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MAJOR- AND TRACE-ELEMENT ANALYSIS OF SULFIDE ORES BY LASER-ABLATION ICP–MS, SOLUTION ICP–MS, AND XRF: NEW DATA ON INTERNATIONAL REFERENCE MATERIALS

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ABSTRACT

International reference materials representing a diverse suite of sulfide ores and related lithologies have been analyzed for major and trace element concentrations by XRF, solution ICP–MS, and laser-ablation ICP–MS (LA–ICP–MS) after fusion of the sample to a lithium borate glass. Reference materials analyzed for this study include a wide variety of bulk compositions, including ores of Pb–Zn sulfides, Fe sulfides, Cu–Mo sulfides, and silicate matrices. Concentrations of 33 elements were determined, including lithophile and chalcophile elements of particular interest to economic geochemistry and ore deposit studies. The results of LA–ICP–MS analyses were calibrated using a fused glass standard prepared specifically for the analysis of sulfides. Accuracy of the LA–ICP–MS technique is established by comparison with results obtained by the other methods for abundance variations over several orders of magnitude. Replicate analyses demonstrate a precision of 2–8% (1σ RSD) for the LA–ICP–MS data at rock-equivalent concentrations >1 ppm. Matrix effects were not a significant problem at the scale of compositional variation represented by these samples, and no significant differences in the results were produced with the laser operating in either fixed-spot or line-scan mode. LA–ICP–MS analysis of fused glasses effectively overcomes problems related to insoluble phases such as cassiterite that are resistant to acid dissolution. Whole-rock analysis of sulfide ores by XRF and LA–ICP–MS provides a fast and convenient approach for determinations of major- and trace-element concentrations in a variety of ores and related materials without the need for wet-chemical dissolutions.

Keywords: laser-ablation ICP–MS, trace elements, sulfide ores, X-ray fluorescence, CANMET standards.

SOMMAIRE

Nous avons analysé des étalons de référence internationaux représentant une variété de minerais sulfurés et assemblages associés pour en établir les concentrations en éléments majeurs et éléments traces par fluorescence X, analyse ICP–MS de solutions, et analyse ICP–MS avec ablation au laser suite à une fusion de l'échantillon pour en faire un verre à base de borate de lithium. Parmi les matériaux de référence analysés se trouve une grande variété de compositions globales, y compris des minerais contenant des sulfures de Pb–Zn, de Fe, de Cu–Mo, et des matrices silicatées. Nous avons établi les concentrations de 33 éléments, y inclus des éléments lithophiles et chalcophiles d'intérêt particulier en géochimie économique et en gîtologie. Les résultats d'analyses ICP–MS avec ablation au laser ont été calibrés avec un étalon de verre préparé spécifiquement pour l'analyse de sulfures. La justesse de la technique ICP–MS avec ablation au laser est établie par comparaison avec les résultats d'autres techniques, les concentrations variant sur plusieurs ordres de grandeur. Des analyses répétées démontrent une précision entre 2 et 8% (1σ écart-type relatif) pour les données obtenues par analyse ICP–MS avec ablation au laser, à des concentrations équivalentes dans la roche dépassant 1 ppm. Les effets de matrice ne constituent pas un problème important à l'échelle des variations en composition représentées par ces échantillons; de plus, nous n'avons pas vu de différences importantes dans les résultats obtenus avec le rayon laser employé avec un foyer fixe ou bien traversant l'échantillon de façon linéaire. L'analyse de verres par ICP–MS avec ablation au laser analysis est un moyen efficace de surmonter les problèmes liés à la présence de phases insolubles, comme la cassitérite, qui résiste à la dissolution dans un acide. L'analyse de minerais entiers par fluorescence X et par ICP–MS avec laser est une façon commode et rapide d'établir les concentrations des éléments majeurs et traces dans une variété de minerais et matériaux associés sans avoir recours à des dissolutions par voie humide.

(Traduit par la Rédaction)

Most-clés: analyse ICP–MS avec ablation au laser, éléments traces, minerais sulfurés, fluorescence X, étalons CANMET.

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INTRODUCTION

Trace-element compositions of sulfide minerals and related ores represent an underutilized aspect of economic geochemistry that holds considerable promise for generating innovative and cost-effective research applications in mineral exploration and ore-deposit studies. Trace-element distributions in sulfide ores and minerals can provide useful information about the distribution of base and precious metals, the definition of trace-element vectors in alteration halos associated with hydrothermal and magmatic ore deposits, and the physicochemical controls on ore deposition, such as temperature, redox conditions, and metal sources.

X-ray fluorescence (XRF) and inductively coupled plasma – mass spectrometry (ICP–MS) are both well-established geochemical techniques capable of determining the concentrations of a wide variety of economically and petrogenetically useful elements in geological materials. Sample-preparation procedures for XRF analysis are relatively simple, but sulfide ores require specialized handling compared to silicate rocks. For example, sulfur may be volatilized, and elements such as Cu, Fe and Sn may be lost to the platinum crucibles typically used for preparation of fused glasses (Norrish & Thompson 1990). Matrix effects and spectral interferences can be significant, with high Pb contents in particular posing difficulties for many elements in the accurate analysis of sulfide samples by XRF. In comparison, ICP–MS analysis can provide improved detection limits and an expanded list of elements, but the conventional approach using solution nebulization requires the sample to be completely dissolved, which can be difficult if minerals that are resistant to acid attack are present (*e.g.*, zircon, cassiterite). An alternative approach applied here is to determine major- and trace-element concentrations by laser-ablation ICP–MS (LA–ICP–MS) analysis of ore samples that have been fused to a glass with a suitable flux. A similar approach has been applied previously to silicate rocks (Perkins *et al.* 1993, Nesbitt *et al.* 1997, Ødegård & Hamester 1997, Ødegård *et al.* 1998, Becker & Dietze 1999, Nutman *et al.* 1999, Pickhardt *et al.* 2000, Sylvester 2001, Günther *et al.* 2001). Here, we demonstrate the utility of this method for analysis of a variety of sulfide ores and related materials through a comparison with data obtained by XRF and solution ICP–MS analysis.

INSTRUMENTATION AND ANALYTICAL METHODS

Samples

A suite of reference materials acquired from CANMET (Canada Centre for Mineral and Energy Technology) and the U.S. Geological Survey was analyzed, with emphasis on sulfide ores and related lithologies. Samples include ores rich in pyrrhotite (RTS–4), sphalerite and galena (CZN–1, CPB–1, MP–1), a Cu–Mo ore from a low-grade porphyry deposit (HV–1), iron sulfide ore tailings (RTS–3), a jasperoid (GXR–1), and a mill-head sample of unoxidized porphyry-Cu ore (GXR–4). The bulk compositions of these reference materials are highly variable, with matrices dominated by Fe, Cu, Zn, and Pb, as well as predominantly silicate matrices with modest sulfide contents.

Major- and trace-element compositions were determined by LA–ICP–MS analysis of samples fused to a glass with a lithium borate flux, XRF, and solution ICP–MS. Two sets of solution ICP–MS data were obtained: one by quadrupole ICP–MS following acid dissolution of whole-rock powders, and the other on dissolved splits of the fused glasses using a Finnigan Element magnetic-sector ICP–MS. All facilities are located in the CODES SRC/Earth Sciences laboratories at the University of Tasmania, with the exception of the Element, which is operated by the Central Science Laboratory, also at the University of Tasmania. The data produced in this study are compared with available reference values reported by CANMET (1972, 1978, 1994) and Govindaraju (1994). Note that different splits of the GXR standards may be heterogeneous for some elements (Kane *et al.* 1992).

