THE MINERAL CONTENT OF SOME CALCIUM CARBONATE DEPOSITING MARINE ORGANISMS

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DEPOSITION OF CARBONATES

BARAKAT

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AN ABSTRACT OF THE THESIS OF

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Title: The Mineral content of Some Calcium Carbonate-Depositing Marine Organisms.

This study is conducted to determine the mineral content of some calcium carbonate-depositing marine organisms and to establish correlations between this content and that of the sea-water. The mineral content of the organisms collected here, and determined spectroscopically and gravimetrically, is higher than that of organisms collected from the Pacific coast of North America. This is due to the higher salinity and temperature in this area which have a direct effect on the rate of deposition. The average salinity between June and December of 1965 is 39.74‰, as determined by the Mohr titration of the chloride ion. This higher salinity is attributable to the nature of the area and to the construction of the High Dam over the Nile River which has reduced the amount of fresh water runoff.

The incorporation of any element in an organism is a function of both genetic and environmental factors. Some show a magnesium content higher than calcium although they are considered calcium carbonate depositing forms, and others show a low concentration of both calcium and magnesium thus suggesting that other elements are more abundant than calcium or magnesium.

The mineral content of some of the rocks of the terraces seems to be related to either plant or animal origin, but any definite or further conclusion needs to be supported by a complete analysis of the minerals that might be associated or deposited in these terraces.

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I. INTRODUCTION

The coast of the Republic of Lebanon reaches some 220 km. from the Nahr el-Kabir in the north to Ras Nakoura in the south. Limestone baserock headlands dominate a series of gravely and sandy bays. In addition to limestone features, calcareously cemented sandstone forms a reef which is frequently exposed as islands and at headlands (George et al. 1964). Some beaches are formed from gravel which is derived from sea cliffs or streams and other beaches are formed from sand derived from the local watershed, calcium carbonate depositing organisms, and sediments from the Nile River in order of decreasing importance.

Limestone and calcareous organisms are a prominant and dominant feature in many areas along the coast of Lebanon and particularly the American University of Beirut frontage. Consequently, a study dealing with the mineral content of these calcium carbonate-depositing organisms helps to elucidate the role these organisms play in their continuous building activity.

The characteristic features of the Eastern Mediterranean namely, a higher salinity because the rate of evaporation exceeds that of precipitation, the relatively higher temperatures, and the negligible freshening effects, may affect the organisms inhabiting it in a distinctive manner.

The purpose of this study is to determine the calcium, magnesium and strontium content of some local calcium carbonate-depositing marine organisms, and to compare the mineral content of these organisms with organisms from other seas in order to find if the existing conditions these organisms live under affect their mineral content in any appreciable manner. Analysis of the mineral content of the sea water was also done and possible correlations between the mineral content of the organisms and sea water are considered.

II. HISTORICAL REVIEW

The presence of strontium in sea water was first reported by Sonstadt (1870) who mistook the spectral lines of calcium and strontium for those of rubidium and cesium but later corrected the observational error. Dittmar (1884) detected the element spectroscopically in sea water and marine organisms. The first quantitative data on strontium was given by Desgrez and Meunier (1926) who reported 0.154 mg-atom/L for the waters of the English Channel. Thompson and Robinson (1932) cite the data of Thomas and Thompson who obtained a value of 0.145 mg-atom/Kg, calculated for 19‰ chlorinity for waters of the San Juan Channel in the State of Washington. Later results by Ramage (1933) showed 0.456-0.470 mg-atom/L. The above information was taken from Thompson and Chow (1955). Thompson and Chow (1955a), using an elaborate technique called "Internal Standards" report that strontium exists in the oceans in constant proportions to chlorinity as 0.0048 ± 0.0002, the lowest ratio was obtained for sea waters taken at 1000 m in the Pacific Ocean. Sverdrup, Johnson and Flemming (1942) report a value of 0.15 mg-atoms/L for 19‰ chlorinity, and Harvey (1963) as 0.04%.

Since the contamination of the Earth's surface with radioactive fallout, attention has been paid to the fate of the radioactive isotope of strontium in marine environments.

Studies were conducted to examine the horizontal and vertical mixing of the isotope in the sea in order to see the extent of its incorporation and its effect on marine organisms. Bowen and Sugihara (1956) discussed horizontal mixing of water masses in the north Atlantic on the basis of strontium-90 content of the surface and subsurface waters. Hiyama and Ichikawa (1957) reported the strontium-90 content of fishes and clams in the vicinity of Japan.

Concurrent with these studies, laboratory experiments on the uptake, accumulation, and loss of the isotope of strontium by marine organisms were carried out in connection with the problem of radioactive waste disposal in the sea. Rice (1956) studied the uptake of strontium-90 in planktonic algae, Spooner (1949) by seaweeds, and Boroughs et al. (1956) by marine fishes. The latter found that the marine fish Tilapia descriminates against strontium relative to calcium. Rosenthal (1957) showed that fresh water fishes do not descriminate between strontium and calcium and attributes this lack of descrimination to differences between fresh water and marine fishes in the absorption of the isotope by the gills, skin, and intestinal tract, rather than fundemantal alterations in the metabolism of mineral elements.

Elaborations on the factors that affect the incorporation of strontium and calcium were made by many workers in the field. In their extensive investigation, Thompson and Chow (1961) showed that organisms belonging to different

phyla, genera, or even species, had different strontium content. Different species sharing the same habitat, where conditions of salinity and temperature were the same, were found to have different strontium content. Specimens of the same species, on the other hand, living in different habitats where conditions of salinity and temperature were different had the same strontium content. They feel that the strontium incorporation is genetically determined. Kulp et al. (1952) state that the primary factor determining the Sr/Ca ratio in calcareous organisms is the ratio of these elements in sea water, which in turn is related to salinity. Odum (1951a) using artificial sea water of varying Sr/Ca ratio demonstrated that this ratio in the calcareous shell of Physa is directly related to that of the media.

Lowenstam (1954) whose work deals mainly with the mineralogic composition of calcium carbonate secreting organisms and the factors that affect the composition, relates the amount of strontium incorporated to the calcareous composition. He observed that specimens from different latitudes showed different mineralogic composition, although they belonged to the same species. Specimens collected from the tropical and subtropical regions showed aragonitic composition and had a high strontium content. Specimens of the same species living in higher latitudes showed calcitic deposition. In a habitat where there are wide fluctuations in temperature, such as the Bermuda Islands having temperature

ranges between 16 and 30 degrees C, specimens showed different mineralogic compositions where the specimens living under the high temperatures showed aragonitic composition. Harris (1963) supports this last hypothesis of the effect of environment on the organism in relation to strontium and other trace elements. In his study of trace elements in the marine alga Caulerpa racemosa, he says that the general distribution of trace elements in algae depends on the species, portion of structure analysed, and the time of collection. He also adds that laboratory studies on ionic equilibria between the alga and the surrounding media have demonstrated that certain elements are selectively absorbed by the algae as a result of special physiological functions such as metabolic control, carbon dioxide fixation, and the rate of photosynthesis.

