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ORGANIZER:

Troy A. Dexter

Executive Director
Gerace Research Centre
University of The Bahamas
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PALEOSOL AND CAVE MINERALOGY FROM ELEUTHERA, THE BAHAMAS

Jonathan B. Sumrall[1], Kaitlyn L. Gauvey[1], Jeanne L. Sumrall[1], Kristin E. Sides[2], and Erik B. Larson[3]

[1]Department of Geosciences, Fort Hays State University
600 Park Street, Hays, KS 67601

[2]Department of Geography and Geology, Sam Houston State University
1905 University Avenue, Huntsville, TX 77340

[3]Department of Natural Sciences, Shawnee State University
940 2nd Street, Portsmouth, OH 45662

ABSTRACT

Paleosols on Eleuthera were sampled to determine the clay mineralogy from outcrops and inside Hatchet Bay Cave. In addition, cave mineral samples were collected from other flank margin and littoral sea caves. K-saturation, Mg-saturation, heating, and gylcolnation were used to determine the specific clay mineralogy of each sample. Petrographic thin sections were prepared to determine characteristics of each type of paleosol. Cave samples were powdered and analyzed using powdered X-ray diffraction (XRD).

The dominant clay mineral present in the paleosols on Eleuthera was Fe-rich chlorite ($(Fe^{+2},Mg,Al,Fe^{+3})_6(Si,Al)_4O_{10}(OH,O)_8$) and Illite ($K_{0.6}(H_3O)_{0.4}Al_{1.3}Mg_{0.3}Fe^{+2}_{0.1}Si_{3.5}O_{10}(OH)_2\cdot(H_2O)$) based on the 14Å and 10Å peaks of samples. The larger [002] 7Å peak compared to the [001] 14Å peak indicates a Fe-rich chlorite. In addition, a peak shift from 14Å to 6.1Å in several samples, possibly suggests the presence of Boehmite ($AlO(OH)$). Non-clay materials include low-Mg calcite and quartz.

Cave minerals included carbonates (calcite and aragonite), sulfates (gypsum), phosphates (hydroxyapatite, fluorapatite, chlorapatite, and woodhouseite), and Mn-oxides. All minerals except woodhouseite have previously been reported from Bahamian caves. Woodhouseite ($CaAl_3(SO_4)(PO_4)(OH)_6$) is part of the Alunite supergroup, previously reported as the product of bat guano in cave environments. Woodhouseite samples came from Hatchet Bay Cave, specifically from small crusts found on the exposed paleosol within the cave. The presence of woodhouseite was confirmed in three samples spatially distributed in the cave. Woodhouseite formation in this instance likely represents phosphate-rich leachate derived from seawater and guano interacting with the various aluminum-rich phases found in the clay fraction of the paleosol. Previous studies of Bahamian cave minerals did not have access to exposed paleosols within caves, making this an interesting addition to the diverse inventory of cave minerals of The Bahamas.

GEOGRAPHIC AND GEOLOGIC SETTING

The Bahamas in the Atlantic Ocean stretches over 1000 km from the coast of Florida to Great Inagua just off the coast of Cuba (Figure 1). Eleuthera is located on the western edge of the Great Bahama Bank is less than 15 km across at its widest point, and is approximately 125 km long (Figure 1). Unlike some islands in The Bahamas (e.g. San Salvador), Eleuthera occupies the northeastern margin of the Great Bahama Bank. This means that the island of Eleuthera becomes part of a much larger island when sea level drops and exposes the Great Bahama Bank.

The large Bahama Banks represent a Mesozoic to present tectonically stable platform with more than 5 km of shallow water carbonates (Melim and Masaferro, 1997). Today, surficial geology is almost entirely Quaternary limestone that has been modified by karst processes (Carew and

Mylroie, 1995; Mylroie and Carew, 1995; Mylroie and Mylroie, 2007).

