

COPPER IN THE NORTH MOUNTAIN BASALTS,
NOVA SCOTIA

by

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ABSTRACT

The North Mountain basalts are quartz-normative tholeiites stretching from Cape Split to Whipple, Nova Scotia. The lavas have been subjected to zeolite facies metamorphism. Native copper occurs in trace quantities associated with zeolites and in some fault zones such as the ones at Cap d'Or from which copper was mined between 1900 and 1907.

A total of 56 rocks were analysed for Cu, Zn, Mn, Co, Ti, Cr and Ni, using atomic absorption spectroscopy. Variation diagrams of Ti, Cr and Ni show a rather well-defined differentiation trend indicating that these metals probably remained relatively immobile during burial metamorphism. The Cu does not correlate with Zn, while poor co-variances exist between Zn and Mn, and Cu and Mn. On a Cu - Zn - Mn diagram, zinc enrichment occurs only at Ross Creek and in a fault zone at Cape Split.

When Cu, Zn, and Mn were plotted against the differentiation index, $\frac{\text{Ti}}{\text{Cr} + \text{Ti}}$, generally poor correlations were obtained, showing that the distribution of Cu, Zn and Mn was controlled by different processes from those affecting Ti and Cr. Prior to alteration, Cu, Zn and Mn are found in interstitial glass or replace Fe^{2+} in magnetite and pyroxene. During alteration by hydrothermal brines Cu, Zn and Mn were liberated, first from the glass and then from pyroxene and magnetite. Copper was precipitated by reduction

to Cu^0 indicating a low f_{S_2} . Oxidation of magnetite to hematite supplied electrons for copper reduction. Precipitation of Zn is made difficult by the lack of sulphide. Some Zn, Mn and Cu may be adsorbed by clays, chlorite or zeolite.

The North Mountain basalts have not been metamorphosed to the same degree as the Keweenaw lavas (prehnite-pumpellyite facies). The behavior of Cu, Zn and Ni in the North Mountain basalts is similar to the Keweenaw lavas, where Cu^0 is deposited, Zn is leached away and Ni remains unchanged except for zeolite dilution. However, at North Mountain, copper concentration does not reach economic levels as in the Keweenaw Peninsula.

I. GENERAL INTRODUCTION

A. Introduction

The North Mountain Basalts of Nova Scotia are Triassic extrusives on the south shore of the Bay of Fundy. They, along with associated Triassic sediments, were first referred to as the North Mountain by Powers (1916). The lithology of the basalts has been described by Crosby (1962), Klein (1962), Sinha (1970), Burton (1972), Smitheringale (1973), and Stevens (1975). The Zeolites have been described by Aumento (1966). The Titano-magnetites have been described by Carmichael and Palmer (1968). Radiometric ages have been given by Carmichael and Palmer (1968) and Poole (1968). The occurrence of native copper at Cap d'Or was described by Douglas (1942).

The object of this thesis is to investigate the primary and secondary distribution of copper. Other analysed elements include Zn, Mn, Co, Ti, Cr and Ni. An attempt is made to relate the occurrence of native copper in the North Mountain Basalts to the copper deposits of the Keweenaw Peninsula, Michigan.

B. Native Copper In Basalts

Cornwall (1956) lists more than 30 occurrences of basalts with native copper. Prominent examples include Lake Superior district, U.S.A.; Southeastern U.S.A.;

Connecticut; Copper and White Rivers, Alaska; Coppermine River, Northwest Territories; and Novoya Zemlya, U.S.S.R. Copper concentrations are highest in the pegmatitic and vesicular parts of flows (Cornwall, 1956). Some of the secondary minerals associated with native copper include calcite, quartz, epidote, chlorite, prehnite, chalcedony, zeolites, and dotalite.

Native copper has been reported in spilitic, amygdaloidal pillow basalts from La Désirade, Lesser Antilles Island Arc (Nagle, et. al., 1973). Copper-bearing lavas (0.5 - 1.5% Cu) are restricted to hematite-rich flows, although not all hematite-rich flows are copper-bearing. Sulphides are totally lacking in these basalts and in any other rocks on La Désirade. The authors suggest that the occurrence of native copper with hematite and secondary calcite indicates that copper was precipitated in the presence of strongly oxidizing, Fe-rich solutions.

Andrews (1977) reports the occurrence of native copper in oceanic layer 2 basalts from DSDP Leg 37. Native copper was found in a vein and in the adjacent oxidation zone. The altered wall rock contained remnant silicate cores, hematite, Fe-Mn hydroxides, and small quantities of secondary magnetite. Andrews (1977) suggests that copper may have been removed from seawater by Fe-Mn hydroxides.

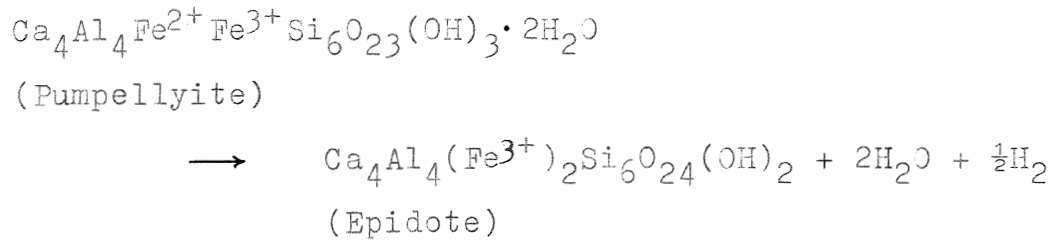
The native copper deposits of the Keweenawan lavas in Michigan have been described by Broderick (1929), Cornwall

and Rose (1957), Jolly (1974), and others. In the 100 years before 1956 a total of 5 billion pounds of copper was mined from six deposits on the Keweenaw Peninsula. (Cornwall, 1956).

Primary copper may occur as disseminations in the native state, and may be found in massive basalt or pegmatitic segregations (Cornwall, 1956). Copper concentration in massive basalt varies from 10 to over 400 ppm. A third or more of the copper is found in rock-forming minerals such as magnetite (200 - 880 ppm), ilmenite (90 - 300 ppm), augite (51 - 320 ppm) and chlorite (50 - 280 ppm) (Cornwall, 1956). The Cu^{2+} is believed to replace Fe^{2+} because of its similar atomic radius (Cornwall, 1957).

Secondary copper occurs in the native form particularly in amygdular zones, breccias, conglomerate units, and along joints and faults. Jolly (1974) has related the behavior of Cu, Zn, and Ni to prehnite-pumpellyite rank metamorphism. Copper is leached from a deeper zone of dehydration. Greatest dehydration occurs in permeable areas where epidote has formed. Above this zone of dehydration occurs a zone of hydration belonging to the prehnite-pumpellyite facies. The permeable zones are the most hydrated and contain pumpellyite. Native copper is concentrated in the lower part of the zone of hydration, usually corresponding to the first appearance of epidote. Copper was transported by chlorine complexes as Cu^+ . The Cu^+ was reduced to Cu^0

when magnetite oxidized to hematite, and pumpellyite oxidized to epidote. The latter reaction was given by (Jolly, 1974).



Zinc is leached from the basalts and is not able to precipitate because there is no sulphide present, and it is not able to reduce to the native state. Nickel is concentrated mostly in olivine, with lesser amounts in ilmenite, magnetite, augite and chlorite (Cornwall, 1957). It has remained immobile during the period of metamorphism (Jolly, 1974).

Other mechanisms for the formation of native copper have been proposed. Primary copper could have occurred as sulphides. The action of steam at 300°C could reduce the copper in sulphides, and oxidize the sulphides to sulphates (Park, 1931). Hematite would be produced from iron sulphides. One possibility proposed for La Désirade is that copper sulphides settled on top of, or crystallized with the lavas, producing native copper and hematite at the same time (Nagle et. al., 1973).

C. General Geology

The North Mountain basalts make up a prominent ridge

stretching from Cape Split to Whipple on the southwestern tip of Digby Neck, a distance of 200 km, and with widths of 3 to 6 km. The North Mountain is a cuesta capped by resistant basalt. A steep escarpment slope occurs on the southern flank, while the gently dipping northern side is a dip slope. At one time the North Mountain was part of the Atlantic Upland which was a continuous, level surface rising northwesterly from southern Nova Scotia to the level of the south highlands near Wolfville. Where the Atlantic Upland was not capped by basalt, extensive erosion took place producing the Annapolis - Cornwallis Valley (Crosby, 1962).

The basalts conformably overlie Triassic sediments consisting of the Wolfville Formation overlain by the Blomidon Formation. The Wolfville Formation is composed of red conglomerate and sandstone with minor red shale. The Blomidon rocks consist of red shale and argillaceous sandstone. The basalts are disconformably overlain by small pockets of the Scots Bay Formation in the Wolfville area. The rocks contain arenaceous limestone and calcareous sandstone with occasional jasper concretions. Erosion of the Scots Bay Formation and much of the basalt has produced an unconformity extending to the Pleistocene. The amount of sediment and basalt which has been removed from above the present land surface is not known.

The thickness of the lava pile varies from 175 metres at Bridgetown to about 427 metres at Petite Passage at Digby Neck (Smitheringale, 1973). There is a general thickening southwestward towards Digby.

The total number of flows in the North Mountain is not clear. In the Bridgetown map area at least 6 flows are present, while more than 17 are exposed northeast of Digby Gut. Many flows pinch out locally. Others have imbricating tongues which protrude from a parent flow and may be later overrun by the same flow. This presents a problem of establishing criteria which define a flow or the products of a single eruption. Some authors would prefer to distinguish each flow unit no matter how closely it is associated with its neighbor, while others such as Sinha (1970) prefer to lump together flow units believed related to the same extrusion. Sinha (1970) has attempted to categorize the North Mountain into four major flows on the basis of lithology. The lower Blomidon flow is massive, dark grey to greenish black, and with virtually no zeolites. Columnar jointing is common. Above this occur the Cape Split flows which are amygdaloidal. The older Cape Split flow is dark green while the younger is colored brown by iron oxides. The youngest flow is the Scots Bay flow which is massive, dark grey, and locally has a vesicular top. The local nature of the vesicular top is due to various degrees of erosion.

Although Sinha claims to have traced these flows the full length of the North Mountain, a continuous profile is not given as evidence. No attempt at chemical correlation has been made. Smitheringale (1973) suggests that a massive basal flow can be traced along the length of the North Mountain. However, as flow contacts are sometimes difficult to trace over distance, and since a detailed profile of the entire North Mountain does not exist, the division of the basalts into four flows is an over simplification, if not mere speculation. However, Sinha's 4 flows do illustrate the type of lithology found in the basalts.

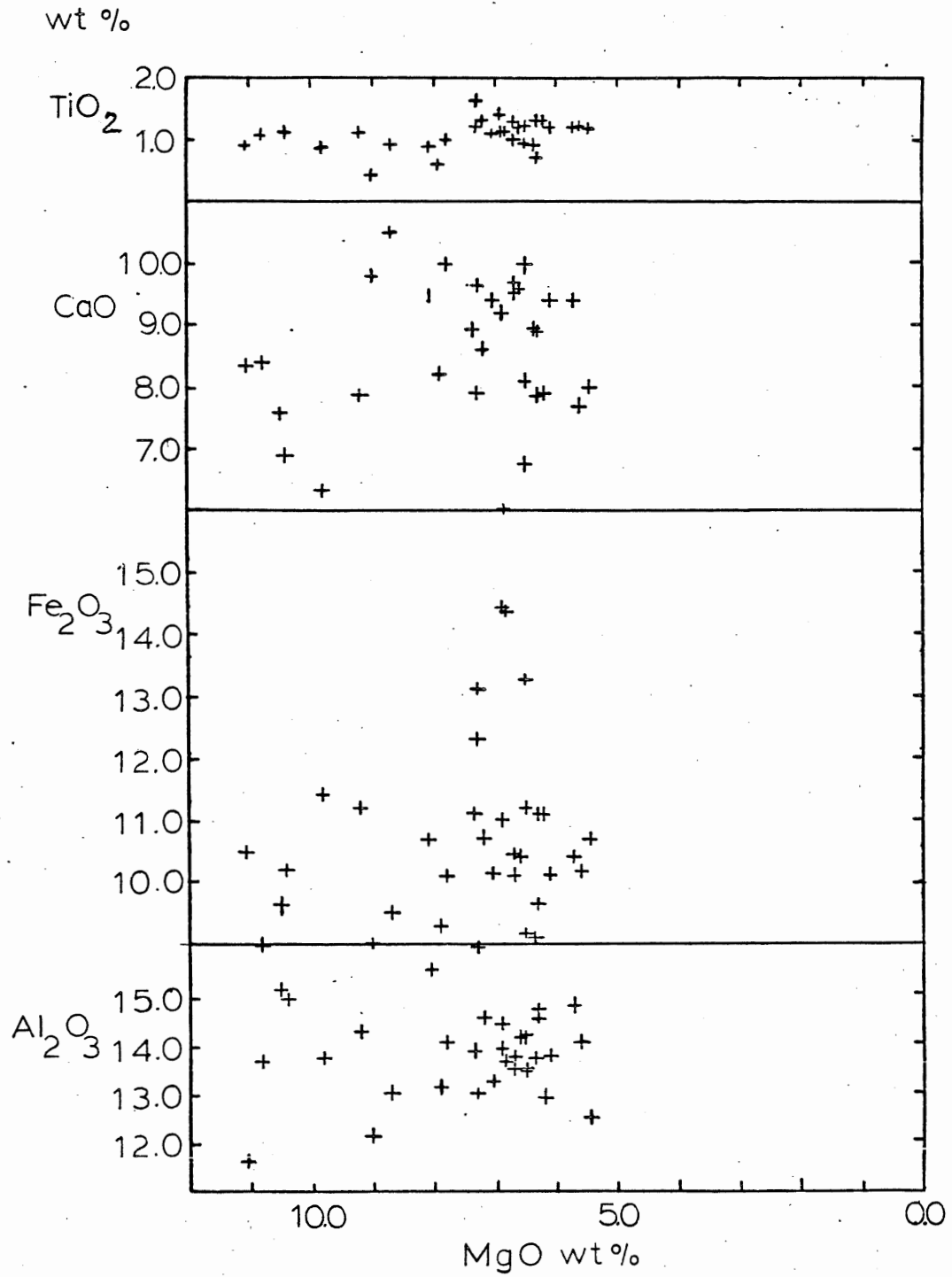
The lavas dip from 3° to 10° northwest into the Bay of Fundy. The existence of Scots Bay can be explained by a generalized cross-section sketch from Stevens (1975). Scots Bay occupied a syncline, with flows at Cape Split forming the northwestern limb. The main part of the North Mountain forms the southeastern limb. This syncline is termed the Minas Syncline and gently plunges to the west. According to the cross-section the basalts at Cape d'Or and Ile Haute are a down faulted extension of Cape Split. At several localities open folds are found with axes plunging several degrees to the northwest.

Major elements and phases: The major-element analyses of Sinha (1970) show the North Mountain basalts to be quartz-normative tholeiites. When the molar proportions of MgO, CaO, Al₂O₃, FeO, Fe₂O₃, K₂O, Na₂O and TiO₂ are plotted against SiO₂ no obvious differentiation trends were noted (Sinha, 1970). A plot of oxides versus MgO wt% was made from Sinha's data, and confirmed the absence of a regular variation (Fig. 1).

The major phases found in the basalt are plagioclase and pyroxene with minor iron-titanium oxides. The plagioclase crystals are often zoned with cores varying from An₄₁ to An₇₈ and rims from An₃₁ to An₇₁ (Sinha, 1970). A slight decrease in An from the Blomidon flow (An₆₆) to the upper Scots Bay flow (An₅₈) is also reported by Sinha. The pyroxenes have been identified by optical methods to be augite, subcalcic augite, pigeonite, and rarely orthopyroxene. The existence of pigeonite and orthopyroxene has not been confirmed with the electron microprobe (Clarke, personal communication). Apatite occurs as an accessory mineral.

Four types of iron-titanium oxides have been identified in the North Mountain (Carmichael and Palmer, 1968).

(1) Low oxidation state magnetites which appear as maltese crosses were found to contain 34% ulvospinel. (2) Titanium-bearing magnetites of intermediate oxidation state were



(Fig1) Oxide - MgO Variation. Data from Sihna (1970)

17% ulvospinel. They showed exsolution lamella of ilmenite.

(3) A titanium-bearing hematite has formed by oxidation of magnetite. An amorphous hematite occurs in fissures.

(4) Large primary magnetite grains occur which have networks of cracks filled with silicate. No exsolution is shown.

Other secondary minerals include zeolites, quartz, amethyst, agate, chalcedony, calcite, and mineraloids such as chlorophaeite.

Age and origin: The age of the North Mountain is Triassic since it is bracketed by the Triassic Blomidon and Scots Bay Formations. The age of the Blomidon Formation is given by the presence of Isoura ovata (Klein, 1962). The latter, along with fish remains pinpoint a Triassic age to the Scots Bay Formation. Carmichael and Palmer (1968) give a K-Ar age of 200 ± 10 M.Y. An average K-Ar age of 198 M.Y. is given by Poole et. al. (1968).

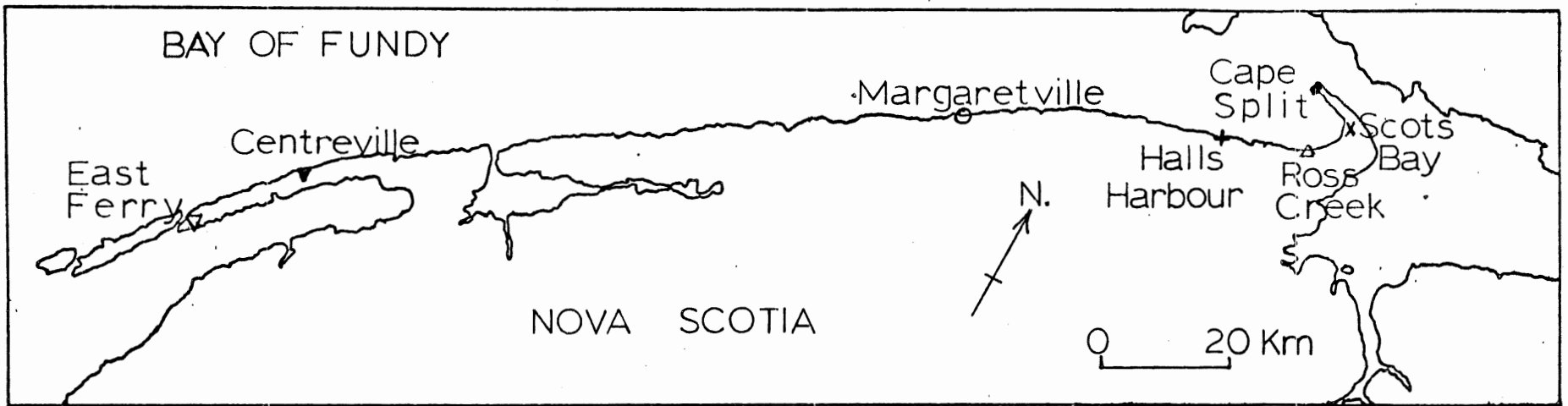
The basalts constitute a subaerial eruptive sequence. Evidence for a subaerial eruption is given by the absence of pillow lavas and the presence of reddened flow tops and soil horizons. The pillow lavas reported by Sinha (1970) represent various stages of spheroidal weathering in which the columnar joints have been altered or filled with chert. A glassy crust found at Scots Bay represents the chilled crust of a subaerial flow.

The source of the basalt eruption was to the northwest

(Smitheringale, 1973) and possibly from the Five Islands region. Burton (1972) suggests that intrusives near Goshen, Guysborough County might have been the basalt source which has since been offset by a major dextral fault. Evidence given includes (1) a similar major element chemistry as well as (2) a large contact aureole around the Goshen plugs suggesting the passage of a large volume of magma. However, more conclusive evidence would have to include a comparative isotope, trace-element and rare-earth element study.

In the initial stages of the opening of the North Atlantic Ocean, extensive block faulting occurred on both sides of the present ocean. Clastics and basalt lavas were deposited in the grabens. Burton (1972) has made an attempt to correlate the Triassic basalts of Nova Scotia with extrusives along the eastern seaboard of the United States. Evidence cited includes (1) a close age relationship, (2) a similar sequence consisting of sandstone overlain by shales, overlain by basalt, and (3) a close similarity in the mineralogy and major element chemistry.

Bertrand and Coffront (1977) have noted that, along both sides of the Atlantic, there is a northward increase in the silica content of the Triassic lavas. The authors used chemical data from the literature and multivariant statistical methods to correlate Triassic lavas across the



(Fig. 2) Sample Locations

Atlantic to their predrift positions. Their work places Nova Scotia with Morocco in predrift times as previously suggested by Schenk (1971).

The most notable occurrence of native copper is at Cap d'Or (Douglas 1942). From 1900 to 1907 the Colonial Copper Company had made an attempt to mine the copper at Cap d'Or. The native copper is found in fault zones which are one to nine metres wide. Highest copper values appear where the copper-bearing fault zones cut red, loosely compacted lava. Douglas doubted that the copper grade exceeds one percent. The volume of copper is not great enough to be of economic value.

D. Sampling

The collection of samples was carried out in the summer and autumn of 1977. The sample locations include Cape Split, Scots Bay, Ross Creek, Halls Harbour, Margaretville, Centreville, and East Ferry (Fig. 2). Vertical sections of a flow were sampled at Margaretville, Halls Harbour, and Ross Creek. Partial vertical sections were obtained from East Ferry and Centreville. Sampling was carried out along a native copper-bearing fault zone at the tip of Cape Split. Some lateral sampling of a massive flow, with altered jointing was done at Scots Bay. Along with the vertical profile, sampling was done along a coastal section northeast of the wharf at Margaretville (Fig. 18).

