RELATIONSHIP BETWEEN BITUMEN AND COPPER-LEAD-ZINC MINERALIZATION

IN THE MID-SILURIAN CARBONATES IN THE VICINITY OF

HAMILTON, ONTARIO


BY


SHA-PAK CHEUNG


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ABSTRACT

Previous workers in the Hamilton area have pointed out the occurance of lead and zinc mineralization within the Mid-Silurian carbonate beds. They also mentioned the existance of bitumens in these rock units.

Analysis of 30 dolomite samples and seperated bitumens by atomic absorption for Cu, Pb, Zn showed that the localization of the metals in the carbonates was controlled by the concentration of the bitumens in the rocks.

Analysis of 5 bitumens samples by atomic absorption for Cu, Pb, Zn suggested that the bitumens act merely as a reducing agent and are not preferred sites for base metal accumulation.

## ACKNOWLDEGEMENTS

The author wishes to express his sincere gratitude to
Dr. J. H. Crocket who suggested the topic and supervised the
project. Without his patient guidence, the completion of this
thesis would have been impossible.

The author is also indebted to Mr. P. Fung for his assistance
and advice in the analysis procedures.

# TABLE OF CONTENTS

# INTRODUCTION

As early as 1919 (Williams, 1919) there was report on the presence of lead and zinc deposits in the Paleozoic rocks of the Niagara Escarpment and the Bruce Peninsula.

Most of the lead and zinc minerals occured as sulphides especially galena and sphalerite and the deposits were likened to the Mississippi Valley Type Deposits. (Guillett, 1967)

Arround Hamilton, Ontario, galena and sphalerite occur in small amounts in the carbonate rocks of the Niagara Escarpment. However, very little work has been done on them.

As with other Mississippi Valley Type Deposits, galena and sphalerite in the Niagara Escarpment usually occur in the carbonate rock units with organic bitumeneous compounds. The main purpose of this thesis is to study the relationship between the occurrence of the base metal minerals and the bitumens, and to see if the bitumens have any control over the localization of the sulphide minerals.

# GEOLOGY

The geology of the Niagara Escarpment has been discribed by Hewitt (Hewitt, 1971). In general, the exposed bed rocks of the Niagara Escarpment in the Hamilton area are sedimentary rocks of Ordovician (minor) and Silurian ages. These rocks dips about 13' (20 feet per mile) towards the south west. The rocks have remained undisturbed by any major faulting, folding or igneous activity since the beginnning of Paleozoic time.

The classification of the stratigraphy of the Niagara Escarpment in Hamilton area is given in Table 1 (after Bolton, 1957, p.5). The description for each formation or member is given in Table 2. (after Hewitt, 1971, p.25 & Bolton, 1957)

| | | | | Formation | Member |
|---|---|---|---|---|---|
| Silurian | Niagaran Series (M. Silurian) | | Ambemarle Group | Guelph | |
| | | | | Lockport | Eramosa Goat Island Gasport |
| | | Clinton Group | Upper | DeCew Rochester Irondequoit | |
| | | | Mid | | |
| | | | Lower | Reynales Neahga Thorold | |
| | Alexandrian Series (L. Silurian) | Cataract Group | | Grimsby Power Glen Whirlpool | |
| Ordovician | | | | Queenston | |

Table 1. Representative Stratigraphic Section of the Niagara Escarpment in the Hamilton area, Ontario. (after Balton, 1957)

| Formation or Member | Description |
| --- | --- |
| Guelph | light creamy buff, fine or medium crystalline porous dolomite, generally thick bedded; also characterized by reef facies |
| Eramosa | medium to dark brownish grey, aphanitic to sugary, medium to thin bedded, bituminous dolomite with dark grey shale partings, locally solution breccia prominebt. |
| Goat Island | aphanitic to fine crystalline, light buff, brownish grey dolomite containing abundant chert especially near the base |
| Gasport | dolomite, light grey, dense to very fine grey, massive with thin bedded rare thin crinoidal lenses. |
| DeCew | dolomite, grey, dense to very fine crystalline thin to thick bedded, conchoidal fracture mud galls. |
| Rochester | Shale, dark grey, calcareous interbedded with limestone and dolomite. |
| Irondequoit | limestone, dolomitic, grey to reddish brown, massive, dense to crystalline. |
| Reynales | light grey to blue, thin bedded, fine crystalline dolomite with shaly partings, Pentameras abundant, near the base fossiliferous. |
| Nealiga | absent. |
| Thorald | sandstone, grey to blue, fine to medium, crystalline. |
| Grimsby | sandstone, red, green mottled, irregularly bedded, interbedded with red shale. |
| Power Glen | shale, dark grey, to greenish grey, interbedded with calcareous sandstone. |
| Whirlpool | sandstone, white to light grey, massive. |
| Queenston | shale, brick red, green mottled to streaked. |

Table 2.  Description for each Formation and Member in the
Niagara Escarptment around Hamilton, Ontario.

# FIELD WORK

Most of the field work for this thesis had been done on the road cut on Highway 403 and the New Dundas Quarry. Locations are shown in Fig.1.

Stratigraphic sections for the outcrops studied in both areas are shown in Fig. 2.
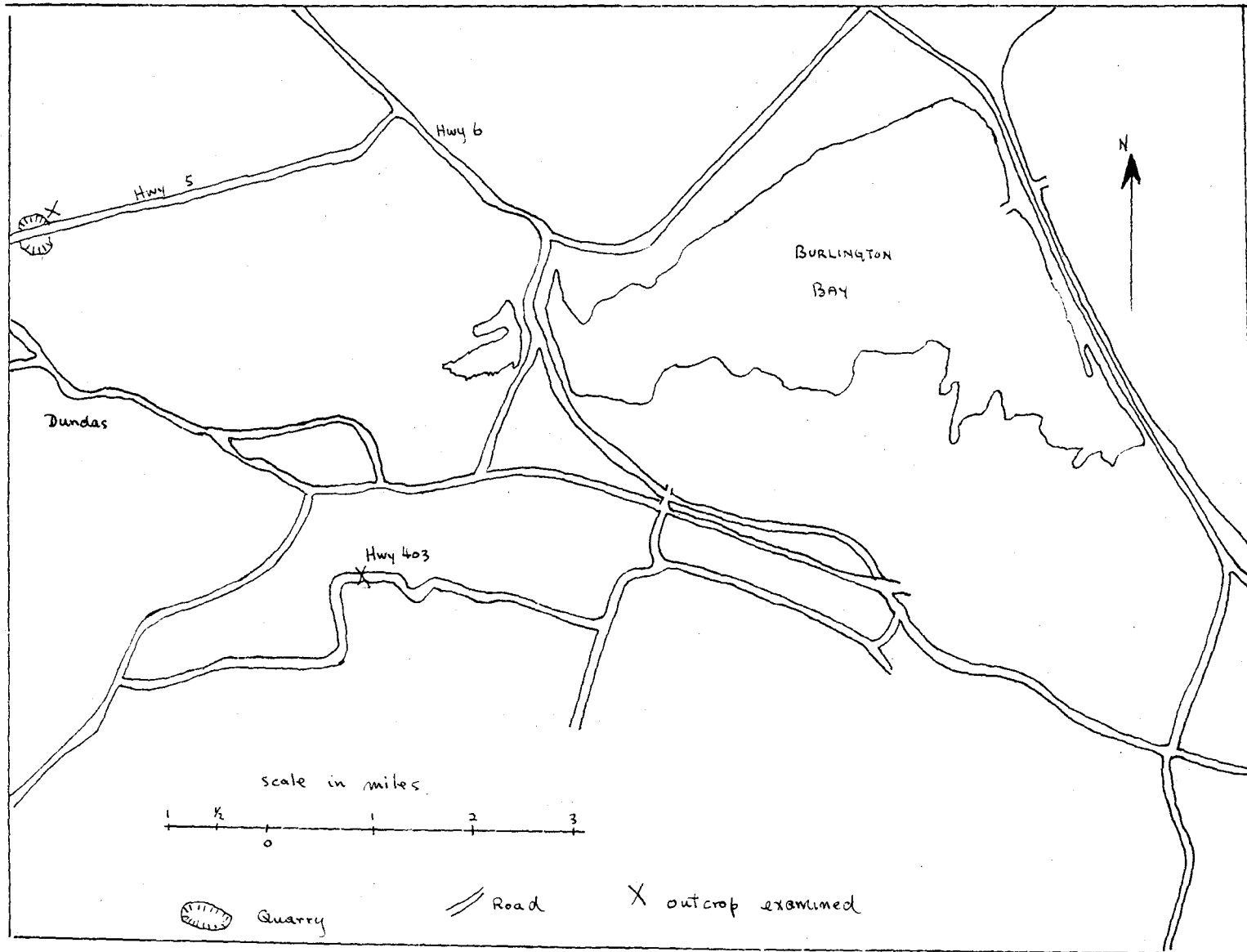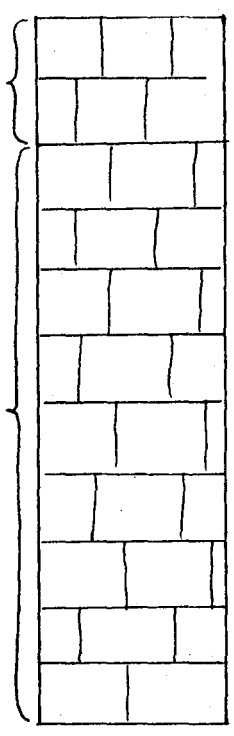
Fig. 1  Map of Dundas Valley Showing Location of Outcrop Visited.
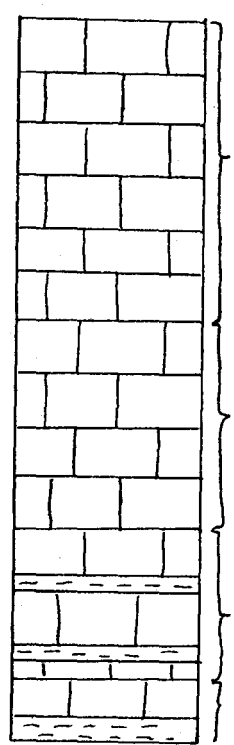
Guelph (8')    Massive, grey dolostone
               with reef facies at base

