Electronic Supplementary Material (ESI) for JAAS.

Capabilities of Laser Ablation Inductively Coupled Plasma Time-of-Flight Mass Spectrometry

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Table S1. Poisson LODs and quantitative results as observed in high-dispersion- and low-dispersion LA-ICP-TOFMS analyses using a 44-µm diameter laser spot. Quantitative results for analyses of NIST 612 are compared to the preferred values reported in the GeoReM database.

isotope	Poisson LODs 44 um, 10 Hz, line scanning, mg/kg	Poisson LODs 44 um, 10 Hz, hole drilling, mg/kg	Poisson LODs 44 um, single pulse, mg/kg	NIST 612							
				reference		high-dispersion				low-dispersion	
						line scanning		hole drilling		single pulse	
				preferred value (mg/kg)	uncertainty preferred value (mg/kg)	quantified concentration (mg/kg)	standard deviation (mg/kg) (N = 4)	quantified concentration (mg/kg)	standard deviation (mg/kg) (N = 4)	quantified concentration (mg/kg)	standard deviation (mg/kg) (N = 9)
Na23	3.33	5.96	17.8	$1.016\ 10^5$	$2.2\ 10^3$	$9.7\ 10^4$	$1.1\ 10^3$	$1.016\ 10^5$	$1.3\ 10^3$	$9.91\ 10^4$	$8\ 10^2$
Mg25	0.98	1.88	11.7	68	5.1	60.5	1.1	57.9	1.0	61	19
Al27	0.20	0.41	2.00	$1.075\ 10^4$	$2.1\ 10^2$	$1.075\ 10^5$	-	$1.075\ 10^5$	-	$1.075\ 10^5$	-
Si29	82.9	129	333	$3.071\ 10^5$	$2.8\ 10^3$	$3.34\ 10^5$	$1.1\ 10^4$	$3.53\ 10^5$	$2.2\ 10^4$	$3.309\ 10^5$	$2.2\ 10^3$
P31	3.54	6.21	23.7	46.6	6.9	42.5	3.4	69	9	69	17
S34	66.8	94.9	336.7	377	70	350	60	360	38	<LOD	n.d.
K39	0.84	1.55	4.63	62.3	2.4	124	22	62	2	70	40
Ca44	12.6	23.8	50.5	$8.51\ 10^4$	$7\ 10^2$	$8.66\ 10^4$	$7\ 10^2$	$8.47\ 10^4$	$1.1\ 10^3$	$8.27\ 10^4$	$3.2\ 10^3$
Sc45	0.07	0.14	0.69	39.9	2.5	41.8	0.4	43.1	0.8	52.3	2.7
Ti49	0.78	1.50	8.99	44	2.3	40.21	0.18	41.2	1.3	50	10
V51	0.05	0.08	0.59	38.8	1.2	37.32	0.37	38.6	1.1	38.6	2.3
Cr53	0.45	0.84	5.71	36.4	1.5	34.83	0.34	36.2	1.4	38	11
Mn55	0.05	0.10	0.47	38.7	0.9	37.46	0.14	37.9	0.5	37.4	2.1
Fe56	0.25	0.43	0.55	51	2	46.4	1.2	47.4	1.1	40	5
Co59	0.09	0.15	0.56	35.5	1	33.62	0.28	35.0	1.1	35.0	2.4
Ni60	0.51	0.85	2.57	38.8	0.2	36.4	1.3	38.6	0.6	38	4
Cu65	0.18	0.31	1.80	37.8	1.5	35.6	0.6	38.5	1.1	34	5
Zn66	0.23	0.38	2.18	39.1	1.7	38.3	0.4	37.3	1.1	39.1	2.7
Ga71	0.04	0.07	0.57	36.9	1.5	35.69	0.12	36.3	0.7	33.7	1.5
Ge74	0.08	0.13	0.92	36.1	3.8	38.5	0.6	39.6	0.9	36.8	2.5
As75	0.42	0.72	2.08	35.7	5.5	28.7	1.7	36.7	2.6	30.0	3.3
Se77	1.99	3.23	13.9	16.3	1.9	17.3	0.8	19.2	1.6	<LOD	n.d.
