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1 Isotopic evolution of prehistoric magma sources of Mt. Etna, Sicily: Insights 2 from the Valle Del Bove

3
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17 Abstract

18
19 Mount Etna in NE Sicily occupies an unusual tectonic position in the convergence zone between the
20 African and Eurasian plates, near the Quaternary subduction-related Aeolian arc and above the down-
21 going Ionian oceanic slab. Magmatic evolution broadly involves a transition from an early tholeiitic
22 phase (~500 ka) to the current alkaline phase. Most geochemical investigations have focussed on
23 either historic (>130 years old) or recent (<130 years old) eruptions of Mt. Etna or on the ancient basal
24 lavas (ca. 500 ka). In this study, we have analysed and modelled the petrogenesis of alkalic lavas from
25 the southern wall of the Valle del Bove, which represent a time span of Mt. Etna's prehistoric
26 magmatic activity from ~85 to ~4 ka. They exhibit geochemical variations that distinguish them as six
27 separate lithostratigraphic and volcanic units. Isotopic data (¹⁴³Nd/¹⁴⁴Nd = 0.51283-0.51291; ⁸⁷Sr/⁸⁶Sr
28 = 0.70332-0.70363; ¹⁷⁶Hf/¹⁷⁷Hf = 0.28288-0.28298; ²⁰⁶Pb/²⁰⁴Pb = 19.76-20.03) indicate changes in the
29 magma source during the ~80 kyr of activity that do not follow the previously observed temporal
30 trend. The oldest analysed Valle del Bove unit (Salifizio-1) erupted basaltic trachyandesites with
31 variations in ¹⁴³Nd/¹⁴⁴Nd and ⁸⁷Sr/⁸⁶Sr ratios indicating a magma source remarkably similar to that of
32 recent Etna eruptions, while four of the five subsequent units have isotopic compositions resembling
33 those of historic Etna magmas. All five magma batches are considered to be derived from melting of
34 a mixture of spinel lherzolite and pyroxenite (± garnet). In contrast, the sixth unit, the main Piano
35 Provenzana formation (~42-30 ka), includes the most evolved trachyandesitic lavas (58-62 wt. % SiO₂)
36 and exhibits notably lower ¹⁷⁶Hf/¹⁷⁷Hf, ¹⁴³Nd/¹⁴⁴Nd, and ²⁰⁶Pb/²⁰⁴Pb ratios than the other prehistoric
37 Valle del Bove units. This isotopic signature has not yet been observed in any other samples from Mt.

38 Etna and we suggest that the parental melts of the trachyandesites were derived predominantly from
39 ancient pyroxenite in the mantle source of Etna.

40

41 **Keywords: prehistoric Etna; Sr-Nd-Pb-Hf isotopes; mantle heterogeneity**

42

43 **Highlights:**

44 • Sr, Nd, Pb, and Hf isotope compositions were measured on stratigraphically constrained
45 prehistoric lavas from Etna ~85-4 ka.

46 • Temporal trend of isotope compositions was interrupted during this ~80 kyr period.

47 • Lava compositions switch between those of “recent” and “historic” Etna.

48 • Lavas from Piano Provenzana show a unique isotope composition for Etna with unusually low
49 $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{206}\text{Pb}/^{204}\text{Pb}$.

50

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61

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65 **Conflicts of interest/Competing interests:** not applicable

66 **Availability of data and material** (data transparency): All new data are provided in tables presented
67 in this paper

68 **Code availability** (software application or custom code): Not applicable

69 **Authors' contributions:** HD conceived and designed the study. Material preparation was performed
70 by AS, with analytical preparations and data produced by JBT, JB, EH, and PZV. The first draft of the
71 manuscript was written by AS and all authors contributed with data analysis, interpretation, and

72 writing. PDK performed the modelling and wrote the second draft of the manuscript, which all
73 authors again contributed to.

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74 Introduction

75

76 Mount Etna, Europe's largest active volcano, is located on the Mediterranean island of Sicily (Fig. 1)
77 and lies in a complex tectonic setting near the convergence of the African and Eurasian plates.
78 Eruptions of submarine and subaerial tholeiitic basalts between ~500 and 300 ka were gradually
79 replaced by transitional to alkaline volcanism after ~250 ka via a succession of eruptive centres; this
80 activity continues to the present day (McGuire 1982; Chester et al. 1985; Kieffer and Tanguy 1993;
81 Scarth and Tanguy 2001; Patanè et al. 2006; Branca et al. 2008, 2011b). The magmatic evolution of
82 Mt. Etna has been the subject of intense geochemical and isotopic research (e.g., Armienti et al. 1989;
83 Marty et al. 1994; Tonarini et al. 1995, 2001; D'Orazio et al. 1997; Tanguy et al. 1997; Gasperini et al.
84 2002; Viccaro and Cristofolini 2008; Viccaro et al. 2011; Correale et al. 2014; Di Renzo et al. 2019),
85 mainly using samples of recent (defined here as <130 years old) and historic lavas, i.e., those erupted
86 from the start of historic records to ca. 1890 CE. Sampling of prehistoric lavas on Mt. Etna is generally
87 hampered by the widespread cover of these younger (historic and recent) eruptive products. Note the
88 age boundary between historic and prehistoric is undefined, due to lack of data; the youngest
89 prehistoric samples included here are < ~15 kyr old (D'Orazio et al. 1997), whereas the oldest historic
90 lavas are from the 18th century CE (Viccaro and Cristofolini 2008). Nevertheless, some basal tholeiites
91 (here termed "ancient Etna") and prehistoric (i.e., < ~250 ka) alkaline lavas from the eastern flank
92 (Carter and Civetta 1977; Marty et al. 1994; D'Orazio et al. 1997; Tanguy et al. 1997; Tonarini et al.
93 2001; Corsaro et al. 2002) have been previously analysed, as have some of the older Plio-Pleistocene-
94 age Iblean Plateau lavas (Fig. 1; Carter and Civetta 1977; Tonarini et al. 1996; Trua et al. 1998; Miller
95 et al. 2017).

96 Several authors have discussed the isotopic evolution of the magma sources beneath Sicily
97 and Mt. Etna (Marty et al. 1994; Tonarini et al. 2001; Corsaro and Pompilio 2004; Branca et al. 2008;
98 Viccaro and Cristofolini 2008). Strontium, Nd, and Hf isotopic compositions of eruptive products from
99 the Iblean Plateau and Mt. Etna show a broad temporal evolution from DMM-like (depleted MORB
100 [mid-ocean-ridge basalt] mantle) for the Iblean Plateau toward BSE (bulk silicate Earth) for recent
101 (<130-year-old) eruptions. This has been interpreted by some authors as evidence for subduction of
102 Ionian oceanic lithosphere beneath Mt. Etna and modification of the sub-Etna mantle by subduction-
103 derived fluids (Gvirtzman and Nur 1999). Doglioni et al. (2001) and Gasperini et al. (2002) considered
104 that differential slab rollback between the Sicilian and Ionian segments of the Apennines slab may
105 have opened a slab window that has enabled upwelling and decompression partial melting of

106 underlying asthenospheric mantle. Schiano et al. (2001) also suggested that subduction-derived fluids
107 might be metasomatising the upwelling asthenospheric mantle beneath Mt. Etna. In contrast,
108 Kamenetsky et al. (2007), Viccaro and Cristofolini (2008), Nicotra et al. (2013), Correale et al. (2014),
109 Miller et al. (2017), and Viccaro and Zuccarello (2017) considered Etna's isotopic variation to be the
110 result of melting of a heterogeneous mixture of mantle spinel lherzolites and pyroxenites.

111 In this paper we investigate prehistoric lavas from Mt. Etna that erupted during a poorly
112 known period in the evolution of the volcano between ~85 and ~4 ka. The lavas are exposed in the
113 southern wall of the Valle del Bove (latitude 15° 00' 53"–15° 01' 42"; longitude 37° 42' 50"–37° 42'
114 32") and were collected in 1988 from four separate near-vertical sections (Fig. 1). They consist of
115 several moderately evolved, geochemically distinct lava groups that correlate stratigraphically across
116 the sections (Spence and Downes 2011). These lavas were previously considered to be products of a
117 single eruptive centre referred to as "Vavalaci" (Lo Giudice 1970; McGuire 1982; Guest et al. 1984).
118 They are now, however, reinterpreted as derived from several discrete volcanic centres dating from
119 ~85 ka to ~4 ka (Calvari et al. 1994; De Beni et al. 2011; Branca et al. 2011a). Thus, they represent an
120 ~80 kyr time span between the older magmatism of Mt. Etna and the present day, providing a link
121 between the earlier eruptive phases and historic eruptions.

122 In this study, we provide new radiogenic isotope data (Sr, Nd, Pb, and Hf) for these prehistoric
123 Valle del Bove units to investigate whether the broad trends in magma source evolution from ancient
124 Etna eruptions to the modern day continued systematically throughout the ~80 kyr period that they
125 cover. We also investigate whether variations in isotopic compositions are the result of melting of
126 subducted Ionian oceanic lithosphere or rather a consequence of melting of ambient heterogeneous
127 mantle.

128

129 **Background and sampling**

130

131 Mount Etna is located near the convergence of the African and Eurasian tectonic plates (Fig. 1a). North
132 of Mt. Etna, the Quaternary Aeolian volcanic arc formed by northwards subduction of the Ionian
133 oceanic plate. The Iblean Plateau, situated ~100 km south of Etna (Fig. 1a), represents the relatively
134 undeformed foreland that was uplifted and underwent discontinuous intraplate volcanism during the
135 Tertiary and Quaternary (Tonarini et al. 1996; Trua et al. 1998).

136 All samples for this study were collected from four stratigraphic sections in the southern wall
137 of the Valle del Bove (Spence and Downes 2011). The sections from east to west are: Section A – Valle

138 del Tripodo; Section D – west of Serra dell’Acqua; Section E – Serra Pirciata; and Section C – Serra
139 Vavalaci (Fig. 1c). The stratigraphy, field relations, and petrography of the lavas can be inferred from
140 the recent geological map of Etna by Branca et al. (2011b). In combination with the $^{40}\text{Ar}/^{39}\text{Ar}$ ages of
141 De Beni et al. (2011) (Table 1), they comprise six discrete lithological units (Fig. 1d). From oldest to
142 youngest, these are: (1) Salifizio-1; (2) Salifizio-2; (3) Cuvigghiuni; (4/5) the Valle del Tripodo member
143 of the Piano Provenzana formation (Tripodo member) and Piano Provenzana; and (6) Mongibello.
144 Note that we have tried to follow the terminology of Branca et al. (2011b), choosing terms from the
145 geological map of Etna that was published after field sampling had been completed. However, we
146 have inadvertently employed a mixture of terms relating to different volcanic centres (e.g.,
147 Cuvigghiuni, Mongibello) and lithostratigraphic units (e.g., Piano Provenzana, Tripodo). To improve
148 clarity, Table 1 and the table legend at the bottom of Fig. 1 explain the equivalence between the terms
149 used in this study and those of the geological map of Branca et al. (2011b).

150 The stratigraphically lowest lavas in sections A and D (Fig. 1c, d) are basaltic trachyandesites
151 belonging to the Valle degli Zappini formation (Salifizio-1) and are therefore older than 85.6 ka.
152 Basaltic trachyandesite lavas from the Serra del Salifizio formation (Salifizio-2), dated at 85.6 ± 6.8 ka,
153 overlie this unit and are present in all four sections (Table 1). Both formations are considered to belong
154 to the Salifizio volcano (Branca et al. 2011b). The overlying trachybasalt and basaltic trachyandesite
155 lavas in sections D, E, and C are from the Canalone della Montagnola formation, dated at 79-70 ka and
156 defined by Branca et al. (2011b) as eruptions of the Cuvigghiuni volcano. The uppermost lavas in
157 section A (Fig. 1c, d) are less evolved trachybasaltic lavas from the Tripodo member of the Piano
158 Provenzana formation of the Ellittico volcano (Branca et al. 2011b), dated at 42-30 ka. In sections E
159 and C, trachyandesitic lavas form the uppermost member of the Piano Provenzana formation, also
160 dated at 42-30 ka. Precise age relationships between the Tripodo and upper Piano Provenzana
161 members have not been determined (Branca et al. 2011b). We assume from field evidence (Spence
162 and Downes 2011) that the upper member (Piano Provenzana) lavas are younger than those of
163 Tripodo, but our conclusions are not affected by this assumption. The two units are mineralogically
164 and texturally distinguishable and are also compositionally distinct. The basaltic trachyandesitic lavas
165 at the top of sections E and C form the top of the southern wall of the Valle del Bove at the Schiena
166 dell’Asino. These are products of the Mongibello stratovolcano and are younger than 15 ka (Branca et
167 al. 2011b; De Beni et al. 2011).

168 The sampled lavas are extremely fresh, and most are vesicular to highly vesicular (>20%). They
169 range from aphyric to strongly porphyritic (25–40% phenocrysts), with plagioclase as the most
170 common phenocryst phase. Some of the larger plagioclase phenocrysts exhibit zoning and/or sieve

171 textures. Clinopyroxene (augite) phenocrysts/megacrysts range up to 5 mm in size; they typically
172 exhibit oscillatory zoning and ophitic textures, enclosing aligned plagioclase laths and FeTi oxides.
173 Glomeroporphyritic aggregates of plagioclase, augite and Ti-magnetite are also common. Although its
174 modal abundance is relatively low, olivine is present as phenocrysts and in the groundmass of all but
175 the most evolved and aphyric lavas. Kaersutite occurs rarely as small, ragged and broken, partially
176 reabsorbed crystals with reaction rims of titanomagnetite, indicating instability during low-pressure
177 fractionation. Accessory apatite is also present as inclusions in augite and some plagioclase. Further
178 details of sample petrography can be found in Spence and Downes (2011).

179

180 **Sample preparation and methods**

181

182 All the sampled Valle del Bove lavas were ground to a powder using a tungsten carbide mortar and
183 analysed by X-Ray Fluorescence (XRF) at Royal Holloway University of London (Spence and Downes
184 2011). XRF data for ten of the samples were reported in Spence and Downes (2011), others are
185 presented in Table 2. Strontium and Nd isotopic analyses were initially obtained on 11 samples at the
186 University of London radiogenic isotope facility at Royal Holloway in the 1990s (data published in this
187 study) but were unevenly distributed among the six lithostratigraphic units. Therefore, for the present
188 study, 12 additional samples were analysed for Sr, Nd, Pb, and Hf isotopic ratios in other laboratories
189 (see below for details).

190 Strontium and Nd isotopic ratios on the 11 samples analysed at Royal Holloway University of
191 London (Table 3) were determined following the method described by Thirlwall (1991) and Thirlwall
192 et al. (1997). Strontium and Nd isotopic compositions were determined multi-dynamically using a
193 VG354 5-collector mass spectrometer, following conventional dissolution and chemical separation
194 without prior sample leaching. Data were collected during several analytical sessions (methods in
195 Thirlwall 1991), with reference materials reproducible to ± 0.000020 and ± 0.000008 (2SD) for $^{87}\text{Sr}/^{86}\text{Sr}$
196 and $^{143}\text{Nd}/^{144}\text{Nd}$, respectively. For a few samples, small machine bias-corrections were made based on
197 the difference between the means of the measuring period for NIST SRM 987 and a Nd in-house
198 standard. The machine bias corrections were never more than $+0.000009$ and -0.000006 , respectively.
199 The long-term laboratory averages for SRM 987 were $^{87}\text{Sr}/^{86}\text{Sr} = 0.710248$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.511420$
200 for the Nd house standard (equivalent to La Jolla of 0.511857; Thirlwall 1991). Measured Nd and Sr
201 procedural blanks were not significant with respect to the sample concentrations.

202 The new Sr and Nd isotope analyses (Table 3) were carried out at the Department of Earth and
203 Environmental Sciences, Ludwig-Maximilians-Universität of Munich, following the methods described

204 in Hegner et al. (1995). No sample powder leaching was employed. Strontium and Nd isotopes were
205 measured as metals on single W and double Re-filament configurations, respectively. Total procedural
206 blanks of <500 pg for Sr and <100 pg for Nd are not significant for the processed amounts of Sr and
207 Nd. Isotope analyses were performed on an upgraded MAT 261 multi-collector thermal ionisation
208 mass spectrometer. Strontium isotope abundance ratios were measured with a dynamic double-
209 collector routine, while Nd isotope compositions were measured using a dynamic triple-collector
210 routine, with corrections made for interfering ^{87}Rb and ^{144}Sm . $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were
211 normalised for instrumental mass bias relative to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, using a
212 Rayleigh fractionation law. During the period of this study the NIST SRM 987 Sr reference material
213 yielded $^{87}\text{Sr}/^{86}\text{Sr} = 0.710234 \pm 0.000006$ (2SD of population, n=8) and the La Jolla Nd reference material
214 $^{143}\text{Nd}/^{144}\text{Nd} = 0.511847 \pm 0.000008$ (2SD of population, n=10). The long-term external precision for
215 $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ is estimated at ca. 1.1×10^{-5} (2SD).

216 The Pb and Hf isotope analyses (Table 3) were carried out at the Ecole Normale Supérieure in
217 Lyon (ENSL) by solution chemistry (Hf only; Pb separated at University of New Hampshire; see below)
218 and MC-ICP-MS (both Hf and Pb; Nu Plasma 500 HR) following the methods of Blichert-Toft et al.
219 (1997) and Blichert-Toft and Albarède (2009). $^{176}\text{Hf}/^{177}\text{Hf}$ ratios were corrected for instrumental mass
220 fractionation relative to $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$ using an exponential law. The JMC-475 Hf standard was
221 run every two samples and averaged 0.282163 ± 0.000007 (2σ ; n=14) for $^{176}\text{Hf}/^{177}\text{Hf}$ during the single
222 run session of this work. Since this is identical to the accepted value of 0.282163 ± 0.000009 (Blichert-
223 Toft et al. 1997) for JMC-475, no corrections were applied to the data. ϵ_{Hf} values (Table 3) were
224 calculated using $^{176}\text{Hf}/^{177}\text{Hf} = 0.282772$ (Blichert-Toft and Albarède 1997).

225 Samples were prepared for Pb isotope analyses at the University of New Hampshire (UNH)
226 geochemical laboratories. Samples were first leached in hot 6 M HCl to remove surficial contaminants.
227 Lead was then isolated from the sample following procedures adapted from Bryce and DePaolo (2004).
228 The Pb isotope data obtained by MC-ICP-MS at the Ecole Normale Supérieure in Lyon were corrected
229 for instrumental mass fractionation by thallium normalization and adjusted for machine drift by
230 sample-standard bracketing (White et al. 2000; Albarède et al. 2004) using the values of Eisele et al.
231 (2003) for NIST SRM 981. Three NIST SRM 981 standard analyses run within the bracketed sample
232 suite yielded results (with external reproducibility) of $^{208}\text{Pb}/^{204}\text{Pb} = 36.726(4)$ $^{207}\text{Pb}/^{204}\text{Pb} = 15.498(3)$,
233 and $^{206}\text{Pb}/^{204}\text{Pb} = 16.941(3)$. Total procedural Hf and Pb blanks were <20 pg and <100 pg, respectively,
234 negligible relative to the abundances of these elements processed for study.

