# ANALYSIS AND INTERPRETATION OF FOSSILS IN THE ONONDAGA FORMATION USING CATHODOLUMINESCENCE AS COMPARED WITH PETROGRAPHIC TECHNIQUE OF EXAMINATION

By

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ABSTRACT

From the analysis of fossils, using the cathodoluminescence technique, it is seen that there is a pattern to the luminescence colours exhibited by dolomite, calcite and quartz, depending on the amount of the trace element $Mn^{2+}$ present in the structure of the minerals. In the experiment

| | | |
|---|---|---|
| Dolomite | luminesces | turquoise blue, |
| Calcite | luminesces | pale pink & bright red, |
| & Quartz | luminesces | sea blue. |

The calcite and quartz colours agree well with the observation of both Agrell et al. (1965) and Sippel et al. (1965). However, the dolomite luminescence colour definitely agrees better with the colour described by Agrell et al. than with that observed by Sippel et al.

Selective replacement of material occurs in Rugosa corals of the Devonian Onondaga formation of Southern Ontario. Quartz replacing material in the cavities of fossils is common, with the fringe wall of the fossil being of calcite as was previously observed by Middleton (1958). The matrix around the fossils consists mainly of quartz and calcite with minor dolomite.

A systematic difference in style of replacement (with respect to the various heights from which the fossils came in the section) occurred when considering replacement of the fossils by quartz. Replacement of calcite by quartz followed by slight dolomitization of the matrix in the Onondaga is suggested by luminescence observation. Also suggested by luminescence observations is: 1) Dolomitization by a downward influx of $Mg^{2+}$ ions, and 2) Homogenous and heterogenous micritic mud fillings in Rugosa corals' cavities.

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# INTRODUCTION

This thesis deals with the different luminescence colours exhibited by dolomite, quartz and calcite, when they appear as replacements of fossil parts or as infilling between these parts. From the cathodoluminescence patterns exhibited by calcite, dolomite and quartz in the matrix or fossils of the Onondaga formation, some attempt is made to:

1) give a history of the replacement,
2) tell whether there are variations in the process of replacement of the fossils with sample height in the formation (whether there is a vertical trend to the style of the replacement process), and
3) give an explanation for the variations in luminescence colours of the quartz, calcite and dolomite.

## CAUSES OF CATHODOLUMINESCENCE AND ITS COLOURS

A brief account will be given on the two above topics; for detailed work on the above consult Smith et al. (1965) and Medlin (1963a). Cathodoluminescence is the emission of light from a crystal during electron bombardment, and because variations in luminescence in individual minerals can be seen readily and related to texture and chemical composition, geologists have used it as a petrographic tool for the past 13 years.

The emission of light from calcite, quartz and dolomite (and a host of other minerals) is caused by the release of energy stored as electrons in energy levels of trace elements in the mineral. It should be noted that cathodoluminescence is closely related to thermoluminescence (which Medlin used in his experiments); the difference being that in thermoluminescence, electrons lost from an activator ion (e.g., $Mn^{2+}$) during radioactive bombardment, and trapped in the calcitic structure are made to recombine with the $Mn^{2+}$, etc., by heating the crystal, whereas in cathodoluminescence the specimen is bombarded with an external source of ions which excite an $Mn^{2+}$ ion, allowing it to de-excite by fluorescent radiation of a characteristic wavelength. In thermoluminescence it is the recombining of the electron with the $Mn^{2+}$ that causes the emission of light. In both cases the same activators and depressants are at work.

According to experiments carried out by Medlin (1963a, b, c) the chief trace elements that promote fluorescence are $Mn^{2+}$, $Pb^{2+}$, $Zn^{2+}$, and $Sb^{3+}$ in that order. His experiment was essentially based on measuring the emission spectra for principal glow peaks due to the activating ions. He found that divalent Mn is the most important activator and accounts for a prominent glow peak in most natural samples of calcite at 6500 Å. Divalent Pb, which is rarely found in calcite, shows glow peaks at 4800 Å and 6200 Å (see Fig. 1 (from Medlin 1963a)). Similarly, in the dolomites $Mn^{2+}$ was found to be the most important activator in natural samples. It produced glow peaks at 3800 Å and 6700 Å and accounts for the x-ray excited luminescence of most samples of dolomite (see Fig. 2 (from Medlin 1963a)). By using synthesised calcium carbonate, Medlin also introduced calculated quantities of $Fe^{3+}$, $Co^{2+}$, and $Ni^{2+}$ in the structure and noted that there was a dramatic decrease in the fluorescence colour exhibited by the activator ions ($Mn^{2+}$ and $Pb^{2+}$) in the synthetic calcite; thus the conclusion that these ions act as depressing agents in natural calcites and dolomites.

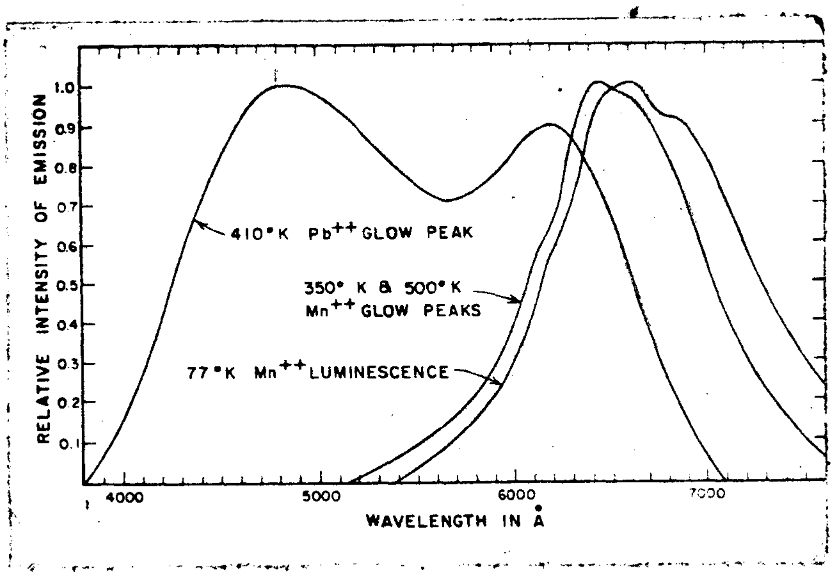



Fig. 1: Emission spectra for principal glow peaks due to $Mn^{2+}$ and $Pb^{2+}$ and for luminescence due to $Mn^{2+}$ in calcite (Medlin 1963a).

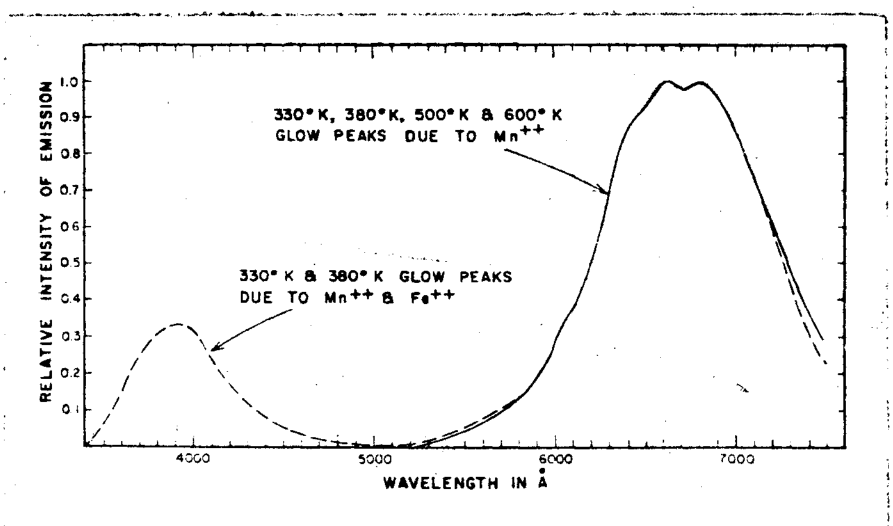



Fig. 2: Emission spectra for principal glow peaks due to $Mn^{2+}$ in dolomite (Medlin 1963a).

There are two factors that determine the colour of fluorescence by any one mineral: 1) the amount of activator ions in the structure ($Mn^{2+}$, and $Pb^{2+}$) and 2) the quantity of depressing ions in the structure ($Fe^{3+}$, $Co^{2+}$, and $Ni^{2+}$). To cite a classic example of the mineral dolomite exhibiting two entirely different fluorescent colours, we may note that R. F. Sippel (1965) working on dolomites found that dolomite luminesces bright red, whereas Agrell and Long (1965) found their dolomite samples to fluoresce turquoise blue. The vast difference in luminescing colours between the dolomites of Sippel's observations and those of Agrell et al. can be accounted for by the difference in $Mn^{2+}$ and $Fe^{2+}$ ion content of the dolomites.

$Mn^{2+}$ contents of 0.07 ± 0.02%,
and $Fe^{2+}$ contents of 0.80 ± 0.10%

occurred on an average in the dolomites studied by Agrell and Long. The dolomites studied by Sippel had much higher $Mn^{2+}$ contents and since it is this high content of $Mn^{2+}$ in the minerals which gives the fluorescent colours, the dolomites showed bright red luminescing colour. Concentrations of iron in excess of 0.5% in any of the minerals extinguish the Mn-induced cathodoluminescence colours (Agrell and Long 1965). It should be noted that in a few samples of calcite and dolomite anomalous colours may appear, that have no direct relation to the quantity of activator ions present, in these cases Medlin (1963b) using x-ray analysis of the fluorescent regions showed that the structures of the calcite and dolomite were faulty and thus the fluorescence in this case was due to a defect structure.

Luminescence thus depends on defect structures and on the concentration and interaction of a variety of trace elements, which act as activators, for example manganese. The absence of luminescence does not necessarily indicate the absence of these trace elements, but rather: 1) the low concentrations of the activator ion, or 2) the presence of a depression ion such as $Fe^{2+}$ in major quantities.

## REVIEW OF PREVIOUS WORK DONE USING THE CATHODE LUMINESCENCE TECHNIQUE

### 1) J. V. P. Long and S. O. Agrell (1965)

They examined the different luminescence colours exhibited by the various minerals. In Fig. 3, reproduced from their paper, the authors show calcite and dolomite from a section of a carbonatite from Palabora, South Africa. The calcite luminesces a typical orange-red fluorescence produced by the presence of $Mn^{2+}$ ions. The exsolved dolomite show a weak bluish fluorescence, which appears blackish brown in the coloured photostat. The respective $Mn^{2+}$ and $Fe^{2+}$ contents determined by microprobe are given below.

