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# Mineralogical and geochemical features of the Allan Hills tephra, South Victoria Land: Implications for mid-Pleistocene volcanic activity in Antarctica

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1 **Mineralogical and geochemical features of the Allan Hills tephra, South**  
2 **Victoria Land: Implications for mid-Pleistocene volcanic activity in**  
3 **Antarctica**

4  
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17

18 **Abstract:** More than 100 volcanoes have been discovered in Antarctica, however, the  
19 sources of many Antarctic tephras are not yet constrained. In this study, four tephra samples  
20 recovered from the environment of Site 27 on an area of blue ice at Allan Hills, South  
21 Victoria Land, provide information on magma and crustal sources for the tephra erupted in  
22 Antarctica. We report data on the chemistry of Antarctic tephra glasses and minerals  
23 analysed by electron microscopy, electron probe microanalysis and laser ablation  
24 inductively coupled plasma mass spectrometry. The tephra amphibole chemistry indicates  
25 magma residence at ~1 GPa and ~1100 °C. Abundant Ca-Al-Si-rich minerals imply that the  
26 magma ascended from a reservoir at  $29.4 \pm 2.7$  km depth was affected by the assimilation  
27 of calc-silicate crust. The high Fe and Ti contents in the magmatic minerals and the trace  
28 element patterns of the glasses typical of a hydrothermally altered oceanic crust suggest that  
29 the Allan Hills tephra originated from a mantle plume-derived magma. The fragmented  
30 morphology of the glasses implies that the magmatic activity was associated with explosive  
31 eruptions during the mid-Pleistocene. The chemistry of the glasses and the presence of  
32 rhönite and Al-rich spinel minerals suggest that the magma might be genetically related to  
33 the currently active McMurdo volcanic group.

34

35 **Keywords:** volcanic tephra; Antarctica; Allan Hills; mantle plume; Pleistocene;

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37 **1. Introduction**

38 Antarctica is a volcanically active region (Kyle et al., 1990; Wörner, 1999; Van Wyk de  
39 Vries, 2017; Iverson et al., 2017). A number of “dust” bands visible on the surface of blue  
40 ice at Allan Hills, South Victoria Land are reported to be volcanic ashes (tephra) (Nishio et  
41 al., 1985; Dunbar et al., 1995; Spaulding 2012; 2013; Iverson et al., 2014; 2017). Tephra

42 layers in blue ice result from explosive eruptions, thus providing excellent time-lines for the  
43 assessment of climate change, thermal anomalies and volcanic activity in polar regions (Keys  
44 et al., 1977; Ponomareva et al., 2013; Dunbar et al., 2017; Narcisi et al., 2012; 2016; 2017).  
45 However, the sources and ages of many Antarctic tephra are not yet constrained. This fact  
46 hampers the use of tephra for establishing correlations with paleo-climatic archives. This  
47 study aims to (i) identify the mineralogical and chemical composition of the dated tephra  
48 particles from the environment of Site 27 in the Allan Hills blue ice area (BIA), South  
49 Victoria Land, (ii) interpret this information in terms of the physical-chemical conditions of  
50 magmatic crystallization and (iii) obtain better constraints on the origin of tephra. Moreover,  
51 the results presented here may be used to improve our interpretation of paleo-environmental  
52 records (Keeling and Whorf, 2004) in Antarctica. In this study, we investigate four tephra  
53 samples recovered from the environment of Site 27, allowing us to elucidate the presence of  
54 multiple magma sources in the Southern Victoria Land.

55

## 56 **2. Materials and Methods**

57 Four samples (labelled BIT10, BIT12, SURF and CORE) were collected from englacial  
58 tephra at Site 27 in the Allan Hills BIA (Fig. 1, Table 1). Glaciological studies suggest  
59 steady-state conditions allowing the long-term continuity of the ice areas as well as that old  
60 ice is located at the surface (Spaulding et al., 2012; 2013). Each tephra sample is derived  
61 from a cubic meter of ice. The ice is first melted, followed by decantation of the water and  
62 storage of the complete (unfiltered) sample. The insoluble residue of the tephra is extracted  
63 from melted ice samples using 0.2- $\mu\text{m}$  Nuclepore polycarbonate filters. The melt water  
64 volume for each of these samples is from ~150 mL to ~250 mL. Map coordinates for each  
65 sample are given in Table 1. SURF was collected from the same ash layer as BIT10, while  
66 CORE was sampled 24.25 m up flow from SURF, extracted from an ice core at a depth of

67 ~3.5 m. Stratigraphically, BIT10, SURF and CORE all represent the same tephra layer,  
68 which is dated at ~114.7 ka, according to a time scale developed for Site 27 or ice core S27  
69 (Spaulding et al., 2012; 2013; Higgins et al., 2015), whereas the glass-rich BIT12 sample  
70 (Fig. 2) is dated by  $^{40}\text{Ar}/^{39}\text{Ar}$  method at  $202 \pm 7$  ka (Iverson, 2017).

71 The tephra samples were carefully embedded into epoxy resin, polished with SiC paper  
72 and diamond pastes and then investigated at the Géosciences Environnement Toulouse  
73 (GET) laboratory in France using a JEOL JSM-6360 LV scanning electron microscope, with  
74 energy dispersive spectroscopy (EDS) coupled with an automatic particle analyzer controlled  
75 by the “Esprit” program working in the “Feature” module. The backscattered electron (BSE)  
76 imaging was performed coupled with EDS mapping (Table 1, Supplementary Dataset)  
77 following the analytical protocol previously developed (Borisova et al., 2012; 2013) and  
78 described below. The solid particles (glasses and minerals) in each sample were initially  
79 distinguished based on their grey tones on the BSE images, being classified using the EDS  
80 technique (Table 1, Supplementary Dataset), and then analysed by electron probe  
81 microanalysis (EPMA) (Figs. 2, S1–S3). The most representative particles include glass,  
82 plagioclase, quartz, alkali feldspar, albite, spinels, iron silicate, clinopyroxene,  
83 orthopyroxene, kaersutite and Ca-Al-rich amphibole, ilmenite, rhönite and carbonates. These  
84 latter particles, together with other unclassified particles, are then used to interpret the tephra  
85 provenances. The minimum size of the analysed particles is 12 to 80  $\mu\text{m}$ , with a maximum  
86 size ranging from 100 to 200  $\mu\text{m}$ , depending on the sample (see Figs 2, S1-S3). The number  
87 of compositionally homogeneous particles analyzed by BSE-EDS method ranges from 190  
88 to 270 per sample. Table 1 and the Supplementary Dataset summarize the mineral and glass  
89 contents in the four tephra samples obtained by back-scattered-electron-energy-dispersive X-  
90 ray spectroscopy (BSE-EDS) mapping.

91 Major- and minor-element compositions of glasses and minerals were determined on  
92 embedded samples using a CAMECA SX-50 instrument (GET, Toulouse, France), following  
93 the analytical protocol previously developed (Borisova et al., 2012; 2013). Additionally, the  
94 BIT12 glasses were analysed using a CAMECA SX-Five instrument (Centre Castaing,  
95 Toulouse, France). Tables 2, S1–S9 and the Supplementary Dataset present the complete  
96 dataset and analytical conditions applied during EPMA and femtosecond laser ablation  
97 inductively coupled plasma mass spectrometry (fs-LA-ICP-MS). For the spot analyses and  
98 mineral profiling, the electron beam was set at an accelerating voltage of 15 kV, with a probe  
99 current of 10–20 nA for minerals, 10 nA for glasses and a spot diameter on the sample of 4  
100  $\mu\text{m}$  (CAMECA SX-50) to defocused 10  $\mu\text{m}$  (CAMECA SX-Five). Sodium was analysed first  
101 of all to assure minimal loss during EPMA; the applied analytical conditions allowed an  
102 optimal signal for the major and minor elements and a better internal precision. Such  
103 conditions are in accordance with recommendations given by Kuehn et al. (2011) for use in  
104 tephrochronology to ensure minimal sodium loss during EPMA. The following synthetic or  
105 natural reference materials were used: albite (Na), periclase (Mg), corundum (Al), sanidine  
106 (K), wollastonite (Si and Ca), pyrophanite (Ti), hematite (Fe), chromium oxide (Cr), and  
107 topaz (F). An acquisition time of 10 s was used per element on the peak (by CAMECA SX-  
108 50 and CAMECA SX-Five) in glasses and minerals and an acquisition time of 5 s was used  
109 per peak of Na (by CAMECA SX-Five) in the BIT12 glasses and 5 s per element on the  
110 background (by CAMECA SX-50 and CAMECA SX-Five). The analytical uncertainties (1–  
111 3 wt.% relative for major elements) are evaluated using MPI-DING reference glasses (T1-G,  
112 ATHO-G and StHs6/80-G, Table S3) as described by Jochum et al. (2006). The detection  
113 limits for major and minor elements in the main minerals, as well as glasses, are similar to  
114 those previously described by Borisova et al. (2012). The detection limit for F under the  
115 CAMECA SX-50 conditions is 700 ppm.

116 The major and trace element composition of the BIT12 glasses and minerals, as well as  
117 the glass-hosted inclusions of micrometric size, were measured and identified by fs-LA-  
118 ICP-MS at the Max Planck Institute for Chemistry, Mainz, Germany (Jochum et al., 2014)  
119 (see Table 2, Tables S1 and S2). Nine line scan analyses of 500  $\mu\text{m}$  length each were  
120 performed on the BIT12 sample. Each of nine scan fs-LA-ICP-MS spectra has been  
121 thoughtfully analysed, and the spectra of the predominant “matrix” have been identified and  
122 separated from the “inclusion” spectra based on the characteristic peaks of Si and Na in those  
123 of “inclusions” (Fig. 2). The both analyzed “matrix” glasses and “inclusions” are essential  
124 components of the tephra analyzed by fs LA-ICP-MS (Fig. 2). The “matrix” composition was  
125 obtained based on 333 single measurements by fs LA-ICP-MS, whereas “inclusions” have  
126 been quantified based on the well-known method of inclusion analysis by laser ablation (e.g.,  
127 Borisova et al., 2012; 2013). The analyzed “inclusions” are not always visible on the images  
128 obtained by electron microscopy (Fig. 2), since their identification and quantification is based  
129 solely on the fs LA-ICP-MS spectra. For the evaluation of the “matrix” and “inclusions” data,  
130 we have rejected the first 1 to 4 measurements per a scan line corresponding to a range of  
131 unstable conditions (unstable laser; relative higher proportion of (contaminated) surface  
132 material).

