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## **CARBONATE WATER MIXING IN A MODERN FLANK MARGIN CAVE**

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### **ABSTRACT**

The purpose of this paper is to test the idea that flank margin caves form by mixing between fresh water and seawater, resulting in water that is undersaturated with respect to calcite. Majors Cave, a flank margin cave, located in an interior Pleistocene dune ridge on San Salvador Island, Bahamas contains pools of water with salinities that suggest that they form from mixing of fresh water and seawater. With the exception of the upper-most sample, water from the pools have Na/Cl, K/Cl, Mg/Cl, and SO<sub>4</sub>/Cl ratios that are within 3% seawater ratios, suggesting that the source of solutes is from seawater. The same samples have Ca/Cl ratios that are 9 to 17% higher than seawater ratios. We believe the excess Ca may derive from dissolution of calcite as meteoric water percolates through the epikarst into the cave. Water in the pools is supersaturated with respect to calcite, which may result from degassing of CO<sub>2</sub>, increased salinity following evaporation, or from the excess Ca. While the primary development of flank margin caves is attributed to mixing of fresh water and seawater, supersaturation with respect to calcite after their formation may limit their continued growth.

### **INTRODUCTION**

San Salvador Island has lakes, low plains and eolian dunes that contain caves of phreatic

origin. These caves formed during Oxygen Isotope Substage 5e (ca. 125 kybp), when sea level was 4 to 6 m above present (Myroie et al., 1995). During the sea level highstand, the island consisted only of small eolian dunes (Figure 1; Carew and Myroie, 1997) separated into islands by seawater, each containing individual freshwater lenses (e.g. Vacher, 1988). The modern caves are believed to have formed by dissolution during mixing of the fresh water and seawater at the distal margin of the lens under the flank of the dune and are thus referred to as flank margin caves (Myroie and Carew, 1990). Since the highstand was above present sea level for less than 15,000 years (Carew and Myroie, 1995), the caves must have formed during this time-frame. Myroie et al. (1995) report dissolution chambers with volumes up to 14,000 m<sup>3</sup> suggesting dissolution rates of ~1 m<sup>3</sup>/yr. Because the rate of dissolution is controlled by the saturation state of the mixed water (e.g. Plummer, 1975), these rates suggest a high degree of undersaturation.

The purpose of this study is to assess water chemistry variability within a modern flank margin cave to determine its saturation state with respect to calcite and whether the cave is continuing to grow with modern mixing of fresh and seawater. Information on the chemistry of the cave water also should provide insight into vadose zone hydrology and recharge of aquifers in young, eogenetic limestones. The chemical results

indicate that the cave water is supersaturated with respect to calcite as a result of hydrology and chemical reactions in the vadose zone.

## SETTING

Majors Cave is located on Hog Cay, an interior eolian ridge of Pleistocene age located north of the San Salvador International Airport runway (Figure 1). Flamingo Pond is on the east side of the cay and contains water with salinities of at least 64‰. An overflow pond wraps around the southern end and west side of the cay which, during the dry, summer months, can reach salinity of up to ~120‰, four times seawater values. Majors Cave is the second largest known cave on San Salvador (Moore et al., 2004) and contains one large pool of water near one of its entrances and smaller, linear pools in the back of the cave toward the axis of the dune ridge (Figure 2). The pools are tidal, and a free dive at the entrance pool in 2000 revealed continuing passage (Gulley, pers. comm.), yet to be fully explored. Limited measurements indicate that the pools have surface salinities ranging from 23.7‰ during the wet season to 29.1‰ during the dry season.

## METHODS

### Sampling and Analyses

In January 2004 we collected water samples at 0.5 m intervals from the Water Entrance pool of Majors Cave from the surface to 2.0 m depth. Samples were collected by diving into the pool. A profile of salinity was measured prior to diving and compared with the salinity-depth profiles of the samples. The profiles have similar variations in salinity with depth suggesting that little mixing of the water occurred during sample collection. At each depth, grab samples were collected in Nalgene<sup>®</sup> HDPE bottles rinsed three times with pool water prior to collection. Specific conductance, salinity, pH and temperature were measured in the field at the time of collection. Temperature, salinity and specific conductance were measured with an ATI Orion

