# Using titanite to determine magmatic thermal histories of granites

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## Introduction

Granite, the most abundant rock in the continental crust, is primarily comprised of the minerals quartz ($SiO_2$), potassium feldspar ($KAlSiO_8$) and plagioclase feldspar [$(Na,Ca)Al_{1-2}Si_{2-3}O_8$], but also contains minor abundances of zircon, titanite, amphibole, and biotite. The crystallization temperatures and cooling rates of granites are critical factors for understanding the formation and evolution of magmas in the crust, yet both (particularly cooling rates) are poorly constrained. Titanite ($CaTiSiO_5$), also known as *sphene* , can be an important tool for analyzing the cooling histories of granites. The diffusion of elements can be observed in titanite zoning patterns, which can then be analyzed to determine the cooling rate of their host granite. Additionally, thermobarometry that utilizes the substitution of $Zr^{4+}$ for $Ti^{4+}$ in titanites can be used to calculate the temperature at which the granite crystallized. The goal of this study is to better understand the thermal histories of granites, and in doing so gain knowledge of the process of continental crust formation.

## Applications

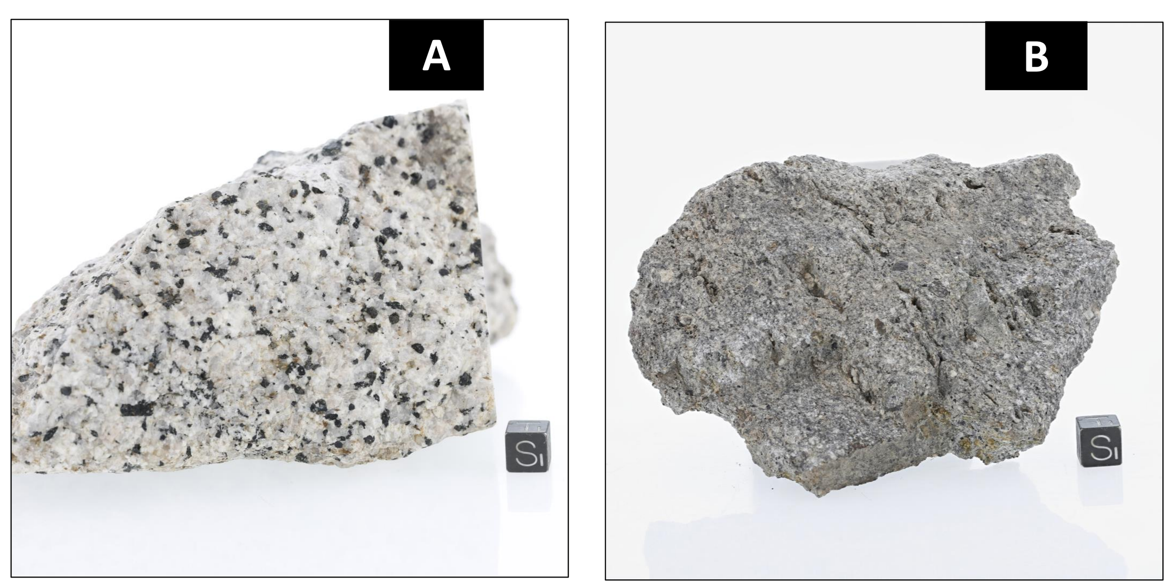



**Figure 1 – (A) Half Dome granodiorite; (B) Fish Canyon Tuff dacite**. The die is 1cm$^3$.

The Half Dome Granodiorite in Yosemite National Park (Fig. 1A) and the volcanic dacite of the Fish Canyon Tuff in Southwest Colorado (Fig. 1B) share almost the exact same mineral composition. Curiously, the granites of Yosemite cooled peacefully in the crust, whereas the Fish Canyon Tuff comes from the largest volcanic eruption in Earth's history—releasing 5000 km$^3$ of volcanic material instantly to the surface. One potential reason for the differences between these two systems is differences in their thermal histories: at what temperatures did they form and how long did they reside in the crust? Analysis of titanites can help quantify this phenomenon.

