Magmatic Crystalization of Sulfides in the Ellicott City Granodiorite: Implications on Ore Metals

GEOL 394

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Abstract
The Ellicott City granodiorite is an epidote-bearing pluton containing sulfide minerals observable in outcrop. The granodiorite is c. 460 Ma old and formed during the Taconic Orogeny. Epidote in the granodiorite is of magmatic origin (Mario, 1985). Pressure estimates for an epidote-bearing granitoid place the crystallization depth of epidote at 0.6-0.8 GPa (Zen and Hammarstrom, 1984). Corresponding to 25-30 km under the earth's surface.

At these pressures a magmatic vapor phase is unlikely to form (Philpots, 1990). If sulfides had crystallized from the magma prior to exsolution of a vapor phase, the sulfides will contain high chalcophile element abundances. However, sulfide phases can be susceptible to a magmatic ore-fluid which would grab the chalcophile elements from the sulfides. The magmatic origin of sulfides is established from petrographic analyses of polished thin sections. The electron microprobe analysis identified two sulfide phases in the ECG, pyrite and chalcopyrite. Trace elements such as As, Te, Ag, and Pb are measured by the LA-ICP-MS. Trace lement abundance in pyrite and chalcopyrite grains are found to be heterogeneous with the exception of Ag.

Introduction

Igneous epidote is an important mineral for constraining the pressure and temperature of crystallization in a pluton. Research done by Zen and Hammarstrom (1984) on plutons from the northern Cordillera in Northwestern U.S. to Alaska have indicated that the presence of epidote indicates a crystallization pressure of at least 0.6GPa-0.8GPa. This would correspond to a depth of about 25-30 km under the earth's surface. After crystallization the pluton could have either moved closer to the surface or stayed in place. Based on pressure estimates by Zen and Hammarstrom (1984) for the crystallization of epidote, it can be assumed that a magmatic vapor phase did not form. For an andesitic melt at pressures of 0.6-0.8 GPa the weight percent of H_2O would have to be greater than 10% (Philpotts, 1990) for a vapor phase to form. When a vapor phase is present metals can partition in to it stripping the of elements that partition into this phase. Assuming a volatile phase did not form, chalcophile metals will be taken in by the sulfides.

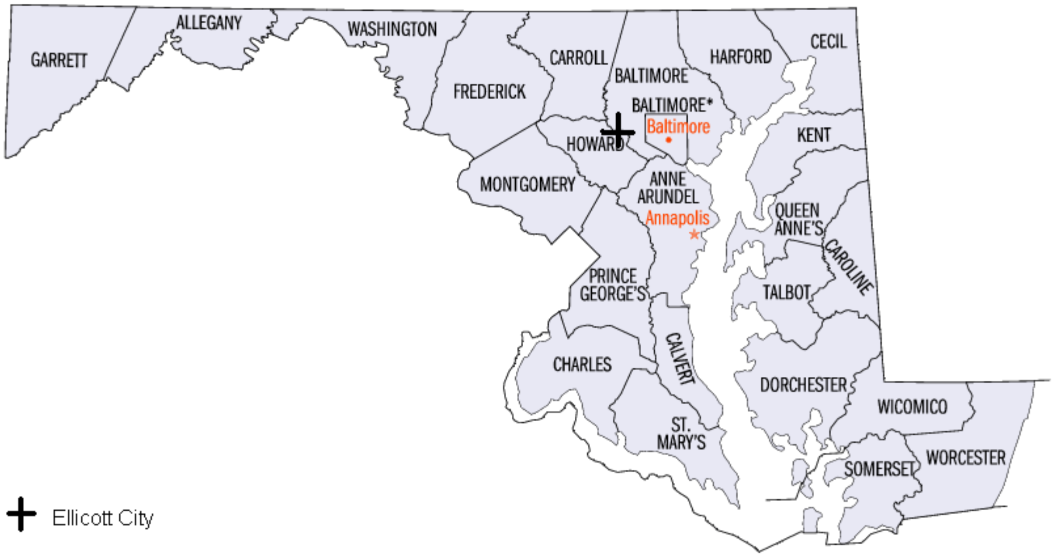
Hypothesis

The Ellicott City granodiorite is an epidote-bearing pluton, suggested to have crystallized at high pressure and observed to contain sulfides. At such high pressure a magmatic vapor phase is not likely to form, and metals would not have been partitioned into the vapor phase. Sulfides in the Ellicott City granodiorite crystallized from the magma before exsolution of a magmatic vapor phase and therefore may contain high metal concentrations.

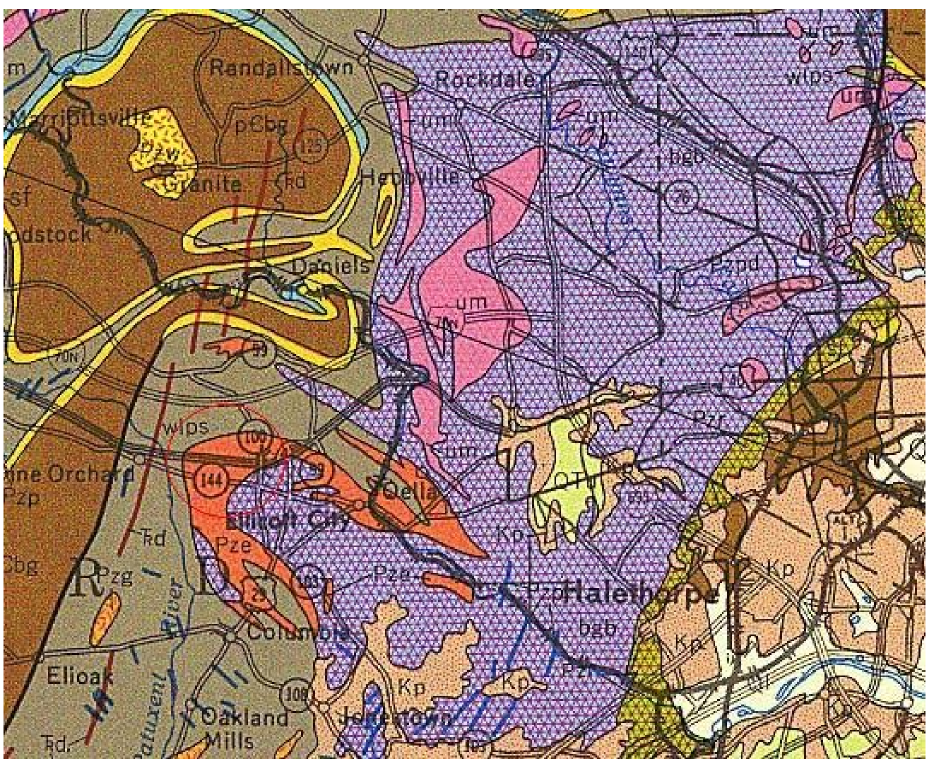
Geology

The Ellicott City granodiorite is located southwest of Baltimore on the Howard-Baltimore county line (map 1). The pluton broke through along a thrust fault between amphibolites and mica schists, the Cambrian Baltimore Gabbro Complex and the Cambro-Ordivician Whissahickon Formation, respectively (Hopson, 1964). The granodiorite is largely composed of quartz, plagioclase, and biotite. Other minerals making up the granodiorite matrix are epidote, hornblende, allanite, and sphene. Epidote forms euhedral crystals that surround euhedral allanite. Biotite and other major minerals surround the euhedral epidote. Sulfides are also present.

