Geochemistry of meteoric diagenesis in carbonate islands of the northern Bahamas: 1. Evidence from field studies

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Abstract:

Processes driving carbonate diagenesis in islands of the northern Bahamas are investigated using major ion, dissolved oxygen and dissolved organic carbon analyses of water samples from surface and ground waters, and measurements of soil gas P_{CO_2}. Meteoric waters equilibrate with aragonite, but reactions are water controlled rather than mineral-controlled and drive dissolution rather than concurrent precipitation of calcite. Surface runoff waters equilibrate with atmospheric P_{CO_2} and rapidly recharge the vadose zone, limiting subaerial bedrock dissolution to only 6·6–15 mg l^{-1} Ca. P_{CO_2} of soil gas measured in the summer wet season (($7·4 \pm 3·7) \times 10^{-3}$ atm) is elevated compared with that of the atmosphere, despite the thin skeletal organic nature of the soil and the discontinuous soil cover. Soil waters retained in surface pockets are equilibrated with respect to aragonite and have dissolved 51 ± 19 mg l^{-1} Ca. This is substantially less than the 93 ± 18 mg l^{-1} Ca in samples from pumping boreholes that sample meteoric waters from the freshwater lens. The high P_{CO_2} of the freshwater lens (($16 \pm 8·3) \times 10^{-3}$ atm for pumping boreholes) suggests that significant additional CO_2 may be derived by oxidation of soil- and surface-derived organic carbon within the lens. The suboxic nature of the majority of the freshwater lens and the observed depletion in sulphate support this suggestion, and indicate that both aerobic and anaerobic oxidation may take place. Shallow lens samples from observation boreholes are calcite supersaturated and have a lower P_{CO_2} than deeper lens waters, indicating that CO_2 degasses from the water table, driving precipitation of calcite cements. We suggest that the geochemical evolution of waters in the vadose zone and upper part of the freshwater lens may be determined by the presence of a body of ground air with P_{CO_2} controlled by production in the freshwater lens and soil and by degassing to the atmosphere. Copyright © 2007 John Wiley & Sons, Ltd.

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INTRODUCTION

Early meteoric diagenesis is an important control on both the porosity and permeability of young carbonate rocks, and their later diagenesis and compaction (Budd, 2001; Moore, 2001). In young, partially stabilized carbonates, the simultaneous occlusion of primary porosity and development of dissolutional secondary porosity results in an increasingly heterogeneous distribution of porosity and may significantly enhance permeability with only a minor change in total porosity (Halley and Evans, 1983). To predict the distribution and extent of early diagenesis in carbonates adequately (Whitaker *et al.*, 1997), we need first to understand the nature of the processes, their controls and the rates at which they operate in present-day carbonate settings. A particular challenge is to understand fully the complex interplay between factors critical for creating and preserving porosity and developing permeability.

The traditional geological approach is to study diagenetic products. Thus, rates of stabilization have been estimated for well-dated Pleistocene sequences, e.g. in

Bermuda (Land *et al.*, 1967; Vacher *et al.*, 1990). It is also possible to infer the origin of cements from their petrography and/or geochemistry (Moore, 2001). However, the morphology of dissolutional voids offers little diagnostic potential. An alternative approach is to examine the hydrology and geochemistry of surface water and groundwater of modern carbonate islands. Aqueous geochemistry is a relatively sensitive indicator of diagenesis, and enables some geochemical process responsible for diagenesis to be determined from the distinctive geochemical signature often present in diagenetic fluids. In addition, it has the potential to provide an understanding of both the large-scale distribution of processes and the rates of diagenesis. The work of Budd (1988) and McClain *et al.* (1992) on rates and processes of stabilization in Holocene grainstones are excellent examples of this approach.

James and Choquette (1984) recognize two sets of processes that drive early diagenesis in carbonates: mineral- and water-controlled reactions. Mineral-controlled reactions involve stabilization of primary metastable high-magnesium calcite (HMC) and aragonite to low-magnesium calcite (LMC), and are driven by differences in the solubility of the carbonate phases. Under closed-system conditions, these reactions are mass

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conservative, with only minor porosity change due to differences in mineral density. There may also be some local redistribution of porosity, with occlusion of primary depositional porosity and generation of a more heterogeneous secondary porosity distribution. Under open-system conditions, the efficiency of conversion (percentage of metastable carbonate converted locally to LMC; Budd, 1988) can be less than 100%, with loss of dissolved carbonate in circulating groundwater. However, efficiency can locally also exceed 100% due to precipitation of carbonate derived from dissolution at the surface and/or in the shallow aquifer. Water-controlled reactions are dominant in stabilized (LMC) carbonates, and have been extensively studied in continental karst areas (White, 1988; Palmer, 1991). Dissolution is driven primarily by carbonic acid derived from CO_2 in soil air, which derives from root respiration and bacterial decomposition of organic matter (White, 1988). Some workers have also suggested that CO_2 generated or stored in the vadose zone (ground air) may be important (Atkinson, 1977; Wood and Petriakis, 1984). Others have emphasized dissolution due to the mixing of waters of differing chemistry (Bögli, 1964), although mixing can drive dissolution or precipitation, depending on the nature of the waters mixed.

Mineralogically stabilized oceanic carbonate terrains are different in many ways to continental carbonate terrains (Wright and Smart, 1994). As the former are often areas of contemporary carbonate deposition, the climate is generally warm with high evapotranspiration. There is, thus, the potential for reprecipitation of dissolved carbonate driven by evaporation and degassing of CO_2 (Esteban and Klappa, 1983; Perry et al., 1989). Oceanic carbonates are also characterized by retention of a relatively high intergranular porosity and the presence of saline waters at depth beneath a freshwater lens of often limited thickness (Vacher and Mylroie, 2002). Relief is often low, and the depth of the vadose zone can be quite small (Wright and Smart, 1994). Furthermore, the absence of clastic sediments limits the potential for development of mineral soils (Newell and Rigby, 1957). These differences limit the applicability of studies in continental carbonate terrains to the understanding of early meteoric diagenesis. However, surprisingly few studies have been undertaken in mineralogically stabilized oceanic carbonate terrains, notable exceptions being the classic study of Plummer et al. (1976) in Bermuda and the less well-known study of Irabu Island, Japan, by Matsuda et al. (1995).

This paper examines the processes driving carbonate diagenesis within the meteoric system of Pleistocene carbonate islands of the northern Bahamas using field sampling of waters from different hydrochemical environments. In an associated paper we undertake geochemical modelling to explore the evolution of poorly known parts of the hydro-chemical system and generate a distributed dissolution budget for the northern Bahamas (Whitaker and Smart, 2007).
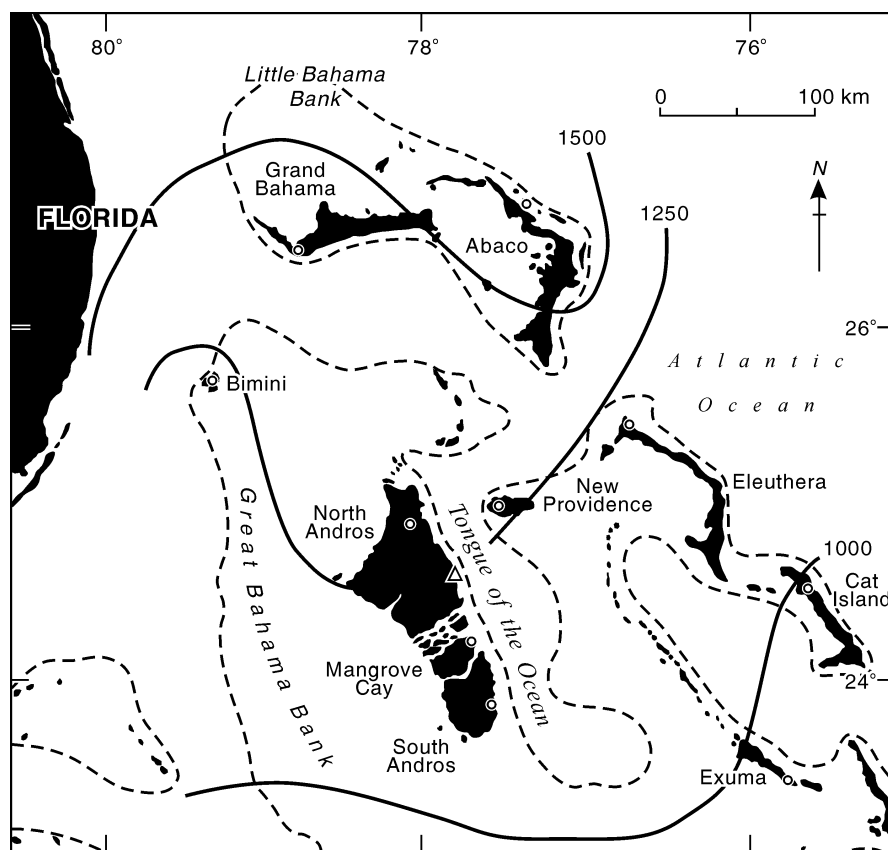

Figure 1. Map of the northern Bahamas showing location of named islands, regional variation in rainfall (contours in mm year^{-1}), rainfall monitoring sites (circles) and Autec Naval Base (triangle)

GEOLOGY, PHYSIOGRAPHY AND HYDROLOGY OF THE STUDY AREA

The northern Bahamas consists of two large coalesced platforms, i.e. the Great and Little Bahama Banks (Figure 1). Andros Island lies on the windward side of the northwest part of the Great Bahama Bank, and is the largest of all the Bahamian islands, extending some 180 km north–south and averaging 35 km in width. Andros is dissected by wide, shallow tidal creeks and channels ('bights') that create three separate islands (North Andros, Mangrove Cay and South Andros), as well as numerous small cays. Grand Bahama is slightly smaller than Andros, extending some 155 km east–west across the southern part of the Little Bahama Bank, with an average width of 8 km.

On both islands the subaerial and subsurface carbonates hosting meteoric groundwater are dominated by poorly stratified non-skeletal shallow-water limestones of the late Pliocene–Pleistocene Lucayan Formation, within which there are frequent subaerial exposure horizons (Beach and Ginsburg, 1980). This formation also includes complex sequences of low linear and arcuate aeolian and beach dune ridges, which dominate present-day relief (Garrett and Gould, 1984). Terrain is determined largely by subtle differences in elevation, grading from dry rocklands, through zones of marsh, lagoon and swamp, to shallow lakes. Subaerial Holocene deposits comprise locally distributed narrow ridges of unconsolidated beach sands on exposed coasts, and broad tidal flats on the platform interior coasts.

