GALENA AND SPHALERTIE IN THE MID-SILURIAN CARBONATES IN THE VICINITY OF HAMILTON, ONTARIO

BY

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ABSTRACT

Field observation at seven outcrops and subsequent polished section studies reveal that lead and zinc mineralization in the Hamilton vicinity occurred after the lithification of the host carbonates. The availability of open structures and the presence of potential reducing agents are the main controlling factors of sulphide deposition. The absence of an igneous source demands an origin of the metals from the sedimentary country rocks. Analysis of 14 shales and 12 dolomites by atomic absorption for Cu, Pb, and Zn indicates that the argillaceous rocks are potential source of the heavy metals. Furthermore, a simple leaching experiment has demonstrated that concentrated brine (sodium chloride solution) can preferentially leach lead and zinc from the shales. A mode of origin involving preferential leaching can then adequately explain the scarcity of copper minerals in the Mississippi Valley-Type ore. It is suggested that better controlled leaching experiments at various temperatures should be done in conjunction with more extensive field work to check the plausibility of such a theory.

ACKNOWLEDGEMENTS

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 Dr. J. R. Kramer and his graduate student Mr. Dean S. Jeffries. Dr. J. R. Kramer kindly gave the author permission to use his apparatus for doing atomic absorption analysis. Mr. Jeffries' assistance and advice in the analysis procedure were invaluable.

Mr. H. J. Down of the Gemini Gem and Mineral Club of Burlington and Mr. D. Lee of the Hamilton Geological Society have kindly shown the author part of their personal mineral collection from the Niagara Escarpment. Mr. Down has also offered the author some specimens. Their generosity and enthusiasm are heartedly appreciated.

The management of Canada Crushed Stone Co. Ltd.granted permission for the author to enter their properties and collect samples. It is hereby acknowledged with thanks.

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INTRODUCTION

Small but widespread occurrence of lead and zinc mineralization in Paleozoic rocks of the Niagara Escarpment and Bruce Peninsula, Ontario, was reported as early as 1919 by Williams (1919). Guillett (1967) has gathered descriptions on various reported occurrences and remarked the similarity of these occurrences with the Mississippi Valley (U.S.A) and Pine Point (Canada) deposits. While the mode of occurrence of these sulphides, especially sphalerite, in the Bruce Peninsula has been studied fairly thoroughly and corresponding modes of origin suggested (B. A. Liberty, 1966, R. Shklanka, 1969, Sangster, 1970, Sangster and Liberty, 1971), little has been done on the sulphide occurrences of the Hamilton district. Although these sulphides occur in too small amounts to constitute a mine, it is of interest to investigate their mode of occurrence and their bearing on the controversial origin of the Mississippi Valley type lead-zinc ore.

GEOLOGY

The exposed bedrocks in and around Hamilton are sedimentary strata of Ordovician (minor) and Silurian age which dip gently, about 13' (20 ft. per mile), towards the southwest. Structurally speaking the area has remained undisturbed by any major faulting, folding or igneous activity since the beginning of Paleozoic time. The general succession of the Middle Silurian Strata (after Bolton, 1957) is presented in Table 1 together with a brief description of each formation/member.

Table 1, Mid-Silurian stratigraphy in the Hamilton Vicinity (modified from Bolton, 1957)

		Formation	Member	Description
Abemarle Group		Guelph		light creamy buff, fine or medium crystalline porous dolomite, generally thick-bedded; also characterized by reefy facies.
		Lockport	Eramosa	medium to dark brownish grey, aphanitic to sugary, medium to thin-bedded, bituminous dolomite with dark grey shaly partings; locally, solution breccia prominent.
			Goat Island	aphanitic to fine crystalline, light buff brownish grey dolomite containing abundant chert especially near the base.
			Gasport	bluish grey to light buff, medium crystalline crinoidal dolomite; massive to thick bedded.
Clinton Group	Upper	De Cew		grey, fine crystalline thin-bedded dolomite with mud. galls; either absent or grade into Rochester shale.
		Rochester		dark grey, calcareous shale with many dolomite interbeds
		Irondequoit		grey to reddish brown, massive, crystalline dolomite limestone.
	Mid	▨		discontinuity
	Lower	Reynales		light grey to blue thin-bedded, fine crystalline dolomite with shaly partings; *Pentameras* abundant near the base
		Neahga		absent
		Thorold		white sandstone with green or red shale interbeds

FIELD WORK AND POLISHED SECTIONS

A. METHOD

Seven easily accessible road cuts/quarries were investigated in detail. At each outcrop, details of each stratigraphic unit (thickness, mineral composition, rock texture, etc.) were recorded and/or checked against published work, if any. Samples of both the mineralized and unmineralized portions of the same unit were collected for later reference. Polished sections were made whenever possible from the mineralized rock sample for closer investigation of the host rock-ore textural relationships.

Fig. 1 shows the location of the outcrops visited and Fig. 2 depicts the relative abundance of the sulphides in the stratigraphic section of each outcrop. Finally, Figs. 3-17 show the textures of the more prominent occurrences on both a megascopic and microscopic scale.

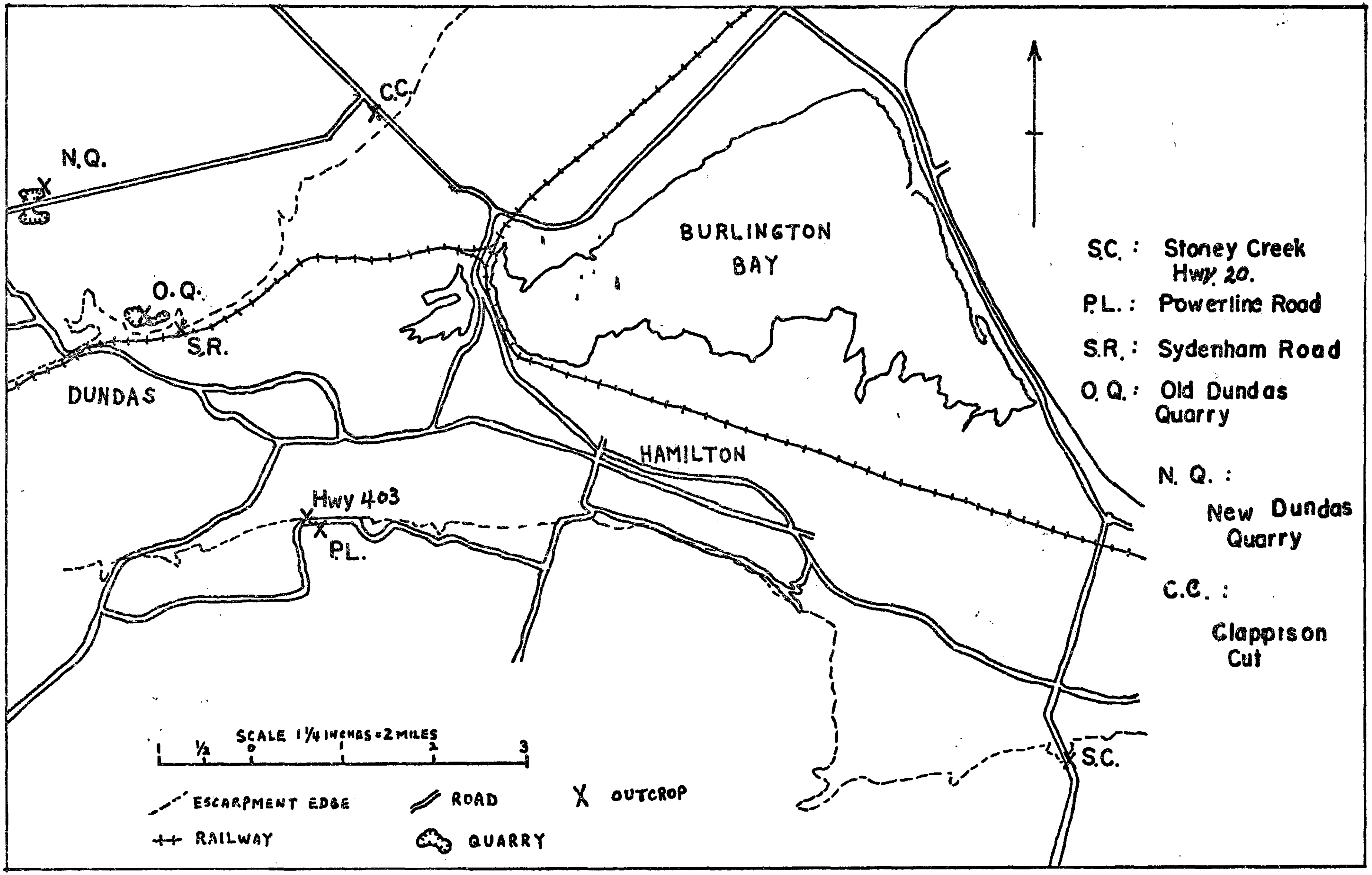
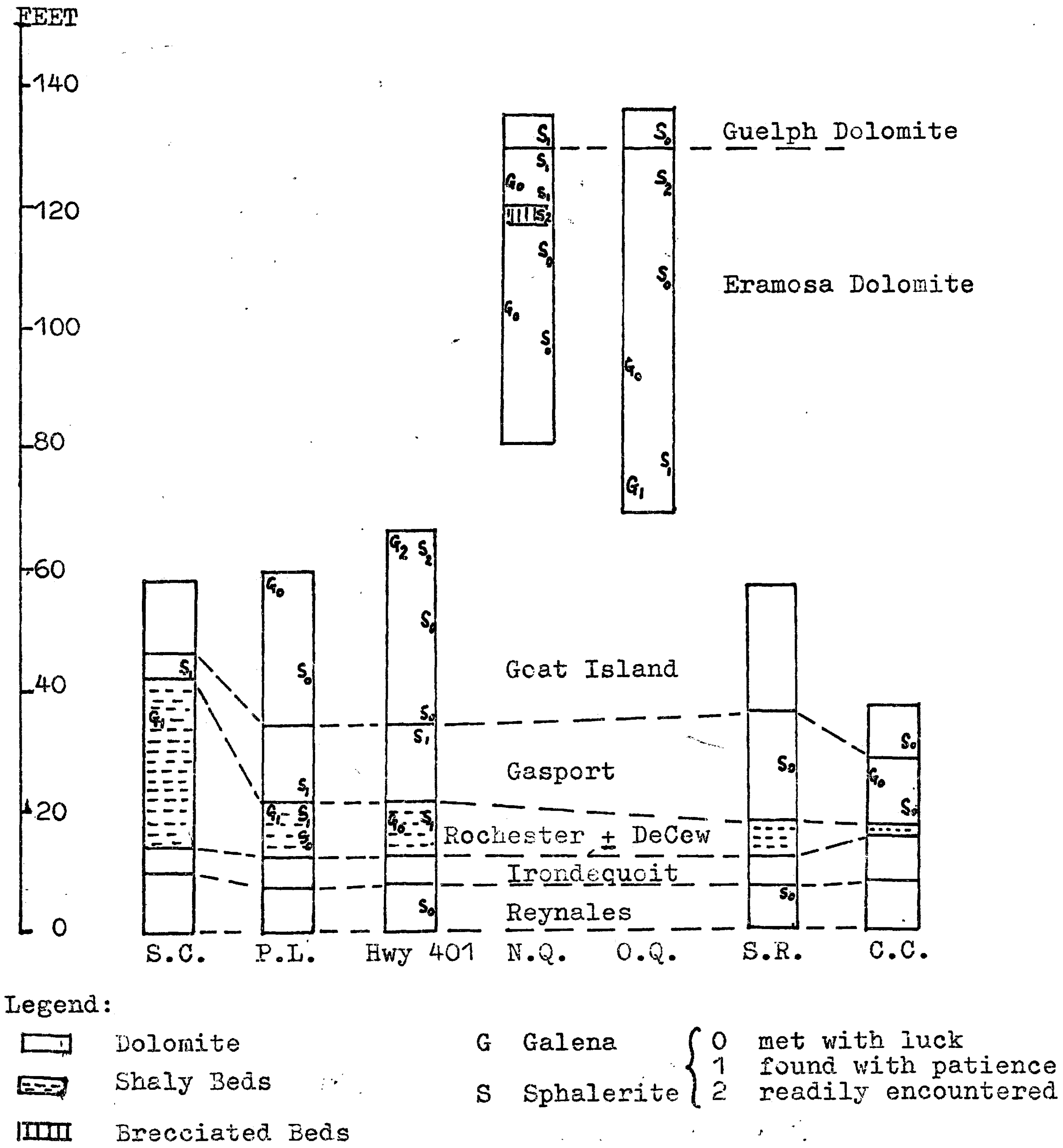