235

236 Results

237

238 Valle del Bove lavas are moderately evolved (50-62 wt. % SiO₂, Fig. 2a) and, based on the ratio of Na₂O
239 to K₂O (1.9-2.8), the rocks are mildly sodic basaltic trachyandesites and trachyandesites, including one
240 trachyte sample. Figure 2a also shows fields that encompass the range of compositions for recent (i.e.,
241 <130 years old) and historic (i.e., >130 years old) Etna lavas, along with the field for prehistoric and
242 ancient Etna magmatic products. The Valle del Bove lavas overlap the field for previously analysed
243 prehistoric and ancient Etna lavas, but most of these rocks, including Valle del Bove, have higher
244 concentrations of SiO₂ and total alkalis than recent and historic Etna lavas. In a K₂O versus SiO₂
245 discrimination diagram (Fig. 2b) (Peccerillo and Taylor 1976) most Etna rock samples, including Valle
246 del Bove, fall within the high-K field. Recent Etna samples, however, are distinct, being more enriched
247 in K₂O for a given SiO₂ concentration than all other Etna lavas, as shown previously by Clocchiatti et
248 al. (1988). Within the Valle del Bove suite, samples from Salifizio-1 and Piano Provenzana have
249 consistently lower concentrations of K₂O and total alkalis for a given SiO₂ concentration than those of
250 Salifizio-2, Cuvigghiuni, the Tripodo member, or Mongibello.

251 Although the higher SiO₂ concentrations for prehistoric and ancient Etna samples suggest that
252 these rocks are all more evolved than recent and historic Etna samples, plots of major element oxides
253 versus MgO (Fig. 3) show that the least evolved lavas from Valle del Bove, particularly those from
254 Salifizio-1, have similar MgO concentrations (and Mg numbers; see Online Resource 1, Fig. S1) to
255 recent and historic Etna, suggesting similar degrees of magmatic evolution. Valle del Bove lavas are
256 distinct in having higher SiO₂ for a given MgO concentration (Fig. 3a). They also have lower CaO, Al₂O₃,
257 TiO₂, and FeO_{total} concentrations and CaO/Al₂O₃ ratios. Recent Etna lavas have significantly higher K₂O
258 for a given MgO concentration (see Online Resource 1, Fig. S1) than either historic or
259 ancient/prehistoric Etna, including the Valle del Bove lavas, consistent with their higher K₂O shown in
260 Figure 2b. Only two samples from the Tripodo member, A14 and A15 (Table 2), are as enriched in K₂O
261 at similar MgO concentration as recent Etna lavas. Other samples from the Tripodo member are more
262 evolved (MgO <3.3 wt. %), yet they have lower K₂O concentrations, i.e., opposite of what would be
263 expected from fractional crystallisation of the observed phenocryst phases. Samples A14 and A15
264 occur stratigraphically below the more evolved Tripodo member samples and below a 20 m interval
265 with lack of exposure (Spence and Downes 2011); hence, the relationship between these two groups
266 of Tripodo samples is unclear, but they may not be petrogenetically related.

267 The Valle del Bove lavas overlap the compositional fields for ancient and prehistoric Etna in
268 Fig. 3, with a few notable exceptions. Salifizio-1 lavas, the oldest rocks in the suite, have SiO₂
269 concentrations higher than those of recent and historic Etna, but also higher than most other ancient

270 and prehistoric Etna rocks (Fig. 3a). They also have lower Al_2O_3 and TiO_2 (Figs. 3c, e). Ancient and
271 prehistoric Etna samples, including those from Valle del Bove, extend to more evolved compositions
272 (i.e., lower MgO and higher SiO_2) than recent or historic Etna lavas.

273 Figure 4a shows the primitive-mantle-normalised incompatible element patterns for the Valle
274 del Bove samples compared with those of ocean island basalts (OIB) representative of EM (enriched
275 mantle) and HIMU (mantle with high time-integrated U/Pb) sources, as well as average global
276 subducted sediments (GLOSS) and bulk continental crust. Figure 4b shows the data normalised to the
277 composition of average recent Etna lavas. All Valle del Bove samples are enriched in most of the
278 incompatible trace elements relative to recent and historic Etna basalts (Fig. 4b). Two units
279 (Mongibello and Piano Provenzana) exhibit particular enrichment in nearly all incompatible trace
280 elements except Sr and Ti, consistent with their evolved compositions (MgO concentrations <2.6 wt.
281 %, Table 2; see also Figs. 2 and 3). In contrast, the least evolved samples (e.g., from Salifizio-1 and the
282 Tripodo member) have compositions typical of intraplate alkaline magmas, e.g., OIB-like, although
283 with relative enrichments in Ba, Th, and Pb and depletions in Ti and K (Fig. 4a). Of note in this context
284 are the high La/Nb ratios relative to average OIB compositions. The Tripodo member has a trace
285 element pattern that is distinct from most other Valle del Bove units. It is more akin to historic Etna,
286 particularly in terms of its low Th/Nb and Th/Ba ratios (Fig. 4b). However, the least evolved Tripodo
287 samples, A14 and A15, have higher concentrations of nearly all incompatible trace elements (Table 2)
288 than the most evolved samples, further supporting the idea that these two groups of samples are not
289 related by fractional crystallisation.

290 The Valle del Bove lavas show significant variations in $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70334-0.70364), $^{143}\text{Nd}/^{144}\text{Nd}$
291 (0.51284-0.51290), $^{176}\text{Hf}/^{177}\text{Hf}$ (0.28288-0.28298), and $^{206}\text{Pb}/^{204}\text{Pb}$ (19.76-20.03) ratios with clear
292 differences between the six units (Fig. 5). Samples from the oldest unit (Salifizio-1) have the highest
293 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of all the Valle del Bove units (>0.7035). These rocks contrast with those of similar age
294 from the northern wall of the Valle del Bove, i.e., the Rocca Capra (ca. 81-78 ka) (D'Orazio et al. 1997)
295 and the prehistoric/ancient Etna rocks reported by Marty et al. (1994), all of which have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios
296 < 0.70325 and $^{143}\text{Nd}/^{144}\text{Nd}$ > 0.51291. Instead, Salifizio-1 samples overlap the field of recent high-
297 $^{87}\text{Sr}/^{86}\text{Sr}$ Etna lavas (Figs. 5a, b) in a Sr-Nd isotope diagram. They also have overlapping to lower
298 $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios relative to recent Etna lavas (Figs. 5c, e). Their Hf isotopic
299 compositions overlap those of most younger Valle del Bove units (except Piano Provenzana), but their
300 $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are lower. Thus, the isotopic data suggest that Salifizio-1 magmas were derived from
301 a source isotopically similar to that of recent Etna magmas and distinct from that of other ancient and
302 prehistoric Etna rocks. In contrast, the slightly younger (~85-70 ka) Salifizio-2 and Cuvigghiuni lavas

303 have lower $^{87}\text{Sr}/^{86}\text{Sr}$ and higher $^{176}\text{Hf}/^{177}\text{Hf}$ ratios and plot within or near the field of historic Etna lavas
304 (Figs. 5a, c, e), as do lavas from the Tripodo member. However, even these samples have higher
305 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than most samples of ancient and prehistoric Etna (Marty et al. 1994; D’Orazio et al.
306 1997). All VdB units, however, have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the unusual prehistoric picrite, FS
307 (pyroclastic fall deposit), analysed by Correale et al. (2014). The higher Sr isotopic ratio for this sample
308 (0.70391) was attributed to crustal contamination, although the authors did not distinguish between
309 contamination occurring in a shallow crustal magma chamber or via subduction modification of the
310 mantle source.

311 The Piano Provenzana lavas have the lowest $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of all the analysed prehistoric
312 lavas and almost the lowest $^{143}\text{Nd}/^{144}\text{Nd}$ (the Nd isotope values overlap those of Salifizio-1). The
313 youngest Mongibello lavas return to isotopic ratios that are more typical of historic Etna, with higher
314 $^{143}\text{Nd}/^{144}\text{Nd}$ (Figs. 5b, d, f). The Hf and Sr isotopic compositions thus indicate the existence of at least
315 three different components, two of which are predominant, i.e., the isotopically distinct sources of
316 recent Etna lavas and historic/prehistoric Etna lavas, with five of the six Valle del Bove units
317 overlapping these two fields. The third component, with an unusually low Hf isotopic composition for
318 a given Sr or Nd isotopic composition, is seen only in the Piano Provenzana unit (Figs. 5c, e). This
319 component has not previously been observed in samples from Mt. Etna, regardless of eruption age or
320 major element composition.

321 Strontium, Nd, and Hf isotopic ratios (Fig. 5) show a change over time from more depleted
322 DMM-like compositions (e.g., ϵ_{Nd} of $\sim +10$) for ancient Iblean tholeiites to less depleted isotopic
323 compositions for recent Etna eruptions. However, this simple trend breaks down during the ~ 80 kyr
324 time span of the Valle del Bove eruptions (Fig. 5). Instead, a wider range of compositions appears to
325 have been available for prehistoric Etna than exists today, particularly with addition of the new data
326 of this study for Salifizio-1 and Piano Provenzana.

327 Lead isotope data for lavas from the Iblean Plateau and Mt. Etna (Fig. 6) also show a trend
328 from depleted towards more enriched source compositions over time. However, some of the variation
329 in the literature data, particularly in $^{207}\text{Pb}/^{204}\text{Pb}$, may result, in part, from the greater analytical
330 uncertainty of the older data collected using thermal ionisation mass spectrometry as compared with
331 modern MC-ICP-MS data, which better control instrumental mass discrimination. There may also be
332 some differences in sample preparation, particularly with regards to whether pre-dissolution leaching
333 was applied. Lead isotope compositions of the Valle del Bove samples analysed using MC-ICP-MS with
334 TI-normalisation and sample-standard bracketing show tight linearity in Pb isotope space over the ~ 80

335 kyr time span considered (Fig. 6). The Valle del Bove units have relatively radiogenic Pb isotope
336 compositions, overlapping the fields for recent, historic, and prehistoric / ancient Etna, and extending
337 to higher $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios than those from the Iblean Plateau. Among the Valle del
338 Bove units, the Piano Provenzana lavas have the lowest $^{206}\text{Pb}/^{204}\text{Pb}$ (19.76-19.80), whereas the Tripodo
339 member is the most radiogenic (i.e., its source shows the highest time-integrated U/Pb of all samples).
340 The radiogenic Pb isotope composition of the Tripodo member contrasts with its lower $^{87}\text{Sr}/^{86}\text{Sr}$ than
341 in the other samples (Fig. 5a), which suggests a source that is more incompatible element depleted
342 (i.e., time-integrated depletion in Rb relative to Sr) than that of most other Valle del Bove lavas.

343

344 **Discussion**

345

346 *Fractionation of Valle del Bove prehistoric magmas*

347

348 The data points in the TAS diagram (Fig. 2a) suggest that most of the prehistoric Valle del Bove lavas
349 are more evolved than recent and historic Etna eruptions (Tanguy et al. 1997), with the Mongibello
350 and Piano Provenzana lavas amongst the most evolved. Salifizio-1 and Piano Provenzana lavas exhibit
351 lower concentrations of total alkalis for a given SiO_2 concentration and are transitional to silica
352 oversaturated in composition (i.e., up to 4.3 wt. % normative quartz), whereas the Mongibello lavas
353 are all silica undersaturated, with up to 6 wt. % normative nepheline (see Online Resource 1, Fig. S2a).
354 The lavas from Mongibello and Piano Provenzana are clearly the most evolved of the Valle del Bove
355 samples, with Differentiation Indices (DI = normative q + or + ab + ne + lc) of 63 to 77 (Fig. S2a), but
356 they lie along two different differentiation trends (Fig. S2b). Samples from the Tripodo member,
357 Cuvigghiuni, Salifizio-2, and Mongibello become more silica undersaturated as they become more
358 evolved, whereas those from Salifizio-1 and Piano Provenzana become more silica saturated as
359 differentiation increases.

360 To better understand the effects of fractional crystallisation on the Valle del Bove lavas, we
361 have modelled isobaric fractionation using alphaMELTS 1.9 (Ghiorso and Sack 1995; Asimow and
362 Ghiorso 1998; Smith and Asimow 2005). The results are shown in diagrams of MgO versus major
363 element oxides SiO_2 , Al_2O_3 , CaO, $\text{FeO}_{\text{total}}$, as well as $\text{Na}_2\text{O} + \text{K}_2\text{O}$ versus SiO_2 (Fig. 7); details of the
364 calculations are provided in Online Resource 2. Given the observation that the Valle del Bove suite
365 includes at least two distinct differentiation trends, two different parental compositions have been
366 assumed, one to represent the trend of increasing silica saturation (i.e., Salifizio-1 sample A5; Spence

367 and Downes 2011) and the other to represent the trend of increasing silica undersaturation with
368 increased differentiation (i.e., Tripodo member sample A15; Table 2). Figure 7 shows that, for both
369 starting compositions, fractional crystallisation at low pressure (i.e., 1 kb or ~3 km) fails to reproduce
370 the data, particularly the observed increase in Al_2O_3 and decreasing $\text{FeO}_{\text{total}}$ with decreasing MgO
371 concentration. It also fails to reproduce the distribution of data on the TAS diagram (Figs. 7i, j), with
372 low-pressure fractionation resulting in excessive enrichment in total alkalis. For these low-pressure
373 calculations, we assumed 'dry' conditions (H_2O of 0.01 wt. %), because of the low loss on ignition of
374 the studied samples (Table 2). However, even if we assume higher water concentrations (e.g., 2 wt.
375 %), the model curves at low pressure (not shown) do not reproduce the data, particularly for Al_2O_3 ,
376 $\text{FeO}_{\text{total}}$, and total alkalis.

377 In contrast, at moderate pressure (3.5 to 4 kb or ~10-12 km) and H_2O concentrations in the
378 melt of ~3 to 4 wt. %, the model curves reproduce the shape of the observed data distributions well.
379 The difference in the residual melt pathways for low vs. moderate pressure is due to the expansion of
380 the olivine stability field as pressure increases. At low pressures, plagioclase is the liquidus phase,
381 followed by olivine and clinopyroxene in fairly rapid succession (see Online Resources 2 for details).
382 The early stabilisation of plagioclase leads to a rapid depletion in Al_2O_3 as fractionation proceeds. At
383 higher pressures, the olivine stability field expands, and the crystallisation sequence is typically spinel
384 followed by olivine, followed closely by clinopyroxene, with plagioclase appearing much later. Under
385 these conditions, Al_2O_3 increases until plagioclase starts to fractionate.

386 None of the models accurately reproduce the high Al_2O_3 concentrations of some samples from
387 Cuvigghiuni and the Tripodo member (Figs. 7c, d). The MELTS models also fail to reproduce the
388 variations in TiO_2 versus MgO (not shown). These discrepancies may, in part, be a function of
389 uncertainties in the thermodynamic data used in the MELTS calculations and are associated with an
390 over-stabilisation of spinel, a recognised problem of the MELTS software (Ghiorso et al. 2002). This
391 leads to depletion in Al_2O_3 , FeO, and TiO_2 in the calculated melts in excess of that in the actual rocks.
392 Nonetheless, some of the Valle del Bove samples are plagioclase-rich, particularly the Tripodo lavas
393 (Spence and Downes 2011). Hence, some of the observed compositional variation, particularly the
394 enrichment in Al_2O_3 , may be due to plagioclase accumulation at low pressures prior to eruption.

395 In summary, modelling with alphaMELTS 1.9 indicates that fractionation of the Valle del Bove
396 lavas occurred in a magma chamber at moderate depths of ~10-12 km, which is consistent with
397 interpretations based on geophysical data for the depth of present-day magma storage (Paonita et al.
398 2012; Mollo et al. 2015; Miller et al. 2017; Cannata et al. 2018). For the Valle del Bove lavas,

399 fractionation is dominated by olivine and clinopyroxene. This contrasts with models for recent Etna in
400 which the fractionation sequence is typically described as plagioclase, followed by clinopyroxene,
401 olivine, titaniferous magnetite, and, in some cases, amphibole (Viccaro et al. 2011), all of which
402 suggest a stronger imprint from shallower fractional crystallisation processes. Water concentrations
403 of 3-4 wt. % are consistent with the compositions of melt inclusions in olivine (Spilliaert et al. 2006),
404 studies of Etna magma ascent rates (Armienti et al. 2013), and thermodynamic modelling (Kahl et al.
405 2015). Low values of loss on ignition (Table 2) suggest the Valle del Bove lavas were thoroughly
406 degassed before eruption.

407

408 *Source components of Etna magmatism – evidence from major and trace elements*

409

410 Fractional crystallisation has clearly affected the compositions of the Valle del Bove lavas (Figs. 2, 3,
411 7). Nonetheless, some of the major and trace element variations observed may be an indication of
412 differences in mantle source composition or variations in percentage of melting, rather than
413 differences in extent of fractionation.

