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Front Cover: Crinoids in waters of San Salvador, Bahamas. Photograph by Sandy Voegeli, 2003.

Back Cover: Dr. H. Leonard Vacher, University of South Florida, Keynote Speaker for the 12^{th} Symposium and author of "Keynote Address – Plato, Archimedes, Ghyben Herzberg, and Mylroie", this volume , p. ix. Photograph by Don Seale.

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AN ANALYSIS OF THE MUDS OF MOON ROCK POND, SAN SALVADOR, BAHAMAS: ORGANICALLY OR INORGANICALLY PRECIPITATED?

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ABSTRACT

An analysis of muds (clay size fraction) from Moon Rock Pond show that compositionally they are >90% aragonite with Sr in the aragonite values close to 1.0%. This would indicate that they are mostly inorganically precipitated (Milliman, 1967, 1974; Loreau 1982; Milliman et al., 1993). The silt and very fine sand of the pond has a slightly lower aragonite value and a much lower Sr value than the clay-size fraction indicating input from the molluscan assemblage of the pond, which is 100% aragonite but only an average of 0.26% Sr. The high Sr content of the aragonite within the fine fraction (<63µm) is consistent with an inorganically precipitated origin with some minor addition of the calcareous green alga *Acetabularia* (97% aragonite and approximately 0.9% Sr), which is ubiquitous in the pond, but found in low density, and may produce a small amount of the needle-size aragonite sediments. The lower Sr content of the silt and fine sand would indicate that it is the breakdown product of the shell material.

INTRODUCTION

Hyper-saline ponds are supratidal bodies of water that have extremely high salinities. These ponds are common throughout the Bahamas and are very prevalent on San Salvador Island, Bahamas (Figure 1). The interior of the island is dotted with these ponds which range in size from a few meters across to several kilometers long (Teeter, 1995). Some of the ponds on the island are home to a diverse community of flora and fauna (Teeter, 1995). Most of these ponds fill sinkholes and areas between old dune ridges (Teeter, 1995). They tend to be shallow and range from less than 1m to almost 3, with an average maximum depth of 2m (Davis and Johnson, 1989; Teeter, 1995). The biotic assemblages are euryhaline and thrive in salinity ranges from 10 to 100 ppt (Teeter, 1995). The series of ponds in the northern part of the island (southeast of the Gerace Research Center) are mostly fed through meteoric water, seeps from the surrounding rock formations, as well as through conduits that link them to the sea (Davis and Johnson, 1989). The size and development of these conduits coupled with elevation, rainfall, proximity and contact with freshwater lenses, and size of the pond can affect the salt concentration within each pond (Davis and Johnson, 1989; Teeter, 1995). These northern ponds are all clear and salinities are similar to those of seawater (Davis and Johnson, 1989). Tides influence the flow of water through the conduits in the ponds; however, depending on the elevation of the pond with respect to maximum high tide or minimum high tide, the flow of water in and out of the pond may not equally match the 6 hour period of flood and ebb tide, so in effect, water may flow out of the pond for the entire tidal cycle or for 9 hours depending on the height of the high tide with respect to the elevation of the pond (Davis and Johnson, 1989). These ponds have a substrate that generally consists of fine muds. In general, hypersaline ponds in tropical areas are primarily underlain by a fine organic brown fluc with some amounts of calcium carbonate lime muds, comprised of both clay- and silt-sized carbonate particles of both authigenic and detrital sources, comprising the rest (Yamamoto, 2002).

Moon Rock Pond (Figure 1), a saline pond in the interior northern part of San Salvador Island, Bahamas, is sedimentologically dissimilar to the other ponds of the area, which primarily contain a coarse-grained molluscan shell debris substrate and a brown organic fluc. Moon Rock Pond is floored by a fine white carbonate mud (principally <63μm in size). Davis (In Godfrey et al., 1994) has speculated that the mud in Moon Rock Pond is an inorganic precipitate. The result of meteoric dissolution of the surrounding rock and the mixing with the hypersaline waters of Moon Rock Pond.

At Moon Rock Pond the molluscan assemblage is dominated by gastropods. The assemblage of organisms includes *Batillaria minima, Cerithidea costata, Cerithium lutosum, Codakia orbiculata, Mytilus exustus, Nassarius albos, Rissoina cancellata,* and *Tellina mera* (Edwards et al., 1990; Godfrey et al., 1994). In addition, two chlorophytes are present in relative abundance, *Acetabularia spp.* and *Bataphora spp.*

The debate about whether or not carbonate lime muds are mostly inorganically precipitated or organically produced has been an on going one among carbonate sedimentologists. Early workers favored a biologically mediated inorganic precipitation calling into play the supersaturated calcium carbonate rich warm hypersaline waters of Great Bahama Bank (Drew, 1911; Vaughan, 1914; Smith, 1940). By the mid 1950's the work of Lowenstam and