Eramosa (38')   Massive, grey dolostone,
                bitumenous, sphalerite &
                galena easily observed

New Dundas
Quarry

Hwy. 403

Goat Island (20')   Grey to brown, fine to medium
                    grained dolomite, sphalerite &
                    galena at the upper beds with
                    grey chert at the lower beds

Gasport (16')   grey and buff, medium grained
                dolostone and lomestone

DeCew &
Rochester (10')   grey dolomite and silty shale

Irondequoiut (4')   light grey dolomitic limestone

Fig 2. Stratigraphic Section for the Two Outcrops Visited.

## OBSERVATIONS ON THE OCCURRENCE OF GALENA AND SPHALERITE

From study on the Highway 403 and Dundas Quarrys outcrops,
it is observed neither galena nor sphalerite is restricted to a
particular horizon though some beds seems to be enriched sulphide
mineralization relative to others.  It seems that the beds which
are the most favourable locations for the sulphides are the lower
Guelph, Eramosa and the Upper Goat Island.  Lower in the strati-
graphic column fewer sulphides are observed and, if any sulphide
is present, it is usually the sphalerite.  This agreed quite well
with observation by Kwong (1973).

Other minor minerals associated with galena and sphalerite
in the carbonate rocks are calcite, celesite, gypsum and barite.
Some pyrite and marcasite are also present in the shaly parts of
the carbonate beds.

In field, galena usually appears as a dull grey smear on
exposed carbonate rock surfaces and when scratched by a knife
gives a diagnostic metallic grey luster.  Much of the galena
also occurs as veinlets filling small fractures  (about 1-2 mm.)
in the host rock and gives some estimate of average vein width.
A few galena crystal with angular outline are also observed.  Some
of the galena is present as replacements of crinoid stem fragments.

Sphalerite occurs as deep orange to black crystals in

the carbonate rocks. It is usual to find sphalerite as irregular patches sitting or impregnated in the carbonate rocks. Exposures of the Eramosa Member in the New Dundas Quarry are characterized by bedded structures thought by the author to be reefs or reefs which have undergone collapse. These structures are characterized by length to thickness ratio of about 10 to 1, occur predominatly at the same stratigraphic horizon and are generally 10 t0 20 feet in length (dimension along or within the plane of bedding). They consists of a fossiliferous, chaotic, jumble or breccia of dolomite marked by numerous solution cavities (vugs of diameter about 1 to 3 inches) and are highly porous. In many of these vugs are sphalerite patches. These sphalerites may or may not have calcite linings alon the contacts. Fissures fillings and fossil replacements are also observed but not as common as in galena.

Large amounts of dark coloured organic materials, bitumens, which look like dark resin are found in the Guelph, Eramosa and the upper Goat Island rocks. The Eramosa seems to be especially enriched in bitumens. There is little or no such organic compounds in the lower beds. Some of the bitumens occur as large nodules and often with sphalerite found in close proximity. In the Eramosa and the upper Goat Island some of the bitumen occurs preferentially along the bedding plane of the carbonate rocks.

In the field, it was observed that these seems to be a closer relation between the bitumens and the sphalerite than bitumens

and galena. The author's experience was that when large bitumen nodules are found, it is usual to find some sphalerite nearby.

No copper sulphides were observed in the field. If they are present they must be very fine grained and not easily seen with the unaided eye.

## RELATIONSHIP BETWEEN SULPHIDE MINERALS AND BITUMENS

The presence of bitumens in most if not all of the Mississippi Valley Type deposits shows that these compounds may play some important role in the localization of these minerals. It is believed that these organic compounds probably acted as reducing agents which reduced sulphate ions, $SO_4^{--}$, to sulphide ions, $S^-$. The sulphide ions would then precipitate any metallic ions that were present in the ore solution, commonly thought to be brine. Barton (1967) suggested the following reaction :-

$$CH_4 + H^+ + SO_4^{--} + Mg^{++} + ZnCl_2 + 3CaCO_3 =$$
$$ZnS + CaMg(CO_3)_2 + 2Ca^{++} + 2Cl^- + H_2O + 2HCO_3^-$$
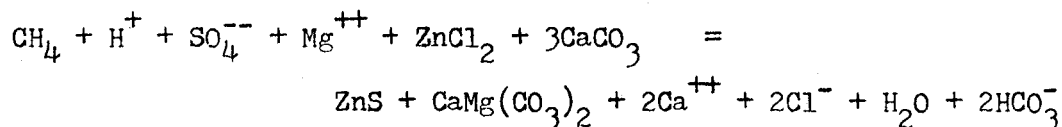
approximately described the sulphide depositional process.

If this is the case, then two situations may arise, i) the reduction of the sulphate ocurred at the site of the bitumen and the sulphide ions then migrated to some other site and contacts the brine solution and precipitate any metallic ions, or, ii) the brine solution may carry sulphate and metallic ions and where reduction and sulphide precipitation takes place.

Should the first hypothesis be right, then high concentration of organic bitumen may not be found at the immediate site of metal sulphides concentration because the reduction of sulphate occurred at one place and the precipitation of metal sulphides occurred elsewhere. However, if the second hypothesis is correct metal

sulphides should be found in close association with the bitumen.

Experiments were therefore carried out to precisely define the spatial relationships of the bitumens and sulphide minerals.

## EXPERIMENTS

Three different sets of experiments were carried out with
the following objectives,

A.) Objective: To identify the functional groups in the bituments
and thus to determine the best kind of solvents to dissolve the
bitumens

Procedure: Some of the bituments were chipped out of the rock and
sperated from any carbonates or rock minerals under a binocular.
The bitumens were then ground to very fine powder and mixed with
nujol. The infra-red spectrum was then taken.

