

EPIGENETIC GROWTH OF CALCITE-CEMENTED NODULES
WITHIN A POROUS DOLOMITE MATRIX--AVON PARK FORMATION
OF CENTRAL FLORIDA

by

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ABSTRACT

Unusual epigenetic calcite-cemented nodules occur in the Middle Eocene Avon Park Formation, a porous dolomitic packstone, exposed along the Cross-Florida Barge Canal in Citrus County, Florida. These nodules incorporate dolomite rhombohedrons from the host rock and are nearly spherical with innumerable calcite scalenohedrons radiating from an indefinite central point. The scalenohedrons occur as individuals, as well as accumulations in beds and ledges. Their geographic distribution seems to be contingent upon the location of certain organic-rich sand lenses incorporated within the overlying formations.

The Avon Park Formation of Claiborne Age is overlain by the Inglis Formation of Jackson Age (a granular, fossiliferous limestone), which in turn is overlain by the Pamlico Formation of Sangamon Age, composed of unconsolidated sands with variable facies.

It is within the Pamlico Formation that the above mentioned richly organic sand lenses occur. Surface waters percolating through these organic sand lenses become acidic, then dissolve calcium carbonate from the Inglis and precipi-

tate it in the Avon Park, at the coincident sea-level/water table. The growth of nodules through crystallization of this calcite has decreased the previous pore space (30 to 50 percent by point count) of the dolomitic host rock to nearly zero at these sites of nodular growth.

Available evidence indicates that this process is active today and has operated during at least the past 130,000 years.

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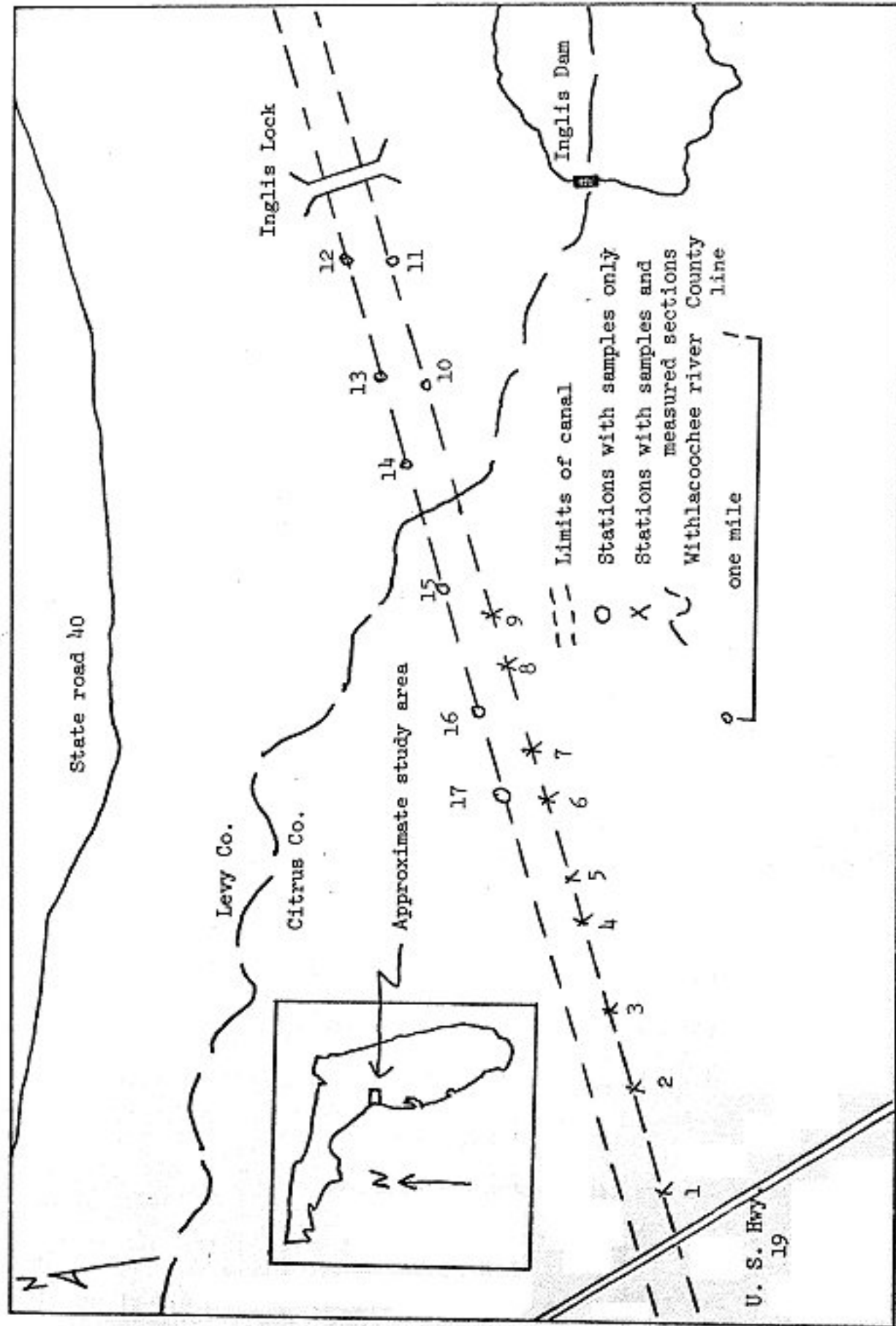
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INTRODUCTION

The geologic literature includes many descriptions of nodular masses of differing compositions ranging in age from Paleozoic to Recent. Daly (1900) describes Mississippian concretions from Ontario, Mathias (1931) cites the occurrence of Cretaceous nodules in Colorado, and Tarr (1935) discusses the Pleistocene concretions of the Connecticut Valley. However, with a few exceptions, the genesis of the nodules has not been detailed by the writers; and, in fact, these processes may be impossible to determine from the rock evidence usually available. Several specific points that normally lack clarification are: (1) the age of the nodules relative to the age of the host formations; (2) the geochemical circumstance that provided solutions of the ions for the nodules; and (3) the physio-chemical reasons for precipitation of the ions at specific locations or horizons within the host rocks.

Answers to some of these questions for one important nodule type are provided by detailed examination of the Middle Eocene Avon Park Formation along the Cross-Florida Barge Canal in Citrus County, Florida (Fig. 1). Exposures in the

Figure 1. Map of study area showing locations of sampling stations.



study area (Fig. 2) were examined intermittently over a three-year period following excavation of the canal in 1966; and an extensive collection was made of the nodules, the Eocene host rock, the Inglis Formation, and the overlying Pleistocene sands. Stratigraphic sections were measured at nine stations over a distance of approximately two miles east of the U. S. Highway 19 bridge. Collection was keyed to the measured sections at stations 1-9, as shown on Figure 1. A typical stratigraphic section, beginning at the sea level datum, shows 10 feet of Avon Park Formation (Eocene), overlain by 2 feet of Inglis Limestone (Eocene), overlain by 12 feet of Pamlico Formation (Pleistocene) (Fig. 3).

Field observations of the stratigraphy, fossil types, and lithology were supplemented by extensive laboratory analyses, including X-ray measurements of calcite/dolomite ratios and diadochic substitution of magnesium within the calcite-type lattice, thin sections and point counts, selective staining of calcite and dolomite on slabs and thin sections, pH measurement of filtrates passed through specimens, and Carbon-14 age determination (kindly arranged by Dr. Paul Enos of Shell Development Company).

The major site of nodule growth is in the Middle Eocene, Avon Park Formation, a friable, granular dolomite with extensive fractures and interconnected secondary porosity. The



Figure 2. Panoramic view of the Cross-Florida Barge Canal, Citrus County, Florida, View westward from the south bank near Withlacoochee River, with U. S. Highway 19 bridge in background.



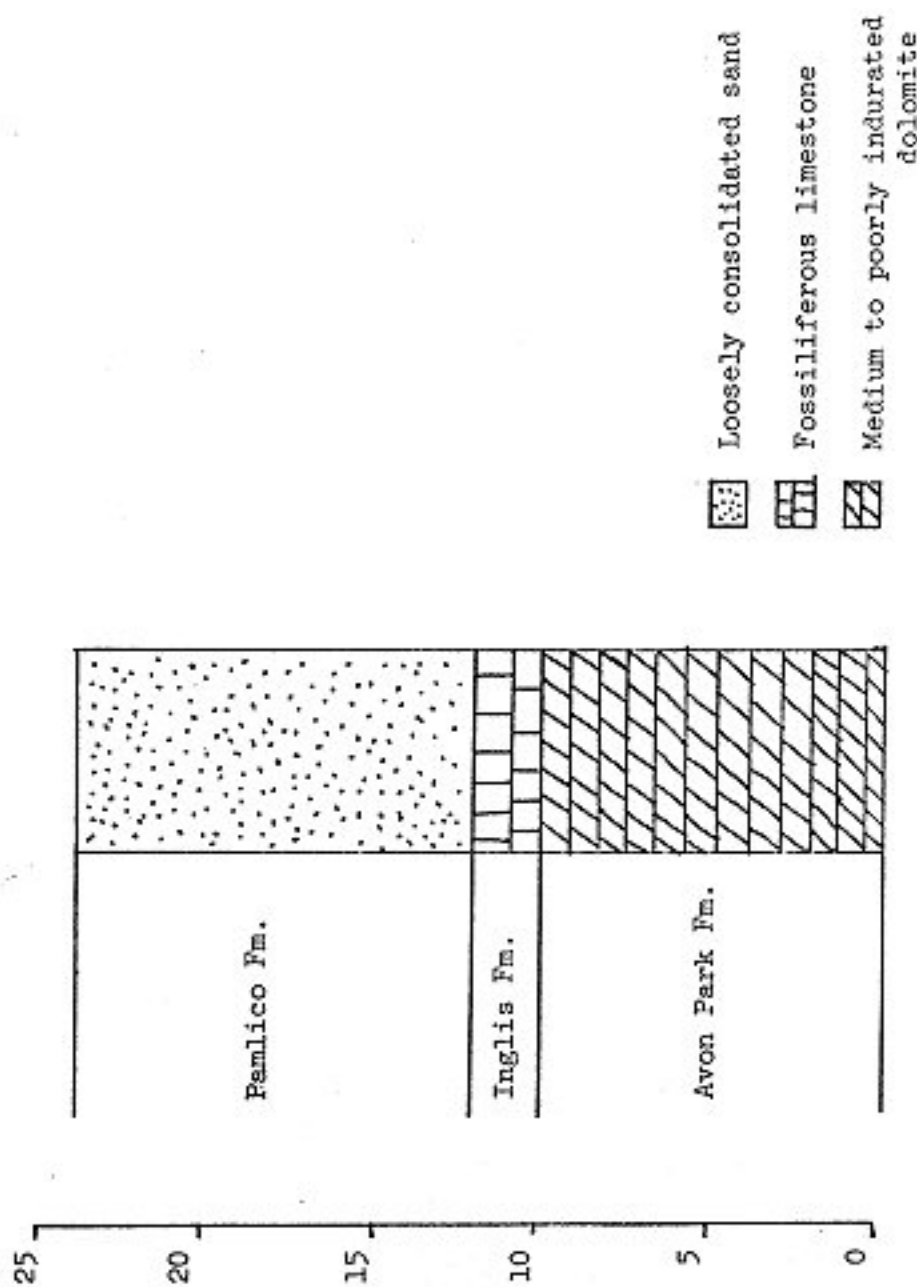


Figure 3. Generalized cross section of strata exposed at the Barge Canal, Citrus County, Florida.

nodules are concentrated in sites separated by relatively nodule-barren areas. At each site they occur in multiple, superimposed, ill-defined lenses. Vertical location of the lowermost nodular layers may possibly be related, in part, to an increase in pH at the modern coincident sea-level/water table within the lower exposed part of the formation. As the pH of sea water is in the mildly alkaline range (7.5 to 8.3, Garrels and Christ [1965], p. 102) it would neutralize the acid waters effectively and promote calcite precipitation at this level. It can be hypothesized that other layers of nodules in the Avon Park Formation correlate with former sea level stands and water table fluctuations due to seasonal or tidal influences, although this cannot be stated with certainty. Other more planar, calcite-cemented forms occur along fractures and bedding planes within the Avon Park and illustrate the importance of permeable zones in controlling ion transport and precipitation sites.

Nodule growth is accomplished primarily by addition of ions to the apexes of calcite scalenohedrons which radiate outward from an ill-defined nucleus. The calcite crystals completely fill the pores within the perimeter of the nodules, and incorporate host rock dolomite rhombs in poikilitic fashion, as in sand-crystals. Thus the nodule has no pore space while the country rock retains its porosity essentially

unchanged. Concentric rings indicate intermittent growth stages, and dominant downward growth is shown by the sharply terminated scalenohedrons that project in that direction, resulting in inverted, irregular, tear-drop shapes for most individual nodules.

As a result of these observations, several conclusions have been reached: (1) The time of nodule formation is known definitely to extend into the Recent Epoch, and growth of some nodules is apparently still active. (2) The donor of the calcium carbonate ions for the nodules is the Upper Eocene, Inglis Limestone that overlies the nodular Avon Park Formation. Localized solution of the Inglis is promoted by organic acids that percolate downward from peaty pods in the overlying organic-rich Pleistocene sands of the Pamlico Formation. (3) Precipitation of secondary nodular calcite occurs in the Avon Park Formation when the pH of the downward percolating waters is raised sufficiently (to approximately 7.8) by contact with the coincident sea-level/water table. Precipitation also occurs because of evaporation in both the Inglis and Avon Park Formations and possibly for other undelineated reasons. Variations in permeability of the Avon Park are also important in dictating the sites of nodule growth. These conclusions are amplified in the following sections after a review of previous literature on

similar concretions.

REVIEW OF LITERATURE CONCERNING SIMILAR NODULES

Daly (1900), in one of the earliest studies of nodules in the American literature, describes the occurrence of large calcareous concretions in Mississippian age shale at Kettle Point, Ontario, on Lake Huron. Composed of almost pure calcite, these nodules range from one to three feet in diameter (averaging two feet), and show a definite radiate structure, with a less obvious concentric pattern. Daly indicates that the nodules formed after the shale was deposited and at least partially lithified, inasmuch as the shale is deformed for a short distance about the nodules' perimeters.

The Ohio Shale, in northcentral Ohio, which can be compared with the Kettle Point material described above, also contains large spheroidal calcareous concretions, with a maximum diameter of approximately nine feet (Clifton, p. 114, 1957). Because beds of shale are deformed around the nodule, both above and below, he considers these nodules to be formed before the compaction of the shale. Clifton believes that during compaction, the shale contained a large percentage of interstitial water relatively saturated with calcium carbonate, which was free to migrate. Then, upon

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some undefined sites of crystallization, calcite began to precipitate, forming regions of local lithification. The nodules were more consolidated than the shale; hence, during compaction the shale beds were deformed by the nodules. Differential compaction is evidenced by the relative states of deformation of fossil organisms (ostracodes, plant fragments, and fish bones) found in the concretions and the shale. Fossils in the shale are compressed, while those in the concretions remain almost completely undistorted.

Barbour (1901) discusses the formation of sand-calcite crystals and their relation to certain types of concretions. These sand-calcite crystals have the external appearance of "barrel-shaped" doubly-terminated scalenohedrons with rounded corners and usually form multiple crystals. Crystals of this type are very impure. Quartz and heavy mineral sand may compose as much as sixty percent of the crystal (p. 170).

Spherical concretions are often found in the same beds as the crystals, but invariably overlying them. Barbour offers no explanation for this. The concretions are composed of a large number of equidimensional sand crystals, twinned or intergrown through a central point. Thin section analysis indicated that the calcite was precipitated throughout the connected pore network as large, optically continuous

crystals. The crystals had enveloped the quartz grains as they grew.

George P. Merrill of the U. S. National Museum described concretions from an oil field in northeastern Mexico as composed of concentrically layered, radiating calcite, but with some carbonaceous material disseminated throughout (as quoted in White, 1912). They ranged from one-half to five inches in diameter.

Merrill concluded that the concretions seem to be forming in a hot salt-water spring (approximately 165° F). The spring has a strong boil, and Merrill theorizes that this current keeps the particles agitated so that calcite can be deposited equally on all sides of the growing concretionary structures.

Mathias (1931) noted the presence of large calcareous concretions in the Cretaceous Fox Hills Sandstone of Colorado. He considers the concretions to be genetically related to decay of certain organisms, especially plants. Mathias proposes several ways in which calcite precipitation may be thus influenced. The plants may have contained calcareous particles upon which calcite could crystallize when the organism disaggregated after death, thereby furnishing a nucleation point for further precipitation; or, that decay

of the organic tissue produced ammonium bicarbonate which reacted with calcium ions in solution to provide the necessary geochemical conditions to precipitate calcium carbonate within a localized area around the organisms. $(2\text{NH}_3\text{HCO}_3 + 2\text{Ca}^{++} + 1/2\text{O}_2 \rightarrow 2\text{CaCO}_3 + 2\text{NH}_3 + \text{H}_2\text{O})$. The influence of the plant debris seems substantiated in that many of the concretions represent local areas of a greater degree of cementation of the sandstone around organic debris.

Weeks (1957) further examined the role of organic material in the formation of Cretaceous calcareous concretions. He cited South American examples of calcareous nodules which originally enclosed decomposed fish remains. Weeks concluded that a localized alkaline environment is created around the decaying fish as nitrates are converted to ammonia; this highly basic microenvironment is quite conducive to calcite precipitation. Being a product of a very local environment, the concretion is restricted in size and shape to the approximate dimensions as the fish or other similarly enclosed organic object.

However, there are certain limitations to this method of forming concretions. Even though the physiochemical conditions may be generally favorable for nodule formation about a decaying organism, no precipitation can possibly

take place if no calcium carbonate is available in solution. Similarly, no concretion can be formed if low permeability restricts the movement of solutions.

Tarr (1935) discussed concretions occurring in varved Pleistocene glacial clays of the Connecticut Valley. Because the concretions are confined strictly to the silty and sandy layers, which are thin laminae, the concretions are disk-shaped or layers of poorly-joined contiguous disks. Diameters of individual disks range from less than an inch to approximately six inches, but clusters of concretions are fairly common. Tarr surmised that they are restricted to the silt and sand layers because of the greater permeability.

Tarr deduced that the concretions formed some time after the compaction of the varves. Considering the varves were formed as Pleistocene lake deposits, the concretions probably had less than two million years to develop.

Tarr suggests that calcite within the glacial debris acted as the source of CaCO_3 . This was partly dissolved by the cold melt water streams, washed into the lakes, and accumulated as interstitial water in the silty, more permeable varve layers. With the decline of glaciation, increasing temperatures produced supersaturation and precipitation of

calcium carbonate in the silty varve layers.

Crystallization of calcite may have occurred around a pre-existing grain of calcite, although Tarr found no evidence of any distinct grains as nuclei. He, then, favors a supersaturated environment to be a requisite in initiating nucleation. Apparently, loss of carbon dioxide from supersaturated solutions through evaporation will cause spontaneous nucleation and further precipitation of calcite (Gee, et al, [1932] as quoted by Tarr). Once nucleation has been effected, crystal growth can proceed even from unsaturated solutions.

