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VARIATION IN GOLD CONTENT OF MINERALS OF THE MARYSVILLE QUARTZ DIORITE STOCK, MONTANA

BY

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A

DISSERTATION

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Dr. A. H. Brownlow Dissertation Supervisor

ABSTRACT

The purpose of this thesis was to study the amount and distribution of gold in the minerals of the Marysville quartz diorite stock, Montana. Twenty-eight rock samples were collected from various parts of the Marysville Stock, using a NS-EW grid sample pattern. Thirty additional samples were collected from selected localities and from the vicinity of the gold mines which occur around the periphery of the stock.

By use of a hand magnet and a Frantz isodynamic separator, the magnetite, biotite, hornblende, and quartz-feldspar portions of the various rock samples were isolated and purified to between 90-99 percent purity. Eighteen thin sections of selected samples were made and studied.

Because of the small quantity of gold believed to be present in the samples, neutron activation was chosen as the method of analysis. A non-destructive method of activation analysis was established because of the time saved in analyzing a large number of samples. Activation and counting procedures were carried out by use of a swimming pool reactor and 400 channel pulse height analyzer located at the University of Missouri at Rolla. Samples were compared with a granite standard. Analytical data were compiled, programmed and calculated using the Fortran statement method. A total of 44 biotite samples, 37 hornblende samples, 44 magnetite samples, 10 quartz-feldspar samples, and five whole rock samples were analyzed.

Nineteen samples were chosen at random and rerun to obtain an estimate of precision for the method of analysis. The average deviation from the mean of the duplicate values is ± 34 percent. The accuracy of the method is unknown because of the lack of rock and mineral standards with known values of gold. The results show slightly higher gold values in the minerals as compared to previously reported values for igneous rocks.

The following results were obtained. The gold content of the biotites ranged from 0.002 - 0.924 ppm and averaged 0.076 ppm; for the hornblendes, 0.003 - 0.823 ppm and averaged 0.100 ppm; for the magnetites, 0.002 - 0.329 ppm and averaged 0.037 ppm; for the quartz-feldspar, 0.006-0.176 ppm and averaged 0.065 ppm; for the whole rock, 0.004 - 0.089 ppm and averaged 0.034 ppm.

The gold values were plotted and contoured on the Marysville Stock and indicate a tendency for the gold to be concentrated in the mine areas, generally in the southern portion of the stock. The biotite and hornblende results show a very strong concentration in the Drumlummon Mine area, the highest gold-producing area.

The concentration of gold in the various minerals does not appear to be an ionic substitution between diadochic elements, but rather an entrapment of the gold, which is a function of the chronological sequence of mineral crystallization and of the types of crystal lattice. The concentration of the gold in the various minerals closest to the mine areas and the existence of a finer-grained quartz diorite in the central portion of the stock seems to indicate a cooling trend of the Marysville magma from the interior, enriching the residual fluids in gold toward the stock's periphery. Hence, the results seem to indicate a genetic relationship of the gold with the Marysville Stock, which supports Barrell's (1907) theory of origin for the gold deposits.

When the minerals from the Marysville Stock were compared with minerals from a gold-producing quartz monzonite at Searchlight, Nevada, and from a non-producing granite in Rhode Island, the results indicated that the Marysville Stock at the present time contains about the same amount of gold as the other two igneous bodies. However, it is believed that the original gold content of the Marysville magma was much higher than that for the other two.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

CHAPTER I

INTRODUCTION

A. Purpose and Scope of Investigation

This work is concerned with trace element analysis of minerals of the Marysville quartz diorite stock. The principal objective of this investigation was to determine the amount and variation of gold in the biotite, hornblende, magnetite, and quartz-feldspar of rock samples from various parts of the intrusive. A second objective was to determine if a relationship existed between the gold content of the minerals and their proximity to the gold mines located around the periphery of the stock.

In order to carry this out, it was necessary to establish a sensitive and fairly precise method of analysis for trace amounts of gold in the major minerals of igneous rocks. Neutron activation analysis was selected for this work. A non-destructive method of activation analysis was used because of the time saved in analyzing a large number of samples.

Twenty-eight rock samples were collected from various parts of the stock by use of a grid sample pattern. Thirty additional samples were collected from the vicinity of the mines and from the periphery of the stock. From each rock sample the major minerals were separated and purified. Gold analysis was carried out on 44 biotite samples, 37 hornblende samples, 44 magnetite samples, 10 quartz-feldspar samples, and five whole rock samples. Analysis of a few mineral samples from other areas was also completed.

Seventeen representative thin sections of the Marysville Stock were studied to determine variation in mineral content and general mineral relationships.

B. Location of Area

The Marysville Stock is situated in the Lewis and Clark Range of the Northern Rockies. On the Marysville, Montana 7' quadrangle map, the stock lies between 112° 18' - 112° 21' W. longitude and 46° 44' - 46° 47.5' N. latitude and occurs in sections 27, 34, 35 and 36 of T 12 N, R 6 W and in sections 1 and 2 of T 11 N, R 6 W. It is located in Lewis and Clark county, approximately 20 miles N.W. of Helena, the state capitol of Montana. Marysville can be reached from Helena by going approximately 8 miles north on Highway 91, 10 miles W - NW on Highway 279 and 6 miles due West on a dirt road (Figure 1).

C. Collection of Samples

Fifty-eight rock samples were collected during the summer of 1963 from the Marysville Stock and surrounding rocks. These samples consisted of 48 quartz diorites, 38 coarse-grained and 10 fine-grained; three porphyries, two of which Barrell (1907) describes as the Drumlummon and

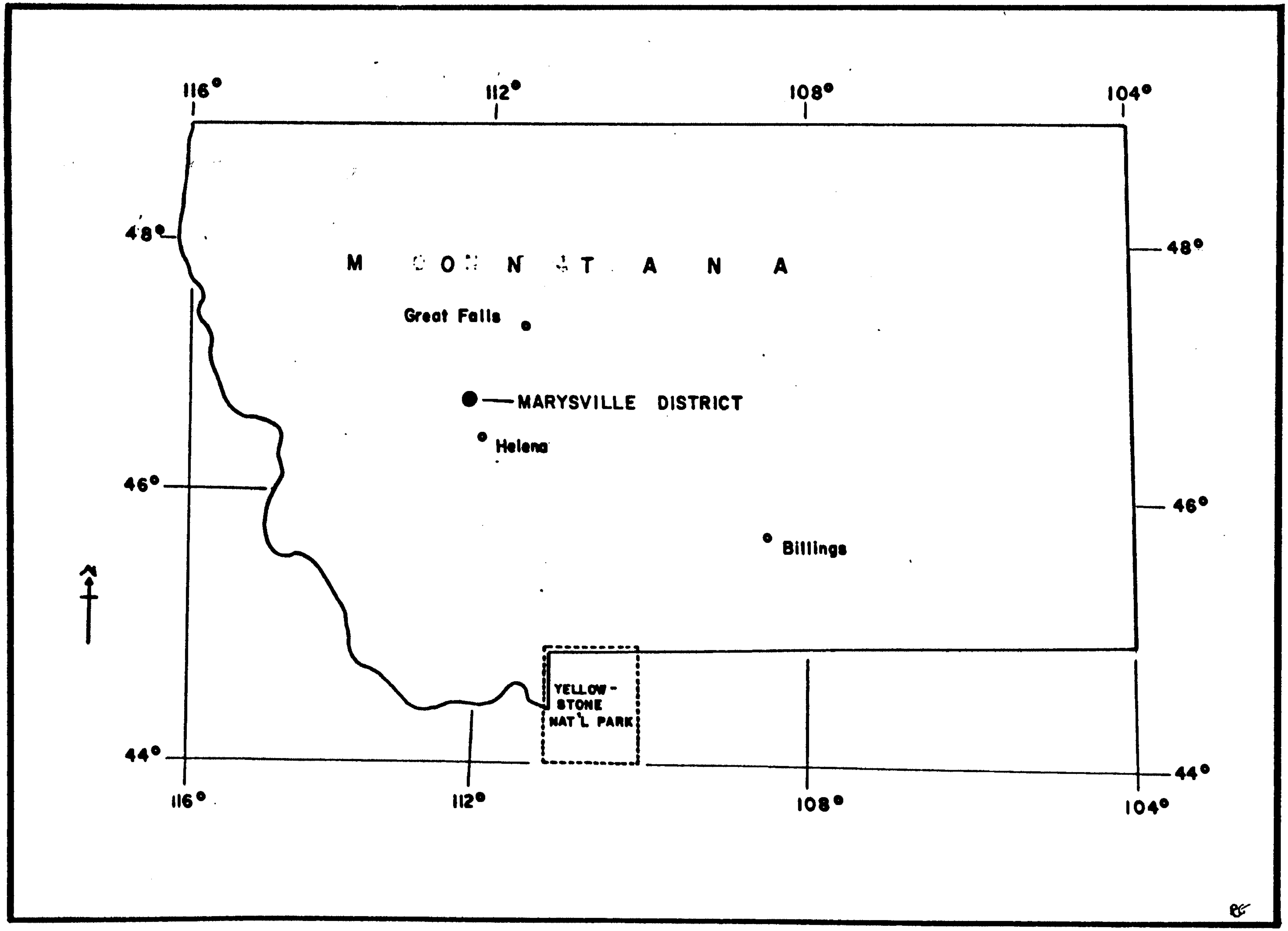

Fig. I INDEX MAP OF AREA 0 100 mi.

Belmont porphyries; one microdiorite; two microgabbros; one diabase; and three quartz diorite rubble samples. All samples except the three rubble samples were collected from outcrops.

A NS - EW grid pattern was established across the stock, and 28 outcrop samples were collected along this pattern at approximately 1,300 foot intervals (Plate I). Three additional samples were collected within 500 feet of each of the Belmont and Cruse mines, and 4 additional samples from the Drumlummon Mine. Two isolated quartz diorite samples were collected outside the stock. Five quartz diorite samples were taken at the contact between the quartz diorite and surrounding metamorphics, inside the stock but off the grid system.

The Brunton compass and pace method was employed for measurement and direction. Some samples were collected slightly off the grid points because of the lack of outcrops at many of the selected grid positions. If an outcrop did not appear in a radius of about 400 feet from the grid point, a bedrock sample was not collected. On three occasions, no outcrop was observed within this limiting radius, hence, nearby rubble samples were collected instead.

In order to obtain a fresh representative sample from an outcrop, the weathered portion of the outcrop was broken off and a relatively unweathered sample of 2-4 pounds was taken. The particles of these samples ranged from larger than a hand specimen to pieces 1-2 inches in diameter. A geologic hammer was used to obtain samples and in some cases a steel wedge was employed to help loosen the material. The samples were then wrapped in paper bags and labeled.

D. Laboratory Methods

Separation of magnetite, biotite and hornblende was carried out on the rock samples. By using a small hand magnet, the magnetite was extracted from the pulverized sample. By employing a Frantz isodynamic separator, the biotite and hornblende were extracted and separated. Details are given in Chapter IV, C.

A semi-quantitative spectrographic analysis was used to check for possible traces of silver and gold in seven reconnaissance samples. The magnetite, biotite, and hornblende of each sample was arced along with standards containing a number of elements in concentrations from 5 - 5000 ppm. Traces of silver below 5 ppm were observed in many samples along with possible minute amounts of gold. The gold 2427.95Å line and the silver 3280Å line were used for analysis.

In order to get high sensitivity in the determination of the very small amounts of gold and silver present in the minerals, neutron activation was chosen as the method of analysis. Other advantages of this method are speed and preservation of the sample. Very little work has been published on the use of this method to measure gold and silver in minerals. The method has been used for analyses of rocks and meteorites. A neutron flux and flux time had to be established in order to give satisfactory sensitivity for the trace elements while also eliminating the interference of the undesired minor and major elements. Further, a "cooling down" period was needed in order to calculate the half lives of the various elements as well as to permit the interfering elements to decay. It was found later that what was thought to be the 0.88 mev silver γ peak was actually the 0.89 mev peak of scandium. This was accomplished by setting up a more accurate half-life chart on the peak. A half life value of 89 days was obtained instead of the silver 249-day half-life. Some of the scandium is primary and some produced possibly by the β^- decay of Ca^{45}.