## Methods

We utilized the following techniques:

- Sample-collecting in Southwest Colorado
- Micro X-ray Computed Tomography (μ-XRCT)
  - Gather 3-D images of titanite crystals to identify the exact positions of their zoning patterns
- Scanning Electron Microscopy (SEM)
  - Analyze zoning patterns and collect data via x-ray line scans
- Electron Probe Microanalysis (EPMA)
  - Improve upon analysis of SEM
- Identify $S_0$ from line scan diffusion step profiles to calculate cooling rates
- Zr-in-sphene thermobarometry
  - Obtain crystallization temperatures

## Results

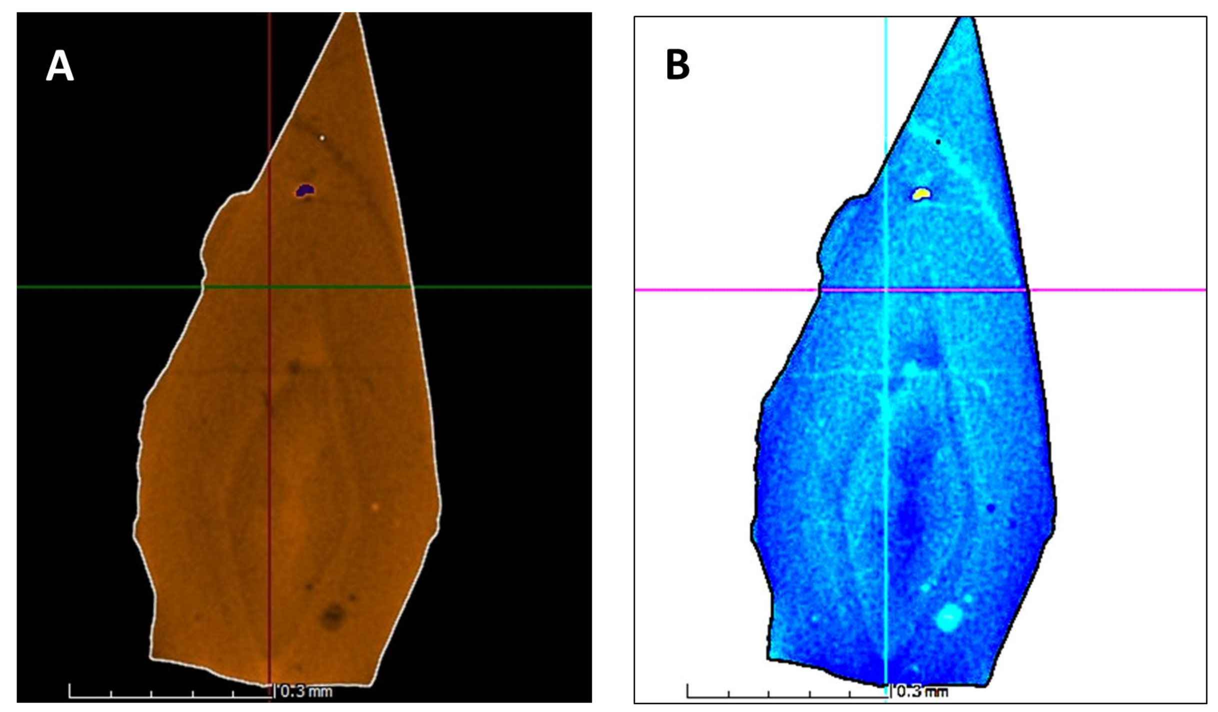



**Figure 2 – Cross-section viewing of a titanite crystal that was 3D imaged by μ-XRCT**. (A) Oscillatory zoning (concentric diamond-shaped ring patterns) and sector zoning (central bowtie-shaped patterns) are indicative of the how the crystal grew. As a titanite grows, elements diffuse across these zoning boundaries. (B) A color-inverted image of Fig. 2A with increased contrast to highlight these zoning arrays. The crosshairs are axis planes left over from the imaging software