Although most large-scale landforms are depositional in origin, the exposed limestones are subject to subaerial dissolution. At a small scale this is evidenced by karren, kamenitzas, solution pipes and shallow subsurface channels, and metre-diameter dissolution pits locally termed 'banana holes' (Smart and Whitaker, 1989; note that our usage of this term differs from that of Harris *et al.* (1995)). In the northern Bahamas, subaerial caves are generally limited in size, but there are numerous 'blue holes', i.e. entrances to underwater cave systems that can be vertically and laterally very extensive (Whitaker and Smart, 1997a). Lucayan Caverns on Grand Bahama, for example, has more than 14 km of explored passage, whereas other systems developed on a bank-marginal fracture system on the east coast of Andros have been explored to depths in excess of 93 m (Whitaker, 1998).

The northern Bahamas has a subtropical marine climate, with persistent trade winds, a warmer rainy season from May to October and a cooler, drier season from November to April. There is a broad north–south climatic gradient (Figure 1), with the wetter, northern Bahamas having almost twice the annual rainfall of the more arid southern islands. Within the study area, mean annual rainfall reduces from 1496 mm in Freeport (Grand Bahama) to 1175 mm at Kemps Bay (South Andros). Potential evapotranspiration has been estimated for the northern Bahamas from Bahamas Meteorological Office data as 1581–1610 mm year^{-1} (Whitaker, 1992). However, rates of actual evapotranspiration are likely substantially lower than the potential rate, and are estimated at approximately 75% of total rainfall (Little *et al.*, 1973). A proportion of this evaporative demand is satisfied from interception retained on vegetative surfaces, which range from pine forest on Grand Bahama and North Andros to coppice woodland on the drier islands, including South Andros (Campbell, 1978).

The high permeability of the karstified limestones gives rapid infiltration of recharge and there are no surface streams or rivers. However, particularly in the rainy season, many freshwater ponds and lakes form where the water table intersects the ground surface. The depth of the vadose zone is controlled largely by topography, and over large areas remains less than 1 m, although it may exceed 5 m beneath aeolianite ridges. Over much of the islands tree roots reach the shallow water table, from which evapotranspiration can occur directly.

In the Bahamas, phreatic meteoric groundwater occurs as Ghyben–Herzberg lenses overlying denser saline groundwater. The nature and size of the freshwater lens is determined by island size and shape, climate and aquifer characteristics (Cant and Weech, 1986; Whitaker and Smart, 1997a). Throughout the study area, the actual freshwater lens is thinner than the theoretical Ghyben–Herzberg lens because the hydraulic conductivity of the upper Lucayan Limestone aquifer increases substantially with depth (Whitaker and Smart, 1997b). On North Andros the freshwater lens reaches a maximum thickness of 34 m, limited by the distance between tidal creeks, which function as estuaries discharging fresh and brackish groundwater (Whitaker and Smart, 1997a). On the Little Bahama Bank, where rates of subsidence are relatively low, the base of the lens is truncated at 21 m at the boundary between the Lucayan Formation and the older, more conductive limestones below (Cant and Weech, 1986). Meteoric water discharges largely through the fresh-water–salt-water mixing zone both along the coast and via tidal creeks (Whitaker, 1992).

METHODS

A total of 103 samples of meteoric water were collected during the rainy season (June–July) from a range of sites and geochemical environments on North and South Andros and Grand Bahama (Figure 1). Rainfall was sampled ~250 m inland of the eastern coast of North Andros. Samples of runoff, collected during and immediately after storm events, include water running over a variety of bare and vegetated bedrock surfaces. Water retained at the bedrock surface for periods from a few hours to a few days was collected from ephemeral surface pools (including shallow puddles and kamenitzas) and soil-filled solution hollows (including banana holes). There were no active drips within any subaerial caves visited, but water dripping from the roof of cave entrances during a storm was sampled at two sites at Lucayan Caverns, Grand Bahama.

The meteoric freshwater lens was sampled using unpumped observation boreholes, pumped abstraction boreholes, shallow hand-dug wells (up to 2 m diameter) and large (30 cm) diameter boreholes drilled to provide road drainage. In addition, specialized cave-diving techniques were used to collect samples from flooded caves. These include predominantly horizontal cave systems (including the Lucayan Caverns and Owls Hole–Mermaids Lair systems on Grand Bahama), very large diameter open circular shafts ('cenotes') on North Andros, and vertically extensive linear caves developed on a bank-marginal fracture system on South Andros (Whitaker and Smart, 1997c). Samples from flooded caves were collected to a maximum depth of 20 m using 1·5 l plastic tubes, 7 cm diameter, which were filled by forward motion of the diver and capped underwater. In addition samples of surface water were collected from cave-entrance pools along the bank-marginal fracture. Because they potentially represent rather different geochemical environments, the data for each of these types of freshwater lens sampling site are presented separately.

Field measurements included temperature, conductance, pH ($\pm$0·02 pH units) and, for cave and borehole samples, dissolved oxygen ($\pm$1%). Subsamples were taken for immediate analysis of alkalinity and calcium by titration, and after pressure filtration and acidification to pH < 2 with HNO_3 for analysis of other major ions (major cations by atomic adsorption spectrophotometry, chloride by mercurimetric or Mohr titration and sulphate by turbidimetry). Selected samples ($n = 26$) were also analysed for strontium by atomic adsorption spectrometry. All dilutions were weighed, and analytical uncertainty was less than $\pm$1%, except sulphate and strontium with uncertainties of $\pm$4% and $\pm$5% respectively. Ion balance errors are normally distributed about a mean of $0·24 \pm 4·40\%$ (one standard error: 0·44%). Selected waters ($n = 44$) were subsampled and analysed for dissolved organic carbon (DOC) using high-temperature catalytic oxygenation with a Shimadzu TOC-500 analyser.

Soil-air CO_2 was measured during the wet season (June–July) using a Miotke soil CO_2 probe with Gastech gas analysis tubes. Measurements were made in humus–clay soils from pockets and banana holes up to 60 cm depth (the maximum soil depth encountered) at 35 sites across North Andros.

The aqueous speciation model PHREEQC (Parkhurst, 1995) was used to calculate the distribution and activities of all aqueous species, the partial pressure of CO_2, ion activity products (IAP), and saturation states (log IAP/K) of aragonite (SI_A) and calcite (SI_C) using thermodynamic equilibrium constants of Plummer and Busenberg (1982). Uncertainties in saturation indices and P_{CO_2} values are typically 0·036 log units and $0·28 \times 10^{-3}$ atm respectively, with >95% of uncertainty deriving from measurement of pH.

We use chloride as a conservative tracer to differentiate between conservative processes and those involving reactions between gas, mineral and organic phases. The concentrations of calcium, strontium, magnesium and sulphate in excess of those predicted from simple dilution of local Tongue of the Ocean (TOTO) seawater were calculated:

$$Ca_{XS} = Ca_{SAMPLE} - (Ca_{TOTO} \times Cl_{SAMPLE}/Cl_{TOTO})$$

(1)

Root-mean-squared errors were calculated by combining uncertainties in estimates of sample and TOTO concentrations. The combined error for an average pumping borehole water amounts to $\pm$3·3 mg l^{-1} Ca_{XS}, $\pm$0·44 mg l^{-1} Sr_{XS}, $\pm$7·8 mg l^{-1} Mg_{XS} and $\pm$14 mg l^{-1} $SO_{4\ XS}$, where XS signifies 'excess'. Because the majority of the error derives from uncertainty in TOTO concentrations, combined errors do not vary greatly between different meteoric waters.

RESULTS

Chloride

Chloride concentrations for all waters sampled are summarized in Table I. Only two rainfall samples are available, varying in chloride concentrations from 1·7 mg l^{-1} for a heavy convective storm (such as account for the majority of rainy-season recharge events) to 9·2 mg l^{-1} for a storm following an extended dry period. Runoff from bare and vegetated surfaces contains 17 ± 17 mg l^{-1} chloride and is probably representative of rapid groundwater recharge. Waters retained at the surface and sampled in banana holes (31 ± 64 mg l^{-1}) and ephemeral pools (104 ± 83 mg l^{-1}) have relatively elevated chloride concentrations. Samples from boreholes and wells in the freshwater lens have a large range of chloride concentrations (33–3995 mg l^{-1}). However, chloride concentrations in unpumped observation boreholes and hand-dug wells are much lower than those from pumped boreholes and drainage wells (175 ± 106 mg l^{-1} and 193 ± 49 mg l^{-1} respectively compared with 458 ± 340 mg l^{-1} and 1640 ± 1950 mg l^{-1} respectively), and are comparable with July–August values of 202 ± 157 mg l^{-1} ($n = 73$) for unpumped observation boreholes sampled across North Andros by Little et al. (1973). Samples of the freshwater lens from flooded caves generally have a higher and more variable chloride concentration than those from boreholes and wells. Samples from cenotes have the lowest chloride concentration of the cave-derived freshwater lens samples (375 ± 209 mg l^{-1}), whereas those from horizontal cave systems and particularly bank-marginal fracture caves, which connect directly with the ocean, are much higher (833 ± 662 mg l^{-1} and 3590 ± 1042 mg l^{-1} respectively). A more extensive helicopter-based survey of cenotes by Little et al. (1973) found an average surface water chloride concentration of 597 ± 474 mg l^{-1} ($n = 78$, excluding 12 sites with Cl >2000 mg l^{-1}), with a median for the strongly negatively skewed distribution of 420 mg l^{-1}.