Calcite: $Mn^{2+}$ content = 0.13 ± 0.02%
$Fe^{2+}$ content = 0.20 ± 0.02%

Dolomite: $Mn^{2+}$ content = 0.07 ± 0.02%
$Fe^{2+}$ content = 0.80 ± 0.10% .

Figure 4 shows a zoned calcite crystal from a hydrothermal vein from Strontian, Scotland. The alternation

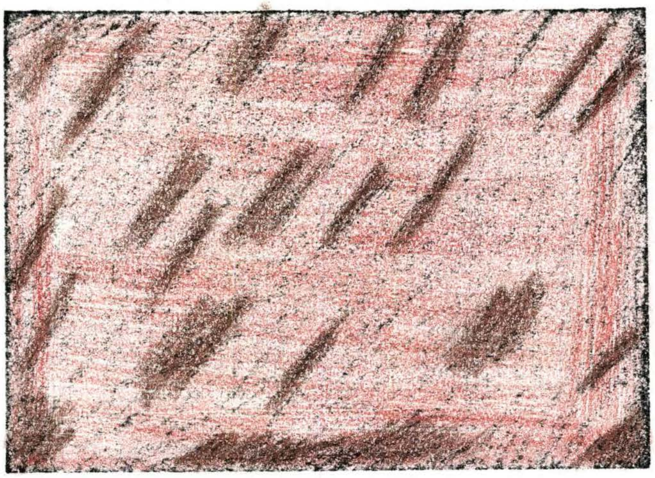


Fig. 3: Cathodoluminescence of a thin section of a calcite (Red)-dolomite (Blackish brown) intergrowth from Palabora.

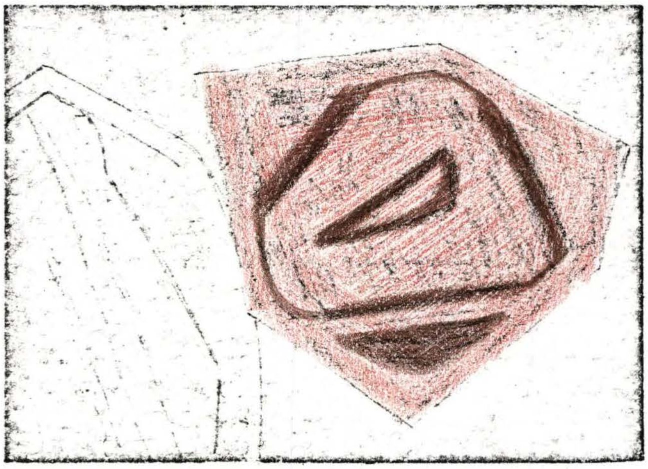


Fig. 4: Cathodoluminescence of a single crystal of calcite showing rhythmic variations in colour due to fluctuating Mn/Fe ratio.

in zonation suggested by the different fluorescent colours does not correlate with any obvious change in optical properties, and in plane transmitted light the authors see no evidence of zonation except for occasional alignments of opaque inclusions parallel to the crystal faces. The respective $Mn^{2+}$ and $Fe^{2+}$ contents are given below.

| | |
|---|---|
| Orangish Red Calcite zone: | $Mn^{2+}$ content = 1.0% |
| | $Fe^{2+}$ content = 0.1% |
| Dark Calcite zone: | $Mn^{2+}$ content = 0.1% |
| | $Fe^{2+}$ content = 1.0% . |

Their observation and chemical analysis thus suggest that concentrations of iron in excess of 0.3 - 0.5% were effective in extinguishing the Mn-induced cathodoluminescence of calcite, and because dolomite is able to substitute more $Fe^{2+}$ in its structure, the luminescence colour of this mineral will be very low (bluish black, to blackish blue to pale blue - depending on the amount of iron in the particular dolomite).

The authors saw two types of luminescence for quartz. The majority of grains of quartz show a faint blue to a dark blue luminescence colour, whereas overgrowth material of quartz on detrital grains luminesce red. They also examined

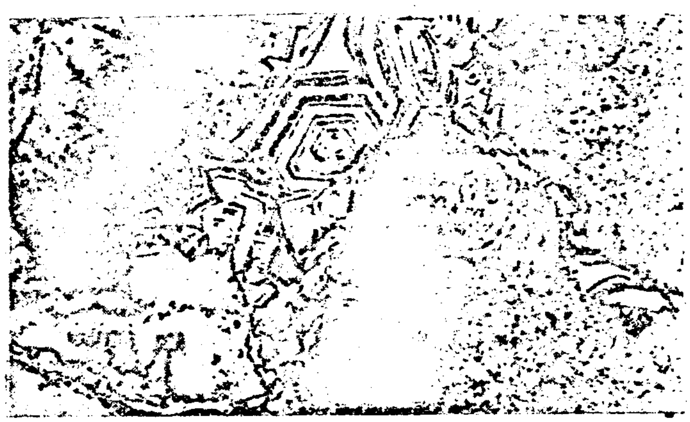
2 feldspars in the coarse perthite of the Madoc granite. They both gave different intensities of a "bluish-purple fluorescent colour, thus suggesting the unequal partition of an activator between the two phases".

2) R. F. Sippel and E. D. Glover (1965)

They used the cathodoluminescence technique to observe: 1) vein fillings, 2) crystal growth, 3) overgrowths, and 4) cementation phenomena in carbonates. Sometimes none of the above four can be seen under plane polarized light or transmitted light, because the vein fillings may be of the same mineral as the wall rock, etc.

A typical case in which the structure of calcite cannot be determined in plane light, but where, under cathodoluminescence, the grain shows fifty successive growth bands, is shown in Fig. 5 (reproduced from their paper). Overgrowths and healed cracks in dolomite were also quite nicely shown in luminescence light. The colour of the overgrowth appears different from the initial grain.

Fig. 5: Calcite infilling in dolomite. Crossed nicols (Sippel et al. 1965).



Luminescence.

3) R. F. Sippel (1968)

He compared the luminescence colour of quartz with the luminescence colour of the minerals below.

| MINERAL | | LUMINESCENCE COLOUR |
|---|---|---|
| Potash Feldspar | | Various intensities of Blue |
| Dolomite | | Bright Red |
| Calcite | | Brilliant Orange |
| Apatite and Zircon | | Yellow |
| Plagioclase | Oligoclase | Bright Green |
| | Albite | Blue or Red . |

He found that quartz when compared to the above minerals shows a dull blue luminescence colour. He also used the variation in colours of quartz in luminescent light to show: 1) overgrowth, and 2) fracturing and healing of quartz grains which cannot always be seen under crossed nicols. The only means of telling quartz overgrowth under crossed nicols is if there are inclusions in the quartz that rims the initial detrital grain. Fractured and healed quartz shows up as polycrystalline quartz in crossed nicols, but sometimes the quartz is fractured and undergoes no rotation whatsoever. In this case the fracture cannot be seen in crossed nicols. An example showing overgrowth that cannot be seen in crossed nicols is shown in Fig. 6. The blue

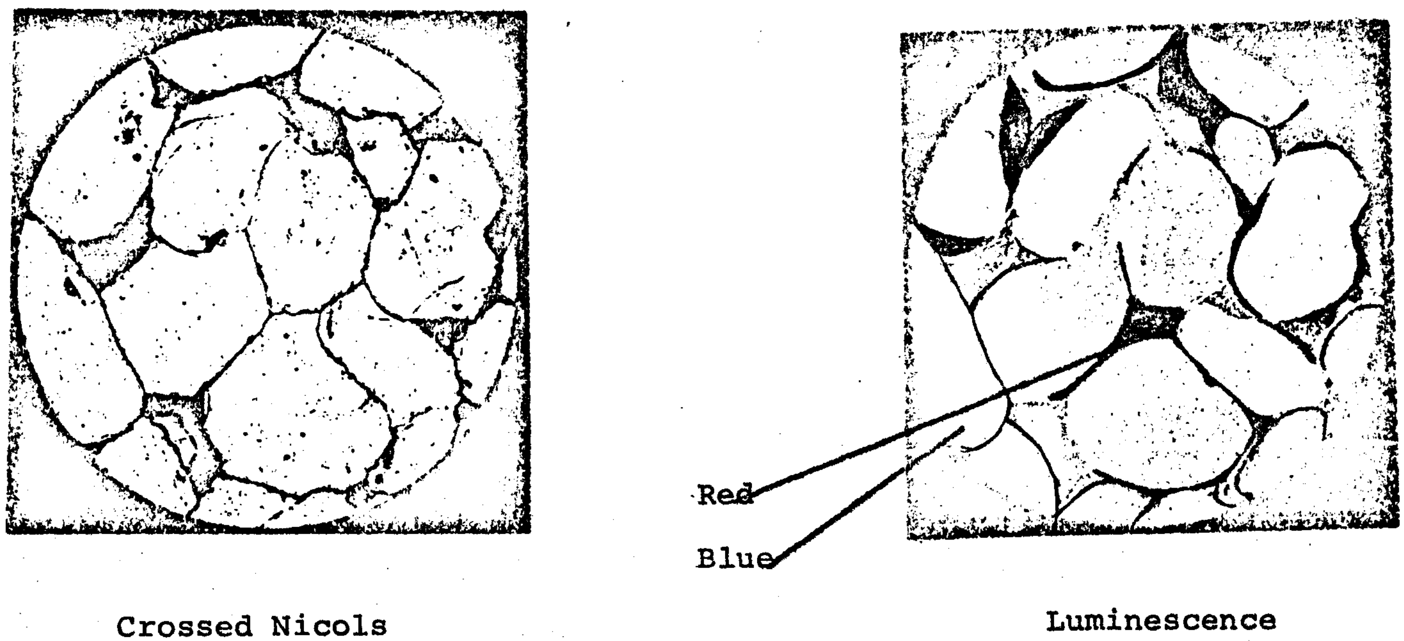



Fig. 6

overgrowth in the figure = Red luminescence and the grey overgrowth in the figure = Blue luminescence. Sippel also used the luminescence colours to tell the amount of rotation through which a fractured grain turned, before it was cemented by quartz solution.

4) T. Freeman (1971)

He used the luminescence technique to study the calcitic content in fossils as opposed to the calcite in the cement. His experiment was done on a crinoidal biosparite.

> "In plane polarized light and crossed nicols, there is no suggestion of a difference between the calcite in the fossils and that in the matrix, apart from druse on polycrystalline grains or morphological or compositional discontinuities within the calcite cement."

Under luminescence light, however, there are seen to be two zones of calcite, - an earlier non-luminescent calcite which is restricted to the underside of fossil fragments and the later pore - occluding luminescent calcite which surrounds the fossil fragments. From this experiment the author shows that multiple generations of calcite cement can be recognized under luminescence light although this phenomenon is invisible by normal optical means.

