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A Quantitative Study of the Copper Content in Granite Rocks

Samir F. Al-Mandwee

Western Michigan University

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A QUANTITATIVE STUDY OF THE COPPER CONTENT IN GRANITE ROCKS

by

Samir F. Al-Mandwee

A Thesis
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Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Arts
Department of Physics

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A QUANTITATIVE STUDY OF THE COPPER CONTENT IN GRANITE ROCKS

Samir F. Al-Mandwee, M.A.
Western Michigan University, 1984

A spectrographic analysis was conducted on ten granite samples of different geological origin from the Pioneer Mountains in Central Idaho. A qualitative analysis was performed first and then a quantitative analysis to determine the presence and relative amounts of copper in the various samples. This spectrographic analysis employed a direct current arc source of 340 volts and 4 amperes to excite the samples which were dissolved in acid and dried on the ends of high purity carbon electrodes. The emitted light passed through a step sector and a medium quartz spectrograph to a photographic plate. The optical density of the spectral lines on the photographic plate was determined with a microdensitometer. The optical density is related to the percentage of copper present in the rock samples. In order to compensate for many uncontrolled variables which could alter the optical line density, an internal control element, indium, was added to each sample. By comparing the copper line density to the internal control line density, the influence of such variables as sample mass, exposure time, or slit width is controlled. The analysis of the ten samples found that the copper content varied from approximately 25 parts per million to 400 parts per million.

This information augments and confirms previous analytical and geological knowledge concerning these granite samples from the Pioneer Mountains.
ACKNOWLEDGEMENTS

My thanks go to my advisor, Dr. Stanley K. Derby. Additional thanks go to Dr. Robert Poel and Dr. John Grace for their review of the manuscript.

Samir F. Al-Mandwee
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CHAPTER I

INTRODUCTION

Emission spectrographic analysis of an unknown material involves identifying which elements are present (qualitative analysis) and, if desired, the amount of the elements present (quantitative analysis). Qualitative analysis was first used more than a century ago by Kirchhoff and Bunsen (1860) for a study of alkali elements. Kirchhoff and Bunsen noted that certain spectral lines not belonging to the pure spectra of known alkalies appeared in the light from their preparations. Search for the origin of those lines led to the discovery of two new alkali elements, cesium and rubidium. Since that time, several other new elements have been discovered by emission spectrographic analysis.

Spectrographic quantitative analyses are based on the assumption that at very low concentrations of an element in a sample, the amount of light emitted by that element is directly proportional to the number of atoms of that element present, if all other factors are constant.

Although qualitative spectrum analysis has been a useful scientific tool for 120 years, the basic methods for successful quantitative analyses have existed for less than 60 years. It was not until after the development of the Bohr model (Bohr, 1913) of the atom that light emission from atoms was understood well enough to create useful quantitative spectrographic methods. All modern spectrographic methods are based on the assumption that the number of photons emitted by an element are directly proportional to the number of atoms present in
that element. This assumption, of course, presumes all other factors are constant. This assumption, however, is less valid for samples with very high concentration of an element.

The general process by which a qualitative and quantitative spectrographic analysis is made involves exciting the atoms of the unknown material to give off their characteristic light. This is usually accomplished by placing the sample in the center of an electric arc or electric spark. The electron bombardment excites the atoms of the sample such that each element gives off its own characteristic light. That special "fingerprint" light, in turn, is used to demonstrate the presence of that particular element in the sample. In order to sort out all of the different kinds of light coming from the sample, the emitted light is passed through a spectrograph with a prism or a grating. The prism or grating will spread out the different kinds of sample light according to the wavelengths, with the short wavelengths at one end and the long wavelengths at the other. This wavelength dispersion is called a spectrum. Each element has its own unique spectrum which is different from the spectrum of all other elements. This fact is the foundation for qualitative spectrum analyses. A quantitative analysis must accurately measure the amount of light occurring at a chosen wavelength for the desired element. The amount of the element present can be quantitively determined from an analysis of the amount of light given off by the element. Two common ways of measuring the quantity of that light are by photographic film or by photomultiplier tube.

This study is concerned with the application of spectrographic analysis techniques to the analysis of geological samples for trace element
content. The trace element of interest is copper and the particular rock samples that were investigated in this study were from a prospective granite porphyry stock located in Idaho. The samples selected were specifically chosen to measure both areal and vertical variations in copper content. Such information is of great value in aiding exploration geologists and mining engineers to explore and develop such rock bodies for metal resources.
CHAPTER II

SPECTROSCOPIC APPARATUS

Hilger Medium Quartz Spectrograph

White light is a composite of light of all the colors of the visible spectrum. That is, white light is a mixture of many radiations, each of which has a different wavelength. It is possible to separate these different wavelengths by using an instrument called a spectroscope which disperses the various wavelengths into a spectrum. In a spectroscope, the spectrum is observed visually. A spectrograph is a similar instrument for producing a photographic image of the spectrum. This photograph is called a spectrogram.

The spectrograph, in general, consists of: (1) a dispersing device which gives different emergent angles to different wavelengths passing through it; (2) an optical system of mirrors or lenses to bring the different wavelengths to a focus; (3) an entrance aperture, usually a rectangular slit, whose images, formed by the optical system in light from different wavelengths, are the spectral "lines" which are observed or photographed.

There are several important characteristics distinguishing different spectrographs. They are: (1) the dispersive ability or power to spread different wavelengths out so that they emerge from the system at different angles and are focused at different positions in the focal plane of the spectrograph; (2) the resolving power which is a measure of the ability of
the instrument to separate adjacent images of slightly different wavelengths. The resolving power is defined as the ratio of the wavelength observed to the smallest difference between two wavelengths which can just be resolved or distinguished as two separate lines; (3) the brightness of image which depends on the focal length and the aperture of the lenses, and the reflection and transmission losses within the instrument; (4) the illumination which depends upon the way in which the slit is illuminated by the external light sources used. A condensing lens may be used in front of the slit to form an image of the source at the slit, thereby increasing the illumination of the spectrum.