133 The LA-ICP-MS system was equipped with a femtosecond laser NWRFemto200  
134 (Electro Scientific Industries, New Wave Research Division, Portland, OR, USA) (Jochum  
135 et al., 2014) and coupled with a Thermo Finnigan sector-field ICP-MS Element 2. Table S2  
136 lists the main operating parameters, in addition to a detailed description of the Thermo  
137 Element 2 mass spectrometer at MPIC already given by Jochum et al. (2007). This system is  
138 fitted with a Ti-sapphire-based ultra-fast amplifier delivering laser pulses shorter than 130 fs.  
139 The amplifier produces a laser output wavelength of 200 nm via highly efficient harmonic  
140 generation of the fundamental wavelength. The laser beam is introduced into a high-

141 performance New Wave Large Format cell, which is a two-volume ablation cell capable of  
142 generating wash-out times <1 s and accommodating multiple samples and reference  
143 materials. We used NIST 610 as the calibration material and new reference values (Jochum  
144 et al., 2011). Spot size and repetition rate (used for the investigation of the tephra “matrix”  
145 and the reference glasses) were 40  $\mu\text{m}$  and 50 Hz, respectively, at a fluence of 0.7  $\text{J cm}^{-2}$ .  
146 We used line scan analysis, with a scan speed of 5  $\mu\text{m s}^{-1}$ . The micro-size “inclusions” were  
147 investigated with a spot size of 25  $\mu\text{m}$  at a fluence of 0.6  $\text{J cm}^{-2}$ , with a scan speed of 1  $\mu\text{m}$   
148  $\text{s}^{-1}$ .

149 The ICP-MS measurements were performed in low mass resolution mode ( $M/\Delta M =$   
150 300), using a combination of magnetic and electrical scan modes. The analysis time for a 1-  
151 pass measurement is about 1.5 s, while the whole ablation time is 100 s for the “matrix” and  
152 50 s for “inclusions” numbered 1 to 10. The following isotopes were used in the multi-  
153 element analyses:  $^7\text{Li}$ ,  $^{11}\text{B}$ ,  $^{23}\text{Na}$ ,  $^{25}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ,  $^{43}\text{Ca}$ ,  $^{47}\text{Ti}$ ,  $^{51}\text{V}$ ,  $^{53}\text{Cr}$ ,  $^{55}\text{Mn}$ ,  $^{57}\text{Fe}$ ,  $^{59}\text{Co}$ ,  $^{62}\text{Ni}$ ,  
154  $^{65}\text{Cu}$ ,  $^{66}\text{Zn}$ ,  $^{75}\text{As}$ ,  $^{85}\text{Rb}$ ,  $^{88}\text{Sr}$ ,  $^{89}\text{Y}$ ,  $^{90}\text{Zr}$ ,  $^{93}\text{Nb}$ ,  $^{133}\text{Cs}$ ,  $^{137}\text{Ba}$ ,  $^{139}\text{La}$ ,  $^{140}\text{Ce}$ ,  $^{141}\text{Pr}$ ,  $^{146}\text{Nd}$ ,  $^{147}\text{Sm}$ ,  
155  $^{151}\text{Eu}$ ,  $^{157}\text{Gd}$ ,  $^{159}\text{Tb}$ ,  $^{163}\text{Dy}$ ,  $^{165}\text{Ho}$ ,  $^{167}\text{Er}$ ,  $^{169}\text{Tm}$ ,  $^{173}\text{Yb}$ ,  $^{175}\text{Lu}$ ,  $^{178}\text{Hf}$ ,  $^{181}\text{Ta}$ ,  $^{208}\text{Pb}$ ,  $^{232}\text{Th}$ , and  
156  $^{238}\text{U}$ . Offline data reduction was performed by the same mode by calculating the gas blank  
157 corrected ion intensities of the trace element isotopes of interest, relative to  $^{43}\text{Ca}$ . Routine  
158 calculations programmed in Excel rejected obvious outliers by Jochum et al. (2007). In  
159 addition, the major element concentrations (including CaO wt.%) were adjusted  
160 (independently from trace elements) to a total oxide content of 97 wt.%, which is minimal  
161 content of the total oxide sum obtained by EPMA (Table S3, the Supplementary Dataset).  
162 The reproducibility (% RSD, relative standard deviation) of the fs-LA-ICP-MS analyses is  
163 1–3% as demonstrated by the analyses of the most homogeneous glasses, such as, basaltic  
164 glass KL2-G (MPI-DING series) (Borisova et al., 2010; Jochum et al., 2006). For example,  
165 the concentration data for KL2-G agree with the reference values within 1–5% (Jochum et



166 al., 2014). Because of sample heterogeneities, the reproducibility of the “matrix”  
167 measurements of BIT12 tephra is lower (about 10–25%). The uncertainty of the data of the  
168 small ( $\mu\text{m}$ -size) “inclusions” is strongly dependent on the concentration and generally varies  
169 between 10% and 30%. The proposed contents of  $\text{K}_2\text{O}$  in the BIT12 tephra glasses given in  
170 Figure 3 are calculated according to the measured  $\text{Na}_2\text{O}$  contents and an average  $\text{Na}_2\text{O}/\text{K}_2\text{O}$   
171 ratio characteristic of that measured in the BIT12 glasses by EPMA (see Table S3,  
172 Supplementary Dataset).

173

### 174 **3. Results**

175 The common feature of the investigated tephra samples is the presence of magmatic Ca  
176 amphiboles, titanomagnetites (up to 20 rel.%, Table 1), Ti-augites (up to 19 rel.%),  
177 plagioclases (up to 18 rel.%), and mildly peralkaline to alkaline glasses with quartz-  
178 normative compositions (up to 84 rel.%, see Fig. 2, Table S3, Supplementary Dataset).

179 BIT10 is a fine grained tephra ( $\leq 100 \mu\text{m}$ ) with fragments and agglomerations of the  
180 volcanic particles composed of ferrokaersutite, kaersutite, ferro-edenite and plagioclase, as  
181 well as Ti-augite, apatite, anorthoclase, olivine, ilmenite, rhönite grains, and glasses of  
182 trachyandesitic, trachytic to phonolitic composition (Figs. 3, S1). The amphiboles are  
183 identified according to the classification of Leake et al. (1997). Table 1 and Tables S4–S9  
184 show that the BIT10 sample contains magmatic Ca amphibole (Mg# 37–47,  $\text{TiO}_2 = 3.8\text{--}5.8$   
185 wt.%), Ti-augite ( $\text{TiO}_2 = 4.7\text{--}5.7$  wt.%), olivine ( $\text{Fo}_{77\text{--}80}$ ,  $\text{CaO} = 0.4\text{--}1.0$  wt.%), plagioclase  
186 ( $\text{An}_{40\text{--}66}$ ,  $\text{FeO} = 1.2$  wt.%), titanomagnetite ( $\text{Usp}_{89}$ ), ilmenite ( $\text{Ilm}_{92\text{--}94}$ ) and F-apatite. Two Ca-  
187 Mg-Fe carbonate and two quartz particles are detected by the BSE-EDS method (Table 1,  
188 Supplementary Dataset). Moreover, abundant metamorphic Ca-Al-rich tschermakite  
189 amphiboles are identified in this sample. Three ilmenite particles (P216, P217 and P218)  
190 were detected and analysed by BSE-EDS mapping of the sample, being used here to estimate

191 the magmatic temperature and oxygen fugacity ( $f_{O_2}$ ) based on the Fe-Ti oxide  
192 geothermobarometer (Ghiorso and Evans, 2008) (Table S8). Pairs of ilmenite–  
193 titanomagnetite reflect the magmatic mineral equilibrium at a temperature of  $1105 \pm 15$  °C  
194 with redox conditions (expressed in logarithmic units,  $\log(f_{O_2})$ , relative to the redox buffer of  
195 nickel-nickel oxide, NNO) varying from NNO-1.3 to NNO-0.8 (Table S8).

196 BIT12 is a fragmented glass-rich tephra sample composed of 50 – 200  $\mu\text{m}$ -sized glass  
197 fragments of trachytic composition with typical bubble-wall appearance and fluidal texture  
198 ( $\text{SiO}_2 = 58 - 68$  wt.%;  $\text{Na}_2\text{O} + \text{K}_2\text{O} = 7.6 - 9.4$  wt.%), plagioclase ( $\text{An}_{33-57}$ ,  $\text{FeO} = 0.14 -$   
199  $0.34$  wt.%), titanomagnetite ( $\text{Usp}_{83-86}$ ) analysed by EPMA (Fig. 3, Tables S3, S5, S8), as  
200 well as  $\text{SiO}_2$  grains and glass-hosted “inclusions” identified and analysed by fs-LA-ICP-MS  
201 (Figs. 2, 4, Table 2). Additionally, we have found particles of anorthoclase, Ca-Fe-rich  
202 pyroxene and rhönite (see Table S9, Supplementary Dataset). Compared to the “particles”  
203 identified by BSE-EDS and analysed by EDS and EPMA method, the analyzed “inclusions”  
204 are not always visible on the images obtained by electron microscopy (Fig. 2), since their  
205 identification and quantification is based solely on the fs LA-ICP-MS spectra.

