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The fertilization of the Bahamas by Saharan dust: A trigger for carbonate precipitation?

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ABSTRACT

The enigma of the Bahamas is that this highly productive carbonate system has existed for at least 100 m.y., building a vast edifice of carbonates, thousands of meters thick, in an essentially nutrient-poor environment. Based on measurements of the insoluble material, the Fe and Mn in the carbonate fraction, and the $\delta^{15}N$ of the sedimentary organic matter, we suggest a paradigm shift in order to explain the formation of the Bahamas and possibly other similar platforms. We propose that the Great Bahama Bank is currently, and may in the past have been, fertilized by atmospheric dust, promoting the fixation of atmospheric N_2 by cyanobacteria. These cyanobacteria provided a source of nitrogen to the rest of the community in this nutrient-poor environment. The fixation of N has imparted a characteristic $\delta^{15}N$ signal and has been responsible, through the drawdown of CO_2, for initiating the precipitation of carbonate in the shallow waters. This phenomenon might be responsible for the formation of vast amounts of sediments in the oceans, not only within recent times, but throughout geological history, particularly in the early history of the Earth prior to the existence of calcium carbonate–secreting organisms.

INTRODUCTION

The Great Bahama Bank (GBB) is a large (>100,000 km^2) shallow-water carbonate complex that contains numerous semiemergent islands and is situated to the east of the Florida Straits. These islands are composed primarily of calcium carbonate and have no significant siliciclastic component. Great Bahama Bank has built up over at least the past 100 m.y. (Eberli and Ginsburg, 1987; Schlager et al., 1988) in a nutrient-poor environment. Because high concentrations of nutrients promote macro-algal and micro-algal growth, reducing water transparency and limiting the growth of carbonate producers such as corals and calcareous algae (Hallock and Schlager, 1986), it has been suggested that carbonate platforms flourish in oligotrophic environments. In the Bahamas, the activities of various carbonate-secreting organisms and the inorganic precipitation of calcium carbonate have produced large amounts of sediment, which has been deposited on the platform surface and transported off the platform, allowing the GBB to build laterally. The modern sediments on the GBB are mainly nonskeletal, composed of ooids, peloids, and carbonate muds (Purdy, 1963b; Traverse and Ginsburg, 1966). The muds are ingested by worms, generating pellets that harden and eventually form the central portions of peloids and ooids. All of the surface sediments on the GBB have essentially similar $\delta^{13}C$ and $\delta^{18}O$ values, suggesting that at least the nonskeletal materials are genetically related (Swart et al., 2009) and have a common precursor, the mud. The source of Bahamian muds has long been a mystery. One suggested origin is the direct precipitation from surface waters producing intensely white areas of water known as whitings (Black, 1933; Cloud, 1962; Shinn et al., 1989). Conversely, it has been postulated that the whitings might result from sediment reworking (Broecker and Takahashi, 1966; Morse et al., 2003, 1984). The occurrence of whitings is of much more than academic interest, particularly if they result from direct precipitation from seawater. For billions of years, during the early history of Earth, such precipitation may have been the only method of carbonate formation, and therefore the processes occurring on the GBB may provide a valuable insight into carbonate precipitation during early Earth history.

A large amount of research has supported both sides of the whitings argument. Proponents of direct precipitation point to the absence of mechanisms whereby the sediments could be stirred up (Shinn et al., 1989), the different structures of the aragonite crystals obtained from the whitings compared to bottom sediments (Loreau, 1982; Reid and MacIntyre, 2000), and the absence of sufficient quantities of possible calcium carbonate–producing organisms on the platform surface (Shinn et al., 1989). Alternatively, the supporters of a reworked origin point to the fact that radiometric dating of the whitings indicates an old, rather than modern, age (Broecker et al., 2000; Morse et al., 1984), and the absence of changes in the carbonate alkalinity between the whiting and the surrounding waters (Morse et al., 2003, 1984) that would be expected if direct precipitation occurred; these workers favor an explanation that the mud is ultimately derived from the breakdown of the skeletons of calcareous green algae (Neumann and Land, 1975).

