

Electronic Supplementary Information

Determination of Major and Trace Elements in Geological Samples by Laser Ablation Solution Sampling-Inductively Coupled Plasma Mass Spectrometry

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Table S1. Isotopes selected for the determination and limits of detection (LOD) for LA-ICP-MS analysis of the solution sample.

Table S2. Determination of forty-five elements in six international geological reference materials by laser ablation solution sampling ICP-MS.

Calculation for limits of detection

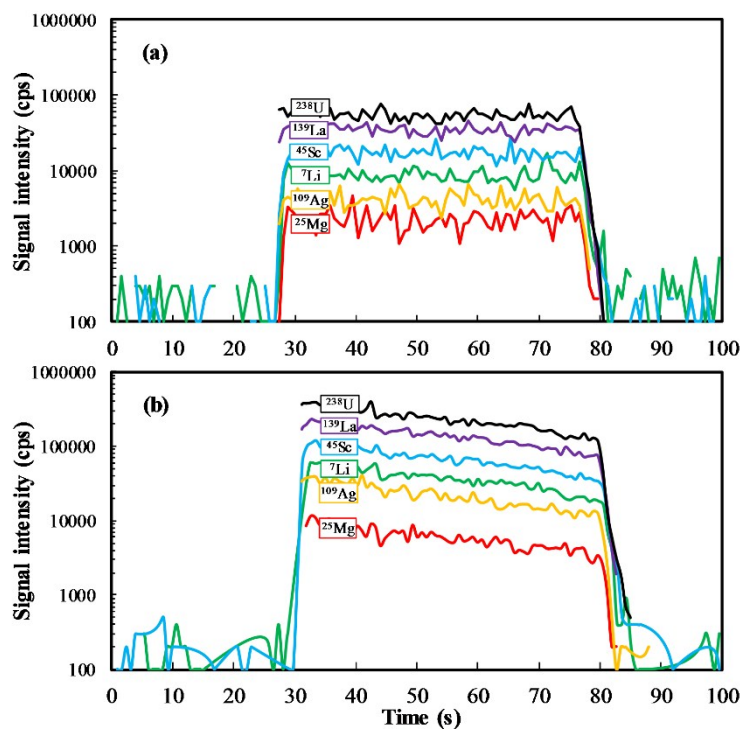


Fig. S1. Time-resolved signals of ^7Li , ^{25}Mg , ^{45}Sc , ^{109}Ag , ^{139}La and ^{238}U in the ablation of (a) a multi-element solution with all elements in the concentration of $0.1 \mu\text{g ml}^{-1}$ and (b) NIST SRM 610 silicate glass, in which the elements concentration are 400 to $500 \mu\text{g g}^{-1}$. Both samples were ablated by static ablation and other conditions cited in Table 1.

Table. S1. Isotopes selected for the determination and limits of detection (LOD) for LA-ICP-MS analysis of the solution sample.

Element	Analytical mass	Isotope Abundance(%)	LOD (ng g⁻¹)	Element	Analytical mass	Isotope Abundance(%)	LOD (ng g⁻¹)
Li	7	92.41	0.956	In	115	95.71	0.165
Na	23	100.00	2.899	Cs	133	100.00	0.744
Mg	25	10.00	0.563	Ba	137	11.23	0.170
Al	27	100.00	1.140	La	139	99.91	0.026
K	39	93.26	15.09	Ce	140	88.45	0.032
Ca	42	0.65	64.11	Pr	141	100.00	0.017
Sc	45	100.00	0.339	Nd	146	17.20	0.083
Ti	47	7.44	1.779	Sm	147	14.99	0.098
V	51	99.75	0.243	Eu	153	52.19	0.045
Cr	52	83.79	2.118	Gd	158	24.84	0.058
Mn	55	100.00	1.382	Tb	159	100.00	0.016
Fe	57	2.12	16.18	Dy	163	24.90	0.058
Co	59	100.00	0.155	Ho	165	100.00	0.023
Ni	60	26.22	13.67	Er	166	33.61	0.094
Cu	63	69.17	0.899	Tm	169	100.00	0.021
Zn	66	27.90	0.550	Yb	173	21.83	0.106
Ga	71	39.89	0.575	Lu	175	97.41	0.037
Rb	85	72.17	1.999	Hf	178	27.28	0.043
Sr	88	82.58	0.063	Ta	181	99.99	0.023
Y	89	100.00	0.111	Tl	205	70.50	0.044
Zr	91	11.22	0.382	Pb	208	52.40	0.069
Nb	93	100.00	0.080	Th	232	100.00	0.042
Mo	97	9.55	0.274	U	238	99.27	0.024

Table. S2. Determination of forty-five elements in six international geological reference materials by laser ablation solution sampling ICP-MS.

