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THE GEOCHRONOLOGY OF THE KEWEENAWAN ROCKS
OF MICHIGAN AND THE ORIGIN
OF THE COPPER DEPOSITS

DISSERATION

Presented in Partial Fulfillment of the Requirements for the
Degree Doctor of Philosophy in the Graduate School of
The Ohio State University

By
Sambhudas Chaudhuri, B.Sc., M.Sc., A.M.

The Ohio State University
1966

Approved by

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PREFACE

An objective of the present study was to determine the ages of the Keweenawan igneous and sedimentary rocks in the Upper Peninsula of Michigan by the whole-rock Rb-Sr method. The purpose of the age determinations of the Keweenawan igneous bodies and sediments was to define their relative stratigraphic positions which have not been clearly established by field evidence and to evaluate the applicability of the whole-rock Rb-Sr method to dating sediments.

A second objective was to analyze the isotopic composition of leads in copper sulfide deposits of the Keweenawan Nonesuch Shale with the purpose of determining the time of mineralization by using the Russell-Farquhar model. The lead data were used to shed some light on the controversial origin of the strata-bound copper sulfide deposits of the Nonesuch Shale.

The results obtained in this investigation were used to interpret the geologic history of the Keweenaw Peninsula of Michigan during Late Precambrian time.
CHAPTER I

REGIONAL GEOLOGY

Introduction

The northern peninsula of Michigan has long been an important copper-producing area. The economic importance of the copper deposits has attracted many investigators who have studied different aspects of the ore bodies. The geology of the Michigan copper district has been described in detail by Irving (1883), Van Hise and Leith (1911), Lane (1911), Butler and Burbank (1929) and others. A general geologic map of this area is shown in Figure 1.

The Keweenaw peninsula of Michigan is underlain by a thick series of lava flows interbedded with conglomerates and sandstones. These rocks lie on the southern flank of the Lake Superior syncline. The regional dip is to the northwest toward Lake Superior. The formations which make up this structural limb are: from oldest to youngest, the Portage Lake Lava Series, Copper Harbor Conglomerate, Nonesuch Shale, Freda Sandstone and Jacobsville Sandstone. A columnar section of the Keweenawan rocks is shown in Figure 2.

The major structural feature of the region is the Keweenaw fault, which can be traced for about 100 miles from Keweenaw Point southwestward to Lake Gogebic in Ontonagon County, Michigan (Figure 3).
Acidic intrusive and extrusive
Jacobsville and younger rocks
Upper Keweenawan sediments
Basic extrusives and interbedded sediments

Fig. 1. General Geologic Map of the Keweenawan and Associated Rocks in the Lake Superior District of Michigan (After Butler and Burbank, 1929)
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Fig. 2. STRATIGRAPHY OF THE MICHIGAN KEWEENAN ROCKS
(Modified after Butler and Burbank, 1929)
Fig. 3. Geologic Map of the Keweenawan Intrusives in Northern Michigan. (After Broderic et al., 1946)
It is a reverse fault bringing the Keweenawan lavas of the northern block into contact with the Jacobsville Sandstone of the southern block. The fault strikes east to northeast and dips from 20 degrees to 70 degrees to the northwest. Since the fault is a brecciated zone and not a single surface, its attitude is difficult to ascertain in most localities.

**Portage Lake Lava Series**

The Portage Lake Lava Series, of Middle Keweenawan age, is a thick sequence of basalts and andesites interbedded with conglomerates and sandstones of variable thickness. The total thickness of the series is at least 15,000 feet (Broderick, Hohl and Eidemiller, 1946). The flows are capped in many places by amygdaloidal lavas 1 to 50 feet thick. Conglomerate and sandstone beds, 1 to 1,000 feet thick, lie between a few of the lava flows. The pebbles and granules are predominantly of acidic igneous rock types. The matrix of the conglomerates is composed of coarse to fine sand of the same lithologic character as the coarser pebbles. The conglomerate beds are lenticular and thin out rapidly along the strike. Most of the pebbles are fairly well rounded. Butler and Burbank (1929) believed that the pebbles were not of immediate local derivation, as suggested by Lane (1911), but came from long-lived uplands composed mainly of felsite and quartz porphyry. Most of the sedimentary beds in the Portage Lake Lava Series are identified either by a number or name acquired by the local occurrence.
The Portage Lake Lava Series contains the commercially important native copper deposit of Keweenaw peninsula. The native copper occurs chiefly in the sandy matrix of the conglomerates and in vesicles and brecciated tops of the lava flows. Minor amounts also occur in veins along fractures that parallel or cross the beds. Most of the production has come from specific flows and conglomerates.

**Copper Harbor Conglomerate**

The Copper Harbor Conglomerate, probably of Middle to Upper Keweenawan age (Butler and Burbank, 1929), overlies the Portage Lake Lava Series of Middle Keweenawan age and underlies the Nonesuch Shale of Upper Keweenawan age. The formation interfingers slightly with both the Portage Lake Lava Series and the Nonesuch Shales. The Copper Harbor Conglomerate is divided, from oldest to youngest, into Great Conglomerate, Lake Shore Trap and Outer Conglomerate (Butler and Burbank, 1929). The pebbles in the conglomerates are mainly of acidic igneous rock type with a minor amount of mafic lava. The Lake Shore Trap consists primarily of basaltic flows with a few interbedded conglomerate. The total thickness of the Copper Harbor Conglomerate is estimated to be over 6,000 feet (Broderick, Hohl and Eidemiller, 1946). In the vicinity of White Pine, Ontonagon County, native copper with minor amounts of chalcocite occurs in the top 5 to 10 feet of the formation which is a medium-grained sandstone (White and Wright, 1954).
Nonesuch Shale

The Nonesuch Shale, of Upper Keweenawan age, is a sequence of dominantly grey, well-bedded siltstone and shale. It crops out on the north side of the Keweenaw trap range, which is upheld by the Portage Lake Lava Series. The formation is transitional into both the underlying Copper Harbor Conglomerate and the overlying Freda Sandstone (White and Wright, 1954). The thickness of the Nonesuch Shale ranges from 250 feet at the Bad River, north of Mellen in Wisconsin, to more than 700 feet near Calumet, Michigan. Ripple marks, channel fills, and other shallow water depositional features are present in the rocks of this formation. The Nonesuch Shale contains many rock and mineral particles which were derived from basic igneous rocks; minor amounts of sedimentary and metamorphic grains are also present (Van Hise and Leith, 1911). Most of these particles are sub-angular. Presence of channel sands and ripple marks in many beds of the Nonesuch Shale probably indicate that the formation was largely deposited in a near-shore or deltaic environment (White and Wright, 1954).

In the vicinity of White Pine, Ontonagon County, Michigan, the lower 25 feet of this formation contain economic copper concentrations. Chalcocite and some native copper occur primarily as disseminated grains; some native copper, chalcocite, chalcopyrite and bornite are also found in veins along fractures and faults that parallel or cross the beds.
Freda Sandstone

The Freda Sandstone is exposed along the western shore of the Keweenaw peninsula and can be traced southward into Wisconsin. This formation, considered to be the youngest formation of the Keweenawan sequence, lies conformably upon the Nonesuch Shale. The Freda Sandstone, consisting primarily of fine arkosic sandstone and red silty shale, attains a thickness of more than 14,000 feet (Hamblin, 1961). Ripple marks, mud cracks and rain imprints are found at numerous horizons throughout the formation. The heavy mineral assemblage of the Freda Sandstone strongly suggests that the main source rocks were the Keweenawan flows and the Huronian Iron Formation (Hamblin, 1961).

Jacobsville Sandstone

The Jacobsville Sandstone, about 2,000 feet thick, consists primarily of buff-colored sandstones and shales. The Jacobsville sandstones are primarily quartzose, whereas the underlying Freda Sandstone is primarily arkosic. Current and oscillation ripple marks in the Jacobsville formation are not as abundant as in the Freda Sandstone. The relationship between the two formations has been a matter of conjecture for many years. In Michigan, east of the Keweenaw fault, the entire Upper Keweenawan section is absent, and the Jacobsville rests directly upon Middle Keweenawan basalts and older rocks with marked angular unconformity. Hamblin (1961) noted a significant break in sedimentation between the Upper Keweenawan rocks and the Jacobsville formation and suggested that the Jacobsville sediments are
post-Keweenawan. Thwaites (1943), on the other hand, recognized the structural and lithological similarities of Jacobsville rocks in northern Michigan to rocks in Wisconsin, which are definitely Upper Keweenawan. He suggested that the Jacobsville Sandstone is probably the last phase of Keweenawan sedimentation.

**Intrusive Rocks**

The Keweenawan series in northern Michigan is cut in many places by igneous bodies ranging from laccoliths to small dikes. These igneous bodies, mostly of rhyolite, quartz porphyry and felsite, are considered by some to be intrusive and by others extrusive. A large intrusive occurs at Mount Bohemia, where the intruded rocks show pronounced contact metamorphic effect. The Mount Houghton quartz porphyry and some igneous bodies north of Lake Gogebic in Michigan are considered to be sills or laccoliths. The rhyolite of the Porcupine Mountains has been regarded by many geologists to be extrusive (Thade, 1950), while others (Butler and Burbank, 1929) considered it to be intrusive. Figure 3 shows the occurrence of several intrusives near the Keweenaw fault of Michigan.

The ages of these rhyolites and porphyries are not definitely known. The dominance of rhyolite and quartz porphyry fragments in the conglomerate beds of the Portage Lake Lava Series and younger formations indicates only that these igneous bodies were exposed over a considerable area during Middle and Upper Keweenawan time.
Origin of Copper in the Portage Lake Lava Series

It is generally accepted that the native copper deposits in the Portage Lake Lava Series are related to igneous activity on the Keweenaw peninsula. However, there is much disagreement about the mode of origin. Butler and Burbank (1929), Broderick, Hohl and Eidemiller (1946) and others favored an epigenetic theory, which postulates deposition from ascending solutions that emanated from an underlying intrusive. Lindgren (1933), Lane (1935), and Cornwall (1951), on the other hand, proposed a syngenetic origin and preferred the theory that ascending hydrothermal solutions dissolved primary copper, which was syngenetically concentrated in certain sediments and amygdaloids within the lava series and redeposited to form commercial deposits.

Geology of the White Pine Area,
Ontonagon County, Michigan

Because of the occurrence of copper at the base of the Nonesuch Shale, the geology of the White Pine area is of special interest. Irving (1883), Van Hise and Leith (1911), Lane (1911), Butler and Burbank (1929) and others mentioned the Nonesuch Shale and described the occurrence of copper in the White Pine area. The most complete description of lithology, structure and occurrence of copper in the Nonesuch Shale of the White Pine area is that of White and Wright (1954). A generalized geologic map, adapted from Butler and Burbank (1929, Plate 14) is shown in Figure 4.
Fig. 4. GENERAL GEOLOGIC MAP OF WHITE PINE AREA, MICHIGAN
The Nonesuch Shale

The Nonesuch Shale, dominantly, is a gray-colored siltstone and shale unit that lies on the southern flank of the Lake Superior syncline. The thickness of this formation is about 600 feet in the White Pine area. The beds generally dip 15 to 45 degrees northward or northwestward toward Lake Superior. The Nonesuch Shale in the White Pine area is transitional both into the overlying Freda Sandstone and the underlying Copper Harbor Conglomerate (White and Wright, 1954). A generalized columnar section of the formation is shown in Figure 5.

According to White and Wright (1954), the lower 25 feet of the Nonesuch Shale and the upper 5 feet of the Copper Harbor Conglomerate in the White Pine area contain economic copper deposit. This cupriferous zone of about 30 feet thick has been subdivided, from oldest to youngest, into: the lower sandstone, the parting shale, the upper sandstone, and the upper shale. Figure 6 is a columnar section of the cupriferous zone.

**Lower Sandstone.** The lower sandstone unit comprises the uppermost 5 to 20 feet of the Copper Harbor Conglomerate. This zone of the Copper Harbor Conglomerate is generally grayish, in contrast with the reddish or brownish color of the formation as a whole. The sandstone is fine- to coarse-grained, the detrital grains being predominantly of mafic lava. Calcite and chlorite are the common matrix of the sandstone. The upper five feet of this unit contains about 1 per cent copper.
Pinkish-gray fine-grained sandstone and dark-gray laminated siltstone.

Very massive light-gray fine-grained sandstone; above and below are dark-gray laminated siltstones and interlaminated siltstone and shale.

Rippled interlaminated gray siltstone and reddish-gray shale

Massive gray siltstone with interbedded evenly laminated gray siltstone and reddish-gray shale

Dark-gray laminated siltstone and shale with arkosic sandstone beds near base.

Red fine- to coarse-grained arkosic sandstone, gray in upper 20 ft.

---

**Fig. 5. A TYPICAL SECTION OF THE NONESUCH SHALE NEAR WHITE PINE, MICHIGAN.**
(After White and Wright, 1954)
<table>
<thead>
<tr>
<th>Layer</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower Sandstone</td>
<td>Gray fine-to medium-grained sandstone, with locally interbedded gray siltstone and red shale.</td>
</tr>
<tr>
<td>Parting Shale</td>
<td>4' Evenly laminated gray siltstone and shale.</td>
</tr>
<tr>
<td>Upper Sandstone</td>
<td>4 1/2' Massive gray siltstone, reddish near bottom, with calcareous concretions.</td>
</tr>
<tr>
<td>Upper Shale (part)</td>
<td>1' Thinly interlaminated gray siltstone and black shale.</td>
</tr>
<tr>
<td>Evenly laminated gray siltstone and greenish-gray shale.</td>
<td>10'</td>
</tr>
<tr>
<td>Massively laminated gray siltstone, locally laminated.</td>
<td>3 1/2'</td>
</tr>
<tr>
<td>Thinly interlaminated gray siltstone and black shale.</td>
<td>1'</td>
</tr>
<tr>
<td>Gray fine-to medium-grained sandstone, with locally interbedded gray siltstone and red shale.</td>
<td>4 1/2'</td>
</tr>
<tr>
<td>Evenly laminated gray siltstone and shale.</td>
<td>2'</td>
</tr>
<tr>
<td>Massively laminated gray siltstone, locally laminated.</td>
<td>4'</td>
</tr>
<tr>
<td>Calcareous seam 1/4&quot;-1&quot; thick</td>
<td>1/2'</td>
</tr>
<tr>
<td>Thinly interlaminated gray siltstone and black shale.</td>
<td>1/2'</td>
</tr>
<tr>
<td>Gray fine-to coarse-grained sandstone, locally pebbly.</td>
<td>5'</td>
</tr>
</tbody>
</table>

Fig. 6. TYPICAL STRATIGRAPHIC SECTION OF CUPRIFEROUS ZONE, WHITE PINE AREA MICHIGAN. (After White and Wright, 1954)
Parting Shale. The parting shale unit, which is dominantly siltstone, has a thickness of about 7 feet. A transition zone of 3 to 6 inches thick separates the parting shale from the lower sandstone. The transition zone is marked by fine- to medium-grained sandstone with numerous discontinuous thin black shale partings. The parting shale unit is composed of thinly laminated gray siltstone and black shale. There is a remarkably persistent limestone layer, 1/4 to 1 inch thick, near the base of the parting shale unit. The top of the parting shale has abundant mudcracks and sand-filled channels.

The base of the parting shale generally contains 1 to 5 per cent copper as chalcocite and native metal, while the upper part typically contains 1 to 2 per cent copper.

Upper Sandstone. The upper sandstone, which is generally fine-grained, is very similar in appearance to the lower sandstone. This bed shows more conspicuous change in lithology and thickness from place to place than do the other beds of the cupriferous zone. In some places the upper sandstone is a single massive bed of more or less even-grained sandstone, while in others it consists of several conspicuously graded beds a few inches to over a foot thick. The upper sandstone locally contains about 1 per cent or less of chalcocite and native copper.
Upper Shale. The upper shale, which includes about 40 feet of the rock above the upper sandstone unit, consists of a sequence of beds that is very similar to the parting shale unit. The boundary between the upper shale and the upper sandstone is marked by a transition zone which resembles the one at the base of the parting shale. The lower 10 feet of the upper shale contains economic copper deposits. The base of this copper-bearing zone contains 1 to 5 percent copper as chalcocite or native metal, like its counterpart at the base of the parting shale.

The lithology of rocks above the cupriferous zone of the Nonesuch Shale consists of well-bedded to laminated gray siltstone. These rocks contain numerous shallow-water depositional features, such as mudcracks and current ripple marks.

Paleobiology of the Nonesuch Shale

The parting shale and the upper shale units of the cupriferous zone contain sporadically distributed vugular structures which often contain small amounts of crude oil. Liquid hydrocarbons also occur associated with fractures in these strata. Finely disseminated carbonaceous material, locally but scantily present in the two sandy units, is relatively abundant throughout the shale units. In general, the distribution of copper in the Nonesuch Shale appears to vary in direct proportion to the amount of organic matter present. Sales (1959) and White (1960) indicated that the precipitation of copper minerals in
the basal Nonesuch Shale was probably facilitated by the presence of organic material.

Barghoorn, Meinschein and Schopf (1965) studied the organic matter and crude oils from the parting shale unit of the Nonesuch formation. They noted that porphyrins were common in the siltstones, while the crude oils lacked in porphyrins. The presence of porphyrins within the fine-grained strata and their absence in the petroleum present in the associated vugular structures of the parting shale unit have been regarded as an indication of limited mobility of the porphyrins within the formation. They considered these porphyrins to be indigenous to the siltstone.

It has been suggested that porphyrins are preserved only under a mild geothermal condition. Barghoorn, Meinschein and Schopf calculated the thermal stability of porphyrins and found that these chemical fossils could not have persisted longer than about 100 years in a lithologic environment subjected to temperatures of 250°C. Therefore, they proposed that the Nonesuch Shale was never subjected to more than a low-temperature condition.

Depositional History of the Nonesuch Shale

The constituents of the sandstone in the Nonesuch Shale are quartz, feldspar, epidote, tourmaline, apatite, mica, chlorite and fragments of basalts and felsites. According to White and Wright (1954), the presence of considerable amounts of quartz, feldspar and
mica in the formation suggests that the streams supplying sediment to the local basin had their headwaters in pre-Keweenawan igneous rocks. Weise (1960) suggested that the presence of detrital epidote and chert in the sandstone beds indicate that both metamorphic and sedimentary rocks may have contributed minor amounts of detritus. The considerable amount of unstable mineral and rock fragments present in the Nonesuch Shale is indicative of a proximate source area. White and Wright (1954) noted the alignment and character of sediments in the channels penetrating the top of the shale units and suggested that the dominant sediment source was southwest of the White Pine area.

Although the presence of thin calcareous zones in the Nonesuch Shale might easily be attributed to marine conditions, the numerous shallow-water depositional features, such as ripple marks, mud cracks, and mud chips, seem to indicate a deposition partly at least in a sub-aerial terrestrial environment (Van Hise and Leith, 1911). According to White and Wright (1954), the tonguelike form of the upper sandstone unit and the presence of mudcracks and channels at its base suggest that the rocks were deposited in a deltaic or near-shore environment.

