1	Late Glacial-Holocene tephra from southern Patagonia and Tierra del Fuego (Argentina,
2	Chile): a complete textural and geochemical fingerprinting for distal correlations in the
3	Southern Hemisphere
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- 25 1. Abstract

26 Explosive volcanoes from the southern Andes are able to disperse ash over wide areas of the 27 Southern Hemisphere, potentially as far as Antarctica. With the aim of improving correlations between sources and tephra in southernmost South America and, possibly, Antarctica, this work 28 presents new field, textural and geochemical data on tephra layers from southern Patagonia and 29 Tierra del Fuego (Argentina and Chile). Major- and trace-element data, obtained on single glass 30 shards allowed to identify tephra sources in Late Glacial-Holocene eruptions from Hudson, Reclus 31 and Mt Burney volcanoes, located in the Southern and Austral Volcanic Zone of the Andean 32 Cordillera. Twelve new radiocarbon age determinations of charcoals, peats and soils have further 33 constrained the correlations between the studied tephra layers and known eruptions from Hudson, Mt 34 Burney and Reclus volcanoes. Therefore, this study contributes to expand the geochemical dataset on 35 volcanic glasses valuable for tephra correlations in South America, and improves the current 36 37 tephrostratigraphic framework of this region. Furthermore, we revised literature data by compiling a database including Neogene-Quaternary volcanic tephra found in Antarctic ice cores, marine 38 sediments, blue ice and continental outcrops as well as tephra produced by volcanic sources located 39 in Antarctica and circum-Antarctic areas. This revision shows that Antarctic tephra can be correlated 40 with confidence to Antarctic and circum-Antarctic (South Shetlands and South Sandwich Islands) 41 volcanic sources, whereas correlations with South American sources are arguable, and a complete 42 geochemical fingerprinting is needed for validation. 43

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## 50 2. Introduction

51 Tephra layers preserved in geological records represent a valuable tool for reconstructing the past 52 volcanic activity of a given area. Moreover, they are isochronous marker horizons providing timestratigraphic information whenever they are geochemically fingerprinted and tied to a known, dated 53 eruption (Lowe, 2011; Lowe and Alloway, 2015). Volcanoes of southernmost South America have 54 been proposed as possible extra-Antarctic sources of some tephra recovered in Antarctic glacial 55 archives (Kurbatov et al., 2006; Narcisi et al., 2010; Narcisi et al., 2012), along with those from the 56 South Sandwich Islands and New Zealand (Dunbar et al., 2017; Narcisi et al., 2005; Narcisi et al., 57 2012). Thus, in this perspective, tephra recovered from southern Patagonia and Tierra del Fuego 58 (hereafter SPTF) have additional value as a tool for the correlation of geological, paleoclimatic and 59 paleoenvironmental archives at intercontinental scale. 60

Late Glacial to Holocene tephra layers in SPTF (Argentina and Chile) have been recovered in different sedimentary archives including terrestrial outcrops, marine and lacustrine cores (Fontijn et al., 2014). They have been produced by several volcanoes during tens of eruptions some of which are characterized by intensities up to a Volcanic Explosive Index (VEI) of 6 (Naranjo and Stern, 1998). Some of these eruptions emplaced volumes of tephra larger than 20 km<sup>3</sup> (e.g., Hudson Ho eruption; Weller et al., 2014), with a dispersal area covering almost the whole SPTF and extending over the surrounding oceans.

Despite their significance, and with the exception of few cases (Haberle and Lumley, 1998; Kilian et 68 al., 2003; Kratzmann et al., 2010; Stern, 2008; Weller et al., 2014), most of the eruptions occurred in 69 70 the SPTF have been solely characterized by the chemical composition of the bulk tephra deposit or the bulk rock analysis of the juvenile component. Conversely, textural and mineralogical 71 72 characterization, as well as major- and, even most, trace-element analyses of glasses are scarce. This issue represents a significant limitation when correlating tephra at both proximal to distal scale (i.e., 73 SPTF) and distal to ultra-distal, Southern Hemisphere-wide scale (e.g., with the Antarctic ice 74 75 records). In fact, the major- and trace-element compositions of the bulk deposit may significantly differ from that of individual glass shards, commonly recovered and analyzed in ultra-distal 76

77 locations, since the former may be variably affected by sample heterogeneity, and inter-shard 78 variations (Pearce et al., 2004). Moreover, the bulk rock composition will correspond to that of glass fraction only if the first one is aphyric and formed only by juvenile material with no accidental 79 lithics. Finally, many explosive eruptions are rhyolitic or dacitic in composition and almost 80 indistinguishable using the major-element chemistry alone. In such cases, the study of textural and 81 mineralogical features of tephra (e.g., nature and abundance of the components, particles 82 morphology, vesicle size and distribution and crystal content) associated with single-glass-shard 83 trace-element data is an invaluable help for the identification of their eruptive sources and for the 84 correlation of different tephra layers (Pearce et al., 2004). This approach, typical of modern 85 tephrostratigraphy, has never been fully applied to Patagonian tephra and only few papers report on 86 the textural and physical features of studied deposits as well as on the mineralogical assemblage of 87 88 distal tephra.

In this work, we present and discuss new data on texture, mineralogy, major- and trace-element 89 geochemical composition performed on single glass shards of several tephra layers occurring in 90 different, mostly unreported, stratigraphic sections in SPTF (Argentina and Chile). In addition, we 91 provide new radiocarbon ages of charcoals, peats, and soils that further constrain the correlation 92 between tephra layers and known volcanic eruptions. Findings of this investigation implement the 93 existing tephrostratigraphic framework for the SPTF by also increasing the inventory of known 94 outcrops. In the light of these results, we discuss the provenance of some tephra layers found in the 95 96 Antarctic ice-records and previously attributed to the volcanoes of Southern and Austral Volcanic 97 Zone of the Andean Cordillera.

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#### 101 **3.** Volcanological framework

In South America, most of the explosive Holocene volcanism is produced by the Andean Arc, a segmented volcanic arc along the Andean Cordillera (Stern, 2004). Volcanism formed as a result of the subduction of the Nazca and Antarctic plates underneath the South American Plate (Fig. 1), and is subdivided into four main volcanic zones separated from each other by volcanic gaps (Stern et al., 1984): the Northern (NVZ), the Central (CVZ), the Southern (SVZ), and the Austral Volcanic Zone (AVZ). The SVZ and AVZ are the closest to the area under study.

108 The SVZ comprises 60 volcanic centers aligned along a 1400 km-long, continuous volcanic arc 109 active since the Late Quaternary. Similarly, the AVZ volcanic arc comprises six volcanic complexes 110 active since the Late Quaternary: Lautaro, Viedma, Aguilera, Reclus, Mt Burney and Fueguino, also 111 known as Cook (Corbella and Lara, 2008; Stern and Kilian, 1996).

Tephrostratigraphic and tephrochronological studies conducted in the Patagonia-Tierra del Fuego region have shown that explosive volcanism has been extremely active during the Holocene and Late Glacial period, often with high magnitude eruptions (Fontjin et al., 2104). In geological records, tephra layers have been correlated to large eruptions from four principal sources: Hudson, Mt Burney, Reclus and Aguilera volcanoes (Stern, 2008; Fig. 1).

The Hudson volcanic complex is the most active in the southern SVZ. Tephrostratigraphic records count at least a dozen of large-scale explosive eruptions since the Late Glacial period (Fontijn et al., 2014). The major explosive events of Hudson volcano occurred at ca.17,400 cal yrs BP (Ho) (Weller et al., 2014), at 7,750 cal yrs BP (H<sub>1</sub>) (Fontijn et al., 2014; Prieto et al., 2013), at 3,920 cal yrs BP (H<sub>2</sub>) (Naranjo and Stern, 1998), and in AD 1991 (H<sub>3</sub>) (Scasso et al., 1994). All these eruptions produced a considerable volume of pyroclastic material, possibly ranging between >20 km<sup>3</sup> (Ho) to ca. 4.3 km<sup>3</sup> (H<sub>3</sub>).

Mt Burney is a volcanic complex formed by a somma and an inner stratocone. The study of tephra over the Patagonia and Tierra del Fuego has yielded evidence for several eruptions from Mt Burney volcano, including two large Plinian eruptions named MB<sub>1</sub> and MB<sub>2</sub> (Stern, 2008). Radiocarbon dating indicates an age for MB<sub>1</sub> eruption comprised between 8,851 and 9,949 cal yrs BP (Kilian et 128 al., 2003; Stern, 2008). The age of MB<sub>2</sub> tephra has also been determined at several sites between 3,818 and 4,711 cal years BP (Kilian et al., 2003; McCulloch and Bentley, 1998; McCulloch and 129 Davies, 2001; Stern, 2008). Both the Plinian eruptions producing MB<sub>1</sub> and MB<sub>2</sub> tephra were VEI 5 130 and produced volumes of tephra exceeding 3 and 2.8 km<sup>3</sup>, respectively (Stern et al., 2008). Some 131 other minor tephra layers have been identified possibly emplaced after smaller eruptions of Mt 132 Burney (Kilian et al., 2003). These have been dated from the oldest to the youngest at >9,511 cal yrs 133 BP, between 9,175±111 and 9,511±121 cal yrs BP and between 2,026±48 to 2,063±90 cal yrs BP 134 (Kilian et al., 2003). 135

Reclus is a small stratovolcano that has erupted mainly dacite lavas and pyroclastic ejecta 136 (Harambour, 1988). The present tephrostratigraphic and tephrochronologic framework in southern 137 Patagonia points to three main tephra layers sourced form Reclus volcano. The widespread R<sub>1</sub> tephra 138 139 layer (Tephra I of Auer, 1974) is attributed to a Plinian eruption of Reclus volcano dated at ~12,700 <sup>14</sup>C yrs BP (McCulloch and Davies, 2001; McCulloch et al., 2005; Stern, 2008; Stern et al., 2011) 140 and possibly involving a volume of ca. 5 km<sup>3</sup> of pyroclastic material (Stern et al., 2011). Several 141 other Holocene tephra layers chemically compatible with Reclus volcano, but much thinner and 142 considerably less spatially dispersed than R<sub>1</sub>, have been identified in several localities of southern 143 Patagonia. In particular, two tephra, R<sub>2</sub> and R<sub>3</sub>, derived from Reclus have been found in sediment 144 cores from Torres del Paine National Park, southern Chile (Villa-Martínez and Moreno, 2007) and 145 have been dated at 1789 cal yrs BP and 1035 cal yrs BP, respectively (Breuer et al., 2013; Moy et al., 146 147 2008).

