



# THE DIAGENESIS OF SHELL MIDDENS ALONG THE GULF COASTS OF TEXAS AND FLORIDA

Nicole M. Villarreal<sup>1</sup>, Henry Chafetz<sup>2</sup>, and John Meredith<sup>3</sup>

<sup>1</sup>*Southwestern Energy Company, 10000 Energy Dr., Spring, Texas 77389, U.S.A.*

<sup>2</sup>*Department of Earth and Atmospheric Sciences, University of Houston, 312 Science & Research Bldg. 1, Rm. 312, Houston, Texas 77204, U.S.A.*

<sup>3</sup>*Retired – Anadarko, 1201 Lake Robbins Dr., The Woodlands, Texas 77380, U.S.A.*

## ABSTRACT

Dissolution, mechanical fracturing, color bleaching, and mineralogical conversion of aragonite to calcite within shells from three recent midden sites along the Gulf Coast provide evidence of early, shallow burial diagenesis. Composed of refuse from premodern daily life by indigenous peoples, such as the harvested shells of marine invertebrates after consumption of their soft parts, midden piles offer a unique opportunity to study post-depositional alteration of carbonates within settings well-constrained in terms of both time and environment. It is evident that both physical and chemical diagenesis in subaerial carbonates take place within as few as two thousand years. Hand sample observation and petrographic microscopy display evidence of physical and chemical manifestations of diagenesis, including dissolution, fracturing, and color bleaching of shells, and x-ray diffraction (XRD) confirms mineralogical changes from aragonite to calcite. This study infers that carbonate analyses are more likely to elucidate the influences of introduced waters and not the environmental conditions or length of time since deposition.

## INTRODUCTION

### Shell Middens and their Geologic Potential

Shell middens appear alongside aquatic environments on every continent except Antarctica (Erlandson, 2001). They are sites where people dumped the refuse from their daily lives, such as the shells of marine invertebrates after they had harvested and eaten their contents (Fig. 1). Andrus (2011, p. 2893) stated that shell middens generally refer to “mollusk shell-rich archaeological sites.” This definition seems to agree with most literature, although Andrus’s (2011) designation of a mollusk population is more exacting than most others. Some abandoned shell middens date back to the late twentieth century, whereas others, particularly several located in South Africa, date to more than 160,000 yr B.P. (Andrus, 2011). Inhabitants used these sites as waste dumps, and they can contain artifacts such as the shells of harvested marine invertebrates, the bones of various vertebrates, e.g., mammals, birds, and fish, as well as broken pottery vessels,

or even previous dwellings (Kratt et al., 2008). Human remains are also commonly discovered, as the dead were commonly interred in these piles (Martindale et al., 2009). After dumping utilized materials, people would continue to live on and above the discarded remnants. Geochemical (e.g., stable isotope analysis) and physical characteristic studies (e.g., growth band analysis) of the shells collected from these piles indicate that habitation occurred throughout the year in some sites and was seasonal or only occupied in association with ritualistic feast activities in others (Thompson and Worth, 2011). Middens can be quite extensive and cover several thousand square meters with thicknesses greater than five meters. These larger deposits are thought to have taken hundreds or even thousands of years to develop (Martindale et al., 2009).

The mineralogy of midden piles, predominantly calcite and aragonite, allows for the possibility of extensive diagenesis, namely cementation, dissolution, replacement, recrystallization, physical or mechanical compaction, chemical compaction, or fracturing, to take place (Scholle and Ulmer-Scholle, 2003). Effects, such as fractures, neomorphic calcite replacement of aragonite, and the color bleaching of shells, are evidence of these diagenetic processes (Folk, 1965; Bathurst, 1994; Maliva et al., 2000; and Beitler et al., 2005). Additionally, those shell middens that have remained subaerially exposed exhibit excellent preservation of carbonate materials and, therefore, allow for the extensive study of any diagenetic changes. There are several reasons



**Figure 1.** Habitation at Historic Spanish Point, one site where samples were obtained, began 4500 yr ago and was sustained for over 3000 yr (Bullen and Bullen, 1976). This image shows a portion of one midden at Historic Spanish Point that is over three meters thick. Note the abundance of mollusk shells that create distinct layers within the midden pile.

for this preservation effect: the massive amount of carbonate materials present within the pile buffers acidic waters; fragile shells are sheltered due to the density of layering; and pile depths focus erosion on surface shells (Andrus, 2011).

In addition to more costly methods of dating, e.g., carbon dating, oxygen isotope variation, radiogenic methods, particularly  $^{230}\text{Th}/\text{U}$  and  $\text{U}-\text{Pb}$  or, more recently, electron-spin resonance

(ESR) dating (Rasbury et al., 1997; Glaser, 2003; Titschack et al., 2009; Andrus, 2011), the nature of midden piles allows for an alternative and less costly method for dating: relating structural layering of the midden, itself, to the human artifacts that lie within. This method, termed “seriation,” can provide a shorter period of uncertainty, several hundred to several thousand years, due to previous anthropological studies of human artifacts (Wylde, 2013, p. 15). Whereas this dating scheme would not provide an absolute age of the diagenesis itself, it allows for a shortening of the time range during which the midden could have existed and, therefore, provides a much shorter time frame during which diagenesis could have occurred (creation of the midden to the present).

In the case of the middens studied for this work, the amount of time allowable for diagenesis is, at most, 4500 yr, as the oldest midden analyzed for this study was created between 2500 B.C.E.–500 B.C.E. (Murphy, 2013). Furthermore, archaeologists have extensively studied the environmental conditions surrounding many shell middens in order to better understand the settings in which indigenous people lived. These two facts combined lead to well-documented and easily time-constrained sampling areas for a study on timing and developmental conditions of diagenesis. Within this study, previously-obtained radiocarbon ages are utilized with the use of seriation to corroborate ages of shells analyzed for this study.

### Settings

Four middens at three geographic sites were sampled for this study: Sea Rim State Park, the Pineland Site Complex, and two midden piles at Historic Spanish Point (Table 1). The midden at Sea Rim State Park lies 5.5 km from the Texas coast. It is connected to the Gulf of Mexico by a saline lake to its south that possesses an outlet to the sea. The Pineland Site Complex and Historic Spanish Point are situated on Florida’s west coast (Fig. 2). The middens at the Pineland Site Complex and Historic Spanish Point are situated directly on bays that connect to the Gulf of Mexico.

#### Sea Rim State Park

Sea Rim State Park is located in Jefferson County, Texas. The park is run by the Texas Parks and Wildlife Department (TPWD). It is a 3000 ac system of brackish lakes situated directly adjacent to the Gulf of Mexico. Freshwater is introduced into the park via rainfall, runoff, and through the Sabine and Neches Rivers (Wern, 1993). There is an abundance of wildlife present within the park, which would have made the site an excellent choice for habitation by native peoples. There are several middens located within Sea Rim State Park, but only one was accessible for sampling at the time of this study due to low water levels.

The midden sampled within Sea Rim State Park is designated as state archaeological landmark 41JF47. The midden shall be referred to within this work as the Sea Rim State Park Midden. Its surface, at its highest point, lay 1 m above sea level. Pottery found at the site during the excavations for this study was determined to be of the Goose Creek Series, which, according to the head archaeologist present during sampling, indicates construction by the Atakapan Indians and most likely began from 100 B.C.E.–1000 C.E. (Ruth Mathews, 2013, personal communication).

#### Pineland Site Complex

The Pineland Site Complex was built by the Calusa Indians and is located on the wetlands of the northern tip of Pine Island, adjacent to the Pine Island Sound (Marquardt, 2013). The sampled midden, 8LL33 (Pineland), is one of several archaeological sites within the complex (Walker and Marquardt, 2013). This

**Table 1. Age of creation and a short description of each midden and its location. All are located within predominantly siliciclastic, as opposed to carbonate, depositional systems.**

Site	Midden	Earliest Year of Creation	Length of Existence (in years)	Characteristics
Sea Rim State Park	41JF47	100 B.C.E.	2100	Documented only within state park literature. Lower volume of shell material than Pineland and Historic Spanish Point middens but densely packed with shells nested within one another.
Pineland Site Complex	8LL33	200 C.E.	1800	Midden extensively studied (e.g., Walker and Marquardt, 2013). Shells were concreted in a hardened, dark matrix. Thick packing of shell material.
Historic Spanish Point	Chapel Midden/Shell Ridge	300 B.C.E.	2300	Extent clearly demarcated, most notably by Bullen and Bullen (1976). Likely thousands of years of occupation (300 B.C.E.–1100 C.E.) (Bullen and Bullen, 1976; Murphy, 2013). Midden several meters thick and shells directly nested in one another.
Historic Spanish Point	Hill Cottage Midden	2500 B.C.E.	4500	Studied previously, most extensively by Bullen and Bullen (1976). Period of occupation ranged from 2500 B.C.E.–500 B.C.E. (Bullen and Bullen, 1976; Murphy, 2013). Midden is several meters thick and shells are stacked directly atop one another.

region of Florida is designated as the Caloosahatchee region by archaeologists. Habitation at the Pineland Site Complex began during the Late Holocene approximately 50 C.E.—part of the time period known as the Caloosahatchee I cultural period (Marquardt, 2013).

