A SPECTROGRAPHIC ANALYSIS OF THE DIKES OF THE GOGEBIC RANGE, MICHIGAN

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A SPECTROGRAPHIC ANALYSIS OF THE DIKES OF THE GOGEBIC RANGE, MICHIGAN

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ABSTRACT

The primary ore controls on the Gogebic iron range are a series of eastward pitching dikes which intersect the footwall quartzite and impermeable layers of the iron formation to form plunging troughs, the locus of the majority of the ore bodies. The dikes are mineralogically similar, being classified essentially as diabase intrusives in their unaltered phases. At depths, the dikes form complex patterns due to their intersecting nature, and are further complicated by the effects of the geologic processes of faulting, alteration by leaching solutions, and possibly metamorphism.

Hence in sub-surface diamond drilling and mining development, the identification and correlation of specific dikes, which is of considerable economic importance, has become a difficult problem.

It was the author's contention that whereas the dikes were essentially mineralogically similar, a spectrochemical analysis might reveal considerable differences in trace element content, either quantitatively and/or qualitatively upon which identification and correlation could be made.

In an effort to identify and correlate the dikes of the Gogebic iron range, a spectrochemical analysis was made on 20 dike samples, 15 from the Davis dike, which is associated with major ore production on the range, and 5 from two associated dikes, the Geneva dike and the Ironton dike, which are also related to ore production.

The Davis dike was set up as a control to test the homogenity of a single dike as to its trace element content and to serve for correlative purposes in the identification of the other dikes of the range. The 15 samples taken from the Davis dike were chosen so as to include a lateral coverage of approximately 3,300 feet along strike and 1,000 feet along dip.

A qualitative analysis showed virtually no variations in the elements present with the exception of minor traces of scandium and lithium distributed erratically among the samples analyzed. The same elements found in the Davis dike were also found in the Ironton and Geneva dikes. A semi-quantitative analysis revealed varying degrees of intensity of the spectral lines of the elements identified, thus indicating varying concentrations of these elements in the samples studied. Further investigation along these lines, utilizing ratios of chemically related elements (Mg/Fe, Sr/Ca etc.) revealed marked differences in elemental ratios between varying locational samples of the Davis dike and also between the Davis dike and the Ironton and Geneva dikes.

These variations appear to be related to the degree of alteration, environmental control and structural trends of the dikes. It appears that though a single dike may have been homogeneous at the time of its intrusion, the geologic factors mentioned above, operating either singularily or in combination with each other, have succeeded in destroying this innate homogenity. Hence, any identification or correlation of the dikes on these grounds must await further study.

GENERAL GEOLOGY

THE GOGEBIC RANGE

The Gogebic district lies south of the west half of Lake Superior in the states of Michigan and Wisconsin, extending from Lake Numakagon in Wisconsin approximately N30°E to Lake Gogebic in Michigan, a total distance of about 80 miles. (Figure 1)

The major topographic features of the district are dependent upon the relative resistance of the formations, the strike of the harder formations being the primary directional controls of the ridges on the range. (Van Hise, 1911)

Two main ridges trending somewhat south of west and separated by a valley from one to two miles in width exist. The crest of the southern-most ridge is formed by the iron formation or the formations immediately underlying it, quartzite and Archean granite and greenstone, while the northern ridge is formed by the Keweenawan trap rocks (lava flows) (the copper bearing series of Michigan). The valley in between is underlain by the Tyler graywacke and slate formation. (W. O. Hotchkiss, 1933)

The present area streams cut an unorthodox path almost directly across the ranges and the longitudinal valley between them and pursue a staggered course of a few miles to Lake Superior, which is about one thousand feet lower than the iron range.

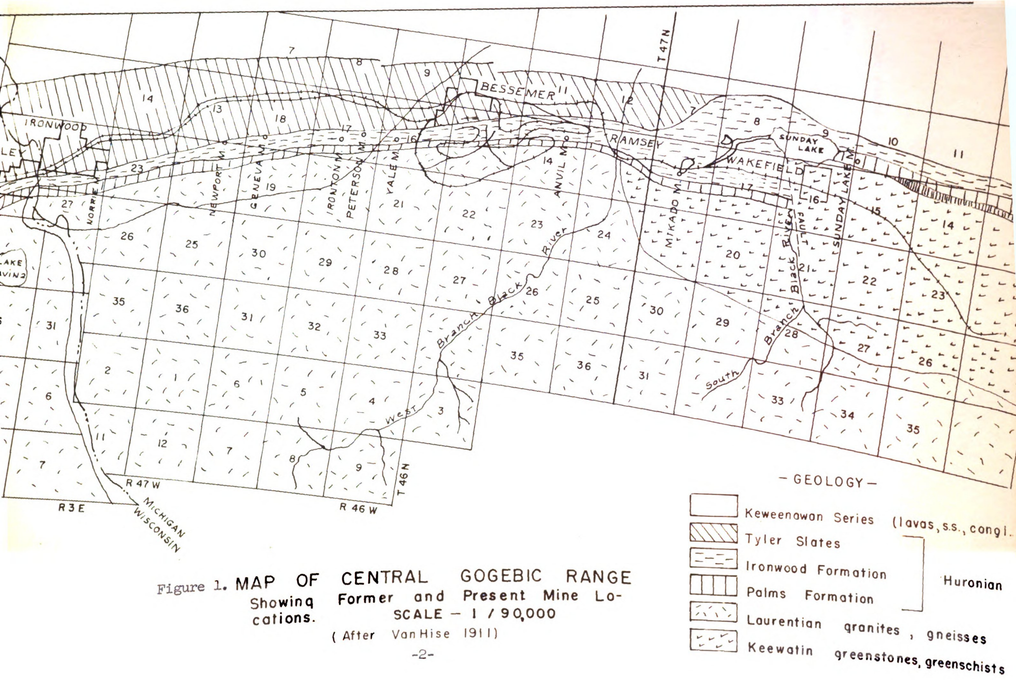

Figure 1. MAP OF CENTRAL GOGEBIC RANGE Showing Former and Present Mine Locations.
SCALE – 1 / 90,000
(After Van Hise 1911)

The rocks of the Gogebic range dip about 60°N and form the south limb of the Lake Superior syncline, with the conformable overlying Keweenawan lava flows and sandstones extending continuously from the northeast end of the Keweenawan Peninsula into Minnesota. (W. O. Hotchkiss, 1933)

A generalized stratigraphic column after W. O. Hotchkiss (1933) is shown in Figure 2.

The oldest rocks of the district, occurring to the south, are primarily granites, greenstones, and green schists, igneous in origin and immediately underlying the Huronian rocks. The Bad River cherty dolomite lies unconformably on this base and is generally found as isolated remnants, most of it having been eroded away before the succeeding formation was deposited. In the eastern part of the district, the dolomite has a rather pure quartzite base, known as the Sunday Lake quartzite. Upon the dolomite, or lower formations where it is absent, lies the Palms formation. It is generally 400 to 500 feet in thickness, reaching a maximum thickness of 800 feet at Sunday Lake. It is marked by a slight unconformity with only thin lenses of conglomerate being discernible at its base. The lower part of this formation is a quartz slate displaying thin to irregular ripple marked beds. The upper portion of this formation is a hard, glassy quartzite, 30 to 100 feet thick, forming the footwall of most of the ore-bodies found on the range. The Ironwood formation, which is conformable on the Palms formation, is the economically important iron bearing stratum of the Huronian series. It is dominantly a chert formation; interbedded with the chert are

STRATIGRAPHIC COLUMN

Gogebic Range

Post Keweenawan			Pleistocene Cambrian S. S. (N. E. part of district) Great Unconformity	
ALGONKIAN	Keweenawan		Basic Intrusive Sandstone, Shale and Conglomerate Acidic Lava Flows Basic Lava Flows S. S. and Conglomerate Unconformity	
	Huronian	Upper	Tyler Slates -	Graywacke Slates Iron Carbonate Slates Pabst (cherty and fragmental) Ferruginous slate beds Unconformity(?)
		Middle	Basic Intrusives Ironwood Iron Formation — Palms Quartzite	Upper: Anvil-wavy bedded ferruginous chert Pence-even bedded (some magnetite) Norrie-wavy bedded ferruginous chert Lower: Yale-even bedded thin ferruginous chert and slate Plymouth-irregular wavy bedded chert Errosional Unconformity
		Lower	Bad River Dolomite (cherty, limestone) Sunday Lake Quartzite Great Unconformity	
Archean	Laurentian Granite		Granite and Granitoid Gneiss (Intrusive into Keewatin)	
	Keewatin		Greenstones and Green Schists	

Figure 2.

thinner beds of iron minerals. The iron minerals in the unaltered part of the formation are siderite, magnetite and hard blue hematite, while in the productive part, the siderite is completely replaced by or altered to hematite. This formation is divided into five members based on differing lithologic characteristics of the material, as demonstrated by both iron content and specific gravity. In order of succession from the footwall quartzite, they are the Plymouth member, characterized for the most part by irregular wavy-bedded chert with iron minerals occurring both in the bands between the chert layers and also in small particles throughout the chert; the Yale member which is chiefly a thin, even bedded ferruginous chert and slate member; the Norrie member, a dominantly wavy-bedded ferruginous chert; the Pence member, preceded by a slight erosion interval, which is unusally even bedded throughout most of the range and contains a moderate amount of magnetite; and the Anvil member, which is also a wavy-bedded ferruginous chert composed largely of rounded chert granules and differing from the other wavy-bedded members in this respect.

The Tyler formation lies upon the Ironwood formation throughout most of the district except in those places where it has been removed through erosion. It is primarily a slaty formation reaching a maximum thickness of 10,000 feet and divisible by material content into a ferruginous slate member, cherty and fragmental member (Pabst), iron carbonate slate member and a graywacke slate member. The deposition of the Tyler was followed by the formation of the great Sunday Lake fault which moved the beds east of it up and to the northwest. This was

followed by an erosion interval of sufficient length to remove the Tyler and part of the Ironwood east of Sunday Lake. The Keweenawan sediments were laid down on this unconformable surface, the lower portion varying from sandstones in some localities to quartzites in others, followed by successive volcanic flows, mostly dark green diabases and amygdaloids with porphyries and syenites.

STRUCTURAL HISTORY

A discussion of the geologic processes of folding, faulting, and intrusive activity which have occurred in the Gogebic range and their relationship to ore development and its localization now follows:

Folding: Extensive folding in this area has occurred only in the non-productive east and west ends of the range. Folding in the productive portion of the range is of a minor character, being confined to small drag folds only a few feet across. These folds as far as known, have not played any part in ore localization.

Faulting: Faulting throughout the extent of the iron formation and the rocks associated with it is very common. (W. O. Hotchkiss, 1937) The influence of faults in ore development has been cited previously and hence, the discussion which follows is in reference to the types of faults and their age relationships.

On the basis of the evidence on hand, four types of faults of relative age occurring throughout the range have been described.

An adapted description of these faults after Hotchkiss, 1937 follows:

1. Transverse faults - Faults striking nearly perpendicular to the formation and nearly vertical in dip.
2. Eureka type faults - Faults striking nearly parallel to the strike of the formation or parallel to eastward-pitching dikes, and nearly perpendicular to the beds.
3. The great Sunday Lake fault, the only one of its type.

4. Bedding faults - Faults parallel to the beds of the iron formation.

The transverse faults are the only ones known to affect the Keweenawan volcanic rocks and are probably the latest faults to be formed. Horizontal displacement by this type of fault ranges upward to 1500'; though in general the displacement by these faults throughout the Ironwood formation is of the order of 20 - 100'. Vertical movement is undeterminable.

The Eureka faults are named after a type of fault found in the Eureka mine, which dips toward the footwall and strikes nearly parallel to it. This type of fault which offsets the iron formation has also been observed in the Asteroid and Mikado mines to the east, and in the Plymouth and Wakefield mines.

The Eureka fault is offset by the transverse faults and so is older. It in turn offsets the bedding fault and the sill so that these must be still older. (W. O. Hotchkiss, 1937)

The Sunday Lake fault, which represents the greatest fault movement on the range, has a northwest strike and is nearly vertical in dip. The base of the iron formation on the east side of the fault has been displaced horizontally one and one-half miles to the northwest relative to the base of the iron formation on the west side. (M. C. Lake, 1917)

The movement along this fault plane, which took place while the beds of the iron formation were still horizontal, was such that the beds on the east side of the fault were over-thrust upward in a westerly direction. (W. O. Hotchkiss, 1937)

Following the formation of this fault, there was a period of erosion which almost completely removed the Tyler slates on its eastern side allowing the outpouring of the Keweenawan lava flows to rest directly on the iron formation in many places.

As far as known, this fault does not cut the Keweenawan volcanics and is not affected by the bedding fault. Rather, it seems probable that the Sunday Lake fault must have displaced the bedding fault since smaller bedding faults believed contemporaneous with the main bedding fault are known in the iron formation east of the Sunday Lake fault.

Bedding faults within the iron formation are found near the base of the Plymouth member, in the Yale member, the Pence member and also in the Pabst member of the Tyler formation. The movement on these fault planes is relatively small except for the great bedding fault found in or near the black ferruginous slate of the Yale member. (H. O. Hotchkiss, 1937)

The main movement along this fault plane was such that the beds above were moved to the east, with minor movements up or down the dip of the beds. The main movement resulted in displacements, where measurable, up to 950 feet.

The bedding fault is displaced by the transverse faults and by faults of the Eureka type which indicates this fault was older than the two latter types. In turn, the main bedding fault is known to displace at least one intrusive in the iron formation and possibly affects others.

A discussion on the intrusives and extrusives originating in the Huronian and the Keweenawan geologic periods in this area now follows. Particular emphasis is given to this phase of the geologic setting due to its intrinsic relationship to the problem at hand, namely, that of dike identification and correlation. A real problem arises because of the similar mineralogic and structural relationship of these rocks. Although the author is primarily concerned with those dikes on the range which have been instrumental in the formation of the ore-bodies, the innate geologic behavior of the sum total of all intrusives is so integrated that a solution to this immediate problem necessarily involves postulation as to the origin and age relationships of all intrusives on the range; because of their interrelated characteristics, extrusives are also included in this discussion.

Geologists have yet to agree on any absolute means of differentiating Keweenawan intrusives from those of the Huronian, although partial evidence related to metamorphic effects, rank and mineral assemblages, chemical analyses, and to some extent structural behavior and the concept of polarity have been introduced in this respect.

W. O. Hotchkiss (1933) describes the intrusives in the Huronian as numerous basic dikes whose structural behavior is that of near perpendicularity to the beds of the iron formation which they intrude. This structural relationship has also been observed by the author.

Two of these dikes are known to intrude both the Ironwood formation and the Keweenawan lava flows, but most of them cannot be traced into the Keweenawan.

At Bessemer, a thin sill, which thickens toward the east until it reaches a maximum thickness of 450 feet at the old Mikado mine, is found near the great bedding fault. It is intruded by a dike, but is not known to cut any dikes. The other significant intrusive is found at the east end of the area near Lake Gogebic, where Huronian formations are intruded by Presque Isle granite. (W. O. Hotchkiss, 1933)

Hotchkiss reserves any opinions as to definite age relationships of the sum total of intrusives found in this region though suggesting two different periods of intrusive activity and hinting that the Presque Isle granite may be pre-Keweenawan in age.

