

# Multiple sources for tephra from AD 1259 volcanic signal in Antarctic ice cores

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#### **Abstract**

Strong volcanic signals simultaneously recorded in polar ice sheets are commonly assigned to major low-latitude eruptions that dispersed large quantities of aerosols in the global atmosphere with the potential of inducing climate perturbations. Parent eruptions responsible for specific events are typically deduced from matching to a known volcanic eruption having coincidental date. However, more robust source linkage can be achieved only through geochemical characterisation of the airborne volcanic glass products (tephra) sometimes preserved in the polar strata. We analysed fine-grained tephra particles extracted from layers of the AD 1259 major bipolar volcanic signal in four East Antarctic ice cores drilled in different widely-spaced locations of the Plateau. The very large database of glass-shard geochemistry combined with grain size analyses consistently indicate that the material was sourced from multiple distinct eruptions. These are the AD 1257 mega-eruption of Samalas volcano in Indonesia, recently proposed to be the single event responsible for the polar signal, as well as a newly-identified Antarctic eruption occurred in AD 1259. Finally, a further eruption that took place somewhere outside Antarctica has contributed to tephra deposition. Our high-resolution, multiple-site approach was critical to reveal spatial heterogeneity of tephra at the continental scale. Evidence from ice-core tephra indicates recurrent explosive activity at the Antarctic volcanoes and could have implications for improved reconstruction of post-volcanic effects on climate from proxy polar records.

#### Submission Files Included in this PDF

#### File Name [File Type]

AD1259\_text\_Jan\_2019.docx [Manuscript File]

Fig1 sample position dic18.pdf [Figure]

figura 2\_v3.JPG [Figure]

Fig3 micro foto dic 2018.pdf [Figure]

Fig4\_TAS\_AD1259\_thin+ comp.pdf [Figure]

Fig5\_TASthin\_trend TD.pdf [Figure]

Supplementary AD1259 rev2019.docx [MethodsX]

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#### Research Data Related to this Submission

There are no linked research data sets for this submission. The following reason is given:

Microprobe single-grain data are given as Supplementary Material along with details of analytical conditions

## MULTIPLE SOURCES FOR TEPHRA FROM AD 1259 VOLCANIC SIGNAL IN ANTARCTIC ICE CORES

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#### **Abstract**

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Strong volcanic signals simultaneously recorded in polar ice sheets are commonly assigned to major low-latitude eruptions that dispersed large quantities of aerosols in the global atmosphere with the potential of inducing climate perturbations. Parent eruptions responsible for specific events are typically deduced from matching to a known volcanic eruption having coincidental date. However, more robust source linkage can be achieved only through geochemical characterisation of the airborne volcanic glass products (tephra) sometimes preserved in the polar strata. We lysed fine-grained tephra particles extracted from layers of the AD 1259 major bip volcanic signal in four East Antarctic ice cores drilled in different widely-spaced locations of the Plateau. The very large database of glass-shard geochemistry combined with grain size analyses consistently indicate that the material was sourced from multiple distinct eruptions. These are AD 1257 mega-eruption of Samalas volcano in Indonesia, recently proposed the the mgle nt responsible for the polar signal, as well as a newly-identified Antarctic, eruption occurred in A 59. Finally, a further eruption that took place somewhere outside Antarctica has contributed to tephra deposition. Our high-resolution, multiple-site approach was critical to reveal spatial heterogeneity of tephra at the continental scale. Evidence from ice-core tephra indicates recurrent explosive activity at the Antarctic volcanoes and could have implications for improved reconstruction of post-volcanic effects on climate from proxy polar records.

#### 35 Highlights

- Significant tephra concentration in AD 1259 volcanic signal from four Antarctic ice cores
- Compositional heterogeneity of tephra suggests sourcing from multiple distinct eruptions
- Linkage of the Antarctic ice signal with the Samalas AD 1257 eruption confirmed
- A new Antarctic eruption that occurred in AD 1259 has been also identified
- Antarctic regional-scale effects of local volcanic activity conceivable
- 41 **Key words**: Cryptotephra; Antarctica; Ice Cores; Volcanic isochron; Glass shard
- 42 microanalysis; Antarctic rifting volcanism; Samalas AD 1257 eruption

#### 1. Introduction

As it is documented in the vast literature produced during the last four decades, continuous volcanic profiles from polar ice sheets reconstructed by electric conductivity (ECM) and sulphate measurements are punctuated by prominent spikes recording explosive eruptions of the past (e.g., Hammer, 1980; Delmas et al., 1992; Langway et al., 1995; Severi et al., 2012; Sigl et al., 2014, 2015). These signals can be used both as reference horizons to provide independent age constraints for the ice core series, and to reconstruct the history of explosive volcanism and its relationship with climate. Volcanic events with bipolar occurrence are particularly interesting in this respect. These are typically interpreted as related to massive low-latitude events capable to produce sulphuric acidic deposition all over the world with the potential of forcing global climate (e.g., Langway et al., 1995; Sigl et al., 2015). Their record in both polar regions also enables direct north-south synchronisation of ice stratigraphies, which is of crucial importance to reconstruct the phasing of climatic events and understanding underlying mechanisms (Svensson et al., 2013).

Among the most outstanding volcanic deposition events of the last millennia (Sigl et al., 2014), peak fallout of volcanic aerosols over the poles dated 1259 represents a fundamental age marker for ice chronologies. Its signal is recorded in several Greenland and Antarctic ice cores, and was initially identified by Langway et al. (1988), who suggested that the parent volcano could be probably located in the Northern Hemisphere close to Equator. Since then, numerous papers have considered various aspects of this event (e.g. Delmas et al., 1992; Zielinski, 1995; Stothers, 2000). Particularly, its source has been a matter of debate as until recently no record of large volcanic eruption around that date was known. On the basis of analysis of tiny glass shards, Palais et al. (1992) suggested that the material from Greenland and South Pole (SP) ice levels is indeed from the same volcano, and identified El Chichón, Mexico, as the probable source, despite the chemical match was not perfect in detail. Oppenheimer (2003) presented the hypothesis of a super-eruption of global significance or a smaller eruption enriched in sulphur. Baroni et al. (2008) used sulphur isotope analysis to indicate a stratospheric nature for the volcanic signals at the Antarctic Dome C and SP sites. More recently, a major caldera explosive event was identified at Samalas volcano, on Lombok Island, Indonesia (Lavigne et al., 2013, Vidal et al., 2015, 2016; Alloway et al., 2017). Based upon chronostratigraphic and geochemical studies nearby the source, and the analysis of historical texts, this eruption of exceptional size was dated at AD 1257, placed at the end of the Medieval Warm Period (ca. 900-1250 A.D., Mann et al., 2009). It has been inferred to be the single counterpart of the AD 1259 bipolar spike. In particular, according to a recent reconstruction of Antarctic continental-scale volcanic aerosol deposition, the sulphate injection greatly exceeded that of the AD 1815 cataclysmic Tambora eruption (Sigl et al., 2014).

When strong explosive volcanic eruptions occur, large quantities of solid particles (tephra) and gases penetrate the tropopause and rise to altitudes well within the stratosphere, where they can be distributed all around the globe. Tephra fallout can affect vast regions, and small particles can be deposited thousands of kilometres from active sources forming invisible horizons (e.g., Lowe, 2011; Ponomareva et al., 2015, and references therein). The fingerprint of volcanic material preserved in distant sites can univocally identify source areas and could be employed to disentangle the origin of volcanic glacio-chemical signals in polar ice cores

(e.g., Yalcin et al., 2006; Dunbar et al., 2017), that otherwise is conjectured from the record of documented eruptions. However, especially for tropical-equatorial eruptions the amount of tephra that could be dispersed towards the poles is typically very small and the material very fine-grained, making such tephra study very challenging.

A preliminary exploratory investigation of a shallow Antarctic ice core from the Concordia-Dome C site revealed evidence of an appreciable concentration of cryptotephra in connection with the AD 1259 sulphate peak (Petit et al., 2016). This intriguing observation prompted us to carry out a detailed tephra study in order to make inferences about source(s) that produced the tephra and to discuss the related atmospheric implications. In this work we describe the characteristics of the glassy volcanic material associated with the AD 1259 signal in different sectors of the East Antarctic Plateau (EAP). We took advantage of having access to various good-quality ice cores covering the last millennium to apply a multiple core approach that allows highlighting the spatial distribution of volcanic products. Note that while attempts to identify the parent eruption of major polar signals through a tephra study often rely on few shards (e.g., Zielinski et al., 1997; Barbante et al., 2013), here we obtained a large dataset based on a considerable amount of electron probe microanalyses that allows recognizing compositional heterogeneities within tephra, in association with ash grain size measurements. We also considered an inventory of candidate source volcanoes more extended than that employed in previous studies.

#### 2. Materials and Methods

In this study we used 4 EAP ice cores located at elevations between 1950 and 3488 m (Figure 1 and Table S1). Two core sites, Dome C-Concordia (DC) and Vostok (VK), are located ~ 600 km apart in the central, inner sector of the Plateau, and two, Talos Dome-TALDICE (TD) and GV7, are ~ 200 km apart in peripheral position facing the Ross Sea. They show different modern climate and atmospheric characteristics (e.g., Masson-Delmotte et al., 2011) as well as distance from the Quaternary volcanoes of the Antarctic rift provinces. All the cores used have an undisturbed stratigraphy and are provided with a detailed volcanic aerosol profile, either as sulphate or ECM measurements. They all show the broad and pronounced signal unambiguously related to the AD 1259 event that occurs at variable depth depending on the accumulation rate of the site (between 29.6 m at VK and 181.9 m at GV7, Figure 1a).

