

1 **Frequent activity on Vulcano (Italy) spanning the last 80 ky: new insights from the**
2 **chemo-stratigraphy of the Brown Tuffs**

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17 ABSTRACT

18 The Brown Tuffs (BT) are widespread reddish-brown to grey, ash-rich pyroclastic deposits
19 recognized in the stratigraphic sequences of the Aeolian Islands and Capo Millazzo
20 peninsula (Sicily) that span the last 80 ky. They have very homogeneous lithological, textural
21 and sedimentological features which make it difficult to reliably correlate units on the islands
22 to proximal units in the source areas. Here we carefully re-interpret the stratigraphic profiles
23 of the BT on Vulcano and Lipari where the deposits are thickest and present the most
24 complete succession. The investigation is based on a large dataset of major and minor
25 element geochemistry of juvenile glass components for the majority of the recognized BT
26 depositional units, whilst also providing new radiocarbon ages. The distinctive chemical
27 groupings observed within the glass analyses, both temporally and spatially, allow us to
28 fingerprint the three main stratigraphically defined macro-units in which the BT succession
29 can be sub-divided using prominent tephra marker beds, the Ischia Tephra (Monte Epomeo
30 Green Tuff; 56 ky) and Monte Guardia pyroclastics from Lipari (herein radiocarbon dated to
31 27-26 ky). The Lower (80-56 ky; LBT), Intermediate (56-27 ky; IBT) and Upper BT (here
32 dated at 24-6 ky; UBT) macro-units display K-series volcanic glasses ranging from basaltic
33 trachy-andesites, through trachy-andesites, to more evolved trachytes, all consistent with
34 an origin on Vulcano. The UBT are clearly distinguished from the lower macro units by their
35 higher-SiO₂ trachy-andesite to trachytic glasses, which extend to noticeably lower TiO₂, CaO
36 and MgO contents. These features make it possible to re-define the geochemical-
37 evolutionary boundary between IBT and UBT as corresponding to the 24 ky Spiaggia Lunga
38 scoria bed on Vulcano, which is stratigraphically higher (and younger) than the previous
39 boundary marker (Monte Guardia). The glass compositions of the LBT, IBT and UBT are
40 used to: (1) assess links to known proximal eruption units outcropping on Vulcano; (2)
41 validate medial-distal BT occurrences across the Aeolian archipelago (Salina, Filicudi and
42 Panarea) and on Capo Millazzo; (3) confirm that the BT are responsible for distal volcanic
43 ash layers preserved in Central Mediterranean marine sedimentary archives. Interestingly,
44 the glass compositions of the UBT are very similar to those of the Punte Nere unit, the
45 earliest pyroclastic products erupted from the currently active La Fossa cone on Vulcano,
46 indicating the corresponding magmatic system has likely erupted similar melts and products
47 over the last 24 ky and thus extending its life cycle. Such information is crucial for evaluating
48 the long-term eruption scenarios underpinning hazard assessment of the La Fossa caldera
49 magmatic system.

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52 1. INTRODUCTION

53 Explosive volcanic eruptions can disperse volcanic ash (< 2 mm) to distances of tens
54 to thousands of kilometers from their source and cause multi-hazard impacts on human
55 activities and the environment, potentially forcing climate variability (e.g. Martin et al., 2009;
56 Le Pennec et al., 2011; Bonasia et al., 2012; Sulpizio et al., 2012; 2014; Biass et al., 2014;
57 Dingwell and Rutgersson, 2014; Scaini et al., 2014). Pyroclastic deposits from these
58 eruptions are crucial for reconstructing the volcanic history of a volcano, and understanding
59 the frequency and the impact of its eruptive activity on the surroundings. Where the age of
60 the corresponding eruptions is known, ash (tephra) deposits preserved in distal sedimentary
61 records are also powerful chronological and stratigraphic markers in complex stratigraphic
62 sequences across the region (Narcisi, 1996; Machida, 1999; Shane, 2000), and can be used
63 in age-depth models and to synchronize disparate sedimentary palaeoclimate archives
64 (Paterne et al., 1986; 1988; Sulpizio et al., 2010; Zanchetta et al., 2011).

65 In this paper, the Brown Tuffs (BT) are presented as a case study of widespread, ash-
66 rich pyroclastic deposits. These deposits have metric thickness and are recognized in the
67 stratigraphic sequences of most of the Aeolian Islands and on the Capo Milazzo peninsula
68 in northern Sicily. Their interpretation as paleosols, reworked or primary pyroclastic
69 products, as well as their vent locations, areal distribution, chronology and eruptive
70 processes has been long debated (Bergeat, 1899; Pichler, 1980; Keller, 1967; Keller, 1980a,
71 b; Crisci et al., 1981, 1983, 1991; Manetti et al., 1988, 1995; Morche, 1988; Gioncada et al.,
72 2003). Stratigraphic and tephrochronological studies have suggested that the BT are
73 composed of a number of depositional units emplaced in the 80-5 ky time interval by
74 pyroclastic density currents (PDCs) and fallout from hydromagmatic explosive activity of a
75 vent (or multiple vents) located within the La Fossa caldera on Vulcano (Lucchi et al., 2008;
76 2013b). This is also confirmed by measurements of the anisotropy of magnetic susceptibility
77 of BT sequences on Lipari and Vulcano (Cicchino et al., 2011) and combined textural,
78 petrological methods on glass fragments of the BT on Lipari (De Rosa et al. 2016). However,
79 in most outcrops the BT show a very homogeneous lithology, whilst sedimentological
80 characteristics and textural features, reflecting similar eruptive mechanisms, transport and
81 deposition. Moreover, preliminary glass compositional data indicate the deposits have a
82 dominant, albeit variable, trachy-andesite glass composition and overall K-series affinity,
83 extending towards subsidiary rhyolitic components (Lucchi et al., 2008). As a consequence,

84 the individual BT depositional units generally cannot be distinguished from each other, and
85 only separated by localized erosive surfaces or reworked horizons and the interbedding of
86 other volcanic units or exotic tephra deposits erupted from within, and outside the Aeolian
87 Islands. A stratigraphic subdivision into three macro-units, namely the Lower (LBT),
88 Intermediate (IBT) and Upper BT (UBT), has been proposed by Lucchi et al. (2008, 2013b)
89 based on the interbedding of two stratigraphic markers correlated on a regional scale,
90 namely the i) Ischia Tephra (56 ky) from Campania and the ii) Monte Guardia pyroclastics
91 (27-24 ky) from Lipari. Unfortunately, the discontinuous recognition of these marker-beds
92 makes difficult to correlate directly the BT macro-units between one island and another, and
93 throughout the Aeolian archipelago. The similar componentry and mineral assemblage, and
94 the rather small glass compositional variability reported so far (Lucchi et al. 2008, 2013b;
95 De Rosa et al., 2016), has meant that the LBT, IBT and UBT could not be clearly
96 discriminated or correlated across the islands in the absence of the interlayered marker-
97 beds. Because of all these difficulties and fragmentary stratigraphic, petrological and
98 geochemical data, a largely accepted framework of the distribution and depositional area of
99 these units and their correlation to proximal counterparts on the island of Vulcano (for the
100 LBT and IBT) has been missing.

101 Here we present a large dataset of major and minor element geochemistry of juvenile
102 glass components for most BT depositional units using grain-specific micro-analytical
103 techniques. The BT were sampled from exposed stratigraphic profiles on the islands of
104 Vulcano and Lipari, which are fully representative of the complete stratigraphic succession,
105 together with selected stratigraphic sections from the islands of Salina, Filicudi, Panarea
106 and on Capo Milazzo peninsula (northern Sicily) for strengthening the correlations. A revised
107 stratigraphic analysis of the BT exposures has taken advantage of the local successions,
108 new radiocarbon ages and correlation of marker beds to the regional tephrostratigraphy (e.g.
109 Albert et al., 2017). This provides an improved reconstruction of the stratigraphy, dispersal
110 and chronology of the different BT depositional units. The LBT, IBT and UBT macro-units
111 are geochemically fingerprinted in order to investigate the compositional variability both
112 temporally and spatially, supporting inter-island and regional correlations. Previously the BT
113 were largely overlooked as correlatives of volcanic ash recorded in distal land and deep-sea
114 archives (Paterne et al., 1986, 1988; Siani et al., 2004; Di Roberto et al., 2008; Albert et al.,
115 2012; Caron et al., 2012; Insinga et al., 2014; Matthews et al., 2015; Tamburrino et al.,
116 2016), mostly due to an inadequate characterization of their glass geochemistry. This

117 contribution instead illustrates that the BT are potentially proximal (high-volume) equivalents
118 of widespread ash dispersals, with the associated tephra layers being suitable to correlate
119 volcanic and tectonic events across the whole Aeolian archipelago and southern Tyrrhenian
120 Sea. Finally, the glass geochemical data of the LBT, IBT and UBT, combined with
121 stratigraphic and lithological information, are also used to infer links to proximal units on
122 Vulcano, providing insights into the eruptive and magmatic history and long-term hazard
123 assessment in the La Fossa caldera magmatic system.

124 **2. STUDY AREA**

125 The Aeolian Islands (Alicudi, Filicudi, Salina, Lipari, Vulcano, Panarea and Stromboli;
126 Fig. 1a), and the surrounding seamounts, are an active volcanic system in the southern
127 Tyrrhenian Sea (Barberi et al., 1973; Beccaluva et al., 1985; De Astis et al., 2003; Chiarabba
128 et al., 2008; Ventura, 2013). Subaerial volcanism developed from c. 270–240 ky to the
129 present (Leocat, 2011; Lucchi et al., 2013b), through successive eruptive epochs subdivided
130 by volcanic collapses or major quiescent (erosional) stages (De Astis et al., 2013; Forni et
131 al., 2013; Francalanci et al., 2013; Lucchi et al., 2013 a,c,d,e), and the erupted melts range
132 from basaltic andesites to rhyolites, covering a large spectrum of differing magmatic suites
133 from calc-alkaline (CA), high-K calc-alkaline (HKCA), shoshonitic (SHO) and K-Series (KS)
134 (Ellam et al., 1988; Francalanci et al., 1993; Peccerillo et al., 2013). Vulcano, which is the
135 suggested source area of the Brown Tuffs (BT), is a complex volcanic system made up of
136 various eruptive centres and two multi-stage calderas (Il Piano and La Fossa), and
137 characterized by the active La Fossa cone (De Astis et al. 2013). The BT have been
138 deposited during distinct time intervals over the last c. 80 ky (Lucchi et al., 2008, 2013b),
139 and are interlayered with widespread fall deposits from major explosive eruptions of Lipari,
140 Stromboli, Salina and Campania (Keller, 1981; Lucchi et al., 2013b; Albert et al., 2017).

141 **3. METHODS**

142 **3.1. Fieldwork**

143 Stratigraphic analysis and sampling was conducted principally on the islands of
144 Vulcano and Lipari, whilst also on Salina, Panarea, Filicudi and Capo Milazzo peninsula
145 following the correlations between islands as defined by Lucchi et al. (2008, 2013b).
146 Stratigraphic logging and lithostratigraphy focussed on identifying all the individual
147 depositional units of the BT, and obtain a comprehensive set of samples of the tephra

deposits. Following Lucchi (2013), a “depositional unit” is generically referred to as the pyroclastic material deposited during an individual, relatively continuous eruptive event (PDC or fallout), and is delimited by features indicative of interruptions of deposition or energy variations (e.g. erosive surfaces, paleosols, reworked horizons, angular discordances, sharp grain-size variations, fine ash layers), or other volcanic units.

Once the stratigraphic correlations of the BT across the islands had been fixed, 65 ash deposits were sampled covering most of the BT depositional units that were stratigraphically recognized, together with several lapilli (12) and ash (19) samples from the interbedded tephra layers. We also sampled near-vent pyroclastic deposits on Vulcano which either represent potential proximal equivalents of the BT (Monte Molineddo 1-3 and Punte Nere formations; De Astis et al., 2013), and/or offer useful constraints on the known chemical signature of the volcano.

3.2. Laboratory analyses

Juvenile (glass) fragments from the selected samples were washed, dried and mounted in Streurs epoxy resin. Mounts were ground, polished and carbon coated in preparation for chemical analysis. Major and minor element micron-beam volcanic glass data was determined using the wavelength-dispersive JEOL 8600 and the JEOL 8200 electron microprobes (WDS-EMP) at the Research Laboratory for Archaeology and the History of Art (RLAHA), University of Oxford. Details of the analytical operating conditions, monitoring of data accuracy and precision, and post-analysis data treatment are provided in Supplementary Material A.1. The full geochemical dataset, along with MPI-DING reference glasses (Jochum et al., 2006) run alongside the unknown samples are available in Supplementary Material B. Data presented in plots are normalised (e.g., water-free) and error bars represent reproducibility, calculated as 2 x standard deviation of replicate analysis of StHs6/80-G reference glass.

Charcoal fragments embedded within the BT deposits were collected for radiocarbon (^{14}C) dating to provide further age constraints. Charcoals were chemically pre-treated at the Oxford Radiocarbon Accelerator Unit (ORAU) using the acid- base-acid (ABA) methodology outlined by Brock et al. (2010). The ^{14}C analyses were subsequently performed using a 2.5 MV HVEE tandem Accelerator Mass Spectrometry (AMS) system at ORAU (Ramsey et al., 2004). These new radiocarbon ages, together with previously published BT radiocarbon

179 ages (Pichler, 1980; Crisci et al., 1981, 1983; De Astis et al., 1997), were then calibrated
180 and modelled using the Bayesian statistical program of OxCal v4.4 (Bronk Ramsey, 2009),
181 using the IntCal20 Northern Hemisphere calibration curve (Reimer et al., 2020).

182 **4. RESULTS**

183 **4.1. Overview of the stratigraphy and age of the Brown Tuffs (BT)**

184 The BT are made up of reddish-brown to grey fine to coarse ash in weakly coherent to
185 coherent depositional units, which comprise glass shards, minor crystals (with abundant
186 clinopyroxene) and a negligible lithic content. They form thick massive successions (up to
187 15-25 m on Vulcano and Lipari) with considerable thickness variations due to the paleo-
188 topography and erosion. In some exposures on Vulcano and southern Lipari there are
189 internal grain size variations, color banding and plane-parallel to cross bedding stratification
190 (De Astis et al, 1997; Lucchi et al., 2008). The stratigraphy of the BT has been reviewed
191 through a careful investigation of the majority of the outcrops on the islands of Vulcano and
192 Lipari (Fig. 1), where the BT obtain their maximum thickness, and where there are
193 radiocarbon (^{14}C) age constraints. Outcrops on Salina, Filicudi, Panarea and Capo Milazzo
194 (Fig. 1) were also studied to verify BT occurrences and extend the correlations established
195 on Vulcano and Lipari. The outcrops of the BT on Capo Milazzo, originally described by
196 Morche (1988), are now largely eroded and partially destroyed by anthropogenic activity.
197 The BT outcropping on the islands of Alicudi and Stromboli are not considered here due to
198 their poor stratigraphic and chronologic constraints (Francalanci et al., 2013; Lucchi et al.,
199 2013d). The most important features of the Campanian and Aeolian tephra layers ultimately
200 used to subdivide and correlate the BT are provided in Table 1, and the suite of radiocarbon
201 ages adopted in the present work is provided in Table 2.

202 The most complete succession of the BT is reconstructed on the island of Lipari,
203 furtherly detailing the stratigraphy previously proposed by Lucchi et al. (2008, 2013b) by
204 identifying a few more interlayered tephra beds and localized erosional surfaces. The BT
205 succession is distinguished into (at least) 16 depositional units (Fig. 2), superimposed on
206 the three-fold subdivision into the Lower (LBT), Intermediate (IBT) and Upper BT (UBT)
207 macro-units based on the interbedded Ischia Tephra and Monte Guardia pyroclastics from
208 Lipari (see Lucchi et al., 2013b and references therein). The most important features of this
209 succession are hereafter described, outlining correlations between the main outcrops on

210 Lipari and Vulcano, and the other Aeolian Islands and the Capo Milazzo peninsula.
211 Correlations with the island of Vulcano are described below in Section 4.1.1.

212 The LBT are constrained at the base by the late marine (oxygen) isotope stage (MIS)
213 5 conglomerate deposits (c. 80 ky) along the west coast of Lipari, as well as on Salina,
214 Filicudi, Panarea and the Capo Milazzo peninsula. A lower chronological boundary is also
215 provided by lapilli and ash correlated to the 77-75 ky Petrazza Tuffs from Stromboli found at
216 the base of the LBT succession on Panarea and Capo Milazzo (Lucchi et al. 2008 and
217 references therein). The Grey Porri Tuffs (GPT) from Salina (70-67 ky; Sulpizio et al., 2016
218 and references therein) are important for stratigraphic correlations in the lower portion of the
219 LBT on Salina and Lipari, with distal occurrences on Panarea and Capo Milazzo.

220 The IBT are defined as above the Ischia Tephra, which is widely exposed on Lipari,
221 Salina, Filicudi and Panarea. This marker bed is the distal equivalent of the Monte Epomeo
222 Green Tuff of Ischia (Tomlinson et al., 2014), and dated distally in Lake Fucino (Italy) at 56.1 ± 1.0 ky [2 σ] (Giaccio et al., 2017). The IBT are best exposed in southern-central Lipari (Fig.
223 3A-B) where they are split into (at least) 6 depositional units by the local pumiceous
224 successions of Punta di Perciato (undated) and Falcone (43-40 ky; Forni et al 2013 and
225 references therein), the Lower Pollara Tuffs from Salina and a couple of other tephra layers
226 (Fig. 2, Table 1). Particularly, the Lip1 tephra has a rhyolitic composition (cf. 4.2.2.1) and
227 provides evidence of a previously unknown explosive eruption in the southern dome-field of
228 Lipari.
229

230 The IBT and UBT macro-units are subdivided on Lipari (Fig. 3A-D) and across much
231 of the archipelago by the Monte Guardia marker bed (Lucchi et al., 2008), until now dated
232 to between 27 and 24 ky (Lucchi et al. 2013b; Albert et al., 2017 and references therein).
233 Here we provide new radiocarbon ages of charcoal remnants embedded within the BT
234 above the Monte Guardia (Table 2), yielding calibrated (IntCal20) eruption ages of 25,845-
235 26,310 cal y BP (95.4%; sample LIP07/17) and 23,830-24,240 cal y BP (95.4%; sample
236 LIP14/17) for the host BT depositional unit. Here we incorporate these new ages, together
237 with all the available and stratigraphically relevant BT ¹⁴C ages from the literature (Table 2),
238 into the Bayesian age-model developed by Albert et al. (2017) (Supplementary Material A.3)
239 to provide a more precise age of between 25,920-27,025 cal y BP (95.4%) for the Monte
240 Guardia eruption. The modelling also provides an age of 26,425-27,585 cal y BP (95.4%)
241 for the Lower Pollara eruption (Salina).