414 We test this hypothesis using Th, a highly incompatible trace element, as a proxy for alkaline
415 magma fractionation (Wilson et al. 1995) (Fig. 8). Thorium correlates positively with Differentiation
416 Index in the Valle del Bove suite ($R^2 = 0.75$), further justifying this trace element approach (see Online
417 Resources 1, Fig. S3). In the absence of significant crustal contamination, the ratio of two highly
418 incompatible elements (i.e., $D \ll 1$) should remain largely unchanged during fractional crystallisation.
419 Therefore, plots of Th versus other highly incompatible trace elements should produce linear arrays
420 that project back to the ratio of the two elements in the parental magma, providing an indication of
421 source composition and possible heterogeneity (e.g., Allegre et al. 1977; Joron and Treuil 1989). Given
422 that the Valle del Bove lavas are characterised by an anhydrous phenocryst assemblage consisting of
423 clinopyroxene + plagioclase + magnetite \pm olivine (Spence and Downes 2011), elements such as Nb,
424 Zr, and Ba should have similar incompatibility during fractional crystallisation in this system (see GERM
425 database, <https://earthref.org/KDD/>). Figure 8a shows that most Valle del Bove lavas overlap the field
426 of prehistoric/ancient Etna and form arrays with Nb/Th ratios similar to recent and historic Etna. Some
427 lavas from Salifizio-1, however, appear to have evolved from a parental magma that was more
428 enriched in Th relative to Nb. Moreover, if the Piano Provenzana lavas evolved from a
429 transitional/silica-saturated parent similar to Salifizio-1, as suggested by Figs. 2 and S2, these lavas are
430 significantly more enriched in Nb (or depleted in Th) than expected by fractional crystallisation alone.
431 In the plots of Ba and Zr vs Th (Figs. 8b and c), the Valle del Bove samples again largely overlap the

432 field for prehistoric/ancient Etna, but the slopes of the data at the highest degrees of fractionation are
433 shallower than expected within individual units; that is, at the highest Th concentrations (i.e., highest
434 fractionation), Ba and Zr concentrations are lower than expected. Instead, the data are better
435 described by second-order polynomials ($R^2 > 0.86$), as shown in Figs. 8b and c. At lower Th
436 concentrations (lower fractionation), the curves indicate similar Ba/Th and Zr/Th ratios for recent and
437 historic Etna, but as magma differentiation increases, they deviate to lower Ba/Th and Zr/Th. This
438 could be due to fractionation of trace phases with higher D values for these elements that appear later
439 in the fractionation sequence, such as amphibole, biotite, or K-feldspar (for Ba), and zircon (for Zr).
440 Nonetheless, as for Nb vs. Th, lavas from Salifizio-1 appear to have evolved from a parent that was
441 enriched in Th relative to Ba and Zr, and the Piano Provenzana lavas have higher concentrations of Ba
442 and Zr relative to Th than would be expected if they were derived from a silica-saturated parent similar
443 to Salifizio-1. In addition, the two least evolved Tripodo member samples, A14 and A15 ($MgO > 4.75$
444 wt. %; samples circled in Figs. 8a-c), clearly have *higher* concentrations of incompatible trace elements
445 than the more evolved lavas from this unit ($MgO < 3.3$ wt. %), opposite to what would be expected if
446 the rocks were related by fractional crystallisation.

447 The data, therefore, demonstrate that at least some of the trace element variations observed
448 are unrelated to fractional crystallisation (Fig. 8). These findings further suggest that crustal
449 contamination is unlikely to be responsible for the trace element variations, since average continental
450 crust (Rudnick and Gao 2003) has concentrations of Nb (8 ppm), Zr (132 ppm), Ba (456 ppm), and Th
451 (6 ppm) that are lower than those in the least evolved Valle del Bove samples. This conclusion is
452 consistent with similar trace element arguments against significant crustal assimilation put forward
453 for recent Etna by Corsaro et al. (2007). In addition, D'Orazio et al. (1997) observed Sr and Nd isotope
454 equilibrium between clinopyroxene and host lavas from the north wall of the Valle del Bove, which
455 indicates that if crustal contamination occurred, it could not have taken place after clinopyroxene
456 began to crystallise. Similar evidence for phenocryst-melt isotopic equilibrium was also reported by
457 Miller et al. (2017) for the older Timpe lavas. As shown by our alphaMELTS 1.9 modelling,
458 crystallisation of clinopyroxene occurs very early in the fractionation sequence at moderate pressures,
459 thus limiting the potential for impact from shallow-level crustal contamination.

460 Despite the similarities in incompatible element ratios and, hence, potential source regions
461 for recent to ancient Etna as suggested by Fig. 8, Figure 4b shows that even the most primitive of the
462 Valle del Bove samples, i.e., some samples from Salifizio-1 and the Tripodo member, are enriched in
463 Ba, Th, Nb, Pb, and Zr relative to recent and historic Etna magmas. Furthermore, these two units are
464 not only distinct from recent and historic Etna, but also different from one another, suggesting

465 differences in source composition or petrogenesis. The Tripodo member has a trace element pattern
466 similar to average historic Etna lavas, just at higher overall concentrations, consistent with the lavas
467 being slightly more evolved (Fig. 3). In contrast, Salifizio-1 lavas have higher Rb and Th, but lower light
468 rare earth elements (LREE) and Sr. Strong relative depletions in Sr indicate a role for plagioclase
469 fractionation, and the trough at Ti reflects magnetite fractionation (Fig. 4b). The low K concentration
470 would be consistent with fractionation of a K-bearing phase, such as biotite or K-feldspar, but neither
471 of these phases is observed in the rocks. Instead, the relative depletion in K is more likely an indication
472 of derivation from a source in which a K-bearing phase, such as phlogopite or amphibole, was residual
473 during partial melting, as suggested by Viccaro and Cristofolini (2008) for recent Etna lavas.

474 This interpretation is consistent with our own modelling of K and Rb systematics for the Valle
475 del Bove lavas (Fig. 9). In a plot of K/Rb ratio versus Rb concentration, the Valle del Bove samples
476 overlap the fields for historic and recent Etna but extend to higher concentrations of Rb for a given K
477 than seen in the younger Etna rocks, particularly for the highly evolved lavas from Piano Provenzana
478 and Mongibello. The effects of clinopyroxene and amphibole fractionation are shown as the solid and
479 dashed lines, respectively. Fractionation in the absence of a hydrous phase would increase Rb
480 concentrations but have little effect on the K/Rb ratio (solid lines). Because K is more compatible in
481 amphibole than Rb, fractionation of this phase would decrease the K/Rb ratio while increasing the Rb
482 concentration (dashed lines). While some of the Valle del Bove data are consistent with a small
483 amount of amphibole fractionation, in most cases, our modelling suggests that fractionation is
484 dominated by anhydrous phases, in support of our MELTS modelling (Fig. 7).

485 However, fractionation of the observed phenocryst phases cannot account for the lower Rb
486 and higher K/Rb values of some Tripodo or Mongibello samples, assuming parental magma
487 compositions like those of the most primitive lavas in the suite. Indeed, the most primitive lavas, e.g.,
488 A5 from Salifizio-1 and A15 from the Tripodo member, overlap the field of recent Etna, whereas the
489 more evolved samples from the Tripodo member overlap the field for historic Etna, and evolved rocks
490 from Mongibello have both higher K/Rb ratios and Rb concentrations (Fig. 9). These differences
491 suggest either different source compositions or differences in the degree of melting that gave rise to
492 the parental magma, or both.

493 We evaluate these two alternatives via a simple batch partial melting model of a spinel
494 lherzolite source containing either 1% amphibole or 1% phlogopite in the mode (Fig. 9). The two curves
495 have similar shapes and show similar trajectories of increasing K/Rb ratios with decreasing Rb
496 concentration as degree of partial melting increases, similar to the distribution shown by the Etna
497 data. The phlogopite-bearing source, however, produces lower concentrations of Rb and higher K/Rb

498 ratios for the same degree of partial melting relative to the amphibole-bearing source. More
499 sophisticated melting models, such as non-modal batch melting or fractional melting, tend to produce
500 higher Rb concentrations and K/Rb ratios for smaller degrees of partial melting. In contrast, partial
501 melting of an anhydrous peridotite source would produce a nearly horizontal array on this diagram
502 given the similar partition coefficients for the relevant mineral phases.

503 Collectively, the data suggest that the Etna lavas were derived by partial melting of a source
504 containing hydrous phases, such as amphibole or phlogopite. The trend of increasing K/Rb with
505 decreasing Rb concentration as a function of degree of partial melting is more consistent with the
506 observed data distribution than melting of an anhydrous source. The offset of the Tripodo member
507 samples and historic Etna to lower Rb and higher K/Rb relative to recent Etna suggests these magmas
508 were either derived by larger degrees of partial melting or from a different source.

509 The modelling results in Fig. 9 do not allow unambiguous distinction between these two
510 options, because details of source mineralogy and elemental concentrations can only be assumed.
511 However, several lines of evidence lead us to conclude that the Tripodo member lavas were derived
512 by smaller degrees of partial melting than the Salifizio-1 lavas, e.g., their more silica undersaturated
513 compositions (Figs. 2 and S1), higher La/Y, and lower Rb, Th, and K relative to Ba, Nb, and La (Fig. 4).
514 Therefore, source heterogeneity has likely played a significant role in generating the compositional
515 variations observed.

516

517 *Source components of Etna magmatism – evidence from Sr-Nd-Pb-Hf isotopes*

518

519 Many authors have interpreted the compositional variations in recent Etna lavas as evidence
520 for source heterogeneity (e.g., Carter and Civetta 1977; Tanguy et al. 1997; Tonarini et al. 2001;
521 Armienti et al. 2004; Viccaro and Cristofolini 2008; Viccaro et al. 2011, Correale et al. 2014 and
522 references therein). Models to explain this source heterogeneity are broadly of two types. One calls
523 for modification of the mantle source via subduction-derived melts and fluids, a model consistent with
524 the complex geodynamic setting in which Etna is located (e.g., Armienti et al. 2004; Tonarini et al.
525 2001; Viccaro et al. 2011). The other attributes source heterogeneity to lithologic variations in which
526 a predominantly lherzolitic matrix is crosscut by pyroxenite (\pm garnet) veins (Correale et al. 2014;
527 Miller et al. 2017; Viccaro and Zuccarello 2017). Correale et al. (2014) further argue that the
528 pyroxenitic component contributes about 10% to the melts that give rise to recent Etnean lavas.

529 Constraining the proportion of pyroxenite to peridotite in the mantle source is challenging
530 because (a) pyroxenite compositions can vary widely (Downes 2007; Lambert et al. 2016) and (b)

531 phase relations, and hence melt compositions, are pressure and temperature sensitive. Nonetheless,
532 in broad terms, partial melts involving high proportions of pyroxenite in the source tend to be higher
533 in CaO/Al₂O₃ and TiO₂ but lower in SiO₂ for a given MgO concentration than those derived from
534 peridotite melting (Kogiso et al. 2003; Condamine et al. 2016). Thus, the higher SiO₂, lower CaO/Al₂O₃,
535 FeO, and TiO₂ of prehistoric Etna magmas relative to recent and historic Etna (Fig. 3) are consistent
536 with an increase in the proportion of pyroxenite in the source of Etna magmas over time.

537 Variations in isotopic composition also allow us to examine source heterogeneity and to assess
538 several different processes that may be involved in the petrogenesis of the Valle del Bove lavas: 1)
539 melting of isotopically distinct asthenospheric mantle sources; 2) variable degrees of partial melting
540 of metasomatised mantle domains; 3) addition of a subduction-related component to the mantle
541 source; and 4) crustal contamination of magmas during fractionation. In the following sections we
542 consider the relative contributions of these various processes.

543 Recent and historic Etna lavas are generally considered to have been derived from an
544 asthenospheric mantle source (Wilson and Downes 2006), known variously as the low-velocity
545 composition (LVC) of Hoernle et al. (1995), the European asthenospheric reservoir (EAR) of Cebrià and
546 Wilson (1995), the common component ('C') of Hanan and Graham (1996), or the FOcal ZOne (FOZO)
547 of Hart et al. (1992). This mantle component may itself be a mixture, with contributions from DMM
548 (low ⁸⁷Sr/⁸⁶Sr and radiogenic (high) Nd, Hf, and Pb isotopic compositions) and possibly EM1 sources
549 (enriched mantle-1) (Stracke et al. 2005; Viccaro et al. 2011). The isotopic compositions of the Iblean
550 Plateau lavas (Figs. 5, 6) indicate an origin from a more depleted mantle source than that feeding
551 present-day Mt. Etna (Tonarini et al. 1996; Trua et al. 1998). Hence, modern Etna is no longer tapping
552 the depleted mantle source of the older Iblean tholeiitic magmatism. Instead, modern Etna is being
553 fed by an isotopically heterogeneous mantle source more typical of intra-plate ocean islands (Armienti
554 et al. 1989; Tonarini et al. 2001; Viccaro and Cristofolini 2008). Surprisingly, our study shows that
555 Salifizio-1 lavas, the oldest lavas in our suite, have isotopic compositions similar to those of recently
556 erupted Etna lavas, whereas four slightly younger units (Salifizio-2, Cuvigghiuni, Tripodo, and
557 Mongibello) have tapped a source very similar to that of historic Etna lavas (Fig. 5). In contrast, Piano
558 Provenzana lavas show a unique isotopic signature that has not previously been recognised in the data
559 for Mt. Etna. Although major and trace element data provide no evidence for significant involvement
560 of crustal contamination in the petrogenesis of Valle del Bove lavas, we still need to consider this
561 process with regard to the isotope data before we can confidently interpret this new isotopic signature
562 as an indication of source heterogeneity.

563

564 *Crustal contamination versus a subducted sediment component – evidence from Sr-Nd-Pb-Hf isotopes*

565

566 The composition of the lower crust beneath NE Sicily is not well constrained, since the only crustal
567 xenoliths available are derived from the upper crust and have experienced extensive thermal
568 metamorphism (Michaud 1995). The outcropping basement NE of Mt. Etna is composed of a variety
569 of metasedimentary rocks intruded by Hercynian granitoids (Fiannacca et al. 2008) and thus closely
570 resembles the crust of the Calabrian arc and other areas of Hercynian crust throughout southern
571 Europe, but there are few studies of the geochemistry and isotopic compositions of these rocks. We
572 have therefore used Sr, Nd, and Pb isotopic data for metaigneous and metasedimentary lower crustal
573 xenoliths from the Hercynian French Massif Central (Downes et al. 1990) as proxies in concert with
574 the limited information available on Calabrian basement (Caggianelli et al. 1991; Rottura et al. 1991).
575 The average Hf isotope composition of the same Hercynian lower crustal xenoliths (Vervoort et al.
576 2000) has been used here as a proxy for the crust underneath Mt. Etna.

577 Lead isotope data for the Valle del Bove lavas show a tightly constrained linear array in
578 comparison to circum-Tyrrhenian volcanic rocks (Fig. 10). Most samples plot within or near the
579 FOZO/EAR/LVC/C field with high $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, while the Piano Provenzana lavas have lower
580 $^{206}\text{Pb}/^{204}\text{Pb}$ and trend towards the general fields of sediments or continental crust. The solid black
581 arrows in Figs. 10a and b indicate possible mixing trajectories that could explain the Valle del Bove Pb
582 isotope arrays. The data are inconsistent with assimilation of Hercynian-type upper continental crust,
583 but could be explained by incorporation of subducted sediment like that seen in the eastern
584 Mediterranean (Klaver et al. 2015) or Ionian Sea (Kempton et al. 2018) into a FOZO/EAR-type source.
585 Assimilation of Calabrian-type basement is also consistent with the Pb isotope data, and we cannot
586 distinguish these alternatives using Pb isotope data alone.

587 However, Calabrian basement has an average $^{87}\text{Sr}/^{86}\text{Sr}$ value of ca. 0.717 (Caggianelli et al.
588 1991; Rottura et al. 1991), so assimilation-fractional crystallisation processes involving such a
589 contaminant would likely have also affected $^{87}\text{Sr}/^{86}\text{Sr}$, which is not observed (Fig. 5). Furthermore, all
590 analysed Etna lavas have >700 ppm Sr (compared to <250 ppm for Calabrian basement), so it is unlikely
591 that assimilation of continental crust would strongly affect their Sr isotope compositions.
592 Nevertheless, the Piano Provenzana lavas clearly provide evidence for the presence of a component
593 with a lower ϵ_{Hf} and ϵ_{Nd} composition beneath Etna (Fig. 5d, f).

594 The uniqueness of this component is particularly apparent in comparisons of the Valle del
595 Bove units in $^{176}\text{Hf}/^{177}\text{Hf}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ in the context of the wider regional data set (Fig. 11a). Most of
596 the Valle del Bove lavas again show a well-constrained array with one end-member in the FOZO/EAR

597 field; the data partially overlap the field for recent and historic Etna, but are clearly distinct from the
598 sources of the Iblean Plateau and Aeolian arc (Alicudi and Filicudi), the compositions of which indicate
599 greater time-integrated incompatible element depletion. Paired Hf-Pb isotopic data for other
600 prehistoric Etna rocks are limited, but four analyses from the Timpe Santa Caterina phase of activity,
601 i.e., 220-100 ka (Miller et al. 2017), have high Hf isotope values that overlap the composition of the
602 Iblean Plateau. The Pb isotope compositions of these rocks are, however, more HIMU-like than those
603 from the Iblean Plateau and, instead, are similar to the most radiogenic lavas from Valle del Bove.
604 Thus, based on currently available data, the low Hf isotope values of the Piano Provenzana lavas are
605 unlike any known Etna magmatic products.

606

607 *Piano Provenzana – a new component in Etna magmatism?*

608

609 Figures 5 and 11 indicate that the lavas from Piano Provenzana are isotopically unique among Etna
610 magmatic products. One interpretation is that a brief episode of melting of an unusual sediment
611 component in the slab beneath Sicily may have given rise to the source of the Piano Provenzana lavas.
612 Comparisons of $^{176}\text{Hf}/^{177}\text{Hf}$ and Nd/Zr (Fig. 12a) show that all the prehistoric lavas analysed in this
613 study have lower Nd/Zr than recent or historic Etna, while only the Piano Provenzana lavas have Hf
614 isotope compositions lower than recent and historic Etna. Thus, the lower Hf isotope signature in the
615 Piano Provenzana unit might be related to zircon-rich sediments introduced into the mantle wedge
616 prior to mixing with an upwelling melt generated from a more depleted mantle end-member, i.e., the
617 “zircon effect” (Patchett et al. 1984; White et al. 1986; Blichert-Toft et al. 1999; Carpentier et al. 2009).
618 Mixing calculations (Fig. 11b) show that isotopic signatures of most Valle del Bove samples can be
619 explained by incorporation into a FOZO/EAR-type mantle source of < 2 wt. % sediment similar in
620 composition to that of the Ionian Sea (Kempton et al. 2018). The Piano Provenzana samples, however,
621 require a sediment contaminant with a lower Hf isotope composition, such as the Zr-rich sediments
622 of the eastern Mediterranean (Klaver et al. 2015). A similar model was used recently to explain the Hf-
623 Nd isotope systematics of Miocene subduction-related rocks from Sardinia (Kempton et al. 2018).

624 However, if a subduction component is involved in the mantle source of the Piano Provenzana
625 lavas, this addition must have occurred prior to 42-30 ka, the age of the Piano Provenzana lavas
626 according to De Beni et al. (2011). Moreover, $^{87}\text{Sr}/^{86}\text{Sr}$ appears to have been largely unaffected by this
627 process relative to other lavas of Ellittico. The Tripodo member, for example, comprises low-SiO₂ lavas
628 with an age range similar to that of the upper Piano Provenzana formation (Branca et al. 2011a; De
629 Beni et al. 2011), and these lavas exhibit low $^{87}\text{Sr}/^{86}\text{Sr}$ and high $^{176}\text{Hf}/^{177}\text{Hf}$ (Fig. 5). Furthermore, the

630 degree of isotopic offset of the Piano Provenzana lavas from other prehistoric Etna lavas (Figs. 5, 6,
631 and 12) decreases in the order: Hf > Nd > Pb > Sr. In other words, the fluid-immobile elements Hf and
632 Nd show a greater offset than the fluid-mobile elements Pb and Sr.