An adaptation of the direct precipitation hypothesis is that the whitings are produced as a result of the photosynthetic activity of cyanobacteria (Robbins, 1992). These organisms remove CO_2, raising the saturation state of $CaCO_3$ and inducing the precipitation. Although such a mechanism has been shown to be responsible for precipitation in many locations (Davis et al., 1995; Hodell et al., 1998), carbonate platforms such as the GBB are generally Fe poor despite the fact that this element has proved to be critical for the growth of nitrogen-fixing organisms such as cyanobacteria (Brand, 1991; Chappell et al., 2012), the proposed agent inducing the whitings. One possible source of Fe that might promote such blooms on the GBB is atmospheric dust originating in the Sahara and Sahel regions of Africa. Airborne materials from this and other regions, including North America, are the only likely source of noncarbonate material in the region (Muhs et al., 2007; Prospero et al., 1970). In order to investigate the hypothesis that atmospheric dust might be an important source of Fe in the GBB, we measured the percentage of insoluble residue and the concentration of trace elements (Fe and Mn) characteristic of atmospheric dust (Trapp et al., 2010) in the carbonate-soluble portion of ~250 samples of surface sediments from the GBB. In addition, we measured the $\delta^{15}N$ values of organic material in these sediments. The results of these analyses were compared with the distribution of whitings as documented by satellite observations (Robbins et al., 1997).

METHODS

During 2001–2004, ~270 grab samples were collected from the GBB (Oehlert et al., 2012; Reijmer et al., 2009; Swart et al., 2009). Concentrations of trace elements in the carbonate fraction were determined by dissolving 100 mg of sediment in 100 cm^3 of 4% nitric acid. The resultant solution was filtered and the percentage of insoluble material was determined by weight difference. The dissolved sample was analyzed using an inductively coupled plasma emission spectrometer (Varian Vista Pro)

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[1]GSA Data Repository item 2014251, locations of the samples, percentage insoluble, and concentrations of Mn and Fe, is available online at www.geosociety.org/pubs/ft2014.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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and standardized using matrix matched solutions. The limit of detection for Fe and Mn was ~1 ppm in the sample or 1 ppb in the solution. The δ^{15}N was analyzed by combusting the entire sample, without pretreatment, in a Costech elemental analyzer and measuring the N_2 produced using a Thermo Advantage V stable isotope ratio mass spectrometer. The δ^{15}N values are reported relative to atmospheric nitrogen using conventional delta (δ) notation. Correlations between the various measured components were determined using a Spearman's rank correlation coefficient.

RESULTS

The average concentrations, standard deviations of the percentage insoluble, Fe and Mn, and the correlation coefficients are shown in Table 1. In addition, previously published data on the mineralogy have been included (Table 1; Reijmer et al., 2009). The surface sediments of the GBB are nearly pure calcium carbonate (m = 99.3%); the mineralogy consists mainly of aragonite (91.6%) with smaller amounts of high-Mg calcite (HMC = 7.5%), and low-Mg calcite (LMC < 0.1%) (Reijmer et al., 2009). The concentration of insoluble residue in the sediments ranges from essentially zero to a maximum of 3.4% and is statistically significantly positively correlated with the concentrations of Fe (Figs. 1A and 1B) and Mn in the carbonate fraction (see the GSA Data Repository[1]) (Table 1). The highest concentrations of insoluble material and Fe are located immediately to the west of the island of Andros, while the areas to the north and south show lower values (Fig. 1A). The mean δ^{15}N of the organic material is 0.1‰ (n = 256, σ = 0.7). Although there are no distinct west-east spatial patterns in the distribution of the δ^{15}N, the most positive values (+3‰) occur on the northern margin of the GBB. In addition, there are more negative values to the south (–1‰ to 0‰) (Fig. 1C).

