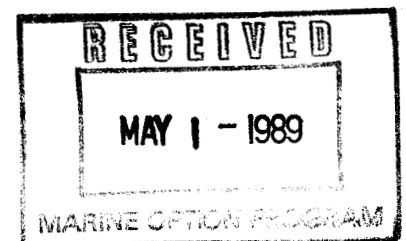


SEDIMENTATION IN CHRISTMAS ISLAND PONDS

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## INTRODUCTION

Christmas Island, with a surface area of approximately 350 square kilometers, is the largest atoll in the Pacific Ocean. It is located due south of the Hawaiian Islands, the southernmost atoll in the Line Island chain (Figure 1). An interesting geologic feature of the atoll are the hundreds of ponds that cover approximately 25% of the atoll's interior. These ponds vary in size, salinity, temperature, water chemistry, and the amount of isolation from lagoonal waters.

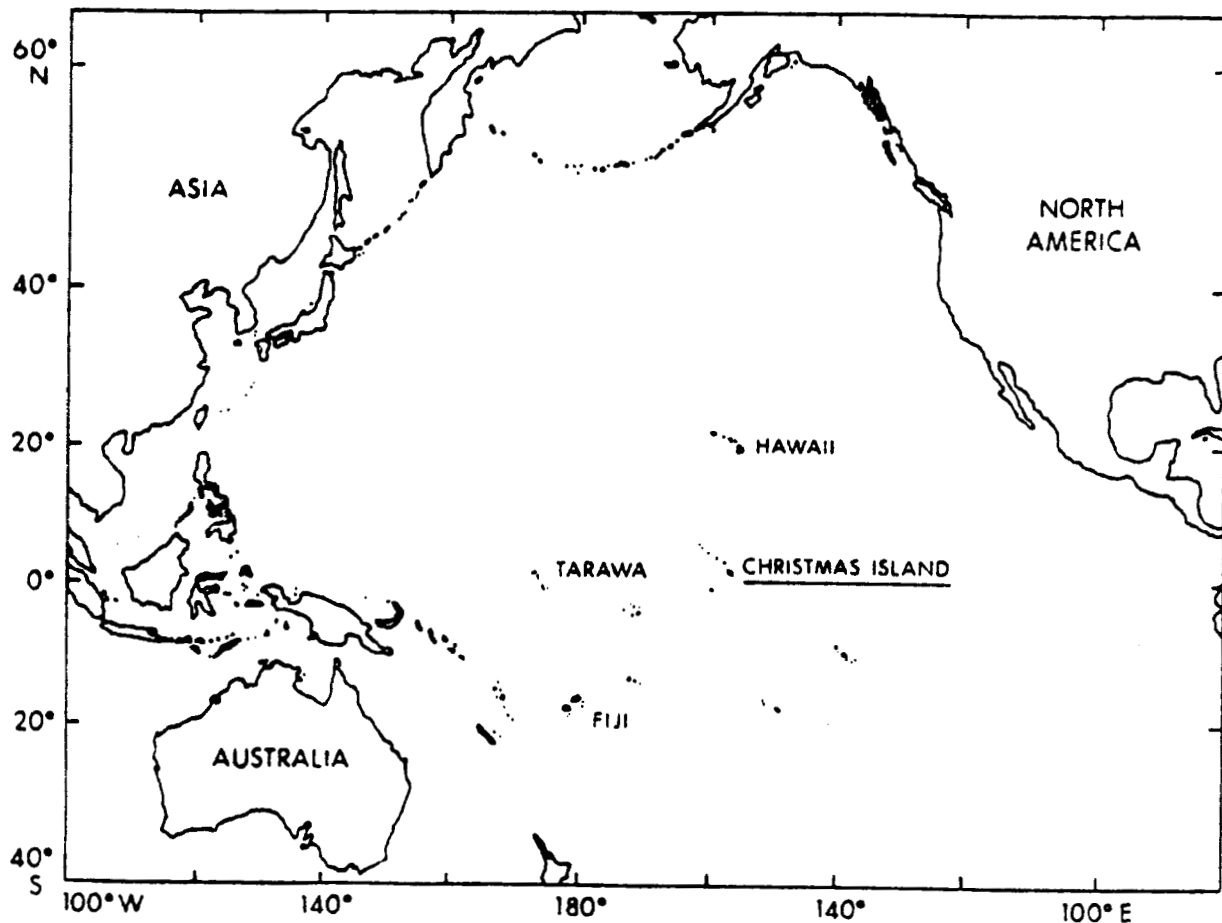


Figure 1. Generalized index map, showing location of Christmas Island, in the Central Pacific Ocean

