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DEPARTMENT OF
MINERALS AND ENERGY

BUREAU OF MINERAL RESOURCES, GEOLOGY AND GEOPHYSICS

Record 1973/113

CATION ELECTRODE MEASUREMENTS IN THE CAPRICORN AREA, SOUTHERN GREAT BARRIER REEF PROVINCE

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SUMMARY

Solution by sea water is of great importance in removing carbonate in the intertidal zone. This process is faster than solution by rain water. Measurement of salinity, alkalinity, pH, oxygen, calcium, magnesium, and temperature, in water associated with beach rocks and the reef flat in two reefs in the Capricorn Group indicate a massive day time solution of carbonate, and a night time precipitation. This effect is opposite to that reported in the literature. In addition, marked but unsystematic variations in the solubility of carbonate minerals is indicated, this further suggesting that unsystematic complexing of calcium and magnesium, possibly as hydrates, is occurring in the water. These halmyrolitic reactions are the result of organic attack on carbonate grains, especially those composed of high Mg - calcite.

INTRODUCTION

Work on coral reefs has in the past been almost totally concentrated on their constructional nature, and on the processes which have aided in their lithfication into solid units. Little work has been carried out on destructive processes, evidence of which is abundant on coral reefs throughout the world. Much of this destructive work appears to have been due to corrosive forces. However, past workers have been intimidated by the conclusions of chemists that tropical waters are saturated or even supersaturated with respect to lime, thus precluding the possibility of the solution of limestone. Also the geological evidence for solution on the intertidal zone of reefal areas is in conflict with the results of laboratory studies on the solubility of calcium carbonate in sea water. The fact remains however, that visual observations in such environments suggest that corrosive processes are playing a major part in the fashioning of the intertidal coral reef environment. Keunen (1933, 1950), convinced by his observations, yet concerned by the experimental data stated -

> 'Whether it is the greater range in temperature, the contact with the atmosphere, some influence of surface tension, the alternate wetting and drying, or some other unsuspected influence which was overlooked in the experimental work, I am unable to say' (Keunen, 1933, p. 75).

What then is the observational evidence indicating that corrosive processed are operative in the tropical intertidal environment? It has been reported by many workers (Keunen, 1933, Fairbridge, 1952; Guilcher, 1953; Revelle and Emery, 1957; Davies and Kinsey, 1973), that solution basins, nips, and caves are common in reefal areas. The jagged crater-like appearance of beach rock and reef flat surfaces on cays in the Coral Sea and Great Barrier Reef Province also testifies to the action of corrosive zones, as does the friable, rapidly disintegrating beach rock in Shark Bay on Heron Island. Accepting that the visual observations of many workers are valid, the problem therefore crystallizes into two parts: (a) can solution of Ca CO_2 be shown to occur quantitatively? and (b) if so, what mechanism can be involked to explain the experimental results?

In the present contribution, experimental data published for Bikini and Guam are compared with data obtained by the writer from Heron Island and One Tree Island in the southern Great Barrier Reef Province. In these four areas, in situ measurements of chemical parameters have been conducted on small bodies of water which remain in the intertidal environment after tidal withdrawal. Results from such experiments are probably more valid in estimating gross chemical changes than similar experiments in large water bodies (main body of sea water) because the magnitude of the changes are such that large water volumes render the changes difficult to detect.

BIKINI AND GUAM

Revelle and Emery (1957) published the results of in situ experiments on chemical erosion of beach rock and exposed reef rock on Bikini and Guam. The results of this experimental data shown in Figure 1A and B, and are summarized below.

1. Diurnal chemical variation was detected in the pool waters. Oxygen, temperature, and pH were seen to rise in the day, and drop at night. Both the oxygen and pH changes were interpreted as due to biologic metabolic effects. Carbon dioxide (not measured) concentration was inferred to be largely inversely proportional to the oxygen variation.

No alkalinity determinations were made at Bikini. However, measurements made at Guam showed that the alkalinity variations were large, and in any one basin inversely proportional to pH (Fig. 1B). The alkalinity data are seen to reflect alternate precipitation (in the day) and solution (in the night) of calcium carbonate.

2. Calcium and magnesium variations in the pools were not examined. However, by assuming that the magnesium variation is negligible, and also that

$$\Delta \text{ Alkalinity}/_2 \text{ (m. equivs/litre)} = \Delta \text{ Ca}^{2+} \text{ (mg atoms/litre)},$$

it was calculated that 9 mg/litre of calcium would dissolve at night, and 5 mg/litre would precipitate during the day.

3. Not all night time alkalinity changes are the direct result of solution. At Guam, some are due to the reduction of sulphate to sulphide. However, such changes could only form a small part of the total alkalinity change.

ONE TREE ISLAND

At One Tree Island, in situ measurements were made in pools, the floor of which carried a large algal community. In situ measurements were made for salinity, temperature, and pH. Alkalinity was measured on the same water samples within 24 hours and calcium and magnesium was measured on acidified samples by atomic absorption spectroscopy within 7 days of collection. The calcium, magnesium, and pH variations for one cycle of measurements are shown in Figures 2 and 3. The alkalinity is not plotted because it showed the normally expected trend of an alkalinity drop in the day and a rise at night. The calcium and magnesium data are plotted because they form significant gaps in the Bikini and Guam data. The pH is plotted because it exhibits interesting variation. The results may be summarized as follows:

1. Magnesium exhibits a marked variation throughout the day and night. At night there is a systematic increase in the magnesium concentration which cannot be accounted for by salinity increases. The day time variation is more complex. A rise is seen in the morning with a gradual decrease towards the later part of the day.

