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by Sarah M. Malcolmson for
[Full Name(s)]

Undergraduate course number 4K06 at McMaster
University under the supervision/direction of Dr. J. R. Kramer

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Silver Substitution into Common Metal Sulphides from Cobalt, Ontario

Silver Substitution into Common Metal Sulphides from Cobalt, Ontario

by

Sarah Malcolmson

A Thesis

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in Partial Fulfilment of the Requirements for the
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AUTHOR: Sarah Malcolmson

SUPERVISOR: Dr. J. R. Kramer

Abstract

The occurrence of silver in galena, chalcopyrite, sphalerite, and pyrite as well as tailings from Cart Lake, Cobalt Ontario were investigated to compare with the undetectable ($<10^{-11}$ g/g) Ag found in runoff water from the Cobalt area.

Silver was detected at very low levels: 0.012 wt% \pm 0.009 wt%, 0.015 wt% \pm 0.01 wt%, and 0.0062 wt% \pm 0.02 wt% for pyrite, galena and chalcopyrite, respectively.

Attempts to characterize the mineralogical associations of silver were not successful. The silver sequence of pyrite > galena > chalcopyrite is contrary to results from other studies. This may be due to the maximum thermal stabilities of the minerals in relation to the ions available for replacement.

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1. INTRODUCTION

The concentration of silver in the ecosystem has become an environmental concern. Although once thought to be a non-accumulative, non-toxic metal, a recent study by Luoma (1994) has shown that even in trace amounts, silver can accumulate in benthic organisms. Currently, research is focusing on the speciation and solid forms of silver in the environment. This information will be used in defining the toxicity and eventual fate of silver.

Silver, in conjunction with sulphur, can form both organic and inorganic compounds. Within the inorganic realm silver sulphides are extremely insoluble and the concentration of silver ions in the aquatic environment is low. Sources of silver can be both natural and anthropogenic, although the latter appear to dominate (Benjamin and Honeyman, 1992). A study by Bruland *et al.* (1974) indicates that, in relation to a century ago, present anthropogenic emissions of silver exceed natural rates. The environment affected by the disposal of industrial waste is extremely complex. In order to fully comprehend the effects of silver disposal it is first important to understand the system itself. Within waste systems it is not known which association predominates, organic or inorganic silver sulphides. Due to the low solubility of both inorganic and organo-silver sulphides either of these associations is possible. To ascertain which type of sulphide complex predominates it is important to characterize organo-silver sulphide and inorganic silver sulphide complexation.

The inorganic properties of silver are important in understanding the eventual fate of silver emissions. The release of silver through weathering is difficult due to the

insolubility of silver sulphide minerals, the most common silver containing minerals.

This study considers the inorganic associations of silver with sulphides only.

The ability to liberate silver from sulphide minerals depends not only on the expected solubility of the mineral but also its stability. General characteristics, solubilities, and stabilities of common silver containing sulphides, i.e. acanthite (Ag_2S), are well known (Sugaki, Scott, Hayashi, and Kitakaze, 1987, Goates, Cole, Gray, and Faux, 1951, and Ribbe, 1974). The difficulty in characterising this system arises from a poor understanding of the effects of silver substitution on common metal sulphides, i.e., galena (PbS). Although substitution of silver for Fe, Cu, Zn, or Pb in metal sulphides is documented, (Viets, Hopkins, and Miller, 1992, Fleischer, 1955) there is little understanding of its association with these metals and of its effect upon the unit cell. The possible destabilisation of the unit cell of common metal sulphides through the substitution of silver could provide a means for silver to enter the environment. To characterize changes to the unit cell, knowledge of the associations of silver with metals from common metal sulphides must be gathered.

This thesis is concerned with the characterisations of silver substitution within four major sulphides: galena (PbS), chalcopyrite (CuFeS_2), sphalerite (ZnS), and pyrite (FeS_2). It is intended to provide an understanding of how substitution of silver for common metals within sulphides may occur. With this knowledge in hand it may be possible to hypothesize which substitutions may change, and even destabilise, the unit cell.

2. MINERALOGY OF SILVER

2.1 The Element

Silver is labelled a Group 1b transition metal, meaning it has a single 5 *s* electron beyond a completely filled 4 *d* shell, but this occurs only in its monovalent state. When the element is divalent or trivalent the *d*-subshell is incomplete and therefore behave more like transition metals (Steele, 1966). It is classified as a B-type metal cation (Stumm and Morgan, 1981), meaning, low electronegativity with highly polarisable soft spheres. B-type metals preferentially form bonds with sulphur creating insoluble sulphides. Silver preferentially bonds with sulphur as seen by its incredibly low K_{sp} value of $10^{-53.4}$ (Licht, 1988). This bonding is due to covalent and ionic bonding (Fleischer, 1955, Stumm and Morgan, 1981). The covalent nature of most sulphides dictates that substitution of silver for other metals be based upon its covalent radii of 1.445 Å (Pearson, 1972, pg 151). An exception to this rule is lead. This element is ionically bound to sulphur in galena and therefore substitution is based on the ionic radii of 1.26 Å for Ag 1.20 Å for Pb (Fleischer, 1955, pg 973).

Elemental silver can occur in the +1, +2, and +3 oxidation states, as described above, but most commonly appears in the +1 form. The coordination of Ag^{+1} is variable but most commonly occurs as 2 or 4, (Cotton and Wilkinson, 1966). Cotton and Wilkinson (1966) state that the reasoning for the 2 (most common) and 4 (less common) coordination is that Ag^{+1} is sensitive to the nature of the ligand with which it bonds. Cotton and Wilkinson (1966) also note that Ag^{+1} predominantly occurs in the linear, two fold coordination. This coordination is due to a small energy difference

between the 4 *d* and 5 *s* shells which form two linear hybridized orbitals. This concept is pictorially represented in figure 1. A central area of high electron density forces the ligands into the areas above and below the ring. Two hybrid orbitals for the formation of linear covalent bonds occur when mixing of the $\psi_{d_{z^2}}$ with the p_z orbital.

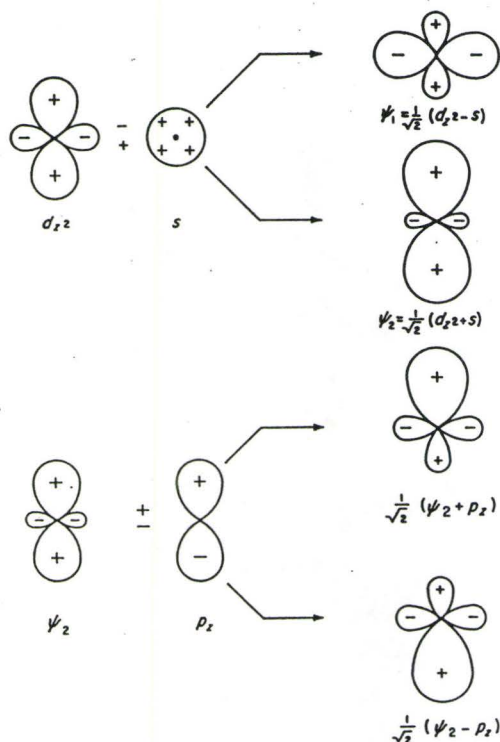


Figure 1. The hybrid orbitals: top from d_{z^2} and *s* orbitals, bottom from $\psi_{d_{z^2}}$ and p_z orbitals. The *z* axis is vertical. (From Cotton and Wilkinson, 1966).

The complexity of silver coordination becomes apparent upon examination of the silver-sulphide association.

2.2 Sulphides

2.2.1 Silver Sulphides

Silver sulphide occurs in many different forms the simplest of which is Ag_2S . The Ag-S system contains three polymorphs, acanthite, argentite, and an amorphous form for which the maximum thermal stabilities are 177 °C, 586-622 °C, and 838 °C respectively (Taylor, 1970). The low temperature of acanthite produces a cubic structure whereas the elevated temperature of argentite creates a monoclinic structure.

There are many well documented occurrences of silver within sulphides (Hawkey, and Nichol, 1961, Fleischer, 1955). This can occur in the expected form of silver sulphides or silver metal sulphides or it may be due to substitution or diffusion into the mineral (Slinkina, Zhukovskii, and Zhukovskaya, 1985 (a) and (b)). The sulphosalts are a group of sulphides with the general formula $[\text{M}_1 \text{M}_2]_n \text{R}_m \text{S}_n$. The bonding for sulphosalts between the metal and the ligand is primarily covalent. The M_1 positions are predominantly taken by Ag, Cu, and Hg at 9 percent, Ti at 12%, and Zn at 18%. At the M_2 site Pb, Ti, and He primarily occur (Kostov, and Minceva-Stefanova, 1982). This general formula is well represented with respect to silver-metal-sulphides and therefore can be considered an expected source of silver ions.

