

JAAS

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50

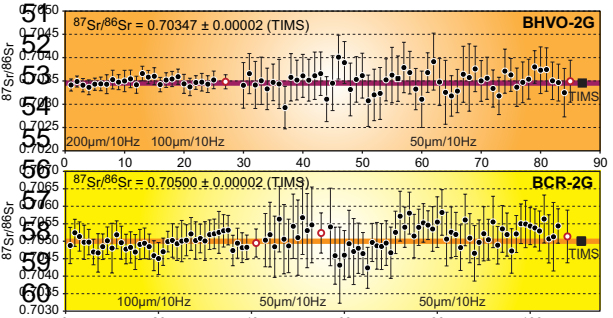


Table of contents entry.
An analytical protocol using LA-MC-ICP-MS for precise Sr isotope ratio analysis from small glass samples is presented.

TECHNICAL NOTE**In situ Sr isotope measurement of small glass samples using multiple-Faraday collector inductively coupled plasma mass spectrometry with $10^{12}\text{-}\Omega$ resistor high gain Faraday amplifiers†**Qing Chang^{*a}, Jun-Ichi Kimura^a, and Bogdan Stefanov Vaglarov^a

An analytical protocol was developed for correcting Kr baseline-induced bias and Rb isobaric overlap factors to analyse Sr isotope ratios for small glass samples using excimer laser ablation (LA) with an Aridus II desolvating nebuliser dual-intake system and multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS). Combined use of a low-oxide interface setup, along with high-gain Faraday amplifiers with a $10^{12}\text{-}\Omega$ resistor, enabled precise determination of Sr isotope ratios from 50- and 100- μm diameter craters at 10-Hz laser repetition rate. Residual analytical biases of $^{84}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios, obtained from Kr baseline suppressions (Kimura et al., 2013, Journal of Analytical Atomic Spectrometry, 28, 945–957), were found to be nonlinear, but the correction method was applicable to 50–200- $\mu\text{m}/10\text{-Hz}$ craters. We also found that the $^{85}\text{Rb}/^{87}\text{Rb}$ overlap correction factor changed with time with a change in the surface condition of the sampler–skimmer cones. The correction factor of $^{85}\text{Rb}/^{87}\text{Rb}$ was thus determined at least once per five unknown measurements using the Aridus solution intake line. We determined $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios from MkAn anorthite (Sr = 305 ppm, Rb = 0.07 ppm), BHVO-2G, KL2-G, ML3B-G (Sr = 312–396 ppm, Rb = 5.8–9.2 ppm), and BCR-2G (Sr = 337 ppm, Rb = 48.5 ppm) basalt glasses using a 50–100- $\mu\text{m}/10\text{-Hz}$ crater. The results agree well with their reference values, determined by

1
2
3
4
5
6 25 thermal ionisation mass spectrometry, even with the high Rb/Sr ratio (0.14) in the
7
8
9 26 BCR-2G glass. The internal/intermediate precisions were ± 0.0002 (two-standard
10
11 27 deviation: 2SD) for 100- μm craters and ± 0.0005 for 50- μm craters. The new instrument
12
13 28 settings and analytical protocol improved the precision by a factor of two compared to
14
15 29 the previous report using LA-(sector field)-ICP-MS and enables the analysis of sample
16
17 30 volumes that are ten times smaller than those used in previous LA-MC-ICP-MS
18
19 31 analyses with equal precision.

20
21
22 32 (298 words in abstract, 6836 words in all document)
23
24
25 33

26
27 34 ^a Department of Solid Earth Geochemistry (DSEG), Japan Agency for Marine-Earth
28
29 35 Science and Technology (JAMSTEC), 2–15 Natsushima-Cho, Yokosuka 237-0061,
30
31 36 Japan.
32
33

34
35
36 37 E-mail: qchang@jamstec.go.jp; Fax: +81-46-867-9634; Tel: +81-46-867-9765
37
38

39 39 † Electronic supplementary information (ESI) available: Data Table 1: Analytical results
40
41 40 of Sr isotope ratios. See DOI:10.1039/c4jaxxxxxg
42
43
44
45 42
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

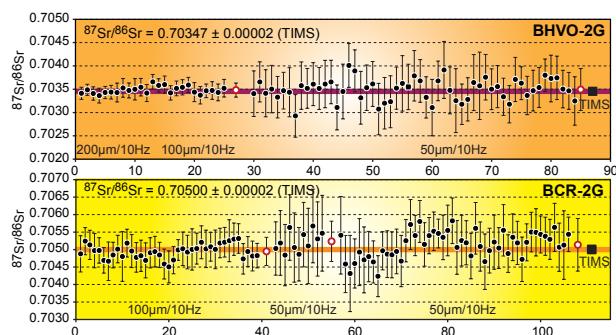


Table of contents entry.

An analytical protocol using LA-MC-ICP-MS for precise Sr isotope ratio analysis from small glass samples is presented.

1. Introduction

1.1. In situ Sr isotope ratio analysis by LA-ICP-MS

Strontium isotope analysis using in situ laser ablation multiple collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) has been a useful geochemical tool for the analysis of plagioclase crystals or carbonate materials and glasses.¹⁻⁶ Complex isobaric overlaps from Ar gas blanks and isobaric ions, oxides, and doubly charged ions from the samples are of concern for four naturally occurring Sr isotopes, ⁸⁴Sr, ⁸⁶Sr, ⁸⁷Sr, and ⁸⁸Sr. Data correction protocols are therefore very complex, prompting rigorous examination. These problems and their resulting solutions have been summarized by Vroon et al.⁷

The most commonly employed Sr isotope measurement protocol⁷ for the geochemical samples is the use of on-peak background subtraction, which corrects for Kr gas blanks and instrumental memories of Sr and Rb,^{1, 2, 5, 6, 8-13} although iterative subtraction of the Kr baselines is also a useful technique.^{3, 13} Overlap correction of ⁸⁷Rb using ⁸⁵Rb is achieved by an external mass bias correction from Sr, determined as $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$.^{1, 2, 5, 6, 8-12} but is successful only with the actual determination of ⁸⁵Rb/⁸⁷Rb, either by measurement of a Rb-doped Sr standard solution, using a solution-laser aerosol-dual intake system,¹⁴ or by measurement of both natural and synthetic glasses with known ⁸⁷Sr/⁸⁶Sr isotope ratios.^{2, 3, 15} Interferences from Ca dimers, CaAr, and ²³Na⁶⁰⁻⁶⁴Ni molecular ions are usually negligible for plagioclase crystals and carbonates.^{6, 7, 10} Oxide interferences on ⁸⁵Rb and ⁸⁷Sr, from ⁶⁹Ga¹⁶O and ⁷¹Ga¹⁶O are significant for samples rich in Al, such as plagioclase and glass, as Ga has a chemical affinity for Al and is highly partitioned in these samples.¹⁴ Therefore, by using particular MC-ICP-MS settings,¹⁶ high oxide yields are avoided.^{6, 10} Interference from doubly

1
2
3
4
5
6 67 charged rare earth element (REE) ions are also obvious,^{10, 12, 17} and care must be taken
7
8 68 to exclude REE-rich Sr-poor samples (e.g., clinopyroxene) and co-ablation of REE-rich
9
10 69 mineral inclusions (e.g., apatite). The REE double charges such as $^{166}\text{Er}^{++}$, $^{168}\text{Er}^{++}$, and
11
12 $^{170}\text{Er}^{++}$ for ^{83}Kr , ^{84}Sr , and ^{85}Rb , respectively, and $^{170}\text{Yb}^{++}$, $^{172}\text{Yb}^{++}$, $^{174}\text{Yb}^{++}$ and $^{176}\text{Yb}^{++}$
13
14 for ^{85}Rb , ^{86}Sr , ^{87}Sr and ^{88}Sr , respectively, can be monitored, or even corrected for, by
15
16 71 placing the Faraday collectors at half-mass positions of $^{83.5}\text{M}$ ($^{167}\text{Er}^{++}$) and $^{86.5}\text{M}$
17
18 72 ($^{173}\text{Yb}^{++}$).^{10, 17} Finally, analytical results are obtained by the internal mass fractionation
19
20 73 correction of Sr given that $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$.⁷ Additional bias corrections for Kr
21
22 74 baseline suppression caused by LA aerosols were recently introduced for $^{87}\text{Sr}/^{86}\text{Sr}$
23
24 75 measurements to further improve analytical precision and reproducibility for samples
25
26 76 low in Sr (e.g., 300 ppm), for which large amounts of LA aerosols needed to be
27
28 77 introduced.¹⁴
29
30
31
32
33

34 79

35 80 **1.2. Analysis of Sr isotope ratios in glass samples**

36
37 81 Analysis of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio from a small glass sample, such as olivine-hosted
38
39 82 small glass inclusions (diameters of 50–200 μm or less), is particularly useful for the
40
41 83 identification of the source processes in the genesis of basalt magmas. These glass
42
43 84 inclusions can preserve information regarding the primary magma generated in the deep
44
45 85 mantle and is unaffected by chemical modifications during ascent to the surface by
46
47 86 encapsulation of tiny drops of the deep, quenched magmas.^{3, 18} Attempts to analyse a
48
49 87 basalt glass were described by Christensen et al. in the first paper published on in situ
50
51 88 $^{87}\text{Sr}/^{86}\text{Sr}$ isotope analysis using LA-MC-ICP-MS, in which they analysed the
52
53 89 groundmass glass of Long Valley basalt from a 300- μm /20-Hz crater (approximate
54
55 90 sample volume: $V = \sim 2.1 \times 10^{-5} \text{ cm}^3$), sampled by an infrared (IR) Nd-YAG laser with
56
57
58
59
60

