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► To cite this version:

Johan Villeneuve, Marc Chaussidon, Yves Marrocchi, Zhengbin Deng, E. Bruce Watson. High-precision in situ silicon isotopic analyses by multi-collector secondary ion mass spectrometry in olivine and low-calcium pyroxene. *Rapid Communications in Mass Spectrometry*, 2019, 33 (20), pp.1589-1597. 10.1002/rcm.8508 . hal-02357497

HAL Id: hal-02357497

<https://hal.univ-lorraine.fr/hal-02357497>

Submitted on 10 Nov 2019

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1 High-precision In situ silicon isotopic analyses by MC-SIMS in olivine and low-Ca pyroxene

2

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12 Abstract

13

14 **Rationale:** High-precision determination of silicon isotopes can be achieved by *in situ* multi-collector
15 secondary ion mass spectrometry. The analyses accuracy is however sensitive to ion yields and
16 instrumental mass fractionations (IMFs) induced by the analytical procedure. These effects vary from
17 an instrument to another, with the analytical settings, and with the composition and nature of the
18 sample. Because ion yields and IMF effects are not predictable and rely on empirical calibrations,
19 high-accuracy analyses require suitable sets of standards.

20 **Methods:** Here, we document calibrations of ion yields and matrix effects in a set of 23 olivine
21 standards and 3 low-Ca pyroxene for silicon isotopic measurements in both polarities using Caméca
22 IMS 1270 E7 and IMS 1280 HR2 ion probes set with the cesium or radiofrequency (RF) source.

23 **Results:** Silicon ion yields show (i) strong variations with the chemical composition, and (ii) an
24 opposite behavior between the secondary positive and negative polarities. The magnitude of IMF
25 along the fayalite-forsterite (olivine) series shows a complex behavior, increasing overall by $\approx 7\%$
26 (secondary positive) and $\approx 15\%$ (secondary negative) with increasing olivine Mg#. A drastic change in
27 olivine IMF occurs at Mg# ≈ 70 in both polarities. The magnitude of IMF for low-Ca pyroxene from
28 Mg# = 70-100 is almost constant in both polarities, i.e. $\approx 0.1\%$ in secondary positive and $\approx 0.15\%$ in
29 secondary negative. Analytical uncertainties on individual analyses were $\pm 0.05\text{--}0.15\%$ (2 S.E.) with

30 both sources, and external errors for each standard material were $\approx \pm 0.05\text{--}0.5\%$ (2 S.E.) with the Cs
31 source and $\approx \pm 0.03\text{--}0.15\%$ (2 S.E.) with the RF source.

32 **Conclusions:** The IMF effect of Si isotopes in silicates shows complex behaviors that vary with the
33 chemistry and the settings of the instrument. We developed a suitable set of standards in order to
34 perform high-accuracy *in situ* measurements of Si isotopes in olivine and low-Ca pyroxene
35 characterized by varying chemical compositions by MC-SIMS.

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37 **Keywords:** Secondary ion mass spectrometer, silicon isotopes, ion yield, matrix effects

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51 Introduction

52 Natural stable isotopic variations result from various processes that affect geological materials during
53 their formation. Because H, C, N, O, and S commonly show large isotopic fractionations, they have
54 been widely used in Earth and planetary sciences during the last half-century. Owing to recent
55 considerable improvements in analytical methods, high-precision isotopic measurements of a large
56 number of typically less-fractionated elements (Mg, Si, Fe, Cr, Zn, *etc.*) are now possible, providing
57 insights into various processes such as evaporation and condensation during planetary formation¹,
58 igneous differentiation², or metal-silicate fractionation³. Among the instruments allowing *in situ*
59 isotopic analyses, the latest generation of ions probes, allowing multi-collector secondary ion mass
60 spectrometry (MC-SIMS), is the most versatile with unique advantages: (i) high spatial resolution (5–
61 20 μm beam diameter and 1–2 μm depth); (ii) high sensitivity, allowing detection limits below the
62 ppm level for most elements; (iii) high mass-resolution analysis, thus removing most isobaric
63 interferences; and (iv) a good level of analytical precision, usually better than 1‰ at 2σ depending on
64 the element analyzed^{4–7}. These advantages make ion probes powerful tools for studying isotopic
65 fractionations in complex mineralogical assemblages and zoned minerals. Regardless of the
66 technique used, high-precision *in situ* isotopic analyses have always been challenging and rely on the
67 use of suitable reference materials. Ion probes measurements can be particularly sensitive to
68 differences in ion yields between elements and to mass-dependent instrumental isotopic
69 fractionation. This latter effect is usually referred to as instrumental mass fractionation (IMF) and
70 corresponds to the difference between the natural isotopic composition of a sample and the value
71 measured with the ion probe. Ion yield and IMF essentially depend on the physics of the mass
72 spectrometer, the analytical settings, and the nature and composition of the sample, *i.e.* the so-
73 called “matrix effects”⁷. Neither ion yields nor IMF effects are predictable by physical models; they
74 thus require empirical calibrations based on appropriate mineral and glass standards^{8,9}.

75 Because the electronic and electrical and physical environment of an ion probe are, in theory, stable
76 during an analytical session, IMF variations that limit the accuracy of *in situ* isotopic measurements
77 are, for a given analytical setting, mainly due to matrix effects. IMF can be understood as an
78 incomplete ionization and transmission of the isotopes of an element through the mass
79 spectrometer; *i.e.* 100% ionization and transmission would eliminate IMF. Therefore, extraction and
80 ionization yields of secondary atoms (or molecules) are sensitive to variations in the chemical
81 composition and/or crystalline structure of samples^{8,10,11}. Indeed, the efficiency of breaking chemical
82 bonds between atoms and the ionization of atoms in the plasma relies on the binding energies
83 between atoms, *i.e.* chemical composition and structure, and the elemental concentrations in the
84 plasma¹². Matrix effects are well known for ion probes, and previous studies have shown that IMF

85 variations can be estimated from empirical calibrations with various parameters describing changes
86 in the chemical composition of the matrix. For instance, it has been shown that (i) IMF varies linearly
87 with the mass-to-charge ratio of octahedral cations (e.g. Mn, Mg, Fe, Ti) as they impact the strength
88 of the OH and OB bond¹³⁻¹⁵ for analyses of ²H/¹H in micas and amphiboles and ¹¹B/¹⁰B in tourmaline,
89 (ii) IMF during ¹⁸O/¹⁶O analyses in silicates depends on the SiO₂ and FeO contents¹⁶⁻¹⁸, (iii) IMF during
90 ¹⁸O/¹⁶O analyses in carbonates depends on Fe, Mg, and Mn contents^{19,20}, and (iv) IMF during ³⁰Si/²⁸Si
91 and ⁴⁴Ca/⁴⁰Ca analyses in CaO–MgO–Al₂O₃–SiO₂ (CMAS) glasses varies linearly with optical basicity²¹.
92 Thus, for a given isotopic system, it is often possible to build an empirical calibration from
93 measurements of a limited number of well-chosen standards, and interpolate IMF values for
94 different (but related) compositions. This is particularly the case for minerals belonging to the same
95 solid solution (e.g. olivine, garnet, and tourmaline) and glasses.

