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LA THÈSE A ÉTÉ
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AN INVESTIGATION OF BIOEROSION AND INORGANIC
EROSION IN SHORE PLATFORM ROCK POOLS AT
IPPERWASH PROVINCIAL PARK, ONTARIO, CANADA

by



Donna Paraschak

A Thesis
submitted to the Faculty of Graduate Studies
through the Department of Geography
in partial fulfillment of the requirements
for the degree of Master of Arts at the
University of Windsor

Windsor, Ontario, Canada

1982

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ABSTRACT

Shore platform rock pools located at Ipperwash Provincial Park, Ontario, which is a northern latitude, fresh water, non-tidal environment, were studied for inorganic and organic solutional erosion. The rock pools were sampled on a 24-hour basis, through spring, summer and fall, for free CO_2 , pH, calcium concentrations, magnesium concentrations and alkalinity. A laboratory experiment which simulated spring and fall on site conditions was set up to observe differences between inorganic and organic solutional erosion.

The results of the multivariate analysis of variance test indicated that the seasons factor, which was interpreted as the biological factor, had the greatest influence on all of the variables but pH. To a lesser extent, the location of the rock pools and the 24-hour variation of temperature both affected the variability of free CO_2 , alkalinity, and calcium concentration. The partial correlation analysis between air temperature and the dependent variables sampled on site showed a negative, moderate strength relationship with alkalinity and magnesium, and a negative weak relationship with free CO_2 and calcium.

Overall, biological solutional erosion was more effective as an erosional factor than the inorganic factor, and together they are not important in the development of this northern latitude fresh water, non-tidal environment

shore platform. Although the biological factor needs to be studied in more depth, and there is a need for a more direct method of erosion measurement such as the use of a microerosion meter, this investigation did show that organic solutional erosion does occur, but is only a minor component in the development of a northern latitude fresh water, non-tidal environment, shore platform.

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Lastly, I would like to thank my mother for putting in the long hours typing my thesis and my father, Vicky, Carol, Linda, Michael and Daryl for their unfailing support through it all.

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CHAPTER ONE

INTRODUCTION

1.1 The Nature of the Problem

A shore platform can be generally understood to refer to a horizontal or gentle sloping rock surface (0 to 3 degrees) extending from the base of a cliff to the water's edge, generally being less than 100 m in width. Although the process of platform development has been a controversial subject, mechanical wave erosion and weathering are generally considered the dominant processes operating on platforms. Of recent interest is the role of solutional erosion of shore platforms--both inorganic and organic.

Little is known on the contribution of inorganic and organic solutional erosion to shore platforms development. In previous studies, it has been established that bioerosion does occur in rock pools in saline, tidal environments (Emery 1946, Schmalz and Swanson 1969, Schneider 1976). The processes of respiration and photosynthesis of plants and animals are responsible for disequilibrium in ionic content of the water, causing calcium precipitation or erosion. Bioerosion has been defined as the removal of lithic substrate by direct organic activities (Neumann 1966 in Trenhaile, 1980a). Inorganic erosion, which comes about by temperature variation control on capacity of the water to dissolve carbon dioxide, is also

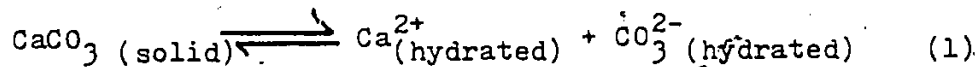
thought to occur. Since most studies on this type have been situated in warm, tidal, salt water environments, or in laboratory situations, it would be of interest to observe the amount of erosion by solution in a northern non-tidal fresh water environment. Another important question to consider is, what is the seasonal effect of inorganic and organic erosion? The quantification of the effects of bioerosion and inorganic erosion on rock pools found on shore platforms will further the understanding of processes occurring in shore platform development.

1.2 Review of Literature

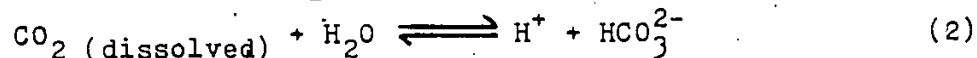
Mechanical wave erosion and weathering are generally considered to be the dominant processes operating on platforms. But the destruction of coastal limestones in areas where mechanical wave action is judged to be ineffective, has long been a contentious issue (Trenhaile, 1980a). Even though much work has already been done on the process-response relationships of platform morphology (platform gradient and cliff platform junction), and the morphogenic environment (tidal range, fetch, tidal levels), very little work has occurred on the destruction of limestone shore platforms by chemical solution and biological activity. Recent work suggests that whereas platform gradient is directly related to tidal range, width is largely a function of the erosion rate (Trenhaile, 1980a). Solutional erosion can be effected by organic and inorganic processes. Calcium minerals

are of primary interest when discussing erosion rates of limestone shore platforms. The solution of calcium is determined by the rock type, the wave environment, the biomass present, and the temperature variations.

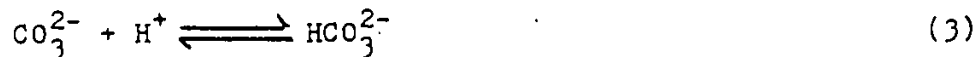
In a three-phase system (air-water-rock), when limestone is the rock involved, the following processes occur (King, 1963). Between the rock and water:



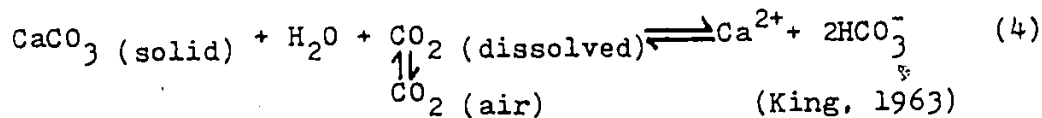
With respect to the CO_2 in the air and the water interface:



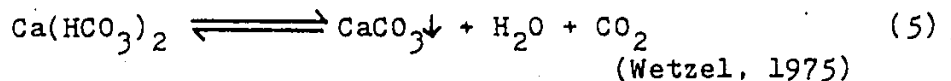
Then the carbonic ions from the dissolved limestone react instantaneously with the hydrogen ions to produce bicarbonate ions.



Since the last reaction upsets the equilibrium of equations (1) and (2), more limestone goes into solution to keep the product $[\text{Ca}^{2+}] [\text{CO}_3^{2-}]$ constant and more dissolved CO_2 reacts with the water to produce more carbonic acid (H_2CO_3). This last phase causes a disequilibrium to exist between the CO_2 partial pressure of the air and water, so that a diffusion of CO_2 from the air to the water takes place, causing further solution of limestone through the chain of events. The complete process of limestone corrosion may be simplified in the following way:



The bonding in CaCO_3 is strong. If a H^+ ion drifts within electrical sensing distance of CaCO_3 , the H^+ ion gets a pull from the negatively charged CO_3 . Then CO_3 comes out and bonds with the H^+ ion to produce HCO_3^- (bicarbonate ion). Then Ca^{2+} floats out into solution. The HCO_3^- in water stays in this state or encounters another H^+ ion floating around to form H_2CO_3^0 (carbonic acid molecule). The HCO_3^- ion may also dissociate into H^+ and CO_3^{2-} because the bonding is weak. The possible species in solution because of these processes are H^+ , Ca^{2+} , HCO_3^- , CO_3^{2-} , OH^- , and H_2CO_3^0 . Each reaction proceeds at a characteristic rate, the overall rate being controlled by the slowest reaction, which is the hydration of CO_2 gas in this three-phase system. Rates are proportional to the concentration of reactants, reaching a state of dynamic equilibrium for the given set of physical conditions imposed on the system (Ford and Gascoyne, 1978). If solution in equilibrium loses a portion of the CO_2 required to maintain the equilibrium, CaCO_3 will precipitate until the equilibrium is reestablished by the formation of CO_2 :



The controls imposed on the system are temperature, CO_2 concentration, pressure, and the additional H^+ concentration. Henry's Law states:

The total amount of limestone which can be dissolved at saturation equilibrium per unit volume of water is overall a direct function of the PCO_2 of the air with which the water is in contact and an inverse function of the latter's control of the dissolved CO_2 saturation equilibrium.

(King, 1963)

Temperature therefore, exerts control over inorganic solution. Carbon dioxide is more soluble in waters of lower temperatures, so that in northern climates, where water temperatures vary greatly in a year, a diurnal cycle and a seasonal rhythm due to temperature variation would be expected.

In free atmosphere, the mean PCO_2 is 0.03% of volume. Solubility is proportional to the partial pressure of CO_2 ; the higher the partial pressure, the greater the solubility. The concentrations of CO_2 are much higher in soil and snow. The freezing and thawing of a snow surface leads to a greater concentration of CO_2 (approximately 0.1% of CO_2), so that when rain and meltwater pass through the snow they become highly charged with CO_2 . The erosional effect of these highly charged waters on the limestone is another inorganic solutional effect. Corbel (1959), basing his arguments upon the fact that a gas (CO_2) is more soluble at lower than higher temperatures, thought that snow was a more effective solvent of limestone than rainwater. This view has recently been challenged by the work of Miotke (1968) in the Pyrenees, which indicates.

that snow is both a slower and a smaller dissolver of limestone than rainwater (Sweeting, 1969).

The rate of solution is greater with greater turbulence or agitation of the water because the products of the reactions are removed from the solid--liquid interface. The length of time that CO_2 --charged water is in contact with the rock face affects the amount of solution accomplished, as well as the presence of chemical impurities. For example, the presence of lead or iron sulphides increases their solution due to oxidation of the sulphides to H_2SO_4 , while Na and K are considered to increase the solubility of calcite because of the ion pair effect. Recently, Terjesen and others have indicated that small traces of heavy metals such as lead, scandium, copper and manganese have an inhibiting effect on the solution of calcite (Sweeting, 1973). There is also the potential enrichment in CO_2 content from industrial pollution (Wetzel, 1975). Another control on solution is the common ion effect, which acts as a depressant to calcium solution. When an ion common to the solid is introduced from a foreign source, there is a reduced amount of room for Ca from CaCO_3 to come from, which depresses the solubility of CaCO_3 . The presence of Mg^{2+} in solution for example, reduces the saturation level with respect to calcium carbonate by forming ion-pairs which hinder the activity of the carbonate ions (Trenhaile, 1980a). Chemical effects on the solution of limestone are not thoroughly understood.

The porosity and the permeability of the limestone is important in regulating the rate of solution, as the pore space determines the amount of water the rock can take up, and permeability determines the ease with which water can pass through the rock. The orientation of the grains in a limestone affects its solubility, solution being more effective in limestones in which there is a diverse rather than a preferred orientation of the crystals (Sweeting, 1969). In addition, the rougher the rock surface (greater the surface area), the more soluble the rock.

The hardness of water is due to alkaline earth metal content, calcium and magnesium being the principle alkaline earths in natural waters. The hardness is expressed in terms of alkalinity, which can be expressed as the calcium carbonate and magnesium content of the sample under test. For a given concentration of calcium bicarbonate and magnesium bicarbonate in solution, there is a certain quantity of free CO_2 whose presence is necessary to avoid the decomposition of the bicarbonates, or the precipitation of the corresponding carbonates. This free CO_2 is known as the equilibrium CO_2 , which if the total carbonic acid in the water is greater than the amount of equilibrium CO_2 , the excess is the aggressive CO_2 which permits the solution of more carbonates (Douglas, 1968). Such measurements of Ca and Mg are only an indirect measure of the rate of limestone solution because they record the amount of

dissolved Ca and Mg in parts per million present in the waters, and do not record directly the lowering of a limestone surface. It has been suggested that nocturnal falls in temperature and the production of CO_2 by respiration of pelagic biota at night (not being balanced by photosynthetic uptake of CO_2) will enhance the solution of calcite at night (Trudgill, 1975). Indeed, Ranson (1955, 1959) considered that the dissolution of limestones by sea water is impossible without the intervention of biological processes (Trenhaile, 1980b). Schmalz and Swanson (1969) stated that field and laboratory observations have established the occurrence of diurnal cycles in pH, dissolved CO_2 , and carbonate saturation of natural marine waters in a wide range of tropical and subtropical environments. They believe that the cycles are the result of changing rates of the opposing reactions--respiration and photosynthesis. In a study of biological and inorganic factors causing destruction of a limestone coast on the Northern Adriatic, Schneider (1976) concluded that inorganic solution of carbonate could not be responsible for the destructive relief forms, but is significant in the destructive processes only as a preparation of the rock surface for colonization. He felt that the destructive processes are of biological origin.

The following processes take place in the water of a rock pool which is densely populated with epi and endolithic

microflora and fauna (Schneider, 1976). By day photosynthesis is the dominant process whereby plants use CO_2 which raises the pH and results in the removal of CO_2 and HCO_3^- . The alkalinity is then reduced. At night, the dominant process is respiration, which causes an addition of CO_2 to the water, lowering the pH, and raising the alkalinity.

The reactions can be described as shown below:

At pH values above 8.0,



(Schneider, 1966)

A majority of the carbon in freshwater systems occurs as equilibrium products of carbonic acid.

$$\text{total CO}_2 = \text{CO}_2 + \text{HCO}_3^- + \text{CO}_3^{2-} \quad (9)$$

(Wetzel, 1975)

Figure 1 shows the proportion of CO_2 , H_2CO_3 , HCO_3^- and CO_3^{2-} in solution at different pH values. Below pH 5, only free CO_2 is of any quantitative importance, and between pH 7 and pH 9, bicarbonate is of the greatest significance. Above pH 9.5, carbonate begins to be of importance (Wetzel, 1975).

Free CO_2 is utilized by nearly all algae and larger aquatic plants, but many algae and aquatic vascular plants are capable of assimilating bicarbonate ions when free CO_2 is in low supply, and HCO_3^- is abundant. A few species

of algae require HCO_3^- and cannot grow with free CO_2 alone. There is no clear evidence that algae or higher aquatic plants assimilate CO_3^{2-} directly as a carbon source, although it has been implicated strongly in growth at very high pH values (Wetzel, 1975).

Rock pools are attributed to organic erosion, although there may be an initial inorganic stage (Emery, 1946). Organisms are arranged according to the frequency of moistening; the average frequency of wetting decreasing with increasing distance from the sea and height above sea level. Schneider (1976) found that there is a corresponding decrease in the intensity of the biological corrosion by the boring algae, fungi and lichen and of the dependent abrasive activity of the grazing gastropods. He also found an approximately five-fold increase in the erosion rates in the pools compared to their surroundings.

Emery (1946) found a diurnal cycle of pH in 21 rock pools in La Jolla California. For example, the pH rose to 9.00 in the afternoon and decreased to 7.56 just before sunrise, in contrast to the normal variation in the open sea of between 8.0 and 8.2. He attributed the change in pH to the diurnal variation of CO_2 in the tide pools from 43.3 mg l^{-1} in the afternoon to 107.3 mg l^{-1} just before sunrise. He concluded that at night the plants and animals may have liberated more CO_2 in respiration than the water analysis indicated, as the remainder would have escaped into the air. He found that during the day, due to high

temperatures, high pH and low CO_2 content, much of the CaCO_3 is precipitated. At night, due to low temperatures, low pH, and high CO_2 content, the calcium of water combines with bicarbonate ions, so that the water is unsaturated with calcium. Some of the CaCO_3 of the rock cement is then converted to $\text{Ca}(\text{HCO}_3)_2$ which dissolves in the water. Once the cement between sand grains is removed, the grains are easily loosened and washed away by waves and, as in this case, ingested by snails (Emery, 1946).

Field and laboratory experiments conducted by Schmalz and Swanson (1969) demonstrated that the amplitude of diurnal changes is related to the volume of water in the aquaria. This presumably reflects the difference in biomass, and suggests that smaller diurnal changes would be observed in large open waters. In the laboratory, systems from which macro-organisms were excluded did not exhibit the cycles, which indicates that the cycles resulted from changing rates of metabolic production and photosynthetic extraction of CO_2 in the affected water (Schmalz and Swanson, 1969).

The types of organisms causing erosion are basically borers and grazers. The process by which organisms bore into substrates, or otherwise bring about their destruction, is a contentious issue (Trenhaile, 1980a). Microflora, such as algae, fungi, lichens, and bacteria, and fauna which lack hard parts may erode by purely chemical means, but many fauna use a combination of mechanical and chemical

means, initially weakening the rock by secreted fluids, followed by abrasion by teeth, bristles, hooks, shields, valvular edges, and other hard parts (Trenhaile, 1980a).

Epilithic algae inhabit the rock surface, whereas endolithic algae penetrate the rock to a depth of several millimetres, both contributing to rock destruction. Rock borers directly remove rock material, rendering the residual mass much more susceptible to break down by destructive processes, and they also enhance a rock environment for algal colonisation and increase the rock surface which is exposed to other physical and chemical processes. By developing aerobic conditions in rock pools, these grazers make them suitable for colonisation. Grazing on epilithic microflora and the ends of endolithic forms, commonly results in mechanical rasping of the rock surface, which has been weakened by biochemical processes associated with the microflora, or by the penetration of their filaments into the rock (Trenhaile, 1980b). Considerable erosion may be caused by the consumption of epi-endolithic or shallow endolithic forms. An added complication is that protective marine organisms exist in the lower intertidal and upper subtidal zones, which form organic crusts which protect the underlying substrate from wave and physio-chemical attack. For example, Schneider (1976) found that rock pool floors were densely populated by epi- and endolithic algae, fungi and lichens which prevented any direct exchange between the water and the

carbonate substrate, and consequently inhibits inorganic dissolution.

Little is known about the biological activity contributing to erosion of shore platforms. Generally the activity of the organisms is determined by type, population density, animal size, depth of algal penetration, the effect of grazers, the environment, the characteristics of the substrates, rock hardness, mineralogy, grain size, and porosity (Trenhaile, 1980a).

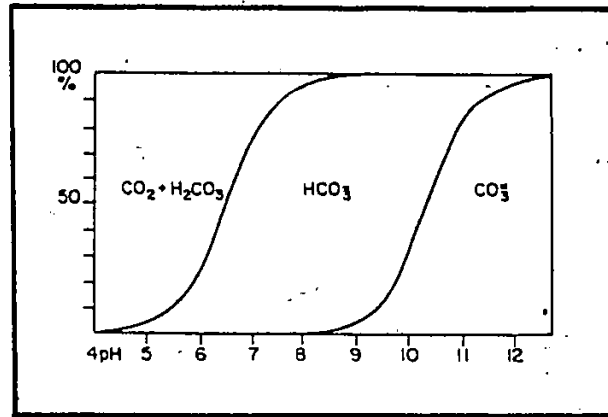
Phytoplankton is the algae of the open water of lakes, consisting of the assemblage of small plants that have no, or very limited powers of locomotion, and are more or less subject to distribution by water movements (Wetzel, 1975). Each of the species populations coexist in the phytoplankton according to physical, chemical and biotic requirements. Factors such as inorganic and organic nutrient supply, herbivorous predation, parasitism, self-shading, temperature, light and seasonal variations affect population type and distribution.

The growth of algae and photosynthetic rates are directly related to light intensity (Wetzel, 1975). For example, on a seasonal basis, there is a preponderance of diatoms at colder temperatures and an increasing diversity of algae as the water warms. Further, blue-green algae (Cyanophyta) as a group are generally much more tolerant of higher temperatures than other algae. Some algae, such as Skeletonema adapt to lower temperatures by increasing

enzyme concentrations so that the same rate of photosynthesis is achieved per given light intensity at high and low temperatures (Wetzel, 1975). Although not greatly affected, rates of respiration do increase with increasing temperatures. On bright days it is very common to observe a distinct depression of rates in situ photosynthesis near the surface. As far as diurnal changes in phytoplanktonic rates are concerned, most studies have shown that diurnal periodicity of photosynthesis often is not proportional to the daily insolation curve. The maximum photosynthetic rates occur in the morning hours, followed by a reduction at midday and sometimes recovery in the afternoon. This diurnal periodicity is particularly acute at the surface, and undoubtedly is partly related to photoinhibition and increased rates of extracellular release of organic photoassimilates (Wetzel, 1975).

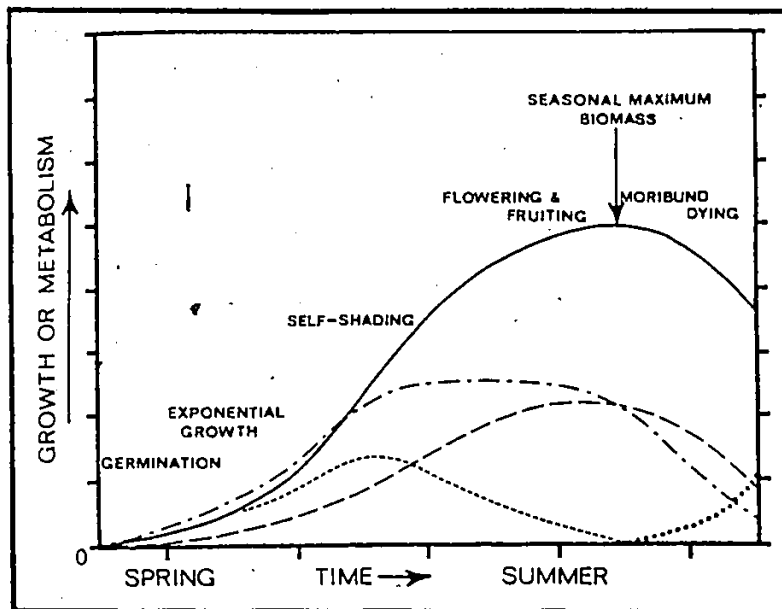
A seasonal periodicity in the biomass of phytoplankton occurs in temperate fresh waters. During winter conditions of low light and temperatures, growth is greatly reduced or negligible. Under improved spring light conditions, phytoplankton numbers and biomass greatly increase to a spring maximum, even though water temperatures are still low. This spring maximum can begin under the ice in late winter and often consists predominately of diatoms such as Asterionella, which are adapted to low temperatures (Wetzel, 1975). This maximum lasts less than three months and is followed by a period of low biomass that may extend

FIGURE 1: PROPORTIONS OF CO_2 (AND H_2CO_3), HCO_3^- , AND CO_3^{2-} IN SOLUTION AT DIFFERENT pH VALUES



(Source: Buch in Wetzel, 1975)

FIGURE 2: GENERALIZED GROWTH AND METABOLIC PATTERNS FOR A TYPICAL ANNUAL AQUATIC MACROPHYTE



LEGEND

- biomass
- current gross productivity
- - - current net productivity
- - - current respiration rate
- death losses

(source: After Westlake, in Wetzel, 1975)

throughout the summer. This decline is the result of physical and biotic factors, such as a reduction of nutrient availability, and self-shading by the organisms which reduce the light flux into the rock pool. A secondary maximum occurs in the autumn which is not as strongly developed as the spring maximum. In more eutrophic lakes of the temperate region, the summer minimum is often brief and phases into a late summer profusion of blue green algae that persists into the autumn until the disruption of thermal stratification begins. In oligotrophic lakes, the second maximum in autumn is predominantly diatoms. Predation of phytoplankton by animals such as the microcrustacea is considered a significant factor in the seasonal decline of the algae population (Wetzel, 1975). Although it is difficult to make generalizations from lake to lake, the successional season periodicity of phytoplanktonic biomass is reasonably constant from year to year, and the seasonal amplitude of changes in phytoplanktonic numbers and biomass is usually very great, on the order of a thousandfold in temperate and polar fresh waters (Wetzel, 1975).

Aquatic macrophytes are found in the littoral zone. This classification refers to macroscopic forms of aquatic vegetation and encompasses macroalgae, mosses, and ferns adapted to the aquatic habitat and the true angiosperms. Submerged macrophytes consists of a heterogeneous group of plants that include the following (Wetzel, 1975):

^

1) filamentous algae that may become pseudo-attached to the substrata of the littoral zone in massive mats; 2) certain macroalgae; 3) mosses; 4) totally submerged ferns; and 5) vascular submerged macrophytes. Their leaves have a tendency to elongation which maximally uses the reduced available light and maximizes the efficiency of gaseous exchange and nutrient absorption. Also, their form has a mechanical advantage in water movement.

As with phytoplankton, the rates of photosynthetic carbon fixation in submerged macrophytes is correlated with the intensity of solar radiation on a daily basis, exhibiting the highest rates of photosynthesis in the morning and a midday and afternoon depression of carbon fixation. The generalized growth and metabolic patterns for a typical annual aquatic macrophyte has an annual component as well (Fig. 2). Although aquatic macrophytes can assimilate bicarbonate ions as a carbon source supplementary to carbon dioxide, the physiological mechanisms of bicarbonate uptake are not fully understood. However, among certain submerged angiosperms the process is as follows (Wetzel, 1975): carbon dioxide and bicarbonate ions are taken up through both leaf surfaces and the CO_2 is fixed; then, hydroxyl ions equivalent to the amount of bicarbonate used pass out through the adaxial leaf surface; a quantity of cations, primarily calcium, which is equivalent to the amount of bicarbonate taken in through the abaxial leaf surface, is transported from the abaxial to the adaxial

leaf surface, thereby achieving a charge balance; and the passage of bicarbonate, calcium, and hydroxyl ions to the adaxial leaf surface usually results in precipitation of CaCO_3 on the surface.

In rock or tidal pools of warmer, tidal, saline environments, diurnal variations in pH, free CO_2 , alkalinity, and calcium and magnesium ion concentrations have been observed. Although these rock pools may be started by inorganic erosion, they are thought to be largely developed by organic erosion. It would be of interest to observe whether bioerosion and inorganic erosion processes occur on shore platforms in a fresh water, non-tidal, northern environment. If bioerosion and inorganic erosion do take place, "it is of interest to know whether basic-forming processes have an annual, as well as a diurnal cycle" (Emery, 1946). The organisms of the phytoplankton and aquatic macrophytes undergo changes in type, number and biomass through the seasons. Diurnal changes in pH, free CO_2 , alkalinity, calcium and magnesium have been attributed to diurnal processes in biological processes, which result in the erosion of limestone at night. The relative contributions of inorganic and organic solution in shore platform rock pools have not been established in a fresh water environment. Also, the annual cycle of bioerosion and inorganic erosion of rock pools is of interest. A study of these aspects would add to the knowledge of shore platform development.

CHAPTER TWO

STUDY AREA

The area under study is a shore platform located on the east shore of Lake Huron at Ippeewash Provincial Park, Ontario, Canada ($81^{\circ}9'0''\text{W}$, $43^{\circ}2'5''\text{N}$) (Fig. 3). It is approximately 9m wide and 90 m in length. It is located in a fresh water northern environment where there are four distinct seasons--winter, spring, summer and fall. The area is snow covered for approximately six months of the year (Table 1). The rock type is a grey argillaceous limestone and it is part of the youngest unit of the Devonian formation, the Ippeewash Member, exposed as a bedrock outcrop in Ippeewash Provincial Park (Ontario Division of Mines, 1976). The actual mineral content is unknown, but the percentage of calcite and dolomite was determined by a quantimetric gasometric method devised by Dreimanis (1962).

Bioerosion experiments have never been undertaken in such an environment, and it is of interest to observe the daily variation in pH, free CO_2 , alkalinity, Ca, and Mg content due to temperature and biomass differences in the rock pools. This environment's seasonal climatic component makes it ideal for a seasonal study of bioerosion and inorganic erosion.

Winter samples were not taken because the area is snow and ice covered in winter. However, in the other

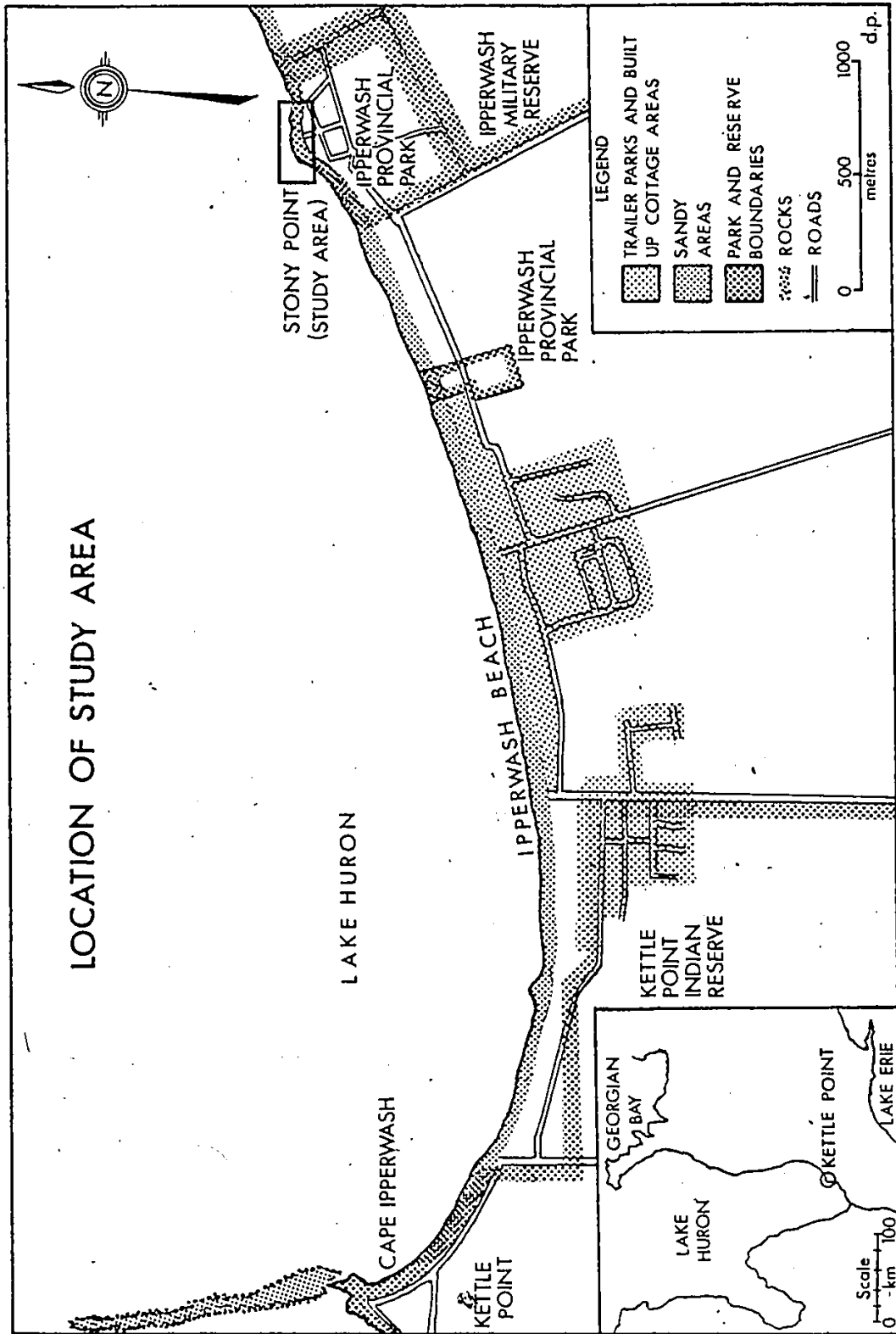


Fig. 3

MEAN MONTHLY TEMPERATURE AND TOTAL
RAINFALL AND SNOWFALL, SARNIA, 1981

MONTH	MEAN TEMP (°C)	TOTAL RAINFALL (mm)	TOTAL SNOWFALL (cm)
JAN	- 7.5	0	26.5
FEB	- 2.5	64.2	18.6
MARCH	1.5	18.4	10.7
APRIL	8.3	97.2	TR
MAY	11.2	72.7	0
JUNE	18.3	76.0	0
JULY	21.2	64.2	0
AUG	19.8	96.1	0
SEPT	15.8	230.1	0
OCT	7.7	101.5	TR
NOV	4.3	39.3	1.0
DEC	- 2.5	16.9	33.2

TR = trace
(Source: Monthly Meteorological
Summary, 1981. Sarnia, Ontario)

Table 1

seasons, fluctuations in pH, alkalinity, free CO_2 , Ca and Mg ion concentrations due to biomass and inorganic solution were studied, and used to indicate the contribution of these two processes towards platform development in a northern environment.