206 The glasses analysed by EPMA and fs-LA-ICP-MS, using several line scans on a  
207 micrometric scale, are characterized by a nearly homogeneous trachytic “matrix”  
208 composition (Table 2, Figs. 2, 4) with high concentrations of Cs, Rb, Pb, REE, Nb, Th, U,  
209 As and Zr relative to primitive mantle composition (Lyubetskaya and Korenaga, 2007). The  
210 “matrix” glass has a quartz-normative composition (Table S3). The primitive mantle-  
211 normalized pattern of the average composition is similar to the patterns of the McMurdo  
212 trachyte rocks (Kyle, 1981; Kyle et al., 1992; Kelly et al., 2008), marine sediments (Ben  
213 Othman et al., 1989) and global subducting sediment (GLOSS) (Plank and Langmuir, 1998).  
214 The BIT12 glasses also show an inhomogeneous distribution of large-ion lithophile elements  
215 (LILE) (Li, B, As, Ba, Rb, Sr and LREE), which can be distinguished on the laser ablation

216 patterns as sub-micrometric “inclusions” in the host “matrix” glass. An inclusion of the SiO<sub>2</sub>  
217 mineral (number 4, Fig. 2, Table 2) has very low Na<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> contents (Na<sub>2</sub>O<sup>SiO<sub>2</sub></sup> and  
218 Al<sub>2</sub>O<sub>3</sub><sup>SiO<sub>2</sub></sup> contents are below detection limits by fs-LA-ICP-MS). An inclusion of Si-Al-rich  
219 glass with relatively low Na<sub>2</sub>O and high Rb (~270 ppm), Ba (~9000 ppm), Sr (~550 ppm),  
220 and Eu (3.4 ppm) contents (number 6, Table 2), is also detected by fs-LA-ICP-MS. The glass  
221 and mineral “inclusions” numbered 1 to 3 and 7 to 10 have elevated SiO<sub>2</sub> (66–68 wt.%),  
222 Al<sub>2</sub>O<sub>3</sub> (15–22 wt.%), Na<sub>2</sub>O (6.5–8.0 wt.%) contents comparable to alkali feldspar (Na-rich  
223 plagioclase or anorthoclase). The most abundant “matrix” glasses of trachyte composition  
224 are characterized by a X<sub>nf</sub>/X ratio of 0.74 ± 0.04 (the X<sub>nf</sub>/X value necessary for the estimation  
225 of amphibole-melt partitioning is the sum of the molar fractions of network-forming cations  
226 (X<sub>nf</sub>) normalized to the molar fraction of the total number of cations (X) in the melt)  
227 according to Tiepolo et al. (2007). A single Ca-rich carbonate particle in this sample was also  
228 detected using BSE-EDS (Table 1, Supplementary Dataset).

229 SURF is a tephra sample with fragmented volcanic particles 50–200 μm in size. Table  
230 1, Tables S4–S6, S8 and S9 report the mineralogy in the analysed zone of this sample, which  
231 contains plagioclase (An<sub>37-57</sub>, FeO = 0.25–0.85 wt.%), magmatic Ca amphibole (Mg# 40–62,  
232 TiO<sub>2</sub> = 3.2–5.3 wt.%), titanomagnetite (Usp<sub>54-82</sub>), rhönite, olivine (Fo<sub>68-85</sub>, CaO = 0.3–1.0  
233 wt.%), Ti-augites (TiO<sub>2</sub> = 2.7–3.8 wt.%), glasses of trachyandesite, trachyte to phonolite  
234 composition (Figs. 3, S3) and dolomite (SURF-20). Moreover, abundant metamorphic Ca-  
235 Al-rich tschermakite amphiboles are identified (see Supplementary Dataset). Four Ca-Mg-  
236 Fe carbonate particles are also detected using the BSE-EDS method (Table 1, Supplementary  
237 Dataset).

238 CORE is a finely grained tephra sample with particles of volcanic material finer than 50  
239 μm. Table 1 and Tables S4–S8 show that the sample contains plagioclase (An<sub>33-68</sub>, FeO =  
240 0.6–1.0 wt.%), Ti-augite (TiO<sub>2</sub> = 2.3–5.5 wt.%), magmatic Ca amphibole (Mg# 38–76, TiO<sub>2</sub>

241 = 3.9–5.6 wt.%), olivine ( $\text{Fo}_{84-87}$ ,  $\text{CaO} = 0.2\text{--}0.4$  wt.%), titanomagnetite ( $\text{Usp}_{49-70}$ ), ilmenite  
242 ( $\text{Ilm}_{0.91\text{--}1.0}$ ), glasses of trachyandesite to trachyte compositions (Figs. 3, S2), and rhönite  
243 particles. One Ca-Mg-Fe carbonate particle is detected using the BSE-EDS method (Table 1,  
244 Supplementary Dataset). Moreover, abundant metamorphic Ca-Al-rich tschermakite  
245 amphibole and four particles of Al-rich oxide of spinel group are identified (see Table S8 and  
246 Supplementary Dataset). The composition of the magmatic ilmenite particle (P171) detected  
247 and analysed by BSE-EDS method, coupled with that of titanomagnetite, yields a  
248 temperature of  $1092 \pm 100$  °C and redox conditions slightly below the NNO buffer (from  
249 NNO-0.58 to NNO-0.19, Table S8).

250 Thus, in addition to typically magmatic minerals (ferrokaersutite, kaersutite, ferro-  
251 edenite, and plagioclase, along with Ti-augite, apatite, anorthoclase, olivine, ilmenite), and  
252 rhönite – a mineral belonging to the aenigmatite group (Kyle and Price, 1975) – as well as  
253 quartz-normative glasses of mildly peralkaline to alkaline composition (Table 2), all tephra  
254 samples contain metamorphic phases, such as carbonates, quartz, metamorphic Ca-Al-rich  
255 amphiboles and Al-rich spinels.

256

## 257 **4. Discussion**

### 258 *4.1. Derivation of Allan Hills tephra from a mantle plume*

259 A magmatic system that evolves as an open system (e.g., through assimilation-fractional  
260 crystallization, magma mixing) may nevertheless provide evidence of local equilibrium. For  
261 example, the mineral and glasses found in volcanic ashes formed due to crustal assimilation  
262 and magma mixing frequently coexist in local equilibrium at the  $\mu\text{m}$  scale (e.g., Borisova et  
263 al., 2012; 2013). In the investigated system, we applied partition coefficients between

264 magmatic minerals and mafic melts, principally those of alkaline affinity, to determine  
265 whether the mineral phases could be in equilibrium with the co-existing glasses.

266 In contrast to mid-ocean ridge magmas, mantle plume-derived or intraplate magmas  
267 typically represent high-temperature melts that are regularly enriched in Fe and Ti (e.g.,  
268 Hawaii and Iceland) (Giehl et al., 2013). The investigated samples contain abundant  
269 differentiated glasses and associated Fe-Ti-rich minerals (e.g., Ti-augite, titanomagnetite,  
270 ilmenite and rhönite). The average  $\text{TiO}_2$  content of  $0.32 \pm 0.23$  wt.% in the BIT12 glasses  
271 (Table 2 and Table S3) corresponds to the value obtained by assuming a theoretical  
272  $D^{\text{TiO}_2}_{\text{Amph/melt}}$  partition coefficient of  $6 \pm 2$  according to the  $X_{\text{nf}}/X$  ratio described by Tiepolo  
273 et al. (2007). This Ti partitioning between amphibole and melt means that the BIT12 tephra  
274 glasses are close to equilibrium with the magmatic amphiboles in BIT10, SURF and CORE,  
275 with an average  $\text{TiO}_2^{\text{Amph}}$  content of  $4.9 \pm 0.6$  wt.% (Table S4). The predominant “matrix”  
276 glass is also enriched in iron (average  $\text{FeO}^{\text{glass}}$   $5.2 \pm 0.6$  wt.%, Table 2 and Table S3), similar  
277 to the alkaline melts produced under water-saturated magmatic conditions (Giehl et al.,  
278 2013). According to experimental Fe partitioning between plagioclase and melt,  $D^{\text{FeO}}_{\text{Plag/melt}}$   
279 = 0.14–0.22 for  $\text{An}_{40-60}$  (Bindeman et al., 1998), the BIT12 trachytic glasses are in  
280 equilibrium with the plagioclases  $\text{An}_{55 \pm 12}$ , with average  $\text{FeO}^{\text{Plag}}$  content of  $0.84 \pm 0.25$  wt.%  
281 (BIT10, SURF, CORE, Table S5). A common volcanic origin is implied by the mid-  
282 Pleistocene age of the Allan Hills tephra samples (BIT12 is estimated to have been formed  
283 ~202 ka ago (Iverson, 2017), while samples BIT10, SURF, and CORE represent a tephra  
284 layer dated at ~115 ka) and the similar major element compositions of the mineral and glass  
285 particles in all tephra samples. The typical chemical features of the Allan Hills tephra glasses,  
286 mostly of trachytic to phonolitic composition, suggest that they originated from a common  
287 magma generated by mantle plume activity. The fragmented morphology and micrometric  
288 size of the analysed particles and glass fragments, as well as the typical bubble-wall

289 appearance and fluidal texture of the glasses (BIT12, Fig. 2), suggest a Plinian- or Subplinian-  
290 type explosive eruption (e.g., Ponomareva et al., 2013; Borisova et al., 2012; 2013).

