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1 Silicon isotope analyses of soil and plant reference materials: an inter-comparison of seven
2 laboratories

3

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27

28 **Keywords**

29 silicon isotopes, reference materials, soil, plant, inter-comparison of measurements

30

31 **Mots clés**

32 Isotopes du silicium, matériaux de référence, sol, plante, intercomparaison de mesures

33

34 **Main message**

35 This inter-laboratory comparison exercise establishes the $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ values for four new

36 soil reference materials and one plant reference material, for future use as secondary Si

37 isotope reference materials.

38 **Abstract**

39 The use of silicon (Si) isotopes has led to major advances in our understanding of the Si
40 cycling in modern and past environments. This inter-laboratory comparison exercise
41 provides the community with the first set of soil and plant reference materials with an
42 analytically challenging matrix containing organic material, known to induce isotopic bias, for
43 use as secondary reference materials in Si isotope analysis. Seven laboratories analysed four
44 soil reference materials (GBW-07401, GBW-07404, GBW-07407, TILL-1) and one plant
45 reference material (ERM-CD281). Participating laboratories employed a range of chemical
46 preparation methods and analytical setups but all analyses were performed by MC-ICP-MS.
47 Irrespective of the chemical preparation method or analytical conditions, the results show
48 excellent agreement among laboratories within their respective external reproducibilities
49 (2SD). Data were combined together to calculate $\delta^{29}\text{Si}$ and $\delta^{30}\text{Si}$ average values (relative to
50 NBS 28) and their uncertainties (U , expanded uncertainty; $k = 2$, coverage factor). The $\delta^{30}\text{Si}$
51 values are as follow: GBW-07401: -0.27 ± 0.06 ‰, GBW-07404: -0.76 ± 0.12 ‰, GBW-07407:
52 -1.82 ± 0.17 ‰, TILL-1: -0.16 ± 0.06 ‰ and for ERM-CD281: -0.28 ± 0.11 ‰. Also, a
53 compilation of published data provides an up-to-date average $\delta^{30}\text{Si}$ for BHVO-2 of $-0.28 \pm$
54 0.08 ‰.

55

56

57 **1. Introduction**

58

59 Silicon (Si), the second most abundant element in the Earth's crust, is a ubiquitous rock-
60 forming element and is considered as a key component of global biogeochemical cycles, due
61 to links with carbon cycling and other nutrient systems. Chemical weathering of silicate
62 minerals controls atmospheric CO₂ concentration and thus regulates climate over geological
63 timescales (e.g., Berner et al., 1983). Silicate weathering also releases dissolved Si into the
64 hydrosphere, and thereby ultimately controls the biological pump, because Si is an essential
65 nutrient in marine and freshwater ecosystems (Nelson et al., 1995; Ragueneau et al., 2006).
66 Although the oceanic Si cycle has been a key research focus for decades, the terrestrial Si
67 cycle has since attracted more scientific attention after the important and complex role of
68 vegetation was recognized (Conley 2002; Street-Perrott and Barker, 2008; Struyf and Conley,
69 2012). Processes occurring at the land-ocean interface and anthropogenic impacts are now
70 actively studied using Si isotopic variations or "fingerprints" (Engström et al., 2010; Hughes
71 et al., 2011, 2013; Mangalaa et al., 2017; Vandevenne et al., 2015).

72 Silicon has three stable isotopes: ²⁸Si, ²⁹Si, ³⁰Si with average relative isotope abundances of
73 92.23%, 4.67% and 3.10%, respectively (Barnes et al., 1975; De Bièvre and Taylor, 1993).

74 Pioneering Si isotope investigations in natural systems showed the potential to provide
75 better understanding of the biogeochemical cycle of Si in both modern and past
76 environments (see Basile, 2006, for an early review). However, studies remained limited
77 because of sometimes hazardous, but often delicate and time-consuming analytical
78 methods. The advent of MC-ICP-MS instruments, combined with improved sample
79 preparation techniques (e.g., Georg et al., 2006), have subsequently allowed Si isotope

80 measurements to flourish and led to great advances in our understanding of the global Si
81 cycle (see Poitrasson, 2017, for a more recent review).