2. Calcium exhibits a sharp rise in the early part of the night after which it remains steady before rising again as the dawn approaches. The plot in Figure 3 are results not incorrected for salinity increases due to evaporation. When this is done, calcium in fact shows a drop throughout the night from 0040 hours to 0440 hours. Once again, as with magnesium, the daytime calcium picture is more complex. The trend however, suggests an increase in calcium throughout the morning and afternoon, followed by a decrease in calcium in the later part of the day. Daytime calcium values are higher than the night time values. It is apparent therefore that calcium and magnesium are exhibiting similar trends. However, the overall variation in magnesium is far greater than calcium.

3. At night pH is steady at around 8.1. However, a marked increase occurs around 0300 hours to 8.4. The day time picture shows a gradual increase throughout the day with a fall in pH preceding the dusk.

The calcium and magnesium variations are very surprising when viewed against the alkalinity and pH variations. During the day, both cations show strong increases as the pH rises. At night magnesium increases in solution while Ca^{2+} effectively decreases. During this period, pH remained relatively steady except for a sharp rise in one sample. Generally, the alaklinity and pH picture is similar to that reported from Bikini and Guam. However, the calcium and magnesium variation bears little relation to the theoretically calculated calcium variation for these localities. The One Tree Island results also indicate that large scale variations in magnesium are occurring in solution which invalidates any possibility of a relationship between Δ Alkalinity/$_2$ and = Δ calcium concentration.

HERON ISLAND

At Heron Island, a long series of experiments have been conducted, the results of some of which have been reported elsewhere (Davies and Kinsey, 1973). However, as these results are the most complete, and as they have an important bearing on the problems of chemical variation in the intertidal environment, they are reported here in summary. In both natural and artifical pools, total alkalinity, oxygen concentration, pH, salinity, water temperature, dissociated calcium, and total calcium and magnesium were studied. The total analytical data is given in Davies and Kinsey (op. cit.). The principal natural pool on the beach rock at Heron Island was estimated to hold approximately 5000 litres of sea water, a depth of 15 cms being attained immediately after tidal withdrawal. Almost all of the bottom of the pool was covered with an algal mat. It represents an environment in which biological activity is at a maximum. The results obtained from the beach rock pool are presented in Figures 4 and 5, and are summarized below.

1. Salinity increases in the day. It also increases at night, but is interrupted by periodic salinity dilutions.

2. The pH increases in the day (9.4 max.) and in the night (8.4 max.).

3. Alkalinity decreases in the day, and increases in the night.

4. Oxygen concentration increases in the day, while at night it decreases to levels below saturation.

5. Temperature rises in the forenoon and falls towards dusk. Temperature drops at night.

6. Calcium values rise during the day, and fall at night. The data plotted are corrected to zero salinity, so that the calcium variation is true, and not a function of salinity increases. Daytime calcium values are consistently higher than night time values.

7. Daytime magnesium values show an increase throughout the early part of the day, and a fall in the afternoon. The early part of the night shows a magnesium fall, but this is followed by a rise throughout the rest of the night.

It can be seen from the above, that the salinity, alkalinity, temperature, and oxygen data agree substantially with that from Bikini and Guam. They also agree with data from One Tree Island. The calcium and magnesium data agree with that shown for One Tree Island. The daytime pH data is similar in all localities. The night time rise in pH at Heron Island has been consistently measured at that locality on many different occasions. Similar pH rises, and marked fluctuations have also been noticed at One Tree Island. The Guam data (Fig. 1B) show a slight pH rise throughout the night. In fact the Guam data are very similar to the Heron Island data.

The conclusions drawn from the One Tree Island data are also valid for the Heron Island data. However, at the latter locality, they can be taken further because additional information is available, i.e. at Heron Island, both total and dissociated calcium were measured (Fig. 5). Thus the following comments are relevant to complexing of calcium in such environments.

(a) Large scale variation in the concentration of complex calcium occurs during both day and night. This is shown in Table 1.

TABLE 1:	Experiment 1	Experiment 2	Experiment 3
Day	4.5%-25% (mean = 15%)	11%-29% (mean = 20%)	20%-38% (mean = 28%)
Night	7.8%-23.5% (mean = 16%)	4.7%-1.3% (mean=13%)	7%-30% (mean = 18%)

(b) In two of the three experiments, it can be shown that the percentage of complexed calcium varies directly with termperature (Fig. 6 and 7). It can be shown that the amount of complexing is almost directly proportional to the temperature during both day and night cycles. As the temperature rises, so does the amount of calcium complexed. Conversely, as the temperature drops, so does the amount of complexed calcium. This is independent of the fact that calcium is increasing in the pools in the day and is decreasing at night. Therefore the addition and removal of calcium must be due to a process significantly different from that producing the complexing.