FIG. I MAP OF DUNDAS VALLEY, SHOWING LOCATION OF OUTCROPS VISITED

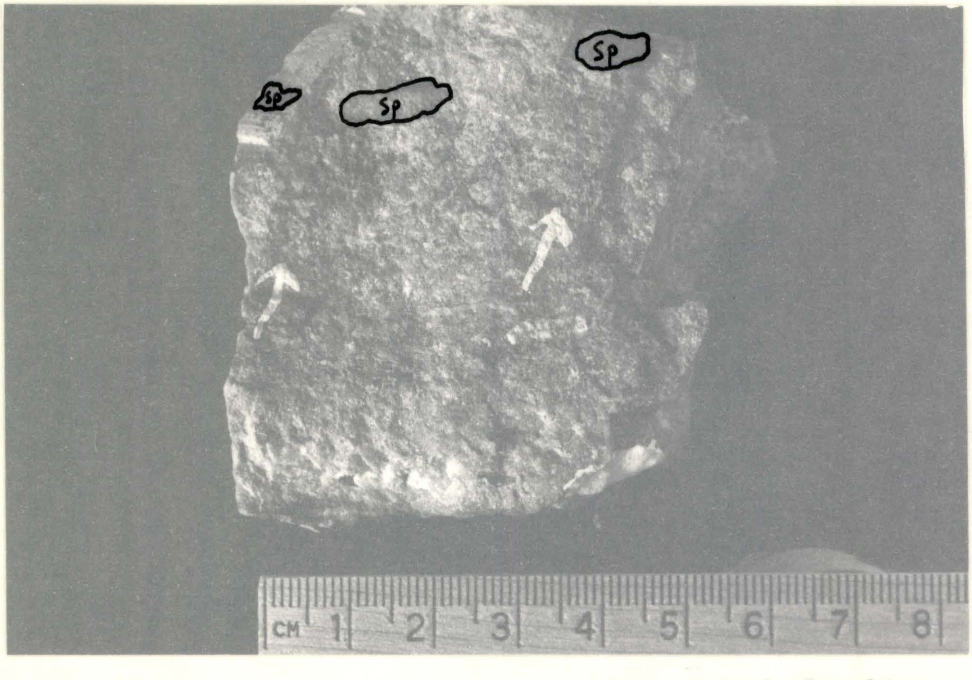
FIG.2 ABUNDANCE OF SULFHIDES AT VARIOUS HORIZONS AT EACH OUTCROP



Note that abbreviations for names of outcrops are the same as in fig.1

Fig.3 Sphalerite (deep yellow) replacing coral(?), Eramosa dolomite, Old Dundas Quarry. Note also the porosity contrast of the carbonate host adjacent to the sulphite.

Fig.4 Sphalerite replacing crinoids, Gasport dolomite, Hwy.403. The white arrows point to disseminated pyrite.



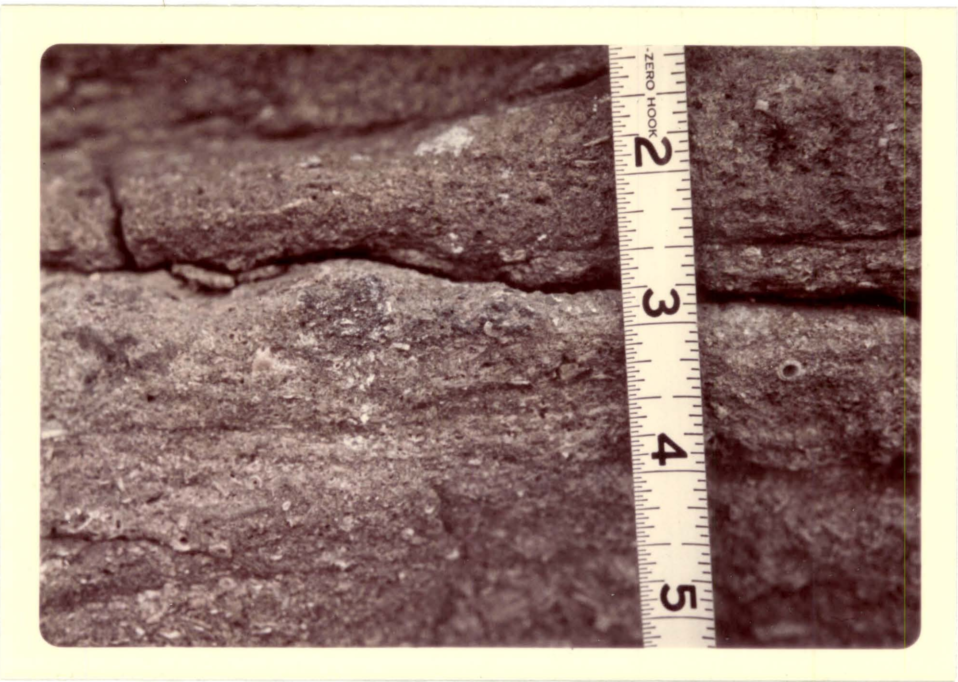
sp = sphalerite


CM 1 2 3 4 5 6 7 8

Fig.5 Galena replacing crinoid columnals;
Rochester Formation, Powerline Roadcut.

a) Photograph showing the actual field appearance. The blue patch (central left) is the galena.

b) Micrograh at 4X. The white mineral is galena.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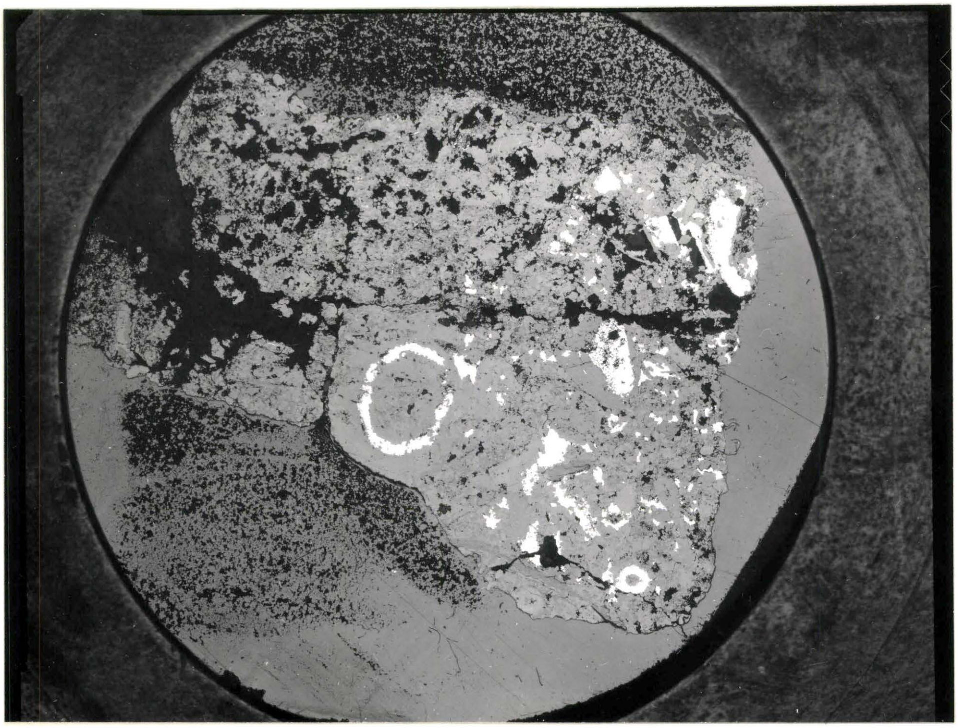
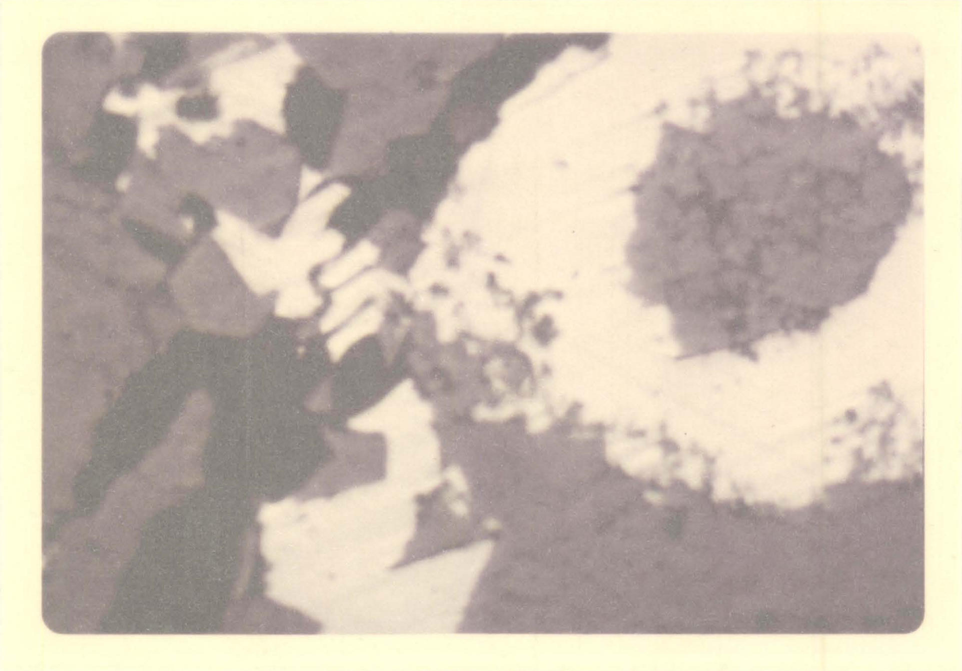
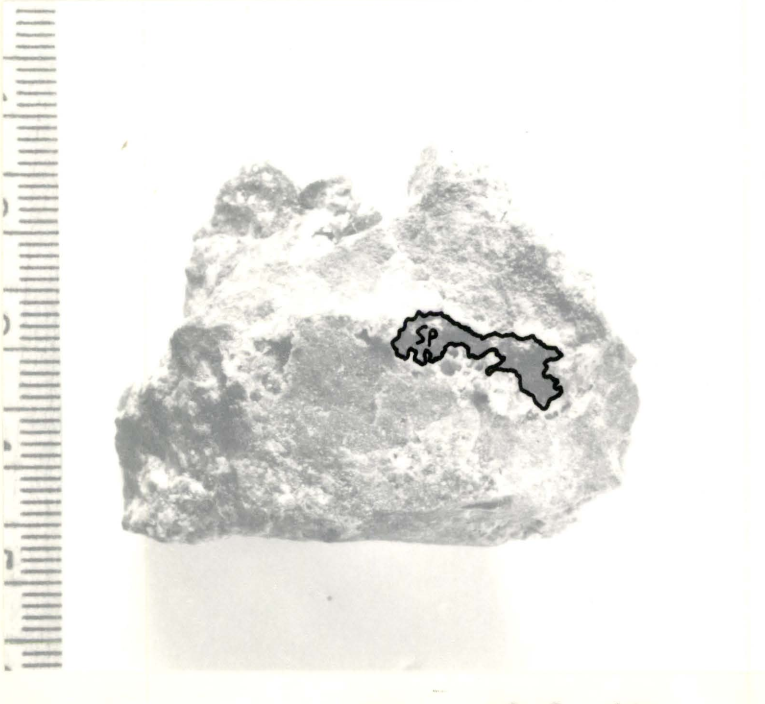


Fig.5c Micrograph 16X showing the replacement texture. Note especially in the lower middle, galena (white) is pseudomorphic after dolomite (grey).

