Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry.

Appendix for "Precise Measurement of $^{41}K/^{39}K$ Ratios Using A Single Focusing Collision Cell Multi-Collector ICP-MS"

1. Column chemistry procedure for K purification
2. Detailed mass spectrometer settings
3. Typical mass scan for a K solution
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1. Column chemistry procedure for K purification

Stage 1. Removal of Na, Al, and Ca from K

Column detail	Custom-made quartz column (6mm OD) Resin bed dimensions: 4mm × 10cm long 20 ml reservoir
Resin	Biorad AG50W-X12 cation exchange resin, 100-200 mesh
Procedure	
Clean	3ml 4.5M HNO_3
Clean	1ml H_2O
Equilibrate	3ml 1.5M HNO_3
Load sample	In 0.5ml 1.5M HNO_3
Elute Na, Al	4.5ml 1.5M HNO_3
Collect K	12 ml 1.5M HNO_3
Clean (Elute Ca)	5ml 6M HCl
Clean	5ml H_2O

Stage 2. Removal of Ti and Mg from K

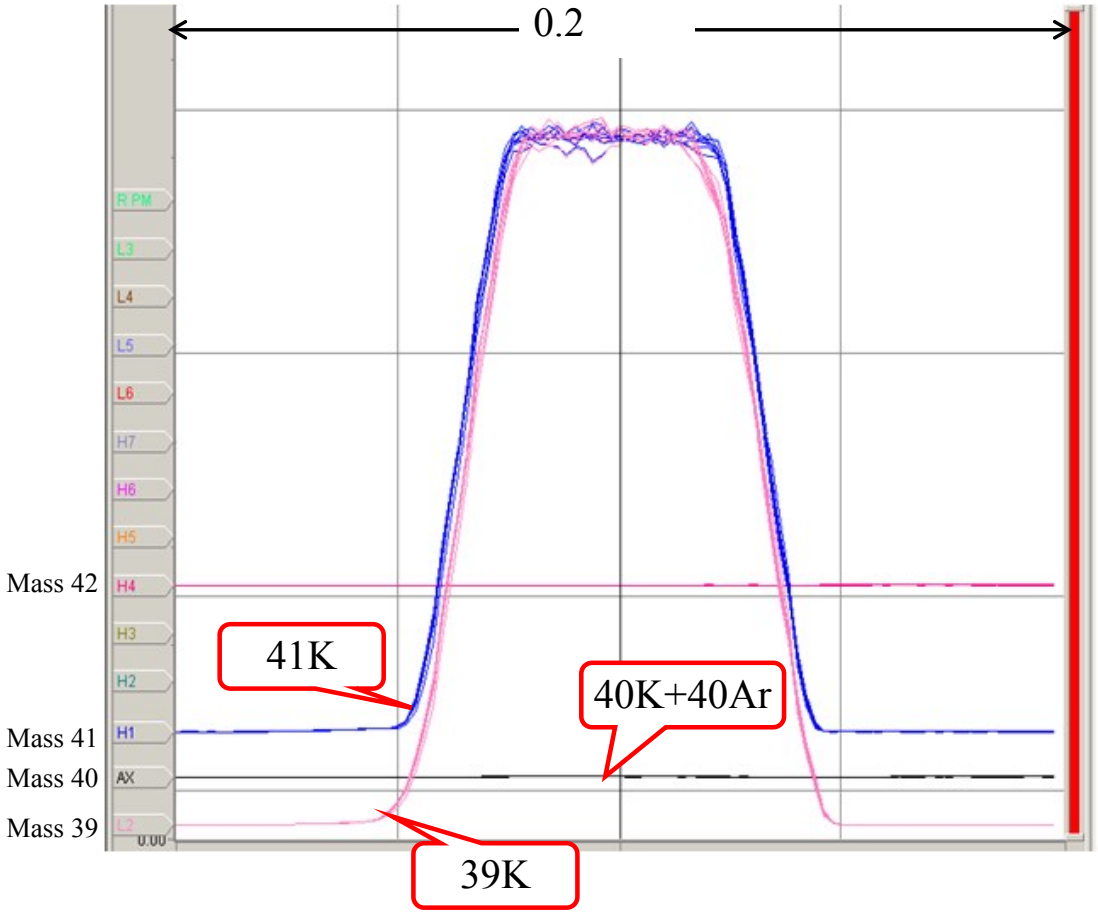
Column detail	Custom-made shrinkable Teflon column Resin Bed dimensions: 4mm × 4.2cm long 1.5 ml reservoir
Resin	Biorad AG50W-X8 cation exchange resin, 100-200 mesh
Procedure	
Clean	1ml 4.5M HNO_3
Clean	1ml H_2O
Equilibrate	1ml 0.2M HNO_3+0.05M HF
Load sample	in 0.5ml 0.2M HNO_3+0.05M HF
Elute Al, Ti	5ml 0.2M HNO_3+0.05M HF
Elute Na	1.5ml 0.5M HNO_3
Collect K	9 ml 0.5M HNO_3
Clean (Elute Mg)	2ml 6M HCl
Clean	2ml H_2O

