The Role of Crustal Contamination throughout the 1329–2005 CE Eruptive Record of Mt. Etna Volcano, Italy

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The nearly continuous volcanic eruption record at Mt. Etna dating back ~700 years provides an excellent opportunity to investigate the geochemical evolution of a highly active volcano. Of particular interest is elucidating the cause of selective enrichment in alkali elements (K and Rb) and 87Sr/86Sr observed in various episodes of past activity. More recently, this alkali enrichment trend started to manifest in the 17th century and accelerated after 1971, and was accompanied by an increase in the volume, frequency, and explosivity of eruptions. Explanations for this signature include recharge of alkali-enriched magmas and/or crustal contamination from the subvolcanic basement. This study quantitatively examines the role of crustal contamination in post-1971 Etnean magma compositions via hundreds of open-system phase equilibria and trace element calculations based upon whole-rock major oxides, trace elements, 87Sr/86Sr ratios, and mineral compositional data. Available pre-1971 petrochemical data are satisfactorily reproduced by fractional crystallization of a high whole-rock MgO (12–17 wt.%), Ni (135–285 ppm), and Cr (920–1330 ppm) parental magma composition that is documented in Etna’s ~4-ka fall-stratified deposit. Observed post-1971 whole-rock and glass trends and phase equilibria are reproduced via modeled assimilation of a skarn and flysch mixture, lithologies that represent the uppermost 10 to 15 km of sedimentary rocks beneath Etna. Notably, models show that K2O (wt.%) and Rb (ppm) behave incompatibly during partial melting of skarn/flysch. Additionally, the observed elevation of 87Sr/86Sr in post-1971 samples is consistent with the addition of radiogenic Sr from wallrock partial melts. In best-fit models, which yield observed post-1971 K2O, Rb, and 87Sr/86Sr trends, ~17% anatectic melt is assimilated and there may be a subordinate stopped wallrock component of <2% (percentage is relative to the starting mass of pristine magma). Previous work has shown that metasomatized spinel lherzolite and garnet pyroxenite can be melted in different proportions to reproduce long- and short-term changes observed in Etna’s geochemical products. We propose that the alkali enrichment signature observed after 1971 can be fully explained through the combination of mantle heterogeneity and crustal contamination. In particular, up to ~20% crustal input coupled with mantle heterogeneity of primitive melts explains the geochemical signals quite well. The influence of crustal contamination on post-1971 lavas is, in part, the result of frequent recharge of magmas that thermally primed the middle to upper crust and enhanced its partial melting.

Key words: Mt. Etna; crustal contamination; assimilation; thermodynamic modeling; Magma Chamber Simulator

INTRODUCTION

Mt. Etna is a largely trachybasaltic stratovolcano that developed since ~500 ka on what is now the densely populated coast of eastern Sicily, Italy (Figs. 1 and 2a), and is among the most active and well-monitored volcanoes in the world (Kahl et al., 2011; Branca et al., 2011a; Corsaro & Miraglia, 2014; Cannata et al., 2018). Etna experienced a recent shift from sodic to potassic affinity in its alkalic series (Fig. 2b) (Corsaro & Pompilio, 2004a) as well as Rb enrichment and more radiogenic 87Sr/86Sr (Fig. 2d-e) compared to earlier stages of magmatism. The alkali enrichment trend started in the 17th century and increased dramatically starting in the 1970s. Since then, lavas with the most radiogenic Sr isotopes and melts with the highest K concentrations ever produced at comparable differentiation degrees were emitted (Fig. 2c, e) (Tanguy & Kieffer, 1976; Tanguy & Clocchiatti, 1984; Barbieri et al., 1993; Armienti et al., 1994a, 2007; Condomines et al., 1995; Tonarini et al., 2001; Corsaro & Pompilio, 2004a). This geochemical signature is accompanied by a striking change in the volcano’s eruptive behavior after 1971 with increases in the explosivity, frequency, and volume of eruptions. The alkali enrichment and accompanying eruptive activity shift at Etna remains a prevailing scientific problem.

Endmember ideas proffered to explain the alkali enrichment include: (1) crustal contributions in the form of alkali-rich fluids or melts (e.g. Clocchiatti et al., 1988, Condomines et al., 1995), and (2) changes to the mantle source delivered to the shallow plumbing system by mafic recharge (e.g. Tonarini et al., 2001; Armienti et al., 2007). A variable mantle source for Etna has been shown to produce compositional differences in Etna’s erupted products’ via resident magmas mixing with recharge magmas originating from a source that is either heterogenous (Armienti et al., 1989; Barbieri et al., 1993; Viccaro & Cristofolini, 2008; Corsaro & Métrich, 2016; Viccaro & Zuccarello, 2017), has been partially melted to different degrees (Clocchiatti et al., 1998) or in varied proportions (Casetta et al., 2019), and/or metasomatized
by carbonatite (Bragagni et al., 2022) or subduction-related fluids from the adjacent Ionian slab (Schiano et al., 2001; Tonarini et al., 2001; Armienti et al., 2004). For example, Viccaro & Zuccarello (2017) propose that variable metasomatism of the mantle source, changing degrees of partial melting of lherzolite and pyroxenite, and magma mixing can account for some of Etna’s temporal geochemical variations, whereas Casetta et al. (2019) suggest varied proportions of amphibole and phlogopite melting in the source linked to heterogenous H2O and CO2 activity drives Etna’s geochemical changes. Regardless of the exact mantle source, magma mixing has been an important process during at least the last ~700 years (La Della et al., 2001; Clocchiatti et al., 2004; Viccaro et al., 2006, 2010, 2015; Armienti et al., 2007; Corsaro et al., 2009; Ferlito et al., 2009, 2012; Andronicos & Corsaro, 2011; Kahl et al., 2011, 2013, 2017; Corsaro & Miraglia, 2014; Giacomoni et al., 2016; Giaffrida & Viccaro, 2017, 2019; Ubide & Kamber, 2018; Salem et al., 2019; Magee et al., 2021 and more). Furthermore, Etna has been active for decades, with recent volcanic activity increasing in volume and frequency (Branca & Del Carlo, 2004, 2005), which likely implies the replenishment of magma chambers from deeper reservoirs in the lower crust or mantle.

The wide array of previous works demonstrates the importance of magma recharge and mixing to produce the spectrum of erupted products at Etna. Still, other proponents argue that carbonate/flysch basement assimilation also contributes to the changing geochemical signature in Etnean magmas (e.g. Clocchiatti et al., 1988; Condonesmes et al., 1995; Tanguy et al., 1997). These subvolcanic sedimentary strata are ≤15 km thick and composed of variable carbonates, shales, siltstones, and sandstones. Collectively, these crustal lithologies are rich in alkali elements with relatively high 87Sr/86Sr (e.g. Clocchiatti et al., 1988; Armienti et al., 1989), providing a potential source of the alkali and 87Sr/86Sr enrichment observed.

Effects of carbonate assimilation at volcanoes with carbonate basements are extensively recognized, for example, in the following locations: the Colli Albani volcanic district (Iacono Marziano et al., 2007; Freda et al., 2008; Di Rocco et al., 2012), Mt. Vesuvius (Del Moro et al., 2001; Iacono Marziano et al., 2008, 2009; Jolis et al., 2009).
GEOLOGICAL BACKGROUND

At present, Etna reaches a maximum elevation of 3357 m a.s.l. with an ellipsoidal base covering 1250 km² (Patanè et al., 2011). The island of Sicily upon which Etna developed lies near the center of the Mediterranean Basin, a region marked by complex tectonic and geodynamic features (Fig. 1a, b). Etna formed in an area of roughly north–south Neogene-Quaternary convergence of the African and Eurasian plates (Dewey et al., 1989; Lentini et al., 2006). Here, there are two primary tectonic domains: (1) the orogenic domain to the north composed of the Apenninic-Maghrebian Chain, and (2) the foreland domain to the south composed of the Gela-Catania foredeep, Hyblean foreland, and Ionian basin (Fig. 1b). Etna’s magmatism is focused at the intersection of these domains, and the magma storage system is in the Sicilian continental crust where the Gela-Catania foredeep and Apenninic-Maghrebian chain meet (Cristofolini et al., 1985; Bousquet & Lanzafame, 2004; Lentini et al., 2006; Patanè et al., 2011). The sedimentary basement beneath Etna is uplifted to 700 to 1300 m a.s.l. and capped by 2000 to 2600 m of Etna’s volcanic...
products (Catalano et al., 2004); the lower 8 to 10 km are comprised of Hyblean Plateau carbonate rocks (Loddo et al., 1988; Yellin-Dror et al., 1997; Corsaro & Pompilio, 2004b) overlain by 2 to 5 km of varied carbonates, shales, slithstones, and sandstones including sequences of flysch from the Apenninic-Maghrebian chain and Gela-Catania foredeeped nappes (Fig. 1c; Lentini, 1982; Loddo et al., 1989; Tibaldi & Groppelli, 2002; Bousquet & Lanzafame, 2004; Corsaro & Pompilio, 2004b).