5) M. Kastner (1971)

She examined: 1) authigenic feldspar samples in carbonate rocks, and 2) albites from low-grade metamorphic rocks under cathodoluminescence light. Her findings were that neither the albites nor the authigenic feldspar showed any detectable characteristic luminescence. She noted that, by contrast, Smith and Stenstrom (1965) had examined feldspars from a variety of igneous rocks using the cathode luminescence technique and found that all the feldspars showed either blue or red luminescence.

Kastner thus suggested that cathodoluminescence may be used to distinguish the different geological origins of the feldspar grains, and thus tell authigenic from detrital grains. To the present writer this seems a good field for experimentation, but it should be undertaken with the recognition as indicated in the work by past authors, that various samples of the same mineral when examined under cathodoluminescence give vastly different colours.

In conclusion to this brief discussion on past work luminescence has been shown to depend on defect structures and on the concentration and interaction of a variety of trace elements, which act as activators, for example manganese.

## GENERAL GEOLOGY OF THE ONONDAGA FORMATION FROM WHICH MOST OF THE FOSSILS WERE TAKEN

The Onondaga formation is a "fossiliferous, cherty and slightly dolomitic limestone" of Devonian age (Middleton 1958). The basal section of the formation is the Springvale sandstone. The formation is exposed in the quarries of Hagersville, Ontario where active excavation is in progress. Samples were collected from the South Quarry and a vertical section was made from which the samples came. From the top of the section to the bottom measured 23'4". The base of the section was a shaly, glauconitic chert Table 1 shows the "heights" from which the corals came. The corals from these heights are then examined to see if there is any difference in replacement in the cavities of the fossils, by using the luminescence technique.

It should be noted here that no great attention has been paid to minerology in this section, except to say whether the rock is calcareous chert, limestone, chert, etc.

From the previous section it is seen that Rugosa corals seem to occur over the whole section and these seem to be the dominant fossils. Thus experimentation was

TABLE 1

| Section | | Coral Samples |
|---|---|---|
| Top | 0 | |
| | 1' | Calcareous mud matrix - Rugosa Corals |
| | 2' 5" | Calcareous mud matrix - Devoid of corals |
| Onondaga Limestone | 3'10" | Calcareous mud with Rugosa Corals |
| | 10'10" | No fossils in this sample - silty limestone |
| | 13' | Cherty calcareous mud with Rugosa Corals |
| | 15' | Cherty calcareous mud with Rugosa Corals |
| Base of Onondaga | 17' 6" | Cherty calcareous mud with Rugosa Corals |
| Springvale | | |
| Sandstone | 21' | Quartzite |
| | 23' 7" | Glauconitic chert |

carried out mainly on the corals, using the cathodo-luminescence to see variations in replacement of parts of the coral and thus trying to determine something about the history of the replacement.

## PREPARATION OF SAMPLES FOR OPTICAL ANALYSIS

Polished sections of the chips were made for all samples examined. Fossils were taken from both the Onondaga formation and from other areas, together with matrix material from the Onondaga. The chips were cut $1\frac{1}{2}$" by 1" and about $\frac{1}{2}$" thick. Using the $\frac{1}{2}$" thickness as a "handle", one face of the chip was ground down and the edges "buffed" on the coarse lap, using carborundum powder as the grinding agent. The chip was then washed and ground down to a smoother surface using the finer mesh of carborundum as the grinding agent on a glass plate. On completion of this step, the chip was washed off and polished on a high speed lap using tin oxide as the polishing agent.

In order to fit the specimen in the examination chamber of the luminoscope such that the beam would fall on the chip's surface and not fall on the edge of the chip, the chip had to be about $\frac{5}{16}$" thick. To get this thickness, the chip was stuck with balsam to the frosted face of a glass slide and cut by the vacuum cutter to about $\frac{5}{16}$", then ground down to smooth the back of the chip. Finally it was removed from the slide, cleaned of the mounting medium, and was then ready for cathodoluminescence analysis.

## CHEMICAL STAINING OF THE CHIPS

Chemical staining of the chips was necessary for the positive identification of the mineral viewed under luminescing light. The staining technique used was one suggested by Dickson (1965). The chips were first immersed in a solution of dilute HCl ($\frac{1}{200}$) for 30 sec to remove any dirt on the surface and to partially etch the chip. The chip was then immersed for 45 sec in a solution of HCl acid ($\frac{1}{100}$) and a few drops of potassium ferricyanide (0.5 - 1.0%). The dolomite was stained blue whereas the calcite was not affected. To stain for calcite, the chips were immersed for 45 sec in a solution of 100 cc 0.2% cold acid + 0.1 gm Alizarin Red S. The calcite was stained pink (and in some cases, deep red) and the dolomite was still blue. Thus,

| | | | |
|---|---|---|---|
| | Dolomite | stains | blue, |
| | Calcite | stains | red, |
| and | Quartz | shows no | staining. |

Another diagnostic feature of quartz as distinct from dolomite and calcite is that it does not etch and thus the polished side of the chip is still slightly polished in areas of chert, chalcedony, etc.

## DESCRIPTION AND OPERATIONAL USE OF THE CATHODOLUMINOSCOPE

The cathodoluminoscope consists essentially of: 1) a high voltage source, 2) a specimen chamber, 3) a cathode ray tube, and 4) a vacuum pump. The apparatus is shown in Fig. 7. The mechanism behind the production of the discharge is as follows: The cold-cathode discharge consists of an electron-ion current, started and sustained by ions and ionizable gases in the specimen chamber's atmosphere. The discharge begins when ions in the cathode tube are accelerated by the difference in potential between the cathode and the ground potential (Anode). If the pressure in the chamber is low, then these ions will create more ions by intermolecular collisions. Bombardment of the surface of the cathode frees electrons which are then accelerated towards the anode.

If the pressure in the chamber is too high, then the path between collisions is too short and the acceleration of ions falls below the critical point and no discharge occurs in the chamber. If the pressure is lower than 5 millitorrs, not enough collisions occur for a discharge to be sustained; thus the author had to manipulate the air vent attached to

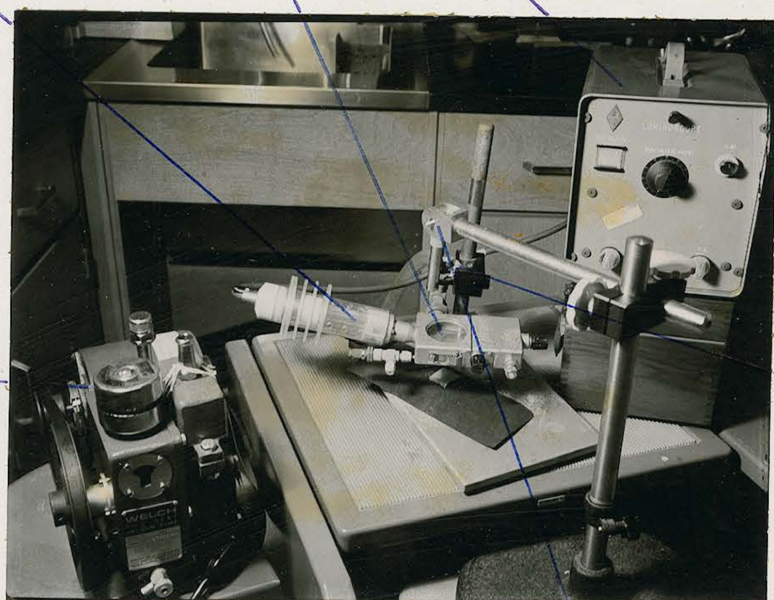



Fig. 7: The Cathodoluminoscope

the chamber to get the "correct vacuum" range, in order to produce a sustained discharge in the vacuum chamber.

The vacuum pump used was a new welch Duo-Seal pump. Actually any pump capable of producing a pressure range of approximately 25 - 50 millitorrs is quite suitable. At a pressure range of about 25 - 50 millitorrs a sustained discharge sufficient to produce luminescence of a specimen was obtained.

For the operation of the luminoscope the equipment is attached as shown in Fig. 7. The pump button on the control panel of the luminoscope is switched on. The "pump isolation valve" is then raised vertically allowing the vacuum pump to suck air out of the chamber; also the vent valve and vacuum control valve are shut tightly. If a specimen is already in the specimen chamber, the light in the room is turned off and a binocular microscope light is used to position the chip in the centre of the chamber. After about 3 - 5 minutes the high voltage button is depressed and the control potentiometer set to about 20 on the high voltage dial. After 30 sec the potentiometer is set to the 40 mark (7 KV) when more air is let into the chamber, through the vent valve, if the discharge becomes too faint (the pressure by this time may be too high in the chamber). There was found to be a severe leak along the stem of the control valve. Therefore, no adjustments were made with this valve, but rather the vent valve served a dual purpose.

The luminescence area obtained was about $\frac{1}{2}$" - $\frac{3}{4}$" long and about $\frac{1}{8}$" wide; this area is very small and it was only able to illuminate a very small area of the specimens. One gets the feeling that originally the ray illuminated a much wider area. In the manual it is said that the pump should be running for at least 30 minutes before the high voltage source is turned on; however, the author got satisfactory results after about 5 minutes with the pump on. The high voltage control was never put higher than the 45 mark (8 KV), because the F-1 fuse (controlling the high voltage source) blew within $\frac{1}{2}$ minute. A useful voltage figure was about 40 - 45 marks. With the specimen in the chamber and the luminescence beam on it, to maneuver the specimen, the x-motion and y-motion knobs on the vacuum chamber were turned. The illuminated section of the specimen was first viewed through a binocular microscope, and once an interesting part of it was observed, the binocular microscope light was turned on, and a note was made as to what mineral was luminescing and in what colours (note that the specimens were all stained, so that the author could tell what was calcite, dolomite and quartz). The binocular microscope was then removed and a stand with a camera attached was then moved into place, focused and a picture taken. The light in the room was then turned on and another specimen placed in the specimen chamber.

## PHOTOGRAPHY TECHNIQUE

After several "experiments" with a standard single lens Reflex camera, using various extension tubes to get in close to the specimen chamber, it was found best to use a lens of focal length 35 mm with two short extension tubes placed about 8 inches above the specimen chamber (the camera is mounted on the T bar in the position shown in the photo Fig. 7). When seen through the viewing lens, the luminescing area appeared about $1\frac{1}{2}$ times as big as its true area. A shutter release cable was attached to the camera and the time of exposure for the shot was set at between 3 and 4 minutes. The film type used was Kodak High Speed Ektachrome Film EHB 135-36. The film was then developed, blown up to about 5 - 6 times the original size, and the prints made of the blown up negatives.