The geographic location of Christmas Island greatly influences the types of ponds found on the atoll's interior. Located at approximately 2° N latitude, the atoll exists in a very dry climate, producing net evaporative systems. As pond waters evaporate, dissolved ions are left in solution and allowed to reach high concentrations, resulting in hypersaline waters. If evaporation continues long enough, concentrations of ions eventually reach levels that cause ions to combine and precipitate as minerals. The concentration of ions in solution determines what minerals will precipitate. Precipitation generally proceeds as follows: at approximately twice the concentration of seawater, calcium carbonate minerals (calcite and aragonite) may precipitate out of solution; at approximately five times the concentration of seawater, calcium sulfate minerals (gypsum) may precipitate out of solution; and at eleven to twelve times the concentration of seawater, halite may precipitate.

While Christmas Island ponds are generally net evaporative systems, there are periods where much water is added to the pond system. El Nino events periodically dump unusually high rainfall over the atoll every 5 to 7 years. The addition of freshwater to the pond systems is marked by a decrease in surface water salinities. Occasionally, some ponds develop a vertical stratification in which the diluted surface waters lie over denser bottom waters. This stratification may be strong enough that as solar heat is added to the pond, only the surface pond

waters circulate, give off heat and maintain a constant temperature. The denser bottom waters are not able to circulate to the surface, absorb heat and experience a temperature increase. The addition of freshwater to the pond systems which results in a decrease in salinity and possible temperature increase may greatly affect pond water chemistry and sediment formation.

In July 1983 and June 1984, samples were taken from a number of the Christmas Island ponds. Core samples of sediments and pond waters were analyzed in detail for the first time (Schoonmaker et al., 1985). Core analyses indicated significant, rapid changes in pond sedimentation. Pond sediments were made up of layers of microbial mats, fish excrements, carbonates and evaporite salts. Schoonmaker et al. (1985) interpreted that the changes in sedimentation must be correlated with the changes in pond water chemistry, temperature, salinity and productivity.

The objective of my project was to sample surface sediments from ponds at Christmas Island (Figure 2), and correlate these sediment samples to the water chemistry of the ponds in which they formed, specifically to the saturation states for calcium carbonate and calcium sulfate minerals. The formation of a particular mineral phase within a pond should indicate that the pond water was oversaturated with respect to that mineral.