The analytical work was carried out using the nuclear reactor and associated equipment on the campus of the University of Missouri at Rolla. Details of this work are given in Chapter IV, D.

Thin sections of a number of the samples were studied. The results of this work are given in Chapter III, D.

E. Acknowledgments

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To the other members of the geology and chemistry staffs at the University of Missouri at Rolla and to those who have helped him in any way, the author expresses his gratitude.

CHAPTER II

REVIEW OF LITERATURE

A. Thesis Area

The first published report on the gold mines of the Marysville district was written by Weed (1903). He briefly describes the geology of the area and states that the vein systems around the edge of the stock show three distinct directions: NE, NW, and NS.

The major contributions concerning the Marysville mining district have been made by Barrell (1907) and Knopf (1913, 1950). Using field studies and petrographic, chemical, and mineralogical analyses, Barrell published an exhaustive report on the Marysville stock and the surrounding metamorphic rocks. This is now considered a classic paper in geology because of Barrell's emphasis on the distinction between contact metamorphism and contact metasomatism. Barrell concluded that the Marysville stock is probably an outlier of the Boulder batholith. The associated precious-metal veins he thought to have been produced by contraction effects on the margin of the stock and to have been filled by mineral matter deposited from emanations released from the solidifying magma. From petrographic studies, Barrell concluded that the stock was a quartz diorite. He noted further that within the stock two types of quartz diorite occur. The normal type is a fairly coarse-grained rock, very uniform in appearance and containing hornblende and biotite in equal amounts. The second phase is somewhat finer-grained and has a lesser portion of hornblende and biotite. Knopf (1913) stated that although the stock is an outlier of the Boulder batholith, the geographically associated gold-silver veins are not genetically allied to the stock and differ greatly in their principal features from the deposits genetically related to the batholith. Knopf mentions no definite contact or transition of a finer- and coarser-grained rock within the stock but considered the stock to be a medium-grained quartz diorite composed essentially of andesine, quartz, orthoclase, biotite, and hornblende.

Very little scientific work was done on the gold mines of the Marysville area in the period from 1913-1933. Pardee and Schrader (1933) accepted the idea that the Marysville veins were formed during an epoch of ore deposition that was later than the mineralization accompanying the cooling of the Boulder Batholith, but maintained that the veins are genetically related to the Marysville Stock. Thus, they felt that the stock is not an outlier of the Boulder Batholith.

Additional studies have been made of the Marysville stock by Knopf (1950). He described the stock, its contact aureole, and the surrounding rocks. Further evidence obtained during more recent detailed investigation of the region supported Knopf's original 1913 theory. In this report, Knopf changed his original rock name for the stock from quartz diorite to granodiorite but gave no explanation. Included is a compilation of previous work and of the major theories for the origin of the gold deposits.

Wolle (1964) compiled an interesting "Guide to Mining Camps of the Treasure State". She discusses the history and development of every mining camp in Montana with interesting sketches of each mining area, including Marysville.

B. Neutron Activation Analysis

Many papers have been published since 1949 discussing the various aspects of activation analysis. The major reviews and papers pertinent to this work will be mentioned here. Meinke (1955) discusses activation analysis in terms of trace element sensitivity and compares the method with other analytical methods. An article on "How to Minimize Errors in Neutron Activation Analysis" by Plumb and Lewis (1955) explains the major sources of error of the method, including incomplete chemical separations, radioactive contaminations in the carrier, errors in activation due to competing transmutations, flux inhomogeneties, and self absorption. Connally (1956) discusses instrumental methods of X-ray spectrometry and emphasises the γ scintillation spectrometer. "Methods of Geochemistry" by Smales and Wager (1960) contains two excellent chapters dealing with activation analysis. One chapter is on "Radiochemical Methods" by S. Moorbath and the other is on "Radioactive Analysis" by D. Mapper. They discuss the various aspects of activation analysis and their application to geochemistry. Tables of the nuclides according to their gamma energies and half-lives have been listed by Crouthamel (1960). An article in Industrial Research written by Guinn (1964) gives a concise outlook of the uses of activation analysis in the various branches of science and engineering. "A Guide to Activation Analysis" by Lyons (1964) is an excellent compilation of information presented in text book form.

C. Trace Metal Studies

An activation analysis study on 45 meteorites by Goldberg, Uchiyama and Brown (1951) showed the gold content to range from 0.5-2 ppm. A chemical and radioactivation method for gold in igneous rocks using activation analysis was developed by Vincent and Smales (1956). Vincent and Crockett (1960), working on basic and ultramafic rocks along with stony meteorites, used the same procedure but modified it slightly. Using a chemical separation, they found 0.1-10 ppm gold in most rock samples, with no notable preference of that element to concentrate in any silicate mineral. Vincent and Crockett (1960a) made a study of the gold content of the rocks and minerals of the Skaergaard intrusion of East

Greenland. They believe the initial magma contained 0.0046 ppm gold, the content found in a chilled marginal gabbro. Most of the other results were between half and twice this amount. A study on gold contents of rocks by DeGrazia and Haskin (1964) gives a procedure of analysis plus results for gold content in various rock types. The spread in gold concentrations was found to be relatively narrow, between 0.6 and 44 ppb for a fairly wide variety of samples. A crustal gold abundance of about 2.5 ppb is indicated. Baedecker and Ehmann (1965) have studied the distribution of gold, iridium and platinum in meteorites and natural materials. Platinum is more concentrated in the chrondrites, followed by iridium and then gold. Results are shown for concentration of these elements in achondrites, siderites, tektites, and some deep sea sediments. A small article on the gold content of the standard granite G-1 is given by Sarma, Sen, and Chowdhury (1965). The gold values reported by various investigators range from 0.0045 ppm to 0.0112 ppm. Goldschmidt (1954) approximated the gold content in magmatic rocks to be 1 ppb. Rankama and Sahama (1955) state that gold is enriched in the late magmatic products and state that the abundance of gold in igneous rocks appears to be about 6 ppb.

Base metals in biotites of monzonitic rocks associated with ore deposits were studied by Parry and Nackowski (1960). Results showed a copper content from 26-4600 ppm. They concluded that the high concentrations of copper in biotites probably represents not only biotite lattice substitution but also chalcopyrite inclusions. Theobald and Havens (1960) discuss base metals in biotite and magnetite and their alteration products in a hydrothermally altered quartz monzonite porphyry. In the unaltered rock, the copper, lead, and zinc are in the magnetite and to a lesser degree in the biotite. As the biotite alters, the base metal content decreases, while the copper, lead, and zinc content in the magnetite varies little with alteration. Theobald and Havens observed the base metals in the rocks to be enriched near strongly mineralized areas. Putman and Burnham (1960) analyzed spectrographically biotites from 223 rock samples. Results showed that the areas of known copper mineralization are reflected in anomalously high copper content of the associated plutonic bodies.

CHAPTER III

GEOLOGY OF AREA

A. Geologic Setting

According to Barrell (1907), the history of the Marysville district opens with the subsidence of a basin in the late Precambrian. Within this down-warping basin was deposited between 11,000-12,000 feet of sediment called the Belt Group and consisting of the Greyson-Spokane Formation, Empire Shale Formation, Helena Limestone Formation, and Marsh Shale Formation listed in chronological order from oldest to youngest.

The period of sedimentation was followed by warping, which brought portions of the formations within the reach of erosion. The erosion was sufficient enough to reduce the region to an advanced stage of peneplanation before the transgression of the Middle Cambrian sea. Barrell considered the age of the entire Belt Group to be Precambrian because of the length of the erosion interval, along with the absence from the Belt rocks of the characteristic Lower Cambrian fauna.

Whatever Paleozoic and Mesozoic formations were once deposited in the Marysville area have now been removed by erosion. During that time there was little change in the structure of the Belt Group. However, during Paleozoic and Mesozoic time, the area was subjected to widespread oscillation which lowered it first to the bottom of a shallow sea, then raised it into a low-lying land surface.

Near the close of the Cretaceous or at the beginning of the Tertiary, uplift and volcanic activity began throughout the entire Cordilleran region of North America, producing folded mountains, great domes, arches, and plateaus along with lava eruptions and granitic intrusions, the extent of which has never been exceeded or equaled in the earth's history.

The initial igneous activity which took place in the Marysville district was the injection of basic and intermediate dikes and sheets. This was followed by a large granitic intrusion of quartz diorite, now named the Marysville Stock. It may be an outlier of the much larger Boulder Batholith, which occupies over 2,000 square miles and occurs about six miles to the south of the Marysville Stock.

The invasion of the stock produced a great deal of fracturing and faulting in the surrounding rocks. The result of the intrusion was a doming of the overlying material and alteration of the limy sediments into hornfels and marble. The stock intrudes and has profoundly metamorphosed the Empire Formation and the Helena limestone of the Belt Group.

Pegmatitic injections from still fluid portions of the magma at greater depths, along with the intrusion of porphyry dikes, followed the crystallization of the stock. As the stock cooled, shrinkage cracks appeared, roughly paralleling the stock's periphery.

Erosion of long duration followed, removing some thousands of feet of strata and reducing this portion of Montana to a mature topography. The lack of adequate stream flowage through old valleys in contrast to nearby gorges seems to indicate a new uplift period occuring at some time in the Miocene or Pliocene. Profound faulting, tilting and warping of the rocks took place during this time, causing breakage of the old drainage system. Also, uplifts and volcanic eruptions occured, resulting in the formation of andesite-dacite flows, tuffs, and breccias.

Finally, a series of gravels covered the Belt rocks in Tertiary time, followed by the deposition of Quaternary alluvium.

B. Ore Deposits

1. General Historical Background and Description of Ore Deposits

Placer gold was first discovered in Last Chance Gulch, in Helena, on July 14, 1864. The original discovery is now thought to have been at the present site of the Masonic Temple. Soon placer miners spread from the original site and uncovered placers in the surrounding area. In 1864 the first placers in the Marysville area were worked along Silver Creek. Generally, little interest was paid to the possibility of lode deposits until the placers were almost exhausted. In 1876, the veins of the Drumlummon Mine at Marysville were discovered by Thomas Cruse. Later, the Cruse and Belmont mines were opened along with other small mines and prospect pits.

Total production of the Marysville area is valued at about $35,150,000, mostly in gold and silver, but with appreciable amounts of lead and some copper and zinc (Sahinen, 1959). The Drumlummon lode, itself, has yielded nearly $16,000,000. Other richly productive mines were the Belmont and Cruse mines along with the Bald Butte, Penobscot, Empire, and Piegan-Gloster mines, which surround the edge of the Marysville Stock or occur nearby.

The ore deposits are steeply-dipping fissure veins bearing gold and silver that occur both in the metamorphic rocks and in the stock. The veins occur around the edge of the stock, with no veins found in the central portion of the stock. Pardee and Schrader (1933, p. 67-68) state that the ore in all the veins occurs in shoots. High-grade ore was found above the 200 foot level, but in depth the ore rapidly decreases in value until the veins are no longer workable. None of the veins in the district except those of the Drumlummon, which was opened to a depth of 1,600 feet, were developed more than 500 feet below the surface. The gold is finely divided and not usually visible. The gangue has a characteristic composition and structure and contains quartz, commonly platy, and calcite in broad, thin plates. The calcite carries some iron and manganese, resulting in some highly manganiferous outcropping veins.

Pardee and Schrader state further that brecciated wall rock forms the bulk of the vein filling. The fragments are cemented chiefly with cerusite, iron oxides, calamine, and green-blue carbonates of copper.

In places there are remnants of unoxidized sulfides, chiefly galena and chalcopyrite, of which the galena is the younger and has replaced part of the chalcopyrite. Fluorite seems to be one of the first minerals introduced while the carbonates and oxides along with calamine are secondary minerals due to oxidation of the vein.

The ores contrast strongly in metallic content with the copper and silver ores of the nearby Butte district. Although this area is in the same metallogenic province as Butte, the Marysville region has a scarcity of copper deposits.

2. Theories of Origin

There have been three main theories proposed for the origin of the Marysville ore deposits. Barrell (1907) believed the Marysville veins to be genetically related to the intrusion of the stock. Since he felt the stock was related to the Boulder Batholith, the age of the veins would be Late Cretaceous or early Tertiary. He believed the veins were due to contraction effects on the margins of the stock, that is, formation of fractures at the margins of the stock and then filling of the fractures soon after. The fillings or veins were considered to be due to the crystallization of the stock's residual fluids.