The Bahama Banks are steep-sided platforms with an average water depth of ~10 m. Glacioeustatic sea level controls the geology of The Bahamas. For example, Eleuthera is a relatively small island on a larger platform that is exposed during glacioeustatic lowstands to form a much larger island. However, during highstands, the platforms are mostly submerged by marine water, initiating carbonate production. These carbonate sediments are carried by waves and currents and deposited as beach sediments, where eolian processes deposit these sediments as calcareous sand dunes (eolianites). During the initial transgressive phase of platform flooding, eolianites are produced as wave action constantly keeps lagoon and beach sediment mobilized, forming transgressive-phase eolianites. Transgressive-phase eolianites are often characterized by lacking trace fossils of colonizing vegetation referred to as vegemorphs (Birmingham et al., 2008; Mylroie et al., 2017).

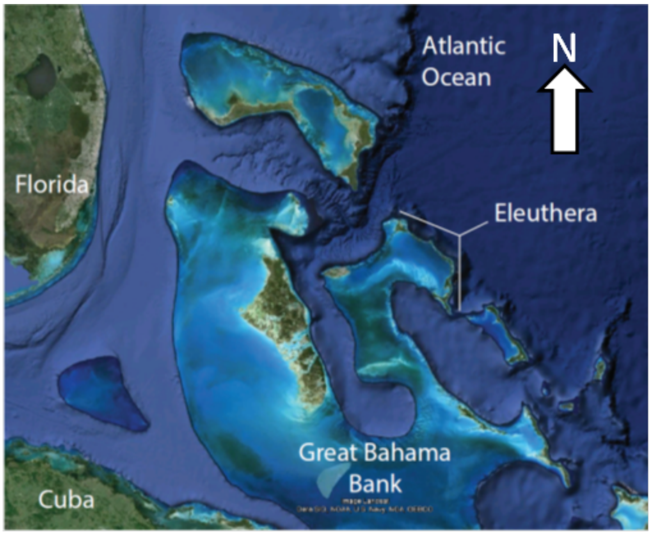


Figure 1. Location of Eleuthera, The Bahamas (Source: Google Earth ©).

Coral reefs grow to wave-base, producing quiescent lagoons during highstands. This causes a reduction in eolian production, causing strand plains to prograde into lagoons (Infante, 2012). During sea level regression, the declining wave base mobilizes lagoonal sediments. This produces regressive-phase eolianites. These regressive-phase eolianites often overstep reefs and subtidal deposits (Carew and Mylroie, 1995). Regressive-phase eolianites are also colonized by vegetation and contain abundant vegemorphs (Birmingham et al., 2008; Mylroie et al., 2018).

Platform exposure causes epikarst development and pedogenic processes to initiate. Collection of insoluble material from African dust produces fossilized soil horizons called terra rossa paleosols (Muhs et al., 1990). Carbonate paleosols have been studied to determine the main source of Bahamian soils and paleosols to be consistent with an airborne source. The Quaternary stratigraphy of The Bahamas consists of depositional packages separated by *terra rossa* paleosols formed during sea level lowstands. The stratigraphy of Eleuthera consists of the Middle Pleistocene Owl's Hole Formation, which contains several *terra rossa* paleosols; the Late Pleistocene Grotto Beach Formation, which consists of the French Bay Member, the Cockburn Town Member, and is topped by a *terra rossa* paleosol; the Late Pleistocene Whale Pont Formation, bounded by *terra rossa* paleosols and only reported on Eleuthera; and the Holocene Rice Bay Formation, which consists of the North Point Member and the Hanna Bay Member (Figure 2). The Holocene units are too young to have developed a terra rossa paleosol.

Bahamian karst

The young rocks of The Bahamas represent carbonate sequences that have only undergone eogenetic diagenesis. All of the karst features present in The Bahamas must be explained within this constraint. There are specific types of karst features found on islands that are specific to carbonate coastlines, that include surface karst, such as karren and kamenitza; pit caves; blue holes (many of these are the result of the collapse of large conduit caves at depth produced by sea-level lowstands (Larson and Mylroie, 2014)); and flank margin caves. This study specifically focuses on cave minerals, so flank margin caves will be the main type of karst discussed. Another type of cave exists in The Bahamas; however, these caves are erosional, pseudokarst features called littoral caves or sea caves produced by wave action, and tafoni produced by wind action.

