A worthwhile contribution

Geology 9

The Use of Etching Reagents For The Determination of Zinckenite

by

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Acknowledgements

The writer wishes to thank Dr. H. V. Warren, professor of Mineralogy, for his keen interest which has been an inspiration at all times and especially when the work was progressing slowly, and for his many helpfull suggestions. The writer also wishes to thank Mr. Robert Thompson for his assistance in etching with standard reagents and Mr. Jim Donnan for his aid in preparing and super-polishing the sections.

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The Use of Etching Reagents For The Determination of Zinckenite

1. Introduction

Dr. H. V. Warren, in suggesting to the writer the suite of ores from the Robson Group as a topic for a Geology 9 thesis, stated that he would like to see a little more work done on the ore as the occurrence of zinckenite in British Columbia is noteworthy. Although specimens of zinckenite have been proven by X-ray analysis to be zinckenite, it was thought that there was a definite possibility that the zinckenite might be accompanied by minor amounts of minerals from the same series. Thus it was decided, as the polished surfaces of these related minerals were not distinctive, that suitable etches might be used to separate these minerals. The common etching reagents were used first of all and found to be unsatisfactory. It was logical, therefore, to follow A. M. Gaudin's work described in his paper, "The Indentification of Sulphide Minerals by Selective Iridescent Filming", whereby he was able to distinguish betwen Chalcostibite and Stibnite in synthetic aggregate.

2. Location

The Robson Group, consisting of 16 claims, is situated near Bonanza Creek in the Tyaughton Lake area. The workings are approximately at 6000 feet elevation and maybe reached from Minto via 18 miles of wagon road to Empire Mercury mine, thence by pack trail for 6 miles up Tyaughton Creek.

3. General Geology

The Robson Group is situated in the Eldorado Series which are lower Cretacious and upper Jurassic in age. The series consists mainly of argillite but with many beds of sandstone, conglomerate and lenses of limestone as well as a few layers of volcanic material. The upper and lower horizons contain predominantly argillite with some fine sandstones, whereas, the central part of the formation is a well-defined zone to which almost all the conglomerates, limestones, and volcanic material are confined but which also contain much argillaceous material. The beds of the Eldorado Series are steeply dipping and in places intricately folded. In general, however, they conform to a large anticlinal fold the axis of which strikes and plunges fairly steeply towards the west from a point a few miles east of Castle mountain. To the northeast of this fold in the neighborhood of the head of Tyaughton Creek, the dips are reversed indicating an anticlinal axis in this vicinity. The relation of the Eldorado series to the Coast Range batholith is clearly an intrusive one and considerable metamorphism is in evidence.

(a) Porphory Stocks

A short distance east of the Coast Range batholith, the Cretaceous sediments and volcanics are cut by many sills and stocks, of various kinds of light colored porphories, some of the larger of which lie east and west of Tyaughton Creek. The majority of the porphories are coarse-grained, light grey diorites, consisting of large phenocrysts of andesine and smaller ones of hornblende crowded together in a matrix of the same minerals plus small amounts of magnetite. Some of the porphories have abundant quartz phenocrysts and are similar in composition to a quartz-diorite.

The age of the porphories is not determined beyond the fact that they cut the Cretacious sediments and volcanics as well as the Coast Range batholith. They are a persistent feature throughout the eastern contact of the batholith and are believed related to it both time and origin.

4. Detailed Geology

The main showing is a strong fissure vein containing widths of sulphides varying from stringers to 1.0 feet. The sulphides consist mainly of pyrite, arsenopyrite, sphalerite, zinckenite and tetrahedrite. From an assay it was shown that the main vein also contained 1.68 ounces of gold and 22.95 ounces of silver per ton.

(a) Megascopic Appearance of the Ore

The wall rock consists mainly of light grey silicified argillite which undoubtedly has been altered by the mineralizing solutions. ~~This alteration is substantiated by~~ the finely disseminated pyrite in the silicified argillite for at least an inch beond the vein. At some time later the wall rock has been fractured and veined by calcite.

