

1 REVISED VERSION

2 **Discovery of moissanite in a peralkaline syenite from the Azores Islands**

3  
4  
5 SABRINA NAZZARENI<sup>A,\*</sup>, FABRIZIO NESTOLA<sup>B</sup>, VITTORIO ZANON<sup>C</sup>, LUCA BINDI<sup>P</sup>, ENRICO SCRICCIOLO<sup>A</sup>,  
6 MAURIZIO PETRELLI<sup>A,E</sup>, MARCO ZANATTA<sup>F</sup>, GINO MARIOTTO<sup>F</sup>, GABRIELE GIULI<sup>G</sup>

7  
8 <sup>a</sup>Dipartimento di Fisica e Geologia, Università di Perugia, Perugia, Italy;

9 <sup>b</sup>Dipartimento di Geoscienze, Università di Padova, Padova, Italy

10 <sup>c</sup>Instituto de Investigação em Vulcanologia e Avaliação de Riscos / Universidade dos Açores, Ponta Delgada, Portugal

11 <sup>d</sup>Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Firenze, Italy

12 <sup>e</sup>INFN, Perugia, Italy

13 <sup>f</sup>Dipartimento di Informatica, Università di Verona, Verona, Italy

14 <sup>g</sup>Scuola di Scienze e Tecnologie – sez. Geologia, Università di Camerino, Camerino, Italy

15  
16 \*Corresponding author: Sabrina Nazzareni ([sabrina.nazzareni@unipg.it](mailto:sabrina.nazzareni@unipg.it))

## Abstract

23  
24 Our discovery of moissanite grains in a peralkaline syenite from the Água de Pau Volcano (São  
25 Miguel, Azores Islands, Portugal) represents the first report of this mineral in present day oceanic  
26 geodynamic settings. Raman spectroscopy and single-crystal X-ray diffraction show the presence of  
27 both the  $6H$  and  $4H$  polytypes with the predominance of the first one. The distribution of trace  
28 elements is homogeneous, except for Al and V. Azorean moissanite often hosts rounded inclusions  
29 of metallic Si and other not yet identified metallic alloys. A process involving a flushing of  $\text{CH}_4\text{-H}_2$   
30 ultra-reducing fluids in the alkaline melts might be considered as a possible mechanism leading to  
31 the formation of natural SiC, thus calling for strongly reducing conditions that were locally met in  
32 the crust-mantle beneath the São Miguel Island.

33

34

## 35 1. Introduction

36 Since its discovery in 1893, moissanite (SiC) was recovered in an increasing number of  
37 terrestrial tectonic settings: as inclusions in diamonds (Klein-BenDavid et al., 2007), in kimberlites  
38 (Marshintsev et al., 1967; Leung et al., 1990; Mathez et al., 1995; Shiryaev et al., 2011), in  
39 ophiolites (Trumbull et al., 2009), in granulites and metamorphic rocks (Perraki and Faryad, 2014;  
40 Janák et al., 2015; Machev et al., 2018), and in volcanic breccias (Di Pierro et al., 2003;  
41 Dobrzhinetskaya et al., 2018). However, despite the increased findings from continental crust  
42 sources, moissanite has never been reported from present-day oceanic geodynamic settings.

43 Doubts often raised on the natural origin of SiC grains because they are commonly recovered in  
44 heavy fractions after separation, and only rarely *in situ* (Di Pierro et al., 2003; Dobrzhinetskaya et  
45 al., 2018; Machev et al., 2018). Nevertheless, both the morphology and the occurrence/nature of  
46 inclusions inside moissanite usually support a natural origin.

47 The presence of moissanite in such different rocks opened an intense debate to explain its origin  
48 (Shiryaev et al., 2011; Di Pierro et al., 2003; Griffin et al., 2016; Dobrzhinetskaya et al., 2018,  
49 Machev et al., 2018), mainly because it only forms at extremely reducing conditions, i.e.  $f\text{O}_2$  5-7 log  
50 units below Iron-Wustite (IW) for mantle conditions ( $P = 2\text{-}10$  GPa  $T = 1000\text{-}1700^\circ\text{C}$ ; Ulmer et al.,  
51 1998; Schmidt et al., 2014). How a silicide (like moissanite) or native elements (like  $\text{Si}^0$  or  $\text{Fe}^0$ )

52 could coexist with silicates and oxides is still far to be explained.

53 Moissanite phase diagrams (including polytype stability) applicable to geologically meaningful  
54 conditions are scarce and, even when recovered *in situ*, moissanite is never in equilibrium with the  
55 coexisting mineral assemblage supporting the idea of its xenocrystic nature.

56 Here we report discovery of moissanite grains recovered from a concentrated diamagnetic  
57 fraction from a peralkaline syenite from the Água de Pau Volcano, at São Miguel (Azores Islands,  
58 Portugal). Moissanite has been characterised by micro-Raman spectroscopy ( $\mu$ -RS), single-crystal  
59 X-ray diffraction (SC-XRD) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry  
60 (LA-ICP-MS). Beside, inclusions hosted in moissanite were characterized by  $\mu$ -RS .

61

## 62 **2. Geological setting**

63 The Azores region includes nine volcanic islands and several seamounts located in the central-  
64 north Atlantic Ocean which constitute the Azores Triple Junction between the Eurasia, Nubia and  
65 North America tectonic plates.

66 Magmatism at the volcano of Água de Pau in São Miguel easternmost island started about 270  
67 ka (Sibrant et al., 2016) with the emission of submarine basalts. The last eruption was in 1563 and  
68 involved the formation of a subplinian eruptive column of trachytic pumices. The Holocene activity  
69 was dominantly explosive, with two caldera-forming events: Ribeira Chã (8–12 ka BP) and Fogo A  
70 (4.6 ka BP) (Wallenstein et al., 2015).

71 Syenites are relatively common products of this volcano. Three generations of syenite suites  
72 have been recognised so far (Widom et al., 1993): they are weakly peralkaline and strongly  
73 enriched in trace elements (Ridolfi et al., 2003). The peculiar enrichment determined the formation  
74 of REE, Zr and Nb accessory (rare) minerals during late stage of crystallization, in the presence of  
75 fluids (Widom et al., 1993).

76

## 77 **3. Sample description and methods**

78 Samples were collected from the Lombadas ravine, on the northern flank of the volcano. The  
79 water stream bed at the bottom of the ravine shows the frequent occurrence of syenite rocks ranging  
80 in size from boulders to cobbles. Three texturally different syenites can be found. Metasomatised  
81 miarolitic syenite composed mostly of zoned feldspars and acicular amphiboles are rarely found  
82 irregularly shaped cobbles. Leucocratic pegmatitic syenite consisting mostly of large perthitic  
83 feldspars, plagioclase, biotite and amphibole are frequently found in form of large boulders.  
84 Saccaroid-textured medium-grained syenite consisting mostly of sanidine, plagioclase, aegirina-  
85 augite, biotite, brown amphibole, apatite, zircon and quartz can be sometimes found as rounded  
86 cobbles and pebbles. These rocks host numerous rare REE-bearing minerals the object of the  
87 present study. These Syenites are feldspar dominated, with minor amphibole, clinopyroxene, Fe-Ti  
88 oxides and quartz (Fig 1), similar to those described by Ridolfi et al. (2003). Accessory minerals are  
89 apatite, titanite, eudyalite, aenigmanite, zircon, chevkinite-(Ce), pyrochlore, dalyite, Fe-katophorite,  
90 chiappinoite-Y, steacyite, Nb-Zr-bearing astrophillyte and monazite.