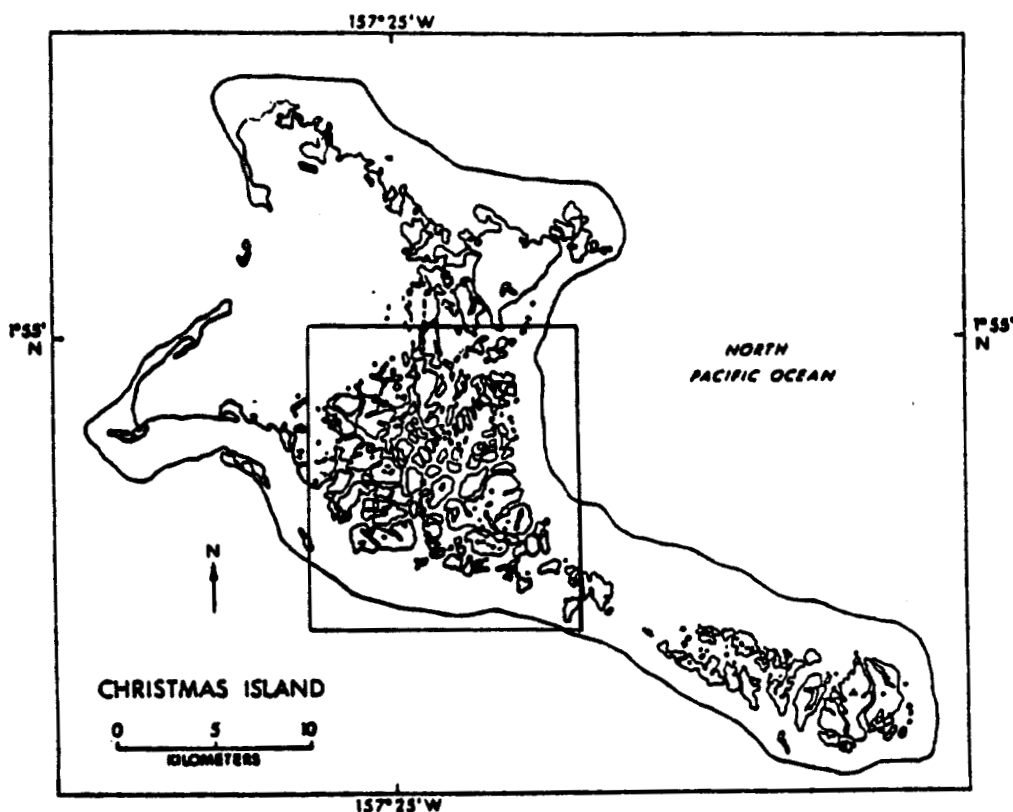


Figure 2. Map of Christmas Island. Box indicates area of pond study.

## METHODS

In October 1988, twenty three ponds on Christmas Island were sampled for analysis of water chemistry. Of these ponds, twelve were sampled for surface sediment analysis. Water chemistry analysis in the field included measurements of temperature with the temperature probe of the pH meter, pH using a Ross electrode, salinity with an American Optical refractometer, and dissolved oxygen using both a YSI field oxygen meter and a Winkler Titration method. Filtered water samples were also taken for analyses of major elements and nutrients back at the University

of Hawaii. Unfiltered water samples were taken for alkalinity and chlorinity analyses. All water samples to be analyzed back at the UH were refrigerated immediately. Surface sediments were collected by scooping the uppermost sediments in contact with pond waters by hand, or if necessary, using gardening tools. Descriptions were made for each sample in regard to sediment layering, and the presence or absence of organic material. These sediment samples were stored in Ziploc bags and kept frozen until they were analyzed at the UH.

Upon return to the University of Hawaii, major cations (calcium, magnesium, sodium, strontium) were analyzed using Inductively Coupled Plasma (ICP) spectroscopy. Potassium was measured with Atomic Absorption (AA) spectroscopy. Chlorinities were measured electrochemically using a Metrohm automated titroprocessor (after Jagner and Aren, 1970). Sulfate concentrations were measured by ion chromatography. Alkalinities were determined potentiometrically using a modified Gran titration. Determination of surface sediment mineralogy was made using a Scintag x-ray diffractometer.

Pond water saturation states with respect to the minerals aragonite, calcite and gypsum were calculated as the ratios of ion activity products (IAP) to the solubility products for these minerals. IAP's were calculated from measurements of ion concentrations ( $M_i$ ) and approximate ion activity coefficients ( $G_i$ ) (e.g.  $IAP_{CaCO_3} = A_{Ca^{2+}} A_{CO_3^{2-}} = M_{Ca^{2+}} G_{Ca^{2+}} M_{CO_3^{2-}} G_{CO_3^{2-}}$ ). Ion activity coefficients for  $Ca^{2+}$ ,  $CO_3^{2-}$ ,  $HCO_3^-$ , and  $SO_4^{2-}$  were calculated using

the following modified Debye-Huckel equation (Helgeson, 1969):

$$\log G_i = - \frac{Z^2 A_i I^{1/2}}{1 + a_i B_i I^{1/2}} + B_i^* I$$

where  $G_i$  = individual ion activity coefficients

$Z$  = charge of the ion

$A, B, B^*$  = temperature dependent parameters taken from Helgeson (1969)

$a$  = values for each species from Garrels & Christ (1965)

$I$  = ionic strengths for pond waters from water chemistry data

Carbonate ion concentrations were calculated from measurements of pH and alkalinity.

