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Micro-PIXE analysis of silicate reference standards

GERALD K. CZAMANSKE, THOMAS W. SISSON
U.S. Geological Survey, 345 Middlefield Road, Menlo Park, California 94025, U.S.A.
JOHN L. CAMPBELL, WILLIAM J. TEESDALE
Department of Physics, University of Guelph, Guelph, Ontario N1G 2W1, Canada

ABSTRACT

The accuracy and precision of the University of Guelph proton microprobe have been evaluated through trace-element analysis of well-characterized silicate glasses and minerals, including BHVO-1 glass, Kakanui augite and hornblende, and ten other natural samples of volcanic glass, amphibole, pyroxene, and garnet. Using the 2.39 wt% Mo in a NIST steel as the standard, excellent precision and agreement between reported and analyzed abundances were obtained for Fe, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, and Nb; all materials were analyzed at least twice by obtaining three to ten individual spot analyses. For BHVO-1 and Kakanui hornblende, the precision of individual point analyses was evaluated by five replicate measurements at a single location. For Kakanui hornblende, the precision of these analyses expressed as relative percent [(standard deviation/mean) × 100] is Fe, <1; Ni, 10; Zn, 5; Ga, 5; Rb, 12; Sr, 1; Y, 12; Zr, 6; Nb, 4; and Ba, 33. This precision of individual analyses is sufficiently high that studies of trace-element zoning and diffusion are feasible. Count rates were stable for the five replicate measurements, indicating that higher precision could be obtained simply by repeatedly analyzing the same spot. It is our hope that this demonstration of the ease, accuracy, and precision of in situ trace-element analysis by proton microprobe will lead to greater appreciation and application of the micro-PIXE technique by the geologic community.

INTRODUCTION

In situ microanalysis of major elements with the electron microprobe (EMPA) has been routine in petrologic and geochemical investigations since the late 1960s. The successful development of nondestructive analytical methods, including instrumentation, standards, and data reduction procedures, has led to great advances in the fields of phase equilibria and kinetics, and in their application to geologic problems. Development of techniques for in situ microanalysis of elements present in abundances of <500 ppm has been slower, and such analyses have only been feasible within approximately the last 10 yr. In situ trace-element analyses are now used in studies of trace-element partitioning, diffusion, and zoning, as well as ore genesis, mantle melting and heterogeneity, and melt volatile contents (Shimizu, 1981; Sneeringer et al., 1984; Johnson et al., 1990; Sisson, 1991; Dunbar and Hervig, 1992; Hickmott and Spear, 1992).

Three types of instrument have been developed for in situ trace-element analysis: the ion microprobe, the proton microprobe, and the synchrotron X-ray microprobe. The ion microprobe, or secondary-ion mass spectrometer, was applied first to geologic problems in 1978 (Shimizu et al., 1978) and then to ore mineralogy in 1984 (McIntyre et al., 1984); it has found the widest subsequent application. That instrument employs a mass spectrometer to determine the relative abundances of secondary ions sputtered from a polished specimen surface by a primary ion beam. Because the sputtering process and secondary ion formation are not well understood, conversion of ion intensities to elemental abundances requires working curves developed from standards similar in major-element composition to the unknown samples. With appropriate standards, elemental abundances can be measured at levels below that of parts per million, with precisions of ±10% relative for single-point analyses, with spatial resolution of 10–20 μm. Development of trace-element standards for each phase of interest has proved, however, to be very laborious and has been a major impediment to the wider application of the ion microprobe.

The development of electron storage rings at synchrotron laboratories has facilitated recent progress on the microbeam version of X-ray fluorescence analysis, usually referred to as SXRF. Lu et al. (1989) have published a review that compares SXRF with other microanalytical techniques in the context of mineral analyses. To date, the volume of work reported using SXRF is significantly less than that accomplished with the ion microprobe or with micro-PIXE.

The proton microprobe also was brought to the attention of the geologic community in 1978 (Bosch et al., 1978) and applied to ore mineralogy in 1984 (Cabri et al., 1984a, 1984b; Harris et al., 1984). The proton microprobe operates with a proton beam of 0.5–4 MeV (hence the acronym PIXE, for proton-induced X-ray ex-

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citation) that is focused on the polished surface of a sample. The generation of characteristic X-rays by MeV-energy protons and keV-energy electrons is quantitatively similar. However, the *bremsstrahlung* background, which is the primary determinant of detection limits, is very much lower in the case of protons. This allows simultaneous measurement of the abundances of many elements down to parts per million. Because the generation of characteristic X-rays and their subsequent absorption and secondary fluorescence are well understood, determination of absolute abundances is readily accomplished without the need for standards and unknowns to have comparable matrices.

Much of the pioneering work on quantitative micro-PIXE analysis of geologic specimens was done at Heidelberg and Los Alamos. At Heidelberg, Bosch et al. (1978) and Blank et al. (1982) studies partitioning in lunar rocks from several Apollo missions. At Los Alamos, Rogers et al. (1984) studied terrestrial, meteoritic, and synthetic materials. Again at Heidelberg and subsequently at Guelph, Cabri and various colleagues (Cabri et al., 1984a, 1984b, 1985; Harris et al., 1984) demonstrated the potential of micro-PIXE for quantitative analysis of trace elements in sulfide minerals. Over 40 proton microprobes exist presently, varying significantly in their analytical mission, in their accessibility, and in the degree to which they are tailored to provide conveniently the desired visual and spatial control of beam position and quality of data. For example, two-dimensional imaging of micrometer-scale trace-element zoning was demonstrated at Oxford for samples of secondary dolomite (Fraser et al., 1989). In the late 1980s the facilities at Guelph and North Ryde (Campbell et al., 1990; Ryan et al., 1990) were constructed, the latter specifically for analysis of mineralogical and geochemical specimens. In both cases, provisions were made for optical viewing along the lines used in EMPA, and in each case highly automated analysis and sophisticated spectrum-processing software were developed to cope accurately with large numbers of specimens. These two laboratories are involved in both fundamental studies and commercial analyses; presently, the North Ryde laboratory leads the proton-microprobe field in the volume of geologic work accomplished. Recent examples of the capabilities of these laboratories, as well as Los Alamos, include Czamanske et al. (1992; Guelph), Hickmott and Spear (1992; Los Alamos), Griffin et al. (1992; North Ryde), and Heinrich et al. (1992; North Ryde). A current list of all known, uncited references to applications of micro-PIXE to geologic problems is provided in Appendix 1.