291 The occurrence of olivine Fo<sub>68-87</sub> micro-crystals in samples BIT10, CORE and SURF,  
292 which are likely from the same eruption, implies their common magmatic source. According  
293 to experimental data on equilibrium Ca partitioning between olivine and aluminosilicate melt  
294 ( $D^{\text{CaO}}_{\text{Ol/melt}} = 0.14\text{--}0.28$  at Fo<sub>68-87</sub>) (Libourel, 1999), the Allan Hills olivines with CaO<sup>Ol</sup> =  
295 0.3–1.0 wt.% (Table S6) were crystallized from silicate melt with CaO<sup>melt</sup> ranging from 1.1  
296 to 5.2 wt.%. The fact that the BIT12 glasses have comparable CaO<sup>glass</sup> of  $1.0 \pm 0.6$  wt.%  
297 (Tables 2, S3) indicates that the Allan Hills olivines (BIT10, CORE and SURF) are mostly  
298 represented by magmatic crystals close to equilibrium with the analysed BIT12 trachytic  
299 glasses. By contrast, the most CaO-rich (~ 1.0 wt.% CaO) olivine may have also crystallized  
300 from Ca-rich melt formed due to the assimilation of calc-silicate crust (Deegan et al., 2010;  
301 Borisova et al., 2013).

302 Furthermore, the BIT12 Allan Hills trachytic glasses are also strongly enriched in trace  
303 elements such as Cs, Rb, Ba, Pb, B, La, Ce, Nb, Th, U, As and Zr compared to the primitive  
304 mantle composition (Fig. 4). A hydrothermally altered oceanic lithosphere, which is similar  
305 in composition to oceanic sediments, is enriched in volatiles (H<sub>2</sub>O, B, As), LILE (such as Rb,  
306 Ba, Cs, Pb, LREE), and high field strength elements (HFSEs; such as Al, Zr, Nb, Th, and U)  
307 relative to heavy rare earth elements (HREE). High concentrations of volatiles (B, As), LILE,  
308 and HFSE elements relative to HREE in the BIT12 glasses (e.g., “matrix” Table 2 and Table  
309 S3) are signatures of either highly altered silicate rocks or pelagic sediments, such as GLOSS.  
310 Similar to the Icelandic hot spot (Borisova et al., 2012), an altered oceanic lithosphere is an  
311 appropriate candidate for a mantle plume source for the Allan Hills magma. This similarity  
312 suggests that the Allan Hills magma draws its origin from a mantle plume derived from a  
313 hydrothermally altered oceanic lithosphere. Indeed, the West Antarctic Rift System may be

314 related to a hot spot activity (Behrendt, 1999); the magmatic activity of Mount Erebus, Ross  
315 Island, is related to a mantle plume known as the Erebus plume (Kyle et al., 1992). The Allan  
316 Hills glass compositions are different from the Cenozoic rift magmas, which are  
317 characterized by negative Pb anomalies in the primitive mantle-normalized patterns (Rocchi  
318 et al., 2003). Therefore, the Allan Hills tephra glasses are chemically distinct from magmatic  
319 products related to intraplate strike-slip tectonic activity. The alkalinity of the Allan Hills  
320 glasses is similar to that of the McMurdo volcanic rocks and glasses (Fig. 3). Moreover, the  
321 Allan Hills “matrix” trachytic glass displays mantle-normalized trace element patterns which  
322 are similar to those of the McMurdo trachytes (Fig. 4); in addition, the Allan Hills tephra  
323 contain a rare mineral called rhönite (Tables 1, S9, Supplementary Dataset). Similarly, the  
324 Erebus and Melbourne volcanic products in the currently active McMurdo volcanic group  
325 include rhönite-bearing- and Al-rich spinel-bearing trachytic lavas as well as pyroclastic fall  
326 deposits related to explosive volcanism, (e.g., Kyle and Prie, 1975; Kyle, 1981; 1990; Iverson  
327 et al., 2014; Kelly et al., 2008). These data strongly support a hypothesis that the studied  
328 Allan Hills tephra may be genetically related to the currently active McMurdo volcanic  
329 group. Thus, the Allan Hills tephra represent mid-Pleistocene ashes produced due to  
330 intraplate magmatism, likely derived from mantle plume activity (Kyle et al., 1992), and  
331 likely associated with the magmatic activity of the McMurdo volcanic group, in particular,  
332 Erebus volcanic province.

333

#### 334 *4.2. Physical-chemical conditions of magma crystallization*

335 In the Allan Hills tephra, the abundant mildly peralkaline to peralkaline glasses, together  
336 with the presence of Ca amphiboles in the volcanic tephra, and the fragmented morphology  
337 of the tephra particles (Figs. 2, S1–S3), imply an explosive eruption of the volcanic material  
338 due to saturation of the magma with an aqueous fluid, (Martel et al., 1998). Application of

339 the amphibole geobarometer equation (Schmidt, 1992) to the Allan Hills amphiboles (Table  
340 S4) yields an average pressure of  $0.98 \pm 0.09$  GPa for magma residence in a deep reservoir,  
341 likely in the presence of an H<sub>2</sub>O-CO<sub>2</sub> fluid. Similarly, application of the amphibole  
342 geobarometer of Ridolfi et al. (2010) implies a pressure of  $1.1 \pm 0.1$  GPa. These high-pressure  
343 conditions suggest that the magma may have resided in a chamber under mantle lithospheric  
344 conditions ( $29.3 \pm 2.7$  km depth, Fig. 5), below the continental crust (Behrendt, 1999; Cooke  
345 and Foden, 2016), rather than below a thick oceanic crust (e.g., Central Kerguelen Plateau)  
346 (Borisova et al., 2014; 2017).

347 The high Ti contents in the BIT10, CORE, and SURF amphiboles ( $Ti^C \geq 0.5$  apfu, atoms  
348 per formula unit, Table S4) and Ti-augites ( $X^{Cpx}_{CaTi}$  up to 0.20, Table S7) reflect an  
349 enrichment in the Ca-Ti-Tschermak's molecule (CaTiAl<sub>2</sub>O<sub>6</sub>). This signature suggests a high  
350 temperature during the magmatic crystallization. Given that TiO<sub>2</sub> contents in the amphibole  
351 vary from 3.2 to 6.8 wt.%, the graphical method of Ernst and Liu (1998) implies magmatic  
352 temperatures above 900 °C at a pressure of ~1 GPa. Calculations according to Equation (4)  
353 from Féménias et al. (2006) and geothermometer of Ridolfi et al. (2010) suggest  
354 crystallization temperatures of  $1135 \pm 80$  °C and  $1057 \pm 50$  °C, respectively (Table S4). The  
355 clinopyroxene-only geothermometer indicates  $1196 \pm 90$  °C at 0.9 GPa (Putirka, 2008)  
356 (Table S7). These pressure-temperature conditions suggest deeper and hotter magmatic  
357 reservoir(s) compared to the shallow magmatic system feeding the Erebus lava lake over the  
358 last 20 kyr (Moussalam et al., 2013).

359 Moreover, the composition of rare ilmenite–titanomagnetite pairs from samples CORE  
360 and BIT10 (Table S8) indicates reducing conditions below the NNO buffer (NNO-1.0 to  
361 NNO-0.19, Table S8). These reducing conditions are also corroborated by the presence of  
362 rhönite containing Ti<sup>3+</sup> (Kyle and Price, 1975). These redox conditions are comparable to  
363 those (between QFM and QFM-1.0) established by Moussallam et al. (2017) for the shallow



364 magmatic system feeding the Erebus lava lake over the last 20 kyr. The presence of abundant  
365 Ca-Al-rich tschermakite (Table 1, Supplementary Dataset) in the tephra suggests high  
366 temperature-pressure conditions of magma residence or transport in deep crustal rocks (e.g.,  
367 Cooke and Foden, 2016).

368

#### 369 *4.3. Evidence for mineral dissolution and calc-silicate crust assimilation*

370 Calc-silicate crust xenoliths observed in different volcanic products are systematically  
371 enriched in Ca-Al-rich minerals (e.g., amphibole, anorthite), carbonates, Ca-rich glasses and  
372 SiO<sub>2</sub>-rich phases such as metamorphic quartz (Deegan et al., 2010; Borisova et al., 2013;  
373 2016). Several carbonates, SiO<sub>2</sub> particles and an inclusion of SiO<sub>2</sub> with low Na<sub>2</sub>O contents  
374 are also detected in the BIT10 and BIT12 tephra samples (Tables 1 and 2). Low Na<sub>2</sub>O and  
375 Al<sub>2</sub>O<sub>3</sub> contents in the SiO<sub>2</sub> “inclusion” (number 4, Fig. 2, Table 2) are detected by fs-LA-  
376 ICP-MS in the host “matrix” glass. This implies that the mineral phase is a quartz micro-  
377 xenocryst rather than magmatic cristobalite (Borisova et al., 2013) crystallized from the  
378 associated melt with high Na<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> contents (Table 2).

379 The occurrence of dolomite and mylonitized limestones is documented in the Ross  
380 orogenic structures (Kleinschmidt et al., 2002), and metamorphic calc-silicate rocks are  
381 present elsewhere in Antarctica (Yamakawa et al., 2001). The presence of dolomite, other  
382 carbonates and quartz particles, as well as the “matrix” glass-hosted inclusion of quartz  
383 (number 4, Table 2 and Table S9) formed as micro-xenocrysts strongly supports crustal  
384 assimilation by the magma. Indeed, available experimental data suggest a dolomite-quartz  
385 stability limit at 500 °C at low pressures (Müller et al., 2004). Moreover, the thermal stability  
386 of limestone is below 820–870 °C at 0.1 MPa pressure (Ar and Doğu, 2001). Given that the  
387 established temperature conditions of the peralkaline magma crystallization are ~1100 °C,

388 the crustal dolomite was also likely thermodynamically unstable with the magma at high  
389 pressure. Therefore, the crustal quartz-carbonate association may have briefly survived in the  
390 magma as crustal micro-xenoliths, (e.g., Borisova et al., 2013; 2016), and could have been  
391 incorporated into the volcanic tephra due to very rapid ascent of the Allan Hills magma from  
392 its reservoir during an explosive (Plinian- or Subplinian-type) eruption.