Van Hise (1892) proposes that the Keweenawan eruptives above the Penokee (Huronian) series are the volcanic equivalents of the Penokee dikes and sheets, their contacts being sometimes intricately related. "These facts strongly suggest that the Penokee dikes are the pipes through which the volcanics passed. The identical lithological character of the dikes and sheets suggests that the former fed the latter. We are thus led to the hypothesis that all of these eruptives belong to a single period, the Keweenawan." (C. R. Van Hise, 1892)

The author at this time wishes to reserve any personal opinions in regard to this controversial issue and instead present a more detailed description of these intrusive rocks, particularly of those found in the Ironwood formation.

These dikes are essentially typical diabase rocks in their unaltered form, but within the range they are commonly altered to what is referred to by mining personnel as soapstones.

The lithologic significance of this term (soapstone) is that of a rock which is soft, friable and greasy to the touch in which little, if any, of the original constituent minerals of the primary basic rock remains.

These dikes, however, even in their most altered form, frequently retain a relict diabasic texture and can be traced in many instances into comparatively unaltered phases which are true diabases.

Alteration of these rocks has extended furthest in those portions of the iron formation which contain the ore-bodies. The feldspars in the dike having been altered to kaolin or replaced by chlorite and the pyroxene being converted to hornblende, biotite, or chlorite. The continuation of these dikes into their unaltered portions, usually finds them cutting relatively impermeable beds of the upper slates.

Van Hise (1892) suggests that the contrast between the altered and unaltered portions of the dikes is a result of the influence of environment upon decomposition, the diabases enclosed in the impervious upper slate being kept in a well preserved condition since their intrusion, whereas the portions of these same dikes in a formation which contains evidence of having been subject to the leaching action of percolating waters have been almost totally decomposed.

It is assumed that the alteration by leaching solutions is postmetamorphic in origin.

Because of their intimate association with the iron ores, the structural trends of the dikes are given with reference to the iron formation in which they occur. The iron formation has a general east-

west strike and dips to the north at 60°. The dikes, however, though varying considerably in their dip and strike at various mines, always dip to the south with a southernly component of 20° - 40° and generally pitch to the east with a pitch as high as 35°, but this amount may vary to horizontal or even a slight western pitch. (Van Hise, 1911) From these observations, it can be concluded that if the iron-bearing strata were returned to a position of horizontality, the dikes would be nearly vertical. This suggests that the dike intrusion took place before the sediments were tilted to their present attitude.

The intrusives vary greatly in thickness ranging from a few inches to as great as 90 feet; at depths some of the main dikes are known to split into tongues or stringers and ore is occasionally found between these components.

The function of these dikes as ore controls has initiated diversified opinions among geologists.

Van Hise (1912) proposes the leaching action of downward percolating waters as the main contributary cause to ore formation and hence assigns the role of the dikes to be due to their orientation and relationship to the land surface and the forces of gravity acting upon meteoric waters.

S. A. Tyler (1949) suggests that the escaping water from the dike magma plays the more important role in ore formation, whereas J. W. Gruner, (1930) proposes that the dikes served as conduits for ore-concentrating hydrothermal solutions.

In either of these latter cases, the structural position of the

dikes in secondary concentration is not of primary importance.

Structural and mineralogical data and ore-dike relationships tend to support Van Hise's theory of downward percolating waters as the primary enriching agent contributing to the formation of ore-bodies. For this reason the discussion of ore development in relation to structural controls which follows is intricately related to this theory.

The dikes in intersecting the more impermeable layers of the iron formation and the footwall quartzite form eastward pitching structural troughs which acted as the main circulatory controls for downward percolating surface waters, the agents which enhanced the formation of the iron-ores. Structural controls are also formed by the intersection of two or more dikes. The channelways which carried these solutions were generally fault and fracture zones or the more permeable members of the iron-bearing series. In almost every case the ore-bodies are found immediately overlying the dikes in the apices of these troughs. The alteration of these dikes (through decomposition) appears to be taking place from their structural tops downward, thus supporting the hypothesis of enrichment of the iron formation by downward percolating surface waters. A generalized cross section across the Gogebic iron formation is shown in Figure 3.

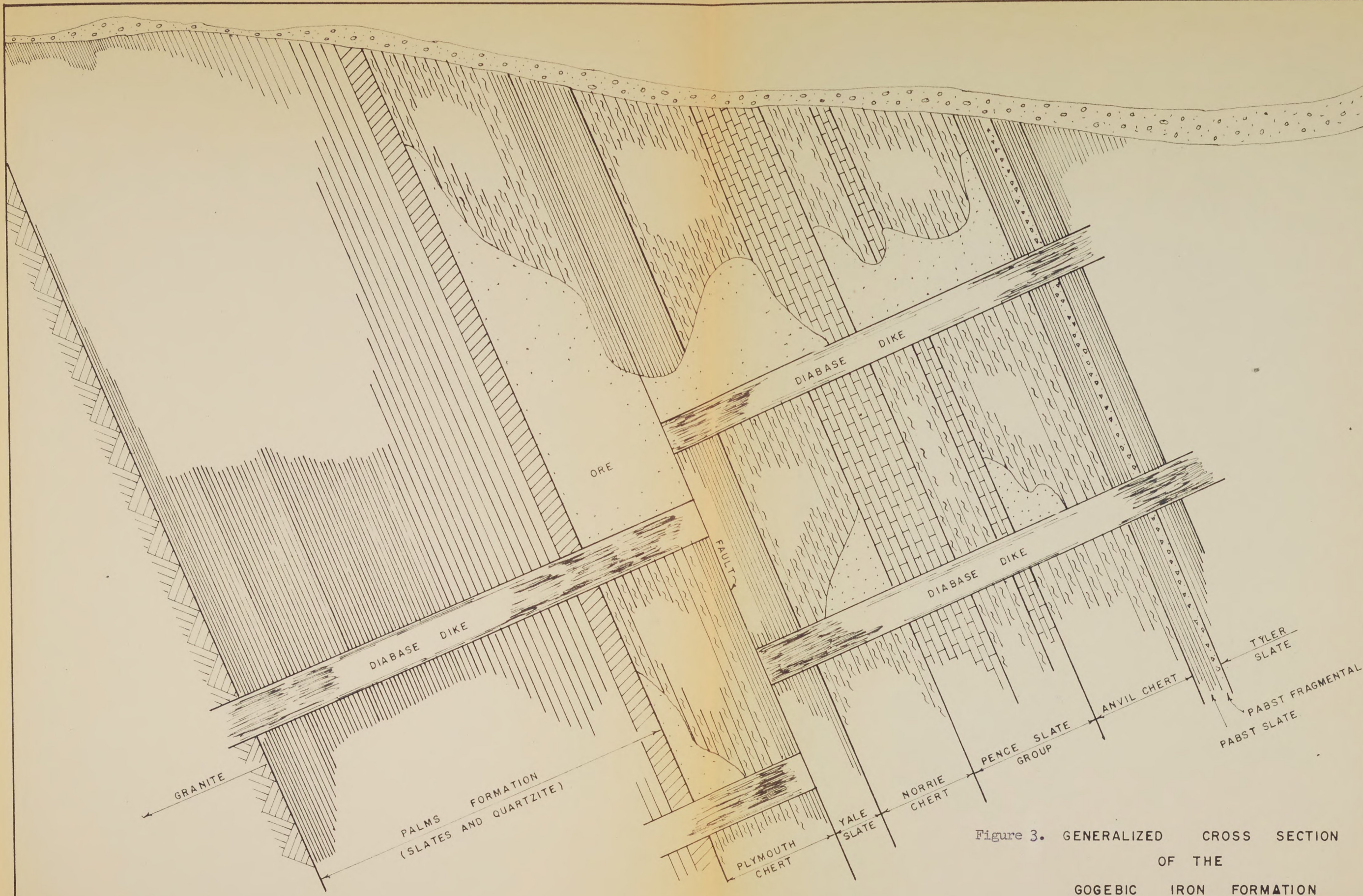

Figure 3. GENERALIZED CROSS SECTION OF THE GOGEBIC IRON FORMATION
SCALE 1= 100'
(PICKANDS & MATHER COMPANY)

INTRUSIVES AT THE PETERSON MINE

The dikes of the Peterson mine are typical of most of the dikes of the range as previously described. They have a diabasic texture which is persistant even in their altered phases, and correlate closely with the general mineralogic description of the sum total of dikes on the range as described by Leith and Van Hise having approximately 51% feldspar, 40% ferromagnesium minerals, 1% quartz, 5.3% magnetite, 1.5% ilmenite and small amounts of calcium-magnesium carbonates and apatite in their less altered portions.

These dikes are approximately parallel to each other, generally forming low angles in those instances where they do intersect. Their horizontal traces on the footwall are inclined about 14° east, these intersections forming the axes of eastward pitching troughs as previously described.

The main ore carrying dikes at the Peterson Mine are the Davis, Geneva, Ironton and Puritan dikes. Ore production along the Davis and Puritan have now ceased.

The Davis, Geneva and Ironton dikes were selected for this study and sampling was confined within the limits of their boundaries.

Their structural positions are described as follows: The Davis dike has an average strike of N 65°E, a variable dip ranging from 25° to 50° southeast and pitches (rake on iron formation) from 0° to 20° northeast; the Ironton dike has a strike varying from N40°E to N62°E, has a dip of 23° southeast and pitches 13° to 24° northeast; the Geneva

dike has a strike varying from N56°E to N78°E, dips 41° southeast and has a pitch which varies from near horizontality to 16° northeast.

LOCATION AND FIELD PROCEDURE

The samples utilized in this study were obtained from diamond drill core and underground workings at the Peterson Mine located in Bessemer, Michigan, in the heart of the Gogebic iron range, seven miles from the eastern border of northern Wisconsin, and 16 miles south of the southern shore of Lake Supeior. This mine, one of the six still active on the range is operated by Pickands Mather and Company affiliated with Bethlehem and Youngstown Steel Corporation.

Due to the nature of the ore-bodies as to shape, size and manner of formation, the majority of the mines on the range are confined to the underground type utilizing sub-level caving mining methods for extraction of the ore. Since the dikes are the main ore controls and hence the locus of the majority of ore bodies, most of the mining development is close to the dikes making them accessible to geologic investigation. Because of the otherwise inaccessible nature of the dikes, samples had to be confined to those portions of a dike exposed by underground workings and diamond drill core which had intersected the dikes during preliminary exploration.

The Davis dike has been one of the larger "ore producing" dikes of the range, its lateral and vertical extent and structural trends being confirmed through numerous exposures as a consequence of preliminary exploration and mining development. Mining along this dike has been carried on extensively at the Peterson Mine, hence the choice of this particular dike for preliminary sampling.

The spacing of the samples was not as selective as the author would have preferred, but they were taken at all accessible exposures to include a lateral coverage of 3,300 feet along the strike and approximately 1,000 feet along the dip of this particular rock unit. Two additional samples of the Ironton and three of the Geneva dike were taken for correlation.

The locations and field descriptions of the various samples are given below:

Davis Dike

#1. 27th Level "A" shaft x-cut 2220E, 1885N, 1702 Elevation strike N80E, Dip 50°SE, pitch 0°.

Hard, fine grained, dark gray-black, fresh appearing, unaltered diabase rock. Some red-hematite stain along joint planes and fractures. Overlain by iron formation above and quartz slate below. Sample taken 4 feet from iron formation contact.

#2. 27th Level "A" shaft x-cut, E. Drift, 125 feet from x-cut. 2340 E., 1740 N., Elevation 1702, strike N70°E, Dip 35° SE pitching 6°NE.

Hard fine-grained, dark gray-black, unaltered diabase rock. Sample taken 12 feet from lower quartz slate contact.

#3. 27th Level shaft x-cut, E. drift, 75 feet from 2600 E loading sub. 2525 E., 1845 N, Elevation 1701, strike N65°E, Dip 42° SE, pitching 0°-30' NE.

Semi-hard, fine grained, partially altered, light green-gray diabase rock with red-hematite stain along fractures and evidence of

#3. kaolinization and chlorite alteration taking place.

#4. 27th Level, 2740 x-cut North 2730 E, 1060 N, Elevation 1700, strike N80° E, Dip 45° SE, Pitching 2° NE.

Soft, friable, red-hematite stained altered diabase rock (soapstone). Green argillacious material along joints and fractures. Sample taken 3 feet from iron formation contact.

#5. 4th Sub above 27th Level, 1800 E. Raise 1800 E, 1840 N, Elevation 1520, strike N80° Dip 40° SE, Pitch 0°.

Semi-hard, fine grained, red hematite-stained partially altered diabase rock. Soft white clay-like mineral insinuated along fractures and joints planes. Hard blue hematite ore above dike. Sample taken 4 feet from ore contact.

#6. 7th sub above 27th Level, 1550 E. Raise, 1550 E, 1800 N, Elevation 1470, strike N80° E, Dip 40° SE, Pitch 0°.

Soft, friable, extremely fine grained, red hematite-stained altered diabase rock. Soft white clay-like mineral insinuated along fractures and joints planes. Hard blue hematite ore above dike. Sample taken 4 feet from ore contact.

#11. 28th Level foot drift, 3200 E, 2065 N, Elevation 1898, strike N50E, Dip 40°SE, Pitching 20°.

Hard, fine to medium grained, partially altered, dark gray to green-black diabase rock. Upper contact with quartz slate. Sample taken 7 feet from this contact.

#12. 28th Level, "A" shaft x-cut 2330E, 1375N, Elevation 1902, strike N50°E, Dip 40°SE, Pitching 20°.

#12. Hard, fine to medium grained, unaltered, fresh appearing, green-black diabase rock. Soft, orange-brown translucent mineral along a joint plane (talc). Contact with granite at its base and quartz slate at its top. Sample taken 15 feet from granite contact.

#14. 29th Level "A" shaft x-cut, 200 feet S. of car-shifter cutout 2380 E, 1080N, Elevation 2104, Strike N55E, Dip 25°SE, Pitch is undeterminable (dike intruded into granite)

Hard, fine to medium grained, generally fresh appearing dark gray to green-black diabase rock. Slight kaolinization along fractures. Sample taken 2 feet from upper contact with granite.

Davis Dike (Diamond Drill Hole Samples)

#15. Diamond Drill Hole 512, 3075E, 2525N, Elevation 1179, Strike N65E, Dip 30°S, Pitching 10°NE, dike from 213-271 feet.

Semi-hard, fine to medium grained, partially altered, dark gray diabase rock, with thin (1/64 inch) white, clay-like laminae 1/4 inch apart throughout. Slight red-hematite stain discernible. Ore immediately above dike, cherty iron formation below. Sample taken at 240 feet.

#16. Diamond Drill Hole 508, 1365E, 1315N, Elevation 1203, Strike N60E, Dip 30°S, Pitching 13°NE, dike from 484-526 feet.

Hard fine to medium grained, unaltered, green-black diabase rock, intrusive within footwall quartz slates. Sample taken at 510 feet.

#17. Diamond Drill Hole 507, 2290E, 1795N, Elevation 1192, Strike N63°E,

#17. Dip 39°S, Pitching 11°NE, dike from 502-540 feet.

Hard, medium grained, unaltered, fresh appearing, dark gray-black diabase rock. Some quartz discernible but only in minor amounts. Dike intrusive within the quartzite phase of the Palms formation. Fault zone immediately above. Sample taken at 520 feet.

#18. Diamond Drill Hole 509, 2200E, 2355N, Elevation 1185, Strike N63E, Dip 39°S, Pitching 11°-30°NE, dike from 0-34 feet.

Hard, fine to medium grained, slightly altered, dark gray to green-black diabase rock. Wavy-bedded cherty iron formation at bottom and top. Sample taken at 15 feet.