Holmes (1965, p. 129) states that the Magnesian Limestone of Durham (England) contains an ". . . extraordinary variety of concretionary structures . . ." Many spheroidal forms are found, ranging from less than one inch to greater than eight inches in diameter; other concretions are described as "reticulate," being networks of "rods and spindles." The concretions occur in a powdery or granular matrix of dolomite with a slight amount of calcium carbonate, whereas the concretions themselves are composed of calcite with only a small amount of dolomite. Holmes suggests that: ". . . Under the influence of percolating waters, the original fine-grained and intimately-mixed deposit of CaCO_3

(calcite) and $\text{CaMg}(\text{CO}_3)_2$ (dolomite) has been reconstituted into large-scale spheres and networks of calcite embedded in dolomite . . ." (Ibid, p. 130). In this respect, the concretions have a number of factors in common with those found by the writer at the Cross-Florida Barge Canal at Inglis, Florida.

METHODS OF STUDY

Field Methods

The study area extended along both sides of the Cross-Florida Barge Canal from the U. S. Highway 19 bridge eastward to the Inglis Lock, a distance of two and one-half miles. Nodule concentrations were marked by numbered stakes and the locations mapped. The stakes are referred to later by station numbers (Fig. 1). Stratigraphic sections were measured at each location and dip of cross-bedding in one area was measured with a Brunton Pocket Transit. At each station, and at many intervening places, samples of the nodules, Avon Park Formation, Inglis Formation, and Pamlico Formation were collected; fossils were also collected at nearly every site along the canal bank.

Laboratory Analysis

Selected samples were washed and dried at room tempera-

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ture. Indurated samples were cut into slabs with a diamond¹⁶ saw to expose internal structures. Poorly indurated samples were vacuum impregnated with polyester resin and cut into slabs. Twenty samples were then thin sectioned.

Slabs and thin sections were stained to distinguish calcite/aragonite areas from dolomite areas, using methods proposed by Friedman (1959): i.e., calcite and aragonite are selectively stained dark red by alizarine red-S in a 0.5 per cent HCl solution, while dolomite is not affected. Dolomite is selectively stained dark purple by alizarine red-S in a 30 percent NaOH solution that leaves calcite and aragonite unaffected.

X-ray powder diffractometer analyses were made from five samples to determine calcite/dolomite ratios and diadochic magnesium substitution in the calcite-type lattices (Fig. 4) (after Chave, 1952). Using the methods suggested by Griffin (1969) calcium fluoride was added as an internal standard for measurement of peak locations, and peak intensity ratios were converted into dolomite percentages by use of a working curve (Fig. 5).

The effect of the sediments on ground water pH was assessed by mixing unconsolidated rock samples with distilled water. After five days the pH change in the water was measured with a Corning Model 12 Research pH meter.

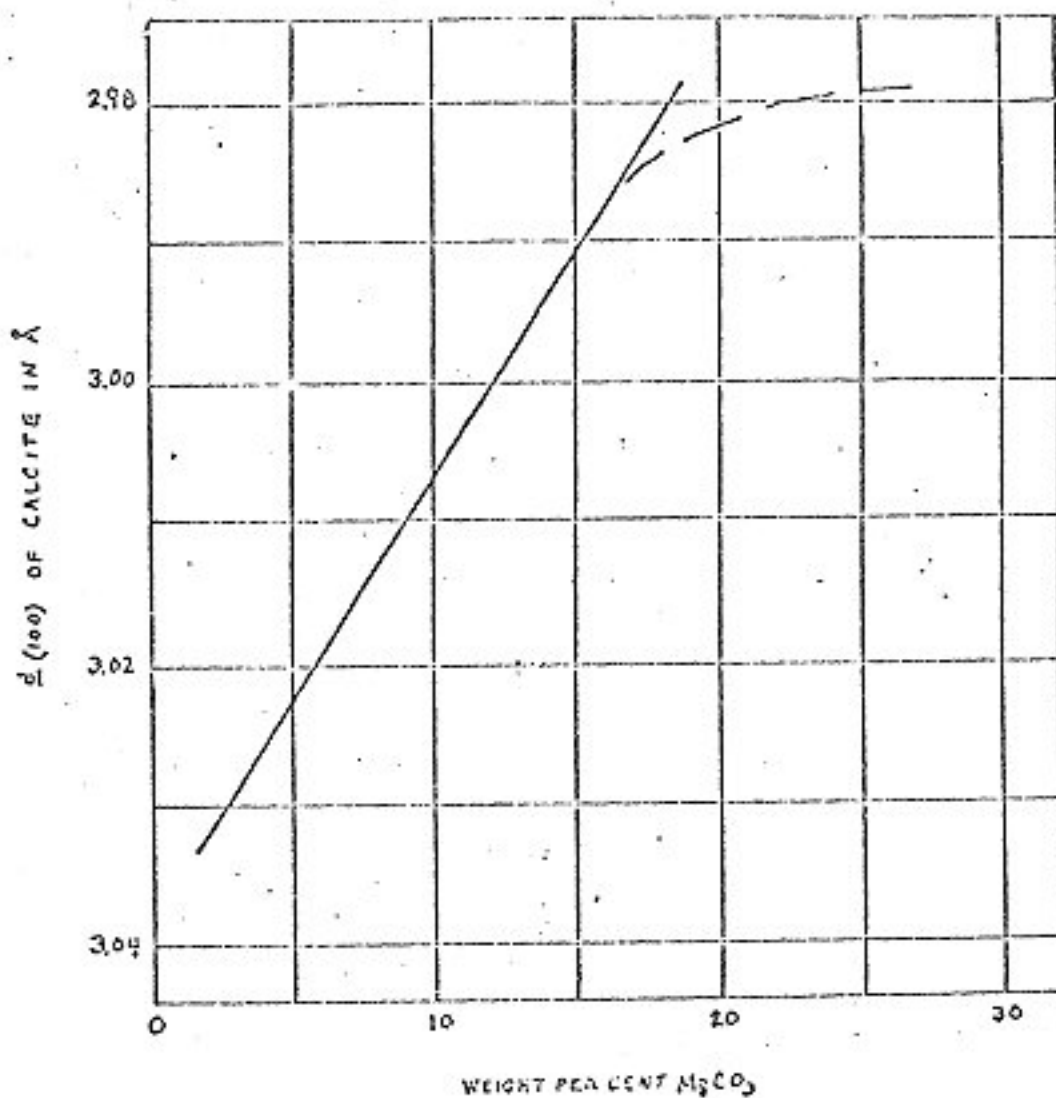
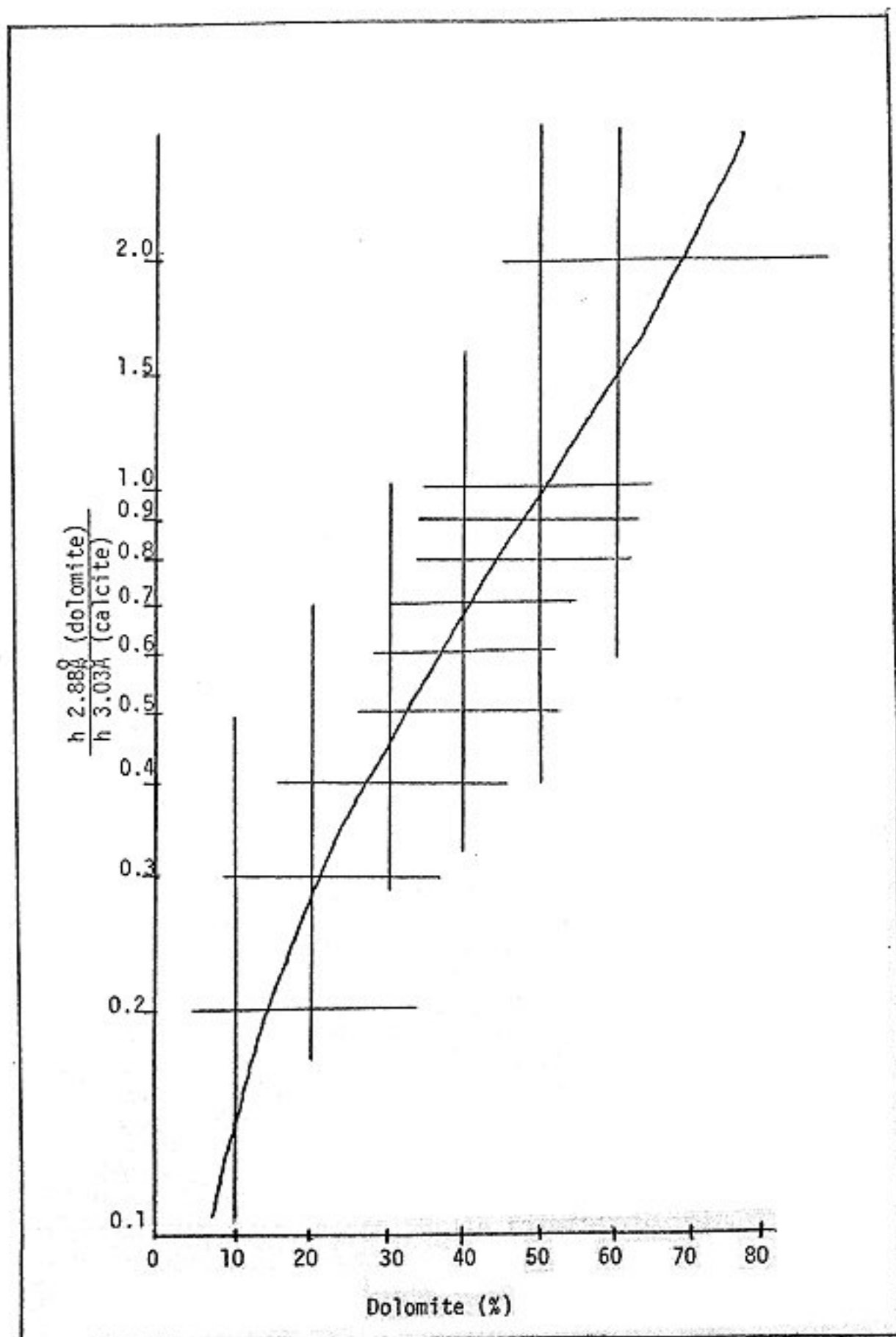


Figure 4. Graph for the determination of weight percent magnesium calcite from X-ray d-spacings (Chave, 1952, p. 191). Note the $d(100)$ peak of calcite is commonly known as the (014) peak.

Figure 5. Working curve used in the determination of dolomite percent from X-ray peak height ratios. Reproduced from Griffin (1969).



Percentage of organic material was determined by ignition as described by Carlisle and Caldwell (1964, p.53). Samples of the organic-rich sand were placed in a crucible and heated for an hour over an open flame, cooled in a desiccator, and weight loss calculated. Prior drying of the sample was not advocated by Carlisle and Caldwell; however, the writer found that by overnight oven-drying, the weight loss due to evaporation of water was approximately 19 percent of the total weight loss due to ignition.

Porosity of the Avon Park country rock was estimated by point-count analysis on thin sections. Approximately 300 points were counted on each of four slides.

GEOLOGIC SETTING

Dredging of the Cross-Florida Barge Canal in 1966 has exposed in the area of Inglis, Florida, a partial section of two of the oldest formations that outcrop in the state. The lowest beds of this section are the Avon Park Formation of Middle Eocene (Claiborne) age. Unconformably overlying the Avon Park is the Inglis Formation, the lowest member of the Ocala Group (Vernon, 1951, p. 115) of Upper Eocene (Jackson) age. Pleistocene sands, probably of the Pamlico Formation, unconformably overlies the Inglis Formation. All these formations dip westerly at one to two feet per mile.

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Superimposed on the regional dip are irregularities due to disconformities between each formation.

The Avon Park Formation outcrops only in a relatively small area around Inglis, primarily along the banks of the Withlacoochee River. The river intersects the Barge Canal approximately 1.7 miles east of the U. S. Highway 19 bridge (Fig. 1).

The Inglis Formation also outcrops in this area, its type locality. The disconformable contact between the Inglis and Avon Park Formations is easily recognized by a deep red limonite zone, one inch to nearly one foot thick, as well by distinct difference in lithologies. (See section below on petrology).

From the coast to the Inglis Lock, some four or five miles eastward, the Barge Canal cuts through at least two Pleistocene terraces. The eight-foot or Silver Bluff terrace is observed west of the Highway 19 bridge, where elevations range from zero to ten feet above sea-level. East of the bridge to the Inglis Lock, the elevation ranges from ten to twenty-five feet, approximating the Pamlico terrace.

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PETROLOGY

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Puri and Vernon (1964) described a section of the Avon

Park Formation at Inglis as (p. 52) ". . . tan to brown, extremely platy and laminated by alternate layers of plant remains and silt-size euhedral crystals of dolomite . . ."

And another section is described as (p. 53) ". . . cream to white, mottled, hard ledge of dense, very fossiliferous, marine limestone . . ." An underlying bed was described as similar (p. 53) ". . . but softer and containing hard nodules . . ."

Sections studied by the writer along the banks of the Barge Canal have remarkably homogeneous lithologies. The Avon Park Formation in this area is composed dominantly of dolomite euhedra 40 to 80 microns in diameter, medium to poorly indurated, and containing individual and composite ledges of calcite-cemented nodules. When originally deposited, it was probably a foraminiferal packstone, but subsequently the matrix was dolomitized and the organically formed grains leached away, to leave only a loose framework of dolomite rhombs, secondary after the original matrix.

The calcite nodules occur in lenses not more than thirty to forty feet long and less than ten feet thick. The lateral distribution of these nodular lenses superficially appears intermittent and random; however, detailed examination showed that the lenses lie beneath organic-rich zones in the overlying Pleistocene sands. This relationship is explained in a

later section on the petrogenesis of nodules.

Despite the lithologic uniformity of the Avon Park beds along the canal banks, detailed examination reveals significant variations in the degree of induration. For example, between the Withlacoochee River and the Inglis Lock, a 0.8-mile stretch, the degree of induration varies from "powdery" to samples so consolidated that they will "ring" when struck with a hammer. There are also several grades of induration between these two extremes.

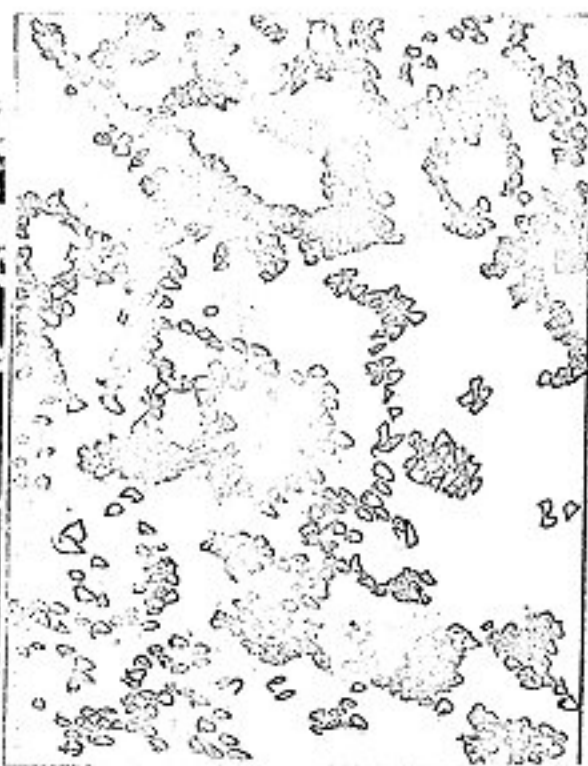
All Avon Park deposits in this area have high secondary porosity (Figs. 6a and 6b). Thin sections reveal less than 30 percent porosity in the better indurated rocks, whereas those which are poorly indurated contain as much as 50 percent open pore space (Table I). This value exceeds the theoretical limit for packed spheres, probably because the grains are rhombs loosely packed. A small amount of residual, possibly primary, calcite acts as a cement, binding the loosely arrayed dolomite crystals. No other original grains remain.

Plant fragments are irregularly distributed within the Avon Park beds. They are specific age and stratigraphic indicators of Avon Park rocks. The plant fragments occur as thin films of completely carbonized leaves (Fig. 7a), stems, and some uncompressed branches. These plant remains suggest

- Figure 6a. (upper left) Photomicrograph of Avon Park host rock at station 4. (crossed nicols).
- b. (upper right) Sketch of previous picture. Light areas are pore space.
 - c. (lower left) Photomicrograph of same sample (plane light).
 - d. (lower right) Sketch of previous picture. Light areas are pores.