91 Syenites were crushed in a steel mortar and then sieved. Diamagnetic component (mainly  
92 feldspar, quartz, pyrochlore and zircon) was separated from paramagnetic/ferromagnetic material  
93 using a Frantz Isodynamic Magnetic Separator apparatus. Neither further laboratory preparation,  
94 nor cutting and polishing treatments on the original syenite were done.

95 About 500 moissanite grains were recovered from 63 gr of the fraction < 0.5 mm of the  
96 diamagnetic material (78 gr is the total diamagnetic/para-ferro-magnetic fraction < 0.5 mm). They  
97 show deep-blue to green-bluish colours and exhibit a morphology that spans from hexagonal to  
98 anhedral.

99 Single-crystal X-ray diffraction was carried out using an Oxford Diffraction Xcalibur  
100 diffractometer (X-ray radiation  $\text{MoK}\alpha$ ,  $\lambda = 0.71073 \text{ \AA}$ ) fitted with a CCD detector. After absorption  
101 correction reflections data were used for the structural refinement by using SHELXL (Sheldrick,  
102 2008). The refinement was done in  $P6_3mc$  space group using the atomic coordinates reported by  
103 Capitani et al. (2007). The occupancy of all the sites was left free to vary (Si vs. vacancy and C vs.

104 vacancy) and resulted in a full occupancy by Si and C, respectively. At the last stage, with  
105 anisotropic atomic displacement parameters for all atoms and without constraints, the residual value  
106 settled at  $R1 = 1.47\%$  for 153 observed reflections [ $F_o > 4\sigma(F_o)$  level] and 20 parameters and at  $R1$   
107  $= 1.83\%$  for all 200 independent reflections.

108 Micro-Raman measurements were carried out in backscattering geometry using two different  
109 instrumentations. A Horiba Jobin-Yvon Labram HR800 spectrometer with a focal length of 800  
110 mm and equipped with a 600 lines/mm grating. The excitation wavelength was the 633 nm line of a  
111 He-Ne laser and detected by a CCD detector cooled by liquid nitrogen. Micro-sized regions with a  
112 diameter of  $\sim 1.5 \mu\text{m}$  were probed by an  $80\times$  long working distance objective. The laser power at the  
113 sample surface was  $\sim 6 \text{ mW}$  and the experimental resolution was about  $1.5 \text{ cm}^{-1}$ . The second  
114 instrument is a Thermo Scientific DXR2 Raman microscope equipped with a long-working distance  
115  $50\times$  objective. The excitation source was a 532 nm laser, the spatial resolution  $1.1 \mu\text{m}$  and the  
116 minimum spectral resolution was  $2.2 \text{ cm}^{-1}$ . Un-polarized spectra were collected between 150 and  
117  $3570 \text{ cm}^{-1}$  in confocal mode through a laser power of 10 mW. The exposure times varied between 5  
118 and 40 s with a 2-5 accumulations per spectrum.

119 Trace element compositions were estimated by LA-ICP-MS. The instrumentation is a Teledyne  
120 Photon Machine G2 laser ablation device, equipped with a two-volume HeEx 2 cell, and coupled to  
121 a Thermo Fisher Scientific iCAP Q quadrupole mass spectrometer (Petrelli et al., 2016a). A circular  
122  $65 \mu\text{m}$  spot size, a repetition rate of 8Hz, and a laser fluence of  $\sim 3.5 \text{ Jcm}^{-1}$  was used. Ablation times  
123 were  $\sim 50 \text{ s}$  per spot, preceded by a 30-s background measurement and followed by 30 s of washout.  
124 Data reduction was performed by the Iolite 3 software (Paton et al., 2011). The NIST SRM 610  
125 (Pearce et al., 1997) glass and the USGS BCR2G reference materials were used as calibrator and  
126 quality control, respectively. Si was used as internal standard. Under the reported analytical  
127 conditions, the precision is better than 10% for concentrations above  $\sim 0.1 \text{ ppm}$ , and better than 5%  
128 above  $\sim 2 \text{ ppm}$ ; accuracy is always better than 10% (Petrelli et al., 2016b).

129

## 130 **4. Results**

### 131 *4.1. Crystal structure*

132 Moissanite has a closed packed structure of C (or Si) where the other cation is located in a  
133 tetrahedral site. The basic structure is cubic *3C* polytype (zincblende structure) having the shortest  
134 period of repetition of the Si-C layer. The different modes in which this basic layer can repeat along  
135 the *c* axis give a unit cell with *n* formula units and is *n* time larger than the basic polytype. The most  
136 common polytypes in synthetic material are *4H* and *6H* (hexagonal), *15R* (rhombohedral) and *3C*  
137 (cubic). The *3C* polytype was found in shocked meteorites and only rarely in terrestrial rocks  
138 (Machev et al., 2018); on the other hand, *6H*, *4H* and *15R* were found in kimberlitic, ophiolitic and  
139 volcanic rocks (i.e. Di Pierro et al, 2003; Shiryayev et al., 2011, Dobrzhinetskaya et al., 2018).

140 Hexagonal *6H* unit-cell parameters were measured by single-crystal X-ray diffraction on three  
141 Água de Pau moissanite grains resulting nearly identical. They are very similar to those reported by  
142 Capitani et al. (2007) for terrestrial moissanite and those measured for synthetic *6H*-SiC  
143 (RRUFF#R061083, La Fuente et al., 2015). The difference in colour (deep blue and green crystals  
144 were measured by SCXRD) is not related to a stabilization of different polytypes but to the presence  
145 of peculiar trace elements (Al, B, N) and vacancies (colour centres).

146

### 147 *4.2. Raman spectroscopy study*

148 Micro-Raman spectroscopy has been already exploited to discriminate among the different SiC  
149 polytypes (i.e. Shiryayev et al., 2011; Dobrzhinetskaya et al., 2018). The presence of strong covalent  
150 bonds in SiC leads to a strong Raman scattering of the vibrational modes. Moreover, *4H* and *6H*  
151 polytypes show characteristic spectra that allow an unambiguous identification. Figure 2 shows a  
152 comparison between a typical experimental spectrum acquired on a *6H* crystal (upper panel) and  
153 that obtained on a *4H* one (lower panel). The positions of the observed modes measured on ca. 40  
154 samples are in good agreement with literature data (Feldman et al., 1968a,b; Nakashima et al.,  
155 1997). The identification can be carried out using the low wavenumber planar acoustic modes (see

156 insets) and the strongest planar optic ones at  $790\text{ cm}^{-1}$  ( $6H$ -SiC) and  $777\text{ cm}^{-1}$  ( $4H$ -SiC). It is worth  
157 mentioning that, in addition to relative peak intensity effects, due to polarization, the position of  
158 some modes in SiC polytypes also shows a dependence on the angle between the direction of the  
159 incident laser beam and the crystal  $c$ -axis (Feldman et al., 1968a,b). In particular, this is true for the  
160 peaks occurring in the region between  $750\text{ cm}^{-1}$  and  $1000\text{ cm}^{-1}$ , with the notable exception of the  
161 mode at about  $797\text{ cm}^{-1}$ , which is angle and polytype independent.