Different solvents such as methanol, ethanol, diethyl ether,
benzene and acetone were tried to determine which would be best
to dissolve the bitumens.

Results: The infra-red spectra showed strong absorption at about
2900 $cm^{-1}$ and 1400 $cm^{-1}$. Other adsorption peaks were very
weak. This suggested that the bitumens are mainly saturated
carbon-carbon chains, i.e. aliphatic hydrocarbons. This agrees
with the observations of Pering (1973) on bitumens from comparable
carbonate rocks of North Derbyshire, England. Although no gas
chromatography were done, the bitumens must be of high molecular
weight, possibly a $C_{17}$ chain as Pering observed. If the bitumens
were of low molecular weight, they would vaporized very easily
and probly not be preserved.

Warm benzene-methanol (benzene : methanol = 9:1) mixture was found to be the best solvent and was chosen as the solvent for the extraction of the bitumens.

B.) Objective: To extract the bitumens from the rock samples and to determine the organic carbon concentration in the carbonate rocks.

Procedure: All the rock samples were ground to about 0.1cm - 0.3cm in grain size. About 40 gm of the ground rock was weighed accurately for each sample. This was then put into an extraction assembly shown in Fig. 3.

After extraction the solution was evaporated to dryness at about 30 C in weighed porcelain crucibles. After all the solvents had evaporated a dark coloured tar was left behind in the crucibles. The mass of the organic was than determined by weighing on a micro-balance.

Results: The concentrations of the bitumens in the rocks were calculated and tabulated in Table-4. The concentration are given in ppm.

C.) Objective: Determination of copper, lead, and zinc concentration in rock and bitumens samples.

Procedure: Rock samples were ground to a very fine powder. Bitumens were chipped out and seperated from any rock fragments under a binocular microscope. The bitumens were also fround to fine powder.

cold water "out"

condenser

cold water "in"

extraction shell

rock chips

. . . > route for solvent

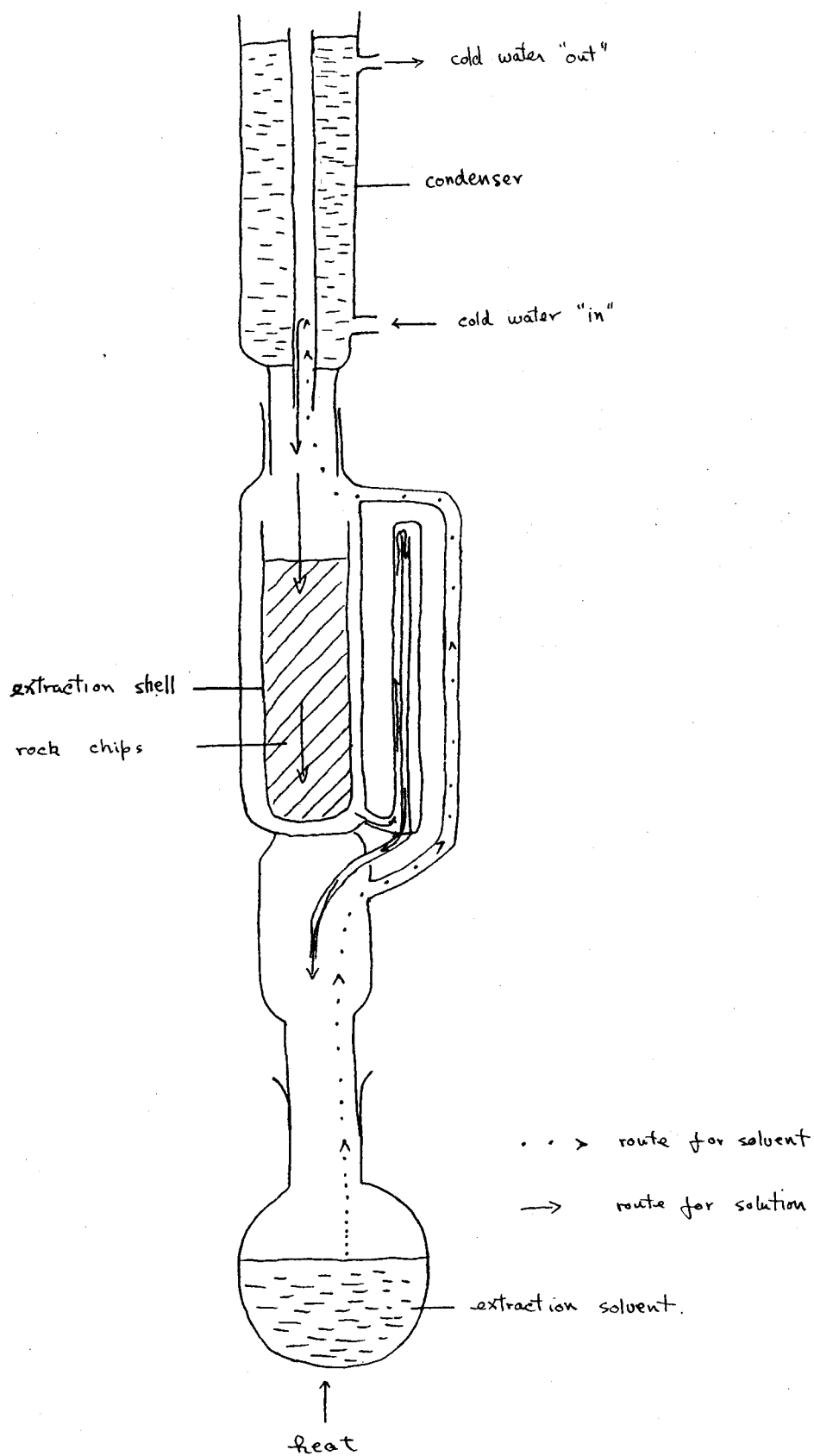——→ route for solution

extraction solvent.

heat

Fig. 3 Apparatus Set Up for Extraction Experiments.

About 1 gm of each rock and bitmen samples were weighed accurately and digested overnight in 20 ml of HF and 5 ml of $HClO_4$ solution. Then the solution was evaporated to dryness and redissolved in 5 ml of 1N NaCl solution ( $Na^+$ isused to inhibit any interference by other ions, such as $Ca^{++}$ in the rock, during atomic absorption analysis.) Each solution was then diluted to 100 ml with deionized water.

Standard solution were also prepared in similar way using cuprous oxide CuO, lead nitrate $Pb(NO_3)_2$, and zinc chloride $ZnCl_2$.

The concentration of copper, lead and zinc were then determined by means of the atomic absorption technique. (The instrument used was a Perkin Elmer model 303)

Fig 4. shows a flow chart of the analytical procedure. Results: The data for Cu, Pb, Zn are presented in Table 4.

Any samples with a concentration of metal beyond the range of the atomic absorption unit were diluted further.

It should be noted that the samples analysed were all carbonate rocks and that most have visible galena and/or sphalerite. Descriptions of the hand specimens and locations for each sample are listed in Appendex I.

