

Table ES11. ESRs for solution nebulization (SN) and laser ablation of SRM 612 and BCR-2G measured using regular cones.

	SN	SRM 612	BCR-2G		SN	SRM 612	BCR-2G
Li	0.32	0.54	0.67	In	4.60	3.50	4.94
Be	0.12	0.13		Sn	4.02	4.93	4.24
B	0.21	0.26	0.14	Sb	1.45	2.05	2.34
Na		2.50	1.45	Te	0.92		
Mg	1.00	1.00	1.00	Cs	4.99	6.28	7.37
Al	1.47	0.64	1.28	Ba	5.46	5.53	7.33
Si		0.67	0.51	La	4.87	3.66	6.66
P		0.25	0.07	Ce	4.98	4.94	7.00
Ca		2.11	3.30	Pr	5.59	4.52	7.25
Sc	1.95	1.48	2.61	Nd	5.95	3.94	6.56
Ti	1.68		2.11	Sm	6.58	3.78	6.05
V	1.95	2.72	2.99	Eu	6.63	5.07	9.11
Cr	1.94	1.72	2.28	Gd	6.31	4.12	8.30
Mn	2.28	1.89	2.30	Tb	6.77	4.27	8.56
Fe		2.34	1.84	Dy	6.35	3.71	7.34
Co	2.47	2.25	2.49	Ho	6.19	3.65	7.22
Ni	2.03	1.81	1.83	Er	6.14	3.72	6.91
Cu	1.60	1.68	1.19	Tm	7.39	3.75	6.84
Zn	0.83	1.75	0.87	Yb	7.69	4.35	10.19
Ga	2.94	2.83	3.05	Lu	7.37	4.23	9.89
Ge	1.62	2.98	3.13	Hf	5.39	4.40	9.68
As	0.23	0.63		Ta	4.16	3.20	7.66
Se	0.79	0.34		W	5.03	4.19	7.04
Rb	3.62	4.60	4.66	Re	5.60	6.05	7.91
Sr	3.93	3.47	4.54	Os	5.85		
Y	3.58	2.33	3.84	Ir	5.09		
Zr	2.57	2.37	3.65	Pt	4.26	2.91	1.70
Nb	2.51	2.42	2.91	Au	1.07	1.76	
Mo	3.07	3.25	4.60	Tl	6.95	5.79	6.53
Ru	4.26			Pb	6.49	6.62	7.74
Rh	4.03			Bi	5.48	5.82	6.79
Ag	3.34	2.92	4.03	Th	7.30	4.39	11.22
Cd	2.76	2.45	4.46	U	7.98	7.50	11.53

Table ESI2. ESRs for SRM 61X glasses measured on the Element 1 in a single analytical session using regular cones.

	SRM 616	SRM 614	SRM 612	SRM 610		SRM 616	SRM 614	SRM 612	SRM 610
Li	0.90	0.95	0.87	0.80	In	4.72	4.29	4.29	4.63
Be			<u>0.02</u>	<u>0.02</u>	Sn	6.51	5.97	5.60	5.80
B	1.12	0.71	0.36	0.29	Sb	3.74	3.33	2.91	3.51
Mg	1.17	1.12	1.07	1.45	Cs	6.61	6.95	6.46	6.21
Al	0.99	0.92	0.97	1.03	Ba	5.28	5.00	5.80	6.41
Si	1.00	1.00	1.00	1.00	La	3.74	3.39	3.97	4.21
P				<u>0.38</u>	Ce	5.22	5.06	5.48	5.92
Ca	2.77	2.59	2.78	3.09	Pr	5.16	4.77	5.35	6.03
Sc			2.17	2.36	Nd	4.64	4.27	4.83	5.39
Ti			3.88	3.28	Sm	4.32	4.24	4.83	5.39
V	3.86	3.68	3.52	3.55	Eu	5.38	4.96	5.54	5.65
Cr		2.33	2.77	2.95	Gd	4.02	3.98	4.58	5.40
Mn			2.69	2.57	Tb	4.06	3.84	4.47	4.84
Fe		2.39	2.42	2.79	Dy	3.63	3.81	4.31	5.05
Co		2.26	2.86	2.86	Ho	3.46	3.67	4.21	4.79
Ni			2.15	2.34	Er	3.83	3.66	4.23	5.05
Cu	6.33	3.00	2.45	2.28	Tm	3.99	3.77	4.35	5.27
Zn	<u>3.61</u>	<u>1.83</u>	<u>1.77</u>	<u>1.64</u>	Yb	3.77	3.92	4.41	4.98
Ga	2.67	3.14	3.74	3.56	Lu	3.97	3.73	4.24	4.90
Ge	3.19	3.79	3.54	3.12	Hf	4.39	3.89	4.65	5.08
As	<u>0.87</u>	<u>0.98</u>	<u>0.78</u>	<u>0.94</u>	Ta	3.47	3.22	3.53	4.92
Se			<u>0.59</u>	<u>1.79</u>	W	7.80	4.84	4.86	4.94
Rb	10.24	5.54	4.95	4.70	Re	8.96	7.30	6.80	6.47
Sr	3.69	3.45	4.00	4.18	Pt	<u>3.80</u>	<u>8.02</u>	<u>3.73</u>	<u>3.64</u>
Y	2.43	2.17	2.69	3.14	Au	<u>2.45</u>	<u>1.95</u>	<u>2.20</u>	<u>2.37</u>
Zr	2.46	2.30	2.76	2.99	Tl	16.71	7.07	6.61	6.28
Nb	2.92	2.79	3.15	3.76	Pb	8.15	7.88	7.02	6.57
Mo	5.30	4.57	3.97	4.49	Bi	7.28	7.67	7.28	6.37
Ag	4.81	4.41	3.94	3.76	Th	4.77	4.18	4.84	5.33
Cd		3.29	3.12	3.09	U	8.67	9.23	8.99	8.82

