Kaitlyn Nelson

**Title:** Timing and Source of Alkali-Enrichment at Mt. Etna, Sicily: Constraints from Clinopyroxene Geobarometry and *in situ* Sr Isotope Data

**Location:** Mt. Etna, Sicily, Italy

**Introduction and Purpose:**

Understanding the magmatic processes that occur within the magma storage and transport system of a volcano is essential for the improvement of associated eruptive hazards prediction and mitigation. For example, documenting eruption frequency, magnitude of ground deformation prior to eruption, and volume of erupted material informs scientists about the temporal and spatial evolution of a magma chamber (Caricausi et al. 2003; Patane et al. 2005). Furthermore, the collection and analysis of compositional data allows volcanologists to document the thermo-chemical origin and evolution of magmas within a magma chamber, providing insight into subvolcanic processes that influence eruption style and volatility (Metrich et al. 2004; Schiano et al. 2001; Tonarini et al. 2001). As such, characterization of the magmatic processes that impact a volcanic system is crucial for the improved assessment of volcanic hazards, and ultimately helps to preserve both property and life.

Mt. Etna stands as Europe’s largest and most active volcano, its location proximal to areas of population and commerce. Since 1971, the volcano has exhibited increased ground deformation, seismicity and volcanic activity, emphasizing the need for hazard evaluation and prediction (Kamenetsky et al. 2007). However, improved prediction of eruptive hazards requires constraints on the extent of its magma plumbing system and characterization of associated magmatic processes. Lavas erupted over the last 700 years have yielded data (Figure 1), such as whole-rock and mineral geochemical and isotopic signatures, which indicate a complex subvolcanic magma reservoir (Tanguy et al. 1997).

In addition, associated with the increased volcanic activity displayed by Etna post-1971, magmas have exhibited increased abundances of some alkali elements such as K and Rb as well as elevated $^{87}$Sr/$^{86}$Sr (Figures 1a and 1b). The source of this alkali-enrichment has been hotly debated, with opposing hypotheses of mantle vs. crust. Some researchers favor enrichment due to subduction that has changed the character of the mantle source region (Tonarini et al. 2001; Schiano et al. 2001; Metrich et al. 2004). Additionally, differences in Sr/Ba ratios and anorthite
content of plagioclase in historic and recent lavas is interpreted by Viccaro et al. (submitted, Bulletin of Volcanology), to be due primarily to recharge of a geochemically distinct magma derived from a heterogeneously metasomatized mantle.

Collecting plagioclase data in conjunction with whole-rock and geochemical analysis, Pitcher (2011) produced strong evidence for alkali enrichment of an upper crustal origin. However, because plagioclase crystallization is limited to depths of $<10$ km below the Earth’s surface, information about crystallization pathways below this level is necessary in order to build a crustal-scale understanding of Etna’s magma storage system as well as to fully elucidate the origin of alkali-enrichment. Because clinopyroxene crystallizes at deeper crustal levels than plagioclase (e.g., Armienti et al. 2007), I propose to use geobarometry and in situ Sr isotope data from clinopyroxene in 3 pre- and 3 post-1971 lavas to probe the timing and depth of the enrichment, as well as to characterize the mid- to lower-crustal magma chamber history of the volcano. These new data may help resolve a longstanding debate among volcanologists regarding the source of alkali-enrichment, as well as provide information about the processes that influence eruption style, aiding in eruptive hazard prediction and mitigation.

**Background:** Mt. Etna is a composite volcano located in eastern Sicily, Italy within the compressive foreland of the subduction zone between Europe and Africa, and directly south of
the calc-alkaline Aeolian arc (Figure 2). This dominantly basaltic volcano is characterized by low-K\textsubscript{2}O tholeiites that erupted from \( \sim 0.5-0.7 \) Ma. Eruption of more alkaline magmas began ca. 220 ka. Since 1971, magmas have exhibited a marked increase in elements such as K and Rb and in Sr isotopes (Tanguy et al. 1997; Armienti et al. 2007). The source of this recent alkali-enrichment event is controversial: one hypothesis proposes that mantle has been infiltrated by subduction fluid due to a slab tear near Mt. Etna (Tonarini et al. 2001). The second hypothesis involves magma-upper crustal interaction in which a carrier fluid or melt adds alkalis to magma (Michaud 1995; Pitcher 2011), (Figure 3b). As a consequence of this compositional shift, eruptions have become more voluminous and explosive in recent decades (Viccaro et al. 2009).

Thermodynamic modeling and geobarometry show that Mt. Etna's magma system extends from the Moho to the upper crust (\( \sim 0.2 \) GPa, \( \sim 6-6.6 \) km), with plagioclase crystallizing at shallow depths (Putirka et al. 2003; Armienti et al. 2007; Moses 2009). Based on a study by Pitcher et al. (2011), higher K is displayed exclusively in the rims of post-1971 plagioclase, compared to rims of pre-1971 crystals and cores of both pre- and post-1971 plagioclase. In addition, in situ Sr isotope analyses of groundmass are more radiogenic than whole-rock, which in turn are more radiogenic than plagioclase (Figure 3, Pitcher 2011). These data strongly indicate that a component of the alkali-enrichment is late-stage and due to interaction of magma with upper crust.

