PROCEEDINGS

OF THE FOURTH SYMPOSIUM

ON THE GEOLOGY OF THE BAHAMAS

Editor

John E. Mylroie

Production Editor

Donald T. Gerace

Sponsored by the Bahamian Field Station

June 17 - 22, 1988

ISBN 0-935909-31-1

Printed by Don Heuer in the U.S.A.

CONTROLS ON THE RATE AND DISTRIBUTION OF CARBONATE BEDROCK DISSOLUTION IN THE BAHAMAS

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ABSTRACT

Three 'water-controlled' reactions are of importance for bedrock dissolution in the Bahamas: generation of carbonic acid in the soil, *in situ* oxidation of organic matter and mixing of water of different composition. All share certain common controls, which depend primarily on climate, and specifically on the balance between actual evapotranspiration and rainfall which directly controls groundwater flux. However this balance is also critically dependent on relief, because at high sea-levels the saturated zone is not decoupled from the effects of evaporation. Under arid conditions caliche crusts may develop, further reducing net groundwater recharge, but also causing it's concentration at breaks in the crust. Where mineral soils are not present a similar increase in concentrated recharge with time may result from the strong positive feedbacks between micro-topography, organic soil accumulation and soil CO_2, involved in the formation of solution pockets (banana holes) and shafts. In the saturated zone mixing at the water table and transition zone generates further dissolution, which is enhanced by oxidation of organic matter introduced in fissures. Major fracture systems and pre-existing cavernous horizons exert a strong control on the thickness of the fresh water lens and the degree of mixing at the transition zone. There is thus a change with time in the distribution of dissolution from a shallow, relatively homogeneous distribution to the deeper, heterogeneous pattern characteristic of karst terrains.

INTRODUCTION

Given the importance of the Bahamas as a natural laboratory for the study of carbonate sedimentation and diagenesis, it is surprising that relatively little work has been undertaken on the distribution and magnitude of bedrock dissolution. Such studies are needed both to understand the evolution of landforms in the area, and to provide models of the extent and distribution of secondary porosity within the platform (Craig 1988).

In this paper we present a brief review of some of the factors controlling bedrock dissolution based on results of field work on Andros Island and San Salvador. Emphasis is placed on '<u>water-controlled</u>' dissolution reactions (James and Choquette 1984), which in the Bahamas include dissolution by carbonic acid derived from the soil atmosphere, dissolution due to mixing of waters of differing chemical composition, and dissolution due to *in situ* microbial oxidation of organic matter. Only brief attention is focused on '<u>mineral-controlled</u>' reactions which are important in recent carbonate sediments, and involve the conversion of metastable high-magnesium calcite and aragonite to low-magnesium calcite (Walter 1985). Although this process gives rise to a change in the size distribution of porosity, creating larger vuggy pores with a heterogeneous distribution in the unsaturated zone (Harrison 1975), recent studies on Schooner Cays in the Bahamas (Budd 1988) suggest that it is a conservative process, with little loss of carbonate (overall efficiency c. 90%).

For both stable and unstable carbonate minerals the rate of bedrock dissolution is predominantly controlled by two sets of factors: 1. those controlling the inorganic and organic processes generating undersaturation with respect to calcite - <u>the chemical potential</u> - and 2. those controlling the supply and removal of reactants and products - <u>the groundwater flow regime</u>. Information on the former may be readily obtained by sampling and analysis of surface and groundwaters, but it is much more difficult to convert these concentrations to rates of dissolution because of the difficulties of measuring groundwater flux.

1. CLIMATE - PRECIPITATION

At present the major climatic gradient in the Bahamas is between the wetter, cooler northwestern islands and the drier, warmer southeastern islands. The contrast in temperatures (mean annual temperature 24-27^{o}C) is however much smaller than that in rainfall (mean annual rainfall 1550-690mm). It is therefore the latter which is most important in controlling both spatial differences in present bedrock dissolution, and it's temporal variation with paleoclimate. The balance between annual rainfall and annual actual evaporation (currently about 1150mm), has an important control on soil type and on the magnitude and form of the freshwater lens. These both affect dissolution and are discussed further below. However, effective precipitation is the major direct control on the rate of carbonate dissolution because of it's effect on the net groundwater flux. This is demonstrated by the strong positive relationship between net denudation rates and the mean annual runoff for karst areas, as shown in Fig. 1 (derived from the literature by Smith and Atkinson 1976). This predominant effect is also clear from the theoretical model developed by White (1984).