Structure

The Nonesuch Shale of Michigan lies on the southern flank of the Lake Superior syncline and dips gently northward or northwestward toward the basin. The slightly sinuous course of its outcrop is interrupted by the structural dome of the Porcupine Mountains, around which the outcrop belt makes an almost closed loop with beds dipping
away from the dome (Figure 4). The Nonesuch Shale is broken in many places by faults, with offshoots ranging from as large as a mile to as small as a foot (White and Wright, 1954).

The most prominent structural feature near the White Pine mine is the northwest-trending White Pine fault. This fault is a right-hand tear fault with a horizontal displacement of over a mile and a vertical displacement of about 1500 feet (Carpenter, 1963). The present White Pine mine is located on the crest of an anticline northeast of the White Pine fault. This anticline is thought to be the result of drag accompanying vertical movement along the fault.

Minor faults and fractures are numerous in the White Pine mine, particularly near the White Pine fault. Most of these minor faults and fractures strike west of north, but near the White Pine fault they assume an easterly trend. The hook-shaped patterns of minor faults are clearly related to the White Pine fault (White and Wright, 1954).

Numerous small fractures are present in the southwestern portion of the mine. The number of fractures increases toward the faults, and the strikes of the fractures generally parallel the strikes of the faults.

Butler and Burbank (1929) attributed all these structural features to intrusion of an igneous core of the Porcupine Mountains.
Distribution of Copper in the Nonesuch Shale

According to White and Wright (1954), the copper mineralization in the lower and upper sandstone beds is characterized by native copper with minor amounts of chalcocite. The parting shale and the upper shale, on the other hand, contain abundant chalcocite with only minor amounts of native copper. Chalcocite and native copper occur principally as fine disseminations in shale, siltstone and sandstone. This type of copper mineralization forms the dominant facies. Also, there is a second minor facies of mineralization, which occurs as vein deposit in fractures and faults.

White and Wright (1954) observed that the lines of equal copper content in the shales trend northeast, more or less parallel to isopachs and facies boundaries. They suggested that the copper contents in the parting shale and upper shale members are independent of structure. Copper in the upper and lower sandstone, on the other hand, is clearly most abundant near the White Pine fault. The general distribution of copper in the sandstones yields a pattern that would be expected if the copper was deposited from solutions moving up from the vicinity of the White Pine fault (White and Wright, 1954).

Carpenter (1963) made a detailed study of the distribution and nature of copper minerals in joints and small faults. He recognized two types of fracture-controlled mineralization: (1) fracture-filled veins, and (2) halos. The halos are chalcocite-bearing zones in wall rock adjacent to the veins and symmetrical with respect to the vein.
Carpenter (1963) observed that the halos are minerallogically and chemically distinct from the wall rock in that the native copper is absent, the average copper content is lower and the sulfur content is higher. The halos are confined to chalcocite-bearing veins, and the width of each is approximately proportional to the amount of chalcocite in the central vein.

**Origin of Copper in the Nonesuch Shale**

White and Wright (1954) made a detailed study of the distribution of copper in the shale, siltstone and sandstone beds of the Nonesuch formation in the White Pine mine. The lack of structural control and the very definite stratigraphic control on the distribution of copper in the parting shale and the upper shale members led White and Wright (1954, p. 712) to conclude "... the copper is believed to have been introduced before the rock was lithified, deeply buried and deformed." Thus, they interpret the mineralization in the shales and siltstones to be syngenetetic in origin. They noted an increase of copper in the sandstones in the direction of the White Pine fault and concluded that the copper in the sandstone is hydrothermally redistributed copper, possibly derived in large part from the beds at the base of the Nonesuch Shale on the southwest side of the White Pine fault.

Carpenter (1963) studied the characteristics of some of the vein deposits and halos, which are chalcocite-bearing zones in
wall-rock adjacent to the veins. He concluded that the mineralization in the veins is due to remobilization of copper by solutions diffusing into walls. Thus, he added another line of evidence in support of the syngenetic origin.

Sales (1959) and Joralemon (1959) strongly questioned this conclusion of syngenetic origin. Sales advocated that all the copper in the Nonesuch Shale near White Pine mine was brought by the uprising solutions through the White Pine fault. His conclusion in favor of the epigenetic origin is based on the following evidence:

1. The fan-like spread of the copper mineralization in the sandstone and shale from the White Pine fault.

2. The irregular vertical distribution of copper throughout the cupriferous zone.

3. The presence of native copper and chalcocite in close association through the chemical reactions between a high copper-low sulfur and the hematite-carbon-bearing beds of the ore zone.

4. The increase in ore grade in the sandstone and in the richest shale bed as they approach the White Pine fault.

Joralemon (1959), in support of an epigenetic origin, cited the presence of many chalcocite seams, an inch or more wide, on steep fractures that cut the bedded White Pine ore.

Butler and Burbank (1929) suggested that the copper in the Nonesuch Shale was probably brought in by solutions ascending along
the White Pine fault and therefore it should be epigenetic hydrothermal in origin.

**Intrusives**

In the vicinity of the Porcupine Mountains and north of Lake Gogebic several scattered exposures of igneous bodies have been noted. A small body of quartz-feldspar porphyry is exposed in a road cut on highway M-64 about 8 miles south of White Pine. The Bergland Lookout Tower is situated on a porphyritic felsite body, which may be a flow. A prominent south-facing scarp about one-and-a-half miles west of Bergland exposes a tabular body of porphyritic rhyolite and basalt. Leonardson (1966), who studied the petrography of these rocks, suggested that they are shallow intrusives.

The Porcupine Mountains are the most prominent topographic features in the vicinity of the White Pine. According to Butler and Burbank (1929), the mountains are a domical uplift. The center of the dome is occupied by fine-grained felsite and rhyolite. The Portage Lake Lava Series and the younger formations dip away from the mountains. These beds are cut by numerous faults in the vicinity of the Porcupine Mountains. Butler and Burbank suggested that the deformation in the Porcupine Mountains region could be a result of intrusion of an igneous mass from below. Lane (1911), Thaden (1950) and others, however, regarded the rhyolite in the Porcupine Mountains as effusive.
The importance of the intrusives in this area stems from the fact that they lie close to the present White Pine copper mine. This has led Sales (1959) and others to postulate a genetic relationship of the copper mineralization in the Nonesuch Shale with these intrusives.
CHAPTER II

RUBIDIUM-STRONTIUM METHOD OF GEOCHRONOLOGIC INVESTIGATION

Introduction

Rubidium has two natural isotopes, \( \text{Rb}^{85} \) (72.15%) and \( \text{Rb}^{87} \) (27.85%). Thomson (1905) observed that rubidium is naturally radioactive. Hahn, Strassman and Wahling (1937) recognized the radioactivity as originating from the decay of \( \text{Rb}^{87} \) to \( \text{Sr}^{87} \) with an emission of beta particle. \( \text{Rb}^{87} \) has a half life of 50 billion years.

Four stable isotopes of strontium are known to occur in nature. These are: \( \text{Sr}^{84} \), \( \text{Sr}^{86} \), \( \text{Sr}^{87} \), and \( \text{Sr}^{88} \). Since \( \text{Rb}^{87} \) decays to \( \text{Sr}^{87} \), the abundance of \( \text{Sr}^{87} \) relative to the other strontium isotopes increase with time at a rate dependent on the relative amounts of rubidium and strontium in the sample. Therefore, the present isotopic abundance of \( \text{Sr}^{87} \) in any rock or mineral sample depends on the initial abundance of \( \text{Sr}^{87} \) at the time of formation of the rock or mineral, on the age of the sample, and on the ratio of rubidium to strontium. The natural abundance of four stable isotopes of strontium in common reagents are: \( \text{Sr}^{84} \) (0.58%), \( \text{Sr}^{86} \) (9.87%), \( \text{Sr}^{87} \) (7.09%), and \( \text{Sr}^{88} \) (82.52%).
Goldschmidt (1937) was the first to suggest the use of the rubidium-strontium method for dating old geological materials. The Rb-Sr method of dating was initially applied to rubidium-rich minerals. With advancement of methods and analytical techniques, the Rb-Sr method of dating can now be applied successfully to various kinds of rocks and minerals.

**Principle of Age Determination**

**by Radioactive Decay**

The fundamental law of radioactive decay states that the number of atoms disintegrating per unit time is proportional to the number of atoms present. This is expressed by the differential equation:

\[-dN/dt = \lambda N\]

(1)

where \(\lambda\), the proportionality factor, is called the decay constant and \(N\) is the number of atoms present at any time \(t\).

On integration, the equation (1) yields

\[N = N_0 e^{-\lambda t}\]

(2)

where

- \(N\) = number of atoms present at time \(t\), and
- \(N_0\) = number of atoms present at \(t = 0\).

Because it is impossible to know the value of \(N_0\), for geologic materials, equation (2) can not be used to determine \(t\). However, this equation can be rearranged in terms of the number of radiogenic daughter atoms present and then can be solved for \(t\). The mathematical treatment is shown below.
Let $D$ be the number of radiogenic atoms at any time $t$. The total number of radiogenic atoms $"D"$ is equal to the total number of parent atoms which have disintegrated, i.e., $N_0-N$. Therefore,

$$D = N_0 - N$$

or, $$D = N_0 e^{\lambda t} - N$$

or, $$D = N (e^{\lambda t} - 1).$$  \(3\)

The equation (3) is an expression for the total number of radiogenic atoms produced in time $t$ since decay started.

**Rb-Sr Age Determination**

The abundance of the Sr$^{87}$ isotope relative to the other strontium isotopes increases with time as Rb$^{87}$ decays to Sr$^{87}$. Since the abundance of Sr$^{87}$ is closer to that of Sr$^{86}$ and the number of Sr$^{86}$ is known to be constant in nature, it is customary to use the Sr$^{87}$/Sr$^{86}$ ratio as a measure of the relative abundance of Sr$^{87}$. The Sr$^{87}$/Sr$^{86}$ ratio of a system is a function of both time and the Rb/Sr ratio.

The Rb-Sr method is now a well-established technique for the dating of many geological materials. The first application of the Rb-Sr method for age determination was on individual mineral. However, it was soon discovered that different minerals of the same rock yielded discordant ages. These discrepancies in the ages were thought to be the result of redistribution of radiogenic Sr$^{87}$ among minerals during periods of metamorphism or base exchange effects by ground water. In other words, the mineral phases do not always behave closed systems
with respect to Rb and Sr since its first crystallization.

Nicolaysen (1961) and others suggested that the retentivity of whole rock specimens for Rb and Sr is greater than that of the constituent minerals and the whole-rock method of dating is therefore more reliable for the age determination.

To determine the age of whole rocks from the measured \( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \) ratio, which is a function of time and the Rb/Sr ratio, a correct choice of initial \( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \) ratio is very critical. However, a new method for Rb-Sr dating of rocks was devised to calculate both the age of the rock and the initial \( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \) ratio. This method is commonly called the isochron method or the whole-rock Rb-Sr method. The mathematical expression used in calculating ages by the whole-rock method is outlined below.

\[
\frac{\text{Sr}^{87}}{\text{Sr}^{86}} \text{ ratio in a rock today} = \text{Initial } \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \text{ ratio of the rock} + \text{Radiogenic } \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \text{ ratio produced since decay started.}
\]

Therefore, we can write

\[
\left( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \right)_t = \left( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \right)_o + \left( \frac{\text{Rb}^{87}}{\text{Sr}^{86}} \right)_t \left( e^{\lambda t} - 1 \right) \quad (4)
\]

where

\[
\left( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \right)_t = \text{Sr isotopic ratio today,}
\left( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \right)_o = \text{Sr isotopic ratio present initially, i.e. } t=0
\left( \frac{\text{Rb}^{87}}{\text{Sr}^{86}} \right)_t = \text{the ratio today, and}
\lambda = \text{decay constant.}
\]
The expression \( \frac{Rb^{87}}{Sr^{86}}(e^{\frac{\lambda t}{2}} - 1) \) in the equation (4) is an expression obtained from equation (3) for the total amount of radioogenic strontium produced in time \( t \).

The equation (4) is that of a straight line of the form \( Y = mx + b \) for the case that \( t = \) constant.

If several rock samples having the same age and same initial \( \frac{Sr^{87}}{Sr^{86}} \) ratio but different Rb/Sr ratio are plotted on \( \frac{Sr^{87}}{Sr^{86}} \) ratio as ordinate and \( \frac{Rb^{87}}{Sr^{86}} \) ratio as abcissa, they will define a straight line whose slope is a function of time. This line is called the isochron. The intercept of the isochron at \( Rb/Sr = 0 \) indicates the initial \( \frac{Sr^{87}}{Sr^{86}} \) ratio. This isochron method of dating is very suitable for cogenetic igneous rocks, since fractional crystallization of magma can produce rocks having a wide range of Rb/Sr ratios. Figure 7 is an example of an isochron for cogenetic igneous rocks.

**Application of the \( \frac{Sr^{87}}{Sr^{86}} \) Ratio in Geologic Problems**

Beside the application of the Rb-Sr method in dating rocks, the strontium isotopic composition of rocks has widespread use for solving many petrogenetic problems. Some of its applications are summarized below.

The values of the initial \( \frac{Sr^{87}}{Sr^{86}} \) ratio is now used to deduce the genesis of rocks. Faure and Hurley (1963) have suggested that the difference between the \( \frac{Sr^{87}}{Sr^{86}} \) ratio of the upper crust and the source regions of basalt is sufficient to make the initial
Fig. 7. A WHOLE-ROCK Rb-Sr ISOCRHN DIAGRAM
Sr$^{87}$/Sr$^{86}$ ratio of igneous rocks a useful criterion for determining their origin from either of the two sources. Since the upper part of the crust is relatively enriched in Rb, igneous rocks formed by remelting or assimilation of old crustal material should have higher values for the initial Sr$^{87}$/Sr$^{86}$ ratio than rocks derived directly from the source regions of basalt.

Faure and Hurley (1963) studied the alkaline rocks of the Monteregian Hills and obtained a well-defined isochron for the different alkaline rocks of the Hills. They concluded that the isochron method of dating is a useful technique to determine whether or not a suite of magmatic rocks is a result of the fractional crystallization of a common magma.

Powell and Hurley (1963) observed that the carbonatites of differing geological age are characterized by very low and constant Sr$^{87}$/Sr$^{86}$ ratios of about 0.706. The limestones have an average Sr$^{87}$/Sr$^{86}$ ratio which is significantly higher than the initial Sr$^{87}$/Sr$^{86}$ ratio for the carbonatites. Therefore, they concluded that the carbonatites have been derived from depth in a low Rb/Sr environment and these are not formed by the remobilization of limestones.

The oceans constitute a well-mixed reservoir with respect to both rubidium and strontium and, therefore, a variation with time in the abundance of Sr$^{87}$ were to be expected. Wickman (1948) suggested that the Sr$^{87}$/Sr$^{86}$ ratio may be used to calculate the age of certain marine limestones. Gast (1955) analyzed four limestones ranging in age
from 320 to 2700 million years and found a change in the $^{87}\text{Sr}$ content that was less than one-tenth of the predicted change calculated from the rubidium and strontium content of igneous rocks and from the half-life of $^{87}\text{Rb}$. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of modern sea water is 0.7092, while the 3.0 b.y. old Bulawayan limestone of South Africa has a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of about 0.7000. Thus it has been suggested that all normal marine limestones should have the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios within this narrow range depending upon their ages. Therefore, it is possible to determine the environment of deposition of a limestone from its strontium isotopic composition.

It can be seen that the increase in the Sr content of sea water throughout the geologic time is very small. At one time it was felt that the marine limestone cannot be dated by its Sr isotopic composition, since the analytical technique is not sufficiently improved to detect a small difference in the isotopic composition. However, with much improved technique and instrumentation, it is now realized that these small differences in the isotopic composition can be detected and a meaningful age can be obtained for the marine limestones (Hurley, 1965).

**Sample Preparation**

Fresh rock samples were collected in the field. A portion of each sample was broken into small fragments in a cleaned steel mortar. The fragments were then completely pulverized in a Spex mixer mill until a size of -140 mesh was obtained. The powder was thoroughly
mixed and stored in a screw-cap vial. Preliminary estimates of Rb/Sr ratios for the rock samples were made by x-ray fluorescence in order to select the rocks most suitable for the establishment of a satisfactory isochron.

Reagents and Apparatus

Reagent grade hydrochloric acid and nitric acid were distilled in vycor glass as constant-boiling acid. The water used in the analytical treatments was demineralized and stored in a polyethylene container. The A-R grade hydrofluoric, sulfuric and perchloric acids were used without further treatment.

All glass or plastic beakers used in the analytical work were soaked in dilute hydrochloric acid, washed with detergent, rinsed in tap water and then thoroughly washed with demineralized water and 2·25N distilled hydrochloric acid. Ion exchange columns, 60 cm. x 1 cm., were made up of pyrex glass and fitted with fritted glass-discs at the bottom. The columns were about half-filled with Dowex 50W-X8 cation exchange resin. The cation exchange columns were thoroughly washed with 2·25N distilled hydrochloric acid before each use. Rock samples were dissolved in teflon crucibles.

Decomposition of Rock Samples

A desired amount of sample was placed in a clean teflon crucible. The sample was digested in a mixture of 15 ml hydrofluoric acid and 5 ml sulfuric acid per gram of sample. The digestion was allowed
to continue overnight by placing the crucible on a hot plate adjusted
to a low heat. This was followed by evaporation to a mush, which was
then dissolved in about 50 ml of about 1N hydrochloric acid and
evaporated again until the solution was reduced to a volume of about
20 ml. The solution was then cooled and filtered for ion exchange
separation of Rb and Sr.

**Separation of Sr and Rb**

A small quantity of radioactive Sr$^{89}$ tracer was added to the
solution prepared for ion exchange separation of Sr. The solution was
then poured gently into the ion exchange column. After the solution
passed completely through the resin, the column was eluted with a 2·25N
HCl acid. The position of Sr within the column was monitored by a
gasger counter. The Sr was collected in 15 ml portions in several
clean beakers. About two beakers that had the highest concentrations
were chosen for Sr analysis. The solution in these two beakers was
evaporated to dryness. The strontium concentrates were transferred to
a clean 5 ml beaker with a small quantity of distilled hydrochloric
acid, followed by evaporation with a few drops of perchloric acid. The
sample was then stored carefully for mass spectrometric analysis.

The identification of Rb in the eluate of the ion exchange
column was achieved by a flame test using a clean platinum wire. The
collection of rubidium was done in the same manner as that for the
strontium.
**Isotope Dilution Analysis**

In the isotope dilution method the quantity of an element is measured from the change produced in its isotopic composition by the addition of a known quantity of a stable isotope of that element. The measurement of Sr concentrations of a rock by the isotope dilution method is done by an addition of a solution enriched in one of its stable isotope to the solution of the rock. The solution enriched in one of its stable isotope is known as a "spike" solution.

