

# PhD Proposal

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## Motivation

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## Background

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The Ora Ignimbrite (277 +/- 2 Ma) is a welded crystal-rich supereruption-sized deposit located in the southern Alps of northern Italy. Ora represents the final eruptive pulse of the Athesian Volcanic Group (285-274 Ma), a slab-rollback ignimbrite flareup resulting from the oblique subduction of the Paleo-Tethys ocean under Eurasia in the Permian (Marocchi et al., 2008; Best et al., 2016). This volcanic terrain escaped alpine deformation and has been scoured by glacial incision, exposing intracaldera deposits reaching thicknesses of 1350 m. Outflow deposits are less than 250 m thick and are stratigraphically similar to the late-erupted deposits (Willcock et al., 2013) (Fig 1). The Ora eruption is interpreted to have had an early caldera collapse, based on the large amount of intracaldera fill and the fact that the outflow correlates with the late-erupted units of the intracaldera deposit (Willcock et al., 2013). Furthermore, Willcock et al. (2015) identify two discrete collapse calderas (northern and southern) and variations in bulk rock compositions and biotite content between the two calderas suggest that multiple magma chambers were evacuated to form the Ora Ignimbrite.

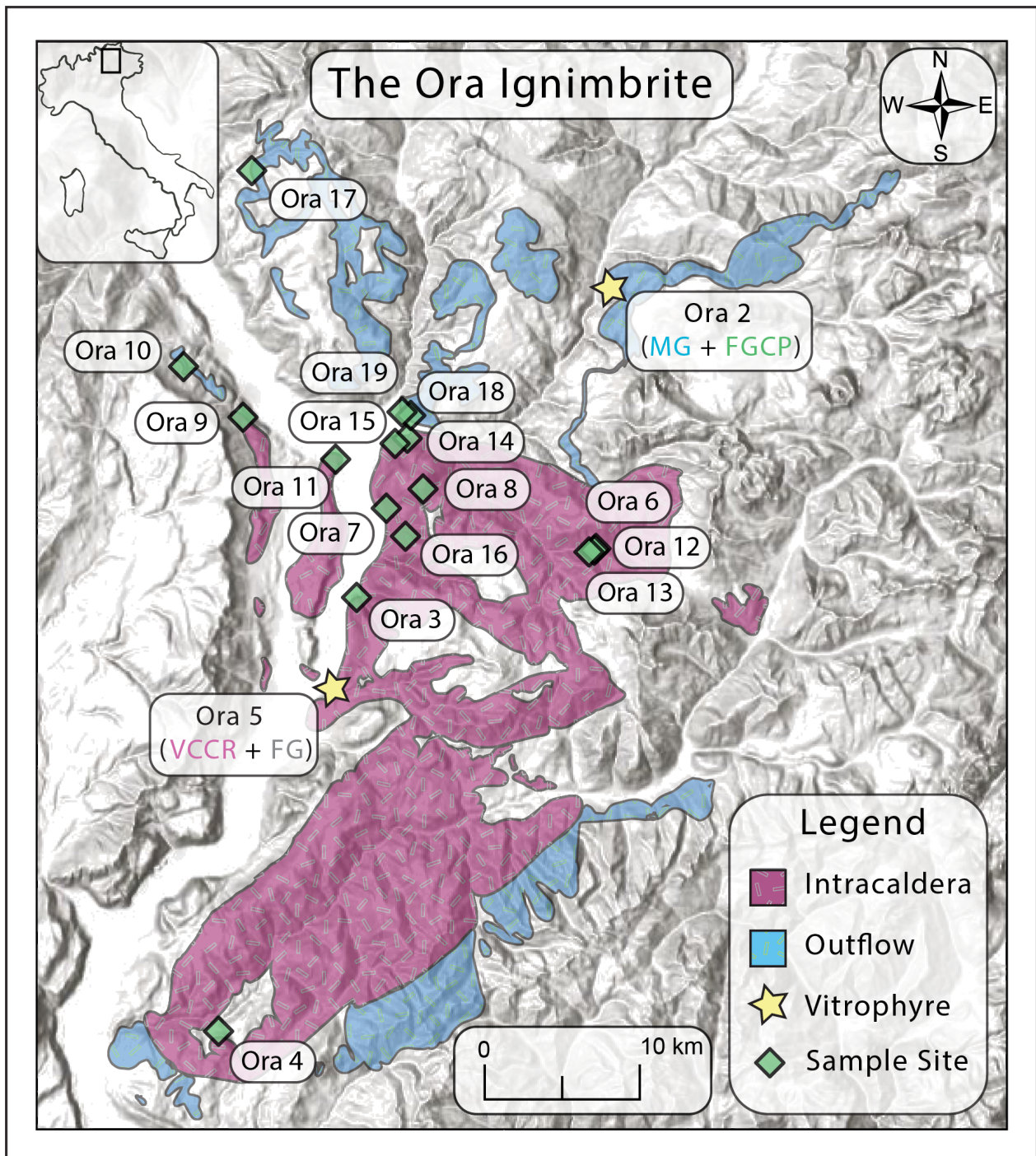


Figure 1: A map of the field location. The four fiamme types identified in Chiaro et al. (in prep) are listed with their corresponding vitrophyre locations.

Table 1: Samples collected in Fall 2017 and Spring 2019. Sample locations are shown in Fig. 1. The number of bulk tuff samples and fiamme are listed.

| Samples:     | Location:               | Type:         | Bulk Tuff: | Fiamme: |
|--------------|-------------------------|---------------|------------|---------|
| <b>ORA 2</b> | Outflow Vitrophyre      | Vitrophyre    | 1          | x       |
| <b>ORA 3</b> | Northern Intracaldera   | Bulk Tuff     | 1          | 1       |
| <b>ORA 4</b> | Odorizzi Quarry         | Bulk Tuff     | 2          | 50      |
| <b>ORA 5</b> | Intracaldera Vitrophyre | Vitrophyre    | 1          | x       |