1
2
3
4
5
6 91 an internal/intermediate precision of $^{87}\text{Sr}/^{86}\text{Sr} =$ approximately ± 0.0005 (two-standard
7
8 deviation: 2SD).¹
9

10
11 The attempt continued with development in an ultraviolet 213-nm YAG laser
12
13 and a third-generation MC-ICP-MS, allowing analysis from a smaller crater of
14
15 120- $\mu\text{m}/20\text{-Hz}$ ($V = \sim 7.9 \times 10^{-7} \text{ cm}^3$) with a similar internal/intermediate precision of
16
17 approximately ± 0.0005 2SD.³ An alternative approach was to use a sector field
18
19 (SF)-ICP-MS with rapid peak jumping using a single ion counter (IC) connected to a
20
21 193-nm excimer laser (ExLA). This allowed analysis of a smaller sample volume, a
22
23 crater from 50 $\mu\text{m}/10 \text{ Hz}$ ($V = \sim 9.8 \times 10^{-8} \text{ cm}^3$), with an intermediate precision of
24
25 approximately ± 0.0010 2SD.¹⁹ Analysis of the small sample volume was achieved
26
27 through use of the high-sensitivity IC, whereas use of the IC with peak jumping resulted
28
29 in poor intermediate precision.
30
31
32
33

34 103 35 36 104 **1.3.Focus** 37

38
39 In this study, we present an improved analytical technique for Sr isotope analysis of
40
41 glass samples. We apply a 193-nm ExLA laser sampling method, with simultaneous
42
43 introduction of Aridus II solution aerosols (dual intake system),¹⁴ connected to an
44
45 MC-ICP-MS. In order to prevent any potential oxide interferences, the interface of the
46
47 MC-ICP-MS was set to achieve the lowest oxide molecular yield.²⁰ Low instrumental
48
49 sensitivity with the interface was accounted for by the use of a high-efficiency rotary
50
51 pump at the interface^{14, 20-22} and the application of high-gain Faraday amplifiers using a
52
53 $10^{12}\text{-}\Omega$ resistor.
54
55
56

57
58 Use of these amplifiers increases sensitivity by 10 times by reducing the
59
60 signal-to-noise ratio to half of what would be obtained from an amplifier with a $10^{11}\text{-}\Omega$

1
2
3
4
5
6
7 115 resistor. This can in turn reduce analytical error generated during the analysis by more
8
9 116 than half for low electron currents.^{23, 24} We also examine the Kr baseline-induced bias¹⁴
10
11 117 during loading of smaller samples to the ICP and temporal changes in the Rb overlap
12
13 118 correction factor for glass samples with high Rb content. The small sample size and the
14
15 119 internal/intermediate precision achieved in this study are keys to the successful
16
17 120 application of LA-MC-ICP-MS to small glass inclusions.
18
19
20
21

22 122 **2. Instrument setting, data acquisition/reduction**

23 123 **2.1.Laser ablation (LA) and dual-intake sample introduction**

24
25
26
27 124 The instrumentation for our LA-multiple correction (MC)-ICP-MS has been reported
28
29 125 elsewhere for the in situ Sr isotope analysis of plagioclase crystals^{14, 15, 25} In brief, the
30
31 126 instrument consists of an LA-Aridus II dual-intake system including a 193-nm excimer
32
33 127 LA system with a COMPex 102 laser source (Coherent, Göttingen, Germany) combined
34
35 128 with an Aridus II desolvating nebuliser (CETAC Technologies, Omaha, USA). The laser
36
37 129 aerosols in the He gas flow and the Aridus II solution aerosols in the Ar gas flow were
38
39 130 mixed in a T-piece connector just prior to the ICP torch in the MC-ICP-MS. The
40
41 131 excimer laser operated with a fluence of 20 J cm^{-2} , a 50–200- μm crater diameter, and,
42
43 132 in most cases, a 10-Hz repetition rate, which resulted in craters with depths of $\sim 50 \mu\text{m}$
44
45 133 after ablation for $\sim 35 \text{ s}$ (idle time, 10 s; data acquisition, 25 s), indicating a drilling rate
46
47 134 of $0.125\text{-}\mu\text{m}$ per shot.
48
49
50
51

52 135 53 54 136 **2.2.MC-ICP-MS**

55
56
57 137 A NEPTUNE MC-ICP-MS was used (Thermo Fisher Scientific, Bremen, Germany) and
58
59 138 was modifications at the interface for a high sensitivity as has been reported
60

1
2
3
4
5
6 139 elsewhere.^{14, 20} The settings of the ion interface were normal (N) Ni sampling and
7
8 140 normal (H) Ni skimmer cones with the guard electrode (GE) turned off (electrically
9
10 141 disconnected) (**Table 1**). This allowed minimisation of the oxide molecular ion yields
11
12 142 ($^{238}\text{U}^{16}\text{O}^{+}/^{238}\text{U}^{+} < 1\%$, analysed in solution by Aridus II) and thus, any oxide based
13
14 143 interference (e.g., GaO^{+}) was avoided. The important doubly charged REE ions were
15
16 144 monitored by half mass Faradays set at $^{83.5}\text{M}$ for $^{167}\text{Er}^{++}$ and $^{86.5}\text{M}$ for $^{173}\text{M}^{++}$ (**Table**
17
18 145 **1**),²⁰ and these were almost completely absent (grand averages of the per cent REE^{++} on
19
20 146 the most affected ^{84}Sr signals were $^{168}\text{Er}^{++}/^{84}\text{Sr} < 0\%$ and $^{168}\text{Yb}^{++}/^{84}\text{Sr} = 0.004\%$;
21
22 147 calculations from **ESI Data Table 1†**) for glass samples.
23
24
25
26

27 148 With the interface designed to maintain low oxide levels, as noted above, the
28
29 149 system sensitivity was maintained at 200 V/ppm Sr (~11 Gcps/ppm) measured from the
30
31 150 Aridus II solution.^{3, 10} Analysis of ~300–400 ppm of Sr in glasses yielded a ^{88}Sr signal
32
33 151 of 0.5–0.8 V and ~0.1–0.2 V from 100- $\mu\text{m}/10\text{-Hz}$ and 50- $\mu\text{m}/10\text{-Hz}$ laser craters,
34
35 152 respectively (**ESI Data Table 1†**). These values were sufficient for an internal analytical
36
37 153 precision of $^{87}\text{Sr}/^{88}\text{Sr} = \pm 0.0002$ to ~0.0010 (2SE) after ~25 s of data acquisition. This
38
39 154 was achieved by the application of high-gain Faraday amplifiers, equipped with $10^{12}\text{-}\Omega$
40
41 155 resistors,²³ to all naturally occurring Sr isotopes (^{84}Sr , ^{86}Sr , ^{87}Sr , and ^{88}Sr) and ^{85}Rb
42
43 156 (**Table 1**).
44
45
46
47

48 157

50 158 **2.3.Laser ablation protocol**

51
52 159 We especially focused on optimizing the LA analytical protocol for the use of $10^{12}\ \Omega$
53
54 160 high-gain amplifiers because of their slow response to transient signals.^{23, 26} One cycle
55
56 161 of data acquisition consisted of: (1) two 30-s baseline measurements made on-peak
57
58 162 before laser firing; (2) subsequent firing of the laser for 10 s without data acquisition,
59
60

163 allowing stabilisation of the LA signal and the current applied to the Faraday amplifiers
164 in order to avoid the acquisition of transient signals during LA signal growth; and (3)
165 data acquisition for ~25 s using a time slice of ~0.524 s for 50 scans, completed while
166 the signal output was flat and stable (**Fig. 1**). The detailed setup parameters of the laser
167 system and the MC-ICP-MS, including the Faraday collector setup in the mass
168 spectrometer, are listed in **Table 1**.

169

170 **2.4. Correction of Rb isobaric overlap**

171 Correction of interference from the ^{87}Rb isobar on ^{87}Sr is particularly important in the
172 precise analysis of glasses because natural basaltic glasses contain Rb in the range 0.02–
173 0.15 or more times the amount of Sr.^{19, 27} Previous studies used both synthetic² or
174 natural glasses^{3, 19} of known contents of Rb and Sr and of known $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio.
175 This allows determination of the overlap correction factor of Rb by adjusting the
176 $^{85}\text{Rb}/^{87}\text{Rb}$ isotope ratios to reproduce the known $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio of the glasses.

177 We have been using a different approach for determination of the Rb overlap
178 correction factor, using a LA–Aridus solution aerosol dual-intake system. This system
179 has been applied to Hf, Nd, and Sr isotope analyses of zircon,²⁸ monazite/apatite and
180 rutile,²⁰ and plagioclase,¹⁴ respectively. The advantage of this method is its ability to
181 simultaneous fine-tune the MC-ICP-MS instrument for both the solution and the LA
182 aerosols from the dual-intake lines, by using solution aerosols while LA firing is off and
183 the laser cell gas is on. Precise determination of an overlap correction factor (e.g., ^{176}Yb
184 and ^{176}Lu on ^{176}Hf ;²⁸ ^{144}Sm on ^{144}Nd ;²⁰ and ^{87}Rb on ^{87}Sr ¹⁴) is simple by using mixed
185 solutions with known (not necessarily accurate) concentrations of the
186 interfering-interfered elements and known isotope composition.

