

# **<sup>PS</sup> Micromorphological, Stable Isotope, NMR, Geomicrobial and Crystallographic Analysis of Quaternary Calcrete Formation, Puerto Rico\***

**Katherine B. Kuklewicz<sup>1</sup>, Luis A. Gonzalez<sup>2</sup>, Jennifer A. Roberts<sup>2</sup>, and Chi Zhang<sup>2</sup>**

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<sup>1</sup>KICC (Kansas Interdisciplinary Carbonates Consortium), Department of Geology, University of Kansas, Lawrence, Kansas, United States ([kkuklewicz@ku.edu](mailto:kkuklewicz@ku.edu))

<sup>2</sup>KICC (Kansas Interdisciplinary Carbonates Consortium), Department of Geology, University of Kansas, Lawrence, Kansas, United States

## **Abstract**

Pedogenic calcretes are widely used as evidence for subaerial exposure and are commonly used as sequence boundaries. Due to their association with exposure in dry regions, calcretes are commonly used as indicators for arid and semiarid paleoclimates. Yet in the literature calcretes have been reported from areas with as much as 990 mm/year, and more recently we have documented calcretes in tropical settings with precipitation over 1600 mm/year. To improve our interpretation of environment of deposition (EOD) using calcretes, this study aims to produce quantitative diagnostic criteria to identify semiarid versus humid calcretes in the rock record. Such EOD criteria is useful for carbonate reservoir characterization since calcretes have the potential to affect subsurface fluid flow. Fieldwork results reveal that semiarid calcretes are laterally extensive, continuous, and impermeable and thus, if preserved, they have the potential to compartmentalize (locally) reservoirs. In contrast, humid calcretes are patchy, discontinuous, and semipermeable which may not affect reservoir quality. Identifying exposure surfaces in these humid areas may be difficult given the paucity of the calcretes' extent. Microscopy results show that semiarid profiles are extensively recrystallized with micrite, microspar, and pseudospar leading to decreased primary porosity. Humid profiles contain well-preserved original fabrics and uncemented voids leading to preserved primary porosity. Laboratory results from NMR illustrate that semiarid calcretes have lower porosity relative to the host sediment, which is inferred to result from the extensive cementation and recrystallization, indicating high amounts of diagenesis, hence, tight carbonates (local traps?). Humid calcretes have higher porosity relative to the host sediment, reflecting the incomplete cementation and infilling of voids, indicating minimal diagenesis, thus porous carbonate deposits. Integrated calcrete field observations, micromorphology, and geophysics improve EOD interpretation of secondary carbonates in marine and terrigenous settings as well as provide useful information about carbonate reservoir characteristics.

### **References Cited**

Jones, B., 1988, The Influence of Plants and Micro-Organisms on Diagenesis in Caliche: Example from the Pleistocene Ironshore Formation in Cayman Brac, British West Indies: *Bulletin of Canadian Petroleum Geology*, v. 36, p. 191-201.

Semeniuk, V., and D.J. Searle, 1985, Distribution of Calcrete in Holocene Coastal Sands in Relationship to Climate, Southwestern Australia: *Journal of Sedimentary Petrology*, v. 55, p. 86-95.

Shinn, E.A., R.S. Reese, and C.D. Reich, 1994, Fate and Pathways of Injection-Well Effluent in the Florida Keys: U.S. Geological Survey, Open-File Report 94-276, 122 p.

Torres-Valcárcel, A., J. Harbor, C. González-Avilés, and A. Torres-Valcárcel, 2014, Impacts of Urban Development on Precipitation in the Tropical Maritime Climate of Puerto Rico: *Climate*, v. 2, p. 47-77.



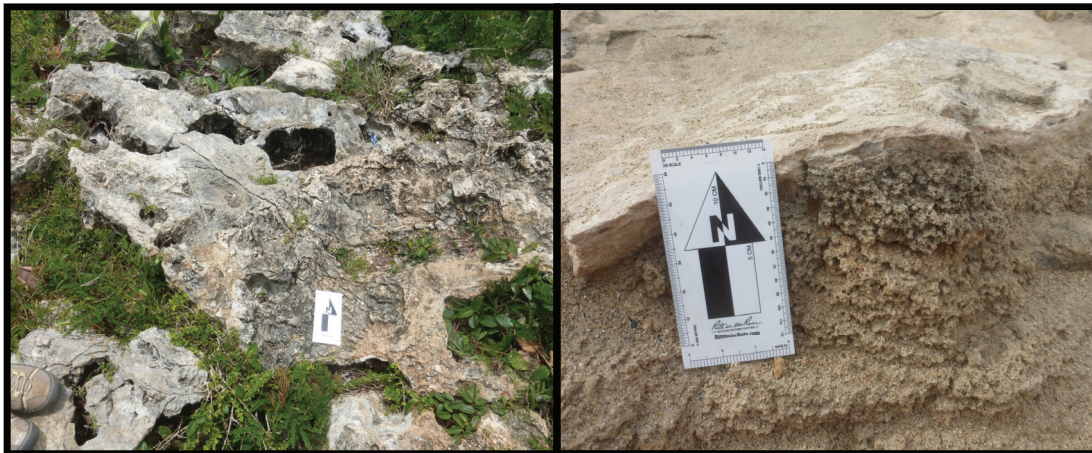
# Micromorphological, Stable Isotope, NMR, Geomicrobial and Crystallographic Analysis of Quaternary Calcrete Formation, Puerto Rico