Supporting data for the Bahamas are not available, but Pierson and Shinn (1985) report preservation of high-magnesium, calcite and aragonite cements in sediments greater than 300 ka in age at Hogsty Reef in the dryer southern Bahamas. At the much wetter Joulters Cay, to the north of Andros Island, more rapid leaching occurs and stabilization would be complete within 10 to 20ka (Halley and Harris 1979). Note however that the latter sediments have not been exposed to freshwater and Budd (1988) reports rates of stabilization between two and three times lower in the saline transition zone than in fresh water. Furthermore, mixed mineralogy sediments such as these transform more slowly than wholly aragonitic sediments (Halley and Harris 1979).

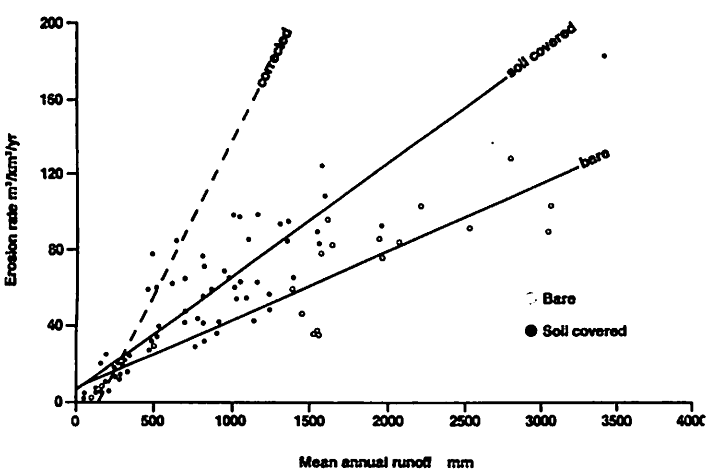

Fig. 1. Denudation rates for soil covered and bare limestone terrains (Smith and Atkinson 1976). Note the change to the observed relationship if solution rate is corrected for the presence of non-carbonate rocks in the catchment, the relationship which would apply in the Bahamas.

2. ORGANIC SOILS - DEPTH AND DISTRIBUTION

The presence of a soil cover has a significant effect upon the rate of denudation, this being higher for soil covered than for bare terrain (Fig. 1). True mineral soils are rare in the Bahamas at present except in areas improved for agriculture. Most soils comprise a thin litter layer underlain by an Ah horizon of decomposing humus, often with many roots. This may continue down into a rubbly C hoizon with corroded limestone blocks, or have a sharp basal transition to the limestone. Soil depth is very variable with the thicker soils accumulating in lows on the bedrock surface, such as topographic basins, pockets and joints. In the case of the larger basins, laterally continuous soils may develop, and often a discontinuous red clay-loam mineral horizon is observed above the bedrock surface.

Carbonic acid, formed by dissolution of carbon dioxide generated by microorganisms and root respiration in the soil, provides the major chemical potential driving dissolution in most karst areas. The PCO_2 of soil gas is controlled both by the rate of CO_2 production (discussed below), and the rate of removal by diffusion to the soil surface. Soil PCO_2 therefore increases with depth and with the bulk density of the soil matrix. This is shown for organic soils from North Andros Island in Fig. 2. The humified organic soils have higher CO_2 concentrations than those comprising only highly porous undecomposed litter, but for both types PCO_2 increases with depth.