The veins have a typical banded appearance and the general sequence from the wallrock inwards is as follows:

1. Wallrock - silicified argillite with finely disseminated pyrite.

2. Massive white quartz up to 1/8 of an inch in width.

3. Arsenopyrite crystals indefinately oriented with fairly large inclusions of massive to crystalline pyrite. In places, however, number 3 is absent.

4. Arsenopyrite and quartz crystals forming a band 1/8 to 1/4 of an inch wide. In general, the arsenopyrite and quartz crystals are intergrown, with the length of the crystals perpendicular to the vein.

5. A large band 1 to 6 inches wide consisting mainly of fibrous zinckenite with tetrahedrite, scattered crystals of arsenopyrite and irregularly rounded blobs of sphalerite and calcite. In sections cut perpendicular and parallel to the vein, the fibrous zinckenite often appears as rosettes. The sphalerite may occur as bands of irregular masses in the zinckenite but it is noticeable that it does not occur at the arsenopyrite-zinckenite contact. The calcite occurs as subhedral crystals up to 1 inch in size. There are a few cavities that have been partially or wholly filled with quartz crystals as in the manner of a geode. This appears to be a second generation of quartz.

(b) Paragenesis

The writer did little work on the paragenesis of the sulphides as W. Lynott and P. Beley had previously worked with the ore and were concerned with the order of precipitation of the minerals and their occurrence. The writer, however, did come to the following conclusion that there was a fairly orderly precipitation of minerals in the following order with a noted break between the deposition of the high and low temperature minerals.

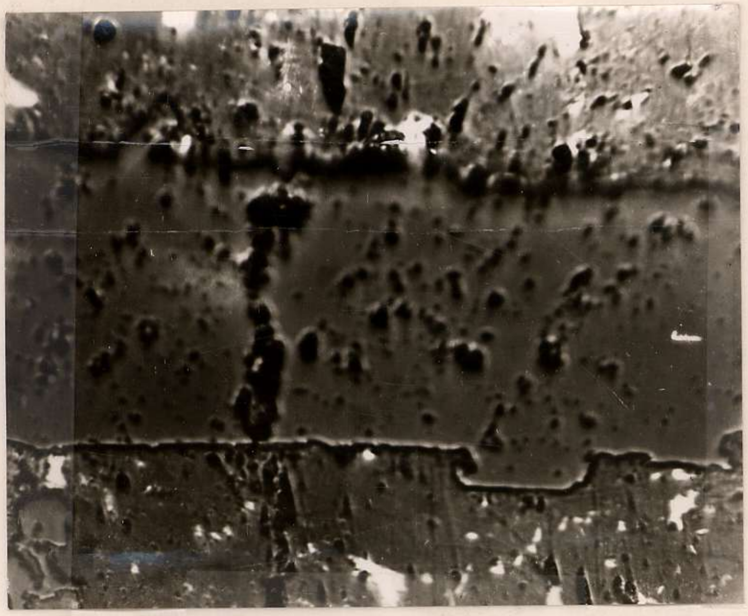
High Temperature	Arsenopyrite Quartz (1) Pyrite
Moderate to Low Temperature	Zinckenite Tetrahedrite Quartz (2) Shalerite and Chalcopyrite Calcite

The following photographs illustrate some of the age relations of the minerals.

No. 1

Quartz (1) veining arsenopyrite.

X 150



No. 2
Quartz (2) veining unetched zinckenite with inclusions of tetrahedrite
X 150

No. 3
Etched zinckenite, pseudo-morphous after arsenopyrite, enclosed in tetrahedrite
X 150

5. <u>Preparation of Specimens</u>

Specimens of ore were picked partially to show the age relations of the different sulphides but primarily to contain substantial amounts of zinckenite. The specimens were sawen with the diamond saw and then polished. As it is very difficult to distinguish between zinckenite and tetrahedite in the hand-specimen the microscope was used to pick out good areas of zinckenite. These areas were marked and the sections resawen. The selected chips then were mounted in bakelite, and hand polished.

