Estimating the temperature of equilibration of quartz in the Tuolumne Intrusive Suite

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Abstract

Felsic magmas emplaced within the crust undergo a long history of crystallization and possibly subsequent alteration. The Skaergaard intrusion, for example, contains rocks that appeared pristine (i.e. magmatic) but stable isotope studies revealed that extensive hydrothermal alteration has taken place. In the research presented here, I will use the titanium content of quartz to estimate the temperatures of equilibration (using the TitaniQ geothermometer) to determine if the quartz retains magmatic temperatures in the relatively pristine granites of the Tuolumne Intrusive Suite.

Quartz crystals from each pluton (Johnson Granite Porphyry, Kuna Crest, Cathedral Peak, and the Half Dome Equigranular) of the Tuolumne Intrusive Suite (TIS) was analyzed using electron probe microanalysis to determine the concentrations of titanium. It has been found previously (Wark and Watson, 2006) that the concentration of titanium in quartz can record the temperature conditions during formation in rutile-saturated systems. The temperature of the solidus for granodioritic rocks, like those of the TIS, emplaced at a pressure of 2 kilobars, is approximately 680 degrees Celsius: temperatures above the solidus are most likely magmatic, and those below are or sub-solidus and could be effected by hydrothermal alteration.

The following equation calibrated by Wark and Watson (2006) describes the relationship between titanium and temperature as: $T\,°(C) = \frac{-3765}{\log\left(X_{Ti}^{qtz}\right) - 5.69} - 273,$ where X_{Ti}^{qtz} is the titanium concentration in quartz (in ppm by weight). They estimate accuracy to be within 5 degrees Celsius (two sigma). Further research by Thomas et al. (2010) suggested a more complex relationship, and accounted for the pressure at which the rocks formed and the activity of TiO_2 in the system: $RTlnX_{TiO_2}^{quartz} = -60952 + 1.520 * T(K) - 1741 * P(kbar) + RTlna_{TiO_2}$ where R is the universal gas constant, T is temperature in kelvin, X is the mole fraction of TiO_2 in quartz, P is the pressure in kilobars, and a is the activity of TiO_2 in the system. As part of this work, I rearranged the equation and solved for T: $T(K) = \frac{60952 + 1741 * P(kbar)}{-RlnX + 1.52 + Rlna_{TiO_2}}$. As part of this research, I hypothesized that the titanium concentrations in each sample would record magmatic temperatures for each pluton. The geothermometers described above rely on the presences of rutile, or a correction needed to be made. There is no record in the literature of rutile being present in the TIS rocks, therefore the activity of TiO2 needed to be estimated. The activity of rutile of these rocks was calculated by use of the rhyolite-MELTS program; the program calculated the affinity of rutile A_{rutile} of the system, which was then used to calculate the activity a of TiO_2 using the equation $a_{TiO_2}^{liquid-rutile} = exp(A_{rutile}/RT)$ (Gualda and Ghiorso, 2014). The calculated affinities were 7245, 6227, 7051, and 4879 for the Kuna Crest, Half Dome Equigranular, Johnson Granite Porphyry, and Cathedral Peak rocks, respectively. Assuming a pressure of emplacement of 2 kilobars, the average calculated temperatures of three crystals from the Kuna Crest sample calculated using the thermobarometer calibrated by Thomas et al. (2010) were found to be 772 °C, 761 °C, and 660 °C. The Half Dome equigranular crystals output temperatures of 687 °C, 658 °C, and 668 °C. The Cathedral Peak crystals yielded temperatures of 639 °C, 638 °C, and 598 °C. For the Johnson Granite Porphyry rock, the measured temperatures were 725 °C, 610 °C, and 718 °C. Excluding two grains from the Kuna Crest and two grains from the Johnson Granite, all temperatures were approximate to or below 680 °C, the solidus for this system.

Introduction

Quartz is stable over an extensive range of pressures and temperatures, evident by its prominence in crustal rocks (Thomas et al. 2010). It is becomingly increasingly recognized that trace element concentrations in quartz yield petrologic evidence of the conditions during crystallization (Wark and Watson, 2006). Titanium substitutes for silicon in quartz and as a result is found in concentrations extending from 1 to 100 ppm (Wark and Watson, 2006). In magmatic and metamorphic systems where quartz and rutile are present and in equilibrium, the measured concentration of titanium in quartz has been found to correlate with the temperature at which the quartz crystallized. Wark and Watson (2006) calibrated this correlation between titanium concentration in quartz and its temperature of crystallization, and a geothermometer commonly called "TitaniQ" was developed and is described by the following equation: $T\,°(C) = \frac{-3765}{\log\left(X_{Ti}^{qtz}\right)-5.69} - 273,$ where $X_{Ti}^{qtz}$is the mole fraction of TiO2 in quartz. Wark and Watson (2006) calibrated TitaniQ using experiments conducted between 600 and 1,000 degrees Celsius within the presence of rutile, but determined rutile does not have to be present as an equilibrium phase if titanium activity can be constrained, by using Fe-Ti oxide pairs or the program rhyolite MELTS. For this research, the latter was used. Initially, TitaniQ was believed to be minimally affected by pressure, but subsequent experiments using the geothermometer conducted at 2 and 10 kbar suggested that pressure has a more substantial effect on titanium in quartz solubility than originally believed.

Thomas et al. (2010) recalibrated TitaniQ to include the pressure factor, modeled as $RTlnX_{TiO_2}^{quartz} = -60952 + 1.520 * T(K) - 1741 * P(kbar) + RTlna_{TiO_2}$, where T is temperature in Kelvin, R is the universal gas constant, P is the pressure in kilobars, and a is the activity of TiO_2. This recalibration of TitaniQ was originally thought to only be applicable to quartz in rocks formed at pressures between 5 and 20 kbar, but Huang and Audetat (2012) expanded the application of the recalibrated TitaniQ to lower pressures. This research was reliant upon the expansion to lower pressures.

Titanium concentrations of four quartz crystals from the Tuolumne Intrusive Suite, crystallized at 2 kbar, (Piccoli and Candela, 1994), were measured via electron probe microanalysis (EPMA). Using the calculated values, along with activity values obtained from the rhyolite MELTS program, this research aimed to determine if the calculated temperatures would be magmatic or subsolidus, and what those temperatures suggest for the formation of the crystals.

Geologic Setting and Hypothesis

The Tuolumne Intrusive Suite formed during the Late Cretaceous Epoch and is located in the Sierra Nevada mountain range. It is composed of four different plutons: the Kuna Crest Granodiorite, the equigranular and porphyritic Half Dome Granodiorite, the Cathedral Peak Granodiorite, and the Johnson Granite Porphyry. Figure 1 below illustrates the zoning of the Tuolumne Batholith; Kuna Crest is the outermost pluton, followed by the equigranular Half Dome Granodiorite, the porphyritic Half Dome Granodiorite, Cathedral Peak, and the Johnson Granite Porphyry at the interior.