Aguilera is a remote stratovolcano identified in 1985 and indicated as the source of a regionally widespread Holocene tephra named A<sub>1</sub>, mostly found close to Lago Argentino just east of this volcano. The A<sub>1</sub> tephra has an estimated age of~3,067-3,339 cal yrs BP (Stern, 2008). Several other thinner and less widely distributed tephra layers have been identified in the vicinity of Lago Argentino and Torres del Paine, and correlated to Aguilera volcano. The age obtained for one of these layers is older than the age of  $A_1$  tephra layer around <4,560 <sup>14</sup>C yrs BP. The age of tephra layers younger than  $A_1$  was not constrained.

The three remaining volcanoes of the AVZ, namely Lautaro, Viedma, and Fueguino (Fig. 1) erupted in the Holocene and during historical time. Lautaro and Viedma are two stratovolcanoes located in the northernmost AVZ (Corbella and Lara, 2008), yet no tephra layers in SPTF have attributed to their activities. Fueguino represents the southernmost Holocene volcanic occurrence of the Andes (Corbella and Lara, 2008). It produced a cluster of small pyroclastic cones (<150 m) and columnarjointed lava domes (Puig et al., 1984); this small to moderately energetic activity makes unlikely that widely dispersed tephra sourced from this complex.

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#### 163 4. Sampling and Methods

Stratigraphic logging and sampling of tephra layers were performed (February 2015 field work) in 164 SPTF (Fig. 1 and Table 1 for coordinates of stratigraphic sections). Sampling sites have been 165 selected in medial-distal locations, with respect to the potential Holocene volcanic sources of tephra, 166 and following criteria of easy accessibility and good exposure of the outcrops. From north to south, 167 168 the stratigraphic sections here reported are: Arroyo Robles close to the Potrok Aike Lake (Argentina; section AR-1), Río Rubens (Argentina; section RR-1), Estancia Otway (Chile; sections EO-1, EO-2), 169 Río O'Higgins (Tierra del Fuego, Chile; section ROH-2); Punta Arenas (Chile; section PA-1), Río 170 Tres Brazos (Chile; sections RTB-1, RTB-2), Laguna de los Cisnes (Tierra del Fuego, Chile; section 171 172 LA-1). These are all unreported outcrops but one (ROH-2) (Stern, 1991). Tephra layers with a 173 thickness ranging from 1 to 16 cm have been identified mainly in natural exposures including banks of alluvial and meandering channels, peat bogs, alluvial terraces, as well as in trenches dug for 174 livestock beverage and road cuts, yielding 16 samples. 175

Samples were first washed with deionized water in an ultrasonic bath to disaggregate them and to remove impurities. Hydrochloric acid (10% v/v) was added to the samples to dissolve carbonates. Afterward, hydrogen peroxide (35% v/v) was repeatedly added to the samples that were successively heated at 120°C to further disaggregate the matrix, remove organic matter and soluble compounds.
Samples were then dried at 60°C, mounted with epoxy resin in 1-inch stubs, polished and prepared
for textural and geochemical analyses.

Tephra samples were described under a petrography microscope. The texture, components and 182 mineral assemblage of tephra were studied at the Istituto Nazionale di Geofisica e Vulcanologia, 183 Sezione di Pisa (INGV-Pisa) with a scanning electron microscope (SEM) Zeiss EVO MA and 184 images have been collected in back-scattered electrons (BSE) mode. Major-element glass 185 compositions were determined at the Laboratorio Microsonda Elettronica C.N.R.-I.G.G. of Florence 186 using a JEOL JXA-8600 microprobe (EMP) equipped with 4 wavelength dispersive spectrometers 187 (operating conditions:15 kV accelerating voltage, 10 nA beam current, 10 µm probe diameter and 20 188 s (10 s for Na and 40 s for Cl and F) and 20 s acquisition time for peak and background (40 s for Cl 189 190 and F), respectively) and at HPHT Laboratory INGV-Roma using a JEOL JXA 8200 electron microprobe (EPMA) equipped with five wavelength-dispersive spectrometers (operating conditions: 191 192 15 kV accelerating voltage, 8 nA beam current, 5 µm probe diameter, 10 and 5 s acquisition time for peak and background, respectively). Standards of glass and natural mineral phases were analyzed to 193 test the accuracy of data during the analyses (see Supplementary Material 1). 194

The trace-element concentrations were determined on single glass shards by Laser Ablation-195 Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) at the Università di Perugia, 196 Dipartimento di Fisica e Geologia. The analyses were carried out with a Teledyne Photon Machine 197 198 G2 laser ablation system coupled to a Thermo Fisher Scientific iCAP-Q, quadrupole based, ICP-MS (Petrelli et al., 2016a, 2016b; Petrelli et al., 2008). The LA-ICP-MS operating conditions were 199 200 optimized before each analytical session by continuous ablation of NIST SRM 612 glass reference material (Pearce et al., 1997) to provide maximum signal intensity and stability for the ions of 201 202 interest while suppressing oxides formation (ThO+/Th+ below 0.5%). The U/Th ratio was also monitored and maintained close to 1. The stability of the system was evaluated on <sup>139</sup>La, <sup>208</sup>Pb, <sup>232</sup>Th, 203 and <sup>238</sup>U by a short-term stability test. It consisted of 5 acquisitions (one minute each) on a linear 204

scan of NIST SRM 612 glass reference material (Petrelli et al., 2016a, 2016b). Tephra glasses were analyzed by using a circular laser beam with a diameter of 20  $\mu$ m, a frequency of 8 Hz, and an energy density at the sample surface of 3.5 J/cm<sup>2</sup>. NIST SRM 610 reference material (Pearce et al., 1997) was used as the calibrator and <sup>29</sup>Si as the internal standard. USGS BCR2G reference material was analyzed as unknown to provide a quality control (Jochum et al., 2005). Under these operating conditions, precision and accuracy are better than 10 % for all the investigated elements (Petrelli et al., 2008; Petrelli et al., 2016a, 2016b).

Age of tephra was obtained by <sup>14</sup>C-AMS radiometric dating of organic matter (charcoal, soil and peat samples) that are intercalated with tephra layers. Unfortunately, organic matter was present only in 9 of the studied sections. Analyses have been performed at the CIRCE laboratories, Caserta, Italy. Radiocarbon dates were converted to calendar years before present (cal years BP) with the CALIB 7.01 program (Stuiver et al., 2018), using the IntCal13 radiocarbon ages calibration curve (Reimer et al., 2013).

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## **5.** Results: chemical composition, tephra texture, mineral assemblage and age

A synoptic view of the features of the studied tephra layers is reported in Table 1 including grainsize, nature and relative abundance of components, texture of volcanic particles and mineral assemblage. Figures 2 and 3 report the photographs and the schematic representation of the studied stratigraphic sections, respectively. Figures 4, 5 and 6 show selected SEM-BSE images of the studied tephra. The major- and trace-element compositions of each sample are reported in Table 2 as averages of multiple point analyses by EPMA and LA-ICP-MS, and the whole analytical data set is reported in Supplementary Material 1.