Because of the relative softness of zinckenite and tetrahedrite in comparision with the associated minerals, quartz, arsenopyrite, and pyrite, considerable relief was evident, and the fibrous zinckenite was severely plucked. The sections were repolished with considerable care but it was found that the zinckenite could not be polished highly enough to bring out the details without causing it to pluck and relief to be shown at the quartz-zinckenite contacts. Super-polishing also was tried with indifferent success, as the zinckenite would not polish and small plucks were numerous.

6. Etching With Ordinary Reagents.

Mr. R. Thompson and the writer etched polished-sections containing known stibnite, plagionite, zinckenite and chalcostibite with the following results; table No. 1

Table No. 2 consists of Shorts' etch tests for the Lead-Antimony group of minerals and chalcostibite.

(a) Conclusions

Table No. 1 and more especially table No. 2 show that ordinary etching solutions are of little use in indentifying individual members of the Lead-Antimony group.

Mineral	$HgCl_2$	$FeCl_3$	KCN	KOH	HCl	HNO_3 1:1	Remarks
Chalcostibite Carbon Hill Section #1	Neg.	Neg.	light brown shows up scratches	Neg.	Neg.	Neg	
Stibnite Carbon Hill	Neg.	Neg.	Shows up scratches	Orange-red ppt. (Sb_2S_3)	Neg.	Differentially irid.	Multiple twinning
Plagionite Carbon Hill Section #8	Neg.	Neg.	Neg.	light brown rubs off. 2 minutes	light brown rubs off	Dark grey irid. at edges.	Some tiny blebs not etched by HNO_3. Are anisotropic - may be Chalcostibite
Zinckenite Poppoa	Neg.	Irid. rubs off	Neg.	slight irid. rubs of. 2 minutes	light brown rubs off.	Dark grey effervesces	Typically fibrous
Zinckenite Robson Group	Neg	Neg.	Neg.	slight irid. rubs off. 2 minutes	light brown rubs off	Dark grey with effervescence. Irid. at edge.	HCl reacts on calcite
Plagionite Hartz	Neg.	Neg.	Neg.	slight brown tarnish - rubs off. - 2 minutes	Negative to slight tarnish rubs off	Dark grey with effervescence Irid. at edge	

Name	Composition	Anisotrop.	Color	$HgCl_2$	$FeCl_3$	KCN	KOH	HCl	HNO_3
Zinckenite	PbS, Sb_2S_3	White to dark grey	Grey	Neg.	Neg.	Neg.	Irid.	Fumes Tarnish	Effervesces & darkens
Plagionite	$5PbS, 4Sb_2S_3$	Light to dark grey	White	Neg.	Neg.	Neg.	Grey to brown	Fumes tarnish some.	Effervesces & stains black
Jamesonite	$4PbS, FeS, 3Sb_2S_3$	Strong grey-brown	Galena white	Neg.	Neg.	Neg.	Irid.	Fumes tarnish	Tarnish irid. slow efferv.
Semseyite	$9PbS, 4Sb_2S_3$	Light to dark grey	Grey	Neg.	Neg.	Neg.	Irid.	Fumes tarnish some.	Effervesces & stains black
Boulangerite	$5PbS, 2Sb_2S_3$	White to dark grey	Galena white	Neg.	Neg.	Neg.	Neg.	Fumes tarnish	Effervesces & darkens
Meneghenite	$4PbS, Sb_2S_3$	Grey brown, blue	White	Neg.	Neg.	Neg.	Neg.	Fumes tarnish some	Effervesces & darkens
Geocronite	$5PbS, Sb_2S_3$	Brown-blue	Grey	Neg.	Neg.	Neg.	Neg.	Fumes tarnish	Effervesces & darkens
Chalcostibite	Cu_2S, Sb_2S_3	pink-grey	White	Neg.	Neg.	Brown	Neg.	Neg.	Fumes tarnish

