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CALCIUM CARBONATE PRECIPITATION IN THE CUEVA DI WATAPANA ON BONAIRE, NETHERLANDS ANTILLES

BY

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SUMMARY

Calcium carbonate precipitates as low Mg-calcite and aragonite in slightly brackish water in a cave in the Pleistocene Middle Terrace of southern Bonaire. The calcium carbonate precipitates at the atmosphere-water interface forming floating calcite scales (calcite ice). Aragonite crystals frequently link the calcite scales together. The juxtaposition of calcite and aragonite is explained by calcite precipitation at the water-surface in nearly fresh water, with low Mg/Ca ratio, followed by the formation of aragonite near the bottom of the pool in more saline water with higher Mg/Ca ratio. The saline water with a higher magnesium content is most likely Caribbean sea water working its way inland through underground fissures.

INTRODUCTION

In the Pleistocene Middle Terrace of southern Bonaire (Netherlands Antilles) several sinkholes and caves have been formed. Two caves, Cueva di Watapana and Pos Calbas (Fig. 1) have been visited briefly by the author and dr. P. Wagenaar Hummelinck in 1970. Purpose of this visit were pools of stagnant water in the Cueva di Watapana (Fig. 2) in which little scales composed of calcite are floating on the water.

Cueva di Watapana was mentioned and described by Wagenaar Hummelinck in 1940 and 1943. This cave is formed in the Pleistocene Middle Terrace which lies here 5–8 m above sea-level. Pos Calbas lies about 300 m north of Cueva di Watapana. It was visited en route and will only be mentioned briefly. A sketch map of the Cueva di Watapana (Fig. 2) was published by Wagenaar Hummelinck in 1943. It shows a cave with a length of about 80 m whose entrance is almost blocked by limestone rubble from the overlying coral limestone. Inside the cave are small pools with stagnant water. During the author's visit in March 1970 only two pools, at the very end of the cave were filled. The atmosphere inside the cave was very damp, and the cave proved to serve as a hiding place to numerous bats. Along one side of the cave the floor is covered by blocks of limestone fallen from the ceiling, the rest of the cave floor is covered by a laminated carbonate sediment. Travertine is being formed on some places in the deeper parts of the cave (Wagenaar Hummelinck, 1943). Wagenaar Hummelinck (1940, vol. II, p. 9) gives the following description of the pools:

Approximate size	5×3×1 m
Movement of water	stagnant
Permanency	permanent
Origin	natural
Soil in neighbourhood	coral limestone
Bottom	rocks and crystals
Vegetation	none (too dark)
Turbidity	clear
Colour	colourless
Temperature	30°C
pH	7.4–7.6

Tiny aggregates of calcite crystals could be observed floating on the water-surface. Such aggregates are generally called floating calcite scales, or calcite ice. The bottoms of the two pools which were filled with water during the author's visit, as well as their immediate surroundings, are covered with semiconsolidated calcite scales, several of which were cemented together into lumps by tiny aragonite crystals.

OBSERVATIONS

The composition of the water

Water samples were taken from two pools in the back of the cave. The samples, one of each pool, were taken by simply pushing an open polyethylene bottle under the water surface and closing it when it was full. The samples can only be considered representative for the upper part of the waterbodies in the pools. These samples were analyzed at home for their chlorine, calcium and magnesium contents. The results are presented in a table and compared with normal Caribbean sea water sampled on the southeastern side of Bonaire.