#### DATA

The ponds at Christmas Island varied in size, salinity, amount of organic material, as well as proximity to the lagoon. Ponds 5, 8, 14, 16, 43 and 49 were located in the interior of the island atoll, well isolated from the lagoonal waters. Ponds 10, 13, 22 and 40 were located closer to lagoonal waters. All of these ponds except Pond 43 had salinity values one and a half to five times greater than normal seawater, which is approximately 35 o/oo. Pond 43 had an unusually low salinity of 21 o/oo. All of the ponds sampled contained microbial mat layers. These mat layers varied in color (red, green, brown, and purple), thickness (millimeters to a couple centimeters), and number of layers (single to multiple). An interesting feature seen on the banks of three ponds (Ponds 5, 10 and 14) was the dissolution of carbonate material (corals and seashells) which were in lithified materials.

Analyses of pond water and sediment analyses show a wide range of values (Table 1). Salinities varied from 21.57 o/oo in Pond 43 to 202.55 o/oo in Pond 14. Calcite saturation values vary from 4.74 in Pond 40 to 11.84 in Pond 14, whereas gypsum saturation values vary from 0.11 in Pond 40 to 0.71 in Pond 8. Analyses of surface sediment mineralogy show variations in percentages of three minerals, aragonite ( $\text{CaCO}_3$ ), magnesian-calcite ( $\text{Ca}_x\text{Mg}_{1-x}\text{CO}_3$ ), and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). Ponds 16 and 22 had sediments of 100% gypsum, while Pond 14 had sediments of 100% aragonite. The other ponds had mixed percentages of gypsum, aragonite and magnesian-calcite.

Table 1. Water Chemistry and Sediment Mineralogy

<u>Pond</u>	<u>Salinity</u>	<u>Saturation Values</u>		<u>Mineralogy (%)</u>		
		<u>Calcite</u>	<u>Gypsum</u>	<u>Aragonite</u>	<u>Mg-Calcite</u>	<u>Gypsum</u>
5*	69.59	10.63	0.29	60.86	18.74	20.40
8	69.15	10.93	0.71	51.82	48.18	0.00
10*	155.91	5.76	0.44	20.51	2.31	77.18
13*	63.03	7.40	0.23	52.12	7.20	40.68
14	202.55	11.84	0.67	100.00	0.00	0.00
16*	174.58	10.67	0.64	0.00	0.00	100.00
22	148.97	8.97	0.64	0.00	0.00	100.00
40	45.07	4.74	0.11	45.47	54.53	0.00
43	21.57	8.39	0.29	31.89	68.11	0.00
49*	109.91	10.83	0.43	82.96	17.04	0.00

\* Mineralogy values averaged from two surface sediment samples



## PROBLEMS

A few problems were encountered during the course of this project. First, our trip to Christmas Island was delayed for about three months when one of the principal investigators (our microbial mat specialist), Dr. Yehuda Cohen of the Steinitz Marine Biology Laboratory, Elat, Israel, was called away for a few months. Second, two of the surface samples I collected were partially defrosted on our return trip and were mixed up enough that I could not analyze the surface sediments for those ponds. Finally, the Scintag x-ray diffraction system I was using for mineralogical analysis was not working well for several weeks. These problems have delayed my analysis and final report for approximately four months.

## RESULTS

Figures 3 and 4 are plots of mineral saturation states versus salinity. Saturation states were calculated with respect to two carbonate minerals, calcite and aragonite. On Figure 3, calcite has a saturation value of 1.0. A saturation value above 1.0 indicates that the waters are supersaturated with respect to calcium carbonate and theoretically should precipitate the mineral calcite. The other calcium carbonate mineral, aragonite, has a saturation value of 1.6. Waters with calcium carbonate saturation values above 1.6 should precipitate the mineral aragonite. All ponds analyzed had saturation values above 1.6 and were oversaturated with respect to both calcite and