Within the metal sulphides the relationship between silver and its respective metal- sulphides is complex. Iron, copper, and lead-silver sulphides present expected stoichiometric ranges:

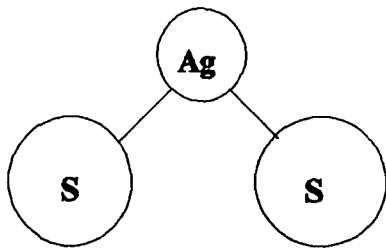
Ag-Fe-S from AgFe_2S_3 to $\text{Ag}_2\text{Fe}_5\text{S}_8$

Ag-Cu-S from Cu/Ag of 0.29 to >1

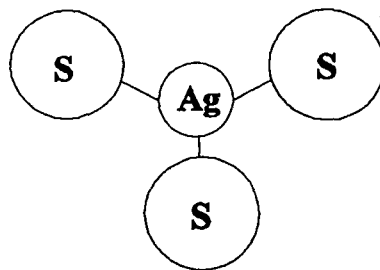
Ag-Pb-S from variable stoichiometry due to solid solution

which can be used as a guide when investigating silver substitution (Craig, and Scott, 1974). The coordination of silver is extremely complicated due to its variable oxidation states of 1^+ , 2^+ , and 3^+ . A generalisation of the associations of silver leads to three expected coordinations within sulphides: 2-Fold, Triangular, and Distorted Triangular .

2-Fold



Triangular



Distorted Triangular

(modified tetrahedral)

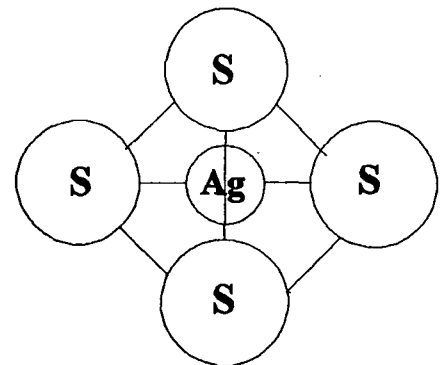


Figure 2. Coordination of Ag with sulphur.

These expected coordinations can be used to create a simplistic hypothesis of the type of structure to expect after silver substitution.

2.2.2 Galena

Galena is a lead sulphide, PbS . Its structure is similar to rock salt excepting that lead is surrounded by six sulphur and each S by six Pb (Deer, Howie, and Zussman, 1992)(Fig. 3).

Galena

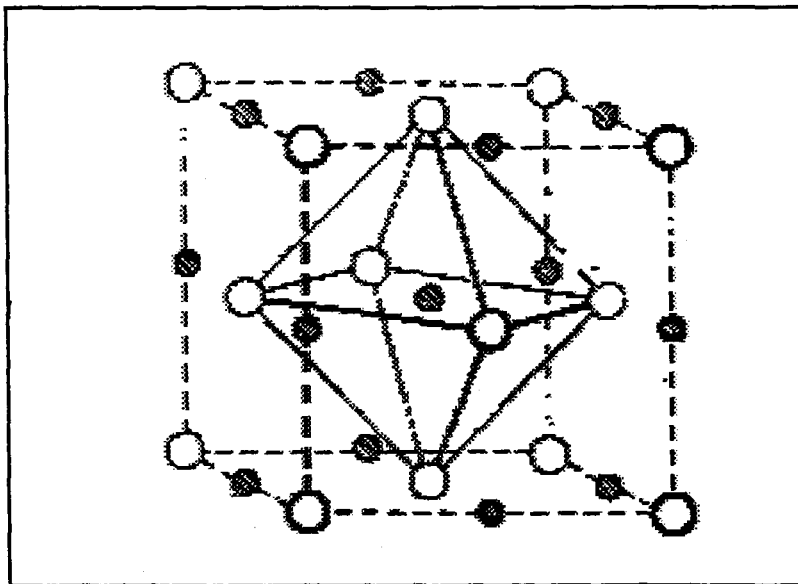
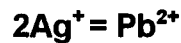


Figure 3. Structure of Galena. Hollow circles are Pb, solid circles are S.

Unlike most sulphides, galena is characterized by ionic bonding and therefore any substitution into the structure must be based on ionic radii. Since the ionic radii of Pb (1.26 Å) and Ag (1.20 Å) are close substitution is feasible (Fleischer, 1955, pg 973).

The substitution of Ag^+ for Pb^{2+} is expected to be in the form of:



Sharp and Buseck (1993) revealed that the simple substitution of silver for Pb is limited to 0.4 mol.% Ag_2S at 700 °C. This quantity decreases as temperature decreases due to the requirement that half of the Ag be placed in the interstitial sites. This study also revealed an increase in Ag^+ substitution for Pb^{2+} when coupled with Bi^{3+} or Sb^{3+} to maintain the charge balance. Upon substitution of silver for Pb displacement of S atoms from the ideal position may exceed 1Å but only 3 or 4 S atoms may be displaced. One of the greatest problems noted by this experiment is difficulty in distinguishing between silver located within the solid solution and that which is contained in inclusions. Most inclusions of diaphorite ($\text{Pb}_2\text{Ag}_3\text{Sb}_3\text{S}_8$) (Fig. 4) found by Sharp et al (1993) are less than 1 µm in diameter and none greater than 20 nm were found. Raster-beam analysis was performed on the samples and the silver concentration was found by subtracting the concentration in the inclusions from the total mineral silver concentration.

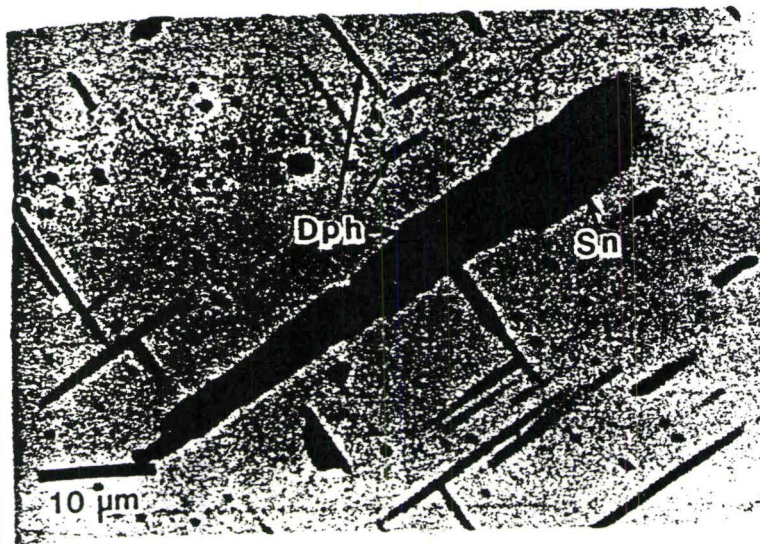


Figure 4. Inclusions of Diaphorite in Galena.

Silver concentrations that were less than 0.5 wt. % were considered in the solid solution.

Within the Cobalt-Gowganda region galena is a common metal sulphide. Microprobe analysis of galena samples from this region have shown that there is Ag within the structure. The silver is available in trace amounts only and therefore characterisation of the silver is difficult (Petruk *et al.*, 1971).

Based on the probability that silver will substitute into galena for Pb and the generalised coordinations for silver within sulphides the suggested coordination is distorted triangular (Wuensch, 1971 (a) and (b)).

2.2.3 Chalcopyrite

Chalcopyrite is a Cu-Fe-sulphide, CuFeS_2 . The structure is a superstructure of sphalerite (Deer *et al.*, 1992, and Pearson, 1972) where the Zn is replaced by Cu and Fe and the S positioning remains the same. The bonding within chalcopyrite is controversial because of conflicting information. The Cu-S and Fe-S interatomic distances dictate that the bonding is ionic whereas the sp^3 hybridization indicates strong covalent bonding (Kostov and Minceva-Stefanova, 1982). Since there is no clear answer to this debate the bonding will be considered a combination of the two. As seen in Figure 5 each metal atom is coordinated by a tetrahedron of sulphur creating the cubic closed packed system.