242 The youngest UBT units, above the Monte Guardia marker-bed, are best exposed in
243 the north-eastern sector of Lipari, where they are further subdivided into (at least) 4 distinct
244 depositional units by local pyroclastic deposits (Fig. 2). Most of the UBT are found
245 stratigraphically below the Vallone Canneto Dentro pyroclastic unit (currently undated) (Fig.
246 3D), with no occurrences between Vallone Canneto Dentro and the widespread Vallone del
247 Gabellotto pyroclastic marker bed (8,430–8,730 cal y BP; Siani et al., 2004; Albert et al.,
248 2017). The most recent UBT depositional unit is recognized between Vallone del Gabellotto
249 and the Monte Pilato pyroclastic unit (dated to 776 CE; Forni et al. 2013, and references
250 therein) (Fig. 3E), and is capped by an irregularly thick reddish paleosol with a maximum
251 age of 5,445-5,610 cal y BP based on previous ¹⁴C age determinations (Pichler, 1980; Table
252 2).

253 **4.1.1. Stratigraphy and age of the BT on Vulcano**

254 The BT deposits are recognized in different sectors of Vulcano, interlayered between
255 various other local volcanic units at different stratigraphic levels (Fig. 2). They do not outcrop
256 in the northern sector of the island (except to the south of M. Lentia) and within the La Fossa
257 caldera owing to their burial by the most recent volcanic products related to the La Fossa
258 and Vulcanello eruptive centres (younger than 5.5 ky).

259 The youngest UBT are best exposed in the central sector of Il Piano, beyond the south-
260 eastern rim of the La Fossa caldera, and match stratigraphically and lithologically the so-
261 called Piano Grotte dei Rossi tuffs (Lucchi et al., 2008 and references therein). The UBT are
262 subdivided by the widespread Cugni di Molinello scoria fallout layer that is the marker bed
263 (currently undated) separating the lower and upper portions of the Piano Grotte dei Rossi
264 tuffs ('Tufi di Grotte dei Rossi' in De Astis et al. 1997). As with the UBT, the source area of
265 the Cugni di Molinello unit is interpreted as being within the La Fossa caldera (De Astis et
266 al., 2013; Dellino et al., 2011). The UBT below Cugni di Molinello contain most of the deposit
267 volume (Fig. 2), with a maximum thickness of 8-10 m along the border of La Fossa caldera,
268 whilst the UBT above the marker bed are only 2-3 m thick and are further subdivided into
269 (at least) 3 depositional units based on the interlayered Monte Saraceno unit (8.3 ky; De
270 Astis et al. 1989) and the Vallone del Gabellotto tephra layer from Lipari (8.7-8.4 ky). Outside
271 of the main depositional area of Il Piano, the UBT are recognized above the Monte Guardia
272 in the areas of Gelso (south-east) and Monte Luccia (central-north Vulcano), and above the
273 Spiaggia Lunga unit (24 ky; Soligo et al. 2000) along the western slopes of the island (Fig.

274 3F), cropping out very discontinuously due to erosion along steep and exposed slopes. The
275 UBT are not recognized along the western rim of La Fossa caldera, stratigraphically above
276 the intermediate Monte Lentia lava domes (15-13 ky). This suggests that most of the UBT
277 were emplaced before 15-13 ky, likely corresponding to the part of UBT below the Cugni di
278 Molinello marker bed. One of the youngest UBT depositional units has a calibrated
279 radiocarbon age of 8,305-8,655 cal y BP (Table 2). At the top, the UBT are unconformably
280 covered by the Grotta dei Palizzi 1 and 2 pyroclastic successions from the intermediate La
281 Fossa cone (2.9-2.1 ky; De Astis et al., 2013 and references therein) along the border of La
282 Fossa caldera, whereas there are no clear stratigraphic contacts or field-based correlations
283 with the Punte Nere pyroclastics (Fig. 2) that represent the oldest portion of La Fossa cone
284 succession (5.5-3.8 ky; De Astis et al., 2013 and references therein).

285 Delimiting the areal distribution of LBT and IBT on Vulcano is challenging, and their
286 separation is made difficult by the absence of the Ischia Tephra marker bed. LBT-IBT
287 deposits with a maximum thickness of 5-6 m are found in south Vulcano near Gelso, below
288 the Monte Guardia marker bed. Whilst, they are generically recognized below the Spiaggia
289 Lunga scoriae in west Vulcano near to Grotta dei Pisani (Fig. 3G), where they show a
290 thickness of 7-8 m, and the absence of the Monte Guardia makes it difficult to define the
291 boundary with the UBT. In this outcrop the LBT-IBT boundary is represented by a high-angle
292 erosional unconformity.

293 Noteworthy, there are no typical LBT-IBT deposits in the area of il Piano, where the
294 stratotype of UBT is identified. There, three thick pyroclastic successions (Fig. 3H), namely
295 the Monte Molineddo (MM) 1-3 formations (De Astis et al., 2013), are stratigraphically
296 recognized above the Monte Aria/Timpa del Corvo lava flows (78-77 ky; De Astis et al., 2013
297 and references therein) and below the UBT, matching the stratigraphic position of the LBT-
298 IBT units. Local volcanic units (Monte Rosso, Monte Luccia, Passo del Piano) dated to 53-
299 48 ky (De Astis et al. 2013, and references therein) are interlayered between the MM1-2
300 and MM3 successions (Fig. 2). The MM1-3 are massive to stratified, grey to varicoloured
301 ash successions with interlayered layers of black to yellow scoria lapilli, which are related to
302 an undefined source area within the La Fossa caldera based on a substantial
303 southeastwards thickness and grain size decrease (De Astis et al., 2013). They share some
304 lithofacies observed in LBT-IBT deposits, but a clear lithostratigraphic correlation has not
305 yet been defined. Remarkably, black to yellow scoria lapilli resembling those of the MM3

306 succession are found embedded, in places aligned in trails, within the IBT in south Lipari
307 (above the Falcone domes) and near Grotta dei Pisani and Gelso on Vulcano, thus
308 suggesting a possible correlation between the MM3 and IBT.

309 **4.2 Volcanic glass geochemistry of the BT**

310 Following the stratigraphy outline above, in the following sections we report the
311 compositional data (major and minor elements) of volcanic glass (ash and scoria) sampled
312 from throughout the BT successions outcropping on Vulcano and Lipari. Owing to more
313 extensive exposures the chemical analysis of the LBT and IBT stratigraphic macro-units
314 concentrated predominantly on outcrops studied on Lipari, whilst chemical investigations of
315 the UBT instead largely focused on the outcrops exposed on Vulcano (Fig. 4).

316 For each stratigraphically defined macro-unit outlined below, in the first instance we
317 report the glass data relating to dominant glass component or melt composition tapped
318 during the eruptions responsible for the emplacement of the BT deposits. Overall the juvenile
319 BT glasses range from basaltic trachy-andesites through trachy-andesites to more evolved
320 trachytes (Fig. 5A) and show a clear K-series affinity (Fig. 5B). Major and minor element
321 glass analyses of representative BT depositional units analysed are reported in Table 3 and
322 4, whilst the full glass dataset is reported in the Supplementary Material B.

323 Separately, some minor chemical components with distinct compositions are observed
324 within some of the individual BT depositional units (Table 5) and are also described below.
325 We attribute these chemical components to the stratigraphic units underlying the BT, and
326 as such are considered ‘secondary’ components unrelated to the juvenile products of the
327 BT source eruptions. Specifically, some depositional units in the IBT and UBT contain HKCA
328 rhyolitic glasses, whilst transitional CA to HKCA andesite to dacitic glasses are recognised
329 in some LBT depositional units (Fig. 5A).

330 To assess links between the BT depositional units and proximal eruptive units on
331 Vulcano we provide additional major and minor element glass data for the Monte Molineddo
332 (MM) 1-3 successions, and the Punte Nere Formation (Table 6). A detailed description of
333 their glass compositions is reported in Supplementary Material A.2.

334 **4.2.1 Glass geochemistry of the LBT outcropping on Lipari and Vulcano**

335 The sampled units representative of the LBT (Bt1-6) outcropping on Lipari are
336 dominated by volcanic glass compositions ranging from basaltic trachy-andesites to trachy-
337 andesites and tephri-phonolites ($\text{SiO}_2 = 52.4\text{-}57.2$ wt.%; $\text{Na}_2\text{O} + \text{K}_2\text{O} = 7.7\text{-}11.5$ wt.%; [$n =$
338 109] Fig. 5A), and these glasses have a clear K-series affinity ($\text{K}_2\text{O} = 4.2\text{-}6.3$ wt.%; Fig. 5B).
339 Using increasing SiO_2 content as a fractionation index for the LBT glasses, CaO (4.9-7.5
340 wt.%), MgO (1.8-3.5 wt.%), and Na_2O (2.8-5.9 wt.%) contents noticeably decrease, whilst
341 K_2O content increases. There is no evidence of clear chemo-stratigraphic variation in the
342 glass compositions of the LBT depositional units (Table 3). Trachy-andesite glasses ($n=22$)
343 from the limited LBT exposures accessible on Vulcano, at Grotta dei Pisani, display a
344 consistent K-series affinity, and evolutionary trends similar to those from LBT deposits
345 examined on Lipari (Fig. 5-8).

346 A secondary glass component ($n=14$), with glasses ranging from andesite through to
347 dacite ($\text{SiO}_2 = 56.5\text{-}62.6$ wt.%; $\text{Na}_2\text{O} + \text{K}_2\text{O} = 4.5\text{-}8.3$ wt.%) and a transitional CA to HKCA
348 affinity (Fig. 5A), is observed in the LBT units outcropping on Lipari interlayered with (Bt3)
349 and overlying (Bt4) the GPT (Fig. 2).

350 **4.2.2 Glass geochemistry of the IBT outcropping on Lipari and Vulcano**

351 The sampled units representative of the IBT (Bt7-11) that outcrop on Lipari are
352 dominated by volcanic glass compositions ranging from basaltic trachy-andesite to trachy-
353 andesites and tephri-phonolites ($\text{SiO}_2 = 50.8\text{-}57.2$ wt.%; $\text{Na}_2\text{O} + \text{K}_2\text{O} = 7.0\text{-}12.3$ wt.%; [$n =$
354 279] Fig. 5A), and these glasses display a clear K-series affinity ($\text{K}_2\text{O} = 3.6\text{-}7.5$ wt.%; Fig.
355 5B). Using increasing SiO_2 content as a fractionation index the IBT glasses show decreasing
356 CaO (4.0-9.1 wt.%) and MgO (1.3-4.4 wt.%) content, while K_2O increases with evolution (Fig.
357 5B). The FeOt, TiO_2 , Na_2O and Al_2O_3 contents remain broadly constant with increasing SiO_2 .
358 No clear chemo-stratigraphic relationship exists in the IBT succession on Lipari (Table 3).
359 The least evolved products observed within the IBT relate to layers of diffuse scoria lapilli
360 (Fig. 7-8; Table 3). The limited IBT exposures on Vulcano at Grotta dei Pisani are relatively
361 homogeneous and chemically consistent with the trachy-andesite/tephri-phonolitic glasses
362 of the IBT on Lipari (Fig. 5A), and these glasses conform to the same evolutionary trends
363 (Fig. 8).

364 Minor secondary glass components ($n = 34$) observed in distinct IBT depositional units
365 sampled on Lipari (bt8-10) are homogeneous high- SiO_2 rhyolites ($\text{SiO}_2 = 76.0 \pm 0.4$ wt.%;

Na₂O + K₂O = 8.9 ± 0.3 wt.%; Fig. 5A), and are characterized by variable K₂O contents, but all show a clear HKCA affinity (K₂O = 5.6 ± 0.8 wt.% [2 s.d.]; Fig. 5B). No rhyolitic glasses were observed in the IBT (Bt7) that underly the lowermost Punta di Perciato pumice deposits in southern Lipari (Fig. 2). Separating Bt9 and Bt10 in southern Lipari (Fig. 4; Loc. 3) a previously unreported whitish tephra layer (Lip1, sample LIP01/16; Table 1) was identified, which displays a homogeneous HKCA rhyolitic glass composition (SiO₂ = 75.8 ± 0.6 wt.% [2 s.d.]; K₂O = 5.3 ± 0.4 wt.% [2 s.d.]; *n* = 15; *Supplementary Material 2*).

4.2.2.1 IBT ‘upper’ unit that outcrops on Lipari and Vulcano

A further subdivision of the BT succession is introduced here on the basis of the presented volcanic glass chemistry. The glasses analysed from the basal portion of the UBT macro-unit, as previously defined by Lucchi et al. (2008) immediately overlying the Monte Guardia tephra on Lipari and Vulcano (Gelso), and labelled the Bt12 depositional unit here, are actually chemically consistent with the underlying IBT compositions described above (Section 4.2.2; Fig. 6), and distinct from the UBT (Bt13-16). Thus, we prefer to attribute the Bt12 deposits, directly overlying the Monte Guardia, to the IBT macro-unit, and herein name them as the IBT ‘upper’.

On Lipari, the IBT ‘upper’ have a dominant juvenile glass component that ranges from trachy-andesites to higher alkali content tephri-phonolites (SiO₂ = 53.1-55.9 wt.%; Na₂O + K₂O = 8.4-12.3 wt.%; [*n* = 157] Fig. 5A), and these glasses display a clear K-series affinity (K₂O = 5.4-7.5 wt.%; Fig. 5B). At Gelso on Vulcano (VUL09/17), the IBT ‘upper’ is characterised by tephri-phonolitic glasses (Fig. 5A), with a K-series affinity (Fig. 5B), that are consistent with the IBT ‘upper’ glasses observed on Lipari. With increasing SiO₂ content these IBT ‘upper’ glasses show broadly increasing K₂O content, decreasing CaO and MgO, whilst FeO_t, TiO₂, Na₂O and Al₂O₃ contents remain largely constant. The evolutionary trends of the IBT ‘upper’ glasses characterised here on both Lipari and Vulcano are entirely consistent with the underlying IBT deposits (Section 4.2.2; Fig. 6).

Minor secondary glass components (*n*=19) observed in the IBT ‘upper’ on Lipari and Gelso (Vulcano), above the Monte Guardia marker bed, are relatively homogeneous high-SiO₂ rhyolites (SiO₂ = 74.2-77.2 wt.%; Na₂O + K₂O = 8.5-9.9 wt.%; Fig. 5A), these glasses show a clear HKCA affinity (K₂O = 4.8-6.0 wt.%; Fig. 5B).

4.2.3 Glass geochemistry of the UBT

397 **4.2.3.1 UBT units that outcrop on Vulcano, and the Cugni di Molinello Formation**

398 Here we refer to the UBT depositional units (from Bt13 upwards) as those above the
399 IBT 'upper' (Bt12) (Fig. 2). Overall the juvenile glass compositions of the UBT on Vulcano
400 show a considerable range in evolution and are dominated by trachy-andesitic through to
401 trachytic glasses ($\text{SiO}_2 = 55.7\text{-}64.5$ wt.%; $\text{Na}_2\text{O} + \text{K}_2\text{O} = 8.3\text{-}11.6$ wt.%; $n = 242$; Fig. 5A), all
402 showing a clear K-series affinity ($\text{K}_2\text{O} = 5.1\text{-}7.3$ wt.%; Fig. 5B). The UBT glass compositions
403 display increasing K_2O and decreasing CaO (2.6-5.7 wt.%), MgO (1.3-2.9 wt.%), and FeOt
404 (3.9-7.3 wt.%) with increasing SiO_2 content, whilst Na_2O (2.6-4.8 wt.%), TiO_2 (0.5-0.8 wt.%;
405 Fig. 5C) and Al_2O_3 (16.4-18.1 wt.%) contents remains broadly constant. They plot along a
406 distinct evolutionary trend with higher SiO_2 contents at overlapping CaO and MgO contents
407 relative to the IBT and IBT 'upper' glasses (Fig. 6).

408 The most voluminous UBT, corresponding to unit Bt13, likely results from numerous
409 amalgamated depositional units, and was sampled directly above the Spiaggia Lunga (24
410 ky) marker bed at Grotta dei Pisani. Glass compositions of Bt13 extend to the most evolved
411 products observed in the entire Vulcano UBT succession (58.1-63.3 wt.% SiO_2). Where Bt13
412 glasses overlap in SiO_2 content with the younger BT depositional units, the latter are typically
413 dominated by glasses with higher K_2O content (e.g., Bt15; Fig. 6). The highest SiO_2 glasses
414 observed within the Bt13 samples display the lowest CaO , FeOt and MgO contents within
415 the entire UBT succession (Fig. 6). Stratigraphically higher in the Bt13 unit on Vulcano,
416 above the Quadrara marker bed (21 ky), glasses are more restricted in their degree of
417 evolution (VUL09/19; 56.1-59.3 wt.% SiO_2). Whilst, the uppermost portion of Bt13 on
418 Vulcano (sample bt02/16), collected immediately below the Cugni di Molinello scoria bed,
419 displays some of the least evolved compositions observed through the entire Bt13 unit (55.7-
420 58.5 wt.% SiO_2).

