CLASSIFICATION OF COPPER DEPOSITS

USING COPPER, GOLD, SILVER RATIOS

By

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A Thesis
Submitted to the Faculty of Arts and Sciences
in Partial Fulfillment of the Requirements
for the Degree
Bachelor of Science

McMaster University
May 1973
ABSTRACT

An attempt was made in this study to classify copper deposits using the ratio of copper, gold and silver in the deposits. Data were accumulated from a literature search and neutron activation analysis of samples. Triangular diagrams were plotted and fields for each type of deposit were defined. Porphyry, volcanogenic, and sedimentary fields were most easily defined due to the amount and quality of data available for these deposits. It is found that the size of the field for any type of deposit is a function of its mineralogy. This is illustrated by the data spread for the copper and lead-zinc zones in volcanogenic deposits.

A clear separation of deposit types could not be obtained due to a partial overlap of the data fields; however, it is suggested that further work using more metals might yield a clear separation of deposits.
ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Dr. J. H. Crocket, McMaster University, and Dr. R. V. Kirkham, Geological Survey of Canada. Dr. Crocket supervised this project and provided invaluable assistance in the development of neutron activation procedures needed for analysis of copper, gold, and silver. Dr. Kirkham provided samples for analysis as well as some of his own analytical data for use in this study.
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INTRODUCTION

A) PURPOSE

A genetic classification of copper deposits has been proposed (Kirkham, 1972) in which it was suggested that the physico-chemical conditions related to the formation of an orebody should be reflected in the metal content of the resulting deposit. It was further stated that "for certain types of deposits major metal content or ratios of major metals should adequately define the kind of deposit involved..." (Kirkham, 1972).

In this study the author has attempted to determine whether the trace metals gold and silver singly, or in combination with the major element copper, can be used to distinguish the different deposits of Kirkham's classification (Table 1). Nickel-copper and carbonatite deposits were not dealt with in this work due to a scarcity of data and the ease with which the deposits can be identified using other criteria such as type of host rock.

B) CHOICE OF METALS

Copper, gold and silver were chosen for a number of reasons, both practical and theoretical.

Although in most deposits gold and silver are not found above trace values their high dollar values make them economic to produce. This means there is an abundance of both production and assay data for these two elements in the literature.
<table>
<thead>
<tr>
<th>Suggested Names</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Magmatic nickel-copper or simply nickel-copper deposits</td>
</tr>
<tr>
<td>2. Carbonatite or alkaline complex deposits</td>
</tr>
<tr>
<td>3. Porphyry copper deposits</td>
</tr>
<tr>
<td>4. Contact metasomatic or skarn deposits</td>
</tr>
<tr>
<td>5. Volcanogenic polymetallic (massive iron sulphide) or volcanic exhalative deposits</td>
</tr>
<tr>
<td>6. Copper sulphide-native copper deposits in volcanic sequences</td>
</tr>
<tr>
<td>7. Sedimentary or alternatively concordant and peneconcordant deposits in sedimentary sequences</td>
</tr>
<tr>
<td>8. Miscellaneous deposits</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Inferred Genetic Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. magmatic deposits associated with mafic and ultramafic igneous rocks</td>
</tr>
<tr>
<td>2. &quot;late stage&quot; magmatic and/or magmatic-hydrothermal deposits associated with carbonatites and alkaline complexes</td>
</tr>
<tr>
<td>3. magmatic-hydrothermal</td>
</tr>
<tr>
<td>4. magmatic-hydrothermal</td>
</tr>
<tr>
<td>5. volcanic-hydrothermal-exhalative</td>
</tr>
<tr>
<td>6. volcanic (?)-hydrothermal(?)</td>
</tr>
<tr>
<td>7. sedimentary (includes aspects of diagenesis)</td>
</tr>
<tr>
<td>8. mainly hydrothermal and magmatic-hydrothermal vein and replacement deposits</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Characteristic Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni, Cu (Co, Pt)</td>
</tr>
<tr>
<td>Cu (Ti, Fe, P₂O₅, Zr, Mo, etc.)</td>
</tr>
<tr>
<td>Cu, Mo (Au, Ag)</td>
</tr>
<tr>
<td>Cu (Fe, Mo, W, Zn, Au, Ag, etc.)</td>
</tr>
<tr>
<td>Cu, Zn (Pb, Au, Ag)</td>
</tr>
<tr>
<td>Cu (Ag)</td>
</tr>
<tr>
<td>Cu (Mo, Co, Pb, Zn, Ag, V, U, etc.)</td>
</tr>
<tr>
<td>Cu, Pb, Zn, Ag, Au As, Sb, etc.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sudbury district, Great Lakes Nickel, Giant Mascot</td>
</tr>
<tr>
<td>Palabora, South Africa</td>
</tr>
<tr>
<td>Bethlehem, Brenda, Granisle</td>
</tr>
<tr>
<td>Gaspé Copper, Craigmont, Phoenix</td>
</tr>
<tr>
<td>Noranda district, Bathurst district, Whalesback, Western Mines</td>
</tr>
<tr>
<td>Keweenaw Peninsula, Coppermine River area, Mamainse Point</td>
</tr>
<tr>
<td>White Pine, Redstone, Dorchester</td>
</tr>
<tr>
<td>Chibougamau district, Icon-Sullivan, Alwin, Churchill</td>
</tr>
</tbody>
</table>