1
2
3
4
5
6 187 The tuning solution can easily be prepared by mixing standard solutions. The
7
8
9 188 determined correction factor can be used for the LA aerosols while Aridus II introduces
10
11 189 deionised water (DIW). The matrix effect of the concomitant major elements from LA
12
13 190 aerosols has been examined by major element-doped solutions²⁸ or by comparisons to
14
15 191 the known TIMS values of the LA analytes.^{14, 20, 28} The bias was found to be negligible
16
17 192 within the level of intermediate precision of ± 0.00002 for Hf (~90-ppm offset in
18
19 193 naturally occurring $^{176}\text{Hf}/^{177}\text{Hf}$), Nd (~40-ppm offset in $^{143}\text{Nd}/^{144}\text{Nd}$), and Sr (~30-ppm
20
21 194 offset in $^{87}\text{Sr}/^{86}\text{Sr}$) isotope analyses.^{14, 20, 28} It should be noted that the majority of these
22
23 195 analyses were mostly done with a crater size smaller than 200 $\mu\text{m}/20$ Hz and with the
24
25 196 same instruments used in this study. The effectiveness and stability of Rb overlap
26
27 197 correction are discussed in **Section 3.2**, particularly for glass samples high in Rb
28
29 198 content.
30
31
32

33

34 199 **2.5.Data reduction**

35

36 200
37
38 201 First, the peak intensities of ^{84}Sr , ^{86}Sr , ^{87}Sr , ^{88}Sr , and ^{85}Rb were measured using on-peak
39
40 202 background subtraction. ^{87}Sr intensity was corrected for ^{87}Rb overlap by using the
41
42 203 pre-determined $^{85}\text{Rb}/^{87}\text{Rb}$ isotope ratio (**Section 2.4**) and the measured ^{85}Rb intensity.
43
44 204 $^{84}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios were calculated from the intensities of ^{84}Sr , ^{86}Sr and
45
46 205 ^{87}Sr (employing the correction for ^{87}Rb overlap), while ^{88}Sr was determined by the
47
48 206 exponential law given that $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. Further Kr baseline bias was corrected by
49
50 207 using $^{84}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with the following equation:
51
52

53

$$54 \quad ^{87}\text{Sr}/^{86}\text{Sr}_{\text{corrected}} = ^{87}\text{Sr}/^{86}\text{Sr}_{\text{original}} / (-0.14121 \times ^{84}\text{Sr}/^{86}\text{Sr} + 1.0081)$$

55

56 209 using the empirical correction coefficients proposed by Kimura et al.¹⁴ The above
57
58 210 calculations were applied off-line to all 50 scans in a given run. An average and twice
59
60

1
2
3
4
5
6 211 the standard error (2SE) were calculated for each spot; in this case, all the errors that
7
8 212 propagated from each isotope measurement were included in the calculated 2SE, while
9
10 213 errors from the Rb overlap correction factor and the coefficients used for Kr baseline
11
12 214 bias were not included because of their minimal effect.

13
14
15 215 Kr bias correction itself does not improve internal or external precision caused
16
17 216 by the short or long term drift in Kr baselines, a feature that is described elsewhere for
18
19 217 iterative Kr baseline subtraction.¹³ The major role of this technique is to account for Kr
20
21 218 baseline suppression due to the mass loading of LA aerosols; the improvement in this
22
23 219 bias can be as high 250 ppm, which is far greater than the Kr baseline drift.¹⁴ The effect
24
25 220 of the Kr baseline bias with regards to this study is discussed in **Section 3.1**.
26
27
28
29
30
31

32 **3. Results**

33
34 223 Although the analytical protocol for Sr isotope measurements using LA-MC-ICP-MS
35
36 224 has been rigorously examined and researchers have been largely in consensus regarding
37
38 225 the analytical protocol, special care must nevertheless be taken with Kr baseline
39
40 226 suppressions and the Rb overlap correction. We identified new features of these factors,
41
42 227 as described below.
43
44
45
46
47

48 229 **3.1.Kr baseline suppression with varied sample loading**

49 230 **3.1.1. Mass loading and Kr baselines: a basic test**

50
51
52 231 We tested the effect of mass loading of LA aerosols by analysing an ~5 ppb SRM 987 Sr
53
54 232 standard solution, along with introduction of LA aerosols at different laser crater sizes
55
56 233 obtained from an olivine crystal in a picrite lava from St. Helena Island.²⁹ The SRM 987
57
58 234 is free from any interference from concomitant elements, while Sr and Rb signals from
59
60

1
2
3
4
5
6 235 the tested olivine were both below the detection limits. Kr outgassing during LA was
7
8 236 reported from olivine in the JP-1 peridotite¹⁴ but this was not detected from the olivine
9
10 237 in the picrite. The olivine sample is therefore suitable for mass loading tests.

11
12
13 238 The ⁸⁸Sr intensity from ~5-ppb SRM 987 was ~0.5 V, which was approximately
14
15 239 the same signal size as that from a 100- μm /10-Hz crater on a plagioclase/glass
16
17 240 containing ~300-ppm Sr. The SRM 987 solution was first analysed for ⁸⁷Sr/⁸⁶Sr without
18
19 241 LA firing. Subsequent analyses used 50- μm /10-Hz (rate of LA aerosol loading: $V_t = 2.5$
20
21 242 $\times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$), 100- μm /10-Hz ($V_t = 9.8 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$), 200- μm /10-Hz ($V_t = 3.9 \times$
22
23 243 $10^{-8} \text{ cm}^3 \text{ s}^{-1}$), and 200- μm /20-Hz ($V_t = 7.8 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$) craters with increasing
24
25 244 loaded mass from the olivine aerosols. The Sr signals vary with different LA aerosol
26
27 245 loading when analysing a Sr-bearing material with a different crater size; therefore, the
28
29 246 absolute role of Kr baseline suppression cannot be tested, particularly for small aerosol
30
31 247 loading due to large internal analytical errors in ⁸⁷Sr/⁸⁶Sr (see **Section 3.1.2**).

32
33
34 248 Analytical results are given in **Fig. 2**. The results show a nonlinear relationship,
35
36 249 indicating a small suppression of the Kr baseline with 50–100- μm /10-Hz craters,
37
38 250 whereas an obvious increase in the uncorrected Sr isotope ratio occurs in 200- μm /10–
39
40 251 20-Hz craters. This confirmed the necessity for correction of the Kr baseline
41
42 252 suppression. The first report of this suppression was on a 200- μm /5–10-Hz crater for
43
44 253 plagioclase analysis,¹⁴ the necessity of which may have been questioned, but our new
45
46 254 analysis clearly demonstrates the necessity of the correction when the sample loading of
47
48 255 LA is greater than $3.9 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$. Even with a low mass loading, corrected data are
49
50 256 closer to the reference value of SRM 987, indicating the importance of this bias
51
52 257 correction (**Fig. 2**).

53
54
55 258 The baseline bias correction with the heaviest sample loading at $7.8 \times 10^{-8} \text{ cm}^3$
56
57
58
59
60

259 s^{-1} from a 200- $\mu\text{m}/20\text{-Hz}$ crater appears to be invalid, showing a large offset in the
260 corrected Sr isotope ratio (**Fig. 2**). In this particular analysis, we saw ~10% suppression
261 of the ^{88}Sr signal for the SRM 987 solution during loading of the olivine LA aerosols,
262 suggesting suppression of Sr in the ICP (not shown). This was not observed with the
263 smaller sample loading. The nonlinear response of the Sr signal might originate from
264 the nonlinear response described by Saha's equation^{30, 31} where an increase in the
265 electron number density causes a sigmoidal decrease of the ionisation efficiency.^{21, 30-32}
266 Sr signal suppression relative to Kr was not taken into account for the Kr baseline bias
267 correction in the previous paper;¹⁴ therefore, the proposed correction could apply only
268 to the LA aerosol loading smaller than $7.8 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ with the 200- $\mu\text{m}/20\text{-Hz}$ crater
269 used in this study. The effect of signal suppression is discussed further in **Section 3.2.1**.

270

271 **3.1.2. Effect of Kr baseline suppression in plagioclase analysis**

272 We conducted a series of experiments using an extremely homogeneous anorthite
273 plagioclase MkAn.^{14, 25} The Sr isotope composition of the crystal is homogeneous,
274 $^{87}\text{Sr}/^{86}\text{Sr} = 0.70345 \pm 0.00002$ (error in 2SD, $n = 4$) confirmed by TIMS and
275 LA-MC-ICP-MS.^{14, 25} This crystal contains minuscule amounts of Rb (0.07 ppm), with
276 $\text{Sr} = 305 \text{ ppm}^{21}$ and thus it is the best suited for examination of the Kr baseline
277 suppression without considering the effect of Rb overlap.