Table I. Geochemistry of freshwater samples from Andros and Grand Bahama[a]

Water type	N[b]	Cl (mg l⁻¹)	Ca (mg l⁻¹)	Ca$_{XS}$ (mg l⁻¹)	Sr$_{XS}$/Ca$_{XS}$ (10⁻² mg l⁻¹)	P_{CO_2} (10⁻³ atm)	SI$_A$ (SI$_C$) (log IAP/K)	SO$_4$ $_{XS}$ (mg l⁻¹)
Rainfall	2 (0)	1·7 and 9·2[c]	1·2 ± 0·14	1·1 ± 0·05		0·48 ± 0·25	−3·29 (−3·14) ± 0·48	+0·5 ± 0·8
Runoff	7 (0)	17 ± 17	8·1 ± 2·7	7·7 ± 2·5		0·39 ± 0·25	−1·37 (−1·23) ± 0·47	+0·2 ± 2·1
Surface detention								
Shallow ephemeral pools	7 (1)	104 ± 83	33 ± 11	31 ± 12	0·9	0·50 ± 0·47	+0·62 (+0·76) ± 0·31	+3·8 ± 9·0
Banana holes[d]		31 ± 64[e]	52 ± 20[f]	51 ± 19	1·1 ± 0·2[e]	4·5 ± 2·8	+0·02 (+0·16) ± 0·47	−2·2 ± 9·5
Vadose cave drips	2 (0)	64 ± 42	70 ± 6·4	68 ± 5·4		1·1 ± 0·06	+0·80 (+0·94) ± 0·01	+0·1 ± 0·6
Freshwater lens								
Pumping boreholes	12 (3)	458 ± 340	106 ± 26	93 ± 18	1·3 ± 0·1	16 ± 8·3	+0·07 (+0·22) ± 0·13[f]	−21 ± 26
Drainage boreholes	4 (0)	1640 ± 1950	140 ± 50	105 ± 7·9		21 ± 13	−0·10 (+0·05) ± 0·19	−77 ± 81
Observation boreholes	6 (1)	175 ± 106[f]	72 ± 4·8[f]	69 ± 3·6[f]	2·1	4·0 ± 1·1	+0·33 (+0·47) ± 0·15	−2·8 ± 12
Hand-dug wells	3 (1)	193 ± 49	88 ± 17	84 ± 16	1·3	9·1 ± 2·6	+0·07 (+0·21) ± 0·04	+9·3 ± 3·6
Horizontal cave systems	11 (0)	833 ± 662	97 ± 17	79 ± 8		8·6 ± 3·6	+0·01 (+0·16) ± 0·09	−9·4 ± 17
Bank-marginal fracture cave (3–18 m)	14 (4)	3800 ± 872	171 ± 18	90 ± 12	1·3 ± 0·1	10 ± 2·6	+0·01 (+0·15) ± 0·11	−51 ± 63
Bank-marginal fracture cave <3 m	16 (5)	3410 ± 1170	154 ± 21	82 ± 11	1·6 ± 0·3	3·1 ± 2·0	+0·56 (+0·70) ± 0·26	−70 ± 34
Cenotes	6 (6)	375 ± 209	67 ± 13	57 ± 10	0·9 ± 0·2	2·4 ± 1·5	+0·34 (+0·48) ± 0·26	+43 ± 34
All freshwater lens samples	72 (20)	1890 ± 1710	124 ± 42	83 ± 16	1·3 ± 0·4	8·8 ± 7·3	+0·22 (+0·35) ± 0·31	−31 ± 52

[a] Values given are the mean plus/minus one standard deviation for concentrations of chloride, calcium, calcium excess, molar ratio of calcium to strontium excess, partial pressure of CO_2, aragonite (and calcite) saturation indices and sulphate excess.
[b] Number of samples. Subset of samples analysed for strontium in parentheses.
[c] Values for the two types of rainfall event, as described in the text.
[d] Deeper/soil-filled dissolutional hollows.
[e] Excluding two outliers greater than plus/minus two standard deviations from the mean.
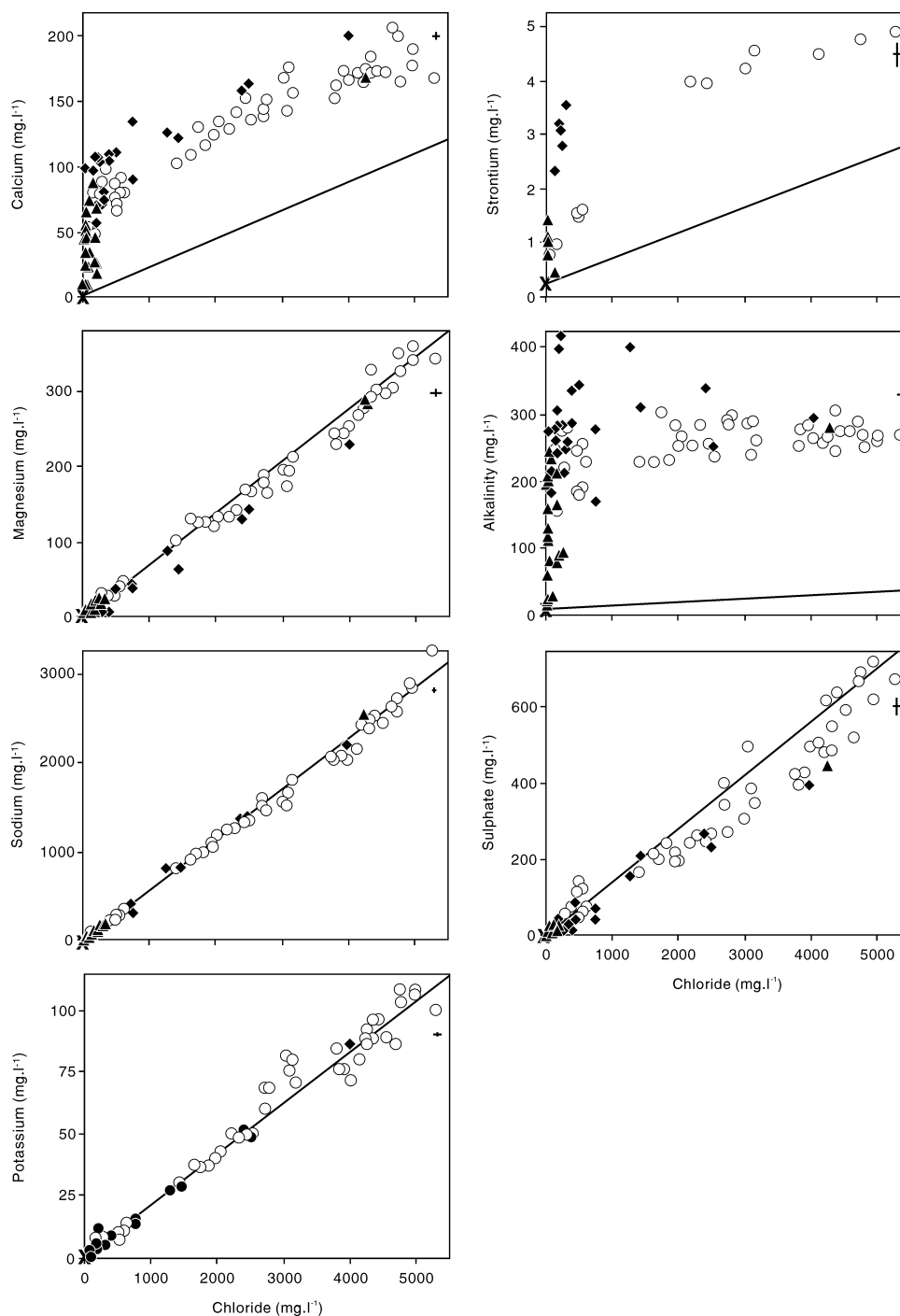[f] Excluding one outlier greater than plus/minus two standard deviations from the mean.

Figure 2. Cross-plots of major cations and anions versus chloride concentrations in rain ($\times$), surface waters and drips (triangles), and lens water from boreholes and wells (diamonds) and caves (circles). Solid line is conservative mixing line between rainwater and Tongue of the Ocean seawater. Cross shows representative analytical uncertainties

Calcium, P_{CO_2} and saturation with respect to calcite and aragonite

All meteoric waters are significantly enriched with calcium (and bicarbonate) to varying degrees (Figure 2) due to reaction with carbonate minerals. This is measured by Ca_{XS}, which is summarized, together with data for P_{CO_2}, SI_C and SI_A, in Table I. Rainfall samples have an average Ca_{XS} of $1\cdot1$ mg l^{-1}, are equilibrated to atmospheric P_{CO_2} and are substantially undersaturated with respect to both calcite and aragonite. Runoff waters remain close to

atmospheric P_{CO_2} but have, on average, dissolved a further $6\cdot6$ mg l^{-1} Ca. They remain significantly undersaturated with respect to both aragonite and calcite, although two orders of magnitude less so than rainfall. Surface detention waters from the shallow, ephemeral pools have a much larger range of P_{CO_2} but are, on average, equilibrated with a CO_2 value only marginally above that of the atmosphere $((0\cdot50 \pm 0\cdot47) \times 10^{-3}$ atm). The calcium concentration is much higher $(31 \pm 12$ mg l^{-1} $Ca_{XS})$ than in runoff, and the waters are supersaturated with

respect to aragonite ($+0.62 \pm 0.31$). In contrast, surface detention water sampled from banana holes has a significantly elevated P_{CO_2} ((4.5 ± 2.8) $\times 10^{-3}$ atm), a higher calcium concentration (51 ± 19 mg l^{-1} Ca$_{XS}$), and are close to equilibrium with respect to aragonite. The two samples that may be representative of vadose percolation (the rapid flow waters entering Lucayan Caverns during a heavy storm) are considerably supersaturated with respect to aragonite. However, their average P_{CO_2} is more than twice that of ephemeral pools, and in terms of Ca$_{XS}$ they are more similar to surface detention sampled in banana holes (Table I).

Samples of the freshwater lens from pumping boreholes are aragonite equilibrated and have a P_{CO_2} of (16 ± 8.3) $\times 10^{-3}$ atm. (Table I). The latter is significantly higher than determined for surface detention in banana holes ((4.5 ± 2.8) $\times 10^{-3}$ atm). Slightly higher P_{CO_2} and Ca$_{XS}$ are measured in freshwater sampled from drainage wells ((21 ± 13) $\times 10^{-3}$ atm and 105 ± 7.9 mg l^{-1} respectively), and on average these waters are marginally undersaturated with respect to aragonite (-0.10 ± 0.19). Water sampled from shallow depth in the freshwater lens in hand-dug wells and in unpumped observation boreholes has significantly lower P_{CO_2} (and also Ca$_{XS}$) than that from pumped boreholes: (9.1 ± 2.6) $\times 10^{-3}$ atm and (4.0 ± 1.1) $\times 10^{-3}$ atm respectively, compared with (16 ± 8.3) $\times 10^{-3}$ atm. Observation borehole waters are also considerably supersaturated with respect to aragonite ($+0.33 \pm 0.15$). Samples from unpumped observation boreholes are comparable in terms of carbonate chemistry to those from cenotes, whereas those from hand-dug wells are more similar to samples from horizontal cave systems (Table I). Shallow samples from fracture caves have the highest aragonite supersaturation of all freshwater lens samples ($+0.56 \pm 0.26$). Both these and cenote waters have a lower P_{CO_2} than measured in detention waters from banana holes ((3.1 ± 2.0) $\times 10^{-3}$ atm and (2.4 ± 1.5) $\times 10^{-3}$ atm compared with (4.5 ± 2.8) $\times 10^{-3}$ atm respectively).

Sodium, potassium and magnesium

In contrast to calcium and bicarbonate, sodium and potassium are essentially conservative with respect to chloride (Figure 2). A few of the samples from the freshwater lens from the fracture blue holes have potassium concentrations slightly higher (five samples) or lower (three samples) than expected. However, some 15 (21%) of the samples from the freshwater lens have magnesium concentrations more than 2σ analytical uncertainty lower than expected from conservative mixing (up to 45 mg l^{-1}), with only 6% of samples showing significantly magnesium enrichment. Magnesium depletion generally increases with chloride concentration and is most common in waters sampled from the deeper fracture cave sites (57% of samples).

