CSL - CENTER FOR CARBONATE RESEARCH RESEARCH PROGRAM PROSPECTUS 2013



UNCONVENTIONAL FOCUS: VACA MUERTA CONVENTIONAL FOCUS: DEEP WATER CARBONATE SYSTEMS, PETROPHYSICS, & CLUMPED ISOTOPE DIAGENESIS

UNIVERSITY OF MIAMI ROSENSTIEL SCHOOL of MARINE & ATMOSPHERIC SCIENCE



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MISSION OF THE CSL – CENTER FOR CARBONATE RESEARCH

The mission of the CSL – Center for Carbonate Research (CSL-CCR) is to conduct fundamental science for improved carbonate reservoir prediction and characterization.

The research conducted within the CSL-CCR is intended to provide valuable and comprehensive information for emerging topics in exploration and production as well as to advance fundamental knowledge in carbonates. In addition, CSL-CCR aims to inform its industrial associates on the newest research techniques and topics that potentially can be incorporated into the workflow of projects or help to solve longstanding problems.

The projects during 2013 combine observational, laboratory and theoretical data and integrate geology, geophysics, geomicrobiology and geochemistry. These integrated studies are grouped into five areas:

- Unconventional Reservoirs
- Carbonate Systems and Reservoir Characterization
- Petrophysics and Near-Surface Geophysics
- Geobiology and Microbialites
- Geochemistry and Diagenesis of Carbonates

The individual projects are designed to address various aspects of these themes. They are described in detail in this prospectus and are retrievable on the website <u>www.cslmiami.info</u>.

KNOWLEDGE TRANSFER

The CSL – Center for Carbonate Research transfers the research results to our industry partners through annual meetings, our website, and publications. We also offer field seminars and short courses as continuing education for geoscientists in the participating companies.

We present the research results at the **Annual Review Meeting** and provide each company with a CD of our presentations and the publications stemming from CSL sponsored research. On our **website** research results from previous years can be viewed in the archive section, providing a comprehensive data base for many topics and areas. Upon request, we also share original data sets with participating companies.

In 2013, we offer 2 seminars.

PERSONNEL

PRINCIPAL INVESTIGATORS

- **Gregor P. Eberli**, Ph.D. 1985, Geological Institute ETH Zürich, Switzerland Research Interests: Shallow and deep-water carbonate systems; seismic facies analysis and sequence stratigraphy, petrophysics of carbonates, and mixed carbonate/siliciclastic systems.
- Mark P. Grasmueck, Ph.D. 1995, Geophysical Institute ETH Zürich, Switzerland Research Interests: Applied geophysics, reflection seismic, Ground Penetrating Radar, 3-D and 4-D near surface imaging, reservoir characterization.

James S. Klaus, Ph.D. 2005, University of Illinois Research Interests: Evolution and extinction of Cenozoic to Recent reef corals, paleoecology of Cenozoic reefs, geo-microbiology of modern coral reef ecosystems.

- **Donald F. McNeill**, Ph.D. 1989, University of Miami/RSMAS Research Interests: Sedimentology and stratigraphic correlation of carbonate and mixed systems, integrated stratigraphy (bio-, Sr-isotope-, magnetostratigraphy).
- Peter K. Swart, Ph.D. 1980, King's College, University of London, England Research Interests: Sedimentary geochemistry, stable isotope geochemistry, organic geochemistry, global climate change, coral reef sedimentation.

ASSOCIATE SCIENTISTS

Mara R. Diaz Greta Mackenzie Ralf J. Weger

SCIENTIFIC COLLABORATORS

Christian Betzler and colleagues Dierk Hebbeln and colleagues Janos Urai and colleagues Thierry Mulder and colleagues University of Hamburg, Germany University of Bremen, Germany University of Aachen, Germany University of Bordeaux, France

VISITING SCIENTIST

Alex Bastos, PhD

Universidade Federal do Espirito Santo, Brasil

STUDENTS

Monica M. Arienzo, Deniz Atasoy, Caitlin Augustin, Quinn Devlin, Viviana Diaz, Ben Galfond, Kelly L. Jackson, Andrew Jo, Deniz Kula, Pierpaolo Marchesini, Irena Maura, Sean Murray, Jan Norbisrath, Amanda M. Oehlert, Erica Parke, Chelsea Pederson, Alan M. Piggot, Laura Rueda, Jara Schnyder, Rani Sianipar, Hasan Calgar Usdun, Noelle J. Van Ee, Michael Zeller

RESEARCH ASSOCIATE

Amel Saied

STAFF

Karen Neher Cory Schroeder Office Manager Technical Specialist

2013 RESEARCH FOCUS

In 2013 the CSL will place extra focus on three research directions in addition to the core projects in shallow-water carbonates and petrophysics. The first of these is an expansion of projects relevant to **unconventional reservoirs**. In this focus area we build on results from three years of fieldwork in the Neuquén Basin, which we will revisit, and extend our theoretical and experimental studies of limestone-shale mixtures. The second focus is a large research effort in **deep-water carbonates**, in particular the slope and basin west of Great Bahama Bank. In this local, a series of research cruises have assembled an unprecedented data set allowing comprehensive characterization of the morphology of, and the processes operating in, this slope-to-basin environment. The third focus is in **clumped isotope geochemistry**. After testing and refining the methodology, a full suite of research questions can now be addressed.

The **unconventional reservoir focus** uses the results of the outcrop studies in the Neuquén Basin, Argentina, as a starting point to assess the rules used to improve prediction of the distribution of TOC, and carbonate-shale ratios in this and other basins. Dense sampling and measurement of these three components within a sequence stratigraphic framework of the Vaca Muerta system is key to achieving this goal. Synthetic seismic modeling has proved that changes in limestone-shale ratios can potentially be detected on seismic data. In order to assess this potential and its limits we plan to combine a theoretical and laboratory study of the three-component system (TOC-shale-limestone). We expect that these projects will yield results that are applicable in a variety of basins with unconventional reservoirs.

The projects in **reservoir characterization of carbonate systems** are subdivided into two main research areas. The **deep-water environment focus** is possible because five research cruises along the western margin of Great Bahama Bank have collected a comprehensive geophysical and geological data set that allows the geomorphology and the processes operating along the entire slope-to-basin transect to be investigated for a lateral distance of over 400km. Hitherto underestimated lower slope failures and resultant mass wasting complexes, as well as mud-lean channelized slope sections, are just some of the new findings on this modern slope. The results will add much-needed information regarding the lateral variations of slope anatomy and facies that exist along a single carbonate platform.

The focus of the projects in the **shallow-water environment** is on processes that determine the stratigraphic architecture and the fluid flow in carbonate reservoirs. The recognition of sea-level oscillations within highstands is important in regards to the stratigraphy and the evolution of flow units. These oscillations potentially add heterogeneity within an existing flow unit and potentially create depositional cycles of short, suborbital duration. Both are important when assessing or modeling reservoir flow units. Outcrops and cores from the Bahamas and Florida are used to examine the sedimentary record of these oscillations within the last sea-level highstand. A second thrust regarding shallow-water carbonate reservoirs is examining the interplay between facies and diagenesis. The study site for this topic is the southern coast of the Dominican Republic where the CSL has mapped and drilled prograding reef successions over the past several years. Low-frequency GPR will be used to delineate the subsurface geometry of these successions. Subsequently, an additional 350 m of core will be drilled and finally hydrologic experiments will be conducted to assess the fluid-flow behavior of these reef successions.

Clumped Isotope Geochemistry focus: There has been a recent revolution in the application of stable oxygen isotopes to understand carbonate precipitation and recrystallization. Namely it has been recognized that deviations in the measured abundance of the ${}^{13}C^{18}O$ in CO₂ released through the digestion of carbonate minerals, as measured at mass 47, differs from that predicted by the rule of means and is solely a function of temperature. This is the so-called clumped isotope method. The method allows us to determine both the temperature and the δ^{18} O of the fluid from one measurement. The importance of the clumped isotope method to the study of carbonate diagenesis cannot be over-emphasized. Previous applications of the δ^{18} O method to carbonate paragenesis can be considered obsolete, in that they analyzed one variable (δ^{18} O) to determine two unknowns (temperature and the isotopic composition of the fluid). The projects outlined in this prospectus will attempt to calibrate the behavior of the clumped isotope method under well-constrained diagenetic conditions including early fresh-water diagenesis and dolomitization. These projects will allow the clumped isotope method to be applied towards the understanding of paragenesis in reservoir development.

Geo-microbiology: The ubiquitous presence of microbes and their ability to mediate carbonate precipitation requires appraisal of the importance of microbial influence on the formation of grains like ooids and during diagenesis. Three projects address these aspects. Based on the results of the functional gene analysis of the microbial community associated with ooids, in vitro precipitation experiments will be conducted to assess the roles of microbial metabolism and biofilm/EPS in carbonate precipitation. In a second study, cores through mud banks of Florida Bay are evaluated with microbiological techniques to assess the role of microbes in the early diagenesis of carbonate mud. Likewise, cores from the cyanobacterial mats and marl deposits in freshwater environments of the Florida Everglades will be used to characterize the microbial communities and document the diagenetic and textural changes through various diagenetic stages.

The **petrophysical and near-surface geophysical projects** cover experimental studies on resistivity, the petro-acoustic characterization of microbialites and unconventional reservoir facies, and a combined theoretical and field study approach to the use of diffractions as direct indicators of fracture intersections. Last year we studied the effects of cementation and dissolution on the porosity, permeability and sonic velocity. This year we will include resistivity into these experiments to further assess the influence of pore structure on the petrophysical properties of carbonates. For the same reason we started collaborating with colleagues from the University of Aachen to image the pores at sub-micron scales using the BIBSEM method (Broad-Ion-Beam cross-sectioning with subsequent SEM-image mosaic acquisition). These direct measurements of the pore network will be compared to indirect methods of pore size distributions derived from mercury injection (MICP) and magnetic resonance (NMR).

In the last two years a combined approach of GPR diffraction analysis and Ray-Born modeling produced results that promote the seismic diffractions from noise to valuable signal. The follow-up project integrates 3D synthetic modeling, 3D GPR data, outcrop observations, and 3D seismic data to reveal the geologic source of the diffractions and apply the findings to reservoir depth seismic data.

Below is the list of all planned projects. The detailed objectives and deliverables of each project are outlined further in the 2013 research prospectus.

2013 PLANNED PROJECTS

UNCOVENTIONAL RESERVOIR PROJECTS

- Outcrop Analogs for the Quintuco Vaca Muerta System Guidelines for Conventional and Unconventional Exploration
- Sequence Stratigraphic Control on the Source Rock Quality in the Vaca Muerta System, Neuquén Basin, Argentina
- Forward Modeling Acoustic Properties from Unconventional Mineral Combinations
- Acoustic Properties of Shale-TOC-Limestone Mixtures

CARBONATE SYSTEMS AND RESERVOIR CHARACTERIZATION

- A) Deep-water Carbonates
 - Morphology and Sedimentation Processes on the Slope of Great Bahama Bank
 A Multi-Institutional Research Effort
 - Anatomy of Slope Channels, Debris Fields and Slope Scars: Great Bahama Bank
 - Current Influence on Slope and Basin Sedimentation
 - Slope to Basin Geomorphology and Processes along Southwestern Great Bahama Bank
- B) Shallow-water Carbonates
 - Suborbital Sea-Level Oscillations during the Last Interglacial Highstand (MIS 5e): Evidence from the Bahamas
 - Influence of Sea-Level Oscillations During Highstands on Pleistocene Carbonate Shoals (year 2)
 - Facies and Diagenetic Progression in Deep, Windward Margin Grainstones, New Providence Platform, Bahamas
 - Quantitative Characterization of Mixed System Clinothems: Gurabo Formation, Dominican Republic
 - Depositional and Diagenetic Controls on Fluid Flow Properties of Plio-Pleistocene Shallow-water Carbonates of the Dominican Republic

GEOCHEMICAL PROJECTS

- Using Clumped Isotopes to Understand Early Diagenesis
- New Insights into Dolomitization Using Clumped Isotopes
- Speleothems as a Model System For The Study of Clumped Isotopes and Fluid Inclusions
- Geochemical Evidence of a Mississippian Anoxic Event from Carbon and Sulfur Isotopes?

GEOBIOLOGY PROJECTS

- The Potential Role of Microbes in the Genesis of Ooids and Carbonate Precipitation
- Microbial and Geochemical Characterization of Carbonate Mud Islands from Florida Bay
- Freshwater Microbial Carbonates of South Florida: Biological, Geochemical, and Textural Characterization

PETROPHYSICS AND (NEAR-SURFACE) GEOPHYSICS

- Diffractions as Direct Indicators of Fracture Intersections and Reservoir Connectivity
- Facies Geometry and Regional Correlation of Pleistocene Reefal Limestones: A Low Frequency 2D GPR Survey on Rough Terrain
- Pore Size Distributions and Electrical Resistivity in Carbonates and Shales
- Variability of Electrical Resistivity during Controlled Precipitation and/or Dissolution
- Petrophysical Properties and Pore Structures of Microbialites (Stromatolites, Travertine and Tufa)

Costs

The contribution of each Industrial Associate towards the research is **\$55,000**. The CSL-CCR raises additional research grants from national funding agencies such as the National Science Foundation and the Petroleum Research Fund for many of the proposed projects. For example, funding for the data acquisition of the deep-water carbonates project, and most of the funds for new equipment for the geochemical studies, have been made possible by grants from federal funding agencies.