Rb85	0.032	0.05	0.36	31.4	0.4	30.89	0.18	30.6	0.5	31.5	1.2
Sr88	0.014	0.028	0.18	78.4	0.2	76.7	0.4	75.7	1.0	76.8	1.9
Y89	0.013	0.027	0.16	38.3	1.4	36.8	0.5	36.8	0.4	39.5	1.5
Zr90	0.028	0.06	0.33	37.9	1.2	36.6	0.7	37.2	0.7	39.8	0.9
Nb93	0.017	0.032	0.19	38.9	2.1	36.0	0.6	37.7	1.1	37.6	1.6
Mo98	0.06	0.10	0.62	37.4	1.5	35.1	0.7	36.7	1.2	35.8	2.4
Rh103	0.015	0.02	0.13	0.91	0.02	0.92	0.04	0.94	0.06	0.81	0.12
Pd104	0.020	0.04	1.21	1.05	0.1	0.93	0.18	1.16	0.08	0.40	0.13
Ag107	0.04	0.06	0.35	22	0.3	21.8	0.7	22.2	0.7	20.8	0.8
Cd111	0.18	0.31	1.42	28.1	1.1	29.2	1.1	29.6	0.6	28.2	3.5
In115	0.008	0.013	0.10	38.9	2.1	35.64	0.25	35.4	0.7	37.6	1.0
Sn120	0.029	0.05	0.31	38.6	1.3	36.59	0.31	36.8	0.8	34.4	1.5
Sb123	0.04	0.07	0.37	34.7	1.8	32.6	0.6	34.0	1.2	31.8	2.0
Cs133	0.017	0.03	0.12	42.7	1.8	40.90	0.38	39.8	0.9	41.5	0.7
Ba137	0.06	0.12	0.67	39.3	0.9	39.85	0.24	38.8	0.5	36.4	2.6
La139	0.007	0.014	0.08	36	0.7	35.12	0.28	34.1	0.5	34.2	1.2
Ce140	0.008	0.015	0.08	38.4	0.7	37.29	0.27	36.7	0.9	36.6	1.0
Pr141	0.008	0.015	0.06	37.9	1.0	36.71	0.30	35.9	0.7	36.6	0.7
Nd146	0.035	0.07	0.34	35.5	0.7	35.02	0.33	34.3	0.6	33.1	1.2
Sm147	0.04	0.09	0.39	37.7	0.8	37.2	0.4	36.7	0.6	36.0	1.2
Eu153	0.010	0.020	0.09	35.6	0.8	34.77	0.21	34.1	0.5	34.2	1.0
Tb159	0.005	0.011	0.05	37.6	1.1	35.5	0.5	34.8	0.5	36.6	0.5
Gd160	0.024	0.05	0.20	37.3	0.9	36.8	0.6	36.3	0.6	36.9	1.4
Dy163	0.022	0.05	0.19	35.5	0.7	35.0	0.5	34.49	0.38	35.1	2.1
Ho165	0.005	0.011	0.04	38.3	0.8	36.4	0.5	35.9	0.5	39.2	1.1
Er166	0.016	0.03	0.13	38	0.9	37.1	0.5	36.9	0.6	39.3	0.8
Tm169	0.005	0.012	0.04	36.8	0.6	35.7	0.5	35.0	0.4	37.1	0.5
Yb172	0.022	0.04	0.18	39.2	0.9	38.01	0.34	37.08	0.35	37.4	1.5
Lu175	0.005	0.010	0.04	37	0.9	35.2	0.6	34.7	0.4	37.0	0.9
Hf178	0.018	0.04	0.13	36.7	1.2	35.6	0.7	36.1	0.8	39.5	1.1
Ta181	0.006	0.012	0.04	37.6	1.9	34.2	0.8	36.0	1.5	37.0	0.5
W182	0.029	0.05	0.19	38	1.1	35.3	0.8	38.3	1.9	35.6	1.8
Re185	0.016	0.028	0.11	6.63	0.61	6.65	0.17	6.89	0.25	6.2	0.5
Pt195	0.023	0.04	0.15	2.51	0.1	1.67	0.04	1.76	0.09	1.86	0.25
Au197	0.018	0.033	0.10	4.77	0.31	3.93	0.16	4.53	0.33	4.2	0.5
Tl205	0.009	0.014	0.05	14.9	0.5	15.9	1.1	16.4	0.6	13.6	0.6
Pb208	0.010	0.017	0.07	38.57	0.2	38.3	0.6	37.3	1.1	36.2	1.7
Bi209	0.008	0.014	0.05	30.2	2.3	33.5	0.6	32.8	1.1	30.5	0.6
Th232	0.005	0.010	0.030	37.79	0.08	36.2	0.7	35.8	0.7	36.3	0.8
U238	0.004	0.009	0.027	37.38	0.08	35.5	0.5	36.2	1.5	34.3	0.6

Table S2. Quantitative results for analyses of NIST 614 and USGS BCR-2G using high-dispersion- and low-dispersion LA-ICP-TOFMS with a 44-µm laser spot. Results are compared to the preferred values reported in the GeoReM database.