The following descriptions of the Cambrian Baltimore Gabbro Complex and the Cambro-Ordivician Whissahickon Fromation reflect the fieldwork done by Hopson (1964) and Mario (1989). The granodiorite-gabbro contact is relatively distinct. The granodiorite has "intruded through the Whissahickon Formation like a pen wedged up through a book" (Hopson, 1964). The granodiorite is dated by U-Pb at c. 460 Ma and



Map 1: Map of the state of Maryland and Ellicott City shown.



Map 2: Ellicott City granodiorite in orange labeled Pze. Outcrop circled in red.

likely formed during the collision between an island arc and the continent Laurentia during the Taconic Orogeny (Mario, 1989).

The Whissahickon Formation is composed mainly of pelitic schist, semipelitic schist, and crystalline granulose psammitc rocks (Hopson, 1964). The pelitic schists are medium- to coarse-grained and dominated by a muscovite and biotite matrix. The semipelitic schists are fine-grained and have higher contents of quartz and feldspar than the pelite. Mica in the semipelitic schist is also considerably less abundant than the pelite. The psammitic rocks are fine-grained and contain high abundances of quartz. However, biotite, oligoclase, and muscovite are common.

The Baltimore Gabbro Complex is composed of three main ultramafic rocks: websterite, lherzolite, and dunite. Plagioclase, orthopyroxene, and olivine are the main minerals in these rocks (Hopson, 1964).

Samples

Samples of the Ellicott City granodiorite were taken from an outcrop on Old Frederick Rd, Maryland state highway 144 from three main locations. The outcrop site on 144 is circled in red on map 2. The first site visited is behind the nursery and the High's convenience store. The next samples were taken from the creek bed next to the High's. The final site was approximately 200-300 yards up Old Frederick Road or Maryland 144, visible on map 2, towards the coffee shop. This site is where the abundant sulfides were found. Epidote was relatively abundant in outcrop. It was found in all three locations identified with hand lens.

I received two hand specimens of the Golden Sunlight mine latite. Two thin sections were made from these hand specimens in order to make petrographic observations. The GSL consists of plagioclase feldspar (approxximately 80 %), orthoclase feldspar, hornblende and pyrite. The pyrites range from 2 um to 200 um.

Methods

In order to measure the compositions of the sulfides present in the Ellicott City granodiorite several steps needed to be taken. Collecting samples from the field was the first step. Consequently, samples that contained sulfides were of necessity. Although several samples were taken from three major sites from the outcrop, only one site supplied the sulfide minerals that were needed in the experiment. Noticeable in outcrop was a dark reddish stain resulting from a chemical weathering (Fig 1). After cutting the samples into 1/2 inch slabs sulfides were located using a

Fig. 1: Reddish stain from chemical weathering used to identify potential rocks containing sulfides.

binocular microscope. The sulfide-bearing samples were then cut into billets and sent out for preparation of polished thin sections. Thins sections were examined by petrographic microscope using both transmitted and reflected light. These are described below. The electron probe microanalyzer was used to determine the composition of the sulfides. The electron probe microanalyzer was used to measure Cu, Fe, Ni and Zn concentrations. Concentrations of Fe, S, and Cu from this analysis allowed identification of the pyrite and chalcopyrite. Following this, Fe, Mo, W, Au, Ag, Cu, and Zn were measured in the sulfides by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Statistical errors will be determined later in the project.

Petrography

I studied five thin sections from Clair Coyne's senior thesis project (courtesy of Dr. Piccoli), and eleven polished thin sections of samples taken during my own field expedition. The Coyne thin sections were used as an introduction to petrographic analysis to the Ellicott City granodiorite. A typical thin section of the Ellicott City granodiorite consists of quartz, plagioclase, biotite, epidote, hornblende, and allanite. In transmitted light quartz and plagioclase are clear. Biotite is brown and is easily distinguished from the bird's eye texture in cross polarized light. Epidote is primarily euhedral. Euhedral allanite is often seen as a core inside the euhedral epidote (Fig. 2). Epidote can be seen in contact with hornblende, sharing a euhedral edge (Fig. 3). The Coyne thin sections did not contain any obvious sulfides.

In the polished thin sections, all of the phases noted above were also observed, in addition to sulfides. The rest of this discussion focuses on the color and textural relationships of sulfides. There were two different sulfides observed based on color and textural

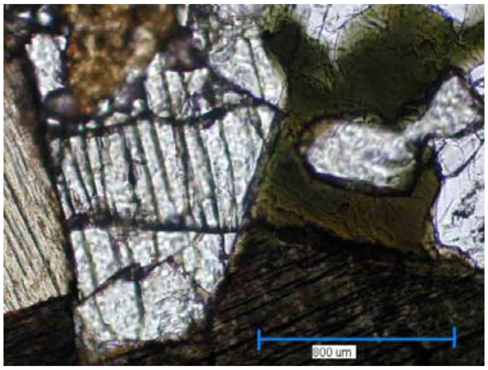


Fig 3: Euhedral epidote contact with euhedral hornblende.

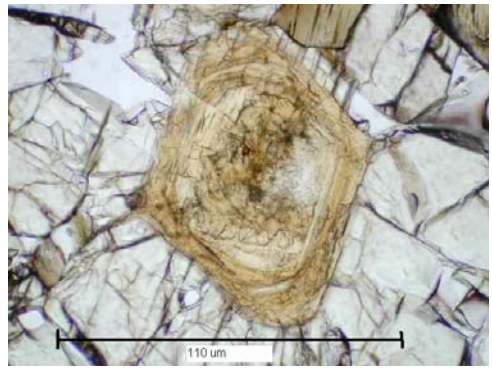


Fig 2: Euhedral allanite surrounding euhedral epidote.