421 The Cugni di Molinello scoria is a key marker bed within the UBT succession on
422 Vulcano (Fig. 2). Here we present glass data for the Cugni di Molinello scoria to help assess
423 their geochemical relationship. Glasses ($n = 19$) are relatively homogeneous trachy-
424 andesites (52.3-54.3 wt.% SiO_2) with a K-series affinity (5.2-6.2 wt.% K_2O), and show most
425 significant variability in their MgO (2.9-4.0 wt.%) and CaO (6.3-8.0 wt.%) contents (Fig. 6).
426 The Cugni di Molinello scoria are more primitive than all the UBT deposits.

427 Above the Cugni di Molinello scoria bed, the UBT (Bt14) are quite homogenous (55.9-
428 57.9 wt.% SiO₂) (Fig. 6). The Bt15 unit displays some of the most potassic glasses
429 throughout the UBT macro-unit, with a dominant population containing ca. 7 wt.% K₂O.
430 Juvenile glasses from both the Bt15 (56.3-60.7 wt.% SiO₂) and Bt16 (56.9-61.2 wt.% SiO₂)
431 units are more heterogeneous than those of Bt14, and display some of the most evolved
432 UBT glass compositions after the basal portions of the Bt13 unit (Fig. 6).

433 A minor, silicic, secondary glass component is identified in the Bt16 depositional unit
434 sampled on Vulcano immediately above the Vallone del Gabellotto tephra erupted from
435 Lipari. These secondary rhyolitic glasses (SiO₂ = 75.0 ± 0.3 wt.%; Na₂O + K₂O = 9.2 ± 0.5
436 wt.%; Fig. 5A) display a clear HKCA affinity (K₂O = 5.3 ± 0.5 wt.%; Fig. 5B). Also, two glass
437 analyses (ca. 53 wt.% SiO₂) from the Bt14 unit are chemically consistent with the underlying
438 Cugni di Molinello scoria (Fig. 6),

439 **4.2.3.2 UBT units that outcrop on Lipari**

440 The UBT on Lipari are sampled above the IBT 'upper', exclusively belonging to the
441 Bt13 depositional unit. Overall the juvenile glasses sampled at Chiesa Vecchia (north Lipari)
442 and Vallone Canneto Dentro (central-eastern) are broadly consistent, with a heterogeneous
443 composition ranging from tephri-phonolites to trachytes (SiO₂ = 57.7-64.2; Na₂O + K₂O =
444 8.2-11.3 wt.%; $n = 63$; Fig. 5A) and a K-series affinity (K₂O = 5.1-7.1 wt.%; Fig. 5B). With
445 increasing SiO₂ content these UBT juvenile glass display decreasing CaO (2.3-5.5 wt.%;
446 Fig. 6B), FeOt (4.4 -6.7 wt.%), MgO (0.9-2.8 wt.%; Fig. 6C), TiO₂ (0.5-0.8 wt.%) and Al₂O₃
447 (15.5-17.7 wt.%) content, whilst K₂O content increases, and Na₂O (2.9-4.6 wt.%) remains
448 broadly constant. In central-eastern Lipari, the juvenile glasses of the basal Bt13 unit
449 (LIP09/19) are largely distinct from those overlying (LIP07/19), whereby the latter are
450 typically offset to higher SiO₂ at overlapping CaO, MgO and K₂O contents (Fig. 6). The same
451 compositional heterogeneity is shown by glasses of the Bt13 unit collected at Chiesa
452 Vecchia (north Lipari). A secondary component of higher SiO₂ glasses (66.1-68.8 wt.%; $n =$
453 7) is observed in the upper sample of Bt13 sampled at Chiesa Vecchia (LIP03/19),
454 recognised on the basis of a clear compositional gap (ca.64-66 wt.%; Fig. 6) which
455 separates them from the dominant juvenile component.

456 **5. DISCUSSION**

457 Stratigraphic relationships and detailed geochemical characterization of the BT on
458 Lipari and Vulcano are integrated to give constraints on their areal distribution and
459 correlations with proximal near-source units. This provides the basis for proximal-medial-
460 distal tephra correlations, and fundamental insights into hazard assessment in this active
461 sector of the Aeolian Islands.

462 **5.1 Geochemical characteristics of the BT volcanic glasses and a proximal link to** 463 **Vulcano**

464 Major and minor element glass geochemistry of the juvenile component of individual
465 BT depositional units reveals that they are relatively homogeneous with K-series populations
466 ranging from basaltic trachy-andesites, through trachy-andesites and tephri-phonolites, up
467 to more evolved trachytes (Fig. 5A). The minor outlying HKCA rhyolitic glasses, and CA to
468 HKCA andesite to dacite glasses recognized in some depositional units of the LBT, IBT and
469 UBT are considered as “secondary” components, which do not reflect the juvenile magmas
470 feeding the BT. Their origin is discussed in Section 5.2. Consequently, the overall
471 compositional field of BT volcanic glasses is significantly more restricted when compared to
472 the one proposed by Lucchi et al. (2008). A narrower compositional range centred
473 exclusively around K-series volcanic glasses reinforces the correlation of the BT with the
474 Vulcano magmatic system. During its intermediate to youngest stages of evolution, Vulcano
475 has been the dominant source of K-series products within the Aeolian archipelago (Fig. 5A-
476 C). The evolutionary trends observed here within the overall BT dataset are entirely
477 consistent with the previously characterised near-source Vulcano volcanic glasses (Fig. 5C-
478 D). Indeed, the only other source of K-series magmas within the archipelago, and similar to
479 those of the BT, is the Stromboli volcano, specifically during the Neostromboli period (~13-
480 4 ky; Francalanci et al., 2013; Albert et al., 2017; Fig. 5). An association between the BT
481 and eruptive activity on Stromboli is, however, implausible owing to their greater thicknesses
482 on Vulcano and Lipari relative to the rest of the archipelago (including Stromboli).
483 Furthermore, K-Series activity on Stromboli is temporally incompatible with the longer-term
484 emplacement of the BT succession. Finally, in terms of glass compositions, at overlapping
485 SiO₂ content, the BT glasses display TiO₂ content more consistent with Vulcano products
486 (lower-TiO₂) rather than those erupted on Stromboli (Fig. 5C). This final observation is
487 pertinent when assessing the provenance of distal K-series marine tephra layers which
488 might be related to the eruptions responsible for the BT.

489 Resolving unique geochemical fingerprints for the LBT and IBT glasses is a significant
490 challenge given their large degree of chemical overlap. They are broadly consistent in terms
491 of their SiO₂ content (~52-57 wt.%), and across most other major and minor elements (Fig.
492 8). Some subtle differences may offer potential to help provenance medial-distal equivalents
493 of the BT deposits, particularly where chrono-stratigraphy is poorly constrained. The least
494 evolved IBT glasses contain higher MgO, CaO and FeO_t relative to those analysed
495 throughout the LBT (Figs. 5 and 8). More useful is that the IBT glasses range to higher K₂O
496 content than those of the LBT, thus at overlapping SiO₂, where K₂O content exceeds 6.3
497 wt.%, an attribution to the IBT is more likely (Fig. 7C).

498 The UBT glasses can be distinguished from those of the IBT (and LBT) owing to their
499 higher SiO₂, trachy-andesitic to trachytic compositions (Fig. 5). The UBT glasses extend to
500 lower TiO₂ contents compared to the underlying IBT units, again consistent with the overall
501 trends observed in the glasses of known Vulcano erupted products (Fig. 5C). The UBT
502 glasses also plot on subtly different evolutionary trends from those of the IBT, and this is
503 well illustrated by CaO and MgO content plotted against SiO₂ (Fig. 6), where both CaO and
504 MgO contents of the UBT extend to lower values than those of the IBT glasses (Fig. 6).

505 The stratigraphic boundary between the IBT and UBT macro-units had been previously
506 defined by the identification of the widespread Monte Guardia tephra marker bed (Lucchi et
507 al. 2008) and dated here at 25,920-27,025 cal y BP. The observed geochemical distinction
508 between the IBT and UBT makes it possible to define a different geochemical-evolutionary
509 boundary between the two successions. The lowermost depositional unit (Bt12) of the
510 stratigraphically defined UBT macro-unit, immediately overlying the Monte Guardia tephra
511 on both Vulcano (Gelso) and at various locations across Lipari (Fig. 6), is in fact chemically
512 consistent with the IBT (those deposits beneath the Monte Guardia; Fig. 6), and
513 consequently this depositional unit is re-defined in this study as the IBT '*upper*'. On Vulcano,
514 the IBT/UBT chemical transition is observed relative to the Spiaggia Lunga scoria unit in the
515 western sector of the island, whereby IBT type compositions are not observed in BT deposits
516 above the Spiaggia Lunga, instead exclusively evolved UBT compositions are recognized.
517 The age of 24 ± 5 ky for Spiaggia Lunga (Soligo et al., 2000) allows us to redefine the
518 chronological boundary between IBT (56-24 ky) and UBT (24-8 ky). Unfortunately, where
519 the Spiaggia Lunga scoria is not present, the IBT to UBT chemo-stratigraphic boundary is
520 more difficult to identify, and this is the case on Lipari where no obvious unconformities are

521 recognized at the corresponding stratigraphic level. However, charcoal dated from within the
522 IBT 'upper' on Lipari is dated here at 25,800-26,190 cal y BP and this eruption age is in good
523 chrono-stratigraphic agreement with the inferred Spiaggia Lunga boundary-transition age
524 on Vulcano. The Spiaggia Lunga scoria unit crops out along the south-western border of the
525 La Fossa caldera, which is the likely source area of the BT. Interestingly, Nicotra et al. (2020)
526 have proposed that the emplacement of the Spiaggia Lunga scoria unit is directly linked to
527 a volcano-tectonic (caldera) collapse event on Vulcano. It can be thus postulated that a
528 collapse of the La Fossa caldera has coincided with a reconfiguration of this magmatic
529 system, and the production of more evolved magmas which feed the UBT.

530 The more evolved depositional units that form the UBT (Bt13-16) show considerable
531 compositional variability (Fig. 6). The most evolved glasses erupted within the UBT are
532 associated with the most voluminous and oldest portion of Bt13, below the Cugni di Molinello
533 scoria marker bed (Fig. 6). There is clear chemical overlap between the Bt13 depositional
534 unit sampled on Vulcano and further north on Lipari. For instance the lowermost Bt13
535 samples from Vallone Canneto Dentro on Lipari (LIP09/19) are very consistent with the
536 analysed deposits from the lowest portions of Bt13 on Vulcano. However, there are some
537 noticeable spatio-chemical variations associated with unit Bt13. The remaining Lipari Bt13
538 samples (LIP07/19, LIP04/19 and LIP03/19) are dominated by glasses which reside on a
539 subtly distinct evolutionary trend to those prevalent in the Vulcano deposits, this is best
540 illustrated by a subtle offset to higher SiO₂ at overlapping K₂O, CaO and MgO content (Fig.
541 6). Importantly, from a correlation and provenance perspective, these higher SiO₂ glasses
542 are also observed in the basal Bt13 deposit closer to source on Vulcano, albeit as a lower
543 proportion of the glasses analyzed. Published data (sample VL328) stratigraphically
544 equivalent to Bt13 reported on Vulcano (Lucchi et al. 2008) is also consistent with the data
545 presented here from Lipari. The most obvious explanation for a lower proportion of higher
546 SiO₂ UBT glasses in our Vulcano dataset is because our sampling concentrated at the top
547 and bottom of the thick Bt13 depositional unit, whereby the intermediate portion was not
548 analysed. In contrast on Lipari, further from vent, this depositional unit is thinner and more
549 compact, for instance at Vallone Canneto Dentro the analyses appear to reveal a more
550 heterogeneous Bt13 signature, with data reflecting both the subtly offset UBT evolutionary
551 trends (Fig. 6). There is a return to less evolved trachy-andesite compositions (ca. 57 wt.%)
552 in the uppermost portion of unit Bt13 (sample bt02/16), directly underlying the Cugni di
553 Molinello scoria bed. This variability suggests that Bt13 does not represent a single

554 depositional unit, but an amalgamation of lithologically homogeneous deposits, as also
555 testified by the occurrence of localized erosional surfaces throughout the thickness of Bt13.
556 The upper portion of Bt13 and Bt14 on Vulcano are indistinguishable in their composition,
557 and are merely stratigraphically separated by the less evolved Cugni di Molinello scoria (Fig.
558 6), seemingly sourced from a separate vent within the La Fossa caldera (Dellino et al., 2011).
559 Bt15 and Bt16 return to more evolved trachytic glass compositions, more consistent with
560 those deposits from Bt13 (Fig. 6), making independent stratigraphic control important when
561 distinguishing depositional units throughout the UBT. Bt15 is distinctive in terms of its
562 prevalence of higher-K₂O glasses at overlapping SiO₂ content relative to other UBT
563 deposits, a feature that is also apparent in published data from the same stratigraphic level
564 (sample VL151; Lucchi et al. 2008).

565 **5.2 The secondary glass compositions: insight into the BT depositional mechanisms**

566 In addition to the dominant juvenile K-series glass components of the BT, a small
567 proportion of chemical outliers are recognized in some depositional units of the LBT, IBT
568 and UBT on both Vulcano and Lipari. These glasses are genetically unrelated to magmas
569 feeding the eruptions responsible for the BT and are termed here as “secondary glasses”.
570 HKCA rhyolitic glass compositions identified in some IBT and UBT units are entirely
571 consistent with the silicic activities on Lipari during the past ca. 50 ka (Fig. 5A-B).
572 Specifically, the rhyolitic glasses observed in the depositional units Bt8 and Bt9-10 of the
573 IBT on Lipari, Bt12 of the newly defined IBT ‘upper’ on Lipari and Bt16 of the UBT on
574 Vulcano. Lipari HKCA rhyolitic glasses can be most easily distinguished using their SiO₂ and
575 K₂O content. On this basis we see that the rhyolitic glasses observed as secondary glasses
576 can be compositionally linked to the pumice beds stratigraphically underlying each of the
577 above-mentioned BT depositional units. The Bt8 and Bt9-10 depositional units of IBT contain
578 high-SiO₂ (~76 wt.%) rhyolites with high K₂O (~5.5-6.2 wt.%), largely consistent with the
579 underlying Falcone and Punta di Perciato tephra deposits related to eruptive activity in
580 southern Lipari (Fig. 9A-B). There is also a degree of chemical overlap with rhyolitic glasses
581 of the Lip1 tephra. This newly identified tephra layer separating the Bt9 and Bt10
582 depositional units, clearly documents a previously un-reported explosive eruption in the
583 southern dome-field of Lipari given its glass composition spans those of the underlying
584 (Falcone) and overlying (Monte Guardia) eruption units (Fig. 9A-B). The Bt12 (IBT ‘upper’)
585 deposits across Lipari and in southern Vulcano (Gelso) contain minor components of high-

586 SiO₂ rhyolites (~76 wt.%) with far more variable K₂O content (4.7-6.0- wt.%), consistent with
587 the pumice and ash compositions of the underlying Monte Guardia eruption deposits (Fig.
588 9A-B). Whilst the HKCA rhyolitic glasses within the Bt16 unit of UBT on Vulcano are more
589 consistent with the underlying Vallone del Gabellotto tephra deposits from Lipari (Fig. 9).

590 Similarly, CA to HKCA andesitic glass compositions are identified in the depositional
591 units Bt3-4 of the LBT that outcrop on Lipari and are either interbedded within, or directly
592 overly the GPT deposits from neighbouring Salina (Fig. 9, C-D). These glass compositions
593 are entirely consistent with the GPT deposits characterised proximally on Salina (Sulpizio et
594 al., 2016), but also include new glass data for the proximal GPT, and medial-distal
595 occurrences sampled on Lipari (LIP41/17; SME4/5), Vulcano (VUL05/18) and Panarea
596 (PAN07/17). The additional occurrence of basaltic-andesite to andesite glass compositions
597 consistent with the GPT in the depositional units Bt1-2 of the LBT in western Lipari (Fig. 9C-
598 D) is instead likely to be attributed to an underlying tephra deposit (reported as I1 tephra by
599 Forni et al. 2013) which shares a similar composition to the products of the GPT (Fig. 9C-
600 D).

601 Furthermore, unit Bt14 of the UBT on Vulcano contains a minor component of K-series
602 glasses which are entirely consistent with the juvenile products of the underlying, more
603 primitive, Cugni di Molinello scoria bed (Fig. 6).

604 The presence of a minor component of glass fragments within some BT depositional
605 units that compositionally correlate to the underlying pyroclastic units is the result of clast-
606 embedding, ripped up from the incoherent substratum by PDCs laterally spreading from the
607 source area on Vulcano. This is clearly observed in the field where pumice and/or scoria
608 from the underlying incoherent pyroclastic units are ripped-up and embedded at the base of
609 the individual BT depositional units in the sampled outcrops, a feature first observed by
610 Lucchi et al. (2008; 2013b). These authors suggested that PDC erosion and abrasion was
611 limited to proximal to mid-proximal areas, whereas here we suggest that clast-embedding
612 could be effective even at a greater distance up to at least the northern sector of Lipari (more
613 than 10 km from the source).

614 **5.3 BT links with proximal units on Vulcano**

615 Here our volcanic glass dataset for the LBT, IBT and UBT is used to assess
616 correlations with proximal units on Vulcano, to further constraint source/vent location. For

617 this purpose we discuss the geochemical affinity of the LBT, IBT and UBT with the volcanic
618 units belonging to the corresponding chrono-stratigraphic windows that currently outcrop
619 along the borders of the La Fossa caldera, which have been considered as the most
620 probable BT source area (Lucchi et al., 2008, 2013b). Lucchi et al. (2008, 2013b)
621 established a univocal lithostratigraphic correlation between the UBT and the Piano Grotte
622 dei Rossi Tuffs, which are best exposed along the south-eastern rim of La Fossa caldera, in
623 the area of Il Piano and crop out discontinuously on western and southern Vulcano. These
624 show a regular decrease of deposit thickness from the caldera rim towards southern Vulcano
625 that indicate an origin from a (undefined) vent within the La Fossa caldera.

