Geosci. Instrum. Method. Data Syst., 4, 75–80, 2015 www.geosci-instrum-method-data-syst.net/4/75/2015/doi:10.5194/gi-4-75-2015 © Author(s) 2015. CC Attribution 3.0 License.





Alkali element background reduction in laser ICP-MS

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Received: 16 September 2014 - Published in Geosci. Instrum. Method. Data Syst. Discuss.: 17 November 2014

Revised: 3 March 2015 - Accepted: 3 March 2015 - Published: 17 March 2015

Abstract. Alkali backgrounds in laser ablation ICP-MS analyses can be enhanced by electron-induced ionisation of alkali contamination on the skimmer cone, reducing effective detection limits for these elements. Traditionally, this problem is addressed by isolating analyses of high-alkali materials onto a designated cone set, or by operating the ICP-MS in a "soft extraction" mode, which reduces the energy of electrons repelled into the potentially contaminated sampling cone by the extraction field. Here we present a novel approach, where we replace the traditional alkali glass tuning standards with synthetic low-alkali glass reference materials. Using this vitreous tuning solution, we find that this approach reduces the amount of alkali contamination produced, halving backgrounds for the heavy alkali elements without any change to analytical procedures. Using segregated cones is still the most effective method for reducing lithium backgrounds, but since the procedures are complimentary, both can easily be applied to the routine operations of an analytical lab.

1 Introduction

In solution ICP-MS, tuning and calibration are performed using carefully selected, high-purity aqueous solutions. In contrast, laser ablation ICP-MS (LA-ICP-MS) tuning and calibration are often conducted using natural or multi-element glass reference materials such as the NIST 600-series glasses, which are generally not specifically chosen or synthesised for the purpose of tuning a plasma source mass spectrometer. This can create a host of contamination issues (Eggins and Shelley, 2002).

The LA-ICP-MS Agilent 7500 lab in operation at the Research School of Earth Sciences (RSES), Australian National University (ANU), during 2006, was a general-purpose, multidisciplinary analytical facility. Samples analysed included zircon and other minerals for U–Pb geochronology; geological, synthetic, and biogenic carbonates for paleoclimatology; mantle minerals for diamond indicator studies; igneous, metamorphic, and synthetic minerals and silicate melts for the study of petrogenesis of various mantle and crustal rocks at a variety of pressures and temperatures; synthetic and natural sulfides for thermodynamic or ore-genesis research, and occasional solution (no laser ablation) ICP-MS analyses of platinum group elements. The extensive variety of analytical procedures performed led to a number of potential contamination and cross-contamination issues.

Of particular concern were the alkali elements. Once alkali elements are introduced to the skimmer and sampler cones, electron-induced secondary ionisation can create large sample-independent backgrounds. Analytical protocols such as the soft extraction technique (Tye and Sakata, 2000) will reduce these backgrounds, but at the expense of overall sensitivity, especially for low-mass ions.

Two experiments were performed in the LA- ICP-MS Agilent 7500 lab, in order to determine the ease and effectiveness of reducing alkali loads and backgrounds without changing analytical procedures. The first method involved segregating cones into high, low, and average expected alkali concentrations. This is standard procedure in many labs, and served as a baseline for effectiveness, to which we could compare our new procedure. The second experiment replaced the NIST612 standard with a custom-built alkali-free glass (Tune-1) with a composition especially chosen for tuning and evaluation of laser ablation and ICP-MS performance.

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This was, in effect, the vitreous equivalent of a tuning solution, with the tuning elements dissolved into a glass instead of dilute nitric acid. While this may seem to be an obvious approach, we do not know of any previous attempts to dissolve tuning species into a glass with a composition chosen to eliminate unwanted contaminants.