278 Using the MkAn, analyses of Sr isotope ratios were performed with ablation
279 conditions of 200 $\mu\text{m}/20 \text{ Hz}$, 200 $\mu\text{m}/10 \text{ Hz}$, 100 $\mu\text{m}/10 \text{ Hz}$, and 50 $\mu\text{m}/10 \text{ Hz}$ (**Fig. 3a**
280 and **ESI Data Table 1†**). We rearranged the data using the Kr baseline bias uncorrected
281 data of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{84}\text{Sr}/^{86}\text{Sr}$ based on the crater size (**Fig. 3b**). The data from the
282 200- $\mu\text{m}/10\text{-}20\text{-Hz}$ plot on the same negatively sloped linear regression line, which is

1
2
3
4
5
6
7 283 sub-parallel to the theoretical fractionation line of Kr baseline suppression proposed by
8
9 284 the previous study.¹⁴ The amount of LA aerosols from a 200- μm /20-Hz crater is about
10
11 285 0.7 times smaller than that from olivine because of the poorer coupling of 193-nm
12
13 286 excimer laser light to the transparent (Fe- and Mg-poor) plagioclase. This would be the
14
15 287 reason for the lack of offset from the Kr baseline bias for this sample amount. In
16
17 288 contrast, the regression lines of the 100 μm /10 Hz and 50 μm /10 Hz data are
18
19 289 sub-parallel, but with shallower slopes than those from 200- μm craters. Kr baseline
20
21 290 corrections, made by the theoretical model of Kimura et al.,¹⁴ resulted in an almost flat
22
23 291 regression line for the data from 200- μm craters (**Fig. 3c**), indicating almost perfect
24
25 292 correction of the bias. The same correction made for the data from 100–50- μm craters
26
27 293 showed slight over-reductions as shown by the positively sloped regression lines in **Fig.**
28
29 294 **3c**.

30
31
32
33
34 295 This examination clearly indicates that the Kr baseline suppression is due to
35
36 296 mass loading of the plagioclase aerosols, but the degree of suppression could be
37
38 297 nonlinear against the amount of aerosol loaded. The mass loading from 200- μm craters
39
40 298 clearly showed the bias, whereas 50–100- μm craters showed the same bias, but to an
41
42 299 apparently smaller extent. The systematic errors from the potential nonlinearity,
43
44 300 deduced from the slopes of the regression lines of 50–100- μm craters, are well within
45
46 301 the typical internal precision of ± 0.0002 for these small craters both before and after the
47
48 302 bias corrections (**Fig. 3b** and **3c**). Therefore, we corrected for the baseline bias even for
49
50 303 the small 50–100- μm craters. As shown, the $^{87}\text{Sr}/^{86}\text{Sr}$ from SRM 987 solution showed a
51
52 304 closer match to the reference value after the bias correction for a small aerosol loading
53
54 305 (**Fig. 2**), which also supports our approach. The analytical results of MkAn are given in
55
56 306 **Fig. 3a** and **ESI Data Table 1†**, and show an almost perfect match with the isotope

307 ratios measured by TIMS ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70345 \pm 0.00002$) for all sample sizes; $0.7035 \pm$
308 0.0002 , 2SD, $n = 26$, 200- μm craters; 0.7034 ± 0.0002 , 2SD, $n = 10$, 100- μm craters;
309 and 0.7035 ± 0.0008 , 2SD, $n = 40$, 50- μm craters.

310

311 **3.2.Rb overlap correction factor and its temporal drift**

312 **3.2.1. Determination of the Rb correction factor**

313 We determined the $^{85}\text{Rb}/^{87}\text{Rb}$ correction factor using the dual-intake system over the
314 period of analyses of this study and found a temporal change of the value obtained (**Fig.**
315 **4a** and **4b**). The correction factor was obtained by analysing an ~5-ppb NIST SRM 987
316 standard solution ($^{87}\text{Sr}/^{86}\text{Sr} = 0.71024$)²⁷ doped with an ~1-ppb Rb, in which Rb/Sr =
317 ~0.2 is higher than all target glasses. The acquisition was done by the same protocol as
318 for the LA analysis but with a longer time slice of ~4.25 s for 50 scans in order to obtain
319 high-precision results. In this measurement, instrumental mass fractionation of Sr was
320 determined by a stable isotope ratio of $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$.³³ The mass fractionation was
321 corrected by the exponential law for both Sr and Rb isotope ratios, assuming the same
322 mass fractionation factor over the mass range ^{84}M – ^{88}M . This calculation protocol is the
323 same as that used for the LA analyses.

324 We determined the $^{87}\text{Sr}/^{86}\text{Sr} = S_1$ ratio of the mixed solution with a provisional
325 $^{85}\text{Rb}/^{87}\text{Rb}$ value (e.g., 2.5926, the canonical value of $^{85}\text{Rb}/^{87}\text{Rb}$ from the IUPAC isotopic
326 abundances of $^{85}\text{Rb} = 72.165$ and $^{87}\text{Rb} = 27.835$).³³ The obtained $^{87}\text{Sr}/^{86}\text{Sr}$ was always
327 incorrect because of the difference between the proper and the given $^{85}\text{Rb}/^{87}\text{Rb}$ ratio,
328 due to the different elemental sensitivity between Rb and Sr, which altered the ratio of
329 $^{87}\text{Rb}/^{87}\text{Sr}$ (see the similar example between Sm and Nd).^{20, 34} The second cycle of the
330 calculation was done using the same analytical data with a different $^{85}\text{Rb}/^{87}\text{Rb}$ value

331 (e.g., 2.470) to obtain the second $^{87}\text{Sr}/^{86}\text{Sr} = S_2$ ratio. The correct $^{85}\text{Rb}/^{87}\text{Rb} = R_{\text{Rb}}$ ratio
332 should be on the linear regression line passing through the coordinates (X, Y) =
333 (S_1 , 2.5926) and (S_2 , 2.470), obtaining R_{Rb} at (0.70124, R_{Rb}) for the Rb doped SRM 987
334 standard solution. R_{Rb} does not represent its natural value but represents the value
335 including the correction factor (see the similar example between Lu, Yb, and Hf).²⁸

336

337 **3.2.2. Possible origin of enhanced Rb correction factor**

338 The averaged $R_{\text{Rb}} = ^{85}\text{Rb}/^{87}\text{Rb}$ value on Day 5 was 2.4688 (**Fig. 4b**), expressed as a
339 mass fractionation factor of $\Delta M(\text{Rb}) = 2.417\%$ in comparison to the canonical value of
340 $^{85}\text{Rb}/^{87}\text{Rb} = 2.5926$.³³ This fractionation factor is systematically larger than that
341 measured for $^{86}\text{Sr}/^{88}\text{Sr}$ which gave $\Delta M(\text{Sr}) = 2.317\%$ assuming $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ (**Fig.**
342 **4c**). This is due to the difference in elemental sensitivity between Rb and Sr as noted in
343 **Section 3.2.1**, showing a 4.35% enhancement of Rb relative to Sr. Note that the $\Delta M(\text{Rb})$
344 values in **Fig. 4c** are derived from the measured and interpolated values shown in **Fig.**
345 **4b**; the values have therefore been corrected for temporal drift (see **Section 3.2.3**).

346 The enhanced $\Delta M(\text{Rb})$ values are consistent with the higher ionisation
347 efficiency of Rb than Sr in the ICP, where the first ionisation energy of Rb (640 kJ
348 mol^{-1}) is lower than Sr (660 kJ mol^{-1}), and the boiling and dissociation temperatures of
349 Rb (312.2 and 961 K, respectively) are both lower than those of Sr (1042 and 1657 K,
350 respectively) promoting together the higher ionization efficiency of Rb than for Sr.³⁵
351 When the local plasma equilibrium of Saha's equation^{30, 31} and electron number density
352 $ne = 1.47 \times 10^{20} \text{ m}^{-3}$ are assumed, plasma temperature at $T = 5514 \text{ K}$ is calculated to
353 yield a 4.35% enhancement in the ionization efficiency of Rb (92.05%) relative to Sr
354 (88.21%). This temperature is far lower than that of a standard ICP ($T = 6680 \text{ K}$),³⁶ but

1
2
3
4
5
6 355 is still similar to the apparent ionization temperature ($T = \sim 5500$ K) estimated for
7
8 356 element fractionation between a refractory SRM 612 glass and a more easily ionized
9
10 357 BCR-2G basalt glass (see Fig. 2F in Kimura and Chang).²¹ The large particle size of LA
11
12 358 aerosols (10–500-nm with ~ 100 -nm median diameter)^{21, 37} and short transit time in the
13
14 359 ICP may be the source of this apparently low ionization temperature.²¹

15
16
17 360 It is worth noting that the $^{85}\text{Rb}/^{87}\text{Rb}$ factor determined by the solution aerosols
18
19 361 should differ from that for the LA aerosols owing to the change in the plasma conditions
20
21 362 when mass loading of the LA aerosols occurs.^{21, 32} This was not the case with the
22
23 363 volume of LA aerosols and the internal/intermediate precision being dealt with in this
24
25 364 study, or in our previous studies, as shown by the intermediate level of analytical
26
27 365 precision of the standard materials (**Sections 3.1.1** and **3.3**). In the case of heavy mass
28
29 366 loading, however, determination of the $^{85}\text{Rb}/^{87}\text{Rb}$ factor by LA aerosols should be
30
31 367 recommended.