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## Motivation

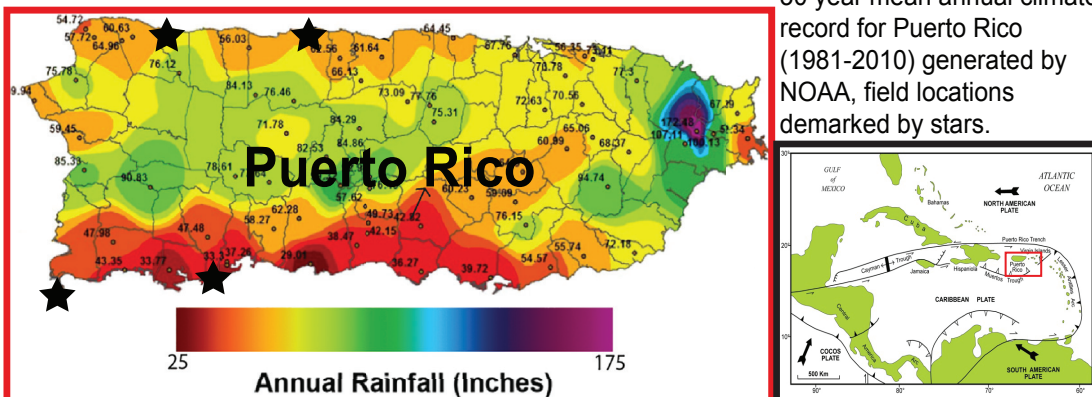
- Calcrete crusts are early diagenetic subaerial exposure surfaces widely used as indicators of paleoclimate and environments of deposition (EOD)
- They are often interpreted as arid climate indicators, however they occur in areas with rainfall up to 1650 mm/year
- To improve our interpretation of paleoclimate and EOD using calcrete, this study will produce quantitative diagnostic criteria for distinguishing between semiarid and humid calcretes



Humid calcrete (left), semiarid calcrete (right)

## Location

- The study area, Puerto Rico, contains modern calcrete deposits forming along climatically different coasts which exhibit distinct vegetation coverage: the north coast is classified as Tropical Monsoon, whereas the south coast is classified as Tropical Savanna
- Calcretes on the north coast are developing on Miocene carbonates and Pleistocene eolianites; south coast are on Miocene carbonates



30 year mean annual climate record for Puerto Rico (1981-2010) generated by NOAA, field locations demarked by stars.

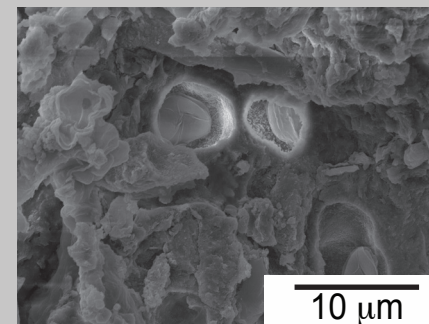
## Methods

- 1) Map the spatial variability (i.e. lateral extent and thickness) of calcrete deposits under each climate.
- 2) Systematically sample to capture a diversity of textures, surficial geometries and associated biota.
- 3) Characterize textures of calcretes using conventional binocular, detailed polarized light microscopy on thin or thick sections as appropriate.
- 4) Quantify microbial abundance and distribution using a SEM to determine the role of microbes in the formation of calcrete.
- 5) Perform geochemical and isotopic analysis of calcrete using an ICP-OES to evaluate the geochemical variations at each site.
- 6) Use NMR, specifically  $T_2$  relaxation measurements, to quantify the porosity, and pore size distribution on humid and arid calcrete.

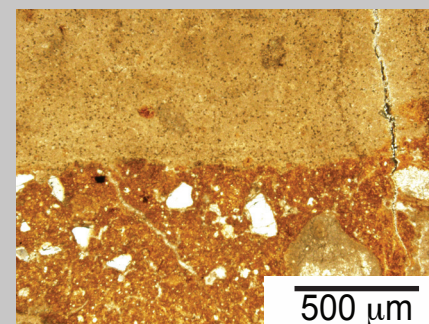
## Is this calcrete modern forming?

