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STRATIGRAPHIC DISTRIBUTION AND ASSOCIATIONS OF TRACE ELEMENTS IN VADOSE-ALTERED MULTICOMPONENT CARBONATE ASSEMBLAGES

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ABSTRACT

Trace element geochemistry is being increasingly used to determine diagenetic trends in carbonates (Pingitore, 1978; 1982; Veizer, 1983; Brand and Veizer, 1980). Recent studies have developed theories on the mechanisms involved in the redistribution of trace elements in carbonates and laid the groundwork for further research. However, the effects of vadose diagenesis on the distribution of trace elements in carbonate assemblages remains poorly understood.

Analysis of multicomponent carbonates (i.e., stable and metastable carbonate minerals, oxides, organic matter, and non-carbonate minerals) from Andros Island and San Salvador Island, Bahamas provides information on trace element associations among various components within carbonate units and the vertical and lateral stratigraphic distribution of trace elements, particularly in relation to paleosol horizons. Three geochemically distinct zones may be observed within a single vadose-altered carbonate dune: 1. paleosols; 2. "zone of influence"; and 3. host rocks. Each of these zones can be recognized by the trace element signatures associated with the exchangeable carbonate and oxide fractions of multicomponent carbonates.

Multivariate statistical analysis reveals the presence of five geochemically-distinct groups within the Pleistocene and Holocene dunes of the Bahamas: 1. paleosols; 2. early diagenetic dune sands; 3. recrystallized dune sands; 4. soil influenced type I; and 5. soil influenced type II.

A statistical model (polar ordination) is developed to account for the diagenetic trends observed within the Bahamian carbonate dune sands. Variability among the units studied is accounted for by progressive aragonite to diagenetic low-Mg calcite transformation and by varying degrees of pedogenesis. Although time is a factor in the development of the trends recognized, other factors related to vadose diagenesis are more important. The trace element signals associated with vadose diagenesis result from the degree of chemical diagenesis, the type

and timing of paleosol development, and the extent of bioturbation and fracturing of the host unit. These mechanisms play the most important role in the geochemical signature present in vadose-altered carbonate sands.

INTRODUCTION

Carbonate rocks and sediments are comprised of a variety of constituents, including: the carbonate minerals aragonite, high-Mg calcite, and low-Mg calcite; oxides; organic matter; and non-carbonate minerals. Such "multicomponent" carbonates have diagenetically-mobile and immobile trace elements associated with various constituents of the rock or sediment.

In recent years, studies concerning the occurrence and mobility of trace elements in carbonate rocks and sediments have provided both practical and theoretical models for chemical controls and pathways during carbonate diagenesis (Land, 1967; Kinsman, 1969; Friedman, 1969; Pingitore, 1978; 1982; Brand and Veizer, 1980; and Veizer, 1983). The precipitation or dissolution of calcium carbonate is a wet chemical reaction, and trace elements from solution such as Sr^{++} , Mg^{++} , Fe^{++} , Mn^{++} , and Na^+ can substitute for Ca^{++} in the CaCO_3 lattice (Bathurst, 1975; Brand and Veizer, 1980). Trace elements can be incorporated into carbonate minerals in several ways: 1. substitution for calcium in the CaCO_3 lattice; 2. interstitially between lattice planes; 3. in lattice positions that are open due to defects in the structure; and 4. in non-carbonate inclusions, such as silicate impurities and fluid inclusions (Veizer, 1983).

The original carbonate minerals, aragonite (A) and high-Mg calcite (HMC), will possess a trace element signature derived from the ambient sea-water in which they formed. Some modification by biogenic processes may occur. This is particularly important for low-strontium molluscan aragonite. Upon exposure to meteoric waters,

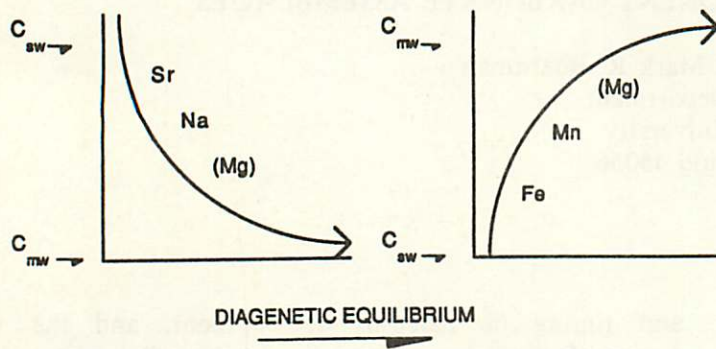


Fig. 1. Elemental changes expected during increasing diagenetic equilibrium with meteoric water. C_{mw} and C_{sw} are calcium carbonate in equilibrium with meteoric water and sea-water, respectively. Sr and Na, present in higher concentrations in sea water, show a decrease in concentration as diagenetic equilibrium with meteoric water is approached. Fe and Mn, present in higher concentrations in meteoric water, should show a concomitant increase. Mg can either increase or decrease with progressive equilibrium with meteoric water, depending on original mineralogy; high-Mg calcite, low-Mg calcite, or aragonite (after Brand and Veizer, 1980).

these minerals partly or completely dissolve, exchange, and mix their trace elements with those of the meteoric water, and subsequently reprecipitate as diagenetic low-Mg calcite (dLMC) (Pingitore, 1978; 1982; Brand and Veizer, 1980). This dLMC will have a trace element signature shifted in the direction of equilibrium with the meteoric water from which it precipitated (Brand and Veizer, 1980). As fresh water diagenesis proceeds, a progressive loss of strontium and sodium, along with a concomitant increase in iron and manganese should occur (Fig. 1). Such elemental behavior is identifiable after extensive diagenetic equilibration, as in the Silurian Read Bay Formation and the Mississippian Burlington Limestone (Brand and Veizer, 1980); but what role does early vadose diagenesis play in the establishment of these trends, and are they identifiable in younger subaerially-exposed carbonates?

Previous workers have collected samples from wide geographic areas and/or concentrated on examining specific allochems (Brand and Veizer, 1980; Pingitore, 1978). In doing so, 1. the stratigraphic variability in trace element composition has been neglected and remains unknown, and 2. the relative importance of the non-carbonate fractions in determining trace element compositions of a multicomponent carbonate system has been ignored or brushed aside. In addition, previous workers have utilized single-dissolution procedures for the extraction of trace elements from carbonate rocks and sediments (Veizer and Demovic, 1974; Pingitore, 1978; Brand and Veizer, 1980; and others). These treatments commonly consist of dilute HCl solutions aimed at dissolving the calcium carbonate component of limestones. However, experimental studies show that while treatment of rocks and sediments with

dilute HCl is effective at dissolving calcium carbonate, trace elements can be leached from oxides, organic matter, and the lattices of some clay minerals (Heath and Dymond, 1977; Tessier et al., 1979; Pelle, 1989). As a result of these shortcomings, the modes of occurrence (associations), sources and stratigraphic variability of trace elements in subaerially-exposed carbonates, and the physical controls responsible for the redistribution of trace elements through a carbonate section are not well documented.

The objective of this study is to examine carbonate dune sands and the exposure surfaces/paleosols associated with them to determine the effects of early vadose diagenesis, paleosol formation, and mineral insoluble residue on the distribution of trace elements in eolian carbonate sands. In particular, the associations of trace elements with various fractions of multicomponent carbonate rocks, and the vertical and lateral stratigraphic variability of trace elements as related to diagenetic changes produced in the vadose environment are examined. This study attempts to develop a model for vadose diagenesis in the Pleistocene and Holocene vadose-altered carbonate sands of the Bahamas. It is hoped that the diagenetic trends and processes identified in this study can be useful to the interpretation of ancient carbonate sequences.

METHODOLOGY

Field Methods

Sites on San Salvador Island and Andros Island, Bahamas (Fig. 2) were chosen for this study because of the geographic isolation from most sources of non-carbonate minerals and

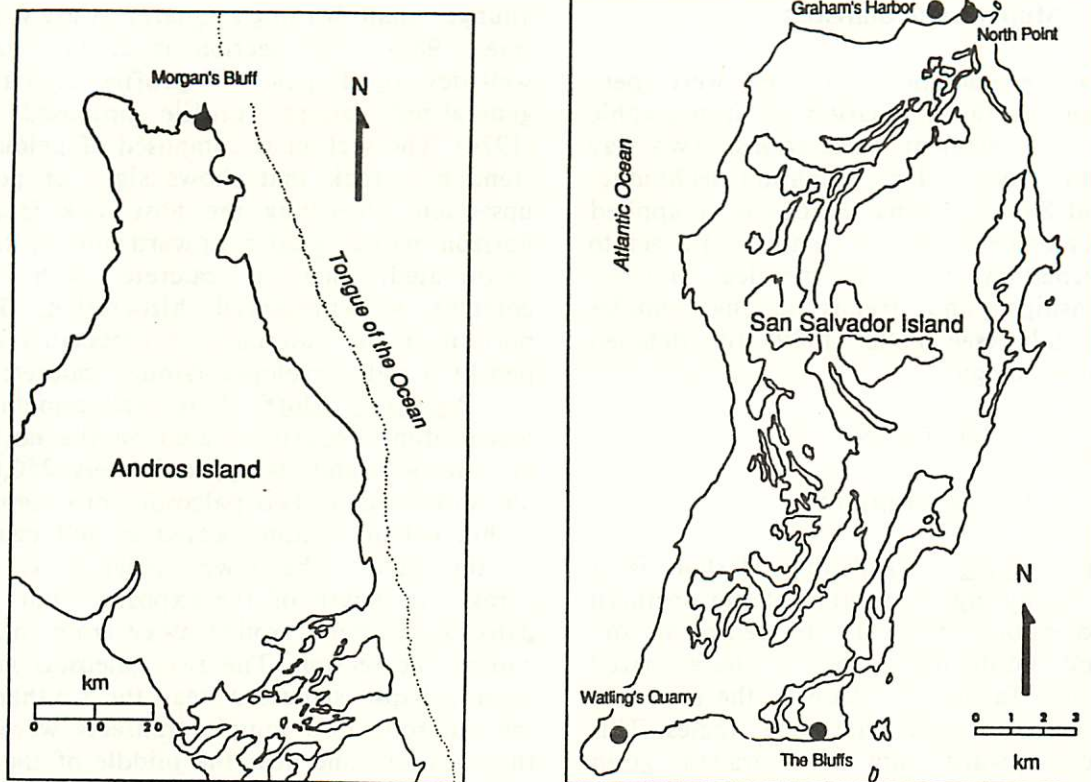


Fig. 2. Sample sites on Andros Island (A) and San Salvador Island (B), Bahamas.

because of the well-developed paleosols present on both islands. A total of 122 limestone and paleosol samples were collected from eolian dune localities on San Salvador Island and Andros Island. In addition, ten sediment samples were obtained from a core taken from Graham's Harbor, a lagoon north of San Salvador Island, to provide a baseline or starting point for measuring diagenetic alterations in subaerially-exposed, vadose-altered rocks.

