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

P. D. Kempton1 · A. Spence2 · H. Downes2 · J. Blichert-Toft3 · J. G. Bryce4 · E. Hegner5 · P. Z. Vroon6

Received: 5 January 2021 / Accepted: 18 May 2021 / Published online: 25 June 2021
© The Author(s) 2021

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

Keywords Prehistoric Etna · Sr:Nd:Pb:Hf isotopes · Mantle heterogeneity

Introduction
Mount Etna, Europe’s largest active volcano, is located on the Mediterranean island of Sicily (Fig. 1) and lies in a complex tectonic setting near the convergence of the African and Eurasian plates. Eruptions of submarine and subaerial tholeiitic basalts between ~ 500 and 300 ka were gradually replaced by transitional to alkaline volcanism after ~ 250 ka via a succession of eruptive centres; this activity continues to the present day (McGuire 1982; Chester et al. 1985; Kieffer and Tanguy 1993; Scarth and Tanguy 2001; Patanè et al. 2006; Branca et al. 2008, 2011b). The magmatic evolution of Mt. Etna has been the subject of intense geochemical and isotopic research (e.g., Armienti et al. 1989; Marty et al. 1994; Tonarini et al. 1995, 2001; D’Orazio et al. 1997; Tanguy et al. 1997; Gasperini et al. 2002; Viccaro and Cristofolini 2008; Viccaro et al.
2011; Correale et al. 2014; Di Renzo et al. 2019), mainly using samples of recent (defined here as < 130 years old) and historic lavas, i.e., those erupted from the start of historic records to ca. 1890 CE. Sampling of prehistoric lavas on Mt. Etna is generally hampered by the widespread cover of these younger (historic and recent) eruptive products. Note the age boundary between historic and prehistoric is undefined, due to lack of data; the youngest prehistoric

**Fig. 1**  
(a) Public domain outline map of southern Italy with areas of interest indicated.  
(b) Outline of Mt. Etna with Valle del Bove, adapted from Chester et al. (1985).  
(c) Map of the southern wall of the Valle del Bove, adapted from the Geological Map of Etna Volcano (Branca et al. 2011b). Widths of sections A, D, E, and C are exaggerated for clarity. All samples analysed in this study were collected from one of the four sections labelled A, D, E and C.  
(d) Lithology of the six volcanic units as exposed in the four sections A, D, E and C.
samples included here are < ~ 15-kyr old (D’Orazio et al. 1997), whereas the oldest historic lavas are from the eighteenth century CE (Viccaro and Cristofolini 2008). Nevertheless, some basal tholeiites (here termed “ancient Etna”) and prehistoric (i.e., < ~ 250 ka) alkaline lavas from the eastern flank (Carter and Civetta 1977; Marty et al. 1994; D’Orazio et al. 1997; Tanguy et al. 1997; Tonarini et al. 2001; Corsaro et al. 2002) have been previously analysed, as have some of the older Plio-Pleistocene-age Iblean Plateau lavas (Fig. 1; Carter and Civetta 1977; Tonarini et al. 1996; Trua et al. 1998; Miller et al. 2017).

Several authors have discussed the isotopic evolution of the magma sources beneath Sicily and Mt. Etna (Marty et al. 1994; Tonarini et al. 2001; Corsaro and Pompilio 2004; Branca et al. 2008; Viccaro and Cristofolini 2008). Strontium, Nd, and Hf isotopic compositions of eruptive products from the Iblean Plateau and Mt. Etna show a broad temporal evolution from DMM-like (depleted MORB [mid-ocean-ridge basalt] mantle) for the Iblean Plateau toward BSE (bulk silicate Earth) for recent (< 130-year-old) eruptions. This has been interpreted by some authors as evidence for subduction of Ionian oceanic lithosphere beneath Mt. Etna and modification of the sub-Etna mantle by subduction-derived fluids (Gvirtzman and Nur 1999). Doglioni et al. (2001) and Gasperini et al. (2002) considered that differential slab rollback between the Sicilian and Ionian segments of the Apennines slab may have opened a slab window that has enabled upwelling and decompression partial melting of underlying asthenospheric mantle. Schiano et al. (2001) also suggested that subduction-derived fluids might be metasomatising the upwelling asthenospheric mantle beneath Mt. Etna. In contrast, Kamenetsky et al. (2007), Viccaro and Cristofolini (2008), Nicotra et al. (2013), Correale et al. (2014), Miller et al. (2017), and Viccaro and Zuccarello (2017) considered Etna’s isotopic variation to be the result of melting of a heterogeneous mixture of mantle spinel lherzolites and pyroxenites.

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

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

### Background and sampling

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

All samples for this study were collected from four stratigraphic sections in the southern wall of the Valle del Bove (Spence and Downes 2011). The sections from east to west are: Section A—Valle del Tripodo; Section D—west of Serra dell’Acqua; Section E—Serra Pirciata; and Section C—Serra Vavalaci (Fig. 1c). The stratigraphy, field relations, and petrography of the lavas can be inferred from the recent geological map of Etna by Branca et al. (2011b). In combination with the 40Ar/39Ar ages of De Beni et al. (2011) (Table 1), they comprise six discrete lithological units (Fig. 1d). From oldest to youngest, these are: (1) Salifizio-1; (2) Salifizio-2; (3) Cuvigghiuni; (4/5) the Valle del Tripodo member of the Piano Provenzana formation (Tripodo member) and Piano Provenzana; and (6) Mongibello. Note that we have tried to follow the terminology of Branca et al. (2011b), choosing terms from the geological map of Etna that was published after field sampling had been completed. However, we have inadvertently employed a mixture of terms relating to different volcanic centres (e.g., Cuvigghiuni, Mongibello) and lithostratigraphic units (e.g., Piano Provenzana, Tripodo). To improve clarity, Table 1 and the table legend at the bottom of Fig. 1 explain the equivalence between the terms used in this study and those of the geological map of Branca et al. (2011b).

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

The sampled lavas are extremely fresh, and most are vesicular to highly vesicular (> 20%). They range from aphyric to strongly porphyritic (25–40% phenocrysts), with plagioclase as the most common phenocryst phase. Some of the larger plagioclase phenocrysts exhibit zoning and/or sieve textures. Clinopyroxene (augite) phenocrysts/megacrysts range up to 5 mm in size; they typically exhibit oscillatory zoning and ophitic textures, enclosing aligned plagioclase laths and FeTi oxides. Glomeroporphyritic aggregates of plagioclase, augite and Ti-magnetite are also common. Although its modal abundance is relatively low, olivine is present as phenocrysts and in the groundmass of all but the most evolved and aphyric lavas. Kaersutite occurs rarely as small, ragged and broken, partially reabsorbed crystals with reaction rims of titanomagnetite, indicating instability during low-pressure fractionation. Accessory apatite is also present as inclusions in augite and some plagioclase. Further details of sample petrography can be found in Spence and Downes (2011).

### Table 1

| Synthemic units | Lithostratigraphic units | Present |
|-----------------|--------------------------|---------|
| **Stratovulcano Synthemic** | - | - |
| Il Piano Synthemic | Torre del Filosofo f | - |
| | Pietracannone f. | - |
| Concaze Synthemic | Portella Giumenta f. | - |
| | Monte Calvario f. | - |
| | Piano Provenzana f. | - |
| | Pizz Dei Arei f. | - |
| | Serra della Concaze f. | - |
| **Prehistoric** | - | - |
| Valle del Bove Synthemic | Canalone della Montagna f. | - |
| | Serra Cuvigghiuni f. | - |
| | Aqua della Rocca f. | - |
| | Serra del Saliitto f. | - |
| | Valle degli Zappini f. | - |
| | Serra Giannicola Grande f. | - |
| | Monte Fior di Cosimo f. | - |
| | Monte Scosone f. | - |
| Croce Menza Synthemic | Piano del Trifaglittio f. | - |
| | Roccheta f. | - |
| | Contrada Passo Cannelli f. | - |
| **Ancient** | - | - |
| Tempo Synthemic | S. Affo Synthemic | - |
| | Valverde f. | - |
| | Moscardello f. | - |
| | Calanna f. | - |
| Aciare Synthemic | Timpa f. | - |
| | Timpa di Don Masi f. | - |
| Andranco Synthemic | S. Maria di Licodia f. | - |
| Aci Trezza Synthemic | Aci Castello f. | - |
| **Recent (<130 yrs) & Historic (>130 yrs)** | - | - |

**Valle del Bove sections with associated lithostratigraphy and isotope age ranges**

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

| Volcanic Unit | Formation Name, Valle del Bove sections, this study | Section A | Section D | Section E | Section C |
|---------------|---------------------------------------------------|----------|----------|----------|----------|
| Mongibello | Tripode member (Piano Provenzana) (42-30 ka) | - | - | - | - |
| Ellittico | Piano Provenzana (42-30 ka) | - | - | - | - |
| Cuvigghiuni | Canalone della Montagna (79-70 ka) | - | - | - | - |
| Salifizio-2 | Serra del Salifizio (85.6±6.8 ka) | - | - | - | - |
| Salifizio-1 | Valle degli Zappini (>85.6 ka) | - | - | - | - |

Formation designations, volcanic units, synthems, supersynthems and isotopic ages from Branca et al. (2011b) and adapted from DeBeni et al. (2011); colour coding using above corresponds to that in subsequent figures.
Sample preparation and methods

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

Strontium and Nd isotopic ratios on the 11 samples analysed at Royal Holloway University of London (Table 3) were determined following the method described by Thirwall (1991) and Thirwall et al. (1997). Strontium and Nd isotopic compositions were determined multi-dynamically using a VG354 5-collector mass spectrometer, following conventional dissolution and chemical separation without prior sample leaching. Data were collected during several analytical sessions (methods in Thirwall 1991), with reference materials reproducible to ±0.000020 and ±0.000008 (2SD) for 87Sr/86Sr and 143Nd/144Nd, respectively. For a few samples, small machine bias-corrections were made based on the difference between the means of the measuring period for NIST SRM 987 and a Nd in-house standard. The long-term laboratory precision for 87Sr/86Sr and 143Nd/144Nd is estimated at ca. 1.1 x 10^{-5} (2SD).