The main structural evidence which led Barrell to the contraction theory was his observation that the location of the veins was parallel or nearly parallel with the contact. The branching character of the fissures, the general shattered and infiltrated character of the walls, the dying out of the vein fissures, and the absence of marked throw along the fissure planes were additional support for his theory.

Mineralogical evidence favoring his theory was found by Barrell largely in the Bald Butte mine. Fluorite is a characteristic mineral in this mine and was considered by Barrell to be indicative of magmatic emanations, although the deposition may have taken place under hydrothermal as well as pneumatolytic conditions.

The second theory completely disagrees with Barrell's ideas. Knopf (1913) states that the structural evidence of Barrell can hardly be accepted as proof of the contraction origin of the Marysville fissures. He pointed out that these same features are of common occurrence in late Tertiary veins which cut surface lava flows and are therefore as indicative of fracturing under light load as they are of contraction during the cooling of plutonic rocks. Knopf rejects Barrell's idea of contraction for the origin of the veins, on the basis that continuity of the Marysville veins occur across intrusive contacts, as exemplified in the

Belmont, Cruse, and Drumlummon mines. He feels a contraction fissure could not extend from the stock into the country rock.

The mineralogical evidence given by Barrell is unfortunately chosen, according to Knopf. The Bald Butte mine, which is the only mine in which fluorite is found, is not characteristic of the mines which have yielded 95% of the production of the Marysville district. Nor is fluorite always to be considered indicative of magmatic emanations. Knopf states that the characteristic veins of Marysville have a gangue identical in structure and composition with that of veins in nearby districts of proven post - Miocene age. Knopf (1913, p. 10) states that the ores in the area of the Boulder Batholith are of two distinct ages. The older group is of pre-volcanic origin and is genetically related to the intrusion of the batholith. The older bodies consist mainly of silver-lead and gold-silver deposits. The younger post - Miocene ores are related to volcanic extrusives and are essentially precious metal deposits. They are characterized by the tendency of the quartz gangue to display a very fine-grained, cryptocrystalline, porcelain-type texture as contrasted with coarse-grained quartz in the older vein-type deposits. Knopf states that the Marysville quartz is generally dense and fine-grained, indicating the veins belong to the younger group. He also mentions that tourmaline, which is so conspicuously developed in most of the older deposits of the Boulder Batholith, is entirely absent in the Marysville deposits.

Pardee and Schrader (1933) proposed the third theory of origin and it is probably the least well-known. They accepted the idea that the Marysville veins were formed during an epoch of ore deposition that was later than the metalogenesis accompanying the cooling of the Boulder Batholith, but they maintained that the veins were genetically related to the Marysville stock. Since Barrell concluded that the depth to the Marysville granitic body was comparatively shallow at the time of the intrusion, Pardee and Schrader concluded that it was probably not until well along in the Oligocene that about 10,000 feet of sedimentary cover had been lowered to the shallow extent indicated.

C. Description of the Marysville Stock

The Marysville stock is approximately four square miles in surface exposure (Plate I). The irregular, pear-shaped stock trends in a NW direction in plan view. The intrusion has metamorphosed the surrounding sediments up to a distance of two miles into hard dense rocks (hornfels) composed of calcite and silicates such as diopside, wollastonite, tremolite and biotite.

The stock, itself, exhibits two different grain sizes (Plate I). The majority of the rock is rather coarse and even-grained and constitutes the outer portion of the stock. Generally, upon traversing the coarse-grained portion of the stock from the inner area to the periphery, the rock appears to be more brittle and weathered. The trend is especially apparent in the southern portion near the St. Louis - Drumlummon mine area and also in the NW and east portions of the stock in the area of samples 23 and 27 and in the area of sample con-2 (Plate I). The magnitude of fracturing also increases outward to the periphery. Quartz filling occurs at the periphery and is best observed again in the area of samples 23 and 27, in the area of the St. Louis - Drumlummon mines, and in the area of sample con-2. No decrease in grain size could be observed at or toward the periphery.

There are four areas of quartz diorite outlier outcrops. One lies northeast of the northern portion of the stock, one in the northeast portion of the stock, another just southwest of the southern-most portion of the stock, and the largest about 2600 feet north of the finger-like projection in the western edge of the stock. All the outlier outcrops lie about the same distance from the stock (Plate I).

The finer-grained rock in the inner portion of the stock shows very little or no weathering, along with a greater strength in relation to the coarser-grained rock.

Barrell, although not studying the stock in detail, thought that the appearance of the whole mass gave the impression that the magma had varied slightly in its development and the absence of contacts suggested that it was probably due to one continued period of invasion. On the other hand, Dr. Whitman Cross, making a reconnaissance trip across the stock in 1904, noted a contact of the fine-grained rock against the coarse-grained rock in certain places (Barrell, 1907). Dr. Cross stated that the finer-grained rock appeared to be a distinct intrusion filling a large channel through the coarser-grained rock. The author has studied these areas and although there seems to be a definite contact, the contact in some places is not very clear.

Within the inner area of finer-grained rock, there is an area of bluish quartz diorite. Within this area, as well as in adjacent areas, there outcrops a blue porphyry. The bluish quartz diorite is harder than either the coarse- or fine-grained diorite.

About 1250 feet southwest of the St. Louis mine and near the periphery of the stock a brownish porphyry dike outcrops. Barrell (1907) has called it the Drumlummon porphyry. It trends almost due north, dips nearly verticallyand is about ten feet thick. The rock is spotted with numerous phenocrysts of feldspar not over one-eighth inch in diameter. According to Barrell, the brown color is due to greater oxidation at the surface compared to the pale gray to greenish gray color found in the mines. Since the porphyry dike cuts the stock at the surface, the porphyry is younger (Plate I).

About 1500 feet due south of the Belmont mine on the southeast slope of Mt. Belmont, finger-like projections of diorite porphyry outcrop. This porphyry has been called the Belmont diorite porphyry by Barrell (1907). Since this porphyry has not been found within the stock, it seems that the porphyry is older. On the other hand, since this porphyry resembles the Drumlummon porphyry, a younger origin could be possible. Microscopic study by the author confirms a mineralogical relationship of both porphyries.

A microgabbro outcrop occurs on the southeast flank of Mt. Belmont, possibly a coarser-grained equivalent of the microdiorite found at Bald Butte.

A large microdiorite dike outcrops on Drumlummon Hill near the St. Louis mine and conforms with the bedding planes of the metamorphosed Belt series. The dike is about two feet thick and dips about 12° to the north. Quartz stringers cut the dike. The relationships of the microdiorite indicate it to be the oldest of all igneous rocks in the district. According to Barrell (1907), there is nothing within the Marysville district to fix the age of these early intrusives. Since they are mostly unaltered, the microdiorites are thought to be Late Cretaceous or early Tertiary.

The aplite dikes in the area of sample con-2 are observed to cut the quartz diorite as well as the wall rocks, but within short distances they fade out in the quartz diorite and are not noted very far from the border. The inner stock is almost completely free from these dikes. They probably originated from late residual fluids after the stock had solidified. The fluids found their way up through the fractures, collected in the cooling stock, and then crystallized. The dikes would concentrate at the margin of the stock because of the abundance of fractures there.

A basic diorite occurs about 1100 feet southeast of sample con-3 and has been called by Barrell a basic quartz diorite (Plate I).

A small metamorphic inclusion occurs within the stock near sample con-3, about thirty feet southwest of the contact. It is about thirty feet long and ten feet wide (Plate I).

D. Petrography Study

Barrell (1907) stated that the Marysville Stock, although having local variations in its content of hornblende, generally does not vary mineralogically in any part of the stock. According to him, the only variation in the stock occurs at the basic portions located in some peripherial positions.

Eighteen thin sections of representative samples taken across the stock were studied. Ten sections were grid samples, nine of which were the normal coarse-grained type, one of the finer-grained blue granite from the center of the stock, two coarse-grained contact samples, two coarse-grained samples collected from the mine areas, and three porphyries, one at the periphery of the stock and the other two nearer the central portion of the stock.

Study of the sections showed no significant changes in the mineralogical composition for 16 samples. Among these 16 samples, 13 were of the normal coarse-grained type with the following mineralogy:

Feldspar	57%	Plagioclase	44%
		Orthoclase	13%
Quartz	20%		
Biotite	7%		
Hornblende	5%		
Titanite	1%		
Alteration Products	6%	Kaolinite-sericite	4%
		Chlorite	2%
Magnetite	2%		
Apatite	1%		
Calcite	1%		

The remaining two samples, both porphyries, differed mainly in their lower feldspar content and higher degree of alteration. The two fine-grained specimens also had a lower hornblende content than the other rocks.

All the samples showed zoning of their plagioclase feldspar, which in every case consisted of andesine or labradiorite. All sections had at least some pericline, albite, and Carlsbad twinning in the feldspar. One sample was so extremely altered that twinning was difficult to observe.

Titanite occurred around the magnetite in many cases although other titanite crystals were isolated from the magnetite.

Kaolinite and sericite appeared to be the main alteration products, although chlorite was found in many sections forming from biotite and hornblende. Also small amounts of calcite appeared as an alteration product of hornblende.

The above mineralogical composition of the Marysville Stock resembles closely that given by Barrell and Knopf. However, in their analyses, no percentages of alteration products are listed. Hence, from the above mineralogical composition, the author has decided to call the rock a quartz diorite, although it is on the border and may be classified as a granodiorite. Barrell (1907) and Knopf (1913) called the rock a quartz diorite. Knopf (1950) called the rock a granodiorite.

CHAPTER IV

NEUTRON ACTIVATION ANALYSIS

A. Theory of Method

Activation analysis is actually a relatively simple process. The material to be analyzed is bombarded with nuclear particles, converting some of the atoms in the sample into new isotopes. Often the isotopes are radioactive and their characteristic radiations can be observed and measured. From this, the chemistry of the isotopes can be determined. The bombarding particles can be neutrons, protons, deuterons, alpha particles, or high energy photons. The most useful bombardment particle is the neutron, hence the name neutron activation analysis (N.A.A.).

There are essentially two different ways in which the activation analysis method can be used - one involving post-irradiation chemical separation, and the other a purely instrumental approach.

The purely instrumental method is more rapid and is non-destructive to the material being analyzed, but can be more complicated in certain cases. Often greater sensitivity can be obtained with the chemical separation method.

The following steps outline the chemical separation method.

1) The samples and standards are separately weighed into polyethylene or silica containers and sealed.

2) The containers are placed in a reactor and irradiated for equal times.

3) After irradiation, the samples are dissolved in the presence of a known amount of the inactive element or elements being determined.

4) The solution containing the sample is then treated so that there is complete chemical exchange between the active tracer and the inactive carrier.

5) A number of chemical separations are then carried out, in which the desired element in a compound form is isolated and freed from all other contaminating radio-nuclides.

6) The standards are treated, at some convenient time during the separation, in a similar manner.

7) The isolated compounds from the samples and standards are next weighed to check the chemical yield of the added carrier.

8) Finally, the samples and standards are compared under identical counting conditions, by first qualitatively finding the peak of the element in question, and then quantitatively reading the counting rate of both sample and standard. A simple equation can be used to fine the quantity of unknown:

$$(1) \quad \frac{\text{Counting rate of sample}}{\text{Counting rate of standard}} = \frac{\text{Weight of element in sample}}{\text{Weight of element in standard}}$$

The purely instrumental approach is much more simple in practice.

1) The samples and standard are weighed separately in

polyethylene or silica containers and sealed.

2) The containers containing the unknown and standard are irradiated for the same time, under the same flux conditions.

3) The samples and standard are allowed to "cool" until any interfering elements have decayed, exposing the desired isotope. A decay curve can be plotted.

4) The samples and standard are then compared under identical counting conditions, first by qualitatively finding the element in question and then quantitatively reading the counting rates of both the sample and standard. Equation 1 is then used to find the quantity of unknown in the sample.

Both the chemical and the purely instrumental procedure have their advantages and disadvantages. The chemical separation method is much longer, requires chemical reagents, and incomplete chemical combination, adsorption, and recovery may occur. On the other hand, the method eliminates any element or elements which may act as an interfering obstacle and gives a rather pure spectrum. The completely instrumental method is fast, requires no reagents, and the possibility of losing an amount of sample is theoretically nill. However, interference may occur and is proportional to the quantity of various elements present. If interference does occur, a definite flux and flux time along with a "cooling" period of the samples must be established for best results. All of the analytical results reported here were obtained by the instrumental method.