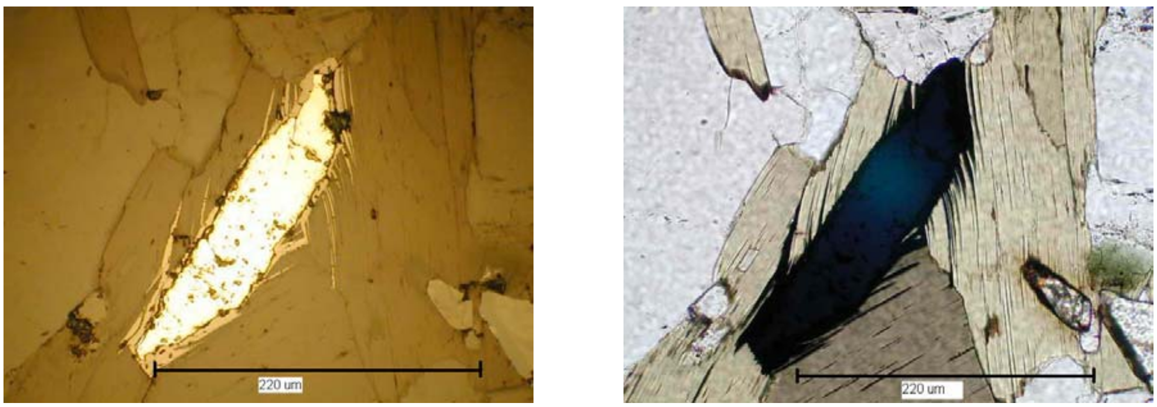


Fig. 4: Pyrite and thin gray oxide rime surrounded by biotite in reflected light (left) and transmitted light (right).

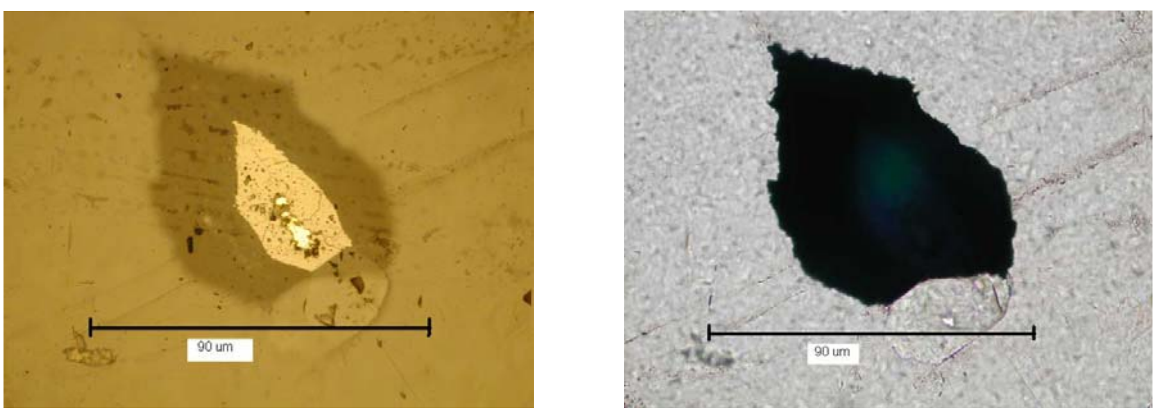


Fig. 6: Pyrite under reflected light (left) and transmitted light (right). The sulfide is surrounded by quartz except for the noticeable high relief to the bottom right. This is most likely apatite.

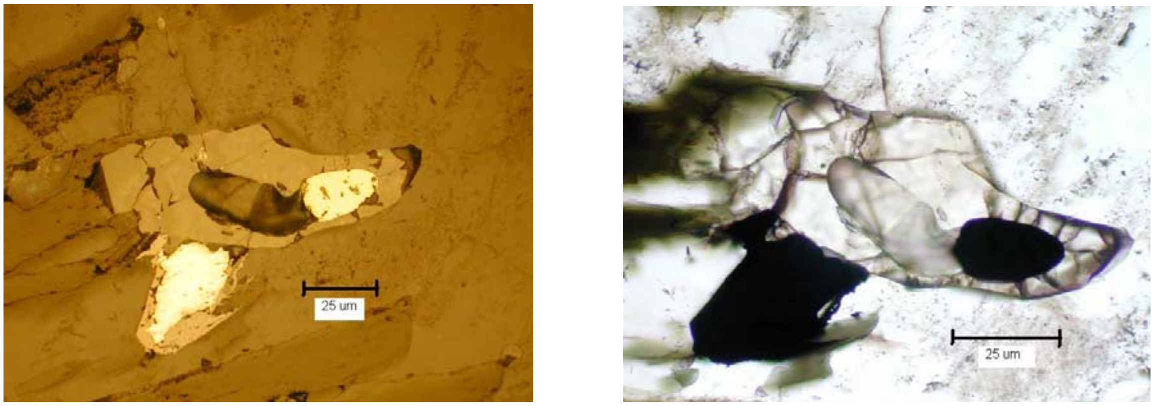


Fig. 7: Chalcopyrite (yellow) inclusion in epidote under reflected light (left) and transmitted light (right). Notice the stronger yellow chalcopyrite compared with the paler yellow pyrite crystallized outside of epidote, and the lack of oxide tims on the ccp comapred with pyrite.

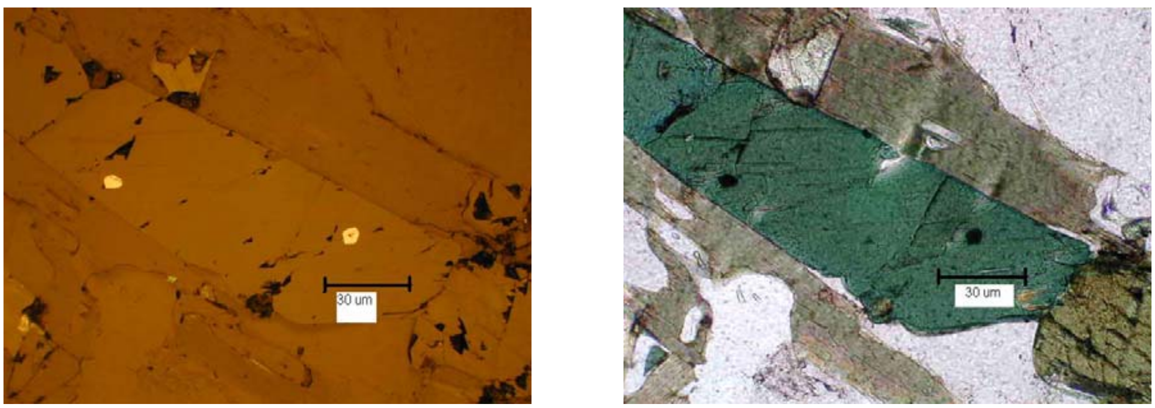


Fig. 8: Chalcopyrite inclusions in hornblende under reflected light (left) and transmitted light (right).