2. Mass spectrometer settings

Sample introduction system	
Self aspirating glass expansion spray chamber	
Glass expansion nebulizer	
Uptake rate	~90-100 μL/min
MC-ICP-MS instrument	IsoProbe
RF Power	1350 W
Cooling gas	13.1 L min^{-1}
Auxiliary gas	0.8-1.2 L min^{-1}
Nebulizer gas	0.8-1.2 L min^{-1}
Analysis mode	Static
Mass resolution	Low resolution (400)
Cone Voltage	20-40 (Hard Extract)
Collision gas conditions (optimum)	
Ar	0 ml/min
He	10 ml/min
D_2	6 ml/min
Ion detection	Analogue by Faraday cup, static mode 10^{10} Ω for m/z 39 (^{39}K), 10^{11} Ω for m/z 40 (^{40}Ar, ^{40}Ca), 41 (^{41}K, ^{40}ArH), 42 (^{40}ArD), and 43
Data acquisition	
On-peak background subtraction	60 s
Signal integration time	200 s (40 × 5s)
Wash time between samples	400 s
Mass bias correction	Sample-standard-sample bracketing.
Typical signal intensity	7-11×10^{-11}A ^{39}K

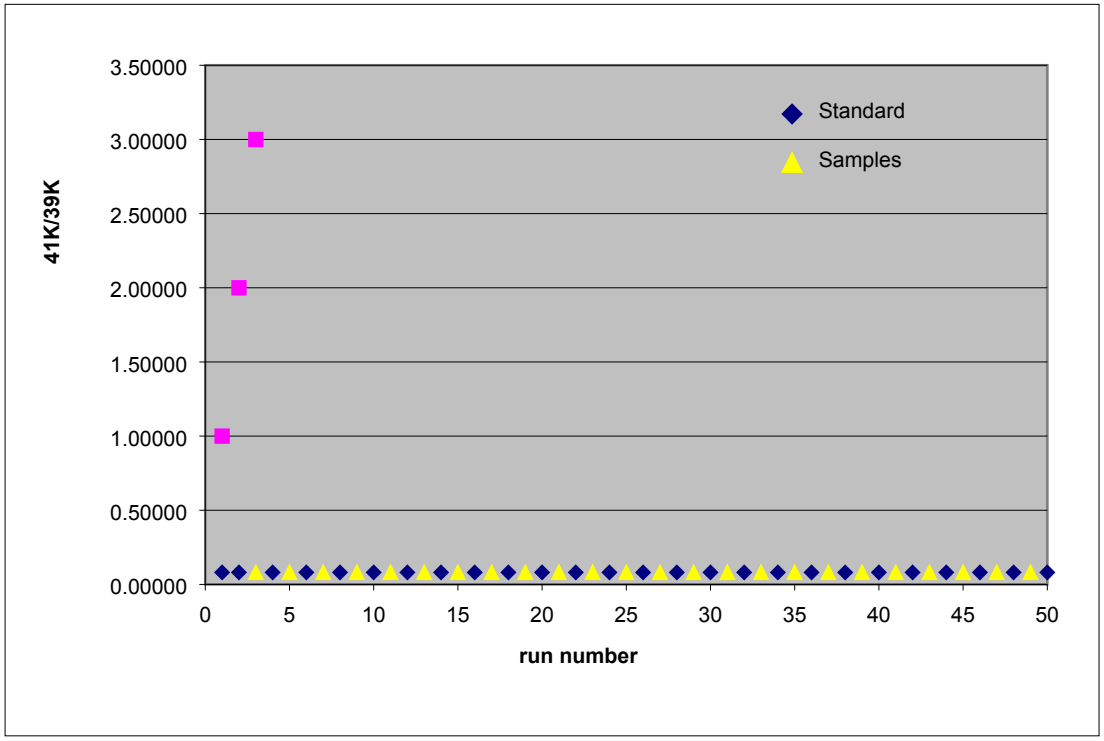
Note that 400 second washout was sufficient to reach steady state conditions in K background measured in clean acid. Use of an Aridus desolvating nebulizer required much longer wash out times to avoid increasing K signals in blank acid during analysis sessions.