The quantitative estimation of Sr by the isotope dilution method is illustrated by a mathematical treatment outlined below.

Let \( N \) = Total number of strontium atoms present in a known amount of rock.

\( S \) = Total number strontium atoms in a "spike" solution.

\( A_n^{88}, A_n^{86} \) = Abundances of \( \text{Sr}^{88} \) and \( \text{Sr}^{86} \) respectively in the rock.

\( A_s^{88}, A_s^{86} \) = Abundances of \( \text{Sr}^{88} \) and \( \text{Sr}^{86} \) respectively in the "spike."

\( R = \) Measured \( \text{Sr}^{86}/\text{Sr}^{88} \) ratio of the mixture of "spike" strontium and strontium of the rock.

Therefore,

\[
R = \frac{A_n^{86} \times N + A_s^{86} \times S}{A_n^{88} \times N + A_s^{88} \times S}
\]
The above equation is solved for (N/S) atomic ratio. This atomic ratio is transformed into a weight ratio through multiplication by a "weight factor," which is the ratio of the atomic weight of strontium in the rock to the atomic weight of "spike" strontium. The weight ratio is then solved for N, the weight of Sr in the sample, by substituting appropriate value for S, the weight of spike strontium added.

Mass Spectrometric Measurements

All the mass spectrometric runs were made on a six-inch, 60° sector, single filament solid source, Nier type instrument (Nuclide Corporation, Model 6-60-S). The ion current was amplified by a vibrating reed electrometer and was recorded on a strip chart recorder. Operating pressures varied from $4 \times 10^{-8}$ to $1 \times 10^{-7}$ mm of Hg during the Sr isotopic measurement, while it was about $1 \times 10^{-7}$ to $8 \times 10^{-7}$ mm of Hg during the isotope dilution runs.

In order to obtain the best possible precision for the mass spectrometric measurements, the following precautions were taken:

1. Measurements were made only when the ion emission was steady.
2. Care was taken to focus the ion beam by adjusting voltages applied to plates in the source of the mass spectrometer.
3. The base line was checked periodically during the course of each run.
4. The resolution was monitored carefully by observing the "valley" between Sr$^{87}$ and Sr$^{88}$. Data were taken only when the bottom of this "valley" was flat and on zero.

The peaks recorded during an analysis were summed in groups of six and the ratios were determined for each group. This procedure minimizes minor statistical fluctuations in emission intensity. Generally seven to nine groups of six-peak sets were measured for isotope ratios, while five to seven groups were measured for isotope dilution. Figure 8 is an illustration of a portion of a strontium isotope ratio analysis record.

**Calibration of Sr$^{86}$ Spike Solution**

The calibration of the spike solution consists of the determination of both the isotopic composition and its concentration. The isotopic composition of Sr$^{86}$ spike (Oak Ridge, "Batch No." LH1368-A) was determined by a single isotope ratio run. The atomic abundance obtained from this single measurement is given below.

\[
\begin{align*}
\text{Sr}^{84} &= 0.00014 \\
\text{Sr}^{86} &= 0.97644 \\
\text{Sr}^{87} &= 0.00654 \\
\text{Sr}^{88} &= 0.01687.
\end{align*}
\]
Fig. 8. A TYPICAL MASS SPECTROMETER RECORD
The Oak Ridge analysis of this spike was:

\[
\begin{align*}
Sr^{84} & = < 0.0005 \\
Sr^{86} & = 0.976 \\
Sr^{87} & = 0.0068 \\
Sr^{88} & = 0.0173.
\end{align*}
\]

The results obtained at the Ohio State laboratory are identical to the Oak Ridge analysis within the experimental error.

A strontium "shelf" solution of normal isotopic composition and of known concentration was used for determining the concentration of the spike solution by the isotope dilution method. Two measurements were made on the strontium spike solution during the course of the present investigation. The concentration of the \(Sr^{86}\) spike solution is shown in Table 1.

**Calibration of \(Rb^{87}\) Spike Solution**

The atomic abundance of the \(Rb^{87}\) spike (Oak Ridge - Batch no.: LY 1448-A) was measured by a single isotope ratio run. The results of this measurement are given below:

\[
\begin{align*}
Rb^{85} & = 0.00805 \\
Rb^{87} & = 0.99195.
\end{align*}
\]

The Oak Ridge analysis of the spike was:

\[
\begin{align*}
Rb^{85} & = 0.0084 \\
Rb^{87} & = 0.9916.
\end{align*}
\]
The two analyses are identical within the experimental error.

The Rb$^{87}$ spike solutions used in the present study were of two different concentrations: dilute spike and concentrated spike. The dilute spike prepared volumetrically had a concentration two-fifths that of the concentrated spike. The concentrations of the Rb spike solutions were measured by the isotope dilution method using a Rb "shelf" solution of normal isotopic composition and of known concentration. The results of the analyses are given in Table 1.

**TABLE 1**

**CONCENTRATION OF Rb and Sr SPIKE SOLUTIONS**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Date</th>
<th>Sr $\mu$gm/ml</th>
<th>Analyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>76</td>
<td>1/27/66</td>
<td>23.35</td>
<td>Faure</td>
</tr>
<tr>
<td>102</td>
<td>3/3/66</td>
<td>23.54</td>
<td>Chaudhuri</td>
</tr>
</tbody>
</table>

**AVERAGE** = 23.45 ± 0.10

**Concentration of Rb$^{87}$ Spike Solution**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Date</th>
<th>Type of Spike</th>
<th>Rb $\mu$gm/ml</th>
<th>Analyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>3/19/66</td>
<td>Concentrated</td>
<td>49.08</td>
<td>Chaudhuri</td>
</tr>
<tr>
<td>145</td>
<td>4/8/66</td>
<td>Dilute</td>
<td>19.64</td>
<td>Chaudhuri</td>
</tr>
</tbody>
</table>
Accuracy of Rb and Sr Analyses

Rb and Sr analyses were made on samples of G-l and W-l in order to check the accuracy of isotope dilution analyses and the spike calibrations. The analytical data obtained in the present study along with the values obtained by other investigators are shown in Table 2.

TABLE 2

Rb AND Sr DATA ON G-l AND W-l

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb p.p.m.</th>
<th>Sr p.p.m.</th>
<th>Analyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-l</td>
<td>215.8</td>
<td>248.8</td>
<td>Present work</td>
</tr>
<tr>
<td></td>
<td>239.</td>
<td>--</td>
<td>Smales et al. (1955)</td>
</tr>
<tr>
<td></td>
<td>217.</td>
<td>233.</td>
<td>Herzog et al. (1955)</td>
</tr>
<tr>
<td></td>
<td>219.</td>
<td>--</td>
<td>Cabell et al. (1957)</td>
</tr>
<tr>
<td></td>
<td>--</td>
<td>252.</td>
<td>Smales et al. (1957)</td>
</tr>
<tr>
<td></td>
<td>--</td>
<td>236.</td>
<td>Cabell et al. (1957)</td>
</tr>
<tr>
<td></td>
<td>220.</td>
<td>250.</td>
<td>Taylor et al. (1964)</td>
</tr>
<tr>
<td></td>
<td>214.</td>
<td>--</td>
<td>Smales et al. (1958)</td>
</tr>
<tr>
<td></td>
<td>224.</td>
<td>258.</td>
<td>Pinson et al. (1962)</td>
</tr>
<tr>
<td></td>
<td>--</td>
<td>262.</td>
<td>Turekian et al. (1957)</td>
</tr>
<tr>
<td>W-l</td>
<td>21.6</td>
<td>191.8</td>
<td>Present work</td>
</tr>
<tr>
<td></td>
<td>28.5</td>
<td>177.</td>
<td>Herzog et al. (1955)</td>
</tr>
<tr>
<td></td>
<td>--</td>
<td>178.</td>
<td>Turekian et al. (1957)</td>
</tr>
<tr>
<td></td>
<td>--</td>
<td>172.</td>
<td>Smales et al. (1957)</td>
</tr>
<tr>
<td></td>
<td>--</td>
<td>180.</td>
<td>Smales et al. (1957)</td>
</tr>
<tr>
<td></td>
<td>21.3</td>
<td>--</td>
<td>Smales et al. (1958)</td>
</tr>
<tr>
<td></td>
<td>21.3</td>
<td>--</td>
<td>Cabell et al. (1958)</td>
</tr>
<tr>
<td></td>
<td>23.2</td>
<td>194.</td>
<td>Pinson et al. (1962)</td>
</tr>
<tr>
<td></td>
<td>22.</td>
<td>160.</td>
<td>Taylor et al. (1964)</td>
</tr>
</tbody>
</table>

A comparison of the recommended values, as suggested by Fleischer (1965), with the data obtained in the present study is shown in Table 3. The data in Table 2 show considerable disagreement in the
results obtained by different investigators. Fleischer and Steven (1962) suspected that the disagreement may be partly real but possibly due to sample inhomogeneity. However, the data presented in Table 3 indicate that the results obtained by the present investigator is in good agreement with the recommended values as suggested by Fleischer (1965).

TABLE 3

COMPARISON OF Rb AND Sr DATA ON G-1 AND W-1

<table>
<thead>
<tr>
<th>Analyst</th>
<th>DATA ON G-1</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rb p.p.m.</td>
<td>Sr p.p.m.</td>
<td>Rb/Sr</td>
<td></td>
</tr>
<tr>
<td>Values recommended by Fleischer (1965)</td>
<td>220.</td>
<td>250.</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>Present work</td>
<td>215.8</td>
<td>248.8</td>
<td>0.87</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Analyst</th>
<th>DATA ON W-1</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rb p.p.m.</td>
<td>Sr p.p.m.</td>
<td>Rb/Sr</td>
<td></td>
</tr>
<tr>
<td>Values recommended by Fleischer (1965)</td>
<td>22.</td>
<td>180.</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Present work</td>
<td>21.6</td>
<td>191.8</td>
<td>0.11</td>
<td></td>
</tr>
</tbody>
</table>
Strontium Isotope Ratio Analyses

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in natural strontium is believed to be fixed in nature. A standard value of 0.1194 has been assigned to the natural $^{86}\text{Sr}/^{88}\text{Sr}$ ratio. However, the measured ratios are variable both in replicate analyses of the same sample and between different samples. This variation in $^{86}\text{Sr}/^{88}\text{Sr}$ ratio is believed to be due to the isotopic fractionation in the mass spectrometer. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were adjusted by an amount proportional to half the observed deviation of $^{86}\text{Sr}/^{88}\text{Sr}$ from 0.1194. That this assumption of isotopic fractionation is valid is borne out by the fact that for a large number of replicate analysis the corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios exhibit a greater reproducibility than the measured values.

Nine analyses of the strontium carbonate standard (Eimer and Amend Lot 492327) shown in Table 4, were made during the course of this investigation. These replicate analyses gave a mean corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7083 and a standard deviation of an individual analysis of 0.0001. This value agrees well with the average of 0.7082 as determined by seven independent analyses in an inter-laboratory comparison (M. I. T. Grochronology Laboratory, 11th Ann. Prog. Rep., p. 161).
## TABLE 4

**SUMMARY OF DATA ON \( \text{Sr CO}_3 \) STANDARD**  
(Eimer and Amend Lot Number 492327)

<table>
<thead>
<tr>
<th>Record Number</th>
<th>Date</th>
<th>((\text{Sr}^{87}/\text{Sr}^{86})) corr.</th>
<th>(\text{Sr}^{87}/\text{Sr}^{86})</th>
<th>(\text{Sr}^{86}/\text{Sr}^{88})</th>
<th>Analyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6/24/65</td>
<td>0.7084</td>
<td>0.7135</td>
<td>0.1177</td>
<td>Faure</td>
</tr>
<tr>
<td>4</td>
<td>9/ 9/65</td>
<td>0.7080</td>
<td>0.7107</td>
<td>0.1185</td>
<td>Chaudhuri</td>
</tr>
<tr>
<td>16</td>
<td>9/23/65</td>
<td>0.7084</td>
<td>0.7138</td>
<td>0.1176</td>
<td>Chaudhuri</td>
</tr>
<tr>
<td>34</td>
<td>10/26/65</td>
<td>0.7089</td>
<td>0.7140</td>
<td>0.1179</td>
<td>Chaudhuri</td>
</tr>
<tr>
<td>36</td>
<td>11/ 8/65</td>
<td>0.7074</td>
<td>0.7125</td>
<td>0.1177</td>
<td>Chaudhuri</td>
</tr>
<tr>
<td>55</td>
<td>12/ 7/65</td>
<td>0.7083</td>
<td>0.7119</td>
<td>0.1182</td>
<td>Faure</td>
</tr>
<tr>
<td>66</td>
<td>12/28/65</td>
<td>0.7084</td>
<td>0.7144</td>
<td>0.1174</td>
<td>Kovach</td>
</tr>
<tr>
<td>192</td>
<td>5/24/66</td>
<td>0.7082</td>
<td>0.7124</td>
<td>0.1180</td>
<td>Chaudhuri</td>
</tr>
<tr>
<td>206</td>
<td>6/13/60</td>
<td>0.7084</td>
<td>0.7009</td>
<td>0.1189</td>
<td>Montigny</td>
</tr>
</tbody>
</table>

**AVERAGE** = 0.7083 0.7126 0.1180  

\(\bar{\sigma}_{\text{corr.}}\) = 0.0001  

\(\bar{\sigma}\) = 0.0005
CHAPTER III

Rb-Sr AGE OF INTRUSIVES AND EXTRUSIVES
OF THE WHITE PINE AREA, MICHIGAN

Introduction

A few large and small igneous bodies of felsic nature are exposed in the vicinity of the White Pine, Ontonagon County, Michigan. These igneous bodies make the prominent topographic highs in this region. The low areas, generally underlain by rocks of the Middle Keweenawan Portage Lake Lava Series and the younger formations, are covered by glacial deposits. As a result the relative stratigraphic positions of the felsic bodies have not been clearly established.

The felsic bodies have been called as rhyolite or felsite by different investigators. The relative ages of these rocks are critical, because a few investigators (Butler and Burbank, 1929; Sales, 1959; Joralemon, 1959), who favor an epignetic hydrothermal origin for the White Pine copper deposit, considered some of these igneous bodies to be possible sources for the copper in the Nonesuch Shale. White (1960) and Thaden (1950), on the other hand, regarded the rhyolites in the White Pine area as extrusives and therefore older than the Nonesuch Shale.
The whole-rock Rb-Sr ages were measured on these rhyolites in order to settle the dispute of the relative age of the rocks. In all the age calculations made in this study, the decay constant, $\lambda$, for Rb$^{87}$ was taken to be $1.39 \times 10^{-11}$ yr$^{-1}$.

Whole-Rock Rb-Sr Age of Bergland Rhyolite

A tabular rhyolite body is exposed in a road cut about 1.5 miles west of Bergland, Ontonagon County, Michigan. The rock contains a few quartz and feldspar phenocrysts of 2 to 3 mm in size. The rhyolite body encloses a lens-shaped basaltic flow and intrudes a graywacke type sandstone. Spherules are present near the top few feet of the rock. The rhyolite also contains large xenoliths of graywacke type sandstone. Leonardson (1966) made a detailed petrologic study of this Bergland rhyolite and concluded that the rhyolite is a shallow intrusive, because it contains no vesicular or brecciated top, has a micropegmatitic core and shows complete absence of spherules except in the top few feet of the rock.

For the purpose of obtaining a whole-rock Rb-Sr age of the Bergland rhyolite, samples were collected from an exposure in a small quarry about 1.5 miles west of Bergland. The sample location is shown in Figure 4. Six whole-rock samples were analyzed for Rb$^{87}$/Sr$^{86}$ and Sr$^{87}$/Sr$^{86}$ ratios. The analytical data are shown in Table 5. The Sr$^{87}$/Sr$^{86}$ and Rb$^{87}$/Sr$^{86}$ ratios are plotted in an isochron diagram (Figure 9). The best-fit straight line through these six total-rock points has been determined by least-squares analysis. The slope of
the line yields an age of 1042 ± 6 m.y. The initial Sr\textsuperscript{87}/Sr\textsuperscript{86} ratio is 0.7042 ± 0.0002.

**TABLE 5**

**ANALYTICAL DATA FOR BERGLAND RHYOLITE-BASALT ASSOCIATION, BERGLAND, MICHIGAN**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Rb p.p.m.</th>
<th>Sr p.p.m.</th>
<th>( \frac{\text{Rb}^{87}}{\text{Sr}^{86}} )</th>
<th>( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} ) (corr.)</th>
<th>( \frac{\text{Sr}^{86}}{\text{Sr}^{88}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>203</td>
<td>165.02</td>
<td>14.09</td>
<td>35.610</td>
<td>1.2167</td>
<td>0.1183</td>
</tr>
<tr>
<td>204</td>
<td>76.36</td>
<td>237.14</td>
<td>0.933</td>
<td>0.7185</td>
<td>0.1180</td>
</tr>
<tr>
<td>205</td>
<td>223.62</td>
<td>12.34</td>
<td>56.678</td>
<td>1.5386</td>
<td>0.1187</td>
</tr>
<tr>
<td>206</td>
<td>179.59</td>
<td>118.27</td>
<td>4.422</td>
<td>0.7672</td>
<td>0.1164</td>
</tr>
<tr>
<td>207</td>
<td>82.16</td>
<td>201.26</td>
<td>1.184</td>
<td>0.7216</td>
<td>0.1176</td>
</tr>
<tr>
<td>208</td>
<td>184.27</td>
<td>86.26</td>
<td>6.642</td>
<td>0.8058</td>
<td>0.1187</td>
</tr>
</tbody>
</table>

**PORCUPINE MOUNTAINS RHYOLITE, MICHIGAN**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Rb p.p.m.</th>
<th>Sr p.p.m.</th>
<th>( \frac{\text{Rb}^{87}}{\text{Sr}^{86}} )</th>
<th>( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} ) (corr.)</th>
<th>( \frac{\text{Sr}^{86}}{\text{Sr}^{88}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>225</td>
<td>183.88</td>
<td>22.13</td>
<td>24.900</td>
<td>1.0638</td>
<td>0.1190</td>
</tr>
</tbody>
</table>
Fig. 9. WHOLE-ROCK ISOCHEM DIAGRAM FOR BERGLAND RHYOLITE, BERGLAND, MICHIGAN.
(Φ RHYOLITE OF THE PORCUPINE MOUNTAINS, MICH.)
Whole-Rock Rb-Sr Age of the Porcupine Mountains

The Porcupine Mountains in Ontonagon County of Michigan are a prominent structural feature on the south limb of the Lake Superior syncline. According to Butler and Burbank (1929), these mountains are a domical uplift with a rhyolitic core in the center. The dome-shaped mountains cover an area of about 12 to 15 miles long and 4 to 6 miles wide. The rocks of the Portage Lake Lava Series and the younger formations, which include the Nonesuch Shale, are exposed around the mountains and dip away from them. Butler and Burbank (1929) noted that the domical uplift caused the Portage Lake Lava Series and the younger rocks to be faulted so that the rhyolite is brought against very steeply inclined Nonesuch Shale on the southeast side of the mountain. They concluded that all the structural features, including the White Pine fault, in the Porcupine Mountains area are the result of a laccolithic intrusive of the Porcupine Mountains. Thus, they interpreted the rhyolite as a post-Nonesuch intrusion.