1 gm of

Powdered Sample

(rock or bitumens)

↓

Digest overnight

in 20ml of HF

+ 5ml of $HClO_4$

↓

Evaperate to

Dryness

↓

Cool & redissolve

in 5ml 1N NaCl

↓

Dilute to

100 ml

↓

Brun Extract

in atomizer

↓

Absorbance    conc. of metal
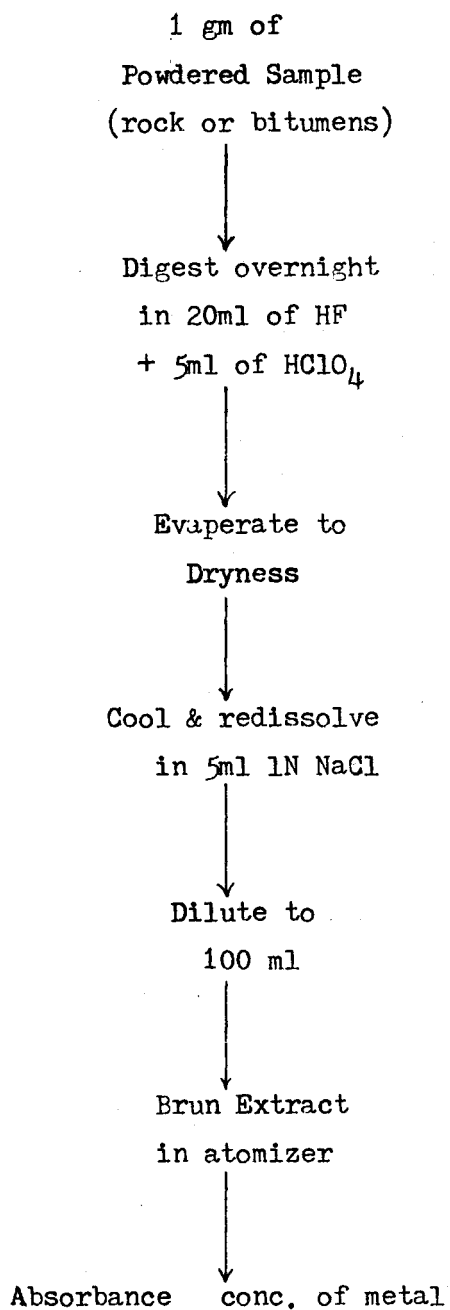
Fig. 4 Flow Chart for Atomic Absorption Analysis

| Sample No. | Cu | Pb | Zn | Organic Carbon |
|---|---|---|---|---|
| D-1 | 19 | 6 | 99 | 283 |
| D-2 | 9 | 2 | 6 | 220 |
| D-3 | 4 | 11 | 23 | 173 |
| D-4 | 8 | 5 | 22 | 315 |
| D-5 | 5 | 4 | 40 | 290 |
| D-6 | 10 | 6 | 490 | 134 |
| D-7 | 10 | 5 | 1000 | 338 |
| D-8 | 38 | 5 | 31 | 634 |
| D-9 | 193 | 39 | 1000 | 1295 |
| D-10 | 32 | 7 | 1000 | 470 |
| D-11 | 12 | 6 | 42 | 367 |
| D-12 | 20 | 7 | 19 | 512 |
| D-13 | 20 | 107 | 32 | 563 |
| D-14 | 8 | 4 | 12 | 190 |
| D-15 | 23 | 7 | 120 | 382 |
| D-16 | 8 | 126 | 23 | 227 |
| D-17 | 13 | 14 | 32 | 171 |
| D-18 | 13 | 6 | 12 | 247 |
| D-19 | 57 | 8 | 135 | 236 |
| D-20 | 28 | 29 | 119 | 600 |
| D-21 | 19 | 9 | 25 | trace |
| D-22 | 65 | 8 | 83 | 885 |
| D-23 | 13 | 7 | 9 | trace |
| D-24 | 50 | 10 | 73 | 680 |
| D-25 | 57 | 4 | 69 | 820 |
| D-26 | 25 | 7 | 64 | 463 |
| D-27 | 28 | 5 | 53 | 297 |
| D-28 | 54 | 7 | 58 | 617 |
| D-29 | 25 | 9 | 48 | 730 |
| D-30 | 27 | 15 | 36 | 418 |

Table 4a. Concentration of Cu, Pb, Zn and organic carbon (in ppm.) carbonate roaks, mainly from Eramosa and Goat Island Member

| Sample No. | Cu | Pb | Zn |
|:----------:|:--:|:--:|:--:|
| B-1 | 19 | 3 | 5 |
| B-2 | 7 | 2 | 5 |
| B-3 | 6 | 10 | 20 |
| B-4 | 7 | 6 | 11 |
| B-5 | 14 | 4 | 8 |

Table 4b.   Concentration of Cu, Pb and Zn in bitumen samples
from the Eramosa and Goat Island Members.

Noted that in table 4a. Sample #D-1 to D-18 are samples from
New Dundas Quarry.   Sample #D-19 to D-30 are samples from Highway 403.

## PRESENTATION OF DATA

To examine the relationship between bitumens (organic carbon) and different base metal concentrations and between different individual base metals, six graphs were plotted including:

Fig. 5 - a plot of concentration of organic carbon Vs concentration of copper.

Fig. 6 - a plot of concentration of organic carbon Vs concentration of lead.

Fig. 7 - a plot of concentration of organic carbon Vs concentration of zinc.

Fig. 8 - a plot of concentration of copper Vs concentration of lead.

Fig. 9 - a plot of concentration of copper Vs concentration of zinc.

Fig. 10- a plot of concentration of lead Vs concentration of zinc.