The samples from this work were found within the Northwest Pasture (8LL33). Previous work on the Northwest Pasture at Pineland has dated its time of occupation to the Caloosahatchee I and early IIA periods, 500 B.C.E.–500 C.E. and 500–800 C.E., respectively (Marquardt, 2013; Walker and Marquardt, 2013). The concreted portion of this midden from which these samples were taken is located 1.5 m below present day ground surface, which stands at modern day sea level (Karen Walker, 2013, personal communication). The samples themselves were hardened masses with dark brown matrix and shell material within and had been radiocarbon dated previously to approximately 200 C.E. (Karen Walker, 2013, personal communication).

**Historic Spanish Point**

Historic Spanish Point, archaeological site designation Palmer Site 8SO2, is located in Osprey, Florida (Murphy, 2013). Original excavations established four main archaeological components to the site: Hill Cottage Midden (2500–500 B.C.E.), Chapel Midden (300 B.C.E.–300 C.E.), Shell Ridge (100–1100 C.E.), and Palmer Burial Mound (300–900 C.E.) (Bullen and Bullen, 1976; Murphy, 2013). More recent works (e.g., Kozuch, 1998), have purported that the Shell Ridge is actually a westward continuation of the Chapel Midden. This amendment to the components at Historic Spanish Point would alter the number of middens on the site to three, two of which, the Hill Cottage Midden and the Chapel Midden/Shell Ridge, were sampled for this study. Dates for each pile were taken from previously performed radiocarbon dating (Bullen and Bullen, 1976; Kozuch, 1998; Murphy, 2013). Historic Spanish Point is located directly on Little Sara-

sota Bay, which connects to the Gulf of Mexico. At their highest elevation, the middens at this site reach a maximum of 3 m above sea level. The site today is a museum owned and operated by the Gulf Coast Heritage Association, Inc. (Bullen and Bullen, 1976; Murphy, 2013).

**Effects of Sea Level**

The importance of the effects of sea-level rise and fall on diagenesis within middens cannot be overstated. Were sea level to rise and cover a midden at any point during its existence, different diagenetic conditions, i.e., submarine versus subaerial, would determine which products, if any, occurred. In Texas, the earliest potential date for the commencement of construction of the midden at Sea Rim State Park is 100 B.C.E. The oldest midden sampled for this study in Florida is the Hill Cottage Midden at Historic Spanish Point, the building of which is estimated to have commenced around 2500 B.C.E. (Murphy, 2013). Therefore, only sea-level rise and fall after these times in each location is significant for this study.

Human settlements along the coastline of Texas appear to correspond with periods of stable sea level from 3900–2200 B.C.E., and after 1000 B.C.E. (Ricklis and Blum, 1997). In the interim, stepwise periods of sea-level rise and fall occurred. Sea level at or near modern levels was reached in Texas around 1000 B.C.E., roughly 900 yr before the building of the Texas midden examined for this work (Ricklis and Blum, 1997).

Sea levels in Florida followed the same pattern of rise and falls as Texas during the Holocene. In the more recent past, i.e., approximately 5000 B.C.E., the sea level along the Gulf Coast of Florida began steadily, but slowly rising to reach its current position (Scholl et al., 1969). Therefore, in Florida, as well as Texas, sea level has been below present conditions throughout the entire history of the middens sampled there. As all of the middens sampled in this study fall within 4 m of current sea level, it is likely

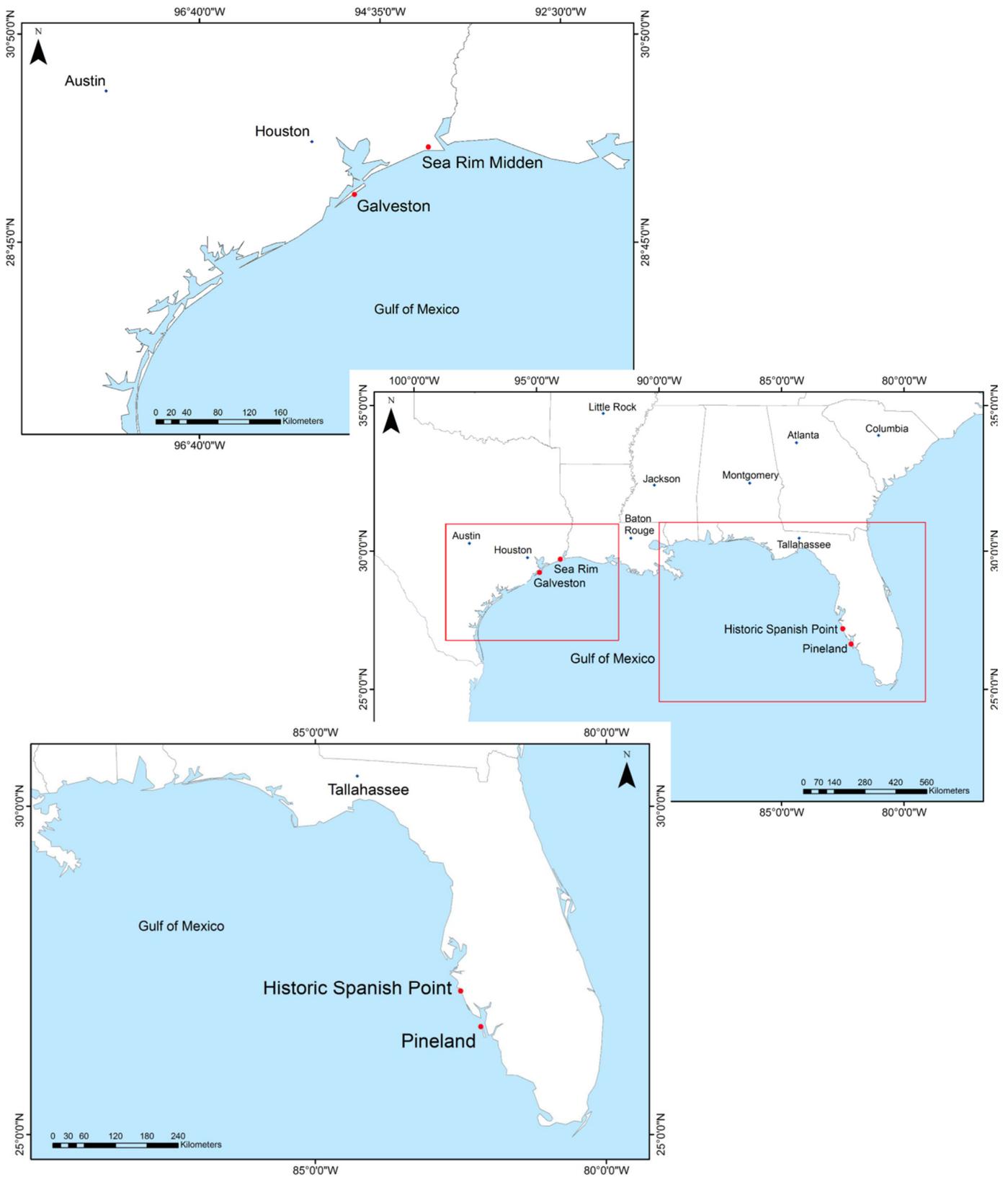


Figure 2. The center map shows the four sampling sites (red dots) located along the Gulf Coast. The red box on the left of the center map corresponds with the map on the top, and the red box on the right of the center map corresponds with the map at the bottom of the figure. The location of Follets and Galveston islands, the modern sample collection locations, are represented by a single dot called “Galveston.”

that they were covered by water for short periods, such as during storm activity, but not consistently enough to maintain subaqueous conditions.

## OBJECTIVES

The rapidity and extent of diagenetic changes within carbonate systems seems to be underestimated in many analyses. The primary purpose of this work was firstly to evaluate whether enough time had passed for carbonate diagenesis to have occurred in deposits laid down between 2500 B.C.E.–200 C.E. Secondary goals were to evaluate any existing early diagenesis and to document which forms of diagenesis occurred, e.g., dissolution, mineralogical alteration, and fracturing.