Yes, the calcrete is modern forming because:

- The presence of living microbes within isolated cavities



- Preserved rootlets near the surface suggests organic matter is currently being incorporated



## Spatial Distribution

North Coast



Spatial Extent:

- Discontinuous and patchy

Thickness:

- Approximately 10 cm thick

South Coast



Spatial Extent:

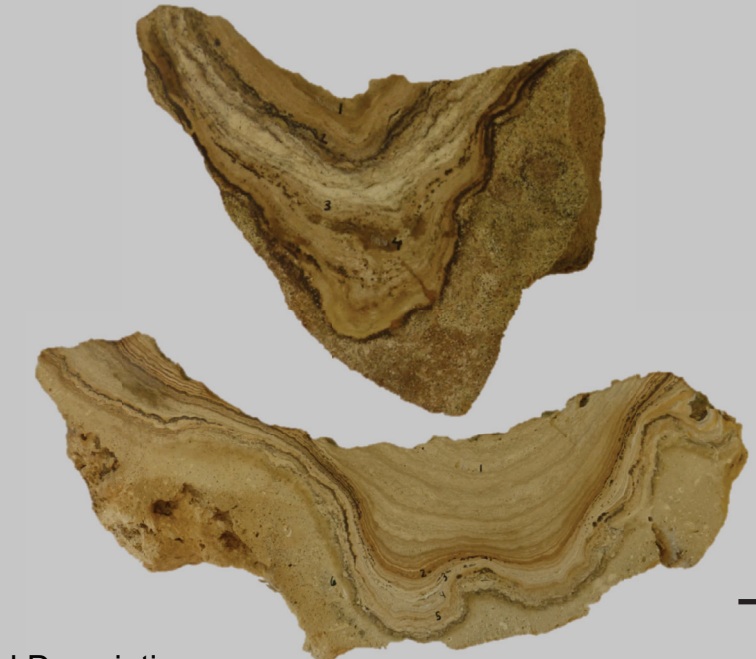
- Continuous and extensive

Thickness:

- Approximately 1.5 m thick

## Macrostructures

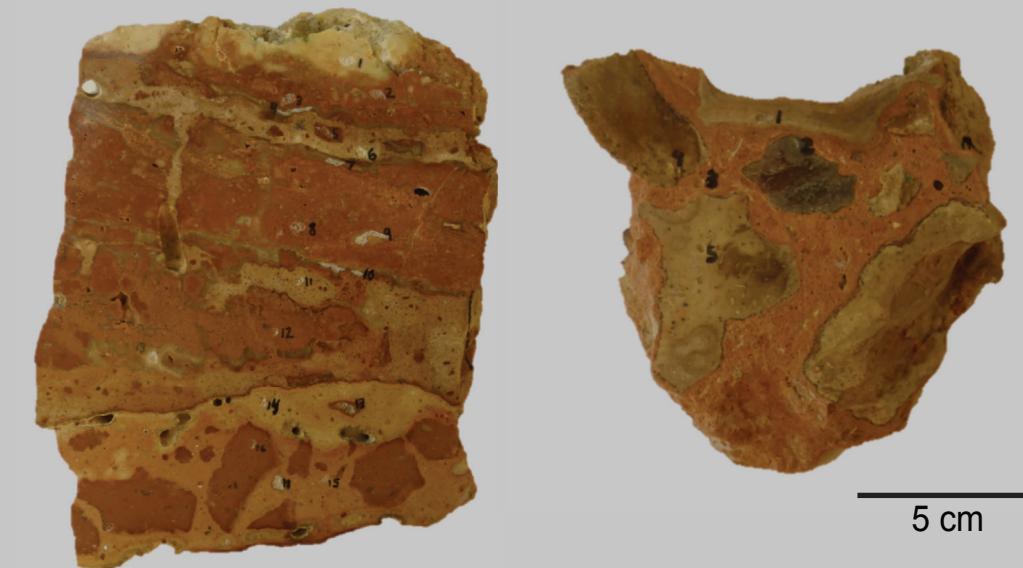
North Coast



General Descriptions:

- Continuous, thin and wavy laminations

South Coast



General Descriptions:

- Multiple cementation and recrystallizations events
- Breccia
- Thick calcite cement zones



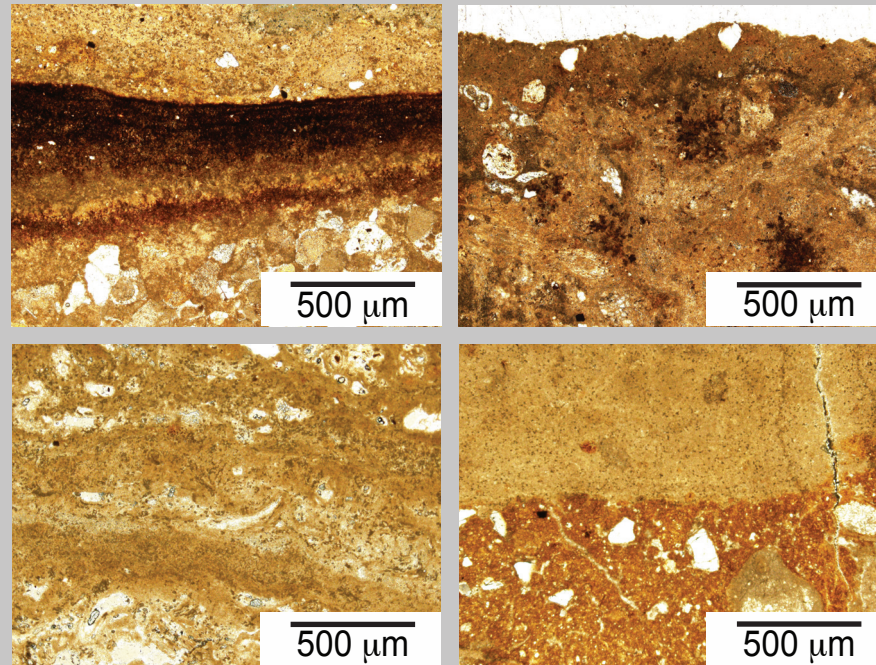
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## Petrography