DISCUSSION

The work of Revelle and Emery (1957) is an important step in recognizing that chemical solution occurs in environments which are supersaturated with respect to calcium carbonate. Diurnal variations in chemical parameters of water due to physico chemical and biologic processes lead to the belief that day time precipitation and night time solution of $CaCo_3$ is possible in the intertidal environment. This conclusion is based on the assumption that the Δ Alkalinity/2 = Δ Ca^{2+} in the waters. The present writer believes that this conclusion is unsound for waters of the intertidal environment. First it is based on a physico-chemical system that ignores any biologic affects other than photosynthesis. Secondly, even if it did operate in such a physico/organic system, it ignores any contribution by magnesium. Revelle and Emery (op. cit.) did not analyse for calcium or magnesium. Magnesium was ignored because it was thought to have little effect, and calcium was calculated.

When the salinity and alkalinity data from Heron Island are recalculated to express expected calcium carbonate variations (in the manner of Revelle and Emery, 1957, p. 704) figures are produced comparable with the Bikini and Guam data. However, the actual measurements of calcium variation indicates that this sort of calculation is misleading and the computations totally erroneous.

The present work shows that active solution of calcium and magnesium is occurring in the intertidal environment. It indicates also that reactions within the pools are complex, and that purely physico/chemical interactions are being outbalanced by reactions induced by other sources. These sources are thought to be biological for two major reasons, (a) the pools examined were floored by an algal community composed essentially of species of Kyrtuthrix, Calothrix, and Rivularia; (b) similar reactions were not observed in a control pool which simulated the inorganic environment, i.e. where the above algae were not present.

It is tempting to ignore the temperature-aided calcium complexing, which is especially a feature of the daytime regime. It is, however, pertinent to point out that complexing of calcium, in itself, may have an effect on the solution process in these environments. Concurring with Revelle and Emery (1957), if sufficient calcium in solution is complexed, then this would reduce the level of calcium actively to a level where the possible $CaCo_3$ concentrations times the activity coefficient is less than the solubility product, leading to solution. An appraisal of this possibility is at present in hand.

ACKNOWLEDGEMENTS

I wish to express my thanks to the members and staff of the Geology Department, University of Queensland; to Miss K. Lundgren, and Mr B. Radke for aid in the sampling at One Tree Island, and to Dr D.W. Kinsey who has been physically and mentally involved in most of the work presented. My gratitude is extended also to the Australian Research Grants Committee, and to the Australian Museum for logistic support and for permission to work on One Tree Island. Mrs M. Muir of the Baas Becking Geobiological Laboratories, undertook some of the atomic absorption analysis. Technical facilities were provided by the Bureau of Mineral Resources.

REFERENCES

DAVIES, P.J., & KINSEY, D.W., 1973 - Organic and inorganic factors in Recent beach rock formation, Heron Island, Great Barrier Reef: J. Sediment. Petrol., 43(1), 59-81.

FAIRBRIDGE, R.W., 1952 - Marine erosion: Seventh Pacific Sci. Congr. Proc., New Zealand. 3, 347-59.

GUILCHER, A., 1953 - Intertidal erosion on the Florida Keys: Marine Science of the Gulf and Caribbean Bull. 3, 59-69.

KEUNEN, Ph. H., 1933 - THE SNELLIUS EXPEDITION - GEOLOGY OF CORAL REEFS. Leyden, Brill, V.S. pt. 2, 126 p.

KEUNEN, Ph. H., 1950 - MARINE GEOLOGY: Wiley, New York, 568 p.

REVELLE, R., & EMERY, K.O., 1957 - Chemical erosion of beach rock and exposed Reef Rock: U.S. Geol. Surv. Prof. Paper 260-1. 699-709.