96 Silicon has three stable isotopes, ²⁸Si, ²⁹Si, and ³⁰Si, with mean abundances of 92.23, 4.67, and 3.10%
97 respectively²². It is a major and ubiquitous element in the Solar System that mainly occurs in the
98 tetravalent oxidation state to form silicate minerals or amorphous forms of silica in rocks. In low
99 oxygen fugacity environments such as the solar nebula, it is believed to occur as divalent gaseous
100 species SiO or SiS. Silicon also exists as Si⁰ in metallic alloys in inclusions in meteorites and iron
101 meteorites²³⁻²⁵ and presumably in the metallic cores of terrestrial planets. Silicon isotopic research
102 has taken full advantage of the recent rise of new generation multi-collector inductively coupled
103 plasma mass spectrometers as well as *in situ* analytical devices such as laser-coupled multi-collector
104 inductively coupled plasma mass spectrometers and the latest generation multi-collector secondary
105 ions mass spectrometers (referred hereafter as ion probes) such as the Caméca IMS 1270/1280
106 series. Ion probes are versatile mass spectrometers allowing *in situ* isotopic measurements of major
107 and trace elements, isotopic mapping or depth isotopic profiles in solid material, through the use of a
108 focalized and accelerated primary beam of O⁻ or Cs⁺ ions with a spatial resolution from 50 nm to a
109 few tenth of μm. These developments have allowed the use of Si isotopes to address various
110 problems in Earth sciences such as the formation and metal-silicate differentiation of planetary
111 bodies, magmatic differentiation during igneous processes, the biogeochemical cycle of silicon, and
112 the weathering of the continental crust or past terrestrial environments³. The overall variability of Si
113 isotopes in bulk terrestrial and extra-terrestrial samples does not generally exceed a few per mil,
114 making reliable IMF corrections essential³. *In situ* Si isotopic measurements have been performed
115 via SIMS for the past 30 years, first applied to presolar grains from primitive carbonaceous
116 meteorites that yielded large mass-independent Si isotopic fractionations with δ³⁰Si variations of
117 ~2000‰²⁶. These measurements were performed on first-generation ion probes, *i.e.* Caméca IMS 3f,
118 that did not allow good analytical precision. With the development of large-radius ion probes, *i.e.*

119 Caméca IMS 1270 and 1280, that allow multi-collection capability, high mass resolution and high ion
 120 transmission, analytical uncertainties were significantly reduced and reproducibilities much better
 121 than 1‰ on $\delta^{30}\text{Si}$ values were obtained: *e.g.* $\sim \pm 0.7\text{‰}$ in silcretes²⁷, $\sim \pm 0.1\text{--}0.4\text{‰}$ in CMAS synthetic
 122 glasses^{21,28}, and $\sim \pm 0.3\text{‰}$ in quartz and precambrian cherts^{6,29–31}.

123 In the present study, we have characterized the ion yield and IMF variations for Si isotopes measured
 124 by SIMS in a set of 23 natural and synthetic olivine standards, 3 natural low-Ca pyroxene standards,
 125 and 2 quartz standards used as a reference. We show that ion yields and IMFs in olivine standards do
 126 not follow any simple trend and must be carefully characterized to avoid inappropriate sample
 127 corrections. In contrast, IMFs in low-Ca pyroxenes seem to evolve linearly with simple compositional
 128 parameters over restricted compositional ranges and thus are more predictable.

129

130 **Nomenclature and analytical approach**

131 Si isotopic compositions are reported using the classical delta notation as per mil (‰) variations of
 132 the $^{29}\text{Si}/^{28}\text{Si}$ or $^{30}\text{Si}/^{28}\text{Si}$ ratio in a sample normalized to that of the NBS28 (international quartz
 133 standard SRM 8546, provided by the National Institute of Standards and Technology):

$$134 \quad \delta^{29,30}\text{Si} = \left[\frac{\left(\frac{^{29,30}\text{Si}}{^{28}\text{Si}} \right)_{\text{sample}}}{\left(\frac{^{29,30}\text{Si}}{^{28}\text{Si}} \right)_{\text{NBS28}}} - 1 \right]$$

135

136 The absolute Si isotopic composition of NBS28 used here is $^{29}\text{Si}/^{28}\text{Si} = 0.0508229$ and $^{30}\text{Si}/^{28}\text{Si} =$
 137 0.0335336 ³². Because $^{29}\text{Si}/^{28}\text{Si}$ and $^{30}\text{Si}/^{28}\text{Si}$ ratios show similar behaviors in regard to IMF (except for
 138 the amplitude which is twice higher for $^{30}\text{Si}/^{28}\text{Si}$ ratios compared to $^{29}\text{Si}/^{28}\text{Si}$ ratios) only the $^{29}\text{Si}/^{28}\text{Si}$
 139 ratio will be used herein. The IMF for $^{29}\text{Si}/^{28}\text{Si}$ is defined by:

$$140 \quad a_{\text{instr}}^{29/28} = \frac{\left(\frac{^{29}\text{Si}}{^{28}\text{Si}} \right)_{\text{measured}}}{\left(\frac{^{29}\text{Si}}{^{28}\text{Si}} \right)_{\text{true}}},$$

141 and can be approximated to the first order by:

$$142 \quad \delta^{29}\text{Si}_{\text{instr}} = \delta^{29}\text{Si}_{\text{measured}} - \delta^{29}\text{Si}_{\text{true}},$$

143 with

$$144 \quad \delta^{29}\text{Si}_{\text{instr}} \approx \ln(\alpha_{\text{instr}}^{29/28}).$$

145 Our in-house quartz standards (NL615 and Sonar) were measured and used as an internal reference
146 to allow comparison between analytical sessions and to follow the stability of the ion probes (Fig. 1),
147 *i.e.* $\delta^{29}\text{Si}_{\text{norm}}$ values are normalized to NL615 or Sonar (Tables 2, 3; Fig. 3).

148 In the case of our study, the Si ion yield is expressed as the efficiency with which Si atoms from a
149 given matrix are sputtered, ionized, and transmitted to the mass spectrometer:

$$150 \quad {}^{28}\text{Si yield} = {}^{28}\text{Si}^{+,-} / [\text{SiO}_2]$$

151 with ${}^{28}\text{Si}^{+,-}$ the count rate of ${}^{28}\text{Si}$ ions in positive or negative polarity depending on the primary ion
152 source used and $[\text{SiO}_2]$ the SiO_2 content of the sample. The count rate of ${}^{28}\text{Si}^{+,-}$ was normalized to the
153 primary beam intensity (expressed in nA) and thus is given in counts/s/nA.