White (1960) pointed out that most of rhyolites in the Porcupine Mountains are finer-grained than would be expected in a laccolith. He recommended a pre-Nonesuch age for these rhyolites, because the Keweenawan rocks in and below the Nonesuch Shale contain abundant rhyolite fragments. Thaden (1950), who studied the petrology of the rhyolites, interpreted them as flows in the upper part of the Middle Keweenawan Lava Series.
Several samples of rhyolite were collected from Government Peak, shown in Figure 4, of the Porcupine Mountains. Preliminary Rb-Sr study on these samples by x-ray fluorescence indicated a very narrow range of Rb/Sr ratios. Since it was not possible to obtain an isochron because of the narrow range of Rb/Sr ratios, the $\text{Rb}^{87}/\text{Sr}^{86}$ and $\text{Sr}^{87}/\text{Sr}^{86}$ ratios were determined for one whole-rock sample. The analytical data are shown in Table 5. The $\text{Sr}^{87}/\text{Sr}^{86}$ and $\text{Rb}^{87}/\text{Sr}^{86}$ ratios for this sample were then plotted on the isochron for the Bergland rhyolite (Figure 9) and found to be in good agreement with it. Therefore, an age of $1042 \pm 6$ m.y. and an initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of $0.7042 \pm 0.0002$ has also been assigned to the rhyolite of the Porcupine Mountains.

**Whole-Rock Rb-Sr Age of Quartz-Feldspar Porphyry**

**Near White Pine, Michigan**

An igneous body of quartz-feldspar porphyry is exposed in a road cut on highway M-64 about eight miles south of White Pine, Michigan. The porphyry is reddish-brown to brown in color. The rock contains abundant euhedral to anhedral phenocrysts of feldspar and quartz. The phenocrysts are about 10 to 15 mm. in size and account for approximately 25 per cent of the rock.

The porphyry is cut in few places by basaltic dikes about one inch thick. Jointing is quite common in the porphyry. According to Butler and Burbank (1929, Plate 32), the quartz-feldspar porphyry
probably assumes an elliptical shape and covers an area of 16 square miles. The quartz-feldspar porphyry is believed to have been intruded into the Portage Lake Lava Series (Butler and Burbank, 1929).

Five samples of the quartz-feldspar porphyry were analyzed for the whole-rock Rb-Sr age study. Analytical data for these samples are shown in Table 6. The $\text{Rb}^{87}/\text{Sr}^{86}$ and $\text{Sr}^{87}/\text{Sr}^{86}$ ratios for these samples were plotted as an isochron. A line has been fitted to these whole-rock points by a least-squares method (Figure 10). The age of the porphyry, calculated from the slope of the line, is $978 \pm 40$ m.y. The initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio is $0.7181 \pm 0.0006$.

**Whole-Rock Rb-Sr Age of the "Chippewa" Felsite in the White Pine Area, Michigan**

The Bergland Lookout Tower in Ontonagon County of Michigan is situated on a hill capped by felsite rock. The felsite is a dark-brown to purplish-brown rock and contains numerous phenocrysts of feldspar. Quartz is abundant in the groundmass, although a very minor amount is also present as phenocrysts. The feldspar phenocrysts approach approximately 15 mm. in size. The felsite near the Bergland Lookout Tower has been called "Chippewa" felsite (Butler and Burbank, 1929, Plate 14).

Gordon and Lane (1907), who studied the felsite in the Chippewa Hill of Gogebic County, Michigan, observed numerous indications of flow structure in the Chippewa felsite. The felsite at the Bergland Lookout Tower in Ontonagon County is separated from the felsite of the
Fig. 10. WHOLE-ROCK ISOCHRON DIAGRAM FOR QUARTZ-FELDSPAR PORPHYRY NEAR WHITE PINE, MICHIGAN.

Age = 978 ± 40 m.y.
Initial \( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} = 0.7181 ± 0.0006 \)
Chippewa Hill in Gogebic County by a distance of over 25 miles. The correlation of these two rocks has not been clearly demonstrated. Butler and Burbank (1929) considered the "Chippewa" felsite to be intrusive. Thaden (1950), who studied the "Chippewa" felsite of the Porcupine Mountains in Ontonagon County, Michigan, regarded the felsite as a flow. The "Chippewa" felsite has been thought to be a member of the Ashbed group in the Portage Lake Lava Series of Middle Keweenawan age (Butler and Burbank, 1929).

### TABLE 6

**ANALYTICAL DATA FOR THE WHITE PINE QUARTZ-FELDSPAR PORPHYRY, WHITE PINE, MICHIGAN**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Rb p.p.m.</th>
<th>Sr p.p.m.</th>
<th>Rb$^{87}$/Sr$^{86}$</th>
<th>Sr$^{87}$/Sr$^{86}$(corr.)</th>
<th>Sr$^{86}$/Sr$^{88}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>209</td>
<td>205.94</td>
<td>61.93</td>
<td>9.767</td>
<td>0.8538</td>
<td>0.1191</td>
</tr>
<tr>
<td>210</td>
<td>195.65</td>
<td>98.41</td>
<td>5.806</td>
<td>0.7950</td>
<td>0.1188</td>
</tr>
<tr>
<td>211</td>
<td>206.44</td>
<td>60.76</td>
<td>9.979</td>
<td>0.8541</td>
<td>0.1192</td>
</tr>
<tr>
<td>212</td>
<td>201.53</td>
<td>45.53</td>
<td>13.051</td>
<td>0.8941</td>
<td>0.1176</td>
</tr>
<tr>
<td>213</td>
<td>206.30</td>
<td>66.43</td>
<td>9.115</td>
<td>0.8467</td>
<td>0.1183</td>
</tr>
</tbody>
</table>

Samples of the "Chippewa" felsite were collected from the Bergland Lookout Tower hill for a whole-rock Rb-Sr age determination. The sample location is shown in Figure 4. Four samples were studied for Rb-Sr analysis. The analytical data are shown in Table 7. The
Rb$^{87}$/Sr$^{86}$ and Sr$^{87}$/Sr$^{86}$ ratios are plotted on an isochron diagram. A best-fit straight line is drawn through these "whole-rock" points by least-squares analysis (Figure 11). The age calculated from the slope of the line is $1100 \pm 25$ m.y., using $\lambda$ for Rb$^{87} = 1.39 \times 10^{-11}$ yr$^{-1}$. The initial Sr$^{87}$/Sr$^{86}$ ratio is $0.7038 \pm 0.0008$.

### TABLE 7

ANALYTICAL DATA FOR FELSITE FROM BERGLAND LOOKOUT TOWER, BERGLAND, MICHIGAN

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Rb p.p.m.</th>
<th>Sr p.p.m.</th>
<th>Rb$^{87}$/Sr$^{86}$</th>
<th>Rb$^{87}$/Sr$^{86}$ (corr.)</th>
<th>Sr$^{86}$/Sr$^{88}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>166</td>
<td>169.65</td>
<td>208.64</td>
<td>2.361</td>
<td>0.7401</td>
<td>0.1205</td>
</tr>
<tr>
<td>169</td>
<td>125.07</td>
<td>214.77</td>
<td>1.688</td>
<td>0.7294</td>
<td>0.1210</td>
</tr>
<tr>
<td>170</td>
<td>131.87</td>
<td>224.50</td>
<td>1.703</td>
<td>0.7299</td>
<td>0.1208</td>
</tr>
<tr>
<td>171</td>
<td>140.87</td>
<td>334.06</td>
<td>1.221</td>
<td>0.7227</td>
<td>0.1200</td>
</tr>
</tbody>
</table>

The analytical work was done in the geochronological laboratory at the University of Minnesota. The Sr$^{87}$/Sr$^{86}$ ratio, after normalizing to Sr$^{86}$/Sr$^{88} = 0.1194$, of the Eimer and Amend SrCO$_3$ standard measured at the University of Minnesota was 0.7074. The ratio measured on the same standard at the Ohio State University was 0.7083. Since most of the Rb-Sr work for the present study was done at the
Fig. II. WHOLE-ROCK ISOCHRNON DIAGRAM FOR FELSITE AT BERGLAND LOOKOUT TOWER, BERGLAND, MICHIGAN

Age = 1100 ± 25 m.y.  
Initial $\frac{Sr^{87}}{Sr^{86}} = 0.7047 ± 0.0008$
Ohio State University, a correction of + 0.0009 should be made to the initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the "Chippewa" felsite for comparison with the rest of the Rb-Sr data. This correction, however, has no effect on the age calculation, because each "whole-rock" point on the isochron will be affected by the same amount and thereby the isochron maintains the same slope. Therefore, the initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio for the Chippewa felsite is considered to be 0.7047 ± 0.0008.

**Discussion of the Rb-Sr Ages of Intrusives and Extrusives**

The Rb-Sr age of the "Chippewa" felsite is 1100 ± 25 m.y. The present study indicates that the Chippewa felsite is oldest of the igneous bodies studied here. The quartz-feldspar porphyry seems to be the youngest intrusive in the White Pine area.

The initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of 0.7181 ± 0.0006 for the quartz-feldspar porphyry is significantly higher than would be expected for common igneous rocks. This high initial ratio would suggest that the parent material originated in a Rb-enriched environment. The scattering of "total-rock" points about the isochron may suggest a possibility of crustal contamination.

The rhyolite sample from the Government Peak of the Porcupine Mountains lies on the isochron for the Bergland rhyolite within the experimental error. Therefore, it is suggested that the Bergland rhyolite and the Porcupine Mountains rhyolite are of the same age and offshoots from a common magmatic source.
CHAPTER IV

WHOLE-ROCK Rb-Sr AGE OF THE NONESUCH SHALE

Introduction

The first report on dating sedimentary rocks by the whole-rock Rb-Sr method was that of Compston and Pidgeon (1962). Later works include that of Whitney and Hurley (1964), Peterman (1965), Faure and Chaudhuri (1965), Allsopp and Kolbe (1965), Kovach and Faure (1966), and Faure and Montigny (1966).

Of three shales studied by Compston and Pidgeon (1962), two had apparent ages that were in good agreement with the known stratigraphic age; the third gave scattered results which yielded an age considerably in excess of the stratigraphic age. The results obtained by Whitney and Hurley (1964) on an unmetamorphosed Middle Devonian shale showed an apparent age 15 per cent in excess of the actual age of the Middle Devonian. Kovach and Faure (1966) analyzed the Gunflint sediments and observed an age 15 per cent lower than the actual age. Peterman (1965) and Faure and Montigny (1966) dated metamorphosed sediments and found the ages considerably lower than the expected age.

The present study is an attempt to date the Precambrian Nonesuch Shale by the whole-rock Rb-Sr method and to evaluate the meaning of this age. The Nonesuch formation, which is about 600 feet thick in
the White Pine area, consists of an unmetamorphosed sequence of dominantly gray, well-bedded siltstone and shale with a minor amount of sandstone.

Mineralogy of the Nonesuch Shale

The petrology of the sandstone in the Nonesuch formation has been described in detail by White and Wright (1954) and Wiese (1960). The sandstone contains numerous angular to subangular rock fragments, quartz, feldspar, and mica. Calcite is quite common as cement.

The mineralogy of the shales and fine-grained siltstones of the formation was studied by x-ray diffraction analysis. Nickel-filtered copper Ka radiation at 45 KV and 15 MA was used in the x-ray analysis. The size fraction less than 62 microns for each sample was x-rayed as a random powder through 65° two theta (2θ) to determine the general clay mineral composition, the non-clay mineral composition, and to pick up certain nonbasal reflections. Random orientation of samples for x-ray analysis was obtained by sprinkling the powdered sample on a glass-slide coated with a mixture of "Duco" cement and acetone.

In the case of the oriented aggregates, the <2 micron fractions were x-rayed through at least 40° two theta (2θ). Oriented aggregate slides for each sample were treated with ethylene glycol by allowing it to remain in a saturated atmosphere for 48 hours. The oriented aggregate slides were also heated to 450° C for twelve hours and again to 600° C for twelve hours. These slides were then immediately x-rayed.
Qualitative Study of the Mineralogy

Random Powder X-ray. Five samples from the parting shale member of the Nonesuch formation were chosen for the x-ray study. On the basis of basal and non-basal reflections, the major components were observed to be quartz, potash feldspar, plagioclase, mica and chlorite with trace amounts of chalcocite and calcite. According to the method of Yoder and Bugster (1956), the presence of both the 1M and 2M mica polymorphs were shown.

In every sample the 1.50 Å and 1.54 Å peaks were observed. These two peaks are generally considered to be the (060) reflections of dioctahedral and trioctahedral 2:1 layer-type silicates. It is possible that in the present analysis the (060) peak at 1.50 Å is that of dioctahedral mica-type mineral and the peak at 1.53 Å is the (060) reflection from a trioctahedral biotite and/or chlorite. However, Ross (1964) recently pointed out that the (060) reflection overlap the equally strong 331 reflection of the 1M and 2M micas. In this case the distinction of dioctahedral and trioctahedral nature of the 2:1 layer-type silicates in the present analysis may not be valid.

Oriented Aggregate X-ray Study

For a detailed study of clay minerals the oriented aggregate technique is useful. Here the basal reflections are greatly enhanced due to the preferred c-axis orientation. The oriented x-ray study was made on particles less than two microns. In the preparation of the
samples for the study of the basal reflections, the shales were crushed to about very coarse sand size particles. Approximately 10 gms. of each sample was placed in 600 ml of double-distilled water. Further disaggregation was obtained by ultrasonic treatment. The sample was then allowed to settle for the time sufficient to permit withdrawal particles of the two micron fraction (Krumbein and Pettijohn, 1938, p. 110). This withdrawal was then concentrated by evaporation. Each concentrate was then put on two glass slides to form air-dried oriented aggregates. These oriented aggregates were then examined for x-ray diffraction study.

A total of fifteen shale samples were analyzed for determining the clay mineral composition of the Nonesuch Shale. Out of these fifteen samples, ten were collected from the mineralized zone and five from the non-mineralized part of the Nonesuch Shale.

The air-dried oriented x-ray patterns indicated the presence of only two groups of clay minerals, the illite (10 Å) group and the chlorite (14 Å) group. No difference in the type of clay mineral composition was observed between the samples of mineralized and non-mineralized zones. The characteristics of the illite and chlorite reflections are summarized below.

**Illite (10 Å) Group**

The (001) reflections on air-dried samples are observed at 10.5 Å to 10.1 Å. The peaks are broad and asymmetric to the low angle side. The 10.5 Å peaks are shifted to 10.1 Å on glycolation, while
the 10.1 Å peaks remain unchanged. Upon heating the untreated air-dried slides to about 450°C, the (001) reflections showed a decrease in intensity and in d-spacing. The samples heated to 600°C showed a further decrease in the intensity of the (001) reflections and 10.1 Å d-spacings were observed for all samples. The nature of the 10 Å peak suggests that the illite may be slightly interstratified with expandable material.

**Chlorite (14 Å) Group**

The (001) reflections occur at 14.6 Å on air-dried samples. None of the samples treated with ethylene glycol showed any sign of expandable clay mineral. Upon heating the slides to 450°C, all the basal reflections showed a decrease in intensity except the (001) reflection, which was slightly increased. The samples heated to about 600°C showed the shift of (001) reflection to 14.1 Å with an increase in intensity. All other basal reflections were nearly absent. A higher intensity of the even-order reflections compared to the odd-order reflections suggests that the chlorites in the Nonesuch Shale are iron-rich.

Figure 12 is a representation of the x-ray pattern of an oriented aggregate.

Because of the coincidence of chlorite (002) and kaolinite (001) reflection at 7 Å, it was necessary to make tests for the presence of kaolinite. In the present study the absence of kaolinite is
Fig. 12. X-RAY DIFFRACTOMETER TRACES OF A SAMPLE OF THE NONESUCH SHALE VARIOUSLY TREATED
indicated by the following observations:

1. No peak was observed for kaolinite at 2.37 Å (003) at 37.5°.

2. No peak for kaolinite 3.57 Å (002) was resolvable from chlorite 3.55 Å (004) even at a goniometer scan-rate of one-eighth of a degree per minute.

3. If kaolinite is present, as shown by the presence of a small 7 Å reflection after heating to 450°C, it occurs in a very small amount.

Quantitative Study of the Clay Minerals

A general observation of the x-ray patterns for all of the fifteen samples gives an impression that there is little or no difference in the clay-mineral composition. However, detailed observation showed that a difference does exist.

An attempt was made to determine the illite/chlorite ratio of these fifteen samples from the Nonesuch Shale. The method involving quantitative estimation was based on peak height ratios, without attempting to make any percentage calculation. The choice of the reflections was arbitrary. The most intense reflections for illite and chlorite were thought to be better for an estimation of the relative amounts of clay mineral groups. Each sample analyzed in the present study showed that the intensity of the chlorite (002) reflection is higher than that for the chlorite (001) reflection.
The illite/chlorite ratio was, therefore, obtained by dividing the peak height of illite (00l) by that of chlorite (002). In every case the total peak height was measured from background.

Two slides of each sample were made for x-ray study. Duplicate runs were made on both slides for three samples. The reproducibility of the illite (00l)/chlorite (002) ratio for these three samples was found to be within 5 to 8 per cent.

**Illite/Chlorite Ratio**

Five samples from the non-mineralized zone of the Nonesuch Shale had illite (00l)/chlorite (002) ratios of 0.09 to 0.56. The ratios for ten samples from the mineralized zone ranged from 0.11 to 1.33.

Four out of the ten samples from the mineralized zone were collected from the same stratigraphic horizon, known as "Tiger" in the White Pine mine. This bed is about a foot thick. The illite/chlorite ratios for these four samples ranged from 0.23 to 1.33. The location of these samples and their illite/chlorite ratios are shown in Figure 13. It can be seen from the figure that there is an apparent northward increase in the illite/chlorite ratio. The amount of increase is about 500% within a distance of about 2-1/2 miles.

White and Wright (1954) suggested that the Nonesuch Shale had a source to the south of the present site of the formation. It appears that the trend of increase in the illite/chlorite ratio for "Tiger" is more or less parallel to the presumed direction of transportation of the sediment.
Fig. 13. Distribution of Illite/Chlorite Ratio in "Tiger" Horizon of the Nonesuch Shale Near White Pine, Michigan.
An increase in the illite/chlorite ratio implies that either the amount of illite had increased or the amount of chlorite had decreased. However, a careful examination showed that the illite (001) peak-height is nearly constant for these four samples. In contrast to this, the chlorite (002) peak-height decreases and the peak broadens with increasing illite/chlorite ratio. The apparent decrease in the chlorite peak-height and the peak sharpness may then be correlated to the increasing distance of transportation. It may be that the large chlorite flakes became thinner with transport and that this caused the apparent increase in the illite/chlorite ratio.