| <b>ORA 6</b> | Northern Intracaldera   | Rhyolite Dike | 4          |         |

| Samples:      | Location:                     | Type:                           | Bulk Tuff: | Fiamme: |
|---------------|-------------------------------|---------------------------------|------------|---------|
| <b>ORA 7</b>  | Base of Northern Intracaldera | Bulk Tuff                       | 1          |         |
| <b>ORA 8</b>  | Northern Intracaldera         | Bulk Tuff                       | 1          |         |
| <b>ORA 9</b>  | NW Outflow 1                  | Biotite-Rich Fiamme             |            | x       |
| <b>ORA 10</b> | NW Outflow 2                  | Medium-Grained Fiamme           |            | x       |
| <b>ORA 11</b> | Castel Firmiano               | Ash/Ignimbrite Contact          | 3          |         |
| <b>ORA 12</b> | Rhyolite Dike                 | Granite Dike                    | 4          |         |
| <b>ORA 13</b> | Rhyolite Dike                 | Potential Fiamma                |            | 1       |
| <b>ORA 14</b> | Caldera Rim Cutting Dike      | Porphyritic Coarse-Grained Dike | 1          |         |
| <b>ORA 15</b> | Caldera Rim Cutting Dike      | Medium-Grained Dike             | 1          |         |
| <b>ORA 16</b> | Cava Flor Quarry              | Fine and Coarse-Grained Fiamme  |            | 4       |
| <b>ORA 17</b> | NW Outflow 3                  | Fine to Medium-Grained Fiamme   |            | x       |
| <b>ORA 18</b> | Magdalena Hike                | Pseudotachylite                 | 1          |         |
| <b>ORA 19</b> | Magdalena Hike @ Sculpture    | Fine and Coarse-Grained Dikes   | 1          |         |

Recent work has attempted to understand the pre-eruptive architecture of the Ora system by using textural, mineralogical, and geochemical features of fiamme (Chiaro et al., in prep). Fiamme were collected from two vitrophyre horizons: an early-erupted intracaldera deposit and a late-erupted outflow deposit in order to find well-preserved glass. These fiamme were initially grouped into four types based on crystal content and biotite content (Table 2). Glass major elements further verified the categorization scheme.