REPORTING

The results of the projects will be presented at the **Annual Review Meeting in Miami**, **October 14-15**, **2013**. In conjunction with the meeting, a fieldtrip to the Exumas is scheduled for **October 16-20**, **2013**.





FIELD SEMINAR 1:

OFFERED BY THE CSL – CENTER FOR CARBONATE RESEARCH

FACIES SUCCESSIONS ON GREAT BAHAMA BANK

IMPLICATIONS FOR EXPLORATION AND RESERVOIR CHARACTERIZATION

JUNE 17 – 22, 2013

Leaders: Gregor P. Eberli, Paul M. (Mitch) Harris and G. Michael Grammer

Location: Begins and ends in Miami, Florida. The first day is a seismic and core workshop in Miami, followed by five days on a chartered boat that will cross Great Bahama Bank with stops at all important facies belts.

Objectives:

- illustrate the depositional processes and dimensions of facies belts on an isolated platform.
- improve the interpretation of subsurface data of carbonate systems.
- relate filling of accommodation space and facies heterogeneities to reservoir models.

Who Should Attend: Petroleum geologists, geophysicists and reservoir engineers who are working in carbonates and need to understand facies heterogeneities and porosity distribution at exploration and production scales.

Content: This seminar explores the vertical and lateral facies successions and heterogeneities of Great Bahama Bank. The seismic and core workshop on day 1 illustrates the architecture of the prograding western margin of Great Bahama Bank. Cores across the platform margin provide a unique opportunity to examine the sequence stratigraphic distribution of facies and diagenetic modification in platform carbonate reservoirs. Log and laboratory data from these cores provide insights into porosity/velocity relationships and permeability distribution in platform carbonates.

As modern analogs, the facies belts on Great Bahama Bank display the depositional heterogeneities that may occur in ancient hydrocarbon reservoirs. We explore the spatial heterogeneity within a carbonate platform, a facies belt or individual facies bodies, while simultaneously exploring the fundamental controlling processes. In particular, sedimentary structures, dimensions and lateral variability of classic reservoir facies are examined during the seminar. Field stops include the leeward platform margin (Cat Cay Ooid Shoal), the platform interior, the tidal flats of Andros, the ooid shoals of Joulters Cay, patch reefs, and the Andros Island barrier reef. Pleistocene outcrops on Bahamian islands show how these facies are preserved in the ancient rock record.

For the complete program visit: http://www.cslmiami.info/learning/fieldSeminars





In the water at Joulters Cay

In an Andros Island tidal channel

Cost: \$4,300.-, Flights to and from the Bahamas, all ground transportation, on-board boat accommodation in the Bahamas, meals, and course notes are included.

Contacts:

Gregor P. Eberli	(305) 421 4678	geberli@rsmas.miami.edu
Karen Neher	(305) 421 4684	kneher@rsmas.miami.edu

Registration: A soon as possible but no later than May 1, 2012

Karen Neher (305) 421-4684 <u>kneher@rsmas.miami.edu</u> Comparative Sedimentology Laboratory 4600 Rickenbacker Causeway, Miami, FL 33149, USA





CSL – CENTER FOR CARBONATE RESEARCH

FIELD SEMINAR 2: IN CONJUNCTION WITH THE ANNUAL MEETING

LATERAL AND VERTICAL HETEROGENEITY AT THE EXUMAS BANK MARGIN

CAUSED BY SUBORBITAL SEA-LEVEL OSCILLATIONS

OCTOBER **15** – **19**, **2013**

Leaders: Kelly L. Jackson, Donald F. McNeill, Gregor P. Eberli, and Paul M. (Mitch) Harris

Location: New Providence Island and several locations in the Exuma Cays are visited to illustrate the influence of sea-level oscillations within the last interglacial highstand (MIS 5e) on the lateral and vertical heterogeneity of the platform top facies. In addition, several stops will document the dynamic development of the grainstone dominated, high-energy carbonate platform margin during the Holocene sea-level rise. The seminar begins and ends in **Nassau** on New Providence Island, **Bahamas**.

Objectives:

- show the evidence for the stratigraphic record of sea-level oscillations and the resultant heterogeneity along the windward margin, and
- illustrate the dynamic evolution and accretion of grainstone facies during the Holocene sea-level rise that cause reservoir-scale heterogeneity within these grainstone facies.

Who Should Attend: Exploration and production geoscientists and reservoir modelers working in grainstone reservoirs or on platform margin settings.

Content: The seminar focuses on the vertical and lateral facies relationships that are created by sea-level oscillations within sea-level highstands and resultant depositional topography that influence the facies distribution in the subsequent sea-level cycle.

Pleistocene islands together with the surrounding Holocene facies illustrate the influence of the antecedent topography. Cores through the Pleistocene strata document the vertical juxtaposition of bank-margin lithofacies that is controlled by oscillations of sea level within the latest highstand. We will discuss the implications for reservoir heterogeneity of these sub-orbital sealevel fluctuations. The modern environment displays the sedimentary products that are produced by the physical and biological processes that evolved during the Holocene sea-level rise. Cemented Holocene beach ridges and eolianites in juxtaposition to the un-cemented Holocene. We will study the accumulation of sand in tidal channels and tidal deltas and examine the various sub-environments with differing grain-composition and sedimentary structures. Corals and stromatolites in normal, open marine environments and tidal channels will display the location of the reef building communities in these high-energy environments.



Cambridge Cay with an offshore relic of cemented Holocene dune and a backstepping beach/dune complex.

Cost: \$3,900.-, Includes all ground transportation, boat, meals, and course notes.

Contacts:

Kelly L. Jackson	(305) 421 4811
Donald F. McNeill	(305) 421 4790
Gregor P. Eberli	(305) 421 4678

kjackson@rsmas.miami.edu dmcneill@rsmas.miami.edu geberli@rsmas.miami.edu

Registration: A soon as possible

Karen Neher (305) 421-4684 <u>kneher@rsmas.miami.edu</u> Comparative Sedimentology Laboratory 4600 Rickenbacker Causeway, Miami, FL 33149, USA

OUTCROP ANALOGS FOR THE QUINTUCO - VACA MUERTA SYSTEM – GUIDELINES FOR CONVENTIONAL AND UNCONVENTIONAL EXPLORATION

Michael Zeller, Ralf J. Weger, and Gregor P. Eberli

PROJECT OBJECTIVES

- Connect existing large scale analog studies to each other and the producing field areas
- Examine conventional and unconventional potential in relation to the sequence stratigraphic framework
- Develop guidelines for seismic identification of reservoirs and sweet spots for fracturing

PROJECT RATIONALE

The Quintuco – Vaca Muerta System in the Neuquén Basin recently received much attention due to its potential as a major unconventional play within the distal shale portions. Moreover the system contains a highly heterogeneous shelfal succession, which offers conventional reservoir potential. However, sedimentological studies are generally restricted to 1D reference sections and do not cover the lateral architecture or heterogeneities within the depositional system. Combining fieldwork, satellite imagery and seismic modeling closes this gap and helps to establish rules for predicting facies and heterogeneities from subsurface data sets.



Figure 1. Sequence Stratigraphic Models at the distal Sierra de la Vaca Muerta (left) and the proximal Picún Leufú Anticline (right).

APPROACH

Over the last few years, we developed high-resolution sequence stratigraphic models of large-scale outcrop analogs (Figure 1) in proximal and distal paleogeographic positions and were able to document potentially brittle zones within the system based on the sequence stratigraphic framework. Moreover we derived synthetic seismic models based on the petrophysical properties of outcrop samples in order to investigate the resulting of seismic expressions of the systems. In the next

step we want to combine our results and, based on them, develop a new set of guidelines for exploration.

EXPECTED RESULTS

We plan to present a summary of observations from the outcrop analogs based on (i) the sequence stratigraphic facies distribution, (ii) the identification of this sequence stratigraphy from seismic sections, and (iii) the seismic expressions of reservoirs and sweet spots for fracturing.



REGIONAL SEISMIC LINE OF QUINTUCO - VACA MUERTA SYSTEM

OUTCROP SYNTHETIC SEISMIC MODELS (SAME SCALE AS SEISMIC)



thick, with breaks

thin, with gentle shelves

Figure 2. Comparison Outcrop Synthetic Seismic Models with regional seismic line. All in same scale. Green transparent area is approximate extent of Vaca Muerta Shale succession. (Seismic Line modified from Leanza et al. (2011))

REFERENCE

Leanza, H., F. Sattler, R. S. Martinez, and O. Carbone, 2011, La Formacion Vaca Muerta y Equivalentes (Jurassico Tardio - Cretacico Temprano) en la Cuenca Neuquina, *in* H. Leanza, C. Arregui, O. Carbone, J. C. Danieli, and J. M. Valles, eds., Geologia y Recursos Naturales de la Provincia del Neuquen, Relatorio del XVIII Congreso Geologico Argentino: Buenos Aires, Asociacion Geologica Argentina, p. 113-130.

SEQUENCE STRATIGRAPHIC CONTROL ON THE SOURCE ROCK QUALITY IN THE VACA MUERTA SYSTEM, NEUQUÉN BASIN, ARGENTINA

Max Tenaglia, Michael Zeller, Gregor P. Eberli, and Peter K. Swart

PROJECT OBJECTIVES

- Document organic carbon content distribution within the existing sequence stratigraphic framework in the large scale Vaca Muerta outcrop exposures.
- Evaluate source rock quality, maturity and preservation in the studied sections
- Identify controlling processes on organic matter distribution in mixed carbonate siliciclastic systems to establish a predictable model for subsurface exploration.
- Establish a δ 13C stratigraphy in the carbonate and organic carbon from the shelf to the basin for high-resolution correlation.

PROJECT RATIONALE

The Vaca Muerta Formation is one of the most prolific source rocks of South America and a key tight oil/shale gas target within the petroleum system of the Neuquén Basin. In order to develop this potentially large reservoir, understanding of shale characteristics is of paramount value to define sweet spots for drilling and hydraulic fracturing.

Organic Carbon Content (TOC) is one of the key parameters and its distribution within the sedimentary succession is thought to be a function of production, preservation and dilution of organic material (Katz, 2005). Understanding the relative impact of these factors can help to identify trends within the sequence stratigraphic framework and help to develop predictive models for sweet spots (high TOC) within unconventional tight oil reservoirs



Figure 1. Sequence Stratigraphic Models at the distal Sierra de la Vaca Muerta (right) with an outcrop picture of section S1. Carbonate content (and with it brittleness) are higher in regressive hemicycles (red triangles) of the successions.

Identify the distribution of organic carbon content within the high-resolution sequence stratigraphic models by dense sampling of the studied sections used for building the sequence stratigraphic framework. We plan to determine carbonate content and organic matter and add RokEval measurements for source rock type, maturity and quality assessment.

A δ^{13} C analysis of the organic and inorganic carbon in the samples will be performed. The isotope analyses will be used to strengthen the stratigraphic correlation between the shelf and the basinal sections and refine the sequence stratigraphic framework within the measured sections. In addition, they will provide new insight as to whether the enrichment of the organic material is related to ocean anoxia or to the sea-level fluctuations that form the mixed sequences in the Neuquén Basin

If access to core material becomes available, samples from the subsurface will be incorporated. These subsurface samples will also be used to relate the geochemical properties to the petrophysical properties, in particular acoustic velocity and resistivity.

EXPECTED RESULTS

The tie of source rock quality to the sequence stratigraphic framework will document the distribution of organic carbon content during changing depositional conditions. While studies on pure carbonate and pure siliciclastic successions revealed the control of sea level in these two-phase systems (e.g. Figure 2, Van Buchem et al. (2005)). This new model for mixed carbonate siliciclastic systems will help in understanding the processes dominating source rock distribution in these more complex 3-component systems.



Figure 2. Example of Sequence Stratigraphic Model for TOC Distribution in the Natih Formation in Oman (modified from Van Buchem et al. (2005)). The main source rock deposition is around maximum flooding phase.

REFERENCES

- Katz, B. J., 2005, Controlling factors on source rock development a review of productivity, preservation, and sedimentation rate, *in* N. B. Harris, ed., Deposition of Organic-Carbon-Rich Sediments: Models: SEPM Special Publication, v. 82, p. 7-16.
- Van Buchem, F. S. P., B. P. Huc, and M. M. Stefani, 2005, Stratigraphic patterns in carbonate source-rock distribution: Second-order to fourth-order: control and sediment flux, *in* N. B. Harris, ed., Deposition of organic-carbon-rich sediments: Models: SEPM Special Publication, v. 82, p. 191-223.