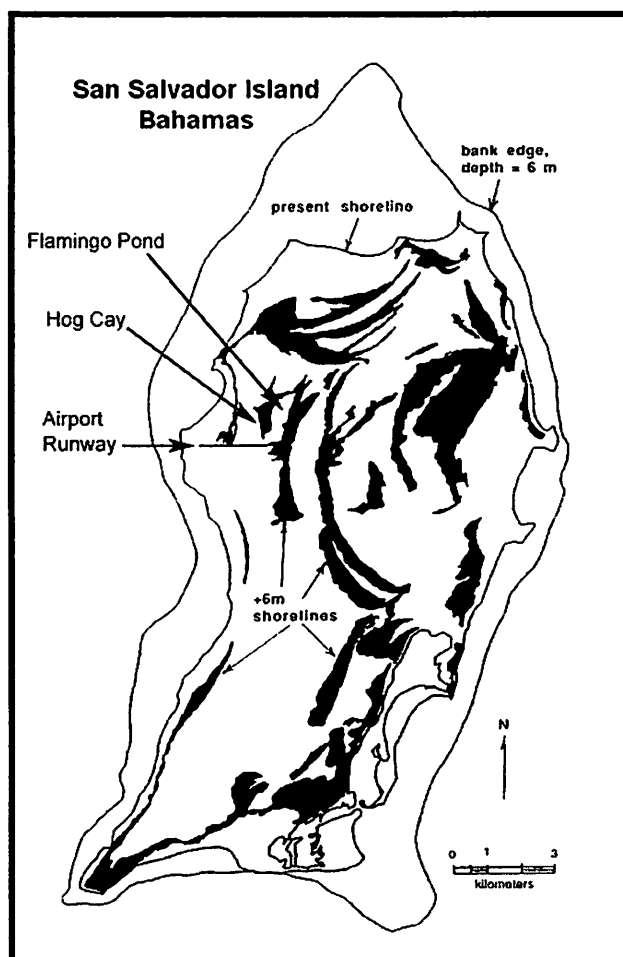


Figure 1. San Salvador today compared to substage 5e (~125 ka) when sea level was 6m above present. Black shading represents exposed +6 m land during 5e high stand. Hog Cay was a small strip-island with a freshwater lens during this time (modified from Carew and Mylroie, 1997).

portable conductivity meter Model #130. Measurement of pH was made with an Orion portable pH meter Model #250A calibrated at the beginning of the sampling period using 7.0 and 10.0 buffers.

Following collection the samples were brought back to the University of Florida for laboratory analysis of various solutes including Ca, Mg, K, Na, and SO<sub>4</sub>. These solutes were measured using a Dionex Model DX500 ion chromatograph in the Department of Geological Sciences at the University of Florida. Chloride concentrations were measured by titration with