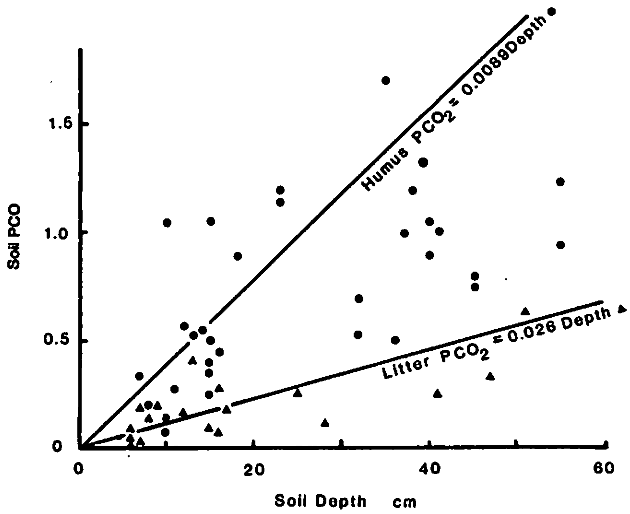

Fig. 2. Relationship between soil depth and PCO_2 measured during the wet season (July) on North Andros using a Miotke soil CO_2 probe with Gastec gas analysis tubes. Quoted regression lines are constrained to pass through the origin, and give R^2 values of 0.84 (humus) and 0.76 (litter).

In the Bahamas decomposition of organic matter by soil microorganisms is limited not by temperature but by soil moisture. During dry periods the litter layer and thinner organic soils become desiccated, and only the deeper soils retain sufficient moisture for decomposition to continue. An elevated PCO_2 is therefore maintained for longer in deeper sites. Furthermore, erosion of the desiccated soils by rainsplash and runoff along the bedrock surface occurs, emphasizing the contrast in soil thickness between 'accumulating' and 'shedding' sites. Observations on North Andros indicate that much of the thin organic mat is lost from the bedrock surface after fires, and only that in deeper moister pockets survives. These sites also accumulate ash and mineral particles washed down from the bare bedrock, providing a possible source for the mineral material observed at the base of these profiles.

Thus the direct effect of soil depth on PCO_2, the persistance of decomposition at deeper, moister sites, the tendency for organic material to erode from micro-topographic highs and accumulate in lows, and for vegetation to preferentially colonize these accumulating sites, gives a series of positive feedback mechanisms, developing and amplifying topographic lows in the bedrock surface (Fig. 3A). This gives rise to the development of 'banana holes' (Fig. 3B), soil filled pockets. These are initially small with a diameter of 0.2-1.0m and depth of 0.2-0.5m, but with continuing bedrock dissolution, increase in size to 1.0-2.0m diameter and 0.5-2.0 m depth. With development, capture of adjacent shallower pockets may occur, increasing the catchment of the main pockets where soil becomes concentrated. Penetration of tree roots into cracks and fissures at the base of the pocket encourages dissolution