Table 1. Classification of Copper Deposits Proposed by Kirkham (1972)
Copper, gold and silver are all members of group IB on the periodic table and as such have many similar properties. They all have face-centred cubic crystal structure, high density, and similar atomic and covalent radii. Copper and gold, and gold and silver are mutually soluble, copper and silver are not.

In nature both gold and silver have been reported to occur in chalcopyrite (Fleischer, 1955). However, gold and silver are also present in other common sulphides such as pyrite, galena, and sphalerite.
DATA

A) SOURCES AND EVALUATION OF DATA

Most of the data in this study come from two sources, one being published data, the other neutron activation analysis of samples by the author.

Published data either consisted of assay data, or production data, both of which have problems associated with their accuracy. Production data is useful since it is possible to calculate accurate gold and silver values which represent a large tonnage of ore. However, in some mines the circuit for gold or silver is only used when ore of sufficient metal content to be economic is mined. Therefore, large tonnages of low grade ore which could contain, in total, an appreciable quantity of the trace metals of interest would not be included in the production data. Another problem is the percentage of each metal that can be recovered from the ore.

In the present study these problems cannot be quantitatively evaluated since individual mines were not studied in sufficient detail.

The major difficulty with assay data is that silver and especially gold are only determined to a level which is necessary to assess their economic feasibility. In some cases this is not accurate enough to give reasonable metal ratios.

Due to the experimental method used (neutron activation analysis), the data generated by the author should not suffer from problems of accuracy. In all, 31 samples were analysed. These samples,
provided by Dr. R. V. Kirkham (Geological Survey of Canada), were from Granisle, B.C., San Manuel-Kalamazoo, Ariz., and Ajo, Ariz., all porphyry deposits, and from Redstone, N.W.T. and other occurrences of copper mineralization in sedimentary sequences.

B) PROCESSING OF DATA

Statistical analysis and plotting of data was carried out using a computer program written by the author for a CDC 6400 computer and associated Benson-Lehner plotter.

Simple linear regression analysis was done for individual deposits where sufficient data was available. The range, mean and standard deviation values for each metal were also calculated.

Both triangular and X-Y plots could be done using the program, however the latter type were not used since in many cases only the ratios of metals and not their absolute values were known.

Data was used in "assay form" in that on all plots copper is in percent, gold and silver being in ounces per ton. Gold values have been multiplied by 10 on the triangular plot so that effects of small variations in the gold content can be seen. This means that if all the data were placed on an equivalent weight scale with the copper being x1, silver would be x320 and gold x3200. When "trace" values were encountered in the assay data the amount of the metal was assumed to be one-half of the assay sensitivity limit for that metal.
ANALYTICAL DETERMINATIONS

A) PROCEDURES

A brief summary of the experimental methods used will be given here, the detailed chemical method needed for the analysis of gold and silver being presented in figure 1 and appendix I.

The method used was NAA\(^1\), all irradiations being carried out in the reactor at McMaster University (flux of \(5 \times 10^{13}\) neutrons/cm\(^2\)/sec).

In preparation for analysis the samples were crushed on enamel and seived through 100 mesh nylon seives. 200 \(\pm\) 30 mg of the powdered sample was loaded into quartz ampoules which were then sealed for irradiation. Two ampoules of Cu + Ag standard and two ampoules of Au standard were included with the samples for each irradiation.

Two irradiations were done for each set of samples, the first being for 15 minutes. Copper was then determined non-destructively (ie. by direct counting) after an initial decay period of 20 hours. Specificity of the photopeak was checked by decay measurements and gamma energy calibration. The samples were then reirradiated for 48 hours in order to determine gold and silver. The longer irradiation was needed due to the 250 day half-life of the silver. After this irradiation the samples were allowed to cool for five days to obtain a safe radiation level. Gold and silver were then determined by normal wet chemical,

\(^1\) NAA will be used to signify Neutron Activation Analysis.
Figure 1. Flowsheet for Wet Chemical Analysis. Numbers refer to steps in respective methods. (Appendix I)

Ag Standard (note 1)
- dissolve, filter into centrifuge tube,
ppte AgCl (1-4)
- centrifuge and discard supernatant
- Ag Procedure (note 2)
  - dissolve in NH₄OH (2)
  - ppte—centrifuge—supernatant
  - SiO₂, discard
    - acidify & ppte AgCl (3)
    - wash, slurry into counting vial (4)

SAMPLE
- Fusion (1,2)
  - dissolve cake, acidify; add Na₂S to ppte sulphides (3,4)
  - ppte—centrifuge—supernatant
  - dissolve, digest, discard (contains take up in 2M HCl(5) Na, K etc...)
  - ethyl acetate extraction (6,7)
  - Au Procedure (note 3)
    - HCl discard evaporate ethyl acetate (1)
    - Au Procedure (note 3)
      - dissolve, digest up in 2M HCl (4)
      - ppte & wash Au (5, 6), slurry into counting vial

Note 1. Ag Standard is processed during fusion since HCl vapour will not be present in the lab at this point in the experiment.