The total alkali vs silica diagram (TAS, Fig. 7a; Le Bas et al., 1986) shows two main compositional clusters for the glasses of the studied tephra in the trachyte and rhyolite fields, respectively. In detail, samples EO-2H, EO-1B, ROH-2C and AR-F1 plot overall in the trachyte field, with SiO<sub>2</sub> ranging

- between 63.7 and 68.6wt%. All the other samples plot into the rhyolite field with SiO<sub>2</sub> comprised
  between 73.4 and 79.8 wt%.
- In the K<sub>2</sub>O vs SiO<sub>2</sub> diagram (Fig. 7b), which is commonly regarded as the most significant plot to 232 233 discriminate tephra from Patagonia and Tierra del Fuego (Stern, 2008), the samples form three main compositional groups. The first one (Group Tr) consists of the four trachyte samples. The rhyolite 234 samples compositions define two distinct clusters. Among these, the Group Rh1 is characterized by a 235 SiO<sub>2</sub> ranging between 73.4 and 79.8 wt% and K<sub>2</sub>O between 1.19 and 2.25 wt% (samples ROH-2B, 236 RTB-1B, EO-1C, EO-2D, EO-2L, AR-1B, AR-1D, RR-2B, and PA-1B). On the contrary, the Group 237 Rh2 shows more restricted SiO<sub>2</sub> values comprised between 77.1 and 78.4 wt% and higher K<sub>2</sub>O, 238 ranging between 2.46 and 2.95 (samples EO-2B, RTB-2B, and LA-1B). 239
- The distribution of the incompatible elements of the 16 samples analyzed by LA-ICP-MS (Fig. 8) is that typical of orogenic magmas, with negative anomalies of Nb, Ta and Ti and positive anomalies of Pb. However, some significant differences between samples belonging to groups Tr, Rh1 and Rh2 can be observed. On average Group Tr shows higher content for most incompatible elements than the other two groups and particularly from Nd to Lu. Moreover, Rh1 glasses are less enriched in Rb than those belonging to Groups Tr and Rh2 (Fig. 8).
- These differences are emphasized in the diagrams Nb/Ba vs La/Zr, Rb/Ba vs Ti/Sm, Rb/Ba vs Sr/Nd 246 and Ce/Pb vs Ba/Th (Fig. 9). In these diagrams, samples belonging to Group Tr are well separated 247 from samples of groups Rh1 and Rh2. Indeed, these trachytes have distinctly higher Nb/Ba and 248 249 lower Sr/Nd and Ba/Th ratios. Rocks of Group Tr also have slightly higher Rb/Ba and Ce/Pb ratios. The higher Nb/Ba and Ce/Pb ratios of Group Tr with respect to Groups Rh1 and Rh2 denotes a less 250 251 marked orogenic signature of the former. Groups Rh1 and Rh2 are less clearly discriminated from each other, even though Rh1 samples have distinctly lower La/Zr and Rb/Ba, and higher Ba/Th with 252 253 respect to Rh2 samples. More in detail, the Rh1 samples PA-1B, RTB-1B, EO-1C and EO-2L have 254 lower La/Zr and higher Ti/Sm ratios, whereas samples RR-2B, AR-1B and AR-1D share higher

La/Zr and lower Ti/Sm ratios. Samples EO-2D and ROH-2B are characterized by intermediate values of these trace element ratios (Fig. 9).

The textural features and the mineral assemblage of the studied samples (Table 1) are consistent with the groups identified with the compositional data. In fact, Group Tr tephra are mainly composed of blocky, y-shaped or platy-cuspate, poorly-vesicular glass fragments ( $<100 \mu$ m) along with a minor amount of micropumices with spherical to slightly elongated and deformed vesicles. They contain scarce amounts of loose crystals of plagioclase (pl), orthopyroxene (opx), clinopyroxene (cpx), quartz (qz) and apatite (ap) (Table 1).

Group Rh1, conversely, is mostly composed of highly- to moderately-vesicular micropumices with spherical to coalesced and collapsed vesicles; micropumices occasionally bear microlites of pl, qz, opx, cpx and Fe-Ti oxides (Table 1). Samples from Group Rh1 commonly contain also abundant loose crystals of pl, qz, opx, Fe-Ti spinels and ap coated with volcanic glass (Table 1).

Group Rh2 is composed of moderately- to poorly-vesicular, blocky and y-shaped glass shards, bubble walls and bubble junctions together with a minor amount of micropumices with tubular, coalesced and collapsed vesicles (Table 1). Glass fragments are mostly aphyric with rare microlites of pl, opx and ap. The tephra also contains scarce loose crystals of pl, opx and ap and holocrystalline volcanic rock fragments (Table 1).

Radiocarbon ages obtained from studied successions are reported in Table 3. Ages span from Late
Glacial (EO-2A) to modern age (RR-2B), yet mostly comprised within the Holocene.

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#### 275 6. Discussion

#### 276 **6.1. Sources of tephra**

To assess the volcanic provenance of the studied tephra, we compared their glass compositions with those available in the literature. Moreover, we used the nature and abundance of components and the texture of juvenile particles (e.g. particle shape, vesicularity, type and abundance of microlites) forming pyroclastic deposits and the relevant constraints provided by radiocarbon ages. 281 It is worth to note that the geochemical characterization and provenance of tephra layers from 282 southern Andes volcanoes have been mainly performed through the analysis of the major-element compositions on bulk tephra up to recent times. The use of trace elements to improve the success of 283 the identification process is scarce. Furthermore, major- and trace-element determinations on single 284 glass shards analyses are even rarer. These latter should be preferred to bulk analyses because bulk 285 tephra often contain abundant phenocrysts, volcanic-lithic fragments, and non-volcanic material, and 286 therefore may not represent the actual composition of the melt fraction quenched at the time of 287 eruption (Pearce et al., 2004), which is indeed represented by glass shards (Shane et al., 2008). 288

The comparison between our microprobe major-element data on glass shards and the only available literature data (see references in the legend of Figs. 10 and 11) on glass shards and bulk tephra as well, shows that the three compositional groups Tr, Rh1 and Rh2 match very well three volcanic sources located in the Southern and Austral Volcanic Zone of the Andean Cordillera (Figs. 10 and 11): Hudson (Tr), Mt Burney (Rh1) and Reclus (Rh2) volcanoes.

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## 295 Compositional Group Tr - Hudson

The major- and trace-element glass compositions of samples belonging to Group Tr closely match 296 297 that of tephra erupted by Hudson volcano during the Holocene (Figs. 10a and 11a,b). Radiocarbon determinations constrain the age of Tr-tephra between 7,026±49 and 4,219±241 yrs BP (Figs. 3 and 298 12), suggesting they were most likely produced by the mid-Holocene H<sub>1</sub> eruption. This represents the 299 largest Holocene volcanic event of the southern Andes, with a volume of erupted materials >18 km<sup>3</sup> 300 (Naranjo and Stern, 1998; Stern, 2008) and an age of 7,750±95 cal yrs BP obtained as the best 301 average among several samples from TF (Prieto et al., 2013). Thickness of tephra belonging to 302 Group Tr is fully compatible with that of tephra previously identified in the SPTF region and 303 304 correlated with  $H_1$  eruption (Prieto et al., 2013).

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306 Compositional Group Rh1 - Mt Burney

307 Major element glass composition of samples belonging to Group Rh1, which includes the majority of the studied tephra, match that of the products erupted by Mt Burney volcano during the Holocene 308 (Fig. 10b). Within compositional Group Rh1, samples EO-2D, ROH-2B and AR-1D are well 309 310 bracketed in age between 9,299±65 and 7,325±46 yrs BP (Fig. 3). This age is compatible with the age of MB<sub>1</sub> eruption which is dated either at 8,851-9,949 cal yrs BP (Stern, 2008) or in the range of 311 9,009-9,175 cal yrs BP (Kilian et al., 2003). The compositions of Group Rh1 match also those of 312 tephra layer 5022-2T1 identified between 12.32-12.34 m in the ICDP core 5022 from Laguna Potrok 313 Aike in southern Patagonia, Argentina, correlated with the MB<sub>1</sub> tephra layer from Mt Burney 314 (Wastegård et al., 2013). The age-depth model reported for the core (Kliem et al., 2013) indicates 315 that the tephra layer has an age of ~9,545 cal yrs BP ( $2\sigma$  range 8851–10238 cal yrs BP) which 316 overlaps the range reported for MB<sub>1</sub> eruption (Stern, 2008) (Fig.12). Thickness of studied tephra 317 318 layer is compatible with that of tephra layers attribute to MB<sub>1</sub> eruption and previously identified in the SPTF region (Stern, 1991; Kilian et al., 2003; Stern, 2008). 319

320 Remarkably, in our Arroyo Robles section, a 2.5 cm thick tephra layer occurs under the MB<sub>1</sub> tephra separated by a 2 cm-thick peat horizon (Fig. 3). This tephra (AR-1B) has the same petro-chemical 321 322 characteristics (Fig. 9) of the overlying  $MB_1$  tephra (AR-1D) and can be attributed to an explosive activity of the Mt Burney slightly older than MB<sub>1</sub>. Several pre-MB<sub>1</sub>, tephra layers, dated between 323 ~20 and ~50 ka, have been identified in the Laguna Potrok Aike lacustrine record (Wastegård et al., 324 2013) and attributed to Mt Burney activity. Accordingly, tephra AR-1B could represent the first 325 326 report of a Mt Burney eruption occurred between MB1 and the those documented in the Potrok Aike record. 327

The age of the rest of Group Rh1 samples (EO-2L, EO-1C, PA-1B, RR-2B, and RTB-1B) is not fully constrained. We obtained a maximum age of 4,219 $\pm$ 241 yrs BP from a sample at the very base of sample EO-2L, but no age constraints at the top (Figs. 2, 3 and 12). In this regard, we do not observe any evidence of a sedimentological break or hiatus occurring between the dated peat sample and EO-2L tephra. EO-2L can be thus correlated with the Mid-Holocene Plinian eruption MB<sub>2</sub> of Mt Burney 333 volcano dated 3,818-4,711 cal yrs BP (Kilian et al., 2003; McCulloch and Bentley, 1998; McCulloch and Davies, 2001; Stern, 2008). Similarly, sample EO-1C is separated by a few cm of sediment from 334 EO-1B tephra (Figs. 2 and 3), which is in turn correlated with the Hudson  $H_1$  eruption dated at 335 7,750±95 cal yrs BP (Prieto et al., 2013). The age of the tephra EO-1C is thus younger than the age 336 of H<sub>1</sub> allowing a possible correlation to MB<sub>2</sub> eruption from Mt Burney, that in the investigated area 337 is reported to reach 5 cm of thickness (Stern, 2008), which is compatible with the 2-4 cm thickness 338 reported here. For PA-1B tephra, we obtained only a minimum age of 1,259±32 cal yrs BP, whereas 339 for RTB-1B tephra a modern age (Figs. 3 and 12). The RTB-1B age, however, is not coherent with 340 the stratigraphic framework, thus suggesting a considerably older age for this eruption. In addition, 341 we observe that samples PA-1B and RTB-1B have the same textural, mineralogical and 342 compositional characteristics as samples EO-2L and EO-1C (Fig. 10b). Thus we suggest their 343 344 correlation with MB<sub>2</sub> eruption.