CHAPTER THREE

THEORETICAL CONSIDERATIONS

3.1 Model and Hypotheses

The rock pools on the shore platform being studied can be thought of as process-response systems, within which biological processes and temperature variations cause changes in the water chemistry that result in erosion at night and precipitation of CaCO_3 during the day. Processes within these rock pools will vary spatially and temporally. With respect to the spatial frame, rock pools from different platform environments were sampled. With respect to the temporal frame, sampling took place over a 24-hour period and seasonally--late spring, summer and fall. As well as observing the type and quantity of biomass from rock pool to rock pool, and over the seasons, samples of temperature, pH, free CO_2 , alkalinity, and Ca content, and Mg concentrations were determined.

The most direct method of determining whether CaCO_3 is precipitated or dissolved by the water in the basins would be to measure the change of calcium ion in the water samples collected at intervals during the day and night (Emery, 1946). Schneider stated in his paper that the level of CaCO_3 saturation can be evaluated from the pH, temperature, Ca-content and titration alkalinity (1976). Diurnal pH variation may be monitored and related more or less directly to the diurnal CO_2 cycle, and to organic

productivity (Schmalz and Swanson, 1969). In order to discover just how important biological and inorganic erosion are in rock pools, the following relationships were studied.

During daylight hours plants are taking in CO_2 for photosynthesis, which lowers the CO_2 content of the rock pool water, which raises the pH and results in a reduction of the alkalinity, and the Ca and Mg content. At night, when respiration is the dominant process, CO_2 is given off, raising the CO_2 content of the water, lowering the pH, and raising the alkalinity and the Ca and Mg content of the pool water. At the same time that biological activities are affecting the pool water, temperature will affect the pool water chemistry. In the day time when temperatures are relatively higher, the CO_2 content of the water will diminish, raising the pH and lowering the alkalinity, and the Ca and Mg content. During the night, the lower water temperatures allow more CO_2 to dissolve in the water, so that the CO_2 content of the water rises, the pH falls, and the alkalinity, and the Ca and Mg content rises (Fig. 4). On a daily basis, diurnal cycling of the variables mentioned was expected.

In late spring, after the ice has broken up, it was expected that a biomass maximum will be present in the rock pools, consisting basically of diatoms. The biomass maximum would be indicated by a large diurnal fluctuation

A Model of Inorganic, Organic and the Seasonal Effects on the 24-Hour
Variation of free CO₂, pH, alkalinity, and Calcium and Magnesium Concentrations

	LATE SPRING		SUMMER		FALL	
	DAYTIME	NIGHTTIME	DAYTIME	NIGHTTIME	DAYTIME	NIGHTTIME
Inorganic Factor	CO ₂ content↑ pH↓ alkalinity↑ Ca content↑ Mg content↑	CO ₂ content↑ pH↓ alkalinity↑ Ca content↑ Mg content↑	CO ₂ content↑ pH↓ alkalinity↑ Ca content↑ Mg content↑	CO ₂ content↑ pH↓ alkalinity↑ Ca content↑ Mg content↑	CO ₂ content↑ pH↓ alkalinity↑ Ca content↑ Mg content↑	CO ₂ content↑ pH↓ alkalinity↑ Ca content↑ Mg content↑
Organic Factor	CO ₂ content↑ pH↓ alkalinity↑ Ca content↑ Mg content↑	CO ₂ content↑ pH↓ alkalinity↑ Ca content↑ Mg content↑	CO ₂ content↑ pH↓ alkalinity↑ Ca content↑ Mg content↑	CO ₂ content↑ pH↓ alkalinity↑ Ca content↑ Mg content↑	CO ₂ content↑ pH↓ alkalinity↑ Ca content↑ Mg content↑	CO ₂ content↑ pH↓ alkalinity↑ Ca content↑ Mg content↑
Seasonal Factor	Maximum fluctuations in free CO ₂ , alkalinity, pH, Ca and Mg concentrations will occur due to spring biomass maximum	Maximum fluctuations in free CO ₂ , alkalinity, pH, Ca and Mg concentrations will occur due to spring biomass maximum	Lowest fluctuations in free CO ₂ , pH, alkalinity, Ca and Mg concentrations will occur due to summer biomass minimum	Lowest fluctuations in free CO ₂ , pH, alkalinity, Ca and Mg concentrations will occur due to summer biomass minimum	Intermediate fluctuations in free CO ₂ , pH, alkalinity, Ca and Mg concentrations will occur due to secondary fall biomass bloom	Intermediate fluctuations in free CO ₂ , pH, alkalinity, Ca and Mg concentrations will occur due to secondary fall biomass bloom

Fig. 4

in free CO_2 , pH, alkalinity, and Ca and Mg concentrations.

The following hypothesis was formalized:

- 1) In late spring, due to the biomass present, the rock pools will experience a diurnal fluctuation in free CO_2 , pH, alkalinity, Ca and Mg concentration, such that a relatively low free CO_2 , high pH, low alkalinity, and low Ca and Mg concentration occurs during the daylight hours.

Since a biomass maximum is expected in late spring, the second hypothesis was:

- 2) The relative diurnal fluctuations of free CO_2 , pH, Ca, Mg and alkalinity experienced in the rock pools will be greater than those experienced in the summer and fall.

Summer weather brings a lower biomass than in the spring, such that the following was expected:

- 3) In the summer when the warmer temperature-tolerant species take over, the diurnal fluctuations in free CO_2 , pH, alkalinity, Ca and Mg concentrations will vary such that during daylight hours there will be a relatively low free CO_2 , high pH, low alkalinity, and Ca and Mg concentration, but this fluctuation will be less than that experienced in the spring and fall.

The autumn brings an increase in biomass such that the following result was expected:

- 4) In the fall, the diurnal fluctuations in free CO_2 , pH, alkalinity, Ca and Mg concentrations will

vary such that during daylight hours there is relatively low free CO_2 , high pH, and low alkalinity. These fluctuations will be larger than the summer fluctuations, but smaller than the spring fluctuations. To observe whether the temperature differences (inorganic solution) is the major control in the erosion of limestone in this setting, a laboratory experiment was carried out such that a rock sample from site, which has been treated to void it of any biological material and put in a container with sterile, distilled water, was set under similar temperature and light conditions as in a rock pool on site. The temperatures occurring on site through the three seasons was simulated and a comparison was made between the pH, free CO_2 , alkalinity, and Ca and Mg concentration fluctuations of the laboratory situation and the fluctuations on site. The following result was expected:

- 5) In a comparison of the laboratory situation where the temperature and light is varied like that of the actual field situation, fluctuations of free CO_2 , alkalinity, pH, and Ca and Mg concentration will be much lower than that of the rock pools which contain biomass.

In comparing rock pools in different environments along the shore platform, it was expected that the rock pools with the greatest amount of biomass will have a relatively higher erosion rate. Thus,

6) The rock pools with the greatest biomass will exhibit the greatest fluctuations of free CO_2 , pH, alkalinity, Ca and Mg concentrations on a given trip, and these rock pools will be the largest in size and depth of those surveyed.

Since the high latitude fresh water environment was expected to have a lower biomass on the whole than that in a low latitude saline tidal environment, the last hypothesis was:

7) The fluctuations in free CO_2 , pH, alkalinity, Ca and Mg concentrations will indicate that bioerosion and inorganic erosion are of relatively little importance in the development of fresh water, northern environment shore platforms.

To evaluate these hypotheses, both field work at the shore platform located at Ipperwash Provincial Park and laboratory work was performed.

3.2 Methodology

The actual contribution of biological and inorganic erosion to the formation of rock pools in a northern fresh water environment was studied. The study variables that were evaluated were biomass, temperature, pH, alkalinity, free CO_2 , and Ca and Mg content. The outline and depth of the rock pool water were determined with a 5x5 cm grid (2"x2"), indicating how the shape and depth of the rock pool water changes over the three seasons.

The relative amounts of biomass in each rock pool over late spring, summer and autumn was recorded. The temperatures were taken with a temperature probe, and pH was measured with a pH meter. The free CO₂ content of the water was measured with a portable CO₂ kit. Ca concentrations, Mg concentrations and alkalinity analysis were made on a IL 51 Series Atomic Absorption/Emission Spectrophotometer, which can determine 69 metallic and semi-metallic elements, at concentration levels ranging down to traces.

Eight rock pool sites, with varying environmental settings were sampled every three hours over a 24-hour period, for a total of 64 readings. These tests were carried out in late spring, summer and autumn. Temperature, free CO₂ and pH values were recorded immediately, whereas airtight containers were filled with water samples, and taken back to the laboratory for alkalinity, Mg and Ca testing on the Atomic Absorption/Emission Spectrophotometer. If pH and free CO₂ testing were accomplished within five minutes of sample extraction, the recorded result was considered very accurate. If the water samples were filtered on site and put in containers from which no evaporation took place, and were analyzed within a one week period, the resulting concentrations of calcium and magnesium were considered accurate (Stenner, 1969).

The depth and extent of the rock pool water were depicted using the mapping programs Symap and Symvu (Harvard University, 1963).

To test for inorganic solution, the field temperatures were simulated in the environmental chamber. Rock samples were taken back and treated in an autoclave to kill all biological material. Then, three hour water samples were extracted over a 24-hour period, and tested for free CO_2 , pH, alkalinity, Ca and Mg concentrations. These results will then be compared to on site results. As mentioned before, dense biological material on the bottom of rock pools is thought to prevent interaction between the water and the rock surface. Therefore, one of the rock samples was brought back and put in a similar light and temperature situation as the fall trip. The rock sample was in the environmental chamber for one week to allow the biological material to become active. Then three hour samples over a 24-hour period were extracted and tested for free CO_2 , pH, alkalinity, Ca and Mg concentrations.

3.3 Statistical Techniques

To evaluate the hypothesis, an analysis of variance test and a partial correlation test was performed on the data. The analysis of variance technique involves separating the total variance into various components or

sources. Both the differences in means and in the variances are considered simultaneously. The S.A.S. general linear model (GLM) of multivariate analysis of variance (Barr et. al., 1976) were used to determine which of the independent variables is the most significant in explaining variability of free CO_2 , pH, Ca, Mg, and alkalinity. In this test, the null hypothesis was that free CO_2 , pH, Ca, Mg and alkalinity variations were equal for each treatment and for the combinations of the treatments. The treatments describe the independent variables which were seasons (biomass), temperature, and rock pool location. If the null hypothesis is rejected for any treatment, this will suggest that a statistically significant relationship exists for the variables in question.

To test whether relationships exist between the independent variable temperature and the dependent variables free CO_2 , pH, Ca, Mg and alkalinity, the S.A.S. GLM partial correlation test was performed. This test clarifies relationships between two or more variables by measuring the strength of the correlation between two variables while the other variables are held fixed. In this test, the null hypothesis suggests that no significant relationship exists between the two variables.

Before these analyses can be performed, the assumption that the populations from which the samples were obtained can be closely approximated with a normal distribution

having the same variance was tested by the use of a Kolmogorov-Smirnov test (Ks test for normality), and the Bartlett's test for homogeneity of variances.

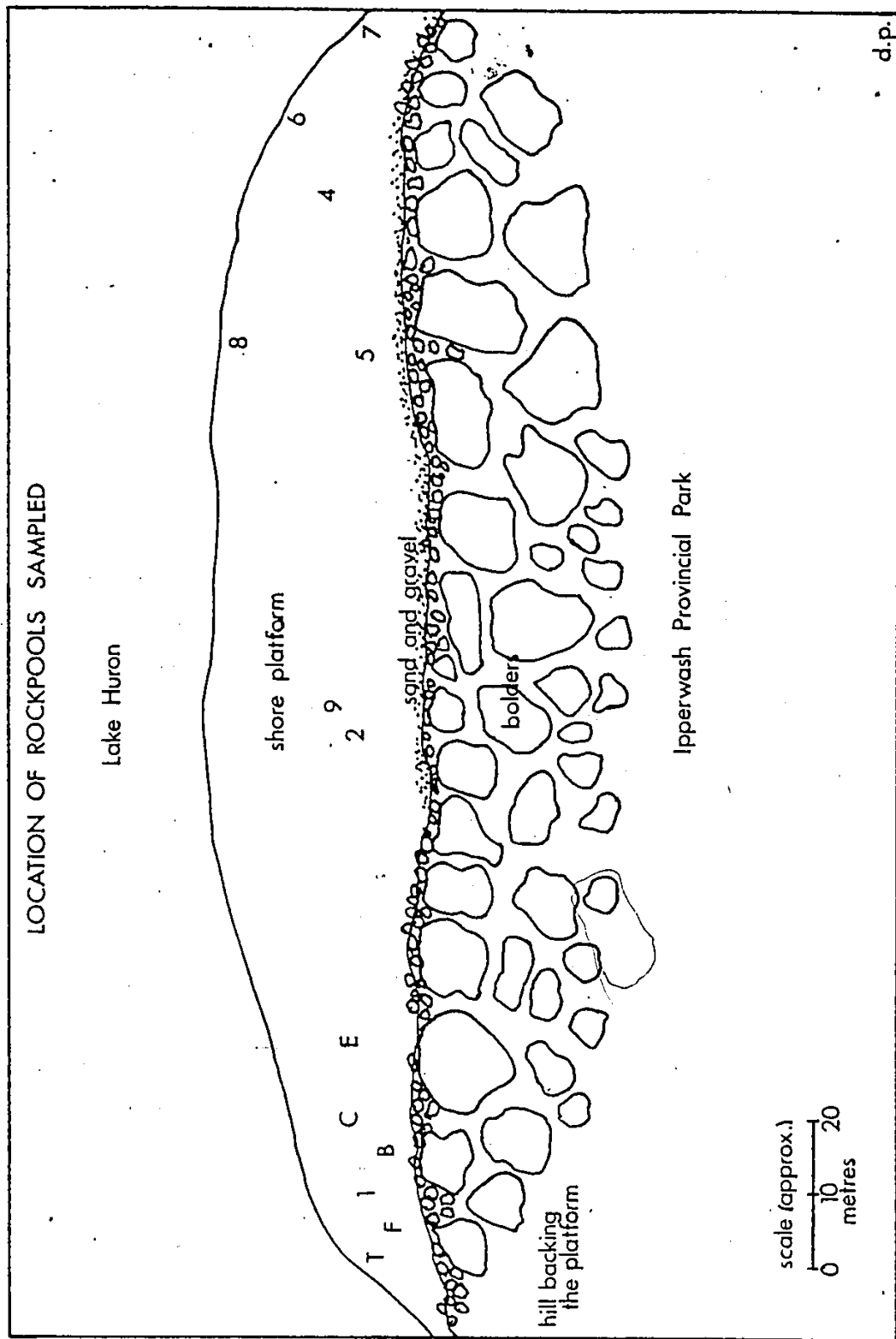
In summary, testing in eight rock pools for temperature, free CO_2 , pH, alkalinity, and Ca and Mg concentrations was performed every 3 hours over a 24-hour period in late spring, summer and fall. A laboratory setup simulated the light and temperature experienced at the rock pool sites with and without biomass, allowing comparison between inorganic and organic erosion. The partial correlation test will suggest the relationship of the temperature variable with the dependent variable, and the 3-way analysis of variance test will suggest any statistically significant relationships between the variables in question.

CHAPTER FOUR
ANALYTICAL FINDINGS

4.1 Descriptive Characteristics of the Data

Collection of data took place on May 18/19, 1981, July 17/18, 1981 and Sept. 25/26, 1981. Wind conditions were a major factor as to whether sampling from the rock pools could occur. If the winds were blowing onshore from the north to northwest, lake water tended to cover the whole platform. If the winds were blowing onshore from the south to southeast, the protection offered by Kettle Point tended to keep the lake water from washing onto the shore platform. This phenomenon lessened through the summer and fall as the lake level gradually lowered from its highest level in May.

Eight rock pools were sampled along the platform, their locations chosen to vary in environment as much as possible. Rock pools 1, 2, 4, 5, 6, 7, 8 and 9 were used on the first trip (Fig. 5). On the July trip, rock pools T, E, F, C, B, 1, 2 and 8 were used because out of the original eight rock pools, only 1, 2 and 8 contained water for sampling. Rock pools 4 and 7, which were fed through rock joints under the main top block of the platform, were dry on the July trip because the level of the lake water was down. On the September trip, rock pools E, C, B, 1, 9, 2, 8 and 5 were used. The only rock pools which could be sampled on every trip were numbers 1, 2 and 8.



Their water content and surface area changed from trip to trip as can be seen by the Symvu diagram of each (Figs. 6 to 8).

Sampling for the first trip began at 1715 hours on May 18, 1981. There was a north wind blowing at that time, which died down around 0515 on May 19, 1981. The minimum temperature recorded on this trip was 1.8°C and the maximum temperature was 11.9°C . The Canadian Coast Guard who record Lake Huron wave height every 6 hours, reported 0.9 to 1.9 meter waves on May 17. On May 18, waves were 0 to 0.9 meters until just after midnight when they increased to 1.9 meters in height. On the 19th, the waves were 0 to 0.9 meters in height. Every rock pool was self-contained throughout the 24 hour sampling time.

Sampling for the second trip began at 1200 hours on July 17, 1981, at which time a southwest wind was blowing. It was a very hot day, with a minimum temperature reading of 17°C and a maximum temperature of 29.5°C . At the second reading, rock pools 1 and 8 had dried up, and on the third reading rock pools T, C, 1, 2 and 8 had dried up. On the fourth reading all of the rock pools were dry. From 1945 to 2130 hours there was a violent storm with rain, lightning and high winds which caused rock pools E, F and C to overflow for the 2400 reading. At the 0300 hour reading all rock pools were self-contained again, and there was a great deal of free standing water over the platform. At 0900 hours the sun was out again.

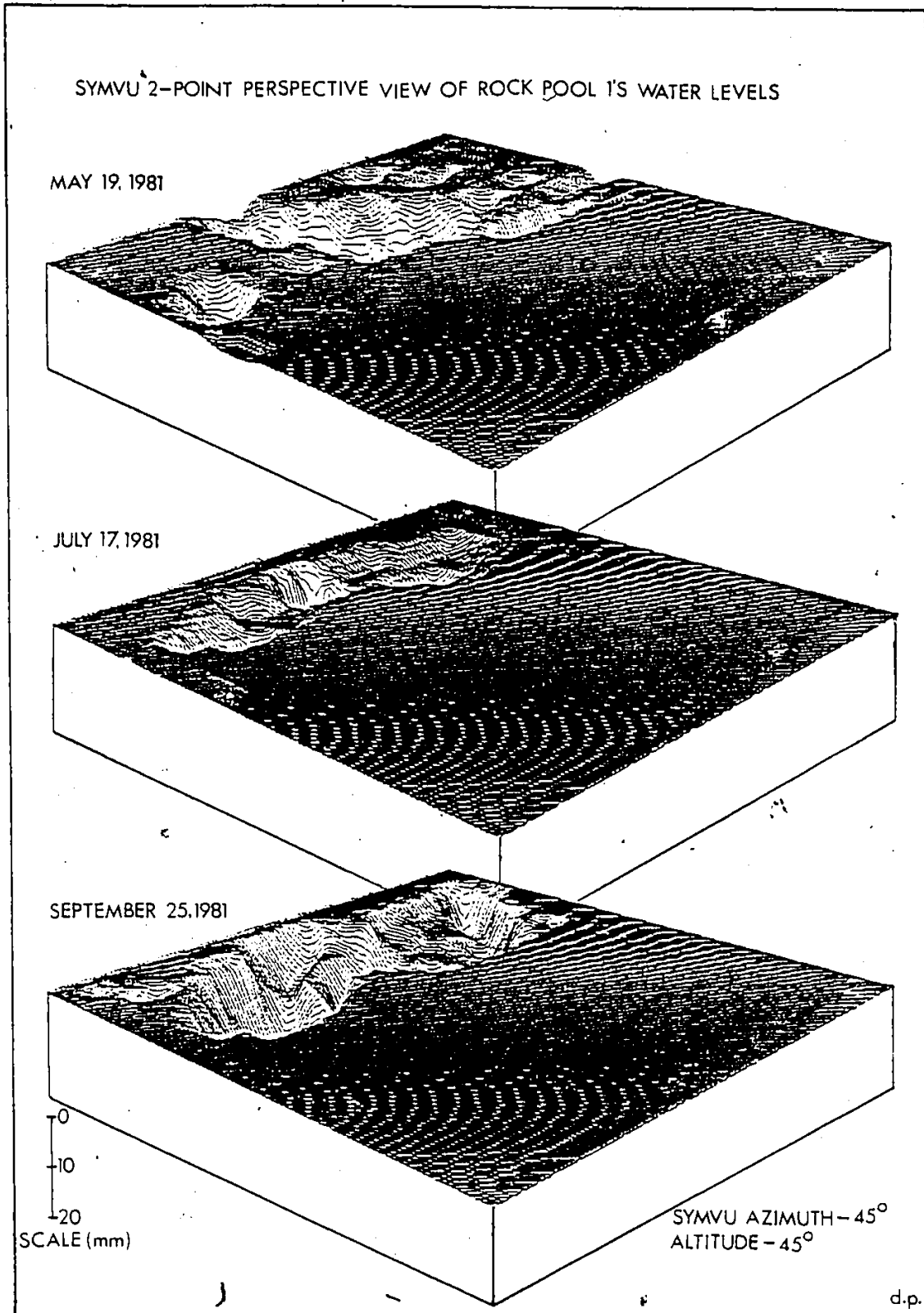


Fig. 6

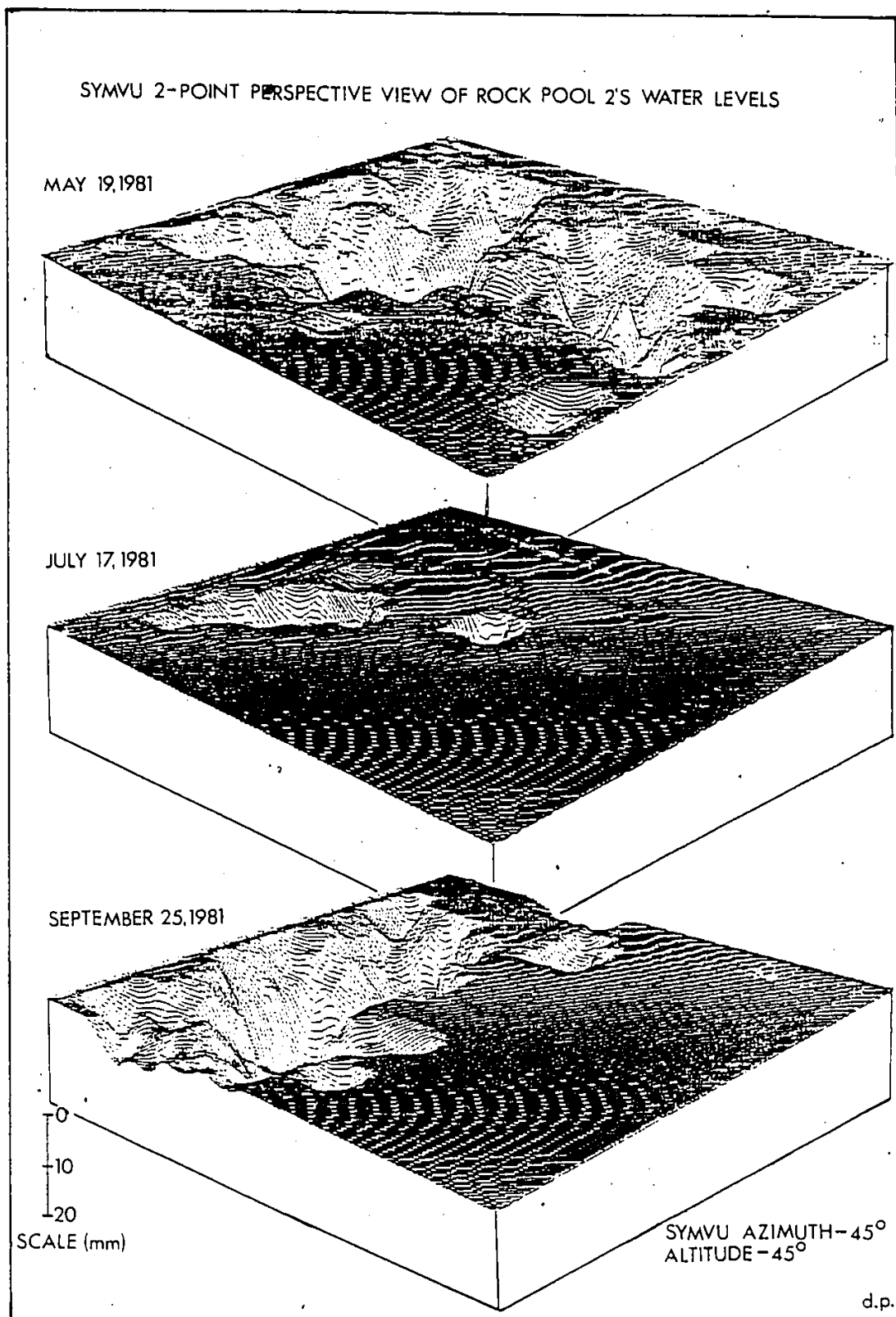


Fig. 7

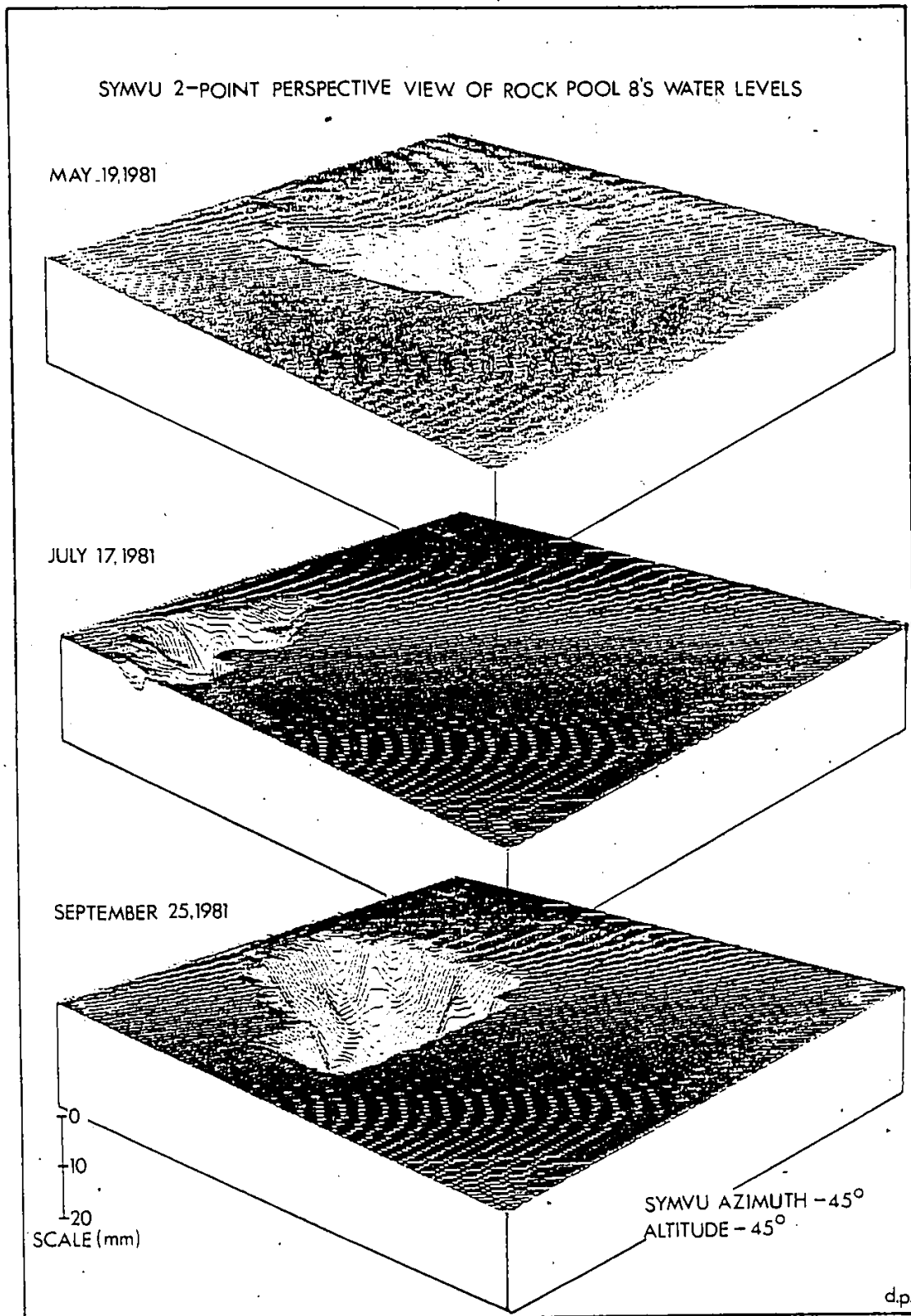


Fig. 8

The Canadian Coast Guard reported waves less than 0.9 meters on July 16. In the morning of July 17, waves were less than 1 meter, changing to .9 meters to 1.9 meters in the evening. In the late evening the waves increased to 3.8 meters and on July 18, they were recorded as greater than 1 meter.