1. Neutrons

Since this thesis deals with neutron activation analysis, the main emphasis of the following discussion will be on the thermal or slow neutron as the activating agent. The other activating agents will be sporadically mentioned. The most suitable source of the neutrons is that obtainable in a nuclear reactor of the natural or enriched uranium type, in which the fast neutrons released in fission are slowed down to desired energies by moderators such as graphite, heavy water, etc. The lighter the moderator nucleus with which a neutron collides, the greater is the fraction of the neutron kinetic energy that can be transferred in the elastic collision. For this reason hydrogen-containing substances such as water and paraffin are most effective as moderators. The number of collisions is important in the moderation of the fast neutron and, therefore, an appropriate equation is applied to calculate the number of collisions a neutron must make in a given substance in order to slow down the faster neutron to a desired energy range:

$$(2) \qquad C = \frac{\ln\left(\frac{E}{E_o}\right)}{1 - \left(\frac{(A-1)^2}{2A}\right) \ln\left(\frac{A+1}{A-1}\right)}$$

where C = number of collisions of the neutron with the nuclei of the substance.

E = initial energy of neutron (eV).

E_o = desired energy of neutron (eV).

A = atomic mass of substance.

At room temperature, the kinetic energy of thermal or slow neutrons is about 0.025 eV which corresponds to a velocity of about 2200 m/sec. A neutron with this energy will give radiative capture (n, γ), the reaction desirable in neutron activation analysis. Any faster neutrons (0.025 eV - 14 x 10^6eV) may give reactions such as the (n, n^1), (n, p) or (n, α) type or $(n, 2n)$, (n, pn) type for even faster neutrons (15 x 10^6eV).

There are two advantages of using thermal neutrons. They can easily enter into the nucleus because of the zero charge. Other particles such as protons, alpha particles, etc., which have protons in their nucleus, are repelled from the target nucleus because of the coulomb repulsion. The neutrons can also be readily incorporated into the nucleus because of their relatively slow velocity.

2. Cross-sectional area of nucleus

The interaction of the neutron with the nucleus is of importance in considering what possible types of reactions can occur. The cross-section area of the nucleus is of major importance since this area is the target area of an approaching neutron and also is a measure of the probability that the neutron will strike and interact with the nucleus. Cross-sections of nuclei are measured in cm^2 and a convenient conventional unit is the "barn", which is equal to 1 x 10^{-24} cm^2.

The total cross-section consists of three partial cross-sections, each of which is responsible for various neutron-nuclei interactions. This relationship can be shown in the form:

$$\sigma_T = \sigma_s + \sigma_c + \sigma_a$$

where

σ_t = total cross-section

σ_s = scattering cross-section

σ_c = capture or activation cross-section

$\sigma_{\bar{a}}$ = absorption cross-section

The scattering cross-section (σ_s) refers to all scattering processes, the capture cross-section (σ_c) refers to only the (n, γ) process, and the absorption cross-section (σ_a) applies to all processes other than the (n, γ), where the neutrons are absorbed. Some of these reactions are (n, p), $(n \alpha)$, (n, n^1), etc., and can be the result of intermediate energy neutrons (100 eV - 100 KeV) (Friedlander and Kennedy, 1960, p. 67). Sometimes the σ_a and σ_c are confused when σ_a is used to mean all absorption reactions including the (n, γ) type.

The capture cross-section, sometimes referred to as the activation cross-section, is the reaction area of importance in neutron activation analysis. Theoretical considerations show that the capture cross-section is proportional to the inverse of the neutron velocity ($1/V \sim \sigma_c$). Therefore, for a given element, the probability of the (n, γ) reaction will increase as the velocity of the slow neutrons decreases.

3. Interaction of Neutron with Nucleus

When an atom is irradiated with thermal or slow neutrons, the resulting reaction can be represented by:

$$(3) \qquad {}^{A}_{N}X + {}^{1}_{0}n \longrightarrow {}^{A+1}_{N}X + \gamma$$

where

A = atomic weight

N = atomic number.

The result is the formation of an isotope with an atomic mass one unit larger than the original element. A γ photon is emitted immediately after the formation of the excited compound nucleus (10^{-14} sec., Lyons, 1964, p. 108).

Since the new isotope may decay by β^- radiation (because of higher neutron-proton ratio), an element with the same atomic weight but larger atomic number will form. The total reaction is then,

$$(4) \qquad {}^{A}_{N}X + {}^{1}_{0}n \longrightarrow {}^{A+1}_{N'}X \longrightarrow {}^{A+1}_{N}X + \gamma$$

$${}^{A+1}_{N}X \longrightarrow \gamma + {}^{0}_{-1}\beta + {}^{A+1}_{N+1}Y^{+}$$

in which a neutron breaks up into a proton and electron or beta particle, increasing the original nucleus by one and retaining the original atomic mass. At about the same time ${}^{A+1}_{N}X$ changes to ${}^{A+1}_{N+1}Y^{+}$, through emission of a β^- and characteristic γ decay which actually takes place after ${}^{A+1}_{N+1}Y^{+}$ has formed. This is the measured γ for the Au^{198} isotope.

If 1 gram of $^{A}_{N}X$ were completely irradiated with slow neutrons, after one full half-life of element $^{A+1}_{N}X$, 0.5 gram of the $^{A+1}_{N}X$ would have decayed and would no longer be emitting the original γ energy. At the end of the second half-life only 0.25 gram of the original $^{A+1}_{N}X$ would emit the original energy, etc. The decay of the new isotope is explained by the equation.

(5)
$$N = N_o e^{-\lambda t}$$

where

N = number of nuclei remaining after time t.

N_o = number of nuclei at time 0.

λ = decay constant related to half-life:

$$\lambda = \frac{.693}{T_{\frac{1}{2}}}$$

t = time of decay.

Problems can occur if an element of atomic number one unit less than that of the element being determined in the sample undergoes a (n, γ) reaction followed by β^- decay and then further (n, γ) reaction. This forms additional quantities of the radio-nuclide under consideration and is a result of an induced impurity. Smales and Wager (1960, p. 326) give an example of an analysis on $^{75}_{33}As$ with $^{74}_{32}Ge$ being changed to As in the following way:

$$^{74}_{32}\text{Ge}\ (n, \gamma)\ ^{75}_{32}\text{Ge}$$

$$^{75}_{32}\text{Ge} \xrightarrow{\beta^-} {}^{75}_{33}\text{As}$$

$$^{75}_{33}\text{As}\ (n, \gamma)\ ^{76}_{33}\text{As}$$

4. Activity of Irradiated Isotope

The factors which determine the amount of radioactivity formed from a given stable isotope due to slow or thermal neutron irradiations are:

1) The amount of the desired isotope present.

2) The isotopic composition.

3) The activation or capture cross-section of the desired isotope.

4) The neutron flux.

5) The flux time.

6) The half-life with which the radioactive species decays.

In order to calculate the number of atoms transformed by neutron irradiation for any element, the same principles used in calculations on growth and decay in naturally occurring radioactive elements are applied. The number of atoms of the isotope present in a sample can be given by,

$$n = \frac{w_g}{m} \times \theta \times 6.02 \times 10^{23} \qquad (6)$$

where

n = number of atoms of isotope

w_g = weight of element (gm)

m = mass of element (atomic)

θ = % abundance or atom fraction of a given isotope in the element

and the rate of formation of the radioactive isotope is given by:

$$V = f\,\sigma\text{act}\ n \qquad (7)$$

where

V = rate of formation of radioactive atoms

f = neutron flux n/cm^2 sec.

σact = activation or capture cross-section

n = number of atoms of isotope under consideration.

Upon sample activation, the growth rate of an isotope can be calculated by subtracting the rate of formation of radioactive atoms from their decay rate. Hence, the equation can be given by:

$$\frac{dn^*}{dt} = f\,\sigma\text{act}\ n - \lambda n^* \qquad (8)$$

where

$\frac{dn^*}{dt}$ = rate of growth of a radioactive isotope

$f\,\sigma\text{act}\ n$ = rate of formation of a radioactive isotope

λn^* = rate of decay of a radioactive isotope.

Since n (total number of isotope nuclei) is much larger than n*, n can be considered constant during irradiation. Integration of equation 8 gives,

$$f\,\sigma\text{act}\ n_{e}-^{\lambda t} = f\,\sigma\text{act}\ n - \lambda n^* \qquad (9)$$

Rearranging equation 7, the amount of activity, A_t can be obtained:

$$\lambda n^* = f\ \sigma\text{act}\ n\ (1 - e^{-\frac{.693t}{T_{\frac{1}{2}}}}) = A_t$$

Substituting in equation 6 for n gives,

$$(10)\quad A_t = 6.02 \times 10^{23} \times f\ \sigma\text{act} \times \theta \times \frac{w_g}{m}\ (1 - e^{-\frac{.693t}{T_{\frac{1}{2}}}}).$$

Hence, while a sample is being irradiated, the γ activity of a given isotope can be calculated after a given time. That part of the equation represented by $6.02 \times 10^{23} \times f\ \sigma\text{act} \times \theta \times \frac{w_g}{m}$, is the maximum possible activity. If the irradiation time t equals the half-life of the isotope, then only 0.5 of the maximum activity can be obtained, since the second portion of the equation would equal 0.5. If, however, t is very long compared to $T_{\frac{1}{2}}$ (about 7 times, Smales, 1960, p. 307), then the maximum activity is obtained since now the second part of equation 10 approaches 1.

When the irradiation of the sample has been stopped, the isotope or activity will decay with its own characteristic half-life. Therefore, after a given time (x) from the end of irradiation, the activity $A_{(x)}$ will be,

$$(11)\quad A_{(x)} = 6.02 \times 10^{23} \times f\ \sigma\text{act}\ \theta\ \frac{w_g}{m} \left(1 - e^{-\frac{.693t}{T_{\frac{1}{2}}}}\right)\left(e^{-\frac{.693t_{(x)}}{T_{\frac{1}{2}}}}\right)$$

This shows that high activity (hence, high sensitivity) is proportional to the flux, activation cross-section and relative abundance, and inversely proportional to the atomic weight of an element.

Calculations can be made on the production of radioactive isotopes from stable elements having a definite thickness such as standards which are in thin-sheet form. For a beam of particles striking a thin target standard, in which the beam is attenuated only infinitesimally the rate of interaction is defined by the equation,

(12) $$N = In \sigma x$$

where

N = rate of processes of the type under consideration occurring at the target

I = incident flux $(\frac{\text{particles}}{\text{sec.}})$

n = number of target nuclei per cm^3 of target

σ = cross-section for a specific process (a, c, etc. cm^2)

x = target thickness (cm).

For the (n, γ) reaction, N is the rate of radioactive isotope produced as well as the number of characteristic γ's which will be given off. I is the neutron flux and σ the activation cross-section. Note the similarity of equations 12 and 7.

If a beam of particles strikes a thicker target standard, in which the beam is attenuated, an equation similar to the absorption of light can be used where

$$-dI = In \sigma dx$$

and upon integration,

$$I = I_o e^{-n \sigma x}$$

or

$$(13) \qquad I_o - I = I_o \left(1 - e^{-n\sigma x}\right)$$

where

I_o = intensity of incident flux $\left(\frac{\text{particles}}{\text{sec.}}\right)$

I = intensity of beam after traversing a thickness (x) $\left(\frac{\text{particles}}{\text{sec.}}\right)$

$I_o - I$ = rate of reactions occurring $\left(\frac{\text{particles}}{\text{sec.}}\right)$

n = number of target nuclei per cm^3 of target

σ = cross-section area under consideration (cm^2)

x = thickness traversed by particles.

For the (n, γ) reaction, $I_o - I$ would be the rate of formation of the radioactive isotope, as well as the number of characteristic γ's which will be given off.