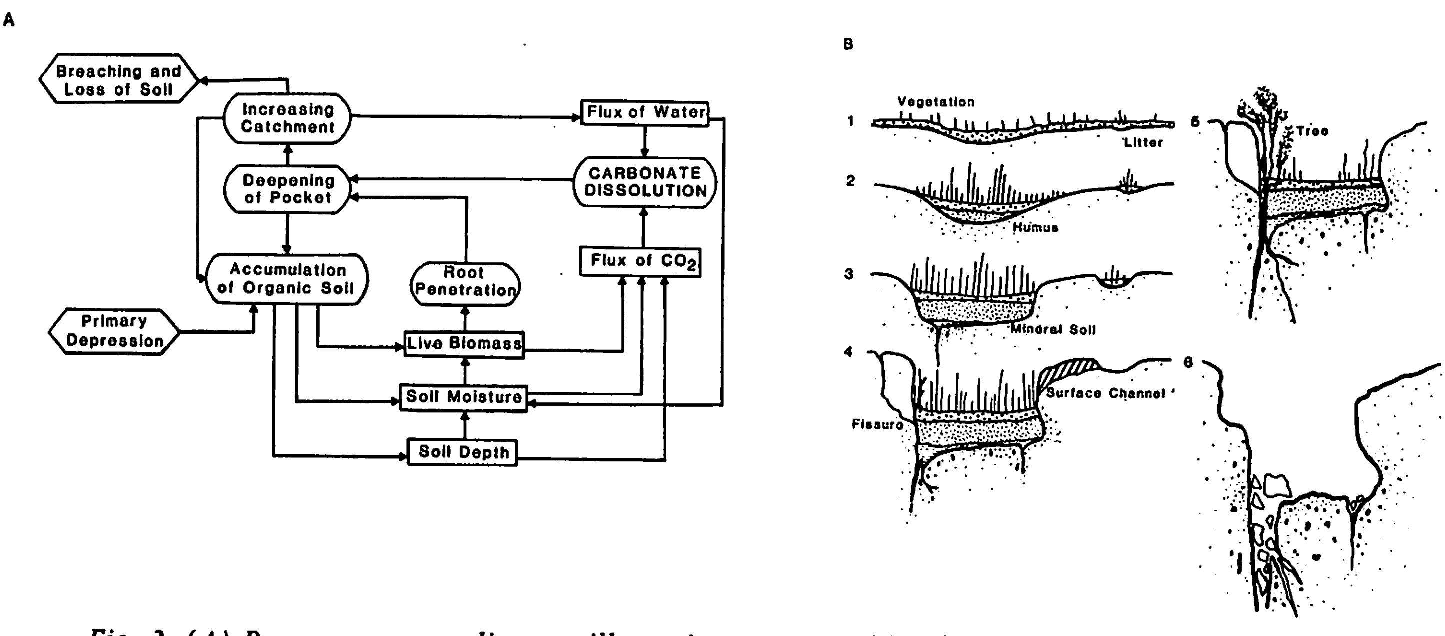

Fig. 3. (A) Process response diagram illustrating strong positive feedback mechanisms in the development of solutional pockets (banana holes). (B) Schematic diagram showing evolution of a solution pocket (banana hole). Density of stipple is proportional to vuggy and mouldic secondary porosity in the limestone. Note the important role of penetration of tree roots towards the water table in draining the pocket, eventually leading to breaching and soil loss.

of a drain, which discharges aggressive soil water from the pocket. This concentrated input rapidly dissolves fissures in the unsaturated zone, so that soil will eventually be lost downwards, and the development of the pocket by sub-soil dissolution will cease.

3. MINERAL SOILS - EVIDENCE FROM PALEOSOLS

There is considerable evidence that mineral soils derived from the accumulation of atmospheric dust (Glaccum and Prospero 1980) were widespread in the Bahamas in the past (Foos 1987, McCartney and Boardman 1987, Carew and Mylroie 1989). Although the preservation of these soils is often poor, they may be up to 1m deep, and unlike present organic soils were laterally continuous, as demonstrated by the paleosol at Crab Cay, San Salvador (Brown 1984). The paleosols are predominantly of the terra rossa type, indicating leaching of silica and accumulation of iron and aluminum rich residues. A second type of paleosol has also been reported from Singer Bar Point, San Salvador (Foos 1987, McCartney and Boardman 1987). In this the presence of the mineral boehmite is indicative of even more intense leaching under a more humid climate, giving the development of a latosol.

The high bulk density of these soils would give a much higher soil PCO_2 than the present organic soils; the relation of Brook et al (1983) predicting a mean growing season soil PCO_2 of 1.78 % compared to the mean of 0.74±0.37 % for the soils sampled on North Andros. Thus the combination of more intense leaching, high soil PCO_2 and a continuous soil cover would be expected to generate both more uniform and more intense sub-soil dissolution than occurs at present.

Preservation of the sub-humid terra rossa soils is often due to subsequent cementation by caliche (Foos 1987), indicating a change in the soil-water balance to much drier semi-arid or arid conditions, with evapotranspiration exceeding rainfall. Accumulation of pedogenic calcium carbonate results in sealing of the bedrock surface by development of laminated micrite crusts. Thus, even during periods with a positive water balance, recharge is restricted and the groundwater flow is substantially reduced (Brown 1984). In the Yucatan Ward (1973) reported preservation of high-magnesium calcite in Pleistocene aeolinantes 25-30ka old, which are overlain by a caliche crust. In contrast, on Holocene deposits where a crust is absent, stabilization will occur in 20ka.

