Microchim Acta (2008) 160: 153–163
DOI 10.1007/s00604-007-0819-7
Printed in The Netherlands

Microchimica Acta

Original Paper

Laser-ablation ICP-MS analysis of siliceous rock glasses fused on an iridium strip heater using MgO dilution

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Received 1 February 2007; Accepted 5 June 2007; Published online 31 July 2007

Abstract. Trace element determination in rocks by fusion on an iridium strip heater followed by LA-ICP-MS analysis of the glass beads is extended here to SiO_2-rich rocks; rapid fusion of samples with >55 wt% SiO_2 is facilitated by dilution by high purity MgO. The method developed here can rapidly and accurately determine numerous trace elements in a large range of rock compositions in a short time (about 50 samples/day). Systematic evaluation for a large range of rock compositions (natural rocks and reference materials AGV-2, GSP-2, JG-1a) with SiO_2 contents between 45 and 80 wt% shows that reproducibility and accuracy within 10% can be routinely achieved for most of the 28 trace elements investigated (Rb, Sr, Cs, Ba, Ti, Zr, Hf, Nb, Ta, Sc, V, Cr, Ni, Pb, Th, U, REE). The 40 mg sample size is smaller than for XRF, INAA or solution-ICP-MS, detection limits are lower, and trace element palettes more complete than XRF and INAA. This microchemical method is thus attractive for the analysis of all natural geological materials as well as for experimental applications with small samples. Samples with SiO_2-contents >55 wt% require hot and long melting to achieve homogeneous glasses and eliminate all residual minerals, particularly refractory accessory phases. Melting conditions of 1600 °C and 20 s for samples are recommended for SiO_2 contents between 55 and 70 wt%, whereas 1800 °C and 20–30 s are often required for samples with >70 wt% SiO_2. Problems are encountered for Pb and Cs due to volatilization on the Ir strip, for Sc due to interferences, and Zr and Hf due to their sequestration in refractory accessory minerals.

Keywords: Iridium strip heater; LA-ICP-MS; geochemistry; trace elements; glass

Introduction and summary of previous studies

Precise determination of bulk rock trace element contents is required for most geochemical studies. Several standard analytical techniques for trace element analysis are available (e.g. XRF, ICP-MS, INAA), which have particular advantages and disadvantages in routine use. Amongst the disadvantages are the need for chemical dissolution of samples and problems of incomplete dissolution (ICP-MS), high detection limits (XRF) or time consuming processing (INAA). A relatively new and rather simple microanalytical tool for trace element determination is direct fusion of rock powder on an Iridium strip heater and analysis of trace elements by Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS). This method provides low detection limits for a large range of elements and can be performed rapidly and easily, by-passing the need for sample dissolution. This is an improvement

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over the use of lithium borate glasses [1], whose analysis by ICP-MS eliminates the possibility of Li determination and may contaminate the instrument for Li analysis in other samples.

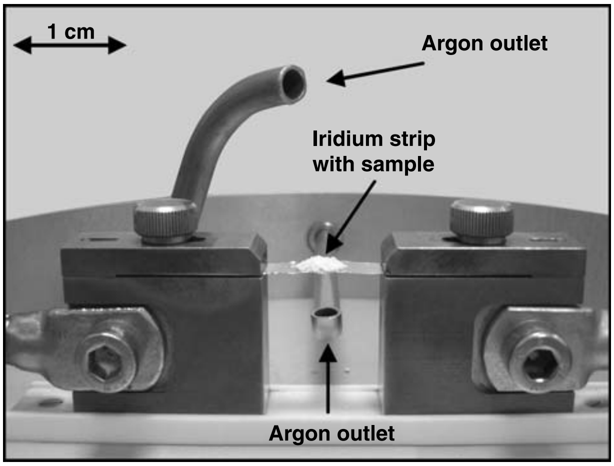

Fig. 1. The strip heater cell at the Department of Geosciences, Johannes Gutenberg-University, Mainz, showing the Iridium strip clamped between two copper electrodes. During fusion and quenching, argon flows through the cell via two outlets to prevent oxidation. An Ar jet directly below the Ir strip helps to quench the glass

The Ir-strip fusion method was first described by Nicholls [2] for determination of major element concentrations on glass beads by electron microprobe and was later extended with slight modification (Tungsten strips) to determine trace element concentrations [3]. The procedure is well established and unproblematic for mafic compositions (<55 wt% SiO_2) that can easily be fused at 1200 °C with routine accuracies better than 10% (pers. comm. K.P. Jochum, Max-Planck-Institute for Chemistry, Mainz). Fusion of siliceous samples is more problematic, because rapid homogenization during melting on the strip is hindered by high melt

Table 1. LA-ICP-MS operating parameters

Laser	new wave UP 213, Nd:YAG laser
Wavelength	213 nm
Pulse energy	0.36–0.45 mJ
Repetition rate	spot: 10 Hz line scan: 20 Hz/20 µm sec^{-1}
Spot size	100 µm
ICP-MS	Agilent 7500ce
Forward power	1200 W
Plasma gas flow (Ar)	15 L min^{-1}
Carrier gas flow (Ar)	1.2 L min^{-1}
Cone material	Ni
ThO^+/Th^+	<0.5%

