

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

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2012-2013 PROJECTS

TECTONIC EVOLUTION OF THE CHUGACH-PRINCE WILLIAM TERRANE: SHUMAGIN ISLANDS AND KENAI PENINSULA, ALASKA

Faculty: *JOHN GARVER*, Union College, *CAMERON DAVIDSON*, Carleton College

Students: *MICHAEL DELUCA*, Union College, *NICOLAS ROBERTS*, Carleton College, *ROSE PETTIETTE*, Washington & Lee University, *ALEXANDER SHORT*, University of Minnesota-Morris, *CARLY ROE*, Lawrence University.

LAVAS AND INTERBEDS OF THE POWDER RIVER VOLCANIC FIELD, NORTHEASTERN OREGON

Faculty: *NICHOLAS BADER & KIRSTEN NICOLAYSEN*, Whitman College.

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

Faculty: *DAVID GILLIKIN*, Union College, *DAVID GOODWIN*, Denison University.

Students: *ROXANNE BANKER*, Denison University, *MAX DAVIDSON*, Union College, *GARY LINKEVICH*, Vassar College, *HANNAH SMITH*, Rensselaer Polytechnic Institute, *NICOLLETTE BUCKLE*, Oberlin College, *SCOTT EVANS*, State University of New York-Geneseo.

METASOMATISM AND THE TECTONICS OF SANTA CATALINA ISLAND: TESTING NEW AND OLD MODELS

Faculty: *ZEB PAGE*, Oberlin College, *EMILY WALSH*, Cornell College.

Students: *MICHAEL BARTHELMES*, Cornell College, *WILLIAM TOWBIN*, Oberlin College, *ABIGAIL SEYMOUR*, Colorado College, *MITCHELL AWALT*, Macalester College, *FREDY, AGUIRRE*, Franklin & Marshall College, *LAUREN MAGLIOZZI*, Smith College.

GEOLOGY, PALEOECOLOGY AND PALEOCLIMATE OF THE PALEOGENE CHICKALOON FORMATION, MATANUSKA VALLEY, ALASKA

Faculty: *CHRIS WILLIAMS*, Franklin & Marshall College, *DAVID SUNDERLIN*, Lafayette College.

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CRETACEOUS TO MIOCENE EVOLUTION OF THE NORTHERN SNAKE RANGE METAMORPHIC CORE COMPLEX: ASSESSING THE SLIP HISTORY OF THE SNAKE RANGE DECOLLEMENT AND SPATIAL VARIATIONS IN THE TIMING OF FOOTWALL DEFORMATION, METAMORPHISM, AND EXHUMATION

Faculty: *MARTIN WONG*, Colgate University, *PHIL GANS*, University of California-Santa Barbara.

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THE ROLE OF GROUNDWATER IN THE FLOODING HISTORY OF CLEAR LAKE, WISCONSIN

Faculty: *SUSAN SWANSON*, Beloit College, *JUSTIN DODD*, Northern Illinois University.

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PALEOENVIRONMENTAL RECORDS AND EARLY DIAGENESIS OF MARL LAKE SEDIMENTS: A CASE STUDY FROM LOUGH CARRA, WESTERN IRELAND

Faculty: *ANNA MARTINI*, Amherst College, *TIM KU*, Wesleyan University.

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INTERDISCIPLINARY STUDIES IN THE CRITICAL ZONE, BOULDER CREEK CATCHMENT, FRONT RANGE, COLORADO

Faculty: David Dethier, Williams College, Will Ouimet, U. Connecticut.

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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**

Faculty: DAVID GILLIKIN, Union College, DAVID GOODWIN, Denison University.