Table 2: The four fiamme types and their location, crystal content, maximum phenocryst size, and mafic content (Chiaro et al., in prep).

| FIAMMA TYPES:  | DESCRIPTION:                                   | LOCATION     | CRYSTAL CONTENT: | MAX PHENOCRYST SIZE: | MAFICS: |
|----------------|--|--------------|------------------|----------------------|---------|
| <b>TYPE 1:</b> | <b>Very Coarse-Grained Crystal-Rich (VCCR)</b> | Intracaldera | ~40-50%          | >5 mm                | ~2-3%   |
| <b>TYPE 2:</b> | <b>Medium-Grained (MG)</b>                     | Outflow      | ~20-40%          | 1-3 mm               | <0.5%   |
| <b>TYPE 3:</b> | <b>Fine-Grained (FG)</b>                       | Intracaldera | ~20%             | ≤1 mm                | <0.1%   |
| <b>TYPE 4:</b> | <b>Fine-Grained Crystal-Poor (FGCP)</b>        | Outflow      | ~10%             | ≤1 mm                | ≤0.15%  |

Glass trace elements illuminate at least three distinct populations for both the VCCR and MG fiamme, suggesting the presence of multiple magma batches within the Ora system (Fig. 2). Pre-eruptive storage pressures were calculated using the Rhyolite-MELTS (Q2F) geobarometer (Fig. 3). This work suggests that there were two potential scenarios for the pre-eruptive architecture of the Ora magma system. Either there were two distinct crystal mush zones located at slightly different depths within the crust, or there was a continuous crystal mush present with multiple heterogeneous zones located throughout (Chiaro et al., in prep).

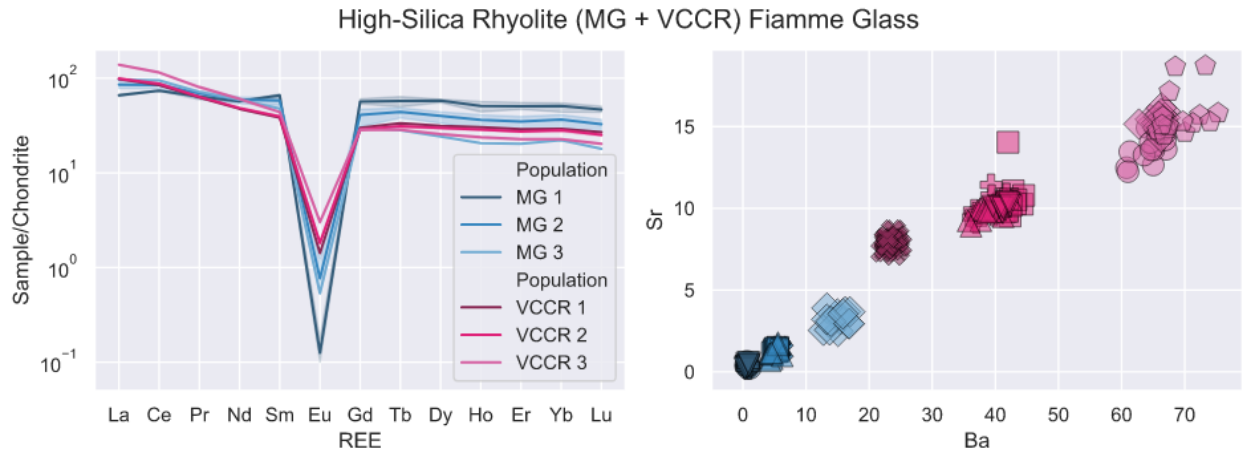


Figure 2: Rare earth element diagrams and a plot of strontium vs. barium illustrate the six discrete glass populations in the Medium-Grained (MG) and Very Coarse-Grained Crystal-Rich (VCCR) fiamme.