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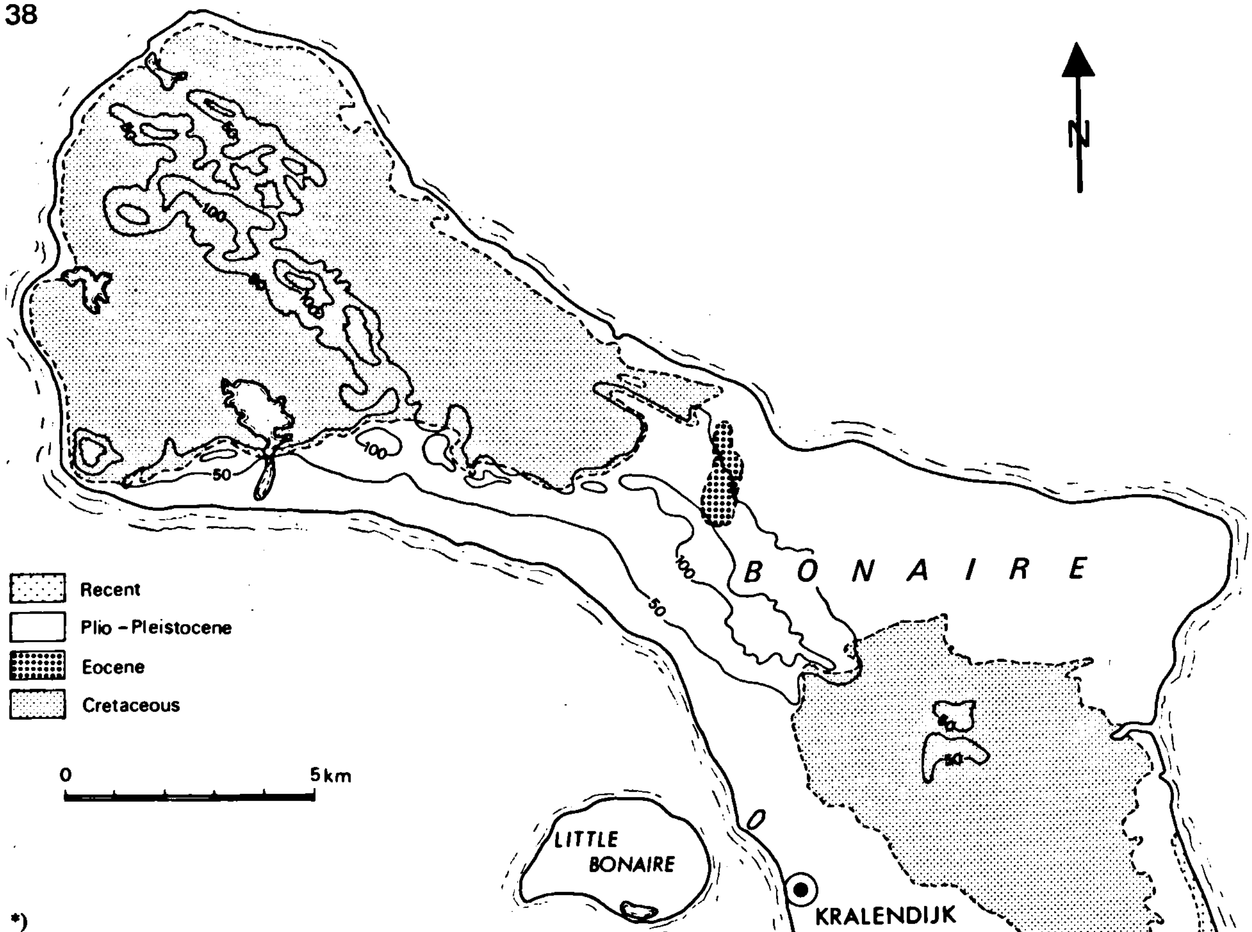
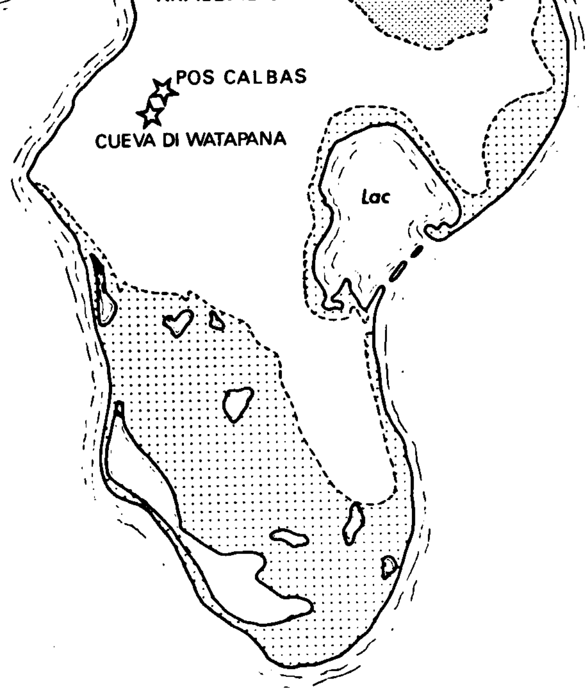

Fig. 1. Sketch map of Bonaire with the locations of the Cueva di Watapana and Pos Calbas.

*)

	Pool 1		Pool 2		Caribbean sea water	
	ppm	mmol/l	ppm	mmol/l	ppm	mmol/l
Ca	117 126	2.93 3.15	109 123	2.73 3.08	562	14.02
Mg	75 83	3.03 3.36	73 81	3.— 3.31	1393	57.11
Cl		34.5		34.5		580
Mg/-Ca	1.05		1.09		4.07	

*) The Sr-concentrations for pools 1 and 2 are 0.44×10^{-2} and 0.56×10^{-2} mmol/l.

