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# “Careful Mr. Frodo – It’s hot!”

## Using pyroxene thermometry to estimate pre-eruptive temperatures of Mt. Ngauruhoe (Mt. Doom) lavas

## Abstract

The erratic eruptive behavior of strato-cone volcanoes, like Mt. Ngauruhoe in New Zealand, presents a significant volcanic hazard. Therefore attempts at understanding them are critical. This study uses pyroxene thermometry with basaltic andesite samples from Ngauruhoe to help further constrain pre-eruptive temperatures, which can greatly affect eruption style. However the use of petrographic rather than more quantitative data created enough uncertainty that the temperature data calculated predicts a wider range than previous estimates do.

## Introduction

Mt. Ngauruhoe (Mt. Doom from the Lord of the Rings) is the most active vent in the Tongariro Volcanic Complex (TVC) at the southern end of the Taupo Volcanic Zone (TVZ), an 180km long swathe of volcanoes that runs NE-SW across New Zealand’s North Island. The TVZ consists of many discrete volcanic cones and shows a cyclic change in lava composition along its length from basaltic andesites and basalts at its NE extreme to volumetrically dominant pumices with silica contents of up to about 70% near its center. At its SW end, where Ngauruhoe is located, volcanic activity again produces more mafic material.

Although Ngauruhoe lies with the popular Tongariro National Park and is a highly active volcano with 5 major eruptions in the past 140 years, a lack of data severely limits our current understanding of this potentially dangerous volcano. One short paper (Hobden, et al. 1999) presents a study of the geochemical evolution of Ngauruhoe lavas, but has only sparse citations and is at odds with other papers (such as Cole et al. 1986 and Cole 1978) as well as petrographic evidence on some properties of Tongariro Volcanic Center (TVC) lavas. Additionally, few studies have been undertaken to determine possible pre-eruptive conditions for Ngauruhoe lavas. A paper by Graham et al. (1987) gives an estimate of pre-eruptive conditions, concluding from the use of a simple phase diagram that pressures were likely around 1kbar and temperatures were at least 775ºC. Other than this, pressure and temperature conditions do not appear to have been considered in detail.

Therefore, this study focuses on a very simple, inexpensive, and therefore easily applied method to estimate pre-eruptive temperatures. A paper by Lindsley, (1983) outlines a way to estimate such temperatures using the composition of clinopyroxenes (known for this paper as cpx). However, the method I used to estimate the compositions themselves incorporated so much uncertainty that the final estimated temperature range was larger than the 1050ºC to 1200ºC range presented in Graham et al. (1995). A discussion of the imprecise methods I used, the trivial conclusions that resulted, and the possible sources of the method's tremendous uncertainty follows.

## Methods

Lindsley (1983) presents a method for estimating pre-eruptive temperatures in lavas based primarily on the composition of calcic pyroxenes. Orthopyroxenes, (opx) so named because their crystallographic structure is a rectangular (orthogonal) box, tend to have low concentrations of calcium (Ca), while clinopyroxenes, ones with monoclinic (non-orthogonal) crystal systems contain more Ca. The details of Ca content, however, vary predictably with temperature: clinopyroxenes become depleted in Ca with increasing temperature, while opx are conversely enriched. Therefore, the relative abundances of Ca can be used to estimate the temperature of a lava before eruption.

The simplicity and elegance of this method are, however, diminished by the techniques needed to gain the necessary Ca data. In the case of this investigation, I didn't have access to an ion-microprobe, meaning that the composition of pyroxenes had to be derived through other less precise methods (see below). Since the actual Ca content of opx is usually very low, (comprising less than 5% of the major cations in Tongariro lavas (Cole et al.,1986)) for the purposes of this study, opx was assumed to contain no appreciable amounts of Ca. Rather cpx was used as the basis for estimating temperature, which also allowed for the application of a simplified version of Lindsley's method.

To obtain and contextualize the geochemical data I needed in order to apply Lindsley's method, I spent several days mapping lava flows and collecting a total of 19 samples from 16 different flows in the Mangatepopo Valley below Ngauruhoe. To estimate the Ca content of the cpx, I obtained bulk elemental compositions for our samples using X-ray Fluorescence (XRF). I then chose 5 samples that showed a wide difference in Ca, iron (Fe), and magnesium (Mg) contents – the primary cations in cpx – to further analyze. Using thin sections and the Michel-Lévy method averaged over at least 10 plagioclase grains, I obtained an estimate for the anorthite (Ca) content of the plagioclase in each of the 5 samples. Since Na is known to be scarce in the cpx of Tongariro lavas, (Graham et al. 1987) I assumed that all Na identified by XRF was accommodated in plagioclase (see figure 1 for behavior of Na, Ca content between samples). Combining this assumption with the anorthite content of the plagioclase allowed me to estimate how much of the Ca that the XRF measured was likely in plagioclase, and how much was left over and therefore likely incorporated in cpx. Since the cpx compositions that Lindsley considers are presented in ternary diagrams of Mg, Fe, and Ca, (i.e. they are given as ratios of the form $Ca_{\alpha}Mg_{\beta}Fe_{\gamma}$ where $\alpha+\beta+\gamma=100$ so that α is the percent of Ca cations in a non-tetrahedral site, β is the percent of Mg cations in the same kind of site, etc.) the relative amounts of Fe and Mg in the cpx were also needed.