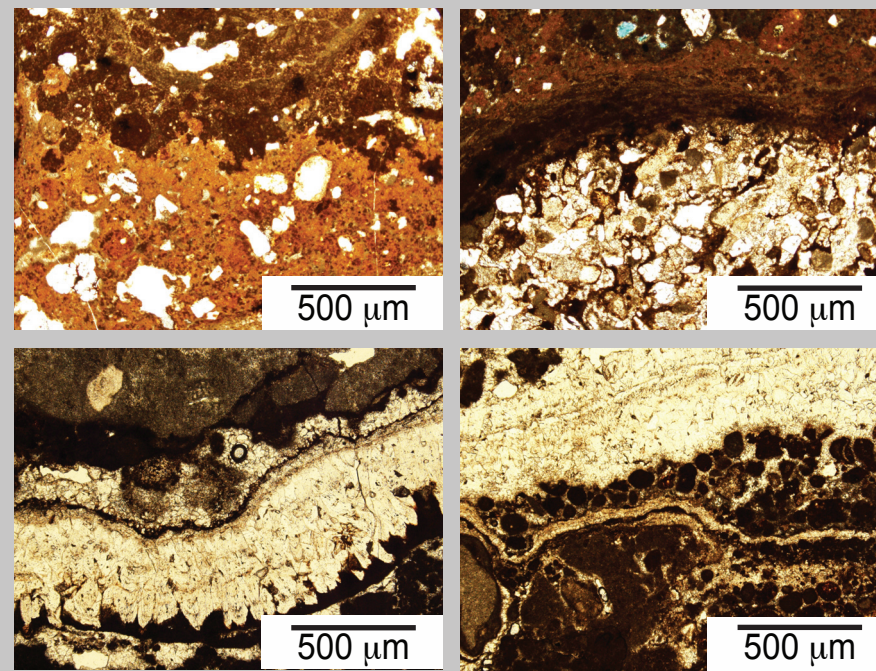
### North Coast



#### Observations:

- Lime mud, micrite, microspar, rhizoliths, recrystallized grains, dark brown clusters of cells (patches and layers)

### South Coast

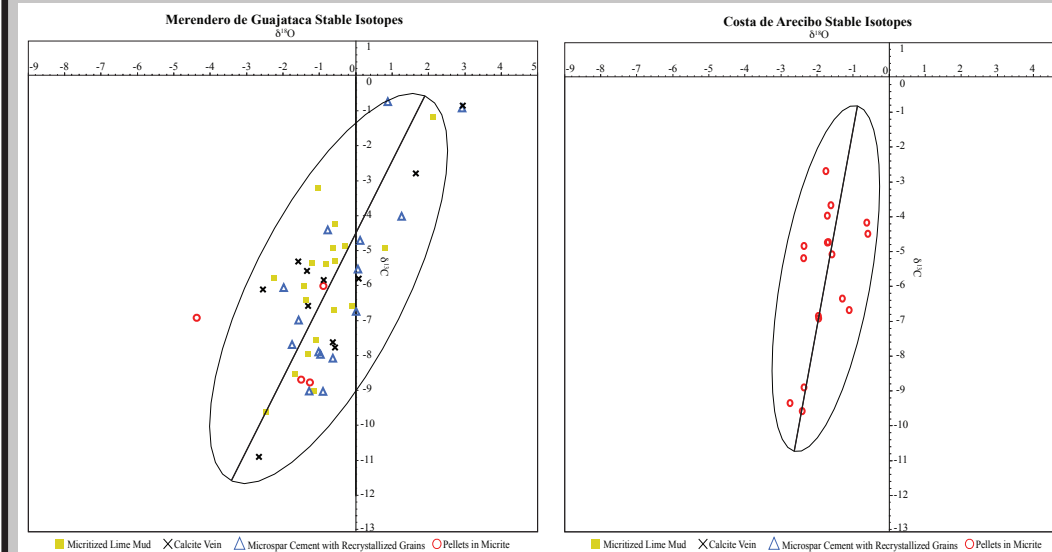


#### Observations:

- Pelids in pseudospar cement, bladed and blocky calcite cements, cemented fractures, recrystallized grains, lime mud, micrite

