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# CARBONATE AND EVAPORITE MINERALOGY OF HOLOCENE (<1900 RCYBP) SEDIMENTS AT SALT POND, SAN SALVADOR ISLAND, BAHAMAS: PRELIMINARY STUDY

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ABSTRACT

Dolomite in association with gypsum, bassanite, and high magnesium calcite (HMC) has been found in a 84 cm core of Holocene (< 1900 RCYBP) algal sediments from Salt Pond, San Salvador Island, Bahamas. Crystals of gypsum and hexagonal bassanite occur in nodules and rosettes between 0-21 and 38-75 cm. XRD analysis indicates that HMC ranges in composition from 9 to 12 mol% $MgCO_3$ (mean ≈ 11 Mol% $MgCO_3$ for 8 analysis). SEM analysis indicates that HMC is undergoing dissolution and is being replaced by submicron, rhombic dolomite crystals.

The 104 x-ray reflection of HMC displays a pronounced shift, with increasing depth, towards a smaller *d* spacing below 38 cm depth , suggesting the presence of carbonate phases with increasing higher Mg concentrations. The presence of such phases is consistent with a step-wise dolomitization process involving several HMC intermediates. A distinct carbonate phase with near dolomite stoichiometry first appears below 38 cm and increases in volume with depth. Attenuated dolomite superstructure (ordering) reflections appear in X-ray diffraction patterns below 65 cm.

Paleosalinity data from Salt Pond ostracodes (Teeter, *et al.*, 1987) indicates that the saline waters were too dilute (< 100°/₀₀) to precipitate gypsum during some periods earlier in the Holocene. Gypsum begins precipitation at salinities above 131°/₀₀. Modern brines with salinities ranging from 89-356°/₀₀ are precipitating sulfates above 17.5 cm. Correlation of paleosalinity minimum events with sulfate free zones suggests the existence of a distinct Holocene sulfate precipitating brine between 1900 and 1360 Radio Carbon Years Before Present (RCYBP) (corresponding to 32 to 75 cm depth). This suggests that precipitation of sulfates from sporadic Holocene evaporite brines increased the $Mg^{2+}/Ca^{2+}$ ratio promoting the formation of dolomite since about 1900 RCYBP.

## INTRODUCTION

Salt Pond lies on the east coast of San Salvador Island at the south end of Storr's Lake just north of the Holiday Tract Settlement (Fig. 1).

