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1 Silicon isotope measurement in zircon by laser ablation  
2 multiple collector inductively coupled plasma mass  
3 spectrometry

4  
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22 **ABSTRACT**

23 **This study reports the first Si isotope data measured in zircon using nanosecond  
24 laser ablation multiple collector inductively coupled plasma mass spectrometry.**

25 **Long-term (>2 years) external reproducibility obtained on the 91500 zircon  
26 standard is 0.13‰ and 0.21‰ (2SD) for  $\delta^{29}\text{Si}$  and  $\delta^{30}\text{Si}$  (per mil deviation from the**

27 quartz reference NBS 28), respectively, and typical precision on a single run is on  
28 the order of 0.10‰ and 0.12‰ (2SE) for  $\delta^{29}\text{Si}$  and  $\delta^{30}\text{Si}$ , respectively. Our results  
29 show good consistency between laser ablation multiple collector inductively  
30 coupled plasma mass spectrometry (LA-MC-ICP-MS) and solution multiple  
31 collector inductively coupled plasma mass spectrometry (S-MC-ICP-MS) /  
32 secondary ionization mass spectrometry (SIMS) data demonstrating that the Si  
33 isotopic composition of zircon can be accurately measured by LA-MC-ICP-MS.  
34 Obtained  $\delta^{30}\text{Si}$  values on natural zircon standards range from  $-0.32 \pm 0.23\text{‰}$  (2SD)  
35 for 91500 to  $-0.47 \pm 0.17\text{‰}$  for MudTank, whereas the MUN (synthetic) zircon  
36 standards have lower  $\delta^{30}\text{Si}$  values around  $-2.0\text{‰}$  (e.g.  $-2.08 \pm 0.17\text{‰}$  for MUN-1-  
37 2b). Silicon isotope measurements by LA-MC-ICP-MS open new possibilities for  
38 studying zircon formation in various geological contexts.

39

## 40 1. Introduction

41 Silicon is the third most abundant element on Earth (e.g., [McDonough, 2003](#)) and it  
42 commonly bonds with oxygen to form  $\text{SiO}_4$  tetrahedrons that represent the building  
43 blocks of all silicates. Silicon is therefore deeply involved in a lot of processes within  
44 and at the surface of the Earth. Silicon has three stable isotopes;  $^{28}\text{Si}$  (92.23%),  $^{29}\text{Si}$   
45 (4.68%), and  $^{30}\text{Si}$  (3.09%), and the measurement of their relative abundances has long  
46 been developed for various applications in planetary and Earth sciences, as well as in  
47 biological and environmental studies (e.g., [Poitrasson, 2017](#); [Ding et al., 2018](#); [Sutton  
48 et al., 2018](#)). Most studies have focused on bulk sample measurement (e.g., [Clayton et  
49 al., 1978](#); [Ziegler et al., 2005](#); [André et al., 2006](#); [Van den Boorn et al., 2010](#); [Savage  
50 et al., 2011](#); [Opfergelt et al., 2012](#); [Zambardi et al., 2013](#); [Deng et al., 2019](#)) but  
51 analytical development and scientific needs have conducted to the analysis of Si

52 isotopes with *in-situ* techniques such as secondary ionization mass spectrometry  
53 (SIMS) and laser ablation multiple collector inductively coupled plasma mass  
54 spectrometry (LA-MC-ICP-MS) (e.g., [Robert and Chaussidon, 2006](#); [Shahar and](#)  
55 [Young, 2007](#); [Chmeleff et al., 2008](#); [Marin-Carbonne et al., 2010](#)). SIMS measurements  
56 successfully helped decipher small scale heterogeneities and processes in SiO<sub>2</sub>-rich  
57 materials and some silicates such as quartz and olivine (e.g., [Marin-Carbonne, 2014](#);  
58 [Kleine et al., 2018](#); [Villeneuve et al., 2019](#)). This *in-situ* approach is required to study  
59 crystals with complex histories such as zircon (ZrSiO<sub>4</sub>) which has recently been  
60 investigated by [Trail et al. \(2018\)](#) using SIMS. The major limitation of these SIMS  
61 measurements is the analytical precision which is on average ~0.4‰ (2SE) and, hence,  
62 prevents good resolution between a large amount of data given that high-temperature  
63 processes induce limited Si isotope fractionation (e.g., [Savage et al., 2014](#)). A few  
64 studies utilized LA-MC-ICP-MS to measure Si isotope signatures in rocks and minerals  
65 (e.g., [Shahar and Young, 2007](#); [Chmeleff et al., 2008](#); [Ziegler et al., 2010](#); [Janney et al.,](#)  
66 [2011](#); [Schuessler and Blackenburg, 2014](#); [Chen et al., 2016](#); [Frick et al., 2016](#)) and  
67 consistently showed that analytical precisions can be better than 0.2‰ (2SE).  
68 Therefore, LA-MC-ICP-MS could be an alternative and very likely useful technique  
69 for *in-situ* studies of Si isotopes in zircon. These studies also underpinned that the type  
70 of laser used (i.e., nanosecond or femtosecond) plays a very important role as SiO<sub>2</sub>-rich  
71 matrices (e.g., quartz, chert) do not always couple well with nanosecond laser beams,  
72 thereby inducing poor external reproducibility (e.g., [Poitrasson and D'abzac, 2017](#)).  
73 However, other types of silicate matrices, such as glass, olivine, and zircon, commonly  
74 behave very well with such lasers. Given that the vast majority of LA-MC-ICP-MS  
75 facilities are equipped with nanosecond lasers (excimer or solid-state), it seemed more

76 useful for the scientific community to develop Si isotope measurements using  
77 nanosecond LA-MC-ICP-MS.

78 Zircon is a mineral extensively used in Earth Sciences because it can provide  
79 precise geochronological information using U-Th-Pb isotope systems (e.g., [Tilton et al., 1957](#);  
80 [Schoene, 2014](#)), as well as source characteristics using Hf and O isotopes  
81 ([Patchett, 1983](#); [Valley, 2003](#)). In addition, it is ubiquitous in granite (*sensus largo*),  
82 very resistant to weathering and erosion, and most elements diffuse very slowly within  
83 its lattice ([Lee et al., 1997](#); [Cherniak and Watson, 2003, 2007](#)). Given that granite is the  
84 main constituent of continents, zircon in magmatic rocks and detrital sediments has  
85 long been used to study the growth of continents, which remains one of the major  
86 unresolved issues in Earth Sciences (e.g., [Fedo et al., 2003](#); [Iizuka et al., 2005](#); [Guitreau  
87 et al., 2012](#); [Roberts and Spencer, 2015](#)). Silicon stable isotopes have been used to  
88 discriminate some granite types from others ([Savage et al., 2012](#); [André et al., 2019](#);  
89 [Deng et al., 2019](#)) and their application to zircon is promising to study the growth of  
90 continents, granite petrogenesis, and lithosphere-hydrosphere interactions in deep-time  
91 geology ([Trail et al., 2018](#)). Theoretical work predicted that Si isotope fractionation  
92 should occur between minerals and their parental melt as a function of temperature,  
93 melt polymerization, mineral chemistry and Si-O bond lengths (e.g. [Méheut et al.,  
94 2009](#); [Méheut and Schauble, 2014](#); [Qin et al., 2016](#)). According to [Qin et al. \(2016\)](#),  
95 enrichment in  $^{30}\text{Si}$  linked to fractionation follows the sequence quartz > albite >  
96 anorthite > olivine ~ zircon > enstatite > diopside. Consequently, zircon is expected to  
97 be enriched in light isotopes compared to its parental melt. This was recently confirmed  
98 by measurements on natural zircons ([Trail et al., 2018](#)) as well as by experimental work  
99 ([Trail et al., 2019](#)). The present contribution explores the capability of nanosecond LA-

100 MC-ICP-MS to measure Si isotopes in individual zircons for future applications in  
101 Earth Sciences.

102

## 103 **2. Material and Methods**

### 104 **2.1. Standard material**

105 Reference materials in the form of glass and crystallized matrices (i.e., olivine and  
106 zircon) were used for the optimization of the analytical conditions and the  
107 determination of an appropriate protocol for silicon isotope measurements by LA-MC-  
108 ICP-MS. Glass reference materials used in this study were SRM NIST 612, USGS  
109 BHVO-2 and GSC-1G (e.g., [Jochum et al., 2005, 2011](#)). The San Carlos olivine  
110 reference material (e.g., [Jarosewich et al., 1980](#)) was also investigated together with  
111 zircon standards 91500 (syenite-derived; [Wiedenbeck et al., 1995](#)), MudTank  
112 (carbonatite-derived; [Black and Gulson, 1978](#)), KIM (kimberlite-derived; [Valley, 2003](#);  
113 [Trail et al., 2018](#)), AS3 (gabbro-derived; [Paces and Miller, 1993](#)), R33 (monzodiorite-  
114 derived; [Black et al., 2004](#)), QGNG (Quartz-gabbronorite-derived; [Black et al., 2003](#)),  
115 Peixe (Alkaline-rich granitoid-derived; [Chang et al., 2006](#)), Plešovice (hyperpotassic  
116 granulite-derived; [Sláma et al., 2008](#)), and the artificial standards MUN from the  
117 Memorial University of Newfoundland ([Fisher et al., 2011](#)).