Strontium

Strontium data are only available for a limited subset of samples and are presented in Table I in terms of the molar ratio to calcium. The average Sr$_{XS}$: Ca$_{XS}$ for all meteoric waters is (1.2 ± 0.4) $\times 10^{-2}$ ($n = 26$). Surface detention waters are only marginally less strontium enriched ((1.0 ± 0.2) $\times 10^{-2}$ Sr$_{XS}$: Ca$_{XS}$, $n = 6$) than samples from the freshwater lens ((1.3 ± 0.4) $\times 10^{-2}$ Sr$_{XS}$: Ca$_{XS,}$, $n = 20$). However, there are significant differences in freshwater lens Sr$_{XS}$: Ca$_{XS}$ between different sample sources. Cenote samples are relatively strontium depleted ((0.9 ± 0.1) $\times 10^{-2}$ Sr$_{XS}$: Ca$_{XS}$, $n = 6$), with values comparable to those of surface detention. In contrast, there is relative strontium enrichment in samples from fracture surface waters ((1.6 ± 0.3) $\times 10^{-2}$ Sr$_{XS}$: Ca$_{XS}$, $n = 5$) and boreholes ((1.3 ± 0.1) $\times 10^{-2}$ Sr$_{XS}$: Ca$_{XS}$, $n = 4$), with Sr$_{XS}$: Ca$_{XS}$ of 2.1 in the single sample from an observation borehole.

Sulphate

Sulphate appears to be conservative relative to chloride in most surface waters sampled (Figure 2 and Table I). In contrast, some 44 (61%) of the groundwater samples from boreholes and caves have sulphate concentrations more than 2σ analytical uncertainty lower than expected from conservative mixing. The average SO$_{4 \; XS}$ for all samples from the freshwater lens is -31 ± 52 mg l^{-1}. However, this average includes samples from cenotes which show significant sulphate enrichment (up to 80 mg l^{-1}). In contrast, all samples from fracture caves are significantly depleted in sulphate (up to 137 mg l^{-1}), whereas those from horizontal cave systems show minor depletion. Sulphate depletion is also evident in waters from drainage boreholes and to a lesser extent from pumping boreholes, but in only one of six samples from observation boreholes. Sulphate concentrations in waters from most observation boreholes and the hand-dug wells are close to those expected from conservative mixing

Dissolved organic carbon and dissolved oxygen

The concentration of DOC is very similar in all surface waters and drips, collectively averaging 20 ± 6.1 mg l^{-1}, $n = 18$ (Table II). The DOC of freshwater sampled in pumping boreholes, cenotes and fracture caves is only slightly lower than that of the surface waters, collectively averaging 17 ± 4.2, $n = 23$. However, the DOC of cave waters from predominantly horizontal cave systems (with few entrances) is only 7.5 ± 7.6 mg l^{-1} ($n = 7$), and that of observation boreholes is lower still 4.8 ± 1.6 mg l^{-1} ($n = 3$). One of the two analyses from drainage boreholes resembles the observation borehole waters, and the other approximates the average for high DOC lens waters.

The average dissolved oxygen content of freshwater samples from observation boreholes and horizontal caves is identical, with slightly lower but comparable values for pumping boreholes (Table II). Collectively, this group has a dissolved oxygen content of $49 \pm 14\%$ ($n = 24$). Rather lower values are obtained for samples from drainage boreholes and fracture caves, averaging $19 \pm 6.0\%$ and $27 \pm 25\%$ saturation respectively. Samples from large-diameter cenotes approach saturation at the

Table II. DOC and dissolved oxygen (DO) concentrations of a subset of freshwater samples from Andros and Grand Bahama (values are mean plus/minus one standard deviation; number of samples n in parentheses)

Water type	DOC (mg l^{-1})	DO (%)
Surface detention		
Shallow ephemeral pools	$20 \pm 8{\cdot}0$ ($n = 9$)	—
Banana holes	$19 \pm 5{\cdot}2^a$ ($n = 7$)	—
Vadose cave drips	$15 \pm 1{\cdot}3$ ($n = 2$)	—
Freshwater lens		
Pumping boreholes	$17 \pm 6{\cdot}7$ ($n = 7$)	44 ± 15 ($n = 4$)
Drainage boreholes	$12 \pm 8{\cdot}0$ ($n = 2$)	$19 \pm 6{\cdot}0$ ($n = 4$)
Observation boreholes	$4{\cdot}8 \pm 1{\cdot}6$ ($n = 3$)	50 ± 11 ($n = 9$)
Horizontal cave systems	$7{\cdot}5 \pm 7{\cdot}6$ ($n = 7$)	50 ± 16 ($n = 11$)
Bank-marginal fracture cave	$17 \pm 4{\cdot}2$ ($n = 12$)	27 ± 25 ($n = 16$)
Cenotes	$16 \pm 1{\cdot}7$ ($n = 4$)	$76 \pm 9{\cdot}5$ ($n = 6$)
All freshwater lens samples	$14 \pm 6{\cdot}5$ ($n = 35$)	40 ± 25 ($n = 50$)

[a] Excluding two outliers greater than plus/minus two standard deviations from the mean.

surface and average $76 \pm 9{\cdot}5\%$. However, most lens waters are sub-oxic, following the terminology of Tyson and Pearson (1991). Dissolved oxygen was not measured in surface waters, which are assumed to be in equilibrium with the atmosphere.

Soil-atmosphere carbon dioxide

Soil CO_2 concentrations increase with depth (Figure 3), with an average P_{CO_2} for organic soils of $(7{\cdot}4 \pm 3{\cdot}7) \times 10^{-3}$ atm, and significantly higher values for humic soils than for more gas-permeable litter. Higher values $((11–17) \times 10^{-3}$ atm) are found in banana holes which contain soils with a higher fraction of more mineral-rich clays at depth (although clay content was not quantified).
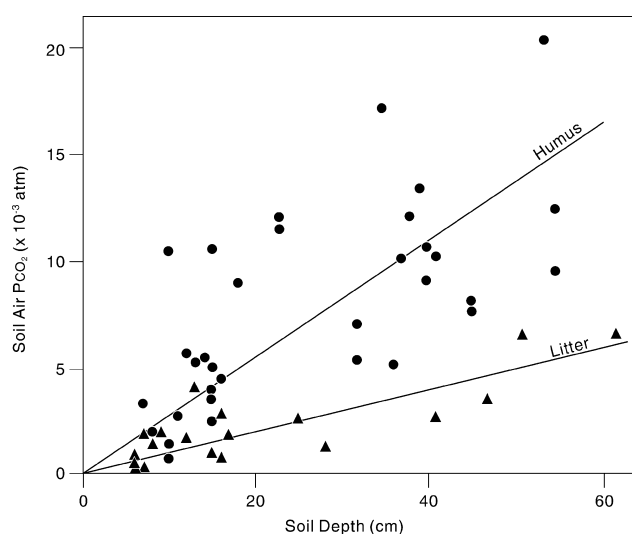

Figure 3. Relationship between soil depth and soil-air P_{CO_2} for humus (circles) and litter (triangles) measured during the rainy season on North Andros. Solid lines are regressions for humus (P_{CO_2} (10^{-3} atm) $= 28 \times$ depth (m), $n = 34$, $r^2 = 0{\cdot}39$, significant at $>98\%$ confidence interval) and litter (P_{CO_2} (10^{-3} atm) $= 9{\cdot}8 \times$ depth (m), $n = 18$, $r^2 = 0{\cdot}69$, significant at $>99{\cdot}9\%$ confidence interval), constrained to pass through the origin

INTERPRETATION

Evaporation and mixing of meteoric and saline waters: conservative processes

In the absence of shallow evaporites in the Bahamas (Newell and Rigby, 1957; Beach, 1982), the only significant source of chloride in the meteoric system is seawater. Chloride can thus be used as a tracer of conservative processes, including wet and dry deposition, natural and anthropogenic mixing with groundwater of near-seawater composition underlying the freshwater lens, coastal sea-spray and/or periodic inundation by seawater during storm surges.

The elevation of chloride (by some 15 mg l^{-1}) in surface runoff compared with rainfall may be in part due to the presence of dry deposition or evaporated residues. However, this effect is likely to be small compared with evaporation from water retained at the surface, which probably accounts for most of the increased chloride concentration in waters sampled from banana holes (31 ± 64 mg l^{-1}) and ephemeral pools (104 ± 83 mg l^{-1}). In contrast to areas with thick vadose zones, the limited depth to the water table on these low-lying islands allows additional direct evapotranspiration from the freshwater lens by deep-rooted vegetation, and capillary and vapour transfer through the vadose zone. This may account for the elevated chloride concentrations measured in observation boreholes and shallow wells (175 ± 106 mg l^{-1} and 193 ± 49 mg l^{-1} respectively) in this study and that of Little et al. (1973).

Little et al. (1973) also reported that 40% of the observation boreholes sampled across North Andros showed increases of 20–30 mg l^{-1} chloride by January–February (mid dry-season) compared with summer (wet-season values). This is strongly suggestive of direct evapotranspiration from the top of the freshwater lens. Weekly records from a pumping well field at the Autec Naval Base, North Andros, over 1 year also indicate seasonal variation from a minimum of 110 mg l^{-1} at the end of the wet season in November to >200 mg l^{-1} by the end of the dry season in May (Figure 4; Whitaker and Smart

1997a). The much larger seasonal difference observed here, compared with the data of Little *et al.* (1973), probably reflects the additional influence of pumping of the coastal well field and thinning of the lens during the dry season.

A proportion of the evapotranspirative demand is satisfied by evaporation of intercepted rainfall. Surface retention in subtropical pine forests is estimated as 10–20% of total rainfall (Balek, 1983; Crockford and Richardson, 1990). This gives estimates of total interception that are comparable to those derived from the product of retention (1–3 mm per event; Falkland and Brunel, 1993) and the number of events (approximated by the number of rain days; 122 on Grand Bahama and 76 on South Andros). The residual evapotranspirative deficit, equivalent to 55–65% of total rainfall, is satisfied from the subsurface.

The ratio of subsurface evapotranspiration to effective recharge indicates an evaporative concentration factor of approximately 2·4 for the northern Bahamas. If we assume recharge has a similar composition to rapid surface runoff, then evapotranspiration from the subsurface would increase chloride concentrations in the freshwater lens by some 24 mg l^{-1}, giving a total of 39 ± 41 mg l^{-1} chloride. Chloride concentrations in the all but two of the samples from the freshwater lens are much higher than this (1890 ± 1710 mg l^{-1} for all samples). There must,

therefore, be a major input of chloride upwards from the underlying saline groundwater.