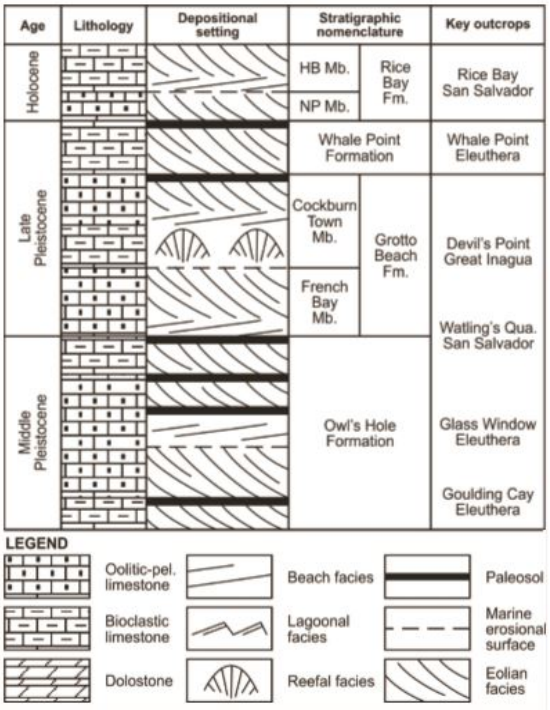


Figure 2. Complete stratigraphy of The Bahamas with key outcrops included (from Kindler et al., 2010).

Flank margin caves are the largest karst features on Eleuthera. These caves develop in the distal margin of the freshwater lens at the flank of the enclosing landmass (Mylroie and Carew, 1995). Three factors at this location result in increased solubility of carbonates: 1) mixing dissolution at the vadose-phreatic mixing zone at the top of the lens superimposed with mixing dissolution at the marine-fresh water mixing zone located at the bottom of the lens, 2) decomposition of organic material that collects at density interfaces (e.g. top and bottom of the lens), and 3) increase in flow velocity as lens cross section decreases at the lens margin. Another type of cave, called Banana Holes, found in The Bahamas forms by a similar mechanism as flank margin caves, in prograding strand plains during highstands as syndepositional voids (Infante, 2012; Mylroie et al., 2015).

Caves and types of speleothems and cave minerals

Fifteen caves were investigated in January 2016 on Eleuthera. Seven of these caves were flank margin caves, four were littoral caves, two were blue holes, one was a pit cave, and the final cave was a overprinted cave (likely flank margin with littoral overprinting). In the present study, the majority of speleothems investigated were collected from caves assigned to the flank margin category.