Fig.6 Isometric sphalerite (black) resting on coral(?) remains. Eramosa dolomite, New Dundas Quarry.





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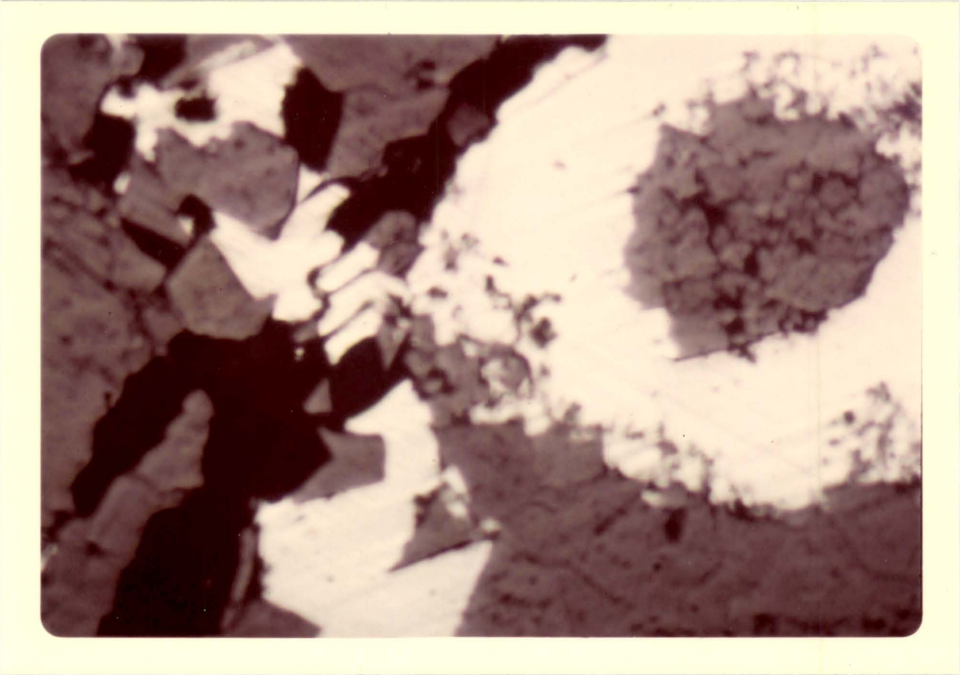


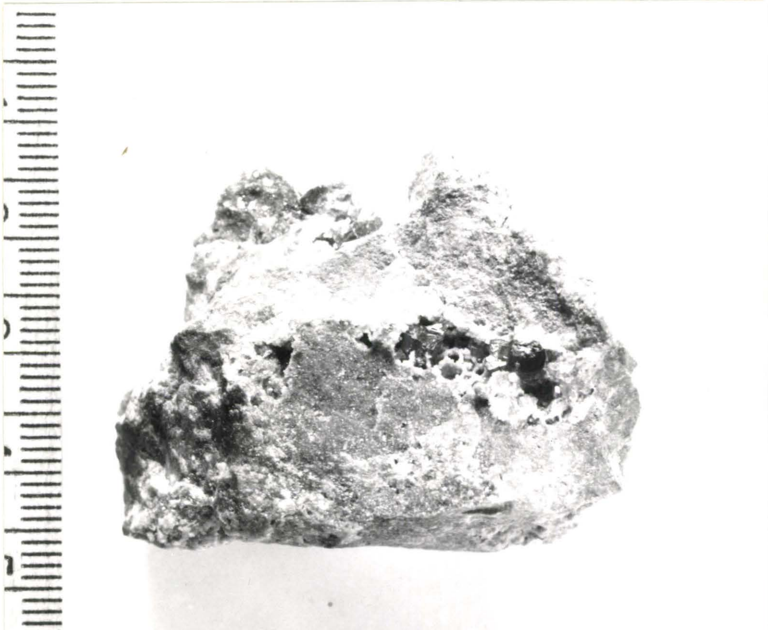
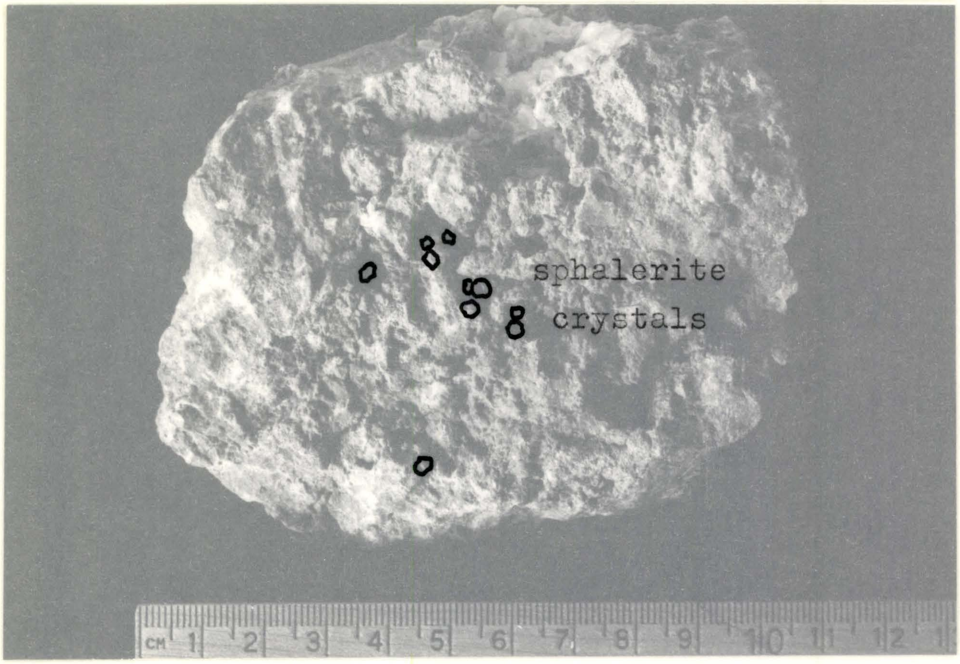
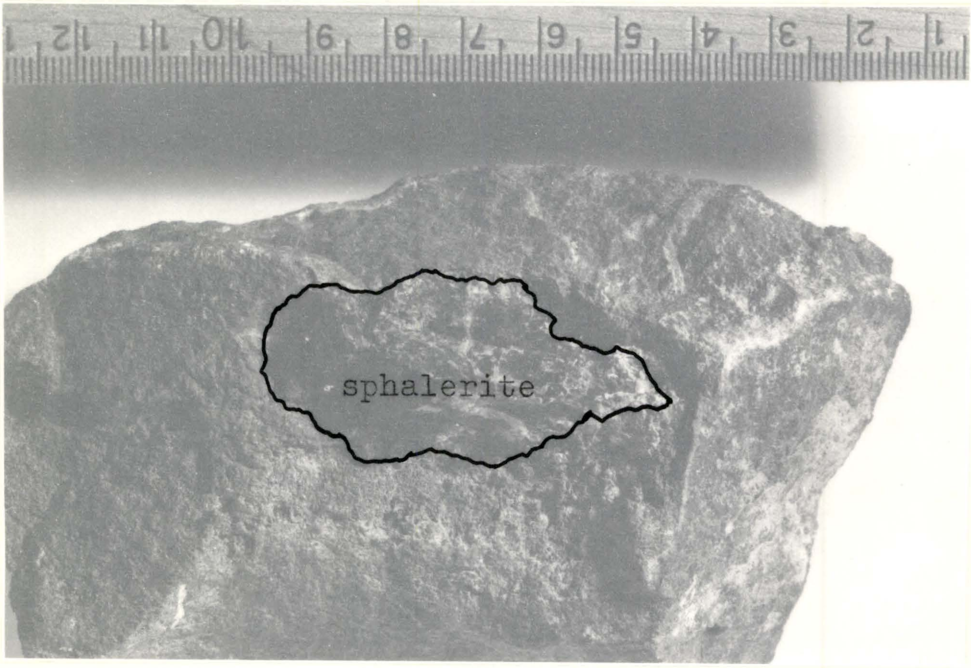


Fig.7 Sphalerite crystals in brecciated Eramosa dolomite, New Dundas Quarry.