The pH of the water samples could not be measured on the spot since a pH-meter was not at hand. The pH measured in the laboratory was 7.9 which is close to the value reported by Wagenaar Hummelinck (1940).

The floating calcite scales

These are crystal aggregates of variable size and thickness. In their simplest form the scales consist of a thin, delicate slightly saucer-shaped layer of calcite crystals (Photo 1b). Their size lies in the order of 3 mm and their thickness is about 100 mu. They are composed of a single layer of calcite crystals. Closer examination under a binocular microscope and with a scanning electron microscope reveals the following characteristics:

1. The scales have a somewhat saucerlike shape due to the fact that the rim of the scales curves slightly upward (Photo 1b).
2. The concave side of the scales has a glossy, polished, appearance when looked at through a binocular microscope (Photo 1b). When that side is studied in a scanning electron microscope the crystal surfaces appear to be corroded and somewhat pitted on that side (Photos 2 & 3). The crystals have also a zonar structure (Photo 2).
3. Near the rim of the scales the crystals seem to grow outward (Photo 1b). In the central part of the scales, the crystals are generally oriented normal to the scale.
4. On the convex side of the scales the individual crystals show no signs of corrosion (Photo 4).

Roentgen diffractograms of these scales revealed that they consist mainly of almost pure calcite with a minor amount of magnesium. The chemical analysis made of the scales showed that they contain approximately 5 percent $MgCO_3$. The calcite scales sampled from the bottom of the pools were often linked together at random to form larger aggregates. The cementing agent turned out to be aragonite (Photos 1a, 5 & 6) which occurs as clusters of radiating, 100–300 mu long, needle-like crystals: aragonite-anthodites (Photo 7).

The sediment on the cave floor
This is a brittle, slightly consolidated carbonate sediment. It consists of parallel laminae of microcrystalline calcite with abundant fragments of calcite scales (Photos 8 & 9) and a few scattered remnants of aragonite-anthodites. The thickness of the laminae varies from 2 to 5 mm. The sawcut of a handspecimen reveals very pale orange (10 YR 8/2) bands of carbonate sediment alternating with much thinner light brown (5 YR 6/4) layers (Photo 8). The surface of the sediment also has this light brown colour.

INTERPRETATION OF THE DATA

The presence of floating calcite scales suggests that the water in the pools is supersaturated with calcium carbonate. An interesting feature is that both calcite and aragonite are present in the sediment collected from the bottom of the pools. Calcite is known to precipitate from fresh water, while aragonite, although unstable under normal atmospheric conditions, precipitates from sea water. This is generally accepted to be caused by the high magnesium concentration in sea water.

Lippmann (1973) studied the precipitation of $CaCO_3$ from homogeneous solutions at 20°C in the presence of varying amounts of magnesium. He came to the conclusion that "...A ratio Mg/Ca between 3 and 4 appeared to be sufficient for the complete suppression of calcite..." (Lippmann, 1973, p. 110). Solutions with a Mg/Ca ratio higher than 3 or 4 yielded aragonite. According to Folk (1974) the formation of aragonite can take place in waters with a Mg/Ca ratio of over 2:1.

This leads to the assumption that the Mg/Ca ratio in the pools, being 1.05 at the time of sampling might show seasonal variations. It is possible that the near-surface