162 Inclusions with unusual composition (metallic Si, Mg-, Cr-, Ti-, Fe-silicides, silicon oxy-  
163 carbides, tistarite, CAS minerals, Fe-Ti-Si-C-P metallic alloys) are reported in natural moissanite  
164 (Marshintsev et al., 1967; Mathez et al., 1995; Di Pierro et al., 2003; Shiryaev et al., 2011; Griffin et  
165 al., 2016; Dobrzhinetskaya et al., 2018). A detailed characterization of the inclusions could provide  
166 constrains about SiC crystallisation in terms of  $fO_2$ , related fluids and ultimately on the  
167 crystallization pressure as already achieved for diamonds (i.e. Anzolini et al., 2018; Nestola et al.,  
168 2018).

169 In Azorean moissanite we identified at least two types of nanometric to micrometric ( $< 40$   
170 microns) inclusions: 1) elongated transparent, 2) round-shaped dark (Fig. 3). The inclusions of type  
171 1 did not provide any Raman signals and were not identified; on the contrary, spectra of type 2  
172 inclusions show a strong peak at  $\sim 520\text{ cm}^{-1}$  not belonging to the  $6H$  host moissanite (Fig. 3). Even if  
173 we did not release the inclusions, we are confident that it can be identified as  $Si^0$ . We have  
174 compared the Raman shift of the  $Si^0$  inclusion band at about  $520\text{ cm}^{-1}$  with respect to the position of  
175 the same band measured for a synthetic  $Si^0$  using the same instrumentation during the same Raman  
176 session.

177 The band position of the synthetic  $Si^0$  measured in this work is at  $520.72\text{ cm}^{-1}$  with a full width  
178 half maximum (FWHM) equal to  $7.06\text{ cm}^{-1}$ ; the band position of our  $Si^0$  inclusion is positioned at  
179  $519.65\text{ cm}^{-1}$  with a FWHM totally comparable to the synthetic one (i.e.  $6.07\text{ cm}^{-1}$ ). Based on  
180 Weinstein and Piermarini (1975) Raman calibration performed on  $Si^0$ , such Raman band variation  
181 would correspond to a negative residual pressure  $P_{inc} = 0.2\text{ GPa}$  (see Anzolini et al., 2018 and

182 Nestola et al., 2018 for more details about the  $P_{inc}$ ). From the residual pressure and knowing the  
183 thermoelastic properties of host and inclusion, we can back-calculate the depth of formation. For  
184 example, a residual pressure of 0.2 GPa for a kyanite inclusion within a diamond provides a  
185 pressure of about 5.3 GPa at  $T = 1120^{\circ}\text{C}$  (Nestola et al., 2018). However, in case of the moissanite-  
186  $\text{Si}^0$  host-inclusion system, our data is providing a negative residual pressure, meaning that the  
187 inclusion is stretched. To explain such behavior, we can use the yield strength of moissanite, which  
188 was determined up to 18.3 GPa and  $1200^{\circ}\text{C}$  by Zhang et al. (2002). At the maximum temperature  
189 reached by the authors, the yield strength of moissanite is 4.2 GPa, at the same temperature the  
190 yield strength of diamond is about 13 GPa (Weidener et al., 1994), which means that diamond has a  
191 much bigger resistance to the plastic deformation. Therefore, during exhumation to the surface at  
192 high temperature the moissanite host, and as a consequence, the cavity around the  $\text{Si}^0$  inclusion,  
193 may have undergone a plastic expansion in addition to the elastic deformation, resulting in a  
194 stretched inclusion with negative  $P_{inc}$  at retrieval. Therefore, the application of a purely elastic  
195 geobarometry approach (see Nestola et al., 2011) to such inclusions may lead to wrong estimate of  
196 the initial conditions of entrapment.

197

#### 198 *4.3. Trace element distribution*

199 A general low content of trace elements was measured in 16 moissanite samples (Table 1  
200 APPENDIX), confirming what already observed in moissanite from kimberlite (Shiryaev et al.,  
201 2011). The few trace elements measured above the detection limits in Azorean moissanite are B, Sc,  
202 Ti, Al and V. They have a quite homogeneous distribution with values of B = 1.8 - 6.6 ppm  
203 (average 4.4 ppm), Sc = 15.5 - 17.2 ppm (average 16.2 ppm), Ti = 10.5 - 26 ppm (average 14.1  
204 ppm). The higher variability was observed for vanadium (from 0.2 to 17 ppm) and aluminium (from  
205 190 to 1415 ppm) contents.

206 As reported by Shiryaev et al. (2011) even synthetic SiC has very few trace elements content that  
207 overlaps the values of natural samples. They observed that moissanite, like diamond, is able to host



208 only atoms that can substitute Si (or C) in its structure like Al, N, B, and that most of the trace  
209 elements partition preferentially into the syngenetic inclusions (alloys, carbides and silicides).  
210 Although low, the trace elements content in kimberlitic SiC shows some variability (see Mir vs  
211 Udachnaya SiC in Shiryaev et al., 2011), and show lower B, Al, Ti and V values than the Azorean  
212 samples whereas the Sc content is similar to Aikhal SiC (Shiryaev et al., 2011).

213 The scarcity of trace elements data on moissanite and its inclusions from different rock types  
214 prevents any deep geochemical considerations.

215

216

#### 217 **4. Discussion and conclusions**

218 Two main questions must be addressed: where the Azorean moissanite originated, and how the  
219 remarkably reduced conditions were achieved in the environment. Several models have been  
220 proposed to explain how natural SiC could occur under extremely different geological settings,  
221 especially whether it has or not a mantle origin (i.e., Mathez et al., 1995; Ulmer et al., 1998; Rogers  
222 et al., 1989; Schmidt et al., 2014; Shiryaev and Gaillard, 2014; Griffin et al., 2018; Ballhaus et al.,  
223 2018). Common point of these models is the very low oxygen fugacity ( $fO_2 = 7-5$  log units below  
224 the IW buffer) and high temperature (from 700°C to 2500°C).

225 The current models are related to experiments in the peridotitic system (Ulmer et al., 1998;  
226 Schmidt et al., 2014) or to thermodynamic calculations (Mathez et al., 1995; Shiryaev and Gaillard,  
227 2014). These models also suggest that these conditions could occur locally, even at the grain scale,  
228 since the redox conditions at mantle or crustal conditions are usually oxidising (QFM-buffered).