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

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

Results

Valle del Bove lavas are moderately evolved (50–62 wt% SiO2, Fig. 2a) and, based on the ratio of Na2O to K2O (1.9–2.8), the rocks are mildly sodic basaltic trachyandesites and trachyandesites, including one trachyte sample. Figure 2a also shows fields that encompass the range of compositions for recent (i.e., <130-years old) and historic (i.e., >130-years old) Etna lavas, along with the field for prehistoric and ancient Etna magmatic products. The Valle
## 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: Serra Pirciata |
|----------------|------------------------------|--------------------------------------|--------------------------|
|                | A1<sup>a</sup>               | A14<sup>a</sup>                      | A15<sup>d</sup>          | A18b<sup>d</sup>        |
| SiO<sub>2</sub> | 57.57                        | 50.37                                | 50.55                    | 51.14                   |
| TiO<sub>2</sub> | 0.87                         | 1.49                                 | 1.50                     | 1.35                    |
| Al<sub>2</sub>O<sub>3</sub> | 19.36                      | 17.41                                | 17.61                    | 20.33                   |
| Fe<sub>2</sub>O<sub>3</sub> | 5.85                       | 9.23                                 | 9.26                     | 7.96                    |
| MnO            | 0.12                         | 0.17                                 | 0.17                     | 0.17                    |
| MgO            | 1.95                         | 4.76                                 | 4.86                     | 7.78                    |
| CaO            | 5.84                         | 8.17                                 | 8.10                     | 7.93                    |
| Na<sub>2</sub>O | 5.84                         | 8.17                                 | 8.10                     | 7.93                    |
| K<sub>2</sub>O | 2.59                         | 4.96                                 | 4.72                     | 4.83                    |
| LOI            | 0.25                         | 0.77                                 | 0.77                     | 0.68                    |
| Total          | 100.21                       | 100.21                               | 100.21                   | 100.21                  |
| Mg #           | 43                           | 54                                   | 54                       | 45                      |
| Rb             | 66                           | 52                                   | 53                       | 29                      |
| Sr              | 976                          | 1143                                 | 1156                     | 1662                    |
| Ba              | 953                          | 877                                  | 881                      | 943                     |
| La              | 90                           | 96                                   | 96                       | 80                      |
| Ce              | 152                          | 179                                  | 179                      | 152                     |
| Nd              | 50                           | 67                                   | 67                       | 63                      |
| Zr              | 324                          | 296                                  | 299                      | 223                     |
| Nb              | 82                           | 100                                  | 102                      | 63                      |
| Y              | 26                           | 30                                   | 29                       | 23                      |
| Th              | 21                           | 19                                   | 19                       | 12                      |

|                | Section C: Serra Vavalaci   |
|----------------|------------------------------|
| SiO<sub>2</sub> | 51.93                       |
| TiO<sub>2</sub> | 1.19                         |
| Al<sub>2</sub>O<sub>3</sub> | 19.75                     |
| Fe<sub>2</sub>O<sub>3</sub> | 8.14                     |
| MnO            | 0.16                         |
| MgO            | 3.04                         |
| CaO            | 7.63                         |
| Na<sub>2</sub>O | 5.30                         |
| K<sub>2</sub>O | 2.04                         |
| P<sub>2</sub>O<sub>5</sub> | 0.64                      |
| LOI            | -0.06                        |
| Total          | 99.75                       |
| Mg #           | 46                           |
| Rb             | 53                           |
| Sr              | 1460                         |
| Ba              | 909                          |
| La              | 81                           |
| Ce              | 151                          |
| Nd              | 56                           |
| Zr              | 283                          |
| Nb              | 83                           |
| Y              | 26                           |

|                | Section C: Serra Vavalaci   |
|----------------|------------------------------|
| SiO<sub>2</sub> | 59.98                        |
| TiO<sub>2</sub> | 1.39                         |
| Al<sub>2</sub>O<sub>3</sub> | 16.93                     |
| Fe<sub>2</sub>O<sub>3</sub> | 6.02                     |
| MnO            | 0.17                         |
| MgO            | 1.76                         |
| CaO            | 3.74                         |
| Na<sub>2</sub>O | 5.94                         |
| K<sub>2</sub>O | 2.04                         |
| P<sub>2</sub>O<sub>5</sub> | 0.46                      |
| LOI            | -0.04                        |
| Total          | 99.55                       |
| Mg #           | 40                           |
| Rb             | 70                           |
| Sr              | 1460                         |
| Ba              | 909                          |
| La              | 81                           |
| Ce              | 151                          |
| Nd              | 56                           |
| Zr              | 283                          |
| Nb              | 83                           |
| Y              | 26                           |
del Bove lavas overlap the field for previously analysed prehistoric and ancient Etna lavas, but most of these rocks, including Valle del Bove, have higher concentrations of SiO$_2$ and total alkalis than recent and historic Etna lavas. In a K$_2$O versus SiO$_2$ discrimination diagram (Fig. 2b) (Peccerillo and Taylor 1976) most Etna rock samples, including Valle del Bove, fall within the high-K field. Recent Etna samples, however, are distinct, being more enriched in K$_2$O for a given SiO$_2$ concentration than all other Etna lavas, as shown previously by Clocchiatti et al. (1988).

Within the Valle del Bove suite, samples from Salifizio-1 and Piano Provenzana have consistently lower concentrations of K$_2$O and total alkalis for a given SiO$_2$ concentration than those of Salifizio-2, Cuvigghiuni, the Tripodo member, or Mongibello. Although the higher SiO$_2$ concentrations for prehistoric and ancient Etna samples suggest that these rocks are all more evolved than recent and historic Etna samples, plots of major element oxides versus MgO (Fig. 3) show that the least evolved lavas from Valle del Bove, particularly those from Salifizio-1, have similar MgO concentrations (and Mg numbers; see Online Resource 1, Fig. S1) to recent and historic Etna, suggesting similar degrees of magmatic evolution. Valle del Bove lavas are distinct in having higher SiO$_2$ for a given MgO concentration (Fig. 3a). They also have lower CaO, Al$_2$O$_3$, TiO$_2$, and FeO$_{total}$ concentrations and CaO/Al$_2$O$_3$ ratios. Recent Etna lavas have significantly higher K$_2$O for a given MgO concentration (see Online Resource 1, Fig. S1) than either historic or ancient/prehistoric Etna, including the Valle del Bove concentration than those of Salifizio-2, Cuvigghiuni, the Tripodo member, or Mongibello.

Although the higher SiO$_2$ concentrations for prehistoric and ancient Etna samples suggest that these rocks are all more evolved than recent and historic Etna samples, plots of major element oxides versus MgO (Fig. 3) show that the least evolved lavas from Valle del Bove, particularly those from Salifizio-1, have similar MgO concentrations (and Mg numbers; see Online Resource 1, Fig. S1) to recent and historic Etna, suggesting similar degrees of magmatic evolution. Valle del Bove lavas are distinct in having higher SiO$_2$ for a given MgO concentration (Fig. 3a). They also have lower CaO, Al$_2$O$_3$, TiO$_2$, and FeO$_{total}$ concentrations and CaO/Al$_2$O$_3$ ratios. Recent Etna lavas have significantly higher K$_2$O for a given MgO concentration (see Online Resource 1, Fig. S1) than either historic or ancient/prehistoric Etna, including the Valle del Bove concentration than those of Salifizio-2, Cuvigghiuni, the Tripodo member, or Mongibello.

The Valle del Bove lavas overlap the compositional fields for ancient and prehistoric Etna in Fig. 3, with a few notable exceptions. Salifizio-1 lavas, the oldest rocks in the suite, have SiO$_2$ concentrations higher than those of recent and historic Etna, but also higher than most other ancient and prehistoric Etna rocks (Fig. 3a). They also have lower Al$_2$O$_3$ and TiO$_2$ (Fig. 3c, e). Ancient and prehistoric Etna samples, including those from Valle del Bove, extend to more evolved compositions (i.e., lower MgO and higher SiO$_2$) than recent or historic Etna lavas.

Figure 4a shows the primitive-mantle-normalised incompatible element patterns for the Valle del Bove samples compared with those of ocean island basalts (OIB) representative of EM (enriched mantle) and HIMU (mantle with high time-integrated U/Pb) sources, as well as average global subducted sediments (GLOSS) and bulk continental crust. Figure 4b shows the data normalised to the composition of average recent Etna lavas. All Valle del Bove samples are enriched in most of the incompatible trace elements relative to recent and historic Etna basalts (Fig. 4b). Two units (Mongibello and Piano Provenzana) exhibit particular enrichment in nearly all incompatible trace elements except Sr and Ti, consistent with their evolved compositions (MgO concentrations < 2.6 wt%, Table 2; see also Figs. 2 and 3). In contrast, the least evolved samples (e.g., from Salifizio-1 and the Tripodo member) have compositions typical of intra-plate alkaline magmas, e.g., OIB-like, although with relative enrichments in Ba, Th, and Pb and depletions in Ti and K (Fig. 4a). Of note in this context are the high La/Nb ratios relative to average OIB compositions. The Tripodo member has a trace element pattern that is distinct from most other Valle del Bove units. It is more akin to historic Etna, particularly in terms of its low Th/Nb and Th/Ba ratios (Fig. 4b). However, the least-evolved Tripodo samples, A14 and A15, have higher concentrations of nearly all incompatible trace elements (Table 2) than the most-evolved samples, further

| Table 2 (continued) |
|---------------------|
| Serra Pirciata      |
| E8 $^c$ 15 24 21 14 21 21 21 21 28  |
| C19 $^c$ 21 20 26 21 21 21 21 21 28  |
| C19 $^c$ 21 20 26 21 21 21 21 21 28  |
| C21 $^c$ 21 20 26 21 21 21 21 21 28  |
| C22 $^c$ 21 20 26 21 21 21 21 21 28  |
| C24 $^c$ 21 20 26 21 21 21 21 21 28  |
| C25 $^c$ 21 20 26 21 21 21 21 21 28  |
| C26 $^c$ 21 20 26 21 21 21 21 21 28  |
| C27 $^c$ 21 20 26 21 21 21 21 21 28  |
| Section C: Serra Vavalaci |
| E8 $^c$ 15 24 21 14 21 20 26 21 21 28  |
| C19 $^c$ 21 20 26 21 21 21 21 21 28  |
| C19 $^c$ 21 20 26 21 21 21 21 21 28  |
| C21 $^c$ 21 20 26 21 21 21 21 21 28  |
| C22 $^c$ 21 20 26 21 21 21 21 21 28  |
| C24 $^c$ 21 20 26 21 21 21 21 21 28  |
| C25 $^c$ 21 20 26 21 21 21 21 21 28  |
| C26 $^c$ 21 20 26 21 21 21 21 21 28  |
| C27 $^c$ 21 20 26 21 21 21 21 21 28  |

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

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

2011); hence, the relationship between these two groups of Tripodo samples is unclear, but they may not be petrogenetically related.

The Valle del Bove lavas overlap the compositional fields for ancient and prehistoric Etna in Fig. 3, with a few notable exceptions. Salifizio-1 lavas, the oldest rocks in the suite, have SiO$_2$ concentrations higher than those of recent and historic Etna, but also higher than most other ancient and prehistoric Etna rocks (Fig. 3a). They also have lower Al$_2$O$_3$ and TiO$_2$ (Fig. 3c, e). Ancient and prehistoric Etna samples, including those from Valle del Bove, extend to more evolved compositions (i.e., lower MgO and higher SiO$_2$) than recent or historic Etna lavas.