393 The calc-silicate assimilation process is supported by the elevated concentration of  $\text{Sr}^{\text{glass}}$   
394 in one glass ( $\text{Sr} \approx 550$  ppm content in glass “inclusion” number 6) and the calculated  $\text{Sr}^{\text{melt}}$   
395 content up to 620 ppm (based on the Sr content in plagioclase “inclusion” 5, Table 2) in the  
396 host BIT12 “matrix” glass (Deegan et al., 2010; Borisova et al., 2013; 2016). Moreover, the  
397 observed Al-rich spinels are either representative of carbonate-rich metamorphic rocks (e.g.,  
398 galaxite) (Essene and Peacor, 1983) or crystallized in the melt due to incongruent dissolution  
399 of calc-silicate minerals such as anorthite (Morgan et al., 2006). The high abundance of the  
400 main Ca-rich minerals (plagioclase, augites with elevated molar fractions of Ca-Tschermak  
401  $X^{\text{cpx}}_{\text{CaTs}}$  up to 0.1, and Ca-Al-rich tschermakite amphiboles, accounting for up to 58 rel.%,  
402 Tables 1, S7), as well as accessory dolomite and other carbonates, quartz and the Al-rich  
403 spinel particles in the tephra samples (Tables S8 and S9; Supplementary Dataset), are  
404 signatures of calc-silicate crust assimilation (e.g., Mollo et al., 2010; Deegan et al., 2010). In  
405 addition, the observed dispersion in alkalinity of the glasses of trachyandesitic, trachytic and  
406 phonolitic to tephri-phonolitic composition (Fig. 3) may be also directly related to the  
407 carbonate-bearing material assimilation by magmas (Mollo et al., 2010).

408 The compositions of the BIT12 glass “inclusion” imply inhomogeneity of the melt with  
409 respect to most major, volatile and LILE trace elements (Li, B, As, Ba, Rb, Sr, REE, Fig. 4)  
410 on a sub-micron scale, suggesting magma mixing. For example, the “inclusions” numbered  
411 1 to 3 and 7 to 10 analysed by fs-LA-ICP-MS have elevated  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Na}_2\text{O}$  contents,  
412 and are variably enriched in REE, Sr, Rb and Ba (Table 2). These inclusions may be formed

413 as glasses or as minerals due to progressive dissolution/crystallization of alkali feldspars in  
414 the melt. Indeed, the presence of anorthoclase particles in the BIT12 sample is recorded in  
415 our work (see Supplementary Dataset) and by Iverson (2017).

416 Additionally, formation of Si-Al-rich glass of dacite/rhyolite composition with high Sr,  
417 Rb, Ba and Eu contents (glass “inclusion” number 6, Table 2) is likely due to the dissolution  
418 of quartz  $\pm$  plagioclase, and also requires thermodynamic instability triggered, for example,  
419 by crustal assimilation. Indeed, similar rhyolite series TD 1387B-iii is recently recorded by  
420 Narcisi et al. (2016) in the Talos Dome ice core (Northern Victoria Land); and it is dated at  
421  $\sim 116 \pm 2$  ka. Although such felsic glasses are regularly considered to be genetically related  
422 to an extra-Antarctic source (Narcisi et al., 2012; 2016), the presence of the described  
423 inclusions within the Allan Hills trachytic “matrix” glass requires an *in situ* origin due to  
424 mineral (quartz  $\pm$  plagioclase) dissolution during magma differentiation in the lithosphere of  
425 Antarctica. The volcanic particles might be accumulated during a single volcanic eruption  
426 and represent a result of syn-eruptive processes of mineral dissolution e.g., (Borisova et al.,  
427 2012; 2013). Mineral dissolution and mixing of melts by chemical diffusion can be directly  
428 related to magmatic events, in particular magma recharge and crustal assimilation (e.g.,  
429 Deegan et al., 2010; Borisova et al., 2013; 2016; 2017). In the case of the Allan Hills tephras,  
430 which are chemically similar to the McMurdo volcanic group rocks and associated glasses  
431 (Fig. 3), the hypothesis of calc-silicate crust assimilation is strengthened by the presence of  
432 crustal xenoliths and xenocrysts in the Erebus and Melbourne Volcanic Province trachytes  
433 and more highly differentiated volcanics. These latter are characterized by variably  
434 radiogenic Sr isotope composition (Wörner et al., 1989; Kyle, 1990; Kyle et al., 1992;  
435 Wörner, 1999), providing additional arguments for either magma mixing or crustal  
436 assimilation associated with fractional crystallization or a combination of both.

437 Thus, the 202 – 115 ka Allan Hills magma might be derived from a mantle plume, likely  
438 currently located beneath the McMurdo volcanic group, and then accumulated in a deep  
439 magmatic reservoir at  $29.4 \pm 2.7$  km depth. The magma was affected by calc-silicate crust  
440 assimilation in the crustal reservoir(s) under pre-eruptive and/or syn-eruptive conditions.  
441 Alternatively, lower crust of McMurdo volcanic region composed of altered oceanic crust  
442 (which may partially include calc-silicate materials) might be partially melted by underlying  
443 hot plume to produce the trachytic melts. This hypothesis may better explain differentiated  
444 and hydrous compositions of the Allan Hills tephra, and incorporation of partially dissolved  
445 crustal materials into the magma. The magma was explosively erupted due to an excess of  
446 H<sub>2</sub>O-CO<sub>2</sub> fluid phase in the pre-eruptive reservoir(s) (Fig. 5). The existence of such  
447 reservoir(s) may be interpreted based on the total oxide contents of the well-polished glasses  
448 measured by EPMA (Table S3, Supplementary Dataset), which indicate up to 3 wt.%  
449 volatiles (H<sub>2</sub>O-CO<sub>2</sub>) dissolved in the melts upon quenching. Such dissolved volatile contents  
450 imply the melt saturation with H<sub>2</sub>O-CO<sub>2</sub> fluid at pressure below 0.7 GPa corresponding to  
451 crustal depths (<20 km depth) (Iacovino et al., 2013), assuming the fraction of  $X_{\text{H}_2\text{O}}^{\text{fluid}}$  ranges  
452 from 0.1 to 0.2.

453

## 454 **5. Implications and conclusions**

455 This study provides evidence for the origin of the mid-Pleistocene Allan Hills tephra in  
456 Antarctica, which are considered to represent volcanic products due to the explosive activity  
457 of a mantle plume-derived magma. Our data indicate that the mantle plume responsible for  
458 the origin of the S27 tephra is currently located beneath the McMurdo volcanic group. The  
459 chemistry of the magmatic Ca amphiboles implies that the magma resided at a depth of  $29.3$   
460  $\pm 2.7$  km. The presence of abundant magmatic Ca-rich minerals (e.g., plagioclase and augite),  
461 metamorphic Ca-Al-rich amphiboles, Ca-Fe pyroxenes as well as dolomite and other

462 carbonate minerals, Al-rich spinel, quartz xenocrysts and felsic glass “inclusions”, suggests  
463 that the magma assimilated Ca-Si-Al-rich calc-silicate crustal material. The formation of Si-  
464 Al-rich glass of dacite/rhyolite composition (glass “inclusion” number 6, similar to rhyolite  
465 series TD 1387B-iii recorded by Narcisi et al. (2016) in the Talos Dome ice core, Northern  
466 Victoria Land, and dated at ~116 ka) requires an *in situ* origin due to mineral (quartz ±  
467 plagioclase) dissolution during magma differentiation in the lithosphere of Antarctica. The  
468 obtained data suggest that an attention should be made to interpret correctly isotopic  
469 composition of the contaminated lavas and glasses in terms of mantle plume composition.

470 We assume that the elevated atmospheric CO<sub>2</sub> concentrations recorded in the Antarctica  
471 region during the mid-Pleistocene (Higgins et al., 2015) might be due to at least two  
472 processes: (1) mantle plume activity and magma degassing due to saturation with a H<sub>2</sub>O-CO<sub>2</sub>  
473 fluid phase (Ernst and Liu, 1998; Kelly et al., 2008), and (2) contact metamorphic  
474 decarbonation reactions due to interactions of the magma with calc-silicate crust. Since  
475 volcanic activity is frequently related to an elevated CO<sub>2</sub> flux (e.g., Ernst and Liu, 1998;  
476 Toutain et al., 2009), the mantle plume activity may also be responsible for the high CO<sub>2</sub>  
477 anomalies recorded in Antarctica ice cores. Such coupling of the volcanic tephra hosted in  
478 Antarctic ice cores and the host ice core composition is a highly promising approach for  
479 developing robust models of the terrestrial climate. This represents a high priority objective  
480 for Antarctic Science according to the current scientific programs (e.g., Antarctic Roadmap  
481 Challenges) (Kennicutt et al., 2016).

482

483 **Supplementary Materials:** Figure S1: Back-scattered electron image and the BSE-EDS  
484 mapping of the BIT10 Allan Hills tephra sample from site S27, Figure S2: Back-scattered  
485 electron image and the BSE-EDS mapping of the CORE Allan Hills tephra sample from site  
486 S27, Figure S3: Back-scattered electron image and the BSE-EDS mapping of the SURF Allan

487 Hills tephra sample from site S27, Table S1: Operating parameters of the laser ablation  
488 system used for the fs-LA-ICP-MS analyses, Table S2: Typical operating parameters of the  
489 ICP mass spectrometer used for the fs-LA-ICP-MS analyses, Table S3: Composition of  
490 glasses in the BIT12 sample (EPMA and CIPW norms in wt.%) and the ATHO-G reference  
491 material, Table S4: Compositions of calcic amphiboles in the tephra samples (EPMA in  
492 wt.%), formula units, Table S5: Compositions of anorthoclases and plagioclases in the tephra  
493 samples (EPMA in wt.%) Table S6: Compositions of olivines in the tephra samples (EPMA  
494 in wt.%), Table S7: Compositions of Ti-augites in the tephra samples (EPMA in wt.%),  
495 formula units, Table S8: Compositions of titanomagnetites and Al-rich spinel in the tephra  
496 samples (EPMA in wt.%), Table S9: Compositions of apatite, dolomite, and rhönite in the  
497 tephra samples (EPMA in wt.%), Supplementary Dataset: BSE-EDS mapping and EPMA  
498 data for the BIT10, BIT12, SURF and CORE samples.