If the Sr/Ca ratio in the organisms is environmentally controlled, then the Sr/Ca ratio in the organisms reflects the chemical composition of the water the organisms live in. Thus, the analysis of unaltered fossils could be used as a valid method of measuring the Sr/Ca ratio of ancient seas. Odum (1951b) after analysing some unaltered fossils concludes that the Sr/Ca ratio of ocean waters has been of the same order of magnitude since the Paleozoic, because the ratio of the fossils resembles that of the modern counterparts.

Works dealing with calcium and magnesium are covered in the discussion.

III. MATERIALS AND METHODS

1. Collection Technique:

Specimens were collected by skin diving or use of SCUBA gear, depending on depth. Some specimens were collected from the inshore drift for purposes of comparison with specimens of the same species living in the sea.

2. Preliminary Preparation of the Sample:

The sample was cleaned from adhering parasites and epiphytes, washed several times with fresh water, then crushed into small particles with an electric grinder. In the shellfish, only the shells were analysed. Crushed samples were dried at 104 degrees C for 24 hours, weighed, then heated to 350-400 degrees C to burn off the organic material, weighed again then heated in an electric oven to 1100-1200 degrees C for removal of carbon dioxide thus leaving only the mineral oxides.

3. Determination of Strontium:

The differential solubility of the hydroxides and sulfates of strontium, calcium and magnesium, made their separation possible. The mineral oxides were hydrolyzed to the corresponding hydroxides in carbon dioxide free water. This required three hours. The hydroxides of calcium and magnesium are slightly soluble in water whereas strontium hydroxide is more soluble as is seen from the following:

Gms dissolved in 1000 cc water at 20 degrees C	$Ca(OH)_2$	$Mg(OH)_2$	$Sr(OH)_2$
	1.65	0.01	35.64

The filtered sample contains, other than strontium hydroxide impurities of alkaline metals and a small amount of the hydroxides of calcium and magnesium. A concentrated solution of sulfuric acid (1 ml/15 gms of sample) is added to the filtrate and left ten hours to secure complete precipitation. The sulfates of calcium, magnesium and other alkaline metals go into solution while strontium sulfate precipitates because it is less soluble. Thus pure strontium sulfate can be seperated from the solution:

Gms dissolved in 1000 cc water at 20 degrees C	$CaSO_4$	$MgSO_4$	$SrSO_4$
	1.93	107.16	0.99

The white bar shaped crystals of strontium sulfate are collected on a filter paper (pore size of 0.80 micra), dessicated and weighed (Tsuchia 1948).

This method is quite feasible for the determination of strontium in calcareous organisms. However, photometric determinations are more accurate and easier to perform. This method was particularly followed for two main reasons; 1) the intention to seperate and isolate strontium in crystal form in order to determine the concentration of the radioactive isotope (strontium-90) in the organisms analysed. This could be done only if strontium was determined gravimetrically. 2) There was no possible access to any machine,

such as a flame photometer, through which more accurate determinations could be made.

4. Determination of Strontium-90:

The isolated strontium sulfate is weighed and transferred to a Geiger-Muller counter. Strontium-90 has a half-life of 20 years and decays into yttrium-90 which has a half-life of 60 hours. It takes 21 days to reach equilibrium after which yttrium will be decaying at the same rate as it is formed. In an equilibrium like this, one measures the Beta particles of yttrium-90 which is a direct measurement of the strontium-90 as the yttrium-90 is decaying as rapidly as it is being formed (Comer 1955).

Background radioactivity was measured for one month at an average of two hours daily, and average counts per minute calculated. The radioactivity of the strontium sulfate was measured after which the sample counts per minute were subtracted from average background counts per minute to determine the amount of radioactive strontium per sample.

5. Determination of Calcite or Aragonite:

Leitmeier and Feigel's test (Read 1962) was used for distinguishing calcite and aragonite. A solution of manganese sulfate (11.8 gms in 100 cc of distilled water) is prepared to which solid silver sulfate is added. It is then heated, cooled and filtered. One or two drops of 50%

sodium hydroxide is added and after two hours, the precipitate is filtered and the filtrate stored in an opaque bottle.

The powder or small slices of the sample are completely covered with the solution. Aragonite turns grey at once and finally black, whereas calcite turns only greyish after one hour. This is a reliable test to differentiate between fine intergrowths of the two minerals.

6. Determination of Calcium:

Calcium was determined by a Perkin-Elmer Atomic Absorption Spectrophotometer, Model 303. A stock solution of Calcium ions of 500 ppm is prepared by dissolving calcium carbonate in a minimal volume of hydrochloric acid and then diluting with distilled water. From this stock solution suitable aliquots are taken and diluted with distilled water to make standard solutions of .5, 1, 2, 3, and 4 ppm. The absorption is measured and a standard curve plotted. Determination of the absorption of the standards was made by following the operating conditions as stated in the manual.

To determine the calcium concentration of the samples, the sample is powdered, heated at 650 degrees C for ten hours, and cooled. 100 mgs are dissolved in the minimal volume of hydrochloric acid and then properly diluted with distilled water to bring them within the range of measurment of the machine. Additional dilutions are necessary

with samples having very high calcium content. The concentration of calcium in ppm is obtained by comparing with the standard curve and then converted to percentage. This is quite an accurate method for the determination of any element provided the proper cathode is available. Typical analyses show coefficients of variation of less than 1% of the amount present. Analyses of samples are fully as accurate as the standard samples used for calibration.

7. Determination of Magnesium:

Magnesium was also determined by the Perkin-Elmer Atomic Absorption Spectrophotometer Model 303 with the special cathode for magnesium. A stock solution of magnesium of 1000 ppm was prepared by dissolving magnesium powder (analytical grade) in the minimal amount of hydrochloric acid (analytical grade), and then diluting with distilled water. From this solution suitable aliquots are taken and diluted to make standard solutions of 0.125, 0.25, 0.50, and 0.75 ppm. The absorption of these standards was measured by following the operating conditions as stated in the manual and a graph plotted.

Determination of magnesium in the samples follows the same procedure as that for calcium.

8. Determination of Calcium and Magnesium in Sea Water:

The determination of both elements was done by using the Atomic Absorption Spectrophotometer. 1 ml. of

sea water was diluted with distilled water to bring it within the range of the machine and the concentration of each element found in the same way as for the organisms.

9. Determination of Salinity:

The salinity was determined by the standard Mohr titration of the chloride ion. Special Knudsen-type burettes and pipettes were used (Strickland and Parsons 1965). Conversion to salinity was made by using the Standard Hydrographical Tables (e. Knudsen 1959).

