

An Analysis of Apatite Chemistry in Garnet Porphyroblasts and in the Matrix of Metamorphic Rocks

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Abstract

Apatite is an accessory phase found in both metamorphic and igneous rocks. In this study I looked at apatite found in garnet porphyroblasts and in the matrix of rocks from Coos Canyon, Maine. Extensive petrographic analysis and the Electron Micro Probe were used to analyze samples collected in a previous study. Analysis of the samples showed that there was no difference in chemistry between apatite found inside of garnet porphyroblasts and of that found in the matrix of the rocks.

Introduction

There is a relatively small amount of data available relating to apatite chemistry in metamorphic rocks. In this paper I will attempt to analyze apatite in garnet porphyroblasts and in the matrix of metamorphic rocks to determine if petrographic location has an effect on the chemistry of the apatite. The analysis will focus mostly on apatite's halogen end members fluorine and chlorine. In order to accurately assess any measured difference the relative timing of garnet growth must also be determined.

Background

General Information on Metamorphism

Metamorphism is, in the most general sense, a change in rocks due to exposure to elevated temperatures and pressures. There are two different types of metamorphism: contact and regional. Contact metamorphism occurs near igneous intrusions. The metamorphism is caused primarily by heat and only occurs very close to the intrusion. The rocks that I am studying have been metamorphosed due to regional metamorphism. This occurs in large areas due to a tectonic event (i.e. plate collision). During regional metamorphism the rocks are exposed not only to high temperatures but elevated pressures as well. The pressure causes foliations to form as planes through the rocks. These foliations appear to be flat planes or show an infinite variations of folds and twists. It is during metamorphism that garnet porphyroblasts like the ones that I will be analyzing form.

Geologic Framework

The samples for this study were collected for another University of Maryland undergraduate research project in Coos Canyon, Maine. The rocks exposed at Coos Canyon are part of the Perry Mountain Formation. The Perry Mountain Formation is part of the Silurian clastic wedge, which was deposited on top of a very thick Late Ordovician clastic sequence in the Merrimack Synclinorium (Osberg et al. 1968; Bock et al. 2004). The rocks found here are bedded quartzite and sillimanite schist containing garnet (up to

0.5 cm diameter) porphyroblasts sharply interbedded with light gray plagioclase-quartz granofels and granular to vitreous light-gray quartzite (Burton et al. 2000).

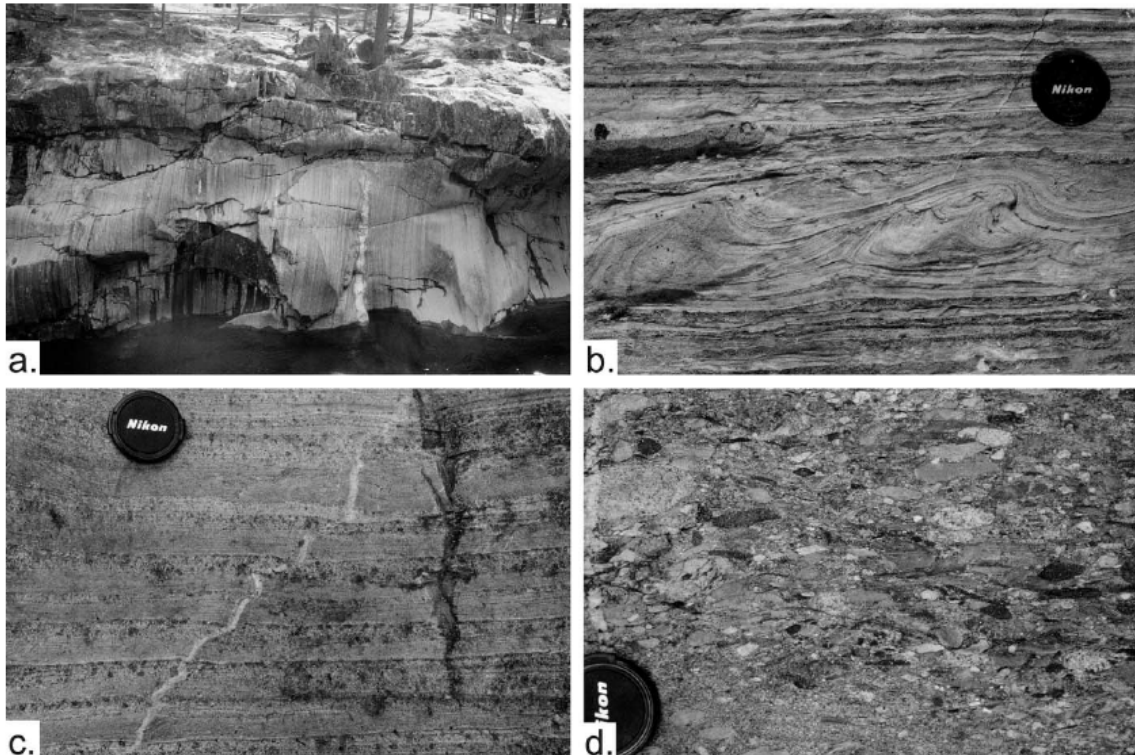


Fig. 1. (a-c) Metamorphic rock of the Perry Mountain Formation from Coos Canyon in Byron, Maine. Photos highlight different metamorphic structures that are visible at Coos Canyon. (d) Conglomerate of the Rangeley Formation which was metamorphosed during the same orogenic event. (After Solar and Brown 2001)

Much of the structural research has been done on this area by Solar and Brown who concluded that deformation occurred during the Early Devonian (Acadian) oblique convergence which developed zones of apparent flattening strain and zones of apparent constrictional strain which is highlighted in figure 1 (Solar and Brown 2001).