a



b

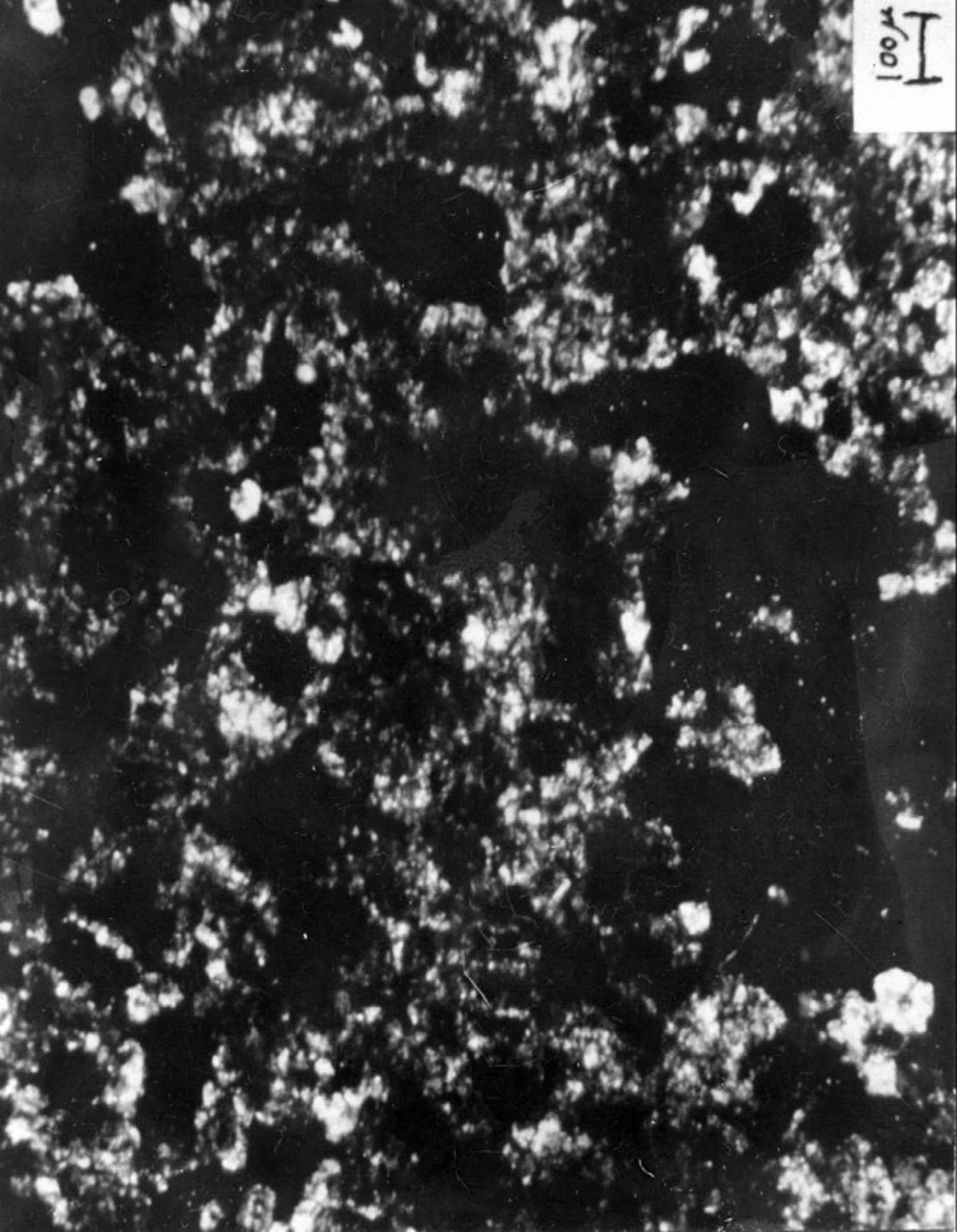


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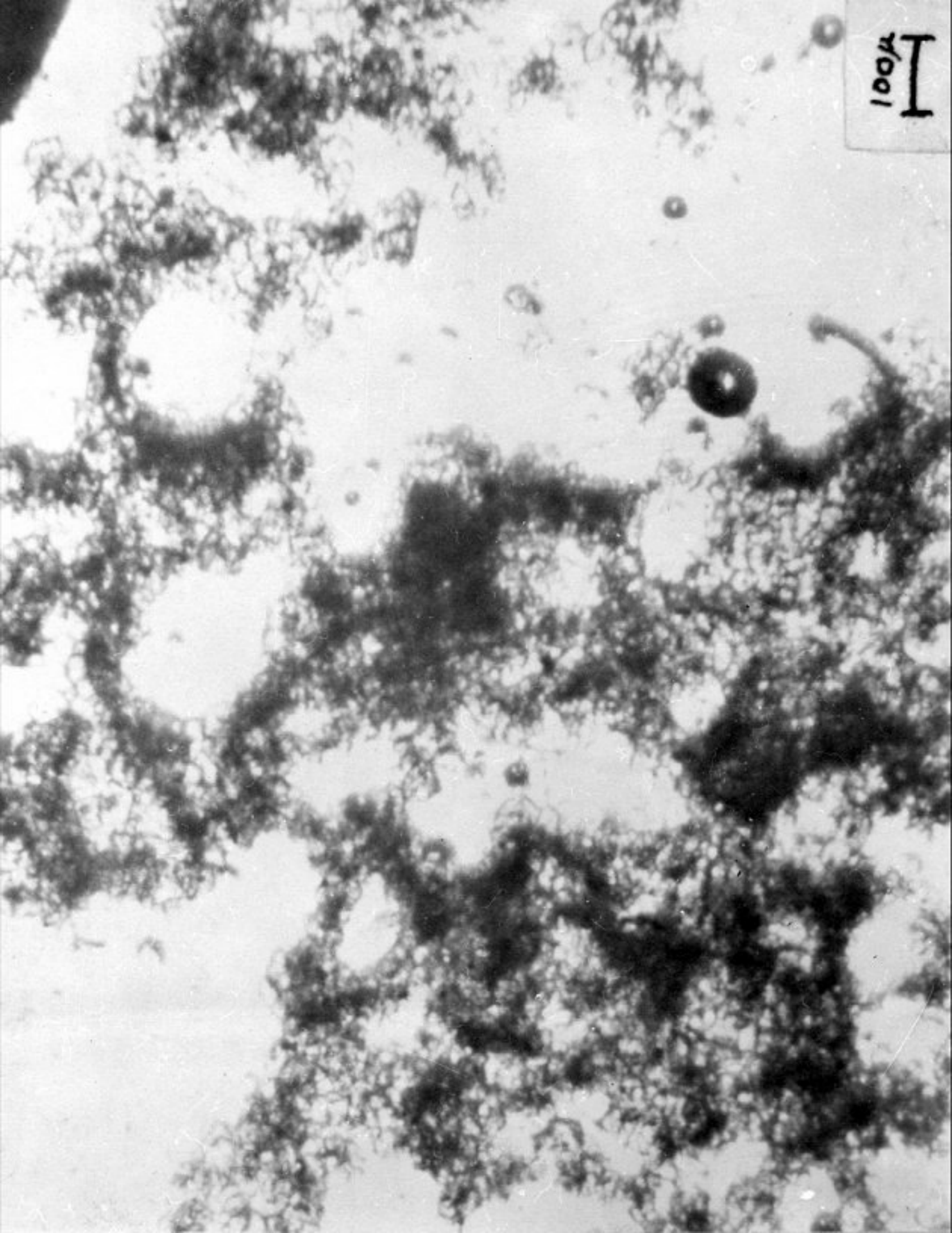


TABLE I. Laboratory Data on Porosity, pH, and Organic Content of Several Representative Samples.

<u>Sample Number</u>	<u>Points Counted</u>	<u>Dolomite Grains</u>	<u>Pores</u>	<u>Percent Porosity</u>	<u>pH 1 day</u>	<u>Percent Organic</u>
Host rock Station 1	322	241	81	25.2	---	----
Host rock Station 3	339	173	166	48.9	---	----
Host rock Station 5	334	194	140	41.8	7.9	----
Host rock Station 6	332	213	119	35.7	---	----
*Organic-Rich Sand, Sta. 2	---	---	---	----	6.1	6.78
*Organic-Rich Sand, Sta. 5	---	---	---	----	6.0	9.80
*Organic-Rich Sand, Sta. 6	---	---	---	----	6.1	4.81
*Organic-Rich Sand, Sta. 7	---	---	---	----	6.0	4.36
(continued)						

(TABLE I. continued)

<u>Sample Number</u>	<u>Points Counted</u>	<u>Dolomite Grains</u>	<u>Pores</u>	<u>Percent Porosity</u>	<u>pH 1 day 5 days</u>	<u>Percent Organic</u>
**Non-organic Sand, Sta. 6	---	---	---	----	---	0.06
**Organic-Rich Sand, Sta. 6	---	---	---	----	---	2.65

* Carlisle and Caldwell method does not allow for weight loss of water.

** Oven dried to remove water previous to ignition

Figure 7a. Avon Park host rock showing leaf imprint. Carbonized print is about 1.5 inches long.

b. Echinoid, Eupatagus clevei, found at station 7 within the Inglis Formation. Numbered intervals are inches.

c. Echinoid, Eupatagus clevei, from station 8, Avon Park Formation. Numbered intervals are inches.



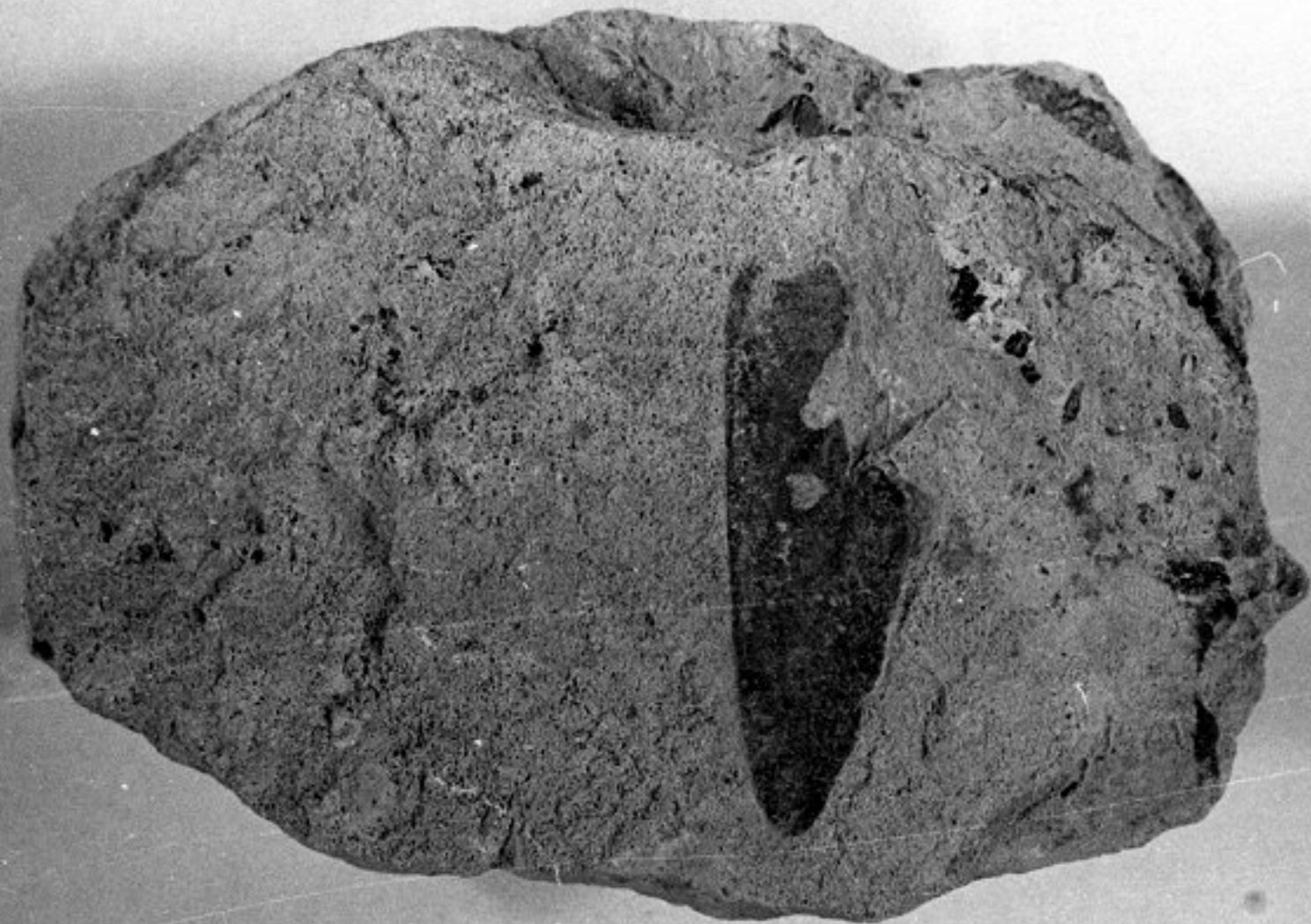
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STERLING

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deposition of the Avon Park Formation in a very nearshore environment. They occur sporadically throughout the entire area sampled. However, most fragments were concentrated in a rather small area midway between the intersection with the Withlacoochee River and the Inglis Lock.

Other biotic evidence is sparse due to leaching of nearly all calcareous material; however, a few large echinoid steinkerns are found in the Avon Park at several locations (stations 5, 6, and 8) along the Canal. The echinoids are mostly Eupatagus clevei (Cotteau) (Figs. 7b and 7c); although a few specimens of Cassidulus sp. were noted. One partial specimen of Periarchus lyelli (Conrad) was noted in a detached boulder that appeared to be of Avon Park composition, but because of its detachment, the Periarchus is of uncertain stratigraphic position.

The Eupatagus clevei specimens reveal a paleontological problem. They were collected in place and are certainly within the Avon Park Formation as defined by lithology and position beneath the Inglis/Avon Park unconformity. However, Cooke (1942) states that Eupatagus clevei is restricted to the lower part of the Upper Eocene Inglis Formation or equivalent age rocks. A possible explanation may be in the statement of Vernon (1951, p. 97) that in Polk County, the Avon Park Formation includes abundant echinoids, principally

specimens of Peronella dalli (Twitchell), an Inglis guide fossil, and appears to be transitional into the overlying Jackson beds. Although no Peronella dalli were identified from the beds at the Barge Canal, Vernon's ideas on the transitional nature of the Inglis/Avon Park contact may verify the writer's observations that the ranges of other echinoids, specifically Eupatagus clevei, extend into the Avon Park rather than being restricted to the Inglis beds.

The Avon Park Formation has undergone at least two diagenetic or physiochemical alterations since it was deposited. A knowledge of the post-depositional alteration of these beds is beneficial in understanding the occurrence of presently observed physical features--for instance, the origin of the porosity in these beds composed of nearly pure dolomite and uniform, silt-size euhedral crystals:

Examination suggests the following brief paragenesis for the Avon Park Formation. During Upper Middle Eocene time it accumulated in a very nearshore area as a carbonate packstone, with grains composed of molluscan fragments and foraminiferal tests, and a matrix of carbonate mud. (Presently these fossils are observed as molds.) By analogy with Recent carbonate muds in south Florida (Ginsburg 1964) it is assumed that the mud was composed largely of aragonite. Because aragonite is unstable at atmospheric conditions,

it is more easily dolomitized than calcite (Adams and Rhodes, 1960, p. 1917), and is likely to have suffered alteration into the secondary dolomite rhombs of the Avon Park sediments. Leaching of calcite constituents followed sub-aerial exposure at an indefinite time, leaving little of the original rock intact. Later infilling by nodular secondary calcite has occurred recently, probably during the Neogene. Several of these tentative conclusions will be amplified in the following paragraphs.

The origin of dolomite has been a problem for many years. As yet, no one has suggested a method of dolomitization to satisfy every situation, although the formation of dolomite in the supratidal zone has been clarified by two studies published since 1960.

Adams and Rhodes (1960) suggested that in evaporite lagoons, dense, highly saline water develops in which magnesium is relatively concentrated. The dense water percolates downward ("refluxes") through slightly older carbonate sediments on the lagoon floor and dolomitizes the metastable carbonate minerals of these sediments.

Deffeyes, Lucia, and Weyl (1965), Illing, Wells, and Taylor (1965), and Shinn, Ginsburg, and Lloyd (1965), introduced the idea that water evaporating from the supratidal zone after storm tides reaches magnesium concentrations 40

times that of sea water. This Mg-rich solution accumulates in the more permeable zones of the surface crust and selectively alters the more unstable CaCO_3 components to $\text{CaMg}(\text{CO}_3)_2$. The resulting euhedral dolomite crystals are one to five microns in diameter.

The application of Adams and Rhodes' theory to the dolomitization of the Avon Park Formation is difficult. No adjacent evaporite deposits (gypsum, anhydrite, halite, etc.) are found in Avon Park rocks. Evaporitic sequences with dolomite are an essential part of their theory, but are not necessary to the supratidal idea.

The Avon Park Formation is recognized in the subsurface over much of peninsular Florida; however, only a few areas are completely dolomitized (Vernon, 1951). The localized occurrence of the dolomite in the Avon Park at the Barge Canal would seem most likely if it had been altered in the supratidal zone instead of by some more widespread process. Formation of the dolomite in the supratidal zone is suggested further by the abundant low angle (approximately 3°) cross-bedding noted along the canal banks in the Avon Park beds (Fig. 8). The carbonaceous remains previously mentioned could also be expected to accumulate in a supratidal environment.

The time of dolomitization is relatively fixed between the time of deposition of the Avon Park sediments (Upper



Figure 8. Section of the Canal bank showing low-angle cross-bedding in the Avon Park Formation. Bank is approximately 25 feet high. 0.5 mi. east of U.S. Highway 19.



Middle Eocene) and the deposition of the undolomitized Inglis beds of the Ocala Group (Lower Upper Eocene). Time must also be allowed for the development of the limonitic unconformity between the Inglis and Avon Park Formations. Hence, dolomitization must have occurred within a few thousand years after the deposition of these Avon Park beds.

Subaerial leaching has occurred at one or more times since deposition of the Avon Park, and each time the remaining calcitic components could have been leached away. Because leaching will preferentially remove the more soluble calcite, the Avon Park Formation was reduced to an extremely porous rock consisting of poorly consolidated dolomite euhe-dra, representing the original carbonate mud matrix of the lime packstone.

This is the present stage in which the Avon Park beds are found, except for the secondary addition of calcite forming the nodules (discussed in detail below). The geologic history of these Avon Park beds, as summarized in Table II, is: original deposition in the supratidal zone as a foraminiferal/molluscan lime packstone; penecontemporaneous dolomitization in the supratidal zone; leaching of molluscan and foraminiferal tests some time after subaerial

TABLE II. Brief Summary of Geologic History of the
Avon Park Formation, Cross-Florida Barge
Canal, Citrus County, Florida.

<u>Time(Epoch)</u>	<u>Event</u>	<u>Environment</u>
Pleistocene - Recent	Precipitation and growth of calcite to form nodules	Vadose zone and water table
Miocene - Recent	Leaching of remaining calcium carbonate (organically formed) by ground water	Vadose zone
Upper Middle Eocene	Dolomitization of metastable carbonates	Supratidal zone
Upper Middle Eocene	Deposition of molluscan and foraminiferal packstone	Supratidal zone

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a period of leaching which has removed secondary intergranular carbonate cement.

Within the study area, the thickness of the Inglis Formation varied from zero to five feet. At other areas near the Barge Canal, as much as twenty-five feet of Inglis Limestone has been reported (Vernon, 1951).

Pamlico Sand

Unconformably overlying the Inglis beds is an unconsolidated quartz sand layer believed to be the Pamlico Formation on the basis of elevation. The sand is dominantly white (N9) or light gray (N8), but includes irregular lenses of dark (N2), peaty sand with in situ roots and stumps (Figs. 9a, 9b, and 9c). These dark layers evidently represent small bogs similar to the cypress hammocks still growing nearby. The cumulative thickness of the sand beds is approximately 10 to 12 feet.

Brooks (1968) correlated deposits of the Pamlico "terrace" with those of the Key Largo and Miami Oolite Formations and the Sangamon interglacial stage. Osmond, Carpenter, and Windom (1965) radiometrically determined (by $\text{Th}^{230}/\text{U}^{234}$) the age of these formations in south Florida as approximately 130,000 years $\pm$ 2%.

These sands contain considerable cross-bedding and

- Figure 9a. Slump section at top of Canal bank. Note dark organic-rich layer and exhumed tree stump above and left of shovel.
- b. Close-up of organic-rich sand from station 6. Numbered intervals are inches.
- c. Tree fragment, right and below hammer. Station 5.



a



b



c







numerous, tubular burrows, probably of pelecypods or polychaete worms. One small lens of whole and fragmental molluscan remains was observed.

DISTRIBUTION AND PETROGENESIS OF THE NODULES

General Features

Although the Avon Park beds in the study area are, as a whole, poorly indurated, as described above, isolated areas of dense calcite lithification (Figs. 10a and 10b) occur in the form of nodules. Internally, the nodules are composed of radiating scalenohedrons of nearly pure calcite that fill the pores and incorporate host rock grains in a poikilitic, sand crystal, manner. The nodules occur in a variety of forms, ranging individually from spheroidal to planar layers, and as single nodules or aggregates of beds and ledges (Figs. 11, 12a). Single nodules range in diameter from less than one inch to greater than five inches (Figs. 12b and 12c). Many of the aggregates of spheroids are apparently formed by coalescence of adjacent nodules (Fig. 13a), whereas the planar forms are usually fillings along joints or bedding planes.