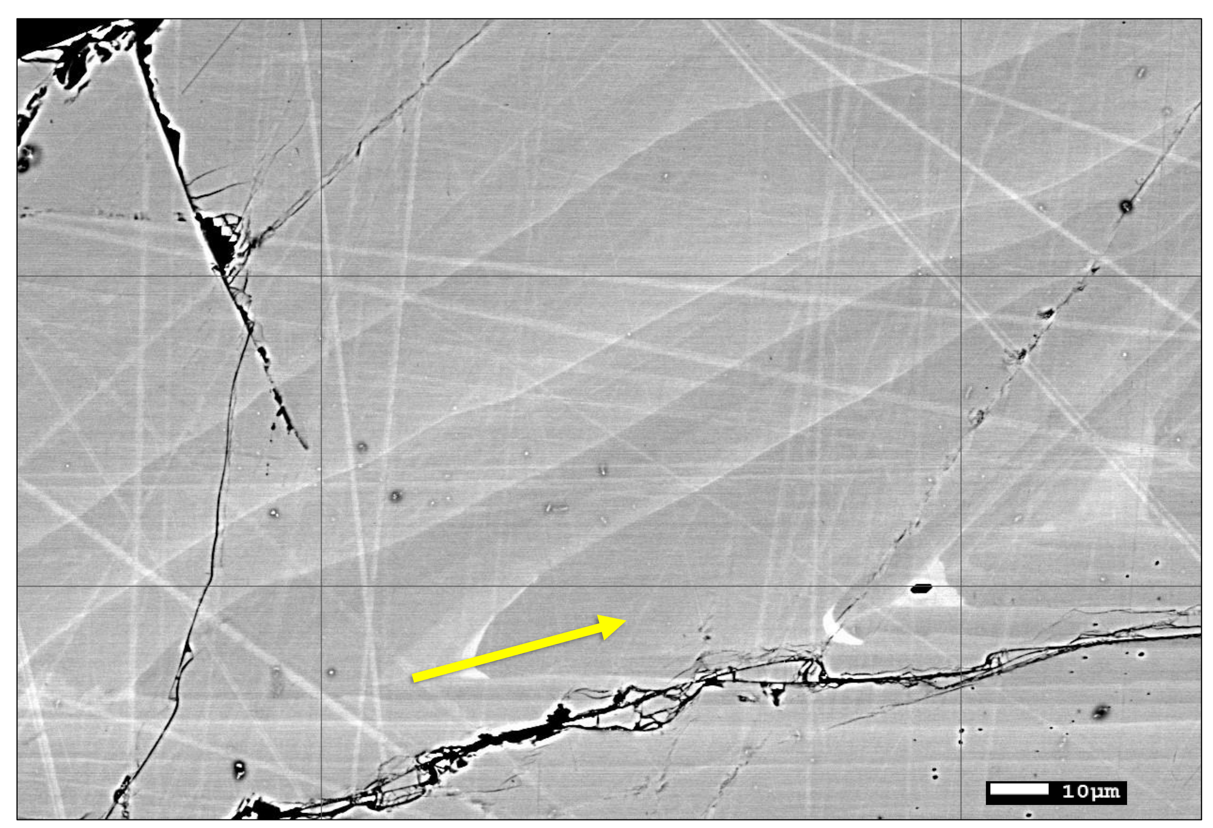