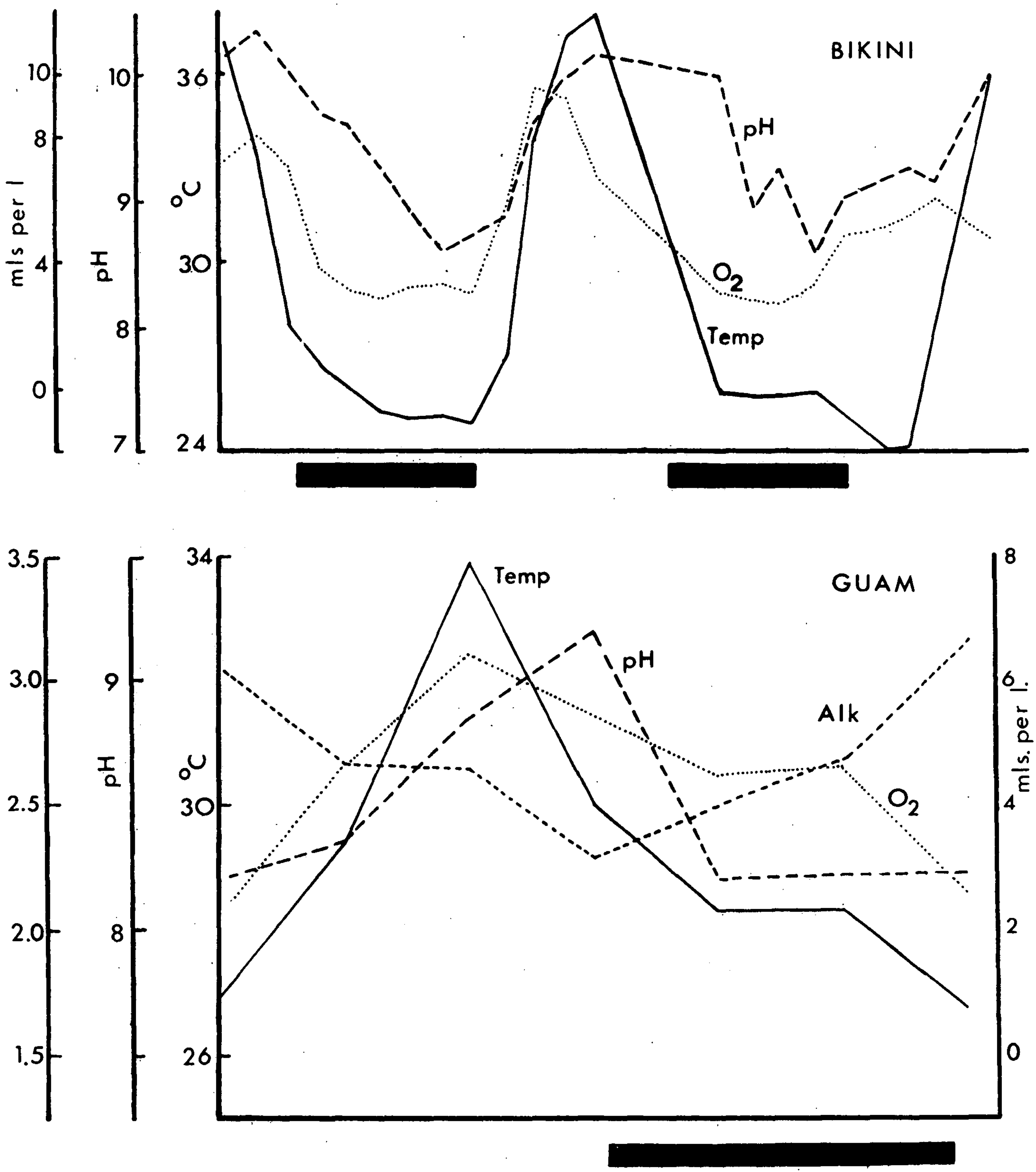

Fig. I Insitu measurements of chemical parameters made on water in intertidal pools at
A. Bikini.
B. Guam.
Black bars below graphs indicate night time periods. Alkalinity measurements at Guam expressed in milli-equivelents per litre.
(Data from Revelle and Emery 1957)

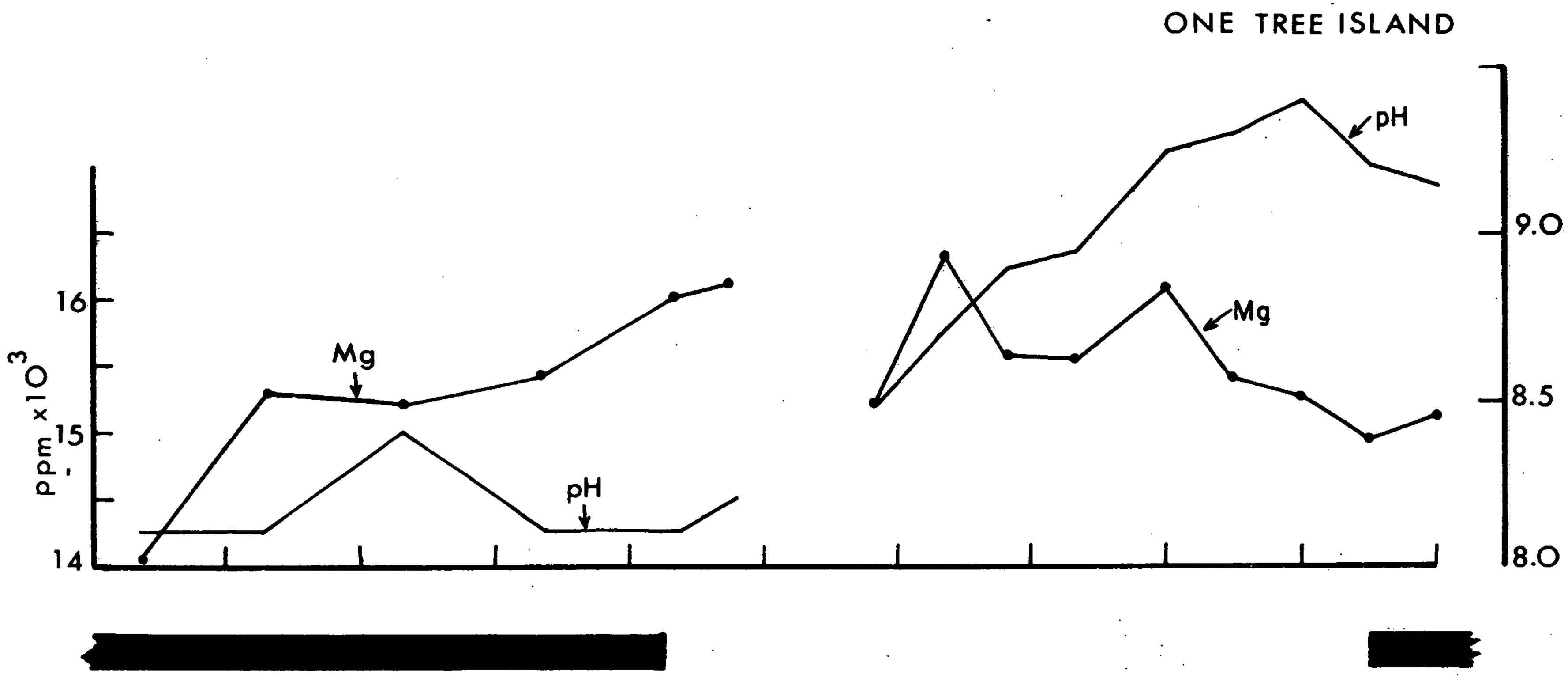

Fig. 2 Magnesium and hydrogen ion variation in intertidal pool at One Tree Island, Great Barrier Reef Province. Black bars below graphs denote night time periods.