10. Identification:

The identification of the coralline algae was through personal communcation with Dr. J. Powell of the Biology Department of A.U.B., of the mollusks through personal communication with Dr. Rosewater and Mr. Erickson (check list of molluscs collected in Lebanon by Erickson and identified by Rosewater of the U.S. National Museum), and Riedl's (1963) Fauna und Flora der Adria.

IV. RESULTS AND DISCUSSION

Figure (1) shows the salinity, calcium and magnesium concentrations of 25 samples of sea water collected over a period of seven months from June to December of 1965. The average salinity for this period is 39.74 ppt. This value is quite high as compared with the average salinity of the same period of 1931 obtained by Dr. Liebman (1935) of the waters of Palestine who found a value of 36.95 ppt, and very close to the one obtained by George and Allen (unpublished data) for the same period of 1964 (39.39‰). This difference in the average salinity (as well as on monthly basis) might be attributable to the following reasons: 1) The building of the High Dam over the Nile River, which was a source of fresh water runoff. With the reduction of the fresh water runoff, the salinities are rising. 2) These 25 samples were stored in glass bottles which were not tightly closed nor filled to the top. Thus some evaporation might have taken place. In general, however, the Eastern Mediterranean has a higher salinity than other seas because the rate of evaporation exceeds that of precipitation, and also because fresh water runoff is low.

The concentration of elements in the sea water is subject to many factors, and the absolute concentration of an element might vary from one area to another, depending on the conditions that affect the concentration of that

particular element. But it has been found that regardless of the absolute conentration of the total solids, the ratios between the more abundant solids are virtually constant (Sverdrup et al. 1942).

The concentration of calcium in the sea is related to both the carbon dioxide of the atmosphere and to the calcium carbonate deposited at the bottom from shell fragments, precipitation of the dissolved calcium carbonate in the water and inflowing calcium carbonate from rivers and streams. Carbon dioxide reacts with water to form a weak acid which dissociates into the carbonate ion and hydrogen ions, as is shown in equation (1):

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad \text{Eq. (1)}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^=$$

The solubility of calcium carbonate depends on temperature. It is more soluble in cold water than it is in hot water, as is shown in equation (2):

$$CaCO_3 \underset{\text{Hot water}}{\overset{\text{Cold water}}{\rightleftharpoons}} Ca^{++} + CO_3^= \qquad \text{Eq. (2)}$$

Thus in colder water the solubility of both carbon dioxide and calcium carbonate increases. These two compounds affect the concentration of calcium in an opposing manner. With the increased solubility of calcium carbonate in cold water, the calcium content should increase (Eq. 2) whereas with

magnesium ion concentration, drop in almost the same proportion.

The values obtained for the concentration of the magnesium ion follow a pattern close to that of salinity and calcium except that the fluctuations are more accentuated. Again I attribute these fluctuations to storage problems and adsorption of magnesium to the glass bottles in which the samples have been stored. It is usually advised that sea water samples are stored in polyethylene bottles to avoid possible interference from glassware.

Table I shows the percentage of organic matter, mineral content, calcium, magnesium, strontium, and the mineralogic composition (whether the calcium carbonate deposited is calcite or aragonite) of the organisms analysed. Examination of the table reveals that generally the algae have a higher percentage of organic matter than the animals regardless of whether the former were whitened or fresh. This is because only the shells of the shellfish were analysed and these contain very little organic matter. The corals, although whitened, show a relatively higher percentage of organic matter than the shells and this is probably because not all of the protoplasm has been removed during the process of whitening.

The cabon dioxide content of the samples after the organic matter has been burnt off, is in the range of 35-45% thus demonstrating that the minerals deposited are mainly

carbonates. This is particularly true of the algae for according to Lewin (1962) the presence of associated sulfates and phosphates has apparently not been reported in algal skeketons. This does not necessarily mean that all organisms having a hard covering deposit carbonates, for the acantharians and radiolarians deposit strontium sulfate.

The carbon dioxide content should not be used as a measure for the carbonate content of the organisms as chances of error in the determination are considerable. Errors might be brought about if the oven door is opened during the process of cooling of the already formed oxides, thus allowing fresh air to enter the oven. The carbon dioxide of the incoming air will react with the oxides to reform the carbonates. Thus the difference in weight between the carbonates and the formed oxides does not necessarily mean that all the carbon dioxide has been driven off, and hence the determination is not quantitative.

The amount of calcium carbonate dissolved in sea water has a considerable effect on the distribution of calcareous organisms. It has commonly been assumed that the calcium carbonate deposition in the algae is the result of the extraction of the carbon dioxide from the water during the process of photosynthesis, thus shifting the equilibrium of equation (3) to the right:

$$Ca^{++} + 2HCO_3^- \longrightarrow CaCO_3 + H_2O + CO_2 \quad \text{Eq. (3)}$$

One should therefore expect all photosynthetic algae to be coated with calcium carbonate. But this is not the case. Even among the calcareous algae, there are certain parts which are not calcified (articulations). Consequently the distribution of calcium carbonate is not necessarily correlated with the distribution of photosynthetic tissues. Studies of a number of calcareous marine algae suggest that metabolic processes other than photosynthesis are involved in the precipitation. Evidences are accumulating from a number of experiments with isotopes of carbon (C^{13}) in the mineralized and organic parts of calcified algae which are in agreement with the observation that large amounts of magnesium carbonate are somehow metabolically incorporated to form a solid solution in algal calcite (Lewin 1962). Thus the metabolic or physiological processes involved in the deposition are not well known yet. However Parke and Adams (1960) presented evidence that the secretion of coccoliths inside the cells of coccolithophorids originates in a vesicle deep within the cell, though how they are formed and how they are later arranged on the cell surface is not known If these observations are correct then the accumulation of calcium carbonate cannot be merely a reaction occuring at the cell surface as a result of the exchanges in carbon dioxide tension due to photosynthesis,

since the calcium carbonate has somehow first to be accumulated and incorporated within the cell (data from Parke and Adams (1960) is from Lewin 1962).