633 Thus, the lower $^{176}\text{Hf}/^{177}\text{Hf}$ values (relative to all other Etna lavas) could imply melting of an
634 additional (ancient?) component in the source of the Piano Provenzana lavas, rather than recent fluid
635 transfer during subduction. The unique isotope composition is consistent with small-scale
636 heterogeneity in the form of veins or metasomatic minerals in the mantle source, i.e., mantle
637 metasomes. Such a process has been described from numerous localities worldwide in which low-
638 degree melts, enriched in highly incompatible elements, ascend and undergo fractional crystallisation,
639 producing a spectrum of mineral assemblages ranging from anhydrous veins (chiefly pyroxenites \pm
640 garnet) to hydrous cumulates that contain amphibole and phlogopite (e.g., Frey and Prinz 1978; Irving
641 1980; Kempton 1987; Bodinier et al. 1990; Harte et al. 1993; Downes 2007). Viccaro and Zuccarello
642 (2017) recently showed that partial melting of a mixed peridotite-pyroxenite mantle source could
643 produce alkaline compositions similar to those of recent Etna magmas. In their model the peridotite
644 component is a spinel lherzolite that contains hydrous metasomatic phases, whereas the pyroxenite
645 component is a garnet pyroxenite formed by crystallisation of silicate melts. They concluded that the
646 pyroxenite to lherzolite ratio required to explain the compositions of recent Etna lavas ranges from
647 10% to 35%.

648 This model is consistent with the Valle del Bove data as shown in Fig. 12b, a plot of $^{87}\text{Sr}/^{86}\text{Sr}$
649 vs. Zr/Nb. Zr and Nb are relatively immobile in fluids mobilised during subduction, and since both are
650 moderately incompatible, variation in the Zr/Nb ratio as a function of partial melting of a
651 homogeneous source should be relatively small. Isotope ratios are obviously not fractionated during
652 mantle melting, so any variation observed is a function of source heterogeneity. The data show a
653 broad correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and Zr/Nb for ancient Etna and most Valle del Bove lavas.
654 Historic and recent Etna lavas plot at the high-Zr/Nb end of the array, although recent Etna lavas
655 have consistently higher $^{87}\text{Sr}/^{86}\text{Sr}$ for a given Zr/Nb relative to older lavas. If modification of the
656 mantle source via subduction-derived fluids was the primary control on isotopic and trace element
657 variations, there should be no obvious correlation between Zr/Nb and $^{87}\text{Sr}/^{86}\text{Sr}$.

658 It could be argued that the trend is due to a fortuitous combination of subduction
659 enrichment, which produces a vertical trend on the diagram through addition of radiogenic Sr, plus
660 variation in Zr/Nb as a function of degree of partial melting induced by that fluid addition. This
661 scenario implies that the degree of subduction modification correlates systematically with the
662 degree of partial melting of the metasomatized mantle. However, the difference in degree of partial

663 melting required to create the observed range of Zr/Nb ratios is at least a factor of 10, which would
664 have a significant impact on the major element compositions of the magmas produced. In such a
665 scenario, the lowest Zr/Nb should be significantly more enriched in other incompatible trace
666 elements and probably more silica undersaturated than those at the high Zr/Nb end of the array,
667 and such systematic variation is not observed for the data set as a whole (see Online Resources 1,
668 Fig. S4). While we cannot entirely rule out this scenario, the impact from garnet pyroxenite in the
669 source, which has a Zr/Nb of >25 based on data for Iblean ultramafic xenoliths (Correale et al. 2012),
670 is likely to outweigh the impact of varying degrees of partial melting of a homogeneous lherzolitic
671 source, which typically has a Zr/Nb ratio <4. As such, the broad positive correlation is more likely
672 due to a heterogeneous source consisting of variable proportions of lherzolite and pyroxenite.

673 This suggests there is a compositional, i.e., source heterogeneity, control involved in the
674 genesis of Etna magmas, particularly ancient and prehistoric Etna. Melts derived from a pyroxenite-
675 rich source should have higher Zr/Nb than those from a lherzolitic source. The positive correlation
676 between Sr isotopes and Zr/Nb, therefore, suggests a role for ancient veins in the mantle rather than
677 recent subduction influences. On the other hand, the offset of recent Etna lavas to higher $^{87}\text{Sr}/^{86}\text{Sr}$
678 may reflect a more significant role for metasomatism of the mantle source via subduction-derived
679 fluids for these rocks.

680 We therefore agree with the interpretations of Viccaro and Cristofolini (2008), Correale et al.
681 (2014), Miller et al. (2017), and Viccaro and Zuccarello (2017) that the mantle beneath Etna is
682 heterogeneous, consisting of a lherzolite matrix crosscut by streaks or veins of 'ancient' pyroxenite
683 of variable composition. More recent modification by subduction-derived fluids and/or melts may
684 contribute to the petrogenesis of historic and recent Etna magmas.

685 The isotopic variation seen in the prehistoric lavas from Mt. Etna may be related to a
686 decreasing degree of mantle melting relative to that producing Iblean tholeiites, so that less depleted
687 low-T melting components of the heterogeneous mantle are preferentially tapped (Conticelli et al.
688 1997; Pilet et al. 2011; Correale et al. 2014). In this scenario, the LREE and large-ion lithophile element
689 (LILE) component of these rocks is likely to be related to decompression melting of a fusible part of
690 the fluid-metasomatised upper mantle enriched with pyroxenites and/or hydrated minerals such as
691 phlogopite or amphibole, as found in mantle xenoliths from the Iblean Plateau (Tonarini et al. 1996;
692 Scribano et al. 2009; Bianchini et al. 2010). The Piano Provenzana parental melt may have formed in a
693 discrete metasomatic zone in the mantle with an enriched crust-like signature (Downes 2007), i.e.,
694 veins with a lower Hf isotopic composition than the surrounding mantle but similar Sr isotopic

695 composition, thus affecting the isotope composition of Hf more than that of Nd and Pb, and with little
696 effect on $^{87}\text{Sr}/^{86}\text{Sr}$.

697

698 **Summary and conclusions**

699

700 i) Analysed Valle del Bove samples represent six lithostratigraphic units of prehistoric Etna
701 lavas ranging in age from ~85 ka to ~4 ka. They show differences in element and
702 radiogenic isotopic compositions that vary between the signatures of recent and
703 historic Etna samples, suggesting melting of two main mantle components in the
704 asthenospheric mantle source over the past ~100 kyr.

705 ii) Although, in broad terms, the source of magmatism in the region has changed over time
706 from more DMM-like (for Iblean Plateau lavas) to a more enriched (FOZO/EAR/LVC/C-
707 like) end-member for Etnean magmatism, variations in Sr-Nd-Pb-Hf isotopic
708 compositions do not support a smooth transition. Instead, some of the oldest rocks for
709 which data are available, e.g., Rocca Capra (~80 ka; D'Orazio et al. 1997) and Salifizio 1
710 (>86 ka), encompass almost the entire range in Sr and Nd isotope values for Etna
711 (0.70317 and 0.51293 for Rocca Capra, 0.70363 and 0.51283 for Salifizio-1).

712 iii) Most of the prehistoric Etna eruptions tapped the FOZO/EAR/LVC/C asthenospheric
713 mantle component. In contrast, evolved trachyandesites from the Piano Provenzana
714 unit were derived from a source that is unique amongst analysed lavas from Mt. Etna,
715 having a less radiogenic Hf isotope signature.

716 iv) The low $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of the Piano Provenzana lavas suggest they formed by melting
717 of an unusual piece of metasomatised lithospheric mantle. Indeed, the data for Valle
718 del Bove as a whole support the existence of a heterogeneous marble-cake-style mantle
719 source variably metasomatized by hydrous phases (amphibole and/or phlogopite) and
720 pyroxenite veins as suggested by several previous studies (Viccaro and Cristofolini 2008;
721 Correalle et al. 2014; Miller et al. 2017; Viccaro and Zuccarello 2017). The proportion of
722 pyroxenite appears to be greater in historic to recent Etna than in the Valle del Bove.

723 v) The degree of magmatic differentiation of Valle del Bove lavas is similar to that of recent
724 and historic Etna, but parental magmas were different and those for recent Etna were
725 more silica undersaturated. Differences may be a function of degree of partial melting

726 but are more likely due to different source compositions and, particularly, different
727 proportions of pyroxenite in the source.
728 vi) MELTS modelling, together with isotopic and trace element data, suggest that the Valle
729 del Bove parental magmas contained ~3 to 4 wt. % H₂O and fractionated in a magma
730 chamber at moderate depths of ~10-12 km.

731

732 **References**

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1095

1096 **Figure Captions**

1097

1098 Figure 1 (a) Public domain outline map of southern Italy with areas of interest indicated. (b) Outline
1099 of Mt. Etna with Valle del Bove, adapted from Chester et al. (1985). (c) Map of the southern
1100 wall of the Valle del Bove, adapted from the Geological Map of Etna Volcano (Branca et al.
1101 2011b). Widths of sections A, D, E, and C are exaggerated for clarity. All samples analysed in
1102 this study were collected from one of the four sections labelled A, D, E and C. (d) Lithology of
1103 the six volcanic units as exposed in the four sections A, D, E and C.

1104

1105 Figure 2 (a) Total alkalis versus silica (TAS) diagram with relevant fields labelled according to the
1106 classification of Le Maitre (1984). (b) K_2O wt.% versus SiO_2 wt. % with discriminant boundaries
1107 from Peccerillo and Taylor (1976). Data for Valle del Bove from Spence and Downes (2011)
1108 and this study. Data for recent Etna samples (<130 years old) from Armienti et al. (1989),
1109 Tonarini et al. (1995), Viccaro and Cristofolini (2008), and Wijbrans (unpublished). Historic
1110 Etna samples (>130 years old) from Viccaro and Cristofolini (2008). Prehistoric/ancient Etna
1111 from D’Orazio et al. (1997).

1112

1113 Figure 3 Major element variation diagrams for (a) SiO_2 , (b) FeO_{total} , (c) Al_2O_3 , (d) CaO, (e) TiO_2 , and (f)
1114 CaO/Al_2O_3 versus MgO wt. %. Data sources for ancient to recent Etna magmatism as in Fig. 2.
1115 Data for Iblean Plateau tholeiites from Tonarini et al. (1996) and Trua et al. (1998).

1116

1117 Figure 4 Primitive-mantle-normalised incompatible element diagram (normalising values from Sun
1118 and McDonough 1989) for the six Valle del Bove units and historic and recent Etna. GLOSS (=
1119 global subducted sediment) average from Plank and Langmuir (1998); bulk continental crust
1120 average from Rudnick and Gao (2003). Representative EM OIB and HIMU OIB based on
1121 average compositions of St. Helena and Tristan da Cunha from Willbold and Stracke (2006).
1122 (b) Recent-Etna-normalised incompatible element diagram for the six Valle del Bove units. The
1123 Mongibello and Piano Provenzana lavas are the most highly enriched in LILE and HFSE (high
1124 field-strength elements) compared to average recent eruptions. Data sources as in Fig. 2.

1125

1126 Figure 5 (a) $^{143}Nd/^{144}Nd$ versus $^{87}Sr/^{86}Sr$ (c) $^{176}Hf/^{177}Hf$ versus $^{87}Sr/^{86}Sr$, and (e) $^{176}Hf/^{177}Hf$ versus
1127 $^{143}Nd/^{144}Nd$ ratios for the six Valle del Bove units, compared with data from the literature for
1128 prehistoric/ancient, historic, and recent lavas from Etna and tholeiitic and alkali lavas from the
1129 Iblean Plateau. Five of the six units fall within the fields for recent and historic Etna lavas,
1130 whereas the Piano Provenzana unit (encircled) lies outside of these fields. Data sources for Nd
1131 and Sr isotopic compositions of recent Etna samples from Armienti et al. (1989), Marty et al.
1132 (1994), Tonarini et al. (1995, 2001), and Viccaro and Cristofolini (2008). Historic Etna data from
1133 Marty et al. (1994), Tonarini et al. (2001), and Viccaro and Cristofolini (2008).

1134 Ancient/prehistoric Etna data from D’Orazio et al. (1997) and Marty et al. (1994). Iblean
1135 Plateau data from Tonarini et al. (1996) and Trua et al. (1998). Hafnium isotopic ratios for
1136 historic and recent Etna from Viccaro et al. (2011), and for prehistoric Etna and Iblean Plateau
1137 from Gasperini et al. (2002), Miller et al. (2017), and Kempton (unpublished). The unusual
1138 prehistoric (3930 ± 60 y BP; Coltelli et al. 2005) picrite sample, FS, plots outside the range of
1139 Sr isotope values shown in panel (a), with an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70391 (Correale et al. 2014);
1140 its $^{143}\text{Nd}/^{144}\text{Nd}$ ratio, however, overlaps the field for prehistoric/ancient Etna as shown. Figures
1141 (b), (d), and (f) show isotopic compositions for the six Valle del Bove units from this study.
1142 Arrows and dates indicate temporal trends in Nd and Sr isotopic ratios for the six units over
1143 their ~80 kyr eruption period. Analytical uncertainties (2SD) for Valle del Bove data in panels
1144 (a), (c), and (e) are within the size of the symbols; analytical uncertainties (2SD) in panels (b),
1145 (d), and (f) are as shown by the error bars.

1146
1147 Figure 6 (a) $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ and (b) $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ ratios for the six Valle
1148 del Bove units; prehistoric/ancient, historic, and recent Etna lavas; and tholeiitic and alkali
1149 lavas from the Iblean Plateau. Data for historic and recent Etna lavas from Carter and Civetta
1150 (1977) and Viccaro and Cristofolini (2008). Prehistoric/ancient Etna data from Carter and
1151 Civetta (1977) and Miller et al. (2017). Data for Iblean tholeiitic and alkali lavas from Carter
1152 and Civetta (1977), Tonarini et al. (1996), and Trua et al. (1998). Analytical uncertainties (2SD)
1153 for Valle del Bove data are within the size of the symbols

1154
1155 Figure 7 Major element variation diagrams for (a) SiO_2 , (b) $\text{FeO}_{\text{total}}$, (c) Al_2O_3 , (d) CaO , (e) K_2O , and (f)
1156 TiO_2 versus MgO wt. % showing fractional crystallisation pathways calculated using
1157 alphaMELTS 1.9. Details of calculations in Online Resources 2. Panels a, c, e, g, and i assume a
1158 starting composition of Salifizio-1 lava A5. Figures b, d, f, h, and j assume Tripodo member A15
1159 as the starting composition. Three model scenarios are presented for both starting
1160 compositions: (1) 1kb, QFM, ‘dry’; (2) 3.5kb, QFM, 4 wt. % H_2O ; (3) 4kb, NNO, 3 wt. % H_2O .
1161 Data sources for recent, historic, and ancient Etna as in Fig. 3.

1162
1163 Figure 8 (a) Nb versus Th, (b) Ba versus Th, and (c) Zr versus Th concentrations. Thorium is used as a
1164 proxy for alkaline magma fractionation of the six Valle del Bove units. Data sources for ancient
1165 to recent Etna magmatism as in Fig. 3.

1166
1167 Figure 9 K/Rb ratios versus Rb concentrations showing calculated trends for partial melting of a source
1168 containing 1 modal % phlogopite (dotted line) and 1 modal % amphibole (dot-dash line).
1169 Variations due to fractional crystallisation of amphibole from starting compositions A5
1170 (Salifizio-1) and A15 (Tripodo member) shown as dashed lines. Variations due to fractional
1171 crystallisation of clinopyroxene from starting compositions A5 and A15 shown as solid lines.

1172 Data sources for ancient to recent Etna samples as in Fig. 3. Fractional crystallisation modelled
1173 using the equation $C_L = C_o * F^{(D-1)}$, where C_L is the calculated liquid composition, C_o is the initial
1174 concentration, D is the bulk distribution coefficient and F is the fraction of liquid remaining.
1175 Partial melting calculations assume simple batch melting, i.e., $C_L = C_o / (D + F - DF)$, where C_L is the
1176 calculated liquid composition, C_o is the initial concentration, D is the bulk distribution
1177 coefficient and F is the degree of partial melting. Mineral modes are based on anhydrous
1178 lherzolite xenoliths from the Iblean Plateau (ol = 72%; opx = 15%; cpx = 12%, Correale et al.
1179 2014) modified to include 1% amphibole or 1% phlogopite. Partition coefficients from GERM
1180 (<https://earthref.org/KDD/>); Rb partition coefficients as follows: ol = 0.0003; opx = 0.001; cpx
1181 = 0.01; amph = 0.023; phlog = 1.5; K partition coefficients: ol = 0.0001; opx = 0.0003; cpx =
1182 0.004; amph = 1.36; phlog = 3.
1183

1184 Figure 10 (a) $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ and (b) $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ ratios for volcanic
1185 rocks of the circum-Tyrrhenian area. Calculated trend line indicates potential mixing of
1186 FOZO/EAR/LVC/C source components with a crustal or sedimentary component. Data sources
1187 as in Fig. 6 with additional data from Ayuso et al. (1998), Barnekow (2000), Beccaluva et al.
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1189 and Peccerillo (1992), Conticelli (1998), Conticelli et al. (2009), Crisci et al. (1991), D'Antonio
1190 and Di Girolamo (1994), D'Antonio et al. (1996, 1999), DeAstis et al. (2000, 2006), Del Moro
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1198 Wilson 1995); LVC = Low Velocity Composition (Hoernle et al. 1995); FOZO = FOcal ZOne (Hart
1199 et al. 1992); 'C' = Common component (Hanan and Graham 1996); NHRL = Northern
1200 Hemisphere Reference Line (Hart 1984).
1201