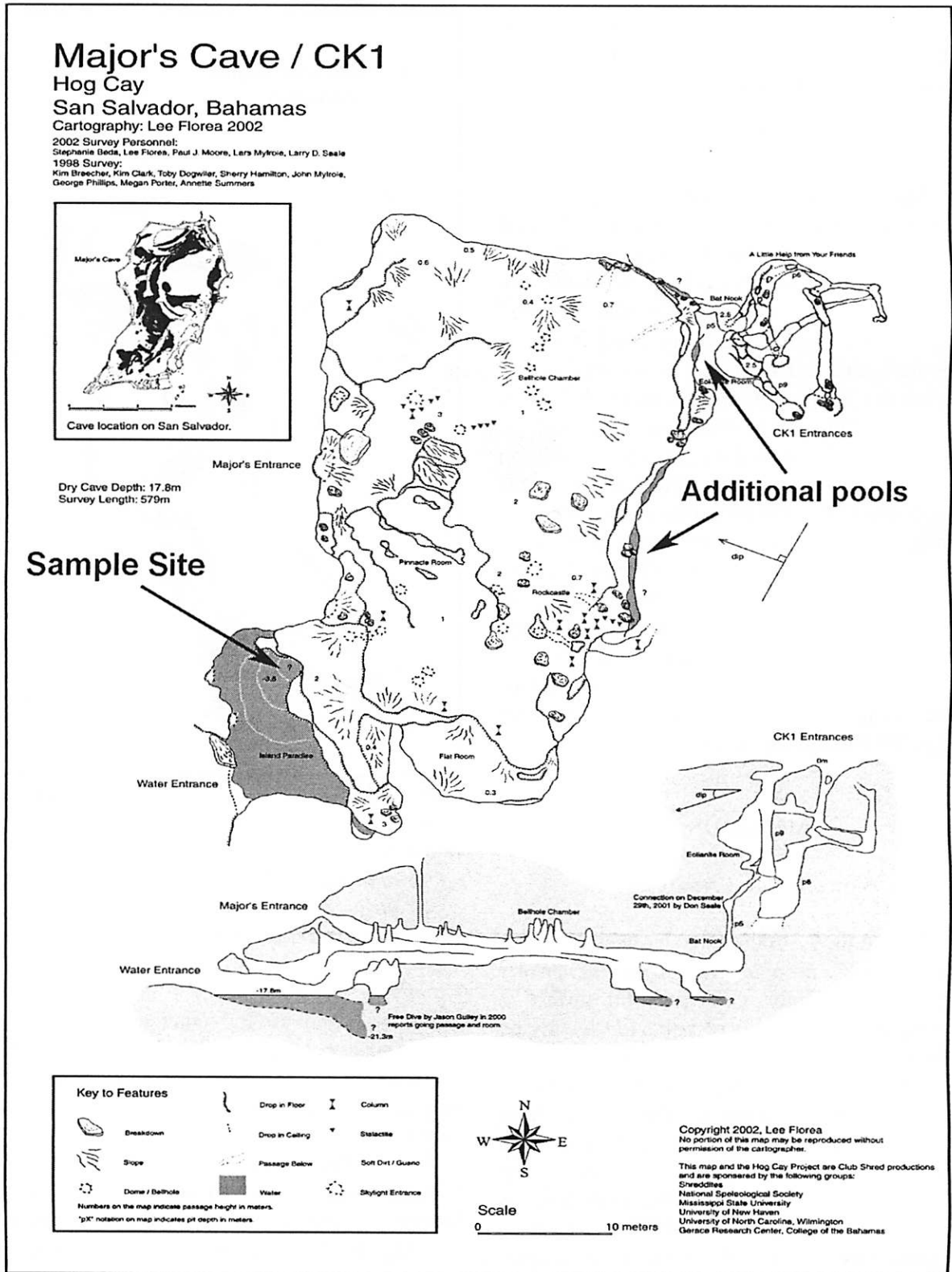


Figure 2. Map of Major's Cave located on Hog Cay. Sample site is a pool near one of the cave entrances containing density stratified water (modified from Moore et al, 2004; Cartography by Lee Florea, used with permission).

AgNO<sub>3</sub> using seawater standards. Alkalinity was not measured but HCO<sub>3</sub> concentrations were calculated using the geochemical speciation program, PHREEQC (Parkhurst and Appelo, 1999).

## RESULTS

Results of analysis show stratification of the water in the pool (Figure 3). The temperature of the water increases from 22.1° C to 22.5° C, salinity increases from 23.70 to 26.40 and conductivity increases from 33.80 mS/cm to 36.80 mS/cm, resulting in water that is density stratified from 1.016 g/cm<sup>3</sup> in the upper layer to 1.018 g/cm<sup>3</sup> in the deepest sample collected. In addition to temperature and salt changes, pH decreases from 7.95 to 7.68 as the stratified water becomes more saline. Deviation from linear trends between 1.5 and 2.0 m depth may result from mixing of water during sampling (Figure 3). Most solutes (Mg, K, Na, Cl, and SO<sub>4</sub>) have concentration ratios similar to seawater ratios when compared to Cl. The exception is Ca/Cl ratios (Figure 4), which are greater than seawater ratios by 9 to 17%. The measured concentrations and calculated bicarbonate concentrations suggest that the mixed water is supersaturated with respect to calcite with saturation indices of +0.5 to +1.3 (Figure 5).