3. **Typical mass scan for the spectra of a 1 ppm K solution in 0.1% HNO3, using mass spectrometer settings as tabulated in Appendix section 2.**



Note: The ion intensities on mass 39, 40, 41, and 42 were ca. 10V, 0.003V, 0.8V, and 0.001V, respectively. The flap top and symmetrical shape of peaks on mass 39 and mass 41 indicate that the ion beam is well thermalized (i.e., tight distribution of kinetic energy of ions). The very low signals on mass 40 and mass 42 indicate efficient suppression of Ar^+ and ArD^+ interferences. These are all key features required for high precision measurement of $^{41}K/^{39}K$ ratios. Note that a small ^{40}K signature was present in the signal on mass 40. The abundance of ^{40}K is very small (0.01%) as compared to ^{39}K and ^{41}K, making it a less attractive isotope for evaluating naturally occurring mass dependent variations in K as compared to the analysis of $^{41}K/^{39}K$ ratios.

4. Trace of measured $^{41}K/^{39}K$ ratios for a typical session



5. Collision gas experiments data for Figure 2 in main text of the paper

Notes prior to data table:

(1) During analyses, a $10^{10}\Omega$ resistor was used for measuring ^{39}K (L2 Faraday), whereas $10^{11}\Omega$ resistors were used for other Faraday cups. Such amplifier bias has been corrected in the following tables by multiplying L2 Faraday cup readings by a factor of 10.

(2) Because sensitivity of the MC-ICP-MS instrument changes in respond to different collision gas conditions, in order to allow comparison of Ar^+, HAr^+, and DAr^+ interference intensities between different gas conditions, a normalization process was performed. This is done by two sets of measurements. In the first set of measurement, signal intensities on masses 39, 40, 41, and 42 were recorded for a clean blank acid (see columns "L2, Ax, H1, H4, H7" in the following tables). In the second set of measurement, a 1ppm K solution was aspirated into ICP at different collision gas conditions, and the signal intensity on L2 Faraday cup was recorded accordingly.

Because the peak on mass 39 is interference free, ^{39}K intensity is an excellent indicator of instrument sensitivity. We arbitrarily set a normalization target of 11V ^{39}K signal for 1ppm K solution, and thus can calculate an normalization constant in each collision gas condition experiment accordingly. All blank acid data, therefore, are normalized to a constant sensitivity for discussion of ArH^+/ArD^+ production and suppression.

(3) Because both $^{41}K^+$ and ArH^+ contribute to signals on mass 41, for a valid discussion on ArH+, the K41+ contribution to signals on mass 41 was corrected. This is done by assuming L2 recorded ^{39}K signal and a $^{39}K/^{41}K$ ratio of 93.3/6.7, and subtracting the calculated 41K signal in each set of data.