Another technique tried was to use "tubes" to get right down on the specimen chamber; the time of exposure in this case being about 8 - 10 minutes, however, the author was not very successful using this technique. Only one fossil (Ludivigia) gave a decent picture. The first approach was deemed the better one; and all the photos were taken by this method.

## DISCUSSION OF RESULTS OF EXPERIMENT

The discussion of the results of the experiment will be broken down into three main subheadings:

1) Replacement History and Diagenesis of the Onondaga Limestone according to Middleton, as based on examination of his thin sections from the Formation.

2) Replacement History and Diagenesis of the Onondaga Limestone according to the Author, as based on his cathodoluminescence observations on fossils from the Formation.

3) Comparing and Contrasting the above two Replacement and Diagenetic Histories.

1) Replacement History and Diagenesis of the Onondaga Limestone according to Middleton, as based on Examination of his Thin Sections from the Formation

The author examined thin sections from G. V. Middleton's collection on the formation, and essentially found the same replacement history as was reported by Middleton (1958). The thin sections examined are given in Table 2.

TABLE 2

ONONDAGA LIMESTONE FORMATION

| Top | Thin Sections |
|---|---|
| Top | |
| 0 - 5.0' | -58038 |
| 5.0' - 9.4' | |
| 9.4' - 12.6' | -58040 |
| 12.6' - 16.6' | |
| 16.6' - 20.4' | -55042 |
| 20.4' - 28.4' | -58043 (upper) |
| | -58044 (lower) |
| Base | |

(a) Author's interpretation of Middleton's thin sections

Figure 8: 58044 (20.4' - 28.4' - Lower Section)

This slide shows very clearly opalescent void-fillings in the internal cavities of fossils, and not so clearly mottled chert nodules. Brown (mottled) chert is mixed together irregularly with unreplaced calcilutite. The opalescent void fillings show chalcedonic texture and well-developed colloform banding. On the inside of the void fillings is a quartz mozaic. The outer fringe of the coral was not noted.

What seems to have happened here is that the inside of the fossil (internal cavities) are first half-filled with calcilutite and half-filled with opalescent silica; however, the calcilutite mud was itself replaced partially by chalcedony. The calcilutite matrix is also partially replaced by irregular patches of brown chert, with rhombs of dolomite occurring in both calcilutite and chert. Thus we note the sequences: 1) filling of cavities of fossils by colloform chalcedony, and 2) partial replacement of calcilutite by irregular patches of brownish colloform chert.

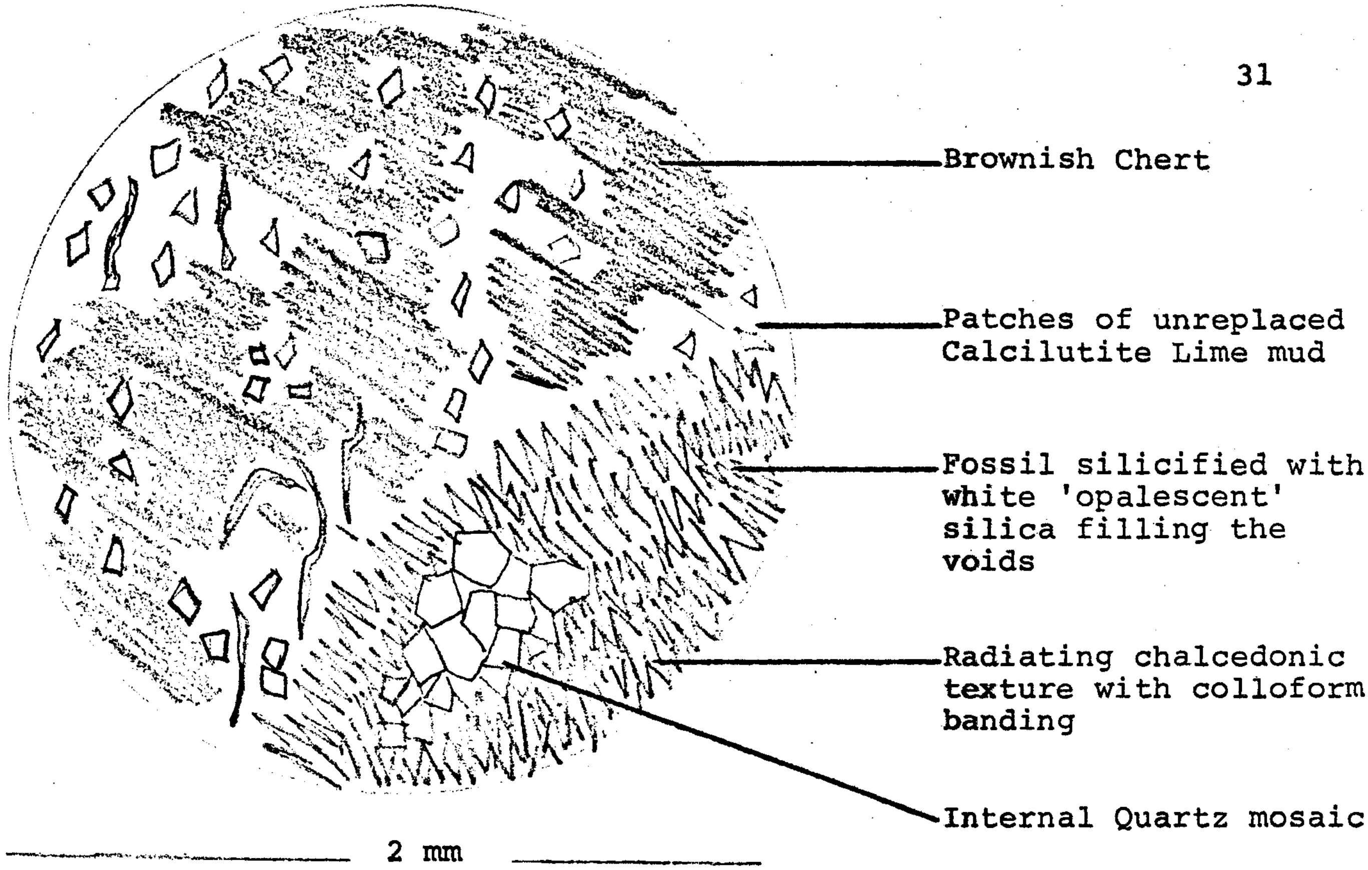



Fig. 8: Thin Section Number:- 58044

Height - 20.4' - 28.4' (LOWER)

Texture: Biomicrite - partially replaced by chert nodules

Bioclastic calcilutite (fossils broken up and hard to see)

Figure 9: 58043 (20.4' - 28.4' - Upper Section)

This slide consists of calcilutite lime mud with broken fossils (partially dolomitized). One fossil which looks like a horizontal cut across a Rugosa Coral is well shown in the diagram. The inside of the fossil is partially filled with opalescent silica (quartz mozaic) and a combination of microcrystalline quartz and dolomite. The shells of the fossils are of calcite (now partially dolomitized). This slide did not show the partial replacement of calcilutite lime mud by brown colloform chert; however, this is already well seen in 58044.

Figure 10: 58042 (16.6' - 20.4')

This slide consists of very fine grained nodular calcilutite dolomite mud with a few silicified fossils (clear chert - no colloform texture). In the matrix there are very fine grained glauconite particles (green). Thus following from the diagenetic steps of 58044 and 58043, the replacement history in this slide should be: 1) replacement of calcareous material from fossils by clear chert with no colloform banding, and 2) introduction of glauconite in the matrix.

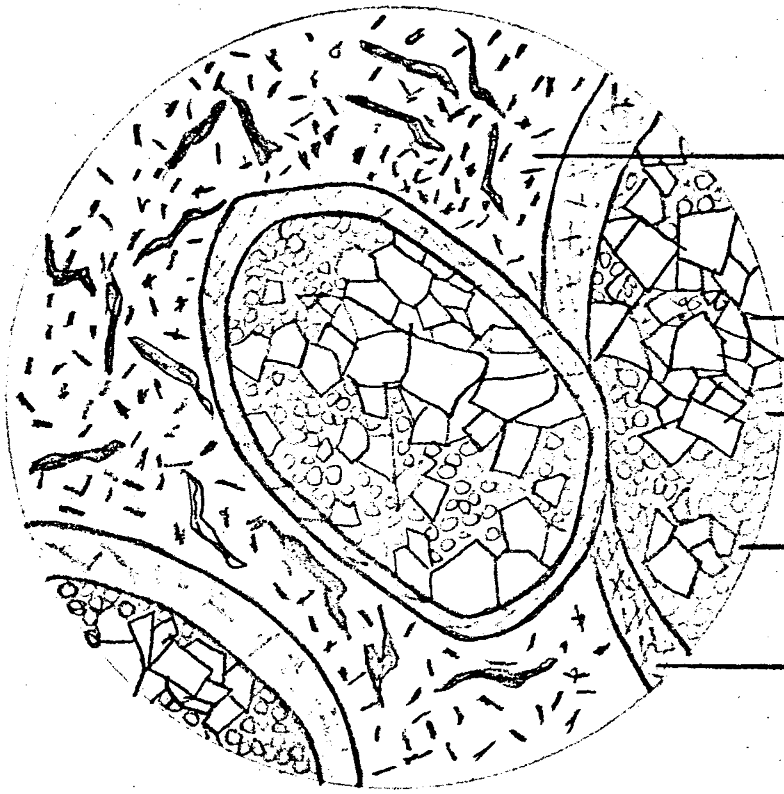



Fig. 9: Thin Section Number:- 58043

Height - 20.4' - 28.4' (UPPER)

Texture: Biomicrite which is slightly dolomitized

Some fossils broken into fine bits

Some fossils are whole showing replacement by chert and dolomite

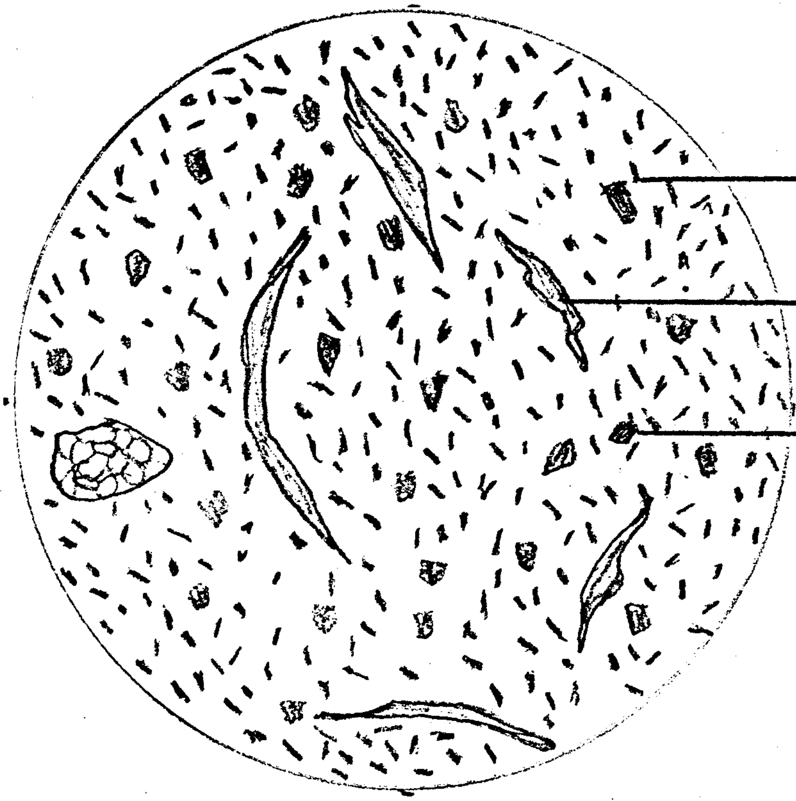



Fig. 10: Thin Section Number:- 58042

Height - 16.6' - 20.4'