626 Instead, there remains a challenge in defining correlations and areal distributions of
627 the LBT-IBT (80-24 ky) because deposits with their typical lithofacies are absent in the area
628 of Il Piano, given the UBT stratotype is observed here, it should represent the main
629 depositional area of the LBT-IBT units, assuming that their source area has not changed
630 over time. In this area, the MM1-3 pyroclastic successions occupy the chrono-stratigraphic
631 window corresponding to the LBT-IBT (in addition to other minor units). Specifically, the
632 MM1-2 are found interlayered between Vulcano products dated at 78-77 ky and 53-48 ky,
633 which broadly corresponds to the 80-56 ky chrono-stratigraphy of the LBT, whilst the IBT
634 (56-24 ky) are more likely to correspond to the MM3 that is loosely defined in the
635 stratigraphic interval above 53-48 ky and the UBT (<24 ky). In addition to a compatible
636 chrono-stratigraphic position, the MM1-3 share many lithological and textural features with
637 the LBT-IBT deposits, consisting of massive ash with discontinuous lamination and planar
638 to inclined bedding, with abundant clinopyroxene crystals and internal banding of colour and
639 grain-size. Furthermore, distinctive black to yellowish scoria lapilli of MM3 are recognized in
640 a number of stratigraphic positions within the IBT including at Grotta dei Pisani and Gelso
641 on Vulcano, or along the southern sector of Lipari. These lines of evidence were responsible
642 for Lucchi et al. (2008, 2013b) proposing that the MM1-3 could represent the near source
643 counterpart of the LBT-IBT units. However, a clear lithostratigraphic correlation between the
644 LBT-IBT units and the MM1-3 has not yet been established, and thus geochemical support
645 becomes particularly important.

646 The K-series basaltic trachy-andesitic, tephri-phonolitic and trachy-andesitic glasses
647 of the LBT and IBT are indeed broadly consistent with the volcanic glasses erupted during
648 the emplacement of the proximal MM1-3 (Fig. 7-8). Our samples and subsequent glass

analyses, reported in Supplementary A, are unlikely to be representative of the full compositional variability of these thick eruptive successions, particularly owing to the poor preservation of the hydrothermally altered MM3 deposits. Regardless of this, the MM1 glasses show some overlap with both the LBT and IBT, although they are dominated by subtly more evolved glass compositions, particularly with respect to those LBT-IBT on Lipari (Fig. 8). There is significant geochemical overlap between the LBT and MM2 glasses (Fig. 8), whilst the IBT appear to show subtle offsets, for instance MM2 glasses do not fully satisfy the higher K₂O (Fig. 7C) or lower TiO₂ observed in the IBT glasses. Whilst a link between the MM1 and the earliest LBT cannot be completely excluded, an assignment of the MM2 as a near-source counterpart of the LBT on Vulcano seems the most probable, consistent with the reconstructed chrono-stratigraphy. Indeed, the correlation is also supported by the occurrence of a layer of grey pumice lapilli (VUL05/18) observed within the MM2 (Fig. 4; sec. 2 on Vulcano). These lapilli display glass compositions consistent with those of the GPT from Salina, which critically is also found interlayered within the LBT on Lipari (Fig. 9), Salina and Panarea (See Section 5.4).

Coarse proximal MM3 scoria fall (sample BT03/20), along with the more evolved component of a black to yellowish MM3 scoria fall deposits traced to southern Vulcano (Gelso; VUL04/17), are consistent with the IBT (Fig. 7-8). The proximal MM3 (BT03/20) glasses are chemically consistent with the least evolved ash deposits of the IBT observed on both Vulcano and Lipari (Fig. 8), while the most evolved scoria (54.4 wt.% SiO₂) analysed displays higher K₂O, and lower CaO and MgO content consistent with the dominant IBT glass compositions (Fig. 8D-F). These proximal MM3 scoria fall (BT03/20) also shows broad chemical consistency with the scoria fall identified within the IBT on Lipari (Fig. 8), albeit these MM3 glasses are offset to higher K₂O content (Fig. 7C). MM3 fall sampled in southern Vulcano (Gelso) is bimodal, while one population is more primitive (~ 49 wt.% SiO₂) than the IBT deposits, the second is chemically consistent with the IBT glasses, even extending to the same more elevated K₂O contents, and further supporting a link between the MM3 and the IBT (Fig. 7C; 8D-F). Combining the proximal and medial MM3 scoria fall data reveals a substantial compositional variability, and this variability appears to correspond to a significant proportion of overall IBT chemical variability observed. However some of the more evolved IBT glass compositions are not satisfied by the available MM3 data, and again this is likely to reflect MM3 preservation related sampling biases. Both in terms of limited stratigraphic coverage of the proximal MM3 succession sampled, and the associated

difficulties of being able to chemically compare the same lithofacies. For instance, proximal MM3 alternates between scoria fall and ash-rich PDC deposits, here we are only able to analyse the fresh scoria fall, whilst the IBT characterised clearly relate to PDCs. Overall, there is sufficient chemical agreement to support the chrono-stratigraphic link between the MM3 and the IBT.

Our geochemical dataset shows that the juvenile UBT glasses (trachy-andesites to trachytes) are very similar to glass compositions of the early to intermediate products of La Fossa cone, namely the Punte Nere and Grotta dei Palizzi deposits (Fig. 6). Interestingly, volcanic glasses of the Punte Nere pyroclastic succession can be chemically distinguished and lie on separate evolutionary trends (Fig. 6). The lowermost Punte Nere (VUL01/17) deposits, and ultimately the earliest La Fossa products recognized in the volcanic stratigraphy, are entirely consistent with the UBT (Fig. 6). Whilst these lowermost Punte Nere deposits are slightly more evolved than the products of the youngest UBT depositional unit (Bt16), they are entirely consistent with the older Bt13 deposits sampled across Vulcano and Lipari, and the Bt15 deposits (Fig. 6). This geochemical link is important given that the Punte Nere pyroclastics are massive to cross-laminated, dark grey ash deposits, lithologically very similar to UBT, yet direct stratigraphical relationships between the two successions are lacking in the field (Fig. 2). The geochemical similarity between the UBT and the earliest Punte Nere products suggests that the UBT may be associated with the earliest activities of the La Fossa cone too, probably sharing the same magmatic plumbing system. It is even plausible that some of the older Punte Nere products recognized in the field may actually equate to the uppermost UBT. Either way this outlines a direct relationship between the UBT and the active La Fossa cone which was not fully demonstrated by previous studies, and illustrates a possible continuity in the evolution of the magmatic and eruptive system of La Fossa cone starting (at least) from the onset of UBT activity at ~24 ky, which extends its life cycle.

As highlighted, the glass compositions within the basal Punte Nere succession are variable. Whilst the oldest Punte Nere deposits (VUL01/17), are chemically consistent with the UBT, the overlying Punte Nere glasses analysed (VUL02/17; VUL03/17) are offset in terms of their CaO, MgO and K₂O content (Fig. 6). Interestingly, these glasses, and those of the younger Grotta dei Palizzi successions (cf. Albert et al., 2012), lie on the same evolutionary trends as the older IBT glasses, albeit extending to more evolved end-member

714 (Fig. 6). Our heterogeneous Punte Nere data, which are consistent with published Punte
715 Nere and Grotta dei Palizzi glass data (Fig. 6), suggest that the La Fossa explosive activity
716 at this time was fed by a complex magmatic system comprising of more than one magma
717 batch

718 **5.4 Proximal-medial-distal correlations**

719 *5.4.1 BT occurrences on Salina, Panarea, Filicudi and Capo Milazzo (Sicily)*

720 Here we use new glass analyses (Supplementary Material B) of BT occurrences from
721 across the Aeolian archipelago (Salina, Filicudi and Panarea) and Capo Millazzo (Sicily) to
722 help constrain the dispersal of volcanic ash associated with the successive eruptions on
723 Vulcano. Considerable geochemical overlap between the juvenile glass components of the
724 LBT and IBT macro units (Section 5.1) means that correlations rely on the stratigraphic
725 context at individual localities throughout the Aeolian islands, and often relying upon key
726 stratigraphic markers beds (e.g., the Ischia Tephra or GPT).

727 BT depositional units observed on Salina underlying the Ischia tephra in the
728 stratigraphic window of the LBT have relatively homogeneous glass chemistries that overlap
729 with the glasses of the LBT elsewhere, and the proximal MM1-2 on Vulcano (Fig. 7B; Fig.
730 8A-C). These LBT deposits observed on Salina lack secondary glass components from the
731 underlying strata, coherent with their occurrence on the lava flows related to the final activity
732 of Monte dei Porri stratocone dated at 67-57 ky (Lucchi et al. 2013a) and the absence of
733 significant abrasion effects.

734 Ash deposits chemically consistent with the LBT and IBT are recognised on Panarea
735 and these are attributed to the former owing to the presence of GPT from Salina interbedded
736 within (Fig. 7B; 8A-C). Deposits with relatively homogeneous glasses consistent with the
737 LBT also outcrop on Capo Milazzo peninsula (Fig. 7B; 8A-C), although without the
738 stratigraphic constraints coming from other tephra marker beds, a link to the IBT cannot be
739 excluded. This highlights the importance of external chrono-stratigraphic markers, or dating
740 (^{14}C) to constrain the timing of the source eruptions on Vulcano and their associated ash
741 dispersals.

742 K-series ash deposits on Filicudi island (FIL07/18), northwest of Vulcano, are entirely
743 consistent with the LBT and IBT glass compositions (Fig 7C; Fig. 8D-F). However, based on
744 their stratigraphic position above the Ischia tephra these deposits are firmly attributed to the

745 activity of the IBT. A second Filicudi ash unit (FIL08/18) is also interpreted as IBT based on
746 its position above the Ischia tephra and its glass compositions being broadly consistent with
747 the most evolved IBT (Fig. 8D-F).

748 *5.4.2 Possible BT occurrences in the sedimentary records of the Central Mediterranean*

749 Given their significant near-source thickness on Vulcano and Lipari and wide
750 distribution throughout the Aeolian Islands (Salina, Panarea and Filicudi), the successive BT
751 depositional units potentially represent the source equivalents of volcanic ash layers
752 recorded in sedimentary archives (marine and lacustrine) across the Central Mediterranean.
753 The region has a well-established distal tephrostratigraphic framework (e.g., Keller et al.,
754 1978; Paterne et al., 1988, Calanchi and Dinelli 1998; Wulf et al., 2004; Sulpizio et al., 2010;
755 Giaccio et al., 2017) with many widespread ash layers tied into the well-dated eruption
756 stratigraphies of the productive central Mediterranean volcanoes, particularly those in
757 Campania (e.g., Campi Flegrei, Ischia). Therefore, the identification of BT deposits within
758 this tephrostratigraphic framework would not only provide information on the distribution and
759 scale of explosive activity on Vulcano, it also offers chronological constraints on the timing
760 of eruptions on the island. With some exceptions, the presence of BT deposits in regional
761 sedimentary archives is largely underexplored (e.g. Paterne et al., 1988; Calanchi et al.,
762 1994; Di Roberto et al., 2008; Albert et al., 2012; Tamburrino et al., 2016), probably due to
763 an inadequate knowledge of their stratigraphy, and most importantly their geochemical
764 (juvenile glass) signatures, essential to reliable source attributions. Here we use our
765 extensive volcanic glass dataset to evaluate the distribution and timing of distal BT
766 occurrences.

767 In the chrono-stratigraphic window of the LBT (80-56 ky), Tyrrhenian (and Adriatic) Sea
768 marine cores, including those investigated by Paterne et al. (1986; 1988), do not reveal any
769 obvious ash layers candidates for distal LBT in the deep-sea realm. In terms of IBT and UBT
770 occurrences, Tamburrino et al. (2016) explored the ash deposits preserved in the Marsili
771 Basin core, MD01-2474G (Fig. 1a), situated on a topographic high. They proposed the
772 possible occurrence of ash layers associated with the IBT (MD27, MD22, MD15) and UBT
773 (MD11 and MD3) eruptions, although it is worth noting that these correlations were made in
774 the absence of reliable BT reference glass data. Albert et al. (2012) reported the occurrence
775 of 'pre-La Fossa' Vulcano tephra (TIR2000-50cm) in another Marsili Basin core, TIR2000-
776 C01 (Fig. 1a), situated more than 20 km ENE of the Stromboli Canyon mouth, a major source

777 of volcanoclastic material into the Basin. The Marsili Basin captures volcanoclastic turbidites
778 relating to pyroclastic material deposited on the islands, and directly into the marine
779 environment, consequently we carefully re-evaluate the available data from these Marsili
780 cores. Unfortunately, with TIR2000-C01, the age of ash layers below the Soccavo 1 tephra
781 (Campi Flegrei) at ~ 12 ky (TIR2000-93cm) were not well constrained in the absence of
782 reliable chrono-stratigraphic or biostratigraphic markers. Conversely, the Marsili core MD01-
783 2474G has a more reliable chronology developed using radiocarbon dating, and orbitally-
784 tuned chronological tie-points (Tamburrino et al., 2016). Broad agreement exists between
785 the independent chronology of the record and the preferred ages of key chrono-stratigraphic
786 markers, particularly those in the deeper portion of the core. For instance, layer MD28 (54.8
787 ky) correlates to the widespread marine ash layer, the Y-7, equivalent to the Ischia Tephra,
788 dated at 56.1 ± 1.0 ky (Giaccio et al., 2017), thus providing a direct tie-point between the
789 onland BT stratigraphy and the marine core. Furthermore, our GPT (Salina) glass data
790 corroborates its distal occurrence in MD01-2474G (MD33 [58.9 ky]; Fig. 9C-D), offering
791 another terrestrial-marine chrono-stratigraphic tie point. Crucially, co-located tephras in the
792 Marsili cores now facilitate the transfer of age information from MD01-2474G to TIR2000-
793 CO1.

794 The oldest ash layer in MD01-2474G, MD27, previously linked to the IBT (Tamburrino
795 et al., 2016), comprises a dominant component of transitional HKCA/SO trachy-andesitic
796 glasses. This layer is dated using the cores age-model at 42.7 ky, an age which is further
797 corroborated by the presence of a secondary Pantellerite glass shards linked to the
798 Pantelleria Green Tuff (Tamburrino et al., 2016) that is $^{40}\text{Ar}/^{39}\text{Ar}$ dated at 45.7 ± 1.0 ky
799 ([95.4%]; Scaillet et al., 2013). Compared to our juvenile BT data it is apparent that these
800 SHO glasses are generally too low in K_2O content, and too high in TiO_2 to be associated
801 with IBT activity on Vulcano (Fig. 10). Glass data indicates they reside on an evolutionary
802 trend more akin to glasses erupted on Stromboli during the Paleostromboli epoch, rather
803 than the central sector of the Aeolian archipelago..

804 Ash layer MD22 (MD01-2474G) dated at 36.9 ky was linked to the IBT (Tamburrino et
805 al., 2016), our data clearly indicate that this layer is inconsistent with the IBT the and Vulcano
806 magmatic system (Fig. 10). Tamburrino et al. (2016) linked this 8.3 cm thick tephra deposit
807 to a layer in TIR2000-C01, namely TIR2000-417 cm. Here we suggest that there is better
808 chemical agreement between MD22 and the overlying tephra in TIR2000-C01, TIR2000-

809 398cm, a 20 cm thick coarse-grained volcanoclastic turbidite (Di Roberto et al., 2008; Albert
810 et al., 2012). MD22 appears to contain both chemical components of the TIR2000-398cm
811 deposit (Fig. 10), the transitional CA/HKCA glasses which extend from basaltic-andesites
812 through andesites and dacites, to a low-SiO₂ rhyolites (Component-1), and HKCA basaltic-
813 andesites (Component-2). This clear chronological tie-point between MD01-2474G and
814 TIR2000-C01 means we can import the MD01-2474G age of 36.9 ky to the TIR2000-398cm
815 tephra unit. This offers useful chronology to the basal sediments of TIR2000-C01, critical
816 when assessing the age of other ash deposits in this core. The sedimentological features of
817 MD22/TIR2000-398cm, including grain-size and layer thickness, combined with the different
818 chemical arrays observed, indicate this deposit is linked with a major volcanic collapse. The
819 data from this deposit are clearly inconsistent with Vulcano and the central sector of the
820 Aeolian archipelago. The high TiO₂ content of the glasses (Fig. 10B) may prompt future
821 investigations of a link to one of the many collapse events to have occurred on Stromboli
822 island (Francalanci et al., 2013).

823 MD15 (29.7 ky) in MD01-2474G, a 10.8 cm thick tephra, was linked to IBT activity on
824 Vulcano, its trachy-andesitic glasses are transitional between HKCA/SHO (Tamburrino et
825 al., 2016). Importantly these glasses display lower K₂O content than the IBT volcanic glasses
826 at overlapping SiO₂ content, and more elevated TiO₂ content is again inconsistent with the
827 BT and Vulcano (Fig. 10). Two trachy-andesite ash layers, MD11 (16.7 ky) and MD3 (6.9
828 ky), in the MD01-2474G core were attributed to the 'Tufi di Grotte dei Rossi inferiori', here
829 equivalent to the UBT (Tamburrino et al., 2016). Whilst both layers display glasses that
830 overlap with those of the UBT, they show more elevated TiO₂ content at particular SiO₂
831 contents, which is again more consistent with Stromboli than the UBT and Vulcano (Fig.
832 10B).

833 Returning to Marsili core TIR2000-C01, in light of new age constraints, with 36.9 ky
834 placed on the coarse-grained volcanoclastic turbidite (CGVT; TIR2000-398cm = MD22), we
835 are able to evaluate the timing of potential distal BT deposits found in the core
836 stratigraphically above this CGVT. Between the Campi Flegrei tephra Soccavo 1 (TIR2000-
837 93cm) found at 93 cm depth in TIR2000-C01, and the CGVT (TIR2000-398) at 398 cm a
838 crude sedimentation rate of 12.4 cm/ky⁻¹ is calculated. This is a noticeable increase from a
839 rate of 7.72 cm/ky⁻¹ observed in the upper portion of the core between the 776 CE Monte
840 Pilato tephra from Lipari (TIR2000-7cm), found at depth of 7 cm, and the Soccavo 1

841 (TIR2000-93cm). However, given the frequent occurrence of volcanoclastic turbidity current
842 deposits (Di Roberto et al., 2008), a highly variable sedimentation rate is expected; indeed,
843 such variability was also recognised in Marsili core MD01-2474G (Tamburrino et al., 2016).
844 Without calculating an event-free sedimentation rate, our TIR2000-C01 tephra age
845 estimates are tentative.

