CONDENSATION CORROSION IN CAVES ON CAYMAN BRAC AND ISLA DE MONA

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Many speleothems in caves on Cayman Brac and Isla de Mona have suffered considerable dissolution. It is suggested that this is a consequence of condensation corrosion rather than of aqueous flooding of the entire cave. A program of temperature and relative humidity measurements during the rainy seasons showed that the entrance zones are areas of comparatively large diurnal variation where condensation from warm air onto cooler walls may occur. Artificial condensation was induced using ice bottles: chemical analysis of the condensation waters determined that they were generally undersaturated with respect to calcite and/or dolomite but that this changes over space and time. Gypsum tablets were suspended inside three sample caves on Cayman Brac and one on Isla de Mona for 16 and 13 months, respectively. At the end of this period, tablets close to the entrances and to the floor were found to have undergone considerable dissolution; this could only have been the result of condensation corrosion

Where water condensing onto cave walls in soluble rocks is undersaturated with respect to the mineral (calcite, dolomite, gypsum, etc.), the potential exists for dissolution to occur; the process is termed "condensation corrosion" (Ford & Williams 1989: 309). It may create some characteristic speleogen features. The most widespread are "air scallops" (Hill 1987: 89), shallow, rounded recesses on walls and ceilings, with lengths ranging from decimeters to several meters. Less common are corrosion channels in ceilings or furrows in floors where condensation water has dripped from above. "Punk rock" (Hill 1987: 89; cavernous weathering with some decomposition of the inter-cavern partitions) may be seen where particularly corrosive air attacks bedrock of heterogeneous solubility. In hydrothermal caves, such speleogens are often large and easily recognized; this is because of the large temperature differences between the thermal water sources of vapour and the bedrock, and also because of greater CO_2 partial pressure and/or the formation of H_2SO_4 from discharged H_2S, both of which will increase the aggressivity of the condensation water. In other categories of caves condensation water is normally less abundant and probably also less aggressive: the resulting speleogens are readily confused with those caused by other processes, primarily phreatic dissolution (Cigna & Forti 1986). This has led to much misinterpretation in some past cave genetic studies.

Small holokarstic oceanic islands in young rocks are ideal sites to study the development of condensation corrosion features. They constitute closed systems without strong external influences: the only fresh water derives from condensation or infiltrating rain because areas above the caves are too small to support surface streams, and the comparatively high primary porosity of the rock dampens the amplitude of any rain floods underground. As a consequence, prolonged flooding (establishing or re-establishing phreatic hydrodynamic conditions) will only be the result of a relative rise in sea level that is due to eustatic or tectonic effects.

The climate in caves is often described as being constant, but in reality this is found only in deep interiors where there is minimal interaction between the cave and the outside environment. Condensation will occur where the air is cooled below its dew-point temperature by mixing with colder air or through contact with colder walls. Condensation should be negligible in cave interiors that have stable temperatures close to the mean annual exterior temperatures of their region and, in humid regions, relative humidities of ~100%. However, it might be observed in the entrance or transition zones. For nearly horizontal caves with single entrances (broadly, the conditions found on Cayman Brac and Isla de Mona) the climate model available is one developed by Wigley and Brown (1971). They modeled the entrance and transition zone for three seasonal conditions - summer, winter and transitional periods (fall or spring) - in humid temperate and alpine climates (i.e. those with warm summers and cold winters). The longitudinal temperature distribution was calculated by:

$$T_{mean} = T_a + (T_0 - T_a)\, e^{-X} + (L/c)(q_0 - q_a)Xe^{-X} \qquad (1)$$

where T_{mean} is the mean temperature of the air in the cave (°C), T_a is the wall temperature (°C), T_0 is the temperature of the air entering the cave (°C), L is the latent heat of vaporization provided that the thermal diffusivity of the wall is much less than that of the air (J/kg), c is the specific heat (at constant pressure) of the air (J/kg/K), q_0 is the specific humidity of the air entering the cave (g/kg), q_a is the specific humidity at the wall (g/kg) and X is a non-dimensional length defined by

$$X = x/x_0 \qquad (2)$$

where x is the distance measured from the entrance (m). In caves external temperature and humidity fluctuations decay with increasing penetration distance into a cave. This decay, or damping of specific humidity/temperature in the absence of moisture is characterized by a relaxation length (or "e-folding" length), x_0. The latter is determined by the Prandtl, Reynolds and Nusselt numbers, which are non-dimensional groups frequently used in heat transfer and fluid mechanics. Eventually, x_0 only depends on the radius of the cave and the flow velocity as defined by Wigley & Brown (1971):

$$x_0 = 36.44\, a^{1.2} V^{0.2} \tag{3}$$

Accordingly, the longitudinal humidity distribution was calculated by

$$q_{mean} = q_a + (q_0 - q_a)\, e^{-x} \tag{4}$$

Wigley and Brown (1971) suggest that equilibrium is reached in about 5 x_0 to 6 x_0 from the entrance of the cave. This model is for the most ideally simple case: a pipe of circular cross-section and fixed radius. Where the cross-section is tapered or irregular with many constrictions, the relaxation length remains x_0 but it is no longer a constant. Most coastal caves show either taper or irregularities with constrictions or both, and will thus have a changing x_0.

During the winter and the transition seasons evaporative cooling will occur for all x where T_a is greater than the outside dew-point temperature. In the summer months the situation is reversed and condensation occurs on the cave walls, increasing the air temperature (Wigley & Brown 1971).

The Caribbean region has a tropical marine climate where seasonal temperature variations are small compared to the diurnal variations that occur. This permits measurement of the Wigley-Brown parameters within a short period of time: daytime corresponds with the summer situation and nighttime with the winter situation. The configuration of the caves on Cayman Brac and Isla de Mona is also relatively simple: large entrances give access to large rooms close to coastal cliff faces, from which smaller passages radiate modest distances into the rock. The caves show many of the types of speleogens associated with condensation corrosion. They are also richly decorated with vadose speleothems, many of which are dry and show signs of dissolution, indicating that they are no longer growing. Often a corrosion pocket will cut across both bedrock and speleothem in a uniform facet. Since many caves are well above sea level at present, flooding is unlikely to have occurred. Condensation corrosion is believed to have been the cause of the later phases of dissolution of the cave walls and speleothems. Analysis of the cave microclimate can help establish whether the present-day conditions are suitable for condensation corrosion and if the process is still continuing.

The objectives of the study reported in this paper were to investigate the microclimatology and water chemistry of selected caves on Cayman Brac and Isla de Mona to determine whether significant condensation corrosion could be occurring there at present.

STUDY AREAS

Cayman Brac (19°43'N 79°47'W) and Isla de Mona (18°05'N 67°55'W) are very similar in appearance, size and geology (Fig. 1). Both islands have cores of Tertiary (mainly Miocene) carbonates. Their coastlines are vertical cliffs partially fringed by narrow coastal plains of Pleistocene limestones. The bedrocks are very pure because the islands are located far from any mainland or continental shelves where rivers might supply clays or sands. The Tertiary strata are extensively dolomitized and have been tectonically uplifted in the past, tilting the islands. Isla de Mona was uplifted 20 m in the south, increasing to 90 m in the north. Cayman Brac displays zero uplift in the west, rising steadily to 45 m at the east end. The presence of horizontal Pleistocene coastal plains and marine erosional notches in the cliffs above them indicates that both islands have been tectonically stable since at least the last interglacial period (oxygen isotope substage 5e, 125,000 years BP; Woodroffe *et al.* 1983; Taggart & González 1994; Frank *et al.* 1998).

Hydrological conditions on both islands are similar and relatively simple. There are no stream channels. Infiltrating rain water creates shallow freshwater lenses which float on top of denser saline water.