Figure 4a shows the primitive-mantle-normalised incompatible element patterns for the Valle del Bove samples compared with those of ocean island basalts (OIB) representative of EM (enriched mantle) and HIMU (mantle with high time-integrated U/Pb) sources, as well as average global subducted sediments (GLOSS) and bulk continental crust. Figure 4b shows the data normalised to the composition of average recent Etna lavas. All Valle del Bove samples are enriched in most of the incompatible trace elements relative to recent and historic Etna basalts (Fig. 4b). Two units (Mongibello and Piano Provenzana) exhibit particular enrichment in nearly all incompatible trace elements except Sr and Ti, consistent with their evolved compositions (MgO concentrations < 2.6 wt%, Table 2; see also Figs. 2 and 3). In contrast, the least evolved samples (e.g., from Salifizio-1 and the Tripodo member) have compositions typical of intra-plate alkaline magmas, e.g., OIB-like, although with relative enrichments in Ba, Th, and Pb and depletions in Ti and K (Fig. 4a). Of note in this context are the high La/Nb ratios relative to average OIB compositions. The Tripodo member has a trace element pattern that is distinct from most other Valle del Bove units. It is more akin to historic Etna, particularly in terms of its low Th/Nb and Th/Ba ratios (Fig. 4b). However, the least-evolved Tripodo samples, A14 and A15, have higher concentrations of nearly all incompatible trace elements (Table 2) than the most-evolved samples, further
## Table 3 Isotopic compositions of the Valle del Bove samples

| Section A: Valle del Tripodo | Section D: West of Serra dell’Acqua | Section E | E8^1,2 | E12^1,2 | E13^1 |
|-----------------------------|-------------------------------------|-----------|-------|---------|-------|
| 87Sr/86Sr                   | 0.703390 ± 0.09                    | 0.703407  | 0.703410 ± 0.11 | 0.703417 ± 0.12 | 0.703420 ± 0.13 |
| εSr                        | −15.8                              | −14.6     | −15.5                        | −16.0                  | −16.7                  |
| 143Nd/144Nd                 | 0.512908 ± 0.06                    | 0.512865 ± 0.11 | 0.512886 ± 0.06 | 0.512893 ± 0.07 | 0.512902 ± 0.07 |
| εNd                        | 5.4                                | 4.6       | 5.0                        | 5.3                  | 4.2                  |
| 176Hf/177Hf                 | 0.282883 ± 0.03                    | 0.282886 ± 0.05 | 0.282887 ± 0.04 | 0.282940 ± 0.04 | 0.282974 ± 0.04 |
| εHf                        | 3.9                                | 4.0       | 3.7                        | 5.9                  | 7.2                  |

| Section E: Serra Pirciata (cont) | Section C: Serra Vavalaci |
|----------------------------------|---------------------------|
| E8^1,2                           | E12^1,2                    | E13^1      |
| C7^1,2                           | C19^1,2                    | C21^1,2    |
| C22^1,2                          | C24^1,2                    | C25^1,2    |
| C26^1,2                          | C27^1,2                    |
| 87Sr/86Sr                        | 0.703470 ± 0.08            | 0.703480 ± 0.10 | 0.703482 ± 0.07 | 0.703421 ± 0.08 | 0.703404 ± 0.07 |
| εSr                              | −14.6                       | −14.5      | −15.3                       | −15.6                  | −15.7                  |
| 143Nd/144Nd                      | 0.512864 ± 0.05             | 0.512848 ± 0.05 | 0.512847 ± 0.09 | 0.512896 ± 0.11 | 0.512904 ± 0.10 |
| εNd                              | 5.0                          | 4.2       | 5.2                        | 5.3                  | 5.4                  |
| 176Hf/177Hf                      | 0.282887 ± 0.04             | 0.282940 ± 0.03 | 0.282974 ± 0.04 | 0.282970 ± 0.04 |
| εHf                              | 7.0                          | 7.2       | 7.2                        | 7.0                  |

| 206Pb/204Pb                      | 19.803                      | 19.795     | 19.794                      | 19.746                 | 19.746                 |
| 207Pb/204Pb                      | 15.680                      | 15.677     | 15.677                      | 15.677                 | 15.677                 |
| 208Pb/204Pb                      | 39.548                      | 39.551     | 39.629                      | 39.667                 | 39.672                 |

---

Salifizio-1; Salifizio-2; Cuvigghiuni; Tripodo Member; Piano Provenzana; Mongibello

Sr and Nd isotopic analyses by E. Hegner, analyzed at LMU; Hf and Pb isotopic analyses by J. Blichert-Toft and J. Bryce, analyzed at ENSL and UNH; 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. ε Nd and ε Hf calculated using the parameters of Bouvier et al. (2008) and Blichert-Toft and Albarède (1997), respectively.
supporting the idea that these two groups of samples are not related by fractional crystallisation.

The Valle del Bove lavas show significant variations in $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70334–0.70364), $^{143}\text{Nd}/^{144}\text{Nd}$ (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 differences between the six units (Fig. 5). Samples from the oldest unit (Salifizio-1) have the highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of all the Valle del Bove units (> 0.7035). These rocks contrast with those of similar age from the northern wall of the Valle del Bove, i.e., the Rocca Capra (ca. 81–78 ka) (D’Orazio et al. 1997) and the prehistoric/ancient Etna rocks reported by Marty et al. (1994), all of which have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios < 0.70325 and $^{143}\text{Nd}/^{144}\text{Nd}$ > 0.51291. Instead, Salifizio-1 samples overlap the field of recent high-$^{87}\text{Sr}/^{86}\text{Sr}$ Etna lavas (Fig. 5a, b) in a Sr–Nd isotope diagram. They also have overlapping to lower $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios relative to recent Etna lavas (Fig. 5c, e). Their Hf isotopic compositions overlap those of most younger Valle del Bove units (except Piano Provenzana), but their $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are lower. Thus, the
isotopic data suggest that Salifizio-1 magmas were derived from a source isotopically similar to that of recent Etna magmas and distinct from that of other ancient and prehistoric Etna rocks. In contrast, the slightly younger (~85–70 ka) Salifizio-2 and Cuvigghiuni lavas 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 (Fig. 5a, c, e), as do lavas from the Tripodo member. However, even these samples have higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than most samples of ancient and prehistoric Etna (Marty et al. 1994; D’Orazio et al. 1997). All VdB units, however, have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the unusual prehistoric picrite, FS (pyroclastic fall deposit), analysed by Correale et al. (2014). The higher Sr isotopic ratio for this sample (0.70391) was attributed to crustal contamination, although the authors did not distinguish between contamination occurring in a shallow crustal magma chamber or via subduction modification of the mantle source.

The Piano Provenzana lavas have the lowest $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of all the analysed prehistoric lavas and almost the lowest $^{143}\text{Nd}/^{144}\text{Nd}$ (the Nd isotope values overlap those

Fig. 3 Major element variation diagrams for a $\text{SiO}_2$, b $\text{FeO}_{\text{eq}}$, c $\text{Al}_2\text{O}_3$, d $\text{CaO}$, e $\text{TiO}_2$, and f $\text{CaO}/\text{Al}_2\text{O}_3$ versus $\text{MgO}$ wt%. Data sources for ancient to recent Etna magmatism as in Fig. 2. Data for Iblean Plateau tholeiites from Tonarini et al. (1996) and Trua et al. (1998)
of Salifizio-1). The youngest Mongibello lavas return to isotopic ratios that are more typical of historic Etna, with higher $^{143}$Nd/$^{144}$Nd (Fig. 5b, d, f). The Hf and Sr isotopic compositions thus indicate the existence of at least three different components, two of which are predominant, i.e., the isotopically distinct sources of recent Etna lavas and historic/prehistoric Etna lavas, with five of the six Valle del Bove units overlapping these two fields. The third component, with an unusually low Hf isotopic composition for a given Sr or Nd isotopic composition, is seen only in the Piano Provenzana unit (Fig. 5c, e). This component has not previously been observed in samples from Mt. Etna, regardless of eruption age or major element composition.

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

Lead isotope data for lavas from the Iblean Plateau and Mt. Etna (Fig. 6) also show a trend from depleted towards more enriched source compositions over time. However, some of the variation in the literature data, particularly in $^{207}$Pb/$^{204}$Pb, may result, in part, from the greater analytical uncertainty of the older data collected using thermal ionisation mass spectrometry as compared with modern MC-ICP-MS data, which better control instrumental mass discrimination. There may also be some differences in sample preparation, particularly with regards to whether pre-dissolution leaching was applied. Lead isotope compositions of the Valle del Bove samples analysed using MC-ICP-MS with Tl-normalisation and sample-standard bracketing show tight linearity in Pb isotope space over the ~ 80 kyr time span considered (Fig. 6). The Valle del Bove units have relatively radiogenic Pb isotope compositions, overlapping the fields for recent, historic, and prehistoric/ancient Etna, and extending to higher $^{206}$Pb/$^{204}$Pb and $^{208}$Pb/$^{204}$Pb ratios than those from the Iblean Plateau. Among the Valle del Bove units, the Piano Provenzana lavas have the lowest $^{206}$Pb/$^{204}$Pb (19.76–19.80), whereas the Tripodo member is the most radiogenic (i.e., its source shows the highest time-integrated U/Pb of all samples). The radiogenic Pb isotope composition of the Tripodo member contrasts with its lower $^{87}$Sr/$^{86}$Sr than in the other samples (Fig. 5a), which suggests a source that is more incompatible element depleted (i.e., time-integrated depletion in Rb relative to Sr) than that of most other Valle del Bove lavas.

Discussion

Fractionation of Valle del Bove prehistoric magmas

The data points in the TAS diagram (Fig. 2a) suggest that most of the prehistoric Valle del Bove lavas are more evolved than recent and historic Etna eruptions (Tanguy et al. 1997), with the Mongibello and Piano Provenzana lavas amongst the most evolved. Salifizio-1 and Piano Provenzana lavas exhibit lower concentrations of total alkalai for a given SiO$_2$ concentration and are transitional to silica oversaturated in composition (i.e., up to 4.3 wt% normative quartz), whereas the Mongibello lavas are all silica undersaturated, with up to 6 wt% normative nepheline (see Online Resource 1, Fig. S2a). The lavas from Mongibello and Piano Provenzana are clearly the most evolved of the Valle del Bove samples, with
Differentiation Indices (DI = normative q + or + ab + ne + lc) of 63–77 (Fig. S2a), but they lie along two different differentiation trends (Fig. S2b). Samples from the Tripodo member, Cuvigghiuni, Salifizio-2, and Mongibello become more silica undersaturated as they become more evolved, whereas, those from Salifizio-1 and Piano Provenzana become more silica saturated as differentiation increases.
To better understand the effects of fractional crystallisation on the Valle del Bove lavas, we have modelled isobaric fractionation using alphaMELTS 1.9 (Ghiorso and Sack 1995; Asimow and Ghiorso 1998; Smith and Asimow 2005). The results are shown in diagrams of MgO versus major element oxides SiO$_2$, Al$_2$O$_3$, CaO, FeO$_{total}$, as well as Na$_2$O + K$_2$O versus SiO$_2$ (Fig. 7); details of the calculations are provided in Online Resource 2. Given the observation that the Valle del Bove suite includes at least two distinct differentiation trends, two different parental compositions have been assumed, one to represent the trend of increasing silica saturation (i.e., Salifizio-1 sample A5; Spence and Downes 2011) and the other to represent the trend of increasing silica undersaturation with increased differentiation (i.e., Tripodo member sample A15; Table 2). Figure 7 shows that, for both starting compositions, fractional crystallisation at low pressure (i.e., 1 kb or ~3 km) fails to reproduce the data, in particular the observed increase in Al$_2$O$_3$ and decreasing FeO$_{total}$ with decreasing MgO concentration. It also fails to reproduce the distribution of data on the TAS diagram (Fig. 7i, j), with low-pressure fractionation resulting in excessive enrichment in total alkalis. For these low-pressure calculations, we assumed ‘dry’ conditions (H$_2$O of 0.01 wt%), because of the low loss on ignition of the studied samples (Table 2). However, even if we assume higher water concentrations (e.g., 2 wt%), the model curves at low pressure (not shown) do not reproduce the data, in particular for Al$_2$O$_3$, FeO$_{total}$, and total alkalis.