32
33
34 368 Finally, the clear correlation between $\Delta M(\text{Rb})$ and $\Delta M(\text{Sr})$ (**Fig. 4c**) confirms
35
36 369 that the Rb overlap correction factor of $^{85}\text{Rb}/^{87}\text{Rb}$, no matter the determination method,
37
38 370 should be used in combination with the $^{86}\text{Sr}/^{88}\text{Sr}$ mass fractionation factor in each
39
40 371 analytical run (see **Section 1.1**). Nevertheless, temporal drift in the Rb correction factor
41
42 372 occurs regardless (**Fig. 4b**), and should be closely monitored, determined, and applied
43
44 373 (**Section 3.2.3**).

45
46
47 374

48 375 **3.2.3. Temporal drift of Rb correction factor**

49
50
51 376 The $^{85}\text{Rb}/^{87}\text{Rb}$ correction factor drifted with time, most likely reflecting a temporal
52
53 377 change in elemental sensitivity between Rb and Sr. The general trend showed a rapid
54
55 378 increase in $^{85}\text{Rb}/^{87}\text{Rb}$ with time after the plasma was on (**Fig. 4a**). The drift stabilised

1
2
3
4
5
6 379 after 2–3 h but problematic changes could have occurred (see Days 5 and 7 in **Fig. 4a**).
7
8
9 380 The absolute $^{85}\text{Rb}/^{87}\text{Rb}$ value changed with different sampler and skimmer cones as
10
11 381 shown for Days 7 and 8 in **Fig. 4a**. In more detail, the change showed a continuous
12
13 382 increase from 2.4669 to 2.4706 and dropped to 2.4694 between runs 39 and 40,
14
15 383 followed by a further increase to 2.4698 on Day 5 (**Fig. 4b**). The sudden drop correlates
16
17 384 to a longer interval of 1 h with no introduction of LA aerosols. We interpreted the
18
19 385 increase in the ratio as being caused by the change in the surface conditions of the
20
21 386 interface cones. This daily trend is common to all examples and is significant when
22
23 387 using a new sampler-skimmer cone for the first time (Day 7 in **Fig. 4b**). It is likely that
24
25 388 the systematic difference between the cones (Day 5–6 and Day 7–8 in **Fig. 4a**) results
26
27 389 from their different geometries.
28
29
30

31
32 390 The change of the $^{85}\text{Rb}/^{87}\text{Rb}$ factor from 2.4669 to 2.4706 causes a systematic
33
34 391 bias increase of $^{87}\text{Sr}/^{86}\text{Sr} = 0.0014$ for BCR-2G (337-ppm Sr, 48.5-ppm Rb, Rb/Sr =
35
36 392 0.144) and $^{87}\text{Sr}/^{86}\text{Sr} = 0.0002$ for BHVO-2G (396-ppm Sr, 9.2-ppm Rb, Rb/Sr = 0.023).
37
38 393 Considering the temporal change of the factor, frequent measurement of $^{85}\text{Rb}/^{87}\text{Rb}$ is
39
40 394 crucial for glass samples with a high Rb content. We used the same, ~5-ppb Sr SRM
41
42 395 987 solution doped with ~1-ppb Rb for this purpose and determined the $^{85}\text{Rb}/^{87}\text{Rb}$
43
44 396 factors for every five unknown LA analyses. The temporal change in $^{85}\text{Rb}/^{87}\text{Rb}$ was the
45
46 397 linearly interpolated for the five unknown calculations.
47
48
49

398

399 **3.3. Analyses of basalt glass samples**

400 With the instrument settings and the analytical protocols described in the above sections,
401 we then analysed the BHVO-2G, KL2-G, ML3B-G, and BCR-2G glasses, which have
402 also been analysed in the previous LA-ICP-MS studies^{18, 19} and TIMS reference values

1
2
3
4
5
6 403 are thus available.²⁷
7

8
9 404 The basalt glasses of BHVO-2G (basalt from the Hawaiian Volcano
10
11 405 Observatory), KL2-G (from Kilauea volcano), and ML3B-G (from Mauna Loa volcano)
12
13 406 are all from the Big Island of Hawaii. As shown in **Table 2** and **ESI Data Table 1†**, the
14
15 407 results of BHVO-2G were: $^{87}\text{Sr}/^{86}\text{Sr} = 0.70345 \pm 0.00020$ ($n = 15$) from 100- $\mu\text{m}/10\text{-Hz}$
16
17 408 craters and 0.7035 ± 0.0005 ($n = 55$) from 50- $\mu\text{m}/10\text{-Hz}$ craters, for the TIMS value of
18
19 409 $^{87}\text{Sr}/^{86}\text{Sr} = 0.703469 \pm 0.000010$ (**Fig. 5a**); those of KL2-G were: $^{87}\text{Sr}/^{86}\text{Sr} = 0.70352 \pm$
20
21 410 0.00013 ($n = 5$) from 100- $\mu\text{m}/10\text{-Hz}$ craters for the TIMS value of 0.703517 ± 0.00002 ;
22
23 411 and those of ML3B-G were: $^{87}\text{Sr}/^{86}\text{Sr} = 0.70386 \pm 0.00027$ ($n = 10$) from
24
25 412 100- $\mu\text{m}/10\text{-Hz}$ craters for the TIMS value of 0.703805 ± 0.000020 . The LA results are
26
27 413 all in excellent agreement with the TIMS values, indicating that the appropriate
28
29 414 correction factor was used in this study.
30
31
32
33

34 415 BCR-2G (Columbia River Basalt) glass, with $\text{Rb}/\text{Sr} = 0.144$, is the most
35
36 416 difficult sample for analysis of the isobaric corrections of the concomitant Rb in this
37
38 417 study. The results of BCR-2G also showed excellent agreement with the TIMS reference
39
40 418 value of $^{87}\text{Sr}/^{86}\text{Sr} = 0.705000 \pm 0.000020$,²⁷ as shown by $^{87}\text{Sr}/^{86}\text{Sr} = 0.70495 \pm 0.00040$
41
42 419 ($n = 39$) from 100- $\mu\text{m}/10\text{-Hz}$ craters and $^{87}\text{Sr}/^{86}\text{Sr} = 0.7051 \pm 0.0008$ ($n = 50$) from
43
44 420 50- $\mu\text{m}/10\text{-Hz}$ craters (**Fig. 5b**). This proves that the method can be applied to many
45
46 421 natural basalt melts of interests.³
47
48
49

50 422 The intermediate precisions were ± 0.00010 for 200- $\mu\text{m}/10\text{-Hz}$ craters,
51
52 423 ± 0.00013 – 0.00040 for 100- $\mu\text{m}/10\text{-Hz}$ craters, and ± 0.00050 – 0.00080 for 50- $\mu\text{m}/10\text{-Hz}$
53
54 424 craters (**Table 2** and **Fig. 5**). These internal/intermediate precisions are a factor of
55
56 425 approximately two smaller than those obtained by LA-SF-ICP-MS for a 50- $\mu\text{m}/10\text{-Hz}$
57
58 426 crater in year 2009.^{18, 19} The intermediate precisions of ± 0.00050 – 0.00080 for a
59
60

1
2
3
4
5
6 427 50- μm /10-Hz crater are comparable to those obtained for a 120- μm /20-Hz crater using
7
8 428 216-nm YAG-LA-MC-ICP-MS in year 2006³ but from an ~10 times smaller sample
9
10 429 volume. If compared with the first report of 1064 nm by YAG-LA-MC-ICP-MS in year
11
12 430 1995,¹ the necessary sample amount for a ± 0.00010 internal/intermediate precision is
13
14 431 ~200 times smaller, reflecting significant improvements in both the instruments and the
15
16 432 analytical protocols. These improvements are useful for the analyses of small melt
17
18 433 inclusions.
19
20
21

22 434

23
24
25 **4. Conclusions**

26
27 436 We evaluated analytical protocols using LA-MC-ICP-MS for accurate Sr isotope
28
29 437 analysis of small glass samples. The Kr baseline suppression during LA analysis was
30
31 438 found to be nonlinear; small for small sample aerosol loading and large for an extreme
32
33 439 sample loading. We corrected the baseline bias for the all sample amounts from the LA
34
35 440 crater of 50–200 μm /10 Hz and found it to be applicable over the range. Precise Rb
36
37 441 overlap correction using a Rb-doped standard solution and temporal variation of the
38
39 442 correction factor were also examined. The results showed that frequent measurement of
40
41 443 the correction factor was required for a high Rb content basalt glass. These correction
42
43 444 methods were applied to the in situ Sr isotope analyses of the basalt glass standards of
44
45 445 BHVO-2G, BCR-2G, KL2-G, and ML3B-G. The internal/intermediate precisions
46
47 446 achieved for the glass standards were $^{87}\text{Sr}/^{86}\text{Sr} = \pm 0.00010$ (200 μm /10 Hz) to 0.00080
48
49 447 (50 μm /10 Hz), dependent on the crater size and Rb content. The results were a factor of
50
51 448 two more precise than the previous method using a 50- μm crater with
52
53 449 ExLA-SF-ICP-MS and were achieved with a ten times smaller sample volume than
54
55 450 those in 213-nm Nd-YAG-MC-ICP-MS. The results demonstrate the wide application of
56
57
58
59
60

1
2
3
4
5
6 451 this method to many naturally occurring melt inclusions in olivine, which typically have
7
8 452 a diameter of 30–200 μm with Sr levels of 200–300 ppm.
9
10
11 453