The majority of the cave entrances are in the coastal cliffs. The caves are confined to narrow zones behind them, extending inland no more than 50 m from the cliffs on Cayman Brac

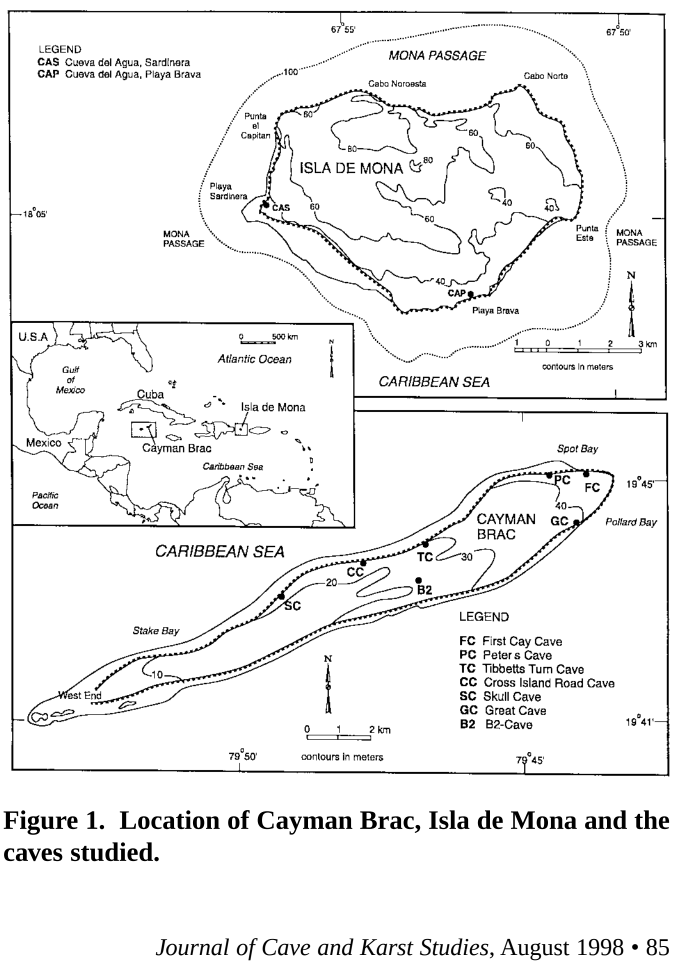


Figure 1. Location of Cayman Brac, Isla de Mona and the caves studied.

and 250 m on Isla de Mona. This suggests that the caves developed around the edges of the islands and were opened up by cliff recession. There are two spatially distinct groups of caves on Cayman Brac: "notch caves" which are located at, or 1 to 2 m above, the +6 m, stage 5e marine notch, and upper caves with entrances at irregular elevations more than 2 m above the notch. The caves of Isla de Mona and the notch caves on Cayman Brac fit the flank margin cave development model, according to which caves form at the discharging margins of the freshwater lens prior to uplift (Mylroie *et al.* 1994; Mylroie & Carew 1990). The upper caves on Cayman Brac are also interpreted to have formed in the phreatic zone around the margins of the island, but they appear to have been influenced by pre-existing structures in the bedrock to a greater extent. The caves on Isla de Mona are bigger than those of Cayman Brac, which might be partially due to the different configuration of the islands; Isla de Mona is larger in area and quite circular, whereas Cayman Brac is very elongated. Island shape greatly influences the extent and thickness of the freshwater lenses and, thus, the magnitude of the formation of flanking caves. On the plateaus above them, the karst features are limited to dissolution pits, sometimes associated with small cave chambers or shafts.

The sample caves on Cayman Brac include First Cay Cave (FC), Peters Cave (PC), Tibbetts Turn Cave (TC), Cross Island Road Cave (CC) and Skull Cave (SC) located on the north side of the island, Great Cave (GC) on the south side and B2-Cave (B2) on the plateau (Fig. 1). FC and GC are developed in the Brac Formation (late Early Oligocene) - FC being in limestone and GC in dolostone: all other caves in the sample are formed in dolostones of the Cayman Formation (Lower to Middle Miocene; Jones *et al.* 1994). CC, SC and GC are notch caves. They have less speleothem growth than the upper caves. In general, the speleothems far inside the caves are still growing, whereas those closer to the entrances show increasing amounts of corrosion. In FC, speleothem dissolution is very clearly zonal: in the entrance, speleothems have been corroded to the point where their original shape can no longer be recognized; this is succeeded by a zone of corroded speleothems with still recognizable shapes and finally, deep inside the caves, there are actively growing speleothems (Fig. 2). Because of its greater size and this very clear zonation, FC was studied in more detail than the other caves.

On Mona, Cueva de Agua, Sardinera (CAS), is located in the Isla de Mona Dolomite (Late Miocene to Early Pliocene) in the southwest corner of the island (Fig. 1). Cueva de Agua, Playa Brava (CAP) is at the southeast corner (Fig. 1) and has a more complicated geologic history. Initially, a large cave developed in Lirio Limestone (Miocene) which was then filled with reef rubble of Pleistocene age that became lithified. A relative sea level change submerged the site and the present day cave was dissolved in both the Pleistocene rubble and the Miocene limestone (Frank 1993).

The climate on the islands is of the tropical marine type with very small seasonal temperature variations. Annual precipitation averages 1025 mm on Cayman Brac and 800 mm on Isla de Mona and is concentrated mainly in the summer months. Proximity to the sea causes comparatively high relative humidity at all times in the caves.

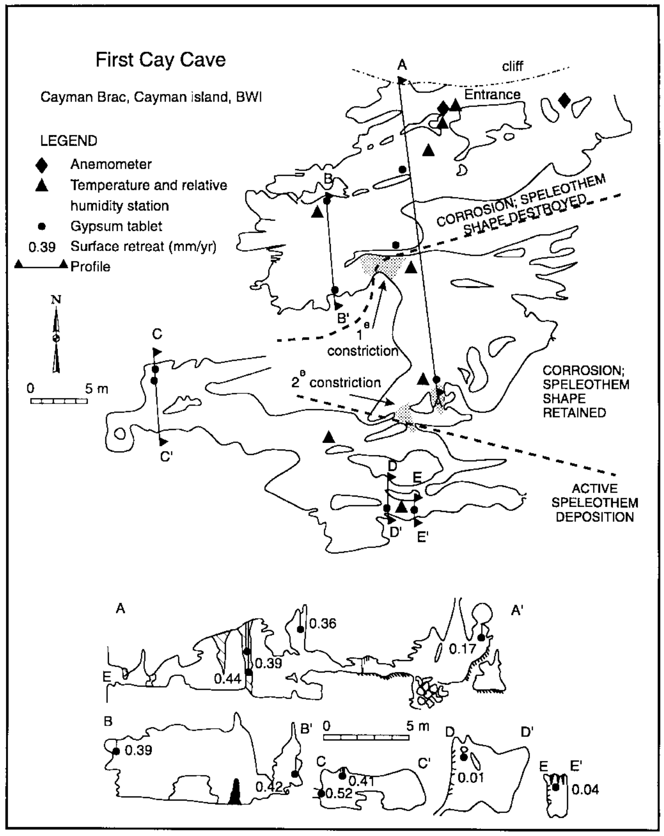


Figure 2. Zonation of speleothem corrosion, meteorological instrument set up, location of gypsum tablets with their surface retreat rates, First Cay Cave, Cayman Brac.

METHODS OF STUDY

Field measurements were taken during two rainy season months (May 1994 and September 1995) in seven caves on Cayman Brac, and in June 1994 in two caves on Isla de Mona (Fig. 1).

TEMPERATURE AND RELATIVE HUMIDITY

Temperature and relative humidity profiles were taken at five caves on Cayman Brac (FC, PC, TC, GC and SC) from the entrances inward, twice daily (~10:00 hr and ~17:00 hr). Wet and dry bulb temperatures were measured with a T-type thermocouple to a resolution of 0.1 °F. The measurements were taken at three heights: 5 cm above the floor, midway between floor and ceiling and about 5 cm below the ceiling (in very high rooms, readings were made at 3.5 m above the floors). The Fahrenheit scale was used to increase the precision of calculation of relative humidity and later converted to degrees Celsius.