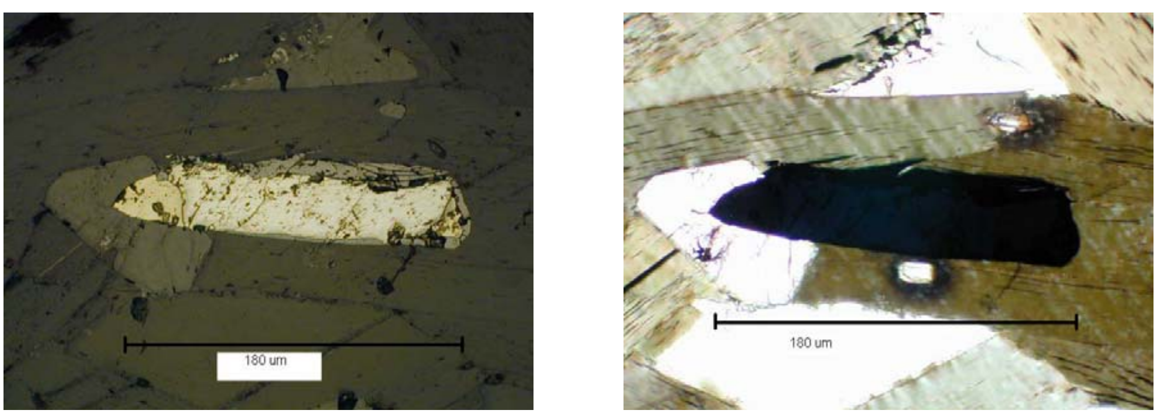


Fig. 9: Stronger yellow chalcopyrite crystalled in epidote under reflected light (left) and transmitted light (right). The paler yellow pyrite is crystallized outside of the epidote.

relationships. The first sulfide that will be discussed is a paler yellow sulfide, identified as pyrite. Pyrite was commonly associated with biotite, quartz, and a gray oxide, which commonly rims pyrite and extrudes cleavage planes into surrounding biotite (Fig. 4). The majority of the pyrites share a euhedral edge with biotite (Fig. 4). The relation between epidote and biotite can be observed from a larger scale (Fig. 5). This shows the frequent association with sulfides specifically pyrite found in clusters of biotite. Other pyrites are surrounded by quartz (Fig. 6).

The stronger yellow sulfides, which were identified as chalcoyrite empa, are observed to be associated with inclusions of epidote and hornblende and large matrix sulfides. This sulfide was identified as chalcopyrite. Chalcopyrites are rarely associated with the gray oxide without the paler yellow oxide present. The chalcopyrites are visible under reflected light in both epidote (Fig. 7) and hornblende (Fig. 8). Fig. 9 shows pyrite crystallized just outside of the epidote. This picture shows clearly the contrast in color between the pyrite and chalcopyrite. The chalcopyrite inclusions display a stronger yellow than pyrite surrounded by biotite, quartz, and plagioclase. Under polarized light the sulfides are opaque and look black (Fis. 4-9).

Sulfide Data

A total of eight thin sections were examined using the electron probe microanalyzer. Seven of these samples were from the ECG and another that was a latite from the Golden Sunlight Mine near Whitehall, Montana. This sample was used as a comparison. It is from an active Au mine, where the Au is contained solely within the pyrites in the latite would contain high abundances of metals.

Finding sulfides was not a difficult task when looking at the Ellicott City granodiorite in polished thin section. Fe and S compositions for both sulfide phases were homogeneous.

Pyrite has an average composition (in weight percent) of 46.8 % ±0.8Fe and 53.2 % ±1.4 S (Appendix A). The pyrites throughout the rock are homogenous. Chalcopyrite contained an average of 30.5% ± 0.4Fe, 35.1% ±0.6 S, and 34.5% ± 0.5 Cu. Chalcopyrite grains are also very homogenous individually and relative to each other. Statistical errors for pyrite and chalcopyrite can be seen in Appendix A and Appendix B, respectively for all grains sampled. The electron probe was also used for determining the concentrations of Ni, Co, Zn, and Mn. Of these, Co was the only element that was found in measurable quantities in both phases.

The LA-ICP-MS was used to measure the trace element content in the pyrite and chalcopyrite grains in the ECG. Assistance from undergraduates Dusty Aikers and Ashley McCleaf helped in reducing LA-ICP-MS data. Many chalcophile elements were chosen for analysus based on their preferential tendency to crystallize in sulfide minerals these are: As, Se, Mo, Ag, Cd, Sb, Te, W, Au, Tl, and Pb. The high number of elements was determined as an introduction to the sulfides. We have also measured sulfides a second time on the LA-ICP-MS reducing the number of elements measured by focusing on elements that returned with good results in the first round of analysis.

Pyrite data from the LA-ICP-MS is presented in Appendix C. Mo, Cd, Sb, W, Au, Tl, and Bi were generally below detection limits. However, elements such as Ag, Se, As and Pb returned data above the detection limits for several grains. Concentrations of Se and Ag are relatively homogenous within grains but not between grains. Pb is very heterogeneous and ranges from as high as 1300 ppm and as low as 3 ppm within the same grain. As and Se contents in the pyrites are relatively homogenous within grains. Se is also homogeneous.

The LA-ICP-MS analysis of chalcopyrite are presented in Appendix D. Chalcopyrite returned similar results to the pyrite. The elements that returned with measured values above the detection limits were Ag, Se, As and Pb. All four elements were homogeneous to each other. Data sets for elements did not fluctuate on order of magnitudes as previous measurements on the pyrite have shown.

Samples from a latite from the Golden Sunlight mine in Whitehall, Montana were acquired to measure element content. These sulfides were identified as pyrite with the electron probe microanalyzer (Appendix E). Metal contents of these sulfides were also measured with the LA-ICP-MS (Appendix F). Of the trace elements measured, only Tl and Ni were below detection. One relationship to note is that the spots tested had high trace elements content all around. Metal content of a spot is not more than one magnitude different for any other element. The metal content of each spot seems relative to one another. The metal contents for all elements in the GSM compared to abundance that were detectable in the ECG samples are much higher.

Discussion

Importance of Magmatic Epidote

In determining a pressure estimate for the Ellicott City granodiorite the conclusion must be made that the epidote crystallized as a magmatic mineral. Zen and Hammarstrom (1984) studied three epidote-bearing plutons in a tonilitic and granodiorite belt between northern California and southeastern Alaska. They concluded that epidote was crystallized from the magma. In thin section Zen and Hammarstrom (1984) saw epdiote in euhedral form against biotite. Also, euhedral epiodte commonly formed around euhedral allanite cores. However, the most important observation by Zen and Hammarstrom (1984) was the epidotes' relationship with hornblende. Rounded hornblendes were found as inclusions in the epidote.

Pressure estimates for a magmatic epidote have been discussed by Zen and Hammarstrom (1984), Naney (1983), and Schmidt and Poli (2004). Naney (1983) found that phase equilibria of synthetic granodioritic melts indicated epidote is stable in a temperature interval just above the solidus at O.8 GPa. Since epidote is stable so close to the solidus, Zen and Hammarstrom's (1985) suggest that epidote could not have risen any significant distance before it had completely crystallized.

Petrographic observations in the ECG lead to the conclusion that epidote is magmatic. Euhedral crystals of epidote and hornblende are often observed in contact, without any noticeable alteration (Fig. 3). Euhedral allanite cores surrounded by euhedral epidote are very common (Fig. 2). This is a strong evidence for epidote in the ECG to be magmatic in origin (Zen and Hammarstrom, 1984).