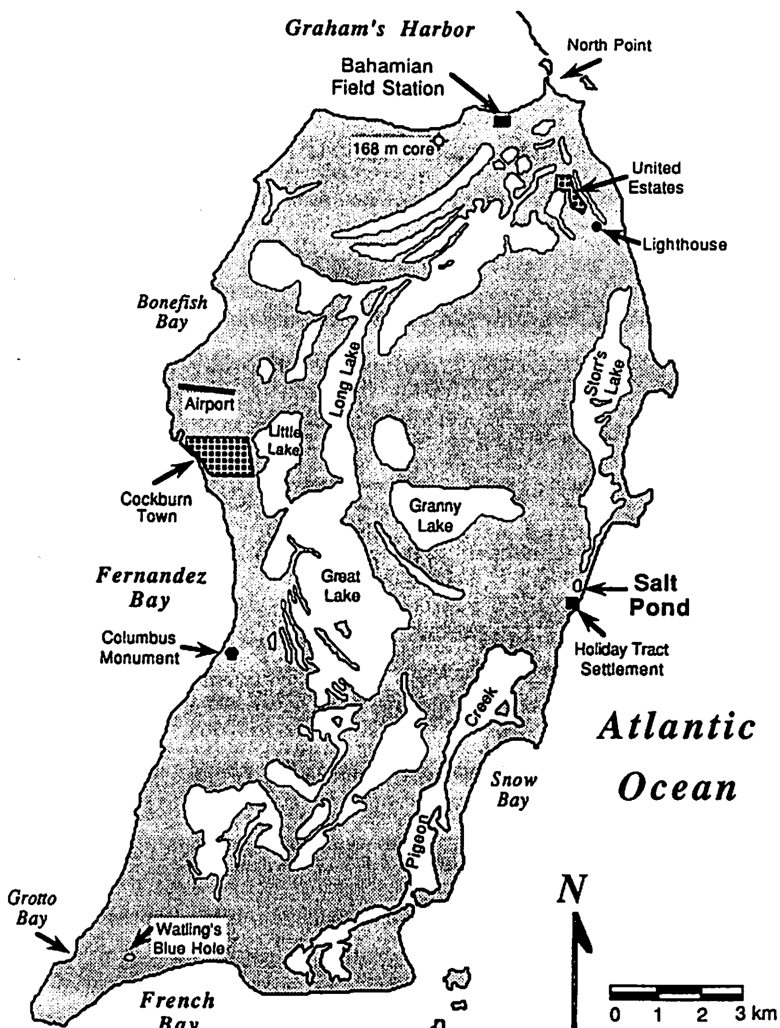


Figure 1. Index map of San Salvador Island, Bahamas showing the location of Salt Pond on the east side of the island at the southern end of Storr's Lake just north of the Holiday Tract Settlement.

The pond derives it name from the historical harvesting of salt at that locality (Teeter, *et al.*, 1987). According to Tom Hanna, a local resident of the area, about every seven years the pond makes salt (Foos, oral communication, 1992). Salt Pond is separated from Storr's Lake to the north by the coastal road, and the Atlantic Ocean to the east by a low, narrow Pleistocene bedrock ridge capped by Holocene Sand dunes (Teeter, *et al.*, 1989). To the west Fortune Hill, a 30 meter high bedrock ridge, rises separating the pond from Granny Lake. Salt Pond is slowly replenished by seawater that seeps through bedrock during high tide (Teeter, *et al.*, 1987).

## Previous Work

This is the first time modern dolomitization in association with HMC, gypsum and bassanite formation has been documented in San Salvador hypersaline lakes. "Protodolomite" in association with HMC and gypsum was reported at the north end of Storr's Lake (Zabielski and Neumann, 1990; Zabielski, 1991). It was not reported whether cation ordering, characteristic of dolomite, was observed. The insoluble residue and ostracodes of Salt Pond have been extensively studied (Teeter, *et al.*, 1987; Teeter, 1989), but the carbonate fraction was not extensively investigated. Dolomite has also been found in a middle Miocene to late Pliocene core at the north end of the San Salvador (Supko, 1977; Dawans and Swart, 1988). The Salt Pond occurrence is similar to the Pekelmeer on the south end of Bonaire, Netherlands Antilles. There Deffeyes, *et al.* (1965) proposed an evaporite seepage reflux model for the dolomitization of Plio-Pleistocene at the north end of the island. Subsequent work at Pekelmeer found no evidence of dolomitization beneath the lake (Lucia, 1968) possibly due to the restriction of reflux flow (Murray, 1969). Supko (1970) proposed a similar model for the Cenozoic San Salvador dolomites, but subsequently considered evaporative reflux highly unlikely or sporadic, due to lower salinity ($\approx 40°/_{\infty}$) and the absence of dolomite in sediments of Great Lake (Supko, 1977) (Fig. 1). It has since been proposed that the core was dolomitized during the late Miocene and Pleistocene (Swart, *et al.*, 1987; Dawans, and Swart, 1988), and therefore unrelated to the Holocene dolomitization.

## Salinity and Temperature Conditions

The salinity of Salt Pond ranges from 89 to $356°/_{\infty}$ (Teeter, *et al.*, 1987, oral communication 1991; Foos, written communication 1992). Gypsum crystal rosettes were observed in sediments in 1991 and both gypsum and large halite crystals were observed at the surface of the pond during mid June 1992. Gypsum begins precipitating out of seawater at salinities of 131.4 $°/_{\infty}$, and halite at 275.3 $°/_{\infty}$, (Arkhangel'skaya and Griror'yev, 1960). By mid June, 1992 the pond level had dropped approximately 15 cm from that observed during late June, 1991. This drop exposed black organic rich sediments that were partially covered by a layer of pink algae and gypsum. The black layer had dried enough to form a crust with the development of early tepee structures filled with gypsum (Plate 1).

Plate 1. Salt Pond with white halite crust in the background, and black organic HMC sediments, and early tepee structure filled with gypsum in the foreground.

Temperatures measured in Salt Pond on June 12, 1992 decreased from 40°C at the top of the water level to 28°C at 1.5 meters depth into the sediments (Table 1). Temperature of exposed organic rich black crusts range from a high of 54°C, decreasing to 36°C at a depth of .075 meters. The presence of a white halite crust on parts of the pond may have resulted in cooler sediment temperature than in those areas (or during seasons) when the halite is not present.