154 We use the Mg number parameter to characterize ion yield and IMF variations, expressed as:

$$155 \quad \text{Mg\#} = \frac{[\text{Mg}]}{[\text{Mg}] + [\text{Fe}]},$$

156 with $[\text{Mg}]$ and $[\text{Fe}]$ the Mg and Fe contents in atomic percent. Mg# describes olivine compositions
157 along the solid solution from the magnesian (forsterite, Mg# = 100) to the ferroan endmember
158 (fayalite, Mg# = 0) or low-Ca pyroxene compositions from enstatite (Mg# = 100) to ferrosilite (Mg# =
159 0).

160 We studied a set of 2 in-house quartz standard, 23 olivines (9 synthetic⁷ and 14 natural olivines³³)
161 spanning nearly the entire Mg# range from fayalite to forsterite, including two slightly different San
162 Carlos olivine grains, and 3 low-Ca pyroxenes with Mg# from 70 to 100. The 2 sets of natural and
163 synthetic olivine have already been characterized and are used for Mg and Fe isotopes
164 measurements^{7,33}. The chemical compositions of these samples have been precisely determined and
165 are summarized in Table 1^{7,33}. The Si isotopic compositions of synthetic (determined from the started
166 silica powder: Alfar Aesar amorphous silica powder, lot number D13Y012) and San Carlos olivines,
167 quartz, and low-Ca pyroxenes are given in Table 1³⁴. The true Si isotopic compositions of the other
168 olivines are not known, but since samples with chemical compositions close to San Carlos olivine or

169 the synthetic olivines, *i.e.* with similar matrix effects, show identical (within analytical errors) $\delta^{29}\text{Si}$
170 and $\delta^{30}\text{Si}$ values measured with the ion probe, we expect that they yield similar Si isotopic
171 compositions (Table 1). This assumption is strengthened by the fact that the overall variation of $\delta^{30}\text{Si}$
172 values in terrestrial igneous, magmatic, and mantellic rocks does not exceed 0.4‰ ³ and is thus
173 negligible relative to the overall IMF observed on the ion probe ($\sim 15\text{‰}$, Table 2). Therefore, the Si
174 isotope value for San Carlos olivine ($\delta^{30}\text{Si}_{\text{true}} = -0.3 \pm 0.04$ and $\delta^{29}\text{Si}_{\text{true}} = -0.16 \pm 0.02$)³⁴ is considered
175 at first order the real value for all unknown olivine samples (Table 1).

176 Isotopic analyses were performed on the multi-collector Cameca IMS 1270E7 and 1280HR
177 instruments at CRPG-CNRS (Nancy, France) during 4 different analytical sessions. We used primary
178 Cs^+ and O^- beams to characterize the ion yields and IMFs of Si isotopes in positive and negative
179 polarity.

180 *Cs source settings*

181 Samples were sputtered with a ~ 5 nA intensity and $\sim 15\text{-}20\mu\text{m}$ diameter primary Cs^+ beam set in
182 Gaussian mode (the size of the primary beam is controlled by the primary column lenses and the
183 primary intensity distribution is gaussian) and accelerated at 10 kV. Secondary negative $^{28,29,30}\text{Si}^-$ ions
184 were accelerated at 10 kV and analyzed in multi-collection mode on three off-axis Faraday cups (L'2,
185 C, and H1, respectively). Charge accumulations on the sample surface were neutralized by the use of
186 an electron gun. The mass resolving power (MRP) was set at $M/\Delta M = 5000$ (slit 2 - $250\mu\text{m}$ - on the
187 multicollection) using the entrance opened at $120\mu\text{m}$; at this MRP, interferences on different masses
188 are completely resolved. The transfer magnification was set at $100\mu\text{m}$ to insure an efficient
189 transmission of secondary ions. The field aperture was set at $2000\mu\text{m}$ and the energy slit was closed
190 at 40 eV in order to remove most of lens aberrations and secondary ions with too high energy. The
191 typical vacuum during analysis was 5×10^{-9} tor. Yields of the amplifier electronic cards of the Faradays
192 cups were calibrated at the beginning of each analytical session. Automatic centering of the transfer
193 deflectors and mass was implemented in the analysis routine. A $10 \times 10\mu\text{m}$ raster was applied to the
194 primary beam to ensure flat-bottomed pits. Measurements typically consisted of a 90-s pre-
195 sputtering during which electric noise backgrounds of the Faraday cup are measured, automatic
196 mass and beam centering, and 40 cycles of 4-s integrations separated by 1-s waiting times. Thus,
197 each measurement took ~ 7 min. Under these conditions, the typical count rate for ^{28}Si , ^{29}Si and ^{30}Si in
198 San Carlos olivine was $\sim 1.2 \times 10^8$, $\sim 6 \times 10^6$, $\sim 4 \times 10^6$ counts per second respectively, and the internal
199 precision on $\delta^{29}\text{Si}$ value was $\pm 0.05\text{-}0.15\text{‰}$ (2σ standard error) depending on the sample. Repeated
200 analyses of the NL615 quartz internal standard showed an external reproducibility of $\pm 0.2\text{‰}$ (2σ
201 standard deviation, Fig. 1) and an external error of $\pm 0.04\text{‰}$ (2σ standard error on 25 data, Table 3).

202 Other samples were measured five to ten times and yielded external errors between ± 0.05 and
203 $\pm 0.5\%$ (2σ standard error, Table 3).

204 *Radiofrequency source settings*

205 Samples were sputtered with a ~ 40 nA intensity and ~ 10 - 15 μm diameter primary O^- beam set in
206 Gaussian mode and accelerated at 13 kV. As for the Cs settings, secondary positive $^{28,29,30}\text{Si}^+$ ions were
207 accelerated at 10 kV and analyzed in multi-collection mode on the same 3 off-axis Faraday cups with
208 MRP = 5000 (slit 2). Settings for the entrance and energy slits, as well as transfer magnification and
209 field aperture were also the same. The typical vacuum during analysis was 5×10^{-9} tor. Relative yields
210 of the amplifier electronic cards of the Faradays cups were calibrated at the beginning of each
211 analytical session. The analytical routine was the same as that for Cs settings, except that the
212 automatic control of the energy centering was added to the routine in order to compensate for slight
213 electrical charges changes on the sample surface. A 5×5 μm raster was applied to the primary beam
214 to ensure flat-bottomed pits. Measurements typically consisted of a 90-s pre-sputtering during which
215 the electric noise background of the Faraday cup is measured, automatic mass and beam centering,
216 and 40 cycles of 4-s integrations separated by 1-s waiting times. Thus, each measurement took ~ 7
217 min. Under these conditions, the typical count rate for ^{28}Si , ^{29}Si and ^{30}Si in San Carlos olivine was
218 $\sim 1.5 \times 10^8$, $\sim 7.5 \times 10^6$, $\sim 5 \times 10^6$ counts per second respectively, and internal precision on $\delta^{29}\text{Si}$ value was
219 ± 0.05 – 0.10% (2σ standard error) depending of the sample. Repeated analyses of the Sonar quartz
220 internal standard showed an external reproducibility of $\pm 0.11\%$ (2σ standard deviation, Fig. 1) and
221 an external error of $\pm 0.03\%$ (2σ standard error on 20 data, Table 2). Other samples were measured
222 five times and yielded external errors between ± 0.03 and $\pm 0.15\%$ (2σ standard error, Table 2).