Source of CaCO_3 Solutions

The nodules are formed when calcium-carbonate-bearing solutions deposit calcite in the pores of the Avon Park

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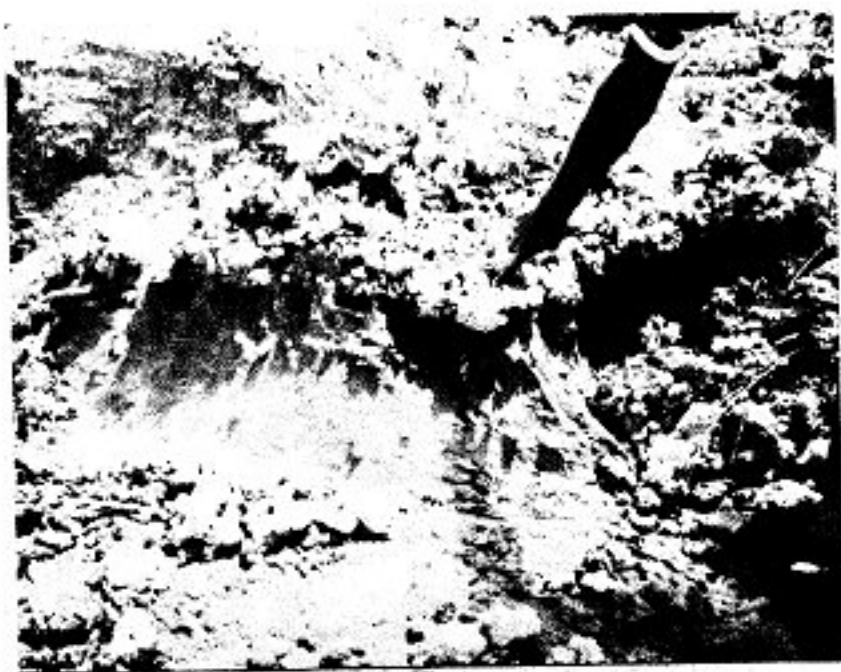
The nodules are formed when calcium-carbonate-bearing solutions deposit calcite in the pores of the Avon Park

Figure 10a. Nodule rubble washed
from Avon Park Formation
near the water table at
Station 6.

- b. Flat ledge of nodules
occurring above the
present water table.
This ledge may repre-
sent an earlier water
stand.



a



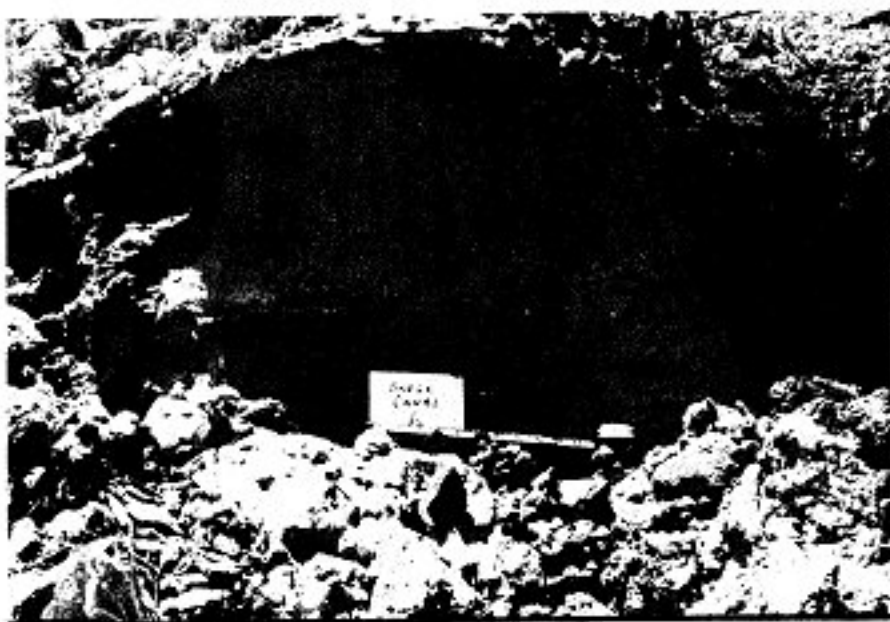
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SAGE
CANAL
6



- Figure 11a. Hydraulically excavated section of bank. Note fine-grained, light-colored Avon Park matrix with nodules interspersed, some in definite layers.
- b. Close-up of Fig. 11a. Note downward elongation in some nodules. Station 6. Scale is inches.



a



b



BARGE
CANAL

6



A black and white photograph of a geological specimen, possibly a fossilized skull, embedded in a matrix. The specimen is characterized by several rounded, bulbous structures. A ruler is placed horizontally below the specimen for scale, showing markings from 1 to 8. A small white label with handwritten text is positioned above the ruler. The foreground shows some loose, light-colored material, likely sediment or rock fragments.

BARGE
CANAL
6

Figure 12a. Nodules washed out of a ledge near the water table. Station 3.

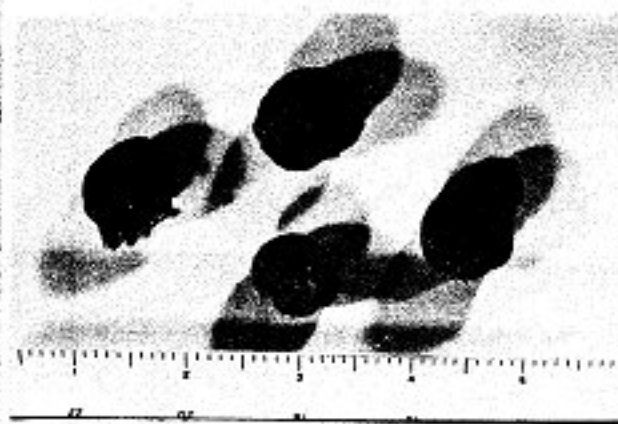
- b. Large spherical concretion with knobby surface. Numbered intervals are inches. Station 5.
- c. Small spherical concretions. Note triangular crystal protrusions on surface. Numbered intervals are inches. Station 1.



a



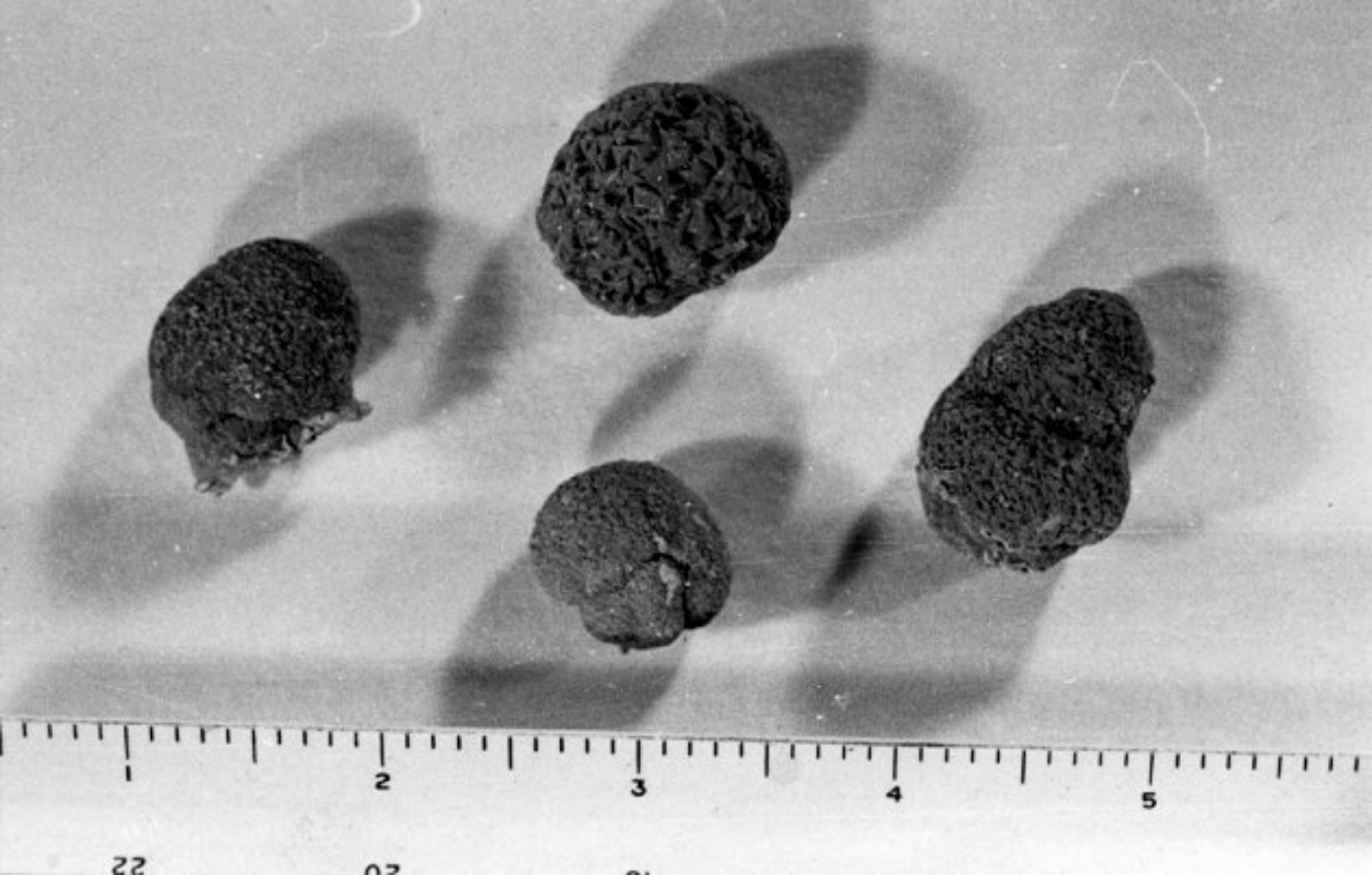
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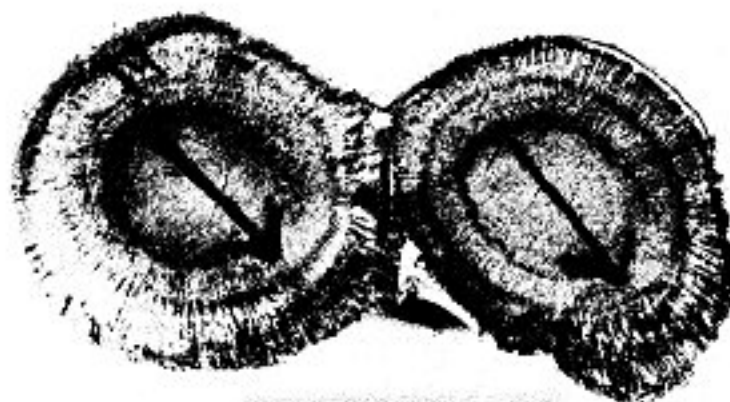