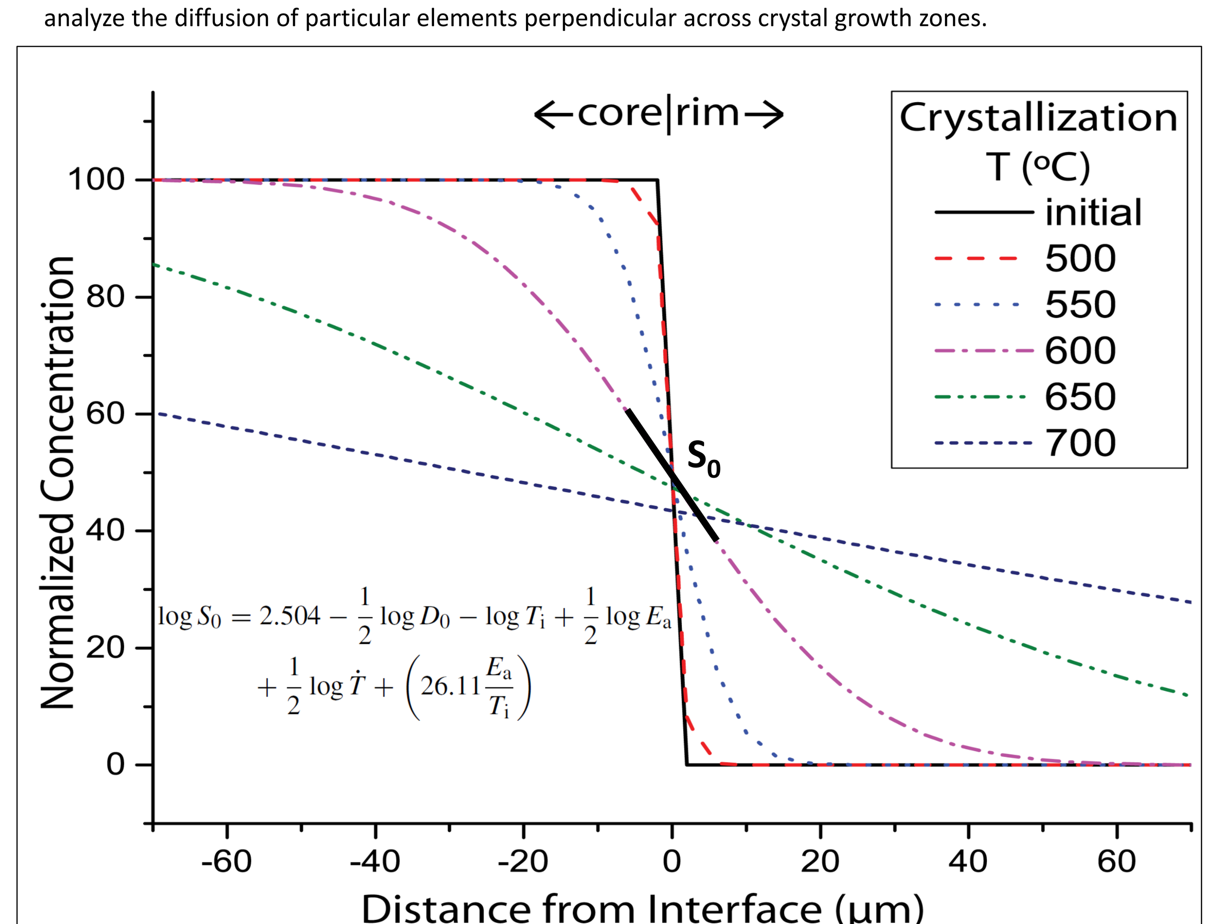