Laser-ablation ICP–MS

Trace-element abundances were determined by LA–ICP–MS analyses of fused glass discs. An Agilent HP4500 quadrupole ICP–MS and a Merchantek LUV266X laser-ablation system were used for these analyses. The glass discs were prepared with a conventional XRF major-element fusion technique by mixing 0.400 g of rock powder with 4.121 g of 12:22 flux (a mix of 12 parts lithium tetraborate and 22 parts lithium metaborate) and 1 mL of 60.6% lithium nitrate solution. The mix was pre-ignited in a platinum crucible at 700°C for 10 minutes, followed by fusion at 1050°C. Slices from the discs prepared with a wafer saw were mounted in epoxy and polished. For each analysis, data were collected in time-resolved mode using 30 ms dwell times per mass, one point per mass, and 90 s total acquisition time, which includes 30 s of instrumental background (terminology following Longerich 2001). After initiation of ablation, approximately 5–10 s were required for the signal to stabilize; these data were excluded on the basis of a visual inspection of each spectrum. Concentrations and detection limits were calculated using the LAMTRACE data-reduction program (van Achterbergh *et al.* 2001) following procedures outlined by Longerich *et al.* (1996). Each set of analytical results was normalized to the Fe content of the sample as an internal standard, and the data reported on a rock-equivalent (flux-free) basis. Four analyses of the calibration standard are made for every 16 unknowns, with drift corrections applied using a weighted mean of the standard compositions. Solution ICP–MS analyses of the flux used for these fusions indicate negligible contributions for the elements of interest here. However, some elements (*e.g.*, Sn, Mo, Ni) appear to show low levels of contamination from the crucible used for fusion, as discussed below.

Most of the LA–ICP–MS analyses were obtained with a spot 100 μm in diameter, a laser-repetition rate of 4 or 5 Hz, and a power setting of 1.0–1.2 mJ/pulse. This choice produced steady signals and count rates sufficient for the analysis of most samples. A few samples ablated poorly under a fixed laser spot, producing weak or rapidly dying signals. These included MP–1, HV–1, and GXR–4, which tend to be poor in Fe or rich in Cu. In order to improve the results, these samples were analyzed with the laser operated in line-scan mode with a repetition rate of 10 Hz and a beam 50 μm in diameter. As shown below, no significant differences result from analyses using spot *versus* line-scan mode for the fused sulfide ore glasses. A second problem encountered was the extremely high Pb signals produced from CPB–1 and CZN–1. Under the conditions used for these analyses, ^{208}Pb signals from these samples were 10^7–10^8 counts per second (cps), well beyond the linear operating range of the pulse mode of the electron multiplier detector. To overcome this problem, these two samples (CPB–1, CZN–1) were re-analyzed with Pb data collected using the analogue detector mode, with a calibration of the pulse-analogue detector established by solution aspiration prior to the laser session.

A significant problem in the past has been the lack of calibration standards appropriate for quantitative analysis of sulfides for trace elements by LA–ICP–MS. Standards commonly used for analysis of silicate phases are not well characterized for chalcophile elements, and natural materials are either heterogeneous or do not carry the entire range of elements at sufficient concentrations to make them useful as primary calibration standards. To enable the quantitative analysis of sulfide minerals and ores, we prepared an in-house calibration standard designed specifically for analysis of sulfides by fusing a mixture of CANMET standards in proportions designed to give adequate signal intensities for most elements (75% RTS–4 and 25% CZN–1. The composition of this standard, designated STDGL–1, was determined by XRF and solution ICP–MS (Tables 1, 2), and it was used for calibration of the LA–ICP–MS data presented here.

Solution ICP–MS analysis of fused discs

Splits of the same fused glasses analyzed by LA–ICP–MS were dissolved, and the solutions analyzed using a Finnigan Element magnetic sector ICP–MS. For

TABLE 1. RESULTS OF SOLUTION ICP–MS ANALYSES OF FUSED ORE STANDARDS, AS DETERMINED WITH A FINNIGAN ELEMENT APPARATUS

	1	2	3	4	5	6	7	8	9	10
Na_2O wt%	23 (M)	0.73	0.18	0.13	0.20	0.13	2.53	0.12	0.77	0.12
MgO wt%	24 (M)	3.64	0.36	0.18	0.46	0.05	0.50	0.36	2.77	0.32
Al_2O_3 wt%	27 (M)	8.09	0.73	0.34	0.33	3.59	11.37	5.54	14.96	0.56
CaO wt%	42 (M)	3.18	0.52	0.93	0.42	4.76	1.51	1.17	1.45	0.40
S wt%	32 (M)	10.0	32.3	17.9	19.2	12.2	0.4	0.4	2.0	24.1
P	31 (M)	403	48.0	28.2	35	238	458	640	1331	37
K	39 (M)	5170	827	606	683	1654	37762	677	61203	652
Ti	47 (M)	3850	1096	128	174	808	1380	331	3408	734
V	51 (M)	127	54	4	4	10	57	100	113	37
Mn	55 (M)	1772	148	426	2385	388	228	813	142	624
Co	59 (M)	289	215	4.6	9.2	3.3	3.0	8.0	15.5	156
Ni	60 (M)	157	8481	87	63	48	43	71	139	6092
Cu	63 (M)	2615	268	2339	1401	20617	4244	1016	6083	530
Zn	66 (M)	1264	160	32784	315307	99852	60	529	71	73735
Ga	69 (M)	46.6	1.5	0.9	5.9	121	16.1	11.9	20.3	1.9
As	75 (M)	18.9	262	688	304	8516	7.1	398	105	267
Rb	85 (M)	14.6	3.1	2.5	6.6	25.7	54.5	5.9	183	2.6
Sr	88 (L)	57.5	14.9	4.7	5.1	11.0	540	335	298	9.7
Zr	90 (L)	91	14.3	11.2	20.1	186	83.8	26.9	250	10.9
Mo	95 (L)	12.9	11.1	11.2	15.7	170	616	26.3	420	12.1
Ag	107 (L)	14.5	2.0	587	93	61	2.7	28.2	5.3	26.6
Sb	121 (L)	3.9	2.5	3738	594	27.9	1.7	117	5.3	138
Ba	137 (L)	147	38.7	19.1	15.4	14.7	954	789	2518	29.0
Tl	205 (L)	2.92	0.72	39.2	7.6	1.50	0.58	0.56	1.6	1.7
Pb	208 (L)	199	212	759553	80152	22677	52	792	83	21340
Bi	209 (L)	117	11.3	278	27.2	265	1.8	1528	23.4	10.4
U	238 (L)	0.67	0.49	1.0	1.3	31.6	1.6	40.6	8.6	0.57

The data are normalized to Fe and reported on a rock-equivalent (flux-free) basis. All data are expressed in ppm except as noted. Column headings: 1: Mass (resolution), 2: RTS-3, 3: RTS-4, 4: CPB-1, 5: CZN-1, 6: MP-1, 7: HV-1, 8: GXR-1, 9: GXR-4, and 10: STDGL-1. Column 1 indicates the mass and resolution used for the analysis, where L stands for low resolution, and M, medium resolution.