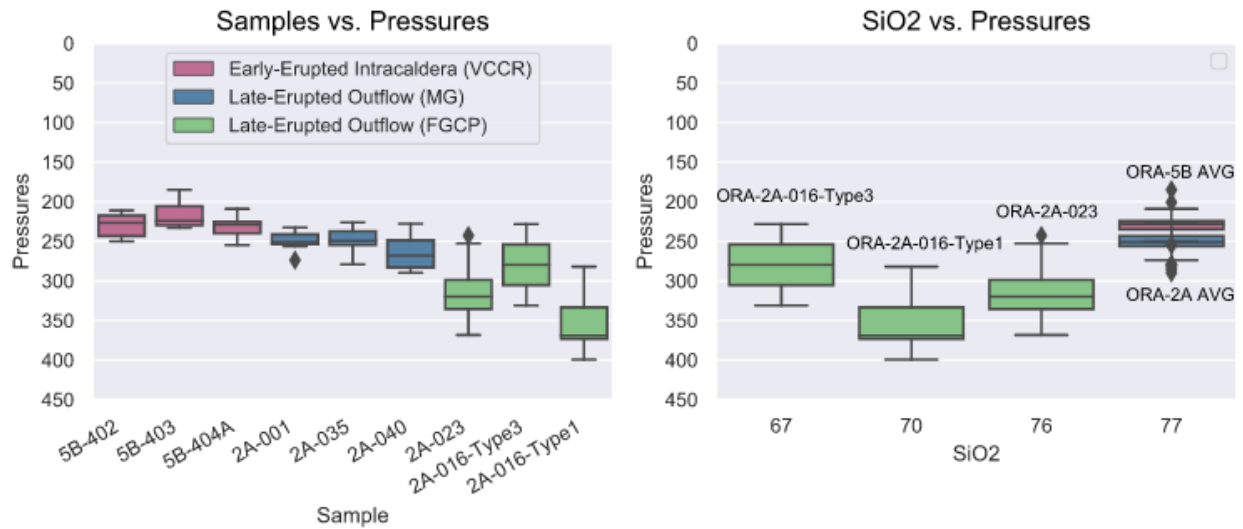


Figure 3: Different fiamme types were stored at different pressures in the crust, with a progression of erupting shallower to deeper magmas through time. Silica content vs. pressure shows variable storage depths for the fine-grained crystal-poor melt, suggesting that there were multiple, small melt bodies located at different depths throughout the magma chamber (from Chiaro et al., in prep).

## Approach

Building on the work from Chiaro et al. (in prep), we propose to use mineral compositions in order to apply this characterization scheme to the entire Ora deposit. Since unaltered glass is only present in the vitrophyre horizons, we plan to use mineral compositions to classify each fiamma. We will collect trace and major elements of plagioclase, alkali feldspar and biotite in fiamme. Preliminary work shows that biotite and plagioclase major elements can be used to differentiate intracaldera vs. outflow fiamme. Furthermore, biotite major element compositions can be used to infer both fiamme type and population (Fig. 4).





Figure 4: Biotite and plagioclase major element compositions from fiamme. Fiamme are divided into population based on hue. Both plagioclase and biotite can be used to determine fiamme type, and biotite can also determine fiamme population (from Chiaro et al., in prep).

### *Hierarchical Clustering and Machine Learning in Python:*

The foundation for this project involves obtaining mineral compositions for the entire crystal. After creating biotite and feldspar EDS maps and collecting trace element profiles, I plan to utilize a hierarchical agglomerative clustering algorithm for major elements in order to statistically determine how many clusters of minerals are present in the fiamme. Another clustering algorithm will be run using trace elements and we will compare the results. Once the clusters are identified, we can observe whether they correlate with fiamme type and population (Chiaro et al., in prep). If we see a correlation, we can confidently use mineral populations to classify fiamme throughout the Ora Ignimbrite. We can also use the mineral maps to visualize core to rim cluster evolution (Fig. 5). By visualizing where the clusters occur in each mineral and by looking at a large enough population of core to rim clusters, we can infer whether crystals experienced similar histories. This approach may reveal information regarding the magmatic processes which occurred prior to the Ora eruption (injection, decompression-driven growth, etc).