#19. Diamond Drill Hole 510, 3215E, 1785N, Elevation-1184, Strike N65E, Dip 39°S, Pitching 10°NE, dike from 205-226 feet.

Semi-hard, medium grained, partially altered, gray-green, diabase rock. Some kaolinization, but primarily chlorite alteration throughout. (A green mineral which may be epidote, present.) Contact with quartzite slate above and quartzite below. Sample taken at 210 feet.

#21. Diamond Drill Hole 511, 3010E, 2600N, Elevation 1177, Strike N65E, Dip 39°S, Pitching 10°NE, dike from 138-187 feet.

Hard, fine to medium grained, slightly altered, gray-black diabase rock. Some chlorite alteration and red-hematite stain along fractures. Wavy-bedded iron formation above and below. Sample taken at 155 feet.

Geneva Dike

#7. 27th Level, W. Drift of 1300E. x-cut, 850 E, 2130N, Elevation 1690, Strike N78°E, Dip 45°SE, Pitching 2°NE.

Semi-hard, fine grained, altered red hematite-stained, diabase rock. Extensive kaolinization throughout. Sample taken 4 feet from contact with iron formation.

#13. 29th Level, x-cut N., 2550E, 2275N, Elevation 2093, Strike N65E, Dip 45°SE, Pitching 2°NE.

Semi-hard to soft, medium grained, altered, green-dark gray diabase rock. Chlorite alteration common throughout. Schistose like structure along a joint plane. (Caused by alteration of a fiberous mineral?) Sample taken 10 feet from upper contact with Yale slates.

#20. Diamond Drill Hole 505, (1215E), 2100N, Elevation 1190, Strike N56°E, Dip 43°S, Pitching 16°NE, dike from 614-703 feet.

Semi-hard, medium to coarse grained, partially altered light to dark gray diabase rock. Kaolinization and chlorite alteration common throughout. Some red-hematite granules scattered throughout, believed to be alteration of magnetite crystals. Hard blue-hematite ore immediately above dike, cherty iron formation below. Sample taken at 660 feet.

Ironton Dike

#8. 27th Level, main drift, 400W, 1280N, Elevation 1675, Strike N40°E, Dip 45°SE, Pitching 24°NE.

8. Semi-hard to soft, medium grained, altered light to dark green-gray diabase rock. Extensive kaolinization and chlorite alteration throughout (talc present along joint plane). Sample taken 2 feet above floor 5 feet from quartzite contact.

#10. 28th Level foot drift OE, 1460N, Elevation 1880, Strike N62E, Dip 40°SE, Pitching 13°NE.

Hard, medium grained, generally fresh appearing gray-black to green-black diabase rock. Some chlorite alteration along with transversing veinlets of white argillaceous-like material. Some red-hematite stain along fractures and joint planes. Sample taken 3 feet from upper contact with quartz slates.

The samples taken from underground workings were carefully removed from exposures with extra precaution being taken not to contaminate the sample with foreign matter. This was done in the following manner. First, a portion of the immediate wall exposure was pried away with a geologic pick exposing a section of the dike free from contamination likely to occur during mine operations. A sample was then removed from this exposure, the portion of it touched by the pick being broken off, using another piece of the rock as an improvised chisel and striking it with the pick. Similar procedures were used on all other samples collected. A representative sample approximately 2 inches by 2 inches was obtained from all locations. These were placed in doubled paper bags, marked and stored. (See Figure 4 for sample locations)

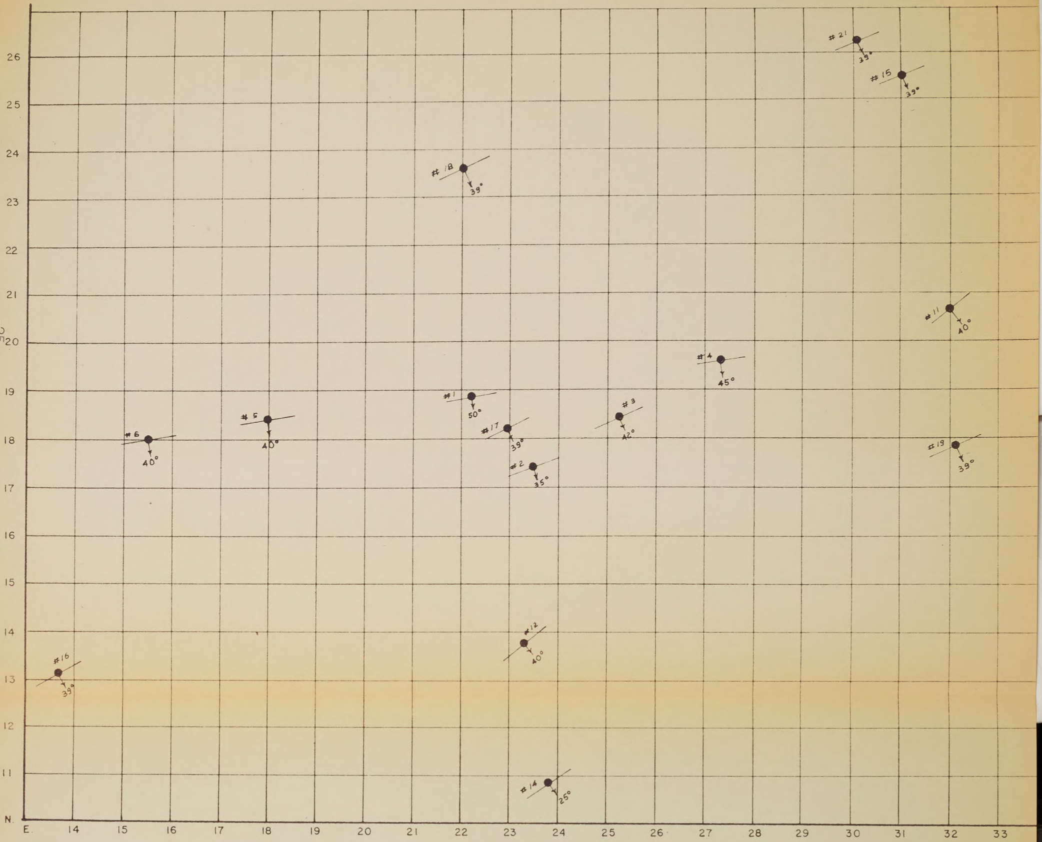

Figure 4. SAMPLE LOCATION MAP
DAVIS DIKE
Scale 1" = 200'

DETERMINATIONS OF STRUCTURAL ATTITUDES OF DIKES

Determinations were made of the structural trends and thicknesses of the dikes at their various sample locations. No direct thicknesses were measured in the field, but rather computed from mine map data.

All rakes (pitches) and plunges of the dikes were computed by the sterographic projection method as described by Walter H. Bucher (1944).

In every instance, the rake (pitch) computed, was that of the dike on the intruded formation. The results disclosed that these dikes all pitch to the northeast, contrary to the southeasterly pitch as described in previous literature. See Figure 5 for an illustrative example of the method used to derive these results.

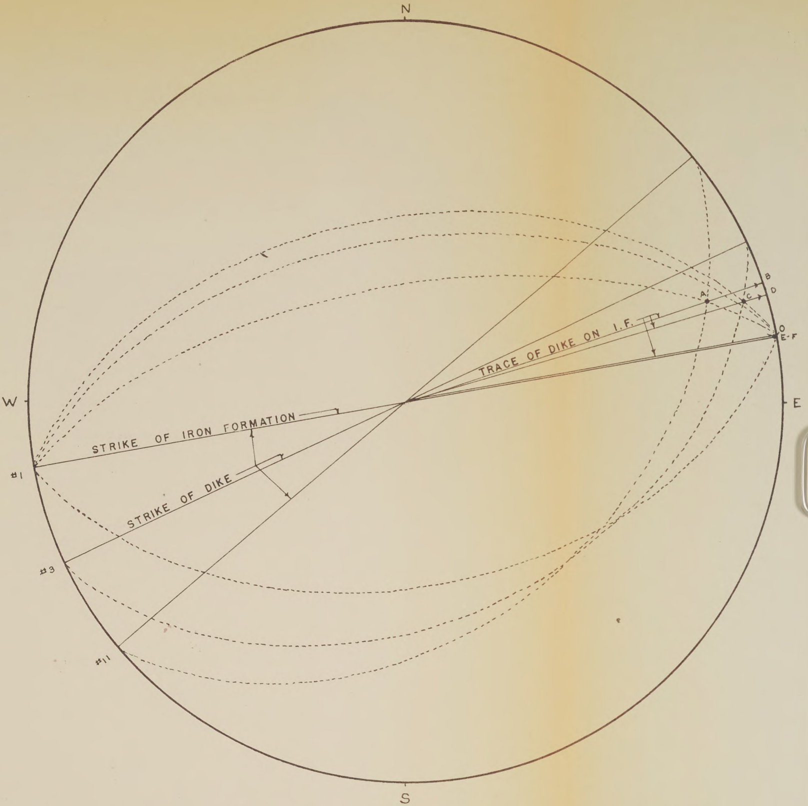

Figure 5. Stereographic Projection of intersection of Davis dike and iron formation at sample locations #1, #3 and #11. A-B, C-D, E-F are plunges of dike, O-A, O-C, O-E are pitches of dike as measured by its trace on iron formation.

AGE DIFFERENTIATION

As was indicated previously, the determination of age relationships of these dikes still remains a controversial issue. Some of the evidence uncovered in this respect based on particular mineral assemblages, more common to either the Huronian or Keweenawan intrusives is related below.

Huronian Dikes: The Huronian dikes are generally metamorphosed, the original plagioclases being recrystallized with a greater Ab/An ratio since calcium is removed during metamorphism. Hence, a metamorphic mineral assemblage, dependent on the metamorphic rank attained (in this case, most likely that of the chlorite sub facies rank) is to be expected in dikes of Huronian age. These dikes presumably never reached the preexisting surface, and hence, most alteration is concluded to be the results of the effects of downward percolating surface waters.

The two contributory causes to the present physio-chemical makeup of these dikes are thus believed to be the effects of metamorphism with resulting new mineral assemblages and the alteration of these minerals through the action of leaching solutions.

Keweenawan Dikes: The Keweenawan dikes are unmetamorphosed and generally fresh appearing, with the original mineral content being preserved. The altered phases are a result of weathering and not due to metamorphic effects. A number of these dikes reached the surface and no doubt served as conduits for the Keweenawan lava flows. The original mineral content typical of diabases is present with an abundance of calcium rich plagio-

clase, monoclinic pyroxene, some olivine, magnetite and/or ilmenite and biotite.

PETROGRAPHY

The extent of the petrographic study of these dikes was confined to that of a supporting role in an effort to predict the geo-chemical behavior of the trace elements found therein and deduce their origin and also possibly supply evidence in regard to age relationships of these rocks.

For a more complete discussion of the petrography of these dikes, the author makes reference to literature by Irving and Van Hise (1892) and the work of George A. Hoffman (1950).

An adapted description of the diabases of the Gogebic range after Irving and Van Hise (1892) is as follows:

"The diabases usually have a well developed ophitic structure, the augites being of large size and including many somewhat idiomorphic lath-shaped plagioclases. In the diabases in which this structure reaches the extreme, the feldspars have a tendency toward two generations, there being aside from the smaller lath-shaped plagioclases, larger, somewhat porphyritic appearing ones. The rocks vary from ophitic diabases to true gabbro, all grades of variation being observed. The gabbro occurs in only a few localities and is of little importance as compared with the diabases.

The original minerals are apatite, magnetite, olivine, plagioclase and monoclinic (augite) and orthorhombic pyroxene. The latter occurs only in one exposure and in the most widespread phase of rock, the only important original minerals are magnetite, plagioclase and augite. The

order given is that of crystallization. In some of the rocks, this succession can be made out with a good deal of sharpness, each mineral present having nearly completed its crystallization before the succeeding one began to separate. This is particularly true of the ophitic diabases and becomes less and less true in passing toward the gabbros."

The environments were peculiar to each sample utilized in this study, selected in such a manner as to permit a petrographic investigation from the most altered to unaltered phases of these rocks, thus allowing the observation of the mineralogic changes taken place through processes (and possibly metamorphic effects).

Four thin sections were prepared from samples of the Davis dike. The samples utilized came from three environments; namely, granite, footwall quartz-slates and the iron formation. An additional thin section of the Geneva dike was prepared from a sample taken close to relatively unaltered iron formation.

The degree of alteration showed a marked increase in going from the granitic environment through the footwall quartz slates and into the iron formation.

In the slides examined, the minerals present consisted of labradorite, olivine (questionable), augite, magnetite, some ilmenite and biotite, along with leucoxene, hematite, biotite, chlorite, sericite and kaolinite.

The iron oxides were for the most part (except in altered phases) magnetite and some ilmenite, occurring as subhedral crystals or linear masses scattered throughout the thin section. They are primary constituents of the rock and fairly abundant. The ilmenite is generally

represented by its alteration product, leucoxene, and is intimately associated with the magnetite. Some oxidation to red hematite is discernible within individual magnetite grains. In the more altered phases, the iron oxides consist wholly of red hematite, the magnetite having been completely oxidized. Because of the deep penetration by red-hematite stain, the other constituent minerals of the thin sections representing the altered phases of this dike could not be determined, with only the ophitic structure being preserved.

The feldspars are restricted to the calci-rich end of the plagioclase series being essentially labradorite with the possibility of some andesine. They are generally found as small idiomorphic, striated, lath-shaped individual crystals displaying polysynthetic twinning and on rare occasions also Carlsbad twinning. In the fresher portions of this rock they are well preserved and extremely abundant, whereas in approaching the altered phases they are frequently altered to sercite and in some cases kaolinite (the determination of kaolinite was based on x-ray study). Determination of specific plagioclase was based on indicative refractive indices and extinction angles.

The pyroxenes are essentially those of the augite-ferroaugite series with some indications of associated pigeonite, although this variety is minor in the rock slides examined. They are roughly equidemensional, stubby to elongated crystals displaying prismatic cleavage on the 110 plane and 100 parting. In the unaltered portions of this rock the individual grains are fairly well preserved, their crystal boundaries being sharply defined in some instances, but for the most

part controlled by the plagioclase laths. In the altered phases, the pyroxenes have been converted almost wholly to a pale green chlorite. In some instances augite can be found growing around plagioclase laths indicating that the mineral is later than the feldspars.

Biotite was present in these rock specimens in which alteration had begun to pass from that of intermediate to an advanced stage. In these slides no pyroxene is apparent, magnetite is abundant and chlorite and kaolinite alteration is extreme. The biotite which is quite pleochroic in shades of brown frequently surrounds magnetite grains. Some of this mineral appears to be secondary after the pyroxenes and for the most part is an alteration product or a reaction mineral. Biotite is conspicuously absent from the sections of the unaltered rock that were examined.

The presence of olivine is suspected in only one instance where an area of what appears to be serpentine alteration maintains a roundish boundary suggesting the former presence of an olivine granule. The exact determination of the secondary mineral serpentine, however, is uncertain due to the obliterating effects of a red-hematite stain.

The order of crystallization of these minerals as indicated by petrographic evidence, appears to be, ilmenite, magnetite, olivine (?), labradorite, pyroxene. Some biotite may have been formed from the residual liquid phases of the magma or as a reaction mineral during the final stages of solidification.