TABLE 2. XRF DATA ON MAJOR- AND TRACE-ELEMENT CONSTITUENTS IN ORE STANDARDS

	1	2	3	4	5	6	7	8	9
Na_2O wt%	0.74	0.10				2.99		0.74	<0.1
MgO wt%	4.12	0.37		0.31	0.13	0.72	0.32	2.91	0.08
Al_2O_3 wt%	9.10	0.65	0.27	0.25	6.32	14.49	6.57	16.1	0.53
CaO wt%	3.27	0.46	0.90	0.24	4.4	1.75	1.29	1.39	0.39
S wt%	10.01	35.8		30.1	11.6	0.345		1.80	24.94
P	395	<200			260	570	700	1350	131
K	3550	500	420	460	1160	29100	830	39850	4151
Ti	3140	898	600	180	600	1380	420	2760	780
V	108	43	5	<3	4	54	86	92	
Mn	2000	150	620	2310	430	260	845	150	620
Fe	209900	544400	84630	109200	51100	14200	251000	30080	451700
Co	262	185					7.2	13.8	
Ni	82		10	28	53	6	42	41	
Cu	2830	337		1400	20300		1270	6460	500
Zn	2120	207		458000	153000	43	870	73	103300
Ga							16	20	
As	7	222	709	323	6300	4	447	101	300
Se	68	76			7.5	1.2	17.3	5.6	
Rb	10.1	3.1				48	14	148	
Sr	41	9		3	6	466.00	279	229	
Zr	75	9		17	121	59.00	39	211	
Mo	2.4	4	22	7	123	543	21	330	
Cd	9.1	<2	139	1274		<1	3	<1	
Ag	14.2	<3	600	99	53	2	35	5.4	
Sn	280	<2	192	54		3	58	7.2	
Sb	2.2	<2	3570	602		<2	132	4.6	
Ba	111	35	10	18		808	670	1810	
Tl								3.0	
Pb	142	47		77200	17700	11.3	833	50	17300
Bi	91	2	210	28	154	<2	1700	19	
U	<2	<2					36	6.1	

Data in ppm except as noted. Column headings: 1: RTS-3, 2: RTS-4, 3: CPB-1, 4: CZN-1, 5: MP-1, 6: HV-1, 7: GXR-1/1720, 8: GXR-4/542, 9: STDGL-1.

these analyses, a 0.1 g aliquot of each glass disc was powdered and dissolved in dilute HNO_3. Each solution was brought to a dilution factor of 0.1% total dissolved solids (flux + sample) and spiked with 10 ppb Rh as an internal standard to correct for instrument drift. A 10 ppb synthetic multi-element solution was used for calibration of instrument sensitivity. The following elements were analyzed in low-resolution mode: Rb, Sr, Zr, Mo, Ag, Sb, Ba, Tl, Pb, Bi, and U. The following elements were run in medium-resolution mode: Na, Mg, Al, P, S, Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, and As. Each solution was analyzed twice, and the average is reported here. As for the LA–ICP–MS analyses, the solution data on the fused glasses were normalized to Fe, and the results reported on a rock-equivalent (*i.e.*, flux-free) basis.

Solution ICP–MS analysis of rock powders

An independent set of solution ICP–MS data on unfused whole-rock powders of the ore standards was obtained using the Agilent HP4500 quadrupole ICP–MS. Solutions were prepared by dissolving 0.02 g of each sample in aqua regia followed by HF–HNO_3, and diluting the solution to 100 mL (dilution factor 5000×) with a final concentration of acid of 2% HNO_3. A high dilution-factor was used for these experiments in order to minimize matrix effects. Samples were dissolved in duplicate, and the average results are reported here. A 10 ppb multi-element solution was used for calibration, with corrections applied for procedural blanks and for instrument drift based on replicate analyses of the calibration standard. No internal standards were used for these analyses.

X-ray fluorescence

The XRF data were obtained on fused lithium borate discs (major elements) and pressed powders (trace elements). Fusion discs were prepared as described above. Pressed powder pills (32 mm in diameter) were prepared by mixing 10 g of sample powder with a PVP–MC (polyvinylpyrrolidone–methylcellulose) binder, and compaction at 3.5 tonnes cm^{-2} (Watson 1996). A Philips PW1480 wavelength-dispersion X-ray spectrometer with a ScMo tube was used for all elements except V, Ag, Sn, Sb, and Ba (Au tube) and Mo (Rh tube). $K\alpha$ lines were used for all elements except As ($K\beta$), Bi and Ba ($L\alpha$) and Pb ($L\beta$). We used a mixture of pure oxides and silica as calibration standards, along with a large range of international and in-house reference rocks and minerals. Line-overlap corrections were determined from very pure chemicals mixed with silica. Corrections for mass absorption were calculated using Philips X40 software with De Jongh's calibration model and Philips alpha coefficients. Compton scattering was also used for many trace elements.

RESULTS

Results of the LA–ICP–MS, solution ICP–MS, and XRF analyses are presented in Tables 1–4. This study provides a considerable amount of new information about the compositions of these international standard reference-materials, as few data exist in the literature for some of these standards, *e.g.*, HV–1 and MP–1. Element concentrations in these materials span a broad range, *e.g.*, Zn, Pb, As, Sb, Sn, and Bi concentrations each extend over 3–4 orders of magnitude. Concentrations of 33 elements were determined by the various techniques employed in this study. The dataset includes lithophile elements found predominantly in the silicate, carbonate, phosphate, or oxide fraction (Al, Ca, Mg, Na, K, P, Mn, Ti, V, Ga, Ge, Rb, Sr, Zr, Ba, U), base and precious metals (Cu, Zn, Pb, Ag), and other chalcophile elements, with a variety of lithological affinities and potential economic significance (S, Ni, Co, As, Se, Mo, Cd, In, Sn, Sb, Te, Tl, Bi). In the following section, we discuss these results in terms of: (1) sensitivity and precision of the LA–ICP–MS analyses, (2) effects of operating the laser in line scan *versus* fixed-spot mode, and (3) a comparison of results among the different analytical methods.

DISCUSSION

LA–ICP–MS: sensitivity, precision, detection limits

Relative sensitivity (cps/ppm) for the LA–ICP–MS analyses showed a typically flat mass-response pattern that varied from ~800–1000 cps/ppm for light-mass elements such as Mg and Al, up to ~2000–5000 cps/ppm for heavy-mass elements such as Pb and Bi. Figure 1 shows typical mass-response curves for different operating conditions of the laser, based on replicate analyses of the standard glass STDGL–1. Structure in these curves, *e.g.*, the low sensitivity for S, Zn, As, and Sb relative to adjacent elements, primarily reflects differences in the ionization efficiency of these elements in the plasma. These curves are based on absolute concentrations in the fused glasses rather than rock-equivalent compositions.

Replicate analyses of the fused glasses by LA–ICP–MS indicate typical 1σ RSD values of 2–8% relative for rock-equivalent concentrations >1 ppm (Table 3). The 16 analyses of STDGL–1 that were used for calibration of the LA–ICP–MS data show 1σ RSD values for each element ranging from 1.0 to 8.1%, with an average value of 3.4%. For these analyses, relative precision was <2% (1σ RSD) for Ti, Mn, Co, Ni, Cu, Zn; 2–5% for MgO, Al_2O_3, S, CaO, V, As, Ag, Sb, Ba, Au, Pb, and Bi, and 5–8% for Sn, Mo, and Tl, with the relatively low count-rates for Mo and Tl accounting for the higher RSD values for these elements. These RSD values are comparable to those found in previous studies using LA–ICP–MS analyses of fused silicate rocks (Sylvester 2001). However, the replicate calibration analyses of STDGL–1 show a greater scatter (*i.e.*, larger RSD) than would be expected simply from counting statistics, as approximated by 1/√cps (Fig. 2). This finding contrasts with results for the NIST 612 glass