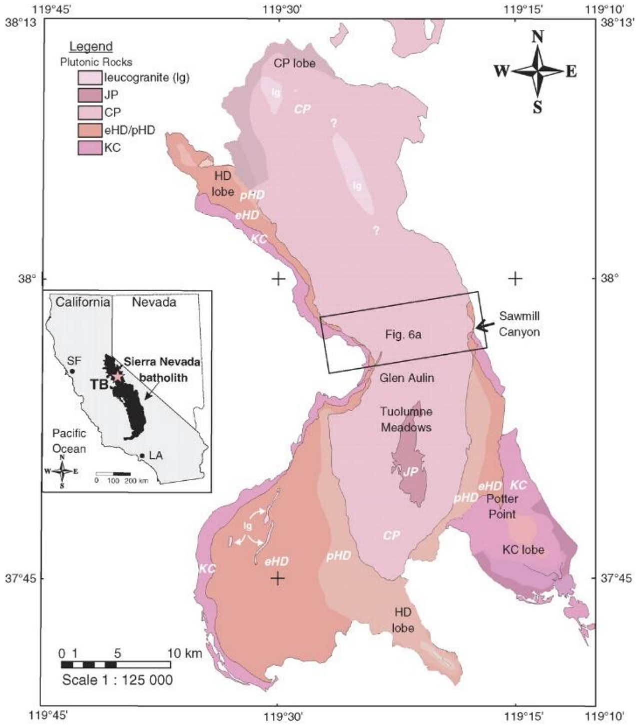


Figure 1: Map of Tuolumne Batholith with labeled plutons(Paterson, 2003)

This research analyzed one quartz crystal from one rock from each pluton.

The significance of this research stemmed from previous work done by Taylor and Forester (1979). Their work focused on analyzing rocks from the Skaergaard intrusion in eastern Greenland. The rocks appeared pristine in hand sample but isotopically it was evident that the rocks had come into contact with hydrothermal fluids. This research aimed to address a similar problem, determining whether the titanium levels in the quartz crystals suggest that the rocks equilibrated at magmatic temperatures (above the solidus) or below were subsequently altered (below the solidus, possibly by hydrothermal fluids.

Before beginning this research, I hypothesized that the titanium levels in quartz from each pluton would be consistent with magmatic temperatures of crystallization when estimated using the TitaniQ geothermometer.

Limitations due to absence of rutile

TitaniQ was calibrated using quartz equilibrated with rutile, but application of the geothermometer is not solely restricted to rutile-bearing rocks. The thermometer can be applied in the absence of rutile if the activity of TiO_2 in the system is known or can be calculated, using the equation: $T\,°(C) = \frac{-3765}{\log\left(\frac{X_{Ti}^{qtz}}{aTiO_2}\right) - 5.69} - 273$, where $aTiO_2$ is the activity of TiO_2. Activity of TiO_2 is 1 for rutile-present conditions, and $0 < a < 1$ if rutile is absent. If rutile is absent then simply scale temperature calculations by the activity of TiO_2: in a melt, for example, if the concentration of TiO_2 is 75% of the amount required for rutile saturation, it is assumed that the titanium concentration in the quartz will be reduced by the same factor (0.75) for a given temperature.

Using the wrong value for the activity will yield erroneous temperature estimates. This is shown below (Figure 2), where Wark and Watson quantified the amount that temperature may be under- or over-estimated in l rutile-absent crustal rocks. If an accurate estimate of TiO2 activity can be made, the error in calculated temperature is low: for rocks equilibrated at T below 700°C, a ± 0.2 error in aTiO2 estimation yields temperatures off by no more than –30° if the activity is overestimated or + 50°C if the activity is underestimated (Wark and Watson, 2006). If the activity is known to within ±0.1, the calculated T will be off by no more than ±20°C.

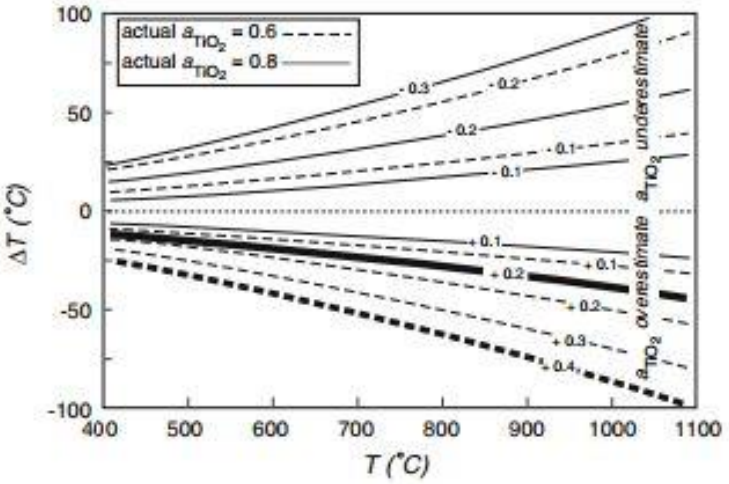


Figure 2: Plot showing possible error in calculated TitaniQ temperature for rutile-absent systems if an incorrect activity of TiO_2 is used. Source: Wark and Watson (2006)

Rhyolite-MELTS

Excluding the titanium concentration, the only variable in the Thomas equation that had to be determined was the activity. This was done by using rhyolite-MELTS, a program designed to simulate and compute phase relations in igneous systems ranging in temperatures of 500 to 2000 degrees Celsius. MELTS is a program that allows for the modeling of crystalline phases from magmatic systems, yielding the affinity for the ending phases. Over a temperature range from 500 to 2,000 degrees Celsius and pressures from 0 to 20 kilobars, crystalline phases are modeled incrementally with changes in temperature and pressure, temperature and volume, enthalpy and pressure, and entropy and pressure. Additionally, the program can be constrained to model these systems with respect to constant enthalpy, constant entropy, or constant volume. Another software program, rhyolite-MELTS, is largely similar to MELTS but differs because the enthalpies of formation of quartz and $KAlSi_3O_8$ are adjusted to model the invariant behavior in naturally occurring melts.

To run rhyolite-MELTS, the starting composition of the each pluton in the Tuolumne Intrusive Suite was first entered. The compositions were found in the work of Bateman and Chappell (1979). Then, three values of H_2O weight percent were entered: 4, 3, and 2 weight percent H_2O. 4 weight percent was entered due to the presence of amphiboles seen in the samples (Naney, 1983), and the weight percentages of 2 and 3 were entered to observe the effect of water content on the activity of TiO_2. These rhyolite-MELTS runs were conducted with respect to temperature and pressure as intensive variables.