Fig.8 Sphalerite occurring as cleavable mass; Eramosa dolomite, New Dundas Quarry.


sphalerite
crystals
CM 1 2 3 4 5 6 7 8 9 10 11 12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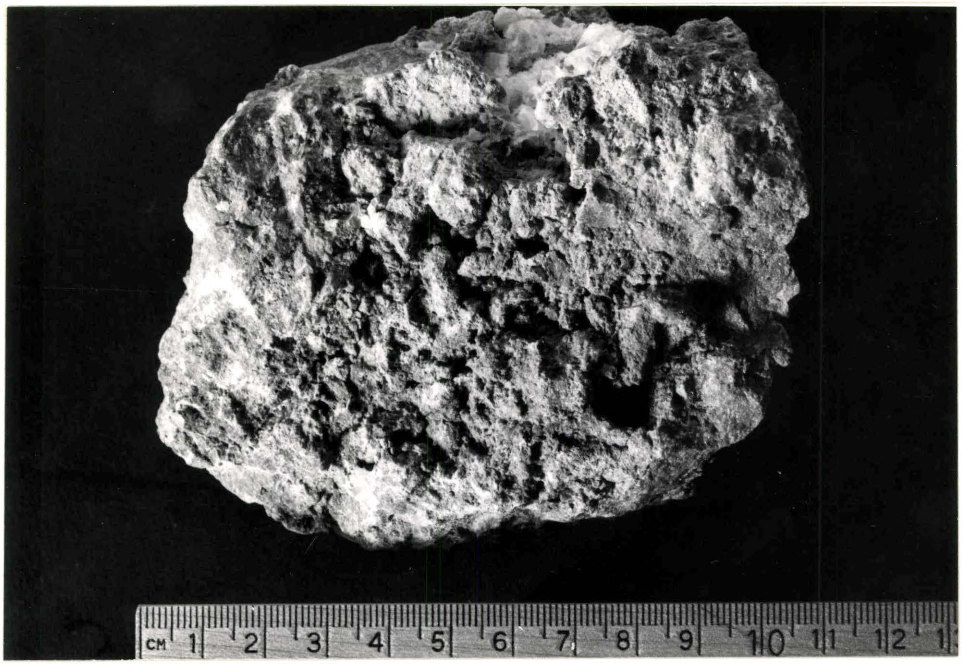
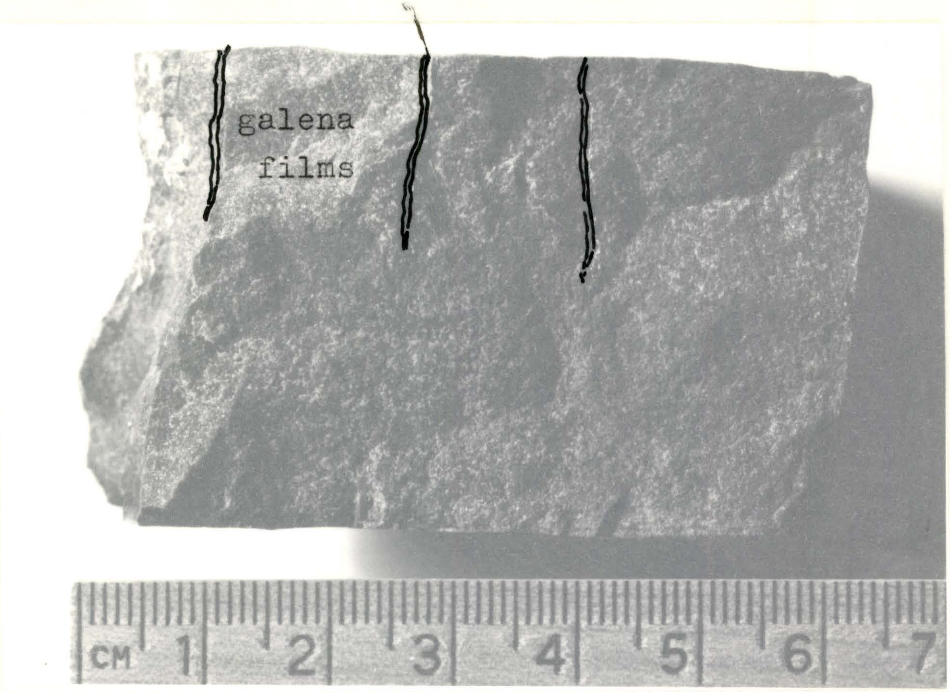
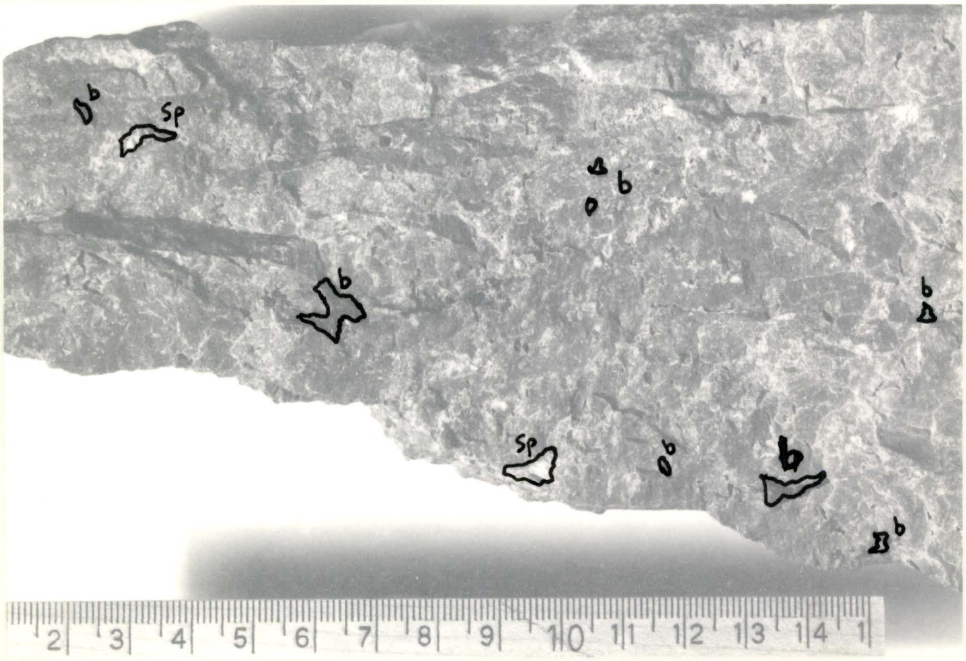


Fig.9 Films of galena in aphanitic Erasmosa dolomite, New Dundas Quarry.

Fig.10 Sphalerite and bitumen filling porous Guelph dolomite, New Dundas Quarry.





sp = sphalerite
b = bitumen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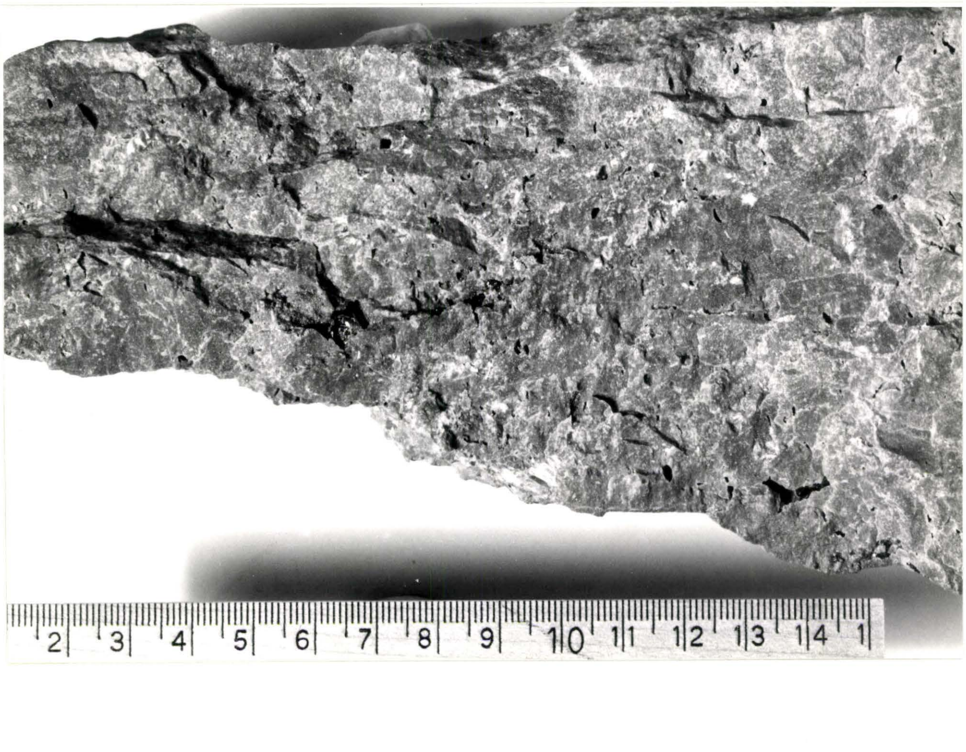
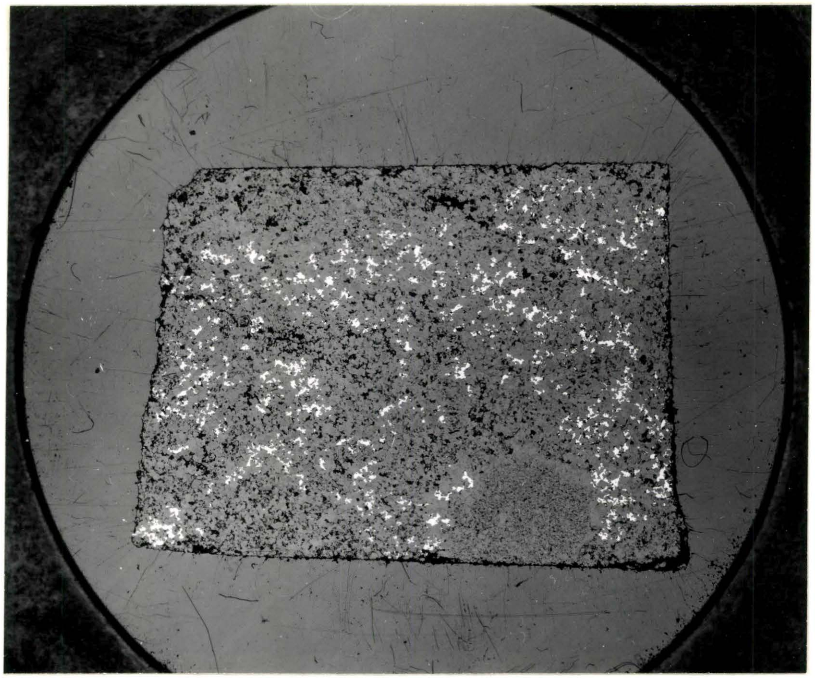

2 3 4 5 6 7 8 9 10 11 12 13 14 1

Fig.11 a) Disseminated galena (white) in the dolomite interbeds of the Rochester Formation. Hwy.20, Stoney Creek. 4X.

b) Micrograph (16X) of the same showing that galena (White) essentially fills pores in the host dolomite (grey).



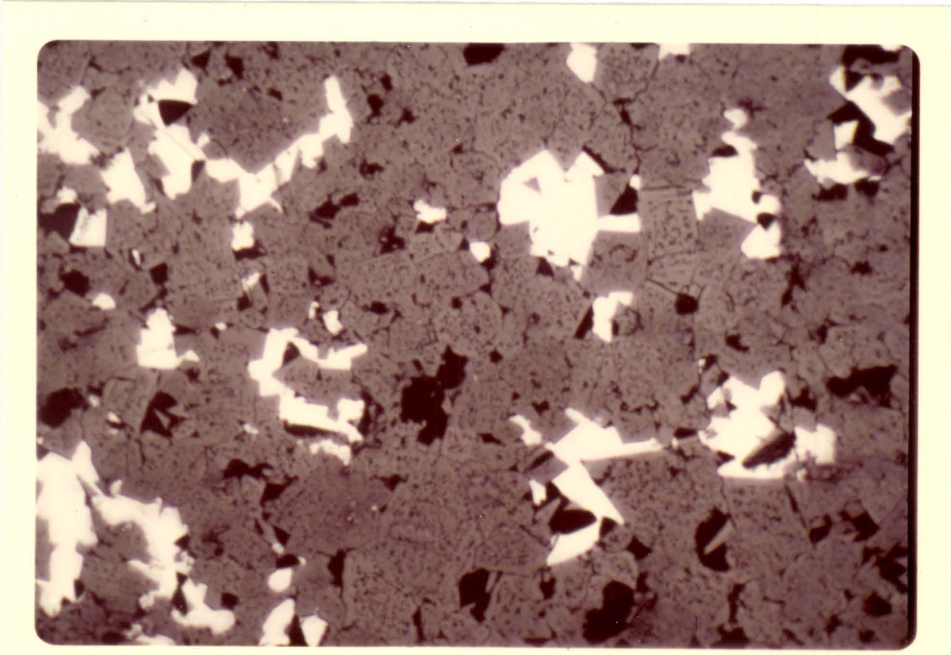


Fig.12 a) Micrograph (4X) of sphalerite (light grey) filling small cavity in Gasport dolomite, Hwy.403.

b) Micrograph (16) of the same showing chalcopyrite (light yellow) enclosed in sphalerite (greyish) and disseminated along the contact zone of sphalerite and dolomite (brown). The white disseminated mineral is marcasite.