Texture: Micrite - 1% fossils in matrix

Essentially a Limestone which is partially dolomitized

Figure 11: 58040 (9.4' - 12.6')

In this slide we have a matrix of bioclastic calcilutite lime mud which is poorly sorted with irregular grains of angillaceous material. This sketch slide shows one solitary tetracoral, the rim of which is of microcrystalline quartz and the inside of which is of irregular patches of microscopic chalcedonic silica, and partially dolomitized calcilutite mud. This slide shows: 1) partial replacement of internal cavities by chalcedonic silica, 2) replacement of the rim of the coral by chert, and 3) partial dolomitization.

Figure 12: 58038 (0.0' - 5.0')

This slide shows a dolomitic limestone which is nodular and fine grained bioclastic calcilutite. The sketch slide shows a silaceous nodule and fossil with replacement by microcrystalline quartz and dolomite (initially calcareous mud).

The slide shows: 1) replacement of calcareous material (partial) by clear chert, and 2) partial dolomitization of the limestone bioclastic calcilutite mud.

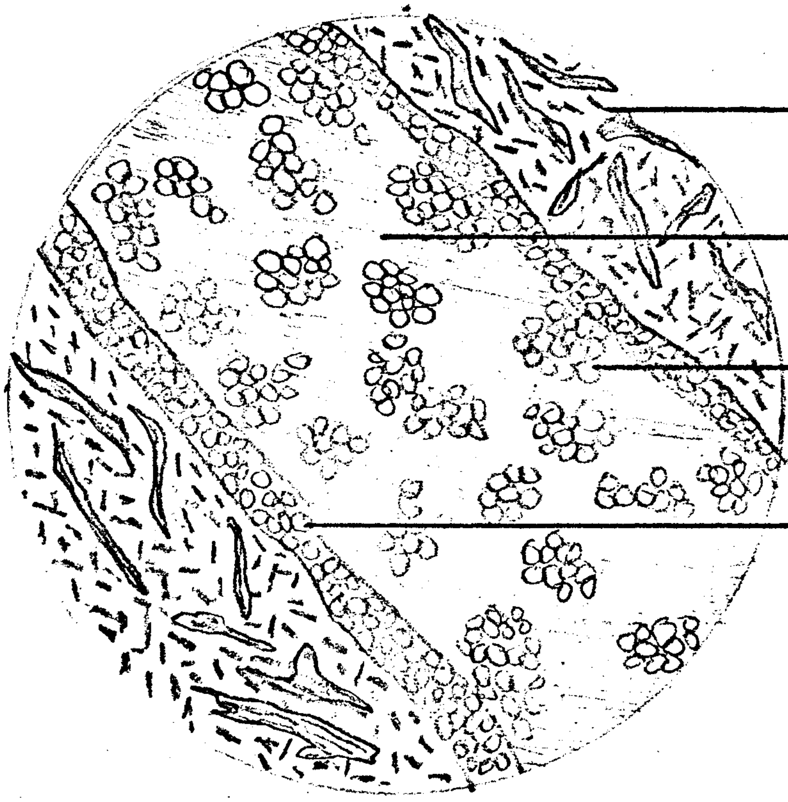



Fig. 11: Thin Section Number:- 58040

Height - 9.4' - 12.6'

Texture: Bioclastic Calcilutite Lime mud

A Limestone which is partially dolomitized

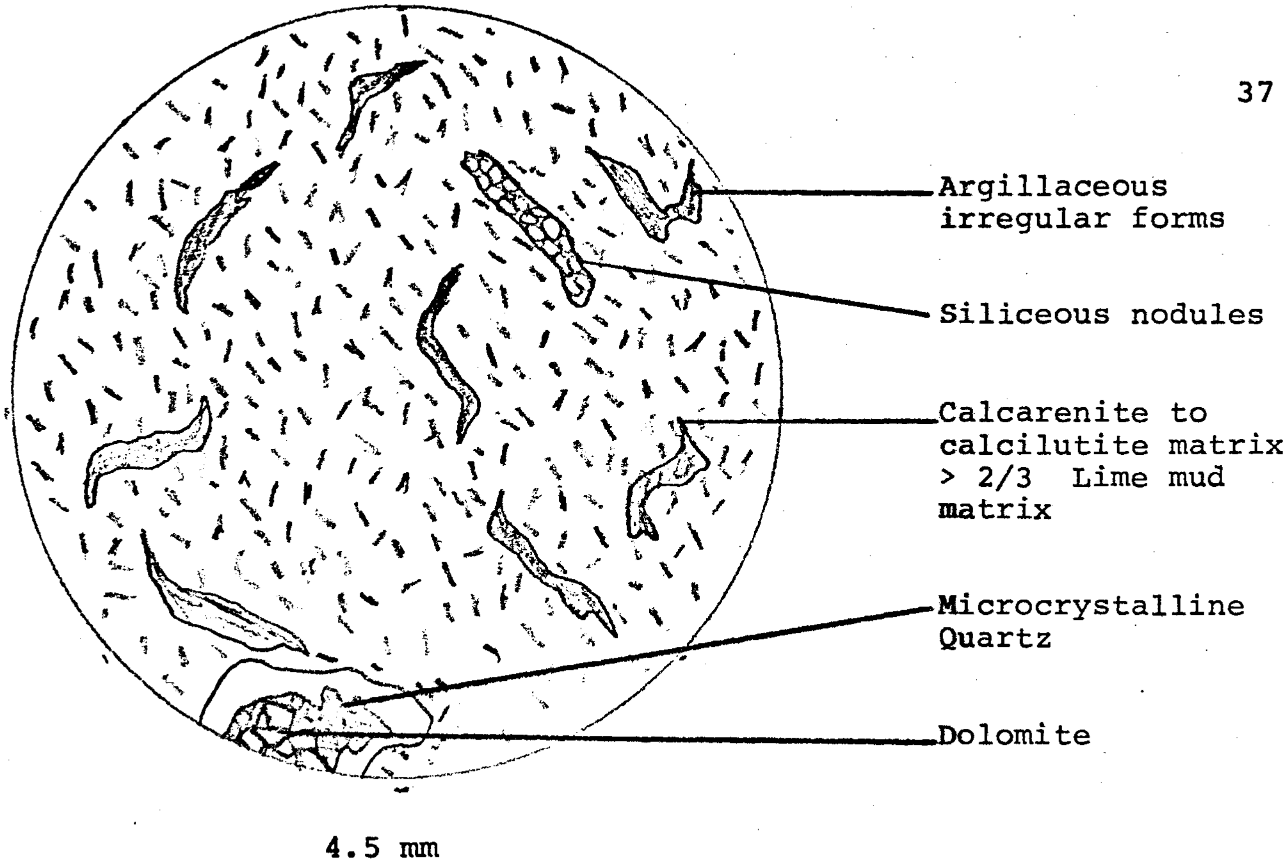



Fig. 12: Thin Section Number:- 58038

Height - 0.0' - 5.0'

Texture: Biomicrite

A Limestone which is partially dolomitized

Putting all the data from the thin sections together, the author gets the same diagenetic replacement history as that suggested by Middleton (1958).

(i) Cavity fillings of fossils by opalescent silica and calcilutite mud, preceeded by rimming of the calcareous fossils by calcite (Slides 58044, 58043),

(ii) Replacement of the calcilutite lime mud by chalcedony (Slide 58044),

(iii) Replacement partially of calcareous material by brownish colloform chert giving the mottled appearance (Slide 58044),

(iv) Replacement of calcareous material by clear chert (no colloform textures) (Slides 58042, 58038),

(v) Dolomitization (shown by all slides).

2) Replacement History and Diagenesis of the Onondaga Limestone according to the Author, as based on his Cathodoluminescence Observations on Fossils from the Formation

For each sample specimen, pictures were taken using luminescence light and reflected light, so that the reader might see what area of the slide had luminesced. The heights in the section from which the chips came, are listed in Table 3.

TABLE 3

ONONDAGA LIMESTONE FORMATION

| Section | Photo Number |
|---|---|
| Top | |
| 1' | Photo 1 |
| 2' 5" | |
| 3'10" | Photo 2 |
| 10'10" | |
| 13' | Photo 3 - Photo 4 |
| 15' | Photo 5 - Photo 6 |
| 17' 6" | Photo 7 - Photo 8 |
| Base | |

In the coloured photos:

Q = Quartz

C = Calcite

D = Dolomite

R = Red Impregnation .

Photo 1: 1' Rugosa Coral

This photo shows two types of colour, turquoise blue and pale pink. The author thinks that the turquoise blue colour from the luminescence beam on the chip is caused by trace elements in dolomite; however, H. P. Schwarcz on his examination thinks that this may be a luminescence colour exhibited by quartz. It is quite true that quartz has replaced large quantities of this coral, but the author suggests that the typical turquoise blue colour exhibited under luminescence must be dolomite. It is possible that the area indicated in the plane light photo is not really the area luminesced, since it does not seem to match properly. Quartz was also noted in the fossil, though it was not photographed. The suggested diagenetic replacement is: 1) micritic mud fillings interstitial to the septa of the coral, 2) replacement by quartz partially, of both the hard parts of the coral and the interseptal areas, and 3) partial dolomitization of the micrite, and complete dolomitization of the calcitic coral.