## DISCUSSION

The similarity to seawater ratios for most of the measured major element/Cl ratios suggest the sampled water is a mixture of fresh water and seawater, which can produce water that is undersaturated with respect to calcite. We assume the excess Ca derives from dissolution of calcite in the vadose zone as meteoric water percolates down towards the freshwater lens. If true, and assuming that Cl is conservative, then the Ca concentration in the meteoric water following dissolution can be calculated using the following equation:

$$Ca_{excess} = Ca_{measured} - \left[ \left( \frac{Cl_{measured}}{Cl_{seawater}} \right) \times Ca_{seawater} \right] \quad (1)$$

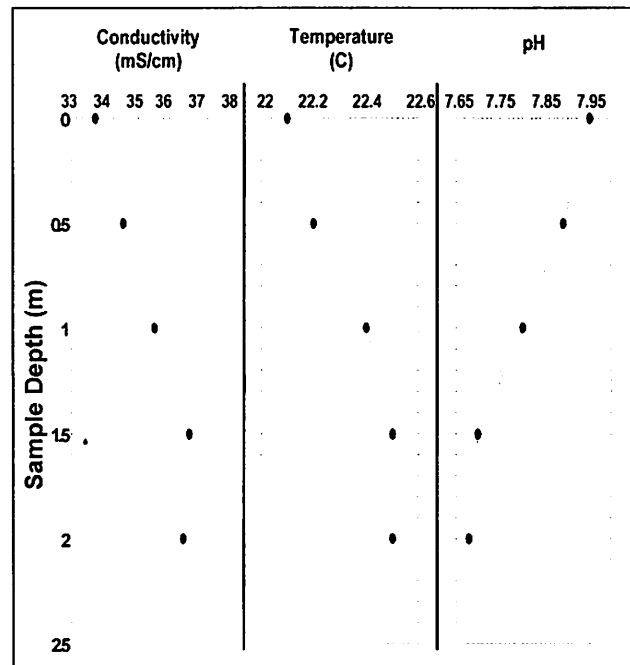


Figure 3. Conductivity (mS/cm), temperature (°C) and pH of sample water from Majors Cave.

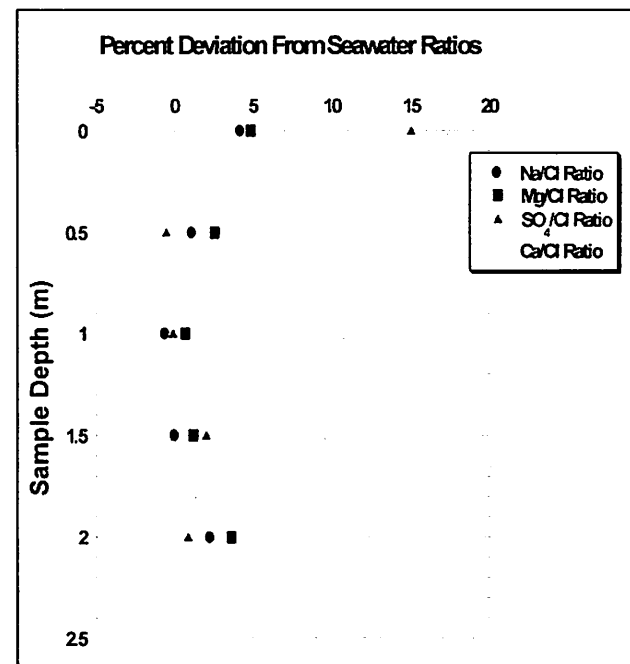


Figure 4. Major ion/Cl ratio percent deviations from seawater value. Ratio of Ca/Cl shows 9 to 17% increase suggesting excess Ca in mixed water.

where  $Ca_{\text{excess}}$  is the excess Ca in sample water,  $Ca_{\text{measured}}$  is the measured concentration of Ca (mM) in sample water,  $Ca_{\text{seawater}}$  is the concentration of Ca in seawater (10.5 mM),  $Cl_{\text{measured}}$  is the measured concentration of Cl in sample water, and  $Cl_{\text{seawater}}$  is the concentration of Cl in seawater (559 mM).