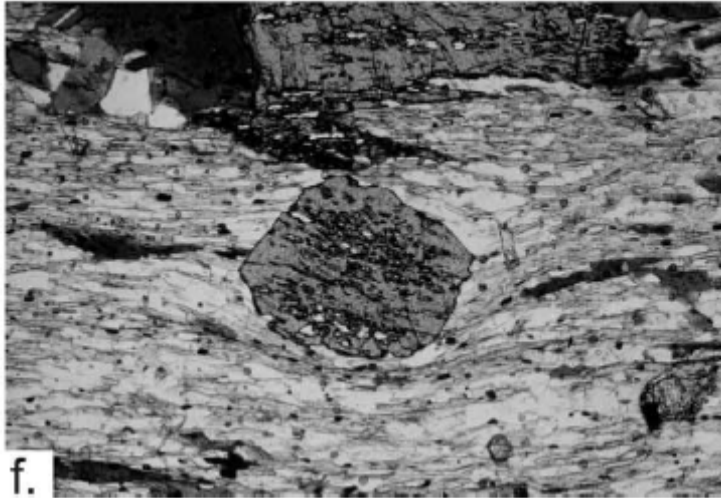


Fig. 2. Photomicrograph of a garnet porphyroblast from Coos Canyon. Apparent σ tails in quartz and mica strain shadows suggest a top-to-the-right sense of shear which indicates shear was along foliation in the direction of lineation. Long side of picture is 3.5 mm. (After Solar and Brown, 2001)

Apatite in Metamorphic Systems

Apatite is found in metamorphic rocks as an accessory phase (Kapustin 1986). It is found in rocks of all metamorphic grades, ranging from those found in transitional diagenetic environments to ultra high-pressure samples, and in rocks of different compositions including pelites, carbonates, basalts and ultramafics (Spear and Pyle 2002). Apatite is one of the accessory phases found in garnet porphyroblasts in metamorphic rocks.. Apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$, is usually found in metamorphic systems as fluorapatite (i.e. F as the primary end-member) but in a very small number of samples it is found as chlorapatite (i.e. Cl as the primary end-member) (Spear and Pyle 2002). Because the composition of apatite is defined by the end member concentrations there are an infinite number of possibilities for compositions of apatite.

While studying accessory phosphates in metamorphic rocks Spear and Pyle (2002) hypothesized that there were four possibilities for the reaction between two different phases in a metamorphic system. The two phases that were examined are garnet and monazite. It was hypothesized that: (a) the monazite and the garnet would both grow, (b) the monazite would be consumed while the garnet grew, (c) the monazite grows while the garnet is consumed, and (d) both the monazite and the garnet are both consumed (Spear and Pyle 2002). These relationships were studied to show that the presence of a mineral such as monazite or apatite alone does not mean it is part of an equilibrium assemblage. These relationships are important in my study so that if there is a difference in apatite chemistry the reaction relationship between the garnet and the apatite must be analyzed to determine if there is any significance in the measured chemical difference.

Yang and Rivers (2002) studied major and trace element zoning in garnets containing apatite and other minerals show LREE-enriched, chondrite-normalized patterns with negative Eu-anomalies in apatite crystals as shown in Fig. 3. LREE stands for light rare earth elements which are the lanthanide group on the periodic table of elements. Looking at the LREE's in a mineral gives us an idea of its metamorphic history

because the LREE's are highly insoluble and thus are not changed during metamorphism. The negative Eu-anomaly arises from the fact that Eu has a charge of 2+ while all the other REE's have a charge of 3+. This causes Eu to substitute readily for Ca^{2+} and is found in higher abundance in plagioclase feldspar and lower abundances in other phases like apatite in this case (White 2005).

Relative Timing

When examining garnets and other porphyroblasts in metamorphic systems, one must consider their timing of formation relative to foliation. There has been a considerable amount of work done on analyzing porphyroblasts to determine just that. Porphyroblasts can be put into three categories, they may be *prekinematic* (*predeformational*), *synkinematic* (*syndeformational*), or *postkinematic* (*postdeformational*) (Vernon 2004). A chart of general end members in each category under different types of strain is shown by the red arrows in figure 3.

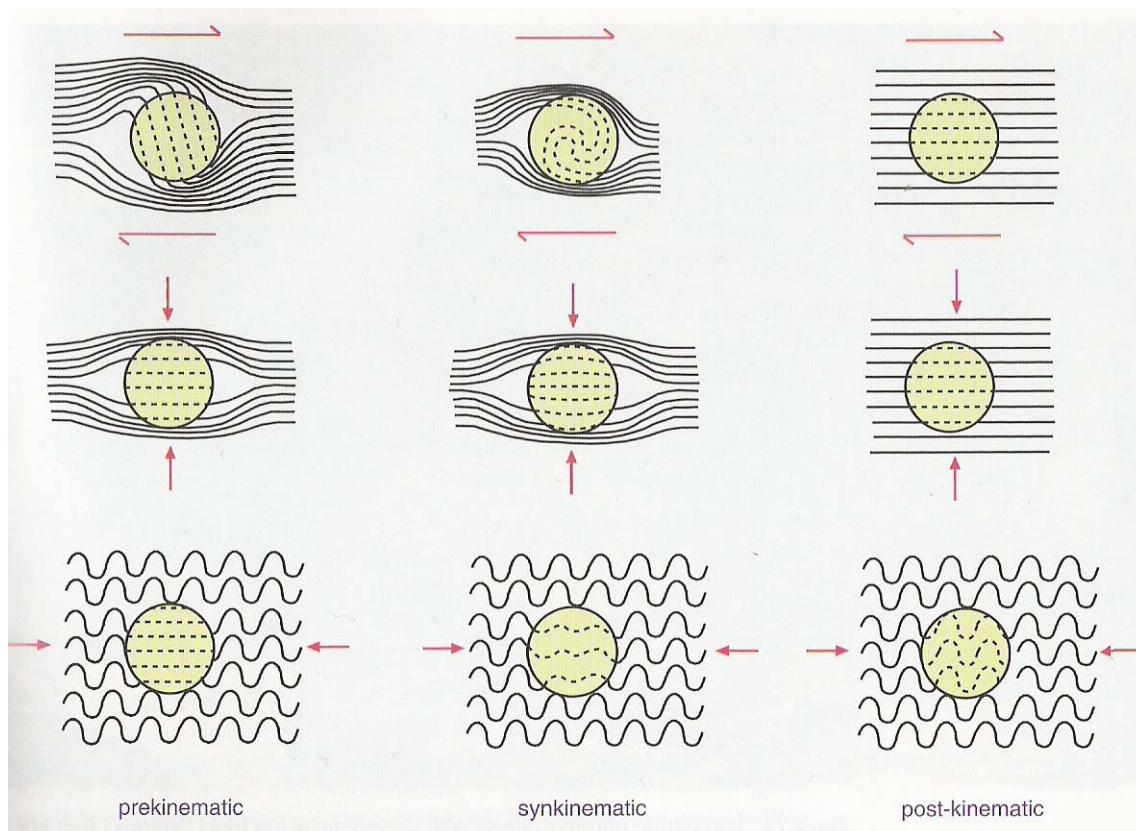


Fig 3. A chart showing relative timing of porphyroblast formation after Vernon (2004)

There are many problems that arise when trying to analyze the relative timing of porphyroblast growth in a metamorphic system. A major precaution that must be taken before analyzing a thin section is to determine the orientation of the cut relative to the

foliation. Figure 4 shows how a cut parallel to microfolding can look completely different than a cut that is perpendicular to fold direction.