LUMINESCENCE LIGHT

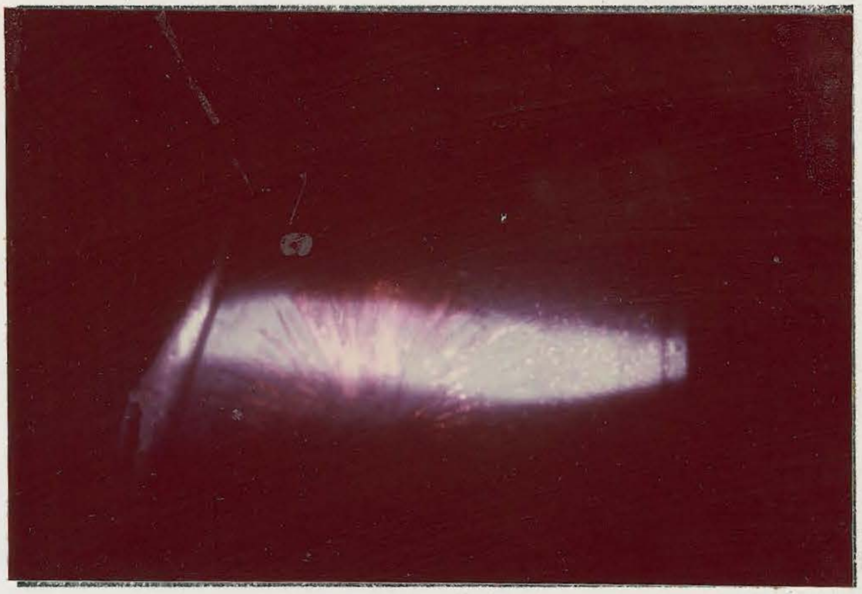


PHOTO 1

PLANE LIGHT

C = Calcite: D = Dolomite

LUMINESCENCE LIGHT

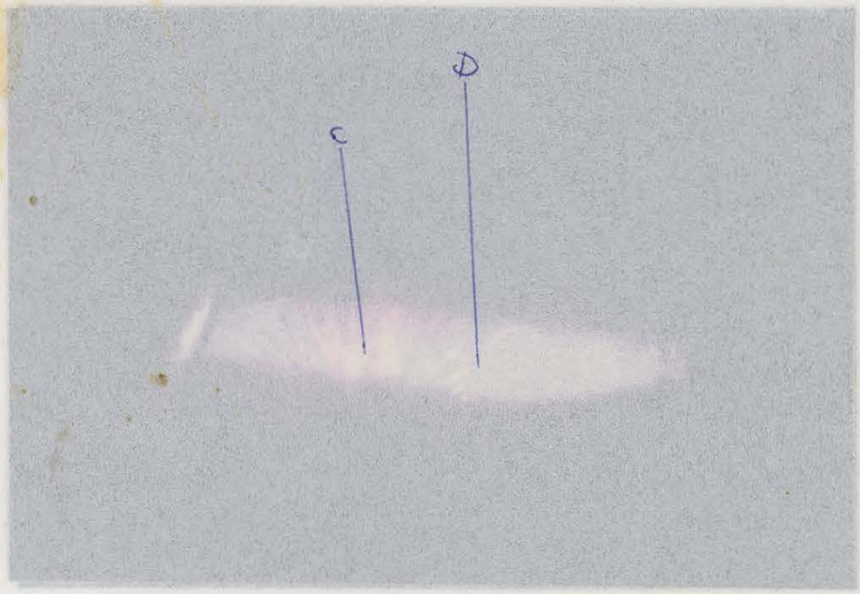



PHOTO 1

PLANE LIGHT

C = Calcite: D = Dolomite

Photo 2: 3'10" Rugosa Coral

In this photo the author had the difficulty of matching the exact spot luminesced with the spot on the plane light photo. The photograph was taken partially in the coral and partially outside.

The Blue (sea blue) = Quartz,

Pinkish = Calcite,

Turquoise blue impregnations = Dolomite.

As seen from the coloured photo, replacement of calcite by quartz occurs both inside and outside the fossil. There are several fine grains that luminesce bright pink. These may be a mineral species with high $Mn^{2+}$, or replaced calcite remnants with a higher $Mn^{2+}$ content.

It should be noted here that nothing can be said about the time of emplacement of the activator ion in the calcitic, dolomitic or quartz structure. The diagenetic process in this slide would be: 1) filling of interseptal areas by micritic mud, 2) invasion and partial replacement by quartz of both the septal and interseptal areas, and 3) partial dolomitization.

The coloured photograph also suggests that the micritic material was not homogenous, but rather heterogenous, because there is preferential replacement of the calcite by both quartz and dolomite on a grain by grain basis. Thus a grain of quartz may have a grain of dolomite next to it on one side, and a grain of calcite next to it on the other.

LUMINESCENT LIGHT

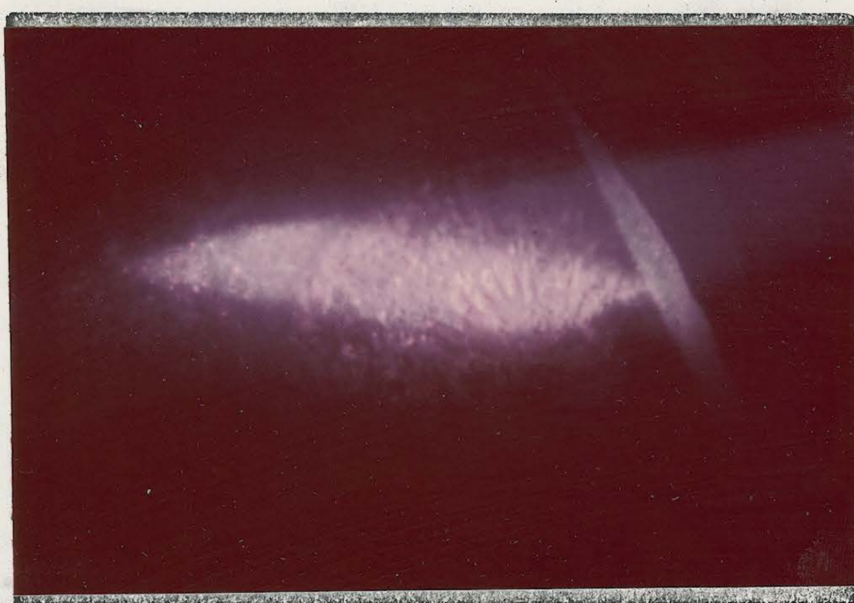
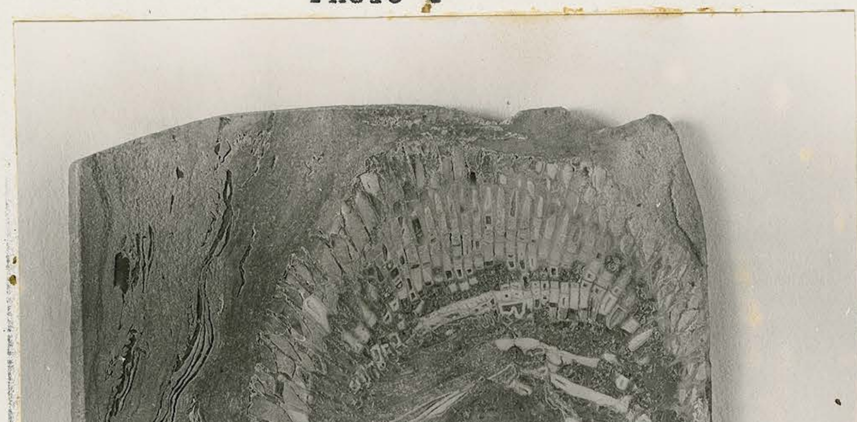


PHOTO 2



PLANE LIGHT

D = Dolomite: Q = Quartz: C = Calcite

LUMINESCENT LIGHT

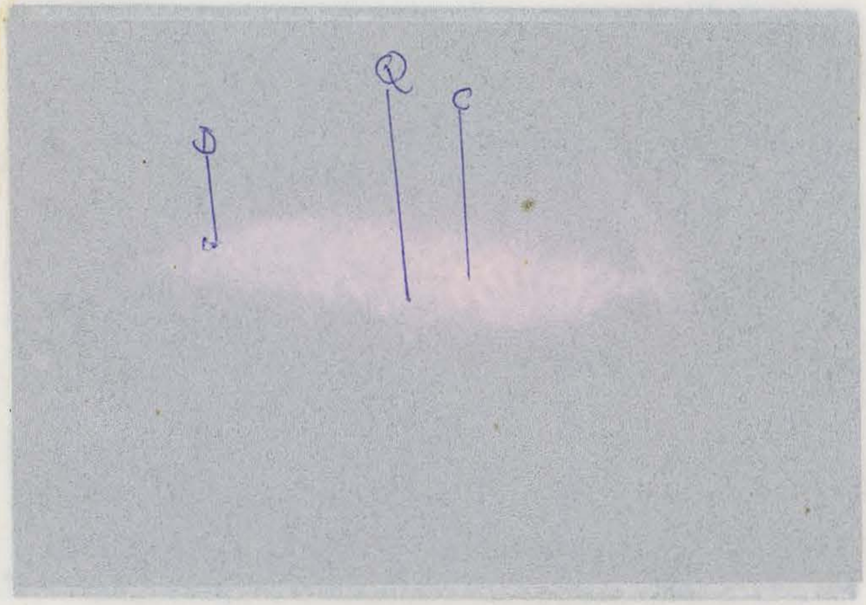



PHOTO 2

PLANE LIGHT

D = Dolomite: Q = Quartz: C = Calcite

Photo 3: 13' Space Filling

The reason this particular photo was taken was to show the spectacular contrast between dolomite, calcite, and quartz under cathodoluminescence light. Replacement of the calcite by quartz in the space filling has taken place. Later on during diagenesis, preferential dolomitization of the remaining blebs of calcite in the quartz matrix occurs. Because of the pink calcite, there arises the problem again of different grains of calcite, sitting side by side, having different calcitic compositions - thus the preferential replacement. Whether the red impregnations represent remnants of previously replaced calcite, or the most recent introduction of some mineral high in $Mn^{2+}$ is not known.