2 Methods

Cone segregation involved analysing samples with different expected alkali contents on different cones. A "dirty" cone set (C-5) was assigned to use for lithium borates (Eggins, 2003), stoichiometric sodium and potassium minerals, and doped or felsic glasses. Another cone set (E-1) was set aside for low-level lithium, rubidium, and caesium work. The remaining cones were used for routine mineral analyses that did not fall into either of these two categories. The backgrounds of Li, Na, Rb, and Cs for the various cone sets were monitored during the daily tune-up from March to July 2006. Potassium was not recorded, as the backgrounds of both stable K isotopes are complicated by argon hydrides and the shoulder of the intense 40 Ar⁺ peak from the argon plasma. 40 K⁺ was completely obscured by 40 Ar⁺.

Tuning the instrument in the morning before the analysis can comprise 5–25 % of the total daily plasma load, depending on the duration (2–12 h) and type of analyses performed. The concentrations of Li, Na, and Rb in NIST 612 and 610 are significantly higher than MORB (Sun and McDonough, 1989), while the Cs concentration in these synthetic glasses is many times higher than most natural samples (Table 1). A nominally alkali-free glass (Tune-1) was synthesised to replace the NIST 612 glass previously used in tuning. Tune-1 was used from August to December 2006, and backgrounds and machine performance were recorded in a similar fashion.

Tune-1 was designed to be an anorthite-wollastonitediopside-quartz eutectic CMAS glass (Longhi, 1987). This composition was chosen for the low melting point (1129 °C) and low silica content, which allows for more rapid diffusive homogenisation of the dopants. The dopants were chosen according to the following criteria: (1) the element must be soluble in the glass. (2) The element must be refractory enough not to evaporate during fusion in the one atmosphere furnace. (3) To minimise interferences, elements with few isotopes were favoured over those with many. (4) A decent mass range was desired, with a dopant every 40 to 50 AMU. (5) Rare earth elements were avoided, as it was unclear how well separated the available reagents were. (6) An element with an isotopic ratio greater than 10:1 but less than 20:1 was desired for performing deadtime corrections to the electron multiplier (138Ba / 135Ba~11 was eventually chosen). (7) If possible, elements which ionised well in the ICP were selected. (8) The element had to be available on the shelf of the experimental petrology store, as this project was unfunded. (9) U and Th were both included, as their relative behaviour was of interest to geochronologists at the time.

To satisfy these requirements as best as possible, Tune-1 was doped with 50 micromols mol⁻¹ of Be, Mn, Nb, Ba, Ta, Th, and U. The glass was synthesised via the silica gel process (Hamilton and Henderson, 1968), with the Ca, Mg, Al, Be, Mn, Ba, Th, and U dissolved as nitrates, and the Nb, Ta, and Si added as ethoxides. The Tune-1 measured composition is given in Table 2.

The major element (Ca, Si, Al, Mg) composition of the glass was determined using WD spectrometry on the Cameca SX100 electron microprobe at RSES. The beam conditions were 15 kV and 10 nA, with the spot purposefully defocused to 5 μ m. The following synthetic standards were used for calibration: Ca and Si, wollastonite/CaSiO₃, Al, CaAl₂O₄, Mg, and periclase/MgO. All standards were prepared at RSES from high-purity powders (B. Hibberson, personal communication, 2006) and appropriate conditions of synthesis. Forty points across the sample were analysed and the results statistically collated to give the standard deviation reported.

The trace elemental composition of the glass was determined using laser ICP-MS. LA-ICP-MS analysis was performed at RSES using the Agilent 7500 series mass spectrometer. The Lambda Physik lpx 120i 193nm excimer laser laser supplied by Resonetics was attenuated by using a 25 % reflectance mirror on the final bend of the custom-built laser flight tube, yielding a power output of approximately 2–3 J cm⁻². The custom-built two-volume mixing cell is the predecessor to both the Laurin Technic RESOlution cell and the Helix cells sold commercially, with the details described in Eggins et al. (2003), and references therein. Ablation took place at 5 Hz.