**Figure 3 – Electron backscatter image of a Half Dome titanite**. The scratches are imperfections from polishing. The arrow indicates the direction of the EPMA line scan. The scan uses an electron beam to generate x-rays from the atoms along the line to identify the elements present. This method is used to analyze the diffusion of particular elements perpendicular across crystal growth zones.




$$\log S_0 = 2.504 - \frac{1}{2}\log D_0 - \log T_\mathrm{i} + \frac{1}{2}\log E_\mathrm{a} + \frac{1}{2}\log \dot{T} + \left(26.11\frac{E_\mathrm{a}}{T_\mathrm{i}}\right)$$

**Figure 4 – Model of a diffusion step profile**. Before diffusion occurs, one side of the sector zone will have a 100% relative concentration of a particular element compared to the other side with a relative 0% concentration of the same element. Diffusion may occur more rapidly for different elements depending on a number of factors. A fast diffusion profile is represented above as the dotted dark blue line, and a slow diffusion profile would be the dashed red line. We can take the slope $S_0$ that is tangent to the point at exactly the interface of the sector zone and apply it to the equation from Watson and Cherniak (2015) to calculate a cooling rate $\dot{T}$ for the crystal. $D_0$, $T_i$, and $E_a$ are known constants. Comparing two elements can also yield potential crystallization temperatures.