846 Many ash rich, volcanoclastic turbidites within TIR2000-C01 have not been chemically
847 characterised (Di Roberto et al., 2008; Albert et al., 2012), here we provide new glass data
848 from some which reinforce the occurrence of marine deposits chemically consistent with the
849 BT in the Marsili Basin, and highlight the need for future investigations of similar sedimentary
850 successions from the southern Tyrrhenian Sea. A thin (3 mm) ash deposit sampled at a
851 depth of 297 cm, TIR2000-297cm, has a homogeneous K-Series (Fig. 10), basaltic trachy-
852 andesite to trachy-andesite affinity, with an age of ~28.7 ky. The glass compositions are
853 generally consistent with the eruptive products of the IBT on Lipari, and in particular the
854 diffuse scoria fall (LIP27/17; Fig. 8D-F) observed in the depositional unit above the Falcone
855 dome (~43-40 ky), although we must acknowledge a subtle offset in FeO_t content (Fig. 8F).
856 With an age of ~28.7 ky for TIR2000-297cm we tentatively suggest this marine tephra pre-
857 dates the widespread 25,885-27,055 cal y BP Monte Guardia eruption, and therefore it is
858 plausible that the tephra relates to IBT activity preserved on Lipari Island between the local
859 Falcone and Monte Guardia tephra beds (Bt10 or Bt11).

860 Stratigraphically higher in the TIR2000-C01 succession, a thin (2 mm) ash rich tephra,
861 TIR2000-160cm, has a relatively heterogeneous (57.4-61.4 wt.% SiO₂) K-series (Fig. 10),
862 trachy-andesite to trachyte compositions with an age of ~16.7 ky. These glasses are entirely
863 consistent with the UBT on Vulcano, whilst restricted by a limited number of analyses the
864 compositional variability and chrono-stratigraphic position means a link to the eruptions
865 responsible for Bt13 is most likely (Fig. 6). This marine tephra reinforces a chemical link to
866 the La Fossa magmatic system deeper in time.

867 The K-series trachytic tephra TIR2000-50 (Fig. 10) has an age of ~6.7 ky, and its origin
868 was the focus of previous debate. Di Roberto et al. (2008) initially attributed this layer to a
869 collapse during the Secche di Lazzaro eruption on Stromboli (Neostromboli epoch).
870 However, chemical investigations revealed that this tephra was actually more consistent
871 with the eruptive products of Vulcano (Albert et al., 2012; 2017). Based on the diagnostic
872 lower TiO₂ content of these volcanic glasses they were akin to the evolutionary trend of

873 Vulcano products and thus suggested pre- or early La Fossa activity (Fig. 10B). Interestingly,
874 the dominant K-series glasses are consistent with the UBT (Fig. 10A), whilst a secondary
875 glass component of HKCA rhyolites are consistent with those of the Vallone del Gabellotto
876 (Lipari). This feature is consistent with the onland Bt16 depositional unit, immediately
877 overlying the Vallone del Gabellotto (8.7–8.4 ky) tephra on Vulcano. A correlation of
878 TIR2000-50cm to Bt16 would be consistent with the chrono-stratigraphy given the marine
879 tephra deposits age (~6.7 ky). The overlying TIR2000-46cm unit is compositionally
880 indistinguishable from the dominant K-series component of the underlying TIR2000-50 (Fig.
881 10), although this younger tephra (~6.1 ky) has no secondary rhyolitic component. It is
882 plausible that this tephra also relates to the Bt16, and would imply that Bt16 depositional
883 unit is the product of more than one eruption. These correlations give us new age constraints
884 for the youngest portion of the UBT on Vulcano, which post-date the 8.5 ky (radiocarbon)
885 age obtained by De Astis et al. (1997b).

886 Away from the Marsili Basin, two noticeable distal occurrences of potential IBT are
887 worthy of discussion. The E-10 Tyrrhenian Sea ash layer preserved in KET8003 north of
888 Salina (Fig. 1a) and dated to 35.2 ky (Paterne et al., 1988) appears to have a glass chemistry
889 (Fig. 10) and chrono-stratigraphic position consistent with the IBT positioned between the
890 Falcone and Monte Guardia tephra deposits outcropping on Lipari. Whilst Matthews et al.
891 (2015) reported a basaltic trachy-andesite tephra, T1567, dated at between 35,693-34,064
892 cal y BP in the Southern Adriatic (core SA03-11; Fig. 1a) and positioned immediately above
893 the 40 ky Campanian Ignimbrite (Y-5/C-13) tephra. The glass compositions of this tephra
894 are entirely consistent with those of the IBT, and specifically to the diffuse scoria fall
895 observed in the IBT above the 43-40 ky Falcone dome on Lipari (LIP27/17; LIP15/18;
896 LIP16/18). The chrono-stratigraphy of this correlation is compelling and indicates a
897 widespread ash fall event associated with the IBT at ~35 ky. Whilst there are clear chemical
898 differences between the E-10 and T1567, their ages (~ 35 ky) are entirely compatible,
899 indicating that the two distal tephra layers may reflect either; (1) closely spaced eruptions or
900 eruptive phases on Vulcano, which cumulatively form part of the IBT eruptive cycle; or (2)
901 different eruptive processes during the same IBT eruption. According to this hypothesis, the
902 E-10 (Tyrrhenian Sea) marine tephra, which is chemically compatible with the IBT emplaced
903 from PDCs across Lipari at this time, may relate to ash fall from a co-PDC plume. While in
904 contrast T1567 (Adriatic Sea), is compositionally consistent with a phase of scoria fall
905 embedded within these PDC deposits on Lipari and perhaps reflects ash dispersed from a

906 quasi-sustained eruptive column. This would be consistent with the observed lithological
907 features of the IBT and their likely proximal counterpart in Vulcano, the MM3, which are
908 characterized by ash layers from PDCs, alternated with scoria lapilli fall.

909 6. CONCLUSIONS

910 Revised stratigraphic investigations combined with new radiocarbon ages and a large
911 dataset of grain-specific volcanic glass compositional data for the different depositional units
912 of the ash-rich Brown Tuffs (BT) on Lipari and Vulcano provide constraints on their large-
913 scale correlations across the Aeolian archipelago and the southern Tyrrhenian Sea, along
914 with insights for hazard assessments. The main outcomes of this work are the following:

- 915 (1) Juvenile BT eruptive material displays relatively homogeneous glass compositions,
916 particularly in the case of individual depositional units. Overall these units range from
917 basaltic trachy-andesites and trachy-andesites to trachytes, broadly evolving
918 through the succession, with the most evolved glass compositions observed in the
919 UBT macro unit. The LBT (80-56 ky) and IBT (56-24 ky) macro units are most
920 challenging to chemically distinguish, with alkali variability most diagnostic. While the
921 UBT macro unit can be distinguished on the basis that their glasses display higher
922 SiO₂ and extend to lower TiO₂, CaO, MgO and FeO_t contents.
- 923 (2) Secondary glass compositions within some of the BT depositional units are related
924 to a minor component of embedded pumice and/or scoriae from the underlying
925 incoherent pyroclastic units during the emplacement of the PDCs that deposited the
926 BT in proximal-medial areas.
- 927 (3) The time interval of the eruptions that deposited the UBT has been re-defined to
928 between 24 and 6 ky based on the observed chemo-stratigraphic transitions which
929 coincides with the age of the Spiaggia Lunga marker bed on Vulcano, and thus
930 replaces the older previously adopted Monte Guardia stratigraphic marker.
- 931 (4) Correlations between the LBT, IBT and UBT macro-units and proximal units on
932 Vulcano are proposed, providing a more robust framework for the long-term hazard
933 assessment related to explosive activity within the La Fossa Caldera. A clear
934 geochemical link is suggested between the UBT and the early products of the La
935 Fossa cone, suggesting a shared magmatic system during the last 24 ky, and thus
936 extending the life cycle of this currently active eruptive source area.

(5) Unequivocal evidence that ash deposits preserved across the Aeolian archipelago and in Tyrrhenian and Adriatic Sea marine cores are chemically consistent with the IBT and UBT erupted on Vulcano offers important insights into the scale of these eruptions and the associated hazards.

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1191 CAPTIONS

1192 **Fig. 1.** Sketch maps of the islands of Vulcano, Lipari, Salina, Filicudi and Panarea (Aeolian
1193 archipelago) and the Capo Milazzo in northern Sicily showing the outcrop areas of the BT.
1194 The inset (a) shows the location of the Aeolian Islands and seamounts in the southern
1195 Tyrrhenian sea (depth contour lines in metres below sea level). Coordinates conform to the
1196 Gauss-Boaga System (IGM). The sites of marine cores TIR200-C01 (Albert et al., 2012),
1197 KET8003 (Paterne et al., 1988), MD01-2474G (Tamburrino et al., 2016) and SA03-11
1198 (Matthews et al., 2015), that have BT units, are also outlined.

1199 **Fig. 2.** Generalized stratigraphic correlations of the BT successions and age constraints in
1200 the study area. The most complete BT succession is recognized on the island of Lipari,
1201 subdivided into several depositional units (Bt1-16) superposed to the LBT, IBT and UBT
1202 macro-units by means of interlayered volcanic units and tephra layers, erosive surfaces and
1203 reworked horizons. The Bt12 depositional unit immediately overlying the Monte Guardia
1204 tephra is considered as part of the IBT (namely IBT 'Upper') following the chemical evidence
1205 presented here (whilst it was part of the UBT macro unit as defined by Lucchi et al., 2008).
1206 The LBT, IBT and UBT are then correlated with distinct sectors of the island of Vulcano, the
1207 islands of Salina, Filicudi, Panarea and the Capo Milazzo peninsula. Please note that the
1208 recognized depositional units are a minimum number as some lithologically-homogeneous
1209 units could have be amalgamated. References for the stratigraphic units in the different sites
1210 are: Forni et al., 2013 (Lipari); De Astis et al., 2013 (Vulcano); Lucchi et al., 2013a (Salina);
1211 Lucchi et al., 2013e (Filicudi); Lucchi et al., 2013c (Panarea); Morche, 1988 (Capo Milazzo).
1212 The Lip1 and Lip2 tephras are described in Table 1, whilst 'ext' is an external tephra not
1213 discussed here. On Salina, the Sal III and Sal IV tephra layers (Lucchi et al., 2008 and
1214 references therein) are correlated with tephra layers C(i)-8 and C(i)-7 in the Tyrrhenian sea
1215 core KET 8011 (Paterne, 1985; Paterne et al., 1988). Some additional tephra layers
1216 interlayered within the BT succession (not displayed here) provide stratigraphic boundaries
1217 between distinct depositional units of BT (not correlated between the islands), and based on
1218 their glass geochemistry they are likely to correlate with widespread central Mediterranean
1219 isochronous markers derived from the Campanian volcanic zone and recorded in marine
1220 and lacustrine successions.

1221 **Fig. 3.** Field evidence and main sampling outcrops of the BT on Lipari and Vulcano. A)
1222 Vallone Canneto Dentro, central-eastern Lipari: LBT and IBT macro-units with interlayered

1223 Grey Porri Tuffs (gpt), Ischia Tephra (it) and the local Punta di Perciato (pe), Falcone (fa)
1224 and Monte Guardia pumice pyroclastics (gu). B) Valle Muria, south-western Lipari: IBT
1225 interlayered with the local Punta di Perciato (pe), Falcone (fa) and Monte Guardia pumice
1226 pyroclastics (gu). C) Canneto, eastern Lipari: IBT 'upper' (see the text for explanation) and
1227 UBT above the Monte Guardia marker bed (gu). D) Vallone Canneto Dentro, central-eastern
1228 Lipari: IBT 'upper' and UBT above the Monte Guardia marker bed (gu), bounded at the top
1229 by the local Vallone Canneto Dentro (cd) pumice succession. E) Vallone Fiume Bianco,
1230 central-northern Lipari: top portion of the UBT interlayered between the local Vallone del
1231 Gabellotto (vg) and Monte Pilato (mp) pumice successions. F) Grotta dei Pisani, western
1232 Vulcano: UBT located above the Spiaggia Lunga scoria marker bed. G) Grotta dei Pisani,
1233 western Vulcano: IBT and LBT below the Spiaggia Lunga scoria marker bed (sl),
1234 characterized by massive ash deposits alternated with scoria lapilli layers (*). H) Il Piano,
1235 central Vulcano: Monte Molineddo 1, 2, 3 (mm3) pyroclastic successions outcropping in the
1236 stratigraphic window of the LBT and IBT.

1237 **Fig. 4.** Correlation of selected stratigraphic sections showing the main sampled outcrops of
1238 the BT on Lipari and Vulcano (the scale is only approximate). Labels for the shown
1239 stratigraphic units: pv=Paleo-Vulcano, sl=Spiaggia Lunga, ma=Monte Aria; mm1=Monte
1240 Molineddo 1, mm2=Monte Molineddo 2, mm3=Monte Molineddo 3, mr=Monte Rosso,
1241 pp=Passo del Piano, qd=Quadrara, cm=Cugni di Molinello, sa=Monte Saraceno, pn=Punte
1242 Nere, gp=Grotta dei Palizzi, co=marine deposits, lf='leaf-bearing pyroclastics', gpt=Grey
1243 Porri Tuffs, it=Ischia-Tephra, pe=Punta di Perciato, fa1=Falcone pumice, fa2=Falcone
1244 domes, lip1=lip1 tephra, exl=external tephra (not discussed here), lpt=Lower Pollara Tuffs,
1245 gu=Monte Guardia, lip2=lip2 tephra, cd=Vallone Canneto dentro, vg=Vallone del Gabellotto,
1246 rw=reworked horizon. References for the stratigraphic units herein are Forni et al., 2013
1247 (Lipari) and De Astis et al., 2013 (Vulcano).

1248 **Fig. 5.** Major element (wt.%) glass geochemical variations of the BT glasses analysed in
1249 this study compared to the volcanic glasses of explosive eruption deposits produced on
1250 Vulcano, Lipari, Salina and Stromboli during the last 50 ky. (A) TAS classification diagram
1251 of BT glasses, also shown are the compositional ranges of the whole rock (WR) data for
1252 Vulcano, Lipari, Salina and Stromboli; (B) SiO₂ vs K₂O classification diagram; (C) SiO₂ vs.
1253 TiO₂ diagnostic plot used for distinguishing the potassic eruptive products of Vulcano and
1254 Stromboli, and illustrating the BT clear link to volcanism on Vulcano and useful when

1255 considering the provenance of distal marine tephra layers; (D) MgO vs. CaO plot further
1256 illustrating that the BT juvenile glasses conform to the compositions of eruptive products
1257 known to have been produced on Vulcano (including the Quadrara Formation, Casa Lentia,
1258 Grotta dei Palizzi 1 and 2, Caruggi formation/Breccia di Commenda, Lower and Upper Pietre
1259 Cotte). Error bars represented 2*standard deviations of replicated analyses of the StHs6/80-
1260 G secondary standard glass run alongside the BT samples. References: (1) Albert et al.,
1261 2017; (2) De Astis et al., 2013; (3) Forni et al., 2013; (4) Francalanci et al., 2013; and (5)
1262 Lucchi et al., 2013a.

1263 **Fig. 6.** Major element (wt.%) glass geochemical variation diagrams (A-C) showing the
1264 different UBT depositional units sampled on Vulcano and Lipari (D). Shown are the
1265 compositions of the newly defined IBT 'upper' which immediately overlie the Monte Guardia
1266 tephra at various outcrops on Lipari and Vulcano (Gelso). These deposits are re-classified
1267 as the IBT 'upper' owing to their chemical similarity to the IBT found below the Monte
1268 Guardia marker bed. A minor secondary component of more evolved trachyte is shown
1269 within the Bt13 (LIP03/19) deposits at Chiesa Vecchia, Lipari and these share a similar
1270 chemical affinity to the explosive products of the Casa Lentia eruptive succession on
1271 Vulcano. HKCA rhyolitic secondary glass component are also observed in Bt16 on Vulcano,
1272 these are not shown here, instead refer to Figure 9. New glass data is presented for the
1273 Cugni di Molinello scoria bed which is interbedded between the Bt12 and Bt13 depositional
1274 units on Vulcano, these more primitive fall out scoria deposit are also believed to derive from
1275 activity within the La Fossa caldera, albeit erupted from a separate vent area to the UBT
1276 (Dellino et al., 2011). Glass data collected from a marine ash sample TIR2000-160cm taken
1277 from the Marsili Basin marine core is also shown to have a clear UBT affinity. Error bars
1278 represented 2*standard deviations of replicated analyses of the StHs6/80-G secondary
1279 standard glass run alongside the BT samples. References: (1) Lucchi et al., 2008 and (2)
1280 Albert et al., 2017.

1281 **Fig. 7.** Major element glass geochemical variation diagrams for the juvenile component of
1282 the LBT, IBT and IBT 'upper' outcropping on Lipari and Vulcano compared to near-vent
1283 deposits on Vulcano and distal tephra layers. The near-vent eruption deposits on Vulcano
1284 considered responsible for the LBT and IBT are Monte Molineddo 1-3. Also shown are the
1285 proximal deposit of the younger Punte Nere succession and the Cugni di Molinello (CM).
1286 Here more distal occurrences of the LBT and IBT units focus on deposits found outcropping

1287 across the archipelago on Salina, Panarea, Filicudi and Capo Milazzo (Sicily). The similarity
1288 between fallout components of the IBT deposits and a distal marine tephra layers in the
1289 Tyrrhenian (Paterne et al., 1988) and Adriatic Seas (Matthews et al., 2015) is explored. (A)
1290 TAS classification diagram of LBT and IBT glasses, (B, C) SiO_2 vs K_2O classification
1291 diagrams of the LBT and IBT deposits and distal equivalents. Error bars represented
1292 2*standard deviations of replicated analyses of the StHs6/80-G secondary standard glass
1293 run alongside the BT samples.