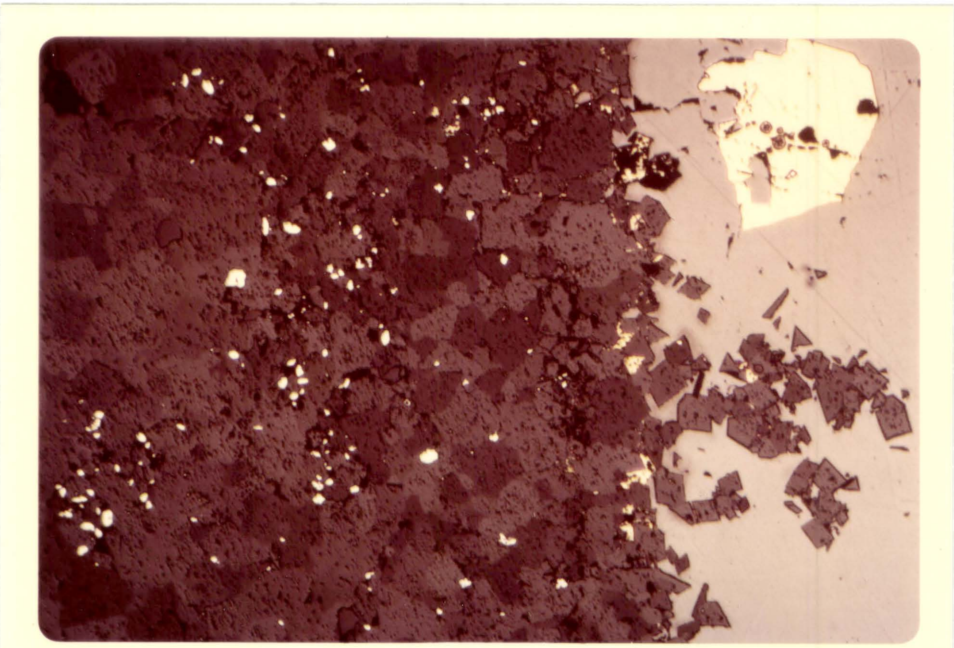
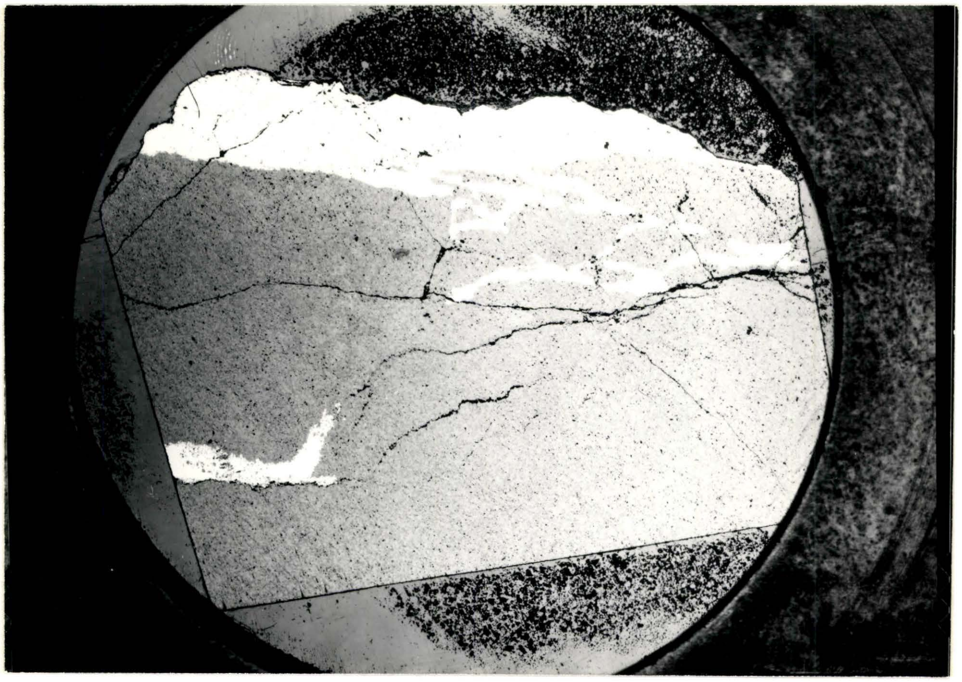


Fig.13 a) Fissures of sphalerite (white) in fine grained Eramosa dolomite, Old Dundas Quarry. (4X).

b) Micrograph (16X) of the same showing the replacement texture. (sphalerite--blue, dolomite--grey.)



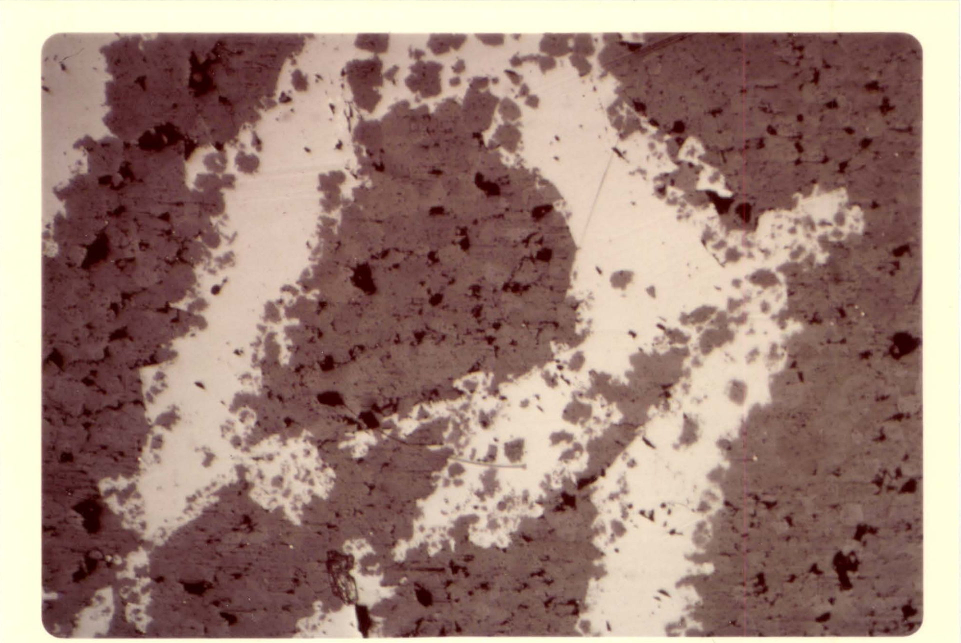


Fig.14 a) Veinlet of galena (white) in Eramosa dolomite, Old Dundas Quarry. (4X).

b) Micrograph (16X) of the same showing that little replacement feature is apparent along the galena-dolomite contact.

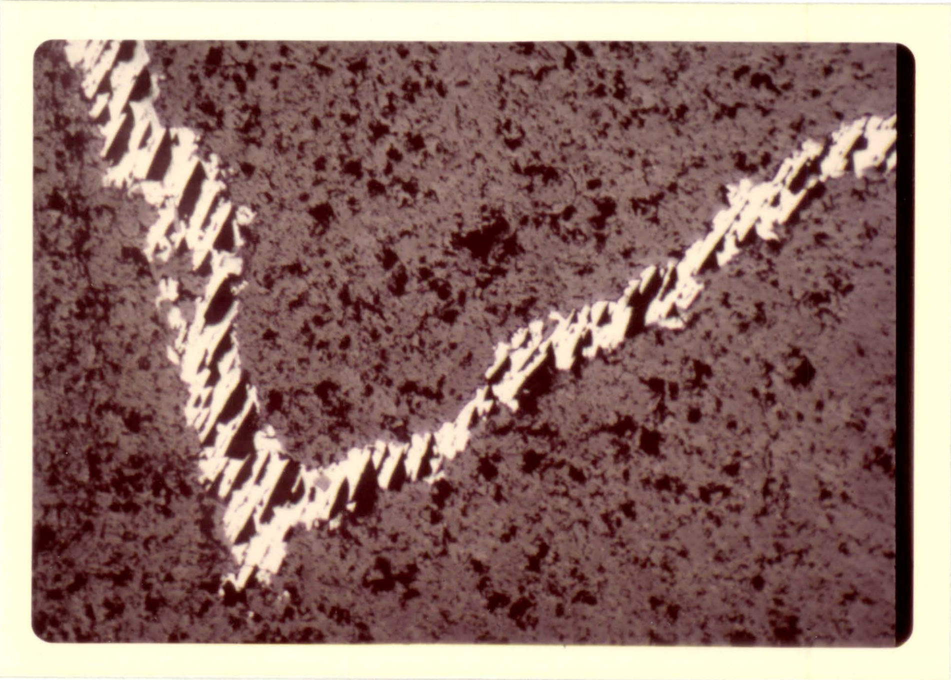


Fig.15 a) Lenticular mass of sphalerite (light grey) containing shale fragments (dark grey to black). Eramosa dolomite, Old Dundas Quarry.

b) Micrograph (4X) of the same.