Element	Unit	BCR-2			BHVO-2			W-2A		
		Liquid (n=11)	RSD (%)	Ref value	Liquid (n=11)	RSD (%)	Ref value	Liquid (n=11)	RSD (%)	Ref value
Li (7)	ppm	9.26	3.4	9.13	4.43	6.5	4.5	9.28	2.2	9.6
Na ₂ O (23)	wt%	3.06	3.6	3.12	2.19	5.5	2.219	2.02	2.5	2.21
MgO (25)	wt%	3.27	1.4	3.599	6.29	4.8	6.8	5.68	3.5	6.24
Al ₂ O ₃ (27)	wt%	14.3	2.0	13.48	14.2	2.7	13.44	15.2	3.8	15.45
K ₂ O (39)	wt%	1.92	3.2	1.83	0.52	5.8	0.513	0.68	1.2	0.63
CaO (42)	wt%	7.23	2.5	7.114	10.4	2.8	11.4	10.5	2.7	11.04
Sc (45)	ppm	32.7	3.1	33.53	29.8	3.1	31.83	32.3	1.6	35
TiO ₂ (47)	wt%	2.04	3.8	2.265	2.14	3.7	2.731	1.00	4.8	1.078
V (51)	ppm	422	1.9	417.6	317	4.1	318.2	264	2.6	262
Cr (53)	ppm	16.8	10	15.85	293	5.1	287.2	90.8	3.4	87
MnO (55)	wt%	0.20	2.0	0.1966	0.16	3.8	0.169	0.17	3.5	0.166
Fe ₂ O ₃ (t) (57)	wt%	13.4	2.9	13.77	12.7	4.0	12.39	9.94	3.2	10.54
Co (59)	ppm	37.4	2.2	37.33	45.7	3.9	44.89	44.9	1.3	45
Ni (60)	ppm	12.7	6.8	12.57	126	5.6	119.8	74.9	3.6	70
Cu (63)	ppm	20.5	6.1	19.66	125	5.7	129.3	109	4.3	104
Zn (66)	ppm	131	4.5	129.5	99.8	5.9	103.9	75.9	4.4	79
Ga (71)	ppm	22.4	3.7	22.07	21.9	4.9	21.37	18.0	5.1	17
Rb (85)	ppm	46.5	3.5	46.02	9.37	5.5	9.261	20.0	4.5	19
Sr (88)	ppm	335	1.9	337.4	359	4.8	394.1	193	3.2	194
Y (89)	ppm	36.1	1.6	36.07	24.5	4.7	25.91	20.9	2.4	19.5
Zr (91)	ppm	178	2.4	186.5	155	6.1	169	83.8	4.0	84
Nb (93)	ppm	11.1	5.3	11.2	15.9	4.6	16.95	5.99	5.0	6.4
Mo (97)	ppm	246	5.1	250.6	3.41	4.1	3.5	0.43	17.8	0.46
Cs (133)	ppm	1.10	5.5	1.16	0.10	15	0.0996	0.98	10.2	0.93
Ba (137)	ppm	679	2.4	683.9	130	4.4	130.9	171	4.0	172.74
La (139)	ppm	25.6	1.0	25.08	15.3	4.9	15.2	10.7	4.2	10.71
Ce (140)	ppm	53.9	2.5	53.12	38.2	3.1	37.53	23.3	3.0	23.24
Pr (141)	ppm	6.90	1.7	6.827	5.46	4.5	5.339	3.15	4.1	3.01
Nd (143)	ppm	29.4	2.5	28.26	24.0	5.9	24.27	13.4	7.3	13.08
Sm (147)	ppm	6.78	4.7	6.547	6.66	6.5	6.023	3.24	9.3	3.29
Eu (153)	ppm	1.98	5.2	1.989	2.14	5.9	2.043	1.14	5.8	1.11
Gd (155)	ppm	7.03	4.6	6.811	6.47	6.8	6.207	3.64	4.3	3.74
Tb (159)	ppm	1.04	5.2	1.077	0.92	7.0	0.94	0.62	5.1	0.61