Outcrops were sampled at approximately 50cm intervals along vertical transects to provide information on the vertical stratigraphic distribution of trace elements within a single outcrop. Parallel transects were sampled on two outcrops (Morgan's Bluff, Andros Island and Watling's Quarry, San Salvador) to examine lateral variability in trace element distributions on the outcrop scale.

Lab Methods

A selective sequential dissolution procedure, modeled after the method developed by Tessier and others (1979) was utilized in this study for the extraction of trace elements from rock and sediment samples. This procedure is capable of chemically separating trace elements into distinct fractions (Tessier et al., 1979), including: 1.

exchangeable (adsorbed trace elements); 2. bound to carbonates; 3. bound to Fe-Mn oxides; and 4. bound to organic matter (see Pelle, 1989, for detailed methodology). A fifth fraction, composed of trace elements in lattices of stable minerals, is not considered to be diagenetically mobile (Tessier et al., 1979), and this "residual fraction" is considered to be beyond the scope of this study.

Calcium, magnesium, strontium, sodium, potassium, manganese, iron, aluminum, and silicon concentrations were determined on a Beckman SpectraSpan V argon plasma spectrometer (DCP). All discussion concerning elemental concentrations in the carbonate fraction is based on the total carbonate (insoluble residue-free) basis.

Percent insoluble residue was determined by dissolving the calcium carbonate from 1 g (dry weight) of each sample in 10% (v/v) HCl. The insoluble residue was collected on pre-weighed 0.45 μ m Millipore filter paper, dried, and re-weighed.

Mineralogy was determined by x-ray diffraction on a Phillips XRG-3000 x-ray diffractometer using Cu-K α radiation. Percent aragonite was calculated using ratios of peak areas of aragonite and calcite and comparison to mixtures of biogenic carbonates (Neumann, 1965; Boardman, 1976).

Multivariate Statistics

Multivariate statistical analyses were performed to aid in the evaluation of stratigraphic trends and trace element associations. Two-way cluster analysis and polar ordination techniques (Sepkoski and Sharry, 1976a; 1976b) were applied to the mineralogical and geochemical data set to provide information on the geochemical similarities, relationships, and trends among samples within the study (see Pelle, 1989, for detailed statistical methodology).

RESULTS

Site Descriptions

Graham's Harbor. Graham's Harbor is a silled, high-energy lagoon located at the northern tip of San Salvador Island. The 3m sediment core extracted from Graham's Harbor is characterized by three distinct facies. The base of the core is a grapestone/bioclast "wacke-packstone" facies. This facies grades upward into an abraded grain "grapestone" and is capped by a *Halimeda*, foram-rich "packstone" facies (Colby and Boardman, 1988).

North Point. North Point is a Holocene eolian dune complex comprised of peloidal sands less than 6500 years old, based on C-14 dates of bulk sand (Boardman et al., 1987). This dune is characterized by fresh exposures adjacent to Graham's Harbor. North Point does not contain a paleosol, but is characterized by a poorly-developed soil and minor development of rhizcretions.

Watling's Quarry. Located in the southwest portion of San Salvador Island, Watling's Quarry is an 8.5m Pleistocene dune ridge approximately 120,000 years old (Carew and Mylroie, 1985). This outcrop is characterized by a lower paleosol that separates an underlying eolian skeletal grainstone from the overlying oolitic eolianite. The outcrop is capped by a thin laminar calcrete that extends down the flank of the dune. This calcrete has numerous micritic stringers (Braithwaite, 1983) associated with it that extend well below the exposure surface into the main body of the rock along fractures and more permeable laminae. Two sampling transects were taken at this location: one through the middle of the exposed dune, and a second along a cut near the dune flank.

The Gulf. The Gulf was formed from the coastal erosion of a Pleistocene dune somewhat

younger than Watling's Quarry (Carew and Mylroie, 1985). This section is characterized by a well-developed paleosol profile similar to the generalized calcrete profile proposed by Read (1974). The section is composed of peloidal grainstone host rock that shows signs of pedogenesis upsection. Overlying the host rock is a mottled horizon which grades upward into a thoroughly bioturbated, massive calcrete with extensive, complex, well-preserved rhizcretions. The upper portion of the outcrop is a brecciated zone capped by a well-developed laminar calcrete.

Morgan's Bluff. This well-cemented Pleistocene dune deposit, located on the northern end of Andros Island, is approximately 250,000 years old and contains two paleosol units, separated by a thin eolian section located at and near the top of the dune. The lower paleosol is preserved across the length of the exposure, but the upper paleosol has been eroded away from the northern end of the section. The two paleosols merge in a karst collapse structure near the southern end of the outcrop. Two sample transects were taken at this location, one near the middle of the exposure and another to the south, through a zone where the two paleosols mix.

Geochemical Results

In agreement with Walls and others (1977) and Brand and Veizer (1980), analyses of element concentrations in this study indeed show that carbonate rocks and sediments are a "multicomponent" geochemical system. Each component or fraction within the system contains diagenetically-mobile elements that contribute to the geochemical signature of the whole rock. Although the carbonate fraction dominates, other fractions (exchangeable and oxides) are important in understanding the diagenetic processes operating within the system as a whole.

Exchangeable Fraction. Elements associated with the exchangeable fraction include calcium, sodium, potassium, and strontium. High concentrations of calcium and strontium in marine sediments from Graham's Harbor indicate that treatment of samples with 1M MgCl₂ to strip away the adsorbed cations results in the dissolution of a small percentage of the total calcium carbonate available. Calculations and experimental results indicate the dissolution of no more than 0.6% of the total calcium carbonate available (Pelle, 1989). While this analytic problem increases the apparent concentrations of exchangeable cations, the over-

Exchangeable Fraction

Elemental Concentrations

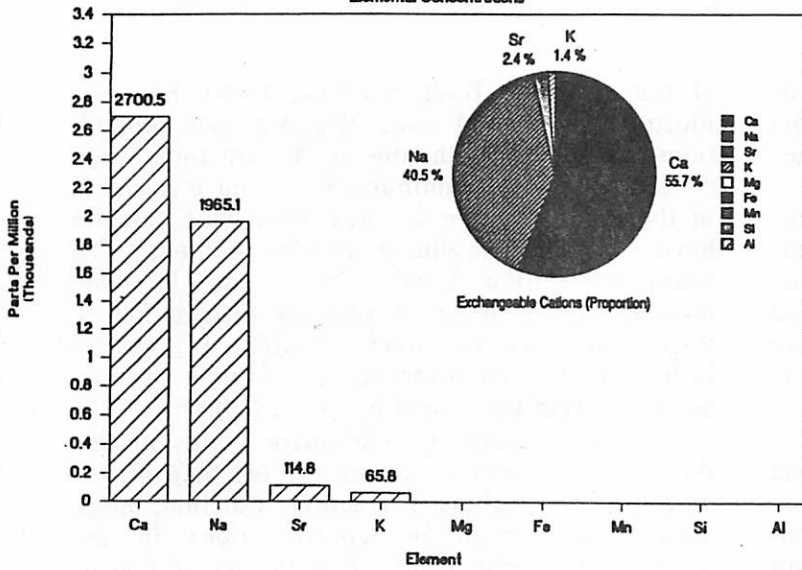


Fig. 3A.

Carbonate Fraction

Elemental Concentrations

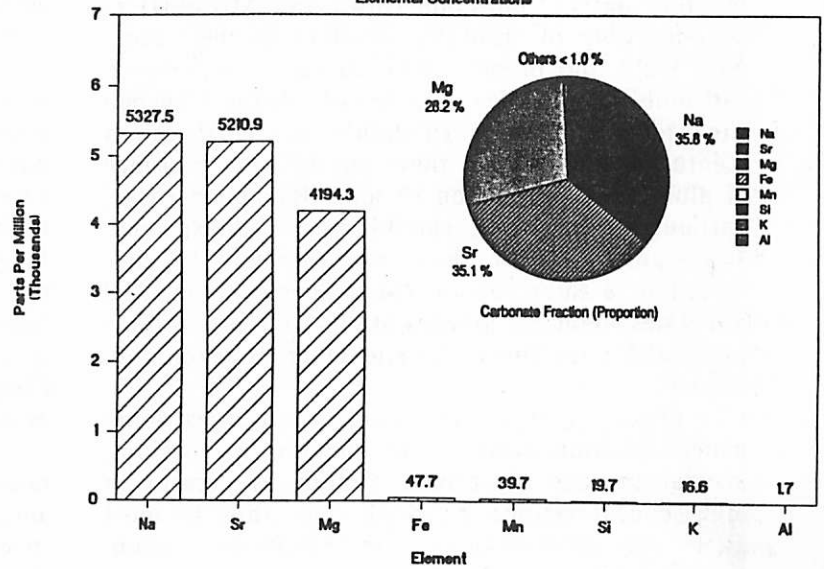


Fig. 3B.