229 Ultra-reducing C-O-H fluids were invoked to obtain such an environment that stabilizes SiC and  
230 metallic alloys (Schmidt et al., 2014; Griffin et al., 2018; Dobrzhinetskaya et al., 2018). Such  
231 reducing C-O-H fluids can be obtained for example by change the H/O ratio as a result of H<sub>2</sub>O  
232 subtraction, at carbon saturated conditions, moving the isopleths towards CH<sub>4</sub>-rich fluid, without  
233 changing  $fO_2$  (Schmidt et al., 2014). At low pressure during magma ascent, decompression can

230 trigger redox reactions in carbon-saturated melt with high-silica activity to form moissanite at  
231 around 1300°C (Shiryaev and Gaillard, 2014). Griffin et al. (2018) suggested a worldwide process  
232 in which reduced C-O-H-N fluids may be transported from deep Earth up to at least the base of the  
233 lithosphere and, depending on its thickness, different redox reactions can be triggered (i.e., with  
234 diamond or SiC formation). Mt. Carmel moissanite formation is based on this model: mantle-  
235 derived fluids dominated by CH<sub>4</sub> + H<sub>2</sub> interacted with an alkaline basalt melt at 60-100 km ( 2-3  
236 GPa) depth and 1000 °C ≥ T ≤ 1660 °C (Griffin et al., 2018; Dobrzhinetskaya et al., 2018).  
237 Nevertheless, there are no evidences of CH<sub>4</sub> dominant fluids in ol and cpx-hosted fluid inclusions at  
238 the Azores (Zanon and Frezzotti, 2014; Métrich et al., 2015; Zanon, 2015).

239 We recovered ca. 500 moissanite grains in 78 gr. of fine-grained (<0.5 mm) syenite, lacking  
240 textural information. However, the mineral assemblage of the syenite (feld, ± amph, cpx, ann, Fe-Ti  
241 oxides and sodalite or quartz) cannot be in equilibrium with extremely reduced phase like SiC or  
242 metallic Si. The Água de Pau syenites are characterised by a wealth of accessory minerals enriched  
243 in REE, Zr, and Nb are the ultimate stage of crystallisation of a trachyte (Ridolfi et al., 2003). Even  
244 if during this late stage of the chemical evolution a decrease in  $fO_2$  has been proposed (Ridolfi et al.,  
245 2003), it seems very unlikely that  $fO_2$  reached the extremely reduced conditions requested for the  
246 SiC formation. Moreover, SiC is not stable together with Fe-rich minerals like those occurring as  
247 accessory in the Água de Pau syenite.

248 Azorean moissanites are 90% the 6H polytype, suggesting that they grew at similar  $P$ - $T$   
249 conditions and degree of impurities, and that no polytype transformation occurred since their  
250 formation. The presence of Si<sup>0</sup> inclusions supports the natural origin of these grains but currently it  
251 does not provide any indication of pressure as the actual depth of formation was somehow reset to  
252 the HT-LP conditions typical of the syenite crystallization. In case of moissanite and its inclusions,  
253 it is not trivial to apply the elastic geobarometry approach unless the crystal is erupted rapidly from  
254 HP conditions like happens for the typical kimberlitic magmas. In order to prove such hypothesis, a  
255 systematic study of inclusions present in the Azorean and in kimberlitic moissanites is currently

256 under progress, aiming at applying the elastic geobarometry to all typologies of inclusions.  
257 However, such approach requires a complete revision of all thermodynamic parameters for host and  
258 inclusion, information not at moment available for many inclusions found in moissanite.

259 Furthermore, without considering the influence of pressure, assuming that Si metal was  
260 entrapped as a liquid phase by moissanite, a temperature of  $\sim 1400^\circ\text{C}$  (melting point for  $\text{Si}^0$ ) was  
261 needed. Actually, the temperature of evolved liquids at São Miguel is  $\sim 730\text{-}780^\circ\text{C}$  (Renzulli and  
262 Santi, 2000), whereas São Miguel basalts are originated at  $\approx 3\text{-}4$  GPa and  $T \approx 1300^\circ\text{C}\text{-}1400^\circ\text{C}$   
263 (Beier et al., 2008).

264 Hardly we can directly apply the current models to explain the formation of Azorean moissanite.  
265 Azores Islands are located in oceanic extensional setting; nevertheless, the enriched geochemical  
266 signature of the São Miguel magmas likely derives from the recycle of an old ( $\approx 3$  Ga) crustal  
267 component into the mantle (Béguelin et al., 2017; Schaefer et al., 2002).

268 Even if we lack textural information, starting from the point that moissanite is not a phase that  
269 normally crystallises in syenitic melts, we may hypothesise that our grains were formed by ultra-  
270 reducing (metasomatic/hydrothermal) fluids possibly reacting with the alkaline melt at some stage  
271 of the syenite formation/emplacement. The current data cannot solve whether this process occurred  
272 when alkaline magma formed by partial melting in the lithosphere or at some stage between the  
273 formation and ascent to the magma chamber.

274 A more detailed study of inclusions and the recovery of *in situ* moissanite would help to convey  
275 on a more reliable model. As far as we know, this is the first report of moissanite in a non-  
276 continental geodynamic settings, widening the tectonic settings where SiC occurred.

277

278

279

### Acknowledgments

280 This study was partially funded by Fundação para a Ciência e Tecnologia, Portugal (MARES  
281 project PTDC/GEO-FIQ/1088/2014). FN thanks the European Research Council for funding the

282 research (agreement n. 307322). Editor Marco Scambelluri, Larissa Dobrzhinetskaya and an  
283 anonymous reviewer are greatly acknowledged for their constructive comments and suggestions.  
284

## Figure and Table captions

285

286

287 **Figure 1.** Microphotograph of a typical saccaroid-textured syenite, showing the presence of  
288 sanidine, two amphiboles, apatite, quartz, pyroxene and aenigmatite.

289

290 **Figure 2.** Typical micro-Raman spectra of *6H* (upper panel) and *4H* (lower panel) polytypes. Insets:  
291 insight of the low wavenumber region; peaks position of *6H*-SiC is  $236\text{ cm}^{-1}$ ,  $242\text{ cm}^{-1}$  and  $267\text{ cm}^{-1}$   
292 peaks position of *4H*-SiC is  $196\text{ cm}^{-1}$  and  $204\text{ cm}^{-1}$ . The uncertainty on the peak positions is  $\pm 1$   
293  $\text{cm}^{-1}$ .

294

295 **Figure 3.** Analysis of two typical  $\text{Si}^0$  inclusions enclosed in *6H*-SiC crystals (A1 and A2). From left  
296 to right: low magnification image of the crystal with the inclusion, high-magnification detail of the  
297 inclusion, and  $\mu\text{RS}$  spectrum acquired on the inclusion. The  $\text{Si}^0$  peak at  $520\text{ cm}^{-1}$  is marked with a  
298 red arrow.

299

300

## Appendix material

301

302

303 **Table 1.** Trace elements composition of moissanite crystals.