-------------------- a) Remnant Calcite

Possible Diagenetic History

(1) Calcite and Micrite mud

(2) Replacement by Quartz — either a) <u>or</u> b)

(3) Dolomitization

-------------------- b) Recent introduction of mineral high in $Mn^{2+}$

LUMINESCENT LIGHT

PHOTO 3

PLANE LIGHT

R = Red Impregnation: C = Calcite: Q = Quartz: D = Dolomite

LUMINESCENT LIGHT

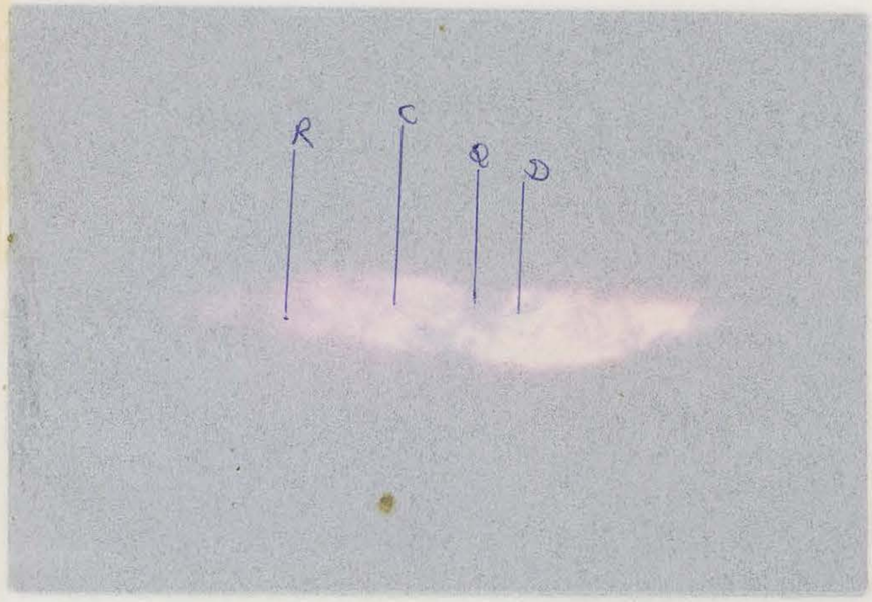



PHOTO 3

PLANE LIGHT

R = Red Impregnation: C = Calcite: Q = Quartz: D = Dolomite

Photo 4: 13' Rugosa Coral

This is a photo taken of part of an angular cut through a rugosa coral. Again the typical three colours are seen:

Pink = Calcite,

Turquoise Blue = Dolomite,

Sea Blue = Quartz.

It is difficult to tell in this specimen whether the septal areas are being replaced by quartz, or the interseptal areas are the replacement sites, but the replacement quartz shows some type of preferential replacement in the fossil.

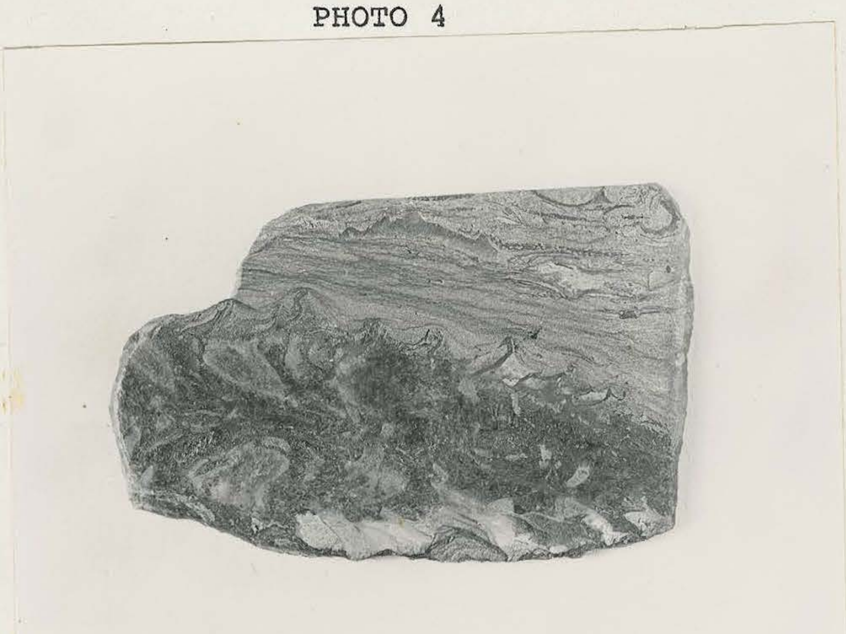
The diagenetic history of replacement for this photo is:

1) filling of interseptal areas by micritic mud,
2) preferential replacement by quartz of the septal or interseptal areas, and
3) partial dolomitization of the calcite.

It should be noted that the dolomitization in all the fossils seem to be rather limited, especially as seen in this photo.

LUMINESCENT LIGHT

PHOTO 4



PLANE LIGHT

D = Dolomite: C = Calcite: Q = Quartz

LUMINESCENT LIGHT

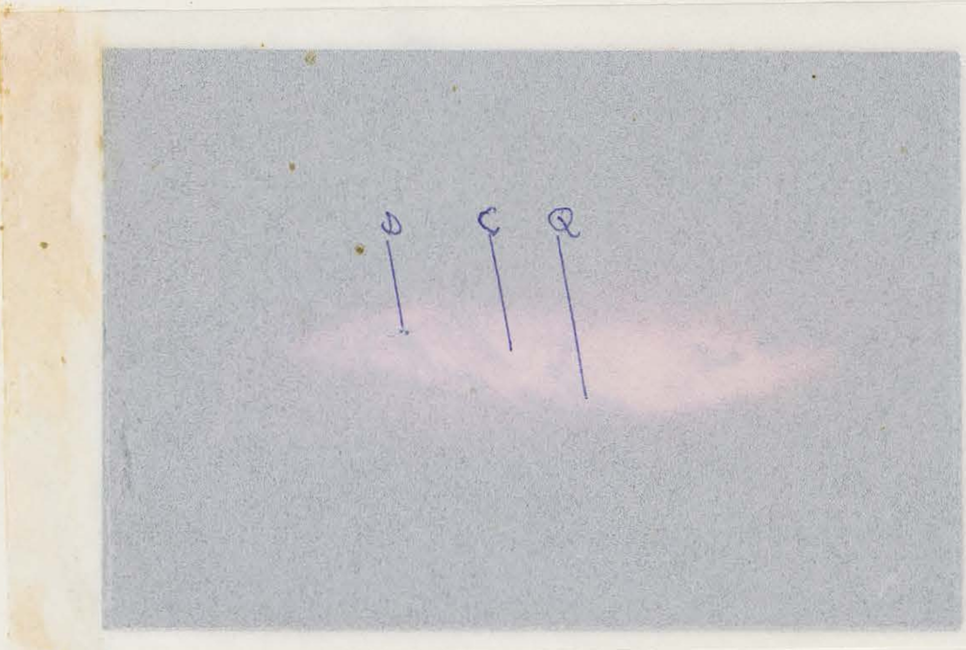



PHOTO 4

PLANE LIGHT

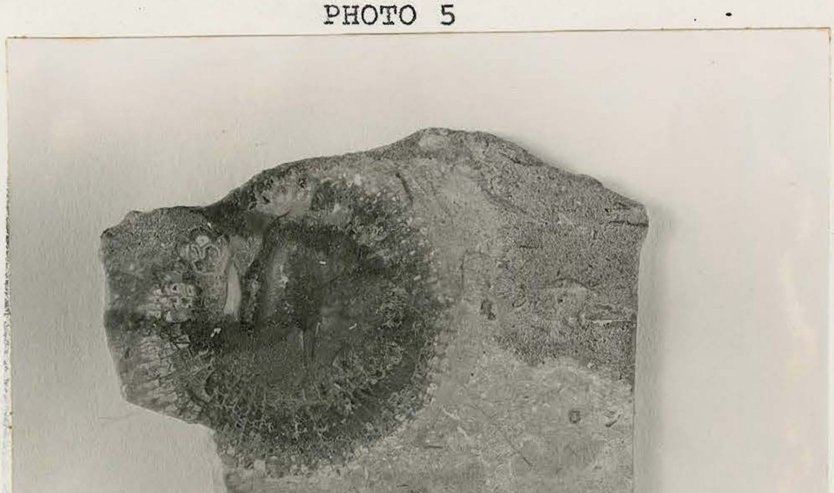
D = Dolomite: C = Calcite: Q = Quartz

Photo 5: 15' Rugosa Coral

In this sample there is both replacement of the Rugosa Coral and void filling taking place. The pink material is the calcite. The red impregnations can be: 1) preferential replacement of a previous calcite infilling, or 2) some accessory mineral with a high content of $Mn^{2+}$. The blue phase in the matrix is quartz and the blue material showing zonation is also quartz. The zonation shows up optically under reflected light, but to a much lesser extent than that shown under luminescent light. There is no dolomite present in this area. As seen from the plane light photo, the quartz is filling a void on the outer edge of the fossil in zone like bands, and is also selectively replacing the calcareous interseptal areas of the fossil. It should be noted that the internal part of the fossil is untouched by the invading quartz solution. Assuming that intensely luminescing red impregnation is another generation of calcite, then this demonstrates how cathodoluminescence displays contrasts between adjacent calcite grains otherwise optically indistinguishable. The brightly fluorescing grains are uniformly distributed through the pink fluorescing background, selectively replacing certain calcite grains rather than certain areas. Note that the red impregnations did not come out well in the photograph, but can be clearly seen by visual inspection under cathodoluminescence light.

LUMINESCENT LIGHT

PHOTO 5



PLANE LIGHT

C = Calcite: R = Red Impregnation: Q = Quartz

LUMINESCENT LIGHT

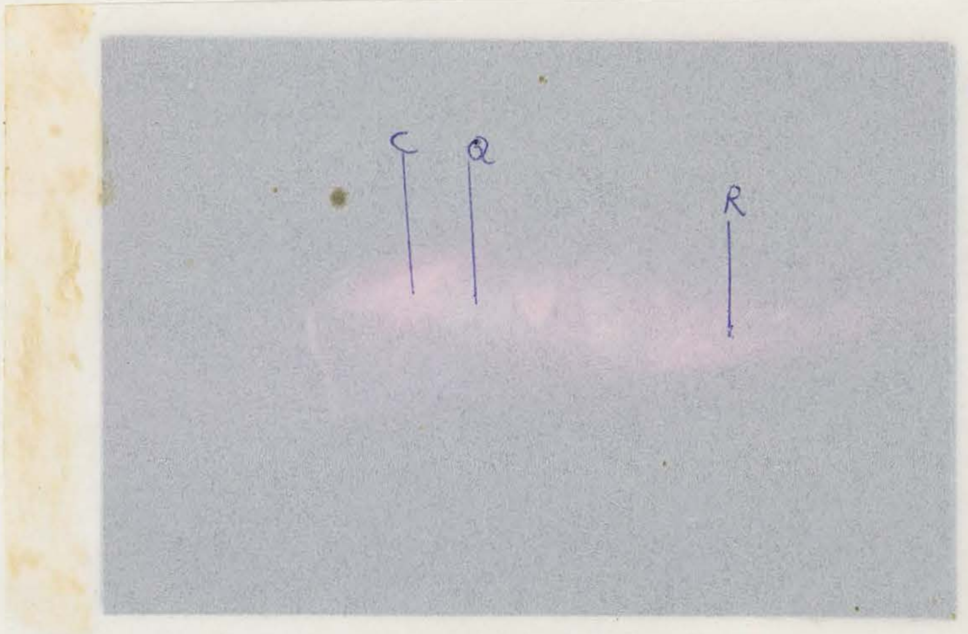



PHOTO 5

PLANE LIGHT

C = Calcite: R = Red Impregnation: Q = Quartz

Photo 6: 15' Rugosa Coral - Matrix and Unknown Fossil

This photo in luminescent light shows the replacement of the calcite material by quartz in the fossil is restricted to the areas in between the septa and not to the septal areas themselves. The unknown fossil is totally replaced by quartz, with a few minor horizontal bands still consisting of calcite. There are turquoise blue impregnations throughout the luminesced area which signify that some of the calcite has undergone dolomitization during diagenesis.