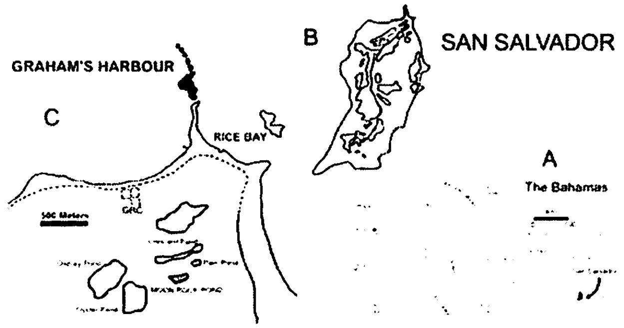

Figure 1. A) Map of the Bahamas, San Salvador indicated with an arrow. B) Map of San Salvador (approximately 8Km E-W and 15 Km N-S), note the large number of inland lakes in the interior. C) Close up of inland lakes near the Gerace Research Center (GRC) on the northern side of the island, Moon Rock Pond shaded.

Epstein (1957), using stable isotope data on codiacean algae, particularly *Halimeda* and *Penicillus* coupled with scanning electron photomicrographs by Lowenstam (1955) of the aragonite needles produced by the algae and those of the muds strongly favored an organically precipitated origin for carbonate muds. More recently, data can be found to support both arguments depending on locality and environmental conditions. The calcareous (Codiacean) algal assemblage in the Bight of Abaco exists in sufficient quantity for the muds in that locality to be organically produced (Neumann and Land, 1975). On Great Bahama Bank, however, the standing algal crop is insufficient to account for the lime mud productions and chemical analysis (Sr content) demonstrated an inorganically precipitated origin for those lime muds (Milliman et al. 1993).

In 1993, Dr. R. Laurence Davis (University of New Haven) developed the hypothesis that Moon Rock Pond has a carbonate mud that is mostly inorganically precipitated (Godfrey et al., 1994). Davis' hypothesis is based on the paradoxical chemical mechanism, which states that when two saturated solutions of differing calcium carbonate concentrations mix it becomes an unsaturated solution. Due to its high salinity and temperature, this solution begins to dissolve the limestone surrounding the pond. The water of the pond is already supersaturated with carbonate; however, it is at a different concentration than the incoming meteoric water as it cascades over the surrounding limestone. As the supersaturated, cooler meteoric water enters the pond, it mixes with the saline pond water. As the sun heats the water the excess calcium carbonate precipitates out as aragonite needles due to the sudden change in water temperature and concentration (Godfrey et al., 1994), thus forming the white mud substrate characteristic of the pond. This is very similar to the inorganic precipitates known as whitings that occur on western Great Bahama Bank and which have been extensively described and explained in the literature (Cloud, 1962; Steinen et al., 1988; Shinn et al., 1989). Davis supported his hypothesis in May 1993 when he saw a milky precipitate appear throughout the pond after a heavy rainfall the night before. The present study is based on the idea that Sr content in the aragonite is a useful tool in separating organically vs. inorganically precipitated origins for carbonate muds (Milliman, 1967, 1974; Loreau 1982). This work is based on calculating Sr content within the aragonitic phase of the sediment in Moon Rock Pond and comparing these values with the Sr content of calcareous algae and molluscan invertebrates, as well as the Sr signature of inorganically precipitated carbonate muds by using values of ooids as a proxy.

The premise of this paper is modeled after an experiment by Milliman (1974) and others (Loreau, 1982; Milliman et al., 1993), and will attempt to support Davis' idea that the lime muds in Moon Rock Pond are, in fact, inorganically produced. This will be done by comparing the Sr values within the aragonite phase of the carbonate muds with those in the molluscan shell and algal material of the organismal assemblage of the pond.

An argument exists that by analyzing Sr content in the aragonite, one can discriminate between organically derived calcium carbonate and inorganically precipitated calcium carbonate. The aragonite produced by codiacean algae, for instance, ranges between 0.8%-0.9%, while those of inorganically precipitated ooids range from 0.95%-1.0% (Milliman, 1974; Loreau, 1982; Milliman et al., 1993). Milliman (1974) developed a formula where he assumed a Sr value of 0.2% in the magnesian calcite and calcite. Per Milliman and others (1993) one can then calculate the percentage of Sr within the aragonitic phase of an aragonite-magnesian calcite mixture by a simple two-part mixing equation:

% Sr (bulk) = [% Sr (in aragonite)] (% aragonite) + 0.2 (% calcite)

Leading to

% Sr (in aragonite) = [% Sr (bulk) -0.2(% calcite)]/ %aragonite

This will give a percent value of Sr content, which can then be used to gauge whether the sample was inorganically or organically precipitated calcium carbonate.

