

PROCEEDINGS OF THE TWENTY-SIXTH ANNUAL KECK RESEARCH SYMPOSIUM IN GEOLOGY

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Pomona College, Claremont, CA

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Keck Geology Consortium: Projects 2012-2013

Short Contributions— Bivalve Geochemistry Project

BIOGEOCHEMICAL CARBON CYCLING IN FLUVIAL SYSTEMS FROM BIVALVE SHELL GEOCHEMISTRY - USING THE MODERN TO UNDERSTAND THE PAST

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Research Advisor: David Goodwin

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Research Advisor: David P Gillikin

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THE LIFE AND AFTERLIFE OF HELL CREEK UNIONIDS

NICOLLETTE BUCKLE, Oberlin College

Research Advisor: Karla Parsons-Hubbard

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THE LIFE AND AFTERLIFE OF HELL CREEK UNIONIDS

NICOLLETTE BUCKLE, Oberlin College
Research Advisor: Karla Parsons-Hubbard

INTRODUCTION

Non-marine Mollusca are the most abundant animal macrofossil in the upper most Cretaceous and Paleogene strata of Western North America (Hartman 1989). Their fossil record is continuous and a distinct faunal change, marked by a reduction of abundance, can be observed through the Paleocene (Hartman 1998). The family of bivalves known as Unionids are taxonomically conservative and therefore are assumed to have occupied the same ecological and morphological spaces as their modern counterparts (Scholz and Hartman 2007a). Because of their taxonomic conservatism, fossil unionid bivalves have often been used for reconstruction of paleoenvironments.

Unionids incorporate ambient fluids into nacreous shell material. Isotopic data retrieved from the unionids of Cretaceous and Paleogene depositional sequences of Northern Montana have been used for paleoenvironmental reconstructions (Dettman and Lohmann 2000; Fan and Dettman 2009). Several projects are underway to refine the resolution of isotopic data and the processes before and after preservation that affect original isotopic values. The goal of this project is to establish the pristine nature of shells from Fort Union and Hell Creek formations so that geochemical information collected from these shells can be judged reliable. Through the evaluation of gross and microscopic taphonomic clues as well as the analysis of trace element and isotope concentrations in these bivalves, we can learn about seasonal variation and change in habitat over geologic time.

The objectives of this project are to analyze the overall condition of the shells collected from Cretaceous and Paleogene fluvial environments. Although outwardly pristine shells were collected in the field, it is important to ensure that degradation has not taken place, even at the micro scale. To establish their condition, four independent lines of evidence were analyzed.

1) We began an ongoing analysis of taphonomic pathways in modern non-marine unionids. Macro- and micro-scale examination of shell degradation over time will be used to assess the rate and effect of diagenesis in burial experiments in modern fluvial environments. 2) Taphonomy and diagenesis in fossil and modern material is evaluated using Scanning Electron Microscopy (SEM) and compared to an established preservation index. Pristine specimens are less affected by diagenetic processes and are more reliable for use in chemical analysis. 3) X-Ray diffraction (XRD) analysis of shell structure is used to gain insight about whether the structure of the fossil shell has altered from aragonite to calcite. If alteration has occurred then the chemical data is not reliable because of diagenetic effects. 4) A sclerochronological interpretation of paleoenvironmental conditions is made using thin section analysis of growth patterns in bivalves to give us insight into the living conditions experienced by the unionids before and after the K/Pg extinction boundary.

METHODS AND MATERIALS

MATERIALS

In August 2012, shells from the Cretaceous, and Paleocene periods were collected for taphonomic and sclerochronological analysis. The material that

was used in this study was selected for high macro taphonomic grade at the start of the experiment. Each group of shells was divided into subcategories and photographed. The three shells of the Cretaceous group (Group K) identified as *Proparresysia pyramidatoides*, *plethobasus aseopiformis*, and *Quadrula cylindricoides* were collected by Keck crew members at location L2333b as described by Hartman (1998). All cretaceous shells were collected whole and were analyzed using SEM, thin section and XRD. The six Paleogene (Group PG) aged shells identified as *Rhabdotophorus sp.* were collected at location L6897 (areas a, c, and f). Three PG shells were found at location L6897a and were used for thin section and SEM analysis. These shells were treated with glue on site to keep the shell material in place. One shell from L6897c and two shells from L6897f were not glued on site and were slightly more fragmented than the glued specimens. Specimens not treated with glue were used for XRD analysis.