Sampling on the third trip of September 25, 1981 began at 1600 hours, when a south wind was prevailing. The minimum temperature recorded was 12.5°C and the maximum temperature recorded was 18°C. The skies were overcast, and a very light drizzle started around 1900 hours, which continued intermittently until 0700 hours. The light drizzle started again at 1000, and the winds began picking up around 1300 hours. The Canadian Coast Guard reported waves of 0.9 to 1.9 meters on September 24 and waves of 0.9 to 1.9 meters on September 25. Waves of 4.7 to 5.7 meters were recorded in the morning of September 26, followed by waves of 2.8 to 3.8 meters in the evening. The lake level was even lower than observed on the July trip, and the secondary platform became evident being no longer covered with water. The platform on this trip was covered with a very slimey, slippery, greenish brown algae. This condition probably occurred because of the 23.2 mm of rain that had fallen on September 21, four days before sampling took place (Fig. 10).

The perimeter and water depth of the rock pools were subject to the variability of the weather and lake conditions. For instance, a rock pool located near the

WEATHER CONDITIONS AT IPPEWASH PROVINCIAL PARK FOR THE PERIODS OF May 11, 1981-May 19, 1981, July 10, 1981-July 18, 1981 and Sept. 18, 1981-Sept. 26, 1981									
DATE	TEMPERATURE (°C)			TOTAL PRECIPITATION (mm)	WIND		BRIGHT SUNSHINE INSOLATION EFFECTIVE (HOURS)		
	MAX	MIN	MEAN		AVERAGE SPEED (km/hr)	PREVAILING DIRECTION			
May 11	6.9	3.0	5.0	8.9	31.2	N	0.0		
May 12	9.6	1.8	5.7	TR.	20.7	N	5.5		
May 13	17.2	-0.4	8.8		13.7	NW	13.2		
May 14	9.7	2.6	6.2	4.0	11.5	N	1.3		
May 15	8.6	5.6	7.1	4.8	25.3	N	0.0		
May 16	15.1	6.0	10.6		18.0	N	12.4		
May 17	8.6	4.7	6.7		19.8	N	11.0		
*May 18	9.5	0.2	4.9		17.3	N	14.1		
*May 19	12.5	2.8	7.7		9.6	N	12.9		
July 10	28.4	15.2	21.8		10.1	NW/N	14.7		
July 11	32.0	14.1	23.1		7.1	S	10.6		
July 12	33.2	19.9	26.6	TR	18.0	S	7.0		
July 13	28.3	20.7	24.5		18.4	NE	9.1		
July 14	23.0	17.0	20.5		20.4	N	10.4		
July 15	24.0	14.2	19.1	TR	8.3	N	7.2		
July 16	26.4	16.4	21.4	TR	6.8	NE	9.6		
*July 17	20.9	13.5	22.2	7.7 (Thunderstorm)	10.8	SW	12.0		
*July 18	31.1	16.9	24.0	3.4 (Thunderstorm)	8.6	SW	9.3		
Sept. 18	14.4	9.4	11.9	0.6	12.7	NE	0.4		
Sept. 19	21.0	9.8	15.4	0.2	18.7	SW	6.3		
Sept. 20	15.9	6.5	11.2		15.1	W	8.7		
Sept. 21	12.5	6.0	9.3	23.2	11.6	NE	0.0		
Sept. 22	14.0	7.2	10.6	0.4	27.6	NE	6.9		
Sept. 23	14.0	7.9	11.0		19.3	W	9.7		
Sept. 24	19.0	11.7	15.3		7.2	W	9.6		
*Sept. 25	16.5	10.1	13.3	3.8	8.9	S	0.0		
*Sept. 26	23.6	13.4	18.5	0.6	18.3	S	0.0		

Source: Monthly Meteorological
Summary, Sarnia (A), Ontario, 1981

Table 2

*Days over which sampling occurred

shore platform edge may evaporate during the day and if the winds caused the waves to pick up, the lake water might splash into the rock pool, and perhaps overflow it. If a storm occurred, the whole platform might be totally underwater for days. The rock pool's sensitivity to the weather conditions is exemplified by the fact that only three rock pools could be sampled on every trip, and their size and shape changed significantly over these three time periods (Figs. 6 to 8). In general, the rock pools were largest in extent and depth on the May trip and the smallest on the July trip.

The 24-hour readings for air temperature, water temperature, pH, free CO_2 , Ca, Mg and alkalinity are recorded on Tables 3 to 5, and the individual results are graphed on Figures 9 to 35. The May air temperatures for the eight rock pools peaked at 0100 to 1200 hours, and the water temperatures peaked three hours later at higher temperatures. The pH curve was similar in shape to the temperature curve but had a peak lag time of approximately three hours. This phenomenon was especially obvious in rock pools 2 and 9 which were both located toward the back of the platform and not affected by wave splash. The free CO_2 curves generally have an inverse relationship to temperature, experiencing a minimum at temperature maximums. There tend to be two peaks in free CO_2 which occur around early morning and early evening, with the exception of rock pools 4 and 5. These free CO_2 curves

THE 24-HOUR READINGS OF TEMPERATURE, PH, FREE CO ₂ , CALCIUM, MAGNESIUM AND ALKALINITY FOR EIGHT ROCK POOLS AT UPPERWASHI PROVINCIAL PARK - MAY 18, 1981								
ROCK POOL NUMBER	TIME	AIR TEMP. (°C)	WATER TEMP. (°C)	PH	FREE CO ₂ (PPH)	CA (PPH)	MG (PPH)	ALKALINITY (PPH)
1	1715	9.5	16.25	8.5	10.0	55	23	78
1	2015	8.3	10.2	8.1	6.0	56	19	75
1	2315	8.5	8.0	7.8	8.0	50	19	60
1	215	7.0	7.9	8.0	4.5	57	21	78
1	515	1.8	4.5	7.68	5.0	59	22	81
1	815	9.2	7.5	7.6	7.0	58	22	80
1	1115	11.9	15.5	8.48	0	44	17	61
1	1415	10.5	20.5	9.3	0	31	18	49
2	1715	9.5	14.5	9.2	0	31	18	49
2	2015	8.3	9.5	7.94	3.5	57	20	77
2	2315	8.5	7.9	8.05	4.5	58	22	80
2	215	7.0	6.8	7.4	4.0	61	24	85
2	515	1.8	4.5	7.6	5.0	61	25	86
2	815	9.2	7.7	7.8	4.5	60	25	85
2	1115	11.9	17.2	8.3	0	51	21	72
2	1415	10.5	21.0	8.85	0	39	23	62
4	1715	9.5	13.5	7.89	37.5	83	28	111
4	2015	8.3	8.1	7.5	6.5	86	26	112
4	2315	8.5	7.5	7.58	18.5	92	26	118
4	215	7.0	6.1	7.65	18.5	91	28	119
4	515	1.8	4.5	7.48	10.0	90	29	119
4	815	9.2	8.0	7.41	28.0	87	27	114
4	1115	11.9	15.8	7.7	18.0	86	26	112
4	1415	10.5	22.5	7.7	11.5	81	31	112
5	1715	9.5	13.5	9.6	0	31	28	59
5	2015	8.3	8.0	9.4	0	51	21	51
5	2315	8.5	8.0	8.8	0	30	22	52
5	215	7.0	6.2	8.45	0	32	20	52
5	515	1.8	4.5	8.0	20.5	33	23	56
5	815	9.2	9.2	8.2	2.0	34	21	55
5	1115	11.9	17.5	9.2	0	30	20	50
5	1415	10.5	21.0	9.8	0	37	19	56

Table 3

THE 24-HOUR READINGS OF TEMPERATURE, PH, FREE CO ₂ , CALCIUM, MAGNESIUM AND ALKALINITY FOR EIGHT ROCK POOLS AT IPPEKAWASHI PROVINCIAL PARK - MAY 18, 1981								
ROCK POOL NUMBER	TIME	AIR TEMP. (°C)	WATER TEMP. (°C)	PH	FREE CO ₂ (PPM)	CA (PPM)	MG (PPM)	ALKALINITY (PPM)
6	1715	9.5	12.9	8.0	12.5	77	29	106
6	2015	8.3	8.0	7.82	12.5	85	28	113
6	2315	8.5	7.9	7.75	6.5	82	27	109
6	215	7.0	6.5	7.65	11.0	84	29	113
6	515	1.8	5.0	7.5	20.5	96	20	116
6	815	9.2	8.9	7.6	20.5	84	27	111
6	1115	11.9	18.0	7.71	18.5	93	28	121
6	1415	10.5	23.0	7.79	5.0	83	30	113
7	1715	9.5	12.5	7.78	18.5	101	25	126
7	2015	8.3	8.1	7.6	16.0	83	16	99
7	2315	8.5	7.5	7.4	21.5	88	15	103
7	215	7.0	6.5	7.6	27.0	91	28	119
7	515	1.8	4.0	7.39	27.0	92	35	127
7	815	9.2	9.5	7.48	29.0	125	25	150
7	1115	11.9	18.0	7.82	9.5	114	25	139
7	1415	10.5	22.0	7.97	6.5	81	35	116
8	1715	9.5	14.5	9.1	0	38	19	57
8	2015	8.3	9.5	8.01	13.5	54	22	76
8	2315	8.5	7.8	7.95	4.0	54	21	75
8	215	7.0	6.8	7.7	6.5	56	24	80
8	515	1.8	4.5	7.48	5.5	57	28	85
8	815	9.2	8.0	7.75	5.0	55	24	79
8	1115	11.9	16.2	8.42	0	46	26	72
8	1415	10.5	20.2	9.01	0	32	21	53
9	1715	9.5	15.0	9.2	0	34	17	51
9	2015	8.3	8.1	8.0	7.0	59	22	81
9	2315	8.5	7.9	8.05	4.5	60	20	80
9	215	7.0	6.5	7.57	3.5	60	24	84
9	515	1.8	4.5	7.62	7.0	59	27	86
9	815	9.2	7.5	7.75	7.0	57	23	80
9	1115	11.9	17.0	8.22	0	50	31	81
9	1415	10.5	21.5	8.78	0	39	21	60

Table 3 (cont.)

THE 24-HOUR READINGS OF TEMPERATURE, PH, FREE CO ₂ , CALCIUM, MAGNESIUM AND ALKALINITY FOR EIGHT ROCK POOLS AT IPPERWASH PROVINCIAL PARK - JULY 17, 1981									
ROCK POOL NUMBER	TIME	AIR TEMP. (°C)	WATER TEMP. (°C)	PH	FREE CO ₂ (PPH)	CA (PPH)	MG (PPH)	ALKALINITY (PPH)	
T	1800	29.5	DRY	DRY	DRY	DRY	DRY	DRY	
T	2100	24	DRY	DRY	DRY	DRY	DRY	DRY	
T	2400	21	18	7.1	7.0	15	13	28	
T	300	20	17.5	7.1	4.0	15	7	22	
T	600	17	19.5	7.55	3.0	16	11	27	
T	900	21.5	DRY	DRY	DRY	DRY	DRY	DRY	
T	1200	28.5	28.5	--	0	16	10	26	
T	300	28	31.5	8.4	0	14	11	25	
E	1800	29.5	29	8.5	0	14	7	21	
E	2100	24	DRY	DRY	DRY	DRY	DRY	DRY	
E	2400	21	ROCK POOL OVERFLOW	7.18	4.0	15	7	22	
E	300	20	17.5	7.55	4.0	15	13	28	
E	600	17	19.5	7.78	0	14	10	24	
E	900	21.5	21.5	--	0	17	9	26	
E	1200	28.5	27	--	0	14	9	23	
E	300	28	31.5	8.4	0	14	9	23	
F	1800	29.5	27.5	9.25	0	12	6	18	
F	2100	24	DRY	DRY	DRY	DRY	DRY	DRY	
F	2400	21	ROCK POOL OVERFLOW	7.3	5.0	15	6	21	
F	300	20	17.5	7.6	5.0	15	14	29	
F	600	17	19.8	7.75	0	15	7	22	
F	900	21.5	21.3	--	0	15	8	23	
F	1200	28.5	26.5	--	0	15	8	23	
F	300	28	20	9.25	0	13	7	20	
G	1800	29.5	DRY	DRY	DRY	DRY	DRY	DRY	
G	2100	24	ROCK POOL OVERFLOW	7.1	6.0	15	13	28	
G	2400	21	18	7.3	5.5	16	6	22	
G	300	20	17.5	7.59	5.0	16	15	31	
G	600	17	19	7.7	0	15	9	24	
G	900	21.5	21.9	--	0	16	8	24	
G	1200	28.5	28	--	0	16	8	24	
G	300	28	30	9.7	0	18	3	21	

Table 4

THE 24-HOUR READINGS OF TEMPERATURE, PH, FREE CO ₂ , CALCIUM, MAGNESIUM AND ALKALINITY FOR EIGHT ROCK POOLS AT IPPERWASH PROVINCIAL PARK - JULY 17, 1981								
ROCK POOL NUMBER	TIME	AIR TEMP. (°C)	WATER TEMP. (°C)	PH	FREE CO ₂ (PPH)	CA (PPM)	MG (PPH)	ALKALINITY (PPH)
B	1800	29.5	28	9.1	0	13	6	19
B	2100	24	DRY	DRY	DRY	DRY	DRY	DRY
B	2400	21	18	7.1	12.5	15	13	28
B	300	20	17.5	7.42	5.0	16	6	22
B	600	17	18.5	7.6	4.5	16	15	31
B	900	21.5	22	7.7	0	15	8	23
B	1200	28.5	28	--	0	15	14	29
B	300	28	30	9.2	0	13	7	20
1	1800	29.5	DRY	DRY	DRY	DRY	DRY	DRY
1	2100	24	DRY	DRY	DRY	DRY	DRY	DRY
1	2400	21	18	7.05	7.0	15	11	26
1	300	20	17.5	7.38	5.0	16	7	23
1	600	17	19	7.63	6.0	16	14	30
1	900	21.5	22	7.7	0	16	9	25
1	1200	28.5	28	--	0	18	17	35
1	300	28	DRY	DRY	DRY	DRY	DRY	DRY
2	1800	29.5	DRY	DRY	DRY	DRY	DRY	DRY
2	2100	24	DRY	DRY	DRY	DRY	DRY	DRY
2	2400	21	18	7.1	10.0	17	13	30
2	300	20	18	7.35	6.0	17	10	27
2	600	17	18.5	7.7	6.0	18	16	34
2	900	21.5	21.8	7.7	0	17	10	27
2	1200	28.5	28.5	--	0	23	19	42
2	300	28	30	8.8	0	20	13	33
8	1800	29.5	DRY	DRY	DRY	DRY	DRY	DRY
8	2100	24	DRY	DRY	DRY	DRY	DRY	DRY
8	2400	21	18	7.1	7.5	16	10	26
8	300	20	18	7.5	6.0	17	10	27
8	600	17	18	7.65	7.0	18	16	34
8	900	21.5	21.8	7.65	0	16	7	23
8	1200	28.5	28	--	0	19	2	21
8	300	28	DRY	DRY	DRY	DRY	DRY	DRY

Table 4 (cont.)

THE 24-HOUR READINGS OF TEMPERATURE, PH, FREE CO ₂ , CALCIUM, MAGNESIUM AND ALKALINITY FOR EIGHT ROCK POOLS AT UPPERWASH PROVINCIAL PARK - SEPTEMBER 25, 1981									
ROCK POOL NUMBER	TIME	AIR TEMP. (°C)	WATER TEMP. (°C)	PH	FREE CO ₂ (PPH)	CA (PPH)	MG (PPH)	ALKALINITY (PPH)	
E	400	18	16.5	9.6	0	29	13	42	
E	700	13	15	7.1	0	19	10	29	
E	1000	12.75	14	8.6	0	18	11	29	
E	1300	12.5	13.5	8.8	2.5	19	14	33	
E	1600	13	13.5	7.8	2.0	21	13	34	
E	1900	14	13.25	7.6	2.5	19	14	33	
E	2200	14.5	14.25	7.5	0	19	14	33	
E	100	22	19.75	9.5	0	16	9	25	
C	400	18	16.5	10.3	0	18	11	29	
C	700	13	15	7.1	0	19	7	26	
C	1000	12.75	14	8.8	0	19	6	25	
C	1300	12.5	13.5	8.0	2.5	20	13	33	
C	1600	13	13.25	7.65	4.0	23	12	35	
C	1900	14	13.25	7.0	4.0	21	13	34	
C	2200	14.5	14.25	7.5	0	19	12	31	
C	100	22	20	10.2	0	16	6	22	
B	400	18	16.5	10.35	0	17	7	24	
B	700	13	14.5	7.05	0	19	5	24	
B	1000	12.75	13.75	7.75	3.0	13	8	21	
B	1300	12.5	13	6.6	4.0	21	12	33	
B	1600	13	13	7.6	5.0	26	14	40	
B	1900	14	13.25	7.2	3.5	25	15	40	
B	2200	14.5	14.5	8.5	0	19	13	32	
B	100	22	20.25	10.2	0	16	5	21	
L	400	18	17	10.28	0	17	9	26	
L	700	13	15	7.25	0	19	6	25	
L	1000	12.75	13.75	8.00	3/0	21	6	27	
L	1300	12.5	13	7.3	2.0	19	10	29	
L	1600	13	13.25	7.6	5.0	23	11	34	
L	1900	14	13.25	6.85	2.5	24	14	38	
L	2200	14.5	14.5	8.45	0	21	13	34	
L	100	22	20	9.9	0	16	7	23	

Table 5

THE 24-HOUR READINGS OF TEMPERATURE, PH, FREE CO ₂ , CALCIUM, MAGNESIUM AND ALKALINITY FOR EIGHT ROCK POOLS AT IPPERWASH PROVINCIAL PARK - SEPTEMBER 25, 1981								
ROCK POOL NUMBER	TIME	AIR TEMP. (°C)	WATER TEMP. (°C)	PH	FREE CO ₂ (PPH)	CA (PPH)	MG (PPH)	ALKALINITY (PPH)
9	400	18	17	10.1	0	18	10	28
9	700	13	15	7.25	0	19	9	28
9	1000	12.75	14	8.4	0	20	9	29
9	1300	12.5	13.5	5.9	2.5	19	10	29
9	1600	13	13.5	6.7	4.0	25	11	36
9	1900	14	13.25	6.7	3.5	20	11	31
9	2200	14.5	14.25	6.3	0	20	11	31
9	100	22	21	9.05	0	17	6	23
2	400	18	17	10.1	0	18	11	29
2	700	13	15	7.0	0	19	9	28
2	1000	12.75	14	7.6	0	19	9	28
2	1300	12.5	13.5	6.7	0	15	10	25
2	1600	13	13.25	7.4	2.0	21	11	32
2	1900	14	13.25	6.75	2.5	20	11	31
2	2200	14.5	14.25	6.4	0	18	10	28
2	100	22	20.5	9.9	0	17	7	24
8	400	18	16.5	10.13	0	23	6	29
8	700	13	14.75	7.05	0	21	4	25
8	1000	12.75	14	9.0	0	25	5	29
8	1300	12.5	13	8.35	2.0	17	7	24
8	1600	13	13.5	7.3	5.5	21	9	30
8	1900	14	13.25	7.8	2.5	20	10	30
8	2200	14.5	15	8.15	0	17	9	26
8	100	22	20	10.3	0	20	5	25
5	400	18	16.5	10.8	0	24	5	29
5	700	13	14.5	7.1	0	26	2	28
5	1000	12.75	14	9.0	0	23	5	28
5	1300	12.5	14.5	8.3	0	21	6	27
5	1600	13	13.25	7.8	2.5	19	10	29
5	1900	14	13	7.35	2.5	21	10	31
5	2200	14.5	15	9.2	0	17	10	27
5	100	22	19.5	10.35	0	23	10	33

Table 5 (cont.)