(4) The sensitivity in Experiments H_2-a and H_2-b was about a factor of 2 lower than that in Experiments D_2-a to D_2-d, this is tentatively attributed to existence of trace water molecules in the collision cell in Experiments that used D_2 gas, as D_2 gas has lower purity compared to H_2. It is important to note, however, that even discounting the difference in sensitivity, the basic observation discussed in the main text remains, that ArH^+ and ArD^+ signals decrease with increasing collision gas flows. On the other hand, the higher sensitivity obtained using D_2 suggests that D_2 is preferable for K isotope analysis.

Table A5-1. Measured (L2, Ax, H2, H4, H7) and calculated (Ar, HAr, DAr) signal intensities for Experiment H_2-a

He (ml/min)	H2 (ml/min)	L2* (Mass39)	Ax (Mass40)	H1 (Mass41)	H4 (Mass 42)	H7 (Mass43)	1ppm K Sensitivity*	Ar+**	HAr**	DAr**
	LSO-closed	-0.0005	-0.0006	-0.0045	-0.0005	-0.0006				
10	**7**	0.0035	0.0015	-0.0041	-0.0004	-0.0004	5.5	0.0042	0.0002	0.0002
10	**6**	0.0036	0.0014	-0.0041	-0.0004	-0.0004	5.5	0.0040	0.0002	0.0002
10	**5**	0.0036	0.0015	-0.0039	-0.0005	-0.0005	5.5	0.0042	0.0006	0.0000
10	**4.5**	0.0037	0.0015	-0.0037	-0.0003	-0.0004	5.2	0.0044	0.0011	0.0004
10	**4**	0.0038	0.0016	-0.0028	-0.0004	-0.0003	5.0	0.0048	0.0031	0.0002
10	**3.5**	0.0039	0.0016	-0.0003	-0.0003	-0.0004	5.1	0.0047	0.0084	0.0004
10	**3**	0.0038	0.0017	0.0075	-0.0003	-0.0004	5.0	0.0051	0.0257	0.0004
10	**2.5**	0.0039	0.0016	0.0345	-0.0003	-0.0004	4.9	0.0049	0.0868	0.0004
10	**2**	0.0040	0.0017	0.1330	-0.0003	-0.0004	4.9	0.0052	0.3079	0.0004
10	**1.5**	0.0042	0.0017	0.5210	-0.0002	-0.0004	4.8	0.0053	1.2035	0.0007
10	**1**	0.0052	0.0023	2.2000	0.0000	-0.0003	4.5	0.0071	5.3878	0.0012
10	**0.9**	0.0057	0.0027	3.0500	0.0003	-0.0003	4.5	0.0081	7.4655	0.0020

Table A5-2. Measured (L2, Ax, H2, H4, H7) and calculated (Ar, HAr, DAr) signal intensities for Experiment H_2-b

He (ml/min)	H2 (ml/min)	L2* (Mass39)	Ax (Mass40)	H1 (Mass41)	H4 (Mass 42)	H7 (Mass43)	1ppm K sensitivity	Ar+**	HAr**	DAr**
	LSO-closed	0.0005	-0.0006	-0.0045	-0.0005	-0.0006	L2 reading*			
10	5	0.0036	0.0016	-0.0039	-0.0004	-0.0004	4.7	0.0051	0.0007	0.0002
9	5	0.0037	0.0017	-0.0037	-0.0004	-0.0004	4.7	0.0054	0.0012	0.0002
8	5	0.0037	0.0017	-0.0031	-0.0004	-0.0004	4.8	0.0053	0.0025	0.0002
7	5	0.0037	0.0017	-0.0021	-0.0003	-0.0003	4.8	0.0053	0.0048	0.0005
6	5	0.0037	0.0017	0.0000	-0.0003	-0.0004	4.7	0.0054	0.0098	0.0005
5	5	0.0037	0.0016	0.0045	-0.0004	-0.0004	4.5	0.0054	0.0213	0.0002
4	5	0.0034	0.0015	0.0130	-0.0003	-0.0004	4.0	0.0058	0.0474	0.0006
3	5	0.0030	0.0010	0.0270	-0.0003	-0.0004	3.6	0.0049	0.0955	0.0006
2	5	0.0024	0.0007	0.0450	-0.0004	-0.0004	2.8	0.0051	0.1936	0.0004
1	5	0.0019	0.0004	0.0680	-0.0004	-0.0005	2.2	0.0050	0.3616	0.0005