The calcium content of the algae collected from this area is markedly higher than that of the algae collected and analysed in other areas. Thompson and Chow's (1961) analysis of calcium in some coralline algae collected in California shows an average of approximately 27%, whereas those analysed here show approximately 30% of the mineral weight. This higher percentage of calcium of the local algae is probably due to the higher concentration of calcium in sea water, for according to Horn of Rantzein (1959) calcification of the vegetative parts of the thallus appears to be correlated with the high concentration of calcium bicarbonate in the habitat. Concentration of this element in the animals on the other hand, seems to be independent of its concentration in sea water. Animals collected from Puget Sound on the Pacific coast of North America show a calcium content approximately equal to related species collected here (table I). However, the corals from Aqaba show a relatively higher percentage of calcium than any of the other groups collected in Lebanon. This might be due to the differences in temperature of the waters. According to Sverdrup et al. (1942) temperature influences to a marked extent the rate at which calcium carbonate can be precipitated by animals in the formation of skeletal parts, shells

and spicules. The chemical reactions involved in the deposition are not clearly understood but they proceed more rapidly at high temperatures; hence organisms that utilize calcium compounds in their supporting and protective skeletal structures are notably abundant in warm tropical waters, for in this environment shells can be grown faster and heavier than in cold waters of higher latitudes. The coral reefs are an outstanding example of this in tropical seas. However, since the process of reef formation is a result of biological precipitation of calcium from the sea water by the corals, the rate of deposition is thermally controlled. This does not support the observation that the shells collected from Puget Sound show a close content of calcium to the shells collected here. The differential content of calcium in the organisms leads to two different hypotheses; either the incorporation is genetically controlled or it is environment dependent.

If the incorporation of calcium is genetically determined then members of the same species, or perhaps genus, should show relatively close calcium concentrations. The differences between the calcium content of Corallina mediterranea collected here (average 37% of mineral wt.) and that collected from the Pacific, (av. 29% Thompson and Chow 1961), does not support this hypothesis. There should be no variation in the content of calcium in members of the same species if the incorporation is genetically determined.

If, on the other hand, the incorporation is environment dependent, then one should not expect fluctuations in the percentage of calcium among different groups living in a similar habitat where conditions of temperature and salinity are the same because the environmental conditions will affect the organisms equally. The mollusks (table I.), however, show such a case. Murex and Eutritonium which are not directly related, collected from Rabbit Islands show close calcium contents. If the incorporation of any element is environment dependent, then one should expect that the magnesium content of all organisms to be much higher than that of the calcium, since magnesium is three times as concentrated in the sea as calcium. Yet we find that all organisms used in this study, except the coralline algae, incorporate much less magnesium. It is quite obvious therefore, that the organisms are exerting some sort of selective mechanisms, which are most likely genetically controlled, otherwise, one would expect that the ratio of incorporation of calcium to magnesium to be close to that of sea water. However, when one considers the individual elements, there is little concrete evidence for rigid genetical control. I feel that with the evidence now available, we have to say that the incorporation of any element in the majority of organisms is a function of both factors, genetic determination and environmental control. Genetically, an organism can incorporate a certain maximal amount of a given element, but

the concentration of that element incorporated is related to the abundance of the particular element in the organism's habitat.

Magnesium carbonate is another important constituent of calcareous organisms. Chave (1952) showed that magnesium carbonate forms a solid solution with calcium carbonate in calcite skeletons, although in natural minerals such a solid solution is only formed under high temperatures. Aragonitic skeletons of coralline algae are lower in magnesium than are those composed of calcite. Moreover in all groups of calcitic organisms, a linear relationship exists between the magnesium content of the skeletons and the temperature of the water in which the organisms lives (Lewin 1962). Haas et al. (1935) studying calcium and magnesium metabolism in calcareous algae such as Corallina squamata, found seasonal changes in the amount of these elements on a dry weight basis. Chave (1952) showed that the ratio of Mg/Ca in the calcite laid down by Lithothamnion sp. during the summer is 2-4% higher than in the calcite deposited in winter. Table I. reveals that the coralline algae have a magnesium content up to 69%, the corals values of about 6%, and the other animals relatively low magnesium content of about 2%. Johnson (1961) states that among the Corallinaceae, the amount of calcium carbonate and magnesium carbonate varies relatively little. The coralline algae contain higher percentages of magnesium carbonate than have been

found in skeletons of any other animals or plants. This chemical characteristic of being particularly rich in magnesium carbonate is very distinctive of this family of algae and distinguishes them from all other lime-encrusting and lime-secreting algae. Thus the higher values obtained with the algae (table I) could be due to a combination between the distinctive characteristic of the Corallinaceae and the higher temperatures that prevail in the waters of this area.

The lower values of magnesium in the two samples of Jania sp. (7.40% and 6.70%) were from preserved samples (for two years) which apparently affected the magnesium of the alga but did not affect the calcium in an appreciable manner. This matter bears further investigation.

The higher percentage of magnesium in the corals, might also be due to temperature effects.

Strontium occurs in traces in animals and plants but does not seem to be an essential element. Little is known about its vitality in the metabolism of organisms. Although it resembles calcium in chemical and physiological properties, the ionization constant, solubility products and other properties differ by a factor of from 2-200, so that most of the natural processes act on the two elements differentially (Odum 1951b). The factors that affect the incorporation of strontium in the body of the organisms are very speculative. Some authors (Thompson and Chow 1961)

attribute this incorporation to genetical differences between organisms. Others (Kulp et al., Lowenstam 1954) to environmental factors. But all agree that the amount incorporated is directly related to the mineralogic composition of the organism. In aragonitic skeletons strontium was found to be higher than it is in calcitic ones. Again contradictory points of view arise regarding the factors that affect the mineralogic compositions of organisms and the controversy between genetic and environmental factors persists here too.

Table I reveals several important points. The values of strontium obtained for the coralline algae are very close to those obtained by Thompson and Chow (1955), who got an average of 0.37% of strontium carbonate. The animals on the other hand show a lower content of strontium than those they analysed.

Regarding the mineralogical composition, the calcareous algae, unlike some animals, have either calcite or aragonite deposition but no mixture of the two, the corals mostly aragonite, and other animals varied deposition from calcite or aragonite to a mixture of both in different proportions. It has been suggested (Lowenstam 1954) that with the higher temperature of the sea water, the calcareous deposition is aragonite. This might be correct of the corals for many of the ones analysed showed aragonitic deposition. The Gulf of Aqaba is a region of higher minimal

temperatures and this might explain the aragonitic deposition found in the corals. Associated with this aragonitic deposition, is a high strontium content. This higher concentration of strontium in aragonitic forms is attributed (Kulp et al. 1952) to the fact that calcite has a crystal lattice which is less amenable to strontium than aragonite. However the results obtained in this study in relation to strontium and the mineralogical composition, do not show a significant difference except perhaps in the coral Herpolitha, which has aragonitic deposition and a relatively high strontium content.

The specimens which were collected from the Pacific showed little or not strontium content, in their calcitic depositions. This calcitic deposition is probably due to the lower temperatures of the waters they live in. But the lack of strontium in them is really questionable. The waters of the Pacific contain around 13 ppm of strontium (Sverdrup et al. 1942), plus an additional amount from fallout and radioactive wastes, which are minute in concentration. If the hypothesis that deposition is a function of both genetic and environmental factors holds, then one should expect that the strontium content of these animals to be lower than animals collected here. The strontium content is lower in the Pacific, because the salinity is lower, and the temperatures which might be responsible for the deposition are also lower. Consequently, the

environmental conditions do not favor a high concentration of strontium, and one should expect that the genetic factor in these organisms to be more important than the environment in determining the strontium content.