118

### 119 **2.2. Measurements**

#### 120 **2.2.1. Solution MC-ICP-MS characterization of zircon standards**

121 In order to determine the Si isotope composition of zircons and to check the validity of  
122 results obtained using LA-MC-ICP-MS, we have analyzed several well-known zircon  
123 reference materials using solution mode technique (S-MC-ICP-MS) modified from that  
124 described in [Deng et al. \(2019\)](#). Crushed powders of 91500 and Plešovice zircons (1.5-

125 6.8 mg), as well as MUN-1 (0.6 mg), were dissolved using a NaOH fusion method  
126 revised after [Georg et al. \(2006\)](#). The samples were fused in Ag crucibles with proper  
127 additions of NaOH pellet (120 mg for 91500 and Plešovice zircons and only 40 mg for  
128 MUN-1) at 720 °C for 15 min in a furnace. Afterwards, the glassy samples were  
129 dissolved in Milli-Q H<sub>2</sub>O by heating and ultrasonication. The samples were, then,  
130 transferred into pre-cleaned tubes by Milli-Q H<sub>2</sub>O rinsing, achieving total volumes of  
131 the solutions for 91500 and Plešovice zircons to 30-40 ml and 10 ml for MUN-1 zircon.  
132 This step control in dissolution volume maintains Si concentrations in the sample  
133 solutions to be sufficiently high (at µg/g or sub µg/g level) for subsequent isotopic  
134 measurements. For the digestions on  $\geq 1$  mg samples, purified 16 M HNO<sub>3</sub> (0.1-0.3  
135 mL) were properly added to acidify the solutions until they became clear.

136 Sample aliquots containing 20 µg of Si were passed through columns hosting  
137 1.8 mL BioRad AG50X-12 (200-400 meshes) cation exchange resin ([Pringle et al.,](#)  
138 [2014](#)). At neutral conditions, the dissolved Si would be eluted by 5 mL Milli-Q H<sub>2</sub>O  
139 rinsing, whereas the cations would be retained on the columns by the resin. Note that  
140 the resin was discarded after every single use to avoid any memory effect of any neo-  
141 formed insoluble Zr particles under weak-acids. After purification, the solutions were  
142 further diluted and acidified into 10 mL (2 µg/g) Si solutions in 0.2 M HNO<sub>3</sub>. The  
143 sample solutions were measured for the Si isotopic compositions on the Thermo  
144 Scientific Neptune Plus multi-collector inductively coupled plasma mass spectrometer  
145 (MC-ICP-MS) at the Institut de Physique du Globe de Paris (IPGP). The solutions were  
146 introduced via a quartz-made spray chamber. The typical sensitivity was 10-12 V on  
147 <sup>28</sup>Si<sup>+</sup> for 2 µg/g of Si with an uptake rate of 100 µL/min under a medium resolution  
148 mode (M/ΔM ~5000). In order to avoid isobaric interferences from <sup>14</sup>N<sup>16</sup>O<sup>+</sup> on <sup>30</sup>Si<sup>+</sup>,  
149 the measurements of ion intensities were conducted at the lower masses of peaks 28,

150 29 and 30 (e.g., [Shahar and Young, 2007](#); [Chmeleff et al., 2008](#); [Zhang et al., 2015](#)).  
151 Reference materials NBS 28 and BHVO-2 were processed following the same  
152 protocols as for zircon standards, and the purified NBS 28 was used as the bracketing  
153 standard. A standard-sample bracketing method was used, meaning that NBS 28  
154 solutions were measured before and after each analysis of BHVO-2 and zircon  
155 reference material. Each sample was analyzed 3-6 times, and each measurement  
156 consisted of 25 cycles with 8.389 s of integration time per cycle. After every analysis,  
157 a wash-out with 0.5 M HNO<sub>3</sub> and 0.2 M HNO<sub>3</sub> in steps was carried out. The Si blank  
158 from the whole procedure was  $\leq 15$  ng, which is much lower than the Si masses of the  
159 samples (40-2000  $\mu$ g). After Si purification, each solution was checked using Q-ICP-  
160 MS and no Zr was detected whereas other elements, when detected, were all below 1  
161 ppb. Note that we managed to strictly match the NO<sub>3</sub><sup>-</sup> contents and Si concentrations  
162 of the bracketing NBS 28 solutions to the corresponding sample solutions, which  
163 minimizes possible matrix effects.

164

### 165 **2.2.2. Silicon isotope measurements by LA-MC-ICP-MS**

166 Laser ablation multiple collector inductively coupled plasma mass spectrometry  
167 measurements were conducted at Laboratoire Magmas et Volcans (LMV, Clermont-  
168 Ferrand, France) using a Resonetics Resolution M-50 coupled to a Thermo Scientific  
169 Neptune Plus. Analytical conditions are provided in [Table 1](#). The abundance of silicon  
170 isotopes was measured in high resolution mode ( $M/\Delta M=7800$ ) and on the low-mass  
171 shoulder of 28, 29, and 30 peaks to avoid isobaric interferences (e.g., [Shahar and](#)  
172 [Young, 2007](#); [Chmeleff et al., 2008](#); [Janney et al., 2011](#); [Schuessler and Von](#)  
173 [Blackenburg, 2014](#); [Frick et al., 2016](#)). Silicon isotope analyses were performed in  
174 standard-bracketing (i.e., single measurement of an unknown bracketed by two



175 analyses of a matrix-matched standard, or batch of two unknowns bracketed by two  
176 measurements of a matrix-matched standard). During the development of the  
177 technique, we analyzed quartz, notably NBS 28, and silica-rich matrices (e.g., chert,  
178 opale), but observed either very noisy signals or even breakage of crystals during  
179 ablation. As a consequence, we could not analyze the international quartz reference  
180 standard NBS 28 (NIST RM 8546) to normalize our data to. Instead, we used NIST 612  
181 or the zircon standard 91500 as our normalizing reference and recalculated all data  
182 relative to NBS 28. Results are reported in delta notation,  $\delta^{29}\text{Si}$  and  $\delta^{30}\text{Si}$ , which express  
183 per mil deviations from a reference, and are calculated using the following equations.

$$184 \quad \delta^x\text{Si} (\text{‰}) = \left( \frac{\left( \frac{{}^x\text{Si}}{28\text{Si}} \right)_{\text{sample}}}{\left( \frac{{}^x\text{Si}}{28\text{Si}} \right)_{\text{reference}}} - 1 \right) \times 1000 \quad (1)$$

185 with x being either 29 or 30. Several ways of reporting analytical uncertainties have  
186 been adopted in the literature (e.g., 1 SD, 1 SE, 2 SD, 2 SE, 95% confidence). For the  
187 sake of consistency, we report internal precision (i.e., within-run error or analytical  
188 precision) as 2 standard-errors (2SE), also called reduced-error, which is 2 times the  
189 standard-deviation divided by the square-root of the number of measurements. This is  
190 the case for single zircon measurement. Note that the internal precision reported for  
191  $\delta^{29}\text{Si}$  and  $\delta^{30}\text{Si}$  of single measurements include a quadratic addition of the errors on the  
192 bracketing standards. The external reproducibility (e.g., mean of measurements on the  
193 same zircon standard) is, however, reported as 2 standard-deviations (2SD). When we  
194 quote literature data and their associated uncertainties, we report them in the same way  
195 as our data and, hence, recalculated them if they were reported differently in the original  
196 publications. We processed Si isotope data both with and without applying background  
197 correction and observed no difference in the obtained  $\delta^{29}\text{Si}$  and  $\delta^{30}\text{Si}$ . However, data  
198 that were corrected for background exhibited poorer external reproducibility likely due

199 to the limited signal-over-noise ratio (Fig. 1). As a consequence, all data presented in  
200 this contribution were not corrected for background. We also applied a 2SD filter to  
201 remove outliers.

202 A critical issue with high-temperature Si isotope geochemistry is the limited  
203 fractionation which, in turn, results in small isotopic variability (e.g., [Savage et al. 2014](#),  
204 [Deng et al., 2019](#)). This requires an appropriate analytical precision so as to be able to  
205 discriminate distinct isotopic compositions. Consequently, we compared Si isotopes  
206 measurements obtained by spot and line modes on synthetic glass, olivine, and zircon  
207 standards. We adjusted spot size and frequency together in order to obtain highest and  
208 most stable signals, and set the fluence to  $\sim 3 \text{ J/cm}^2$  regardless of spot size and frequency  
209 used because it corresponds to ablation conditions that are optimal for other isotope  
210 systems (i.e., U-Pb and Lu-Hf; [Guitreau et al., 2019](#)).