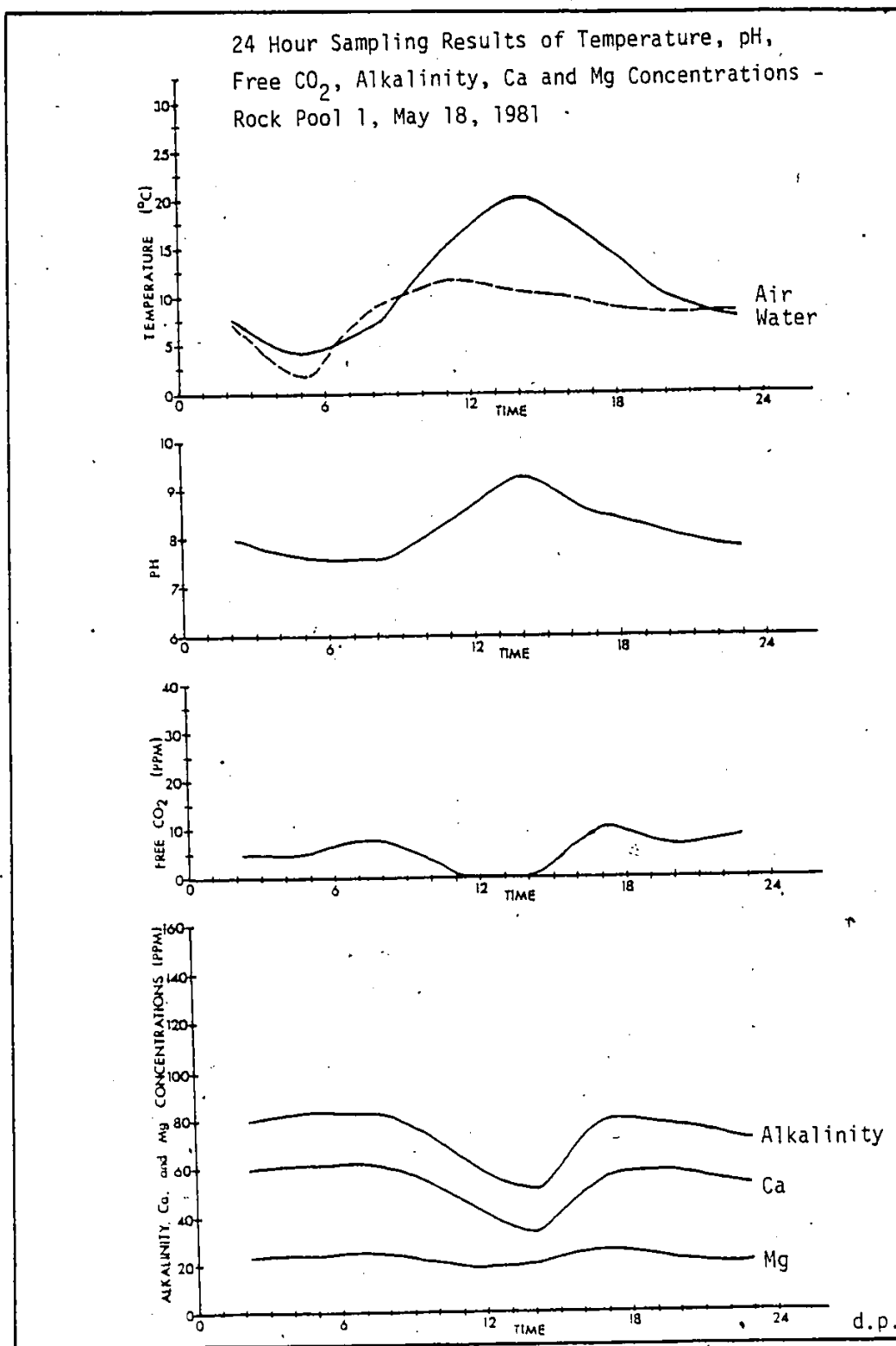


Fig. 9

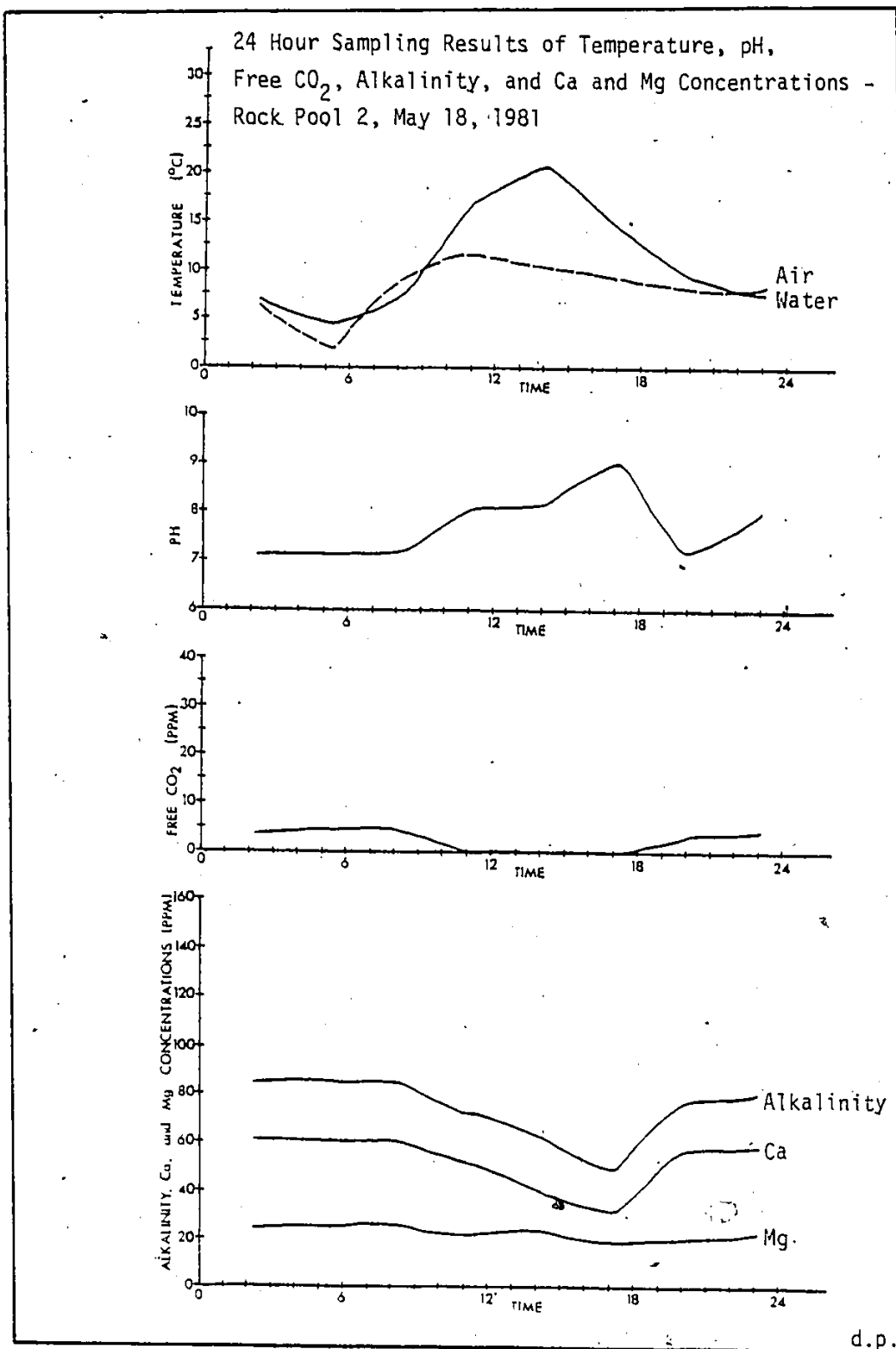


Fig. 10

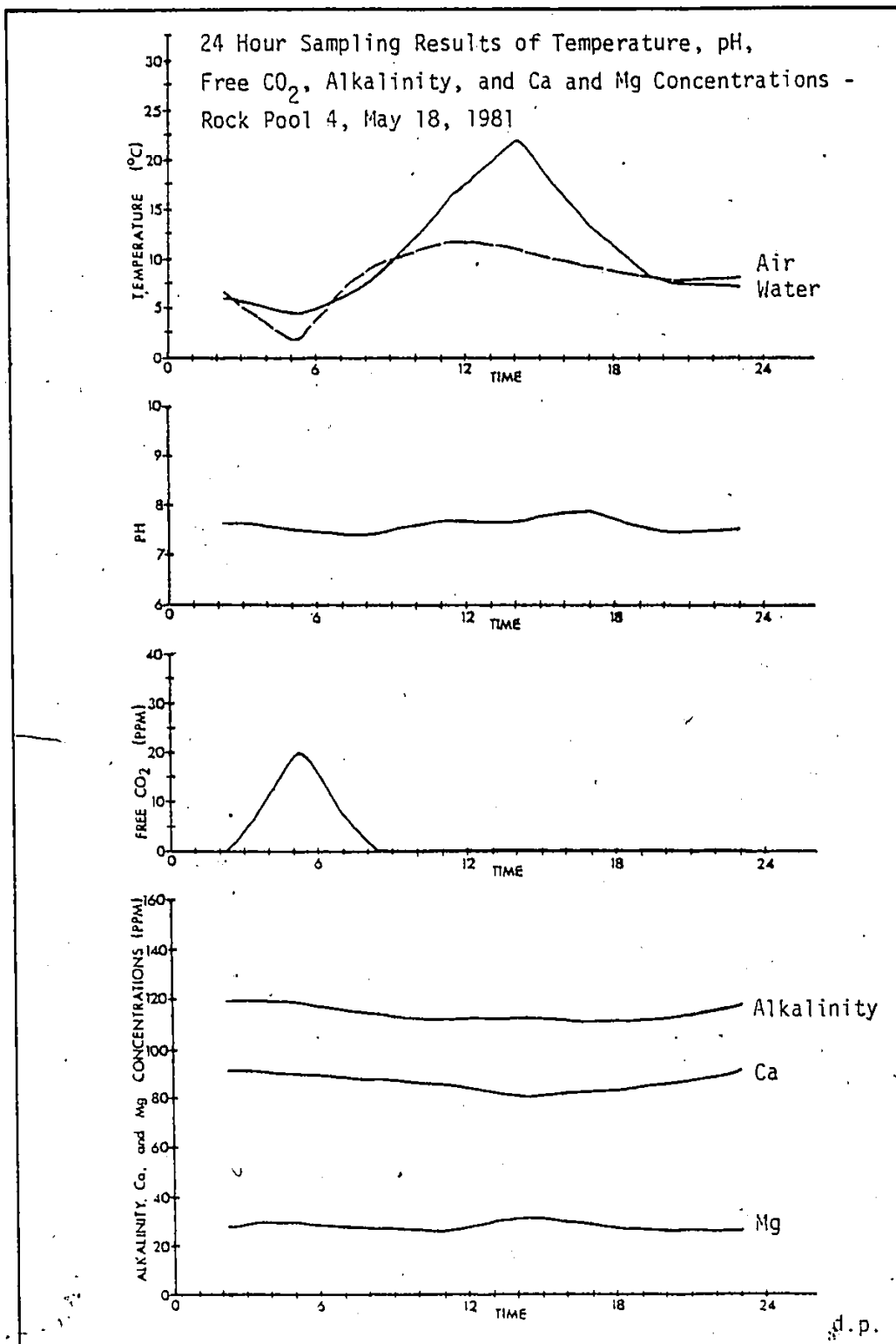


Fig. 11

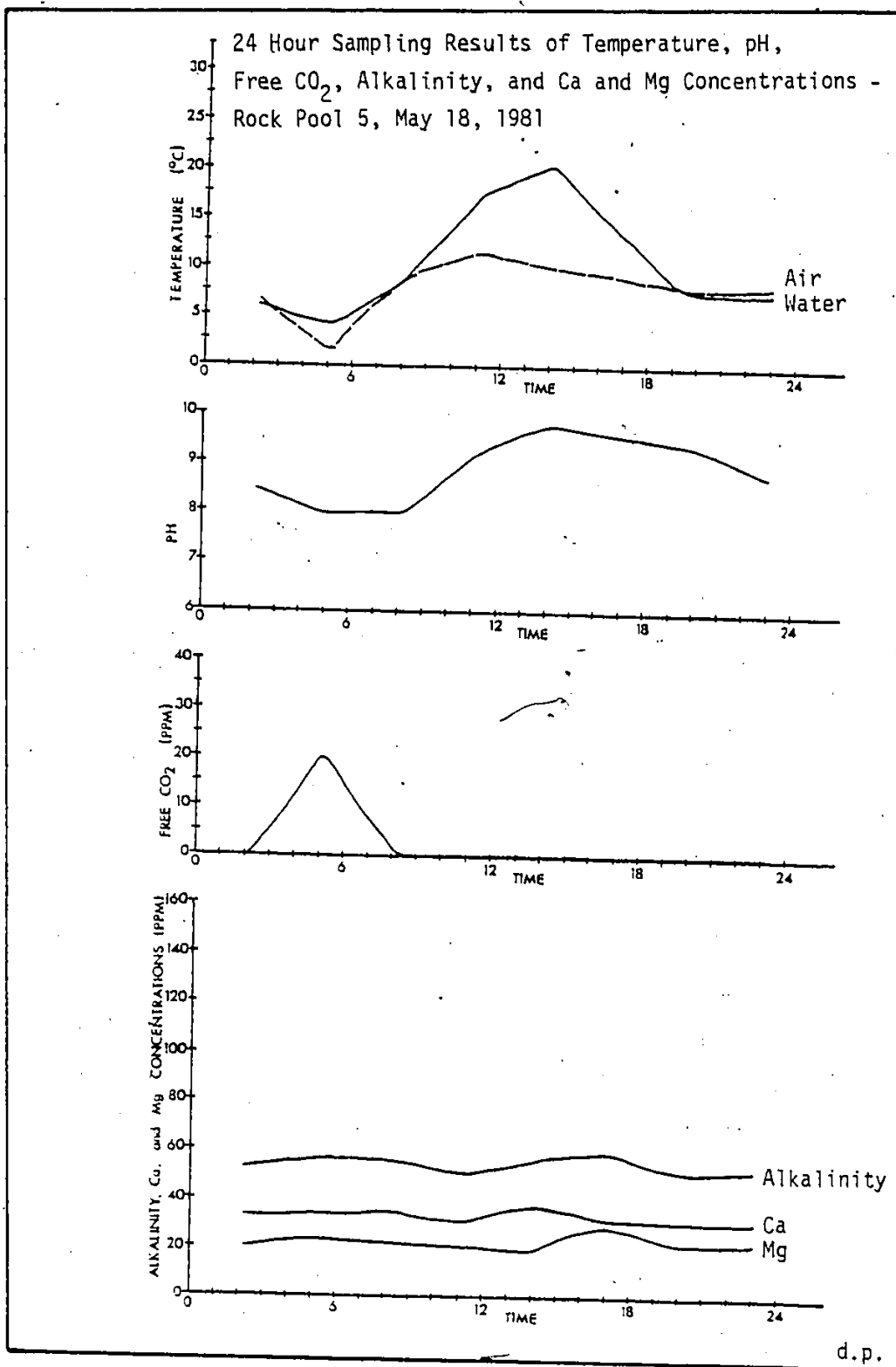


Fig. 12

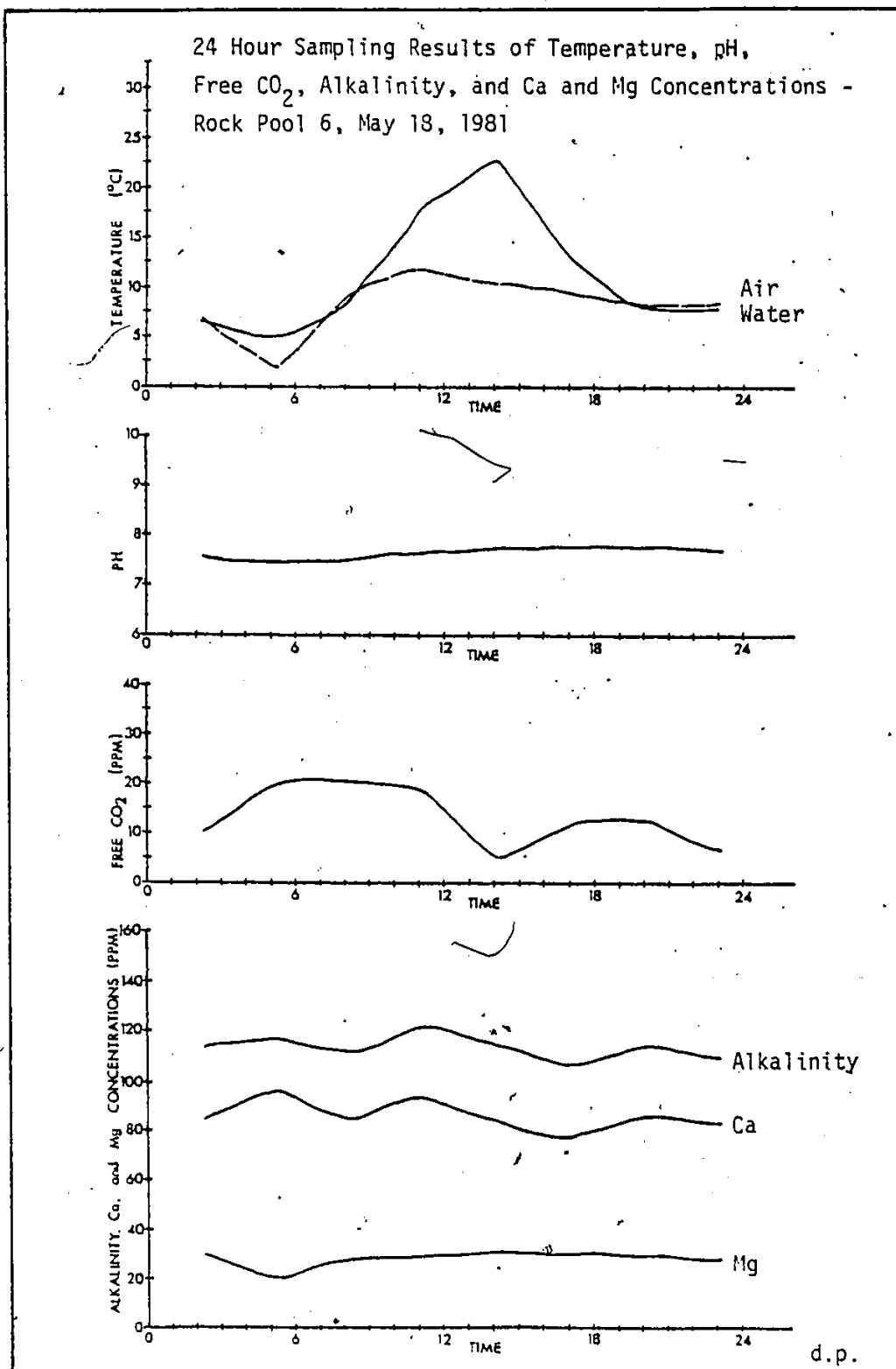


Fig. 13

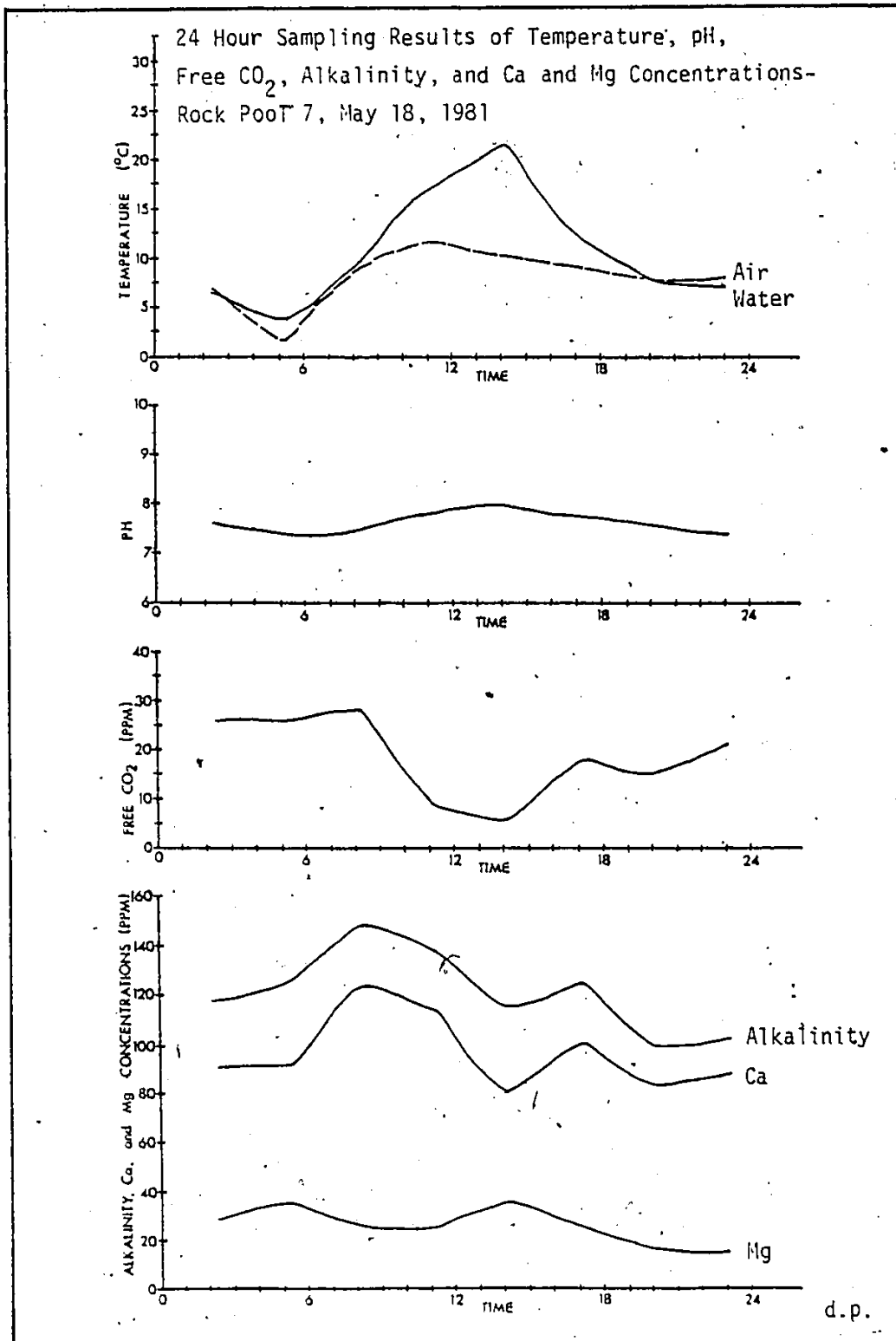


Fig. 14

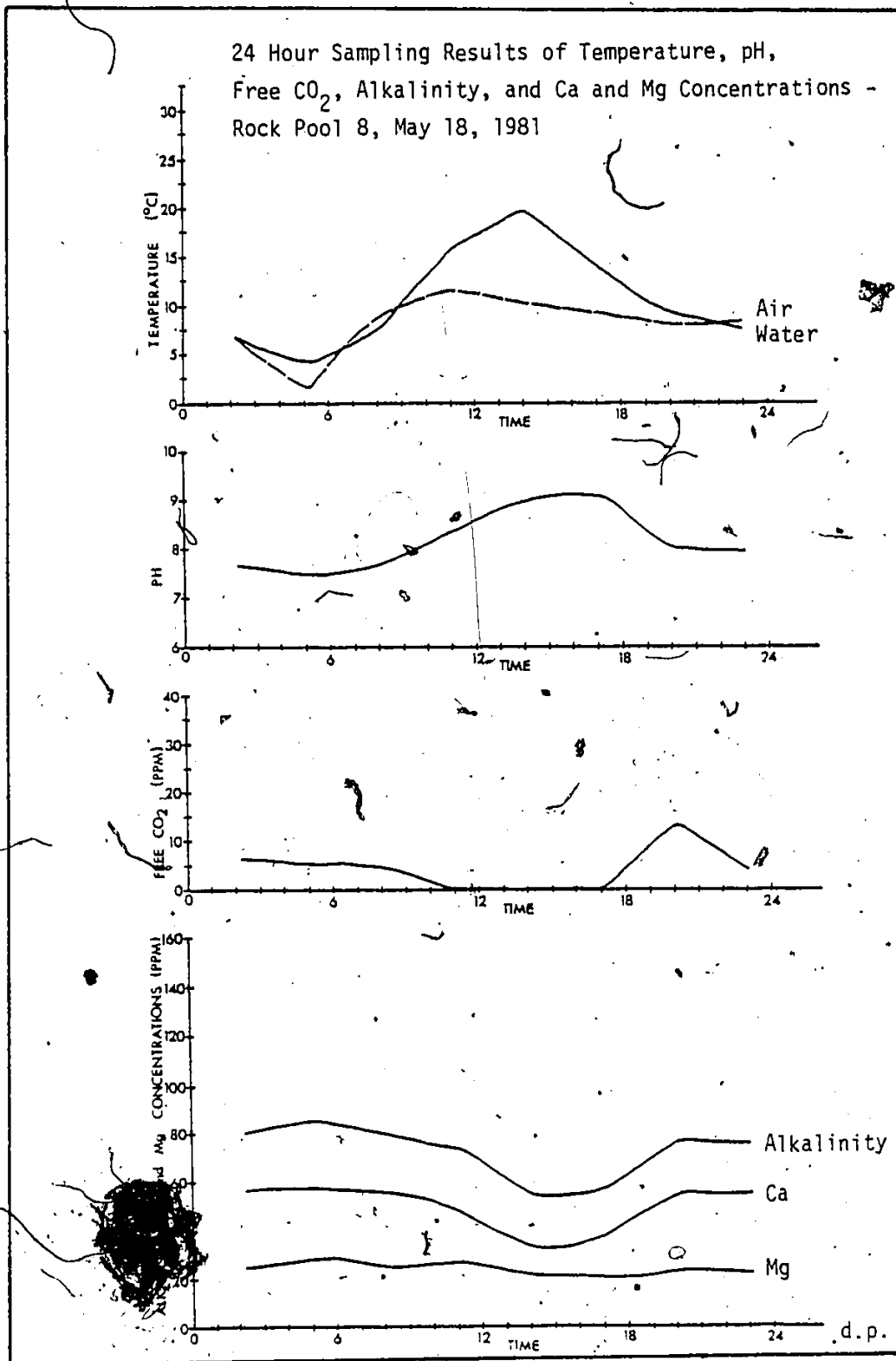


Fig. 15.