Development of a protective caliche crust under arid conditions will thus have a marked effect on bedrock dissolution rates, augmenting the direct reduction due to a decreased groundwater flux.

4. HYDROLOGICAL ROUTING IN THE UNSATURATED ZONE

The primary intergranular permeability of the relatively coarse grained aeolianites found on many Bahamian islands is very high, although in finer grained deposits it is much lower (Enos and Sawatsky 1981). Thus on initial exposure, recharge is via diffuse routes with the development of vuggy and mouldic dissolutional porosity, which may be locally concentrated (Harrison 1975). Under these conditions bedrock dissolution will be limited to a shallow irregular zone immediately below the developing soil. There will be little or no dissolution at depth as recharge waters rapidly reach equilibrium, and there is no renewal of their dissolutional potential. The dominance of diffuse recharge and low runoff will allow mineral soils to accumulate providing there is a sufficient supply of atmospheric dust, as has occurred on Bermuda (Ruhe et al 1961).

With time, recharge will switch to more concentrated routes, with cementation and case-hardening of exposed carbonates shedding water laterally into pockets and fissures (Fig. 3B). Even where mineral soils are present the development of an impermeable caliche crust may result in flow concentration. The role of tree roots may be significant in both these cases. In the latter, disruption and brecciation of the micrite crust by penetration of roots provides concentrated outlets for locally perched soil waters, with the development of rhizomorphs into the underlying porous carbonates (Brown 1984). In the former, direct bedrock dissolution and the mechanical action of roots growing downward toward the saturated zone may give rise to discrete continuous channels on root decay, which bypass the diffuse-flow part of the unsaturated zone. Such concentrated recharge routes are characteristic of mature karst terrains, and are best seen where there is a thick unsaturated zone, as in the Sandy Point area of San Salvador. Here Mylroie (1988) has mapped the resulting shaft complexes, and the dominant role of shallow tributary runnels and shallow sub-surface fissures is clearly apparent.

Concentrated recharge routes, once established, will tend to be self-perpetuating and will give a dramatic change in the distribution of bedrock dissolution. Rapid recharge will allow chemically aggressive water to penetrate the unsaturated zone, resulting in a very heterogeneous development of secondary porosity to a considerable depth. Rapid recharge may also result in mixing corrosion where chemical contrasts exist between the recharge waters and long residence evolved groundwaters of the saturated zone.

Finally transport of particulate organic matter into the upper part of the saturated zone via fissure flow may occur. Here aerobic decomposition generates additional chemical potential for dissolution. A plot of the calcium concentration and PCO_2 of present day fresh groundwaters from North and South Andros, shows a parallel increase in PCO_2 and calcium concentration as water passes from the surface to the saturated zone (Fig. 4). This suggests open system dissolution with a PCO_2 similar to that measured in the organic soils. In practice however recharge waters are actually saturated, and two of the fresh water samples have a PCO_2 substantially higher than the maximum measured in the organic soils. The clear conclusion is therefore that carbon dioxide is generated by microbial decomposition of organic matter within the fresh water lens.

5. DEPTH AND DISTRIBUTION OF THE TRANSITION ZONE

In carbonate islands, such as the Bahamas, the contrast in density between fresh and saline waters results in the development of a lens-shaped body of fresh water underlain by saline water. The interface between the two waters is known as the transition zone. Residence times within the fresh water lens (Vacher and Bengtsson 1989) are long compared with times to reach chemical equilibrium, and bedrock dissolution is therefore limited unless chemical potential is renewed. However in the transition zone considerable potential for dissolution may be generated by mixing of waters of different salinity, demonstrated theoretically by Plummer (1975).