This input occurs by hydrodynamic mixing and upward dispersion, as indicated by the progressive increase in chloride with depth through the freshwater lens (Whitaker and Smart, 1997a,c). Mixing is enhanced by oscillations in the position of the fresh-water–salt-water mixing zone, both semi-diurnally due to ocean tides, and from periodic and seasonal variations in recharge. On North Andros, a reduction in fluctuation ratio (amplitude of tidal water-level fluctuation in boreholes as a ratio of that at the coast) at a rate of 3% km^{-1} from the coast is paralleled by a reduction in chloride in the upper part of the lens by 20 mg l^{-1} km^{-1} (Whitaker, 1992). However, this may also in part reflect progressive advective mixing and evapotranspiration along the groundwater flow path. In addition, pumping-induced upconing of the base of the freshwater lens increases chloride in pumped boreholes compared with observation wells, which are only affected by tidal and seasonal dispersive mixing.

The higher chloride concentration of cave water samples compared with those from boreholes reflects enhanced mixing within the cave voids, particularly towards the margins of the lens. For instance, the bank-marginal fracture caves experience exceptionally active tidal mixing, developing a markedly brackish rather than fresh lens that increases in chloride with flow along the fracture (Whitaker and Smart, 1997c). Chloride concentrations in the horizontal cave systems that connect directly with the ocean are also higher than in the cenotes (average 833 ± 662 compared with 375 ± 209 mg l^{-1} Cl). The only exception to this general pattern are the waters sampled from drainage wells, which have much higher chloride concentrations than other borehole and well samples, and are more comparable to the cave waters. This is because, unlike other boreholes, they frequently penetrate more transmissive units within and below the fresh-water–salt-water mixing zone, and are affected by both tidal mixing and enhanced fluctuations in mixing-zone position during times of recharge.

We can thus calculate a chloride budget for the freshwater lens using measurements of chloride concentration and estimates of rainfall, evapotranspiration and interception discussed above. Approximately 8% (17 mg l^{-1}) of chloride in the freshwater lens sampled in non-salinized wells and boreholes (average chloride of 212 ± 126 for 18 samples with Cl <500 mg l^{-1}) derives from wet and dry deposition and evaporation of interception. Following recharge, chloride concentrations within the freshwater lens increase due to both evapotranspiration from the upper part of the lens and to mixing with underlying saline groundwater. Subsurface evapotranspirative concentration of recharge water may be responsible for some 12% (24 mg l^{-1}) of the chloride in the freshwater lens. A further 12% to 42% may be generated by evapotranspiration from the upper part of the lens (estimated from seasonal increases of 25 mg l^{-1} to 90 mg l^{-1} in observation and pumping boreholes respectively). Mixing with saline groundwater contributes the balance, or 38–69%
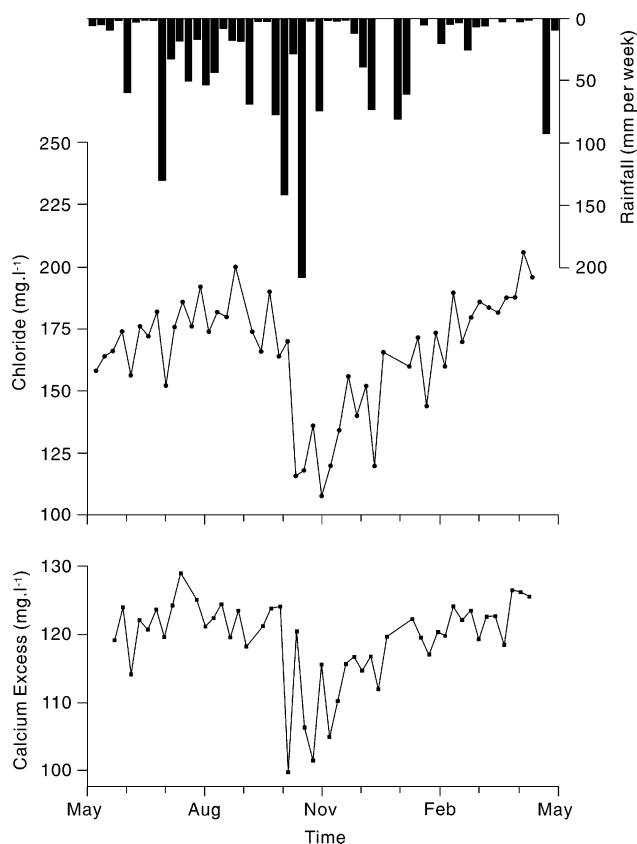

Figure 4. Variation over 1 year in rainfall (weekly total) and concentration of Cl (mg l^{-1}) and Ca$_{XS}$ (mg l^{-1}) in bulked water samples from pumping boreholes in the abstraction well field, Autec Naval Base, North Andros. Tick marks on *x*-axis show start of given month (after Whitaker and Smart (1997a))

$(81–146$ mg $l^{-1})$, of the chloride in boreholes, and a considerably greater proportion in the more brackish lens waters in the caves.

Mineral-controlled reactions

The importance of mineral-controlled reactions can be examined using the molar ratios of Mg_{xs}, Sr_{xs} and Ca_{xs} in solution (e.g. Budd, 1988; McClain *et al.*, 1992). HMC is transformed to LMC rapidly because of its highly metastable nature (Walter, 1985), with release of magnesium to solution from both dissolution of HMC and conversion of HMC to LMC. Forams and echinoderm fragments suggest that HMC bioclasts were present in the Lucayan Limestone on deposition, but have since been completed stabilized to LMC (Beach 1982; Williams, 1985). Even in the much younger Holocene sediments from North Andros (5–6 ka), Pelle and Boardman (1988) report a complete absence of HMC. As expected, therefore, there is no evidence of elevated Mg_{xs} within modern water samples from Andros and Grand Bahama (Figure 2), strongly suggesting that stabilization of HMC is unimportant at present.

Dissolution of aragonite adds strontium and calcium in proportion to their molar ratio in aragonite (average Sr : Ca molar ratio 1.1×10^{-2} for Holocene sands from the central Bahamas; Budd, 1988). However, stabilization of aragonite to LMC (Sr : Ca molar ratio 1.7×10^{-3}; Budd, 1988) yields water with a molar ratio considerably in excess of 1.1×10^{-2}. Meteoric waters from North Andros plot around the line for aragonite dissolution, suggesting that they derive their calcium from dissolution of aragonite, rather than inefficient aragonite stabilization (Figure 5). The overall average $Sr_{XS} : Ca_{XS}$ is $(1.2 \pm 0.4) \times 10^{-2}$, but there are subtle differences between samples from different site types. With the exception of samples from fracture caves, cave waters generally have a lower $Sr_{XS} : Ca_{XS}$, perhaps indicating dissolution of both aragonite and LMC. The higher $Sr_{XS} : Ca_{XS}$ of shallow samples from the fracture caves is probably indicative of calcite precipitation (as inorganic cements or in calcareous algae growing in lakes along the fracture) rather than aragonite stabilization. This suggestion is supported by a progressive decline in Ca_{XS} as groundwater flows along the fracture system (Whitaker and Smart, 1997c). Precipitation of calcite cement as a result of degassing (see below) would also account for the much higher molar $Sr_{XS} : Ca_{XS}$ of the two samples from an observation borehole and a hand-dug well, relative to those from other (pumping) boreholes.

Beach (1982) reports a general decline in aragonite abundance with depth in cores from North Andros, and a similar trend is seen in Grand Bahama (Williams, 1985). Aragonite comprises up to half the carbonates at the surface, but is absent below depths ranging from 7·6 m to 19·8 m below the surface. Similarly, wall-rock samples from within the brackish lens of a fracture cave on South Andros (Whitaker and Smart, 1998) indicate aragonite is only present $(8 \pm 2\%)$ up to 10 m below
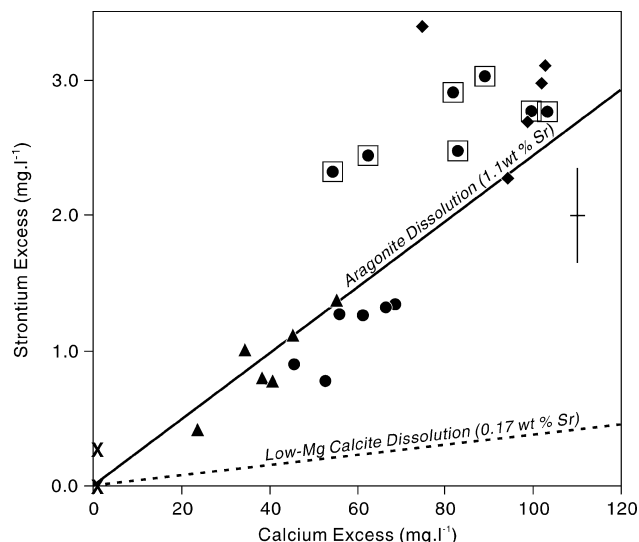

Figure 5. Variation of Ca_{XS} with Sr_{XS} in rainwater ($\times$), surface waters and drips (triangles) and lens water from boreholes and wells (diamonds) and caves (circles). Samples from fracture caves are boxed to differentiate them from cenote cave waters. Samples are compared with ratio expected from dissolution aragonite (solid line) and LMC (solid line). Stabilization of aragonite would produce waters highly enriched in Sr, which plot far above these lines. Cross shows representative analytical uncertainties

the water table. Although aragonite is volumetrically far less abundant than LMC, apparently sufficient of this more thermodynamically unstable phase is present to dominate carbonate dissolution. This suggestion is strongly supported by the observation that fresh water from pumped boreholes, large-diameter wells, horizontal cave systems and brackish water from depth in the bank-marginal fracture caves is equilibrated with respect to aragonite rather than calcite (Table I).

Water-controlled reactions

Water-controlled reactions include all reactions driven by changes in the P_{CO_2} of waters, which may occur as a result of CO_2 uptake or degassing, or by fluid mixing. As would be expected, both rainfall and runoff waters are equilibrated with respect to atmospheric P_{CO_2}. Rainfall contains a minor amount of calcium derived by dissolution of $CaCO_3$ aerosols from terrestrial dust, but much more calcium (a further 6·6 mg l^{-1}) is dissolved during runoff over the bare limestone surface. However, the residence times are short and waters do not reach equilibrium before infiltration occurs (Table I).