![Figure 2: Location map and tectonic setting of Mt. Etna and surrounding volcanism](http://www.explorevolcanoes.com/volcanoimages/Italy_map_modern.png)
Methods and Logistics:

I will analyze clinopyroxene from six Etna eruptions dating from 1329 to 2004, including three before and three after the 1971 transition. Clinopyroxene textures will be documented using a petrographic microscope and Back-scattered electron (BSE) imaging. BSE imaging and microscopy will provide textural characterization of complex zoning displayed in the crystals as well as identify a subset of clinopyroxene phenocrysts to be further analyzed using the electron microprobe. Electron microprobe analysis will then be performed at Washington State University in Pullman, WA in order to determine major and selected trace element concentrations. Such analyses will be combined with existing whole-rock data (Graham and Bohrson, unpublished) in order to calculate depth of clinopyroxene crystallization based on the

Figure 3: Sr Isotopes of Plagioclase, Whole-rock and Groundmass for Historic and Recent Eruptions (Pitcher, 2011; 2013); Whole-rock Data from Graham, Spera, Giacobbe
geobarometer of Putirka et al. (2003). This depth estimation will utilize temperature- and pressure-sensitive mineral-melt equilibria to determine the pressures under which the individual clinopyroxenes or parts of clinopyroxene formed. The geobarometer to be utilized for these calculations is that of the equilibrium constant ($K_{eq}$) for the jadeite ($\text{NaAlSi}_2\text{O}_6^{\text{cpx}}$) crystallization equilibrium:

$$\text{NaO}_{0.5} + \text{AlO}_{1.5} + 2\text{SiO}_2 = \text{NaAlSi}_2\text{O}_6^{\text{cpx}}$$

Due to the significant difference between the volume ($\Delta V_r$) of its products and reactants (23.5 cm$^3$/mol), this equation acts as an excellent determinant of crystallization pressures for the system (Putirka et al. 2003). In addition, due to the entropy change of this reaction being non-zero (Richet et al. 1993), the equilibrium is also temperature dependent. Acting as a clinopyroxene thermometer, the following equation may be used to determine the $K_{eq}$ of jadeite (Jd)—diopside (Di) + hedenbergite (Hd) exchange equilibrium:

$$\text{CaFmSi}_2\text{O}_6^{\text{cpx}} + \text{NaO}_{0.5} + \text{AlO}_{1.5} = \text{NaAlSi}_2\text{O}_6^{\text{cpx}} + \text{CaO}^{\text{cpx}} + \text{FmO}^{\text{cpx}}$$

where Fm = FeO + MgO, and CaFmSi$_2$O$_6$ represents Ca(Fe,Mg)Si$_2$O$_6$, or DiHd.

These together comprise a thermobarometry calculation for jadeite crystallization and jadeite-diopside + hedenbergite exchange equilibria which will be utilized to determine the depths of formation for the clinopyroxene:

$$P(\text{kbar}) = -88.3 + 2.82 \times 10^{-3} T(K) \ln \left[ \frac{[\text{Jd}^{\text{cpx}}]}{[\text{Na}^{\text{cpx}}\text{Al}^{\text{cpx}}(\text{Si}^{\text{cpx}})^2]} \right] + 2.19 \times 10^{-2} T(K) - 25.1 \ln[\text{Ca}^{\text{cpx}}\text{Si}^{\text{cpx}}] + 7.03[\text{Mg}^{\text{cpx}}] + 12.4 \ln[\text{Ca}^{\text{cpx}}]$$

$$\frac{10^4}{T(K)} = 4.60 - 4.37 \times 10^{-3} \ln \left[ \frac{[\text{Jd}^{\text{cpx}}\text{Ca}^{\text{cpx}}\text{Fm}^{\text{cpx}}]}{[\text{DiHd}^{\text{cpx}}\text{Na}^{\text{cpx}}\text{Al}^{\text{cpx}}]} \right] - 6.54 \times 10^{-3} \ln[\text{Mg}^{\text{cpx}}] - 3.26 \times 10^{-3} \ln[\text{Na}^{\text{cpx}}] - 6.32 \times 10^{-3} P(\text{kbar}) - 0.92 \ln[\text{Si}^{\text{cpx}}] + 2.74 \times 10^{-3} \ln[\text{Jd}^{\text{cpx}}]$$

These depths of crystallization are expected to vary from deep to shallow within the Etnean plumbing structure, representing a crystallization array from below the Moho (~27 km) to ~0.2 GPa (~6 km).