I applied a similar method for both Fe and Mg, using olivine, opx, and magnetite instead of plagioclase as these are the primary Fe and Mg bearing phases recorded in literature (Graham, et al. 1987) and observed under thin section. Once I had this data, I was able to estimate the composition of cpx in the form $Ca_{\alpha}Mg_{\beta}Fe_{\gamma}$, which allowed me to use the diagrams in Lindsley 1983 to estimate pre-eruptive temperatures. Using diagrams to predict results is a great way to introduce error; however the uncertainty in other areas of this study was large enough to render any error from the use of diagrams inconsequential (see Table 1.).

## Concluding the Trivial and Discussing the Trivial Conclusion

The petrographic method I used in this study proved so imprecise that the final uncertainty in composition was well over ±100%.

| Final ternary formula | Final molecular formula | Uncertainty as percent of measured value |
|---|---|---|
| $Ca_{32}Mg_{51}Fe_{18}$ | $Ca_{(0.64)}Mg_{(1.01)}Fe_{(0.35)}Si_2O_6$ | >100 |
| $Ca_{10}Mg_{51}Fe_{39}$ | $Ca_{(0.21)}Mg_{(1.02)}Fe_{(0.77)}Si_2O_6$ | >100 |
| $Ca_{41}Mg_{36}Fe_{23}$ | $Ca_{(0.81)}Mg_{(0.73)}Fe_{(0.46)}Si_2O_6$ | >100 |
| $Ca_{34}Mg_{52}Fe_{15}$ | $Ca_{(0.68)}Mg_{(1.03)}Fe_{(0.29)}Si_2O_6$ | >100 |
| $Ca_{47}Mg_{43}Fe_{10}$ | $Ca_{(0.93)}Mg_{(0.86)}Fe_{(0.20)}Si_2O_6$ | >100 |

**Table 1. Calculated values of cpx composition**

This means that the cpx composition in my samples couldn't be distinguished from $Ca_{100}Mg_0Fe_0$ , $Ca_0Mg_{100}Fe_0$ , or $Ca_0Mg_0Fe_{100}$. In fewer words, the results themselves were trivial and imply that this method needs significant improvement. Estimates of the Ca content in cpx were negative for two samples, implying not only some error in the determination of plagioclase composition, but also suggesting that these samples should not have cpx. In fact, the estimated cpx abundance was about 5% for all samples. If the Lindlsey method is assumed to be valid for such a range in composition, it predicts that pre-eruptive temperatures were likely in the range of 900°C ± 500°C. Indeed, 400°C seems unlikely to liquefy a basaltic andesite enough that it could erupt effusively, while 1300°C is at the uppermost limit of current magma temperatures.

Furthermore, these results are uncertain enough that they do not even acknowledge the compositional distinction between opx and cpx. Allowing 100% variation in cpx composition covers the entire range of Na-poor pyroxenes, so opx and cpx, which have different concentrations of Ca, Mg, and Fe, cannot be distinguished from each other compositionally. Orthopyroxene, with its pleochroism and low birefringence, visibly coexists with cpx under thin section. In this case, the results from this study are less enlightening than simply looking down a petrographic microscope. Indeed, when it does not state the obvious – that the lavas of Ngauruhoe likely experienced pre-eruptive temperatures within the range best described as possible – the data from this study contradicts the obvious. Therefore, this study is best viewed as proof that the simple method it employs does not generate meaningful results, at least for Ngauruhoe lavas. Given the extremely high uncertainty, and therefore low applicability, of the results presented here a review of possible error sources seems necessary.

## A Review of Possible Error Sources

The most likely and likely most significant sources of error derived from the use of thin sections and petrographic techniques rather than more reliable ones to estimate plagioclase composition and mineral abundances. Using the Combined Carlsbad-Albite Twinning Method to estimate the composition of several dramatically zoned plagioclase grains revealed an average core composition of about $An_{85}$ (i.e. Ca accounted for 85% of the non-tetrahedral cation sites with Na occupying the remaining 15%) and an average rim composition of about $An_{65}$.