The type of spectrograph used in this investigation was a Hilger Medium Quartz Spectrograph (see Figure 1).

Figure 1. Hilger Medium Quartz Spectrograph

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Quartz-prism spectrographs are frequently used because many chemical elements have their sensitive analysis lines in the ultraviolet region. Quartz transmits the ultraviolet radiation whereas glass does not. It also has an advantage in industrial laboratories, where there may be dust and corrosive vapor, in that quartz optics resists corrosion and withstands cleaning better than diffraction gratings.

The prism spectrograph used in this research has two lenses: the collimator lens and the camera lens. Each lens has a focal length of about 60 centimeters for the sodium D lines. The length of the spectrum is 221 mm, ranging from 2000 Å to 10000 Å and the spectrum is recorded on a single photographic plate. The camera lens is designed to give an almost flat spectrum so that thin plates are not required. The Hilger instrument has a fixed adjustment for the prism and lenses. Small focus corrections to allow for temperature or other changes are made by small displacements of the slit. The slit itself is of unilateral design with micrometer adjustment. Each micrometer division equals 2.5 microns or 0.0025 mm.

Microphotometer

In order to quantitatively determine how much of an element is present, some additional apparatus must be used. Specifically, a step sector is used to calibrate the photographic plate and a microphotometer (or microdensitometer) is used to measure the optical density of the spectral lines.

The quantitative determination of the intensities of the spectral lines depends upon measuring the optical density of the photographic
image. This measurement involves a determination of the amount of light transmitted through the spectral line. In this study, the instrument used to measure optical density of the lines is called a microphotometer or a microdensitometer. In this instrument, (see Figure 2), the photographic plate is traversed by a beam of light from a constant light source, and means are provided for comparing the brightness of the beam which has passed through the spectral line with that of a beam which has passed through a clear part of the plate.

From the microphotometer reading, photographic density is computed by \[ D = \log \frac{I_0}{I} \], where \( I_0 \) is the light intensity of the measuring beam incident on the plate, and \( I \) that transmitted by the selected area on the plate. The measurements required are \( d \), the clear-plate reading; \( d' \), the reading through the area photometered; and \( d_0 \), the full opaque dark reading. Then,

\[
D = \log \frac{I_0}{I} = \log \left( \frac{d - d_0}{d' - d_0} \right) = \log \left( \frac{d - d_0}{d' - d_0} \right) \]

If \( I_0 \) and \( d_0 \) are constant, as they should be, they need to be checked only infrequently and \( d' \) need be observed only on individual lines.

The microphotometer used in this research has the following characteristics which maximize precision and facilitate measurements:

1. A constant voltage supply provides a constant temperature light source.
Figure 2. Microphotometer

B = Concentrated filament bulb at constant voltage
C = Condenser lenses
S₁ = Shield with 1 mm or 2 mm slit
P = Spectrogram mounted on sliding carriage
M = Micrometer screw which moves carriage

S₂ = Screen on which image of spectrogram is focused
Pc = Photocell mounted behind slot in screen
L = Projection microscope
G = Galvanometer

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2. The response of the photocell is linear.
3. The microphotometer slit has uniform illumination.
5. Freedom from scattered light.
7. Ease of plate adjustment.
8. Scale graduated in percent transmission.
9. Galvanometer adjustment of maximum deflection and zero deflection are rapid and simple.
10. The photocell has small fatigue.

Step Sector

For spectrographic quantitative analysis, it is necessary to know the relationship between the amount of incident light and the degree of blackening observed on the plate. The process for determining this relationship is called photographic plate calibration or simply plate calibration.

One common method of plate calibration involves the use of a step sector (see Figure 3). A step sector permits the slit to be illuminated with light which varies in intensity from one end of the slit to the other. Either a spectral or a continuous source may be used with the step sector method.

The step sector is a metal disk with portions removed which is rotated in front of the spectrograph slit. In practice, one adjusts the sector in front of the slit so that light is permitted to pass over the top of the sector as well as to pass through it. The light which
passes through the sector is attenuated by various amounts depending on the area of metal cut out. The light which passes over the top of the sector is, of course, unattenuated. For example, the sector used in this research allows 100% of the light to reach the slit, while the light which passes through the top step is 50% of the incident light, the light through the next step is 25% of the incident light, and so on. The sector used permitted eight different intensity values. The eight different attenuation factors are given in Appendix D.

Figure 3. Step-Sector
Source

The direct-current low voltage arc is a widely used source that combines high detection sensitivity with adequate reproductibility for quantitative analysis. The low voltage direct current arc was selected for this research instead of a high voltage (20,000 volts) spark because, although the high-voltage spark is generally more precise, it cannot detect low concentrations as well. The direct current circuit used in this analysis is shown in Figure 4.

A low-voltage arc can be ignited by momentarily bringing into contact the electrode tips, or by touching both with the tip of a third graphite rod having an insulated handle.

![Diagram of the D.C. Arc Source]

Figure 4. D.C. Arc Source

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SPECTROGRAPHIC ANALYSIS

Qualitative Analysis

The work by Kirchhoff and Bunsen (1860) constituted the first spectroscopic qualitative analysis. In their investigations of several new spectral lines they were led to the discovery of two new elements: cesium and rubidium. Continual improvement in techniques in the following century has made qualitative spectrographic analysis an extremely rapid and accurate method for identifying elements in a given sample.