Since at the visual core inspection no macroscopic evidence for the presence of tephra was detected, the core depth intervals corresponding to the volcanic spike were sub-sampled continuously, albeit with different resolution (5 to 15 cm) depending on the local accumulation rate. Processing of subsamples for laboratory measurements was carried out under clean conditions. To reduce contamination of samples to a minimum, the outer portion of porous firn samples was removed with a clean ceramic knife while ice pieces were washed thrice in ultrapure water. The resulting decontaminated samples were then melted and an aliquot was used for quantitative measurements of dust concentration and size distribution using a Coulter Counter set up in a class 100 clean room (Delmonte et al., 2002). The only exception relates to the GV7 core, where presence of abundant drilling fluid prevented accurate Coulter Counter measurements. A separate aliquot of meltwater from levels showing unusually high concentration of particles with respect to the local background was filtered (nucleopore polycarbonate membranes) for tephra recovery. Filters were examined using light and scanning electron microscopes, and typical tephra grains were

- photographed (Figure 27. To investigate the source for the recovered material, we 132
- 133 determined the major element composition of individual shards using the electron
- 134 microprobe set up at the Institut des Sciences de la Terre (ISTerre) of Grenoble. The
- 135 operating details are given in the Supplementary Material.
- From the initial geochemical dataset (over 900 analyses) collected during different sessions, 136
- we cautiously discarded analytical data showing total oxide sums ≤ 60% and those obviously 137
- related to pure minerals (quartz, plagioclase, metals, etc.). The rest, consisting ~ 320 138
- 139 measurements generally made on very small individual glass particles, was normalised to
- 140 100% total oxide values for subsequent interpretation. We expect a decrease of precision but
- 141 after normalisation all the elements with oxide contents > 1% can be considered robust
- 142 enough for interpretation (Iverson et al., 2017).

#### 3. Results

- EAP core samples selected at the culmination of the volcanic spike show microparticle 144
- 145 concentrations well above background levels for each site (Fig. 2). Central Plateau samples
- show concentrations higher (a factor 6 to 10) than background levels for firn (~ 8 ppb, 146
- 147 Delmonte et al., 2013) and mass size distributions well-defined around modal values smaller
- 148 than background (~ 2 µm on average during Holocene, Delmonte et al., 2005). For DC, the
- 149 mode is around 1.7 μm, while for VK it is between 1.3 μm and 1.9 μm respectively for samples.
- VK-16 and VK-14, although some very large particles up to ~ 20 μm were included in 💭 150
- 151 latter.

- TD sample 87-1 from the base of the volcanic sulphate peak shows very large particles with 152
- mass modal values as high as ~ 6  $\mu$ m, associated concentration levels higher than ~ 10 153
- times background levels for firn (~ 12 ppb, Delmonte et al., 2013). From the lowermost to the 154
- 155 uppermost part of the volcanic spike (see Figure 1a for stratigraphic position of the samples),
- a progressive decrease in microparticle concentration and size can be observed. A 156
- 157 population of particles larger than  $\sim 5 \, \mu m$  is present in the two deepest samples (TD 87-1 and
- 158 86-4), while the relative abundance of particles smaller than 2 µm increases upward within
- 159 the peak. We note that sample 86-4 shows a bimodal distribution with a first mode smaller
- 160 than 2 μm and a larger mode around 4-6 μm.
- At the microscopic inspection, glass particles generally display well-preserved textures with 161
- no traces of abrasion strongly suggesting that the material was not subject to reworking 162
- 163 (Figure 3). Among the examined samples, TD 87-1 and 86-4 contain pumice particles with
- elongated vesicles up to ca. 40-50 µm long along with fine-size shards remnants of thin 164
- 165 vesicle walls. Particles in the filters from the inner EAP cores are typically represented by tiny
- curved and platy-like shards. Material from ple VK-14 contains glass particles up to 15-20 166
- um in size. Microscopic observations counted with grain size analysis exclude that the 167
- 168 volcanic material belongs to background dust, and instead provide compelling evidence of
- 169 primary tephra deposition at levels within the AD 1259 acidity peak.
- 170 Results of grain-specific geochemical analysis are illustrated in Figs 4-5, where the data are
- 171 plotted on the total alkali-silica (TAS) diagram. Silica co-variations with K<sub>2</sub>O, CaO, FeO and
- 172 Al<sub>2</sub>O<sub>3</sub>, not shown here, are coherent in providing the same chemical pattern. Representative
- 173 analyses of individual glass shards are presented in Table S3, along with biplot comparisons

of selected major-oxide ratios in the present data and in published literature for further potential source volcanoes and equivalents (Supplementary Material).

The analysed glass shards, taken altogether, display variable silica contents, from intermediate to evolved compositions (SiO<sub>2</sub> > 52 wt %). No basic and ultrabasic geochemistries are represented. Within the glass heterogeneous composition spreading over three TAS fields, we identify two main separate clusters of data, one trachytic falling in the alkaline field, ~ 63-65 wt %, and the other showing sub-alkaline affinity and straddling the trachyte-dacite-rhyolite boundaries (for brevity referred to hereafter as 'dacitic'), ~ 70 wt %. A third subpopulation, subordinate in terms of frequency, shows a siliceous rhyolitic composition ( $SiO_2 > 74$  wt %).

Volcanic glass composition also varies spatially (Figure 4a). Ice core shards from the Central EAP sites are predominantly sub-alkaline in composition. However, the three analysed samples display different characteristics. The very fine-grained DC sample and sample VK-14 also dominantly dacitic. Sample VK-16 displays two clusters of geochemical data. The main glass population is dacitic in composition and appears comparable with that in sample VK-14 and in DC, the subordinate population is a siliceous rhyolite. Sparse analyses from both VK samples fall within the trachytic glass group.

In all six ice sections from the two peripheral EAP sites trachytic tephra particles are dominating, but with occurrence of subordinate glass with different signature (Fig. 4a). At TD, we observe an interesting compositional variation with respect to the time-stratigraphic position of the samples (Figure 5). Volcanic ash on the TD 87-1 filter, situated at the very beginning of the sulphate fallout (Figure 1) and containing coarse particles, is mainly trachytic in composition. The adjacent TD 86-4 from the acme of the sulphate volcanic signal shows two main coexisting glass populations. This is consistent with the striking bimodal grain size distribution of this sample (Figure 2). According to scanning electron microscopic check during microprobe analysis, coarser particles correspond to trachyte, finer particles are mostly dacitic. Glass from the upper TD 86 samples -3 and -2, stratigraphically located at the later part of the spike and populated by fine particles, is trachytic. GV7 ice shows coexisting trachytic and dacitic geochemistries (Figure 4a). The two analysed samples are equally heterogeneous (not shown). In all samples from the peripheral cores, only one shard from TD falls within the rhyolite cluster identified in VK-16 (Figure 4a).

#### 4. Interpretation and discussion

4.1 *Identification of tephra sources* 

Filters from all studied cores contain significant volcanic glass that appears heterogeneous both in grain size and geochemistry and present variable spatial characteristics.

Taken as a whole, the composition of glass shards allows two prevailing and a third subsidiary populations to be distinguished. Trachytic shards are more abundant in the samples from peripheral EAP sites, which are characterised by coarser grain size. Dacitic shards occur in all sites but are dominating in the Central EAP samples, typically characterised by smaller particle size. This pattern already suggests that tephra transport

and deposition could be controlled by different atmospheric dynamics over the Plateau.

219 Although tephra transport is very different from background dust input onto the EAP (Narcisi

220 et al., 2005), mineral dust investigations highlighted that the periphery of the ice sheet in fact

is influenced by regional atmospheric circulation dynamics of the Western Ross Sea, while

sites from the inner part of the EAP are more sensitive to long-range high-altitude transport

above Antarctica (e.g., Delmonte et al., 2013).

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224 Focusing on the geochemical signature of volcanic glass as a major criterion for source

identification, we first point out that compositional heterogeneity in a tephra horizon could

be related to magmatic differentiation during a single parent explosive episode or to coeval

deposition from separate events. Several examples of both types of tephra are known in

Antarctic ice (e.g., Narcisi et al., 2016). Since alkaline (i.e. trachytic) composition and sub-

alkaline (i.e. dacitic) composition typically pertain to different tectonic settings, here we

230 interpret co-existing trachytic and dacitic tephras in the studied samples as related to

231 contemporaneous eruptions from independent sources.

Alkaline trachytic compositions are characteristic of Antarctic volcanoes, belonging to one of the largest active alkali rift systems of the world (Wover, 1989). Indeed, the identified trachytic glass shards, particularly copious in the filters from peripher pres that are adjacent to Victoria Land volcanic provinces, is chemically very consistent with compositions of the tephra layers in the TALDICE core originated from local sources during the last climatic cycle (Narcisi et al., 2012, 2016, 2017) (Figure 4b). We therefore deduce that the trachytic glass in the studied samples was produced by a local Antarctic explosive eruption occurred at AD 1259. The coarse particle size observed at TD which is ~ 200 km distant from the inferred source area, further surrets this interpretation. This event dispersed material mostly over the adjacent ice sheet region, but the ash deposition involved also more inland areas of the EAP, as the occurrence of sporadic trachytic shards in the VK samples demonstrates. Infrequent ash layers of Antarctic derivation in long cores from the EAP have been already observed within the last four glacial-interglacial cycle ice series (e.g., Narcisi et al., 2010). We infer that the Antarctic volcanic plume entered into the polar vortex circulation and then rapidly reached the inner sectors of the Plateau. Based on the available data, it is unclear whether the plume from the AD 1259 Antarctic eruption dispersed particulate material onto the SP area. In the early tephra investigation by Palais et al. (1992), no trace of trachytic glass is reported for the Antarctic ice core. That tephra study however, was based upon the analysis of a handful of volcanic particles, representing a limitation for the detection of compositional heterogeneity and multiple fingerprints within individual horizons. Finally, similarly to other local eruptions, this Antarctic event likely delivered sulphate aerosols, but this is difficult to detect as it is combined with the coincidental broad signal peaking at AD 1259 related to long-range stratospheric transport and deposition of aerosols and generated during an extra-Antarctic source event (see discussion below). Note that examples of circacoeval multiple eruptions manifesting as a single volcanic signal are known in the Antarctic ice record (Cole-Dai and Mosley-Thompson, 1999; Cole-Dai et al., 2000). They represent tricky case studies for estimation of atmospheric aerosol loadings by related eruptions, with implications for assessment of the real impact on climate (e.g., Timmreck et al., 2009).