499

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501 data analysis and led the drafting of the manuscript. K.P.J. provided access to LA-ICP-MS  
502 and analytical data. S.G. and A.Y.B. performed the EDS/SEM analyses and mapping, and  
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522

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750



**FIGURE CAPTIONS:**

751

752

753 **Figure 1.** Map of the Allan Hills Blue Ice Area (BIA) in South Victoria Land,  
754 Antarctica. The ash layers crossing transect A–B are shown. The ice core S27 was  
755 collected from the main icefield (marked as MIF) of the Allan Hills BIA during field  
756 seasons in 2010 and 2011. Maps are modified after Spaulding et al. (2012).

757

758 **Figure 2.** (A) Back-scattered electron image of the BIT12 Allan Hills tephra sample  
759 from site S27. (B) Result of BSE-EDS mapping for sample BIT12. The color coding  
760 identifies a given class of particles (see Figs. S1-S3), representing the glasses and  
761 minerals. The image represents volcanic glass (beige), alkali feldspar (yellow) and  
762 the plagioclase (violet) and not identified (grey). (C) The fs LA-ICP-MS spectra of  
763 quartz inclusion number 4. For the evaluation of the data, we have rejected the first  
764 4 measurements corresponding to the range of unstable conditions (unstable laser;  
765 relative higher proportion of (contaminated) surface material). The identification  
766 and quantification of the “inclusions” and “matrix” are based solely on the fs-LA-  
767 ICP-MS spectra. The glasses and minerals analyzed by the scan lines are not always  
768 visible on the BSE images.

769

770 **Figure 3.** Total alkalis versus silica (TAS) diagram ( $\text{Na}_2\text{O}+\text{K}_2\text{O}$  versus  $\text{SiO}_2$ , wt.%)  
771 for the S27 Allan Hills tephra glass particles analysed using EPMA, fs-LA-ICP-MS  
772 and BSE-EDS. The composition of the predominant “matrix” analysed by fs-LA-  
773 ICP-MS is indicated. The BIT12 glasses analysed using EPMA and fs-LA-ICP-MS

774 are of trachytic composition. The glass compositions are compared to the bulk-rock  
775 and matrix glass composition of the Erebus volcano lavas (labelled as McMurdo  
776 volcanic rocks and glasses), from Kyle (1981; 1990); Kyle et al. (1992) and Kelly  
777 et al. (2008). The plotted BSE-EDS data points can be found in the Supplementary  
778 Dataset. CA = carbonate crust assimilation; FC = fractional crystallization; CSA =  
779 calc-silicate assimilation via quartz-bearing rock dissolution.

780

781 **Figure 4.** Pattern of the trace element compositions normalized to primitive mantle  
782 for S27 Allan Hills BIT12 glasses analyzed by femtosecond laser ablation-  
783 inductively coupled plasma-mass spectrometry (fs-LA-ICP-MS). The “matrix” (red  
784 diamonds) and “inclusions” (rose field) are normalized to composition from  
785 (Lyubetskaya and Korenaga, 2007). The “matrix” and “inclusions” patterns are  
786 compared to the patterns of the bulk-rock composition of the McMurdo volcanic  
787 group trachyte lavas and pyroclastic rocks (labelled as McMurdo trachyte lavas)  
788 (Kyle, 1981; 1990; Kyle et al., 1992; Kelly et al., 2008), marine sediments (Ben  
789 Othman et al., 1989), and global subducted sediments (GLOSS) (Plank and  
790 Langmuir, 1998). The order of elements on the plot corresponds to the increasing  
791 ratio of charge to ionic radius (Borisova et al., 2012). The arrow indicates an increase  
792 in the Sr concentration in the glass “inclusion” (number 6) compared to the average  
793 Sr content in the “matrix” glass (Table 2).

794

795 **Figure 5.** Scheme of the proposed model for residence and transport of the Allan  
796 Hills magma during mid-Pleistocene explosive eruptions. The magma was derived  
797 from a mantle plume currently located beneath the McMurdo volcanic group. The

798 magma crystallized in a magma chamber located within a deep reservoir at a depth  
799 of  $29.4 \pm 2.7$  km. The magma was then affected by calc-silicate crust assimilation  
800 and mixing, and explosively erupted likely due to an excess of CO<sub>2</sub>-bearing fluids  
801 in the pre-eruptive reservoir(s) or during eruption.

802

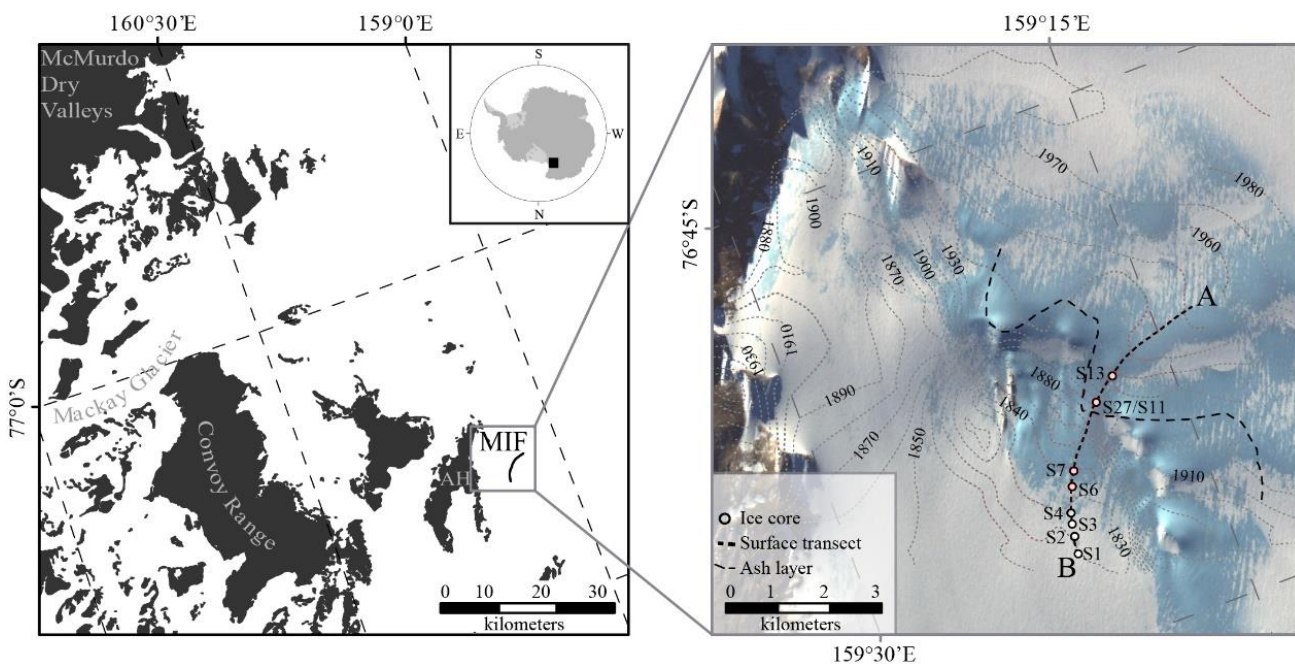
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**FIGURES:**

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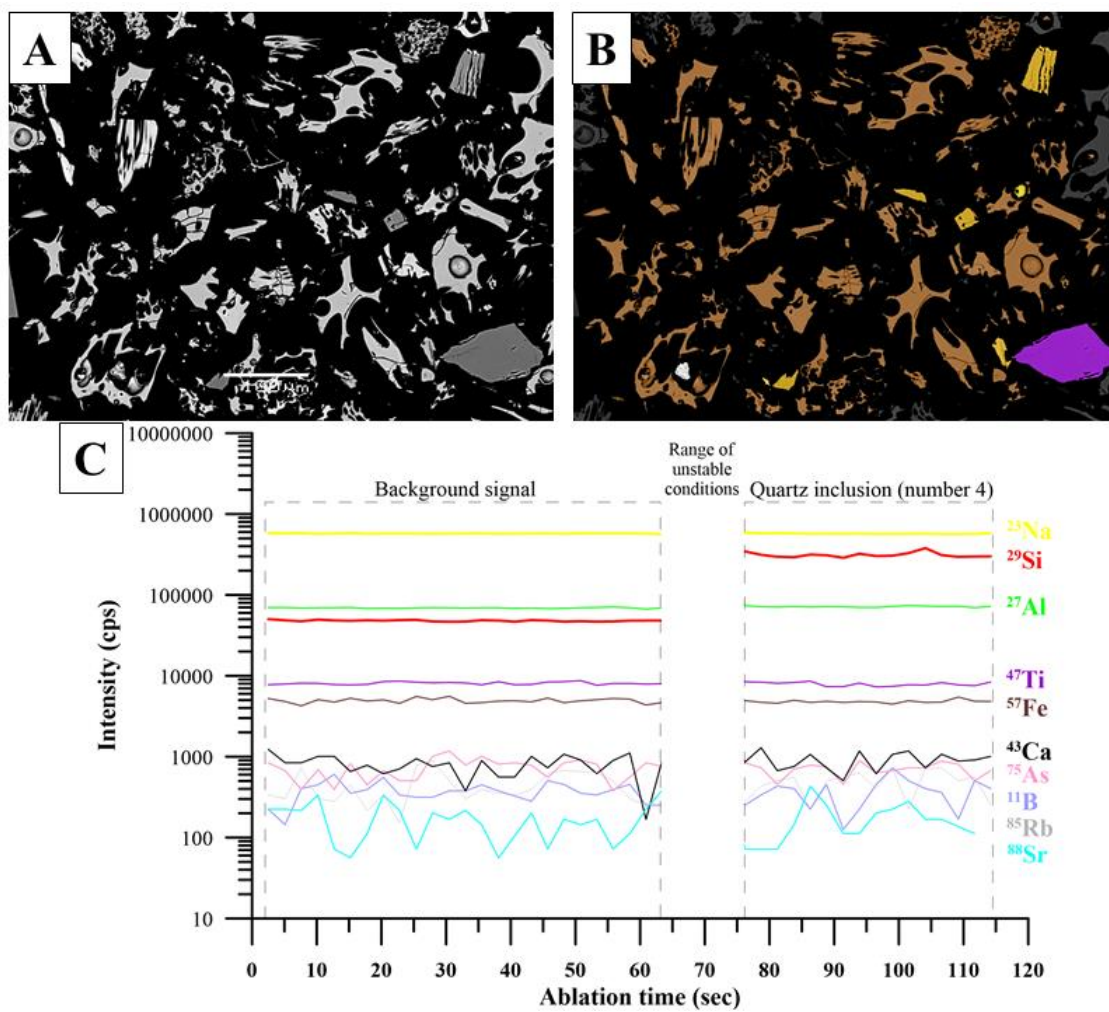
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808 **Figure 1.**