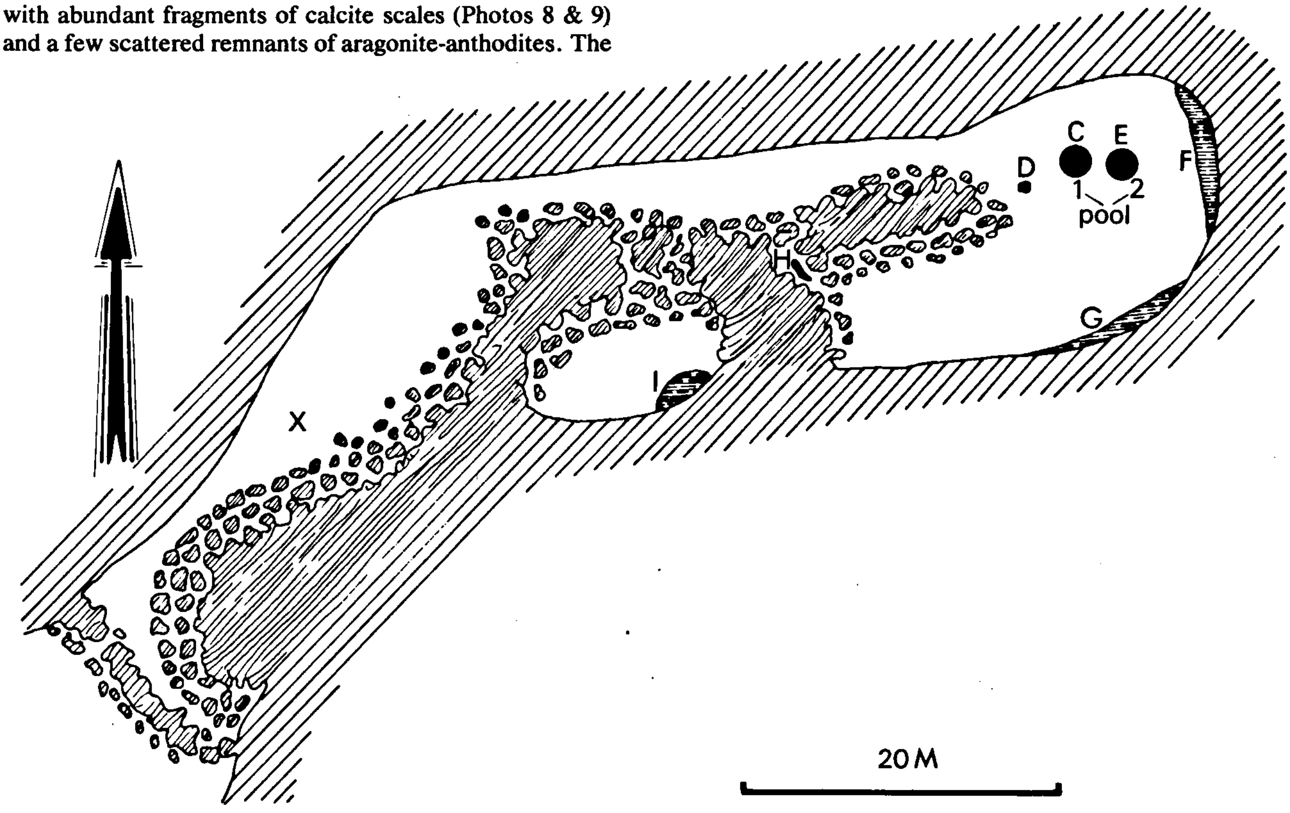

Fig. 2. Sketch map of the Cueva di Watapana. On locations C, D, E, F, G, H and I, Wagenaar Hummelinck (1943) observed pools with floating calcite scales. During the author's visit in 1970 only pool C (= pool 1 in this paper) and pool E (= pool 2 in this paper) contained water. Cross (×) indicates the location of the laminated carbonate sediment described in this article. After Wagenaar Hummelinck (1943).

water in the pools is fresh water which floats on deeper lying saline water with a higher Mg/Ca ratio.

During the wet season, from October to January, significant amounts of meteoric water will flow down through fissures in the limestone. This fresh water will be overlying denser brackish water which owes its salinity, and a high Mg/Ca ratio, to sea water from the nearby Caribbean Sea which reaches the area via underground fissures. The water in the pools will therefore be layered. In Pos Calbas, Wagenaar Hummelinck (1940, p. 9) observed that the water table in a pool fluctuated with the tide.

Meteoric water will reach the pools by passing through several meters of overlying Pleistocene limestone which is covered by underbrush. The water will pick up CO_2 in the thin top soil and dissolve some calcium carbonate in the limestone. This solution will enter the cave. Once in the cave and in contact with the atmosphere the water will loose excess CO_2 (Weyl, 1970). The loss of CO_2 from the solution will result in supersaturation in calcium carbonate which precipitates as travertine along the walls of the cave or as crystals floating on the water-surface of the pools. Since the upper part of the water in the pools is fresh water, which has a low Mg/Ca ratio, calcite is being formed.

The floating calcite crystals will form scales (see below) which eventually become too heavy to be kept afloat by surface tension and sink downward. At the bottom of the pool they arrive in water which came in from the Caribbean Sea and which has a much higher Mg/Ca ratio. Here aragonite crystals will form and link the calcite scales, randomly oriented on the bottom, together. During an appreciable influx of fresh water its lower boundary will move downward. When it reaches the aragonite crystals, corrosion of the crystals (Photo 10) may occur.