211

### 212 **3. Results**

#### 213 **3.1. S-MC-ICP-MS results**

214 Results for basalt (BHVO-2) standards are in good agreement with literature values as  
215 we obtained  $\delta^{29}\text{Si}$  and  $\delta^{30}\text{Si}$  of  $-0.14 \pm 0.09$  and  $-0.28 \pm 0.15\text{‰}$  ( $n = 60$ ; 2SD),  
216 respectively which compares well with a  $\delta^{30}\text{Si} = -0.29 \pm 0.05\text{‰}$ ; from [Schuessler and](#)  
217 [Von Blackenburg \(2014\)](#) ([Table 2](#)).

218 The two different fragments of 91500 analyzed by S-MC-ICP-MS, labeled  
219 91500-MG and 91500-Corfu, exhibit very consistent  $\delta^{30}\text{Si}$  values of  $-0.39 \pm 0.10$  and -  
220  $0.36 \pm 0.02\text{‰}$  (2SD; [Table 2](#)). This is also true for  $\delta^{29}\text{Si}$  with values of  $-0.19 \pm 0.09$  and  
221  $-0.20 \pm 0.02\text{‰}$  (2SD; [Table 2](#)). The 4 different fragments of Plešovice zircon standard  
222 similarly gave consistent  $\delta^{30}\text{Si}$  values between  $-0.39 \pm 0.10$  and  $-0.34 \pm 0.24\text{‰}$  (2SD;  
223 [Table 2](#)). The artificial zircon standard MUN-1, which corresponds to MUN-1-2b from

224 MUNzirc second series (Hanchar personal communication), gave a mean  $\delta^{30}\text{Si}$  value  
225 of  $-2.08 \pm 0.17\text{‰}$  (2SD; [Table 2](#)), which is very light compared to natural zircons. The  
226 standards 91500 and Plešovice exhibit similar Si isotope values with those obtained by  
227 S-MC-ICP-MS and SIMS in [Trail et al. \(2018\)](#).

228

### 229 **3.2. LA-MC-ICP-MS results**

230 The results are given in [Tables 3-5](#) and [S1-S5](#), and illustrated in [Figures 1-5](#). Figure 1  
231 shows typical LA-MC-ICP-MS measurements of 91500 in spot and line modes and it  
232 is visible that Si isotopic ratios are stable throughout a run for both modes. The spot  
233 measurement (Fig. 1A) is affected by intensity decrease over the course of the analysis  
234 which is due to deepening of the laser pit. On the contrary, line mode produces more  
235 stable intensities that also translate into more reproducible signals and isotopic ratios.  
236 Note that Si backgrounds are high which is common with laser ablation measurements.  
237 [Table 3 and Figure 2](#) further show that line mode provides better internal precision and  
238 external reproducibility than spot mode regardless of the type of matrix analyzed and  
239 laser setting used. Such observation is consistent with those reported by [Schuessler and](#)  
240 [von Blanckenburg \(2014\)](#). In order to test LA-MC-ICP-MS measurement accuracy, we  
241 analyzed San Carlos olivine and 91500 zircon and used NIST 612 as a normalizing  
242 reference. It can be seen in [Table 4](#) that obtained  $\delta^{29}\text{Si}$  and  $\delta^{30}\text{Si}$  for San Carlos and  
243 91500 are inconsistent with expected values. [Schuessler and Von Blackenburg \(2014\)](#)  
244 showed that differences in Si intensity between a sample and its bracketing standard  
245 could result in inaccurate  $\delta^{29}\text{Si}$  and  $\delta^{30}\text{Si}$ . The synthetic glass, NIST 612, has a much  
246 higher Si concentration than olivine and zircon and, hence, we have adjusted the Si  
247 intensity between San Carlos olivine and NIST 612 by changing the frequency of the  
248 laser and by doing measurements in line mode. However, obtained values for San

249 Carlos olivine are still inaccurate (Table 4) which highlights the matrix-sensitive nature  
250 of isotope measurements by LA-MC-ICP-MS using nanosecond lasers. Therefore, all  
251 zircon analyses presented in what follows correspond to line mode (Fig. 1B) that were  
252 conducted with a frequency of 6 Hz, a spot size of 33  $\mu\text{m}$ , a fluence of 3  $\text{J}/\text{cm}^2$ , a traverse  
253 rate of 1.6  $\mu\text{m}/\text{s}$ , and normalized to 91500. The spot size and frequency were selected  
254 to obtain the highest and most stable signal according to the MC-ICP-MS sensitivity  
255 without compromising spatial resolution too much.. Data for 91500 gathered over a  
256 period of more than 2 years show an external reproducibility of 0.21‰ on the self-  
257 bracketed  $\delta^{30}\text{Si}$  (2SD; Fig. 3), while internal precisions vary between 0.09 and 0.16‰  
258 (2SE; Table S3).

259 Figure 4a illustrates that LA-MC-ICP-MS data align along a least-squares  
260 regression line of  $0.5132 \pm 0.0034$  ( $R^2 = 0.98$ ) which falls right in between theoretical  
261 predictions for mass-dependent fractionation (i.e., equilibrium = 0.5178 and kinetic =  
262 0.5092; e.g. Zambardi and Poitrasson, 2011; Savage et al., 2014). Moreover, both S-  
263 MC-ICP-MS and LA-MC-ICP-MS measurements have consistent fractionation  
264 behavior along the terrestrial mass-dependent fractionation lines (Figure 4b). Finally,  
265 Figure 5 demonstrates that our new LA-MC-ICP-MS data comply well with Si isotope  
266 data obtained with other techniques on the same zircon standards (i.e., S-MC-ICP-MS  
267 in this study and S-MC-ICP-MS/SIMS techniques in Trail et al., 2018).

268 Silicon isotope data for natural zircon standards overall show very little  
269 variability with  $\delta^{30}\text{Si}$  ranging from  $-0.32 \pm 0.23\text{‰}$  for 91500 to  $-0.47 \pm 0.17\text{‰}$  for  
270 MudTank (2SD; Table 5). These values are consistent with Si isotope data on zircon  
271 published elsewhere (Trail et al., 2018, 2019, Figure 5 and Table 5). 91500 zircon  
272 analyzed in this study by LA-MC-ICP-MS and by S-MC-ICP-MS gave consistent  $\delta^{30}\text{Si}$   
273 of  $-0.32 \pm 0.23\text{‰}$  and  $-0.39 \pm 0.10\text{‰}$ , respectively. AS3 zircon analyzed in this study

274 by LA-MC-ICP-MS gave a  $\delta^{30}\text{Si}$  of  $-0.44 \pm 0.23\text{‰}$  which is consistent within  
275 uncertainty-with the value of  $-0.36 \pm 0.35\text{‰}$  (2SD; [Table 5](#)) obtained by SIMS in [Trail](#)  
276 [et al. \(2018\)](#). KIM zircon gave a LA-MC-ICP-MS  $\delta^{30}\text{Si}$  of  $-0.40 \pm 0.23\text{‰}$  identical to  
277 the S-MC-ICP-MS value of  $-0.41 \pm 0.01\text{‰}$  from [Trail et al. \(2018\)](#). Kuehl Lake zircon  
278 gave a LA-MC-ICP-MS  $\delta^{30}\text{Si}$  of  $-0.38 \pm 0.12\text{‰}$  which is also consistent within  
279 uncertainty with the S-MC-ICP-MS value of  $-0.29 \pm 0.04\text{‰}$  published in [Trail et al.](#)  
280 [\(2018\)](#). MudTank zircon displays a LA-MC-ICP-MS  $\delta^{30}\text{Si}$  of  $-0.47 \pm 0.17\text{‰}$  which is  
281 consistent, within error, with the S-MC-ICP-MS value of  $-0.34 \pm 0.03\text{‰}$  from [Trail et](#)  
282 [al. \(2018\)](#). Plešovice zircon gave a LA-MC-ICP-MS  $\delta^{30}\text{Si}$  of  $-0.38 \pm 0.18\text{‰}$  identical  
283 to S-MC-ICP-MS analyses from this study ( $\delta^{30}\text{Si} = -0.39 \pm 0.06\text{‰}$ ). The artificial MUN  
284 zircon standards exhibit consistently lighter Si isotope compositions compared to those  
285 shown by natural standards. MUN zircons have slightly variable  $\delta^{30}\text{Si}$  that range from  
286  $-1.67 \pm 0.14\text{‰}$  for MUN-0 to  $-2.05 \pm 0.30\text{‰}$  (2SD; [Table 5](#)) for MUN-4. The value of  
287  $-2.00 \pm 0.22\text{‰}$  obtained for MUN-1 using LA-MC-ICP-MS ([Table 5](#)) is identical within  
288 uncertainty to that obtained by S-MC-ICP-MS (i.e.,  $-2.08 \pm 0.17\text{‰}$ ; [Table 2](#)), hence,  
289 confirming the enrichment of this synthetic zircon in light Si isotopes.