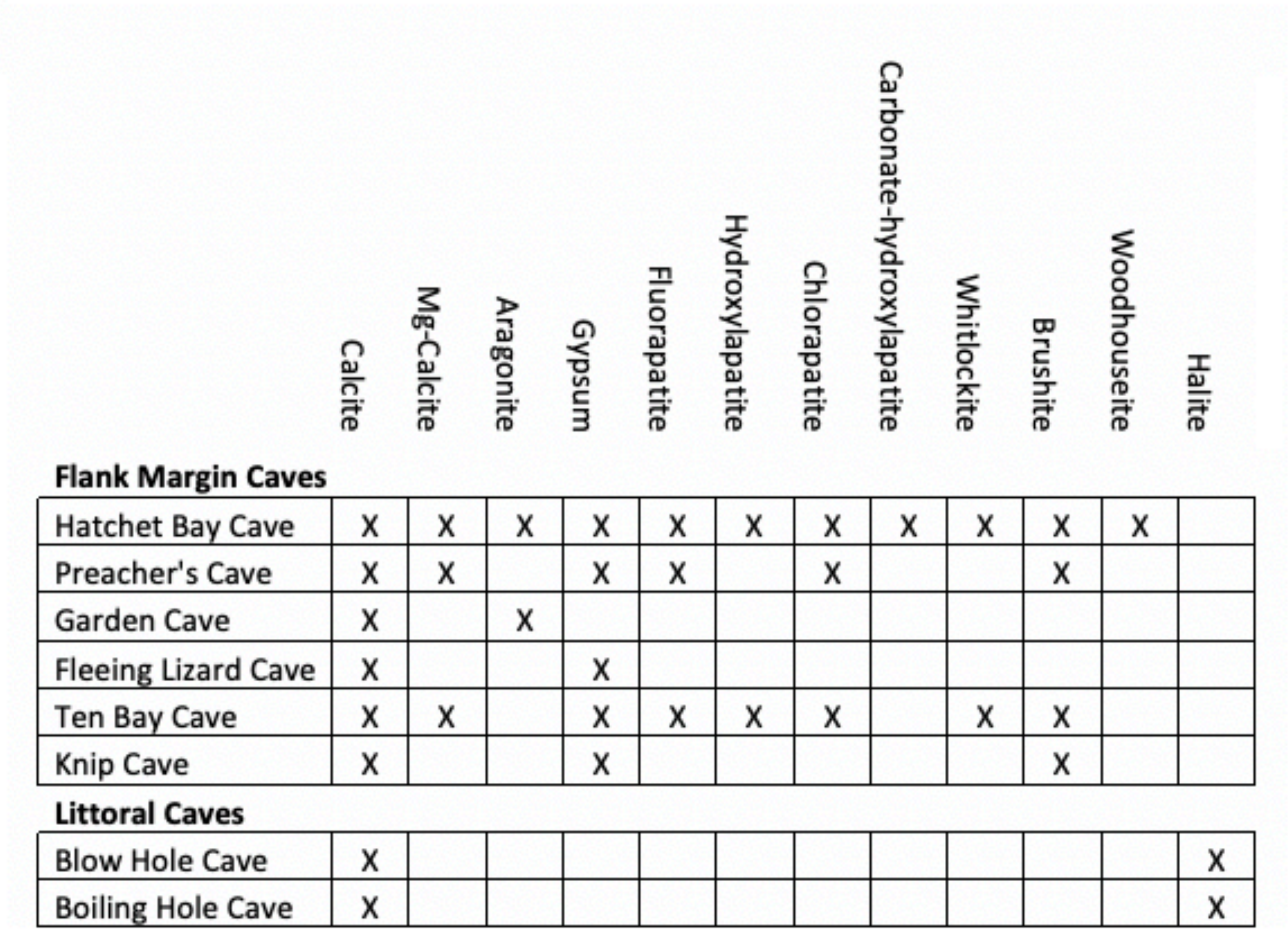
Previous investigations of cave minerals on San Salvador Island in The Bahamas revealed the presence of approximately twenty minerals despite the limited carbonate lithology (Onac et al., 2001, 2009). The presence of bat guano and marine ions provide the necessary chemistry for formation. In addition, the two previous studies expanded sample collection to crusts and earthy aggregates collected within fresh and desiccated guano piles instead of focusing on traditional speleothems. The main goal of this study is to investigate the mineral diversity on Eleuthera and compare to previous studies on San Salvador Island.

METHODS

Paleosol sample

One sample was collected from a paleosol within Hatchet Bay Cave. The sample was air-dried, powdered using a low-speed dental drill, sieved through 45 µm mesh, and analyzed for bulk mineralogy. Bulk mineralogy was analyzed by a Rigaku Miniflex 600 diffractometer. XRD patterns were obtained as follows: continuous mode, 0.002° per step, 4° 2θ per minute, 3° -70° 2θ CuKα radiation. Relative mineral percentages were estimated from relative intensities of peak heights of XRD lines. In addition to bulk mineralogy, the paleosol sample was processed to remove carbonates and organics before fractionating by size. Treatments (K-saturation, Mg-saturation, heating, and gylcolnation) were used to determine the specific clay mineralogy.