TABLE 3. RESULTS OF LASER-ABLATION ICP–MS ANALYSES
OF FUSED ORE STANDARDS

			RTS-3			RTS-4			CPB-1			CZN-1		
	mass	DL	avg	1σ	CIV	avg	1σ	CIV	avg	1σ	CIV	avg	1σ	CIV
MgO	25	5.5	4.1	0.2	4.1	0.32	0.01	0.30	0.16	0.01	*0.15*	0.32	0.01	*0.32*
Al_2O_3	27	2.0	8.0	0.3	9.1	0.70	0.03	0.64	0.32	0.01	0.28	0.27	0.01	0.25
CaO	44	80	3.2	0.2	3.1	0.57	0.04	0.46	0.89	0.07	*0.88*	0.31	0.03	*0.25*
S wt%	34	0.55	10.2	0.6	10.0	36.7	1.8	35.9	19.1	1.8	17.8	19.8	1.7	30.2
Ti	47	3.7	2346	126	*3200*	971	21	*800*	444	21		499	49	
V	51	0.2	98	2		49	2		12	1		13	2	
Mn	55	4.0	1890	33	*2000*	132	3	*150*	400	3	390	2234	81	2190
Fe wt%	57	120	21.04	IS		56.70	IS		8.43	IS		10.93	IS	
Co	59	0.2	272	7	260	207	3	186	3.9	0.1		8.3	0.3	
Ni	60	1.1	103	2	71	7974	174	7940	55	1		41	3	
Cu	65	1.5	2717	150	2820	290	12	280	2233	67	2540	1378	39	1440
Zn	66	3	1996	92	1850	209	12	158	45858	1297	44200	397661	25685	447400
As	75	0.9	15.0	0.8	9	267	14	207	593	25	560	267	25	260
Mo	98	1.2	6.2	0.4		6.7	0.4		6.2	0.3		9.9	0.6	
Ag	107	0.2	13.9	0.6	*<8*	2.2	0.1	*<2*	589	21	626	92	8	93
Sn	118	0.4	293	10		8.7	0.7		218	10	190	84	4	65
Sb	121	0.3	2.7	0.2		0.7	0.2		3729	156	3600	573	36	520
Ba	138	0.2	154	5	*98*	41	2	*27*	14.6	0.5		14.1	0.7	
Tl	205	0.07	2.7	0.1		0.21	0.05		38	2		6.63	0.59	
Pb	208	0.2	185	4	146	84	3	60	637934	18683	647400	75198	5413	74500
Bi	209	0.03	97	5	*100*	3.6	0.3	*3*	230	5	230	23	2	27

			MP-1			HV-1			GXR-1			GXR-4		
	mass	DL	avg	1σ	CIV	avg	1σ	CIV	avg	1σ	CIV	avg	1σ	CIV
MgO	25	5.5	0.03	0.01	*0.01*	0.52	0.01	*0.56*	0.35	0.02	*0.36*	3.0	0.1	2.8
Al_2O_3	27	2.0	6.0	0.4	*6.9*	11.1	0.2	*12.5*	5.8	0.2	*6.6*	13.7	0.5	13.6
CaO	44	80	4.3	0.4	*4.7*	1.6	0.1	*2.0*	1.12	0.10	*1.34*	1.34	0.02	1.41
S wt%	34	0.55	13.3	0.8	*11.8*	<0.5		*0.35*	<0.3		*0.26*	1.70	0.17	1.77
Ti	47	3.7	852	29	*700*	1178	9	*1450*	537	32	*380*	2222	84	2870
V	51	0.2	18	1		57	1	*70*	81	2	*80*	95	4	87
Mn	55	4.0	403	13	*500*	261	5	*280*	797	12	*880*	157	2	150
Fe wt%	57	120	5.68	IS		1.42	IS		23.60	IS		3.09	IS	
Co	59	0.2	3.5	0.3		3.2	0.1		8.1	0.2	*8.2*	15.0	0.4	15
Ni	60	1.1	34	2		30	2		58	3	*41*	59	1	42
Cu	65	1.5	21857	1086	20900	5063	183	5200	1090	17	*1110*	6160	308	6520
Zn	66	3	162161	8909	159000	78	3		772	47	*760*	90	4	73
As	75	0.9	8222	345	7700	8.9	0.6		410	12	*427*	109	6	98
Mo	98	1.2	144	10	140	607	22	580	23	1	*18*	427	14	310
Ag	107	0.2	64	2	58	3.0	0.1		32	2	*31*	4.1	0.3	4
Sn	118	0.4	22965	1412	24300	12.7	0.3		59	3	*54*	15	1	5.6
Sb	121	0.3	25.1	1.9		1.3	0.1		118	5	*122*	4.4	0.2	4.8
Ba	138	0.2	10.7	0.5		1204	22	*810*	989	30	*750*	2558	142	1640
Tl	205	0.07	0.82	0.05		0.14	0.01		0.12	0.02	*0.39*	1.2	0.1	3.2
Pb	208	0.2	18848	829	18800	53	8		815	54	*730*	75	4	52
Bi	209	0.03	232	9	240	1.6	0.1		1478	78	*1380*	19.1	0.6	19

The data are expressed in ppm, except as noted, and represent an average result of eight analyses per sample, except HV-1 (n = 4) and Pb for CPB-1 and CZN-1 (n = 4). IS indicates the value of Fe used for internal standardization. DL represents average detection-limits (ppm) for 80 analyses calculated on a rock-equivalent (flux-free) basis. Detection limits for Mg, Al, Ca, and Fe given as ppm of the elemental abundance. CIV are certified or information (italics) values from references cited in the text.

described by Norman *et al.* (1996), and indicates that other sources of uncertainty, such as sample heterogeneity, element fractionation, or instrumental instability (ICP–MS or laser) also contribute to the reproducibility of the LA–ICP–MS data for this glass.

Detection limits for each individual LA–ICP–MS analysis are calculated from the gas background and apparent sensitivity of the calibration standard following the approach of Longerich *et al.* (1996). Average detection-limits calculated on a rock-equivalent (flux-free) basis for the approximately 80 LA–ICP–MS analyses obtained for this study are given in Table 3. These rock-equivalent detection limits are somewhat arbitrary, as they depend on the ratio of sample to flux, but they do provide a realistic basis for evaluating the technique. Actual concentrations of trace elements in the glass disc are ~10× lower than the rock-equivalent abundances used for calibration values, so detection limits based on absolute concentrations in the glass would be lower than those shown in Table 3 by a factor of ~10. For example, detection limits based on absolute analytical sensitivity and not corrected for dilution of the sample with flux would be 550 ppm for S and 12 ppm for Fe, extending down to values as low as 3 ppb for Bi and 7 ppb for Tl (Table 3). This example demonstrates the ability of high-sensitivity LA–ICP–MS instrumentation to obtain useful precision even at very low concentrations.

TABLE 4. SOLUTION ICP–MS DATA ON POWDERED ORE STANDARDS, OBTAINED USING A QUADRUPOLE ICP–MS APPARATUS

	mass	RTS-3	RTS-4	CPB-1	CZN-1	HV-1	MP-1	GXR-1	GXR-4
Mn	55	2019	128	512	2973	266	439	966	147
Co	59	293	209	4.6	10	2.9	3.0	8.9	14
Ni	60	75	8220	8.6	8.4	6.2	14	43	38
Ge	73	18	22	4.5	6.6	3.0	4.9	11	3.4
As	75	13	252	745	360	5.9	8835	468	102
Se	77	65	61	33	6.1	1.1	13	16	6.1
Sr	88	41	8.7	3.2	2.6	436	6.9	307	217
Mo	95	2.5	2.2	1.2	6.0	576	141	20	321
Cd	111	9.5	0.9	176	1596	0.4	596	2.7	0.4
In	115	3.2	0.03	13	104	0.1	746	1.1	0.2
Sn	118	66	0.4	214	60	2.8	3490	49	6.5
Sb	121	2.2	0.3	4188	625	1.2	25	120	4.2
Te	125	8.1	0.8	0.6	0.1	0.3	3.2	14	0.8
Tl	205	4.6	0.2	37	13	0.2	0.8	0.4	2.9
Bi	209	92	2.6	230	25	1.3	240	1546	18

All data in ppm.