Qualitative analysis with a spectrograph is a relatively simple process. A small sample of the material to be analyzed is placed in an electric arc, spark, or other suitable source of excitation so that when excited, the molecules of the sample will be disassociated into their constituent atoms which are then stimulated to emit their characteristic light. This light is sent through the spectrograph, which separates the various wavelengths and records these individually as spectrum lines on a photographic plate or film. Each chemical element emits a well-known group of lines whose wavelengths are recorded in wavelength tables which are printed in many spectroscopy books. Therefore, it is possible to measure the wavelength of an unknown spectral line and then refer to these tables to identify what element emitted that radiation. Although many wavelengths are emitted by each kind of atom, only one or two lines are needed to give positive identification of the element.
Quantitative Analysis

Quantitative analysis of materials by emission spectroscopy is frequently referred to as spectrochemical analysis. The spectrochemical method has many advantages over the traditional "wet" chemical method. These advantages are the small size of the sample that can be analyzed, the simplicity of the operations needed, the sensitivity available for determining very low concentration of material, the precision obtainable, and the speed with which the analysis can be completed.

Probably the greatest usefulness for spectrochemical methods arise in carrying out routine procedures where similar analyses are to be made on hundreds or thousands of samples, as in production composition control. Here the time and effort consumed in preparing standard samples and in setting up special procedures are soon returned in time saving compared to individual tests, and in consequent reductions of operating costs in plants and laboratories. In most of the metals industry and in many chemical laboratories, spectrochemical analysis is now a routine control process.

A fundamental concept of a quantitative spectrochemical analysis concerns the amount of radiation emitted by the atoms of an element in the sample. As a first approximation, one may anticipate that the radiation output from the atoms is directly proportional to the number of atoms of the element present. The total light output of an atom, however, may be influenced by the other elements which exist in the sample.
One of the most common methods of detecting this atomic radiation is to record it on photographic film (or plate) after it has passed through a spectrograph. Greater amounts of an element are recorded as darker spectral lines on the film. This photographic recording process is as follows:

When a photon of radiation is absorbed by a silver halide particle of the photographic emulsion, the radiant energy is stored in the form of a latent image. Treatment with a reducing agent (called a developer) results in the formation of a number of silver atoms for each absorbed photon. The number of black silver particles formed and thus the darkness of the exposed area, is a function of the exposure $E$, which is defined by:

$$E = I \cdot t$$

where $I$ is the intensity of radiation and $t$ is the exposure time. For quantitative purposes the exposure $t$ is held constant for both samples and standards. Under these circumstances, exposures are directly proportional to the line intensity and thus to the concentration of the emitting species. (Skoog and West, 1980)

Preparation for the Quantitative Analysis

Quantitative emission analyses demand precise control of the many variables involved in sample preparation and the excitation (and also in film processing with spectrograph). In addition, quantitative measurements require a set of carefully prepared concentration standards for calibration of the analysis technique. These calibration standards should approximate as closely as possible the composition and physical properties of the sample to be analyzed.
Internal Standard (Control)

The central problem in the quantitative emission analysis is the very large number of variables that affect the blackness of a spectral line on a photographic plate. Most variables that are associated with the excitation and the photographic processes are difficult to control. In order to compensate for their effect, an internal standard is generally employed.

An internal standard is an element incorporated in a fixed concentration into each sample and each calibration standard. The darkness of a chosen spectral line of the internal standard is then determined for each sample and standard. These measurements serve as standards of comparison for the spectral line darkening measurements of the analytical elements.

A ratio of the intensity of the analytical line to intensity of the internal control line is then employed for the concentration determination. It is found experimentally that a direct proportionality exists between this ratio and the concentration.

Some Properties of an Ideal Internal Standard

1. It should have the same concentration in samples and standards.
2. Its chemical and physical properties should be as similar as possible to those of the element being determined.
3. It should have an emission line that has about the same excitation and ionization energy as the one for the element being determined.
4. The lines of the standard (control element) should be similar in intensity and should be in the same spectral region as those of the analytical element.

It is seldom possible to find an internal standard element that will meet all of these criteria.

The element indium was chosen for the control element for this study because indium has two strong radiations at wavelengths 3256 Å and 3258 Å which are in close proximity to the copper wavelengths 3247 Å and 3274 Å. In addition, these indium radiations originate from electronic levels of four electron-volts, the same value as the copper radiations. Similarly, both the indium and the copper radiations terminate on lower levels near zero electron-volts. This similarity of the excitation levels enhances the likelihood that the ratio of the radiations will remain constant even if the direct current source voltage changes.

Photographic Emulsion Requirement

In order to reduce photometer errors it is desirable that the photographic emulsion used have small grain size, low chemical fog, and uniform sensitivity and contrast over a wide spectral range to avoid the necessity of more than one calibration curve. Also, low sensitivity to radiation is often desirable to permit long enough exposures for good sampling of the material.

The Kodak Spectrum Analysis No. 1 (SA1) Emulsion, developed especially for the spectrochemistry of metals, combines most of the desired properties of emulsions with rapid processing, made possible by a thin,
hard, gelatin layer. Nevertheless, whatever the emulsion used, a significant source of experimental error is the variability of silver bromide grain size in the emulsion which leads to variations in microphotometer reading in successive settings on the same line because of the difference in the number of grains included.

Errors also arise from variation in emulsion sensitivity from point to point on the plate. Since these errors tend to increase with distance, it is highly desirable to have the reference pair of lines close together on the plate, within a millimeter or two, if possible.

The Analytical Curve

In general, for quantitative analysis with the spectrograph, it is necessary to obtain an exposure on the photographic plate which is proportional to the light intensity, which in turn bears some fixed relation to the concentration of atoms in the arc. These data are plotted as logarithms because the logarithm of the exposure of the spectral line is proportional to the logarithm of the concentration of the variable to be determined.