1294 **Fig.8.** Major element glass geochemical variation diagrams for the juvenile component of
1295 the LBT, IBT and IBT ‘upper’ outcropping on Lipari and Vulcano compared to near-vent
1296 deposits on Vulcano and distal tephra layers found on the neighboring islands and in the
1297 marine setting. LBT are considered in the context of Monte Monlineddo 1 and 2 units on
1298 Vulcano, whilst the IBT are compared to the limited glass data available for the Monlineddo
1299 3 unit. Error bars represented 2*standard deviations of replicated analyses of the StHs6/80-
1300 G secondary standard glass run alongside the BT samples.

1301 **Fig. 9.** Major element geochemical variability diagram of the secondary glass components
1302 found within a selection of BT depositional units outcropping primarily on Lipari, but also
1303 Vulcano. These minor populations are chemically related to the underlying stratigraphic units
1304 which were subject to clast embedding and erosion processes. Error bars represented
1305 2*standard deviations of replicated analyses of the StHs6/80-G secondary standard glass
1306 run alongside the BT samples.

1307 **Fig. 10.** Major element geochemical variability of the BT deposits compared to marine tephra
1308 deposits considered here to be related to the BT eruption units, or have been previously
1309 ascribed as distal BT deposits in the literature. (A) SiO_2 vs K_2O classification diagram; (B)
1310 SiO_2 vs. TiO_2 diagnostic plot used for distinguishing the potassic eruptive products of
1311 Vulcano and Stromboli, and very useful when considering the provenance of distal marine
1312 tephra layers associated with the two islands. Error bars represented 2*standard deviations
1313 of replicated analyses of the StHs6/80-G secondary standard glass run alongside the BT
1314 samples. TIR2000 Marsili Basin cores samples are from Albert et al. (2012) and Albert
1315 (2012); the MD Marsili Basin marine tephra layers are from Tamburrino et al. (2016), the
1316 marine layers E-11 (Tyrrhenian Sea) and T1567 (Adriatic) are reported in Paterne et al.
1317 (1988) and Matthews et al. (2015) respectively.

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Table 1
Main characteristics of tephra layers and marker beds used for the subdivisions of BT depositional units and correlations (listed in stratigraphic order starting from the older one). Recognition area: Str=Stromboli, Pan=Panarea, Sal=Salina, Lip=Lipari, Vul=Vulcano, Fil=Filicudi, Ali=Alicudi, Mil=Capo Milazzo. Chemical composition of juvenile glass fragments (w.r.=whole rock) is reported by referring to: (1) present work; (2) Albert et al (2017); (3) De Astis et al 2013: CA=calcalkaline, HKCA=high-k calcalkaline, SHO=shoshonite series; Bas=basalt, Bas-And=basaltic andesite, And=andesite, Dac=dacite, Rhy=rhyolite, Lat=latite, Sho=shoshonite, Tra=trachyte). Correlations with proximal stratigraphic units refer to: (1) Lucchi et al. (2008); (2) Forni et al. (2013); (3) Lucchi et al., 2013a; (4) De Astis et al. 2013. Age references: (1) Morche, 1988; (2) De Astis et al 1989; (3) Soligo et al 2000; (4) Siani et al., 2004; (5) Leocat, 2011; (6) Lucchi et al., 2013a, b; (7) Sulpizio et al. 2016; (8) Giaccio et al. 2017; (9) present work.

Tephra	Marine tephra	Lithology	Dispersal area	Chemistry (glass)	Source area	Proximal stratigraphic unit	Age (ky)
Grey Porri Tuff		Grey (to whitish) scoria and pumice lapilli and ash	Sal, Lip, Pan, Mil	CA Bas-And to Dac	Sal	Rocce di Barcone Fm. (3)	70–67 (1,6,7)
		Grey fine to coarse ashes, with abundant mm-sized cpx crystals and interlayered yellowish scoriaceous lapilli	Vul		Vul	M. Molineddo 1 (4)	
		Varicoloured ash, locally with beds of scoriaceous lapilli and isolated bombs	Vul		Vul	M. Molineddo 2 (4)	
Ischia Tephra	Y-7	White-yellowish ash	Str, Pan, Sal, Lip, Fil	Tra-Pho (1)	Ischia	Epomeo Green Tuff –Monte Sant’Angelo (1)	56.1±1.0 (8)
		Black to yellowish scoriaceous lapilli and bombs and grey coarse to fine ashes with abundant mm-sized euhedral cpx crystals	Vul		Vul	M. Molineddo 3 (4)	
Punta di Perciato		Whitish pumice lapilli and ash	Lip	Rhy (1)	Lip	Punta di Perciato Fm., member pe ₂ (2)	
Falcone		Whitish pumice lapilli and ash	Lip	Rhy (1)	Lip	Falcone Fm., member fa ₁ (2)	43-40 (5)
lip1		Whitish ash	Lip	Rhy (1)	Lip		
Lower Pollara Tuff		Lapilli and ash of yellow pumice and black scoria	Sal, Lip	CA- to HKCA Bas-And to And	Sal	Punta Fontanelle Form. (3)	27.6-26.4 (9)
Monte Guardia		White and grey pumice (and obsidian) lapilli and ash	Lip, Vul, Sal, Pan	Rhy (1,2)	Lip	Monte Guardia Fm. (2)	27-26 (9)
Spiaggia Lunga		Red to black scoria lapilli and bombs	Vul	SHO Bas to Sho (w.r.) (3)	Vul	Spiaggia Lunga Fm. (4)	24±5 (3)
Cugni di Molinello		Black scoria lapilli	Vul	Sho	Vul	Cugni di Molinello Fm. (4)	
lip2		Pumice and obsidian lapilli and ash	Lip	Rhy (1)	Lip		
Monte Saraceno		Red to black scoria lapilli	Vul	Sho (w.r.) (3)	Vulc	Monte Saraceno Fm., member sa ₁ (4)	8.3±1.6 (2)
Vallone Canneto dentro		Pumice and obsidian lapilli and ash	Lip	Rhy (1)	Lip	Vallone Canneto dentro Fm., member cd ₁ (2)	
Vallone del Gabelotto	E-1	White pumice ash and lapilli	Lip, Pan, Vul, Str	Rhy (1,2)	Lip	Vallone del Gabelotto Fm. (2)	8.7 – 8.4 (4)
Punte Nere		Dark grey lapilli and ash	Lip	Tra-Pho (1)	Vul	Punte Nere Fm., member pn ₁ (4)	5.3 +2.2/-1.1 (3)

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Table 2

Radiocarbon age determinations of charcoals sampled from within the BT succession and the palaeosol overlying the UBT. (A) Radiocarbon age determinations presented here from between the Monte Guardia Tephra and the Vallone Cannetto Dentro on Lipari Island. Charcoal LIP14/17 was collected at Location 9 (Fig. 3) and LIP07/17 was collected at Location 8 (Fig. 3). Ages are calibrated using IntCal20 (Reimer et al., 2020) and OxCal v4.4. Calibrated age-distribution plots are provided in supplementary information A. (B) Radiocarbon ages from the literature recalibrated using IntCal20 (Un-modelled), while some of the age determinations have been incorporated into an Bayesian age-depth model which is used to provide new age constraints on the Monte Guardia and Lower Pollara eruption deposits used as chrono-stratigraphic markers in the Aeolian Islands. Details of the Bayesian age model are reported in Supplementary Material A. * Age range represents 82.2% probability, with 8.7% probability range of 5325-5390 cal y BP.

Eruption Unit	Location	Sample ID	Material	Oxford Lab Code	¹⁴ C age	Error (68.2%)	δ ¹³ C	cal y BP (95.4%; IntCal20)				cal y BP (95.4%; IntCal20)				Reference
								(Un-modelled)				Modelled Age				
(A) This study																
IBT Upper	Lipari	LIP014/17	Charcoal	OxA-36000	20020	90	-24.83	23830	-	24240		23830	-	24260	This Study	
IBT Upper	Lipari	LIP07/17	Charcoal	OxA-35999	21760	100	-24.73	25845	-	26310		25830	-	26295	This Study	
(B) Re-calibrated published data + Bayesian Modelling																
-	Lipari		palaeosol (bulk Sed)	-	4810	60	-	5445*	-	5610*		-	-	-	Pichler, 1980	
UBT	Vulcano		Charcoal	-	7680	100	-	8305	-	8655		-	-	-	De Asilis et al., 1997	
UBT	Lipari	-	Charcoal	-	16800	200	-	19825	-	20845		-	-	-	Crisci et al., 1983	
IBT Upper	Lipari		Charcoal	-	20500	200	-	24155	-	25200		24240	-	25240	Crisci et al., 1983	
IBT Upper	Lipari		Charcoal	-	20300	700	-	22950	-	26005		24110	-	25980	Crisci et al., 1983	
Monte Guardia (mgl)												25920	-	27025	This Study	
IBT	Lipari		Charcoal	-	22480	1100	-	24570	-	29500		26125	-	27295	Crisci et al., 1983	
IBT	Lipari		Charcoal	-	22600	300	-	26100	-	27460		26300	-	27275	Crisci et al., 1981	
Lower Pollara Tuff (lpt)												26425	-	27585	This Study	
IBT	Lipari		Charcoal	-	22940	340	-	26445	-	27770		26575	-	27760	Monche, 1988	
IBT	Lipari		Charcoal	-	23500	900	-	26985	-	29850		26495	-	28100	Crisci et al., 1983	

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Table 3

Average of major and minor element composition of juvenile glass of selected Lower and Intermediate Brown Tuffs units included in the study. Totals are pre-normalised analytical totals. n = number of analyses used to calculate the average. Locality is referred to Fig.4. A complete geochemical dataset is provided in Supplementary material B.

Macro Unit	LOWER BROWN TUFF													
Locality	1 (Lipari)	8 (Lipari)	8 (Lipari)	1 (Lipari)	8 (Lipari)	8 (Lipari)	1 (Vulcano)							
Unit	bt 1	bt 1/2	bt 3	bt 4	bt 4	bt 6	?							
Sample	bt06/16 (L) 2φ	LIP10/18 3φ	LIP05/18 3φ	bt09/16 (L) 3φ	LIP04/18 3φ	LIP02/18 3φ	VUL10/18 3φ							
Material	ash	ash	ash	ash	ash	ash	ash							
n	10	10	11	8	19	11	16							
	mean	1σ	mean	1σ	mean	1σ	mean	1σ	mean	1σ	mean	1σ	mean	1σ
(wt%)														
Total	96.83	1.50	96.70	0.60	97.07	1.80	97.57	1.11	97.66	1.40	98.19	0.78	98.66	1.15
SiO ₂	54.68	0.80	54.01	0.62	56.68	0.33	56.13	0.42	53.76	0.49	53.41	0.93	56.77	1.10
TiO ₂	0.99	0.03	0.84	0.10	0.87	0.07	0.99	0.09	0.79	0.05	0.73	0.11	0.97	0.05
Al ₂ O ₃	16.58	0.13	17.03	0.63	16.44	0.38	16.39	0.20	17.55	0.38	17.78	0.91	16.35	0.37
FeO	9.22	0.61	8.63	0.64	8.18	0.38	8.83	0.35	8.03	0.26	8.02	1.08	8.15	0.56
MnO	0.21	0.05	0.19	0.03	0.20	0.04	0.22	0.04	0.16	0.02	0.17	0.05	0.16	0.03
MgO	2.76	0.37	2.83	0.17	2.13	0.20	2.29	0.26	2.69	0.15	2.78	0.39	2.09	0.38
CaO	6.09	0.64	6.24	0.26	5.38	0.21	5.54	0.40	6.02	0.28	6.23	0.67	5.22	0.68
Na ₂ O	3.61	0.25	4.19	0.32	3.89	0.23	3.57	0.45	4.50	0.25	4.43	0.74	3.97	0.25
K ₂ O	5.10	0.58	5.16	0.37	5.33	0.23	5.16	0.22	5.66	0.25	5.63	0.49	5.47	0.45
P ₂ O ₅	0.61	0.05	0.69	0.04	0.66	0.07	0.68	0.04	0.68	0.03	0.70	0.09	0.67	0.03
Cl	0.15	0.02	0.20	0.04	0.23	0.07	0.19	0.06	0.15	0.03	0.12	0.03	0.18	0.05
Macro Unit	INTERMEDIATE BROWN TUFF													
Locality	2 (Lipari)	4 (Lipari)	10 (Lipari)	6 (Lipari)	6 (Lipari)	2 (Lipari)	1 (Vulcano)							
Unit	bt 7	bt 9	bt 8/9	bt 9	bt 10	bt 11	?							
Sample	bt11/16 (L)	LIP14/18 3φ	LIP45/17	LIP27/17	LIP36/17 -1φ	bt15/16 (L) 2 φ	VUL09/18 2φ							
Material	ash	ash	scoria	scoria	ash	ash	ash							
n	10	27	10	18	20	10	10							
	mean	1σ	mean	1σ	mean	1σ	mean	1σ	mean	1σ	mean	1σ	mean	1σ
(wt%)														
Total	97.46	1.27	96.19	0.91	98.59	0.74	97.01	1.18	98.16	0.62	97.83	1.28	99.07	0.83
SiO ₂	54.77	0.45	54.17	0.57	51.15	0.69	53.61	0.54	53.85	0.40	54.44	0.41	55.12	0.32
TiO ₂	0.83	0.05	0.77	0.05	0.77	0.07	0.90	0.03	0.82	0.05	0.75	0.05	0.85	0.05
Al ₂ O ₃	17.21	0.40	17.25	0.36	17.22	0.48	17.17	0.17	17.02	0.27	17.35	0.26	16.59	0.31
FeO	8.24	0.29	8.14	0.37	9.34	0.52	8.68	0.29	8.64	0.27	8.21	0.32	8.65	0.20
MnO	0.18	0.05	0.20	0.04	0.19	0.04	0.18	0.06	0.19	0.06	0.21	0.06	0.19	0.04
MgO	2.20	0.29	2.19	0.17	4.21	0.59	3.05	0.24	2.60	0.31	2.09	0.16	2.29	0.05
CaO	5.31	0.56	5.38	0.23	8.86	0.87	6.92	0.43	5.88	0.45	5.25	0.36	5.52	0.14
Na ₂ O	4.00	0.35	4.75	0.17	3.72	0.32	3.95	0.28	4.20	0.18	4.27	0.31	4.17	0.18
K ₂ O	6.26	0.49	6.02	0.16	3.88	0.53	4.65	0.27	5.87	0.34	6.46	0.47	5.61	0.18
P ₂ O ₅	0.75	0.05	0.83	0.06	0.49	0.08	0.60	0.04	0.73	0.05	0.71	0.03	0.73	0.02
Cl	0.25	0.04	0.31	0.03	0.17	0.02	0.29	0.02	0.20	0.04	0.25	0.04	0.28	0.02

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Table 4

Average of major and minor element composition of juvenile glass of selected Upper-Intermediate and Upper Brown Tuffs units included in the study. Totals are pre-normalised analytical totals. n = number of analyses used to calculate the average. Locality is referred to Fig.4. A complete geochemical dataset is provided in Supplementary material B.

Macro Unit	INTERMEDIATE BROWN TUFF 'UPPER'									
Locality	7 (Lipari)		12 (Lipari)		9 (Lipari)		13 (Lipari)		3 (Vulcano)	
Unit	bt 12		bt 12		bt 12		bt 12		bt 12	
Sample	bt01/16 (L) 3 φ		LIP18/17 1φ		LIP06/17 -1φ		LIP21/17 -1φ		VUL09/17 1φ	
n	11		17		26		24		10	
	mean	1σ	mean	1σ	mean	1σ	mean	1σ	mean	1σ
(wt%)										
Total	97.10	1.26	97.73	0.64	97.18	0.96	97.88	0.61	97.83	0.97
SiO ₂	54.55	0.68	54.26	0.62	54.89	0.38	54.73	0.42	54.09	0.49
TiO ₂	0.78	0.05	0.71	0.03	0.71	0.03	0.73	0.05	0.72	0.05
Al ₂ O ₃	17.48	0.14	17.77	0.21	17.64	0.18	17.67	0.23	17.86	0.34
FeO	8.19	0.32	7.65	0.24	7.70	0.21	7.62	0.19	7.73	0.34
MnO	0.21	0.06	0.19	0.04	0.19	0.03	0.18	0.04	0.16	0.07
MgO	2.10	0.22	2.13	0.22	1.95	0.15	2.00	0.10	2.18	0.17
CaO	5.15	0.42	5.03	0.40	4.74	0.32	4.80	0.19	5.15	0.22
Na ₂ O	4.45	0.39	4.72	0.24	4.56	0.29	4.58	0.59	4.71	0.23
K ₂ O	6.08	0.50	6.51	0.24	6.57	0.30	6.66	0.25	6.42	0.30
P ₂ O ₅	0.73	0.06	0.80	0.05	0.79	0.04	0.79	0.05	0.76	0.07
Cl	0.29	0.04	0.24	0.03	0.25	0.02	0.23	0.04	0.21	0.02

Macro Unit	UPPER BROWN TUFF									
Locality	9 (Lipari)		5 (Vulcano)		4 (Vulcano)		5 (Vulcano)		5 (Vulcano)	
Unit	bt 13		bt 13		bt 14		bt 15		bt 16	
Sample	LIP07/19		VUL17/19		bt03/16 (V) 2 φ		bt04/16 (V) 2 φ		bt05/16 (V) 3 φ	
n	17		17		17		19		17	
	mean	1σ	mean	1σ	mean	1σ	mean	1σ	mean	1σ
(wt%)										
Total	97.90	1.00	99.17	1.03	97.82	0.79	98.31	0.61	98.00	1.06
SiO ₂	60.80	1.95	59.12	0.65	56.96	1.03	58.16	0.87	58.06	1.38
TiO ₂	0.64	0.04	0.65	0.05	0.68	0.05	0.68	0.03	0.68	0.04
Al ₂ O ₃	16.37	0.41	17.30	0.36	17.12	0.26	17.14	0.17	17.47	0.41
FeO	5.72	0.61	5.94	0.56	6.88	0.53	6.32	0.38	6.28	0.28
MnO	0.11	0.02	0.12	0.04	0.16	0.05	0.15	0.05	0.15	0.04
MgO	1.85	0.52	1.78	0.11	2.20	0.29	1.86	0.29	1.94	0.27
CaO	3.89	0.97	3.87	0.19	4.73	0.53	3.99	0.59	4.25	0.58
Na ₂ O	4.09	0.43	4.38	0.14	4.24	0.19	4.39	0.25	4.27	0.45
K ₂ O	5.85	0.48	6.19	0.21	6.18	0.24	6.53	0.38	6.12	0.34
P ₂ O ₅	0.43	0.06	0.47	0.07	0.61	0.04	0.57	0.04	0.54	0.05
Cl	0.23	0.02	0.18	0.05	0.24	0.04	0.21	0.02	0.25	0.01

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Table 5

Average of major and minor element composition of secondary glass components inside Brown Tuffs units across the macro units included in the study. Totals are pre-normalised analytical totals. n = number of analyses used to calculate the average. Locality is referred to Fig.4. A complete geochemical dataset is provided in Supplementary material B.