## Results

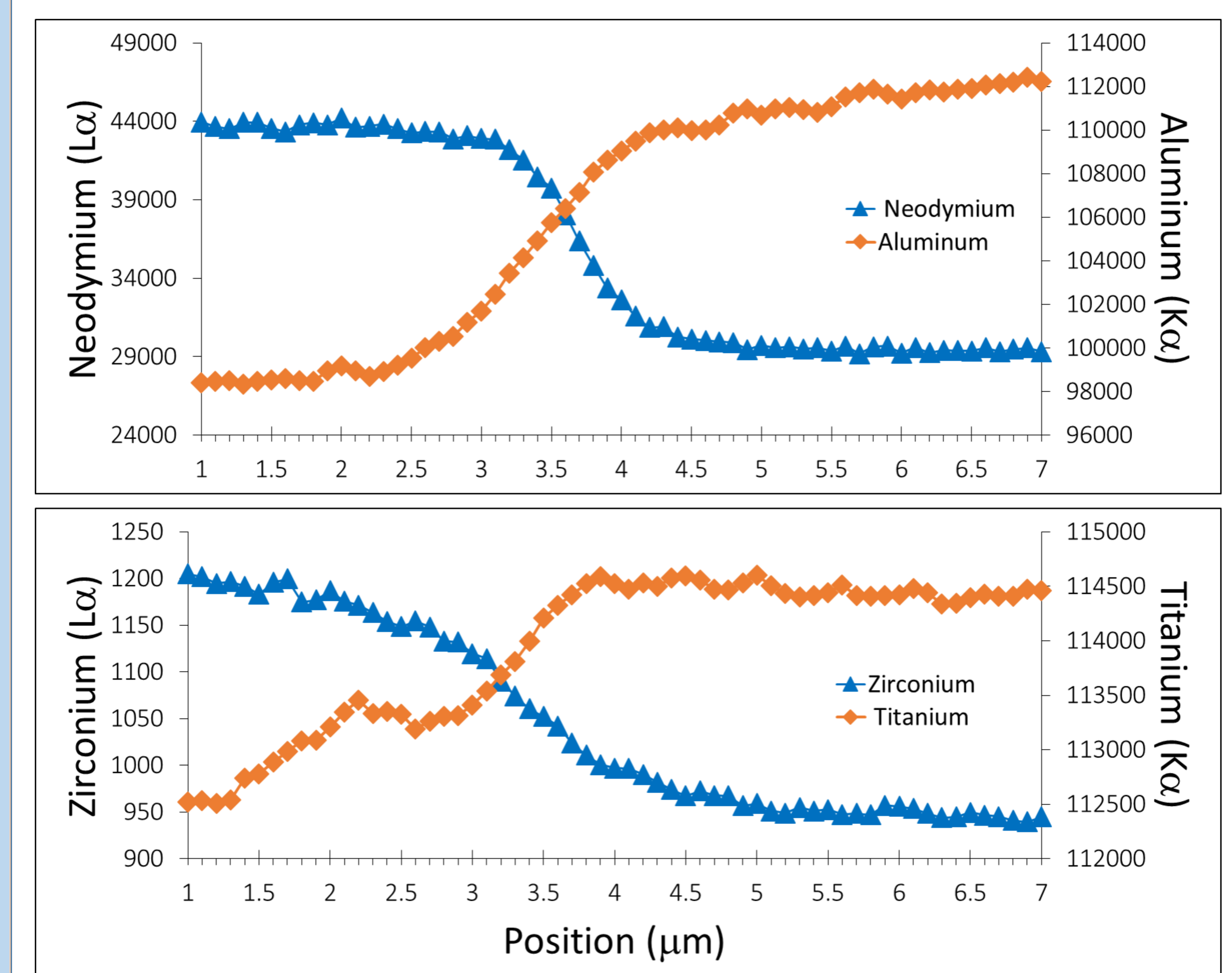



**Figure 5 – Diffusion step profiles for Nd/Al and Zr/Ti from a porphyritic Half Dome granodiorite**. Data was obtained using the EPMA line scan that is imaged in Figure 3. Diffusion profiles represent the activity of the elements as the crystal cools, including how charges balance themselves in the mineral's structural assemblage. (Top) As a titanite grows, Nd diffuses across sector zones in an inversely proportional relationship with Al. Nd usually exists in the (3+) oxidation state, and so when the concentration of Nd decreases, [$Al^{3+}$] increases to compensate. (Bottom) A similar relationship is demonstrated in which a decrease in [$Zr^{4+}$] is balanced by an increase in [$Ti^{4+}$].