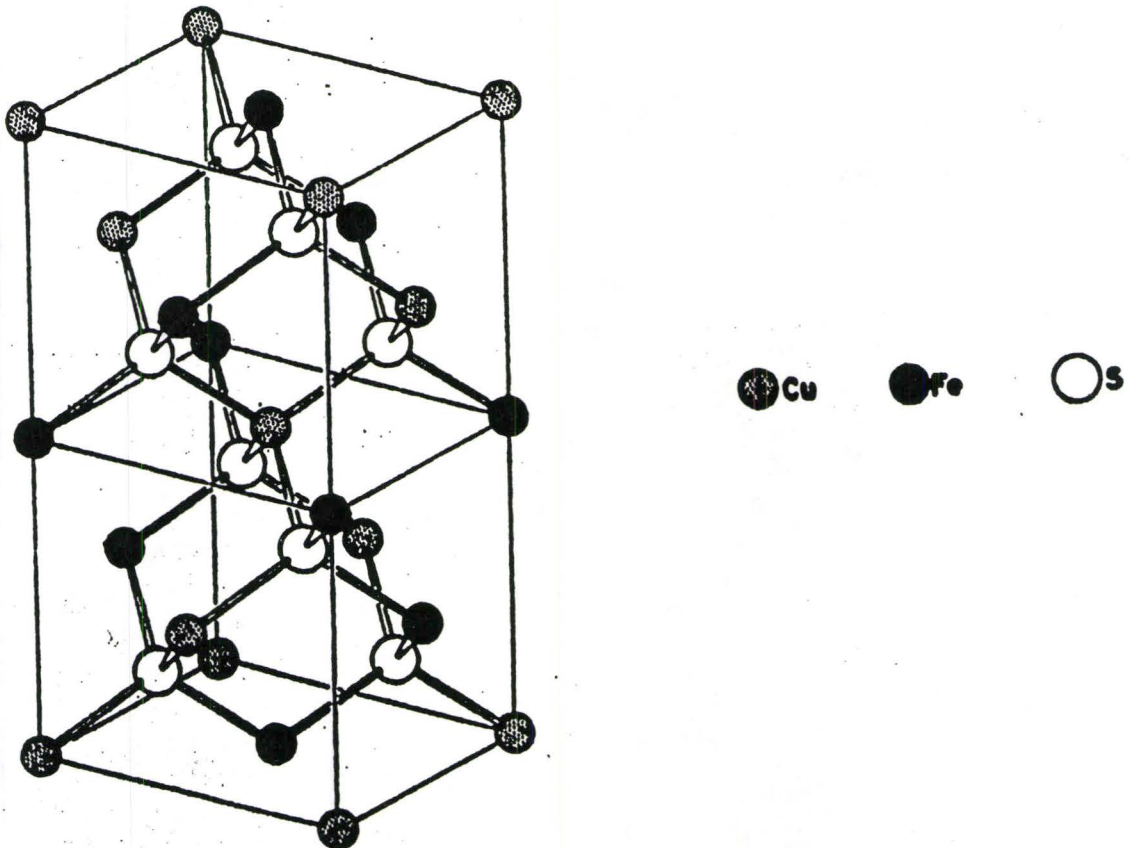


Figure 5. Structure of Chalcopyrite.

The superstructure is very open and can accept additional metal ions. Upon addition to the supercell the chalcopyrite can change from cubic to tetragonal or orthorhombic proving that the cell is relatively sturdy (Deer *et al.*, 1992).

Within the Cobalt-Gowganda area chalcopyrite is one of the most common sulphides but no significant levels of impurities have been found, including silver (Petruk *et al.*, 1971). Although no silver was found in these samples this fact does not negate its existence within the chalcopyrite solid solution. Harris, Cabri, and Nobling, (1984) and Hawley and Nichol, (1961) show that silver is contained within the solid solution of chalcopyrite even though the covalent radii of Ag^{+1} and Cu^{+1} are relatively different, 1.445 Å and 1.273 Å respectively (Pearson, 1972). There may be some dynamic between the radius and charge of Ag^{+} and Cu^{+} to make substitution feasible. The rapid tarnish effect explained by Harris *et al.* (1984) is said to indicate silver within chalcopyrite solid solution but this fact has not been fully documented. The rapid tarnishing of the surface of chalcopyrite does suggest the diffusion of silver onto the mineral. Electron- and Proton- Microprobe analysis done by Harris *et al.* (1984) did find that there was silver contained within the chalcopyrite solid solution.

There is no suggested coordination for silver substituted into the chalcopyrite structure. Based on the placement of Cu within the unit cell the hypothesised coordination for the silver ion would be 2-Fold.

2.2.4 Sphalerite

Sphalerite is a low temperature face-centred cubic Zn sulphide, ZnS . The

sphalerite, as seen in Figure 6, is used as a basis for many monosulphides and shows that each sulphur is coordinated by four zincs.

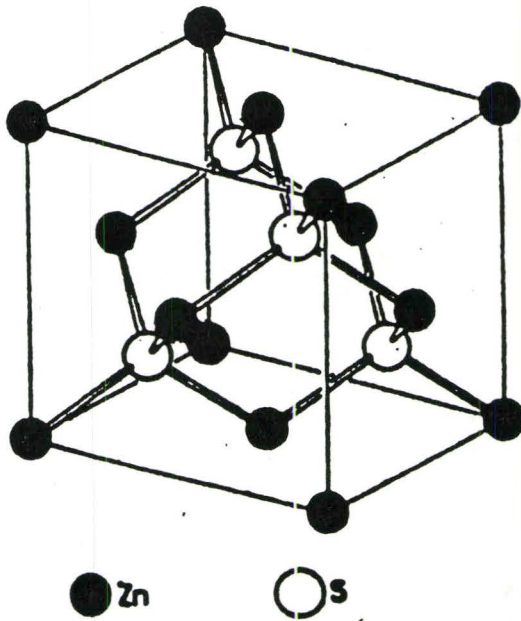


Figure 6. The Structure of Sphalerite.

At an inversion temperature of 1020 °C sphalerite is thought to convert to its polytype wurtzite, but there is much debate on this point (Craig and Scott, 1974). The debate centres around the non-stoichiometry of sphalerite, meaning its composition deviates from proper proportions (Craig and Scott, 1974). Early studies on the structure of sphalerite concluded that there is a high-sulphur form (sphalerite) and a low-sulphur form (wurtzite). Further study on this topic revealed that under high Zn pressure, zinc

entered the lattice creating the hexagonal polytype known as wurtzite (Fig. 7).

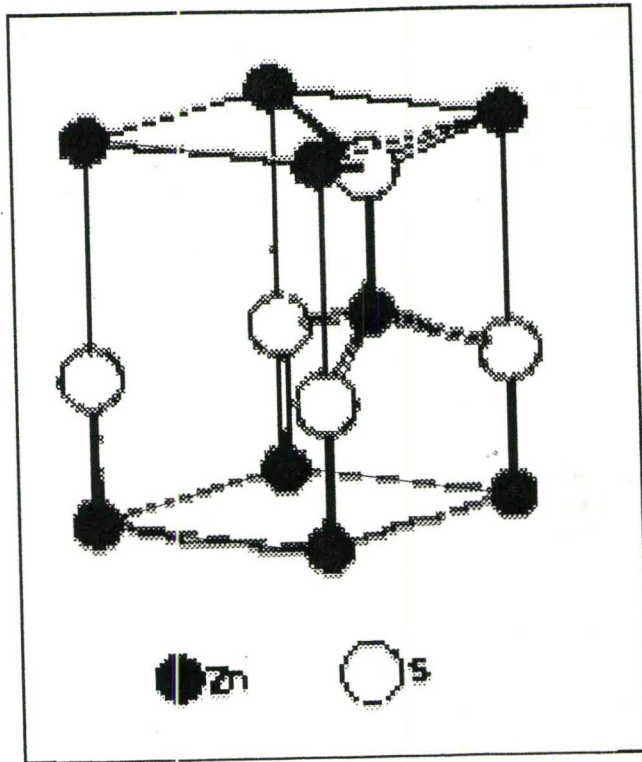


Figure 7. The Structure of Wurtzite.

The bonding of ZnS is predominantly covalent and therefore any substitution into the cell would depend on covalent radii. The covalent radii of Ag and Zn are 1.445 Å and 1.394 Å respectively (Pearson, 1972) making substitution feasible. Silver that has substituted for Zn will have a similar non-stoichiometric behaviour that may increase the feasibility of this substitution, although the deviation is unlikely to be greater than one atomic percent (Craig and Scott, 1974).

Sphalerite is a common mineral in the Cobalt-Gowganda region but there is no

documented evidence of silver that could be found. In studies by Fleischer (1955) and Viets *et al.* (1992) silver is reported within ZnS although there is discussion as to the form of the Ag. Fleischer (1955) states that the silver is probably due to impurities, i.e., galena. Further to this point, Fleischer (1955) also states that any concentration of silver in pure sphalerite is probably very small.

Research by Viets *et al.* (1992) indicates that the concentration of silver within sphalerite may be due to its stage of formation. Sphalerite, from the Viburnum Trend, formed in the main stage event was found to contain 117 times the amount of silver reported for ZnS formed in the later cubic galena-stage sphalerite. From this research it may be possible to predict the expected silver concentration within the sphalerite of the Cobalt-Gowganda area based on the stage in which it was formed.