Table A5-3. Measured (L2, Ax, H2, H4, H7) and calculated (Ar, HAr, DAr) signal intensities for Experiment D_2-a

He (ml/min)	D2 (ml/min)	L2* (Mass39)	Ax (Mass40)	H1 (Mass41)	H4 (Mass 42)	H7 (Mass43)	1ppm K sensitivity	Ar+**	HAr**	DAr**
	LSO-closed	0.0132	-0.0005	-0.0046	0.0006	-0.0012	L2 reading*			
10	**5**	0.018	0.0009	-0.0040	0.0008	-0.0010	10.0	0.0015	0.0003	0.0003
9	**5**	0.018	0.0009	-0.0040	0.0009	-0.0010	10.3	0.0015	0.0002	0.0003
8	**5**	0.019	0.0009	-0.0040	0.0009	-0.0010	10.2	0.0015	0.0003	0.0003
7	**5**	0.019	0.0010	-0.0039	0.0010	-0.0010	10.9	0.0015	0.0003	0.0004
6	**5**	0.019	0.0010	-0.0038	0.0011	-0.0010	11.1	0.0015	0.0004	0.0005
5	**5**	0.019	0.0011	-0.0036	0.0012	-0.0010	11.3	0.0015	0.0006	0.0006
4	**5**	0.019	0.0010	-0.0032	0.0015	-0.0010	10.7	0.0015	0.0010	0.0009
3	**5**	0.019	0.0010	-0.0025	0.0021	-0.0010	11.2	0.0015	0.0016	0.0015
2	**5**	0.019	0.0010	-0.0013	0.0030	-0.0010	10.8	0.0015	0.0029	0.0024
1	**5**	0.018	0.0008	0.0001	0.0045	-0.0010	9.6	0.0015	0.0050	0.0045
0.5	**5**	0.018	0.0007	0.0011	0.0054	-0.0010	9.5	0.0014	0.0062	0.0056
0.1	**5**	0.018	0.0007	0.0025	0.0064	-0.0010	9.2	0.0014	0.0081	0.0069

Table A5-4. Measured (L2, Ax, H2, H4, H7) and calculated (Ar, HAr, DAr) signal intensities for Experiment D_2-b

He (ml/min)	D2 (ml/min)	L2* (Mass39)	Ax (Mass40)	H1 (Mass41)	H4 (Mass 42)	H7 (Mass43)	1ppm K sensitivity	Ar+**	HAr**	DAr**
	LSO-closed	0.0132	-0.0005	-0.0046	0.0006	-0.0012	L2 reading*			
10	**2**	0.019	0.0009	0.0136	0.0097	-0.0010	10.7	0.0015	0.0183	0.0094
9	**2**	0.019	0.0009	0.0290	0.0158	-0.0010	11.2	0.0014	0.0326	0.0149
8	**2**	0.019	0.0010	0.0533	0.0262	-0.0010	11.2	0.0015	0.0564	0.0251
7	**2**	0.019	0.0010	0.0900	0.0410	-0.0010	10.8	0.0015	0.0959	0.0411
6	**2**	0.019	0.0010	0.1390	0.0620	-0.0010	9.9	0.0017	0.1591	0.0682
5	**2**	0.018	0.0009	0.2010	0.0830	-0.0010	9.5	0.0017	0.2376	0.0954
4	**2**	0.018	0.0009	0.2720	0.1050	-0.0010	8.4	0.0018	0.3617	0.1367
3	**2**	0.017	0.0008	0.3210	0.1230	-0.0010	7.0	0.0020	0.5112	0.1923
2	**2**	0.017	0.0008	0.3450	0.1290	-0.0010	5.4	0.0025	0.7116	0.2616
1	**2**	0.016	0.0008	0.3200	0.1230	-0.0010	4.3	0.0033	0.8299	0.3131
0.5	**2**	0.016	0.0011	0.2720	0.1100	-0.0011	3.8	0.0045	0.8001	0.3167
0.1	**2**	0.016	0.0012	0.2460	0.1060	-0.0011	3.2	0.0060	0.8608	0.3623