304

305

- 307 Anzolini, C., Prencipe, M., Alvaro, M., Romano, C., Vona, A., Lorenzon, S., Smith, E.M., Brenker,  
308 F.E., Nestola, F. (2018) Depth of formation of super-deep diamonds: Raman barometry of CaSiO<sub>3</sub>-  
309 walstromite inclusions. *American Mineralogist*, 103, 69-74.
- 310 Ballhaus, C., Wirth, R., Fonseca, R.O.C., Blanchard, H., Pröll, W., Bragagni, A., Nagel, T.,  
311 Schreiber, A., Dittrich, S., Thome, V., Hezel, D.C., Below, R., Cieszynski, H., 2017. Ultra-high  
312 pressure and ultra-reduced minerals in ophiolites may form by lightning strikes. *Geochemical*  
313 *Perspective Letters* 5, 42–46.
- 314 Béguelin, P., Bizimis, M., Beier, C., Turner, S., 2017. Rift–plume interaction reveals multiple  
315 generations of recycled oceanic crust in Azores lavas. *Geochimica Cosmochimica Acta* 218, 132-  
316 152.
- 317 Beier, C., Haase, K.M., Abouchami, W., Krienitz, M.-S., Hauff, F., 2008. Magma genesis by rifting  
318 of oceanic lithosphere above anomalous mantle: Terceira Rift, Azores. *Geochemistry, Geophysics,*  
319 *Geosystems* 9, Q12013.
- 320 Capitani, G.C., Di Pierro, S., Tempesta, G., 2007. The 6H-SiC structure model: Further refinement  
321 from SCXRD data from a terrestrial moissanite. *American Mineralogist* 92, 403–407.
- 322 Di Pierro, S., Gnos, E., Grobety, B.H., Armbruster, T., Bernasconi, S.M., Ulmer, P., 2003. Rock-  
323 forming moissanite (natural  $\alpha$ -silicon carbide). *American Mineralogist* 88, 1817–1821.
- 324 Dobrzhinetskaya L, Mukhin P, Wang Q., Wirth R., O'Bannon E., Zhao W., Eppelbaum L.,  
325 Sokhonchuk T., 2018. Moissanite (SiC) with metal-silicide and silicon inclusions from tuff of  
326 Israel: Raman spectroscopy and electron microscope studies. *Lithos* 310-311, 355-368.
- 327 Feldman, D.W., Parker Jr., J.H., Choyke, W.J., Patrick, L., 1968a. Raman Scattering in 6H SiC.  
328 *Physical Review* 170, 698-704.
- 329 Feldman, D.W., Parker Jr., J.H., Choyke, W.J., Patrick, L., 1968b. Phonon dispersion curves by  
330 Raman scattering in SiC, polytypes 3C, 4H, 6H, 15R, and 21R. *Physical Review* 173, 787–793.

331 Griffin, W. L., Huang, J-X., Thomassot, E., Gain, S. E. M., Toledo V., O'Reilly, S. Y., 2018.  
332 Super-reducing conditions in ancient and modern volcanic systems: sources and behaviour of  
333 carbon-rich fluids in the lithospheric mantle. *Mineralogy and Petrology*  
334 <https://doi.org/10.1007/s00710-018-0575-x>.

335 Griffin, W.L., Gain, S.E.M., Adams, D.T., Huang, J-X., Saunders, M., Toledo, V., Pearson, N.J.,  
336 O'Reilly, S.Y., 2016. First terrestrial occurrence of tistarite (Ti<sub>2</sub>O<sub>3</sub>): ultra-low oxygen fugacity in  
337 the upper mantle beneath Mt. Carmel, Israel. *Geology*, 44, 815–818.

338 Janák, M., Froitzheim, N., Yoshida, K., Sasinková, V., Nosko, M., Kobayashi, T., Hirajima, T.,  
339 Vrabec, M., 2015. Diamond in metasedimentary crustal rocks from Pohorje, Eastern Alps: a  
340 window to deep continental subduction. *Journal of Metamorphic Geology* 33, 495–512.

341 Klein-BenDavid, O., Wirth, R., Navon, O., 2007. Micrometer-scale cavities in fibrous and cloudy  
342 diamonds — a glance into diamond dissolution events. *Earth and Planetary Science Letters* 264,  
343 89–103.

344 Lafuente, B., Downs, R.T., Yang, H., Stone, N. 2015. The power of databases: the RRUFF project.  
345 In: *Highlights in Mineralogical Crystallography*, T Armbruster and R M Danisi, eds. Berlin,  
346 Germany, W. De Gruyter, pp 1-30.

347 Leung, I., Guo, W., Freidman, I., Gleason, J., 1990. Natural occurrence of silicon carbide in a  
348 diamondiferous kimberlite from Fuxian. *Nature* 346, 352–354.

349 Machev, P., O'Bannon, E.F., Bozhilov, K.N., Wang, Q., Dobrzhinetskaya, L., 2018. Not all  
350 moissanites are created equal: New constraints on moissanite from metamorphic rocks of Bulgaria.  
351 *Earth and Planetary Science Letters* 498, 387–396.

352 Marshintsev, V.K., Shchelchkova, S.G., Zol'nikov, G.V., Voskresenskaya, V.B., 1967. New data on  
353 moissanite from the Yakutian kimberlites. *Geologiya i Geofizika* 12, 22–31.

354 Mathez, E.A., Fogel, R.A., Hutcheon, I.D., Marshintsev, V.K., 1995. Carbon isotopic composition  
355 and origin of SiC from kimberlites of Yakutia, Russia. *Geochimica et Cosmochimica Acta*, 59,

356 781–791.

357 Métrich, N., Zanon, V., Créon, L., Hildenbrand, A., Moreira, M., Marques, F.O., 2015. Is the  
358 “Azores hotspot” a wetspot? Insights from the geochemistry of the fluid and melt inclusions in  
359 olivines of Pico basalts. *Journal of Petrology* 55(2), 377-393.

360 Nakashima, S., Harita, H., 1997. Raman investigation of SiC polytypes. *Physica Status Solidi*  
361 A162, 39–64.

362 Nestola, F., Nimis, P., Ziberna, L., Longo, M., Marzoli, A., Harris, J.W., Manghnani, M.H.,  
363 Fedortchouk, Y., 2011. First crystal-structure determination of olivine in diamond: Composition  
364 and implications for provenance in the Earth's mantle. *Earth and Planetary Science Letters*, 305,  
365 249-255.

366 Nestola, F., Prencipe, M., Nimis, P., Sgreva, N., Perritt, S.H., Chinn, I.L., Zaffiro, G., 2018. Toward  
367 a robust elastic geobarometry of kyanite inclusions in eclogitic diamonds. *Journal of Geophysical*  
368 *Research – Solid Earth*, 123, 6411-6423.

369 Paton C., Hellstrom J., Paul B., Woodhead J., Hergt J., 2011. Iolite: Freeware for the visualisation  
370 and processing of mass spectrometric data. *Journal of Analytical Atomic Spectrometry* 26, 2508-  
371 2518.

372 Pearce J.G.N., Perkins W.T., Westgate J.A., Gorton M.P., Jackson S.E., Neal C.R., Chenery S.P.,  
373 1997. A compilation of new and published major and trace element data for NIST SRM 610 and  
374 NIST SRM 612 glass reference materials. *Geostandards Newsletter* 21, 115-144.

375 Perraki, M., Faryad, S.W., 2014. First finding of microdiamond, coesite and other UHP phases in  
376 felsic granulites in the Moldanubian Zone: implications for deep subduction and a revised  
377 geodynamic model for Variscan Orogeny in the Bohemian Massif. *Lithos* 202, 157–166.

378 Petrelli, M., Laeger, K., Perugini, D., 2016a. High spatial resolution trace element determination of  
379 geological samples by laser ablation quadrupole plasma mass spectrometry: Implications for glass  
380 analysis in volcanic products. *Geosciences Journal*, 20, 1–13.



381 Petrelli, M., Morgavi, D., Vetere, F., Perugia, D., 2016b. Elemental imaging and petro-  
382 volcanological applications of an improved Laser Ablation Inductively Coupled Quadrupole Plasma  
383 Mass Spectrometry. *Periodico di Mineralogia* 85(1), 25-39.