The results of this petrographic study provided no conclusive evidence that might be used in age differentiation of these intrusives. The

apparent lack of olivine in the sections studied suggest dikes of Huronian age, since Keweenawan intrusives and extrusives (if the dikes are related to the flows) are generally reported to be quite rich in olivine. A Huronian age for these dikes is also supported by structural evidence. Yet, the abundance of calci-rich plagioclase and monoclinic pyroxene and the lack of amphibole suggests dikes of Keweenawan age. Biotite offers no clue to the solution of this problem, as it is conspicuously absent in one section and particularly abundant in another. No flow structures were noted in any of the sections that might postulate intrusives of Keweenawan age, such as might be expected had the dikes furnished the pipes through which the Keweenawan lavas poured out.

This suggests that age determinations based on petrographic evidence alone is inconclusive and hence a more fundamental approach involving research on the physical chemistry of magmatic differentiation and crystallization in these rocks is necessary in the final analysis.

QUALITATIVE AND QUANTITATIVE SPECTROSCOPY

The basic theory of spectroscopy is outlined briefly in the following paragraph, succeeded by a discussion on qualitative and quantitative methods of analysis. For a more detailed discussion on the theory of spectroscopy, the author makes reference to the works of Ahrens (1950), and Willard, L. L. Merritt, J. A. Dean (1948).

The quantum theory introduced by Planck to explain the emission of radiant energy from the excitation of an atom or ion, predicts that each atom or ion has definite energy states in which the various electrons can exist. In the normal or ground state, the electrons are in the lowest energy state, but upon addition of sufficient energy by thermal, electrical, or other means, one or more electrons may be removed to a higher energy state farther from the nucleus. This condition is an unstable one and the electrons upon returning to their original orbital position emit radiant energy of specific wave lengths which can be recorded as spectral lines on a photographic plate.

Since radiant energy when dispersed produces a spectrum unique for each particular atom or ion, identification of a mixture of unknown elements is made possible by interpretation of their characteristic spectra emitted during excitation. Final identification is achieved by visual comparison with known standard charts and tables.

Quantitative analysis of these elements is achieved through the measure of the intensity or optical density of their characteristic spectral lines which is reflected on the photographic plate as varying

degrees of blackening of a particular line. This immediately follows since the radiation emitted by any element is directly proportional to its concentration in the sample and the intensity or blackening of a spectral line on the plate is in turn proportional to the radiation emitted.

Various techniques utilizing this concept have been employed in the semi-quantitative determination of trace elements from spectrochemical analysis.

Harvey (1947) describes a method by which weighed amounts of samples are completely volatilized and selected line to background ratios are determined on a microphotometer. The background continuum is used in principle as an internal standard and the conditions of arcing must be closely controlled. This method is applicable to the analysis of a wide number of elements.

Van Tongeren (1938) has made use of a method involving cathode layer excitation on carefully weighed samples diluted with N_2CO_3 in which successive exposures were made on each of the samples at varying amperages and exposure times. Semi-quantitative determinations were made visually by comparing line responses of the unknown with those of standards which had been prepared in a base of quartz and Na_2CO_3.

Another general method which employs cathode layer excitation is that described by Mitchell (1948). This method which has been widely applied to the analysis of soils, minerals and rocks, requires that a small accurately weighed quantity of specimen be loaded into a cathode cavity and arced at a predetermined amperage. Three successive exposures of about one minute are made. To facilitate visual comparison of the line response, a step sector is employed and the plates are examined in a comparator.

The semi-quantitative methods just described are designed to handle a relatively large number of elements and are applicable to a wide variety of materials. The value of these methods is that of enabling the analyst to obtain much information about many elements in a short time.

The method employed by the author is similar to that as described by Mitchell with some modifications, and is described later on in this work.

Strictly quantitative methods utilizing internal standards and possessing a greater degree of accuracy have been described by Ahrens (1950). In these methods, intensity ratios are measured, that is, the ratio of the analysis line to that of a line of an element, the "internal standard". The advantage of using an internal standard is that it affords compensation for various factors affecting the intensity of line emission such as arc wandering, change in length of arc column, failure to time the exposure exactly, and lack of uniformity in the technique of photographic development. The main disadvantage of internal standardization is that each element or a limited number of elements may require a separate internal standard, and a complete and accurate analysis becomes very tedious.

Since this study was designed to cover a wide range of elements, it did not seem feasible to employ internal standardization, but rather utilize semi-quantitative techniques with close control on those factors influencing the intensity of line emission.

PREPARATION OF SPECIMEN PRIOR TO ARCING

The laboratory techniques and procedures utilized in this study followed a preliminary investigation of crushing and grinding methods as described by Ahrens (1950).

Because it was necessary to obtain a small and accurately representative powder sample from a rock specimen whose physical-chemical properties made it quite resistant to ordinary crushing and grinding techniques, certain modifications in these techniques had to be employed in the procedure followed by the author.

First, the original rock specimen was cracked into two smaller pieces approximately 1" x 1" in size with the aid of a porcelain pestle and mortar. One of these pieces was then selected for further preparation of the powder sample, and washed with dilute HNO_3 in order to remove the oxide minerals (particularly red hematite dust which had collected on dike exposures from mine operations) as soluable nitrates. The specimen was then rinsed in de-ionized water, placed in an electric furnace and heated to 600° C. for 25 minutes. The specimen was removed, chilled in de-ionized water and placed in an electric oven for drying (30 minutes).

This procedure not only facilitated secondary crushing and grinding but also served to drive off volatile components (primarily H_2O) which are often the cause of the erratic behavior (spattering effect) of silicate minerals during initial arcing.

After being removed from the dryer, the specimen was crushed and

ground in a mullite mortar. Final grinding in an agate mortar was continued until the bulk of the sample was homogenous and reduced to about - 150 mesh. A one-half gram weight of this sample was accurately weighed out, mixed with an equal portion by weight of purified powdered carbon and stored in a clean glass vial.

All samples were prepared in this manner with particular care being taken to cleanse all laboratory equipment used in their preparation between samples. Such procedures limited possible contamination.

Control samples were then run in an effort to determine moisture loss during preliminary heating in the electric furnace. The results disclosed an average moisture loss of 3.5% by weight.

The addition of powdered carbon to the samples in a 1:1 ratio was made to facilitate arcing. Ahrens (1950) states that "The presence of powdered carbon speeds up volatilization rates considerably, without affecting total line intensity, provided the specimen is arced to completion and the change in composition does not alter the arc temperature significantly".

Arcing to completion, is referred to as the total energy method since it allows the total intensity of emission to be recorded. For this reason, the total energy method can be effectively employed in semi-quantitative analysis and was utilized by the author. The main requirements imposed upon this method are accurately weighed samples, a carefully controlled excitation source, a smooth burning arc, and arcing to completion.

SPECTROGRAPHIC TECHNIQUES

The spectrographic techniques employed for the respective sample analyses were designed to maintain uniform rate of volatilization and a constant temperature range which insured equal levels of excitation and hence the consistency of treatment of each particular sample. Preliminary samples were first run to determine the optimum operating conditions of the spectrograph relative to the unknowns to be analyzed.

The instrument used for these analyses was a Bauch and Lomb large Littrow Spectrograph possessing a range of 2100 to 8000Å and capable of recording this entire range in three photographs on 25.4 cm. photographic plates. The dispersing media is a quartz Littrow prism, with the dispersion being about 0.4 mm/Å at 2500Å and 0.10 mm/Å at 4000Å. An interchangeable glass prism can be inserted for increased dispersion in the visible region.

For the purposes of this study the quartz Littrow prism was used exclusively and the computed dispersion for the particular spectral range used was 0.7 mm/Å . A direct current arc energized at 70 volts and 3 amperes was used as the excitation source with an average exposure time of two minutes.

The reason for D.C. excitation is as stated by Willard, Merritt, Jr., Dean (1948), "The D.C. arc is a very sensitive source and is used for the determination and identification of substances present in very small concentrations. A comparatively large amount of the substance being analyzed passes through the arc, and on this account, an average or more representa-

tive value of the concentration is shown provided the complete sample is burned".

The recording device used were Kodax Spectrum Analysis Number One plates of size 10.2 by 25.4 cm, which were developed by use of Kodak Developer D-19 for 4 minutes at 70°F, followed by a 30 second stop bath, a 15-20 minute acid fix, a 30 minute washing period and a final rinsing with distilled water.

BURNING OF THE SAMPLE

The procedure involved in the actual burning of the sample is outlined as follows:

Eight milligrams of a sample were accurately weighed out and placed into the drilled out recess of the lower electrode. Transferal of the sample to the recess was done by means of a beveled carbon rod of electrode material, thus eliminating the introduction of any foreign impurities. The upper electrode was beveled to a point to prevent arc wandering and maintained at a distance of 1/4 inch from the lower electrode during all arcings, a condition which is described by many spectroanalysts as optimum for a smooth, continuous burning arc.

A power supply unit furnished the amperage and induced voltage, controlled by a rheostat to the particular requirements deemed necessary for optimum results in these analyses; arcing was induced by means of a striker electrode. The spark image was then centered on a plastic screen and the shutter opened with exposure time necessary for complete consumption of the sample. The shutter was closed and the plate racked up 3 millimeters, allowing an interval spacing of 1 millimeter between successive spectra. A slit width of 2 millimeters was used in all exposures. The original procedure was then repeated until the spectra of a sufficient number of unknowns were recorded on one plate. A copper spectrum and FeCl spectrum were then recorded immediately above and below the unknowns to act as a guide and external standard for qualitative purposes.

Final identification of the recorded spectrums was achieved by

comparative methods with known standard charts and tables.

The definite presence of any particular element was confirmed through the identification of at least two of its most persistent lines.

A semi-quantitative evaluation of these elements was achieved by setting up an intensity scale (1-10) designed to measure the relative concentration of an element in a particular sample. A persistent line of an element was chosen from the spectrum in which it appeared to be most intense and given an intensity rating of ten. The same line was then examined in the other spectra and an intensity rating from 1-10 assigned to it accordingly. In this manner, the relative concentration of each element, as it appeared in a particular sample, was determined.

The emulsion factor between a number of spectrum analysis plates has been known to vary, causing an apparent deviation in the concentrations of elements recorded on these plates. Since the author used two plates in recording the total samples analyzed, and since the intensity of the recorded iron spectra between the two plates varied, the relative concentrations of the elements in one plate had to be multiplied by a variance factor (1.4), computed as the proportional difference in the intensities of a persistent iron line as it appeared in the iron spectra of the two plates.

The trace elements listed in the following table along with their identifying spectral lines were studied semi-quantitatively in this work. Photographs of the spectra used in this analysis are depicted in Figure 6.

SPECTRAL LINES USED IN ELEMENT IDENTIFICATION

Element	Spectral Lines - Wavelength in A°
Iron (Fe)	3099.90, 3100.31, 3100.67
Magnesium (mg)	3096.92, 3336.89, 3832.31
Aluminum (Al)	3082.16, 3092.72, 3944.03, 3961.54
Vanadium (V)	2891.65, 2908.81, 2923.63, 3118.38, 3183.99, 3703.57
Silicon (Si)	2881.59, 3905.52
Cobalt (Co)	3158.76, 3254.20, 3377.06, 3385.23, 3453.51
Chromium (Cr)	3578.69, 3593.48, 4254.34, 4289.73
Nickel (Ni)	3243.06, 3380.56, 3433.57, 3446.26, 3461.66, 3619.89
Copper (Cu)	3247.55. 3273.96, 3307.95, 4062.75
Titanium (Ti)	3088.03, 3199.92, 3222.84, 3341.87, 3372.80, 3642.68, 3685.19, 3956.34, 3958.21
Potassium (K)	3217.1
Sodium (Na)	3302.34, 3302.94
Calcium (Ca)	3158.87, 3179.33, 3644.39, 4302.53
Lead (Pb)	3739.95
Platinum (Pt)	3628.11, 3672.00
Beryllium (Be)	3130.72, 3131.06, 3321.08, 3321.35
Antimony (Sb)	3232.52, 3267.47
Cadmium (Cd)	3261.05, 3466.20, 3467.66

Element	Spectral Lines - Wavelength in A°
Molybdenum (Mo)	3112.12, 3132.60, 3327.31
Strontium (Sr)	4077.84
Barium (Ba)	4304.00
Scandium (Sc)	3589.66, 3590.52, 3642.81
Zirconium (Zr)	3106.57, 3165.97, 3438.23, 3496.09
Lithium (Li)	3232.67

By relative concentrations, silicon, magnesium, aluminum, calcium and iron are by far the most abundant of the elements studied. Some potassium and possibly some barium might be attributed to the presence of potash feldspar and barium feldspar which are known to occur within the limits of the intermediate plagioclase feldspar series. Some manganese may be present as a specific mineral or on rare occasion replacing the ferrous iron in the alteration product of chlorite. Petrographic study also indicates that a greater proportion of titanium is the result of the presence of ilmenite in these rocks.

The remaining elements do not form common rock making minerals and their presence is hence concluded to be due to substitution in the silicates, oxides and possibly sulfides (pyrite) of the rocks.

The occurrence and behavior of some of these elements in igneous rocks follows.

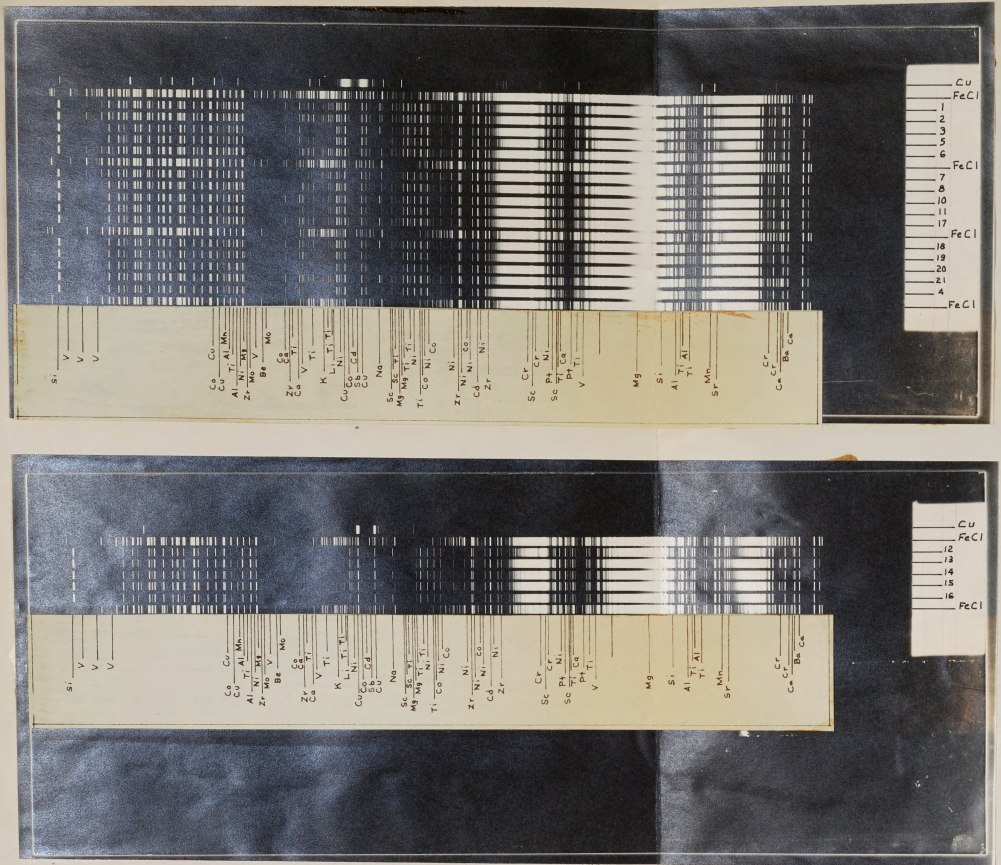

Figure 6. Photographs of Spectra

GEOCHEMICAL NATURE OF TRACE ELEMENTS

Because of the important role assigned to trace elements in this work, a discussion on their occurrence, abundance and physio-chemical relations with rocks of magmatic origin is deemed necessary before presenting the results and their interpretation as derived from this spectrochemical study.