290

#### 291 **4. Discussion**

292 Comparisons between Si isotope signatures of natural and synthetic zircons analyzed  
293 by LA-MC-ICP-MS and S-MC-ICP-MS in this study, as well as data from the literature  
294 (S-MC-ICP-MS and SIMS, [Trail et al., 2018](#)), exhibit general good consistency that  
295 indicates that zircon data by LA-MC-ICP-MS are accurate and robust. Moreover,  
296 although less precise than S-MC-ICP-MS analyses ( $\delta^{30}\text{Si}$  within-run 2 standard error  
297 of  $\sim 0.02\text{-}0.05\text{‰}$ ), LA-MC-ICP-MS data ( $\delta^{30}\text{Si}$  within-run 2 standard error of  $\sim 0.10\text{-}$   
298  $0.15\text{‰}$ ) are more precise than currently available SIMS data ( $\delta^{30}\text{Si}$  within-run 2

299 standard error of ~0.30-0.40‰) and, hence, represent a relevant compromise between  
300 precision and spatial resolution. Therefore, Si isotope measurements in zircon by LA-  
301 MC-ICP-MS open new possibilities for zircon studies in various geological contexts  
302 (e.g., magmatic differentiation, crustal growth).

303 This technique could be improved further in the future by reducing the high Si  
304 background which is visible in [Figure 1](#) and likely influences external reproducibility  
305 of Si isotope signatures. Moreover, as shown in [Zambardi and Poitrasson \(2011\)](#) silicon  
306 isotopic fractionation induced by MC-ICP-MS instruments evolve non-linearly over  
307 time, which requires a strict standard-bracketing procedure to be applied when  
308 measuring Si isotopes by LA-MC-ICP-MS. However, if ways to stabilize the time-  
309 induced drift in Si isotope ratios in MC-ICP-MS are found they would certainly help  
310 improve external reproducibility of  $\delta^{29}\text{Si}$  and  $\delta^{30}\text{Si}$ .

311 One pitfall of LA-MC-ICP-MS analysis, compared to SIMS, is the quantity of  
312 material required to achieve reasonable precision. In this contribution, we have decided  
313 to conduct analyses in line mode so as to obtain the best internal precision and external  
314 reproducibility. In the context of zircon studies, processing by lines over spots has the  
315 advantage of better coupling internal textures observed in cathodoluminescence (CL)  
316 and back-scattered electron (BSE) images to the obtained isotopic information.  
317 However, such lines require a rather large part of zircons to be swept across (~100  $\mu\text{m}$   
318 long traverse). Possible chemical/isotopic heterogeneities may be invisible at the  
319 sampling scale. One may compromise the precision for spatial resolution by doing spots  
320 but would likely reduce the precision and hence the resolvability. This issue can be  
321 dealt with on a case-to-case basis depending on the size and complexity of zircons  
322 studied.

323

324 **5. Conclusions**

325 In this contribution, we have set up a protocol for Si isotope measurements in zircon by  
326 nanosecond LA-MC-ICP-MS. Analyses performed in line mode were preferred to those  
327 obtained by spot mode because of their better internal precision and external  
328 reproducibility. Within-run error on zircon  $\delta^{30}\text{Si}$  are on the order of  $\sim 0.10\text{-}0.15\text{‰}$  (2SE)  
329 and external precision of  $\sim 0.15\text{-}0.30\text{‰}$  (2SD). Our LA-MC-ICP-MS data are in line  
330 with those acquired with S-MC-ICP-MS and SIMS, therefore highlighting the accuracy  
331 of silicon isotope measurements in zircon by LA-MC-ICP-MS. This technique,  
332 therefore, offers an additional way to existing methods aiming to study zircon formation  
333 in different geological contexts.

334

335 **Conflicts of interest**

336 The authors have no conflicts to declare.

337

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351

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544

545 **Figure and Table captions**

546 Table 1. LA-MC-ICP-MS operating conditions

547

548 Table 2. Silicon isotope results for zircons analyzed by S-MC-ICP-MS

549

550 Table 3. External reproducibility of self-normalized standards

551

552 Table 4. Summary of Si isotope measurements by LA-MC-ICP-MS of San Carlos and  
553 91500 normalized to NIST 612

554

555 Table 5. Silicon isotope results for zircons analyzed by LA-MC-ICP-MS

556

557 Figure 1. Signal and isotope ratio evolutions throughout a typical analysis of the zircon  
558 standard 91500 in spot (A) and line (B) modes using the same analytical conditions  
559 (i.e., spot size of 33  $\mu\text{m}$ , frequency of 6 Hz, fluence of 3  $\text{J}/\text{cm}^2$  and sweeping rate of  
560 1.6  $\mu\text{m}/\text{s}$  for the line mode, and). In the insets,  $\delta^{29}\text{Si}$  and  $\delta^{30}\text{Si}$  values were calculated  
561 by normalization to the average  $^{29}\text{Si}/^{28}\text{Si}$  and  $^{30}\text{Si}/^{28}\text{Si}$  of the corresponding analysis.  
562 Note that during ablation both the isotope ratios are stable, despite high intensities of  
563 Si in the background (laser off)..

564



565 Figure 2. External reproducibility of Si isotopes in different matrices. Delta values are  
566 self-normalized for each standard. Note the general better external reproducibility of  
567 line analyses compared to spots regardless of the matrix analyzed

568

569 Figure 3. Long-term (>2 years) reproducibility of Si isotope signatures in 91500 (self-  
570 bracketed).

571

572 Figure 4. Silicon isotope results for zircon analysed by LA-MC-ICP-MS and S-MC-  
573 ICP-MS. Figure A shows the relationship between  $\delta^{29}\text{Si}$  and  $\delta^{30}\text{Si}$  for all single LA-  
574 MC-ICP-MS measurements whereas B exhibits the relationship between  $\delta^{29}\text{Si}$  and  
575  $\delta^{30}\text{Si}$  for averages of all zircon standards analyzed by LA-MC-ICP-MS and S-MC-ICP-  
576 MS. Note that MUN artificial zircon standards have very light Si isotope signatures  
577 compared to natural zircons and that data align along the terrestrial mass-dependent  
578 fractionation lines, labeled EMFL and KMFL for equilibrium and kinetic fractionation,  
579 respectively.

580

581 Figure 5. Comparison between LA-MC-ICP-MS and S-MC-ICP-MS/SIMS data for  
582 zircon standards (MUN-1, 91500, AS3, KIM, Kuehl Lake, MudTank, and Plešovice)  
583 from this study and [Trail et al. \(2018\)](#). All data align along a line with a slope of 1,  
584 therefore, indicating very good agreement between techniques.