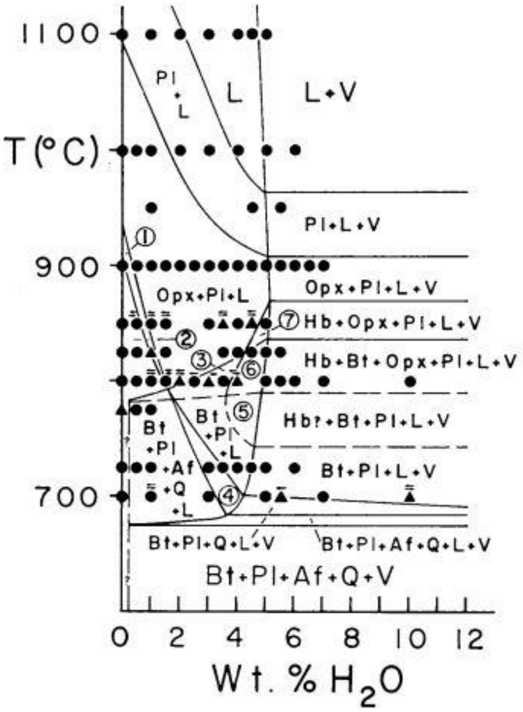


Diagram from Naney (1983) depicting the phases equilibrating out of a melt at 2 kilobars at differing water content. Quartz begins to crystallize around 725-750 degrees

Pressure was kept constant at 2 kilobars, and three different temperatures were entered: 1300 degrees Celsius, the starting melt temperature (well above the liquidus), 750 degrees Celsius which is where quartz is expected to begin to crystallize, and 700 degrees Celsius which is 20 degrees higher than the solidus of 680 degrees. Rhyolite-MELTS cannot do calculations at the solidus of 680 degrees Celsius or lower temperatures due to an inability to iterate at low temperatures. These runs were also conducted with respect to fugacity of oxygen, fixed at nickel-nickel oxide. The program simulated the cooling at one degree increments of a melt with these variables, starting at 1300 degrees Celsius, past the liquidus temperature for each melt simulation, down to 750 degrees where quartz was expected to begin equilibrating out of the melt. After reaching 750 degrees, the simulation was then set to proceed further down to 700 degrees Celsius. At the liquidus, 750 degrees, and 700 degrees, rhyolite-MELTS reported out the dominant mineral phase, as well the chemical affinities of saturation for liquid rutile and liquid quartz. Using the affinity of rutile A_{rutile} given at each temperature, different values of activity of TiO_2 a were calculated using the following equation found in Ghiorso and Gualda (2013): $a_{TiO_2}^{liquid-rutile} = exp(A_{rutile}/RT)$. The data from rhyolite-MELTS are shown in Table 1 below.

Table 1: Rhyolite-MELTS results

🟨 Kuna Crest	🟦 HDE	🟥 JP	🟩 CP

H2O Percent	Temperature (°C)	Liquidus phase	Affinity$_{\text{Rutile}}$	Affinity$_{\text{Quartz}}$	Calculated activity (affinity$_{\text{rutile)}}$
4	1049	Opx	17186	4772	0.14
	750		6501	42	0.35
	725		7245		0.30
3	1067	Opx	19173	4531	0.12
	750		4113		0.52
	700		7483		0.28
2	1088	Opx	21334	4232	0.09
	750		6505	42	0.35
	700		8294		0.24
4	1035	Opx	21136	3507	0.09
	750		6111		0.38
	700		6227		0.34
3	1054	Opx	23047	3259	0.07
	750		6212		0.37
	700		7609		0.27
2	1075	Opx	25163	2946	0.06
	750		6291		0.36
	700		7607		0.27
4	1064	Feldspar	32866	532	0.02
	750		7796		0.29
	700		7051		0.30
3	882	Feldspar	889	17790	0.89
	750		6135		0.37
	700		6673		0.32
2	932	Feldspar	21994	852	0.06
	750		6389		0.36
	700		6674		0.32
4	921	Opx	11780	2190	0.21
	750		6337		0.36
	700		4879		0.43
3	947	Feldspar	14148	2078	0.17
	750		6341		0.36
	700		4100		0.49
2	994	Feldspar	17961	2043	0.11
	750		6399		0.36
	700		11667		0.13

Experiment Design

Rocks from each of the four plutons in the intrusive suite were collected by Dr. Philip Piccoli, and parts were made into sections. Petrography was performed using standard petrographic techniques, in order to identify appropriate quartz grains for analysis (see Figure ##-thin section scans). The titanium content of the quartz was analyzed via electron probe microanalysis (EPMA) in the Advanced Imaging and Microscopy Lab in the Maryland Nanocenter. EPMA determines concentrations of elements in a sample by bombarding a stream of electrons at the targeted sample. The beam interacts with elements in the sample and causes atoms of each element to emit x-rays at diagnostic frequencies, which are then detected by the microprobe. They can either be detected by their energy (EDS) or their wavelength (WDS). When using WDS, detection limits of concentrations of 10s of ppm can be attained in some cases. The operating conditions for the analyses employed here were: 20 kV accelerating voltage, 240 nA cup current, and a 30 micron beam diameter. Titanium was the only element analyzed: silicon was calculated by difference. Analysis of pure, synthetic rutile was used as the standard for Ti, the results of which are shown in Table 2. Titanium was counted for 300 seconds on peak, and 150 seconds on each background. The detection limit for Ti using this setup was 8 ppm.

Table 2: Results of standard analysis

	[Ti] in ppm
610 RNO	**458**
Line 1 NIST 610	**439**
Line 2 NIST 610	**442**
Line 3 NIST 610	**449**
Line 4 NIST 610	**448**
Line 5 NIST 610	**450**

Results

Table 3

Kuna Crest			
	Average weight % TiO2	Average [Ti] (ppm)	Average temperature (°C)
Region 1	0.0088	52	772
Region 2	0.0081	49	761
Region 3	0.0036	22	660

Figure 3

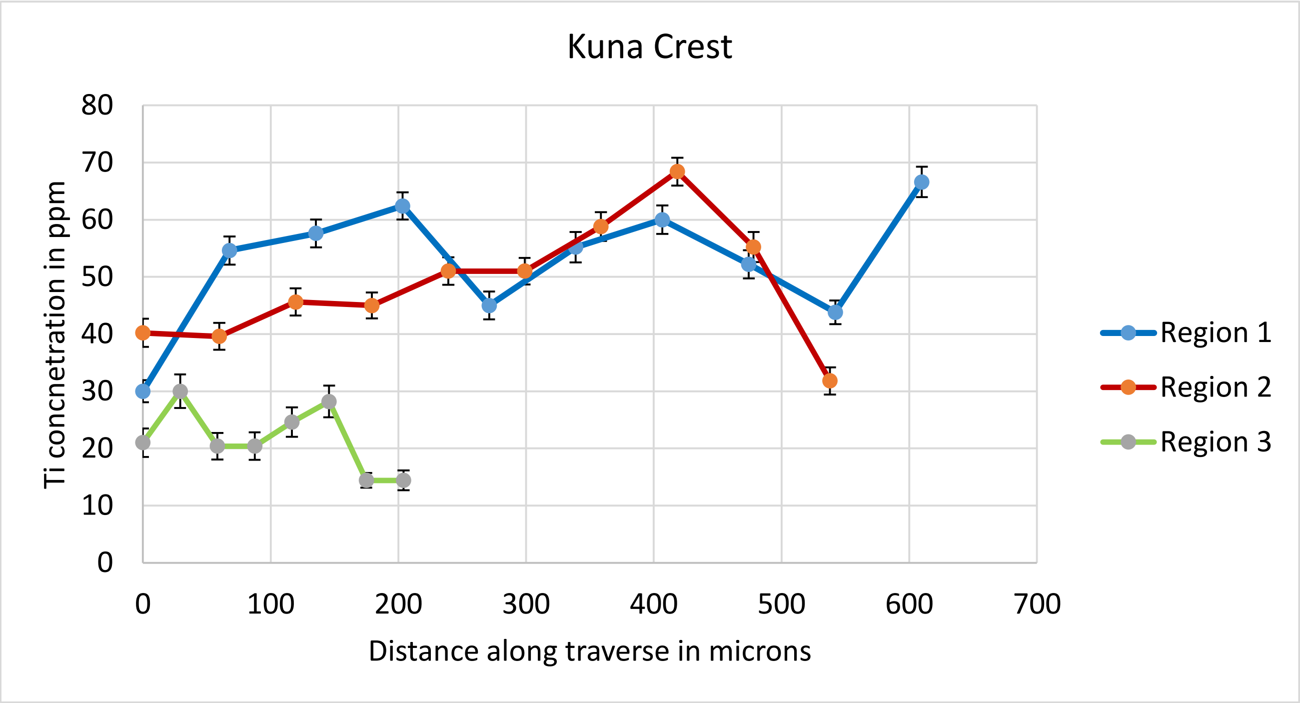


Table 4

Johnson Granite Porphyry			
	Average weight % TiO2	Average [Ti] (ppm)	Average temperature (°C)
Region 1	0.0064	38	725
Region 2	0.0044	26	610
Region 3	0.0059	35	718