The next point to consider are the characteristics of the calcite scales. The tiny crystals floating at the water-surface can only accrete downward or sideways. Gradual accretion sideways and on the bottom side of a scale increases its weight and pulls it slightly down into the solution. Meanwhile crystal growth continues at the rim of the scale. This will lead eventually to the slightly saucer-like shape of the crystals since the rim of the scale will be slightly higher than its center. This process is somewhat similar to the formation of salthoppers as suggested by Dellwig (1955).

While the scale is growing on the water-surface of the pool, its upper, concave, side is in contact with the damp, poorly circulated air in the cave. This damp air contains CO_2 which will not only be present in the air but also in the very small water droplets in the air and in thin water films covering the top of the scales. In this film HCO_3^- and CO_3^{2-} ions will be present which corrode the tiny calcite crystals on the upper side of the calcite scales.

Visible clouds, from which no precipitation takes place, usually contain water droplets with a diameter of about 5 mu and a concentration of about 200 per cubic cm. The pits observed on the concave side of some scales have a diameter of about 20 mu and could have been formed by a number of water droplets settling on the scale's surface.

During movements of an extreme supply of meteoric water into the cave the pools probably expand in size. Wagenaar Hummelinck noticed six pools in the Cueva di Watapana. During the author's visit in 1970 there were only two pools filled with water. The presence of a laminated carbonate sediment containing fragmented calcite scales near the entrance of the cave points at a periodic flooding of most of the cave's floor. It indicates some transportation of the calcite scales from the area where they are almost constantly produced to the incidentally flooded parts.

ACKNOWLEDGEMENTS

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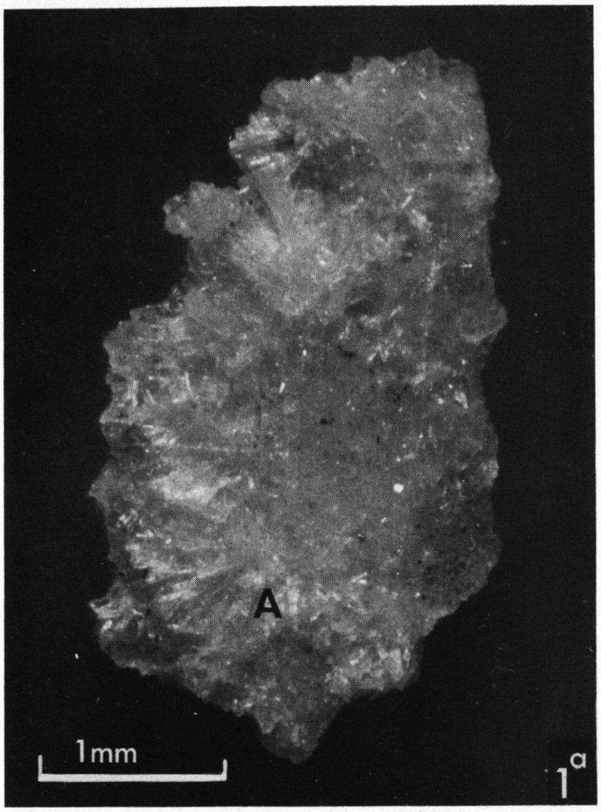
PHOTOGRAPHS

Photo 1a. Clusters of needle-like aragonite crystals (A) on a calcite scale.

Photo 1b. Small calcite scale showing radial-grown calcite crystals at the rim and a smoothly polished concave center (C).

Photo 2. Corroded zonar calcite crystals on the upper; concave side of a calcite scale. S.E.M.-photo 854/23, enlargement 2500 times.