Oxide Fraction

Elemental Concentrations

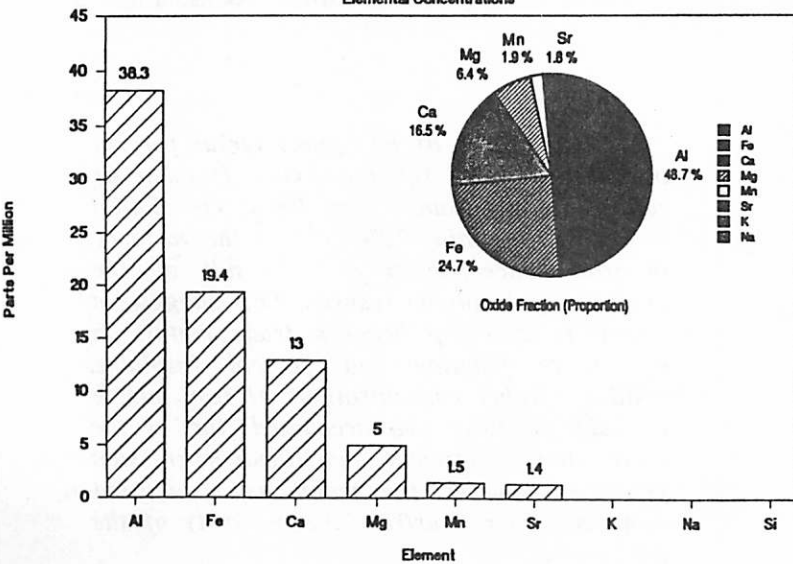


Fig. 3C.

Fig. 3. Average element concentrations associated with the (A) exchangeable fraction, (B) carbonate fraction, and (C) oxide fraction of samples studied. Pie charts illustrate relative proportions of cations present in each fraction.

all elemental trends and relationships are little affected. Fig. 3-A illustrates uncorrected element concentrations and proportions in the exchangeable fraction.

Carbonate Fraction. Elements associated with the carbonate fraction in this study include calcium, magnesium, strontium, sodium, potassium, iron, manganese, aluminum, and silicon. Elemental concentrations observed are in general agreement with previous studies (Kinsman, 1969; Pingitore, 1978; Dulin, 1984; Span and Gaillard, 1986).

The presence of aluminum and silicon associated with the carbonate fraction may seem surprising at first glance. However, Brand and Veizer (1980) attribute aluminum concentrations in the Read Bay Formation (Arctic Canada) and the Burlington Limestone (Iowa and Missouri) to acid leaching of insoluble residues in their samples. Walls and others (1975) discuss the presence and mobility of silica in paleosols of the Newman Limestone (Slade Formation) of northeastern Kentucky. In light of these studies, the presence of aluminum and silicon in some Bahamian rocks, particularly paleosols, should not be unexpected. The significance of these elements will be discussed in a later section (on paleosols). Fig. 3-B illustrates element concentrations and proportions associated with the carbonate fraction (excluding Ca).

Oxide Fraction. The oxide fraction is dominated by aluminum, iron, calcium, magnesium, manganese, and strontium. Sodium is present in high concentrations as well, but this is most likely due to insufficient rinsing of the sodium acetate-acetic acid leach used in the dissolution

of the carbonate fraction (Pelle, 1989). Fig. 3-C illustrates elemental concentrations and proportions associated with the oxide fraction. High concentrations of aluminum, iron, and manganese in the oxide fraction are associated with samples having a high insoluble residue content. The linear correlation between iron and insoluble residue (Fig. 4) indicates that the distribution of trace metals in the oxide fraction is strongly influenced by the presence of insoluble residue, an observation also noted by Dulin (1984).

Oxide coatings on carbonate grains protect them from dissolution during the leaching procedure for the carbonate fraction. Calcium, magnesium, and strontium concentrations in the oxide fraction may result from the dissolution of carbonate grains after their protective oxide coatings are dissolved.

Organic Matter Fraction. Elemental analysis reveals no significant concentrations of trace elements associated with residual organic matter. Although organic matter is thought to be an excellent scavenger for trace elements, particularly in soil horizons, the well-drained, sandy soils in this semi-arid environment apparently permit the rapid oxidation of organic matter, leaving behind a paraffin-like material and resistant structural (non-humified) organic matter residues (Tessier et al., 1979). Oxidation effectively releases any scavenged trace elements into the system.

Geochemical/Mineralogical Profiles. Geochemical analyses performed on samples collected along vertical transects at each of the outcrops reveal distinct vertical trends in the geochemistry of the vadose-altered dune rocks. Figs. 5

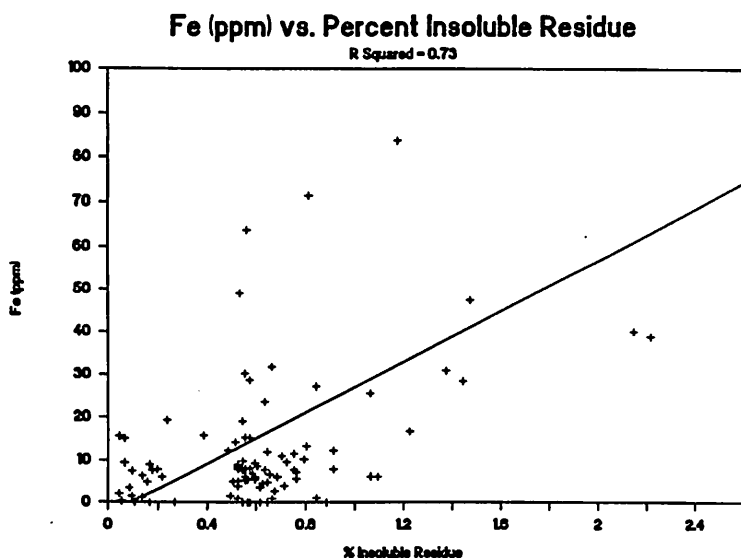


Fig. 4. Plot of Fe (ppm) versus percent insoluble residue for the oxide fraction of vadose-altered sands. The linear correlation ($r = 0.85$) explains 73% (r^2) of the variance in iron concentration as a result of the presence of insoluble residue. This suggests a strong relationship between trace metals in the oxide fraction and percent insoluble residue. Higher concentrations of iron and % insoluble residue are accounted for in the correlation coefficient and linear regression pictured; however, the scales were adjusted down to better illustrate the majority of the data points.

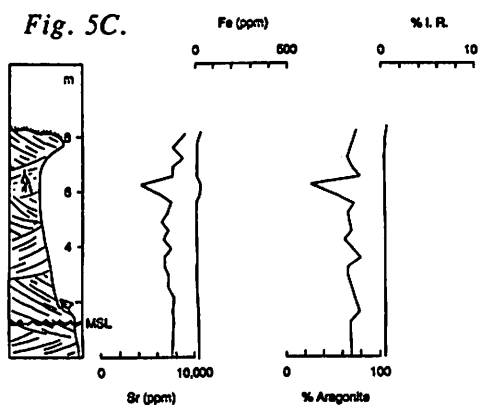
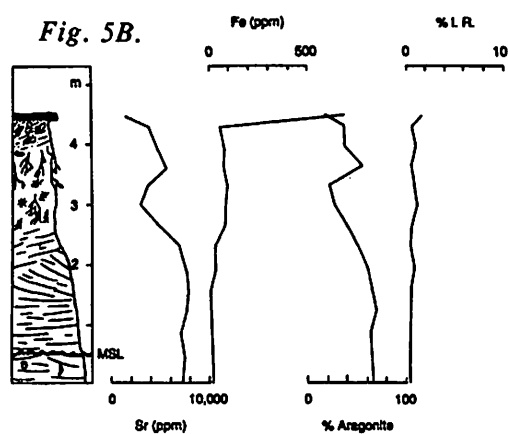
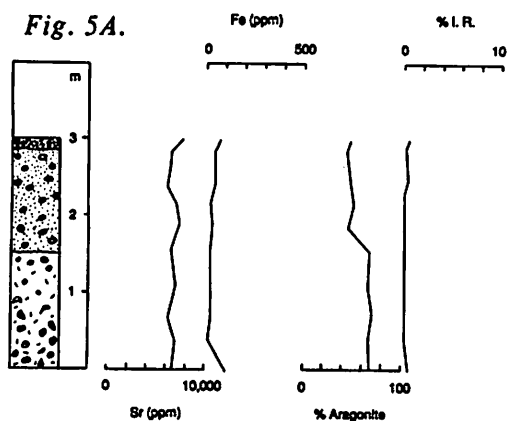


Fig. 5. Geochemical/mineralogical profiles for the carbonate fractions of (A) Graham's Harbor, (B) the Gulf, and (C) North Point.

and 6 illustrate geochemical/mineralogical profiles for the carbonate fraction along each of the outcrops examined in this study. The carbonate fraction was chosen to illustrate the results of these analyses because it contains the highest concentrations of diagenetically mobile elements. Strontium and iron concentrations, percent insoluble residue, and percent aragonite are illustrated in the profiles because they are useful indicators of diagenetic trends that will be discussed in later sections.

Cluster Analysis. Two-way cluster analysis was used to compare 132 samples, each with 11 variables. Results of the two-way cluster analysis (Fig. 7) performed on geochemical and mineralogical data indicates the presence of five geochemically-distinct rock types within Bahamian dune units. A sixth cluster represents samples from the sediment core extracted from Graham's Harbor. The diagenetic significance of these clusters and names assigned to them will be discussed in a later section.

DISCUSSION

The stratigraphic variability of trace elements in vadose-altered carbonates can be discussed as vertical or lateral stratigraphic variability within a single outcrop (intra-outcrop) and lateral variability between outcrops (inter-outcrop). Diagenetic trends and processes responsible for variability in the stratigraphic distribution of trace elements are identified and discussed.