TABLE 1. GEOCHEMICAL DATA AND CORRELATION COEFFICIENTS BETWEEN VARIOUS MEASURED PARAMETERS

	Mean	s.d.	Fe	Mn	A	LMC	HMC	Insoluble
Fe (ppm)	42.0	50.0						
Mn (ppm)	1.4	1.3	**0.79**					
A (%)	91.6	5.3	0.15	0.04				
LMC (%)	0.1	0.4	**0.31**	**0.24**	0.01			
HMC (%)	7.5	5.3	0.76	0.11	**−0.21**	0.03		
Insoluble (%)	0.7	0.6	**0.35**	**0.35**	−0.08	**0.16**	0.11	
δ^{15}N (‰)	0.1	0.7	0.05	**0.18**	−0.11	**0.15**	0.06	**0.22**

Note: Relationships that are statistically significant at the 95% confidence limits are in bold type. A—aragonite; LMC—low-Mg calcite; HMC—high-Mg calcite; s.d.—standard deviation.

DISCUSSION

The surface waters in the lee of Andros Island possess the highest salinity of any in the Bahamas (to 40 PSU), the longest residence time (Broecker and Takahashi, 1966; Traverse and Ginsburg, 1966), the greatest number of whitings (Morse et al., 1984; Robbins et al., 1997; Shinn et al., 1989), and the highest amount of carbonate mud (Purdy, 1963a, 1963b; Reijmer et al., 2009; Traverse and Ginsburg, 1966). This study also documents that the sediments in this region have the highest amounts of insoluble materials and concentrations of Fe and Mn. To the north and the south, the sediments become coarser (Reijmer et al., 2009) and the percentage of insoluble materials and the trace elements decrease. We propose that the relatively high concentrations of insoluble material, as well as Fe and Mn, are derived from atmospheric dust. The sediments may also receive Fe derived from Andros Island, which like many islands in the Bahamas receives significant quantities of atmospheric dust leading to high concentrations of Fe in the soils (Rossinsky et al., 1992). We suggest that this Fe has a fundamental role in producing whitings, because the Fe is needed by the N-fixing cyanobacteria, the photosynthetic activity of which removes CO_2 and induces carbonate precipitation. Although the Fe derived from dust is very insoluble in seawater, and only a small proportion (~1%–4%) dissolves directly in oceanic water (Sholkovitz et al., 2012), its impact upon coastal oceans is well established (Elrod et al., 2004), and atmospheric dust is considered to be a major input of Fe into the oceans (Mahowald et al., 2005). In the case of the GBB we do not know whether the Fe is utilized directly as the dust settles through the water column or whether it is cycled through the pore waters of the bottom sediments. One possible model is that within the uppermost portion of the sedimentary pore waters, above the sulfate reducing zone, Fe^{3+} is utilized as an electron acceptor during the oxidation of organic material and converted to Fe^{2+}, a more soluble form than Fe^{3+}. As the Fe^{2+} diffuses out of the sediment pore waters it is utilized by cyanobacteria growing at or near the surface of the sediments. Occasionally the surface sediments are resuspended by the action of currents, winds, and/or by burrowers such as shrimp. Within the shallow water column the cyanobacteria promote the formation of algal blooms and the precipitation of carbonate sediments through the removal of CO_2. The bloom continues until the cyanobacteria, eventually starved of Fe, stop photosynthesizing and active carbonate precipitation ceases. However, the whiting may persist for some time in a nonactive mode, particularly during the summer when the surface waters are calm and highly saline. These active and nonactive phases might explain the observations by previous workers, who in some instances were unable to measure anticipated differences in the chemistry of the water (Morse et al., 2003, 1984) between the interior and exterior of whitings. In addition, this model would imply that the whiting had some contribution from the bottom sediment, as previously suggested (Shinn et al., 1989), and therefore also would explain the old ages previously measured (Broecker et al., 2000). A key component of this model is the shallow water depth on the GBB that allows the Fe from the dust to sink to the bottom, be reduced to Fe^{2+}, and then be available for the cyanobacteria to utilize. Such a cycle would be unique to shallow-water environments.