The level of exploitation of micro-PIXE by the geologic community remains low. We attribute this situation in part to lack of realization that a novel technique has matured and that outside users are welcomed in various PIXE laboratories. However, if micro-PIXE is to gain wider acceptance within this community, the various dedicated facilities must demonstrate the accuracy and precision of their methodology in a geochemical context. The CSIRO group (Ryan et al., 1990) analyzed glasses prepared by fusing three rock powder standards from the U.S. Geological Survey. The homogeneity of such glasses can be expressed by the average, over all trace elements, of the ratios of the standard deviations in the elemental abundances for a set of analyzed spots to the errors of single measurements, the optimal value of this average being 1.0. Although the means of their measurements agreed well with reported values, calculated homogeneity values of 1.8, 2.4, and 5.6 reflect considerable heterogeneity in the contents of some elements, apparently as a result of difficulty with the fusions. Consequently, we felt that the methodology developed at the Guelph instrument merited testing by means of a diverse suite of well-characterized, homogeneous samples.

Operating parameters

For micro-PIXE analysis at Guelph, a 3-MeV proton beam is magnetically focused to a spot on the surface of the specimen. This spot, which may be located under 60× magnification, is ultimately viewed optically by a 300× microscope equipped with a charge-coupled-device television camera. A large-area (80 mm^2) Link Analytical plc Si (Li) X-ray detector of nominal resolution 150 eV at 5.9 keV is placed as close as possible to the specimen ($\sim$25 mm). The specimen stage is insulated to permit integration of the incident-beam charge.

For silicate analysis, an Al foil nominally 250 μm thick is located between the specimen and detector to heavily attenuate the X-rays of the light major elements, thereby enhancing the relative content of spectral information for the much less intense X-rays of the trace elements, which are only slightly attenuated because of their higher energy. Except in special cases (e.g., analyzing near grain boundaries or along zoning or diffusion profiles) there is little merit in focusing the proton beam to the 1–3 μm that is available on an increasing number of proton microprobes. Local heating is less with a broader beam, which also confers the advantages of improving detection limits through the use of higher currents and averaging over heterogeneities. In this study we used a beam 5 × 10 μm, with a typical beam current of 10–15 nA; each analysis took only 3–4 min.

Standardization of the micro-PIXE technique is ultimately based solely on accurate determination of an instrumental constant, H (Appendix 2, Standardization; Cabri et al., 1985). For this study, H was determined on the basis of the 2.39 wt% Mo contained in NIST standard reference steel SRM 1155. Ten spots were analyzed, with the beam rastered over an area 400 × 400 μm to average over heterogeneities. Minimal details about the more technical aspects of the data reduction procedure are presented in Appendix 2, and fuller details may be found in the reports referenced there. A tremendous advantage of the most modern micro-PIXE facilities is the ability to provide the analyst or scientist with rapid on-line data computation. Once procedures are established for a particular problem, the complete results of an individual measurement typically are printed within 4–5 min, allowing real-time adjustments in data collection.

Attractive stepping and rastering options are available on the Guelph instrument. Three techniques allow analysis of points along a traverse: (1) preset mechanical stepping for as much as 2.5 cm, with increments as small as 2.5 μm; (2) definition of end points as much as 560 μm apart, with the beam deflected electrostatically to n discrete points between; (3) electrostatic sweeping of the beam back and forth along a line as much as 560 μm long, with location coordinates and X-ray energies stored on disk for later playback and choice of spatial resolution. In addition to obtaining bulk analyses over a heterogeneous sample area (e.g., two exsolved phases), the rastering mode can reduce the thermal damage to relatively unstable materials. Rastering over an area 400 × 400 μm may also be used to obtain images of elemental distribution. At present, images of the distributions of as many as 12 elements can be viewed simultaneously on screen during data accumulation; all data are stored on disk to permit eventual changes in the choice of elements and production of color hard copy or photographs.

Rectangular or round, standard thin-section shapes are accommodated, or mineral grains may be potted in appropriate mounts. Samples are prepared precisely as for the electron microprobe by C coating a well-polished surface. The use of metal mounts must be avoided because polishing will cause surface contamination of the specimens. As the densities of our samples decrease from about 3.8 (MNAG garnet) to 2.36 g/cm^3 (RLS-158 rhyolite glass), the depth, D(90); from which 90% of the observed X-rays originate, increases from 19–20 to 30–33 μm, over the range of Z, from 26 (Fe) to 92 (U). It is thus prudent to prepare sections that are >50 μm thick and to be aware of the grain-boundary orientation. [If standard thin sections (30 μm thick) are desirable for any reason, significant Rb, As, and Zr signals can be derived from the underlying glass; hence, silica mounting slides should be used.]

It seems doubtful that micro-PIXE analyses of silicate minerals will be undertaken without substantial EMPA support. However, a very relevant question concerns the degree to which measured X-ray intensities might be affected by variable matrix compositions in zoned grains. In Appendix 2 we show that this will rarely be an important limitation.

SAMPLE SELECTION

Our goal in this experiment has been to test the accuracy and precision of the Guelph micro-PIXE facility for trace-element analyses of silicate materials. We assembled samples of minerals and natural glasses and one synthetic glass that are thought to be relatively homogeneous and that had been analyzed for some trace elements. Although many mineral and natural glass samples have been shown to be homogeneous with respect to major elements and are in use as EMPA standards, we discovered that very few have also been analyzed for trace elements. Accordingly, U.S. Geological Survey basalt standard BHVO-1 was carefully prepared as a glass (see Appendix 2) and forms our primary reference for the accuracy of the micro-PIXE technique. Glass-standard NIST-610, with over 60 elements present at nominal abundances of 500 ppm, was analyzed as an ancillary test of the spectrum-analysis software.