Intra-Outcrop Variability

Vertical Trace Element Distribution. Three geochemically-distinct zones are recognized within a single vadose-altered outcrop: 1. paleosols; 2. zone of influence; and 3. diagenetically-altered host rock. Development of the three zones results from the progressive meteoric diagenesis of the exposed multicomponent carbonate sands and the geochemical interaction between the exchangeable,

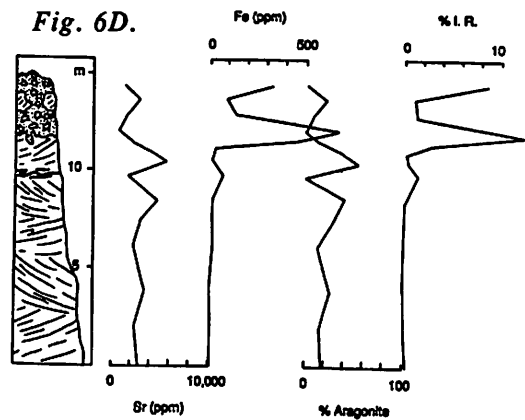
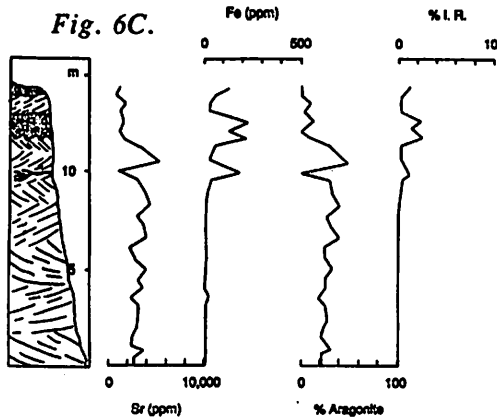
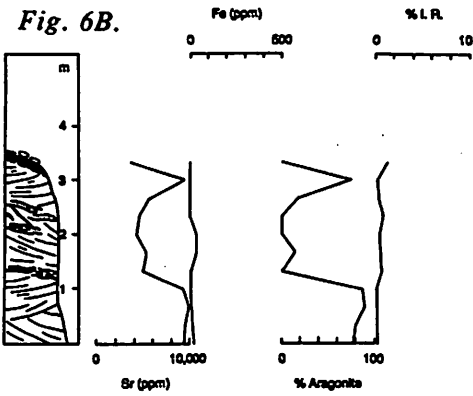
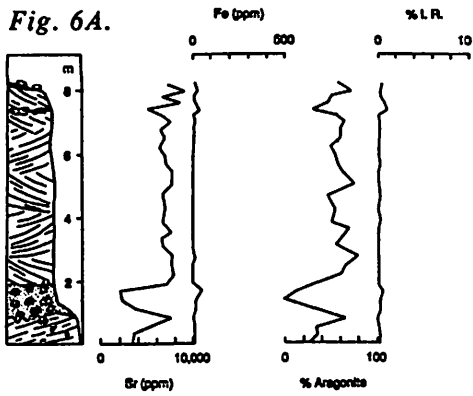
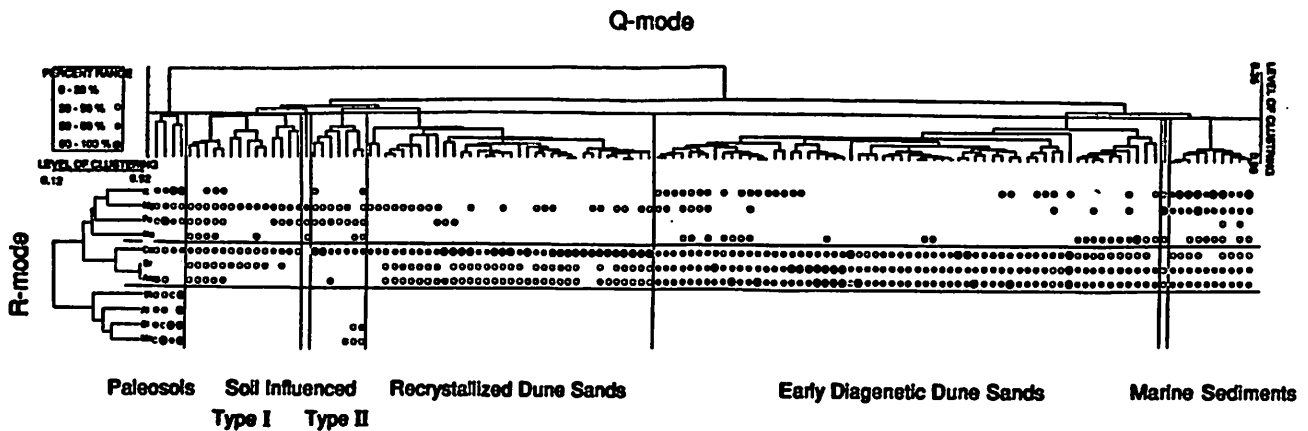


Fig. 6. Geochemical/mineralogical profiles for the carbonate fractions of Watling's Quarry transects 1 and 2 (A and B, respectively) and Morgan's Bluff transects 1 and 2 (C and D, respectively).



TWO-WAY CLUSTER ANALYSIS: VADOSE-ALTERED EOLIAN SANDS

Fig. 7. Symbols shown in the two-way cluster diagram refer to percent-range transformed data. That is, the sample with the highest value for a given variable is assigned a value of 100%. The sample with the lowest value for the same variable is assigned 0%. All remaining samples are expressed as a percentage of the maximum value. This data transformation is repeated for each variable, thus eliminating problems in comparing samples with variables having different orders of magnitudes (e.g., percent insoluble residue and ppm Sr).

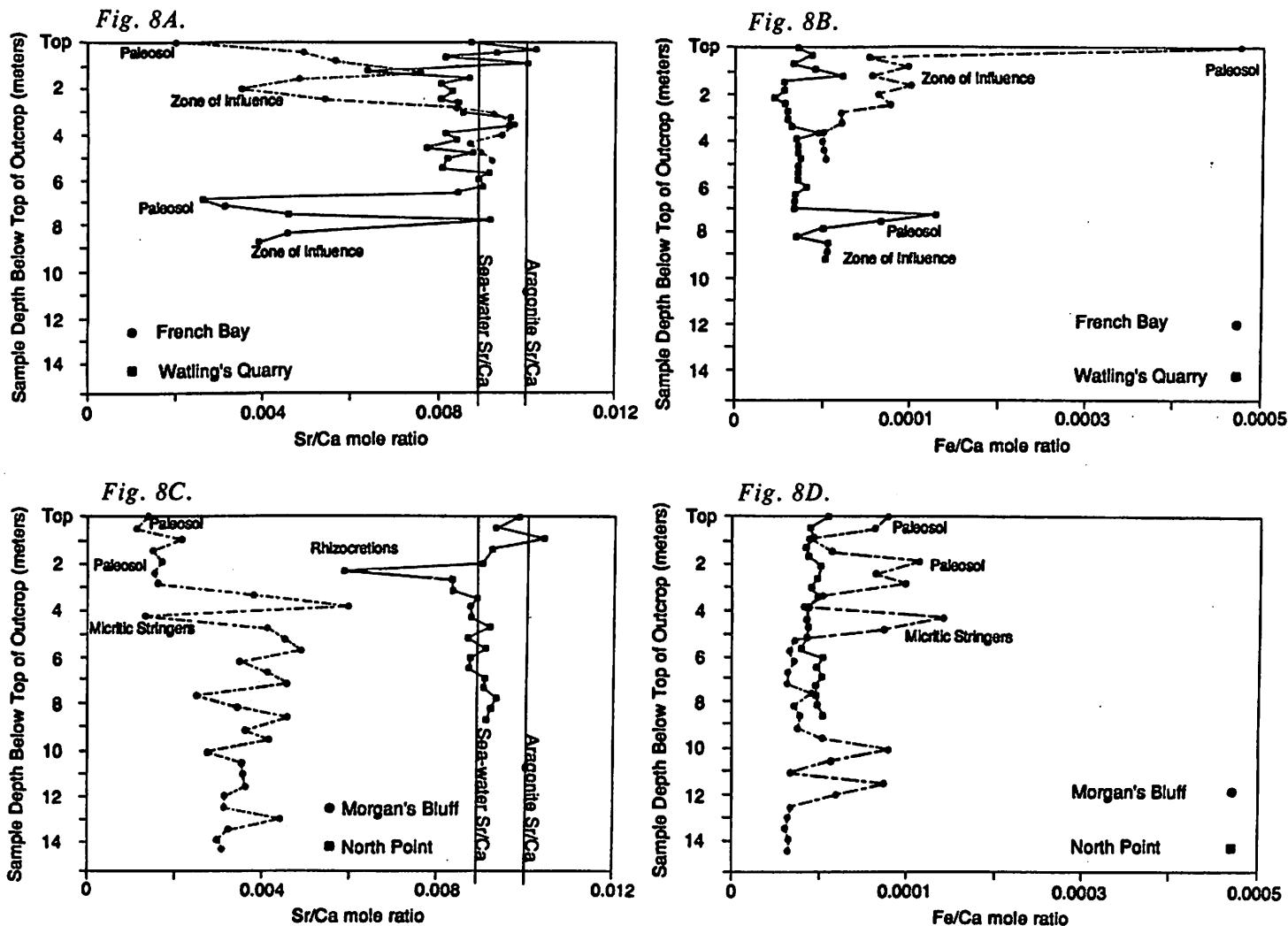


Fig. 8. Sr/Ca ratios for Watling's Quarry and French Bay (A), Fe/Ca ratios for Watling's Quarry and French Bay (B); Sr/Ca ratios for North Point and Morgan's Bluff (C); Fe/Ca ratios for North Point and Morgan's Bluff (D).

carbonate, and oxide fractions. The three diagenetic zones are recognizable from the trace element geochemistry associated with each fraction of the multicomponent system, but the carbonate fraction has the highest trace element concentrations and provides the most information about the diagenetic alterations occurring within the carbonate sands. Fig. 8 illustrates the vertical stratigraphic variability of strontium and iron in terms of Me/Ca ratios in the carbonate fraction of outcrops examined in this study.

Paleosols: Paleosols (caliche, calcrete, etc.) are deposition and diagenetic products of soil-forming processes acting on limestones exposed to meteoric waters (Braithwaite, 1983). In terms of trace element composition, the most important processes operating in the development of paleo-

sols on exposed carbonate sands are the accumulation of insoluble residues and the dissolution of metastable carbonate minerals and reprecipitation of diagenetic low-Mg calcite.