Despite the sparse nature, limited thickness and open structure of the predominantly organic soils in the Bahamas, wet-season soil CO_2 concentrations are elevated compared with the atmospheric concentration $((7.4 \pm 3.7) \times 10^{-3}$ atm), and increase with depth (Figure 3). As is generally recognized, soil CO_2, therefore, provides a major drive for bedrock dissolution (White, 1984). The North Andros soil CO_2 concentrations, however, are substantially lower than would be predicted from general climate–soil P_{CO_2} relationships, such as that of Brook *et al.* (1983). They are, however, similar to the value Brook *et al.* (1983) report for Florida

$(5.0 \times 10^{-3}$ atm), which is a major outlier from their general trend. For both the Bahamas and Florida this is probably due to desiccation limiting CO_2 production and rapid diffusive loss of soil CO_2 from the thin skeletal soils.

The elevated P_{CO_2} of water samples from banana holes and cave entrance drip waters indicates significant uptake of soil CO_2 by waters in the upper vadose zone. Calcium concentrations are also elevated compared with those in surface runoff, indicating that carbonate dissolution has occurred (Figure 6 and Table I). However, although waters from soil-filled banana holes have sufficient contact with the soil atmosphere to attain an elevated P_{CO_2} and remain close to aragonite equilibrium, vadose drips have partially degassed (indicated by their lower P_{CO_2}), resulting in aragonite supersaturation. This also accounts for the composition of shallow ephemeral pools sampled after rainfall, which have completely degassed. Chloride concentrations indicate progressive evapotranspiration of surficial waters occurs during dry periods, and significant redeposition of dissolved carbonate may occur in the soil as calcrete or as micritic crusts at the bedrock surface (Rossinski and Wanless, 1992). The ephemeral pool and cave drip-water samples are probably representative of such waters, having elevated Ca_{XS} and chloride concentrations, but also high calcite supersaturation.

There is a large range in the P_{CO_2} of samples from the freshwater lens depending on their source. Samples from cenotes have the lowest P_{CO_2} ($(2.4 \pm 1.5) \times 10^{-3}$ atm), whereas drainage boreholes have the highest ($(21 \pm 13) \times 10^{-3}$ atm). Most types of sample from the freshwater lens are equilibrated with respect to aragonite, indicating, as might be expected, that residence times in

the freshwater lens are sufficient for geochemical equilibration with the least stable aquifer mineral and that significant additional carbonate dissolution has occurred since recharge. Notable exceptions include samples from the unpumped observation boreholes, cenotes and the shallow samples from fracture caves, all of which are substantially aragonite and calcite supersaturated. These sites are also those that have the lowest P_{CO_2}. For fracture cave sites, the low P_{CO_2} of surface samples compared with those from depth strongly suggests loss of CO_2 by degassing from the open water surface, which then results in calcite supersaturation and carbonate precipitation (Figure 7). In the more restricted entrances of the fracture caves, this affects only the upper 2–3 m of the water column, but the large surface area of cenotes permits wind-driven mixing and extends degassing to much greater depths (some 15 m; Whitaker, 1992). The low P_{CO_2} of observation boreholes and hand-dug wells in comparison with pumped boreholes, their supersaturation with respect to aragonite and their reduced Ca_{XS} (Figure 7, Table I), therefore, also suggest loss of CO_2 by degassing. The North Andros data thus suggest both a substantial amount of dissolution within the subsurface and considerable potential for degassing to drive redeposition of this dissolved carbonate as cements near the water table.

Ground air within the vadose zone can be enriched in CO_2 relative to atmospheric values (Atkinson, 1977; Wood and Petriakis, 1984). In the Bahamas, potential sources of elevated CO_2 in ground air include downward diffusion of CO_2 from the surface soil, production by tree roots that penetrate the rock to depths of several metres, bacterial oxidation of organic matter washed down from the surface, and upwards diffusion of CO_2 from the freshwater lens. The similarity of the P_{CO_2} of waters sampled from the observation boreholes from the upper freshwater lens and banana holes which are in
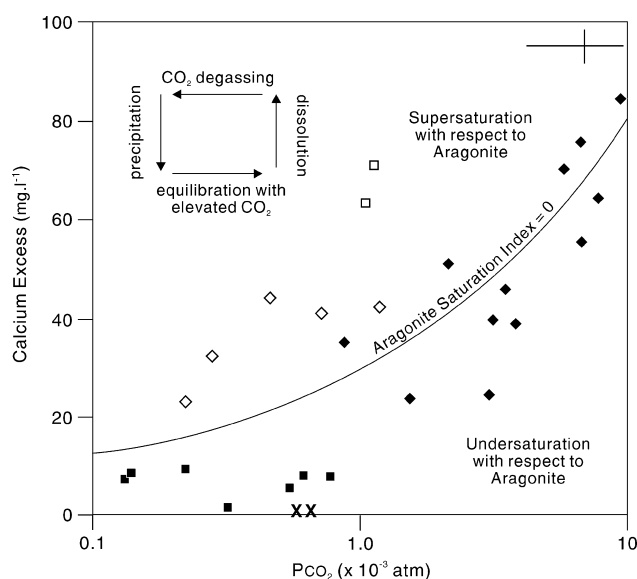

Figure 6. Relationship between P_{CO_2}, Ca_{XS}, and aragonite saturation in rainwater ($\times$) and surface waters, including runoff (black squares), shallow pools (white diamonds), banana holes (black diamonds) and cave drips (white squares). Schematic details some of the important processes influencing P_{CO_2} and Ca_{XS}. Cross shows representative analytical uncertainties. Schematic inset details effects of CO_2 uptake and degassing carbonate dissolution and precipitation and on P_{CO_2} and Ca_{XS}
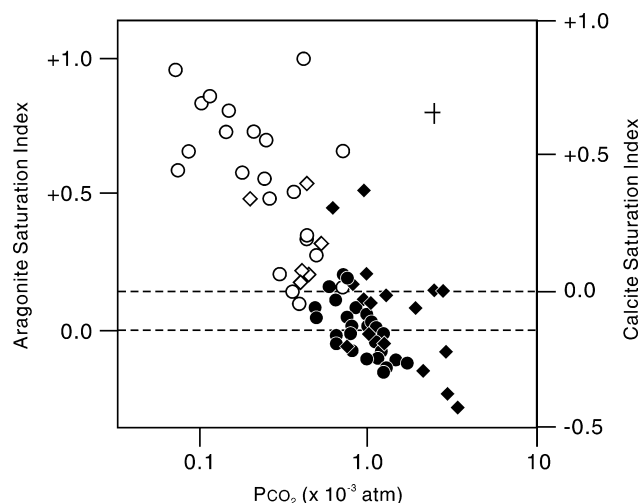

Figure 7. Relationship between P_{CO_2} and aragonite and calcite saturation in freshwater lens samples from degassed observation boreholes (white diamonds) and caves (white circles), and non-degassed pumping and drainage boreholes and wells (black diamonds) and caves (black circles). Cross shows representative analytical uncertainties

contact with the soil atmosphere ($(4 \cdot 0 \pm 1 \cdot 1) \times 10^{-3}$ atm and $(4 \cdot 5 \pm 2 \cdot 8) \times 10^{-3}$ atm respectively) suggests the presence of a body of ground air limiting degassing from the freshwater lens. In the wet season there is an increase in the P_{CO_2} of the shallow organic soils due to enhanced organic decomposition and root respiration. This may result in downward diffusion of CO_2 into the vadose zone. During the following dry season, desiccation of the soils will lower soil CO_2 and an upward loss of CO_2 from the vadose zone may occur. Such seasonal variations have been quantified by Hendry *et al.* (1999) for a sandy unsaturated zone. These surface-controlled CO_2 fluxes will be moderated by *in situ* production within the vadose zone and by degassing from the top of the freshwater lens. We do not have any indication of the relative magnitudes of these fluxes in the Bahamas at present; however, we believe that ground air may be an important control on the maximum P_{CO_2}, and thus the calcium excess of shallow waters in the freshwater lens.

Redox reactions

The much higher P_{CO_2} of waters from pumping boreholes and drainage wells ($(16 \pm 8 \cdot 3) \times 10^{-3}$ atm and $(21 \pm 13) \times 10^{-3}$ atm respectively) compared with those measured in soil air ($(7 \cdot 4 \pm 3 \cdot 7) \times 10^{-3}$ atm) strongly suggests the presence of a further source of carbonic acid, other than soil CO_2. Although comparably high P_{CO_2} values are observed in the thin mineral soils sometimes found in the base of banana holes, our field sampling suggests these are very uncommon. There is a significant concentration ($17 \pm 6 \cdot 7$ mg l^{-1} in pumping boreholes) of DOC in the freshwater lens, oxidation of which might generate additional carbonic acid. Much of this organic carbon probably originates at or near the bedrock surface and is washed underground by storm runoff, although a proportion will be derived from *in situ* decomposition of plant roots and bacteria. The high P_{CO_2} (and resulting elevated Ca_{XS}) of drainage borehole waters, which are derived directly from surface runoff, and their aragonite undersaturation, may thus be due to oxidation of surface-derived organic matter episodically washed into the borehole. Oxidation of organic matter within the freshwater lens may similarly explain the elevated P_{CO_2} of pumped borehole waters.

This suggestion is strongly supported by the sub-oxic nature of most freshwater lens samples ($40 \pm 25\%$ dissolved oxygen), indicating consumption of oxygen by aerobic decomposition of organic matter (Equation (2)). Furthermore, dissolved oxygen is more depleted in waters from fracture and drainage boreholes, which have elevated DOC concentrations, compared with other samples from the freshwater lens.

$$CH_2O + O_2 \leftrightarrow CO_2 + H_2O \leftrightarrow H_2CO_3 + H^+ \qquad (2)$$
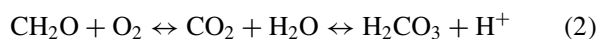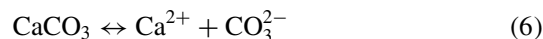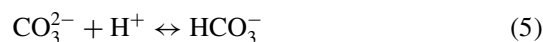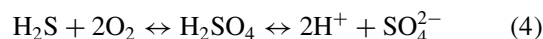
The widespread presence of sulphate depletion observed in samples from the freshwater lens (61% of all samples; Figure 8) indicates that organic matter oxidation

by sulphate reduction must also occur within microenvironments and/or at depth within the lens:

$$2CH_2O + SO_4^{2-} \leftrightarrow 2HCO_3^- + H_2S \qquad (3)$$

Within the common pH range of carbonate groundwater, this drives carbonate dissolution, as the impact of lowered pH due to partial dissociation of H_2S is greater than that of increased alkalinity (Morse and Mackenzie, 1990).