Unconformity-bound stratigraphy emphasizes four major evolutionary phases, or ‘supersyntheses’, of submarine transitioning to subaerial eruptive activity at Etna (De Beni et al., 2011; Branca et al., 2011a, 2011b). Following Branca et al. (2011a), these are Basal Tholeiitic (542–320 ka), Timpe (221–112 ka), Valle de Bove (106–65 ka), and Stratovolcano (Ellittico and Mongibello; <57 ka) (Fig. 2). Etna’s alkaline series (Timpe and younger) is dominantly Na-alkaline except for post-1971 eruptive products with potassic affinity (Fig. 2b). Volcanics in the Stratovolcano phase range from alkalai basalt to trachytes (Fig. 2a) and the most common products in the Ellittico and Mongibello volcanoes are mugearites and hawaiites, respectively. Plagioclase is the predominant phenocryst during this phase followed by clinopyroxene, olivine, and Ti-magnetite. Apatite is sometimes an accessory phase (Corsaro & Pompilio, 2004a), and Ca-amphibole and orthopyroxene are documented in select eruptions (Ciocchiatti et al., 2004; Viccaro et al., 2006). For eruptions between 1329 and 2005 CE, lavas typically exhibit 10% to 40% by volume of phenocrysts (Armi enti et al., 1994a; Corsaro et al., 2007, 2009; Viccaro & Cristofolini, 2008; Ferlito et al., 2009; De Beni et al., 2011), and rarely >40 vol% (Corsaro et al., 1996; Nicotra & Viccaro, 2012; Kahl et al., 2017). Etnean magmas often contain ~1 to 4 wt.% H2O (Del Carlo & Pompilio, 2004; Métrich et al., 2004; Corsaro & Pompilio, 2004a, 2004b; Spilliaert et al., 2006; Moretti et al., 2018; Zuccarello et al., 2021, 2022) with H2O up to 6 wt.% found more recently in the ~4–ka fall-stratified tephra (Gennaro et al., 2019).

There are multiple well-documented zones of crystallization in the crust beneath Etna spanning from just below the edifice (~1–2 km) to near the crust–mantle boundary (~20–24 km) (Sharp et al., 1980; Trigila et al., 1990; Murru et al., 1999; Chiarabba et al., 2000; Armienti et al., 2004, 2007; Nelson, 2015; Giuffrida & Viccaro, 2017; Ubide & Kamber, 2018; Giuffrida et al., 2023). Furthermore, the ratio of plagioclase to mafic minerals (plagioclase/[clinopyroxene + olivine + Ti-magnetite]) for Etna’s historical magmas is often >1, which suggests shallow crystallization is predominant (Métrich & Rutherford, 1998; Métrich et al., 2004; Corsaro et al., 2013).

**GEOCHEMICAL AND MINERALOGICAL DATA UTILIZED IN STUDY**

To evaluate the feasibility of the computational models, each model is compared to analytical data for 538 whole-rock samples and glass compiled from 18 studies spanning Etnean eruptions from 1329 to 2005 CE. For analytical details of these studies refer to the original papers in Electronic Appendix 1. This study focuses on eight major oxides (SiO2, TiO2, FeO* = FeO + Fe2O3 * 0.8998), Al2O3, MgO, CaO, Na2O, and K2O), five trace elements (Rb, Sr, Ba, La, Nd, and 87Sr/86Sr). Other than Rb, which undergoes post-1971 enrichment, trace elements that do not undergo enrichment but are otherwise well-characterized at Etna were selected to cover a range of partitioning behaviors. Note that 87Sr/86Sr is not the only isotopic ratio to experience a shift in the post-1971 geochemical signature. There are corresponding decreases in whole-rock Nd–Pb–Hf isotopes (e.g. Viccaro et al., 2011; Correale et al., 2014). Sr isotopes are targeted for modeling here because they are extensively characterized in whole-rock samples and select crystal phases (Joron & Treuil, 1984; Armienti et al., 1989, 2007; Barbieri et al., 1993; Condones et al., 1995; Tonarnini et al., 1995). In this document, all observed major element oxides are reported in wt.% and trace elements in ppm (equivalent to µg/g).

Observed mineral proportions of ubiquitous phases are taken from a 1977 to 2005 sample subset (Electronic Appendix 2), which are consistent with limited reports of proportions for older eruptions in the studied period. The average observed phase assemblage is dominated by plagioclase feldspar (63%), followed by clinopyroxene (30%), olivine (7%), and Ti-magnetite (<1%).

**THERMODYNAMIC MODEL AND PARAMETERS**

Magma Chamber Simulator

The Magma Chamber Simulator (MCS) (Bohrson et al., 2014, 2020; Heinonen et al., 2020) is a thermodynamic model that represents the integration of MELTS (Ghiorso & Sack, 1995; Asimow & Ghiorso, 1998; Ghiorso et al., 2002; Gualda et al., 2012; Ghiorso & Gualda, 2015) and the energy- and mass-constrained theory of open magmatic systems developed in Spera & Bohrson (2001). MCS quantifies the chemical evolution (major and trace elements, isotopes, phase equilibria) of a magma body affected by concurrent and/or serial recharge via magma mixing (R), mush entrainment (E), crustal assimilation via partial melting (A) or stopping (S), and fractional crystallization (FC). Stopping is used to simulate the physical process by which wallrock is fractured and incorporated en masse into pre-existing magma. Stopped mass is thermodynamically treated the same as recharge magma or entrained mush (Bohrson et al., 2014, 2020), and we simplify phrasing to only include stopped wallrock in the explanation below.

There are four subsystems (residual melt + cumulates [crystals formed during fractional crystallization] + wallrock + stopped wallrock) for which initial model parameters are defined. A run begins with 100 mass units (m.u.) of resident magma at its liquidus temperature and with a user-defined composition and cooling increment (e.g. 5 °C). Also required are compositions, masses, and temperatures of the assimilated and stopped wallrock, as well as a critical melt fraction of wallrock (FMzero in MCS), which represents a percolation threshold for anatectic melt mobility (typical values for crustal magmatic systems are 0.04 to >0.12; Bohrson et al., 2020; see Bohrson et al., 2014 for assumptions related to percolation threshold in MCS). Wallrock is modeled in isotopic equilibrium (i.e. all wallrock phases have identical 87Sr/86Sr). When models are run with unconstrained fO2, initial Fe2O3 and FeO compositions for each subsystem at a given pressure and temperature are defined using rhyolite-MELTS along a specified buffer and thereafter the fugacity of the oxygen is buffered by the ferrous/ferric Fe ratio of the melt. All masses reported here are either in m.u. (e.g. 5 m.u. of olivine formed in the resident melt) or percent, using the initial mass of magma as the comparison (e.g. 5% olivine formed); in MCS all masses are relative and can be scaled to any absolute amount.

An 8Sr–8Sr AFC (n < 30) simulation proceeds as follows: (1) The resident magma, initially at its liquidus, cools and fractionally crystallizes; crystal phases are removed at each temperature decrement into a cumulate reservoir. The cumulate crystals are chemically isolated from but remain in thermal equilibrium with resident melt as cooling and crystallization proceeds. Sensible and latent heat from magma cooling and concomitant crystallization is transferred to wallrock, which heats up and may begin to melt.
(2) If the percolation threshold for the wallrock is surpassed, all partial melt produced over this critical value is instantaneously removed and added to the resident melt. (3) Stopped wallrock defined by its unique state (composition, mass, and temperature) is added to the magma body via bulk addition at any chosen resident melt temperature step. Upon stopping, the resident melt and newly added mass homogenize and thermodynamically re-equilibrate. Each simulation concludes when the magma body and wallrock are in thermal equilibrium or when a user-specified temperature is reached (Bohrson et al., 2014). Each step in the initial stage of the simulation utilizes mass and energy balance and thermodynamic constraints to provide major elements, masses, and temperatures for magma melt + fluid phase, associated crystals, and residual wallrock, as well as the state of the stopped block at the instant before stopping. After solving for solid phases and major element compositions, MCS can calculate trace elements and isotopes with input of user-defined initial concentrations, isotopic ratios, and relevant partition coefficients (Heinonen et al., 2020). Output includes trace element concentrations and isotope ratios for all parts of MCS subsystems.

Here, MCS modeling was originally broken into two steps (Fig. 3). Step one modeled pre-1971 data with the goal of defining a primitive parent magma composition to represent an uncontaminated starting material as well as its storage location and intensive parameters. Step two modeled post-1971 data with the goal of examining possibilities of crustal contamination of the parental magma through wallrock assimilation and stopping. Lastly, alternative parental magmas were re-examined due to unsatisfactory model fit of Na2O and TiO2 versus MgO. Modeling in all steps included sensitivity testing to identify parameters that exerted the most control on model outcomes. Best-fit MCS models were determined by phase equilibria comparison and visual inspection of modeled trends with the goals of capturing the main observed data trends and/or ‘bracketing’ the observed data (i.e., capturing the lower and upper limits of these data). Best-fit FC, AFC, SFC, and SAFC model inputs and outputs are available electronically and they include the trace element partition coefficients used. Since Etnean magmas typically erupt between 1000 °C and 1100 °C (e.g., Corsaro & Miraglia, 2005), models stop when the resident magma cools below 1000 °C. The magma cooling increment in models shown here is 5 °C. Model runs included in figures in this paper are intended to highlight the most distinguishing trends used to assess model fit. To examine any models that are referenced but not plotted here, see Supplementary Figs. 1–14 in Electronic Appendix 3. Finally, modifications made to initial compositions (e.g., changes to initial H2O content) are summarized in Electronic Appendix 4.