In contrast, at moderate pressure (3.5 to 4 kb or ~10–12 km) and H$_2$O concentrations in the melt of ~3–4 wt%, the model curves reproduce the shape of the observed data distributions well. The difference in the residual melt pathways for low vs. moderate pressure is due to the expansion of the olivine stability field as pressure increases. At low pressures, plagioclase is the liquidus phase, followed by olivine and clinopyroxene in fairly rapid succession (see Online Resources 2 for details). The early stabilisation of plagioclase leads to a rapid depletion in Al$_2$O$_3$ as fractionation proceeds. At higher pressures, the olivine stability field expands, and the crystallisation sequence is typically spinel followed by olivine, followed closely by clinopyroxene, with plagioclase appearing much later. Under these conditions, Al$_2$O$_3$ increases until plagioclase starts to fractionate.

None of the models accurately reproduce the high Al$_2$O$_3$ concentrations of some samples from Cuvigliani and the Tripodo member (Fig. 7c, d). The MELTS models also fail to reproduce the variations in TiO$_2$ versus MgO (not shown). These discrepancies may, in part, be a function of uncertainties in the thermodynamic data used in the MELTS calculations and are associated with an over-stabilisation of spinel, a recognised problem of the MELTS software (Ghiorso et al. 2002). This leads to depletion in Al$_2$O$_3$, FeO, and TiO$_2$ in the calculated melts in excess of that in the actual rocks. Nonetheless, some of the Valle del Bove samples are plagioclase-rich, in particular the Tripodo lavas (Spence and Downes 2011). Hence, some of the observed compositional variation, particularly the enrichment in Al$_2$O$_3$, may be due to plagioclase accumulation at low pressures prior to eruption.

In summary, modelling with alphaMELTS 1.9 indicates that fractionation of the Valle del Bove lavas occurred in a magma chamber at moderate depths of ~10–12 km, which is consistent with interpretations based on geophysical data for the depth of present-day magma storage (Paonita et al. 2012; Mollo et al. 2015; Miller et al. 2017; Cannata et al. 2018). For the Valle del Bove lavas, fractionation is dominated by olivine and clinopyroxene. This contrasts with models for recent Etna in which the fractionation sequence is typically described as plagioclase, followed by clinopyroxene, olivine,
Fig. 7 Major element variation diagrams for a SiO$_2$, b FeO$_{total}$, c Al$_2$O$_3$, d CaO, e K$_2$O, and f TiO$_2$ versus MgO wt% showing fractional crystallisation pathways calculated using alphaMELTS 1.9. Details of calculations in Online Resources 2. a, c, e, g, and i assume a starting composition of Salifizio-1 lava A5. b, d, f, h, and j assume Tripodo member A15 as the starting composition. Three model scenarios are presented for both starting compositions: (1) 1 kb, QFM, 'dry'; (2) 3.5 kb, QFM, 4 wt% H$_2$O; (3) 4 kb, NNO, 3 wt% H$_2$O. Data sources for recent, historic, and ancient Etna as in Fig. 3.
titaniferous magnetite, and, in some cases, amphibole (Viccaro et al. 2011), all of which suggest a stronger imprint from shallower fractional crystallisation processes. Water concentrations of 3–4 wt% are consistent with the compositions of melt inclusions in olivine (Spilliaert et al. 2006), studies of Etna magma ascent rates (Armienti et al. 2013), and thermodynamic modelling (Kahl et al. 2015). Low values of loss on ignition (Table 2) suggest the Valle del Bove lavas were thoroughly degassed before eruption.

Source components of Etna magmatism: evidence from major and trace elements

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

We test this hypothesis using Th, a highly incompatible trace element, as a proxy for alkaline magma fractionation (Wilson et al. 1995) (Fig. 8). Thorium correlates positively with Differentiation Index in the Valle del Bove suite ($R^2 = 0.75$), further justifying this trace element approach (see Online Resources 1, Fig. S3). In the absence of significant crustal contamination, the ratio of two highly incompatible elements (i.e., $D \ll 1$) should remain largely unchanged during fractional crystallisation. Therefore, plots of Th versus other highly incompatible trace elements should produce linear arrays that project back to the ratio of the two elements in the parental magma, providing an indication of source composition and possible heterogeneity (e.g., Allegre et al. 1977; Joron and Treuil 1989). Given that the Valle del Bove lavas are characterised by an anhydrous phenocryst assemblage consisting of clinopyroxene + plagioclase + magnetite ± olivine (Spence and Downes 2011), elements such as Nb, Zr, and Ba should have similar incompatibility during fractional crystallisation in this system (see GERM database, https://earthref.org/KDD/). Figure 8a shows that most Valle del Bove lavas overlap the field of prehistoric/ancient Etna and form arrays with Nb/Th ratios similar to recent and historic Etna. Some lavas from Salifizio-1, however, appear to have evolved from a parental magma that was more enriched in Th relative to Nb. Moreover, if the Piano Provenzana lavas evolved from a transitional/silica-saturated parent similar to Salifizio-1, as suggested by Fig. 2 and S2, these lavas are significantly more enriched in Nb (or depleted in Th) than expected by fractional crystallisation alone. In the plots of Ba and Zr vs Th (Fig. 8b, c), the Valle del Bove samples again largely overlap the field for prehistoric/ancient Etna, but the slopes of the data at the highest degrees of fractionation are shallower than expected within individual units; that is, at the highest Th concentrations (i.e., highest fractionation), Ba and Zr concentrations are lower than expected. Instead, the data are better described by second–order polynomials ($R^2 > 0.86$), as shown in Fig. 8b, c. At lower Th concentrations (lower fractionation), the curves indicate similar Ba/Th and Zr/Th ratios for recent and historic Etna, but as magma differentiation increases, they deviate to lower Ba/Th and Zr/Th. This could be due to
fractionation of trace phases with higher $D$ values for these elements that appear later in the fractionation sequence, such as amphibole, biotite, or K-feldspar (for Ba), and zircon (for Zr). Nonetheless, as for Nb vs. Th, lavas from Salifizio-1 appear to have evolved from a parent that was enriched in Th relative to Ba and Zr, and the Piano Provenzana lavas have higher concentrations of Ba and Zr relative to Th than would be expected if they were derived from a silica-saturated parent similar to Salifizio-1. In addition, the two least evolved Tripodo member samples, A14 and A15 (MgO > 4.75 wt%; samples circled in Fig. 8a–c), clearly have higher concentrations of incompatible trace elements than the more evolved lavas from this unit (MgO < 3.3 wt%), opposite to what would be expected if the rocks were related by fractional crystallisation.

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

Despite the similarities in incompatible element ratios and, hence, potential source regions for recent to ancient Etna as suggested by Fig. 8, Fig. 4b shows that even the most primitive of the Valle del Bove samples, i.e., some samples from Salifizio-1 and the Tripodo member, are enriched in Ba, Th, Nb, Pb, and Zr relative to recent and historic Etna magmas. Furthermore, these two units are not only distinct from recent and historic Etna, but also different from one another, suggesting differences in source composition or petrogenesis. The Tripodo member has a trace element pattern similar to average historic Etna lavas, just at higher overall concentrations, consistent with the lavas being slightly more evolved (Fig. 3). In contrast, Salifizio-1 lavas have higher Rb and Th, but lower light rare earth elements (LREE) and Sr. Strong relative depletions in Sr indicate a role for plagioclase fractionation, and the trough at Ti reflects magnetite fractionation (Fig. 4b). The low K concentration would be consistent with fractionation of a K-bearing phase, such as biotite or K-feldspar, but neither of these phases is observed in the rocks. Instead, the relative depletion in K is more likely an indication of derivation from a source in which a K-bearing phase, such as phlogopite or amphibole, was residual during partial melting, as suggested by Viccaro and Cristofolini (2008) for recent Etna lavas.

This interpretation is consistent with our own modelling of K and Rb systematics for the Valle del Bove lavas (Fig. 9). In a plot of K/Rb ratio versus Rb concentration, the Valle del Bove samples overlap the fields for historic and recent Etna but extend to higher concentrations of Rb for a given K than seen in the younger Etna rocks, particularly for the highly evolved lavas from Piano Provenzana and Mongibello. The effects of clinopyroxene and amphibole fractionation are shown as the solid and dashed lines, respectively. Fractionation in the absence of a hydrous phase would increase Rb.
conclude that the Tripodo member lavas were derived by partial melting or from a different source. Etna suggests these magmas were either derived by larger degrees of partial melting is more consistent with increasing K/Rb ratios with decreasing Rb concentration as degree of partial melting increases, similar to the distribution shown by the Etna data. The phlogopite-bearing source, however, produces lower concentrations of Rb and higher K/Rb ratios for the same degree of partial melting relative to the amphibole-bearing source. More sophisticated melting models, such as non-modal batch melting or fractional melting, tend to produce higher Rb concentrations and K/Rb ratios for smaller degrees of partial melting. In contrast, partial melting of an anhydrous source tends to be higher in CaO/Al2O3 and TiO2 but lower in SiO2 for a given MgO concentration than those derived from peridotite melting (Kogiso et al. 2003; Condamine and Medard 2016). Thus, the higher SiO2, lower CaO/Al2O3, FeO, and TiO2 of prehistoric Etna magmas relative to recent and historic Etna (Fig. 3) are consistent with an increase in the proportion of pyroxenite in the source of Etna magmas over time.