223 **Results and discussion**

224 *Si ion yields in olivine and low-Ca pyroxene*

225 As shown in Fig. 2 and Tables 2 and 3, Si ion yields were clearly different between the different
226 matrices studied (olivine, low-Ca pyroxene, and quartz) and the two primary ion sources used (one
227 session using the RF source and three using the Cs source, producing positive and negative secondary
228 ions, respectively). Indeed, Si ion yields with the Cs source were ~ 1.5 times better than with the O
229 source for quartz, ~ 2.5 – 4 times better for low-Ca pyroxene, and ~ 2 – 7 times better for olivine
230 standards (Fig. 2, Tables 2, 3). The Si ion yield evolves differently depending on the primary ion
231 source; the $^{28}\text{Si}^+$ yield is stable with Mg# whereas the $^{28}\text{Si}^-$ yield slightly decreases in low-Ca pyroxene
232 (Fig. 2). Olivine positive and negative ion yields similarly show opposite behaviors (Fig. 2).

233 Clear differences in ion yields between different matrices have been previously observed^{8,35}. In
234 olivine, the evolution of the Si ion yield with Mg# is not linear; ²⁸Si⁻ yields increase until Mg# ≈ 70–75,
235 then decrease, whereas ²⁸Si⁺ yields decrease until the same SiO₂ content and then increase (Fig. 2).
236 The same systematic for ²⁸Si⁺ was previously observed by Steele *et al.*³⁵ who indicated a minimum
237 near Mg# = 65 (they did not investigate ²⁸Si⁻). Chaussidon *et al.*⁷ showed a similar systematic for the
238 Mg ion yield in olivine with a change in behavior also at Mg# = 75. These complex changes of Si (and
239 Mg) ion yields that affect both polarities are puzzling, since olivine is a solid solution with nothing
240 particular in its chemical and structural properties at Mg# ≈ 70–75. Since olivines have relatively
241 restricted Si atomic contents, these changes must be in some way related to changes in their Fe and
242 Mg contents, and therefore related to the ionic bonding between Si and Mg/Fe in the olivine
243 structure. A kind of ‘competition’ between elements for ionization, which would enhance or suppress
244 the emissivity of a specific element depending on its atomic environment during sputtering, has been
245 previously proposed to explain some complex ionization behaviors^{8,9}. Thus, Chaussidon *et al.*⁷
246 proposed an empirical model based on the difference in enthalpies of atomization between Fe and
247 Mg (used as a proxy for bond strength difference between Fe and Mg) that successfully fit Mg ion
248 yields and IMF in olivine standards and CMAS and basaltic glasses. They showed that Mg ion yields
249 and IMFs can be modeled with a two-component ionization including (i) a simple ionization process
250 correlated with the Mg content and (ii) an enhanced ionization process amplified by the presence of
251 Fe. A similar approach might be possible for Si ion yields in olivine, but the problem is more complex
252 since Si ionization relies on the variations and interactions of both Mg and Fe. Therefore, we did not
253 find a satisfactory way to model the evolution of the Si ion yield in olivine.

254 In low-Ca pyroxene, variations of ion yields are limited for Mg# between 70 and 100 for both ²⁸Si⁺ and
255 ²⁸Si⁻ (Fig. 2). Such behavior is consistent with Steele *et al.* study³⁵.

256 *IMF of Si isotopes in olivine and low-Ca pyroxene*

257 To our knowledge, no systematic study of Si isotopic analyses in olivine and low-Ca pyroxene by SIMS
258 has been reported in the literature. IMF variations in olivine as a function of Mg# are shown in Fig. 3
259 (complete data are available in Tables 1–3). Obviously, IMF in olivine strongly relies on the
260 abundances of FeO and MgO. In secondary positive polarity, $\delta^{29}\text{Si}_{\text{instr}}$ decreases non-linearly by ~3‰
261 over the range Mg# ≈ 10–70, then increases linearly by ~6‰ up to Mg# = 95 (Fig. 3). In secondary
262 negative polarity, $\delta^{29}\text{Si}_{\text{instr}}$ value increases nonlinearly by ~15‰ from Mg# ≈ 0 until reaching a plateau
263 at Mg# ≈ 70 (Fig. 3). IMF with the RF source can be fitted with a polynomial regression over the range
264 Mg# ≈ 10–70 and then a linear regression yielding residual of 0.16‰, whereas IMF with the Cs source
265 can be fitted with a polynomial function yielding a residual of 0.22‰ (and even better over Mg# =

266 70–95; Fig. 3, Table 4). IMF with the Cs source is very well constrained above Mg# = 45 and is thus
267 useful for IMF corrections in high-MgO olivines. In contrast, it may be preferable to analyze high-FeO
268 olivines with the RF source, although the Si ion yield is lower. In any case, as with Mg and O isotopic
269 measurements in olivine^{7,17}, a comprehensive set of standards is needed to avoid artificial isotopic
270 fractionations and to ensure high precision IMF corrections for Si isotopes.

271 IMF in low-Ca pyroxene shows very small and linear variations with Mg# from 70-100 (Fig. 3). In
272 secondary positive polarity, $\delta^{29}\text{Si}_{\text{instr}}$ value decreases linearly by $\sim 0.1\text{‰}$ whereas it increases linearly
273 by $\sim 0.15\text{‰}$ in secondary negative polarity (Fig. 2). Therefore, IMF can be fitted with linear
274 regressions yielding a residual of 0.01 for both sources.

275 *Conclusions*

276 Ion yields and IMFs in olivine show complex behaviors that rely on variations in both MgO and FeO
277 content (Fig. 2, 3). In secondary negative polarity, IMF is well constrained above Mg# = 45, and
278 particularly in the range Mg# = 70–100 where $\delta^{29}\text{Si}_{\text{instr}}$ value does not vary. Therefore, these settings
279 are appropriate for high-accuracy Si isotopic analyses of high-MgO olivines. In contrast, $\delta^{29}\text{Si}_{\text{instr}}$ value
280 does not vary much over Mg# = 0–70 in positive polarity; such settings are thus appropriate for
281 analyses of high-FeO olivine. Ion yields and IMFs in low-Ca pyroxene are more predictable as they
282 show limited variations over Mg# = 70-100.

283 **Acknowledgment:** This work was supported by PNP-INSU (French national program of planetology)
284 and ANR CASSYSS (ANR-18-CE31-0010-01, PI J.V.). This is CRPG publication #2705.