5. Sample Form for Irradiation

The sample form is important in neutron activation analysis. According to Smales and Wager (1960, p. 310), if the sample or standard is brittle it should be in a powdered form and if ductile or malleable, in the form of small pieces or shavings, since the largest practical surface area is desired. When a sample is subjected to a flux, there is absorption of the slower neutrons in the outer portion of the sample. The faster neutrons are, therefore, left to react with the inner nuclei of the sample. This self-shielding, by removing the slower neutrons in the outer part of the sample, hardens the flux and since the activation cross-section varies inversely as the velocity of the neutron, ($\sigma c \sim 1/V$), the σc will be smaller in the interior of the sample. Hence, when elements of large capture or absorption cross-section are irradiated, suitable precautions must be taken. Such variations of flux may be caused not only through neutron absorption by the elements being determined, but, as is the general case, by other elements normally present in much larger amounts in the sample. If the matrix material or major constituent has a large capture or absorption cross-section, the sample weight must be restricted to a minimum. If necessary, the samples can be diluted with low cross-section materials such as alumina, magnesia or silica. It can be seen that pure samples and standards of dilute solution ($\frac{\mu g}{ml}$) are desired, since there is now relatively no self-shielding errors caused by milligram quantities of solid standards.

6. Counting of γ Energies from Isotopes

Counting the radioactive particles emitted by the sample is the next major step after the irradiation. Various types of counting devices can be used, but for γ spectrometry a scintillator with a thallium-activated sodium iodide crystal connected to a photomultiplier tube is used.

There are three ways in which energy is absorbed in a scintillator crystal from the incident gamma radiation. According to Smales and Wager (1960, p. 277), absorption by the "photoelectric" effect results in pulses which have the same energy as the incident gamma ray. According to Willard, Merrit, and Dean (1962, p. 22), the incident gamma ray must have a larger energy than the emitted photoelectron from the crystal by an amount equal to the work necessary to free the electron from the surface. That is,

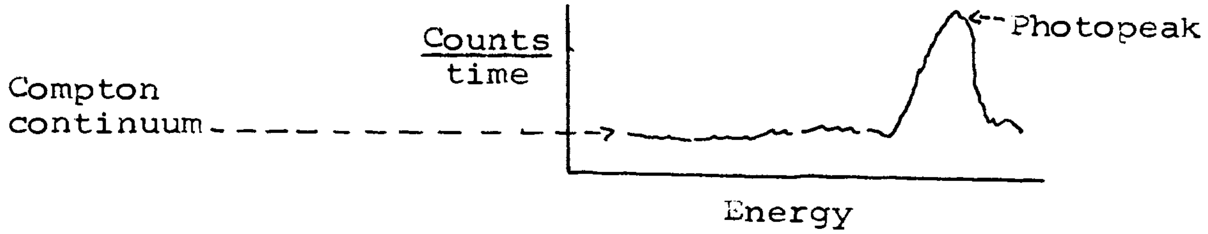
$$\frac{1}{2} mV^2 = hv - hv_o$$

where

$\frac{1}{2} mV^2$ = kinetic energy of emitted photoelectron
hv = energy of incident photon
hv_o = energy necessary to free the photoelectron from the crystal.

The energy emitted from the photoelectron from the crystal is then absorbed in the NaI crystal, resulting in a photon of light. This results in a total absorption or photoelectric peak characteristic for each isotope. Also X-rays may form. The γ particle imparts all of its energy to the electron of the iodine atom. The photoelectron produced leaves a vacancy in the iodine atom which then emits a characteristic iodine X-ray of 0.028 Mev. The second way energy can be absorbed is by the "Compton scattering" effect, which yields a spectrum of pulses with a maximum energy which is less than the energy of the incident gamma ray. The third process, known as "pair production", occurs with high energy γ rays and need not be considered here.

A plot of a pure isotope containing both the photoelectric and Compton effects can be shown as follows:

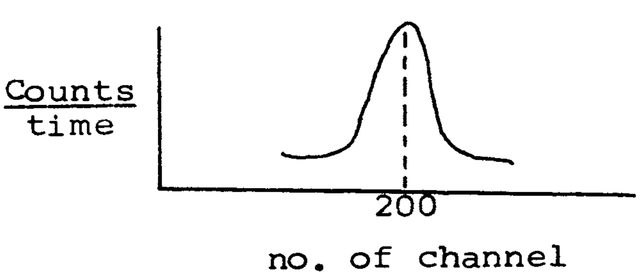


The photopeak of a pure isotope caused by the photoelectric effect will be constant for each encounter of the incident gamma ray with the sodium iodide crystal, giving one definite peak for a given isotope. The Compton continuum varies in energy since the incident gamma radiations will strike the electrons of the sodium iodide crystal each at a different angle, resulting in various energies of the photons. Hence, the characteristic gamma energy photopeak of an isotope analyzed on a disintegration rate vs gamma energy plot is the result of the photoelectric effect of radiation on the NaI crystal in addition to a multiplication of the radiation by a photomultiplier tube. The photomultiplier tube may increase the intensity of the radiation from the NaI crystal up to 10^6 times. Because of background radiation, such as cosmic rays and other nearby radioactive materials, the scintillation counter should be encased in a lead shield.

A multi-channel scintillometer can be attached to a small memory unit which stores the information of the sample and standard gamma radiations. The sample and standard at different instances can be placed at a definite distance from the sodium iodide crystal in order to eliminate as much "dead time" as desired. In case of a large flux and flux time, more gammas are given off per unit time. Because of the recovery time needed by the counter, although very small, there will be a dead time which is proportional to the rate of gammas it counts and inversely to the distance the source and crystal are from each other. There will always be a dead time. If the counter were set for a ten minute counting time, the actual time for waiting would be ten minutes plus the factor of dead time.

The memory unit can be played back after the counting, and a relative number will be typed out corresponding to each of the channels in the scintillation counter. The number of channels as well as the energy of gamma radiation correspond to the abscissa of a plot which can also be obtained from the memory unit. For more accuracy in qualitative measurements, a determined peak in a definite channel should match up with the abscissa peak value of the plot.

For instance, if the machine types out the following,
198: 109472, 199: 109475, 200: 109600, 201: 109500,
there is a definite peak in channel 200 which should correspond to the plot as follows:



The ordinate of the plot represents the rate of disintegrations of a given isotope. It is proportional to the amount of isotope and is where the quantitative results are observed.

Shifting of the counts in the various channels during counting procedures may offer serious limitations to the application of instrumental technique in gamma spectral resolution. According to Lyons (1964, p. 106), these shifts may arise from several sources. The most usual cause is changes in the photomultiplier tube. Such shifts may occur because of high counting rates.

In order to obtain the actual peak height of an isotope, the background must be subtracted from the peak value. Using a chemical separation on the isotope gives a relatively pure spectrum with low background. However, when no primary separation is made, other elements may give a larger background. Edwards (1964, personal communication) stated that the peak to background ratio should be in the order of at least 4-1 to obtain reasonably good statistics (1-3%). The percent statistical error in obtaining the desired peak of an isotope can be given by the equation.

$$A = \frac{N_1 - N_2 \pm \sqrt{N_1 + N_2}}{N_1 - N_2} \times 100 \tag{14}$$

where

A = % statistical error

N_1 = peak value

N_2 = background value.

Hence, a peak value of 5800 counts, and a background value of 600 counts will give a statistical error of 1.5% in the system, while a peak value of 600 and background of 200 counts will give a statistical error of 6.3%. It can also be seen that higher amounts of N_1 and N_2 result in a lower statistical error and are proportional to a number of items (equation 11, p. 38).

Equation 11 could theoretically give semi-quantitative results if the exact number of counts were known, the number of counts observed being the function of the efficiency of the counter. If this actual rate of γ were known then w could be calculated and, since the weight of the sample is known, a quantitative analysis could be obtained.

The half-life of a given isotope can be calculated by observing its original peak and then waiting a given time and observing the decrease. Most radionuclides encountered in practice will have a half-life between several hours to several years. An equation similar to equation 5, p. 35, can be used to obtain the half-life of an isotope giving a definite peak,

$$A = A_o e^{-\frac{.693t}{T_{\frac{1}{2}}}} \tag{15}$$

where

A = peak activity after a given time interval t

A_o = peak activity at time zero or first peak

$T_{\frac{1}{2}}$ = half-life of isotope under consideration

t = time of decay or time between two peaks.

It is very important that the analyst establish a decay curve or determine a half-life for a given peak where many isotopes of various elements with similar gamma energies may occur. Often, more abundant isotopes of various elements may shield desired trace element isotopes, but because of their smaller half-lives, they will decay faster and after a given "cooling" period, the desired isotope peak will become distinct. Hence, knowing the gamma energy of given isotope peak along with the calculated half-life, a given isotope can readily be obtained.

There should not be too much dependence upon equation 15 to give good results in the single calculation of the half-life of an isotope. Since there is a statistical counting error, the reliability of equation 15 is proportional to the number of counts used for A and A_o. The percent counting error of a given number of counts is proportional to one over the square root of that number. Hence, for a large number, 10,000, the percent counting error would be $\frac{1}{\sqrt{10,000}}$ or 1% while a smaller value for A or A_o such as 900 would give a counting error of $\frac{1}{\sqrt{900}}$ or 3.33%. This is the standard deviation. Smales and Wager (1960, p. 256) show a graph of the percent probable error of a measurement plotted as a function of the total number of counts taken.

A decay curve will give more satisfactory half-life results by plotting four or more points using a given sample. A half-life curve for gold is shown on page 49, (Figure 2).

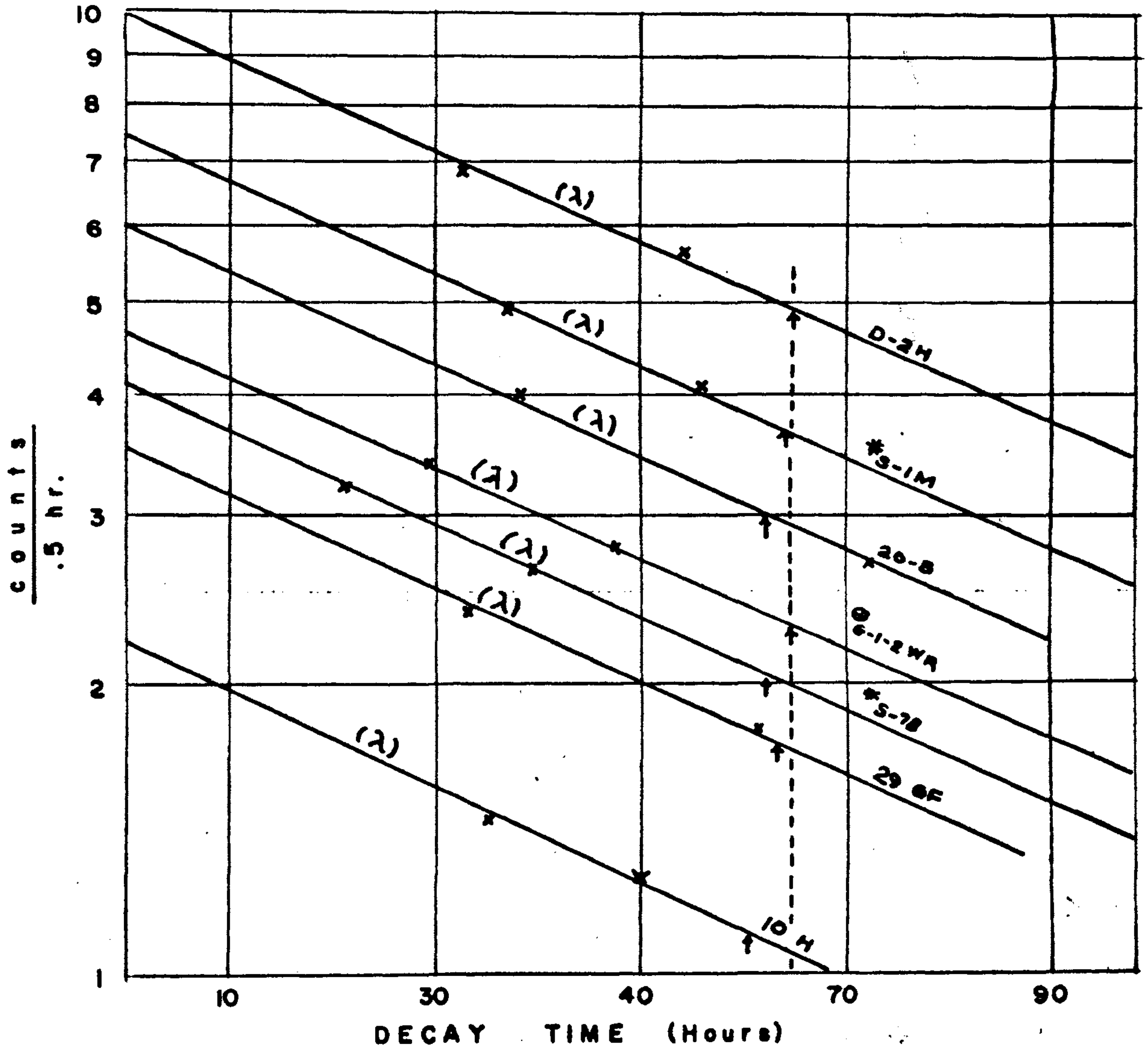
The sensitivity of neutron activation analysis is hard to excel in analyses for trace elements. According to Guinn (1964, p. 32), under slow neutron flux, detection limits range from to 10^{-7} - 10^{-6} micrograms to as high as 1-10 micrograms, with a median sensitivity of 10^{-3} micrograms.