Table A5-5. Measured (L2, Ax, H2, H4, H7) and calculated (Ar, HAr, DAr) signal intensities for Experiment D_2-c

He (ml/min)	D2 (ml/min)	L2* (Mass39)	Ax (Mass40)	H1 (Mass41)	H4 (Mass 42)	H7 (Mass43)	1ppm K sensitivity	Ar+**	HAr**	DAr**
	LSO-closed	0.0132	-0.0005	-0.0046	0.0006	-0.0012	L2 reading			
10	**1**	0.019	0.0012	0.4320	0.1350	-0.0010	11.1	0.0017	0.4322	0.1332
9	**1**	0.019	0.0013	0.6310	0.1900	-0.0010	10.9	0.0018	0.6410	0.1911
8	**1**	0.019	0.0014	0.8740	0.2570	-0.0010	10.5	0.0020	0.9200	0.2686
7	**1**	0.019	0.0016	1.1630	0.3250	-0.0010	9.9	0.0023	1.2968	0.3604
6	**1**	0.019	0.0016	1.4500	0.3780	-0.0010	8.8	0.0027	1.8177	0.4718
5	**1**	0.019	0.0017	1.7300	0.4200	-0.0010	7.6	0.0032	2.5101	0.6070
4	**1**	0.018	0.0020	1.8840	0.4510	-0.0010	6.2	0.0044	3.3501	0.7991
3	**1**	0.017	0.0025	1.7010	0.3840	-0.0010	4.9	0.0067	3.8282	0.8607
2	**1**	0.017	0.0032	1.4430	0.3430	-0.0010	3.5	0.0115	4.5489	1.0761
1	**1**	0.016	0.0041	1.0190	0.2630	-0.0011	2.6	0.0196	4.3297	1.1102
0.5	**1**	0.015	0.0046	0.7370	0.2160	-0.0011	2.1	0.0268	3.8837	1.1283
0.1	**1**	0.015	0.0056	0.5560	0.1870	-0.0012	1.7	0.0395	3.6266	1.2061

Table A5-6. Measured (L2, Ax, H2, H4, H7) and calculated (Ar, HAr, DAr) signal intensities for Experiment D_2-d

He (ml/min)	D2 (ml/min)	L2* (Mass39)	Ax (Mass40)	H1 (Mass41)	H4 (Mass 42)	H7 (Mass43)	1ppm K sensitivity	Ar+**	HAr**	DAr**
	LSO-closed	0.005	-0.0006	-0.0045	-0.0005	-0.0006	L2 reading			
10	**7**	0.018	0.0008	-0.0041	0.0008	-0.0011	10.6	0.0013	0.0002	0.0002
10	**6**	0.018	0.0009	-0.0040	0.0009	-0.0010	11.0	0.0014	0.0002	0.0003
10	**5**	0.019	0.0009	-0.0040	0.0009	-0.0010	11.1	0.0014	0.0002	0.0003
10	**4.5**	0.019	0.0009	-0.0039	0.0009	-0.0010	11.3	0.0014	0.0003	0.0003
10	**4**	0.019	0.0010	-0.0039	0.0010	-0.0010	11.4	0.0014	0.0003	0.0004
10	**3.5**	0.019	0.0011	-0.0037	0.0011	-0.0010	11.5	0.0015	0.0005	0.0005
10	**3**	0.019	0.0011	-0.0028	0.0016	-0.0010	11.6	0.0015	0.0013	0.0009
10	**2.5**	0.019	0.0011	0.0004	0.0033	-0.0010	11.2	0.0016	0.0045	0.0027
10	**2**	0.019	0.0011	0.0142	0.0095	-0.0010	11.8	0.0015	0.0171	0.0083
10	**1.5**	0.019	0.0011	0.0773	0.0338	-0.0010	11.9	0.0015	0.0753	0.0307
10	**1**	0.019	0.0013	0.3867	0.1380	-0.0010	11.8	0.0017	0.3644	0.1281
10	**0.9**	0.019	0.0015	0.5730	0.1800	-0.0010	11.8	0.0018	0.5380	0.1672
10	**0.8**	0.019	0.0016	0.7540	0.2190	-0.0010	11.7	0.0020	0.7128	0.2053
10	**0.7**	0.020	0.0019	1.1500	0.3000	-0.0010	11.6	0.0023	1.0944	0.2839
10	**0.6**	0.020	0.0025	1.6400	0.4120	-0.0010	11.6	0.0028	1.5591	0.3901
10	**0.5**	0.021	0.0037	2.4400	0.5950	-0.0098	11.4	0.0041	2.3583	0.5735