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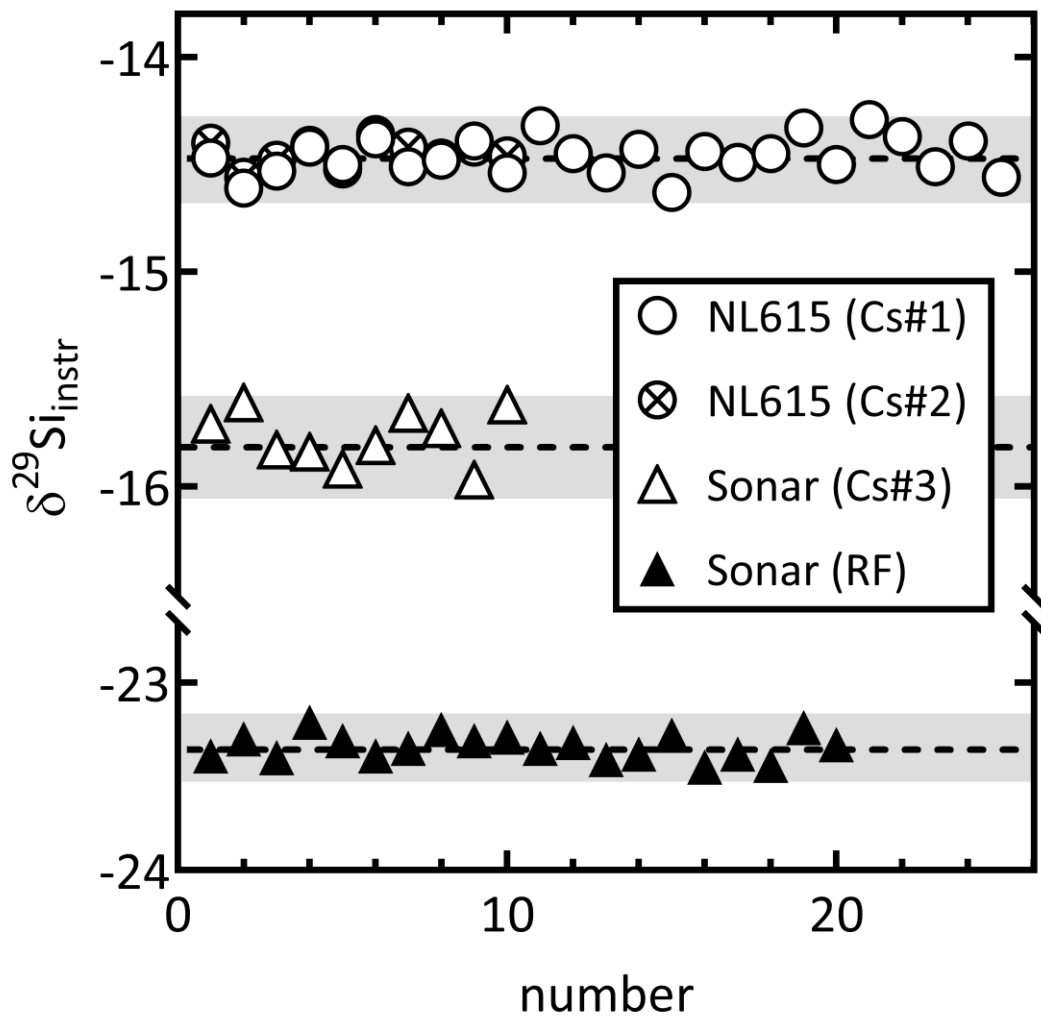
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377

378 **Figures captions**

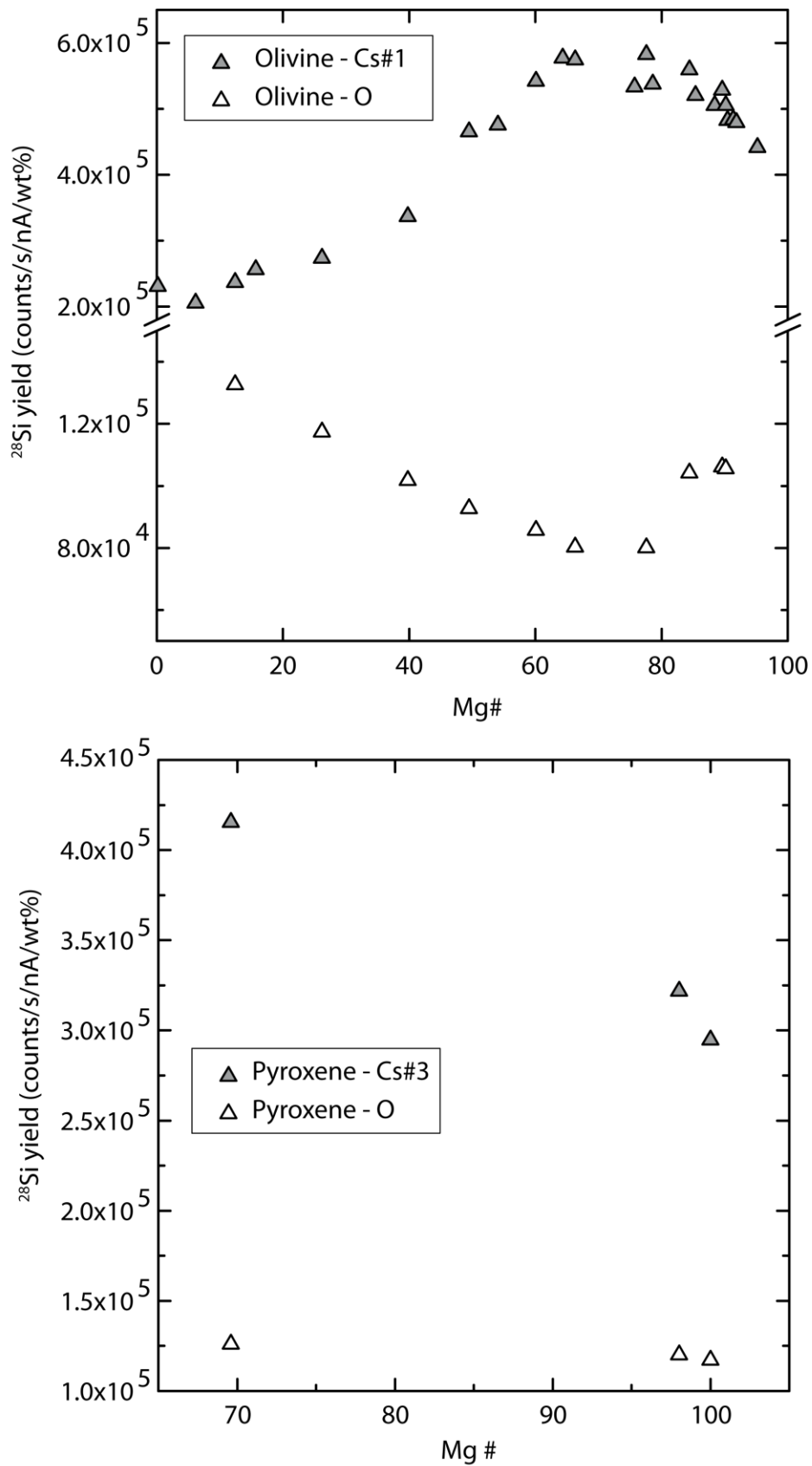
379 Fig. 1: Stability of NL615 and Sonar quartz standards over the different analytical sessions (see tables
380 2 and 3). Dashed lines and grey boxes correspond to average values and external reproducibilities (2σ
381 standard deviation) respectively.