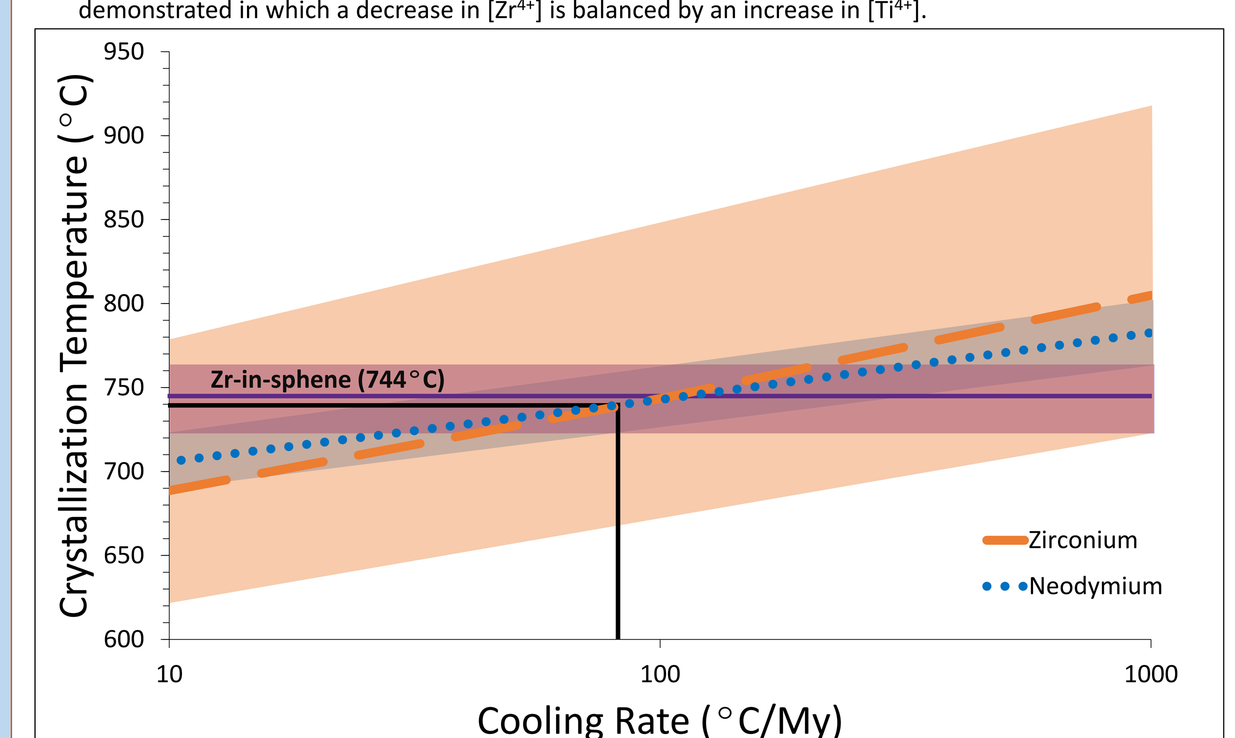



**Figure 6 – Crystallization temperature (°C) vs. cooling rate (°C/My) for Zr and Nd**. Using known diffusivities from Watson & Cherniak and Holder *et al.*, we see that applying EPMA data to their equations yields potential crystallization temperatures and cooling rates for titanites. For a particular Half Dome granodiorite we calculate a titanite crystallization temperature of about 740°C and a cooling rate of just under 100°C per million years. Zr-in-sphene thermobarometry (purple) gives a crystallization temperature of 744°C ±20°C. The shaded regions are error ranges for the data of their respective color. The solid black lines clarify the point of intersection between Nd and Zr.

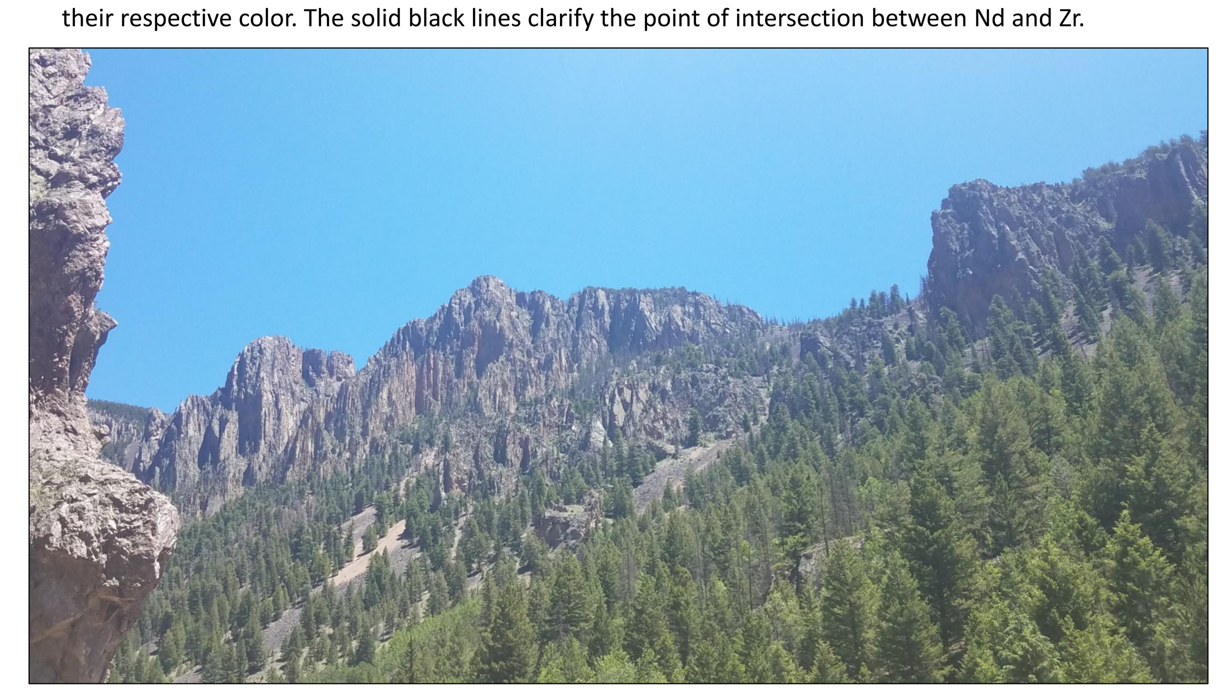


**Figure 7 – Volcanic outcrop near Creede, Colorado**. Field work was conducted in and around the Rocky Mountains and the San Juan basin to collect samples for the project. Sample locations included the Mt. Princeton batholith, Wall Mountain tuff, Pagosa Peak, Fish Canyon tuff, Nutras Creek, Cochetopa Creek, Saguache Creek, and Masonic Park. In addition to the relationship between Half Dome and Fish Canyon, we sampled some of these other sites because they too are plutonic-volcanic counterparts.