Table 1. Cave mineral occurrence by cave type



	Calcite	Mg-Calcite	Aragonite	Gypsum	Fluorapatite	Hydroxylapatite	Chlorapatite	Carbonate-hydroxylapatite	Whitlockite	Brushite	Woodhouseite	Halite
Flank Margin Caves												
Hatchet Bay Cave	X	X	X	X	X	X	X	X	X	X	X	
Preacher's Cave	X	X		X	X		X			X		
Garden Cave	X		X									
Fleeing Lizard Cave	X			X								
Ten Bay Cave	X	X		X	X	X	X		X	X		
Knip Cave	X			X						X		
Littoral Caves												
Blow Hole Cave	X											X
Boiling Hole Cave	X											X

Cave mineral samples

A total of 36 samples were collected from flank margin caves on Eleuthera plus another 12 samples from littoral caves, pit caves, and blue holes. All 48 samples were analyzed for mineral identification. The location of mineral samples varied from cave to cave due to several factors including: number of entrances, humidity, presence of guano (fresh and degraded), presence of excavation pits within guano, and accumulations of crusts on walls and ledges. Most samples collected from Eleuthera caves were weathered crusts, earthy nodules, residual rinds beneath mined guano layers, and precipitates beneath active drips.

The identification of minerals was primarily done by means of XRD and inspection using a binocular microscope. Samples were air-dried, pulverized, sieved through a 45 micron mesh, and analyzed on a Rigaku Miniflex 600 at Sam Houston State University. XRD patterns were obtained as follows: continuous mode, 0.02^{o} 2θ per step, 2^{o} 2θ per minute, 3^{o}–70^{o} 2θ, CuKa radiation. An internal quartz standard was used. The overall results of the XRD analyses are tabulated in Table 1, and the representative XRD patterns are shown in figures 3 and 9.

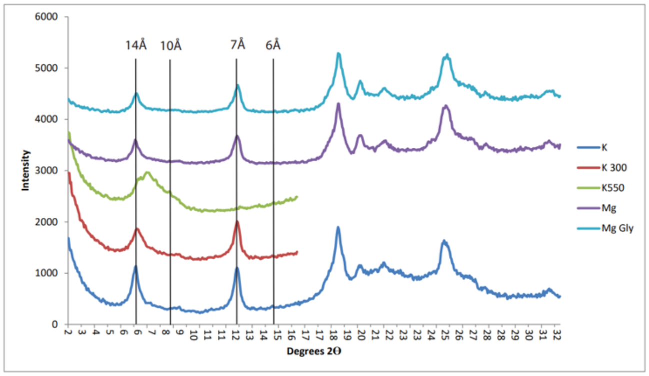


Figure 3. XRD analysis showing the various treatments of clay fractions of the paleosol sample from Hatchet Bay Cave.

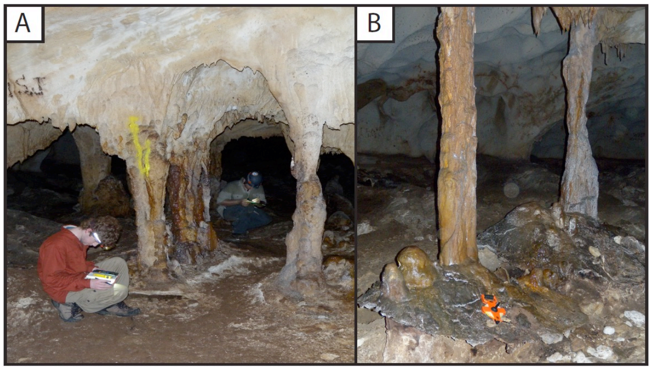


Figure 4. Both inactive (A) and active (B) carbonate speleothems in Hatchet Bay Cave.