In these plot zinc concentration of three samples were greater than 1000 ppm and were not plotted because of the limited scope of the graph.
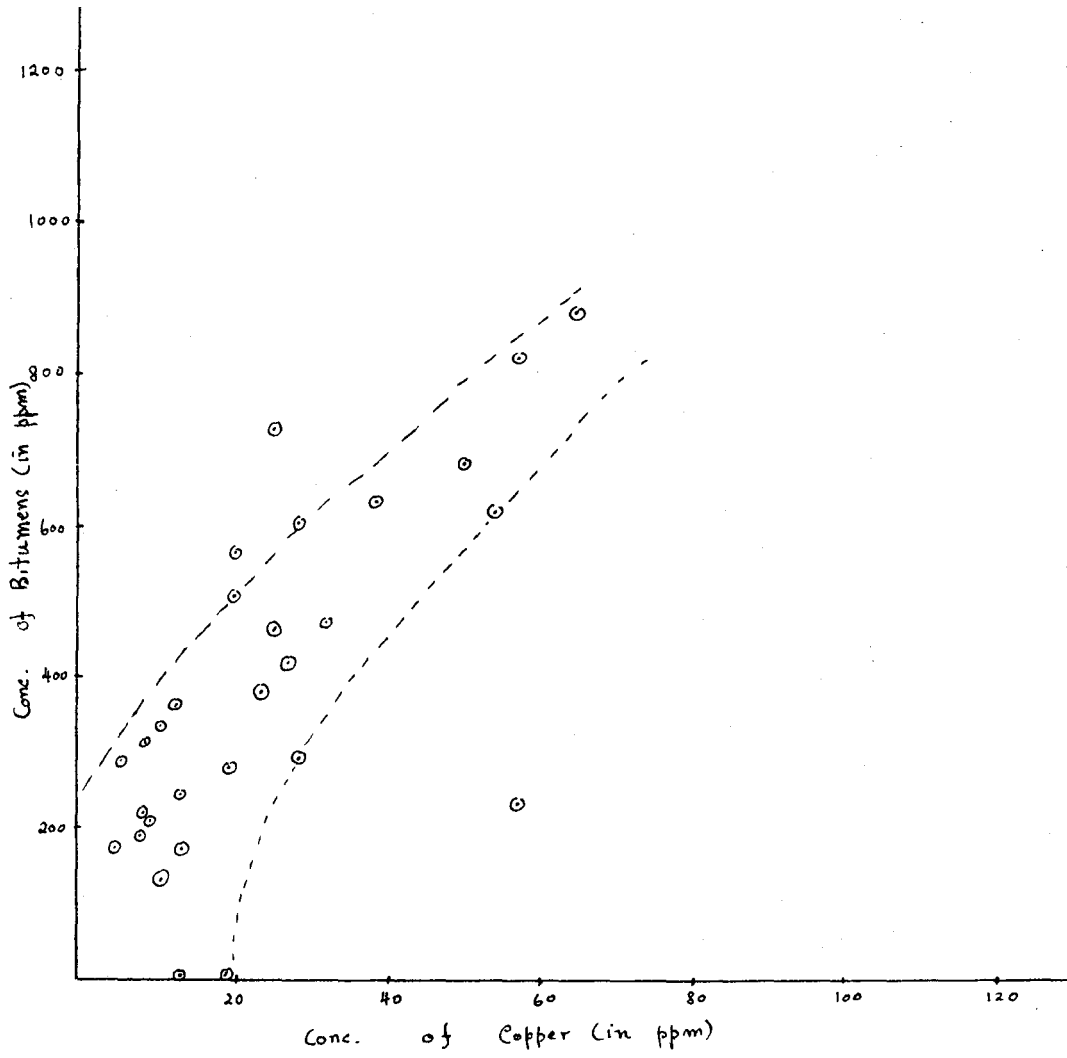
Fig. 5 Concentration of Bitumens Vs Concentration of Copper.
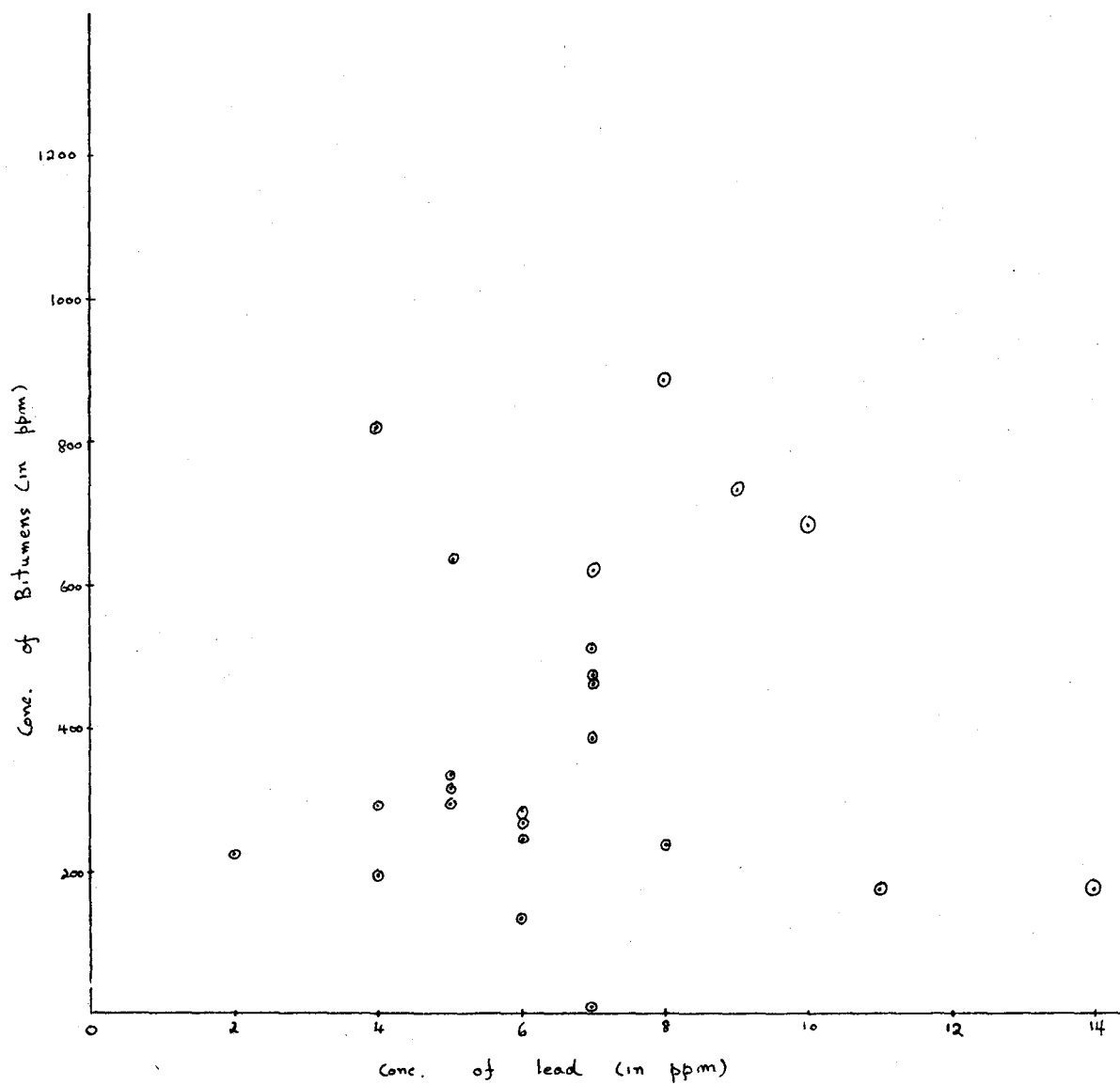
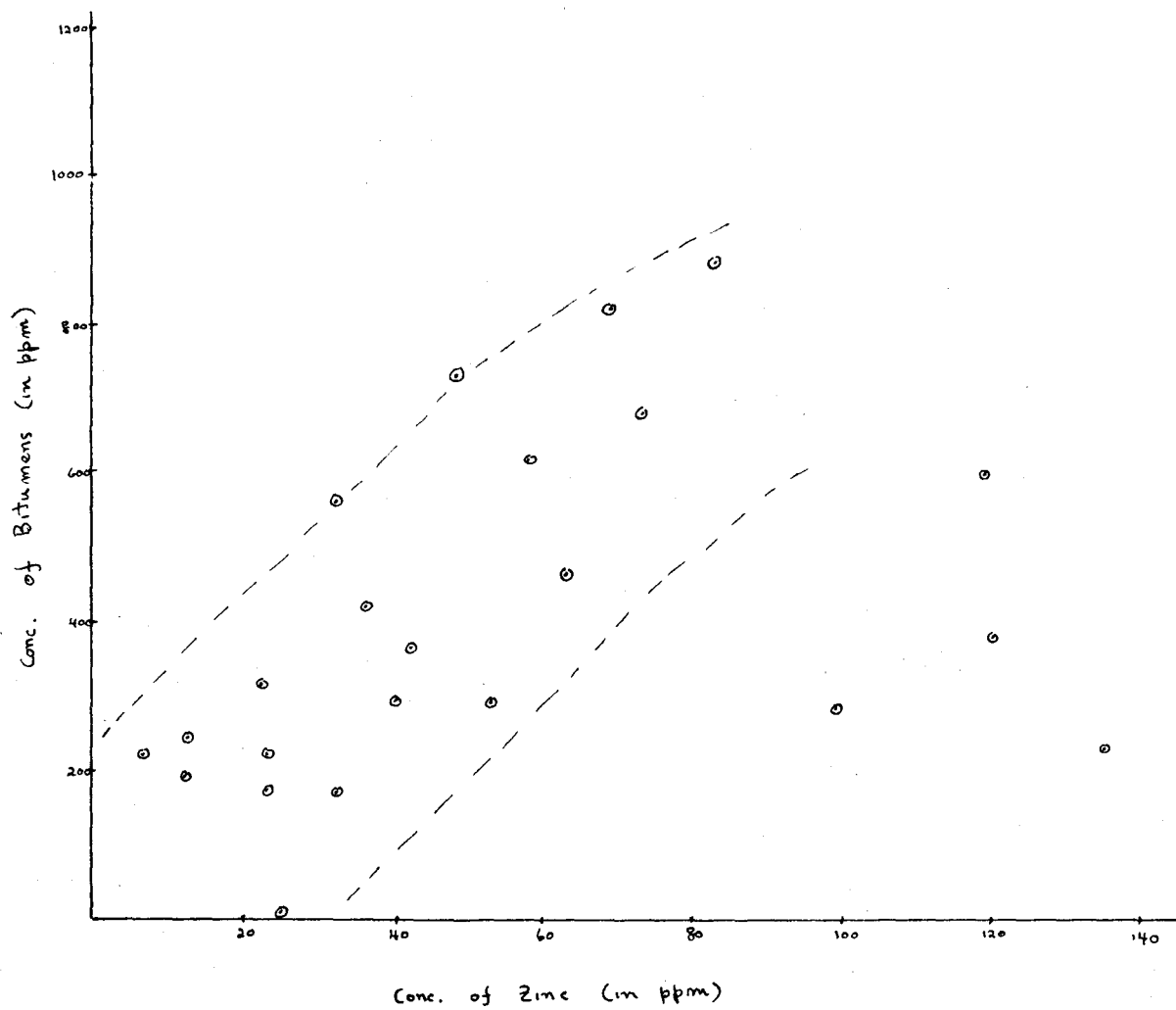Fig. 6 . Concentration of Bitumens Vs Concentration of Lead.