Temperature and relative humidity maps were constructed for FC, PC, SC and GC using one-time temperature readings at the three heights at sufficient points to cover all areas of the caves satisfactorily. Due to time limitations, only simpler line (transect) profiles could be constructed for CAS and CAP on Isla de Mona.

In First Cay Cave a more elaborate system was installed, consisting of two anemometers, two wind vanes, and two sets of dry bulb-wet bulb thermocouples connected to a datalogger (Fig. 2). This permitted continuous measurements during the period, September 12 - October 5, 1995. The wind measurements were taken at the two main entrances to the cave, and the psychrometric temperature measurements at 2 m (entrance) and 8 m (middle of the entrance room) inward from the cliff line.

Relative humidity was calculated from the equation:

$$RH = \frac{m\cdot\exp\left\{\dfrac{aT_w}{T_w+b}\right\} - 6.6\cdot10^{-4}\left(1+1.5\cdot10^{-3}T_w\right)\cdot P\cdot\left(T_d-T_w\right)}{m\cdot\exp\left\{\dfrac{aT_d}{T_d+b}\right\}} * 100 \quad (5)$$

where RH is relative humidity (%), T_w is wet bulb temperature (°F), T_d is dry bulb temperature (°F), P is barometric pressure (kPa), and m, a and b are empirically-derived coefficients optimized for the 0 to 50°C temperature range (m = 0.61121, a = 17.368 and b = 238.88; Boudreau 1993).

Air density was calculated by the formula of Cigna and Forti (1986):

$$k = [3.484(P - RH\cdot P_w)\cdot(273.15 + T)^{-1}] + RH\cdot k_w \quad (6)$$

where k is air density (kg/m^3), P is atmospheric pressure reduced at 0°C (kPa), RH is relative humidity (1 = for 100%), P_w is vapor partial pressure reduced to 0°C (kPa), T is air temperature (°C) and k_w is the vapor density (kg/m^3).

WATER CHEMISTRY

Conductivity was measured with a YSI Model 33 S-C-T (salinity-conductivity-temperature) meter. Measurements were converted to specific conductivity at 25°C using the function:

$$SpC(25°) = 1.81\cdot SpC(T)\cdot e^{-0.023T} \quad (7)$$

where SpC (T) is the measured conductivity at T°C, T is the temperature (°C). The equation is derived empirically from karst water data in Pennsylvania and is valid between 0 to 40°C (White 1988).

pH was determined with an ATC pH meter with an accuracy of 0.01 pH. The meter was standardized against buffers pH = 4.00 and pH = 7.00 before each series of measurements. Temperature was taken with a dual-sensor digital thermometer having a resolution of 0.1 °C and an accuracy of $\pm$ 1.0 °C in the range -10 to + 50 °C. Alkalinity, calcium and total hardness were measured using a Hach Digital Titrator. The saturation indices for calcite and dolomite, the partial pressure of CO_2 with which the water would be in equilibrium and ion balance errors were calculated using the program WCHEM3.

No water analyses were made on Isla de Mona. On Cayman Brac, the caves are quite dry in general and there are few drip sites. Only during heavy rains were the drip rates fast enough to allow satisfactory water collection; on these occasions samples were collected from as many sites as possible.

Condensation was induced by chilling the cave air. Half-gallon plastic milk containers that had been filled with water and then frozen solid were used as condensers. The condensation water was collected in 250 ml sample bottles, via funnels with small apertures to reduce evaporation. In each sample run three bottles were suspended in the selected cave for a minimum of six hours, by which time all the ice had melted; one was placed close to the entrance, one halfway and one close to the back of the cave. A total of 12 condensation experimental runs were completed in six different caves (B2, CC, GC, PC, SC and TC), including up to three repeat runs at the same positions in a given cave on separate days.

GYPSUM TABLETS

Gypsum tablets of known weight were suspended on nylon fishing line away from direct drip sites and walls for 16.5 months (May 1994 to October 1995) in four caves on Cayman Brac (B2, FC, PC and TC) and for 13 months (June 1994 to July 1995) in CAS, Isla de Mona. The tablets were dried overnight at 60°C in an oven before weighing prior to and after exposure. In each cave they were so located as to form a profile perpendicular to the cliff, from the entrance inward (Fig. 2). On each island one sample was retained unexposed to be used as a reference sample. The gypsum was >90% pure $CaSO_4\cdot2H_2O$ donated by the Canadian Gypsum Co., Hagersville, Ontario, Canada. Surface retreat rates were calculated by:

$$r = s\cdot10^{-3}\cdot\rho^{-1}\cdot\varepsilon\cdot365 \quad (8)$$

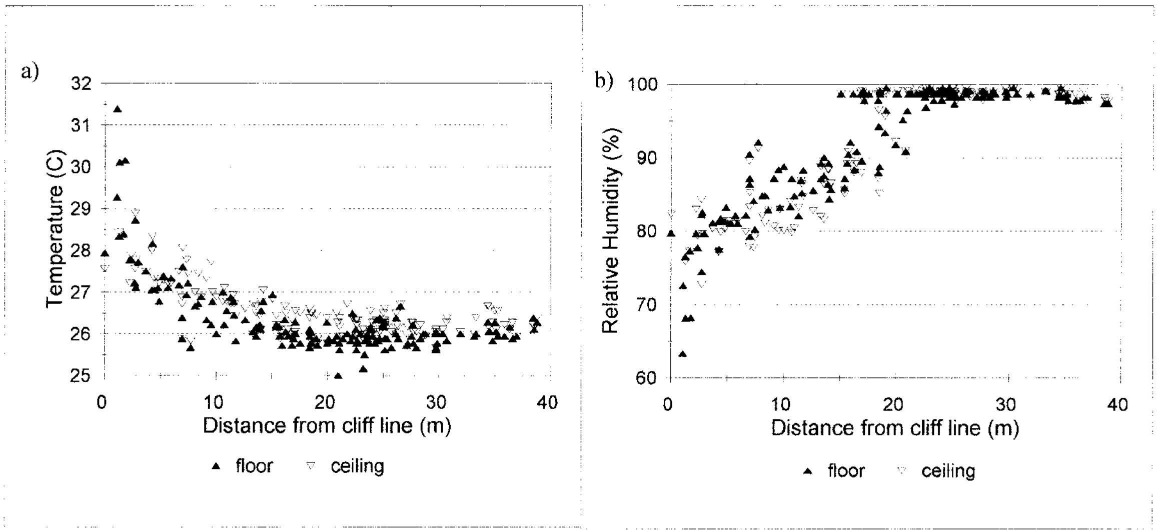
where r is surface retreat rate (mm/a), s is solubility of gypsum (2.5 g/L), ρ is density of gypsum (2.35 g/cm^3) and ε is the amount of condensation water accumulated on the surface in one day, expressed as the water film thickness this amount of condensation water would form on the surface of the tablet (mm/day), given by

$$\varepsilon = W\cdot(A\cdot t)^{-1}\cdot10 \quad (9)$$

where A is surface area of the gypsum tablet (cm^2), t is duration of exposure (days) and W is amount of water in thermodynamic equilibrium with gypsum that is needed to dissolve the observed weight loss (cm^3) i.e.

$$W = (w_1 - w_2)\cdot s^{-1}\cdot10^3 \quad (10)$$

Figure 3. Temperature (a) and relative humidity (b) profiles in First Cay Cave, Cayman Brac, measured in May 1994.



where w_1 and w_2 are weight before and after exposure respectively. The minimum amount of condensation water needed per day (C) to dissolve the observed weight loss is thus:

$$C = W/t = \varepsilon \cdot 10^3 \cdot A \qquad (11)$$

RESULTS AND DISCUSSION

AIR TEMPERATURE AND RELATIVE HUMIDITY

LONGITUDINAL PROFILES

A constant climate with a temperature of 25.5 to 26.5°C on Cayman Brac and 25 to 25.5°C on Isla de Mona and a relative humidity of 95% to 100% was reached deep inside the larger caves and behind constrictions (Fig. 3). In the smaller caves, the relative humidity did not reach its stable level, but rather remained between 90% and 95% even behind some constrictions (Fig. 4). Both on maps and profiles, it is clear that quite short constrictions in cave passages can substantially reduce the penetration of outside climatic effects.