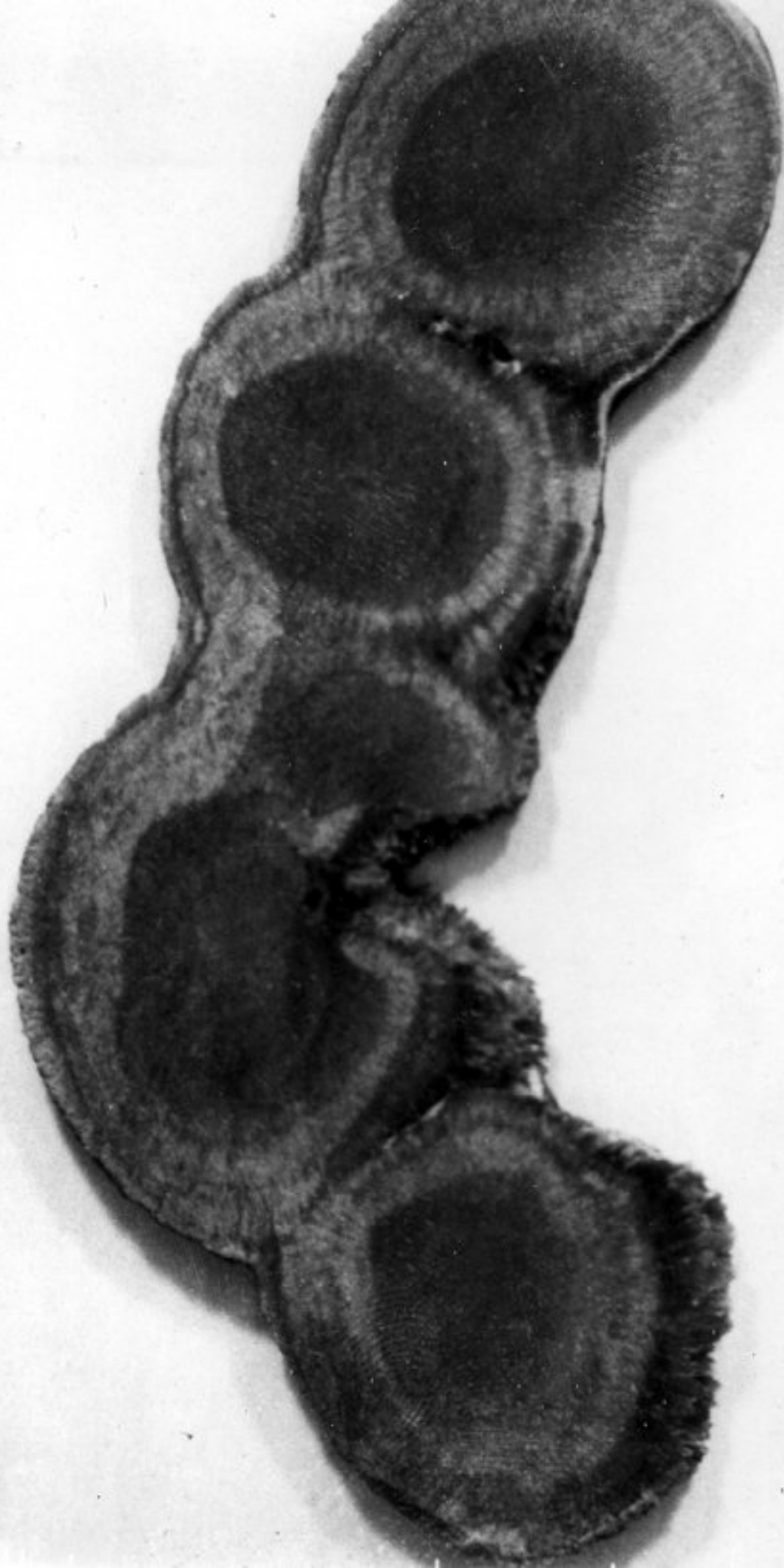


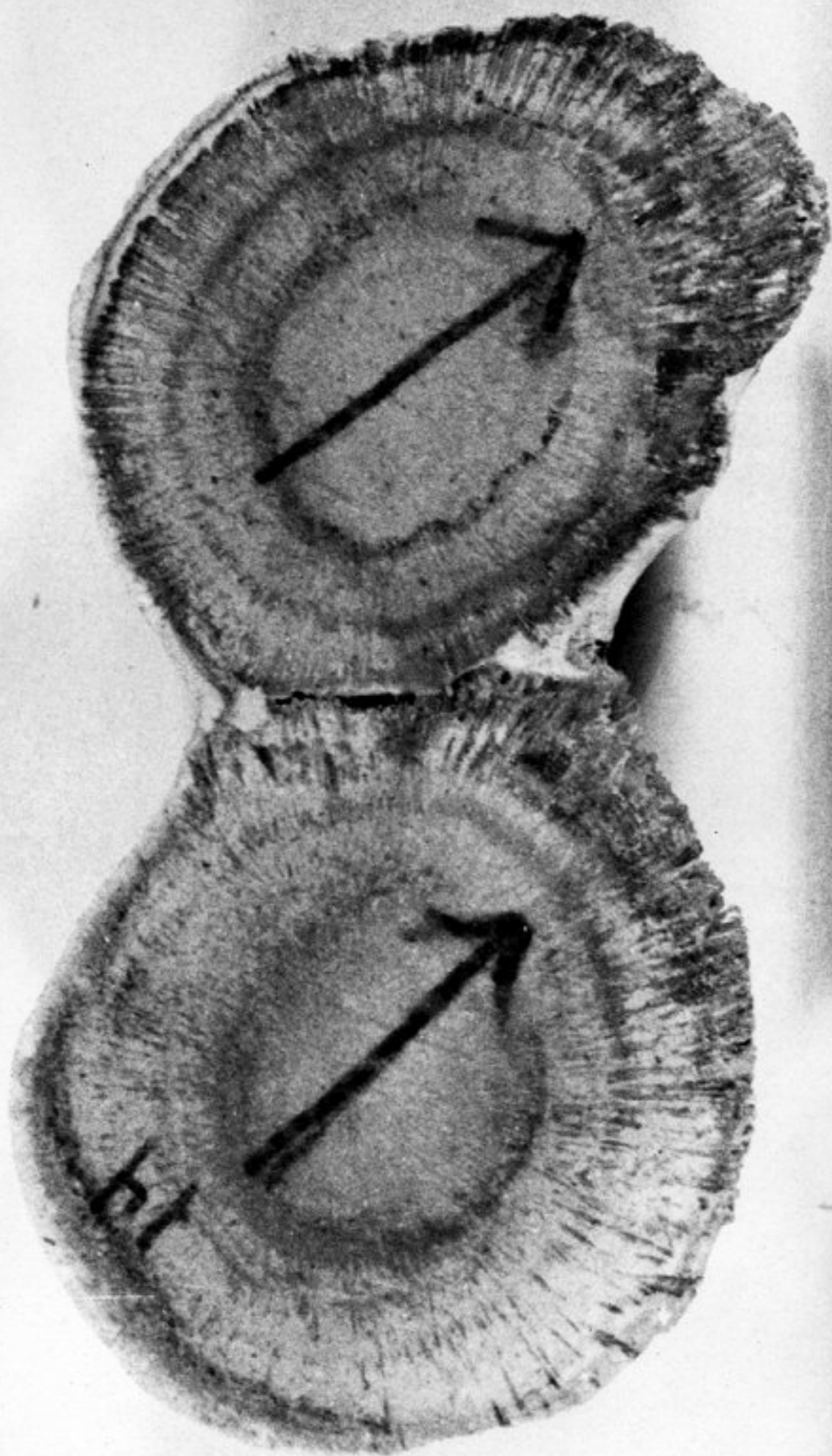


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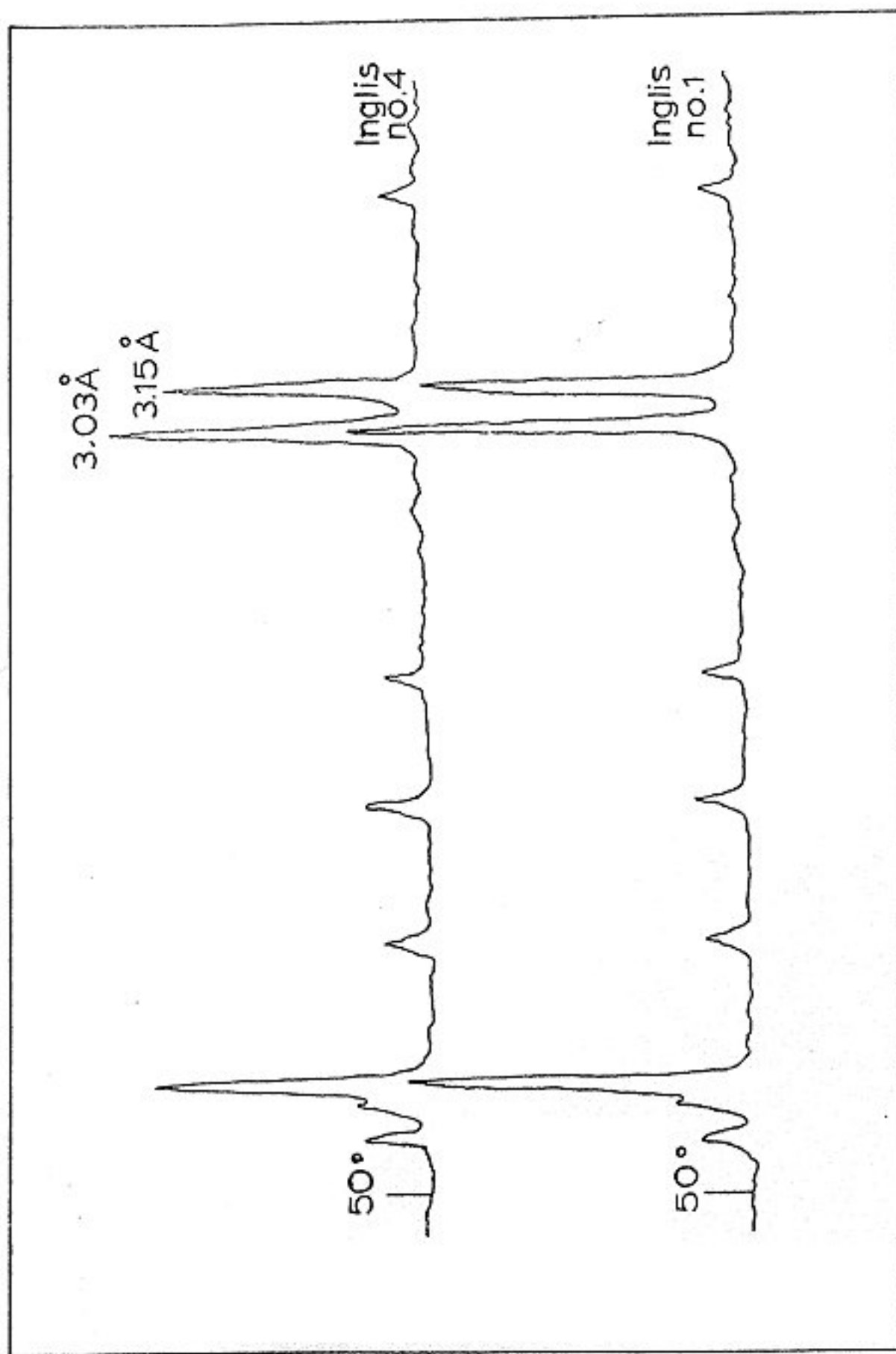


Formation. Because the Avon Park beds in the Inglis area are nearly devoid of calcite, the source of calcium carbonate must be sought elsewhere. The overlying Inglis Formation provides such a source. The Inglis beds are now composed almost entirely of echinoid and foraminifera tests, which are low-magnesium calcium carbonate, having from 5.0 to 5.1 mole percent MgCO_3 in a calcite-type lattice. (Figs. 14, 15, and 16). It is assumed that the Inglis, as originally deposited, contained considerable aragonite and metastable, high-magnesium calcite (Illing; 1954, Ginsburg, 1957, 1964), which leached from the Inglis beds and precipitated as stable low-magnesium calcite in the underlying Avon Park Formation.

Location of Nodular Lenses

Location of nodular lenses is dictated by the distribution of organic-rich layers in the overlying Pleistocene sands. Detailed field observations indicate that dark organic-rich sand lenses directly overlie the nodule concentrations and that the lenses pinch out at both ends, coincident with a decline in abundance of nodules (Fig. 17). The organic-rich sands contain large amounts of woody fragments (Fig. 7b), and large in situ tree stumps and roots may be seen embedded in these sands at many places along the Canal

Figure 14. Two x-ray patterns of the Inglis Limestone showing pure calcite and fluorite (internal standard). Calcite ($3.03\text{\AA}$) and fluorite ($3.15\text{\AA}$). Sample numbers indicate station numbers.



- Figure 15a. X-ray pattern of Eupatagus antillarum (Cooke) predominant Inglis echinoid (completely calcite).
- b. X-ray pattern of calcite nodule from Inglis Formation. Note abundance of quartz rather than dolomite of the Avon Park nodules. Quartz ($3.35\text{\AA}$).

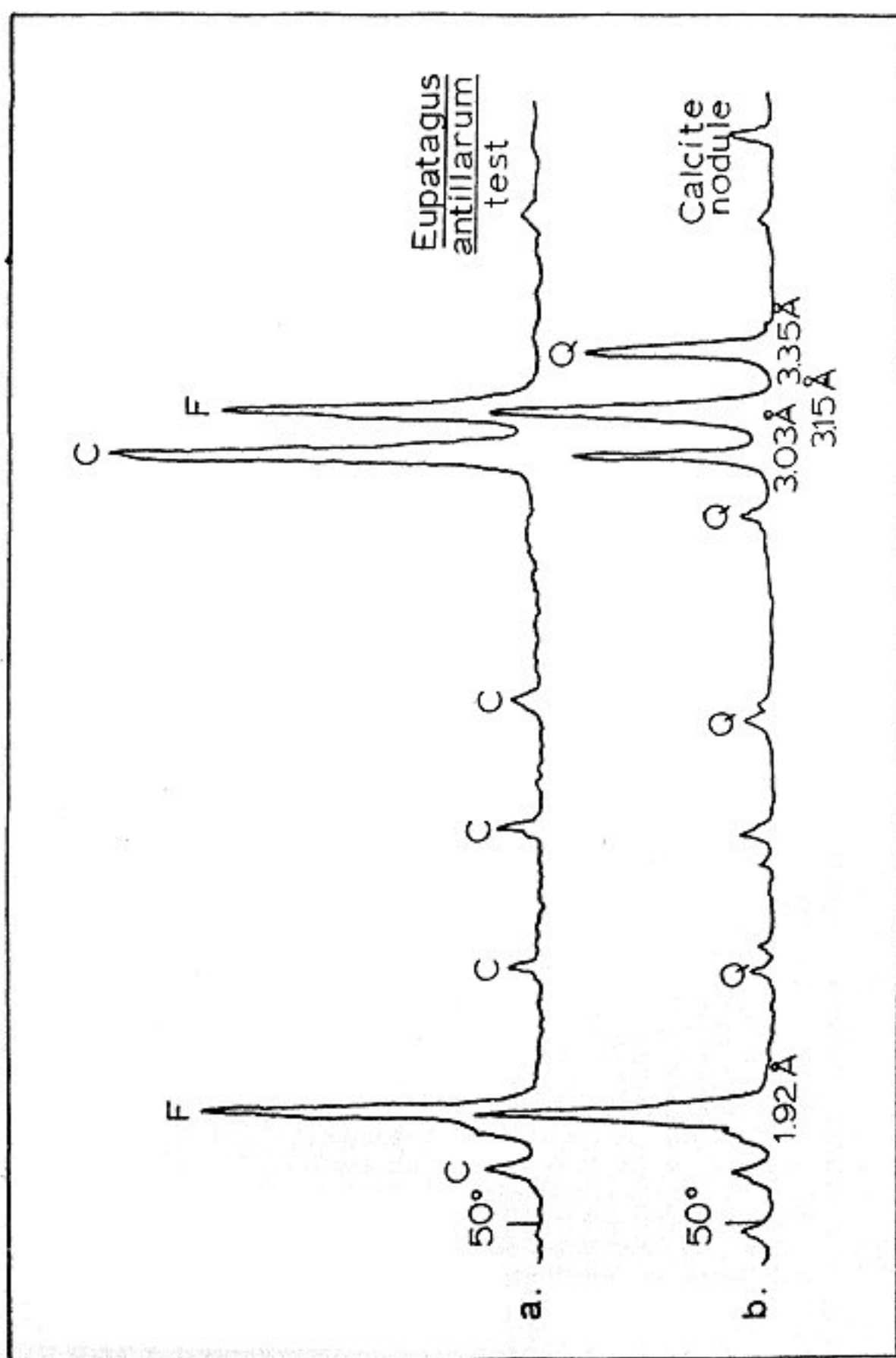


Figure 16. X-ray patterns showing mole percentage MgCO_3 in Eupatagus antillarum test and two Inglis Limestone samples. Scan speed $2^\circ - 2\theta/\text{min}$. Sample number is station number.

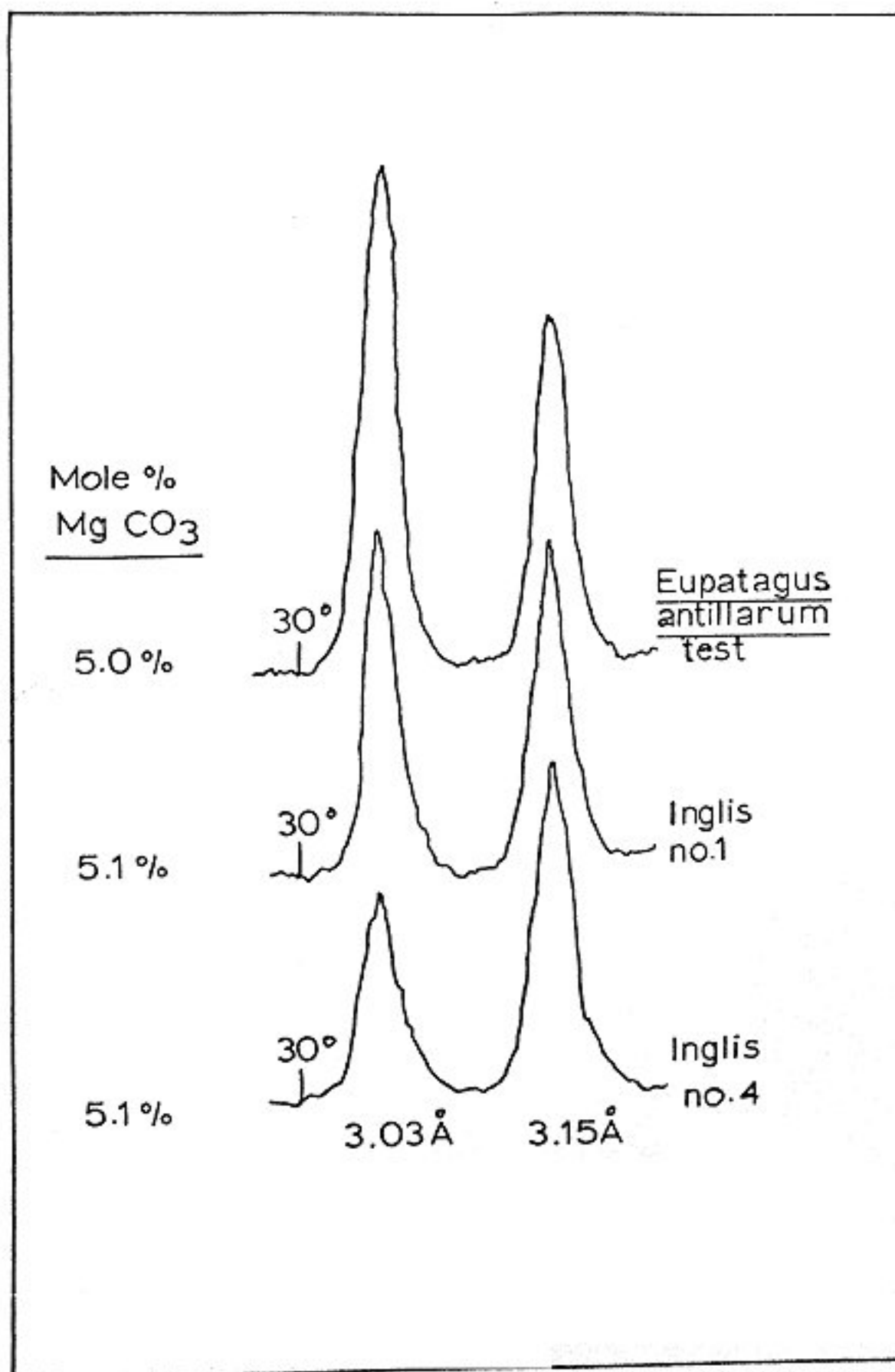
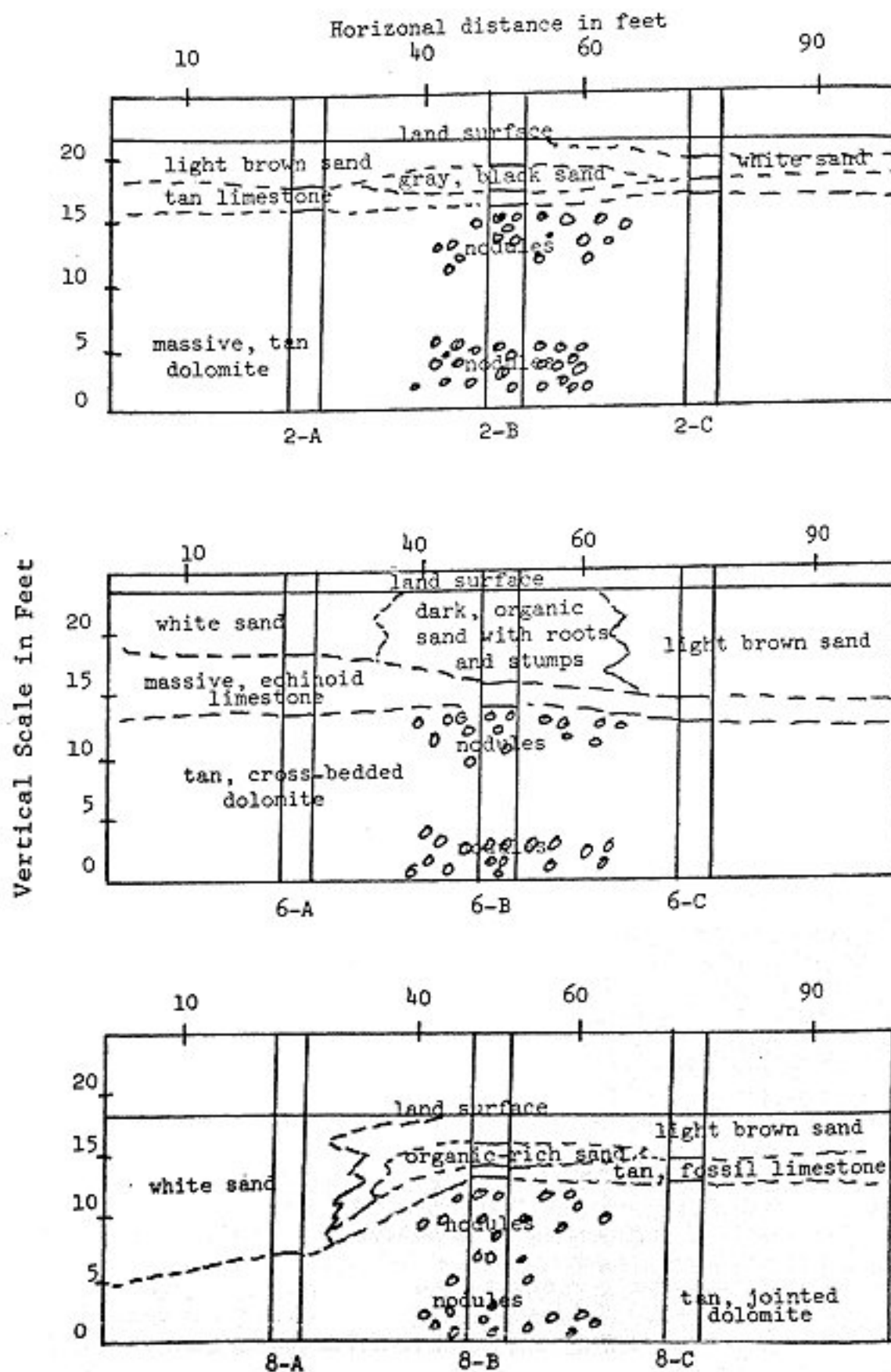


Figure 17. Idealized cross-sections at three stations along the Canal showing sand facies and occurrence of calcareous nodules. Note correspondence of organic sand and nodules.



banks (Fig. 9a and 9c). The average content of organic material in four samples of these sands is 6.5 percent as determined by ignition, and a sample of non-organic sand yields very nearly no organic percentage (0.06%) (Table I). Modification of the original method for organic determination (p. 26) lowered the previously determined organic values by approximately 19 percent. This data is also listed in Table II. Ground water percolating downward through these organic-rich lenses assume an acid pH (approximately 6.0), to dissolve CaCO_3 from the underlying Inglis Formation. This effectively dictates the sites of dominant precipitation of nodules in the deeper Avon Park Formation (Fig. 17). Evidently, percolation is essentially vertical.

Reference to organic-rich sands as a source for acidic waters which dissolve underlying calcitic rocks is unusual but not unique in the literature. Morgan and Treadwell (1954) cite examples of calcite-cemented sandstone slabs on beaches in the Chandeleur Islands of Louisiana. They suggested that lagoonal waters percolating through mangrove marshes on the shoreward side of the islands became acidic and dissolved finely pulverized calcareous shell fragments incorporated into the sediment. This calcium carbonate is then, according to Morgan and Treadwell, precipitated by evaporation in the immediately underlying and seaward beach

sands forming cemented ledges of sandstone one-fourth to two inches thick near sea-level.

Spackman, Scholl, and Taft (1964) show diagrams that indicate solution of limestone beneath organic deposits in the Everglades. Their figures 10 and 11 indicate that the limestone beneath cypress and mangrove "hammocks" is dissolved and that the resultant cavities as deep as seven feet below the land surface are filled with peat. The limestone outcrops, or is present within one foot of the surface, in areas outside the organic "hammocks." It is not known whether secondary calcite is precipitating in deeper layers beneath the hammocks.

To determine what acidic effects were produced by water passing through the organic sand, six samples from three different sand lenses were suspended in distilled water and the pH of the filtrate measured after one and five days. The original pH of the distilled water was 6.8. After one day, the average pH had decreased to 6.0, and after five days, to 5.3. This pH is believed sufficient to dissolve CaCO_3 efficiently. The Krumbein and Garrels' fence diagram (Krumbein & Garrels, 1952, p. 3) indicates that solutions below 7.8 will dissolve calcite.