82 For analyses, external matrix-matched reference materials are required to allow inter-
83 laboratory comparisons and to check for data quality for everyday analytical work –
84 particularly in systems where standard-sample bracketing is the traditional way to measure
85 isotope ratios. To date, only three inter-laboratory comparisons have been published for Si
86 isotopes (Reynolds et al., 2007; Hendry et al., 2011; Grasse et al., 2017). The first one
87 focused on three pure SiO₂ materials: Diatomite ($\delta^{30}\text{Si} = +1.26 \pm 0.20 \text{ ‰}$; from hereon, all
88 reproducibilities will be given as 2 standard deviations unless otherwise stated), IRMM-018
89 ($\delta^{30}\text{Si} = -1.65 \pm 0.22 \text{ ‰}$) and Big Batch ($\delta^{30}\text{Si} = -10.48 \pm 0.54 \text{ ‰}$; Reynolds et al., 2007). The
90 Diatomite reference material is still commonly included in analytical sequences to check for
91 accuracy and precision; however, the last two are less frequently utilised because they are
92 either highly fractionated (Big Batch) or potentially inhomogeneous (IRMM-018; Reynolds et
93 al., 2007). For a better matching between $\delta^{30}\text{Si}$ values of external standards and samples,
94 and to account for any microstructural effect, a second inter-laboratory comparison
95 reported on a Southern Ocean sponge material as an additional reference material for
96 sponge spicule analyses (Hendry et al., 2011). A third inter-calibration study was motivated
97 by the need to reliably compare the increasing number of Si isotope datasets of natural
98 waters. External standards such as Diatomite (which is provided as a powdered, near-pure
99 SiO₂ sample) cannot account for any biases introduced by the specific sample preparation
100 and matrices involved when dealing with natural waters. These samples may contain Si with
101 concentration below 20 $\mu\text{mol l}^{-1}$, which may require pre-concentrations steps or the
102 processing of large amounts of sample, with potentially high salinity. With this in mind,
103 Grasse et al. (2017) characterised two seawater samples (ALOHA 300, $[\text{Si}] = 9 \mu\text{mol l}^{-1}$, $\delta^{30}\text{Si} =$

104 $+1.66 \pm 0.13 \text{ ‰}$; ALOHA 1000, $[\text{Si}] = 113 \text{ } \mu\text{mol l}^{-1}$, $\delta^{30}\text{Si} = +1.25 \pm 0.06 \text{ ‰}$);). The analyses of
105 these “ALOHA” standards is now recommended when laboratories are reporting on
106 seawater Si isotope data. In addition to this collection of reference materials, there are more
107 than a dozen silicate rock reference materials that have enough extant published data to be
108 suitable as external standards for silicate rock analyses (e.g., Abraham et al., 2008; Hughes et
109 al., 2011; Zambardi and Poitrasson, 2011; Savage et al., 2014). Among these reference
110 materials, the Hawaiian basalt BHVO-2 (provided by the USGS) is the most commonly
111 analysed. A valuable compilation of $\delta^{30}\text{Si}$ values suggest that the reference value for BHVO-2
112 is $\delta^{30}\text{Si} = -0.28 \pm 0.03 \text{ ‰}$ (Savage et al., 2014) and more data are added continuously (see the
113 GeoReM database).

114 Among the possible matrix effects on Si isotope measurements, the presence of anions such
115 as sulfate (Van den Boorn et al., 2009) or dissolved organic carbon (DOC) (Hughes et al.,
116 2011) has been reported to produce mass bias changes during MC-ICP-MS analysis. The issue
117 remain debated as matrix effects induced by sulfate on Si isotopes were not subsequently
118 confirmed (Georg et al., 2006 ; Zambardi and Poitrasson, 2011; de Souza et al., 2012) and
119 could potentially depend on plasma conditions of the MC-ICP-MS (Fietzke and Frische, 2015;
120 Yu et al., 2020). A recent study provides constraints on matrix anion threshold
121 concentrations and the extent of resulting biases, but the role of instrument type and
122 different sample introduction systems (wet and dry plasma) has not been fully addressed
123 (Oelze et al., 2016). However, as far as we are aware, there are no Si isotope data for
124 reference materials with an organic-rich matrix. Because such a matrix is prone to induce
125 $\delta^{30}\text{Si}$ bias during MC-ICP-MS analysis, a lack of suitable reference materials is an issue of
126 major importance for the analysis of soil or plant material.

127 The aim of this paper is to provide the community with a set of easily available, well-
128 characterized reference materials containing organic material as part of the matrix for use as
129 secondary reference materials in Si isotope analysis. We propose four soil reference
130 materials (i.e., GBW-07401, GBW-07404, GBW-07407, TILL-1), representative of solid
131 samples with a complex matrix with various Si-bearing phases (i.e., amorphous and/or
132 crystalline silicate minerals, refractory minerals like iron oxy-hydroxides) and organic matter.
133 In addition, the plant reference material ERM-CD281 (rye grass) was selected to represent
134 the chemical composition of vegetation. It contains both organic matter and amorphous
135 silica, which represents the form of Si generally accumulated in grass and then soils upon
136 plant decay. This approach is an essential step in supporting $\delta^{30}\text{Si}$ data comparison among
137 and within laboratories over time.