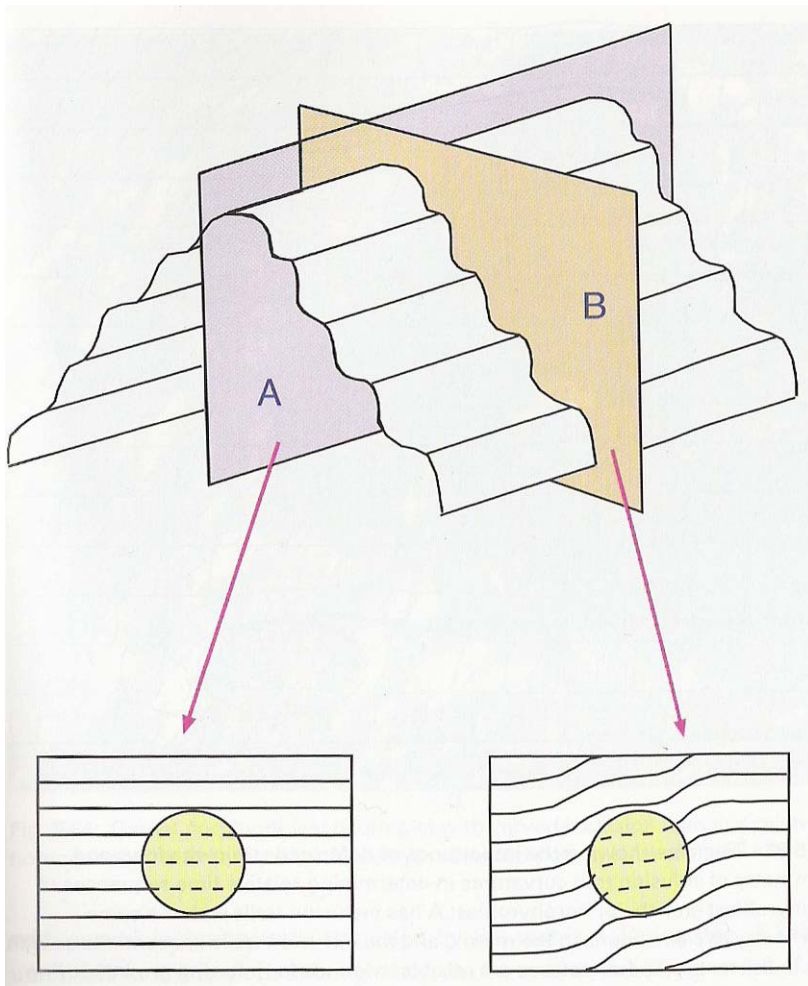


Fig. 4 shows how foliation and inclusions can look different depending on cut angle. (A) Shows a cut parallel to foliation and (B) shows cut perpendicular to foliation after Vernon 2004.

To avoid making mistakes in analysis cuts from multiple angles relative to folding should be analyzed to ensure accurate interpretation (Vernon 2004).

Methodology

To accurately assess the question I have proposed I am using two different methods to analyze my samples. The first method I am using is petrographic analysis with a petrographic microscope. The petrographic analysis I am doing serves a two fold purpose: (1) to look at samples to find garnets with a large number of inclusions and to find what possibly might be apatite in the matrix and (2) to analyze the garnets, inclusion orientation, and foliation orientation to determine time of growth relative to metamorphism. After analysis of the covered thin sections that were previously made from my samples I have determined that the garnet growth is most likely synkinematic

(top row, middle in figure 2). As I have previously discussed there are precautions that must be taken before the relative timing can be determined. I have analyzed thin sections of my samples that were cut both perpendicular and parallel to foliation. Some of the sections I have selected to analyze for apatite chemistry do not show relative timing in the thin sections that already exist. I will be using those samples because they have larger garnets with more inclusions of apatite both in the garnets and in the matrix.

After I have identified apatite in the garnets and in the matrix I will be using a JEOL 8900R WDS Electron Probe Microanalyzer (EPMA) to analyze the chemical composition of apatite. The EPMA works by creating an X-ray signature from the mineral that is being analyzed and identifying those X-rays. Electrons are liberated by heating a tungsten cone to 2300K causing it to release electrons. The beam then passes through a hole in a positively charged plate which concentrates the electrons into a beam. The electrons are funneled through the hole creating a beam between 5 and .5 μm in diameter, which is directed at the mineral to be analyzed. For my analysis I used a 5 μm beam. The beam has three properties that are important. First is the acceleration voltage. This is measured in kV and determines the speed of the electrons that are directed at the mineral to be analyzed. For my analysis I will be using an acceleration voltage of 15 kV. The next important thing to consider is the cup current. This current is measured in nA. For my analysis a cup current of 10 nA was used. The spectrometers were looking for F, Cl, Fe, Mn, P, and Ca.

For the initial set of data, an analysis of 12 apatite grains was done using the EPMA. Four of the apatite crystals that were analyzed were located inside of a garnet. The remaining eight were located in the matrix, four of those were associated with quartz grains and the other four were most likely associated with biotite.

More petrographic analysis was done to select 6 samples to be made into uncovered thin sections for use in the EPMA. When the new sections arrived the sections were scanned to use as maps while using the probe. More petrographic analysis was then done to locate apatite grains both inside garnets and in the matrix. The sections were then taken to the EPMA for analysis. Analysis was run on approximately 150 different points spread across the six sections noting the approximate size of each grain and the other phases that the apatite was associated with. The number of elements that were analyzed in the preliminary analysis was increased from 6 to 14. This was done to ensure a more thorough analysis of the apatite.

After the samples were run in the probe the data was compiled into a table so that the results could be analyzed. From there the standard deviations from the mean of elemental weight percent were calculated. In order to find a trend in the data the charts were arranged by sample number, mineral association and apatite grains that were found in garnet versus those associated with other mineral phases. The final step was to create ternary diagrams so that the data could be analyzed visually.

Results

. Table 1 below shows the concentrations for the 6 elements that were analyzed in the 12 different locations. The raw x-ray counts were corrected using the ZAF algorithm.