The entrance zone was the area most affected by the outside climate. The penetration of external influences was greatest near the ceiling and varied with the cave configuration and the temperature and relative humidity differences between the two environments (Fig. 4).

VERTICAL PROFILES

On most occasions, the temperature near the ceiling was greater than the floor temperature. This temperature difference was highest in the entrance zones, which usually consist of large rooms where the air can circulate most readily (Fig. 4 & 5).

During the periods of study, outside daytime temperatures were higher than the inside temperature. Air was drawn into the caves along the ceilings, was cooled down in the interiors and drained out again along the floors. Because warmer air can contain more water vapour, the air along the ceilings had lower relative humidities than that at the floors (Fig. 5). In areas with poor air exchange (e.g. deep inside the cave or behind constrictions), the relative humidity was either stable up the vertical profile or increased slightly from the floor to the ceiling.

According to the Wigley-Brown model temperature and relative humidity equilibrium will be attained after 5 x_0 to 6 x_0: thus, x_0 was calculated by dividing the distance required to arrive at equilibrium in the sample caves by six. On Cayman Brac average x_0 = 5 m; however, because of the changing cross-section of the passages in these caves, it varies with distance from the entrance, as illustrated in detail in figure 4. As noted, the Wigley-Brown model was developed for a simple pipe of constant radius. The configuration of the caves on Cayman Brac and Mona is that of series of chambers/high passages separated by constrictions. This configuration is an extreme test of the Wigley-Brown model. Values of x_0 for these caves calculated according to the model are at least one order of magnitude higher than the actual measured average. This discrepancy is most likely explained by the presence of the constrictions. The implication is that the basic Wigley-Brown model needs to be considerably modified into a "chamber-constriction-chamber" model - which was not the objective of this paper.

A quite different pattern of air circulation can be established in these caves by convective processes. Convection may occur if denser air can accumulate initially at the ceilings rather than at the floors and then settle downwards, setting up a vertical cellular circulation. In general this will correspond to cooler air flowing along the ceilings. This pattern is not expected to occur in every cave and is temporary and superimposed on the general circulation described above. In First Cay Cave this situation tended to occur during the nights and early mornings and was recorded at distances up to 30 m from the entrance. It is a consequence of the daytime "hot" general circulation inward at the ceiling and outward along the floor being sustained into the night by inertia. In Peters Cave, one-

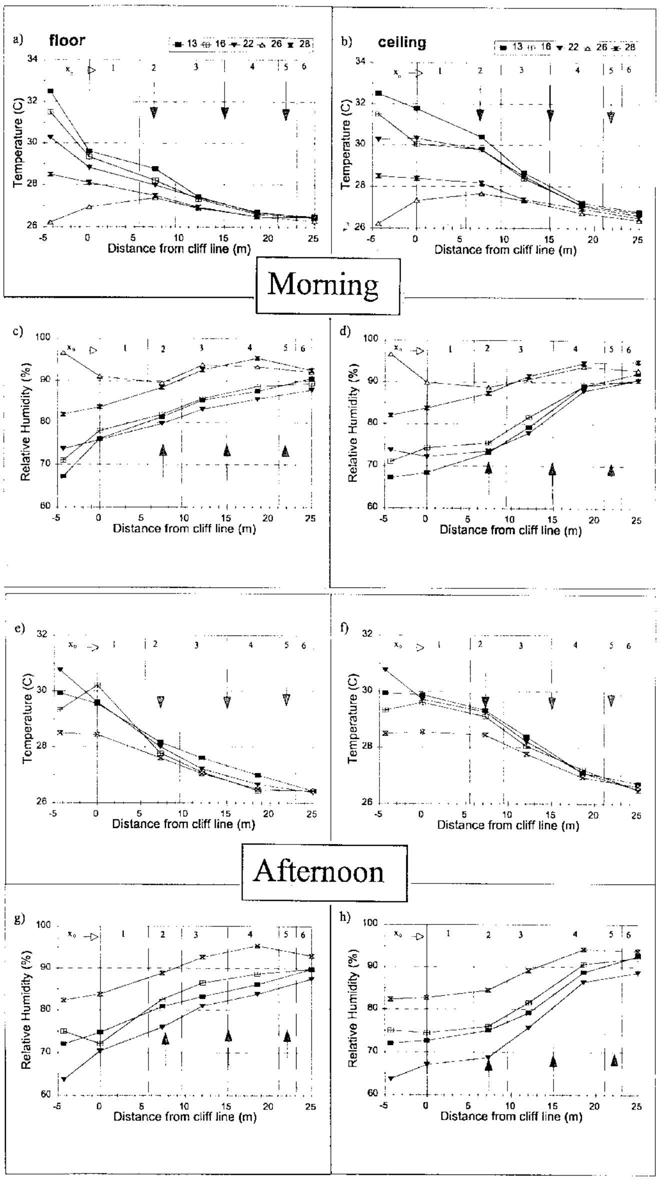


Figure 4. Temperature and relative humidity profiles for September 13, 16, 22, 26 and 28, 1995 in Skull Cave, Cayman Brac. The relaxation lengths, x_0, are indicated along the top of each profile. Note the varying length of x_0 with distance away from the entrance as a result of the cave configuration. Arrows indicate the location of constrictions. a) Morning temperature profile along the floor; b) Morning temperature profile along the ceiling; c) Morning relative humidity profile along the floor; d) Morning relative humidity profile along the ceiling; e) Afternoon temperature profile along the floor; f) Afternoon temperature profile along the ceiling; g) Afternoon relative humidity profile along the floor; h) Afternoon relative humidity profile along the ceiling.

fifth of the stations used for the temperature and relative humidity maps recorded such temperature inversions (Fig. 6). Convection cells could form at these locations. They were distributed throughout the cave, indicating that the process occurs only on a small scale but it is likely to be of local significance.

As noted in the introduction, the climate on Cayman Brac and Isla de Mona is dominated by diurnal rather than seasonal variations and this permits measurement of the Wigley-Brown parameters within a short period of time. Daytime corresponds with the summer situation, when the wall temperature is less than the outside dew-point temperature and condensation occurs on the walls. At night the situation is similar to the winter condition and inside temperature is greater that the outside dew-point temperature resulting in evaporation. This diurnal variation between condensation and evaporation will be greatest in the area of greatest diurnal temperature and relative humidity differences, i.e. the entrance zones. It is very likely that this alternation plays a major role in condensation corrosion because energy is needed to evaporate water and this will cool the walls. No droplets or sheet flow were observed to occur on the walls, indicating that the condensation water was not substantial enough to form droplets or water films thick enough to overcome the surface tension and flow down, removing dissolved material in the process. During evaporation some material might be removed in the vapour phase, which would explain the high concentrations of calcium and magnesium observed in the condensation waters. At the same time, dissolved material could crystallize as small individual particles when evaporation is fast enough to prevent molecules of the dissolved material from rejoining the crystalline structure of the bedrock. As such, they can then be removed as aerosols by gravity, dislodgment by air circulation or some other process.

WATER CHEMISTRY

The chemical characteristics of water samples collected on Cayman Brac are presented in Table 1. Drip water could be collected only on rainy days when the drip rates were high. Relative humidity was then close to 100% and thus evaporation, which would increase mineral concentrations in the water, was assumed to be negligible.

Figure 7 compares the specific conductivity (SpC) of the drip waters with their total hardness. The solid line is the relationship between these two parameters that has been established for bicarbonate waters of Pennsylvania by White (1988). The drip waters fall mainly above the bicarbonate water line, indicating that they have a higher SpC due to the presence of significant quantities of ions other than calcium and magnesium. These foreign ions are believed to have come from sea salt particles in the air or deposited on vegetation.