FORWARD MODELING ACOUSTIC PROPERTIES FROM UNCONVENTIONAL MINERAL COMBINATIONS

Ralf J. Weger, Michael Zeller, and Gregor P. Eberli

PROJECT OBJECTIVES

- Create several different forward model scenarios of different mineral combinations representative of unconventional reservoir settings.
- Analyze feasibility of detection and delineation of both brittleness (E) and Kerogen content from seismic frequency acoustic signals.

PROJECT RATIONALE

Unconventional plays rely heavily on both the success of fracturing in low porosity shale intervals in order to exploit as much volume as possible, and the presence of high quantity and quality TOC contents. Mechanical properties are key for defining the most economic well locations, but the nature of unconventional reservoirs presents a new set of challenges. Petrophysical characteristics of shales in different stratigraphic levels are highly variable; fracability or brittleness is often enhanced by carbonate content; and both are highly influenced by frational TOC content. The most pressing question for geophysicists in unconventional reservoirs is the determination of both brittleness and TOC content from seismic data (lambda-mu plots), and several published examples exist in different unconventional settings in the US (e.g. Eagle Ford, Treadgold et al., 2011 or Barnett, Goodway et al., 2007).



Figure 1. Realistic scenarios forward model of varying mineral combinations and porosity to illustrate and outline the basic property requirements for successful determination of brittleness and delineation of TOC content.

However, given the high variability in shale properties enhanced by the presence of TOC, there are no standardized rules for all unconventional shales. In order to improve the understanding of acoustic behavior in varying carbonate/shale/TOC combinations we plan to create a variety of "template type" forward models of different shales with variable carbonate and TOC content.

SCOPE OF WORK

Starting with known acoustic properties of the component minerals, we intend to forward model varying mineral combinations and porosity in systematic fashion to illustrate and outline the basic property requirements for successful determination of brittleness and delineation of TOC content. Artificial sections of realistic scenarios will be created, their elastic properties will be modeled using a variety of different rock models, synthetic seismic will be created from the resulting sections, and lambda-mu plots will be analyzed to determine their ability to detect high TOC and brittleness under the different scenarios.

EXPECTED RESULTS

The results are expected to produce a better understanding of the physical/acoustic behavior of unconventional reservoirs using a variety of different shales and combinations with carbonates as a guide for delineating crucial parameters from seismic or logs. This study is to provide a basic template for feasibility of Brittleness and TOC content determination usable in different unconventional shale scenarios.

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ACOUSTIC PROPERTIES OF SHALE-TOC-LIMESTONE MIXTURES

Ralf J. Weger, Jan Norbisrath, and Gregor P. Eberli

PROJECT OBJECTIVES

- Systematically measure samples with variable amounts of shale, TOC, and limestone to assess the acoustic and electrical response of the various mixtures.
- Correlate acoustic properties to carbonate content and TOC to asses a) the degree of enhanced fracability of carbonate-bearing shales and b) the seismic response of potential sweet spots in shale basins.



Figure 1. Example of seismic response of mixtures of carbonates and shales in the Vaca Muerta Formation of the Neuquén Basin. The proposed project aims to systematically assess the acoustic response to mixtures of shale-TOC-limestone and evaluate their seismic response (modified from Zeller et al. 2012).

PROJECT RATIONALE

Unconventional plays rely, to a large extent, on recognizing sweet spots on seismic data and the success of fracturing the shale intervals. For both, the mechanical properties are of key importance. These properties are largely dependent on composition of the shale, and the TOC content and carbonate content. The aim of this study is to measure the physical properties of rocks containing these components to assess the respective influence of each on the petrophysical properties of such rocks. This assessment is important for relating the seismic facies and log signature to variations of these three components, which in turn is a prerequisite to predict shale-TOC-limestone composition from subtle changes in amplitude.

SCOPE OF WORK

We plan to measure porosity, permeability, and velocity and resistivity under variable confining pressure and correlate these physical properties to the carbonate content, TOC and shale portion. In addition, the composition of the mineralogy of the shale will be determined by XRD. We plan to assemble data from a variety of settings and stratigraphic ages but will concentrate on formations that contain, or are potential, unconventional reservoirs. Some samples from the Devonian (Perdrix Fm) and the Neuquén Basin (Vaca Muerta Fm) collected in earlier studies are in hand. A new sampling campaign is planned in the Neuquén Basin. In addition, samples from the mixed system in the Dominican Republic (Gurabo Fm) and from the basinal portions of the Bahamas Transect that consist of marl-limestone alterations with variable amounts of TOC will be incorporated in the study. We also will seek access to subsurface samples from intervals drilled through unconventional reservoirs.

In a second step the seismic response of these mixtures are assessed with synthetic seismic modeling. Modeling of the Vaca Muerta Formation using a 2-component limestone-shale system indicates a detectable response of limestone-rich versus more shaly intervals (Figure 1). Likewise, the lower velocities of the marls and shales of Mt. Hawk and Perdrix Formations are responsible for the strong seismic reflections in the Western Canadian Basin (Figure 2).



Figure 2. Velocity model used for a synthetic seismic model of Miette buildup and the adjacent onlapping basinal shales (5 -9)(Perdrix and Mt Hawk Fms.). The shales with slower velocity (yellow and orange) are intercalated with limestone (Schwab et al., 2000).

EXPECTED RESULTS

The proposed study will add much needed information on the controls of petrophysical properties of rocks containing variable amounts of carbonates, shale, and TOC, and their seismic and log response.

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MORPHOLOGY AND SEDIMENTATION PROCESSES ON THE SLOPE OF GREAT BAHAMA BANK - A MULTI-INSTITUTIONAL RESEARCH EFFORT

Gregor P. Eberli, Mark Grasmueck, Deniz Kula, Dierk Hebbeln¹, Christian Betzler³, Thierry Mulder², Paul Wintersteller¹, Jara Schnyder, Thomas Lüdman³, Emmanuelle Ducassou², and shipboard participants

> ¹MARUM, University of Bremen, Germany ²University of Bordeaux, France ³University of Hamburg

RESEARCH EFFORT OBJECTIVES

- Provide a comprehensive documentation of the variability in morphology and composition of the western slope of Great Bahama Bank and the adjacent Straits of Florida using multibeam, side scan sonar, and seismic data together with geological data from cores, and grab samples from several research cruises.
- Document and assess the importance of the different sedimentation processes on the slope and in the basin, including off-bank transport, mass-gravity flows, slope failures and ocean currents.
- Relate the sedimentation processes to the sedimentary products, their distribution and dimensions.

BACKGROUND AND RATIONALE

Studies on the modern Bahamian slopes in the eighties were the first to describe the slope anatomy and facies distribution on modern carbonate platform slopes (Mullins et al., 1984; Schlager and Camber, 1986). Drilling these slopes in two Ocean Drilling Program (ODP) legs added insight into the slope processes through time. ODP Leg 101 had as one of its objectives a test of the concept of slope evolution from accretionary, bypass and erosional slopes (Austin et al., 1988). Seismic imaging and coring during ODP Leg 166 placed the slope processes within a sequence stratigraphic framework (Eberli et al., 1997, Betzler et al., 1999, Anselmetti et al., 2000). Several of these studies have been made into textbooks as modern analogs for carbonate slopes (Playton et al., 2012).

What is still missing, however, is a comprehensive overview of the seafloor geomorphology of the different facies elements of the margin and slope. New multibeam and seismic data, combined with piston cores and visual observation with a Remote Underwater Vehicle (collected during recent cruises in the Bahamas by several groups), provide for the first time a data set that will refine existing models of processes, morphology and facies distribution along carbonate slopes. In particular, these data indicate the importance of slope instability on the lower slope, the lateral variability of slope canyons and the extent of debris fields on the toe-of slope that serves as the habitat of diverse deep-water ecosystems (Mulder et al., 2012; Correa et al., 2012; Hebbeln et al., 2012).

These data sets, combined with a new data set that will be acquired in the spring of 2013 will give nearly complete coverage of the entire western slope of Great Bahama Bank (GBB). This comprehensive data set will allow an investigation of the morphologic variability and different sedimentation processes along more than 400 km of platform margin.

THE DATA SETS

The principal data sets for this research initiative area were acquired by several groups. The older multichannel seismic data along western GBB were collected in the nineties by the CSL in preparation for ODP Leg 166. The new generation of data were collected over the last 10 years from a multitude of platforms (Figure 1): NOAA Explorer funded an AUV- based high-resolution multibeam, side scan sonar and subbottom profile at five sites in the Straits of Florida in 2005. NIH and NOAA funded subsequent submersible dives to ground truth the AUV data.

In 2010, the CSL was invited to participate in a cruise financed by the French National Science Foundation that collected multibeam, single- and multichannel seismic data and piston cores onboard R/V Le Suroit with Thierry Mulder and Emmanuelle Ducassou as co-chiefsd. Last year the Bahamas Petroleum Company made a multibeam/sub-bottom profiler data set from the southern portion of the Santaren Channel available to the CSL.

In the spring of 2012, the German financed WACUM expedition (R/V Maria S. Merian cruise MSM20-4) investigated two sites at the western side of GBB with multibeam and single-channel seismic data, grab samples and piston cores, as well as visual observations with an ROV with a focus on cold-water corals (Hebbeln et al., 2012). For the spring of 2013 Christian Betzler received funding for another expedition into the Straits of Florida. Meteor cruise M-90 will conduct seismic and hydro-acoustic surveys and do geological sampling (grab and gravity cores) to link the geophysical data with sedimentological and facies data



Figure 1. Left) Geographical distribution of the data sets along the western Great Bahama Bank. Right) Vessels and dates of the acquisition of the data sets. With the completion of the upcoming survey 4 over 400 km of the slope and basin along western Great Bahama Bank will be hydro-acoustically imaged and sampled for composition and facies.

SHARE OF THE RESEARCH EFFORT WITHIN THE CSL

The five surveys together provide an unprecedented data set regarding the scale, resolution, and amount of geophysical and geological sampling of a modern carbonate slope. This vast amount of data is mostly worked up in institutions that

wrote the proposals and received funding for these cruises. Fortunately, the CSL has been invited to collaborate with all these groups and, in return, the CSL is sharing data from their earlier surveys. This allows the CSL to work and collaborate in the following projects:

- Two cores, the multibeam and some seismic data from the CARAMBAR cruise are available for the investigation of the cold-water coral mounds in the Straits of Florida. This project is well underway and will be finished within 2013 (Sianipar et al., 2012).
- Projects dealing with sedimentation processes and morphology of the slope and basin system are addressed with three data sets.
 - The MACUM expedition (MSM20-4), in its effort to image the habitat of the cold-water corals, collected a high-quality multibeam data and singlechannel data set of channelized slope north of Bimini and a partly buried debris field in and around the AUV site GBB-1. Scientists from the CSL and MARUM will use this data, the ROV visual imagery and the core and grab samples for a project on the slope processes in these areas.
 - The **CICARB expedition** will collect data to study both the mass gravity flow processes on the slope as well as the current related sedimentation.
 - The **BDP** data set is the southern-most area along the investigated slope. The multibeam and sub-bottom profile data are used to examine variations in slope instabilities close to the Cuban-American collision zone.

EXPECTED RESULTS

The combined results of these data sets will give a very comprehensive documentation of the anatomy of the western slope of GBB. It will provide information about the size, composition and lateral juxtaposition of the different geomorphologic elements that build this margin-slope-basin system. Because of the large coverage it will also allow for a quantitative assessment of the various elements and their variations from north to south. For example, the increase in slope and margin failures towards the south (Cuban-American plate boundary) can be quantified.

The combined geophysical and geological data from the deep ODP cores, the numerous piston cores and grab samples will allow sedimentary processes to be related to their products. We especially expect new insights into the formation of mass transport complexes in carbonates, the role of slope creeping, and the interaction between mass-gravity flows and current sedimentation along the slope.

The calibration of the geophysical data (backscatter and side scan sonar) with core and grab samples will allow a facies map to be constructed along the entire slope and basin.

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ANATOMY OF SLOPE CHANNELS, DEBRIS FIELDS AND SLOPE SCARS: GREAT BAHAMA BANK

Gregor P. Eberli, Paul Wintersteller¹, Dierk Hebbeln¹, Deniz Kula, and Jara Schnyder,

¹University of Bremen, Germany

PROJECT OBJECTIVES

- Document the facies and geometries in a channelized slope segment north of Bimini and the partly buried debris field further south.
- Determine the thickness and stability of the muddy sediment in both areas using sub-bottom profiles to document lateral variability of the mud wedge off GBB.
- Delineate the sedimentary processes responsible for the observed slope morphology and facies.

PROJECT RATIONALE

The western slope of Great Bahama Bank (GBB) has long been thought to be mainly composed of an up to 90 m thick mud wedge that onlaps a cemented upper slope and thins basinward to a few meters (Wilber et al., 1990). Multibeam, seismic and coring data acquired during the CARAMBAR and WACUM cruises, however, reveal lateral transitions into coarse-grained channelized slope segments that can be as wide as 30 km (Figure 1, Mulder et al., 2012). Other unexpected findings of these surveys are the recognition of large-scale slumping, mass transport complexes and scars within the slope that extend for kilometers. In order to provide a more comprehensive understanding of the sedimentation processes and the resultant deposits, an examination of the depositional geometries as seen on the geophysical data, supplemented by facies retrieved with grab samples and piston cores and video footage from the ROV are needed.