Note 2. Ag samples and standards are run through this step after HCl fumes from initial digestion have disappeared and before Au digestion. This avoids unwanted precipitation of AgCl.

Note 3. If Cu was to be done by wet chemical methods this solution would not be discarded as it contains the Cu.
carrier based activation analysis.

Many problems were initially encountered with the wet chemistry, most of them involving the unwanted precipitation of silver chloride at the wrong point in the method (see notes on figure 1). After these difficulties were overcome both gold and silver gave good yields. Average yields were 70% for gold and 80% for silver.

In counting the samples the 0.511 MeV peak of $^{64}$Cu and the 0.412 MeV peak of $^{198}$Au were used. The spectrum of $^{110}$Ag shows four peaks (see figure 2), however in this work only the large compound peak at approximately 0.66 MeV was used in the counting.

B) RESULTS

The NAA results are presented in table 2 along with a very brief description of the type of rocks analysed. Gold and silver data have been converted to oz/ton for plotting and comparisons with literature data.

NAA data should not suffer from problems of accuracy since the concentrations of metals in the samples are above the sensitivity limits of the method. Major sources of error are the standard solutions and non-representative sampling when loading powder for analysis. This second source of error is unimportant in this work since the copper, gold and silver determinations were carried out on the same sample of powder and only ratios of the metals were used in the analysis of data.
Figure 2. Spectrum of $^{110}$Ag. Peak used in counting was large compound peak at .66 KeV.
Table 2. Results of neutron activation analysis of samples.

<table>
<thead>
<tr>
<th>Property, and sample description</th>
<th>Cu (in %)</th>
<th>Au ppb</th>
<th>oz/ton</th>
<th>Ag ppm</th>
<th>oz/ton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granisle, B.C.</td>
<td>3.75</td>
<td>837.</td>
<td>.027</td>
<td>9.33</td>
<td>.299</td>
</tr>
<tr>
<td></td>
<td>3.55</td>
<td>8150.</td>
<td>.261</td>
<td>3.44</td>
<td>.110</td>
</tr>
<tr>
<td>two vein and several lower grade feldspar porphyry samples were analysed.</td>
<td>.99</td>
<td>479.</td>
<td>.015</td>
<td>13.4</td>
<td>.428</td>
</tr>
<tr>
<td></td>
<td>.37</td>
<td>37.5</td>
<td>.001</td>
<td>1.38</td>
<td>.044</td>
</tr>
<tr>
<td></td>
<td>.34</td>
<td>174.</td>
<td>.006</td>
<td>4.91</td>
<td>.157</td>
</tr>
<tr>
<td></td>
<td>.39</td>
<td>72.9</td>
<td>.002</td>
<td>.82</td>
<td>.026</td>
</tr>
<tr>
<td>San Manuel-Kalamazoo, Ariz.</td>
<td>.05</td>
<td>1.6</td>
<td>.00005</td>
<td>1.03</td>
<td>.033</td>
</tr>
<tr>
<td>two granite samples and six porphyries analysed</td>
<td>.04</td>
<td>2.6</td>
<td>.00009</td>
<td>.30</td>
<td>.010</td>
</tr>
<tr>
<td></td>
<td>.78</td>
<td>29.9</td>
<td>.0010</td>
<td>1.84</td>
<td>.059</td>
</tr>
<tr>
<td></td>
<td>.40</td>
<td>18.1</td>
<td>.0006</td>
<td>.72</td>
<td>.023</td>
</tr>
<tr>
<td></td>
<td>.21</td>
<td>9.9</td>
<td>.0003</td>
<td>.41</td>
<td>.013</td>
</tr>
<tr>
<td></td>
<td>.77</td>
<td>30.5</td>
<td>.0010</td>
<td>1.59</td>
<td>.051</td>
</tr>
<tr>
<td></td>
<td>.59</td>
<td>13.3</td>
<td>.0004</td>
<td>1.47</td>
<td>.047</td>
</tr>
<tr>
<td></td>
<td>1.09</td>
<td>77.5</td>
<td>.0025</td>
<td>2.65</td>
<td>.085</td>
</tr>
<tr>
<td>Ajo, Ariz.</td>
<td>.08</td>
<td>3.1</td>
<td>.0001</td>
<td>.31</td>
<td>.010</td>
</tr>
<tr>
<td>a range of rocks from granite to feldspar porphyry analysed</td>
<td>.43</td>
<td>38.7</td>
<td>.0012</td>
<td>1.25</td>
<td>.040</td>
</tr>
<tr>
<td></td>
<td>1.24</td>
<td>542.</td>
<td>.017</td>
<td>11.6</td>
<td>.370</td>
</tr>
<tr>
<td></td>
<td>1.57</td>
<td>446.</td>
<td>.014</td>
<td>12.2</td>
<td>.392</td>
</tr>
<tr>
<td></td>
<td>.30</td>
<td>93.9</td>
<td>.003</td>
<td>1.07</td>
<td>.034</td>
</tr>
</tbody>
</table>
Table 2 (continued)