In the determination of strontium-90, the radioactive isotope of strontium, the average background count was 18 counts per minute. None of the samples analysed for strontium showed any significant deviation from this average background. The highest count was obtained in the coralline algae which had only four counts per minute for a weight of 50 mgs. of strontium sulfate, a value which is definitely insignificant. A great part of strontium-90 in the sea is related to radioactive fallout from nuclear tests. Since most of the tests are carried out in the Pacific Ocean and over continental Asia, the major portion of the fallout will occur in the North Pacific and on the continental masses of Asia and North America. The Levant receives little or no strontium-90 fallout, and oceanic currents are such that it will take a number of years before any degree of stabilization (equal distribution of strontium-90 in all seas) is reached. Consequently one should expect little or no strontium-90 in this area, and this explains the absence of this radioisotope in the organisms analysed.

Padina pavonia (table I) has a calcium content of 8.5% and 3.00% of magnesium out of the total mineral weight. This plant has always been considered a depositor of calcium

carbonate. The calcium content obtained, however, does not show that calcium is the dominant constituent. There should be some other element which makes up the rest of the bulk of the mineral deposition. It has always been believed that the dominant depositions in calcareous organisms are the carbonates of calcium and magnesium. Other elements have not been investigated in detail. There might be some elements which are more important than calcium in Padina sp. or some other organisms as well. In order that characterization of the mineral constitution is established, analyses of the elements that are found in the sea should be carried out on the organisms. Padina sp. might concentrate an element which is not as abundant as calcium as in the case of the acantharians which deposit strontium sulfate.

Table II shows the same analyses as Table I for substances other than living organisms. The sand samples show approximately equal percentages of organic matter, mineral weight, and carbon dioxide. But the calcium content increases as one moves away from the shore line, whereas the magnesium content decreases. This is probably because the sand near the waves contains more silica than sand further away. One should also note that most of the sand found along the beach of Rabbit Islands is made of the calcareous shells of animals and deposits from the calcareous algae. Analysis for the calcium carbonate content of these sand samples reveals 94.5% for the near-

waves sample, 97.1% for the midway sand, and 99.9% for the faraway sample. This means that as one moves away from the shore line, the calcium carbonate content increases and this might explain the increase in the calcium concentration in these samples. The strontium content for the three samples does not show any significant difference and the mineral character was calcitic.

The biogenic rock, although collected from different localities showed no difference in the organic matter content, mineral content, nor carbon dioxide content. But there is a significant difference in the calcium and magnesium contents. This might be due to either the temperatures that prevailed during deposition or to the organisms making up the majority of this biogenic rock. Temperature differences might account for the variation in the strontium content as well. If two organisms are responsible for the building of each sample, and these samples show differential incorporation of the elements, then the rock content of these elements will be related to the contents of these organisms that make it up.

The terrace samples were collected as shown in figure 2. The first three samples show a higher organic matter content than the rest. In the first two samples, this higher organic matter content is because they were collected from the outer lip of the terrace (figure 2), which has a layer of living organisms sometimes reaching

a thickness of 10 cms. The higher organic content in sample three (3) is because it was covered with barnacles (Chthamalus sp.) which usually grow in that region of the terrace. The carbon dioxide content of samples 2 and 3 is approximately the same, rises in samples 3 and 4, and then drops sequentially in the rest of the samples, whereas the calcium concentration of these samples rises successively from sample 1 to sample 7 (table II). The magnesium content in the first three samples and in sample 6 is higher than it is in the rest of the samples and is close to the magnesium content of the plants analysed (table I) at the same time. This resemblence in the magnesium (as well as in the strontium) concentration suggests a possible origin of these rocks from plant depositions whereas the other samples might have originated from animal deposition due to their resemblence in the mineral content of the two (tables I and II). It is interesting at least to hypothize the origin of the rocks from the analysis of the mineral content of these rocks and associated organisms.

The decrease of the carbon dioxide content and the increase in the calcium content, as one moves from sample 1-7, might be explained by two reasons, 1) the carbon dioxide determination might not have been accurate because the intention was to drive it off in order to convert the carbonates to oxides, without paying a great attention to a quantitative determination of the gas. Sources of error might enter if the furnace in which the samples were heated

was areated during the cooling of the samples. The carbon dioxide of the incoming air will react with the oxides to reform the carbonate. 2) The calcium and magnesium might be found in the rock associated with radicals other than the carbonate.

Although the highly magnesian material of the terraces seems related to plant origin, and the low with animal origin, any definite or further conclusion would need to be supported by a complete analysis of the minerals that might be associated or deposited in these terraces.

Future research with the problem of deposition should focus on one or two species. Systematic collections and analyses should be done in order to follow seasonal changes, if any. Any conclusion related to the factors that might affect the uptake and accumulation of any element should be supported by controlled laboratory experiments. Also, more attention should be given to other mineral constituents.

V. SUMMARY AND CONCLUSIONS

1. The average salinity for the sea water in this area between June and September is 39.74‰. This higher salinity (average oceanic salinity is 35‰ for surface waters) is probably due to the construction of the High Dam on the Nile River which reduced the amount of fresh water runoff in the Eastern Mediterranean.
2. The average calcium ion concentration for the same period is 460 ppm and that of magnesium is 1219 ppm which are 60 and 19 ppm higher than the concentration in other seas. The higher values are related to the higher salinity that prevails here.
3. The organisms collected here show a higher concentration of calcium, magnesium and strontium than other organisms collected elsewhere. This might be due to either the higher temperatures that prevail in this area which affect the rate of deposition directly, or to the higher concentration of these elements in the water.
4. The magnesium content of some coralline algae is much higher than the magnesium content of all organisms that were analysed. In some of these algae, the magnesium content exceeds that of calcium.
5. The deposition of any element is a function of genetic and environmental factors. Genetically, an organism can incorporate a certain maximal amount of a given element,

but the concentration of that element incorporated is related to its abundance in the organism's habitat.

6. Although the carbonates of calcium and magnesium are considered to be the dominating depositions in calcareous organisms, compounds of other elements might be more important than calcium or magnesium in organisms such as Padina pavonia.

7. Strontium occurs in traces in all the organisms that were collected here. The absence of the radioactive isotope (strontium-90) in all the organisms analysed is because of the absence of this isotope in the waters these organisms inhabit.

8. Analysis of the mineral content of the organisms and that of the terrace, might give a clue to the origin of the rocks which make up the terrace.

9. Although the mineral content of the terrace seems to be related to either animal or plant origin, any definite or further conclusion would need to be supported by a complete analysis of the minerals that might be associated or deposited in these terraces.