A large variation of the illite/chlorite ratios both laterally and vertically in the Nonesuch Shale appears to be the result of transportation. Thus, it may be inferred that the clay minerals in the Nonesuch Shale are mainly detrital in origin.

Rb-Sr Analytical Data

For the purpose of dating the Nonesuch Shale by the whole-rock Rb-Sr method, eight samples from distinct stratigraphic horizons of the cupriferous parting shale member and one sample from the non-mineralized part of the Nonesuch Shale were chosen. All these samples were collected from the White Pine Mine, Ontonagon. The analytical data are presented in Table 8. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of each sample were plotted against the corresponding $^{87}\text{Rb}/^{86}\text{Sr}$ ratio on an isochron diagram (Figure 14). The slope and zero intercept of the isochron were calculated by a least-squares analysis. The age, calculated from the slope,
is 1075 ± 50 m.y., using λ for Rb$^{87} = 1.39 \times 10^{-11}$ yr$^{-1}$. The initial Sr$^{87}$/Sr$^{86}$ ratio is 0.7080 ± 0.0008.

### TABLE 8

ANALYTICAL DATA FOR THE NONESUCH SHALE, WHITE PINE, MICHIGAN

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Rb (p.p.m.)</th>
<th>Sr (p.p.m.)</th>
<th>Rb$^{87}$/Sr$^{86}$</th>
<th>Sr$^{87}$/Sr$^{86}$ (corr.)</th>
<th>Sr$^{86}$/Sr$^{88}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>241</td>
<td>61.2</td>
<td>222.8</td>
<td>0.797</td>
<td>0.7205</td>
<td>0.1202</td>
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<tr>
<td>241 (carbonate fraction)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>242</td>
<td>109.6</td>
<td>101.3</td>
<td>3.144</td>
<td>0.7552</td>
<td>0.1184</td>
</tr>
<tr>
<td>243</td>
<td>107.27</td>
<td>118.4</td>
<td>2.630</td>
<td>0.7454</td>
<td>0.1190</td>
</tr>
<tr>
<td>244</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.7065</td>
<td>0.1192</td>
</tr>
<tr>
<td>245</td>
<td>105.5</td>
<td>93.6</td>
<td>3.278</td>
<td>0.7568</td>
<td>0.1207</td>
</tr>
<tr>
<td>247</td>
<td>147.9</td>
<td>172.1</td>
<td>2.498</td>
<td>0.7456</td>
<td>0.1182</td>
</tr>
<tr>
<td>248</td>
<td>90.5</td>
<td>110.4</td>
<td>2.381</td>
<td>0.7439</td>
<td>0.1194</td>
</tr>
<tr>
<td>249</td>
<td>55.22</td>
<td>137.08</td>
<td>1.168</td>
<td>0.7255</td>
<td>0.1194</td>
</tr>
<tr>
<td>250</td>
<td>54.30</td>
<td>224.89</td>
<td>0.700</td>
<td>0.7180</td>
<td>0.1188</td>
</tr>
</tbody>
</table>

In addition, Sr isotopic analysis was made on a sample of limestone bed in the parting shale member. The Sr$^{87}$/Sr$^{86}$ ratio of the limestone is 0.7065.

A fraction of carbonate cement in a sample of sandstone from the lower sandstone unit was analyzed for Sr isotopic ratio measurement.
Fig. 14. WHOLE-ROCK ISOCRON DIAGRAM FOR NONESUCH SHALE, MICHIGAN.

Age = 1075 ± 50 m.y.
Initial Sr$^{87}$/Sr$^{66}$ = 0.7060 ± 0.0008
The $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the carbonate cement is 0.7085.

**Rb-Sr Ages of Pebbles from Lower Sandstone Unit**

Several pebbles of the lower sandstone were collected from the White Pine mine area. These pebbles are fresh, rounded and light-brown to chocolate-brown color. The lithology of the pebbles vary from basalt to rhyolite. A dark-brown-colored felsite pebble and a light-brown-colored rhyolite pebble were analyzed for the whole-rock Rb-Sr age determination. These two pebbles were sawed into thin slices in order to obtain a fresh portion of the rocks.

The analytical data and results obtained from these two pebbles are shown in Table 9. An initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of 0.7045 was assumed in calculating the ages. The assumption of this initial ratio is based on the measurements from rhyolites and felsites of this area. The age of the rhyolite pebble is 1107 m.y., while the age of the felsite pebble is 1180 m.y.
TABLE 9
ANALYTICAL DATA FOR THE PEBBLES
IN THE LOWER SANDSTONE,
WHITE PINE, MICHIGAN

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Rb p.p.m.</th>
<th>Sr p.p.m.</th>
<th>Rb(^{87}/)Sr(^{86})</th>
<th>Sr(^{87}/)Sr(^{86}) (corr.)</th>
<th>Sr(^{86}/)Sr(^{88})</th>
</tr>
</thead>
<tbody>
<tr>
<td>251</td>
<td>33.03</td>
<td>74.19</td>
<td>1.291</td>
<td>0.7257</td>
<td>0.1196</td>
</tr>
<tr>
<td>252</td>
<td>122.49</td>
<td>60.04</td>
<td>5.958</td>
<td>0.7962</td>
<td>0.1197</td>
</tr>
</tbody>
</table>

Discussion

The collinearity of the total-rock points, which define the isochron for the Nonesuch Shale, is remarkable. The apparent age of the shale calculated from the slope of isochron in Figure 14 is 1075 ± 50 m.y. This apparent age is regarded as a maximum estimate for the time of deposition of the shale. The actual age of the formation may be significantly less than the apparent age of 1075 ± 50 million years. This interpretation is based on the fact that the initial Sr\(^{87}/\)Sr\(^{86}\) ratio of 0.7080 for the Nonesuch Shale is higher than the initial Sr\(^{87}/\)Sr\(^{86}\) ratio of about 0.7045 for the igneous rocks in this locality, and thereby suggests the presence of inherited radiogenic strontium in the sediments at the time of deposition. In the presence of inherited radiogenic strontium the isochron could have had a finite positive slope at the time of deposition of the sediments since the rocks having a high Rb/Sr ratio had a higher Sr\(^{87}/\)Sr\(^{86}\) ratio than those having a lower Rb/Sr ratio. This would then lead to an overestimate of the
actual age of the sediment.

Hurley (1965) studied the increase of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in sea water during the history of the earth. In this analysis he considered the modern sea water as a reference standard and reported all variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ values of marine limestone of different ages as being the difference between the observed value and that of modern sea water. This difference in the $^{87}\text{Sr}/^{86}\text{Sr}$ value was plotted against time in order to obtain a growth curve for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the sea water. The resulting diagram is shown in Figure 15. The mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of modern sea water is known to be $0.7093 \pm 0.0005$, relative to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ (Faure et al., 1965).

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the limestone in the parting shale member of the Nonesuch Shale was found to be 0.7065. The difference in the $^{87}\text{Sr}/^{86}\text{Sr}$ value between this limestone and the modern sea water is $-27 \times 10^{-4}$. This difference of $-27 \times 10^{-4}$ in $^{87}\text{Sr}/^{86}\text{Sr}$ value is plotted against an age of 1075 ± 50 m.y. on Hurley's marine geochron diagram (Figure 15). The apparent close fit of this value on Hurley's diagram may suggest that the parting shale member of the Nonesuch formation was deposited in a marine environment.

The carbonate fraction extracted from a sample of the lower sandstone has a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7085. This value appears to be significantly higher than the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7065 for the limestone in the parting shale, but closer to the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7080 for the parting shale. This close similarity in the $^{87}\text{Sr}/^{86}\text{Sr}$
Primordial Strontium

Archean Sea Water

Nonesuch Limestone

Grenville

Ordovician

Modern

\[
\left( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \right)_{\text{measured}} - \left( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \right)_{\text{modern sea}}
\]
values for the carbonate fraction and the initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the sediments may indicate an approach of strontium isotopic equilibrium between connate water and the sediment during diagenesis.

Since the initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the shale is higher than the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the limestone, it is suggested that the strontium in detrital sediments did not equilibrate isotopically with that of the water at the time of deposition of the sediments. Similar non-equilibrium relationship was noted by Compston and Pidgeon (1962), Allsopp and Kolbe (1965) and others.
CHAPTER V

EVALUATION OF THE WHOLE-ROCK

Rb-Sr AGE OF SEDIMENTS

Introduction

The basic equation used for dating sediments by the whole-rock Rb-Sr method can be written as:

\[
\frac{\text{Sr}^{87}}{\text{Sr}^{86}} \text{ today} = \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \text{ initial} + \frac{\text{Rb}^{87}}{\text{Sr}^{86}} \text{ today} \ (e^{\lambda t} - 1)
\]

where \( \lambda \) = decay constant for Rb\(^{87} \), and \( t \) = the age of the rock.

If a series of rock samples with the same age and the same initial Sr\(^{87}/\)Sr\(^{86} \) ratio but different Rb/Sr ratios is plotted in Sr\(^{87}/\)Sr\(^{86} \) and Rb\(^{87}/\)Sr\(^{86} \) coordinates, a straight line will be obtained as long as they remain closed systems to Rb and Sr. This line is called the "isochron" and the age of the rock is directly proportional to the slope of the isochron.

It should be emphasized that in order to obtain the actual age of the sediments by the whole-rock Rb-Sr method, the bulk samples must have had essentially the same initial strontium isotopic composition during sedimentation. However, Whitney and Hurley (1964) have already pointed out that the major source of error in Rb/Sr age determinations
on whole-rock samples of argillaceous rocks is the presence of inherited radiogenic strontium in the detrital fraction of the rock. The ages obtained are then necessarily maxima. They concluded that in cases where the provenance of the detrital material was young or where there was a major enrichment of Rb relative to Sr during sedimentation, this maximum age may be close to the true age.

An attempt has been made to obtain information concerning the relative behavior of rubidium and strontium during weathering, transportation and deposition of sediments. This information was gathered of the literature.

**Geochemical Behavior of Rb in Sediments**

Rubidium forms no mineral of its own and is admitted into potassium-bearing minerals. Ahrens (1953) reported a relative enrichment of rubidium in pegmatitic feldspars and micas. Thus detrital feldspar and mica can contribute a significant amount of Rb to the sediments. Turekian and Wedepohl (1961) calculated an average Rb content of 140 p.p.m. in shale, 60 p.p.m. in sandstone and 3 p.p.m. in carbonates.

Because of the close similarity in bond type and ionic radius, Rb is expected to follow K in the sediments. However, Horstman (1957) in a study of several sedimentary rocks ranging in age from Precambrian to Recent observed a decrease in the K/Rb ratio during weathering. Although the trend was toward absolute loss of both K and Rb, there was relative enrichment of Rb. Horstman suggested that adsorption may
play an important role in the concentration of Rb relative to K in the late stages of weathering.

In argillaceous rocks clay minerals make up a major component. Rb can be present in the clay minerals either as interlayer cation or as adsorbed ions on the clay mineral surface. Major clay mineral groups exhibit large variations in their Rb content. Horstman (1957) found that the kaolinite group had the extreme variation in Rb content from 10 p.p.m. to 580 p.p.m. The average Rb content in the kaolinite group was observed to be 110 p.p.m. On the other hand, montmorillonite, illite and mixed-layer clays showed much less variation, the average Rb content being 25 p.p.m., 190 p.p.m., and 180 p.p.m., respectively.

Degens, Williams and Keith (1957) noticed that Rb was more abundant in a group of marine shales than in fresh-water shales. The average Rb content for marine shales was 281 p.p.m. and for fresh-water shales 139 p.p.m.

Hirst (1962) made a study of modern sediments from the Gulf of Persia. He observed an increase of the K/Rb ratio from clay to sand. This was explained as due to more favorable adsorption of Rb than K by clay minerals. Both Young (1954) and Wedepohl (1960) observed that the abundance of Rb is similar in both near-shore and deep-sea clays.

**Geochemical Behavior of Sr in Sediments**

Following Goldschmidt's concept that there is a tendency of certain minor elements to follow the major elements which are similar
to them in radius and bond types, it is believed that Sr will follow Ca to a large extent. However, it has been found that sedimentary rocks do not always show a marked universal covariance between these two elements.

From a study on 62 shales, Turekian and Kulp (1956) calculated a Sr/Ca ratio of 0.06 for "pure" shale. Hirst (1962) observed that the Sr/Ca ratio of sediments from the Gulf of Persia is much lower than the average Sr/Ca ratio of 0.06 for "pure" shale estimated by Turekian and Kulp. This low value was attributed to the loss of Sr relative to Ca during weathering.

Mohr (1959) noticed a similar low value of the Sr/Ca ratio for a Cambrian shale. The Sr/Ca ratio for this shale was found to be 0.018 compared to the sea-water value of 0.03. This low value of the Sr/Ca ratio for the shale probably suggest that relatively more Sr remained in solution than Ca.

El Wakeel and Riley (1961) noticed an increase of Sr content from near-shore sediments to deep-sea clays. They suggested that most of the Sr in sediments are carried by clays.

Schachtschabel (1940) made experiments of ionic exchange of NH₄-kaolinite, NH₄-montmorillonite and NH₄-mica with solution of alkaline-earth chlorides. He noticed that Sr⁺⁺ in competition with equivalent concentrations of Ca⁺⁺ would be taken up preferentially by mica, while kaolinite and montmorillonite did not show such discrimination.
Evaluation of the Whole-Rock Rb-Sr Dating of the Nonesuch Shale

The present study on the Nonesuch Shale yielded the following information:

1. Co-linearity of the "whole-rock" points on an isochron diagram; and
2. the presence of inherited radiogenic strontium in the sediments at the time of deposition.

Similar information was obtained by other investigators from dating sediments by the whole-rock Rb-Sr method.

The apparent co-linearity of the "whole-rock" points for the Nonesuch Shale indicates a homogeneous strontium isotopic composition during some time before the lithification of the sediments. The homogeneity of the strontium isotopic composition in sediments could probably be achieved through any one of the following mechanisms:

1. The provenance was homogeneous in regard to the age and the initial Sr\textsuperscript{87}/Sr\textsuperscript{86} ratio.
2. The homogenization of the Sr isotopic composition could be a result of metamorphism of the sediment after lithification.
3. Authigenic minerals in the sediments may cause a homogenization of the Sr isotopic composition.
4. The homogenization could be the result of diagenesis.
The achievement of a homogenous Sr isotopic composition either through provenance or through metamorphism is of significance to the Rb-Sr age of the sediments. If the homogenization is the result of provenance, the age obtained would then be a maximum estimate for the time of deposition of the sediment and would reflect the age of the source rocks. On the other hand, if it is the result of metamorphism, the age obtained would indicate the time of the metamorphism and hence the age would be a minimum estimate for the time of sedimentation.

An attempt has been made to explore plausible mechanisms for the homogenization of Sr isotopic composition for the Nonesuch Shale. The purpose of this investigation is to evaluate the whole-rock Rb-Sr age of the Nonesuch Shale.

It has been reported that the Nonesuch Shale contains detrital particles which were derived from igneous, sedimentary and metamorphic rocks. Some of these particles were probably derived from pre-Keweenawan rocks (Van Hise and Leith, 1911). However, the Nonesuch Shale contains many unstable rock and mineral fragments. These fragments indicate a proximate source area for these sediments. Thus it is believed that the major amount of detritus was derived from Keweenawan rocks. The present study measured ages on two pebbles from the lower sandstone unit, which transitionally underlies the Nonesuch Shale. The whole-rock Rb-Sr ages for these two boulders are 1107 and 1180 m.y. The lithological and geochronological data do not favor the case that the Nonesuch Shale was derived by weathering of a source area
of uniform age.

The Nonesuch Shale has been considered to be an unmetamorphosed sedimentary rock. It hardly contains minerals that are typical of metamorphic origin. A few grains of epidote have been reported, but they are considered to be detrital (Weise, 1960). The mineralogical and textural characters of the Nonesuch Shale do not indicate any obvious metamorphic effect. The present study measured the Sr isotopic composition of a thin limestone bed in the parting shale unit of the Nonesuch formation. The $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the limestone is 0.7065, whereas the initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the Nonesuch Shale is 0.7080. The difference between these two values is significant within the experimental error. If there had been any metamorphism, even of a very low grade, the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the limestone should be identical to the initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the sediments. Thus, it appears that homogenization can not be the result of metamorphism.

A large amount of authigenic minerals in sediments may facilitate the homogenization of Sr isotopic composition. However, the clays that make up a major component of the Nonesuch sediments are believed to be detrital in origin. Moreover, if the sedimentary particles were authigenic, the initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the sediment should be identical to the $\text{Sr}^{87}/\text{Sr}^{86}$ of the limestone. Therefore, it may be concluded that the homogenization of Sr isotopic composition in the Nonesuch Shale is not caused by the presence of authigenic minerals.

From the study of the geochemical behavior of Rb and Sr in sediments it has been observed that there is an apparent increase in
Rb/Sr ratio of sediments during weathering and transportation. There are also reports on exchange of Sr by clays with the surrounding medium. Thus it is expected that there would be some change in the Sr isotopic composition of the sediments by reaction with the surrounding medium during weathering and transportation. However, it does not seem probable that such exchange reactions cause homogenization of the Sr isotopic composition of the sediment during transportation, since the general consensus is that the sediments generally contain higher Sr$^{87}$/Sr$^{86}$ ratios than the water.

A complete homogenization of the Sr isotopic composition during diagenesis has never been demonstrated or observed. It is generally believed that there is some chemical exchange between the sedimentary particles and the connate water. If widespread homogenization occurs through circulation of the connate water during diagenesis, the initial Sr$^{87}$/Sr$^{86}$ ratio of the sediments would be expected to have the same value as that of carbonate cement present in the sediments.

In the present study an attempt was made to extract carbonate cement from a sample of the lower sandstone. The Sr$^{87}$/Sr$^{86}$ ratio measured on the carbonate fraction was found to be 0.7085. By comparison, this value is identical within the experimental error to the initial Sr$^{87}$/Sr$^{86}$ ratio of 0.7080 for the Nonesuch Shale. Unless the similarity of these two ratios is fortuitous, it may indicate that the homogenization of the Sr isotopic composition for the Nonesuch Shale is a result of diagenesis.
If the above assumption is correct, then the whole-rock Rb-Sr age of 1075 ± 50 m.y. would be close to the true age of deposition of the sediments. If, on the other hand, the isochron had a finite positive slope at the time of deposition of the sediments, then the age of 1075 ± 50 m.y. would be a maximum estimate for the time of deposition of the Nonesuch Shale.