Choice of parent magma and initial conditions

To choose a parent magma, we initially consider samples from sources outlined in Electronic Appendix 1 encompassing eruptions since 1329 (Fig. 2). Magmas with MgO <8 wt.% dominate this sample suite, and thus may have experienced crustal assimilation as they differentiated and are rejected. Another possible parent magma comes from Etna’s ~4-ka fall-stratified tephra deposit (FS tephra; Kamenetsky et al., 2007). This tephra contains euhehedral crystals of olivine (<8% modal abundance; Fo80-83), clinopyroxene (<3%; Mgr 96–92.5), and Cr spinel (<0.1%). The combination of mineral identities and compositions including high whole-rock MgO (12–17 wt.%), Ni (135–285 ppm), and Cr (920–1330 ppm) concentrations are interpreted by Kamenetsky et al. (2007) to represent a primitive, unfractuated magma that may be the parent for more recent eruptive products. An FS tephra sample is thus used as a proxy for a parent magma (PM) composition for pre- and post-1971 Etnean lavas (Tables 1 and 2).

Via fractional crystallization, variations in pressure, initial H2O content, and initial fO2 of PM are examined to determine the best-fit initial conditions of the parent magma (n ∼75 models); these conditions are then utilized as the starting point for assimilation and stopping models. A summary of the range of parameters tested in PM FC modeling is listed in Table 3. Saturation of plagioclase in these models is a key determining factor in choosing initial conditions. Plagioclase phenocrysts in both historic to recent activity are sizeable (1–5 mm, sometimes <10 mm) and have complex growth patterns (e.g., Viccaro et al., 2010; Kamenetsky & Lanzafame, 2007). It is unlikely, then, that these phenocrysts grew exclusively late and upon ascent. Modeled initial H2O >1 wt.% delays the onset of plagioclase crystallization and thus yields a poor model fit for whole-rock Al2O3 versus MgO (Supplementary Fig. 1). Figure 4 shows models of PM with 1 and 4 wt.% initial H2O fractionally crystallizing at 0.2 and 0.5 GPa. Plagioclase crystallization is suppressed completely during FC of PM with 4 wt.% initial H2O at 0.5 GPa, and only 1.7 m.u. crystallizes in the final 10 °C of cooling at 0.2 GPa (Fig. 4b). Although H2O ≤6 wt.% is recorded in the FS tephra (Gennaro et al., 2019), plagioclase behavior suggests that high magma water contents are unlikely to be the prevailing conditions leading to generation of historical to recent Etnean magmas. High H2O contents observed in olivine- and clinopyroxene-hosted melt inclusions in historical and recent lavas can, therefore, be explained assuming complex dynamics of degassing and/or flushing of volatiles (H2O-CO2) occurring in the range of 0.2 to 0.4 GPa (e.g., Métrich et al., 2004; Spiliaert et al., 2006; Ferlito et al., 2008; Gennaro et al., 2019; Zuccarello et al., 2021, 2022), together with H2O acting incompatibly during crystallization. In this regard, at 0.2 GPa pressure, fractional crystallization of the model PM yielded derivatives with MgO of 1 to 8 wt.% and H2O from 1.6 to 5.0 wt.%. In addition, primary magmas with initial H2O of 0.5 wt.% are unlikely, as volatile-poor (<1.0 wt.% H2O+CO2) Etnean magmas would likely stall at ~22 km deep in the crust from insufficient buoyancy relative to basement rocks (Corsaro & Pompilio, 2004c). Therefore, a parent magma with ~1.0 wt.% initial H2O is a reasonable starting composition based on model results and literature constraints. Crystallization of PM with 1.0 wt.% initial H2O at 0.5 GPa also suppresses plagioclase crystallization with just 1 m.u. forming in the final 45 °C of cooling (Fig. 4b), and pressures exceeding 0.5 GPa produce exceptionally poor model fits relative to observed whole rock SiO2, Al2O3, and FeO+ versus MgO (Supplementary Fig. 2). Thus, to produce a phase assemblage consistent with observations, we eliminate pressures >0.2 GPa. Pressures of 0.2 and 0.1 GPa are virtually indistinguishable for TiO2, FeO+, Na2O, and K2O and similar for SiO2 and CaO versus MgO. Plagioclase saturates earlier during FC at 0.1 GPa, and the model reaches only the lowest values of Al2O3. Therefore, a pressure of 0.2 GPa (~6 km depth) is preferred as the best-fit, which is in agreement with studies that place at least part of the major crystallization zone in the upper-middle crust within the sedimentary basement (2–15 km depth; Loddo et al., 1989; Yellin-Dror et al., 1997; Tibaldi & Groppelli, 2002; Bousquet & Lanzafame, 2004; Corsaro & Pompilio, 2004b). Interaction between the magma’s transport and storage system and the sedimentary basement is further supported by sedimentary and metamorphic xenoliths recovered from Etnean lavas (e.g., Michaud, 1995; Lanzafame et al., 2003; Corsaro et al., 2007; Coulson et al., 2011).

Changes in the initial ferric and ferrous iron content are determined under oxygen buffers from QFM-2 to QFM+2 via rhyolite-MELTS version 1.2.0; using these initial fO2 conditions, the models
are run unconstrained (i.e. no oxygen buffer was used). This range of $fO_2$ produced models with different TiO$_2$ and FeO$^*$ in the evolving melt but has negligible effects on all other oxides (Supplementary Fig. 3). Variations in this parameter does capture different ranges of whole-rock FeO$^*$ values, suggesting the oxygen fugacity has varied through time. We use QFM as the $fO_2$ for all remaining models, which is reasonable for Etnean lavas (Kahl et al., 2015, 2017).

In summary, best-fit results for the FC model trend of PM include an initial H$_2$O content of 1.0 wt.%, pressure of 0.2 GPa, and initial ferric and ferrous iron composition determined by an oxygen buffer of QFM (Fig. 4). FC of PM under these conditions yields olivine, clinopyroxene, plagioclase, and minor spinel and apatite, which is in excellent agreement with the dominant observed phase assemblage. Notably, PM’s K$_2$O-MgO evolution successfully captures the pre-1971 whole-rock trend as opposed to the enriched post-1971 trend. Fractionation of PM effectively captures the middle range of the observed data when SiO$_2$ and CaO are plotted versus MgO, and the upper range of FeO$^*$ and its glass compositions, while it is consistently low in Na$_2$O and TiO$_2$ vs MgO. The slope of the model’s MgO-Al$_2$O$_3$ evolution aligns with the observed data but does not reach the upper range from approximately 17 to 20 wt.% Al$_2$O$_3$ at <6 wt.% MgO.

The initial parental magma $^{87}$Sr/$^{86}$Sr is estimated based on the least radiogenic sample in the data compilation (~0.7033) and is not addressed further because this value does not vary in FC models. Initial concentrations of Rb, Sr, Ba, La, and Nd are estimated based on the range of values from the ~4-ka FS tephra analyzed by Kamenetsky et al. (2007). This FC trace element model (Fig. 5h-m) captures the pre-1971 Rb trend exceptionally well, and
Table 1: Initial magma and wallrock compositions utilized in MCS models reported by wt.%

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<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>FeO</th>
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<th>K₂O</th>
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<td><strong>Initial Resident (Parent) Magma Compositions</strong></td>
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<tr>
<td>PM</td>
<td>47.13</td>
<td>0.85</td>
<td>9.99</td>
<td>1.51</td>
<td>7.87</td>
<td>0.17</td>
<td>16.93</td>
<td>12.22</td>
<td>1.31</td>
<td>0.61</td>
<td>0.22</td>
<td>0.99</td>
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<td>ET75</td>
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<td>1.43</td>
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<td>1.76</td>
<td>9.14</td>
<td>0.20</td>
<td>11.61</td>
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<td>2.20</td>
<td>1.08</td>
<td>-</td>
<td>1.91</td>
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<td>45.12</td>
<td>1.66</td>
<td>14.78</td>
<td>1.74</td>
<td>9.14</td>
<td>0.17</td>
<td>11.42</td>
<td>9.93</td>
<td>2.88</td>
<td>0.99</td>
<td>-</td>
<td>2.19</td>
<td>-</td>
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<tr>
<td>Post-1971</td>
<td>44.99</td>
<td>1.73</td>
<td>14.75</td>
<td>1.75</td>
<td>9.05</td>
<td>0.17</td>
<td>10.92</td>
<td>10.30</td>
<td>2.68</td>
<td>1.34</td>
<td>-</td>
<td>2.34</td>
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</tr>
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**Initial Wallrock Compositions**

Flysch  
69.69  0.62  14.13  2.98  1.07  0.05  1.71  1.46  2.41  2.95  -  1.78  1.15
Skarn 1  
45.23  0.36  13.42  2.69  0.81  0.06  13.76 21.4  0.36  1.84  0.03 -  -
Skarn 2  
52.61  0.08  0.55  0.67  0.26  0.04  18.41 26.92  0.28  0.07  0.10 -  -
Skarn 3  
37.26  0.97  20.42  5.14  1.27  0.11  13.03 21.70  0.02  0.00  0.08 -  -
90:10  
67.24  0.60  14.06  2.95  1.04  0.05  2.91  3.45  2.20  2.84  0.00  1.60  1.04
80:20  
64.79  0.57  13.99  2.92  1.02  0.05  4.12  5.45  2.00  2.73  0.01  1.42  0.92
70:30  
62.35  0.54  13.92  2.89  0.99  0.05  5.32  7.45  1.79  2.62  0.01  1.24  0.81
60:40  
59.90  0.52  13.85  2.86  0.97  0.05  6.53  9.45  1.59  2.51  0.01  1.07  0.69
50:50  
57.46  0.49  13.77  2.83  0.94  0.06  7.74  11.45  1.38  2.40  0.02  0.89  0.58
40:60  
55.01  0.46  13.70  2.81  0.92  0.06  8.94  13.45  1.18  2.28  0.02  0.71  0.46
30:70 (Mixture 1)  
52.57  0.44  13.63  2.78  0.89  0.06  10.15 15.45  0.97  2.17  0.02  0.53  0.35
20:80  
50.12  0.41  13.56  2.75  0.86  0.06  11.35 17.45  0.77  2.06  0.02  0.36  0.23
10:90  
47.68  0.38  13.49  2.72  0.84  0.06  12.56 19.44  0.56  1.95  0.03  0.18  0.12

See Electronic Appendix 4 for modifications made to original compositions.  
*Original compositions modified from sample spv291-D of Kamenetsky et al. (2007).  
*Original compositions taken from Clocchiatti et al. (1988).  
*Original compositions taken from Di Rocco et al. (2012).  
*Original composition taken from Jolis et al. (2015).  
*Ratios represent wallrock mixtures with varying proportions of Flysch to Skarn 1 (e.g. 90:10 = 90 parts Flysch to 10 parts Skarn 1).