Our discovery of Antarctic-sourced tephra associated with the AD 1259 acidic deposition is remarkable given the postulated tropical source of the eruption responsible for this polar signal (e.g., Sigl et al., 2015). Nevertheless it is not particularly surprising considering that Antarctic volcanoes from Victoria Land and Marie Pyrd Land show evidence of Holocenehistorical activity and ice cores drilled adjacent volcanoes contain numerous locally derived discrete tephra layers, sometimes in the form of invisible horizons, as a result of persistent explosive activity (e.g., Kurbatov et al., 2006; Narcisi et al., 2012). In this respect, we point out that that the local eruption identified here does not correspond to the Antarctic event dated 1254 ± 2 AD that produced widespread tephra deposition over most of the Pacific-facing sector of Antarctica (Narcisi and Petit, 2018, and references therein). At TD and GV7 in fact this eruption occurs as both coarse visible ash and a sharp sulphate spike standing well above the background values and clearly preceding the AD 1259 volcanic peak (e.g., Narcisi et al., 2001; Severi et al., 2012). The newly identified event neither corresponds to the local eruption at AD 1261 detected as both volcanic sulphate deposition and a large particle concentration peak in the West Antarctic Ice Sheet (WAIS) Divide ice core (Koffman et al., 2013) that clearly follows the AD 1259 signal. Therefore, within a decade three distinct local events took place in the Antarctic mainland that left tangible fallout traces in the ice sheet. Such rapid succession of eruptions could be overlooked in low time resolution studies and instead needs to be carefully considered when addressing the attribution of Antarctic ice-core signals, as having implications for reconstructions of volcanic forcing.

The main sub-alkaline component of dacitic composition is genetically linked to subduction-related volcanism. Differently from the trachytic glass, it is not straightforward to identify the source responsible for this tephra. The distant geographic location of the EAP with respect to subduction provinces provides no clues, and the tiny particle size of the volcanic material in the Central EAP ice suggests long-distance transport, thus enlarging the suite of potential source areas to be considered to the whole Southern Hemisphere and even beyond the Equator. Note in this respect that although not very frequently, ash produced in equatorial-tropical volcanoes could have reached Antarctica during past eruptions, as in the case of Pinatubo (15°14'N) tephra (2-10  $\mu$ m) identified in the 1993-94 snow layers at South Pole after the 1991 eruption (Cole-Dai et al., 1997). In the search for possible sources for the dacitic tephra, we therefore considered an extended inventory of volcanoes. A thorough discussion of this piece of our work is presented in Supplementary Material.

The recently discovered volcanic eruption of Samalas in the Indonesian Archipelago (8°33'S) was suggested as the most probable source for the AD 1259 polar spike, due to its exceptional size (estimated VEI and maximum plume height 7 and 43 km, respectively) and appropriate date (Example 2013; Vidal et al., 2015, 2016; Alloway et al., 2017). Indeed, we found positive chemical match with Samalas products over all constituent elements considered (Figure 4b). Thus, the striking geochemical similarities between the Samalas glass and the ice core dacitic glass population along with the significant differences between the ice core glass and products from other potential sources (Figure S2) led us to conclude that our dacitic glass material was sourced from the Samalas AD 1257 eruption. Note that this volcanic material is also chemically coherent with glass shards formerly found in Greenland and SP ice cores (Palais et al., 1992) suggesting a common source eruption (Figure 4b). The cataclysmic AD 1257 Samalas explosive eruption clearly ranks among the greatest volcanic events of the Holocene. Once injected into the stratosphere up to about 40 km (Vidal et al., 2015), the Samalas tephra particles must have been transported poleward. Volcanic particles are supposed to settle in the lower stratosphere and accumulate just

307 above the tropopause, similarly to <sup>10</sup>Be and sulphate. Then, when stratosphere/troposphere 308 exchange of mass and chemical species occurs above Antarctica, sedimentation of volcanic aerosols proceeds within the troposphere the ice sheet surface. The whole process 309 likely occurred on a timescale of 1-2 years, as indicated by the time shift between the 310 311 eruption and deposition. Evidence for stratospheric transport of volcanic ash to Central EAP 312 in association with strong explosive eruptions is not new. At Vostok, it has been observed 313 (Delmonte et al., 2004) that small particles with modal values around 1.5-1.7 µm are associated **stratospheric** 314 generally ash entering the troposphere stratosphere/troposphere folding, jointly with sulphate and likely <sup>10</sup>Be. We believe that in 315 316 case of injection of large quantities of volcanic ash to great heights in the stratosphere also 317 some relatively large particles can be transported in the stratosphere at great distance from the source, as suggested by presence of some large dacitic glasses in VK-14 sample. 318

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volcanic eruptions.

A limited subset of glass analyses from a Vostok sample indicate distinctive high-silica rhyolitic composition with sub-alkaline affinity (Figure 4a). In the TAS diagram, this evolved component appears separated from the two main glass populations previously discussed, suggesting a different source. Note that this rhyolitic glass was not detected in the samples from the peripheral sites characterised by conspicuous deposition of locally-originated trachytic ash, suggesting that it is likely unrelated to the newly identified Antarctic eruption. Indeed, no such composition is known in the recent volcanic record from Antarctic centres (Dunbar et al., 2008; Narcisi et. al, 2012) and neither in the Samalas products (Vidal et al. 2015; Alloway et al., 2017). We therefore infer that this glass could be originated from a further distant event that contributed to the ice-core tephra. Interestingly, this interpretation could be in accordance with previous investigations in the WAIS Divide ice core that show that the stratospheric microparticle deposition during the year 1258 occurred in two pulses (Koffman et al., 2013), thus hinting for the possible contribution of two quasi-coeval tropical

333 In the Southern Hemisphere, rhyolitic products related to subduction processes occur at 334 some active Andean volcanoes and especially in the volcanic centres of New Zealand (~ 39°S, 335 ca. 6000 km from the Vostokeite in direct line), whereas rarely were erupted from West Antarctic intraplate volcanoe rhyolitic ice-core glass shards display higher K<sub>2</sub>O contents 336 compared to glasses of American temporary volcanoes; they are also characterised by 337 338 CaO and FeO contents < 1 wt%, more typical of New Zealand rhyolitic glasses than of the Antarctic (Marie Byrd Land) ones found in the marine realm (Shane and Froggatt, 1992) 339 (Figure S3). Although we are aware that some Andean centres may have been more 340 341 geochemically evolved than it is currently remembered in literature data, none of the considered volcanoes appear compositionally concrete with our ice-core tephra sub-342 343 population (Figure S3).

Considering the recent tephra record of New Zealand volcanoes, we observe that ice-core glass mimics the chemical composition of Kaharoa Tephra, which represents the only rhyolitic deposit during the last 1000 years in the region (Nairn et al., 2004, Lowe et al., 2013) (Figure S3). This plinian eruption however is precisely dated to AD 1314 ± 12 (Lowe et al., 2013, and references therein), thus is ca. 50 years younger than the polar spike (Lowe and Higham, 1998). Therefore, despite the geochemical similarities, the significant age difference prevents this correlation. We conclude that the source for the identified rhyolitic glass, likely

located outside the Antarctic continent, remains undecided. Nevertheless, the New Zealand volcanic province represents the most frequently active rhyolitic zone on Earth (e.g., Smith et al., 2005) and is a suitable source of tephra in Antarctica, despite only one New Zealand tephra layer in Antarctic ice has been identified so far (Dunbar et al., 2017). Our intriguing finding could hopefully provide a hint for future investigations.

#### 4.2 Implications

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Volcanic eruptions are drivers of transient weather and climate disturbances (e.g., Robock, 2000). The possible climate-forcing produced by the Samalas event, the most powerful eruption of the last millennium, has been addressed in several papers using various proxy archives and historical documents, along with estimate of the release of gas during the eruption based upon an independent geochemical approach. The volatile emissions standing as the greatest volcanogenic gas injection of the last few millennia were enough to produce global cooling (Vidal et al., 2016). Indeed, considerable environmental and social postvolcanic effects were reconstructed that along the Central Indonesian archipelago affected also vast regions of Europe (Guillet et al., 2107; Alloway et al., 2017). According to Gennaretti et al. (2014), tree-ring-based temperature reconstruction from northeastern North America displays an abrupt cooling regime shift that chronologically coincides with the occurrence of a series of eruptions centred around the AD 1257 Samalas event suggesting volcanic impact on the local forests and ice-caps. Moreover, indirect geological sources show occurrence of an El Ni ke event in the Americas and SE Asia in the year after the mega-eruption that suggests causal connection between the volcanic event and the climate anomaly (Emile-Geay et al., 2008; Alloway et al., 2017). In the Antarctic record, the 13<sup>th</sup> century appears exceptionally rich in conspicuous volcanic signals, with the AD 1259 being the most prominent (e.g., Cole-Dai et al., 2000). Possible effects of volcanic activity around the date of 1259 have been invoked also for high southern latitudes, but the data are still very sparse. Using a combination of firn/ice core records, Frezzotti et al. (2013) identified middle 13th century as the onset of a 50yrs-long period of negative surface mass balance of the Antarctic ice she the continental scale. This pattern could be related to solar irradiance with other factors volcanic forcing, superimposing (Frezzotti et al., 2013).

Results of ice-core tephra studies presented here and elsewhere (Koffman et al., 2013; Narcisi and Petit, 2018, and references therein) collectively have shown for the first time that three distinct Antarctic eruptions took place in the time span of a decade between AD 1254 ± 2 and AD 1261. These eruptions produced deposition of tephra blanket and atmospheric sulphate aerosols onto the polar ice sheet. In the ice volcanic record local eruptions typically emitting only tropospheric sulphate are represented by strong but short-lived residence times of aerosols in the atmosphere (e.g., Castellano et al., 2005). This pattern suggests that such individual events most likely are incapable of significant large-scale climatic impact. However, here we raise question about the potential consequences of this closely spaced local eruption sequence occurred in association with the tropical Samalas eruption, on the Antarctic climate and environment. Note that owing to the close proximity to the source region the local forcing would be exerted through both the radiative impacts of gas and particulate aerosols and the reduction in ice surface albedo produced by repeated extensive tephra deposition. With respect to the latter factor, recent estimations have shown the significance of volcanic ash deposition onto snow/ice even from mid-sized eruptions at high-

latitudes to alter surface reflectivity and enhance glacier melting (e.g., Dadic et al., 2013; Young et al., 2014; Muschitiello et al., 2017). Given the continuous sustained explosive activity of the Antarctic volcanoes with related large production of tephra and consequent dispersal over the Plateau due to favourable atmospheric conditions (e.g., Scarchilli et al., 2011), we believe that the potential role of forcing caused by locally-derived ash deposits should not be neglected in Antarctic palaeoclimate reconstructions. This factor deserves further more specific investigation in future research.