The following analytical technique was used to determine the Rb and Cs content of Tune-1. Selected chalcophile elements were also measured for a different experiment, and those results are not reported here. Analysis time was 75 s, with 25 s of background collected before ablation commenced. A 187 micron spot was used. The following masses were measured: ⁹Be, ²⁹Si, ⁴³Ca, ⁸⁵Rb, ¹⁰⁷Ag, ¹⁰⁹Ag, ¹¹¹Cd, ¹¹⁴Cd, ¹¹⁸Sn, ¹¹⁹Sn, ¹²¹Sb, ¹²³Sb, ¹³³Cs, ¹⁸²W, ¹⁸³W, ²⁰³Tl, ²⁰⁵Tl, ²⁰⁸Pb²⁰⁹Bi, ²³²Th, ²³⁸U. All isotopes were counted for 30 ms except for Si and Ca, which were measured for 5 ms. Including switching time, this cycle was repeated every 0.6222 s.

For the dopants, Na, and Li, a 54 um spot was used, with a laser rep rate of 4 Hz. Analysis time was 60 s, with 20 s of background collected before ablation commenced. The following masses were measured: ⁷Li, ⁹Be, ²³Na, ²⁵Mg, ²⁷Al, ²⁹Si, ³¹P, ⁴³Ca, ⁴⁷Ti, ⁵⁵Mn, ⁵⁷Fe, ⁹³Nb, ¹³⁷Ba, ¹⁸¹Ta, ²³²Th, ²³⁸U. All isotopes were counted for 30 ms except for Na, Mg, Ca and Fe, which were measured for 20 ms, and Si, which was measured for 10 ms.

Data were reduced via Excel spreadsheet in the manner of Longerich et al. (1996). ⁴³Ca was the internal standard, using the EPMA value of 28.46 % CaO. Trace element abundances

Table 1. Alkali contents of popular natural and synthetic ICPMS reference materials. Li, Rb, Cs in ppm (μ g g⁻¹). Na is weight percent oxide. Values from Govindaraju (1994), Eggins et al. (1997), Norman et al. (1998), Hinton (1999), and Gao et al. (2002). LiBO flux Li content is an estimate; exact content depends on tetraborate / metaborate ratio, and rock type fluxed.

Element	LiBO flux	610	612	BCR	BHVO	Tune-1	Units
Li	≈ 83000	484	41	9.6	4.9	0.184	$\mu g g^{-1}$
Na ₂ O	variable	13.76 %	14 %	3.15 %	2.26 %	0.0021 %	$%gg^{-1}$
Rb	variable	431	32	49	9.5	0.012	$\mu\mathrm{g}\mathrm{g}^{-1}$
Cs	variable	360	41	1.1	0.1	0.01	$\mu\mathrm{g}\mathrm{g}^{-1}$

Table 2. Major and trace elemental composition of glass Tune-1. Errors are 1σ . Major elements from EPMA, minor elements from ICPMS.

$\%gg^{-1}$					
$28.5\% \pm 0.1\%$					
$2.16\% \pm 0.04\%$					
$13.1\% \pm 0.1\%$					
$56.5\% \pm 0.2\%$					
$\mu \mathrm{g}\mathrm{g}^{-1}$	μmol mol ^{−1}				
42.1 ± 0.2	80.1 ± 0.3				
186.3 ± 0.9	58.1 ± 0.3				
314.1 ± 0.8	57.9 ± 0.2				
429.9 ± 1.2	53.7 ± 0.1				
612.8 ± 2.7	58.0 ± 0.3				
704.1 ± 2.5	52.0 ± 0.2				
723.7 ± 14.6	52.1 ± 1.0				
$\mu \mathrm{g}\mathrm{g}^{-1}$	μmol mol ^{−1}				
0.17 ± 0.02	0.43 ± 0.04				
14.8 ± 1.3	11.0 ± 0.9				
0.012 ± 0.002	0.0025 ± 0.0004				
0.010 ± 0.001	0.0013 ± 0.0001				
	28.5% 2.16% 13.1% 56.5% $\mu g g^{-1}$ 42.1 ± 0.2 186.3 ± 0.9 314.1 ± 0.8 429.9 ± 1.2 612.8 ± 2.7 704.1 ± 2.5 723.7 ± 14.6 $\mu g g^{-1}$ 0.17 ± 0.02 14.8 ± 1.3 0.012 ± 0.002				

were standardised using the Pearce et al. (1997) values for NIST 612. The concentrations of dopants and alkali contaminants are listed in Table 2.