7. Selective Iridescent Filming

The principle consists of forming on a polished surface a thin pellicle of a transparent substance, chemically related to the parent substratum and of definitely controlled thickness. The light striking the filmed surface is reflected partly from the top of the film and partly from the bottom of the film, with additional reflections within the film. The various reflections interfere, since they are out of step with reference to each other. The extent of the relative retardations between reflections is controlled principally by the thickness of the film, but also by several of the optical constants characteristic of the film and of the film-substratum interface. All this, however, would fail to bring about a variety of color if monochromatic light were used. With white light, however, rays of the various component wave lengths--violet, blue, green, yellow, orange and red--while retarded equally or substantially so in terms of actual distance, are retarded unequally as to number of wave lengths. This means that a situation may arise for some particular thickness of the film such that the reflected blue rays are in step while the reflected red rays are out of step, with the result that the surface will appear blue instead of white. Actually there is no dye or coloring matter in the film: the fundamental phenomenon that is utilized is that of production of interference colors, also known as Newtonian colors.

Theory indicates that the color perceived on a filmed surface changes as the film thickens, the normal sequence being as follows: first-order colors--white, pale yellow, yellow, orange-brown, brown-violet, purple, dark blue, pale blue, bluish or yellowish white (hiatus); then, second-order colors--yellow, red, violet, blue, green; then, fourth-order colors--dull yellow, dull red, dull slate blue, dull green, etc."

Gaudin recommends that a solution, made up of 1000 ml. from 25.15 grams of chromic trioxide, 200 m. 12 N.HCl and water, be used to etch such minerals as stibnite and chalcostibite.

8. Method of etching

The sections were sprayed with pure methyl alcohol and rubbed with kleenex to loosen any oils adhering to the surface. They were resprayed and allowed to dry. It should be noted that methyl alcohol should not be used to clean polished sections set demar as the alcohol causes the demar to become gummy.

Next, the sections were immersed in the standard hydrochloric acid-chromic trioxide bath for the required time. The sections should be aggitated in the bath as trapped air bubbles or bubbles arising from the reaction of the solution with carbonates in the section, are likely to interfere with fresh solution being in contact with the surface. The solution was stirred thoroughly just before each etch, as it was found that the results were not uniform if the solution was allowed to stand. The sections upon removal from the bath are quickly slushed in a large pan of cold water. The coldness of the water tends to slow down the chemical action and the large volume of water quickly dilutes the solution. The sections were allowed to dry and then lightly rubbed with kleenex.

The etch retained its colors for approximately six hours after which it tended to turn a dark grey color, the intensity of which varied directly with the time exposed. It was found that the solution retained its strength over several days but to insure a standard method of etching, no solution older than 24 hours was used.

9. <u>Test Number 1.</u>

Twelve polished-sections containing zinckenite from the Robson group were etched in a standard solution at 23'C. for 25 seconds each. The sections then were studied under the microscope and it was found that of the sulphide minerals present only the zinckenite was etched. It displayed colors ranging from orange to blue, with blue being the predominant color. Scattered throughout the apparently massive zinckenite were crystals that showed distinctly different colors. These crystals, however, were not all the same color.

Thus it was thought by the writer that if these crystals were other minerals in the lead-antimony group of sulphides that some information might be gained by re-etching the sections and noting the colors displayed by these minerals on a 5, 10, 15 second etch. This idea was founded, perhaps erroniously, on the bases that blue might be the end color reached by the etching; that is a mineral would etch yellow, orange, purple and then blue and would remain blue regardless of further etching. Previously it was found that the massive zinckenite after a 6 second etch was tan and after an 8 second etch was blue, and continued etching up to 2 minutes did not result in a difference in color.

10. Test Number 2

Thus test number 2 was run with polished-section number 7 noting a small area of zinckenite where etching had showed small differentially-etched crystals enclosed in a groundmass of zinckenite. The section was buffed between etches on a billiard cloth sprinkled with magnesium oxide and this was found to remove effectively the etch. After two buffings, however, it was necessary to repolish the sections. Test number 2 used the same standard solution at 23'C.

Time	Groundmass	Crystals
5 sec.	red, purple, blue	yellow
10 sec.	blue	orange
15 sec.	purple to blue	brown
20 sec.	blue	yellow-red
25 sec.	light blue	orange to purple

The table shows that regardless of the etching time there was a distinct, color difference between the groundmass and the crystals. At this point in the experiments, the writer thought the groundmass and crystals were very likely two different minerals.