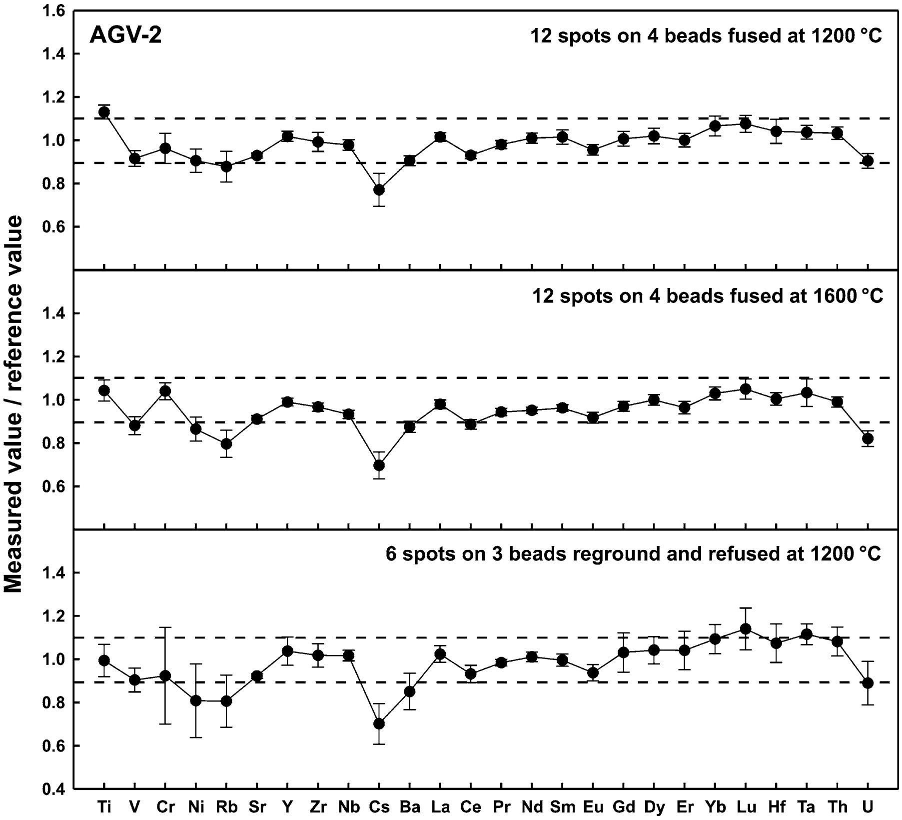

Fig. 2. Data for reference material AGV-2 presented as the ratio of measured value divided by reference value. Stippled lines denote 10% deviation from the reference value. Short melting durations at the lowest temperatures provided the best results for this intermediate rock material

viscosities. Homogeneity in such samples can only be obtained by applying high melting temperatures (1700–1800 °C) and long fusion times (60–120 sec) combined with stirring at high temperatures [2], but this is disadvantageous for elements with high volatility.

Another approach to facilitate rapid fusion and homogeneity is dilution of high SiO_2-concentrations by addition of high-purity MgO [4, 5]. These authors focussed on glass beads of granitic materials for the analysis of major elements by electron microprobe, and discovered that homogeneous beads are best obtained by two sequences of grinding MgO and sample material together in an agate mortar and fusing on the Ir-strip. They documented accuracies better than 5% except for MgO, and encountered problems with trace elements in geochemical reference material JG2; LREE-contents were generally too low, whereas Ni and Cu contents were contaminated by the strip heater electrodes.

In this study, we use an improved Ir-strip heater design with computer-controlled heating and melting under an Ar atmosphere to systematically evaluate melting behaviour of a wide range of rock compositions (55–80 wt% SiO_2) and the dependence of trace element concentrations on the sample/MgO mixing ratio, melting time and melting temperature. The study also employed three commercially available international reference materials (AGV-2, GSP-2 and JG-1a).

Experimental

Instruments and analytical procedure

The Iridium strip heater consists of an Iridium strip (20 mm × 0.5 mm × 0.05 mm in size) clamped between the poles of a

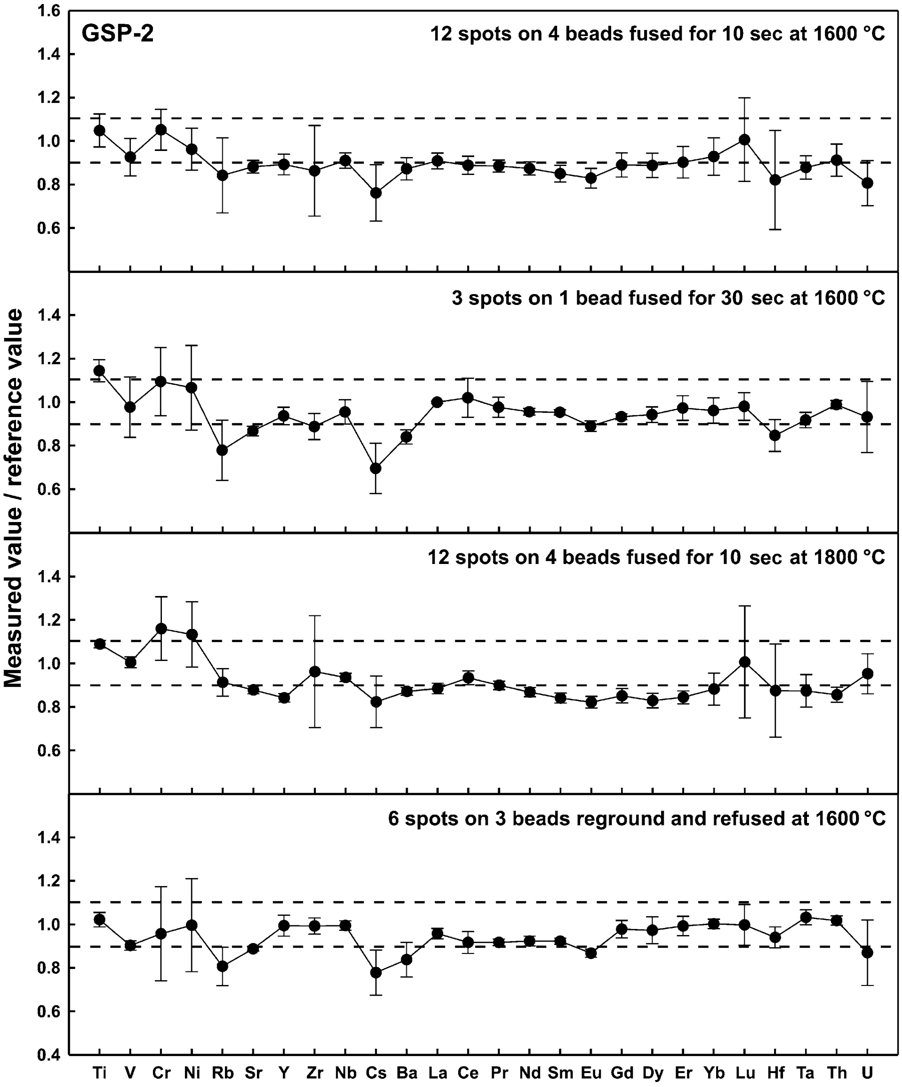

Fig. 3. Data for reference material GSP-2 presented as ratio of measured value divided by reference value. Stippled lines denote 10% deviation from the reference value. Note improvement of results during longer melting (30 sec) and after regrinding and remelting

3 V/250 A electric source, enabling resistance heating (Fig. 1). The heating assemblage is located in a closed chamber flooded with Argon during melting to suppress oxidation of the sample. Temperature is computer-controlled by adjusting the electrical current according to a calibration of melting temperature using a pyrometer. Melts are quenched by a cold argon jet located immediately beneath the Iridium strip.