The non-organic sands similarly treated remained at or

slightly above the distilled water pH (6.8) the first day, then decreased slightly to 6.5 after five days. An analysis was also made upon some powdered Avon Park host rock (dolomite) suspended in distilled water. This water ultimately yielded a pH of 7.3 after five days (Table I).

Controls of Precipitation of Nodular CaCO_3

Once the calcium carbonate is in solution, several factors can influence its precipitation at favorable sites, such as the basic pH in the surrounding rocks, physiochemical changes at the water table, and evaporation. Todd (1903) stated that the water table is the area of predominant growth of concretions, that this is where "precipitating influences" are most active.

Concentrations of nodules into ledges near the sea-level/water table, as observed at the Barge Canal, would uphold Todd's ideas. Interaction with mildly alkaline sea water (pH 7.5-8.3) at that level would increase the ground water pH sufficiently to cause precipitation of CaCO_3 .

Some nodules are found scattered throughout the vadose zone at the Canal which could not be correlated with known, well-defined, Recent or prior sea-level/water table stands, although it is known that sea-level fluctuated through this elevation during the late Pleistocene. It is possible that

while solutions were percolating through this zone a small pH change due to the buffering effect of the dolomitic Avon Park beds, created locally supersaturated environments similar to those at the water table and caused nucleation. Evaporation or perhaps temperature may have also been contributing factors. No evidence of a nucleus was found in any nodules examined (Fig. 13a), which may rule out the former idea of nucleation from prior grains. Therefore, supersaturated microenvironments, probably in pore space, are considered as the areas where nucleation began.

Once the energy boundaries for nucleation are crossed, growth of the calcite may proceed at a rate commensurate with the supply of the calcitic solutions. This growth is principally at the apexes of calcite scalenohedrons radiating from a central nucleating point (Fig. 13a).

This radiating phenomenon is observed in hand specimen, and particularly easily observed in petrographic thin-sections. In these sections euhedral to subhedral crystals of dolomite are seen to be completely enclosed in calcite. Innumerable scalenohedrons are formed, each extinguishing at a different position. In effect, many pores in one area are filled with calcite in optical continuity which compose one scalenohedron (Figs. 18a and 18b).

- Figure 18a. (upper left) Photomicrograph of calcareous nodule in Avon Park at Station 5. (crossed nicols).
- b. (upper right) Facsimile sketch of Fig. 18a. Note uniform extinction (shaded areas) of calcite crystals.
- c. (lower left) Photomicrograph of nodule in Avon Park at Station 9. (crossed nicols). Note dolomite rhombs incorporated within calcite crystals in poikilitic manner.
- d. (lower right) Facsimile sketch of Fig. 18c. Shaded areas represent extinction of calcite crystals.



a



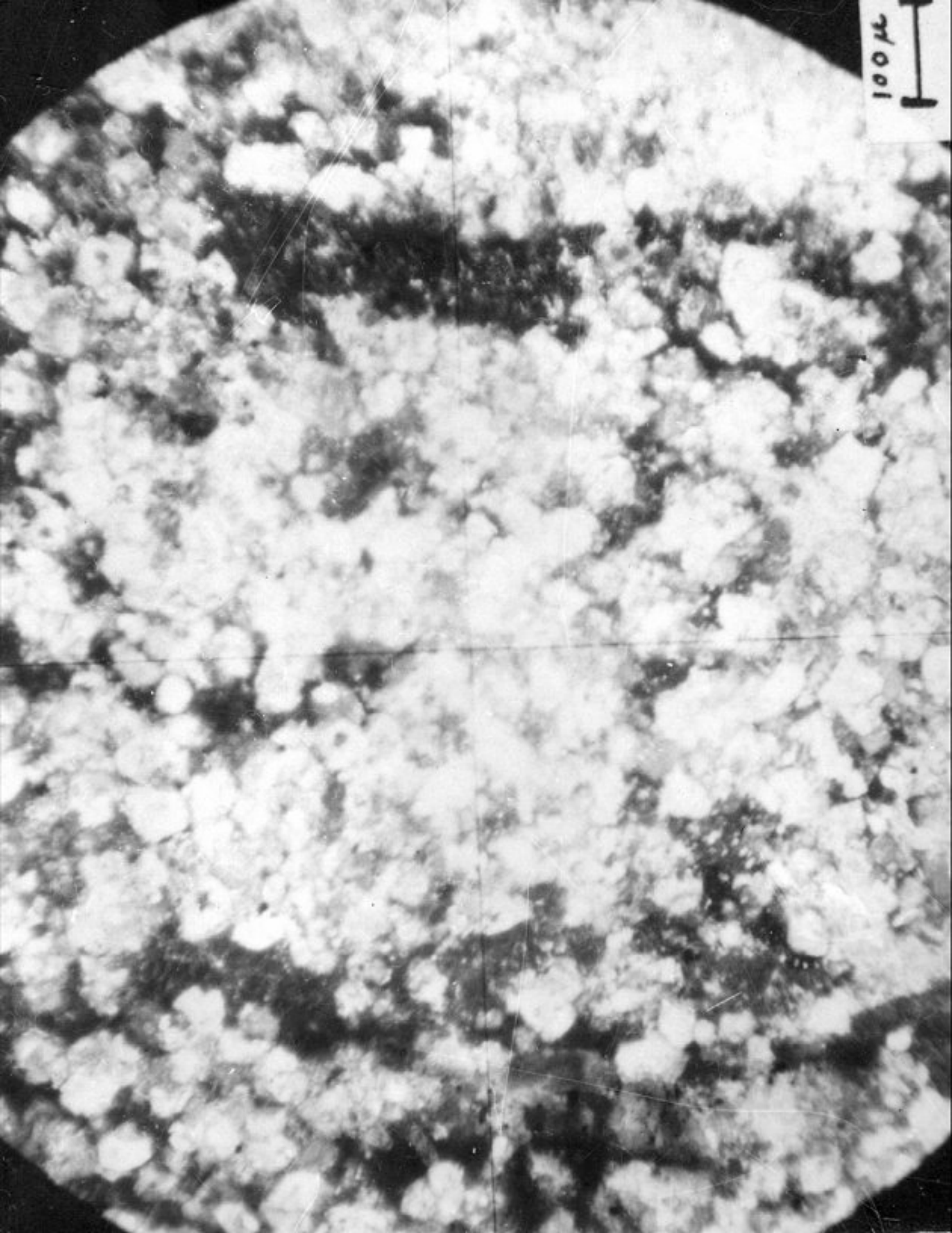
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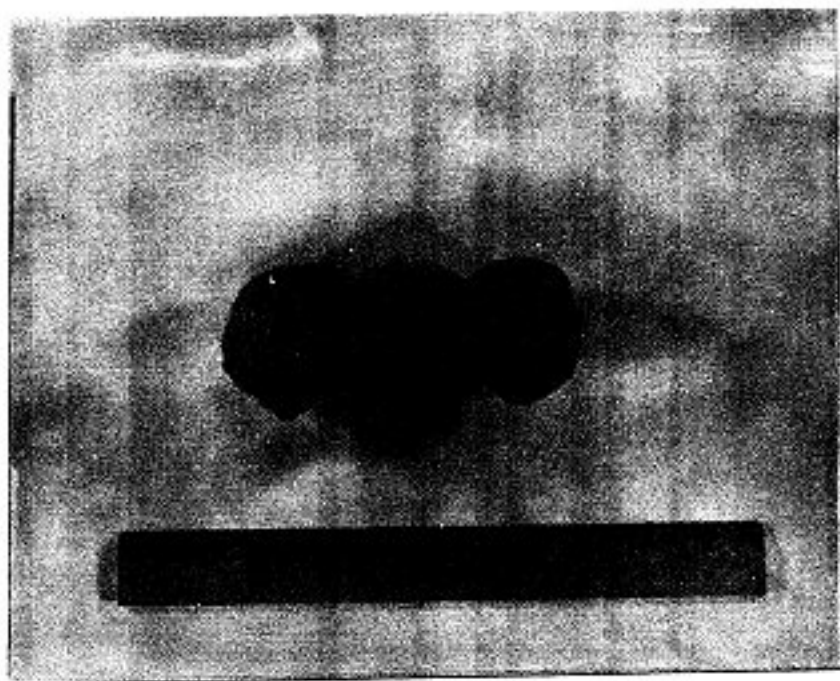


Shape of the Nodules

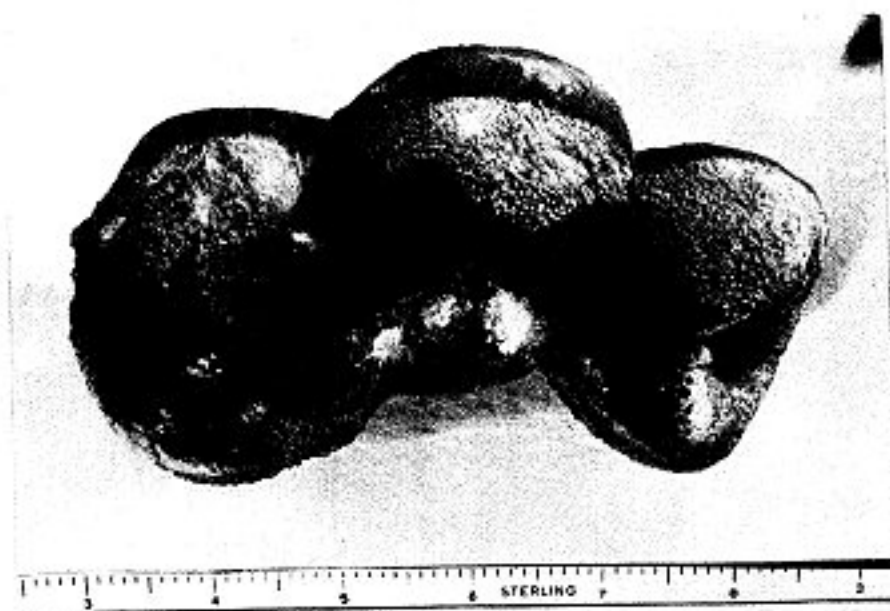
An unusual nodule shape is associated with the near-water table site of nucleation. These nodules are somewhat spheroidal, but show a distinct downward elongation terminating generally in scalenohedrons with sharp points (Figs. 19a and 19b). The downward elongation of the nodules indicates the direction of active crystal growth and is analogous to the formation of stalactites, in that solutions are deposited lastly on the bottom of the concretionary structure. Dunham (1969) reports downward elongation of many pisolites of the backreef facies of the Permian El Capitan sediments in Texas and New Mexico. He states that this downward elongation is indicative of in place growth within the vadose soil zone. The process is also generally similar to the downward growth of pisolites during bauxite development.

The shape of nodules is somewhat contingent upon the fabric of the host rock (Avon Park Formation). If the porosity and permeability are uniform in every direction, the concretion will be spherical. If the porosity and permeability are restricted in any direction, a non-spherical concretion will result (Tarr, 1935) (Figs. 12b, 20a, 20b, 20c, and 20d).

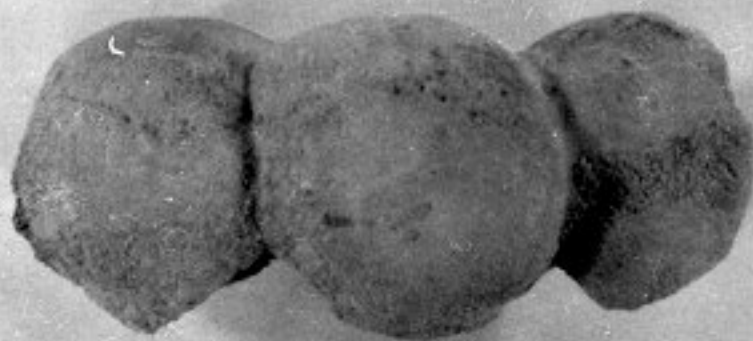
- Figure 19a. Three concretions grown together (Sample No. 10). Note crude inverted "tear-drop" shape. Orientation in the photograph is as the sample was within the formation.
- b. Bottom surface of concretions in Fig. 19a., note protrusion of calcite crystals into cavity.



a



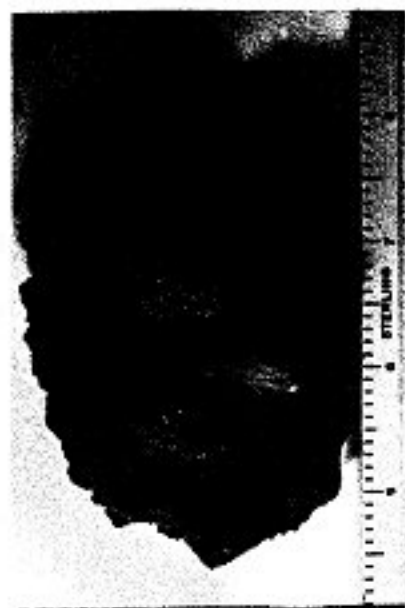
b





- Figure 20a.** (upper left) Irregular concretion with numerous secondary nodules on the surface.
- b. (upper right) Aggregate of small spherical concretions. Station 1.
- c. (lower left) Reticulate and irregular concretions from Station 1.
- d. (lower right) Concretion with protruding crystal terminations and three small secondary nodules on the surface.

In all cases, numbered intervals on scale are inches.



p



c



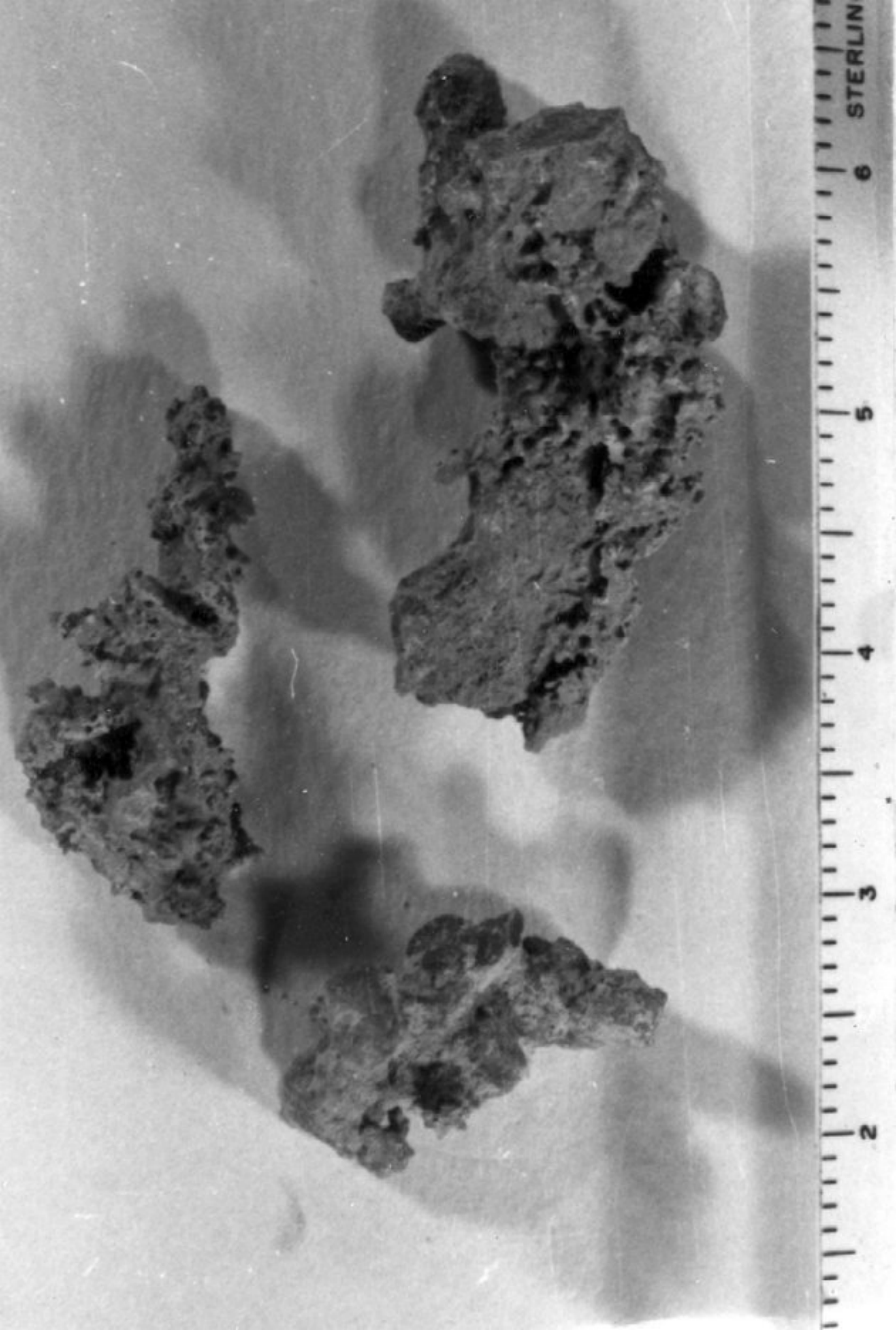
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The pore network of the Avon Park beds is very poorly interconnected in some areas. Such a situation practically prohibits nodule growth by inhibiting the influx of additional CaCO_3 in solution. However, some areas with inadequate porosity are cut by several sets of joints which are very conducive to calcite precipitation because they provide adequate void space for crystallization (Figs. 21a and 21b). Often, the joints are filled with clear calcite, but the calcite-cemented dolomite form also occurs. The general strike of these joints is NW-SE and NE-SW, with indeterminate dips.

Miscellaneous Features of Nodules

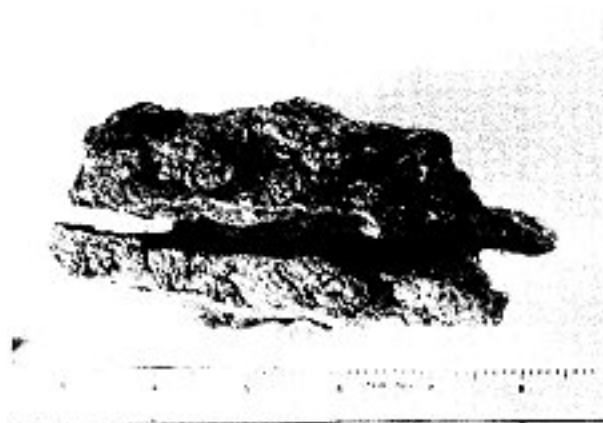
Surface features of the nodules vary. Many have smooth surfaces, sometimes partially studded with "secondary" smaller nodules creating a "knobby" appearance (Figs. 12b, 20a, and 20b). Some of the concretions have scalenohedrons projecting through the surface with terminations of clear and pure, yellow calcite (Fig. 19a, 19b, and 22a). Other nodules exhibit rhombic terminations of impure calcite. These crystals of calcite have incorporated the sucrosic dolomitic host rock (Fig. 22b). Rarely, one finds both types of calcite crystal terminations on the surface of one specimen. A sharp contact can be seen between the two types of crystals

Figure 21a. Vertical view of calcite vein in a joint of the Avon Park Formation. Strike is southwest (toward the top of the picture). Vein just left of penny. Station 7.