10. Any future research that might be done by the author, in the study of calcium carbonate-depositing marine organisms would be focused on one or two species to study seasonal fluctuations and to perform controlled laboratory experiments in order to investigate in greater detail the influence of temperature and that of concent-

ration of the elements on deposition. Possible studies could be conducted with organisms like Halimeda (a coenocytic alga divided into segments) whereby a segment of the plant could be studied in relation to another segment of the same plant. In such a case, where the genetic constitution is identical, the environmental effects could be examined in greater detail. In specimens like Lithothamnion a more detailed study of seasonal fluctuations could be apprehended if one analyses the mineral content of the layers that are laid down seasonally or yearly. Such studies with particular parts of the organism open a broader gate for establishing concrete evidence regarding the effect of the environment in relation to the individual's genetic constitution.

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TABLES

Table I. Mineral content of some calcium carbonate depositing marine organisms. The percentage of carbon dioxide is out of the mineral content which was considered as 100%. The percentage of calcium, magnesium and strontium are calculated from the mineral content without the carbondioxide, i.e. the oxides were considered as 100% and from this the percentages of the latter elements were calculated. In the last column, "A" means aragonite and "C" means calcite.

TABLE I. MINERAL CONTENT OF SOME CALCIUM CARBONATE-DEPOSITING ORGANISMS

Species	Locality	Date	Dry Wt. (Gms)	% Org. Mat.	% Min. Wt.	% CO_2	% from Min. Wt.-CO_2 Ca	Mg	Sr	UMR*	Ca/Mg	A or C
RHODOPHYTA Corallinaceae Jania rubens	AUB	Nov. 66	12.3	18.7	81.3	49.0	32.3	60.0	0.018	3.68	0.54	C
Jania rubens	AUB	Nov. 66	17.7	28.2	71.8	30.7	37.2	40.0	0.017	22.78	0.93	C
Jania rubens	AUB	Oct. 64	59.7	21.7	78.3	47.2	34.2	7.40	0.024	58.38	4.62	C
Jania rubens	AUB	Oct. 64	19.6	20.8	79.2	34.3	23.5	6.70	0.012	69.79	3.51	C
Corallina mediterranea	AUB	Nov. 66	10.7	15.9	84.1	45.5	36.8	50.0	0.003	13.2	0.74	C
Corallina mediterranea	AUB	Nov. 66	32.5	17.8	82.2	43.1	37.0	53.0	0.004	10.0	0.70	C
Corallina mediterranea	AUB	Nov. 66	25.8	19.8	81.2	37.1	37.1	55.0	0.003	7.9	0.67	C
Lithothamnion fruticulosum	RI**	Jul. 66	39.5	14.9	85.1	40.4	30.0	69.0	0.009	1.0	0.43	C
Whitened L. fruticulosum	RI	Jul. 66	29.5	11.8	88.2	41.2	29.5	60.0	0.003	10.5	0.49	C

*Unidentified mineral residue

**Rabbit Islands

TABLE I. (Cont'd)

Species	Locality	Date	Dry Wt. (Gms)	% Org. Mat.	% Min. Wt.	% CO_2	% from Min. Wt.-CO_2			UMR	Ca/Mg	A or C
							Ca	Mg	Sr			
Fresh L. fruticulosum	RI	Jul. 66	27.5	13.9	86.1	41.4	15.0	3.70	0.0007	81.30	4.05	C
Lithophyllum cristatum	RI	Jul. 66	25.6	11.8	88.2	41.8	29.2	6.90	0.003	63.90	4.23	C
Liagora	RI	Jul. 66	29.5	14.6	85.4	49.8	23.6	2.67	0.003	73.73	8.83	A
Lithophyllum racemus	RI	Jul. 66	38.8	2.6	97.4	43.1	30.0	6.65	0.002	63.40	4.51	A
Pseudolitho-phyllum expansum	TAB*	Jun. 66	6.7	14.9	85.1	36.8	20.0	1.5	0.005	78.50	13.33	C
PHAEOPHYTA Padina Pavonia	AUB	Aug. 66	25.5	46.2	53.8	45.3	8.5	3.00	0.004	88.50	2.83	A
COELENTERATA Anthozoa Herpolitha sp.	Aqaba		25.3	4.3	95.7	42.7	33.3	5.75	0.07	59.65	5.79	A
Symphylla sp.	Aqaba		24.0	4.1	95.9	41.3	32.3	6.00	0.003	61.70	5.38	A
Favia sp.	Aqaba		40.2	3.5	96.5	41.8	30.3	6.30	0.005	63.40	4.80	A

*Tabarja

TABLE I. (Cont'd)

Species	Locality	Date	Dry Wt. (Gms)	% Org. Mat.	% Min. Wt.	% CO_2	% from Min. Wt.-CO_2			UMR	Ca/Mg	A or C
							Ca	Mg	Sr			
Madrepora sp.	Aqaba		44.2	3.4	96.5	42.6	31.8	6.17	0.005	62.03	5.15	A
Madrespora sp.	Aqaba		50.8	3.3	96.7	42.8	32.3	6.45	0.005	61.25	5.00	A
Coral	Aqaba		23.9	3.4	96.6	41.8	30.8	6.75	0.008	62.45	4.56	C
Coral	Aqaba		35.2	3.9	96.1	42.6	33.9	6.35	0.006	59.75	5.33	C
MOLLUSKA Gastropoda Monodonta turbinata	RI	Jul. 66	25.7	6.2	93.8	41.9	33.3	0.30	0.008	66.40	111.0	C
Monodonta turbinata	RI	Jul. 66	39.7	5.0	95.0	41.9	23.3	1.00	0.005	75.7	23.3	C
Monodonta turbinata	AUB	Jun. 66	26.5	7.5	92.5	39.2	42.1	1.15	0.000	56.75	36.60	C
Monodonta turbinata	AUB	Jun. 66	50.7	6.8	93.2	37.1	42.1	1.85	0.000	56.05	22.75	C
Murex trunculus	RI	Jul. 66	42.3	3.5	96.5	42.2	27.1	1.90	0.004	72.00	14.26	C

TABLE I. (Cont'd)

Species	Locality	Date	Dry Wt. (Gms)	% Org. Mat.	% Min. Wt.	% CO_2	% from Min. Wt.-CO_2			UMR	Ca/Mg	A or C
							Ca	Mg	Sr			
Eutritonium sp.	RI	Jul. 66	47.7	1.9	98.1	41.7	27.5	0.30	0.004	72.2	91.66	A
Land snail	RI	Jul. 66	30.8	7.1	92.9	41.3	24.3	0.95	0.003	74.75	25.57	A
Bittium reticulatum	AUB	Aug. 66	29.7	8.4	91.6	42.4	34.5	1.20	0.000	64.3	28.75	C
Fasciolaria	AUB	Aug. 66	27.7	2.8	97.2	42.0	23.9	1.73	0.004	74.57	13.81	A
Cassis saburn	RI	Jul. 66	19.5	2.5	97.5	46.8	20.0	1.50	0.003	79.50	13.33	A
Cypraea sp.	RI	Jul. 66	28.1	1.8	98.2	42.5	23.3	1.55	0.0006	75.15	15.03	A
Ostrea lurida	U.S.A.*	Dry	34.7	8.4	91.6	34.9	44.4	2.49	0.000	53.11	17.83	C
Tegula funebralis	U.S.A.	Dry	15.0	6.6	93.4	36.4	41.8	2.13	0.000	56.07	19.62	C
Columbella rustica	RI	Jul. 66	36.1	1.6	98.4	42.2	13.7	1.05	0.002	85.75	13.04	C+A**

*Puget Sound on Pacific Coast of U.S.A.