Diagenetic history of this chip:

1) filling of interseptal areas by micritic mud,
2) complete replacement in places of the micrite by quartz, and
3) partial dolomitization of calcitic septa and micrite filling.

LUMINESCENT LIGHT

PHOTO 6

PLANE LIGHT

LUMINESCENT LIGHT

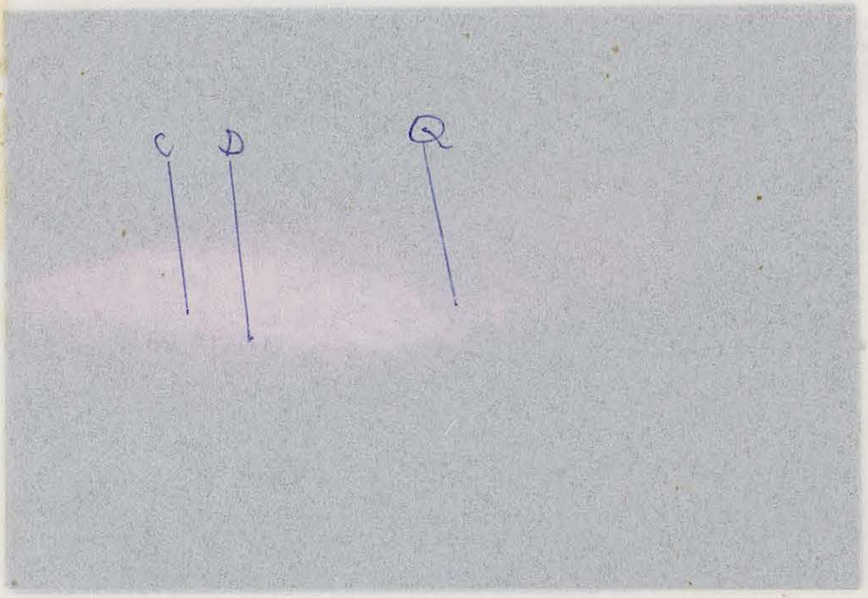



PHOTO 6

PLANE LIGHT

Photo 7: 17'6" Rugosa Coral

This photo shows a vertical cut through a rugosa coral. There is preferential replacement of the septal areas by quartz solutions as opposed to interseptal areas that still consist of micrite. The quartz replacement material is chalcedony. The luminesced area shows the tabulae and septa at the side of the central column of the fossil. The whitish pink material is calcite, and the pale blue material is the chalcedonic chert replacement. Dolomitization if present in this chip is very minor, because no turquoise blue material was observed and also because the carbonate material in the fossil stains red (calcite).

Diagenesis in this slide is as follows:

1) filling of the cavities in the coral by micritic mud, and
2) preferential replacement of the septa, tabulae, etc. by chalcedonic quartz.

LUMINESCENT LIGHT

PHOTO 7

PLANE LIGHT

C = Calcite: Q = Quartz

LUMINESCENT LIGHT


PHOTO 7

PLANE LIGHT

C = Calcite: Q = Quartz

Photo 8: 17'6" Rugosa Coral

The features in this photo are quite similar to that shown in Photo 7. The quartz has preferentially replaced the calcite from the septa, whereas it has left the interseptal area of micrite untouched. Again no dolomitization has taken place in this fossil.

Diagenetic history of this chip is as follows:

1) cavity filling of fossil by micritic mud, and
2) preferential replacement of the septa, tabulae, etc. by chalcedonic quartz.

LUMINESCENT LIGHT

PHOTO 8

PLANE LIGHT

C = Calcite: Q = Quartz

LUMINESCENT LIGHT

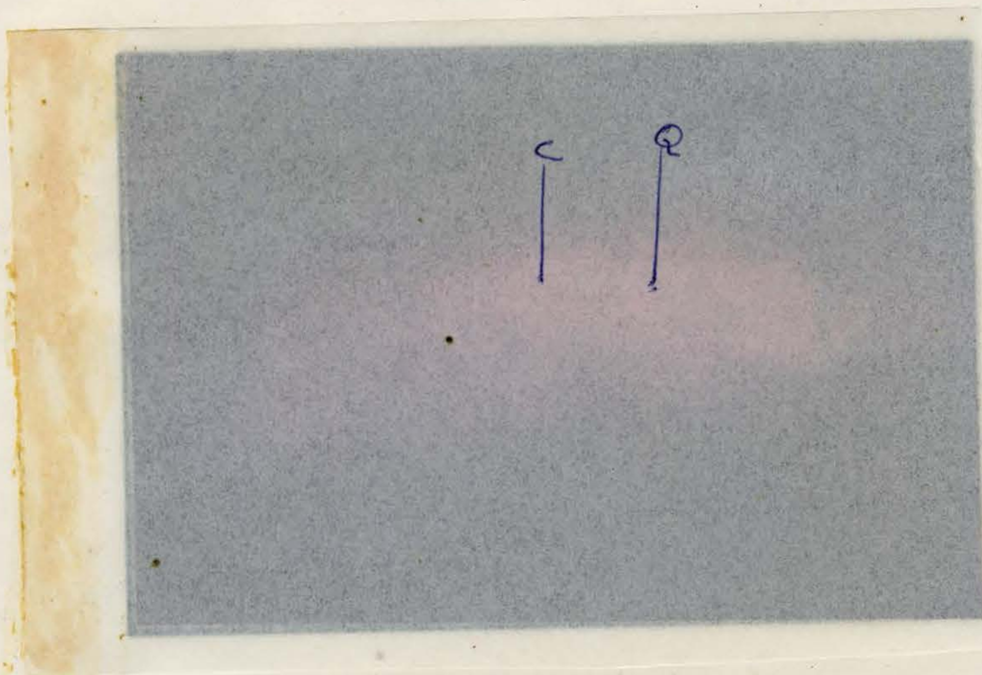



PHOTO 8

PLANE LIGHT

C = Calcite: Q = Quartz

Putting all the data from the luminesced rugosa corals together, the author gets the following diagenetic and replacement history.

(i) Filling of the cavities in the corals by both homogenous and heterogenous micritic muds, depending on from what part in the formation they came: 17'6" = homogenous micritic mud filling,'and
15' & 13' = heterogenous micritic mud filling.

The homogenous mud filling is shown by the absence of red impregnations. The heterogenous mud filling is shown by the presence of red impregnations.

(ii) Replacement by quartz (chalcedony) of calcite septal areas or micritic interseptal areas, depending on from what part in the formation the corals came. In a few cases replacement by quartz of both areas occurred.

Photo 2 : 3'10" = Replacement in both cases,

Photo 6 : 15' = Replacement in interseptal areas alone,

Photos 7 & 8: 17' 6" = Replacement in septal areas alone.

(iii) Partial dolomitization of the calcitic material, with maximum dolomitization at the top of the formation and almost no dolomitization of the fossils at the bottom of the formation.

| | | | |
|---|---|---|---|
| Photo 1 | : | 1' | = Maximum dolomitization, |
| Photos 2 & (3-4) | : | 3'10" & 13' respectively | = Minor dolomitization, |
| Photos 5 - 6 | : | 15' | = Very minor to no dolomitization, |
| Photos 7 - 8 | : | 17' 6" | = No dolomitization whatsoever. |

There is thus considerable strata bound variation in the style of replacement in the formation. The difference in dolomitization at the top and the bottom of the section may be due to the influx of $Mg^{2+}$ ions from evaporite solutions above the formation, seeping downwards.

Interseptal and septal replacements, or a mixture of both by quartz solutions, may depend on the localized Ph-Eh conditions at the various stratigraphic heights in the formation. This is only one interpretation of what may actually have happened. This would mean that at different Ph-Eh conditions the micrite material and the original calcitic septal material may have reacted differently to the replacement quartz solutions.

Because of the dolomitization and silicification of the calcitic mud on a grain by grain basis, this shows that the muds in some instances were heterogenous with respect to their minerology, because preferential dolomitization and silicification took place. These heterogenous and homogenous micritic muds could be due to an intermixing of minute particles from broken calcitic fossils of slightly different compositions (different amounts of trace elements in the structure).

3) Comparing and Contrasting the Replacement and Diagenetic Histories as described by Petrographic and Cathodoluminescence Techniques

Both the petrographic and cathodoluminescence techniques give roughly the same diagenetic histories for the Onondaga formation, but it is possible in the petrographic approach to distinguish many different replacement cycles by silica, whereas in the luminescence approach the quartz only shows up as one colour blue. According to previous workers, the different types of quartz should luminesce different colours; this is not noted in this case. This means either only one replacement by quartz took place in the corals or the different replacements of quartz did not luminesce different colours. For obvious optical detail in the sections it is better to use the petrographic approach, however, for microscopic detail in a fossil, the cathodoluminescence technique is by far the better examination tool.

For example, the zonation described in the photos is much more pronounced in cathodoluminescence light. The other major advantage that the cathodoluminescence technique has, is that it enables the viewer to pick out extremely minor dolomite grains and calcite grains of high $Mn^{2+}$ content that could not be seen by staining or using a petrographic microscope. In the experiment carried out by the author, the presence of the dolomite grains and red impregnation grains was an essential part in the interpretation of the mode of dolomitization and heterogenity of the micritic material in the fossils. Thus from the experiment, there are at least two uses to which the cathodoluminescence technique could be put.

## CONCLUSIONS

Essentially three general features may be noted which could not be seen with the petrographic microscope, but which are visualized with the cathodoluminescent light.

1) The dolomitization as a strata bound process, proceeding downwards in the formation, with maximum dolomitization at the top of the formation and minimum dolomitization at the base.

   Homogenous and heterogenous micritic cavity coral fillings, depending on the different heights in the formation from which they came.

   Preferential replacement of septal and interseptal areas of calcite and micrite mud by quartz solutions depending on localized Ph-Eh conditions in different stratigraphic heights in the formation.

It should be noted that even if the turquoise colour in Photo 1 is not dolomite as suggested by the author, there is still gradation in the amount of dolomite from the top to the base of the formation.

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