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

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

**Source components of Etna magmatism: evidence from Sr:Nd:Pb:Hf isotopes**

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

Constraining the proportion of pyroxenite to peridotite in the mantle source is challenging because (a) pyroxenite compositions can vary widely (Downes 2007; Lambart et al. 2016) and (b) phase relations, and hence melt compositions, are pressure and temperature sensitive. Nonetheless, in broad terms, partial melts involving high proportions of pyroxenite in the source tend to be higher in CaO/Al2O3 and TiO2 but lower in SiO2 for a given MgO concentration than those derived from peridotite melting (Kogiso et al. 2003; Condamine and Medard 2016). Thus, the higher SiO2, lower CaO/Al2O3, FeO, and TiO2 of prehistoric Etna magmas relative to recent and historic Etna (Fig. 3) are consistent with an increase in the proportion of pyroxenite in the source of Etna magmas over time.

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

Recent and historic Etna lavas are generally considered to have been derived from an asthenospheric mantle
source (Wilson and Downes 2006), known variously as the low-velocity composition (LVC) of Hoernle et al. (1995), the European asthenospheric reservoir (EAR) of Cebrà and Wilson (1995), the common component (‘C’) of Hanan and Graham (1996), or the FOcal ZOne (FOZO) of Hart et al. (1992). This mantle component may itself be a mixture, with contributions from DMM (low $^{87}$Sr/$^{86}$Sr and radiogenic (high) Nd, Hf, and Pb isotopic compositions) and possibly EM1 sources (enriched mantle-1) (Stracke et al. 2005; Viccaro et al. 2011). The isotopic compositions of the Iblean Plateau lavas (Figs. 5, 6) indicate an origin from a more depleted mantle source than that feeding present-day Mt. Etna (Tonarini et al. 1996; Trua et al. 1998). Hence, modern Etna is no longer tapping the depleted mantle source of the older Iblean tholeiitic magmatism. Instead, modern Etna is being fed by an isotopically heterogeneous mantle source more typical of intra-plate ocean islands (Armienti et al. 1989; Tonarini et al. 2001; Viccaro and Cristofolini 2008).

Surprisingly, our study shows that Salifizio-1 lavas, the oldest lavas in our suite, have isotopic compositions similar to those of recently erupted Etna lavas, whereas, four slightly younger units (Salifizio-2, Cuvigghiuni, Tripodo, and Mongibello) have tapped a source very similar to that of historic Etna lavas (Fig. 5). In contrast, Piano Provenzana lavas show a unique isotopic signature that has not previously been recognised in the data for Mt. Etna. Although major and trace element data provide no evidence for significant involvement of crustal contamination in the petrogenesis of Valle del Bove lavas, we still need to consider this process with regard to the isotope data before we can confidently interpret this new isotopic signature as an indication of source heterogeneity.

**Crustal contamination versus a subducted sediment component: evidence from Sr:Nd:Pb:Hf isotopes**

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

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

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

The uniqueness of this component is particularly apparent in comparisons of the Valle del Bove units in $^{176}$Hf/$^{177}$Hf vs $^{206}$Pb/$^{204}$Pb in the context of the wider regional data set (Fig. 11a). Most of the Valle del Bove lavas again show a well-constrained array with one end-member in the FOZO/EAR field; the data partially overlap the field for recent and historic Etna, but are clearly distinct from the sources of the Iblean Plateau and Aeolian arc (Alicudi and Flicicudi), the compositions of which indicate greater time-integrated incompatible element depletion. Paired Hf–Pb isotopic data for other prehistoric Etna rocks are limited, but four analyses from the Timpe Santa Caterina phase of activity, i.e., 220–100 ka (Miller et al. 2017), have high Hf isotope values that overlap the composition of the Iblean Plateau. The Pb isotope compositions of these rocks are, however, more HIMU-like than those from the Iblean Plateau and, instead, are similar to the most radiogenic lavas from Valle del Bove. Thus, based on currently available data, the low Hf isotope values of the Piano Provenzana lavas are unlike any known Etna magmatic products.
Piano Provenzana: a new component in Etna magmatism?

Figures 5 and 11 indicate that the lavas from Piano Provenzana are isotopically unique among Etna magmatic products. One interpretation is that a brief episode of melting of an unusual sediment component in the slab beneath Sicily may have given rise to the source of the Piano Provenzana lavas. Comparisons of $^{176}$Hf/$^{177}$Hf and Nd/Zr (Fig. 12a) show that all the prehistoric lavas analysed in this study have lower Nd/Zr than recent or historic Etna, while only the Piano Provenzana lavas have Hf isotope compositions lower than recent and historic Etna. Thus, the lower Hf isotope signature in the Piano Provenzana unit might be related to zircon-rich sediments introduced into the mantle wedge prior to mixing with an upwelling melt generated from a more depleted mantle end-member, i.e., the “zircon effect” (Patchett et al. 1984; White et al. 1986; Blichert-Toft et al. 1999; Carpenter et al. 2009). Mixing calculations (Fig. 11b) show that isotopic signatures of most Valle del Bove samples can be
Fig. 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 data set for Italian/Tyrrhenian volcanic rocks and the field for LVC/EAR/FOZO/C field. Data sources as for Figs. 5 and 10 with additional Hf isotopic data for Italy and the Tyrrhenian Sea from Barnekow (2000), Conticelli and Peccei (1992), Prelević et al. (2010), and Miller et al. (2017). Average Hf isotopic composition for Hercynian lower and upper continental crust from Vervoort et al. (1999, 2000). Mediterranean sediment data from Klaver et al. (2015) and Kempton et al.  

(b) Five representative mixing scenarios between EAR-type mantle and possible subducted sediment calculated using IgPet (Carr and Gazel 2017). EAR mantle modelled using two compositions: EAR a is representative of prehistoric Etna from Timpe 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 HIMU-like and more typical of the most enriched Valle del Bove lavas, i.e., $^{176}\text{Hf}/^{177}\text{Hf}=0.28295$; $^{206}\text{Pb}/^{204}\text{Pb}=20.5$; Hf and Pb concentrations in both cases assume primitive mantle values of 0.309 and 0.185 ppm, respectively (Sun and McDonough 1989). Average Ionian 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; Pb = 12.3 ppm. Eastern Mediterranean Zr-rich sediment from Klaver et al. (2015): $^{176}\text{Hf}/^{177}\text{Hf}=0.28258$; $^{206}\text{Pb}/^{204}\text{Pb}=18.6$; Hf = 3.2 ppm; Pb = 12.5 ppm. Tick marks on the mixing curves represent 1% and 2% mixing of the sediment component into the EAR mantle source; further percentages of mixing omitted from the figure for clarity.
explained by incorporation into a FOZO/EAR-type mantle source of <2 wt% sediment similar in composition to that of the Ionian Sea (Kempton et al. 2018). The Piano Provenzana samples, however, require a sediment contaminant with a lower Hf isotope composition, such as the Zr-rich sediments of the eastern Mediterranean (Klaver et al. 2015). A similar model was used recently to explain the Hf–Nd isotope systematics of Miocene subduction-related rocks from Sardinia (Kempton et al. 2018).

However, if a subduction component is involved in the mantle source of the Piano Provenzana lavas, this addition must have occurred prior to 42–30 ka, the age of the Piano Provenzana lavas according to De Beni et al. (2011). Moreover, $^{87}\text{Sr} / ^{86}\text{Sr}$ appears to have been largely unaffected by this process relative to other lavas of Ellittico. The Tripodo member, for example, comprises low-$\text{SiO}_2$ lavas with an age range similar to that of the upper Piano Provenzana formation (Branca et al. 2011a; De 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 degree of isotopic offset of the Piano Provenzana lavas from other prehistoric Etna lavas (Figs. 5, 6, 12) decreases in the order: Hf > Nd > Pb > Sr. In other words, the fluid-immobile elements Hf and Nd show a greater offset than the fluid-mobile elements Pb and Sr.

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

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

Fig. 12 a $^{176}\text{Hf} / ^{177}\text{Hf}$ versus Nd/Zr ratios for the six Valle del Bove units, recent Etna, and historic Etna. Adapted from a diagram by Nicotra et al. (2013). b $^{87}\text{Sr} / ^{86}\text{Sr}$ versus Zr/Nb ratios for the six Valle del Bove units compared with the data fields for recent, historic, and ancient/prehistoric Etna; prehistoric Etna sample labelled FS is the unusual picrite reported by Correale et al. (2014). Solid black arrows indicate direction of compositional variation from slab-derived fluids and/or recycled sediment melts. Dashed arrow indicates compositional variation for recent Etna as a result of partial melting as proposed by Viccaro and Cristofolini (2008); dotted arrow indicates variation as a result of fractional crystallisation for most evolved VdB compositions where there is potential to fractionate Zr/Nb through crystallisation of phases like titanomagnetite or sphenic. EAR compositional range (double-headed arrow) from Cebrìa and Wilson (1995). Data sources as in Fig. 5
It could be argued that the trend is due to a fortuitous combination of subduction enrichment, which produces a vertical trend on the diagram through addition of radiogenic Sr, plus variation in Zr/Nb as a function of degree of partial melting induced by that fluid addition. This scenario implies that the degree of subduction modification correlates systematically with the degree of partial melting of the metasomatised mantle. However, the difference in degree of partial melting required to create the observed range of Zr/Nb ratios is at least a factor of 10, which would have a significant impact on the major element compositions of the magmas produced. In such a scenario, the lowest Zr/Nb should be significantly more enriched in other incompatible trace elements and probably more silica undersaturated than those at the high Zr/Nb end of the array, and such systematic variation is not observed for the data set as a whole (see Online Resources 1, Fig. S4). While we cannot entirely rule out this scenario, the impact from garnet pyroxenite in the matrix crosscut by streaks or veins of ‘ancient’ pyroxenite beneath Etna is heterogeneous, consisting of a lherzolite matrix crosscut by streaks or veins of ‘ancient’ pyroxenite of variable composition. More recent modification by subduction-derived fluids and/or melts may contribute to the petrogenesis of historic and recent Etna magmas.

This suggests there is a compositional, i.e., source heterogeneity, control involved in the genesis of Etna magmas, particularly ancient and prehistoric Etna. Melts derived from a pyroxenite-rich source should have higher Zr/Nb than those from a lherzolitic source. The positive correlation between Sr isotopes and Zr/Nb, therefore, suggests a role for ancient veins in the mantle rather than recent subduction influences. On the other hand, the offset of recent Etna lavas to higher Zr/Nb than those from the Iblean Plateau (Tonarini et al. 1996; Scribano et al. 2009; Bianchini et al. 2010). The Piano Provenzana parental melt may have formed in a discrete metasomatic zone in the mantle with an enriched crust-like signature (Downes 2007), i.e., veins with a lower Hf isotopic composition than the surrounding mantle but similar Sr isotopic composition, thus affecting the isotope composition of Hf more than that of Nd and Pb, and with little effect on $^{87}$Sr/$^{86}$Sr.