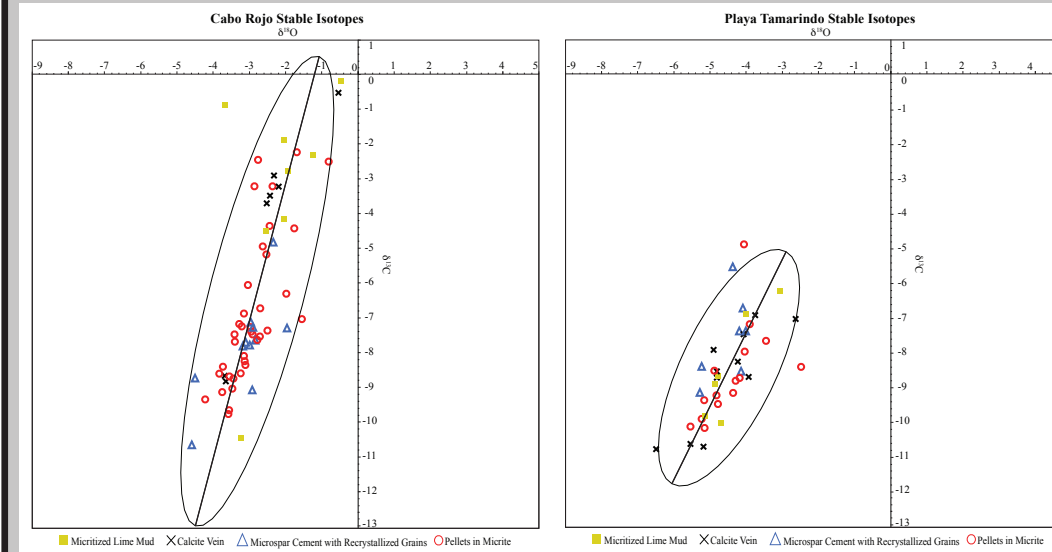
## Stable Isotopes

### North Coast



- Large  $\delta^{18}\text{O}$  ranges due to high precipitation, increased sea spray, increased evapotranspiration
- Large  $\delta^{13}\text{C}$  ranges due to similar contributions of dissolved carbon from the bedrock and the oxidation of organic matter

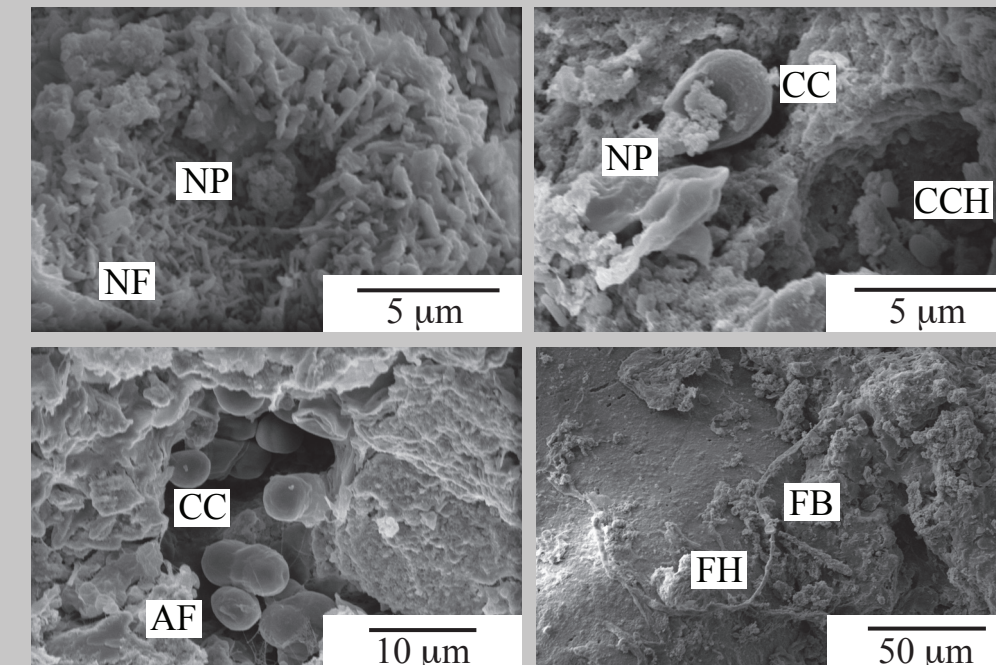
### South Coast



- Similar  $\delta^{18}\text{O}$  values in Cabo Rojo as North Coast despite rainfall difference because higher evaporation and exposure of Cabo Rojo
- Slightly heavier  $\delta^{18}\text{O}$  range in Playa Tamarindo due to increased tropical storms and prevailing east-west wind pattern
- Similar  $\delta^{13}\text{C}$  values as North Coast due to explanations mentioned above
- Lack of correlations between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values with respect to depth could be due to inherent mixing during calcrete formations (episodic dissolution and recrystallization)