With respect to sulphate emission, unfortunately the available data currently do not permit to distinguish between the contribution to the aerosol deposition from the Samalas event and the AD 1259 local Antarctic eruption. These limitations notwithstanding, at this stage we can remark that in Antarctica two distinct volcanic forcings (one tropical and the other of high southern-latitude) may be superimposed around the date of 1259. In conclusion, our results add complexity to interpretation of volcanic aerosol yields from polar records and could have implications for more reliable climate model simulations for the pre-instrumental period (Schneider et al., 2009; Stoffel et al., 2015, and references therein).

#### 5. Conclusions

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Non-visible tephra deposits trapped within polar snow and ice represent precious chronostratigraphic tools. When the material is found associated with a prominent acidic signal, firm attribution to specific eruptions can be given with implications for climate forcing reconstructions. However, tephra detection and fingerprinting is such remote locations is often problematic. We successfully used four cores collected from different sites in the EAP to demonstrate extensive deposition of volcanic dust on the ice/sheet coeval with the large acidity peak at AD 1259, a key time stratigraphic horizon of inter-hemispheric significance. Our compelling data show that the material displays different characteristics from site to site. Geochemical fingerprinting of tephra, obtained with a grain-specific methodology, indicates that altogether multiple distinct explosive events have contributed to the ice core ash deposition, i.e. a newly-identified Antarctic eruption in AD 1259, the great AD 1257 eruption of Samalas, and a further eruption likely occurred somewhere outside Antarctica. Indeed, spatial variations reflecting different atmospher reculation patterns over the EAP were significant in the volcanic deposition on the ice sheet and should not be discounted in order to obtain sound source attribution of volcanic signals in polar sequences. We therefore underline the need of detailed studies based upon a multi-site and parameter approach as well as a large number of chemical analyses for capturing complexities inside tephra. Our results of the chemical composition of hundreds of microscopic particles confirm the inferred linkage of the Antarctic ice signal with the Samalas tropical eruption occurred in AD 1257, but also provide evidence for a coincidental cluster of local explosive events, so far not adequately considered in climate reconstructions derived by ice-core volcanic aerosol records. Local activity instead was important in shaping the Antarctic volcanic record and should be regarded as an agent of potential regional disturbances, not least through dispersion of ash over large areas with consequent radiative impact. We emphasise the potential of tephra investigations with respect to traditional measurements of aerosol concentrations in ice also for identifying superimposition of distinct contemporary events at a single site. Our findings also contribute to a more complete reconstruction of the history of volcanic activity in the Antarctic region.

#### **Aknowledgements**

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#### Figure captions

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- Figure 1. (a) AD 1259 signal (as sulphate in mg/L, or electrical conductivity, ECM, in arbitrary
- units) in the studied Antarctic cores. TALDICE sulphate profile redrawn from Severi et al.
- 465 (2012), GV7 sulphate profile courtesy of R. Nardin. Also shown is the position of samples
- analysed for grain size and geochemistry (grey shaded blocks). The dashed line indicates
- 467 'bag' section limit and/or core break. (b) Map of Antarctica with location of the ice cores and
- 468 main Quaternary volcanoes in Victoria Land (e.g., Mt. Erebus, Mt. Melbourne and The
- 469 Pleiades) and in Marie Byrd Land, West Antarctica (e.g., Mt. Takahe and Mt. Berlin).
- 470 Figure 2. Mass-size distributions (Relative Units, R.U., %) of samples analysed for
- 471 geochemistry. (A): Central EAP samples from Dome C (DC 71-a) and Vostok BH6 (VK-30-14 and
- 472 VK-30-16) ice cores. (B): TD samples 87-1, 86-4, 86-3, 86-2 from the base to the top of the
- 473 volcanic sulphate spike.
- 475 Figure 3. Scanning electron microphotographs of volcanic glass particles from a, DC-71a; b-c,
- 476 VK-14; d-e, TD-87-1; f, TD-86-4.
- 477 Figure 4. (a) Total alkali-silica (TAS) classification diagram and alkaline/sub-alkaline division
- 478 line (Rickwood, 1989, and references therein) showing the normalised analyses of ice-core
- shards. Ph= Phonolite, An = Andesite, T = Trachyte, D = Dacite, Rh = Rhyolite. In the inset the
- 480 TAS diagram with envelopes for the three glass compositional sub-populations is illustrated.
- 481 (b) The TAS classification diagram as above showing the whole data set (in grey-scale)
- 482 compared with glass geochemical analyses for the most likely correlatives (data from
- 483 Alloway et al., 2017; Narcisi et al., 2012, 2016, 2017; Palais et al., 1992). Geochemical
- 484 comparison with further potential sources is provided in Supplementary Material.
- Figure 5. Total alkali-silica (TAS) classification diagram and alkaline/sub-alkaline division line
- 486 (Rickwood, 1989, and references therein) for the normalised analyses of ice-core shards in
- 487 the four TD samples. Data of pertinent samples are superimposed upon the whole data set
- 488 (in grey-scale) for comparative purposes. Ph = Phonolite, An = Andesite, T = Trachyte, D =
- Dacite, Rh = Rhyolite. For the stratigraphic position of samples with respect to the AD 1259
- 490 ice-core volcanic signal see Fig. 1.

#### **Captions for Supplementary Tables and Figures**

- 493 Table S1. Location and characteristics of the studied ice cores.
- 494 Table S2. Composition of reference glasses and Samalas samples measured at different
- 495 analytical conditions.
- 497 Table S3. Representative major element composition of individual glass shards determined
- 498 by electron microprobe analysis. Values are given in weight % oxide and are normalised to
- 499 100%. Total iron is expressed as FeO. MnO not determined. Glass populations as defined in
- the main text.
- 502 Figure S1. World map showing the location of Antarctic ice core sites (blue dots) and of

- selected volcanic sources considered in the text (red triangles). Letters for sources are as
- follows. CH, Chaitén; EC, El Chichón; HU, Hudson; MBL, Marie Byrd Land; NZ, New Zealand;
- 505 PCC, Puyehue-Cordon Caulle; QU, Quilotoa; SM, Samalas; SSh, South Shetland Islands; SSI,
- 506 South Sandwich Islands; VL, Victoria Land.
- 507 Figure S2. Monte Carlo simulation of the interaction and emission volumes of X-rays at 10kV
- for Na-KΔ in Na-Si rich glass considered as A) common polished sample and B) small 1x1 μm
- particle placed on the C-glue. The blue lines show the electron trajectory outside the particle.
- 510
- 511 Figure S3. Major element biplots for the analysed ice-core shards (in grey-scale) compared
- 512 with glass geochemical analyses for selected potential sources and counterparts (data from
- Moreno et al., 2015; Fontijn et al., 2016; Nairn et al., 2004; Kratzmann et al., 2009; Moreno et
- al., 2015; Nooren et al., 2017; Stewart and Castro, 2016; Shane and Froggatt, 1992). Location
- of considered source volcanoes is shown in Supplementary Figure S1.

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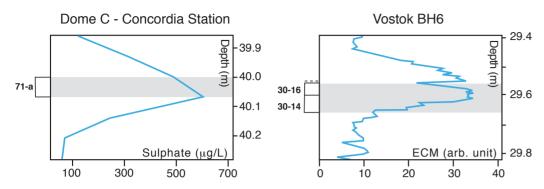
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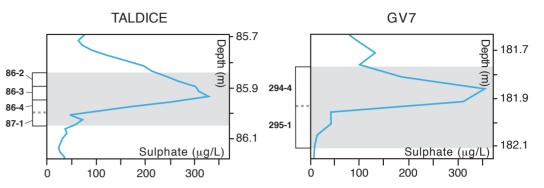
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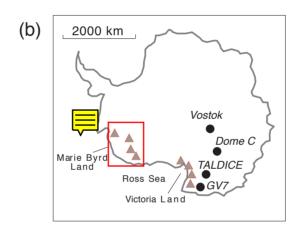
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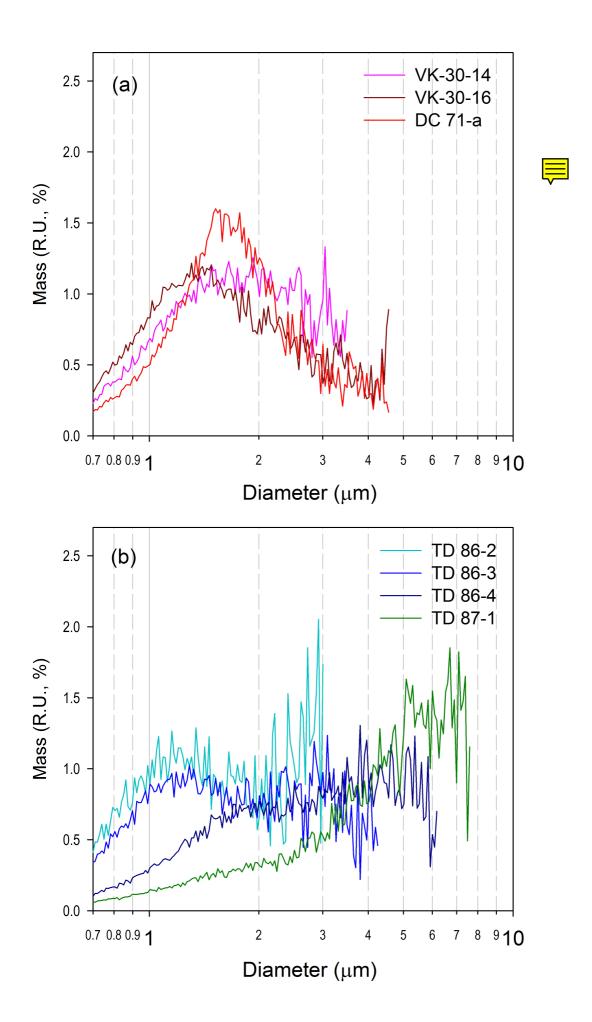
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### Peripheral Plateau