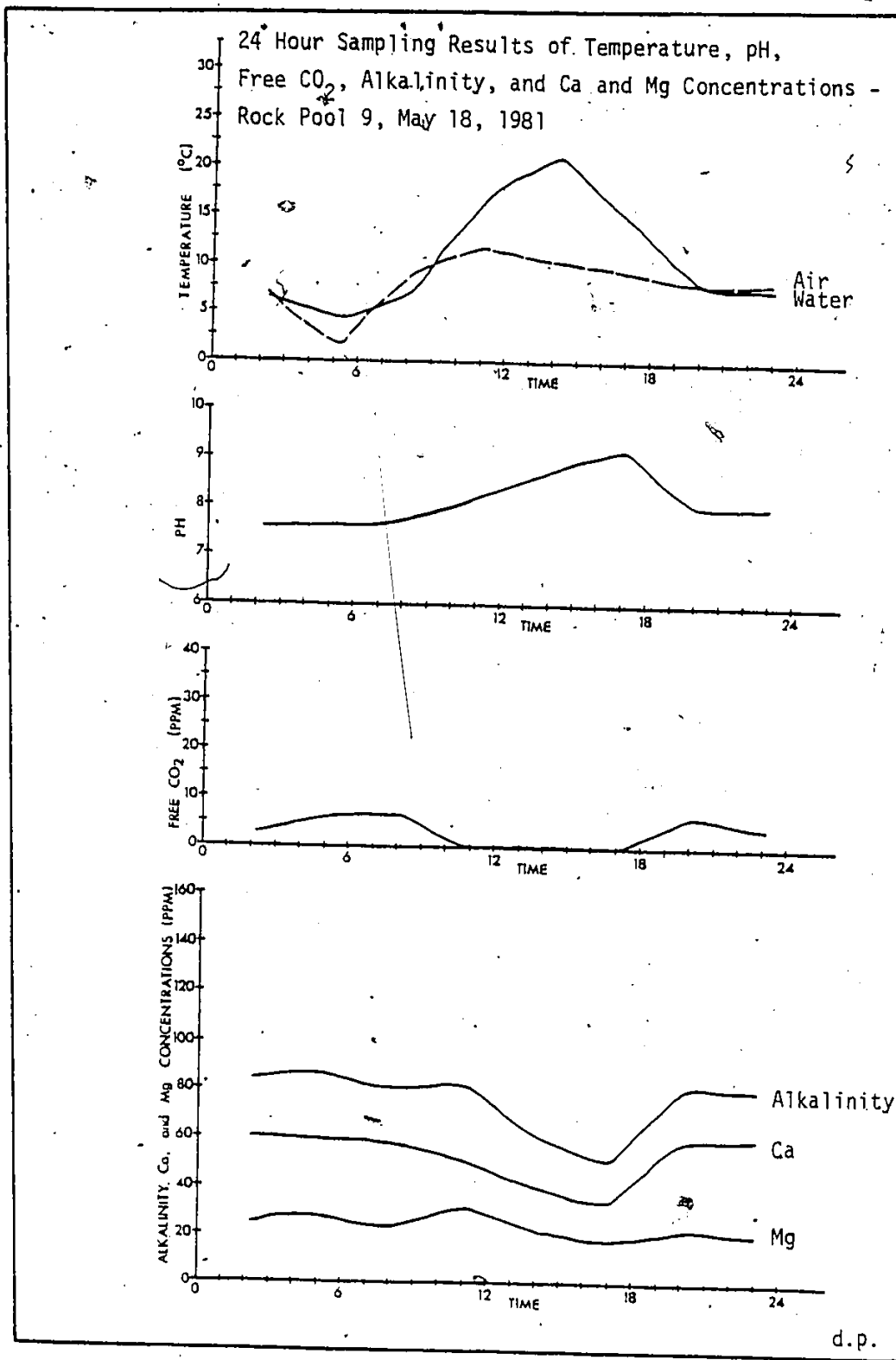


Fig. 16

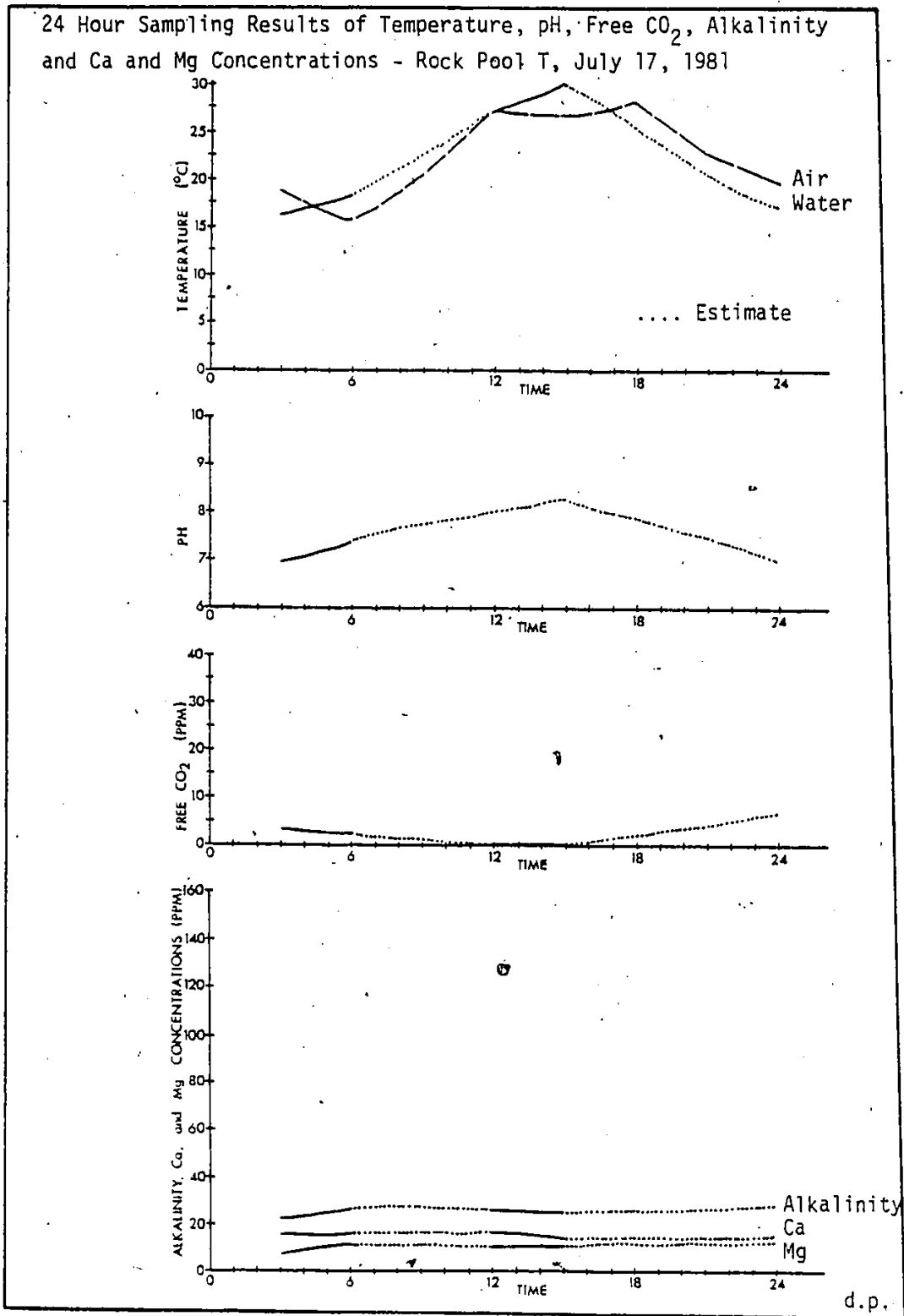


Fig. 17

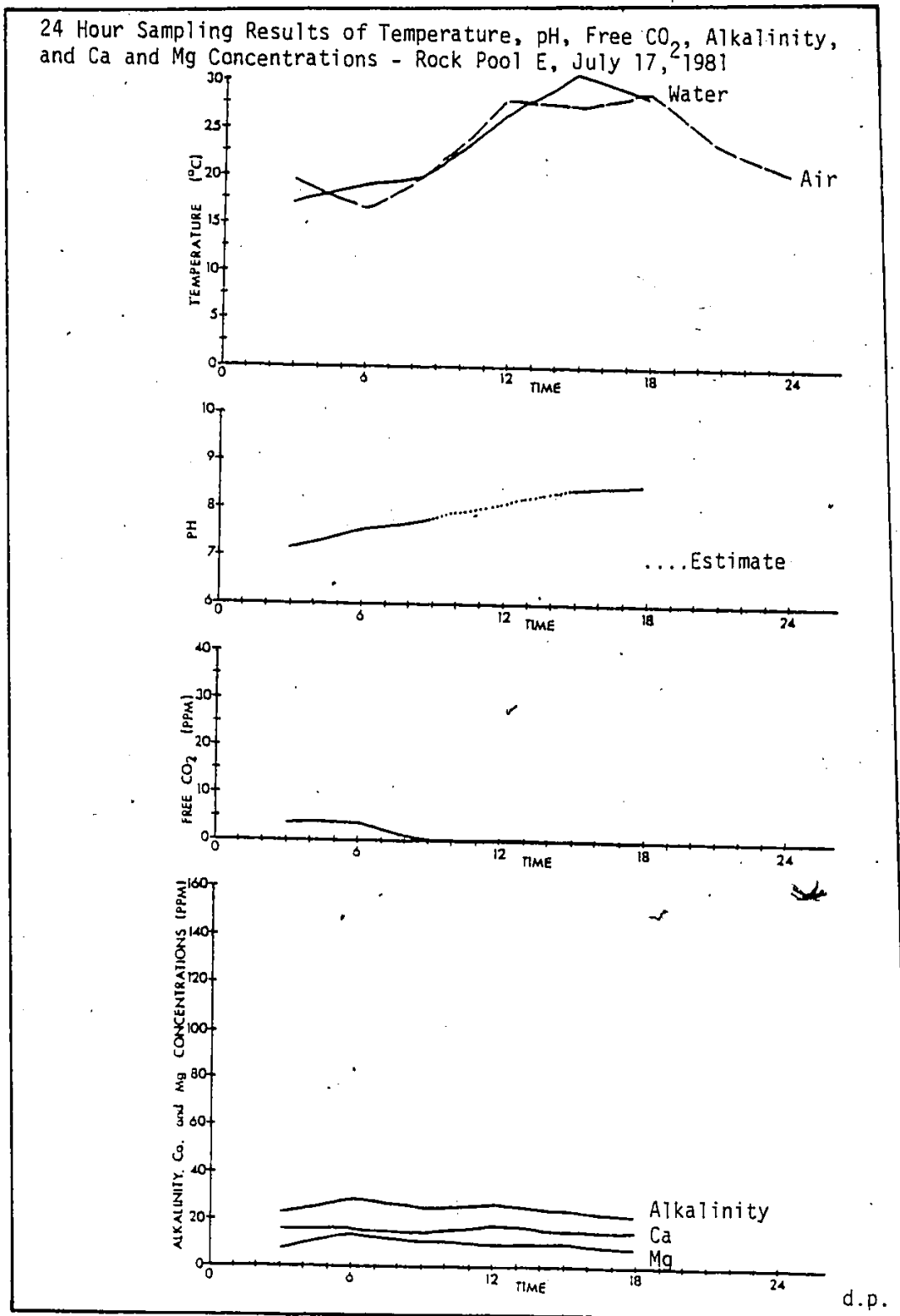


Fig. 18

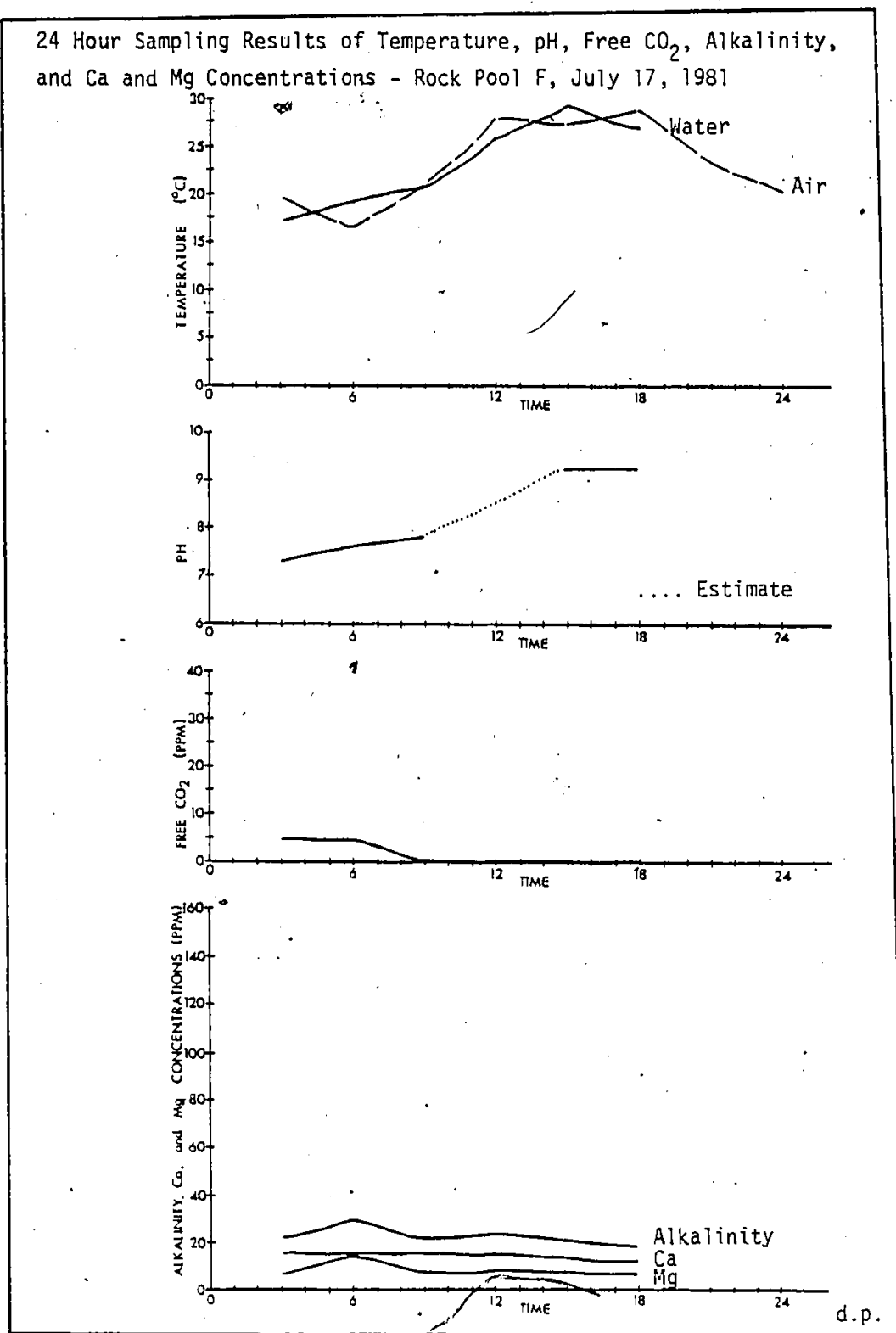


Fig. 19

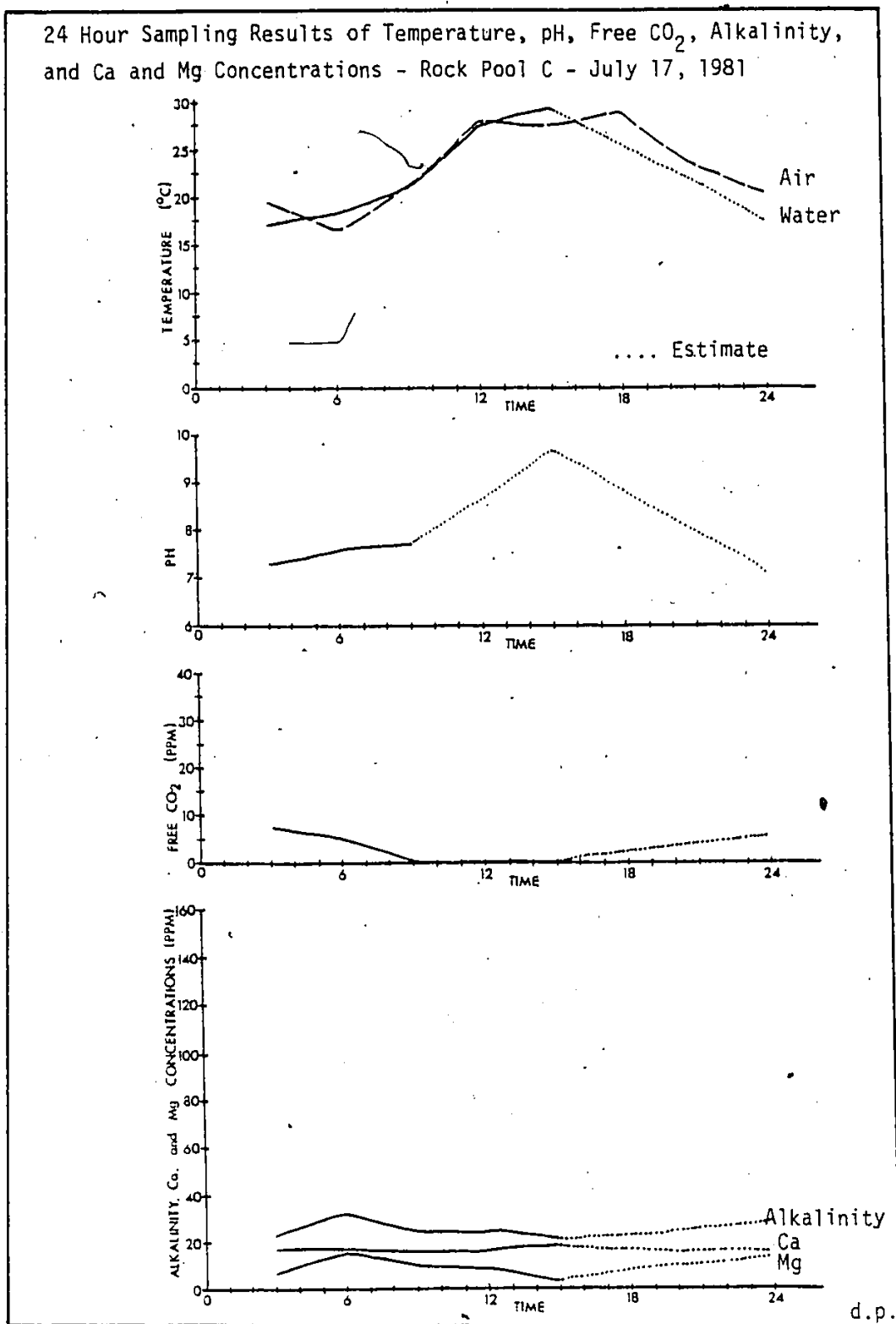


Fig. 20

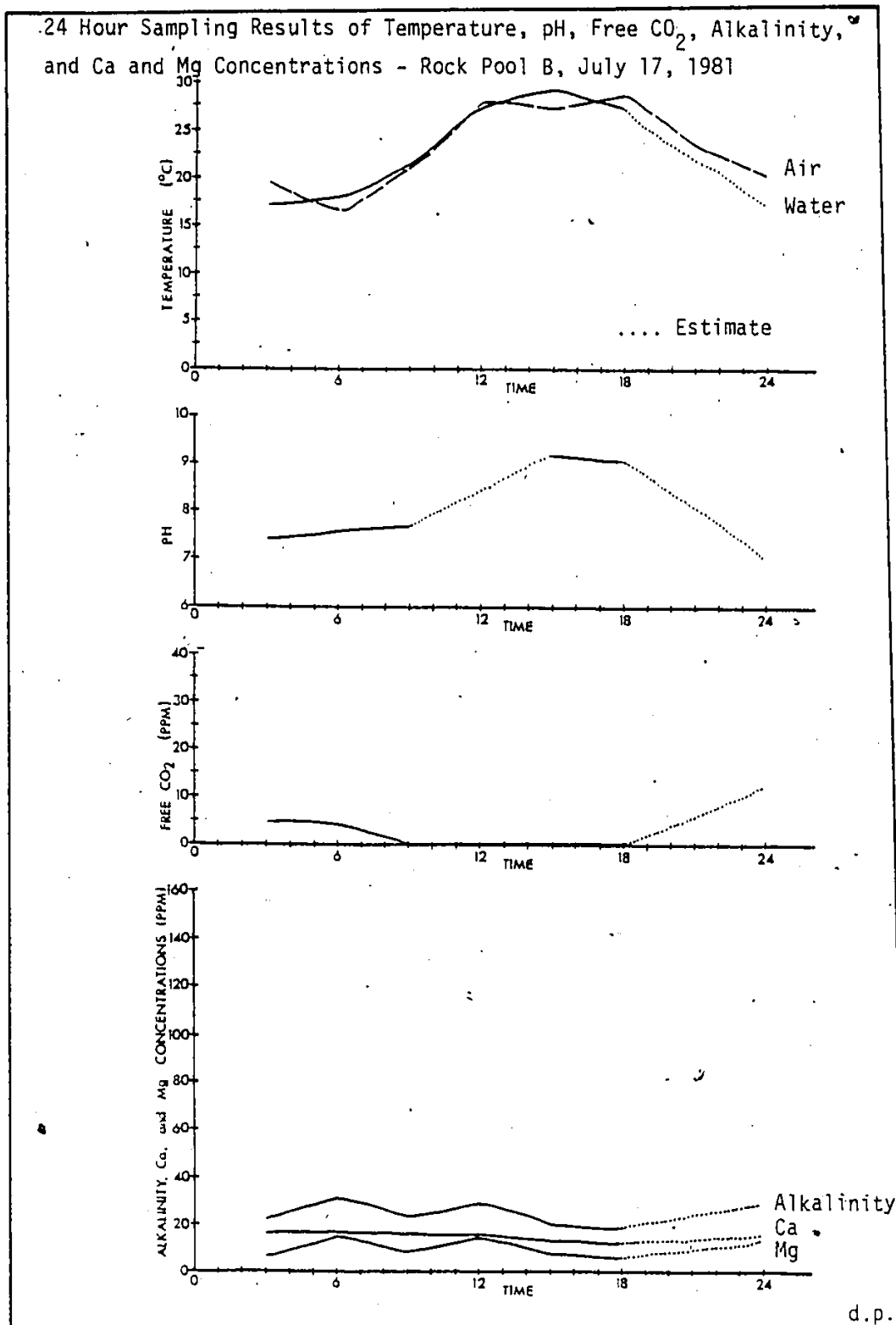


Fig. 21

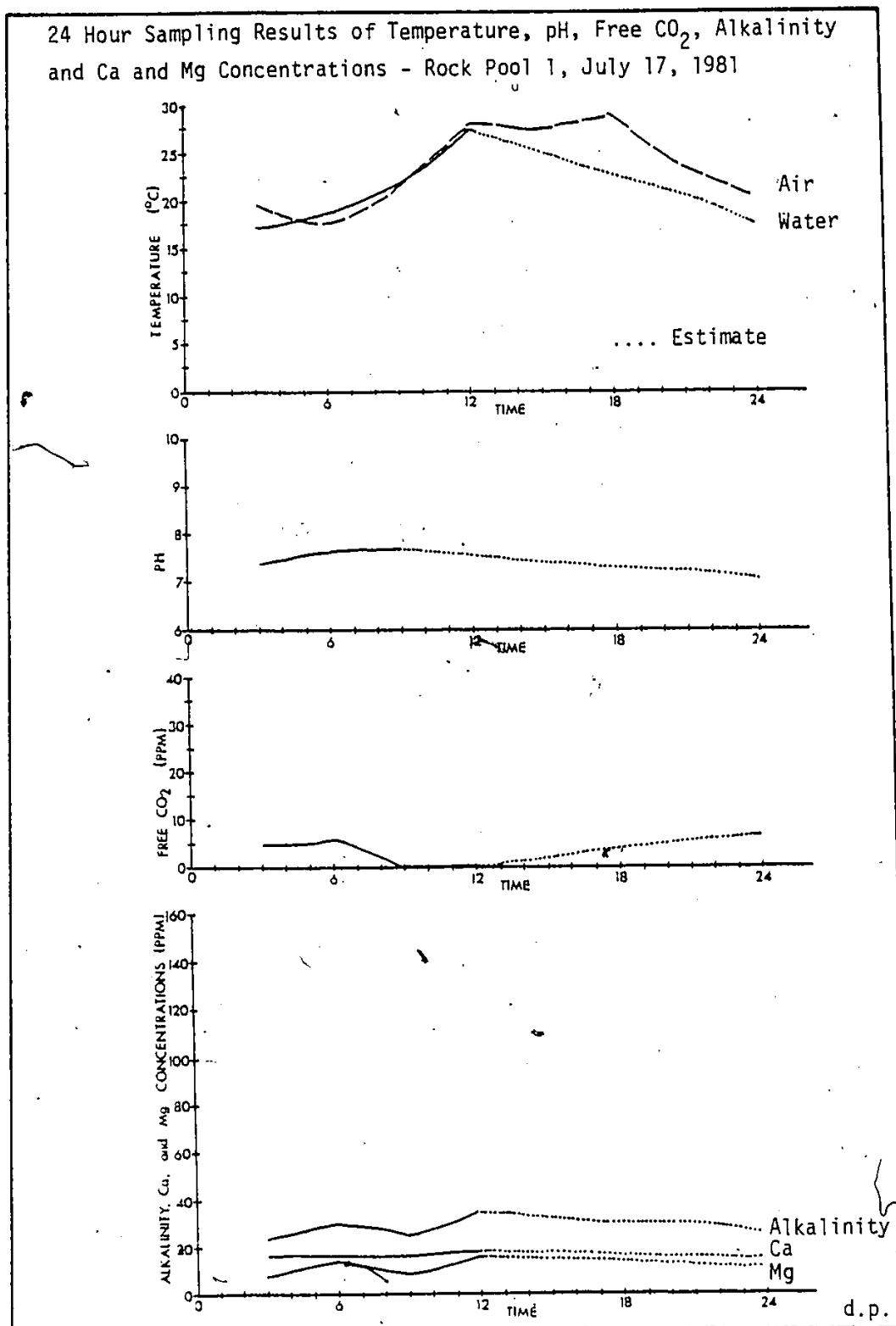


Fig. 22

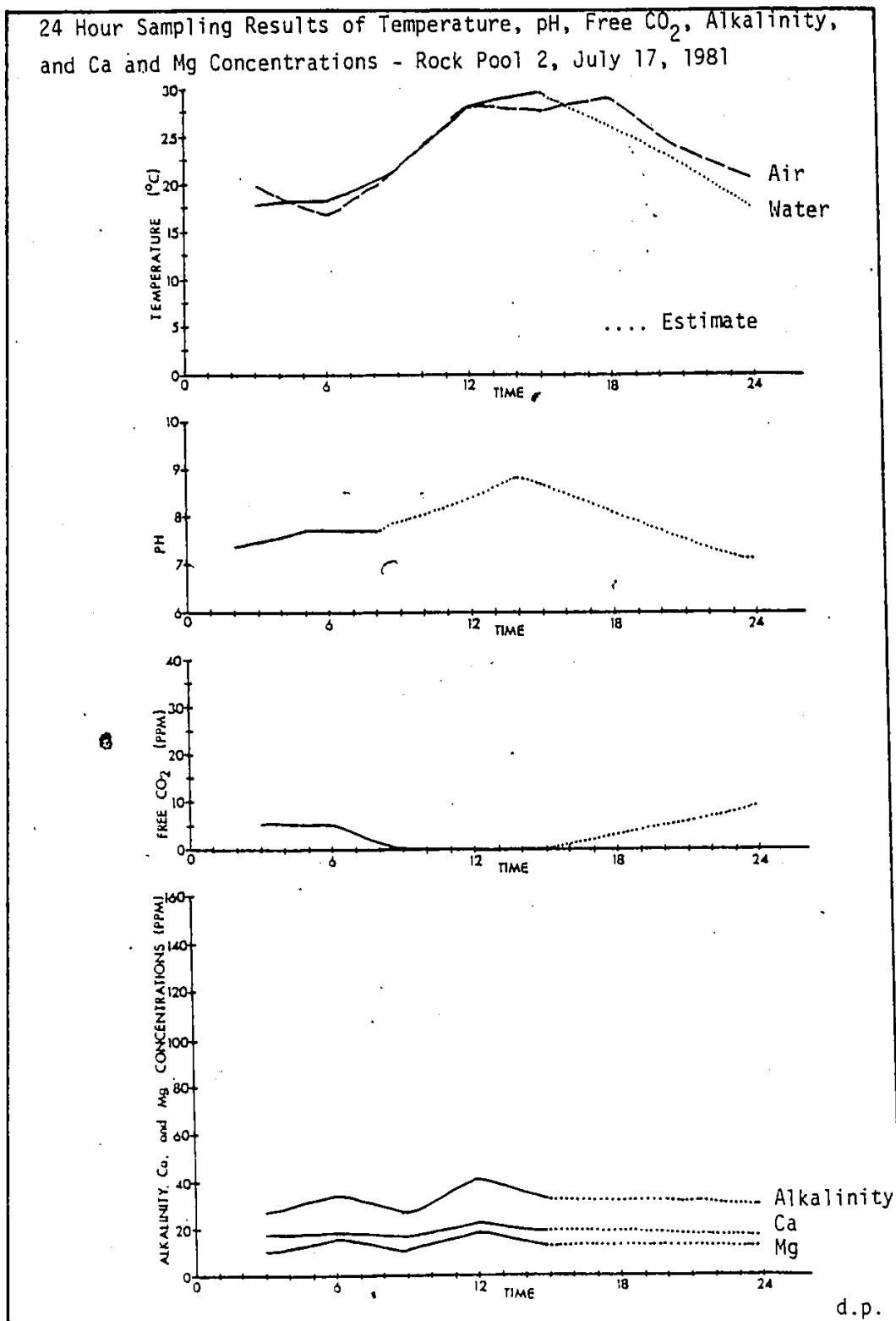


Fig. 23

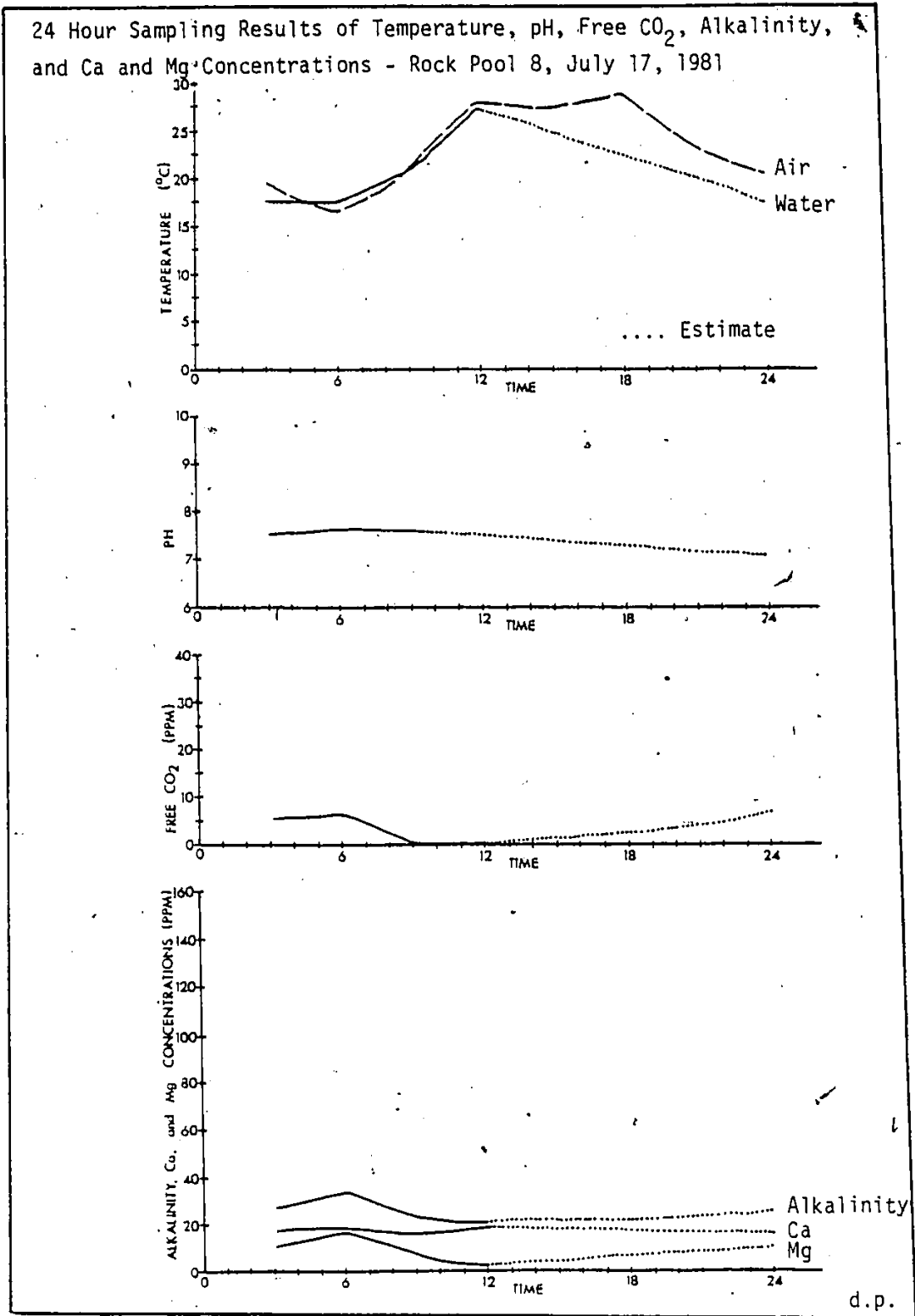


Fig. 24

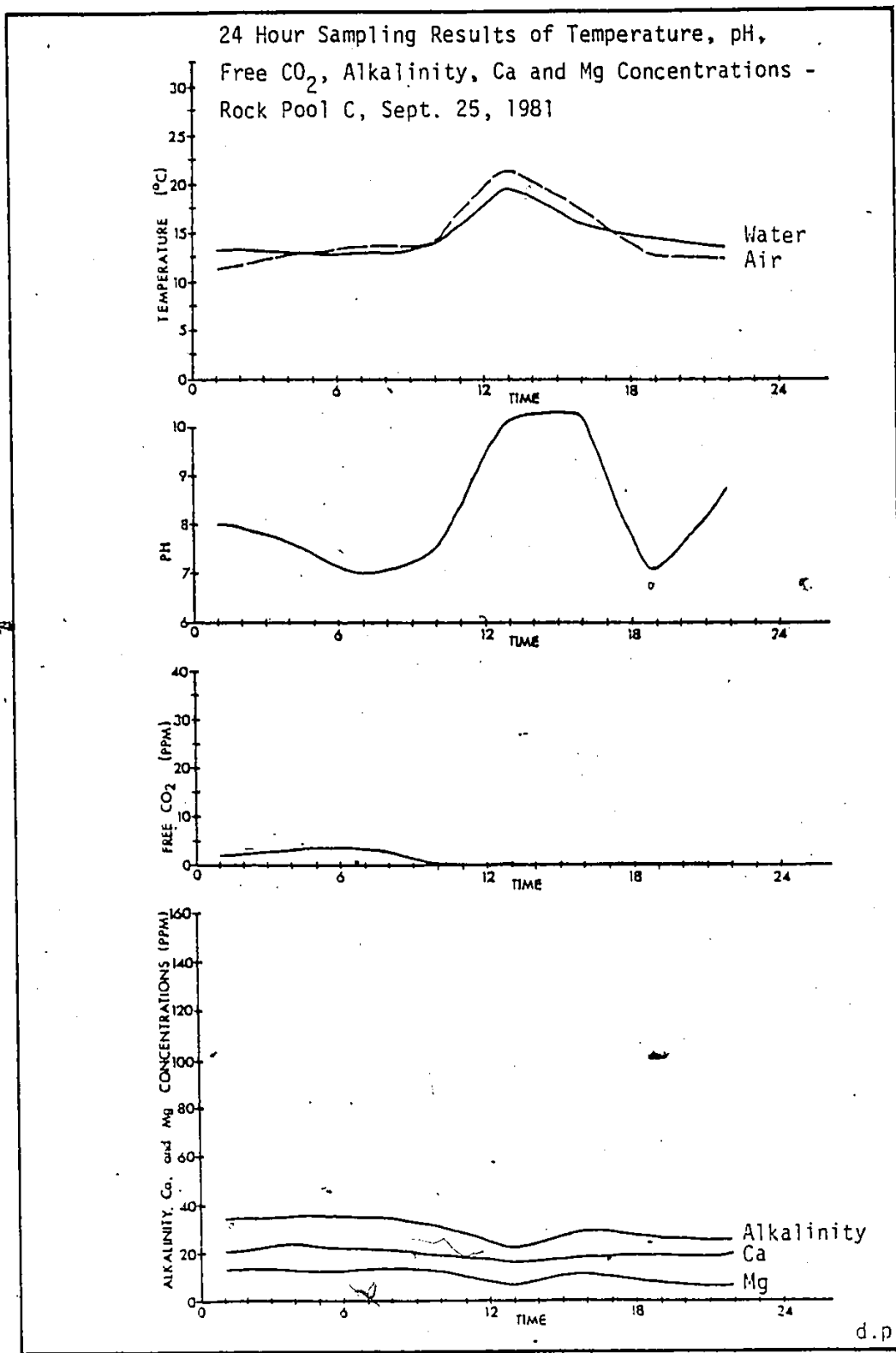


Fig. 25

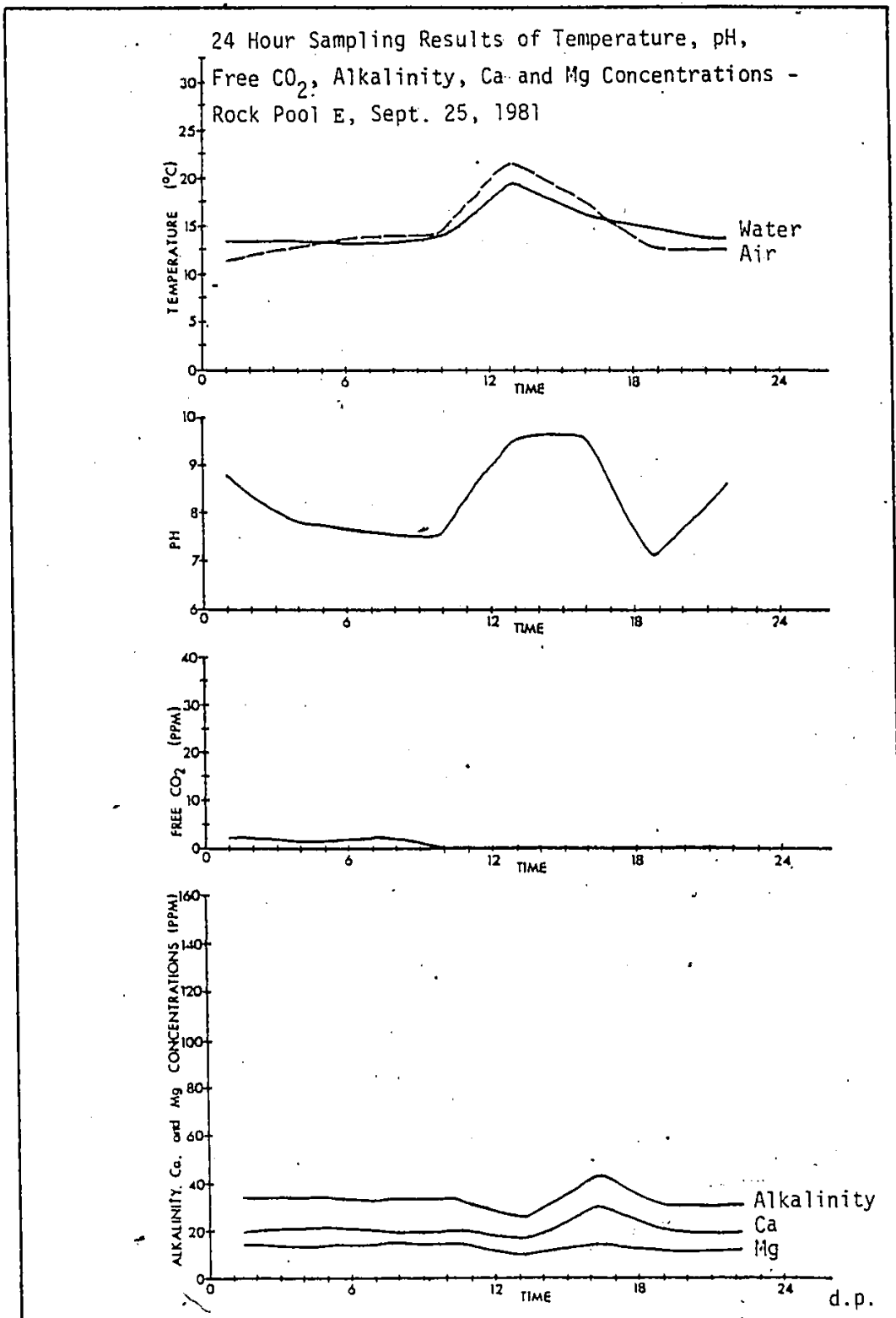


Fig. 26

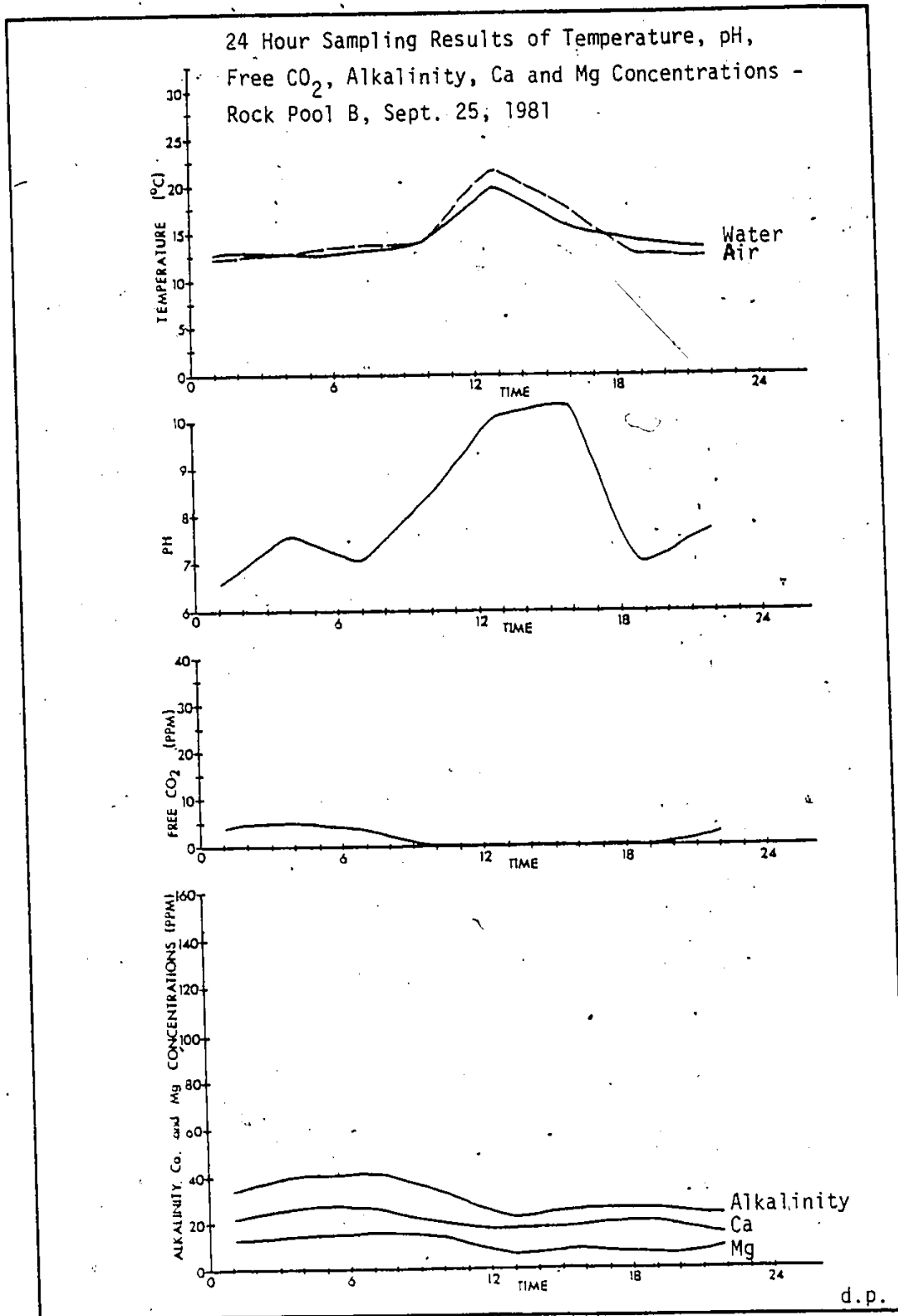


Fig. 27

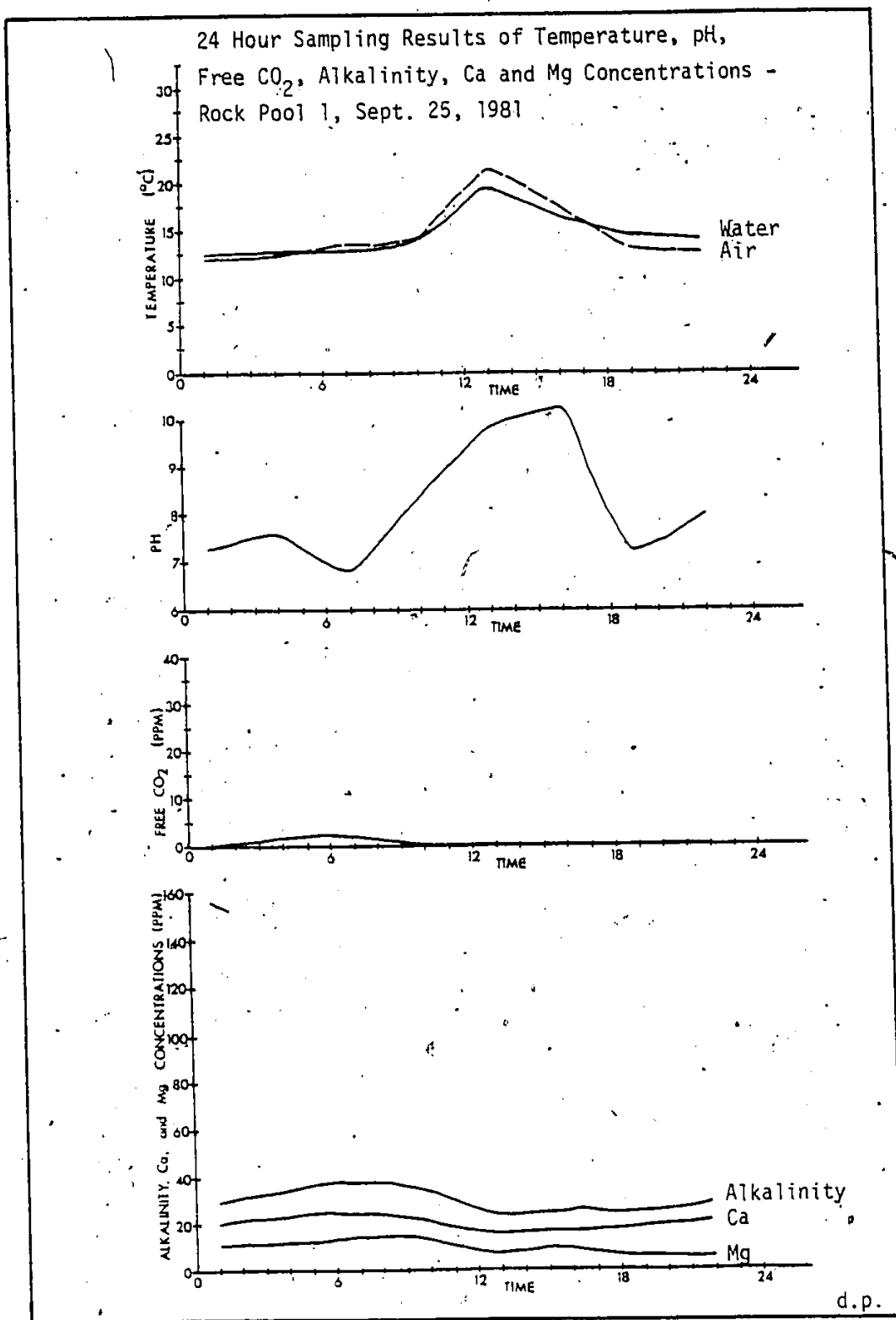


Fig. 28

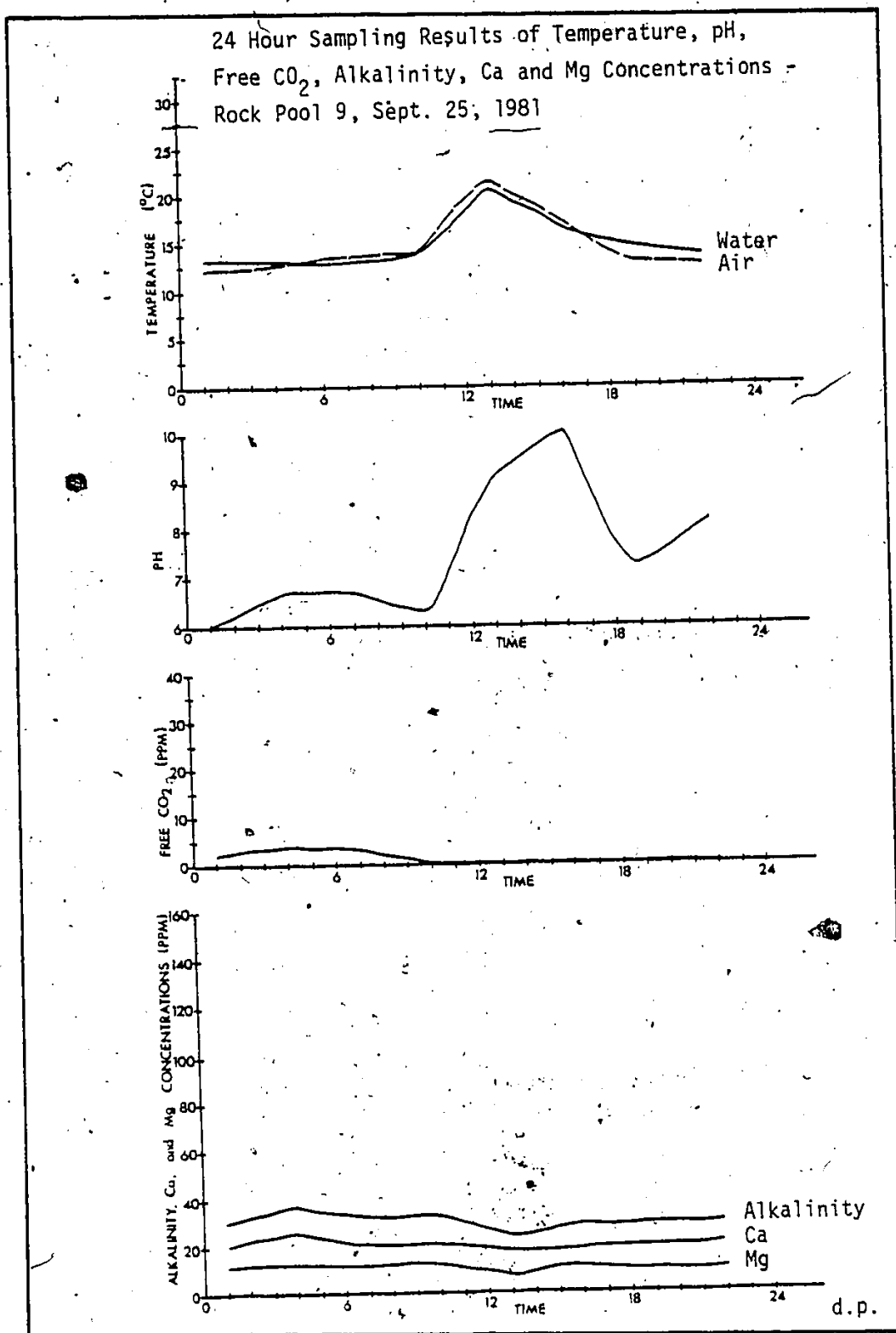


Fig. 29

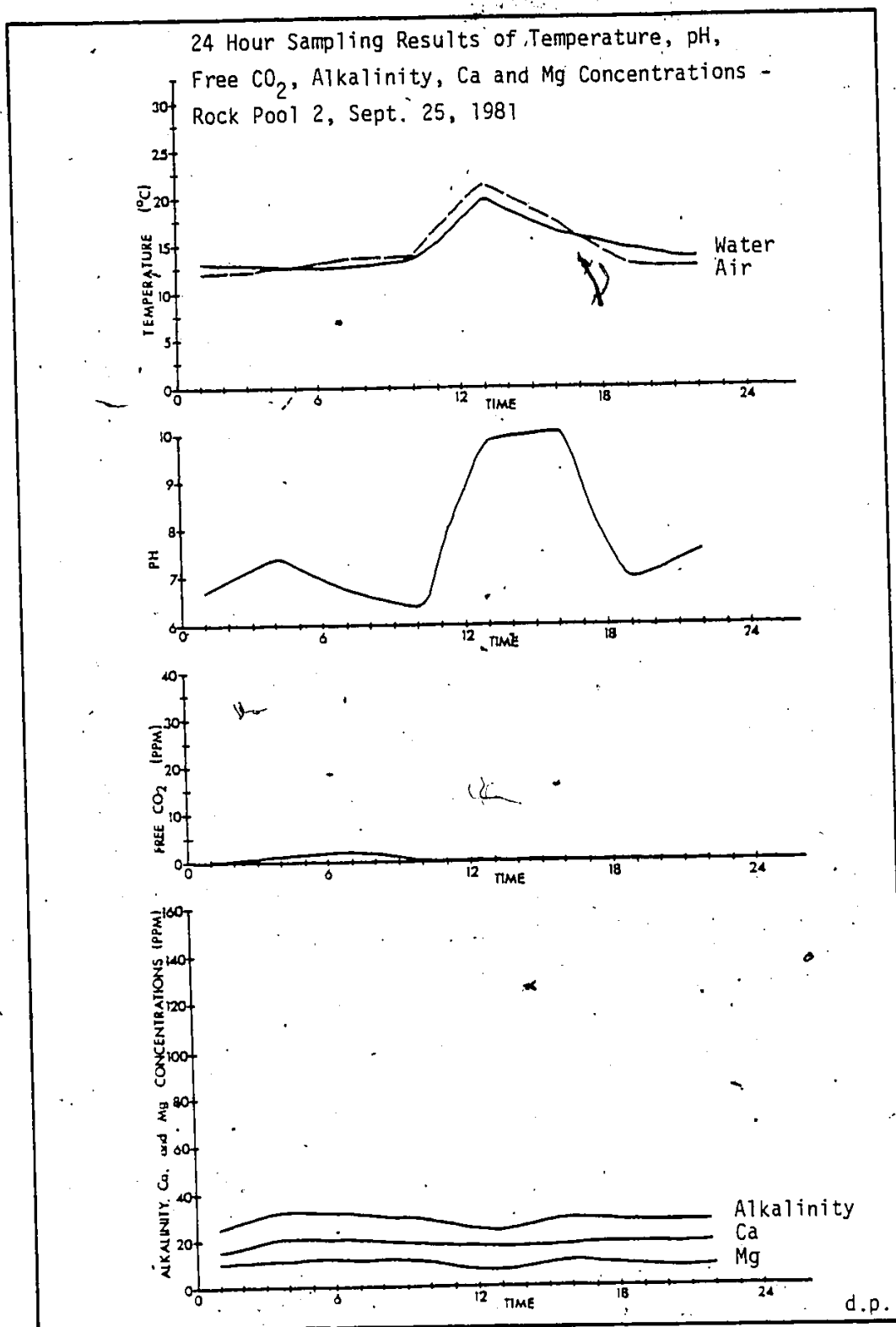


Fig. 30