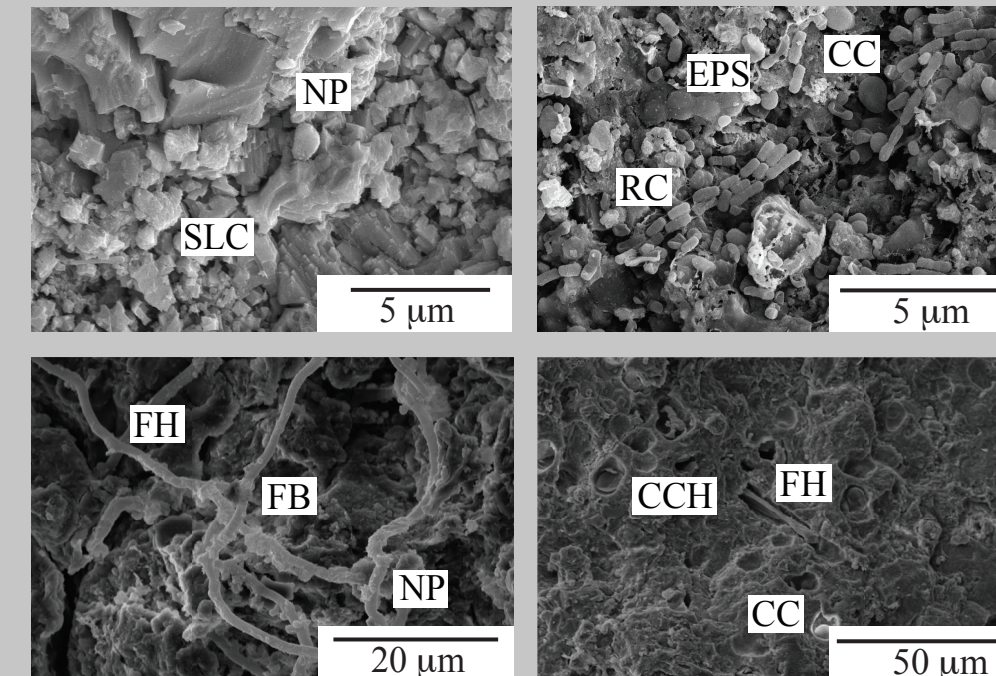
## Scanning Electron Microscope

### North Coast



- Nodular precipitate (NP), needle fibers (NF), cocci cells (CC), cocci cell holes (CCH), attachment filaments (AF), fungal hyphae (FH), fruiting bodies (FB).

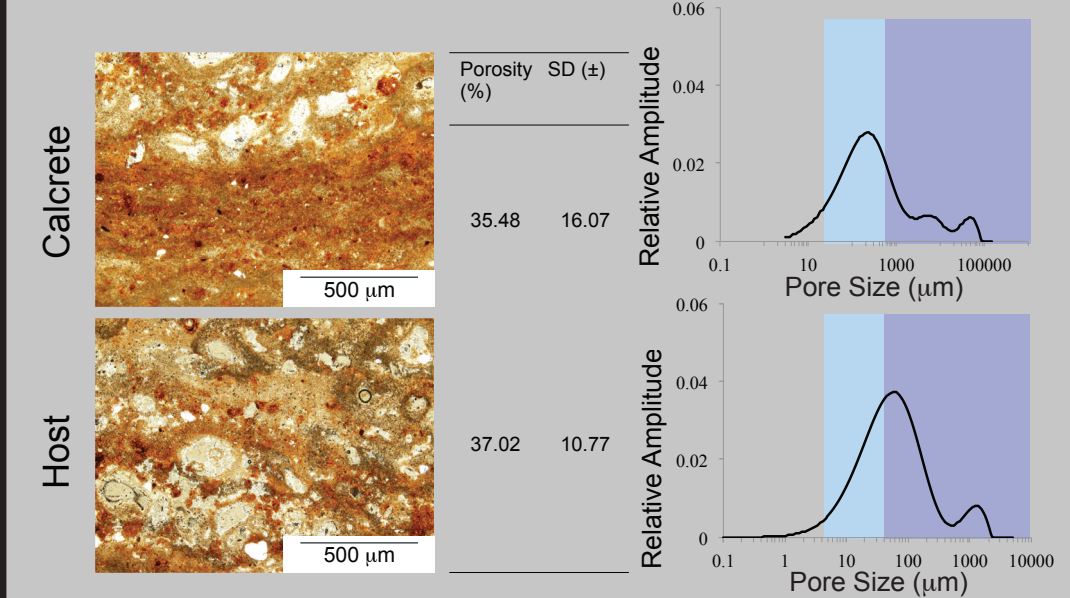
### South Coast



- Nodular precipitate (NP), step like calcite (SLC), extracellular polysaccharides (EPS), cocci cells (CC), rod shaped cells (RC), fungal hyphae (FH), fruiting bodies (FB), cocci cell holes (CCH).