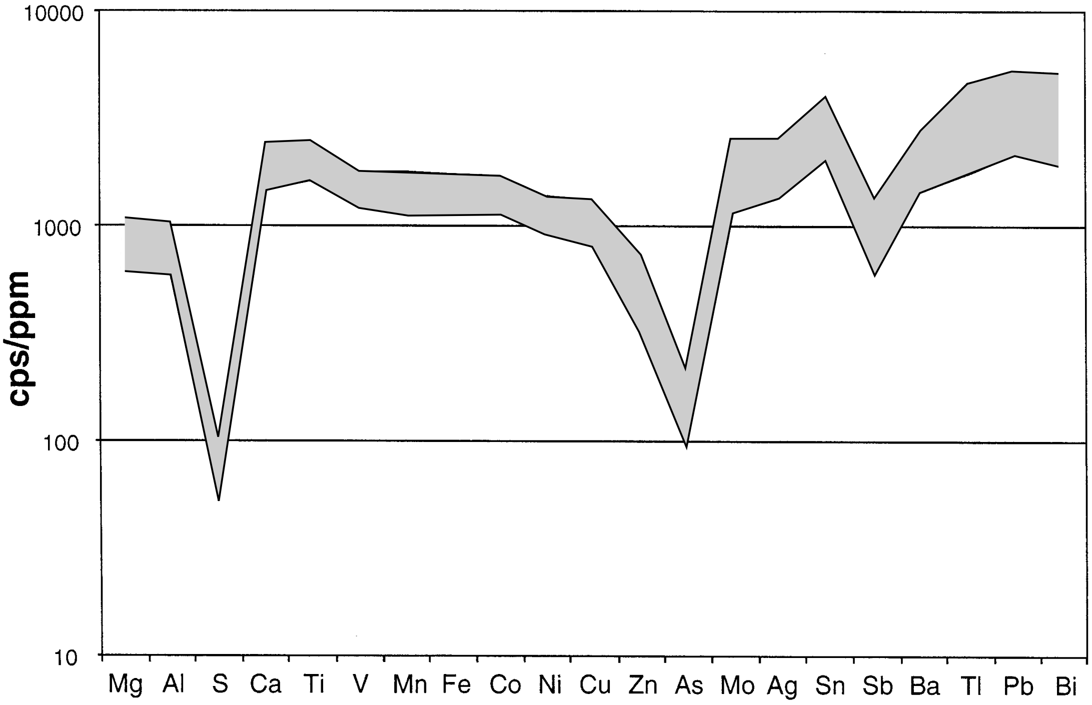

FIG. 1. Relative sensitivities (cps/ppm) of the elements determined on sulfide ores by laser-ablation ICP–MS analysis of fused glasses. Data are based on absolute abundances in the glass and have been normalized for isotopic abundance. The grey field represents the range encountered for the calibration standard STDGL–1 during this study.

Line scan versus fixed-spot mode

The effect of performing LA–ICP–MS analyses with the laser operated in a fixed spot *versus* line-scan mode was evaluated by calibrating results of spot analyses of the STDGL–1 glass against results for this same material analyzed with a line scan. Two experiments were conducted on different days. In the first experiment, both the spot and line-scan analyses were obtained with the laser operating at 4 Hz and a beam diameter of 100 μm. In the second experiment, both spot and line-scan analyses used a beam 50 μm in diameter, but the line-scan analyses were obtained at 5 Hz, and the spot analyses, at 4 Hz. For the line-scan analyses, the sample was traversed under the laser beam for a distance of about 250 μm during a one-minute analysis. In both experi-

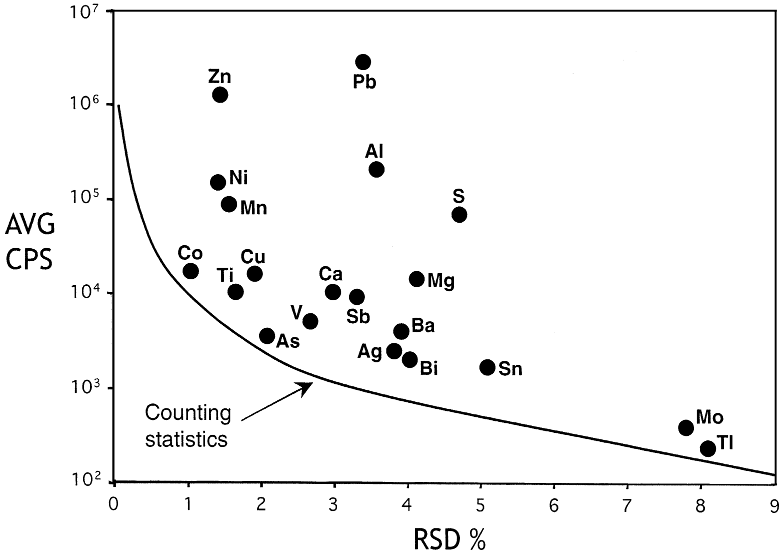

FIG. 2. Analytical precision, as indicated by the 1σ RSD of replicate analyses of the calibration standard STDGL–1, exceeds that expected from counting statistics, indicating additional sources of analytical error.

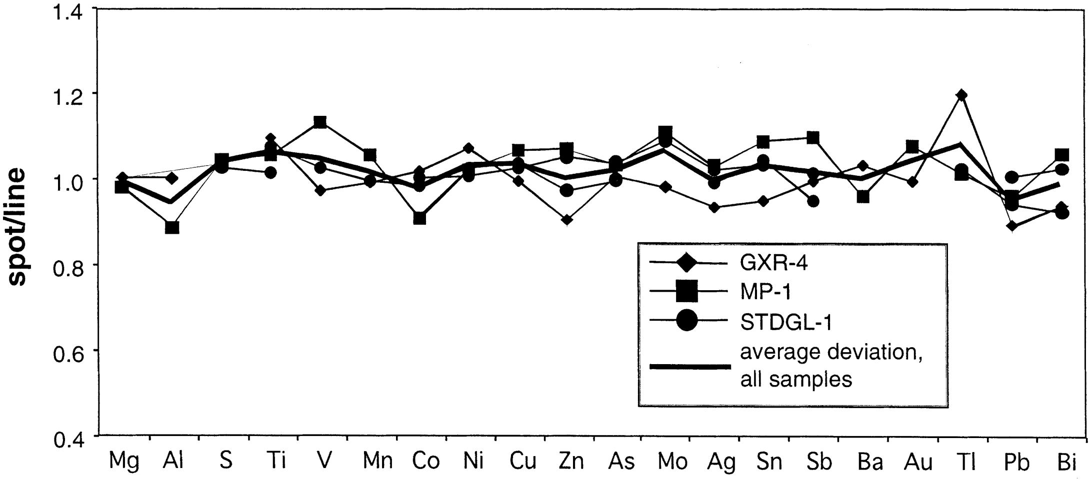

FIG. 3. A comparison of relative sensitivities (cps/ppm) of the various elements determined by LA–ICP–MS, with the laser operated in fixed-spot mode and line-scan mode.

ments, four line-scan analyses were used for calibration, and 4–5 analyses as unknowns were obtained in fixed-spot mode. Results of the spot analyses were averaged and compared with the calibration values used for STDGL–1 (Fig. 3). In addition, two samples (MP–1, GXR–4) were analyzed in both fixed-spot and line-scan modes, against calibration analyses of STDGL–1 analyzed in the same way (*i.e.*, fixed spot *versus* line scan) as the unknowns. The line scans were obtained with the laser operating at 10 Hz with a beam 50 μm in diameter, and the spot analyses were obtained with a beam 100 μm in diameter and a laser-repetition rate of 5 Hz.