**RECONSTRUCTING INTRA-ANNUAL GROWTH PATTERNS OF LAMPSILIS CARDIUM USING
STABLE ISOTOPE GEOCHEMISTRY AND ENVIRONMENTAL PARAMETERS**

ROXANNE BANKER, Denison University

Research Advisor: David Goodwin

VITAL EFFECTS ON STABLE CARBON ISOTOPES IN FRESHWATER BIVALVES

MAX I. DAVIDSON, Union College

Research Advisor: David P Gillikin

**LINEAR AND LANDMARK-BASED MORPHOMETRIC COMPARISON OF TWO POPULATIONS OF
CAMPELOMA, SP. ACROSS THE K-PG BOUNDARY**

GARY LINKEVICH, Vassar College

Research Advisor: Stephanie Peek

**CARBON ISOTOPE CYCLING: A COMPARISON BETWEEN FOSSIL SHELLS ACROSS THE
CRETACEOUS-PALEOGENE BOUNDARY AND TODAY**

HANNAH SMITH, Rensselaer Polytechnic Institute

Research Advisor: Miriam Katz

THE LIFE AND AFTERLIFE OF HELL CREEK UNIONIDS

NICOLLETTE BUCKLE, Oberlin College

Research Advisor: Karla Parsons-Hubbard

**TRACE ELEMENTS WITHIN THE FRESHWATER BIVALVE LAMPSILIS CARDIUM FROM THE
O'SHAUGHNESSY RESERVOIR, OHIO**

SCOTT EVANS, SUNY Geneseo Geology Department, 1 College Circle, Geneseo, NY 14454

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CARBON ISOTOPE CYCLING: A COMPARISON BETWEEN FOSSIL SHELLS ACROSS THE CRETACEOUS-PALEOGENE BOUNDARY AND TODAY

HANNAH SMITH, Rensselaer Polytechnic Institute
Research Advisor: Miriam Katz

INTRODUCTION

The Williston Basin covers portions of North Dakota, South Dakota, and Montana, also extending north into Canada (See Gillikin and Goodwin, this project). In Montana, the Hell Creek (Cretaceous) and Fort Union (Paleogene) formations are bisected by the infamous Cretaceous-Paleogene (K-Pg) boundary which is linked with the demise of the dinosaurs. In the periods surrounding the K-Pg boundary, this area was part of a large prograding alluvial flood plain; this consists of fine grain sediments deposited by meandering rivers (Fastovsky 1987), which eventually emptied into the Western Interior Seaway. The late Cretaceous period was part of a warm period in the Earth's history, and the flood plains surrounding the Western Interior Seaway were rich with a variety of life forms ranging from dinosaurs to plants (Fastovsky 1987, Retallack 1996; Johnson 2002, Scholz and Hartman 2007). The Hell Creek paleo-river system continuously persisted, as shown by the presence of freshwater bivalves, for about two million years (Fastovsky, 1987; White et al.; 1998; Hicks et al. 2002; Lund et al. 2002; Wilson, 2004).

Carbon isotopes in stream water, in the form of dissolved inorganic carbon (DIC), come from a combination of sources, including air, soil, limestone dissolution, and respiration. The process of removing DIC from the water comes from photosynthesis, air-water exchange (degassing), and carbonate precipitation, all which also modify the $\delta^{13}\text{C}_{\text{DIC}}$ value (Mook and Tan, 1991). The soil contribution to DIC results from limestone dissolution and CO_2 among other materials. As the limestone dissolves, it results in a DIC contribution with a $\delta^{13}\text{C}_{\text{DIC}}$ value of $\sim 0\%$ to the system (Mook, 2000). Conversely, soil CO_2 is

around -28% , so when it is transported into rivers due to massive rain events the DIC in rivers becomes more negative (Mook, 2000). Streams that have high respiration typically have very low $\delta^{13}\text{C}$ values (Fig. 1 and Mook and Tan, 1991). Isotopic equilibrium between DIC and atmospheric CO_2 results in a DIC about 9% more negative than air (Mook, 2000); therefore turbulent streams tend to have higher $\delta^{13}\text{C}_{\text{DIC}}$ values. Photosynthesis also makes the $\delta^{13}\text{C}_{\text{DIC}}$ higher by preferentially taking up the lighter carbon (^{12}C) first, leaving the heavier carbon (^{13}C) behind in the water. Modern tropical streams have $\delta^{13}\text{C}_{\text{DIC}}$ values from $\sim +4$ to -28% (see Fig.1), a range we might also expect in the Cretaceous due to the warm climate.