NIST 614				
	reference		low-dispersion	
			single pulse	
isotope	preferred value (mg/kg)	uncertainty preferred value (mg/kg)	quantified concentration (mg/kg)	standard deviation (mg/kg) (N = 9)
Na23	1.016 10^5	2.2 10^3	1.261 10^5	2.3 10^3
Mg25	33.8	1.9	44	18
Al27	1.080 10^4	2.7 10^2	1.080 10^4	-
Si29	3.37 10^5	4 10^3	4.337 10^5	1.4 10^4
P31	11.4	3.9	<LOD	n.d.
S34	291	66	<LOD	n.d.
K39	30	1	60.8	1.6
Ca44	8.51 10^4	1.4 10^3	7.73 10^4	1.7 10^3
Sc45	0.74		<LOD	n.d.
Ti49	3.61	0.25	<LOD	n.d.
V51	1.01	0.04	1.5	0.7
Cr53	1.19	0.12	<LOD	n.d.
Mn55	1.42	0.07	1.8	0.7
Fe56	18.8	6	18.6	3.4
Co59	0.79	0.09	1.19	0.38
Ni60	1.1	0.1	<LOD	n.d.
Cu65	1.37	0.07	<LOD	n.d.
Zn66	2.79	0.38	12	6
Ga71	1.31	0.09	1.3	0.7
Ge74	0.942	0.096	<LOD	n.d.
As75	0.74	0.23	<LOD	n.d.
Se77	0.4	0.08	<LOD	n.d.
Rb85	0.855	0.005	1.3	0.4
Sr88	45.8	0.1	49.8	1.5
Y89	0.79	0.032	0.69	0.17
Zr90	0.848	0.028	0.66	0.33
Nb93	0.824	0.03	1.06	0.25
Mo98	0.8	0.03	1.3	0.6
Rh103	1.54	0.18	1.43	0.28
Pd105	2.05	0.1	0.37	0.13
Ag107	0.42	0.04	0.64	0.33
Cd111	0.56	0.05	<LOD	n.d.
In115	0.79	0.05	0.83	0.23
Sn120	1.68	0.15	1.8	0.6
Sb123	0.79	0.064	1.02	0.36
Cs133	0.664	0.034	0.93	0.22
Ba137	3.2	0.09	3.8	1.2
La139	0.72	0.013	0.67	0.15
Ce140	0.813	0.025	0.83	0.15
Pr141	0.768	0.015	0.74	0.11
Nd146	0.752	0.014	0.56	0.13
Sm147	0.754	0.013	0.7	0.4
Eu153	0.77	0.016	0.79	0.12
Tb159	0.739	0.02	0.62	0.04
Gd160	0.763	0.021	0.65	0.13
Dy163	0.746	0.022	0.59	0.12
Ho165	0.749	0.015	0.54	0.10
Er166	0.74	0.017	0.56	0.12
Tm169	0.732	0.02	0.63	0.08
Yb172	0.777	0.021	0.76	0.23
Lu175	0.732	0.018	0.57	0.11
Hf178	0.711	0.022	0.60	0.16
Ta181	0.808	0.026	0.68	0.11
W182	0.806	0.071	0.92	0.31
Re185	0.17	0.008	0.23	0.13
Pt195	2.36	0.12	1.85	0.31
Au197	0.48	0.07	0.51	0.20
Tl205	0.273	0.02	0.29	0.12
Pb208	2.32	0.04	3.48	0.18
Bi209	0.581	0.043	0.79	0.12
Th232	0.748	0.006	0.65	0.07
U238	0.823	0.002	0.91	0.09