Natural samples were obtained from various investigators. Tahitian seamount basalt glass DR-1-P3-4, Kilbourne Hole augite megacryst KH-1, and Monastery kimberlite garnet megacryst MNAG are in use as trace-element standards, chiefly for the rare-earth elements (REE), at the ion-microprobe facility at Woods Hole Oceanographic Institute and were provided by N. Shimizu. From a suite of obsidians carefully selected for the absence of alteration or crystallites, R. L. Smith, U.S. Geological Survey, donated rhyolitic obsidian glasses from Glass Buttes, Oregon (RLS-158), and Macusani, Peru (RLS-215). C. Neal provided pargasitic amphiboles PHN-4069 and PHN-4074, separated from garnet lherzolite xenoliths from the Solomon Islands, that had been analyzed for Rb, Sr, and REEs by isotope dilution (Neal, 1988). These amphiboles have been found to have relatively homogeneous contents of those elements by ion-microprobe analysis (Sisson, unpublished data). E. Jarosewich, U.S. National Museum, provided the remaining samples, which are in use internationally as electron-microprobe standards, including hornblende and augite megacrysts from Kakanui, New Zealand, that have been analyzed for numerous trace elements (Mason and Allen, 1972). As no trace-element data are available for the USNM basalt-glass electron-microprobe standards, we examined three of these glasses to provide trace-element analyses of widely available standards.

RESULTS

Discussion of our results can conveniently be broken into consideration of (1) the accuracy of the data in comparison with previously reported trace-element abundances, and (2) reproducibility of the data and indications of sample heterogeneity. This report contains twice the amount of data initially envisioned because our first experiment (labeled I in Table 1) was partially compromised by the surface contamination of all specimens prepared in a brass mount. Thus, a second, more comprehensive experiment (II of Table 1) was carried out several months later. Both data sets are reported because of the additional insight afforded into not only the reproducibility of the technique, but also the homogeneity of the samples. In this study, we searched the measured spectrum for all elements from ^{26}Fe to ^{92}U. Only those elements reported in Table 1 were present in abundances considered significant in relation to the MDLs listed in Table 2 (see discussion of MDLs in Appendix 2). Ultimately, a third data set was collected, as noted in Appendix 2 under Filters.

We consider our data for standard BHVO-1 to be most significant as a test of the micro-PIXE analytical tech-

TABLE 1. Proton-microprobe data for selected glass and mineral standards

	Fe*	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Ba
BHVO-1, basalt (fused), Kilauea caldera, Hawaii[A]											
Rept.	*8.64*	*121*	*136*	*105*	*21*	*11*	*403*	*27.6*	*179*	*19*	*139*
II (10)**	8.67	131	161	115	23	9	404	25	173	19	115?
	(8.64–8.73)†	(115–139)	(152–168)	(111–120)	(20–29)	(6–11)	(400–410)	(22–27)	(167–176)	(16–24)	(44–189)
(5-sp.)‡	8.47(0.05)§	126(9)	164(6)	112(4)	22(2)	9(0.9)	396(4)	25(2)	168(7)	18(1.5)	131(32)
I (10)	8.71	123	c.	c.	c.	9.8	398	26	170	17	113
DR-1-P3-4, basaltic glass, Tahitian seamount[B]											
Rept.	—	*58*	*44*	*134*	—	*44.2*	—	*38.3*	*338*	*50.7*	*418*
II (5)	8.82	30	39	130	27	47	907	34	356	58	459
	(8.73–8.91)	(28–32)	(36–44)	(122–137)	(25–29)	(46–48)	(896–916)	(32–36)	(352–364)	(53–62)	(375–575)
I (3)	8.92	23	c.	c.	c.	45	917	36	362	57	470
USNM-111240/52 (VG-2), basaltic glass, Juan de Fuca Ridge (*Rept. Fe = 9.20*)[C]											
II (5)	9.25	49	52	109	22	3??	119	44	145	5?	<
	(9.14–9.32)	(44–52)	(41–63)	(106–112)	(19–24)	(2–3)	(117–121)	(40–46)	(141–152)	(3–7)	
I (3)	9.19	54	c.	c.	c.	3.7?	116	43	138	4?	<
USNM-113498/1 (VG-A99), basaltic glass, Makaopuhi Lava Lake, Hawaii (*Rept. Fe = 10.34*)[C]											
II (5)	10.15	39	204	142	27	13	403	36	259	25	179
	(10.08–10.19)	(32–46)	(197–216)	(137–146)	(25–29)	(11–16)	(396–406)	(33–38)	(253–262)	(22–27)	(114–220)
I (3)	10.44	47	c.	c.	c.	15	412	38	267	26	247
USNM-113716, basaltic glass, Indian Ocean (*Rept. Fe = 7.10*)[C]											
II (5)	6.99	125	56	79	18	<	98	31	81	<	<
	(6.94–7.06)	(112–140)	(50–62)	(77–80)	(16–20)		(97–99)	(30–33)	(78–82)		
I (3)	7.12	133	c.	c.	c.	<	102	31	81	<	<
USNM-143965, hornblende, Kakanui, New Zealand[C,D]											
Rept.	*8.49*	*100–120*	*11*	*40–45*	*19*	*14*	*425*	*8.5*	*50*	*12*	*169–266*
II (10)	8.32	79	<	60	21	15	480	10	57	23	275
	(8.22–8.41)	(62–90)		(57–65)	(20–23)	(13–17)	(468–491)	(7–13)	(54–61)	(21–24)	(183–352)
(5-sp.)	8.15(0.05)‡	87(9)	<	59(3)	20(1)	16(2)	471(5)	11(1.3)	58(3.4)	24(1)	236(79)
I (3)	8.64	82	<	63	21	16	487	9?	58	25	246
USNM-122142, augite, Kakanui, New Zealand[C,D]											
Rept.	*4.92*	*250–465*	*8*	*21–25*	*11*	*0.17–0.36*	*53–66*	*9.7*	*30*	*0.4*	*0.93–1.27*
II (5)	4.78	293	<	30	11	<	59	8	24	<	<
	(4.73–4.80)	(285–299)		(28–33)	(8–14)		(57–63)	(6–11)	(23–25)		
I (3)	4.93	316	c.	c.	c.	<	56	9	23	<	<
KH-1, clinopyroxene megacryst, Kilbourne Hole, New Mexico (*Rept. Fe = 4.70*)[E]											
II (5)	4.56	225	<	27	10	<	49	13	24	<	<
	(4.52–4.64)	(219–232)		(24–30)	(7–11)		(47–52)	(12–14)	(21–26)		
I (3)	4.77	243	c.	c.	c.	<	50	12	24	<	<
PHN-4069, amphibole, Solomon Islands[F]											
Rept.	*3.34*	—	—	—	—	*2.91*	*862*	—	—	—	—
II (5)	3.15	867	<	20	13	<	861	7	15??	27	993
	(3.08–3.19)	(856–893)		(19–22)	(12–14)		(809–886)	(5–12)	(6–21)	(22–32)	(919–1128)
I (3)	3.24	905	c.	c.	c.	3?	892	8	20	31	1114
PHN-4074, amphibole, Solomon Islands[F]											
Rept.	*5.03*	—	—	—	—	*1.85*	*272*	—	—	—	—
II (5)	5.00	908	<	53	28	<	173	12	272	41	<
	(4.96–5.09)	(901–926)		(49–56)	(26–30)		(172–174)	(11–13)	(266–284)	(39–43)	
I (6)	5.01	917	c.	c.	c.	<	176	12	278	43	<
MNAG, pyrope garnet megacryst, Monastery Kimberlite, Africa[B]											
II (5)	7.20	154	<	26	15	<	<	43	128	<	<
		(143–163)		(23–27)	(13–16)			(40–43)	(127–135)		
I (3)	7.34	149	c.	c.	c.	<	<	43	128	<	<
RLS-158, rhyolitic glass, Glass Buttes, Oregon[G]											
Rept.	*0.62*	—	—	*20*	—	*97–102*	*73*	*27*	*88*	*8–11*	*1370*
II (10)	0.63	<	<	26	15	97	68	22	98	6	1199
				(22–28)	(13–17)	(94–100)	(63–72)	(18–25)	(97–100)	(4–7)	(1021–1323)
I (10)	0.56	<	c.	c.	c.	94	65	22	98	7	1200
RLS-215, rhyolitic glass, Macusani, Peru[G,H,I]											
Rept.[G]	*0.39*	—	—	*106*	—	*1100–1174*	*1*	*31*	*28*	*52–60*	*<50*
Rept.[H,I]	*0.40–0.47*	*<10*	*<10*	*92–97*	*42–43*	*1151–1177*	*1.3–1.6*	*4.9–5.6*	*25–39*	*44–51*	*<10*
II (5)	0.38	7?	8	91	38	1109	<	<	13	47	<
		(0–15)	(3–15)	(87–95)	(35–42)	(1059–1152)			(11–15)	(43–50)	
I (5)	0.34	<	c.	c.	c.	1035	<	<	12	44	<
(5)	0.34	<	c.	c.	c.	1062	<	<	10	46	<