The major source for mineral insoluble residues in the Bahamas is aerosol dust carried from the Sahara Desert on trade winds (Dulin, 1984; Eaton, 1986; McCartney, 1987). Saharan dust has also been shown to be a major contributor of insoluble residues in Barbados, West Indies, and Miami, Florida (Savoie and Prospero, 1977). This dust can be identified in deep-sea sediment cores (Eaton, 1986) and in paleosols of the Bahamas (McCartney, 1987). Dulin (1984) identified oxide coatings on Saharan-derived insoluble residues as a major source for the trace elements iron and manganese in Bahamian sediments. Iron and man-

ganese, along with aluminum and silicon, have been shown to be closely associated with insoluble residues in this study, as well (Fig. 4).

Significant concentrations of aluminum and silicon in vadose-altered carbonate sands are restricted primarily to paleosols. Aluminum dominates the oxide fraction of the multicomponent system, and is present in high concentrations in paleosols. In subaerially-exposed carbonate sands, silicon is found in measurable concentrations exclusively in paleosol profiles. These findings agree with the results of Brand and Veizer (1980) and Walls and others (1975), in that both elements are associated with insoluble residues and/or paleosols. The surprising aspect of these two elements is their association with the carbonate fraction in any appreciable concentration.

Aluminum may occupy crystal sites similar to those occupied by magnesium and iron (Hem, 1978), and the aluminum ion is small enough (0.45Å) to fit in interstices in the calcite lattice. However, aluminum rarely occurs in natural water in concentrations greater than a few tenths of a ppm, and the cation Al^{3+} dominates only in solutions with a pH of less than 4.0. At pH between 4.5 and 6.5, polymerization occurs which results in units of various sizes (some small enough to qualify as ions) with structural patterns of gibbsite (Hem, 1978). It is likely, therefore, that the concentrations of aluminum associated with the carbonate fraction are present due to this polymerization process or leaching of insoluble residues, in agreement with Brand and Veizer (1980). Although aluminum is probably not directly associated with the carbonate fraction, its presence is significant because of its relationship to insoluble residues and, in the case of Bahamian carbonate sands, paleosols. A pH below 6.5 is highly unlikely in carbonate rocks. A thick soil with elevated partial pressure of CO_2 could locally create low pH values.

Silica has a low solubility at pH values below 9.0. Localized solutions with a pH above 9 could be attained in soil profiles by the combined effect of calcite precipitation and cation exchange and, under these conditions, silica could be released from clays. Once in solution, silica is present as silicic acid (H_4SiO_4) or as a colloid (Walls et al., 1975). Under some conditions, it is possible for minor concentrations of silica to be mobilized and included in the precipitating carbonate phase, possibly as fluid inclusions, in Bahamian paleosols. This process is believed to be responsible for the formation of chert nodules in

paleosols of the Slade Formation (Walls et al., 1975), and the presence of silica in Bahamian paleosols may be the first stages of chert formation.

Strontium and sodium have low concentrations in paleosols because of the A to dLMC transformation. Under the influence of meteoric waters, metastable carbonate grains (A) dissolve and release strontium, sodium, and calcium into the system. As dLMC precipitates, strontium and sodium are preferentially excluded from the calcite lattice, while iron and manganese are preferentially included (Brand and Veizer, 1980; Pingitore, 1982). Oxide coatings on insoluble residues, concentrated in paleosols, provide the source for iron and manganese, which can substitute for Ca^{++} in the precipitating calcite phase, thereby increasing the concentrations of these two metals. This dissolution and reprecipitation process leads to the progressive depletion of strontium and sodium and an increase in iron and manganese in the carbonate fraction of paleosols, as predicted by Brand and Veizer (1980). Fig. 9 shows the abrupt increase in iron concentrations associated with the carbonate fraction of the paleosol at the Gulf, San Salvador Island.

Zone of Influence: The zone of influence can be thought of as a geochemical gradation between the overlying paleosol and the underlying host rock. The main processes affecting the geochem-

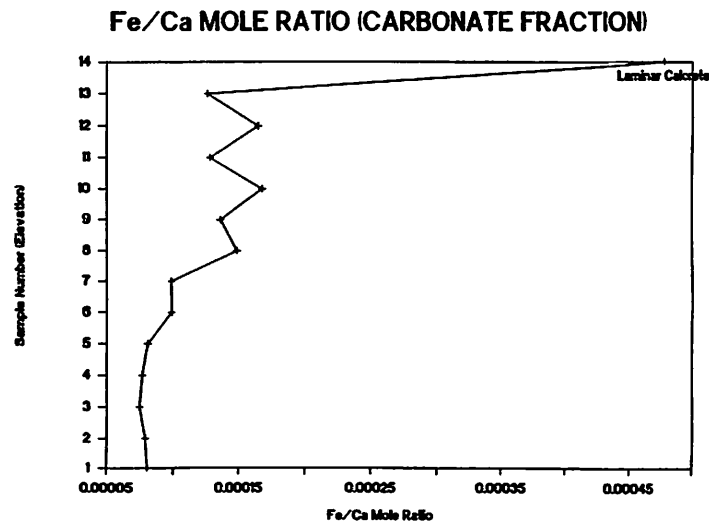


Fig. 9. Iron to calcium mole ratios in the carbonate fraction at the Gulf, San Salvador Island. Note the dramatic enrichment in iron at the laminar calcite (paleosol). The gradual rise through the middle of the section is attributed to the zone of influence.

ical signature of the zone of influence are the A to dLMC transformation and physical alterations to the host rock associated with pedogenesis. The dissolution/reprecipitation of CaCO_3 in the zone of influence operates in much the same fashion as described in the paleosols. However, the geochemical signature within the zone of influence is intermediate between paleosols and the remainder of the host rock.

Important indicators of ongoing diagenesis resulting from the A to dLMC transformation is apparent in the increased Sr/Ca ratios in the exchangeable fraction, high iron and manganese concentrations in the carbonate fraction, and low strontium concentrations in the carbonate fraction. Sr/Ca ratios associated with the exchangeable fraction in the zone of influence are elevated well above those expected for either seawater or aragonite (Fig. 10). Such high ratios can be produced only by the dissolution of A and subsequent reprecipitation of dLMC. As calcium is used in the precipitation of calcite, and strontium is preferentially excluded from the calcite lattice, the ratio of Sr/Ca in the diagenetic solution must increase unless the strontium is removed with the bulk aquifer solution. In Bahamian vadose-altered carbonates, the strontium is retained as exchangeable cations perhaps due to the evaporation of pore waters, thereby increasing the Sr/Ca ratio.

Diagenetic alterations in the zone of in-

fluence are enhanced by pedogenesis. Brecciation, the development of micritic stringers that extend downward along fractures and permeable laminae, bioturbation by land plants aid in the downward movement of meteoric waters, insoluble residues, and trace elements and insoluble residue into the host rock. As such, these features are important physical mechanisms for the redistribution of trace elements throughout a vadose-altered carbonate unit. Roots, preserved in carbonate sands as micritized rhizcretions, enhance the movement of water through the body of rock. As such, roots play a major role in the alteration of aragonite to calcite and the transfer of iron and manganese from the paleosol profile into the underlying zone of influence. While not reaching the elevated values observed in paleosols themselves, micritic calcite within the rhizcretions and in micritic stringers can be much higher in iron, manganese, and insoluble residue than the surrounding host rock (Fig. 8), attesting to their direct connection within the paleosol. In addition, grains in and near these features show varying degrees of alteration, ranging from partial to complete micritization.

Host Rock: The third geochemical zone observed in vadose-altered carbonate sands is characterized by the least diagenetic alteration of the three zones. Much of the original depositional trace element signature is preserved in younger dunes (North Point). Being removed from the effects of paleosol formation, diagenetically-altered host rocks are characterized by low concentrations of iron and manganese and low percentages of insoluble residue, while aragonite and higher strontium concentrations are typically preserved, as illustrated by two-way cluster analysis (Fig. 7).

Known to be the most soluble of the common carbonate minerals (Plummer and McKenzie, 1974; James and Choquette, 1984), high-Mg calcite is virtually non-existent in the Bahamian sand dunes of this study. X-ray diffraction of all samples reveals the presence of HMC in only two dune samples -- both taken from the subtidal portion of outcrops (one from North Point, the other from the Gulf). North Point sands have been dated (C-14) at between 6190 (near the base of the exposure) and 5670 years B.P. (near the top). The presence of HMC in the two subtidal samples and in Graham's Harbor sediments, coupled with the lack of HMC in all North Point sands strongly suggests that the dissolution of HMC is a very rapid process in the vadose en-

Sr/Ca MOLE RATIOS (EXCHANGEABLES)

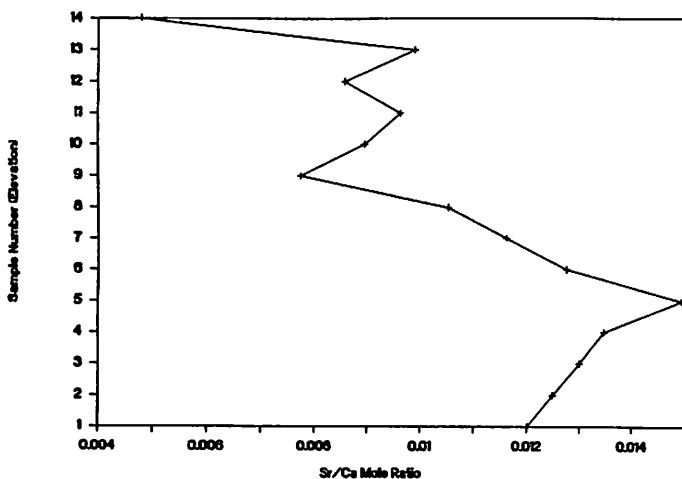


Fig. 10. Strontium to calcium ratios in the exchangeable fraction at the Gulf. Increase in the ratio above that expected for aragonite can only result from the dissolution of aragonite and reprecipitation of diagenetic low-Mg calcite, thereby increasing the Sr/Ca ratio.