Figure 4

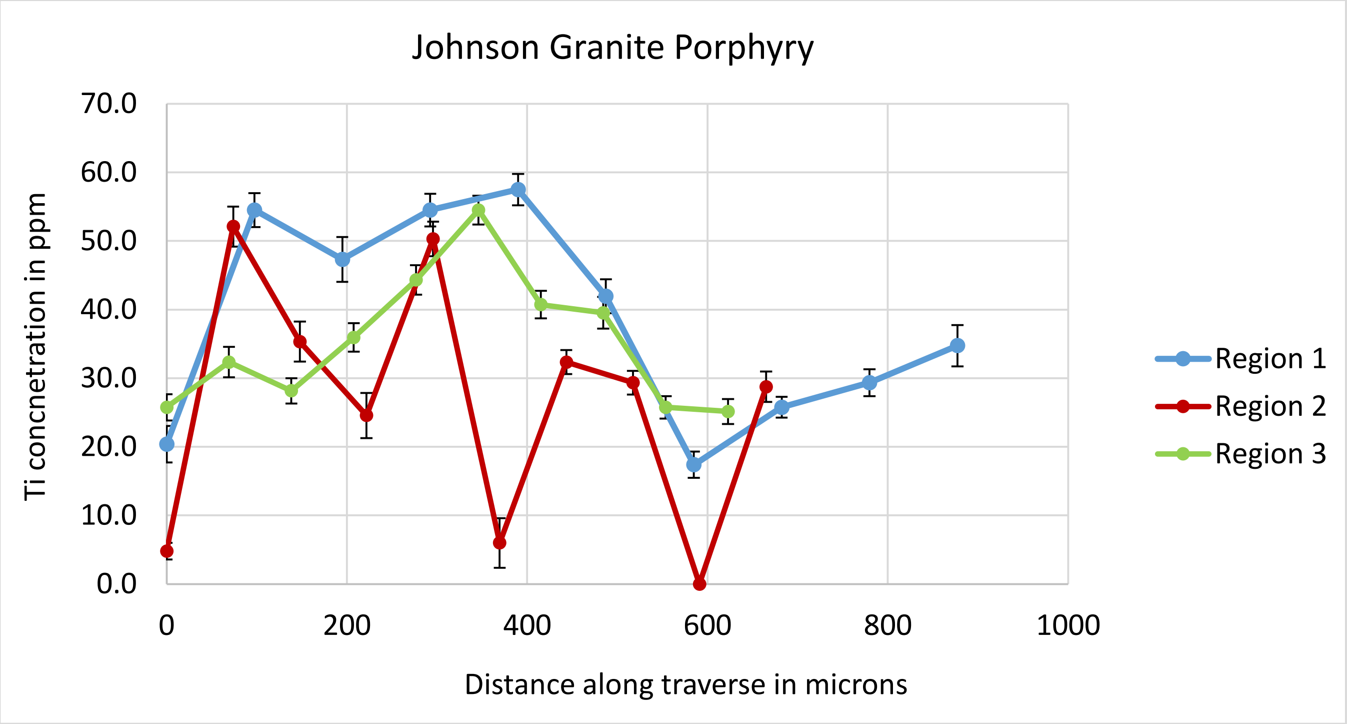


Table 5

Half Dome Equigranular			
	Average weight % TiO2	Average [Ti] (ppm)	Average temperature (°C)
Region 1	0.0060	36	687
Region 2	0.0045	27	658
Region 3	0.0059	35	668

Figure 5

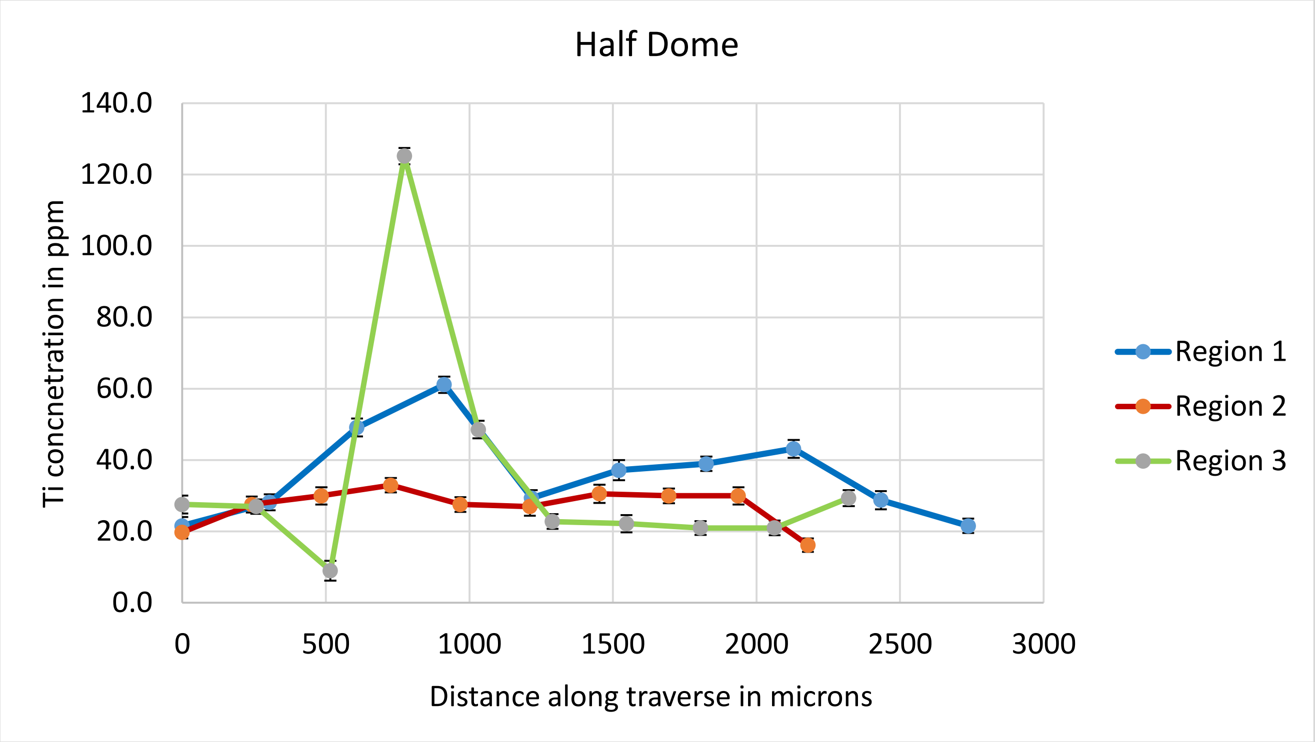
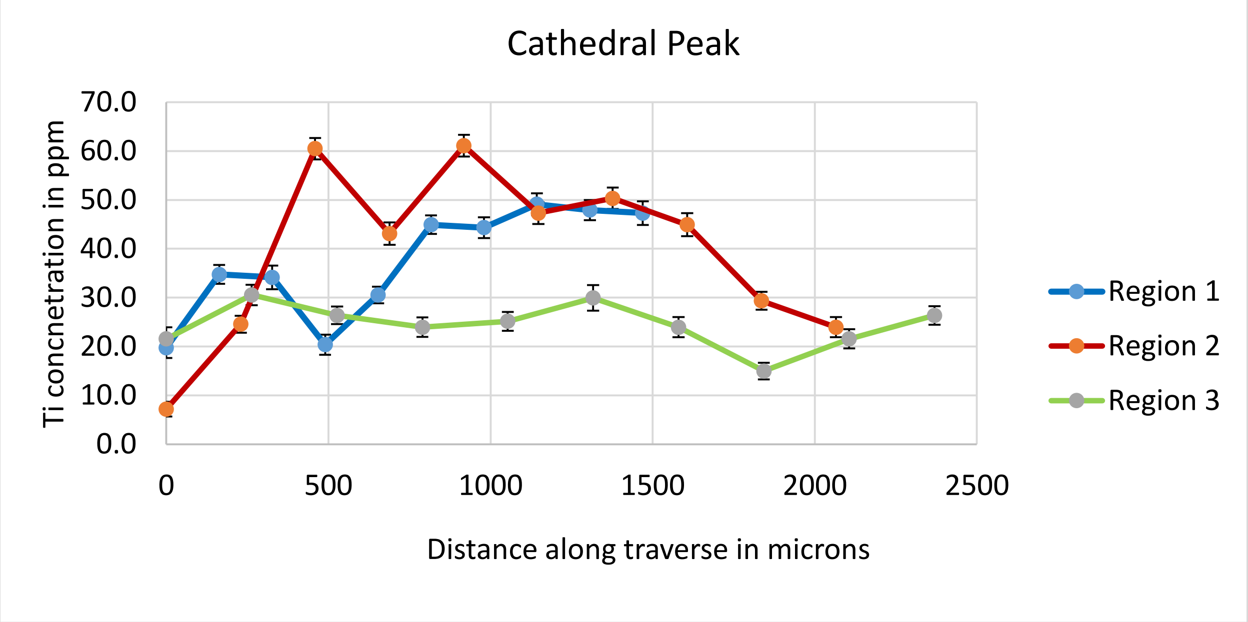