# CHRISTMAS ISLAND POND WATERS

CALCITE SATURATION

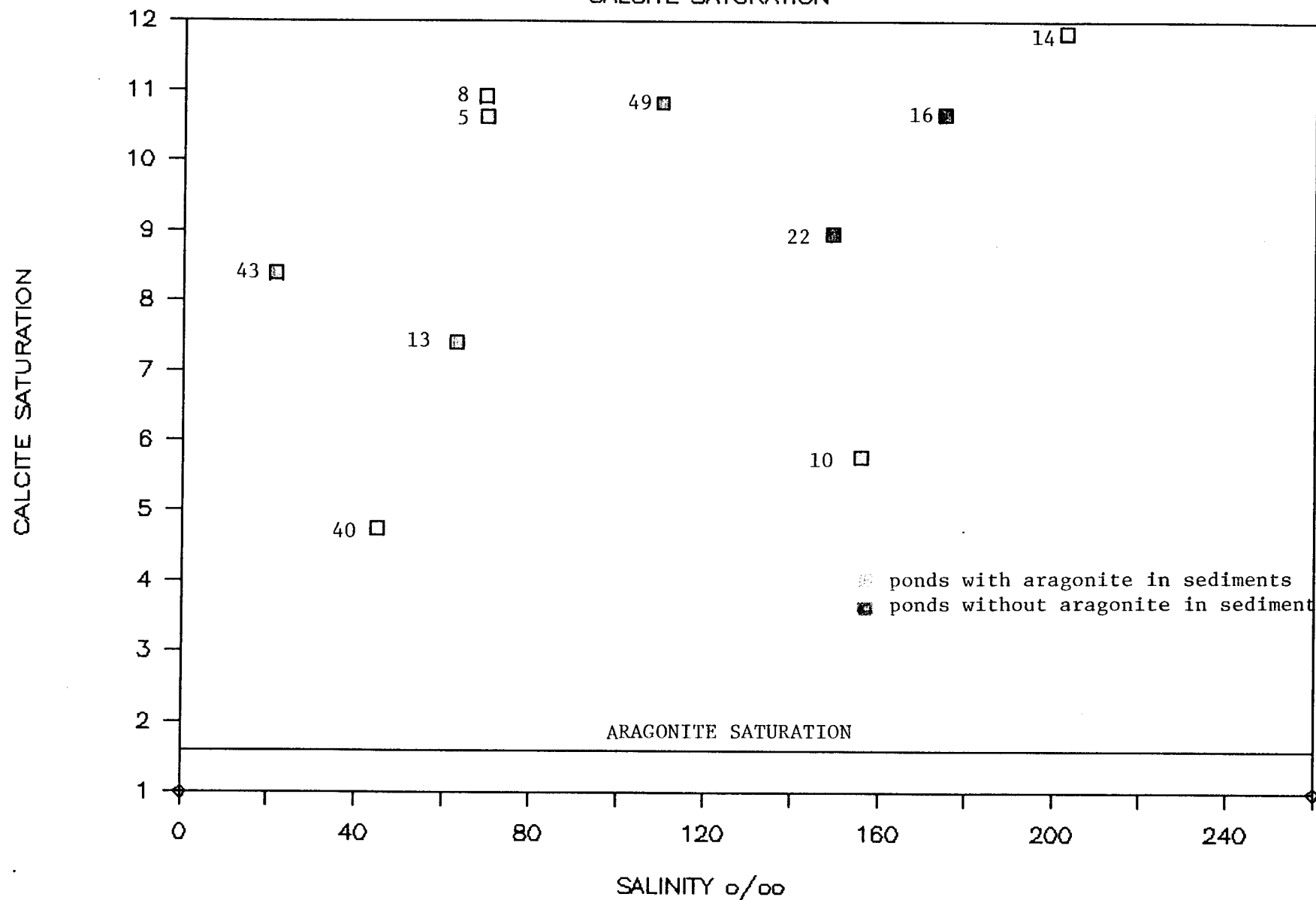


Figure 3. Numbered boxes refer to Ponds.

aragonite (Table 1). This should be reflected in the formation of the mineral aragonite in all pond surface sediments. However, not all the pond sediments had aragonite.