12 **Acknowledgments**

13
14
15 454 The authors wish to thank Dr Y. Tatsumi of JAMSTEC (currently at Kobe University)
16
17 455 for his generous support of this project. We are grateful to Prof. K. P. Jochum of the
18
19 456 Max Plank Institute for Chemistry for providing the MPI-DING glasses. The technical
20
21 457 and engineering support of Mr K. Ohki of OK Laboratory enabled the manufacture of
22
23 458 the high-quality 193-nm excimer LA imaging optics that helped establish the prolonged
24
25 459 stable ablation of plagioclase. Discussions with Dr D. Bouman of Thermo Scientific
26
27 460 were useful for application of the high-gain amplifiers. Finally, the authors are indebted
28
29 461 to the two anonymous reviewers who provided detailed and constructive comments,
30
31 462 which helped to further improve this paper.
32
33 463
34
35 464

36 **References**

- 37
38
39 465
40 466 1. J. N. Christensen, A. N. Halliday, D.-C. Lee and C. M. Hall, *Earth and*
41 467 *Planetary Science Letters*, 1995, **136**, 79-85. DOI: 10.1016/0012-821x(95)00181-6.
42
43 468 2. J. Davidson, F. Tepley III, Z. Palacz and S. Mejan-Main, *Earth and Planetary*
44 469 *Science Letters*, 2001, **184**, 427-442.
45
46 470 3. M. G. Jackson and S. R. Hart, *Earth and Planetary Science Letters*, 2006, **245**,
47 471 260-277. DOI: 10.1016/j.epsl.2006.02.040.
48
49 472 4. T. Takahashi, Y. Hirahara, T. Miyazaki, B. S. Vaglarov, Q. Chang, J.-I. Kimura
50 473 and Y. Tatsumi, *JAMSTEC Report R&D*, 2009, **Special Issue**, 59-64.
51
52 474 5. M. McCulloch, M. Cappel, J. Aumend and W. Müller, *Marine and Freshwater*
53 475 *Research*, 2005, **56**, 637-644. DOI: org/10.1071/MF04184.
54
55 476 6. J. Woodhead, S. Swearer, J. Hergt and R. Maas, *Journal of Analytical Atomic*
56 477 *Spectrometry*, 2005, **20**, 22-27.
57
58 478 7. P. Z. Vroon, B. van der Wagt, J. M. Koornneef and G. R. Davies, *Analytical*
59 479 *and Bioanalytical Chemistry*, 2008, **390**, 465-476, doi:

- 1
2
3
4
5
6 480 410.1007/s00216-00007-01742-00219.
7
8 481 8. R. Barnett-Johnson, F. C. Ramos, C. B. Grimes and R. B. MacFarlane,
9 482 *Canadian Journal of Fisheries and Aquatic Sciences*, 2005, **62**, 2425-2430. DOI:
10 483 10.1139/f05-194.
11
12 484 9. M. Bizzarro, A. Simonetti, R. K. Stevenson and S. Kurszlauskis, *Geochimica et*
13 485 *Cosmochimica Acta*, 2003, **67**, 289-302. DOI: 10.1016/s0016-7037(02)01048-7.
14
15 486 10. F. C. Ramos, J. A. Wolff and D. L. Tollstrup, *Chemical Geology*, 2004, **211**,
16 487 135-158. DOI: 10.1016/j.chemgeo.2004.06.025.
17
18 488 11. S. S. Schmidberger, A. Simonetti and D. Francis, *Chemical Geology*, 2003, **199**,
19 489 317-329. DOI: 10.1016/s0009-2541(03)00125-6.
20
21 490 12. T. Waight, J. Baker and D. Peate, *International Journal of Mass Spectrometry*,
22 491 2002, **221**, 229-244. DOI: 10.1016/s1387-3806(02)01016-3.
23
24 492 13. J. G. Konter and L. P. Storm, *Chemical Geology*, 2014, **385**, 26-34. DOI:
25 493 10.1016/j.chemgeo.2014.07.009.
26
27 494 14. J.-I. Kimura, T. Takahashi and Q. Chang, *Journal of Analytical Atomic*
28 495 *Spectrometry*, 2013, **28**, 945-957. DOI: 0.1039/c3ja30329b.
29
30 496 15. Y. Tatsumi, T. Takahashi, Y. Hirahara, Q. Chang, T. Miyazaki, J.-I. Kimura, M.
31 497 Ban and A. Sakayori, *Journal of Petrology*, 2008, **49**, 1971-2008.
32
33 498 16. J.-I. Kimura, Q. Chang, K. Itano, T. Iizuka, S. B. Vaglarov and K. Tani, *Journal*
34 499 *of Analytical Atomic Spectrometry*, 2014. DOI: 10.1039/C4JA00257A.
35
36 500 17. Y. H. Yang, H.-Y. Wu, J.-H. Yang, D. M. Chew, L.-W. Xie, Z.-Y. Chu, Y.-B.
37 501 Zhang and C. Huang, *Chemical Geology*, 2014, **385**, 35-55. DOI:
38 502 10.1016/j.chemgeo.2014.07.012.
39
40 503 18. A. V. Sovolev, A. W. Hofmann, K. P. Jochum, D. V. Kuzmin and B. Stoll,
41 504 *Nature*, 2011, **476**, 434-437. DOI: 10.1038/nature10321.
42
43 505 19. K. P. Jochum, B. Stoll, U. Weis, D. V. Kuzmin and A. V. Sovolev, *Journal of*
44 506 *Analytical Atomic Spectrometry*, 2009, **24**, 1237-1243. DOI: 10.1039/b905045k.
45
46 507 20. J.-I. Kimura, Q. Chang and H. Kawabata, *Journal of Analytical Atomic*
47 508 *Spectrometry*, 2013, **28**, 1522-1529. DOI: 10.1039/c3ja50109d.
48
49 509 21. J. I. Kimua and Q. Chang, *Journal of Analytical Atomic Spectrometry*, 2012, **27**,
50 510 1549-1559. DOI: 10.1039/c2ja10344c.
51
52 511 22. C. Bouman, M. Deerberg and J. B. Schwieters, *Application Note Thermo*
53 512 *Scientific*, 2009, **30187**, 1-4.
54
55 513 23. J. M. Koornneef, C. Bouman, J. B. Schwieters and G. R. Davies, *Journal of*
56 514 *Analytical Atomic Spectrometry*, 2013, **28**, 749-754.
57
58 515 24. J.-I. Kimura, T. Nozaki, S. R. and K. Suzuki, *Journal of Analytical Atomic*
59
60

- 1
2
3
4
5
6 516 *Spectrometry*, 2014, DOI: 10.1039/c1034ja00092g.
7
8 517 25. T. Takahashi, Y. Hirahara, T. Miyazaki, R. Senda, Q. Chang, J.-I. Kimura and Y.
9 518 Tatsumi, *Journal of Petrology*, 2012. DOI: 10.1093/petrology/egs065.
10
11 519 26. T. Hirata, Y. Hayano and T. Ohno, *Journal of Analytical Atomic Spectrometry*,
12 520 2003, **18**, 1283-1288.
13
14 521 27. K. P. Jochum, U. Nohl, K. Herwig, E. Lammel, B. Stoll and A. W. Hofmann,
15 522 *Geostandards and Geoanalytical Research*, 2005, **29**, 333-338.
16
17 523 28. J.-I. Kimura, K. Tani and Q. Chang, *Geochemical Journal*, 2012, **46**, 1-12.
18
19 524 29. H. Kawabata, T. Hanyu, Q. Chang, J.-I. Kimura, A. R. L. Nichols and Y.
20 525 Tatsumi, *Journal of Petrology*, 2011, **52**, 791-838.
21
22 526 30. H. Bradt, in *Astrophysics Processes*, Cambridge University Press, Cambridge.
23 527 2008, p. 536.
24
25 528 31. M. N. Saha, *Nature*, 1920, **105**, 232-233.
26
27 529 32. I. Kroslakova and D. Günther, *Journal of Analytical Atomic Spectrometry*,
28 530 2007, **22**, 51-62.
29
30 531 33. International_Union_of_Pure_and_Applied_Chemistry, *Pure & Applied*
31 532 *Chemistry*, 1984, **56**, 695-768.
32
33 533 34. T. Iizuka, S. M. Eggins, M. T. McCulloch, L. P. J. Kinsley and G. E. Mortime,
34 534 *Chemical Geology*, 2011, **282**, 45-57. DOI: 10.1016/j.chemgeo.2011.01.008.
35
36 535 35. J. Emsley, *The Elements*, Clarendon Press, Oxford. 1998.
37
38 536 36. G. Horlick and Y. Shao, in *Inductively Coupled Plasma in Analytical Atomic*
39 537 *Spectrometry 2nd ed.*, ed. A. Montaster and D. W. Golightly, VCH Pub. Inc., New York.
40 538 1992, p. 564.
41
42 539 37. F.-X. D'Abzac, A.-M. Seydoux-Guillaume, J. Chmeleff, L. Datas and F.
43 540 Poitrasson, *Journal of Analytical Atomic Spectrometry*, 2012, **27**, 108-119. DOI:
44 541 10.1039/c1ja10145d.
45
46 542
47 543
48
49 544
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6 545 **Figure and Table caption**
7