Table 6

Cathedral Peak			
	Average weight % TiO2	Average [Ti] (ppm)	Average temperature (°C)
Region 1	0.0062	37	639
Region 2	0.0066	39	638
Region 3	0.0041	24	598

Figure 6



Discussion and Summary

As expected, quartz with higher concentrations resulted in higher temperatures output by the Thomas thermobarometer. However, excluding exceptions in the Johnson Granite and Kuna Crest samples, the temperatures were near or below the solidus of 680 degrees Celsius, inconsistent with my hypothesis. The titanium concentrations appear to be fluctuating along the traverses in many of the crystals. In addition, there are obvious outliers in the data. In the analysis of region 2 in the Johnson Granite, one measurement yielded a result of 0 ppm; I attributed this to a crack in the thin section that was likely analyzed instead of the sample itself. The spike in the region 3 analysis of the Half Dome likely could have been an error resulting from electron saturation during analysis. The errors in the plots were calculated by multiplying the measure concentrations by the relative uncertainty, and dividing the product by 100. There is no obvious zoning in these crystals, and the concentration levels could have been affected by diffusion of titanium into or out the crystals, depending on the surrounding phases.

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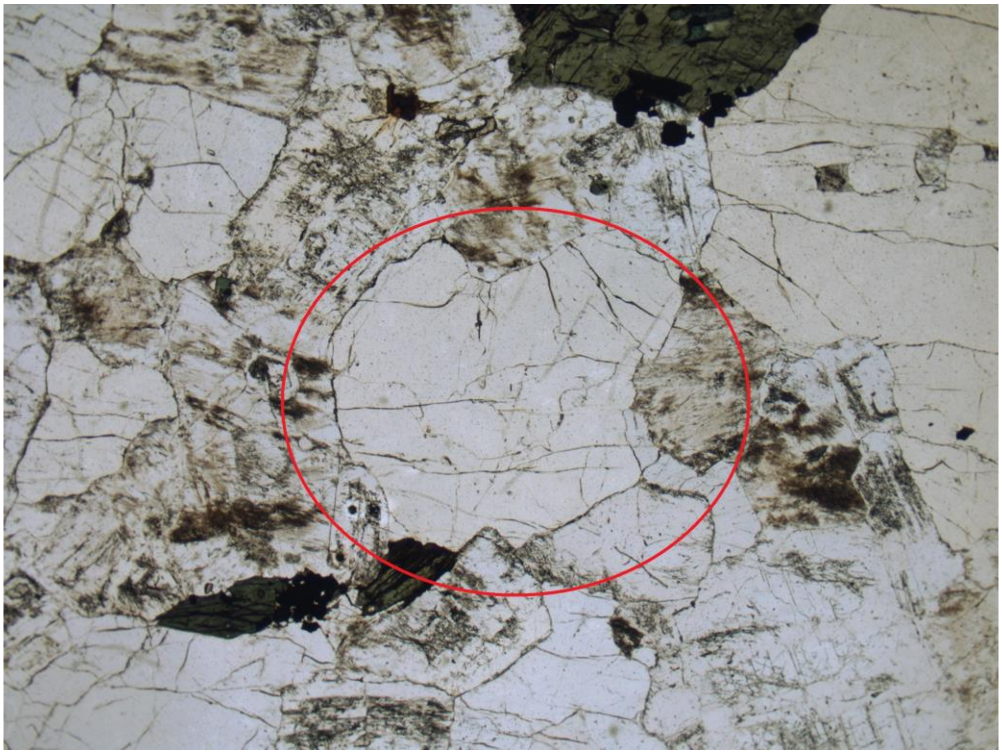
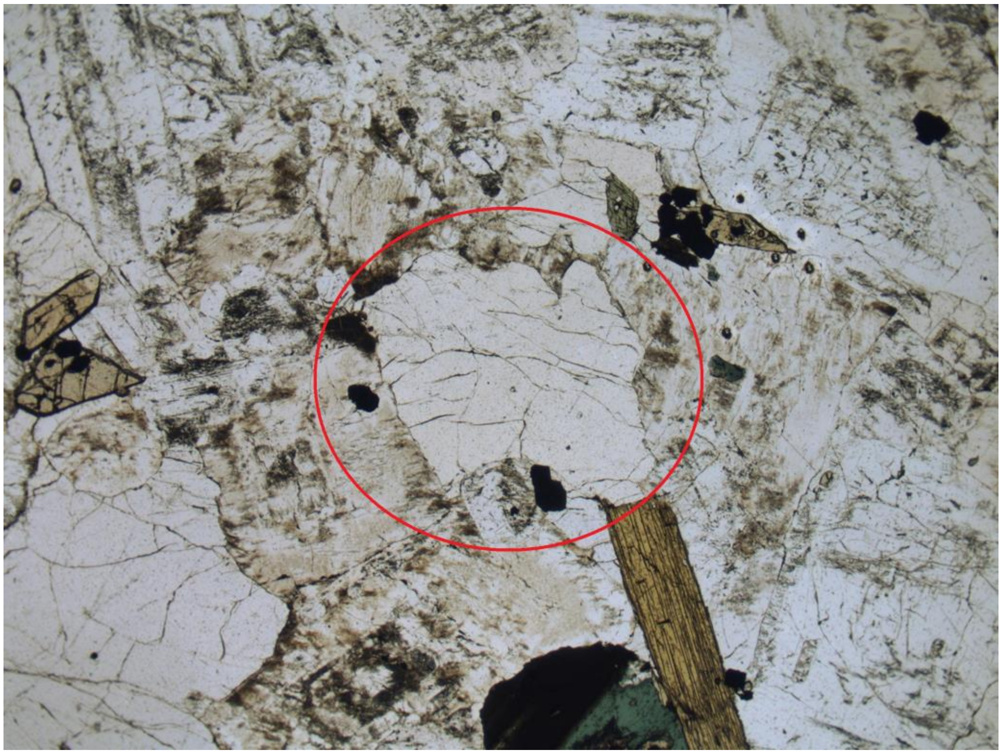
Appendix A: Half Dome