Available research regarding the concentration of silver within sphalerite has not produced a characterization for the substitution of Ag for Zn. As in high temperature metal doped wurtzite, high temperature silver doping may cause deviation from normal cubic coordination to hexagonal coordination. This type of structure can be found in the previously noted main stage sphalerite. Based on the coordination of Zn in this structure it is most probable that the Ag-S coordination will be distorted triangular (modified tetrahedron). Within the previously noted later cubic galena-stage sphalerite the Ag-S coordination is more likely to be two fold, more indicative of the cubic, low temperature sphalerite.

2.2.5 Pyrite

Pyrite is an iron disulphide, FeS_2 , in a face centred cubic structure.

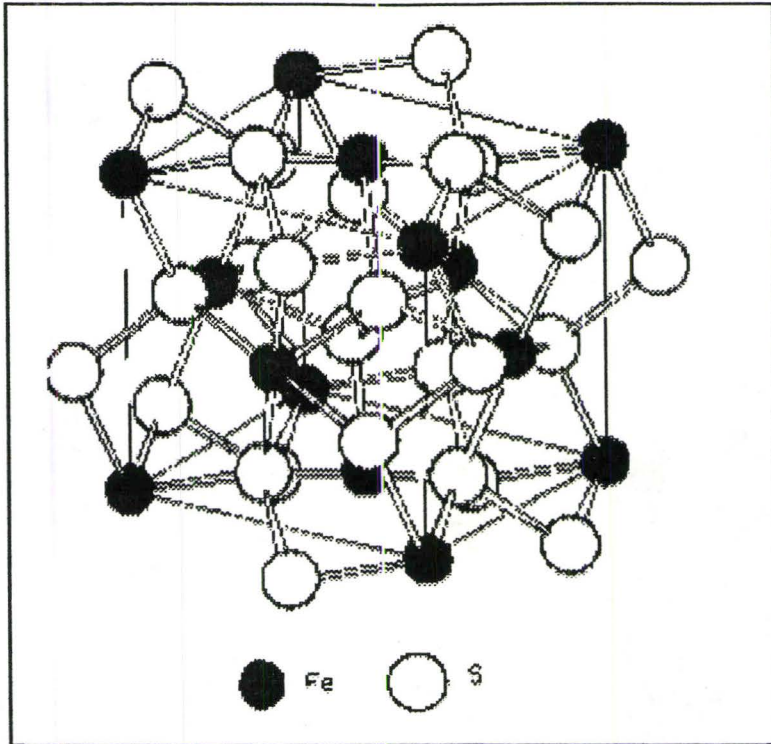


Figure 8. The Structure of Pyrite.

The base structure of the mineral is hypothesised to be three-dimensional networks of interlinked Fe and S_2 (Taylor, 1980). This allows for the octahedral coordination of iron by sulphur. The structure of pyrite is very densely packed in comparison to other sulphides which may inhibit substitution. There is a very large difference between the radius size and charge of silver and iron. This fact, together with the dense packing of the structure, may make substitution of Ag for Fe totally unfeasible.

The interaction of pyrite with Ag is a relatively common topic within the sulphides literature. Several conclusive studies over the last forty years have come to essentially

the same conclusion: there is very little, if any silver within the pyrite solid solution. In a study by Taylor (1970) it was found that the solubility of Ag in FeS₂ is probably less than 0.1 at. %. Taylor (1970) also stated that at 600 °C the solubility of Ag in pyrite was so low that the amount of silver in solid solution would not even affect the cell dimensions. Hawley and Nichol (1961) attempted to show a variation in silver concentration based on formation temperature, the higher the formation temperature the lower the silver content. Although this appears to be backed by Taylor (1970) neither study was truly able to account for either trace impurities or under what conditions the silver was emplaced. A more recent study by Buckley, Wouterlood, and Wood (1989) found that when pyrite was immersed in a sulphuric acid solution containing silver ions, silver sulphide was formed, not Ag-Fe-S.

Pyrite is one of the most common sulphides within the Cobalt-Gowganda sulphides. Microprobe analysis done on pyrite from this area produced no detectable level of Ag (Petruk *et al.*, 1971). Based on the conclusions reached by previous researchers, this may indicate that the pyrite was formed at very high temperatures. Because there is such a small concentration of silver within the solid solution characterization of the substitution of Ag was not available. Based on the size differences of the covalent radii of Ag and Fe, 1.445 Å and 1.274 Å respectively (Pearson, 1972), it is apparent that any large influx of Ag in to pyrite would cause massive destabilisation of the structure.

3. EXPERIMENTAL PROCEDURE

In order to find sulphide samples that were more likely to contain silver, samples from a known high silver concentration area were used in the analysis. Cobalt, Ontario is considered the silver capital of the world and has produced large amounts of silver through mining since the 1920's. Samples chosen from this area were from a silver mine tailings pond at Cart Lake and a bulk conglomerate from Drummond mine.

3.1 Description

3.1.1. Tailings

The tailings sample was provided by Dr. J. R. Kramer from fieldwork done during the summer months. The sample was gathered in bulk form in a large plastic container and stored in the laboratory until analysis could take place. The tailings used were extremely fine grained (62 to 88 μm). They contained a high proportion of Fe-rich chlorite (30%) and a small proportion opaques (2%).

3.1.2. Conglomerate

The conglomerate was provided by the Head Geologist at Cobalt Ontario. It contained large (0.5 cm to 1.5 cm) and small (< 0.5) sulphide mineral grains. The minerals sampled were, galena, chalcopyrite, sphalerite, and pyrite.

3.2 Preparation

3.2.1. Separation techniques (tailings only)

Two different modes of separation were used to attempt to remove the sulphides from the tailings: visual separation and heavy liquid separation.

3.2.1.1. Visual Separation

Visual separation was attempted using a Leitz Laborlux 11 POL light and reflected light microscope. Several problems occurred using this form of separation. Due to the small size of the grains visual separation was almost impossible. Further to the separation of the dark minerals from the sample it was found that it was almost impossible to differentiate between the Fe-rich chlorite and the sulphides present. This method of separation was unfeasible and therefore discontinued.

3.2.1.2. Heavy Liquid Separation

Heavy liquid separation using Na- polytungstate and centrifuging in an I.E.C International was done in four different manners:

- a) with large centrifuge tubes
- b) with small centrifuge tubes
- c) without acid wash, small tubes
- d) with 0.1M nitric acid wash, small tubes

The Na-polytungstate was prepared from a crystal form using Milli-Q water. The

solution was heated until a light crust formed on top. The solution required continuously stirring to ensure that it did not crystallize. As the solution becomes thicker random checks on the density were done using a piece of tooth enamel (density 2.95 g/l). The solution was heated until the tooth began to float in the liquid and then for approximately one half hour after this point. The density was known to approach 3.1 g/l when the liquid continuously formed crystals on its surface.

Large centrifuge tubes were too large for the amount of sulphides recovered by the process. These tubes also did not have a bottom recovery outlet and therefore recovered grains had to be drained from the top leading to contamination of the sample. Smaller centrifuge tubes provided an outlet for the recovered grains and required less fluid and were therefore more feasible.

Several problems occurred during the centrifuge process due to the large proportion of siliceous and calcareous material. To remove the calcareous material a 0.1 M nitric acid wash was prepared and the sample was washed before centrifuging. The sample was rinsed five times in Milli-Q water so no residual acid remained on the tailings. To ensure that the washing of the grains did not reduce the density of the fluid by increasing the water content, the sample was then placed in a Fisher Isotemp oven at 60 °C until dry. This form of preparation was discontinued due to possible removal of some sulphides by the acid.

The process was extremely time consuming for the material recovered and several problems occurred throughout these methods of separation. The large amount of surface tension produced by the liquid made it very difficult to centrifuge the small

sulphides from the larger silicates and calcite grains. Further to these problems, the maximum fluid density was 3.1 g/l whereas the maximum density for the Fe-rich chlorite was 3.3 g/l and for apatite was 3.35 g/l. Most of the resultant grains were Fe-rich chlorite and apatite. Since only 2 percent of the original sample appeared to be sulphides the probability of retaining these grains after all of the problems with the preparation method are considered is minimal.

3.2.2. Preparation of Bulk Conglomerate

The bulk conglomerate was provided in large samples (larger than hand samples) and therefore needed to be broken into smaller pieces. The large rock sample was cut into smaller rock fragments to allow for better access to the grains.

3.3. Preparation for Analysis

Two different forms of analysis were used to deduce the Ag concentration within the samples: Scanning Transmitted Electron Microscopy and X-ray Fluorescence.

3.3.1. Preparation for S.T.E.M.

Both forms of samples were prepared in a similar fashion, which entailed mounting on a copper S.T.E.M. plate and carbon coating.