CM 1 2 3 4 5 6 7

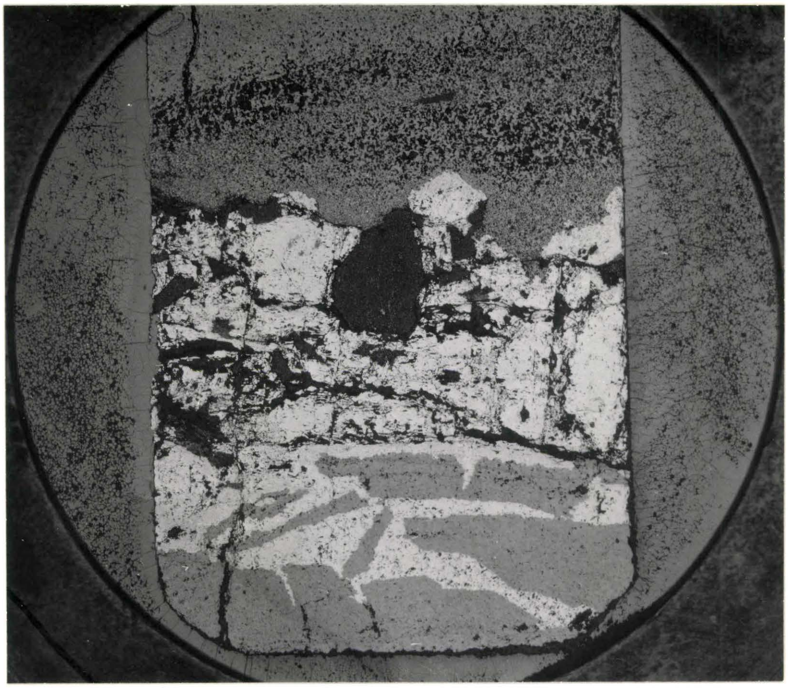
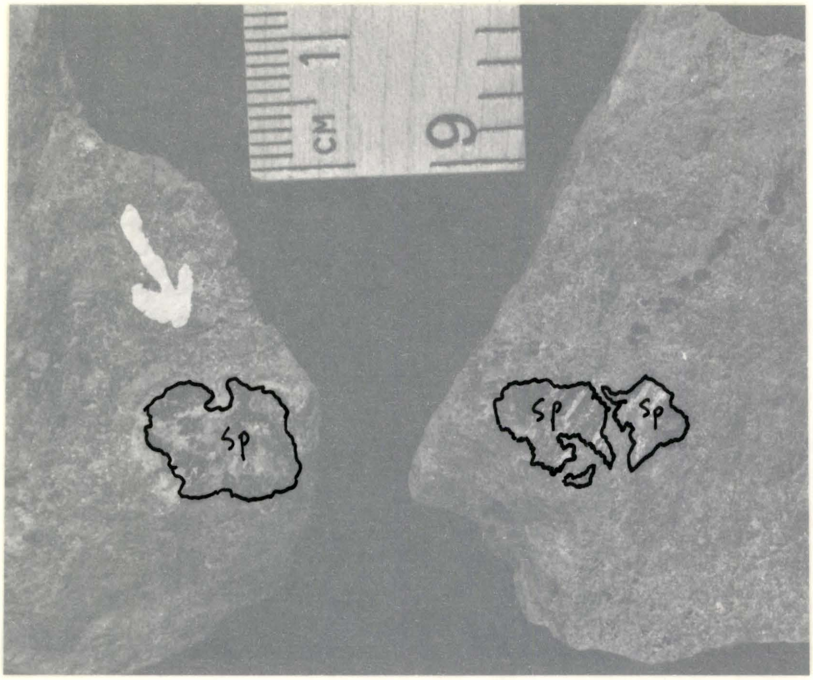
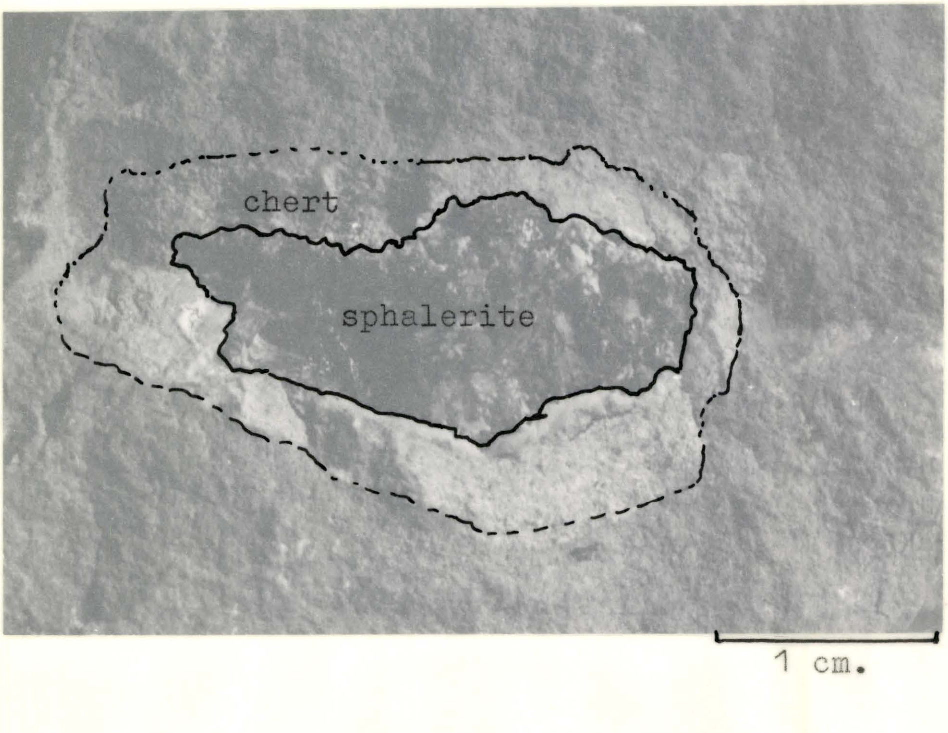


Fig.16 Sphalerite (shiny black) impregnated in slightly argillaceous facies of Goat Island dolomite, Hwy. 403. The white mineral surrounding sphalerite in the left-hand side specimen is calcite.

Fig.17 Sphalerite (dark grey) enclosed in chert nodules (white). Goat Island dolomite, Hwy.403.



sp = sphalerite



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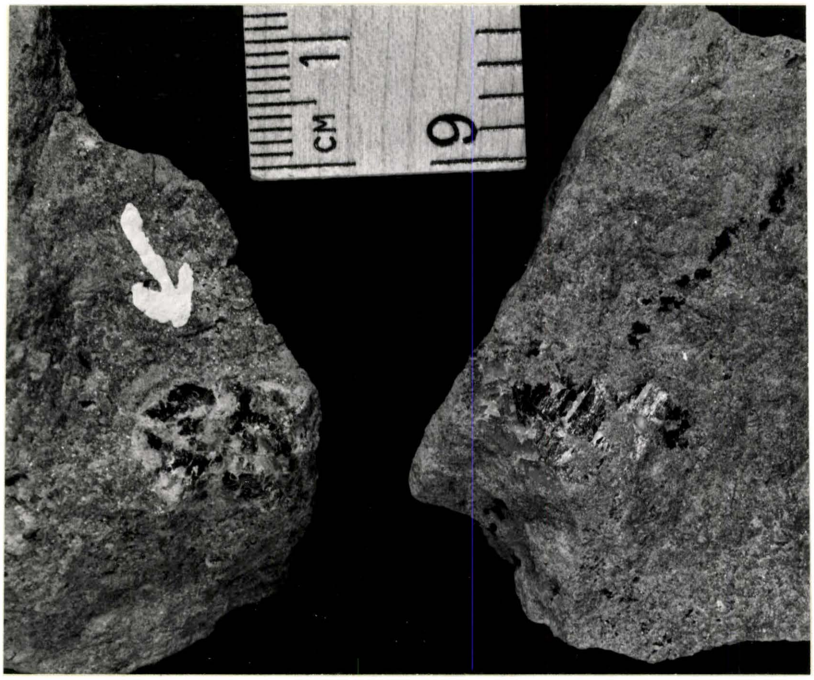
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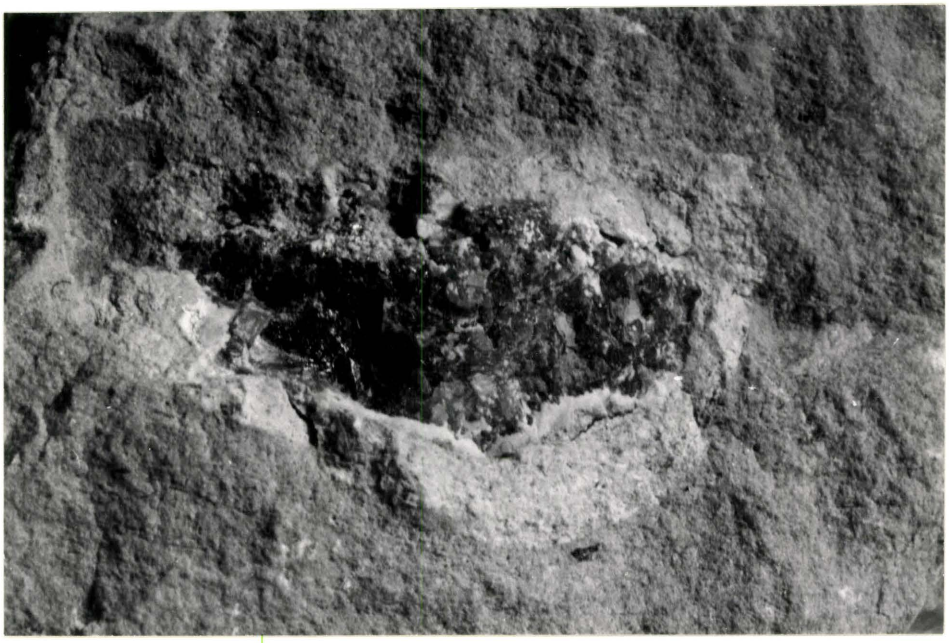


B. OBSERVATIONS

a) Stratigraphic control

Detailed study at the outcrops revealed that neither galena nor sphalerite is restricted to a particular horizon though some beds are more enriched with mineralization than others. Thus in the area covered by this study, the most favourable locations for sulphides are the lower Guelph dolomite adjacent to the contact with the underlying Eramosa, the upper Eramosa dolomite, the argillaceous dolomite just above the Ancaster chert bed (Goat Island) and possibly thick dolomite interbeds (compared to the shale interbeds) in the De Cew - Rochester Formations. In the rest of the stratigraphic column, sparingly small amounts of sulphide (mostly sphalerite) are more readily found adjacent to contacts of two beds especially if a shaly facies is present.

In addition to this distribution of the sulphides, there is an apparent trend of decreasing mineralization down the stratigraphic section.

b) Mode of Occurrence

1) Galena

Galena commonly occurs as films filling small fractures in the finer grained carbonate horizons. (Fig. 9). The rock usually breaks along these fractures so that as a result of weathering, galena frequently forms a greyish white, flaky coating on the rock face. Scratching with knife reveals its characteristic metallic lustre.

Rarely, fine disseminated galena grains are observed having angular outline pseudomorphic after dolomite (Fig. 11). In the Powerline Roadcut, perfect replacement of crinoid stem (pelma) has been found (Fig. 5).

Very rarely, galena also exists as cubic crystals in vugs thinly lined with fine grained crystalline calcite.

2) Sphalerite

Sphalerite usually takes the form of cleavable mass sitting on or impregnated in the vuggy host carbonate with or without a calcite lining along the contact (Figs. 8, 16). It also replaces fossils and fills pores and fissures (Figs. 3, 4, 10, 12, 13). The colour of these sphalerites is commonly light yellow indicating low iron content. In the New Dundas Quarry, isometric sphalerite crystals (up to 4 mm maximum dimension) have been observed resting on, or adjacent to, clusters of black bitumen, white calcite or blue tabular celestite (Figs. 6 & 7) The occurrence is in a prominent fossiliferous solution-brecciated bed about 3 feet thick in the Eramosa 15 feet below the top of the quarry face. The colour of these sphalerite crystals varies from deep orange to nearly black.

Rarely sphalerite of various yellow shades occurs in a lenticular form containing shale fragments (Fig. 15) and also as anhedral grains/mass enclosed in chert nodules. (Fig. 17).

c) Associated Minerals

Besides calcite, celestite and bitumen, gypsum and barite have been found around the middle of the Eramosa dolomite while pyrite and marcasite are more common in the lower shaly portion. In the Lockport Formation, powdery gypsum is occasionally encountered in the cherty beds. Pink dolomites in curved crystals have been observed in the dolomite interbeds of the De Cew-Rochester Formations. Disseminated pyrite/marcasite is fairly common in the Gasport and increases downward, becoming prominently concentrated in the Pentameras casts of the Reynales dolomite.