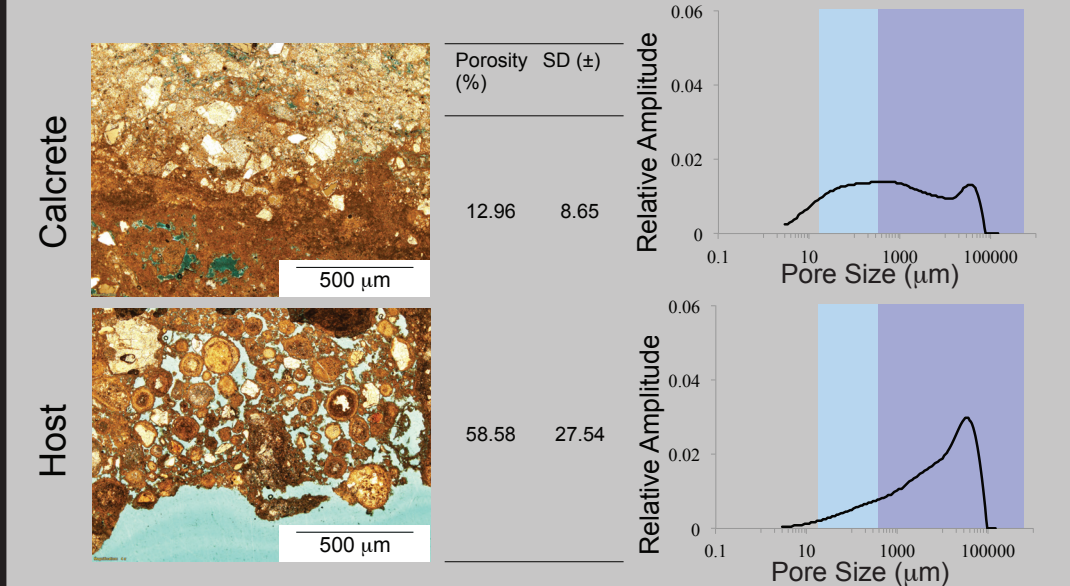
## Nuclear Magnetic Resonance

### North Coast



- Calcrete does not markedly affect porosity from the host
- Macropores → slight shift to more Meso- Macropores

### South Coast



- Calcrete decreases porosity from the host material by fourfold
- Macropores → Micro- Meso- and Macropores



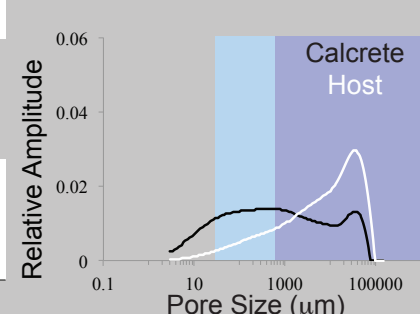
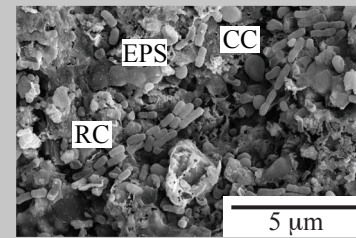
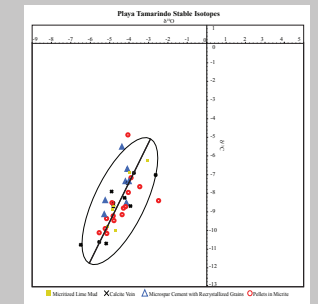
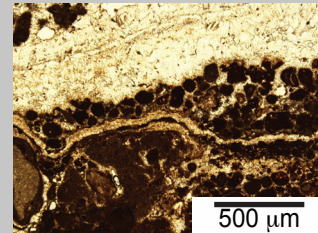
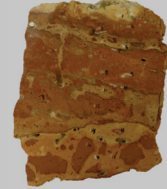
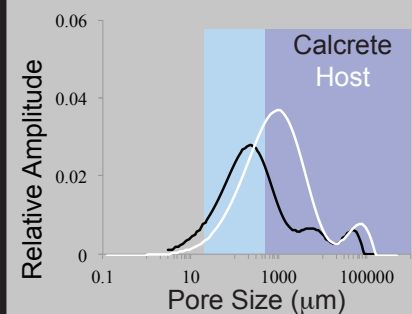
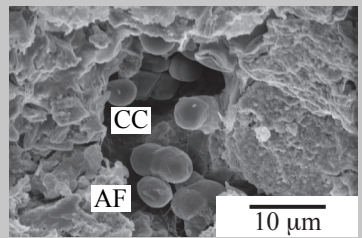
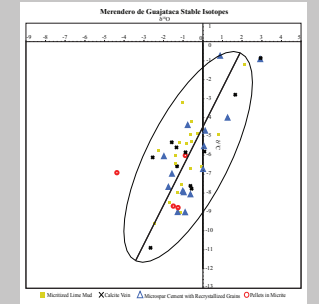
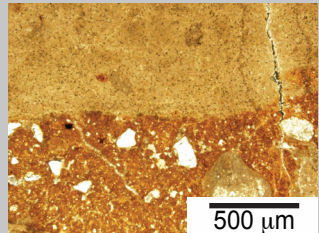
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Summary Table