Hopson determined the order of mineral crystallization in the ECG to be: (1) plagiocalse, allanite, apatite; (2) epdiote, hornblende; (3) biotite; (4) potassium feldspar, quartz, muscovite. Using this sequence of crystallization we can use Schmidt and Poli's (2004) estimates on the correlation between pressure and relative time of epidote crystallization. In a 1.0 to 0.8 GPa system with fO_2 buffered to NNO, Schmidt and Poli (2004) found that the mineral phases crystallize sequentially from the liquidus with: (1) hornblende, (2) plagioclase, (3) epidote, (4) biotite, (5) quartz, and (6) potassium feldspar. As pressure decreases their work shows that epidote crystallization occurs later in the sequence. Therefore, Schmidt and Polis' work can be used as a guide to the presence of epidote crystallization using the relative crystallization sequence for epidote. This relation can be seen in Hopson's (1964) observations. My petrographic analysis confirms this order. Epidote forms euhedral crystals that enclose the euhedral allanite. Allanite could have been an early mineral phase or possibly a crystal remaining from the source region, also called restite (Mario, 1989). Biotite is often surrounding the epidote and allanite crystals.

Sulfide Discussion

The petrographic evidence is clear that the to sulfide phases in the ECG, pyrite and chalcopyrite, crystallized prior a magmatic vapor phase. The crystallization of pyrites and chalcopyrites before and during the crystallization of the epidote phase show this. However, the metal elements abundance measured by ICP-MS in the ECG are low. This would indicate the metal elements were taken out of the sulfides between the time of crystallization of the sulfide phases and the crystallization of the entire rock. Keith et al. (1997) suggest that the metal content of sulfides are available after crystallization to a magmatic ore-fluid. Explaining, the magmatic sulfides are preserved only in the least oxidized and least degassed lavas and vitrophyres. When sulfides are subjected to resorption and oxidation the metal content in the sulfides may be available to this magmatic ore-fluid. Metal elements tested in the ECG such as Ag, Pb, Zn and Au are susceptible to move from the sulfide phases to this ore-fluid. This would explain the relatively low concentrations, compared to the GSL, of metal elements in the pyrites and chalcopyrites.

Another possible explanation for the low metal content measured in the pyrites and chalcopyrites are simply the initial composition of the melt did not contain high metal concentrations.

Conclusion

The Ellicott City granodiorite contains magmatic epidote, which can be determined to crystallize at pressures of 1.0-0.8 GPa. Two phases of sulfides pyrite and chalcopyrite are also observable in the rock. Petrographic analysis of both epidote, pyrite and chalcopyrite show that they are both magmatic. Pyrite and chalcopyrite are found as inclusions in epidote and hornblende (only chalcopyrite) are clear signs of magmatic origin. Elemental abundances of chalcophile metal elements are low. After crystallization of pyrite and chalcopyrite the sulfides contained high abundances of chalcophile elements. Between crystallization of the pyrites and chalcopyrites and the rest of the magma a magmatic ore-fluid was able to take in the metal saturated sulfide phases.

Appendix A: ECG Pyrite electron probe microanalyzer

EC01-Ab grain 1	*Fe*	*Ni*	*Co*	*Cu*	*S*	*Zn*	*Mn*	*Total*
4	47.27	0.04	0.05	0	52.71	0	0.01	100.1
5	46.93	0	0.37	0	52.82	0	0	100.1
6	46.66	0.01	0.15	0	53.57	0	0	100.4
7	46.2	0	0.82	0.01	52.98	0	0	100.1
8	45.13	0	0.99	0.06	53.11	0	0	99.3
Average	46.44	0.01	0.48	0.02	53.04	0	0	99.9
1 sigma	0.74	0.01	0.37	0.02	0.3	0	0	0.37
%RSD	1.59	164	77.81	151	0.56	181	123	0.37
EC01-Ab grain 2								
13	47.01	0.02	0.06	0	53.41	0.01	0	100.5
14	47.08	0.01	0.08	0.01	53.76	0	0	100.9
15	47.43	0.01	0.05	0.01	53.03	0	0	100.5
16	47.28	0.09	0.04	0.03	53.19	0	0	100.6
Average	47.2	0.03	0.06	0.01	53.35	0	0	100.7
1 sigma	0.19	0.04	0.02	0.01	0.31	0	0	0.2
% RSD	0.4	127	26.89	95.75	0.59	137	200	0.2
EC01-Ab grain 3								
19	46.8	0.01	0.08	0.03	53.48	0	0	100.4
20	46.18	0	0.95	0.02	53.13	0.01	0	100.3
21	46.04	0	1.14	0.01	53.05	0	0	100.2
22	47.03	0.03	0.07	0.01	53.01	0	0	100.2
Average	46.51	0.01	0.56	0.02	53.17	0	0	100.3
1 sigma	0.48	0.02	0.57	0.01	0.21	0	0	0.1
%RSD	1.03	165.83	100.94	43.28	0.4	200	90.87	0.1
EC01-Ab grain 4								
23	47.13	0	0.11	0.01	53.09	0	0	100.3
24	47.56	0	0.3	0	52.78	0	0	100.6
25	47.29	0	0.26	0.01	52.95	0	0	100.5
26	47.26	0.02	0.13	0.01	52.91	0.01	0	100.3

	27	47.43	0	0.11	0.02	53.08	0	0	100.6
Average		47.33	0	0.18	0.01	52.96	0	0	100.5
1 sigma		0.16	0.01	0.09	0.01	0.13	0	0	0.15
% RSD		0.34	175.76	49.56	61.58	0.24	218.65		0.15
EC01-Ab grain 5									
	30	46.3	0.01	0.06	0.02	54.18	0.01	0.01	100.6
	31	46.3	0	0.09	0.01	54.04	0	0.01	100.4
	32	46.32	0	0.14	0.01	54.28	0	0	100.7
	33	46.38	0	0.43	0.02	53.46	0	0	100.3
	34	46.76	0	0.22	0.01	54.06	0.01	0	101.1
	34	46.89	0	0.22	0.01	54.09	0.01	0	101.2
	35	46.36	0	0.56	0.02	54.51	0	0	101.4
Average		46.47	0	0.32	0.01	54.08	0	0	100.9
1 sigma		0.25	0	0.16	0.01	0.35	0	0	0.4
% RSD		0.53		49.51	51.24	0.65	122.47	122.47	0.4
EC01-B grain 1									
	41	47.02	0.14	0.04	0.02	53.9	0	0	101.1
	42	47.54	0.06	0.05	0.01	53.95	0	0	101.6
	43	47.1	0.16	0.06	0	53.37	0	0	100.7
	44	47.64	0.02	0.07	0.01	53.48	0	0	101.2
	45	47.43	0.21	0.29	0.06	53.98	0	0	102
	46	45.67	0.02	0.06	0.02	50.07	0.01	0	95.9
Average		47.07	0.1	0.09	0.02	53.13	0	0	100.41
1 sigma		0.73	0.08	0.1	0.02	1.52	0	0	2.28
% RSD		1.54	79.5	107	111	2.86	245	178	2.27
EC-01-B grain 2									
	47	46.71	0.01	1.14	0.01	53.02	0.01	0.01	100.9
	48	47.84	0.02	0.08	0.01	53.78	0	0	101.7
	49	47.73	0.09	0.09	0.03	53.23	0.01	0	101.2
Average		47.43	0.04	0.43	0.02	53.34	0.01	0	101.3
1 sigma		0.63	0.04	0.61	0.01	0.39	0.01	0	0.42
% RSD		1.32	101	141	56.3	0.73	89.3	101	0.41
EC01-B grain 4									
	59	46.88	0.02	0.06	0	52.74	0	0	99.7
	60	46.64	0	0.09	0.01	53	0	0	99.7
	61	47	0.02	0.05	0	54.34	0	0	101.4
	62	47	0	0.05	0	53.98	0	0	101.
Average		46.88	0.01	0.06	0	53.52	0	0	100.5
1 sigma		0.17	0.01	0.02	0.01	0.77	0	0	0.88
% RSD		0.36	100	31.4	131	1.43	200	200	0.88
EC02-Eb grain 2									
	63	46.41	0	0.05	0.01	53.42	0	0	99.9
	64	43.56	0	0.04	0.01	45.45	0.02	0.01	89.0
	65	47.59	0	0.05	0.01	53.3	0	0	101.0
	66	47.56	0	0.05	0.01	55.09	0.01	0	102.7
Average		46.28	0	0.05	0.01	51.81	0.01	0	98.2