LA-ICP-MS measurements were performed at the Department of Geosciences, University of Mainz with an Agilent 7500ce quadrupole ICP-MS coupled with a NewWave Research UP-213 laser. Data acquisition was accomplished in peak-jumping mode with one point per peak and 10 msec dwell time. LA-ICP-MS operating parameters are given in Table 1. Background measurements were performed for each analysis for 60 sec prior to ablation. Plasma conditions were adjusted to oxide formation rates below 0.5% (monitored using the 248/232 mass ratio), so that no further oxide corrections were necessary. Either ^{43}Ca or ^{44}Ca were used as internal standards for the geochemical reference materials and most natural samples, whereas ^{29}Si was used as internal standard for samples with less than 1 wt% CaO. Certified glass reference materi-

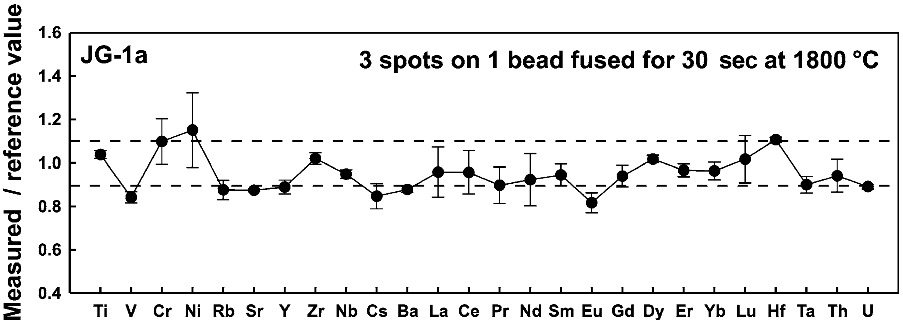

Fig. 4. Data for reference material JG-1a presented as the ratio of measured value divided by reference value. These results within 10% of reference values for this highly siliceous reference material are only obtained if hot and prolonged melting is applied

Table 2. Results obtained for reference material AGV-2. Due to the low SiO_2-content of this samples excellent recoveries are obtained even at low fusion temperature

AGV-2	Reference values		1200 °C 4 beads, $n = 12$			1600 °C 4 beads, $n = 12$		
	Mean	SD	Mean	RSD%	rec.%	Mean	RSD%	rec.%
Li	11	1	10.7	9	97	10.9	10	99
Sc	13	1	15.2	4	117	15.3	3	118
Ti	6300	130	7122	5	113	6570	8	104
V	120	5	110	7	92	106	8	88
Cr	17	2	16.4	13	96	17.7	7	104
Ni	19	3	17.2	11	91	16.4	11	86
Rb	66.7	3.8	58.6	14	88	53.1	14	80
Sr	657	4	610	2	93	598	3	91
Y	18.8	1.5	19.1	4	102	18.6	3	99
Zr	225	14.1	223	8	99	218	4	97
Nb	14.1	0.6	13.8	4	98	13.2	4	93
Cs	1.25	0.08	0.96	17	77	0.87	16	70
Ba	1139	24	1031	4	91	997	5	88
La	36.9	1.3	37.4	3	101	36.1	4	98
Ce	68.8	2.3	64.0	3	93	61.0	4	89
Pr	7.79	0.31	7.63	3	98	7.35	3	94
Nd	30.1	0.5	30.4	4	101	28.6	3	95
Sm	5.4	0.07	5.48	6	101	5.20	3	96
Eu	1.53	0.04	1.46	5	96	1.40	5	92
Gd	4.50	0.05	4.53	6	101	4.36	4	97
Dy	3.44	0.11	3.51	6	102	3.44	4	100
Er	1.80	0.05	1.80	6	100	1.74	5	96
Yb	1.60	0.03	1.71	8	107	1.65	5	103
Lu	0.24	0.01	0.26	6	108	0.25	8	105
Hf	4.97	0.17	5.17	9	104	4.99	5	100
Ta	0.86	0.03	0.89	5	104	0.86	5	103
Pb	13	1	9.49	28	73	8.58	46	66
Th	6.05	0.22	6.25	5	103	5.99	4	99
U	1.82	0.11	1.65	7	90	1.49	8	82

CaO as internal standard measured as ^{43}Ca. All data in μg g^{-1}. Reference values are averages compiled from the GeoReM database [14–17] and from the USGS [27]. rec.% = recovery.

al NIST SRM 612 served as the external standard and was measured at the beginning and at the end of each group of unknowns as well as after every tenth to fifteenth sample measurement during long runs to monitor instrumental drift. Data reduction was carried out using "Glitter" software. Detection limits generally range between 0.001 and 0.5 μg g^{-1}. The elemental concentrations of NIST SRM 612 were taken from Pearce et al. [6] except for Zr for which the preferred value given in the GeoReM database [7] was used. Measured trace elements in NIST SRM 612 have a reproducibility better than 5% (exceptions are Cs, Pb, Th and U at <10%) and correspond within 5% to recommended values.

Instrument performance and stability were monitored by repeated measurements of USGS basaltic reference glass BCR-2G during the analytical sessions. Reproducibility on BCR-2G is better than 10% except for Ni (16%) and Pb (11%), and measured concentrations generally agree within 10%.