In this research, the blackness of each of the chosen spectral lines on the photographic plate was measured with a microdensitometer. A calibration curve (see Figure 8) for the plate was then prepared to convert the blackness measurement of a spectral line to intensity (brightness) of that line. Finally, the analytical working curve was (see Figures 9 and 10) prepared by plotting the logarithm of the element concentration versus the logarithm of the intensity. All intensities of a line are given relative to the intensity of an internal standard line.
CHAPTER IV

Preparation of Samples and Analysis

The samples used in this research were rock samples provided by the Western Michigan University Geology Department. A preliminary investigation was made on a sample of granite rock to determine the detectability of some elements (vandium, molybdenum, and copper) of particular interest to geologists. Although vandium and molybdenum were present, the concentrations were very close to the threshold of detectability and therefore of limited usefulness for analysis. Copper, however, was readily detectable. The granite rocks selected for analysis were from the Pioneer Mountains of Idaho, and the element chosen for analysis was copper. It was hoped that after the completion of the analysis, some relationships could be established between the copper content of the various granite rocks and their original relative location in the ground area where they were mined.

Preparation of Standard Solutions for Analysis

A stock solution of copper was prepared by dissolving 1.252 grams of CuO (= 1.00 grams of copper) in 100 ml of water.

From this primary standard, five secondary standard solutions were prepared by using:

1 - 2 ml Cu from the standard = 20 mg Cu
2 - 0.4 ml Cu from the standard = 4 mg Cu
3 - 0.1 ml Cu from the standard = 1 mg Cu
4 - 0.04 ml Cu from the standard = 0.4 mg Cu
5 - 0.01 ml Cu from the standard = 0.1 mg Cu

A mass of 5.92 mg Indium was added to each of the standard solutions as an internal control. Water was added to make the volume of each solution 100 ml. The final concentrations of all copper standard solutions are given in Table 1.

**TABLE 1**
Concentration for the Copper Standard Solutions

<table>
<thead>
<tr>
<th>Standard No.</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 mg copper + 5.92 mg Indium in 100 ml</td>
</tr>
<tr>
<td>2</td>
<td>4 mg copper + 5.92 mg Indium in 100 ml</td>
</tr>
<tr>
<td>3</td>
<td>1 mg copper + 5.92 mg Indium in 100 ml</td>
</tr>
<tr>
<td>4</td>
<td>0.4 mg copper + 5.92 mg Indium in 100 ml</td>
</tr>
<tr>
<td>5</td>
<td>0.1 mg copper + 5.92 mg Indium in 100 ml</td>
</tr>
</tbody>
</table>
Electrodes and Sample-Support Devices

The electrodes and sample-support system used in this research are shown in Figure 5. This system consists of insulated Post A that supports counterelectrode $E_c$ and sample electrode $E_s$. A direct current potential of 340 volts exists between $V$ and $G$.

Types of Electrodes

A carbon arc is maintained by the carbon vapor boiling off from the tips of the graphite electrodes which conducts current across the gap between electrodes. The electrodes used were those shown in Figure 6.

These electrodes all have a 1/4 inch diameter. Electrode-pair A is most useful when only a very small amount of sample is available for analysis. The other electrode-pair B has flat ends and is useful for analyzing liquid samples. The liquid sample is usually dried on the flat end of both the upper and the lower electrode. On flat electrodes, the arc has a tendency to wander around the edge of the electrodes instead of staying centered. This tends to decrease the precision of the analysis. Spectrographic-grade rods, usually in 12-inch lengths, can be cut and shaped as desired. All tools used for graphite work, such as hacksaw blades, drill bits, files, etc., should be used exclusively for that purpose so that electrodes will not become contaminated with foreign substances.

Electrodes, lenses, and any other accessories required between the light sources and slit must be rigidly mounted on an optical bench fastened to the spectrograph so that they will remain fixed with respect
Figure 5. Sample-support System

A - insulated post
B - electrode holders
E_C - counterelectrode
E_S - sample electrode
V - wire to voltage source (+340 volts)
G - wire to the ground
Figure 6. Two Different Electrode-pair Shapes

to the spectrograph and to one another. The entire system is centered on the optical axis of the spectrograph which is the line through the midpoint of the slit and the dispersing element. The step sector (see Figure 3) is placed on the optical bench directly in front of the slit. The step sector attenuates the incident radiation to provide graduated exposure times for calibrating the photographic emulsion. The sector should rotate fast enough (nominally 600 rpm) to adequately sample the incident radiation.

Microphotometer Measurements

When the photographic emulsion is illuminated by light of intensity I for a length of time t and is developed (development, fixing, washing and drying), a certain degree of blacking is obtained. In order to give a numerical characterization to the blackening obtained,
the processed plate is illuminated by light of intensity $I_0$ and the value of light intensity $I$ after passing through the plate is measured. The photographic transmittance is the ratio of the intensity of the transmitted light to that of incident light.

$$T_p = \frac{I}{I_0} \quad (E1)$$

Compared to photographic transmittance, the $D$ blackening value (density) is the logarithm of the ratio of the intensity of incident light to that of transmitted light.

$$D = \log \frac{I_0}{I} \quad (E2)$$

By substituting $E1$ into $E2$, the following relationship between the photographic transmittance and the optical density can be established.

$$D = \log \frac{1}{T_p} = -\log T_p \quad (E3)$$

In order to establish the intensity ratio of the spectral lines from the photographic transmittance or blackening (density) value, one has to know the relationship between exposure $I \cdot t$ (light quantity) and $T_p$ or $D$. The spectral line density caused by the same amount of exposure is not independent of the values of $I$ and $t$. In the spectrographic evaluation, however, the same time factor always applies for the determination of the intensity of the spectral lines. Thus, the intensity ratio of the spectral lines depends exclusively on the relationship between light intensity $I$ and blackening for a constant time duration.

The relationship between the exposure or light intensity and the blackening is very complex. The physical and chemical processes involved are not clearly understood. These factors can only be dealt with at
best on a rather crude level of approximation. Thus, the exact relationship between the blackening and the intensity can only be established experimentally. If $T_p$, $1/T_p$ or $D$ is plotted versus the intensity, or the logarithm of the intensity, it will be seen that the simplest graph is one depicting the relationship between $D$ and $\log I$. This is because this graph (Figure 7) has a very useful linear portion for relating light intensities to film blackenings. More accurate intensity determinations can be made in this central region because the slope is changing less rapidly there.