382

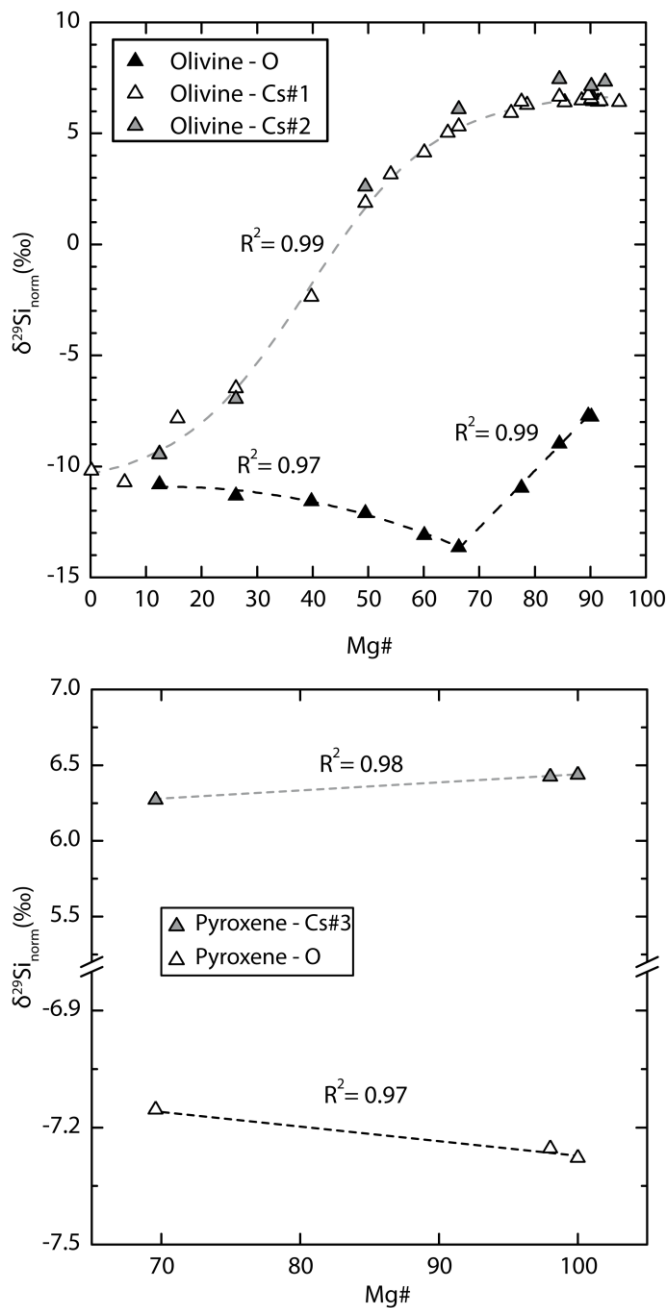
383

384 Fig. 2: ^{28}Si ion yields in both polarities as a function of Mg# in olivine (top) and in low-Ca pyroxene
385 (bottom).



386

387 Fig. 3: $\delta^{29}\text{Si}_{\text{norm}}$ value as a function of Mg# in olivine (top) and in low-Ca pyroxene (bottom). The
 388 polynomial function regression is calculated from the olivine data of session #1 with the Cs source
 389 ($\delta^{29}\text{Si}_{\text{norm}} = -10.19 - 0.09 \times \text{Mg\#} + (1.38 \times 10^{-2}) \times \text{Mg\#}^2 - (1.79 \times 10^{-4}) \times \text{Mg\#}^3 + (6.57 \times 10^{-7}) \times \text{Mg\#}^4$). Data for
 390 olivine with the RF source are fitted with a polynomial function for $\text{Mg\#} < 65$ ($\delta^{29}\text{Si}_{\text{norm}} = -10.98 +$
 391 $0.02 \times \text{Mg\#} - (8.69 \times 10^{-4}) \times \text{Mg\#}^2$) and a linear function for $\text{Mg\#} > 65$ ($\delta^{29}\text{Si}_{\text{norm}} = -30.60 + 0.25 \times \text{Mg\#}$).
 392 Data for low-Ca pyroxene are fitted with linear functions for both polarities, i.e. $\delta^{29}\text{Si}_{\text{norm}} = 5.95 +$
 393 $(4.90 \times 10^{-3}) \times \text{Mg\#}$ with the Cs source and $\delta^{29}\text{Si}_{\text{norm}} = -6.87 + (3.95 \times 10^{-3}) \times \text{Mg\#}$ with the RF source.



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395

396

397 Table 1: Chemical compositions, bulk Si isotopic compositions normalized to NBS 28 (errors are 2 S.E.,
 398 when available), Mg numbers of the studied standards. See text for details and parameter
 399 definitions. Isotopic compositions in italic are estimated (see text for details)