Figure 1. Left) Multibeam bathymetry map of the GBB slope displaying the channelized slope segment north of Bimini (modified from Mulder 2012). Right) Multibeam bathymetry from the same area acquired during MACUM cruise 2012, with positions of the ROV dives and sampling locations. Yellow stippled line is the location of a sub-bottom profile line.

PROJECT DESCRIPTION

Two areas within the large data set collected during the CARAMBAR cruise in 2010 were resurveyed hydro-acoustically during the MACUM cruise in 2012 (Figures 1 and 2). The geophysical data will be examined for the morphologic description of the channelized area north of Bimini, the debris field and the scar surrounding the area GBB-1 that was also surveyed with the AUV in 2005. The geophysical data are complemented with visual observations from video and still cameras collected with a ROV as well as with sediment samples collected with a grab sampler, box corer and piston cores. Visual information and sediment samples will document the facies within the sedimentary geometry and calibrate the backscatter acoustic data for an extensive facies map in these areas.



Figure 2. Left: Sub-bottom profile across a 50 m high scar on the slope, displaying the Holocene sediment that seems to creep downslope. Right: Multibeam bathymetry map displaying the slope from approximately 400- 750m. Large boulders of a partly buried debris field are arranged in a divergent manner. A large scar dissects the slope at ~450m.

EXPECTED RESULTS

The proposed study will document the geomorphology, the dimensions, and the facies within the channelized slope and a debris field associated with massive slope failure. Furthermore the scar along the slope is testament to an incipient slope failure of large lateral extent. The subsurface data should provide information about the roots and the mechanism responsible for this potential failure.

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CURRENT INFLUENCE ON SLOPE AND BASIN SEDIMENTATION

Christian Betzler¹, Thomas Lüdman¹, Gregor P. Eberli, and shipboard participants

¹University of Hamburg, Germany

PROJECT OBJECTIVES

The project objective and the description of the project are taken from the proposal to the German Funding agency that was written by Christian Betzler, Thomas Lüdman and Christian Hübscher.

- To map surface and subsurface variability of platform slope deposits along a platform flank subjected to different current intensities.
- To test the hypothesis that the physical impact of currents is a major controlling factor of tropical carbonate platform evolution and stratigraphy by linking the stratigraphic record of drift in the basin with slope deposits of the platform.
- To develop a model which explains generation of toe of slope mass-flow deposits.

PROJECT RATIONALE

The dynamics and architecture of carbonate platforms and slopes has been related to various factors such as sea-level fluctuations, windward versus leeward position, and the composition of the sediment forming the slope. The influence of ocean currents has not been addressed in many studies, because ocean currents generally do not reach the shallow platform tops. Yet, in their basinal areas most modern or isolated platforms and shelves are exposed to ocean currents. The Straits of Florida, which is the gateway of the Gulf Stream, is an ideal place to study the interaction between the downslope and current controlled sedimentation processes. The flanks of Great Bahama Bank are a particularly ideal natural laboratory, because they are

impacted to a variable degree oceanic bv currents. Strong currents occur in the Strait of Florida, whereas much weaker currents flow in the Santaren Channel (Figure 2). In addition, the entire area is affected bv а comparable wind regime in terms of wind direction and wind speed, and the offbank sediments show little compositional variation.



Figure 1. Bathymetry map of the Straits of Florida, the gateway of the Gulf Stream, displaying the mounded drift deposits. Inset, satellite image of the Gulf Stream whereby the colors give sea surface temperature (red = warm).

PROJECT DESCRIPTION

The main hypothesis in this project is that there is a direct link between current occurrence and slope architecture. To test this model, a detailed analysis of the architectural elements and their controlling parameters will be performed along the flank of the carbonate bank from the Strait of Florida to the Santaren Channel, thus representing a transect from high to low current strength (Figure 2).



Figure 2. Location of the study area at the confluence of the Straits of Florida and the Santaren Channel. Also indicated are the drill sites of ODP Leg 166 that will provide the stratigraphic tie points for the seismic data collected during the cruise. The working area is south of the area covered in Mulder et al. (2012), which is marked in yellow.

The backbone of the cruise from March 28 to April 26, 2013 are seismic and hydroacoustics surveys. To validate the hydroacoustic data, gravity cores and sediment surface samples will be recovered at positions to be defined after a first evaluation of geophysical data. For the interpretation of the geometrical changes in time, a set of seismic lines is collected that crosses the ODP Leg 101 and 166 sites, where a robust lithostratigraphy and chrono-stratigraphy has been developed. A seismic grid will be acquired with a system consisting of 3 GI-Guns and one digital Hydroscience Technologies SeaMUX streamer with 144 channel and 600 m active length. Two 24-channel MicroEel solid streamers with each 100 m active length will be available as backup systems.

EXPECTED RESULTS

A relevant outcome of this work will be the compilation of a sedimentological and stratigraphical model for carbonate platforms subjected to the dual control of sealevel changes and bottom current. Seismostratigraphic linking of the basin floor drifts with the periplatform deposits crossing the ODP Leg 166 drill sites with an established chronostratigraphy and lithostratigraphy along the NW to SE gradient of decreasing current strength will demonstrate the effects of the current control on slope architecture through time.

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SLOPE TO BASIN GEOMORPHOLOGY AND PROCESSES ALONG SOUTHWESTERN GREAT BAHAMA BANK

Andrew Jo, Gregor P. Eberli, Donald F. McNeill, and Mark Grasmueck

PROJECT OBJECTIVES

- Characterize and quantify the morphology of carbonate slope along southwestern Great Bahama Bank.
- Interpret sedimentary processes on the margin and slope by incorporating available 2D seismic data.
- Compare and correlate modern slope processes with subsurface seismic and core data taken in conjunction with Ocean Drilling Program Leg 166.

PROJECT RATIONALE

Carbonate slope and basin floor reservoirs have received limited attention in hydrocarbon exploration. One reason is that the slopes are very heterogeneous in composition, architecture, and lateral continuity because sedimentary processes vary greatly depending on various external and internal controls (Playton, et al., 2010). Multibeam bathymetry and subbottom profile data of modern slopes document the heterogeneity of slope and basin floor geomorphology along dip and strike. Furthermore, analysis of geomorphology the allows interpretation of the processes creating the variability. An over 100 km long data set along the southern Great Bahama Bank is made available by Bahamas Petroleum Company (BPC) to assess the distribution, dimensions and variability of the slope facies between



Figure 1. Location of study area showing BPC multibeam bathymetry data, and the core locations at ODP Leg 166 sites 1008/1009.

Cuba and Great Bahama Bank. Together with borehole and seismic data from ODP Leg 166 sites 1008/1009 this project aims to improve our understanding of slope to basin floor depositional processes close to a plate boundary.

PROJECT DESCRIPTION AND PRELIMINARY RESULTS

Southwestern GBB provides a unique opportunity to study modern carbonate slope and deep water processes in the proximity of the Cuban-Bahamas collision zone. This project will incorporate multibeam bathymetry, backscatter, and sub-bottom profile data acquired by BPC, spec seismic lines in the Santaren Channel and the Strait of Florida, and cores and seismic line from Ocean Drilling Project Leg 166 (Figure 1). Sediment composition will be inferred from backscatter data and correlated with ODP Leg 166 cores 1008 and 1009. We will also investigate the occurrence of pockmarks and document their morphology using seismic data acquired by BPC.

Multibeam bathymetry and backscatter data reveal three depositional environments: platform margin, slope, and basin floor. The steepness of the margin changes from up to 30° in the north to more than 70° in the south. The steep margin is onlapped by a thick mud wedge that has a 30 m deep moat at the upper end and thins basinward.

Regularly spaced gullies incise the middle slope. Large blocks, 20 m high and up to 600 m wide, are scattered along the lower slope in the northern part of the study area. Farther south, sediment lobes and deep water channels funnel coarse-grained sediment to the basin floor. Towards the south, margin failures increase in dimension and frequency. At the southern end of the study area margin both margin failure and slope failure occur, creating multiphase mass transport complexes (Figure 2).

The basin floor in the western part is covered by pockmarks. These surface expressions of fluid escape occur along the northern boundary of the Bahamas-Cuba collision zone.



Figure 2. a) Steepness generated from bathymetric map showing high slope angle ($\sim 76^{\circ} =$ yellow line) in the southernmost area. Slump scars up to 40 m in height are also observed in the lower slope. Debris is dispersed as far as 13 km into the basin. b) View of the multiphase margin and slope failure at the southern end of the study area.

KEY DELIVERABLES

This project will provide a quantitative description of slope and basin floor morphological elements. Based on the surface visualization, we intend to make an interpretation of sedimentary processes and ultimately produce a comprehensive depositional model with all the sedimentary processes from the margin to the basin characterized.

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SUBORBITAL SEA-LEVEL OSCILLATIONS DURING THE LAST INTERGLACIAL HIGHSTAND (MIS 5E): EVIDENCE FROM THE BAHAMAS

Kelly L. Jackson, Gregor P. Eberli, Donald F. McNeill, and Paul M. Harris¹ ¹ Chevron Energy Technology Company, San Ramon, CA

PROJECT OBJECTIVES

- Decipher the amplitude of suborbital sea-level oscillations recorded in core and outcrop in the Exuma Cays and relate findings to Reid (2010) in New Providence.
- Document the stratigraphic heterogeneity produced by oscillations during MIS 5e and assess the significance of this process for heterogeneity within carbonate cycles that are often reservoir flow units.
- Date core and outcrop samples using Amino Acid Racemization (AAR) and Useries to understand the timing of MIS 5e sea-level oscillations on New Providence Platform, Bahamas.

PROJECT RATIONALE

New evidence from New Providence Platform, Bahamas, indicates that sea level oscillated a minimum of 10 m during the last interglacial highstand (MIS 5e), creating early and late substages within the 5e highstand (Figure 1). A 10 m + oscillation exposed Great Bahama Bank, creating two separate depositional cycles within 10,000 years. This highstand oscillation requires a suborbital forcing mechanism of much shorter duration than Milankovitch frequencies and is important because it contradicts the preconceived notion that precession is the controlling factor of high-frequency sequences and the building blocks of carbonate cycles which we assume are reservoir flow units. This new evidence also documents rapid climate changes during warm interglacial periods.



Figure 1. (A) MIS 5e sea level from Thompson and Goldstein (2005). (B) MIS 5e sea interpreted level the facies from successions in the Exumas and New Providence from this study, Halley et al. (1991), Aurell et (1995), and Reid (2010).

SCOPE OF WORK

From 2009-2012 we drilled 14 cores along the Exumas windward margin, dozens of short cores, and mapped the majority of the islands to document vertical and lateral stratigraphy. During 2013, we plan to continue working on dating core and outcrop samples to understand the timing of the MIS 5e sea-level oscillations. Dating is very important for reconstructing the timing of Pleistocene sea-level oscillations but it is not an easy undertaking in these shallow-water carbonates. The approach is to combine the Amino Acid Racemization (AAR) methodology with U-series dating on core and outcrop samples. The goal is to at least be able to separate the two sea-level peaks within MIS 5e.

One final field campaign to New Providence is planned for 2013 to conduct an RTK survey of the downstepping beach ridges on the southern portion of the island to obtain absolute elevations that will in turn be used to construct the amplitude of the MIS 5e sea-level oscillation. Short cores will also be drilled on New Providence to confirm the lateral extent of the calcrete separating subtidal facies dividing early and late MIS 5e substages.

SIGNIFICANCE FOR CYCLOSTRATIGRAPHY AND FLUID FLOW MODELING

The recognition of meter-scale fluctuations of sea level within highstands and the potential that these oscillations produce individual carbonate cycles has far reaching implications for cyclostratigraphy and the driving forces for sea-level changes. Currently, carbonate cycles are mostly related to the frequencies of orbital climate forcing that produce sea-level fluctuations in the 20, 40, and 100 kyr realm. The highstand oscillations with magnitudes of 10+ m would require another, yet unexplained forcing mechanism of much shorter duration. Carbonate cycles of suborbital durations will add an unwelcomed complication in modeling these cyclic successions. The oscillating sea level will also influence the lateral and vertical facies architecture within individual shallow-water carbonate cycles. Understanding the resultant facies juxtapositions and heterogeneities will be paramount for understanding the flow behavior in carbonate strata.

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INFLUENCE OF SEA-LEVEL OSCILLATIONS DURING HIGHSTANDS ON PLEISTOCENE CARBONATE SHOALS (YEAR 2)

Caglar H. Usdun, Gregor P. Eberli, and Donald F. McNeill

PROJECT OBJECTIVES

- Relate the variations in altitude of oolitic grainstone shoals that were deposited during the last interglacial (MIS 5e) to oscillations in sea level during the last highstand.
- Test the hypothesis that oscillations of sea level produce extensive lateral accretion of ooid shoals by examining the evolution of the Miami Oolite.