Note: Underlined elements have FIP > 9 eV.

Table ESI3. Laser operating conditions and Si-normalized ESRs for Ca and Al for measurements on SRM 612, MPI-DING, and USGS glasses.

Session	Sample	Ablation mode	UP-213 operating conditions			Elemental Sensitivity Ratio					
			Spot size (µm)	Laser energy output (%)	Laser energy (mJ)	1		2		3	
						Al	Ca	Al	Ca	Al	Ca
1	SRM 612	line	65	50	0.2	1.37	2.81	1.34	2.79		
2	SRM 612	line	100	50	0.4	1.46	2.99	1.43	2.94	1.37	2.89
2	SRM 612	spot	100	70	1.2	1.70	3.28	1.62	3.24	1.61	3.35
3	SRM 612	line	65	60	0.3	1.47	2.95	1.45	2.94		
4	SRM 612	line	80	75	0.6	0.81	2.03	0.83	1.96	0.83	1.97
1	ATHO-G	line	65	70	0.8	1.96	3.31	1.78	3.02		
1	StHs6/80-G	line	65	70	0.8	2.02	3.40	1.67	3.13		
1	T1-G	line	65	70	0.8	1.86	3.37	1.81	3.28		
1	ML3B-G	line	65	70	0.8	1.91	3.16	1.82	3.23		
1	GOR 128-G	line	65	70	0.8	1.64	2.97	1.58	2.81		
2	ATHO-G	spot	100	70	1.2	1.75	2.94	1.66	2.85		
2	StHs6/80-G	spot	100	70	1.2	1.76	3.26	1.65	3.11		
2	T1-G	spot	100	70	1.2	1.79	3.28	1.79	3.31		
2	BCR-2G	spot	100	60	0.7	1.77	3.25	1.75	3.23		
2	ML3B-G	spot	100	70	1.2	1.75	3.21				
2	BHVO-2G	spot	100	60	0.7	1.76	3.24	1.71	3.16	1.71	3.21
2	GOR 128-G	spot	100	70	1.2	1.58	2.94	1.56	2.82		
3	ML3B-G	line	80	60	0.4	2.07	3.73	1.93	3.56		
4	T1-G	line	65	75	0.4	1.11	2.17	1.05	2.09		
4	ML3B-G	line	65	75	0.4	1.18	2.43	1.12	2.41		
4	KL2-G	line	65	75	0.4	1.00	2.23				
4	BHVO-2G	line	80	75	0.6	1.11	2.27	1.07	2.21	1.26	2.49
4	GOR 128-G	line	65	75	0.4	1.08	2.23	1.07	2.14		

Note: All measurements were performed with an Element 1 at R=4000. For all measurements a Ni-Cu sampler cone and Ni-X skimmer cone were used. Laser repetition rate was 10 Hz for all samples. Travel speed for all lines was 10 µm/s. Spots in Session 2 were ablated for 1 minute.

Table ESI4. Average ESRs for SRM 612, MPI-DING, and USGS glasses measured with X-cones. Averages and RSDs (1 σ) include geologic glasses only.