RESULTS AND DISCUSSION

Paleosols

XRD analysis indicated the paleosol sample consists of a Fe-rich Chlorite, Illite, and Boehmite (Figure 3). Clay minerals observed were Fe-rich Chlorite ($(Fe^{+2},Mg,Al,Fe^{+3})_6(Si,Al)_4O_{10}(OH,O)_8$) and Illite ($K_{0.6}(H_3O)_{0.4}Al_{1.3}Mg_{0.3}Fe^{+2}_{0.1}Si_{3.5}O_{10}(OH)_2\cdot(H_2O)$) based on the 14 Å and 10 Å reflections. Boehmite ($AlO(OH)$) was identified by a reflection peak shift from 14 Å to 6.1 Å (Figure 3). Non-clay minerals included low Mg-calcite and quartz. Illite and chlorite were identified from the presence of 10Å and 14Å reflections which did not shift after treatment with ethylene glycol or collapse after heating to 550° C. The slightly larger [002] 7Å compared to the [001] 14Å peak indicates a Fe-rich chlorite. The origin of chlorite is most likely of a detrital nature from African dust.

Cave minerals

In the fifteen caves investigated, twelve cave minerals were identified. Hatchet Bay Cave contained eleven of the twelve minerals. Overall, flank margin caves contained more diverse accumulations of cave minerals compared to their littoral counterparts. The cave mineral results are summarized in Table 1. Only calcite was identified from pockets in the walls of pit caves and blue holes on Eleuthera, so those results were omitted from Table 1.

Specific mineral groups: Carbonates

Calcite is found in every cave investigated, making up the bulk of most of the speleothems (Figure 4). Aragonite is plentiful in drier portions of flank margin caves, such as Hatchet Bay Cave and Garden Cave, but it is mainly restricted to erratic speleothems, such as small helictites and eccentrics. No further details are given for calcite and aragonite due to their common appearance in the cave environment.

Specific mineral groups: Sulfates

Gypsum ($CaSO_4 \bullet 2H_2O$) was the only documented sulfate mineral found during this reconnaissance. These gypsum deposits form mostly as crusts and blisters in several caves on Eleuthera (Figure 5). There are two mechanisms for Bahamian gypsum crusts: 1) evaporative processes acting on sea spray or saline water bodies in caves and 2) oxidation of biogenic pyrite producing sulfuric acid that reacts with eolianites (Bottrell et al., 1993; Onac et al., 2001, 2009).

Specific mineral groups: Phosphates

The second most abundant (by number) mineral group in Bahamian cave environments is the phosphate group due to the interaction of guano and leachates with carbonate rocks (Figure 6). Four varieties of apatite were documented (with only Hatchet Bay Cave hosting all four varieties). Brushite, whitlockite, and woodhouseite were other phosphates identified in Eleuthera caves. There were no ammonium phosphates identified, possibly because samples were not collected beneath active bat locations.

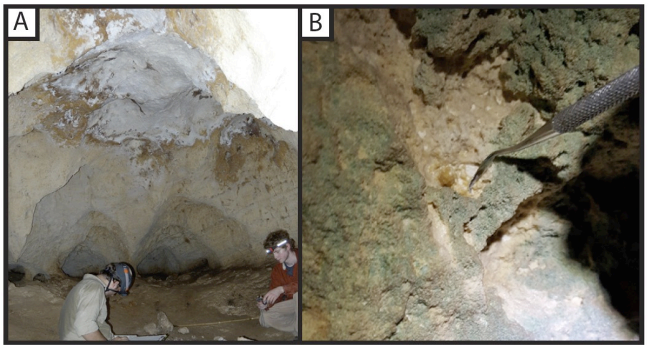


Figure 5. A) Gypsum crust on ceiling pocket of Knip Cave. B) Small gypsum blisters in Preacher's Cave.

Figure 6. Excavated guano pit with earthy phosphatic crusts at the guano-limestone interface and nitrate minerals located in the guano residue within the pit.

The apatite group (hydroxylapaite, $Ca_5(PO_4)_3(OH)$; chlorapatite, $Ca_5(PO_4)_3$ (Cl); carbonate-hydroxylapatite, $Ca_5(PO_4,CO_3)_3$ (OH); and fluorapatite, $Ca_5(PO_4)_3(F)$ was the most common phosphate mineral group identified in Eleuthera caves. The presence of fluorapatite and chlorapatite require marine waters to form and exist stably. These minerals are found in Hatchet Bay Cave, Ten Bay Cave, and Preacher's Cave, which all experience marine water spray. Dryer caves or caves with freshwater pools did not contain these two types of apatite.