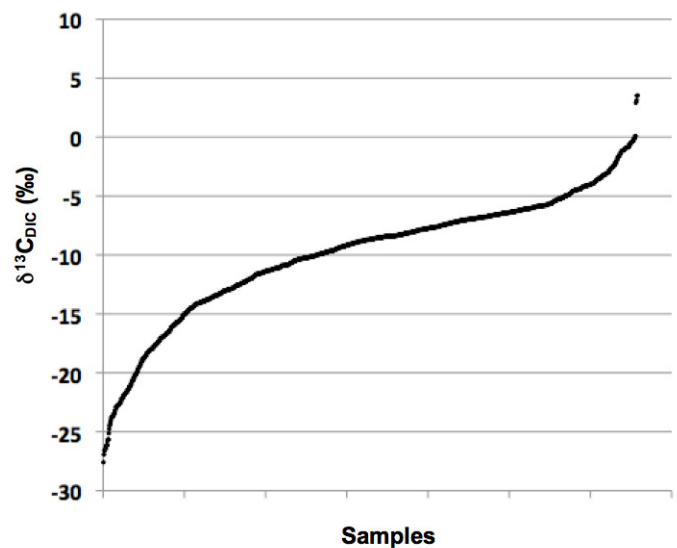


Fig. 1 Compilation of 1,316 modern $\delta^{13}\text{C}_{\text{DIC}}$ data from streams around Africa (compilation of published and unpublished data resulting from the AFRIVAL project). The lowest $\delta^{13}\text{C}_{\text{DIC}}$ values can be as low as -28% , but on average are -10% .

Freshwater bivalves are unique in the fact that they possess high resolution intra-annual growth rings of precipitated carbon which can yield high-resolution snapshots into the life and environment of the shell. Carbon is precipitated from two sources; the DIC which accounts for the majority of the shell's carbon, and metabolic carbon which is incorporated from what the bivalve consumes from its surroundings and incorporates into the shell (McConnaughey and Gillikin, 2008; see Davidson, this project). The isotopes are taken up from both sources and are stored in the precipitated shell layers, which can then be analyzed to give clues as to (paleo)environmental data.

The aim of this project is to 1) understand the carbon cycling within the Williston Basin paleo-river system and 2) establish how carbon cycling has changed (if at all) across the K-Pg within the Hell Creek Formation-Fort Union Formation near Jordan, Montana.

MATERIALS AND METHODS

This study compares carbon isotopes from three shells collected (July 2012) from selected localities in the Williston Basin that span the K-Pg boundary; two of the shells were collected from the Paleogene location (L-6978a), and one from the Cretaceous location (L-5233b). Site location codes are from Hartman (1998), which includes further details regarding fossil molluscan localities within the Williston Basin.

The three shells were selected for isotope analysis on the basis of the shell's completeness along the axis of major growth, as well as its durability (this being the ability of the shell to remain intact throughout the micromilling process). The shells were covered in epoxy (JD Weld) and cut along the maximum growth axis. The shells were then placed under a New Wave Research micromill and milled along the growth lines of the shell at 75 μ m per pass; this process removed about 60 μ g of the shell for analysis and was repeated through several years of continuous growth. Shell carbonate samples were analyzed using an Isotope Ratio Mass Spectrometer (IRMS). All carbonate isotopic analyses were performed at the University of Arizona on a Finnigan MAT 252 IRMS equipped with a Kiel III automated sampling device. Samples were reacted with >100% orthophosphoric acid at 70°C. Results are reported relative to VPDB by calibration

to the NBS-19 reference standard ($\delta^{13}\text{C} = +1.95\%$ and $\delta^{18}\text{O} = -2.20\%$ VPDB).

RESULTS

The results provide continuous data from the two Paleogene shells and one Cretaceous shell for both oxygen isotopes (Fig. 2) and carbon isotopes (Fig. 3). One sample from the Cretaceous shell did not run. The oxygen isotopes clearly show seasonal cycles representing several years of growth (See Banker, this project). These data will not be discussed further because this paper focuses on carbon isotopes. Carbon isotopes also show clear seasonal variation (Fig. 3).

The three shells did not have significant variation between their $\delta^{13}\text{C}_{\text{shell}}$ even though they span across the K-Pg boundary, ranging from -3.5 to -8‰ (Fig. 3).