1. Tailings

The centrifuged grains were filtered and then washed five times in Milli-Q water and dried at 60 °C, placed on copper mount and carbon coated.

2. Conglomerate

A specified area of the rocks were cut into $\frac{1}{2}$ cm x $\frac{1}{2}$ cm x $\frac{1}{2}$ mm (h.w.d.) samples and polished. The finished samples placed on copper S.T.E.M. mount and carbon coated.

3.3.2. Preparation for XRF

The conglomerate was the only sample analyzed by XRF. Larger minerals needed to be broken into small pieces by hand using a blunt hammer. The small particles, of a known weight, were dispersed onto a filter paper for analysis.

4. ANALYSIS

4.1. S.T.E.M. in association with Elemental Analysis

Samples from both the tailings and the bulk conglomerate were analyzed on a Scanning Transmitted Electron Microscope, the Japan Electron Optics LTD. 1200 EXII. The elemental analysis that this tool provides is qualitative only and therefore no actual elemental counts are provided.

There are two basic types of scans S.T.E.M. provides; the point scan and raster mapping. These scans allow for varying degrees of accuracy. The point scan allows for analysis of a point on the sample increasing the sensitivity of the equipment. Raster mapping provides a sweeping analysis of a portion of the sample. Although this increases sampling area, it decreases sensitivity.

4.2. X-Ray Fluorescence

X-ray Fluorescence was done by a Philips PW1480/10 X-Ray Fluorescence Spectrometer that provides a unquant analysis. The analysis provides quantitative data to parts per million and its error is based on statistical unquant analysis of running conditions seen. This provides a useful form of analysis for low concentration analysis.

4.3. ICP-Mass Spectrometry

The silver within the tailings was below the detection limit for XRF (approx. 10 ppm). Silver in the tailings was analyzed by ICPMS after microwave digestion for four hours using aqua regia in Teflon bombs.

5. RESULTS

5.1. S.T.E.M. Analysis

5.1.1. Tailings

Numerous attempts were made to find sulphides within the samples, but none were successful. Figure 9 gives a pictorial representation of the types of grains recovered from the centrifuging process.

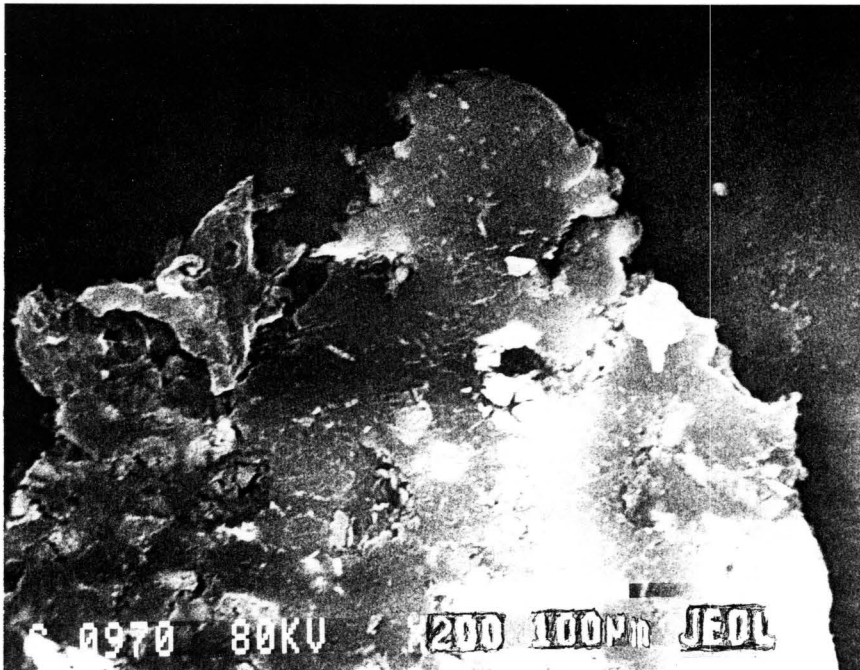


Figure 9. S.T.E.M. picture of tailings grain. Scale is provided on the picture.

When elemental analysis was performed on the samples, the elements shown to exist suggest Fe-rich chlorite and possibly chloro-Apatite (density 3.3-3.35 g/l) only. The graph depicted in figure 10 shows a high count on Fe, Cl, Al, Si, and copper.

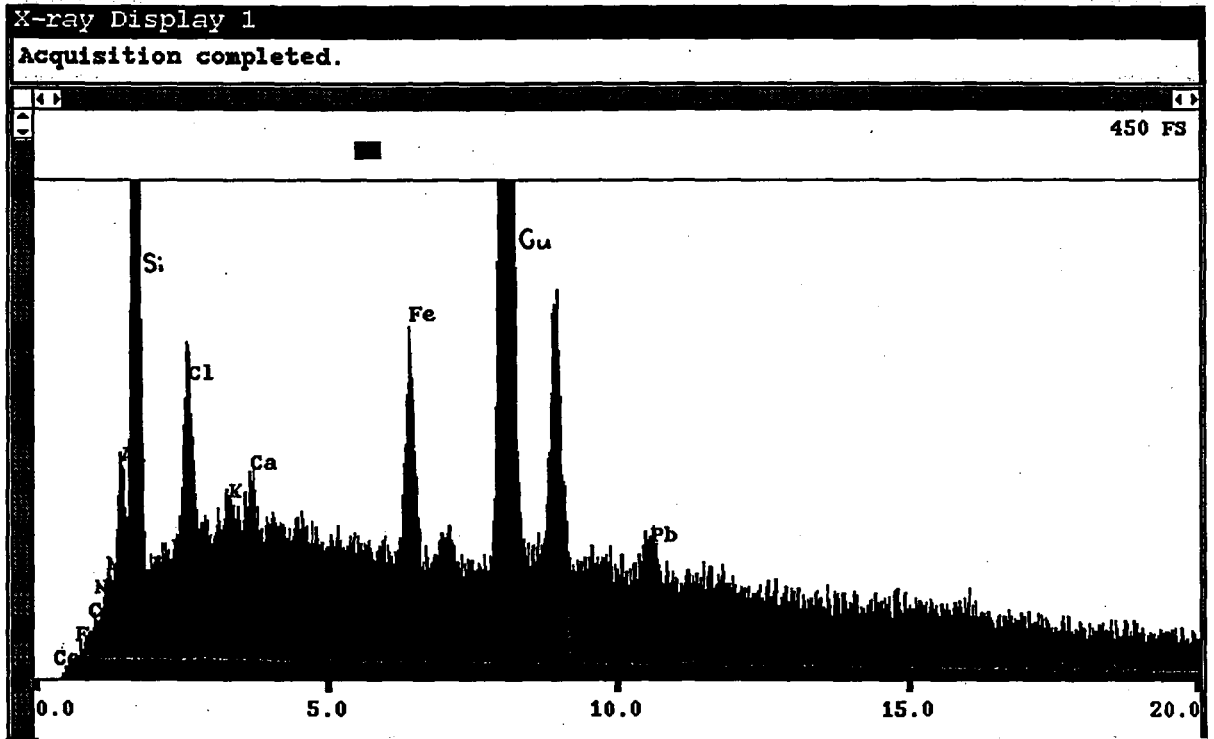


Figure 10. Graphical representation of qualitative analysis of tailings grain.

The Fe probably occurs in Fe-rich chlorite and the Cl is most likely due to Apatite. Both minerals are expected in the Cobalt-Gowganda region within the rock types that these samples would have been taken. A high Si count indicates that the separation

technique used was less successful than hoped as large concentrations of silicates were left in the sample. The high concentration of Cu in the sample may be due to dust from copper S.T.E.M. mount that can contaminate the sample.

5.1.2. Conglomerate

As noted in figures 11 through 14 the elemental analysis gives a clear picture of sulphides being sampled in both a graphical and pictorial manner. Based on the S.T.E.M. analysis the samples chosen were good examples of chalcopyrite, galena, and pyrite. Within the mineral sampled, in both point analysis and raster analysis, no Ag was found within the detection limit ($> 0.1\%$). This may be due to a lack of any concentration of silver or that the concentration was trace only ($< 0.1\%$).

Although sphalerite was expected in the samples no clear representative of sphalerite could be found. Areas within the samples did contain Zn but there was no sample that clearly showed sphalerite. Within the areas that did contain Zn no Ag was found. Samples used in the S.T.E.M. analysis could not be used for the XRF analysis due to their small size and adhesion to the copper S.T.E.M. mount.