Finally, sample RR-2B, which presents trace elements ratios different from EO-2L, EO-1C, PA-1B,
RTB-1B samples (Fig. 9) and a very young age (<200 yrs), may be correlated to the only known</li>
historical eruption of Mt Burney occurred in 1910.

Comparing our compositional data for Mt Burney products with those available in the literature, we 348 observe a good correspondence with major-element compositions but not for trace-element 349 compositions (Fig. 11c and d). For instance, we observe a shift toward lower Rb content and a higher 350 Sr content in the literature data with respect to our compositions. This can be explained with the 351 352 different type of analyses performed: bulk-tephra and glass trace-element compositions determined via energy dispersive XRF analysis (Stern, 2008; Stern and Kilian, 1996) could be affected by the 353 occurrence of microlites/crystals/lithics, whereas space-resolved single-shards LA-ICP-MS are 354 definitely representative of glass. 355

356

357 Compositional Group Rh2 - Reclus

Rhyolitic tephra of Group Rh2 can be correlated to the products erupted by Reclus volcano (Fig. 10c). In this case, the <sup>14</sup>C ages indicate two sub-groups, i.e., samples EO-2B and RTB-2B with age bracketed between 12,240 $\pm$ 54 cal yrs BP and 9,299 $\pm$ 65 cal yrs BP and LA-1B that is considerably much younger and has an age of <3,264 $\pm$ 46 cal yrs BP.

The first sub-group (samples EO-2B, RTB-2B) is compatible in age with R1 eruption from Reclus 362 volcano that was dated between ca 12,700 yrs BP (McCulloch et al., 2005; Stern, 2008). Also the 363 thickness of EO-2B, RTB-2B tephra layers is compatible with that  $R_1$  tephra which in this region is > 364 5 cm (Stern, 2008). As mentioned above, sample LA-1B is considerably much younger and has an 365 age of <3,385-3,585 cal yrs BP. This tephra is thus compatible in age with eruptions R<sub>2</sub> or R<sub>3</sub> dated 366 at 2,000 cal yrs BP (Villa-Martínez and Moreno, 2007). The two groups have very similar trace-367 element signatures (Figs. 11e,f) apart from those compositions deriving from bulk analyses for the 368 369 reasons above explained.

Samples EO-2B, RTB-2B of Group Rh2 match also the composition of tephra layers 5022-2T2,
5022-2T3, and 5022-2T4 recovered at 16.04-16.05 m, 16.48 m and 16.78-16.79 m in the Laguna
Potrok Aike 5022 core and correlated with the Reclus R<sub>1</sub> tephra (Haberzettl et al., 2007; Wastegård et al., 2013).

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375 6.2. South American tephra in Antarctica?

Southern Andes volcanoes, along with New Zealand and South Sandwich Islands volcanoes have 376 377 been considered as potential sources for some Holocene ultra-distal tephra found in ice records at various sites of Antarctica (Dunbar et al., 2017; Kurbatov et al., 2006; Narcisi et al., 2010). Detecting 378 whether these tephra layers are sourced from (i) mid-latitude volcanoes in the southern Andes or 379 New Zealand, (ii) mid/high-latitude circum-antarctic volcanic islands (South Sandwich and South 380 Shetlands) or (ii) high-latitude Antarctic volcanoes, is crucial to understand the atmospheric 381 circulations able to transport tephra onto the Antarctic ice. In this perspective, it urges a detailed 382 textural, mineralogical and geochemical fingerprinting, including major- and trace-element data of 383

tephra layers, in both ultra-distal and proximal-medial sites. This will offer a solid dataset in the framework of which possible stratigraphic correlations among different geological archives would be much more straightforward and reliable. To date, such a dataset is missing, while data are available on the major-element glass composition and on the age of tephra layers based on glacial proxies.

On these bases, it is only possible to define compositional lineages in order to distinguish the main 388 sources of Antarctic tephra. To this aim, we collected major-element data of Neogene-Quaternary 389 tephra from Antarctic ice cores, marine sediments, blue ice, continental outcrops as well as for 390 potential sources located in Antarctica and circum-Antarctic areas (Supplementary Material 2). Then, 391 we critically reviewed the obtained dataset discarding any analysis showing evidence of alterations. 392 In detail, we applied the screening methods for altered specimens reported for Antarctic tephra (Di 393 Roberto et al., 2012), also considering the criteria of alteration and alkali loss (Kilian et al., 2003). 394 395 Figure 13 reports more than 2000 analyses in the widely used K<sub>2</sub>O vs SiO<sub>2</sub> plot where the glass compositions define six clear geochemical lineages. 396

Lineage 1 is a typical alkaline lineage (Fig. 13); this includes glasses erupted by intraplate alkaline 397 volcanoes of the West Antarctic rift system (e.g., McMurdo Volcanic Group, Marie Byrd Land 398 399 volcanoes), most of the Andrill samples (Miocene to Quaternary), and marine and englacial tephra from Antarctica. At higher K<sub>2</sub>O/SiO<sub>2</sub> relative to Lineage 1, nephelinites (1a) and phonolites (1b) are 400 found. A scarcely populated trend is defined by high-silica glasses, with alkali-rhyolite to pantellerite 401 compositions deriving from extreme fractionation of alkali feldspar and quartz (SiO<sub>2</sub>>70 wt%, 402 403 Lineage 1c; Fig. 13) (Armienti et al., 1998; Armienti et al., 2001; Di Roberto et al., 2012; Martin et al., 2010). Most of the tephra layers found in the Antarctic records show compositions that can be 404 405 correlated with alkaline products, typical of Antarctic alkaline volcanoes.

A limited number of Antarctic tephra shows a subalkaline, low-K tholeiitic to calc-alkaline, majorelement signature, typical of subduction zone igneous products. These tephra layers cannot be related to the Antarctic alkaline volcanism, and can potentially derive from subduction-related volcanoes of circum-Antarctic volcanic provinces, such as the Antarctic Peninsula area (South Shetland Islands), the South Sandwich Islands in the southernmost Atlantic Ocean, the southern Andes and New
Zealand volcanic provinces (Fig. 13). These glass compositions define five other sub-alkaline
lineages.

Lineage 2 is potassic calc-alkaline (Fig. 13); this comprises glass compositions of tephra produced or 413 attributed to the Hudson volcano (including also four samples from this study). Also, Hudson 414 volcano has been proposed as the source for a trachybasaltic sample TD193 identified in the Talos 415 Dome core with an assigned age of 2.02 ka BP (Narcisi et al., 2012). This has been correlated to a 416 tephra with basaltic composition that is assumed to be regionally significant and bracketed between 417 uncalibrated radiocarbon ages 1,910±70 and 2,235±130 yrs BP (Naranjo and Stern, 1998). A few 418 Plinian eruptions fed by mafic magmas have been identified worldwide, able to spread ash to ultra-419 distal sites, i.e., Etna 122 B.C. (Coltelli et al., 1998), Fontana Lapilli (ca. 60 ka BP), the Masava 420 421 Triple Layer and the Masaya Tuff from Masaya caldera (2.1 and 1.8 ka BP), Nicaragua (Pérez et al., 2009), and Tarawera, New Zealand in 1886 (Houghton and Gonnermann, 2008). For the Hudson 422 volcano, there is no evidence reported for such an eruption during the Late Glacial period and in the 423 Holocene, thus the correlation between TD193 tephra and Hudson volcano should be reconsidered. 424 Sample TD216, also from Talos Dome ice core, and dated 2,355±54 yrs BP, has been correlated to 425 evolved products from Hudson, based on glass composition (Narcisi et al., 2012) slightly more 426 evolved than most evolved Hudson tephra. In the known volcanological record of this volcano, the 427 HW7 eruption has an age comparable to the one attributed to sample TD216 (Haberle and Lumney, 428 429 1998; Carel et al. 2011). However, the Ti content of TD216 tephra is significantly lower than that present in Hudson samples with comparable SiO<sub>2</sub>, and also the ratios K<sub>2</sub>O/TiO<sub>2</sub> and CaO/Al<sub>2</sub>O<sub>3</sub> are 430 431 different. Therefore, the attribution of this tephra layer to Hudson volcano is not based on solid ground. 432

Lineage 3 is rather K-rich calc-alkaline (Fig. 13) and includes the product erupted by Fueguino, Macá, Cay, and Aguilera volcanoes and also the products from Antarctic Peninsula area (Seal Nunataks) (Kraus et al., 2013). The glass compositions from Siple Dome ice core attributed to an