Two different factors each divide the drip waters into distinct groups. First, samples from rains of May 1994 and September 26, 1995, have greater hardness and lower specific conductivity, in general, than the samples of October 3 and 4, 1995 (Fig. 7a). The difference is attributed to different rainfall

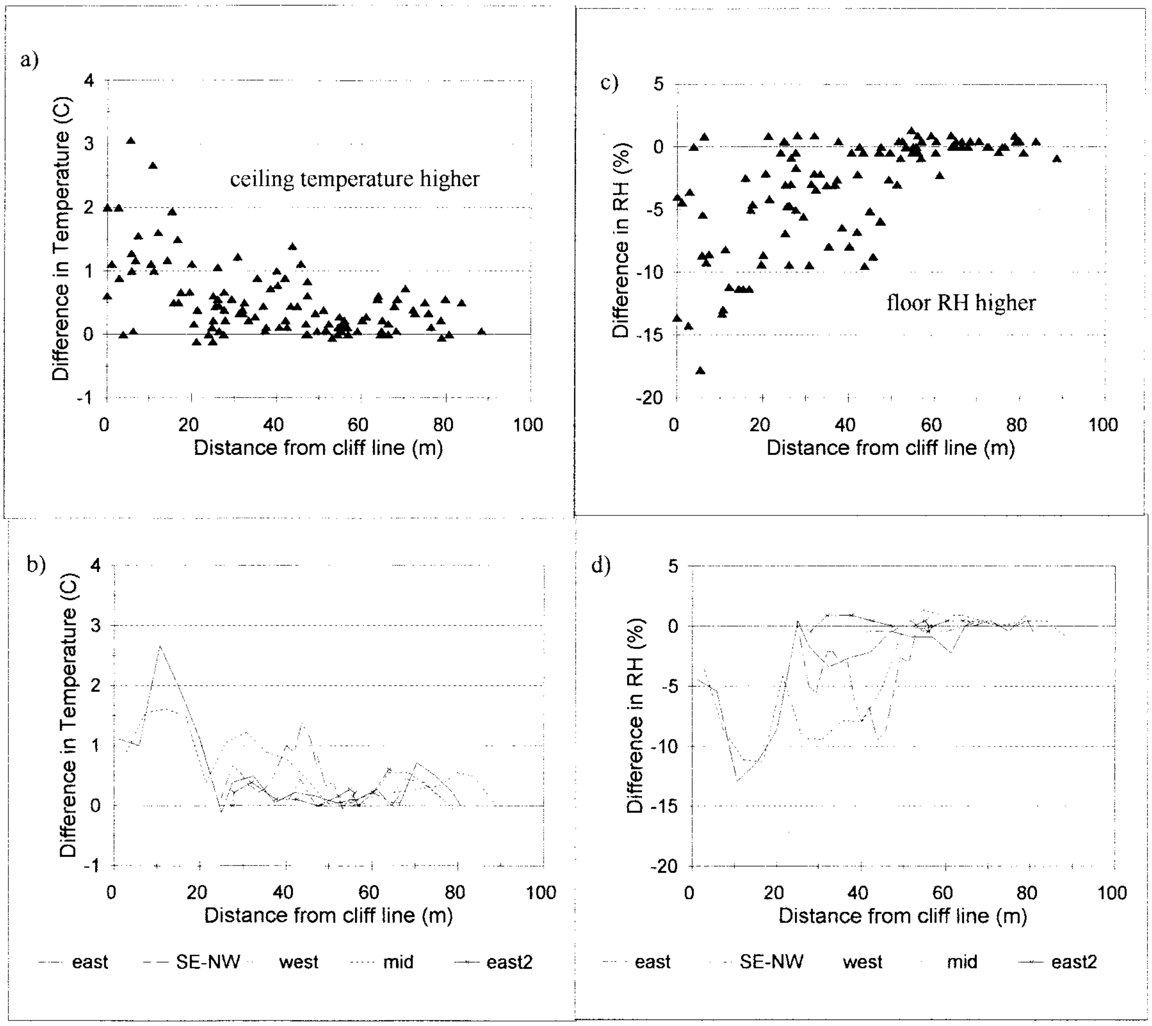


Figure 5. a) Temperature differences between ceiling and floor for all stations, Cueva de Agua Sardinera, Isla de Mona (June 1994); b) Temperature difference between the ceiling and the floor along selected profiles in the cave. Three transects were made NNE-SSW, one in the western end (west), one in the eastern end (east) and one midway between the two (mid). One transect was almost perpendicular to the previous three transects (SE-NW) and transect East2 first goes SSW-NNE and then turns SE-NW to join the eastern transect; c) Relative humidity difference between ceiling and floor for all stations, Cueva de Agua Sardinera; d) Relative humidity difference between the ceiling and the floor along selected profiles in the cave (transect location see 5b).

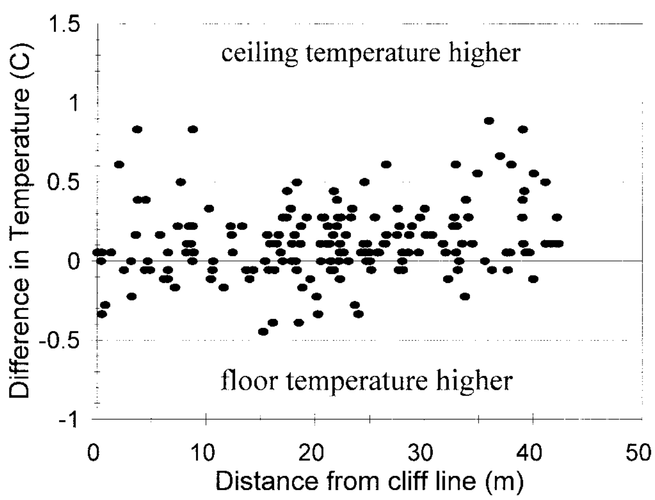


Figure 6. Temperature differences between ceiling and floor for all stations in Peters Cave, Cayman Brac (May 1994).

intensities, duration and amounts. During the night of September 25-26, as well as part of the day it rained steadily, resulting in a mean rainfall of 65 mm for the island. On October 3, the heaviest downpour of the entire study period was experienced due to the influence of Hurricane Opal. Rain fell all day; mean precipitation for the island was 95 mm, varying from 50 mm at the west end to 135 mm in the middle. With a steady rain the amount of water is less and takes longer to penetrate the rock, giving it more time to dissolve the bedrock and, thus, a greater hardness. Heavy downpours will be able to penetrate the bedrock faster and they will flush all the foreign ions through the system as well, increasing the SpC but keeping the hardness relatively low.

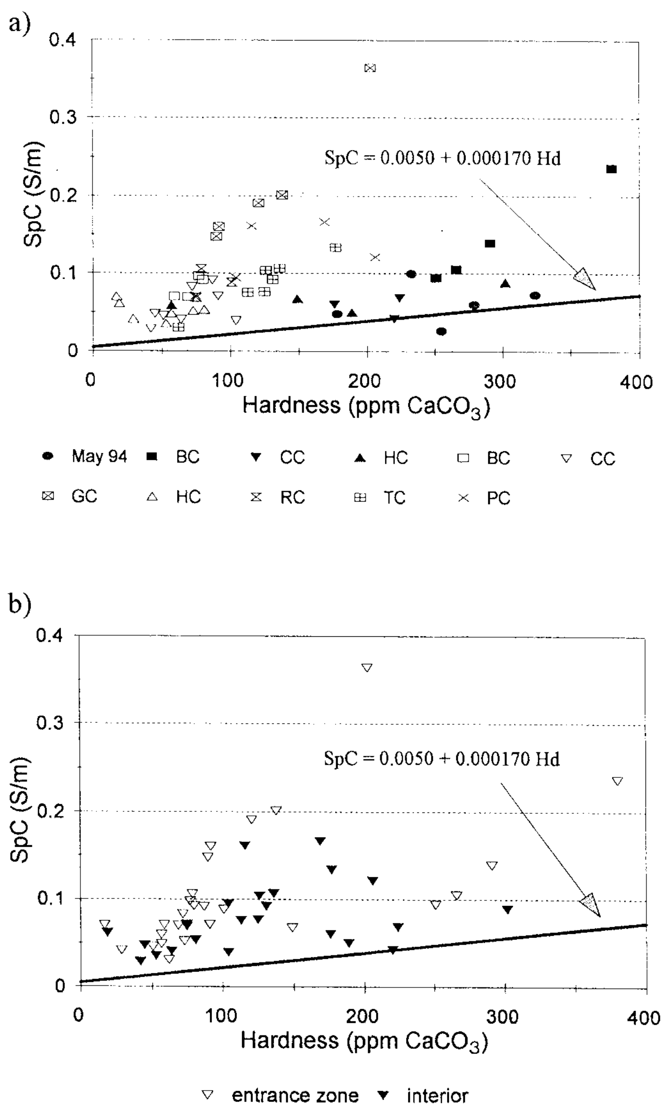


Figure 7. Relationship between specific conductivity and hardness for drip waters. a) Drip waters by cave; closed symbols indicate drip waters from heavy downpours (October 3 and 4, 1995) and open symbols drip waters from steady rain (May 1994 and September 26, 1995); b) Drip waters at the entrances and deep inside caves (Sept-Oct 1995). The solid line is the Pennsylvania water line for inland bicarbonate waters given by White (1988: 137).