Mixing in the transition zone is now widely recognised as a potent process for carbonate dissolution. Back and others (1979) have suggested that the major coastal embayments and underwater cavern systems of the Yucatan Peninsula were formed by this process. Mylroie (1988) has advanced similar arguments to explain the distribution of subaerial caves on San Salvador, which are developed along the flanks of exposed dunes, and stressed the great rapidity of the process. On South Andros Island pervasive dissolution of bedrock in the transition zone has been observed in the walls of blue holes (Smart

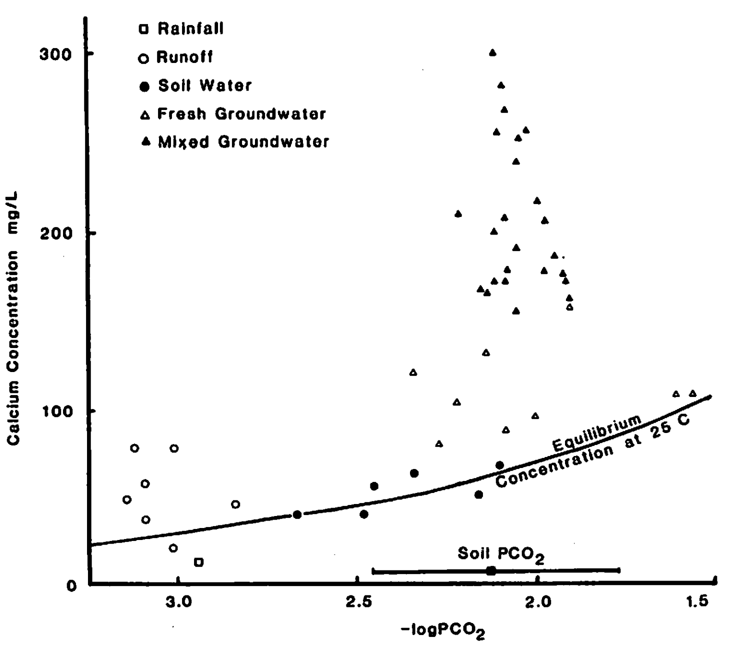

Fig. 4. Relationship between PCO_2 and calcium concentration for samples of rain water, runoff, soil water, and fresh and transition zone groundwaters. Points above the equilibrium line have lost CO_2 by evaporation (runoff) or degassing (groundwaters). Note that mixed transition zone waters have a PCO_2 comparable to fresh groundwaters, although a decrease with increasing percentage seawater would be expected for conservative linear mixing.

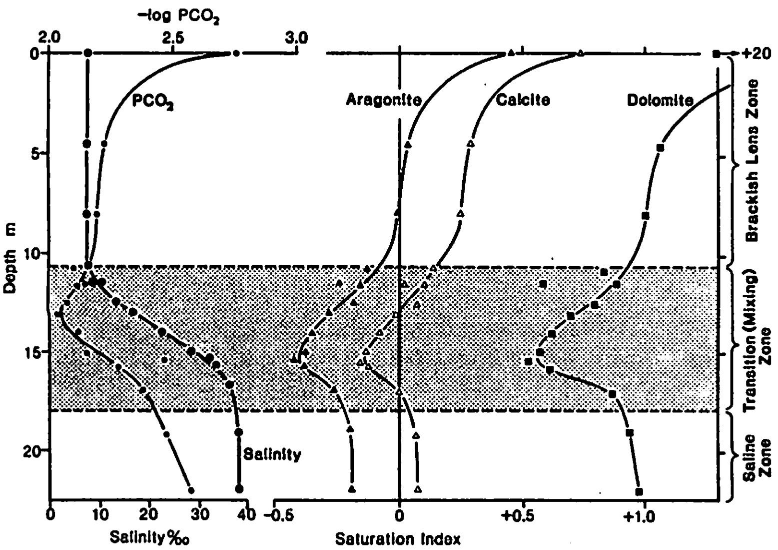

Fig. 5. Vertical variations in salinity, PCO_2, and aragonite, calcite and dolomite saturation indices in Evelyn Green's blue hole South Andros Island (Smart et al 1988). Note chemical undersaturation with respect to both aragonite and calcite, and increasing PCO_2 due to organic decomposition processes in the transition zone.

et al 1988), in association with waters that are undersaturated with respect to both calcite and aragonite (Fig. 5). In these cavernous sites organic particles penetrate the fresh water lens, but due to the density gradient remain suspended in the transition zone. Carbonate dissolution due to inorganic mixing is thus augmented by microbial generation of carbon dioxide. This is also demonstrated by the maintenance of PCO_2 at a level comparable to that in the fresh water lens (Fig. 4), contrary to the decreasing trend expected for linear conservative mixing.