8 546

9
10 547 **Fig. 1.** Signal profiles (a) and isotope ratios (b) acquired from a 50- μm crater in ~ 25 s
11
12 548 on BCR-2G. Stable signals and isotope ratios are obtained after 10 s of idle time with
13
14 549 laser firing. No effect from slow response of the Faraday amplifiers was observed.
15
16

17 550

18
19 551 **Fig. 2.** Variation of $^{87}\text{Sr}/^{86}\text{Sr}$ of SRM 987 solution ($\sim 0.5\text{-V } ^{88}\text{Sr}$) measured with various
20
21 552 amounts of aerosol loading from a St Helena olivine crystal. The bias from Kr baseline
22
23 553 suppression is significant in the crater size 200 $\mu\text{m}/20$ Hz. Uncorrected values are from
24
25 554 isobaric overlap and mass fractionation corrections only. Corrected values are further
26
27 555 corrected for Kr baseline-induced bias. Errors are in 2SE. Aerosol loading without LA
28
29 556 (w/o LA) is provisionally plotted at $1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.
30
31

32 557

33
34
35 558 **Fig. 3.** Analytical results of the MkAn anorthite using different crater sizes for different
36
37 559 amounts of sample aerosol loading (panel a). Uncorrected (panel b) and corrected
38
39 560 $^{87}\text{Sr}/^{86}\text{Sr}$ – $^{84}\text{Sr}/^{86}\text{Sr}$ ratios (panel c) of the Kr baseline-induced biases are compared for
40
41 561 the different sample volumes. Data from large volume aerosols (200- $\mu\text{m}/10$ – 20 -Hz
42
43 562 crater) is plotted on the theoretical fractionation line of the Kr baseline suppression,
44
45 563 while those from the smaller volume aerosols (100–50- $\mu\text{m}/10$ -Hz craters) show slight
46
47 564 over-corrections. Potential biases from these overcorrections are less than ± 0.00020
48
49 565 (thick vertical line), well below the in-run analytical precisions for these data. Thick
50
51 566 shaded lines, thin solid lines, and thin dotted lines are regression lines for the results
52
53 567 from 200-, 100-, and 50- μm craters, respectively. Thin dashed lines show the reference
54
55 568 value of the MkAn as measured by TIMS.
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

569
570 **Fig. 4.** Daily temporal variations of $^{85}\text{Rb}/^{87}\text{Rb}$ correction factors during analyses of
571 basalt glass samples (panel a). The large gap between runs 39 and 40 is due to a long
572 break for 2 h indicating reverse shift of the drift due to no loading of the laser aerosols
573 (panel b). Apparent Rb mass bias and actual Sr mass bias, measured on Day 5 (panel c).
574 Note that open squares show measured values and dots are interpolations in panel b. See
575 details in the text.

576
577 **Fig. 5.** Analytical results of BHVO-2G and BCR-2G glass standards. Internal precisions
578 are given by 2SE, whereas those for averages (open circles) are given by two-standard
579 deviation (2SD). Solid squares and shaded lines are TIMS reference values.

580
581 **Table 1.** Laser and mass spectrometer set-up parameters for the LA-MC-ICP-MS Sr
582 isotope analysis

583
584 **Table 2.** Representative LA-MC-ICP-MS analytical results of Sr isotope ratios in
585 synthetic glass standards

586
587 **ESI Data Table 1.** LA-MC-ICP-MS analytical results of Sr isotope ratios

588
589 **Table of Contents Entry: Graphical abstract**

590 An analytical protocol using LA-MC-ICP-MS for precise Sr isotope ratio analysis from
591 small glass samples is presented

592

Table 1. Laser and mass spectrometer set-up parameters for the LA-MC-ICP-MS Sr isotope analysis

Apparatus	Experimental setting
Excimer laser	OK Laboratory Ltd. (in house)
Source wave length/pulse width	193 nm/20 ns
Energy at source	200 mJ
Focusing lens	Imaging optics using field lens and air spaced doublet objective
Spot size	50, 100, and 200 μm
Fluence at laser spot	20 J cm^{-2}
Repetition rate	10 and 20 Hz
Aridus II	CETAC Technologies
Spray chamber temperature	110 $^{\circ}\text{C}$
Membrane temperature	160 $^{\circ}\text{C}$
Nebuliser flow	1.0 L min^{-1}
Membrane gas flow	$\sim 3.5 \text{ L min}^{-1}$
Additional N_2 gas flow	1.5 mL min^{-1}
MC-ICP-MS	Thermo NEPTUNE
RF-power	1400 W
Guard electrode	off (electronically disconnected)
Sampling cone	N-sample cone (Ni)
Skimmer cone	N-skimmer cone (Ni)
Plasma gas (Ar)	1.0 L min^{-1}
Laser carrier gas (He)	0.7 L min^{-1}
Interface vacuum with E2M80	1.7 mbar with He ablation carrier gas
Acquisition time	0.5 s \times 50 scans for LA and 4 s \times 50 scans for solution
Faraday detector setting	
^{83}Kr (^{83}Kr , $^{43}\text{Ca}^{40}\text{Ca}$, $^{43}\text{Ca}^{40}\text{Ar}$)	FC L4 (10 ¹¹ Ω amplifier)
$^{83.5}\text{M}$ ($^{167}\text{Er}^{++}$)	FC L3 (10 ¹¹ Ω amplifier)
^{84}Sr (^{84}Kr , $^{44}\text{Ca}^{40}\text{Ca}$, $^{44}\text{Ca}^{40}\text{Ar}$)	FC L2 (10 ¹² Ω amplifier)
^{85}Rb (^{85}GaO)	FC L1 (10 ¹² Ω amplifier)
^{86}Sr (^{86}Kr , $^{46}\text{Ca}^{40}\text{Ca}$, $^{46}\text{Ca}^{40}\text{Ar}$)	FC Center (10 ¹² Ω amplifier)
$^{86.5}\text{M}$ ($^{173}\text{Yb}^{++}$)	FC H1 (10 ¹¹ Ω amplifier)
^{87}Sr (^{87}Rb , ^{85}GaO)	FC H2 (10 ¹² Ω amplifier)
^{88}Sr ($^{48}\text{Ca}^{40}\text{Ca}$, $^{48}\text{Ca}^{40}\text{Ar}$)	FC H3 (10 ¹² Ω amplifier)
Background subtraction	on peak background subtraction

632 FC: Faraday cup; isobaric atomic and molecular ions are shown in parentheses

Table 2. Representative LA-MC-ICP-MS analytical results of Sr isotope ratios in synthetic glass standards

Sample	Sr	Rb	Rb/Sr	$^{87}\text{Sr}/^{86}\text{Sr}$	2SD	n	$^{87}\text{Sr}/^{86}\text{Sr}$	2SD	n	$^{87}\text{Sr}/^{86}\text{Sr}$	2SE	Reference
	ppm	ppm		LA-ICP-MS (100 μm)			LA-ICP-MS (50 μm)			TIMS	(GeoREM)	
BHVO-2G	396	9.2	0.023	0.70345	0.00020	15	0.7035	0.0005	55	0.703469	0.00001	This study
				–	–	–	0.7035	0.0010	36	–	–	Jochum et al. (2009)
				–	–	–	0.7035	0.0010	–	–	–	Sovolev et al. (2011)
KL2-G	356	8.7	0.024	0.70352	0.00013	5	–	–	–	0.703517	0.00002	This study
				–	–	–	0.7036	0.0008	43	–	–	Jochum et al. (2009)
				–	–	–	0.7035	0.0008	–	–	–	Sobolev et al. (2011)
ML3B-G	312	5.8	0.019	0.70386	0.00027	10	–	–	–	0.703805	0.00002	This study
				–	–	–	0.7038	0.0008	48	–	–	Jochum et al. (2009)
				–	–	–	0.7038	0.0010	–	–	–	Sobolev et al. (2011)
BCR-2G	337	48.5	0.144	0.70495	0.00040	39	0.7051	0.0008	50	0.705000	0.00002	This study

Note: 2SD = two-standard deviation; 2SE = two-standard error; n = number of analyses. TIMS reference values are from GeoREM²⁷

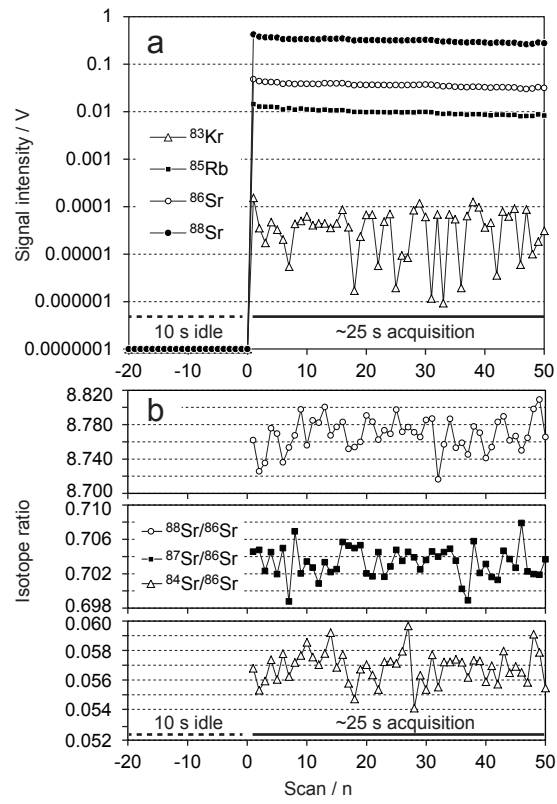


Fig. 1.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

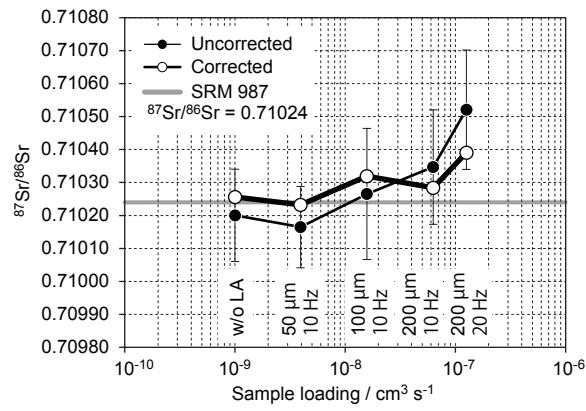


Fig. 2.