Continued Table. S2

Element ($\mu\text{g g}^{-1}$)	Unit	BCR-2			BHVO-2			W-2A		
		Liquid (n=11)	RSD (%)	Ref value	Liquid (n=11)	RSD (%)	Ref value	Liquid (n=11)	RSD (%)	Ref value
Dy (163)	ppm	6.41	4.0	6.424	5.23	5.9	5.28	3.83	5.7	3.83
Ho (165)	ppm	1.31	6.1	1.313	0.97	5.6	0.9887	0.75	6.8	0.78
Er (166)	ppm	3.73	4.0	3.67	2.38	6.2	2.511	2.11	7.2	2.22
Tm (169)	ppm	0.53	6.2	0.5341	0.31	4.7	0.3349	0.33	5.5	0.32
Yb (173)	ppm	3.43	6.9	3.392	1.83	5.6	1.994	1.88	7.8	1.94
Lu (175)	ppm	0.52	5.9	0.5049	0.23	6.8	0.2754	0.28	6.4	0.29
Hf (178)	ppm	4.62	4.2	4.972	4.04	4.8	4.1	2.57	6.9	2.46
Ta (181)	ppm	0.87	5.3	0.8	1.24	6.2	1.154	0.49	5.8	0.46
Tl (205)	ppm	0.25	5.5	0.267			0.0224	0.09	13	0.1
Pb (208)	ppm	10.4	2.3	10.59	1.62	5.9	1.653	9.00	5.0	9
Th (232)	ppm	6.09	2.4	5.828	1.18	8.7	1.224	2.04	4.8	2.19
U (238)	ppm	1.70	4.4	1.683	0.41	4.7	0.412	0.49	5.7	0.51

Continued Table. S2

Element ($\mu\text{g} / \text{g}$)	Unit	GSP-2			AGV-2			RGM-2		
		Liquid (n=11)	RSD (%)	Ref value	Liquid (n=11)	RSD (%)	Ref value	Liquid (n=11)	RSD (%)	Ref value
Li (7)	ppm	36.7	3.2	36	11.3	3.1	10.8	57.3	2.2	58.1
Na2O (23)	wt%	2.72	2.9	2.78	4.21	3.4	4.204	3.81	4.4	3.89
MgO (25)	wt%	0.91	4.0	0.96	1.66	3.1	1.8	0.24	1.8	0.25
Al2O3 (27)	wt%	15.4	2.2	14.9	17.9	4.6	17.03	13.4	5.5	14.3
K2O (39)	wt%	5.37	3.9	5.38	2.19	6.2	2.898	4.24	6.2	4.2
CaO (42)	wt%	2.13	3.4	2.1	5.19	2.7	5.15	1.24	5.9	1.29
Sc (45)	ppm	6.86	4.4	6.3	12.8	2.2	13.11	5.31	2.5	4.89
TiO2 (47)	wt%	0.61	3.3	0.66	0.91	3.1	1.051	0.21	3.5	0.28
V (51)	ppm	52.8	2.9	52	118	4.4	118.5	11.5	4.3	12
Cr (53)	ppm	19.8	5.5	20	17.6	5.9	16.22	3.71	6.1	4
MnO (55)	wt%	0.04	2.4	0.038	0.11	3.5	0.1004	0.03	3.4	0.037
Fe2O3(t) (57)	wt%	4.36	2.0	4.9	6.09	3.0	6.69	1.62	3.5	1.76
Co (59)	ppm	7.51	2.9	7.3	15.5	4.0	15.46	1.82	5.0	1.98
Ni (60)	ppm	17.0	6.5	17	19.3	7.1	18.87	2.40	23	2.5
Cu (63)	ppm	51.4	2.3	47	51.2	5.1	51.51	9.51	4.6	9.95
Zn (66)	ppm	118	5.3	120	91.9	4.6	86.7	34.4	5.0	35
Ga (71)	ppm	23.2	3.6	22	20.5	6.3	20.42	16.4	4.8	16.1
Rb (85)	ppm	239	3.4	245	67.3	2.3	68.6	145	2.8	149
Sr (88)	ppm	236	3.8	240	628	1.4	659.5	105	2.6	107
Y (89)	ppm	25.8	2.9	28	19.1	4.3	19.14	22.9	3.0	21.8
Zr (91)	ppm	508	3.6	550	215	4.8	230	219	3.9	223
Nb (93)	ppm	24.7	5.2	27	13.1	7.0	14.12	8.08	3.1	8.6
Mo (97)	ppm	1.98	9.3	2.1	1.93	6.7	2	2.32	9.4	2.3
Cs (133)	ppm	1.22	3.2	1.2	1.15	3.8	1.173	9.61	2.2	9.83
Ba (137)	ppm	1329	2.5	1340	1091	4.8	1134	777	2.5	812
La (139)	ppm	181	3.9	180	39.9	3.1	38.21	23.2	3.5	22.5
Ce (140)	ppm	442	4.1	410	73.2	4.3	69.43	44.7	3.4	45.1
Pr (141)	ppm	54.7	3.4	51	8.67	4.4	8.165	5.30	4.2	5.12
Nd (143)	ppm	204	1.4	200	29.9	2.5	30.49	19.1	5.9	19.1
Sm (147)	ppm	26.1	3.4	27	5.60	3.7	5.509	4.04	6.8	4.05
Eu (153)	ppm	2.28	5.3	2.3	1.65	5.6	1.553	0.63	5.2	0.65
Gd (155)	ppm	12.5	2.9	12	4.91	4.5	4.678	3.98	6.7	3.84
Tb (159)	ppm	1.21	6.8	1.2	0.62	5.2	0.64	0.57	4.5	0.57
Dy (163)	ppm	5.81	3.9	6.1	3.55	3.3	3.549	3.84	5.1	3.63
Ho (165)	ppm	0.96	5.7	1	0.72	4.6	0.6818	0.74	4.3	0.75
Er (166)	ppm	2.41	3.4	2.43	1.86	4.6	1.825	2.39	4.8	2.32
Tm (169)	ppm	0.29	6.6	0.29	0.25	6.8	0.2623	0.35	6.6	0.35