384 Renzulli, A., Santi, P., 2000. Two stage fractionation history of the alkali basalt-trachyte series of  
385 Sete Cidades volcano (São Miguel Island, Azores). *Europran Journal of Mineralogy*. 12(2), 469-  
386 494.

387 Ridolfi, F., Renzulli, A., Santi, P., Upton, B.G.J., 2003. Evolutionary stages of crystallization of  
388 weakly peralkaline syenite: evidence from ejecta in the plinian deposits of Agua de Pau volcano  
389 (São Miguel Azores Islands). *Mineralogical Magazine*, 67(4), 749-767.

390 Rogers K.A, Courtney S.F. Seelye R., McCulloch B.A., Mulholland I. (1989) An occurrence of  
391 “moissanite” (SiC) from seddonville, west coast, New Zealand. *New Zealand Natural Sciences* 16,  
392 105-108.

393 Schaefer, B.F., Turner, S., Parkinson, I., Rogers, N., Hawkesworth, C., 2002. Evidence for recycled  
394 Archaean oceanic mantle lithosphere in the Azores plume. *Nature* 420, 304-307.

395 Schmidt M.W., Gao G., Golubkova, A., Rohrbach, A., Connolly, J.A.D., 2014. Natural moissanite  
396 (SiC) – a low temperature mineral formed from highly fractionated ultra-reducing COH-fluids.  
397 *Progress in Earth and Planetary Science* 2014, 1-27.

398 Sheldrick, G.M., 2008. A short history of SHELX. *Acta Crystallographica A*64, 112–122.

399 Shiryayev A.A., Gaillard, F., 2014. Local redox buffering by carbon at low pressures and the  
400 formation of moissanite – natural SiC. *European Journal of Minerals*, 26(1), 53-59.

401 Shiryayev, A.A., Griffin, W.L. Stoyanov, E., 2011. Moissanite (SiC) from kimberlites: Polytypes,  
402 trace elements, inclusions and speculations on origin. *Lithos* 122, 152–164.

403 Sibrant, A.L.R., Marques, F.O., Hildenbrand, A., Boulesteix, T., Costa, A.C.G., Catalão, J., 2016.  
404 Deformation in a hyper-slow oceanic rift: insights from the tectonics of the S. Miguel Island (Ter-  
405 ceira Rift, Azores). *Tectonics* 35(2), 425–446.

406 Trumbull, R.B., Yang, J.-S., Robinson, P.T., Di Pierro, S., Vennemann, T., Wiedenbeck, M., 2009.  
407 The carbon isotope composition of natural SiC (moissanite) from the Earth's mantle: new  
408 discoveries from ophiolites. *Lithos* 113, 612–620.

409 Ulmer, G.C., Grandstaff, D.E., Woermann, E., Gobbels, M., Schonitz, M., Woodland, A.B., 1998.  
410 The redox stability of moissanite (SiC) compared with metal-metal oxide buffers at 1773 K and at  
411 pressures up to 90 kbar. *Neues Jahrbuch Mineralogie, Abhandlungen* 172, 279–307.

412 Wallenstein, N., Duncan, A.M., Guest, J.E., Almeida, M.H., 2015. Eruptive history of Fogo  
413 Volcano, São Miguel, Azores. In: Gaspar JL, Guest JE, Duncan AM, Barriga FJAS, Chester DK  
414 (eds) *Volcanic Geology of São Miguel Island (Azores Archipelago)*. Geological Society, London,  
415 *Memoirs*, pp 105–123

416 Weidener, D.J., Wang, Y., Vaughan, M.T., 1994. Strength of diamond. *Science*, 266, 419-422.

417 Weinstein, T., Piermarini, G.J., 1975. Raman scattering and phonon dispersion in Si and GaP at  
418 very high pressure. *Physical Review B*, 12, number 4.

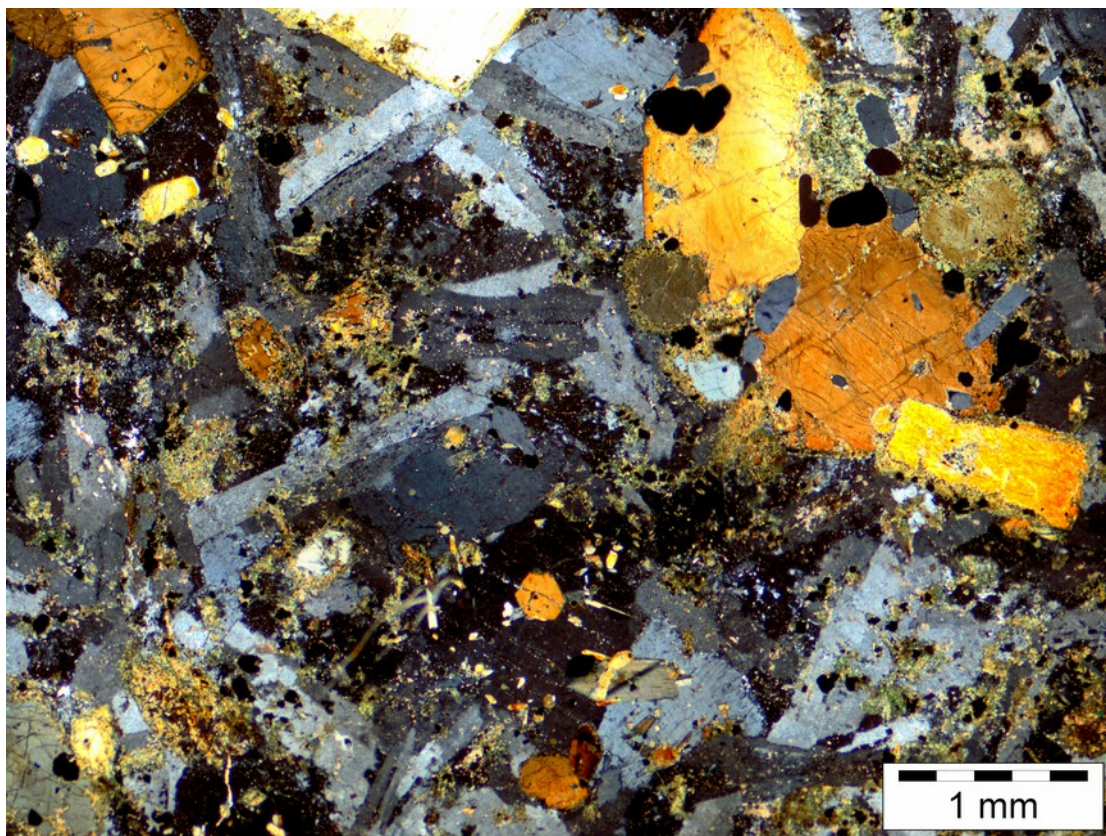
419 Widom, E., Gill, J.B., Schmincke, H.U., 1993. Syenite nodules as long term record of magmatic  
420 activity in Agua de Pau Volcano, Sao Miguel, Azores. *Journal of Petrology*, 34, 929-953.