TABLE 1.—*Continued*

	As	Sn	Cs	W	Pt	Au	Tl	Pb	Bi	Th	U
					RLS-158, rhyolitic glass						
Rept.	—	*1.4*	*3.4*	*1.1*	—	—	—	*21*	—	*8.4*	*3.2*
II (10)	<	<	<	<	<	<	<	16?	<	8?	4.6??
								(12–21)		(4–14)	(0–10)
I (10)	<	<	<	<	<	<	<	25	<	7.6?	3.4?
					RLS-215, rhyolitic glass						
Rept.[G]	—	*180–200*	*503*	*76*	—	—	—	*31*	—	*1.3*	*16.9*
Rept.[H,I]	*314–325*	*155–203*	*516–580*	*59–73*	—	—	—	*7–10*	—	*0.1–2.3*	*18.8–31.7*
II (5)	323	197	464	63	<	<	23?	<	30?	<	21?
	(312–332)	(150–223)	(261–570)	(44–77)			(11–33)		(20–38)		(13–31)
I (5)	308	192	562	49	<	<	26?	<	33?	<	30?
(5)	308	196	527	<	<	<	13?	<	35?	<	29?

Note: Rept. = reported values from cited references, shown in italic type; — = no known reported value; < = value well below MDL (see Table 2); ? or ?? = questionable values near MDL; c. = value compromised by contamination from brass specimen mount. A–F are sources of reported values as follows: A = Govindaraju (1989); B = N. Shimizu, Woods Hole, MA; C = Jarosewich et al. (1980); D = Mason and Allen (1972); E = Irving and Frey (1984); F = Neal (1988); G = MacDonald et al. (1992) and R.L. Smith (personal communication, 1993); H = Pichavant et al. (1987); and I = London et al. (1988).

* Fe in weight percent; all other elements in parts per million.

** Value in parentheses is number of discrete spot analyses upon which mean values are based; I and II signify two entirely independent analytical efforts several months apart with different specimen mounts.

† Range of values represented by mean above.

‡ The (5-sp.) indicates five consecutive analyses on a single spot.

§ Standard deviation calculated for five analyses on same spot.

nique because it is so well analyzed for a broad spectrum of elements. Under routine operating conditions (counting times of 3–4 min, spots 5 × 10 μm), we were able to measure trace elements present in excess of 2–50 ppm (see Table 2), in addition to Fe. For BHVO-1, that encompasses Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, and Ba. Because the limits of detection are largely functions of the total accumulated counts, other elements present below the MDLs of the present study could have been measured by counting for much longer durations with a defocused beam. The accuracy of our micro-PIXE analyses of BHVO-1 ranges from good to excellent (Table 1). Combining experiments I and II and excluding replicate measurements at a single location, the averages of analyses for randomly selected points deviate from accepted abundances as follows (in relative percent, [(measured − accepted)/accepted] × 100): Ni, +5.0; Cu, +18; Zn, +9.5; Ga, +9.5; Rb, −15; Sr, −0.5; Y, −7.6; Zr, −4.2; Nb, −5.3; Ba, −18. The precision of any single analysis, estimated by five replicate measurements at a single location, is (in relative percent [(standard deviation)/mean] × 100): Ni, 7; Cu, 4; Zn, 4; Ga, 9; Rb, 10; Sr, 1; Y, 8; Zr, 4; Nb, 8; and Ba, 24. These numbers correspond closely to the 1-sd errors estimated by the spectrum-fitting procedure. The precision of the Ba analysis is rather poor because of the difficulty of fitting the weak Ba*K* X-ray peaks that are barely distinguishable from background in the high-energy portion of the spectra (see Appendix 2). The homogeneity (defined earlier) of BHVO-1 is 0.98, indicating a very successful fusion. No significant monotonic trend was noted for the five replicate measurements, indicating that more precise abundances could be obtained at a single location by increasing the counting time.