In one of the polished sections, chalcopyrite pseudomorphic after pyrite has been observed enclosed in sphalerite filling a small cavity (Fig. 12). In the field, no copper minerals have been observed.

Lastly, it is noteworthy that even though galena and sphalerite may exist side by side, they are never intermixed or found coating one another. (This statement may not apply to the so called "vein sulphide" from the New Dundas Quarry. In the specimen mentioned by R. L. Wright (1971) and another offered to the author by Mr. H. J. Down, the vuggy pyrite/marcasite masses are successively coated with sphalerite, calcite and galena crystals lining the vugs. This indicates a paragenetic sequence of pyrite/marcasite - sphalerite-calcite - galena. However, the author did not hit upon similar deposits during his three visits to the quarry).

C. INTERPRETATIONS

Summarizing the foregoing descriptions, sphalerite and galena occur in the following modes

(i) pores, fissure and fracture filling
(ii) growing into open space (vugs, cavities, solution breccias)
(iii) fossil replacement

The first two modes of occurrence necessarily require mineralization after lithification of the host carbonates. Simple solution mechanisms (plus subsequent collapse effects) and/or dolomitization can produce the required porosity for ore deposition. As exemplified by the case of galena replacing the crinoid stem, the sulphide is clearly pseudomorphic after dolomite. This indicates that the replacement of fossils most probably also took place after the lithification of the sediments.

The apparent enrichment of sulphides in the upper portion of the stratigraphic column is a consequence of two factors; namely, greater porosity and the presence of potential reducing agents. Recall that only Guelph and Eramosa dolomites are bitumen rich and the underlying carbonates are in general much denser and less porous. The importance of the presence of a percolating route for sulphide deposition is further confirmed by mineralization along the contacts of adjacent beds which gives way more readily to solution effects.

The occurrence of sphalerite of different colours in the same horizon reflect either a change in the composition of ore-bearing fluid or a repetition of ore deposition or both. The presence of discrete sphalerite crystals of different colours in the prominent brecciated layer mentioned above positively implies more than one generation of sphalerites. The fact that sphalerite in small fractures and fissure fillings shows no variation in colour can readily be explained by the size of the opening. If the opening is relatively small and once filled with a fluid it would not be readily displaced though diffusion can bring in the necessary zinc and sulphide ions for the formation of sphalerite. Naturally, once such an opening is filled with sulphide, it would not be open to later generations of ore fluids.

The fact that sphalerite and galena do not intermix and that they occur as large scattered masses rather than tiny disseminated grains probably suggests that the original ore fluid is only slighlty supersaturated with respect to the sulphides. In this situation, rate of crystal growth is greater than rate of nucleation so that like sulphide grows on the seed crystals already present thereby giving rise to the observed texture.

ORIGIN OF THE SULPHIDES

A. PRESENTATION OF THE PROBLEM

The mode of origin of the Mississippi Valley type lead and zinc deposits has long been a matter of debate. Considering the deposits in the districts of the Mississippi Valley alone, most geologists, by 1939 (as reflected in Bastin, 1939) favoured a hydrothermal origin. Twenty years later, Ohle (1959), upon reviewing published information of similar deposits in other parts of the world suggested the grouping of all these into what is called the Mississippi Valley type deposits. He further concluded that all deposits of this type had apparently the same mode of origin. Since then, as remarked by Charles H. Behre Jr. (in Brown, 1966 p. viii), "... the chief contrasts are between the syngenetic or diagenetic, essentially sedimentary theory of origin and the epigenetic, essentially hypogene interpretation." The latest suggestion is that of Jackson and Beales (1967). They argued from the viewpoint of oil geology a process involving transport of the metals by brine expelled from great thickness of sediment during compaction. Plausible as it is, such a theory still does not explain the scarcity of copper accompanying the lead zinc deposits.

An alternative attack on the problem while still keeping the idea that the metals originates from argillaceous rocks is to postulate that lead and zinc are preferentially leached from shales by corrosive fluids. The more likely fluids are solutions of hot brine and bisulphide which are capable of forming stable complexes with the heavy metals. The validity of the suggestion can be established if it is proved that

a) shales are significantly higher in Cu, Pb, Zn contents than unmineralized carbonates and b) copper is inert to the leaching agent concerned.

B. EXPERIMENTAL METHOD

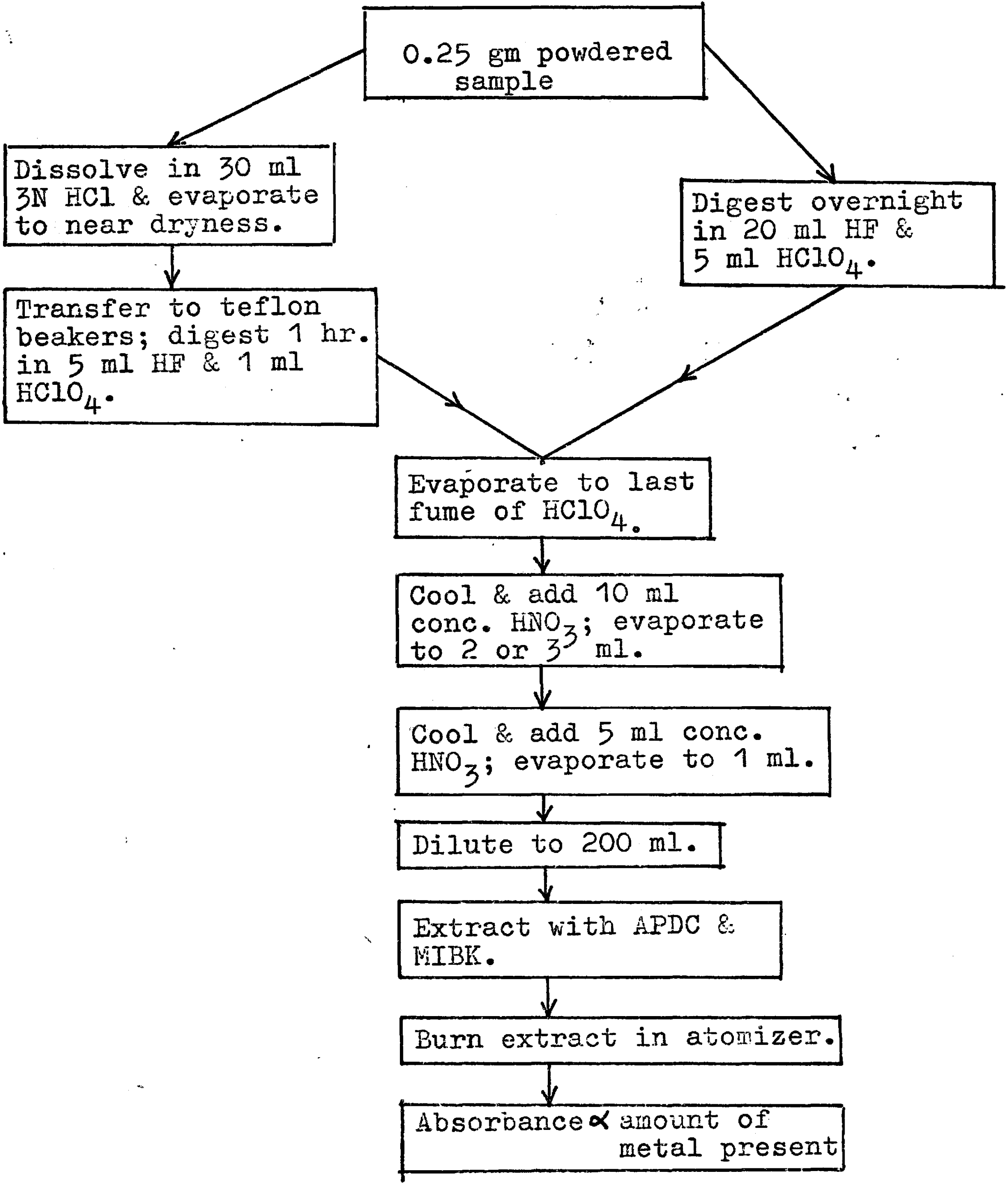
a) Analysis for Cu, Pb and Zn

To assess average copper, lead and zinc contents of argillaceous rocks and carbonates, 14 shales and 12 dolomites containing no visible Cu, Pb or Zn mineralization were analyzed by means of atomic absorption technique. Anticipating a low content of these metals especially in the carbonates and to avoid possible interference by the alkali metals especially calcium, an extraction procedure using APDC and MIBK was followed. Fig. 18 shows a flow chart of the steps of analysis.

Furthermore, to test the validity of the experimental method two analysis of the U. S. Geological Survey standard W-1 (diabase) were done and the result obtained was checked against published values in the literature.

b) Leaching experiments

About two grams of powdered Rochester shale (sample no. S-1, see appendix 1) were weighed accurately to five decimal places and transferred to each of five 35mm x 90 mm test tubes labelled 1 to 5 respectively. 40 mls of 5M NaCl, 3M NaCl, 1M NaCl, 1M NaHS and 0.5M NaHS was added respectively to the test tubes. These were sealed and immersed in a water bath maintained at 78 ± 1° C for 12 days. Fig. 19 shows the set up of the apparatus. The contents of the test tubes were agitated once or twice daily to enhance contact of the solid and liquid phases.



** APDC= 1-pyrrolidinecarbodithioic acid, ammonium salt.

MIBK= methy iso-butyl ketone. **

Fig. 18 Flow chart for atomic absorption analysis.

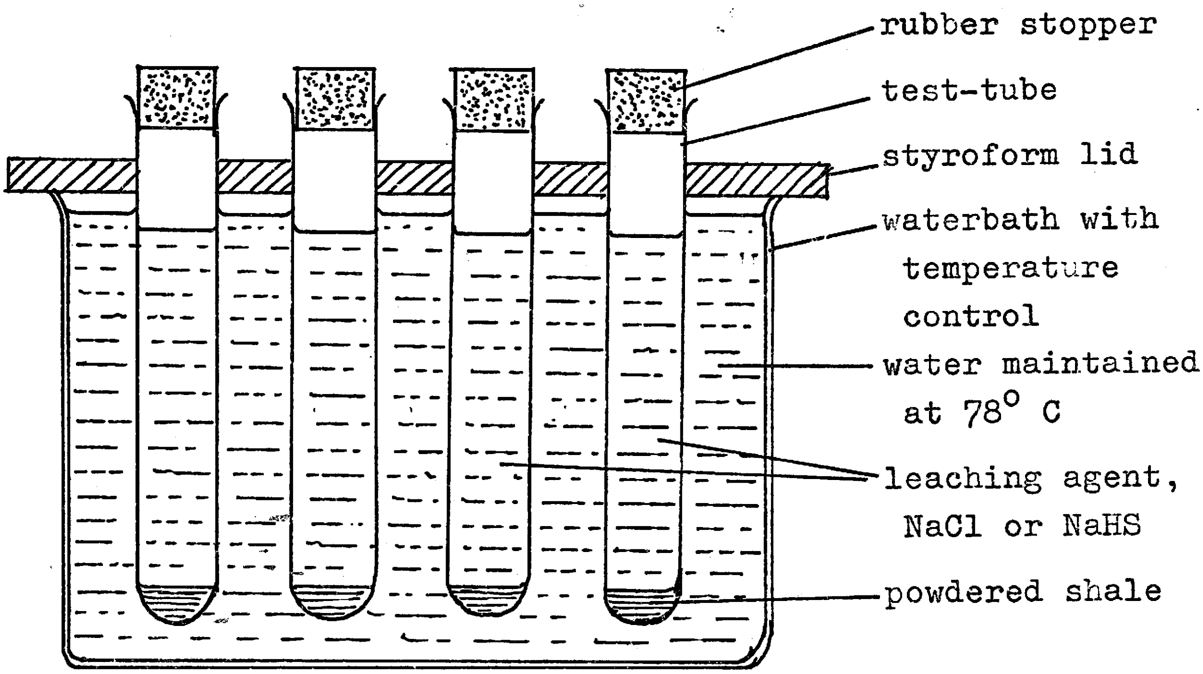


Fig. 19 Apparatus set up for leaching experiments. For simplicity, only four tubes are shown.