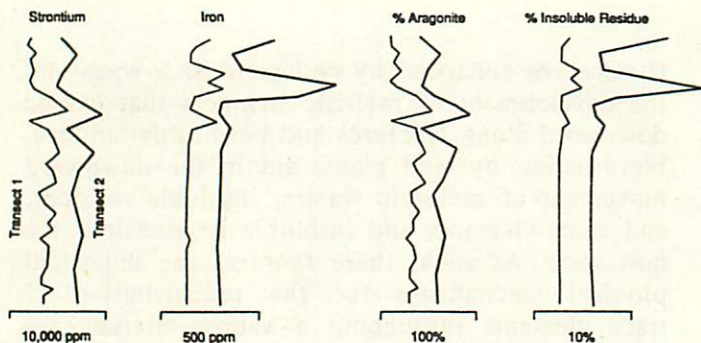


Fig. 11. Geochemical/mineralogical profiles of parallel transects sampled at Morgan's Bluff, Andros Island. Despite the erosion of the upper paleosol in places, the two profiles are remarkably similar.

vironment (near complete dissolution in less than 6000 years).

The host rocks can be altered by more than the loss of HMC. Evidence pointing to the A to dLMC transformation is not recognized in younger rocks. Minor cements in most host rocks may originate from dissolution of HMC or from an external source. Even the oldest, most altered host rocks observed in this study have considerable aragonite preserved. Host rocks at Morgan's Bluff, Andros Island underlay two paleosols and are thus believed to be about 250,000 years old, are very well cemented, and some grains show evidence of micritization and/or dissolution. However, x-ray diffraction of these samples indicates the presence of about 25% aragonite -- significantly more than is found in paleosols or zones of influence in younger rocks on San Salvador. Temporal considerations will be further discussed in a later section.

Lateral Trace Element Distribution: The presence or absence of features associated with paleosols may impart lateral trace element variability with a single outcrop. Parallel transects were sampled on two outcrops (Watling's Quarry and Morgan's Bluff) to identify the lateral variability in trace element distribution. Lateral variability is due primarily to the discontinuous nature of paleosols. Paleosols are typically not laterally continuous over a large area to begin with and, in addition, may be eroded away.

Morgan's Bluff does not display a great amount of lateral variability over the length of the outcrop. The outcrop is characterized by two paleosols across much of the outcrop, but the upper paleosol has been eroded away at some locations. In other locations, the two paleosols merge due to the development of karst collapse structures. This may allow for minor geochemical variability within the outcrop; however, geochemical profiles of the two transects are remarkably similar (Fig. 11). The similarity of the two profiles indicates that the eroded section of paleosol

played a role in the establishment of the geochemical signature, and that this signature has been preserved.

On the other hand, Watling's Quarry shows a great deal of lateral variability over a very short distance. The upper paleosol at Watling's Quarry is a laminated calcrite that extends down the flank of the dune. This calcrite is characterized by numerous micritic stringers that extend well below the surface along more permeable laminae and fractures. Samples taken near the flank of the dune are considerably different from those collected through the exposed center of the dune (Fig. 6-C,D Results), where micritic stringers are less abundant. The presence of the micritic stringers imparts a much more pronounced zone of influence along the dune flank, with higher iron, manganese, and aluminum concentrations and lower strontium and sodium concentrations than samples collected from the middle of the dune.

In short, the major controlling factor for lateral variability within a single outcrop is the presence or absence of features associated with paleosols. However, a section of paleosol missing due to erosion may not cause an increase in variability, as seen at Morgan's Bluff.

Inter-Outcrop Variability

Geographic Variability. The only variability in trace element concentrations of Bahamian carbonate sands solely attributable to geographic location occurs in the exchangeable fraction. Concentrations of exchangeable sodium and potassium are controlled by the proximity of the outcrop to salt water spray. Table 1 compares the average exchangeable concentrations from the four outcrops sampled in this study along with Graham's Harbor marine sediments.

The Gulf and North Point, San Salvador Island are both subjected to almost continual contact with salt water spray. These outcrops are located along the coast and rise directly

	Morgan's Bluff	Watling's Quarry	The Bluffs	North Point	Graham's Harbor	
Na	x	546.41	1526.12	3344.95	4093.15	2550.54
	σ	1127.92	1413.83	1432.95	2220.47	996.46
K	x	14.57	13.07	156.95	207.79	106.55
	σ	29.49	18.99	61.68	115.23	44.43
Sr	x	48.35	221.87	68.98	94.24	72.19
	σ	24.99	42.90	16.68	22.56	10.43
Ca	x	2579.00	2635.65	3064.73	2739.32	2928.87
	σ	557.22	687.74	1057.72	362.61	436.89

Table 1. Mean and standard deviation of exchangeable elements in outcrops and sediment samples. North Point and the Gulf have significantly higher concentrations of sodium and potassium than Morgan's Bluff and Watling's Quarry due to their association with a salt water spray source for the cations.

from sea-level. They also lack vegetation that might baffle the influx of aerosol salts derived from the sea spray. On the other hand, Watling's Quarry and Morgan's Bluff outcrop at higher elevations and are surrounded by vegetation. As such, these outcrops are much less subject to direct contact with salt water.

Samples collected from North Point and the Gulf contain significantly higher concentrations of sodium and potassium than samples from Watling's Quarry and Morgan's Bluff (based on student T-tests), where salt water spray is less of a factor. Fig. 12 illustrates the K/Na ratios of the four outcrops and the salt water dilution line. North Point and the Gulf contain significantly higher concentrations of these two elements and

are slightly enriched in potassium relative to the ratio expected for salt water. This potassium enrichment (sodium depletion) can be accounted for by the relative mobilities of the two cations. Sodium is more mobile than potassium in the exchangeable fraction (Fetter, 1984) and the selective removal of sodium causes enrichment of potassium in the exchangeable.

Watling's Quarry and Morgan's Bluff, on the other hand, are depleted in potassium relative to sodium (Fig. 12). This indicates that the source for these elements in the exchangeable fraction may be something other than sea water. Naturally-occurring carbonates have considerably higher concentrations of sodium than potassium (Fig. 3-B). This leads to the interpretation that the source for sodium and potassium at outcrops not influenced by direct contact with salt water is most likely the dissolution of calcium carbonate.

Statistical Variability. Multivariate statistical analyses, performed on the carbonate fraction of all samples in this study, were used to describe the variability in geochemistry between outcrops of different ages and geographic locations. Cluster analysis identifies five geochemically-distinct clusters, or groups, of diagenetically-altered rocks in the Bahamian dunes studied. A sixth cluster, unaltered marine sediments from Graham's Harbor, was shown to be statistically different from any of the vadose-altered rocks. The two-way cluster diagram illustrated in Fig. 7 depicts the variables (R-mode) that are responsible for clusters of geochemically-different samples (Q-mode; see Results). Table 2 presents averages and standard deviations of values for each variable in the groups identified by cluster analysis. Student T-tests performed on this data indicate that the clusters are indeed statistically significantly different from one another. Table 3 is a dissimilarity matrix showing the percentage of variables that are significantly different between two clusters.

Examination of the rock types present in each of the clusters and the variables responsible for the clusters leads to the interpretation that the six clusters represent varying degrees of progressive meteoric diagenesis related to paleosol formation. Clusters are defined in terms of increasing diagenetic alteration (towards equilibrium with meteoric waters) as follows:

Marine Sediments: All samples in this cluster were taken from the sediment core in Graham's Harbor. These samples have never been subjected

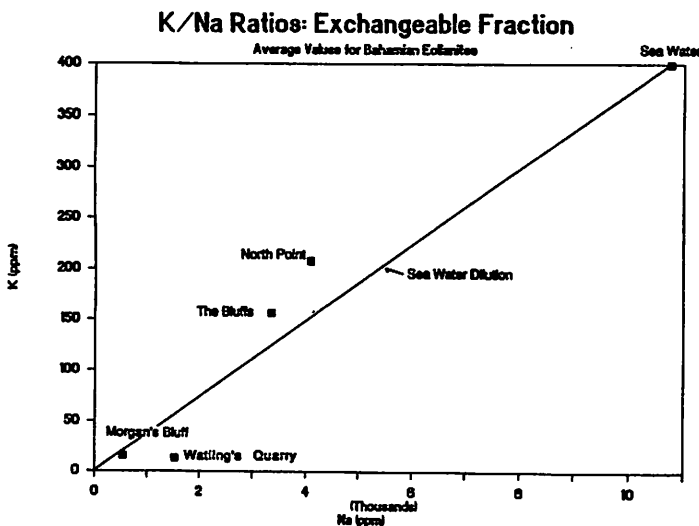


Fig. 12. Potassium to sodium ratios in the exchangeable fraction of Bahamian carbonate dunes.

	% IR	% Aragonite	[Mg]	[Ca]	[Sr]	[Ba]	[Fe]	[Mn]	[Al]	[K]	[Na]
Paleosols	4.4	10.3	6737.6	376038.4	1228.1	392.0	630.2	148.0	45.6	66.6	2788.6
	6.2	6.2	2305.9	12213.7	626.6	131.2	172.4	68.0	29.7	19.2	2306.6
Soil Influenced Type II	1.6	6.4	4093.3	363345.6	1499.0	69.9	151.5	63.0	2.6	14.0	4486.6
	0.4	6.6	717.6	7460.1	406.5	50.3	66.2	13.6	3.6	4.1	3321.6
Soil Influenced Type I	0.6	14.6	6804.2	363550.0	2625.6	3.0	39.4	65.6	0.2	6.3	6323.2
	0.1	14.6	1631.3	6161.3	1311.3	7.6	34.6	19.0	0.3	10.6	2530.6
Recrystallized Dune Sands	0.6	27.1	3626.3	366709.6	3140.4	0.0	13.4	40.6	0.2	4.4	1488.6
	0.1	7.6	686.0	7666.3	616.6	0.1	19.3	15.1	0.6	5.6	675.6
Early Diagenetic Dune Sands	0.6	62.6	2554.7	373117.2	7326.3	2.5	6.5	35.3	0.0	14.6	7571.2
	0.2	11.0	1083.1	13243.2	676.1	4.6	7.6	6.6	0.1	11.6	6667.0
Marine Sediments	0.6	67.4	6566.6	354056.2	6462.3	42.6	62.4	46.3	2.1	66.5	7266.2
	0.1	11.3	617.6	6636.4	266.7	6.7	24.3	16.2	1.3	6.6	766.4

Table 2. Mean and standard deviation of geochemical/mineralogical variables for clusters delineated by cluster analysis.

to meteoric waters and represent a baseline or point of reference against which diagenetic alterations in the subaerially-exposed carbonates can be measured.