Further support for this model is provided by the δ^{15}N results. The δ^{15}N values of the sedimentary organic material from the GBB show a mean value close to 0‰, consistent with N fixation, a process that does not significantly fractionate ^{15}N relative to ^{14}N (Hoering and Ford, 1960). The highest δ^{15}N values (+3‰) are found in three samples retrieved from slightly deeper water off the northern margin of the GBB. Eliminating these samples reduces the mean δ^{15}N to +0.05‰ (σ = 0.5) (Fig. 1C). These deeper samples could be influenced by upwelled waters in which the NO_3^- has more positive δ^{15}N values (~+4.8‰; Leichter et al., 2007; Sigman et al., 2000). In addition to upwelling and fixation, atmospheric dust can be a nitrogen source (Hastings et al., 2003; Knapp et al., 2010; Zamora et al., 2011), with the nitrogen being present in dust as NH_4^+, NO_3^- salts, and organic compounds. Although the Bahamas have not been extensively studied, δ^{15}N values of between ~–4‰ and –2‰ have been reported for atmospheric dust in the region (Hastings et al., 2003). Considering these three sources of nitrogen (i.e., nitrogen fixation, upwelling, and dust), and their δ^{15}N values, it would appear that the majority of the nitrogen in sedimentary organic material on the GBB is derived from nitrogen fixation rather than from upwelling or from atmospheric deposition. The alternative model, that the nitrogen is a mixture of upwelled nitrogen (δ^{15}N ~+5‰) and dust-derived nitrogen (δ^{15}N ~–4‰ to ~–2‰), seems unlikely as there are no spatial patterns in the distribution of the δ^{15}N of the sedimentary organic material that can be attributed to the input of upwelled nitrogen. In contrast, there are some areas, outside the region where the whitings are found, with slightly more negative δ^{15}N values, and these could conceivably have received a greater input of atmospheric nitrogen (Fig. 1C).

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[1] GSA Data Repository item 2014251, locations of the samples, percentage insoluble, and concentrations of Mn and Fe, is available online at www.geosociety.org/pubs/ft2014.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