Each morning, following the daily instrumental tuning regime, alkali backgrounds were recorded as raw counts, and converted to $\mu g \, g^{-1}$ equivalent using a daily cps/ $\mu g \, g^{-1}$ calibration factor. The counts per $\mu g \, g^{-1}$ in routine analysis can vary by a factor of 2 due to the condition of the cones, the laser and optics, the electrostatic lenses, and other unknown factors. This is why a $\mu g \, g^{-1}$ equivalent is reported instead of raw counts.

Once Tune-1 was in use, freshly cleaned cones were installed on those days when low-level analyses of alkali elements were to be performed. This subset of the tune glass backgrounds is representative of the backgrounds that were present during alkali analysis. Low-level alkali analyses were generally standardised against natural basalt BCR-2G, which

Table 3. Mean daily backgrounds in ppm equivalent. Low conc refers to cone set E-5, which was reserved for low-alkali samples. Li free refers to all cones except the dedicated high-alkali set. Clean cones is the background on freshly cleaned cones after tuning on the Tune-1 glass, before any analyses are performed.

Cones	Standard	Li	Na	Rb	Cs
All	NIST 612	86.6	623	0.090	0.037
Li free	NIST 612	4.20	642	0.094	0.039
Low conc	NIST 612	0.29	705	0.090	0.020
Li free	Tune-1	1.83	474	0.044	0.015
Low conc	Tune-1	0.37	499	0.054	0.016
Fresh cones	Tune-1	0.54	161	0.022	0.005

has lower alkali concentrations than NIST 612 or 610 (Table 1).

3 Results

The cone segregation experiment, using NIST 612 as a tuning glass, was performed from March to July 2006. In early August, the custom-made Tune-1 glass replaced NIST 612 as the glass used for tuning. Cone segregation of the high-alkali cone set (C-5) was continued, and data were collected through December 2006.

The mean $\mu g g^{-1}$ equivalent backgrounds for Li, Na, Rb, and Cs are reported in Table 3, and the daily values are in Table 4. The high-alkali cone set (C-5) has significantly higher backgrounds for Li than all other cone sets, but the low-alkali cone set (E-1) is similar to the other cones (sample cones D, J, A, K; skimmer cones 6, 2, 4, 9, 7) for all elements except lithium. Cone segregation was quite effective at reducing Li backgrounds on the low Li cone set (Fig. 1, Table 3). The use of low-concentration cones dropped the Cs background by a factor of about 2. However, cone segregation had no appreciable impact on Na or Rb background levels.

The adoption of Tune-1 approximately halved the backgrounds for Li, Rb, and Cs compared to the backgrounds associated with tuning on NIST 612. Na was reduced by 25 %. However, the background produced by a newly cleaned set of cones (tuned using Tune-1) is 2–3 times lower still (Fig. 1,