## METHODS

This study focuses primarily on six species as well as one genus, for which species identification could not be accomplished, categorized within the phylum Mollusca: *Rangia cuneata*, *Crassostrea virginica*, *Busycon* spp., *Strombus pugilis*, *Mercenaria campechiensis*, *Argopecten gibbus*, and *Argopecten irradians*. Species identification was determined based upon location of discovery, i.e., the Gulf Coast, and shell morphology, e.g., umbo prominence, shell shape, and presence or lack of shell spines. Color is also conventionally used as an additional identification marker; however, it could not be commonly utilized in this study. Many of the shells found within the midden piles were bleached and totally lacking original color, thus obviating any potential for the use of pigmentation as an identifier. For those species within the class Bivalvia, it was not possible to identify both valves from an individual specimen due to disarticulation and the large numbers of specimens within the midden. In addition, species identification was not possible for the samples from the Pineland Site Complex because, although individual shells were readily observable, they were cemented within the matrix of hardened concretions and distinguishing features could not be seen. A comprehensive study of the invertebrate populations within the complex was performed by deFrance and Walker (2013).

### Field Methods

Modern shells were collected from the beach surface at Galveston Island and Follets Island in order to have recent, unaltered samples against which to compare midden samples. Excavations at the Sea Rim Midden were performed from the exposed midden surface down to the depth at which the water table was reached, whereas those at Historic Spanish Point were dug to the extent at which midden walls would have collapsed without the assistance of built supports and machinery. The water table at this site was below the lowest sampled depth and not observed. Shells at both sites were sampled laterally and vertically. Samples from the Pineland Site Complex were obtained from museum collections at the Florida Museum of Natural History.

### Petrography

The purpose of the petrographic analysis within this study was to view shell alteration on a microscopic scale. Diagenesis of carbonates commonly involves dissolution, as well as fracturing. Any dissolution of shells and fractures would be quite obvious after impregnation with a blue epoxy.

Eighty-seven thin sections were created for analysis. As samples from the Pineland Site Complex were concreted, they were first cut with a rock saw. The pieces were then impregnated with blue epoxy in order to preserve and emphasize porosity that originated prior to thin section creation and analysis. Midden

shells, from Sea Rim State Park and Historic Spanish Point, and modern shell specimens, collected from Galveston and Follets islands, were also made into thin sections. Modern shell samples were utilized in order to have unaltered samples that presumably had not undergone diagenesis against which midden samples could be compared. Thin sections were observed for any obvious signs of fracturing, dissolution, or discoloration.

### X-Ray Diffraction

Mollusk shells are composed primarily of calcite and aragonite, along with rarely-present vaterite and solid solution between calcite and dolomite (Compere and Bates, 1973; de Paula and Silveira, 2009; Spann et al., 2010). The unusual presence of vaterite is commonly due to events such as shell regeneration or initial shell formation, and it is the primary mineral within pearls (Spann et al., 2010). Although mollusk shell morphology on a microscopic level is quite complex and can vary between classes, there is a generalized structural model. Calcite and aragonite are present in three layers: an innermost layer of aragonite closest to the soft-tissue of the organism, an intermediate layer which is commonly but not exclusively present, and an outer layer of either aragonite or calcite depending upon the species (de Paula and Silveira, 2009). The internal layer is nacreous and composed 95% volumetrically of aragonite blocks that lie atop one another with their longest axis perpendicular to the shell's exterior (Parker et al., 2010). The other 5% of this layer is an organic matrix that produces a cementing effect between the aragonitic blocks (Parker et al., 2010). The intermediary layer is composed of crystals that cross in an oblique manner to one another, and the exterior layer, either calcite or aragonite, is prismatic (de Paula and Silveira, 2009). Due to their carbonate mineralogy, mollusk shells are prone to diagenesis and fit well within the realm of this study.

XRD was performed on modern shells (the standard against which midden shells were measured) and shells from each layer within each midden in order to obtain information about the calcite/aragonite ratio. Shells from each site were analyzed via powder x-ray diffraction to determine mineralogy and phase distribution. To prepare the shells for analysis, they were first washed with tap water and gently scrubbed with a soft brush to remove any sediment. They were then air dried at room temperature. After drying, the shells were crushed with a mortar and pestle to a fine powder. Shells were not entirely composed of one mineral phase, and, therefore, the whole shell was ground in order to obtain a powder sample that was representative of the average composition of the shell as a whole for analysis. The mortar and pestle were scrubbed with tap water and ethanol between the preparation of each shell in order to prevent cross-contamination. If shells were too large to grind with a mortar and pestle, a handheld air drill was used. When air drilling was utilized, attempts were made to drill the entire thickness of the shell so as not create a bias by only sampling from selective layers. The powdered samples were put into glass vials, which were closed tightly until analysis was performed via XRD. Samples were analyzed at ambient temperatures with a CuK $\alpha$  radiation, operated at 40 kV and 30 mA.

Peak values were determined via Rietveld analysis in X'Pert Highscore. The results were then analyzed by subtracting the modern standard values (presented in Table 2) from the measured value. Presumably, the larger the difference between the values of the standard and the shell being tested, the greater the amount of diagenesis that took place. If a modern specimen of a particular species was not available, values were compared with samples from other depths within the midden. From known standards, the error of this analysis was determined experimentally to be approximately  $\pm 5\%$ .

Table 2. Shell sample numbers, depth from the surface, and species for the modern samples collected at Galveston and Follets islands. Also included are bleaching designations and aragonite to calcite ratios determined for each shell sample. NA means the sample was not analyzed or the values are not reported.

Sample	Depth from Surface (cm)	Species	Bleaching	% Calcite	% Aragonite
23	0	<i>R. flexuosa</i>	none	1	99
24	0	<i>Busycon</i> spp.	none	0	100
25	0	<i>R. cuneata</i>	none	1	99
26	0	<i>C. virginica</i>	none	95	5
27	0	<i>A. irradians</i>	none	NA	NA
28	0	<i>Argopecten</i> (unknown species)	none	NA	NA
145	0	<i>C. virginica</i>	none	NA	NA
146	0	<i>Busycon</i> spp.	none	NA	NA
147	0	<i>R. flexuosa</i>	none	NA	NA