II. PETROGRAPHY

The fault zone at Cape Split occurs in a dark green massive basalt. The plagioclase and pyroxene are moderately altered, and about 5 percent magnetite occurs as primary grains. The fault zone contains brecciated, dark green basalt with local concentrations of native copper along fractures. Most plagioclase crystals appear strongly sericitized and the pyroxenes are strongly altered to the brown oxide which also partially replaces interstitial glass. Magnetite occurs as primary grains in the brown oxide and as secondary coatings on some pyroxenes. In the centre of the fault there is a purple quartz vein with native copper and a green copper oxide (Appendix B).

The flow at Scots Bay is dark grey and massive. The rock has been altered along joints which are often filled with jasper. Due to spheroidal weathering the outcrop resembles pillow lavas. Small patches of a glassy crust may be found at Scots Bay. This crust consists of grains of fresh plagioclase (An_{54}) and pyroxene sitting in a brown glass with variolitic texture. Some primary magnetite grains are also present.

The sampled section at Ross Creek is found in the first cove northeast of the fisherman's wharf. The basalt is unconformably overlain by a small pocket of chert, siltstone and sandstones, probably of the Scots Bay Formation. The

basalt is dark green with increasing amygdales toward the contact. Near the unconformity the basalt becomes increasingly brecciated because of Triassic erosion (Appendix B).

The sampled section at Halls Harbour is located 100 metres southwest along the shore from the wharf. The vertical profile covers most of one flow as well as another part of the same flow which has folded back on itself during extrusion. A massive flow overlies the folded part in the sample area. The basalt is green with increasing amygdales toward the flow top. Amygdales are 2 - 10 mm wide and are rather round spheroids. Most of the plagioclase is sericitized and the pyroxene is fragmented and very altered. Magnetite grains are found in brown oxide which partly replaces glass (Appendix B).

The vertically sampled flow at Margaretville grades upwards from massive green basalt to amygdaloidal brown basalt. In this flow plagioclase appears sericitized, with increasing alteration towards the flow top. The corroded pyroxenes show reaction rims and are often coated with black oxide. Magnetite is also found as primary grains in the brown oxide which partly replaces glass. The sampled flows include massive green-grey basalt, and green amygdaloidal basalt (Fig. 18, Appendix B).

The sampled flow at Centreville is located northeast of the main wharf. It consists of a sea cliff directly

below a small quarry. The rock is a massive green-grey, coarse grained, columnar basalt. Thin cherty veins are noted in fractures. The plagioclase appears relatively fresh. A relatively fresh pyroxene is present as well as an augite which has been altered to amphibole. Some of the phenocrysts are several millimetres long. A black oxide is found closely associated with pyroxene.

At East Ferry samples were collected about 200 metres north of the ferry wharf. The basalts are massive, green-grey with columnar jointing. The petrography appears to be very similar to Centreville samples (Appendix B).

III. TRACE ELEMENT GEOCHEMISTRY

A. Comparison Of Average Concentration

The vertical sections of zeolite-rich basalts of Margaretville and Halls Harbour were compared. Massive rocks from Scots Bay, Margaretville and East Ferry plus Centreville were contrasted. Finally an attempt was made to determine differences between zeolite-bearing and massive basalt at Margaretville and in the total sample population (Table 1).

Sample averages were compared with the T' statistic (Walpole and Myers, 1968) which assumes unknown and unequal population variances. Sample averages were considered unequal if T' exceeded the critical T statistic at the 95% confidence interval (one Tailed test).

Halls Harbour has higher Cu and Zn, but lower Mn than Margaretville. No significant difference was found in Ni, Cr, and Ti.

In the massive samples, Centreville plus East Ferry show higher Ni and Cr and lower Ti and Cu than rocks from Scots Bay and Margaretville. No significant differences are found in Zn and Mn. The averages from Scots Bay and Margaretville could not be statistically separated.

When zeolite-bearing rocks were compared with massive rocks it was found that Cu and Ti were generally higher in amygdaloidal rocks.

To eliminate the imprint of regional differences,

Table 1

Comparison of Average Element Concentration

	Cu	Zn	Mn	Ni	Cr	Ti
	Vertical Sections					
Halls Harbour	116 (25)	70 (10)	875 (194)	*42 (7)	*115 (19)	*4942 (422)
Margaretville	70 (46)	52 (11)	1117 (241)	*46 (11)	*99 (22)	*4914 (399)
	Massive Rocks					
Scots Bay	*58 (23)	*60 (13)	*1109 (136)	*52 (4)	*148 (50)	*4700 (607)
Margaretville	*63 (23)	*81 (36)	*1093 (175)	*51 (2)	*149 (40)	*4945 (607)
Centre-ville + East Ferry	25 (9)	*73 (8)	*1061 (100)	77 (4)	388 (35)	3540 (176)
	Total Samples					
Zeolite-Bearing	103 (48)	*76 (77)	971 (254)	45 (9)	109 (29)	4915 (579)
Massive	48 (26)	*73 (24)	1085 (135)	61 (13)	240 (125)	4371 (785)
	Margaretville Only					
Zeolite-Bearing	*98 (79)	*56 (17)	*1041 (251)	46 (10)	108 (35)	*4968 (679)
Massive	*63 (23)	81 (36)	*1093 (175)	51 (2)	149 (40)	*4945 (607)

* : denotes no significant difference at the 95% confidence interval

() : standard deviation

: The effect of zeolite dilution has not been considered.

a comparison was made of zeolite-bearing and massive rocks only at Margaretville. Again Ni and Cr were lower in the zeolite-rich flows. However, no statistical difference was found in Cu, Mn and Ti. Zinc was higher in the massive rocks. The average of Cu was higher in zeolite-bearing rocks, but due to the large standard deviation (81%) the difference was not statistically significant. It might be worth noting that the standard deviations of all elements except Zn and Cr are higher in zeolite rich sections. This may indicate that the permeable flow tops were subject to greater import or export of trace elements than the less permeable massive sections. No attempt had been made to compensate for the effect of zeolite dilution. Therefore, varying amounts of zeolite will likely contribute to element variation in zeolite-rich zones. Zeolite dilution has had an effect on nickel concentration in the Keweenawan basalts (Jolly, 1974).

B. Vertical Variation in Three Flows

Variations of trace elements were plotted for three flows from Margaretville, Halls Harbour, and Ross Creek. The vertical sections from Centreville and East Ferry were not complete and showed little variation in rock texture. Therefore, they were not plotted. The total thickness of each flow was adjusted to 1.00 and each sample was spaced between 1.00 and 0.00. The vertical variations are given in Figs. 3-9.

Four samples from Halls Harbour represent a regular flow, whereas the remaining five samples represent an imbricated part of the same flow which has folded back on itself. The latter are not included in the vertical profile. At Margaretville samples A8 and A11 represent the top and bottom contacts of the sampled flow, yet they were taken 221 metres and 250 metres northeast of the vertical section. Therefore, any significant variation in these samples is subject to lateral control. Sample A4 and A8 are near zeolite veins. Effects of local alteration are possible.

Copper (Fig. 3) The best copper correlation with height is found at Halls Harbour where copper increases upward ($y = 0.01 x - 0.31$; $r^2 = 0.72$). At Ross Creek the upper contact with sediments is enriched in copper. At Margaretville higher concentrations of copper are found in A8, A4, and A3. Lateral distance may have a bearing on A8 (Fig. 18) while a localized zeolite vein may have affected A4 and A3. If the latter three samples are excluded a poorly defined enrichment may be obtained ($r^2 = 0.62$).

Zinc (Fig. 4) A poor correlation of zinc with height exists at Margaretville. Zinc enrichment from a zeolite vein could have occurred at A4. If A4 is removed a zinc enrichment toward the flow top is noted ($y = 0.06 x - 2.70$, $r^2 = 0.77$). At Halls Harbour a negative but less significant correlation is found between zinc and height ($y = -0.02 x + 1.90$, $r^2 = 0.63$). At Ross Creek zinc is enriched in the

upper part of the flow by a factor of 5.5 over the lower section.

Manganese (Fig. 5) There appears to be no correlation of manganese content with height in flow at Halls Harbour. At Ross Creek the upper contact is enriched by a factor of two in relation to the lower part of the flow. At Margaretville there is little correlation with height. Samples A3 and A4 are enriched, but again lateral flow variation and very localized vein enrichment may play a part.

Chromium (Fig. 7) At Halls Harbour and Ross Creek no distinct trend in chromium can be deduced. At Margaretville no covariance with height exists unless A3 is not considered, in which case a poorly defined negative correlation exists ($y = -0.01 x + 1.21, r^2 = 0.63$).

Nickel, Titanium, Cobalt (Figs. 6, 8 & 9) At Halls Harbour and Ross Creek there is no correlation between flow position and nickel concentration. At Margaretville there is a very poorly defined negative correlation ($y = -.02 + 1.31, r^2 = 0.40$). Titanium and cobalt show no vertical correlation.

Summary Zinc and copper show the best correlation with flow height. Copper may be enriched upward or not greatly affected. Zinc may be enriched or depleted toward the top. Copper, zinc, and manganese are all enriched in the upper flow contact at Ross Creek. Nickel, chromium, titanium, and cobalt show poor negative correlations at Margaretville.

Variation Diagrams. In Figs. 3-9 element variation has been plotted against vertical position in flow. All flow thicknesses have been adjusted to a unitless 1.00. Symbols for vertical sections are:

○ Margaretville

+ Halls Harbour

△ Ross Creek

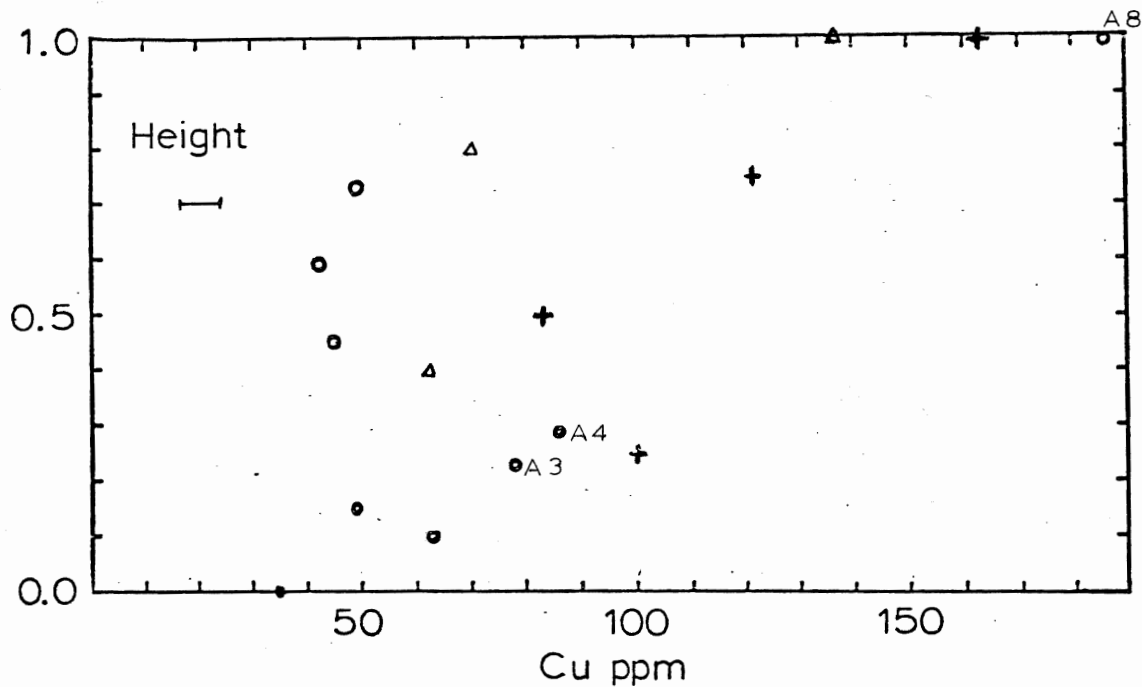
Other symbols used include:

▼ Centreville

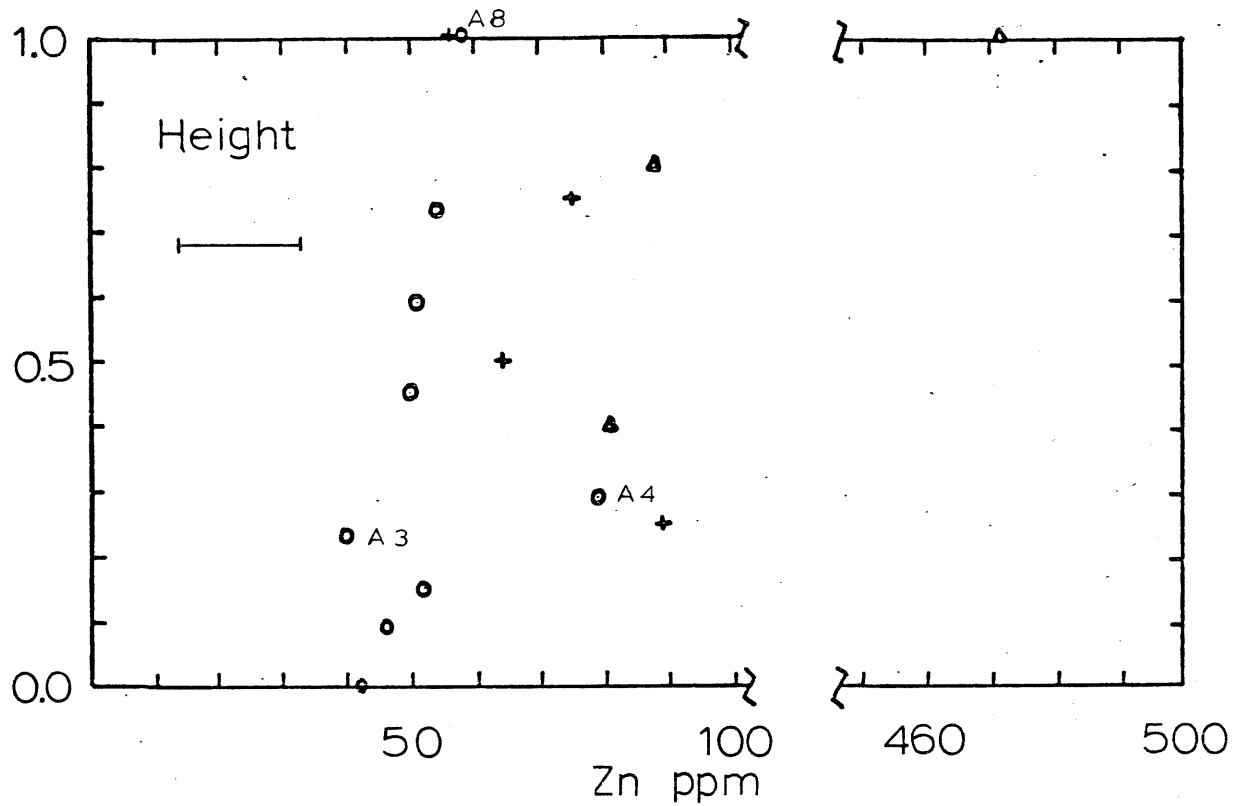
▽ East Ferry

x Scots Bay

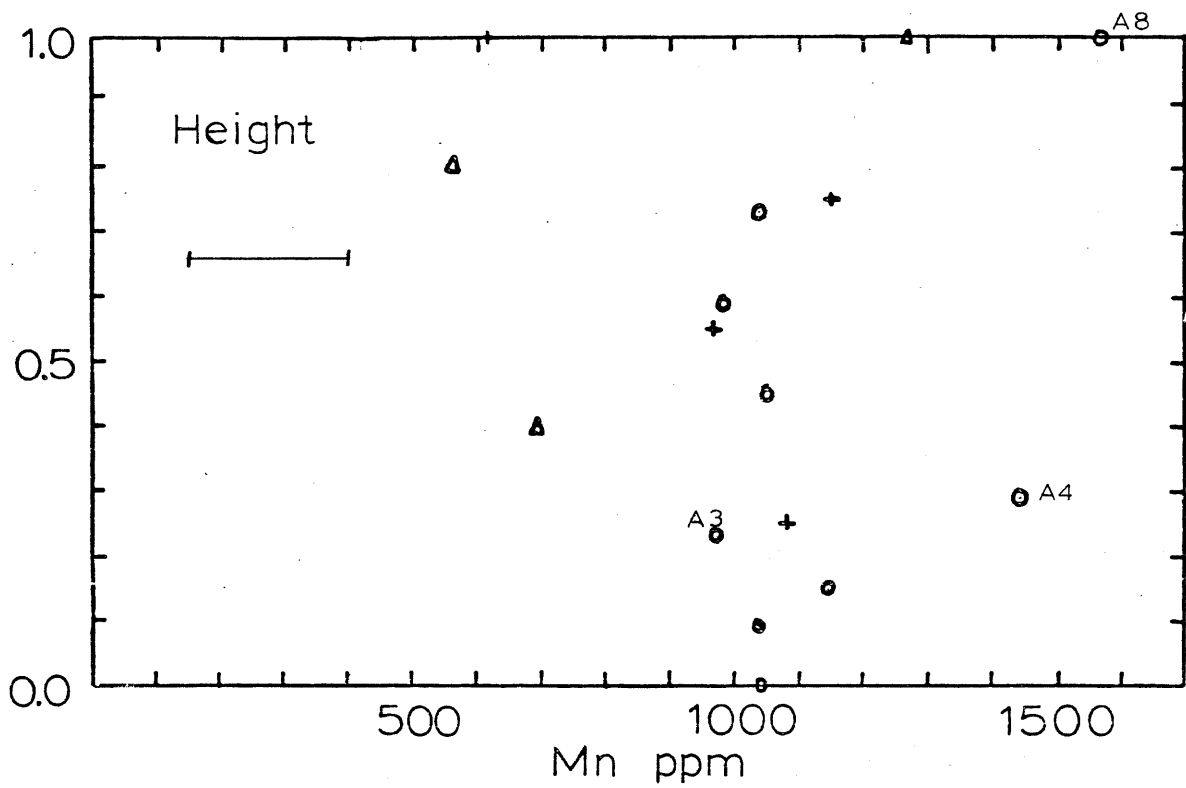
● Cape Split



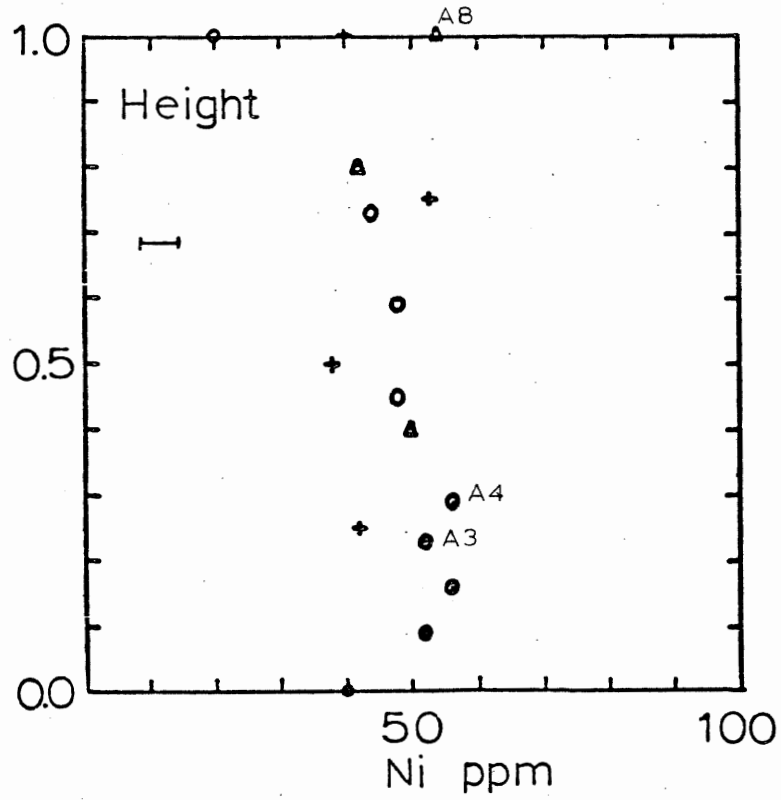
(Fig 3) Copper Variation With Height



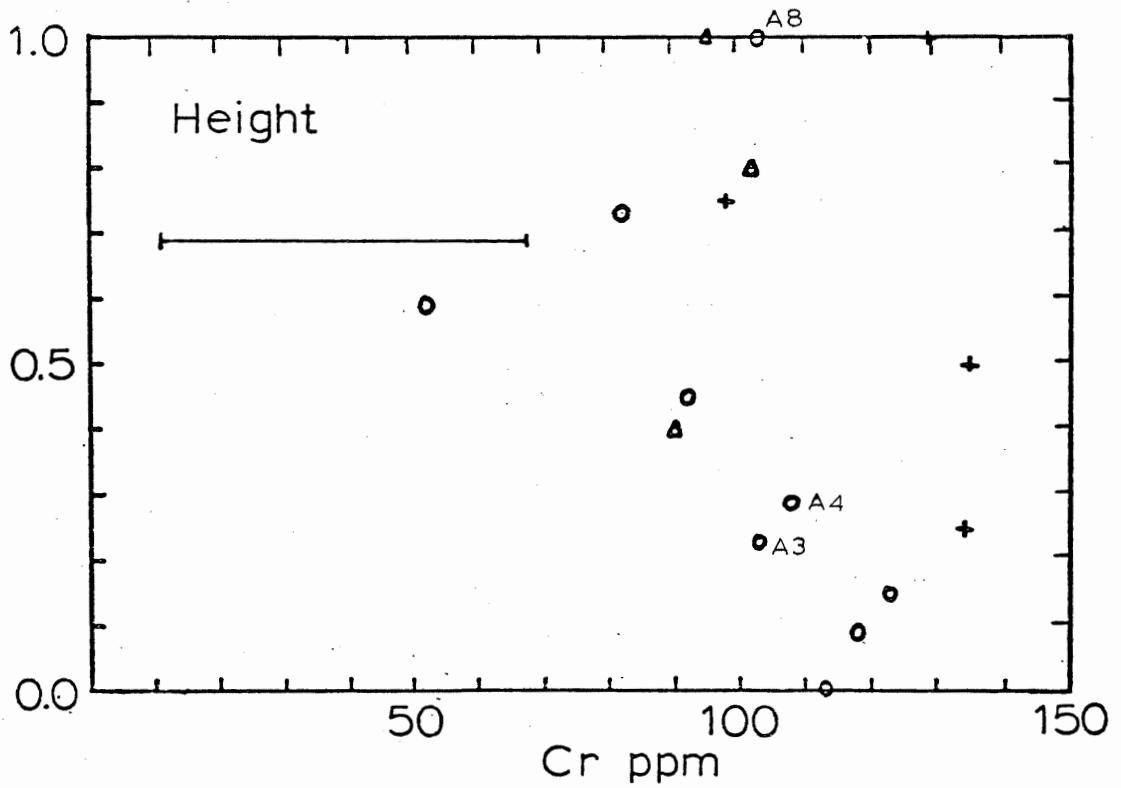
(Fig. 4) Zinc Variation With Height



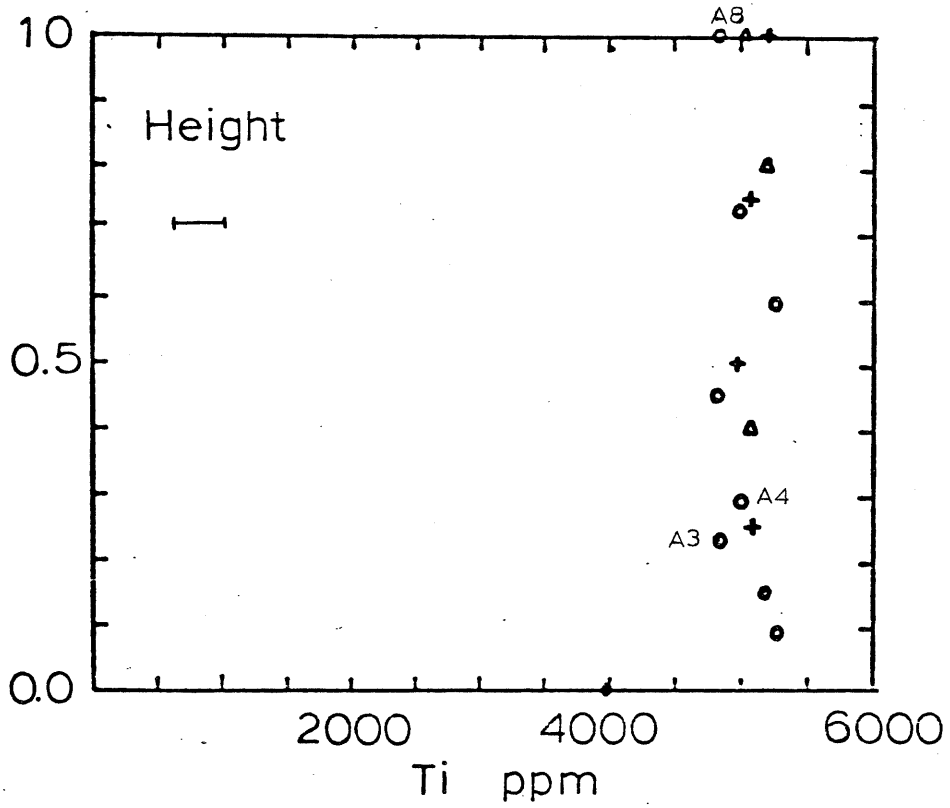
(Fig. 5) Manganese Variation With Height



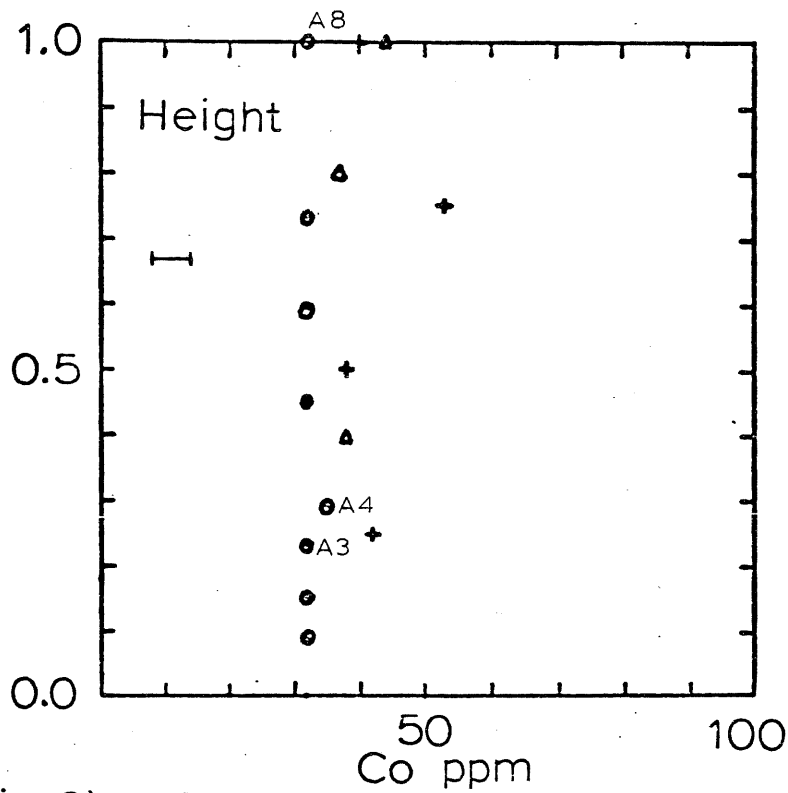
(Fig. 6) Nickel Variation With Height



(Fig 7) Chromium Variation With Height



(Fig 8) Titanium Variation With Height



(Fig 9) Cobalt Variation With Height

C. Metal - Metal Variation

Variation diagrams were plotted for combinations of Zn, Cu, and Mn (Figs. 10, 11 & 12). When exposed to hydrothermal brines these elements are expected to become mobile (Ellis, 1968; Bischoff, 1974; and Jolly, 1974). If Zn, Cu, and Mn correlate with each other, then they may have been distributed by the same mechanism. If no correlations exist, then they were precipitated by different mechanisms, or were preferentially mobilized.

Combinations of Ni, Ti, and Cr were also plotted (Figs. 13 & 14). These elements are preferentially partitioned from an igneous melt into particular phases. For example, Ni would be partitioned into olivine or pyroxene. Titanium would enter pyroxene or the oxide phase. A rock rich in Ni would contain a lot of early crystallized olivine or pyroxene. A Ti-rich rock would represent a more residual liquid with less compatible Ti and Fe^{3+} . The object of the Ni, Cr, and Ti diagrams will be to determine if these elements have been affected by alteration and if not, whether a differentiation can be determined.

Zinc - Copper (Fig. 10) In general a significant covariation cannot be determined between zinc and copper. At Ross Creek, zinc and copper do increase together. At Halls Harbour, on the other hand, there is a very poor negative correlation ($r^2 = 0.37$). This suggests that while

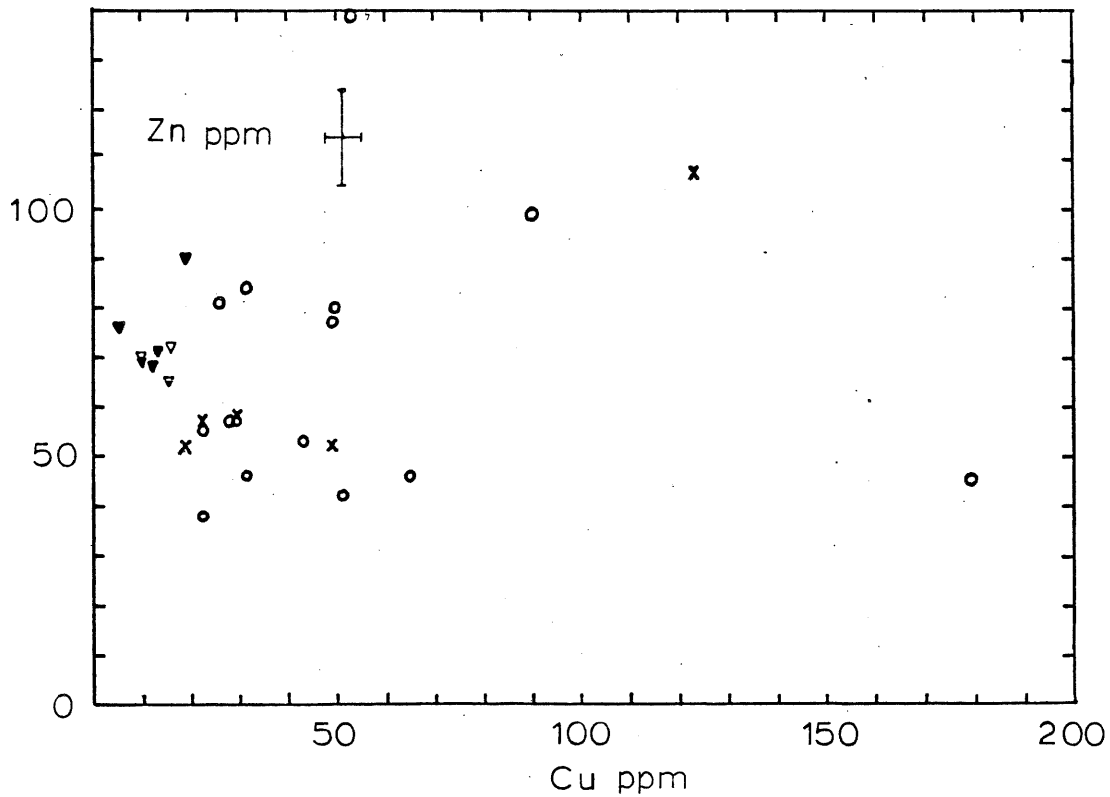
copper is being enriched at Halls Harbour, zinc is being depleted or remains unaffected.

Manganese - Copper (Fig. 11) In general no co-variation between manganese and copper is evident. Within a particular flow some co-variation may exist in a vertical section. Manganese and copper are both enriched upward at Ross Creek. A positive correlation was found in the vertical section at Margaretville ($Mn = 4.32 Cu + 814$, $r^2 = 0.69$). A poor positive correlation appears at Centreville ($r^2 = 0.53$). A very poor negative co-variation exists at Halls Harbour ($r^2 = 0.46$)

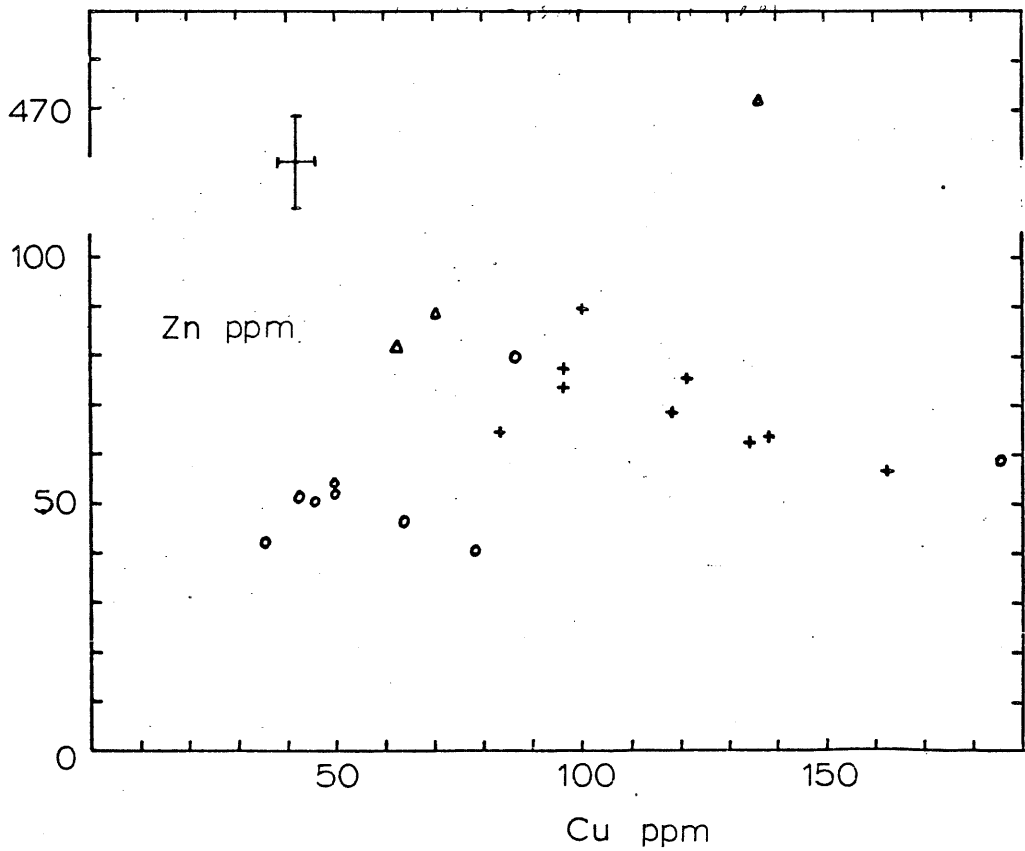
Zinc - Manganese (Fig. 12) A general co-variation is also not apparent. Zinc and manganese both increase at Ross Creek. Poor positive co-variations are found at the Margaretville flow ($r^2 = 0.59$), Halls Harbour ($r^2 = 0.57$) and Scots Bay ($r^2 = 0.58$). Therefore, in individual flows some co-variation does exist.

Nickel - Titanium (Fig. 13) In general there is a rather poorly-defined decrease in nickel with increasing titanium. ($Ni = 0.01 Ti + 103$, $r^2 = 0.45$). A negative co-variation is found at Ross Creek ($Ni = -0.07 Ti + 414$, $r^2 = 0.97$). A poor positive correlation is found at Centreville ($r^2 = 0.62$). In other localities no significant local co-variations are found.

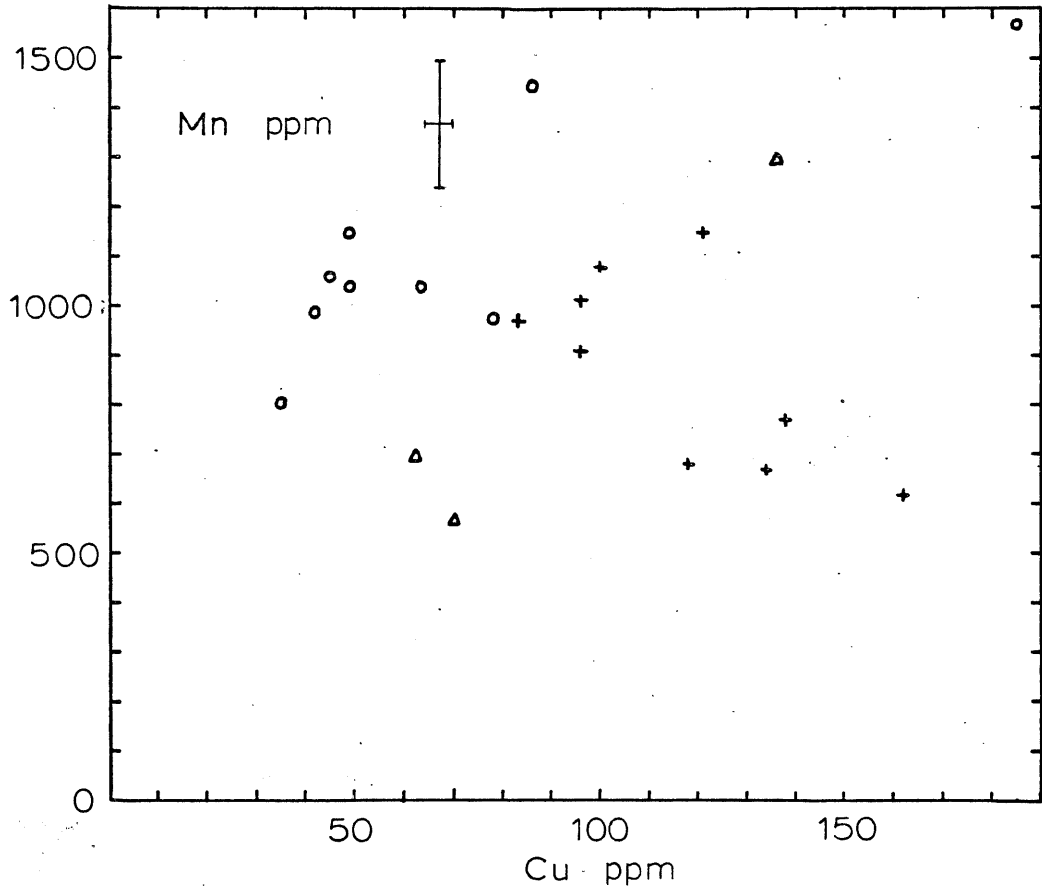
Nickel - Chromium (Fig. 14) There appears to be an increase in nickel with chromium when all the samples are



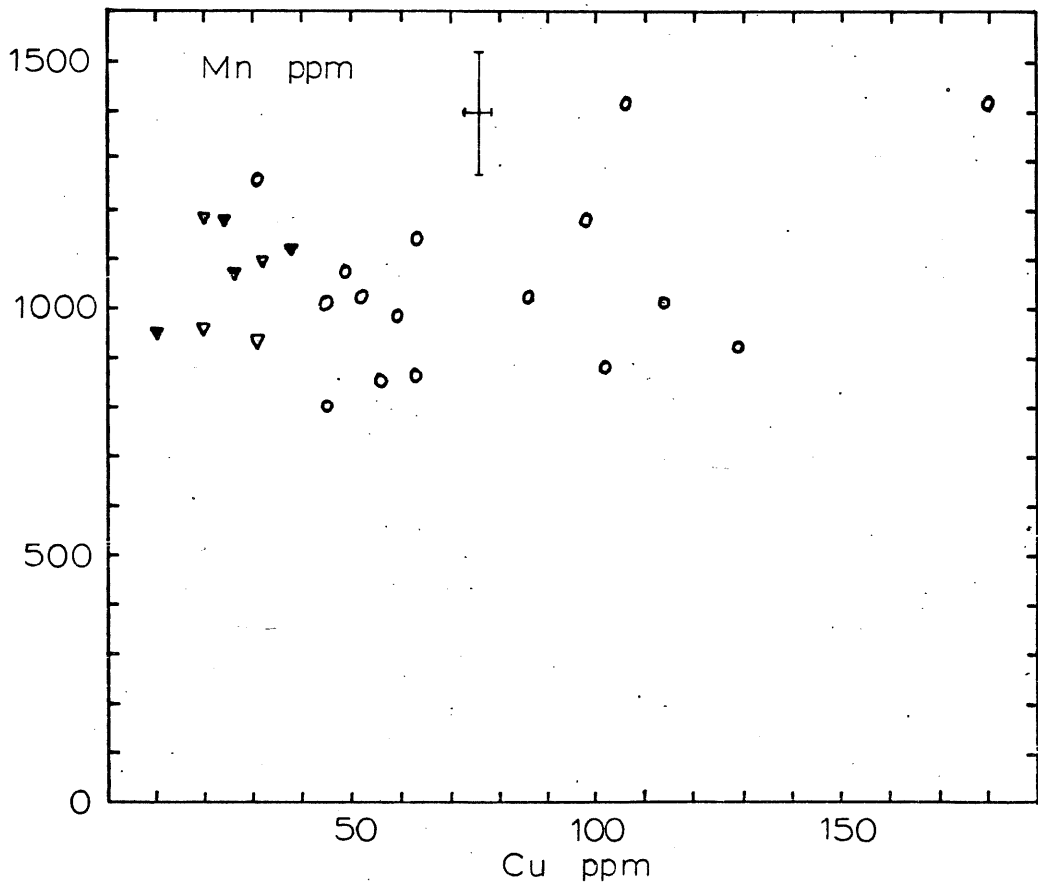
(Fig. 10A) Zinc-Copper Variation



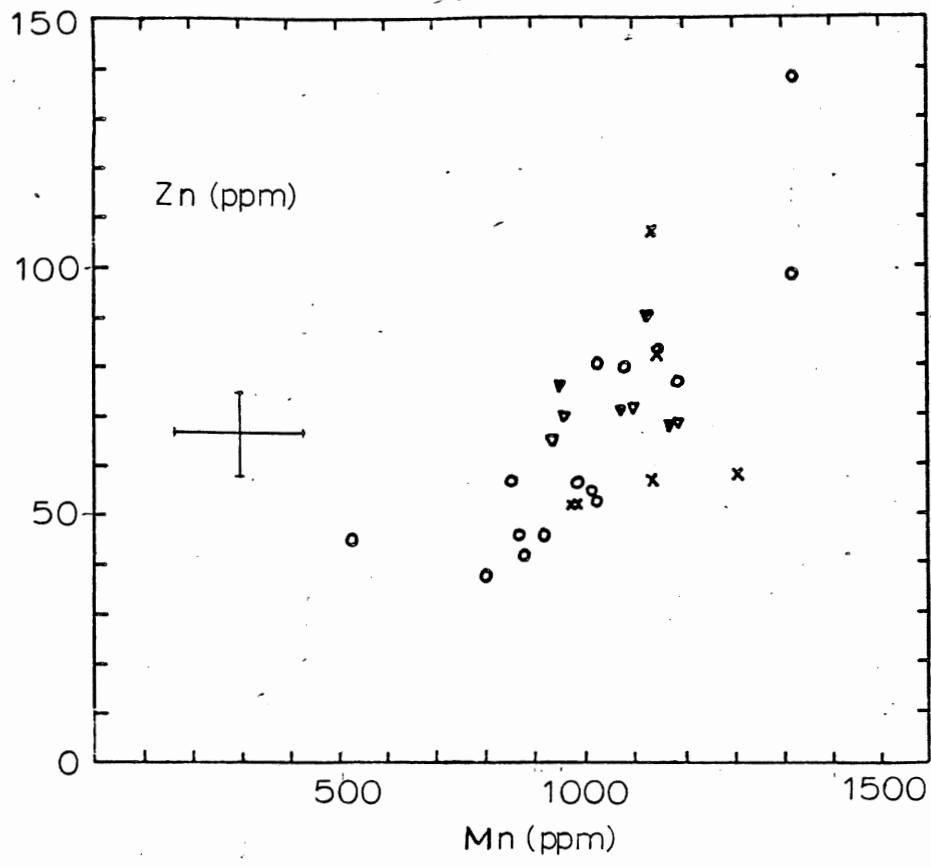
(Fig. 10B) Zinc - Copper Variation in Vertical Sections