Continued Table. S2

Element ($\mu\text{g} / \text{g}$)	Unit	GSP-2			AGV-2			RGM-2		
		Liquid (n=11)	RSD (%)	Ref value	Liquid (n=11)	RSD (%)	Ref value	Liquid (n=11)	RSD (%)	Ref value
Yb (173)	ppm	1.62	6.7	1.6	1.75	4.2	1.653	2.50	5.1	2.56
Lu (175)	ppm	0.22	6.5	0.23	0.26	3.6	0.2507	0.38	5.7	0.4
Hf (178)	ppm	13.5	5.5	14	5.18	1.3	5.137	5.89	3.4	5.87
Ta (181)	ppm	0.81	5.4	0.83	0.78	6.2	0.865	0.87	5.7	0.83
Tl (205)	ppm	1.34	6.0	1.32	0.25	6.7	0.27	2.01	6.0	1.93
Pb (208)	ppm	51.5	2.5	49.8	13.9	3.2	13.14	20.5	4.9	20.1
Th (232)	ppm	109	4.3	105	6.34	4.3	6.174	14.2	4.3	14.6
U (238)	ppm	2.51	3.6	2.4	1.93	4.7	1.885	5.41	2.5	5.37

All of the reference values were taken from the GEOREM database

(<http://georem.mpch-mainz.gwdg.de/>).

Calculation for limits of detection

The limits of detection were calculated according to Longerich et al.¹ and as follows:

$$\sigma_{net} = \sigma_{individual} \sqrt{\frac{1}{n_b} + \frac{1}{n_a}}$$

$$\sigma_{net} \approx \sigma_{individual} \sqrt{\frac{2}{n}}$$

$$LOD = \frac{3\sigma_{net}}{S}$$

where n_a is the number of slices in the ablation time interval that are integrated, n_b is the number of slices in the background time interval that are integrated, and in this research, $n \approx n_a \approx n_b = 50$. $\sigma_{individual}$ refers to standard deviation of the count rate in individual measurements for background. σ_{net} refers to the standard deviation of the net count rate for an analyte in the data acquisition. S refers to sensitivity of the analyte.

Reference

1. H. P. Longerich, S. E. Jackson and D. Günther, *J. Anal. At. Spectrom.*, 1996, **11**, 899-904.