PROJECT RATIONALE

It is well established that the last interglacial highstand during Marine Isotope Stage 5e (MIS 5e) was 6 – 7 m higher than the modern sea level. Tidally influenced carbonate grainstone shoals potentially record the amplitudes of these oscillations with high precision for two reasons: First, the shoal crests fill most accommodation space and are often exposed at low tide and, thus, even small (meter-scale) drops in sea level would expose the shoals. Second, a drop in sea level will also lower the entire tidal range at which point the shoal has the potentially to shift to a lower elevation accreting to the existing one or form a new shoal at a lower level somewhere on the shelf/platform. This process might explain both the lateral extent and lateral heterogeneity in carbonate shoals.

This study aims to decipher the sea-level stand within MIS5e by examining elevations of shoal crests at various locations in Florida and the Bahamas and by searching for stacked shoal complexes in cores from Florida and the Bahamas. In addition, studying the lateral development of the Miami Oolite will test the hypothesis that the process of lateral accretion is caused by meter-scale oscillations within highstands.



Figure 1. Location map and core position with regards to modern sea level for three cores composed of MIS5e ooid shoals. The facies successions in the three cores are similar but the elevation differences indicate deposition during slightly different sea-level positions during the last highstand.

SCOPE OF WORK

In the first year (completed), the facies successions of the MIS5e shoals have been studied in cores and their elevations, referenced to modern sea level, have been plotted (Figure 1). In order to relate these differing elevations to the oscillations proposed by Thompson and Gradstein (2005) and Thompson et al. (2011) precise dating of the successions is necessary. The approach is to combine the Amino Acid Racemization (AAR) methodology with U-series dating on core and outcrop samples. The goal is to assess if different ages exist in the various shoals.

The second task is the test of the hypothesis that the sea-level oscillations produce large-scale lateral accretion on ooid shoals. This test will be performed in the Miami Oolite. A LIDAR-based high-resolution DEM of the Miami Oolite, made available by P.W. Harlem, displays channels, tidal bars and a pronounced repetition of the frontal crest of the shoal (Figure 2). Cross-sections of facies and elevations will document the sedimentologic evolution, while dating of the crests will place them within the known ages of the oscillations.



Figure 2. LIDAR-based high-resolution DEM of the Miami Oolite. The timing and facies of the two frontal crests of the Miami Oolite will be used to decipher the dynamics of the shoal's growth within the context of sea-level oscillations.

EXPECTED RESULTS

The study of the elevations of the Pleistocene ooid shoals is expected to corroborate the evidence for a sedimentary record of sea-level oscillations within the last highstand. The study of the evolution of the Miami Oolite is intended to document a fundamental process of ooid shoal formation and expansion.

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FACIES AND DIAGENETIC PROGRESSION IN DEEP, WINDWARD MARGIN GRAINSTONES, NEW PROVIDENCE PLATFORM, BAHAMAS

Kelly L. Jackson, Kai Lu, Caglar H. Usdun, Donald F. McNeill, Gregor P. Eberli, and Peter K. Swart

PROJECT OBJECTIVES

- Analyze cores from the Nassau Harbor and Bahama Mar and well cuttings from Bell Island, Exumas to provide insight into the pre- and early- Pleistocene geologic evolution of New Providence Platform.
- Extend the search for suborbital sea-level oscillations in the Pleistocne successions on New Providence Platform.
- Relate bank margin dolomitization with progressive burial and repetitive sealevel flushing events.

PROJECT RATIONALE

Cores from New Providence Island and Bell Island are used to evaluate fundamental stratigraphic and diagenetic processes. The early, near surface diagenesis of skeletal and nonskeletal carbonate deposits is well established on several carbonate platforms around the world. However, relatively few intermediate-depth deposits, where burial history and general diagenetic conditions are constrained, have been extensively evaluated. The cores and cuttings from four boreholes to depths of up to 300 m in the Bahamas, provide the opportunity to lithologically and diagenetically assess the progression of early burial changes to grain-rich windward margin deposits. In addition, these cores retrieve the entire Pleistocene and thus potentially record older Pleistocene suborbital carbonate cycles. For example, three sea-level highstands, separated by small sea-level drops during the penultimate interglacial MIS 7, are documented in speleothems from Italy (Dutton *et al.*, 2009). These drops should be recorded in the cores on Great Bahama Bank.



Figure 1. Left: View of Bell Island, Exumas, looking west with yellow stars indicating locations of two disposal wells. Bell Island is approximately 1.5 by 1.5 km in size. Inset photo shows the drill rig set up by Well Done Drilling, Bahamas. Right: Location of the core in Nassau Harbor and Bell Island.

BELL ISLAND WELL CUTTINGS

Well cuttings from two disposal wells drilled to 600 ft (183 m) were collected on Bell Island, Exumas, in May 2012 (Figure 1). Samples were collected every 5 ft during drilling using a large sieve positioned next to the water discharge. Currently, we are preparing and making thin sections of the cuttings every 10 ft and plan to analyze the thin sections for grain composition to infer the environment of deposition. During 2013, we plan to analyze the cuttings mineralogy using XRD. We plan to date the samples using a combination of amino acid racemization, U-series, and Sr isotope dating techniques. The well cuttings represent the deepest dataset collected to date along the Exumas windward margin and the results from this portion of the project will shed light on the growth and evolution of the margin.

NASSAU HARBOR CORE

CSL recently received a core from the Nassau Harbor that was drilled to ~1000 ft. The core is ideally located as it retrieves the subtidal portion of the eolian strata that is exposed in the Queen's Staircase. Thus, it will provide another anchor point of the elevation of transition from the beach to eolian deposits within MIS5e and will thus help calibrate the amplitude of this highstand oscillation on New Providence Island. The core penetrated several older Pleistocene depositional cycles that will be analyzed for the sedimentologic and stratigraphic evolution at this bank margin and can be compared with the margin evolution at Bell Island.

Hydrologic Associates is in the process of drilling another core at Bahama Mar and once the core becomes available to the CSL it will be integrated into this study.

SIGNIFICANCE

The Bell Island well cuttings are currently the deepest data set obtained for the Exumas windward margin. The results from this dataset, combined with the Nassau Harbor core, will provide a unique insight into the evolution of this grain-dominated windward margin.

When combined with existing deep borehole cuttings from New Providence (Caracuel et al., 1995) we can begin to assemble a database on the diagenetic character of intermediate-depth burial and repeated sea-level driven changes in pore fluids and the resultant geochemical signature.

The Nassau Harbor core potentially carries the sedimentary record of one sea-level oscillation within MIS 5E and would thus provide a good measure of the amplitude.

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DEPOSITIONAL AND DIAGENETIC CONTROLS ON FLUID FLOW PROPERTIES OF PLIO-PLEISTOCENE SHALLOW-WATER CARBONATES OF THE DOMINICAN REPUBLIC

Viviana Díaz, Donald F. McNeill, James S. Klaus, Peter K. Swart, and Gregor P. Eberli

PROJECT OBJECTIVES

- Expand packer injection tests along a 5 borehole transect to assess how hydraulic conductivity relates to depositional facies and diagenetic overprint in shallow reefal deposits.
- Provide a facies/diagenesis/acoustic-based correlation of permeability (hydraulic conductivity) data after several stages of post depositional stabilization that can be incorporated as part of the upscaling into reservoir flow simulation models.

PROJECT RATIONALE

Depositional and diagenetic heterogeneities can influence fluid flow and transport parameters. In and carbonates, the porosity permeability structure is dependent on both matrix porosity and the larger development of scale secondary porosity. The resulting complex porosity distribution is best represented by the hydraulicconductivity. If one views



Figure 1. Southern Dominican Republic prograding terraces with core locations.

dissolution zones as discrete heterogeneities, the challenge of predicting transport in carbonate rocks is one of characterizing the hydraulic-conductivity distribution at a scale that captures the variability of these heterogeneities.

Vertical profiles of hydraulic conductivity will be determined from short-interval packer tests performed in a transect of 5 wells drilled perpendicular to the prograding packages of reefal carbonates found in the southern Dominican Republic. These wells vary in both age and diagenetic history (Figure 1). Hydrogeologic data will be integrated with stratigraphic, depositional, diagenetic, and petrophyscial data in order to characterize the hydraulic properties of Plio-Pleistocene reefal limestones of the Dominican Republic.

PROJECT DESCRIPTION

Vertical and lateral variability in hydraulic conductivity will be determined from constant-head injection tests performed in 5 wells varying in depth from 25 m to 70 m using a straddle-packer assemblage with an open interval of 0.7 m (Figure 2). These packer tests provide hydraulic conductivity data on both matrix and dissolution zones. Test intervals will be performed at a resolution of 1m. Hvorslev (1951) developed an equation for analyzing steady-state, constant-head injection tests. Although designed for saturated zones, the method has applications in unsaturated

zones. If L is greater than 5r, as is the case in all testing proposed here, the equation simplifies to:

K = hydraulic conductivity r = the radius of the well L = length of the test interval H = injection head Q = injection rate

Preliminary injection tests obtained from 22 m of core 3 show hydraulic conductivity changes through two shallowing upward sequences (Figure 3). The hydraulic conductivity trend shows a relationship with 1) depositional facies and 2) diagenetic overprint related to secondary dissolution and cementation in the meteoric environment. Phreatic diagenetic overprint in the lower sequence results in the lowest K values (0.007-0.13 cm/s) where original primary porosity is occluded by characteristic fringing cements. In the upper sequence a general trend





Figure 2. Constant-head injection test setup.

of decreasing hydraulic conductivity results from increased cementation in the highenergy reef crest facies where values range from 0.011-0.024 cm/s. Despite poor resolution of plug data, permeability follows a similar trend to K. The similarity between permeability obtained from plugs and hydraulic conductivity suggest that although small scale data might not accurately represent carbonate heterogeneities, in this case it is reasonable to upscale from plugs to borehole data that can be applied to fluid flow reservoir models.



Figure 3. Plot showing hydraulic conductivity with depth in core 3. Measurements span two highstand reef sequences separated by a subaerial exposure surface. Stable isotope data and permeability data from petrophysical cores is included for comparison.

KEY DELIVERABLES

The proposed project will generate an extensive dataset of hydrologic conductivity measurements taken within the Pliocene and Pleistocene reefal deposits of the southern Dominican Republic. This dataset will be integrated with previous depositional and diagenetic studies and used to both statistically evaluate controlling factors in early porosity evolution and constrain transport and flow parameters in reservoir models. The integrated dataset will be made available to all industrial associates of the CSL.

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QUANTITATIVE CHARACTERIZATION OF MIXED SYSTEM CLINOTHEMS: GURABO FORMATION, DOMINICAN REPUBLIC

Donald F. McNeill, James S. Klaus, Peter K. Swart, and Gregor P. Eberli

PROJECT OBJECTIVES

- Divide the mixed system of the Gurabo Formation into high-frequency sequences and their systems tracts.
- Provide quantitative characterization of each mixed system sequence: lithology (siliciclastic & carbonate), mineralogy, and diagenesis across major facies of the clinothem and associated system tracts.

PROJECT RATIONALE

We have completed a regional stratigraphic study of the three mixed-lithology sequences in the Miocene-Pliocene of the Cibao Basin, northern Dominican Republic (McNeill et al., 2012). The next logical step is the detailed sequence-by-sequence documentation of the intra-sequence trends and changes in lithofacies, carbonate-siliciclastic ratios, mineralogy, and how early diagenesis impacts the specific parts (systems tracts) of the sequence. To this end, we propose to focus on the mixed sequence that comprises the Gurabo Formation (late Miocene to early Pliocene) (Figure 1).



Figure 1. Generalized configuration of the Gurabo Formation sequence with proposed sections to be measured and sampled. Two new sections (unnamed) will be added to existing (named sections).

PROJECT DESCRIPTION

The sequence stratigraphic analysis will rely on unconformities and facies shifts observed in the field. A special focus will be the detailed characterization of textures and properties within the topset, foreset (Figure 2), and bottomset of the mixed lithology clinothems. Vertical sections have been selected (Figure 1) based on the preliminary stratigraphic framework to sample the full suite of systems tracts and facies. We will document vertical trends in: lithofacies, percent carbonate (as an indicator of potential diagenesis), bulk stable isotopic composition, carbonate allochem type, carbonate and clay mineralogy, and selected petrophysical properties (porosity, permeability, sonic velocity). We will assess the influence of early diagenesis with respect to cementation and neomorphism of the carbonate dominated lithologies. The measured sections will be integrated with the faunal indicators (benthic foraminifera, molluscs, corals) to isolate water depth trends and overall relationships to sedimentologic and diagenetic trends.



Figure 2. Reefal foreset of Gurabo Formation between Gully and Bridge sections. In situ branching corals build a reef thicket on the upper foreset slope.

Depending on the completeness of the dataset, we will assemble a synthetic seismic model to evaluate the seismic response of the lithologies in these mixed sequences.

KEY DELIVERABLES

The extensive sample and analytical dataset will be synthesized to develop vertical and lateral trends in the composition of the mixed system sequences. These results will be related to, and used to refine, the geometries and attributes of the sequence stratigraphic model. The raw data and integrated dataset will be made available to all industrial associates of the CSL.