Our micro-PIXE trace-element analyses of Tahitian basaltic glass DR-1-P3-4 confirm the accuracy estimated from BHVO-1. Deviations between our averaged micro-PIXE analyses and reported abundances are (in relative percent): Ni, −53; Cu, −11; Zn, −3.0; Rb, +4.6; Y, −9.3; Zr, +6.0; Nb, +14; and Ba, +11. With the exception of Ni, the agreement between reported and analyzed abundances is again good to excellent. The discrepancy between reported and analyzed Ni contents probably results from much of the Ni residing in the olivine crystallites present in the Tahitian glass that were avoided for our in situ analyses.

TABLE 2. Representative minimum detection levels for 39 elements for 3–4 min counts on rhyolite glass RLS-158 (R) and basalt glass BHVO-1 (B)

Element	MDL-R	MDL-B	Element	MDL-R	MDL-B
^{24}Cr	1000	1900	^{46}Pd	3.2	5.2
^{25}Mn	140	310	^{47}Ag	4.0	6.2
^{26}Fe	50	80	^{48}Cd	6.8	7.5
^{27}Co	30	60	^{49}In	6.7	8.5
^{28}Ni	6.5	10.5	^{50}Sn	10.8	10.4
^{29}Cu	3.9	6.9	^{51}Sb	14.9	15.3
^{30}Zn	2.9	4.6	^{52}Te	19.9	15.2
^{31}Ga	2.3	3.3	^{55}Cs	43.2	37.8
^{32}Ge	1.8	2.6	^{56}Ba	25.9	50
^{33}As	2.1	2.7	^{57}La	32.4	66
^{34}Se	1.3	2.4	^{74}W	12.7	26.6
^{35}Br	1.3	1.9	^{78}Pt	9.0	16.7
^{37}Rb	1.5	2.6	^{79}Au	7.2	13.8
^{38}Sr	1.5	2.2	^{80}Hg	6.1	8.5
^{39}Y	4.4	2.5	^{81}Tl	6.6	9.1
^{40}Zr	3.8	10.7	^{82}Pb	5.3	7.5
^{41}Nb	2.8	2.7	^{83}Bi	5.2	7.2
^{42}Mo	4.4	5.2	^{90}Th	5.7	8.0
^{44}Ru	3.2	3.5	^{92}U	12.1	8.7
^{45}Rh	3.1	3.7			

Note: elements Cr through La were detected by means of *K* X-rays and W through U by *L* X-rays. MDLs are in parts per million.

An attractive feature of the micro-PIXE technique is the ability to analyze chemically diverse phases without the need to change operating conditions or standards. The analysis of rhyolitic obsidians RLS-158 and RLS-215, along with the basaltic glasses, provided a test of the ability to accurately analyze samples with widely varying compositions. With the exception of Ni and Cu, which are below the limits of detection, good data were obtained for the same suite of elements as was analyzed in BHVO-1, as well as tentative data for Pb, Th, and U (Table 1). Obsidian RLS-158 is homogeneous with respect to trace elements, as indicated by the nearly identical abundances measured in the different glass chips prepared for experiments I and II. As was found for the basalt samples, the agreement between reported and analyzed abundances is good to excellent. Data from experiments I and II combined, average micro-PIXE analyses deviate from reported abundances as follows (in relative percent): Fe, −4.0; Zn, +30; Rb, −1.6 to −6.4; Sr, −8.9; Y, −19; Zr, +11; Nb, −19 to −41; Ba, −13; Pb, −2.4; Th, −7.1; and U, +25. The ranges for Rb and Nb indicate uncertainties in the reported abundances and not in the micro-PIXE data.

Sample RLS-215 is a highly differentiated peraluminous rhyolite glass from Macusani, Peru, that is exceptionally enriched in F and the alkali trace elements Li, Rb, and Cs; it has been likened to an erupted lithium pegmatite magma (Pichavant et al., 1987; London et al., 1988). Macusani glass occurs as crystal-poor glass pebbles <10 cm in diameter that were apparently weathered from nearby ashflow tuffs (Pichavant et al., 1987). Table 1 shows that our micro-PIXE analysis of sample RLS-215 is in good agreement with either the bulk analysis of RLS-215 (MacDonald et al., 1992) or with analyses of other Macusani glass pebbles (Pichavant et al., 1987; London et al., 1988).

Our data for Macusani glass RLS-215 demonstrate some of the insights that can be gained through micro-PIXE analyses. Determining the compositions of magmatic liquids is one of the first and fundamental steps necessary in understanding the evolution of magmatic systems. As a transparent, unbanded, and crystal-free glass, RLS-215 would be treated as representative of a single magmatic-liquid composition in a petrologic study uitilizing bulk-analytical techniques. Our initial experiment clearly showed that the glass is chemically heterogeneous within millimeter-sized chips because the averages of five analyses on each of two chips differ for several elements (Table 1). As crystals are absent, the chemical variations are not caused by local enrichment or depletion zones around crystals that have grown in situ from a formerly homogeneous melt, and we conclude that bulk RLS-215 is not representative of any single liquid composition. The sample probably formed by the incomplete mechanical mixing of two chemically distinct melts, a discovery that would have been difficult to make without in situ trace-element analyses.

Analyses of augite and hornblende megacrysts from Kakanui, New Zealand, suggest that care should be taken in certifying the source of the Kakanui hornblende used as a major- or trace-element reference material. Good to excellent agreement was obtained between the reported values and analyzed compositions of two fragments of Kakanui augite (Table 1), and our analyses suggest that the material distributed by the U.S. National Museum is homogeneous, with trace-element abundances comparable with those reported in Mason and Allen (1972). Our analyses of Kakanui hornblende are consistent with those reported by Mason and Allen (1972) only for Ga, Rb, and Y. Two other kaersutite megacrysts from the Kakanui locality have been analyzed by Reay et al. (1989) using bulk methods; they show a considerable range in trace-element abundances at nearly constant major-element composition. We conclude that the trace-element contents of the Kakanui hornblende analyzed by Mason and Allen (1972) are not representative of the material being distributed by the U.S. National Museum and recommend use of the new trace-element analyses reported here. The precision of any single Kakanui hornblende analysis was also estimated by five replicate measurements at a single location as (in relative percent): Ni, 10; Zn, 5; Ga, 5; Rb, 12; Sr, 1; Y, 12; Zr, 6; Nb, 4; and Ba, 33—results comparable to those obtained for BHVO-1.