The data at hand are insufficient to make any conclusive statement concerning the actual age of the Nonesuch Shale. Several intrusives in the White Pine area were dated. However, their stratigraphic positions relative to the Nonesuch Shale have not been clearly demonstrated by field data. In this case, the present investigator considers the age of 1075 ± 50 m.y. for the Nonesuch as the maximum estimate for the time of deposition of the sediments.
CHAPTER VI
WHOLE-ROCK Rb-Sr AGE OF THE
MOUNT BOHEMIA INTRUSIVE

Introduction

The Mount Bohemia intrusive is located on the southeast corner of Delaware Quadrangle, Keweenaw County, Michigan. The intrusive body extends for about half a mile up the south slope of Mount Bohemia and has a width of about one-quarter of a mile. The bulk of the intrusive is largely a medium-grained syenodiorite with a central core of fine- to coarse-grained granophyre (Cornwall, 1954). In the older literature the Mount Bohemia intrusive has been termed "gabbro," "gabbro-aplite" or "oligoclase gabbro."

The syenodiorite of the Mount Bohemia is a mottled light red and dark gray colored, medium-grained rock. The essential minerals are hornblende and albite-oligoclase, and the minor constituents are orthoclase, magnetite, apatite, sphene, epidote, and chlorite.

The Mount Bohemia igneous complex is intruded into the basaltic flows and the conglomerates of the Middle Keweenawan Portage Lake Lava Series. The intrusion caused a moderate to intense metamorphism of the basaltic flows. The contact of the syenodiorite with the lavas are steep and the intrusive is thought to be a stock.
In exposed areas, the intrusive is found to cut the Lac La Belle Conglomerate (Conglomerate No. 3?) of early Middle Keweenawan age. This has led many people to believe that the Mount Bohemia intrusive is of Middle Keweenawan age. Butler and Burbank (1929) considered the Mount Bohemia intrusive to be of Middle Keweenawan age but did not exclude a younger age.

Cornwall (1954), who made a detailed study of the bedrock geology of the Mount Bohemia area, considered the Mount Bohemia intrusive to be younger than the Middle Keweenawan Portage Lake Lava Series but older than the Upper Keweenawan Copper Harbor conglomerate.

An attempt was made to obtain a whole-rock Rb-Sr age for the Mount Bohemia intrusive. Five samples of syenodiorite from the intrusive were chosen for the Rb-Sr analysis.

**Results and Discussion**

The analytical data are presented in Table 10. The Rb and Sr concentrations were measured by the isotope dilution method. The \( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \) ratios for these five samples ranged from 0.7150 to 0.7345, while the \( \frac{\text{Rb}^{87}}{\text{Sr}^{86}} \) ratios ranged from 1.867 to 0.709. The \( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \) ratios were plotted against the corresponding \( \frac{\text{Rb}^{87}}{\text{Sr}^{86}} \) ratios on an isochron diagram. The "whole-rock" points on this isochron diagram closely define a straight line (Figure 16). The slope of the line and its intercept was calculated by a least-squares analysis. The age of the intrusive, calculated from the slope of the isochron, is \( 1130 \pm 35 \) m.y., using \( \lambda \) for \( \text{Rb}^{87} = 1.39 \times 10^{-11} \text{ yr}^{-1} \). The initial
Fig. 16. WHOLE-ROCK ISOCHRON DIAGRAM FOR Mount Bohemia Intrusive, Michigan

Age = 1130 ± 35 m.y.

Initial $\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = 0.7045 ± 0.001$
Sr$^{87}$/Sr$^{86}$ ratio is 0.7045 ± 0.001.

Faure (1964) reported a whole-rock Rb-Sr age of 1142 ± 25 m.y. for the Duluth gabbro of Minnesota. It is, therefore, suggested that the age of the Mount Bohemia syenodiorite is identical within the stated limits of errors to that of the Duluth gabbro.

By comparison, the Bergland and the Porcupine Mountains rhyolites of 1042 ± 6 m.y. appear to be younger than the Mount Bohemia intrusive. Both the Mount Bohemia intrusive and the Bergland intrusives are close to the Keweenaw fault. There are many other intrusives on the Keweenaw Peninsula that are close to the Keweenaw fault. It appears from the data at hand that these intrusives may not all be of the same age.

<table>
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<tr>
<th>Sample No.</th>
<th>Rb p.p.m.</th>
<th>Sr p.p.m.</th>
<th>Rb$^{87}$/Sr$^{86}$</th>
<th>Sr$^{87}$/Sr$^{86}$ (corr.)</th>
<th>Sr$^{86}$/Sr$^{88}$</th>
</tr>
</thead>
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<tr>
<td>217</td>
<td>30.95</td>
<td>71.49</td>
<td>1.255</td>
<td>0.7238</td>
<td>0.1177</td>
</tr>
<tr>
<td>219</td>
<td>73.87</td>
<td>114.85</td>
<td>1.867</td>
<td>0.7345</td>
<td>0.1179</td>
</tr>
<tr>
<td>220</td>
<td>55.60</td>
<td>135.23</td>
<td>1.192</td>
<td>0.7223</td>
<td>0.1182</td>
</tr>
<tr>
<td>221</td>
<td>45.67</td>
<td>201.76</td>
<td>0.656</td>
<td>0.7150</td>
<td>0.1151</td>
</tr>
<tr>
<td>222</td>
<td>49.02</td>
<td>200.26</td>
<td>0.709</td>
<td>0.7162</td>
<td>0.1166</td>
</tr>
</tbody>
</table>
CHAPTER VII

LEAD ISOTOPIC AGE MEASUREMENT

Introduction

Lead has four stable isotopes having mass numbers 204, 206, 207, and 208. The last three are known to be produced by the radioactive decay of $^{238}\text{U}$, $^{235}\text{U}$ and $^{232}\text{Th}$, respectively; whereas, $^{204}\text{Pb}$ is not produced by nuclear processes. It has been found that large variations exist in isotopic composition of lead of geologic material. Holmes (1937) measured the atomic weights of various ore leads and found a constant atomic weight of 207.21. He concluded that lead developed in an environment free of uranium and thorium, presumably below the crust. Holmes' conclusion that the isotopic composition of lead in ore deposits did not vary has been proven incorrect. Large variations in the $\text{Pb}^{206}/\text{Pb}^{204}$ and $\text{Pb}^{208}/\text{Pb}^{204}$ ratios exist in nature and this alone will cause a measurable difference in atomic weights. However, these ratios tend to vary together in such a way as to maintain an almost constant atomic weight.

Holmes was a pioneer in lead isotope studies and evolved much of the terminology used today. He defined "common lead" as the ordinary lead obtained from galena, cerussite, and other ores of lead; "radiogenic lead" as the lead generated from the radioactive decay of
uranium and thorium; and "primeval lead" is the lead that was present in the earth at the time of its formation.

Isotope ratios of common leads were first reported by Nier (1938) and Nier, Thompson and Murphy (1941). They found a fairly consistent relationship between lead isotopic compositions and ages of galena deposits and suggested that ore leads are mixtures of primeval lead and radiogenic lead. Since the isotopic composition of radiogenic lead in an isolated uranium-thorium system is time dependent, any mixture of radiogenic lead and primeval lead separated from a source at a various geological time would be expected to show some relation between composition and time of lead mineral formation.

Mathematical treatment of lead data use the basic decay equation,

$$N_t = N_0 e^{-\lambda t}$$

where $$N_t$$ is the number of radiogenic atoms at time $$t$$, $$N_0$$ is the initial number of radioactive atoms, and $$\lambda$$ is the decay constant characteristic of the element.

The number of radiogenic atoms formed from the beginning of geologic time to any time $$t$$, is given by the number of parent atoms decayed during the time. Let us apply this concept to one of the radiogenic lead isotopes. Therefore,

$$(\text{Pb}^{206}) \text{ radiogenic} = (\text{U}^{238}) \text{ at } t = 0 - (\text{U}^{238}) \text{ at } t$$
or,

\[ (\text{Pb}^{206})_{\text{radiogenic}} = (U^{238})_{\text{present}} (e^{\lambda t_0} - e^{\lambda t_1}). \]

To obtain total \( \text{Pb}^{206} \) atoms present in a closed system at time \( t_1 \), \( \text{Pb}^{206} \) present in a primeval lead must be added to the number of radiogenic \( \text{Pb}^{206} \). So, we can write

\[ (\text{Pb}^{206})_{t_1} = (\text{Pb}^{206})_0 + (U^{238})_p (e^{\lambda t_0} - e^{\lambda t_1}). \]

Dividing both sides of this equation by \( \text{Pb}^{204} \), which is assumed to have remained constant, we can write

\[ \frac{\text{Pb}^{206}}{\text{Pb}^{204}} \left( t_1 \right) = \frac{\text{Pb}^{206}}{\text{Pb}^{204}}_0 + \frac{U^{238}}{\text{Pb}^{204}} (e^{\lambda t_0} - e^{\lambda t_1}) \]  \hspace{1cm} (5)

where

\[ \frac{\text{Pb}^{206}}{\text{Pb}^{204}} \left( t_1 \right) = \text{ratio at time } t_1, \]

\[ \frac{\text{Pb}^{206}}{\text{Pb}^{204}}_0 = \text{primeval ratio}, \]

\[ \frac{U^{238}}{\text{Pb}^{204}} = \text{present ratio}, \]

\[ \lambda = \text{decay constant for } U^{238}, \]

\[ t_1 = \text{time measured backward from the present}. \]
We can express in a similar manner to equation (5), the values for
\[ \frac{\text{Pb}^{207}}{\text{Pb}^{204}} \text{ and } \frac{\text{Pb}^{208}}{\text{Pb}^{204}} \]

Therefore,
\[ \frac{\text{Pb}^{207}}{\text{Pb}^{204}} t_1 = \frac{\text{Pb}^{207}}{\text{Pb}^{204}} o + \frac{\text{U}^{235}}{\text{Pb}^{204}} p \left( e^{\lambda' t_0 - \lambda' t_1} \right) \]  

(6)

where \( \lambda' \) is decay constant for \( \text{U}^{235} \).

Equations (1) and (2) must be combined to give the Holmes-Houtermans "isochron" equation. Therefore,
\[ \frac{\text{Pb}^{207}}{\text{Pb}^{204}} t_1 = \frac{\text{Pb}^{207}}{\text{Pb}^{204}} o + \frac{\text{U}^{235}}{\text{Pb}^{204}} p \left( e^{\lambda' t_0 - \lambda' t_1} \right) \]

(7)

From equation (7) it can be seen that compositions of leads with identical ages and simple histories must plot along a straight line or "isochron" passing through the composition of primeval lead. If \( t_0 \) and isotopic composition of primeval lead are accurately known, the Holmes-Houtermans equation can be used to date any lead mineral that fit the simple model.

Meteorites probably represent closed systems with respect to uranium, thorium and lead. Patterson (1956) obtained an age of 4.55
We can express in a similar manner to equation (5), the values for

\[
\frac{\text{Pb}^{207}}{\text{Pb}^{204}} \text{ and } \frac{\text{Pb}^{208}}{\text{Pb}^{204}} 
\]

Therefore,

\[
\frac{\text{Pb}^{207}}{\text{Pb}^{204}} \frac{1}{t_1} = \frac{\text{Pb}^{207}}{\text{Pb}^{204}} \frac{1}{t_0} + \frac{\text{U}^{235}}{\text{Pb}^{204}} \frac{e^{\lambda't_0} - e^{\lambda't_1}}{e^{\lambda't_0} - e^{\lambda't_1}} \quad (6)
\]

where \( \lambda' \) is decay constant for \( \text{U}^{235} \).

Equations (1) and (2) must be combined to give the Holmes-Houtermans "isochron" equation. Therefore,

\[
\frac{\text{Pb}^{207}}{\text{Pb}^{204}} \frac{1}{t_1} - \frac{\text{Pb}^{207}}{\text{Pb}^{204}} \frac{1}{t_0} = \frac{\text{U}^{235}}{\text{U}^{238}} \frac{e^{\lambda't_{0}} - e^{\lambda't_{1}}}{e^{\lambda't_{0}} - e^{\lambda't_{1}}} \quad (7)
\]

From equation (7) it can be seen that compositions of leads with identical ages and simple histories must plot along a straight line or "isochron" passing through the composition of primeval lead. If \( t_0 \) and isotopic composition of primeval lead are accurately known, the Holmes-Houtermans equation can be used to date any lead mineral that fit the simple model.

Meteorites probably represent closed systems with respect to uranium, thorium and lead. Patterson (1956) obtained an age of 4.55
± 0.07 x 10⁹ yrs. for the earth by demonstrating that the earth's uranium-lead system belongs to the array of meteoritic uranium-lead systems. He made the following assumptions concerning meteorites: they were formed at the same time; they existed as isolated and closed systems; they originally contained lead of the same isotopic composition; they contain uranium which has the same isotopic composition as that in the earth.

Murthy and Patterson (1962) recently examined available lead isotope data. They concluded that (1) the primeval lead of meteorites, obtained from troilite, has the composition of Pb²⁰⁶/Pb²⁰⁴ = 9.56, Pb²⁰⁷/Pb²⁰⁴ = 10.42, and Pb²⁰⁸/Pb²⁰⁴ = 29.71; (2) lead in stony meteorites has a wide range of compositions that group closely about the zero isochron; (3) the isotopic compositions of primeval lead of the earth and the terrestrial zero age correspond to the meteoritic zero age isochron. The age of the earth, calculated by substituting the slope of the meteoritic zero isochron in the Holmes-Houtermans equation, is 4.55 ± 0.03 x 10⁹ years.

**Dating of Galena Lead**

Several attempts have been made to interpret common lead isotope abundances in terms of the age of mineral deposition. Common lead models to interpret the history of the lead development are of two types:

1. Single-stage models involving normal lead that developed in a single uranium-thorium-lead system from the beginning of
geologic time until the time of its final deposition as a lead mineral;

2. multi-stage or anomalous lead models concerned with lead that existed in more than one-uranium-thorium system before final deposition as a lead mineral.

Single-Stage or Normal Lead Models

Holmes-Houtermans Model

Holmes and Houtermans assumed that the primordial earth was fluid and homogeneous with respect to the lead isotopic composition and the distribution of uranium, thorium and lead. Subsequently, when the earth became more rigid, small regional differences arose in the uranium/lead and thorium/lead ratios. Lead developed within these closed uranium-thorium-lead systems by the decay of U and Th to lead. At various times lead was extracted from these regions, concentrated, and deposited as lead minerals. After formation of the lead mineral the isotopic composition of lead remained constant.

If these assumptions are correct, normal leads extracted at the same time from several source regions with different U/Pb ratios should define a straight line passing through the composition of the primeval lead when they are plotted in 207/204 and 206/204 coordinates. Figure 17 illustrates this concept of the model.

Holmes (1947) recognized two types of leads that did not appear to fit the simple history postulated by the Holmes-Houtermans model. These are: J-type (Joplin, Missouri) leads, having negative model
Fig. 17. HOLMES-HOUTERMANS MODEL FOR NORMAL LEAD
ages; and B-type (Bleiberg, Austria) leads, having model ages older than the rocks in which the leads occur.

Some limitations to the Holmes-Houtermans model are:

1. J-type leads are not explained;
2. composition of certain suites of normal leads have linear trends unrelated to primary isochrons; and
3. existence of lead in several uranium-thorium environments prior to deposition as lead minerals would probably not produce a lead isotopic composition that could be dated meaningful by a single-stage model.

The above limitations place severe restrictions on the application of the Holmes-Houtermans model to the problem of dating common leads. However, the leads that have had simple histories can be dated with confidence.

Russell-Farquhar Model

The Russell-Farquhar model has several basic assumptions which are in common with the Holmes-Houtermans model. Both models will yield nearly identical ages for normal leads when the same set of constants is used. The fundamental difference from the Holmes-Houtermans model is that Russell and others consider the source region of normal leads to have constant U/Pb and Th/Pb ratios. Russell and others consider the source region for the normal or single-stage lead to be the mantle and/or the lower part of the crust.
The assumption of a homogeneous source for leads results in the following equations for the Russell-Farquhar model:

\[
\frac{\text{Pb}^{207}}{\text{Pb}^{204}} = \frac{\text{Pb}^{207}_{\text{measured}}}{\text{Pb}^{204}_{\text{measured}}} - \frac{\text{U}^{235}}{\text{Pb}^{204}_{\text{present}}} (e^{\lambda t} - 1) \tag{8}
\]

\[
\frac{\text{Pb}^{206}}{\text{Pb}^{204}} = \frac{\text{Pb}^{206}_{\text{measured}}}{\text{Pb}^{204}_{\text{measured}}} - \frac{\text{U}^{238}}{\text{Pb}^{204}_{\text{present}}} (e^{\lambda t} - 1) \tag{9}
\]

\[
\frac{\text{Pb}^{208}}{\text{Pb}^{204}} = \frac{\text{Pb}^{208}_{\text{measured}}}{\text{Pb}^{204}_{\text{measured}}} - \frac{\text{Th}^{232}}{\text{Pb}^{204}_{\text{present}}} (e^{\lambda ' t} - 1) \tag{10}
\]

After defining the equations for the normal lead development they determined the unique growth curve for lead in the mantle. One end of the $\text{Pb}^{207}/\text{Pb}^{204}$ vs. $\text{Pb}^{206}/\text{Pb}^{204}$ growth curve lies at the point (9.50, 10.36) obtained by averaging Henbury and Canyon Diablo troilite lead isotope ratios. The other end of the same growth curve lies on the zero isochron as defined by the meteoritic leads. Accepting Patterson's parameters for this isochron there results the equation

\[
\frac{\text{Pb}^{206}}{\text{Pb}^{204}} = 1.678 \left(\frac{\text{Pb}^{207}}{\text{Pb}^{204}}\right) + 7.87
\]

which modern mantle lead must satisfy. These conditions completely specify the growth curve except for a single parameter representing the present value of the $\text{U}^{235}/\text{Pb}^{204}$. This value was obtained by insisting that the growth curve pass through the point corresponding to analyses from Bathrust, New Brunswick, galena. This deposit is a young
conformable deposit, and the lead is believed to be of single-stage type and not anomalous. The lead in Bathrust galena is, therefore, considered to be a sample of the mantle lead without having any contamination by crustal lead.

In consequence of these assumptions, they obtained the following present-day ratios for the mantle lead:

$$\frac{\text{Pb}^{207}}{\text{Pb}^{204}} = 15.82; \quad \frac{\text{Pb}^{206}}{\text{Pb}^{204}} = 18.72; \quad \frac{\text{U}^{235}}{\text{Pb}^{204}} = 0.0659.$$ 

Using this set of constants, Russell and Farquhar obtained a single growth curve with $\frac{\text{Pb}^{207}}{\text{Pb}^{204}}$ vs. $\frac{\text{Pb}^{206}}{\text{Pb}^{204}}$ values for the mantle lead (Figure 18). Russell and Farquhar suggested that all normal leads should have ratios $\frac{\text{Pb}^{207}}{\text{Pb}^{204}}$ and $\frac{\text{Pb}^{206}}{\text{Pb}^{204}}$ that lie along this single growth curve.