An exponential relationship exists between the analytical concentration and the intensity of the spectral lines,

$$I = A \cdot c^h$$

where $I$ is the intensity of the line, $c$ is the concentration, $A$ and $h$ are constants. Since, this relationship becomes linear in a logarithmic scale ($\log c$ versus $\log I$), the relationship between the intensity of the lines and the analytical concentration becomes very simple in the linear portion of the plot $D$ versus $\log i$. This is why the step sector was used in order to get different amounts of light to vary logarithmically with the blackening.

Standards

After preparation of the five standard solutions (see Table 1), five pairs of electrodes in flat shape (see Figure 6) were prepared, which would be used in the analysis of the standard solutions. In order to prevent the liquid sample from penetrating into the supporting carbon, one drop of n-Heptane was placed on each electrode. Then, five drops
Figure 7. Typical Photographic Plate Emulsion Calibration Curve
from one of the standard solutions was added to each of two electrodes (five drops are approximately .15 ml). One pair of electrodes was prepared for each standard solution in this manner. Thus, the approximate amount of copper on each electrode from most concentrated to the least concentrated are:

\[
\begin{align*}
\text{20 mg Cu} & \quad (0.15 \text{ ml}) = 0.03 \text{ mg Cu} \\
\text{4 mg Cu} & \quad (0.15 \text{ ml}) = 0.006 \text{ mg Cu} \\
\text{1 mg Cu} & \quad (0.15 \text{ ml}) = 0.0015 \text{ mg Cu} \\
\text{0.4 mg Cu} & \quad (0.15 \text{ ml}) = 0.0006 \text{ mg Cu} \\
\text{0.01 mg Cu} & \quad (0.15 \text{ ml}) = 0.000015 \text{ mg Cu}
\end{align*}
\]

A heater at low temperature (approximately 150° C) was used to dry the standard solutions on the electrodes. It should be noted that it is not necessary to know the exact amount of copper added to each electrode because the measurements are only concerned with the ratio of the copper to indium. This ratio is the same for a given concentration, regardless of the number of sample drops or the size of the sample drops added.

**Samples**

Since the rock samples which were to be studied were in powdered form, a different technique of drying was used.

1. Digest a 20 mg rock sample with 5 drops of concentrated nitric acid (HNO₃) and 10 drops of concentrated hydrochloric acid (HCl)
2. Add (1 ml) of Indium internal control standard solution (concentration = 0.0037 mg In/ml).

3. Heat until dry and then mix the residue for uniformity.

4. Add the residue to a carbon electrode for analysis.

Exposure Time and Photographic Plate Processing

Three electrode-pairs were prepared for each standard solution and each rock sample. All standard solution electrodes and all rock sample electrodes were then subjected to the arc discharge for 20 seconds. The light from the discharge passed through the step sector and was dispersed by the spectrograph to form a spectrum on the photographic plate. The photographic plate was processed by a development for 3 minutes in Kodak D-19, followed by a 15 second stop bath and then 3 minutes in Kodak Rapid Fixer. The photographic plates were washed for 5 minutes in running water and rinsed in distilled water. (Additional photographic details are available in Appendix E).
CHAPTER V

Analysis of Samples

All of the samples prepared for analysis were burned in a direct current arc and the resulting spectrogram analyzed with a microphotometer to provide the average light intensity ratio values listed in Table 2 (summarized from raw data in Appendix A). Separate determinations were made using copper wavelength $3247 \, \text{Å}$ and copper $3274 \, \text{Å}$.

Table 2

Logarithms of the Average Light Intensity Ratios of the 10 Rock Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Log$_2$ Cu 3247 Å</th>
<th>Log$_2$ Cu 3274 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.420</td>
<td>-0.860</td>
</tr>
<tr>
<td>2</td>
<td>+1.700</td>
<td>+0.954</td>
</tr>
<tr>
<td>3</td>
<td>+0.830</td>
<td>-0.111</td>
</tr>
<tr>
<td>4</td>
<td>+1.330</td>
<td>+0.525</td>
</tr>
<tr>
<td>5</td>
<td>-0.337</td>
<td>-0.530</td>
</tr>
<tr>
<td>6</td>
<td>-0.361</td>
<td>-0.350</td>
</tr>
<tr>
<td>7</td>
<td>+1.430</td>
<td>+0.483</td>
</tr>
<tr>
<td>8</td>
<td>-0.288</td>
<td>-0.513</td>
</tr>
<tr>
<td>9</td>
<td>-0.430</td>
<td>-0.547</td>
</tr>
<tr>
<td>10</td>
<td>-0.154</td>
<td>-0.323</td>
</tr>
</tbody>
</table>

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All of the standard (known) concentrations were subjected to the same treatment and the resultant light intensity ratios are listed in Table 3.

Table 3

Logarithms of Light Intensity Ratios of Copper to Indium for the Standard Solutions

<table>
<thead>
<tr>
<th>Standards Concentrations in Parts Per Million</th>
<th>( \log_2 \left( \frac{\text{Cu} 3247 \text{ Å}}{\text{In} 3256 \text{ Å}} \right) )</th>
<th>( \log_2 \left( \frac{\text{Cu} 3274 \text{ Å}}{\text{In} 3256 \text{ Å}} \right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>625.000</td>
<td>+1.662</td>
<td>+1.436</td>
</tr>
<tr>
<td>125.000</td>
<td>+0.743</td>
<td>+0.336</td>
</tr>
<tr>
<td>31.250</td>
<td>-0.153</td>
<td>-0.715</td>
</tr>
<tr>
<td>12.500</td>
<td>-0.973</td>
<td>-1.157</td>
</tr>
<tr>
<td>3.125</td>
<td>-1.183</td>
<td>-1.471</td>
</tr>
<tr>
<td>1.250</td>
<td>-1.460</td>
<td>-1.795</td>
</tr>
</tbody>
</table>