Generally, increasing percentages of the mineral aragonite were found in ponds with higher salinity. There is, however, little or no correlation between aragonite abundance and saturation state. Two of the ponds have no aragonite in the surface sediments, despite the high degree of supersaturation. The high levels of supersaturation with respect to aragonite and calcite, and the apparent lack of correlation between carbonate mineral abundance and saturation state, indicate that the ponds are not in equilibrium states. A number of possibilities could help explain this situation. First, the minerals found in the surface sediments may not be actively forming and may reflect some past pond water conditions. Calcium carbonate saturation states depend on many variables and can be affected by changes in alkalinity, pH, temperature and carbon content. Second, the pond waters analyzed were taken from just below the water surface, not just above the bottom of the pond. Pond water chemistry may vary with depth, so chemical analyses may not reflect the conditions in which the sediments were forming. Third, the pore waters within the sediments, which would have a slightly different chemistry from the overlying pond waters, may be a more important control in sediment formation. Furthermore, organic matter is known to inhibit calcium carbonate precipitation from supersaturated solutions (e.g. Chave and Suess, 1970). The

amount of organic material on the pond bottom, from both algal material and/or fish excrement, may effect the pore water or bottom pond water chemistries as well.

Figure 4 shows gypsum saturation values for all twenty three ponds analyzed for water chemistry. Gypsum has a saturation value of 1.0. All pond waters analyzed were undersaturated with respect to gypsum, having values less than 1.0, although saturation state appears to increase with salinity. This undersaturation should be reflected in the lack of the mineral gypsum forming in any ponds. The figure shows that a number of the ten ponds sampled for surface sediments did have gypsum in the surface sediments. Like the calcium carbonate saturation states, the gypsum saturation states do not correspond to the surface sediments formed in the ponds. The explanations for this situation are similar to those presented for the calcium carbonate minerals earlier. The presence of gypsum may reflect precipitation at an earlier stage of supersaturation, or alternatively, the pond surface waters sampled may not reflect bottom and pore water chemistries.

Halite ( $\text{NaCl}$ ) was found in most of the surface sediments. Salinities were too low for the formation of halite to have occurred through evaporation; its presence therefore, may have resulted from the evaporation of pore waters during preparation of sediments prior to mineralogical analysis.

Table 2 shows some possible trends in water chemistry based on three studies of Christmas Island ponds over the past five