No.	F	CaO	P2O5	FeO	Cl	MnO	Total	Comment	F Ap	Cl Ap	OH Ap
	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%				
1	3.07	50.25	40.86	1.965	0.0154	0.165	96.32	in Grt	0.814	0.002	0.184
2	2.66	51.72	43.68	1.994	0.0106	0.143	100.2	in Grt	0.705	0.002	0.293
3	2.47	48.35	42.25	4.533	0.0189	0.18	97.81	in Grt	0.659	0.003	0.338
4	1.77	49.35	42.15	2.035	0.0106	0.034	95.33	in Grt	0.467	0.002	0.531
5	3.94	50.6	39.26	0.916	0.0333	0.076	93.15	in matrix	0.995	0.005	0
6	3.09	55.5	40.67	B.D	B.D	0.034	98.01	in matrix	0.819	0	0.181
7	2.79	50.21	37.77	0.081	B.D	0	89.68	in matrix	0.74	0	0.26
8	2.79	55.23	40.98	B.D	B.D	0.059	97.88	in matrix	0.741	0	0.259
9	2.52	54.88	40.93	0.066	B.D	0.116	97.45	in matrix	0.668	0	0.332
10	3.63	52.17	39.13	B.D	0.0407	0.075	93.5	in matrix	0.962	0.006	0.032
11	3.4	53.54	39.98	B.D	0.0266	0.017	95.53	in matrix	0.903	0.004	0.093
12	3.41	54.47	41.75	0.135	0.0009	0.009	98.33	in matrix	0.904	0	0.095

Table 1. Compositions in weight percent of elements measured in initial analysis and converted data for use in ternary diagram.

$$F \text{ Ap} = \text{Wt\% F} / 3.767$$

$$Cl \text{ Ap} = \text{Wt \% Cl} / 6.809$$

$$OH \text{ Ap} = 1 - F \text{ Ap} - Cl \text{ Ap}$$

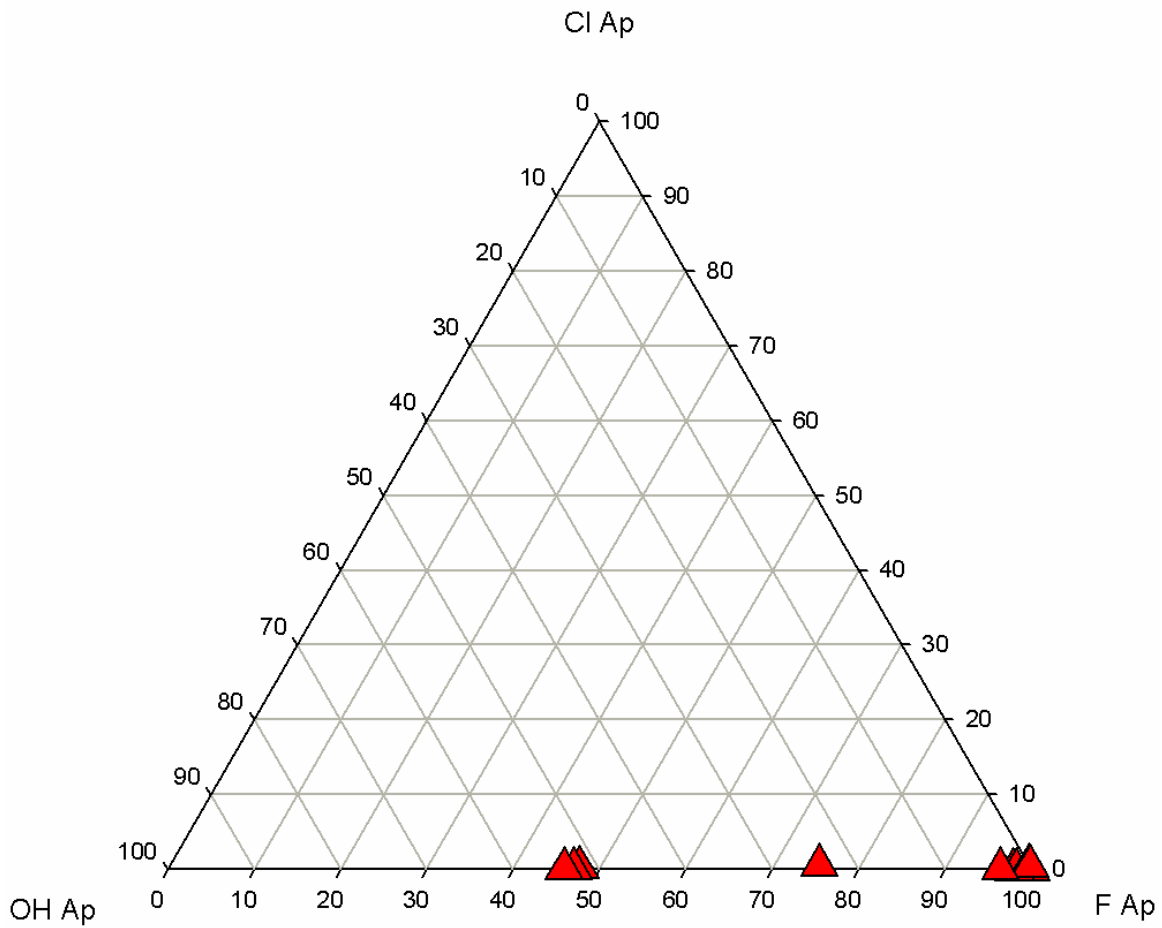


Figure 5. Data from preliminary analysis. The labels on axis refer to F, Cl, and OH concentrations in the apatite. The concentrations are normalized to total 100%. All of the points plot similarly to Spear and Pyle (2004) in figure 6.

The points on the ternary diagram seem to suggest that there could be separate populations in the samples of apatite. But when the data table is compared to the ternary diagram the apatite grains from the matrix are located in both populations as are the apatite grains found in the matrix.