<table>
<thead>
<tr>
<th>Property, and sample description</th>
<th>Cu (in %)</th>
<th>Au ppb</th>
<th>Au oz/ton</th>
<th>Ag ppm</th>
<th>Ag oz/ton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grinnell Fm., Alta., B.C.</td>
<td>1.00</td>
<td>10.0</td>
<td>.0003</td>
<td>8.62</td>
<td>.276</td>
</tr>
<tr>
<td>quartzites containing malachite; some low sulphide contents, no pyrite.</td>
<td>4.32</td>
<td>30.1</td>
<td>.0009</td>
<td>11.7</td>
<td>.437</td>
</tr>
<tr>
<td></td>
<td>4.86</td>
<td>12.3</td>
<td>.0004</td>
<td>17.0</td>
<td>.545</td>
</tr>
<tr>
<td></td>
<td>1.36</td>
<td>2.6</td>
<td>.0001</td>
<td>7.84</td>
<td>.250</td>
</tr>
<tr>
<td></td>
<td>.34</td>
<td>2.8</td>
<td>.0001</td>
<td>4.56</td>
<td>.146</td>
</tr>
<tr>
<td>Purcell Group, Alta.</td>
<td>.09</td>
<td>.6</td>
<td>.00002</td>
<td>.23</td>
<td>.007</td>
</tr>
<tr>
<td>siltstone; low chalcopyrite, mainly malachite.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Redstone, N.W.T.</td>
<td>1.28</td>
<td>1.7</td>
<td>.00005</td>
<td>.91</td>
<td>.029</td>
</tr>
<tr>
<td>siltstones, quartzites, &amp; conglomerates with chalcopyrite, malachite.</td>
<td>.21</td>
<td>4.8</td>
<td>.00015</td>
<td>.81</td>
<td>.026</td>
</tr>
<tr>
<td></td>
<td>.09</td>
<td>.8</td>
<td>.00003</td>
<td>.04</td>
<td>.001</td>
</tr>
<tr>
<td></td>
<td>.05</td>
<td>14.6</td>
<td>.00047</td>
<td>.05</td>
<td>.002</td>
</tr>
<tr>
<td></td>
<td>.09</td>
<td>32.2</td>
<td>.0010</td>
<td>.04</td>
<td>.001</td>
</tr>
<tr>
<td></td>
<td>.27</td>
<td>3.1</td>
<td>.0001</td>
<td>.35</td>
<td>.011</td>
</tr>
</tbody>
</table>
DISCUSSION

A) TWO METAL CORRELATIONS IN INDIVIDUAL DEPOSITS

Seven volcanogenic and three porphyry deposits were examined. For all deposits there is a significant\(^1\) positive correlation of copper and silver (see table 3). Porphyry deposits show significant positive correlations of copper and gold; however, in only one case was the correlation of gold and silver significant. Five of the seven volcanogenic deposits show a significant correlation of copper and gold, although this correlation is not always positive.Brittania, B.C. shows a significant negative correlation of gold and copper and gold and silver. It is interesting to note that the McVicar-Manson property, just north of Britania, also has a similar set of correlations, although they are not high enough to be significant. The various correlations seen for the volcanogenic deposits can perhaps be explained by zonation of metals about a volcanic centre as occurs at Heath Steele, N.B. (Lusk, 1969). Some theoretical zonation patterns have been suggested in figure 3.

B) NAA DATA

i) Two Metal Correlations

Due to the limited number of analyses carried out for each

\(^1\) The 95% level of confidence is used when assessing the significance of correlations.
Table 3. Correlations generated by linear regression analysis of property data.

<table>
<thead>
<tr>
<th>Deposit Type</th>
<th>Name, Location</th>
<th>Relationship (not significant)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cu-Au</td>
</tr>
<tr>
<td>Porphyry</td>
<td>Canam, B.C.</td>
<td>+.22</td>
</tr>
<tr>
<td></td>
<td>Copperado, B.C.</td>
<td>+.29</td>
</tr>
<tr>
<td></td>
<td>Granisle, B.C.</td>
<td>+.47</td>
</tr>
<tr>
<td>Volcanogenic</td>
<td>Britania, B.C.</td>
<td>-.72</td>
</tr>
<tr>
<td></td>
<td>Con. Rambler, Nfld.</td>
<td>+.38</td>
</tr>
<tr>
<td></td>
<td>Iso-Copperfields, Que.</td>
<td>(+.06)</td>
</tr>
<tr>
<td></td>
<td>Le Tac Twp, Que.</td>
<td>+.31</td>
</tr>
<tr>
<td></td>
<td>Mattagami, Ont.</td>
<td>+.26</td>
</tr>
<tr>
<td></td>
<td>McVicar-Manson, B.C.</td>
<td>(-.23)</td>
</tr>
<tr>
<td></td>
<td>Rexdale, Ont.</td>
<td>+.68</td>
</tr>
</tbody>
</table>
Figure 3. Possible metal zonation patterns about a volcanic vent.