Corresponding Pyroclastic Unit	Grey Porri Tuff		Grey Porri Tuff		Grey Porri Tuff		Perciato		Falcone	
Locality	8 (Lipari)		8 (Lipari)		1 (Lipari)		2 (Lipari)		4 (Lipari)	
Unit	bt 1/2		bt 3		bt 4		bt 8		bt 9	
Sample	LIP10/18 3φ		LIP07/18 3φ		bt09/16 (L) 3φ		bt12/16 (L)		LIP16/18 3φ	
n	3		2		3		15		4	
	mean	1σ	mean	1σ	mean	1σ	mean	1σ	mean	1σ
(wt%)										
Total	97.18	0.40	98.68	0.17	97.76	0.17	96.08	0.97	93.94	0.65
SiO ₂	58.19	1.48	57.08	0.43	59.07	0.43	75.92	0.37	76.05	0.30
TiO ₂	1.17	0.13	1.14	0.34	0.91	0.34	0.07	0.02	0.05	0.02
Al ₂ O ₃	16.53	1.80	17.18	2.16	16.11	2.16	12.65	0.15	12.49	0.21
FeO	7.44	1.26	7.72	1.52	8.49	1.52	1.36	0.10	1.48	0.08
MnO	0.13	0.04	0.14	0.04	0.22	0.04	0.04	0.03	0.04	0.05
MgO	2.70	0.64	3.25	0.44	2.59	0.44	0.02	0.02	0.02	0.02
CaO	7.27	1.69	7.38	0.46	6.71	0.46	0.70	0.06	0.69	0.02
Na ₂ O	3.47	0.27	3.44	0.50	3.01	0.50	2.94	0.31	3.75	0.11
K ₂ O	2.47	0.85	2.02	0.35	2.30	0.35	5.99	0.27	5.10	0.14
P ₂ O ₅	0.50	0.07	0.48	0.08	0.35	0.08	0.01	0.02	0.02	0.01
Cl	0.14	0.06	0.16	0.01	0.24	0.01	0.30	0.03	0.31	0.03

Corresponding Pyroclastic Unit	Monte Guardia		Monte Guardia		Monte Guardia		Vallone Del Gabellotto	
Locality	7 (Lipari)		12 (Lipari)		3 (Vulcano)		5 (Vulcano)	
Unit	bt 12		bt 12		bt 12		bt 16	
Sample	bt01/16(L)		LIP17/17		VUL09/17 -1φ		bt05/16 (V)	
n	17		8		3		3	
	mean	1σ	mean	1σ	mean	1σ	mean	1σ
(wt%)								
Total	94.44	1.10	96.43	0.61	94.39	0.91	97.53	0.69
SiO ₂	76.10	0.27	76.42	0.42	75.55	0.16	75.37	0.42
TiO ₂	0.07	0.02	0.05	0.02	0.05	0.05	0.05	0.06
Al ₂ O ₃	12.51	0.07	12.28	0.29	12.59	0.08	12.72	0.32
FeO	1.37	0.10	1.49	0.12	1.45	0.08	1.53	0.16
MnO	0.08	0.04	0.05	0.02	0.05	0.04	0.05	0.01
MgO	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01
CaO	0.69	0.04	0.67	0.05	0.72	0.04	0.71	0.04
Na ₂ O	3.77	0.13	3.72	0.18	3.97	0.07	4.07	0.05
K ₂ O	5.03	0.21	4.94	0.15	5.26	0.01	5.10	0.23
P ₂ O ₅	0.01	0.02	0.02	0.02	0.01	0.01	0.00	0.00
Cl	0.35	0.04	0.35	0.03	0.34	0.02	0.38	0.02

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Table 6

Average of major and minor element glass composition of near-source Vulcano pyroclastic units included in the study. Totals are pre-normalised analytical totals. n = number of analyses used to calculate the average. Locality is referred to Fig.4. A complete geochemical dataset is provided in Supplementary material B.

Pyroclastic unit	Monte Molineddo 1		Monte Molineddo 1		Monte Molineddo 2		Monte Molineddo 3	
Locality	2 (Vulcano)		2 (Vulcano)		2 (Vulcano)		3 (Vulcano)	
Sample	VUL03/18 3φ		VUL04/18 2φ		VUL06/18 2φ		VUL04/17 1φ (component 1)	
n	23		6		10		10	
	mean	1σ	mean	1σ	mean	1σ	mean	1σ
(wt%)								
Total	96.29	0.81	98.54	1.05	98.58	1.23	97.96	1.60
SiO ₂	57.43	0.33	56.73	1.16	53.08	1.35	53.33	0.31
TiO ₂	0.98	0.05	0.99	0.08	0.86	0.07	0.76	0.04
Al ₂ O ₃	16.09	0.33	16.28	0.69	17.06	0.56	17.56	0.24
FeO	7.96	0.19	8.15	0.82	9.09	0.70	8.28	0.33
MnO	0.17	0.03	0.19	0.03	0.17	0.04	0.22	0.04
MgO	1.85	0.14	1.97	0.28	2.66	0.22	2.43	0.11
CaO	4.61	0.14	5.14	0.61	6.39	0.38	5.38	0.80
Na ₂ O	4.12	0.12	4.05	0.18	4.25	0.30	4.56	0.32
K ₂ O	5.85	0.14	5.60	0.29	5.51	0.26	6.39	0.55
P ₂ O ₅	0.76	0.03	0.69	0.05	0.69	0.04	0.73	0.06
Cl	0.19	0.02	0.22	0.08	0.26	0.04	0.36	0.08

Pyroclastic unit	Monte Molineddo 3		Punte Nere		Punte Nere		Punte Nere	
Locality			6 (Vulcano)		6 (Vulcano)		6 (Vulcano)	
Sample	BT03/20		VUL03/17 1φ		VUL02/17 1φ		VUL01/17 1φ	
n	42		13		14		9	
	mean	1σ	mean	1σ	mean	1σ	mean	1σ
(wt%)								
Total	97.79	0.30	97.06	1.17	97.19	1.39	98.54	1.18
SiO ₂	53.51	0.28	56.87	0.55	56.09	0.44	60.32	1.72
TiO ₂	0.73	0.04	0.68	0.04	0.67	0.04	0.60	0.06
Al ₂ O ₃	17.18	0.14	18.18	0.23	18.03	0.17	16.76	0.35
FeO	8.24	0.24	6.14	0.17	6.38	0.50	5.73	0.58
MnO	0.16	0.02	0.16	0.05	0.15	0.04	0.10	0.07
MgO	3.05	0.15	1.66	0.09	1.82	0.18	1.71	0.37
CaO	6.63	0.23	3.74	0.21	4.07	0.32	3.59	0.66
Na ₂ O	3.91	0.13	4.37	0.59	4.46	0.43	4.23	0.20
K ₂ O	5.82	0.15	7.39	0.30	7.50	0.39	6.28	0.51
P ₂ O ₅	0.52	0.05	0.52	0.03	0.54	0.02	0.50	0.11
Cl	0.24	0.02	0.29	0.04	0.28	0.02	0.19	0.06

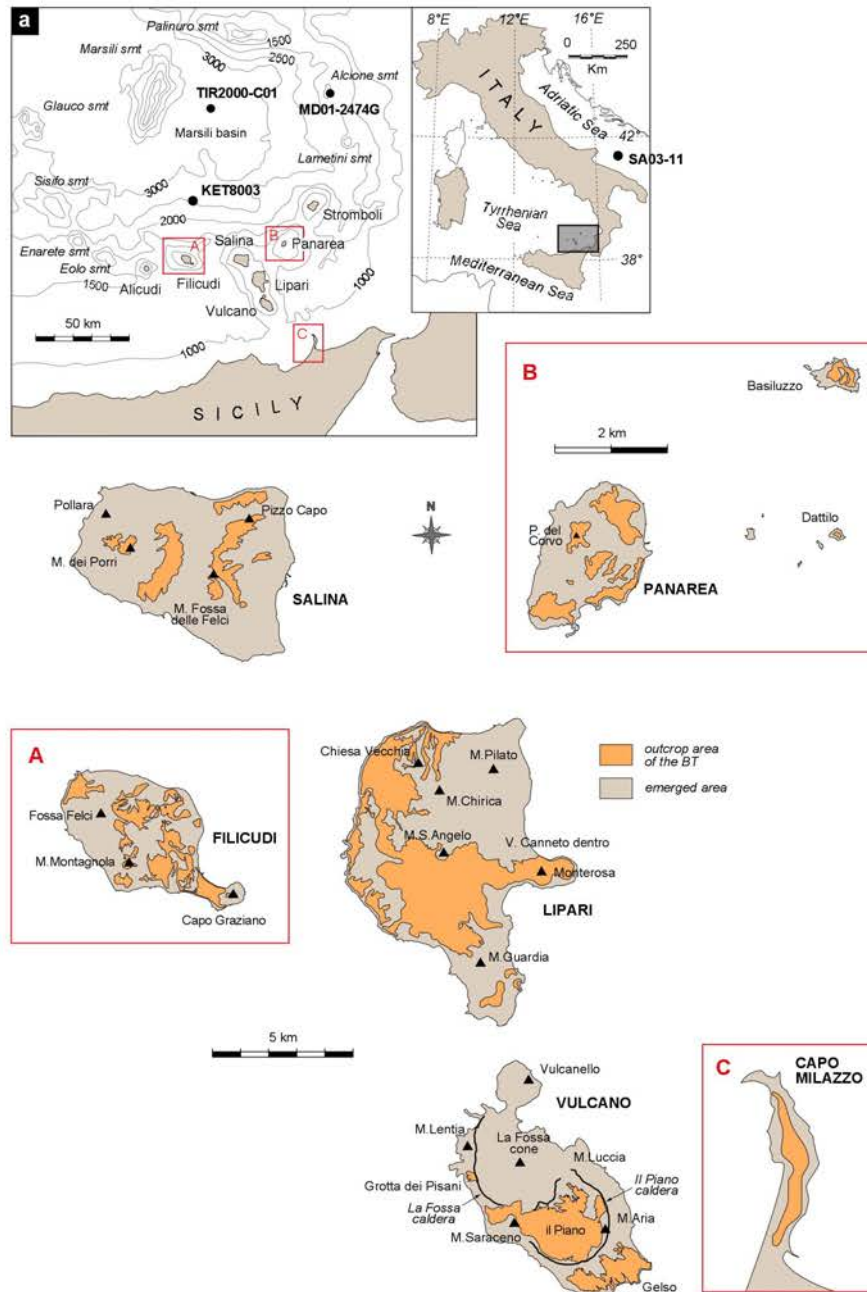
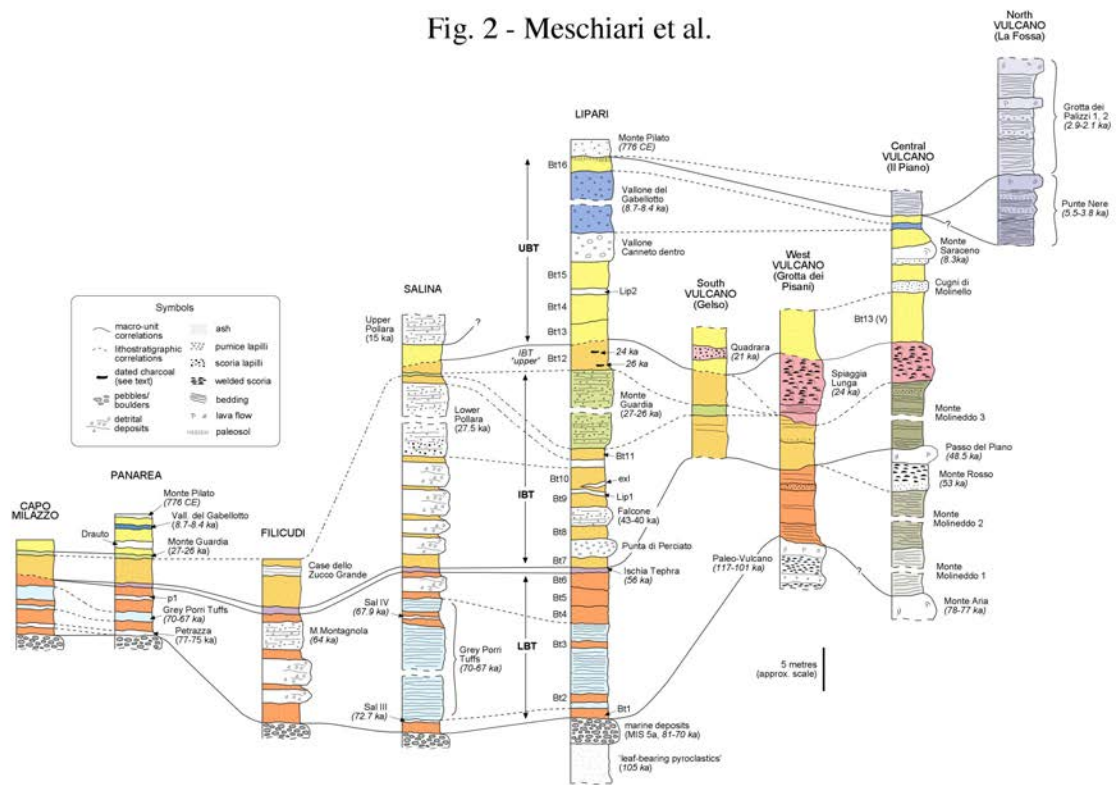


Fig. 1 - Meschiari et al.

Fig. 2 - Meschiari et al.



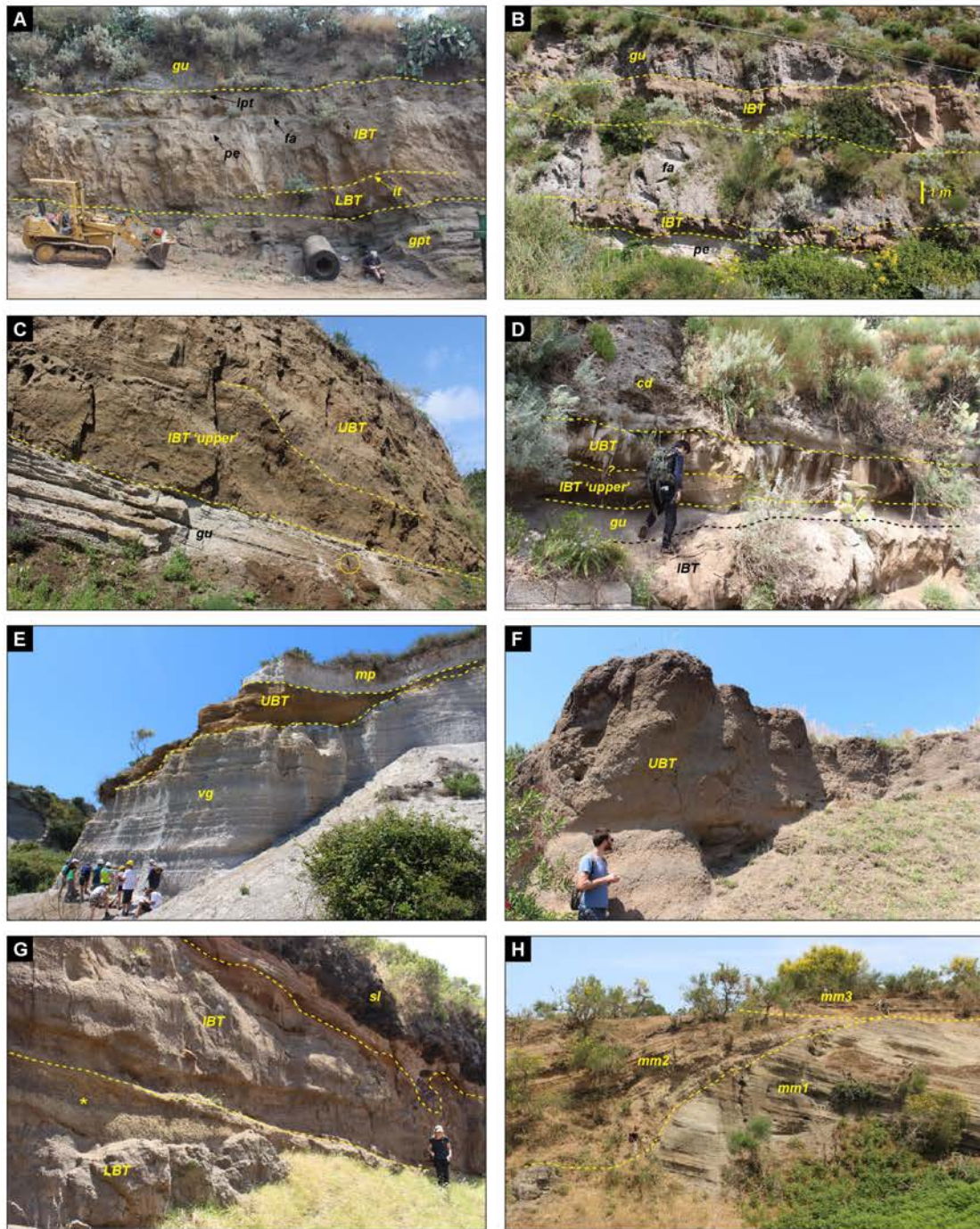


Fig. 3 - Meschiari et al.