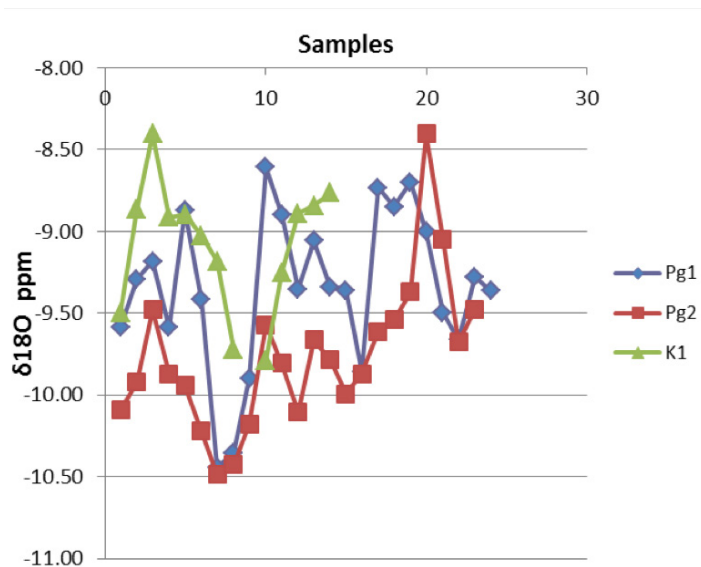


Fig. 2 Shell $\delta^{18}\text{O}$ values (‰) from the three fossil shells plotted versus sample number. Shell growth direction is from right to left.

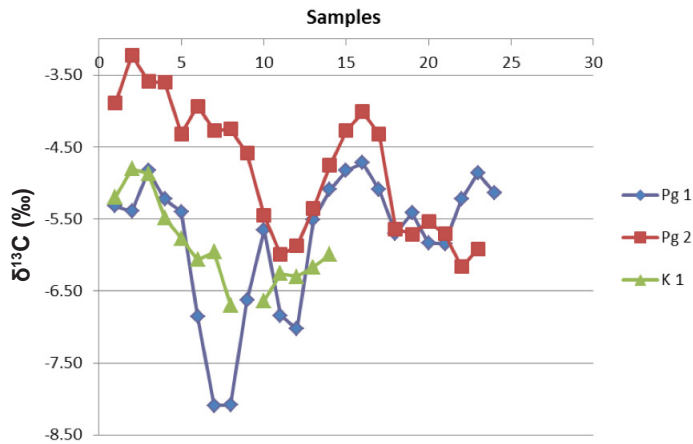


Fig. 3 Shell $\delta^{13}\text{C}$ values (‰) from the three fossil shells plotted versus sample number. Shell growth direction is from right to left.

DISCUSSION

The carbon isotope values from the three shells analyzed are similar, despite the large timespan they cover across the K-Pg boundary. It is hypothesized that these samples were not close enough to the boundary to see any changes resulting from the mass extinction event (cf. Arens and Jahren, 2000). Even though the values are similar between these specimens, it is noticed that the isotope values of these shells are higher than many modern shells that exist in similar warm climate streams (e.g., Graniero, 2011).

Since the shells have survived 65 million years of preservation, it is important to make sure they have not undergone diagenesis. Using the Scanning Electron Microscope (SEM), one can view the crystal lattice structure for any defects that would point to diagenesis (see Buckle, this project). Also used on this project was an X-Ray Diffraction (XRD), which measures the X-rays scattered by [powdered] crystals (see Buckle, this project). Another way that shells can be analyzed for diagenesis is through elemental concentrations; (Evans, this project) showed that the elemental concentrations were not significantly different from the modern shells. With this information it can be concluded that the shells were not impacted by diagenesis.