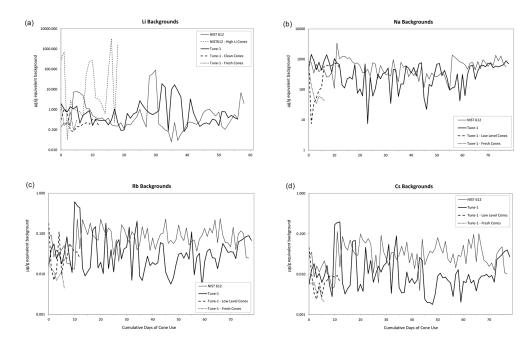


Figure 1. (a) Daily Li backgrounds as $\mu g g^{-1}$ equivalent for high Li cones, standard cones tuned with NIST612, standard cones tuned with Tune-1, low-level cones tuned with Tune-1, and freshly cleaned cones tuned with Tune-1. (b) Daily Na backgrounds as $\mu g g^{-1}$ equivalent for tuning done with NIST 612, Tune-1, and Tune-1 with low-level and freshly cleaned sets of cones for low-level alkali work. (c) Daily Rb backgrounds as $\mu g g^{-1}$ equivalent for tuning done with NIST 612, Tune-1, and Tune-1 with low-level and freshly cleaned sets of cones for low-level alkali work. (d) Daily Cs backgrounds as $\mu g g^{-1}$ equivalent for tuning done with NIST 612, Tune-1, and Tune-1 with low-level and freshly cleaned sets of cones for low-level alkali work.

Table 3), showing that backgrounds can be dropped for those days when low-level alkali elements are to be analysed.

4 Discussion

The analysis of the tune glass reveals a few errors in synthesis. Excess Be is caused by an aborted attempt to dissolve Be metal in concentrated nitric acid before adding Be as a nitrate solution. The Si deficit is probably a result of incomplete hydration of the tetra ethyl orthosilicate, and explains the slightly high trace elemental compositions. The glass appears to be homogenous despite these minor problems. The alkali content, while detectable, is orders of magnitude lower than the NIST 612 glass.

Day-to-day background levels in alkali elements were highly variable throughout the study. Two instances where a lithium borate was run on a cone set other than the designated one are clearly visible in the data (Fig. 1a). Many, but not all, of the other variations can be explained by use of NIST 612 or 610 as a reference material under various spot sizes and ablation times. Cleaning cones generally dropped the backgrounds of all elements except lithium. However, despite the day-to-day noise, some systematic trends were noticed.

Segregating lithium borate flux experiments onto a dedicated cone set produced an order of magnitude decrease in Li backgrounds for non-Li cones, as expected. Replacing the NIST glass used for tuning with a custom-made glass reduced most alkali backgrounds by about a factor of 2. The changes only involved machine set-up, tuning and performance verification, and did not require any changes to methods or standardisation for analysing unknowns. Judging by the alkali levels found on clean cones, a further factor of 2–3 reduction is possible for days when alkali need to be measured at the lowest levels. We note, however, that the lithium backgrounds are lowest for the low-alkali cones tuning with NIST 612. The reason these are higher when the tune glass is used is not clear, but it is possible that the spike in Li backgrounds on the low-level cones at the end of the NIST run was a contamination event that was never properly cleaned, and that persisted into the Tune-1 experiments.

5 Conclusions

When tuning LA-ICP-MS we have observed that use of the low-alkali glass, Tune-1, is an effective means of reducing alkali backgrounds and improving analytical precision and lowering limits of detection. For the heavy alkali in particular, it is more effective than simply segregating cones based on expected target composition.

This reduction in alkali contamination does not preclude use of instrumental methods such as soft extraction (Tye and Sakata, 2000) to further depress the alkali background.

Table 4a. Mean daily backgrounds in $\mu g \, g^{-1}$ equivalent from tuning using the NIST 612 glass.

Table 4b. Mean daily backgrounds in $\mu g \, g^{-1}$ equivalent from tuning using the Tune-1 glass.