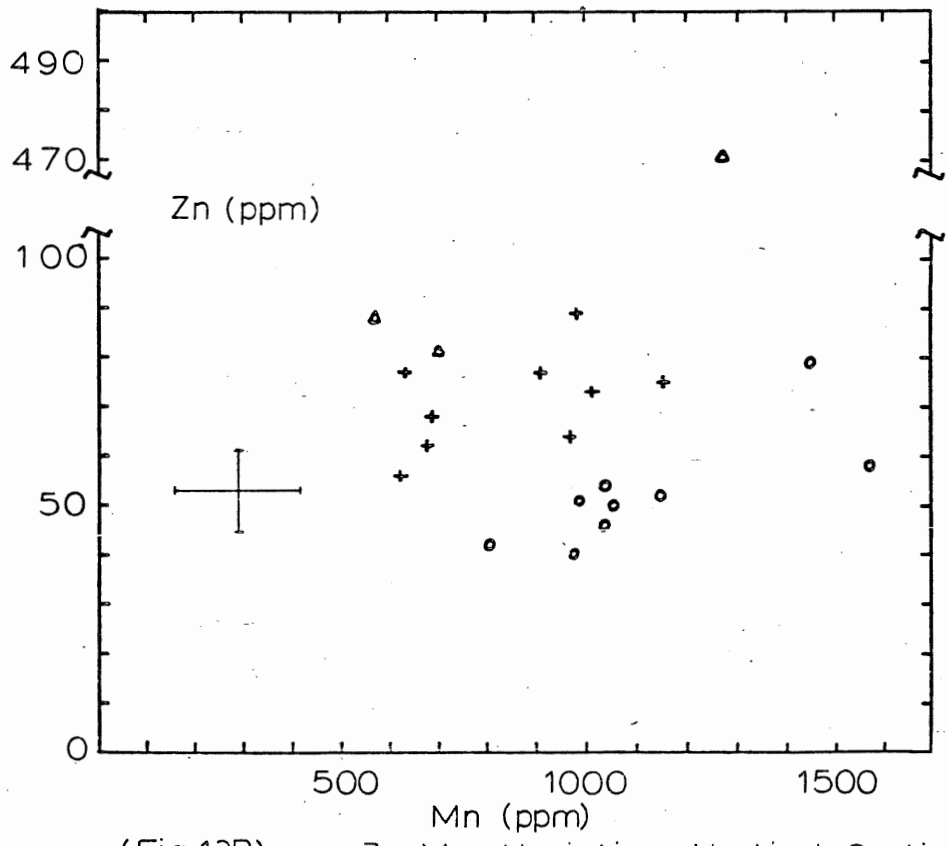
(Fig 11B) Manganese-Copper Variation



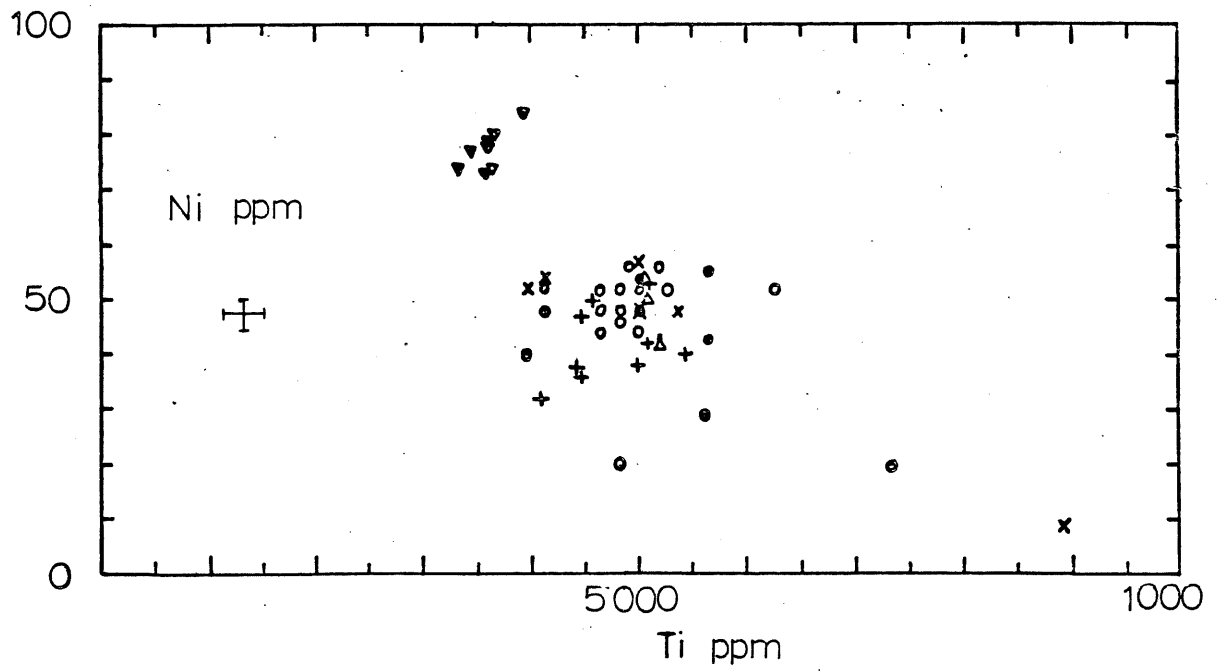
(Fig 11A) Manganese-Copper Variation



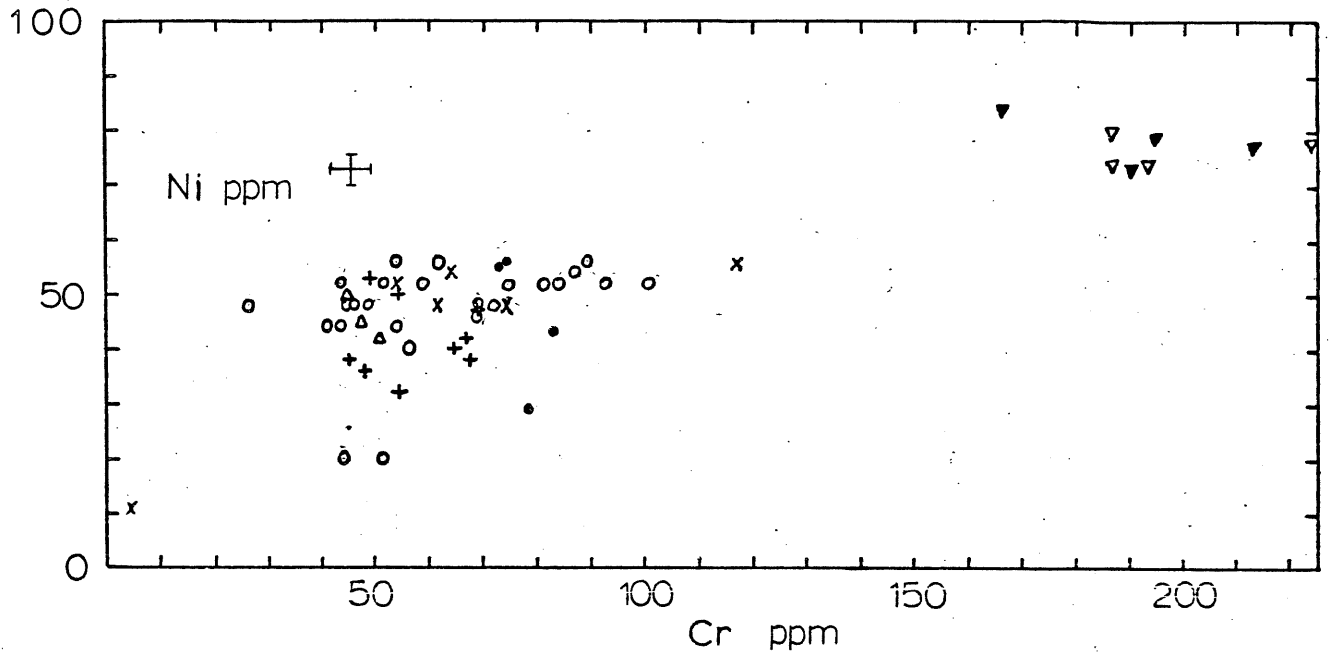
(Fig. 12A) Zn - Mn Variation



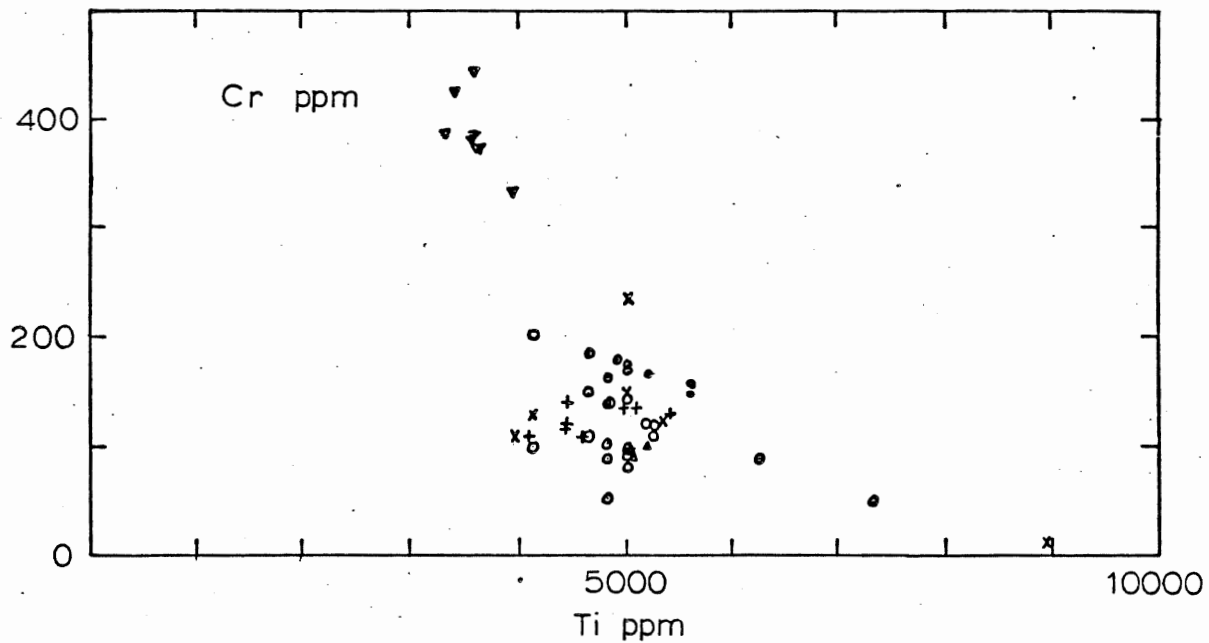
(Fig. 12B) Zn - Mn Variation: Vertical Sections



(Fig 13) Nickel-Titanium Variation



(Fig. 14) Nickel-Chromium Variation



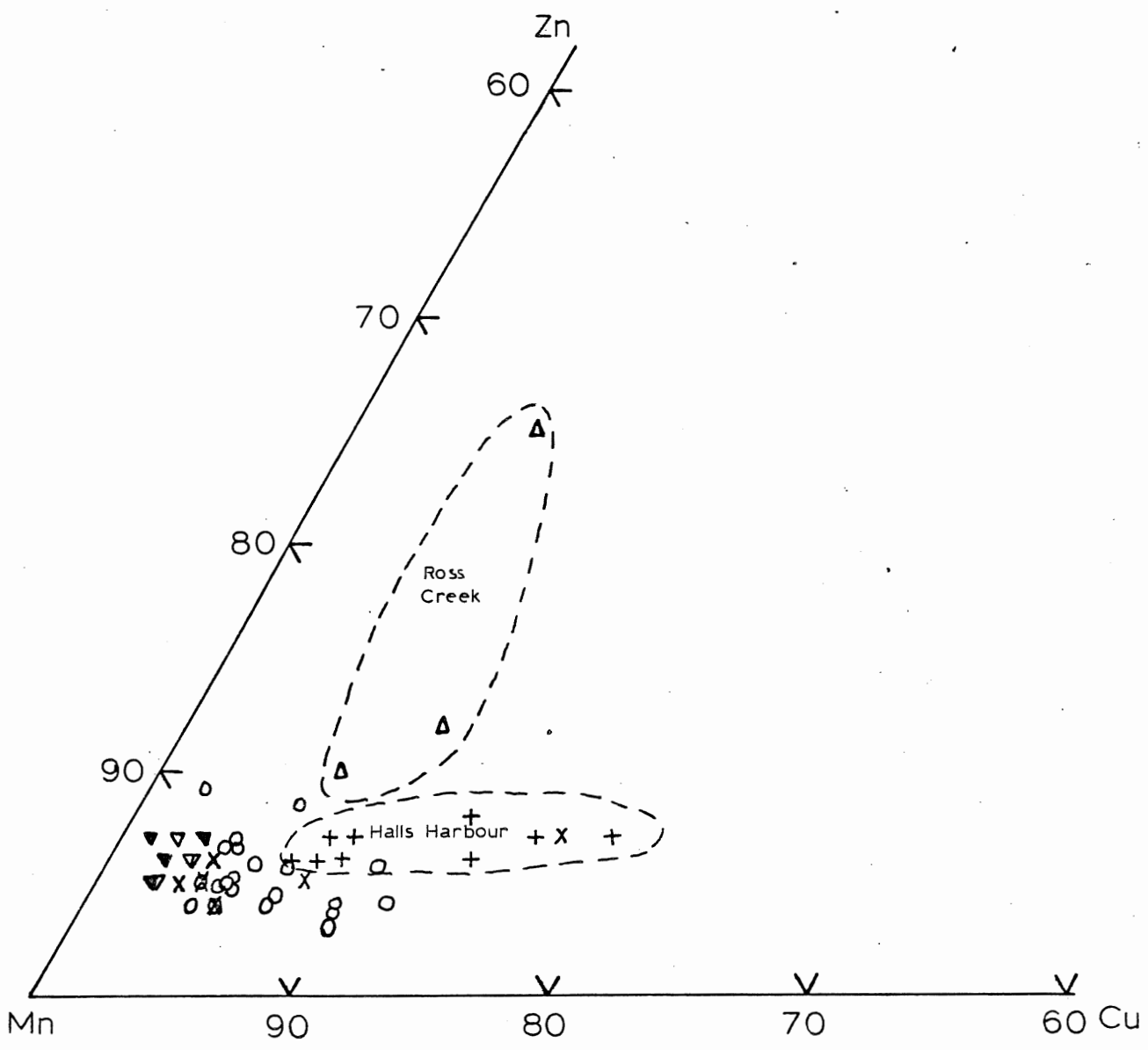
(Fig 14B) Chromium - Titanium Variation

considered. ($\text{Ni} = 0.12 \text{ Cr} + 31.81$, $r^2 = 0.67$). On a local scale little co-variation is noticeable.

Chromium - Titanium (Fig. 14B) As would be anticipated from Ni versus Ti, and Ni versus Cr plots, there is a rather poor negative correlation between chromium and titanium when all samples are considered. On the local level there is little co-variation except at Ross Creek where a positive correlation is found ($r^2 = 0.70$)

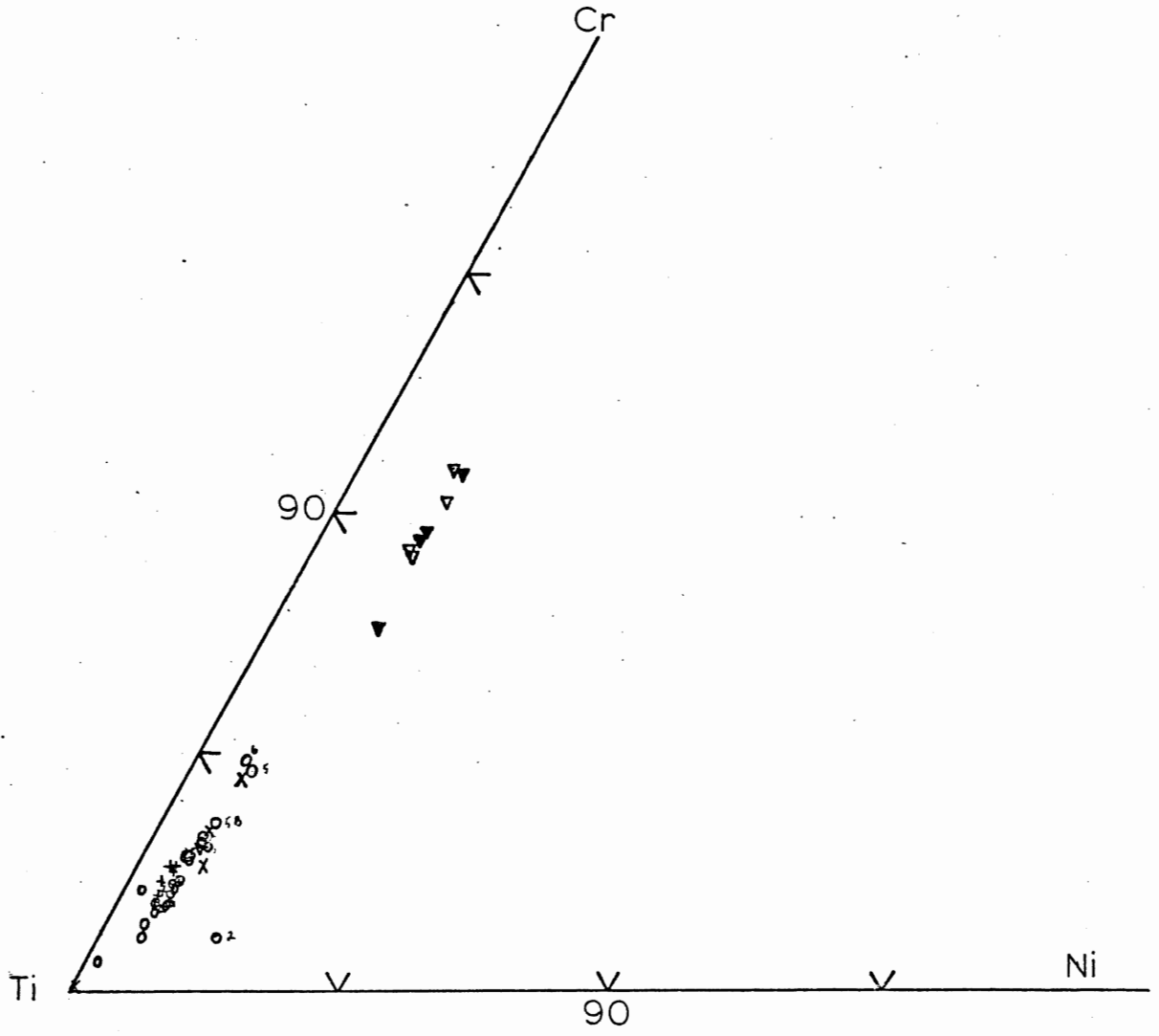
Zinc - Manganese - Copper The Zn - Mn - Cu variation is shown in Fig. 15. The different sampling sites plot along different trends. East Ferry and Centreville are grouped together close to the manganese corner. A trend toward the copper-rich corner is formed by the flow at Halls Harbour. The vertical section at Margaretville and the Scots Bay flow tend to bridge the gap between the samples from Halls Harbour and the manganese-rich corner. The sample from Scots Bay (13), found at the extreme end of the copper-enrichment trend, is a glassy flow crust representing an early quench. Ross Creek is the only locality to show significant zinc enrichment.