138

139 **2. Materials and methods**

140

141 **2.1 Investigated materials**

142

143 This study investigates four soil reference materials GBW-07401, GBW-07404, GBW-07407,
144 TILL-1 and one plant reference material ERM-CD281. The GBW soils “set”, developed by the
145 Institute of Geophysical and Geochemical Exploration (IGGE) of the Chinese Academy of
146 Geological Sciences (CAGS) is not commercially available anymore. Because of this, an
147 aliquot (~g) of the batches analysed in this study can be obtained upon request to Isabelle
148 Basile-Doelsch at CEREGE. Reference material TILL-1 is provided by the CCRMP (Canadian
149 Certified Reference Materials Project) and ERM-CD281 is provided by the EC-JRC (European
150 Commission – Joint Research Center), and both are readily available to the community.

151 The reference material GBW-07401 is described as a dark brown podzolic soil collected in a
152 lead-zinc ore area, Heilongjiang, China; GBW-07404, as a limy-red soil obtained from
153 Guangxi, China, and; GBW-07407, as a lateritic soil developed on basalt collected from
154 Leizhou Peninsula, Guangdong, China (Wang et al., 2013). The reference material TILL-1
155 combines horizons B and C of a soil collected 25 km North-West of Lanark, Ontario, Canada
156 (Lynch 1996). Among those soil reference materials, SiO₂ content ranges from 32.67 to 62.60
157 % *m/m*, organic carbon (C_{org}) content varies from 0.62 to 1.80 % *m/m* and sulfur content
158 varies from 5 to 310 µg g⁻¹ (more details in Table 1). The plant reference material ERM-
159 CD281 is a rye grass, harvested in the United Kingdom in 1983, containing 0.13 % *m/m* Si
160 (C_{org} unknown) and 34 µg g⁻¹ S (Table 1).

161

162 2.2 Sample preparation and silicon isotope measurements

163

164 The reference materials were analysed for their δ²⁹Si and δ³⁰Si values in seven laboratories:
165 University of Bristol Isotope Group, United Kingdom (BIG); Centre Européen de Recherche et
166 d'Enseignement en Géosciences de l'Environnement, France (CEREGE); Géosciences
167 Environnement Toulouse, France (GET); German Research Centre for Geosciences, Germany
168 (GFZ); Institut Français de Recherche pour l'Exploitation de la Mer, France (IFREMER); St
169 Andrews Isotope Geochemistry, University of St Andrews, United Kingdom (STAiG); and
170 Water Quality Centre – Trent University, Canada (WQC). The reference materials, provided
171 as homogeneous powders by suppliers, were split and spread among the different
172 laboratories via mail. Laboratories each received an aliquot of about 1 g of GBW soil
173 reference materials, 0.2 g of TILL-1 and 3 g of ERM-CD281. Each laboratory conducted
174 sample preparation and Si isotope measurements using their own protocols as detailed in

175 Table 2. Sample preparation protocols of all laboratories are adapted from Georg et al.
176 (2006) and hence are similar and consist of an alkaline fusion step followed by purification
177 on a cation exchange resin. In the following, we highlight the differences between the
178 sample preparation and measurement protocols. More details on the procedures used in
179 each participating laboratory are given in previous publications or in Supplementary
180 Materials. For BIG see Hatton et al., (2019); for CEREGE see Supplementary Materials; for
181 GET see Zambardi and Poitrasson (2011); for GFZ see Schuessler and von Blanckenburg
182 (2014) and Oelze et al. (2016); for IFREMER see Bayon et al., (2018); for STAiG see Savage
183 and Moynier (2013); for WQC see Georg et al. (2006).

184 One major difference between protocols relates to the use of calcination to
185 mineralize organic matter. CEREGE, GET and WQC calcinated the samples before fusion
186 while BIG, GFZ and IFREMER did not; STAiG processed replicates both with and without
187 calcination (see Supplementary Materials for detailed calcination procedures). All
188 laboratories performed NaOH fusion in silver crucibles except for IFREMER who used NaOH
189 and Na₂O₂ in glassy carbon crucibles (Bayon et al., 2018). Finally, in order to purify the
190 samples, all laboratories used column chromatography with cation exchange resin (either
191 AG50W-X12 or AG50W-X8, see Table 2) based on the procedure developed by Georg et al.
192 (2006). After alkali fusion, samples are normally taken up in a weakly acidic solution; many
193 laboratories perform a measurement of solution Si concentration here (prior to Si
194 purification), firstly to check for quantitative yield from the fusion step, and also to calculate
195 the required amount of solution for column chemistry.