The analytical curves (Figures 9 and 10) were prepared from the concentrations and the light intensity ratios obtained from the standard copper concentration data of Table 3. Using the analytical curves, Figure 9 and Figure 10, and Table 2 data the concentration in parts per million (ppm) was obtained for each of the unknown rock samples. These values are plotted in Figure 11 and Figure 12. The average values of the rock sample measurements are given in Table 4.
Table 4

Average Copper Concentrations for the 10 Rock Samples (in ppm)

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Geology Department Identification Number</th>
<th>Average Copper Concentration in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>829</td>
<td>21</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>310</td>
</tr>
<tr>
<td>3</td>
<td>834</td>
<td>78</td>
</tr>
<tr>
<td>4</td>
<td>830</td>
<td>185</td>
</tr>
<tr>
<td>5</td>
<td>20C</td>
<td>32</td>
</tr>
<tr>
<td>6</td>
<td>24C</td>
<td>39</td>
</tr>
<tr>
<td>7</td>
<td>831</td>
<td>170</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>35</td>
</tr>
<tr>
<td>9</td>
<td>18</td>
<td>29</td>
</tr>
<tr>
<td>10</td>
<td>23C</td>
<td>46</td>
</tr>
</tbody>
</table>
CHAPTER VI

Conclusion

The geological rocks which were analyzed in this investigation were from the Pioneer Mountains of central Idaho. In general the samples were classified as granite rocks with a high iron, potassium and calcium content (additional geological details concerning the origin of the samples are available in Appendix C). Useful knowledge about the geological history of such samples may be obtained by monitoring the variation in concentration of certain elements such as copper and molybdenum. In the preliminary spectrographic analysis of the selected rock samples, the copper concentrations were great enough to be easily detected. The concentrations of the element molybdenum, however, were near or below the threshold of detection. Since either element can provide a geologist with similar information, this research is concerned with the quantitative spectrographic analysis of granite rock specimens for their relative copper content.

The samples were prepared by digesting the rock powder in nitric acid and drying the residue on high purity carbon electrodes. The samples were then burned in an electric arc and the emitted light was passed through a spectrograph to be recorded on film. The relative light intensities were then evaluated on a microphotometer and the values recorded in Table 2.

These light intensity values were then compared to the copper analytical curves of Figure 9 and Figure 10 which relate copper concentration to relative light intensities.

31
The validity of these concentrations may be evaluated by carrying out a similar analysis on standard rock samples. The relative light intensity values for these samples are given in Table 5 (summarized from Appendix B). The spectrographic concentration values obtained for these standard samples (using copper wavelength 3274 Å) are plotted versus the nominal values (Flanagan, 1967) specified for these standard samples. (See Figure 13.)

This comparison suggests good relative agreement among the measurements on these standard samples. Since the copper concentrations are very low (parts per million), differences in absolute values are expected because of inhomogeneities in the pulverized rock standards.

The range of copper concentration in the ten rock samples from 20 ppm to 310 ppm (see Table 4) represent uneconomical values in reference to the future economic development of this prospect. The relatively higher concentrations from samples 2, 4 and 7 most likely represent effects of secondary enrichment of metals in a weathered horizon within the rock body.

The relative copper concentration information obtained on these ten Idaho samples supplements data on other chemical elements from the Pioneer Mountain region (Hanna, 1983).
TABLE 5

Copper Concentration in the Geological Rock Standard Samples as Determined from Figure 9 (Copper $\lambda = 3247$ Å Data) and From Figure 10 (Copper $\lambda = 3274$ Å Data)

Using Copper Wavelength $\lambda = 3247$ Å for Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Copper Concentration in (ppm)</th>
<th>Flanagan (1967)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGV-1</td>
<td>204</td>
<td>(50-83) ppm</td>
</tr>
<tr>
<td>GSP-1</td>
<td>102</td>
<td>(8-54) ppm</td>
</tr>
<tr>
<td>BCR-1</td>
<td>71</td>
<td>(7-31) ppm</td>
</tr>
</tbody>
</table>

Using Copper Wavelength $\lambda = 3274$ Å for Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Copper Concentration in (ppm)</th>
<th>Flanagan (1967)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGV-1</td>
<td>190</td>
<td>(50-83) ppm</td>
</tr>
<tr>
<td>GSP-1</td>
<td>88</td>
<td>(8-54) ppm</td>
</tr>
<tr>
<td>BCR-1</td>
<td>16</td>
<td>(7-31) ppm</td>
</tr>
</tbody>
</table>

Copper Concentration in (ppm) Figure 9/Figure 10 Average Values Flanagan (1967)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Copper Concentration in (ppm)</th>
<th>Flanagan (1967)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGV-1</td>
<td>197</td>
<td>(50-83) ppm</td>
</tr>
<tr>
<td>GSP-1</td>
<td>95</td>
<td>(8-54) ppm</td>
</tr>
<tr>
<td>BCR-1</td>
<td>44</td>
<td>(7-31) ppm</td>
</tr>
</tbody>
</table>
Figure 8. Photographic Plate Emulsion Calibration Curve
Figure 9. Analytical Curve

A semilog plot of copper concentration in parts per million versus the logarithm of the ratio of the intensity of the copper 3247 A spectral line relative to the intensity of the indium 3256 A spectral line.
Figure 10. Analytical Curve

A semilog plot of copper concentration in parts per million versus the logarithm of the ratio of the intensity of the copper 3274 Å spectral line relative to the intensity of the indium 3256 Å spectral line.