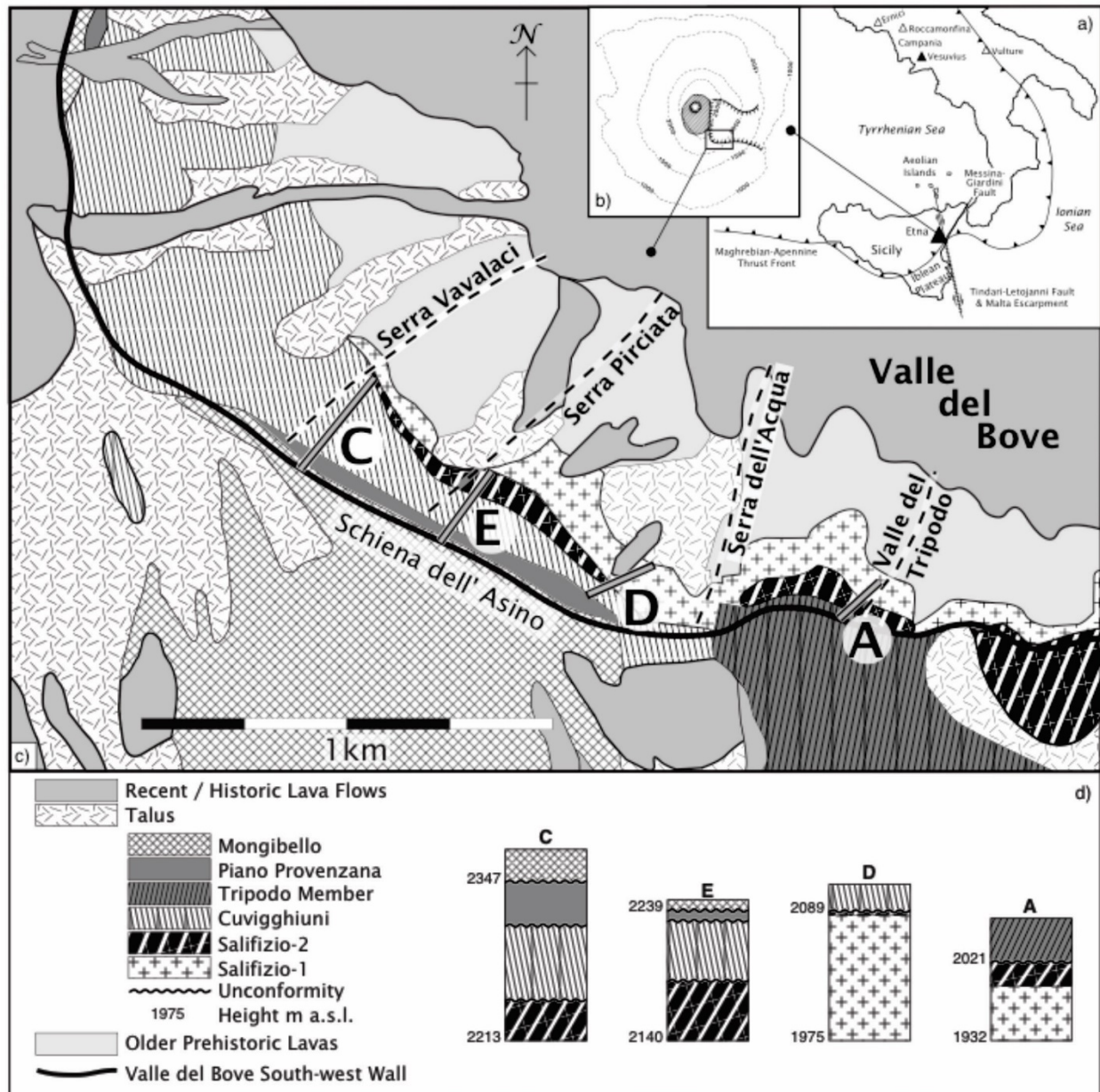
1202 Figure 11 (a) $^{176}\text{Hf}/^{177}\text{Hf}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ ratios for Valle del Bove samples in the context of the wider
1203 data set for Italian / Tyrrhenian volcanic rocks and the field for LVC/EAR/FOZO/C field. Data
1204 sources as for Figs. 5 and 10 with additional Hf isotopic data for Italy and the Tyrrhenian Sea
1205 from Barnekow (2000), Conticelli and Peccerillo (1992), Prelević et al. (2010), and Miller et al.
1206 (2017). Average Hf isotopic composition for Hercynian lower and upper continental crust from
1207 Vervoort et al. (1999, 2000). Mediterranean sediment data from Klaver et al. (2015) and
1208 Kempton et al. (2019). (b) Five representative mixing scenarios between EAR-type mantle and
1209 possible subducted sediment calculated using IgPet (Carr and Gazel 2017). EAR mantle

1210 modelled using two compositions: EAR (A) is representative of prehistoric Etna from Timpe
1211 Santa Catalina (Miller et al. 2017), i.e., $^{176}\text{Hf}/^{177}\text{Hf} = 0.28305$; $^{206}\text{Pb}/^{204}\text{Pb} = 20.2$; EAR (B) is more
1212 HIMU-like and more typical of the most enriched Valle del Bove lavas, i.e., $^{176}\text{Hf}/^{177}\text{Hf} =$
1213 0.28295 ; $^{206}\text{Pb}/^{204}\text{Pb} = 20.5$; Hf and Pb concentrations in both cases assume primitive mantle
1214 values of 0.309 and 0.185 ppm, respectively (Sun and McDonough, 1989). Average Ionian
1215 sediment from Kempton et al. (2018): $^{176}\text{Hf}/^{177}\text{Hf} = 0.28229$; $^{206}\text{Pb}/^{204}\text{Pb} = 18.7$; Hf = 2.6 ppm;
1216 Pb = 12.3 ppm. Eastern Mediterranean Zr-rich sediment from Klaver et al. (2015): $^{176}\text{Hf}/^{177}\text{Hf}$
1217 $= 0.28258$; $^{206}\text{Pb}/^{204}\text{Pb} = 18.6$; Hf = 3.2 ppm; Pb = 12.5 ppm. Tick marks on the mixing curves
1218 represent 1% and 2% mixing of the sediment component into the EAR mantle source; further
1219 percentages of mixing omitted from the figure for clarity.

1220
1221 Figure 12 (a) $^{176}\text{Hf}/^{177}\text{Hf}$ versus Nd/Zr ratios for the six Valle del Bove units, recent Etna, and historic
1222 Etna. Adapted from a diagram by Nicotra et al. (2013). (b) $^{87}\text{Sr}/^{86}\text{Sr}$ versus Zr/Nb ratios for the
1223 six Valle del Bove units compared with the data fields for recent, historic, and
1224 ancient/prehistoric Etna; prehistoric Etna sample labelled FS is the unusual picrite reported
1225 by Correale et al. (2014). Solid black arrows indicate direction of compositional variation from
1226 slab-derived fluids and/or recycled sediment melts. Dashed arrow indicates compositional
1227 variation for recent Etna as a result of partial melting as proposed by Viccaro and Cristofolini
1228 (2008); dotted arrow indicates variation as a result of fractional crystallisation for most
1229 evolved VdB compositions where there is potential to fractionate Zr/Nb through
1230 crystallisation of phases like titanomagnetite or sphene. EAR compositional range (double-
1231 headed arrow) from Cebrià and Wilson (1995). Data sources as in Fig. 5.

1232

Fig. 1



Terminology used in this study	Volcanic Centres	Lithostratigraphic notation
Mongibello	Mongibello	Lower member of Pietracannone Formation
Tripodo	Ellittico	Tripodo member of Piano Provenzana Formation
Piano Provenzana	Ellittico	Piano Provenzana
Cuvigghiuni	Cuvigghiuni	Canalone della Montagnola
Salifizio 2	Salifizio 2	Serra del Salifizio
Salifizio 1	Salifizio 1	Valle degli Zappini

Fig. 2

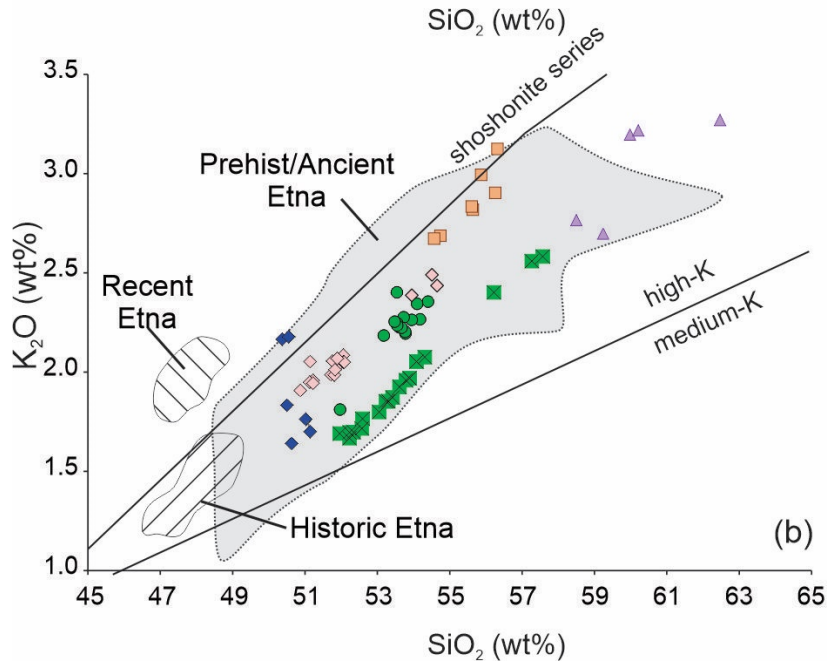
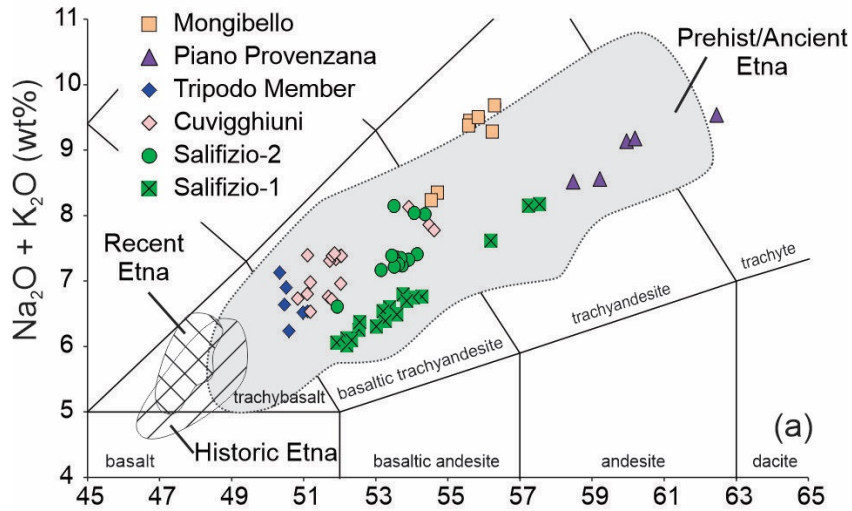