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USING CLUMPED ISOTOPES TO UNDERSTAND EARLY DIAGENESIS

Peter K. Swart, Monica M. Arienzo, Sean T. Murray, and Deniz Atasoy

PROJECT OBJECTIVES

- Define the behavior of the temperature and δ¹⁸O of the fluids determined using the clumped isotope method in well-defined diagenetic sequences.
- These diagenetic sequences will include sub-aerial exposure surfaces, vadose zone, freshwater phreatic zones, mixing-zones, marine diagenesis, and nondepositional surfaces.

PROJECT RATIONALE

Several seminal papers have established patterns in the behavior of geochemical tracers during early diagenesis (Allan and Matthews, 1982; Lohmann, 1987; Matthews, 1968; Melim et al., 1995; Steinen and Matthews, 1973). These include the identification of enrichments in the δ^{18} O at sub-aerial exposure surfaces, the inverted-J isotopic signal, the relatively constant δ^{18} O values within vadose and freshwater phreatic zones, a gradual enrichment within the mixing zone, and heavy δ^{18} O values within the marine phreatic zone. All of these signatures are predicated on the basis of a constant temperature with the δ^{18} O reflecting a change in the source or evaporation history of the water. The use of the clumped isotopic measurements allows an assessment of the temperature and therefore using the conventional δ^{18} O measurement the true δ^{18} O of the water can be measured. This knowledge can lead to substantially improved interpretation of the paragenetic sequence.

SCOPE OF WORK

In order to assess the potential for clumped isotopes to reveal information on the δ^{18} O of the fluids and temperatures during the early diagenesis of carbonates we will choose materials from modern, Holocene, and Pleistocene carbonates. In each of these cases we will measure the Δ 47 to determine the temperature and then use this temperature in conjunction with known temperature- δ^{18} O calibrations to calculate the δ^{18} O of the precipitating fluid. The samples will include the following:

<u>Modern Samples</u>: We will investigate the clumped signatures in a variety of carbonates collected from modern environments including sediments such as those collected from Great Bahama Bank (Reijmer et al., 2009), modern corals, and other biogenic carbonates. The temperature and the δ^{18} O of the waters from these environments will ideally be well known so that a comparison can be made between the δ^{18} O of the water determined from the clumped method with those actually experienced by the carbonates.

<u>Samples Affected by Early Diagenesis</u>: Five distinct isotopic zones were identified in carbonate rocks by Allan and Matthews (1982). These include a characteristic δ^{13} C depletion and δ^{18} O enrichment associated with exposure surfaces, highly variable δ^{13} C and relatively constant (but depleted) δ^{18} O in the vadose zone, more constant δ^{13} C values in the phreatic zone, co-varying δ^{13} C and δ^{18} O values within the mixing

zone, and enriched δ^{13} C and δ^{18} O values in the marine phreatic zone. Another pattern which will be tested will be the inverted J signal, a commonly seen signal in early diagenetic carbonates (Lohmann, 1987). It is believed to result from the alteration of marine sediments by a large pool of meteoric water which imparts its δ^{18} O upon the carbonate leading to the formation of a meteoric carbonate line (MCL). The interpretation of these trends can be tested by combining conventional δ^{13} C and δ^{18} O and $\Delta 47$ measurements. The materials used for determining these trends are taken from cores drilled during the Bahamas Drilling Project and the Dominican Republic Drilling Project, as well as the 100s of cores collected by Bob Ginsburg and his students.

KEY DELIVERABLES

The advent of the clumped isotope method is one of the most exciting methods to be applied to stable isotope geochemistry of carbonates in over 50 years. It makes possible, with a single measurement, the determination of temperature of recrystallization of carbonates as well as the δ^{18} O of the fluid involved. While the calibration in a variety of biogenic proxies appears to be fairly robust, there may be problems with diagenetic carbonates. It is therefore important to calibrate the behavior of the Δ 47 signal in well understood diagenetic environments. The work proposed here will provide valuable base line data in the quest to use the technique in the study of diagenetic carbonates.

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NEW INSIGHTS INTO DOLOMITIZATION USING CLUMPED ISOTOPES

Sean T. Murray, Monica M. Arienzo, and Peter K. Swart

PROJECT OBJECTIVES

- To better constrain the formation kinetics of dolomites by measuring multiply substituted isotopologues to constrain the temperature and isotopic value of the fluid that formed it.
- To analyze and better constrain the formation of the well-studied stochastic dolomites from San Salvador Island, Bahamas. Then use this simple system to predict the most appropriate application of the multiple equations for the δ^{18} O of the fluid for dolomites to the clumped isotope method.
- Apply what is learned from the basic system in San Salvador to more complex and less well understood systems of dolomite formation in the Madison Formation dolomites from Sheep Mountain, Wyoming.

PROJECT RATIONALE

The ever present "Dolomite Problem" has made the understanding of the formation of this mineral difficult in the past. With the advent of the clumped isotope technique, it has become possible to approach questions regarding the formation of dolomite from a new angle, one that is not confounded by unknowns such the δ^{18} O of the fluid. However, despite the promise of an independent thermometer provided by the clumped isotope method, old problems regarding which of the many equations link the δ^{18} O of fluids, temperature, and the δ^{18} O of the dolomite still remain. This study will utilize young dolomites from San Salvador Island in the Bahamas that have formed in a well constrained environment in order to answer this question.

SCOPE OF WORK

In this study we will utilize samples from two localities, a texturally young dolomite whose diagenetic history is reasonably well constrained and a dolomite of Carboniferous age with a more complicated history. The younger rocks are derived from a 168 m deep core drilled on the island of San Salvador in the Bahamas. This core has been extensively studied (Supko, 1977; Dawans and Swart, 1988) and displays an extensive dolomite section replacing middle Miocene to late Pliocene sediments. These dolomites are texturally mature, but formed as recently as 150,000 yr BP (Swart et al., 1987). Extensive isotopic and petrographic studies indicate that these dolomites formed from seawater with near normal composition (Dawans and Swart, 1988).

The older dolomite is derived from the Mississippian Madison Formation in Wyoming. The rocks are fine-crystalline and dolomitized to varying degrees, and are believed to have formed during transgressions (Smith et al., 2004). The source of the dolomite is believed to be the seepage reflux of brines derived from widespread evaporitic lagoons (Moore, 2001). This interpretation is supported by the presence of solution collapse breccias throughout the section (Sonnenfeld, 1996; Katz, 2008).



Figure 1. Left) Dolomite of the Mississippian Madison Formation (field of view 2 mm). Right) Dolomite from the Pliocene from a core in San Salvador (field of view 1 mm).

Samples will be taken from both localities and the $\Delta 47$ measured together with the conventional δ^{18} O and δ^{13} C values. The young dolomites from the Bahamas will be analyzed to place constraints on the most appropriate equation to use relating temperature and dolomite δ^{18} O. These results will not only be used to help refine the model of dolomitization in the Bahamas, but also to help understand the model of dolomitization in the Madison Formation.

KEY DELIVERABLES

The application of multiply substituted isotopologues to the complexities of the dolomite system is expected to be achieved. The well-constrained and ideally stochastic dolomites of San Salvador Island, Bahamas will allow for a better understanding of the effects of the dolomitization process on the measurement of clumped isotope values. After these effects are identified and quantified, they can be applied to more complex dolomite systems.

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SPELEOTHEMS AS A MODEL SYSTEM FOR THE STUDY OF CLUMPED ISOTOPES AND FLUID INCLUSIONS

Monica M. Arienzo, Peter K. Swart, Hubert B. Vonhof¹, and Sean T. Murray ¹Vrije Universiteit Amsterdam, Amsterdam, The Netherlands

PROJECT OBJECTIVES

- To use clumped isotopes and fluid inclusions from speleothems collected from the Bahamas in order to better understand the competing influences of temperature and water isotopic composition in controlling the oxygen isotopic composition of carbonates.
- To use *in situ* monitoring of cave calcite precipitation to aid in the understanding of the relationship between geochemistry and the cave environment.
- To apply these various methods in order to develop a clear understanding of the fluids which form these carbonates and to transfer the lessons learned from these studies to a wide range of diagenetic carbonates.

PROJECT RATIONALE

Traditionally carbon and oxygen isotope analyses have been used to unravel the depositional and diagenetic history of carbonates. However, the $\delta^{18}O$ of a carbonate is dependent both on the variations in temperature and the $\delta^{18}O$ of the water. In order to solve for the second unknown, an additional proxy is needed. Such proxies might include the ratio of certain trace elements relative to calcium, fluid inclusions, and/or clumped isotopes.

The motivation for this study is to utilize speleothems from the Bahamas as a case study for the application of clumped isotopes and stable isotopic analysis of fluid inclusions. Additionally, by monitoring a modern cave a better understanding of the relationship between the cave environment, clumped and fluid inclusion isotopes can be gained and potentially aid in the calibration of these proxies. By applying these various methodologies we hope to better understand the factors which control the oxygen isotopes of the speleothem calcite.

SCOPE OF WORK

We have previously collaborated with Vrije Universiteit, Amsterdam in order to measure the δ^{18} O and δ D of water extracted from fluid inclusions (Vonhof et al., 2006). The results from these studies have allowed us to calculate the temperature of precipitation and help constrain the environment of diagenesis. In addition, clumped isotope (Δ 47) analysis has been conducted on the same samples. The linear relationship between temperature and Δ 47 has been demonstrated by Ghosh et al. (2006) and Dennis and Schrag (2010). However, in a study conducted on speleothems from Israel, although the Δ 47 derived temperatures were similar to those in the literature there was an observed offset in the modern temperature values (Affek et al., 2008). This suggests a need for a separate calibration line for speleothems. The observed offset is thought to be due to the mechanism of calcite precipitation in a speleothem (Affek et al., 2008; Klug et al., 2012). Our results support a change in temperature associated with a change in carbonate δ^{18} O.

absolute temperature value is offset. Further work therefore needs to be conducted to calibrate the clumped isotope to temperature for speleothems and we will be comparing results across multiple speleothems to better understand any species effect.

We have recently acquired a Picarro Cavity Ring-Down Spectrometer for measurement of oxygen and hydrogen isotopes of water. A fluid inclusion extraction device to work in conjunction with the Picarro has been developed, and preliminary results are promising. Initial results demonstrate an average standard deviation of 0.4 ‰ for δ^{18} O and 1.7 ‰ for δ D on a 0.5 µL sized sample. This will enable in house measurements of isotopic ratios of fluid inclusions from a variety of samples. Additionally this will allow for a direct comparison between clumped isotopes and the isotopic ratios of fluid inclusions, further strengthening our interpretations and our understanding of clumped isotopes in speleothems.

In the summer of 2012, cave monitoring began in Eleuthera, Bahamas. The cave is monitored for temperature and relative humidity every 2 hours. Additionally, we are conducting *in situ* monitoring of calcite precipitation. Calcite is "farmed" by placing glass slides on top of actively forming stalagmites within the cave with the slides being collected every 3 to 4 months. This allows for the direct comparison between the cave environment and the chemistry of the calcite. The carbonate is then removed from the glass slide and analyzed for stable C and O isotopes, clumped isotopes and, where possible, fluid inclusions. Through continual monitoring, this work has the potential to aid in the development of a calibration equation to temperature for speleothems.

SIGNIFICANCE

By combining the calcite carbon and oxygen isotopes, clumped and fluid inclusion isotope methods may better aid in our understanding of diagenesis and of the originating fluids for carbonate precipitation. Furthermore, future cave calcite farming may provide valuable insight in to the processes driving geochemical records. The methods utilized in this study are additionally applicable to a range of geochemical studies.

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GEOCHEMICAL EVIDENCE OF A MISSISSIPPIAN ANOXIC EVENT FROM CARBON AND SULFUR ISOTOPES?

Amanda M. Oehlert, Peter K. Swart, Gregor P. Eberli, Samantha Evans¹, and Dave Katz²

¹Boise State University, Boise, ID ²Chevron Energy Technology Company, San Ramon, CA

PROJECT OBJECTIVES

- Characterize the relationship between the isotopic composition of carbonate associated sulfate ($\delta^{34}S_{CAS}$), inorganic, and organic $\delta^{13}C$ records preserved in the Madison Limestone.
- Evaluate the influence of sea-level changes on the relationship between $\delta^{34}S_{CAS}$, inorganic, and organic $\delta^{13}C$ records.

PROJECT RATIONALE

Previous work on Lower Mississippian outcrops have shown a globally correlative positive carbon isotope excursion in Western North America (Katz et al., 2007), the Northern Urals, and the Dinant Basin in Belgium (Saltzman et al., 2004). This positive excursion has been interpreted to be the result of a major global organic carbon burial event which resulted in a period of global anoxia during the Lower Mississippian (Katz et al., 2007; Saltzman et al., 2004). There are two geochemical analyses that can be used to assess the possibility that the positive inorganic $\delta^{13}C$ excursion represents a period of major organic carbon burial: (1) a positive covariation between inorganic and organic $\delta^{13}C$ records, and (2) a positive covariation between inorganic $\delta^{13}C$ and $\delta^{34}S_{CAS}$ records.