In addition to the determinations on Ir-strip glasses, several samples were analysed for comparative purposes for rare earth elements (REE) and Y by solution ICP-MS after Li-metaborate fusion [8], and for Sc, V, Cr, Ni, Zr, Sr and Ba by XRF (MagiXPro) on pressed powder tablets. After Li-metaborate fusion the material was dissolved in 0.42 M HNO_3. Solutions were analysed at the Department of Geosciences at the University of Mainz using a VG Elemental Plasma Quad 3 following routine methods. Quantification of element concentration was carried out by external calibration using reference material AGV-2 processed in the same way as the samples. In and Re were added as internal standards to the sample solutions for instrumental drift correction.

Samples and sample preparation

Geochemical reference materials AGV-2 and GSP-2 (United States Geological Survey, USGS) as well as JG-1a (Geological Survey of Japan, GSJ) were used for the experiments. AGV-2 is an andesite with a SiO_2 content of 59.3 wt%. GSP-2 and JG-1a are granodiorites with SiO_2 contents of 66.6 and 72.3 wt%, respectively. The natural rock samples cover a range of SiO_2-contents from 45 to 80 wt% SiO_2, and represent igneous and metamorphic rocks typical of the continental crust [9]. In addition, paragneisses, sandstones and litharenites [10] were included to test the applicability of the strip heater method to sedimentary rocks.

All samples were milled in an agate rotary mill before fusion. About 40 mg of mafic and intermediate samples with up to 55 wt% SiO_2 were fused directly at 1100–1400 °C at a current of 110–120 A (140–170 W) for 10 sec. Samples with >55 wt% SiO_2 were dried at 1000 °C for 15 min to reduce degassing during the fusion process. Afterwards high purity MgO powder was added to reduce the SiO_2 content of the mixture to ~55 wt%. Trace elements in the MgO as

Table 3. Results obtained for reference material GSP-2. Recoveries are best if a long melting time is applied or if beads are reground and fused again

GSP-2			1600 °C, 10 sec			1800 °C, 10 sec			1600 °C, 30 sec			Reground, 1600 °C		
	Reference values		4 beads, $n = 15$			2 beads, $n = 6$			1 bead, $n = 3$			3 beads, $n = 6$		
	Mean	SD	Mean	RSD%	rec.%	Mean	RSD%	rec.%	Mean	RSD%	rec.%	Mean	RSD%	rec.%
Li	36	2	38.1	13	106	46.4	6	128	34.9	14	97	40.9	4	114
Sc	6.3	0.7	9.46	12	150	9.93	3	158	8.2	1	131	9.80	5	155
Ti	3960	120	4151	7	105	4311	2	109	4538	4	115	4045	3	102
V	52	4	48.2	9	93	52.3	3	101	50.9	14	98	46.9	2	90
Cr	20	6	21.0	9	105	23.2	13	116	21.9	14	110	19.1	23	96
Ni	17	2	16.4	10	96	19.3	13	113	18.2	18	107	16.9	22	100
Rb	247	7	208	20	84	225	7	91	193	18	78	199	11	81
Sr	241	7	213	3	88	212	2	88	209	3	87	214	1	89
Y	27.1	1.2	24.2	5	89	22.8	2	84	25.4	4	94	26.9	5	99
Zr	564	13	487	24	86	543	27	96	502	7	89	560	4	99
Nb	26.8	0.7	24.4	4	91	25.1	2	94	25.6	6	96	26.7	2	99
Cs	1.27	0.12	0.97	17	76	1.05	14	82	0.89	17	70	0.99	13	78
Ba	1373	66	1197	6	87	1197	2	87	1156	4	84	1149	9	84
La	186	11	169	4	91	165	3	88	186	1	100	178	2	96
Ce	436	26	387	5	89	407	3	93	445	9	102	400	6	92
Pr	55	5.1	48.7	3	88	49.5	2	90	53.8	5	98	50.4	2	92
Nd	215	19	188	3	87	187	2	87	206	2	96	198	2	92
Sm	27.5	1.3	23.4	5	85	23.1	3	84	26.3	1	96	25.4	2	92
Eu	2.39	0.15	1.98	5	83	1.96	3	82	2.1	3	89	2.07	2	87
Gd	13	1.3	11.6	6	89	11.1	4	85	12.2	1	93	12.7	4	98
Dy	6.12	0.37	5.43	6	89	5.08	4	83	5.78	4	94	5.95	6	97
Er	2.39	0.21	2.16	8	90	2.02	4	84	2.33	6	97	2.37	4	99
Yb	1.7	0.1	1.58	9	93	1.50	8	88	1.64	6	96	1.70	2	100
Lu	0.24	0.02	0.24	19	101	0.24	26	101	0.24	6	98	0.24	9	100
Hf	15.7	1.5	12.9	28	82	13.7	25	87	13.3	9	85	14.8	5	94
Ta	0.95	0.02	0.83	6	88	0.83	9	87	0.87	4	92	0.98	3	103
Pb	42	3	33.7	34	80	22.8	28	54	39.3	25	94	15.5	46	37
Th	109	7	99.4	8	91	93.3	4	86	108	2	99	111	2	102
U	2.46	0.06	2.0	13	81	2.34	10	95	2.3	18	93	2.14	17	87

CaO as internal standard measured as ^{43}Ca. All data in μg g^{-1}. Reference values are averages compiled from the GeoReM database [14, 15, 18, 19] and from the USGS [27]. rec.% = recovery.

determined by solution ICP-MS are in the range of 0.00002–0.2 µg g^{-1} (pers. comm. G. Brey, Institute Geosciences, University Frankfurt on Main.). The mixtures were blended for several minutes in an agate mortar adding a few drops of acetone. This procedure has the advantage of producing a very fine powder that was easier to fuse than the routinely milled rock powder. About 40 mg of the mixtures were fused for 10, 30 and 70 sec using a current of 116–125 A (160–190 W, 1200–1600 °C). At 1600 °C quench crystals occurred in compositions with more than 70 wt% SiO_2 but even the most siliceous samples yielded homogeneous clear, translucent glass beads at 1800 °C (135 A/220 W). Therefore, melting conditions were chosen according to initial SiO_2 contents as 1200 °C for mafic, undiluted samples, 1600 °C for samples with less than 70 wt% and 1800 °C for samples with more than 70 wt% SiO_2. We also applied grinding of primary glass beads and re-melting of the glass powder. Glass powders melted very easily and always produced optically homogeneous beads.