Chromium - Titanium - Nickel When all samples are plotted on a Cr - Ti - Ni - triangle (Fig. 16) an almost linear co-variation results. The trend starts at the Ti corner and moves toward Cr. The lack of significant deviation from this line suggests that these elements have not been significantly mobilized relative to each other during



(Fig. 15)

Zn-Mn-Cu Variation



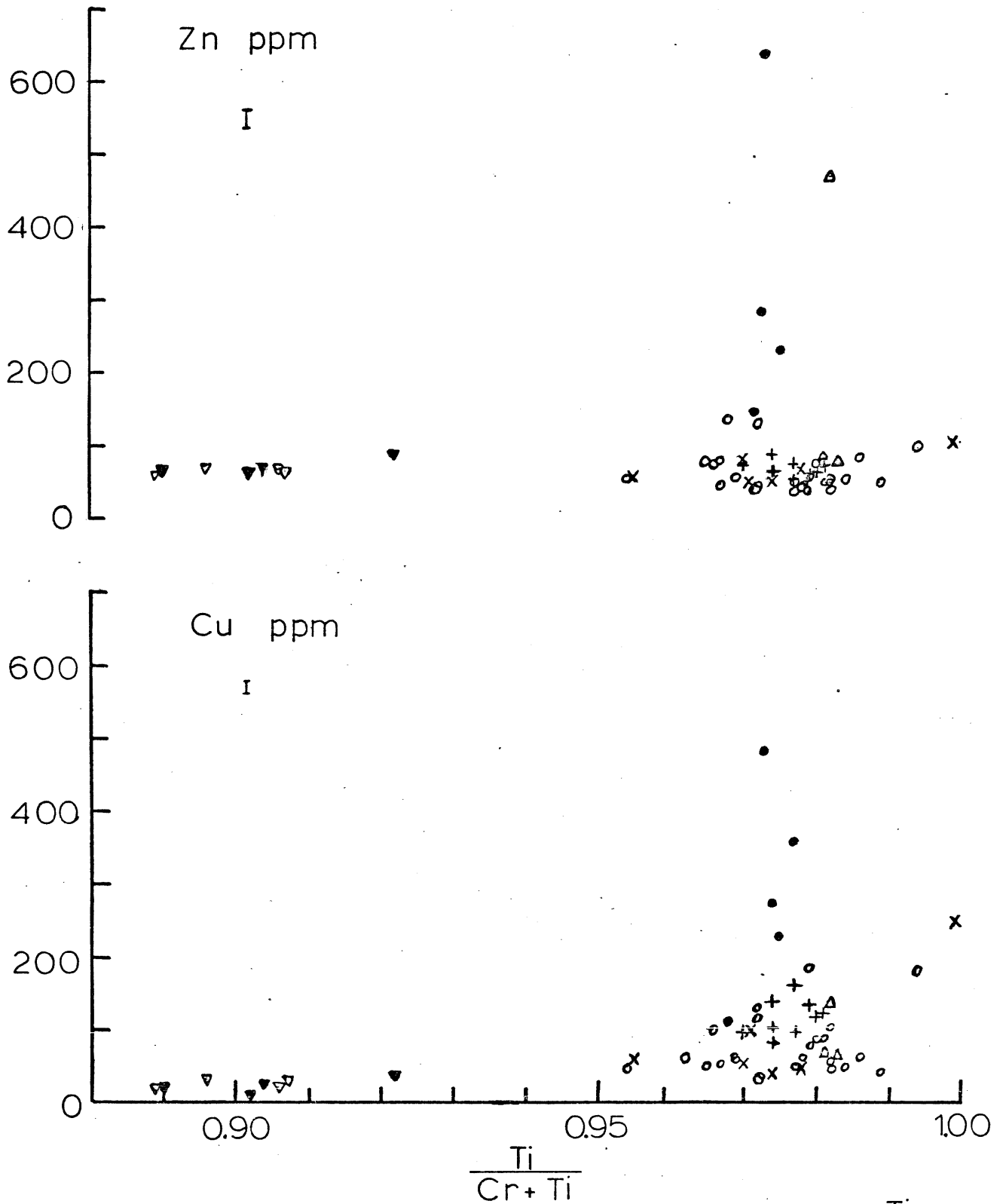
(Fig16)

Cr-Ti-Ni Variation

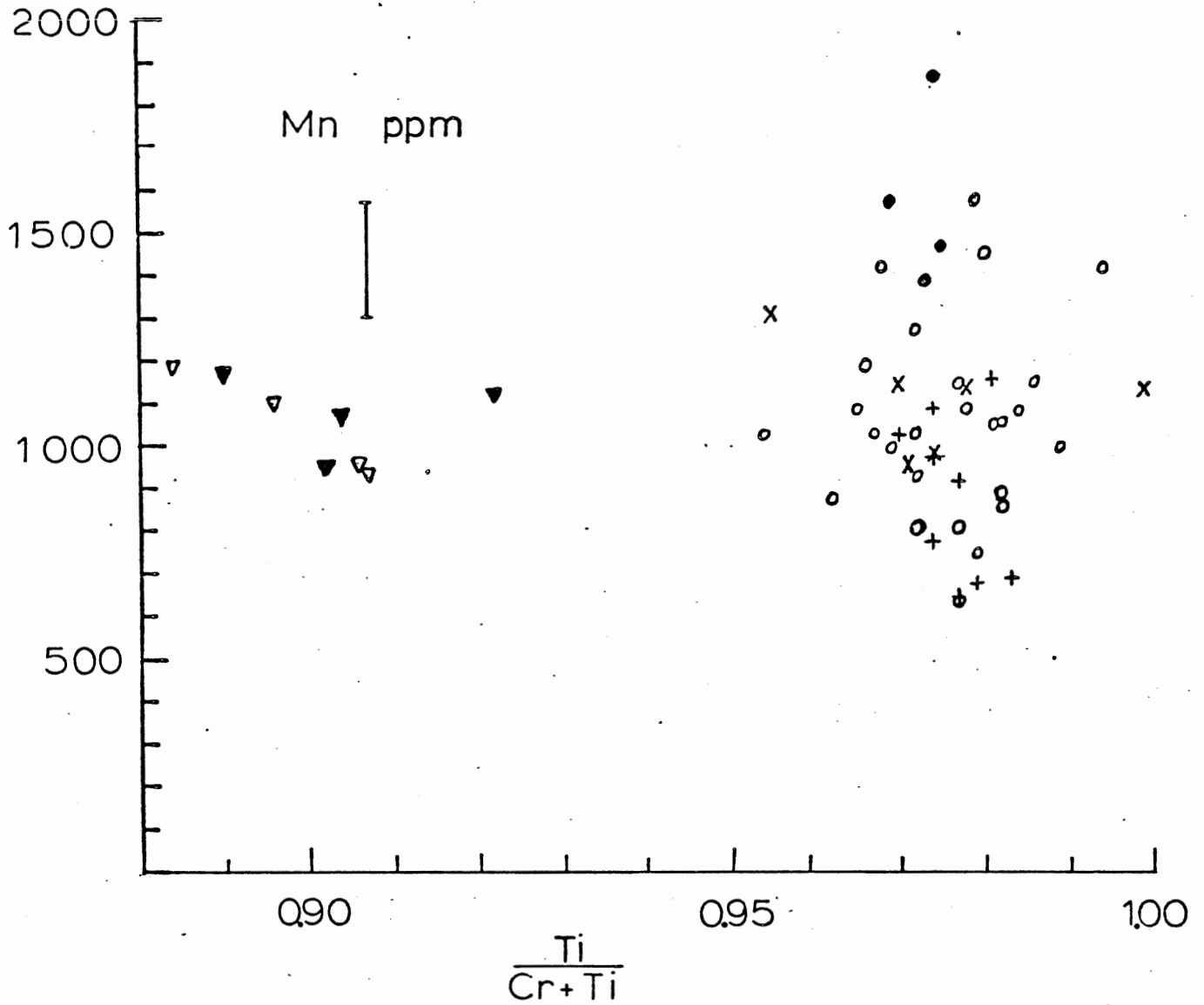
zeolite facies metamorphism. The chromium-rich rocks are coarse grained, pyroxene-bearing basalts from Centreville and East Ferry. The most titanium-rich sample is a chilled crust from Scots Bay.

Differentiation Index and Cu, Mn, Zn During liquid cooling the partitioning of Cr, Ni, and Ti into various phases is a function of their ability to substitute for major elements in particular minerals. The degree of isomorphous substitution between two elements is governed by (1) similarity in ionic radii, (2) similarity in charge(± 1), (3) relative strength of bond formed between each element and the other elements in the phase, and (4) similarity in the covalent character of the bonds (Krauskopf, 1967).

Like Mg^{2+} , Ni^{2+} enters crystal phases early because of its high crystal field octahedral site preference energy and its small ionic radius (Wedephol, 1970). The Cr^{3+} may replace Fe^{3+} and Al^{3+} in spinels such as chromite, and in silicates such as augite, hornblende, and olivine (Rankama and Sahama, 1950). As chromite is one of the first minerals to separate from a crystallizing magma, Cr would be enriched in early cumulates settling from a magma. The Ti^{4+} and Ti^{3+} may substitute for Fe^{3+} or Al^{3+} in pyroxene and particularly in ilmenite. Since Mg enters crystals before Fe^{3+} , Al^{3+} or Ti the latter elements are concentrated in the liquid. Therefore, if the early formed crystals are separated from the liquid, the result will be one rock rich in Cr and Ni and another more evolved rock, rich in Ti and Depleted in Ni and Cr.



(Fig.17A) Zinc and Copper Variation with $\frac{Ti}{Cr+Ti}$



(Fig. 17 B) Manganese Variation with $\frac{\text{Ti}}{\text{Cr} + \text{Ti}}$

With this in mind, a differentiation index of $\frac{\text{Ti}}{\text{Cr} + \text{Ti}}$ was devised since Ti and Cr seemed to be affected the most by differentiation (Fig. 16). Since Ti and Cr have not been greatly affected by metamorphism, a comparison of Cu, Zn and Mn with $\frac{\text{Ti}}{\text{Cr} + \text{Ti}}$ would indicate the degree of mobilization of Cu, Zn and Mn. If a good correlation is obtained with $\frac{\text{Ti}}{\text{Cr} + \text{Ti}}$ then the element in question still has a strong component of igneous differentiation. If Cr and Zn have been concentrated in the residual liquid during differentiation, then they should increase with higher $\frac{\text{Ti}}{\text{Cr} + \text{Ti}}$. A poor covariance would indicate element redistribution by some other mechanism. During burial metamorphism these elements could be more mobile than Ti and Cr, in which case no relation to $\frac{\text{Ti}}{\text{Cr} + \text{Ti}}$ would be shown.

In general there is a rather poor co-variation between Cu, Mn and Zn, and $\frac{\text{Ti}}{\text{Cr} + \text{Ti}}$. Massive flows might retain their primary igneous distribution of elements because they are less permeable and therefore less metamorphosed. An attempt was made to see if a better co-variation could be obtained from massive flows (Table 2).

A negative correlation was found for $\frac{\text{Ti}}{\text{Cr} + \text{Ti}}$ versus manganese at East Ferry ($r^2 = 0.41$). Copper showed a very poor positive correlation at East Ferry ($r^2 = 0.34$), at Centreville ($r^2 = 0.38$), and for massive flows ($r^2 = 0.38$). A slightly stronger positive correlation was shown at Scots Bay ($r^2 = 0.61$). Zinc showed no overall co-variation in

Table 2

Metals vs Differentiation Index

Massive Flows

Mn vs $\frac{Ti}{Cu + Ti}$

Centreville	Mn =	-527x+ 1554	$r^2 = 0.01$
East Ferry		-13676x+13345	$r^2 = 1.00$
Scots Bay		-2756x+ 3798	$r^2 = 0.10$
Massive at Margaretville		4443x- 3216	$r^2 = 0.07$
All Massive Flows		-1x+ 1038	$r^2 = 0.41$

Cu vs $\frac{Ti}{Cr + Ti}$

Centreville	Cu =	533x- 458	$r^2 = 0.38$
East Ferry		373x- 313	$r^2 = 0.34$
Scots Bay		4328x-4128	$r^2 = 0.61$
Massive at Margaretville		599x- 518	$r^2 = 0.07$
All Massive Flows		843x- 742	$r^2 = 0.38$

Zn vs $\frac{Ti}{Cr + Ti}$

Centreville	Zn =	695x-552	$r^2 = 0.89$
East Ferry		- 154x+207	$r^2 = 0.20$
Scots Bay		1085x-990	$r^2 = 0.49$
Massive at Margaretville		624x-524	$r^2 = 0.03$
All Massive Flows		99x- 20	$r^2 = 0.02$

massive flows, although positive variations were shown at Centreville ($r^2 = 0.89$) and Scots Bay ($r^2 = 0.49$).

Summary The variation of Ni and particularly Cr and Ti is a function of fractional crystallization as shown by the Ni - Cr - Ti plot (Fig. 16). The coarse grained basalts of East Ferry and Centreville plot as early differentiates. The chilled crust at Scots Bay plots as a residual liquid. The remaining samples are found between these extremes.

When Zn, Cu and Mn were compared to the differentiation index $\frac{\text{Ti}}{\text{Cr} + \text{Ti}}$, the lack of co-variation suggested that their variation was not controlled by the same factor which controlled the Ti - Cr variation. Therefore, in many places Cu, Zn, and Mn could have moved during burial metamorphism. However, in certain massive flows some of the elements do show a co-variance and may not have been mobilized (Table 2). Greatest deviation from a primary distribution occurred in amygdaloidal sections or fault zones where there is greatest permeability.

Except at Ross Creek, co-variations between Cu - Zn - Mn are generally weak. Zinc and copper show no significant co-variation (Fig. 10). Poor negative and positive co-variations exist between Cu and Mn in some individual flows (Fig. 11). Poor positive co-variations between Zn and Mn occur at Margaretville, Halls Harbour and Scots Bay (Fig. 12). Since both Zn and Mn may substitute for Fe^{2+} in magnetite

(Wedepohl, 1970), the abundance of the iron oxide may influence their co-variance. Since copper has a poor co-variance with zinc and manganese, a different mechanism of distribution must be devised for copper. Ross Creek is the only place where all three metals are significantly enriched together. A slightly different model may have to be constructed for it.

The only places where Zn is enriched relative to Cu and Mn are Ross Creek (Fig. 15), and the brecciated zone at Cape Split (Fig. 23).

D. Lateral Variation at Margaretville

Before a great emphasis is placed on comparing different sampling localities trace element variation on the local scale should be examined. Since the most extensive lateral section was sampled at Margaretville, this locality will be used as an indication of lateral variation.

The various samples are located on the Margaretville cross section (Fig. 18). Stratigraphically flows 1 and 1B appear to be the same. Therefore, the Margaretville samples mostly represent the lateral variance of one flow. One sample below it and several above are included.

When Margaretville samples are plotted on a Cr - Ti - Ni diagram (Fig. 19) a rather straight line occurs. Samples A8 and 2 seem to noticeably deviate from this trend. Both are relatively copper-rich and appear to be part of the

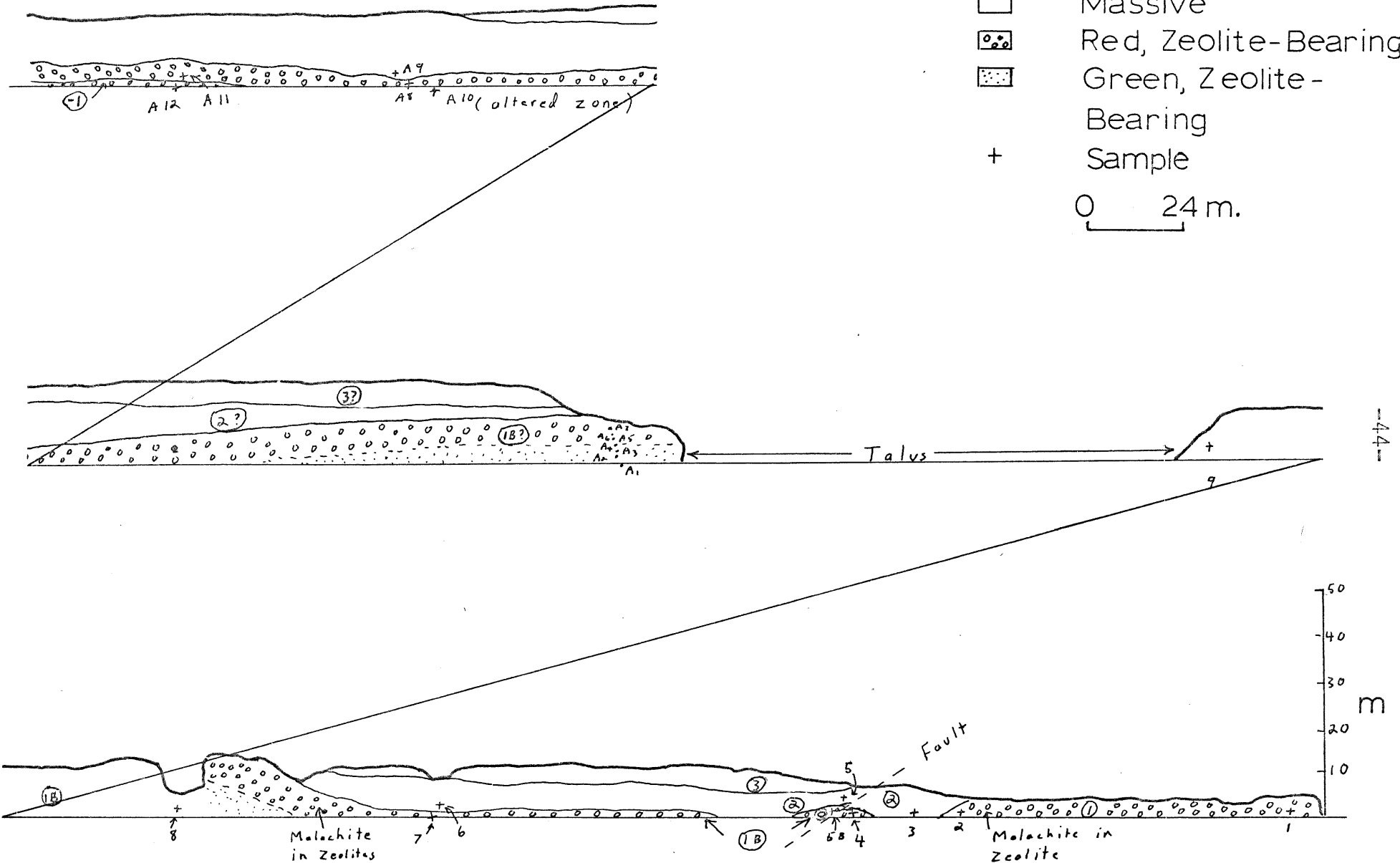
same flow, yet they appear on opposite sides of the Cr - Ti - Ni trend. Both are red, zeolite-bearing basalts so that their deviation from the norm is the result of alteration.

When the element concentrations are plotted on a Zn - Mn - Cr - diagram the majority cluster in the Mn corner. A trend toward the copper-rich corner may be evident in this cluster. Sample 2 tends to emphasize such a trend.

In Fig. 21 manganese, zinc and copper are plotted versus relative horizontal position. These diagrams illustrate extensive variability in element concentration along the lateral extent of a flow. Since the metals do not necessarily increase or decrease at the same time, differences in their ratios could be expected along the same flow. Therefore, comparison of different localities with small local sample areas could be misleading. Element variation which exceeds error bars is greatest for copper and zinc. Manganese variation does not exceed two error bars.

Legend

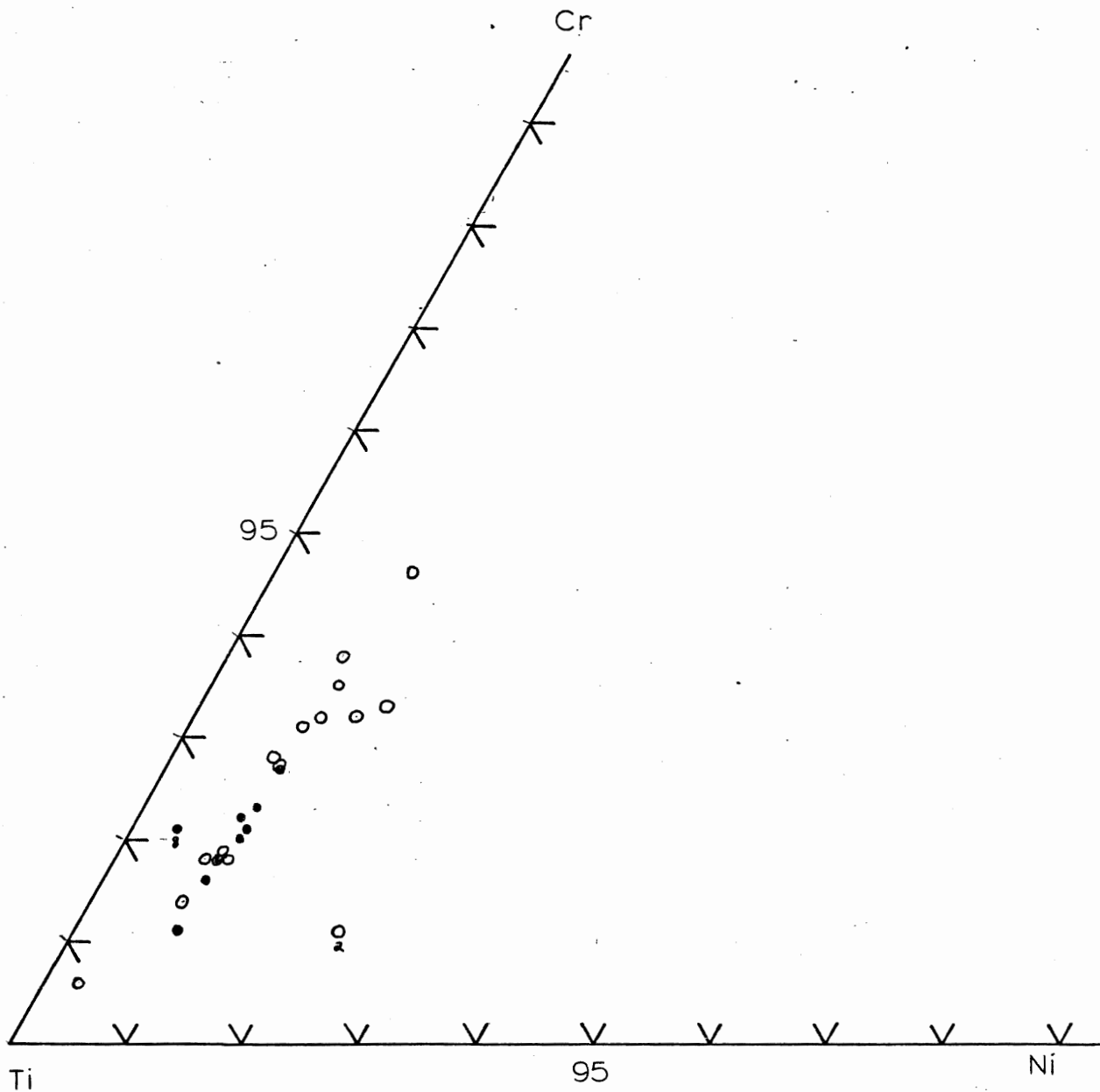
- Massive
 - ◻ with red dots Red, Zeolite-Bearing
 - ◻ with green dots Green, Zeolite-Bearing
 - + Sample
- 0 24 m.