## Coring

A 84 cm long compacted piston core (approximately 175 cm uncompacted) was extracted during late June, 1991. The least compacted upper part of the core (upper 18 cm) is composed of black organic rich sediments (Plate 2). Thin zones of gypsum and bassanite were found at 0 -21 and 38-75 cm depth (Plate 2). The lower 66 cm of the core is gray in color.

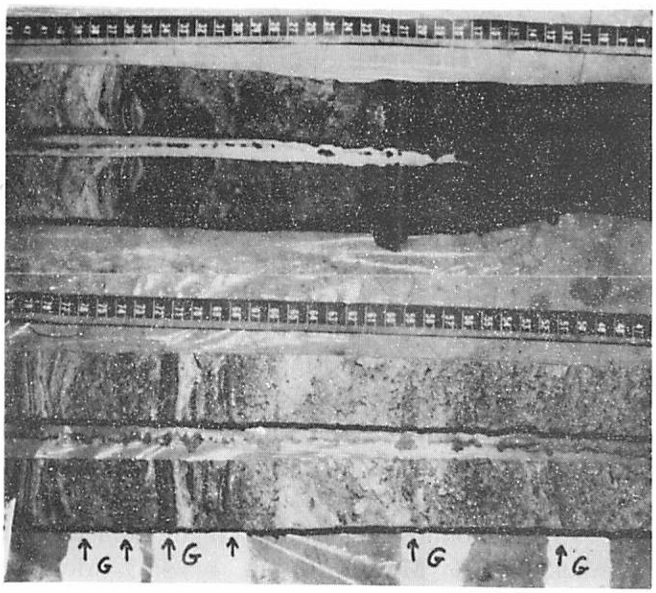

Plate 2. 83 cm piston core from Salt Pond. Note the organic rich upper 18 cm and the gypsum zones at 51, 59, 68, 71, 74 and 76 cm.

| | |
|---|---|
| Air Temperature | 38°C |
| Edge of Salt Pond | |
| Exposed Black Organic Crust | 54°C |
| .075 meters depth black crust | 36°C |
| Central part of Salt Pond | |
| Top of Water | 40°C |
| Top of Halite Crust | 39°C |
| Top of Gypsum Crust | 37°C |
| 0.5 meters sediment depth | 32°C |
| 1.0 meters sediment depth | 29°C |
| 1.5 meters sediment depth | 28°C |

Table 1. Temperature profiles at Salt Pond (June 12, 1992).

## Methodology

The core was split, cut into 5 cm sections and tightly wrapped in plastic wrap to keep the core from drying out. At the University of Missouri-Rolla (UMR) laboratory the core was examined and described using binocular microscopes. Selected crystals were identified out using refraction indices oils. Preliminary X-ray diffraction (XRD) patterns were made of every 5 cm interval on a Phillips PW 1410 X-ray diffractometer at the Department of Geology and Geophysics, UMR. Selected samples, at major breaks in sediment characteristics, were rerun for high quality patterns on a SCINTAG XDS-2000 X-ray diffractometer at the Materials Research Center, UMR. Selected samples were examined with a JEOL JSM-T330A scanning electron microscope (SEM), equipped with a Kevex Delta 1 energy dispersive spectroscopy (EDS) Super Quantum thin window detector.

## MINERALOGY

### Evaporite Mineralogy

Halite

Hopper halite (NaCl) crystals up to 2 cm across were observed forming a 5 cm thick crust on top of gypsum and black organic rich sediments in Salt Pond during June, 1992 (Plate 1). The 9.5 cm rainfall between June 12 and 24, 1992 began to dissolve the halite crust (Foos, written communication, 1992). Halite was observed in all the X-ray diffraction patterns due to the drying of the samples during sample preparation.

Gypsum

Gypsum ($CaSO_4 \cdot 2H_2O$) was observed in a thin pink zone immediately beneath the halite crust and in the upper 2 cm and also in zones at 51, 59, 68, 71, 74 and 75 cm depth (Plate 2). The pink color of the gypsum zone is due to the presence of cyanobacteria. Gypsum occurs usually as untwinned crystals in these intervals.