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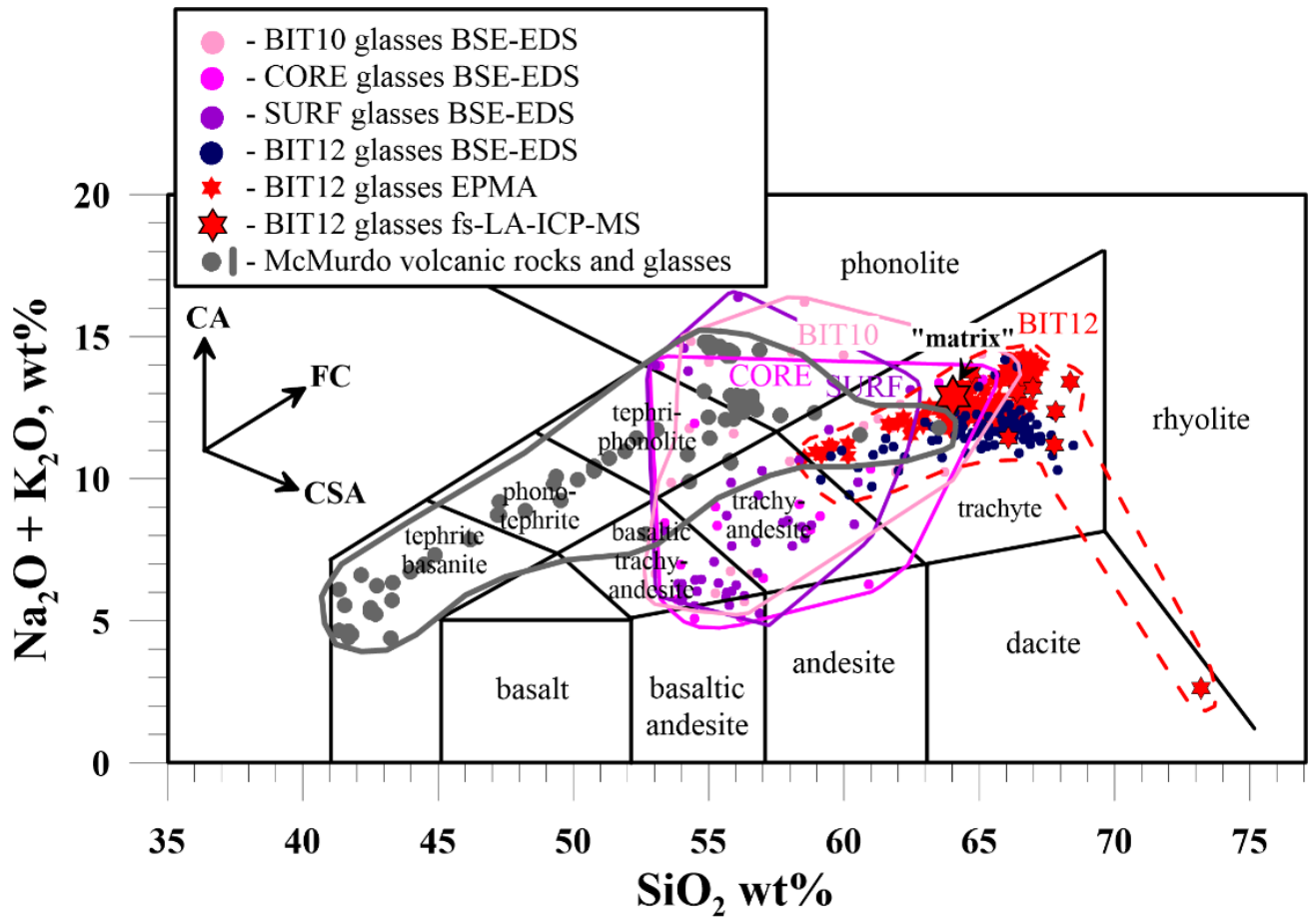


812

813 **Figure 2.**

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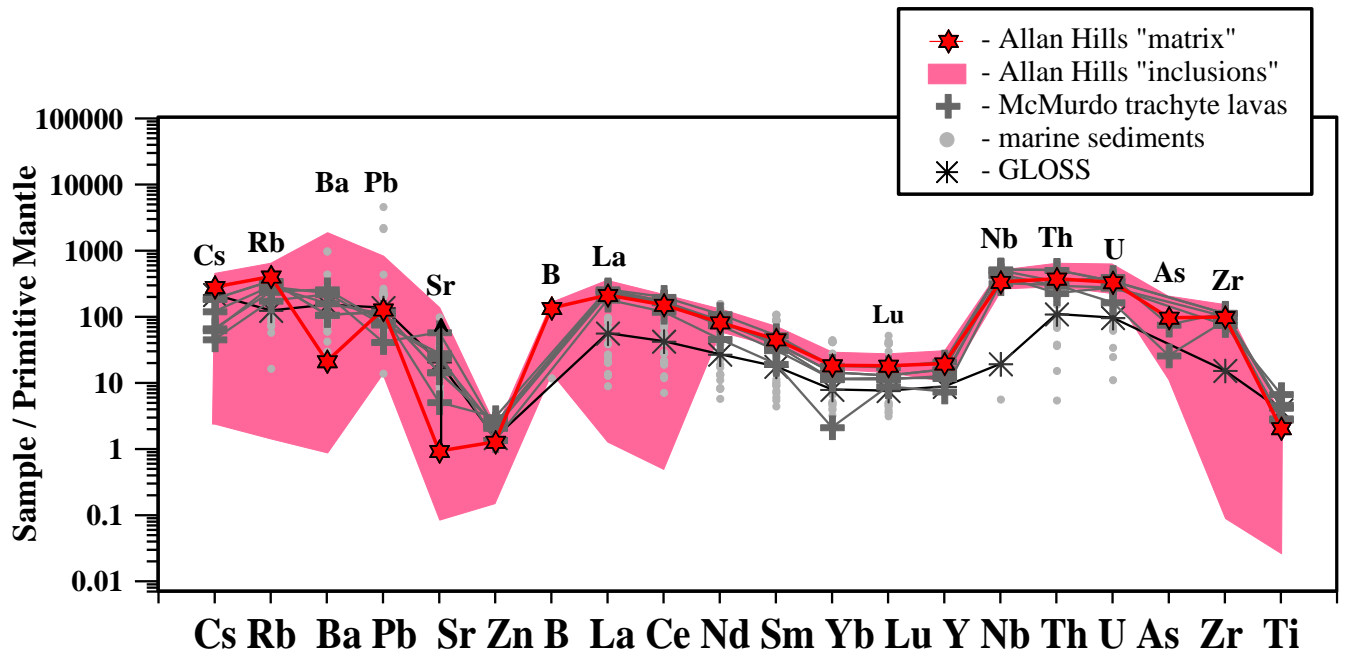
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816

817 **Figure 3.**

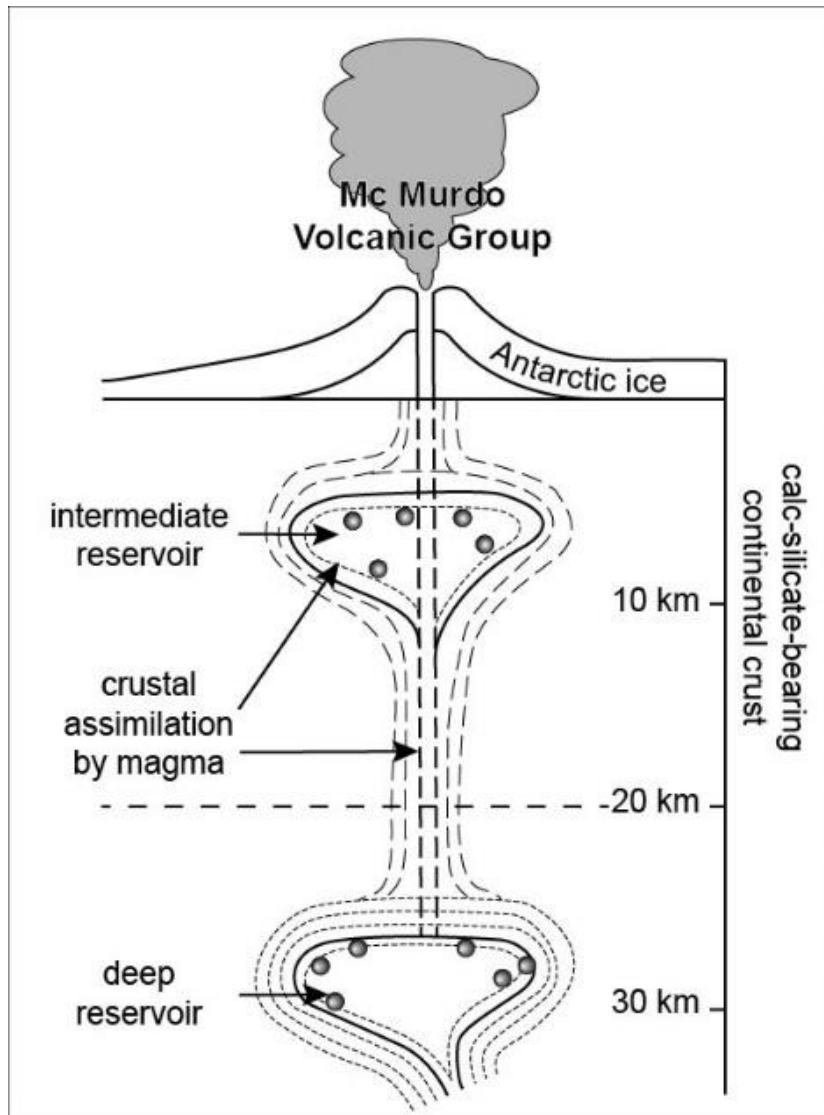
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819