Only limited trace-element data are available for the remaining samples. Our analyses of Sr and Fe in pargasitic amphibole PHN-4069 are in good agreement with those reported by Neal (1988). For pargasite amphibole PHN-4074, we found good agreement with the reported Fe value but found 173 and 176 ppm Sr in two crystal fragments, as opposed to the reported 272 ppm. Insofar as our Sr analyses of other materials are both accurate and precise, either samples were switched or the reported analysis is in error.

The data of Table 1 provide an element-by-element assessment of micro-PIXE's accuracy for geochemically useful trace elements in typical geologic silicates. It is limited more by the availability of accepted abundances than by the measured data. For the elements Rb through Nb, which are of particular interest, the accuracy is usually better than 15% at abundances as low as 10 ppm and can be as good as 1–2 ppm (e.g., for Sr) at abundances of several hundred parts per million. With the exception of Ba, the precision of any single analysis is also usually better than 15% (relative). More precise abundances can be obtained by counting longer or by repeatedly analyzing the same location. For studies relating to mineralogical zoning or diffusion profiles, it is useful to relate variation in trace-element abundances directly to covariation in major-element composition. Thus, the accuracy and precision of the determination of Fe, under the same conditions that are optimal for many trace elements, is an impressive feature of the micro-PIXE technique.

With its ability to perform nearly standardless analyses, micro-PIXE is also useful for developing standard materials for other microanalytical techniques with much lower limits of detection, e.g., the ion microprobe. The excellent agreement among analyses of separate fragments of the USNM basaltic glasses (Table 1) is strong evidence that those materials are homogeneous in trace-element contents at a microscopic level. This, combined with the demonstrated accuracy of our analyses of BHVO-1 and Tahitian basalt glass DR-1-P3-4, indicates that the USNM basaltic-glass reference standards can now be used with our new trace-element analyses as primary or secondary standards for other trace-element microanalytical techniques.

GEOLOGICAL APPLICATIONS

To date, Earth science research utilizing micro-PIXE analysis has principally been concentrated on three types of samples: (1) sulfide ores have been examined to locate the host phases for precious metals; (2) trace elements have been measured in garnet and in some coexisting phases, primarily in mantle-derived rocks, to study metasomatism, partitioning, and metamorphic reactions; and (3) metal, sulfide, oxide, and (rarely) silicate phases have been analyzed in scarce lunar and meteoritic samples. We are aware of no attempts having been made to apply micro-PIXE analysis to the petrogenesis of intermediate-to-silicic igneous rocks. Our results show that such studies are feasible. The ability to analyze diverse phases using a single standard and uniform operating conditions largely obviates the need to perform laborious mineral separations, formerly necessary for studies of the trace-element inventory of such rocks.

Among the most exciting potential applications of micro-PIXE analysis to silicate minerals and glasses are element-partitioning measurements relevant to mineral-melt, mineral-mineral, or melt-melt systems useful in understanding melting and crystallization processes, trace-element zoning studies in igneous or metamorphic minerals to assess the crystallization behavior of magmas or to assess tectonic and metamorphic histories, and diffusion-profile measurements in minerals, melts, or glasses to determine rates of geologic processes. It is a technique ideally suited to analyzing materials or phases available in such low quantities (especially extraterrestrial samples) that bulk analytical techniques are impossible and to using in the fingerprinting of samples in studies of tephrochronology (Sarna-Wojcicki and Davis, 1991) or archeology (Hughes and Smith, 1993), where a spectrum of well-determined elemental abundances may be of critical importance.

CONCLUSIONS

Micro-PIXE analyses of silicate samples are of excellent quality for a broad range of elements at abundance levels of tens to hundreds of parts per million, depending on counting times. Despite this capability, micro-PIXE analysis appears to be underutilized by the wider geochemical community. In a valuable discussion of the application of proton and nuclear microprobes in ore-deposit mineralogy and metallurgy, Cabri (1988) suggested that micro-PIXE had not been widely used because of inaccessibility and relatively unsuitable data reduction capability. These constraints no longer pertain. We feel that underutilization stems from a general lack of awareness of (1) the accuracy, precision, and adjustable spatial resolution of the technique for analysis of geologic materials, (2) the convenience and flexibility of data collection and computation with a modern proton microprobe, and (3) the cost of beam time. The focus of this paper has been on the first two points. As regards cost, there are as yet no commercial micro-PIXE enterprises. However, beam time is available in a growing number of established ion-beam laboratories around the world at a cost that is attractive in comparison with the more widely used techniques. It is our hope that this work will stimulate greater use of micro-PIXE analysis, as well as providing superior in situ analyses of materials in common use by the international electron microprobe community that will be useful for calibration of other microanalytical techniques.

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APPENDIX 1. KNOWN, UNCITED REFERENCES TO GEOLOGICAL APPLICATIONS OF MICRO-PIXE

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APPENDIX 2. ANALYTICAL TECHNIQUES

Standardization

Micro-PIXE analysis differs substantially from EMPA in that the proton travels in a straight path in the specimen and X-ray generation can be described from first principles, without recourse to empiricisms or Monte Carlo methods. The underlying data base of physical quantities, e.g., stopping powers, ionization cross sections, and attenuation coefficients, is well known. All this results (Maxwell et al., 1989; Campbell et al., 1990) in a simple expression for the recorded spectral intensity $I(Z)$ of the principal (e.g., $K\alpha$) X-ray of element Z (content C_Z) in a matrix designated by M: $I(Z) = HQC_Ze_Zt_ZI_1(Z, M)$.

Here I is the theoretical X-ray intensity per unit content, per steradian, per unit charge computed from the data base; H is an instrumental constant that subsumes the detection solid angle and the calibration of the charge integrator; Q is the integrated proton charge; t_Z is the X-ray transmission through the Al absorber; and e_Z is the relative efficiency of the Si (Li) detector (unity over much of the relevant range of X-ray energy). Our assessment of the data base (Campbell et al., 1990) suggests that I_1 can be computed for K X-rays with an accuracy significantly better than 5%. I_1 is analogous to the absorption-weighted integral of $\phi(\rho Z)$ in EMPA, but its determination does not require Monte Carlo techniques or tracer measurements. The major-element contents required for computation of I_1 (Z, M) were obtained from the references cited for Table 1.