- **Positive correlation of metals I and II**
- **Negative correlation of metals I and II**
- **No correlation of metals I and II**

*Volcanic Vent*
property the correlations of metal ratios would not be expected to be very high. However, San Manuel-Kalamazoo, Ajo and the Grinnell data all show significant copper-silver correlations. San Manuel-Kalamazoo and Ajo also show significant correlations of copper and silver with gold.

Although they are not significant, negative correlations with gold are seen for Redstone and Granisle. These deposits show trends from copper to both gold and silver on the triangular plots (figures 4 and 5) and this could account for the negative and low correlations.

The significant correlations with gold for Ajo and San Manuel-Kalamazoo suggest that these are a function of the accuracy of the analyses. Gold contents of rocks tend to be very low and show a restricted range of values. Since with literature data the gold values are commonly a series of steps (due to the sensitivity of the analytical methods used) correlations with gold are frequently low and not significant.

The correlations of elements using NAA data are similar to those obtained from larger amounts of literature data; suggesting that a few accurate analyses can be used in place of larger numbers of less accurate data when developing metal relationships for ore deposits.

ii) Cu-Au-Ag Trends

When plotted on triangular diagrams NAA data show a strong copper-silver trend (figures 4 and 5). Only one sample, a high grade vein from the Granisle deposit, was high in gold (8ppm/.26oz/ton).

The analysed porphyry samples show two distinct levels of gold
PORPHYRY

Figure 4. Plot of all neutron activation analysis data for porphyry deposits.

LEGEND

A  AJO
G  GRANISLE
K  SAN MANUEL-KALAMAZOO
SEDEMENTARY

Figure 5. Plot of all data for sedimentary deposits.

LEGEND

+ REDSTONE
0 GRINNELL FM. 
PURCELL GROUP

WHITE PINE
content; one, represented by San Manuel-Kalamazoo being low in gold (xx ppb/ .000x oz/ton), and the other by Ajo and Granisle which contain a consistently larger concentration (xxx ppb/ .00x oz/ton) of gold. In general the porphyry deposits are low in gold and do not show a wide range of copper-silver ratios.

A good agreement between NAA data (figure 4) and literature data (figure 6) is seen. This suggests that the average metal ratio for all porphyry deposits can be closely approximated by analysis of suites of specimens from a small number of deposits.

Data for sedimentary deposits was limited. Other than the samples analysed in this study, data was found for the White Pine copper deposit. The sedimentary deposits show low absolute gold values (.6 to 32 ppb/ .0000x to .000x oz/ton). This is in part a reflection of the mineralogy of these deposits which contain malachite as the only significant base metal mineral (malachite contains 55% Cu compared to 34% in chalcopyrite).

Low gold values may be a function of the mobility of gold in solution, circulating groundwater removing the gold as gold-chlorides. Silver would not be transported in a chloride rich solution since silver chloride is highly insoluble. The solution of gold would be enhanced by the presence of copper. On a molecular scale the chalcopyrite could go into solution creating a high local concentration of Cu$^{2+}$ ion which would be reduced by the gold as it went into solution as AuCl$_4^-$.

Other oxidizing agents such as MnO$_2$, atmospheric oxygen, and Fe$^{3+}$ also facilitate the solution of gold (see Krauskopf, 1951); however if Cu is
the oxidizing agent then gold could be lost from the system while copper and silver remain.

Alternatively, if copper, gold and silver all go into solution (the silver perhaps as a gel) then copper and silver can be reprecipitated while the gold-chloride remains in solution and is lost. This is due to the effect of high $\text{Cu}^{2+}$ concentrations in solution which inhibit the precipitation of gold.

C) Cu-Au-Ag TRENDS FOR ALL DATA

All available data for the different types of deposits have been plotted on a series of triangular diagrams (figures 6 to 10). Porphyry and volcanogenic deposits have the best coverage due to their prominence in exploration.

Porphyry data clusters in the copper corner of the diagram (figure 6) with limited ranges of data toward gold and silver rich end members. This is in marked contrast to other deposits, particularly the volcanogenic type which shows a wide range of data, especially to silver rich end members (see figure 7).