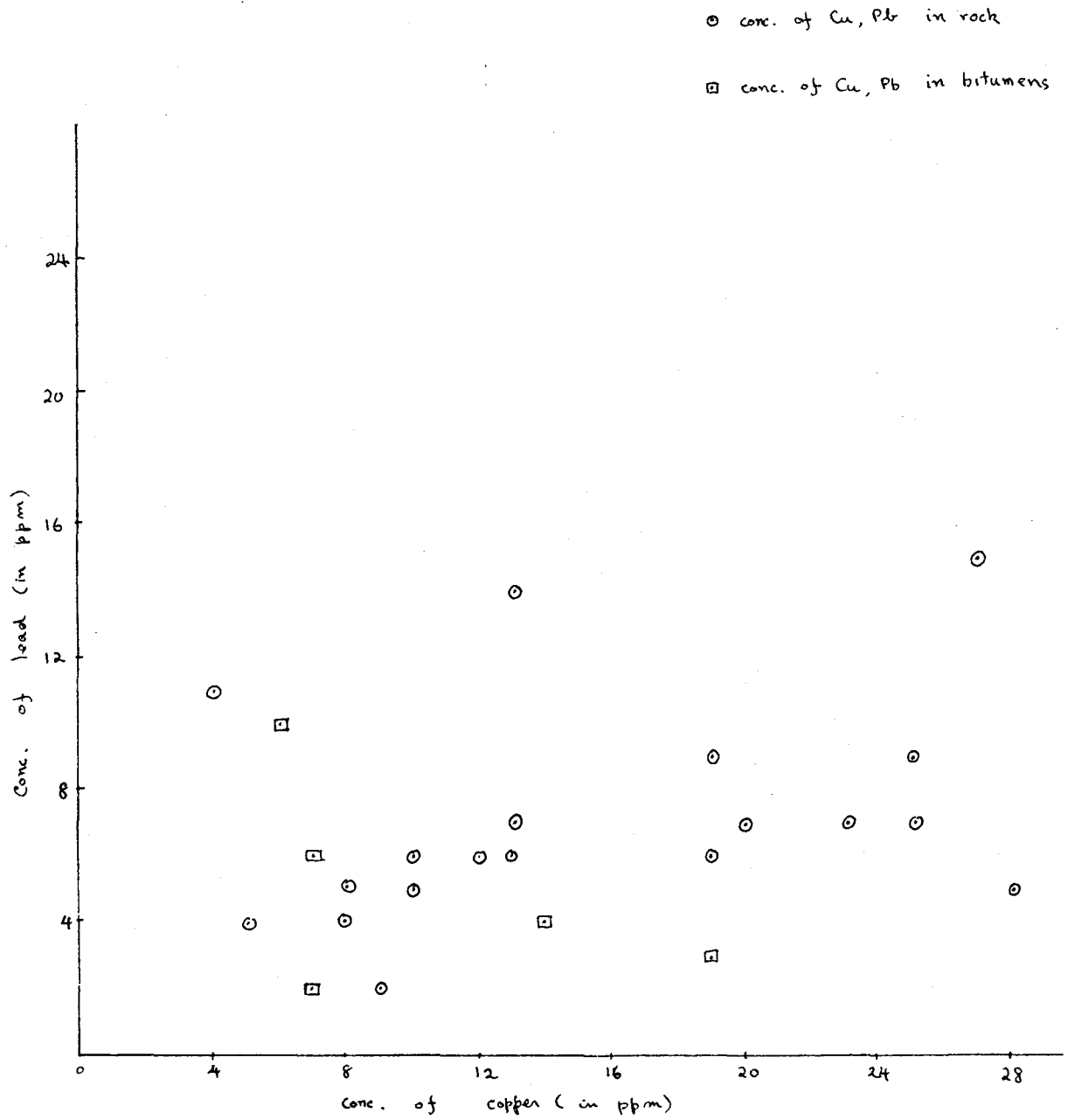Fig. 7  Concentration of Bitumens Vs Concentration of Zinc.

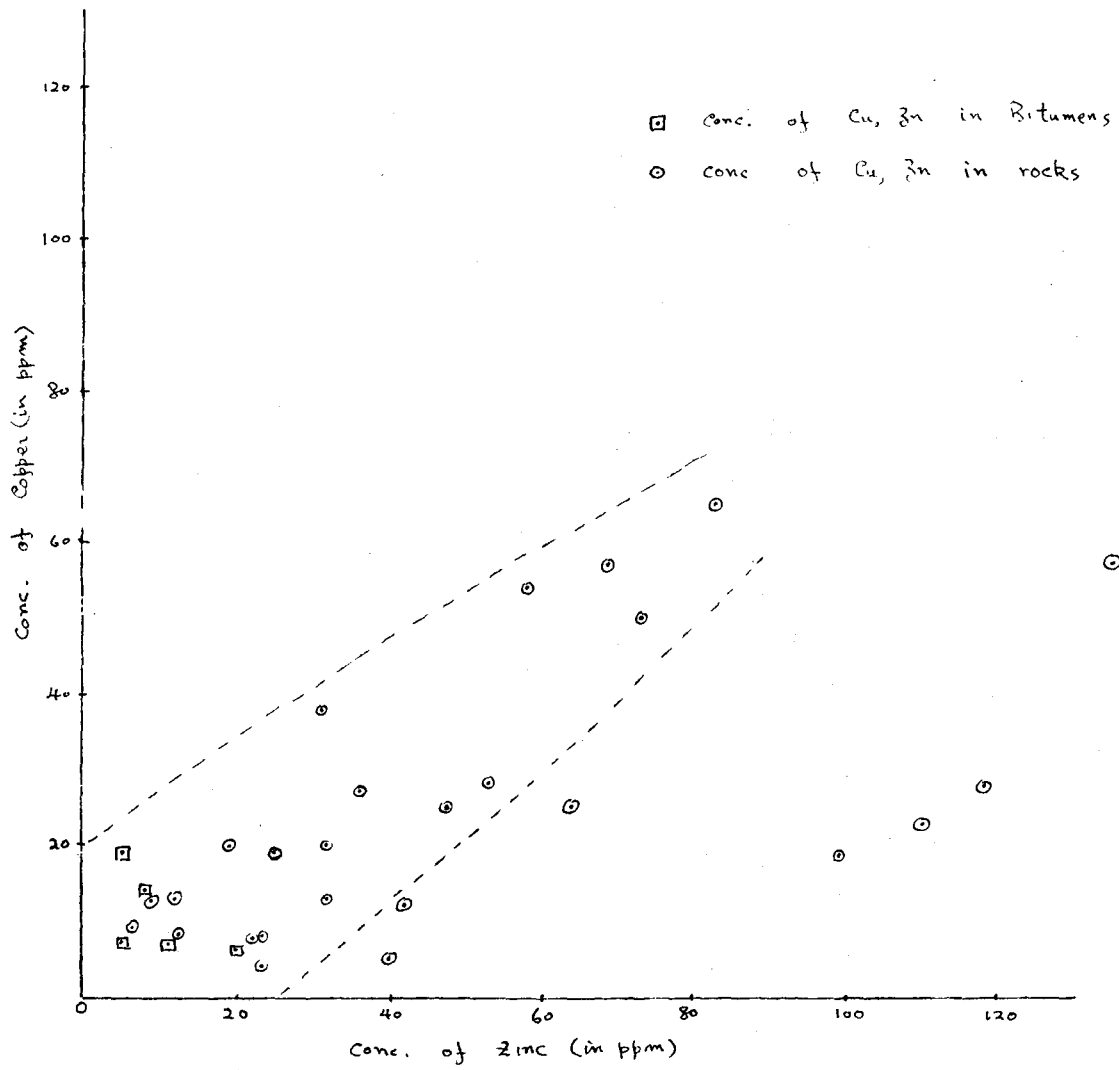Fig. 8  Concentration of Lead Vs Concentration of Copper.