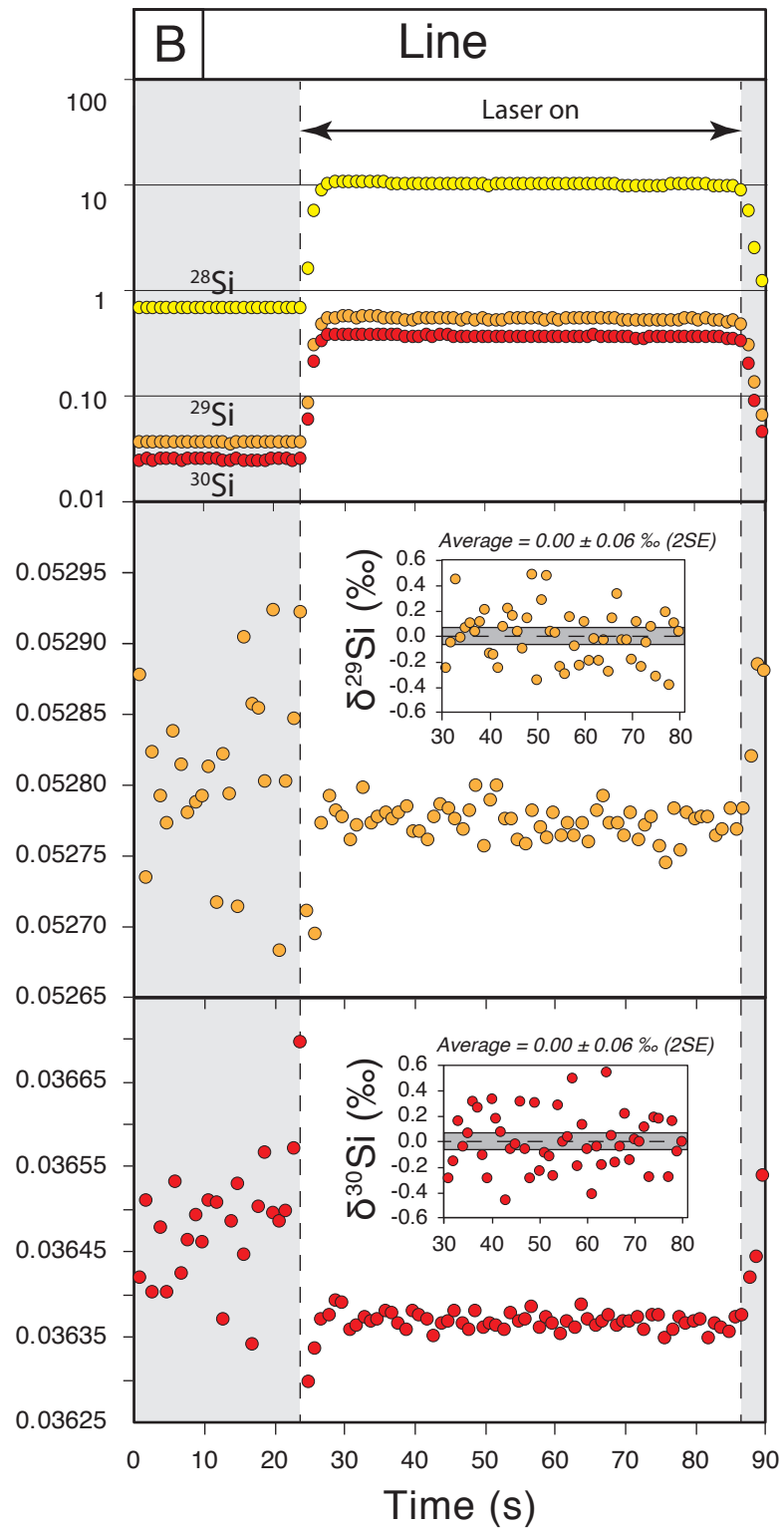
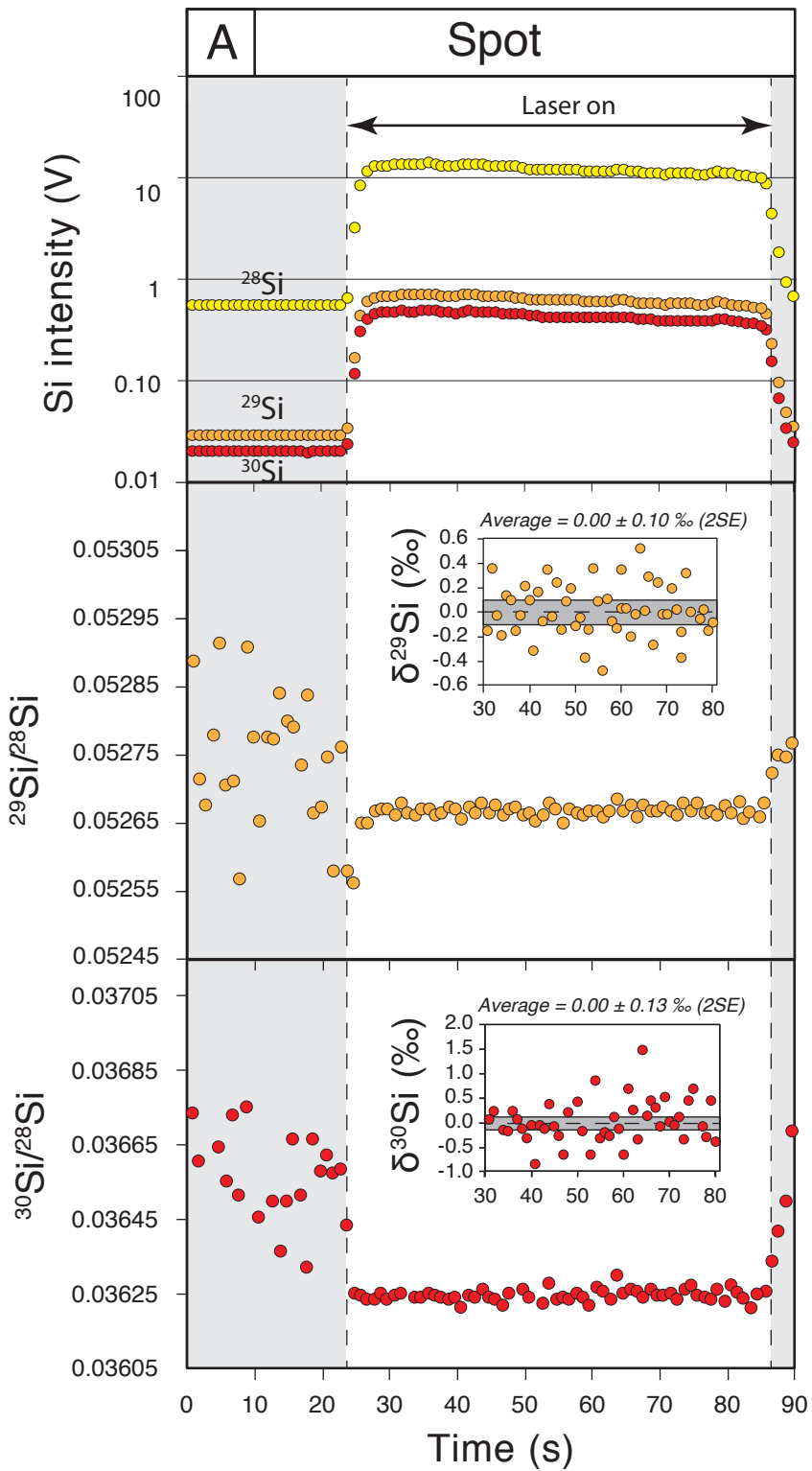
585

### 586 **Supplementary Table captions**

587 Table S1. All LA-MC-ICP-MS results for standards

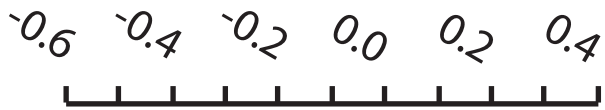
588 Table S2. Results for Si isotope measurements by LA-MC-ICP-MS of San Carlos  
589 olivine and 91500 zircon normalized to NIST 612

590 Table S3. All results for 91500 (self-bracketed) analyzed by LA-MC-ICP-MS in line  
591 mode  
592 Table S4. All Si isotope data for zircon analyzed by LA-MC-ICP-MS in line mode  
593 Table S5. All raw LA-MC-ICP-MS data

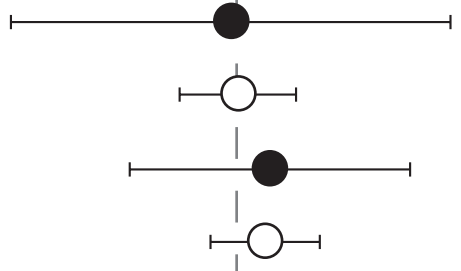
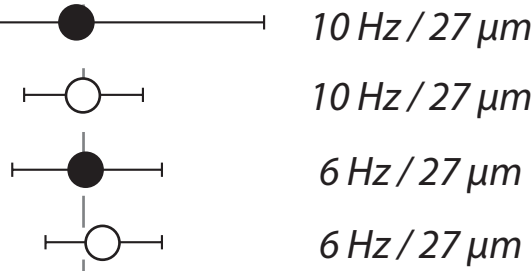


$\delta^{29}\text{Si}$  (‰) self-normalized

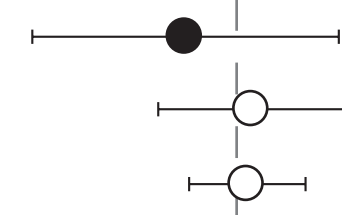
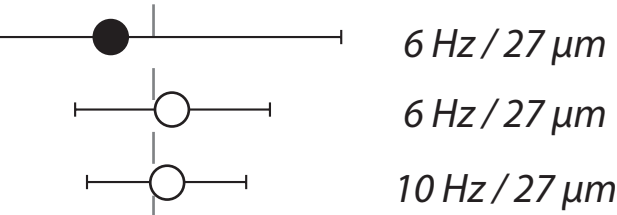
$\delta^{30}\text{Si}$  (‰) self-normalized