Modern unionids were harvested for comparative taphonomic analysis. Streambed samples were collected by Keck crewmembers in Raccoon Creek, Granville, OH. Other material was harvested alive or articulated and in pristine condition by David Goodwin at Denison University. Mollusks from his personal collection were identified, photographed, weighed and placed in groups according to weight and species for long-term observation in the modern taphonomy project.

METHODS

Four distinct analyses were used to establish shell condition for the bivalves. First, because no studies of taphonomic pathways in fresh water bivalves exist in the surveyed literature, we established three sites in local streams to begin a long-term study. Seventy-two modern unionid valves of varying species and taphonomic conditions (Figure 1) were sorted by species and weight, labeled, and then placed in mesh bags. Each bag contained two valves. The bags were deposited October 24th, 2012 at three experimental sites in the Black River drainage area for observation: A bedrock channel (Chance Creek), with the highest energy regime, a tributary of the Black river (Plum Creek) with intermediate flow rates, and a small stream in Oberlin, OH dominated by slow flow and dense

leaf litter (fig. 1). At each site, test groups were placed midstream, buried near the stream in a fine-grained organic rich matrix, or exposed in an area away from the river to simulate possible natural taphonomic pathways experienced by unionids (Fig. 2). One set of shells was collected on January 10, and will continue to be collected periodically for taphonomic analysis.



Figure 1: Project Locations
Different environments and conditions used in our modern stream taphonomy project. Columns A-C show the streams used in the experiments: A) The back yard stream. B) Plum Creek and C) Chance Creek. D) Burying experiments in the flood plain at Plum Creek.



Figure 2: Experimental sites
Stream-related environments that experience different taphonomic pathways: A) exposure, B) deposition in stream and C) burial in floodplain. D) Bagged groups of shells after first collection. From left to right the shell groups had been exposed, buried, or deposited mid-stream.

Shells of varying macro-taphonomic grades and geological ages were also observed using Scanning Electron Microscopy (SEM). Holocene and Paleogene shells were observed using a Zeiss® microscope at Union College, while Cretaceous shells were observed using a JEOL® microscope at Oberlin College (Fig.4). Shells were washed to remove unwanted surface material, mounted on slides and fractured to expose natural micro-structural detail. At least 10 photographs at 1,500x (or 1 micron resolution) were taken of the prismatic and nacreous layers of each shell. Photographs were graded by comparing them to a microscopic preservation index as outlined in Cochran et al. (2010).

After samples were cut and broken for SEM analysis, a portion of the remaining material was scanned using XRD. Nacreous material from six shells from groups K and PG was separated from prismatic fossil material and prepared for X-Ray Diffraction analysis by grinding to a fine powder with mortar & pestle. Diffraction peaks were analyzed using Rigaku® PDXL software to identify any diagenetic alteration from aragonite to calcite.

Finally, shells were cut along the line of maximum growth and mounted on petrographic slides for growth line analysis. Bivalves often exhibit changes in shell density that appears as growth lines when viewed in thin section. Thin sections from group K and PG were cut from shells, lines were analyzed visually, and black and white photomicrographs of the sections were analyzed using the freeware *ImageJ* according to pixel density. *Image J* was used to sharpen the original images, to calculate pixel density, and map the frequency and intensity of the growth bands. Special attention was paid to annual and semiannual bands. The growth banding during the first two years of growth were analyzed for higher resolution short-term growth patterns.

RESULTS

Modern Taphonomy Experiments

A total of 14 shells were recovered from the experimental sites for our initial analysis. The shells that were collected lost an average of 0.175-0.435 g between the months of October and January.

Shells mid stream lost more weight than those that were exposed or buried. The set of shells that were deposited in the smallest of the streams and that experiences lowest flow velocities generally lost more weight than the shells recovered from Chance Creek or Plum Creek.

SEM and XRD analysis

SEM microanalysis shows pristine preservation in the Cretaceous and Paleocene shells. The condition of nacre tablets were comparable to live collected and articulated specimens of unionids that were analyzed as a baseline for this study. Using preservation index (PI) created by Cochran et al., all of the fossil material was ranked at a PI of at least 3, or good condition (Fig. 3). Macroscopically, the Cretaceous material seemed more pristine. Shells that were collected at L5233 displayed little evidence of abrasion, and maintained original structures such as the prismatic layer and internal structures. On the other hand, the Paleogene shells were flaky and were visibly disintegrating. They no longer possessed an outer protective prismatic layer and had lost distinct internal structure. Despite their outward appearance, on the scale of individual tablets observed on the SEM, they still were ranked in very good condition.