Table 2: Measured and estimated trace element concentrations (reported by ppm) and Sr isotopes used in MCS models

<table>
<thead>
<tr>
<th></th>
<th>Rb</th>
<th>Sr</th>
<th>Ba</th>
<th>La</th>
<th>Nd</th>
<th>87Sr/ 86Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM</td>
<td>14</td>
<td>506</td>
<td>240</td>
<td>18.9</td>
<td>18.9</td>
<td>0.7033</td>
</tr>
<tr>
<td>Flysch</td>
<td>49</td>
<td>879</td>
<td>400</td>
<td>40</td>
<td>15</td>
<td>0.71776</td>
</tr>
<tr>
<td>Skarn 1</td>
<td>121</td>
<td>350</td>
<td>1338</td>
<td>20</td>
<td>30</td>
<td>0.7075</td>
</tr>
<tr>
<td>Skarn 2</td>
<td>121</td>
<td>350</td>
<td>1338</td>
<td>20</td>
<td>30</td>
<td>0.7075</td>
</tr>
<tr>
<td>Skarn 3</td>
<td>121</td>
<td>350</td>
<td>1338</td>
<td>20</td>
<td>30</td>
<td>0.7075</td>
</tr>
<tr>
<td>90:10</td>
<td>56</td>
<td>826</td>
<td>494</td>
<td>38</td>
<td>17</td>
<td>0.7173</td>
</tr>
<tr>
<td>80:20</td>
<td>64</td>
<td>773</td>
<td>588</td>
<td>36</td>
<td>18</td>
<td>0.7168</td>
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<td>70:30</td>
<td>71</td>
<td>720</td>
<td>681</td>
<td>34</td>
<td>20</td>
<td>0.7163</td>
</tr>
<tr>
<td>60:40</td>
<td>78</td>
<td>667</td>
<td>775</td>
<td>32</td>
<td>21</td>
<td>0.7156</td>
</tr>
<tr>
<td>50:50</td>
<td>85</td>
<td>615</td>
<td>869</td>
<td>30</td>
<td>23</td>
<td>0.7148</td>
</tr>
<tr>
<td>40:60</td>
<td>92</td>
<td>562</td>
<td>963</td>
<td>28</td>
<td>24</td>
<td>0.7139</td>
</tr>
<tr>
<td>30:70 (Mixture 1)</td>
<td>99</td>
<td>509</td>
<td>1057</td>
<td>26</td>
<td>26</td>
<td>0.7128</td>
</tr>
</tbody>
</table>

*Trace element concentrations taken from the ~4-ka tephra sample set of Kamenetsky et al. (2007); Sr isotope ratio is estimated from the least radiogenic sample in the data compilation provided in Electronic Appendix 1.  
**Trace element concentrations taken from Mikes et al. (2006); Sr isotope ratio taken from Armenti et al. (1989).  
>Rb and Ba concentrations from Jolis et al. (2015); Sr, La, and Nd concentrations estimated based on a range of skarn compositions from Del Moro et al. (2001); Sr isotope ratios estimated based on age of the carbonate Hibléan Plateau (Yellin-Dror et al., 1997) from the Sr seawater curve of McArthur et al. (2001).  
>Ratios represent wallrock mixtures with varying proportions of Flysch to Skarn 1 (e.g. 90:10 = 90 parts Flysch to 10 parts Skarn 1).

Table 3: Summary of parameters tested in fractional crystallization modeling for PM

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range of Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (GPa)</td>
<td>0.1, 0.2, 0.5, 0.8, 1.1</td>
</tr>
<tr>
<td>Initial H₂O content (wt %)</td>
<td>0.5, 1.0, 2.0, 3.0, 4.0, 5.0</td>
</tr>
<tr>
<td>Initial fO₂</td>
<td>QFM-2, QFM-1, QFM, QFM +1, QFM +2</td>
</tr>
</tbody>
</table>

Crustal contamination models

To evaluate the role of crust-magma interaction on post-1971 magmas, we begin with the defined parent magma and initial conditions outlined above; the use of a ~4-ka magma as the parent assumes that the parent magma has broadly remained the same for the last several thousand years (Kamenetsky et al., 2007). To document specific consequences of assimilation versus stoping on the parent magma, a subset of AFC-only and SFC-only runs are presented, followed by combined SAFC models. Subsequently, trace elements are calculated for the best-fit major element models to define the final best-fit model(s) based on major elements, phase equilibria, trace elements, and Sr isotopes.
As illustrated above, FC alone cannot account for the full range of data evidenced in Etna lavas, particularly for post-1971 $\text{K}_2\text{O}$, Rb, and $^{87}\text{Sr}/^{86}\text{Sr}$ versus MgO. Heterogeneous Sr isotopes require crustal contamination and/or mantle heterogeneity manifested through recharge of heterogeneous melts. Contamination via assimilation and stoping are well-documented in the literature as effective mechanisms for contaminating magmas (e.g. Furlong & Myers, 1985; Del Moro et al., 2001; Chadwick et al., 2007; Erdmann et al., 2010; Borisova et al., 2013). Carbonate, calc-silicate, aluminosilicate, and composite xenoliths documented in Etna lavas (e.g. Michaud, 1995) provide evidence that stoned and/or assimilated wallrock may play a role in the alkali enrichment. Although sedimentary xenoliths have been recovered in Etna magmas, no existing studies analyze their whole-rock compositions. Because of this, the Capo d’Orlando flysch, which has been suggested as a source of crustal contamination in Etna lavas (Clocchiatti et al., 1988; Armienti et al., 1989; Marty et al., 1994), is used to represent the sediments in the uppermost 2 to 5 km beneath the volcanic pile (Flysch; Tables 1 and 2). To represent the carbonate-dominated Hyblean Plateau, we attempted to use limestone and dolomite compositions as the wallrock. However, no successful AFC models with carbonate-only wallrock were produced. Nonetheless, the interaction between carbonate rocks and heat supplied by magmatic activity can induce physical, chemical, and mineralogical changes (i.e. contact metamorphism). Due to the thermal alteration evident in Etna carbonate xenoliths such as those documented by Michaud (1995), along with the long-lived (~500 kyr) magmatic activity at Etna, we assume that some carbonate rocks in contact with Etna’s magma storage system were metamorphosed into magmatic skarns. A variety of skarn...
Fig. 5. Modeled SFC trends produced via stoping 10 m.u. of Flysch, Skarn 1, and Mixture 1 compared to observed data, plotted as MgO (wt.%) versus (a) SiO₂, (b) Al₂O₃, (c) TiO₂, (d) FeO*, (e) CaO, (f) Na₂O, (g) K₂O (wt %), (h) Rb, (i) Sr, (j) Ba, (k) La, (l) Nd (ppm), and (m) ⁸⁷Sr/⁸⁶Sr. FC trend of the model PM is shown for comparison to a modeled magma unaffected by crustal contamination. Dashed gray line indicates the FC step after which stoping is triggered. Model progression is as described in Fig. 4. Refer to Tables 1 and 2 for initial magma and wallrock compositions.

MCS stoping and fractional crystallization (SFC) modeling results

Approximately 70 SFC models are examined in this study. For SFC models, additional user-defined variables include the bulk composition, mass, and temperature of the stoped wallrock, and the resident magma body temperature at which the block is stoped (i.e., in MCS, the magma trigger temperature) (tested ranges listed in Table 4). Based on results of models with initial stumped block temperatures of 750 °C to 1250 °C, model sensitivity to the stoped block temperature is negligible (examples of Skarn 1 at 1165 and 1250 °C shown in Supplementary Fig. 4), and thus the stoped block temperature is set near a given composition’s solidus temperature (706–1193 °C). Likewise, assessment of models illustrates variations from 950 °C to 1200 °C in the magma trigger temperature does not affect the overall parental magma’s compositional evolution significantly. For example, evolutionary trends using trigger temperatures of 1095, 1130, and 1165 °C, which are chosen to initiate stoping at various points along the MgO interval of observed data, are nearly indistinguishable except in TiO₂ vs. MgO (Supplementary Fig. 5). Therefore, stoping is triggered in most models at a magma temperature of 1165 °C to capture trends of observed samples with the highest MgO.