436 unreported eruption from Hudson volcano (Kurbatov et al., 2006), together with shards from Talos 437 Dome (Narcisi et al., 2012; Narcisi et al., 2017) ice cores, overlap the compositions of Aguilera rhyolites. Nevertheless, these rhyolitic compositions also plot on the rhyolitic extension of the 438 Antarctic alkaline trend (Lineage 1c), and can therefore represent the extremely evolved alkaline 439 products of an Antarctic volcano. Tephra VK3311-2 and VK3311-4 from Vostok ice core have been 440 potentially attributed to a southern Andes or South Shetland source. Nevertheless, its rather old age 441 (414 ka) and the CaO and TiO<sub>2</sub> content make it difficult to correlate this tephra with either a Macá or 442 Cay source. Layers 1117.1 and 1868.3 from Dome C ice core have been attributed to a South 443 Shetland source (Narcisi et al., 2005) that, despite a rather low Al<sub>2</sub>O<sub>3</sub> content, could be a plausible 444 correlation. 445

Lineage 4 is a rather K-poor calc-alkaline lineage (Fig. 13) that includes products erupted by the 446 447 Reclus volcano (Kilian et al., 2003; Stern and Kilian, 1996)(this work) and by volcanoes in the South Shetlands and South Sandwich Islands. No shards from tephra recognized in Antarctic records plot 448 along this lineage, with the significant exception of a cryptotephra found in the WDC06A ice core, 449 recovered from central West Antarctica and attributed to the Oruanui supereruption from Taupo 450 volcano, at ca. 25.6 ka (Dunbar et al., 2017). Interestingly, the WDC06A ash layer has an average 451 composition closely matching that of Reclus tephra (Fig. 13). The only difference between WDC06A 452 ash layer and Reclus products is a pronounced spread in K<sub>2</sub>O concentration (1.87 to 3.27 wt%), an 453 unusual feature for a strongly evolved, far-distal tephra. Tephra TD282 from Talos Dome ice core, 454 455 dated at 3,392±82 yrs BP (Narcisi et al., 2012) has K<sub>2</sub>O vs SiO<sub>2</sub> relationships compatible with Reclus compositions, but a correlation with Chile's Puyehue-Cordón Caulle has been suggested (Narcisi et 456 al., 2012). However, the K<sub>2</sub>O/TiO<sub>2</sub> ratio (2.63) points out a composition far removed from typical 457 trends of southern Andes volcanoes for which the value of K<sub>2</sub>O/TiO<sub>2</sub> expected at comparable SiO<sub>2</sub> 458 459 content would be around 7, and overlapping instead South Shetlands compositions (Supplementary 460 Material 2).

461 Lineage 5 is a low-K tholeiitic trend (Fig. 13); this includes glass shards from Mt Burney and South 462 Sandwich Islands volcanic arc (Hubberten et al., 1991; Pearce et al., 2014). This lineage overlaps the composition of some tephra layers found in Siple Dome, Vostok, and Talos Dome ice cores. Among 463 464 the latter, the majority of glass compositions with  $SiO_2 < 70$  wt% is consistent with a provenance from South Sandwich Islands (Basile et al., 2001). Conversely, glass with SiO<sub>2</sub> ranging between 70 465 and 75 wt%, cannot be definitively correlated with products of any known volcanic source. More in 466 detail, the SDMA2571 tephra in Siple Dome ice-core, dated at 1805 B.C., was related to the products 467 of Mt Burney (Kurbatov et al., 2006). According to these authors, the age of SDMA2571 tephra is 468 comparable to the MB<sub>2</sub> eruption from Mt Burney dated at 3,818-4,711 cal yrs BP (Kilian et al., 2003; 469 McCulloch and Bentley, 1998; McCulloch and Davies, 2001; Stern, 2008). However, the chemical 470 compositions of SDMA 2571 tephra do not match with the published composition of MB<sub>2</sub> eruption 471 472 tephra (Kilian et al., 2003; Stern, 2008; Wastegård et al., 2013). Our data also confirm this evidence. In fact, although the glass composition of SDMA 2571 tephra lies on the compositional trend defined 473 by the Group Rh1 attributed to Mt Burney eruption, only a partial overlap exists between the most 474 evolved glass of SDMA2571 tephra and less evolved compositions measured in our samples (Fig. 475 13). In Talos Dome ice core, the cryptotephra layer TD299 dated at 3,677±92 yrs BP was correlated 476 to this SDMA2571 tephra, thus in turn possibly correlated to the activity of Mt Burney, even though 477 not to a definite eruption. As reported for SDMA2571, no clear match exists between compositions 478 of TD299 tephra and products of Mt Burney eruptions (Kilian et al., 2003; Stern, 2008; Wastegård et 479 480 al., 2013) (Fig. 13). The glass composition with SiO<sub>2</sub> ranging between 70 and 75 wt% falling on this trend and deriving from Antarctic ice records (mostly Siple Dome) can be correlated either with 481 482 evolved products from Mt Burney or with the most evolved compositions of the South Sandwich Islands. Nevertheless, the drop in Al<sub>2</sub>O<sub>3</sub> contents with increasing SiO<sub>2</sub> is not compatible with a Mt 483 Burney trend, making a South American source poorly feasible also in this case. 484

Also Lineage 6 is again a low-K tholeiitic lineage (Fig. 13), with a slightly lower K content and a modest spread of SiO<sub>2</sub> concentrations than the Lineage 5. This lineage is defined by products of South Sandwich Islands and Fueguino volcano. Tephra layers from Dome C, Siple Dome, Dome Fuji and Vostok ice cores plot on this trend. In more detail, the andesitic layer 9008 from the Antarctic SDMA (Siple Dome) ice core, dated 9,216 yrs B.C., and tentatively attributed to an eruption of the Hudson volcano using geochemical and chronological data (Kurbatov et al., 2006), distinctively plot on this trend (Fig. 13). Additionally, a Hudson tephra characterized by this composition and by a large dispersion such as to justify its transport up to the Antarctic it is not known in Patagonia-Tierra del Fuego. It is therefore plausible this tephra is sourced in South Sandwich volcanic activity.

The result of the comparison between our data and those available in the literature indicates that 494 Antarctic tephra mostly derives from Antarctic or circum-Antarctic volcanoes. For subalkaline 495 tephra, proposed correlations with South American volcanoes are either unfeasible or at least 496 alternative origins are equally feasible. In summary, for Holocene tephra found in Antarctica there is 497 498 no straightforward need to invoke a source at latitude lower than the circum-Antarctic volcanoes. A possible exception could be represented by the cryptotephra found in WDC ice core correlated with 499 500 Oruanui supereruption, from Taupo (Dunbar et al., 2017). However, atmospheric dispersal modeling indicates a significant ash accumulation of 30 g/m<sup>2</sup> on the core site (Dunbar et al., 2017), quite at 501 odds with the extremely fine grain-size of the cryptotephra and the convolute atmospheric path 502 followed by the particles arriving on site more than eight days after the eruption. 503

Possible explanations for the lack of South American tephra in Antarctica can be given in the light of 504 results recently published dealing with the potential ash impact from Antarctic volcanoes (Gever et 505 506 al., 2017). Findings indicate that the potential impact of volcanic ash from Antarctic eruptions is 507 linked to volcano locations and eruption intensities. Eruptions with eruptive plumes <10 km in height and from latitude >70° are likely to be confined in Antarctica due to moderated wind zones encircled 508 by the polar jet stream. Conversely, eruptive plumes >10 km in height have a higher potential for 509 510 extra-Antarctic ash dispersal. Also, eruptions from lower-latitude Antarctic volcanoes as Deception 511 Island are more likely to encircle the globe with ash, even for moderate size eruptions, reaching tropical latitudes (Geyer et al., 2017). This because they are located out of the control of the polar jet 512

513 stream. The lack of ash produced by Austral mid-latitude volcanoes can be due to the effect of the 514 polar jet stream, which acts as a physical barrier on its two sides, hampering their dispersal to 515 Antarctica.

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### 519 7. Conclusions

520 New field occurrences of tephra layers produced by Andean large-scale Holocene eruptions are 521 reported from SPTF. These findings considerably expand the present knowledge of the areal 522 dispersion of these tephra and offer new tie points for future precise eruption volume calculation. A complete stratigraphic, geochronological (whenever possible), textural, mineralogical and 523 compositional characterization of tephra has been carried out including the determination of major 524 and trace elements on single glass shards by EPMA and LA-ICP-MS. These results significantly 525 strengthen the tephrostratigraphic framework of the Patagonia-Tierra del Fuego for the last ca. 13 ka 526 by applying, for the first time in this area, the multidisciplinary approach of the modern 527 tephrostratigraphy and tephrochronology. On this solid ground, we correlated tephra layers across the 528 studied stratigraphic sections and found the volcanic source of studied tephra layers in Hudson, Mt 529 530 Burney and Reclus volcanoes in the southern Andes. In detail, we correlate the tephra layers with major explosive eruptions that affected SPTF during the Late Glacial to Holocene, namely the H<sub>1</sub> 531 532 eruption from Hudson, MB1 and MB2 eruptions from Mt Burney and R1 and R2/R3 eruptions from 533 Reclus.

We compiled a database including major- and trace-element compositional data of Neogene-Quaternary tephra found in Antarctic ice cores, marine sediments, blue ice and continental outcrops as well as tephra produced by volcanic sources located in Antarctica and circum-Antarctic areas. We revised the chemical and petrological soundness of the attribution of some of these tephra to South American volcanic sources. Results indicate that most, if not all, tephra layers identified in Antarctic records can be correlated with Antarctic or circum-Antarctic volcanic sources (South Sandwich and South Shetland Islands). No clear need exists to invoke South American volcanic sources. If confirmed, this result calls for additional unequivocal new data to infer Holocene atmospheric circulation and transport of tephra from mid-latitudes to Antarctica.