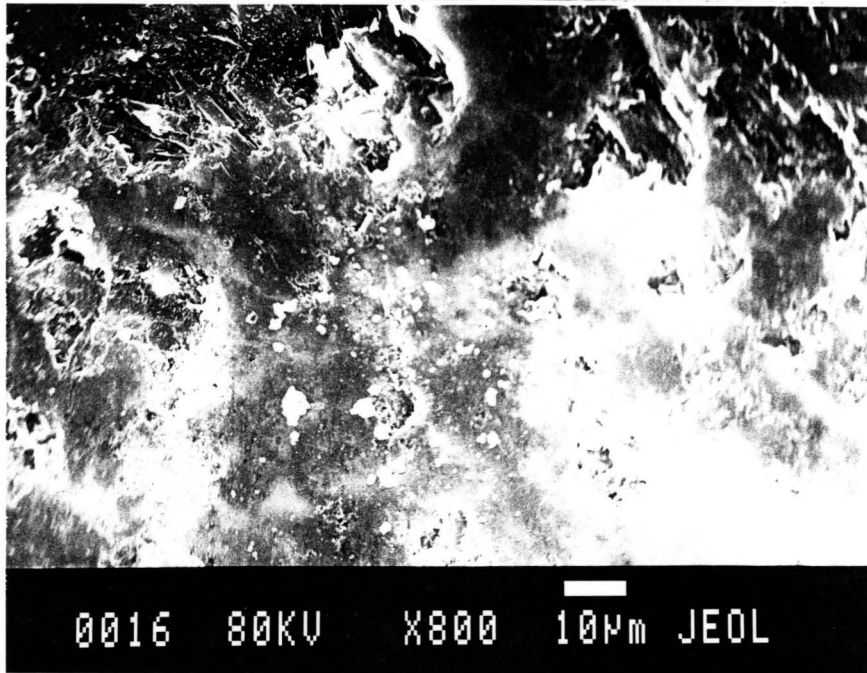
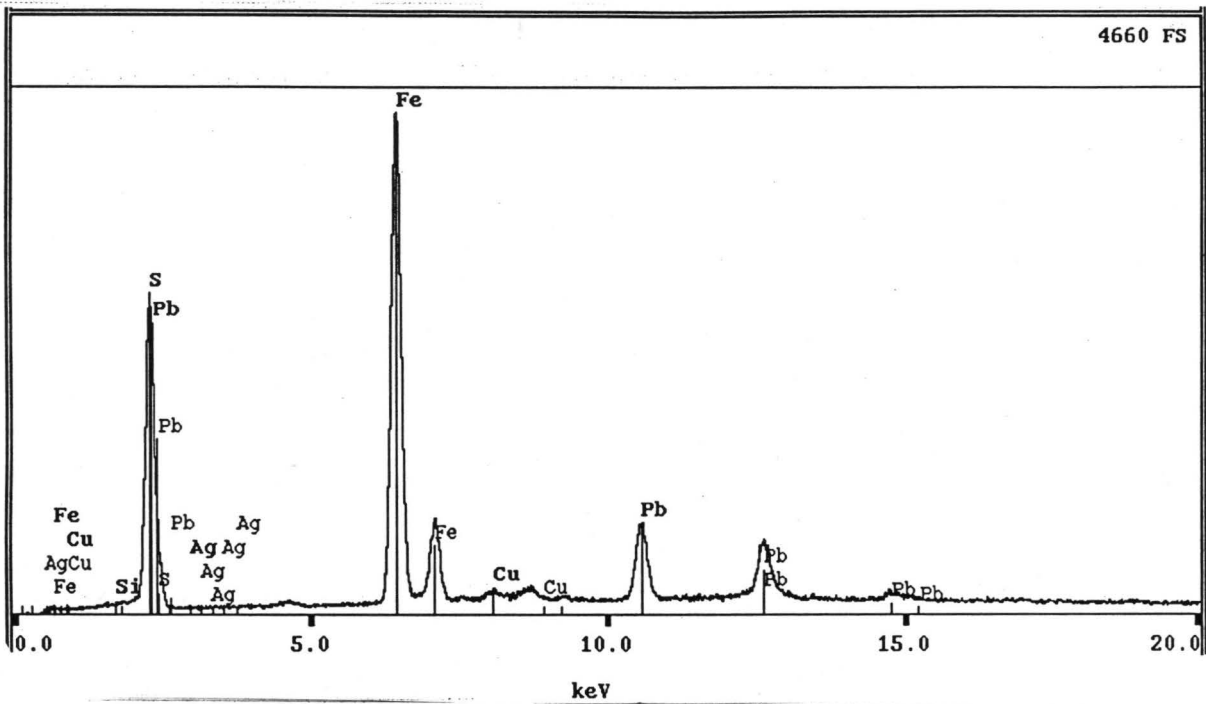


Figure 11. Graphical and pictorial (X800) representation of pyrite grain. A scale is provided on the S.T.E.M. photograph.

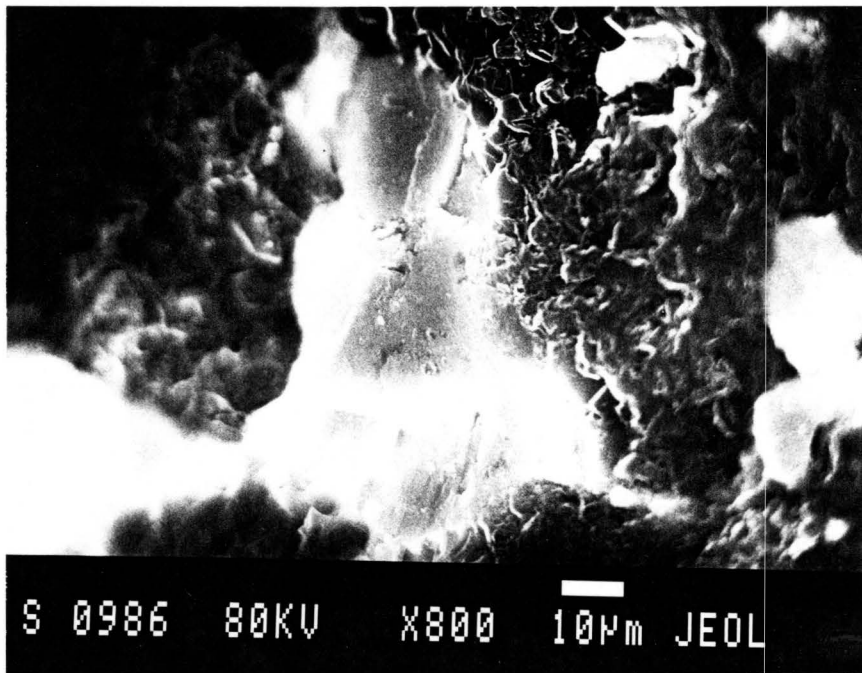
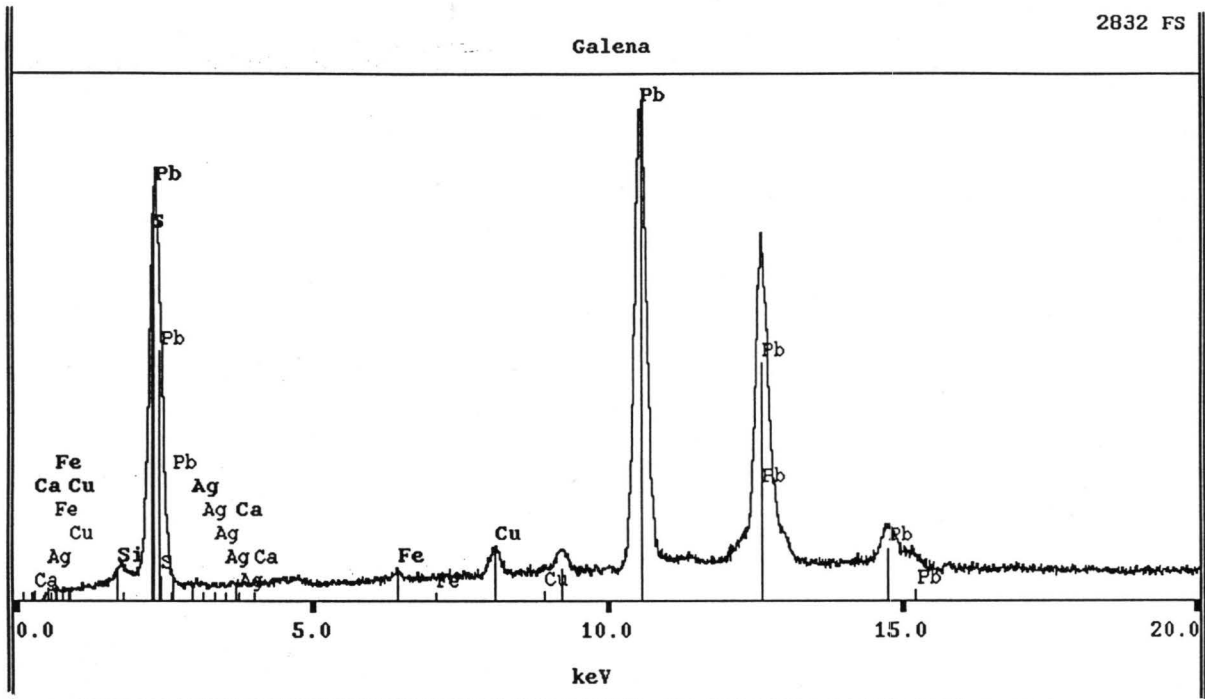


Figure 12. Graphical and pictorial (X800) representation of galena. A scale is provided on the S.T.E.M. picture.