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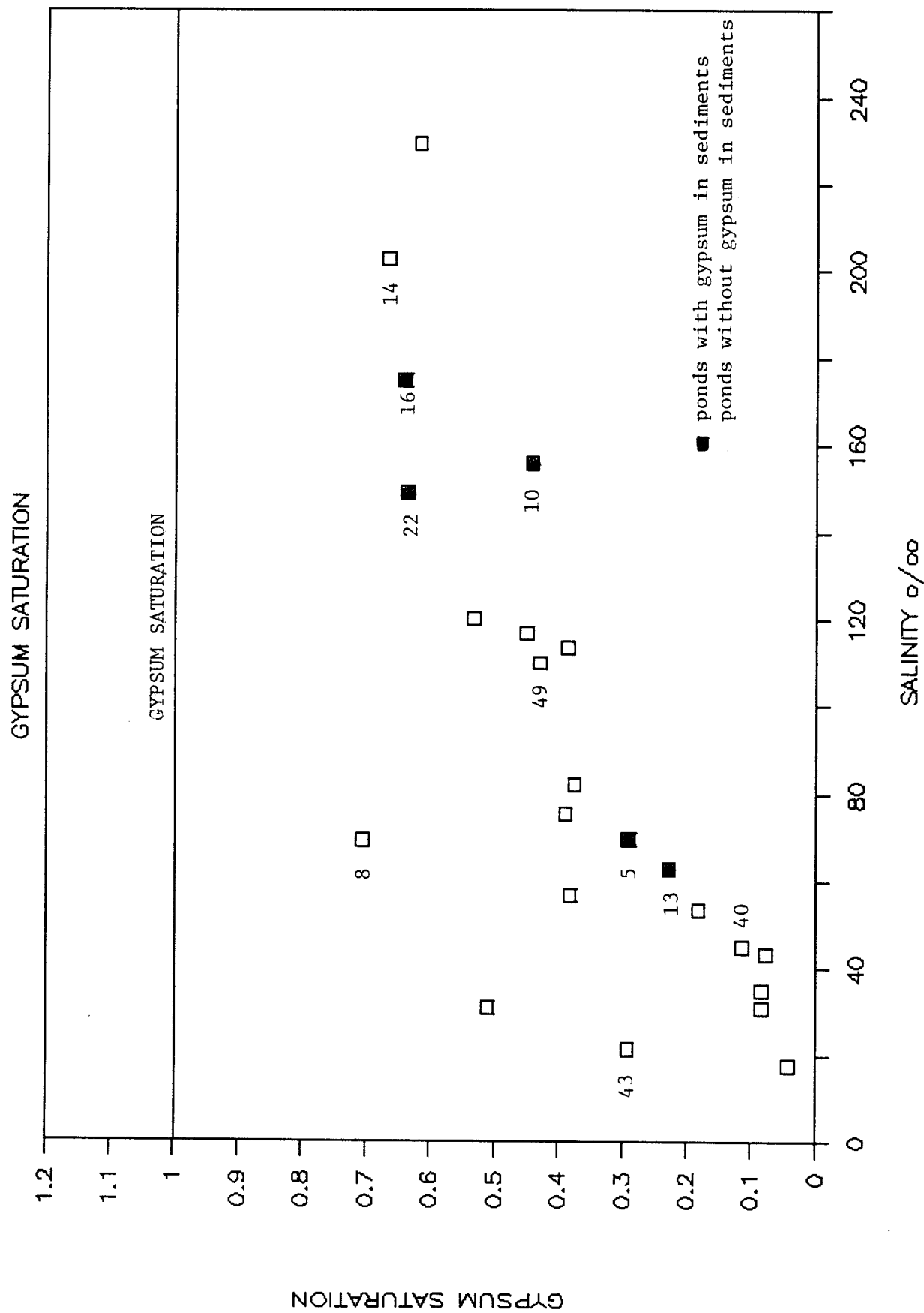


Figure 4. Numbered boxes refer to Pond numbers.

years. Salinity ranges and saturation states for calcite, aragonite and gypsum are similar for both 1983 and 1988 sampling years. This may reflect some type of cyclicity that occurs in Christmas Island ponds over a period of approximately five years. This pattern also correlates nicely to El Nino events which occurred in a similar cycle during those same years. The correlation between El Nino events and pond water chemistry indicates the possibility that sediments which formed within the ponds are records of climate changes that have occurred on the atoll over the years and may thus provide a record of past El Nino events.

Table 2. Summary of Water chemistry, 1983, 1984, 1988

	<u>1983*</u>	<u>1984*</u>	<u>1988</u>
Salinity range	1.5-250	15-142	17-229
Saturation state:			
Calcite	all over	all but Pond 10 over	all over
Aragonite	most over	all but Pond 10 over	all over
Gypsum	all under	some under/ some over	all under

\* after Schoonmaker et al. (1985)

## CONCLUSION

Surface sediments forming in Christmas Island ponds do not appear to directly reflect present pond water chemistries. The

poor correlation between mineral abundance and saturation states indicates that the ponds are not in equilibrium. This suggests that sediments found within ponds reflect either earlier pond water chemistries or that the surface pond waters analyzed have different chemistries from bottom and/or pore waters where the sediments may be forming.

Understanding sediment formation is important because it reflects a particular part of pond water chemistry and subsequently, reflects on climatic conditions of the atoll. When studying the history of Christmas Island by analyzing core samples and the intricate layers the cores contain, interpretations of pond conditions can only be made if sediment formation is fully understood. Therefore, more studies need to be done to identify in which waters sediments are forming, as well as the effect of climatic changes on the atoll in response to El Nino events and the effects of those changes on pond water chemistries.

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