Appendix A1: Thin section of Half Dome rock sample



A2: Photomicrograph of region 1 grain in PPL at 1.5x mag

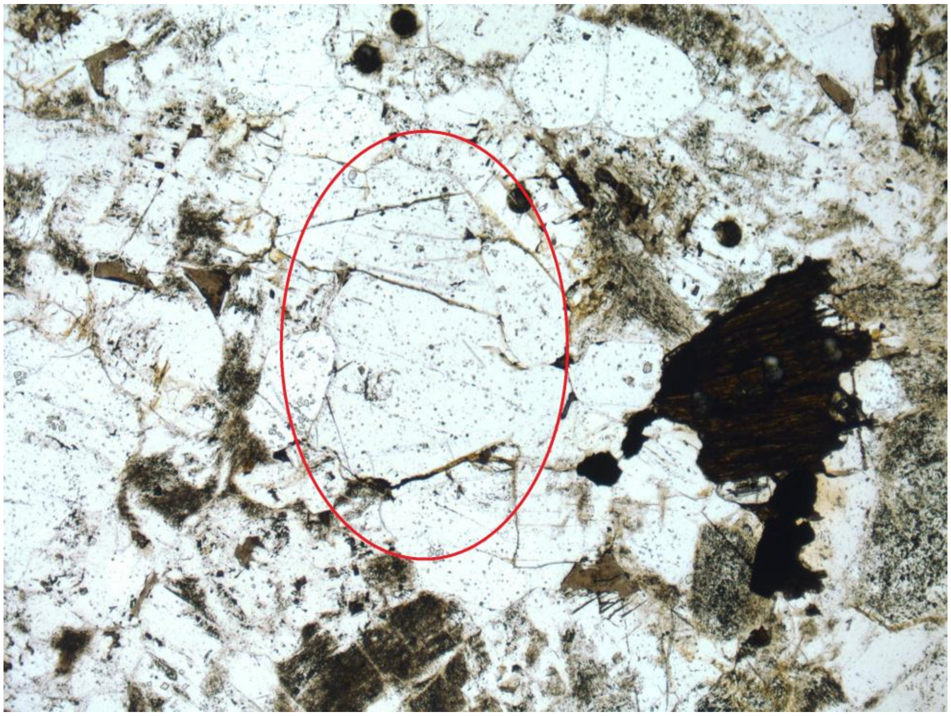


A3: Photomicrograph of region 2 grain in PPL at 1.5x mag

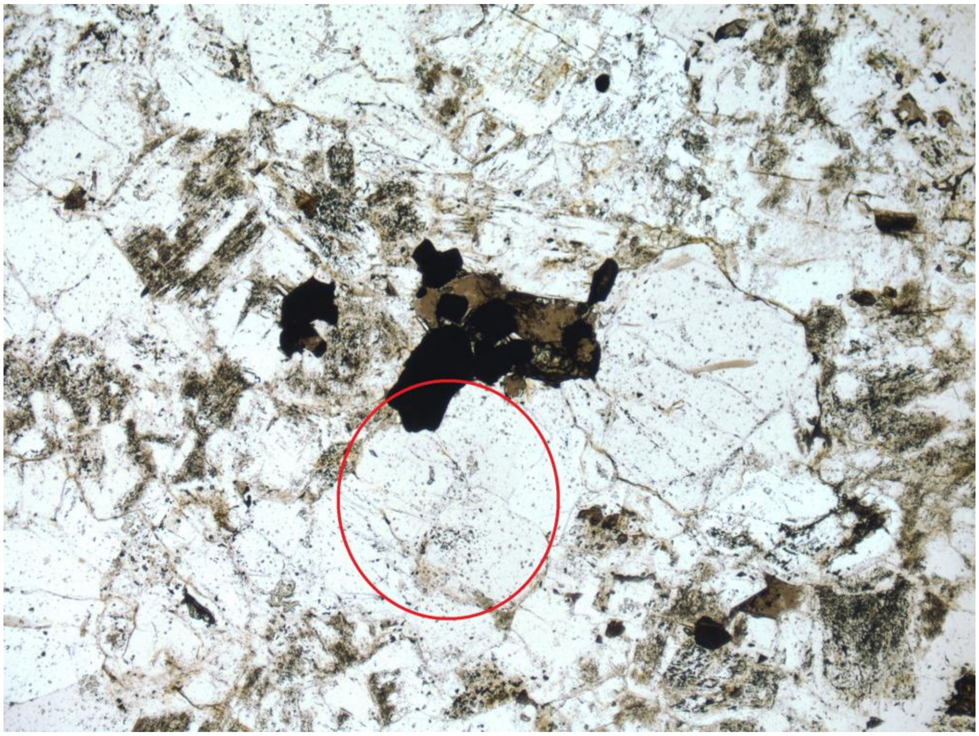
A4: Photomicrograph of region 3 grain in PPL at 1.5x mag