The investigations of Clark and Washington (1922, 1924) based on 5,159 analyses of igneous rocks from all parts of the world, confirmed that the eight elements constituting the bulk of the upper lithosphere were also the primary constituents of all igneous rocks. These main elements, oxygen, silicon, aluminum, iron, calcium, sodium, potassium and magnesium comprise 98.28% by volume of the elemental composition of all igneous rocks; all other elements as a group, accessory or minor or trace elements forming only 1.72% of the total mass of igneous rocks. Of these latter elements, titanium, phosphorous, hydrogen and manganese comprise 1.13% and hence only 0.59% is left for by far the greatest part of the elements.

Rankama and Sahama (1949) define trace elements as those elements not common in the upper lithosphere, that is, all elements other than those which make up the bulk of the upper lithosphere according to the findings of Clark and Washington, and proposes a division of the trace elements into two groups according to their manner of occurrence in igneous rocks. The first of these groups is comprised of the trace elements which ordinarily form independent accessory constituents in igneous rocks; and the second group being composed of those elements which rarely, if ever, form independent minerals, their presence in igneous rocks being the result of incorporation in solution in other minerals.

The author is primarily concerned with the second group of trace elements as it was mostly elements comprising this group that were used in the final quantitative analyses.

Regarding the incorporation of trace elements in mineral structures, Goldschmidt (1944) states that, "Three structurally different types of diadochy regulate the dispersed manner of occurrence of the trace elements".

These are further described as: (1) camouflage, which occurs when a trace element replaces a common element of similar valence (2) capturing, which is the replacement of a common element by a trace element of higher valence, and finally (3) admission, which occurs when a trace element replaces a common element with a valence higher than itself.

Factors governing the introduction of trace elements into minerals are: (1) the effective size of the atom or ion in the structure, which depends upon the bond strength to neighboring atoms or ions, on the electronic configuration of the atom or ion and on its co-ordination (2) the affinity of an element for a particular phase, that is: a silicate, oxide or sulphide phase and the abundance of any of these phases in the particular melt (3) the relative abundance of a particular trace element in the original melt from whence the mineral

crystallized. (Goldschmidt, 1944)

The sizes of the ions or atoms involved in replacement, must be such as not to disrupt the rigidity of the original crystal structure, the tolerance in size difference between any two atoms or ions substituting for each other being about 15% of the larger of the two, as measured by their atomic or ionic radius in terms of angstroms as the unit of measurement. (Rankama and Sahama, 1949). Exceptions to this are probably due to the influence of temperature and pressure at the time of crystallization (Storehouse, 1952).

The deciding factor governing initial substitution is the relative bond strength of two atoms or ions in identical position in a structure, the atom or ion providing greater bond strength being substituted in preference to those contributing weaker bonds. In general, for those atoms or ions with similar valency charge, the larger tends to weaken the bond, while for atoms or ions of similar size, the one with a higher valency charge will tend to strengthen the bond (Goldschmidt, 1937).

Capture of trace elements occurs during the initial stage of crystallization of a magma and hence these are found in the early crystallized minerals, whereas admitted trace elements are incorporated into the structure of later crystallizing minerals.

An illustrative example of this phenomena is that of trivalent scandium (Sc^{3+} 0.83kx) which is captured by magnesium (Mg^{2+} 0.78kx) and is concentrated in basic rocks, whereas (Li 1 0.78kx) is admitted by magnesium and concentrated in acid. rocks.

	<u>Sc ppm</u>	<u>Li ppm</u>
Pyroxenite	46	0
Dunite	0	2.3
Granite	1.3	170.4

(References - Stonehouse, 1952; Goldschmidt, 1937; Strock, 1936)

The following table after Rankama and Sahama (1949) indicates common examples of diadochic substitution in minerals.

Diadochic Substitution With:		
Unchanged Charge	Increasing Charge	Decreasing Charge
Mg^{2+}, Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}	K^{+}, Ba^{2+}, Sr^{2+}, Pb^{2+}	O^{2-}, OH^{-}, F^{-}
Al^{3+}, Ga^{3+}, Mn^{3+}, Cr^{3+}, Fe^{3+}, V^{3+}	K^{+}, Eu^{2+}	Si^{4+}, Al^{3+}, B^{3+}
Si^{4+}, Ge^{4+}, Ti^{4+}	K^{+}, La^{3+}	Si^{4+}, Be^{2+}
P^{5+}, V^{5+}, As^{5+}	Ca^{2+}, Y^{3+}	Ca^{2+}, Na^{+}
K^{+}, Rb^{+}, Cs^{+}, Tl^{+}	Mg^{2+}, Sc^{3+}	Mg^{2+}, Li^{+}
Ca^{2+}, Sr^{2+}, Mn^{2+}	Mg^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}	P^{5+}, Si^{4+}
Zr^{4+}, Hf^{4+}, Th^{4+}	Si^{4+}, P^{5+}	W^{6+}, Cb^{5+}, Ta^{5+}
Sc^{3+}, Y^{3+}	Sc^{3+}, Zr^{4+}, Hf^{4+}	
Cb^{5+}, Ta^{5+}	Zn^{2+}, Ga^{3+}, In^{3+}	
Sr^{2+}, Eu^{2+}	Fe^{2+}, Sc^{3+}	

Nickel Ni^{2+} (0.78kx) and Cobalt Co^{2+} (0.82kx)

Nickel and Cobalt are present in normal igneous rocks of the main stage of magmatic crystallization, their occurrence being due in part to the presence of small quantities of common sulfide minerals such as pentlandite, pyrrhotite and pyrite and of major importance being due to their incorporation into the structures of silicate minerals. This latter case indicates that nickel and cobalt are oxyphile in the upper lithosphere.

The nickel ion, with the same radius and charge as magnesium, is ordinarily camouflaged in magnesium minerals although the high Ni:Mg ratio ion early formed crystals and the steady decline in later formed rocks and minerals indicates its capture in some magnesium minerals, evidently the nickel ion with a valence of greater than +2 is captured. (Mason, 1952).

The bivalent cobalt ion on the other hand is practically the same size as the ferrous ion (0.83Å) and is thus generally camouflaged in ferrous compounds. Sandell and Goldich (1943) found that cobalt varies linearly with magnesium over a wide range of concentrations and hence suggest that this relationship is more apparent than the one between cobalt and ferrous iron.

Both cobalt and nickel are relatively abundant in basic rocks and deficient in silicic rocks, the abundance of cobalt in the latter rocks increasing at the expense of the nickel. (Rankama and Sahama, 1941)

The enrichment of nickel in the early crystallized magnesium and ferromagnesium minerals is due to the suitability of its incorporation into the crystal structure of olivine and hypersthene. Nickel is less abundant in augite, amphibole and biotite (Rankama and Sahama, 1941)

The content of nickel and cobalt present in plagioclase, hypersthene, augite and biotite from a diorite is indicated in the following table after Nockolds and Mitchell (1948).

	Ni ppm	Co ppm
Plagioclase	-	15
Hypersthene	300	100
Augite	200	70
Biotite	150	40

The following tables after Wager and Mitchell (1951) show the relative contents of nickel and cobalt in pyroxene, ilmenite and magnetite from an olivine free gabbro.

	Ni ppm	Co ppm
Plagioclase	-	-
Pyroxene	50	60
Magnetite	50	80
Ilmenite	100	100

These minerals are all present in the diabase dikes sampled. Both of these elements also occur in hornblende.

Manganese Mn^{2+} (0.91kx)

Though manganese forms specific minerals in igneous rocks, they are of minor importance in comparison to the manganese occuring in silicates and oxides. Sulfides are relatively free of manganese

(Stonehouse, 1952).

Divalent manganese replaces Mg^{2+} (0.78kx) Fe^{2+} (0.83kx) and Ca^{2+} (1.06kx). It is admitted in place of magnesium and ferrous iron and is captured in place of Calcium. (Mason, 1952) Nockolds and Mitchell (1948) show a relative increase of Mn:Fe in later differentiates indicating that removal of manganese from magmas is due to a large extent to their admittance to ferromagnesium minerals. Only traces of manganese are found in plagioclases where they replace calcium. This is attributed to the fact that the Mn^{2+} ion is too small to give stability to the feldspar structure. (Mason, 1952)

Figures by Nockolds and Mitchell (1948) and Wager and Mitchell (1951) show that pyroxene is a more important host mineral for the acceptance of manganese than is biotite.

Chromium Cr^{3+} (0.64kx)

Chromium occurs in igneous rocks as chromite or other chrome spinels and as traces in the structures of silicate and oxide minerals. Its most important occurrence is that appearing in silicate minerals where it is camouflaged by aluminum (Al^{3+}, 0.57kx) and iron (Fe^{3+} 0.67kx) and captured by magnesium (Mg^{2+} 0.78kx) and iron (Fe^{2+} 0.83kx). (Stonehouse, 1952)

Chromium is highly concentrated in the early differentiated silicates occurring in magnesium-rich olivine and clinopyroxene though showing a preference for the latter. It also occurs in common augite and hornblende. (Lundegardh, 1946)

Chromium contents in the primary minerals of a diorite as shown

by Nockolds and Mitchell (1948) are listed below:

	Cr ppm
Plagioclase	-
Hypersthene	200
Augite	1500
Biotite	800

Relative contents of chromium in an olivine free gabbro after Wager and Mitchell (1951) follows:

	Cr ppm
Plagioclase	-
Pyroxene	-
Magnetite	800
Ilmenite	300

Copper Cu^{2+} (0.83kx)

The high affinity of copper for sulfur is the primary factor determining the manner of occurrence of copper in igneous rocks. It is almost entirely present as chalcopyrite in unaltered igneous rocks, but small amounts may also replace ferrous iron in mineral structures in the absence of sufficient sulfur.

Ramdohr (1940) believes this replacement would take place in augites. Carobbi and Pieruccini (1947) suggest that copper can replace both Fe^{2+} and Mg^{2+}, for example in tourmaline.

The content of copper in the minerals of a diorite (Nockolds and Mitchell, 1948) is listed below:

	Cu ppm
Plagioclase	-
Hypersthene	150
Augite	100
Biotite	300

Its presence in minerals of an olivine free gabbro (Wager and Mitchell, 1951) follows:

	Cu ppm
Plagioclase	15
Pyroxene	50
Magnetite	50
Ilmenite	50

Titanium Ti^{4+} (0.64kx)

Titanium tends to become strongly enriched in the early products of crystallization and hence occurs in igneous rocks mainly as oxides, the most important of which is ilmenite, although it can replace Al^{+3} and appears, therefore, in pyroxene, hornblende and biotite in which case it is captured by such minerals due to its higher charge. In highly siliceous magmas it is removed as titanite, which is probably the reason for its lack of occurrence in muscovite (Mason, 1952). Though titanium is not generally considered as a trace element, its inclusion here is due to its important geochemical relationship with vanadium.

Vanadium V^{4+} (0.61kx)

Vanadium generally does not form independent minerals in igneous rocks and hence is usually found in the structures of other minerals, essentially as the quadrivalent ion. It is similar to titanium in that it tends to become concentrated in basic rocks. The highest vanadium content in igneous rocks is found in those formed during the initial steps of the main stage of crystallization. (Rankama and Sahama, 1941)

Ramdohr (1940) believes the major content of vanadium found in igneous rocks is due to its presence in magnetite, whereas Lebedev and Levedev (1934) concluded that it was primarily concealed in ilmenite.

Vanadium occurs in additional titanium minerals in igneous rocks such as sphene and rutile where the phenomena is evidently a replacement of Ti^{4+} by V^{4+}.

Quinquevalent vanadium replaces phosphorous (P^{5+}) in apatite. (Rankama and Sahama, 1941)

Feldspars are nearly entirely deficient in vanadium, whereas pyroxenes, amphiboles, micas almost always carry some vanadium as V^{4+} and V^{5+} ions which replace Fe^{3+} and Al^{3+}. (Rankama and Sahama, 1941)

Vanadium, hence occurs in nearly all of the primary constituents of the diabase dikes.

The distribution of vanadium in a diorite and an olivine free gabbro is as follows:

	V ppm		V ppm
Plagioclase	20	Plagioclase	10
Hypersthene	100	Pyroxene	100

	V ppm		V ppm
Augite	200	Magnetite	800
Biotite	400	Ilmenite	300
(Nockolds and Mitchell, 1948)		(Wager and Mitchell, 1951)	

Strontium Sr^{2+} (1.27kx) and Barium Ba^{2+} (1.43kx)

Strontium and Barium ordinarily do not form independent minerals in igneous rocks, but are rather concealed in the rock making minerals. Strontium generally accompanies calcium (1.06kx) in these minerals, whereas barium is usually substituted for potassium (1.33kx).

The behavior of barium in igneous rocks is similar to that of strontium and the presence of one usually indicates that of the other, although, in general, the content of barium in calc-alkali rocks decreases rapidly towards the granites, whereas strontium, though in low concentrations, is more evenly distributed in all igneous rocks.

The most important occurrence of strontium and barium in igneous rocks is in the feldspar structure. Here strontium is admitted by calcium or captured by potassium with an increase in the Sr:Ca ratio in the later differentiates.

Barium being too large to replace calcium or sodium is generally only found in potash feldspars replacing potassium. It also appears in biotite and muscovite.

Strontium also replaces calcium in apatite and the calcium bearing pyroxenes and amphiboles.

Beryllium Be^{2+} (0.34kx)

The studies of Goldschmidt and Peters (1932), Sandell and Goldich

(1943) and Sahama (1945) show that beryllium tends to become enriched toward the late stages of magmatic differentiation, and hence displays a maximum content in both granites and nepheline syenites. In alkalis rocks low in silica, the degree of enrichment is considerably higher than in silica-rich granites.

Sahama and Vahatalo (1939) have also established the concentration of beryllium in the residual solutions of diabase magmas.

The most important occurrence of beryllium in igneous rocks is that contained in other mineral structures since too little of this element is contained in the rocks to allow the formation of its independent minerals.

This occurrence is based on the substitution of Be^{2+} for Si^{4+} (0.39kx) in the SiO_4 tetrahedra. The alkali feldspars, micas, alkali amphiboles and alkali pyroxenes provide suitable structures for the replacement of silicon by beryllium.

Because of its small size and low charge which gives a weaker bond, the main content of beryllium becomes concentrated in the residual solutions and hence enriched in pegmatites.

Zirconium Zr^{4+} (0.87kx)

Though Zirconium resembles titanium chemically in many respects, their manner of occurrence differs considerably.

Zirconium, because of its high charge and relatively high radius, does not enter into any of the common rock-forming minerals, but rather appears exclusively as zircon.

Unlike titanium, the content of zirconium is low in the early

crystalates but tends to become enriched in the last rocks to crystallize.

The following table after Rankama and Sahama (1941) indicates this tendency.

	g/ton
Peridotites, eclogites, dunites	60
Gabbros	140
Diorites	280
Granites	460

Scandium Sc^{3+} (0.83kx)

Goldschmidt and Peters (1931) show that the bulk of scandium present in the upper lithosphere is that concealed in ferromagnesium minerals of the early crystallates and of such ultrabasic and basic rocks as pyroxenites and gabbros.