Date	Skimmer cone	Sampler cone	Li Bkg	Na Bkg	Rb Bkg	Cs Bkg
10 Mar 2006	j	2	0.13	860.74	0.081	0.028
13 Mar 2006	j	2	0.22	783.27	0.093	0.035
14 Mar 2006 15 Mar 2006	j i	2 2	0.20 0.16	350.45 683.83	0.026 0.039	0.009 0.016
16 Mar 2006	j j	2	7.31	384.08	0.039	0.010
17 Mar 2006	j	2	7.85	490.26	0.040	0.016
21 Mar 2006	j	2	6.63	449.75	0.051	0.021
22 Mar 2006	c	5	280.58	258.70	0.018	0.011
23 Mar 2006	c	5	712.95	275.27	0.018	0.008
24 Mar 2006	j	2	4.97	363.73	0.013	0.004
27 Mar 2006 29 Mar 2006	j	2	1.14	109.62	0.013	0.005
29 Mar 2006 31 Mar 2006	k k	4	1.10 0.52	3425.75 1037.87	0.230 0.042	0.115 0.015
3 Apr 2006	k	4	0.40	1208.37	0.223	0.013
4 Apr 2006	k	4	0.34	1261.59	0.143	0.049
5 Apr 2006	k	4	0.39	1068.95	0.095	0.039
6 Apr 2006	k	4	0.28	1119.94	0.182	0.071
7 Apr 2006	d	9	0.38	824.22	0.092	0.039
10 Apr 2006	d	9	0.18	721.55	0.077	0.031
11 Apr 2006	d	9	0.16	756.37	0.068	0.029
13 Apr 2006			0.15	608.52	0.228	0.100
18 Apr 2006 19 Apr 2006			0.22	363.35 362.53	0.138 0.094	0.069 0.059
20 Apr 2006			0.11	469.20	0.094	0.039
21 Apr 2006			0.17	275.83	0.116	0.057
26 Apr 2006	e	1	0.28	772.24	0.029	0.011
27 Apr 2006			0.43	695.87	0.071	0.030
1 May 2006	c	5	0.03	234.94	0.020	0.006
2 May 2006	c	5	2.85	625.57	0.167	0.092
3 May 2006	С	5	1.06	409.54	0.131	0.036
4 May 2006	c c	5 5	0.89 0.81	315.58 330.10	0.083	0.025 0.016
5 May 2006 8 May 2006	c	5	0.43	276.55	0.001	0.010
9 May 2006	j	2	1.03	972.29	0.090	0.035
10 May 2006	,		0.31	361.38	0.040	0.023
11 May 2006			0.14	180.90	0.053	0.030
15 May 2006			45.66	797.04	0.148	0.049
16 May 2006			59.58	542.41	0.076	0.029
17 May 2006			89.88	620.02	0.136	0.063
19 May 2006			0.19	263.64	0.038	0.019
22 May 2006 23 May 2006			0.14	386.39 287.61	0.078 0.041	0.033 0.014
24 May 2006			0.10	420.53	0.065	0.014
29 May 2006	e	1	0.03	185.05	0.097	0.004
31 May 2006	j	2	0.23	540.93	0.102	0.074
1 Jun 2006	e	1	0.03	117.14	0.231	0.017
1 Jun 2006	j	2	0.06	338.97	0.057	0.026
5 Jun 2006			0.10	219.85	0.068	0.038
6 Jun 2006			0.21	352.27	0.057	0.034
7 Jun 2006 8 Jun 2006			0.24 0.21	281.16 266.03	0.071 0.164	0.044 0.081
9 Jun 2006			0.21	306.67	0.164	0.047
13 Jun 2006	j	2	0.15	366.77	0.067	0.033
14 Jun 2006	c	5	54.31	290.85	0.138	0.065
15 Jun 2006	c	5	245.09	158.64	0.052	0.023
16 Jun 2006	c	5	263.34	94.82	0.064	0.019
19 Jun 2006	c	5	3.80	1369.72	0.070	0.032
21 Jun 2006	c	5	3.16	1182.13	0.037	0.014
22 Jun 2006 23 Jun 2006	c c	5 5	1.68	977.39 819.26	0.073	0.030
26 Jun 2006	c	5	0.61 76.51	819.26 764.24	0.090 0.135	0.027 0.052
27 Jun 2006	c	5	3279.83	657.11	0.085	0.032
28 Jun 2006	j	2	0.66	470.63	0.137	0.074
4 Jul 2006	d	4	0.94	748.62	0.104	0.043
5 Jul 2006	d	4	1.04	780.64	0.219	0.098
6 Jul 2006	c	5	0.23	443.88	0.059	0.020
7 Jul 2006	d	4	0.70	843.98	0.236	0.101
12 Jul 2006	d	4	0.48	486.56	0.091	0.044
13 Jul 2006 14 Jul 2006	e	1 1	0.76 0.14	971.26 774.74	0.060	0.022
14 Jul 2006 18 Jul 2006	e e	1	0.14	585.21	0.059 0.047	0.020 0.016
20 Jul 2006	e	1	0.10	787.62	0.047	0.016
21 Jul 2006	e	1	0.32	630.06	0.040	0.012
25 Jul 2006	e	1	0.57	1354.36	0.100	0.032
27 Jul 2006	e	1	0.34	878.88	0.117	0.040
3 Aug 2006	c	5	1575.30	1280.07	0.099	0.048
4 Aug 2006	a a	4	6.87	723.24	0.025	0.011
7 Aug 2006		4	1.99	567.16	0.025	