Where a true fresh water lens is not developed, chemical contrasts in the groundwater body are more limited and thus the potential for mixing dissolution is reduced. Two factors are important in this respect; the balance between rainfall and potential evapotranspiration, and the relief. At present the relief of many Bahamian islands is relatively low, and large areas of open water in continuity with the groundwater permit direct evaporation at the potential rate. However lower sea-levels, as occurred during a substantial part of the Pleistocene, allow the development of a significant unsaturated zone, isolating the groundwater body from direct evaporation. Thus the dry southern islands such as Great Inagua, less than 1 % of which is currently underlain by fresh water (Cant and Weech 1986), would have had well developed fresh water lenses during periods of lower sea-level.

Under static groundwater conditions the contact between fresh and saline groundwaters would be sharp, with mixing generated only by diffusion. In practice there is considerable dispersion at the transition zone, generated by fluctuations in the position of the interface due to semi-diurnal tides (Mather and Buckley 1973) and variations in recharge which are accommodated by expansion and contraction of the lens (Kohout and Kline 1978). These factors enhance groundwater mixing and lead to the development of a zone of transition, the thickness of which may exceed that of the fresh water lens. The reduced density of the mixed waters also leads to the development of a buoyant circulation system in the transition zone, with the entrainment of saline water from below (Cooper 1959). In general there is therefore more active circulation and a thickening of the transition zone towards the coast. A similar effect is observed beneath the creeks which bisect the well developed fresh water lens on North Andros, and discharge large volumes of brackish water. However a small fall in sea-level (in the order of only 2m) would isolate these outlets, and cause the development of a much thicker, more extensive fresh water lens, with reduced mixing of groundwaters and a thinner transition zone.

6. CAVERNOUS POROSITY

It is apparent that bedrock dissolution in the saturated zone is concentrated both at the water-table, and especially in the transition zone. Mylroie (1988) has argued that rates of cave development in the latter may be very rapid. Thus cavernous porosity developed during earlier sea-level still-stands may be present within the bedrock. Because of the extremely high permeability of such zones, they may act to restrict the development of subsequent fresh water lens systems. Thus on Grand Bahama the

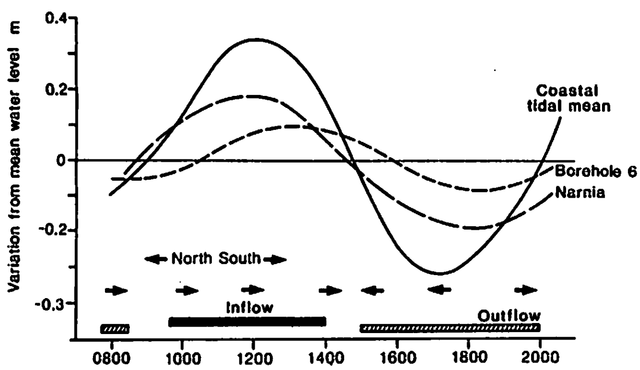

Fig. 6. Comparison of water-level fluctuations over a tidal cycle on South Andros Island, for monitoring stations at the east coast, at Narnia (an inland fracture blue hole) and an adjacent borehole. Arrows indicate the direction of flow observed in the brackish lens at Narnia, shaded bars show periods of inflow and outflow of saline water at an oceanic blue hole where the fracture runs offshore.

present position of the transition zone appears to be constrained by the open passages of Lucayan Caverns, which were developed during earlier high sea-level stands. Indeed Cant and Weech (1986) argue that the depth of the fresh water lens throughout the Bahamas is limited by the thickness of the Pleistocene Lucayn Limestone Formation, which is less cavernous than the older limestones beneath.