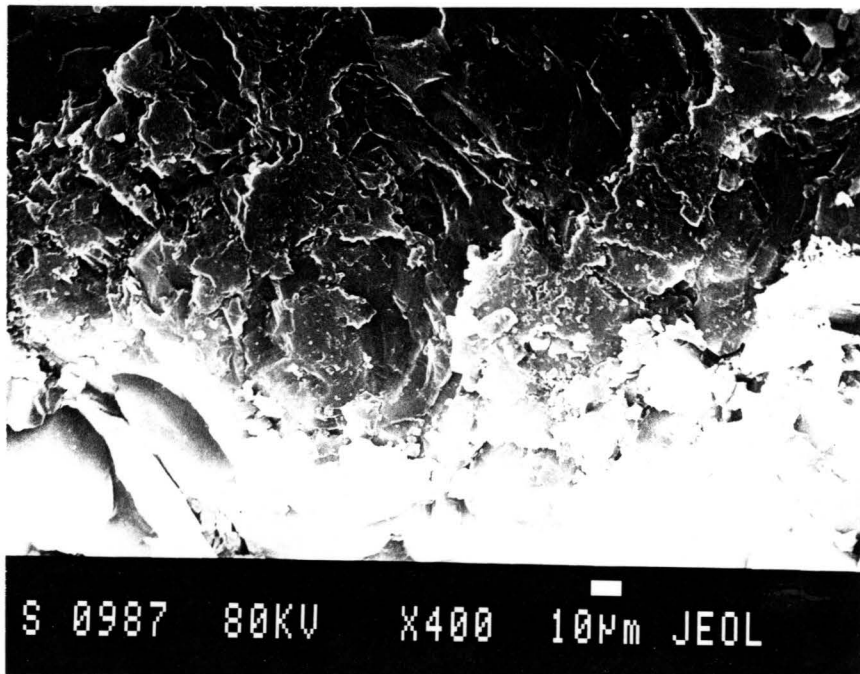
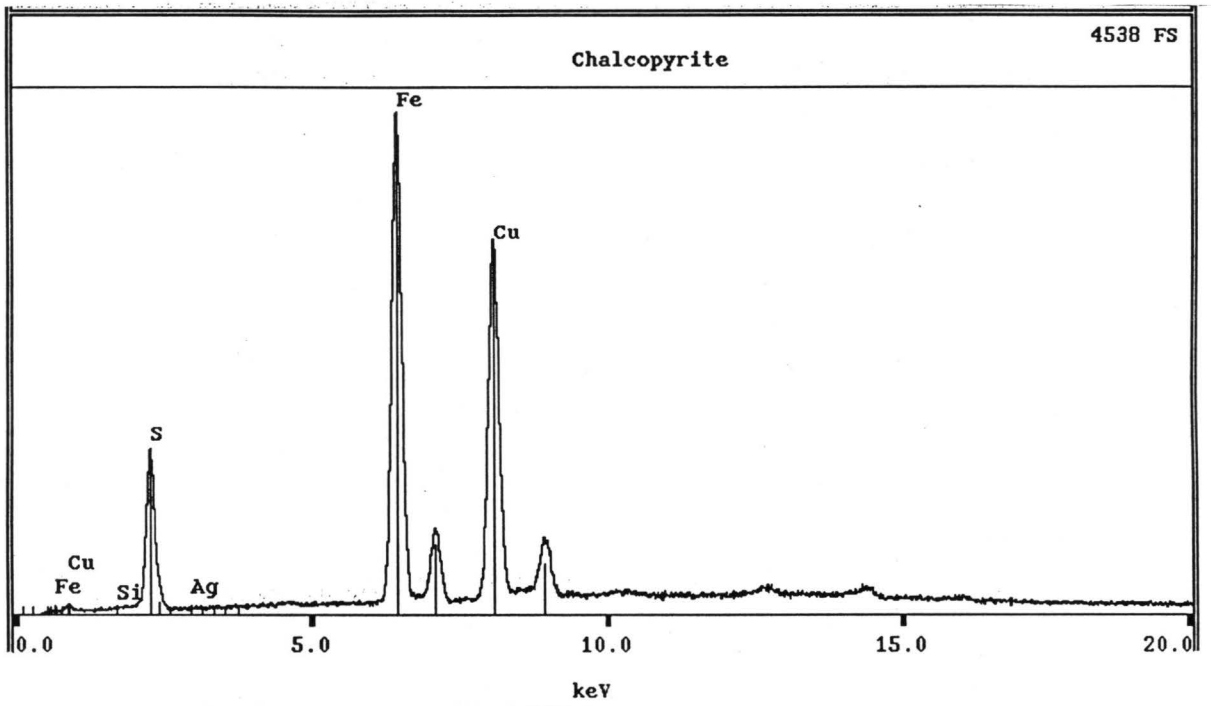


Figure 13. Graphical and pictorial (X 400) representation of chalcopyrite. A scale is provided on the S.T.E.M. photograph.

5.2. XRF Analysis

XRF analysis was done on bulk conglomerate samples of pyrite, galena, and chalcopyrite only. Large samples of centrifuged tailings and sphalerite could not be produced for the analysis therefore making it unfeasible.

Within the samples analyzed Ag and Zn were found in both the galena and the pyrite sample. The levels of Zn and Ag did not fluctuate in the same manner therefore there is no indication that the Ag occurrence is linked to Zn concentrations.

The samples of pyrite, chalcopyrite, and galena did produce low levels of silver as seen in table 1 but the error in galena and chalcopyrite may negate the concentrations found.

Table 1: Silver within sampled sulphides

Pyrite	0.012 wt% \pm 0.009 wt%
Galena	0.015 wt% \pm 0.01 wt%
Chalcopyrite	0.0062 wt% \pm 0.02 wt%

XRF analysis is provided within Appendix A in rough draft form and provides a full documentation of all impurities found within the samples.

5.2.1. Pyrite

The analysis of pyrite established that the sample was relatively impure, and contained many trace elements or compounds. Small but existent level of Ag at 0.012 wt% \pm 0.009 wt%. The error that exists within this analysis is allowable and justifies the statement that Ag does exist within the sample. Levels of Pb, Zn, and S indicate the presence of galena and sphalerite within the pyrite sample providing evidence for the sample's impurity.

5.2.2. Chalcopyrite

The analysis of chalcopyrite suggests that the S is bound completely to Fe and Cu to produce chalcopyrite. No appreciable levels of Ag were found (0.0062 wt% \pm 0.02 wt%) due to the existence of very large error. The sample proved to be relatively pure which has already been documented by previous work in this area (Petruk *et al.*, 1971).

5.2.3. Galena

The galena sample analyzed contained large amounts of impurities even though the sample initially appeared to be pure galena. A small amount of Pb was present in the sample and probably exists as PbS. Large amounts of Zn, Fe, and S exist in the sample in similar concentrations. This may be due to the existence of a solid solution between FeS in ZnS. Although there were many impurities found no appreciable amount of Ag was found (0.015 wt% \pm 0.01 wt%).

5.3. Discussion

The background water levels for silver in the Cobalt area are generally not detectable ($<10^{-11}$ g/g) confirming the very low solubility of silver (unpublished data from Kramer, 1995). A lack of reportable silver in the tailings is feasible and should be expected using the S.T.E.M. as its sensitivity low. Using ICPMS silver was found to be approximately 2 ppm in the Cart Lake area.

The results from XRF analysis for the sulphide minerals samples conflict with other results based on the probability of silver substitution. If the concentrations of silver were due to the substitution of silver for another metal, then the concentration of silver within the minerals should give: chalcopyrite > galena > sphalerite > pyrite.

The actual concentrations of Ag in chalcopyrite, galena, and pyrite were the opposite of the predicted sequence, with pyrite having the highest concentration of silver. I make the prediction that the Ag substitution trend is based on the maximum thermal stability of the minerals which are 743 °C, 1020 °C, 1115 °C, and 557 °C for pyrite, sphalerite, galena, and chalcopyrite respectively. As the mineral reaches its maximum thermal stability higher levels of silver are allowed to substitute into the structure. This theory may need modification. For example, there is a lack of silver within chalcopyrite which, based on my prediction, should have the highest concentration of silver. Silver substitutes for Cu^{+1} therefore a low Ag concentration could be due to low Cu^{+1} levels in chalcopyrite. There is no clear answer for why chalcopyrite did not behave in the manner expected.