The fixed-spot and line-scan data are compared in Figure 3. Relative deviations of the STDGL–1 data obtained in fixed-spot mode range from 0.98 to 1.09 that of the calibration values obtained in line-scan mode, with an average value of 1.02 for all elements. Similar results were obtained for the analyses of MP–1 and GXR–4, with average results for both line-scan and fixed-spot modes agreeing to within 10% (Fig. 3). This is within the 3σ RSD for all elements sought here, suggesting little if any significant or systematic difference in the absolute values obtained by spot *versus* line-scan analysis of this material. The most noticeable difference is a tendency for the line-scan results to generate smoother signals with a somewhat higher average count-rate, producing better detection-limits and relative precision, especially for samples that ablate poorly in fixed-spot mode.

Comparison of the methods

The data obtained by LA–ICP–MS on the fused ores agree well with those collected by the other methods and with the reference values for these materials over several orders of magnitude. A comparison of element abundances obtained by the various methods are presented in Figures 4–9. These data demonstrate excellent correspondence of the LA–ICP–MS data with those obtained by other methods. This finding includes major constituents such as Al_2O_3, CaO, and MgO (Fig. 4), which are present at levels ranging from 0.1 to 10 wt% (rock equivalent), as well as a wide variety of lithophile and chalcophile trace elements. This study demonstrates the accuracy of the LA–ICP–MS technique relative to the other methods, and establishes a useful inter-laboratory calibration for the methods applied here.

Of particular interest for ore-deposit studies is the excellent agreement for base and precious metals such as Cu, Pb, Zn, Ag, and Mn, which vary over several orders of magnitude among the samples (Figs. 4, 5, 6). The concentrations of Cu and Ag are especially well correlated among the various techniques and agree well with the reference values (Fig. 6). At low concentrations

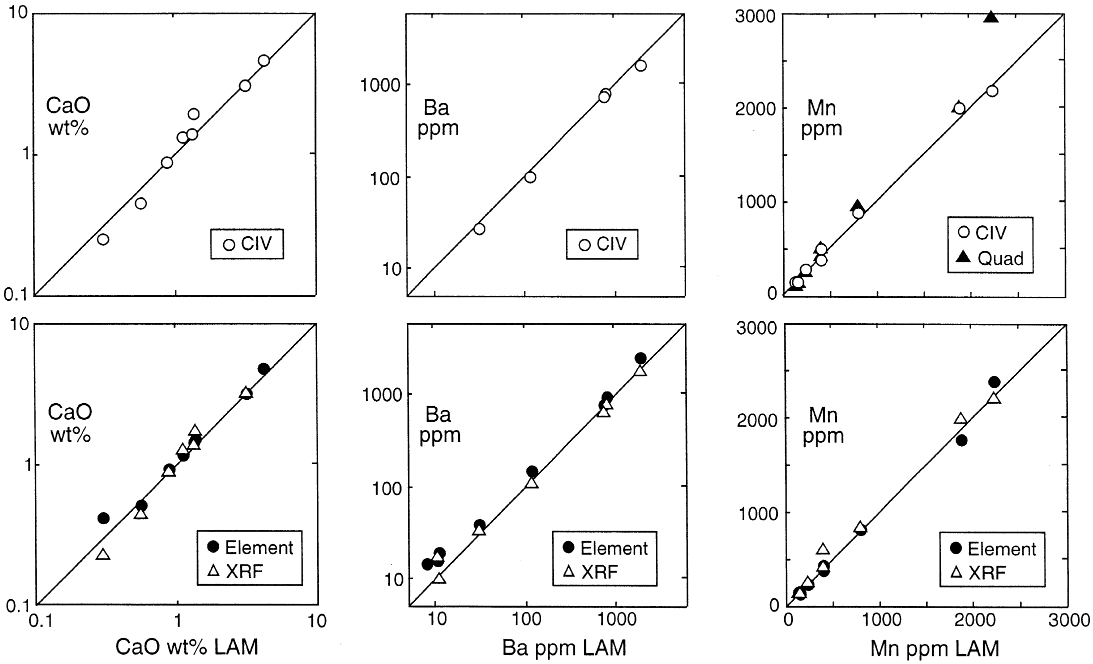

FIG. 4. A comparison of results for CaO, Ba, and Mn obtained on the fused sulfide ore standards by LA–ICP–MS with reference values for these materials (CIV; open circles), solution ICP–MS analysis of the fused glasses (filled circles), XRF (open triangles), and solution ICP–MS of unfused whole-rock powders (filled triangles).

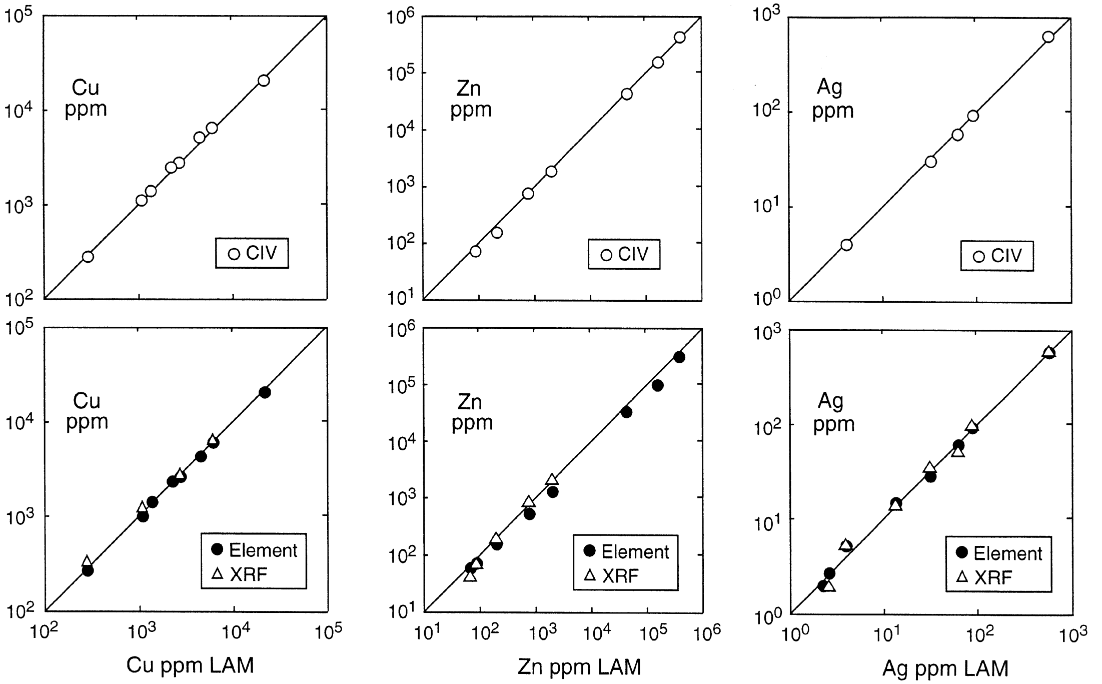

FIG. 5. A comparison of results for Cu, Zn, and Ag obtained on the fused sulfide ore standards by LA–ICP–MS with reference values for these materials (open circles), solution ICP–MS analysis of the fused glasses (filled circles), and XRF (open triangles).