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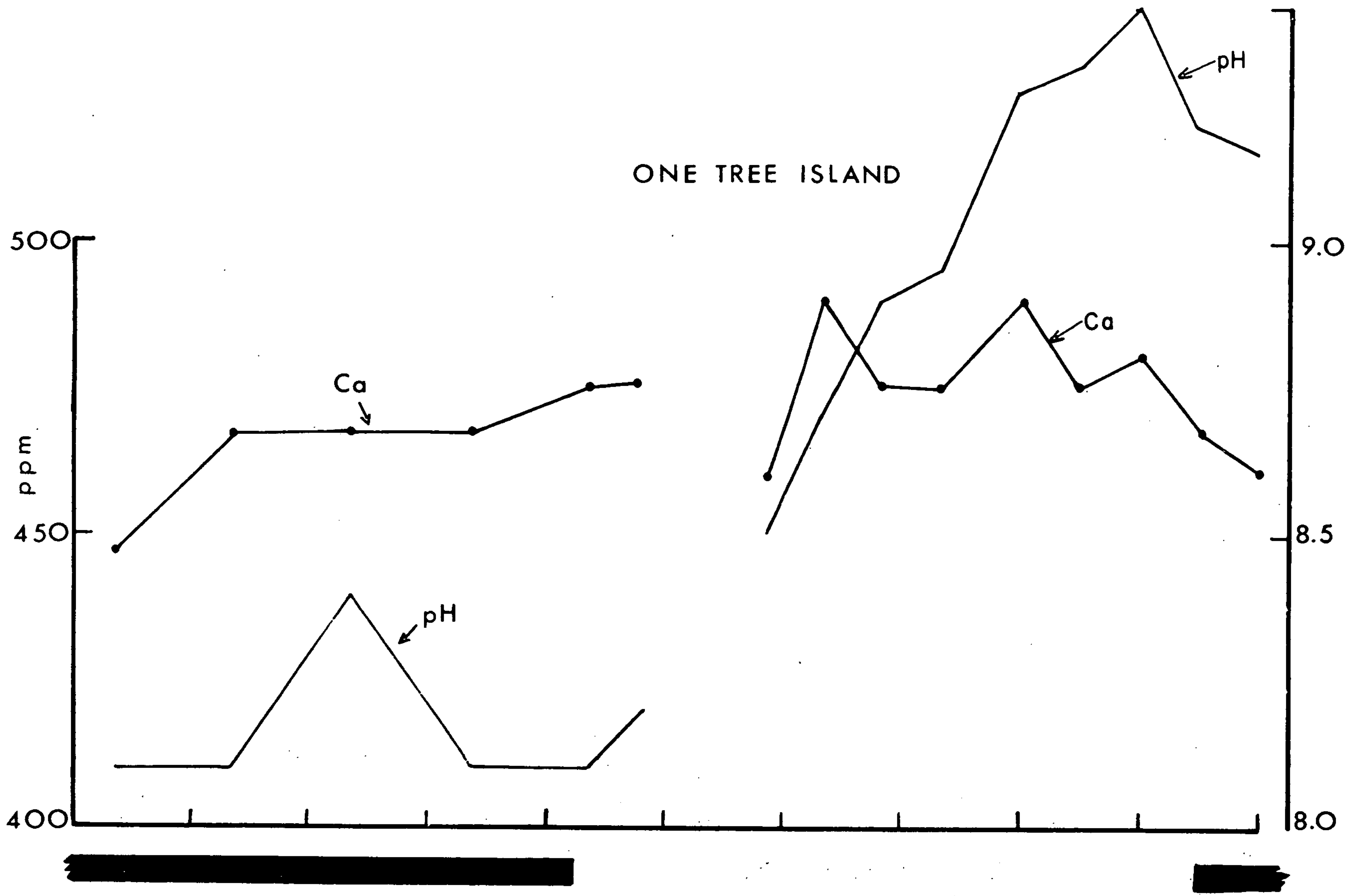

Fig. 3 Calcium and hydrogen ion variation in intertidal pool at One Tree Island, Great Barrier Reef Province. Black bars below graphs denote night time period.