Fig. 3

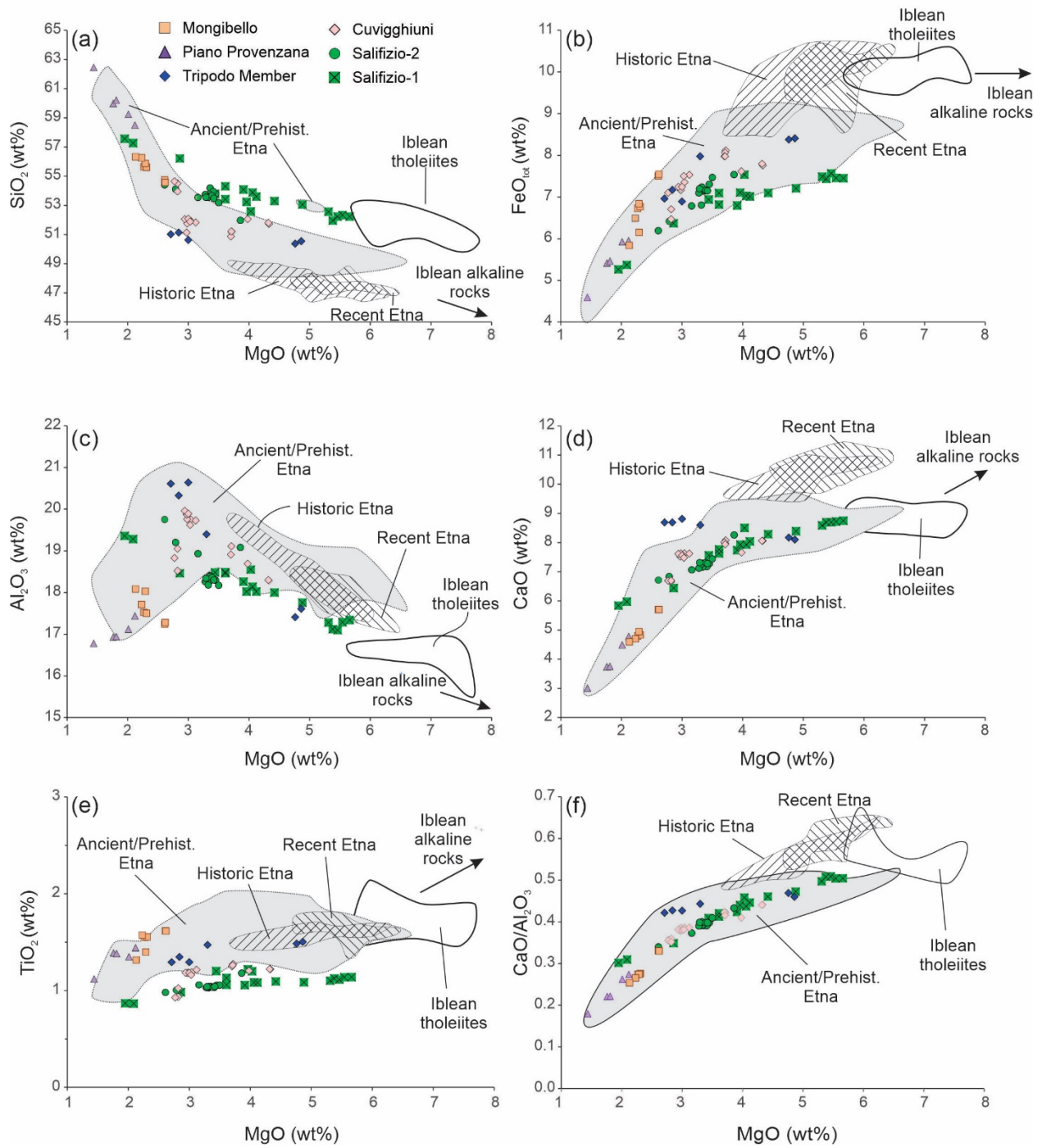


Fig. 4

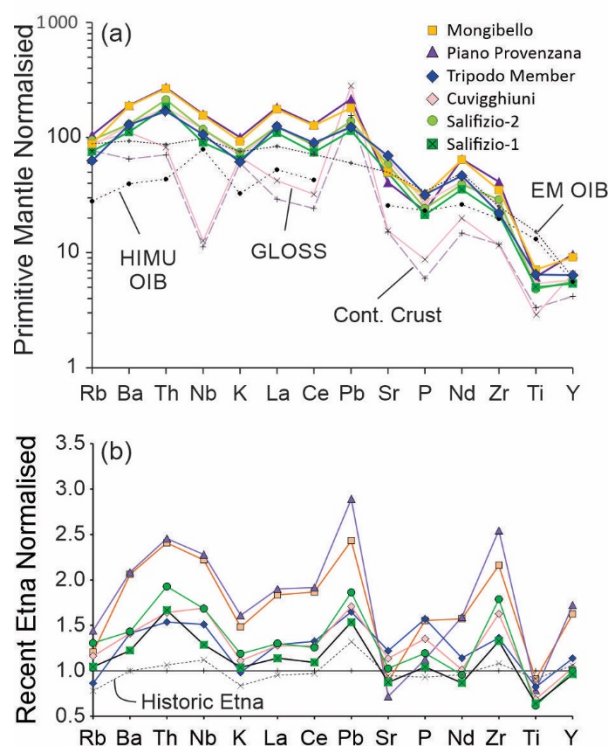


Fig. 5

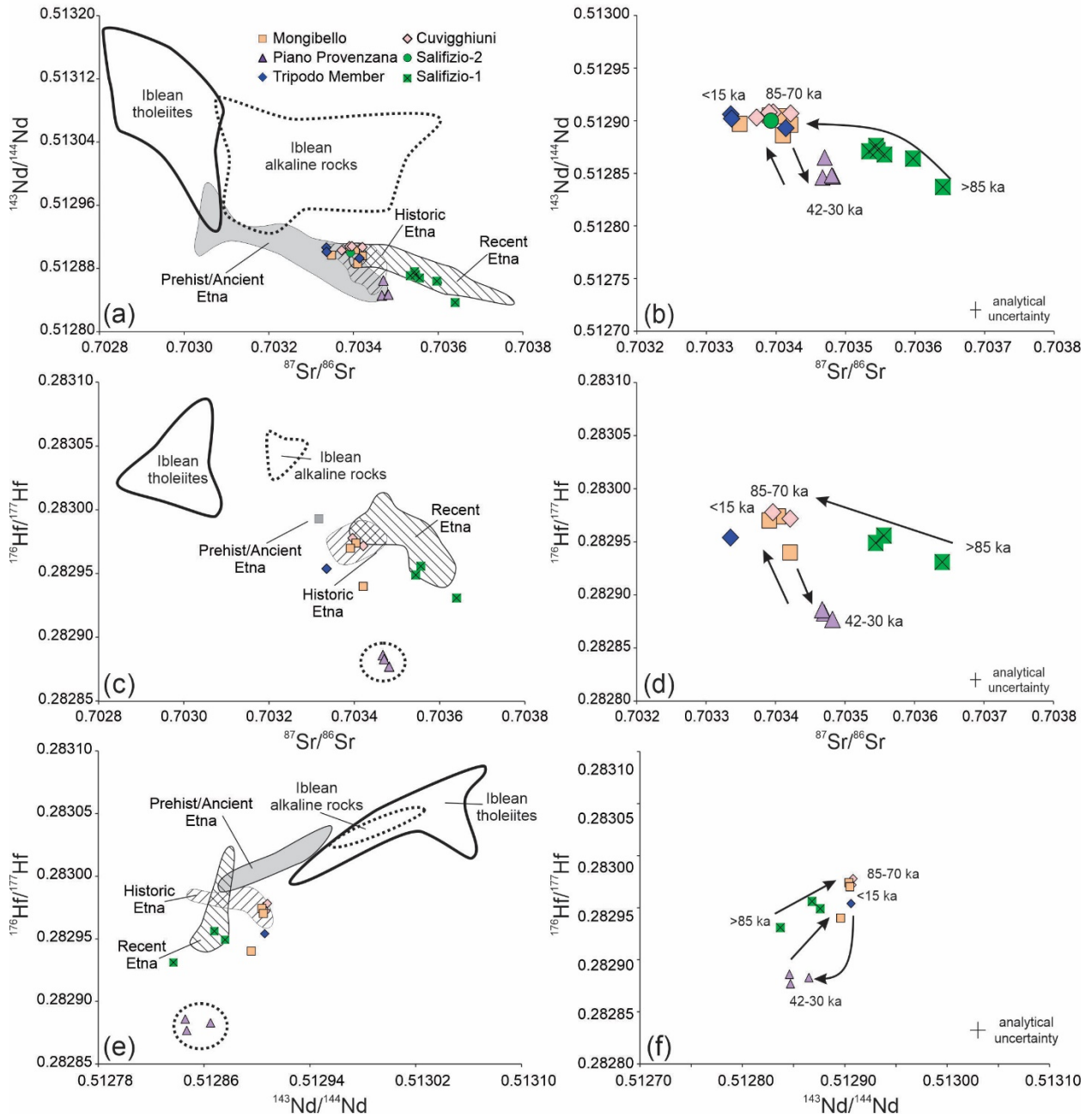


Fig. 6

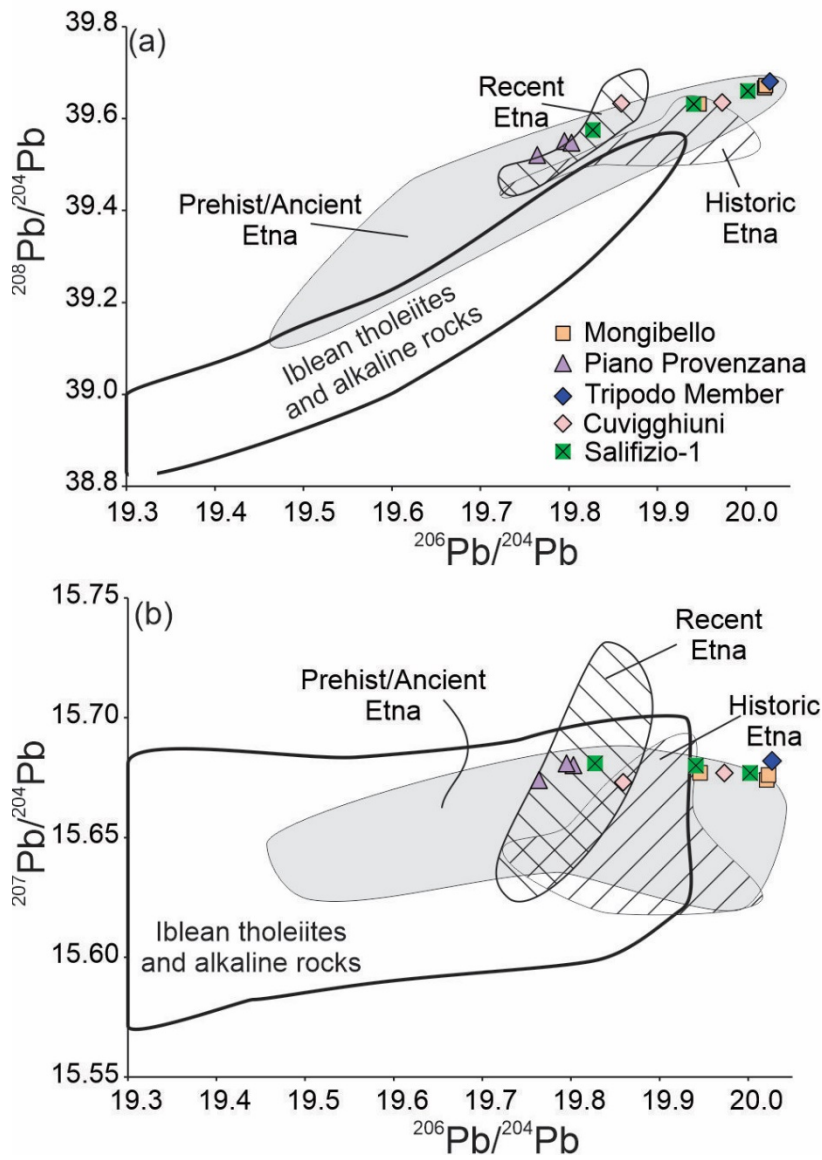


Figure 7

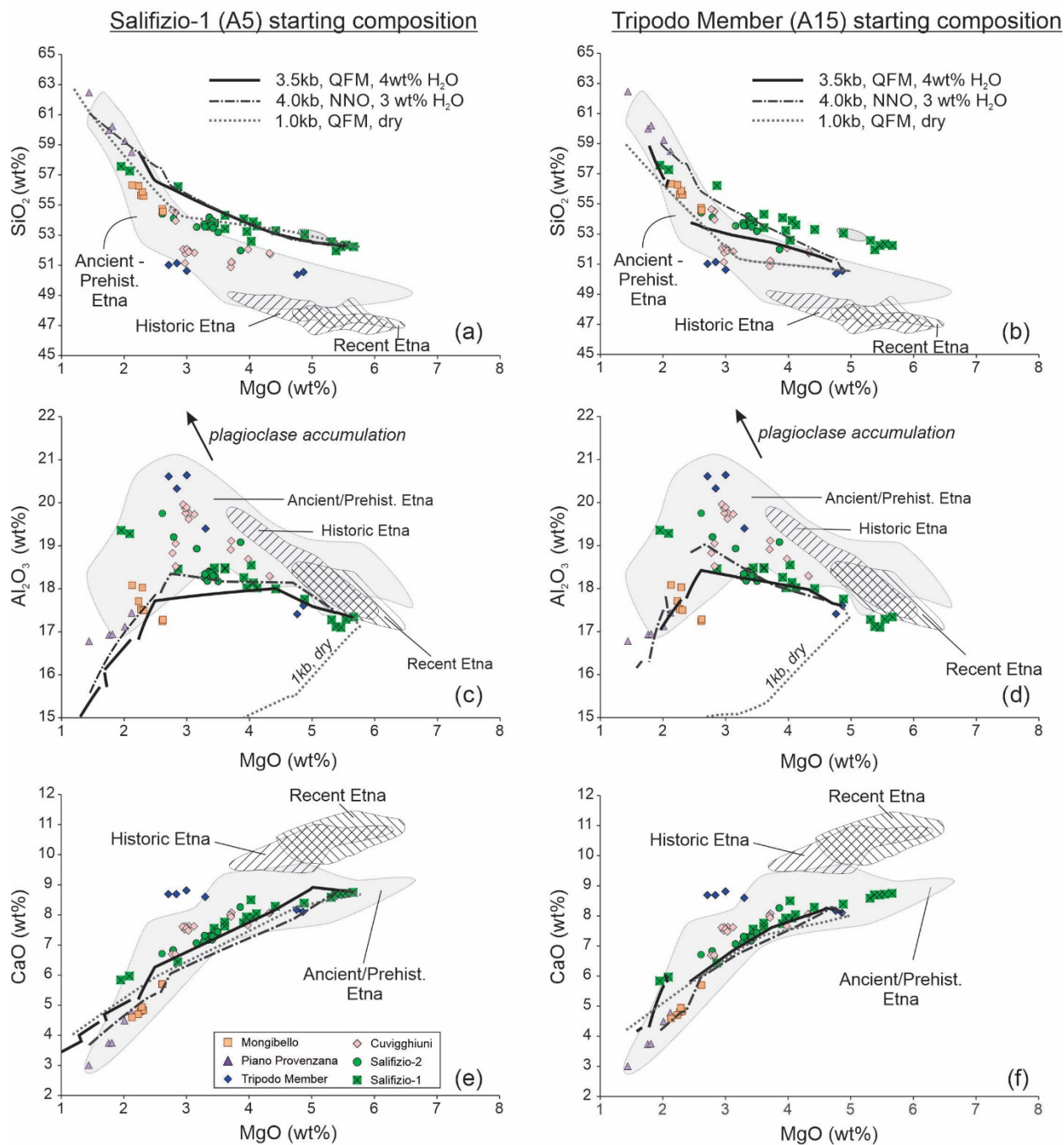
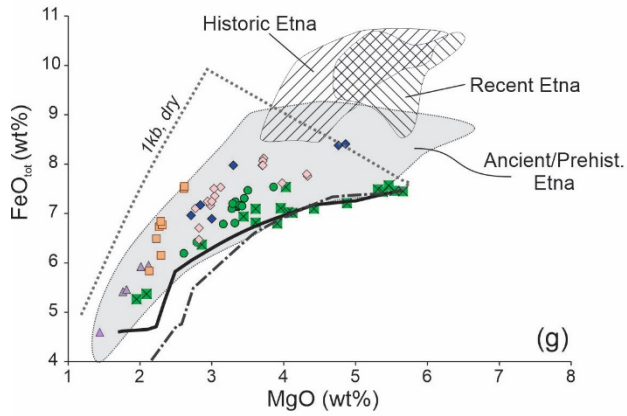


Figure 7 (continued)

Salifizio-1 (A5) starting composition



Tripodo Member (A15) starting composition

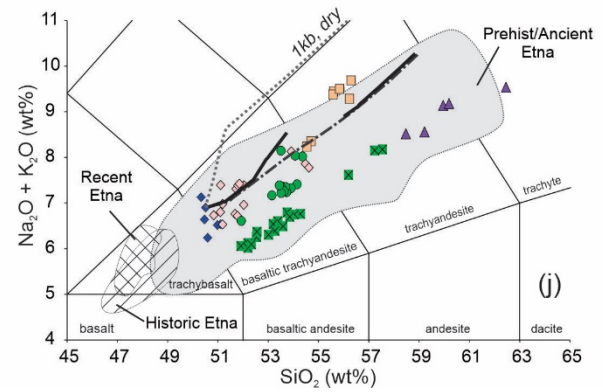
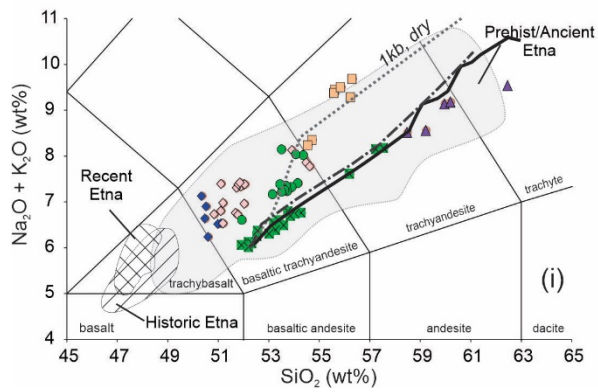
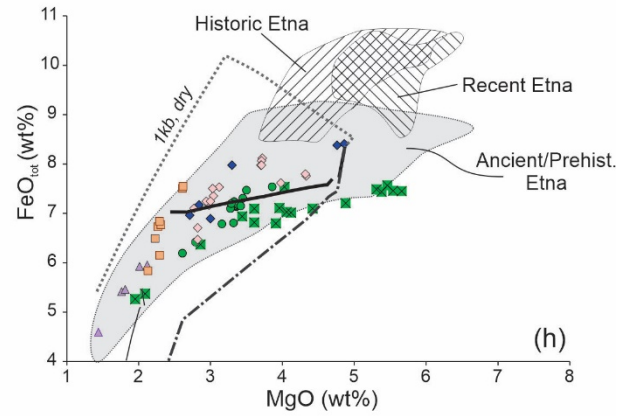