Appendix B: Johnson Granite

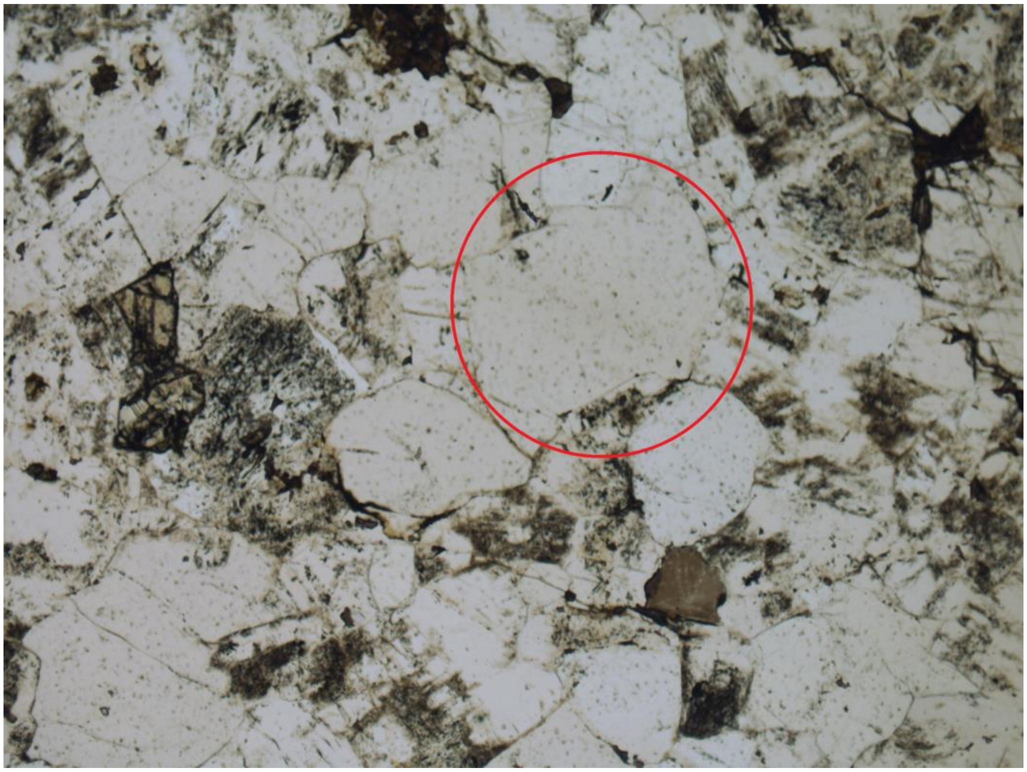
Appendix B1: Thin section of Johnson Granite rock sample



B2: Photomicrograph of region 1 grain in PPL at 5x mag



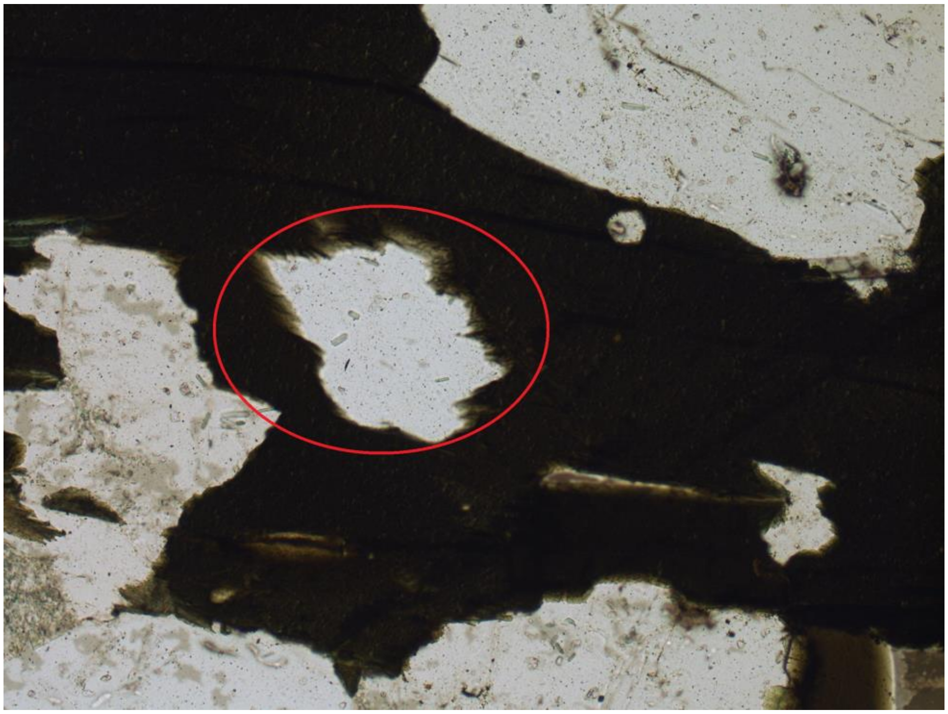
B3: Photomicrograph of region 2 grain in PPL at 5x mag