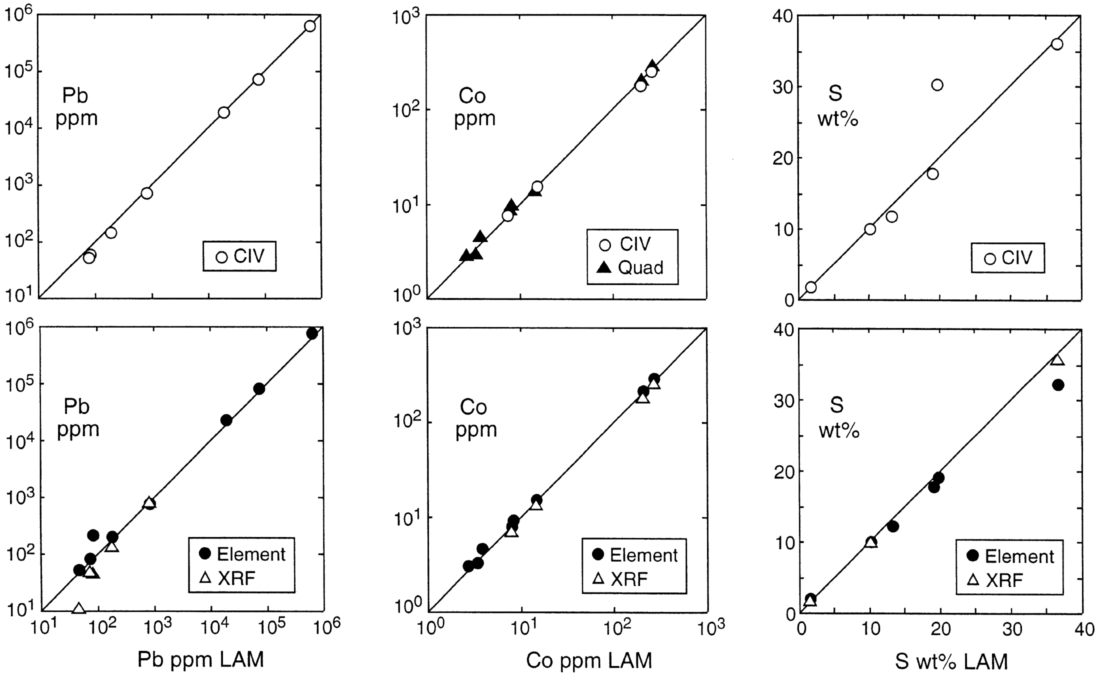

FIG. 6. A comparison of results for Pb, Co, and S obtained on the fused sulfide ore standards by LA–ICP–MS with reference values for these materials (open circles), solution ICP–MS analysis of the fused glasses (filled circles), XRF (open triangles), and solution ICP–MS analysis of whole-rock powders (filled triangles).

of Pb, data for the fused glasses by both LA–ICP–MS and solution ICP–MS show elevated concentrations relative to results by XRF and the reference values (Fig. 7), possibly indicating Pb contamination introduced during preparation of the glasses. There is a tendency for the magnetic sector ICP–MS analysis of the dissolved fused discs to show systematically lower Zn values relative to the other methods, perhaps indicating suppression of the Zn signal in the lithium borate matrix or an offset in the calibration values used for these analyses (Fig. 5).

Other chalcophile elements that may be useful for exploration or petrogenetic studies of ore deposits, such as As, Sb, Bi, and Co, also show very good agreement among the different methods over concentration ranges extending over three or four orders of magnitude (Figs. 6, 7). This agreement demonstrates the robust linear response of the instrument and the ability to obtain useful data for materials with diverse compositions using a single calibration standard. Sulfur contents determined by LA–ICP–MS on the fused glasses show good agreement with reference values and data obtained on the same fused glass discs using the magnetic sector ICP–MS (Fig. 6), despite the relatively poor sensitivity of S by ICP–MS and the need to use a minor isotope (^{34}S) on the quadrupole ICP–MS due to a major interference from $^{16}O_2$ on ^{32}S. Cadmium, In, and Se show good agreement among the data obtained by XRF, solution ICP–MS on whole-rock powders, and the reference values (Fig. 8). These elements were not determined by LA–ICP–MS for this study. Our XRF and solution ICP–MS results suggest that the information value of 100 ppm Se for RTS–4 is probably too high (Fig. 8). Barium also shows excellent agreement among all of the methods used for this study (Fig. 4).

For Sn, Mo, Ni, and Tl, there is good agreement among the various methods at high concentrations, and systematic differences at low concentrations (Figs. 8, 9). Both LA–ICP–MS and solution ICP–MS results on the fused discs show systematically higher Sn, Mo, and Ni at low concentrations compared to XRF and solution ICP–MS analyses on whole-rock powders, whereas the XRF and solution ICP–MS data on the whole-rock powders tend to agree well at low concentrations (Figs. 8, 9). At higher concentrations of these elements, results by all methods converge on the reference values. The discrepancies for Sn, Mo, and Ni at low concentrations may be due to contamination of the samples during fusion, as these elements are known to react with platinum crucibles (Norrish & Thompson 1990). Two samples with moderate to high contents of Sn (MP–1, RTS–3) also show anomalously low values by solution

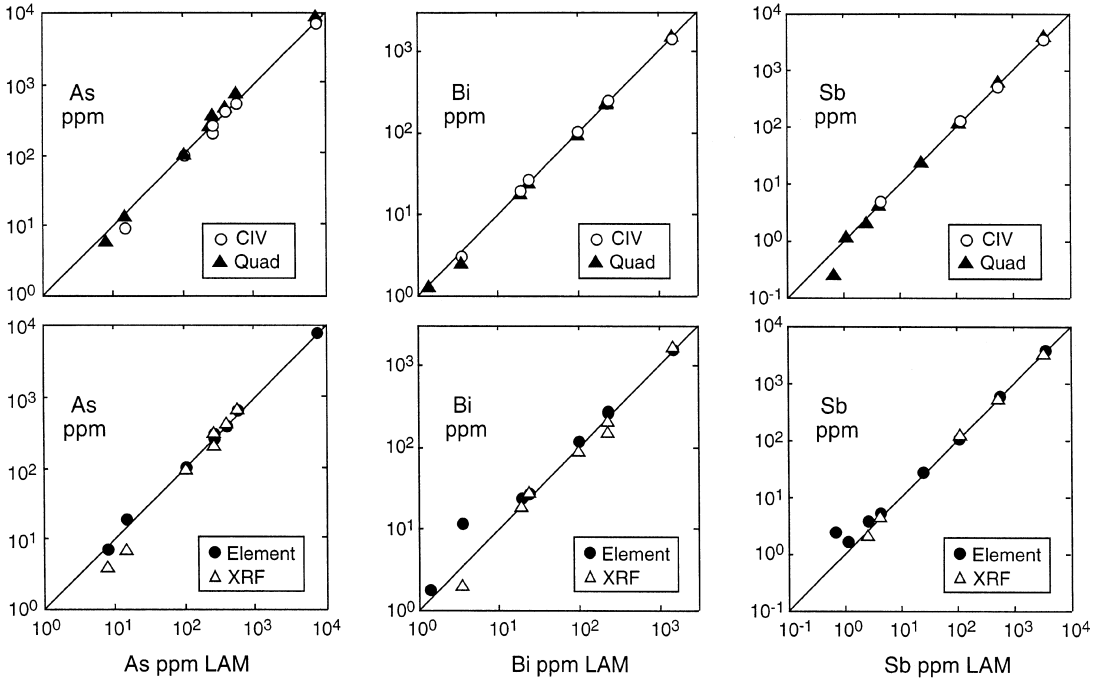

FIG. 7. A comparison of results for As, Bi, and Sb obtained on the fused sulfide ore standards by LA–ICP–MS with reference values for these materials (open circles), solution ICP–MS analysis of the fused glasses (filled circles), XRF (open triangles), and solution ICP–MS analysis of whole-rock powders (filled triangles).