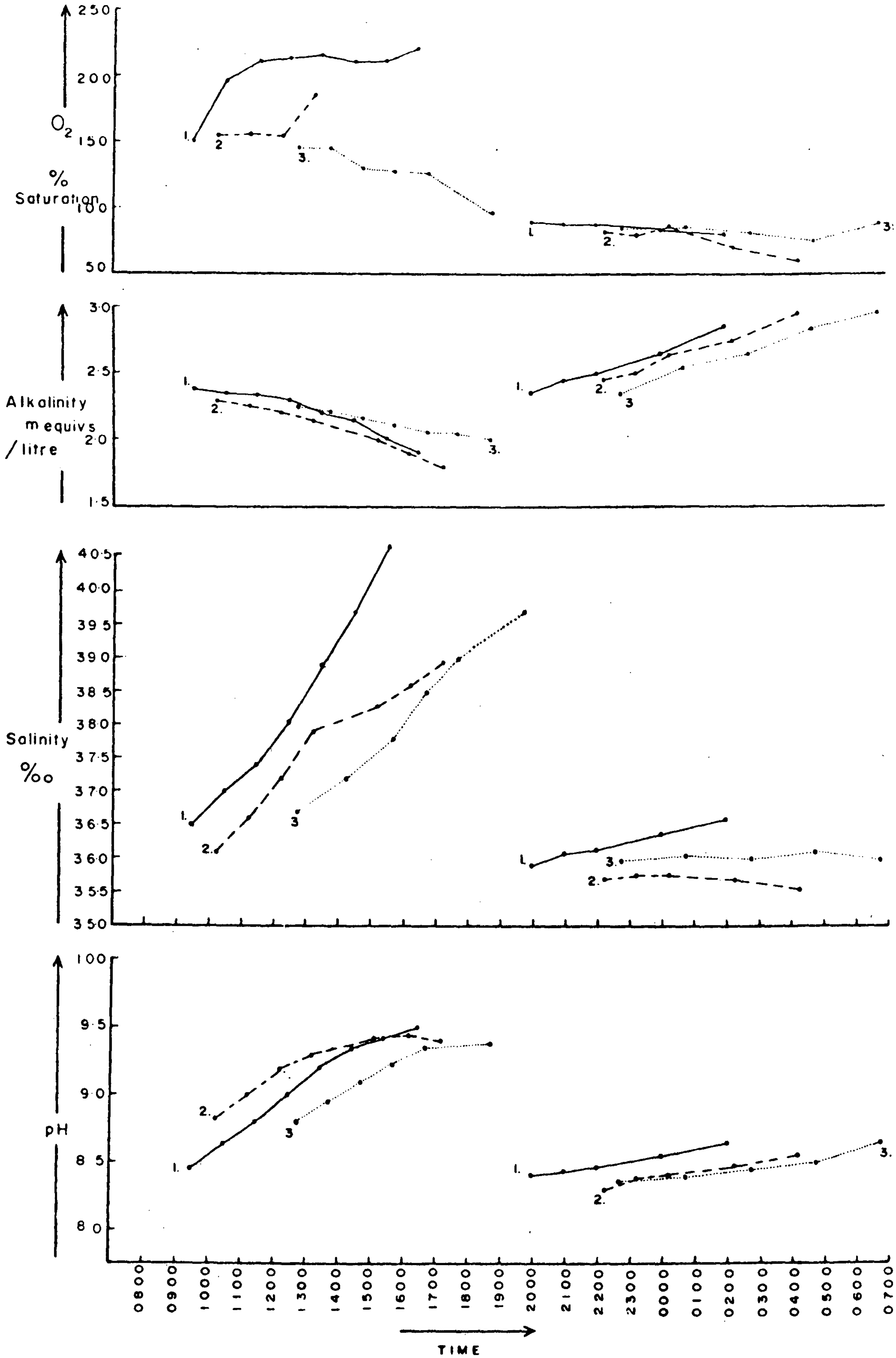

Fig. 4 Variations in oxygen, alkalinity, and hydrogen ion concentration.
Three experiments in intertidal pool at Heron Island, Great Barrier Reef Province
Gaps between graphs reflect tidal incursion.