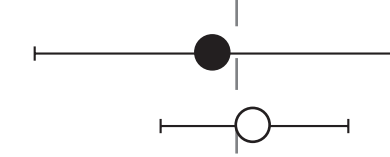
NIST 612



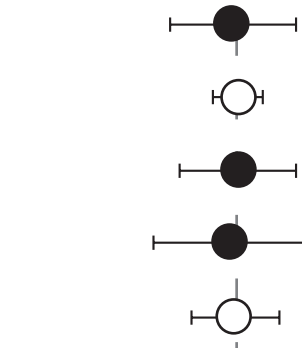
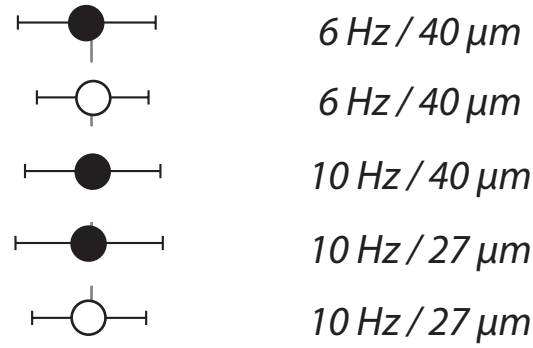
BHVO-2



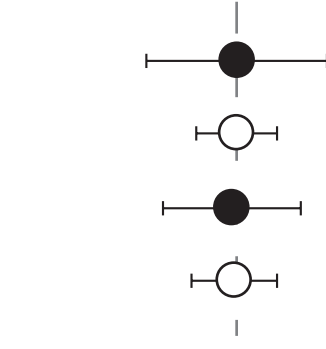
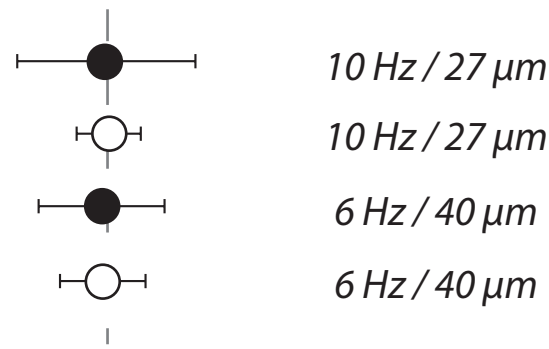
GSC-1G