196 After column chemistry, the purified Si solutions were analysed by ICP-OES, (MC-)ICP-
197 MS or by spectrophotometer using the molybdenum blue colorimetric method to i) verify
198 quantitative Si column recovery (i.e., complete recovery within analytical reproducibilities of

199 the concentration measurements of $100 \pm 5\%$) and ii) check the purity of the Si sample
200 solutions, with a particular focus on confirming the lack of magnesium (Mg) within the
201 sample in the laboratories using Mg doping. Purity was better than 95% for Si, except for the
202 plant ERM CD-281, where elevated levels of phosphorous and sulfur (mass ratios PO_4/Si up
203 to 5 and SO_4/Si up to 6), respectively were still present. Complete removal of these anions
204 was achieved neither by high temperature volatilisation during NaOH fusion at 750°C for 10
205 minutes (without prior calcination; GFZ) or calcination (CEREGE, no SO_4 data), nor by the Si
206 column chemistry. However, as discussed below, all impurities were still within the tolerance
207 limits found to not cause any bias in Si isotope measurements using the MC-ICP-MS setup
208 (instrument, sample introduction system, analyte matrix, Mg doping,...) used by the
209 participating laboratories in this study.

210 Silicon isotope measurements were performed by MC-ICP-MS, either Neptune Plus
211 MC-ICP-MS or Neptune MC-ICP-MS (both from Thermo Fisher Scientific, Germany) (Table 2).
212 The analyses were performed in medium resolution ($m/\Delta m \sim 4500$, 5 and 95% peak side
213 definition, see Weyer and Schwieters, 2003; except for GET which utilised high resolution
214 ($m/\Delta m \sim 7-10000$)) using between $0.5 - 3.6 \mu\text{g}$ Si per analysis, which resulted in a 3 -20 V ion
215 beam on ^{28}Si . Four laboratories carried out analyses in 'wet plasma mode', three in 'semi-dry
216 plasma mode' using a desolvating nebulizer system (ESI Apex-HF, ESI Apex Q). The main
217 advantage of a desolvation unit is to reduce polyatomic interferences from oxygen, nitrogen,
218 carbon and hydrogen and to improve sensitivity. However, use of a desolvation unit
219 increases matrix effects and results in a less stable signal. Subtraction of the blank signal
220 (measured on the pure acid matrix solution) from all sample Si intensities was performed
221 before subsequent data processing by all laboratories (BIG, GFZ, CEREGE, GET, STAiG). For all

222 laboratories, full procedural blank Si intensities did not exceed 1% of the sample Si signal
223 (Table 2).

224 All measurements were performed using the standard-sample-bracketing technique
225 using NBS 28 (also named NIST SRM 8546) as the bracketing standard, except for IFREMER
226 where an in-house standard previously calibrated against the NBS 28 was used. With the
227 exception of STAiG and WQC laboratories, the purified Si solutions were also doped with Mg
228 (Si:Mg ratio of 1 to 3, depending on the laboratories; Table 2) prior to mass spectrometric
229 analysis for an additional online mass bias drift correction using an exponential mass bias
230 equation (Cardinal et al., 2003; Engström et al., 2006; Zambardi and Poitrasson, 2011; Oelze
231 et al., 2016), (Table 2). When Mg-doping was utilised, Mg isotopes were analysed along Si
232 isotopes using dynamic mode (magnet jump alternating between Si and Mg isotopes) for
233 each sample doped with Mg. Magnesium doping is also useful to eliminate variations due to
234 sample matrix effects or insufficiently stable laboratory temperature (Cardinal et al., 2003;
235 Engström et al., 2006; Zambardi and Poitrasson, 2011; Oelze et al., 2016). Additionally, BIG
236 samples were doped with 50 µl 0.01 mol l⁻¹ sulfuric acid per ml of sample to reduce anionic
237 matrix effects. Silicon isotope compositions are reported relative to the NBS 28 in the delta
238 notation as $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$:

$$239 \quad \delta^{30, 29}\text{Si} (\text{‰}) = (R_{\text{sample}}/R_{\text{NBS 28}}) - 1$$

240 where R is the ratio $^{30}\text{Si}/^{28}\text{Si}$ or $^{29}\text{Si}/^{28}\text{Si}$ in a sample, and $R_{\text{NBS 28}}$ the mean value for reference
241 material NBS 28 calculated using the mean of the measured Si isotope ratio immediately
242 measured before and after the unknown sample (i.e., standard-sample bracketing).

243 The well-characterized Diatomite and/or BHVO-2 reference materials, for which large
244 datasets are available in the literature, were measured routinely for quality control as
245 unknown samples during the runs by all laboratories to check for accuracy and precision.

246 These data are provided in Table 2, and are well in agreement with the published values
247 compiled in Table S1 (i.e., mean $\delta^{30}\text{Si} = -0.28 \pm 0.08 \text{‰}$ ($U, k = 2, N = 61$ where N is the
248 number of data published)).