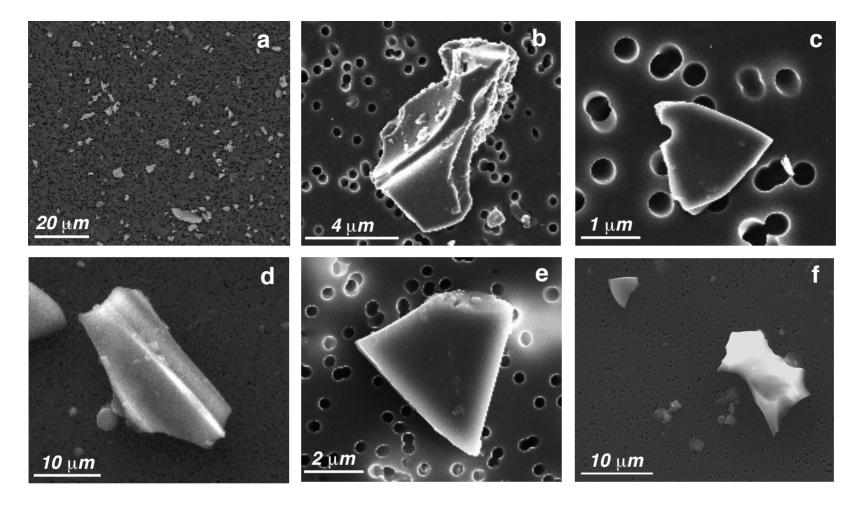
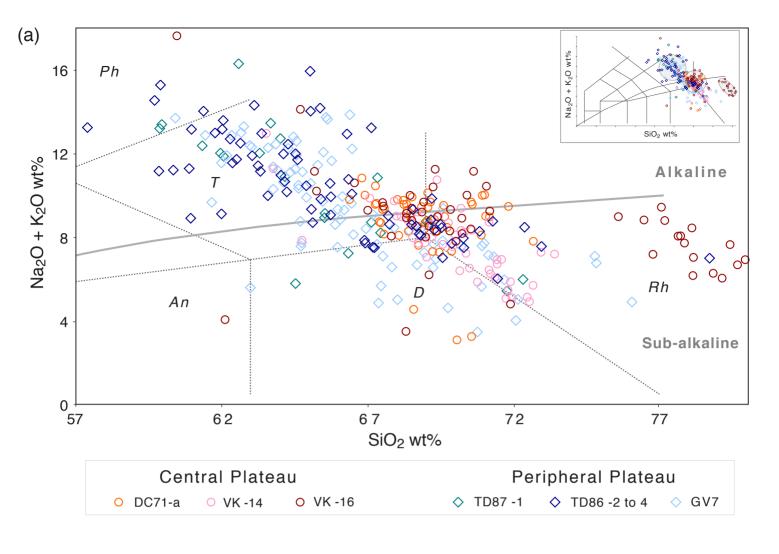
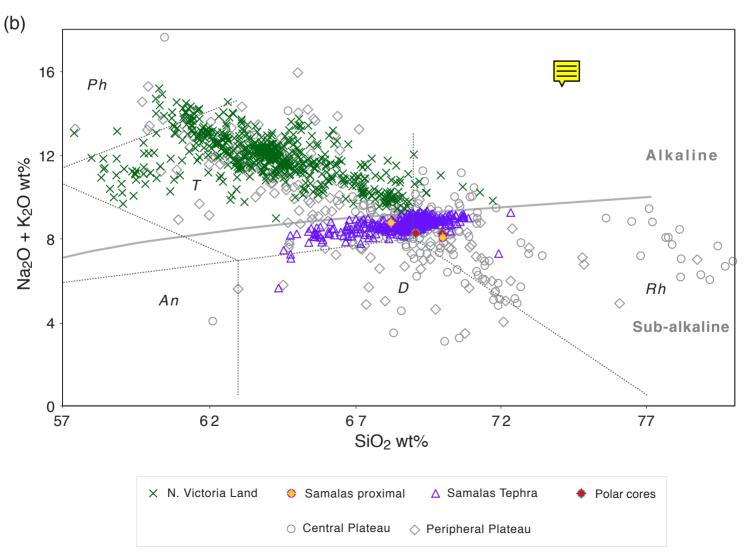
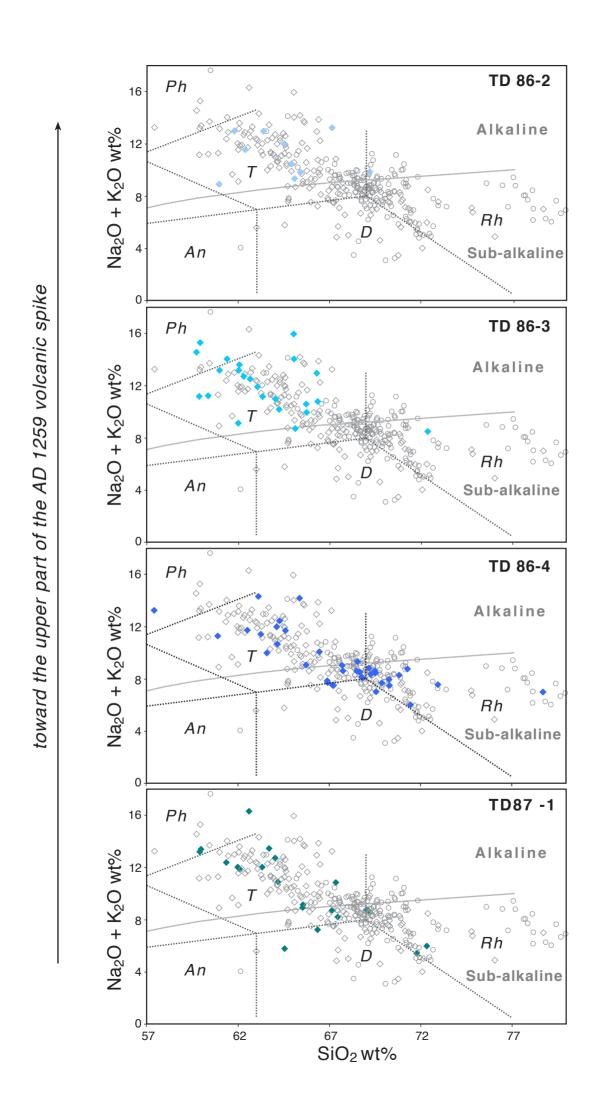


Fig. 3. Scanning electron microphotographs of volcanic glass particles from a, DC-71a; b-c, VK-14; d-e, TD87-1; f, TD86-4.







1	Supplementary Material for
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3	MULTIPLE SOURCES FOR TEPHRA FROM AD 1259 VOLCANIC SIGNAL IN ANTARCTIC ICE CORES
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Drilling Site/Ice core	Short name	Location,ele vation a.s.l.	Accumulation rate (mm we year-1)	Drilling period	Reference	Present sample resolution (cm)
Concordia Station at Dome C	DC	75°06'S, 123°20'E, 3220 m	~25	2013-14	Schwander et al. (2001)	7
Vostok/BH6	VK	78°28'S, 106°48'E, 3488 m	~20	1991- 92	Osipov et al. (2014)	5
Talos Dome/TALDICE	TD	72°49'S, 159°11'E, 2315 m	~80	2004-05	Severi et al. (2012)	5
GV7	GV7	70°41'S, 158°52'E, 1950 m	~240	2013-14	Frezzotti et al. (2007) Caiazzo et al. (2017)	15

15 Table S1. Location and characteristics of the studied ice cores

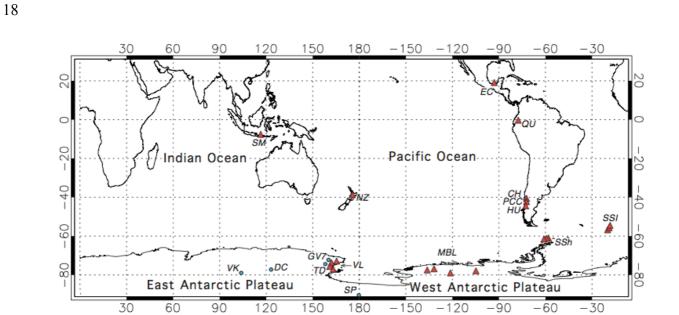


Figure S1. World map showing the location of Antarctic ice core sites (blue dots) and of selected volcanic sources considered in the text (red triangles). Letters for sources are as follows. CH, Chaitén; EC, El Chichón; HU, Hudson; MBL, Marie Byrd Land; NZ, New Zealand; PCC, Puyehue-Cordon Caulle; QU, Quilotoa; SM, Samalas; SSh, South Shetland Islands; SSI, South Sandwich Islands; VL, Victoria Land