Here scandium is captured by Mg^{2+} (0.78kx) and Fe^{2+} (0.83kx) in ferromagnesium mineral structures.

This indicates a concentration of scandium in the pyroxenes, amphiboles and biotite in the basic fractions of a crystallizing magma.

The apparent lack of scandium in the earlier formed olivines is due to the fact that a replacement of Sc^{3+} for Mg^{2+} here would not balance the excess positive charge thus introduced by other suitable replacements. (Mason, 1952)

Scandium may also replace Al^{3+} (0.57kx) in aluminum minerals, but only if the Al^{3+} is in octahedral coordination and in general does not follow aluminum during differentiation.

Only traces of scandium were discernible in the diabases studied.

Molybdenum Mo^{2+}

Molybdenum is preferentially concentrated in the last differentiates during magmatic concentrations and hence appears in notable amounts in granites, and less so in gabbros and norites, the order of magnitude being indicated by the following table:

	g/ton
Gabbros and Norites (Hevesy and Hobbie, 1933)	3
Subsilicic rocks (Sandell and Goldich, 1943)	2
Granite (Hevesy and Hobbie, 1933)	12

The incorporation of Mo^{2+} in mineral structures is rare and it is usually found in the form of the sulfide molybdenite MoS_2. The high affinity of Mo^{2+} for sulfur restricts the formation of sulfides of other metals unless available sulfur is present.

Cadmium Cd^{2+} (1.03kx)

Cadmium closely follows zinc in its manner of occurrence in igneous rocks, although it is much less abundant than the latter.

It remains largely in the residual melts and solutions throughout the main stage of crystallization.

According to Sandell and Goldich (1943) cadmium seems to be concentrated in ferromagnesian minerals of acidic igneous rocks particularly in biotite, although traces of cadmium have also been reported in apatite.

Goldschmidt and Hermann (1937) found notable concentrations of

cadmium in certain plagioclase rocks, but have been unable to determine the manner of occurrence of this element in these rocks, and report that actually cadmium rarely becomes enriched in igneous rocks.

Zinc Zn^{2+} (0.83kx)

Zinc is concentrated in a greater proportion than cadmium in the silicate rocks formed during the main stage of differentiation. The manner of occurrence of zinc is determined by its property of diadochically replacing ferrous iron (0.83kx) and magnesium (0.78kx) in mineral structures. (Rankama and Sahama, 1941)

This similarity of size between zinc and ferrous iron causes the presence of zinc in magnetite and ilmenite. Amphiboles, pyroxenes and some plagioclases are also carriers of zinc. Rankama and Sahama (1941) state that the main carrier of zinc in normal igneous rocks is biotite.

Only traces of zinc were found in the diabases studied.

Antimony Sb^{2+}

The content of antimony in igneous rocks is generally low. Antimony was absent in a composite sample of gabbros analyzed by Preuss (1941) and in a composite analysis of granites only 0.3 ppm was found.

Silicate minerals of antimony are very rare and it is generally found in the oxides or sulfide phase. It forms antimonides with various heavy metals, preferably with copper, iron, nickel and cobalt.

The strong affinity of antimony for sulfur suggests that it is predominantly present in this phase in igneous rocks.

Platinum Pt

Platinum is generally found in nature in the native state due to

its reluctance to combine with other elements. It does, however, form such independent minerals as cooperite (PtS), Braggite (Pt, Pd, Ni S) and Sperrylite (Pt As_2).

Due to its reluctance to combine with other elements and its high melting point, platinum is preferentially enriched in the early-separated fractions during magmatic crystallization and hence is often found in considerable quantities in dunites, pyroxenites and serpentinites. In the ultrabasics, platinum may frequently be concentrated in chromite. (Rankama and Sahama, 1941)

Lithium Li^+ (0.78A)

Since the lithium ion is smaller than any of the other alkali ions (Na^+, 0.98A, K^+, 1.33A) it does not follow these elements during magmatic crystallization, but rather follows magnesium since their ionic sizes are identical. Because of its lower charge, lithium is admitted into magnesium minerals with an increasing Li/Mg ratio in later formed rocks and minerals. Lithium has been found in pyroxenes, amphiboles and particularly in the micas.

SEMI-QUANTITATIVE ANALYSIS

(Davis, Ironton, Geneva Dikes)

Sample No.	Elements																							
	Fe	Mg	Al	Mn	V	Si	K	Na	Ca	Co	Cr	Ni	Ti	Ba	Cu	Bc	Sb	Zr	Mo	Sr	Co	Sc	Pt	Li	Zn
1	7	6	10	10	7	10	9	9	10	9	9	7	10	10	10	10	6	8	8	9	10	T	9	T	8
2	10	8	9	10	10	9	10	8	8	9	9	8	10	7	9	10	5	9	9	8	9	T	8	T	8
3	4	5	6	7	1	9	6	9	9	6	6	5	8	7	9	8	T	7	6	7	9	T	9	0	7
4	7	5	6	8	8	8	7	3	8	7	4	10	8	6	10	9	10	10	10	10	9	0	10	T	9
5	5	1	8	9	1	9	7	3	9	8	6	5	9	7	10	9	T	7	6	8	9	T	7	0	7
6	10	3	9	10	10	8	10	5	8	9	10	9	10	6	9	10	9	8	9	8	10	T	9	T	7
11	7	5	8	8	8	9	7	3	7	7	6	9	8	6	8	8	8	9	6	7	9	T	9	T	8
12	5	4	9	7.5	6	9.5	7.5	10	9.5	7.5	3	9	7.5	9.5	9.5	9	1	7.5	1	9.5	6	0	6	T	6
14	5	3	7.5	9	1	9.5	7.5	10	10	7.5	3	6	7.5	9.5	10	10	1	9	1	10	8	0	9	T	6
15	10	6	7.5	9	6	9.5	9	1	4	10	7.5	9	7.5	7.5	9	10	1	7.5	1	7.5	6	0	6	T	6
16	5	4	9	6	5	10	6	10	9	7.5	5	9	6	9.5	9.5	7.5	1	7.5	1	10	6	0	6	T	6
17	7	7	9	10	10	9	9	9	9	9	9	10	10	10	9	10	9	10	10	9	10	T	9	T	10
18	6	7	10	9	9	9	8	9	9	8	9	8	10	10	8	9	8	9	9	9	10	T	9	T	9
19	6	6	7	8	10	8	7	5	8	7	6	10	8	7	7	8	10	9	9	8	9	T	9	T	9
21	8	7	10	9	10	8	9	10	10	10	10	10	9	10	9	10	9	10	10	8	10	0	9	T	9
7 G	9	7	7	7	5	8	7	3	5	5	4	8	7	4	9	7	6	8	6	9	7	0	9	0	7
13 G	9	10	10	7.5	5	9.5	7.5	1	9	7.5	10	9	7.5	7.5	10	9	T	7.5	1	9.5	6	0	9	T	6
20 G	6	7	7	7	8	8	6	6	7	5	4	9	7	6	8	7	8	10	9	8	7	T	9	0	7
8 I	8	10	9	9	10	10	8	3	5	8	6	9	9	6	8	9	8	10	8	8	9	T	8	T	8
10 I	7	7	9	9	10	9	7	9	10	7	9	9	9	10	8	9	9	8	6	9	9	T	9	T	8

INTERPRETATION OF SPECTROGRAPHIC RESULTS

DIFFERENTIATION

Before proceeding directly with the discussion of the spectrographic results attained in this study it is necessary to consider the phenomena of differentiation as connected with the rocks examined, for there is no doubt that if this factor were ignored a misrepresentation of facts pertaining to semi-quantitative measure of trace elements examined would result.

That this is the case, is due to the fact that the incorporation of various trace elements into different host minerals is a selective process which is intimately connected with the relative time of crystallization of these minerals. If differentiation had taken place in the diabase dikes studied, varying degrees of concentrations of particular minerals in traversing the dike from its base to its structural top or from the center outwards to the structural tops, and hence different levels of concentration of particular trace elements would be expected. Speculation in regard to differentiation along dip must also be included in this particular case, since many of the dikes of the Gogebic range were nearly vertical at the time of their emplacement.

An illustrative example of this is afforded by the Palisades sill of New Jersey. In this igneous body there is a layer near the base greatly enriched in olivine crystals while the rest of the mass except at the chilled contacts is free of olivine.

Since the sampling of these dikes could not be particularly selective, it would be easy to introduce an error in the interpretation of the quantitative results if differentiation, which might have taken place, were neglected in the final analysis.

Because manganese is known to concentrate in the late differentiates, it was used as an index element to determine whether or not any differentiation had taken place. If the dikes represent a case of a vertically differentiated magma, the manganese content would be expected to rise in proportion to the distance from the bottom. Relative concentrations of manganese were determined in 4 traverses of 3 samples, each along the dip of the Davis Dike. Of the twelve samples, four were taken near the original base of the dike, four near the middle, and four near the top of the dike. The results showed that the manganese content was monotonously consistent in the twelve samples studied, indicating that little if any differentiation had taken place. A slight increase in manganese concentration in going up dip appears to be related to alteration rather than differentiation.

A megascopic study of the total samples utilized in this study confirmed this idea, as no visible marked variations, other than those introduced through varying degrees of alteration and slight changes in grain size were observed to occur between specific samples.

The slight variations in grain size do not appear to be related to any particular structural phase of the dike, that is, top, bottom or middle, but are rather erratic in their manner of occurrence and are hence concluded to be the result of nature of the enclosing rock forma-

tions which probably acted as buffers in preventing rapid heat loss.

An attempt was made to correlate mineral assemblages determined from petrographic study with trace element content by establishing if possible a relationship between frequency of occurrence of particular minerals and relative concentrations of trace elements inherent to them.

Two thin sections of samples 11 and 18 were utilized for this purpose. The petrographic study of sample 11 revealed alteration in the intermediate stage with an abundance of biotite and chlorite, little or no pyroxene and quite extensive kaolinization of the feldspars. Sample 18 was relatively unaltered, displayed an abundance of pyroxene, little or no biotite and fresh appearing feldspar. The small amounts of accessory minerals, apatite, sulphides etc., appearing in these sections were neglected in this study since the method was not considered sensitive enough to pick up the variations associated with these minerals.

The results of this study failed to show any correlation between mineral and trace element content with the exception of a decrease in concentration of the alkali earth elements in the altered sample (11). This decrease was anticipated and corresponds very closely to the chemical analyses of fresh and altered dikes.

No relationship was shown to exist between the ferromagnesium minerals and the trace elements common to them although the pyroxene and mica content between the two samples varied considerably.

An interesting point brought out by this study was the sharp decrease in barium content of sample 11 relative to the decrease in potassium, its diadocic counterpart.

The results obtained from the spectrographic analyses are discussed below under the headings of the various trace elements.

Titanium

The values obtained for titanium from the traverses sampled show slight but rather definite trends with a decreasing order of concentration when proceeding down dip and along the plunge in an eastwardly direction.

The higher concentration values are found in those samples which are relatively altered, whereas those of lower values are found in the fresher portions of the dike, those enclosed by relatively impermeable beds, such as, the quartz slate, quartzite, A check on the geologic cross-section of the range discloses that in proceeding along the dip of the dike to the southeast relatively more impermeable formations are encountered and hence, ideally, the unaltered phases of the dike.

The indicated trend then, of a decreasing order of concentration of titanium along dip is warranted by these observations. In proceeding along the strike and down plunge in an easterly direction from the traverse sampled, one encounters the same general trend of titanium concentration, that is, a decrease in content.

This trend is again related to the degree of alteration of the dike which in turn appears to be controlled by environment.

It is concluded from these observations that the higher concentrations of titanium are a result of residual concentrations of ilmenite, left behind during the weathering processes and are not the result of introduction by solutions of meteoric or hydrothermal origin.

We can assume then, within reasonable limits, that the concentrations of titanium throughout any traverse should be constant in an ideal situation (unaltered dike) and any departure from this constancy is primarily the result of the geologic process of weathering.

Vanadium

It was shown that vanadium is similar to titanium in its behavior and manner of occurrence in igneous rocks and since it substitutes diadocically for titanium, it would be expected that the ratio of relative concentrations between these two elements would remain fairly constant, independent of any particular phase of the dike.

This was not the case in three traverses studied. Departure from the ideal was found in samples 3, 5, and 14 where low values for vanadium were recorded. No explanation can be given for the low values of of vanadium in samples 3 and 5 except to mention that the values of most of the elements show a proportional, though not as an extreme, drop in these samples. Sample 14 was the only dike sample taken in a completely granite environment. Since this sample was taken close to the contact between the granite and the dike, it is probable that some vanadium migrated into suitable minerals from the granite. This, however, must remain as pure speculation in view of the lack of supporting evidence.

Manganese

The manganese concentration both along dip, and across strike in an easterly direction, closely parallels that of titanium in a ratio of approximately 1:1. Deviations from this occur in samples 3, 14 and 18

where the relative ratios of manganese content to titanium content is
(.875) (1.33) (.900)
.7:.8, .9:.75, and .9:1. It has been shown that manganese tends to concentrate in the late differentiates, preferentially in the ferromagnesium minerals, with particular concentration in the pyroxenes. A comparison between samples 18 and 11, show similar manganese content, although a petrographic study of these two samples reveals that sample 18 has abundant pyroxenes and is deficient in biotite, and sample 11 is relatively abundant in biotite and deficient in pyroxene. Hence, there is no apparent correlation between particular ferromagnesium minerals and manganese content in these samples.

It seems logical to assume then, that the slight trends of manganese concentration along dip and across strike are related to the same causual factors producing variations in titanium concentration.

Nickel and Cobalt

The behavior of nickel in the traverses departs from constancy, but maintains a fairly consistent ratio between its concentration and that of magnesium.

This is understandable in terms of their same ionic radi (0.78kx) and same charge of 2^+ which enables the camouflage of nickel in early formed magnesium minerals. Significant deviations from their concentration ratio occur in samples 1 and 3. At respective distances of 50' and 60' away from these samples are two thrust faults dipping to the north and displacing the dike somewhat. Whether these faults are associated with the erratic behavior of the Ni:Mg ratio in these two samples cannot be predicted.

In general the Ni:Mg ratio shows a slight increase in going from the unaltered portions of the dikes to the altered portions. This is believed to be attributed to the removal of magnesium from these altered portions during weathering.

The values of cobalt in the traverses studied are strikingly proportional to those values of Fe, Mg and Mn. In general, they all show a slight decrease in concentration down dip and eastward along the strike. Exceptions to this are the low values given for magnesium in samples 5 and 6 which can be explained by their high degree of alteration.

The significance of this intimate relationship between Co, Fe, Mg and Mn is based on the fact that both Co and Mn are capable of substituting diadocically for Fe^{2+} and Mg^{2+} and hence their relative ratios (Co:Fe, Co:Mg, Co:Mn) should be constant throughout this particular rock series. The most consistent of these ratios is the Co:Mn followed by the Co:Fe and then the Co:Mg.

There is no apparent correlation between nickel and cobalt concentrations in these traverses. The somewhat erratic behavior of nickel might be associated with the presence of some early formed sulphide minerals, but this remains at most as pure speculation.