| Standard | Al₂O₃ [wt%] | MgO [wt%] | SiO₂ [wt%] | CaO [wt%] | FeO_T [wt%] | Na₂O [wt%] | $\delta^{30}\text{Si}_{\text{true}}$ [‰] | $\delta^{29}\text{Si}_{\text{true}}$ [‰] | Mg# |
|--|---|---------------------|---------------------------------|---------------------|---------------------------------|---------------------------------|---|---|------------|
| Quartz | | | | | | | | | |
| NL 615 | 0.00 | 0.10 | 99.50 | 0.00 | 0.50 | n.a. | -0.30 ± 0.03 | -0.15 ± 0.03 | n.a. |
| Sonar | 0.00 | 0.00 | 100.00 | 0.00 | 0.00 | n.a. | -0.38 ± 0.06 | -0.21 ± 0.04 | n.a. |
| Olivine (synthetic and natural) † | | | | | | | | | |
| Sio-Mg#0 | n.a. | 0.07 | 29.26 | n.a. | 67.21 | n.a. | -0.30 | -0.16 | 0.17 |
| Sio-Mg#6 | n.a. | 2.46 | 29.99 | n.a. | 67.56 | n.a. | -0.30 | -0.16 | 6.14 |
| Synth Watson #11 | n.a. | 5.06 | 30.60 | n.a. | 64.34 | n.a. | -0.16 ± 0.07 | -0.07 ± 0.01 | 12.40 |
| Sio-Mg#16 | n.a. | 6.48 | 30.94 | n.a. | 62.58 | n.a. | -0.30 | -0.16 | 15.71 |
| Synth Watson #10 | n.a. | 11.19 | 32.05 | n.a. | 56.76 | n.a. | -0.16 ± 0.07 | -0.07 ± 0.01 | 26.20 |
| Synth Watson #9 | n.a. | 17.83 | 33.61 | n.a. | 48.56 | n.a. | -0.16 ± 0.07 | -0.07 ± 0.01 | 39.80 |
| Synth Watson #8 | n.a. | 22.98 | 34.82 | n.a. | 42.20 | n.a. | -0.16 ± 0.07 | -0.07 ± 0.01 | 49.50 |
| Sio-Mg#54 | n.a. | 25.55 | 35.42 | n.a. | 39.03 | n.a. | -0.30 | -0.16 | 54.09 |
| Synth Watson #7 | n.a. | 29.05 | 36.25 | n.a. | 34.71 | n.a. | -0.16 ± 0.07 | -0.07 ± 0.01 | 60.10 |
| SiO-Mg#64 | n.a. | 31.61 | 36.85 | n.a. | 31.54 | n.a. | -0.30 | -0.16 | 64.34 |
| Synth Watson #6 | n.a. | 32.83 | 37.14 | n.a. | 30.04 | n.a. | -0.16 ± 0.07 | -0.07 ± 0.01 | 66.30 |
| Sio-Mg#76 | n.a. | 38.97 | 38.58 | n.a. | 22.45 | n.a. | -0.30 | -0.16 | 75.75 |
| Synth Watson #5 | n.a. | 40.22 | 38.88 | n.a. | 20.90 | n.a. | -0.16 ± 0.07 | -0.07 ± 0.01 | 77.60 |
| Sio-Mg#79 | n.a. | 40.93 | 39.04 | n.a. | 20.03 | n.a. | -0.30 | -0.16 | 78.62 |
| Synth Watson #4 | n.a. | 45.02 | 40.00 | n.a. | 14.98 | n.a. | -0.16 ± 0.07 | -0.07 ± 0.01 | 84.40 |
| Sio-Mg#85 | n.a. | 45.74 | 40.17 | n.a. | 14.09 | n.a. | -0.30 | -0.16 | 85.39 |
| Sio-Mg#88 | n.a. | 48.00 | 40.71 | n.a. | 11.29 | n.a. | -0.30 | -0.16 | 88.44 |
| San Carlos Ol | n.a. | 48.88 | 40.91 | n.a. | 10.21 | n.a. | -0.3 ± 0.04 [‡] | -0.16 ± 0.02 [‡] | 89.60 |
| Synth Watson #1 | n.a. | 49.33 | 41.02 | n.a. | 9.65 | n.a. | -0.16 ± 0.07 | -0.07 ± 0.01 | 90.20 |
| Sio-Mg#90 | n.a. | 49.55 | 41.07 | n.a. | 9.37 | n.a. | -0.30 | -0.16 | 90.49 |
| Sio-Mg#91 | n.a. | 50.21 | 41.23 | n.a. | 8.57 | n.a. | -0.30 | -0.16 | 91.34 |
| Sio-Mg#92 | n.a. | 50.63 | 41.33 | n.a. | 8.04 | n.a. | -0.30 | -0.16 | 91.89 |
| CRPG SC Ol | 0.03 | 50.94 | 41.32 | 0.07 | 7.21 | 0.01 | -0.3 ± 0.04 [‡] | -0.16 ± 0.02 [‡] | 92.68 |
| Sio-Mg#95 | n.a. | 53.25 | 41.94 | n.a. | 4.81 | n.a. | -0.30 | -0.16 | 95.22 |
| Pyroxene | | | | | | | | | |
| St Paul | 1.39 | 24.18 | 52.30 | 1.58 | 19.01 | 0.06 | -0.49 ± 0.05 | -0.21 ± 0.04 | 69.60 |
| Gold En | 0.93 | 38.52 | 58.46 | 0.09 | 1.39 | 0.03 | -0.07 ± 0.08 | -0.06 ± 0.04 | 98.03 |
| OEA En | 0.04 | 39.88 | 60.62 | 0.00 | 0.00 | 0.04 | -0.04 ± 0.04 | -0.02 ± 0.04 | 100.00 |

400 †Chemical composition data from ^{7,33}. ‡ Data from ³⁴

401

402 Table 2: Number of analyses (n), ²⁸Si yield, raw isotopic data, and IMFs normalized to NBS28 from
 403 MC-SIMS analyses with the RF source (positive secondary polarity)

| Standard | n | ²⁸ Si yield [counts/s/nA/wt%] | δ ³⁰ Si _{instr} [‰] | 2 S.E. [‰] | δ ²⁹ Si _{instr} [‰] | 2 S.E. [‰] | δ ²⁹ Si _{norm} [‰] |
|--|----|---|--|---------------|--|---------------|---|
| RF source | | | | | | | |
| Quartz | | | | | | | |
| Sonar | 20 | 1.90E+05 | -41.88 | 0.05 | -23.34 | 0.03 | 0.00 |
| Olivine (synthetic and natural) | | | | | | | |
| Synth Watson #11 | 5 | 1.33E+05 | -63.51 | 0.07 | -34.14 | 0.06 | -10.81 |
| Synth Watson #10 | 5 | 1.17E+05 | -64.31 | 0.29 | -34.66 | 0.15 | -11.32 |
| Synth Watson #9 | 5 | 1.02E+05 | -65.39 | 0.18 | -34.90 | 0.10 | -11.57 |
| Synth Watson #8 | 5 | 9.27E+04 | -66.31 | 0.09 | -35.45 | 0.05 | -12.11 |
| Synth Watson #7 | 5 | 8.03E+04 | -68.22 | 0.23 | -36.43 | 0.10 | -13.10 |
| Synth Watson #6 | 5 | 1.04E+05 | -69.07 | 0.21 | -36.98 | 0.08 | -13.64 |
| Synth Watson #5 | 5 | 1.06E+05 | -63.68 | 0.12 | -34.31 | 0.09 | -10.97 |
| Synth Watson #4 | 5 | 1.06E+05 | -59.92 | 0.14 | -31.81 | 0.05 | -8.47 |
| San Carlos Ol. | 5 | 1.33E+05 | -57.05 | 0.05 | -31.06 | 0.03 | -7.72 |
| Synth Watson #1 | 5 | 1.02E+05 | -57.06 | 0.17 | -31.10 | 0.14 | -7.76 |
| Pyroxene | | | | | | | |
| St Paul | 5 | 1.26E+05 | -55.73 | 0.17 | -30.49 | 0.12 | -7.15 |
| Gold En | 10 | 1.20E+05 | -55.92 | 0.05 | -30.59 | 0.05 | -7.25 |
| OEA En | 5 | 1.17E+05 | -55.99 | 0.09 | -30.61 | 0.07 | -7.28 |

404

405

406 Table 3: Number of analyses (n), ²⁸Si yield, raw isotopic data, and IMFs IMFs normalized to NBS28
 407 from MC-SIMS analyses with the Cs source (negative secondary polarity).