The shells observed in this study showed no evidence of pre or post burial biological erosion. Studies have shown that a large volume of carbonate material is removed from the shells and tests of animals in marine settings (Radke, 1993). This does not seem to be the case in a freshwater living environment.

In addition to being visually pristine, XRD analysis of three shells from each site show that the shells are aragonite and have not converted to calcite (Fig. 4).

Thin Section Analysis

Annual banding is present in all of the thin-sectioned fossil material (Fig. 5). Growth patterns in the Cretaceous show thick annual bands. Individuals were between 6 and 12 years old at the time of death. Paleogene material showed annual banding that was not as strongly defined as that of the Cretaceous material.

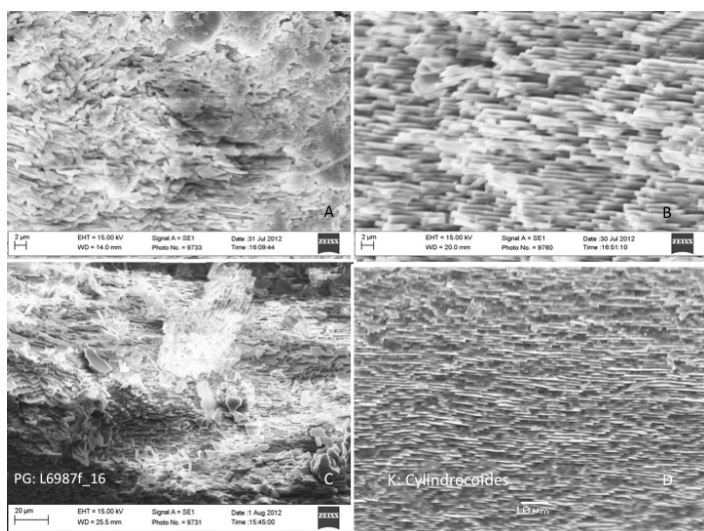


Figure 3: SEM comparison of nacre tablets

Examples of different micro-taphonomic grades.

Shell A was found in the main channel of Raccoon Creek and is rated a 3 (good condition) on the Preservation Index (PI) scale. B is also a modern shell, but was harvested alive and is ranked a PI of 5 (excellent condition). C shows good preservation in a Paleogene shell, while D shows excellent preservation in a Cretaceous sample.

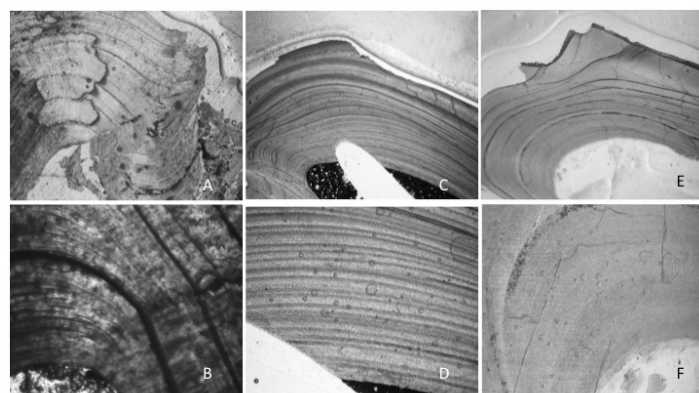


Figure 5. Thin sections of fossil material for growth line analysis

Thin sections of Paleogene (a-b: L6978c-2 *Rhabdotophorus*) and Cretaceous (c-d: L5223c (*Proparresys pyramidaloides*); e-f: L5233c (*Plethobasus aseopiformis*)) growth lines. The above specimens record between 6 and 12 years of sclerochronological data. Figures a, c and e show large-scale growth patterns while the lower panel of images b, d, and f detail sub-annual patterns. Large dark banding is indicative of annual growth cycles in all specimens and smaller bands were indicative of monthly and fortnightly cycles

Annual banding can be observed in all of the material indicating stable and seasonal environments. Some shells also showed evidence of macrostructure as discussed by Good (2004).

DISCUSSION

The modern taphonomy project is an attempt to quantify rates of change experienced by shells prior to the process of diagenesis and while exposed to weathering on Earth's surface. The experiment is in its early stages, and concrete results will only become clear after many months to years. However, preliminary results show that all of the shells lost a comparable amount of material within three months regardless of original weight, size or relative hardness. This suggests that if the project were extended, significant weight would be lost. The fossil shells would have been removed from a taphonomically active environment to avoid dissolution and conversion to calcite.