249 At least three aliquots of each reference material used in this study were processed
250 through the whole sample preparation, hereafter referred to as full procedure replicates,
251 except for GET ($N=1$), WQC ($N=1$) and the additional uncalcinated aliquot of GBW-07401 and
252 GBW-07407 processed by STAiG. Each full procedure replicate was then analysed between 3
253 and 14 times either on different days or on the same day but not consecutively depending
254 on laboratories (see Table 2 for details). Each mass-spectrometric analysis comprises
255 between 20 to 36 signal integrations of 4 to 8.4 s, which is a total 80 to 210 s of Si signal
256 acquisition per analysis. For each laboratory, replicate measurements carried out for each
257 reference material full procedure replicate were averaged using the arithmetic mean and its
258 associated 2 standard deviation (2SD; data are reported in Table S2).

259

260 3. Results and discussion

261

262 3.1. Data quality of participating laboratories

263

264 An essential measurement control is given by the three-isotope plot (Fig. 1). All data (from
265 the reference materials full procedural replicates reported by each laboratory) fall on a
266 straight line with a slope of about $\delta^{29}\text{Si} \sim 0.5103 \times \delta^{30}\text{Si}$ ($r^2 > 99 \%$). The linear correlation
267 encompasses the theoretical slopes calculated for both equilibrium (0.5178) and kinetic
268 (0.5092) mass-dependent fractionation processes (Engström et al., 2008), suggesting no
269 major influence of isobaric interferences or matrix effects. In addition, the $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$

270 values of the Diatomite and BHVO-2 reference materials measured by all laboratories agree
271 well with compiled values (Reynolds et al., 2007; Savage et al., 2014; our compilation in
272 Table S1). The absolute differences between published values and those produced by
273 participating laboratories are smaller than 0.06 ‰ and 0.03 ‰ for $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$,
274 respectively, which are within the 2SD reported by each laboratory (Table 2).
275 WQC reported $\delta^{30}\text{Si}$ calculated from measured $\delta^{29}\text{Si}$ assuming an equilibrium mass-
276 dependent fractionation. Comparing WQC $\delta^{30}\text{Si}$ results with values reported by other
277 laboratories (Fig 2.) shows no notable difference between their calculated $\delta^{30}\text{Si}$ and other
278 laboratories measured $\delta^{30}\text{Si}$, within their respective 2SD. This approach is therefore valid for
279 the set of reference materials analysed in this study. However, this approach should be used
280 with caution since it does not allow a data quality check for mass-dependent fractionation
281 using the three-isotope plot (Fig 1.).

282

283 3.2. Individual results of soil reference materials

284

285 The $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ values obtained for each reference material (representing full procedural
286 replicates) by participating laboratories are illustrated in Fig. 2 and provided in Table S2. The
287 Si isotope composition of the five reference materials reported are indistinguishable within
288 their 2SD, both between the full procedural replicates for a given laboratory, and also
289 between laboratories. The $\delta^{30}\text{Si}$ data range between $-0.30\text{‰} < \delta^{30}\text{Si} < -0.20\text{‰}$ for GBW-
290 07401; $-0.90\text{‰} < \delta^{30}\text{Si} < -0.67\text{‰}$ for GBW-07404; $-2.05\text{‰} < \delta^{30}\text{Si} < -1.71\text{‰}$ for GBW-
291 07407; $-0.21\text{‰} < \delta^{30}\text{Si} < -0.12\text{‰}$ for TILL-1. This range of $\delta^{30}\text{Si}$ values spans the typical $\delta^{30}\text{Si}$
292 spectrum of soil materials ranging from -2.7‰ to $+0.1\text{‰}$ (Poitrasson, 2017). The most
293 negative Si isotope compositions are measured in the reference materials with the lowest

294 SiO₂/Al₂O₃ mass ratio (GBW-07407), i.e., the soil which has undergone the most desilification
295 (Fig. 3). This is consistent with the general weathering trend, wherein the Si isotopic
296 composition of secondary clay minerals formed during chemical weathering is lower than
297 that of the primary silicate material (e.g., Opfergelt et al., 2010; Georg et al., 2009; Savage et
298 al., 2013). Furthermore, the formation of more desilicified 1:1 clays is accompanied by a
299 larger (negative) Si isotopic fractionation than the formation 2:1 clays (Georg et al., 2009;
300 Opfergelt et al., 2012).