**Mineral character is both aragonite and calcite.

TABLE I. (Cont'd)

Species	Locality	Date	Dry Wt. (Gms)	% Org. Mat.	% Min. Wt.	% CO_2	% from Min. Wt.-CO_2			UMR	Ca/Mg	A or C
							Ca	Mg	Sr			
Patella vulgata	RI	Jul. 66	10.3	3.8	96.2	41.4	20.7	1.50	0.000	77.80	13.80	C
MOLLUSCA Pelycepoda Pinna nobilis			25.2	5.2	94.8	41.0	33.0	6.45	0.002	60.55	5.11	A
Pinctada radiata	RI	Jul. 66	36.7	4.8	95.2	41.8	38.5	1.80	0.001	59.70	21.38	A
Pectin hericius	U.S.A		17.5	1.4	98.6	56.6	44.3	1.60	0.000	54.10	27.68	A & C
Mytilus edulis	U.S.A.		24.5	6.1	93.9	38.7	41.8	1.40	0.000	56.80	29.85	C
Donax sp.	KH*	Jan. 67	30.0	2.3	97.7	41.4	21.0	1.15	0.000	77.85	18.26	C
Glycimeris sp.	KH	Jan. 67	30.0	3.8	96.2	40.3	16.8	2.80	0.0001	80.40	6.00	C
ARTHROPODA Lepas anatifera	RI	Jul. 66	28.4	11.3	88.7	44.0	24.6	3.65	0.001	71.75	6.73	C

*Khalde Beach

TABLE I. (Cont'd)

Species	Locality	Date	Dry Wt. (Gms)	% Org. Mat.	% Min. Wt.	% CO_2	% from Min. Wt.-CO_2			UMR	Ca/Mg	A or C
							Ca	Mg	Sr			
Vermetus gigas	RI	Jul. 66	43.4	1.3	98.7	42.0	33.0	1.25	0.000	65.75	26.40	A
ECHINODERMATA												
Sea urchin skeletons	AUB		24.8	4.0	96.0	46.2	50.5	2.65	0.0008	46.85	19.05	C

Table II. Mineral content of sediments and terrace rock.

See legend Table I.

TABLE II. MINERAL CONTENT OF SEDIMENTS AND TERRACE ROCK

Substance	Locality	Dry Wt. (Gms)	% Org. Mat.	% Min. Wt.	% CO_2	% from Min. Wt.-CO_2			UMR	Ca/Mg	A or C
						Ca	Mg	Sr			
Near-waves sand	RI	30.0	1.6	98.4	42.7	26.8	4.20	0.0003	69.0	6.38	C
Midway sand	RI	32.7	1.2	98.8	43.2	27.8	2.45	0.0005	69.75	11.34	C
Faraway sand	RI	32.9	1.5	98.5	42.9	31.4	2.10	0.0006	66.5	14.95	C
Biogenic rock	RI	40.0	1.3	98.3	41.9	26.8	2.35	0.0000	70.85	11.40	C
Biogenic rock	AUB	32.2	2.7	97.3	41.7	23.7	4.80	0.007	71.5	4.93	C
Terrace (1)	AUB	42.5	3.8	96.2	43.8	30.5	60.0	0.001	9.5	0.51	C
Terrace (2)	AUB	33.5	2.2	97.8	43.9	33.0	65.0	0.0006	2.0	0.51	C
Terrace (3)	AUB	41.4	3.9	96.1	44.4	33.0	65.0	0.0009	2.0	0.51	C
Terrace (4)	AUB	41.4	1.4	98.6	45.2	34.3	3.65	0.0003	62.05	9.39	C
Terrace (5)	AUB	32.5	2.2	97.8	40.3	38.0	3.45	0.001	58.55	11.01	C
Terrace (6)	AUB	41.4	1.6	98.4	38.5	38.5	50.0	0.001	11.5	0.77	C
Terrace (7)	AUB	41.4	1.8	98.2	25.6	55.0	4.45	0.002	40.55	12.35	C

FIGURES

Fig. 1. This figure shows the concentration of calcium and magnesium of sea water expressed in PPM for the period between June and December of 1965. The salinity values for the same period expressed in PPT are also included in the upper part of the figure.