USGS BCR-2G								
	reference		high-dispersion				low-dispersion	
			line scanning		hole drilling		single pulse	
isotope	preferred value (mg/kg)	uncertainty preferred value (mg/kg)	quantified concentration (mg/kg)	standard deviation (mg/kg) (N = 4)	quantified concentration (mg/kg)	standard deviation (mg/kg) (N = 4)	quantified concentration (mg/kg)	standard deviation (mg/kg) (N = 9)
Na23	2.40 10^4	5 10^2	2.33 10^4	6 10^2	2.35 10^4	1.1 10^3	1.59 10^4	1.8 10^3
Mg25	2.15 10^4	5 10^2	2.065 10^4	3.0 10^2	1.98 10^4	8 10^2	1.65 10^4	7 10^2
Al27	7.09 10^4	2.1 10^3	7.75 10^4	1.5 10^3	7.58 10^4	3.4 10^3	7.09 10^4	-
Si29	2.543 10^5	1.9 10^3	2.72 10^5	7 10^3	2.82 10^5	7 10^3	2.38 10^5	2.4 10^4
P31	1620	40	1690	90	1570	70	1.60 10^3	3.9 10^2
K39	1.44 10^4	3.3 10^2	1.54 10^4	6 10^2	1.57 10^4	1.2 10^3	3.7 10^3	7 10^2
Ca42	5.05 10^4	8 10^2	5.05 10^4	-	5.05 10^4	-	4.5 10^4	1.9 10^3
Sc45	33	2	36.9	1.2	35.9	1.3	40	9
Ti49	1.4 10^4	10^3	1.409 10^4	2.5 10^2	1.34 10^4	4 10^2	1.15 10^4	5 10^2
V51	425	18	451	12	433	14	405	39
Cr53	17	2	16.9	0.8	17.21	0.13	17	15
Mn55	1550	70	1634	29	1620	60	1450	70
Fe56	9.64 10^4	2.3 10^3	1.052 10^5	2.0 10^3	1.05 10^5	4 10^3	9.32 10^4	2.4 10^3
Co59	38	2	39.8	1.0	40.1	1.6	37	7
Ni60	13	2	13.7	1.4	14.5	1.4	33	13
Cu65	21	5	21.5	0.5	21.8	0.9	26	11
Zn66	125	5	155	6	159	7	129	29
Ga71	23	1	22.0	0.6	23.4	0.9	19	5
Ge74	1.5	0.1	1.68	0.18	1.87	0.37	<LOD	n.d.
Rb85	47	0.5	44.9	1.2	47.3	1.9	43	8
Sr88	342	4	336	5	325	11	322	12
Y89	35	3	31.7	1.1	30.9	1.0	34.6	3.9
Zr90	184	15	176	6	170	6	182	10
Nb93	12.5	1	11.85	0.27	11.31	0.39	11.0	1.8
Mo98	270	30	264	8	265	11	232	30
Ag107	0.5	0.4	0.80	0.10	0.82	0.06	<LOD	n.d.
Cd111	0.2	n.d.	0.66	0.05	0.77	0.08	<LOD	n.d.
In115	0.11	0.02	0.095	0.004	0.104	0.0030	<LOD	n.d.
Sn120	2.6	0.4	2.070	0.033	2.162	0.037	1.7	1.3
Sb123	0.35	0.08	0.28	0.10	0.37	0.020	<LOD	n.d.