Photo 3. Corroded calcite crystals on the pitted (?) upper, concave side of a calcite scale, S.E.M.-photo 855/17, enlargement 2600 times.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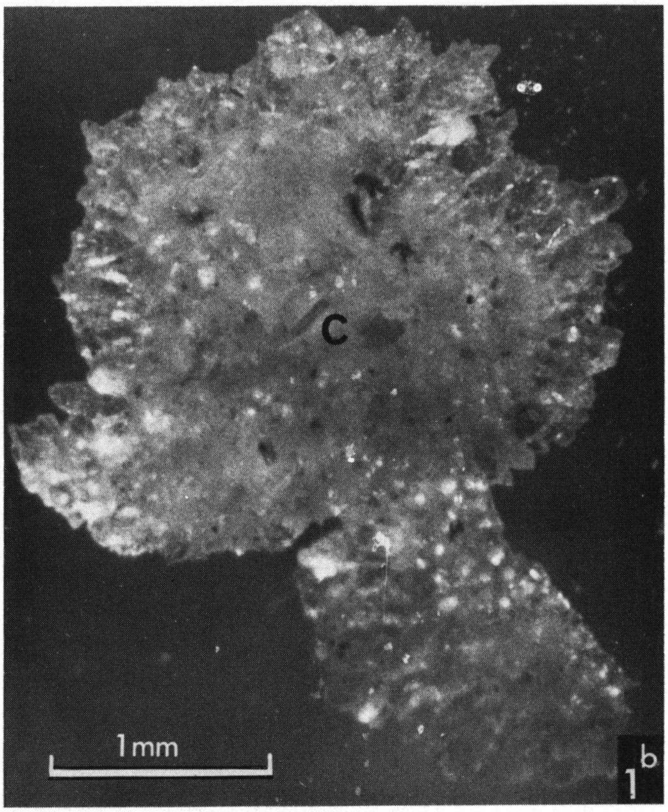
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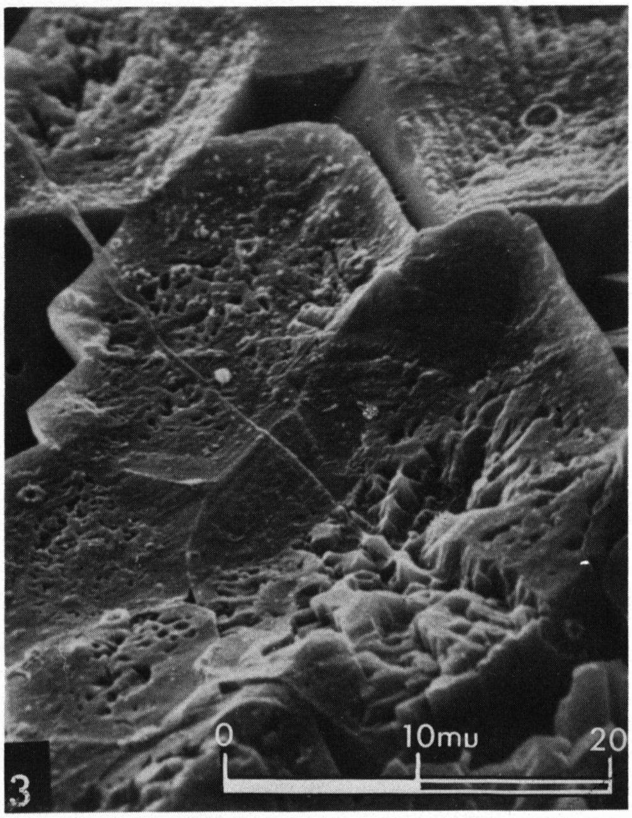
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Photo 4. Calcite crystals on the lower convex side of a calcite scale. S.E.M.-photo 854/29, enlargement 1650 times.

Photo 5. Calcite scales laterally joined together by fibrous aragonite crystals. S.E.M.-photo 855/12, enlargement 25 times.

Photo 6. Radiating bundles of fibrous aragonite crystals (aragonite-anthodites) between two calcite scales. S.E.M.-photo 855/16. Enlargement 140 times.

Photo 7. Radiating fibrous aragonite needles (aragonite-anthodite). S.E.M.-photo 862/21, enlargement 64 times.