Sulphate depletion is significant in pumped boreholes, which draw their water from the full thickness of the freshwater lens (-21 ± 26 mg l^{-1} SO$_4$ $_{XS}$), and in brackish samples from the fracture caves (-61 ± 50 mg l^{-1} SO$_4$ $_{XS}$). As might be expected, the average sulphate depletion is highest in the samples from drainage boreholes (-71 ± 81 mg l^{-1} SO$_4$ $_{XS}$), which also have high DOC concentrations derived from direct runoff. Note, however, that there is a considerable range of sulphate depletions observed in these waters. Cenote waters, which have a considerably higher dissolved oxygen than other water types, are enriched is sulphate (43 ± 34 mg l^{-1} SO$_4$ $_{XS}$). One explanation may be the reoxidation of reduced sulphur species (Equation (4)). Further dissolution of calcium carbonate may thus occur (Equation (6)) in response to a decrease in carbonate ion concentrations (Equation (5)).

$$H_2S + 2O_2 \leftrightarrow H_2SO_4 \leftrightarrow 2H^+ + SO_4^{2-} \qquad (4)$$

$$CO_3^{2-} + H^+ \leftrightarrow HCO_3^- \qquad (5)$$

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-} \qquad (6)$$

Reoxidation of reduced sulphur species, including gaseous H_2S, requires their upward migration from the lower part of the lens where they are generated by anaerobic oxidation of organic carbon to the upper part of
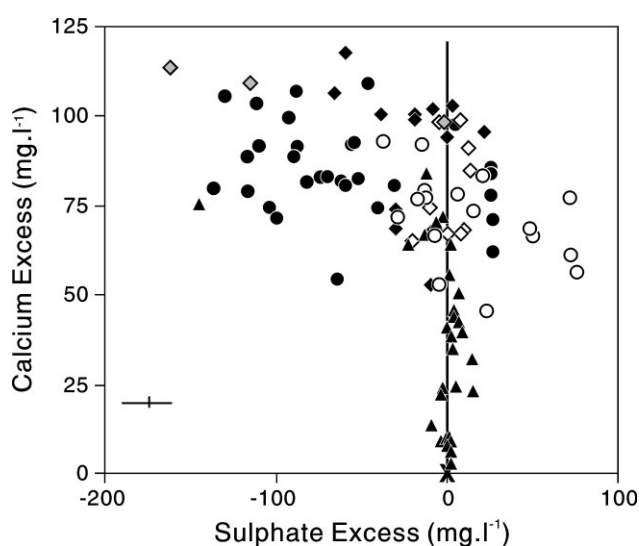

Figure 8. Variation in Ca$_{XS}$ with SO$_{4Xs}$ in rainwater ($\times$), surface waters (triangles), and freshwater lens samples from pumping (black diamonds) and drainage boreholes (grey diamonds), observation boreholes and wells (white diamonds) and cave waters both degassed (black circles) and non-degassed (white circles). Cross shows representative analytical uncertainties

the lens where waters are oxic. Because H_2S concentrations are orders of magnitude lower than that required for degassing, H_2S must diffuse upward driven by the concentration gradient established by the oxidation at the interface with oxic waters. Cavernous porosity extending to deeper anoxic waters could provide a path for more rapid diffusion (as diffusion rate is dependent upon cross-sectional area and the concentration gradient), but may also permit advective transfer. The location of oxidation of reduced sulphur species will vary temporally and spatially in a complex manner in response to variations in input and consumption of oxygen and organic carbon and to groundwater mixing (Whitaker and Smart, 1994). This suggestion is supported by the significantly higher sulphate excess (relative to other types of lens water) of samples from shallow hand-dug wells, which sample only the more oxic upper part of the freshwater lens, and the horizontal cave systems, which sample the distal parts of the meteoric flow system. H_2S may also diffuse upward from the underlying saline groundwaters and the fresh-water–salt-water mixing zone (Smart *et al.*, 1988; Whitaker *et al.*, 1994).

DISCUSSION

Meteoric diagenesis of continental carbonate terrains typically involves the alteration of older, mineralogically stable rocks that have been buried and uplifted, and thus fall within the telegenetic stage of Choquette and Pray's (1970) time–porosity rock cycle. These continental carbonate systems are dominated by the development of secondary karstic porosity. However, for many carbonates deposited in shallow waters, early meteoric diagenesis has a profound impact on the nature of porosity and permeability (Budd *et al.*, 1993; Whitaker and Smart, 1997a). In addition, diagenesis during this 'eogenetic' stage of the time–porosity cycle frequently exerts a significant control on burial compaction and diagenesis (Scholle and Halley, 1985). Where the elapsed time between deposition of the host carbonate and exposure is quite short, meteoric diagenesis differs from that of continental (telegenetic) carbonates in a number of important respects.

Aragonite and HMC present in many carbonate sediments on deposition are generally stabilized to LMC within thousands to tens of thousands of years in the meteoric realm (Vacher *et al.*, 1990). Hydrochemical studies of meteoric waters in Holocene carbonate islands (e.g. Budd, 1988; Anthony *et al.*, 1989) suggest that stabilization occurs throughout the freshwater lens, generating mouldic porosity and inter- and intra-granular cementation (Budd and Land, 1990). The role of mixed mineralogies in carbonate diagenesis is not limited to young sediments. In continental aquifers, the presence of dolomite, gypsum or anhydrite can similarly give rise to incongruent dissolution of dolomite and calcite precipitation (Plummer, 1977; Jones *et al.*, 1993). In the Pleistocene Lucayan Limestone of the northern

Bahamas, HMC stabilization appears to be complete, but minor amounts of aragonite remain (generally $\leq 10\%$; Beach, 1982, Whitaker and Smart, 1998). Waters tend to evolve to equilibrium with respect to the most soluble phase present, which is aragonite rather than calcite for the northern Bahamas, as was also observed in Pleistocene limestones in Bermuda (Plummer *et al.*, 1976). In Bermuda, and also in Holocene settings, in the Bahamas (Budd, 1988; McClain *et al.*, 1992), the $Sr_{XS} : Ca_{XS}$ data suggest that aragonite stabilizes to LMC. In contrast, the $Sr_{XS} : Ca_{XS}$ data for the Pleistocene of the northern Bahamas indicate that the dominant diagenetic processes is aragonite dissolution driven by water-controlled reactions with no concurrent precipitation of calcite.

Carbonate dissolution

Water-controlled reactions in continental carbonates are primarily driven by carbonic acid derived from respiration in the soil (White, 1984). This generates soil CO_2 concentrations up to two orders of magnitude greater than those in rainfall, particularly in terrains with significant siliclastic input (Palmer, 1991). The high P_{CO_2} will increase the solubility of calcium carbonate and cause substantial dissolution, which is greater in more humid areas which have more vegetation (Smith and Atkinson, 1976). CO_2 is derived from root and microbial respiration in the soil, but also from subsurface oxidation of *in situ* and infiltrated organic matter. Even in young metastable carbonates, some studies have found that rates of dissolution and cementation driven by CO_2 can far exceed those of mineral stabilization. Thus, in the Holocene sands of Great Exuma, Bahamas, CO_2 effects generate a highly reactive zone at the water table and in the upper 1·5 m of the phreatic zone (McClain *et al.*, 1992). These effects are also important in the vadose zone of Holocene sands and impact the rates of vadose recharge via changes in pore-size distribution (Brooks and Whitaker, 1997). In contrast to the humic protosols that develop ubiquitously on Holocene deposits in the Bahamas, soils developed on the Pleistocene limestones are limited in thickness and continuity. This limits soil CO_2 concentrations and may also facilitate degassing of CO_2 from the lens. The seasonal aridity of the climate also limits the potential of CO_2 generation in the soil.

On Andros Island, dissolution rates within the freshwater lens appear to vary in response to seasonal rainfall (Whitaker and Smart 1997a; Figure 4). Weekly data from a pumping well field indicate that storm runoff in October causes an immediate reduction in Ca_{XS}, as the base of the lens is depressed and the shallow wells draw from the fresher and less geochemically evolved upper lens. Ca_{XS} then increases steadily by some 25 mg l^{-1} between October and the end of the dry season in March. Superimposed on this seasonal cycle, individual stormy periods cause comparable but smaller scale perturbations in Ca_{XS}. The rapidity of these small-scale changes suggests they are caused by increased biogenic CO_2 in storm recharge waters. The gradual seasonal increase in Ca_{XS} may be

a signal of progressive oxidation of soil- and surface-derived organic carbon organic matter flushed into the lens during the rainy season. It is also possible that, because of the thinning of the lens during the dry season, pumping wells draw water from the deeper part of the lens, where Ca_{XS} is higher. Finally, the delayed response may reflect dissolution kinetics or aragonite and/or calcite within a complex natural water-rock system.

Our hydrochemical data demonstrate that within the freshwater lens the P_{CO_2} increases with depth, with the average P_{CO_2} of pumping borehole' waters four times that of shallow observation wells. This implies *in situ* generation of CO_2 within the freshwater lens and degassing from the water table into the vadose zone. Respiration from roots developed in top few metres of the lens (observed in several caves) may directly contribute CO_2 to the groundwater. However, probably the most significant source of CO_2 within the lens is the oxidation of organic carbon, most of which is probably generated at the surface or in the soil. DOC is a mobile refractory constituent in most groundwaters (Pettersson *et al.*, 1994). In aquifers where the water table occurs at shallow depth, dissolved oxygen tends to be very rapidly depleted due to oxidation of soil and surface-generated labile organic matter (Malard and Hervant, 1999).

In continental karst systems, redox potential reduces from highly oxidized recharge waters into the subsurface (e.g. Edmunds and Walton, 1983) in a manner that is critically dependent on groundwater flow path and rates. However, subsurface microbial activity is generally limited by the availability of organic carbon (Hiscock *et al.*, 1991). In the Bahamas, the thin soils and shallow vadose zone, with its well-developed secondary permeability network, permit rapid infiltration of surface waters. This leads to transport of significant amounts of dissolved (and particulate) organic matter into the lens. Concentrations of DOC in Bahamian lens waters are relatively high, averaging 14 ± 6.5 mg l^{-1}, with higher values not only for waters within cavernous voids with surface openings, but also for pumping boreholes. The latter average 17 ± 6.7 mg l^{-1}, which is more than an order of magnitude greater than the average of 1.2 mg l^{-1} DOC for groundwater DOC measured at 100 US sites in a range of aquifer types (Leenheer *et al.*, 1974). However, it is important to consider in any system that only a fraction of total organic carbon is volatile (estimated <10% of total organic carbon by Barcelona (1984)).

Progressive aerobic oxidation of soil- and surface-generated organic carbon appears to be an important process driving carbonate dissolution in the lens waters in the northern Bahamas. However, sulphate is also abundant because of mixing with saline groundwater (Table I); and where oxidation of organic carbon has consumed available oxygen, oxidation by sulphate reduction occurs, which drives carbonate dissolution. Oxidation of organic carbon was also invoked by McClain *et al.* (1992) to account for rapid and inefficient stabilization of HMC and aragonite in the vadose zone and upper freshwater lens in the southeastern Bahamas. Mineral transformation rates

are greatest at 0·5 m below the water table, corresponding to minimum sulphate concentrations, but Holocene carbonates at depth within the lens remain largely unaltered.