Cs133	1.16	0.07	1.072	0.031	1.098	0.037	1.1	0.5
Ba137	683	7	711	11	668	24	684	26
La139	24.7	0.3	24.7	0.6	23.0	0.8	26.6	2.3
Ce140	53.3	0.5	54.5	0.9	49.0	1.7	55.1	3.1
Pr141	6.7	0.4	6.69	0.16	6.05	0.20	6.7	0.8
Nd146	28.9	0.3	29.0	0.7	26.4	0.8	32	4
Sm147	6.59	0.07	6.64	0.18	6.28	0.29	7.1	1.7
Eu153	1.97	0.02	1.99	0.034	1.86	0.07	2.0	0.5
Tb159	1.02	0.08	0.99	0.035	0.923	0.026	0.96	0.27
Gd160	6.71	0.07	6.68	0.23	6.20	0.22	7.0	1.3
Dy163	6.44	0.06	6.24	0.18	5.92	0.20	6.3	1.4
Ho165	1.27	0.08	1.21	0.033	1.163	0.030	1.26	0.36
Er166	3.7	0.04	3.56	0.12	3.39	0.10	3.9	0.9
Tm169	0.51	0.04	0.49	0.015	0.461	0.008	0.49	0.23
Yb172	3.39	0.03	3.25	0.12	3.12	0.06	3.3	1.0
Lu175	0.503	0.005	0.476	0.015	0.457	0.018	0.47	0.20
Hf178	4.84	0.28	4.94	0.17	4.60	0.14	4.9	1.2
Ta181	0.78	0.06	0.724	0.025	0.685	0.025	0.72	0.25
W182	0.5	0.07	0.571	0.020	0.552	0.012	0.5	0.5
Re185	0.0062	0.0007	<LOD	n.d.	<LOD	n.d.	<LOD	n.d.
Pt195	0.78	0.6	0.28	0.04	0.213	0.020	<LOD	n.d.
Tl205	0.3	0.1	0.265	0.008	0.289	0.005	0.17	0.12
Pb208	11	1	10.82	0.26	11.5	0.5	9.5	2.4
Bi209	0.05	0.01	0.0580	0.0011	0.063	0.006	0.19	0.17
Th232	5.9	0.3	5.97	0.19	5.53	0.13	5.7	0.7
U238	1.69	0.12	1.88	0.06	1.64	0.04	1.70	0.26

Table S3. Bulk composition of regions 1 to 5 (Figure 4). Values reported in standard font are the mean and standard deviation of a Gaussian fitted to the signal intensity distribution derived from evaluation of pixels within the yellow rectangles. Concentrations given in brackets and italic font are the results of a high-dispersion LA-ICPQMS experiment carried out in hole-drilling mode using a 60-µm laser spot and a laser repetition rate of 5 Hz. Uncertainties represent standard deviations calculated from 2 (region 2), 4 (region 3 and 4) and 5 (region 5) individual measurements. Region 1 was analyzed only once. No standard deviation could be calculated in that case.

	region 1	region 2	region 3	region 4	region 5
MgO (wt%)		1.9 ± 0.5 *(2.180 ± 0.030)*	1.00 ± 0.27 *(1.35 ± 0.06)*	1.8 ± 0.4 *(2.232 ± 0.017)*	
Al_2O_3 (wt%)	49 ± 10 *(56.5)*	46 ± 9 *(48.0 ± 1.4)*	34 ± 5 *(32.8 ± 0.7)*	46 ± 8 *(46.86 ± 0.18)*	50 ± 9 *(56.1 ± 0.7)*
SiO_2 (wt%)	47 ± 11 *(42.3)*	38 ± 9 *(34.8 ± 1.4)*	55 ± 7 *(51.6 ± 0.8)*	39 ± 8 *(35.5 ± 0.6)*	47 ± 9 *(42.5 ± 0.6)*
Mn (mg/kg)		660 ± 230 *(686.5 ± 2.7)*		690 ± 240 *(624 ± 29)*	
FeO (wt%)		13.0 ± 2.7 *(14.59 ± 0.36)*	2.5 ± 0.5 *(3.09 ± 0.27)*	12.3 ± 2.4 *(14.7 ± 0.6)*	
Co (mg/kg)		180 ± 120 *(159 ± 5)*		170 ± 110 *(163 ± 4)*	
Ga (mg/kg)		190 ± 120 *(186.3 ± 2.8)*		190 ± 120 *(188.4 ± 1.5)*	
Rb (mg/kg)			390 ± 110 *(326 ± 12)*		
Sr (mg/kg)			240 ± 90 *(237 ± 19)*		
Ba (mg/kg)			2190 ± 480 *(1840 ± 110)*		