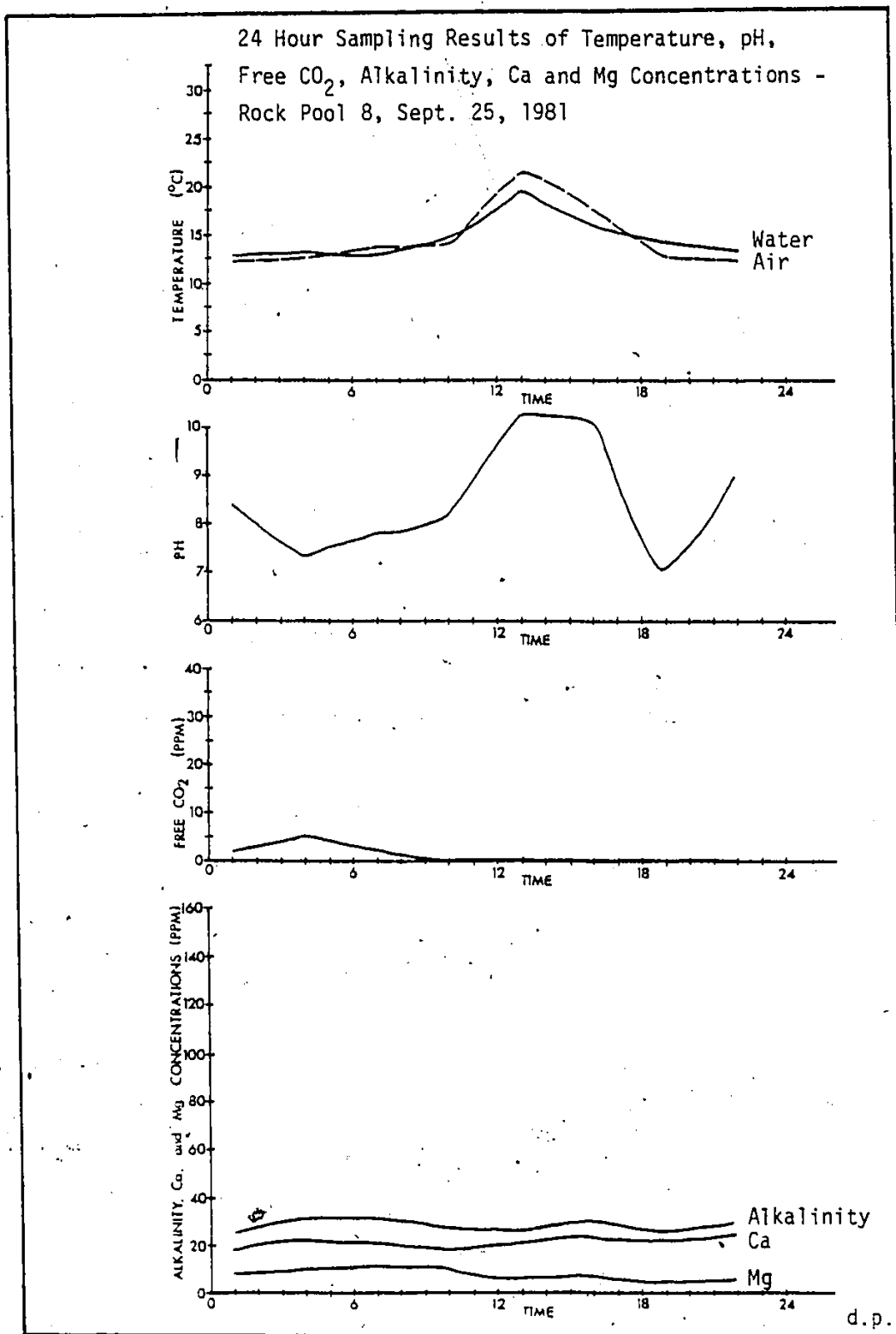


Fig. 31

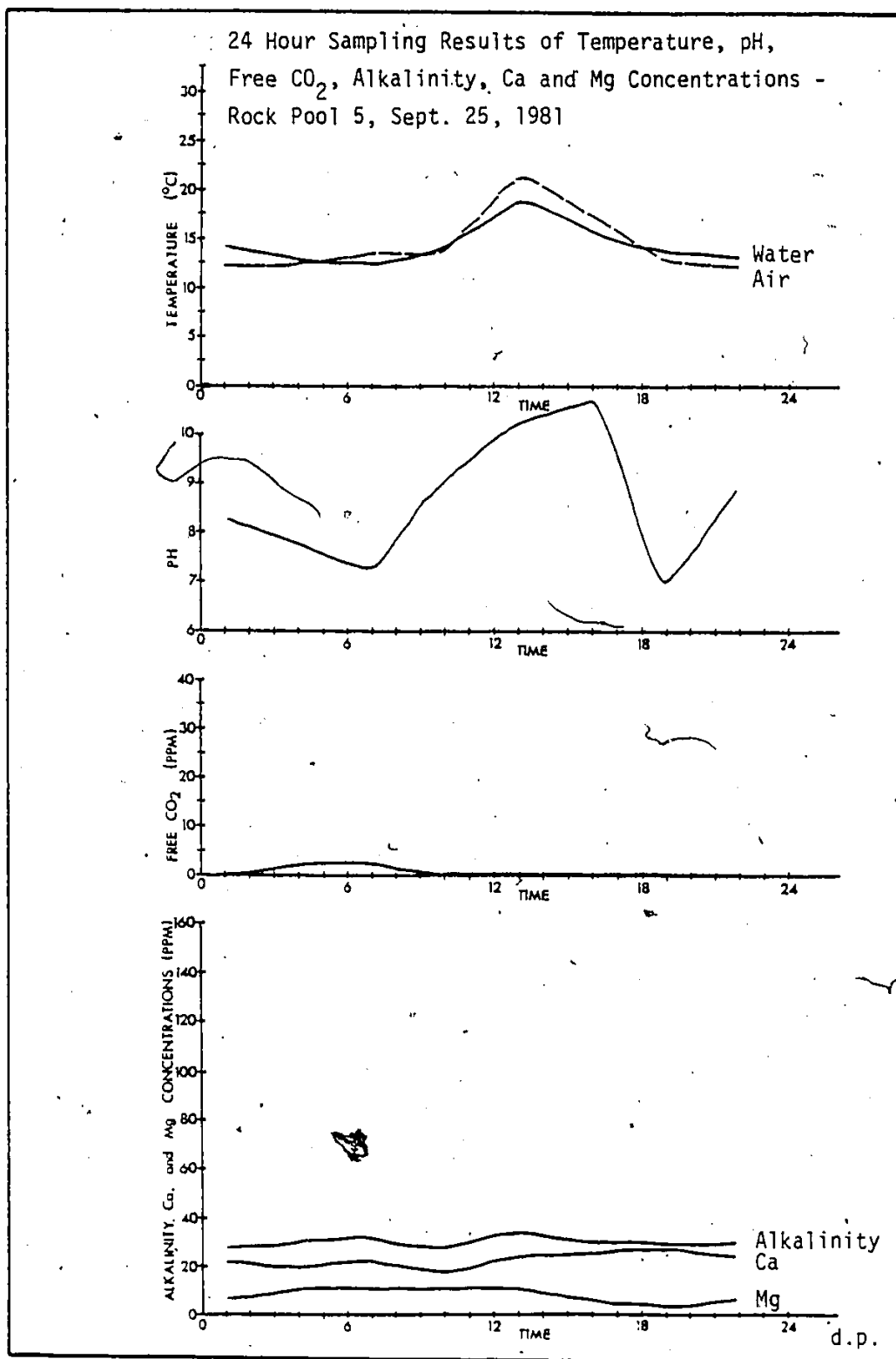


Fig. 32

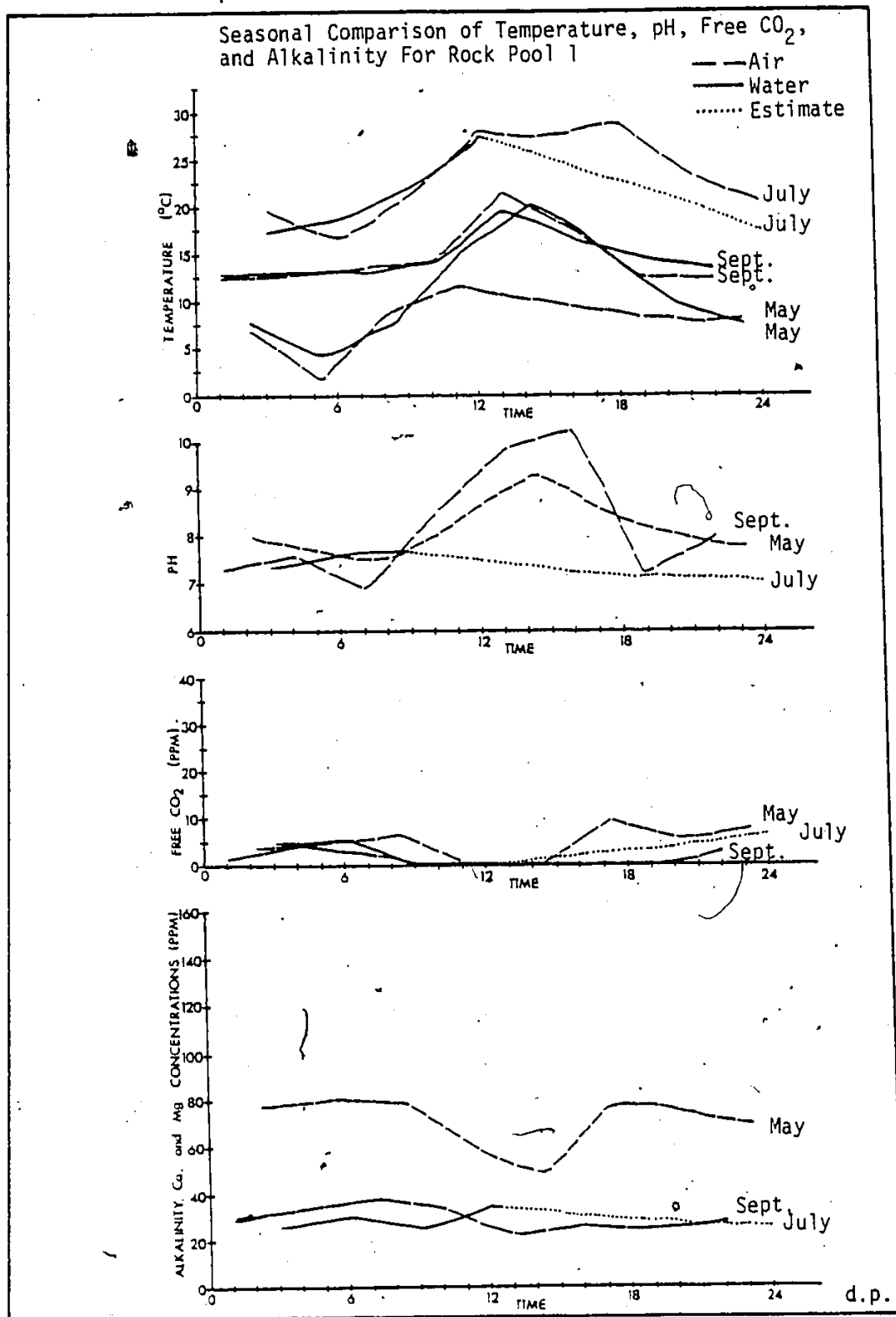


Fig. 33

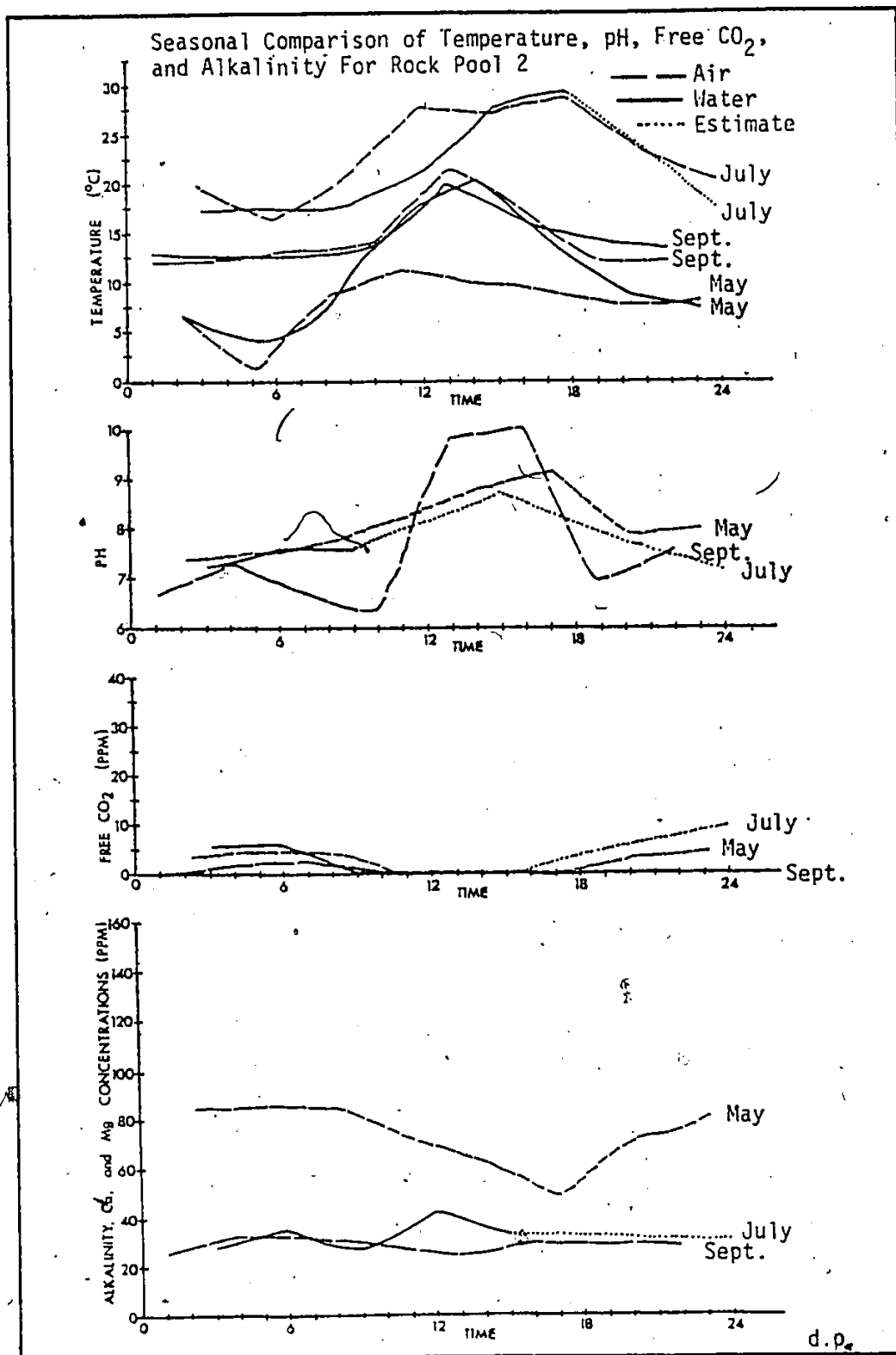


Fig. 34

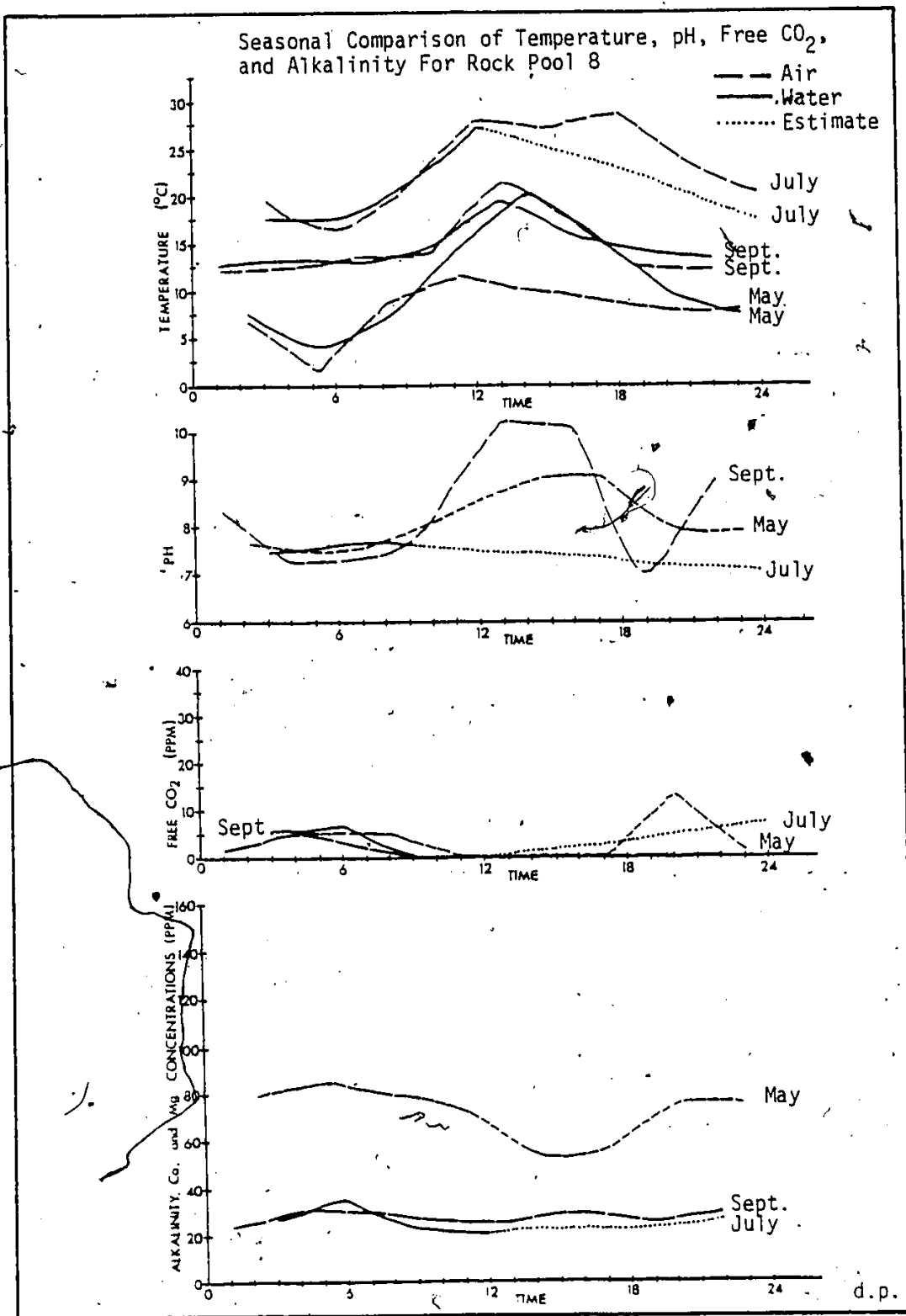


Fig. 35

peak sharply at 0500 hours and fall off to 0 at 0800 hours. All rock pools, with the exception of 6 and 7 experience zero readings from 1100 to late afternoon. The Ca, Mg and alkalinity curves were the same shape, which is inverse to the temperature curve with the exception of rock pools 2, 4, 5 and 7. The Ca and Mg tended to experience minimums between 1400 and 1700 hours. Rock pools 2, 4, 5 and 7 were different in that their Mg graphs had slight peaks at 1700 hours, which was very close to the time the temperature graphs peaked.