(Fig 18) Margaretville Cross Section

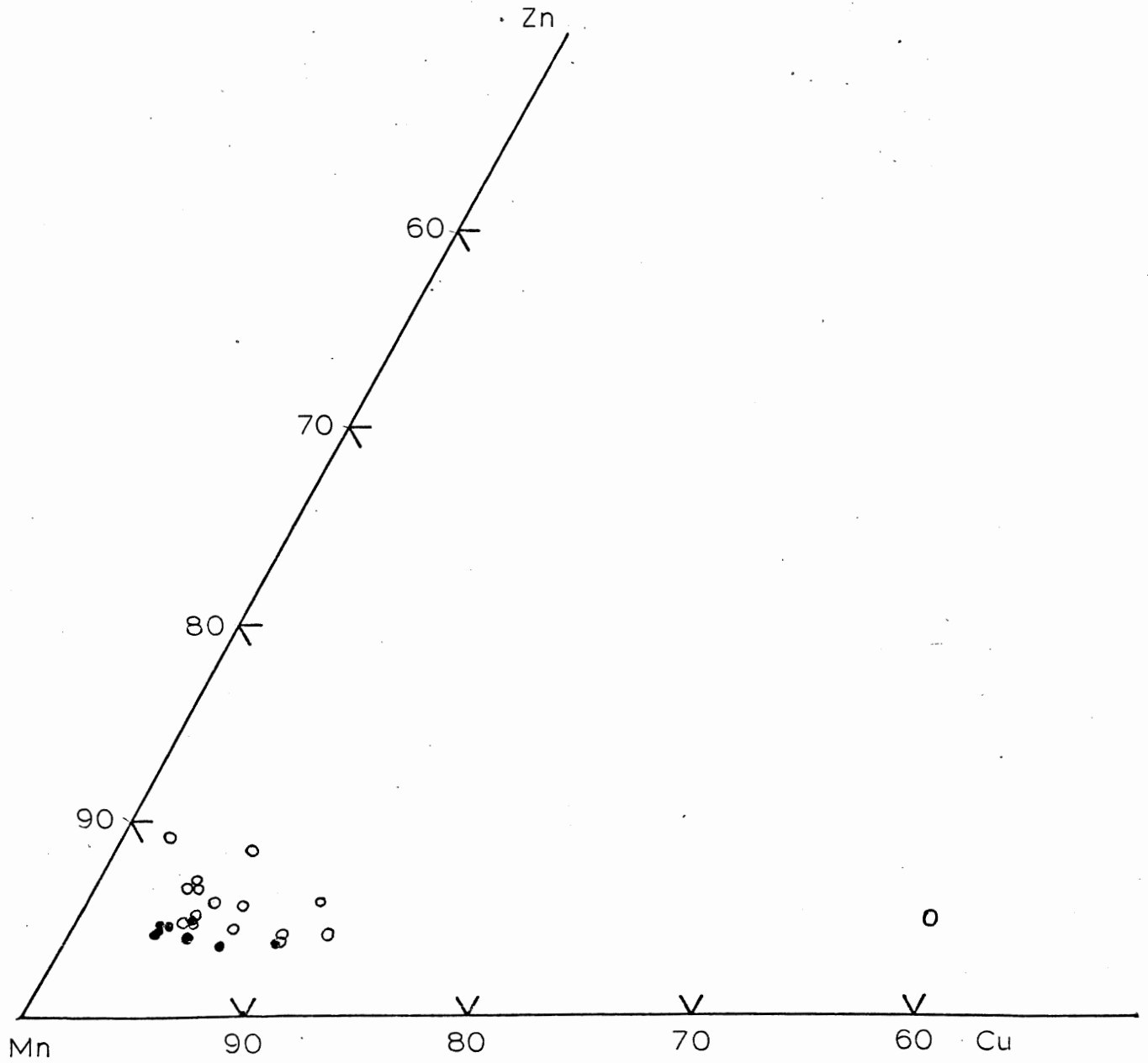
← N.W.

Margaretville →



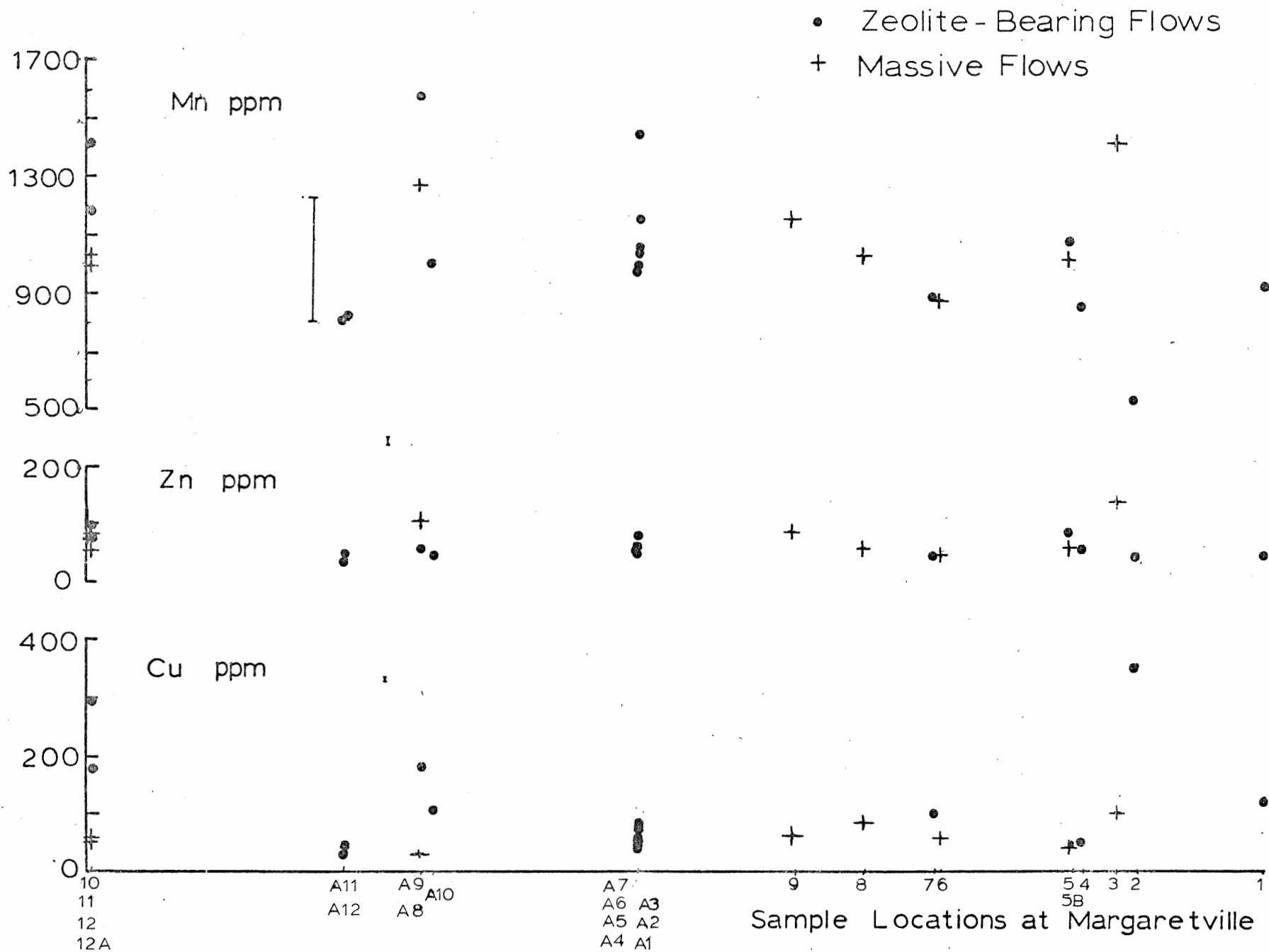
(Fig. 19) Cr-Ti-Ni Variation at Margaretville

- vertical section
- rest



(Fig. 20) Zn-Mn-Cu Variation at Margaretville

- vertical section
- rest



(Fig. 21) Lateral Variation at Margaretville Lateral distance is one kilometre.

IV. DISCUSSION

A. Copper-Bearing Phases

Copper-bearing minerals which are given by Wedepohl (1970) include olivine (6 - 960 ppm Cu), pyroxene (4 - 1000 ppm Cu), and ilmenites and magnetites (5 - 880 ppm Cu).

In an attempt to establish which phases contain the major copper portions, polished thin sections from Margaretville and the Cape Split fault zone were investigated with the electron microprobe. If the count rate at the copper-peak position was less than the average background plus three standard deviations, Cu was considered to be below the detection limit (about .02 wt%). Background was measured at $2^{\circ} 2\theta$ on either side of the copper peak. Since the magnetites from Cape Split were the only ones with detectable copper only their analyses are shown in Table (3).

In sample B-9-10 the magnetite content was estimated to be 2-3%, using a petrographic microscope. If 3 wt% magnetite is assumed, Ti, Zn and Mn are within nine percent of the whole rock analysis so that their concentrations could be explained by magnetite. However, 3% magnetite constitutes only 57 ppm copper of the required 481 ppm copper.

Table 3

Microprobe Analysis of Magnetites
from Cape Split

Magnetites From Cape Split Fault Zone (B-9-10)

wt. %							
Grain	Fe	Ti	Zn	Mn	Cu	Al	Total
1	39.63	17.78	3.49	5.14	0.35	0.70	67.08
2	40.26	15.27	0.63	4.62	-	0.68	61.46
3	41.01	17.12	0.81	3.88	-	0.31	63.14
4	39.56	17.08	3.24	5.13	0.34	0.51	65.86
5	39.27	16.73	2.80	4.22	0.22	0.71	63.95
6	38.99	19.23	2.52	4.38	0.22	0.32	65.67
\bar{x}	39.79	17.20	2.25	4.56	0.19	0.54	

Whole rock concentrations were calculated for 3% magnetite.

	From Magnetite	Actual
Fe	11937 ppm	
Ti	5160 "	5625 ppm
Zn	675 "	638 "
Mn	1368 "	1385 "
Cu	57 "	481 "
Al	162 "	

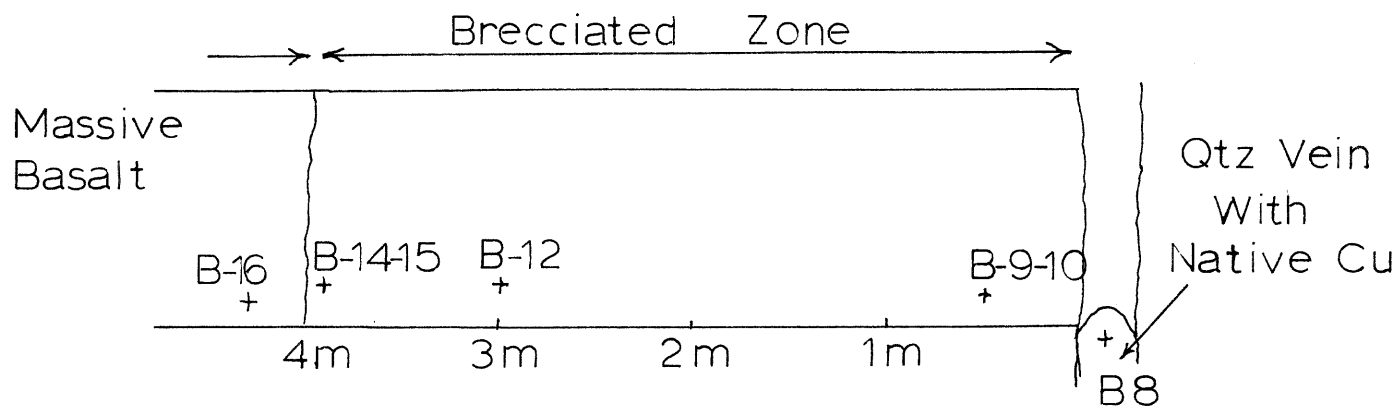
The remaining copper may be accounted for by grains of native copper found in association with B-9-10, and also by trace amounts in the interstitial brown oxide (hematite?) and pyroxene. The concentration of copper in pyroxene and brown oxide is unknown. Assuming all the copper to be in the native state then 0.05 wt% native copper is required to make up the difference.

Grains of native copper were mounted and polished for probe analysis. The copper counts corresponded well with a pure copper standard. Significant quantities of other metals were not detected. Analysis were done for Ag, Zn, As, S, Fe, Pb.

B. Fluid Channels

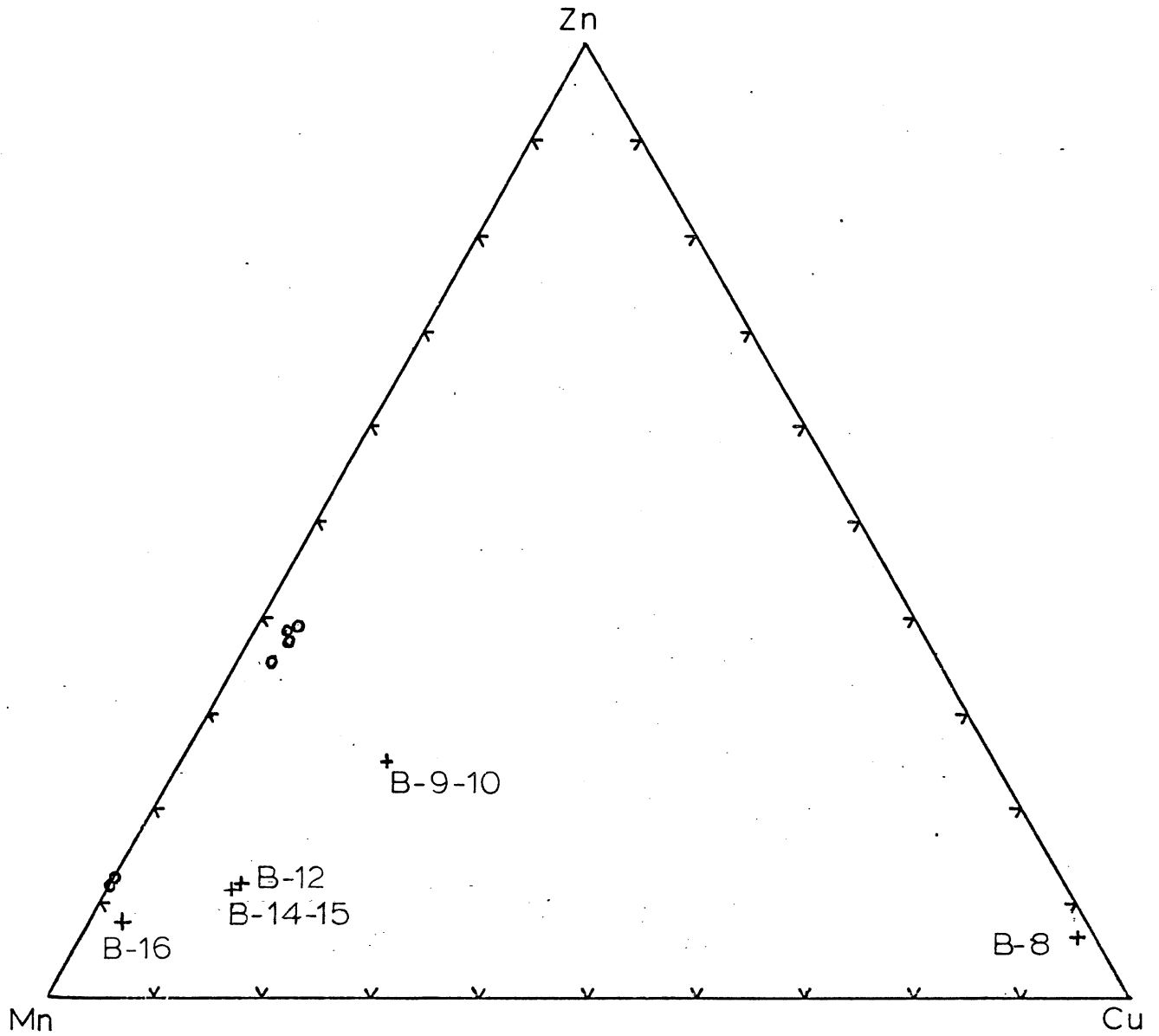
At Margaretville fractures observed in parts of the sampled flow contained zeolites with specks of native copper as well as green copper oxide. A pipe amygdale (12) and the adjacent basalt (12A) were sampled at Margaretville. The pipe amygdale has almost twice the concentration of copper as that in the adjacent basalt. Manganese, titanium, and zinc are slightly higher, while nickel and chromium are reduced by 50%. A brecciated fault zone was sampled at Cape Split. A central fissure (B-8) is filled with purple quartz, surrounding a thin, irregular sheet of native copper with copper oxide, zeolites, and calcite. A four-metre brecciated zone surrounds the quartz vein (Fig. 22). The breccia consists of basalt blocks enclosed in a matrix of

Zoning in the
(Fig 22) Cape Split Fault Zone



Cu	57	271	226	481	636
Zn	146	284	231	638	10
Mn	1572	1868	1467	1385	44

Concentrations are given in ppm.



(Fig. 23) Zinc-Manganese-Copper Variation
in the Cape Split Fault Zone

+ whole rock

o magnetite

highly sheared rock. Plates of native copper up to several centimetres wide are found in this matrix. Samples B-9-10, B-12, and B-14-15 represent a lateral section of the breccia zone. The undeformed host rock is represented by B-16 (Fig. 22). The appearance of native copper and secondary quartz and zeolites in faults and fractures, and the high Cu, Zn, and Mn values in pipe amygdales suggest that these features were once permeable channels for migrating fluids.

The analyses of rocks from Cape Split were plotted on a Zn - Mn - Cu diagram (Fig. 23). The undeformed host basalt and the quartz vein plot on opposite ends of the variation. Copper and zinc are considerably enriched in the breccia. In the breccia Mn decreases from the basalt contact toward the central quartz vein, as Cu and Zn increase. Copper is the only significant metal in the quartz vein.

Magnetite element concentrations are plotted in the Zn - Mn - Cu diagram (Fig. 23). A zinc enrichment at the expense of manganese is apparent. A slight copper enrichment accompanies the higher zinc values, but it is too small to account for copper enrichment in B-9-10.

An explanation must be derived for zinc-copper enrichment in the breccia, and copper-only enrichment in the quartz vein. The fluids migrating through the central fissure probably contained both Cu and Zn. Copper was able to precipitate in the central fissure as well as in the breccia because it was able to form its own phase. Zinc could not

be deposited in the central fissure since it could not form its own phase due to the absence of sulphur. In the breccia zone, zinc may have been adsorbed by clay in the altered glass. The close association of Zn with magnetite suggests that it is found in the magnetite or in the hematite forming by oxidation of magnetite.

The high concentration of Mn in the magnetite suggests that the original Mn concentrations were in magnetite, as in the Keweenaw lavas (Cornwall, 1957). During the oxidation of the magnetite Mn could have been progressively removed toward the central fissure. It is not absolutely clear whether increasing manganese concentrations away from the central fissure are an indication of less alteration or a secondary manganese enrichment.

C. Zeolites

From the evidence presented in Chapter 3, it seems possible that Cu, Zn and Mn were mobilized during zeolite facies metamorphism in the North Mountain basalt. Therefore, in order to obtain a probable temperature range and depth of burial, the zeolite content of various locations was investigated. Previous work on North Mountain zeolites has been done by Walker and Parsons (1922) and Aumento and Friedlander (1966).

Although the primary objective was to investigate

TABLE 4A

Secondary Minerals - Order of Crystallization as
interpreted by Aumento (1966)

First Formed (Low Temperature)	Quartz
	Chabazite-Gmelinite
	Stilbite
	Heulandite
	Laumontite
	Apophyllite
	Analcite
	Thompsonite
Last Formed (High Temperature)	Natrolite-Mesolite

properties of individual zeolites, Aumento did report a sequence of crystallization by observing mineral association in cavities. This is given in Table 4A. Aumento and Friedlander (1966) suggested that the flows in the northeast are at a lower stratigraphic section than in the southwest. They also presented a sketch map showing the westernmost location of certain zeolites.

Using the sketch map as a criterion for the westernmost occurrence of particular zeolites, an attempt was made, in this study to construct zeolite assemblages at the various sampling locations (Table 4B). The constructed assemblages were compared to sodium and calcium zeolite assemblages summarized by Miyashiro and Shido (1970). At each location lower temperature zeolites occurred with higher temperature assemblages. The lowest temperature starts somewhere between 0°C and 150°C and may go up to $260-300^{\circ}\text{C}$. At Cape Split, Halls Harbour and Margaretville the maximum temperature was somewhere between ($150-200^{\circ}\text{C}$) and ($260-300^{\circ}\text{C}$). At Centreville the maximum temperature was a little under ($150-200^{\circ}\text{C}$). According to the map of Aumento et al. (1966), no zeolites should occur at East Ferry.

When compared to the zeolite zones from eastern Iceland (Walker, 1960a), those of Cape Split, Halls Harbour, Margaretville and Centreville would fall into the scolecite-laumontite zone. The first three zones reported by Walker in order of increasing temperature are (1) slightly zeolitized

Table 4B

Icelandic Zones (Walker 1960) Of Zeolites From Aumento's Sketch Map

Location	Zeolites	Slightly Zeolitized	Analcite Heulandite	Scolecite Laumonite
Cape Split	Apophyllite			
	Laumonite			
	Analcite			
	Calcite			
	Heulandite			
	Stilbite			
Halls Harbour	Apophyllite			
	Laumonite			
	Analcite			
	Calcite			
	Heulandite			
	Stilbite			
	Natrolite			
	Thompsonite			
Margaretville	Laumonite			
	Analcite			
	Calcite			
	Heulandite			
	Stilbite			
	Natrolite			
	Thompsonite			
	Centreville			
Calcite				
Heulandite				
Stilbite				
East Ferry				

zone, (2) analcite-heulandite, and (3) scolecite-laumonite zone. Walker estimates that the top of the analcite zone was originally buried 600 metres.