It follows that if the detector and absorber are well characterized, the instrumental constant, H, can be determined with a minimal set of standards. Although Campbell et al. (1993) demonstrate that a single pure-element standard gives a good determination of the H value, geoscientists may be more comfortable with a standard containing several trace and minor elements. For this study, in which H was determined using the NIST standard reference steel SRM 1155, ten spots were analyzed, with the beam rastered over an area 400 × 400 μm to average over heterogeneities. An H value of 0.1004 (sd = 1.2%) was determined from the 2.39 wt% Mo alloyed in this steel. The known Fe content permitted refinement of the Al-foil thickness to 246.5 μm, and the H values for Fe and Ni were, respectively, 0.1006 (sd = 0.9%) and 0.0992 (sd = 2.8%). In earlier work, the same procedure was based on a CANMET synthetic pyrrhotite standard containing 0.1 wt% Pd (e.g., Cabri et al., 1985). To check for consistency of the charge measurement between standard and specimens, H values were measured for Fe in two pyrrhotite samples, a magnetite sample, metallic Fe, and BHVO-1; all values lay within a range of ±0.7%.

Spectrum fitting and minimum detection limits

A model spectrum containing all relevant X-ray lines is fitted to the measured spectrum by nonlinear least squares, the background continuum being removed by digital filtering (Maxwell et al., 1989). The relative intensities of the lines for a given element are adjusted to reflect matrix effects, absorber transmission, and detector efficiency. The line shapes are Gaussian, with low-energy tails determined using pure-element targets. Step features may be included to describe the effect of absorption edges on the background. The principal peak intensity (hence elemental abundance) for each element is accorded a 1-sd error, reflecting both counting statistics and the error from peak overlap. The reproducibility of repeated measurements upon a specimen is determined by this error, by the approximately 1% uncertainty in charge integration, by variations in specimen alignment and surface smoothness, and by specimen heterogeneities.

APPENDIX TABLE 1. Data taken with the 110-μm filter and second detector

Sample	Cr (ppm)	Mn (ppm)	Fe (wt%)	Ni (ppm)	Cu (ppm)	Zn (ppm)
BHVO-1	<	1316(1300)*	8.62	129	163	117
DR-1-P3-4	<	1280	8.99	30	45	145
USNM-111240	<	1650(1700)	9.15	45	56	108
USNM-113498	<	1479(1160)	10.40	40	207	151
USNM-113716	<	1289(1310)	7.09	123	57	80
Kakanui hbl.	<	659(675)	8.29	82	<	63
Kakanui aug.	1010 (785)	1062(982)	4.90	308	<	34
KH-1	<	1076(1316)	4.73	236	<	28
PHN-4069	8500	433(540)	3.26	908	<	20
PHN-4074	7300	741(540)	5.04	936	<	54
MNAG	7300	1849	7.29	152	<	26

Note: data are average of five spot analyses. MDLs (in parts per million): Cr = 300–700; Mn = 40; Fe = 40; Ni = 7; Cu = 5; Zn = 4.

* Reported values in parentheses.

The minimum detection level (MDL) is computed by means of the widely used criterion of three times the standard deviation of the integrated intensity of all events underlying a given X-ray peak, within a region of one full width at half maximum. When a peak intensity or, equivalently, elemental abundance is at the MDL, the element's presence is 99.9% probable; however, although the element has been observed, quantitative use of the data is precluded by the very large associated uncertainty. For this reason we favor the recommendation of Keith et al. (1983) who, in an exhaustive treatment of the subject, defined a "limit of quantitation" (LOQ) as 10σ (where σ is the standard deviation for a single measurement); contents lying in the region of less certain quantitation between the 3σ MDL and the 10σ LOQ should be interpreted with caution. The MDLs attained in this study are in no sense absolute but are determined by counting statistics. In any study, the MDLs will decrease in inverse proportion to the square root of the measurement duration.

In silicate minerals, MDLs of a few parts per million are attained for many trace elements in the absence of interfering X-ray lines. However, MDLs can be worsened considerably by interferences; for example, a difference of 1000 ppm Rb worsens the MDL for Y from 4.4 (RLS-158) to 20 ppm (RLS-215). Relatively high contents of F and rare-earth elements are particularly detrimental to MDLs, the former because of especially strong γ radiation and the latter because of peak complexity and overlap.

The spectrum fits in the present work were very satisfactory, as judged on the basis of the χ^2 values or the overall residue spectrum, which in the case of a good fit should lie within $\pm 3\sigma$.

Filters

In this work, where a major focus was on the elements Sr through Nb, a nominal Al filter thickness of 250 μm was required to suppress the pile up of Fe *K* X-rays, which otherwise would detract from the precision and MDLs of these elements. Unfortunately, this thickness also heavily suppresses the Cr-, Mn-, Co-, and Ni*K* X-rays. We therefore repeated our measurements on all samples other than the obsidians, using a thinner Al filter (110 μm) and a different X-ray detector. The resulting Cr, Mn, Fe, Ni, Cu, and Zn abundances are presented in Appendix Table 1. The Fe, Ni, Cu, and Zn data agree well with those of Table 1, and we consider the Cr and Mn data to be more accurate than any yet reported for this suite.

Co lines are not visible in any spectrum, as the Co*K*α line overlaps with Fe*K*β and the Co*K*β line is very weak. In the absence of prior information, one has a choice as to inclusion of such an element in the fitting list; our choice was to include Co because it was known to be present, albeit in amounts <80 ppm. Because the MDL for Co is 50–80 ppm, Co data are not reported in Table 1 or Appendix Table 1. Nevertheless, we note here that the mean Co contents for ten samples are in fair agreement with accepted values (e.g., 54 ppm in BHVO-1 and 46 ppm in Kakanui augite vs. accepted values of 45 and 41–58 ppm, respectively). We observed that when we excluded Co from the BHVO-1 fits, the Ni value fell by 5 ppm, indicating an additional source of uncertainty for Ni at the lowest abundances reported.

Unavoidably, the use of filters that optimize the determination of trace elements of $Z > 26$ precludes the accurate analysis of minor elements with $Z < 26$ because their X-rays are heavily attenuated or removed entirely. This is not generally a drawback because these elements (e.g., Na, Mg, Al, Si, K, and Ca) can be determined with ease and accuracy by EMPA. In principle, a separate micro-PIXE measurement using no filter can be used for the light elements (e.g., Campbell and Teesdale, 1993) but, because protons scattered off the target damage the Si (Li) detector, the proton energy must be drastically reduced (to 0.75 MeV at Guelph), which worsens detection limits for elements with $Z > 20$.