The excess Ca calculated by Equation (1) correlates linearly with specific conductivity and extrapolates to a concentration of 5.92 mM at a conductivity of 0 mS/cm (Figure 6). If all of the excess Ca represents calcite dissolution during December 2003 when 135 mm of rain fell on Hog Cay (aerial extent  $\sim 6.60 \times 10^5 \text{ m}^2$ ), then assuming the rainwater contained no Ca,  $5.3 \times 10^5$  moles calcite would have dissolved to produce the extrapolated Ca concentration. This amount of calcite represents  $1.96 \times 10^7 \text{ cm}^3$  of calcite dissolution at a molar volume of  $36.934 \text{ cm}^3$  or a linear rate of  $\sim 0.03 \text{ mm}$  over the entire cay.

It is likely this dissolution rate is overestimated but the technique might be useful to quantify bulk dissolution rates within the vadose zone. Better estimates of dissolution could be made with time series observations of variations in pool water chemistry. Although Majors Cave developed by dissolution within a mixing zone (e.g., Mylroie and Carew, 1990), the modern pool water will not drive continued cave growth because of its supersaturation with respect to calcite. Supersaturation may occur from degassing of  $\text{CO}_2$ , evaporative concentration of solutes after water enters the cave environment, or from excess Ca.

Partial pressure values of  $\text{CO}_2$  in solution are typically higher in soil/epikarst water as compared to atmospheric values. This difference in  $P_{\text{CO}_2}$  results in degassing of carbon dioxide once the water enters the cave, thereby elevating the saturation state of the water with respect to calcite. However, extensive formation of calcite precipitates, such as stalactites, was not observed in the cave. Evaporation of water would further the increase of solute concentrations and should increase the saturation state of evaporative minerals. Evaporation would be minimal,

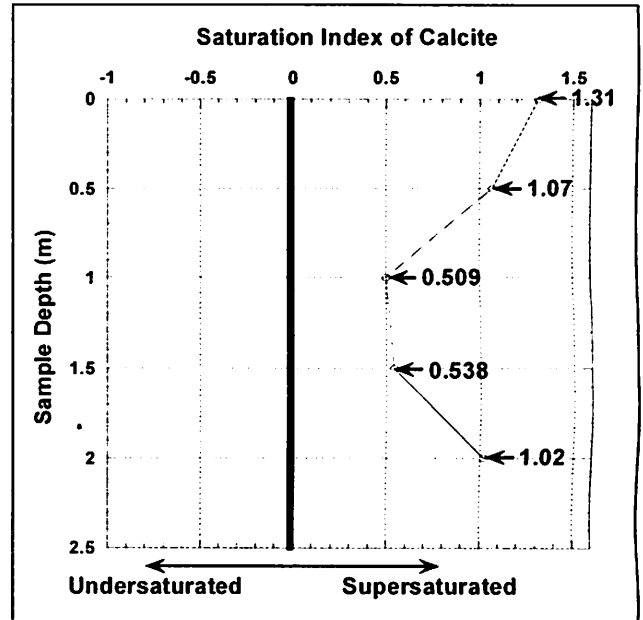


Figure 5. Saturation index (SI) of calcite calculated using speciation program PHREEQC. SI values range from +0.5 to +1.31 suggesting the mixture is supersaturated with respect to calcite. Dark vertical line represents calcite equilibrium ( $SI = 0$ ).

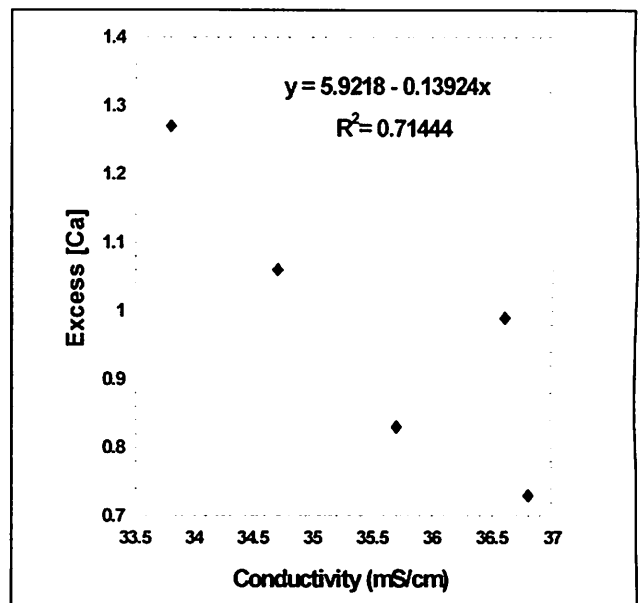


Figure 6. Extrapolation of excess Ca to water with a specific conductivity of 0 mS/cm. The y-intercept is 5.92 mM Ca.