Early Diagenetic Dune Sand: These samples are located within the "diagenetically-altered host rock zone" within the outcrops sampled. Samples belonging to this cluster are characterized by lower magnesium and potassium concentrations than are found in marine sediments. These rocks have been subjected to relatively little diagenesis as shown by the presence of high strontium concentrations and percent aragonite.

Recrystallized Dune Sands: Recrystallized dune sands are characterized by the continued depletion of strontium and the decrease of aragonite preserved in the rock. Sodium is also present in very low concentrations. As such, this cluster represents the next step in the progressive diagenesis of the vadose-altered carbonate sands.

Soil Influenced Type I: This cluster consists of rocks that have been subjected to some degree of pedogenesis. They are altered from the early diagenetic dune sands by soil-forming processes including brecciation and intense bioturbation by land plants. Rocks belonging to this cluster display a further decrease in strontium and aragonite and the incorporation of iron in most samples.

Soil Influenced Type II: Rocks altered by soil-forming processes acting on recrystallized dune sands belong to this cluster. These rocks are characterized by the near total depletion of strontium and aragonite and the incorporation of significant amounts of iron in all samples. Silicon and manganese may also be present in significantly higher concentrations.

Paleosols: This cluster consists of rocks owing their origin to soil-forming processes and meteoric waters. Paleosols are characterized by very low strontium, sodium, and percent aragonite, with significant enrichment in iron, manganese, aluminum, silicon, and percent insoluble residue.

Polar ordination analysis was used to illustrate gradational relationships between the samples in the data set (Fig. 13). This analysis aids in the recognition of the environmental factors responsible for the geochemical variation.

In ordination, samples are plotted along axes whose endpoints represent samples exhibiting maximum statistical dissimilarity (Springer and Bambach, 1985; Pelle, 1989). The spatial arrangement of each sample along the axes de-

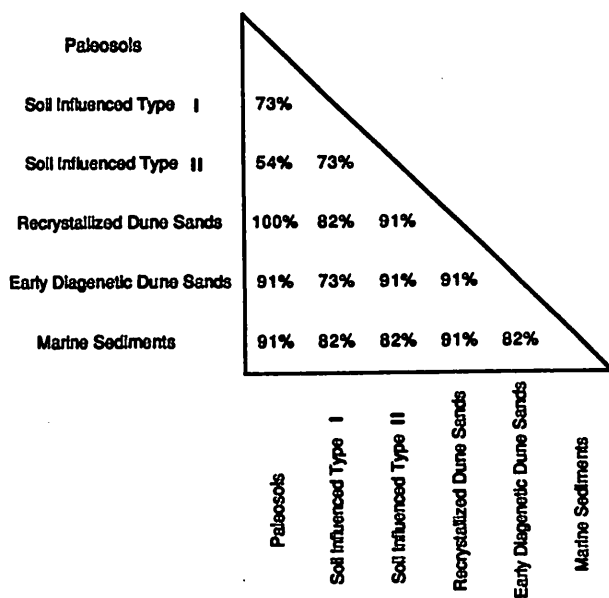


Table 3. Dissimilarity matrix calculated from the results of Student T-tests performed on variables between clusters. Values in matrix are the percentage of variables that are significantly different (at 95% confidence interval) between two groups (i.e., 91% of the variables are significantly different between paleosols and marine sediments).

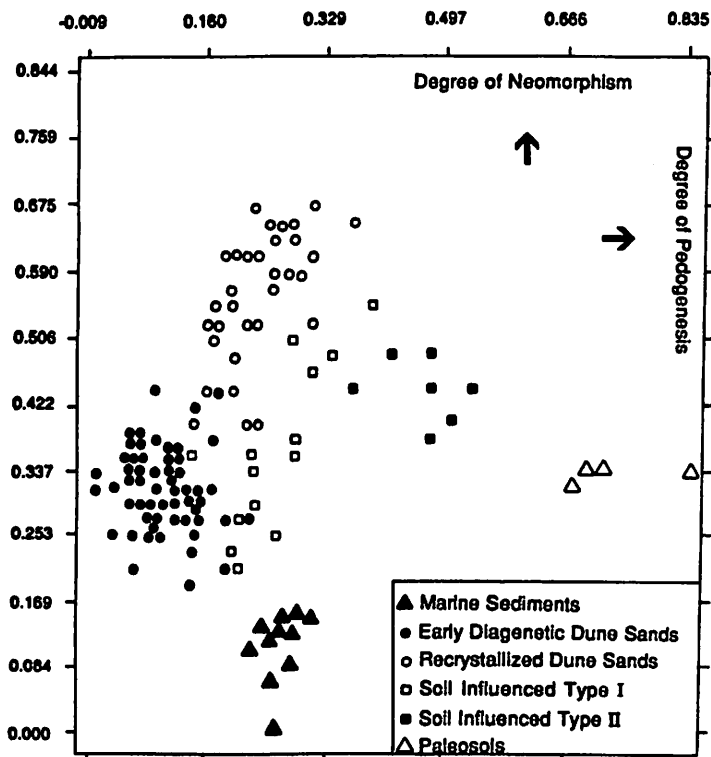


Fig. 13. Polar ordination illustrates gradational relationships (between samples) caused by diagenesis.

depends on the relationships to the endpoints of the axes. That is, the closer a given sample lies to an endpoint, the more similar it is to that endpoint. This allows for the recognition of trends among the samples that can be explained in terms of processes acting on the samples. To aid in the identification of processes responsible for sample locations along the axes, it is useful to examine the nature of the endpoints.

Axis One: Cophenetic Correlation
Coefficient = 0.6883

Endpoint 1: WQ-18 (Watling's Quarry). This sample is a very poorly cemented, friable grainstone. Grains consist of well-rounded peloids and/or ooids, with very few recognizable skeletal grains; there is less than 0.6% insoluble residue. X-ray diffraction reveals the presence of 73% aragonite. Geochemically, it contains high concentrations of strontium (7672ppm) and low manganese (28ppm) and iron (below detection limits).

Endpoint 2: MBL-11 (Morgan's Bluff). This sample is a red, well-indurated brecciated matrix paleosol characterized by a red matrix and partial to complete micritization of grains and intraclasts. Insoluble residue accounts for over 12% of the rock's mass. X-ray diffraction indicates an absence of aragonite. Geochemically, the sample is characterized by very low strontium (763ppm) and

high concentrations of iron (664ppm), manganese (106ppm), silicon (508ppm), and aluminum (75ppm).

Axis One is interpreted as resulting from diagenetic changes associated with soil-forming processes. Samples along this axis grade from being unaffected by pedogenesis to being the product of pedogenetic processes.

Axis Two: Total Cophenetic Correlation
Coefficient (for two axes) = .8601

Endpoint 1: GH-5 (Graham's Harbor).

Graham's Harbor sediments have not been subjected to meteoric diagenesis. The sample is composed of 69% aragonite and 31% HMC. Geochemically, the sediment has high concentrations of strontium (6408ppm), sodium (7582ppm), and potassium (70ppm), and low concentrations of iron (60ppm) and aluminum (<1ppm).

Endpoint 2: MB-15 (Morgan's Bluff). This sample is a very well-cemented oolitic grainstone. Grains show evidence of dissolution and are chalky in appearance. Aragonite has been reduced to 25% of the rock by progressive neomorphism. Geochemically, the sample contains low concentrations of strontium (2094ppm), sodium (779ppm), and potassium (below detection limits). Low concentrations of iron (16ppm), manganese (43ppm), and aluminum (below detection limits) attest to the disassociation of this sample with

soil-forming processes.

Axis Two can be interpreted as resulting from the progressive alteration of sediments exposed to vadose diagenesis. Samples along this axis display a gradation from unaltered marine sediments to highly neomorphosed, well-cemented rocks that have not been influenced by paleosol formation.

Taken as a whole, these samples represent a geochemical continuum in the progressive diagenetic alteration of subaerially-exposed carbonate rocks. The progressive alteration observed in dune sands of widely-different ages and geographic locations is remarkably similar to the theoretical trends envisioned by Brand and Veizer (1980) (Fig. 14).

With increasing diagenetic equilibration with meteoric waters, there is a progressive decrease

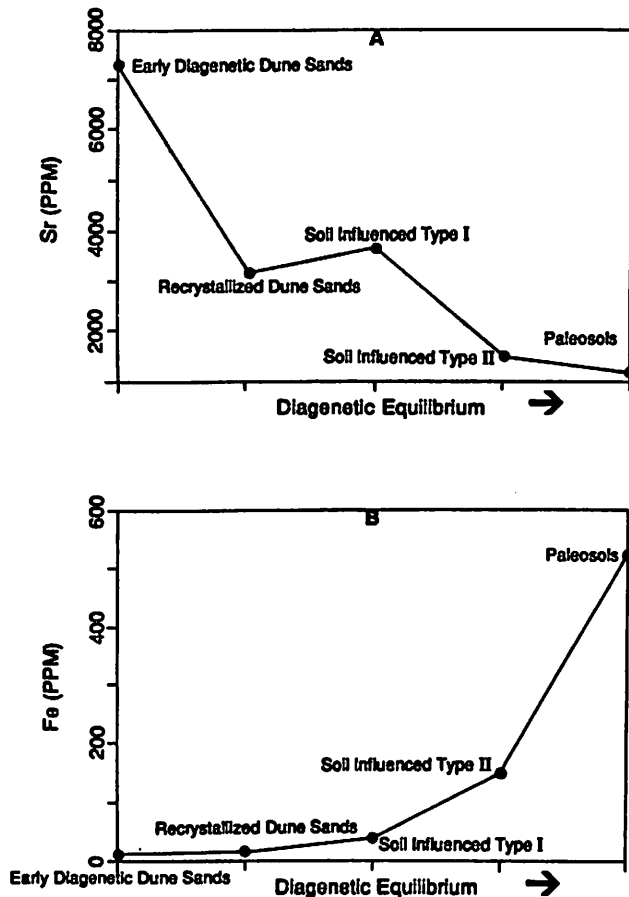


Fig. 14. Loss of Sr as vadose diagenesis progresses toward equilibrium with meteoric waters (A); increase in Fe as vadose diagenesis progresses toward equilibrium with meteoric waters (B). Values reported are average concentrations for each of the diagenetic groups delineated by cluster analysis.

in strontium and sodium and a concomitant increase in iron and manganese. Aluminum and silicon are observed primarily in association with insoluble residues, and therefore show an increase in concentration with alterations due to soil-forming processes. Magnesium does not exhibit a clear pattern of either increase or decrease, and this is believed to result from varying amounts of magnesium in the original mineralogy (Brand and Veizer, 1980).