The great advantage which neutron activation analysis has over other methods is in its freedom from blank or background contributions which often reduce the precision and accuracy of many trace methods although their sensitivity may be high. The accuracy of neutron activation depends mainly on getting away from such factors as self-shielding, conflicting nuclear reactions, etc.

Therefore, it is evident that with care, both a qualitative and quantitative analysis for a given element or elements can be accomplished with good sensitivity, precision, and accuracy using neutron activation analysis. The important item for a quantitative analysis is the treatment of the sample and standard in a similar manner throughout the whole analysis.

B. Equipment

The nuclear reactor at the University of Missouri at Rolla was used for activation. The reactor is housed in a swimming pool which is rectangular in shape, about 19 feet long, 9 feet wide and 27 feet deep. The water is deionized



$-\text{Slope}(\lambda) = \dfrac{\ln(A_2 - A_1)}{t_2 - t_1}$

λ = decay constant
t_1 = time of decay
t_2 = time of decay
A_1 = activity at t_1
A_2 = activity at t_2

¦ = theoretical Au^{198} half-life value
↑ = experimental " " "
✱ = Searchlight samples
● = granite whole rock (WR)

Figure 2

Gamma Half-life Curves of Au^{198} for Some Mineral and Rock Samples and circulated through the pool at a flow of 30 gallons per minute. The fuel consists of 2.7 kilograms of U^{235}. The maximum thermal power of the reactor is 10 kilowatts, with a maximum thermal flux of $1.35 \times 10^{11} \frac{\text{neutrons}}{\text{sec-cm}^2}$ and an average flux of $8.02 \times 10^{10} \frac{\text{neutrons}}{\text{sec-cm}^2}$. The counting equipment consisted of a 1-3/4" x 2" thallium-activated NaI scintillation crystal coupled to a 400 channel pulse height analyzer with a punch tape, graph plot, and a typewriter readout.

C. Preparation of Samples

Each rock sample was broken with a geologic hammer. About 120 grams of sample chips one inch and below in diameter were then washed with distilled water and pulverized in a steel mortar and pestle. They were then sieved through 100-mesh silk bolting cloth extended between two half-sections of a 1000-ml polyethylene wash bottle. The sample was pulverized with light-medium blows to the pestle, which was rotated periodically by lifting it above the sample, rotating it, and placing it back for further pulverization.

About 80 grams of -100 mesh sample were collected in the cap of the polyethylene bottle and then transferred to beakers. The powdered sample was washed three times, once in tap water and twice in demineralized water. In each case, the sample was swirled in the beaker of water and then allowed to settle, the finer dust material which floated being discarded. The larger material was then placed in a muffle furnace and left to dry at a temperature of about 60°C. This procedure was used to rid the sample, which was to be placed in a magnetic separator, of any adsorbed dust particles, thereby giving a better separation.

Because of the large amount of magnetite inclusions in the minerals of the finer-grained rocks, the remaining procedure of separation differed for the coarse-grained and finer-grained rocks.

For the coarse-grained rocks, the magnetite was extracted from the remaining 50 - 60 grams of -100 mesh sample in the following manner. The sample was distributed over a piece of white paper and a magnet passed beneath the paper in a series of to-and-fro and rotating movements. The magnetite was collected and emptied into a labeled plastic vial. The magnetite portion was still impure because of adhering material, mostly quartz and feldspar. The remaining -100 mesh material was placed in labeled vials for later mineral separation on a magnetic separator.

The separated magnetite was then purified. The -100 mesh magnetite was crushed in the mortar and pestle in order to free adhering quartz and feldspar. The magnetite was then distributed over glazed paper and the to-and-fro and rotating method as used before was employed until the magnetite was 98-99% pure. The magnetite was enclosed in labeled plastic vials.

The remaining sample was passed through a Franz isodynamic separator at constant horizontal and vertical axis angles of

25° and 30°, respectively. Because of either slight mechanical magnetic variation within the separator or variations in the magnetic susceptibilities of the biotite and hornblende from sample to sample, small changes in the current had to be made to obtain a clean separation of the biotite from the hornblende. First, the biotite and hornblende were separated from the rest of the sample by adjusting the current to about 0.6 amps. The sample was passed through the separator at a relatively moderate rate several times, depending on the purity of the separation. After each run, the biotite and hornblende were checked under a binocular microscope until the biotite and hornblende portion was about 95% pure. Two to three runs were needed for the average specimen. A little magnetite which adhered to the separator was collected and discarded.

Next, the biotite was separated from the hornblende by adjusting the current to about 0.45 amps. Each of the two mineral fractions were passed through the separator until observation under the binocular microscope indicated approximately 95 - 98% purity. The biotite and hornblende were then placed in labeled vials.

For the finer-grained rocks, the magnetite portion of the sample was collected as before. However, in this portion, along with magnetite, was a large concentration of hornblende, biotite, quartz, and feldspar.

Observation under a binocular microscope indicated a large amount of flaky magnetite inclusions which meant that the material could not be passed through the magnetic separator. This portion was pulverized four to five times in the mortar and pestle and passed, each time, over glazed paper in the same procedure as was used for the coarse-grained rocks. Magnetite of about 95% purity was obtained.

The remaining portion of the sample, unaffected by the hand magnet, was passed through the magnetic separator using the same procedure as was used in the case of the coarse-grained rocks. A large amount of magnetic material still adhered to the walls of the magnetic separator, while an equal amount of non-magnetic biotite and hornblende with quartz and feldspar impurities passed through the separator. The magnetic portion was cleaned from the magnetic separator and placed in labeled vials. The non-magnetic, impure biotite and hornblende portion was purified further by passing it through the magnetic separator at 0.35 amps. The biotite and hornblende were then separated from each other by passing the sample through the magnetic separator at 0.45 amps. Since there was very little hornblende in the original finer-grained rock, there was very little present after separation. Hence, only the biotite could be obtained. The biotite was about 98% pure in each sample.

D. Analytic Procedure

After the samples were purified, an analytical method had to be established for the non-chemically treated samples. With help from the University of Missouri at Rolla reactor personnel, many reconnaissance samples were studied, varying the decay, counting, and irradiation times, the neutron flux, and the weight of the sample. Among many transformations the one under study was the formation of the Au^{198} isotope from the capture of a neutron by the Au^{197} isotope. The characteristic 0.412 mev photon peak with a half-life of 64.80 hours was used. The unstable Au^{198} emits not only its characteristic γ photon but also a β^- particle forming Hg^{198}.

The γ energies along with the half-lives of all the possible major and minor isotopes of the elements in the mineral lattices which could interfere with the gold determinations were considered. Only much shorter lived isotopes such as Te^{52}, Cs^{55}, Pb^{82}, and Cu^{29} (approximately 0.412 mev) could have interfered and were eliminated by a 80-120 hour sample decay period. For the same time, the Au^{198} isotope decayed for less than 2 half-lives.

A 0.5 hour counting period for gold showed good statistics on the number of counts. A decay curve was established for seven samples for what was thought to be the gold peak. Results showed very close values to the true half-life value of gold (Figure 2). Using equation 15, p. 46, for individual samples having large counts, good results on the half-life of gold were obtained.

Because of the large capture cross-section of Au^{197}, a ten hour irradiation period at a power of 10 kilowatts (approximately 3 x 10^{10} n/sec-cm^2) was sufficient. However, the flux differed from this value in each position of each core used.

Generally, a 0.2000 gram sample was used for the analysis. Because of the great sensitivity of the analysis, it was found that good results could be obtained with a sample as small as 0.03 grams. Even smaller portions could be used.

One hundred and ninety-eight samples were then prepared for analysis. A 0.2000 gram sample was prepared for each mineral. Since there were some impurities in the minerals, each sample had to be overweighed by an amount proportional to its percent impurity. Each sample was then sealed in a plastic sheet and placed in a labeled polyethylene bottle 2½" long and 0.8" in diameter. Both the polyethylene sheet and bottle were previously irradiated for impurities. Results showed no interfering impurities.

The sample bottles were then sealed and taped on plastic stringers, lowered into the reactor pool and each stringer placed in its respective core position. The samples were then irradiated for 10 hours under a flux of about 3 x 10^{10} n/cm^{2}sec and a power of 10,000 watts. Twenty-four samples were irradiated during each irradiation period, each stringer usually containing 6 samples, 2 located at each of the stringer's three positions.

After irradiation, the stringers were detached from their core positions and left to decay in the reactor pool for at least 80 hours. Each sample was checked for radiation safety ($< 5 \frac{mr}{hr}$) and then taken off the stringers, unsealed and placed in a cardboard box. The radioactivity at this time usually showed 3-4 mr./hr. Plastic gloves and a metal "grabbing" device were used in the transportation and handling of the samples. It was observed that some of the bottles leaked and were partially filled with H_2O. This did not pose any problems except when the polyethylene bag would break or leak portions of the sample out into the bottle.

This resulted in a larger distribution of the sample in the bottle, hence, part of the sample possibly could be out of the range of the NaI crystal during counting procedures. To insure the exposure of the entire sample to the iodide crystal, all the samples were counted about 4" below the iodide crystal. This gave better geometry, although resulting in fewer counts in relation to a closer position of the sample to the NaI crystal. Each sample was counted for a 0.5 hour period with a dead time between 6-15%. The irradiation time, decay time before counting, counting time, number of counts, and weight of each sample was recorded for later use in equation 16, p. 58. The core position of each sample was also recorded for comparison with a standard irradiated in that position, but at a later period. Assurance was given by reactor personnel that the variation in the flux in a given position at different times would not be great.

Gold foils with aluminum backing were tried first as standards. Twelve foils, varying in weight between 0.1082-0.1167 grams were wrapped in polyethylene bags and placed in bottles in the same position as were the samples. Each was irradiated in one of the 12 positions on the stringers for 9 minutes under 100 watts of power. The gold portion faced the core directly. After irradiation, the standards were checked for radiation, taken off the stringers, and unsealed.

After approximately 4 hours decay time, the standards were counted for 5 minutes in the analyzer in the same position as the samples. The gold portion of the foils faced the NaI crystal. The dead time registered approximately 10-14%. The time of irradiation, decay time before counting, counting time, number of counts and weight of each standard was recorded for later computations. The background was subtracted from total count in peak to obtain peak values.