Summary and conclusions

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

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

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

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

5. The degree of magmatic differentiation of Valle del Bove lavas is similar to that of recent and historic Etna,
but parental magmas were different and those for recent Etna were more silica undersaturated. Differences may be a function of degree of partial melting but are more likely due to different source compositions and, particularly, different proportions of pyroxenite in the source.

6. MELTS modelling, together with isotopic and trace element data, suggest that the Valle del Bove parental magma contained ~ 3–4 wt% H2O and fractionated in a magma chamber at moderate depths of ~ 10–12 km.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00410-021-01804-6.

Acknowledgements JBT acknowledges financial support from the French Agence Nationale de la Recherche (grant ANR-10-BLAN-0603 M&Ms—Mantle Melting—Measurements, Models, Mechanisms). HD is grateful to the University of London for support for fieldwork, and to Dr Giz Marriner for assistance with the XRF analyses at RHUL. EH acknowledges financing of laboratory expenses by the Department of Earth & Environmental Sciences at LMU. JB is grateful to ENSL for a visiting professorship that supported her contributions. We are grateful to Philippe Telouk for support with the ENSL Nu plasma. JBT’s ANR-10-BLAN-0603 M&Ms grant covered the analyses. We thank John Morrison and Richard Spence for their work in production of Fig. 1. Two anonymous reviewers are thanked for their courteous and constructive comments that improved the clarity of the paper.

Author contributions HD conceived and designed the study. Material preparation was performed by AS, with analytical preparations and data produced by JBT, JB, EH, and PZV. The first draft of the manuscript was written by AS and all authors contributed with data analysis, interpretation, and writing. PDK performed the modelling and wrote the second draft of the manuscript, which all authors again contributed to.

Funding JBT acknowledges financial support from the French Agence Nationale de la Recherche (grant ANR-10-BLAN-0603 M&Ms—Mantle Melting—Measurements, Models, Mechanisms).

Availability of data and material (data transparency) All new data are provided in tables presented in this paper.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

Albarède F, Télouk P, Blichert-Toft J, Boyet M, Agranier A, Nelson BK (2004) Precise and accurate isotopic measurements using multiple-collector ICPMS. Geochim Cosmochim Acta 68:2725–2744

Allègre CJ, Treuil M, Minster J-F, Minster B, Albarède F (1977) Systematic use of trace element in igneous process. Contrib Mineral Petrol 60:57–75

Armiénti P, Innocenti F, Pettrini R, Pomplilio M, Villari L (1989) Petrology and Sr–Nd isotope geochemistry of recent lavas from Mt. Etna: bearing on the volcano feeding system. J Volc Geotherm Res 39:315–327

Armiénti P, Tomarini S, D’Orazio M, Innocenti F (2004) Genesis and evolution of Mt Etna alkaline lavas: petrological and Sr–Nd isotope constraints. Period Di Mineral 73:29–52

Armiénti P, Perinelli C, Putirka KD (2013) A new model to estimate deep-level magma ascent rates, with applications to Mt. Etna (Sicily, Italy). J Petrol 54(4):795–813. https://doi.org/10.1093/petrology/egs085

Asimov PD, Ghiorso MS (1998) Algorithmic modifications extending MELTS to calculate subsolidus phase relations. Am Mineral 83:1127–1132

Ayuso RA, De Vivo B, Rolandi G, Seal RR II, Paone A (1998) Geochemical and isotopic (Nd–Pb–Sr–O) variations bearing on the genesis of volcanic rocks from Vesuvius, Italy. J Volc and Geotherm Res 82:53–78

Barnekow P (2000) Volcanic rocks from central Italy: an Oxygen isotopic microanalytical and geochemical study. Ph.D. Thesis, University of Gottingen

Beccaluva L, Bonatti E, Dupuy C, Ferrara G, Innocenti F, Luccinelli F, Macera P, Pettrini R, Rossi PL, Serri G, Seyerl M, and Stena F (1990) Geochemistry and mineralogy of volcanic rocks from ODSP sites 650, 651, 655 and 654 in the Tyrrhenian Sea. In: Stewart NJ (ed) Proc Ocean Drilling Prog, Science Results. U.S. Govt. Print. Office Washington D.C., pp 49–73

Belkin HE, De Vivo B (1993) Fluid inclusion studies of ejected nodules from plinian eruptions of Mt. Somma-Vesuvius. J Volcanol Geotherm Res 58:98–100

Bianchini G, Yoshikawa M, Sapienza GT (2010) Comparative study of ultramafic xenoliths and associated lavas from South-Eastern Sicily: nature of the lithospheric mantle and insights on magma genesis. Mineral Petrol 98:111–121

Blichert-Toft J, Albarède F (1997) The Lu-Hf isotope geochemistry of chondrites and the evolution of the mantle-crust system. Earth Planet Sci Lett 148:243–258

Blichert-Toft J, Albarède F (2009) Mixing of isotopic heterogeneities in the Mauna Kea plume conduit. Earth Planet Sci Lett 282:190–200

Blichert-Toft J, Chauvel C, Albarède F (1997) Separation of Hf and Lu for high-precision isotope analysis of rock samples by magnetic sector-multiple collector ICP-MS. Contrib Mineral Petrol 127:248–260

Blichert-Toft J, Frey FA, Albarède F (1999) Hf isotope evidence for pelagic sediments in the source of Hawaiian basalts. Science 285:879–882

Bodinier JL, Vasseur G, Vernieres J, Dupuy C, Fabries J (1990) Mechanisms of mantle metasomatism: geochemical evidence from the Lherz orogenic peridotite. J Petrol 31:597–628

Bouvier A, Vervoort JD, Patchett PJ (2008) The Lu-Hf and Sm-Nd isotopic composition of CHUR: constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets. Earth Planet Sci Lett 273:48–57

Branca S, Colletti M, De Beni E, Wijbrans J (2008) Geological evolution of Mount Etna volcano (Italy) from earliest products until the first central volcanism (between 500 and 100 ka ago) inferred from geochronological and stratigraphic data. Intl J Earth Sci (geol Rundsch) 97:135–152
Brancato S, Coltellini M, Groppelli G (2011a) Geochemical evolution of a complex basaltic stratovolcano: Mount Etna, Italy. Ital J Geosci (boll Soc Geol It) 130:306–317

Brancato S, Coltellini M, Groppelli G, Lentini F (2011b) Geological map of Etna volcano, 1:50,000. Ital J Geosci (boll Soc Geol It) 130:265–291

Bryce JG, DePaolo DJ (2004) Pb isotopic heterogeneity in basaltic phenocrysts. Geochim Cosmochim Acta 68:4453–4468

Caggianelli A, Del Moro A, Paglionico A, Piccarreta G, Pinarelli L., Rottura A (1991) Lower crustal granite genesis connected with chemical fractionation in the continental crust of Calabria (Southern Italy). Eur J Mineral 3:155–180

Calanchi N, Pecceirillo A, Tranne C, Lucchini F, Rossi PM, Kempton P, Barbieri M, Wu TW (2002) Petrology and geochemistry of the Island of Panarea: implications for mantle evolution beneath the Aeolian island arc (Southern Tyrrenhian Sea, Italy). J Volcanol Geotherm Res 115:367–395

Calvari S, Groppelli G, Pasquare G (1994) Preliminary geological data on the southwestern wall of the Valle del Bove, Mt. Etna. Sicily Acta Vulcanol 5:15–30

Cannata A, Di Grazia G, Giuffrida M, Gresta S, Palano M, Sciotto M, Viccaro M, Zuccarello F (2018) Space-time evolution of magma storage and transfer at Mt. Etna volcano (Italy): The 2015–2016 reawakening of Voragine crater. Geochim Geophys Geosyst 19:471–495. https://doi.org/10.1002/2017GC007296

Carpentier M, Chauvel C, Mauryc R, Mattielli N (2009) The “zircon effect” as recorded by the chemical and Hf isotopic composition of Lesser Antilles forearc sediments. Earth Planet Sci Lett 287:86–96

Carr MJ, Gazel E (2017) Igpet software for modeling igneous processes: examples of application using the open educational version. Miner Planet 70:127–132

Carter SR, Civetta L (1977) Genetic implications of the Isotope and Geochemical characteristics of potassic volcanic from Mt. Etna (Southern Latium, Italy). Contrib Mineral Petrol 59:37–47

Civetta L, D’ Antonio M, Di Girolamo P (1994) Petrological and geochemical studies of basaltic eruptions of the Ischia and Procida Islands. Contrib Mineral Petrol 111:283–289

Cebrià JM, Wilson M (1995) Cenozoic mafic magmatism in Western/ Central Europe: a common European asthenospheric reservoir. Terra Nova Astd Supp 7:162

Chester DK, Duncan AM, Guest JE, Kilburn CRJ (1985) Mount Etna. Stanford University Press, The anatomy of a volcano (ISBN 0-8047-1308-4)

Civetta L, Innocenti F, Manetti P, Pecceirillo A, Poli G (1981) Geochemical characteristics of potassic volcanics from Mt. Etna (Southern Latium, Italy). Contrib Mineral Petrol 78:37–47

Civetta L, D’ Antonio M, Orsi G, Tilton GR (1998) The geochemistry of volcanic rocks from Pantelleria Island, Sicily Channel: petrogenesis and characteristics of the mantle source region. J Petrol 39:1453–1491

Clocchiatti R, Joron J-L., Treuil M (1988) The role of selective alkali contamination in the evolution of recent volcanic lavas of Mt. Etna J Volcanol Geotherm Res 34:241–249

Coltellini M, Del Carlo P, Pompilio M, Vezzoli L (2005) Explosive eruptions of a picrite: the 3930 BP subplinian eruption of Etna volcano (Italy). Geophys Res Lett 32:L23307. https://doi.org/10.1029/2005GL024271

Condamine P, Médard E (2016) Devidal J-L. (2016) Experimental melting of plagiogopy-peridotite in the garnet stability field. Contrib Mineral Petrol 171:95. https://doi.org/10.1007/s00410-016-1306-0

Conticelli S (1998) The effect of crustal contamination on ultrapotassic magmas with lamproitic affinit: mineralogical, geochemical and isotopic data from the Torre Alfina lavas and xenoliths, Central Italy. Chem Geol 149:51–81

Conticelli S, Pecceirillo A (1992) Petrology and geochemistry of potassic and ultrapotassic volcanism in Central Italy: petrogenesis and inferences on the evolution of the mantle sources. Lithos 28:221–240

Conticelli S, Francalanci I, Manetti P, Cioni R, Sbrana A (1997) Petrology and geochemistry of the ultrapotassic rocks from the Sabatini Volcanic District, central Italy: the role of evolutionary processes in the genesis of variably enriched alkali magmas. J Volcanol Geotherm Res 75:107–136

Conticelli S, Marchionni S, Rosa D, Giordano G, Boari E, Avanzinelli R (2009) Shoshonite and sub-ultrapotassic magmas from an ultrapotassic volcano: Sr–Nd–Pb isotope data on the Roccamonfina volcano rocks, Roman Magmatic Province, Southern Italy. Contrib Mineral Petrol 157:41–63