6. K isotope data for test solutions and terrestrial samples ($\delta^{41/39}$K values reported against NIST SRM 3141a)

Sample	$\delta^{41/39}$K	2SD	No. of analysis
Standard			
UW-K (HPS Lot 309921)	**-0.12**	**0.21**	**43**
Test I			
20μg NIST SRM 3141a	-0.01	0.04	2
50μg NIST SRM 3141a	-0.03	0.09	2
80μg NIST SRM 3141a	-0.11	0.02	2
100μg NIST SRM 3141a	0.06	0.03	2
150μg NIST SRM 3141a	-0.06	0.12	2
Average	***-0.03***	***0.13***	
Test II			
50μg UW-K	-0.14	0.13	3
50μg UW-K	-0.08	0.19	3
50μg UW-K + 3mg shale matrix	-0.07	0.06	2
50μg UW-K + 3mg shale matrix	-0.09	0.14	3
50μg UW-K + 1mg corn ash matrix	-0.17	0.05	2
50μg UW-K + 3mg granite matrix	-0.08	0.05	2
50μg UW-K + 20mL river water matrix	-0.08	0.20	3
Average	***-0.10***	***0.08***	
seawater			
Aliquot 1	0.02	0.14	6
Aliquot 2	0.05	0.17	5
Aliquot 3	0.12	0.13	5
Average	***0.06***	***0.10***	
USGS rock standard			
BHVO-2	-0.50	0.19	4
BCR-2	-0.64	0.15	4
AVG-2	-0.48	0.18	4
AVG-2 (replicate)	-0.47	0.12	4
GSP-2	-0.50	0.12	4
GSP-2 (replicate)	-0.51	0.22	5
BCR-2	-0.51	0.19	4
*Australasian tektites**			
Tektite from Thailand (piece 1)	-0.57	0.16	7
Tektite from Thailand (piece 2)	-0.61	0.16	7
Tektite from Viet Nam	-0.40	0.07	4
Tektite from Guangdong, China (piece 1)	-0.49	0.13	3
Tektite from Guangdong, China (piece 2)	-0.26	0.19	3
Tektite from Yunnan, China (piece 1)	-0.64	0.14	6
Tektite from Yunnan, China (piece 2)	-0.72	0.20	3

Tektite from Hainan, China (piece 1)	-0.64	0.10	6
Tektite from Hainan, China (piece 2)	-0.71	0.08	6
Higher plant samples			
Rice grains	-0.98	0.16	2
Wolfberry fruit (*Lycium barbarum*)	-1.12	0.09	8
Tea leaves	-1.26	0.16	8
Chili pepper	-0.90	0.15	8

** Australasian tektites were purchased on taobao.com, a Chinese website similar to ebay.com, from different vendors. Sample localities were taken from the descriptions by the vendors, the authors are not able to verify the correctness of the sample origin statements, other than the reputation of the vendors from the website rating system for the vendors.*