LOCALITY DESCRIPTION

San Salvador Island, Bahamas (24°00N, 74°30'W) (Figure 1) is one of the easternmost islands in the Bahamian Archipelago. Moon Rock Pond is located in the northern part of the island about a kilometer southeast of the Gerace Research Center. Moon Rock Pond is part of a series of seven small ponds in the interior of the island. The pond is one of the smallest in this area (approximately 80m wide x 200m long). The pond itself is surrounded by limestone that has the look of a "moonscape", hence the name (Godfrey et al., 1994) (Figure 2). The substrate at certain times is almost an eerie gray/white color, which is another way this pond got its name. The pond sediments are Holocene, while the surrounding rock is Pleistocene (Teeter, 1995). The conduits that connect it to the ocean are found in the southeastern side. These conduits have an unimpeded flow to the ocean which lies approximately 1km to the east at

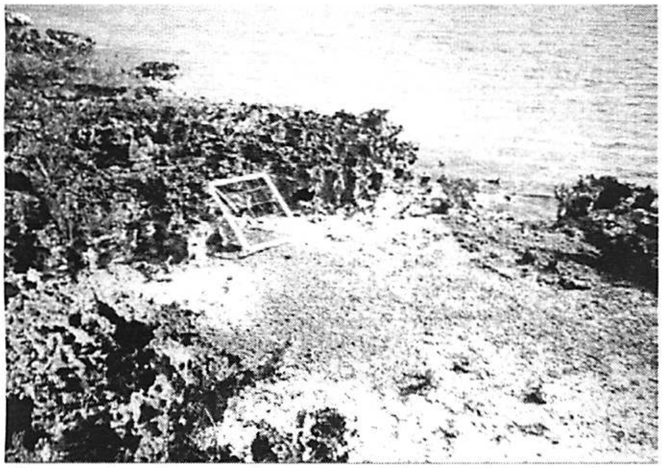

Figure 2. View of Moon Rock Pond, note the epikarst surrounding the pond which gives the pond its 'moonscape' look (quadrat center right of photograph is 0.25m^2).

Hanna Bay (Edwards et al., 1990) allowing the tides and salinities in Moon Rock Pond to be near normal, with a lag and diminished range in the tides (Teeter, 1995).

METHODOLOGY

Sample Collection

The initial samples were collected in July 2000 with more samples collected in May, June, and December 2001. They were collected from Moon Rock Pond and Pain Pond. Samples from Pain Pond were collected to see whether or not any carbonate lime muds existed in this pond. Muds were collected separately from organisms and rock material. The biotic samples were rinsed initially with water at the GRC and bagged. Mollusk shells (of varying species), mud, algae, and rock samples were taken from each site and bagged separately. The ponds varied in composition, with Pain pond having little to no lime mud as a substrate. Pain Pond is representative of the other ponds of the area, which are floored primarily by a brown organic fluc.

Sample Preparation

In the laboratory, all samples were washed with de-ionized water, and then some samples were further washed with a buffered 10% H_2O_2 solution to remove all organic material. These samples were then rinsed again with DI-water. Because Calgon®, which is usually used to disaggregate mud samples interferes with both XRD and AA spectrometry, the sediments were soaked overnight in DI water and disaggregated in an ,ultrasonic bath for 5 minutes. The sediment was sieved through a 63μm sieve and the subsequent slurry decanted several times in order to achieve as close to a <4μm size fraction as possible. All samples were oven dried at 50°C. A portion of each shell sample was cleaned with a 10% HCl solution to remove any epibionts that were attached to the samples, and again they were rinsed with DI-water and oven dried at 50°C for a second time. All samples were crushed into a fine powder in a previously cleaned agate mortar and pestle. The only samples that were treated differently were two Moon Rock Pond mud samples. One was bleached with Clorox® and crushed, while the other was only DI rinsed and then crushed. After the samples were powdered they were dissolved in 2% trace metal grade HCl and filtered through a 0.45-μm syringe filter. This ensured that the sample was pure carbonate and that any other material was kept out of the sample during chemical analysis. The first set of sample solutions were made using ~0.0125g of sample powder and ~25.0000g of acid. These were weighed using an analytical balance, and the weights were recorded so concentrations could be calculated later. The second set of samples were prepared the same way except that 1mL of Li_2CO_3 was added as a matrix modifier for analysis. The samples were placed in HDPE bottles that had been pre-washed in 2% trace metal grade HCl.

Sample Analysis

XRD Analysis. The powder samples were run on a Phillips X-ray diffraction unit to calculate the percent aragonite, calcite, and high Mg-calcite. The instrument scanned the interval from 22° to 38° 2Θ (Cu-Kα) at 1.0° per minute. These ratios were determined using the peak-area method of Milliman and Bornhold (1973) and Milliman et al. (1993). A standard curve was constructed using different percentages of oyster calcite and coral aragonite. Experience with this equipment indicates a reproducibility of 3-4% and an accuracy within 5%.