B4: Photomicrograph of region 3 grain in PPL at 5x mag

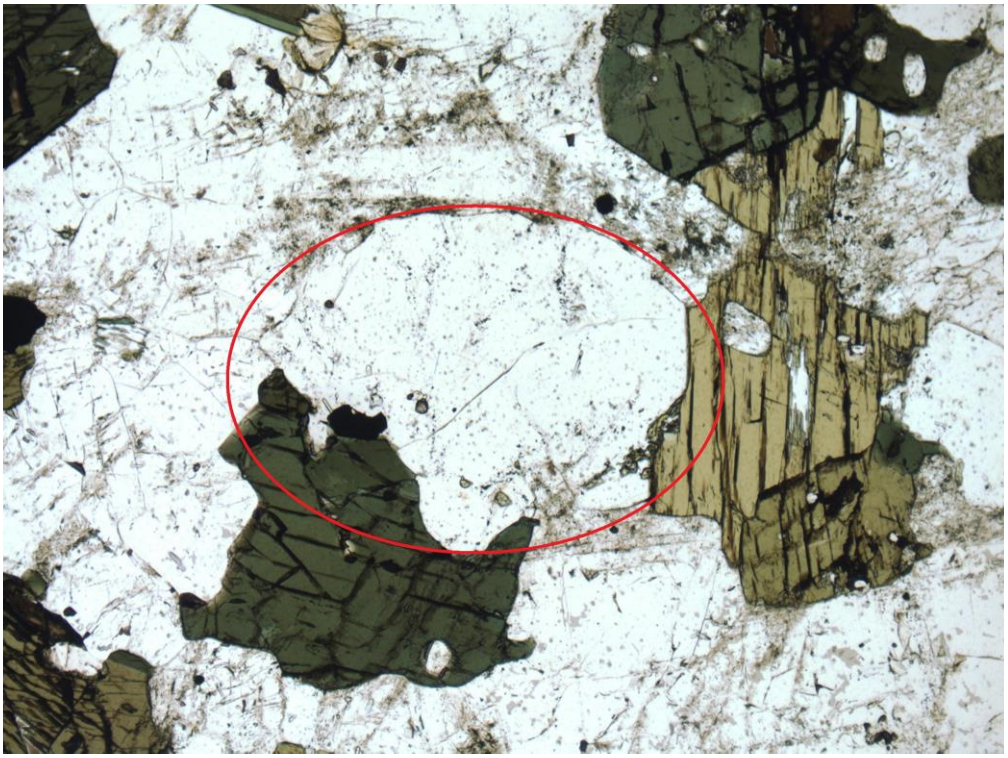
Appendix C: Kuna Crest

Appendix C1: Thin section of Kuna Crest rock sample



C2: Photomicrograph of region 1 grain in PPL at 10x mag

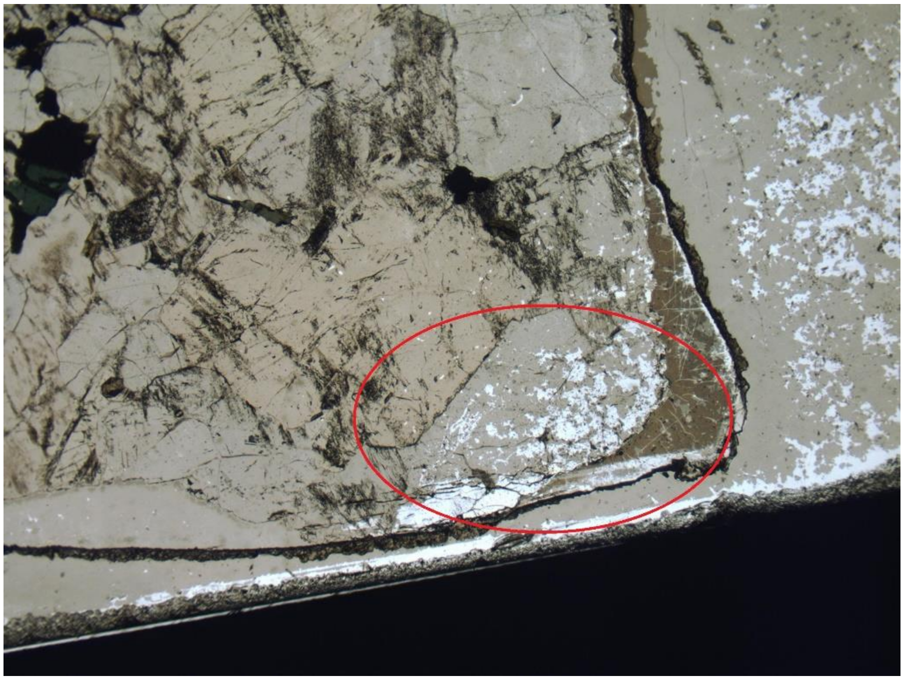
C3: Photomicrograph of region 2 grain in PPL at 5x mag



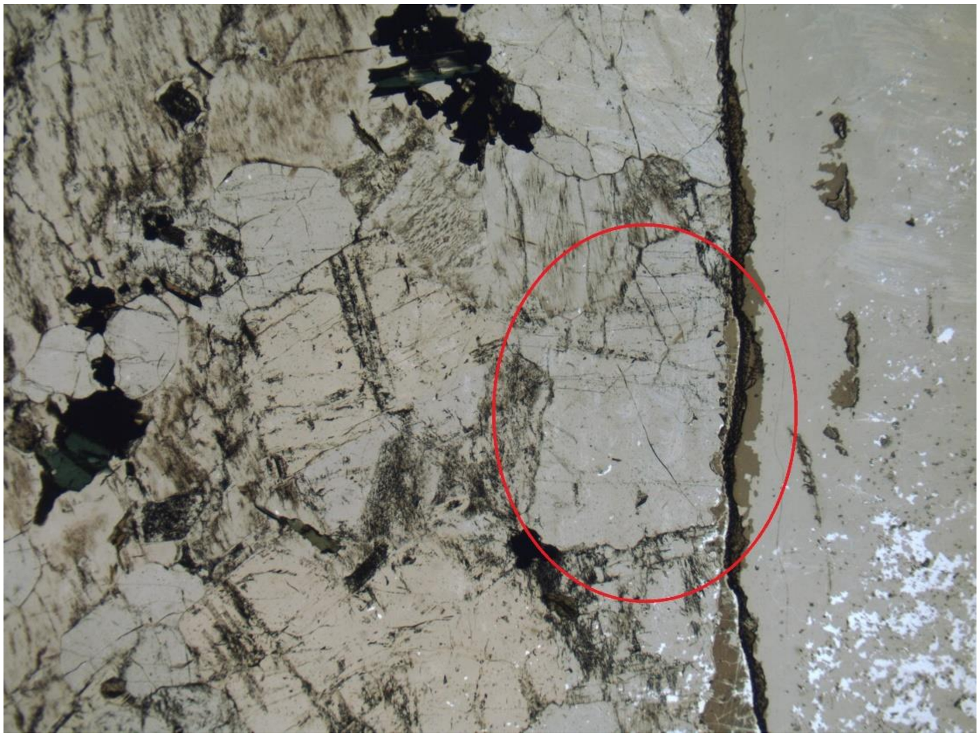
C4: Photomicrograph of region 3 grain in PPL at 5x mag

Appendix D: Cathedral Peak

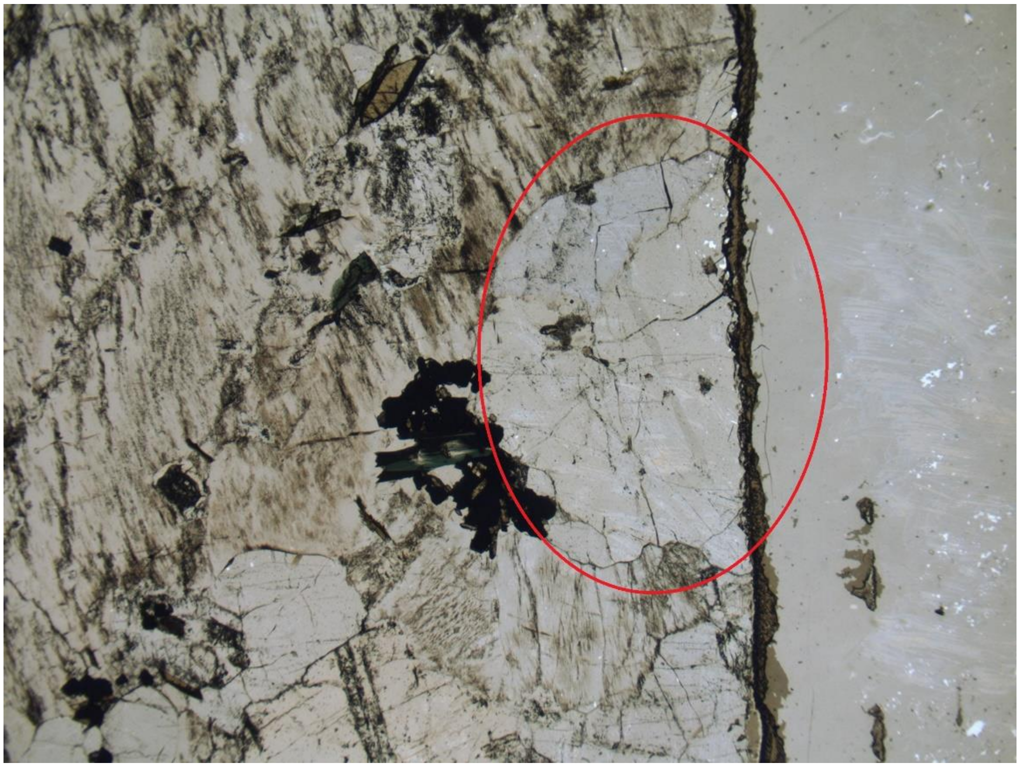
Appendix D1: Thin section of Cathedral Peak rock sample



D2: Photomicrograph of region 1 grain in PPL at 1.5x mag



D3: Photomicrograph of region 2 grain in PPL at 1.5x mag



D4: Photomicrograph of region 3 grain in PPL at 1.5x mag

"I pledge on my honor that I have not given or received any unauthorized assistance or plagiarized on this assignment."