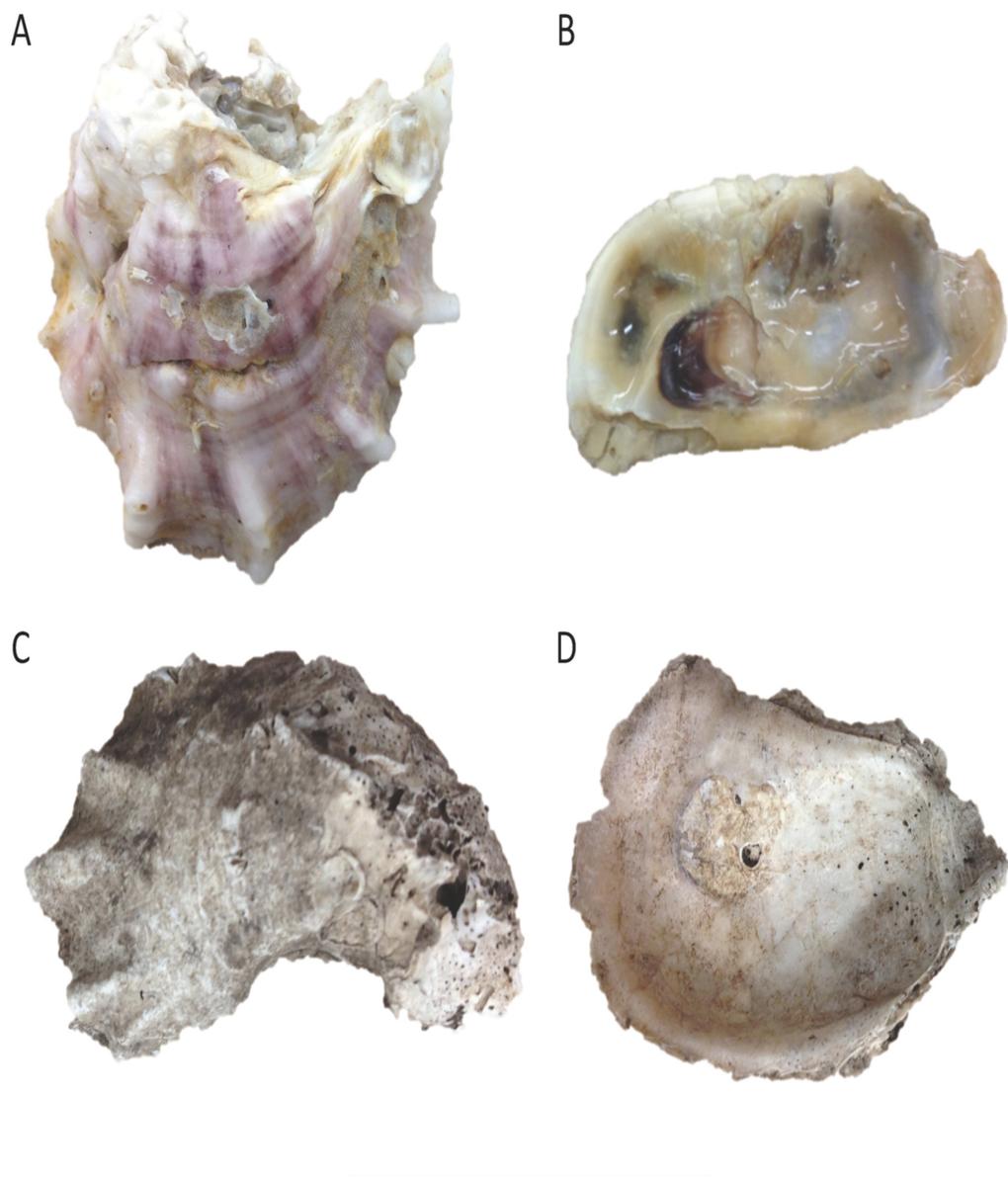


Figure 3. Color bleaching designations demonstrated by specimens of *C. virginica*. This quality is characterized as either “none,” as in modern samples A and B, or “present,” as in midden samples C and D.

## RESULTS

### Hand Sample – Color Bleaching

In life and even for a period of time after its death, an organism’s shell may have quite striking color. The muscle scar of *C. virginica*, for example, is a bright purple. Many of the shells collected from the middens within this study were a stark, bone white. They lacked any of their original color, a state termed “color bleaching” within this study (Fig. 3). For this category, a shell was designated as not bleached, termed “none,” or it was interpreted to be bleached, termed “present.” This category is important when considering diagenesis. Previous studies analyzing this phenomenon have determined that reducing fluids permeating through rock allow for the mixing of rock constituents with exogenous compounds (Beitler et al., 2005). Specifically, bleaching results from materials, e.g., hydrocarbons, methane, or organic acids, such as that found in acidic rainwater, producing CO<sub>2</sub> as a byproduct of their interactions. The CO<sub>2</sub> acidifies pore fluids, which promotes the dissolution of carbonates, commonly in areas of higher permeability (Beitler et al., 2005). Thus, color bleaching is a product of diagenesis.

The modern shells collected at Galveston and Follets islands possessed no color bleaching (Table 2). Of the shells at the Sea Rim State Park Midden, four of the eleven shells tested (36%) were bleached (Table 3). From Historic Spanish Point, 26 of 38 shells sampled (68%) from the Chapel Midden/Shell Ridge and 27 of the 46 (59%) from the Hill Cottage Midden had been bleached of their color (Tables 4–6). Shells from the Pineland Midden were not included in this portion of the study, as they could not be separated from the hardened matrix without causing significant damage. That the bleaching effect occurs only within the midden shells and not the modern comparison shells further corroborates the idea that it is a product of early diagenesis. This diagenetic effect indicates that waters, likely acidic rainwater, percolated down from the surface of the midden and altered the shells as they were drawn downward via gravity.

### Petrography – Fracturing and Dissolution

Shells within the Sea Rim State Park Midden showed pervasive fracturing, and several shells showed signs of oxidation (Fig. 4). Within the concreted midden samples from the Pineland Site Complex, the most notable material is a pervasive, dark brown matrix characteristic of organic matter. This matrix completely

extinguishes in cross-polarized light (XPL). Also present within the concretions were very fine-grained to fine-grained quartz sand grains. Fragmented shell pieces within this midden show evidence of partial dissolution, e.g., void space surrounding shells and pore spaces that would have been too large to support the allochems prior to the hardening of the matrix, i.e., oversized pores (Fig. 5).

Within Historic Spanish Point, the thin sections from the Chapel Midden/Shell Ridge showed fracturing in shells from each depth segment within the midden, and there were patches of alteration in the form of discoloration (Fig. 6). Thin sections from the Hill Cottage Midden exhibited the pervasive diagenesis inherent to this shell accumulation (Fig. 7). The majority of the shells from this midden were fractured, which indicates the existence of physical diagenetic alteration. There were also numerous signs of chemical diagenesis, e.g., dissolution and discoloration, that were likely caused by exposure to meteoric waters.

Extensive physical diagenesis in the form of fracturing was ubiquitous throughout each midden. As modern methods of disarticulating shell valves for consumption do not create extensive damage, it was assumed that these fractures were not created during meal preparation. These physical alterations, therefore, indicate that there was enough overburden stress exerted upon the midden for shells within to break. There was also clear evidence of chemical alterations with the presence of obvious oversized pores. Shell dissolution requires a solution allowing for the exchange of ions within the midden, again indicating the effects of later-introduced water on the midden shells.

### X-Ray Diffraction

There was no evidence for the mineralogical alteration of shells from the Sea Rim Midden. No single midden shell varied more than ±5%, the determined error, from the modern standard (Table 3). Only one shell was analyzed from the Pineland Site Complex samples. The results of the XRD analysis of this shell revealed a mineralogy of primarily aragonite. This outcome shows that if any change of aragonite to calcite had occurred, then it was limited in scope. The XRD analysis from this site served mainly to elucidate that the matrix of the concretions from the Pineland Midden was composed of humified plant matter that was hardened and desiccated.

The Chapel Midden/Shell Ridge at Historic Spanish Point showed minimal shell alteration. Aragonite had converted to

**Table 3. Shell sample numbers, depth from the surface, and species for the Sea Rim State Park Midden. Under the subheading “Hole Number,” 1 indicates hole 1 dug at Sea Rim State Park, and 2 indicates the shell was found in the second hole dug. Also included are bleaching designations and aragonite to calcite ratios determined for each shell sample. “Diff. from Standard” means the difference between the measured value of aragonite or calcite for that shell and that of the corresponding standard from Galveston and Follets islands.**

Hole Number	Sample	Depth from Surface (cm)	Species	Bleaching	% Calcite	Diff. from Standard	% Aragonite	Diff. from Standard
1	3	0–10	<i>R. cuneata</i>	none	1	0	99	0
1	33	10–20	<i>R. cuneata</i>	present	0	-1	100	1
1	2	20–30	<i>R. cuneata</i>	none	0	-1	100	1
1	34	25–30	<i>R. cuneata</i>	present	0	-1	100	1
1	35	30–40	<i>R. cuneata</i>	none	0	-1	100	1
1	36	40–50	<i>R. cuneata</i>	none	0	-1	100	1
1	1	50–55	<i>R. cuneata</i>	none	0	-1	100	1
2	5	0–10	<i>R. cuneata</i>	none	0	-1	100	1
2	37	10–20	<i>R. cuneata</i>	present	0	-1	100	1
2	38	20–30	<i>R. cuneata</i>	present	0	-1	100	1
2	4	30–42	<i>R. cuneata</i>	none	0	-1	100	1

Table 4. Shell sample numbers, depth from the surface, and species for the Chapel Midden/Shell Ridge at Historic Spanish Point. Under the subheading "Hole Number," 1 indicates the shell was located within the first hole dug, 2 indicates the shell was found in the second hole dug, and 3 the third hole. Also included are bleaching designations and aragonite to calcite ratios determined for each shell sample. "Diff. from Standard" means the difference between the measured value of aragonite or calcite for that shell and that of the corresponding standard from Galveston and Follets islands. The acronym NS indicates that there is no modern standard for that species.