As a second effect, these differentiated storm waters also divide in two subgroups according to location within the cave. Waters from the entrance zone have higher SpC for a given hardness than those deep inside, indicating that there is a higher foreign ion content close to the entrances (Fig. 7b). This is in agreement with the temperature and relative humidity observations, which indicated that the entrance zone is most influenced by outside climate. The inflowing air not only conveys heat and moisture into the cave but also sea salt aerosols. Sea salt aerosols are very hygroscopic and can initiate aqueous condensation at relative humidities as low as 80% (Wells 1986). The presence of these particles may therefore cause condensation in the air, increasing the amount of condensation water and the likelihood of condensation corrosion.

Figure 8 displays the saturation index values of the different water samples with respect to calcite (SI_c) and dolomite (SI_d). It is seen that the induced condensation waters are similar to the intense storm drip waters of October 3 and 4, 1995. Condensation waters were undersaturated with respect to both minerals in 75% of the cases and supersaturated in 25%. The calcite index values are the most significant in this study. Their range was from -1.06 to +0.88, the former representing a water capable of dissolving a speleothem quite rapidly and the latter one that would deposit new calcite upon it.

Some measured relationships between the SI_c of sample condensation waters and their distances from cave entrances are shown in Figure 9. They are quite complex, varying between caves and at different dates in the same cave. To generalize, however, a majority of the traverses detected little change in the SI_c state on a given day at distances up to 25 m from the cliff lines but Tibbetts Turn Cave (TC) gave quite aberrant results. Two traverses deeper than 25 m in Great Cave measured significant increases in SI_c, the waters becoming slightly supersaturated. The need for more research here is evident.

GYPSUM TABLETS

The calculated losses by surface retreat on the gypsum, the condensation film thicknesses and minimum quantities of condensation water needed to achieve those losses are given in Table 2. The two reference samples did not display any loss of material. All other tablets recorded losses, which can be represented as surface retreat rates of up to 0.5 mm/a. There was no correlation between the surface areas of the different gypsum tablets and their retreat rates.

With some exceptions, gypsum tablets that were suspended close to the entrances suffered more dissolution than those further inside the caves. Tablets close to the floors were more affected than those close to the ceilings (Fig. 10). Condensation corrosion is the only feasible mechanism for this dissolution: the gypsum tablet experiments reinforce the conclusion from the meteorological work that condensation occurs preferentially in entrance zones and close to the floors.

The greatest number of tablets were placed in First Cay Cave. The amount of surface retreat decreased rapidly beyond a distance of 30 m from the cliff (second constriction; Fig. 10a). Beyond the first constriction at 17 m, the temperature became nearly invariant and the relative humidity stabilized at around 99% (Fig. 2 & 3). Almost no dissolution occurred on tablets where the relative humidity exceeded 95% and remained constant over time. Substantial dissolution was observed at relative humidities less than 95%, i.e. in the entrance areas. These are the zones with the greatest diurnal climatic variations and where alternation of condensation and

Table 1. Chemical analysis of different water types on Cayman Brac.

	Specific Conductivity (muS/cm)			total Ca (mmol/l)			total Mg (mmol/l)			Saturation Index for calcite (SIc)			Saturation Index for dolomite (SId)		
	max	min	mean	max	min	mean	max	min	mean	max	min	mean	max	min	mean
Cayman Brac, May 1994															
Sea	56000	46000	51660	148.13	104.91	116.73	648.56	0.50	265.98	1.86	0.72	1.32	3.62	2.96	3.30
Well	2180	210	1576	6.52	2.55	4.11	4.79	1.51	2.48	0.96	0.20	0.51	1.62	0.40	1.00
Rain	60	24	42	0.05	0.02	0.04	0.03	0.01	0.02	-2.86	-3.92	-3.38	-5.73	-7.81	-6.84
Drip	1000	270	616	1.75	0.96	1.23	2.52	0.81	1.42	0.82	0.43	0.69	2.25	1.08	1.62
Condensation	200	20	103	2.76	0.16	1.11	0.98	0.00	0.31	0.88	-0.98	0.05	1.54	-1.97	0.02
Cayman Brac, Sept-Oct 1995															
Rain	20	9	15	0.04	0.01	0.03	0.01	0.00	0.00	-2.80	-4.22	-3.59	-6.68	-8.62	-6.68
Drip	3646	292	945	2.67	0.07	0.84	1.19	0.00	0.41	1.07	-1.58	0.10	1.83	-2.76	0.10
Condensation	116	27	50	3.32	0.24	0.98	0.46	0.00	0.19	0.77	-1.06	-0.42	0.58	-2.87	-0.89
Drip water for sample caves															
Peters Cave	1664	718	1231	1.24	0.46	0.76	0.86	0.30	0.60	0.30	-0.27	-0.02	0.67	-0.50	0.11
Tibbetts Turn Cave	1337	310	887	1.15	0.48	0.85	0.65	0.14	0.41	0.46	-0.13	0.17	0.88	-0.51	0.23
Cross Island Road Cave	917	292	565	2.09	0.23	0.76	0.71	0.14	0.34	0.95	-0.51	0.12	1.67	-0.47	0.19
Skull Cave	889	358	575	2.01	0.07	0.65	1.12	0.00	0.31	1.05	-1.58	-0.22	1.79	-2.76	-0.56
Rebeca s Cave	1060	694	880	0.74	0.66	0.71	0.29	0.02	0.15	0.42	-0.08	0.19	0.64	-0.89	-0.30
Bats Cave	2367	703	1132	2.67	0.42	1.38	1.19	0.17	0.50	1.07	-0.11	0.46	1.83	-0.43	0.71
Great Cave	3646	1476	2130	1.04	0.56	0.73	1.03	0.33	0.58	0.40	0.06	0.19	1.04	0.18	0.49
Condensation water for sample caves															
Peter s Cave	45	27	31	0.55	0.24	0.43	0.08	0.00	0.03	-0.46	-0.97	-0.77	-1.97	-2.53	-1.09
Tibbettts Turn cave	116	29	59	2.94	0.41	1.16	0.42	0.00	0.22	0.31	-1.06	0.50	-0.17	-2.87	-1.18
Great Cave	107	38	56	3.32	0.44	1.25	0.46	0.18	0.30	0.77	-0.77	0.04	0.58	-1.69	-0.26

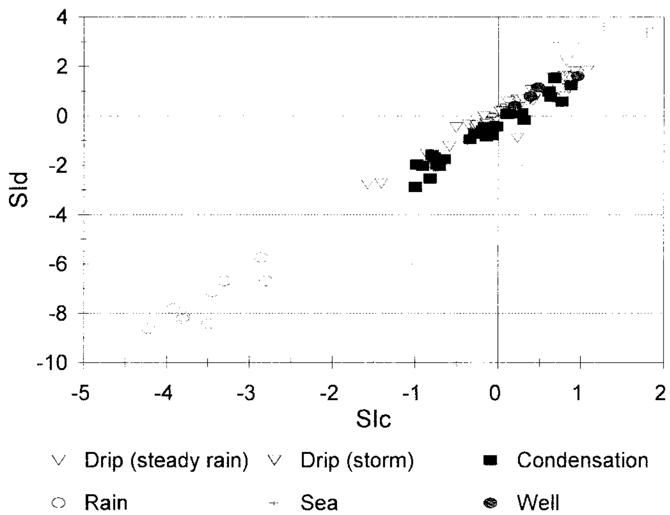


Figure 8. Saturation Index for dolomite (SI_d) versus the Saturation Index for calcite (SI_c) for rain, drip and condensation water on Cayman Brac, 1994 and 1995.