Therefore, estimating a bulk An content for each sample was likely a very imprecise exercise. Furthermore, much of the plagioclase appeared light (1st order) yellow in thin section under crossed polars, suggesting that perhaps the thin sections were slightly thicker than the expected 30μm. A "thick" thin section would increase the path-difference between the two perpendicular planes of light oscillation within the crystal and therefore would be expected to change the direction of polarization upon exiting the crystal. This itself would be expected, then, to influence the extinction angle. Grains showing more standard 1st order grey interference colors were chosen for measurement where possible, but a thick thin section may still have influenced the estimates of An content in these grains.

Despite these difficulties with the estimation of plagioclase content, the visual mineral abundance estimates alone were enough to induce 100% uncertainty. While estimating the modal percents of minerals under thin section, I also estimated an uncertainty for each value. The calculations necessary to convert from modal percents to mole fractions are extensive if not complex, and these initial uncertainties increased through the calculations until they reached 100% of the measured value, at which point they were no longer tracked. Indeed, cpx with a composition like $Ca_{-33}Mg_{-33}Fe_{-33}$ makes little physical sense, but may be within the range of uncertainty if the uncertainty is greater than 100%.

## Conclusions and Moving Forward

This study provided proof that greater accuracy and precision are needed in order to use the Lindsley method on Ngauruhoe lavas. Unfortunately the simple and easy petrographic methods – such as estimating An content of plagioclase and modal percentages – were simply inadequate to produce meaningful results. Gathering X-Ray Diffraction (XRD) data as well as XRF data may provide a simple solution as it would allow for a far more reliable estimate of mineral percentages and therefore a more reliable estimate of the proportion of elements accommodated in each mineral. Additionally, the density of the cpx in the sample was needed to estimate the molar abundance of cpx, resulting in a problem of circular regression: the composition of cpx is needed to calculate the density, which is needed to calculate the composition. XRD data may help with this as well and provide a more reliable estimate of cpx molar abundance. Otherwise, the problem of density may require more creativity. Estimating the bulk density of a sample would give an estimate of cpx density, however these samples are so highly vesicular that bulk density measurements would be difficult to obtain. Alternatively, there may be an iterative way to deal with this problem of circular regression, but this avenue requires more mathematical development and may itself prove problematic. An ion microprobe would certainly be the most straightforward and most accurate way to obtain compositional data.

Finally, an investigation into the chemical equilibria of Ngauruhoe lavas would likely constrain pre-eruptive temperatures even more. Olivine in the samples is visibly altering to opx (see figure 2), suggesting a reaction between it and silica. The compositions of olivine and opx are well described in general in Graham (1985), which may allow an estimation of pre-eruptive conditions based on the reaction of olivine and silica to produce enstatite (a magnesium silicate).