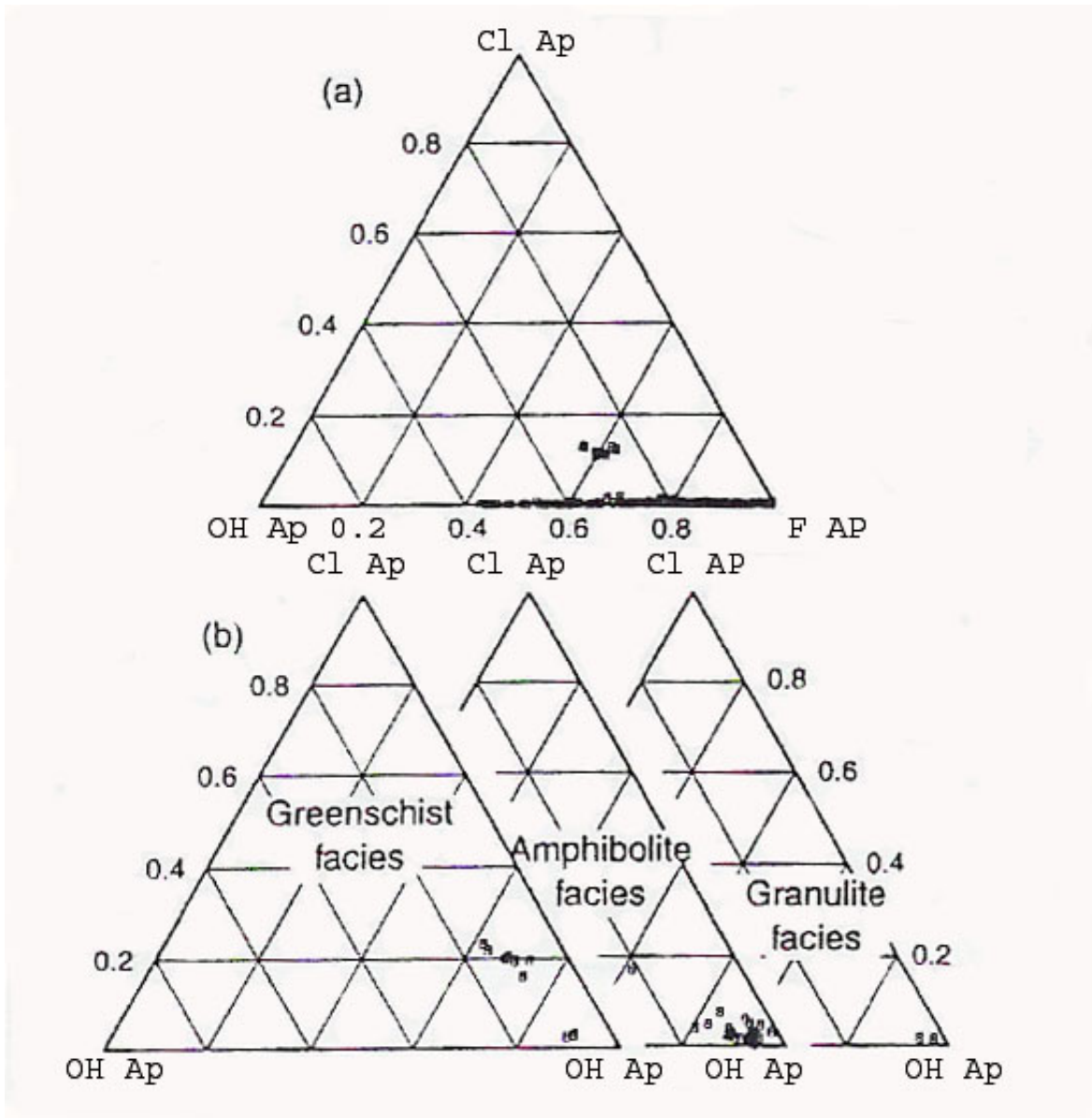


Figure 6 shows ternary diagrams made from data by (a) Pyle and Spear (2002) and (b) Kapustin (1986)

The results of my preliminary data looks similar to the experiment done by Spear and Pyle (2002) with most of the data points falling on the OH-F join, and enriched in F. The data of Kapustin (1986) looks different that what both Pyle and Spear and I have found. No one has been able to reproduce the experiment done by Kapustin (1986) so I do not see his data having an effect on my data.

Table 2 shows a sample of the data collected in the complete analysis that was done. The weight percents were calculated in the same manor that was described above. The conditions and settings of that the probe was run at were also the same as described above.

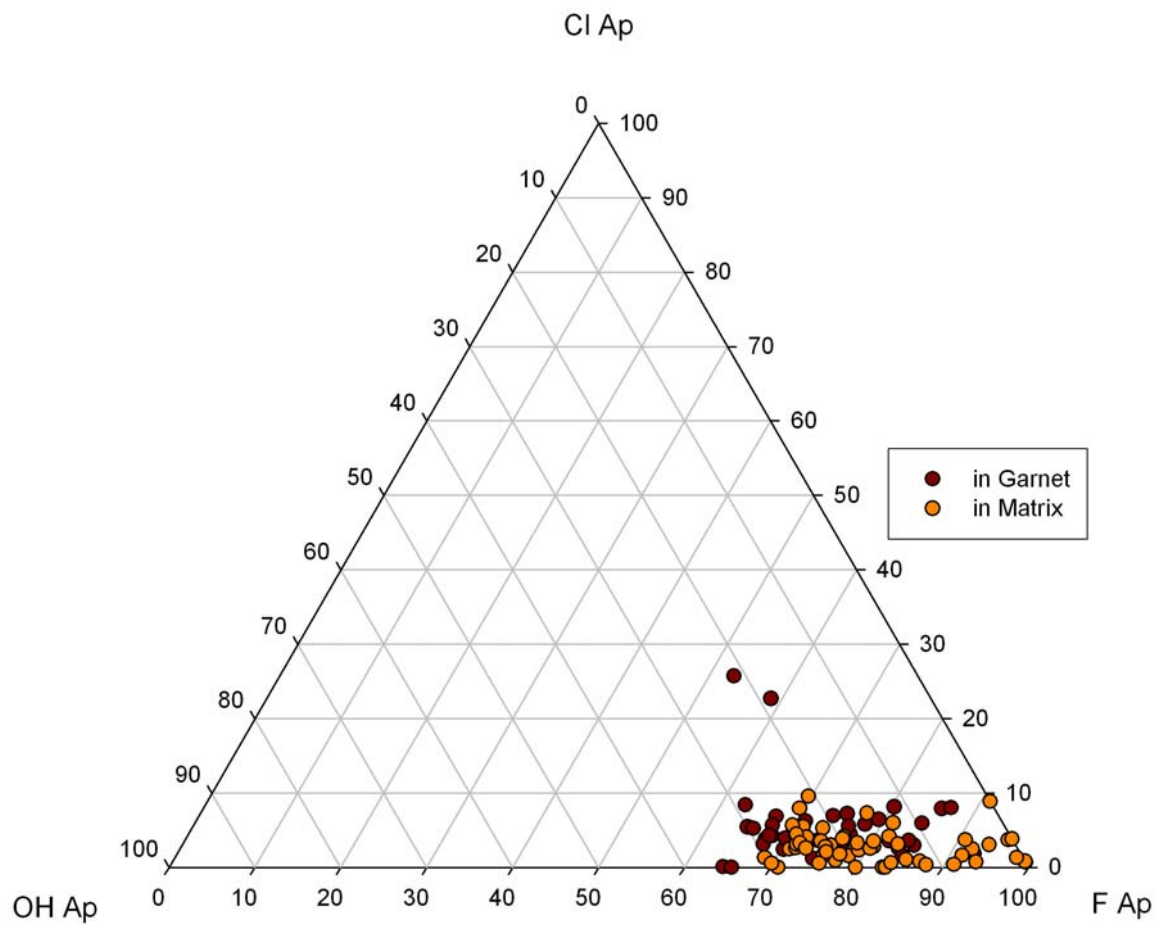


Figure 7. Ternary plot showing apatite grains found in garnet and in the matrix. No significant difference in chemistry can be correlated due to this separation. Chlorapatite content magnified by 40x.