In order to find the sequence of colors exhibited by the groundmass which turned blue in a very short time the writer next used a dilute solution composed of 12.5 gm. chromic trioxide, 100 ml. 12N HCl in a 750 ml. solution.

11. Test Number 3

Polished section number 7 was again etched for varying intervals of time up to $1\frac{1}{2}$ minutes with poor results. The longest etch of $1\frac{1}{2}$ minutes turned a small part of the groundmass blue whereas the remainder was unetched. There was no sequence of colors before the light-blue color appeared.

12. Test Number 4

In order that the etch colors shown by the crystals enclosed in the zinckenite groundmass in test number 2 might be associated with the etch colors of known minerals in the same series, Dr. Warren very kindly supplied sections of known Boulangerite and Meneghenite.

(a) Boulangerite

Each of the 3 sections of boulangerite were etched at 20'c for 10 seconds. The results are as follows:

Section 1. Crystals oriented with the length of the crystals exposed. Some crystals etched light yellow to blue whereas others were unetched.

Section 2. Crystals oriented so the section was parallel to the base of the crystal. The basal sections showed no etch.

Section 3. Crystals oriented at random. A few crystals etched light yellow but the majority remained unetched. A number of unetched crystals, however, showed small micro-crystal inclusions that etched blue. (Photograph No. 4). It is noteworthy and unexplainable that the etched portions photographed white whereas the unetched portions photographed grey. One explanation might be that the oxidized surface reflected the light and photographed, rather than the underlying minerals surface although it may readily be seen with the microscope.

No. 4
Boulangerite crystal, white portions represent etched parts of crystal

(b) Meneghenite

The sections were etched in a standard solution at 20'C. for 10 seconds.

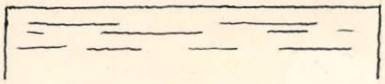
Section 1. Sections cut to expose crystal parallel to the base. The etched parts resulted in a number of colors blue, yellow and orange. The majority of the surface, however, was not etched. Where etched the colors did not blend into one another but appeared to have definate boundaries. (Photograph No. 5) Again the etched parts photographed white.

Section 2. Crystals oriented at random. The same etch effects as in section 1 were seen both on the longtitudinal and basal sections.

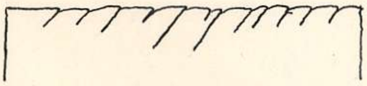
No. 5
White portions etched 3 distinct colors; blue yellow, orange

13. Conclusions

Test number 4 shows that pure minerals were either unetched or etched in different colors. This finding of course, is based on the fact that the minerals were pure, as shown by the X-ray powder photographs. It is logical, therefore, to conclude that the differences in etching were caused by the different orientations of the crystals. This phenomina might be expected in minerals with cleavage, as cleavage surfaces are more susceptible to reaction with the etching solution because of their increased surface due to incipient micro-cleavage cracks.



Cleavage Planes Parallel to the Surface



Cleavage Planes at Random

Further, that as a mineral may have several cleavages, the most prominent cleavage would be most readily attacked by the solution. Thus the amount of chemical action would depend on the orientation of the crystal. The amount of chemical action would determine, therefore, the thickness of the film which in turn controls the color displayed.

It is quite possible that Gaudin was not bothered with the orientation of the crystals in his work as most of his minerals were synthetic and in all probability were very poorly crystallized if not amorphous. Thus, it might be possible, having a complete set of amorphous minerals of the lead-antimony sulphides, to use these as color indicators. This would necessitate extracting pure unknown sulphides and by reheating and sudden cooling cause them to become amorphous. They could then be etched and compared with the standards. This procedure, however, would not be satisfactory unless the unknown sulphides were pure; and at present there is only two methods of assuring the purity of a mineral; namely X-ray powder photograph and assaying.

Thus, the writer concludes that Selective Iridescent Filming is of little use in determining the presence of different members of a family of lead-antimony minerals. Iridescent filming, however, has one important use and that is in etching minerals of different compositions but of like appearance. For example, of the Robson Group minerals, zinckenite was the only one that was etched by the standard hydrochloric acid-chromic trioxide solution. This was very helpful in distinguishing zinckenite from galena and tetrahedrite.