# Figures

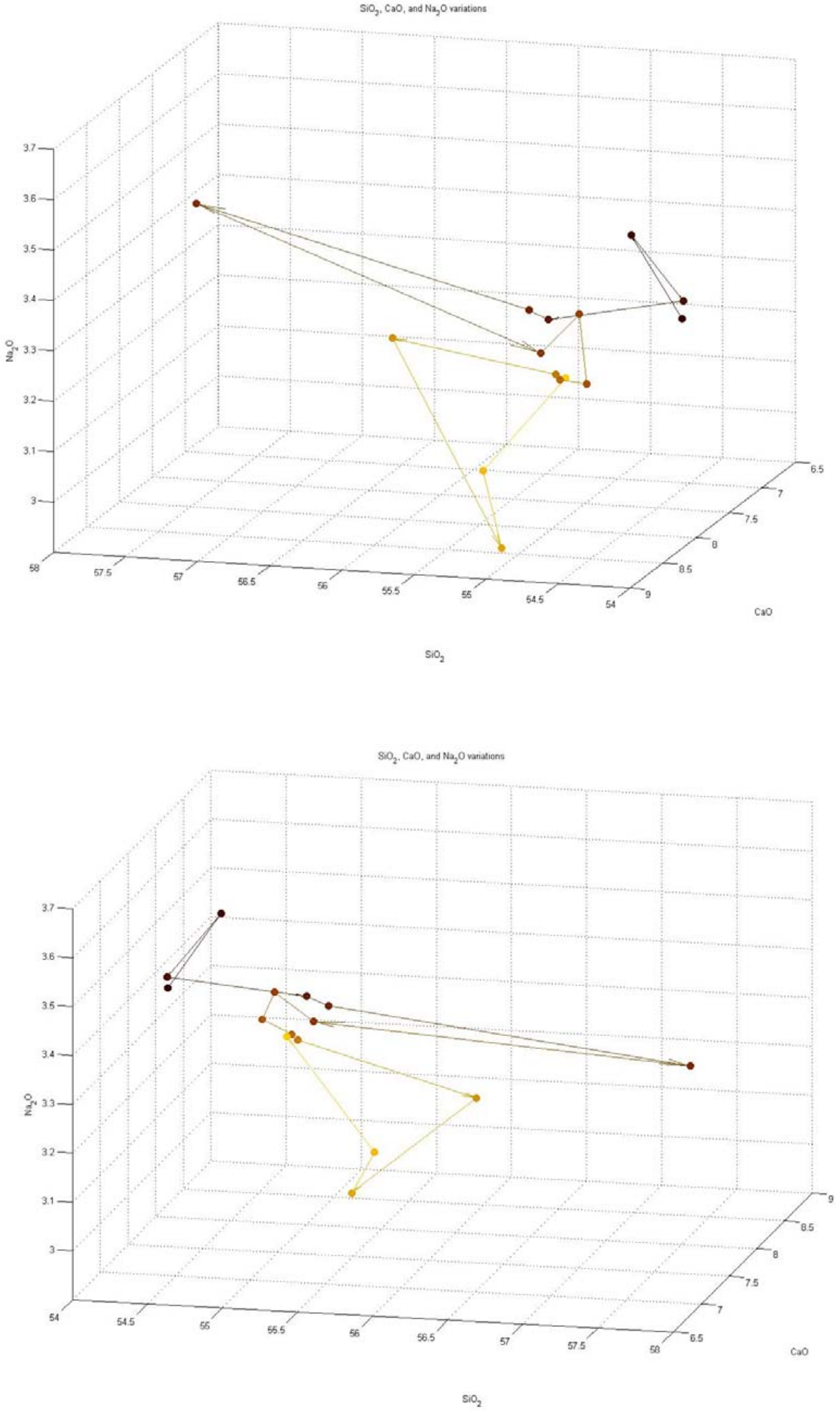

**Figure 1. Two views of the compositions of samples shown in $SiO_2$-CaO-$Na_2O$ space. Darkest points are inferred to be the oldest samples, lighter points are younger based on relative ages obtained during field mapping.**

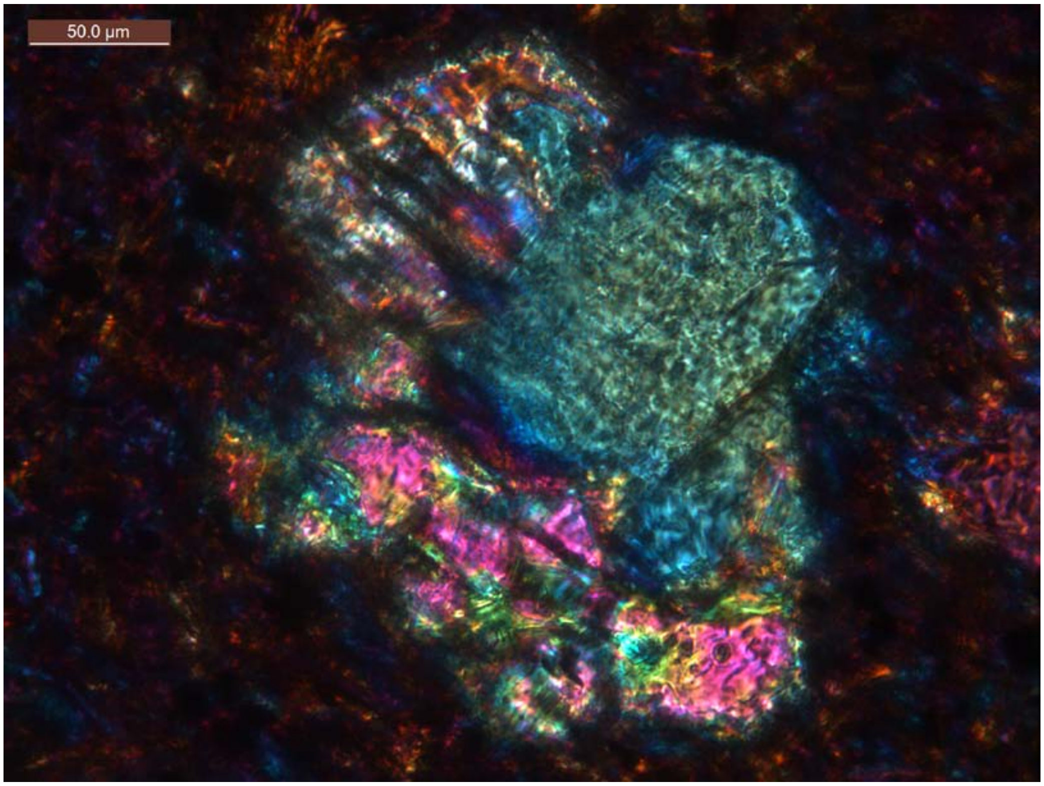

**Figure 2. Olivine (ahedral mass with maximum 3rd order pink intereference color) appears to be altering to opx (euhedral blue grain with hexagonal cross-section). Photograph taken at 40x mag. with crossed polars and standard gypsum plate.**

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