Fig. 8

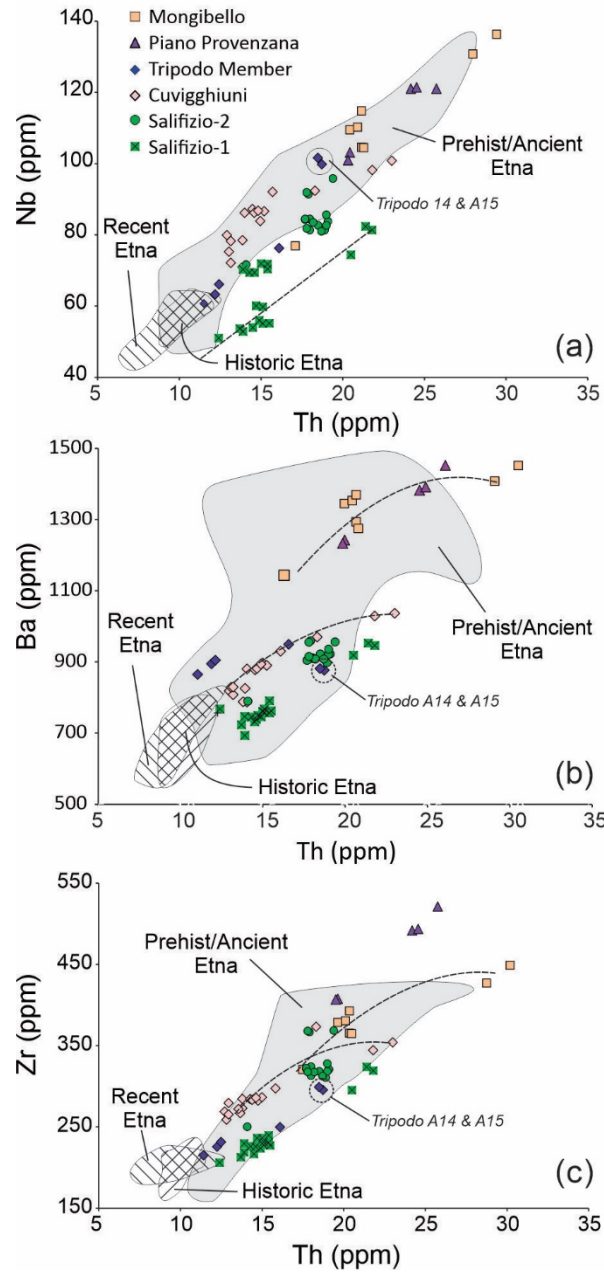


Fig. 9

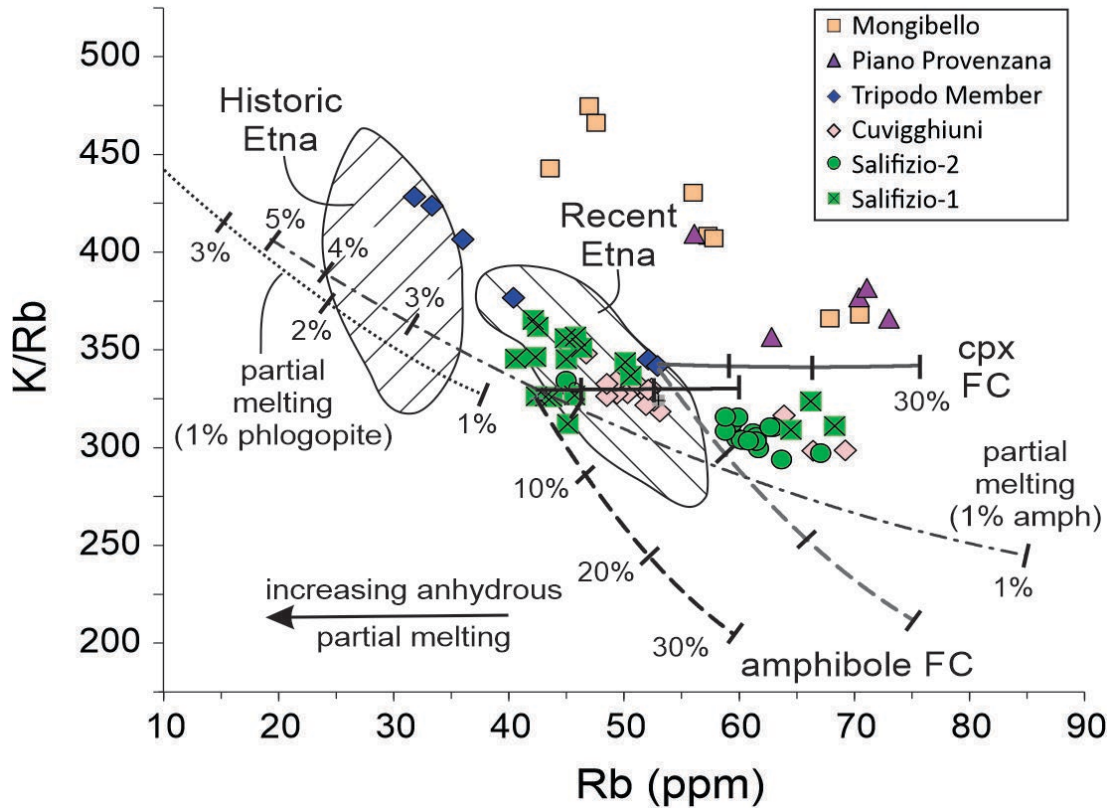


Figure 10

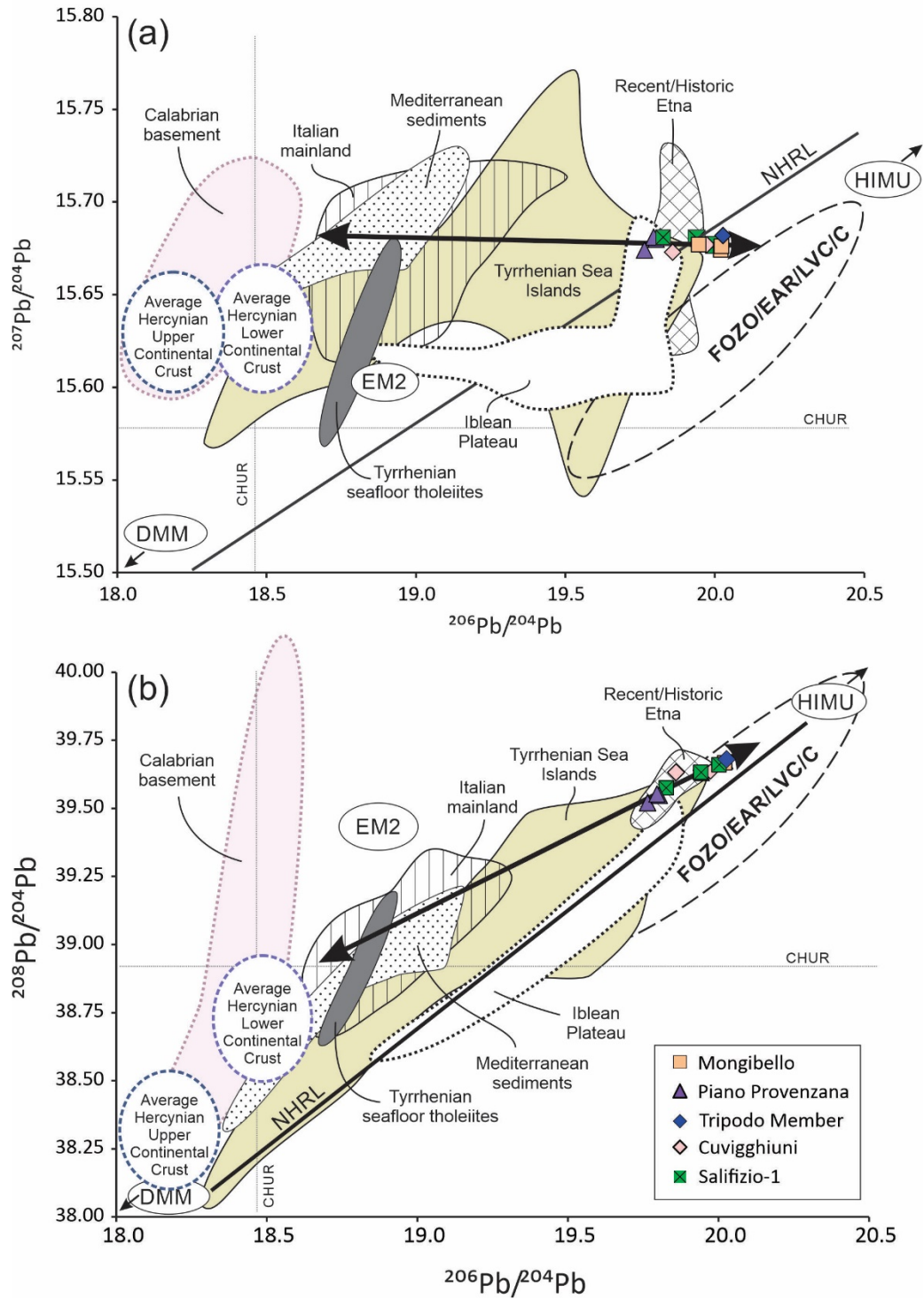
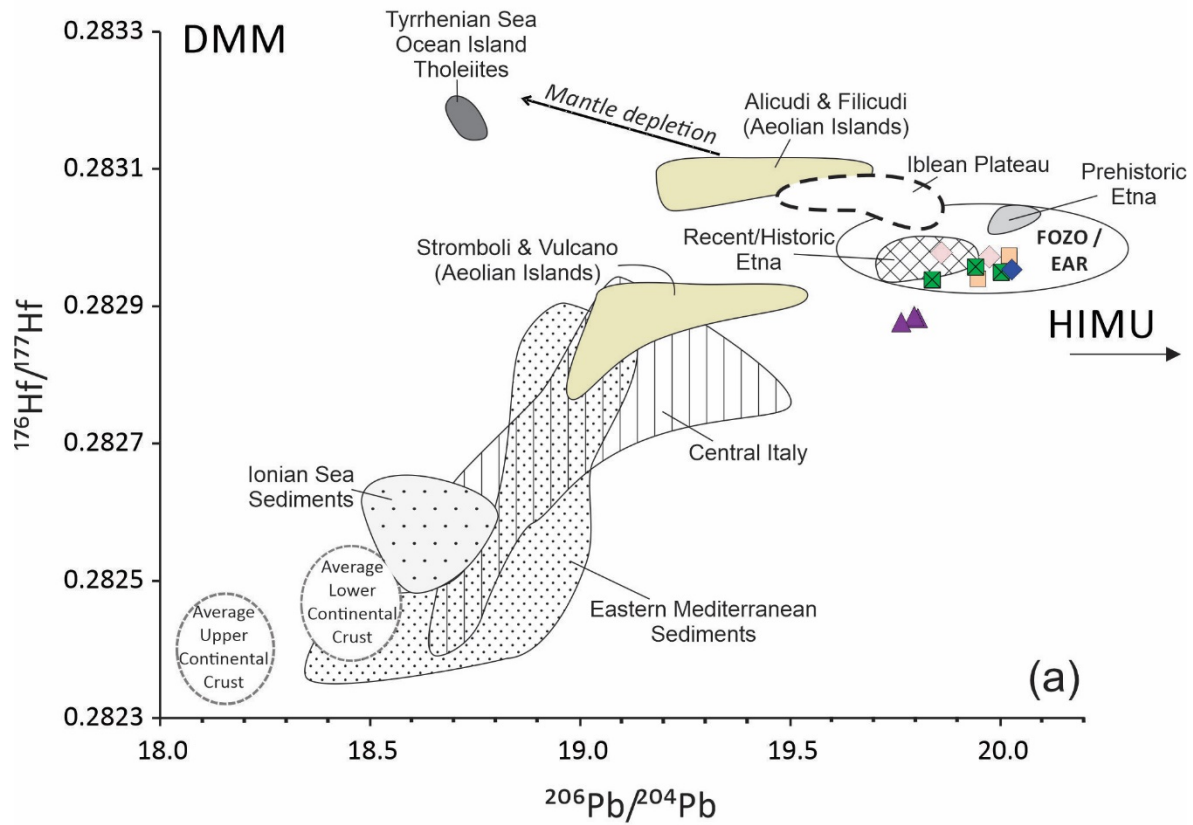
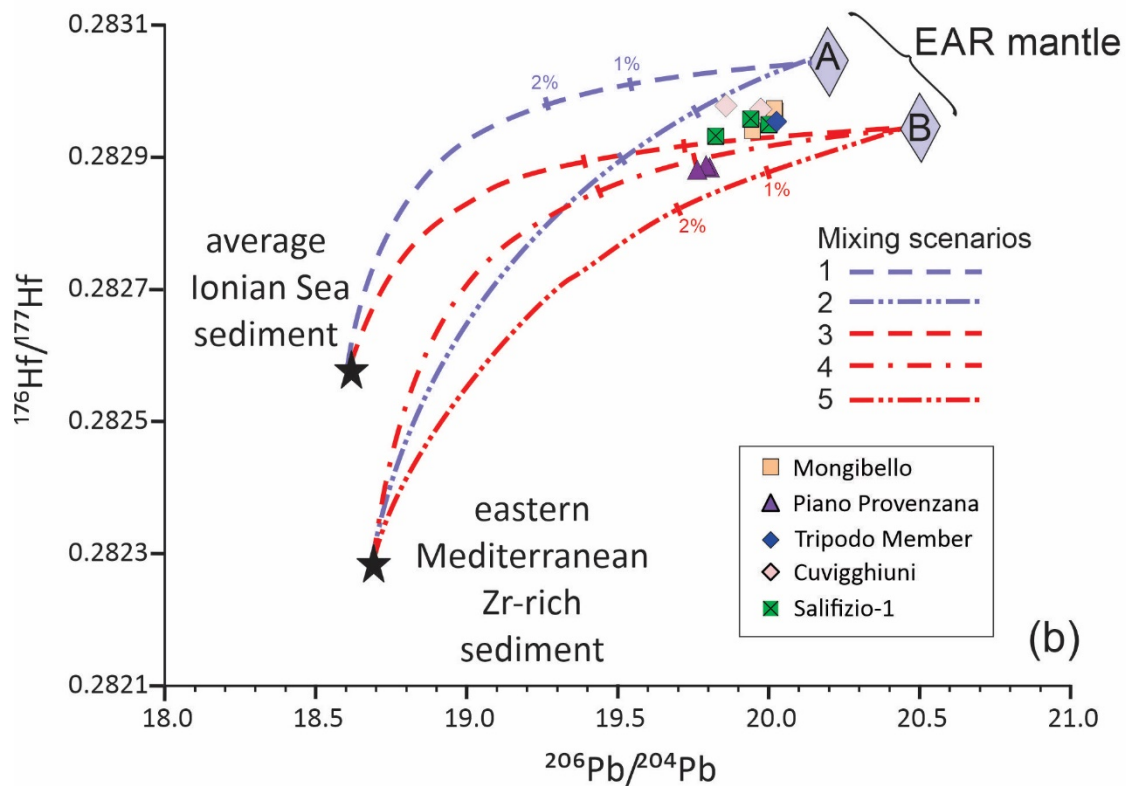


Figure 11



(a)



(b)

Figure 12

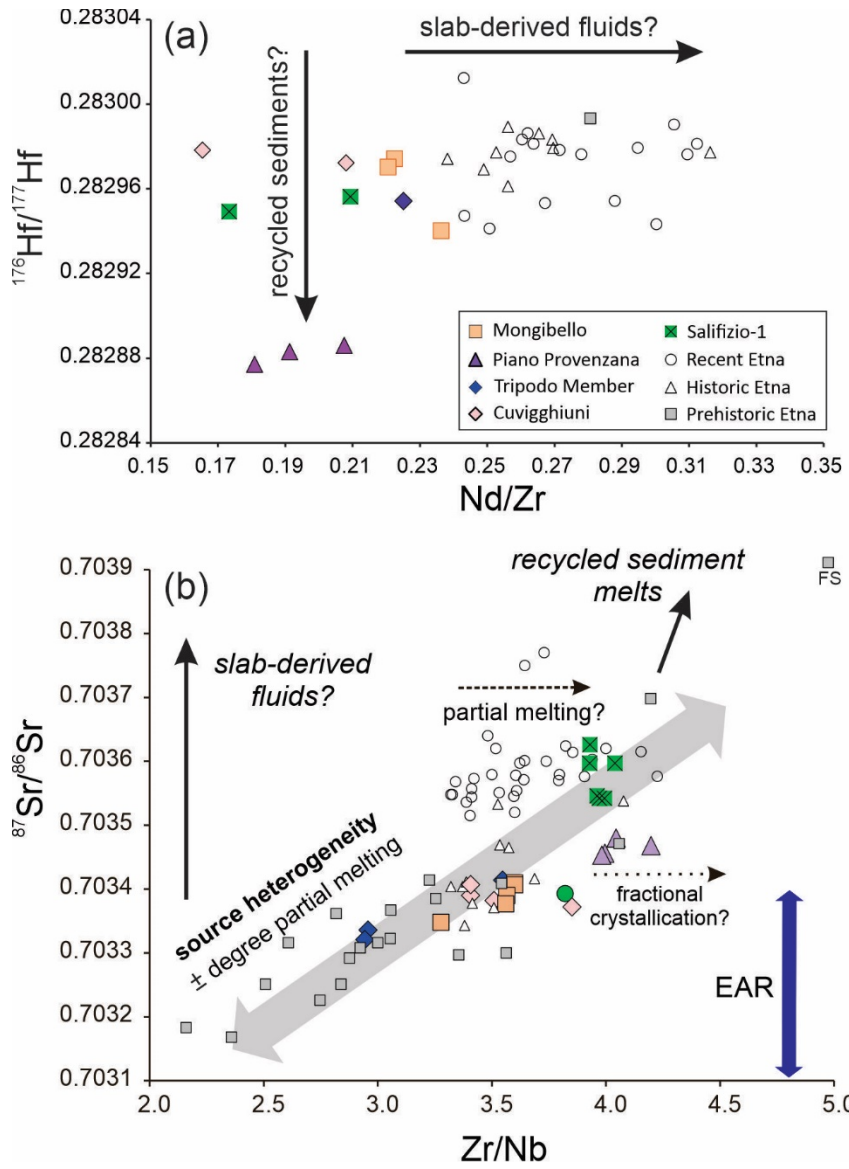


Table 1. Valle del Bove sections with associated lithostratigraphy and isotope age ranges

Recent (<130 yrs) & Historic (>130 yrs)

	Synthetic units		Lithostratigraphic units	Present	Volcanic Unit	Formation Name, Valle del Bove sections, this study			
						Section A	Section D	Section E	Section C
Prehistoric	Stratovolcano Supersynthem	Il Piano Synthem	Torre del Filosofo f. Pietracannone f.	60 ka	Mongibello ■			Pietracannone (lower member) (<15 ka)	Pietracannone (lower member) (<15 ka)
		Concazze Synthem	Portella Giumenta f. Monte Calvario f. Piano Provenzana f. Pizzi Deneri f. Serra della Concazze f.		Ellittico	Tripodo member (Piano Provenzana) (42-30 ka) ◆	Piano Provenzana (42-30 ka) ▲		
	Valle del Bove Supersynthem	Zappini Synthem	Canalone della Montagnola f. Serra Cuvigghiuni f. Aqua della Rocca f. Serra del Salifizio f. Valle degli Zappini f. Serra Giannicola Grande f. Monte fior di Cosimo f. Monte Scorsone f.	110 ka	Cuvigghiuni ◇	Canalone della Montagnola (79-70 ka)	Canalone della Montagnola (79-70 ka)	Canalone della Montagnola (79-70 ka)	Canalone della Montagnola (79-70 ka)
			Croce Menza Synthem		Piano del Trifoglietto f. Rocche f. Contrada Passo Cannelli f.	Salifizio-2 ●	Serra del Salifizio (85.6±6.8 ka)	Serra del Salifizio (85.6±6.8 ka)	Serra del Salifizio (85.6±6.8 ka)
Ancient	Basal Tholeiitic Supersynthem	S. Alfio Synthem	Valverde f. Moscarello f. Calanna f.	220 ka	Salifizio-1 ☒	Valle degli Zappini (>85.6 ka)	Valle degli Zappini (>85.6 ka)		
		Acreale Synthem	Timpa f. Timpa di Don Masi f.						
		Andrano Synthem	S. Maria di Licodia f.	~500 ka					
		Aci Trezza Synthem	Aci Castello f.						

Formation designations, volcanic units, synthems, supersynthems and isotopic ages from Branca et al. (2011b) and adapted from DeBeni et al. (2011). Colour coding used above corresponds to that in subsequent figures.

Table 2 Major and trace element concentrations of the Valle del Bove samples

	Section A: Valle del Tripodo				Section D: West of Serra dell' Acqua						Section E:	
	A1 ^a	A14 ^d	A15 ^d	A18b ^d	D5 ^a	D8 ^a	D10 ^a	D12 ^a	D13 ^a	D21 ^c	E2 ^b	E7 ^c
SiO ₂	57.57	50.37	50.55	51.14	53.89	53.30	53.79	56.22	52.59	54.51	53.78	51.22
TiO ₂	0.87	1.49	1.50	1.35	1.08	1.10	1.20	0.98	1.20	0.93	1.05	1.27
Al ₂ O ₃	19.36	17.41	17.61	20.33	18.14	18.00	18.48	18.46	18.55	18.52	18.29	19.13
Fe ₂ O ₃	5.85	9.23	9.26	7.96	7.78	7.95	7.69	7.09	8.29	7.46	8.06	8.87
MnO	0.12	0.17	0.17	0.17	0.15	0.14	0.14	0.15	0.15	0.16	0.16	0.16
MgO	1.95	4.76	4.86	2.84	4.06	4.42	3.44	2.86	4.03	2.82	3.45	3.72
CaO	5.84	8.17	8.10	8.69	7.93	8.29	7.56	6.44	8.50	6.66	7.27	8.08
Na ₂ O	5.59	4.96	4.72	4.83	4.72	4.53	4.83	5.21	4.60	5.37	5.10	4.57
K ₂ O	2.58	2.17	2.18	1.70	1.97	1.85	1.96	2.40	1.77	2.49	2.19	1.96
P ₂ O ₅	0.40	0.77	0.77	0.68	0.45	0.45	0.46	0.45	0.44	0.56	0.51	0.57
LOI	0.07	-0.20	-0.07	-0.09	0.07	-0.20	-0.11	-0.18	-0.40	0.17	-0.20	0.18
Total	100.21	99.29	99.64	99.59	100.24	99.83	99.44	100.08	99.71	99.66	99.67	99.74
Mg #	43	54	54	45	54	56	42	48	52	46	49	49
Rb	66	52	53	29	46	42	46	65	42	69	60	47
Sr	976	1143	1156	1662	1030	1042	1034	1019	1164	1192	1159	1403
Ba	953	877	881	943	746	723	750	919	768	1030	898	843
La	90	96	96	80	70	73	72	84	67	98	86	79
Ce	152	179	179	152	124	128	125	147	122	170	152	149
Nd	50	67	67	63	47	48	47	51	48	57	52	57
Zr	324	296	299	223	224	213	236	295	206	345	311	272
Nb	82	100	102	63	56	54	60	74	51	98	81	80
Y	26	30	29	29	23	24	26	25	25	27	25	26
Th	21	19	19	12	15	14	15	21	12	22	19	13

Table 2 (continued)

	Serra Pirciata			Section C: Serra Vavalaci							
	E8 ^c	E11 ^e	E13 ^f	C7 ^c	C19 ^e	C21 ^e	C22 ^e	C24 ^f	C25 ^f	C26 ^f	C27 ^f
SiO ₂	51.93	59.98	54.74	51.72	58.50	59.24	62.47	54.57	55.64	55.61	55.87
TiO ₂	1.19	1.39	1.62	1.22	1.44	1.35	1.12	1.61	1.55	1.55	1.40
Al ₂ O ₃	19.75	16.93	17.24	18.28	17.44	17.12	16.78	17.28	17.52	17.50	18.03
Fe ₂ O ₃	8.14	6.02	8.36	8.61	6.64	6.59	5.10	8.40	7.48	7.52	6.84
MnO	0.16	0.17	0.20	0.17	0.17	0.17	0.16	0.20	0.21	0.21	0.21
MgO	3.04	1.76	2.61	4.33	2.12	2.01	1.44	2.62	2.27	2.31	2.29
CaO	7.63	3.74	5.70	8.06	4.78	4.49	3.01	5.70	4.80	4.83	4.94
Na ₂ O	5.30	5.94	5.66	4.77	5.75	5.86	6.27	5.56	6.63	6.54	6.51
K ₂ O	2.04	3.20	2.69	1.99	2.77	2.70	3.27	2.67	2.82	2.83	2.99
P ₂ O ₅	0.64	0.46	0.79	0.53	0.62	0.60	0.35	0.79	0.63	0.62	0.60
LOI	-0.06	-0.04	-0.33	-0.08	0.00	-0.17	-0.01	-0.33	-0.06	-0.01	0.03
Total	99.75	99.55	99.28	99.59	100.23	99.96	99.96	99.07	99.48	99.52	99.71
Mg #	46	40	41	53	42	41	39	41	41	41	43
Rb	53	70	47	50	56	63	71	48	57	58	68
Sr	1460	787	1092	1211	995	995	726	1091	1029	1033	1016
Ba	909	1366	1291	817	1249	1242	1425	1277	1335	1342	1387
La	81	131	124	73	120	111	136	118	117	117	133
Ce	151	243	227	135	222	208	245	226	220	221	244
Nd	56	93	89	51	86	80	92	89	87	86	88
Zr	283	439	378	276	414	413	508	378	389	391	430
Nb	83	121	105	72	104	102	121	105	109	110	131
Y	26	46	42	24	42	38	49	39	43	43	42
Th	15	24	21	14	21	20	26	21	21	21	28

Major-element concentrations in wt%; trace elements in µg/g. Mg # calculated as $[Mg/(Mg+0.9Fe)]*100$

^a Salifizio-1

^b Salifizio-2

^c Cuvigghiuni

^d Tripodo Member

^e Piano Provenzana

^f Mongibello

Table 3 Isotopic compositions of the Valle del Bove samples

	Section A: Valle del Tripodo				Section D: West of Serra dell' Acqua					Section E:		
	A1 ^{a,1,2}	A14 ^{d,3}	A15 ^{d,1,2}	A18b ^{d,3}	D5 ^{a,1,2}	D8 ^{a,3}	D10 ^{a,3}	D12 ^{a,1,2}	D13 ^{a,3}	D21 ^{c,1,2}	E2 ^{b,3}	E7 ^{c1,2}
⁸⁷ Sr/ ⁸⁶ Sr	0.703640 ± 07	0.703336 ± 11	0.703335 ± 09	0.703414 ± 07	0.703556 ± 06	0.703546 ± 10	0.703597 ± 08	0.703544 ± 08	0.703534 ± 08	0.703396 ± 08	0.703393 ± 13	0.703421 ± 08
εSr	-12.2	-16.5	-16.5	-15.4	-13.4	-13.5	-12.8	-13.6	-13.7	-15.7	-15.7	-15.3
¹⁴³ Nd/ ¹⁴⁴ Nd	0.512837 ± 09	0.512902 ± 04	0.512906 ± 11	0.512893 ± 06	0.512868 ± 10	0.512872 ± 06	0.512864 ± 06	0.512876 ± 08	0.512871 ± 04	0.512908 ± 09	0.512900 ± 05	0.512907 ± 11
εNd	4.0	5.3	5.4	5.1	4.6	4.7	4.6	4.8	4.7	5.4	5.3	5.4
¹⁷⁶ Hf/ ¹⁷⁷ Hf	0.282931 ± 04		0.282954 ± 04		0.282956 ± 03			0.282949 ± 03		0.282978 ± 04		0.282972 ± 04
εHf	5.6		6.4		6.5			6.3		7.3		7.1
²⁰⁶ Pb/ ²⁰⁴ Pb	19.827		20.027		19.941			20.002		19.859		19.973
²⁰⁷ Pb/ ²⁰⁴ Pb	15.681		15.682		15.680			15.677		15.673		15.677
²⁰⁸ Pb/ ²⁰⁴ Pb	39.575		39.681		39.632			39.660		39.633		39.635