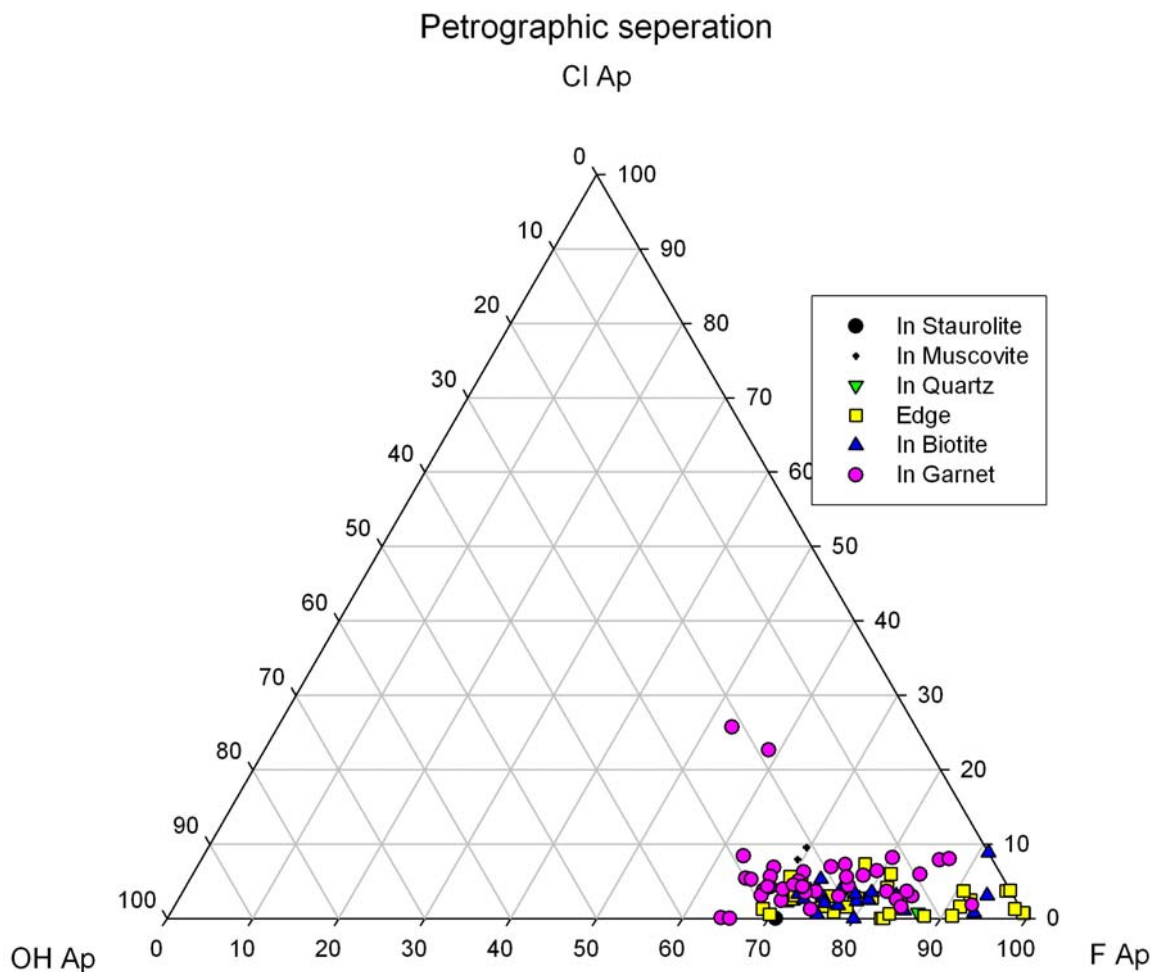


Figure 8. Ternary plot showing apatite chemistry separated by petrographic location of the apatite samples. There appears to be no correlation between chemistry and petrographic location. Chlorapatite content magnified by 40x (Cl on Plot = Cl weight % x 40).

Discussion

Error Analysis

A potential problem in analyzing fluorine with an electron microprobe has been noted in previous studies (Stormer et al.1993). The beam of electrons used in analysis has the potential to cause diffusion of the F rendering counts that are up to 200% of the actual value and then dropping well below the actual value (Stormer et al.1993). To make sure this was not the case the beam was touched to a sample for 3 minutes. If diffusion of F were to occur it would be visible during this extended analysis. The results of this test suggest that no appreciable diffusion occurs using the operating conditions used here. Figure 9 is a representation of counts per second vs. time and clearly shows that the counts remain stable over the whole test period.