- b. Large nodule incorporated in two calcite-filled joints. Station 7.

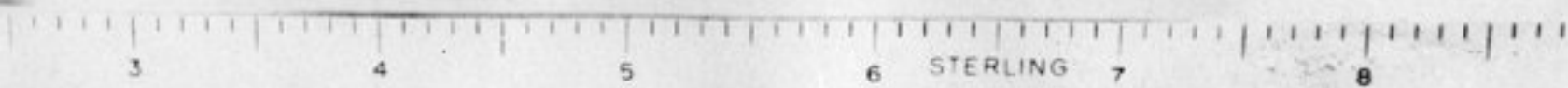


a



b





(Fig. 22c). This phenomenon results when part of the calcite grows into a large void or vug and is free to crystallize without inclusions. The rest of the calcite continues to grow through the dolomite matrix.

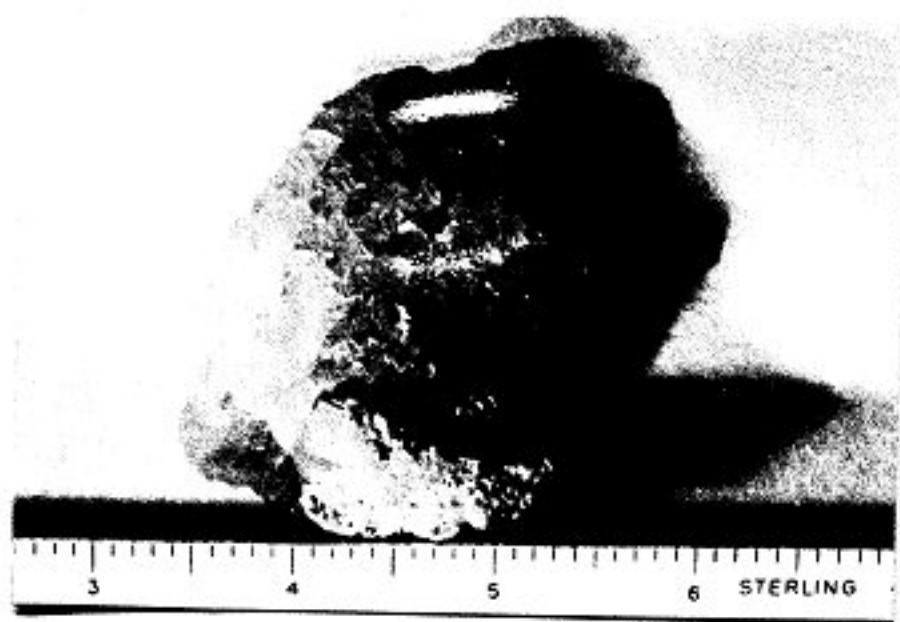
A number of factors may influence the form and shape, as well as the size of the calcite crystals, as a surface expression on the nodules. The amount and rate of supply of ions available to form crystals, the freedom for crystals to grow unobstructed, and later resolution of some calcite by ground water are a few possible factors that modify the calcite crystals.

It would be difficult to establish the quantitative effects of any of these processes without complex laboratory experimentation. However, field observations indicate that well formed crystals occur only in porous areas of the host rock.

A few small concretions were collected within the Inglis Formation near Stations 3 and 7. These concretions are generally similar internally to those in the Avon Park Formation, but include fragments of echinoid tests and quartz grains in lieu of dolomite crystals (Fig. 22d). In thin section, uniform extinction of calcite scalenohedrons is observed; this is also similar to the condition of nodules in the Avon Park Formation. Thus, except for a different host matrix (Fig. 23), these concretions appear

- Figure 22a. (top) Calcite crystals protruding into a vug. Note rhombic terminations. This specimen was used for Carbon-14 age determination. Station 17, just above the water table.
- b. (middle left) Spherical nodule with impure (dolomitic) rhombic calcite terminations on the surface.
- c. (middle right) Close-up of small nodule containing impure and pure calcite rhombic terminations upon surface.
- d. (bottom) Two calcareous sand concretions from the Inglis Formation, composed of detrital quartz grains.

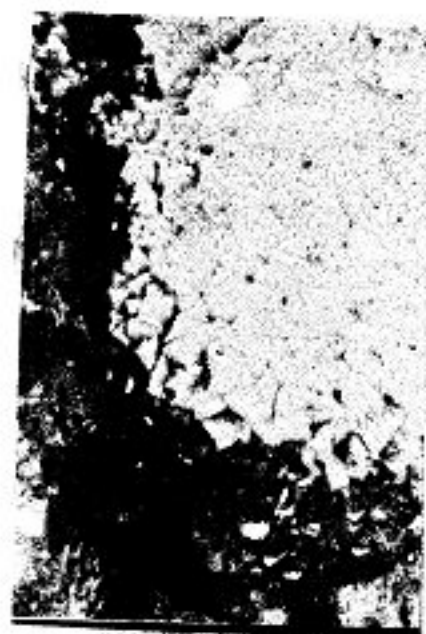
Numbered intervals on scale are inches.



a



b

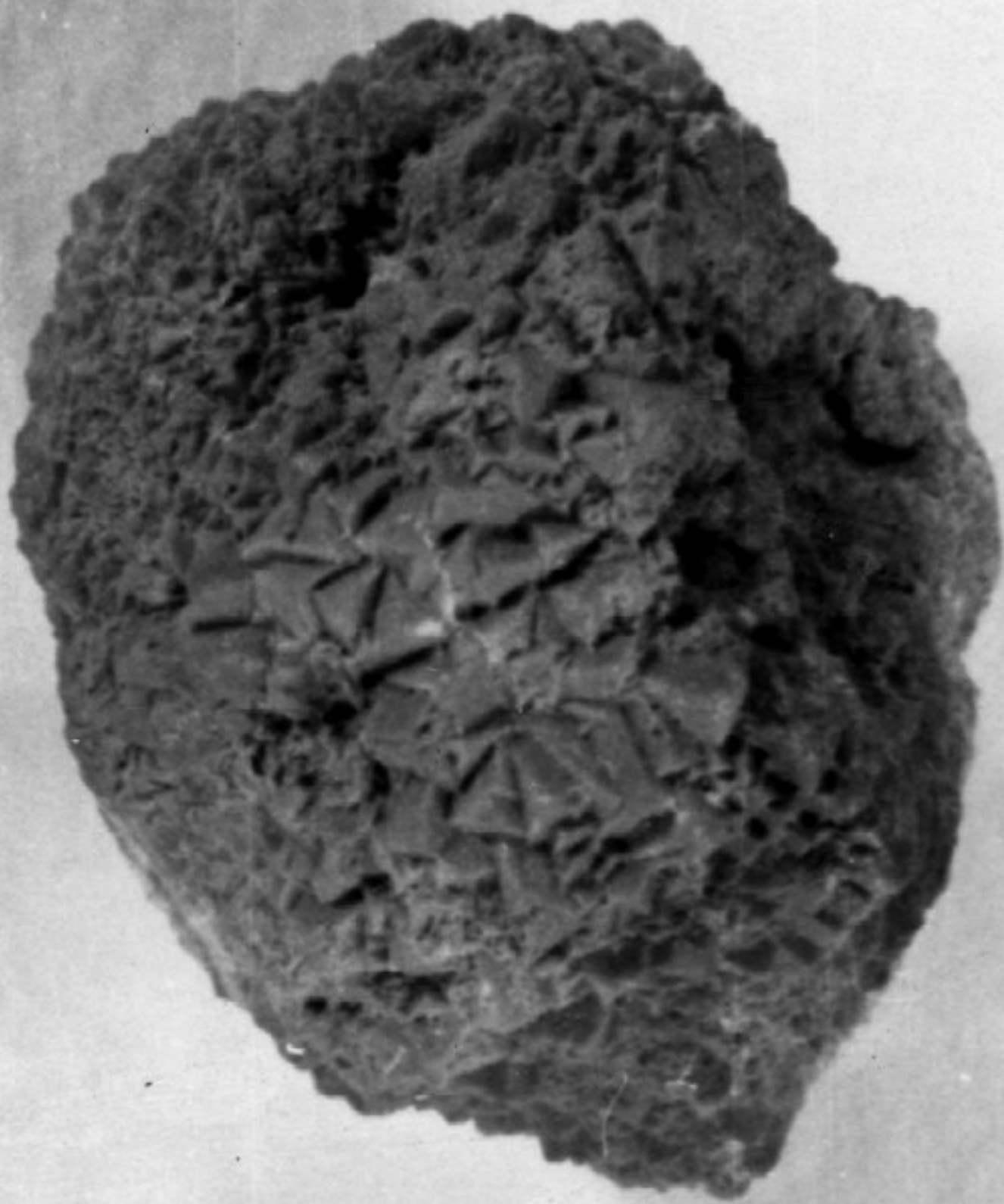


c



d





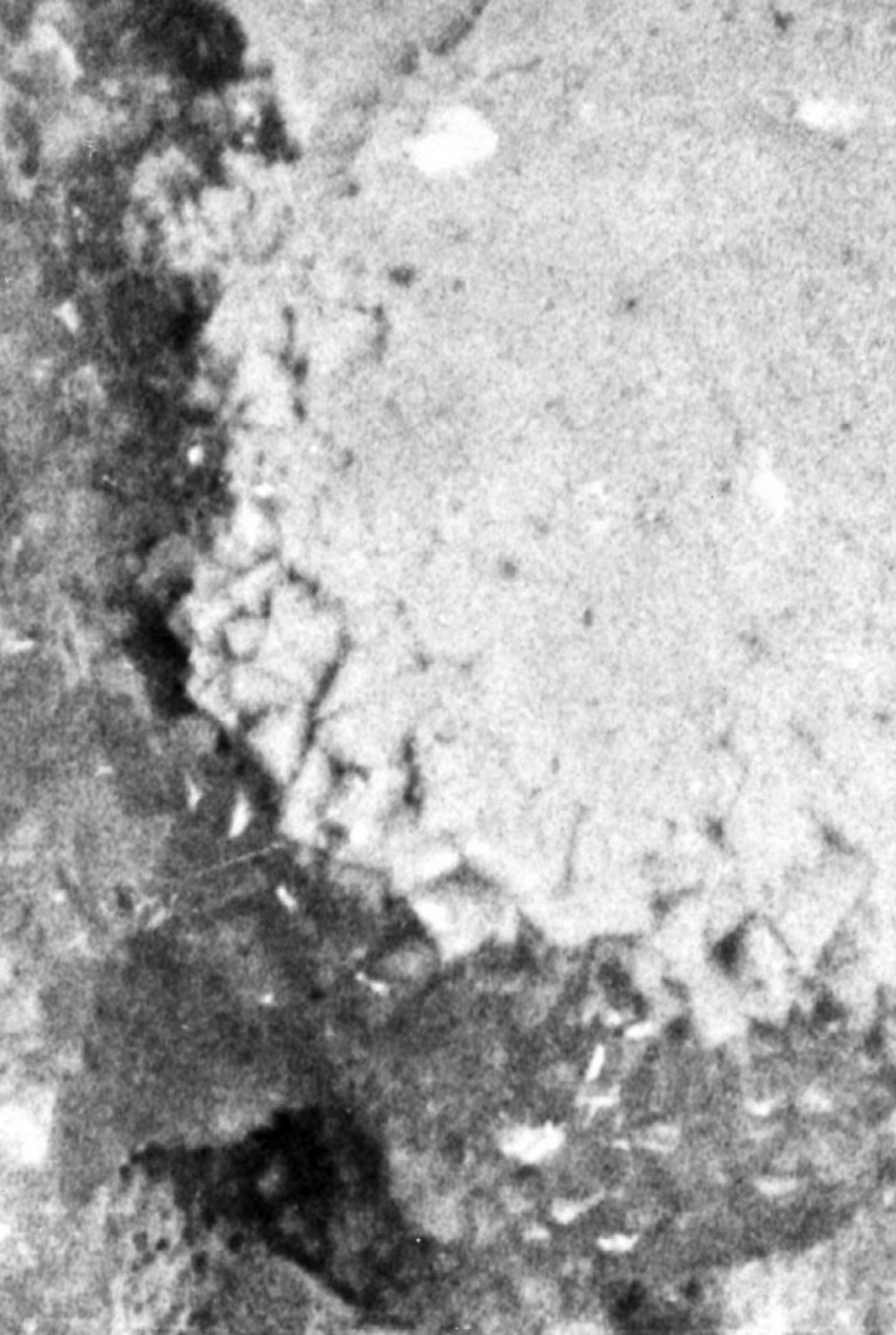
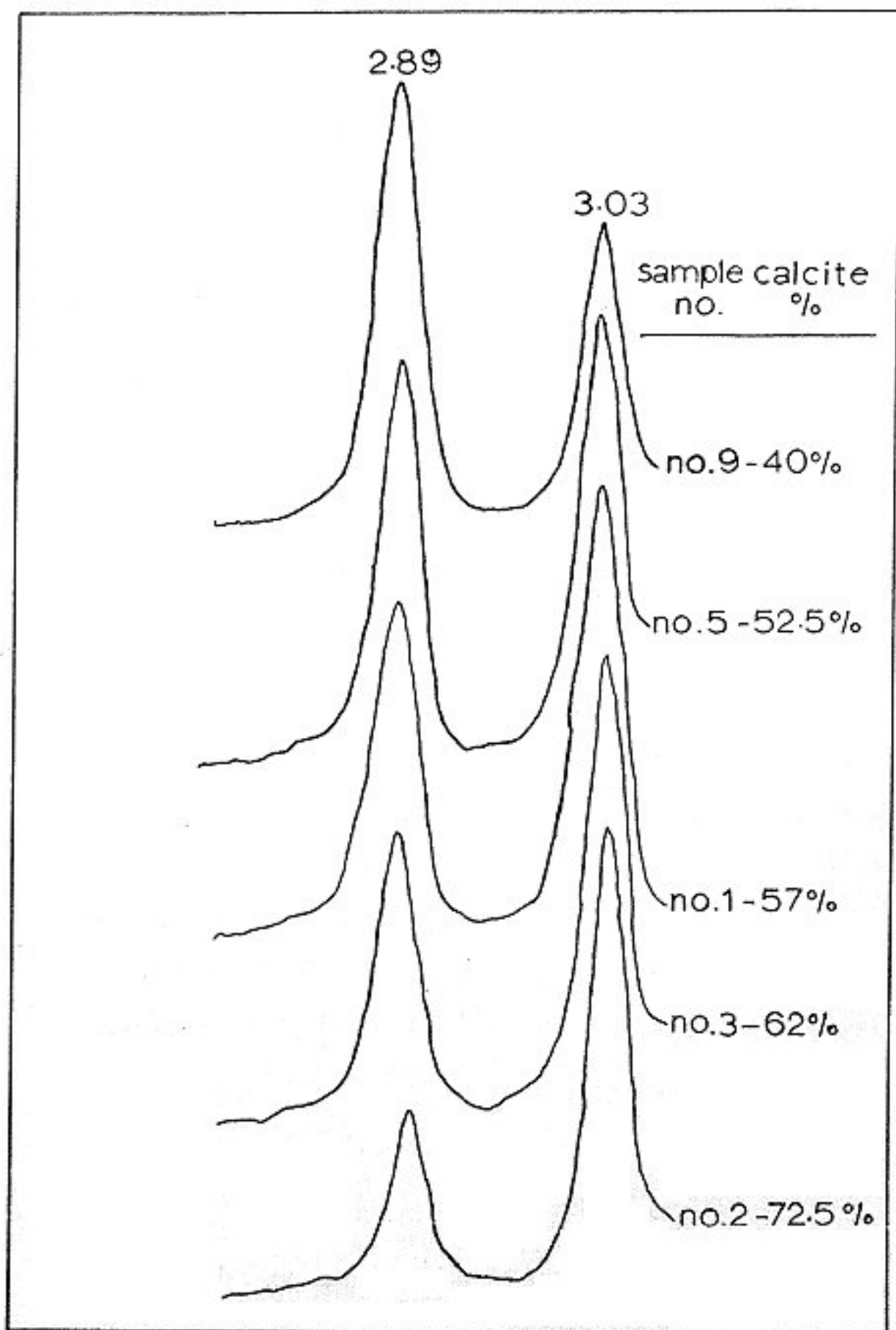




Figure 23. X-ray patterns of several calcareous nodules showing relative peak height of dolomite ($2.89\text{\AA}$) and calcite ($3.03\text{\AA}$). Percentage calcite determined from these patterns (by use of Fig. 5) is listed for each pattern. Sample number represents Station number.



similar to the ones in the Avon Park beds. A minor point of dissimilarity is the lack of distinguishing surface features on the Inglis nodules.

Age of Nodules

The age of the dolomitic concretions varies. Many appear to be growing at present at the water table, as evidenced by downward elongation, with pure, sharply-terminated calcite crystals protruding from the bottom. Other nodules appear to have been arrested in their growth and rounded crystal terminations suggest that some solution has occurred. These observations indicate that several stages of nodule growth occur within the sections at the Barge Canal. The estimated earliest time of initial nodule formation would be sometime after the deposition of the Pleistocene Pamlico sands, approximately 130,000 years ago. A single Carbon-14 age determination was made by Shell Development Company upon some clear calcite from one nodule (Fig. 20b), and its age was determined to be $4,540 \pm 170$ years (Dr. Paul Enos, personal communication, dated October 17, 1968), thus indicating nodule growth continued into the Recent Epoch.

Mineralogy of Nodules

Percentages of calcite and dolomite were measured by the standard x-ray peak height comparison method (described

by Griffin, 1969) (Fig. 4). Data are listed in Figure 23. It was found that the nodules are enriched in calcite with respect to the dolomite host rock (Fig. 24). The nodular calcite ranges from 2.0 to 6.0 mole percent MgCO_3 (Figs. 6a, 6b, and 25).

IMPLICATIONS ON POROSITY

The formation of nodules and ledges of calcite cement in the Avon Park Formation and the removal of calcite from the Inglis beds have distinct and specific effects upon porosity in the study area. Pore space is an essential quality to be looked for when one is in search of occurrences of valuable natural resources, such as minerals, petroleum, or water. Porosity must exist in rocks for these natural resources to occur and especially if they are to be easily extracted. The effects on porosity observed at the Barge Canal, created mostly by organically acid waters percolating from the Pleistocene sands, are fairly easily seen and understood.

Extra pore space is created in the Inglis Formation by leaching, whereas nearly all pore space is filled in areas of calcite cementation within the Avon Park Formation. With an original porosity of thirty to perhaps fifty percent, the Avon Park beds would make ideal reservoir rocks. However,

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Figure 24. X-ray patterns showing comparison of calcareous nodule and host rock at Station 15. Note complete absence of calcite in host rock.