Previous studies have shown that bivalve shell carbon is a mix of respired carbon (estimated using $\delta^{13}\text{C}_{\text{tissue}}$) and DIC (McConnaughey and Gillikin:

2008; Davidson, this project). Respired carbon can be estimated from what the bivalve is consuming, which is typically similar to the carbon isotopic value of terrestrial leaves (Raikow and Hamilton, 2001). Carbon isotope values of fossil Cretaceous leaves range from -23‰ to -26.8‰ (Arens and Jahren 2002). Taking the average of these a value of about -25‰ for $\delta^{13}\text{C}_{\text{tissue}}$ is concluded. If the metabolic contribution to the shell was known, one could estimate the $\delta^{13}\text{C}_{\text{DIC}}$ value of these paleorivers. Estimates of values of the percent metabolic carbon within modern freshwater shells are about 10% - 42% (Gillikin et al, 2009; Davidson, this project). These values were adjusted to 0-40% as upper and lower bounds for the metabolic carbon incorporation envelope and were substituted with the estimated values for $\delta^{13}\text{C}_{\text{shell}}$ (fig. 3) and $\delta^{13}\text{C}_{\text{tissue}}$ (-25‰) to calculate $\delta^{13}\text{C}_{\text{DIC}}$ using a simple mixing model;

$$\delta^{13}\text{C}_{\text{shell}} + 2.7 = (f_{\text{Cm}} * \delta^{13}\text{C}_{\text{tissue}}) + (1 - f_{\text{Cm}} * \delta^{13}\text{C}_{\text{DIC}})$$

(see Davidson this project, for more details). By setting metabolic carbon (f_{Cm}) to 40%, the maximum possible $\delta^{13}\text{C}_{\text{DIC}}$ can be found: by setting metabolic carbon to zero, the minimum $\delta^{13}\text{C}_{\text{DIC}}$ also can be calculated (Fig. 4). By setting the f_{Cm} (%metabolic carbon) to 0%, the lowest $\delta^{13}\text{C}_{\text{DIC}}$ was calculated to be between -3‰ and -11‰ (Fig. 4). With these assumptions, the lowest calculated $\delta^{13}\text{C}_{\text{DIC}}$ values were approximately -11‰, as compared to modern values, which is usually found to be -10‰, but which may be as low as -28‰ (Fig. 1 and Mook and Tan, 1991).

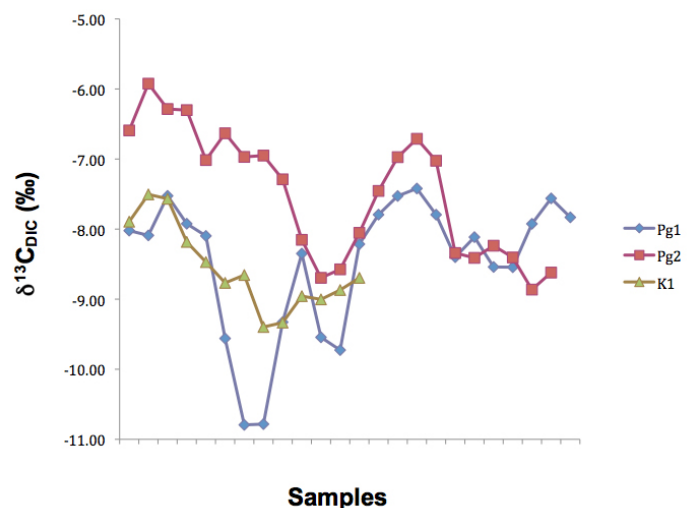


Fig. 4 Calculated $\delta^{13}\text{C}_{\text{DIC}}$ for the three fossil shells based on zero metabolic C incorporation, which show us what our lowest $\delta^{13}\text{C}_{\text{DIC}}$ value only reaches -11‰ which is substantially heavier than modern equivalents.

CONCLUSIONS

From these data our team concluded, through the minimum $\delta^{13}\text{C}_{\text{DIC}}$ calculated values, that the paleoriver systems these shells grew in were not large slow streams with ample respiration occurring. In a slow moving stream with ample respiration, a lower $\delta^{13}\text{C}_{\text{DIC}}$ value is expected, due to our knowledge of streams of similar climate (Fig. 1), and the knowledge of carbon cycling within rivers and streams (Mook and Tan, 1991; Mook, 2000). As higher $\delta^{13}\text{C}_{\text{DIC}}$ values were calculated, it can be concluded that the K-Pg streams from which these shells came from were shallow, well mixed, and did not have ample respiration occurring.

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