Stanton and Russell (1959) recognized a distinct group of sulfide deposits, known as "conformable" deposits. The term conformable has been applied to massive or disseminated, layered sulfide deposits, whose more-or-less tabular or lenticular outlines parallel the layering in enclosing rocks. Moreover, these deposits show a distinct preference for one or a limited number of a sequence of beds, and within these may prefer an off-reef shaley or equivalent facies. Their marked sedimentary affiliations have led some geologists to believe a syngenetic sedimentary origin, while others have attributed them to replacement. Stanton and Russell examined several conformable sulfide deposits and found that lead of individual conformable deposit had mean isotopic
Fig. 18. Russel-Farquhar Model For Normal Lead
composition that plotted on a single primary growth curve, suggested by Russell and Farquhar (Figure 18). The lead of these conformable deposits is, therefore, considered to be a normal lead.

The wide geographic distribution of conformable deposits that plotted on this primary growth curve implied that the uniform source was widespread. Therefore, a subcrustal origin of the lead was postulated on the assumption that only the mantle is uniform with respect to uranium, thorium and lead. The lead in the conformable deposits substantiates the assumption of Russell and Farquhar, who consider the mantle to be the source region for the normal lead.

Stanton and Russell (1959) suggested that the metals in the conformable deposits may have been derived from volcanoes and concentrate without contamination in nearshore sediments around islands in active island arcs. The metal is precipitated as sulfide and incorporated into a syngenetic type deposit.

Criteria for Recognition of Normal Leads

Kanasewich and Farquhar (1965) suggested tentative criteria for recognizing single-stage leads. These are:

1. The isotopic composition of leads for an area should be constant within 0.3 per cent.
2. The $\text{Pb}^{206}/\text{Pb}^{204}$ ratio of an ordinary lead should yield a present day $\text{U}^{238}/\text{Pb}^{204}$ ratio of 8.99 ± 0.07.
3. The $\text{Pb}^{208}/\text{Pb}^{204}$ ratio of an ordinary lead should yield a $\text{Th}^{232}/\text{Pb}^{204}$ ratio of 35.55 ± 0.59.
4. The present-day Th/U ratio for the source region should be 
   \[ 3.92 \pm 0.09. \]

**Anomalous Lead Model**

According to Holmes-Houtermans, the anomalous leads are those 
leads which do not fit their simple model. These are the J-type lead 
and the B-type lead.

Russell et al. (1954) suggested that the anomalous leads are 
those leads which are mixtures of variable proportions of normal lead 
and a radiogenic lead. Anomalous leads recognized by the linear rela­
tionship of the isotope ratios on a plot of \( \text{Pb}^{207}/\text{Pb}^{204} \) versus 
\( \text{Pb}^{206}/\text{Pb}^{204} \) and of \( \text{Pb}^{208}/\text{Pb}^{204} \) versus \( \text{Pb}^{206}/\text{Pb}^{204} \).

Stanton and Russell (1959) recognized that many leads 
occurring as vein fillings are anomalous. The galenas of vein deposits 
have been deposited in fissures whose existence preceded theirs. Such 
galenas are, therefore, younger than the rocks that enclose them and 
may have been derived from a distant source. It is known that all 
crustal rocks, and many sediments in particular, contain uranium, 
thorium, and radiogenic lead. Apart from occasional coincidences, the 
abundances of uranium, thorium, and lead in the crustal rocks is likely 
to be different from those of the main lead source at depth.

Where lead is expelled from a uniform source and commences up­
ward migration, the transporting medium should be capable of collecting 
any lead, radiogenic or otherwise, encountered prior to the deposition 
as lead mineral. Hence, varying quantities of radiogenic lead should
be added to the original lead during the transportation depending upon the distance from source to site of deposition, the duration of transit, and the composition, age and thickness of individual rock units traversed. As the U/Pb ratios of the crustal material would likely to be different from those in the source, the lead in the resultant galenas would become anomalous. Thus all leads which have travelled finite distances through sedimentary rocks are potentially anomalous. Conversely, the normal leads are those leads which represent uncontaminated mantle material and have had a very limited contact with crustal rocks.

Russell and Farquhar (1960) showed a series of numerical calculations to interpret the geologic history of an anomalous lead. The nature of the model on which these calculations are based upon is shown in Figure 19.

According to this figure, the normal lead evolved from the time the earth formed, $t_0$, to time $t_1$. At time $t_2$ uranium and thorium from the mantle were introduced into the crust. At $t_1$ normal leads were deposited in the crust as disseminated or massive minerals. Radiogenic lead evolved from $t_2$ to $t_3$. At time $t_3$ orogeny occurred and mixed the radiogenic lead and normal lead into an ore mineral without further change in the lead isotope ratios. Mixtures of variable amounts of two components, each having a uniform composition, will plot along a straight line on a $\text{Pb}^{206}/\text{Pb}^{204}$ versus $\text{Pb}^{207}/\text{Pb}^{204}$ graph. The slope $R$ of this straight line is the $207/206$ ratio of the
Fig. 19. Schematic Presentation of the Russell-Farquhar Anomalous Lead Model.
radiogenic component and is the basis for the Russell-Farquhar mathematical treatment of anomalous leads.

According to the Russell-Farquhar model, the radiogenic lead generated between time $t_2$ and time $t_3$ has a composition given by the slope $R$, i.e. $\text{Pb}^{207}/\text{Pb}^{206}$ ratio. A maximum age of mineralization, $t_m$, can be calculated, if we assume that the radiogenic lead formed instantaneously, i.e. $t_2 = t_3$. In the case of the instantaneous model, the lead has to be mixed prior to the mineralization. Therefore, the age of the mineralization must be a maximum age. The maximum age of mineralization is calculated in the following manner.

Number of radiogenic lead = number of parent decayed.

Therefore, \[ \text{Pb}^{207} = (\text{U}^{235})_t - (\text{U}^{235})_{\text{today}} \]

or, \[ \text{Pb}^{207} = (\text{U}^{235})_{\text{today}} (e^{\lambda' t} - 1). \]

Differentiating both sides with respect to $t$, we get

\[ \frac{d\text{Pb}^{207}}{dt} = (\text{U}^{235})_{\text{today}} \cdot \lambda' \cdot e^{\lambda' t} \]

Similarly, for $\text{Pb}^{206}$ we can write

\[ \frac{d\text{Pb}^{206}}{dt} = (\text{U}^{238})_{\text{today}} \cdot \lambda \cdot e^{\lambda t} \]
Therefore,

\[
\frac{d\text{Pb}^{207}}{d\text{Pb}^{206}} = \frac{U^{235}}{U^{238}} \cdot \frac{\lambda}{\lambda} \cdot \frac{e^{\lambda't}}{e^{\lambda t}} = R \tag{11}
\]

The equation (11) is simply the ratio in which the lead isotopes were being produced from \(\text{U}^{235}\) and \(\text{U}^{238}\) at time \(t\) years ago. Therefore, from the equation (11), \(t\), the upper limit to the final emplacement of lead mineral, can be calculated.

A second information can be obtained from the slope \(R\) of \(\text{Pb}^{207}/\text{Pb}^{206}\). Assuming that anomalous lead mineralization occurred at the present time, i.e. \(t_0 = 0\), a maximum value for the time of emplacement of uranium-thorium can be calculated. The mathematical treatment of determining this time is shown below:

\[
\frac{\text{Pb}^{206}}{\text{Pb}^{204}}_{\text{radiogenic}} = \frac{U^{238}}{\text{Pb}^{204}}_{\text{today}} \left( e^{\lambda t_2 - \lambda t_3} \right).
\]

Similarly,

\[
\frac{\text{Pb}^{207}}{\text{Pb}^{204}}_{\text{radiogenic}} = \frac{U^{235}}{\text{Pb}^{204}}_{\text{today}} \left( e^{\lambda't_2 - \lambda't_3} \right).
\]

Therefore,

\[
R = \frac{\text{Pb}^{207}}{\text{Pb}^{206}} = \frac{U^{235}}{U^{238}}_{\text{today}} \frac{e^{\lambda t_2 - \lambda t_3}}{e^{\lambda t_2} - e^{\lambda t_3}} \tag{12}.
\]
Assuming $t_3 = 0$, the slope $R$ can be expressed as

$$R = \frac{Pb^{207}}{Pb^{206}} = \frac{U^{235}}{U^{238}} \cdot \frac{e^{\lambda't_2-1}}{e^{\lambda'today}}$$

Equation (13) yields $t_2$, the maximum age for the time of emplacement of uranium–thorium that provided the radiogenic lead. Where there is a geological proof that the age of anomalous lead mineralization cannot be younger than some age $t'$, then the equation (12) should be used by substituting $t'$ for $t_3$.

Additional information can be obtained from a Pb$^{206}$/Pb$^{204}$ versus Pb$^{206}$/Pb$^{204}$ plot. A linear relationship should also exist to satisfy the assumption that the common lead is a mixture of normal lead and radiogenic lead. The slope $R'$ of such a line can be used to calculate the $Th^{232}/U^{238}$ ratio of the source region for the radiogenic component of an anomalous lead. The slope, $R'$, is defined as:

$$R' = \frac{Th^{232}}{U^{238}} \cdot \frac{\lambda''}{\lambda} \cdot \frac{e^{\lambda t}}{e^{\lambda''t}}$$

Lead Isotope Age of the Nonesuch Copper Deposit

Because of the absence of any significant amount of galena in the Nonesuch copper, an attempt was made to study the isotopic composition of lead in the copper minerals in order to determine the time of the copper mineralization. Attempts were made to separate lead by
liquid-liquid and ion-exchange procedures both from native copper and from chalcocite. The method adopted for chemical separation is capable of extracting lead from samples containing about 10 p.p.m. lead. The native copper was observed to be almost devoid of lead, at least beyond the detection limit of the technique adopted. However, two samples of chalcocite yielded lead for isotopic studies.

Lead isotope analyses were made on a chalcocite concentrate (Sample # 0. S. U. 4A) separated from a sample of the "dark gray massive" bed of the cupriferous parting shale unit by treating with dilute nitric acid and a chalcocite concentrate (Sample # 0. S. U. 1) representing mixture of copper sulfides of all the mineralized beds of the parting shale unit. The concentrate representing mixture of chalcocite from different beds of the parting shale was taken from the mill of the White Pine mine. No lead reagents or salts of lead were used in the floatation process to concentrate the chalcocite. The chalcocite concentrate was collected before there was any addition of pyrite to it. Since both samples were found to contain lead of similar isotopic nature, it appears that the contamination of lead, if there was any, during the separation of chalcocite from the rocks was insignificant.

The isotopic composition of lead for these two samples was analyzed by Isotopes, Incorporated. The results of the analyses are shown in Table 11. As a check on the lead isotope analyses presented in this work, a series of measurements were made on standard samples
and the results are given in Table 12.

**TABLE 11**

**LEAD ISOTOPE ANALYSES OF CHALCOCITE FROM THE NONESUCH SHALE**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>204</th>
<th>206</th>
<th>207</th>
<th>208</th>
<th>207/204</th>
<th>206/204</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.S.U.-1</td>
<td></td>
<td>1.313</td>
<td>25.83</td>
<td>20.68</td>
<td>52.18</td>
<td>15.750</td>
</tr>
<tr>
<td>0.S.U.-4A</td>
<td></td>
<td>1.242</td>
<td>27.07</td>
<td>19.78</td>
<td>51.90</td>
<td>15.926</td>
</tr>
</tbody>
</table>

**TABLE 12**

**LEAD ISOTOPE ANALYSES OF STANDARD SAMPLES**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Date</th>
<th>204</th>
<th>206</th>
<th>207</th>
<th>208</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBS-200</td>
<td>8/3/65</td>
<td>1.532</td>
<td>22.46</td>
<td>22.65</td>
<td>53.35</td>
</tr>
<tr>
<td></td>
<td>8/10/65</td>
<td>1.536</td>
<td>22.51</td>
<td>22.67</td>
<td>53.28</td>
</tr>
<tr>
<td></td>
<td>8/26/65</td>
<td>1.534</td>
<td>22.44</td>
<td>22.63</td>
<td>53.40</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>1.534</td>
<td>22.47</td>
<td>22.65</td>
<td>53.34</td>
</tr>
<tr>
<td>(\overline{\sigma})</td>
<td>(\pm 0.001)</td>
<td>(\pm 0.02)</td>
<td>(\pm 0.001)</td>
<td>(\pm 0.03)</td>
<td></td>
</tr>
<tr>
<td>T-1003</td>
<td>7/15/65</td>
<td>1.465</td>
<td>23.43</td>
<td>22.62</td>
<td>52.49</td>
</tr>
<tr>
<td></td>
<td>8/5/65</td>
<td>1.461</td>
<td>23.46</td>
<td>22.62</td>
<td>52.45</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>1.463</td>
<td>23.445</td>
<td>22.62</td>
<td>52.47</td>
</tr>
<tr>
<td>(\overline{\sigma})</td>
<td>(\pm 0.002)</td>
<td>(\pm 0.015)</td>
<td>(\pm 0.00)</td>
<td>(\pm 0.02)</td>
<td></td>
</tr>
</tbody>
</table>
The ratios of 207/204 and 206/204 for the two samples are plotted on a 207/204 versus 206/204 growth curve based on the Russell-Farquhar model. They lie in an area of negative age, i.e. below the "zero-isochron" line (Figure 20). The lead in chalcocite of the Nonesuch Shale, therefore, has a negative age and hence it is a J-type lead.

Since it is impossible to interpret the J-type lead by the Holmes-Houtermans model, the Russell-Farquhar model was used for the anomalous lead of the Nonesuch copper deposits.

A line is drawn through the two data points in Figure 20. This line intersects the model growth curve at about 1900 million years and has a slope, R=0.0829. According to the Russell-Farquhar model, the age of 1900 m.y. is the time when the normal leads were separated from their source and either concentrated to form a lead deposit or disseminated throughout the host rock as lead minerals.

The slope of the line in Figure 20, and hence the Pb$^{207}$/Pb$^{206}$ ratio, enables us to make certain statements concerning the age of deposition of the leads and the age of the rocks from which the radiogenic lead additions were derived. In the present study analyses were made on lead present in the chalcocite of the Nonesuch copper deposits. Therefore, the age of deposition of the leads must be regarded as the age of the copper mineralization in the Nonesuch Shale.

As stated earlier, the equation (11) gives the time of radiogenic addition, assuming that the addition took place instantaneously.
Fig. 20. A plot of $\frac{\text{Pb}^{207}}{\text{Pb}^{204}}$ against $\frac{\text{Pb}^{206}}{\text{Pb}^{204}}$ for leads in chalcolite from the Nonesuch Shale, Michigan.
If the time taken for the radiogenic lead additions was negligible, the value of $t$ calculated from the equation (11) represents the earliest time at which the lead could have been separated from the uranium. In this case the $\text{Pb}^{207}/\text{Pb}^{206}$ ratio of 0.0829 for the lead in chalcocite of the Nonesuch Shale corresponds to a value of 725 million years which is the maximum possible time since the radiogenic addition took place. The lead in the chalcocite is, therefore, certainly younger than 725 million years. Hence the maximum age for the copper mineralization in the Nonesuch Shale is considered to be 725 m.y.

The age of the rocks from which the radiogenic lead additions were derived is calculated from the following equation. If the radiogenic component was generated in the interval between two times $t_2$ and $t_3$, then the ratio of the lead isotopes at time $t$ is given by

$$R = \frac{\text{Pb}^{207}}{\text{Pb}^{206}} = \frac{1}{137.8} \cdot \frac{\lambda' t_2 - e^{\lambda t_2}}{e^{\lambda t_3} - e^{\lambda t_3}}$$

where $1/137.8$ is the present ratio of $\text{U}^{235}/\text{U}^{238}$, $\lambda'$ is the decay constant of $\text{U}^{235}$ and $\lambda$ is the decay constant of $\text{U}^{238}$.

Setting $t_3 = 0$, i.e. assuming that the mineralization is very recent, we can calculate a value for $t_2$ from the above equation. The age $t_2$ for the lead in chalcocite of the Nonesuch Shale is calculated to be 1430 million years. This value of 1430 million years is a maximum estimate for the age of the rocks from which the radiogenic
component of the lead was obtained.

**Discussion of the Lead Age**

White and Wright (1954) noted that the shaley units of the Nonesuch Shale have a higher copper concentration than the associated sandy beds. They believed that the distribution of copper is controlled by the lithology and stratigraphy of the formation and suggested that the copper is strata-bound and syngenetic in origin. The strata-bound copper deposits of the Nonesuch Shale can be regarded as a type example of the "conformable" sulfide deposits, as described by Stanton and Russell (1959).

Stanton and Russell (1959) recognized that the leads from this distinct group of "conformable" sulfide deposits are normal and the lead isotope ratios are remarkably uniform for the same deposit. These deposits are considered to be syngenetic in origin. Stanton and Russell concluded that the sulfide deposits of the "conformable" group have been derived from a deep volcanic source and fairly quickly localized in off-reef or equivalent sedimentary facies around volcanic centers.

The lead isotope data from the chalcocite of the Nonesuch Shale indicate that the lead is a J-type and not a "normal" lead. The lead in the copper minerals of the Nonesuch Shale had a more complex history than a simple normal lead model can explain. Therefore, it appears that the copper in the Nonesuch Shale cannot have been deposited in the manner of the simple model of Stanton and Russell for conformable
strata-bound sulfide deposit.

The model age for copper mineralization in the Nonesuch Shale is 725 million years. According to the Russell-Farquhar model, the age is an upper limit to the time of final mineralization. The whole-rock Rb-Sr age of the Nonesuch Shale is 1075 ± 50 m.y. The age of 1075 ± 50 m.y. is considered to be the maximum estimate of time for the deposition of the Nonesuch Shale.

If the apparent age of 1075 ± 50 m.y. for the Nonesuch Shale is close to the actual time of deposition, then it is quite possible that the time of copper mineralization is significantly less than the time of deposition for the Nonesuch Shale. In this case the copper mineralization is probably hydrothermal and epigenetic in origin.

If, on the other hand, the apparent age of 1075 ± 50 m.y. for the Nonesuch Shale is much higher than the actual time of deposition of the shale, then it cannot be determined from the data obtained in the present study whether or not the time of deposition for the shale is contemporaneous with the time of copper mineralization.

The anomalous nature of the lead in chalcocite of the Nonesuch copper deposits has some significance to the history of the lead and hence the history of the copper deposits. The anomalous leads are thought to have been derived from the "normal" lead by addition of variable amounts of radiogenic lead (Russell et al., 1954). The crustal rocks are known to contain uranium, thorium and radiogenic lead in variable amounts and proportions. Thus any normal lead
emanating from the mantle may have a high probability to be contaminated with the radiogenic crustal lead during its passage through a great thickness of the crustal material and thereby become an anomalous lead.