## Future Directions

Quartz ($SiO_2$) also has the potential to record the cooling histories of granites. Titanium-in-quartz thermobarometry may yield crystallization temperatures, and diffusion profiles may also be obtained to find cooling rates. Future work will determine how the cooling histories recorded in quartz and titanite differ, and what that can tell us about the thermal histories of magmas.

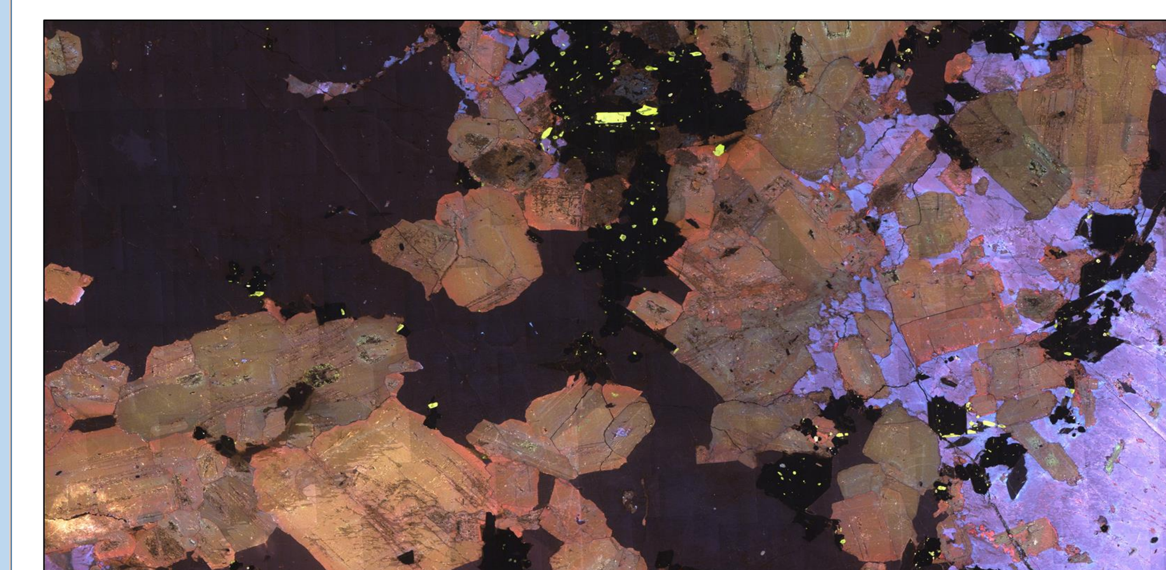


**Figure 8 – Cathodoluminescence image of a thin section of granite**. The deep violets are quartz crystals, oranges are potassium feldspars, blue-purples are plagioclase, and yellow is apatite.

## Conclusion

When magmas cool they crystalize minerals specific to the bulk composition of the magma. These minerals coalesce to form rocks, like granodiorites or dacites. Titanite crystals from the Half Dome granodiorite crystallized at ~740°C and cooled at a rate of ~100°C per million years. The thermal history of the Fish Canyon Tuff is still unknown, and further calculations must be completed in order to identify the magmatic history of a dacite for comparision. Did it crystallize and dwell at high temperatures (>750°C) for thousands of years? Did it crystallize at high temperatures but cool relatively rapidly? Did it crystallize, cool, and stay cold? Each of these scenarios has different implications for how the system evolved and erupted, and future research will elucidate which scenario is most likely. Our present study, in conjunction with future work, will provide a picture of how magmas of similar compositions can produce such drastically different rocks.

## Acknowledgements

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