Bassanite

Small crystals of bassanite, approximately 0.5 mm, were observed in pond sediments (Plate 3). Bassanite, also known as hemihydrite or plaster of Paris ($CaSO_4 \cdot 0.5H_2O$), was found in association with the gypsum (Woody, *et al.*, 1992). Bassanite has two recognizable forms (Flörke, 1952): a low temperature (<45°C) orthorhombic form that is stable under relatively low relative humidity (RH) conditions (RH<5%), and a high temperature (>45°C) hexagonal form that is stable at higher relative humidities

(RH ≈ 40%) (Frik and Kuzel, 1982; Lager, *et al.*, 1984). Only high temperature hexagonal bassanite was observed in the core (Plate 3). The high temperature bassanite was positively identified by its X-ray diffraction pattern (Figure 2), crystal form, its refractive index, and its rehydration to gypsum under high relative humidity conditions in the lab and/or lower temperatures in the pond.

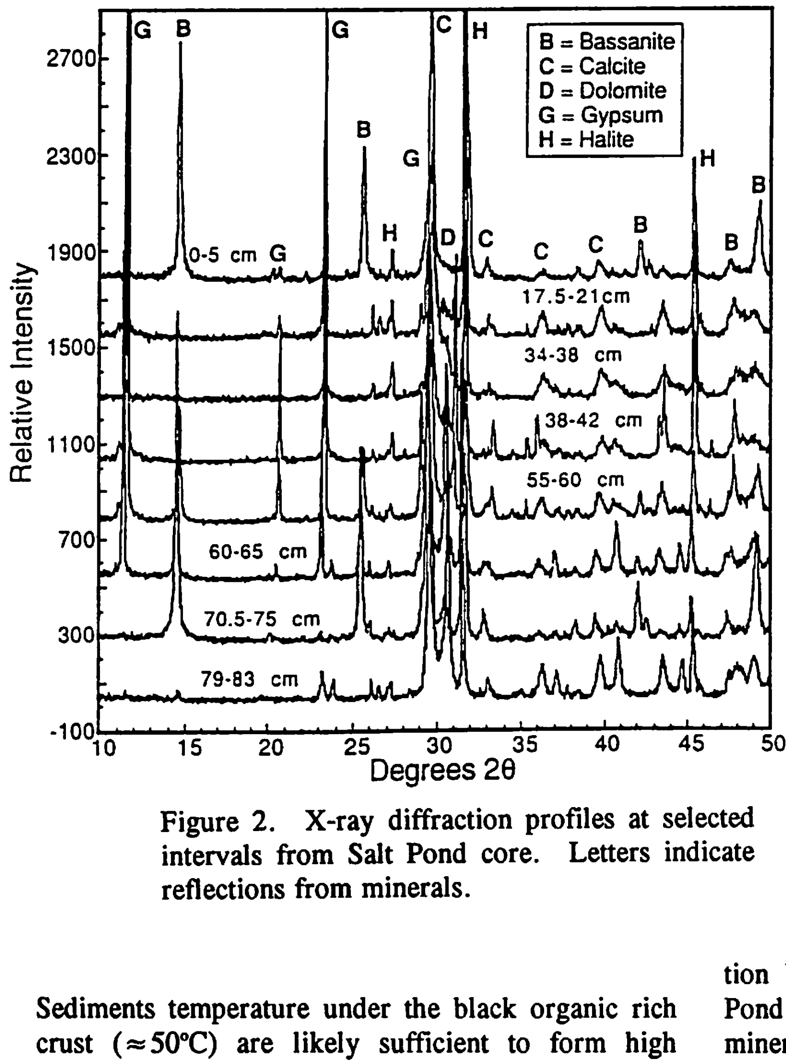


Figure 2. X-ray diffraction profiles at selected intervals from Salt Pond core. Letters indicate reflections from minerals.

Sediments temperature under the black organic rich crust (≈50°C) are likely sufficient to form high temperature hexagonal bassanite (45°C) if conditions are maintained.

Bassanite is a relatively rare mineral being found in continental desert deposits, thin layers in oil sands, fracture fillings in bauxites, and as porphyroblast and nodules in massive gypsum (Sonnenfeld, 1984). It also has been found in continental sabkha lakes, pans, and gypsum dune complexes in Kuwait (Gunatilaka, *et al.*, 1985). The Salt Pond occurrence of bassanite is in a hypersaline supratidal environment similar to the Kuwait sabkha environment.