In order to complement the work of Aumento et al. (1966), zeolites from Cape Split, Halls Harbour, Margaretville, and East Ferry were separated from the sample rocks and analysed by x-ray diffraction. Some problems were encountered with shifting peaks and zeolites masking each other. Since no standard was run, zeolites were identified when the three most prominent peaks of a particular zeolite were found. A small amount of peak shift was taken into account. The identified zeolites are presented in Table 4C. Probably due to the smaller size of the sample area, not all the zeolites that should have been in some localities were detected. Differences in grinding techniques can also alter the diffractograms (Aumento et al., 1966). Using the assemblages reported by Miyashiro and Shido (1970), all the locations had the same maximum temperature, somewhere just under (150° - 200° C). The lack of detected laumonite gave a lower temperature in the east than shown by the zeolite map of Aumento. However, laumonite was seen in some large cavities in the field. The analysed zeolites were taken from vesicles in the sampled rocks. These vesicles may already have been filled during laumonite deposition, which was then restricted to more permeable cavities. Sampling amygdale zeolites only, could miss the laumonite. During

Table 4C

Icelandic Zones (Walker 1960) of Zeolites From X-ray
Diffraction Results

Location	Zeolites	Slightly Zeolitized	Analcite Heulandite	Scolecite Laumonite
Cape Split	Clinoptilolite		-----	
	Heulandite		-----	
	Analcite			
Halls Harbour	Clinoptilolite		-----	
	Heulandite		-----	
	Levynite		-----	
	Analcite			
Margaretville	Scolecite			
	Chabazite		-----	
	Gmelinite?			
	Clinoptilolite		-----	
	Heulandite		-----	
	Analcite			
	Thompsonite		-----	
East Ferry	Natrolite			
	Scolecite			
	Chabazite		-----	
	Heulandite		-----	
	Calcite			
	Celadonite			

alteration to leonardite, laumonite peaks could have been obscured. Therefore, the temperature difference may be due to differences in sampling. All the localities again fall into the Icelandic scolecite laumonite zone.

The temperatures estimated above should be viewed with some caution as they are based on experimental work. In zeolite synthesis $a_{\text{H}_2\text{O}}$ is known, while in natural systems $a_{\text{H}_2\text{O}}$ might be considerably reduced by dissolved salts and gases (Zen and Thompson, 1974). In low grade metamorphism the attainment of equilibrium is much more difficult than under higher temperatures and pressures (Zen and Thompson, 1974). Therefore, when comparing natural and synthetic assemblages, one cannot be sure that either one is in equilibrium. Another problem is that experimental work is normally done with $P_{\text{Fluid}} = P_{\text{Total}}$. In most natural systems under low pressure P_{Fluid} is less than P_{Total} . In such instances actual depths of burial may be considerably less than predicted by pressure-temperature diagrams based on $P_{\text{H}_2\text{O}} = P_{\text{Total}}$.

The presence of zeolites indicates a high $a_{\text{H}_2\text{O}}$ and low a_{CO_2} (Zen, 1961). Otherwise assemblages of calcite-kaolinite-quartz or calcite-pyrophyllite-quartz may dominate.

Comparing a summary of several metamorphic terrains (Zen, 1974), the depth of burial of the eastern zeolites could have been between 0.5 km and 4 km. A comparison of zeolite assemblages in Iceland might suggest a depth

of about 670 metres for most of the North Mountain.

Summary of Zeolite Information:

1. Temperature: from under 150°C to 260-300°C
2. Depth: 0.5 - 4 km
3. High $a_{\text{H}_2\text{O}}$
4. Low a_{CO_2}
5. Possible decrease in grade to the southwest.

D. Mechanisms of Cu, Zn and Mn Distribution

Proposed mechanisms of element redistribution must account for: (1) Lack of Zn-Cu correlation, (2) Lack of Mn-Cu correlation, (3) A poor Zn-Mn correlation (4) Element enrichment at Ross Creek and (5) Zonation in the Cape Split fault zone.

Before construction of a model the following assumptions have been made.

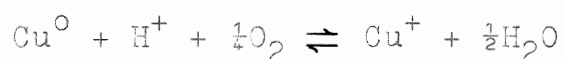
1. Low f_{S_2} is indicated by the general lack of sulphides. Jolly (1974) suggests that in low-pressure environments S^{-2} is oxidized to SO_2 and escapes to the atmosphere.
2. A large percentage of copper precipitates in the native state. Green copper oxides are seen associated with native copper. In most cases the copper oxide is just a stain since x-ray diffraction analyses of copper stained zeolites failed to identify a copper phase. The relation of copper oxide to weathering is not clear. Therefore, precipitation of copper is assumed to take

place as a result of reduction of Cu^+ to Cu^0 .

3. Metal-bearing solutions often have 5 to 40 weight percent NaCl (White, 1968). Jolly (1974) proposed chlorine complexes as a mechanism for moving copper and zinc in the Keweenawan lavas. Since hydrothermal solutions in basalts and other rocks commonly have some amounts of NaCl, it is probable that enough chloride was present in the North Mountain to move metals as chloride complexes.
4. The pH is unknown, but probably is not more than two pH units either side of neutrality (Krauskopf, 1967). Acid solutions are neutralized by hydrolysis with silicates. Basic solutions are neutralized by reaction with silica. The neutral pH varies as the ionization constant of water changes with temperature.
5. From zeolites the given temperature range is 150°C to $(260^\circ\text{C}-300^\circ\text{C})$. The depth is 0.5 - 4km. The a_{CO_2} is low. The origin of fluids responsible for metal transport is not known. They might have been recirculated meteoric water. The fluids may also have been connate water in the underlying sediments. Burial by a lava pile would dehydrate the sediments. The distance of element transport is also unknown. Elements could have been redistributed in the same flow, as indicated by the large variation in copper at the sampled Margaretville flow. The fault zone at Cape Split suggests transport between flows or from underlying sediments. Liberation of metals from basalt could be accomplished by brines at a temperature around 200°C . Bischoff (1975) reacted basalt with seawater at 200°C and 500 bars for

4752 hours. Plagioclase and pyroxene were unaffected, yet glass had altered to montmorillonite releasing Ca, SiO₂, Fe, Mn, Cu, and Ni. The pH was initially lowered to 3.2 from 5.2 as H⁺ was released from glass, but as H⁺ attacked glass and anhydrous silicates pH rose to 4.9.

Precipitation of native copper could be controlled by the equilibrium: (Jolly, 1974)



$$K_t = \frac{(a_{\text{Cu}^+}) (a_{\text{H}_2\text{O}})^{\frac{1}{2}}}{(a_{\text{Cu}^0}) (a_{\text{H}^+}) (f_{\text{O}_2})^{\frac{1}{2}}}$$

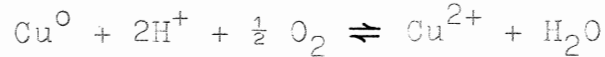
$a_{\text{H}_2\text{O}} = 1$
 $a_{\text{Cu}^0} = 1$
 $a_{\text{Cu}^+} = (\gamma_{\text{Cu}^+}) \times (m_{\text{Cu}^+})$

$$K_t = \frac{(m_{\text{Cu}^+}) (\gamma_{\text{Cu}^+})}{(a_{\text{H}^+}) (f_{\text{O}_2})^{\frac{1}{2}}}$$

- K_t = equilibrium constant)
 - γ_{Cu^+} = activity coefficient of Cu⁺)
 - f_{O_2} = molarity of Cu⁺)
 - m_{Cu^+} = molarity of Cu⁺)
-) calculated by Helgeson (1969)

The presence of magnetite and hematite provides a buffer for oxygen fugacity. Using the data of Helgeson (1969) for values of K_t , γ_{Cu^+} and f_{O_2} , Jolly calculated possible Cu⁺ concentrations at a pH of 7.2 and at various temperatures (Table 5). Using Helgeson's data, concentrations

of Cu^+ have been calculated for $\text{pH} = 6$. Also, corresponding concentrations of Cu^{2+} have been calculated for the possible equilibrium:



From Table (5) it appears that very low concentrations of Cu^{2+} are found in equilibrium with Cu^0 . Although Cu^{2+} may be quickly removed from solution in the presence of copper reduction, it may not be as important for the precipitation of native copper as Cu^+ since the Cu^+ forms the highest copper concentration in chloride solutions (Jolly, 1974). Table (5) illustrates that copper precipitation is favoured by an increase in pH, a decrease in NaCl concentration, and particularly by a drop in temperature from 250°C to 150°C .

Initially Cu^+ would have been more soluble at higher temperature and the slightly lower pH produced by glass alteration. Precipitation of Cu^0 could have occurred as:

- (1) pH returned to a higher level.
- (2) Temperature dropped sharply as the fluid expanded when pressure was released in a fault zone, such as at Cape Split.
- (3) The fluids encountered a strongly oxidizing couple (such as Mt-Hm), which would supply electrons for the reduction of copper.

Zinc and manganese cannot be reduced in the presence of copper reduction (Krauskopf, 1967; p240 and Appendix IX).

A different mechanism is required to explain concentrations of zinc and manganese. Magnetite may hold

Table 5

Concentrations of Cu^+ in Solution (ppm)

I	NaCl	pH	50°C	100°C	150°C	250°C	300°C
	*3 molar	7.2	0.09	1.33	11.56	1,790	34,123
	3 molar	6.0	1.37	21.04	185.37	28,382	547,075
	1 molar	7.2	0.01	0.13	1.17	284	4,346
		6.0	1.37	2.10	18.54	4,498	68,872

Concentration of Cu^{2+} in Solution (ppm)

II	NaCl	pH	50°C	100°C	150°C	250°C	300°C
	3 M	7.2	4.71×10^{-13}	1.08×10^{-11}	2.36×10^{-10}	4.40×10^{-7}	4.93×10^{-6}
	3 M	6.0	1.18×10^{-10}	2.71×10^{-9}	5.93×10^{-8}	1.10×10^{-4}	1.24×10^{-3}

$$I \quad M_{\text{Cu}^+} = \frac{Kt (a_{\text{H}^+}) (f_{\text{O}_2})^{\frac{1}{2}}}{(\gamma_{\text{Cu}^+})}$$

$$\gamma_{\text{Cu}^+} = f(\text{salinity})$$

$$f_{\text{O}_2} = f(\text{Temperature})$$

$$a_{\text{H}^+} = 10^{-\text{pH}}$$

$$II \quad M_{\text{Cu}^{2+}} = \frac{Kt (a_{\text{H}^+}) (f_{\text{O}_2})^{\frac{1}{2}}}{(\gamma_{\text{Cu}^{2+}})}$$

I Illustrates that Cu^+ concentration (solubility) increases with (1) Lower pH, (2) Higher Temperature, (3) Higher Salinity

* Jolly (1974)

significant amounts of Zn and Mn (Wedepohl, 1970). In sample B-9-10 magnetite can account for Zn and Mn concentration. Zinc may substitute for Fe^{2+} in magnetite since both have the same ionic radii and charges and have similar electronegativities. Mn^{2+} is also believed to replace Fe^{2+} in magnetite (Cornwall, 1957).

Table 6 - Comparison of Fe, Zn and Mn

	Fe^{2+}	Zn^{2+}	Mn^{2+}
Ionic Radius	0.74	0.74	0.80
Electronegativity	1.8	1.7	1.5

In most cases the Mn and Zn content of magnetite is primary or has been depleted by remobilization. Since the electronegativity and ionic radius is closer to Fe^{2+} for Zn^{2+} than Mn^{2+} , the Zn might have a tendency to replace Mn in magnetite. A reduction of Mn at the expense of Zn is noted in the magnetite from Cape Split (Fig. 23).

In order to enter the magnetite structure during alteration zinc would have to enter a magnetite which was forming at low temperature. In the Cape Split sample it is not known whether the magnetite is low temperature, and it is also not clear whether the zinc is actually in the magnetite structure. The Zn concentration of 3.49 wt% appears to be rather high for a magnetite. Highest reported Zn in magnetite is 4,000 ppm from a mafic dyke

in North Carolina (Wedepohl, 1970). The Zn at Cape Split probably is loosely associated with magnetite.

In general, it is difficult to find a mechanism of zinc precipitation in the North Mountain basalt because of the low f_{S_2} . Zinc and manganese may substitute for Fe^{2+} in secondary oxides or in chlorite. Zeolites may also have concentrated trace metals by adsorption or cation exchange. Clinoptilolite has been observed to remove Cu and Zn from soils (Mumpton, 1977).

Ross Creek stands out from the other sampled locations because of mutual Cu - Zn - Mn enrichment toward the top of the section. The sampled flow at Ross Creek is overlain nonconformably by siliceous shales and sandstones of the Scots Bay Formation. Fish bones have shown the Scots Bay rocks to have been deposited in a lacustrine environment. Conditions may have been sufficiently oxidizing to permit the formation of manganese oxides in the fractured and vesicular basalt near the lake bottom. Weathering may also have produced clays in the fractures and hollow vesicles of the basalt. During burial and mobilization of Cu and Zn, these metals may have been adsorbed by the Mn hydroxides or the clays.

Further sampling of the basalt and sediments should be carried out to see if the high metal concentrations in the basalt-sediment contact are real and to establish whether the Scots Bay Formation has been enriched with metals from the basalt. If the high metal concentrations are real

an attempt should be made to determine which phases concentrate metals.

E. Conclusions

The North Mountain basalt is a quartz-normative tholeiite which has undergone zeolite facies metamorphism as high as the scolecite-laumonite zone (Walker, 1960). The variation of Ni, Cr, and Ti has not been affected by burial metamorphism as shown by their good co-variation in Fig. 16. The Ni, Cr, and Ti have distributions controlled by fractional crystallization. The Ni^{2+} substitutes for Mg^{2+} in olivine and pyroxene, while Ti^{4+} and Cr^{3+} substitute for Fe^{3+} or Al^{3+} in pyroxene and particularly spinels. The coarse grained rocks at Centreville and East Ferry appear to be earlier differentiates, richer in Ni and Cr and lower in Ti than rocks from Margaretville, Halls Harbour, Ross Creek and Scots Bay.

When Cu, Zn, and Mn are compared to the differentiation index $\frac{\text{Ti}}{\text{Cr} + \text{Ti}}$, poor correlations exist, except in certain massive flows. Variation of Cu, Zn and Mn is greater in zeolite-bearing flows. This might result from a higher degree of element mobility during metamorphism. Average copper concentration tends to be higher in zeolite-rich sections, although the larger standard deviation makes this statistically indistinguishable from massive sections (Table 1). The average concentrations of the remaining elements tend to be

depleted in zeolite-bearing sections (Margaretville), or else show no significant difference. In massive flows, copper and titanium are lower at East Ferry and Centreville, while Ni and Cr are higher.

No co-variance is shown between Cu and Zn. Only some local co-variances are found between Cu and Mn; and between Mn and Zn. With the exception of Ross Creek and Cape Split, there is a trend toward Cu enrichment in a Cu-Zn-Mn diagram (Fig 15).

Copper is probably transported by chloride complexes and precipitated by reduction to Cu^0 . Primary distributions of zinc and manganese are often affected by leaching during burial metamorphism. Enrichment of Cu, Zn, and Mn may occur by adsorption in chlorite, zeolites, or clays. Enrichment of Cu and Zn in the glassy crust at Scots Bay may be due to concentration in clay minerals formed by alteration of glass. The precipitation of Zn is made difficult by the absence of sulphide.

The copper deposits on the Keweenaw Peninsula, Michigan, have apparently undergone a greater degree of burial metamorphism to prehnite-pumpellyite facies while the North Mountain has undergone only zeolite facies metamorphism. Broderick (1929) has described an increase in percent As in native copper with greater depth in the Keweenaw basalts (up to 0.5%). No As was detected in native copper from the North Mountain, possibly indicating a shallower depth.

Copper concentrations found in this study were far below economic levels. Fault zones such as at Cape Split are too small in volume, even if they did have high grade ore. Douglas (1942) did not consider the native copper, occurring in cross-cutting breccia zones at Cap d'Or, to exist in sufficient quantity for economic recovery. Perhaps the grade of burial metamorphism was too low in the North Mountain to have produced adequate copper mobilization and concentration for an economic deposit.

APPENDIX A: ANALYTICAL PROCEDURE

Trace element analyses were carried out on two batches of samples. The first batch was analysed in September of 1977, while the second group was processed in December of 1977. A total of 57 rocks was analysed.

In the preparation of the first batch, sample chips were crushed in an iron cylinder with a rock hammer. The samples were then ground by hand with an agate mortar and pestle.

The rock powders were dissolved in teflon bombs with screw caps. To each bomb 0.500 gm of rock powder was added. This was wetted with one ml of aqua regia (3:1 HCl:HNO₃). Then 6 ml of HF were added and the bombs were tightly sealed. The samples were kept at 80° - 90° C for two hours to allow for complete dissolution.

A solution of H₃BO₃ was prepared for each bomb (5.6 gm of H₃BO₃ in 20 ml of distilled H₂O). Upon cooling, the contents of the bombs were poured into the H₃BO₃ solution. After a thorough rinsing the samples were left overnight to allow for optimum dissolution. The solutions were later bulked to 100 ml.

The solutions were analysed for trace elements at the Bedford Institute of Oceanography, using a Perkin-Elmer 503 atomic absorption apparatus. Readings were given in absorbance by a digital read out and were recorded by a

chart recorder. Analyses were carried out in repeat mode so that strong noise would easily be detected. (Readings are automatically repeated and not integrated over a time period.)

The sample absorbance was calibrated by a synthetic standard prepared by Bob Fitzgerald at B.I.O. A solution of W-1 was analysed for Cu and found to be within 2% of expected standard W-1 value.

The samples processed in December were reduced to powder at Dalhousie University. The rocks were chipped with a hydraulic press. Crushing was done in a porcelain jaw crusher. The crushed samples were ground in a tungsten carbide swing mill.

Sample solutions were prepared in the same way as before. However, this time the amount of sample was a measured value ($\pm .0001$ gm) near 0.5 grams.

The sample absorbances were compared to W-1. Basalt standard 580 acted as an external standard.

Table A1

Comparison with Standard 580

	Clarke (XRF)	Vilks (AAS)
Cu	245	219
Zn	87	127
Mn	1626	1522
Co	-	38
Cr	68	78
Ti	15287	8773*
Ni	79	42

* Value for Ti appears rather low. Problems were encountered with low Ti in the first batch, which probably were related to the synthetic standard used.

Sinha's values range from 2760 to 9830 ppm Ti.

Vilks' values range from 3324 to 6263 ppm Ti.

Table A2

Comparison of W-1 Standard Values

	Values Used	Flanagan (1972)
Cu	110	110
Zn	82	86
Mn	1363	1278
Co	50	47
Cr	120	114
Ni	78	76
Ti	1080	-

Table A3

Duplicate Analysis

Sample	Element	September	December
A 4	Cu	86	79
	Zn	79	85
	Mn	1444	1308
	Co	35	38
	Cr	108	152
	Ti	5278	4894
	Ni	56	51
A 6	Cu	42	35
	Zn	51	69
	Mn	987	717
	Co	32	37
	Cr	52	136
	Ti	4830	5020
	Ni	48	46
1	Cu	129	131
	Zn	46	61
	Mn	921	760
	Co	35	34
	Cr	138	184
	Ti	4830	5169
	Ni	48	42

Table A4

September Analysis

Sample	Cu	Zn	Mn	Co	Ni	Cr	Ti
A 1	63	46	1039	32	52	118	5278
A 2	49	52	1145	32	56	123	5188
A 3	78	40	974	32	52	103	4830
A 4	86	79	1444	35	56	108	5278
A 5	45	50	1053	32	48	92	5009
A 6	42	51	987	32	48	52	4830
A 7	49	54	1039	32	44	82	5009
A 8	185	58	1569	32	20	103	4830
A 9	31	132	1264	35	48	144	5009
A 10	114	45	1013	32	46	138	4830
A 11	35	42	803	32	46	138	4830
A 12	45	38	803	35	44	108	4651
1	129	46	921	35	48	138	4830
2	358	45	529	35	48	97	4141
3	106	139	1417	38	52	168	5009
4	56	57	855	38	52	168	5009
5	45	55	1013	42	52	201	4141
5B	49	80	1079	35	56	179	4919
6	63	46	868	38	52	185	4651
7	102	42	882	20	48	87	4651
8	86	53	1026	20	48	97	5009
9	63	84	1145	20	52	87	6263
10	59	57	987	32	52	149	4651
11	52	81	1026	35	52	163	4830
12	180	99	1417	38	20	48	7338
12A	98	77	1184	38	54	174	5009
13	246	107	1132	35	9	11	8950
14	52	82	1145	38	54	128	4141
15	59	58	1306	42	56	234	5009
16	38	52	987	35	52	108	3976
17	98	52	974	38	48	149	5009
18	45	57	1132	42	48	123	5367
\bar{x}	88	64	1067	34	47	122	5045
s	69	25	212	6	11	46	949

Table A5December Analysis

Sample	Cu	Zn	Mn	Co	Ni	Cr	Ti
HH 1	100	89	1082	38	42	134	5098
HH 2	83	64	971	48	38	135	4982
HH 3	121	75	1151	56	53	98	5090
HH 4	162	56	619	35	40	129	5418
HH 5	138	63	771	38	32	109	4104
HH 6	96	77	909	44	50	109	4593
HH 7	96	73	1011	37	47	138	4477
HH 8	134	62	673	46	36	96	4480
HH 9	118	68	685	40	38	90	4435
Cent. 0	24	68	1170	53	77	426	3442
Cent. 7	26	71	1071	39	73	380	3570
Cent. 15	10	76	950	36	79	389	3593
Cent. 25	38	90	1120	38	84	332	3937
East Ferry 0	20	70	960	45	74	373	3612
East Ferry 10	32	72	1095	37	74	386	3324
East Ferry 15	20	69	1185	39	78	447	3593
East Ferry 50	31	65	935	49	80	373	3650
B-8	636	10	44	36	7	0.0	0.0
B-9-10	481	638	1385	42	29	156	5625
B-12	226	231	1467	37	55	145	5650
B-14-15	271	284	1868	36	56	148	5643
B-16	57	146	1572	37	43	165	5214
F 1	62	81	696	38	50	90	5079
F 2	70	88	567	37	42	102	5210
F 3	136	471	1269	44	54	95	5053
A 4	79	85	1308	38	51	152	4894
A 6	35	69	717	37	46	136	5020
l	131	61	760	34	42	184	5169
\bar{x}	128	120	1009	41	53	204	4587
s	147	135	368	6	20	125	745

Appendix B - Photomicrographs

Cape Split: Sample B-9-10 (Fig. B) from the brecciated zone is dominated by an interstitial brown oxide which appears black in the photo. Magnetite grains tend to be obscured by this oxide. A chlorophaeite is visible in the brown oxide.