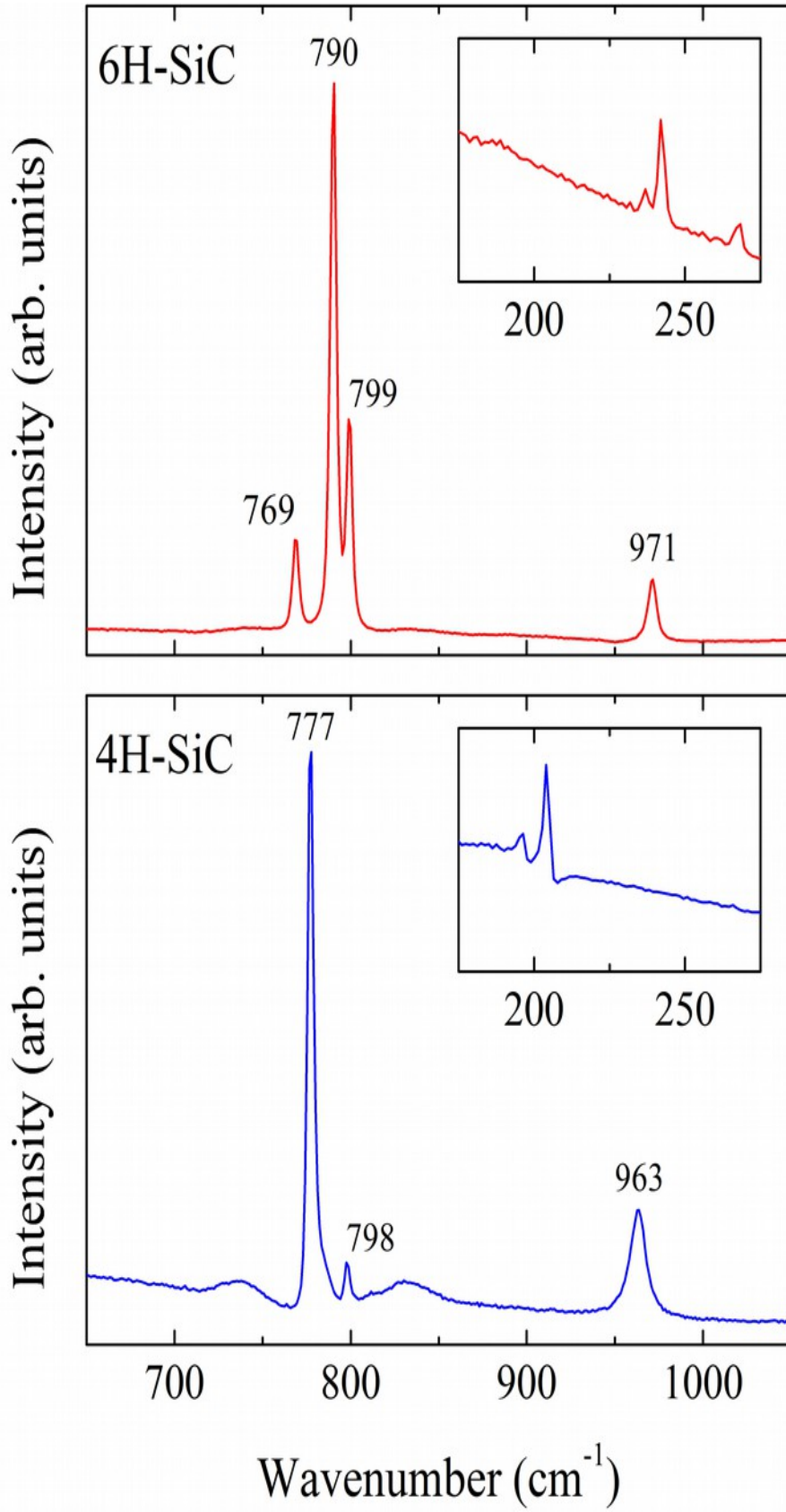
421 Zanon, V., 2015. Conditions for mafic magma storage beneath fissure zones at oceanic islands. The  
422 case of São Miguel island (Azores archipelago). In Caricchi L & Blundy J.D. (eds) *Chemical,*  
423 *physical and temporal evolution of magmatic systems*. Geological Society of London, special  
424 publication, 442, 85-104.

425 Zanon, V., Frezzotti, M.L., 2013. Magma storage and ascent conditions beneath Pico and Faial  
426 islands (Azores Islands). A study on fluid inclusions. *Geochemistry, Geophysics, Geosystems* 14  
427 (9), 3494–3514.

428 Zhang, J. Wang L., Weidner D.J., Uchida, T., Xu J-A., 2002. The strength of moissanite. American  
429 Mineralogist 87(7) 1005-1008.

430

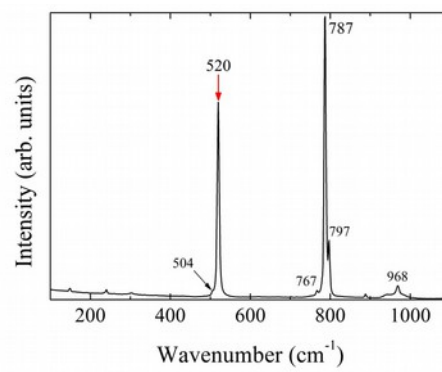




A1



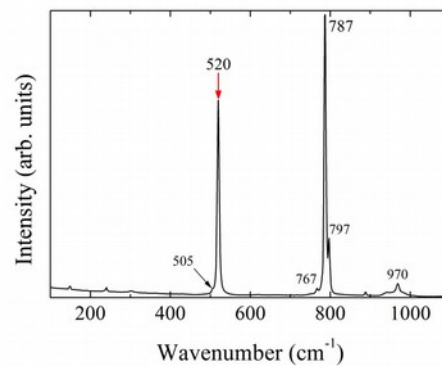
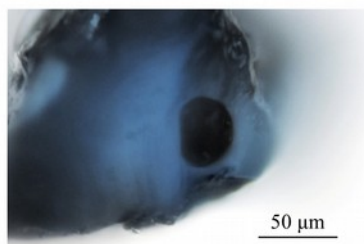
100  $\mu\text{m}$