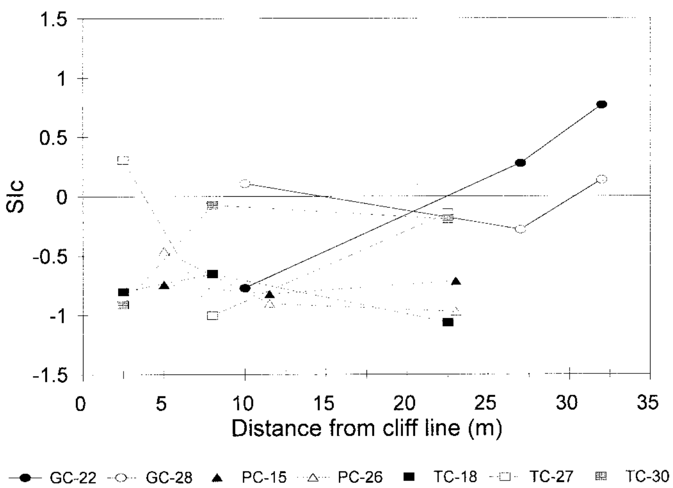


Figure 9. The change in the Saturation Index for calcite (SI_c) of condensation water with distance from the cliff line in three caves on Cayman Brac for September 15, 18, 22, 26, 27, 28 and 30, 1995.

evaporation is believed to occur. As noted above, this cycle of condensation and evaporation might enhance condensation corrosion.

In Peters Cave, the tablets suspended near the ceiling and near the floor displayed similar retreat rates (Fig. 10b). This is believed to be the result of a more homogeneous air mass than in the other caves. The tablets were suspended in the second and third principal passages, which are parallel to the cliff line and in direct contact with the first (or outer) principal passage by an aperture of about 20 cm diameter. The gypsum tablet profile follows a downward slope between the second and third passage. The temperature and relative humidity measurements indicate that convection cells form on a very localized scale in these passages, which might enhance the homogenization of the air mass.

In Cueva de Agua, Sardinera, the highest surface retreat was found on a sample 92 m from the entrance and close to the ceiling (Fig. 10d). A local convection cell might explain this anomaly also, but temperature and relative humidity measurements indicate this was not occurring on the day these measurements were taken. Another possibility might be that the sample was located under or close to an aggressive drip site that was not active at the time of the field measurements.

Excluding the reference samples, the mean surface retreat on the gypsum tablets was 0.36 mm/a. If a ratio of 10:1 is assumed for the ratio of gypsum solubility to calcite solubility (Ford & Williams 1989), the calculated mean calcite (limestone and speleothem) corrosion is 0.036 mm/a or 36 mm/ka.

Table 2. The Gypsum Tablet Experiment.

Cave	Shortest distance to cliff (m)	Measured surface recession (mm/yr)		Estimated aqueous condensation (mm/day)	
		H*	L*	H*	L*
Reference samples					
PC	19	0.01		0.02	
CAS	87	0.00		0.00	
Cayman Brac					
B2-Cave	1	0.37		0.94	
	2		0.08		0.22
First Cay Cave	9	0.39	0.44	1.00	1.14
	13	0.39		1.01	
	16	0.36		0.92	
	21		0.42		1.07
	29	0.41	0.52	1.07	1.33
	31	0.17		0.43	
	40	0.01		0.02	
	40	0.04		0.10	
Peter s Cave	19		0.21		0.55
	23	0.47	0.45	1.21	1.16
	28	0.39	0.40	1.01	1.02
	31	0.02		0.05	
	33	0.09		0.23	
	34	0.40		1.03	
Tibbetts Turn Cave	28	0.01	0.16	0.02	0.42
	30	0.11		0.28	
	33		0.01		0.03
maximum		0.47	0.52	1.21	1.33
minimum		0.01	0.01	0.02	0.03
mean		0.24	0.30	0.62	0.77
Isla de Mona					
Cueva del Agua	1	0.32		0.82	
	8	0.01		0.02	
	13	0.00		0.00	
	63				
	63	0.01	0.26	0.03	0.66
	87		0.02		0.05
	92	0.46		1.18	
maximum		0.46	0.26	1.18	0.66
minimum		0.00	0.02	0.00	0.05
mean		0.16	0.14	0.41	0.36

H* = close to ceiling; L* = close to floor

This must be reduced by a measure that takes into account the greater porosity of gypsum: 33% would seem a likely maximum for this effect, giving a corrosion rate of ~24 mm/Ka for calcites with porosities below ~5%. This remains a considerable loss rate.

Theoretical condensation corrosion rates were also calculated, using

$$R = \alpha(c_{eq} - c) \qquad (12)$$

where R is the dissolution rate in mmol/cm²s, α is the kinetic constant in cm/s, c is the Ca-concentration in the water film and c_{eq} is the equilibrium concentration of calcium in mol/l (= mmol/cm³) with respect to calcite (Buhmann & Dreybrodt 1985; Baker *et al.*, in prep.). An average value of 19 mm/ka was obtained using the Ca-concentrations measured in the induced condensation waters. This corresponds very well with the rates calculated from the gypsum tablet experiments, indicating that (although the methods were crude and the time spans short) the results of the field experiments appear to be meaningful. U-series dating has determined that the growth rates of some larger speleothems on Cayman Brac can be up to 7 mm/Ka but are generally < 1 mm/Ka (Lips 1993). These are far below the corrosion rates that can prevail: thus, for instance, a flowstone 10 cm thick will require about 100,000 years to form and can be dissolved away again in only 4000 - 5000 years.

CONCLUSIONS

Condensation corrosion occurs at present in the entrance zones of caves where the atmospheric variables fluctuate on a daily basis and are highly influenced by the outside climate. The relationships are complicated, however; Figure 11 schematically outlines how they and other environmental variables will contribute to the formation of condensation water and the condensation corrosion inside caves that is a consequence. The climatic variables have both short and long term influences on the climate inside the caves, whereas sea level fluctuations are only of long term importance. The latter influence the size of the entrance, the configuration of the cave and the distance between the sea and the cave.

The physical model for condensation corrosion that is suggested by this investigation is depicted in Figure 12. The typical coastal caves consist of a series of chambers and constrictions. The latter inhibit the free flow of air and dampen the external climatic influences substantially.

The mean condensation corrosion rate was estimated to be ~24 mm/Ka. This corresponds well with a theoretical rate of ~19 mm/Ka that can be calculated from the model of Buhmann and Dreybrodt (1985).