San Carlos



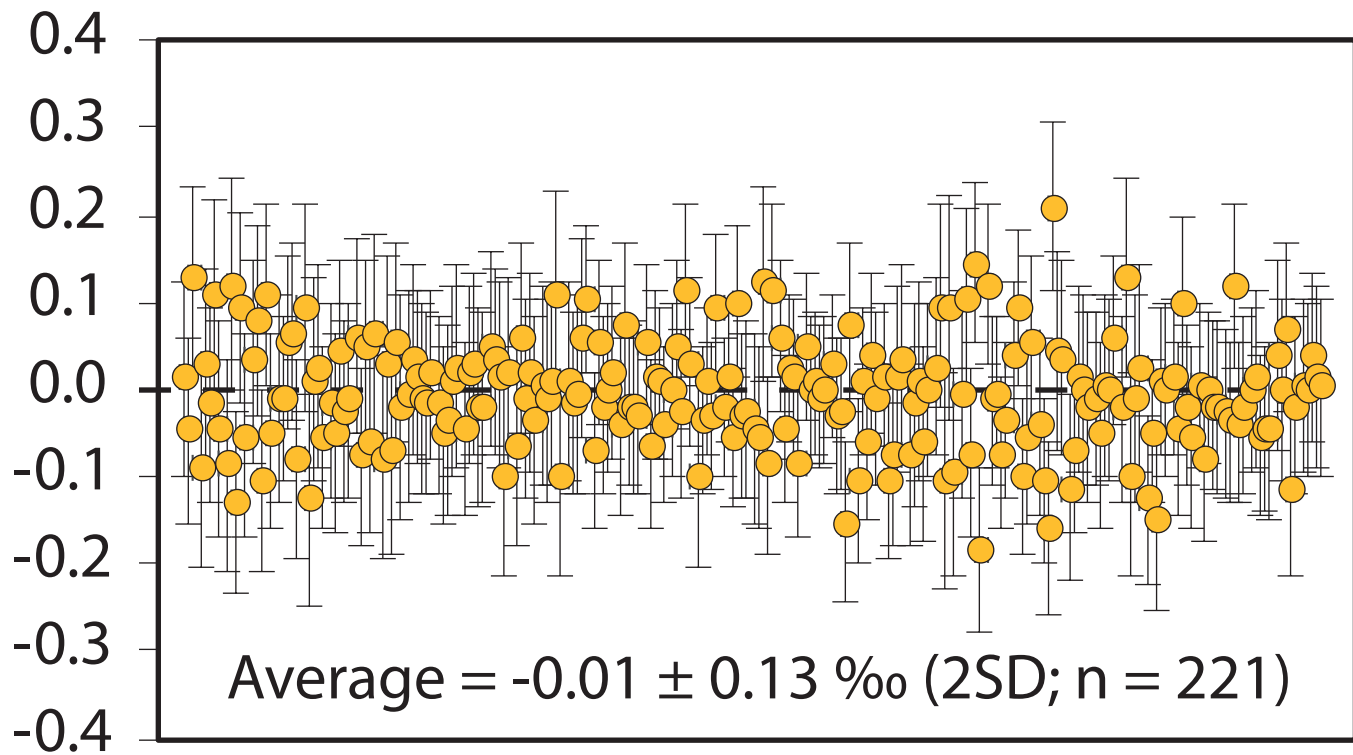
91500



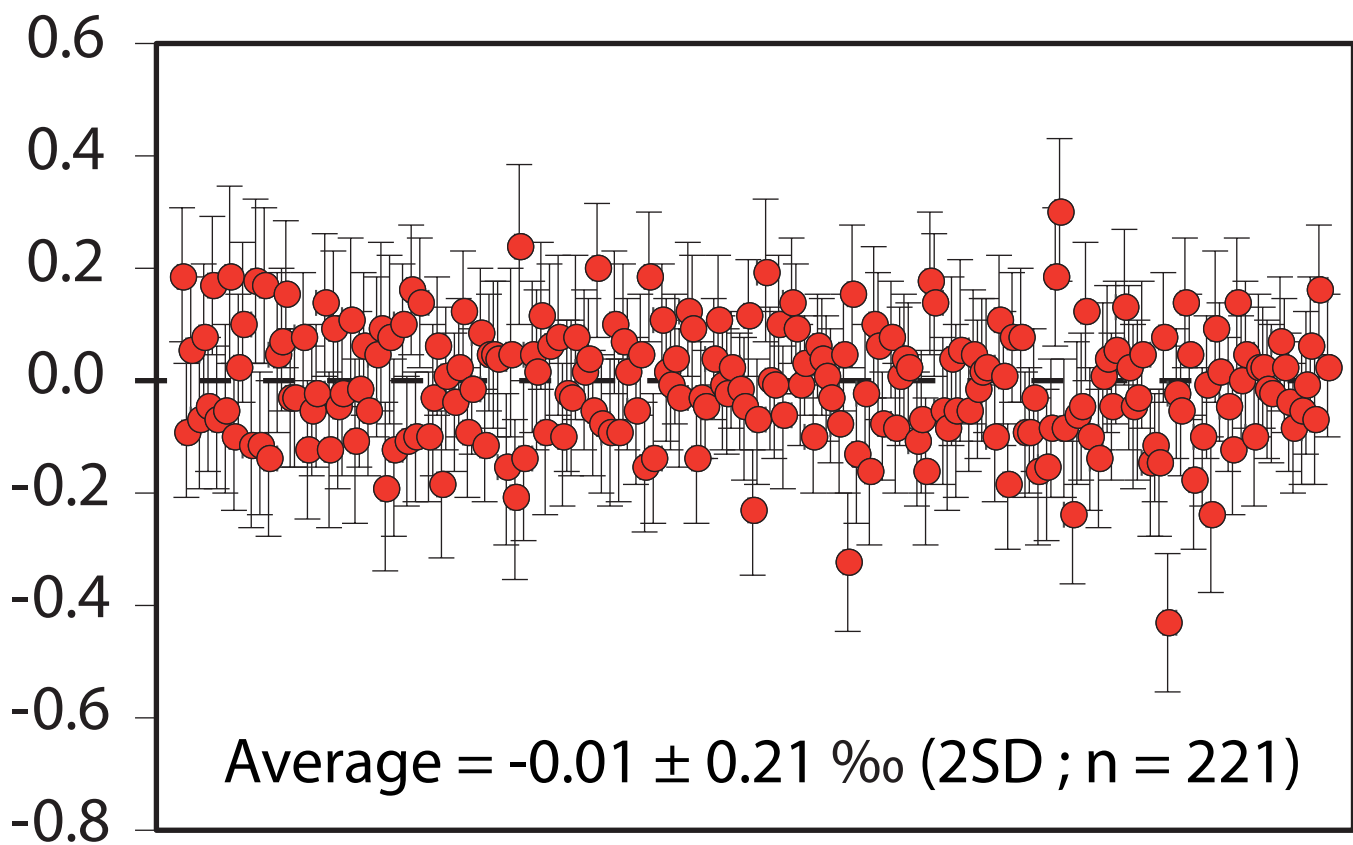
○ Line      ● Spot

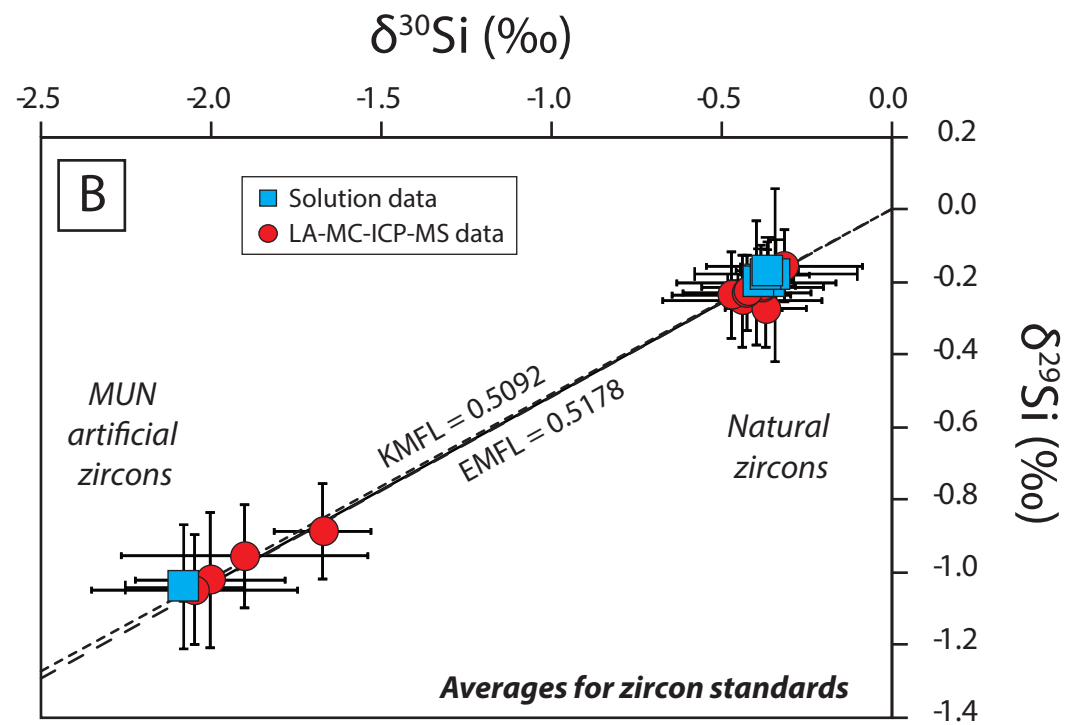
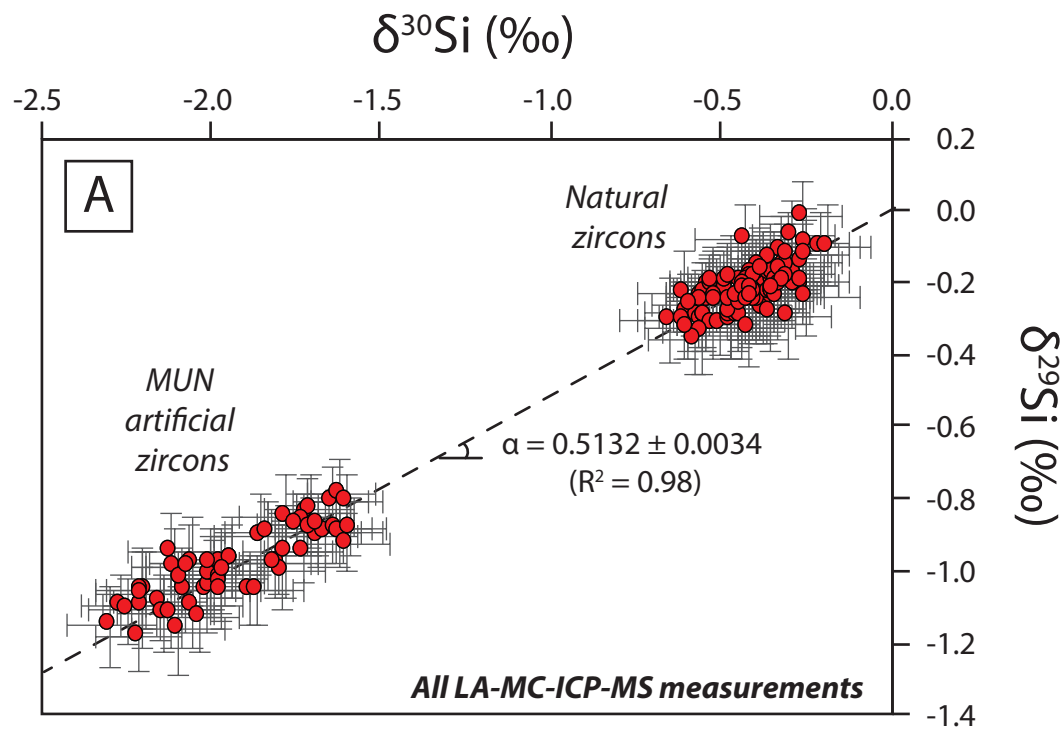
# 91500 zircon standard