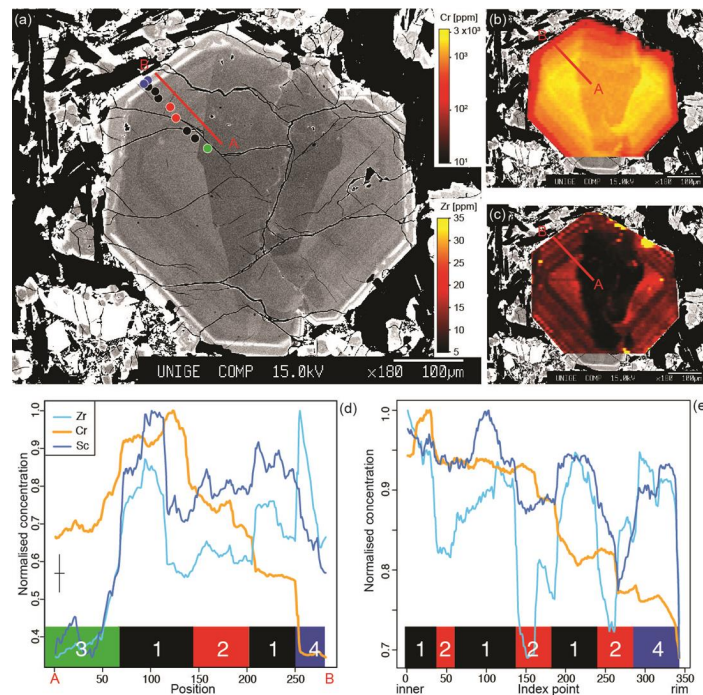


Figure 5: (A-C) BSE and EDS scans of a clinopyroxene phenocryst from the Holuhraun-Bardarbunga eruption in 2014-2015. The circles show the location of the electron microprobe analysis and the color indicates the corresponding cluster from major element analysis. (D) Trace element profiles from A-B.

The colors and numbers at the bottom indicate the corresponding cluster identified with major elements. (E) The same as D, but for another crystal that is not shown (from Luca Caricchi).

We are also interested in identifying the mineral populations that are present in the ignimbrite matrix and seeing whether this varies throughout the deposit. Machine learning algorithms are becoming widely incorporated in scientific studies, and they provide an opportunity to make tedious point-counting obsolete. By utilizing previously determined mineral clusters (major element-based clustering), we can train a machine to classify each mineral in a thin section EDS scan into its associated population. Furthermore, this automatic clustering can be applied to multiple large thin sections, allowing for an estimation of bulk eruptive material. Initial formulation will involve training a supervised machine learning algorithm to identify feldspars. If successful, we will work to develop an unsupervised neural network algorithm. The unsupervised neural network algorithm will effectively create clusters automatically via self-organizing maps and then it will tag each mineral with its identified population.

#### *Spatial Statistics in ArcGIS:*

The spatial distribution of fiamme types and populations has the potential to reveal the locations of eruptive vents that were destroyed during the eruption. Multi-distance spatial cluster analysis (Ripley's k-function) in Arc-GIS investigates the clustering of features over a defined study area. Similarly, this may provide insight on the pre-eruptive magmatic architecture. For example, if the Ora system had two laterally juxtaposed magma chambers that were tapped by different eruptive conduits, we would expect to find two separate clusters with discrete fiamme populations. Integrating spatial statistics and petrology can help us determine how magma was stored in the crust prior to eruption (single chamber, multiple chambers?) and the approximate locations of storage in the x-y plane. If we combine our previously obtained Rhyolite-MELTS data to this model, we can elucidate pre-eruptive storage conditions in three-dimensions.

#### *Sequence Stratigraphy and Ar-Ar Age Dating:*

We propose to investigate whether fiamme type and population change as a supereruption progresses. Our approach will take advantage of the previous work done by Willcock et al. (2013) in which they correlated stratigraphic logs throughout the deposit with observed changes in volcanic lithofacies for 13 intracaldera and 7 outflow stratigraphic sections. More detailed efforts to ascertain the temporal changes of the Ora eruption involved plotting the bulk rock compositions, biotite crystal content, and total crystal content as they varied stratigraphically (Willcock et al., 2015) (Fig. 6). We have identified potential horizons of interest that may signify a change in eruptive material (Fig. 6). By sampling the fiamme types present at these locations, we hope to discover whether there are gradual or instantaneous changes in the fiamme types or populations. Similar to the methodology employed in sedimentary strata with fossil assemblages, we may be able to observe fiamme "extinction horizons" representing the depletion of a magma chamber. We will also utilize this workflow on samples of the ignimbrite matrix with a machine learning algorithm to determine whether we see a change in mineral populations with time. These methods will allow us to extract relative timescales for magmatic events taking place during the Ora supereruption.



Figure 6: Bulk rock compositions, biotite crystal content (Bt), and total crystal content (CF) variation through time. The yellow stars indicate horizons of interest that could show potential changes in eruptive material. Locations 3 and 8 are intracaldera deposits and correlate with Ora 3 and Ora 8. We have yet to sample from location 20, which is just south of the Ora 2 vitrophyre unit. Figure is modified from Willcock et al., 2015.