In order to show the relationship between sample and standard, an equation was developed using the variables from equation 11, p. 38. Along with equation 11, the decay count must be added, hence the number of counts between time (t_o) and time (t_3) is $\int_{t_o}^{t_3} e^{-\lambda t} = (1-e^{-\lambda t_3})$ and the number of counts after a given irradiation time (t_1), decay time (t_2), and counting period (t_3) is $C = f\ \sigma\mathrm{act}\ N\ \theta\ \frac{w_g}{m}\ (1-e^{-\lambda t_1})(1-e^{-\lambda t_3})(e^{-\lambda t_2})$

since

$f = (kP)$

where

f = flux

k = constant

P = power in watts

then

$$C(\mathrm{sample}) = kP_{1a}\ \sigma\mathrm{act}\ N\ \theta\ \frac{w_{g(a)}}{m}\ (1-e^{-\lambda t_{1a}})\ (1-e^{-\lambda t_{3a}})\ (e^{-\lambda t_{2a}})$$

$$C(\mathrm{standard}) = kP_{1b}\ \sigma\mathrm{act}\ N\ \theta\ \frac{w_{g(b)}}{m}(1-e^{-\lambda t_{1b}})(1-e^{-\lambda t_{3b}})(e^{-\lambda t_{2b}})$$

Cancelling out factors and equating the C(sample) and C (standard) gives

$$\frac{C(\mathrm{sample})}{C(\mathrm{standard})} = \frac{P_{1a}}{P_{1b}}\ \frac{w_{g(a)}}{w_{g(b)}}\ \frac{(1-e^{-\lambda t_{1a}})}{(1-e^{-\lambda t_{1b}})}\ \frac{(1-e^{-\lambda t_{3a}})}{(1-e^{-\lambda t_{3b}})}\ \frac{(e^{-\lambda t_{2a}})}{(e^{-\lambda t_{2b}})}$$

and (16)

$$W_{g(a)} = W_{g(b)} \frac{C(\mathrm{sample})}{C(\mathrm{standard})}\ \frac{P(\mathrm{standard})}{P(\mathrm{sample})}\ \frac{(1-e^{-\lambda t_{1b}})(1-e^{-\lambda t_{3b}})(e^{-\lambda t_{2b}})}{(1-e^{-\lambda t_{1a}})(1-e^{-\lambda t_{3a}})(e^{-\lambda t_{2a}})}$$

Dividing $W_{g(a)}$ by the total weight of sample and multiplying everything by 10^6 transfers the answer into ppm. A computer program using the Fortran statement method was established.

Poor results were obtained, apparently because the gold foil standards exhibited self-absorption effects and because of the difference in matrix between standards and samples. Because of the self-absorption, the number of counts for the standard was reduced, giving much higher results than expected. Vincent and Crockett (1960) found that gross errors are introduced in gold analysis unless very small amounts of gold foil are irradiated as standards. They reported results which were 37 percent too high when using a gold foil 0.002 inch in thickness. The gold foil used in this work had a thickness of 0.001 inch and the results appeared to be too high by a factor of 100-1000.

Five samples of a granite were next analyzed using a sulfide ore standard (Webber, 1965) with similar chemical composition and a known gold content (0.11 ppm). The samples and standard were prepared in a manner similar to that for the samples mentioned above. Since the samples and standard were irradiated at the same power, $P_{1a} = P_{1b}$, time t_{1a} = time t_{1b} and counted for the same period, $t_{3a} = t_{3b}$, equation 16 reduces to

$$(17) \qquad W_{g(a)} = W_{g(b)} \frac{C(\text{sample})}{C(\text{standard})} \qquad \frac{e^{-\lambda t_{2b}}}{e^{-\lambda t_{2a}}}$$

Dividing $W_{g(a)}$ by the total weight of sample and multiplying everything by 10^6 again transfers the answer to ppm.

The data were compiled, programmed, and calculated by a computer using the Fortran statement method. Results showed that four of the granite samples contained 0.024, 0.032, 0.033, and 0.041 ppm gold. The fifth sample gave a very high value, apparently an erratic result. The granite was then assigned a value of 0.032 ppm gold and used as a standard.

The mineral samples were next compared with the sulfide standard and with the granite standard by irradiating 12 samples of each standard on separate days in the various core positions. The standards were treated exactly as the samples. A number of erratic results were obtained from the sulfide standard. These were found by comparing counts obtained from the sulfide standard and from the granite standard with those obtained from the gold foils and by comparing sample results from the sulfide standard with results obtained from the granite standard. Therefore, it was decided that sample values obtained by use of the granite standard were of the greatest value. Two possible reasons for obtaining better results from the granite standard are:

1) it is closer in composition to most of the samples analyzed than is the sulfide ore and;

2) the sulfide ore standard may have somehow been treated differently or reacted differently in the analytic procedure.

A few samples appeared to give erratic results. These were run two more times by weighing a new portion of the sample powder, then carrying out irradiation, counting, and computation. Nineteen samples were picked at random and rerun to check the precision of the method.

CHAPTER V

DISCUSSION OF RESULTS

A. Experimental Results

The results of the gold analysis of the various minerals of the Marysville Stock are given in Tables I-VI. Tables I, II, III, and IV show the gold content in the biotites, hornblendes, magnetites, whole rock samples and quartz-feldspar samples. Most of these results are for samples analyzed only once. Table V lists the results of the duplicate analyses on 19 randomly chosen samples. The percent deviation from the mean (precision) is shown in the 5th column of Table V. Table VI gives the results of triplicate analysis of 6 samples. Further analyses were made when two analyses of one sample disagreed by a large amount or when the first analysis seemed to be erratic. Time did not allow duplicate-run samples, D-4-B and con-3M, (Table V), to be analyzed a third time.

In this work the major possible sources of error are:

1) Weighing not exact because of impurity corrections which had to be made;

2) Breaking of the plastic bags during activation so as to scatter part of the sample out of the range of detection of the NaI crystal during counting procedures (this occurred a few times);

3) Variation of reactor flux in a given position from day to day;

TABLE I

Gold Content of Biotites in Marysville Stock, Montana

Biotite Sample Number	Au Concentration (ppm)
1	0.005
2	0.015
3	0.029
4	0.004
5	0.015
6	0.004
7	0.005
8	0.017
9	0.180*
10	0.019
11	0.044
12	0.013
13	0.044
14	0.037
15	0.094
16	0.004
17	0.107*
20	0.155*
21	0.002
22	0.032
23	0.010
24	0.021
25	0.046*
26	0.141
27	0.050
28	0.018
29	0.150*
B-1	0.056
B-2	0.012
B-3	0.054
C-1	0.014
C-2	0.026*
C-3	0.038
D-1	0.159
D-2	0.924*
D-3	0.004
D-4	0.290*
con-1	0.304*
con-1a	0.012
con-1b	0.011
con-3	0.018
con-4	0.007
con-5	0.113
con-D	0.037
Average	0.076 ppm

* Average of two runs.

TABLE II

Gold Content of Hornblendes in Marysville Stock, Montana

Hornblende Sample Number	Au Concentration (ppm)
1	0.823
2	0.033
3	0.046
4	0.005
5	0.015
6	0.024
7	0.060*
8	0.300
9	0.165
10	0.012*
11	0.219
15	0.067
19	0.032
20	0.212
21	0.165
22	0.025
23	0.005
24	0.129
26	0.003
27	0.167
28	0.113
B-1	0.035*
B-2	0.026
C-1	0.012
C-2	0.276*
D-1	0.008
D-2	0.179*
D-3	0.010
D-4	0.056
con-1	0.021
con-1a	0.022
con-1b	0.110
con-2	0.007
con-3	0.022
con-4	0.025
con-5	0.024
con-D	0.231
Average	0.100 ppm

* Average of two runs

TABLE III

Gold Content of Magnetites in Marysville Stock, Montana

Magnetite Sample Number	Au Concentration (ppm)
1	0.055
2	0.012
3	0.014
4	0.006
5	0.052*
6	0.019
7	0.032
8	0.120*
9	0.086*
10	0.008
11	0.003*
12	0.033
13	0.004
14	0.011
16	0.066*
17	0.029
20	0.154
21	0.011
22	0.008
23	0.034
24	0.061
25	0.020
26	0.329
27	0.200
28	0.004
29	0.098
B-1	0.011
B-2	0.006
B-3	0.014
C-1	0.017
C-2	0.002
C-3	0.009
D-1	0.002
D-2	0.003
D-3	0.015
D-4	0.003
con-1	0.007
con-1a	0.007
con-1b	0.013
con-2	0.002
con-3	0.030*
con-4	0.004*
con-5	0.011
con-D	0.026
Average	0.037 ppm

* Average of two runs

TABLE IV

Gold Content of Whole Rock (WR) and Quartz-Feldspar (QF) Samples from Marysville Stock, Montana

Whole Rock (WR) and Quartz-Feldspar (QF) Sample Number	Au Concentration (ppm)
WR-1	0.089*
WR-11	0.004
WR-13	0.010
WR-25	0.015
WR-C-2	0.053
Average	0.034
QF-1	0.037*
QF-11	0.006
QF-13	0.026
QF-22	0.055
QF-25	0.040
QF-29	0.176
QF-B-1	0.144
QF-C-2	0.080
QF-D-2	0.070*
QF-Con-1b	0.011
Average	0.065 ppm

* Average of two runs

TABLE V

Duplicate Results for Gold Content of Samples from Marysville Stock, Montana

Sample Number	Analysis one (ppm)	Analysis two (ppm)	Average (ppm)	% deviation
9B	0.241	0.117	0.180	±35
17B	0.107	0.107	0.107	± 0
25B	0.047	0.044	0.0455	± 3
29B	0.230	0.069	0.150	±55
C-2-B	0.039	0.013	0.026	±50
D-2-B	0.868	0.980	0.924	± 6
D-4-B	0.005	0.575	0.290	Erratic
con-1-B	0.387	0.222	0.305	±27

Average % deviation for biotites = ±25%

Sample Number	Analysis one (ppm)	Analysis two (ppm)	Average (ppm)	% deviation
7-H	0.094	0.025	0.060	±59
B-1-H	0.044	0.026	0.035	±25
C-2-H	0.435	0.122	0.276	±56

Average % deviation for hornblendes = ±47%

Sample Number	Analysis one (ppm)	Analysis two (ppm)	Average (ppm)	% deviation
5-M	0.094	0.015	0.052	±69
8-M	0.190	0.050	0.120	±58
9-M	0.137	0.032	0.086	±63
16-M	0.082	0.049	0.066	±24
con-3M	0.056	0.004	0.030	Erratic
con-4M	0.0033	0.0040	0.0036	±10

Average % deviation for magnetites = ±45%

Sample Number	Analysis one (ppm)	Analysis two (ppm)	Average (ppm)	% deviation
QF-1	0.043	0.031	0.037	±16
AF-F-D-2	0.095	0.050	0.072	±30

Average % deviation for quartz-feldspar=±23%

Average % deviation for all minerals = ±34%

TABLE VI

Triplicate Results for Gold Content of Samples from Marysville Stock, Montana

Sample Number	Analysis one (ppm)	Analysis two (ppm)	Analysis three (ppm)	Average of two best values
WR-1	0.070	0.319	0.108	0.089
20-B	0.005	0.053	0.256	0.155
10-H	0.015	0.166	0.009	0.012
D-2-H	0.004	0.095	0.264	0.179
3M	0.021	0.420	0.007	0.014
11M	0.883	0.002	0.003	0.0025

4) Comparing standards activated at one time with samples activated at another time; (Ideally, a standard should be run contemporaneously with each sample);

5) Incorrect placing of sample holders in the core positions, causing an angle of tilt and producing flux differences on samples run on various days, although in the same position;

6) Leakage of water into bottle resulting in the partial absorption of gammas by the water;

7) Absorption of flux by matrix elements, giving variation of flux and of activity of desired isotope from sample to sample;

8) Gain shift phenomenon, or the wandering of the gold counts in various channels due to the variations in current potential in the electrical system of the counter;

9) Low gold peak counts resulting in relatively high statistical counting errors.

10) Differences in sample matrix and standard matrix.

An estimate of the precision of the method used is given in Table V. The percent deviation (precision) of the duplicate results for a given mineral was obtained by averaging the two analyses, subtracting either of the values from the average and then dividing that number by the average. The percent deviation for the biotites is ± 0% to ± 55%, averaging ± 25%. The magnetites show percent deviations ranging from ± 10% to ± 69%, averaging ± 45% while the two quartz-feldspar samples average ± 23%. The average percent deviation for all samples is ± 34%. Precision would probably have been much better if a standard had been run simultaneously with each sample. However, this would have required a great deal more time and for this reason it was not done.

The accuracy of the analyses is unknown because of lack of rock and mineral standards with known values of gold. The standard granite G-1 has been reported to contain between 0.0045 - 0.011 ppm gold (Sarmo, Sen, and Chowdhury, 1965). DeGrazia and Haskins (1964) report values of 0.0006 - 0.0042 ppm gold for acid igneous rocks and 0.002 - 0.0032 ppm gold for basic igneous rocks. Results obtained here for minerals are in general slightly higher than those values previously reported for igneous rocks.