Since the lead in the Nonesuch copper deposits is highly anomalous, it appears that the normal component of the lead may have travelled through a great thickness of the crustal material and thus contaminated with the radiogenic crustal lead before its final precipitation with chalcocite. Therefore, it is suggested that even if the copper mineralization is syngenetic in origin, the copper may have been derived from a source at great depth and travelled through a great thickness of crustal material before its precipitation as sulfide deposits in the rock. In this case the copper mineralization in the Nonesuch Shale could be hydrothermal and syngenetic in origin.
CHAPTER VIII

GEOLOGICAL HISTORY OF THE KEWEENAWAN ROCKS
OF NORTHERN MICHIGAN

The present investigation yielded the following radiometric ages on the Keweenawan rocks of northern Michigan.

<table>
<thead>
<tr>
<th>Description</th>
<th>Locality</th>
<th>Whole-rock Rb/Sr Age</th>
<th>Pb/Pb Age</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcocite in the Nonesuch Shale</td>
<td>White Pine, Ontonagon County, Michigan</td>
<td>--</td>
<td>725 m.y.</td>
</tr>
<tr>
<td>Quartz-feldspar porphyry</td>
<td>White Pine, Ontonagon County, Michigan</td>
<td>978 ± 40 m.y.</td>
<td>--</td>
</tr>
<tr>
<td>Bergland rhyolite</td>
<td>Bergland, Ontonagon County, Michigan</td>
<td>1042 ± 6 m.y.</td>
<td>--</td>
</tr>
<tr>
<td>Porcupine Mountains rhyolite</td>
<td>Porcupine Mountains, Ontonagon County, Michigan</td>
<td>1042 ± 6 m.y.</td>
<td>--</td>
</tr>
<tr>
<td>Nonesuch Shale</td>
<td>White Pine Mine, Michigan</td>
<td>1075 ± 50 m.y.</td>
<td></td>
</tr>
<tr>
<td>Pebbles from Lower Sandstone</td>
<td>White Pine Mine, Michigan</td>
<td>1107 m.y. and 1180 m.y.</td>
<td>--</td>
</tr>
<tr>
<td>Bergland Lookout Tower felsite</td>
<td>Bergland, Ontonagon County, Michigan</td>
<td>1100 ± 25 m.y.</td>
<td>--</td>
</tr>
<tr>
<td>Mount Bohemia syenodiorite</td>
<td>Mount Bohemia, Keweenaw County, Michigan</td>
<td>1130 ± 35 m.y.</td>
<td>--</td>
</tr>
</tbody>
</table>
Stratigraphic Relationship of the Igneous Rocks

The Mount Bohemia intrusive has a whole-rock Rb-Sr age of 1130 ± 35 m.y. and is the oldest rock dated in this study. Butler and Brubank (1929) considered the intrusive to be a member of the Bohemian Range group, which stratigraphically lies in the lower part of the Portage Lake Lava Series. However, they mentioned at the same time that the intrusive "may be Upper Keweenawan." A later report on the intrusive is that of Cornwall (1954), who stated that the Mount Bohemia intrusive is of Middle or Upper Keweenawan in age. In a columnar stratigraphic section presented in this report, Cornwall placed the intrusive above the Middle Keweenawan Portage Lake Lava Series but below the Upper Keweenawan Copper Harbor Conglomerate.

The whole-rock Rb-Sr age of 1130 ± 35 m.y. for the Mount Bohemia intrusive indicates that the intrusive may be equivalent in age to the Duluth gabbro of Minnesota. Faure (1964) measured a whole-rock Rb-Sr age of 1142 ± 25 m.y. for the Duluth gabbro. Goldich et al. (1961), Silver and Green (1963), and others obtained similar age for the gabbro.

Sandberg (1938), Goldich et al. (1961), Taylor (1964), and others noted that the Duluth gabbro intrudes the North Shore volcanics of Minnesota, which is a thick series of basalt flows interbedded with sediments. Taylor (1964) considered that the period of extrusion of the North Shore volcanics in Minnesota culminated in the intrusion of
gabbroic magma in Keweenawan time. Sandberg (1938) and others correlated the North Shore volcanics in Minnesota with the Portage Lake Lava Series in Michigan.

It appears from the radioactive age measurements and the regional stratigraphic correlation that the Mount Bohemia intrusive is younger than the Portage Lake Lava Series. The whole-rock Rb-Sr age of 1130 ± 35 m.y., therefore, indicates that the Portage Lake Lava Series in Michigan is older than 1130 ± 35 m.y. This interpretation is consistent with the assumed stratigraphic relationship suggested by Cornwall (1954).

The felsite at the Bergland Lookout Tower in Ontonagon County, Michigan has been considered to be a part of the "Chippewa felsite," which is thought to be a member of the Ashbed group in the upper part of the Middle Keweenawan Portage Lake Lava Series (Butler and Burbank, 1929, Plate 14).

The present investigation yielded a whole-rock Rb-Sr age of 1100 ± 25 m.y. for the felsite at the Bergland Lookout Tower. The Mount Bohemia intrusive in Keweenaw County of Michigan has a whole-rock Rb-Sr age of 1130 ± 35 m.y. Since the errors in the two ages overlap, a positive distinction between the two ages cannot be made. It is, however, possible that the two ages are identical within the stated limits of the experimental error.

The Rb-Sr age of 1100 ± 25 m.y. for the felsite at the Bergland Lookout Tower suggests that the felsite is younger than the
Portage Lake Lava Series, which is considered to be older than 1130 ± 35 m.y., and is not a member of the Ashbed group of the Portage Lake Lava Series as suggested by Butler and Burbank.

The Bergland just north of Lake Gogebic in Ontonagon County has a Rb-Sr age of 1042 ± 6 m.y. The same age was obtained for the rhyolite in the Porcupine Mountains. It is believed that these two rhyolites are identical in age and are offshoots from a common source.

The whole-rock Rb-Sr ages of 1042 ± 6 m.y. for the Porcupine Mountains rhyolite and the Bergland rhyolite are significantly lower than the whole-rock Rb-Sr age of 1100 ± 25 m.y. for the felsite at the Bergland Lookout Tower. Therefore, it is concluded that the rhyolite of the Porcupine Mountains and the Bergland rhyolite are younger than the felsite at the Bergland Lookout Tower.

The quartz-feldspar porphyry about 8 miles south of White Pine has been considered to be intrusive into the Portage Lake Lava Series (Butler and Burbank, 1929, Plate 32). The whole-rock Rb-Sr age of the porphyry is 978 ± 40 m.y., which makes the porphyry the youngest of all the igneous bodies investigated in the present study. Its intrusive character appears to be confirmed by the age relationships.

The quartz-feldspar porphyry dated at 978 ± 40 m.y. may have been intruded at the same time as the Mellen granite in Wisconsin and the Endion sill in Minnesota. Goldich et al. (1961) obtained an age of 990 m.y. for the Mellen granite, while Faure (1964) measured an age of 981 ± 40 m.y. for the Endion sill.
Stratigraphic Position of the Nonesuch Shale
Relative to the Igneous Bodies

The stratigraphic position of the Nonesuch Shale in relation to the rhyolites and porphyry has not been clearly established. Sales (1959) considered the porphyry in the White Pine area to be younger than the Nonesuch Shale. Butler and Burbank (1929) regarded the rhyolite in the Porcupine Mountains as a post-Nonesuch laccolith.

In opposition to these views White (1960) suggested the rhyolites and porphyry in the White Pine area to be pre-Nonesuch in age. His conclusion of pre-Nonesuch age for the rhyolites was based on the evidence that there are abundant rhyolite fragments in the rocks in and below the Nonesuch Shale.

Two rhyolite pebbles from the lower sandstone unit in the White Pine mine were dated. The Rb-Sr ages obtained were 1107 m.y. and 1180 m.y. These two ages on the pebbles are definitely higher than the whole-rock Rb-Sr age of 1042 ± 6 m.y. for the Porcupine Mountains rhyolite. It is, therefore, suggested that some of the rhyolites which supplied these pebbles are significantly older than the rhyolite in the Porcupine Mountains.

In the present study the determination of the stratigraphic position of the Nonesuch Shale relative to the rhyolite has been approached from the standpoint of the amount of sediments that may have been deposited between the periods of the cessation of the outpouring of the lava flows in the Portage Lake Lava Series and the emplacement of the rhyolite in the Porcupine Mountains.
Both Cornwall (1954) and White (1960) noted that the Copper Harbor Conglomerate interfingers slightly with the underlying Portage Lake Lava Series. Therefore, it appears that the deposition of Copper Harbor Conglomerate started very shortly after extrusion of lava flows in the Portage Lake Lava Series. The transitional relationship, noted by White and Wright (1954), between the Copper Harbor Conglomerate and the Nonesuch Shale indicates that the period of sedimentation that started in Copper Harbor time continued through Nonesuch time without any large break.

It has already been suggested that the age of the Portage Lake Lava Series, which was intruded by the Mount Bohemia intrusive, is greater than 1130 ± 35 m.y. The age of the Porcupine Mountains rhyolite is 1042 ± 6 m.y. If it is assumed that the Copper Harbor Conglomerate and the Nonesuch Shale were deposited between the periods of emplacement of the Portage Lake Lava Series and the Porcupine Mountains rhyolite, then the total period of sedimentation would be about 60 million years.

The average total thickness of the sediments that make up the Copper Harbor Conglomerate and the Nonesuch Shale is about 4,000 feet. This thickness of sediment is assumed to have been deposited in 60 million years. Then the rate of deposition would be about 70 feet per million years, or 2 cm. per thousand years.

White and Wright (1960) interpreted the conglomerate facies of the Copper Harbor formation as a piedmont fan. Considering the fact
that the conglomerates make up the bulk of the total sediments and that the conglomerates are piedmont fan deposits and that there is no apparent large break in the sedimentation, the rate of deposition of 2 cm. per thousand years is probably a reasonable estimate.

On the basis of the depositional rate of sediments for the Copper Harbor Conglomerate and the Nonesuch Shale, it appears possible that the rhyolite of the Porcupine Mountains is younger than the Nonesuch Shale. It is, therefore, suggested that the whole-rock Rb-Sr age of 1075 ± 50 m.y. for the Nonesuch Shale is a close upper limit to the actual time of sedimentation.

If it is assumed that the limestone in the parting shale unit of the Nonesuch Shale was deposited in a marine environment, then the isotopic composition of Sr in the limestone should plot on the marine strontium geochron determined by Hurley (1965) against the corresponding age of 1075 ± 50 m.y. for the Nonesuch Shale. The fact that the Sr isotopic composition of the limestone plots closely on the strontium development line for marine limestones at the time indicated to be the age of the Nonesuch formation confirms this age and the interpretation of it.

**Origin of Copper in the Nonesuch Shale**

The origin of copper in the Nonesuch Shale is a controversial geologic problem. White and Wright (1954) noted that the copper in the shales and siltstones is independent of any structure and considered it to be strictly strata-bound and syngenetic in origin.
Sales (1959) and Joralemon (1959), on the other hand, suggested that the copper was brought by an uprising hydrothermal solution which came along the White Pine fault and thus the copper deposit is epigenetic hydrothermal in origin.

In the present study attempts were made to analyze the lead in the chalcocite. The isotopic composition of the lead is found to be J-type anomalous, which yields a negative age for the mineralization. The Russell-Farquhar model was used to calculate the time of mineralization for this anomalous lead. The maximum age of mineralization, obtained by this model, is 725 million years.

If the apparent age for the Nonesuch Shale ($1075 \pm 50$ m.y.) is close to the actual time of sedimentation, then the age of 725 m.y. for the mineralization appears to be significantly lower than the age of the Nonesuch Shale. In this case the mineralization should be epigenetic and hydrothermal in origin.

If, on the other hand, the actual age of the Nonesuch Shale is much lower than the apparent age of $1075 \pm 50$ m.y. and the error in the age of 725 m.y. for the mineralization is quite large, then it is possible that the mineralization is contemporaneous with the deposition of the Nonesuch Shale. Under this circumstance, the copper mineralization should be syngenetic. However, the high anomalous nature of the lead in the copper mineralization of the Nonesuch Shale suggests that the copper in the Nonesuch Shale may be hydrothermal in origin.
Environment of Deposition of the Nonesuch Shale

Hurley (1965) obtained a graph showing the change of the strontium isotopic composition of sea-water with geologic time. The present investigator made an analysis of the strontium isotopic composition of the limestone in the parting shale member of the Nonesuch Shale. The $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the limestone is 0.7065. This ratio was plotted on Hurley's graph against the apparent age of 1075 $\pm$ 50 m.y. for the shale. The close fit of the values for the Nonesuch limestone on Hurley's diagram indicates that the parting shale member of the Nonesuch Shale might have been deposited in a marine environment.


APPENDIX
LOCATION AND DESCRIPTION OF DATED SAMPLES

Bergland Lookout Tower (T. 49 N., R. 42 W., Sec. 5):

166. Chocolate-brown colored, fine-grained, porphyritic felsite. Euhedral to subhedral oligoclase-andesine grains occur as phenocrysts, which are as large as 2 mm. in size. Iron oxide and sericite are common secondary minerals. The groundmass is composed of extremely fine-grained quartz.

169. Dark brown, fine-grained felsite. Plagioclase and quartz are primary minerals. Few phenocrysts of plagioclase present are almost completely altered to sericite. Fine-grained feldspars in the groundmass have a somewhat preferred orientation indicative of flowage.

170. Dark brown colored, extremely fine-grained, felsite. Textural characteristic and mineralogical composition are very similar to specimen No. 169.

171. Brown colored, fine-grained, porphyritic felsite. Oligoclase grains, about 1 mm. in size, occur as phenocrysts. Quartz and feldspars are quite common in groundmass. Iron oxide and sericite are common as secondary minerals.

Quarry at Bergland (T. 48 N., R. 42 W., Sec. 6):

203. Brown colored, fine-grained, porphyritic rhyolite. Primary minerals are quartz, orthoclase, and plagioclase with accessory minerals as biotite, muscovite, magnetite, and leucoxene. Secondary minerals are quartz, carbonate, sericite, and chlorite. Phenocrysts are primarily of quartz, which occur as anhedral to subhedral crystals of 2 mm. or less in size. A few micrographic intergrowths between quartz and feldspar are present.

204. Dark colored, fine-grained, basalt. Primary minerals are plagioclase and augite with accessory minerals olivine and magnetite. Olivines are completely replaced by magnetite. Augites are partially replaced by iron oxide. Labradorite crystals, 0.5 mm. or less in size, are enclosed by augites and thus result in an ophitic texture.
205. Brown colored, fine-grained, porphyritic rhyolite with quartz and potash feldspar as primary minerals. Accessory minerals are biotite, muscovite, and magnetite. Secondary minerals are chlorite, carbonate, and sericite. Phenocrysts of quartz and feldspar are about 3 mm. in size. Quartz grains show resorbed edges.

206. Dark colored, fine-grained, basalt with plagioclase and augite as primary minerals. Magnetite and olivine are accessory minerals. Secondary minerals are marked by presence of chlorite, sericite and carbonate. Plagioclase grains are extremely altered to sericite. A typical ophitic texture is present.

207. Dark colored basalt similar to specimen No. 206.

208. Brown colored porphyritic rhyolite with quartz and feldspar as phenocrysts of about 1.5 mm. in size. Orthoclase and albite are highly altered to sericite. Groundmass is composed of extremely fine-grained quartz and coated with hematite.

Road Cut on M-6A South of White Pine
(T. 49 N., R. 42 W., Sec. 9):

209. Chocolate-brown colored, fine-grained quartz-feldspar porphyry. Phenocrysts of quartz, potash feldspar and albite are enclosed in an extremely fine-grained groundmass. Phenocrysts are as large as 8 mm. in size. Feldspars are considerably altered to sericite. Phenocrysts of quartz are resorbed at the edges and are occasionally rimmed by sericite. Groundmass is largely coated with hematite.

210. Dark brown colored, fine-grained porphyry with phenocrystals of quartz, feldspar and few biotite. Quartz and feldspar phenocrysts are fractured in many places and iron oxides fill in these fractures. Sericite, chlorite and hematite are secondary minerals. Feldspars are highly altered to sericite.

211. Light brown colored, fine-grained, quartz-feldspar porphyry. Euhedral phenocrysts of quartz, potash feldspar and plagioclase are quite common. Biotite and magnetite are accessory minerals, while chlorite and sericite are the common secondary minerals. Groundmass is extremely fine-grained and coated with iron oxides.
212. Dark brown, fine-grained, quartz-feldspar porphyry. Phenocrysts of microcline and albite with a minor amount of quartz are quite common. Quartz is primarily present as fine-grained anhedral to subhedral crystals in the groundmass. Biotite and magnetite are the accessory minerals. Feldspars are highly altered and replaced by secondary minerals as sericite and chlorite.

213. Chocolate-brown colored, fine-grained, quartz-feldspar porphyry. The mineralogical composition and textural characteristic are very similar to specimen No. 209.

Mount Bohemia Intrusive (T. 58 N., R. 29 W., Sec. 29):

217-222. Light red and dark gray, medium-grained, hypidiomorphic syenodiorite. Primary minerals are oligoclase and hornblende. Accessory constituents are orthoclase, magnetite, augite, sphene, calcite, spidote and quartz. The plagioclase crystals are highly saussuritized, and augites are uralitized.

Porcupine Mountains Rhyolite (T. 51 N., R. 43 W., Sec. 26):

225. Light brown colored, fine-grained, rhyolite. The primary constituents are quartz and feldspar. Groundmass is composed of extremely fine-grained anhedral crystals of quartz with some iron oxide and feldspar. Quartz and potash feldspar also occur in minor amount as phenocrysts of about 0.5 mm. in size. A small amount of micrographic intergrowth of quartz and feldspar is also present.

Nonesuch Shale, White Pine Mine, Michigan:

241. Greenish gray, medium-grained, sandstone with calcium carbonate as a cement. A sample from the "Lower Sandstone" unit in the uppermost part of the Copper Harbor Conglomerate.

242. Dark gray silty shale from "Lower Transition" unit in the lower part of the Nonesuch Shale.

243. Thin-bedded black shale from the cupriferous "Domino" unit of the Nonesuch Shale.

244. Dark colored, fine-grained, limestone from "Junior" in the lower part of the Nonesuch Shale.

245. Massive reddish gray siltstone from "Red Massive" unit in the cupriferous zone of the Nonesuch Shale.
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246. Massive dark gray siltstone from the cupriferous "Dark Gray Massive" unit of the Nonesuch Shale.

247. Evenly laminated reddish shale from "Tiger" unit in the cupriferous zone of the Nonesuch Shale.

248. Dark gray massive siltstone from the cupriferous "Top Zone" unit of the Nonesuch Shale.

249. Thin-bedded black shale from the cupriferous "Domino" unit of the Nonesuch Shale.

250. Dark gray thin-bedded silty shale about 35 feet above the cupriferous zone of the Nonesuch Shale.

Pebble from Lower Sandstone Unit of the Copper Harbor Conglomerate, White Pine Mine, Michigan

251. Light brown colored, fine-grained, with few phenocrysts of feldspar and biotite.

252. Brown colored, fine-grained, porphyritic rhyolite. Potash feldspar are the common phenocrysts, which are as large as 2 mm. in size.