Chromium

The deviations of chromium values from constancy throughout the traverses is quite pronounced. Relatively high concentrations are found in samples 6, 1, 2, 17, 18 and 21. These values decrease to lows

in samples 12 and 14, as one proceeds down dip. Along the strike, the greatest difference appears in the highs at 6 and 1. Other than these two values, the concentration of Cr in the traverse made along strike remain fairly constant. In two traverses, the chromium values are somewhat proportional to those of titanium. In a third traverse the chromium to manganese ratio remains constant with the only exception being in sample 21. In general it appears that correlative values of chromium decrease with increasing alteration.

Copper

The values for copper remain quite constant throughout all traverses. The consistancy of these values of copper is probably due to its strong affinity for sulphur and hence, existence in these rocks primarily as the sulphides (chalcopyrite) and not as a replacement of sodium in the plagioclase feldspars.

Strontium and Barium

The spectral intensities produced by strontium concentrations vary in a direct proportion with those given by calcium values in the direction of dip of the dike and an almost direct proportion along the strike of the dike, the only exceptions occurring in samples 4 and 5 in which alteration has removed some calcium leaving a higher relatively strontium content. This was anticipated since strontium is admitted by calcium in the plagioclase feldspars.

Barium values are more erratic and do not follow potassium as closely as strontium follows calcium in any of the traverses. As mentioned previously, this is probably due to the presence of minor amounts of independent barium minerals. In general, the Sr:Ba ratio seems to increase with alteration of the dike, but either remains constant or decreases in the unaltered dike.

Beryllium

Beryllium intensity ratios proportional to beryllium concentration vary similarly to the silicon concentration. For the most part they remain constant along the direction of dip, but show a slight erratic decrease in an eastward traverse along the strike. In general, the Be:Si ratio appears to increase with alteration, though in some instances this situation is reversed.

Zirconium

The presence of zirconium in these samples is attributed to the formation of the mineral zircon and not the incorporation of the element into any mineral structures. Its values are somewhat erratic along the strike of the dike, but are proportional to those values of manganese in the direction of dip with an exception in sample 1 where a low value for zirconium relative to that of manganese is recorded. Both zirconium and manganese are believed to be preferentially concentrated in the latter differentiates.

Zinc and Cadmium

The zinc and cadmium concentrations represented by the intensity of their spectral lines are very slight though somewhat constant and invariant with respect to the structural trends of the dike and degree of alteration. Neither of these elements should form independent minerals in this rock type but rather occur in other mineral structures,

the zinc primarily in magnetite and ilmenite replacing ferrous iron and the cadmium in the pyroxene and mica.

The relative concentrations of these elements as recorded are not held to be completely valid due to their low spectral intensities and hence difficulty of semi-quantitative measurement. Their occurrence here is but of general interest.

Molybdenum

The values recorded for molybdenum in these traverses are low and hence, comparison between spectral intensities is difficult. No general trends in the traverses were observed. The element is probably present as its sulfide (molybdenite)

Antimony

As in the case of molydenum, the content of antimony in traverses is very low. This element is also possibly present as its sulfide (stibrite). The non-persistency of occurrence of both molybdenum and antimony in the various traverses might be associated with introduction by solutions of a hydrothermal nature.

Platinum

Platinum concentration in these traverses though low, is quite consistant with exceptions in samples 12, 15 and 16 where slightly lower than average values are recorded. The manner of occurrence of this element in this particular rock cannot be ascertained definitely, although it is suspected to be related to a sulphide phase.

Lithium

Only traces of this element were determined in various traverses,

and hence no trends were observed. The low content of lithium might be attributed to the fact that the spectral range used in this study did not cover the most persistent lines of lithium.

Scandium

Only traces of scandium were determined in the dikes studied, though its occurrence in these rock types is not unusual. It should be present in the pyroxenes, probably only in minor amounts because of the difficulty in balancing the excess positive charge thus introduced by other suitable replacements. Hence, little importance can be placed on its occurrence here as a means of dike identification and correlation.

SUMMARY

It appears, then, that the Davis dike is essentially homogeneous in regard to trace element content from a qualitative viewpoint. It departs from homogeneity in respect to quantitative measurements of these trace elements. This departure from the ideal appears to be related to a number of variables operating either singularly or in combination with each other and are listed here in what appears to be their decreasing order of importance in quantitative control: degree of alteration, environmental control (country rock intruded), structural trends (strike and dip, pitch and plunge), relative thicknesses, and faulting and possibly hydrothermal activity.

The degree of alteration of the dike is closely related to its environment. In the cases where it intrudes more impermeable formations, such as, the quartz slates, quartzites, some members of the iron formation and granite, it is relatively unaltered. This situation is modified by faulting and fracturing which provides channelways for altering solutions. In localities of ore development, by leaching solutions, the dike is subsequently altered.

The elements most susceptible to the leaching action of these solutions are K^{+}, Na^{+}, Li^{+}, Ba^{2+}, Sr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Mg^{2+} and hence their partial removal during this process of weathering. All of these elements are present in the mineralogical makeup of this dike, and in general, their decrease in concentration in the more altered portions is well indicated by the spectrochemical analyses. Exceptions to this

are Mn^{2+} and Sr^{2+}. Manganese shows only a slight decrease in concentration though the Mn/Mg ratio rises at a much faster rate due to the rapid removal of Mg. Some divalent manganese, released from ferromagnesium minerals may remain as MnCO and any Mn^{4+} associated with the oxides (ilmenite) will remain intact during alteration processes. Strontium also, shows only a slight change in concentration with alteration, although the Sr/Ca ratio remains fairly constant. The Sr/K ratio generally increases in going from the altered to unaltered portions of the dike, indicating that most of the strontium occurs as a replacement of calcium in the plagioclase feldspars.

The sharp decrease in Ca^{2+} and Na^{+} in the altered portions of the dike, suggests the altering solutions were slightly acidic. This is also supported by the presence of kaolinite in these altered portions which is favored by an acid environment. Ferromagnesium minerals and calcic feldspars commonly alter to minerals of the montmorillonite group, whose structures are capable of considerable atomic substitution.

According to Mason (1952), the following substitutions are possible in the montmorillonite structure; the aluminum can be partly or wholly replaced by ferric iron, by magnesium, by zinc and by smaller amounts of lithium, trivalent, chromium, manganese and nickel; and the silicon can be partly replaced by aluminum.

This suggests that the behavior of the elements as related above is controlled to a somewhat lesser degree by the mineralogic makeup of the products of alteration in these dikes. Thus, the removal of such elements as Ni^{2+}, Li^{+}, etc: during alteration, as suggested earlier, may not be as effective as would be the case under ideal conditions.

Elements which tend to be more stable under weathering conditions are Zr^{4+}, Al^{3+}, Sc^{3+}, Cr^{3+}, Be^{2+}, V^{3+}, Ti^{4+}, Mo^{6+}, Si^{4+}. Their stability is based on their relatively high ionic potential. Of these elements of hydrolyzates, chromium may also convert to a soluble complex anion and hence be removed in this manner. Its low values in some of the altered portions of the dike may be attributed to this cause. Beryllium concentration remains fairly constant throughout the dike, with a slightly higher Be/Si ratio being observed in the altered portions. This may be due to the removal of some silicon as a colloid during alteration. The concentration of silicon in general, however, remains quite constant throughout the dike. Zirconium, which is present as zircon is quite resistent to alteration and hence its concentration throughout the dike should remain fairly constant, if dependent on this variable alone. In general, this was found to be the case in the samples studied, although some erratic values occur in proceeding along the strike. Higher values of vanadium and titanium appear to be related to residual concentrations of the minerals containing these elements. Only traces of scandium were observed in the dikes and hence its presence in these rocks is relatively unimportant. Again the occurrence of platinum, cadmium, zinc and molybdenum in these rocks remains at best, as a chemical curiosity.

The environmental influence on trace element concentration in these dikes appears to be one of considerable importance. The four major rock types intruded by the dikes are the granite, quartz slate, quartzite, and iron formation. Each of these rock types contain various trace elements in concentrations peculiar to their respective mineral assemblages and hence mutual migration or absorption of these trace elements between these rock types and the dikes at the time of their intrusion is possible. Though migration even in the ideal case would be through relatively short distances and thus confined to the interfaces of these rock types and the dikes, the combined influence of alteration could result in a much deeper penetration of various ions. The most obvious example of this is the high concentration of the Fe^{3+} ion in the altered dike whose immediate environment is that of the iron formation or ore where more complete alteration has taken place.

The specific effects of each of these environments on trace element concentration in the dikes cannot be predicted without further spectrographic analyses on each of these rock types themselves. The high values of Ca^{2+}, Na^{+} and Ba^{2+} in the dike samples associated with the granite environment may suggest the immobility of these and other ions in this type of environment and hence an original trace element concentration in these portions of the dike.

Little can be said about the quartz slate or quartzite environment except that the quartz slate is probably more influential in trace element migration.

The iron formation plays a well marked role in various trace element concentrations as indicated previously. Elements that may be directly affected by this environment are Co^{2+} which can replace Fe^{2+} and Cr^{3+} and V^{3+} which replace Fe^{3+}.

The importance placed on the structural trends of the dike in controlling trace element concentration is primarily that of acting as a circulatory control for the altering solutions. Variations in trace element content across strike and along dip are essentially related to the degree of alteration and environmental influence.

It is possible that the variance in thickness of the dike may have exerted some influence on the concentration of various elements during the earlier stages of solidification. An isopach map of the section of the Davis Dike utilized in this study reveals two linear pinch-out areas running approximately N - S. Whether these areas played any part in restricting uniform trace-element dispersion or not, cannot be predicted until a more thorough sampling of these areas can be made.

In regard to faulting and hydrothermal activity, neither of these appears to have any important bearing on trace element concentration in the dikes. The role of faulting is confined to that of providing channelways for altering solutions and is secondary in importance in this respect. Hydrothermal activity though seemingly lacking in the portions of the dike studied may reveal itself in other areas of this rock with the possible introduction of new elements or increased concentration of those already present.

In regard to correlation of the Davis, Geneva and Ironton Dikes, all three of these rocks have similar trace element assemblages, and in this respect are identical. It has already been shown that a single dike (Davis) varies from homogenenity with respect to particular trace element concentrations and hence differentiation between the Davis, Geneva and Ironton Dikes on these grounds is difficult if not impossible. It appears that the Davis Dike may have a higher Be content than the Ironton Dike and the Ironton a higher Be and Cr content than the Geneva Dike, though this is inconclusive in view of the few samples taken on either the Ironton or Geneva Dikes.

It appears then, that any identification of these dikes, would have to be based on a spectrographic analysis of each in an unique environment (granite, quartz slates or quartzite) common to all of them with further spectrographic analysis of the particular environment selected to determine the effects of migration and absorption of ions on trace element concentrations in any particular dike.

RECOMMENDATIONS

It is recommended that as a supplement to this work and as an aid in dike identification and correlation, further study be pursued along the following lines:

1. Selected sampling of a number of dikes in each of a number of environments common to all of them, along with a close order sampling from their boundaries into the immediate country rocks which they intrude.
2. Spectrochemical analysis of these samples with particular emphasis on those from the country rock in an effort to determine the role played by migration and absorption in the present trace element makeup of the dike.
3. A study of the alteration effects of slightly acidic solutions (generally accepted as nature of leaching solutions) on the mineral assemblages of both the dikes and the intruded country rocks in an effort to predict introduction or removal of trace elements in this manner. In conjunction with this, particular emphasis should be placed on the capacities of alteration products (e.g. kaolin) for admission, capture, or camouflage of individual trace elements.
4. An evaluation of the influence of each of these factors upon trace element content of a single dike.
5. Final dike identification and correlation based on samples selected so as to be least influenced by these factors.

In regard to age differentiation of these intrusives, it is recommended that:

1. A petrographic and spectrographic analysis be made on the Keweenawan extrusives in an effort to delineate any similarities either in mineral assemblages or trace element content which might be inherent to both rock types.
2. A petrographic and spectrographic analysis of a dike known to intrude the Keweenawan sediments, if such a dike is accessible.
3. A petrographic and spectrographic analysis of the great sill which was intruded along the Yale slate member of the Ironwood formation to determine its mineralogic and trace element relationship to the dikes on the range.
4. Further mining development and geologic exploration should allow a more complete investigation of the age relationships between such structural events as folding, faulting, and intrusive activity and hence permit a more accurate reconstruction of the geologic history of the area.

* * * *

APPENDIX

The graphs which follow represent the relative concentrations of the various trace elements in samples along two main traverses of the Davis dike, one along the strike and one parallel to the direction of dip.

In these graphs, the ordinates are represented by an intensity scale from 1 - 10 (described earlier in manuscript on page 44), whereas the absissas are represented by map coordinates in hundreds of feet with indicated sample locations.

In plate 1, (lower half of page) the plunge of the dike at the various sample locations in the traverse along strike is represented graphically, with elevations being given in hundreds of feet. The dip of the dike at these locations is indicated.

In plate 4, (lower half of page) is a graphical representation of the dip of the dike at the sample locations in the traverse parallel to the direction of dip.

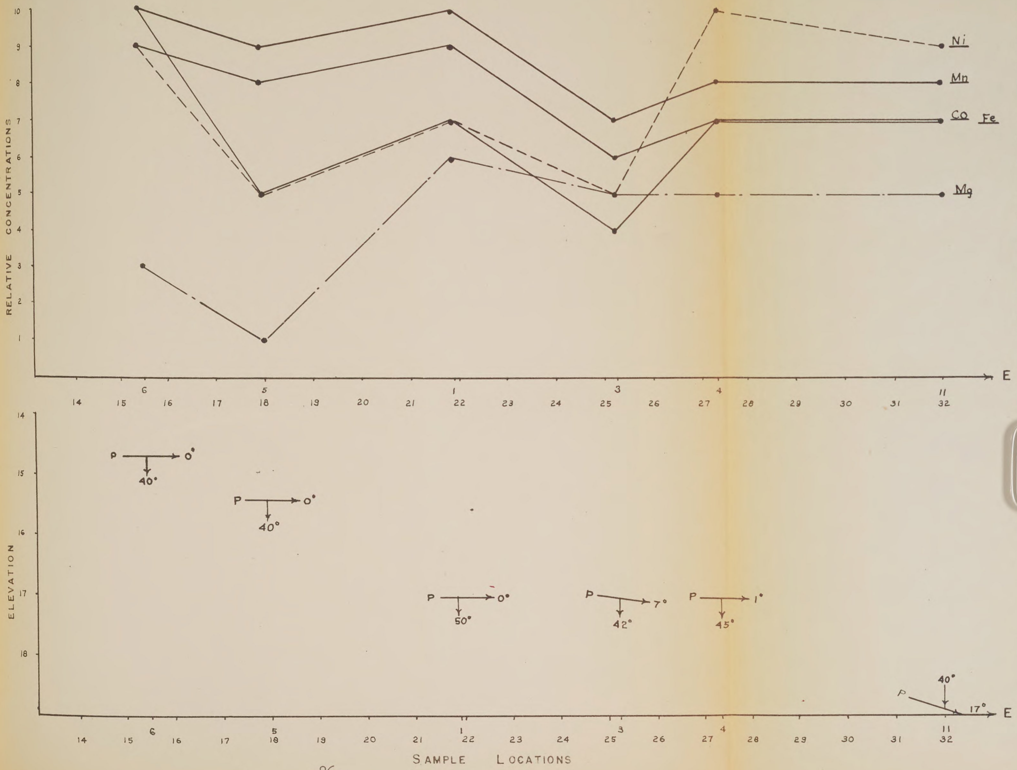
RELATIVE CONCENTRATIONS
10
9
8
7
6
5
4
3
2
1
Ni
Mn
Co
Fe
Mg
E
6
5
1
3
4
11
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
ELEVATION
14
15
16
17
18
P
0°
40°
P
0°
40°
P
0°
50°
P
7°
42°
P
1°
45°
P
40°
17°
E
SAMPLE LOCATIONS