There has not been much work done regarding age dating for the Ora Ignimbrite. Marocchi et al. (2008) obtained single zircon ages for Ora Ignimbrite of  $277 \pm 2$  Ma for the intracaldera fill and  $274.1 \pm 1.6$  Ma for the outflow. These suggest a time break in the eruptive record. Willcock et al. (2015) suggests that Ora experienced a two-stage eruptive history: the southern caldera collapsed first and the northern caldera followed. However, there is no evidence for paleosols or reworked contacts, suggesting that the eruptions were closely spaced in time. The zircon ages are in contrast with the inferred eruption timescale based on stratigraphic evidence. In order to determine whether the Ora eruption lasted for millions of years or was constrained to a shorter time period, we plan to obtain Ar-Ar sanidine ages. Argon is trapped upon eruption so these will provide eruptive ages. We will first determine eruption ages for the intracaldera vitrophyre and the outflow vitrophyre to see if we can resolve discrete ages. If so, Ar-Ar sanidine ages provide a methodology to “deconstruct” a supereruption into distinct volcanic pulses (Kay, 2011). Combined with our work on fiamme type distribution for a stratigraphic column, we may be able to resolve maximum timescales of magma chamber depletion for the Ora system.

## Methods

### *Sample Collection:*

The samples collected during the 2017 and 2019 field seasons are shown in figure 1 and their descriptions are listed in table 1. Currently, we have a disproportionate amount of samples from the northern intracaldera. In order to reduce the sampling bias for our spatial statistics, we will obtain

more samples from the southern intracaldera and southern outflow. Clustering analyses in ArcGIS requires at least 30 features to be reliable. In order to sample a significant number of fiamme, we will make fiamme mounts to maximize sampling potential and analysis speed. The ignimbrite matrix samples will be made into 75 x 50 mm billets.

#### *Analytical Work:*

We plan to obtain EDS scans of individual mineral grains and corresponding BSE images using the Tescan VEGA3 SEM at Vanderbilt University. We will also collect trace element profiles using line scans with consistently spaced laser pits from the ThermoFisher iCAP Qc quadrupole ICPMS at Vanderbilt University.

#### *Hierarchical Clustering and Machine Learning in Python:*

The skills to develop code for this project will be gained from taking DataCamp online courses and also by utilizing the abundant wealth of information on the internet. The hierarchical clustering algorithm will effectively calculate the Euclidean distance between all the points and store them in a proximity matrix. Points with the smallest distances separating them will be merged into clusters until only one single cluster is left. A dendrogram is then created and the optimum number of clusters is determined visually by intersecting the tallest vertical line in the dendrogram. The machine learning algorithm will be trained to classify minerals into these pre-defined clusters based on major element data from an EDS map. In order to test the efficacy of this method, we will first test it on a large thin section of bulk tuff from the vitrophyre. If we can estimate the bulk eruptive material here, we can apply the methodology to a single stratigraphic section. If successful, we can apply this to a stratigraphic horizon in another part of the caldera and see if we observe similar results.

#### *Spatial Statistics in ArcGIS:*

Proficiency in ArcGIS was gained from an Advanced Spatial Analysis course taken in 2018 at Vanderbilt University. ArcGIS skills will be refined by participating in an ESRI MOOC titled Spatial Data Science: The New Frontier in Analytics which runs from February 12-April 9, 2020. The Spatial Analysis Research Laboratory (SARL) at Vanderbilt University will also provide expertise in GIS if any roadblocks may arise.

#### *Ar-Ar Dating:*

Ar-Ar sanidine ages will be obtained from the New Mexico Geochronology Research Laboratory (NMGRL) at New Mexico Tech. Sanidines will be separated, irradiated, and prepared for analysis using a Thermo Scientific Helix Multicollector. Funding for Ar-Ar dating will hopefully be provided by the Awards for Geochronology Student Research 2 (AGeS2) grant which will provide support for one year in 2020.

## **Timeline**

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*Year 1 (2019-2020):*

*Year 2 (2020-2021):*

*Year 3 (2021-2022):*

## **Broader Impacts**

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Developing open-source science with python with hopes of uploading to the ENKI server for distribution.

Mentoring undergraduates! Female Power!!

# References

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