Correale A, Martelli M, Paonita A, Rizzo A, Brusca L, Scibria V (2012) New evidence of mantle heterogeneity beneath the Hyblean Plateau (southeast Sicily, Italy) as inferred from noble gases and geochemistry of ultramafic xenoliths. Lithos 132–133:70–81

Correale A, Paonita A, Martelli M, Rizzo A, Rotolo SG, Corsaro RA, Di Renzo V (2014) A two-component mantle source feeding Mt. Etna magmatism: Insights from the geochemistry of primitive magmas. Lithos 184–187:243–258

Corsaro RA, Pompilio M (2004) Dynamics of magmas at Mount Etna. Geophys Monogr 143:91–110

Corsaro RA, Neri M, Pompilio M (2002) Paleo-environmental and volcano-tectonic evolution of the southeastern flank of Mt. Etna during the last 225 ka inferred from the volcanic succession of the “Timpe”, Acireale. Sicily J Volc Geotherm Res 113:289–306

Corsaro RA, Miraglia L, Pompilio M (2007) Petrologic evidence of a complex plumbing system feeding the July–August 2001 eruption of Mount Etna, Sicily, Italy. Bull Volcanol 69:401–421

Crisci GM, De Rosa R, Esperanza S, Mazzuoli R, Sonnino M (1991) Temporal evolution of a three-component system: the Island of Lipari (Aeolian Arc, southern Italy). Bull Volcanol 53:207–221

D’Antonio M, Di Girolamo P (1994) Petrological and geochemical study of mafic shoshonitic volcanics from Procida–Vivara and Ventotene islands (Campanian Region, South Italy). Acta Vulcanol 5:69–80

D’Antonio M, Tilton GR, Civetta L (1996) Petrogenesis of Italian alkaline lavas deduced from Pb–Sr–Nd isotope relationships. Isotopic Studies of Crust–Mantle Evolution. AGU Monogr 95:253–267

D’Antonio M, Civetta L, Di Girolamo P (1999) Mantle source heterogeneity in the Campanian Region (South Italy) as inferred from geochemical and isotopic features of mafic volcanic rocks with shoshonitic affinity. Mineral Petrol 67:163–192

D’Orazio M, Tonarini S, Innocenti F, Pompilio M (1997) Northern Valle del Bove volcanic succession (Mt. Etna, Sicily): petrography, geochemistry and Sr–Nd isotope data. Acta Vulcanol 9:73–86

De Astis G, Pecceirillo A, Kempton PD, La Volpe L, Wu TW (2000) Transition from calc-alkaline to potassium-rich magmatism in subduction environments: geological and Sr, Nd, Pb isotopic constraints from the island of Vulcano (Aeolian arc). Contrib Mineral Petrol 139:684–703

De Astis G, Kempton PD, Pecceirillo A, Wu TW (2006) Trace element and isotopic variations from Mt. Vulture to Campanian volcanic rocks, Roman Magmatic Province, Southern Italy. Contrib Mineral Petrol 157:133–151

De Beni E, Branca S, Coltellini M, Groppelli G, Wijbrans JR (2011) 40Ar/39Ar isotopic dating of Etna volcanic succession. Ital J Geosci (boll Soc Geol It) 130:292–305

De Beni E, Branca S, Coltellini M, Groppelli G, Wijbrans JR (2011) 40Ar/39Ar isotopic dating of Etna volcanic succession. Ital J Geosci (boll Soc Geol It) 130:292–305

Del Moro A, Gioncada A, Pinarelli L, Sbrana A, Joron JL (1998) Sr, Nd, and Pb isotope evidence for open system evolution at Vulcano, Aeolian Arc, Italy. Lithos 43:81–106

Di Renzo V, Vita MA, Ariento I, Carandente A, Civetta L, D’Antonio M, Giordano F, Orsi G, Tonarini S (2007) Magmatic history of...
of Somma-Vesuvius on the basis of new geochemical and iso-
topic data from a deep borehole (Camaldoli della Torre). J Petrol 48:753–784

Di Renzo V, Corsaro RA, Miraglia L, Pompilio M, Civetta L (2019)
Long and short-term magma differentiation at Mt. Etna as revealed by Sr–Nd isotopes and geochemical data. Earth Sci Rev 190:112–130. https://doi.org/10.1016/j.earscirev.2018.12.008

Doglioni C, Innocenti F, Mariotti G (2001) Why Mt Etna? Terra Nova 13:25–31

Downes H (2007) The origin of spinel- and garnet-pyroxenites in the
Hercynian belt of Western Europe: Evidence from lower-crus-
tal granulitic xenoliths (French Massif Central). Chem Geol 83:209–231

Downes H, Kempton PD, Briot D, Harmon RS, Leyreloup AF (1991)
Pb and O systematics in granulite facies xenoliths, French Mas-
Sif Central: implications for crustal processes. Earth Planet Sci Lett 102:342–357

Downes H, Shaw A, Williamson BJ, Thrillwall MF (1997) Sr, Nd and 
Pb isotopes in Hercynian granodiorites and monzogranites, Massif Central, France. Chem Geol 136:99–122

Downes H, Thrillwall MF, Traylor SC (2001) Moiocene subduction-
related magnetism in southern Sardinia: Sr–Nd– and oxygen isotopic evidence for mantle source enrichment. J Volcan Geotherm Res 106:1–21

Eisele J, Abouchami W, Galer SJG, Hofmann AW (2003) The 320 
kyr Pb isotope evolution of Mauna Kea lavas recorded in the 
HSDP-2 drill core. Geochem Geophysics Geosyst 4:8710. https://
doi.org/10.1029/2002GC000339

Ellam RM, Hawkesworth CJ, Menzies MA, Rogers NW (1989) The 
volcanism of southern Italy: role of subduction and the relations-
ships between potassic and sodic alkaline magmatism. J Geophys Res 94:4589–4601

Esperança S, Crisci GM (1995) The island of Pantelleria: a case 
for the development of DMM-HIMU isotopic compositions in a long-lived extensional setting. Earth Planet Sci Lett 136:167–182

Esperança S, Crisci GM, De Rosa R, Mazzuoli R (1992) The role of the 
crust in the magmatic evolution of the Island of Lipari (Aeolian 
Islands, Italy). Contrib Mineral Petrol 112:450–562

Fiannacca P, Williams IS, Cirrincione R, Pezzino A (2008) Crustal 
contributions to Late Hercynian peraluminous magmatism in the 
southern Calabria-Peloritani orogen, southern Italy: petrogenic 
inferences and the Gondwana connection. J Petrol 49:1497–1514

Francalanci L, Taylor SR, McCulloch MT, Woodhead JD (1993) 
Geochemical and isotopic variations in the calc-alkaline rocks of 
Aeolian arc, southern Tyrrenhenian Sea, Italy: constraints on 
magma genesis. Contrib Mineral Petrol 113:300–313

Frey F, Prinz M (1978) Ultramafic inclusions from San Carlos, Ar-
ozo: Petrologic and geochemical data bearing on their petrogen-
esis. Earth Planet Sci Lett 38:129–176

Gasperini D, Blichert-Toft J, Bosch D, Del Moro A, Macera P, 
Albarède F (2002) Upwelling of deep mantle material through a 
plate window: evidence from the geochemistry of Italian basaltic 
volcanics. J Geophys Res 107(B12):2367

Gertisser R, Keller J (2000) From basalt to dacite: origin and evolution of the calc-alkaline series of Salina, Aeolian Arc, Italy. Contrib 
Mineral Petrol 139:607–626

Ghiorsso MS, Sack RO (1995) Chemical mass-transfer in magmatic 
processes IV. A revised and internally consistent thermodynamic model for the interpolation and extrapolation of liquid-solid equi-
libria in magmatic systems at elevated temperatures and pres-
sures. Contrib Mineral Petrol 119(2–3):197–212

Ghiorsso M S, Hirschmann MM, Reiners PW, Kress VC III (2002) 
The pMELTS: a revision of MELTS for improved calculation of

phase relations and major element partitioning related to partial 
melting of the mantle to 3 GPa. Geochem Geophys Geosyst. 
https://doi.org/10.1029/2001GC000217

Gioncada A, Mazzuoli R, Bisson M, Pareschi MT (2003) Petrology of 
volcanic products younger than 42 ka on the Lipari-Vulcano 
complex (Aeolian Islands, Italy): an example of volcanism con-
trolled by tectonics. J Volcan Geotherm Res 122:191–220

Guest JE, Chester DK, Duncan AM (1984) The Valle del Bove, Mount 
Etna: its origin and relation to the stratigraphy and structure of 
the volcano. J Volcan Geotherm Res 21:1–23

Gvirtzman Z, Nur A (1999) The formation of Mount Etna as the con-
sequence of slab rollback. Nature 401:782–785

Hanan BB, Graham DW (1996) Lead and helium isotope evidence from 
oceanic basalt for a common deep source of mantle plumes.
Science 272:991–995

Hart SR (1984) The DUPAL anomaly: a large-scale isotopic anomaly 
in the southern hemisphere. Nature 309:753–756

Hart SR, Hauri EH, Oschmann LA, Whitehead JA (1992) Mantle 
plumes and entrainment: isotopic evidence. Science 256:517–520

Harte B, Hunter RH, Kinny PD (1993) Melt geometry, movement and 
crystallization in relation to mantle dykes, veins and metasoma-
tism. Philos Trans R Soc Lond Ser A 342:1–21

Hegner E, Walter HJ, Satir M (1995) Pb–Sr–Nd isotopic compositions 
and trace element geochemistry of megacrysts and melilitites 
from the Tertiary Urach volcanic field: source composition of 
small volume melts under SW Germany. Contrib Mineral Petrol 123(3):322–335

Hoernle K, Zhang YS, Graham D (1995) Seismic and geochemical 
evidence for large-scale mantle upwelling beneath the eastern 
Atlantic and western and central Europe. Nature 374:339

Irving AJ (1980) Petrology and geochemistry of composite ultramafic 
xenoliths in alkaline basalts and implications for magmatic pro-
cesses within the mantle. Am J Sci 280A:389–426

Joron J-L, Treuil M (1989) Hygromagmaphile element distributions in 
oceanic basalts as fingerprints of partial melting and mantle het-
erogenecities: a specific approach and proposal of an identification and 
modelling method. Geol Soc Lond Spec Publ 42(1):277–299. 
https://doi.org/10.1144/GSL.SP.1989.042.01.17

Kahl M, Chakroborty S, Pompilio M, Costa F (2015) Constraints on 
the nature and evolution of the magma plumbing system of Mt. 
Etna volcano (1991–2008) from a combined thermodynamic and 
kineti modelling of the compositional record of minerals. J Pet-
rol 56(10):2025–2068. https://doi.org/10.1093/petrology/egv063