1 sigma	1.89	0	0	0	4.32	0.01	0	6.16
% RSD	4.09	71.1	3.79	37.8	8.34	133	127	6.27

	Fe	*Ni*	*Pb*	*Co*	*Cu*	*S*	*Zn*	*Mn*	*Total*
EC-52-1 Grain 5									
1	46.94	0.00	0.01	0.05	0.00	52.76	0.00	0.00	99.76
2	46.92	0.00	0.00	0.06	0.00	52.55	0.00	0.00	99.52
3	46.65	0.00	0.00	0.04	0.10	52.82	0.00	0.00	99.61
4	46.84	0.00	0.01	0.04	0.00	52.61	0.00	0.00	99.50
5	46.91	0.00	0.00	0.04	0.00	52.53	0.00	0.00	99.49
6	48.17	0.00	0.00	0.05	0.00	46.12	0.00	0.00	94.33
7	47.03	0.00	0.00	0.05	0.17	53.30	0.01	0.00	100.56
Average	47.07	0.00	0.00	0.05	0.04	51.81	0.00	0.00	98.97
1 sigma	0.50	0.00	0.01	0.01	0.07	2.52	0.00	0.00	2.08
% RSD	1.06		172	13	177	4.87	265	265	2.10
EC52-1 Grain 4									
8	46.68	0.09	0.00	0.05	0.00	53.05	0.00	0.00	99.87
9	46.95	0.20	0.00	0.10	0.00	53.15	0.00	0.00	100.40
10	47.30	0.17	0.00	0.06	0.00	53.25	0.03	0.00	100.81
11	46.92	0.14	0.01	0.06	0.00	52.81	0.01	0.00	99.95
12	46.98	0.09	0.00	0.04	0.00	53.06	0.00	0.00	100.2
Average	47.0	0.13	0.00	0.06	0.00	53.07	0.01	0.00	100.2
1 sigma	0.22	0.05	0.01	0.02	0.00	0.16	0.01	0.00	0.38
% RSD	0.48	36	185	35		0.31	162	224	0.38
EC52-1 Grain 2									
13	45.07	0.17	0.00	0.13	0.05	51.91	0.00	0.00	97.33
14	45.18	0.03	0.00	0.06	0.00	51.67	0.00	0.00	96.93
15	43.15	0.00	0.00	1.91	0.00	50.67	0.01	0.00	95.74
16	46.42	0.16	0.00	0.07	0.00	51.82	0.00	0.00	98.47
17	45.99	0.06	0.00	0.84	0.00	52.36	0.00	0.00	99.24
Average	45.2	0.08	0.00	0.60	0.01	51.7	0.00	0.00	97.5
1 sigma	1.26	0.07	0.00	0.80	0.02	0.62	0.00	0.00	1.36
% RSD	2.78	90		133	224	1	183	224	1
EC52-1 Grain 1									
23	43.44	0.00	0.00	3.58	0.00	53.34	0.02	0.00	100.38
24	46.83	0.02	0.00	0.06	0.03	53.35	0.05	0.00	100.34
25	46.80	0.00	0.00	0.05	0.00	53.30	0.00	0.00	100.16
26	46.70	0.02	0.00	0.06	0.00	52.99	0.01	0.00	99.79
Average	45.94	0.01	0.00	0.94	0.01	53.25	0.02	0.00	100.17
1 sigma	1.67	0.01	0.00	1.76	0.01	0.17	0.02	0.00	0.27
% RSD	3.63	116		187	200	0.32	109	200	0.27
EC52 –1 Grain 3									
35	46.38	0.17	0.00	0.07	0.00	53.34	0.00	0.01	99.97
36	46.80	0.07	0.00	0.08	0.00	53.20	0.01	0.00	100.16
37	45.95	0.13	0.00	0.12	0.00	51.92	0.01	0.00	98.14

38	46.69	0.18	0.00	0.20	0.00	53.39	0.00	0.00	100.47
Average	46.5	0.14	0.00	0.12	0.00	53.0	0.01	0.00	99.7
1 sigma	0.38	0.05	0.00	0.06	0.00	0.70	0.01	0.00	1.05
% RSD	0.82	38	200	52		1.32	116	182	1.05
EC52-2b Grain 1									
63	45.32	0.01	0.00	0.05	0.00	52.68	0.00	0.00	98.05
64	45.02	0.01	0.00	0.07	0.00	52.20	0.00	0.00	97.30
65	45.84	0.01	0.00	0.05	0.00	52.05	0.01	0.00	97.97
66	45.73	0.08	0.00	0.09	0.00	53.85	0.01	0.00	99.75
67	45.76	0.06	0.02	0.05	0.00	51.94	0.01	0.00	97.84
68	45.68	0.00	0.00	0.03	0.10	52.33	0.01	0.00	98.16
69	45.82	0.03	0.01	0.05	0.15	52.41	0.00	0.00	98.47
70	45.53	0.07	0.82	0.05	0.00	52.14	0.00	0.00	98.62
71	45.86	0.04	0.00	0.05	0.00	52.79	0.00	0.00	98.74
Average	45.6	0.03	0.09	0.06	0.03	52.5	0.00	0.00	98.3
1 sigma	0.29	0.03	0.27	0.02	0.06	0.58	0.00	0.00	0.69
% RSD	0.63	90	289	31	201	1.11	128	181	0.70
EC52-2b Grain 2									
75	44.84	0.22	0.00	0.06	0.19	52.85	0.00	0.00	98.16
76	44.86	0.25	0.02	0.05	0.00	52.60	0.00	0.00	97.80
77	45.56	0.06	0.00	0.06	0.00	52.78	0.00	0.00	98.47
78	45.53	0.05	0.00	0.05	0.00	52.57	0.00	0.00	98.21
Average	45.2	0.15	0.01	0.06	0.05	52.7	0.00	0.00	98.2
1 sigma	0.40	0.10	0.01	0.01	0.10	0.13	0.00	0.00	0.28
% RSD	0.89	71	200	10	200	0.25		200	0.28
EC52-2b Grain 3									
92	45.34	0.00	0.00	0.15	0.00	52.18	0.00	0.00	97.67
93	45.21	0.08	0.00	0.11	0.00	52.54	0.00	0.00	97.94
94	45.22	0.12	0.00	0.09	0.15	52.09	0.00	0.00	97.67
95	45.19	0.05	0.00	0.07	0.06	51.98	0.01	0.00	97.35
96	45.09	0.01	0.00	0.15	0.00	52.16	0.00	0.00	97.41
97	45.09	0.00	0.01	0.10	0.23	52.48	0.00	0.00	97.90
98	44.99	0.02	0.00	0.19	0.00	52.40	0.00	0.00	97.60
99	45.14	0.01	0.00	0.12	0.00	52.57	0.00	0.00	97.85
Average	45.2	0.04	0.00	0.12	0.06	52.3	0.00	0.00	97.7
1 sigma	0.11	0.04	0.00	0.04	0.09	0.23	0.00	0.00	0.22
% RSD	0.24	117	283	33	160	0.43	226		0.22