543

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734

#### 735 Table captions

- Table 1 Synoptic scheme of the features of studied tephra layers.
- Table 2 Major and trace element compositions of glass in studied samples.
- 738 Table 3 Radiocarbon age results.
- 739

# 740 Figure captions

- Figure 1 Map of southernmost South America showing the locations of the Holocene volcanoes, the
  extent of the Austral Volcanic Zone of the Andes, and the tephra outcrops studied in this work.
- Abbreviations: AR, Arroyo Robles; RR, Río Rubens; EO, Estancia Otway; ROH, Río O'Higgins;
- PA, Punta Arenas; LA, Laguna de los Cisnes; RTB, Río Tres Brazos. The inset shows the Southern
- Hemisphere with the localities mentioned in the text: F, Dome Fuji; V, Vostok Station; C, Dome C;

746 T, Taylor Dome; A, Andrill; S, Siple Dome; W, WAIS Divide.

747

- Figure 2 Photographs of the studied stratigraphic sections. a: Estancia Otway 1; b: Estancia Otway
  2; c: Punta Arenas; d: Río Tres Brazos 1; e: Río Tres Brazos 2; f: Laguna de los Cisnes; g: Río
  O'Higgins; h: Arroyo Robles; i: Río Rubens.
- 751
- Figure 3 Logs of studied stratigraphic sections and their correlations.

753

- Figure 4 Scanning electron microscope back-scattered (SEM-BSE) images of tephra samples. a:
  EO-1B tephra; b: EO-1C tephra; c: EO-2B tephra; d: EO-2D tephra; e: EO-2H tephra; f: EO-21 tephra.
- 757
- Figure 5 Scanning electron microscope back-scattered (SEM-BSE) images of tephra samples. a:
  PA-1B tephra; b: RTB-2B tephra; c: RTB-1B tephra; d: LA-1B tephra.
- 760

761	Figure 6 - Scanning electron microscope back-scattered (SEM-BSE) images of tephra samples. a:
762	ROH-2B tephra; b: ROH-2C tephra; c: AR-1B tephra; d: AR-1D tephra; e: AR-1F tephra; f: RR-2B
763	tephra.
764	
765	Figure 7 - a: Total alkali vs Silica diagram (TAS) (Le Bas et al., 1986); b: K <sub>2</sub> O versus SiO <sub>2</sub> diagram.
766	
767	Figure 8 - Primordial mantle-normalized multi-element patterns (McDonough and Sun, 1995). a: all
768	studied samples; b: Group Tr samples; c: Group Rh1 samples; d: Group Rh2 samples.
769	
770	Figure 9 - a: Nb/Ba vs La/Zr; b: Rb/Ba vs Ti/Sm; c: Rb/Ba vs Sr/Nd; d: Ce/Pb vs Ba/Th for the glass
771	shards of tephra layers studied in this work. Each data point represents a single LA-ICP-MS point
772	analysis.
773	
774	Figure 10 - K <sub>2</sub> O vs SiO <sub>2</sub> diagrams reporting literature data compared with data of this work in which
775	the volcanic sources are unambiguously distinguished; a: Hudson (Group Tr); b: Mt Burney (Group
776	Rh1); c: Reclus (Group Rh2).
777	
778	Figure 11 - Selected trace element diagrams for comparison of volcanic sources with this work data.
779	
780	Figure 12 - Volume and age of the major eruptions from Hudson, Mt Burney and Reclus (Watt et al.,
781	2013; Weller et al., 2015) in comparison with the age of eruptions here discussed. Red lines
782	represent intervals for eruption ages defined by two <sup>14</sup> C ages (Table 3), red arrows represent intervals
783	for eruption ages defined by only one <sup>14</sup> C ages bounding the possible oldest or youngest age (Table
784	3).
785	

786 Figure 13 - K<sub>2</sub>O vs SiO<sub>2</sub> plot comparing compositional groups of tephra collected in Antarctic, Peri-787 Antarctic and South American regions. Antarctic tephra come from (i) englacial layers from Marie Byrd Land (MBL) and northern Victoria Land (NVL) (Dunbar et al., 2008; Wilch et al., 1999), 788 http://www.tephrochronology.org/AntT/about.html, and East Antarctica (Curzio et al., 2008; Harpel 789 et al., 2008); in this group highly evolved samples of Lineage 1c are included (Martin et al., 2010; 790 Martin, 2009), (ii) ice cores drilled in Fuji Dome (Fujii et al., 1999; Kohno et al., 2004), Taylor 791 Dome (Dunbar et al., 2003), Siple Dome (Dunbar and Kurbatov, 2011; Kurbatov et al., 2006), 792 http://www.tephrochronology.org/AntT/about.html, West Antarctic Divide-WDC (Dunbar et al., 793 2017), Vostok (Basile et al., 2001; Narcisi et al., 2010), Dome C (Narcisi et al., 2010; Narcisi et al., 794 2005), Talos Dome (Narcisi et al., 2010; Narcisi et al., 2012; Narcisi et al., 2017; Narcisi et al., 2001) 795 and (iii) offshore ANDRILL deep cores (Del Carlo et al., 2009; Di Roberto et al., 2012; Nyland et 796 797 al., 2013) and gravity cores (Del Carlo et al., 2015). Peri-Antarctic tephra are from South Shetland Islands (Hole et al., 1993; Kraus et al., 2013) and from marine tephra attributed to South Sandwich 798 799 sources (Hubberten et al., 1991). Tephra from South America are from semi-distal to distal layers collected in Patagonia and Tierra del Fuego and attributed to an Andean sources, i.e. the volcanoes 800 Hudson (Gutiérrez et al., 2005; Kratzmann et al., 2010; Naranjo and Stern, 1998; Weller et al., 801 2014), Reclus (Kilian et al., 2003; Stern and Kilian, 1996), Mt Burney (Kilian et al., 2003; Stern, 802 2008; Stern and Kilian, 1996), Aguilera (Kilian et al., 2003; Stern, 2008), Cook (Stern and Kilian, 803 1996), Macá and and Cay (Gutiérrez et al., 2005), as well as from layer studied in this work. For 804 805 locations see Figure 1. Specific samples mentioned in the text are labeled (same color as symbol).

806

#### 807 Supplementary Material Table 1

808 Dataset of major and trace elements data and secondary standard analyses.

810

809

# 811 Supplementary Material Table 2

Major- and trace-element data for tephra from Antarctic ice cores, marine sediments, blue ice,
continental outcrops as well as for potential sources located in Antarctica and circum-Antarctic areas.