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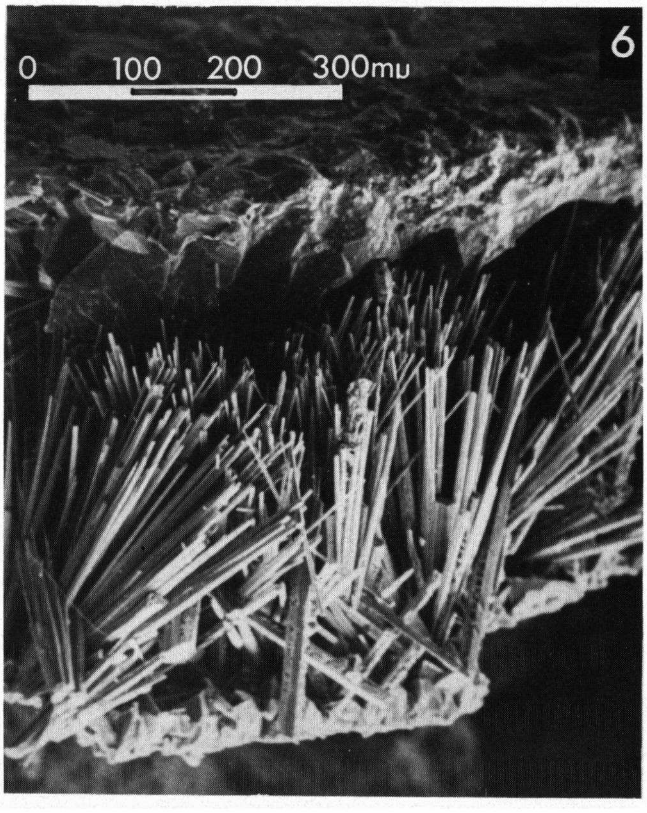
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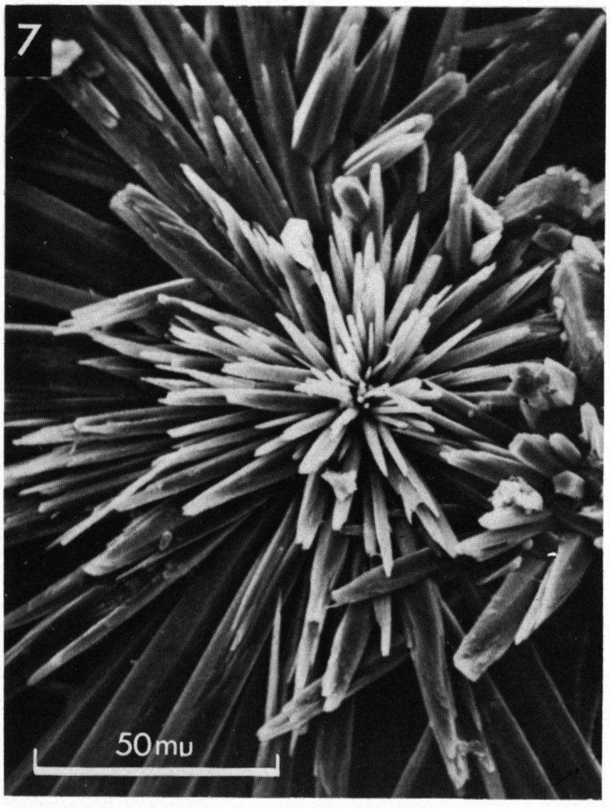
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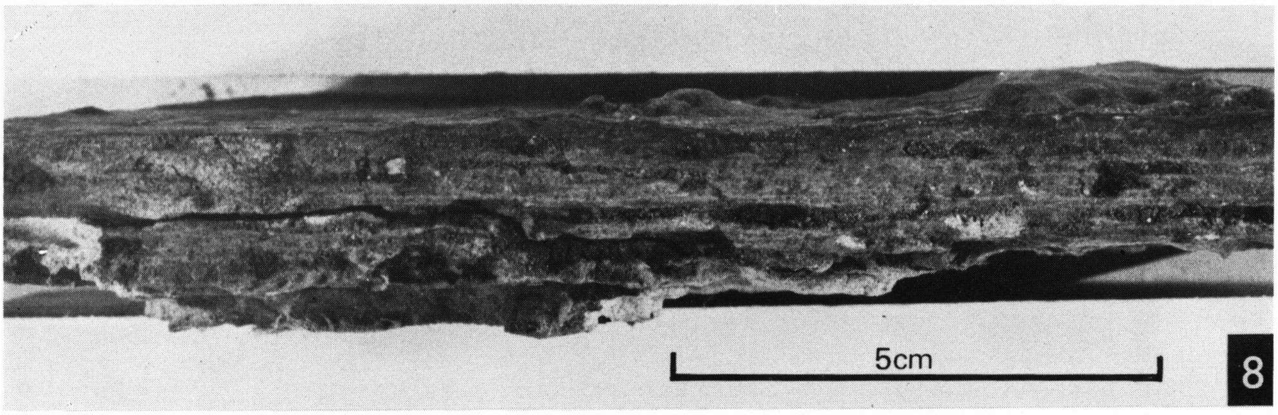
Photo 8. Handspecimen of the laminated carbonate sediment occurring on the cave's floor near the entrance of the Cueva di Watapana.

Photo 9. Thin section of the laminated carbonate sediment shown on photo 8. The arrows on the photo point at the flat upper surface of the scales. Enlargement 28 times.