On South Andros and Grand Bahama cavernous porosity is preferentially developed along major fractures paralleling the bank margin (Palmer 1986). During every tidal cycle considerable volumes of saline water are exchanged between the fracture and the open ocean (Fig. 6). The caverns thus transmit tidal head differences with little attenuation, as shown by the comparable amplitude of water-level fluctuations in blue holes and at the coast. However attenuation of the tidal cycle occurs in the adjacent aquifer penetrated by borehole Number 6. This will cause pumping of saline and brackish waters into the adjacent fresh water diffuse flow aquifer. There is thus considerable potential for bedrock dissolution by groundwater mixing in such systems.

CONCLUSIONS

A major theme in the previous discussion has been the evolution from the homogeneous diffuse intergranular flow found in freshly exposed carbonate rocks, to concentrated recharge via fissures and cavernous flow with time. The resulting concentration of dissolution increases heterogeneity, and also allows the locus of dissolution to move from the surface to greater depth. However climate, and in particular the balance between evapotranspiration and precipitation, is a dominant control on the distribution and rates of bedrock dissolution in the Bahamas. This climatic control is both direct, via the control of groundwater flux, and indirect, via soil type and the extent of the fresh water lens. The latter is also influenced by relief, which is largely dependent on sea-level. Therefore before we can adequately understand the intrinsic changes in the distribution of dissolution (and therefore porosity) with time, it is important to identify the effects of climatic change. The presence of

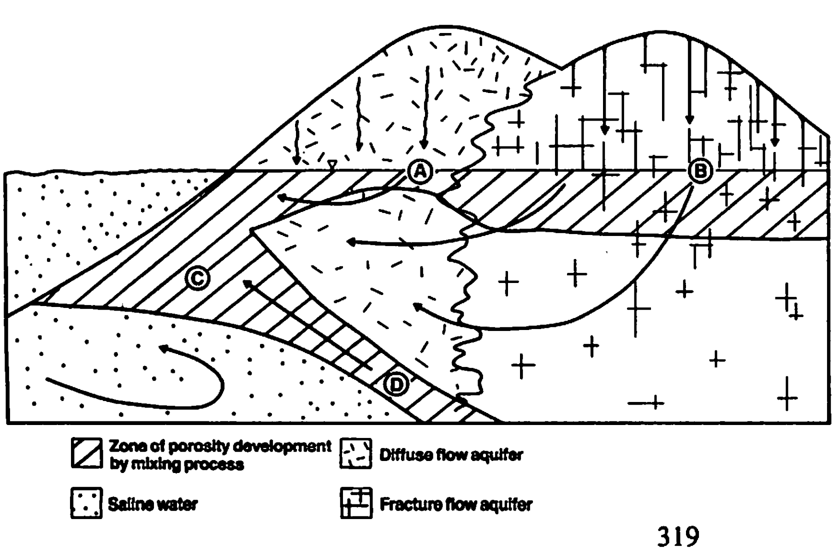

Fig. 7. Schematic diagram illustrating the zones where intense mixing may be expected for intergranular and fracture flow aquifers. At the water table there is limited potential for dissolution by the mixing of diffuse recharge waters and the fresh water lens (A), while fissure flow gives greater chemical contrasts, enhancing dissolutional potential (B). Tidal pumping and buoyant circulation thicken the transition zone near to the coast (C), compared to inland (D) where mixing is reduced.

paleosols ranging from sub-humid to arid in character provides a clear indication of the potential range palaeoclimatic conditions. What is now needed is a radiometrically dated record of these changes, such as may be obtained by the examination of growth periods and the isotopic composition of speleothems from the Bahamas.

ACKNOWLEDGEMENTS

This paper has benefitted from extensive discussion with Richard Cant, John Mylroie, Jim Carew, Neil Sealey, Rob Palmer and J.D. Crummock, and was made possible by financial support from Shell Exploration and Production Ltd, Amoco Ltd, and the National Environmental Research Council (Grant GR3/6694). Logistic support from Virgin Airways, Shell Bahamas, Steve Hobbs, Commander Ian Anderson Royal Navy, and Sue and Jim Phillips is gratefully acknowledged. Finally we thank the Government of the Bahamas for permission to undertake this study, and particularly the Department of Lands and Surveys for their help.

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