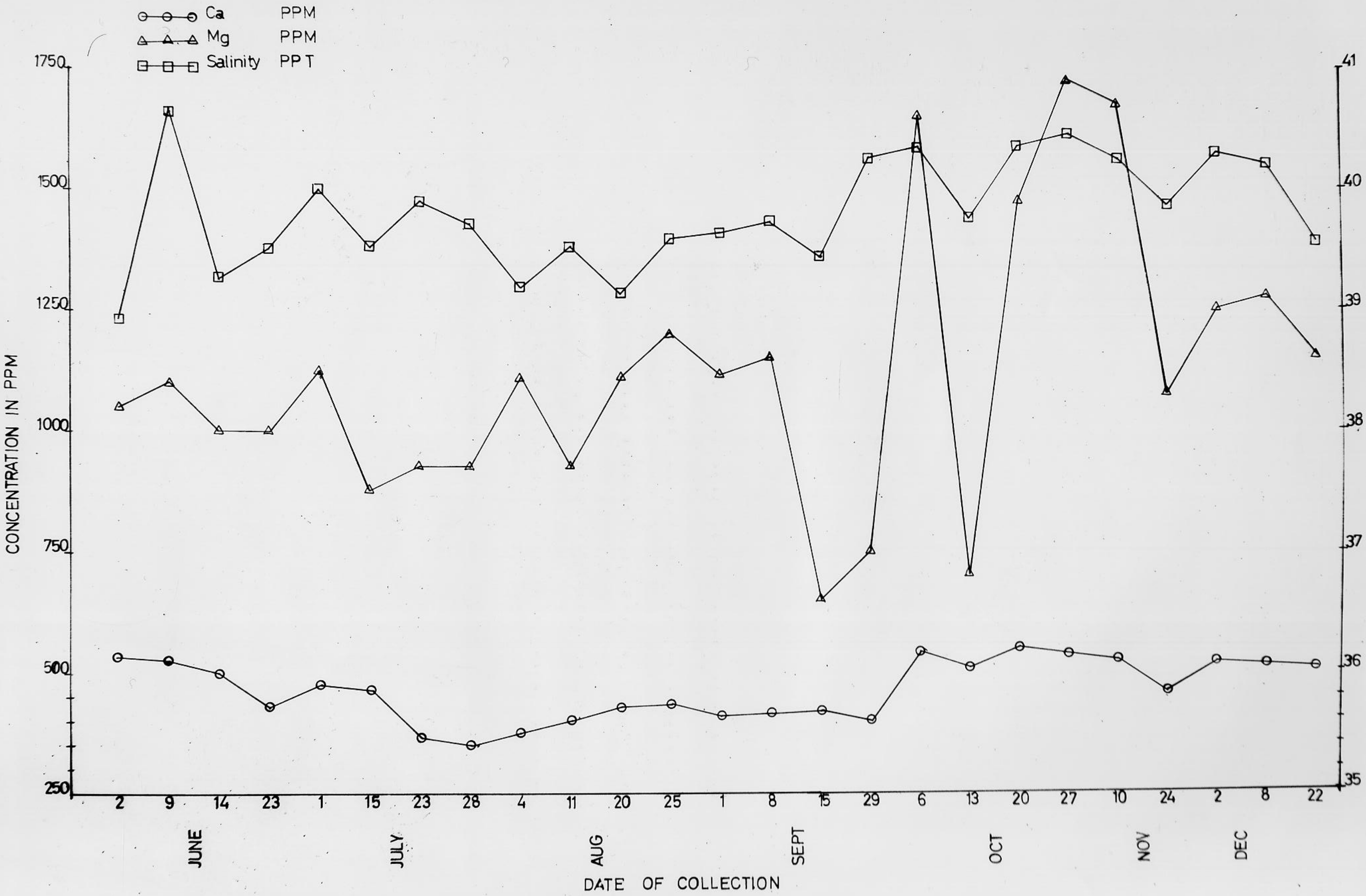
Ca PPM
Mg PPM
Salinity PPT
CONCENTRATION IN PPM
1750
1500
1250
1000
750
500
250
41
40
39
38
37
36
35
2 9 14 23 1 15 23 28 4 11 20 25 1 8 15 29 6 13 20 27 10 24 2 8 22
JUNE
JULY
AUG
SEPT
OCT
NOV
DEC
DATE OF COLLECTION

FIGURE 1

Fig. 2. A schemetic representation of the terrace from which samples were taken and analysed for their mineral content. The diagram does not include the details associated with the profile such as pot holes. The distance between every two samples is not constant because the samples were collected randomly.

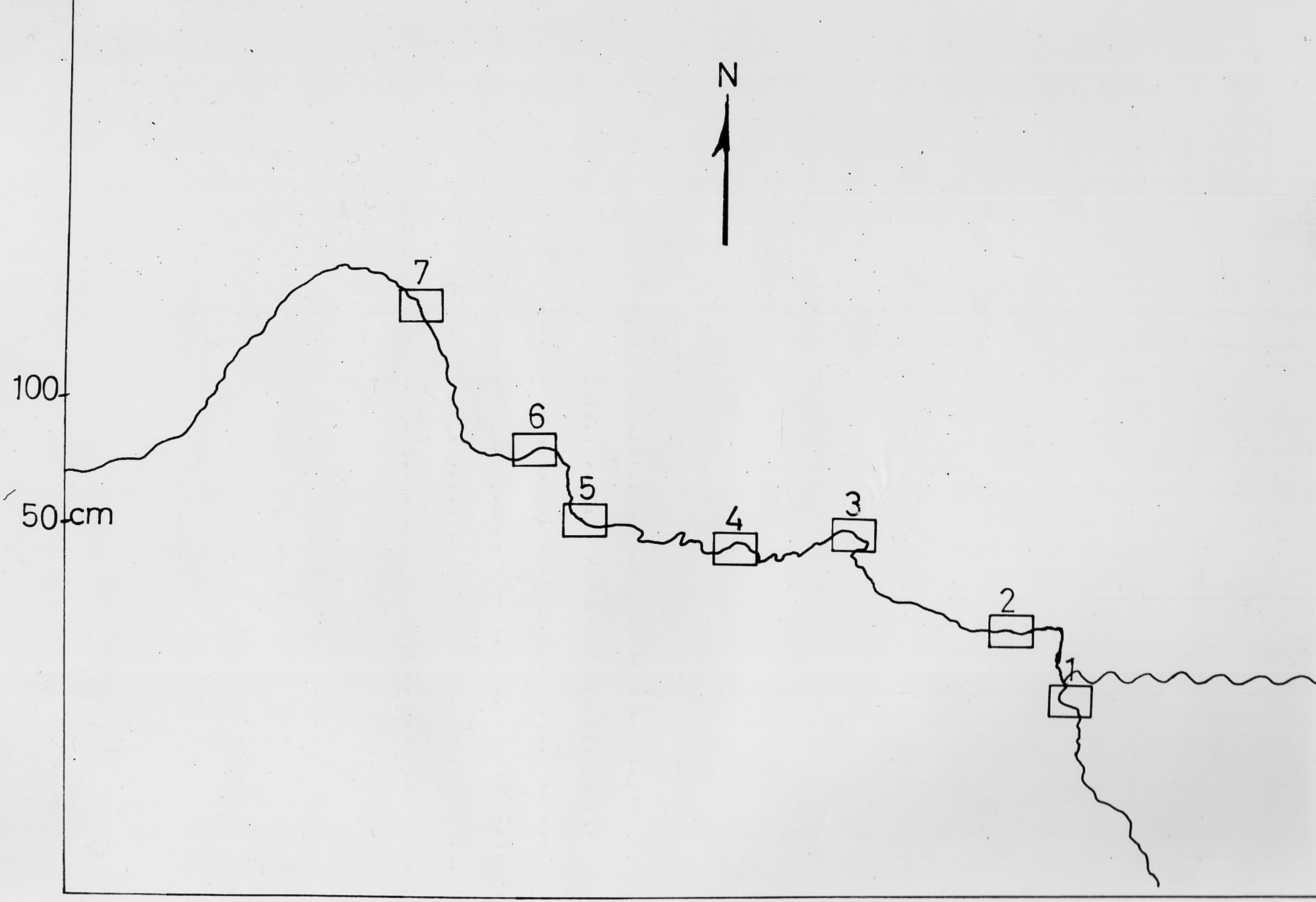

FIG 2.