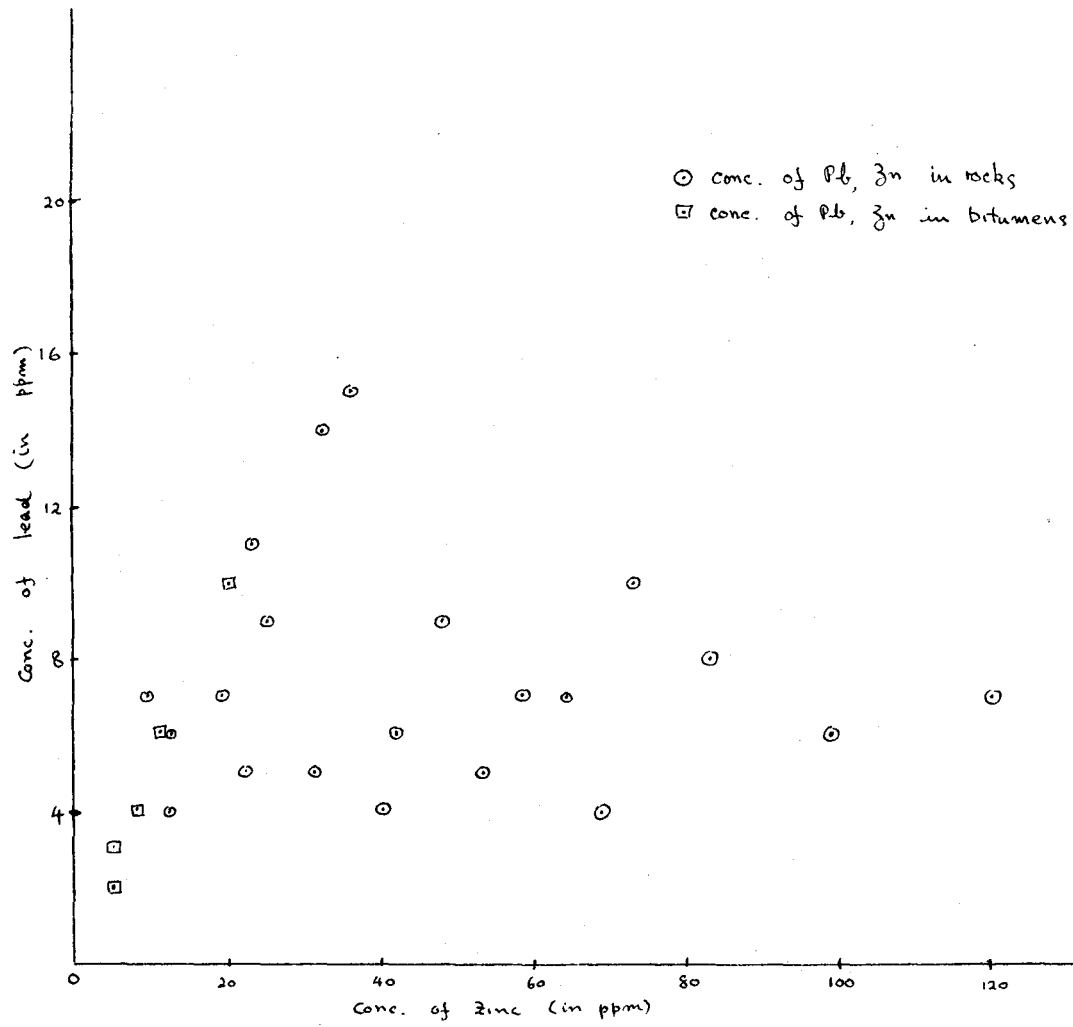Fig. 9 Concentration of copper Vs Concentration of Zinc.

Fig. 10 Concentration of Lead Vs Concentration of Zinc.

DISCUSSION

The following mode of orgin of the galena and sphalerite in

the Paleozic carbonate rocks of the Niagara Escarptment has

been suggested by Kwong (1973).- "ground water running

down the sedimentary pile dissolved some evaporite and progessively

became more saline in character. Upon reaching a depth of a few

thousand feet this brine solution was heated depending upon the

prevailing geothermal gradient and begins to rise, selectively

leaching lead and zinc from consolidated or unconsolidated

argillaceous sediment and carrying them in the form of chloride

complexes. Reaching the present site of sulphide deposition,

the original sulphate dissolved from the evaporite beds and

carried in the brine solution is reduced inorganically by local

concentration of methane or other appropriate reducing agents.

The sulphide ons $S^{--}$ produced combined with lead and zinc ions

to give rise to the sphalerite and galena observed." Kwong

also suggested, based on leaching experiments, that the argilla-

ceous sedimentary rocks could be the potential source rock of

the heavy metals. Kwong's analyses of shales, regarded as a

potential source rock indicated the the Pb/Cu ratio is about

2:1. Also in his leaching experiments he indicated that chloride

rich aqueous fluid are poor solvents for Cu while disulphide rich

solution are some what better.

One thing that puzzled the author from Kwong's experiments was why the concentration of copper is higher than that of lead in the dolomite if lead and zinc were preferrentially leached by the brine solution as kwong had indicated.

The average concentration of Copper, Lead and Zinc from this study are compared with Kwong's analysis in Table 5.

Table 5.  Average concentration of Cu, Pb & zn in dolomite from this study compared with the average of Kwong (1973).

|          | Cu   | Pb  | Zn  |
|----------|------|-----|-----|
| Author   | 30   | 16  | 65  |
| Metal/Pb | 2    | 1   | 4   |
| Kwong    | 4.3  | 1.4 | 8.4 |
| Metal/Pb | 3    | 1   | 6   |

The reason that the author's average Cu, Pb, Zn values are higher than Kwong's analysis is that the latter averages are for dolomite without visible copper, lead and zinc mineralization. Both suites, however, represent samples from the same area and showed fairly similar metal ratio.

Since lead and zinc were selectively leached, why then does copper showed a higher concentration than lead?

The author's opinion is that the organic bitumens must have played a very important role in the precipitation of the base metals.

It has long been suggested that bitumens (or alkanes) are the main reducing agents that reduced the sulphate to sulphide ions (Barton, 1967; Toland, 1960). The latter may potentially precipitate base metals.

# SIGNIFICANCE OF METAL-METAL AND METAL-ORGANIC CARBONE CORRELATION

From the graphs concentration of bitumens Vs concentration of copper (Fig. 5), concentration of bitumens Vs concentration of zinc (Fig.7) we can see roughly that the concentration of these metals increase with an increase of concentration of the organic carbons. The correlation coefficient for these two plots calculated are .791 and .314 respectively. This positive correlation of Cu and Zn content with organic carbon suggested that the bitumens, often localizid in high concentration in highly porous structures such as reefs, have directly or indirectly caused the precipitation of copper and zinc. envesaged is reduction of brine-transported sulphate to sulphide by bitumens.

However, from the plot of concentration of bitumens Vs concentration of lead (Fig.6) no similar trend for lead is seen. The correlation coefficient found for this plot is only .102.

The difference may be due to the differences in solubilities of the various metal sulphides as shown in Table 6.