	ATHO-G	StHs6/80-G	T1-G	BCR-2G	ML3B-G	BHVO-2G	GOR128-G	Ave	RSD	SRM 612
Na	4.2	3.8	3.6	3.4	3.4	3.7	3.6	3.7	7%	3.9
Mg	1.6	1.8	2.0	1.8	1.9	1.9	1.9	1.8	6%	1.5
Al	1.8	1.8	1.8	1.8	1.8	1.7	1.6	1.8	5%	1.5
Si	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0		1.0
P	0.5	0.5	0.5	0.4	0.4	0.4	0.5	0.5	8%	0.6
Ca	3.0	3.2	3.3	3.2	3.2	3.2	2.9	3.2	5%	3.0
Sc	1.4	1.5	1.5	1.8	1.6	1.6	1.6	1.6	7%	1.6
Ti	2.7	2.7	2.7	2.5	2.5	2.4	2.2	2.5	8%	2.0
V	2.8	3.2	3.1	3.6	3.3	3.7	3.2	3.3	10%	3.7
Cr	2.5	2.6	3.1	3.3	3.0	3.8	3.4	3.1	15%	3.8
Mn	3.2	3.2	3.6	3.1	3.2	3.4 ^a	3.4	3.3	5%	3.2
Fe	3.0	2.9	3.0	2.8	2.8	3.1	2.9	2.9	4%	3.2
Co		2.8	2.8	2.9	2.7	3.1 ^a	2.7	2.8	3%	3.0
Ni		2.2	2.4		2.4	3.1	2.4	2.5	13%	2.9
Cu	2.8	2.6	2.8	2.3	2.8		2.8	2.7	8%	3.4
Zn	2.4	2.3	2.5	2.8	2.4	2.5	2.2	2.4	8%	3.3
Ga	3.9	4.4	4.4	4.6	4.3	4.7	4.8	4.4	7%	5.0
Sr	3.4	3.4	3.5	3.4	3.7	3.5	3.5	3.5	3%	3.5
Y	2.0	1.8	1.8	1.9	1.9	1.9	1.9	1.9	4%	1.9
Zr	1.7	1.6	1.4	1.8	1.7	1.8 ^a	1.7	1.6	8%	1.7
Nb	2.1	1.9	1.9	2.0	2.0	1.7	2.8 ^b	1.9	6%	1.9
Sn	7.2	8.1	6.8	5.5	6.9		9.8 ^a	6.9	14%	6.5
Ba	3.5	3.8	3.7	3.7	3.9	4.0	3.8	3.8	4%	3.6
La	2.0	2.0	1.9	2.0	2.1	2.0	1.9	2.0	3%	1.8
Ce	2.8	2.9	2.9	2.6	2.9	2.6	2.9	2.8	5%	2.7
Pr	2.9	2.8	2.9	3.0	3.1		3.0	3.0	3%	2.8
Nd	2.7	2.7	2.5	2.9	2.9	2.8	3.0	2.8	6%	2.9
Sm	2.6	2.6	2.4	2.8	2.7	2.7	2.7	2.7	5%	2.6
Eu	3.2	3.3	3.0	3.6	3.3	3.3	3.3	3.3	5%	3.0
Dy	2.6	2.4	2.1	2.8	2.5	2.7	2.5	2.5	9%	2.5
Er	2.4	2.2	1.9	2.5	2.3	2.5	2.2	2.3	9%	2.3
Yb	2.7	2.5	2.3	3.0	2.7	2.8	2.5	2.6	8%	2.6
Hf	2.0	1.8	1.5	2.1	1.9		2.2	1.9	13%	2.0
Ta	1.5	1.4	1.2	1.6	1.4		1.4 ^b	1.4	10%	1.3
Pb	5.1	4.8	4.7	4.6	4.1	4.9 ^a	3.2	4.4	7%	5.1
Th	1.9	1.8	1.6	2.1	1.9	2.1	2.1 ^b	1.9	10%	1.5
U	4.1	4.0	3.8	3.9	3.6	3.7	3.7 ^b	3.9	5%	4.2

Note: The following ESRs are excluded from the average and RSD: (a) ESRs measured on concentrations with only information values and (b) on concentrations <0.1 ppm. ESRs for elements Co and Ni in ATHO-G are not included because their measured concentrations are more than 35% lower than their reported concentrations (see Table 6 for measured concentrations). Low mass elements (Na to Ga) are measured at R=4000 to avoid interferences. Higher mass elements measured at R=400. Si, used for internal normalization, measured in both.

Table ES15. Variation in ESRs for ML3B-G measured during different analytical sessions with concentrations provided for comparison.

	ESR	ESR*	ESR	RSD	Conc. (ppm)
Na	3.35	3.54	3.30	4%	17800
Mg	1.95	1.80	2.09	8%	39700
Al	1.86	1.75	1.99	6%	72000
Si	1.00	1.00	1.00		240000
P	0.45	0.45	0.46	1%	1000
Ca	3.20	3.21	3.64	8%	75000
Sc	1.57	1.65	2.20	19%	32
Ti	2.53	2.44	2.72	6%	12800
V	3.12	3.72	3.92	12%	268
Cr	2.85	3.39	4.15	19%	177
Mn	3.27	3.19	3.66	8%	1300
Fe	2.79	2.93	3.21	7%	84800
Co	2.65	2.87	3.95	22%	41
Ni	2.37	2.51	3.34	19%	107
Cu	2.77	3.01	3.50	12%	112
Zn	2.39	2.35	2.68	7%	108
Ga	4.08	4.82	5.34	13%	20

Note: ESRs used to calibrate SRM 612 concentrations measured during three sessions at R=4000. ESRs with asterisks (*) were used to calibrate both high and low energy SRM 612 measurements that were run during the same session. RSDs are 1 σ .