However, sulphate reduction is only half as efficient a driver for dissolution as aerobic oxidation. The residual dissolutional potential is realized by reoxidation of H_2S when dissolved oxygen levels become sufficiently elevated. This generates a concentration gradient along which H_2S produced by anaerobic oxidation can diffuse, and a zone of focused dissolution where reoxidation occurs. In continental aquifers, carbonate dissolution by oxidation of H_2S is recognized as important for speleogenesis in the vadose zone, e.g. the Guadalupe Mountains of New Mexico (Hill, 1990). However, Palmer and Palmer (2000) suggest that most caves in the Guadalupes are phreatic in origin, and the dominant sink for H_2S is phreatic dissolution driven by sulphur-oxidizing bacteria beneath the water table (Engel *et al.*, 2004). In such settings, dissolution by oxidation of H_2S relies upon sulphate derived from reduction of gypsum and anhydrite at depth by hydrocarbon-rich fluids. However, in coastal aquifers and islands, mixing with underlying seawater, which in the Bahamas commonly occurs through the entire thickness of the lens, provides a ready source of sulphate. Given that most aquifers are sub-oxic or anoxic at depth (Malard and Hevant, 1999), dissolution in coastal carbonates is then dependent upon availability of organic carbon rather than dissolved oxygen.

At present, the shallow vadose zone across much of the northern Bahamas permits surface-derived organics to reach the freshwater lens, where they are an important drive for dissolution. Depositional relief on the surface of many active carbonate platforms is similarly low. As a consequence, minor changes in relative sea level can cause exposure of extensive areas of the platform, but generate only a limited vadose thickness. Thus, oxidation of surface- and soil-generated labile organic carbon may be an important drive for dissolution within the freshwater lens in many oceanic carbonates under such conditions. However, during glacio-eustatic sea-level low-stands the overall platform relief is much greater (>60–100 m). Physical filtration and bacterial oxidation within the thick vadose zone are both likely to reduce input of organic carbon to the lens significantly, and thus oxidation processes may be considerably less important.

This exhaustion of diagenetic potential as waters percolate through a thick vadose zone accords with the petrographic observations of Melim (1996), which suggest, at core scale, a diagenetically inert freshwater lens during sea-level low-stands. In continental carbonates, uplift and fluvial dissection can give rise to significant relief, and vadose zone thicknesses may similarly be substantial. However, in carbonate aquifers with well-developed secondary permeability and significant allogenic recharge, transmission of recharge waters to the water table is generally rapid. Even in the Pleistocene limestones of Guam, where tectonic uplift has generated a vadose zone up to

180 m thick and autogenic recharge predominates, some 20–40% of recharge reaches the water table within 48 h (Jocson *et al*., 2002). Phreatic dissolution by oxidation of surface- and soil-generated labile organic carbon also appears to be important in this aquifer, and by implication more widely in karstified carbonate platforms during sea-level low-stands (Whitaker *et al*., 2006).

Microorganisms clearly exert an important influence on carbonate dissolution. Bacterial dissolution of carbonates probably involves multiple mechanisms, including organic acids and amino acids, and the effect of the acidic nature of the cell wall (McMahon and Chapelle, 1991; Barker *et al*., 1998) as well as production of CO_2 and reduced sulphur species. Thus, in addition to the macroscale influence of microorganisms on groundwater geochemistry, and hence water–rock equilibria, there are also microscale interactions where attached organisms locally perturb water–rock equilibria (Bennett *et al*., 2000). In this study we have adopted the traditional geochemical view that the chemical composition of groundwater sampled from boreholes or caves is representative of the hydrochemistry of the environment (non-cavernous or cavernous) from which they are sampled. This enables us in a subsequent paper to model and budget water–rock interaction within the meteoric water system (Whitaker and Smart, 2007). However, it important to recognize that this approach, although working well for abiotic reactions, cannot adequately take account of microscale microbial processes where the chemistry of microenvironments may differ substantially from the bulk signature (Bennett *et al*., 2000).

An additional process not explicitly discussed here is mixing, which can drive carbonate dissolution or precipitation dependent upon the nature of waters mixed. This can drive dissolution at depth within continental carbonate aquifers (Bögli, 1964; Kaufmann, 2003). Mixing between meteoric water and seawater is a characteristic feature of eogenetic carbonates. Dissolution due to mixing is of undisputed importance at the fresh-water–salt-water mixing zone that underlies the lens (Wigley and Plummer, 1976). Hydrochemical studies in the Bahamas have shown that significant dissolution occurs in the fresh-water–salt-water mixing zone, which is in part driven simple mixing, but at least as important are organically mediated processes (Smart *et al*., 1988; Bottrell *et al*., 1991; Whitaker and Smart, 1997c). The latter are focused within the fresh-water–salt-water mixing zone due to the density contrast between fresh and saline groundwater. In their 'flank margin' model for caves development in eogenetic carbonates, Mylroie and Carew (1990) suggest that dissolution is particularly active around the island periphery. This is attributed to the coincidence of fresh-water–salt-water mixing and mixing at the water table between infiltrating waters recharging through the vadose and phreatic waters. The chloride budget developed herein for the northern Bahamas clearly shows that meteoric waters of contrasting chemistries mix within the vadose zone, at the water table and throughout the lens, but from the field data it is not possible to isolate the role of mixing from other processes. The significance of this mixing is explored further for the meteoric system of the northern Bahamas using geochemical modelling in our companion paper (Whitaker and Smart, 2007).

Carbonate precipitation

Although dissolution is clearly an important process in the meteoric system of Pleistocene islands of the northern Bahamas, the increasing Ca_{XS} of the evolving meteoric groundwater is the net product of carbonate dissolution and precipitation. Total dissolution may be considerably higher than suggested by Ca_{XS} if it is offset to some degree by LMC precipitation. Precipitation may occur in the subsoil and at or just above the water table by evaporation and/or degassing. As in the case of subsurface oxidation of organic carbon, both these processes will be affected by vadose thickness.

Evaporation is an important mechanism driving precipitation of meteoric cements in the northern Bahamas under the present high-stand conditions. The ratio of subsurface evapotranspiration to effective recharge indicates that evaporation increases the concentration of groundwater by a factor of approximately 2·4. However, this will only drive significant precipitation if evaporation is preceded by equilibration with elevated CO_2 and carbonate dissolution. This suggests two environments where evaporative cementation may be important: at the bedrock surface beneath the soil and at (or slightly above) the water table. Subsoil cementation has undoubtedly been important in the development of case-hardening observed over the present and buried exposure surfaces (Beach, 1982; Rossinski and Wanless, 1992). However, the low moisture retention capacity and sparse distribution of the dominantly humic soils is likely to limit this process beneath modern soils developed on Pleistocene bedrock. The thin vadose zone means that a significant proportion of the total evapotranspirative demand may be met directly from the water table and the lower part of the vadose zone within the capillary fringe.

Degassing of CO_2 at the water table lowers the P_{CO_2} of lens-top waters and can thus also drive significant precipitation. It also generates a body of vadose ground air with an elevated P_{CO_2}. The P_{CO_2} of this ground air is controlled by the rate of degassing of CO_2 from the lens (probably slow) and the soil CO_2, which limits the maximum ground-air P_{CO_2}. There may be a dynamic interaction between soil and ground air, with soil CO_2 moving downward during the wet season when concentrations in soil gas are high relative to those of ground air, and being lost by upward diffusion during the following dry season. Cementation at and just above the water table due to degassing is also affected by the oxidation of soil- and surface-generated organic carbon within the freshwater lens. This generates the upwards CO_2 gradient within the lens that maintains CO_2 degassing at the water table. Where the vadose zone is thin, this process may be augmented by cementation driven by evaporation from the water table.

Finally, dissolution and precipitation reactions are likely to affect different pore types. Dissolution will be focused within larger pores, where vadose recharge, mixing and input of surface-derived organic carbon are all likely to be greatest. In contrast, cements precipitated by degassing and evaporation will preferentially occlude smaller pores with a higher moisture retention capacity (Brooks and Whitaker, 1997). However the $Sr_{XS} : Ca_{XS}$ ratio of groundwater does not suggest precipitation of significant volumes of calcite cements. Any reduction in calcium concentration due to cementation must be off-set by addition of calcium from dissolution of calcite rather than aragonite. This has two important implications. First, any dissolution and consequent cementation would be expected to occur in local environments where all aragonite has already been stabilized, most likely in the subsoil and possibly at the water table. Second, these environments are not adequately sampled by this field study, as waters should be distinct in equilibrating with respect to calcite, not aragonite. Observation well waters appear considerably supersaturated with respect to calcite, and the $Sr_{XS} : Ca_{XS}$ of an observation borehole water (together with fracture surface waters) suggests calcite precipitation. Indeed, calcite was observed encrusting nylon string used to suspend experimental weight-loss tablets within observation boreholes (Whitaker and Smart, unpublished data). Given the challenges in sampling these waters, this will subsequently be explored further using geochemical modelling (Whitaker and Smart, 2007).

CONCLUSIONS

Our hydrochemical investigations indicate that the processes governing early meteoric diagenesis in Pleistocene islands of the northern Bahamas differ in their relative importance, both from those in younger Holocene islands and from older continental carbonate terrains. Meteoric waters equilibrate with minor amounts of aragonite present within the limestones, rather than calcite. However, water-controlled dissolution reactions, rather than mineral-controlled stabilization reactions, dominate diagenesis. Dissolution is organically mediated, and its distribution reflects in part the discontinuous cover and thin skeletal organic nature of the soil, and in part the very shallow depth of the vadose zone.

Much of the rainfall occurs in heavy storms, which runoff rapidly, limiting subaerial dissolution on rock surfaces. Both organic matter and recharge waters are focused into, but only partially retained within, small-scale topographic lows. This generates a locally more aggressive environment with elevated soil-gas P_{CO_2}, at least in the summer wet season, and provides an important mechanism for generation of differential relief. Recharge waters flow rapidly through the shallow vadose zone, transporting surface- and soil-generated organic carbon to the water table. The subsequent oxidation of this organic carbon provides an important drive for

subsurface dissolution. As a result, the freshwater lens is sub-oxic, with sulphate reduction in microenvironments and at depth, and oxidation of H_2S generates further focused acidity. However, at the water table and beneath the soil, degassing of CO_2 and evaporation both increase carbonate saturation and may drive precipitation of calcite cements. Dissolution and precipitation reactions are likely to affect different pore types, with dissolution within larger pores, which focus fluxes of water, CO_2 and organic matter, and cementation of smaller pores with a higher moisture retention capacity.

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