The aqueous solutions were subsequently analyzed for copper, lead and zinc by atomic absorption. To allow for possible contamination in the chemicals and apparatus used, 40 ml of 2M NaCl and 0.75M NaHS solutions were prepared and carried through the same prodedure. These provided the background values for the absorbance record.

C . RESULTS

The data obtained from the Cu, Pb and Zn analysis are presented in appendix 1. In calculating the average value of the heavy metal contents of shale, two sets of data have been ignored due to the possible masking effect of iron. Also, two dolomite analysis were discarded due to later discovery of lead and/or zinc mineralization in the samples. If the metal value was below the detection limit, half the detection limit value (0.025 ppm) was used for calculation of the average. After these modifications, the Cu, Pb, Zn contents of shales are compared with those of the carbonates in Table 2.

The results of the leaching experiments are also tabülarized and presented in Table 3.

D. DISCUSSION

a) Significance of the experimental results

As shown in Table 2 the Cu, Pb and Zn contents of the shales are significantly higher than those of the dolomites. This implies that argillaceous sediments can be a potential source of lead and zinc later precipitated as galena and sphalerite in carbonates. This is especially significant for the Mississippi Valley type lead-zinc deposits where in general an igneous source is absent.

Table 2 Average Cu, Pb, Zn contents of shales and dolomites

Rock Type	No. of samples analyzed	Conc. of elements in ppm.								
		Cu			Pb			Zn		
		range	average	δ	range	average	δ	range	average	δ
Shale	12	5.2-31	15	7.43	0.025-120	28	40.4	6.1-50	24	13.5
Dolomite	10	0.60-11	4.7	4.26	0.025-12	1.4	3.56	0.025-36	8.4	11.6

Table 3 Leaching of Rochester shale with various concentrations of NaCl and NaHS for 12 days at 78 ± 1° C (pH = 9 for the NaHS leaching)

	% leached				
	5 M NaCl	3 M NaCl	1 M NaCl	1 M NaHS	0.5 M NaHS
Cu	N.D	N.D	N.D	4.7	4.5
Pb	2.6	N.D	N.D	11.3	4.3
Zn	49.4	N.D	N.D	1.1	N.D

Table 4 Comparison of the experimental values and literature values (compiled by M. Fleischer 1969) for the Cu, Pb and Zn contents of W-1

	Experimental value in ppm average of 2 analysis	Literature value in ppm	
		range	recommended value
Pb	N. D (< 0.05)	trace - 20	8
Zn	57	42.8 - 91	82
Cu	120	100 - 140	110

The simple leaching experiments render some interesting results. The leaching of powdered shale with various strength of NaCl solutions at 78° C (which is in the temperature range of deposition of the Mississippi Type lead-zinc ore according to fluid inclusion studies) indicates that only a concentration of ≥ 5 M would a brine solution be corrosive enough to leach any signigicant amount of heavy metals from the argillaceous rock. Fluid inclusion studies on the Mississippi type ore show that ore-bearing fluid is near or even reach saturation with respect to sodium chloride. The required concentration is therefore compatible with the natural solutions. What is more significant, however, is the ratio of Zn : Pb : Cu leached from the shale. Although in the original shale, [Pb] > [Zn] > [Cu], Zn : Pb : Cu in the solution is 19 : 1 : 0.025. This agrees with the field observation that sphalerite is more abundant than galena and no copper mineralization is observed. A possible drawback of the result is perhaps the high percentage of zinc (49.4%) leached from the shale. This may suggest that during the experiment, the solution was somehow contaminated with respect to zinc. However, the amount of these heavy metals leached depends on how they are tied up with the shale mineralogy. If zinc is largely adsorpted to the surface layers instead of being bound within the crystal lattice of silicates in the shale, the author can see no reason why it cannot be released in great quantities given the right conditions.

One of the reasons why the bisulphide leaching was carried out is that water percolating through carbonate rocks is usually slightly alkaline in character (in contrast to brine solution which is usually slightly acidic or neutral). Besides, the sour taste of the Ancaster - Dundas ground water is well known indicating that it may contain an appreciable amount of bisulphide ions. It is therefore suspected that bisulphide might be important in the leaching mechanism. Experimental results presented in Table 3, however, show that while bisulphide solution can behave as an effective leaching agent under the laboratory conditions, it leaches copper equally well regardless of the NaHS concentration. This means that if bisulphide solution is responsible for releasing heavy metals from the shale, one should expect to find some copper minerals in addition to sphalerite and galena. Since no copper sulphide has been found, it is logical to conclude that bisulphide cannot be the leaching agent or heavy metal carrier in the genesis of the Mississippi Type ore.

b) Validity of the experimental data

Comparison of the experimental values for Cu, Pb Zn contents of the U. S. Geological Survey standard rock W-1 with those listed by Fleischer (1969) shows that the experimental values for lead and zinc are on the low side (see Table 4). This is probably due to the masking effect caused by the presence of abundant iron. In the shale and dolomite samples analyzed, Fe/Zn, Fe/Pb ratios are not as high as in W-1. Therefore, the masking effect should be tolerably small. The experimental data are considered as valid unless otherwise stated.

E. MODE OF ORIGIN SUGGESTED

Having established that shaly sedimentary rocks can be potential suppliers of heavy metals and that leaching by concentrated brine at moderately elevated temperature can be an effective mechanism for selectively removing lead and zinc, the mode of origin for the sulphide occurrences in the Hamilton vicinity suggested is as follows.

Ground-waters running down the sedimentary pile dissolve some evaporite and become progressively more saline in character. Upon reaching a depth of a few thousand feet, this brine solution is heated depending upon the prevailing geothermal gradient and begins to rise, selectively leaching lead and zinc from consolidated or unconsolidated argillaceous sediments 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 ion, $S^{=}$, produced combines with the lead and zinc ions to give rise to the sphalerite and galena observed. Repetition of the same process produces the several generations of sulphides.

Such an explanation is supported by the absence of an igneous source for the heavy metals, the absence of copper mineral associated with galena and sphalerite, the feasibility of the evolution of a chloride brine by dissolution of subsurface halite beds by ground water (Lerman, 1970) and the agreement of $\delta\ S^{34}$ value for the Dundas sulphide sulphur with that of sulphate sulfur of Devonian evaporites (Wright, 1971) which have probably once been present but are now eroded away.

CONCLUSIONS

1) Field and polished section studies suggest that lead and zinc mineralization of the Silurian dolomites in the Hamilton vicinity occurred after the lithification of the host rocks.

2) The enrichment of sulphides in particular horizons are a consequence of local porosity and the presence of potential reducing agents.

3) Atomic absorption analysis for Cu, Pb and Zn showed that shales are significantly richer in these heavy metals than the corresponding dolomites. Thus they may be a potential source of these elements in absence of an igneous source.

4) Concentrated sodium chloride brine solutions at 78° C appear to leach Pb and Zn selectively from argilleceous rocks leaving Cu behind. Therefore preferential leaching can be a crucial process involved in the genesis of the Mississippi Valley type lead-zinc ore where copper is usually extraordinarily low or absent.

SUGGESTIONS FOR FURTHER STUDY

1) Upper Silurian and Devonian carbonates are abundant to the southwest of Hamilton. These carbonates overlie the mid-Silurian Salina evaporites. Many of them, especially the Detroit River Group, are characterized by reefy assemblage and are bitumen rich. It would be interesting to see whether the generalizations arrived at in this study are applicable to them or not.

2) Fluid inclusion studies on the Mississippi Valley type deposits have shown that the temperature of ore deposition lies in the range of 50-150° C. The leaching experiments can readily be modified to cover the whole range by using high temperature-pressure bombs. Sodium chloride should be purified beforehand e.g. by recrystallization to leviate the problem of contamination. Effect of varying pH of leaching agents could be studied. In addition to copper, other trace elements like nickel, cobalt should be considered. If differential leaching of these trace elements also occurs and agrees with the actual abundance in the host carbonates and/or sulphides the plausibility of the suggested model of mineralization cannot be doubted.

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Appendix 1 Data of Analyses for Cu, Pb and Zn

				conc. of elements in ppm		
Sample No,	Formation	Location	Brief description/Remark	Cu	Pb	Zn
S1	Rochester	Hwy 403	dark grey	27.	77	31
S2	Rochester	"	dark grey, thicker than S1	10	17	17
S3	Grimsby	"	red	5.2	N.D	36
S4	"	"	green	10	N.D	50
S5	Goat Island	"	limey, fossiliferous	14	89	26
S6	Grimsby	Sy. Rd.	green	8.4	N.D	42
S7	Thorold	"	silty	11	N.D	26
S8	Grimsby	"	red, fossilferous *	4.2	N.D	N.D
S9	Rochester	"	greenish grey	19	120	15
S10	Rochester	C. C.	dark grey	16	20	6.8
S11	Eramosa	O.Q.	dark grey, limey	31	16	6.1
S12	Grimsby	Sy. Rd.	yellowish green	8.6	N.D	18
S13	Grimsby	C. C.	greenish grey, silty	14	N.D	9.2
S14	Grimsby	C. C.	thick bedded,red., c.f. siltstone *	43	N.D	N.D
			average	15	28	24
			range	5.2-31	0.025-120	61-50
			stand deviation δ	7.43	40.4	13.5
D1	Gasport	Hwy 403	crinoidal, medium grained	0.83	N.D	N.D
D2	Reynales	"	fine grained, visible pyrite	11	0.80	18
D3	Irondequoit	"		9.4	N.D	1.6
D4	Goat Island	"	trace argillaceous mat.	3.2	12	20
D5	De Cew	"	interbedded with shale †	7.4	> 240	4.6
D6	Goat Island	"	silicious †	2.0	N.D	127
D7	Eramosa	O. Q	bituminous	7.4	0.6	N.D
D8	"	N. Q	bitumen rich	0.60	N.D	4.4
D9	"	"	limey crust (pale yellow)	1.6	N.D	2.4
D10	"	N. Q	porous (+ coral?)	1.2	N.D.	0.40
D11	Reynales	S. C.		11	N.D	1.6
D12	Eramosa	O. Q	associated with celestite	0.6	N.D	36