814

Section Lat. S Long. W	PA-1 53°10'14.9" 070°56'19.3"	RTB-1 53°17'23.70" 71° 1'12.60"	RTB-2 53°17'25.26" 71° 1'12.66"	LA-1 53°14'43.20" 70°18'58.74"	E 52°47'2 71° 5'1			E0 52°44'2 71°20'5			RC 52°56'' 69°25'4			AR-1 51°51'27.77" 70°25'37.54"		RR-2 52° 3'37.14" 71°59'24.78"
Sample	PA-1B	RTB-1B	RTB-2B	LA-1B	EO-1B	EO-1C	EO-2B	EO-2D	EO-2H	EO-2L	ROH-2B	ROH-2C	AR-1B	AR-1D	AR-1F	RR-2B
Thickness (cm)	2-5	12-15	1-3	3-7, discontinuous	1-3	2-4	1-2	2-5	2	2	3-5	12	2.5	10-12	1-16, discontinuous	7, discontinuous
Color	grey-white (Fig. 2c)	white-grey (Fig. 2d)	white (Fig. 2d)	grey (Fig. 2f)	grey (Fig. 2a)	pale yellow (Fig. 2b)	milky white (Fig. 2b)	honey (Fig. 2b)	grey (Fig. 2b)	grey (Fig. 2b)	pale white (Fig. 2g)	pale yellow (Fig. 2g)	white (Fig. 2h)	pale grey (Fig. 2h)	pale yellow (Fig. 2h)	grey-white (Fig. 2i)
Grain size	very fine	fine	very fine	very fine	very fine	fine	very fine	fine to coarse ash	very fine	very fine	fine	very fine	fine to coarse ash	fine to coarse ash	very fine	fine to coarse ash
Glass shards	and cuspate glass shards, bubble	<20 µm blocky to y-shaped or cuspate glass shards (Fig. 5c)	<20 µm, bubble junctions and y-shaped glass shards; poorly-vesicular blocky glass fragments <100 µm with spherical to ellipsoidal and coalesced vesicles	<50 µm, moderately- to poorly-vesicular, blocky glass particles and y- shaped, bubble walls and junctions shards (Fig. 5d); mostly aphyric with scarce pl, opx, ap	blocky, y-shaped or platy-cuspate poorly-vesicular, glass fragments; size from few $\mu$ m up to ~100 $\mu$ m (Fig. 4a)	blocky, <100 μm shards; dense fragments with crystal-rich (pl+ox±opx) groundmass (Fig. 4b)	<30 µm, y- shaped, bubble walls and bubble junctions glass hards (Fig. 4c) and blocky particles		low to moderately vesicular, blocky shards <100 µm with spherical to slightly elongated and deformed vesicles; pl, opx microlites; bubble walls and junctions <50		bubble walls and bubble junctions, y shaped glass shards; moderately vesicular blocky glass few to ~100 µm in size	moderately- to			<100 µm, moderately- to poorly-vesicular, blocky particles and y-shaped shards, bubble walls and bubble junctions; mostly aphyric with sparse pl, opx microlites	
Micropumices	some highly vesicular and almost aphytic micropumices, <300 µm in size with coalesced and collapsed vesicles	moderately- to highly-vesicular micropumices <200 µm	minor highly- to moderately- vesicular micropumices <200 μm (Fig. 5b); micropumices with microities of pl, opx, cpx, Fe-Ti ox, ap	occur with tubular,	few micropumices with tubular vesicles and occasional microlites of pl, opx, Fe-Ti ox, ap	few moderately to highly-vesicular micropumices	coalesced and	moderately- vesicular with coalesced and collapsed vesicles, bearing		few high- to moderately- vesicular micropumices	<300 µm, highly- to moderately- vesicular micropumices with spherical to amoeboid vesicles, coalesced, collapsed, rarely tubular; aphyric, occasionally including microlites of opx, pt, opx, Ti-	some poorly- to moderately- vesicular micropumices with amoeboid to collapsed vesicles	abundant, highly- to moderately- vesicular micropumices with spherical to coalesced and collapsed vesicles; micropumices occasionally bear microlites of pl, qz, opx, cpx, Fe-Ti oxides (Fig. 6c)	abundant highly- to moderately- vesicular micropumices <500 µm in size, with spherical to coalesced and collapsed vesicles (Fig. 6d)	with elongated,	highly- to moderately- vesicular micropumices <1 mm with spherical to coalesced and collapsed vesicles; glass groundmass is aphyric to crystalline with abundant microlites of feldspar and minor
Crystals	cpx, opx, pl and Fe	<ul> <li>(strongly zoned), opx, cpx wetted by</li> </ul>	loose crystals of pl, opx, cpx, Fe-Ti oxides, ap, wetted by vesicular volcanic glass	crystals of pl, opx,	scarce loose crystals of pl <150 µm	subhedral crystals of pl, opx, cpx, ap, Fe-Ti oxides coated with highly- vesicular glass; crystals with cracks and perforation patterns (channels	often coated with vesicular to dense glass	<1 mm-sized, loose crystals of pl, qz, opx, Fe-Ti spinels, cpx and ap coated with highly- vesicular glass	crystals of pl, opx, cpx and ap	abundant loose crystals of pl, qz, opx, Fe-Ti spinels and ap coated with volcanic glass and few µm blocky glass shards, bubble walls and bubble junctions (Fig. 4f)	loose crystals of pl, cpx, opx and qz <400 μm n occur coated with	loose crystals of pl, opx, cpx, qz and apatite	<500 µm, loose crystals of pl, qz, opx, Fe-Ti spinels, cpx and ap coated with vesicular glass	<500 µm, loose crystals of pl, qz, opx, Fe-Ti spinels, cpx and ap often coated with moderately vesicular glass	loose crystals of cpx, pl and opx	<2 mm, loose crystals of pl, opx, cpx, qz often coated with moderately vesicular glass (Fig. 6f); crystals with cracks and alteration textures along the cracks
Lithics	well rounded volcanic rock grains and abundant diatoms	abundant fragments and crystals with cracks and perforation pattems (channels or tunnels)	volcanic rock grains	scarce holocrystalline volcanic rock fragments		or tunnels)	present	present	present	well-rounded lithic fragments of holocrystalline volcanic rocks		rare fragments of holocrystalline rocks		holocrystalline volcanic rocks	holocrystalline rock fragments are scarce	
Stratigraphic notes	layer sandwiched between two soils (PA-1C, above and PA-1A, below), with desiccation cracks (Fig. 2c)	top and bottom of the layer slightly reworked and diffuse; charcoal fragments (sample RTB-1C) dispersed in the uppermost 3 cm of the tephra	conglomerate (Fig. 2e)	several cm-thick (sample LA-1A; Fig. 2f)		emplaced over a peat layer (Fig. 2a)	layer interbedded with peat layer (Fig. 2b)	layer interbedded with peat layer (Fig. 2b)			lowest layers, lying with wavy basal contact over a peat layer several cm-thick (sample ROH-2A; Fig. 2g)		lowermost layer in the section; embedded betwen two peat layers (samples AR-1A, AR-1C, Fig. 2h)	mid layer in the section; sandwitched betwen two peat layers (samples AR 1C, AR-1E, Fig. 2h)	the section (Fig. 2h)	tephra tooped by a soil layer rich in organic matter with dispersed charcoals has been observed (sample RR-2A; Fig. 2i)

Abbreviations: cpx, clinopyroxene; opx, orthopyroxene; pl, plagioclase; ox, oxides; ap, apatite