Table-6. Solubilities of various metal sulphides in cold aqueous syatem.

| Mineral | Solubility in gm/100ml |
|---|---|
| Chalcocite $Cu_2S$ | $1 \times 10^{-14}$ |
| Covellite $CuS$ | .000033 |
| Galena $PbS$ | .01244 |
| Sphalerite $ZnS$ | .000065 |
| Wurtzite $ZnS$ | .000069 |

From the table we can see that galena is the most soluble

sulphide for these different sulphides while chalcocite is the least soluble one. This suggested that even the concentration of copper is low in the brine, at the presence of sulphide ions $S^{--}$ the metal sulphide would be precipitated. Therefore, when the concentration of of organic is high at certain locality the concentration of sulphide ion tends to rise too. In this casem when a brine solution bring in even some low concentration of copper, copper sulphide would be precipitated. So when more and more ascending brine passed this site more and more of the copper sulphide would be precipitated thus give rise to a localized higher concentration of copper when organic concentration is high. For regions where not much organic carbons are present, the concentration of sulphide ion would be lowered and thus lower concentration of copper sulphide should be expected.

For lead, because of the higher solubility, even when the ascending brine met a higher concentration of organic compounds, the sulphide formed would not be totally precipitated at that site. Instead, much of it will be remained in the brine solution. As the solution moved away, it will bring with it some of the sulphide. Thus the galena are apread further away from the site of formation. This lead to a wider geographical distribution with roughly the same concentraton of lead and showed little correlation with bitumens as in Fig 6. where concentration of bitumens is plotted against concentration of lead.

Zinc, with a solubility between that of copper and lead, showed

a weaker correlation with bitumens than copper but a much stronger

correlation than lead did. This is clearly illustrated in fig 7.

It must be noted that the above solubilities only represent

solubilities in pure aqueous solvent and do not apply to well brine

solution where the base metals are carried is chloride complexes.

However, for the chloride complexes, the stability is in the follow-

ing order: Cu Zn Pb. Therefore, the copper-chloride complexes

are the easiest for the $S^{--}$ ion to attack and precipitated while

it is most difficult for the $S^{--}$ ion to attack the lead-chloride

complexes.

Since the bitumens concentration controls the concentration

of copper and zinc deposits we should be able to draw some relation-

ship between the concentration of zinc znd that of copper. From Fig

9. we can see that the concentration of zinc increased with concentr-

ation of copper. This indicates very well that when the concentration

of bitumens are high it will give higher concentratration for both

copper and zinc mineralization. Bitumens showed no control for the

localization of lead deposit while the localization of copper and

zinc deposits are controlled by the concentration of bitumens.

Therefore, we should not expect to find the same kind of correlation

for copper and lead or lead and zinc as we found for copper and

zinc. These are shown pretty well in Fig 8. and Fig 10.

The higher solubity of galena may also be used to explain

why some of the galena exists as smear on exposed rock surface.

This may be because some of the rain water passed into the carbonate rocks dissolver some of the the galena and as the water reached the surface again, the water will evaporate and leave the galena behind as smear on the rock surface.

From the above, we can see that the bitumens act as a reducing agent which reduce the sulphate ion $SO_4^{--}$ to sulphide ion $S^{--}$ for the precipitation of the base metal ions. From the analysis of copper, lead, and zinc in bitumens itself we can see the values are actually very low. In fact, the highest concentration of copper, lead and zinc in the samples tested are all lower than the average values given the dolomite. The figures are shown in Table 7.

Table 7. Comparison of highest Cu, Pb and Zn values in bitumens with average Cu, Pb, and Zn values in dolomites.

|  | Cu | Pb | Zn |
|---|---|---|---|
| Average conc.(ppm) in dolomite | 30 | 16 | 65 |
| Average conc.(ppm) in bitumens | 11 | 5 | 10 |
| Highest value(ppm) in bitumens | 20 | 10 | 19 |

This may be explain by the fact that the bitumens are merely a reducing agent and they are a poor solution for the metals when compared with aqueous solvents.

Another possiblity to explain the higher values of copper than lead in the dolomite may be due to a higher brine solution temperature as suggested by Kwong (1973). At higher temperature, about 300 C the solubity of copper is highly increased and the brine solution will contain, if not more, equal amount of copper and lead.

Now we may have a rough idea that we could expected to find

highly localized concentration of copper and zinc with higher
concentration of bitumens but no such correlation in lead with
bitumens.

However, we should bear in mind that since more lead were
leached out by the brine than copper; the overall extraction of
lead, over a large area, should be higher than copper.

Also since the concentration of copper, in brine, leached out
was so low, and even the copper had been concentration by the bitumens
it would be difficult to observe tha mineralization of copper in
field.

## CONCLUSION

The concentration of bitumens in the carbonate rock played a very
important roe in the localization ofminerals in the Mississippi Valley
Type Deposits. Copper and zinc concentrations seem to be controlled
by the concentration of bitumens shich showed little control over the
concentration of lead. The reason may be due to the differences in
the solubilities between copper, lead and zinc sulphide and also
due the differences in stabilities for the metal-chloride complexes
formed.

The bitumens itself is not a good site for the mineralization
of metal sulphides.

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Appendix 1.  Location and Description for the Samples Collected.

| Sample No. | Location | Description |
|---|---|---|
| D-1 | Dundas Quarry | dolomite, Guelph Formation, no visible sulphide crystal. |
| D-2 | Dundas Quarry | dolomite, Guelph Formation, no visible sulphide crystal. |
| D-3 | Dundas Quarry | dolomite, Eramosa, no visible sulphide. |
| D-4 | Dundas Quarry | dolomite, Eramosa, no visible sulphide. |
| D-5 | Dundas Quarry | dolomite, Eramosa, no visible sulphide. |
| D-6 | Dundas Quarry | dolomite, Eramosa, contain a vug with sphalerite. |
| D-7 | Dundas Quarry | dolomite, Eramosa, containing sphalerite. |
| D-8 | Dundas Quarry | dolomite, Eramosa, with galena smear. |
| D-9 | Dundas Quarry | dolomite, Eramosa, with sphalerite. |
| D-10 | Dundas Quarry | dolomite, Eramosa, with sphalerite. |
| D-11 | Dundas Quarry | dolomite, Eramosa, with sphalerite. |
| D-12 | Dundas Quarry | dolomite, Eramosa, with galena smear. |
| D-13 | Dundas Quarry | dolomite, Eramosa, with sphalerite. |
| D-14 | Dundas Quarry | dolomite, Eramosa, with sphalerite. |
| D-15 | Dundas Quarry | dolomite, Eramosa, with sphalerite. |
| D-16 | Dundas Quarry | dolomite, Eramosa, with galena. |
| D-17 | Dundas Quarry | dolomite, Eramosa, no visible sulphide. |
| D-18 | Dundas Quarry | dolomite, Eramosa, no visible sulphide. |
| D-19 | Hwy 403 | dolomite, Goat Island, with sphalerite. |
| D-20 | Hwy 403 | dolomite, Goat Island, both galena and sphalerite observed. |
| D-21 | Hwy 403 | dolomite, Goat Island, with sphalerite. |
| D-22 | Hwy 403 | dolomite, Goat Island, with sphalerite. |
| D-23 | Hwy 403 | dolomite, Goat Island, with sphalerite. |
| D-24 | Hwy 403 | dolomite, Goat Island, with sphalerite. |
| D-25 | Hwy 403 | dolomite, Goat Island, with sphalerite. |
| D-26 | Hwy 403 | dolomite, Gasport, no visible sulphide. |
| D-27 | Hwy 403 | dolomite, Gasport, no visible sulphide. |

Appendix 1. continued

| Sample No. | Location | Description |
|---|---|---|
| D-28 | Hwy 403 | dolomite, Gasport, no visible sulphide. |
| D-29 | Hwy 403 | dolomite, Goat Island, with sphalerite. |
| D-30 | Hwy 403 | dolomite, Goat Island, with sphalerite. |
| B-1 | Dundas Quarry | bitumens nodules in Eramosa. |
| B-2 | Dundas Quarry | bitumens nodules in Eramosa. |
| B-3 | Dundas Quarry | bitumens nodules in Eramosa. |
| B-4 | Hwy 403 | bitumens nodules in Goat Island. |
| B-5 | Hwy 403 | bitumens nodules in Goat Island. |