301

302 3.3. Individual results of the plant reference material ERM-CD281

303 Of the laboratories involved in this study, two did not analyse the ERM-CD281 rye grass
304 reference material because they had not previously processed highly organic-rich material
305 (i.e., plant matter) and methodological development was beyond the scope of this study.
306 The $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ obtained for the plant reference material full procedure replicates by
307 each laboratory are illustrated in Fig. 2 and provided in Table S2. The Si isotope compositions
308 reported are indistinguishable within the 2SD both between the full procedural replicates for
309 a given laboratory and between laboratories. The $\delta^{30}\text{Si}$ data range between $-0.36\text{‰} < \delta^{30}\text{Si} <$
310 -0.26‰ . In addition to the data acquired during this study, another published result for
311 ERM-CD281 is available ($\delta^{30}\text{Si} = -0.28 \pm 0.08\text{‰}$, 2SD, $n = 3$; Frick et al. 2020). These published
312 analyses were performed at GFZ using the same protocol in the same laboratory as reported
313 for GFZ in this study. The Si isotope values for ERM-CD281 fall within the large range of $\delta^{30}\text{Si}$
314 values reported in the literature for biogenic silica in plants (-2.3 to $+6.1\text{‰}$; Opfergelt and
315 Delmelle, 2012). The range of Si isotope compositions is large because the $\delta^{30}\text{Si}$ values of
316 biogenic silica in plants depend on several factors such as soil parent material lithology, soil

317 weathering degree and on complex isotope fractionation processes during Si uptake and
318 deposition (Opfergelt et al., 2010).

319

320 3.4. Influence of sulfur and DOC contents

321

322 The importance of chemical purification in removing so-called matrix effects has already
323 been described for several isotopes systems measured by MC-ICP-MS (see for example Galy
324 et al., 2001, for Mg isotopes). For Si isotopes, significant effects induced by the presence of
325 sulfur in rock samples were first reported by Van den Boorn et al. (2009), i.e., a Si isotope
326 bias of up to 1.4 ‰ for a SO_4/Si mass ratio higher than 0.02. Subsequent studies have
327 discussed the possibility of sulfur-induced bias on Si isotope measurements (Hughes et al.,
328 2011; Zambardi and Poitrasson, 2011; Chemtob et al., 2015), and highlighted the potential
329 for several parameters to influence the magnitude of the bias, notably in the dry plasma
330 mode (Oelze et al., 2016). Thus, care must be taken when comparing studies and drawing
331 conclusions is not that straightforward. In particular, comparing sulfur-induced bias between
332 S-doped solutions and S-rich rocks is likely irrelevant. However, in this study, sulfur-induced
333 matrix effects are less likely to be significant, because the 720°C fusion step of solid samples
334 used by all laboratories will at least partially remove the sulfur, with full removal achieved by
335 heating at 1350°C (Van den Boorn et al., 2009). Despite different analytical settings, this can
336 partly explain the large decrease from +1.4 to +0.3 ‰ (SO_4/Si mass ratio ~ 0.3) between Van
337 den Boorn et al. (2009) and Hughes et al. (2011) datasets as well as the absence of Si isotope
338 bias measured on rock samples with SO_4/Si mass ratios ≤ 0.14 by Zambardi and Poitrasson
339 (2011). To allow comparison between studies, it would be useful to provide SO_4/Si ratios of
340 the Si analyte solutions in addition to the usual initial sample SO_4/Si ratios before processing.

341 Restricting comparison to S-doped pure Si solutions (usually doped NBS 28), it appears that
342 several parameters may reduce the isotopic bias. Van den Boorn et al. (2009) noticed that
343 HCl 0.1 mol l⁻¹ matrix reduces the bias by a factor about 1.5 compared to a HNO₃ matrix.
344 Also, Chemtob et al. (2015) noticed no significant bias due to sulfur for SO₄/Si mass ratios <1
345 with a 0.002% HF and 2% HNO₃ matrix despite very similar analytical parameters (i.e., the
346 use of a Neptune, a CETAC desolvator and no Mg doping). It appears that the overall sample
347 aliquot matrix plays a role in the magnitude of the S-induced bias in addition to subtle
348 differences in instrumental set-up. Similarly, Georg et al. (2006) noticed no deviation from
349 expected values for SO₄/Si mass ratio up to 48 using a Nu instrument, a CETAC desolvator in
350 a 0.1 mol l⁻¹ HCl matrix without Mg doping. Similarly, Zambardi and Poitrasson (2011) and
351 Oelze et al (2016) investigated the effect with Mg doping. For SO₄/Si ratios < 1, the Mg
352 doping had no effect on the magnitude of the S-induced bias (Zambardi and Poitrasson,
353 2011; Oelze et al., 2016). Moreover, Oelze et al (2016) found that the addition of Mg to the
354 Si analyte solution resulted in higher tolerance to impurities during MC-ICP-MS analyses
355 when an Apex desolvator without a membrane was used. Remaining anionic impurities (PO₄
356 ³⁻, SO₄²⁻, and NO₃⁻) had no effect on the Si isotope mass bias (with accuracy within ± 0.14
357 ‰) if the mass ratio of those anions to Si is lower than 6 (Oelze et al., 2016). To overcome S-
358 induced bias, different techniques were suggested: removal of sulfur by heating the samples
359 up to 1350°C (Van den Boorn et al., 2009) or doping both samples and bracketing standard
360 with significant amounts of sulfuric acid to overwhelm any variation in the sample (Hughes
361 et al., 2011).