Previous work on Wind River Canyon and Sheep Mountain outcrops suggests that inorganic δ^{13} C values are buffered during diagenesis. Conversely, the $\delta^{34}S_{CAS}$ records show opposite trends at the two sections, suggesting that the CAS can be significantly influenced by recrystallization. This year, the transect will be expanded to include a more proximal location, Freemont Canyon, and a more distal ramp setting, Benbow Mine Road, in order to evaluate whether the positive excursion in inorganic δ^{13} C records is the result of a period of anoxia, or a product of diagenesis. If the results of this project show that the excursion resulted from a period of global anoxia, a Lower Mississippian source rock was likely formed as a result of these oceanic conditions.

SCOPE OF WORK

This year, new records of organic δ^{13} C and $\delta^{34}S_{CAS}$ will be produced from samples collected at the Freemont Canyon and Benbow Mine Road outcrops. In addition, mineralogical and elemental assessments will be conducted via X-ray diffraction (XRD) and Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). These new records will be integrated with previously analyzed samples from the Sheep Mountain and Wind River Canyon outcrops.

Correlation analyses will be used to characterize the relationship between the isotopic compositions of carbonate associated sulfate ($\delta^{34}S_{CAS}$), inorganic and organic $\delta^{13}C$ records preserved in the four outcrops of the Madison Limestone. The influence



of sea-level fluctuations will be assessed by conducting correlation analyses on highstand and low-stand samples separately.

Figure 1. Cross-section of the Madison Limestone (from Katz et al., 2007). During this year analyses on Freemont Canyon (proximal) and Benbow Mine Road (distal ramp) will be conducted.

EXPECTED RESULTS

This study will ascertain whether or not the Madison Limestone was deposited during a period of global oceanic anoxia, which may have resulted in the deposition of an organic-rich source rock in Lower Mississippian strata. In addition, organic $\delta^{13}C$ and $\delta^{34}S_{CAS}$ records will be produced for two new locations, extending the transect from roughly 70 km to nearly 410 km. The results of this study will also permit an evaluation of how ancient records of inorganic and organic $\delta^{13}C$ values are influenced by margin type, sea-level fluctuations, and distance from the margin.

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THE POTENTIAL ROLE OF MICROBES IN THE GENESIS OF OOIDS AND CARBONATE PRECIPITATION

Mara R. Diaz, Alan M. Piggot, Peter K. Swart, and James S. Klaus

PROJECT OBJECTIVES

This project investigates the potential role of microbial communities in calcium carbonate precipitation. Towards this end we seek to:

- Determine the isotopic composition of carbonate and intracrystalline organic matter on oolitic grains to gain a better understanding of metabolic pathways and/or chemical processes associated with carbonate precipitation.
- Quantify the amount of biofilm coating carbonate grain surfaces and assess the stability/adherence of sediment biofilms through agitation experiments.
- Perform in vitro precipitation experiments to assess the roles of microbial metabolism and biofilm/EPS in carbonate precipitation.

PROJECT RATIONALE

Oolitic grainstones are one of the predominant sediment types in carbonate platforms of tropical regions. They are characterized by high permeability/porosity, which enable advective exchange of particles and dissolved materials. In the Bahamas, there are hundreds of square kilometers of ooid sands, which form extensive shoal complexes. These ooid sands are important contributors to the global carbonate accumulation, which have been estimated at 3.2GT per year (Milliman, 1993; Milliman and Droxler, 1995). In spite of their abundance and the importance of oolitic grainstones as potential carbonate reservoirs, the genesis of ooids remains controversial. Not disputed is the fact that ooids form in high-energy environments by concentric layers of tangentially or radially arranged aragonite needles around a nucleus. The cause for the precipitation of the aragonite needles, however, is still debated.

Various theories support abiotic processes (Duguid et al., 2010), while others have attributed ooid genesis to biogenic factors (Gerdes et al., 1994). The abiotic theory suggests that carbonate precipitates around a nucleus (e.g. peloid, guartz grain, skeletal particle) within an aquatic solution that is supersaturated with respect to CaCO₃, whereas those supporting a biological origin propose that microbial metabolic processes can control the geochemical environment by altering the alkalinity and pH (Kahle, 2007; Plee et al., 2008). The formation of these alkaline microenvironments can induce carbonate precipitation. Extracellular polymeric substances (EPS) have also been associated with carbonate precipitation (Dupraz and Visscher et al., 2005; Dupraz et al., 2009) and as such three different types of EPS alteration have been proposed to lead to $CaCO_3$ precipitation: 1) microbially mediated decomposition of EPS, liberating HCO_3^- and Ca^{2+} ; 2) organo-mineralization in which the EPS matrix is altered by chemical or biological activity, creating a template for $CaCO_3$ binding and precipitation; and 3) precipitation regulated by the balance of the external cation concentration and binding capacity of EPS (Dupraz and Visscher et al., 2005). Despite the presumed importance of the aforementioned microbial processes, there is scant information about microbial community composition and associated metabolism. This knowledge gap in carbonates is nowhere more evident than in the formation of ooids.

Our previous studies focused on the microbial characterization of oolitic sediments based on 16S rRNA gene sequencing, TRFLP community profiling, and functional gene analysis. These studies showed that sediments from active, non-active and mat-stabilized depositional environments harbor complex microbial communities, some of which play roles in mineralization processes. Functional gene analysis, also established differences in the community structure among sites and suggest that carbonate precipitation in oolitic sediments appears to be regulated by photosynthesizers, sulfate reducers, denitrifiers and ammonifiers (Figure 1). Confocal image analysis (CLSM) as determined by the cyanine dye conjugated lectin and EPS measurements by the sulfuric acid method also, confirm the ubiquitous presence of biofilm communities and their potential involvement in carbonate precipitation (Figure 2).

Ongoing studies will concentrate in three areas: 1) isotopic analysis of the carbonate as well as intercrystalline organic matter; 2) biofilm/EPS dynamics on oolitic grains; and 3) controlled in vitro precipitation studies.



Figure 1. Distribution of biogeochemical cycles as determined by Geochip 4, functional gene analysis. Error bars represent the standard deviation of three replicates.



Figure 2. CLSM images of ooids and measurements of EPS from active, non-active and mat-stabilized environments of Joulter Cay, Bahamas. Ooids were stained with a cyanine dye-conjugated with lectin wheat germ agglutinin (WGA). Blue zones represent aragonite ooid and pink areas extracellular polymeric substances (EPS). Inset bars are EPS measurements based on phenol-sulfuric acid method. Error bars represent the standard deviation of three subsets of samples per environmental site.

Isotopic indicators will be used to assess metabolic processes associated with ooid grains. The use of stable isotopes will provide insights on the predominant chemical processes and/or metabolic pathways of ooid communities, especially those associated with carbonate precipitation e.g. sulfate reduction, denitrification, ammonification, and autotrophic CO₂ fixation. Isotopic measurements will be made from both the carbonate and organic material. Carbonate associated sulfate (CAS) will be measured by the currently accepted methods of Gill et al. (2011). In addition to the carbonate, we will also isolate the intra-crystalline organic matter associated with ooid grains and will follow the protocol established by Ingall et al. (2003). This protocol involves bleaching for carbonate dissolution of oolitic grains followed by analyses on the isotopic composition of organic carbon, nitrogen and sulfur systems e.g. δ^{13} C, δ^{15} N, and δ^{34} S.

CHARACTERIZATION OF SEDIMENT BIOFILM/EPS

We will conduct quantitative analysis of EPS coatings on sediment samples from various hydrodynamic settings. EPS analysis will follow the sulfuric acid assay. Environmental scanning electron microscopy (ESEM) will also be used to obtain high-resolution images of natural sediment biofilms. Together, these analyses will allow quantification and visualization of the spatial distribution of EPS and microbes on sediment grains and the relationship of these two components in sediment biofilms.

In addition, we will test the adherence/stability of EPS within various hydrodynamic conditions. Toward this end, we will perform an agitation assay that emulates various hydrologic conditions found within oolitic shoals. Treatments 1 and treatment 2 will simulate low and high groundwater flow within the pore space. Published reports for groundwater flow range from $0.025 - 4.3 \text{ Lm}^{-2} \text{ min}^{-1}$ (Shellenbarger et al., 2006). Core sediments exposed to treatment 3 will be emptied into a large glass baking dish along with 2 liters of filtered seawater and placed on a laboratory rocker/shaker table set at 10 rpms for a duration equal to the pumping times of treatments 1 and 2. Treatment 4 sediments will be placed into a sterile 4 L polyethylene bottle and vigorously shaken on a reciprocating shaker for the same duration. In treatment 5 we will remove associated microbes from the sediment grains by subjecting them to pulsed ultrasonic treatment (150 s incubation time, 30% of this time pulsed, Bandelin M72 probe, 3mm diameter, 20 kHz, 70W, vials on ice) following an optimized protocol for sandy sediments (Ferguson et al., 2005, Rusch et al., 2006). After the sand grains have settled and the supernatant removed, the remaining sediment will be washed six times with filtered seawater and all supernatants combined. Ultrasonic treatments followed by six washings each will be carried out until no additional microbes can be removed from the sediment. For each treatment the removed EPS will be quantified using the sulfuric acid assay.

PRECIPITATION EXPERIMENTS

To test the effect of microbes and EPS on calcification, a series of precipitation experiments will be performed in flow-through chambers, representing three sediment treatments. Treatment 1 will represent the control group and will consist of ooids devoid of microbes and EPS. In treatment 2, all active microbes will be killed (UV and antibiotic treatment) but the sediment-associated biofilm will remain in place. Treatment 3, will consist of active ooids with biofilms supplemented with seawater growth media. Precipitation in the three treatments will be compared using the buoyant weight method and will be visually inspected under SEM.

KEY DELIVERABLES OR EXPECTED RESULTS

- Documentation of biochemical signals in oolitic sands established by isotopic determinations.
- A quantitative assessment of the stability/adherence of biofilm/EPS to sediment surfaces under varying hydrodynamic regimes.
- Assessment of the role of active microbes and associated EPS coatings in controlled ooid precipitation studies.

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MICROBIAL AND GEOCHEMICAL CHARACTERIZATION OF CARBONATE MUD ISLANDS FROM FLORIDA BAY

Alan M. Piggot, James S. Klaus, and Peter K. Swart

PROJECT OBJECTIVES

This project investigates the microbial influence on pore water geochemistry and early diagenesis of carbonate mud banks and islands. The project objectives include:

- Determining how variations in microbial metabolic processes influence pore water chemistry and diagenetic products in Florida Bay mud island cores.
- Assessing the vertical and lateral heterogeneity in mud mound diagenesis by comparing characteristics of mud banks and mud islands.

PROJECT RATIONALE

Florida Bay has been used as a modern depositional analog to interpret carbonate buildups in low energy environments for production refined strategies. For example, in the middle and upper Wabamun Group on the Peace River Arch, Alberta, Canada, the discovery rate of reservoir grade porosity was shown to improve from 25 to 80% when a depositional-diagenetic model similar to Florida Bay was applied (Saller and Yaremko, 1994). In this settina earlv replacive



Figure 1. Map of Florida Bay showing the sample locations of cores collected from mud islands. Low Key (B), Jimmy Key (C) and Crane Key (D).

dolomitization by marine or slightly hypersaline water is thought to have occurred shortly after deposition preferentially targeting mudstones and peloidal wackestones and packstones on topographical highs or mound-like structures (Saller and Yaremko, 1994).

The Holocene mud islands in Florida Bay provide an ideal opportunity to investigate how microbial processes bring about diagenetic changes in the composition of modern sediments and interstitial pore waters. The low permeability of Florida Bay's fine-grained carbonate mud creates a subsurface environment where changes in carbonate solution chemistry can accumulate in pore waters and be related to different microbial activities. Utilizing this effect, depositional environments can be characterized by the impact of microbial communities on diagenetic processes and improve interpretation of similar ancient environments. The sediment characteristics in Florida Bay are laterally heterogeneous across mud mounds. Mud banks flanking the islands are typically more organic rich and dominated by mollusk wackestone, packestone and windward grainstone packages. The mud islands have significantly less organic matter and are dominated by mudstones and wackestones. This difference in organic matter is used to assess the effect of organic matter on microbial diagenesis. The degradation of organic matter by microbes can affect the pH and alkalinity of pore waters and carbonate saturation (Castenier et al., 1999).

PROJECT DESCRIPTION

Sediment cores were collected from the Florida Bay mud islands of Low Key, Jimmy Key, and Crane key for geochemical and microbial characterization of the carbonate mud. Geochemical and microbial analyses will be conducted every 10 cm from each island core. Pore waters will be extracted using a hydraulic press to squeeze sediment intervals and filter the evacuated water samples. Geochemical analyses will include alkalinity and chloride titrations and trace elements such as calcium, magnesium and strontium measured by standard ICP-OES methods. Carbonate mineralogy will be determined using x-ray diffraction to quantitatively track changes in aragonite, calcite, and dolomite down core. EPS and organic content of sediment intervals will be quantified and normalized per gram of dry sediment.