July is a difficult month to analyze because all of the rock pools dried up at one point and then overflowed due to a storm. The temperature peaked between 1200 and 1800 hours and the water temperatures peaked at slightly higher temperatures 3 hours later. The pH curves were similar to the temperature curves, peaking at approximately 1500 hours. Rock pools 1 and 8 both peaked at approximately 0600 hours, after which they steadily decreased. Both of these rock pools were located on the edge of the platform. The free CO_2 curves have an inverse relationship to temperature, with the exception of rock pools E and F which decrease to zero at 0900. These two rock pools were the smallest of those sampled. Alkalinity and Mg have the same general shape, peaking at 0600 and 1200 hours. Rock pools 1, 2, B, C and E experienced their lowest values at the temperature peak. For all eight rock pools, Ca had a fairly straight curve.

In September both air and water values peaked at 1300 hours, air temperatures being slightly higher. The pH curves have a definite peak between 1300 and 1600 hours, which is a lag time of approximately 3 hours to that of temperature. All pH curves also experienced a definite minimum at 1900 hours. Rock pools B, 1, 2 and 9 had secondary peaks at 0400 hours, and a secondary minimum between 0700 to 0900 hours. Rock pools C, E, 8 and 5 had secondary peaks between 2200 and 0100 hours, and secondary minimums between 0400 and 0700 hours. The free CO₂ curves were at a maximum between 0400 and 0600 hours when temperature values were at a minimum. They all dropped off to zero at approximately 0100 hours and remained there for the remainder of the sampling period. Alkalinity, Ca and Mg were basically the same shape, having an inverse relationship to temperature. These curves tended to peak at 0600 hours and at 1600 hours, and experienced a minimum value around 1300 hours.

Figures 33, 34 and 35 are comparisons of rock pools 1, 2 and 8 through the three sampling periods. There were three distinct ranges of temperature with July having the highest temperatures and May the lowest temperatures. All three rock pools had their highest pH values in September, and the smallest pH readings in July. The September and May pH maximums had a lag time of approximately three hours to that of air temperature. Minimums in pH for all rock pools with the exception of 1 and 8 in July, occurred in the early morning (approximately 0600 hours) and early evening

(approximately 1900 hours): Inverse to the pH curves, free CO_2 curves peaked in the early morning and evening. All rock pools had zero readings between 1100 and 1500 hours. May tended to have the highest values, July had the second highest values, and September the lowest values. May also had the highest alkalinity values. The September alkalinity curve was higher than July for rock pools 1 and 8, while July had slightly higher values compared to September for rock pool 2. Rock pool 1's alkalinity curves for May and September were inverse to the temperature curves, experiencing maximum values between 1600 and 1700 hours, and minimum values between 1300 and 1400 hours. Rock pool 1's July curve was maximum at 1200 hours and at a minimum at 0900 hours. May and September alkalinity curves for rock pools 2 and 8 were inverse to temperature also. These graphs serve to indicate the general trends of the variables over a 24-hour sampling period. Generally, the trends were the following: during the daytime, pH readings were at a maximum and free CO_2 , alkalinity, and Ca and Mg concentration readings were at a minimum; and during nighttime, pH readings were at a minimum and the free CO_2 , alkalinity, Ca and Mg concentrations were at a maximum. These fluctuations were predicted by the experimental model (Fig. 5), and hypothesis one. Hypothesis two predicted that the relative fluctuations of the variables would be greater in the spring than those experienced in the summer and fall and the higher values in

alkalinity, Ca and Mg concentrations tend to support this hypothesis. Although the July and September alkalinity, Ca and Mg concentrations are similar, the September values tend to be higher. Also, the pH and free CO₂ fluctuations are greater in September as compared to July. These results tend to support hypotheses three and four, which predicted the lowest fluctuations of the variables in the summer and fluctuations between those of the spring and summer in the fall. These relationships were investigated further by the analysis of variance and the partial correlation tests.

The results for the laboratory simulation of May and September temperatures are recorded on Tables 6 to 8 and graphed on Figs. 36 to 41. It was difficult to get the temperatures to mimic the site temperatures for two reasons. The first reason is that the environmental chamber was not suited to temperatures much higher than 19°C. The second reason is that even though the air temperatures were simulated, the water temperatures were generally a degree colder than the air temperature which was unlike the water temperatures on site. In an attempt to compensate for this problem the water temperatures of rock pool 2 in May were simulated, which gave better temperature results. Only the May and September temperatures were simulated as the environmental chamber could not go high enough for the July temperatures.

The May organic pH curve remained between 6 and 7, peaking slightly at 0500 hours and 1100 hours. The free CO₂,

THE 24-HOUR READINGS OF TEMPERATURE, PH, FREE CO ₂ , CALCIUM, MAGNESIUM AND ALKALINITY FOR ORGANIC (O) AND INORGANIC (I) ROCK POOLS UNDER LAB SIMULATION CONDITIONS (AIR TEMP.) OF MAY 18, 1981									
ROCK POOL	TIME	AIR TEMP. (°C)	WATER TEMP. (°C)	PH	FREE CO ₂ (PPH)	CA (PPH)	HG (PPH)	ALKALINITY (PPH)	
0	1700	9.0	8.0	6.5	3.5	5	5	10	
0	2000	6.0	6.0	6.5	5.0	5	4	9	
0	2300	7.0	6.0	6.5	5.5	5	4	9	
0	200	6.0	5.0	6.6	6.5	5	5	10	
0	500	1.0	2.0	6.85	5.0	5	5	10	
0	800	8.5	4.0	6.3	3.0	5	5	10	
0	1100	13.0	10.5	6.55	3.0	5	5	10	
0	1400	11.3	9.5	6.5	3.0	5	5	10	
I	1700	9.0	8.0	6.55	3.5	4	0	4	
I	2000	6.0	6.0	7.1	5.0	4	0	4	
I	2300	7.0	6.0	6.8	3.0	4	0	4	
I	200	6.0	5.0	6.7	4.5	4	0	4	
I	500	1.0	2.0	8.15	3.0	4	0	4	
I	800	8.5	4.0	6.6	3.0	4	0	4	
I	1100	13.0	10.5	7.1	3.0	4	0	4	
I	1400	11.3	9.5	6.9	2.5	4	0	4	

Table 6

THE 24-HOUR READINGS OF TEMPERATURE, PH, FREE CO ₂ , CALCIUM, MAGNESIUM AND ALKALINITY FOR ORGANIC (O) AND INORGANIC (I) ROCK POOLS UNDER LAB SIMULATION CONDITIONS (AIR TEMP.) OF SEPTEMBER 25, 1981								
ROCK POOL	TIME	AIR TEMP. (°C)	WATER TEMP. (°C)	PH	FREE CO ₂ (PPM)	CA (PPM)	MG (PPM)	ALKALINITY (PPM)
0	1600	16	15.5	6.9	5.0	7	4	11
0	1900	12	11.5	6.6	5.5	6	4	10
0	2300	12	11	6.7	4.5	6	5	11
0	100	13	12.5	6.6	5.0	7	5	12
0	499	9.5	9.5	6.6	6.0	7	5	12
0	700	10	9	6.5	5.0	6	5	11
0	1000	12	9	7.8	3.0	6	5	11
0	1300	20	15	6.9	4.5	6	5	11
I	1600	16	14	6.8	3.0	3	0	3
I	1900	12	10.5	7.0	4.0	3	0	3
I	2300	12	10	6.8	5.0	3	0	3
I	100	13	10.5	6.8	2.5	4	0	4
I	400	9.5	8.5	6.9	3.0	4	0	4
I	700	10	8.0	6.4	2.0	4	0	4
I	1000	12	8.0	7.3	2.0	4	0	4
I	1300	20	14	6.9	2.5	4	0	4

Table 7

THE 24-HOUR READINGS OF TEMPERATURE, PH, FREE CO ₂ , CALCIUM, MAGNESIUM AND ALKALINITY FOR ORGANIC (O) AND INORGANIC (I) ROCK POOLS UNDER LAB SIMULATION CONDITIONS (WATER TEMP. - ROCK POOL 2) OF MAY 18, 1981								
ROCK POOL	TIME	AIR TEMP. (°C)	WATER TEMP. (°C)	PH	FREE CO ₂ (PPM)	CA (PPM)	MG (PPM)	ALKALINITY (PPM)
0	1700	14.5	13.0	6.4	2.5	5	4	9
0	2000	8.5	7.0	6.0	3.0	5	4	9
0	2300	7.0	5.5	6.4	2.5	5	4	9
0	200	6.0	3.5	7.0	3.0	5	4	9
0	500	8.5	2.5	6.4	5.0	5	4	9
0	800	12.5	5.0	6.25	5.0	5	4	9
0	1100	17.5	12.5	6.9	5.0	5	4	9
0	1400	18.8	16.0	6.6	2.5	5	4	9
I	1700	14.5	12.3	7.1	2.5	60	2	8
I	2000	8.5	5.5	7.1	3.0	5	1	6
I	2300	7.0	5.0	6.8	4.5	5	1	6
I	200	6.0	3.5	7.2	4.0	5	1	6
I	500	8.5	2.0	7.1	4.0	5	1	6
I	800	12.5	4.8	7.0	5.5	5	1	6
I	1100	17.5	11.5	6.75	3.0	5	1	6
I	1400	18.8	15.0	7.4	5.5	5	1	6

Table 8

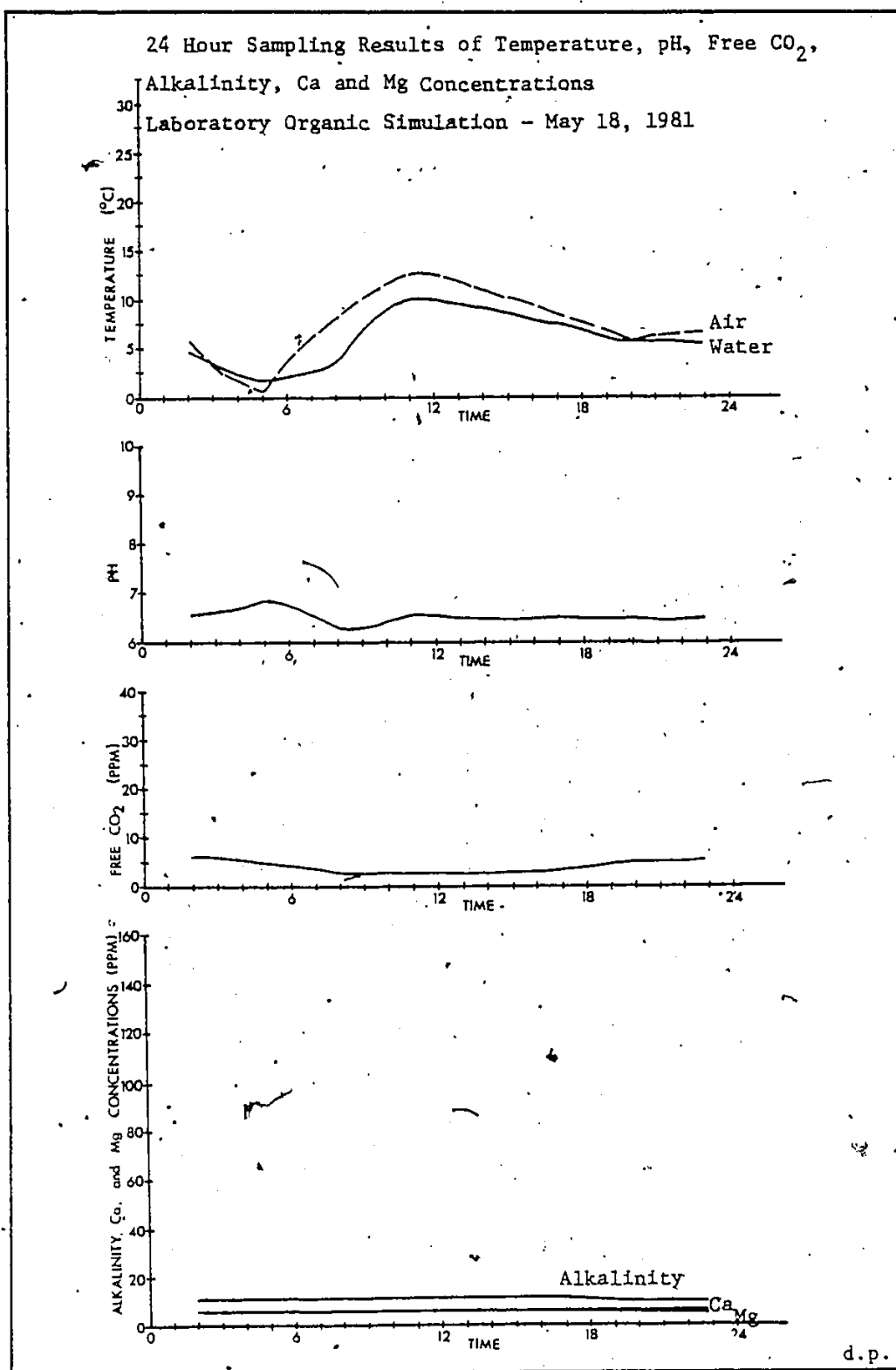


Fig. 36

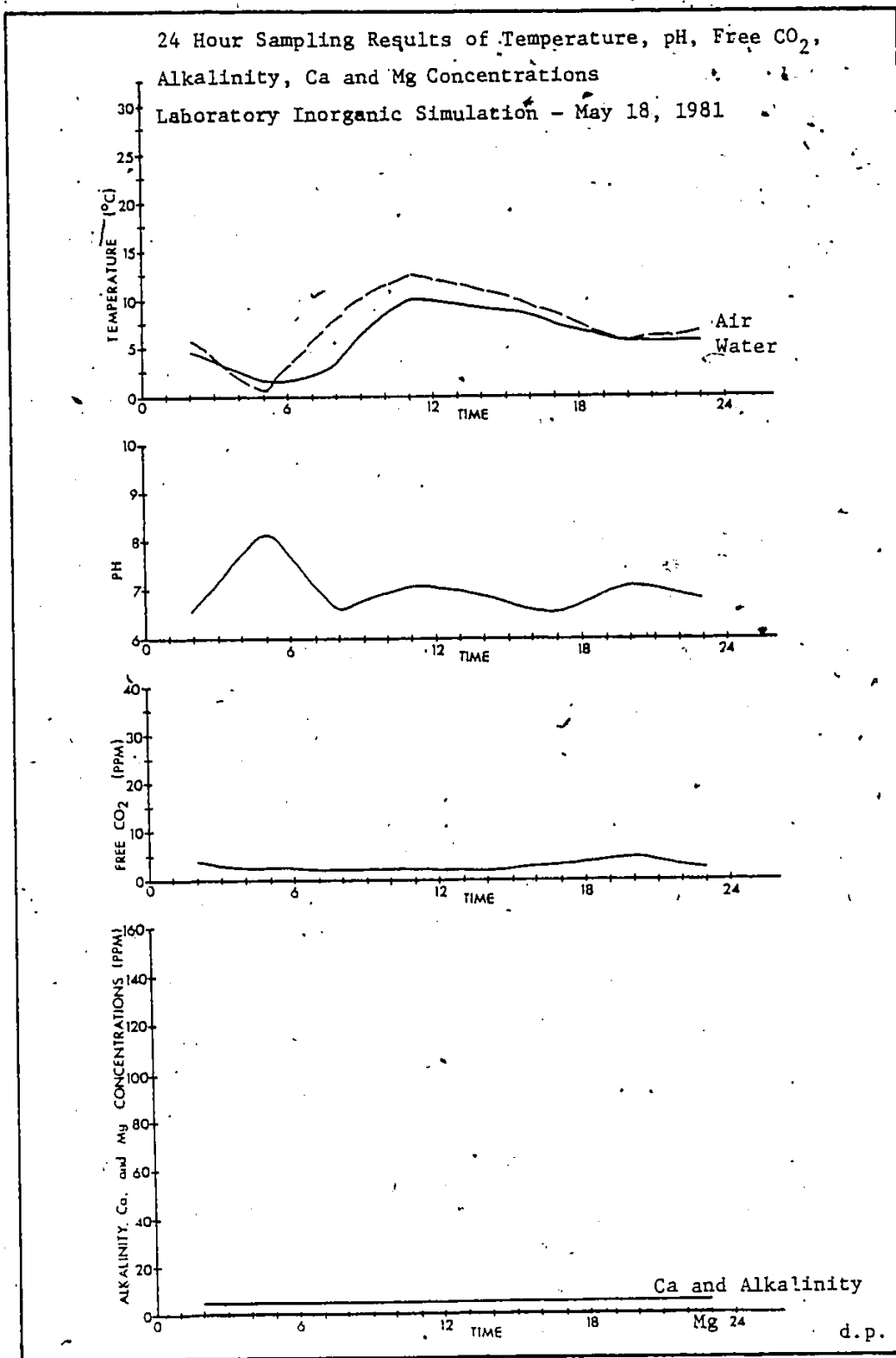


Fig. 37

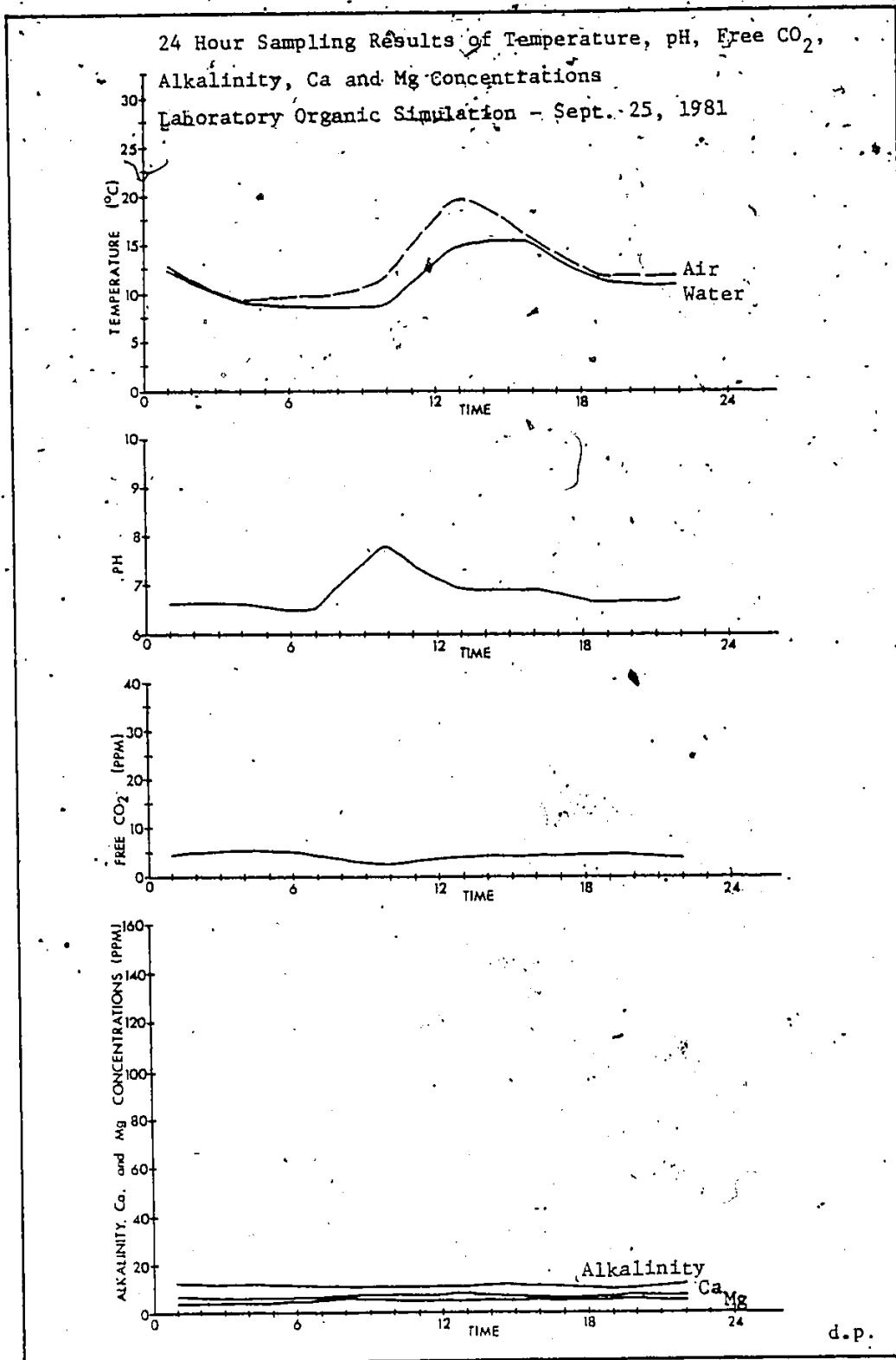


Fig. 38

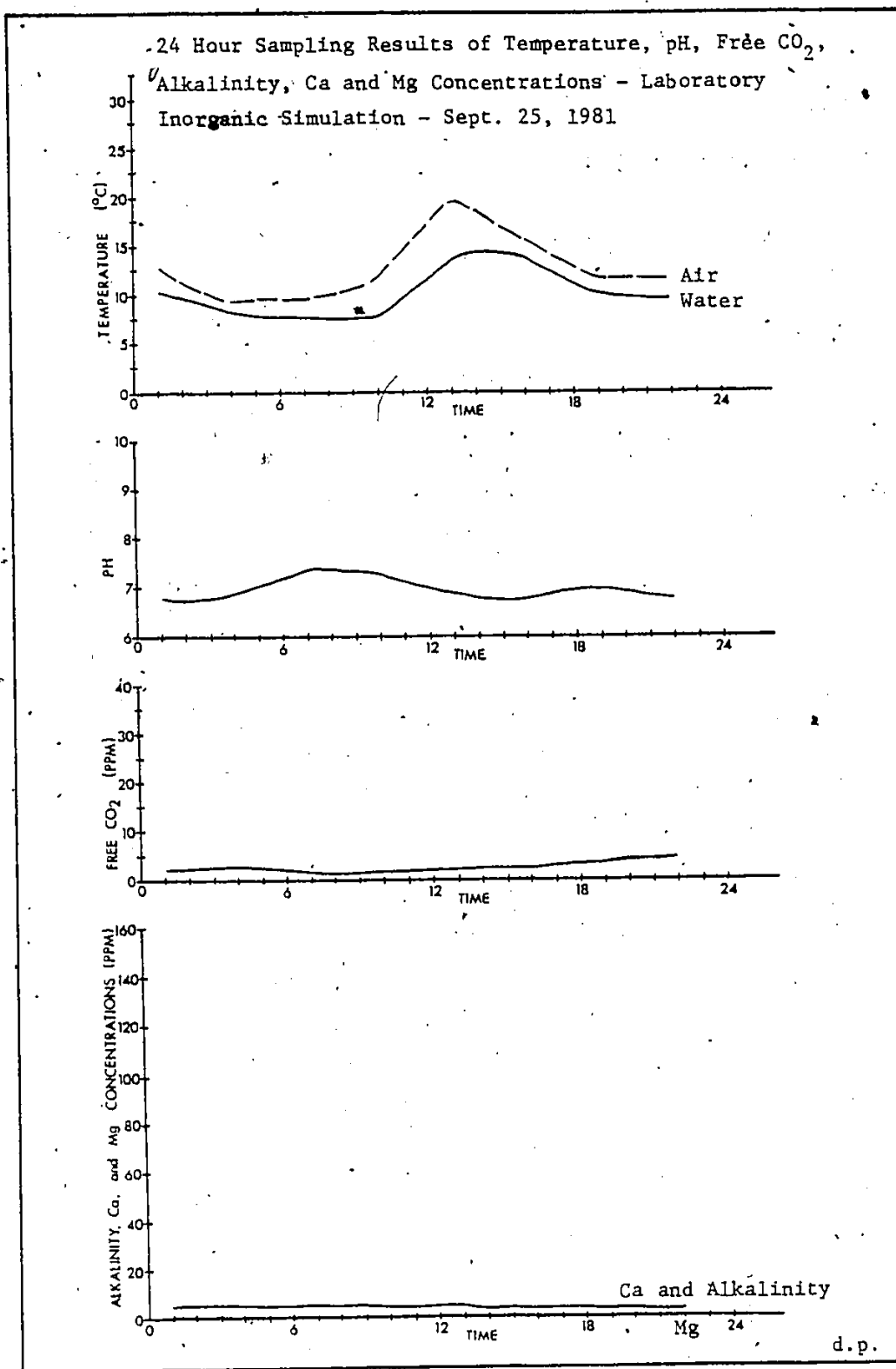


Fig. 39

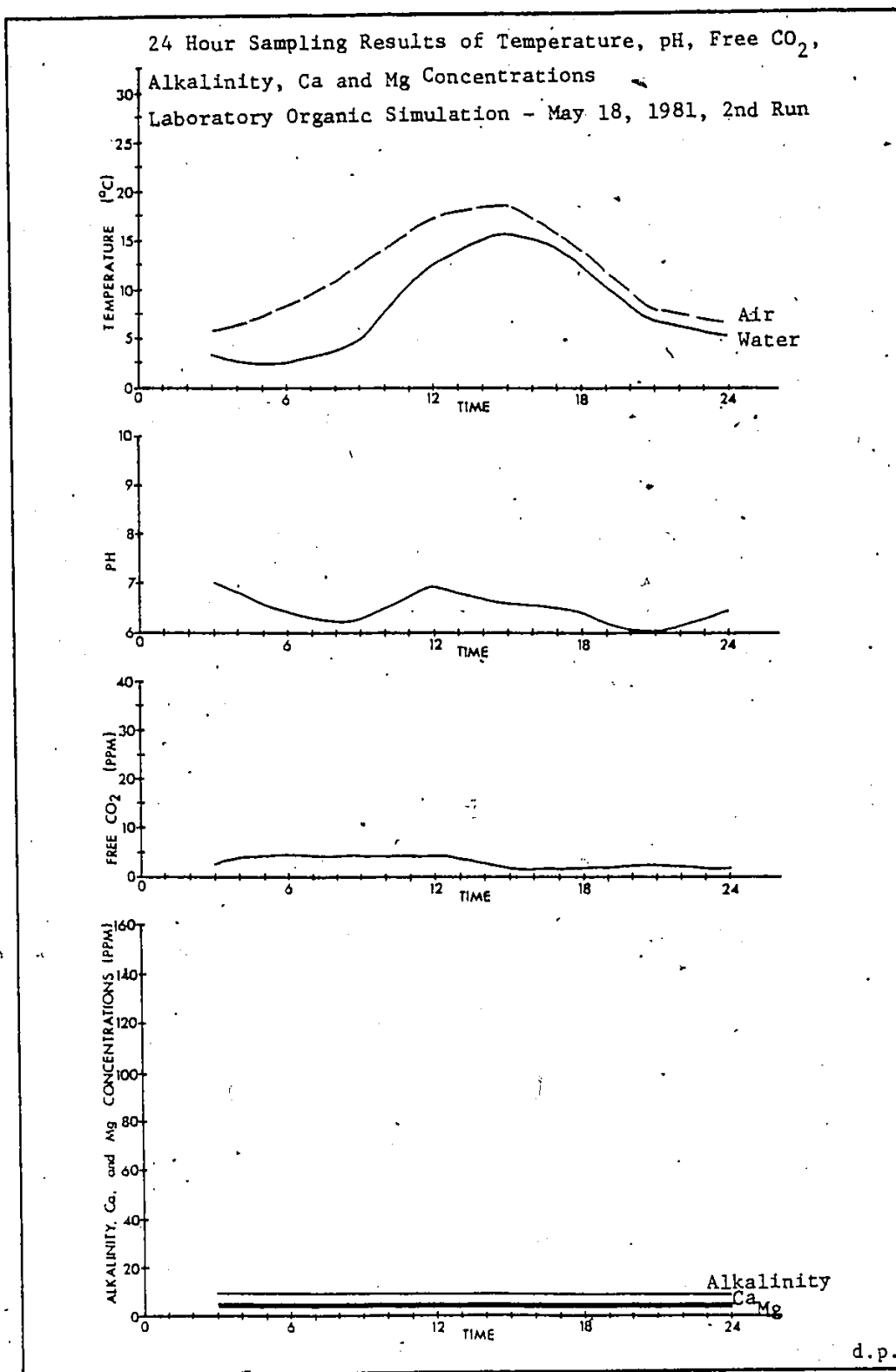


Fig: 40

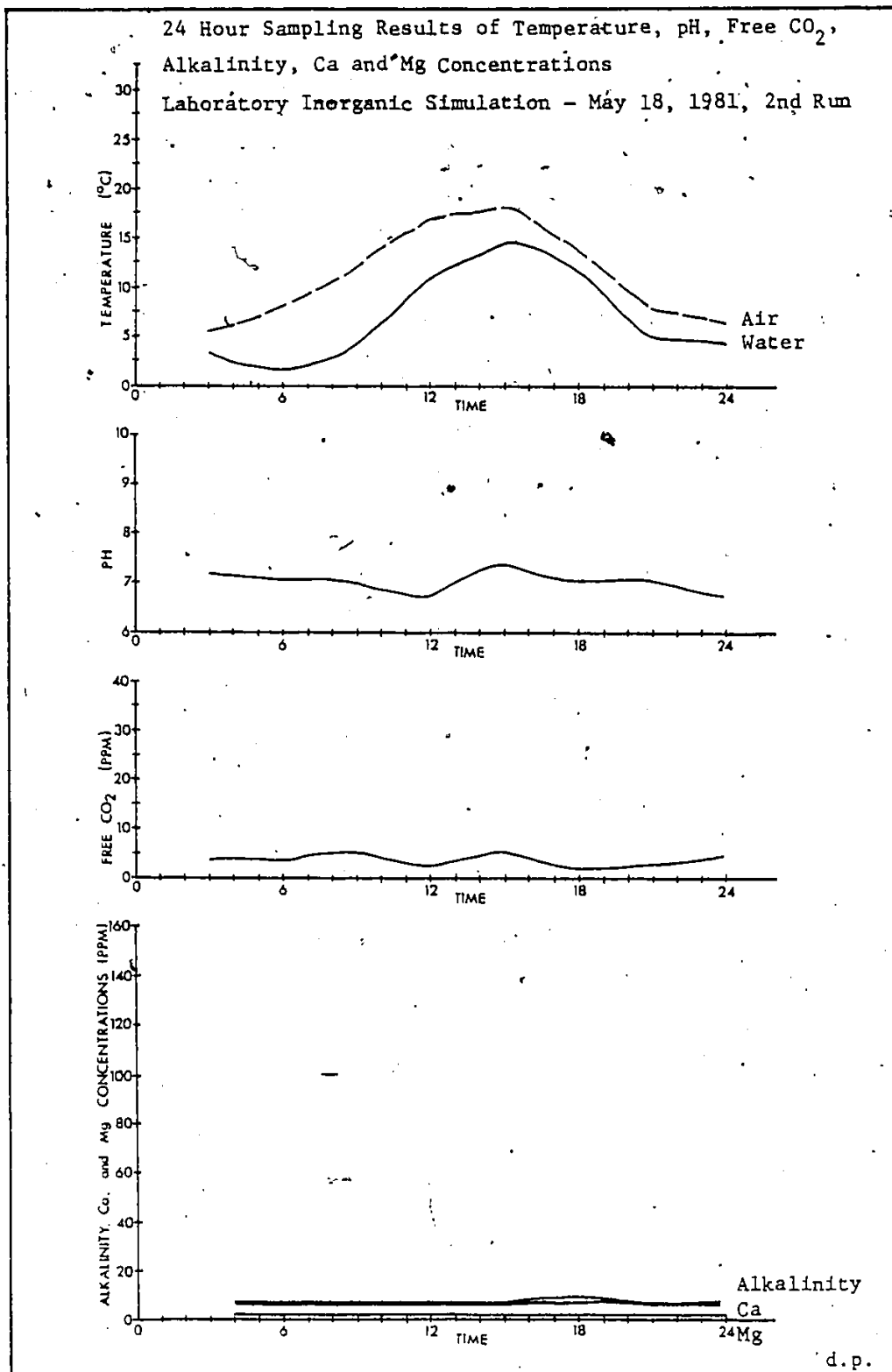


Fig. 41

curve experienced a slight maximum between 2300 and 2400. The Ca, Mg and alkalinity curves were almost straight at very low values. The May inorganic pH curve fluctuated more than the organic curve, maximizing at a value of 8.15 when the temperatures are at a minimum. After peaking, the values fell between 6 and 7. The free CO₂ values were fairly low and steady, similar to the organic curve. The Mg values were zero throughout the whole sampling time and the Ca/alkalinity curve stayed fairly straight at a low value.