The next most abundant phosphate was brushite ($CaHPO_4 \bullet 2H_20$). It formed small light brown crusts near the bottom of walls and on guano covered breakdown blocks. Brushite was almost always found in association with apatite mineral crusts. Similar relationships have been documented between apatite and brushite, which were interpreted to represent brushite replacement of hydroxylapatite (Onac et al., 2009).

Whitlockite ($Ca_9Mg(PO_3OH)(PO_4)_6$) was identified in Hatchet Bay Cave and Ten Bay Cave on wall crusts at the base of cave wall deposits. The whitlockite likely formed by the Mg-enriched solutions derived from sea-spray descending through guano deposits.

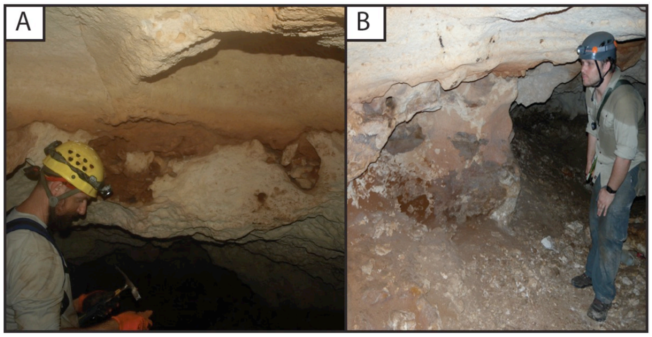


Figure 7. A) Paleosol surface within Hatchet Bay Cave collecting guano in small pockets. B) Sampling location showing bat guano (brownish red) accumulating on paleosol within Hatchet Bay Cave. Dark Brown crust on paleosol was identified as woodhouseite. Whitlockite was also found on the wallrock at the base of the wall, well below the woodhouseite crust.

Woodhouseite ($CaAl_3(SO_4)(PO_4)(OH)_6$) is part of the alunite supergroup and has been previously been reported as the product of bat guano in cave environments (Hill and Forti, 1997). This mineral has not been previously reported from caves in The Bahamas. Woodhouseite samples came from Hatchet Bay Cave, specifically from small crusts found on the exposed paleosol within the cave (Figures 7 and 8). The presence of woodhouseite was confirmed in three samples from various locations within the cave using XRD analysis (Figures 8 and 9). Woodhouseite formation in this instance likely represents phosphate-rich leachate derived from the combination of seawater and guano interacting with the various aluminum-rich phases found within the clay fraction of the paleosol.

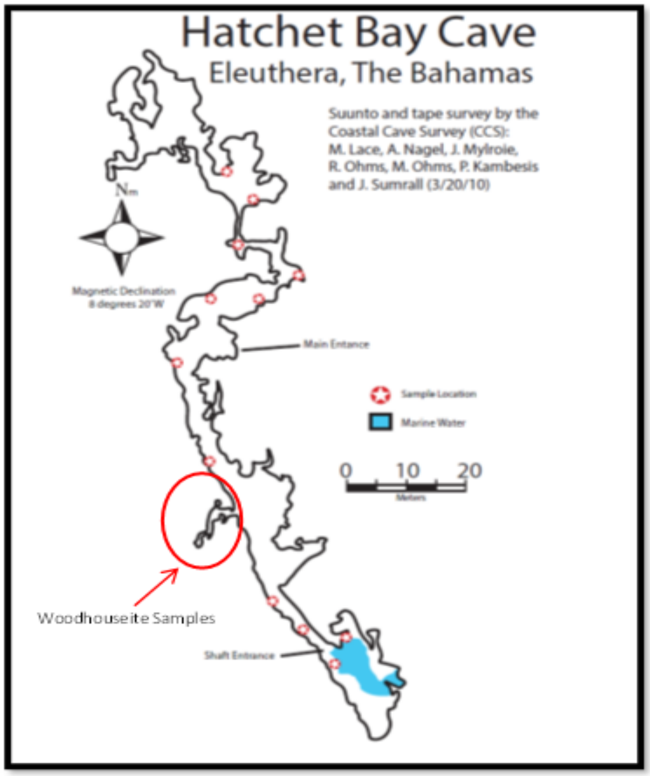


Figure 8. Simplified cave map of Hatchet Bay Cave showing sampling locations, noting the key locations of woodhouseite.