### Carbonate Mineralogy

Aragonite and Low Magnesium Calcite

Trace amounts of aragonite are found in the Salt Pond sediments, being contained in ostracode shells. There are also trace amounts of LMC which is contained in occasional pelecypods and lake gastropods shells (Teeter, *et al.*, 1987).

High Magnesium Calcite

The majority of the Salt Pond sediments is composed of poorly sorted silt sized high magnesium calcite (HMC) derived from algal sediments (Teeter, *et al.*, 1987). The shift in the 104 calcite reflection indicates that HMC composition ranges from 9 to 12 mole % $MgCO_3$ (mean ≈ 11 mole% $MgCO_3$ from 8 analyses) with increasing Mg with depth (using the method of Lumsden and Chimahusky, 1980) (Fig. 3).

Dolomite

A distinct carbonate phase with near dolomite stoichiometry first appears below 34 cm and increases in volume with depth (Fig. 3). Dolomite composition ranges from 40 to 45 mol% $MgCO_3$ (mean ≈ 43.7 Mol% $MgCO_3$ for 5 analysis). There is an increasing dolomite (104) reflection intensity with age, downsection, from 34 cm depth indicating increasing dolomite composition (Fig. 4). Dolomite cation ordering (indicated by the presence and intensity of the 015 reflection at 35° $2\theta$) also increases downsection. SEM analysis indicates that the HMC is undergoing dissolution and is being replaced by submicron rhombic dolomite crystals (Plate 4).

## DISCUSSION AND CONCLUSIONS

There is a strong stratigraphic correlation between paleosalinity data obtained from Salt Pond ostracodes (Teeter, *et al.*, 1987) and evaporite mineralogy after correction for effect of different compaction rates (Fig. 4). Ostracode paleosalinity maxima between 0-15 and 30-75 cm correlate with evaporite rich zones (Fig. 4). The higher salinities, indicated by the presence of gypsum, bassanite (>131.4 ‰), and halite (>275.3 ‰), suggest that intermittent hypersalinity conditions occurred during the dry season, and lower salinity (<100 ‰), indicated by ostracode chemistry during the rainy season in the Holocene (Fig. 4). Modern brine salinities in Salt Pond range from 89 to 356‰, depending on the season. There is, likewise, a correlation between the

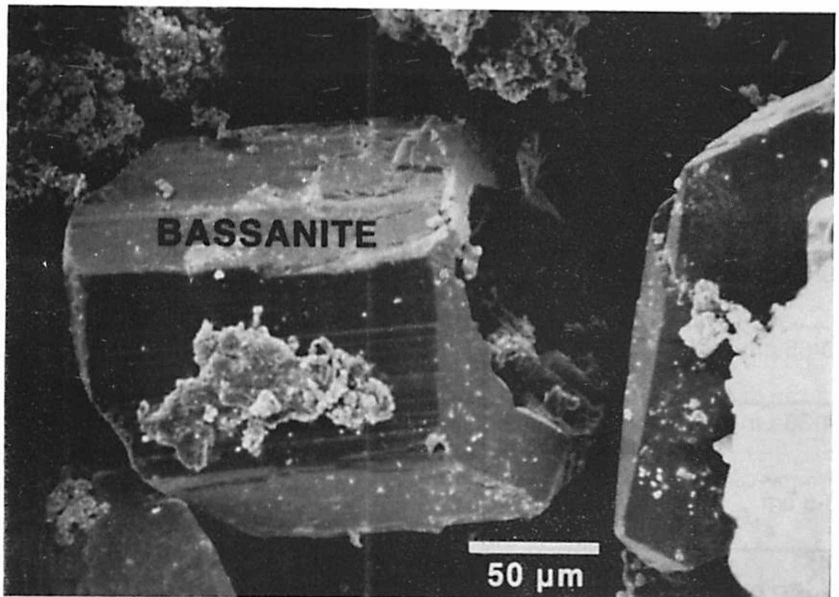


Plate 3. Scanning electron micrograph of hexagonal bassanite.