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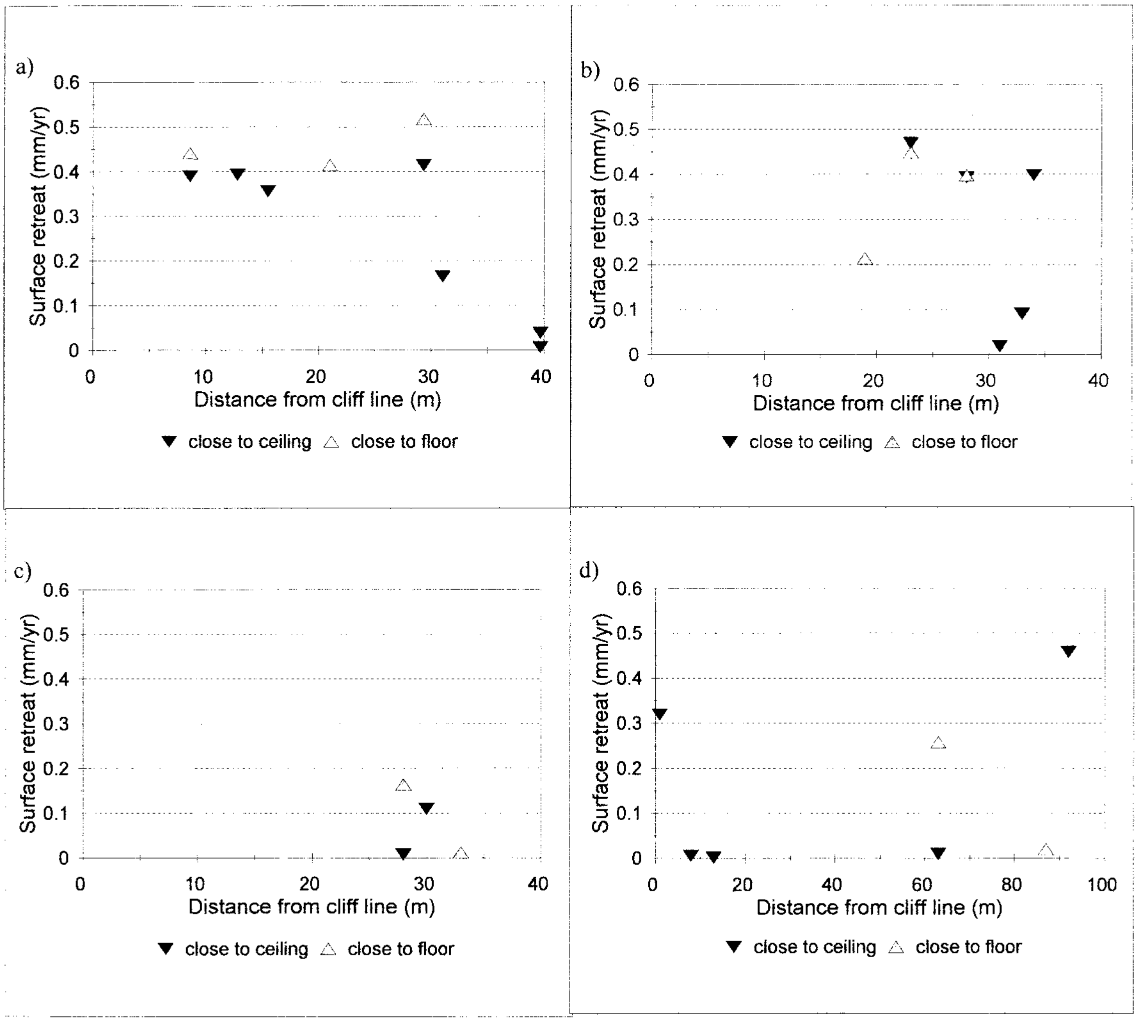

Figure 10. Surface retreat of gypsum tablets in First Cay Cave (a), Peters Cave (b), Tibbetts Turn Cave (c) on Cayman Brac and Cueva de Agua (d) on Isla de Mona.

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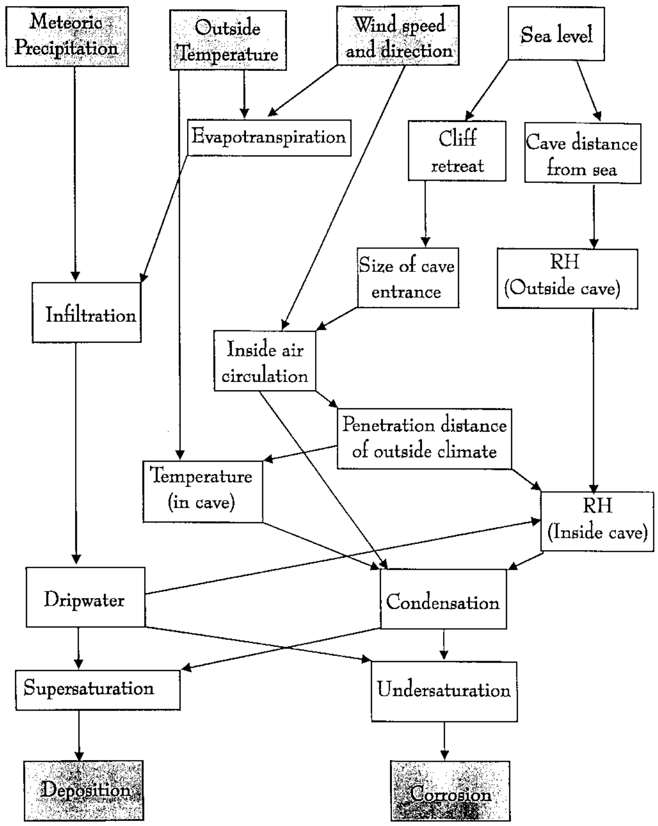

Figure 11. Schematic representation of the interaction between the outside and cave environments.

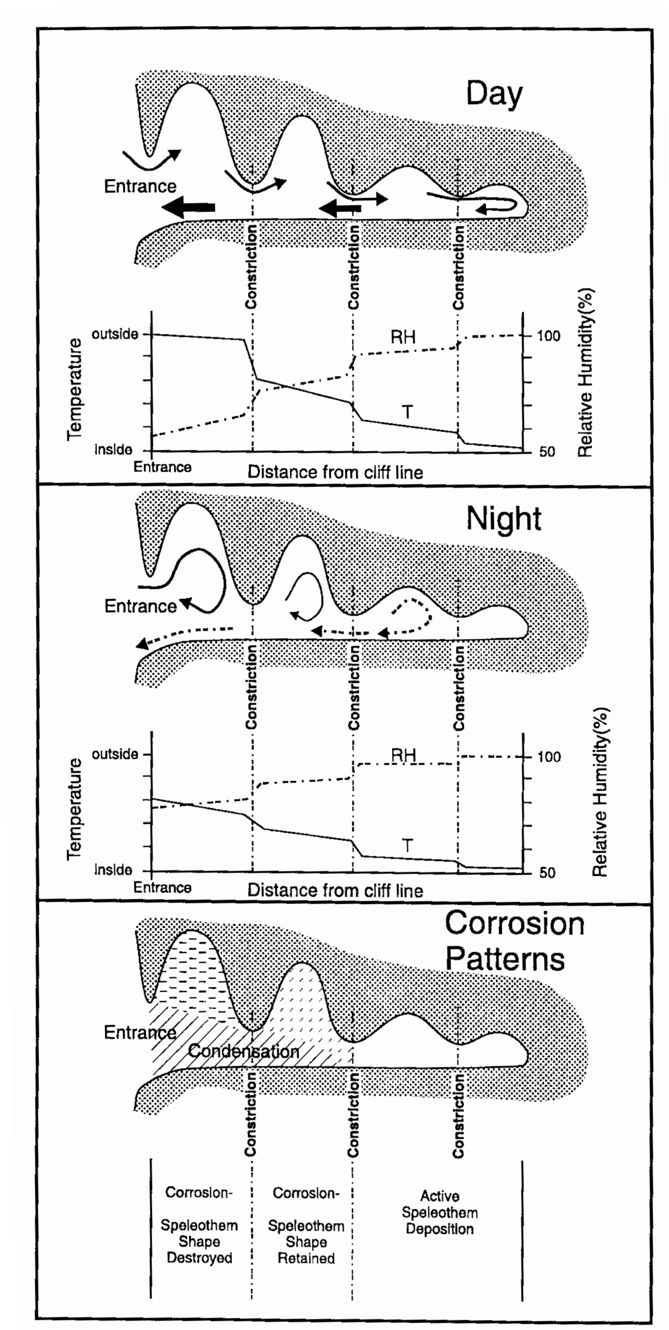

Figure 12. Proposed model of condensation corrosion in coastal caves on small holokarstic oceanic islands with young rocks.

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