Results for gold values in biotites, hornblendes, magnetites, whole rock and quartz-feldspar samples taken from Tables I-IV have been plotted and contoured on the stock to show their relationships to the mine areas. Values obtained from duplicate runs were averaged to get values used on the maps while the two best values of the triplicate runs were averaged to get values for the maps. Areas of 0.08 ppm gold and above have been colored to show more clearly the concentration of the gold.

Plate II shows the gold content of the biotite in the stock. The concentration of gold appears highest in the Drumlummon Mine area. This was the highest gold producing mine in the district (approximately $16,000,000). Concentrations are also found in the area of the St. Louis Mine, just south of the Belmont mine, and north of the Cruse mine.

Smaller concentrations occur in 3 other areas where no mines are located. Hence, the gold content in biotite shows a concentration mainly in the southern portion of the stock, in the areas of the major producing mines.

Comparison of these biotites with biotites from the standard granite, which is not associated with any known gold mines, shows a similarity in gold content. Five biotites from the standard granite samples (which were taken from the same area of Rhode Island as the standard granite G-1) were analyzed and were found to contain, on the average, a little more gold than the Marysville biotites. The 5 biotites averaged 0.108 ppm gold compared to 0.076 ppm gold for the Marysville biotites. The ranges were 0.025 - 0.246 ppm and 0.004 - 0.924 ppm, respectively. One biotite from a stock associated with gold deposits in the Searchlight, Nevada, area was analyzed. The biotite was found to contain 0.259 ppm gold.

Plate III shows the gold content of hornblende in the stock. Again the gold content appears to be highest in the Drumlummon area with concentrations also in the St. Louis, Belmont, Gloster, and Cruse mine areas. A small area of concentration occurs in the northern edge of the stock. The gold content of the hornblende appears to be concentrated also in the southern portion of the stock, in the area of the major producing mines.

No other hornblendes from either a producing area or non-producing area were analyzed and compared to the Marysville hornblendes. The gold content of the hornblende ranges from 0.005 ppm to 0.823 ppm and averages 0.100 ppm.

Plate IV shows the gold content of magnetite in the stock. The gold concentration here shows no definite connection with the major mine areas in the southern portion of the stock. The highest gold values seem to be scattered about the stock with the largest area of concentration, however, appearing in the southern portion of the stock.

The Marysville magnetites were compared to similarly analyzed magnetites from a quartz monzonite stock associated with gold deposits in the Searchlight district, Nevada. Results showed that the average gold content of the Searchlight magnetites was 0.016 ppm while those of the Marysville Stock average 0.037 ppm. The range for the two areas was 0.002 ppm to 0.064 ppm and 0.003 ppm - 0.329 ppm, respectively.

Plate V shows the gold content of whole rock and quartz-feldspar samples. There are only 5 whole rock samples and the largest values of gold are found near the Drumlummon and Cruse mine areas, the smaller values being in the center and northern portion of the stock. The quartz-feldspar samples have their two highest values near the Belmont and Cruse mine areas, the smallest values again being in the center and northern portions of the stock. The range of gold in the whole rock samples is 0.004 ppm to 0.089 ppm and the average is 0.034 ppm. This compares to the granite standard samples which were analyzed and gave an average of 0.032 ppm. Values of gold reported by Sarma, Sen, and Chowdbury (1965) for the standard granite G-1 range from 0.0045 ppm to 0.011 ppm, averaging 0.007 ppm. Gold in the quartz-feldspar samples ranges from 0.006 ppm to 0.176 ppm, averaging 0.065 ppm.

B. Interpretation of Results

The concentration of gold in the various minerals seems to be due to an inclusion or entrapping phenomena rather than to ionic substitution. It would be difficult to oxidize the gold to Au^+ to have the possibility of an ionic substitution. Vincent and Crockett (1960) state that Au^+ and Au^{+++} can not exist in geological environments. The Au^+ state would probably be very hard to obtain since $Au \longrightarrow Au^+ + e^-$ has an oxidation potential of -1.68 ev and in order to oxidize the gold, species must be present with a larger reduction potential than +1.68. Only a few species would oxidize Au. Possibilities are $Co^{+++} + e^- \longrightarrow Co^{++}$ with a reduction potential of +1.82 and $F_2 + 2e^- \longrightarrow 2F^-$ with a reduction potential of +2.65. Since there is some fluorite associated with the gold deposits, it is possible that gaseous fluorine is reduced to the fluoride ion while the gold is oxidized, establishing the environment for the formation of the related fluorite. Possibly the temperature of the magma would be great enough to oxidize the gold.

According to Goldschmidt's rules on substitution, Au^+ with an ionic size of 1.37 Å could substitute for only a few elements, such as Ba^{++} (1.34 Å), and K^+ (1.33 Å). Of these two only K^+ could be diadochic with gold because of its content in biotite, hornblende, and feldspar. However, Goldschmidt's rules of substitution do not consider the effect of the electronegativity of elements and will apply only when the difference of electronegativity between the cations is no greater than 0.1 ev. The elements are treated as if there were no covalency to them. Ringwood (1955) has modified Goldschmidt's rules and considers the covalency or bond weakness character of the bond, which is a function of electronegativity difference between an anion and a cation. When two elements have similar ability to substitute in a crystal structure and there exists an electronegativity difference between them of more than 0.1 ev, the one which will give the greatest difference in electronegativity between itself and the anion will be the first to substitute, since its bond will be more ionic and stronger compared to the other element. The other element will tend to become concentrated or enriched in the residue. Hence, if gold could substitute for an element, reasoning from Goldschmidt's rules, the element it proxys for must have an electronegativity of about 2.3 - 2.5. But there is no such element with the same size and similar charge. According to Ringwood (1955), because of the relatively large electronegativity of 2.4 for Au^+, the difference when subtracted from almost any anion including oxygen would give a small electronegativity difference, hence, a very weak covalent bond, and one which would not prefer to form. Instead elements with much lower electronegativity will proxy and form a stronger ionic bond.

By the use of either Goldschmidt's or Ringwood's rules, gold will be concentrated in the residual fluids. Hence, the author believes the concentration in the various minerals is not an ionic substitution phenomena, but rather a function of the chronological sequence of the formation of the minerals along with the characteristic of open crystal structures which could entrap the gold in either the Au^o or Au^+ state.

As a magma differentiates, gold will be concentrated in the residual fluids. Magnetite would be the first mineral of those considered here to crystallize out. This would take place before the gold has become concentrated in the magma. Also, magnetite has a relatively closed structure and would not entrap the gold to a large extent. This corresponds to the relatively low concentration of gold in the Marysville magnetite of about 0.037 ppm (Table III). Upon further crystallization of the magma, according to "Bowen's reaction series", hornblende and biotite form. By this time the gold has become more concentrated in the residual material and the open structures of hornblende and biotite entrap the gold. This would explain the higher values of 0.100 ppm and 0.076 ppm gold for the Marysville hornblende and biotite, respectively (Tables I and II). About the same time, the andesine portion of the feldspar is being formed, but because of its structure, it will not entrap as much gold as the hornblende or biotite. A mineral which forms later in the sequence is orthoclase feldspar, which will entrap only a little gold because of its relatively closed crystal structure. The gold is enriched even more when quartz crystallizes out. However, quartz has a completely closed tektosilicate structure which is one of the least open structures of all. The average of 0.065 ppm gold for the Marysville quartz-feldspar samples is probably due mainly to gold in the feldspars. Hence, the existence of quartz in the sample probably lowers the gold concentration appreciably. The gold content of the feldspars is relatively high despite their structure because they formed from a melt enriched in gold compared to that from which the earlier minerals formed. At the end of the crystallization sequence, the gold is enriched to the extent of forming the ore veins. These veins would form wherever openings in the country rock and in the cooling igneous mass occurred.

Vincent and Crockett (1960) have made a study of the gold content of rocks and minerals from the strongly differentiated Skaergaard intrusion, East Greenland. They analyzed seventeen whole rock samples and eleven mineral samples (two plagioclase feldspars, two pyroxenes, two magnetites, two ilmenites, one pyrite, one pyrrhotite, and one olivine). With four exceptions, all the rocks and minerals contained between half and twice the value of 0.0046 ppm gold which they reported for the chilled marginal gabbro (believed to represent the initial magma). Because of the constancy of the gold content of the strongly fractionated rocks, they conclude that there was no significant concentration of gold in residual fluids as the magma crystallized. However, the highest gold content (0.073 ppm) was found in a late-forming rock and they state that this may indicate a concentration of gold in the very last hydrothermal solutions.

In discussing the mineral analyses, they conclude that gold shows no preference for any of the various silicate, oxide, and iron sulfide minerals. They believe the gold in the Skaergaard rocks is strongly concentrated in the copper sulfide minerals, but give no analyses of these. The olivine sample was found to contain three to four times less gold than the other minerals. They suggest that this may be due to the densely-packed olivine structure, but point out that the magnetite and ilmenite also have tight structures, yet contain the same amount of gold as do the other silicates.

The migration of the gold-rich residual fluids probably occurred after crystallization of most of the Marysville magma. Since the finer-grained portion of the stock is located in the central part of the stock, and the coarsest material near the periphery, it appears that the crystallization of the stock was from the inner portion outwards. As this proceeded, the gold-rich residual fluids would be pushed outward by the crystallizing magma. The volatiles in the magma would be concentrated near the periphery of the magma, causing this portion to cool slower, and resulting in a coarser-grained rock. The crystallization would appear to have started in the north central portion of the stock, pushing the main residual fluids generally southward. This would cause a slight increase of gold content in the minerals southward to the periphery. There would be smaller concentrations toward the north due to the same process. There appears to be some gold values which are higher in the stock compared to values on the periphery. Possibly these values are the results of a periodic halt in the crystallization rate of the magma at that position and the crystallizing minerals, taking a longer time to form, have a chance to entrap more of the gold in their structures. Similarly, unusually low values could be the result of a relatively more rapid crystallization. The rather low precision of the analytical method makes it hard to compare values which have similar magnitude. The higher concentration of the gold in the southern portion of the stock may also be partially due to the larger two-dimensional size of it compared to the northern portion.

Results show a somewhat larger content of gold for the average of the various Marysville minerals as compared to known values of rock samples taken from non-producing areas. However, the Marysville rock samples average about the same content of gold as rock samples taken from non-producing areas (DeGrazia and Hasken, 1964) (Sarmo, Sen, and Chowdbury, 1965). This is due to the dilution of low-gold minerals in the Marysville rocks. The Marysville magnetites when compared to the Searchlight magnetites show twice as much gold. The Marysville biotites when compared with biotites taken from a non-producing area show smaller gold content. This result may not be too conclusive since only five Rhode Island biotites were analyzed. It appears from the above information that the Marysville Stock now contains about the same amount of gold, on the average, as the non-producing granite in Rhode Island. However, the original Marysville magma was probably much richer in gold. Not too much can be concluded when comparing the Marysville Stock with the Searchlight area since only eight magnetites from Searchlight are being compared. On this basis, however, it would appear that the Marysville Stock may have been richer than the Searchlight Stock.

The results show that the gold has a definite genetic relationship with the Marysville Stock, supporting Barrell's (1907) theory. However, this does not rule out Knopf's

(1913, 1950) theory completely since there may have been another period of mineralization at a much later time with no genetic relationship to the stock.

Future work on gold distribution in minerals could be carried out with more precision by irradiating each sample contemporaneously with a standard. Troubles of variation of flux in a given core position from day to day would be eliminated. Longer irradiation periods may give clearer peaks for elements such as gold and other elements with large thermal neutron capture cross-sections which would ordinarily be camouflaged by the background. Hence, distribution and variation of other elements in minerals may be studied in a similar way. If time and equipment are available, activation analysis with post-irradiation chemical separation can be carried out and may provide better results in some cases.

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VITA

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THE UNIVERSITY OF MISSOURI AT ROLLA

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The undersigned, appointed by the Director of the Graduate School, have examined a thesis entitled:
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presented by Erwin J. Mantei

a candidate for the degree of Doctor of Philosophy in

Geology

and hereby certify that in their opinion it is worthy of acceptance.

Date	Signature
June 22, 1965	Arthur H. Brownlow
June 22, 1965	William H. Webb
July 7, 1965	W D Keller

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Wouter Bosch

Wouter Bosch, Director
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