Sample B-16 (Fig. B2) is the unaltered basalt around the fault zone. Feldspars and pyroxenes are less altered. Primary magnetites are easy to distinguish.

Halls Harbour: HH-4 (Fig. B3-B5) is a flow top with 35% zeolite. Brown oxide partially replaces glass. Plagioclase and pyroxene are very altered. Secondary magnetite is found rimming zeolite filled cavities. A red hematite stains some zeolites.

Sample HH-1 represents the lower part of the same flow (Fig. B6). Plagioclase is sericitized and pyroxenes are fragmented. Secondary magnetite is seen lining some cavities.

Margaretville: Sample A-2 is from the interior of a zeolite-bearing flow (Fig. B7). Only 5% zeolites are present. Primary and secondary magnetite is present. Plagioclase is strongly sericitized. Chlorite gives the rock a green color.

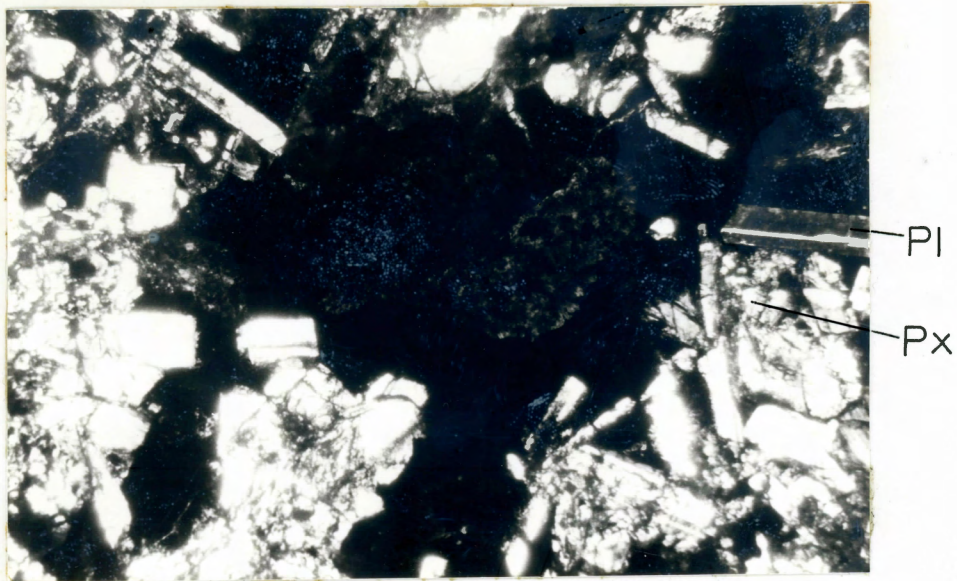
Sample 2 (Fig. B8) is a red zeolite-bearing flow with green copper oxide. The photo shows secondary magnetite in a zeolite matrix. The rock is about 30% zeolite.

Sample A-8 is the red, zeolite-bearing top of a flow (Figs. B11 and B12). The plagioclase and pyroxene are highly altered. Primary and secondary magnetite is present. Fluid inclusions are visible in some zeolites. There are 30% zeolites.

Sample A-7 (Fig. B9) is a massive basalt. Plagioclase is sericitized. Small grains of primary magnetite are visible along with some secondary magnetite around two cavities. Amphibole is seen replacing some pyroxenes.

Sample A-10 (Fig. B10) illustrates an alteration zone of brown oxide surrounding a zeolite cavity.

Centreville: Sample Cent-25 (Figs. B13-B14) is a coarse grained massive basalt. Fig. B13 illustrates an augite pseudomorph replaced by amphibole. Fig. B14 shows another pyroxene phase which remains unaltered. Fresh plagioclase and primary magnetite are present.



(Fig. B1) Cape Split, B-9-10
Crossed nicols

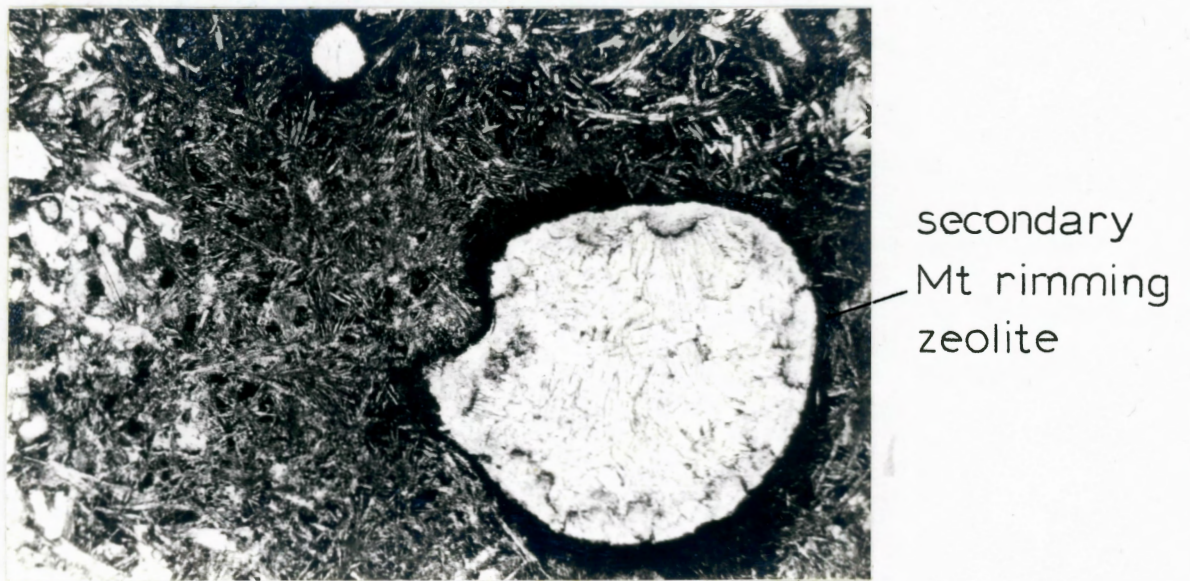


(Fig. B2) Cape Split B-16
Crossed nicols

0 0.5 mm

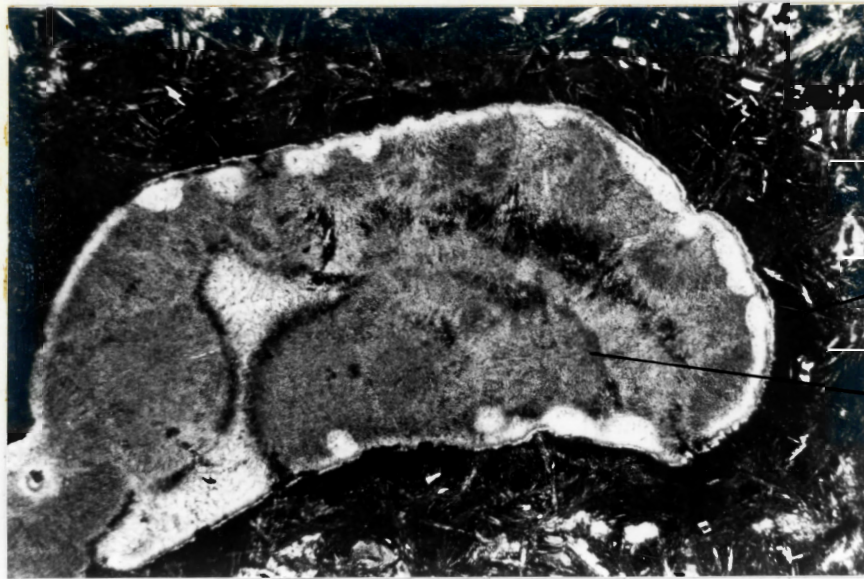


(Fig. B3) Halls Harbour HH-4
Crossed nicols



(Fig. B4) Halls Harbour HH-4

0 0.5



Mt rimming
zeolite
red Hm in
zeolite

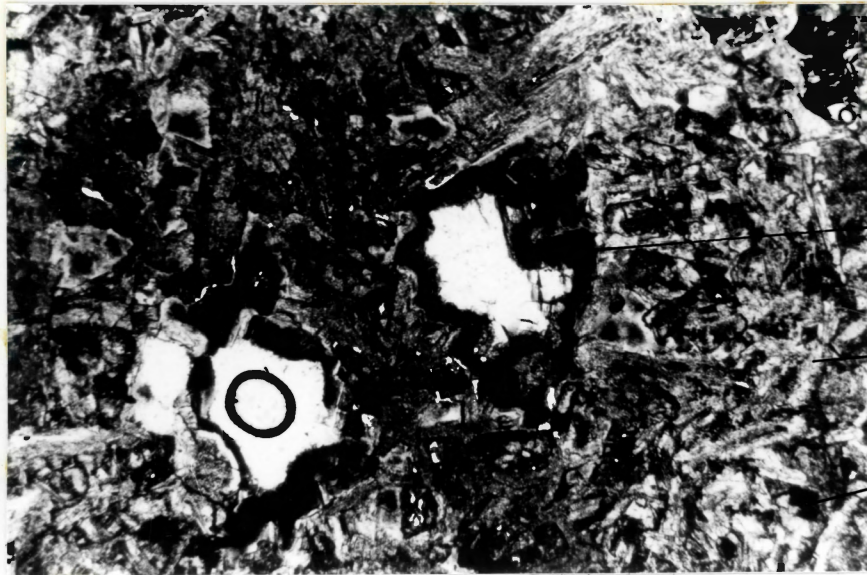
(Fig. B5) Halls Harbour HH-4



sericitized
Pl
primary Mt
secondary Mt

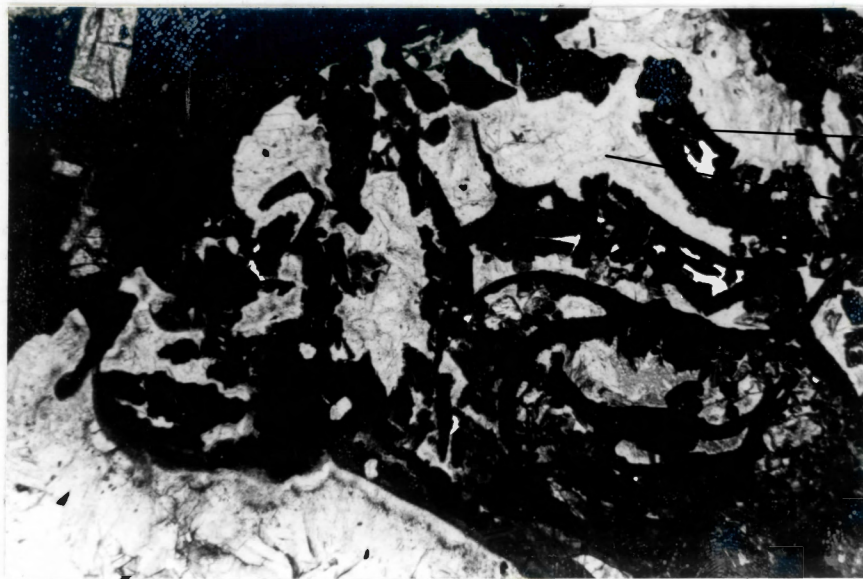
(Fig. B6) Halls Harbour HH-1

0 0.5 mm



secondary
Mt rimming
zeolite
sericitized Pl
primary Mt

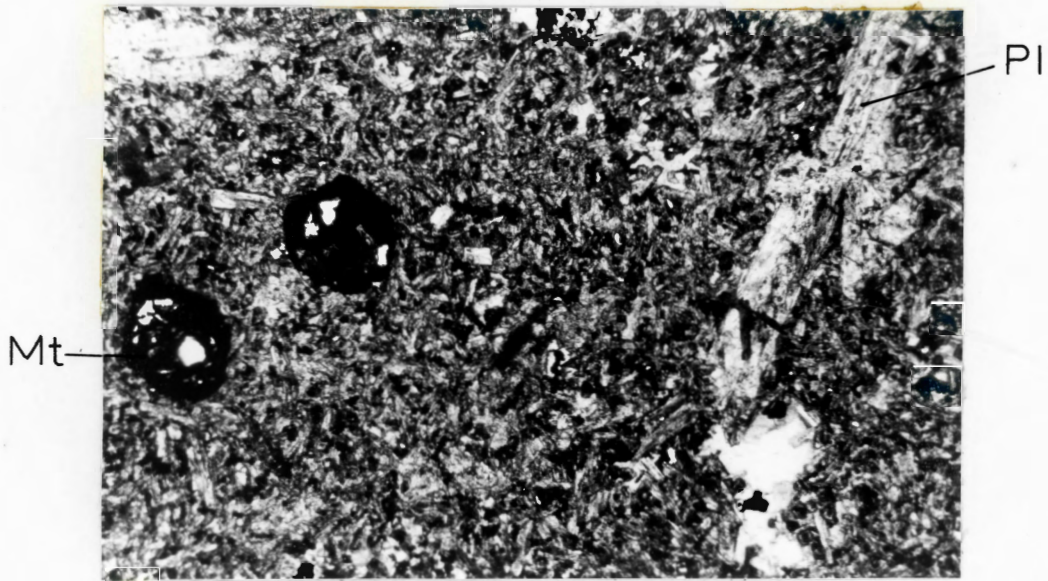
(Fig. B7) Margaretville A-2



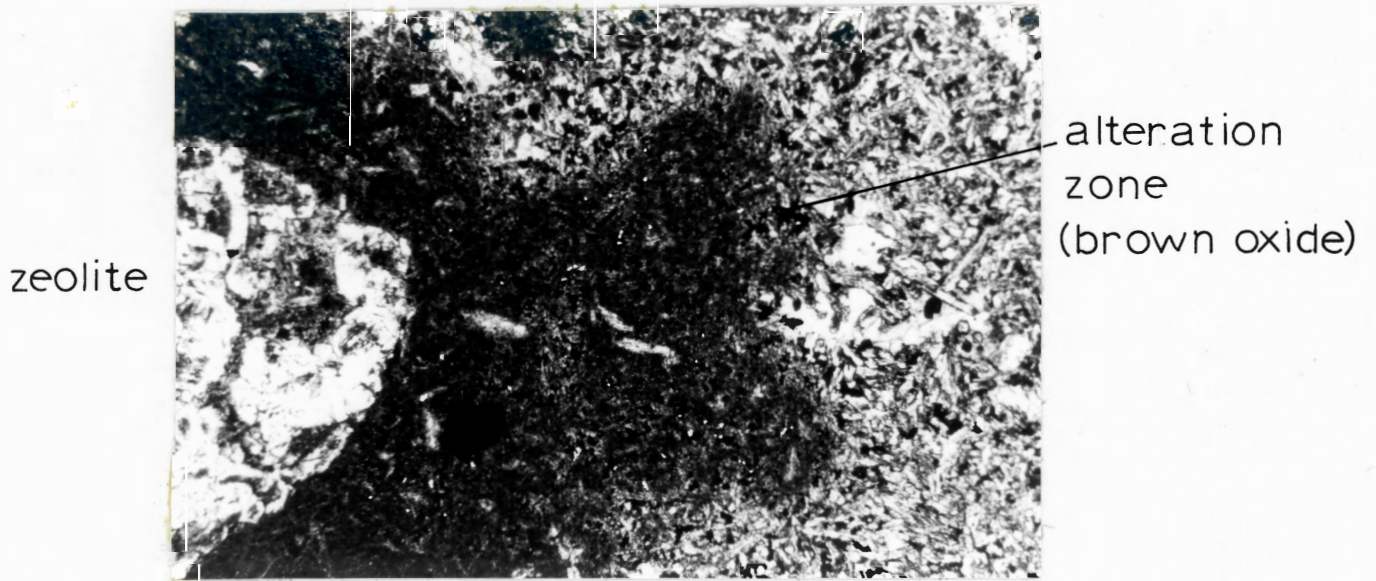
secondary
Mt
zeolite

(Fig. B8) Margaretville

2
0 0.5 mm



(Fig. B9) Margaretville A-9

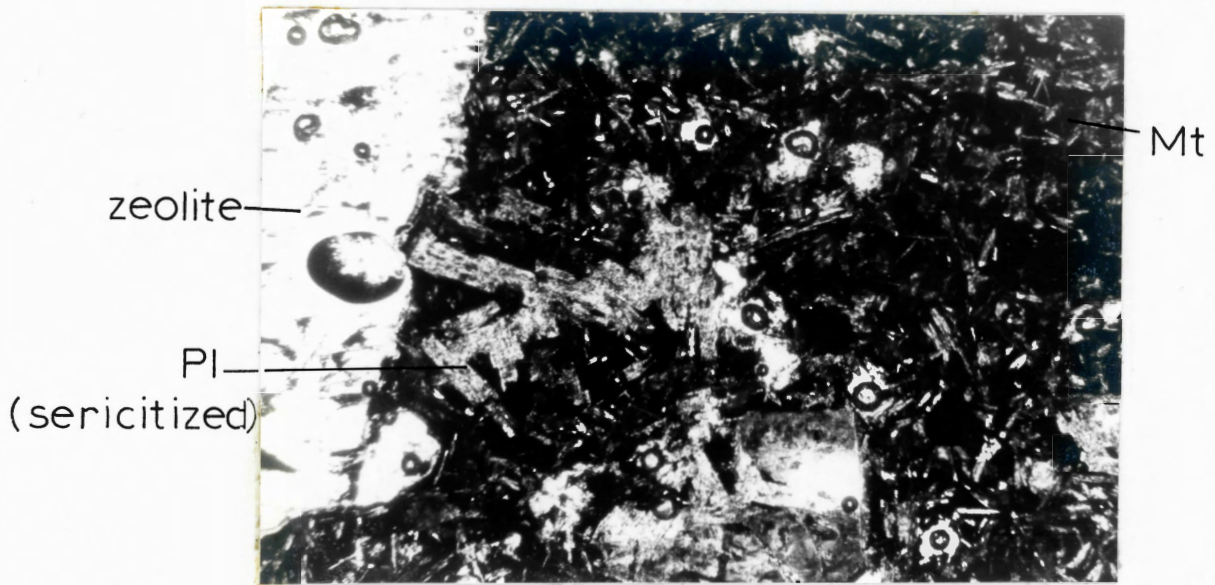


(Fig. B10) Margaretville A-10

0 0.5 mm.

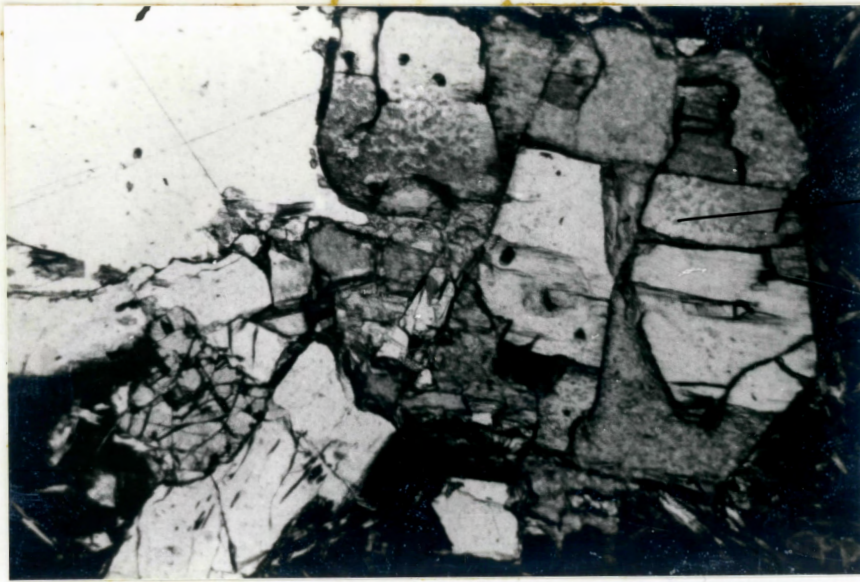


(Fig. B11) Margaretville A-8



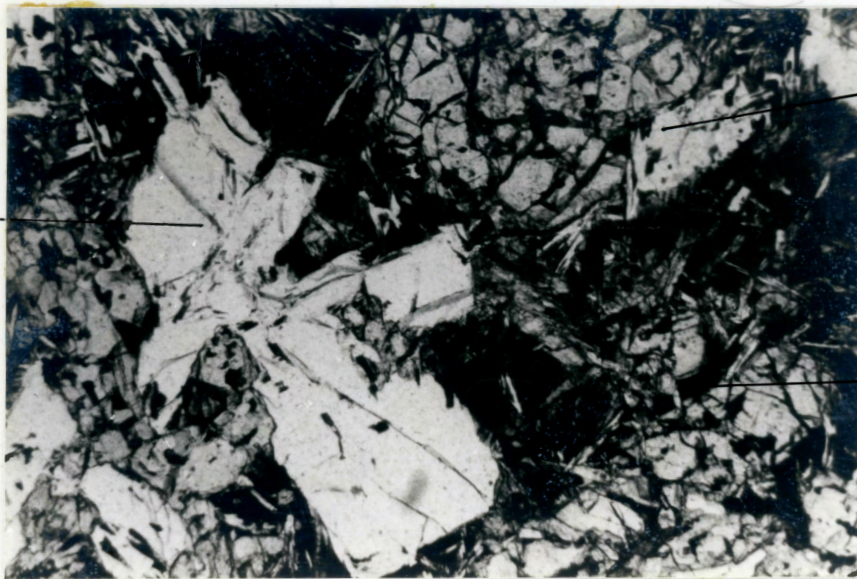
(Fig. B12) Margaretville A-8

0 0.5 mm



augite
replaced by
amphibole

(Fig. B13) Centreville Cent-25



Pl

Px
(unaltered)

Mt

(Fig. B14) Centreville Cent - 25

0 0.5 mm

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