About 55 models are run to assess the impact of stoped block composition and masses on model outcomes. In the remainder
of this section we refer to Figure 5, which shows model results of stoping 10-m.u. blocks of Capo d’Orlando Flysch, Skarn 1, and Mixture 1 for illustrative purposes. Model results from stoping additional skarn compositions (Skarns 1, 2, and 3, Supplementary Fig. 6) and masses (2, 5, 10, and 20 m.u.) for Capo d’Orlando Flysch, Skarn 1, and Mixture 1 (Supplementary Figs. 7–9, respectively) are found in Electronic Appendix 3. Amounts of 2 to 20 m.u. of stoped Capo d’Orlando flysch produce substantial misfits for numerous trends (e.g. MgO versus SiO₂ and $^{87}$Sr/$^{86}$Sr), and stoping this material does not significantly increase the concentrations of K₂O or Rb in the derivative melts. The smallest tested amount of 2 m.u. is the only model that does not overestimate $^{87}$Sr/$^{86}$Sr. Flysch is, therefore, eliminated as a stoped contaminant. In addition, three different skarn compositions (Skarns 1, 2, and 3) and a skarn and flysch mixture (Mixture 1, 30:70 flysch:skarn) are stoped. Mixture 1 is the mixture utilized most in AFC models due to its agreeable solidus temperature and chemical composition as an assimilant (see Tables 1 and 2 and discussion in the following section on wallrock heterogeneity and solidi for further details). In general, the skarns and Mixture 1 are Ca- and Mg-rich relative to the resident magma composition at the instant of stoping (~8 wt% MgO), and their addition results in increases in CaO

Table 4: Summary of parameters tested in crustal contamination models

<table>
<thead>
<tr>
<th></th>
<th>AFC</th>
<th>SFC</th>
<th>SAFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Runs</td>
<td>65</td>
<td>70</td>
<td>40</td>
</tr>
<tr>
<td>WR Compositions Tested</td>
<td>11</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>WR Initial Mass Units (m.u.)</td>
<td>25–100</td>
<td>-</td>
<td>75–100</td>
</tr>
<tr>
<td>WR Initial T (°C)</td>
<td>200–500</td>
<td>-</td>
<td>200</td>
</tr>
<tr>
<td>Fmzero</td>
<td>0.02–0.12</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>S Compositions Tested</td>
<td>-</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>S Mass Units</td>
<td>-</td>
<td>2–80</td>
<td>2–60</td>
</tr>
<tr>
<td>S Trigger T (°C)</td>
<td>750–1250</td>
<td>750–1250</td>
<td>1140–1185</td>
</tr>
</tbody>
</table>

*These runs were performed with PM as the initial composition with the best fit FC parameters outlined in the text. WR, wallrock; S, stoped block. WR initial mass is set relative to the magma body mass, which is always 100 m.u.
and MgO in the contaminated magma melt. Responses of the ~8 wt.% MgO melt with respect to the remaining oxides depend on the composition of a given stoped block. For example, upon stoping, Skarn 1 and Mixture 1 increase the melt K₂O, but Skarn 3 decreases it, and Skarn 3 increases Al₂O₃, whereas Skarn 2 decreases it. Furthermore, the modeled phase assemblages of olivine, clinopyroxene, plagioclase, and spinel ± apatite are still in excellent agreement with observed phase assemblages. Since Skarn 1 and Mixture 1 yield the necessary K₂O increase observed in post-1971 samples, these compositions are used to assess the sensitivity of model results to stoped mass.

Mass variations in stoped blocks (Skarn 1 and Mixture 1) for a given composition produce effects in the resident magma melt proportional to the mass (Supplementary Figs. 8–9). That is, larger stoped masses yield more drastic increases or decreases in affected oxides. Skarn 1 and Mixture 1 both induce changes to the derivative melts needed to capture observed post-1971 trends, including increases in K₂O, Rb, and ⁸⁷Sr/⁸⁶Sr. However, large enough increases in K₂O are not possible without overestimating the Rb, Ba, and ⁸⁷Sr/⁸⁶Sr characteristics of the observed products. Models including 20 m.u. of stoped Skarn 1 and Mixture 1 capture post-1971 K₂O versus MgO, but the addition of Skarn 1 overestimates Rb and Ba, and the addition of Mixture 1 overestimates ⁸⁷Sr/⁸⁶Sr. As a result, stoped masses are limited to rather small amounts. In these models, the derivative magmas generated via 2 m.u. of stoped Skarn 1 and Mixture 1 are selected as the best-fit model in the stoped mass and composition sensitivity tests because crystallizing phases are consistent with observations and these models capture the range of selected major oxides (except TiO₂ and Na₂O), trace elements, and ⁸⁷Sr/⁸⁶Sr characteristics of the observed products. However, minor additions of these wallrocks are insufficient to capture post-1971 K₂O, Rb, and ⁸⁷Sr/⁸⁶Sr trends, and thus stoping alone cannot explain the alkali enrichment.

MCS assimilation and fractional crystallization (AFC) modeling results

For AFC models (n ≈ 65), additional user-defined variables include the initial mass, temperature, and composition of the wallrock, as well as the percolation threshold (Fmzero) (Table 4). The percolation threshold was 0.05 for most runs, which falls within the typical range for crustal magmas (Bohrson et al., 2020). Sensitivity tests demonstrate that a value of 0.05 initiates assimilation earlier than a value of 0.12; however, the overall evolution of the contaminated melts follow similar trajectories (Supplementary Fig. 10). Sensitivity of models to initial wallrock mass primarily changes the point at which assimilation begins, since larger masses require more enthalpy delivered from cooling and crystallization of magma to initiate partial melting in wallrock. The onset of assimilation due to these mass differences produces substantial differences in derivative melts (example masses of 40, 75, and 110 m.u. shown in Supplementary Fig. 11). The wallrock initial mass for most models is 100 m.u., which equates to 0.1 km in diameter (Heinonen et al., 2019). Like initial mass, initial wallrock temperature controls the point at which contamination begins (examples of 50, 200, and 350 °C shown in Supplementary Fig. 12). At the chosen mass, the best-fit initial temperature of 450 °C represents wallrock that is thermally primed at approximately 3x that of a typical geotherm (25 °C/km). The initial composition of the wallrock (and its associated solids) produces the most substantial model variability, and thus is the focus of the discussion below.

A wallrock’s composition affects its solidus, which in turn affects the efficiency with which anatetic melts are produced and thus the fertility of the wallrock to yield contaminated magmas. The Capo d’Orlando flysch has a solidus of 706 °C at 0.2 GPa determined by rhyolite-MELTS. In contrast, investigated skarns are relatively restitic and yield solidi temperatures up to 1193 °C (Figure 6). Because PM’s liquidus is at 1361 °C, for typical geothermal gradients, the amount of enthalpy delivered by its fractionation is likely insufficient to produce substantial anatetic melt from skarns. This idea is confirmed by AFC models with skarn as the wallrock. Magma-wallrock thermal equilibrium is consistently reached before skarn wallrock melts are produced over the range of observed MgO in Etnean lavas, and thus pure skarn is eliminated as a potential assimilant. Wallrock of flysch-skarn mixtures with >80% skarn behave in a similar manner and are also unlikely assimilants.

When skarn and flysch compositions are mixed in various proportions to represent a heterogenous and interbedded sedimentary basement, the solidi fall within the range defined by flysch and skarn endmembers. For example, when just 10% flysch is added to skarn, the solidus decreases >200 °C at 0.2 GPa according to rhyolite-MELTS (Fig. 6). Consequently, assimilation of the sedimentary basement may either involve a pure flysch or a flysch-skarn mixture with ≤70% of a skarn endmember. Initial phase assemblages of these wallrocks according to rhyolite-MELTS are plagioclase, K-feldspar, quartz, biotite, and orthopyroxene ± spinel, rhombohedral oxide, clinopyroxene, garnet, olivine, and sillimanite. Figure 7 illustrates select major oxide and trace element compositions of incremental anatetic melts produced from melting of flysch and 70:30, 50:50, and 30:70 flysch-skarn mixtures. Consistently over all AFC runs, quartz, biotite, and K-feldspar completely melt (Fig 7a). During melting, compared to the initial wallrock composition, wallrock melts display increases in FeO and Na₂O (7c,e). Wallrock melts of the 70:30 mixture and flysch are Si-rich (≤75 wt.% SiO₂), whereas wallrock melts of the 50:50 and 30:70 mixtures have melts with ~58 wt.% SiO₂ (Fig 7b). In each wallrock, quartz is present and melts completely by the end of model runs, but the 70:30 mixture and flysch have significantly more quartz than the wallrock mixtures with more skarn, accounting for the Si-rich melts in the former. Melts of the
Fig. 7. Incremental partial melt compositions of wallrock produced as the wallrock increases in temperature during a given AFC run, with melting phases highlighted in (a), progressing from left to right and plotted as wallrock temperature (°C) versus wallrock partial melt (b) SiO$_2$, (c) FeO$^*$, (d) K$_2$O, (e) Na$_2$O (wt.%), (f) Ba, (g) Rb, (h) La, and (i) Nd (ppm). Bars at the top of the figure indicate the range over which different phases are present in the wallrock for the endmembers of Flysch and Mixture 1. Ratios listed represent the ratio of Flysch to Skarn 1 in a mixed composition. Initial wallrock compositions are given in Tables 1 and 2.