A2



100  $\mu\text{m}$



434

435

Table 1

|    | SiC_146 |       | SiC_147 |      | SiC_148 |      | SiC_149 |      | SiC_150 |       | SiC_151 |      | SiC_152 |      | SiC_153 |      |
|----|---------|-------|---------|------|---------|------|---------|------|---------|-------|---------|------|---------|------|---------|------|
|    | µg/g    | 2s    | µg/g    | 2s   | µg/g    | 2s   | µg/g    | 2s   | µg/g    | 2s    | µg/g    | 2s   | µg/g    | 2s   | µg/g    | 2s   |
| B  | -       | -     | 1.8     | 0.7  | 4.1     | 0.7  | 6.5     | 0.8  | 6.6     | 1.5   | 3.6     | 0.7  | 5.6     | 0.7  | 5.6     | 1.2  |
| Al | 270     | 9     | 453     | 14   | 345     | 7.8  | 192     | 6.4  | 1106    | 43    | 256     | 8.8  | 445     | 18   | 304     | 11   |
| Sc | 16      | 0.5   | 17      | 0.7  | 16      | 0.5  | 16      | 0.6  | 16      | 0.7   | 16      | 0.6  | 16      | 1.1  | 16      | 0.7  |
| Ti | 11      | 1.1   | 11      | 0.9  | 12      | 1.2  | 15      | 1.3  | 27      | 2.8   | 10      | 1    | 15      | 1.6  | 16      | 1.4  |
| V  | 0.4     | 0.06  | 0.9     | 0.1  | 3.6     | 0.2  | 8.6     | 0.3  | 18      | 0.78  | 0.22    | 0.06 | 5.4     | 0.3  | 6.7     | 0.3  |
| Cr | -       | -     | -       | -    | 0.83    | 0.55 | -       | -    | -       | -     | -       | -    | -       | -    | -       | -    |
| Zn | 0.64    | 0.55  | -       | -    | 0.29    | 0.16 | 0.52    | 0.21 | 0.64    | 0.36  | 1       | 1.3  | 0.42    | 0.19 | 0.86    | 0.73 |
| Ga | -       | -     | -       | -    | -       | -    | -       | -    | -       | -     | -       | -    | -       | -    | -       | -    |
| Sr | -       | -     | -       | -    | -       | -    | -       | -    | -       | -     | -       | -    | -       | -    | -       | -    |
| Zr | -       | -     | -       | -    | -       | -    | -       | -    | -       | -     | -       | -    | -       | -    | -       | -    |
| Nb | -       | -     | -       | -    | -       | -    | -       | -    | -       | -     | -       | -    | -       | -    | -       | -    |
| Mo | -       | -     | -       | -    | -       | -    | -       | -    | -       | -     | -       | -    | -       | -    | -       | -    |
| Sn | 0.18    | 0.05  | 0.16    | 0.05 | 0.21    | 0.05 | 0.21    | 0.05 | 0.18    | 0.07  | 0.15    | 0.04 | 0.13    | 0.06 | 0.19    | 0.10 |
| Ba | -       | -     | -       | -    | -       | -    | -       | -    | -       | -     | -       | -    | -       | -    | -       | -    |
| Ce | -       | -     | -       | -    | -       | -    | -       | -    | -       | -     | -       | -    | -       | -    | -       | -    |
| Eu | -       | -     | -       | -    | -       | -    | -       | -    | -       | -     | -       | -    | -       | -    | -       | -    |
| Tm | -       | -     | -       | -    | -       | -    | -       | -    | -       | -     | -       | -    | -       | -    | -       | -    |
| Hf | -       | -     | -       | -    | -       | -    | -       | -    | -       | -     | -       | -    | -       | -    | -       | -    |
| Ta | -       | -     | -       | -    | -       | -    | -       | -    | -       | -     | -       | -    | -       | -    | -       | -    |
| Pb | 0.038   | 0.018 | -       | -    | 0.17    | 0.28 | 0.03    | 0.01 | 0.047   | 0.028 | 0.09    | 0.1  | -       | -    | -       | -    |
| U  | -       | -     | -       | -    | -       | -    | -       | -    | -       | -     | -       | -    | -       | -    | -       | -    |

437

Table 1

| SiC_154 | SiC_155 |      | SiC_156 |       | SiC_157 |       | SiC_158 |       | SiC_159 |      | SiC_160 |      | average | st. dev. | d. l. |       |
|---------|---------|------|---------|-------|---------|-------|---------|-------|---------|------|---------|------|---------|----------|-------|-------|
| µg/g    | 2s      | µg/g | 2s      | µg/g  | 2s      | µg/g  | 2s      | µg/g  | 2s      | µg/g | 2s      | µg/g | µg/g    | µg/g     | µg/g  |       |
| 2.8     | 0.6     | 2.0  | 0.5     | 5.3   | 0.8     | 6.4   | 0.8     | 2.1   | 0.6     | -    | -       | 4.4  | 1.3     | 4.4      | 1.8   | 1     |
| 1237    | 36      | 581  | 18      | 179   | 4.4     | 198   | 5.2     | 751   | 19      | 1415 | 33      | 201  | 6.4     | 529      | 411   | 0.8   |
| 16      | 0.6     | 16   | 0.6     | 16    | 0.6     | 16    | 0.5     | 16    | 0.6     | 16   | 0.5     | 16   | 0.8     | 16.2     | 0.4   | 0.2   |
| 16      | 1.3     | 10   | 0.9     | 14    | 1.2     | 23    | 1.5     | 10    | 0.9     | 11   | 1.1     | 11   | 1.6     | 14       | 5     | 1     |
| 5.3     | 0.3     | 0.45 | 0.18    | 6.9   | 0.3     | 17    | 0.4     | 0.47  | 0.07    | 0.36 | 0.06    | 1.9  | 0.2     | 5        | 6     | 0.1   |
| 1.2     | 0.6     | -    | -       | -     | -       | -     | -       | -     | -       | -    | -       | -    | -       | -        | -     | 0.6   |
| 0.28    | 0.16    | -    | -       | 0.38  | 0.17    | 0.35  | 0.21    | 0.67  | 0.41    | -    | -       | 0.67 | 0.29    | 0.6      | 0.2   | 0.3   |
| -       | -       | -    | -       | -     | -       | -     | -       | -     | -       | -    | -       | -    | -       | -        | -     | 0.02  |
| -       | -       | -    | -       | -     | -       | -     | -       | -     | -       | -    | -       | -    | -       | -        | -     | 0.005 |
| -       | -       | -    | -       | -     | -       | -     | 0.023   | -     | -       | -    | -       | -    | -       | -        | -     | 0.01  |
| -       | -       | -    | -       | -     | -       | -     | -       | -     | -       | -    | -       | -    | -       | -        | -     | 0.006 |
| -       | -       | -    | -       | -     | -       | -     | -       | -     | -       | -    | -       | -    | -       | -        | -     | 0.06  |
| 0.10    | 0.03    | 0.14 | 0.05    | 0.16  | 0.04    | 0.19  | 0.038   | 0.16  | 0.05    | 0.14 | 0.05    | 0.14 | 0.07    | 0.16     | 0.03  | 0.08  |
| -       | -       | -    | -       | -     | -       | -     | -       | -     | -       | -    | -       | -    | -       | -        | -     | 0.02  |
| -       | -       | -    | -       | -     | -       | -     | -       | -     | -       | -    | -       | -    | -       | -        | -     | 0.003 |
| -       | -       | -    | -       | -     | -       | -     | -       | -     | -       | -    | -       | -    | -       | -        | -     | 0.004 |
| -       | -       | -    | -       | -     | -       | -     | -       | -     | -       | -    | -       | -    | -       | -        | -     | 0.002 |
| -       | -       | -    | -       | -     | -       | -     | -       | -     | -       | -    | -       | -    | -       | -        | -     | 0.008 |
| -       | -       | -    | -       | -     | -       | -     | -       | -     | -       | -    | -       | -    | -       | -        | -     | 0.002 |
| 0.034   | 0.015   | -    | -       | 0.023 | 0.012   | 0.037 | 0.017   | 0.037 | 0.044   | -    | -       | 0.09 | 0.053   | 0.060    | 0.05  | 0.02  |
| -       | -       | -    | -       | -     | -       | -     | -       | -     | -       | -    | -       | -    | -       | -        | -     | 0.003 |

439