Melting of silicic glasses is accompanied by degassing of the sample and formation of vesicles in the melt. Degassing can be a result of release of crystal-bound water as well as of water absorbed by the powders during grinding; the latter is indicated by the fact that vesicle formation during fusion of glass powders is especially strong. For analysis by LA-ICP-MS, beads were stuck onto a microscope slide using double-sided adhesive tape.

Results

Homogeneity and accuracy of analyses of reference materials

Homogeneous results can be achieved in the three reference materials (Figs. 2–4) by adjusting the fusion conditions to the SiO_2-content of the sample. For the elements Sr, Ba, Th, U, Ti, Nb, Ta, Th and the Rare Earth Elements (REE), accuracy is usually within 10% of the reference value (Tables 2–4). Reproducibility is also within 10%, which may be due partly to similar fractionation to the internal standard Ca [11, 12] during laser ablation.

Homogeneity of REE in reference material JG-1a and highly siliceous samples is only achieved under the highest temperature fusion conditions applied (1800 °C and 30 sec), whereas the behaviour of Sr, Ba, Th, U, Nb and Ta is evidently not influenced by fusion conditions. This may be due to storage of the REE in refractory accessory phases (zircon, apatite, monazite, allanite) that do not easily dissolve in the melt. Similary, REE contents in reference material GSP-2 only agree with the reference values if the fusion process is prolonged (30–70 sec) or the glass beads are reground and remolten.

Inhomogenously distributed Zr and Hf contents in the glass beads of GSP-2 and JG-1a are most likely related to incomplete melting of microscopic zircon crystals. Re-grinding and a second fusion cycle improved the homogeneity of these elements. However, similar improvements are obtained during hotter and prolonged fusion of the siliceous compositions, which is preferred to re-grinding and re-fusion.

Table 4. Best result obtained for reference material JG-1a. Due to the high SiO_2-content (72.3 wt%) high fusion temperature and a prolonged melting duration had to be applied. At lower temperatures and shorter fusion duration homogeneity was not sufficient. Note that Pb is strongly depleted at these high fusion conditions

JG-1a			1800 °C, 30 sec		
	Reference values		1 bead, $n = 3$		
	Mean	SD	Mean	RSD%	rec.%
Li	79.5	4.5	94.4	5	118
Sc	6.21	0.49	9.74	3	157
Ti	1500	180	1557	2	104
V	22.7	3.8	19.1	3	84
Cr	17.6	4.4	19.3	10	110
Ni	6.91	1.9	7.95	15	115
Rb	182	9	159	5	87
Sr	183	5	160	1	87
Y	30.2	1.3	26.9	4	89
Zr	117	9	119	3	102
Nb	11.1	0.8	10.5	2	95
Cs	11.3	0.5	9.6	7	85
Ba	465	7	408	1	88
La	21.8	1.8	20.9	12	96
Ce	46.4	2.4	44.4	11	96
Pr	5.44	0.35	4.88	9	90
Nd	20.3	1.2	18.7	13	92
Sm	4.6	0.27	4.35	5	95
Eu	0.74	0.08	0.6	7	81
Gd	4.36	0.36	4.09	5	94
Dy	4.36	0.37	4.44	2	102
Er	2.85	0.32	2.75	3	96
Yb	2.96	0.34	2.85	4	96
Lu	0.45	0.05	0.46	11	102
Hf	3.6	0.24	3.98	1	111
Ta	1.85	0.16	1.67	4	90
Pb	26.4	2.8	8.3	39	31
Th	12.8	1.6	12.1	8	95
U	4.63	0.29	4.13	1	89

CaO as internal standard measured as ^{43}Ca. All data in µg g^{-1}. Reference values are averages compiled from the GeoReM database [15, 19–26] and the GSJ [28]. rec.% = recovery.

Reproducibility of Cr and Ni contents is poorer at 10–15%, which may be attributed to less well determined Ni and Cr concentrations in the reference materials (Table 3). Reference values for Cr and Ni contents of AGV-2 are documented with relative standard deviations (RSD%) of 12 and 16%, respectively (Cr 17 ± 2 µg g^{-1}; Ni 19 ± 3 µg g^{-1}) and uncertainties are larger for GSP-2 (Cr ±30%, Ni ±12%) and JG-1a (Cr ±25%, Ni ±27%). Our values lie within the given RSD% of the reference materials.

Pb and Cs are depleted in the glass beads compared to the reference values, which is due to volatilization during melting: their determination by the strip heater method is therefore not recommended. The loss of these elements increases with increasing fusion temperature and time and, hence, is especially strong if a second melting cycle is applied.

We investigated several degrees of dilution to the reference materials AGV-2 and GSP-2. The fusion procedure and the homogeneity of the glasses is not significantly improved by dilution down to 50 wt% SiO_2. On the contrary, accuracy suffered slightly, probably due to mixing problems.

Comparison of scanning mode ablation with spot ablation

Comparison of line scan and single spot ablation analysis showed no advantage of line scans over spot analyses. Considerably higher Rb and Cs contents (up to 30%) were obtained in line scan ablations than in spot ablation analyses. Material ablation in scanning mode is confined to the surface of the bead and has been shown to produce larger particles than spot ablations, resulting in high matrix effects and significant contribution to elemental fractionation effects in the ICP [11, 12]. Large particles may be incompletely ionized in the plasma and elemental fractionation due to preferential ionization of the more volatile elements such as Cs and Rb from the surface of large particles [13] may result. Pb shows contrasting behaviour; it is depleted in the line scans compared to the spot ablation patterns, although it is more volatile than Cs. The time-resolved signal of the spot ablations shows an increase of the Pb signal intensity with increasing depth, indicating that Pb is depleted at the surface of the beads during the melting process. Thus, since line scans only ablate depleted material from the surface, Pb contents are lower than those calculated from spot ablation patterns.