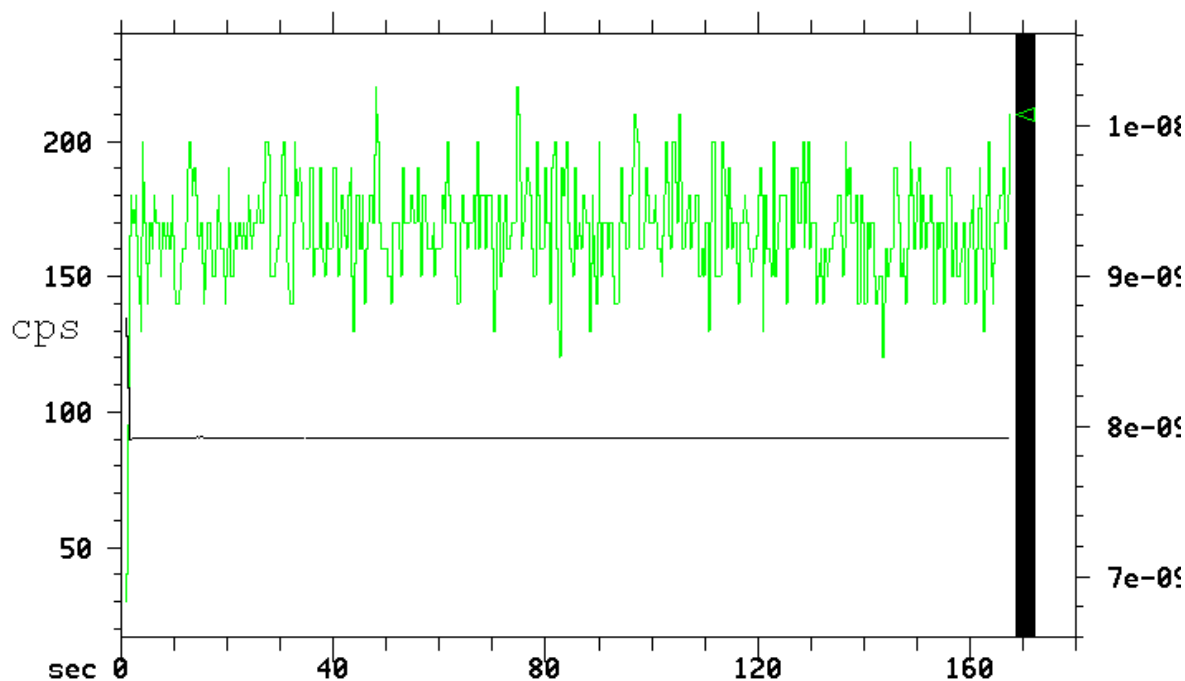


Figure 9. Electron Microprobe image showing that no diffusion of F occurred during analysis. No spike or rapid fall off occurred which are the signs of diffusion noted by Stormer (1993)

Accuracy and Precision

In any scientific study before you can attempt to draw any conclusions it is important to assess the accuracy and precision of the data that has been collected. Accuracy is a measure of how close the measured results that were obtained are to the actual values which are determined with the use of standards. In this study standards were used to calibrate the probe. From these standards error can be measured. If the error in a measurement was found to be above an acceptable level the data was discarded. Doing this ensures that the data is accurate. As a measure of accuracy, for each probe session, I measured the composition of Durango Apatite. Durango Apatite has the accepted value of 3.53 weight % F and 0.41 weight % Cl. The Durango Apatite was analyzed 25 times by the probe and yielded 3.58 weight % F and 0.44 weight % Cl.

Precision is a measure of how close the data points are in proximity to the population of rest of the data. In this study the data is fairly precise with the exception of two points that lie away from the majority of the data.

Findings

After analysis of the data collected there was no distinguishable difference in the composition of apatite based on petrographic location or in any other way the data was correlated. There were two points out of the 100 good points that seemed to be different than the rest. These two points which are from a garnet in slide 27D have a chlorapatite content that is an order of magnitude higher than the rest of the samples (.05 as apposed to .005 in most other samples). There are a few ways that these two anomalous data points can be looked at. First is that these samples were taken from a very small apatite grain and that the beam may have touched another phase which would cause the readings

to be different. Another cause for the difference in chlorine content could be because this apatite grain formed at a different time than the other grains that were looked at. If this is true than the apatite grain that showed a difference in chemistry would have formed under different conditions thus causing a change in chemistry. A third possibility is that in reality the difference in composition between the apatite grain that I have labeled different actually has no significant difference. In the ternary plots it is impossible to notice any difference with out magnifying the chlorapatite content by a factor of 40.

Although zoning has been noted in apatite (Spear and Pyle 2002), I was only able to locate one grain that showed zoning. This zoned grain showed a homogenous chemical make up, and showed no difference in chemistry from all the other un-zoned apatite grains. With regard to the question of whether apatite chemistry was a function of its petrographic location, I found there to be no correlation between chemistry and location. While there was a variation of chemistry between different apatite grains, there is no evidence to suggest that petrographic location is a factor in this difference. The size of the apatite grain also showed to have no significant effect on chemistry.

The data that was obtained is consistent with the findings of Pyle (2001) and Kapustin's (1986) analysis of apatite from amphibolite facies rocks. Both found that metamorphic apatite is found mostly as end member fluorapatite. This is probably not a coincidence because the rocks analyzed in this study and both the studies mentioned above all come from different environments and locations. The reason that fluorapatite is so prevalent in metamorphic rocks is because of the size of a F⁻ ion. The F⁻ ion fits better into the "anion column" than either the Cl⁻ ion or the OH⁻ ion (Spear and Pyle 2002). Moderate amounts of Cl have been found in rocks of the greenschist facies (Kapustin 1986). The validity of this study comes under question because the Electron Microprobe was not used to obtain the data. The study used wet chemistry to determine the halogen content. No one has been able to replicate Kapustin's study so it is unclear whether apatite ever has a Cl content as high as reported in this study.

Conclusion

Analysis of the data on the composition of apatite in metamorphic rocks from Coos Canyon, Maine shows that petrographic location of apatite is not a factor in influencing the chemical make up of apatite. All of the apatite grains analyzed fell somewhere along the F-OH divide with just one grain showing a small amount of Cl. Apatite that was found as an inclusion in garnet porphyroblasts had the same chemistry is apatite found in between grains of biotite, quartz or any other mineral present in the samples. I had speculated that the apatite in the garnet porphyroblasts might have a different chemistry because garnet is much harder than the other phases in the samples. Being very hard and relatively impenetrable, a garnet could theoretically shield an inclusion such as apatite from any change in chemistry that might occur due to metamorphism. One possibility in explaining the findings of this study is that apatite

always occurs primarily as fluorapatite in metamorphic rocks no matter what changes it has undergone.