Date	Skimmer cone	Sampler cone	Li Bkg	Na Bkg	Rb Bkg	Cs Bkg
9 Aug 2006	a	4	2.00	514.40	0.016	0.006
10 Aug 2006	a	4	1.09	1439.83	0.043	0.013
11 Aug 2006	a	4	0.77	902.18	0.055	0.018
14 Aug 2006 15 Aug 2006	a a	4	1.37 1.08	452.61 796.94	0.024	0.008 0.010
16 Aug 2006	a	4	1.48	439.43	0.018	0.006
17 Aug 2006	a	4	0.21	883.06	0.032	0.009
18 Aug 2006	a	4	0.53	1400.18	0.083	0.017
20 Aug 2006 21 Aug 2006	a a	4	0.68 0.90	772.84 368.04	0.024	0.005 0.003
21 Aug 2006	c	5	167.29	1046.24	0.613	0.170
22 Aug 2006	c	5	218.54	759.97	0.488	0.191
23 Aug 2006 4 Sep 2006	c d	5 9	365.30 0.16	664.10 142.18	0.434 0.014	0.198 0.006
5 Sep 2006	d	9	0.10	112.77	0.009	0.003
6 Sep 2006	d	9	0.29	220.22	0.011	0.004
7 Sep 2006	d	9	0.29	257.43	0.014	0.005
8 Sep 2006 12 Sep 2006	d d	9	0.30 0.18	220.43 664.68	0.124 0.149	0.065 0.069
13 Sep 2006	c	5	12.94	76.32	0.014	0.003
14 Sep 2006	c	5	21.09	105.01	0.020	0.006
15 Sep 2006	c	5	17.92	61.70	0.010	0.004
18 Sep 2006 18 Sep 2006	e e	1 9	0.30 1.07	699.00 7.57	0.181 0.014	0.046 0.010
18 Sep 2006	c	5	4.18	260.06	0.040	0.022
19 Sep 2006	d	9	0.22	60.86	0.011	0.006
21 Sep 2006	d	9	0.09	106.44	0.052	0.011
22 Sep 2006 26 Sep 2006	d c	9 5	0.10 10.09	317.45 226.23	0.071 0.024	0.016 0.011
27 Sep 2006	c	5	283.63	337.15	0.042	0.016
28 Sep 2006	c	5	326.27	367.70	0.046	0.019
29 Sep 2006	c	5	826.78	511.94	0.144	0.055
29 Sep 2006 29 Sep 2006	e d	1 9	0.64 0.37	34.97 466.57	0.007 0.085	0.003 0.032
10 Oct 2006	d	9	0.61	438.80	0.203	0.089
10 Oct 2006	j	2	0.73	59.32	0.009	0.005
11 Oct 2006	j	2	2.75	152.15	0.007	0.003
12 Oct 2006 17 Oct 2006	j j	2 2	1.51 0.95	152.68 598.86	0.014 0.028	0.004 0.011
18 Oct 2006	j	2	0.69	507.74	0.016	0.006
19 Oct 2006	j	2	0.56	354.14	0.019	0.008
20 Oct 2006 23 Oct 2006	j	2 2	0.68 0.86	536.71 280.69	0.017 0.019	0.006 0.007
24 Oct 2006	j j	2	19.11	694.11	0.019	0.007
25 Oct 2006	j	2	12.66	771.84	0.055	0.022
27 Oct 2006	e	1	0.09	52.90	0.011	0.002
31 Oct 2006 1 Nov 2006	c c	5 5	6.94 11.89	22.20 147.23	0.008	0.002 0.002
2 Nov 2006	c	5	324.38	128.81	0.008	0.002
3 Nov 2006	c	5	178.84	300.52	0.017	0.003
7 Nov 2006	j	2	9.82	683.59	0.031	0.009
8 Nov 2006 9 Nov 2006	j j	2 2	16.83 8.60	725.89 288.02	0.033 0.025	0.011 0.008
10 Nov 2006	c	5	217.02	432.29	0.034	0.008