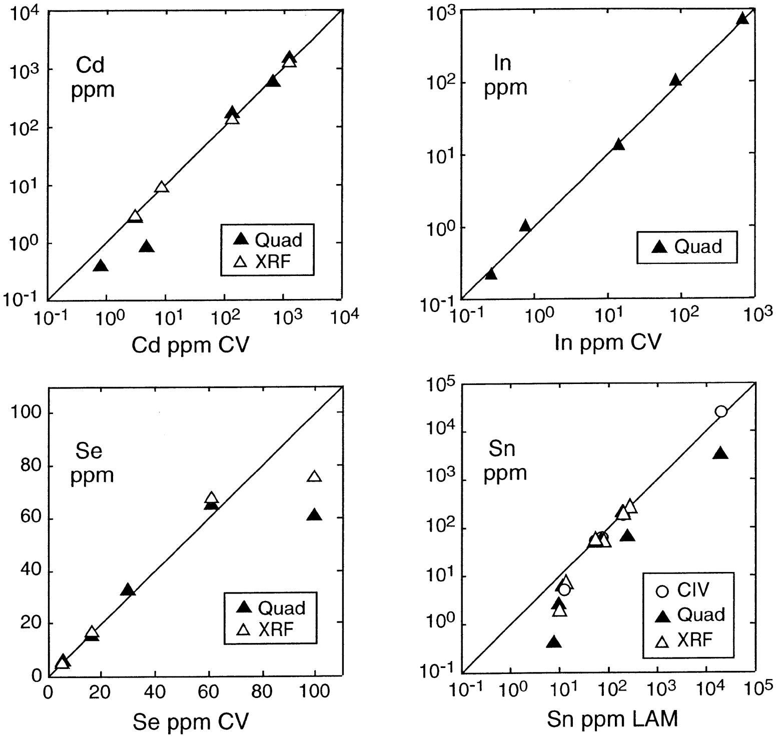

FIG. 8. A comparison of results for Cd, In, Se, and Sn obtained on the sulfide ore standards by solution ICP–MS analysis of whole-rock powders (filled triangles) with data obtained by LA–ICP–MS, XRF, and the reference values for these materials.

ICP–MS analysis of whole rock powders (Fig. 8), probably owing to incomplete dissolution of Sn-bearing phases such as cassiterite during acid digestion of these samples. This situation is especially likely to be a problem for MP–1 (reference value: 24300 ppm), which is known to contain Sn mineralization (CANMET 1972).

The LA–ICP–MS and whole-rock solution data for Tl show good agreement (Fig. 9), especially considering the low absolute concentrations present in the fused discs (down to 10 ppb actual concentrations in the glass). In the samples with the lowest Tl concentrations (HV–1, MP–1, RTS–4), the solution ICP–MS data for the fused discs are systematically high compared to those obtained by LA–ICP–MS (Fig. 9), whereas all of the datasets converge on GXR–4/542, which has the highest Tl content (3.2 ppm). A more detailed evaluation of the Tl data is limited by the lack of consensus or certified values for these materials. Additional work is needed to resolve this and the other discrepancies present at low concentrations for some elements. For many ore-deposit studies, however, relatively small differences in absolute values at low concentrations will not significantly alter the interpretations.

CONCLUSIONS

Whole-rock major- and trace-element compositions of a diverse suite of standard reference materials representing sulfide ores and related rock-types have been measured by laser-ablation ICP–MS (LA–ICP–MS) analysis of fused lithium borate glasses. A comparison with results obtained by solution ICP–MS and XRF demonstrates the accuracy of the LA–ICP–MS technique. Replicate analyses indicate a precision of 2–8% relative (1σ RSD) for the LA–ICP–MS data at concentrations above 1 ppm rock-equivalent, corresponding to actual concentrations of >0.1 ppm in the fused glasses after dilution with flux.

A wide range of bulk compositions can be analyzed using the LA–ICP–MS method described here, including Pb–Zn sulfides, Fe sulfides, Cu–Mo sulfides, and silicates. This sampling covers the range of compositions likely to be encountered in many ore-deposit studies. The good agreement of results for these diverse compositions shows that matrix effects are not a significant problem at the scale of compositional variation represented by these samples. No significant differences in the results were found with the laser operating in either line scan or fixed-spot mode. The LA–ICP–MS analysis of fused glasses overcomes problems related to insoluble phases such as cassiterite, which demonstrably affect solution ICP–MS analysis of whole-rock powders. Minor discrepancies among the various techniques were found for some elements (Sn, Mo, Ni, Tl) at low concentrations, possibly owing to incomplete dissolution of resistant phases or contamination acquired during the fusions. Whole-rock analysis using LA–ICP–MS analysis of fused samples provides a fast and convenient method for measuring concentrations of trace elements in both sulfide ores and silicate rocks without the need for wet-chemical dissolution.

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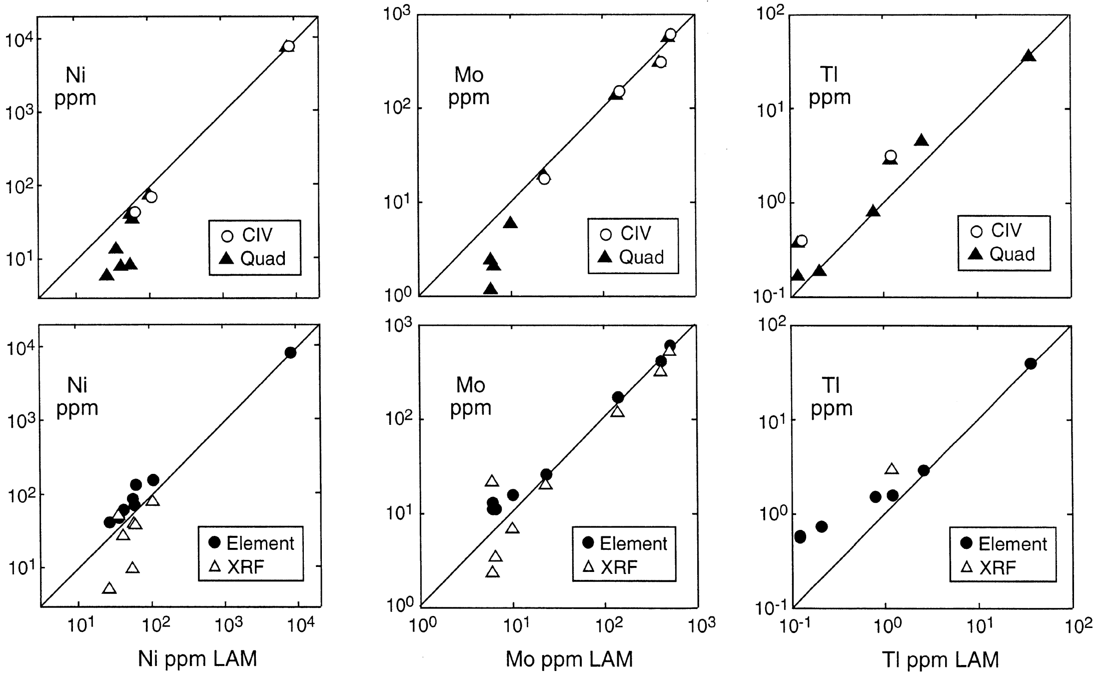

FIG. 9. A comparison of results for Ni, Mo, and Tl obtained on the sulfide ore standards by LA–ICP–MS with reference values for these materials (open circles), solution ICP–MS analysis of the fused glasses (filled circles), XRF (open triangles), and solution ICP–MS analysis of whole-rock powders (filled triangles).

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