Hole Number	Sample	Depth from Surface (cm)	Species	Bleaching	% Calcite	Diff. from Standard	% Aragonite	Diff. from Standard
1	11	0-19	<i>C. virginica</i>	none	95	0	5	0
1	61	0-19	<i>M. campechiensis</i>	present	1	NS	99	NS
1	92	0-19	<i>C. virginica</i>	none	92	-3	8	3
1	62	19-36	<i>M. campechiensis</i>	present	0	NS	100	NS
1	63	36-58	<i>S. pugilis</i>	none	1	NS	99	NS
1	64	58-72	<i>M. campechiensis</i>	present	10	NS	90	NS
1	90A	58-72	<i>C. virginica</i>	present	93	-2	7	2
1	68	82-92	<i>M. campechiensis</i>	none	0	NS	100	NS
1	69	82-92	<i>A. irradians</i>	present	90	NS	10	NS
1	70	92-100	<i>M. campechiensis</i>	none	0	NS	100	NS
1	71	92-100	<i>A. irradians</i>	present	92	NS	8	NS
1	73	100-113	<i>M. campechiensis</i>	present	0	NS	100	NS
1	74	113-126	<i>A. irradians</i>	present	86	NS	14	NS
1	91A	113-126	<i>C. virginica</i>	none	95	0	5	0
1	91B	113-126	<i>C. virginica</i>	present	94	-1	6	1
2	93	0-24	<i>C. virginica</i>	none	94	-1	6	1
2	75	24-46	<i>S. pugilis</i>	present	1	NS	99	NS
2	76	24-46	<i>M. campechiensis</i>	present	0	NS	100	NS
2	77A	46-60	<i>A. irradians</i>	present	88	NS	12	NS
2	77B	46-60	<i>A. gibbus</i>	present	89	NS	11	NS
2	94	60-80	<i>C. virginica</i>	none	94	-1	6	1
2	78	100-120	<i>M. campechiensis</i>	present	0	NS	100	NS
2	95	120-140	<i>C. virginica</i>	none	94	-1	6	1
3	10	1-11	<i>C. virginica</i>	none	94	-1	6	1
3	89	0-11	<i>S. pugilis</i>	none	1	NS	99	NS
3	88	11-21	<i>Busycon</i> spp.	none	1	1	99	-1
3	86	21-31	<i>A. irradians</i>	present	89	NS	11	NS
3	87	21-31	<i>M. campechiensis</i>	present	0	NS	100	NS
3	9	31-41	<i>C. virginica</i>	present	94	-1	6	1
3	84	31-41	<i>Busycon</i> spp.	present	1	1	99	-1
3	85	31-41	<i>M. campechiensis</i>	present	0	NS	100	NS
3	83	41-51	<i>M. campechiensis</i>	present	0	NS	100	NS
3	82	51-61	<i>M. campechiensis</i>	present	0	NS	100	NS
3	7	61-71	<i>C. virginica</i>	present	92	-3	8	3
3	81	61-71	<i>Busycon</i> spp.	present	1	1	99	-1
3	80	71-81	<i>S. pugilis</i>	present	3	NS	97	NS
3	6	81-91	<i>C. virginica</i>	present	94	-1	6	1
3	79	81-91	<i>A. irradians</i>	present	87	NS	13	NS

calcite, but in only one shell sampled within the entire midden (Table 4). Although there was no modern specimen of *M. campechiensis* against which to compare the midden shells, the samples may be compared against the other shells within the midden to see if any displayed a variation of greater than  $\pm 5\%$ . Sample 64 of *M. campechiensis* displayed quite different percentages than the others from the hole. This particular shell was composed of 9% more calcite than the shell with the next highest levels. These results indicate that there is aragonite to calcite diagenesis occurring within this hole.

The Hill Cottage Midden had the most aragonite-calcite conversion of all analyzed midden piles. Of the 46 shells sampled from the Hill Cottage Midden, several shells from two species, *S. pugilis* and *Busycon* spp., showed diagenetically increased amounts of calcite (Table 5). For the *S. pugilis* from the first hole, the maximum percentage of calcite measured was 5% (sample 130). The minimum for this species was 1% (sample 143). The difference between the two is 4% which is reasonably close to a value of statistical viability. As such, it is likely that this value indicates an actual increase in the amount of calcite

Table 5. Shell sample numbers, depth from the surface, and species for the Hill Cottage Midden at Historic Spanish Point. Under the subheading "Hole Number," 1 indicates the shell was discovered in the first hole dug, and 2 indicates the shell was found in the second hole. Also included are bleaching designations and aragonite to calcite ratios determined for each shell sample. "Diff. from Standard" means the difference between the measured value of aragonite or calcite for that shell and that of the corresponding standard from Galveston and Follets islands. The acronym NS indicates that there are no modern standard values for that species.

Hole Number	Sample	Depth from Surface (cm)	Species	Bleaching	% Calcite	Diff. from Standard	% Aragonite	Diff. from Standard
1	144	0	<i>A. irradians</i>	present	87	NS	13	NS
1	143	0	<i>S. pugilis</i>	none	1	NS	99	NS
1	140	7-17	<i>C. virginica</i>	present	94	-1	6	1
1	139	17-31	<i>M. campechiensis</i>	present	1	NS	99	NS
1	138	31-47	<i>M. campechiensis</i>	present	1	NS	99	NS
1	137	47-57	<i>C. virginica</i>	present	95	0	5	0
1	136	57-67	<i>Busycon</i> spp.	none	10	10	90	-10
1	135	67-77	<i>M. campechiensis</i>	none	6	NS	94	NS
1	134	67-77	<i>C. virginica</i>	none	94	-1	6	1
1	132	77-87	<i>M. campechiensis</i>	present	7	NS	93	NS
1	131	87-102	<i>M. campechiensis</i>	none	1	NS	99	NS
1	130	102-115	<i>S. pugilis</i>	present	5	NS	95	NS
1	129	115-123	<i>C. virginica</i>	none	93	-2	7	2
1	128	115-123	<i>S. pugilis</i>	none	1	NS	99	NS
1	127	123-135	<i>A. gibbus</i>	present	91	NS	9	NS
1	126	135-149	<i>S. pugilis</i>	none	2	NS	98	NS
1	125	149-159	<i>S. pugilis</i>	none	2	NS	98	NS
1	124	159-169	<i>C. virginica</i>	none	95	0	5	0
1	123	169-183	<i>A. irradians</i>	present	87	NS	13	NS
1	122	183-190	<i>A. irradians</i>	present	90	NS	10	NS
1	121	190-207	<i>C. virginica</i>	none	90	-5	10	5
1	120	190-207	<i>Busycon</i> spp.	none	10	10	90	-10
2	109	2-11	<i>A. irradians</i>	present	89	NS	11	NS
2	110	2-11	<i>C. virginica</i>	none	95	0	5	0
2	118	2-12	<i>C. virginica</i>	none	94	-1	6	1
2	119	2-12	<i>M. campechiensis</i>	present	0	NS	100	NS
2	102	2-14	<i>C. virginica</i>	present	95	0	5	0
2	103	2-14	<i>M. campechiensis</i>	present	0	NS	100	NS
2	107	11-23	<i>C. virginica</i>	present	95	0	5	0
2	108	11-23	<i>S. pugilis</i>	none	1	NS	99	NS
2	117	12-18	<i>C. virginica</i>	present	95	0	5	0
2	115	18-23	<i>S. pugilis</i>	present	1	NS	99	NS
2	116	18-23	<i>C. virginica</i>	none	95	0	5	0
2	100	14-23	<i>C. virginica</i>	present	95	0	5	0
2	101	14-23	<i>A. irradians</i>	present	88	NS	12	NS
2	98	23-32	<i>M. campechiensis</i>	present	1	NS	99	NS
2	99	23-32	<i>C. virginica</i>	none	95	0	5	0
2	105	23-32	<i>M. campechiensis</i>	present	0	NS	100	NS
2	106	23-32	<i>C. virginica</i>	present	95	0	5	0
2	113	23-32	<i>C. virginica</i>	present	95	0	5	0
2	114	23-32	<i>M. campechiensis</i>	present	1	NS	99	NS
2	96	32-42	<i>C. virginica</i>	none	93	-2	7	2
2	97	32-42	<i>A. gibbus</i>	present	83	NS	17	NS
2	104	32-42	<i>C. virginica</i>	present	94	-1	6	1
2	111	32-42	<i>S. pugilis</i>	present	2	NS	98	NS
2	112	32-42	<i>C. virginica</i>	none	95	0	5	0

**Table 6.** GI = Galveston Island and Follets Island (modern samples), SR = Sea Rim State Park Midden, CM/S = Chapel Midden/Shell Ridge at Historic Spanish Point, and HCM = Hill Cottage Midden at Historic Spanish Point. The values indicated are the total amount of shells analyzed for color bleaching within each midden, the number of shells bleached within said midden, the number of shells without color bleaching, and the percentage of shells with color bleaching.

Location	Shells Analyzed	Shells with Bleaching	Shells without Bleaching	Percentage Bleached
GI	9	0	9	0%
SR	11	4	7	36%
CM/S	38	26	12	68%
HCM	46	27	19	59%

and is not simply due to instrument limitations. There were two *Busycon* spp. shells within the first hole dug (samples 120 and 136) displaying a calcite increase of 10% relative to the modern standard. As such, values of calcite within this excavation have been increased by diagenetic processes within the midden.