	Table 2. Major and	d trace element cor	npositions of gla	ass in the stu	died samples
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	AR	-1F	EO	-1B	EO	-2H	RO	H-2C	AR	-1B	AR	-1D	EC	)-1C	EO	-2D	EC	)-2L	PA	-1B	RO	H-2B	RR	-2B	RTE	3-2B	EO	-2B	LA-	1B	RTB	B-1B
Compositional Group	٦	Γr	т	r	-	Tr		Tr	R	h1	RI	h1	R	h2	Rł	12	R	h2														
	n-11	et dov	n-14	et dev	n-12	et dov	n=12	st.dev	n=10	et dov	n-22	et dov	n-17	et dov	n=6	et dev	n-11	et dov	n-11	et dov	n=10	et dev	n-15	et dov	n=7	et dou	n-11	et dov	n-22	et dov	0-15	et des
SiO <sub>2</sub>	65.4	51.UEV 1	64.6				65.4		77.6		78.3		77.2		76.6		78.2		77.9		78.1		78.1		77.9		77.6		78.0	0.2		0.8
=																																
TiO <sub>2</sub>	1.17		1.29				1.15		0.19		0.16	0.05			0.29	0.11			0.27		0.22		0.16				0.12		0.14	0.04		0.07
Al <sub>2</sub> O <sub>3</sub>	15.9		15.7	0.2			15.8		13.3		12.6		12.9		13.4		12.8		12.7		12.7		12.7		12.8		12.9		12.6	0.1		9.0
MnO	0.28		0.16		0.17		0.29		0.13		0.04	0.02			0.09		0.05		0.03		0.10		0.05				0.14		0.06	0.03		0.02
MgO	1.41		1.52		1.39		1.41		0.30		0.23	0.04			0.46		0.34	0.08			0.44		0.24	0.03			0.23	0.08		0.02		0.05
FeO	4.87		5.04		4.82		4.89		1.26		1.16		1.51		1.73		1.28		1.35		1.48		1.22		1.34		1.33		1.26	0.06		0.2
CaO	2.79		3.12		2.81		2.91		1.45		1.26		1.73		2.03		1.46		1.63		1.54		1.33	0.08			1.55		1.47	0.06		0.2
Na <sub>2</sub> O	4.67		5.29		4.78		4.46		3.96		4.17		4.16		3.65		3.50		4.08		3.64		4.19		3.25		3.43		3.53	0.1		0.4
K₂O	2.95		2.87		2.96		2.98		1.75		2.01		1.79		1.50		1.99		1.73		1.66		1.99		2.68		2.60		2.74	0.07		0.6
P <sub>2</sub> O <sub>5</sub>	0.52		0.39	0.05	0.41		0.68		0.10		0.04	0.02			0.19		0.05		0.05	0.02	0.07		0.05	0.02			0.15		0.03	0.02		0.02
Total	98.8	1	99.4	0.5	98.4	0.8	97.7	0.9	97.4	1	97.6	1	98.3	0.9	96.5	0.9	95.3	2	98.5	0.6	96.4	3	98.3	0.8	94.9	1	96.7	2	96.1	0.9	94.6	0.7
	n=10	st.dev	n=33	st.dev	n=10	st.dev	n=12	st.dev	n=7	st.dev	n=17	st.dev	n=8	st.dev	n=8	st.dev	n=7	st.dev	n=8	st.dev	n=2	st.dev	n=13	st.dev	n=7	st.dev	n=17	st.dev	n=17	st.dev	n=4	st.de
Sc	23.7	2	23.8	2	23.9	2	23.9	2	12.7	1	11.9	1	13.6	2	9.7	1	13.0	1	13.6	0.72	11.5	2	11.3	0.9	13.6	1	11.5	2	10.9	1	15.4	:
	6821	510	6894	700	6594	788	6594	990	849	71	939	75	1578	735	1152	520	1103	144	1451	220	1386	482	898	43	1344	160	877	181	725	76	743	11
v	67	11	60	8	61	12	61	29	4.7	0.7	7.5	3	12.7	8	10.0	9	10.7	2	14.0	3	9.4	4	6.0	1	14.2	5	4.7	3	7.3	4	9.6	6
Cr	bdl		bdl		bdl		bdl		14.0		bdl		31.0		bdl																	
	1287	84	1283	59	1376	90	1376	139	326	19	320	14	341	116	353	72	277	36	335	31	425	125	321	16	306	43	359	26	386	50	597	212
Co	6.0	1	6.2	1	5.4	0.9	5.4	2	0.97		1.61	0.5	2.45		2.70		2.52	1	3.6	1	2.10		1.23	0.2	1.39	0.3	2.54	1	3.7	1	4.1	
Cu	8.3	3	9.2	3	7.8	2	7.8	5	14.6	4	12.7	4	19.1	12	16.6	7	21.4	3	22.3	4	17.9	6	11.1	3	11.9	6	6.9	3	7.8	2	14.0	
Ga	20.6	0.6	24.6	4	20.4	0.7	20.4	0.9	13.8	1	13.9	2	13.8	1	14.9	2	13.1	2	15.6	2	14.6	0.7	14.1	2	13.5	1	15.5	2	17.0	2	17.8	
Rb	66	3	69	3	69	4	69	10	28.2	2	28.2	2	27.7	5	26.0	3	19.3	2	23.7	2	24.6	2	27.7	2	22.8	3	45	4	50	4	50	2
Sr	292	31	268	23	283	57	283	100	174	13	187	15	199	53	206	54	189	50	222	25	247	89	187	24	216	48	275	56	255	43	234	9
Y	46	2	46	4	47	6	47	7	12.0	1.0	12.4	1	15.1	3	11.2	2	8.8	0.9	12.7	2	11.7	1	12.6	1	9.0	1	14.6	3	11.7	1	17.0	ł
Zr	469	13	471	41	475	48	475	61	92	10	99	6	133	39	103	23	115	12	139	20	133	41	99	8	119	14	105	26	78	7	78	8
Nb	19.5	0.7	20.1	1	19.8	2	19.8	2	5.1	0.3	5.3	0.4	5.2	1	4.4	0.6	3.7	0.6	4.7	0.3	4.5	0.6	5.1	0.4	4.0	0.5	9.3	0.8	8.1	0.9	8.4	0.4
Cs	1.63	0.1	1.78	0.2	1.66	0.2	1.66	0.2	0.51	0.05	0.51	0.1	0.55	0.1	0.55	0.2	0.40	0.1	0.54	0.1	0.52	0.05	0.46	0.1	0.67	0.4	0.68	0.1	1.00	0.3	0.81	0.1
Ва	766	28	745	43	788	61	788	84	561	22	563	34	525	40	480	48	352	25	434	42	475	22	559	36	384	33	660	64	679	58	621	42
La	49	2	50	3	50	5	50	6	15.1	0.6	15.9	1	18.5	2	13.6	2	10.7	0.9	14.8	1	15.7	4	15.3	1	10.7	1	28.3	2	25.1	2	25.6	2
Ce	103	5	105	8	103	9	103	10	29.5	2	30.6	2	36	5	27.1	3	21.4	1	28.7	1	30.3	5	29.7	2	21.8	2	52	5	47	4	44	2
Pr	12.1	0.5	12.4	1	12.3	1	12.3	1	3.19	0.2	3.4	0.3	4.1	0.6	3.01	0.4	2.44	0.2	3.4	0.4	3.12	0.3	3.4	0.3	2.35	0.3	5.5	0.5	5.0	0.6	5.1	0.6
Nd	50	3	51	4	51	5	51	6	12.9	1	13.0	1	16.4	3	11.6	2	9.7	0.7	13.3	2	11.7	1	13.4	2	9.6	1	20.2	2	17.5	3	18.9	2
Sm	10.4	1	10.7	2	10.2	2	10.2	1	2.50	0.3	2.72	0.6	3.29	0.9	2.24	0.7	1.99	0.4	2.63	0.7	2.47	0.3	2.88	0.7	1.84	0.4	3.6	0.8	3.13	0.6	3.6	0.8
Eu	2.72	0.2	2.73	0.3	2.62	0.5	2.62	0.3	0.46	0.07	0.54	0.2	0.57	0.3	0.45	0.1	0.45	0.05	0.71	0.2	0.54	0.1	0.48	0.1	0.47	0.1	0.81	0.2	0.73	0.2	0.68	0.2
Gd	9.3	1	9.4	1	9.3	0.7	9.3	1	2.09	0.4	2.46	0.7	2.73	1	2.25	0.7	1.59	0.3	2.44	0.4	1.92	0.1	2.05	0.4	1.81	0.3	3.21	0.9	2.56	0.7	3.26	0.9
ТЬ	1.40	0.1	1.37	0.2	1.37	0.2	1.37	0.2	0.34	0.06	0.33	0.09	0.37	0.1	0.28	0.1	0.24	0.05	0.35	0.06	0.28	0.06	0.34	0.07	0.24	0.06	0.44	0.1	0.35	0.08	0.50	0.09
Dy	8.3	0.5	8.4	1	8.5	1	8.5	1	1.96	0.1	2.14	0.4	2.56	0.7	1.68	0.3	1.44	0.1	2.14	0.2	1.83	0.04	2.02	0.4	1.55	0.5	2.42	0.5	1.94	0.5	2.62	0.9
Ho	1.77	0.1	1.72	0.2	1.82	0.4	1.82	0.2	0.38	0.06	0.45	0.1	0.49	0.08	0.38	0.1	0.30	0.06	0.45	0.09	0.38	0.03	0.44	0.1	0.30	0.03	0.51	0.2	0.41	0.1	0.52	0.2
Er	4.9	0.3	4.9	0.4	4.9	0.6	4.9	0.6	1.05	0.3	1.33	0.3	1.67	0.4	1.05	0.2	0.92	0.2	1.38	0.3	0.93	0.2	1.24	0.3	0.85	0.2	1.41	0.4	1.23	0.3	1.48	0.3
Tm	0.74	0.05	0.71	0.1	0.74	0.2	0.74	0.1	0.18	0.03	0.20	0.07	0.25	0.07	0.14	0.05	0.15	0.03	0.22	0.08	0.20	0.07	0.21	0.05	0.17	0.04	0.22	0.05	0.16	0.06	0.26	0.02
Yb	5.1	0.4	4.9	0.8	5.3	0.8	5.3	1	1.33	0.3	1.50	0.5	1.61	0.5	1.29	0.5	0.95	0.3	1.36	0.4	1.13	0.3	1.55	0.4	1.05	0.3	1.38	0.3	1.26	0.4	1.81	0.6
Lu	0.83	0.08	0.78	0.1	0.82	0.1	0.82	0.2	0.20	0.03	0.22	0.1	0.25	0.05	0.19	0.08	0.18	0.03	0.25	0.09	0.12	0.06	0.23	0.05	0.16	0.05	0.19	0.07	0.17	0.07	0.29	0.08
Hf	10.7	0.6	10.5	1	10.7	2	10.7	2	3.32	0.3	3.5	0.5	4.0	1	2.97	0.6	3.28	0.6	4.0	0.9	3.6	0.7	3.4	0.6	3.11	0.6	3.08	0.8	2.37	0.4	2.33	0.3
Та	1.16	0.1	1.17	0.2	1.18	0.2	1.18	0.2	0.44	0.07	0.40	0.1	0.39	0.1	0.33	0.05	0.28	0.03	0.34	0.09	0.25	0.1	0.40	0.08	0.32	0.07	0.78	0.2	0.72	0.1	0.72	0.1
Pb	14.9	0.3	18.2	3	15.5	2	15.5	1	8.4	2	8.0	1	12.5	9	8.2	0.8	6.7	1	9.3	3	7.6	2	8.3	0.8	6.7	1	11.4	2	14.0	3	11.9	
Th	7.7	0.4	8.0	1	7.9	0.9	7.9	1	2.38	0.3	2.28	0.3	2.49	0.3	1.92	0.3	1.39	0.09	2.14	0.2	2.55	1	2.28	0.3	1.47	0.2	5.9	0.6	5.4	0.6	5.3	0.4
U	1.90	0 1	2.03	03	1.85	04	1.85	0.2	0.64	0.04	0.67	0.2	0.73	0.2	0.71	0.2	0.59	02	0.64	0.1	0.60	0.2	0.66	0.1	0.43	0.08	2.05	0.7	1.52	0.3	2 00	0.4

Abbreviations: n, number of analyses; st.dev, standard deviation; bdl, below detection limit

# Table 3. Radiocarbon age results

Sample Label	Laboratory	Material	<sup>14</sup> C yrs BP	<sup>14</sup> C cal yrs BP	median cal year	∂ <sup>13</sup> C‰ V-
	code		-	(range 2g)	BP	PDB
RTB-1C	RC479	Charcoal	267±37	277-459	321	-38.13±1.43
RTB-2A	RC491	SOM	12240±54	13966-14402	14143	-26.54±2.04
PA-1C	RC475	Charcoal	1259±32	1084-1281	1216	-14.07±0.80
LA-1A	RC494	SOM	3264±46	3385-3585	3495	-24.78±4.40
EO-1A	RC486	SOM	7294±71	7965-8303	8106	-37.29±1.25
EO-2I	RC490	SOM	4219±241	4090-5461	4762	-29.60±0.84
EO-2C	RC488	SOM	9299±65	10276-10661	10490	-24.12±4.63
EO-2E	RC489	SOM	7026±49	7744-7955	7865	-36.02±1.35
EO-2A	RC477	Charcoal	13054±54	15359-15861	15643	-30.77±1.26
ROH-2A	RC493	SOM	9146±48	10224-10482	10308	-33.42±1.73
AR-1E	RC485	SOM	7325±46	8014-8291	8119	-22.32±1.68
RR-2A	RC481	SOM	9±38	Modern	Modern	-24.39±4.54

Abbreviations: SOM, soil organic matter

