Clinopyroxenes exhibiting these varying depths of formation will be selected for in situ Sr isotope microsampling. The NewWave microdriller at WSU will be used to drill cores and
rims of the largest and most complexly zoned crystals that show deep to shallow crystallization depths. Sr separation and analysis of $^{87}\text{Sr}/^{86}\text{Sr}$ by thermal ionization mass spectrometry (TIMS) at New Mexico State University with Dr. Frank Ramos will follow. I plan to analyze cores and rims of 3 crystals per sample, for a total of 36 Sr isotope analyses. Clinopyroxene $^{87}\text{Sr}/^{86}\text{Sr}$ values will be compared with existing in situ plagioclase, groundmass and whole-rock data (Figure 4, Pitcher 2011) to test the contrasting hypotheses regarding the source and timing of the alkali enrichment event.

**Anticipated Results:**

Application of thermobarometry and in situ microsampling for Sr isotopes on clinopyroxene will provide a window into the middle to lower crustal dynamics of the Etnean magma storage system. This will allow for a characterization of crustal and mantle geochemical contributions, further elucidating the origin and timing of the alkali enrichment event. I anticipate that those clinopyroxene which crystallize more deeply in the crust will display similar radiogenic Sr signature between pre- and post-1971 samples. I predict late-stage clinopyroxene will be dominated by the alkali-enrichment Sr isotope signature, supporting the hypothesis that the enrichment event occurs dominantly in the upper crust. I also anticipate that, like the plagioclase core and rim Sr isotope data, the deep vs. shallow clinopyroxene will show a range in Sr isotopes; in particular, $^{87}\text{Sr}/^{86}\text{Sr}$ heterogeneity evident in clinopyroxene that forms in the lower crust and upper mantle will allow constraints to be placed on the contribution from heterogeneous mantle.

**Duration of investigation:**

May-July 2013: A subset of samples representing eruptions between 1329 and 2004 that have detailed plagioclase work were assessed using a petrographic microscope. Three pre- and three post-1971 lavas were chosen based on the clinopyroxene textures, and also based on the size and abundance of clinopyroxene.

August 2013: Electron microprobe work and application of geobarometry will be performed.

Fall Quarter 2013: Microsampling of cores and rims of a subset of clinopyroxene (based on results of geobarometry) will occur at WSU, followed by separation and analysis of Sr at New Mexico State University.

January 2014: Microsampling of cores and rims of a subset of clinopyroxene (based on results of
geobarometry) will occur at WSU, followed by separation and analysis of Sr at New Mexico State University.

Winter 2014: Data analysis will be conducted. Drafts of background and methods will be completed.

Spring Quarter 2014: Thesis writing will take place.

Spring 2014: Thesis defense will take place.

Summer 2014: Final revisions will be completed.

**Budget:**

<table>
<thead>
<tr>
<th>Description</th>
<th>Cost</th>
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<tbody>
<tr>
<td>Sr isotope TIMS Analysis, New Mexico State University</td>
<td>$125 per analysis, 36 analyses = $4500</td>
</tr>
<tr>
<td>Electron Microprobe, Washington State University</td>
<td>Three days, $500 ($50/hr) per day = $1500</td>
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<tr>
<td>Mileage to WSU for BSE and electron probe work, lodging, per diem</td>
<td>$358.50</td>
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<tr>
<td>Airfare to Las Cruces, NM for TIMS work, lodging per diem</td>
<td>$1523.60</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td><strong>$7882.10</strong></td>
</tr>
</tbody>
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**Sources:**

Armienti, P., et al., 2007, Mount Etna pyroxene as tracer of petrogenetic processes and dynamics of the feeding system; Geological Society of America: Special Papers, 418; 265-276.


Kamenetsky, V., et al., 2007, Arrival of extremely volatile-rich high-Mg magmas changes explosivity of Mount Etna; Geology, 35; 255-258.

Michaud, V., 1995, Crustal xenoliths in recent hawaiites from Mount Etna, Italy: evidence for alkali exchanges during magma-wall rock interaction; Chemical Geology, 122; 21-42.

Moses, M., 2009, Thermochemical modeling of crystal populations at Mt. Etna, Italy; Central Washington University; Graduate Thesis.


Pitcher, B., 2011, Crustal Assimilation and Magma Recharge in the Recent Mt. Etna Magma Plumbing System: Evidence From In Situ Plagioclase Textural and Compositional Data; Central Washington University; Science Honors Research Program.

Putirka, K. D., 2008, Thermometers and Barometers for Volcanic Systems; Reviews in Mineralogy & Geochemistry, 69; 61-120.

Putirka, K. D., et al., 2003, New clinopyroxene-liquid thermobarometers for mafic, evolved, and volatile-bearing lava compositions, with applications to lavas from Tibet and the Snake River Plain, Idaho; American Mineralogist, 88; 1542–1554.


Viccaro, M., et al. 2009, Dynamics of magma supply at Mt. Etna volcano (Southern Italy) as revealed by textural and compositional features of plagioclase phenocrysts; Lithos, 113; 659-672.
Figure 4b: Model of the Etna post-1971 magma storage system (Pitcher, 2011)
Figure 4b: Model of the Etna pre-1971 magma storage system (Pitcher, 2011)