An explanation of this difference between copper-silver ratios of deposits can be based upon their mineralogy. Porphyry deposits contain in their mined portions ore that is comprised of pyrite and various copper minerals. These minerals contain small amounts of both gold and silver. The volcanogenic deposits and perhaps the skarns contain galena and sphalerite which have a high content of silver (Fleischer, 1955). Galena from the Bathurst Camp, N.B. has been studied (Boorman, 1968) and
found to contain in some cases discrete crystals of silver minerals. Therefore, any copper deposit with high contents of sphalerite or galena might be expected to show high silver content as well. The high pyrite content of the volcanogenic deposits might account for the higher gold values in these deposits since pyrite does contain some gold.

It appears that, in part, the wider range of values for the volcanogenic deposits is due to the grouping of copper and lead-zinc zones together, the lead-zinc mineralization and not the copper controlling the range of metal ratios seen.

Skarn deposits (figure 8) suffer from a lack of data; however, four of the five deposits show low proportions of gold relative to copper and silver. This distribution is primarily a function of high absolute copper and silver contents rather than a low gold content. High silver values might be due to galena and sphalerite in the ore, or some silver minerals might be present in the deposits.

Vein and replacement deposits show data clustered about the silver rich end member (figure 9). Although these high silver proportions appear to be characteristic of this type of deposit, most of the data is from the vein and replacement deposits peripheral to the Bingham porphyry deposit. Due to this bias of data sources it is unwise to conclude anything about this deposit type. There is a lack of recent data for these deposits due to a lack of exploration, the only recent data being for Alwin Mine, B.C. This deposit plots in the copper rich portion of figure 9.

Native copper deposits in volcanic sequences (figure 10)
Figure 6. Plot of all literature data for porphyry deposits.
VOLCANOGENIC

Figure 7. Plot of all literature data for volcanogenic deposits.
SKARN

Figure 8. Plot of all literature data for skarn deposits.
Figure 9. Plot of all literature data for vein and replacement deposits.
Figure 10. Plot of data for native copper in volcanic sequences. Data all from the Coppermine River Area.
exhibit another problem encountered with assay data. Gold was only found at "trace" levels in all assays and, as was explained previously, "trace" is assumed to be .005 oz/ton in a case such as this. In some assays this level of gold became significant with respect to the copper, silver content; that is, the gold content is probably greatly overestimated. Therefore, instead of the range shown, the native copper deposits should only have a limited range from copper to silver with little or no gold present. This would be consistent with the theory that the native copper in the Coppermine River Area had been remobilized and deposited in fissures in the volcanics (Kindle, 1970). As has been discussed for the sedimentary deposits it is likely that the gold would be lost from the system during any remobilization.

All data have been plotted on one triangular diagram (figure 11). From this plot it is seen that there is a strong data trend from copper to silver and a less well developed trend from copper to gold. No gold-silver trends are seen. As would be expected there is a concentration of data points about the copper rich end member.

The plot has been divided into four areas (see figure 11) and the number of deposits of each type in each area has been tabulated (table 4).

Area I is seen to contain 57% of the data points (total number 23) for the volcanogenic deposits as well as three of the five skarn data points. This area is characterized by a large range of copper-silver ratios and, in general, higher relative gold contents than other areas.
ALL DATA

Figure 11. Plot of all data and definition of fields for different types of deposits.

LEGEND

symbol | deposit type
-------|-----------------|
.       | PORPHYRY        |
.       | VOLCANOGENIC    |
.       | SEDIMENTARY     |
.       | SKARN           |
.       | NATIVE COPPER   |
.       | VEIN / REPLACEMENT

area

I
II
III
IV
Table 4. Number of data points for each type of deposit falling in designated areas of figure 11 (plot of ALL DATA).

<table>
<thead>
<tr>
<th>Deposit Type</th>
<th>Areas</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porphyry</td>
<td></td>
<td>0</td>
<td>18</td>
<td>22</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>Volcanogenic</td>
<td></td>
<td>13</td>
<td>6</td>
<td>3</td>
<td>1</td>
<td>23</td>
</tr>
<tr>
<td>Sedimentary</td>
<td></td>
<td>0</td>
<td>0</td>
<td>13</td>
<td>0</td>
<td>13</td>
</tr>
<tr>
<td>Skarn</td>
<td></td>
<td>3</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Native Copper</td>
<td></td>
<td>0</td>
<td>2*</td>
<td>17</td>
<td>0</td>
<td>19</td>
</tr>
<tr>
<td>Vein / Replacement</td>
<td></td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>18</td>
<td>19</td>
</tr>
</tbody>
</table>

* probably should be in Area III; for reasons see discussion in text.

Table 5. Distinctive areas for each type of deposit.