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Figure 11. A semilogarithmic graph of the rock concentration of copper in parts per million with error bars plotted versus the logarithm of the relative intensity of the copper 3247 Å line compared to the indium 3256 Å line. These data are superimposed on the analytical curve of Figure 9.
Figure 12. A semilogarithmic graph of the rock concentrations of copper in parts per million with error bars plotted versus the logarithm of the relative intensity of the copper 3274 Å line compared to the indium 3256 Å line. These data are superimposed on the analytical curve of Figure 10.
Figure 13. Relative copper concentrations in parts per million obtained in this research for three standard rocks plotted versus the nominal values of copper cited in the literature (Flanagan, 1967).
### APPENDIX A

#### Sample Log Ratio Values

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \log_{2} \left( \frac{\text{cu3247 A}}{\text{In3256 A}} \right) )</th>
<th>( \log_{2} \left( \frac{\text{cu3274 A}}{\text{In3256 A}} \right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.230</td>
<td>-0.600</td>
</tr>
<tr>
<td></td>
<td>-0.600</td>
<td>-1.000</td>
</tr>
<tr>
<td></td>
<td>-0.420</td>
<td>-1.000</td>
</tr>
<tr>
<td>Average</td>
<td>-0.420</td>
<td>-0.860</td>
</tr>
<tr>
<td>2</td>
<td>+1.800</td>
<td>+0.933</td>
</tr>
<tr>
<td></td>
<td>+1.433</td>
<td>+0.930</td>
</tr>
<tr>
<td></td>
<td>+1.860</td>
<td>+1.000</td>
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<tr>
<td>Average</td>
<td>+1.700</td>
<td>+0.954</td>
</tr>
<tr>
<td>3</td>
<td>+1.025</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>+0.600</td>
<td>-0.200</td>
</tr>
<tr>
<td></td>
<td>+0.866</td>
<td>+0.033</td>
</tr>
<tr>
<td>Average</td>
<td>+0.830</td>
<td>-0.111</td>
</tr>
<tr>
<td>4</td>
<td>+1.300</td>
<td>+0.250</td>
</tr>
<tr>
<td></td>
<td>+1.275</td>
<td>+0.850</td>
</tr>
<tr>
<td></td>
<td>+1.425</td>
<td>+0.475</td>
</tr>
<tr>
<td>Average</td>
<td>+1.330</td>
<td>+0.525</td>
</tr>
<tr>
<td>5</td>
<td>-0.300</td>
<td>-0.550</td>
</tr>
<tr>
<td></td>
<td>-0.375</td>
<td>-0.525</td>
</tr>
<tr>
<td>Average</td>
<td>-0.337</td>
<td>-0.530</td>
</tr>
<tr>
<td>6</td>
<td>-0.283</td>
<td>-0.100</td>
</tr>
<tr>
<td></td>
<td>0.000</td>
<td>-0.050</td>
</tr>
<tr>
<td></td>
<td>-0.800</td>
<td>-0.900</td>
</tr>
<tr>
<td>Average</td>
<td>-0.361</td>
<td>-0.350</td>
</tr>
<tr>
<td>7</td>
<td>+1.100</td>
<td>+0.250</td>
</tr>
<tr>
<td></td>
<td>+2.000</td>
<td>+1.200</td>
</tr>
<tr>
<td>Average</td>
<td>+1.430</td>
<td>+0.483</td>
</tr>
<tr>
<td>8</td>
<td>-0.366</td>
<td>-0.566</td>
</tr>
<tr>
<td></td>
<td>-0.375</td>
<td>-0.550</td>
</tr>
<tr>
<td></td>
<td>-0.125</td>
<td>-0.425</td>
</tr>
<tr>
<td>Average</td>
<td>-0.288</td>
<td>-0.513</td>
</tr>
<tr>
<td>Sample</td>
<td>( \frac{\text{Log}_2 \text{Cu3247}^0 \text{ Å}}{\text{In3256}^0 \text{ Å}} )</td>
<td>( \frac{\text{Log}_2 \text{Cu3274}^0 \text{ Å}}{\text{In3256}^0 \text{ Å}} )</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>9</td>
<td>-0.075</td>
<td>-0.325</td>
</tr>
<tr>
<td></td>
<td>-0.800</td>
<td>-0.775</td>
</tr>
<tr>
<td>Average</td>
<td>-0.430</td>
<td>-0.547</td>
</tr>
<tr>
<td>10</td>
<td>-0.183</td>
<td>-0.383</td>
</tr>
<tr>
<td></td>
<td>-0.233</td>
<td>-0.366</td>
</tr>
<tr>
<td></td>
<td>-0.050</td>
<td>-0.225</td>
</tr>
<tr>
<td>Average</td>
<td>-0.154</td>
<td>-0.323</td>
</tr>
</tbody>
</table>
### APPENDIX B

**Standard Sample Log Ratio Values**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Log₂ cu3247 Å</th>
<th>Log₂ cu3274 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGV-1</td>
<td>+0.85</td>
<td>+0.20</td>
</tr>
<tr>
<td></td>
<td>+1.10</td>
<td>+0.55</td>
</tr>
<tr>
<td></td>
<td>+1.10</td>
<td>+0.40</td>
</tr>
<tr>
<td>Average</td>
<td>+1.01</td>
<td>+0.38</td>
</tr>
<tr>
<td>GSP-1</td>
<td>+0.50</td>
<td>-0.20</td>
</tr>
<tr>
<td></td>
<td>+0.57</td>
<td>-0.12</td>
</tr>
<tr>
<td>Average</td>
<td>+0.53</td>
<td>-0.16</td>
</tr>
<tr>
<td>BCR-1</td>
<td>+0.10</td>
<td>-0.90</td>
</tr>
<tr>
<td></td>
<td>+0.50</td>
<td>-1.30</td>
</tr>
<tr>
<td>Average</td>
<td>+0.30</td>
<td>-1.10</td>
</tr>
</tbody>
</table>
APPENDIX C

Abstract of Western Michigan University
Geology Masters Thesis by Thomas Hanna

[This thesis provides information concerning the geological origin of
the sample rocks (Hanna, 1983).]