Photo 10. Corroded aragonite crystals occurring between the calcite scales in the pools of the Cueva di Watapana. S.E.M.-photo 862/25, enlargement 1450 times.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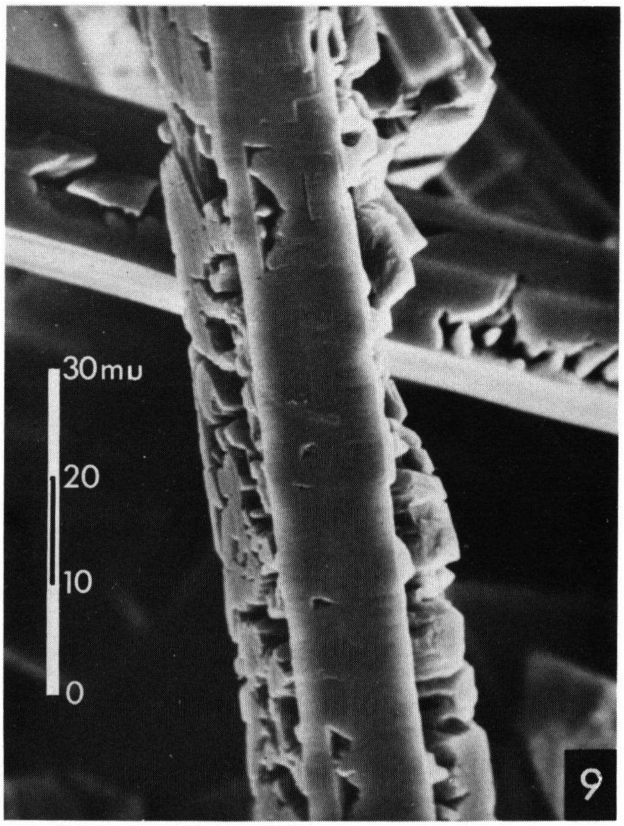
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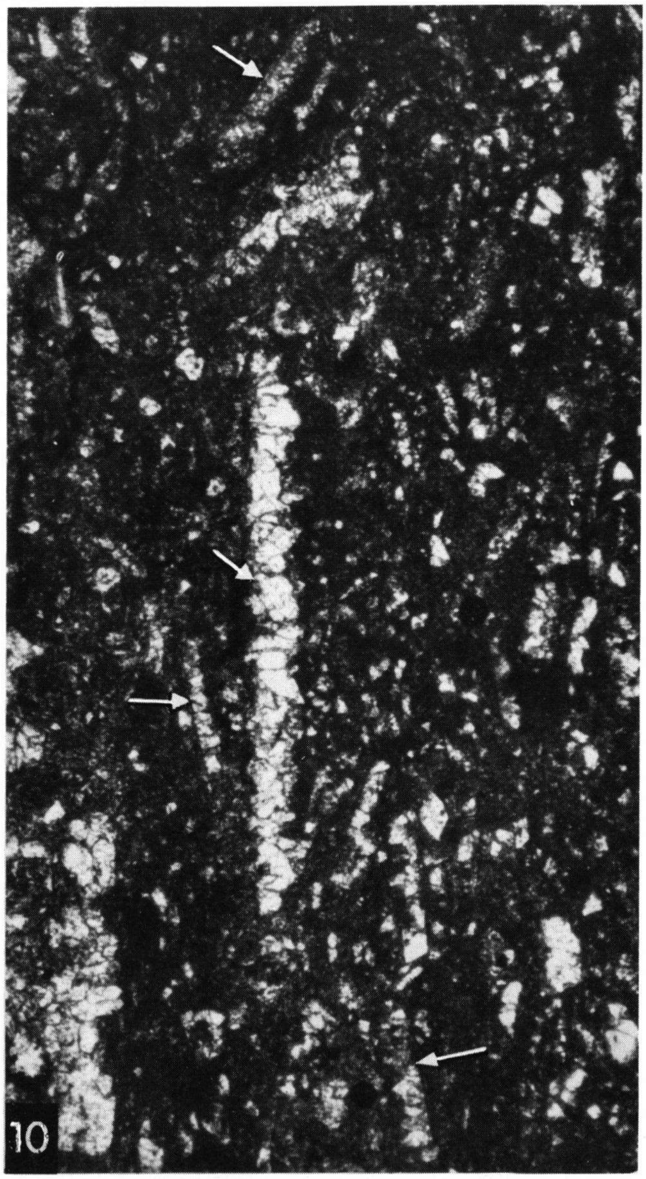
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