820 **Figure 4.**

821



822

823 **Figure 5.**

824



**Table 1.** Coordinates and contents of minerals and glass in the Allan Hills BIA tephra samples (Antarctica).

Sample	Samples							
	BIT10		BIT12		SURF		CORE	
coordinates:	GPS :		76.7101S,		76.7024S		76.7009	
	76.7009S,		159.343E		159.3110		159.304	
	159.304E				E		E	
Minerals and glasses	P	Relative %	PN	Relative %	PN	Relative %	PN	Relative %
	<sup>a</sup>							
SiO <sub>2</sub> <sup>b</sup>	2	0.9	10	N.A.	-	-	-	-
Plagioclase	22	8.6	1	9.5	36	17.8	23	11.9
Alkali feldspars	5	1.1	20	5.5	1	0.07	2	0.31
Olivine	3	1.9	-	-	14	6.5	16	7.8
Clinopyroxene	9	14.8	-	-	15	10.6	29	19.2
Ca-Al-rich amphiboles <sup>c</sup>	52	32.2	-	-	49	16.2	21	26.6
Ca amphiboles <sup>c</sup>	1	0.22	-	-	-	-	3	0.7
Silicate glass	4	0.9	92	84.2	1	0.13	1	0.15
Titanomagnetite	11	1.6	1	N.A.	30	20.1	19	4.2
Ilmenite <sup>d</sup>	3	0.12	-	-	-	-	4	0.7
Rhönite	3	0.30	2	N.A.	1	1.1	4	0.4
Apatite	6	1.4	1	N.A.	-	-	-	-
Dolomite <sup>e</sup>	2	N.A.	1	N.A.	4	N.A.	1	N.A.
Unclassified	11	36.0	2	0.8	120	27.6	70	28.0
	8							
All	23	100	130	100	267	100	192	100
	8							

827 GPS – GPS coordinates. <sup>a</sup> PN = Number of particles investigated by BSE-EDS mapping. Relative%  
828 = Relative percentage by area (normalized to 100%) calculated based on the EDS analysis using the  
829 “Feature” program. N.A.—not calculated, because the particles were identified by EPMA, not by  
830 BSE-EDS. “-” —no data on the mineral or glass particles. <sup>b</sup> SiO<sub>2</sub> particle detected by BSE-EDS  
831 mapping in the BIT10 and BIT12 samples and SiO<sub>2</sub> inclusion analysed by fs-LA-ICP-MS in the  
832 BIT12 glassy sample. <sup>c</sup> Abundant metamorphic Ca-Al rich amphiboles are tschermakites (see  
833 Supplementary Dataset), whereas magmatic Ca amphiboles, such as ferrokaersutite, kaersutite and  
834 ferro-edenite were identified by EPMA in the BIT10, SURF, and CORE samples (see Table S4). <sup>d</sup>  
835 Ilmenite particles from samples BIT10 and CORE (major element compositions obtained by BSE-  
836 EDS) are used for temperature and f<sub>O2</sub> estimations using a Fe-Ti oxide geothermobarometer as in  
837 (Ghiorso and Evans, 2008) (see Table S8). <sup>e</sup> Metamorphic Ca-Mg-Fe or Ca-Mg carbonates are  
838 identified among the unclassified particles (P 44, P 47, P 155, P 157 in the SURF; P 149 in the CORE;  
839 P 50 and P 22 in the BIT10, and P 84 in the BIT12, see Supplementary Dataset). A dolomite particle  
840 (analysis SURF-20, Table S9) is detected by BSE-EDS and analysed by EPMA in the SURF sample  
841 (see Table S9). Four particles of Al-rich spinel are identified (P166, 167, 168, CORE-19) in the  
842 CORE sample (see Table S8; Supplementary Dataset).

843 **Table 2.** Major and trace element compositions of “matrix” glass and “matrix” glass-hosted  
 844 “inclusions” in sample BIT12 (fs-LA-ICP-MS, wt.% and ppm, respectively)

fs-LA-ICP-MS	Inclusions										Matrix (333) <sup>s</sup>	Model
	1	2	3	4	5	6	7	8	9	10		
wt% /ppm	G/ A	G/ A	G	Q	Plag An <sub>57</sub>	G	G	G	G/ A	G	G	Calculated melt * ppm
SiO <sub>2</sub>	67.8	67.	66.	96.	52.2	73.2	64.7	66.4	67.	68.4	64.4	-
TiO <sub>2</sub>	0.02	0.0	0.3	0.0	0.05	0.01	0.28	0.29	0.0	0.23	0.33	-
Al <sub>2</sub> O <sub>3</sub>	21.2	21.	17.		28.1	21.9	17.4	16.2	21.	15.2	18.2	-
MgO	0.002		0.1	-	0.056	-	0.05	0.03	-	0.04	0.16	-
MnO			0.1	-		-	0.16	0.16	-	0.13	0.18	-
FeO	0.21	0.1	5.2	-	0.34	-	5.39	5.53	0.3	4.43	5.18	-
CaO	0.46	0.8	1.2		11.42	0.31	0.96	0.79	0.2	0.75	1.20	-
Na <sub>2</sub> O	7.2	6.5	6.7		4.8	1.5	8.0	7.6	7.7	7.8	7.6	-
Li	1.5		21	-	-		34	42	4.4	29	35	-
B	2.6	2.3	11	-	-	7.7	20	12	-	7.4	23	-
Cu			1.9	2.1	7.7	2.4	12.2	13.2		3.4	11.4	-
Zn	30	93	78		9.0	12	94	96	18	67	75	-
As			9.2	2.9		0.63	5.69	4.23		3.89	4.85	-
Rb	52.9	31.	137	-	0.68	268	200	222	75.	209	185	-
Sr	17.0	56.	7.5	-	1682	548	2.50	2.08	11.	1.40	14.7	619
Y	-		44.	-	-	-	74.6	78.9	-	65.4	66.4	-
Zr	-	0.8	585	-	-	-	100	107	-	908	835	-
Nb	-		125	-	-	-	179	208	-	197	155	-
Cs	0.15	0.0	3.3	-	0.22	2.58	5.42	6.19	-	5.56	4.52	-
Ba	104	794	28.	-	889	899	7.98	7.35	39.	4.47	108	-
La	1.43	2.7	82.	-	3.39	1.34	125	136	0.6	120	108	-
Ce	1.50	2.1	162	-	5.95	0.71	238	264	0.7	248	203	-
Pr	-	0.1	19.	-	0.53	-	27.9	28.0	-	26.1	21.7	-
Nd	-	-	63.	-	-	-	96.1	99.3	-	83.3	81.9	-
Sm	-	-	12.	-	-	-	17.4	20.0	-	13.8	14.8	-
Eu	0.39	2.6	0.8	-	2.94	3.35	0.28	0.63	0.8	0.31	1.07	-
Gd	-	-	9.9	-	-	-	13.5	16.0	-	13.5	13.4	-
Tb	-	-	1.6	-	-	-	2.54	2.12	-	2.14	2.08	-
Dy	-	-	10.	-	-	-	13.0	14.9	-	10.9	12.5	-
Ho	-	-	1.6	-	-	-	2.80	3.23	-	2.26	2.41	-
Er	-	-	3.3	-	-	-	8.94	9.53	-	5.79	7.15	-
Tm	-	-	0.8	-	-	-	0.95	1.09	-	0.73	0.95	-
Yb	-	-	5.9	-	-	-	6.37	8.91	-	6.28	6.39	-
Lu	-	-	1.2	-	-	-	1.22	0.75	-	0.67	0.98	-
Hf	-	-	14.	-	-	-	24.0	24.8	-	18.9	18.5	-
Ta	-	-	6.9	-	-	0.31	11.2	12.6	-	9.71	9.26	-
Pb	1.86	2.4	14.	-	-	113	22.7	26.8	2.1	17.7	18.5	-
Th	-	-	18.	-	-	-	29.4	31.0	-	20.7	23.6	-
U	-	-	4.3	-	-	-	7.51	8.61	-	5.76	5.77	-

845 G = glass; Q = quartz; Plag = plagioclase; A = anorthoclase; \* Melt composition is calculated based  
 846 on the partition coefficients between plagioclase and melt according to (Bindeman et al., 1998) and

847 analysis № 5 for the plagioclase. Blanks in the columns represent values below the detection limits  
848 of fs-LA-ICP-MS. 1–10 are the compositions of minerals and glass “inclusions” in the glassy matrix  
849 (“matrix”). \$ Bracketed number indicates number of points per analysis.

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