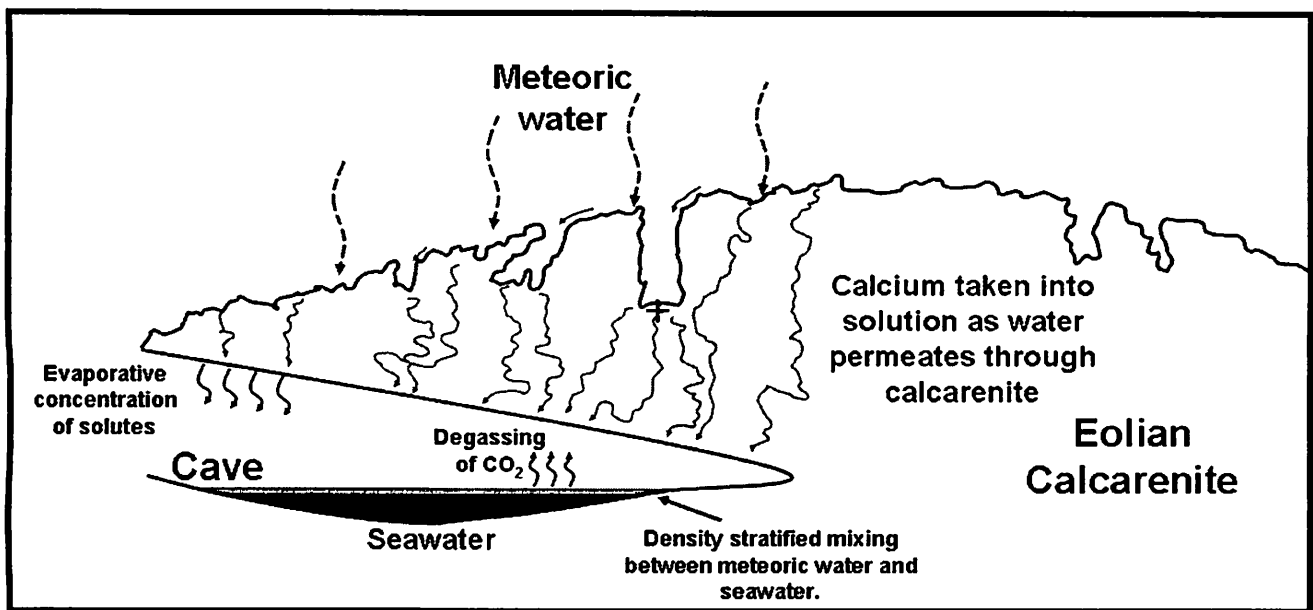


Figure 7. Conceptual model illustrating how excess Ca can go into solution of meteoric water (dashed lines) during infiltration through the vadose zone (solid lines).

however, during storm events that push water through the vadose zone at relatively swift rates, as was observed during a visit to the cave following a storm in June 2004.

Figure 7 shows a conceptual model of dissolution in the epikarst and vadose zone with development of supersaturation of cave water. In this model, dissolution occurs primarily in the vadose zone by interaction of undersaturated meteoric water with limestone of the cay, and is expressed by intensive karstification resulting in the development of vertical shafts and solution chimneys (e.g., Moore et al., 2004). However, the other possible mechanisms for the apparent supersaturation of calcite necessitate further sampling and analysis cave drip-water and pool water.

#### CONCLUSION

Although Majors Cave formed by the mixing dissolution of limestone, the modern cave water will not promote further cave growth because of its supersaturated state. The difference between the environment when the cave formed and the modern cave environment may result from the modern environment now being open to the atmosphere, allowing degassing, evaporative concentration, and/or

input of excess Ca from infiltrated water, but further analysis of temporal changes of cave water chemistry is necessary to quantify excess Ca influences.

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