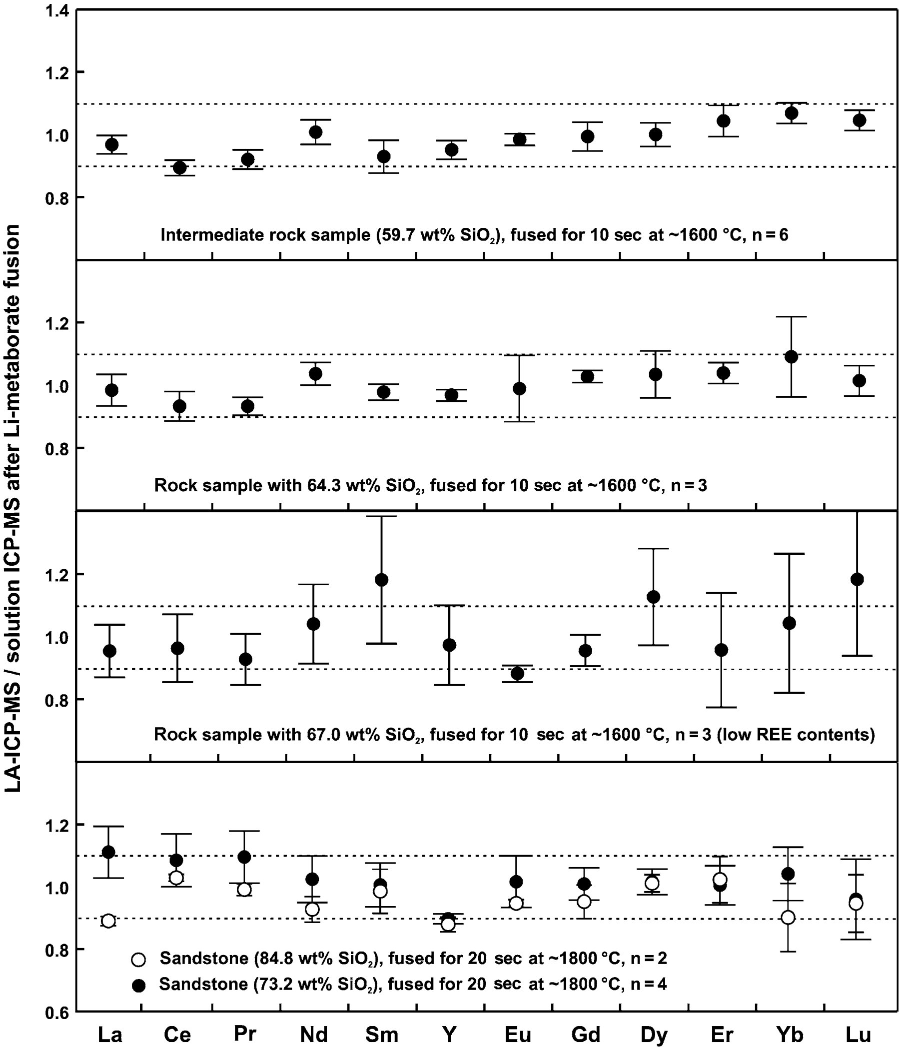

Fig. 5. LA-ICP-MS values compared to total dissolution ICP-MS values for natural rock samples. The deviation for the methods is less than 10% (stippled line) even for samples with exceptionally high SiO_2-contents such as sandstones

Application of LA-ICP-MS on glass beads to natural rock samples

For most trace elements analysed, the results by LA-ICP-MS are comparable to those from other methods. Comparison of LA-ICP-MS data of REE and Y contents in a selection of the natural rock samples with SiO_2 of 59–85 wt% with data from solution ICP-MS indicates agreement within 10% (Fig. 5). Larger deviations in one of the samples (a leucosome with 67 wt% SiO_2) are due to the low contents of HREE in this sample (Lu 0.03 $\mu g\, g^{-1}$). Furthermore, this sample was fused for only 10 sec at 1600 °C and longer melting could improve agreement with solution ICP-MS data (Table 5).

There are, however, a few elements for which problems were encountered, namely Sc, Zr, Hf, Pb and Cs. Scandium contents determined by LA-ICP-MS on glass beads in the highly siliceous samples are consis-

Table 5. Comparison of REE and Y values (mean ± 1SD) of natural rock samples derived by LA-ICP-MS after strip-heater fusion (normal font) with values derived by solution ICP-MS after Li-tetraborate fusion (bold). All data in $\mu g\, g^{-1}$