Appendix B: ECG Chalcopyrite epm data

	Fe	*Ni*	*Co*	*Cu*	*S*	*Zn*	*Mn*	*Total*
EC01-Ab grain 1								
3	30.91	0.00	0.02	34.66	33.26	0.01	0.00	98.86
9	29.83	0.00	0.04	34.93	34.48	0.01	0.00	99.29
10	29.84	0.00	0.03	35.04	34.87	0.03	0.00	99.80
11	29.61	0.00	0.03	35.05	34.60	0.00	0.00	99.29
12	29.41	0.00	0.02	34.80	34.90	0.02	0.00	99.15
Average	29.92	0.00	0.03	34.90	34.42	0.01	0.00	99.28
1 sigma	0.58		0.01	0.17	0.67	0.01		0.34
% RSD	1.94		31.5	0.48	1.96	80.4		0.35
EC01-Ab grain 2								
17	30.38	0.00	0.03	34.89	35.08	0.01	0.00	100.38
18	30.78	0.00	0.02	34.79	34.47	0.03	0.00	100.10
Average	30.58		0.03	34.84	34.78	0.02	0.00	100.24
1 sigma	0.29		0.01	0.06	0.43	0.01	0.00	0.20
% RSD	0.94		26.3	0.19	1.23	57.3	141	0.20
EC01-Ab grain 4								
28	30.39	0.00	0.03	34.74	34.92	0.04	0.00	100.1
29	29.88	0.00	0.04	34.37	34.54	0.04	0.00	98.8681
Average	30.13	0.00	0.03	34.55	34.73	0.04	0.00	99.49
1 sigma	0.36	0	0.003	0.26	0.27	0.001	0.0004	0.88
% RSD	98.3		112.5	98.9	98.9	96.4		98.8
EC01-Ab grain 6								
36	30.47	0.00	0.04	34.05	35.13	0.02	0.00	99.7065
37	30.52	0.00	0.02	34.13	35.24	0.00	0.00	99.9077
38	30.39	0.00	0.03	33.93	34.91	0.03	0.00	99.2878
39	30.29	0.00	0.04	33.87	35.01	0.02	0.00	99.2304

40	30.54	0.00	0.04	34.08	35.24	0.01	0.00	99.9012
Average	30.44	0.00	0.03	34.01	35.10	0.02	0.00	99.61
1 sigma	0.10	0	0.008	0.11	0.14	0.013	0	0.33
% RSD	0.34		26.8	0.32	0.41	81.4		0.33
EC01-B grain 2								
50	30.91	0.00	0.03	34.37	35.13	0.02	0.00	100.5
51	30.79	0.00	0.04	34.40	35.04	0.03	0.00	100.3
52	30.78	0.00	0.02	34.48	35.16	0.00	0.00	100.4
53	30.57	0.00	0.03	35.38	35.18	0.03	0.00	101.2
53	30.71	0.00	0.03	34.38	35.13	0.03	0.00	100.3
54	30.73	0.00	0.04	34.58	35.14	0.03	0.00	100.5
Average	30.75	0.00	0.03	34.60	35.13	0.02	0.00	100.53
1 sigma	0.11	0	0.005	0.39	0.047	0.0119	0	0.33
% RSD	0.36		15.5	1.12	0.13	49.55		0.33
EC01-B grain 3								
55	30.41	0.00	0.02	33.92	35.94	0.02	0.00	100.3
56	30.50	0.00	0.03	33.91	35.58	0.01	0.00	100.03
57	30.58	0.00	0.03	34.15	35.80	0.02	0.00	100.6
58	30.66	0.00	0.02	33.94	35.86	0.01	0.00	100.5
Average	30.54	0.00	0.03	33.98	35.79	0.02	0.00	100.4
1 sigma	0.11	0.00	0.00	0.12	0.16	0.01	0.00	0.25
% RSD	0.36		19.3	0.34	0.44	51.22	200	0.25
EC02-Eb grain 3								
67	30.82	0.00	0.04	34.02	35.83	0.03	0.00	100.7
68	30.30	0.00	0.03	33.42	35.51	0.02	0.00	99.3
69	30.75	0.00	0.03	34.25	35.56	0.01	0.00	100.6
70	30.83	0.00	0.03	34.15	35.92	0.02	0.00	100.95
Average	30.68	0.00	0.03	33.96	35.70	0.02	0.00	100.39
1 sigma	0.25	0.00	0.01	0.37	0.20	0.01	0.00	0.76
% RSD	0.83		16.2	1.10	0.57	38.5	148.5	0.76

Appendix C: ECG Pyrite LA-ICP-MS data

Element	*Mn*	*Fe*	*Co*	*Ni*	*Cu*	*Cu*	*As*	*Se*	*Ag*	*Ag*	*Cd*	*W*	*W*	*Au*	*Tl*	*Tl*	*Pb*	*Pb*	*Bi*
Atomic number	55	57	59	61	63	65	75	77	107	109		182	183	197	203	205	206	207	209
Grain 1		470000	176	2121	61	59		55	7	7			0.2			0.04	4	3	
Grain 2	19	470000	48	1437	56	51	8.7	67	5	6					0.08	0.09	186	165	
Grain 3		300000	52						7	6					0.16	0.11	24	20	
Grain 4			900	1578	9	11		58	4	8							5	4	
Grain 5			218	218	4	5	10	17	2	2							5	5	
Grain 6	4.3		204	218	5	4	9	14	3	2		0.01		0.3			4	3	0.05
Grain 7	12		1157	2130	585	534	40	72	13	13		0.03					15	14	
Grain 8	4.3		1212	2130	965	1079	20	60	16	15				0.7	0.13		18	17	
Grain 9			110	189	4	4	6	8	2	2			0.01		0.03		2	2	0.01
Grain 10		470000	508	880		8									0.05				
Grain 11		470000	11835		7														
Grain 12	22		290	242	137	128	14	31	1	1			0.14			0.02	71	77	
Grain 13			6519		13	15						0.04	2.6		0.05		3		
Grain 14	200		101			1020	17	134	109	94			1.0				1445	1264	0.50
Grain 15		470000	110		84	254			7	7					0.11	0.21	6	4	
Grain 16		470000	54		13	53						0.06	0.23		0.08		16	13	
Grain 17			600					625					0.6		0.40		12		15
Grain 18			600		60	147		697							2.3			13	0.25