#### **Details of microprobe analysis**

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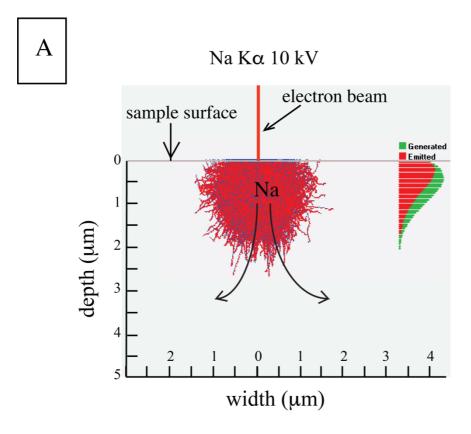
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Although tephra embedding and polishing should be preferred for microprobe analysis, this was not possible here due to the small amount of material and its very fine grain size. Therefore, single-grain geochemical analysis was carried out on unpolished samples using a JEOL JXA-8230 electron microprobe set up at the Institut des Sciences de Terre (ISTerre) of Grenoble. For analysis of small (1-3 μm) and thin (< 2 μm) unpolished tephra shards the analytical protocol with simultaneous WDS/EDS signal acquisition has been applied. We run Ti, Na, Mg, K, and Fe on WD spectrometers and Si, Ca, Al, on ED spectrometers. The following analytical conditions have been used: accelerating voltage 10kV, probe beam current 2 nA and beam diameter 1 µm. The low accelerating voltage was selected to reduce X-ray excitation volume. Natural and synthetic minerals and glasses were used for standardisation: StHs6/80-G (Si, Al, Ca) and GOR132-G (Fe) synthetic glasses (Jochum et al, 2000 and GEOREM database), pure synthetic MgO (Mg), synthetic rutile (Ti), albite (Na), orthoclase (K). During analytical sessions the reference materials StHs6/80-G, ATHO-G (Jochum et al., 2000) and KE-12 (Metrich and Rutherford, 1992) ran as unknowns after each 40-50 analytical points to evaluate analytical accuracy and precision. Even at current as low as 2 nA the migration of sodium could be significant if the diameter of the electron beam is small (1 µm). The results of analysis of reference glasses and polished tephra samples analysed at traditional (Acc. voltage 15kV, probe current 5nA, beam diameter 5 µm, e.g. Narcisi et al., 2016) and non-traditional (Acc. voltage 10kV, beam current 2nA, probe diameter 1 μm, this study) are in Table S2. We estimate that Na loss for polished samples analysed by 1 μm beam and non-traditional analytical conditions described above corresponds to 25% relative for samples with 4-7 wt% of Na<sub>2</sub>O and 67-75 wt% of SiO<sub>2</sub> (ATHO-G, KE-12, and samples RIN1392E and RIN1392A related to the AD 1257 Samalas medial tephra, Vidal et al., 2015) (Table S2). As it has been shown in several studies (e.g. Nielsen and Sigurdsson, 1981; Spray and Rae, 1995; Morgan and London, 1996) sodium migration from the excitation volume is a result of heating of the area of analysis by electron beam. According to Spray and Rae (1995) sodium migrates downward to space-charge layer within the sample. Figure S2 shows Monte Carlo electron trajectory simulation of the interaction volume as well as Na-K $\alpha$  generation and emission volumes for 10kV in common polished sample and unpolished 1x1 μm particle on filter. These figures demonstrated how electron beam penetrates the samples of the different morphology. As follows from the modelling in case of analysis of small shards the Na migration does not take place because of small sample size. Analysis of small tephra shards often displayed low analytical total (30-60 %). Low and variable totals of analysis are result of small size of analytical area (smaller than excitation volume) (Figure S2-B). The analytical precision for the selected analytical conditions is in Table S2. While the analytical precision at 10 kV and 2 nA for the most analysed oxides is significantly lower than for traditional conditions it is still within reasonable error (5-15%).



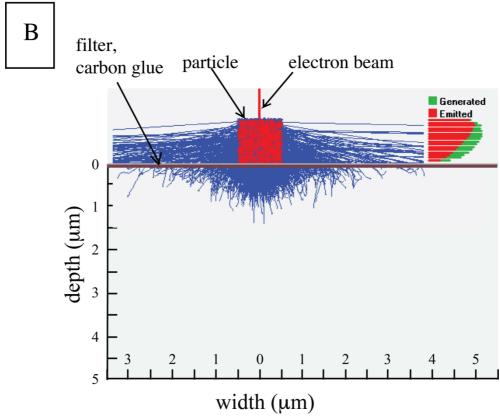


Figure S2. Monte Carlo simulation of the interaction and emission volumes of X-rays at 10kV for Na-K $\alpha$  in Na-Si rich glass considered as A) common polished sample and B) small 1x1  $\mu$ m particle placed on the C-glue. The blue lines show the electron trajectory outside the particle.

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Sample	Reference	Analytical conditions	N	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO <sub>tot</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Total
StHs6/80-G	this work	10kV, 2nA, 1 μm	15	63,56	0,69	17,61	4,46		1,95	5,38	4,33	1,29	99,28
±		_		0,45	0,10	0,33	0,26		0,11	0,33	0,30	0,04	
StHs6/80-G	this work	15kV, 5nA, 5 μm	15	63,73	0,69	17,86	4,29	0,08	1,94	5,26	4,62	1,28	99,75
±		-		0,21	0,01	0,18	0,08	0,03	0,04	0,06	0,12	0,03	
StHs6/80-G	Jochum et al. (2000) (a)			63,70	0,70	17,80	4,37	0,08	1,97	5,28	4,44	1,29	99,63
95%CL				0,50	0,02	0,20	0,07	0,00	0,04	0,09	0,14	0,02	
ATHO-G	this work	10kV, 2nA, 1 μm	12	75,64	0,26	11,95	3,14		0,09	1,72	2,79	2,61	98,20
±				0,59	0,04	0,21	0,27		0,03	0,25	0,47	0,08	
ATHO-G	this work	15kV, 5nA, 5 μm	12	75,88	0,24	12,30	3,14	0,11	0,09	1,71	3,98	2,64	100,08
±				0,32	0,02	0,21	0,06	0,03	0,01	0,03	0,10	0,04	
ATHO-G	Jochum et al. (2000) (a)			75,60	0,26	12,20	3,27	0,11	0,10	1,70	3,75	2,64	99,62
95%CL				0,70	0,02	0,20	0,10	0,01	0,01	0,03	0,31	0,09	
KE-12	this work	10kV, 2nA, 1 μm	12	71,56	0,32	7,92	8,93		0,01	0,39	5,36	4,09	98,60
±				0,45	0,08	0,20	0,45		0,02	0,20	0,23	0,09	
KE-12	this work	15kV, 5nA, 5 μm	12	71,01	0,30	7,84	8,30	0,26	0,03	0,37	7,01	4,23	99,35
±				0,33	0,01	0,11	0,08	0,03	0,02	0,01	0,17	0,04	
KE-12	Metrich and Rutherford (1992) (b)			70,30	0,33	7,60	8,36	0,26	nd	0,35	7,28	4,27	98,75
KE-12	Vidal et al. (2015) (c)		5	69,93	0,33	7,64	8,47	0,31	0,03	0,37	6,91	4,26	98,25
±				0,38	0,05	0,22	0,20	0,08	0,01	0,03	0,34	0,04	
RIN1392E	this work	10kV, 2nA, 1 μm	41	68,25	0,45	15,19	2,43		0,58	1,67	2,90	4,10	96,29
±				0,93	0,06	0,38	0,25		0,11	0,28	0,50	0,24	
RIN1392E	this work	15kV, 5nA, 5 μm	26	68,38	0,45	15,41	2,40	0,12	0,58	1,67	4,52	4,45	97,97
±				0,48	0,01	0,27	0,09	0,02	0,09	0,09	0,29	0,11	
RIN1392E	Vidal et al. (2015) (c)		10	70,09	0,47	15,65	2,51	0,14	0,60	1,80	3,52	4,39	99,17
±				0,69	0,07	0,28	0,10	0,07	0,05	0,21	0,47	0,22	
RIN1392A	this work	10kV, 2nA, 1 μm	48	67,95	0,45	16,05	2,81		0,74	2,22	3,59	3,99	98,68
±				0,65	0,07	0,26	0,22		0,07	0,25	0,35	0,10	
RIN1392A	this work	15kV, 5nA, 5 μm	48	67,67	0,45	16,16	2,66	0,12	0,72	2,18	4,73	4,11	98,81
±				0,49	0,02	0,21	0,07	0,02	0,02	0,05	0,19	0,06	
RIN1392A	Vidal et al. (2015) (c)		16	68,24	0,46	16,11	2,70	0,11	0,73	2,22	4,69	4,16	99,42
±				0,77	0,07	0,31	0,12	0,05	0,04	0,13	0,19	0,11	

Table S2. Composition of reference glasses and Samalas tephra samples measured at different analytical conditions.

#### Potential sources for the ice-core dacitic glass population

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Our attempt over urce identification was based upon comparison with bibliographic information for volcanoes that have been active during post-glacial times. We considered as constraining features the chronostratigraphy of the deposits, the character of volcanic activity and the chemical signature of the material. However, a matching source depends on the data available in the literature. Inaccessible volcanoes may be vided with stratigraphic records that are still incomplete or poorly age constrained. The possibility that our tephra may represent a hitherto unknown eruption in the proximal sequence cannot be entirely excluded. As for chemical features of deposits from proximal contexts, in order to avoid misleading correlations we took into account only sources for which single-shard microprobe data are available. We consider in fact bulk-rock analyses of near-vent samples, often affected by the presence of minerals on xenoliths, unsuitable for comparison with the present shard-specific dataset. However, we are aware that proximal and distal tephra components of the same eruption may have slightly different compositions and this may represent a further problem of our approach. On the other hand, here we considered a large set of possible volcanic sources within and surrounding the Antarctic continent, more extended than that employed in previous studies. This strategy, requiring scrutiny of a high number of relevant published papers, allowed us to confidently rule out clearly dissimilar sources and to ascribe the investigated ice-core tephra to the parent eruption.

Figure S1 illustrates location of a few volcanoes considered in this discussion. Graphical comparison of the composition of individual ice-core shards with glass analyses from proximal source deposits (Figure S3) supports the following considerations.

Regardless of age of proximal activity, we could readily exclude volcanism of South Sandwich Islands (SSI) in the Southern Atlantic Ocean, producing several tephras preserved in Central EAP (e.g., Narcisi et al., 2010, and references therein), because of its low-K tholeiitic nature (e.g., Nielsen et al., 2007), as well as volcanoes in the South Shetland Islands (Antarctic Peninsula region) that display predominantly basaltic and batter compositions (Kraus et al., 2013; Antoniades et al., 2018). Both provinces are clearly dissimilar in composition with the icecore glass.

104 Careful attention was paid to post-glacial volcanoes of the Andean belt representing very 105 efficient producers of sub-alkaline (calc-alkaline) tephra. These could be eligible candidates 106 considering that the westerly atmospheric circulation penetrating the EAP favours the rapid 107 transport and deposition of dust and tephra from South America to Antarctica (e.g., Pitts and 108 Thomason, 1993; Delmonte et al., 2008; Narcisi et al., 2012; Koffman et al., 2017). On the basis of 109 numerous studies over the last decades, the eruptive chronologies of many of these volcanic 110 centres are well constrained, thus helping us to rule out a number of them.