Sample SiO_2	Granulite 59.7 wt%		Leucosome 64.3 wt%		Leucosome 67.0 wt%		Sandstone 73.2 wt%		Sandstone 84.8 wt%	
Method	LA-ICP-MS	ICP-MS	LA-ICP-MS	ICP-MS	LA-ICP-MS	ICP-MS	LA-ICP-MS	ICP-MS	LA-ICP-MS	ICP-MS
Temperature	1600 °C		1600 °C		1600 °C		1800 °C		1800 °C	
Time	10 sec		10 sec		10 sec		20 sec		20 sec	
Spots	$n = 6$		$n = 3$		$n = 3$		$n = 6$		$n = 6$	
La	16.8 ± 0.5	**17.3**	20.7 ± 1.1	**21.7**	10.2 ± 0.9	**10.7**	13.4 ± 1.1	**13.15**	14.6 ± 0.2	**16.4**
Ce	33.3 ± 0.9	**37.2**	38.1 ± 1.9	**40.9**	15.9 ± 1.8	**16.5**	27.5 ± 2.3	**27.28**	33.8 ± 0.4	**32.9**
Pr	4.14 ± 0.13	**4.49**	4.67 ± 0.14	**5.01**	1.64 ± 0.15	**1.77**	3.09 ± 0.26	**3.07**	3.57 ± 0.07	**3.61**
Nd	17.4 ± 0.6	**17.2**	20.4 ± 0.7	**19.7**	6.02 ± 0.73	**5.79**	11.7 ± 0.9	**11.59**	13.6 ± 0.6	**14.8**
Sm	3.35 ± 0.17	**3.60**	4.66 ± 0.12	**4.76**	0.97 ± 0.17	**0.82**	2.32 ± 0.16	**2.32**	2.86 ± 0.21	**2.91**
Y	15.7 ± 0.45	**16.5**	20.0 ± 0.4	**20.6**	2.28 ± 0.30	**2.34**	13.2 ± 0.2	**13.7**	13.8 ± 0.4	**15.7**
Eu	1.02 ± 0.02	**1.04**	1.51 ± 0.17	**1.53**	0.55 ± 0.02	**0.63**	0.48 ± 0.04	**0.47**	0.61 ± 0.01	**0.65**
Gd	3.17 ± 0.14	**3.19**	4.72 ± 0.09	**4.59**	0.69 ± 0.04	**0.72**	2.25 ± 0.12	**2.19**	2.49 ± 0.14	**2.63**
Dy	2.90 ± 0.1	**2.90**	4.23 ± 0.31	**4.09**	0.49 ± 0.07	**0.44**	2.26 ± 0.09	**2.38**	2.56 ± 0.07	**2.54**
Er	1.66 ± 0.07	**1.59**	2.06 ± 0.07	**1.98**	0.19 ± 0.04	**0.20**	1.31 ± 0.08	**1.39**	1.55 ± 0.11	**1.52**
Yb	1.64 ± 0.05	**1.53**	1.84 ± 0.22	**1.69**	0.19 ± 0.04	**0.18**	1.31 ± 0.11	**1.36**	1.39 ± 0.17	**1.55**
Lu	0.25 ± 0.01	**0.24**	0.24 ± 0.01	**0.23**	0.03 ± 0.02	**0.02**	0.20 ± 0.03	**0.22**	0.22 ± 0.02	**0.24**

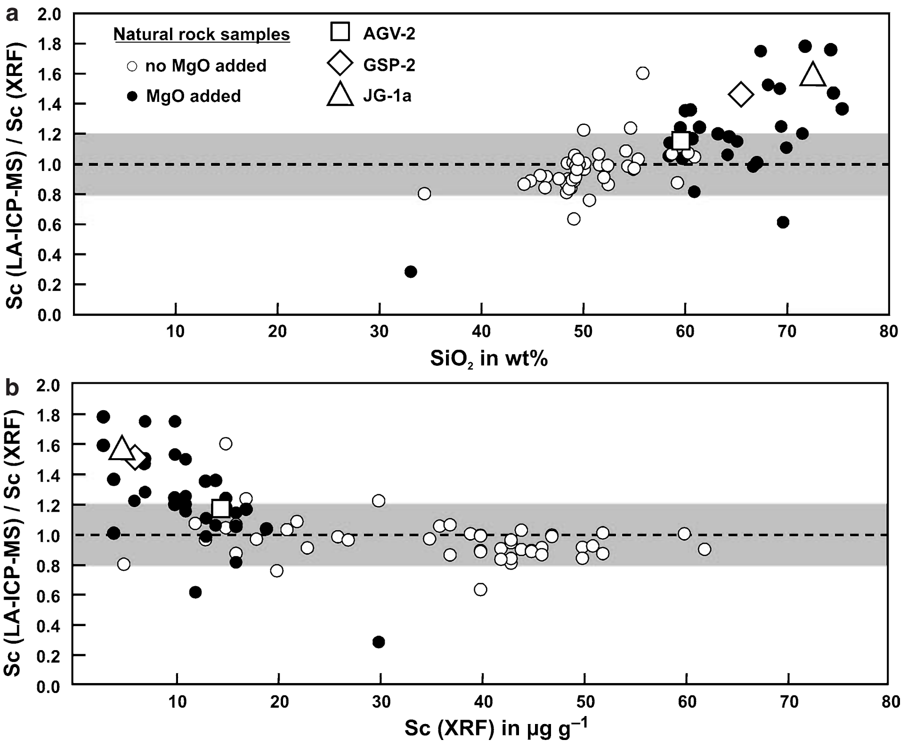

Fig. 6. Comparison of Sc data obtained by LA-ICP-MS versus XRF-data plotted against (a) SiO_2-content of the samples, and (b) Sc values from XRF. Grey fields indicate agreement within 20%. The positive deviation of LA-ICP-MS values is due to $^{28}Si^{17}O$ and $^{29}Si^{16}O$ interferences from the Si-rich samples (see text)