362 In this study, no S-induced bias on Si isotopes measurements is expected for soil reference
363 materials as SO₄/Si mass ratios are below 0.01 (SO₄/Si mass ratio ~0.003 for GBW-07401;
364 0.002 for GBW-07404; 0.005 for GBW-07407 and 0.002 for TILL-1). In contrast, the plant

365 reference material ERM-CD281 has a SO_4/Si mass ratio about 7.8 that could potentially be
366 problematic for Si isotopes measurements. This was verified in Si analyte solutions where
367 elevated levels of phosphorous and sulfur (mass ratios PO_4/Si up to 5 and SO_4/Si up to 6),
368 respectively, were still present after NaOH fusion (with or without prior calcination) and Si
369 column purification. Complete removal of these anions was achieved neither by high
370 temperature volatilisation nor by the Si column chemistry. However, all impurities were still
371 within the limits required to avoid any bias for all different analytical configurations used by
372 different laboratories (prior calcination or not, wet plasma or Apex desolvation, Mg doping
373 or no Mg doping, HCl or HNO_3 matrix). This is consistent with the study of Oelze et al., (2016)
374 where no effect on the Si isotope mass bias is observed if the mass ratio of anions to Si is
375 lower than 6 with an Mg correction (1 without an Mg correction). The Si isotope results of
376 ERM CD-281 measured by laboratories using a regular spray chamber (wet plasma) agree
377 well with those measured using an Apex sample introduction system. Similarly, the prior
378 calcination of the sample has a limited efficiency (Fig. 2) and does not seem mandatory for
379 SO_4 removal in such samples. In all cases, the chemical preparation and analytical settings
380 seem to be robust enough to avoid matrix effects caused by residual impurities in the
381 sample during Si isotope measurements.

382 Hughes et al., (2011) also showed that measurable concentrations of dissolved organic
383 carbon (DOC) in freshwater samples can affect their Si isotopic determination. Given the
384 large spectrum of naturally occurring DOC forms, DOC-induced bias is suspected to be
385 variable from one DOC form to another even before considering combined effects. This
386 would make correcting for the presence of DOC in samples unworkable, due to the near-
387 impossibility of matching the matrix in the bracketing standards. Therefore, removal of

388 organic matter during sample preparation seems to be the best option to ensure reliable
389 analysis of organic carbon-rich samples.

390 The variability of the SiO₂ and organic carbon contents of the soils reference materials used
391 in this study allow for evaluation of the influence of varying matrix to analyte ratios with or
392 without calcination steps. When comparing the results with or without organic matter
393 mineralization, no notable offset is observed, regardless of the considered reference
394 material (Fig. 2). In addition, STAiG laboratory calcinated their reference materials but also
395 processed one aliquot each of GBW-07401 and GBW-07407 without calcination (Fig. 2). The
396 results for both calcinated and uncalcinated aliquots of these two reference materials are
397 identical within their 2SD (Fig. 2 and Table S2). In addition, at GFZ the removal of organic
398 carbon by the NaOH fusion method (750°C, 10 minutes) – without prior calcination – was
399 investigated. Effective organic carbon removal was found for all soil and plant samples
400 processed at GFZ during this study using semi-quantitative ICP-OES analyses (carbon 193.027
401 nm emission line) by evaluation of C remaining in the post-fusion and purified Si solutions
402 prior to Si isotope analyses. All solutions showed C-counts indistinguishable from pure acid
403 used for dilution for the analyses, whereas significant C intensities were recorded in sample
404 aliquots that were not treated by alkali fusion and subsequent Si column purification. It thus
405 seems that the presence of organic carbon has no impact on the accuracy or reproducibility
406 of Si isotopes measurements if the high temperature alkaline fusion digestion is used (with
407 or without prior calcination) as the remaining amount of organic matter is insufficient to
408 induce Si isotopic bias. Several factors could explain this. The amount of organic matter in
409 uncalcinated aliquots was insufficient to induce any bias. Indeed, C_{org}/Si mass ratios of soil
410 reference materials were below 0.1 while Hughes et al. (2011) observed a shift in freshwater
411 samples from DOC/Si > 0.2. However, the Si isotope measurement of the high C_{org}/Si plant

412 reference material ERM-CD281 analysed at IFREMER and GFZ – without prior calcination
413 step – are not affected. In this case, it could be that the organic carbon in this sample is not
414 refractory and is oxidised during the high-temperature fusion step as suggested by C
415 analyses at GFZ. Finally, it is also possible that the DOC form present in soils or plants does
416 not induce bias, at least not on the Thermo Neptune-family of MC-ICP-MS instruments.
417 More tests would be required to determine the critical DOC/Si ratio and if it is DOC-form
418 sensitive.