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Appendix

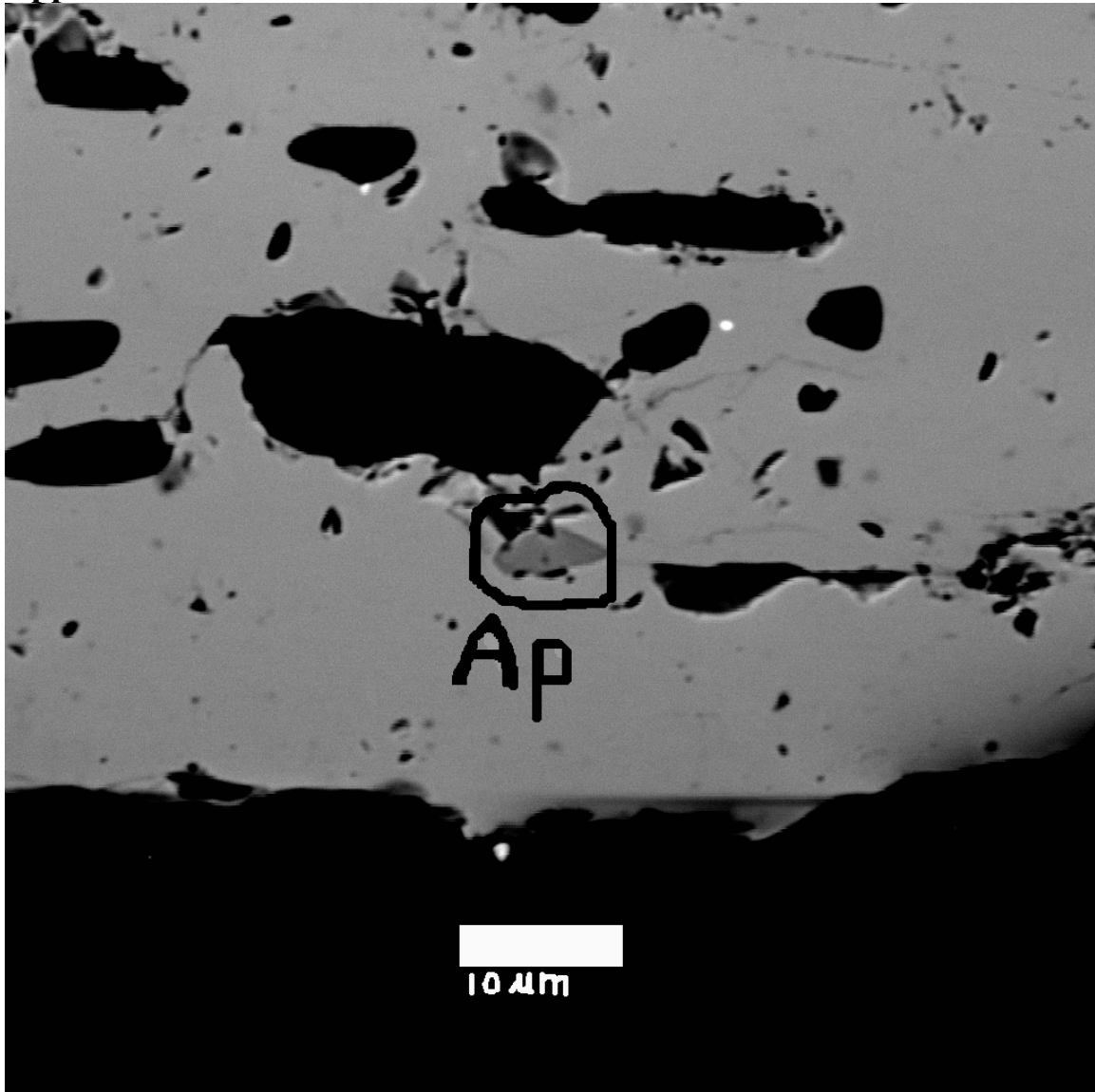


Fig. 10 Photomicrograph of apatite in garnet

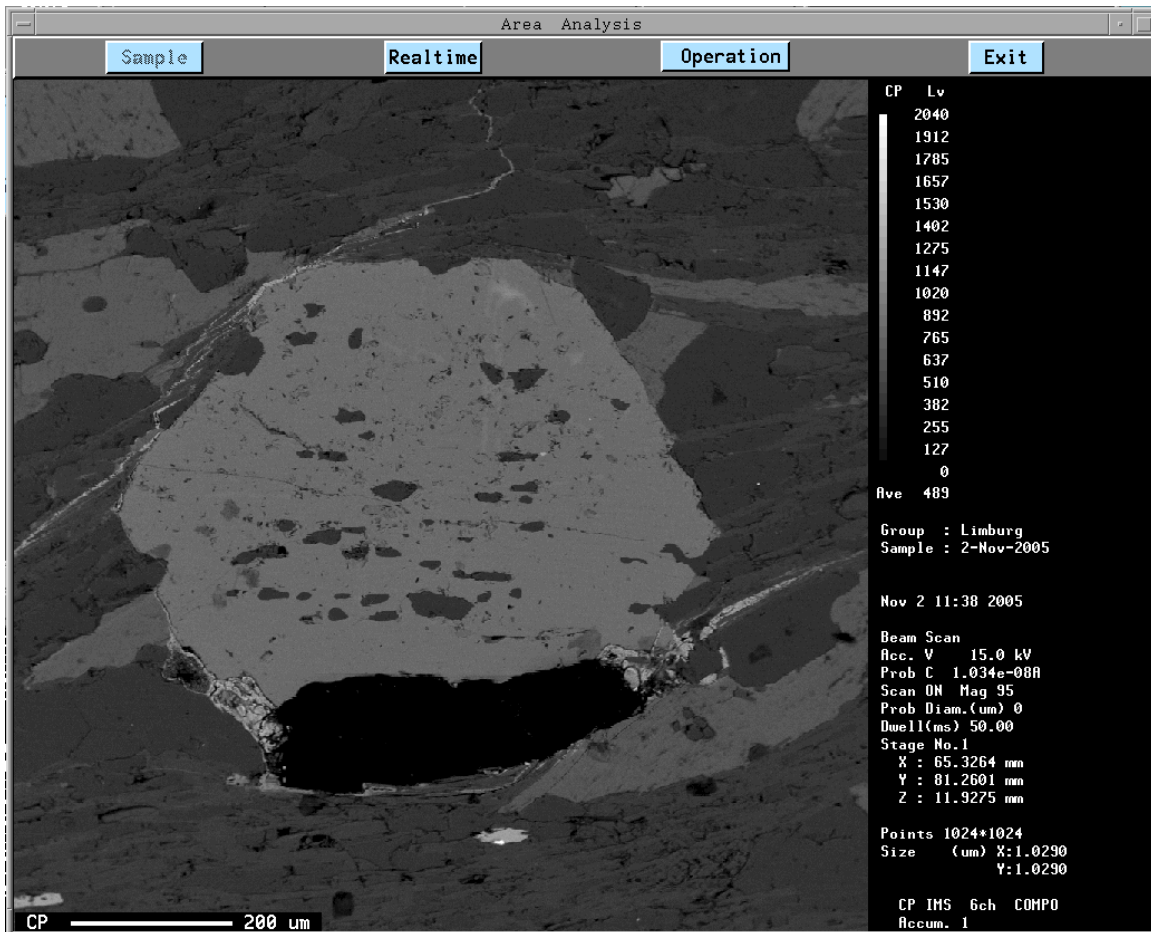


Fig 11. Photomicrograph of garnet containing apatite

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