13 Nov 2006	j	2	4.21	237.98	0.023	0.007
13 Nov 2006	e	1	0.08	97.03	0.110	0.006
14 Nov 2006 15 Nov 2006	e j	1 2	0.14 3.35	112.57 121.40	0.010 0.026	0.003 0.010
16 Nov 2006	j	2	0.67	329.30	0.033	0.013
17 Nov 2006	d	9	0.30	42.56	0.004	0.002
20 Nov 2006 22 Nov 2006	c	5 5	317.87	314.98 62.41	0.020	0.007
24 Nov 2006	c c	5	101.05 83.24	320.34	0.037 0.042	0.006 0.010
27 Nov 2006	e	1	0.15	596.33	0.025	0.006
29 Nov 2006	e	1	0.19	638.18	0.025	0.007
30 Nov 2006 1 Dec 2006	c	5 5	73.62 86.85	217.96 413.92	0.014 0.027	0.004 0.007
2 Dec 2006	c e	1	0.22	598.30	0.027	0.007
4 Dec 2006	e	1	0.19	634.70	0.045	0.009
5 Dec 2006	c	5	155.70	563.94	0.034	0.010
6 Dec 2006 7 Dec 2006	e e	1 1	0.33	741.09 724.49	0.036 0.035	0.008
8 Dec 2006	e	1	0.30	524.38	0.033	0.009
11 Dec 2006	e	1	0.80	596.19	0.062	0.023
12 Dec 2006	e	1	0.77	559.75	0.068	0.026
13 Dec 2006 14 Dec 2006	e e	1 1	0.39 0.51	605.62 659.52	0.075 0.085	0.031 0.037
15 Dec 2006	e	1	0.40	889.42	0.089	0.040
19 Dec 2006	e	1	0.33	712.80	0.068	0.027

Rather, it reduces the build-up of unwanted alkali elements in parts of the instrument where secondary ionisation can reintroduce them into subsequent samples as contamination. As this is only a change to the instrument set-up procedure, it does not require a change to the protocols used by analysts. The lower backgrounds that result from this study have enabled the determination of the alkali content of olivine (Mallmann et al., 2009), feldspar lamellae (Parsons et al., 2009), ultramafic melt inclusions (Kallio and Ireland, 2006), and Martian meteorites (Stopar et al., 2007). Although only a dozen glass beads were cast, limited supplies are available from the authors on request.

Acknowledgements. This project was not funded by any grant or scholarship, but was performed by technical staff as part of our brief to improve instrumental performance. We thank Hugh O'Neill and Stephen Eggins for giving us the latitude to look into this issue, Mike Shelley for instruction on excimer laser and ICP-MS maintenance, and Carl Spandler and two anonymous reviewers for thoughtful reviews of the manuscript.

Edited by: W. Schmidt

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