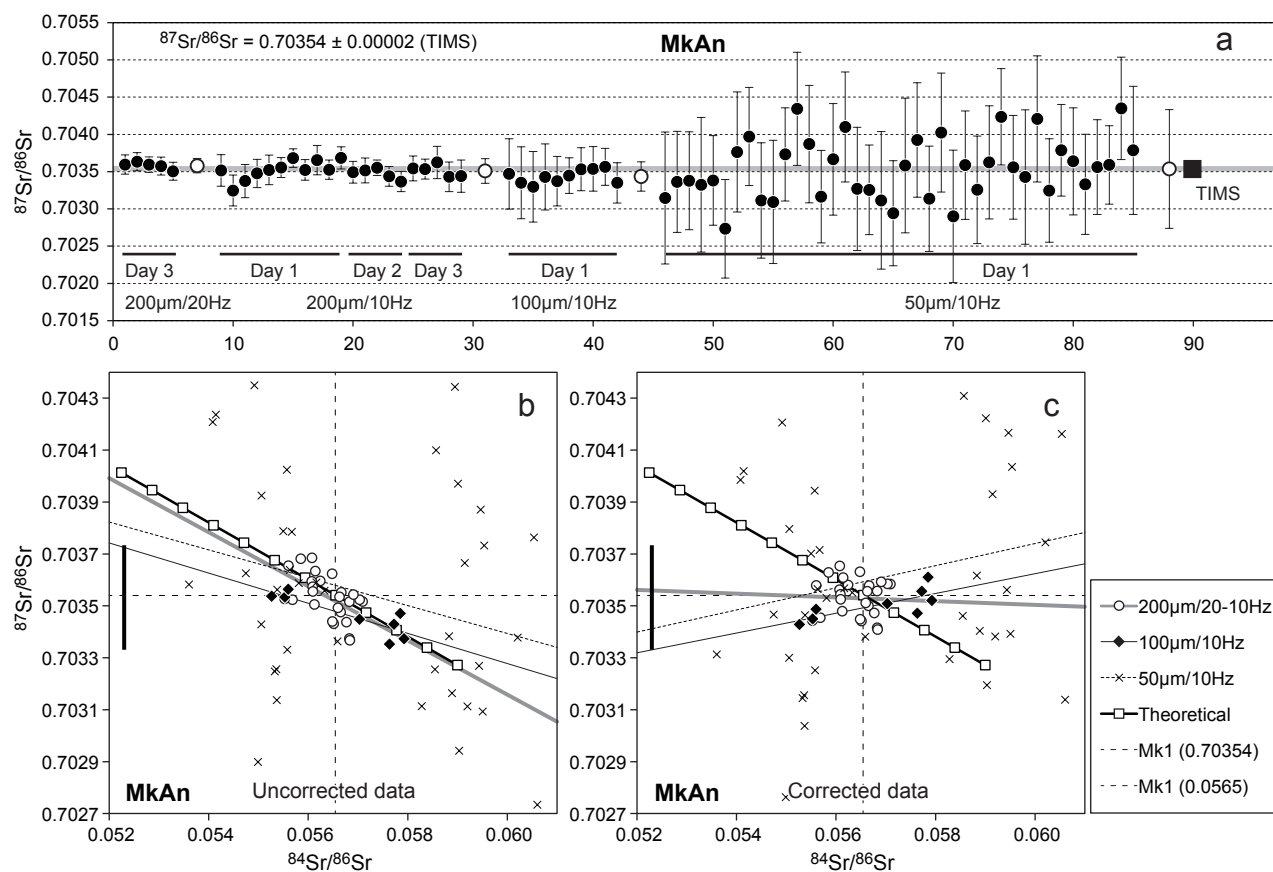


Fig. 3.

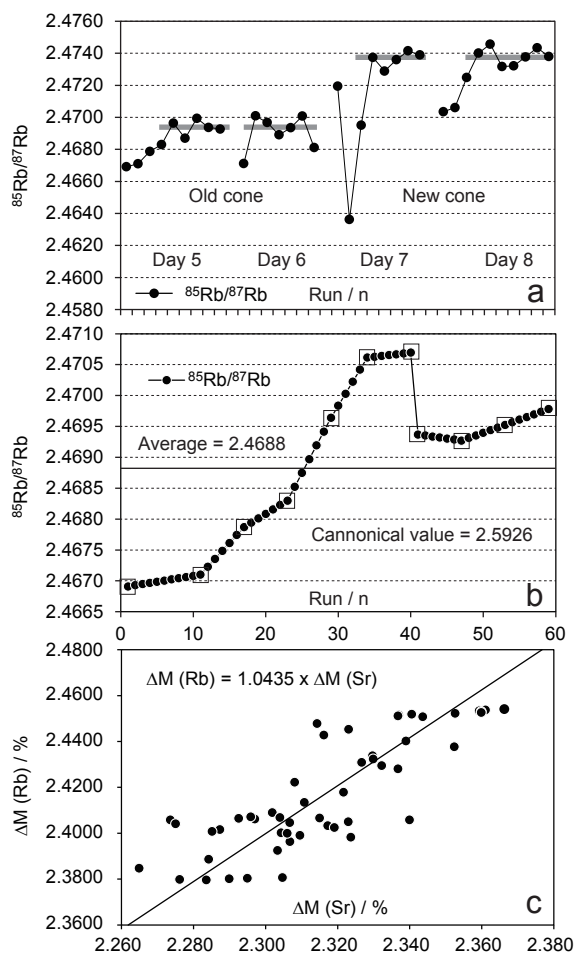


Fig. 4.

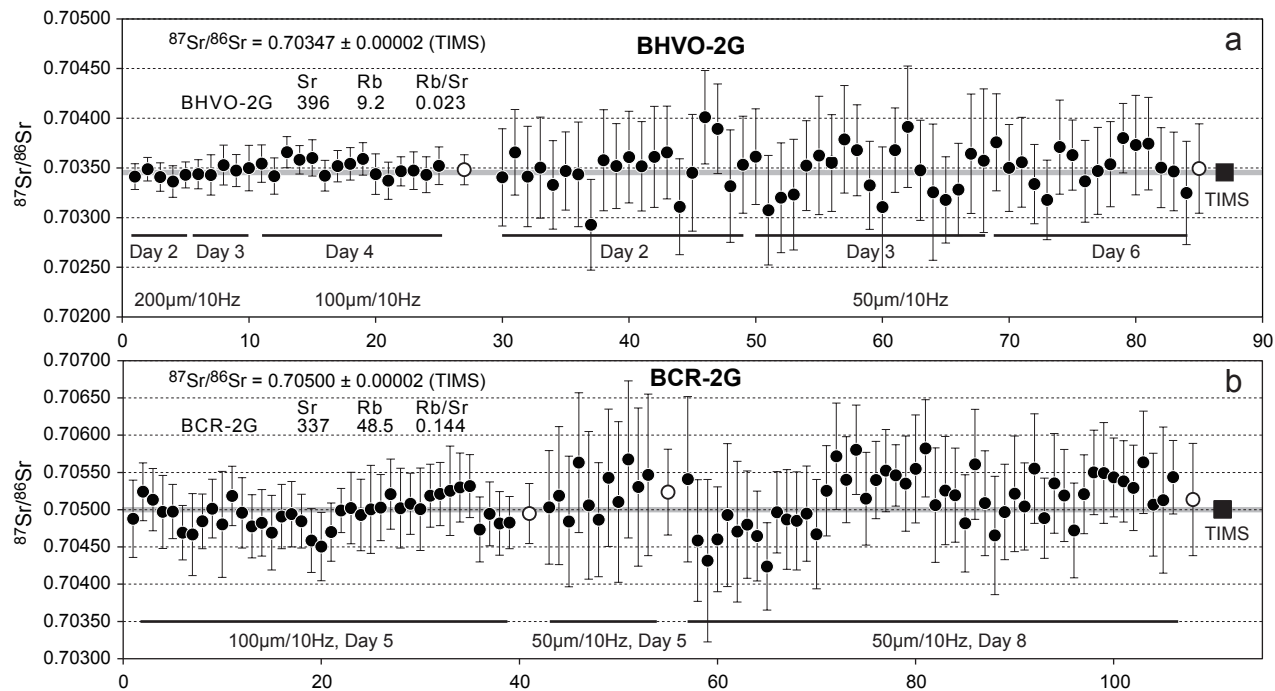


Fig. 5.