Plate 1

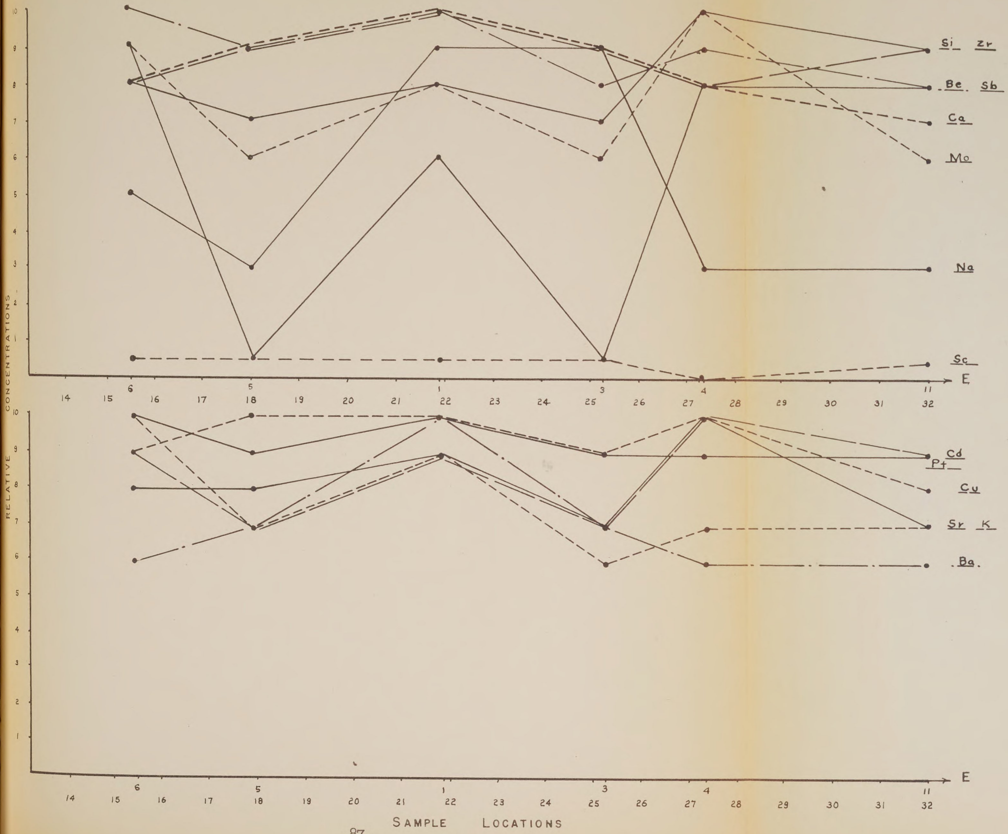
RELATIVE CONCENTRATIONS
10
9
8
7
6
5
4
3
2
1
Si Zr
Be Sb
Ca
Mo
Na
Sc
E
6
5
1
3
4
11
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
10
9
8
7
6
5
4
3
2
1
Cd
Pt
Cu
Sr K
Ba
E
6
5
1
3
4
11
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
SAMPLE LOCATIONS

Plate 2

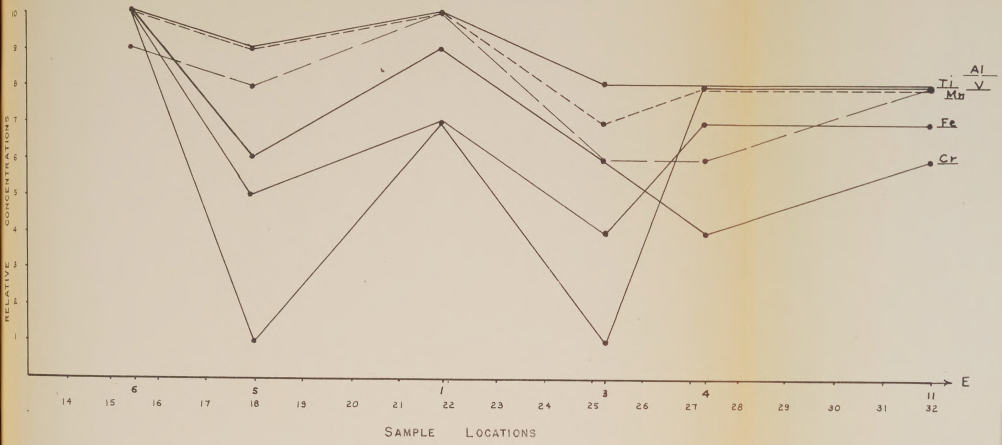
RELATIVE CONCENTRATIONS
10
9
8
7
6
5
4
3
2
1
6
5
1
3
4
11
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
E
SAMPLE LOCATIONS
Al
Ti
V
Mn
Fe
Cr

Plate 3

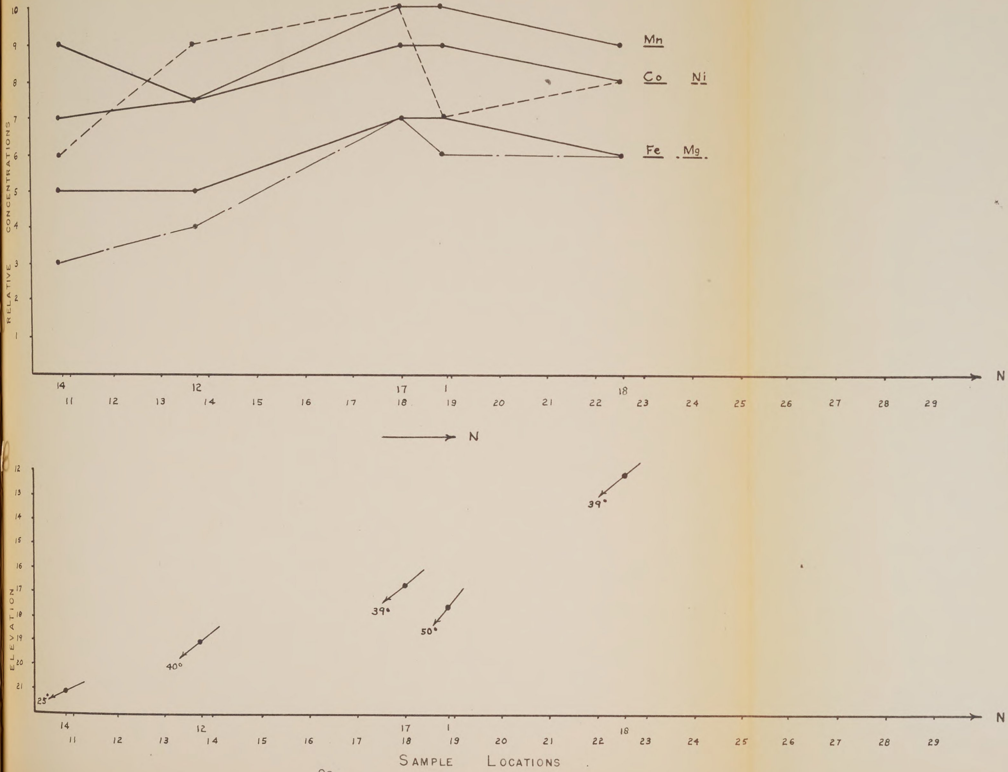
RELATIVE CONCENTRATIONS
1 2 3 4 5 6 7 8 9 10
Mn
Co
Ni
Fe
Mg
N
14 12 17 1 18
11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29
N
ELEVATION
12 13 14 15 16 17 18 19 20 21
39°
39°
50°
40°
25°
N
14 12 17 1 18
11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29
SAMPLE LOCATIONS

Plate 4

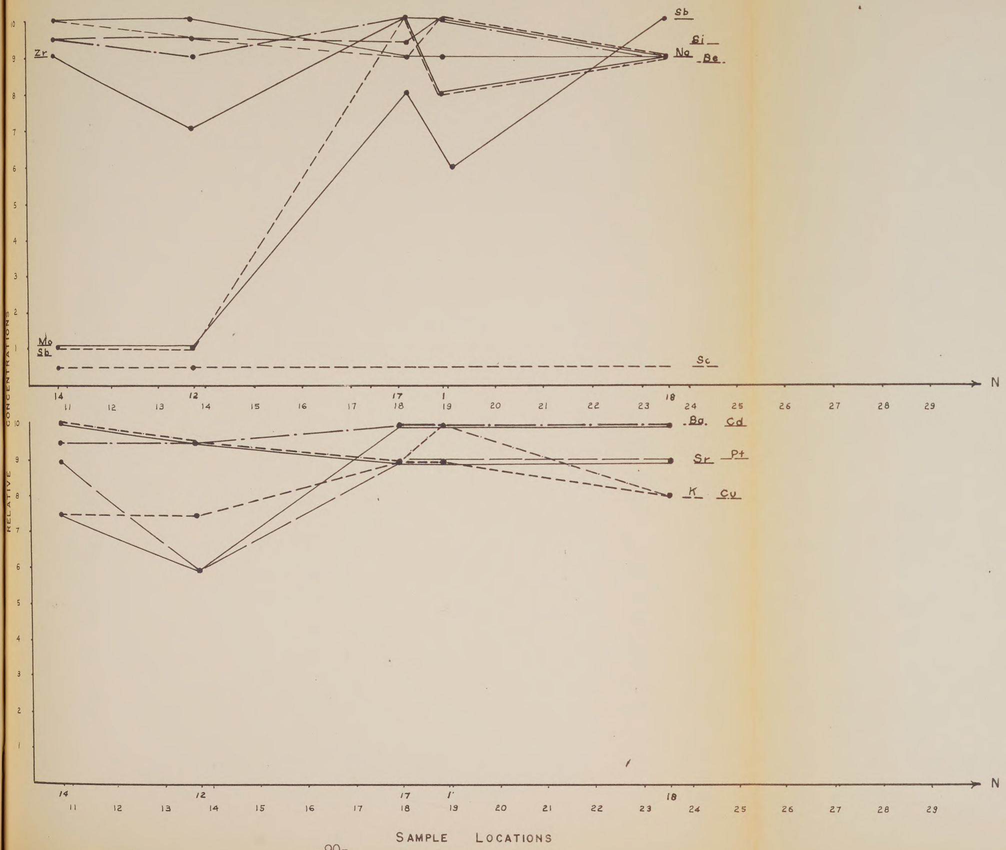
RELATIVE CONCENTRATIONS
Sb
Si
Na
Be
Zr
Mo
Sb
Sc
N
14
12
17
1
18
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
Ba
Cd
Sr
Pt
K
Cu
N
1
2
3
4
5
6
7
8
9
10
SAMPLE LOCATIONS

Plate 5

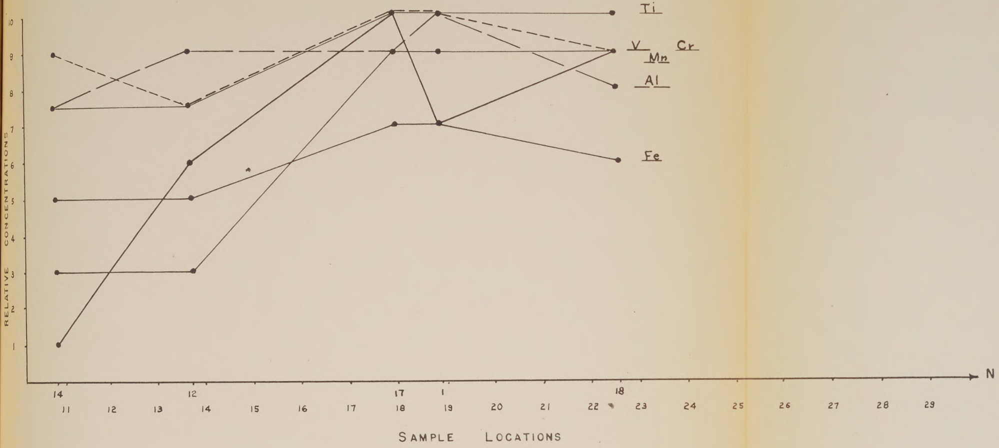
Ti
V
Mn
Cr
Al
Fe
RELATIVE CONCENTRATIONS
1
2
3
4
5
6
7
8
9
10
14
12
17
1
18
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
N
SAMPLE LOCATIONS

Plate 6

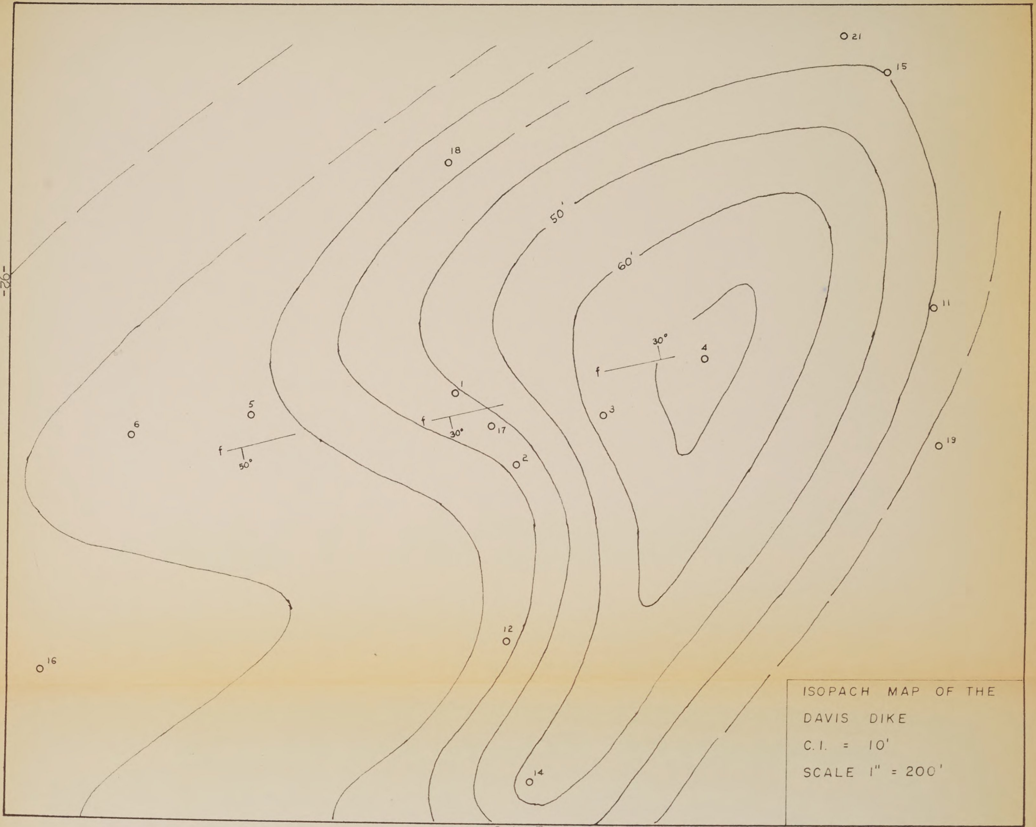
21
15
18
50'
60'
11
30°
4
f
1
3
5
6
f
30°
17
f
50°
2
19
12
16
14
ISOPACH MAP OF THE
DAVIS DIKE
C.I. = 10'
SCALE 1" = 200'

Plate 7

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