<table>
<thead>
<tr>
<th>Deposit Type</th>
<th>Areas</th>
<th>% of data included in specified areas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porphyry</td>
<td>II &amp; III</td>
<td>100</td>
</tr>
<tr>
<td>Volcanogenic</td>
<td>I &amp; II</td>
<td>83</td>
</tr>
<tr>
<td>Sedimentary</td>
<td>III</td>
<td>100</td>
</tr>
<tr>
<td>Skarn</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Native Copper</td>
<td>III</td>
<td>100</td>
</tr>
<tr>
<td>Vein / Replacement</td>
<td>IV</td>
<td>95*</td>
</tr>
</tbody>
</table>

* see discussion in text.
Area II contains the porphyry deposits as well as a few volcanogenic deposits. Two points for native copper deposits occur in this area but they can be disregarded for reasons already discussed. A limited range of gold and silver ratios with copper are seen in this area.

Data points for all types of deposits are in area III. The area is characterized by deposits rich in copper relative to gold and silver. Sedimentary and native copper deposits are only seen in this area; however, porphyry data points (55% of porphyry data) are also prominent.

Area IV is dominated by vein and replacement type deposits but this could be a false distribution due to previously discussed problems with the data.

From table 4 and figure 11 a rough classification can be developed (table 5). Deposits of sedimentary and native copper types are totally confined to area III of the diagram. Porphyry deposits occur only in areas II and III, and 80% of the volcanogenic deposits are in areas I and II. This gives a partial separation of deposits and allows one to say with a fair degree of certainty what type the deposit does not belong to (eg. if a deposit plots in area II it is not a sedimentary or native copper deposit; it could be either a porphyry or volcanogenic deposit). One can only answer in the positive sense if a deposit plots in area I in which case it is most likely volcanogenic.
D) VARIATION OF DATA WITHIN SINGLE DEPOSITS

In order to assess the variation of data within a single deposit, several data suites were plotted. From these plots (porphyry deposits figures 12 and 13; volcanogenic deposits figures 14 and 15) the range of data for an individual deposit is seen to exceed the range assigned to that class of deposits by table 5 and figure 11. This high within deposit variation means that single assays are of little use in plotting to determine the "type" of a deposit.

These variations could be caused by local abundances of silver and gold bearing minerals such as sphalerite, galena or pyrite. Plots of volcanogenic deposit data divide clearly into two areas, thus illustrating the idea of silver being in the lead-zinc ores. In the case of Con. Rambler high silver and gold are seen together, suggesting that the lead-zinc zone might also be an area of abundant pyrite.

The NAA data (figure 4) falls in the assigned range for porphyry deposits. Samples analysed have low copper contents and do not contain any visible sphalerite and galena. Pyrite is also low in most rocks analysed. Therefore, none of the minerals that have been proposed as causing high within deposit variation are present in the samples.
Figure 12. Plot of data for Canam porphyry deposit, B.C. Field for porphyry deposits is shown by dotted line.
Figure 13. Plot of data for Granisle porphyry deposit, B.C. Boundary of field for porphyry deposits is shown by dotted line.
CON RAMBLER

Figure 14. Plot of data for Consolidated Rambler, Nfld., a volcanogenic deposit. Limits of volcanogenic field are shown by dotted line. Copper zone (Cu) and Lead-Zinc zone (P) plot in different areas of diagram.
Figure 15. Plot of data for Sturgeon Lake property of Mattagami Mines. Limits of volcanogenic field are shown by dotted line. Copper zone (Cu) and Lead-Zinc zone (P) plot in different areas of diagram.
CONCLUSIONS

Although a partial separation of deposit types can be achieved using copper-gold-silver ratios it is not possible to delineate areas where one type of deposit is found exclusive to all other types. The closest approach to this ideal is the volcanogenic deposits where 57% of all deposits fall in area I of figure 11.

Most individual deposits show a good correlation of copper and silver; however, correlations of gold with other elements are not as strong. This is perhaps a function of the general accuracy of literature data for gold, particularly sub-ppm quantities. Better correlations with gold are found in the author's analyses where neutron activation techniques allow analysis to .1 ppb gold levels.

Although correlations of elements are strong within one deposit, they are not consistent between deposits of the same type. This fact might be useful in exploration since it could be determined when a new ore zone is found peripheral to a present producer whether it is a continuation of a known orebody or an entirely new deposit.
SUGGESTIONS FOR FURTHER STUDY

The results of this study suggest that one should limit the scope of metal ratio studies only to the copper minerals when determining gold and silver. However, an alternative approach would be to look at the whole rock with either lead or zinc in combination with copper, gold and silver. This would require graphical representation on a tetrahedral diagram and, due to the lead and zinc in volcanogenic deposits, would allow a clear separation of this type of deposit.

Another interesting feature which is worth further work is the determination of metal ratios for each period of mineralization in a porphyry system where intermineral dykes indicate that there have been several mineralization episodes (e.g. Granisle). If each episode had a different set of metal correlations then in areas of overlap it might be possible to sort out the ages of the individual vein systems.

The fact that a partial separation of deposits has been made in this study on the basis of only three metals suggests that with further work using more metals it might be possible to develop a quantitative aid to the classification of copper deposits.
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APPENDIX I

PROCEDURE FOR WET CHEMICAL ANALYSIS OF GOLD AND SILVER

A) Concentrations of Standards and Carriers.