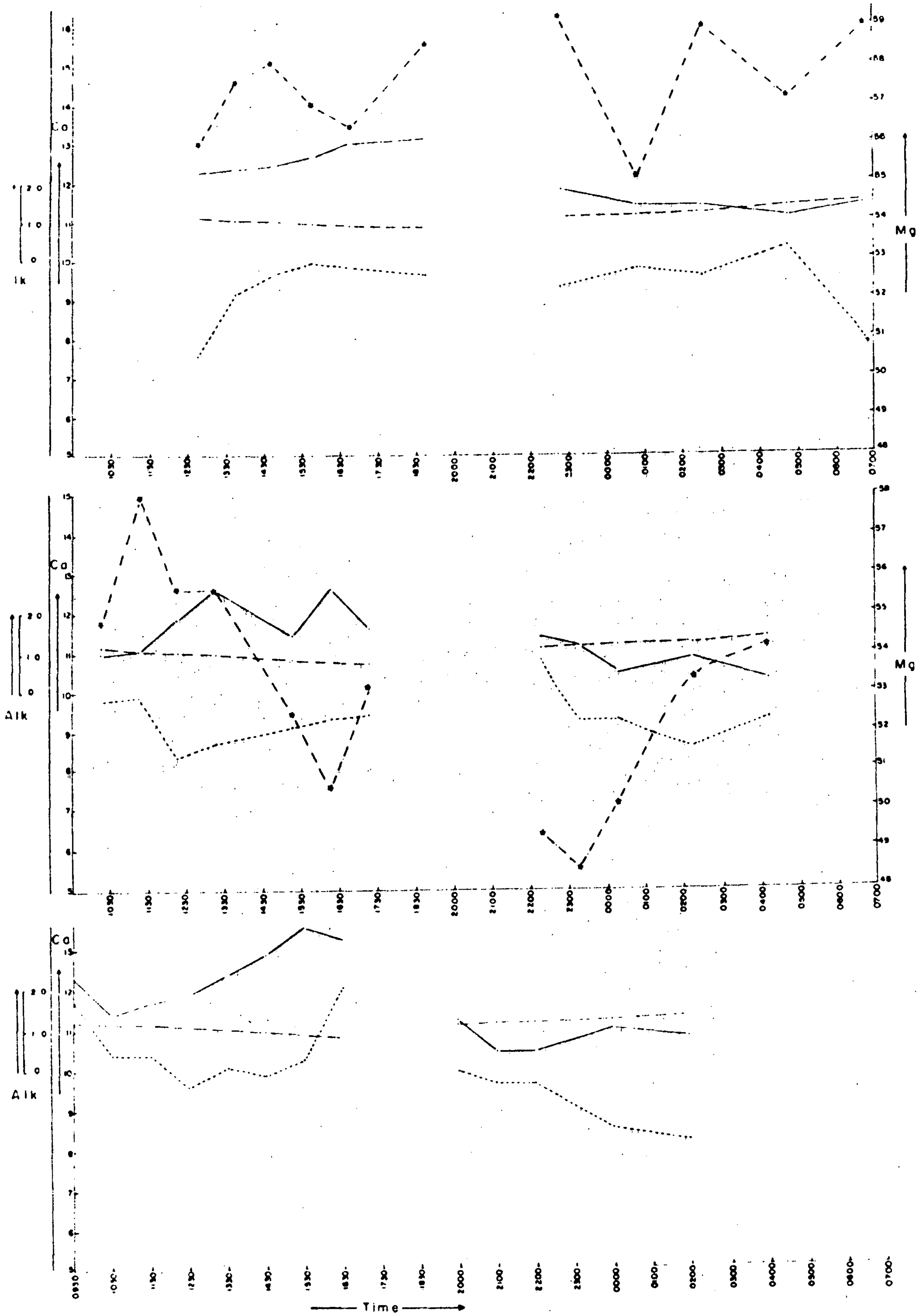

Fig. 5 Variation in Alkalinity/2 (thick broken lines), dissociated calcium (dotted lines), total calcium (full lines), and magnesium (starred point). Both calcium and magnesium are plotted as M.gram atoms/litre. Gaps in the graphs of the three experiments are due to tidal incursion. Data is for pool at Heron Island.

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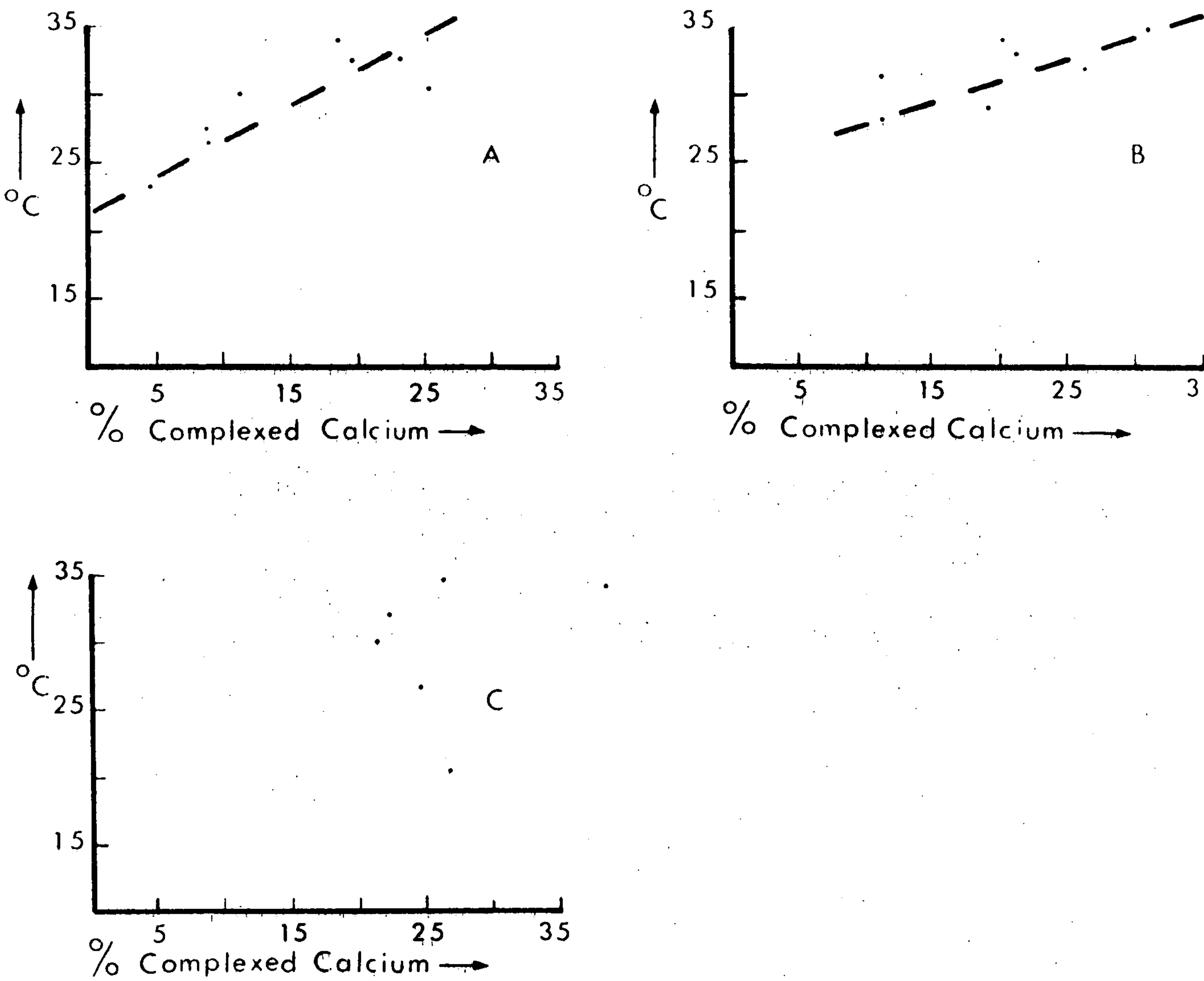