The September organic pH curve peaked at 7.8 when the temperature was at a minimum. The free CO₂ curve was fairly steady, experiencing a slight minimum when the temperature curve was at a minimum. The pH and free CO₂ maximums and minimums from the lab results are opposite to that of the curves from on site data. The Ca, Mg and alkalinity curves were basically straight lines at low values. The September inorganic pH curve peaked at 7.3 when the temperature was also at a minimum. The free CO₂ curve fluctuated slightly downwards when temperature was at a minimum. The Mg line again stayed at zero and the calcium/alkalinity was essentially constant at a low value.

For the first two simulations the rocks were in their environments for three days before sampling. On the second May run, the rocks were left in their environment for one

week before sampling. The May organic pH values were again between 6 and 7, peaking at 7, three hours before the air temperature peaked. The free CO₂ had no apparent pattern, staying fairly steady between 0 and 5 ppm. The alkalinity, Ca and Mg values formed straight lines at very low values.

The May inorganic pH curves fluctuated around 7 with no real pattern. The free CO₂ curve also had no apparent pattern, staying between 0 and 5.5 ppm. For the first time in the laboratory simulation experiments, there were Mg readings above 0 ppm. The Mg, Ca and alkalinity curves were fairly straight at low values. On the whole, both the inorganic and organic results did not behave closely to the site results. Any fluctuations in the variables were minimal, and it is difficult to determine any relationships between them. The analysis of variance and partial correlation will clarify any relationships that may exist between these variables.

According to the literature the biological activity is at a maximum in spring, and at a minimum in the summer. On the spring trip the visual signs of biological activity were recorded. A thin coating of grey biological matter lined the bottom of the rock pools, having air bubbles trapped within it. Also, rock pools 4, 6 and 7 contained an abundance of fibrous looking plants. The coatings on the bottom of the rock pools were thicker on the July trip, and greenish algae covered a great deal of

1
the platform surface.. Grasses and green plants grew in a few of the rock pools, as well as inbetween joints of the platform rock. On the September trip a higher order of plant life was much more evident. There were many grasses and flowering plants growing in the joints of the platform and mosses were evident for the first time. The bulbous material on the bottom and sides of the rock pools was thicker than that found on the July trip. The whole platform was very slippery and slimey, covered with a greenish brown algae. The lake level had lowered on every trip, and on this trip the secondary platform was no longer covered with water, having a thick covering of greenish brown algae upon it. Overall, it is impossible to determine biomass by visual means only. However, the season variable will be interpreted as a biomass difference as the literature predicts that biomass changes in type and numbers through the three seasons in a very distinct manner. Hypothesis six suggested that rock pools with the greatest biomass will exhibit the greatest fluctuation of free CO_2 , pH, alkalinity, and Ca and Mg concentrations on a given trip, and these rock pools would be the largest in size and depth of those surveyed. The only trip which showed significantly different fluctuations between rock pools was in May. On this trip, rock pools 7, 4, and 6 had higher Ca, Mg and alkalinity results compared to the others (Figs. 11 and 12). Rock pools 7 and 4 were both fed from beneath the top rock surface and both had visible fibrous-

type plants that were not observed in any other rock pools. Rock pool six was more self-contained but had three joints feeding in and out of it. All three contained relatively more water than the other rock pools sampled on that trip. This indicates that hypothesis six may be true, but the rock pools are simply too unstable, changing on an hourly basis at times, to make any clear cut distinctions on size.

4.2 Chittick Experiment

Rock samples were brought back from the site and analyzed for Ca and Mg content using a chittick apparatus (Dreimanis, 1962). The calculations from three runs of the experiment resulted in 72.07% Ca and 1.01% Mg. (Appendix 1 and 2). According to Dreimanis, the probable errors for the results of the Chittick apparatus are ± 0.1 for calcite and ± 0.3 for dolomite. This error is increased in that two out of the three experiments were conducted with the smallest weight recommended for the experiment. A rock composed of between 50% and 75% calcite is considered a dirty or impure limestone and will often be described as a sandy limestone (Ford and Gascoyne, 1978). At 72% calcite, this sample is an impure limestone, and in fact, as mentioned earlier, has been classified as a grey argillaceous limestone (Ontario Division of Mines, 1976).

4.3 Data Preparation

The data were grouped into two main divisions for analytical purposes. The first division made was between the three trips made--spring, summer and fall. The data

were then divided into groups according to air temperature, which was the same as grouping the data according to sampling times. Therefore, eight groups were created within each seasonal group because there were eight sampling times per 24-hour sampling period. These groups of eight also consisted of the eight rock pools sampled at one time, so that the data were grouped for rock pool location comparison. Altogether there were twenty-four groups of eight for the variables of water temperature, free CO_2 , pH, Ca, Mg and alkalinity. The lab data were treated separately from the site data. These data were first divided up by the seasonal temperatures simulated, which were the May air temperatures, September air temperatures and rock pool 2's May water temperatures. The second division was made between the inorganic and organic environments. A third division was made according to temperature variations over a 24-hour sampling period. Totally, six groups of laboratory data existed for statistical testing.

Each individual group of eight described above, for all of the variables, was tested for normality using the Ks test. The July data could not be used for this test as there was too much missing data. When the remaining groups were tested, six of the groups were not normal, but five of these six were normalized by \log_{10} , \ln and squaring transformations. The sixth group had no variance at all, and could not be transformed. The Bartlett's test for homogeneity of variances had mixed results. This can be

explained in the way that the data were grouped. If the groups were not homogeneous, it could be attributed to the rock pool location factor, as each group consisted of data from all of the rock pools at one sampling time. The fact will be further explored in the analysis of variance test.

4.4 Analysis of Variance

In the analysis of variance test for the site data, the independent variables of seasons (X1), location of rock pools (X2), and air temperature (X3), and all possible combinations of these treatments were used to compare with the dependent variables of free CO₂, pH, Ca concentrations, Mg concentrations, and alkalinity (Table 9). The key value on the GLM printout is the F-value which is also called a variance ratio. The F-value consists of a ratio of an estimate of variance based on the variation among the means to an estimate of variance based on the variation within the samples. The variation within the samples is the error sum of squares, or experimental error due to chance. If the F-value is less than F_{crit} , it can be concluded that the differences among the sample means may be attributed to chance. Each treatment sum of squares is the quantity which measures the variation among the sample means, whereas the model sum of squares measures the total variation. The DF column gives the degrees of freedom which are required in order to determine the F_{crit}

ANALYSIS OF VARIANCE FOR SEASONS (X1), LOCATION OF ROCK POOLS (X2),
AND AIR TEMPERATURE (X3) WITH RESPECT TO FREE CO₂, pH,
Ca CONCENTRATIONS, MG CONCENTRATIONS AND ALKALINITY

Ca CONCENTRATIONS, MG

DEPENDENT VARIABLE: FREE CO₂

SOURCES OF VARIATION	DF	SUM OF SQUARES	F VALUE	PR > F	R-SQUARE
MODEL	165*	8392.9059	6.43	0.0040	0.992520
ERROR	8	63.2500			
CORRECTED TOTAL	173	8456.1559			
X1	2	1744.6513	110.33*		
X2	12	2848.7375	30.03*		
X1*X2	9	22.8496	0.32		
X3	19	1394.2566	9.28*		
X1*X3	0	0.0000			
X2*X3	123	2382.4110	2.45		
X1*X2*X3	0	0.0000			

DEPENDENT VARIABLE: pH

SOURCES OF VARIATION	DF	SUM OF SQUARES	F VALUE	PR > F	R-SQUARE
MODEL	157	91266912.5370	99999.99	0.0000	1.000000
ERROR	8	1.1163			
CORRECTED TOTAL	165	91266913.6533			
X1	2	872469.1946	99999.99*		
X2	12	4651879.1174	99999.99*		
X1*X2	9	5407488.3736	99999.99*		
X3	18	9935952.8224	99999.99*		
X1*X3	0	0.0000			
X2*X3	116	70399123.0290	99999.99*		
X1*X2*X3	0	0.0000			
X1 (separate run)	2	72469.1946	.79		
X2 (May)	27	10.3719	6.12*		
X3 (May)	?	9.5743	5.34*		
X2 (Sept.)	?	8.4743	0.70		
X3 (Sept.)	?	84.5943	31.86*		

*significant variance
(5% Level of Significance)

Table 9

DEPENDENT VARIABLE: Ca									
SOURCES OF VARIATION					SUM OF SQUARES				
	DF					F VALUE	PR > F		R-SQUARE
MODEL	165				1889692.1681	1053.12	0.0001		0.999954
ERROR	8				87.0000				
CORRECTED TOTAL	173				1889779.1681				
X1	2				379325.1727	17440.24*			
X2	12				27244.0520	208.77*			
X1*X2	9				25234.0211	257.82*			
X3	19				1129748.2652	5467.63*			
X1*X3	0				0.0000				
X2*X3	123				328140.6571	245.32*			
X1*X2*X3	0				0.0000				
DEPENDENT VARIABLE: Mg									
SOURCES OF VARIATION					SUM OF SQUARES				
	DF					F VALUE	PR > F		R-SQUARE
MODEL	165				10445.9655	4.27	0.0159		0.988783
ERROR	8				118.5000				
CORRECTED TOTAL	173				10564.4655				
X1	2				8146.8806	275.00*			
X2	12				479.2885	2.70			
X1*X2	9				209.5810	1.57			
X3	19				613.4894	2.18			
X1*X3	0				0.0000				
X2*X3	123				996.7260	0.55			
X1*X2*X3	0				0.0000				

*significant variance
(5% Level of Significance)

Table 9 (cont.)

DEPENDENT VARIABLE: ALKALINITY					
SOURCES OF VARIATION	DF	SUM OF SQUARES	F VALUE	PR > F	R-SQUARE
MODEL	165	187220.8103	33.07	0.0001	0.998536
ERROR	8	274.5000			
CORRECTED TOTAL	173	187495.3103			
X1	2	142446.1555	2075.72*		
X2	12	35243.1149	85.59*		
X1*X2	19	1501.6091	4.86*		
X3	0	2977.7672	4.57*		
X1*X3	0	0.0000			
X2*X3	123	5052.1638	1.20		
X1*X2*X3	0	0.0000			

Source: SAS GLM printout

Table 9 (cont.)

*significant variance
(5% Level of Significance)

value. The $Pr > F$ is the probability of finding an F_{crit} value similar to the F values, and the R-square value indicates the percentage of variation accounted for in the model for all treatments and their combinations.

The treatments of seasons, rock pool location and temperature all proved to be significant contributors to the explanation of the variation in free CO_2 observed in the rock pools on site. As indicated by the R-square value, all treatments together explained 99% of the total variation in free CO_2 . Individually, the season variable had the largest F -value, which indicates that this treatment has the greatest effect on the variability of free CO_2 . There is a problem in the interpretation of this variable because it can be looked upon in two ways. There is not only a general temperature change over the three time periods, but, according to literature, a very definite change in biomass. The season variable will therefore be considered to be the influence of biomass. To confirm whether this factor is just the influence of biomass would involve using actual biomass measurements in the model.

The fact that the season treatment has the largest F -value is not unexpected as biological metabolic activities cause CO_2 to be taken from the water into the plant or organism and released into the rock pool water. Rock pool location, which has the second largest significant F -value, has an effect on free CO_2 in that the closer the rock pools are to the edge of the platform, the greater is the

tendency for waves to splash into them from the lake, which increases the carbon dioxide in the rock pool. The rock pools further back from the platform are not replenished in the same way. Temperature was the third treatment having an effect on the free CO_2 variance. Temperature which is temperature difference over 24-hour sampling periods, controls to a certain extent how much CO_2 can be dissolved in the rock pool water and more importantly, has an effect on biological metabolic processes. For example, higher temperatures may cause certain species to stop photosynthesizing--the process known as photoinhibition.

For the dependent variable pH, the error measure is almost zero. This indicates that virtually no variance is unaccounted for by the differences within the replicates. Further, the original pH samples are different, each set of replicates having been drawn from separate populations having almost zero variances. However, when the pH values were compared within May and September separately, the temperature treatment had an effect on pH. The location treatment had an effect on pH variation for the May data only. The season factor overall did not explain any of the pH variation.

The treatments of seasons, rock pool location and temperature all had an effect on the variability of calcium. The F-value of the seasonal factor is a great deal larger than the others. This again is explained by biological metabolic rates which vary throughout the

seasons according to the type and quantity of biomass present. Of second importance is the temperature factor which controls to a certain extent the varying metabolic rates of the biomass present over a 24-hour period. The third highest significant F-value is the combined treatment of seasons and rock pool location. This can be interpreted as a result of calcium concentrations varying according to biological metabolic activities. The rock pool location also determines to a certain extent the type and concentration of biomass present within each rock pool. For example, on the May trip, rock pools 4 and 7 had thin, filament-like plants present within them which were not observed in any other of the rock pools sampled. The fourth significant F-value was for the combined treatment of rock pool location and temperature which may just be reflecting the variation of biomass type and numbers across the platform and their changing metabolic rates over a 24-hour period. The last significant factor is that of rock pool location which again affects Ca concentrations by its control over biomass type and numbers.

The season treatment was the only variable which explained the variation in magnesium concentrations. This is expected, as the biological metabolic activities would cause magnesium to vary similarly to calcium. Rock pool location and temperature variation do not have the same effect on magnesium as they did on calcium. This could be because the small percentage of magnesium in the rock

makeup would lead to low concentrations of magnesium in the rock pool water which would not vary significantly over 24 hours or from rock pool to rock pool.

The season, rock pool location, and temperature treatments all contributed in explaining the variability of alkalinity. Again, the F-value for seasons is the largest, which is expected since calcium and magnesium are individually strongly affected by the season treatment. The rock pool location factor is second in importance, and a much weaker third is the combination of seasons and rock pool location. This combination indicates that the effect of rock pool location varies throughout the seasons. For example, as the lake level drops from May to September, the rock pools located on the edge of the platform are less susceptible to splash from the lake, and will be more uniform in reaction to the other rock pools. The temperature treatment F-value indicates that it does weakly affect alkalinity, and this could be attributed to the control of temperature on biological metabolic rates. Overall, the season treatment had the greatest statistical effect on all variables but pH. Location of rock pools and temperature affected all variables but pH.

An analysis of variance test was also performed on the laboratory results (Table 10). In this run X1 was the season factor (May air temperatures, September air temperatures, May water temperatures), X2 was the comparison of the inorganic and organic rock pools, and X3 was the

ANALYSIS OF VARIANCE FOR SEASONS (X1), ORGANIC VS INORGANIC ENVIRONMENTS (X2),
AND AIR TEMPERATURE (X3) WITH RESPECT TO FREE CO₂, PH, Ca CONCENTRATIONS.

MG CONCENTRATIONS AND ALKALINITY

DEPENDENT VARIABLE: FREE CO ₂					
SOURCE OF VARIATION	DF	SUM OF SQUARES	F VALUE	PR > F	R-SQUARE
MODEL	12	26.5833	1.90	0.0699	0.393949
ERROR	35	40.8958			
CORRECTED TOTAL	47	67.4792			
X1	2	0.1354	0.06		
X2	3	16.9688	4.84*		
X3	7	9.4792	1.16		
DEPENDENT VARIABLE: pH					
SOURCE OF VARIATION	DF	SUM OF SQUARES	F VALUE	PR > F	R-SQUARE
MODEL	12	3.3615	2.63	0.0128	0.474461
ERROR	35	3.7233			
CORRECTED TOTAL	47	7.0848			
X1	2	0.2029	0.95		
X2	3	2.1812	6.83*		
X3	7	0.9773	1.31		
DEPENDENT VARIABLE: Ca					
SOURCE OF VARIATION	DF	SUM OF SQUARES	F VALUE	PR > F	R-SQUARE
MODEL	12	38.1667	29.20	0.0001	0.909181
ERROR	35	3.8125			
CORRECTED TOTAL	47	41.9792			
X1	2	3.0417	13.96*		
X2	3	34.3125	105.00*		
X3	7	0.8125	1.07		

*significant variance
(5% Level of Significance)

Table 10

DEPENDENT VARIABLE: ME					DEPENDENT VARIABLE: ALKALINITY				
SOURCE OF VARIATION		DF	SUM OF SQUARES	F VALUE	PR > F	R-SQUARE			
MODEL		12	214.5833	193.82	0.0001	0.985175			
ERROR		35	3.2292						
CORRECTED TOTAL		47	217.8125						
X1		2	0.3750	2.03					
X2		3	219.5625	771.58*					
X3		7	0.6458	1.00					
SOURCE OF VARIATION		DF	SUM OF SQUARES	F VALUE	PR > F	R-SQUARE			
MODEL		12	394.7500	160.65	0.0001	0.982169			
ERROR		35	7.1667						
CORRECTED TOTAL		47							
X1		2	4.6667	11.40*					
X2		3	387.5000	630.81*					
X3		7	2.5833	1.80					

Source: SAS GLM printout

*significant variance
(5% Level of Significance)

Table 10 (cont.)

24-hour temperature factor. The variability caused by the inorganic and organic environments had an effect on both free CO_2 and pH. Although the F-values are relatively low, these results suggest that there is a definite difference between the two environments. Both the season factor and the differing biological environments accounted for variability in calcium concentrations. The most important factor is the difference between the organic and inorganic environments, which is expected since literature suggests that inorganic erosion is of little importance. The season's F-value indicates that the biological metabolic activities varied. Very little weight should be put on these findings as these experiments were run in sequence, such that the biomass present was allowed to multiply and metabolize for a longer period of time for the September and the second May run. The variability of magnesium was accounted for by the difference between the organic and inorganic environments. The variability of alkalinity was explained by the differences in environments, and by the season factor.

The whole laboratory experiment was weak in design. The organic material in the lab was only that which had been lying dormant on the rock samples brought back from on site, whereas on site the lake brings in organisms and plant material which varied over the seasons. However, it can be concluded that there is a difference between

organic and inorganic solution, and inorganic is much lower in its effectiveness toward solution of calcium, magnesium and alkalinity.

4.5 Partial Correlation

A partial correlation test was performed between the independent variable temperature and the dependent variables free CO_2 , pH, calcium, magnesium and alkalinity (Table 11). This test was performed to statistically indicate the strength and direction of the variables with respect to the temperature variable. Their relationships have already been discussed in section 4.1. The partial correlation test describes the strength of the association between two variables when all other variables are held fixed. If the correlation coefficient is less than r_{crit} , the null hypothesis is accepted and it can be concluded that there is no significant relationship between the two variables. This is the case for the pH variable from the on site data, and for all variables from the laboratory simulation. The lab results were expected, as the fluctuations in all the variables were very small. On site, a significant relationship does exist between temperature and free CO_2 , Ca, Mg and alkalinity. Alkalinity had a correlation of -0.67409, which is a negative relationship which is moderate in strength. Magnesium also has a negative, moderate in strength relationship at -0.66934. Free CO_2 has a weak negative correlation with temperature (-0.38376).

Table 11

PARTIAL CORRELATION COEFFICIENTS BETWEEN THE INDEPENDENT VARIABLE TEMPERATURE AND THE DEPENDENT VARIABLES FREE CO ₂ , pH, Ca, Mg AND ALKALINITY					
LOCATION OF SAMPLES	V A R I A B L E				
	FREE CO ₂	pH	Ca	Mg	ALKALINITY
ON SITE	-0.38376 ($>r_{crit}$)	-0.07167 ($<r_{crit}$)	-0.27529 ($>r_{crit}$)	-0.66934 ($>r_{crit}$)	-0.67409 ($>r_{crit}$)
LAB	-0.12662 ($<r_{crit}$)	-0.03027 ($<r_{crit}$)	0.13595 ($<r_{crit}$)	0.01319 ($<r_{crit}$)	0.05365 ($<r_{crit}$)

Source: SAS GLM printout

as does calcium (-0.27529). This test does not imply a cause-effect relationship, but it does indicate statistically the strength and direction of each dependent variable with the independent variable, temperature.

CHAPTER FIVE

CONCLUSIONS

5.1 Problems Encountered In The Study

During the course of the investigation certain problems were encountered. Sampling problems arose because of the vagaries of the weather. Two trips had to be aborted because of the winds switching to northerly directions, causing the platform to be completely covered. It was hoped that a few more trip results could have been used in the investigation. July's trip was short of samples because of evaporation first drying up the rock pools, followed by a storm which caused the platform to be covered in water for a time. When sampling, an attempt was made to always read temperatures and sample from the same location in the rock pool water. This was not always possible because the rock pools would sometimes dry up in these locations. Also, even though flashlights were used to make readings at night, it was difficult to determine the light pink end point in the free CO_2 test. It was also hoped that the same rock pools could be used for every trip, but the rock pools were easily affected by the weather conditions, including evaporation which had a very definite effect in the summer months.

Problems also arose in the use of the A.A. for sample analysis. For example, the July samples were not analyzed within the recommended week because the A.A. broke down.

When the samples were actually analyzed, the higher the concentrations, the more erratic was the reading.

The final problem involved the simulation experiment. The actual temperatures were very difficult to simulate, and were never satisfactorily duplicated. Also, the only biological material involved in the experiment was that which lay dormant on the rock sample brought back from on site. If biological material was brought back from on site and included in the experiment, a more distinct difference between the inorganic and organic might be observed.

As far as the statistical testing is concerned the interpretation of the seasons factor is questionable, as it has been interpreted as the biological change over the three seasons. To further test this assumption actual biomass readings should have been taken and used in the analysis of variance.

5.2 Model Conclusions

The results of the study indicate that there is a diurnal fluctuation in free CO_2 , pH, Ca concentrations, Mg concentrations and alkalinity. Further, these fluctuations change from spring to summer, to fall. The concentrations of calcium, magnesium and alkalinity were much higher for the spring testing compared to the summer and fall readings. The summer and fall concentrations were close together with the fall readings being slightly

higher. The analysis of variance indicates that these fluctuations and concentrations are affected the greatest by the seasons, or the biological factor. Rock pool location affected all of the variables but magnesium, which may be because the platform rock contains only 1.01% magnesium. The 24-hour temperature factor has an influence on all of the variables but magnesium again, its effect being the temperature and light control over biological metabolic activities.

The laboratory simulation suggested that inorganic erosion has very little effect on the variables, although this simulation experimental design could have been improved to show a clearer contrast in organic and inorganic erosion. Hypothesis six stated that the rock pools with the greatest biomass would exhibit the greatest fluctuations of free CO_2 , pH, alkalinity, Ca and Mg concentrations on a given trip, and would be the largest in size and depth of those surveyed. This was difficult to prove as the biological material within each rock pool on a given trip was very similar looking. However on the May trip rock pools four and seven which had relatively higher concentrations of calcium and magnesium were relatively deeper than the other rock pools, and unlike the others, contained filament-type biological material within them. Together, the erratic weather conditions and lake conditions cause the form of the rock pools to be very unstable. The

shallowness of the rock pools indicates that bioerosion and inorganic erosion were of relatively little importance in the development of this fresh water, northern latitude shore platform. Although a 24-hourly cycling of the variables exist, and there seemed to be a seasonal component to the fluctuations, the relatively low concentrations of calcium, magnesium and alkalinity found in the analysis confirm the observation that solution erosion is of relatively little importance.

5.3 Suggestions For Future Studies

Although this study indicated that bioerosion does occur on a fresh water, northern environment shore platform, it would be beneficial to have a measurable reading of the erosion occurring. This could be accomplished by the use of a microerosion meter. Further, biomass identification and density readings should occur in order to relate a measurable value to the free CO_2 , calcium, magnesium and alkalinity results obtained. Literature suggests that bioerosion is greatest in early spring which occurs around mid-May in the Ipperwash area. Therefore, bioerosion studies should really start around that time. Other variables such as evaporation, and rain analysis would also benefit this study. It would also be of interest to study bioerosion on a platform in a different fresh water environment with a different rock type and experiencing different weather conditions. This

would indicate if rock types react differently to bioerosion, and if the weather conditions alter the influence of any of the independent variables studied.

Therefore, future studies should concentrate on measuring erosion rates and biomass present over a greater period of time. This would give a greater understanding of the bioerosion and possible inorganic solutional erosion processes occurring.

Appendix 1

CALCULATIONS FOR CHITTICK EXPERIMENT:

X = First reading

Y = Initial reading

C = Correction factors depending on the atmospheric pressure and temperature (Table 43,

The volume of CO₂ liberated by the reaction is

$$V_{\text{CaCO}_3} = (X - Y - 20.0) \text{ ml and the \% CaCO}_3 \text{ by weight}$$

$$= \frac{100.09}{44.01} \times \frac{V_{\text{CaCO}_3}}{10.0} \times C$$

Z = Second reading

The volume of CO₂ liberated by the reaction is

$$V_{\text{Mg}(\text{CO}_3)_2} = Z - X \text{ and \% dolomite by weight and}$$

$$\frac{184.0}{88.02} \times \frac{V_{\text{CaMg}(\text{CO}_3)_2}}{10.0} \times C$$

SAMPLE ONE:

$$\frac{100.09}{44.01} \times \frac{80}{10} \times 1.04284 = 18.97 (x4) = 75.89\% \text{ Ca}$$

$$\frac{184.0}{88.02} \times \frac{3}{10} \times 1.04834 = 0.66 (x4) = 2.63\% \text{ Mg}$$

SAMPLE TWO:

$$\frac{100.09}{44.01} \times \frac{76.5}{10} \times 1.03863 = 18.07 (x4) = 72.28\% \text{ Ca}$$

$$\frac{184.0}{88.02} \times \frac{0}{10} \times 1.04419 = 0\% \text{ Mg}$$

Calculations (cont'd)

SAMPLE THREE:

$$\frac{100.09}{44.01} \times \frac{144}{10} \times 1.03862 = 34.01 \text{ (x2)} = 68.03\% \text{ Ca}$$

$$\frac{184.0}{88.02} \times \frac{1}{10} \times 1.04982 = 0.20 \text{ (x2)} = 0.40\% \text{ Mg}$$

$$\text{AVERAGE Ca Percentage} = \frac{75.89 + 72.28 + 68.03}{3} = 72.07$$

$$\text{AVERAGE Mg Percentage} = \frac{2.63 + 0.0 + 0.40}{3} = 1.01$$

Appendix 2

CHITTICK EXPERIMENT RESULTS										
SAMPLE NUMBER	SAMPLE SIZE (g)	INITIAL POSITION (ml)	FIRST READING (ml)	DIFFERENCE Ca (ml)	SECOND READING (ml)	DIFFERENCE Mg (ml)	TEMP [*] ₁ (°C)	TEMP ₂ (°C)	BAROMETRIC PRESSURE ₁ (kPa)	BAROMETRIC PRESSURE ₂ (kPa)
1	.425	1	101	100	103	3	23.25	22.25	102.0	102.0
2	.425	0	96.5	96.5	96.5	0	23.75	22.75	101.8	101.8
3	.850	0	164	164	165	1	25	23	102.5	102.5

*TEMP₁ are adjusted for calculations

If the first reading difference is less than 50 ml, add 0.5°C to the room temperature
 If the first reading difference is 50 ml to 100 ml, add 1°C to the room temperature
 If the first reading difference is 100 ml to 200 ml, add 2°C to the room temperature

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