419

420 3.5. Assigning $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ to the reference materials analysed in this study

421

422 Results from all seven laboratories are in excellent agreement for all reference materials
423 (Fig.2), despite the use of different sample preparations (calcination versus no calcination;
424 NaOH fusion versus NaOH and Na_2O_2 fusion) and different analytical settings (Mg doping vs
425 no doping, wet plasma sample introduction vs semi-dry plasma; see Table 2). Therefore, the
426 results reported by the laboratories for each reference material full procedural replicates
427 (with the exception of the $\delta^{30}\text{Si}$ reported by WQC) were weighted and combined together to
428 calculate averages and their associated combined uncertainties ($U, k = 2$). Final isotopic
429 characterisation of the five reference materials analysed here are given in Table 3. Following
430 the EURACHEM/CITAC Guide CG4, the combined uncertainties were calculated by error
431 propagation, assuming independent variables, of the standard deviations obtained on full
432 procedure replicates for each reference material, also including the standard deviation of
433 the averages of full procedure replicates for each reference material. The combined
434 uncertainties were multiplied by a coverage factor of $k = 2$ to obtain the expanded
435 uncertainties for each reference material. The uncertainties ($U, k = 2$) range from 0.04 ‰ to

436 0.12 ‰ for $\delta^{29}\text{Si}$ and from 0.06 ‰ to 0.17 ‰ for the $\delta^{30}\text{Si}$. The larger magnitude of U for
437 $\delta^{30}\text{Si}$ compared to those for $\delta^{29}\text{Si}$ correspond with the lower natural abundance of ^{30}Si
438 compared with ^{29}Si and the concomitant deterioration in counting statistics of the detectors.
439 In addition, the uncertainties of these results (Table 3) are comparable with standard
440 deviation obtained on multiple measurements of the reference materials Diatomite and
441 BHVO-2 (Table 2) used by the laboratories to check for accuracy. Overall, the reference
442 materials homogeneity is valid at the scale of the minimum sample mass used in this study,
443 i.e., >3 mg for the soils reference materials, and at least 50 mg for rye grass ERM CD281. The
444 soils RM GBW-07401, GBW-07404, GBW-07407 and TILL-1 offer a wide range of $\delta^{29}\text{Si}$ and
445 $\delta^{30}\text{Si}$ values comparable to and therefore useful for future Si isotope environmental studies.
446 The uncertainties obtained in this inter-laboratory comparison are more than one order of
447 magnitude lower than the range of $\delta^{29}\text{Si}$ and $\delta^{30}\text{Si}$ measured in natural samples: -5.7 to +6.1
448 ‰ (Opfergelt and Delmelle, 2012) and are therefore sufficient to allow the robust
449 interpretation of small variations in the $\delta^{29}\text{Si}$ and $\delta^{30}\text{Si}$.

450

451 **4. Conclusion**

452

453 In this study, the $\delta^{29}\text{Si}$ and $\delta^{30}\text{Si}$ values of four soil and one plant reference materials were
454 determined and compared between laboratories. Different sample preparation procedures
455 and analytical settings provide consistent results for both $\delta^{29}\text{Si}$ and $\delta^{30}\text{Si}$ values for all
456 reference materials. Therefore, all protocols used by the participating laboratories for Si
457 isotope analysis provide comparable results. Also, no notable isotopic bias was observed
458 between calcinated and uncalcinated reference materials with different C_{org}/Si ratios.

459 However, caution still stands for analyses of organic carbon-rich samples with a C_{org}/Si ratio

460 above the studied reference materials, where biases in $\delta^{30}\text{Si}$ measurements could potentially
461 occur. This is particularly the case when sample preparation does not involve calcination,
462 leading to potential matrix effects during MC-ICP-MS analyses that could be DOC-form
463 dependent. The data for soil and plant reference materials from this study can be reliably
464 used by other laboratories for routine quality control of Si isotope ratio measurements
465 during environmental and geochemical studies. Moreover, the wide range of $\delta^{29}\text{Si}$ and $\delta^{30}\text{Si}$
466 covered by these soil reference materials provided here allows analysts to select the
467 reference materials that are best suited for their study.

468

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470

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484

485 **Data availability Statement**

486 The authors confirm that the data supporting the findings of this study are available within the article
487 and its Supplementary Materials. Detailed datasets are available from the corresponding author
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