Table ES16. Measured concentrations (ppm) for MPI-DING and USGS glasses.

	ATHO-G		StHs6/80-G		T1-G		BCR-2G		BHVO-2G		GOR128-G	
	Ave	Stdev	Ave	Stdev	Ave	Stdev	Ave	Stdev	Ave	Stdev	Ave	Stdev
Na	34000	2000	36000	3000	25000	200	23000	300	16700	700	4300	200
Mg	550	20	11300	400	23000	400	21700	200	46000	1000	159000	2000
Al	64000	3000	93000	8000	89000	2000	71300	500	71000	1000	46000	1000
Si	353000		298000		274000		254000		233000		216000	
P	123	7	720	20	866	8	1530	20	1190	10	112	4
Ca	11500	800	38000	2000	53000	1000	51000	300	82000	2000	40000	1000
Sc	6.2	0.4	10.5	0.6	26.1	0.6	35.26	0.02	32.9	0.8	32	1
Ti	1660	70	4600	200	4810	90	13900	100	16200	300	1500	70
V	3.2	0.1	84	4	191.8	0.2	414	2	316	7	176	2
Cr	4.9	0.2	13.9	0.9	22.9	0.1	16.72	0.02	320	10	2500	200
Mn	810	20	580	20	1080	20	1523.6	0.4	1390	50	1450	20
Fe	26800	600	35000	2000	53000	700	94000	2000	89000	4000	79000	2000
Co	1.36	0.04	13.4	0.3	19.8	0.4	38	1	48	2	90	2
Ni	5.3	0.1	21.0	0.4	10.8	0.4	12.8	0.6	134	5	1070	20
Cu	17.9	0.5	37	1	19.2	0.5	15.8	0.7	125	5	61	2
Zn	150	10	66	5	78	4	149	5	108	5	68	2
Ga	22.2	0.4	20.6	0.8	21.0	0.1	22.0	0.3	20.9	0.6	9.3	0.3
Sr	86	2	450	10	300	20	301.0	0.6	356.5	0.4	29	3
Y	96	6	10.4	0.2	25	3	33.3	0.9	23.97	0.04	12	1
Zr	510	20	111	6	140	20	174	3	156	2	10	2
Nb	66	2	6.72	0.03	9.6	0.5	11.85	0.07	16.4	0.1	0.14	0.02
Sn	5.6	0.2	1.29	0.04	2.23	0.03	1.77	0.02	1.409	0.008	0.33	0.06
Ba	490	20	288.6	14.0	410	10	584	6	116	4	1.0	0.1
La	52	2	11.3	0.3	73	4	21.8	0.1	13.0	0.3	0.11	0.01
Ce	117	6	25.3	0.9	135	8	42.828	0.007	30	1	0.45	0.04
Pr	14.0	0.6	2.9	0.1	13.2	0.7	5.95	0.04	4.5	0.1	0.10	0.01
Nd	58	2	12.2	0.8	43	3	25.6	0.3	21.1	0.7	0.8	0.1
Sm	14.1	0.5	2.7	0.1	7.1	0.6	6.2	0.1	5.6	0.3	0.53	0.07
Eu	2.63	0.09	0.93	0.05	1.3	0.1	1.86	0.03	1.82	0.04	0.26	0.04
Dy	17.1	0.6	2.12	0.09	4.8	0.6	6.2	0.2	4.96	0.05	1.9	0.2
Er	10.6	0.3	1.13	0.05	2.7	0.4	3.6	0.1	2.41	0.01	1.3	0.2
Yb	10.8	0.3	1.08	0.07	2.6	0.3	3.36	0.08	1.91	0.08	1.3	0.1
Hf	14.4	0.3	2.9	0.1	3.8	0.5	4.6	0.1	4.0	0.1	0.41	0.04
Ta	4.2	0.1	0.44	0.02	0.50	0.03	0.77	0.02	1.071	0.003	0.020	0.003
Pb	7.0	0.3	12.0	0.3	15.4	0.5	10.38	0.07	1.50	0.04	0.3	0.1
Th	7.6	0.2	2.2	0.1	34	3	5.4	0.2	1.10	0.01	0.009	0.002
U	2.7	0.1	1.11	0.04	2.14	0.06	1.46	0.01	0.345	0.007	0.013	0.002

Note: For ATHO-G, StHs6/80-G, and GOR128-G, the averages and standard deviations (1 σ) are from 4 measurements over two sessions. T1-G, BCR-2G, and BHVO-2G values are from two measurements during one analytical session.