Chemical Analysis. The Ca, Mg, and Sr content of each sample solution were analyzed using a single element lamp Perkin-Elmer Atomic Absorption Spectrophotometer (AAS). A 5-point (standard) calibration curve for each element was prepared. Li_2CO_3 was added as a matrix modifier for analysis. The concentration of Sr in each sample would allow the comparison of the Moon Rock Pond mud concentration to the shells, algae, and rock. This would ultimately lead to the determination of the origin of the carbonate in the muds. Satlabs, Inc. of Cartersville, GA independently tested some samples using an Inductively Coupled Plasma-Emission (ICP) Spectrophotometer.

RESULTS

The results of the chemical analysrs (Figure 3) indicate that the muds (clay and silt fraction) (particles approx < 64μm) of Moon Rock Pond have a Sr concentration of between 0.47 and 0.97%, indicating that the mud is not purely an inorganic carbonate precipitate. Milliman (1967, 1974) and Loreau (1982) found that pure inorganic carbonates, primarily ooids, have a Sr concentration of between 0.95% – 1.0% (with a mean of 0.98 +/- 0.047% for 15 samples).

When the samples from Moon Rock Pond are further subdivided into silt (>4μm) and clay (<4μm) sizes, however, the finer grained fraction (clay) are definitely of an inorganically

Sample	% Sr in Aragonite
Mud (<4μm)	0.9700 +/- 0.0050
Silt & Clay	0.4700 +/- 0.0096
Bivalve	0.2600 +/- 0.0500
Gastropod	0.2700 +/- 0.0022
Shells (undifferentiated)	0.3000 +/- 0.0700
Acetabularia	0.8400 +/-0.1600

Figure 3. Table showing %Sr in the aragonite fraction of the carbonate constituents of Moon Rock Pond.

precipitated calcium carbonate value closer to 0.97% Sr. While the combined silt and clay fraction have a value of 0.47% Sr. The crushed combined molluscan shells (bivalves (0.26%) and gastropods (0.27%) have mean Sr value of 0.30%, whereas the algal component, *Acetabularia sp.* has a Sr concentration of 0.84%.

The aragonite values for each sample were calculated using the peak-area method by Milliman and Bornhold (1973). The highest values were found in the bivalve component, except for the oysters. Each sample yielded an aragonite value of between 97-100%, as did *Acetabularia.* The oysters are calcitic. This was also the case for the rock samples, which had been altered to either calcite or high Mg-calcite and showed no aragonite fraction. Two of the mud samples, the ones washed in DI and H_20_2, yielded high aragonite values of 90% to 92%, whereas the bleached mud showed only a value of 62.8% aragonite. We believe the bleach had some effect on both the mineral and chemical analysis, thus they are not used for discussion. Some of the clay/silt samples yielded aragonite values of only about 50%, the remainder consisting primarily of Mg-calcite, indicating perhaps detrital input from the surrounding rock.

If we attempt a 2-part mixing equation (see below*), where inorganically precipitated needles have a value of 0.98%Sr (Milliman, 1967, 1974; Milliman et al., 1993; Loreau, 1982) and the combined crushed shells have a value of 0.30%Sr, then the clays would be wholly (99%) inorganically precipitated, while the silt and clay mixture (with a value of 0.47%) would be 75% from organic sources (molluscs) and 25% from an inorganically precipitated source.

*0.98x + 0.30(100-x) = 100 Sr (bulk)

Where x is the percent inorganically precipitated aragonite.

*0.98(25%) + 0.30 (75%)= 47 Sr (For silt &clay)
*0.98 (99%) + 0.30 (1%) = 97 Sr (For clay only)

DISCUSSION

The results obtained from this study appear to support the hypothesis proposed by Davis (In Godfrey *et al.*, 1994). Based on their Sr and aragonite signatures, the bulk of the Sr content in the aragonite of the clays (<4μm) of Moon Rock Pond is of an inorganically precipitated origin. The silt and clay fraction, however, show that the samples have a strong organic (molluscan) source content, 75%. The silt and sand are probably mostly disaggregated shell material, i.e. broken down shell fragments with some detrital rock material. This mixing of organically and inorganically precipitated aragonitic constituents is reflected in the Sr signatures present. One anomaly in the mud analysis is the bleached mud. This yielded a much lower Sr values, which is believed to be the result of the bleach's make-up interfering with both the XRD and AA analysis. The calcareous green alga, *Acetabularia,* which have a high Sr in the aragonite signature, is believed to have little impact on the carbonate source due to its low density at the site, though some impact cannot be discounted.

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