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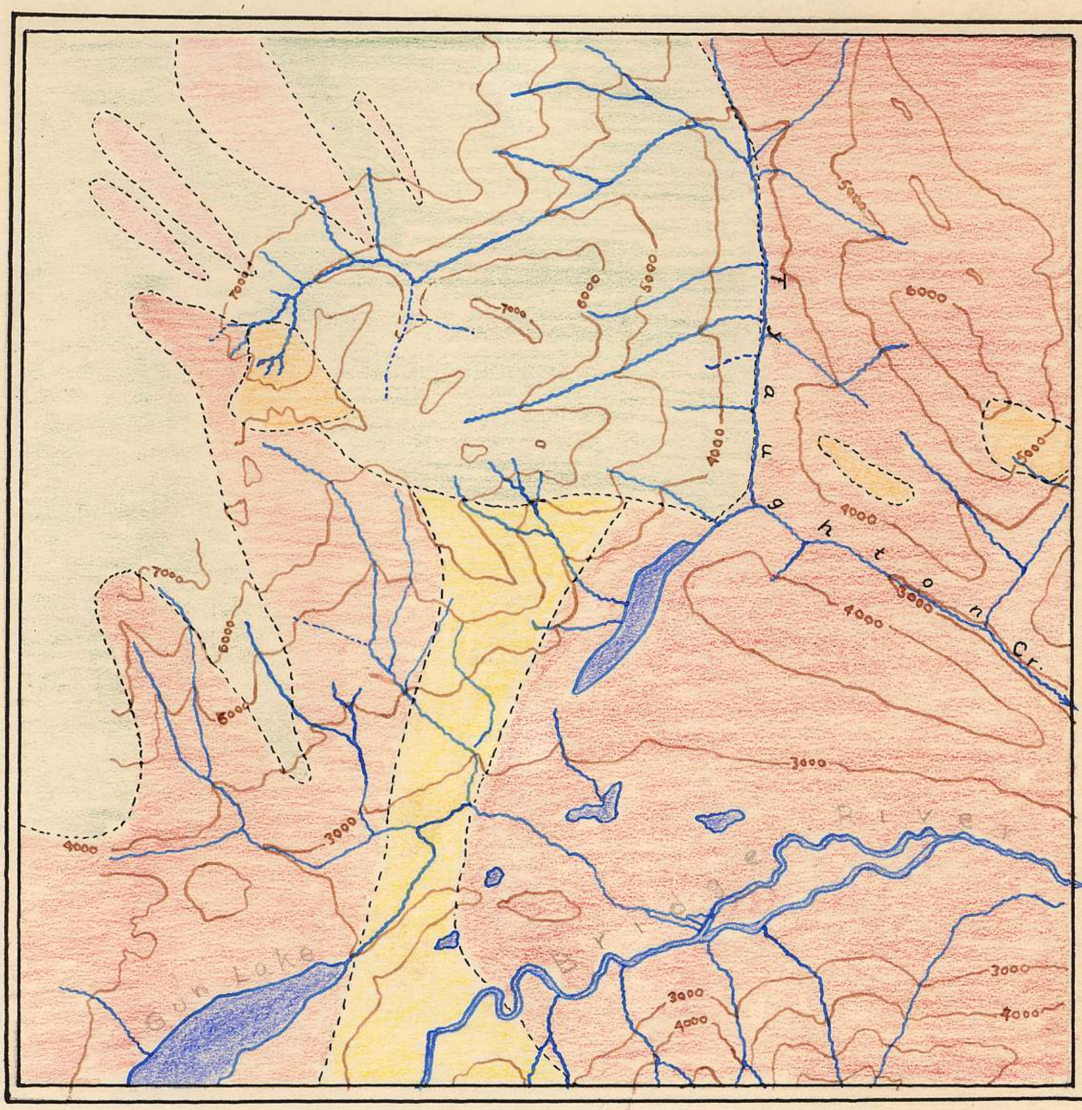
Tyaughton Cr.
Bridge River
Gun Lake