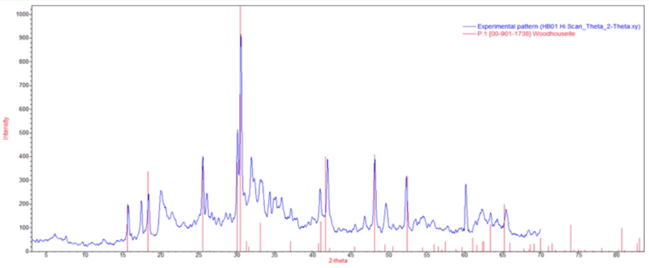


Figure 9. Representative XRD spectrum of woodhouseite from Hatchet Bay Cave.

Specific mineral groups: Halides

Halite (NaCl) was identified by XRD analysis at two locations on Eleuthera, Blow Hole Cave and Boiling Hole Cave. Both locations are littoral caves that fall well within the wave action zone. The origin of halite was interpreted as precipitation from aerosols and wave-splashed seawater inside the cave. The samples were found in ceiling and wall pockets during low tide as white crusts.

Specific mineral groups: Silicates

Clay minerals and quartz were documented in the paleosol found in Hatchet Bay Cave. While these were not considered cave minerals as being the product of a cave environment, their presence inside of the cave is worth documenting. Quartz specifically has an origin as an aerosol dust from Africa.

Relationship between paleosols and cave minerals

Bahamian caves, especially flank margin caves, have shown a relatively high diversity of cave minerals (Onac et al., 2001, 2009). Eleutheran caves show no exception to this trend. One difference that has been documented in Eleutheran caves was sampling from a cave that has a paleosol within it (Hatchet Bay Cave). Paleosol mineralogy was explored after woodhouseite was positively identified in three samples from Hatchet Bay Cave. The mechanism of woodhouseite's origin was dependent upon the identification of an aluminum bearing phase in an environment where both sulfate and phosphate ions were readily accessible. Clay mineral analysis of paleosols from Hatchet Bay Cave revealed that aluminum phases (boehmite, illite, and chlorite) were present. The interaction with phosphatic solutions leached from bat guano coupled with either sea spray or marine groundwater would account for the anion complexes found in woodhouseite. It is hypothesized that the interaction of this leachate specifically with the minerals found in the paleosol in the cave would account for woodhouseite formation, as well as other non-silicate mineral phases. This study suggests that other flank margin caves with exposed paleosols should also contain the appropriate environment for woodhouseite formation. Cave microclimate may have also play a role, especially in determining the humidity, temperature, and other geochemical parameters required for woodhouseite formation in The Bahamas. It is also uncertain the role that previous highstands of sea level (i.e. MIS 5e) would play in older guano deposits. These questions are beyond the scope of this study, but they warrant future study.

CONCLUSIONS

Eleuthera caves contain a wide variety of minerals associated with marine water and bat guano. The presence of paleosols in a flank margin cave environment allowed for the documentation of one particularly rare phosphate mineral, woodhouseite ($CaAl_3(SO_4)(PO_4)(OH)_6$) that has not been previously documented in Bahamian caves. Paleosol analyses revealed the presence of mineral phases capable of forming complex phosphate minerals when exposed to guano in a cave environment. Mineralogic evidence from Hatchet Bay Cave was interpreted to represent the interaction of aluminum phases from an exposed paleosol with leachate from bat guano. In addition to woodhouseite, several mineral groups are well represented in the caves of Eleuthera. However, more samples are needed from additional locations within caves and additional caves to achieve a better cave mineral inventory.

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