Matrix effects and EMPA support

In micro-PIXE analysis, the matrix effects are (1) the slowing down of the proton, which causes a rapidly decreasing generation of X-rays as the proton goes deeper, and (2) the attenuation of emitted X-rays en route from points of origin to the detector. Although EMPA approximates these in the semiempirical ZAF model, for PIXE one can model the X-ray production from first principles with high accuracy. In the above equation, I_1 (Z, M) represents the matrix effects. In this study, we knew the major-element contents and could calculate I_1 directly. In cases where the major-element contents are not supplied from EMPA or some other source, micro-PIXE can be used, as described in the previous paragraph, to determine them. The filter is removed to enable detection of light-element X-rays, and an iterative solution of the equation is effected (precisely as is done in EMPA).

As an example of the potential loss in accuracy that might be associated with traversing a strongly zoned mineral in the absence of site-specific major-element data, we made calculations of the effect of gross compositional variation on X-ray intensities. The calculations of Appendix Table 2 are based on two pyroxene compositions (Deer et al., 1992; Table 18, Analyses 1 and 2) and two amphibole compositions (Deer et al., 1992; Table 24, Analyses 10 and 18) that are far more disparate than would commonly be expected in zoned mineral grains; i.e., the respective Mg numbers are 91.4 and 36.9 for the pyroxenes and 50.2 and 95.1 for the two amphiboles. We conclude that analyses of zoned silicate minerals would rarely be compromised by lack of site-specific matrix compositions. Soon, however, developments in progress may allow simultaneous micro-PIXE determination of the light and heavy elements using two Si (Li) detectors.

Preparation of basalt standard BHVO-1

Basalt standard BHVO-1 was prepared by fusing a 100-mg split of rock powder to liquid and quenching to a glass in H_2O. The rock powder was formed into a pellet by wetting with deionized and doubly distilled H_2O and was compressed in a pellet press. A hole was drilled into the damp pellet, and the pellet was threaded onto a Pt wire hook 0.008 in. in diameter that had previously been brought into equilibrium with BHVO-1 melt by

APPENDIX TABLE 2. Perturbation of X-ray intensities for two cases of variable silicate matrix composition

	Pyroxene*	Amphibole**
Fe	−3.6	−0.92
Ni	25	−5.7
Zn	18	−2.8
Ga	15	−1.6
Rb	2.1	2.5
Sr	0.89	2.8
Y	0.0	3.1
Zn	−1.1	3.4
Nb	−1.8	3.6
Ba	−6.3	4.7
Pb	2.1	0.20
Th	3.5	2.2

* Values are percentages, $100[(Px_1 - Px_2)/Px_1]$, where pyroxene Analyses 1 and 2 are from Deer et al. (1992, Table 18).

** Values are percentages, $100[(Amp_{10} - Amp_{18})/Amp_{10}]$, where amphibole Analyses 10 and 18 are from Deer et al. (1992, Table 24).

APPENDIX TABLE 3. A test of micro-PIXE with NIST-610 glass

		Measured, ten spots				
	Recom- mended	Range	Mean	Error (%)*	Sd (%)	Mean/ recom.
Fe	458	353–456	406	10.3	7.4	0.886
Co	(390)**	376–502	441	6.4	7.7	1.13
Ni	459	456–547	510	15.7	5.7	1.11
Cu	(444)	366–413	392	13.2	4.1	0.883
Zn	(433)	442–488	460	8.5	3.7	1.062
Rb	426	380–431	412	5.5	3.9	0.967
Sr	516	487–518	506	4.1	2.8	0.982
Ag	(254)	243–281	257	3.1	4.7	1.011
Tl	(62)	53–90	66	43.1	17	1.06
Th	457	431–477	458	4.0	3.9	1.003
U	462	431–481	463	4.1	3.9	1.003

Note: abundances are in parts per million.

* Error expressed as the standard deviation for a single measurement.

** Parentheses indicate interim NIST recommendations.

sequentially fusing three other pellets of BHVO-1 to liquid for up to 12 hr each, followed by cleaning in hot HF. The final pellet was fused for 2 hr at 1350 °C in air in a Deltec DT-31-VT furnace and was quenched to crystallite-free glass by being dropped into H_2O. Glass fragments from the interior of the bead were mounted for micro-PIXE analysis.

A note about NIST 610 glass

This reference material, containing over 60 trace elements at nominal contents of 500 ppm, offers the ultimate challenge to micro-PIXE. Despite the complexity of the spectrum, with its multitude of overlapping X-ray lines, the χ^2 values indicated a reasonably good fit. Although we extractetd abundances for 41 elements having $Z \geq 26$, we can only comment usefully on the elements where NIST supplies an interim or final recommendation for content, namely, Fe, Co, Ni, Cu, Zn, Rb, Sr, Ag, Tl, Pb, Th, and U. For these 12 elements, the ratios of our measured values to the recommended abundances are shown in the last column of Appendix Table 3; the mean value of these ratios is 1.01. Micro-PIXE analyses of NIST 610 have also been reported by Rogers et al. (1987). In that work two long (45 min) separate measurements were made using different X-ray filters. In the measurement more closely resembling ours, the mean ratio of measured abundances to recommended values for 14 elements was 1.007.

Although on the surface these results appear encouraging, we prefer to treat them with caution. Our fit was unable to discern a number of the light REE. This may detract from the accuracy of the deduced abundances of 3D transition metals, whose K X-rays fall in the same energy region (5–10 keV). For example, the fit fails to discern Er and Yb; the $L\alpha$ lines of these two elements coincide in energy with the $K\alpha$ lines of Co and Ni; the contents of the latter are overestimated by about 12%. Conversely the Dy content given by the fit is 950 ppm, significantly larger than the nominal 500 ppm; the Dy$L\alpha$ line overlaps the Fe$K\alpha$ line, and the Fe content is 11% low. These overlap problems become less serious for the $K\alpha$ X-rays of Rb and Sr and the $L\alpha$ X-rays of U and Th, and indeed in these cases the discrepancies are below 3.3%. It is unfortunate that the majority of elements in NIST 610 remain uncertified, because that prevents us from evaluating the micro-PIXE results for some 30 elements.

Regardless, we suggest that NIST 610 not be used for a micro-PIXE standard because of the severity of the line overlap in its energy spectra.