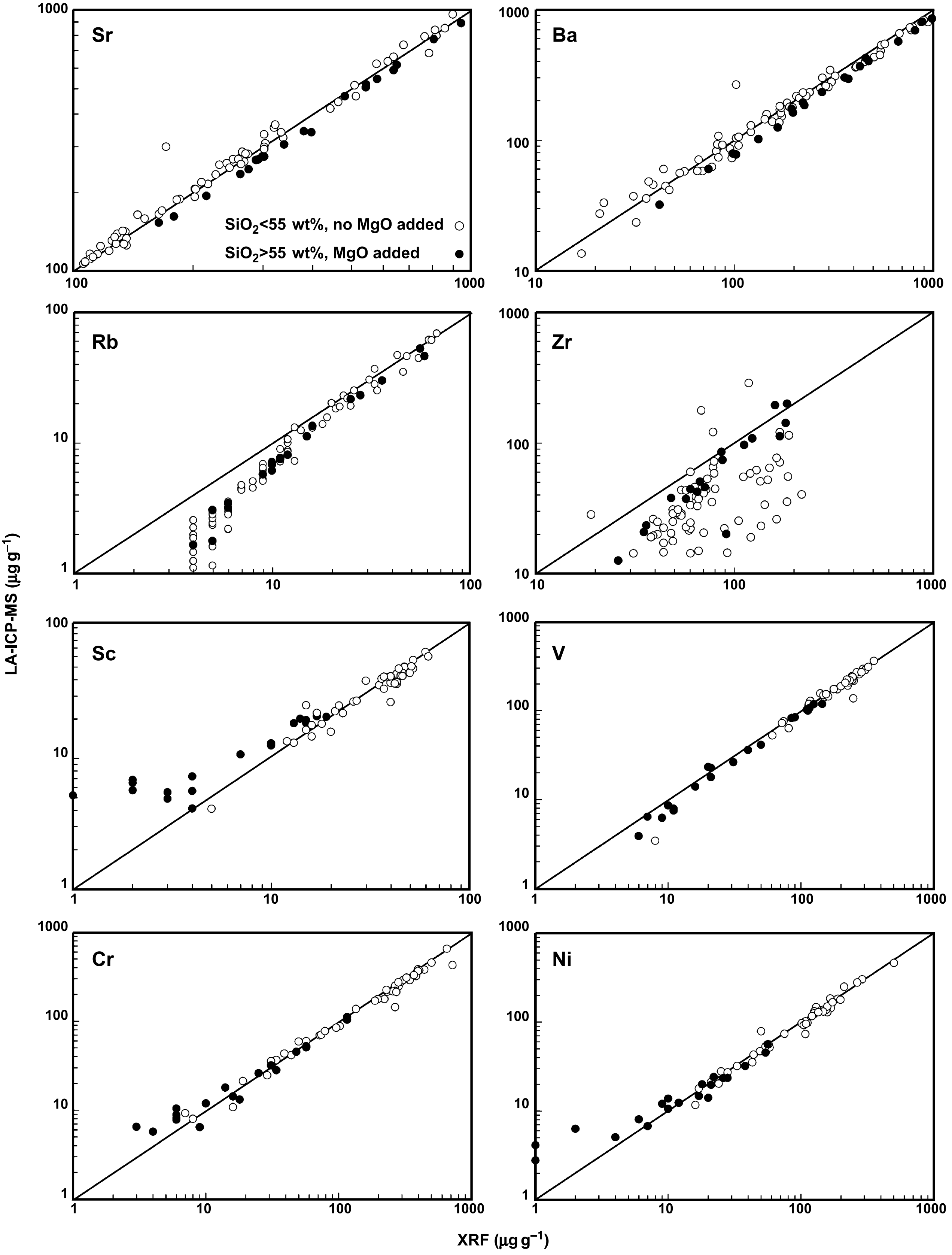

Fig. 7. Comparison of XRF and LA-ICP-MS values for a large group of natural rock samples. In the low concentration range deviation between the methods may be larger than 10%; here LA-ICP-MS values are preferred. See text for further discussion

tently higher than XRF analyses of powdered rocks and the reference values of standard materials. The difference becomes larger with increasing SiO_2-contents and simultaneously decreasing Sc-contents (Fig. 6). This overestimation of Sc by LA-ICP-MS is not related to the fusion process but most likely results from interferences of $^{28}Si^{17}O$ and $^{29}Si^{16}O$ on isotopic mass 45. This becomes more noticeable in samples with higher SiO_2-contents because this trend generally correlates with decreasing Sc in natural rocks.

The determination of Zr and Hf is problematic in both natural rock samples and geological reference materials (Fig. 7). In most cases, concentrations measured by LA-ICP-MS on glass beads are lower than those determined by XRF. The poor correlation between Zr contents in samples with SiO_2 <55 wt% and no added MgO results from a mixture of two effects. Firstly, these samples were melted at 1200 °C which may have prevented complete melting of small zircon crystals. Secondly, mafic rocks have low Zr contents and some of the scatter is related to inaccuracy of XRF determinations these concentrations. This is supported by mass balance calculations obtained for some of the mafic samples by analyzing Zr and Hf concentrations in constituent minerals of the unmelted rocks and combining them into whole-rock concentrations. Results are in accordance with the LA-ICP-MS data, whereas concentrations obtained by XRF are too high.

Comparison with alternative methods for trace element analysis of bulk rocks

X-ray fluorescence spectrometry is a standard tool for the determination of a number of trace elements (Rb, Sr, Ba, Zr, Sc, V, Cr and Ni) in geological materials. Our analyses show that the LA-ICP-MS data on glass beads usually agree well with XRF data and deviations are less than 10% (Fig. 7). At concentrations $<20\,\mu g\,g^{-1}$ the discrepancy increases as detection limits of the XRF method are approached. Highly siliceous samples are more prone to erroneous determination of these elements by XRF since low concentrations of transition metals coincide with high SiO_2-contents of the samples. Therefore we consider the LA-ICP-MS method to be more reliable in the low concentration range.

Both XRF and INAA require larger samples than the strip heater method and are capable of analysing a more limited palette of trace elements, resulting in only partial coverage of the elements generally sought by geochemists. Larger samples (ca. 200 mg) are also used for solution ICP-MS, which, in contrast, permits detection of many more elements at ultratrace concentrations ($<0.01\,\mu g\,g^{-1}$), but these are not generally sought in geological applications. Solution ICP-MS requires acid digestion of samples which may encounter similar problems in the dissolution of accessory minerals, necessitating dissolution in bombs.

In summary, the LA-ICP-MS glass bead method developed here enables accurate and precise simultaneous determination of many trace elements in SiO_2-rich whole-rocks by laser sampling for the first time. It is a rapid and cheap method which does not require acid digestion in a chemical laboratory, and can be practised on much smaller samples, opening the way to many technical and experimental applications. The palette of elements is larger than available to INAA and XRF, and preparation times are quicker (INAA) or comparable (XRF). Specific problems are encountered with Sc (this applies also to solution ICP-MS), and the volatile elements Pb and Cs. Problems with Zr and Hf can be circumvented by further optimization of melting times and temperatures.

Acknowledgements. K.P. Jochum, B. Stoll and K. Herwig are thanked for introduction to the use of the Iridium strip heater and support in setting up the strip heater assemblage in the Department of Geosciences. We are grateful to the workshop of the Max-Planck-Institute for Chemistry in Mainz who constructed the strip heater assemblage. G. Brey and M. Seitz initiated the idea of diluting highly siliceous samples and supplied us with MgO. G. Meinhold provided the metasedimentary sample material.

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