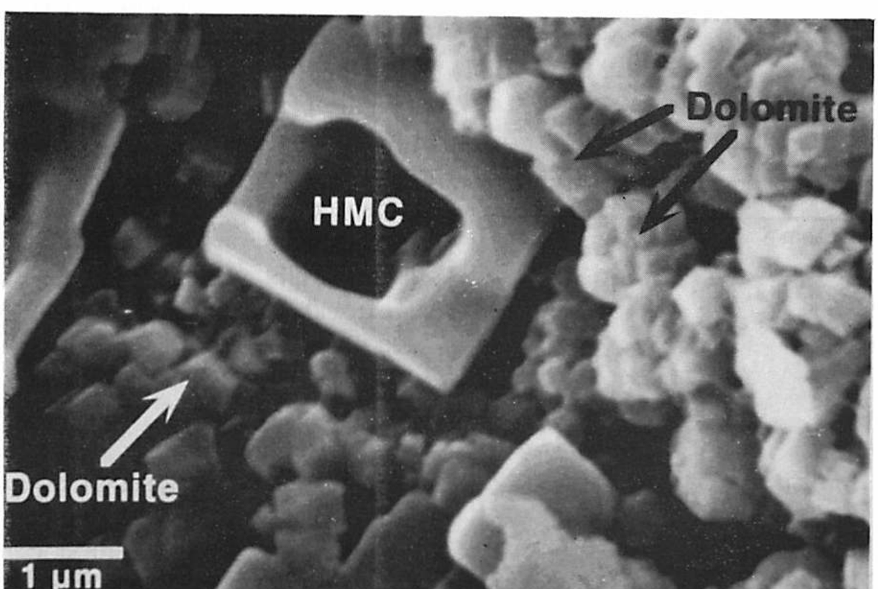


Plate 4. Scanning electron micrograph showing high magnesium calcite (HMC) undergoing replacement by submicron sized encrusting dolomite crystals. The large scale pitting and rounded edges of the HMC crystals indicates that it is undergoing dissolution.

ostracode paleosalinity minimum events at 20 and 80 cm with evaporite free zones (Fig. 4). The gypsum in the upper portion of lowest paleosalinity maximum event (28 to 45 cm) and the upper (0-2 cm) and lower portion (7 to 10 cm) of the upper paleosalinity maximum event has not been transformed to bassanite (Fig. 4). This may be due to the presence of lower salinity waters from the salinity minimum events (Fig. 4), as dehydration of gypsum to bassanite is affected by salinity (Ostroff, 1964). The paleosalinity minimum events can be correlated with similar events at Watling's Blue Hole which have been dated at 1360±90 and 1900±80 RCYBP (Teeter,*et al* 1987; 1989). This suggests the existence of a distinct Holocene sulfate precipitating brine in Salt Pond between 1900 and 1360 RCYBP, that has had minimum reequilibration with surrounding brines due to the low permeability of the sediments.

Presence of the dolomite rich interval below 34 cm with the ostracode paleosalinity maxima and sulfate rich zone (Fig. 4) suggests that precipitation of sulfates from intermittent Holocene evaporite brines increased the $Mg^{++}/Ca^{++}$ molar ratio promoting the formation of dolomite since 1900 RCYBP. At Pekelmeer the molar ratio has been increased from 5.2 in sea water to values near 30 in the dolomitizing lake brine (Deffeyes *et al.*, 1965). Experimental studies suggest that the presence of sulfates is important for dolomite formation (Zeller, *et al.*, 1959). Baker and Kastner (1981) proposed that sulfate may kinetically inhibit dolomite precipitation. Gypsym precipitation lower sulfate to a degree that dolomite can form (Baker, and Kastner, 1981).

Absence of dolomite in the upper 18 cm salinity maximum may be due to the high organic content. Total organic carbon (TOC) reaches a high of 8.1% TOC near the top of the core (Teeter, *et al.*, 1987). Certain amino acids and soluble proteins, which may be present in the sediments, inhibit dolomite precipitation (see Gaines, 1980).