THE GEOLOGY AND GEOCHEMISTRY OF THE SUMMIT CREEK
MOLYBDENUM PROSPECT, CUSTER COUNTY, IDAHO

Thomas Murray Hanna, M.S.
Western Michigan University, 1983

The Summit Creek stock, a molybdenum prospect located in the
Pioneer Mountains of central Idaho, is a 46.7 m.y. old medium grained,
slightly porphyritic quartz monzonite, which has intruded the late
Ordovician Phi Kappa formation. Trend surface analysis shows that the
stock is the product of one intrusive event. Pervasive mineral alteration
usually associated with such porphyry (stockwork) molybdenum deposits
is not present in this pluton, and the alteration that is present is
confined to local faults and fractures.

Geochemical and petrographic evidence suggest that the pluton is a
felsic differentiate from a melt which originated at a depth of 220-260
kilometers along an east-dipping subduction zone. Whole rock major
element geochemical analysis indicates that the stock is a high potassium
calc-alkaline intrusion. Trace element analysis shows similarities to
other stocks associated with economic molybdenum deposits. In addition,
chemical analysis of argillic assemblages are similar to those of
porphyry molybdenum deposits.
APPENDIX D

The Percentage of Incident Light Transmitted Through Each Step of the Step Sector

<table>
<thead>
<tr>
<th>Step No.</th>
<th>The Percentage of Incident Light Transmitted Through Each Step of the Step Sector</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100.00%</td>
</tr>
<tr>
<td>1</td>
<td>50.00%</td>
</tr>
<tr>
<td>2</td>
<td>25.00%</td>
</tr>
<tr>
<td>3</td>
<td>12.50%</td>
</tr>
<tr>
<td>4</td>
<td>6.25%</td>
</tr>
<tr>
<td>5</td>
<td>3.125%</td>
</tr>
<tr>
<td>6</td>
<td>1.56%</td>
</tr>
<tr>
<td>7</td>
<td>0.78%</td>
</tr>
<tr>
<td>8</td>
<td>0.39%</td>
</tr>
</tbody>
</table>

Since the light for each larger step increases by a factor of 2, it is convenient to use logarithms to the base 2 to represent the relative light transmitted.
APPENDIX E

The Photographic Process

Photographic image formation rests not only on the fact that the silver halides are photosensitive, but also on the fact that the action of light on silver halide crystals produces a latent effect which may remain for days, or even years, and which makes it easier to liberate silver from the compound in the area where it has been acted on by light than in the area where this action has not occurred. This liberation is performed by suitable reducing agents or developers, which leave metallic silver in the form of the image; the unreduced silver halide is removed by the aid of a solvent or fixer, usually sodium thiosulphate (sometimes called "hypo").

In practice, the light-sensitive salts are used in the form of an emulsion, a suspension of these small crystals in gelatin, which holds the crystals in position and is transparent to light for a wide range of wavelengths. The emulsion is spread in a thin layer on a support (commonly glass, cellulose-ester film, or paper). The gelatin film, when wet, swells only in the direction perpendicular to the support; the swelling is several times the original thickness. The swollen gelation is readily permeable by water and water solutions, such as developer and fixer, and so is easily processed. Finally, when dry, the gelatin returns to almost exactly its original form and position. All these properties make it a nearly ideal medium for photographic purposes.
Development

As has been pointed out, photographic development is essentially the reduction to metallic silver of the activated silver halide grains of the latent image. The reducing agents used at present are almost exclusively organic compounds, but satisfactory developing formulae contain, in addition to organic reducing agents, preservative, accelerators, restrainers, and, sometimes, special compounds such as hardeners, clarifiers, toning agents, or grain-size reducers. The most common of these are: pyrogallol (pyro), glycine, hydroquinone, metol (elon), p-phenylenediamine, and p-amino-phenol.

The developer which was used in this research was Eastman Kodak D-19. The composition of the developer D-19 is: water (about 50°C)-2.0 liters; metol or elon (Methylaminophenol sulfate)-8.8 grams; Kodak sodium sulfite-384.0 grams; desiccated hydroquinone-35.2 grams; sodium carbonate monohydrate-192.0 grams; potassium bromide-20.0 grams; cold water to make 4.0 liters.

The active agents are metol and hydroquinone—generally known as M.Q., for short. A particular advantage of the M.Q. combination is that it does not stain the gelatin, which would cause trouble in densitometry.

The function of the sulfite is to combine with the oxidation products and to keep the solution stain-free. The carbonate controls the pH of the solution, which in turn controls the ionization of the developing agents and hence, the rate of the reaction. Development action stops completely in an acid medium. The bromide is added to
reduce the build-up of fog. It also slows the rate of development, but its main function is to suppress fog.

The average time of development in a tray is about 3 minutes at 20.0°C.

Fixing, Washing, and Drying

On completion of development, the plate is transferred to the short-stop, a water rinse acidified to about 1% with acetic acid. After a 15 second rinse, the plate is transferred to the hypo bath, where it remains for double the time needed to clear it of the mildly unexposed silver halide deposit. Room lights may be turned on soon after the alkali of the developer has been neutralized.

The composition of the standard fixing bath (Kodak F-5) is as follows: water-(about 50°C)-1.2 liters; Sodium thio-sulfate (hypo)-480.0 grams; Sodium sulfite, anhyd-30.0 g; Acetic acid-18%-96.0 cc; Boric acid, crystalline-15.0 g; Potassium alum-30.0 g; cold water to make 2.0 liters.

The active agent is the thiosulfate, which forms soluble complexes with the residue silver halide. Alum hardens the gelatin and, to prevent the precipitation of aluminum salts, the solution must be buffered on the acid side, which is the function of the boric acid. The small amount of sulfite acts as a preservative of the hypo.
Washing

After fixing, the plate must be washed to remove all soluble salts, a matter of 5-10 minutes if permanency of image is not required, or at least 30 minutes for permanency.

Drying

Drying should be at a uniform rate; uneven drying is a cause of density changes. Photographic plates in this research were dried vertically in a rack at room temperature, about 22°C.
BIBLIOGRAPHY

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