| Humid Calcrete  | Criteria                             | Semiarid Calcrete   |
|---|--------------------------------------|---|
| Discontinuous, patchy, ~10 cm thick   | Lateral Extent                       | Continuous, extensive, ~1.5 m thick   |
| Thin, continuous laminations  | Macrostructures                      | Thick horizons of dissolution and recrystallization, brecciation of underlying material   |
| Lime mud, micrite, rhizoliths, recrystallized grains  | Microstructures                      | Peloids, pseudospar, bladed and blocky calcite cements, cemented fractures, recrystallized grains   |
| Large range due to high precipitation, increased sea spray, increased evapotranspiration                                | Stable Isotope $\delta^{18}\text{O}$ | Similar values in Cabo Rojo as North Coast due to higher evaporation and exposure. Slightly heavier range in Playa Tamarindo due to increased tropical storms and prevailing east-west wind pattern |
| Large range due to similar contributions of dissolved carbon from the bedrock and the oxidation of organic matter       | Stable Isotope $\delta^{13}\text{C}$ | Similar values as North Coast due to similar contributions of dissolved carbon from the bedrock and the oxidation of organic matter   |
| Nodular precipitate, needle fibers, cocci cells, cocci cell holes, attachment filaments, fungal hyphae, fruiting bodies | Microbe Abundance                    | Nodular precipitate, step-like calcite, rod shaped cells, cocci cells, cocci cell holes, extracellular polysaccharides, fungal hyphae, fruiting bodies  |
| 35.48%  | Calcrete Porosity                    | 12.96%  |
| 37.02%  | Host Porosity                        | 58.58%  |
| Calcrete does not markedly affect porosity from the host  | Change in Porosity                   | Calcrete decreases porosity from the host material by fourfold  |
| Pore reduction: slight shift to more Mesopores  | NMR T2 Graphs                        | Pore Reduction: Macropores to Meso- and Micro- pores  |



## Key Findings

- Carbonate coastal plains tend to have considerable variability in meteoric diagenesis, thereby affecting porosity (ranges and variability) and permeability.
- The island of Puerto Rico has calcretes forming along the northern humid coastal plain and along the southern semiarid coastal plain, leading to different calcrete textures, petrographies, isotopic signatures and geophysical attributes.
- Calcrete formation in semiarid environments decreases porosity of the host material by fourfold, which has the potential to form small sized caps and partitions in the subsurface.
- In contrast, calcrete formation in humid environments does not significantly alter porosity, and hence does not affect reservoir character.

## Implications of calcrete formation on Carbonate Reservoir Character

- Humid calcretes did not significantly alter the porosity of carbonates, and hence does not markedly affect reservoir character.
  - In addition, the calcretes produced under humid environments was patchy and discontinuous.



- Semiarid calcretes decreased the porosity of carbonate by fourfold, and as such has the potential to impede subsurface fluid flow.
  - Since the calcretes produced under semiarid environments were laterally continuous and extensive, they have the potential to form small sized caps, which is consistent with the findings of Shinn et al. (1994).



## Future Work

- DNA identification (16S Gene) or microbes
  - Are there differences in microbe species with respect to the hydroclimate (i.e differences between the North and South coast calcretes)?
  - Are there differences in the variability of microbes with respect to the hydroclimate (i.e. number of microbe species on the North vs. on the South coast)?
- Use diagnostic criteria to identify paleoclimate using calcrete in core
- Develop method for dating calcrete deposits
  - Cannot use radiocarbon dating because calcrete formation incorporates inorganic carbon from the atmosphere with carbon from the host material
  - Cannot use U/Th (U series) dating because calcrete incorporates detrital material which has Th, thus altering the relative amounts of U/Th



## References

- Jones, B., 1988, The influence of plants and micro-organisms on diagenesis in caliche: example from the Pleistocene Ironshore Formation in Cayman Brac, British West Indies: Bulletin of Canadian Petroleum Geology 36, p. 191-201.
- Semeniuk, V., and Searle, D.J., 1985, Distribution of calcrete in Holocene coastal sands in relation-ship to climate, southwestern Australia: Journal of Sedimentary Petrology 55, p. 86-95.
- Shinn, E.A., Reese, R.S., Reich, C.D., 1994, Fate and Pathways of Injection-Well Effluent in the Florida Keys: U.S. Geological Survey, Open-File Report 94-276, 122 pgs.
- Torres-Valcárcel, A., Harbor, J., González-Avilés, C., and Torres-Valcárcel, A., 2014, Impacts of urban development on precipitation in the tropical maritime climate of Puerto Rico: Climate, v. 2, p. 47-77.