6. CONCLUSIONS

In theory the presence of silver is expected within the common sulphides in the sequence of chalcopyrite, galena, sphalerite, and pyrite. This conclusion is based on covalent radii, ionic radii (for galena), and charge similarities. Experimentally this sequence was reversed with pyrite containing the highest levels of silver. This may be due to a trend of increasing silver concentration with decreasing maximum thermal stability.

Silver was found at very low levels ($< 0.1\%$) in pyrite, galena, and chalcopyrite samples from Cobalt Ontario. It is impossible to characterize the presence of silver within common metal sulphides at the levels of sensitivity (0.1%) of elemental detection in electron microscopy systems.

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8. APPENDIX A

McMaster University Department Of Geology
 1280 Main Street West,
 Hamilton, Ontario
 L8S 4M1

Tel: (416) 525-9140 Fax: (416) 522-3141

JOB.520

10-Apr-95

Company name..... McMaster ScMo 100kV LiF220 Ge111 PE TIAP

Pyrite 233-1

A Supporting Film is used

BackgroundModel used is Al

Eff. Area calculated: 55.73 mm² (8.4 mm)

Assumed grain size = 0 Micrometer

Given rest is 0 %

Given Diluent/Sample is 0

Given Viewed Mass is 200.00 mg / 4.522 cm² = 0.044 g/cm²

A < sign means that the concentration is < 50 ppm

Z	wt%	StdErr	Z	wt%	StdErr	Z	wt%	StdErr
9 F			32 GeO2			56 BaO	<	
11 Na2O	<		33 As	0.24	0.04	57 La2O3	<	
12 MgO	0.94	0.2	34 SeO2	0.014	0.007	58 Ce2O3	<	
13 Al2O3	1.0	0.04	35 Br	<		59 Pr2O3	<	
14 SiO2	14.2	0.2	37 Rb2O	<		60 Nd2O3	<	
15 F2O5	4.2	0.10	38 SrO	<		62 Sm2O3	0.057	0.03
16 S	38.6	0.2	39 Y2O3	<		64 Gd2O3		
17 Cl	0.16	0.01	40 ZrO2	<		65 Tb2O3		
19 K2O	0.059	0.005	41 Nb2O5	0.0073	0.009	72 HfO2		
20 CaO	5.6	0.1	42 Mo	<		73 Ta2O5	<	
22 TiO2	0.24	0.02	45 Rh	0.0076	0.007	74 WO3	<	
23 V2O5	<		46 Pd	0.0064	0.007	77 Ir		
24 Cr2O3	0.018	0.01	47 Ag	0.021	0.009	78 Pt	<	
25 Mn	0.060	0.010	48 Cd	0.031	0.009	79 Au	<	
26 Fe	23.2	0.2	49 In2O3			80 Hg	<	
27 Co3O4	<		50 Sn	0.016	0.01	81 Tl2O3	<	
28 Ni	<		51 Sb	0.024	0.02	82 Pb	4.0	0.09
29 Cu	<		52 TeO2	<		83 Bi2O3	0.019	0.01
30 Zn	6.4	0.1	53 I	0.73	0.05	90 ThO2	0.033	0.03
31 Ga2O3			55 Cs2O	<		92 U3O8	<	

KnownConc 0

REST= 0

Dil/Smpl= 0

McMaster University Department Of Geology
 1280 Main Street West,
 Hamilton, Ontario
 L8S 4M1

Tel: (416) 525-9140 Fax: (416) 522-3141

JOB.521

10-Apr-95

Company name..... McMaster ScMo 100kV LiF220 Ge111 FE T1AP
 Chalcopyrite 233-2

A Supporting Film is used

BackgroundModel used is Al

Eff. Area calculated: 27.12 mm² (5.9 mm)

Assumed grain size = 0 Micrometer

Given rest is 0 %

Given Diluent/Sample is 0

Given Viewed Mass is 200.00 mg / 4.522 cm² = 0.044 g/cm²

A < sign means that the concentration is < 50 ppm

Z	wt%	StdErr	Z	wt%	StdErr	Z	wt%	StdErr
9 F			32 GeO2			56 BaO	<	
11 Na2O	<		33 As	0.15	0.09	57 La2O3	<	
12 MgO	1.4	0.1	34 SeO2	0.016	0.02	58 Ce2O3	<	
13 Al2O3	1.2	0.05	35 Br	<		59 Pr2O3		
14 SiO2	3.3	0.09	37 Rb2O	<		60 Nd2O3	0.16	0.06
15 P2O5	10.1	0.1	38 SrO	<		62 Sm2O3	0.13	0.05
16 S	24.7	0.2	39 Y2O3	<		64 Gd2O3		
17 Cl	0.26	0.02	40 ZrO2	<		65 Tb2O3		
19 K2O	0.14	0.01	41 Nb2O5	0.018	0.02	72 HfO2		
20 CaO	8.5	0.1	42 Mo	<		73 Ta2O5	<	
22 TiO2	0.29	0.04	45 Rh	0.029	0.02	74 WO3	<	
23 V2O5	<		46 Pd	<		77 Ir		
24 Cr2O3	0.045	0.02	47 Ag	0.0062	0.02	78 Pt	<	
25 Mn	0.086	0.02	48 Cd	0.036	0.02	79 Au	<	
26 Fe	22.0	0.2	49 In2O3			80 Hg	0.044	0.03
27 Co3O4	<		50 Sn	0.037	0.03	81 Tl2O3	0.043	0.04
28 Ni	<		51 Sb	0.058	0.04	82 Pb	3.3	0.09
29 Cu	21.2	0.2	52 TeO2	<		83 Bi2O3	0.039	0.04
30 Zn	1.0	0.07	53 I	1.5	0.09	90 ThO2	0.058	0.06
31 Ga2O3			55 Cs2O	<		92 U3O8	0.015	0.03

KnownConc 0

REST= 0

Dil/Smpl= 0

McMaster University Department Of Geology
1280 Main Street West,
Hamilton, Ontario
L8S 4M1

Tel: (416) 525-9140 Fax: (416) 522-3141

JOB.522

10-Apr-95

Company name..... McMaster ScMo 100KV LiF220 Ge111 PE T1AP
Galena 233-3

A Supporting Film is used

BackgroundModel used is Al

Eff. Area calculated: 44.57 mm2 (7.5 mm)

Assumed grain size = 0 Micrometer

Given rest is 0 %

Given Diluent/Sample is 0

Given Viewed Mass is 200.00 mg / 4.522 cm2 = 0.044 g/cm2

A < sign means that the concentration is < 50 ppm

Z	wt%	StdErr	Z	wt%	StdErr	Z	wt%	StdErr
9 F			32 GeO2			56 BaO	<	
11 Na2O	<		33 As	0.24	0.05	57 La2O3	<	
12 MgO	3.0	0.2	34 SeO2	0.016	0.01	58 Ce2O3	<	
13 Al2O3	3.1	0.08	35 Br	<		59 Pr2O3		
14 SiO2	32.4	0.2	37 Rb2O	<		60 Nd2O3	0.044	0.04
15 P2O5	7.0	0.1	38 SrO	<		62 Sm2O3	0.095	0.04
16 S	8.6	0.1	39 Y2O3	<		64 Gd2O3		
17 Cl	0.19	0.01	40 ZrO2	<		65 Tb2O3		
19 K2O	0.044	0.004	41 Nb2O5	0.014	0.02	72 HfO2		
20 CaO	5.6	0.1	42 Mo	0.0087	0.01	73 Ta2O5	<	
22 TiO2	0.40	0.03	45 Rh	0.013	0.01	74 WO3	<	
23 V2O5	<		46 Pd	0.013	0.01	77 Ir		
24 Cr2O3	0.036	0.02	47 Ag	0.015	0.01	78 Pt	<	
25 Mn	0.11	0.01	48 Cd	0.032	0.01	79 Au	<	
26 Fe	8.1	0.1	49 In2O3			80 Hg	<	
27 Co3O4	0.027	0.03	50 Sn	<		81 Tl2O3	<	
28 Ni	<		51 Sb	0.061	0.03	82 Pb	20.4	0.2
29 Cu	0.28	0.06	52 TeO2	0.015	0.05	83 Bi2O3	0.0075	0.02
30 Zn	8.9	0.1	53 I	1.1	0.07	90 ThO2	0.028	0.05
31 Ga2O3			55 Cs2O	<		92 U3O8	<	

KnownConc 0

REST= 0

Dil/Smpl= 0