Kamenetsky VS, Pompilio M, Métrich N, Sobolev AV, Kuzmin DV, 
Klaver M, Djuly T, de Graaf S, Sakes A, Wijbrans J, Davies G, Vroon 
and trace element geochemistry of megacrysts and melilitites in a 
long-lived extensional setting. Earth Planet Sci Lett 102:342–357

Kieffer G, Tanguy J-C (1993) L’Etna: évolution structurale, magma-
ique et dynamique d’un volcan “polygenique.” Mem Soc Geol 
France 163:253–271

Kieffer G, Tanguy J-C (1993) L’Etna: évolution structurale, magma-
ique et dynamique d’un volcan “polygenique.” Mem Soc Geol 
France 163:253–271

Kipper G, Tanguy J-C (1993) L’Etna: évolution structurale, magma-
ique et dynamique d’un volcan “polygenique.” Mem Soc Geol 
France 163:253–271
Kogiso T, Hirschmann MM, Frost DJ (2003) High-pressure partial melting of garnet pyroxenite: possible mafic lithologies in the source of ocean island basalts. Earth Planet Sci Lett 216:603–617

Lambart S, Baker MB, Stolper EM (2016) The role of pyroxenite in basalt genesis: Melt-PX, a melting parameterization for mantle pyroxenites between 0.9 and 5 GPa. J Geophys Res Solid Earth 121:5708–5735. https://doi.org/10.1002/2015JB012762

Le Maitre RW (1984) A proposal by the IUGS Subcommission on the Systematics of Igneous Rocks for a chemical classification of volcanic rocks based on the total alkali silica (TAS) diagram. Aust J Earth Sci 31:243–255

Lo Giudice A (1970) Caratteri petrografici e petrochimici delle lave del Complesso di Vavalaci (Etna). Rend Soc Ital Mineral Et Petrol 26:687–732

Marty B, Trull T, Lussiez P, Basile I, Tanguy J-C (1994) He, Ar, O, Sr and Nd isotope constraints on the origin and evolution of Mount Etna magmatism. Earth Planet Sci Lett 126:23–39

McGuire WJ (1982) Evolution of the Etna volcano: information from the southern wall of the Valle del Bove caldera. J Volcanol Geotherm Res 13:241–271

Michaud V (1995) Crustal xenoliths in recent hawaiites from Mount Etna, Italy: evidence for alkali exchanges during magma-wall rock interaction. Chem Geol 122:21–42

Miller SA, Myers M, Fahnestock MF, Bryce JG, Blichtert-Toft J (2017) Magma dynamics of ancient Mt. Etna inferred from clinopyroxene isotopic and trace element systematics. Geochim Persp Lett 4:47–52

Mollo S, Giacononi PP, Coltorti M, Fertilio C, Iezzia G, Scarlato P (2015) Reconstruction of magmatic variables governing recent Etnan eruptions: Constraints from mineral chemistry and P-T-fO2–H2O modeling. Lithos 212–215:311–320

Nicotra E, Viccaro M, Cristofolini R, Conticelli S (2013) Changes of magma geochemistry at Mt. Etna during the last 45ka due to sampling of a variegated mantle. Goldschmidt Conf Abstr:1846

Orsi G, Civetta L, D’ Antonio M, Di Girolamo P, Piochi M (1995) Step-filling and development of a three-layer magma chamber: the Neapolitan Yellow Tuff case history. J Volcanol Geotherm Res 67:291–312

Paonita A, Caracausi A, Iacono-Marziano G, Martelli M, Rizzo A (2012) Geochemical evidence for mixing between fluids exsolved at different depths in the magmatic system of Mt Etna (Italy). Geochim Cosmochim Acta 84:380–394

Pappalardo L, Piochi M, D’ Antonio M, Civetta L, Pettrini R (2002) Evidence for multi-stage magmatic evolution during the past 60 kyr at Campi Flegrei (Italy) deduced from Sr, Nd and Pb isotope data. J Petrol 43:1415–1434

Patanè G, La Delfa S, Tanguy J-C (2006) Volcanism and mantle-crust evolution: the Etna case. Earth Planet Sci Lett 241:831–843

Patchett PJ, White WM, Feldmann H, Kielinczuk S, Hofmann AW (1984) Hafnium/rare-earth element fractionation in the sediment and its consequences for the crust and mantle. Chem Geol 45:325–394

Prelević D, Stracke A, Foley SF, Romer RL, Conticelli S (2010) Hf isotope compositions of Mediterranean lamproites: mixing of melts from asthenosphere and crustally contaminated mantle lithosphere. Lithos 119:297–312

Prosperini N (1993) Petrology and geochemistry of the rocces of Capraia (Arcipelago Toscano, Italia): a vulcano calcalkalino di origine complessa. B.Sc. Thesis, University of Perugia, Italy

Rottura A, Del Moro A, Pinarelli L, Pettrini R, Caggianelli PA, A, Bargossi GM, Piccarreta G. (1991) Relationships between intermedie and acid rocks in orogenic granitoid suites: petrological, geochemical and isotopic (Sr, Nd, Pb) data from Cape Vaticano (southern Calabria, Italy). Chem Geol 92:153–176

Rudnick RL, Gao S (2003) Composition of the continental crust. Treat Geochem 3:1–64

Santo AP, Jacobsen SB, Baker J (2004) Evolution and genesis of calc-alkaline magmas at Flicicudi volcano, Aeolian Arc (Southern Tyrrhenian Sea, Italy). Lithos 72:73–96

Scarth A, Tanguy J-C (2001) Volcanoes of Europe. Terra Publish, pp 51–69

Schiano P, Clocchiatti R, Ottolini L, Busa T (2001) Transition of Mount Etna lavas from a mantle-plume to an island-arc magmatic source. Nature 412:900–904

Scrubano V, Viccaro M, Cristofolini R, Ottolini L (2009) Metasomatic events recorded in ultramafic xenoliths from the Hyblean area (Southeastern Sicily, Italy). Mineral Petrol 95:235–250

Smith PM, Asimow PD (2005) Adiabat_1ph: A new public front-end for the MELTS, pMELTS, and pHEMELTS models. Geochim Geophys Geosyst. https://doi.org/10.1029/2004GC000816

Spence A, Downnes H (2011) A chemostatigraphic investigation of the prehistoric Vavalaci lava sequence on Mount Etna: simulating borehole drilling. Lithos 125:423–433

Spilliaert N, Allard P, Métrich N, Sobolev AV (2006) Melt inclusion record of the conditions of ascent, degassing, and extrusion of volatile-rich alkali basalt during the powerful 2002 flank eruption of Mount Etna (Italy). J Geophys Res 111:B04203

Stracke A, Hofmann AW, Hart SR (2005) FOZO, HIMU and the rest mantle. Terra Nova, vol 17:91–104

Sun SS, McDonough WF (1989) Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. In: Saunders AD, Norry MJ (eds) Magmatism in the ocean basins, vol 42. Geol Soc London Spec Publ., pp 313–345

Tanguy J-C, Condomines M, Kieffer G (1997) Evolution of the Mount Etna magma: constraints on the present feeding system and eruptive mechanism. J Volc Geotherm Res 75:221–250

Thirlwall MF (1991) Long-term reproducibility of multicollector Sr and Nd isotope ratio analysis. Chem Geol Isot Geosci Sect 94:85–104

Thirlwall MF, Jenkins C, Vroon PZ, Mattey DP (1997) Crustal differentiation characteristics of oceanic islands: P–Sr–Nd–O isotopic geochemistry of the shield basalts of Gran Canaria, Canary Islands. Chem Geol 135(3–4):233–262

Tonarini S, Armienti P, D’Orazio M, Armienti P, Innocenti F, Pompilio M, Pettrini R (1995) Geochemical and isotopic monitoring of Mt. Etna 1989–1993: evidences for the shallow feeding system. J Volcanol Geotherm Res 64:95–115

Tonarini S, D’ Orazio M, Armienti P, Innocenti F, Scrubano V (1996) Geochemical features of eastern Sicily lithosphere as probed by Hyblean xenoliths and lavas. Eur J Miner 8:1153–1173

Tonarini S, Armienti P, D’Orazio M, Innocenti F (2001) Subduction-like fluids in the genesis of Mt. Etna magmas: evidence from
boron isotopes and fluid mobile elements. Earth Planet Sci Lett 192:471–483
Trua T, Esperança S, Mazzuoli R (1998) The evolution of the lithospheric mantle along the N. African Plate: geochemical and isotopic evidence from the tholeiitic and alkaline volcanic rocks of the Hyblean Plateau, Italy. Contrib Miner Petrol 131:307–322
Vervoort JD, Blichert-Toft J, Patchett PJ, Albarède F (1999) Relationships between Lu–Hf and Sm–Nd isotopic systems in the global sedimentary system. Earth Planet Sci Lett 168:79–99
Vervoort JD, Patchett PJ, Albarède F, Blichert-Toft J, Rudnick R, Downes H (2000) Hf-Nd isotopic evolution of the lower crust. Earth Planet Sci Lett 181:115–129
Viccaro M, Cristofolini R (2008) Nature of mantle heterogeneity and its role in the short-term geochemical and volcanological evolution of Mt. Etna (Italy). Lithos 105:272–288
Viccaro M, Zuccarello F (2017) Mantle ingredients for making the fingerprint of Etna alkaline magmas: implications for shallow partial melting within the complex geodynamic framework of Eastern Sicily. J Geodyn 109:10–23
Viccaro M, Nicotra E, Millar IL, Cristofolini R (2011) The magma source at Mount Etna volcano: Perspectives from the Hf isotope composition of historic and recent lavas. Chem Geol 281:343–351
Vollmer R (1976) Rb-Sr and U-Th-Pb systematics of alkaline rocks: the alkaline rocks from Italy. Geochim Cosmochim Acta 40:283–295
White WM, Patchett PJ, Ben Othman D (1986) Hf isotope ratios of marine sediments and Mn nodules: evidence for a mantle source of Hf in seawater. Earth Planet Sci Lett 79:46–54
White WM, Albarède F, Telouk P (2000) High-precision analysis of Pb isotope ratios by multi-collector ICP-MS. Chem Geol 167:257–270
Willbold M, Stracke A (2006) Trace element composition of mantle eNd–members: Implications for recycling of oceanic and upper and lower continental crust. Geochem Geophys Geosyst 7(4):Q04004. https://doi.org/10.1029/2005GC001005
Wilson M, Downes H (2006) Tertiary-Quaternary intra-plate magmatism in Europe and its relationship to mantle dynamics. Eur Lithosphere Dyn Geol Soc Lond Mem 32:147–166
Wilson M, Downes H, Cebriá J-M (1995) contrasting fractionation trends in coexisting continental alkaline magma series; Cantal, Massif Central, France. J Petrol 36(6):1729–1753. https://doi.org/10.1093/oxfordjournals.petrology.a037272

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.