In particular, in the Southern and Austral Volcanic Zones of the Andes (latitudes between 33 to 55°S) about 20 volcanoes produced explosive eruptions with significant regional or even hemispheric impact (Fontijn et al., 2014). However, the largest Holocene explosive eruptions of volcanoes in the southernmost Andes producing regionally widespread tephra layers are dated back at least to 3 ka (Stern, 2008) and so are too old to be related with the studied tephra. Other volcanoes of the Southern Volcanic Zone that either are too old or do not show geological

evidence of energetic explosive activity in mid-13th century to be considered as likely sources are Calbuco (41°33'S, Watts et al., 2011), Mocho-Choshuenco (39°55'S, Rawson et al., 2015), Quetrupillán (39°30' S, Fontjin et al., 2016), Sollipulli (38°58'S; Naranjo et al., 1993), Lonquimay (38°22'S, Gilbert et al., 2014), Quizapu-Cerro Azul (35°39'S, Ruprecht et al., 2012) San Pedro (36°S, Singer et al., 1997). Similarly, we can exclude volcanoes of the Central Volcanic Zone of the Andes (latitudes between 14° and 29°S) characterised by high-K calc-alkaline compositions. Here, the two last major explosive events were the 2-ka BP plinian eruption of El Misti volcano (Thouret et al., 2001) and the AD 1600 eruption of Huaynaputina volcano (e.g., Lavallée et al., 2006), both inconsistent with age of the ice tephra sample. The remaining explosive activity was small to moderate, so most likely not capable of dispersing ash onto the Antarctic ice sheet. Farther north, also at the Andean volcanoes of Chimborazo (1°28'S, Barba et al., 2008) and Cotopaxi (0°38'S, Hall and Mothes, 2008) the recorded activity is not appropriate as either age or character to suggest a linkage with our tephra. In the Northern Hemisphere, according to marine tephrostratigraphy offshore the southern Central American Volcanic Arc (7-9 °N) documenting explosive activity of Costa Rica and Nicaragua volcanoes, the most recent marker is 3.5 ka old (Schindlbeck et al., 2016), thus much older than our ice-core tephra. Terrestrial volcanostratigraphies of Irazù (9°58'N, Benjamin et al., 2007), Apoyeque (12°14'N, Kutterolf et al., 2011) and Ilopango (13°67°N, Mehringer et al., 2005) do not show any suitable tephra deposit of appropriate age. The voluminous eruption of El Metate (19°32′N, Mexico) dated at ~ AD 1250 was purely effusive (Chevrel et al., 2015), making it an unlikely candidate.

We carried out a comparison between our glass-shard microprobe data and the composition of selected calc-alkaline tephra sources active he last millennium (Figure S3). In particular, we considered recent explosive products of the American volcanoes of Chaitén (42°49'S, Moreno et al., 2015), Puyehue-Cordon Caulle (40°59'S, Mil Hojas tephra, modelled age 0.84 ± 0.18 cal ka BP, Fontijn et al., 2016), Hudson (45°54'S, Kratzmann et al., 2009), Quilotoa (~ AD 1280, 0°51'S, Stewart and Castro, 2016), El Chichón (6<sup>th</sup>-century deposits, 17°22'N, Nooren et al., 2017) along with tephra erupted during the Kaharoa tin New Zealand (AD 1314 ± 12; e.g., Nairn et al., 2004) and from Marie Byrd Land volcanoes found in the marine realm (Shane and Froggatt, 1992). It can be seen that none of these satisfactorily fit the dacitic chemistry of the ice-core tephra component and consequently cannot be likely counterparts. Note that El Chichón volcano was previously suggested as a probable source for the polar tephra in the South Pole (SP) and Greenland ice cores (Palais et al., 1992). Although the El Chichón historic volcanic record does not preclude this possibility (Espíndola et al., 2000), the present comparison highlights appreciable compositional differences between the studied dacitic tephra and the proximal volcanic deposits, thus excluding the former attribution.

We finally found positive chemical match between dacitic glass shards trapped within ice and products of AD 1257 Samalas volcanic eruption, the cataclysmic event occurred in the Indonesian Archipelago (8°33'S) and rate g among the greatest volcanic events of the Holocene (e.g., Lavigne et al., 2013; Vidal et al. 2015, 2016; Alloway et al., 2017) (Figure 4b, main text). Note that our chemical results are also event with microprobe data of Samalas samples analysed within this work (Table S2).

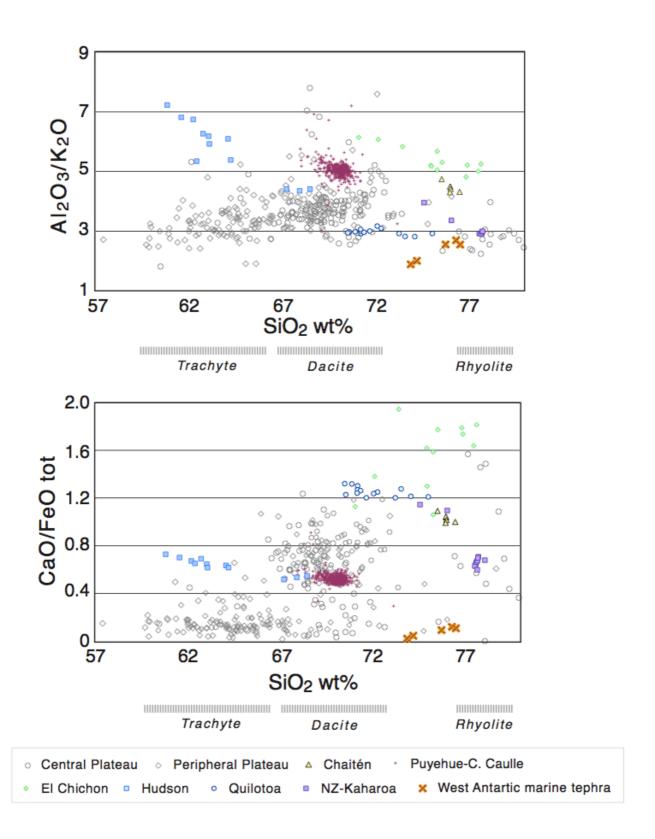


Figure S3. Major element biplots for the analysed ice-core shards (in grey-scale) compared with glass geochemical analyses for selected potential sources and counterparts (data from Moreno et al., 2015; Fontijn et al., 2016; Nairn et al., 2004; Kratzmann et al., 2009; Nooren et al., 2017; Stewart and Castro, 2016; Shane and Froggatt, 1992). Location of considered source volcanoes is shown in Supplementary Figure S1.