Within the second hole of the Hill Cottage Midden, a specimen of *A. gibbus* had a percent calcite value of 83% (sample 97). Other specimens of *A. gibbus* and *A. irradians* found within this midden had an average value of 89% calcite. Thus, this lower value for sample 97 would indicate that the amount of calcite within the shell actually decreased, which is not chemically reasonable. This lower value could perhaps be attributed to specimen variation and machine error, which provides for a range of  $\pm 5\%$ . With this range factored in, the calcite percentage could be as low as 84%. The additional difference beyond that is only 1%, which could easily be accounted for if one considers that living organisms created these shells and may have slightly different regulation capabilities. No other shells have values indicating that their mineralogical content was altered.

## CONCLUSIONS

Hand sample, petrographic, and XRD analyses indicate multiple diagenetic alterations within four relatively modern middens, i.e., created within the last 4500 yr. The effects of diagenesis were found specifically to be chemical, mechanical, and mineralogical in nature. Chemical alterations were predominantly indicated by extensive color bleaching of midden shells and shell dissolution, whereas physical manifestations were represented by shell fractures. XRD analyses revealed the conversion of aragonite to calcite in two of the four middens studied. As the youngest midden samples considered within this study, from the Pineland Site Complex, were radiocarbon dated to be 1800 yr old, it has been clearly demonstrated that recent carbonate deposits can be significantly diagenetically altered. Researchers must, therefore, be aware when studying modern carbonate systems that they may, in fact, be analyzing diagenetic effects and not primary carbonate materials.

## ACKNOWLEDGMENTS

Thanks are given to Ruth Mathews, a state parks regional archaeologist for the Texas Parks and Wildlife Department, for her assistance with the work performed at Sea Rim State Park. Samples from the Pineland Site Complex were provided by Dr. Karen Walker, Assistant Scientist and the Collections Manager at the Florida Museum of Natural History. Species identification was assisted by Dr. Tina Petway, Associate Curator of Malacology at the Houston Museum of Natural Science. Mr. Ryan Murphy, the curator of Historic Spanish Point at the time of this study and now an archaeologist with Sarasota County Historical Resources, provided permission to sample and much guidance while working at Historic Spanish Point. Additionally, personal thanks are given to Dr. Ian Evans, whose counsel during this work was paramount.

## REFERENCES CITED

- Andrus, C. F. T., 2011, Shell midden sclerochronology: Quaternary Science Reviews, v. 30, p. 2892–2905.
- Bathurst, R. G. C., 1994, Neomorphic processes in diagenesis, in R. G. C. Bathurst, ed., Carbonate sediments and their diagenesis: Developments in Sedimentology 12, Elsevier, Amsterdam, The Netherlands, p. 475–516.
- Beitler, B., W. T. Parry, and M. A. Chan, 2005, Fingerprints of fluid flow: Chemical diagenetic history of the Jurassic Navajo Sandstone, southern Utah: Journal of Sedimentary Research, v. 75, p. 547–561.
- Bullen, R. P., and A. K. Bullen, 1976, The Palmer site: The Florida Anthropologist, v. 29, p. 1–53.
- Compere, E. L., Jr., and J. M. Bates, 1973, Determination of calcite:aragonite ratios in mollusc shells by infrared spectra: Limnology and Oceanography, v. 18, p. 326–331.
- deFrance, S. D., and K. J. Walker, 2013, The zooarchaeology of Pineland, in H. Marquardt and K. J. Walker, eds., The archaeology of Pineland: A coastal southwest Florida site complex, A.D. 50–1710: University of Florida Institute of Archaeology and Paleoenvironmental Studies, Gainesville, Florida, p. 305–348.
- de Paula, S. M., and M. Silveira, 2009, Studies on molluscan shells: Contributions from microscopic and analytical methods: Micron, v. 40, p. 669–690.
- Erlandson, J. M., 2001, The archaeology of aquatic adaptations: Paradigms for a new millennium: Journal of Archaeological Research, v. 9, p. 287–349.
- Folk, R. L., 1965, Some aspects of recrystallization in ancient limestones, in L. C. Pray and R. C. Murray, eds., Dolomitization and limestone diagenesis: A symposium: Society of Economic Paleontologists and Mineralogists Special Publication 13, Tulsa, Oklahoma, p. 14–15.
- Glaser, L. L., 2003, Dating fluvial terraces by  $^{230}\text{Th}/\text{U}$  on pedogenic carbonate, Wind River Basin, Wyoming: Quaternary Research, v. 59, p. 139 p.
- Kozuch, L., 1998, Faunal remains from the Palmer Site [(8SO2)], with a focus on shark remains: The Florida Anthropologist, v. 51, p. 177–192.
- Kratt, H. J., Jr., C. L. Coultas, and M. Russo, 2008, The Lewis Camp Mound: An example of a petrocalcic horizon in Jefferson County, Florida: Gulf Coast Association of Geological Societies Transactions, v. 58, p. 561–572.
- Maliva, R. G., T. M. Missimer, and J. A. D. Dickson, 2000, Skeletal aragonite neomorphism in Plio-Pleistocene sandy limestones and sandstones, Hollywood, Florida: Sedimentary Geology, v. 136, p. 147–154.
- Marquardt, H., 2013, The Pineland Site Complex: Theoretical and cultural contexts, in H. Marquardt and K. J. Walker, eds., The archaeology of Pineland: A coastal southwest Florida site complex, A.D. 50–1710: University of Florida Institute of Archaeology and Paleoenvironmental Studies, Gainesville, Florida, p. 1–22.
- Martindale, A., B. Letham, D. McLaren, D. Archer, M. Burchell, and B. R. Schone, 2009, Mapping of subsurface shell midden components through percussion coring: Examples from the Dundas

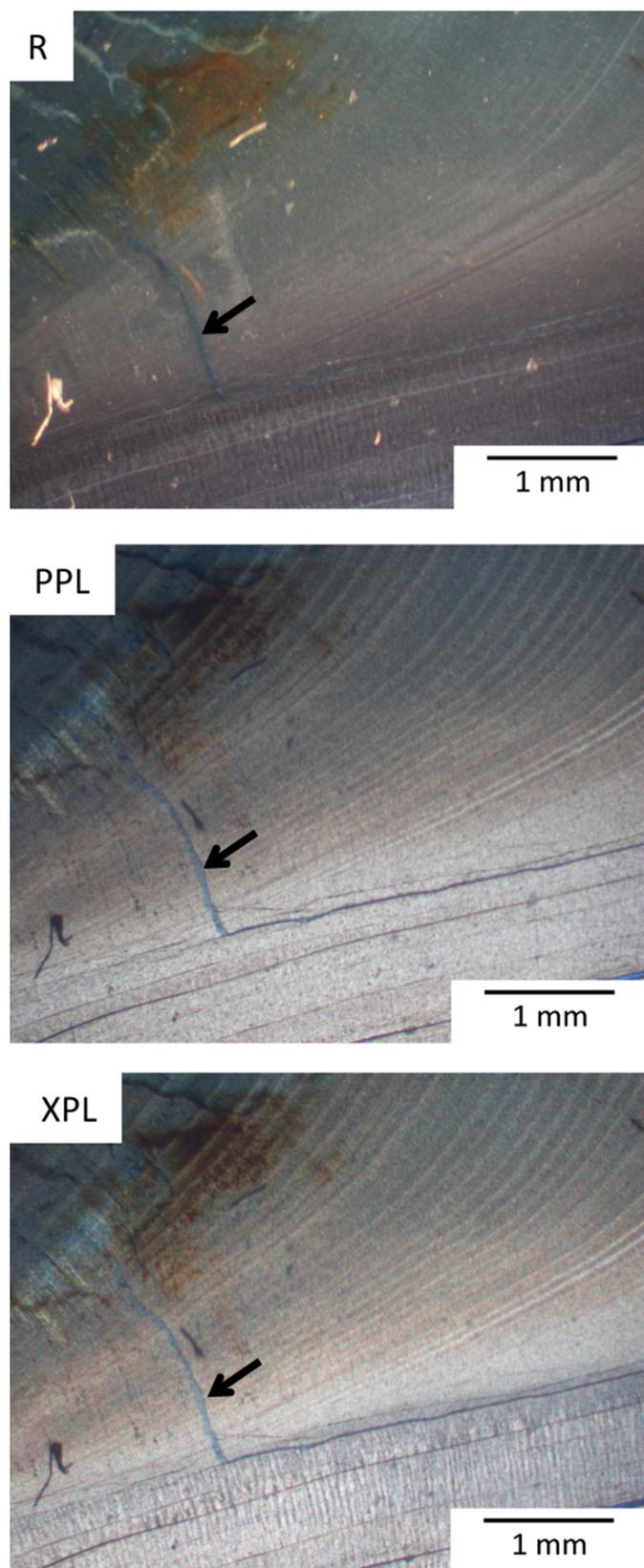


Figure 4. Photomicrographs of *R. cuneata* from the Sea Rim State Park Midden. The black arrows indicate fractures. “R” designates a view in reflected light, “PPL” indicates that the photomicrograph was taken in plane-polarized light, and “XPL” indicates that it was taken in cross-polarized light.