50:50 and 30:70 wallrock mixtures have the highest concentrations of K$_2$O (Fig. 7d). Again, this results from differences in the phase assemblages. The 50:50 and 30:70 mixtures are dominated by clinopyroxene, which does not melt, and plagioclase, which experiences limited melting. Consequently, the effects of melting K-rich biotite and K-feldspar are maximized. In comparison, the 70:30 mixture and Flysch are dominated by quartz, which melt completely and dilute the compositional effects of other melted phases. All wallrock melts display initially high concentrations of La and Nd (Fig. 7h-i), owing to their incompatible nature in the melting assemblage, with their concentrations decreasing over the course of melting. Rb and Ba exhibit a range of behaviors in the wallrock melts (Fig. 7f-g). In these cases, we interpret the melting of biotite and possibly K-feldspar in the wallrocks as the major controls on concentrations of Rb and the melting of biotite and K-feldspar as the likely controls on the concentrations of Ba.

The remainder of this section references Fig. 8, which highlights AFC cases of wallrock compositions just discussed in Fig. 7 (30:70, 50:50, 70:30, and 100:0 flysch:skarn ratios), while AFC cases of the full range of mixed wallrock compositions are shown in Supplementary Figs. 13 (70:30, 80:20, 90:10, and 100:0 flysch:skarn ratios) and 14 (30:70, 40:60, 50:50, and 60:40 flysch:skarn ratios). Compared to the FC trend of PM, AFC of the Capo d’Orlando flysch, and flysch-skarn mixtures with ≥70% flysch (Fig. 8 and Supplementary Fig. 13) induce notable increases in SiO$_2$ and K$_2$O, and decreases in TiO$_2$, FeO$^*$, CaO, and Na$_2$O versus MgO. The maximum concentrations of Al$_2$O$_3$ between fractionated PM derivatives and the assimilation scenarios are similar but occur at very different MgO; assimilation initially decreases Al$_2$O$_3$ compared to the FC case and delays the onset of plagioclase crystallization, which is indicated by the inflection in Al$_2$O$_3$ at ~3 wt.% MgO for most AFC cases. In addition, models that utilize this range of wallrock compositions produce nearly identical major element...
compositional trends, so it is necessary to model trace elements and $^{87}\text{Sr}/^{86}\text{Sr}$ to further evaluate model quality. These models yield magma compositions with increased Rb, La, and Nd concentrations and Sr isotope ratios, and decreased Ba concentrations (compared to the FC case). The resulting increases in Rb are in good agreement with observations, as they reach the highest observed Rb concentrations. However, the modeled $^{87}\text{Sr}/^{86}\text{Sr}$ in each of these scenarios greatly overestimate the observed values.

The four assimilation scenarios of flysch-skarn mixtures with 30% to 60% flysch (Fig. 8 and Supplementary Fig. 14) produce slightly more variation than the assimilants discussed above. Assimilation of these mixtures generates increases in SiO$_2$ and K$_2$O, and decreases in TiO$_2$, FeO*, CaO, and Na$_2$O. Mixture 1 produces the smallest increase in SiO$_2$ relative to the other mixtures, and the slope of its modeled K$_2$O trend is the closest match to observed MgO vs. K$_2$O. Its slope is shallowest from ~6 to 4 wt.% MgO and increases more drastically at <4 wt.% MgO as the observed glass concentrations do, whereas the others increase more drastically from ~6 to 4 wt.% MgO and begin to level off at <4 wt.% MgO. Furthermore, each of these four AFC models generates increases in concentrations of Rb and Nd and in Sr isotope ratios in the contaminated melt. All models except for the 50:50 flysch-skarn mixture produce increases in Ba and La concentrations relative to simple FC. The Sr concentration behavior is more complex. The minimum peak Sr concentration reached is ~1150 ppm (30:70 mixture AFC), which we interpret as a function of plagioclase saturation. Sr is highly compatible in plagioclase and less compatible in the earlier phases crystallizing in these models (spinel, olivine, and clinopyroxene), and as such, Sr concentrations will increase in the melt until plagioclase saturates, at which point Sr will decrease. As a result, in the models where plagioclase saturates in the magma melt at a higher magma temperature (e.g. 30:70 mixture), a lower peak concentration of Sr is reached, whereas in the models where plagioclase saturation is delayed (e.g. 50:50 mixture), the highest peak concentrations are reached.

In summary, due to high solidi temperatures, pure skarn and interbedded flysch-skarn mixtures with ≥80% skarn are unlikely to generate substantial anatectic melt. Although assimilation of wallrock with 70% to 100% flysch produces some of the desired compositional trends, their phase assemblages are dominated by quartz, and the resulting magmas greatly overestimate SiO$_2$ (for a particular MgO), and high anatectic melt production due to low wallrock solidi results in exceedingly high $^{87}\text{Sr}/^{86}\text{Sr}$. As such, flysch-skarn mixtures with 30% to 60% flysch are preferred. Although a variety of these mixtures generate desired increases in K$_2$O and Rb concentrations and Sr isotope ratios while still producing reasonable results for parameters that are unchanged between pre- and post-1971, the 30:70 mixture as the wallrock produces the best-fit results for the combination of major oxides, trace elements, $^{87}\text{Sr}/^{86}\text{Sr}$, and phase equilibria (Mixture 1 AFC, Fig. 8).
Fig. 8. Modeled AFC trends produced via assimilation of wallrock partial melts from the same select initial wallrock compositions shown in Fig. 7, plotted as MgO (wt.%) versus (a) SiO$_2$, (b) Al$_2$O$_3$, (c) TiO$_2$, (d) FeO*, (e) CaO, (f) Na$_2$O, (g) K$_2$O (wt. %), (h) Rb, (i) Sr, (j) Ba, (k) La, (l) Nd (ppm), and (m) $^{87}$Sr/$^{86}$Sr. FC trend of the model PM is shown for comparison. Dashed gray line indicates the FC step after which stoping is triggered. Model progression is as described in Fig. 4. Refer to Tables 1 and 2 for initial magma and wallrock compositions. Note that partial melt assimilation of initial wallrock compositions shown with $\geq$ 50% produce models with substantial misfits for parameters such as SiO$_2$, Sr, and $^{87}$Sr/$^{86}$Sr.

MCS stoping, assimilation, and fractional crystallization (SAFC) modeling results

Although the best-fit AFC model successfully captures post-1971 compositional trends, we modeled SAFC processes to evaluate the possibility of stoping concurrent with assimilation. For consistency, we utilize Mixture 1 as both the stoped block and the wallrock that undergoes melting, since it produced the best-fit AFC model for post-1971 trends.

Compared to the best-fit AFC model, major and trace element trends that result from stoped and assimilated Mixture 1 wallrock are virtually identical (Mixture 1 SAFC, S = 2 and 5 m.u.; Fig. 9). As revealed by previous SFC models, the major limitation on stoped wallrock addition is the evolution of $^{87}$Sr/$^{86}$Sr in the resident magma melt. As little as 5 m.u. of stoped Mixture 1 exceeds the observed post-1971 $^{87}$Sr/$^{86}$Sr values, whereas 2 m.u. bounds the 3 most radiogenic observed samples not captured by AFC alone (Fig. 9m). These models suggest that stoping of minimal amounts of mixed flysch and skarn (e.g. 2% of the initial resident magma body mass) may accompany assimilation of anatectic melt from a similar wallrock.

DISCUSSION OF MODELS AND THEIR IMPLICATIONS

Evaluation of PM fractional crystallization model

The selected parent magma composition and its best-fit initial conditions (pressure, initial wt.% H$_2$O, and initial fO$_2$), in conjunction with information from the literature, provide constraints regarding these conditions of Etna’s magmatic system. In this section, we discuss the overall fit of the models
and consider causes for misfits between the models and observed data.

**Major oxides, trace elements, and Sr isotopes**

Whereas the drivers of short-term changes like those observed in Etna’s post-1971 period include chemical input from a variety of proposed sources (Clocchiatti et al., 1988; Armienti et al., 1989; Barbieri et al., 1993; Condomines et al., 1995; Tanguy et al., 1997; Schiano et al., 2001; Tonarini et al., 2001; Viccaro & Cristofolini, 2008; Viccaro et al., 2011; Viccaro & Zuccarello, 2017), FC has been invoked as the driver of Etna’s geochemical characteristics over long periods of the volcano (Tanguy et al., 1997). It is also noteworthy that Bohrson et al. (2020) show that recharge of a parent magma to a fractionated derivative magma does not profoundly affect magma compositional evolution after the initial compositional deviation (e.g., increase in MgO and decrease in SiO2 are model outcomes to recharge but the SiO2-MgO trend as FC occurs is similar to the trend without recharge). As such, our primary goal of defining a parent magma for this study is to identify an initial composition whose fractional crystallization evolution reproduces the compositional trends of lavas from the pre-1971 period, especially for K2O, Rb, and 87Sr/86Sr. We recognize that recharge is still occurring, but for the purposes of our study we deem models focused on FC sufficient for the pre-1971 period.

The ~4-ka FS tephra (PM; Tables 1 and 2) is selected as the parent magma because it has geochemical and petrographic characteristics and consider causes for misfits between the models and observed data.

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The ~4-ka FS tephra (PM; Tables 1 and 2) is selected as the parent magma because it has geochemical and petrographic characteristics akin to a primary magma (12–17 wt. % MgO, 920–1330 ppm Cr, and 135–285 ppm Ni, olivine with Fo80–91, and clinopyroxene...
with Mg# 96–92.5), and has a low porphyritic index (<10%) so it is not heavily influenced by crystal addition. FC trends of PM successfully capture the observed pre-1971 K2O, Rb, and 87Sr/86Sr trends, reproduce the general trends for SiO2, Al2O3, FeO∗, CaO, Sr, and Ba, and define the lower limits of La and Nd versus MgO.