	Section E: Serra Pirciata (cont)				Section C: Serra Valalaci						
	E8 ^{c,3}	E11 ^{e,1,2}	E13 ^{f,3}	C7 ^{c,3}	C19 ^{e,1,2}	C21 ^{e,3}	C22 ^{e,1,2}	C24 ^{f,1,2}	C25 ^{f,1,2}	C26 ^{f,1,2}	C27 ^{f,3}
⁸⁷ Sr/ ⁸⁶ Sr	0.703390 ± 09	0.703470 ± 08	0.703410 ± 11	0.703372 ± 17	0.703467 ± 08	0.703480 ± 10	0.703482 ± 07	0.703421 ± 08	0.703404 ± 07	0.703391 ± 09	0.703348 ± 07
εSr	-15.8	-14.6	-15.5	-16.0	-14.7	-14.5	-14.5	-15.3	-15.6	-15.7	-16.4
¹⁴³ Nd/ ¹⁴⁴ Nd	0.512908 ± 06	0.512865 ± 11	0.512886 ± 06	0.512903 ± 07	0.512846 ± 11	0.512848 ± 05	0.512847 ± 09	0.512896 ± 11	0.512904 ± 10	0.512905 ± 09	0.512897 ± 07
εNd	5.4	4.6	5.0	5.3	4.2	4.3	4.2	5.2	5.3	5.4	5.2
¹⁷⁶ Hf/ ¹⁷⁷ Hf		0.282883 ± 03			0.282886 ± 05		0.282877 ± 04	0.282940 ± 03	0.282974 ± 04	0.282970 ± 04	
εHf		3.9			4.0		3.7	5.9	7.2	7.0	
²⁰⁶ Pb/ ²⁰⁴ Pb		19.803			19.795		19.764	19.946	20.021	20.023	
²⁰⁷ Pb/ ²⁰⁴ Pb		15.680			15.681		15.674	15.677	15.674	15.676	
²⁰⁸ Pb/ ²⁰⁴ Pb		39.548			39.551		39.521	39.629	39.667	39.672	

^aSalifizio-1; ^bSalifizio-2; ^cCuvigghiuni; ^dTripodo Member; ^ePiano Provenzana; ^fMongibello

¹ Sr and Nd isotopic analyses by E. Hegner, analyzed at LMU; ² Hf and Pb isotopic analyses by J. Blichert-Toft and J. Bryce, analyzed at ENSL and UNH; ³ Sr and Nd isotopic analyses by P.Z. Vroon, analyzed at RHUL. Errors of isotopic ratios are 2σ mean and refer to the last digits of the ratios. εNd and εHf calculated using the parameters of Bouvier et al. (2008) and Blichert-Toft and Albarède (1997), respectively.

Isotopic evolution of prehistoric magma sources of Mt. Etna, Sicily: Insights from the Valle Del Bove

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Contributions to Mineralogy and Petrology

Online Resources

Figure S1 (a) Plot of $\text{CaO}/\text{Al}_2\text{O}_3$ v Mg \# ; (b) plot of K_2O v SiO_2 . Data sources and symbols as in Figure 3, main text.

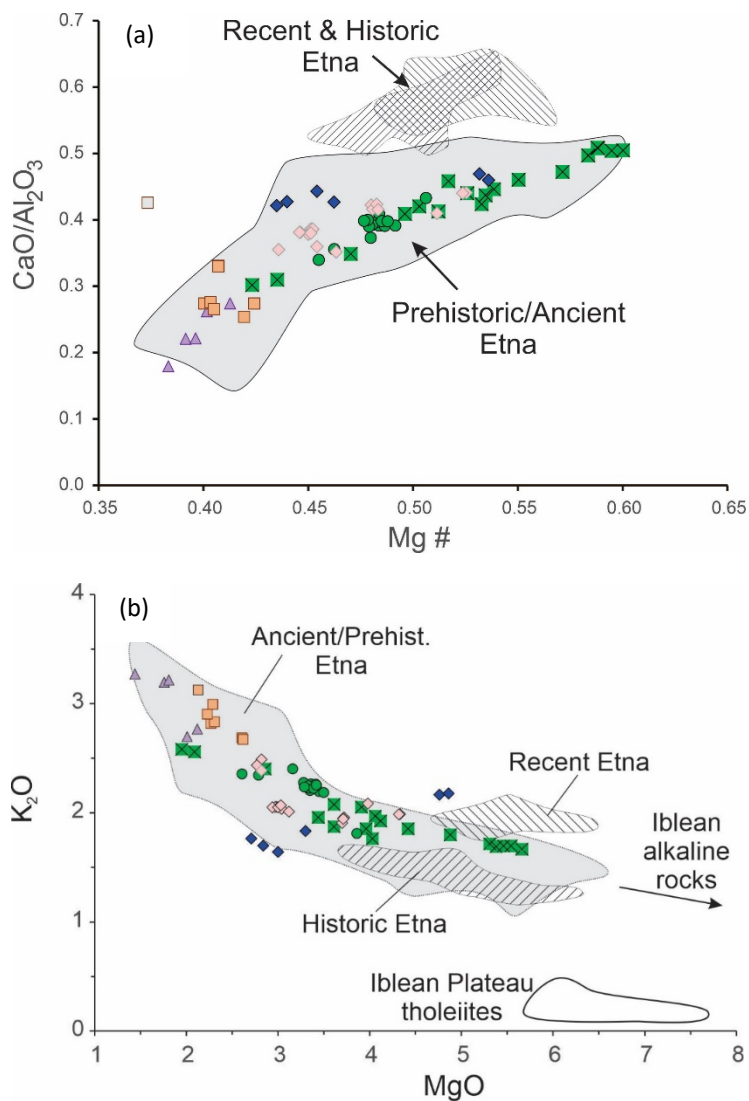


Figure S2 (a) Samples from the six Valle del Bove units plotted as Differentiation Index (DI, where $DI = \text{normative } q + \text{or} + ab + ne + lc$) vs degree of silica saturation / undersaturation, represented here as normative quartz and normative nepheline, respectively. Salifizio-1 samples with no normative quartz or nepheline are transitional, containing normative olivine and hypersthene. (b) Plot of Differentiation Index vs SiO_2 wt. %. Note the two distinct differentiation trends in both diagrams. Lavas from Salifizio-1 and Piano Provenzana become more silica saturated as they become more evolved. Those from Salifizio-2, Cuvigghiuni, Tripodo Member and Mongibello become more silica undersaturated with increasing differentiation.

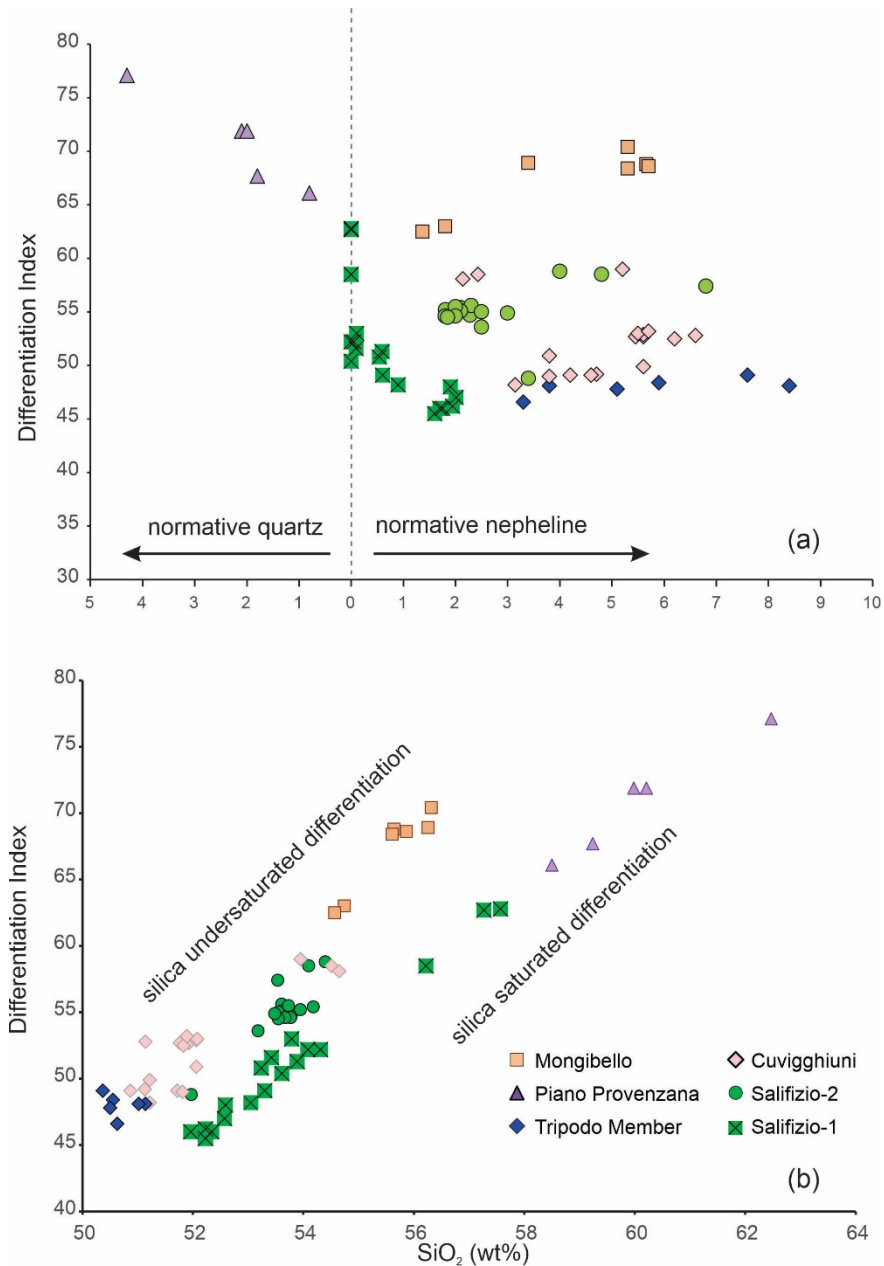


Figure S3 Plot of Differentiation Index versus Th (ppm) for samples from the six Valle del Bove units.

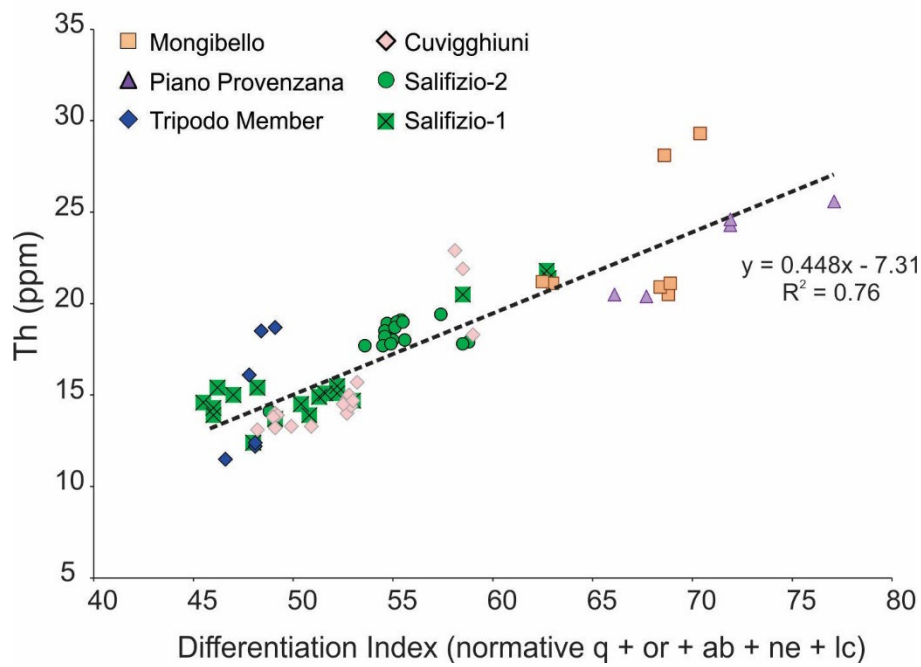
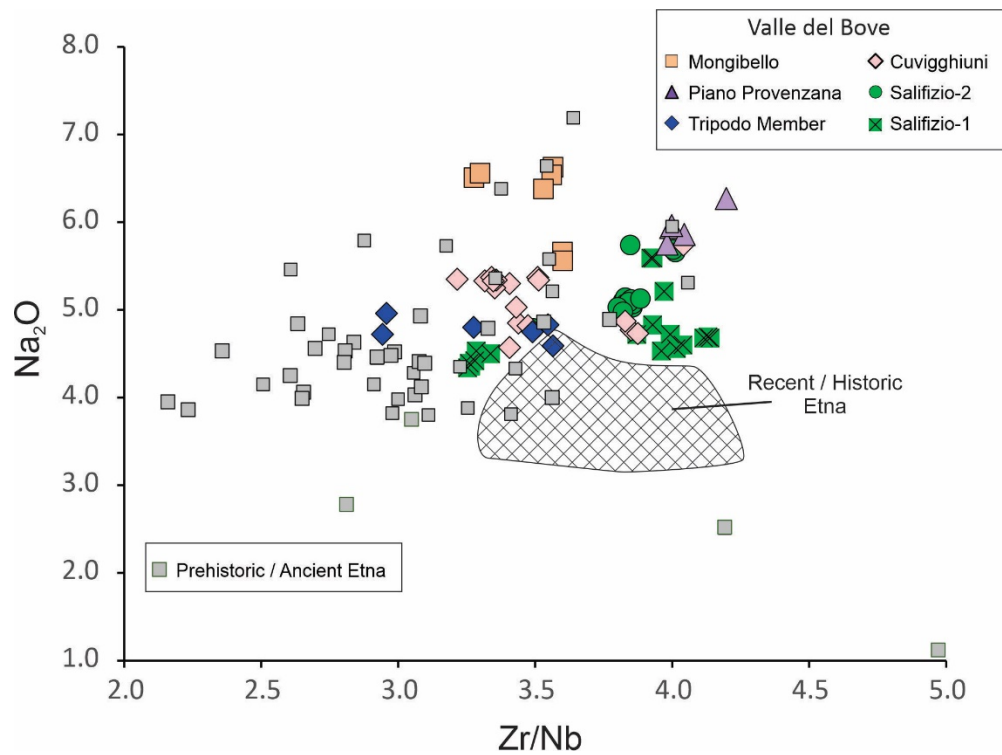


Figure S4. Plot of Na₂O concentrations versus Zr/Nb ratio. Data sources and symbols as in Figure 3 main text.



Isotopic evolution of prehistoric magma sources of Mt. Etna, Sicily: Insights from the Valle Del Bove

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Contributions to Mineralogy and Petrology

Calculation of fractional crystallisation using alphaMELTS 1.9

Isobaric fractional crystallisation pathways were calculated in forward simulation using rhyoliteMELTS 1.2.0 available in alphaMELTS 1.9 (Ghiorso & Sack, 1995; Asimow & Ghiorso, 1998). We chose to model isobaric fractional crystallisation to simulate processes operating in magma chambers at relatively fixed depths, rather than continuous fractional crystallisation over a range of pressures. We have calculated the evolution of each melt composition under 'wet' (initial H₂O content 3.5 to 4.0 wt %) and 'dry' (initial H₂O content 0.1wt %) conditions, and at oxygen fugacities buffered at nickel-nickel oxide (NNO) or quartz–fayalite–magnetite (QFM) using a temperature increment of 1°C. Two different starting compositions were assumed, A5 (Salifizio-1; Spence and Downes 2011) to represent the silica saturated fractionation trend and A15 (Tripodo Member, this study) to represent the silica undersaturated fractionation trend (see Online Resource, Fig. S1 and Table 2, main text). Starting conditions and resulting liquid lines of descent (LLD) for curves presented in Figure 7(main text) are summarised below. Numbers in parentheses are temperatures in degrees centigrade.

A5 liquid lines of descent summary

- (1) Starting conditions: QFM, 3.5kb, 4 wt% H₂O.

LLD: Liquidus T = 1107°C. LLD = spinel → olivine (Fo80) (1101) → cpx (1078) → plag (An71) (999)

Full alphaMELTS outputs in: ***A5 frac QFM 3500b 4H2O.xlsx***

- (2) Starting conditions: NNO, 4 kb, 3 wt% H₂O.

LLD: Liquidus T = 1135°C. LLD = spinel → olivine (Fo81) (1119) → cpx (1112) → plag (An67) (1032) → opx (1010).

Full alphaMELTS outputs in: ***A5 frac NNO 4000b 3H2O.xlsx***

- (3) Starting conditions: QFM, 1kb, dry.

LLD: Liquidus T = 1184°C. LLD = plag (An69) → olivine (Fo80) (1179) → cpx (1152) → spinel (1103).

Full alphaMELTS outputs in: ***A5 frac QFM 1000b dry.xlsx***

A15 liquid lines of descent summary

- (1) Starting conditions: QFM, 3.5 kb, 4 wt% H₂O.

LLD: Liquidus T = 1115 °C. LLD = spinel → ol (Fo77) (1082) → cpx (1078) → plag (An74) (1007).

Full alphaMELTS outputs in: ***A15 frac QFM 3500b 4H2O.xlsx***

(2) Starting conditions: NNO, 4 kb 3 wt% H₂O.

LLD: Liquidus T = 1144°C. LLD = spinel → ol1 (Fo79) (1095) → cpx (1094) → plag (An66) (1028) → ol2 (Fo75) (994)

Full alphaMELTS outputs in: ***A15 frac NNO 4000b 3H2O.xlsx***

(3) Starting conditions: QFM, 1 kb, dry.

LLD: Liquidus T = 1175°C. LLD = plag (An66) → ol (Fo79) (1168) → spinel (1141) → cpx (1129)

Full alphaMELTS outputs in: ***A15 frac QFM 1000b dry.xlsx***

The compiled alphaMELTS output files were produced in Excel format using software provided by Gualda and Ghiorso (2015).

References

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