Appendix D: ECG Chalcopyrite LA-ICP-MS data

	Mn	*Fe*	*Co*	*Ni*	*Cu*	*Cu*	*As*	*Se*	*Ag*	*Cd*	*Sb*	*W*	*Au*	*Tl*	*Pb*	*Bi*
Grain 1	300000						504	17	16					10	9	
Grain 2	300000							47	59					12	10	
Grain 3	300000	677						20	19				0.11	10	7	
Grain 4	300000					172	190	36	36				0.28	3	5	
Grain 5	300000						184	39	38					26	22	
Grain 6	300000						187	34	30						1	
Grain 7	306600			24650	185863		372					0.2	0.42			
Grain 8	306000			52599	207912		379	13				0.4				
Grain 9	309100	490		15103	30158		47	8	7		0.7		0.23	6		
Grain 10	307900			61344	279798			48	42							
Grain 11	307900			35934	260939		226	45	50							

Appendix E: GSL Pyrite epm

GSL-01 Grain 4	*Fe*	*Ni*	*Pb*	*Co*	*Cu*	*S*	*Zn*	*Mn*	*Total*
102	45.78	0	0	0.04	0	53.22	0.02	0	99.06
103	46.08	0.01	0	0.04	0.02	53	0	0	99.14
104	46.14	0	0	0.04	0	53.02	0	0	99.2
105	45.98	0.02	0	0.1	0	53.04	0.02	0	99.16
106	46.95	0	0	0.04	0	53.11	0	0	100.1
107	45.64	0	0	0.04	0.09	51.3	0	0	97.08
108	46.8	0	0	0.06	0	53.13	0	0	99.98
109	46.65	0.01	0	0.36	0.14	53.11	0	0	100.27
110	47.11	0	0	0.05	0	53.29	0	0	100.45
111	46.63	0	0	0.1	0	53.19	0.01	0	99.93
112	46.87	0	0	0.05	0.1	53.07	0	0	100.09
113	46.78	0	0.01	0.05	0	53.29	0.02	0	100.15
114	46.96	0	0	0.04	0	52.96	0	0	99.97
115	46.17	0.01	0.01	0.51	0.02	53.13	0	0	99.84
Average	46.4	0	0	0.11	0.03	53	0.01	0	99.6
1 sigma	0.49	0.01	0	0.14	0.05	0.5	0.01	0	0.86
% RSD	1.04	159	259	131	178	0.94	152	206	0.86
GSL-01 Grain 3									
116	46.74	0	0	0.04	0.08	52.88	0	0	99.74
117	36.24	0	0	0.03	0	38.55	0	0	74.82
118	46.77	0	0.01	0.04	0	52.95	0	0	99.76
119	46.73	0	0	0.04	0	53.07	0	0	99.84
120	46.84	0	0	0.04	0	53.26	0	0	100.15
121	46.66	0	0.01	0.04	0.25	53.22	0	0	100.18
Average	45	0	0	0.04	0.06	50.6	0	0	95.78
1 sigma	4.29	0	0	0.01	0.1	5.93	0	0	10.25
% RSD	10		162	14	182	12	166	164	11
GSL-01 Grain 6									
122	47.23	0	0.03	0.05	0	53.19	0	0	100.5
123	46.73	0	0	0.04	0	52.87	0.01	0.01	99.66
124	46.89	0	0	0.04	0	53.17	0	0	100.09
125	46.69	0.01	0	0.05	0.28	53.11	0	0	100.15
126	46.75	0.01	0	0.05	0	52.76	0	0	99.57
127	47.37	0.01	0	0.04	0	52.14	0	0.02	99.58
128	47.02	0	0	0.03	0	53.41	0.01	0	100.48
129	47.06	0	0.02	0.05	0.05	53.21	0.01	0	100.4
Average	47	0	0.01	0.04	0.04	53	0	0	100.1
1 sigma	0.25	0	0.01	0.01	0.1	0.4	0	0.01	0.4
% RSD	0.52	143	186	15	240	0.75	97	204	0.4
GSL-01 Grain 1									
130	46.9	0.01	0	0.05	0	53.35	0	0	100.31
131	47.01	0	0	0.04	0.06	53.02	0	0	100.14
132	46.8	0	0	0.04	0.37	53.34	0	0	100.55
133	46.81	0.01	0	0.03	0.09	53.24	0	0	100.18
134	46.65	0	0	0.05	0.25	52.88	0	0	99.83
135	46.66	0.03	0	0.05	0.04	53.22	0	0	100
136	46.58	0	0	0.06	0	53.06	0	0	99.7

137	46.11	0	0	0.06	0.03	52.79	0	0	98.98
Average	46.7	0.01	0	0.05	0.11	53.1	0	0	99.9
1 sigma	0.27	0.01	0	0.01	0.14	0.21	0	0	0.48
% RSD	0.59	157		18	128	0.39	283	230	0.48

Appendix F: GSL Pyrite LA-ICP-MS data

	Gold deposit pyrites													
Mn	95	210	287	186	1313	285		61	33	3071	824	229	85	24
Co	48	10		900		440	115	783	5946	5851	46	28	148	6877
Ni	299	212		275		906		908	1086	1070	436	930		1026
Cu	3397	2093	423	1561	12003	127	98	1464	2299	117	40	3872	912	245
Cu	5006	3211	713	5689	15739	149	100	1813	2507	143	43	5796	945	234
As	23	21	12	170	546	288		88	133	201	23	670	94	24
Se	100	100	100	100	100	100		100	100	100	100	100	100	100
Ag	82	895	562	88	364	76	98	359	195	325	28	40	66	49
Ag	72	977	551	76	479	78	86	426	151	345	31	40	70	44
Au	19	243	197	15	40	36		39	46	48	2.1	7.6	1.6	0.6
Pb	301	135	44	6209	698	294	17	74	84	2048	282	213	40	158
Pb	325	132	40	7489	653	271	16	68	82	1910	273	201	49	134
Bi	64	77	49	122	472	21	4.7	16	27	10	45	295	147	261
Comments	GSC-01 py6	GSC-01 py6	GSC-01 py6	GSC-01 py6	GSC-01 py6	GSC-01 py4	GSC-01 py4 *bad*	GSC-01 py4	GSC-01 py4	GSC-01 py4	GSC-01 py3	GSC-01 py3	GSC-01 py3 *low He*	GSC-01 py2

*Values in ppm

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