$\delta^{29}\text{Si}$  (‰) self-normalized



$\delta^{30}\text{Si}$  (‰) self-normalized





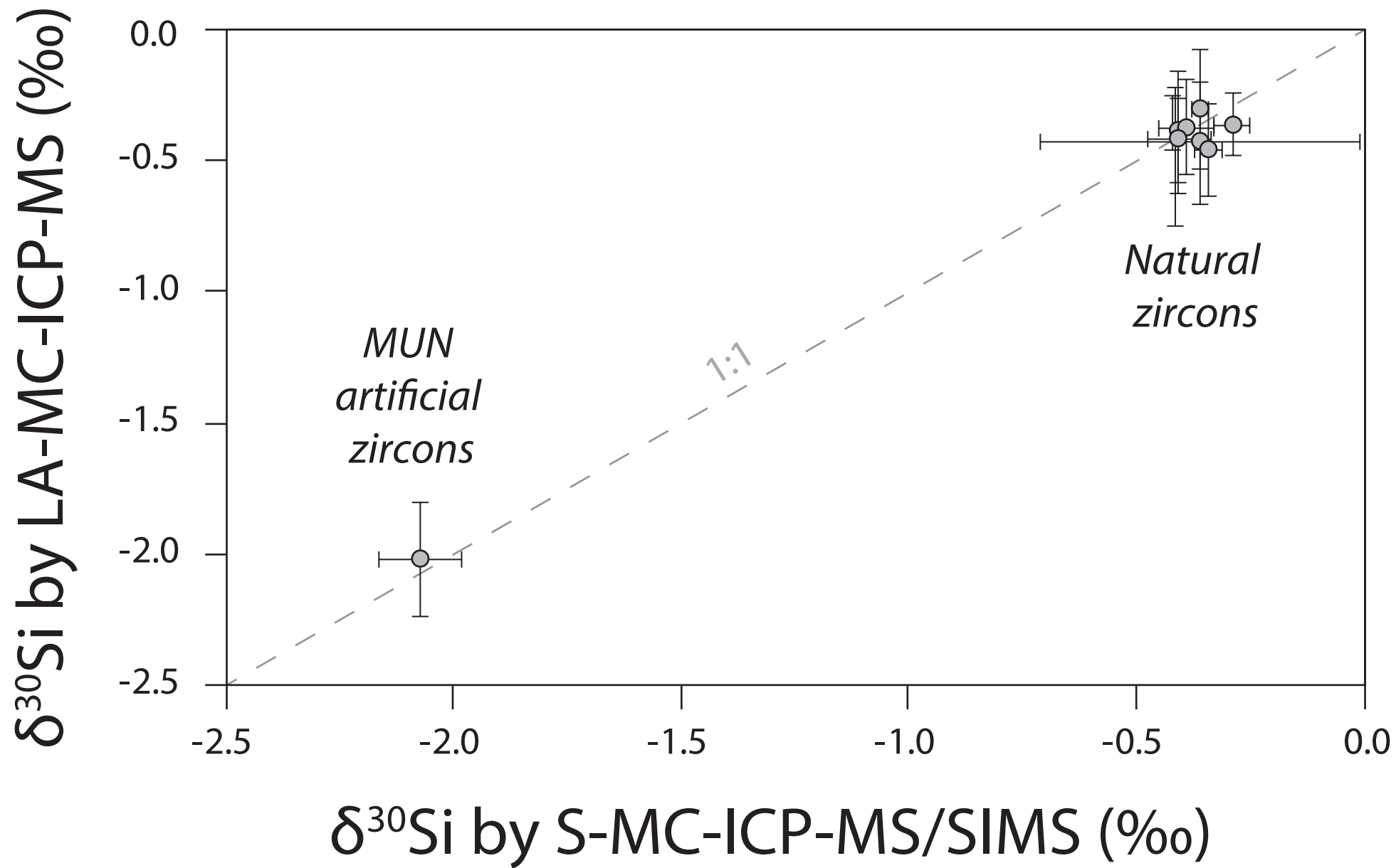


Table 1. LA-MC-ICP-MS operating conditions

<b>Analysis</b>	<i>Si isotopes</i>		
<b>Laboratory</b>	Magmas et Volcans		
Cup configuration	L3	C	H3
Mass measured	28	29	30
MC-ICP-MS model	Thermo Neptune <i>Plus</i>		
Interface type	Jet (high sensitivity)		
Cones	X-Cones		
Resistors	10 <sup>11</sup> Ohms		
Resolution	High (M/ΔM~7800)		
Forward Power	1200 W		
Auxiliary gas (Ar)	0.7-0.8 L/min		
Ar sample	0.9-1.1 L/min		
SQUID	On		
<b>Data acquisition</b>	Time resolved analysis		
Scanning mode	Static multi-collection		
Integration time per isotope	1s		
Background counting time	20-30 s		
Sample measurement time	40-60s		
Measurement type	Standard bracketing		
External standard	NIST 612, 91500		
<b>Laser model</b>	Resonetics Resolution M-50E		
Wavelength	193 nm		
Pulse duration	5 ns		
Energy	2-5 mJ		
Fluence	~3 J/cm <sup>2</sup>		
Frequency	6-10 Hz		
Spot size	27-40 μm		
Carrier gas	He		
Carrier gas flow	0.65-0.75 L/min		
Traverse rate	1.6 μm/s		



Table 2. Si isotope results for zircons analyzed by S-MC-ICP-MS

<b>Sample</b>	<b><math>\delta^{29}\text{Si}^*</math> (‰)</b>	<b>2SD</b>	<b><math>\delta^{30}\text{Si}^*</math> (‰)</b>	<b>2SD</b>	<b>n</b>
NBS 28 (NIST 8546)	0.00	0.08	0.00	0.13	236
BHVO-2	-0.14	0.09	-0.28	0.15	60
91500-MG	-0.19	0.09	-0.39	0.10	4
91500-Corfu	-0.20	0.02	-0.36	0.02	4
Plešovice-MG	-0.20	0.06	-0.39	0.06	4
Plešovice-IPGP	-0.18	0.10	-0.34	0.24	4
Plešovice-IPGP	-0.18	0.03	-0.37	0.07	4
Plešovice-IPGP	-0.17	0.09	-0.37	0.08	4
MUN-1	-1.04	0.04	-2.08	0.17	4

\* normalized to NBS 28

Table 3. External reproducibility of self-normalized standards

Name	$\delta^{29}\text{Si}$ 2SD	$\delta^{30}\text{Si}$ 2SD	Analysis	Repetition rate	Spot size	Fluence	n	
NIST 612	-0.01	0.35	-0.02	0.83 Spot	10 Hz	27 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	4
NIST 612	0.00	0.11	0.01	0.22 Line	6 Hz	27 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	9
NIST 612	0.01	0.14	0.13	0.52 Spot	6 Hz	27 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	9
NIST 612	0.04	0.11	0.11	0.20 Line	6 Hz	27 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	9
BHVO-2	-0.08	0.43	-0.19	0.57 Spot	6 Hz	27 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	4
BHVO-2	0.03	0.18	0.06	0.35 Line	6 Hz	27 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	6
BHVO-2	0.02	0.15	0.04	0.22 Line	10 Hz	27 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	8
GSC-1G	-0.08	0.19	-0.09	0.67 Spot	6 Hz	27 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	4
GSC-1G	0.00	0.20	0.07	0.35 Line	6 Hz	27 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	6
San Carlos	-0.01	0.13	-0.01	0.24 Spot	6 Hz	40 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	9
San Carlos	0.00	0.10	0.00	0.09 Line	6 Hz	40 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	9
San Carlos	-0.01	0.14	-0.02	0.29 Spot	10 Hz	27 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	9
San Carlos	-0.01	0.11	-0.01	0.17 Line	10 Hz	27 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	15
San Carlos	0.00	0.13	0.01	0.22 Spot	10 Hz	40 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	9
91500	0.00	0.17	0.00	0.34 Spot	10 Hz	27 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	9
91500	0.00	0.06	0.00	0.15 Line	10 Hz	27 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	9
91500	-0.01	0.12	-0.02	0.26 Spot	6 Hz	40 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	9
91500	-0.01	0.08	-0.01	0.16 Line	6 Hz	40 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	9
91500	-0.01	0.13	-0.01	0.21 Line	6 Hz	33 $\mu\text{m}$	$\sim 3 \text{ J.cm}^{-2}$	221

Table 4 - Summary of Si isotope measurements by LA-MC-ICP-MS of San Carlos and 91500 normalized to NIST 612

Average	Sample				Laser setup	Mode	Si <sub>S</sub> /Si <sub>NIST</sub> **	Literature				
	δ <sup>29</sup> Si(‰)*	2 SD	δ <sup>30</sup> Si(‰)*	2 SD				δ <sup>29</sup> Si(‰)***	2 SD	δ <sup>30</sup> Si(‰)***	2 SD	Reference
San Carlos	-0.74	0.20	-1.44	0.51	6 Hz 40 μm	Spot	0.5	-0.20	0.10	-0.34	0.15	Schuessler and Von Blackenburg (2014)
San Carlos	-0.85	0.11	-1.67	0.43	10 Hz 27 μm	Spot	0.6	-0.20	0.10	-0.34	0.15	Schuessler and Von Blackenburg (2014)
San Carlos	-0.60	0.08	-1.19	0.22	10 Hz 27 μm	Raster	0.9	-0.20	0.10	-0.34	0.15	Schuessler and Von Blackenburg (2014)
91500	0.19	0.17	0.37	0.21	6 Hz 40 μm	Spot	0.6	-0.20	0.02	-0.36	0.02	<i>This study</i>
91500	0.00	0.31	-0.12	0.48	10 Hz 27 μm	Spot	0.7	-0.20	0.02	-0.36	0.02	<i>This study</i>

\* Delta values are relative to NBS 28 but normalized to NIST 612 that was analyzed in the same conditions except for the rasters for which NIST 612 was analyzed using 6 Hz and 27 μm.

\*\* S refers to sample (San Carlos or 91500) and NIST to NIST 612.

\*\*\* Delta values are relative to NBS 28

Table 5. Si isotope results for zircons analyzed by LA-MC-ICP-MS

Technique	Sample	$\delta^{29}\text{Si}^*$ (‰)				$\delta^{30}\text{Si}^*$ (‰)				<i>Data from other techniques</i>		
		2SD				2SD	n	Technique	$\delta^{30}\text{Si}^*$ (‰)	2SD	Reference	
LA-MC-ICP-MS	91500-MG	-0.15	0.10	-0.32	0.23	5	S-MC-ICP-MS	-0.39	0.10	<i>This study</i>		
LA-MC-ICP-MS	AS3	-0.25	0.13	-0.44	0.23	28	SIMS	-0.36	0.35	Trail et al. (2018)		
LA-MC-ICP-MS	KIM	-0.20	0.17	-0.40	0.23	16	S-MC-ICP-MS	-0.41	0.01	Trail et al. (2018)		
LA-MC-ICP-MS	Kuehl Lake	-0.25	0.11	-0.38	0.12	3	S-MC-ICP-MS	-0.29	0.04	Trail et al. (2018)		
LA-MC-ICP-MS	MudTank	-0.23	0.12	-0.47	0.17	13	S-MC-ICP-MS	-0.34	0.03	Trail et al. (2018)		
LA-MC-ICP-MS	MUN-0	-0.88	0.13	-1.67	0.14	14	-	-	-	-		
LA-MC-ICP-MS	MUN-1	-1.02	0.19	-2.00	0.22	8	S-MC-ICP-MS	-2.08	0.17	<i>This study</i>		
LA-MC-ICP-MS	MUN-3	-0.95	0.14	-1.90	0.36	10	-	-	-	-		
LA-MC-ICP-MS	MUN-4	-1.05	0.15	-2.05	0.30	25	-	-	-	-		
LA-MC-ICP-MS	Peixe	-0.23	0.10	-0.43	0.19	11	-	-	-	-		
LA-MC-ICP-MS	Plešovice-MG	-0.21	0.07	-0.38	0.18	11	S-MC-ICP-MS	-0.39	0.06	<i>This study</i>		
LA-MC-ICP-MS	QGNG	-0.21	0.05	-0.38	0.10	7	-	-	-	-		
LA-MC-ICP-MS	R33	-0.22	0.04	-0.42	0.08	8	-	-	-	-		

\* relative to NBS 28