- Islands: *Journal of Archaeological Science*, v. 36, p. 1565–1575.
- Murphy, R., 2013, The Hill Cottage Midden (8SO2): A contextual study of Late Archaic shell ring sites: M.S. Thesis, California State University, Dominguez Hills, 75 p.
- Parker, J. E., S. P. Thompson, A. R. Lennie, J. Potter, and C. C. Tang, 2010, A study of the aragonite-calcite transformation using Raman spectroscopy, synchrotron powder diffraction and scanning electron microscopy: *CrystEngComm*, v. 12, p. 1590–1599.
- Rasbury, E. T., G. N. Hanson, W. J. Meyers, and A. H. Saller, 1997, Dating of the time of sedimentation using U–Pb ages for paleosol calcite: *Geochemica et Cosmochimica Acta*, v. 61, p. 1525–1529.
- Ricklis, R. A., and M. D. Blum, 1997, The geoarchaeological record of Holocene sea level change and human occupation of the Texas Gulf Coast: *Geoarchaeology: An International Journal*, v. 12, p. 287–314.
- Scholl, D. W., F. C. Craighead, Sr., and M. Stuiver, 1969, Florida submergence curve revised: Its relation to coastal sedimentation rates: *Science*, v. 163, p. 562–564.
- Scholle, P. A., and D. S. Ulmer-Scholle, 2003. A color guide to the petrography of carbonate rocks: Grains, textures, porosity, and diagenesis: American Association of Petroleum Geologists Memoir 77, Tulsa, Oklahoma, 474 p.
- Spann, N., E. M. Harper, and D. C. Aldridge, 2010, The unusual mineral vaterite in shells of the freshwater bivalve *Corbicula fluminea* from the UK: *Naturwissenschaften*, v. 97, p. 743–751.
- Thompson, V. D., and J. E. Worth, 2011, Dwellers by the sea: Native American adaptations along the southern coasts of eastern North America: *Journal of Archaeological Research*, v. 19, p. 51–101.
- Titschack, J., U. Radtke, and A. Freiwald, 2009, Dating and characterization of polymorphic transformation of aragonite to calcite in Pleistocene bivalves from Rhodes (Greece) by combined shell microstructure, stable isotope, and electron spin resonance study: *Journal of Sedimentary Research*, v. 79, p. 332–346.
- Walker, K. J., and W. H. Marquardt, 2013, Excavations and chronostratigraphy at the Pineland Site Complex, in H. Marquardt and K. J. Walker, eds., *The archaeology of Pineland: A coastal southwest Florida site complex, A.D. 50–1710*: University of Florida Institute of Archaeology and Paleoenvironmental Studies, Gainesville, Florida, p. 53–154.
- Wern, J. O., 1993, Ecological studies of the nemertean fauna in an estuarine system of the northwestern Gulf of Mexico: *Hydrobiologia*, v. 266, p. 81–87.
- Wyde, M., 2013, Excavations at Brown’s Complex Mound 5, Pineland Site Complex, Pine Island, Florida: M.S. Thesis, University of Florida, Gainesville, 76 p.

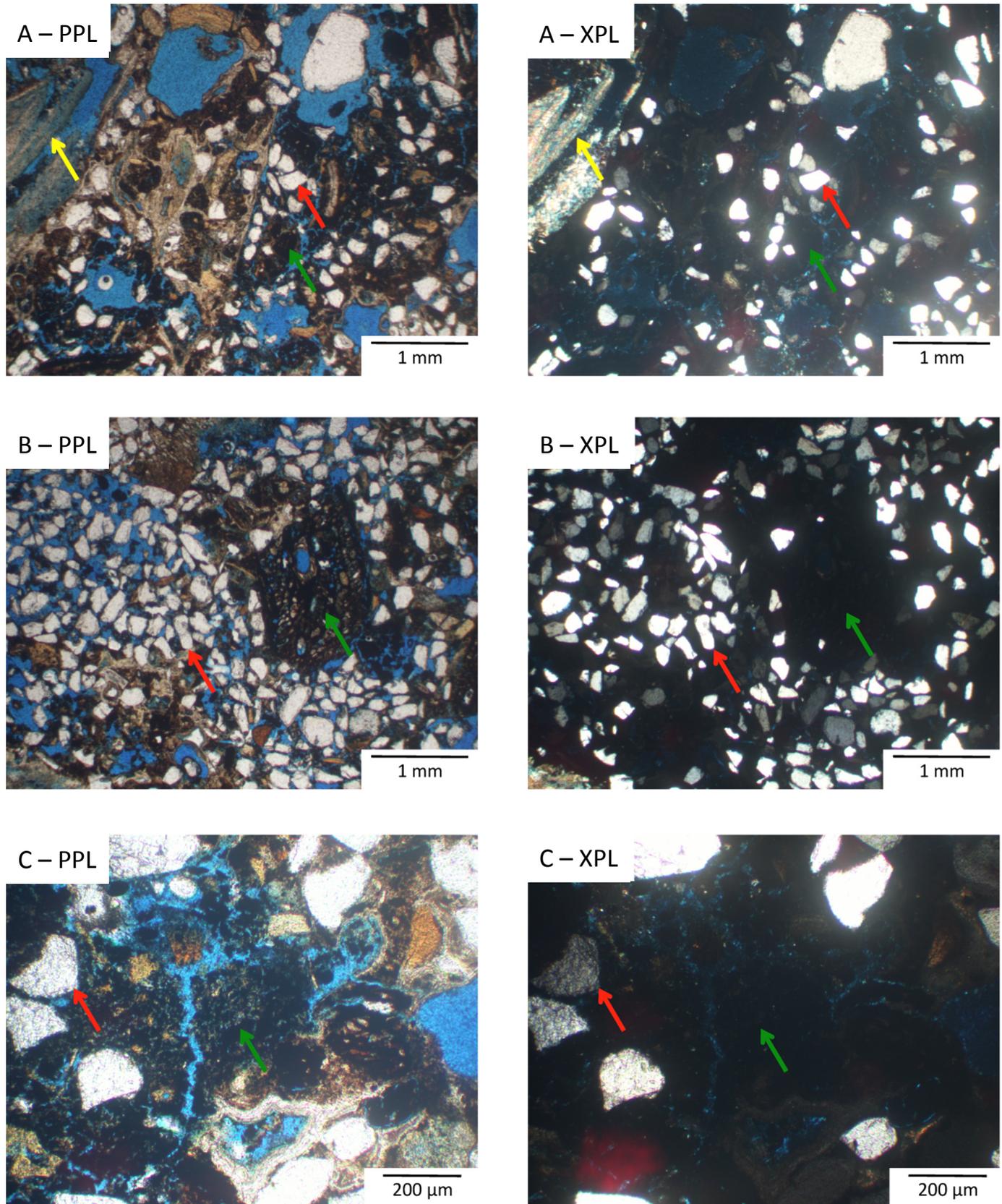


Figure 5. Photomicrographs of various views (A–C) of the concretions from the midden at the Pineland Site Complex. The red arrows point to quartz grains that were deposited due to the midden being formed in a predominantly-siliciclastic environment. The green arrows point to aggregates of humified organic matter, and the yellow arrows indicate a partially-dissolved carbonate shell remnant. “PPL” indicates that the image was taken in plane-polarized light, and “XPL” indicates that it was taken in cross-polarized light.