However, all model results (including the AFC, SFC, and SAFC scenarios) consistently underestimate Na2O and TiO2. We also explore three theoretical parental magmas from Viccaro & Zuccarello (2017) as alternate choices because (1) at the conclusion of FC, AFC, SFC, and SAFC modeling, it is apparent that the FS tephra chosen as the parent magma does not accurately capture whole-rock concentrations of Na2O and TiO2, which are underestimated in every model run; and (2) we want to briefly evaluate the range of major element compositions produced by fractional crystallization of heterogeneous mantle sources. The starting compositions for these trends use average compositions from Etna’s different eruptive periods whose major and trace elements were then re-equilibrated to primary conditions by adding varied proportions of fractionated minerals in two steps (Viccaro & Zuccarello, 2017). Additional FC models using calculated compositions of primary magmas from Viccaro & Zuccarello (2017) are shown in Fig. 10 (VZ2017). Notably, using these primary magma compositions that represent different periods of Etna’s activity, the models still fail to capture most observed TiO2 trends. In addition, these models, which capture the range of observed Na2O, illustrate that the initial Na2O composition of Etna’s ~4-ka FS tephra is likely not representative of magmas generated over the 1329 to 2005 period.

A magma with an additional ~1 wt % Na2O is a more likely primary composition, as illustrated by FC trends of VZ2017 primary magmas. In comparison to FC of PM, the trends of VZ2017 magmas capture a similar range of values for SiO2, Al2O3, CaO, and FeO∗. The Al2O3 trends differ slightly based on the timing of plagioclase saturation noted by the inflection point. The trend of ‘ET-75’ and ‘Pre-1971’ compositions capture observed pre-1971 variability in terms of K2O in addition to PM. The ‘Post-1971’ initial composition produces a fractionation trend that is the most K-enriched of all FC trends and captures the lowest values of observed post-1971 samples, but still fails to capture the datapoints most enriched in K2O. These results suggest that: (1) the mismatch of modeled and observed TiO2 versus MgO for all trends may be rooted in the control of fO2 on modeled Fe-Ti oxides, (2) the primary melts generated to produce the 1329 to 2005 CE magmas are higher in Na2O contents compared to those from the ~4-ka FS tephra, (3) the variability in the data captured by these alternative parent magmas is consistent with the suggestion that Etna is sourced by heterogeneous mantle (e.g. Viccaro & Cristofolini, 2008; Viccaro et al., 2011; Viccaro & Zuccarello, 2017), and (4) although FC of the ‘Post-1971’ initial composition captures the least K-enriched post-1971 lavas, the range of mantle heterogeneity represented by these samples is insufficient to perfectly explain the majority of enriched post-1971 lavas.

There is also an inherent limitation when comparing MCS modeled data to observed whole-rock data. MCS utilizes batch fractional crystallization, in which crystal phases are removed
at each temperature decrement into a cumulate reservoir that interacts thermally but not chemically with the resident magma melt. As such, the model records the compositional evolution of the melt as the resident magma body cools at an incremental temperature step. This step-by-step compositional evolution of the melt is then compared to observed whole-rock data, which is a straightforward comparison if observed data are taken from glass compositions or largely aphyric rocks. However, in samples where the porphyritic index is greater than \( \sim 10\% \), the chemical effects of crystals need to be evaluated to assess modeled versus observed data fit.

For eruptions between 1329 and 2005 CE, lavas typically exhibit 10% to 40% phenocrysts by volume (e.g. Armienti et al., 1994b; Corsaro et al., 2007, 2009; Viccaro & Cristofolini, 2008; Ferlito et al., 2009; De Beni et al., 2011), and infrequently >40 vol.% (e.g. Viccaro & Cristofolini, 2008; Kahl et al., 2017). No models, including the best-fit AFC model, reach the upper limits of observed Al\(_2\)O\(_3\), CaO, and Sr data. To evaluate if the porphyritic nature of the samples can explain the misfits in these elements, we calculated a bulk cumulate composition based on the average mineral proportions (63% plagioclase, 30% clinopyroxene, 7% olivine) taken from the literature for the 1977 to 2005 eruptions (Electronic Appendix 2), and major oxide mineral compositions taken from the average of all FC steps with a melt composition in the range of \( \sim 2 \) to 8 wt.% MgO in the best-fit AFC model. Mineral trace element concentrations were estimated based on GEOROC mineral compilations. Plagioclase trace element concentrations from the GEOROC database were specifically averaged from Etnean trachybasalts from 1600 to 2005 CE (Viccaro et al., 2016), whereas olivine and clinopyroxene trace element estimates included an average of all trachybasaltic rocks in the GEOROC mineral data compilation due to a lack of available trace element data for Etna-specific samples (Electronic Appendix 2). The Sr isotope value of the cumulate was estimated based on the least radiogenic sample in the data collection.
flows represent the heterogenous nature of the crust beneath Etna (Michaud, 1995). Based on these models, mixtures of skarn and flysch may form the dominant wallrock for the shallow crustal Etna magma storage zone. The assimilation of partial melts generated from flysch-skarn mixtures (excluding those with &gt;80% skarn) yield magma compositions with elevated K₂O and Rb concentrations and ⁸⁷Sr/⁸⁶Sr. The skarns beneath Etna have radiogenic Sr values akin to the seawater at the time of their sedimentary protolith formation in the Cretaceous to Jurassic periods. Sr isotope values of skarns in this study were estimated at 0.7075 based on the seawater curve of McArthur et al. (2001), and the Capo d’Orlando flysch has a value measured at 0.71776 (Table 2). Mixtures of these endmembers thus have Sr isotopic values between these two, with the best fit assimilant having ⁸⁷Sr/⁸⁶Sr of 0.7128 (Mixture 1). Therefore, assimilation raises the Sr isotope values of the resident melt as magma evolution progresses. Furthermore, partial melts of these wallrocks are high in Rb (up to ~800 ppm) and K₂O (up to ~12 wt.%) (Fig 7), which causes significant increases in the Rb and K₂O concentrations in the corresponding contaminated magma melts. We interpret the high concentrations of K₂O and Rb in the partial melts to be the result of the mineralogy of these wallrocks. The flysch-skarn mixtures all contain K-feldspar and biotite, which are rich in K and Rb. As the magma delivers enthalpy to the wallrocks and the wallrock temperatures increased, these minerals melt completely over the course of the model runs. Therefore, the partial melts of flysch-skarn wallrocks are rich in K, Rb, and have relatively radiogenic Sr, and via their assimilation, the resident magma body is enriched in these elements and Sr isotopes. The results of this process coincide well with the post-1971 trends observed at Etna. The sensitivity of ⁸⁷Sr/⁸⁶Sr in the models places a general limit on the mass of stoped material of ~2% of the magma body mass when stoping occurs in conjunction with assimilation. This amount of skarn or skarn-dominated mixes, for various compositions, can be added to the modeled magma melt and still maintain the general major oxide and trace element trends observed in Etnal lavas while not exceeding the observed Sr isotopes (Fig. 9).

Based on the best-fit open-system model, crust-magma interaction beneath Etna likely involves assimilation ± minor stoping of wallrock (Fig. 9) in addition to FC. Best-fit results yield mass estimates that indicate the crustal contribution is likely to be &lt;20% of the initial magma body mass (e.g. ~2 m.u. of stoped wallrock and ~17 m.u. of assimilated partial melts). However, reference to Fig. 9 shows that this model does not capture the entire post-1971 data set for any element or oxide. The most likely explanation is that the sedimentary substrata beneath Etna are heterogeneous, crustal xenoliths described by Michaud (1995) exhibit heterogeneity in their geochemistry and phase assemblages, as do carbonate xenoliths at other Italian volcanoes such as Vesuvius (Jolis et al., 2015) and the Colli Albani district (Di Rocco et al., 2012). Consistent with this suggestion, sensitivity models demonstrate that different wallrock compositions yielded different model outcomes. The skarn utilized in flysch-skarn wallrock combinations is Skarn 1 (Tables 1 and 2). Many eliminated skarn xenolith compositions had comparatively lower SiO₂ values (~7–34 wt.%). Mixing a lower SiO₂ skarn composition with the Capo d’Orlando flysch (SiO₂ = 69.7 wt.%) would reduce the amount of SiO₂ in the wallrock, while retaining the necessary elevated K₂O that the skarns provide. Such heterogeneity could explain the overestimation of SiO₂ that results from the assimilation of partial melts from flysch-dominated wallrock mixtures. Similarly, wallrock mixtures dominated by the Capo d’Orlando flysch tend
to overestimate Sr isotope values. The estimated $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the skarns used in this study (0.7075) is taken from the Sr isotope seawater curve of McArthur et al. (2001) and represents a mid-range seawater value for the Cretaceous period in which most of the carbonates in the Hyblean Plateau formed. However, some of the carbonate rocks of the Hyblean Plateau may have formed as far back as the Jurassic period, where Sr isotope seawater values reached as low as ~0.7068. Invoking variable $^{87}\text{Sr}/^{86}\text{Sr}$ to reflect the heterogeneity of the seawater curve over the time periods in which the carbonate protoliths were deposited may explain the mismatch between the modeled and observed Sr isotope data.