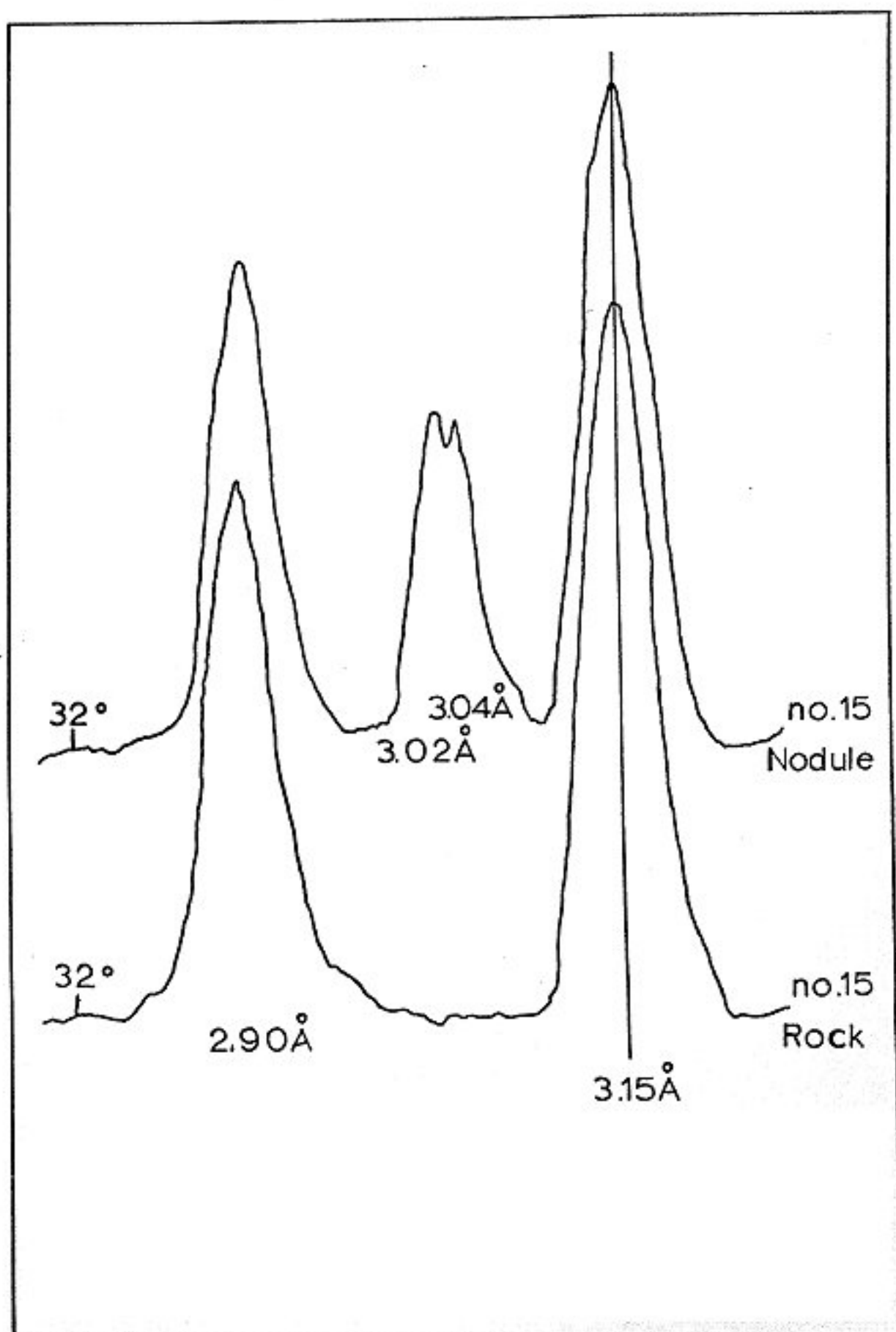
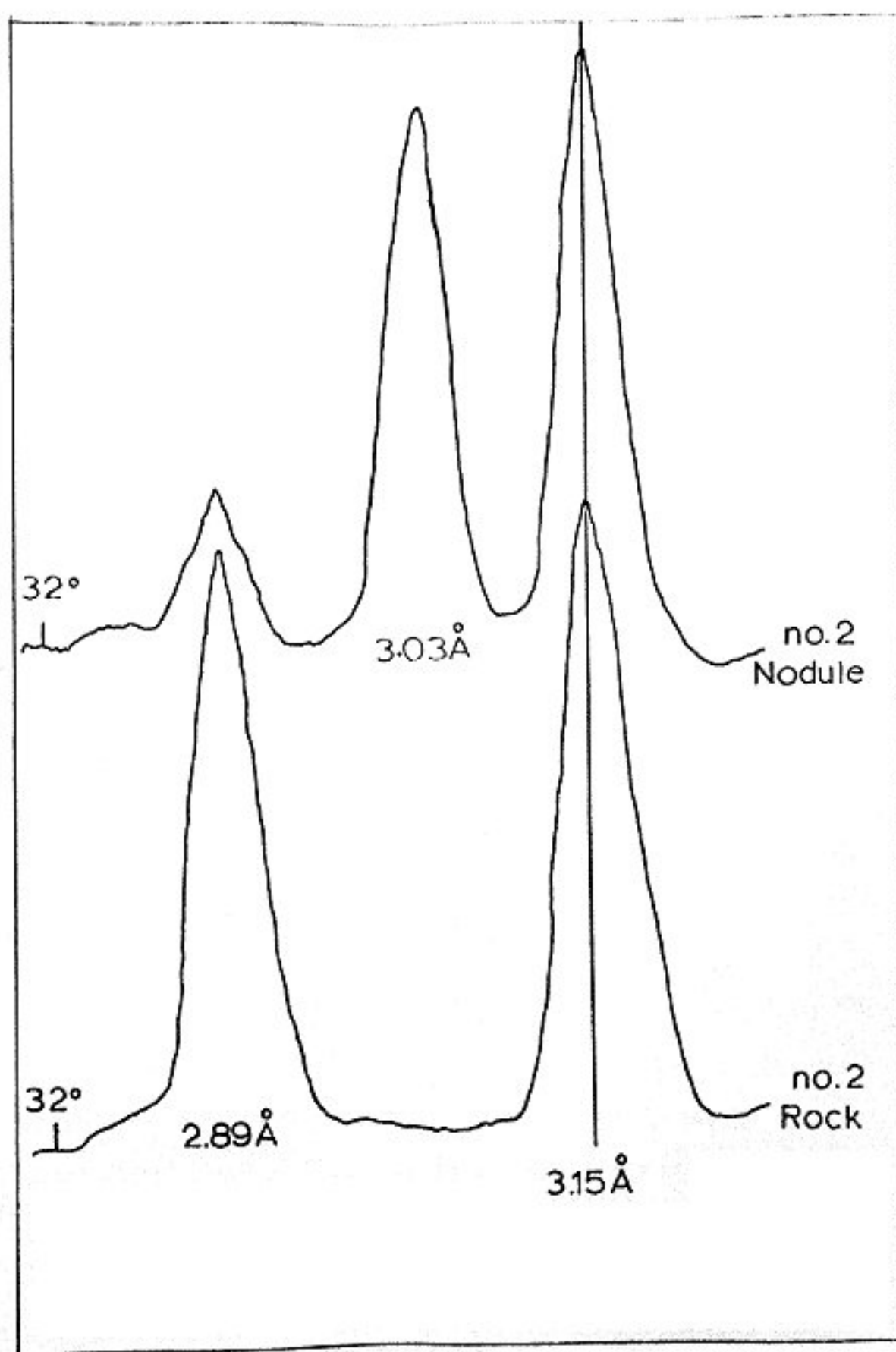


Figure 25. X-ray patterns showing comparison of calcareous nodule and host rock at Station 2. Note complete absence of calcite in host rock.



after cementation with calcite, the porosity is reduced to nearly zero.

If it can be assumed that calcite is filling the pores of the Avon Park rock, then it could be expected that a direct relationship between calcite percentage and porosity decline would be indicated in the Avon Park Formation; however, this was not found (Fig. 26). The reason for lack of correlation is not known, but may be related to the relatively crude point count porosity measurements (Table I), as compared with the more accurate calcite percentage determination by x-ray techniques (Fig. 15). The unconsolidated nature of the Avon Park host rock within this area made it necessary to vacuum impregnate samples therefrom with polyester resin prior to thin sectioning. The resulting sections were thicker than optimum. Counts from these sections gave an apparent porosity near 50 percent, which may well be in error.

If one were able to recognize sections similar to those of the Barge Canal within the geologic record, geologic interpretation of porosity distribution and economic estimations would, perhaps, be facilitated.

CONCLUSIONS

These unusual nodules of calcite and dolomite are

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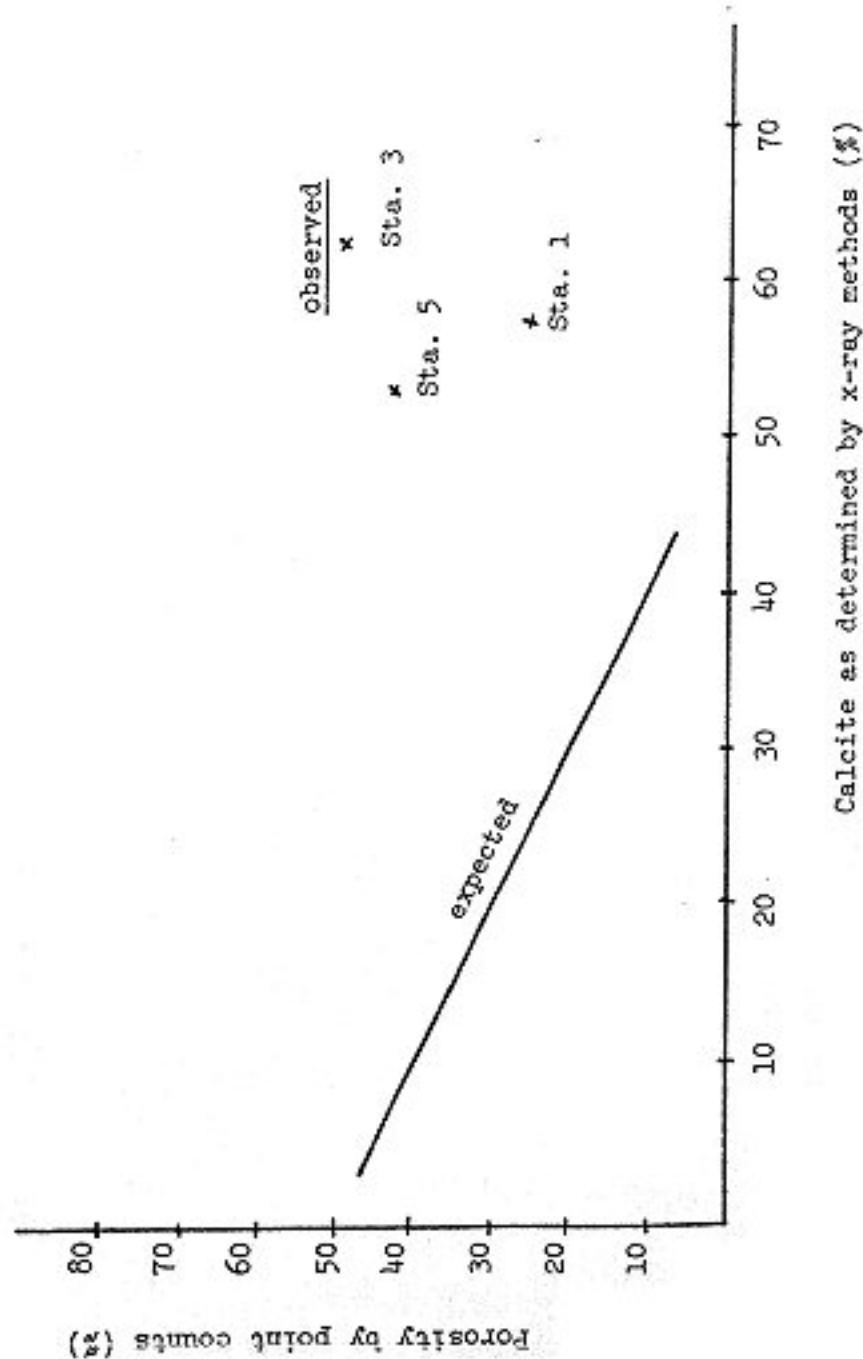
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CONCLUSIONS

These unusual nodules of calcite and dolomite are

Figure 26. Plot of expected and observed relationship between porosity as determined by point count and calcite percentage as determined by x-ray techniques. Note divergence in expected and observed values.



probably forming at present in much the same way as they have in the recent geologic past. Percolating surface waters moving downward through acid-producing, organic-rich sands, dissolution of calcium carbonate from the underlying Inglis Formation and precipitation of calcite at the water table in the Avon Park Dolomite is the method in which these nodules appear to have originated. They increase in size by addition of calcite to the apexes of scalenohedrons, forming concentric rings during intermittent growth stages. Where permeability is good, conditions for epigenetic precipitation are favorable; and the nodules tend to grow together in blocks and ledges separated by nodule-barren areas.

The mechanisms which produce these calcite-cemented nodules therefore bring about marked effects upon porosity.

REFERENCES CITED

- Adams, J. E., and Rhodes, M. L., 1960, Dolomitization by seepage refluxion: Am. Assoc. Petroleum Geologists Bull., v. 44, p. 1912-1920.
- Barbour, E. H., 1901, Sand crystals and their relation to certain concretionary forms: Geol. Soc. American Bull., v. 12, p. 165-172.
- Brooks, H. K., 1968, Late Cenozoic stratigraphy of southern Florida, a reappraisal, Second Annual Field Trip, Miami Geological Society Pub., p. 38.
- Carlisle, V. W., and Caldwell, R. E., 1964, A laboratory manual for introductory soil science: J. S. Swift Co., Inc., St. Louis, Missouri, p. 53.
- Chave, K. E., 1952, A solid solution between calcite and dolomite: Jour. Geology, v. 60, p. 190-191.
- Clifton, H. E., 1957, The carbonate concretions of the Ohio Shale: Ohio Jour. Science, v. 57 p. 114-124.
- Cooke, C. W., 1942, Cenozoic echinoids of eastern United States: Jour. Paleontology, v. 16, p. 1-61.
- Daly, R. A., 1900, Calcareous concretions of Kettle Point, Lambton Co., Ontario: Jour. Geology, v. 8, p. 135-150.
- Deffeyes, K. S., Lucia, F. J., and Weyl, P. K., 1965, Dolomitization of Recent and Pleistocene sediments by marine evaporite waters on Bonaire, Netherlands Antilles: in Dolomitization and Limestone Diagenesis, A symposium (Pray, L. C. and Murray, R. C., editors), Soc. Econ. Paleontologists and Mineralogists, Spec. Publ. No. 13, p. 71-88.
- Dunham, R. J., 1962, Classification of carbonate rocks according to depositional textures: in Classification of Carbonate Rocks, A Symposium, (Ham, W. E., editor), Am. Assoc. Petroleum Geologists, Memoir 1, p. 108-121.

- _____, 1969, Vadose pisolite in the Capitan Reef (Permian), New Mexico and Texas: in Depositional Environments in Carbonate Rocks, A Symposium, (Friedman, G. M., editor), Soc. Econ. Paleontologists and Mineralogists, Spec. Publ. No. 14, p. 182-191.
- Friedman, G. M., 1959, Identification of carbonate minerals by staining methods: Jour. Sedimentary Petrology, v. 29. p. 87-97.
- Garrels, R. M. and Christ, C. L., 1965, Solution, Minerals, and Equilibria: Harper and Row Publishers, New York p. 90-106.
- Gee, H. Moberg, E. G., Breenberg, D. M., and Revelle, R., 1932, Calcium equilibrium in sea water: Scripps Inst. Oceanography Bull., Univ. Calif., Tech. Series, v. 3, p. 145-190.
- Ginsburg, R. N., 1957, Early diagenesis and lithification of shallow-water carbonate sediments in south Florida: in Regional Aspects of Carbonate Deposition, (Le Blanc, R. J., and Breeding, J. G., editors), Soc. Econ. Paleontologists and Mineralogists, Spec. Publ. No. 5, p. 80-99.
- _____, 1964, South Florida carbonate sediments: Guidebook for Field Trip No. 1, Geol. Soc. America, Annual Convention, Miami Beach, Florida, p. 19-20.
- Griffin, G. M., 1969, Geological interpretation of x-ray diffraction data: Chap. 22 in Procedures in Sedimentary Petrology, A Symposium, (Carver, R. E., editor), John Wiley and Sons. (in press).
- Holmes, A., 1965, Principles of Physical Geology, Ronald Press Company, New York, p. 129-131.
- Illing, L. V., 1954, Bahaman calcareous sands: Am. Assoc. Petroleum Geologists Bull., v. 38, p. 1-95.
- Illing, L. V., Wells, A. J., and Taylor, J. C. M., 1965, Penecontemporary dolomite in the Persian Gulf: in Dolomitization and Limestone Diagenesis, A Symposium, (Pray, L. C. and Murray, R. C., editors), Soc. Econ. Paleontologists and Mineralogists, Spec. Publ. No. 13, p. 89-111.

- Krumbein, W. C. and Garrels, R. M., 1952, Origin and classification of chemical sediments in terms of pH and oxidation-reduction potentials: Jour. Geology, v. 60, p. 1-33.
- Lowman, S. W., 1949, Sedimentary facies in the Gulf Coast: Am. Assoc. Petroleum Geologists Bull., v. 33, p. 1939-1964.
- Mathias, H. E., 1931, Calcareous sandstone concretions in the Fox Hills Formation, Colorado: Am. Jour. Science, Ser. 5, v. 22, No. 130, p. 354-359.
- Morgan, J. P., and Treadwell, R. C., 1954, Cemented sandstone slabs of the Chandeleur Islands, Louisiana: Jour. Sedimentary Petrology, v. 24, p. 71-75.
- Osman, J. K., Carpenter, J. R., and Windom, H. L., 1965, Th²³⁰/U²³⁴ age of the Pleistocene corals and oolites of Florida: Jour. Geophysical Research, v. 70, p. 1843-1847.
- Puri, H. S., and Vernon, R. O., 1964, Summary of the geology of Florida and a guidebook to classic exposures: Fla. Geol. Survey Spec. Publ. No. 5, p. 52-64.
- Shinn, E. A., Ginsburg, R. N., and Lloyd R. M., 1965, Recent supratidal dolomite from Andros Island, Bahamas: in Dolomitization and Limestone Diagenesis, A Symposium, (Pray, L. C. and Murray, R. C., editors), Soc. Econ. Paleontologists and Mineralogists, Spec. Publ. No. 13, p. 112-123.
- Spackman, W., Scholl, D. W., and Taft, W. H., 1964, Field guidebook to environments of coal formation in southern Florida: Geol. Soc. of America Pre-Convention field trip guidebook, p. 20-26.
- Tarr, W. A., 1935, Concretions in the Champlain Formations of the Connecticut River Valley: Geol. Soc. of America Bull., v. 46, p. 1493-1534.
- Todd, J. E., 1903, Concretions and their geologic effects: Geol. Soc. of America Bull., v. 14, p. 353-368.
- Vernon, R. O., 1951, Geology of Citrus and Levy Counties, Florida: Fla. Geol. Survey Bull., No. 33, 256 pp.