The 104 reflection of HMC displays a pro-

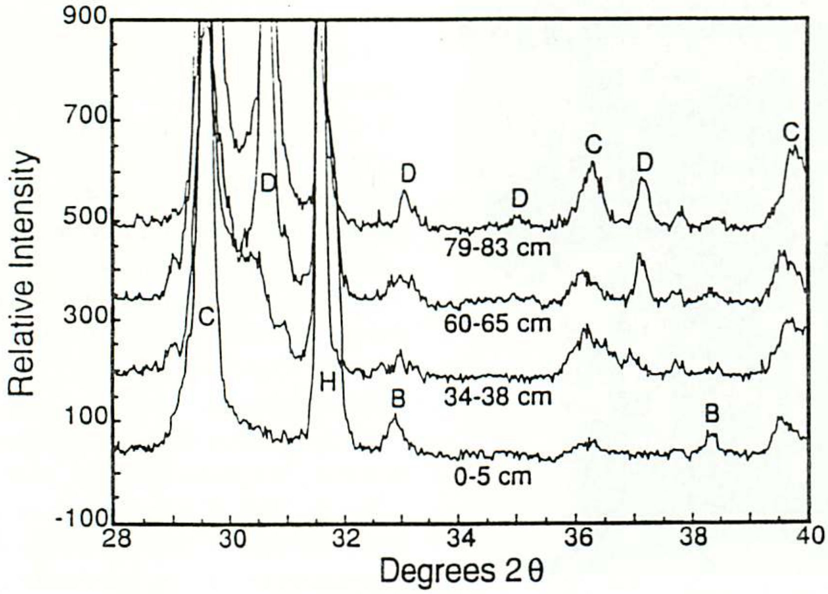


Figure 3. X-ray diffraction profiles at selected intervals from Salt Pond. A strong 104 dolomite reflection is present (30.5° 2θ) at the 60-65 cm interval and the 015 dolomite ordering reflection (35° 2θ) is pronounced in the 79-83 cm interval. Letters indicate reflections for the following minerals: C = HMC, D = dolomite, H = halite, G = gypsum.

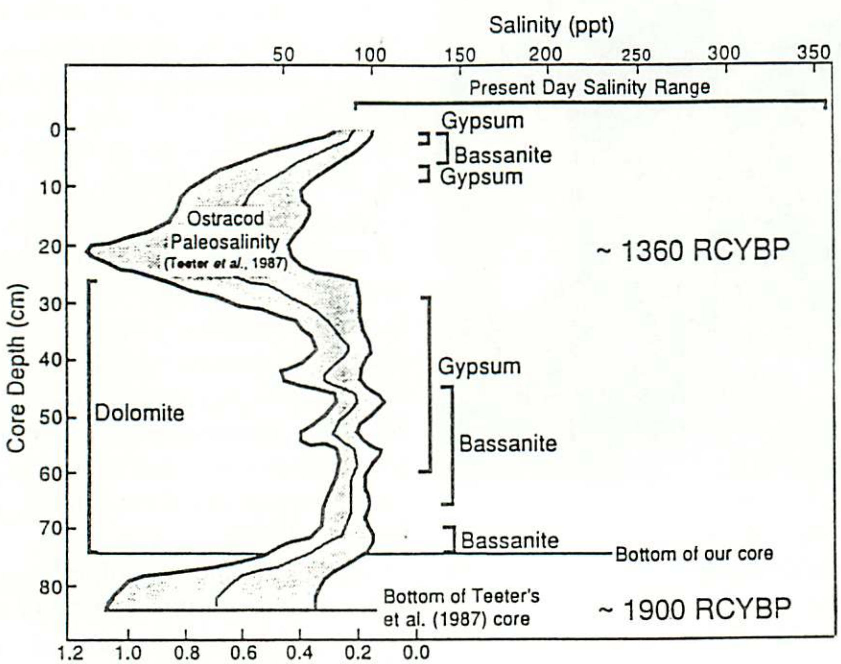


Figure 4. Comparison of Salt Pond ostracod paleosalinity data with evaporite mineralogy after compaction correction. Note the correlation between evaporites and the high salinity ostracod event between 1360 and 1900 RCYBP (25 and 75 cm depth). The higher salinities indicated by the presence of calcium sulfate (> 134 ‰), and halite (> 273‰) suggest hypersalinity conditions occurred intermittently during the Holocene.

nounced shift, with increasing depth, towards a smaller *d* spacing below 38 cm, suggesting the presence of carbonate phases with increasing higher Mg concentrations (Fig. 3). The presence of such a shift is consistent with a step-wise dolomite nucleation process involving several HMC intermediates. A similar pattern of formation of HMC phases with increasing Mg content was observed during experimental dolomite synthesis between 193°C and room temperature by Nordeng and Sibley (in press, see also Sibley, 1990). These authors also interpreted their observations to indicate a step-wise nucleation process during dolomitization (Sibley, 1990; Nordeng and Sibley, in press).

## ACKNOWLEDGEMENTS


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## ADDENDUM

The first recorded example of surficial dolomite on San Salvador Island was in a dolomitic crust in the Reckley Hill Settlement Pond, 1 km east of the Bahamian Field Station (Kwolek, 1984).

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