| Standard | Session | n | ²⁸ Si yield [counts/s/nA/wt%] | δ ²⁹ Si _{instr} [‰] | 2 S.E. [‰] | δ ²⁹ Si _{instr} [‰] | 2 S.E. [‰] | δ ²⁹ Si _{norm} [‰] |
|--|---------|----|---|--|---------------|--|---------------|---|
| Cs source | | | | | | | | |
| Quartz | | | | | | | | |
| NL615 | #1 | 25 | 2.49E+05 | -28.96 | 0.05 | -14.45 | 0.04 | 0.00 |
| NL615 | #2 | 10 | 3.16E+05 | -28.89 | 0.06 | -14.45 | 0.03 | 0.00 |
| Sonar | #3 | 10 | 2.18E+05 | -29.68 | 0.11 | -15.77 | 0.09 | 0.00 |
| Olivine (synthetic and natural) | | | | | | | | |
| Sio-Mg#0 | #1 | 5 | 2.31E+05 | -48.47 | 0.30 | -24.63 | 0.33 | -10.19 |
| Sio-Mg#6 | #1 | 5 | 2.05E+05 | -49.54 | 0.43 | -25.16 | 0.27 | -10.71 |
| Synth Watson #11 | #1 | 5 | 2.37E+05 | -47.32 | 0.50 | -23.87 | 0.49 | -9.42 |
| Sio-Mg#16 | #1 | 5 | 2.56E+05 | -44.24 | 0.40 | -22.32 | 0.22 | -7.88 |
| Synth Watson #10 | #1 | 5 | 2.73E+05 | -41.67 | 0.18 | -20.93 | 0.11 | -6.48 |
| Synth Watson #9 | #1 | 5 | 3.36E+05 | -33.34 | 0.25 | -16.80 | 0.15 | -2.36 |
| Synth Watson #8 | #1 | 5 | 4.65E+05 | -25.08 | 0.21 | -12.57 | 0.12 | 1.88 |
| Sio-Mg#54 | #1 | 5 | 4.75E+05 | -22.52 | 0.42 | -11.29 | 0.26 | 3.16 |
| Synth Watson #7 | #1 | 5 | 5.42E+05 | -20.59 | 0.18 | -10.30 | 0.13 | 4.15 |
| SiO-Mg#64 | #1 | 5 | 5.77E+05 | -18.97 | 0.20 | -9.41 | 0.09 | 5.03 |
| Synth Watson #6 | #1 | 5 | 5.75E+05 | -18.28 | 0.16 | -9.14 | 0.10 | 5.31 |
| Sio-Mg#76 | #1 | 5 | 5.33E+05 | -17.14 | 0.17 | -8.52 | 0.10 | 5.93 |
| Synth Watson #5 | #1 | 5 | 5.83E+05 | -16.31 | 0.17 | -8.02 | 0.13 | 6.43 |
| Sio-Mg#79 | #1 | 5 | 5.37E+05 | -16.54 | 0.14 | -8.16 | 0.04 | 6.28 |
| Synth Watson #4 | #1 | 5 | 5.59E+05 | -15.58 | 0.26 | -7.79 | 0.17 | 6.66 |
| Sio-Mg#85 | #1 | 5 | 5.20E+05 | -16.44 | 0.26 | -8.05 | 0.10 | 6.40 |
| Sio-Mg#88 | #1 | 5 | 5.05E+05 | -16.20 | 0.19 | -7.96 | 0.06 | 6.49 |
| San Carlos Ol | #1 | 5 | 5.29E+05 | -15.67 | 0.17 | -7.72 | 0.15 | 6.73 |
| Synth Watson #1 | #1 | 5 | 5.05E+05 | -16.15 | 0.21 | -7.96 | 0.12 | 6.49 |
| Sio-Mg#90 | #1 | 5 | 4.83E+05 | -16.15 | 0.19 | -7.98 | 0.16 | 6.46 |
| Sio-Mg#91 | #1 | 5 | 4.84E+05 | -16.35 | 0.16 | -8.01 | 0.07 | 6.44 |
| Sio-Mg#92 | #1 | 5 | 4.79E+05 | -16.25 | 0.26 | -7.98 | 0.16 | 6.46 |
| Sio-Mg#95 | #1 | 5 | 4.41E+05 | -16.44 | 0.18 | -8.03 | 0.17 | 6.42 |
| Synth Watson #11 | #2 | 5 | 2.84E+05 | -47.06 | 0.22 | -23.90 | 0.16 | -9.46 |
| Synth Watson #10 | #2 | 5 | 3.19E+05 | -42.41 | 0.55 | -21.41 | 0.53 | -6.96 |
| Synth Watson #8 | #2 | 5 | 5.35E+05 | -23.70 | 0.24 | -11.83 | 0.17 | 2.61 |
| Synth Watson #6 | #2 | 5 | 6.56E+05 | -17.02 | 0.14 | -8.35 | 0.13 | 6.10 |
| Synth Watson #4 | #2 | 5 | 6.49E+05 | -14.36 | 0.12 | -7.00 | 0.06 | 7.45 |
| Synth Watson #1 | #2 | 5 | 5.84E+05 | -14.83 | 0.17 | -7.31 | 0.10 | 7.14 |
| CRPG SC Ol | #2 | 10 | 6.65E+05 | -14.56 | 0.10 | -7.12 | 0.03 | 7.33 |
| pyroxene | | | | | | | | |
| St Paul | #3 | 5 | 4.16E+05 | -17.30 | 0.11 | -9.48 | 0.08 | 6.29 |
| Gold En | #3 | 5 | 3.22E+05 | -17.01 | 0.16 | -9.33 | 0.16 | 6.44 |
| OEA En | #3 | 5 | 2.95E+05 | -17.06 | 0.22 | -9.32 | 0.08 | 6.43 |

408

409 Table 4: Coefficients of determination and average residuals of IMF ($\delta^{29}\text{Si}_{\text{norm}}$) as a function of Mg#
 410 for the different sessions and standard sets.

| Data sets | No. of samples | $\delta^{29}\text{Si}_{\text{norm}}$ vs Mg# | |
|----------------|----------------|---|------------|
| | | R ² | Residuals* |
| Olivine - O | 10 | 0.97-0.99 | 0.16 |
| Olivine - Cs#1 | 23 | 0.99 | 0.22 |
| Pyroxene - O | 3 | 0.97 | 0.01 |
| Pyroxene - Cs | 3 | 0.98 | 0.01 |

411 * Residuals are expressed in ‰ and are calculated as: residual = $(\sum | \delta^{29}\text{Si}_{\text{norm}} - \delta^{29}\text{Si}_{\text{calc}} |) / (\text{no. analyses})$, with $\delta^{29}\text{Si}_{\text{norm}}$ the
 412 isotopic ratio measured for one sample and $\delta^{29}\text{Si}_{\text{calc}}$ the isotopic ratio of the same sample calculated from the regression
 413 curves.

414