Gold Standard  .19775 ugm/gm solution
Gold Carrier    14.2522 mg/gm solution
Silver Standard 10.737 ugm/gm solution
Silver Carrier  14.5310 mg/gm solution
Copper Standard 1.2204 mg/gm solution

B) Pre-Irradiation

1) Add 1.0 ml of each of Au and Ag carriers to each
zirconium crucible along with 4 pellets (about .5 g) of NaOH.
2) Evaporate using heat lamp to dryness.

C) Irradiation

8 samples and 4 standards were irradiated for each experiment.
Irradiation time was 48 hours in a position of high flux. Cooling
time was 5 days. At pick up the radiation field was usually 5 MR/HR
through 2 1/2 inches of lead.

D) Post-Irradiation

1) To the crucible add Na₂O₂, then the sample, then additional
Na₂O₂. Mix together, then add 12 pellets of NaOH and cover with Na₂O₂.
In total 5 gm Na₂O₂ and 2 gm NaOH are used for each .2 gm sample.
2) Fuse contents of crucible at low heat until peroxide melts
then turn up flame to bright red heat for 2 minutes, rotating crucible
two times during fusion. Quench and let crystallize.
3) Dissolve fusion cake with minimal volume of distilled water, clean crucible with 2M H₂SO₄ and wash into solution. Carefully add concentrated H₂SO₄ to acidify the solution to a pH in the range 1 to 3. Pour solution into the centrifuge tube.

4) Add 5 ml of 10% Na₂S, stir to mix thoroughly and centrifuge sulphides of Ag and Au. Pour off supernatant and wash precipitate with 3M NaOH.

5) Dissolve precipitate in aqua regia, take to near dryness two times, adding conc. HCl each time. Add conc. HCl so that 3 ml are present then 17 ml of distilled water to precipitate AgCl. Centrifuge.

6) Pour supernatant (Au) into seperatory funnel and add 20 ml of 10M HCl to give 40 ml of 6M HCl. Precipitate from step 5 goes to silver procedure.

7) Extract Au into 40 ml of ethyl acetate by shaking for two minutes.

8) Run off HCl and discard (contains Cu, Fe).

9) Run ethyl acetate into beaker and go to gold procedure.

D-1) Silver Procedure

1) Wash precipitate with minimal volume of 2M HCl.

2) Dissolve AgCl with about 5 ml of conc. NH₄OH; centrifuge and pour supernatant into new centrifuge tube.

3) Acidify solution with HNO₃ and reprecipitate AgCl with HCl.

4) Wash twice with water and slurry with EtOH into counting vial.

D-2) Gold Procedure

1) Evaporate ethyl acetate to dryness.
2) Add about 5 ml of aqua regia and take to dryness. (Repeat)
3) Add about 3 ml of conc. HCl and take to dryness. (Repeat)
4) Take up in 5 ml of 2M HCl and transfer to centrifuge tube. Wash beaker with 3 ml of 2M HCl and add to solution.
5) Take solution to boil and add hydroquinone (C₆H₄(OH)₂) to precipitate gold.
6) Wash twice with EtOH+water and slurry with EtOH into counting vial.

D-3) Silver Standard
1) Break ampoule into beaker and add 1.0 ml of Ag carrier.
2) Dissolve in 5 ml of warm 2M HNO₃.
3) Filter solution into centrifuge tube, washing filtrate with 0.5M HNO₃.
4) Add 2M HCl to precipitate AgCl; centrifuge and pour off supernatant.
5) Go to step 2 of silver procedure.

D-4) Gold Standard
1) Break ampoule into beaker and add 1.0 ml of Au carrier.
2) Procedure identical to gold procedure, steps 2 to 6, except 2M HCl solution is filtered into centrifuge tube (step 4) to remove quartz powder from solution. Filtrate is washed with 2M HCl.
APPENDIX II

DEPOSITS USED IN THIS STUDY.

Note that number of data points are not equal to the number of properties since for some deposits there were two or more data points.

Porphyry Deposits

B. C. : Bethlehem, Canam, Copper Mountain, Copperado, Granisle
Ont. : Minnitaki Lake, Ryan Lake

Volcanogenic Deposits

B.C. : Bonanza, Britannia, Hidden Creek, Mount Sicker, Western Mines
Appalachians : Buchans, Consolidated Rambler

Skarn Deposits

B.C. : Cambrian Chieftain, Maid of Erin, Phoenix Copper, Squaw Lake Area

Vein / Replacement Deposits

B.C. : Alwin Mines Ltd., Tulsequah Chief
U.S.A. : Bingham Area, Eagle Co. Colorado

Native Copper in Volcanic Sequences

Coppermine River Area, N.W.T.
Sedimentary Deposits

Grinnell Formation, Alta., B.C.; Purcell Group, Alta.;

Redstone, N.W.T.; White Pine, Michigan