Fig. 4 - Meschiari et al.

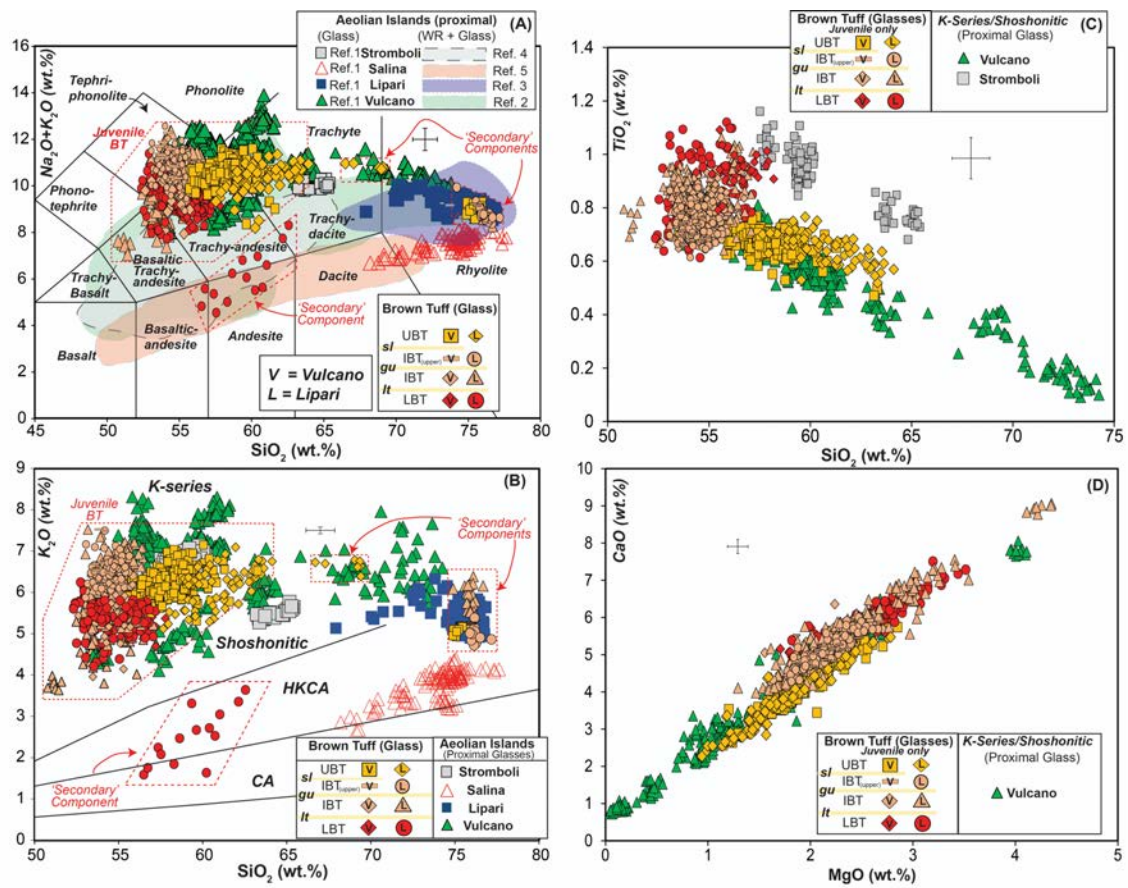


Fig. 5 - Meschiari et al.

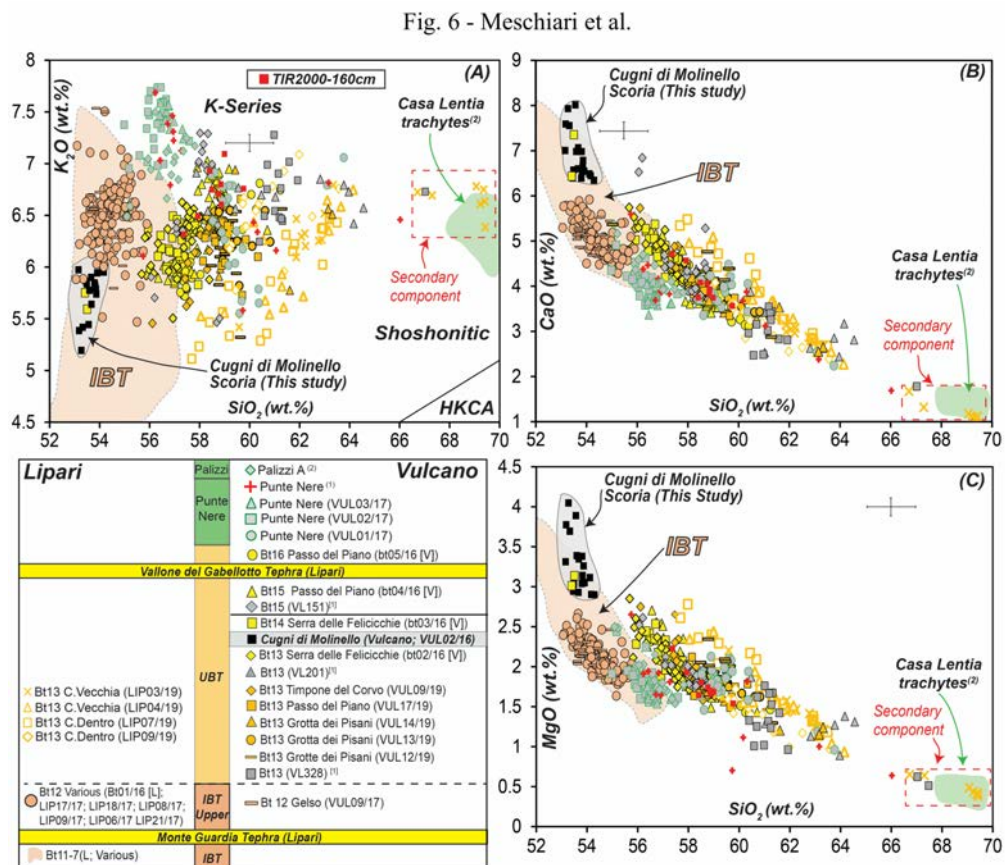


Fig. 6 - Meschiari et al.

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Fig. 7 - Meschiari et al.

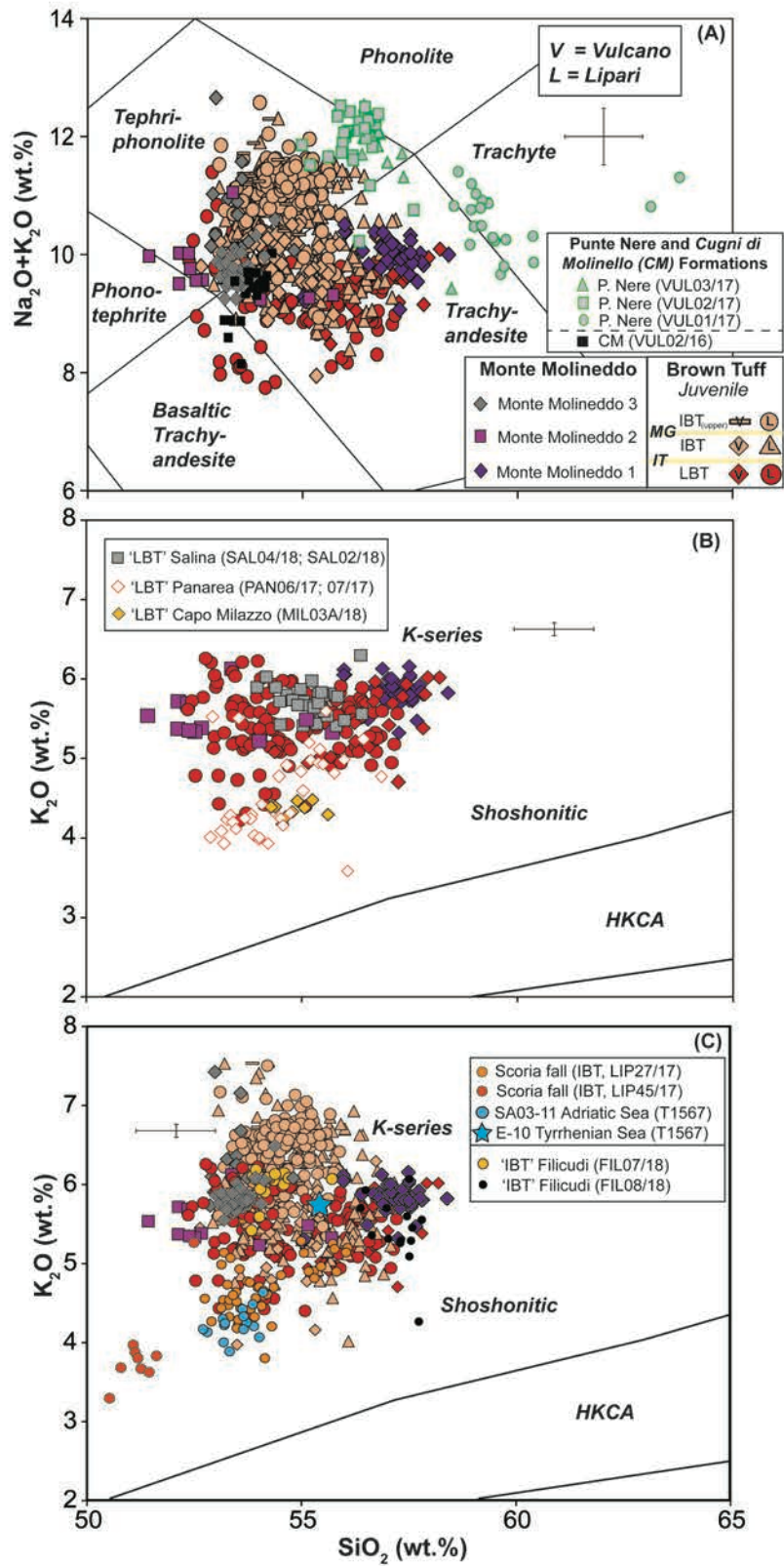


Fig. 8 - Meschiari et al.

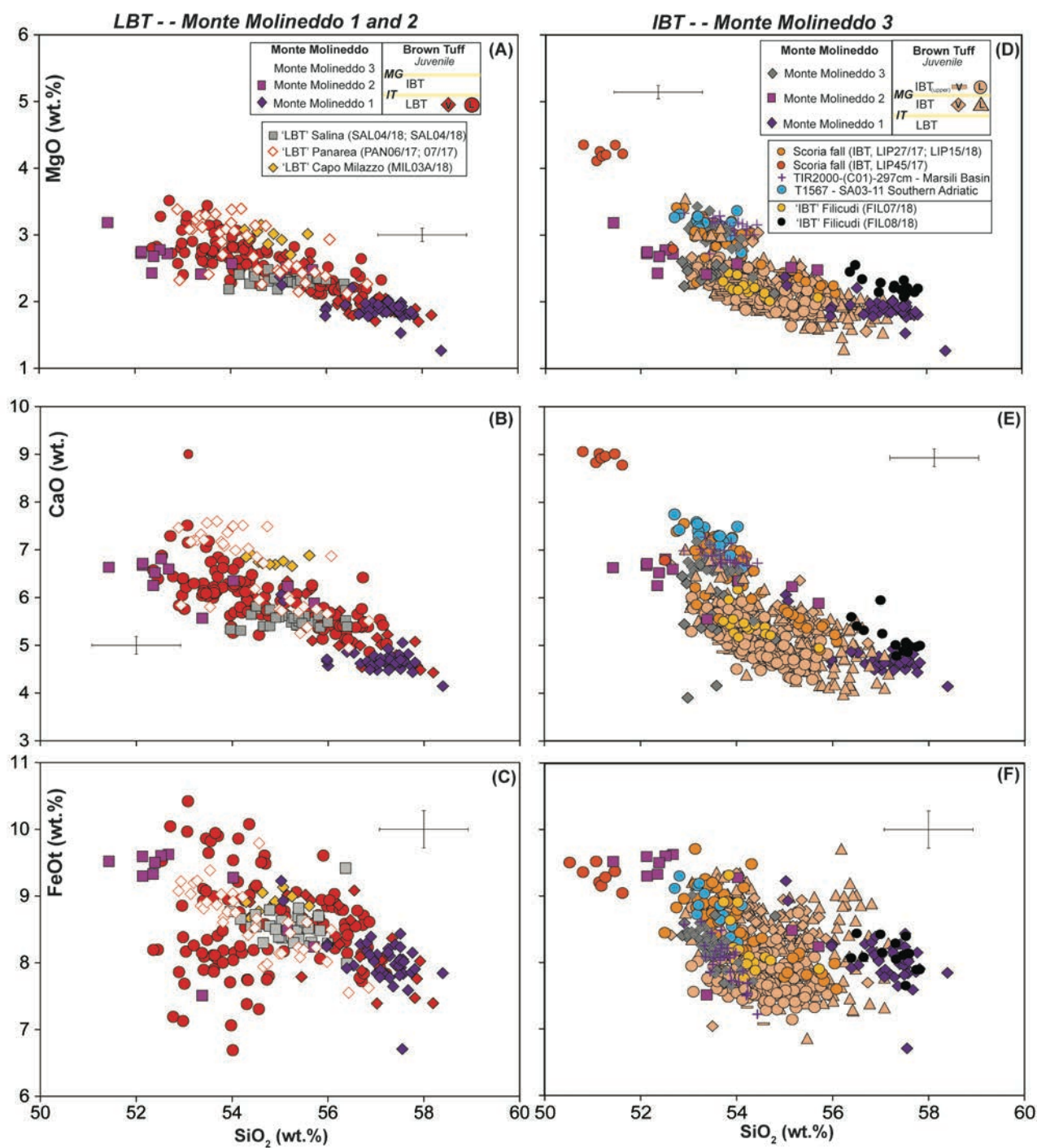


Fig. 9 - Meschiari et al.

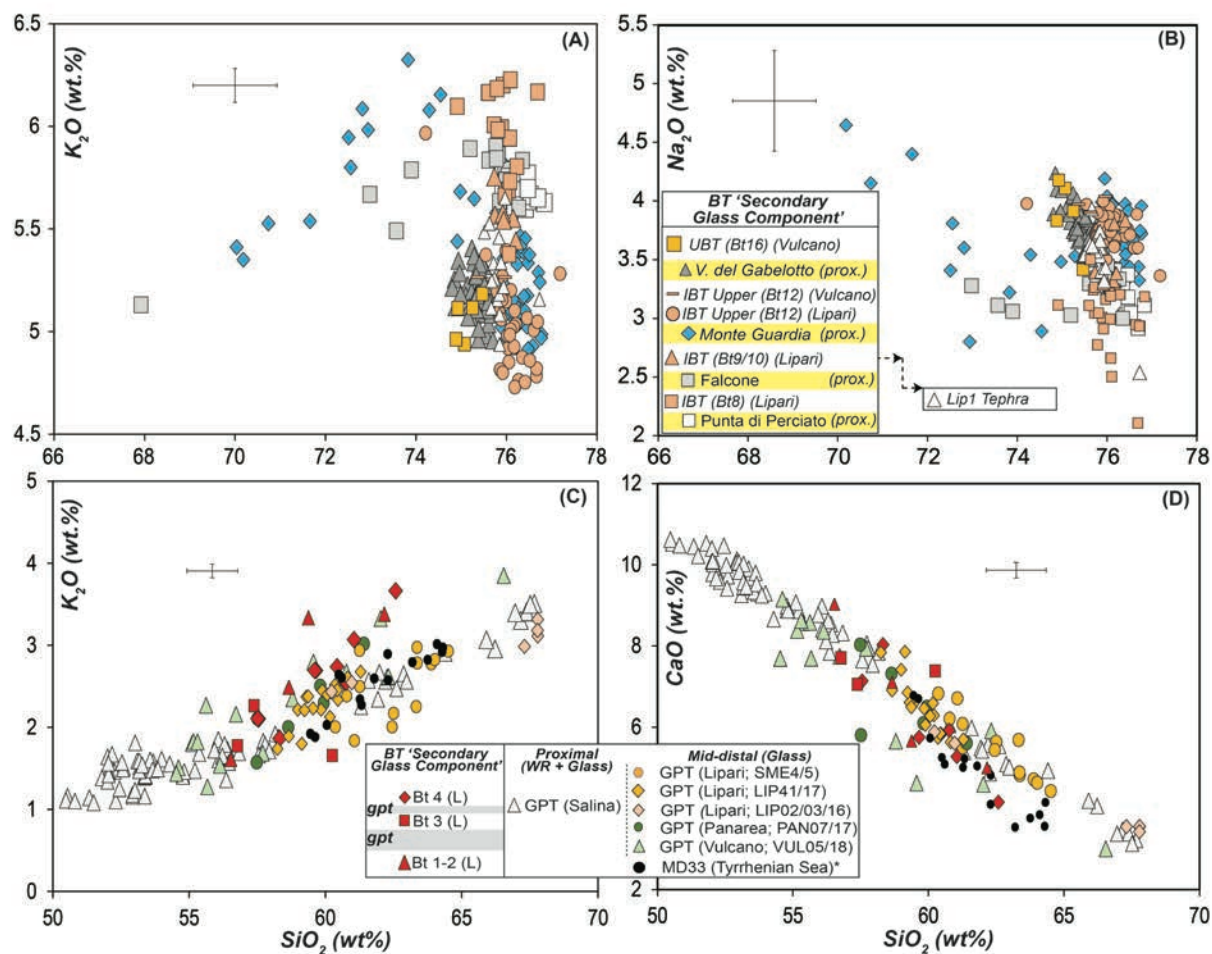


Fig. 10 - Meschiari et al.