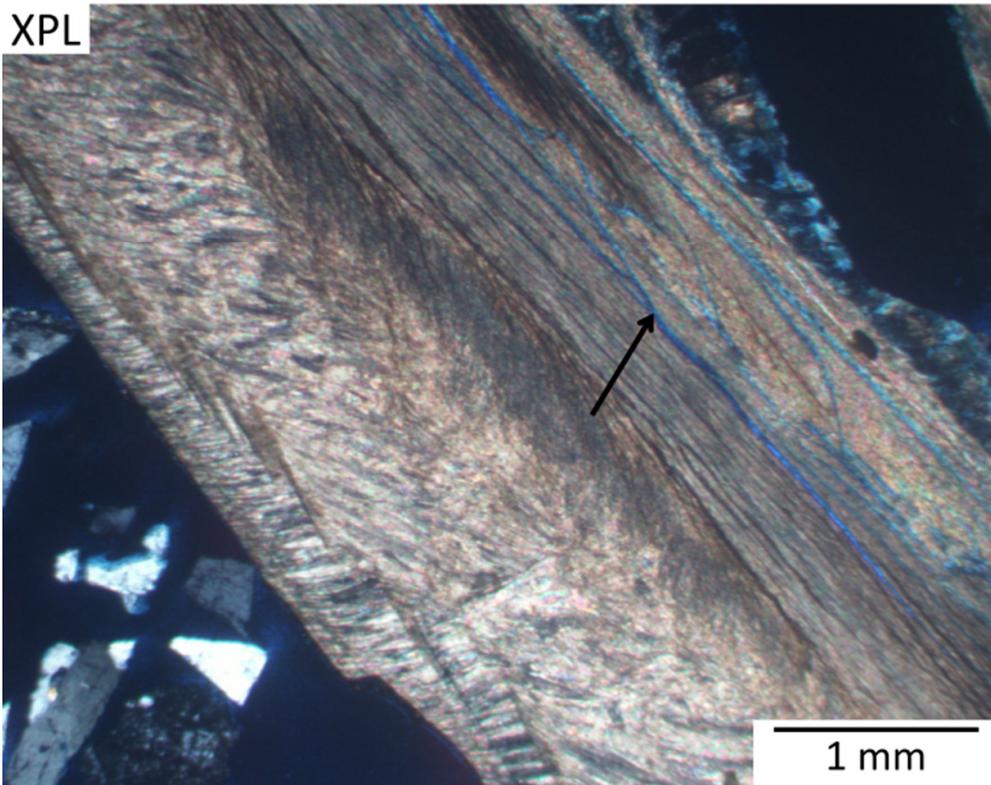
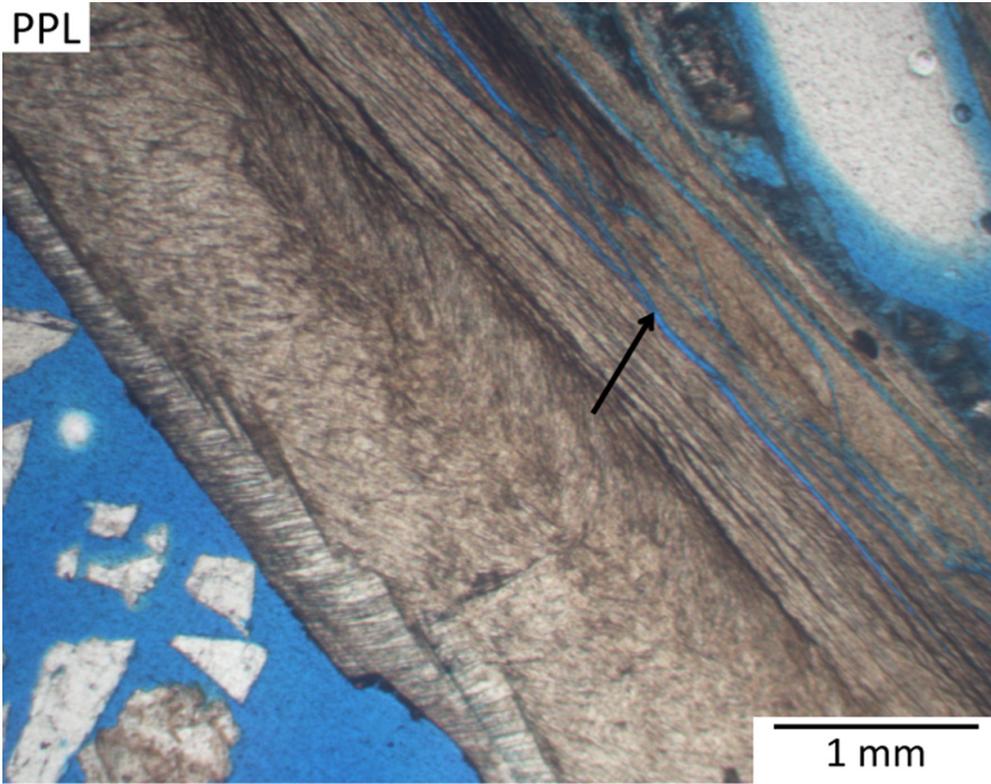


Figure 6. Photomicrographs of *C. virginica* from the Chapel Midden/Shell Ridge. The black arrows indicate fractures. "PPL" indicates that the photomicrograph was taken in plane-polarized light, and "XPL" indicates that it was taken in cross-polarized light.

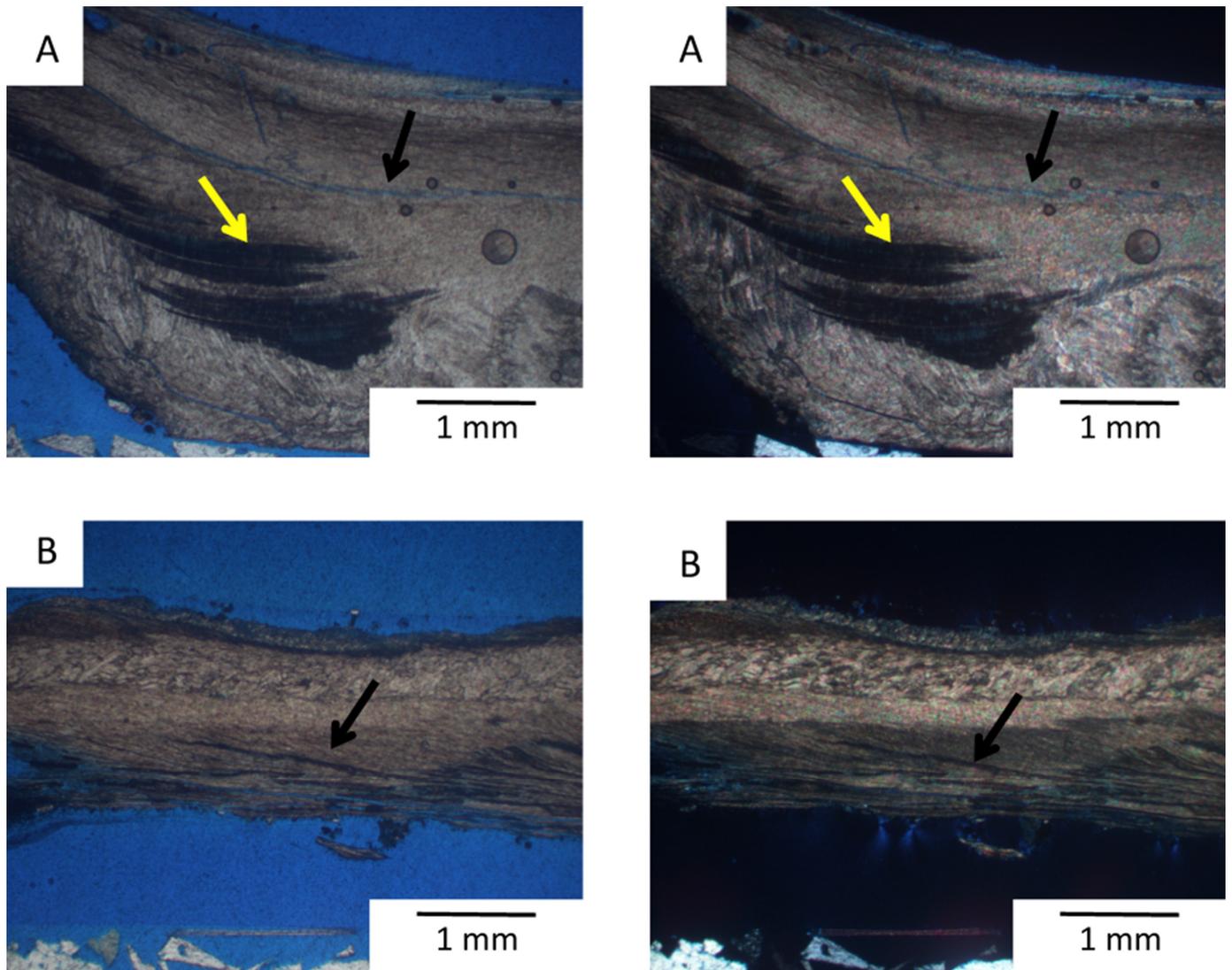


Figure 7. Photomicrographs of two *C. virginica* (A and B) from the Hill Cottage Midden. The images on the left were taken in plane-polarized light (PPL), and the images on the right were taken in cross-polarized light (XPL). Fractures are indicated by black arrows. The yellow arrows point to areas of dissolution and discoloration.