Temporal Considerations

The progressive diagenesis toward equilibrium with meteoric waters in vadose-altered rocks should not be confused with time. Although time is an important factor in diagenetic alterations, other factors are more important and tend to override the effects of time (Fig. 15). The lack of a definite pattern such as the one present in Fig. 14 demonstrates the lack of control of age alone on the formation of the various diagenetic groups.

Early diagenetic dune sands and paleosols are shown to vary widely in age, yet samples within each group are geochemically similar -- regardless of age. The geochemical similarity of paleosols of differing ages is easily explained by the constant nature of pedogenic processes and products through time. In addition, paleosols may be thought of as an end member product of meteoric diagenesis. However, the similarity between the diagenetically-altered host rocks of widely different ages is less easily explained if trends predicted by Brand and Veizer (1980) are primarily time controlled. Examination of geochemical and lithologic characteristics of the outcrops indicates that the primary controls for progressive diagenesis in exposed dune sands are the timing of paleosol development on the exposed sands and the type of paleosol formed.

Samples classified as early diagenetic dune sands range in age from less than 6500 years at North Point (Boardman et al., 1987) to about 125,000 years at Watling's Quarry (Carew and Mylroie, 1984). The geochemical similarity between Watling's Quarry and North Point would be surprising if time were the major consideration. Watling's Quarry would be expected to show a higher degree of vadose alterations including lower strontium concentrations, reduced percentages of aragonite, and increased cementation.

The geochemical similarity between these two outcrops can be explained by the formation

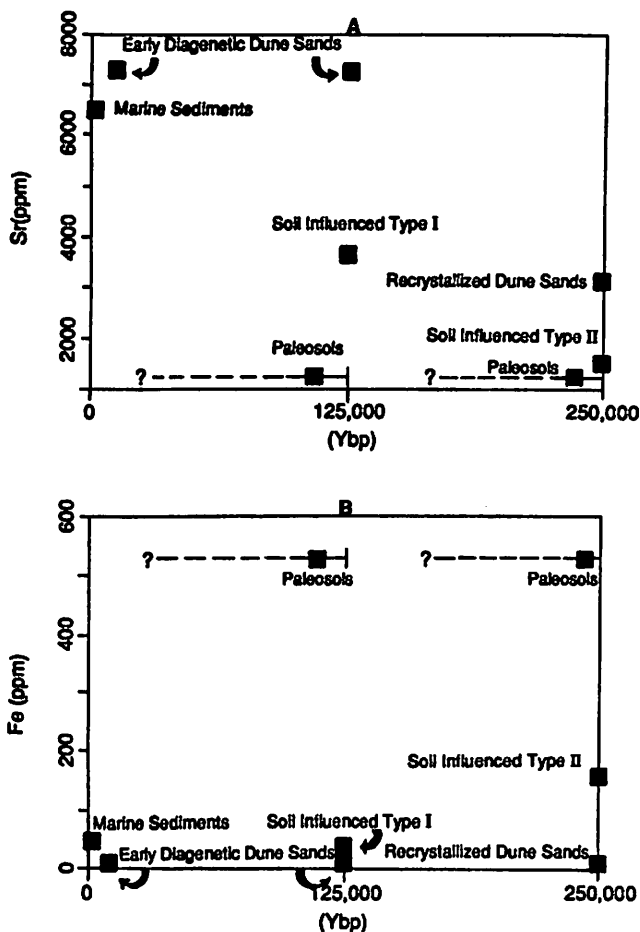


Fig. 15. Sr concentrations of vadose-altered carbonates as related to age (A); Fe concentrations as related to age (B). Values reported are average concentrations for each of the diagenetic groups delineated by cluster analysis.

of the impermeable laminar calcrete cap on Watling's Quarry soon after sand deposition ceased. Such a cap is an effective barrier to the downward movement of meteoric waters, producing a geochemically "closed" dune system. Systems such as this are characterized by low water-rock ratios in which the water, because of its constant interaction with solids, loses its chemical identity and its composition is controlled (buffered) by the rock itself (Veizer, 1983). This closed diagenetic system has effectively preserved the original geochemistry of the rocks at Watling's Quarry.

On the other hand, dune sands that have a permeable, brecciated matrix type paleosol or no paleosol associated with them at all are much more susceptible to meteoric diagenesis. Fresh water is able to move through the permeable soil (if present) and into the rock body. This type of dune system is characterized by high water-rock

ratios, in which the dissolving CaCO_3 does not effectively alter the bulk water chemistry (Veizer, 1983). Morgan's Bluff and the Gulf are examples of outcrops characterized by a diagenetically "open" system. These outcrops show much more diagenetic alterations to the dune sands -- particularly the strong development of zones of influence beneath the paleosols.

SUMMARY AND CONCLUSIONS

The study of trace and minor element concentrations in vadose-altered eolian sands of San Salvador Island and Andros Island, Bahamas, has provided information on trace element associations, stratigraphic variability, and mechanisms for redistribution in carbonate sequences.

Carbonate rocks and sediments are defined as multicomponent systems with trace elements associated with several different fractions in addition to CaCO_3 . The use of a sequential extraction procedure allows for the chemical separation of trace elements into fractions that are useful in identifying trace element sources and trends. This has led to several conclusions about elemental associations in vadose-altered carbonate sands.

Elements associated with the exchangeable fraction include potassium, sodium, calcium, and strontium. Concentrations of K and Na are highly variable and are dependent primarily on geographic location (proximity to the coast). Sr/Ca ratios in the exchangeable fraction are shown to be useful indicators of on-going diagenesis. Sr/Ca ratios elevated above ratios expected in sea-water and aragonite are caused by dissolution of aragonite and subsequent precipitation of diagenetic low-Mg calcite with preferential exclusion of Sr from the precipitating phase.

Elements associated with the CaCO_3 fraction behave in a predictable manner as diagenetic equilibrium with meteoric waters is approached. Na and Sr show a systematic decrease; Fe, Mn, and Al display a concomitant increase in concentration with progressive equilibrium. Sources for trace elements in the carbonate fraction include sea-water, the original carbonate phase, and mineral insoluble residues concentrated in paleosol profiles.

Metals associated with the Fe-Mn oxide fraction include Fe, Mn, and Al. These metals are present in appreciable quantities only in and near (within the zone of influence) paleosol horizons. The abundance of these metals in paleo-

sol horizons and the strong positive correlation with the percentage of insoluble residue suggests that the Fe, Mn, and Al in the carbonate fraction is derived from oxide coatings of insoluble residue within the paleosols.

Organic matter is of minor importance in the distribution of trace elements in vadose-altered carbonate sands. Most organic matter in this environment is readily oxidized, releasing trace elements to the exchangeable fraction or to be carried away in the bulk aquifer solution.

Variability in trace element distribution is best described in terms of vertical and lateral variability within a single outcrop (intra-outcrop) and lateral variability among outcrops of different age and/or geographic location (inter-outcrop).

Three geochemically-distinct zones, related to the presence of a paleosol, may be recognizable within a single vadose-altered outcrop: 1. metal-rich, Sr-depleted paleosols; 2. zone of influence associated with paleosols; and 3. early diagenetically-altered zone that retains much of the original elemental signature. Lateral variability within a single outcrop may be accounted for by the discontinuous nature of paleosols accounts for increase variability at and near exposure surfaces.

Development of the zone of influence and the redistribution of trace elements into the vadose-altered carbonate sands is dependent on several physical mechanisms: 1. simple downward percolation of meteoric waters through metal-rich soil/paleosol horizons; 2. bioturbation, particularly by roots of land plants; and 3. fracturing of the host rock.

Multivariate statistical analyses (cluster analysis and polar ordination) identify five geochemically-distinct groups of rocks present within vadose-altered dunes of differing ages and degree of diagenesis in the Bahamas: 1. paleosols; 2. soil influenced Type I; 3. soil influenced Type II; 4. recrystallized dune sands; and 5. early diagenetic dune sands. A sixth group, marine sediments, is also shown to be geochemically distinct from the vadose-altered sands.

While trace elements associated with the carbonate fraction behave in a predictable manner as diagenetic equilibrium with meteoric waters is approached, it should be clear that diagenetic equilibrium does not necessarily imply increasing age. Although age is certainly a factor in carbonate diagenesis, the timing and type of paleosol that develops on exposed carbonate rock has a direct bearing on the effectiveness of elemental

redistribution through a section.

Early-formed, impermeable laminated calcrites can be an effective seal against the movement of meteoric waters through a carbonate unit, producing a geochemically "closed" system. Permeable, brecciated-matrix soils and/or later-formed soils do not effectively "close" a carbonate section, allowing for the progressive neomorphism of metastable carbonate minerals to diagenetic low-Mg calcite with the accompanying trace element signature. This allows older rocks with impermeable paleosol caps to be preserved with little geochemical alteration (presumably with intact primary porosity), relative to rocks of the same age within the impermeable cap.

The associations, trends, and relationships of trace elements recognized in this study should prove valuable to the interpretation of ancient vadose-altered carbonate sands.

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