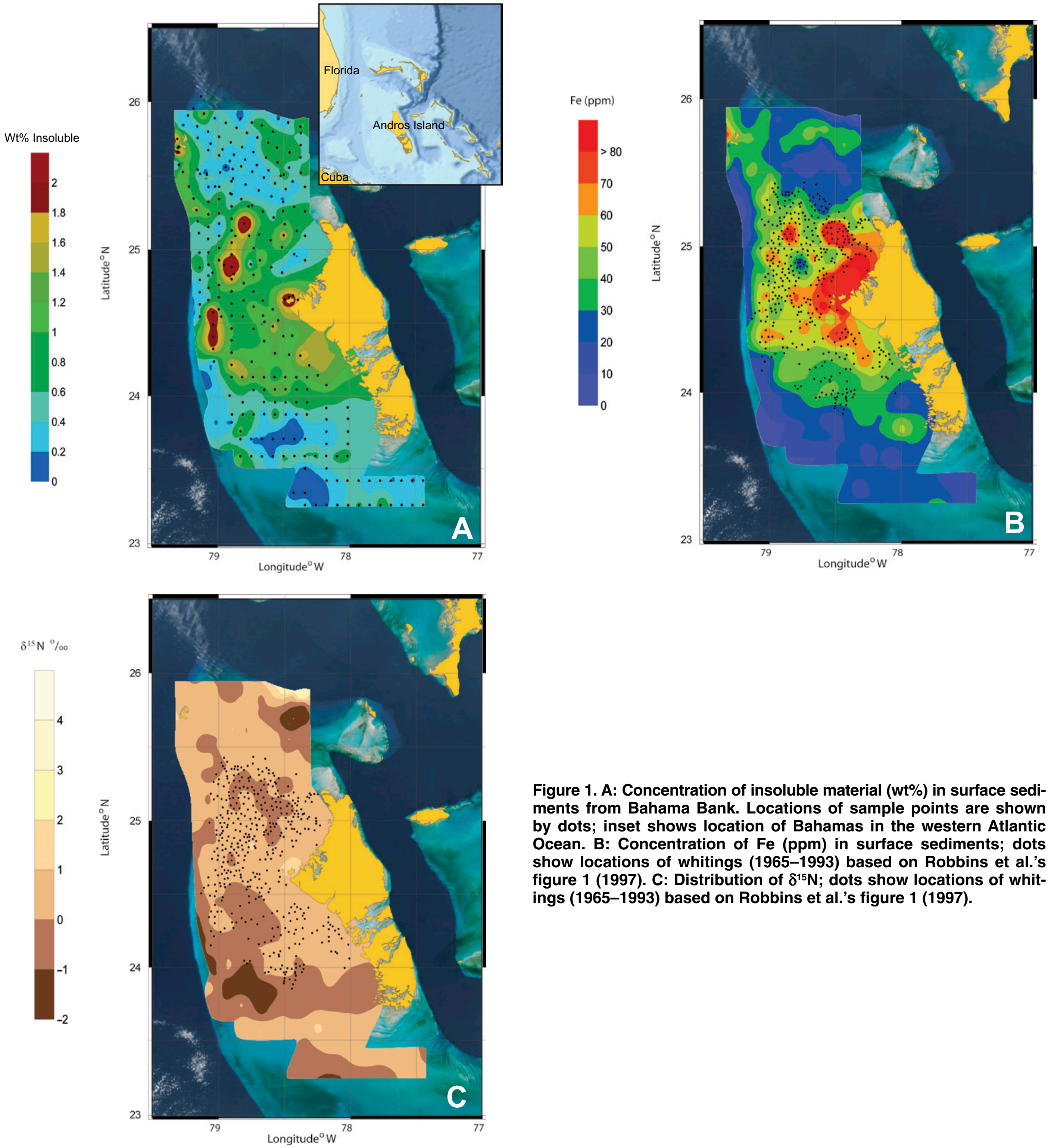

Figure 1. A: Concentration of insoluble material (wt%) in surface sediments from Bahama Bank. Locations of sample points are shown by dots; inset shows location of Bahamas in the western Atlantic Ocean. B: Concentration of Fe (ppm) in surface sediments; dots show locations of whitings (1965–1993) based on Robbins et al.'s figure 1 (1997). C: Distribution of $\delta^{15}N$; dots show locations of whitings (1965–1993) based on Robbins et al.'s figure 1 (1997).

CONCLUSIONS

In this paper, we demonstrated a strong similarity between the distribution of whitings and the Fe in the sediments of the GBB. We believe that the Fe originates from dust deposited either directly or washed in from dust deposited on the adjacent Andros Island. The input of Fe helps induce the precipitation of $CaCO_3$ through the photosynthetic activity of cyanobacteria. Cyanobacteria also fix N_2, which is utilized by all the biological communities on the GBB and is evident in the $\delta^{15}N$ signature, which is close to zero over the entire platform. Such whitings might be responsible for helping to produce vast amounts of sediments, not only within recent times, but also during previous periods of geological history. Evidence of long-term dust deposition is present in other records and has been postulated to account for the accumulation of soils through the Caribbean and the southern United States (Muhs et al., 2007). Such production might be significantly increased during periods of high dust input and could account for variations in rates of accumulation and platform progradation. This model suggests a modification to the paradigm that proposes that high concentrations of nutrients are detrimental to the growth of carbonate platforms. Rather we propose that certain nutrients may promote platform growth, particularly ones dominated by nonskeletal carbonates and the formation of mud by whitings.

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