Fig. 6 Variation of percent complexed calcium as a function of temperature in three daytime experiments conducted in an intertidal pool at Heron Island.

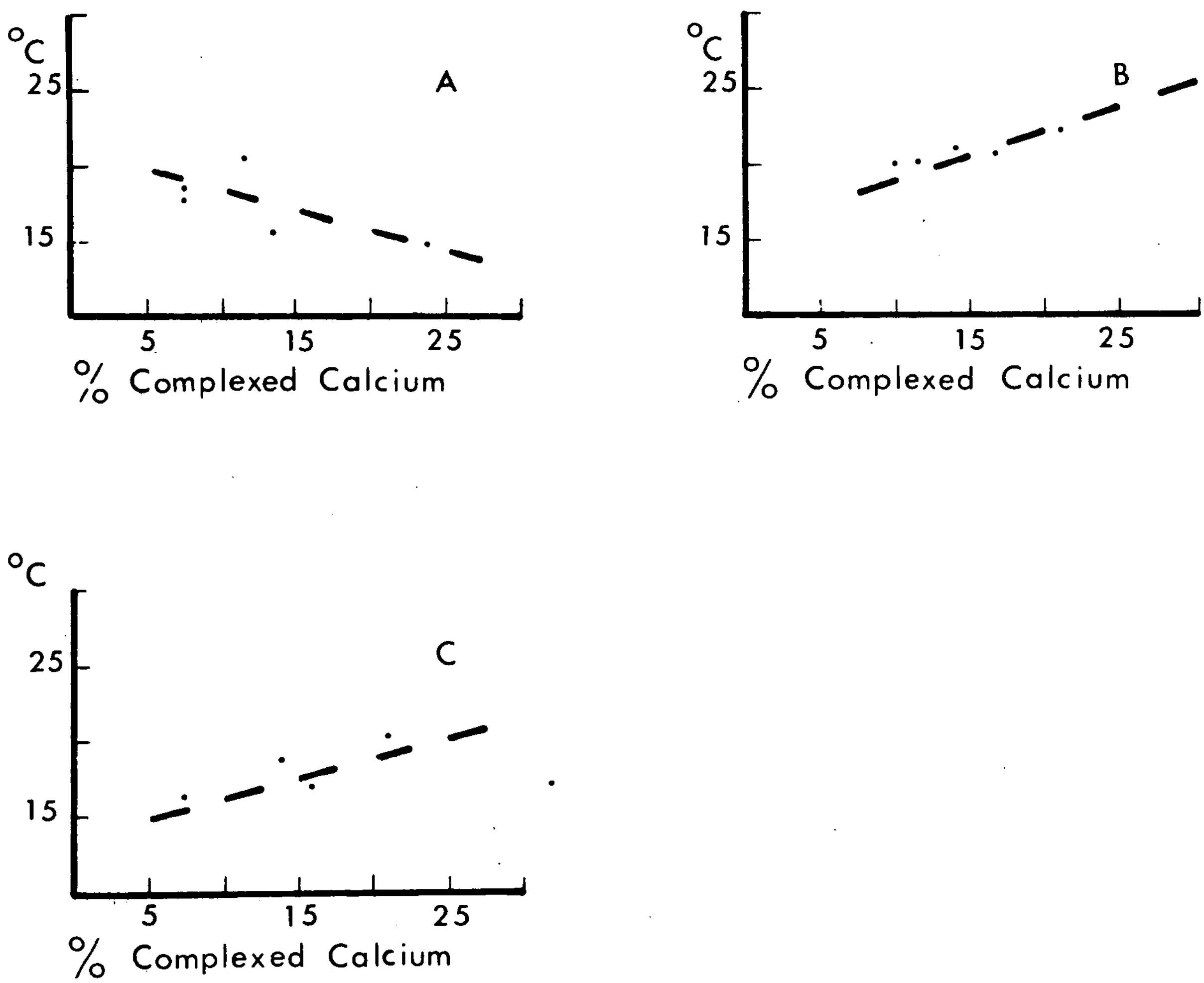

Fig. 7 Variation of percent complexed calcium as a function of temperature in three night time experiments conducted in an intertidial pool at Heron Island.