The fossil material in the K and PG groups ranged from 3-5 (good to excellent) on the micro-preservation index scale. Taphonomic signature varied from specimen to specimen and could also vary within one sample, but all samples that were analyzed are in a condition that is appropriate for reliable geochemical analysis. SEM data proved shells that were collected from the main channel of Raccoon

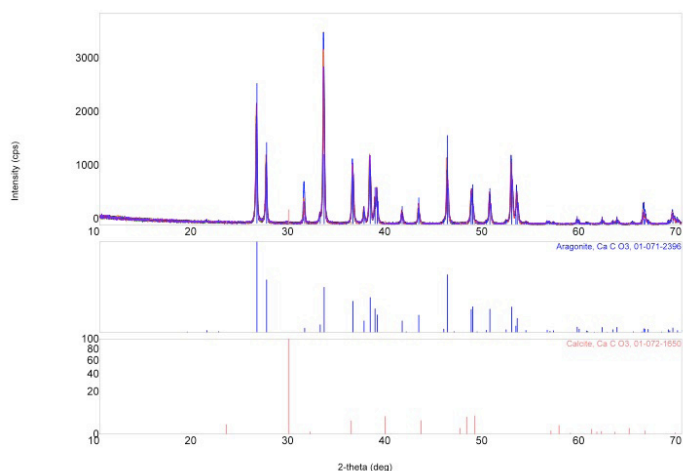


Figure 4: XRD Peak Intensity data

Raw XRD data for three K samples and three PG samples. The first column is a comparison of the average peak intensities for all shells analyzed to the 2-theta values for calcite and aragonite. Structures have been positively identified as aragonite.

Creek to be generally less fit for geochemical analysis than fossil material that was used in this study (Fig. 3). Preferential preservation and the particular taphonomic pathway experienced by the shells in Hell Creek Montana have allowed exceptional preservation over the last 60 million years.

In addition to being pristine on a microscopic scale, XRD analysis shows that all of the nacreous material observed in this study was composed of unaltered aragonite (Fig. 4). It is widely accepted that aragonite easily alters to calcite during diagenesis, especially when exposed to fresh water (Friedman, 1964; Dodd, 1966). Therefore it is significant that these shells have not experienced much alteration in the diagenetic process.

Despite little taphonomic change overall, there were some differences between the K and the PG material. Some differences were morphological. It has been noted that Cretaceous species had more morphological diversity and were more ornamented than those of the Paleogene (Scholz and J. H. Hartman 2007a). Paleogene samples, in addition to having low morphological diversity, were generally softer than the Cretaceous material. Growth lines in the PG group were not visible in hand sample and were hardly discernable in thin section analysis without analytical software (Fig. 5). The drastic change in morphological variability might have been caused by environmental factors that would also affect taphonomic patterns. Further study on the chemical composition of the two groups of fossil material might give insight into the slight differences in preservation. But despite these differences, there remained little alteration visible at the microscopic scale.

The difference in the morphologic and diagenetic styles between the two groups might be attributed to a distinct change in habitat across the K-Pg boundary. The presence of macrostructure in the PG shells suggests less prominent seasonality and a stable environment (Good, 2004). Prior research using Fourier coefficients suggests that the natural habitats of the unionids migrated from fluvial to lacustrine habitats across the K/Pg boundary (Scholz and Hartman 2007b). A rise in the water table and the persistence of large swampy lakes is seen as an explanation for change in species diversity

and dominant morphological characteristics, but interestingly may not have affected their taphonomic history.

CONCLUSION

The fossil material recovered from the lagerstätten in Hell Creek Montana is extremely well preserved as shown by SEM and XRD analysis. Their taphonomic pathway has prevented them from deteriorating in ways that modern shells being deposited in streams and flood plains naturally are prone to. The reasons for their pristine state remain unclear.

Growth patterns observed in the shells show some physical and morphologic changes across the boundary. Despite those differences, taphonomic evidence indicates that fluvial processes acted in similar ways and allowed pristine preservation of the two groups of mollusks. The good preservation of shells from the K/Pg transition in the Hell Creek and Fort Union Formations provide an opportunity for geochemists in conjunction with paleontologists to reconstruct more specific details of past fluvial environments.

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