Analytical session May 2015	DC 71-a	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO <sub>tat</sub>	MgO	CaO	Na <sub>2</sub> O	K,O	Original Total	Glass po
May 2015	1259_1-p3	67,57	0,60	15,68	4,41	0,94	2,65	4,24	3,91	60,66	dacitio
	1259_1-p6	67,27	0,56	15,31	4,33	0,68	2,27	5,16	4,42	64,67	dacitio
	1259_1-p10 1259_1-p14	69,07 68.86	0,37	15,87	2,05	0,82	1,71	5,41 4.75	4,71	77,55 67,51	dacitio
	1259_1-p16	68,37	0,47	15,52	3,22	0,98	2,13	4,68	4,62	67,86	dacitio
December 2015	1259_p6	69,33	0,51	15,68	3,44	0,77	2,02	4.44	3,81	77,58	dacitio
	1259_p13	67,32	0,59	15,59	3,29	0,90	2,69	5,21	4,41	72,66	dacitio
	1259_p16	70,90 68.41	0,44	15,43 16,05	2,81	0,76	1,56	3,67 4,19	4,43	90,67 72.85	dacitio
	1259_p19 1259_p20	67,47	0,62	16,78	3,44	0,84	2,25	4,19	4,09	91,60	dacitio
	1259_p31	69,65	0,52	15,56	3,16	0,60	1,54	4,25	4,75	71,40	dacitio
	1259_p40 1259_p42	68,47 69,05	0,51	14,76 15,07	3,78	1,05	2,29	4,65 4,68	4,49	61,73 67,41	dacitio
	1259_p44	69,61	0,49	15,83	2,08	0,85	1,61	4,92	4,61	66,34	dacitio
Analytical session	VK -14	SIO <sub>2</sub>	TIO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO <sub>tal</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Original Total	Glass po
October 2016	BH6-30-14_p7	69,38	0,50	15,05	2,62	0,59	1,10	5,51	5,25	76,31	dacitio
	BH6-30-14_p8	70,33	0,43	15,96	2,56	0,65	1,81	4,04	4,22	90,59	dacitio
	BH6-30-14_p17 BH6-30-14_p26	68,72 67,09	0,44	15,61	2,80 3,65	0,79	2,43	4,96 4,91	4,24 4,96	77,77 79,05	dacitio
	BH6-30-14_p27	68,17	0,50	16,29	2,89	0,86	2,31	4,97	4,01	95,16	dacitio
	BH6-30-14_p50	69,78 69,21	0,66	16,13 16,56	2,46 2.96	0,70	1,57	4,36	4,33	95,08	dacitio
	BH6-30-14_p75 BH6-30-14_p89	63,54	0,53	16,04	6,18	0,71	0,72	4,02 8,07	4,00	93,55 95,72	dacitio
	BH6-30-14_p90	63,78	0,48	17,30	6,17	0,14	0,86	6,59	4,69	91,31	trachyt
	BH6-30-14_p91 BH6-30-14_p92	68,00 67,92	0,83	15,48 15,67	3,56 3,21	0,77	2,34	4,83 5,13	4,18	66,61 84,58	dacitio
	BH6-30-14_p110	71,16	0,41	16,44	1,40	0,48	1,37	4,29	4,44	96,57	dacitio
	BH6-30-14_p120	70,58	0,49	16,17	2,00	0,79	1,64	4,32	4,02	97,06	dacitio
	BH6-30-14_p146 BH6-30-14_p153	68,56 69,21	0,56	16,12 16,04	2,79 2,54	1,15 0,65	2,17	4,46 4,54	4,19	90,30 87,56	dacitio
Analytical session	VK -16	SIO <sub>2</sub>	TIO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO <sub>tot</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Original Total	Glass po
October 2016	BH6-30-16 p10	69.40	0.50	16.29	2.37	0.75	1,70	4.88	4.11	68.11	dacitie
	BH6-30-16_p22	78,15	0,00	13,81	0,63	0,30	0,94	2,70	3,48	90,33	rhyoliti
	BH6-30-16_p29	69,38	0,43	16,10	2,46	0,60	2,72	4,25	4,06	76,28	dacitio
	BH6-30-16_p63 BH6-30-16_p68	77,19 77.07	0,18	12,70	0,43	0,02	0,68	3,43 4,30	5,38	69,81 82,58	rhyoliti
	BH6-30-16_p76	68,53	0,48	15,22	3,64	0,91	1,82	5,21	4,19	68,17	dacitio
	BH6-30-16_p77	68,86	0,50	16,19	3,50	0,66	1,08	5,05	4,16	82,05	dacitio
	BH6-30-16_p82 BH6-30-16_p83	68,34 65,26	0,82	16,28	3,11 8,55	0,82	1,48 0,76	4,62 5,04	4,52 5,17	71,11 63,35	trachyt
	BH6-30-16_p87	70,24	0,47	15,16	2,98	0,67	1,57	4,59	4,32	70,77	dacitio
	BH6-30-16_p91 BH6-30-16_p95	69,11 67.53	0,42	16,28	2,99 2.78	0,75	1,92	4,51 5.27	4,02	89,56 76.03	dacitio
	BH6-30-16_p99	68,93	0,54	15,49	3,49	0,67	1,20	5,03	4,65	63,47	dacitio
	BH6-30-16_p117	69,85	0,59	15,54	3,09	0,54	1,07	4,53	4,79	60,37	dacitio
	BH6-30-16_p130 BH6-30-16_p134	77,72 67.55	0,05	12,77	0,37 3.85	0,00	1,01	3,38 5.23	4,69 4,26	68,34 73,56	rhyoliti
	BH6-30-16_p140	77,64	0,19	12,44	0,98	0,13	0,56	2,50	5,55	88,98	rhyoliti
Analytical session	BH6-30-16_p160 TD 87-1	68,33	0,40	15,91	3,45	0,84	2,14 CaO	4,78	4,15	79,73 Original Total	Glass po
December 2015	10 01-1	SIO,	TIO,	AI <sub>2</sub> O <sub>3</sub>	FeO <sub>tot</sub>	MgO	Cao	Na,O	K,O	Original rotal	Grass po
	87-1-p27	63,69	0,24	17,06	4,07	0,06	1,42	7,63	5,82	90,22	trachyt
	87-1-p37 87-1-p42	64,03 62.08	0,34	16,21	5,08 7,97	0,20	1,41	6,98	5,75	94,07	trachyti
	87-1-p45	61,97	0,44	16,46	7,54	0,19	1,37	7,09	4,94	89,66	trachyti
	87-1-p47	61,35	0,61	15,99	6,23	0,34	3,09	7,75	4,63	95,15	trachyti
Analytical session	87-1-p50 TD 86-4	63,32 SIO <sub>2</sub>	0,43 TIO <sub>2</sub>	16,57 Al <sub>2</sub> O <sub>2</sub>	6,80 FeO <sub>tal</sub>	0,07 MgD	0,79 CaO	6,52 Na <sub>2</sub> O	5,50 <b>K<sub>2</sub>O</b>	91,35 Original Total	Glass po
December 2015											
	86-4A-14 86-4A-15	69,18 78,72	0,46	15,67	2,75 0,93	0,89	2,20 0,57	4,56 2,63	4,28 4,37	86,15 90,99	rhyoliti
	86-4A-30	69,51	0,45	16,07	2,57	0,58	2,14	4,25	4,37	92,92	dacitio
	86-4A-34	68,83	0,48	16,33	3,31	0,75	2,20	4,11	3,98	89,23	dacitio
	86-4A-38 86-4A-51	64,29 68.56	0,53	14,92	7,44	0,13	0,24 2,18	7,26 4,75	5,19 4,59	79,68 83,72	trachyt
	86-4A-60	63,26	0,45	15,88	7,63	0,13	1,23	6,26	5,16	77,80	trachyt
	86-4A-61 86-4A-65	62,52 69,54	0,43	15,99 15,69	8,23 2,89	0,12	0,98	6,23 4,27	5,50 4,19	71,32 92,31	trachyti
	86-4A-66	64,18	0,40	16,36	7,36	0,14	0,88	6,09	4,15	85,33	trachyt
	86-4A-67	68,78	0,62	16,94	2,35	0,85	2,32	4,06	4,10	88,71	dacitio
	86-4A-89 86-4A-90	64,13 64,61	0,41	16,37 15,50	6,20 6,93	0,10	0,80	6,76	5,23 5,53	75,48 83,29	trachyt
	86-4A-99	69,29	0,43	16,23	3,18	0,68	1,82	4,03	4,34	88,59	dacitio
Analytical session December 2015	TD 86-3	SIO <sub>2</sub>	TIO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO <sub>tel</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Original Total	Glass po
Secender 2015	86-3a-25	62,66	0,27	16,70	7,11	0,12	0,64	7,32	5,18	95,57	trachyt
	86-3a-27	62,04	0,33	16,28	7,05	0,16	0,98	8,31	4,85	91,91	trachyt
	86-3a-30 86-3a-38	62,07 61,39	0,36	16,37 13,81	6,76 8,41	0,08	0,76 1,58	8,60	5,00 5,26	86,71 89,03	trachyt
	86-3a-66	63,06	0,37	16,00	7,78	0,03	0,86	7,48	4,42	67,57	trachyt
	86-3a-72	62,31	0,50	16,07	7,53	0,06	0,83	7,83	4,87	81,62	trachyt
Analytical session	86-3a-75 TD 86-2	64,04 SIO <sub>2</sub>	0,34 TIO <sub>2</sub>	16,86 Al <sub>2</sub> O <sub>3</sub>	6,72 FeO <sub>tel</sub>	0,14 MgO	0,92 CaO	6,41 Na <sub>2</sub> O	4,57 <b>K<sub>2</sub>O</b>	93,13 Original Total	Glass po
December 2015											
	86-2A-7 86-2A-12	61,79 64,54	0,47	15,64 16,68	8,34 5.52	0,14	0,63	7,21	5,79 4,82	63,85 95,52	trachyti
	86-2A-13	69,21	0,68	15,23	3,06	0,77	1,20	5,32	4,54	62,11	dacitio
	86-2A-14	65,09	0,43	17,62 16.38	6,62	0,05	0,85	5,32	4,02 5.39	95,45 91,40	trachyti
Analytical session	86-2A-20 GV7 295-1	63,38 SIO <sub>2</sub>	0,46 TIO <sub>2</sub>	16,38 Al <sub>2</sub> O <sub>3</sub>	6,28 FeO <sub>tel</sub>	0,24 MgO	0,29 CaO	7,58 Na <sub>2</sub> O	5,39 <b>K</b> <sub>2</sub> <b>O</b>	91,40 Original Total	Glass po
February 2016											
	295-1-p12	68,43	0,45	16,67	3,05	0,86	2,20	4,43 5,40	3,91	98,29 100,14	dacitio
June 2016	295-1-p24	64,92	0,46	17,70	6,21	0,07	0,73	0,40	4,50	100,14	trachyt
	295-1-pt27	62,78	0,48	16,50	6,18	0,11	0,64	8,21	5,08	91,29	trachyt
	295-1-pt31	65,06 64,57	0,22	17,98	4,77	0,00	1,39	5,46	5,12	68,02 89,80	trachyt
	295-1-pt56 295-1-pt66	64,57 66,40	0,11	16,83 16,68	5,50 2,10	0,07	1,00 0,54	7,01	4,92 6,11	97,83	trachyt
Application	295-1-pt67	70,93	0,59	15,66	2,95	0,68	1,61	3,38	4,21	88,51	dacitio
Analytical session February 2016	GV7 294-4	SIO <sub>2</sub>	TIO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO <sub>tal</sub>	MgO	CaO	Na <sub>2</sub> O	K,O	Original Total	Glass po
. Seronly £010	294-4-p2	63,78	0,38	16,40	7,22	0,19	1,72	5,75	4,55	83,47	trachyt
	294-4-p3	61,46	0,36	16,52	8,11	0,02	0,66	8,49	4,39	93,18	trachyt
	294-4-p10 294-4-p14	67,92 60.43	0,48	16,29	3,15	0,87	2,82	4,34	4,12	92,97	dacitio
June 2016	294-4-p14	60,43	0,35	15,66	8,91	0,14	0,81	8,49	5,22	68,57	trachyt
	294-4A-pt6	64,65	0,48	16,94	6,10	0,08	1,26	5,77	4,73	96,13	trachyt
	294-4A-pt15 294-4A-pt27	69,27 65,78	0,56	16,09	3,00 5,57	0,86	2,54 0,24	3,81 6,79	3,88 4,87	91,01	dacitio
	294-4A-pt27 294-4A-pt29	65,78 65,31	0,31	16,40	5,57	0,05	1,11	6,79	4,87 5,20	98,08 87,24	trachyt
	294-4A-pt31	64,58	0,33	16,98	3,89	0,08	1,54	8,06	4,54	74,06	trachyt
	294-4A-pt39	62,68	0,33	15,51	8,05	0,04	0,39	8,62	4,38	91,73	trachyt
	294-4A-pt41	62,36	0,33	16,85	6,53 2,60	0,09	0,95 1,81	8,08 3,98	4,80 4,62	95,77 83,73	trachyti
	294-4A-m48										
	294-4A-pt48 294-4A-pt53	69,18 64,29	0,49	16,42	5,83	0,12	0,59	6,69	5,57	88,80	trachyt

Table S3. Representative major element composition of individual glass shards determined by electron microprobe analysis. Values are given in weight % oxide and are normalised to 100%. Total iron is expressed as FeO. MnO not determined. Glass populations as defined in the main text.

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