A model for the alkali enrichment trend at Etna

Together, FC of PM and the best-fit AFC/SAFC models effectively bracket the observed pre- and post-1971 whole-rock data (Fig. 9). This holds especially true for K$_2$O, Rb, and $^{87}\text{Sr}/^{86}\text{Sr}$, where PM defines the lower limit of concentrations (i.e. pre-1971 data) and the AFC/SAFC models define the upper limit of concentrations (i.e. post-1971 data). In this section, we discuss a model for the Etnean magmatic storage and transport system based on these models coupled with information gleaned from the literature.

A variety of studies have identified characteristics of Etna’s magma storage and transport system in the lower- to upper-crust (Sharp et al., 1980; Triglia et al., 1990; Murrri et al., 1999; Chiarabba et al., 2000, 2004; Armenti et al., 2004, 2007; Bonforte et al., 2008; Nelson, 2015; Giuffrida & Viccaro, 2017; Ubide & Kamber, 2018; Giuffrida et al., 2023). Significantly, these studies place the upper crustal portions of Etna’s magmatic transport and storage system within the sedimentary basement (~10–15 km depth). Further evidence for the direct interaction between the sedimentary basement and Etnean magmas is recorded by sedimentary xenoliths, which are generally sampled during ascent of magma. Michaud (1995) carried out a systematic mineralogical and geochemical study on xenoliths and their host magmas from the 1892, 1986, and 1989 Etna lavas. The xenoliths are categorized into siliceous, peraluminous, carbonate, and composite types, reflecting the highly heterogeneous nature of the sedimentary basement, and show evidence of morphological, structural, mineralogical, and geochemical alterations, which were likely induced by thermal and chemical exchanges with the host magma. Michaud (1995) also recognized early and strong mobility of K, Rb, and Cs from the xenolith toward its corresponding aneatic melt and enclosing lava, which identifies these crustal rocks as a potential source of alkali elements.

The location of the storage and transport system, along with evidence from sedimentary-metamorphic xenoliths documented at Etna, indicate that magmas are indeed in direct contact and interact physically and chemically with the flysch and carbonate/skarn substrata. The complex nature of the present storage and transport system as a plexus of dikes and sills (Triglia et al., 1990; Armenti et al., 2004; Chiarabba et al., 2004; Corsaro & Pompilio, 2004c; Andronico et al., 2005; Corsaro et al., 2007) creates even larger areas of contact (compared to a single, large magma chamber) between the magma and wallrock to support these thermal and chemical exchanges.

1329–1971 CE

Based on the best-fit FC model of PM, we suggest that the geochemical signature of lavas in the pre-1971 magma transport and storage system was dominated by the supply of a magma similar to the ~4-ka FS tephra, a composition that Kamenetsky et al. (2007) postulates to be the type of magma supplying more recent eruptions. The major oxide (except Na$_2$O and TiO$_2$), trace element, and Sr isotope characteristics of lavas emitted from 1329 to 1971 can generally be replicated by FC of a parent magma that is a high-Mg (12–17 wt. % MgO) basalt to picrite composition (PM), which has lost part of its pristine volatile cargo through degassing and, therefore, has an initial H$_2$O content of 1.0 wt. % at a pressure of ~0.2 GPa. The early fractionation of olivine and clinopyroxene in MCS models drives the basaltic magma to trachybasalt and basaltic-trachyandesite compositions, which are the dominant rock types during this period. This magma rose through the crust and was eventually stored in the upper crust, at ~6 km depth (Fig. 1c). The magma bodies in the complex storage and transport system were delivering enthalpy to the surrounding wallrock. During this period, we suggest that interactions between the magma and sedimentary crust were dominated by thermal exchange but mass transfer (i.e. assimilation and stopping) was not a dominant process. Perhaps, this phase represents the heating of wallrock by low ambient temperatures to higher values approaching the solidus. This pre-heating history is a requirement because ambient crustal temperatures before magma intrusion were ~200 °C to 300 °C, far below the solidus.

Clinopyroxene, a common phase in skarns (including those modeled here), are identified with high $^{87}\text{Sr}/^{86}\text{Sr}$ in the eruptions of 1886 and 2004, which suggest magmatic skarn was present in the surrounding wallrock and later incorporated into these magma bodies (Nelson, 2015). Furthermore, pre-1971 whole-rock Sr isotopes display slight variations (~0.7033–0.7035) (Fig. 2e). As discussed above, FC models for this period are sufficient for the purposes of this work, but differences over a range of 0.0002 $^{87}\text{Sr}/^{86}\text{Sr}$ documented in pre-1971 magmas suggest recharge of magmas with modest isotopic variability was also occurring. Viccaro & Cristofolini (2008) ascribe this to partial melting of a heterogeneously enriched mantle by ancient metasomatic events where increased melting of plagiophyrite, which may have undergone time-integrated increases in radiogenic Sr, can contribute to increases in $^{87}\text{Sr}/^{86}\text{Sr}$.

1971–2005 CE

Conversely, crustal assimilation is a significant process recorded in post-1971 lavas. The major and trace element and isotopic characteristics of lavas emitted from 1971 to 2005 CE can be generally replicated via assimilation and stopping of the sedimentary basement by a parent magma similar to that of the pre-1971 magma system. Upper crustal skarn and flysch contain elevated abundances of alkali elements (K, Rb, Cs) and radiogenic Sr (Del Moro et al., 2001; McArthur et al., 2001; Mikes et al., 2006; Di Rocco et al., 2012), and thermal and chemical interactions between the wallrock and Etnan magmas have the demonstrated potential (Michaud, 1995) to exchange these alkali elements via aneatic melts or fluid phases (Clocchiatti et al., 1988). Additionally, Chiodini et al. (2011) document a shift to heavier $^{87}$Sr isotopes (~4%) in the 1970s and 1980s to ~1% in 2009) from CO$_2$ measurements in Etna’s volcanic gas plumes, which is consistent with carbonate assimilation.

By 1971, we speculate that the wallrock was thermally primed to undergo partial melting sufficient to generate the observed geochemical signatures via their assimilation into the resident magmas. During this time, recharge magmas of variable compositions mixing with resident magmas also may supply some of the heterogeneity in the observed Etnan lavas (Fig. 10). Partial melting of mantle material heterogeneously containing phlogopite,
which has higher partition coefficients for K and Rb than other mantle minerals, should produce magmas relatively enriched in these elements as well as \(^{87}\text{Sr}/^{86}\text{Sr}\) (Viccaro & Cristofolini, 2008; Viccaro & Zuccarello, 2017). Casetta et al. (2019) also highlight the importance of phlogopite and amphibole in Etna’s mantle source, but instead invoke a modally and compositionally homogenous mantle domain melted to different degrees. Either way, variations in magmas supplied by the mantle are likely to generate a degree of heterogeneity via recharge magmas. Magma recharge can also enhance crustal assimilation by supplying additional heat to the surrounding wallrock (e.g. see RAFC examples in Bohrson et al., 2020). Nelson (2015) recorded post-1971 sample rims that are more enriched in radiogenic Sr than their cores, implying that the alkali enrichment event is a late-stage process, and proposed that an increase in the rates of magma recharge can enhance the assimilation process as well. This idea is also supported by experimental studies, such as Iacono Marziano et al. (2008), that demonstrated limestone assimilation can be induced by interaction with a hot, mafic melt.

Based on the results of >300 MCS models that evaluate whole-rock major oxides, trace elements and Sr isotopes, and mineral assemblage identity, composition, and abundance, late-stage crustal contamination by heterogeneous mixtures of skarn and felsic rocks contributes to the mass balance of the enrichment in alkali elements and radiogenic Sr, in conjunction with geochemical variations introduced by a heterogeneous mantle via recharge/magma mixing. Crustal heterogeneity is indirectly supported by the modeling results, which, even in the case of the best-fit model, do not capture all observed whole-rock and mineral data. The suggestion that the magma storage system is a plexus of dikes and sills is also supported by the variability of the observed data, even within a single eruption (e.g. Behnke & Neri, 2003; Clocchiatti et al., 2004; Andronico et al., 2005; Viccaro et al., 2006; Ferlito et al., 2012; Magee et al., 2021). The complex nature of the magma storage system can allow magmas to be stored in physically isolated chambers, which can interact with spatially heterogeneous wallrock compositions or mix with varied recharge magmas, which means these magma chambers are not equally affected by fractionation and other open-system processes (e.g. recharge and assimilation).

CONCLUDING REMARKS

This research demonstrates the utility of the Magma Chamber Simulator to model crustal contamination processes via its application to Mt. Etna volcano. Quantifying crustal input from 1329 to 2005 CE provides insight into the physical and chemical shift that occurred in post-1971 Etna lavas, which includes an intriguing enrichment in alkali elements and radiogenic Sr, and an increase in the volume, frequency, and explosivity of eruptions. The pre-1971 magma storage and transport system is dominated by magmas similar to those observed in the ∼4-ka FS tephra. Thermal interactions stimulated by repeated recharge of hot, mafic magmas induced melting and reaction of the sedimentary crust. By 1971 the wallrock was primed for a sufficient amount of assimilation that could cause the observed increases in K, O, Rb, and \(^{87}\text{Sr}/^{86}\text{Sr}\). The post-1971 magma storage and transport system thus included felsic and carbonate assimilation and stoping, which is a contributor to the post-1971 alkali enrichment. The crustal signature causing the alkali enrichment is in conjunction with the signature of mantle heterogeneity. Thorough modeling studies such as this may prove useful at other volcanoes where crustal contamination is suggested.

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DATA AVAILABILITY

The data underlying this article are available in its online supplementary material.

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