The microbial diversity and associated metabolisms of core sediments will be analyzed by Terminal Restriction Fragment Length Polymorphism (T-RFLP). T-RFLP is a molecular technique used for profiling microbial communities based on the location of restriction sites within the 16S rRNA gene. Genomic DNA will extracted and the 16S rRNA gene amplified using polymerase chain reaction (PCR) with universal bacterial primers. T-RFLP analysis of 16S rRNA gene will be used track changes in the bacterial communities with sediment depth along the cores and between mud bank locations. Clone libraries will be made and the 16S rRNA gene sequenced to identify dominant populations within the mud cores.

KEY DELIVERABLES

- Molecular characterization of mud island sediment microbial community variation based on 16S rRNA gene sequencing and TRFLP community profiling.
- Preliminary assessment of the variation in mud island sediment bacterial metabolisms and the relationship to sediment characteristics and interstitial pore water chemistry (Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, Sr²⁺).
- Assessment of the spatial variability of microbial communities associated with different islands to determine if specific community profiles are linked to characteristic geochemical gradients and diagenesis of carbonate sediments.

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FRESHWATER MICROBIAL CARBONATES OF SOUTH FLORIDA: BIOLOGICAL, GEOCHEMICAL, AND TEXTURAL CHARACTERIZATION

Chelsea Pederson, James S. Klaus, Donald F. McNeill, Peter K. Swart, and Alan M. Piggot

PROJECT OBJECTIVES

- To characterize the microbial communities in cyanobacterial mats and marl deposits from freshwater environments of the Florida Everglades.
- To provide a geochemical analysis of pore water/organics from cores to characterize the surficial, early diagenetic changes to microbial carbonate.
- To document the diagenetic and textural changes through various stages and conditions of early burial (marine, brackish, fresh) and pore water chemical changes during the Holocene transgression.
- To use the textures of modern and neomodern microbial carbonates to calibrate similar features found in Pleistocene and Pliocene microbial deposits (second phase of project).

PROJECT RATIONALE

Microbial processes are increasingly recognized for their importance in both carbonate precipitation and dissolution. However, the specific microbial processes that influence local environmental conditions of a carbonate system are often poorly understood.

The Florida Everglades has been used as an analogue for paludal, fine-grained carbonate production (marl). However, the nature of the microbial communities and the effect of early diagenetic alteration on the resultant calcitic mud are relatively unknown. Detailed characterization of modern marl formation in the Everglades will provide a means for direct calibration of key identifying microbial features. Furthermore, buried Holocene freshwater carbonate, exposed to changing conditions (freshwater, brackish, marine) during the transgression, can be analyzed to gauge



the impacts of changes in pore water chemistry. These early diagenetic environments can be assessed for changes to carbonate texture, organic matter composition, and survival of key microbial indicators. Future studies will include a characterization of ancient (Pleistocene & Pliocene) deposits, delving into the preservation potential of microbial textures, organic matter, and carbonate diagenesis.

Figure 1. Projected core locations (arrows) in Everglades and Florida Bay

PROJECT SETTING AND SCOPE OF WORK

This project will characterize the microbial communities within carbonate deposits of the Florida Everglades. We aim to analyze the microbial communities and their effect on carbonate diagenesis across conditions of varying burial during the Holocene transgression. Moving from the inland freshwater prairies to the marine environment of Florida Bay, we will discern the microbial community structure and processes occurring within microbial carbonate deposits. Push cores and vibrocores will be collected from four different burial environments (Figures 1 & 2). The *inland freshwater* environment represents the region of active microbial carbonate formation. The *brackish* environment currently overlies transgressed microbial deposits and is marked by organic-rich sediments and seasonal changes in salinity. At Florida Bay, Holocene freshwater marls have been cored beneath the *coastal levee* sediment and in the *marine subtidal* basins. This freshwater to marine progression will provide a window into the various stages of diagenesis for freshwater microbial carbonates.

Microbial communities will be documented across the laterally heterogeneous carbonate facies. Genomic DNA will be extracted and the 16S rRNA gene will be amplified using polymerase chain reaction (PCR) with universal bacterial primers. Terminal restriction fragment length polymorphism (T-RFLP) analysis and genetic sequencing of 16S rRNA gene will be used to track changes in the bacterial communities with sediment depth along the cores. This will give insight to the various microbial processes occurring during the different stages.



Pore water chemistry will be used to determine microbial processes following deposition of the freshwater marls. Geochemical analyses of pore waters will include alkalinity and chloride titrations, and trace elements (Ca, Mg, Sr, S) using standard ICP-OES methods. Carbonate mineralogy will be determined using x-ray diffraction and the inorganic δ^{13} C and δ^{18} O composition of the sediment will be measured. These parameters will help characterize the depositional environment and processes occurring during different stages of diagenesis.

KEY DELIVERABLES

The results of this study will provide a linked modern to ancient calibration and assessment of freshwater microbial carbonate and associated organic content. This project will form the dissertation research for C. Pederson. Data and results from each phase of the study will be available to the Industrial Associates.

DIFFRACTIONS AS DIRECT INDICATORS OF FRACTURE INTERSECTIONS AND RESERVOIR CONNECTIVITY

Mark Grasmueck, Tijmen Jan Moser¹, and Michael A. Pelissier² ¹ Moser Geophysical Services, Den Haag NL ² Marathon Oil Company, Houston USA

PROJECT OBJECTIVES

- Use full resolution 3D Ground Penetrating Radar (GPR) surveys with antenna frequencies ranging from 100-500 MHz to study diffraction signatures of fracture networks and their connectivity of reservoir analogues.
- High-resolution 3D GPR cubes and outcrop observations serve as a bridge between synthetic models and real seismic data.
- Wanted: High resolution 3D seismic dataset examples for diffraction analysis and comparison with outcrop calibrated GPR diffraction signatures.

PROJECT RATIONALE AND HYPOTHESIS

Flow in carbonate and unconventional reservoirs is often controlled by *discontinuities* such as fractures or voids. The reflection seismic method is optimized towards imaging of *continuous* reflectors to delineate stratigraphic boundaries. As a consequence, reflection seismic is of limited use for characterizing small scale fractures and voids. Sub-wavelength discontinuities cause diffractions and generate scattered energy on seismic records. Commonly such scatter is considered as noise and suppressed as much as possible during acquisition and processing. Diffractions present an opportunity to expand the resolution limit of subsurface imaging to the sub-wavelength scale.

Our hypothesis is that seismically recordable diffractions can be caused by intersections of thin fractures with no displacement. Diffraction analysis, following the three main tasks described below, occurred in collaboration with Tijmen Jan Moser and Michael Pelissier.



Figure 1. Illustration of data used for modeling of fracture-induced diffractions. a) Subvolume of larger 3D GPR survey acquired in Cassis Quarry (France). The bright spot in the center of the top face is caused by the intersection of a vertical with a sub-horizontal fracture. b) Intersection of a vertical and horizontal fracture in outcrop. c) Ray-Born synthetic data of a quarter wavelength line cross as observed in outcrop b).

1) Integrate 3D Synthetic Modeling, 3D GPR Data, Outcrop Observations, and 3D Seismic Data:

Synthetic modeling is performed with the Ray-Born method which is a very efficient tool to model both diffractions and reflections in 3D. We use high-resolution 3D GPR data for a direct as possible verification of the modeled diffractions with geophysical data recorded in fractured rock domains (Figure 1). Due to the kinematic similarity of GPR and seismic wave propagation, the GPR data can used as a proxy for seismic data to help develop new diffraction based fracture imaging workflows. Through scaling relationships the GPR findings are applied to the seismic method and provide guidance for the use of diffractions for determining previously seismically unresolvable fracture systems at reservoir depth.

2) Determine Geological Origins of Diffractions:

Geological scattering mechanisms and diffraction detection limits are not well understood. The key question is what geological features generate point diffractions. On well-developed fractures small conjugate fractures cause steps and corners acting as wave scatterers. From our 3D GPR data we see that zones consisting of fractures with one millimeter or less aperture cause abundant diffractions. The non-random distribution of these sub-Rayleigh size discontinuities is caused by fracture trends and patterns providing information about fracture spacing and fracture continuity of fractured domains. By their nature, fracture intersections and hence the resulting diffractions are direct indicators of fracture connectivity. We will use full resolution 3D GPR surveys acquired at various field sites with antenna frequencies ranging from 100-500 MHz to study diffraction signatures of fracture networks and their connectivity.

3) Apply Findings to Reservoir Depth Seismic Data:

Seismic diffraction signals from 4-5 km deep reservoirs are by an order of magnitude weaker than reflections from the same depth. To fully harness diffractions and the information they contain regarding reservoir fracture systems seismic data need to be acquired densely with high signal-to-noise ratio coupled with processing optimized for diffraction signal preservation and separation. To achieve this objective high resolution and high fidelity seismic datasets are needed. We are searching suitable seismic datasets for diffraction analysis and comparison with outcrop calibrated GPR diffraction signatures.

EXPECTED OUTCOME

With the new knowledge about diffractions gained from Ray-Born Modeling, 3D GPR and outcropping reservoir units, seismic diffractions are promoted from noise to valuable signal. Diffractions make sub-wavelength discontinuities caused by intersecting fractures in complex reservoirs visible and quantifiable.

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FACIES GEOMETRY AND REGIONAL CORRELATION OF PLEISTOCENE REEFAL LIMESTONES: A LOW FREQUENCY 2D GPR SURVEY ON ROUGH TERRAIN

Mark Grasmueck, Viviana Díaz, Donald F. McNeill, James S. Klaus, and Gregor P. Eberli

PROJECT OBJECTIVES

- Acquire a low frequency 2D GPR survey grid along a 4-km transect perpendicular to the southern coast of the Dominican Republic.
- Correlate 5 previously drilled cores and constrain facies geometries associated with Pleistocene highstand reef deposits and the transition from low amplitude 40 kyr sea-level cycles to high amplitude 100 kyr sea-level cycles.

PROJECT RATIONALE

The Dominican Republic Drilling Project (DRDP) was initiated with support of the Industrial Associates in the summer of 2010. The project has focused efforts on defining lithofacies, delineating diagenetic zones, characterizing petrophysical properties and establishing the chronostratigraphic framework within five drilled boreholes from the southern coast of the Dominican



Figure 1. The 2D GPR grid will be acquired around the five cored drill holes.

Republic (Figure 1). Despite these detailed characterizations, the absence of shallow seismic data has limited the ability to correlate laterally heterogeneous facies between cores and constrain depositional geometries associated with highstand reef deposition. The acquisition of a low frequency 2D GPR survey grid across the study

area will allow us to better correlate depositional packages between cores and define the internal anatomy and stratal geometry of the individual reef sigmoids and sigmoid sets.

Once completed, the GPR survey will provide the stratigraphic framework necessary to integrate existing depositional, diagenetic, petrophysical and hydraulic conductivity data into a reservoir model.

PROJECT DESCRIPTION

The 2D GPR survey will be conducted in a roughly 4x4 km corridor perpendicular to the southern coast of the Dominican Republic just east of the city of Boca Chica in the area of the drilled reefal cores (Figure 1). To maximize penetration the GPR survey will be conducted at low frequency (30 MHz) using a flexible antenna (Figure 2). The



Figure 2. Example of 30 MHz rough terrain GPR antenna.

"snake" like design of the antenna allows it to be maneuvered easily through the dense vegetation or uneven terrain without affecting ground contact. The most important benefit of the snake antenna will be that we do not need to clear an access path or route prior to the survey. To optimize acquisition parameters preliminary tests will be performed in a number of limestone quarries that allow for subsurface ground truth of up to 20m of penetration.

The acquired GPR data will be used to refine correlations between existing boreholes, and evaluate existing depositional models based solely on vertical facies patterns and the correlation of subaerial exposure surfaces between cores (Figure 3).



Figure 3. Proposed facies map and stratal geometries to be tested by 2D GPR survey.

KEY DELIVERABLES

The proposed project will generate a low frequency pseudo 3D GPR survey in a 4x4 km area on the southern coast of the Dominican Republic and provide a basis for correlating previously drilled cores in the area and constraining facies geometries associated with the transition from low amplitude 40 kyr sea-level cycles to high amplitude 100 kyr sea-level cycles. This dataset will be integrated with previous depositional, diagenetic, and petrophysical studies to evaluate porosity evolution, distribution and influence on transport and flow parameters. The integrated dataset will form the basis of a simulated reservoir model and will be made available to all Industrial Associates of the CSL-CCR.



Figure 4. Example of 3D GPR regional facies model based on Coll et al. CSL 2008.

PORE SIZE DISTRIBUTIONS AND ELECTRICAL RESISTIVITY IN CARBONATES AND SHALES

Jan H. Norbisrath, Ben Laurich¹, Guillaume Desbois¹, Janos Urai¹, Gregor P. Eberli, Ralf J. Weger, and Klaas Verwer² ¹ RWTH Aachen, Germany; ² Statoil, Bergen, Norway

PROJECT OBJECTIVES

- Expand the digital imaging of pore structures of various carbonate rock types and shales to sub-micron scales using the BIBSEM method (Broad-Ion-Beam cross-sectioning with subsequent SEM-image mosaic acquisition).
- Test if fractal Pore Size Density Distributions (PSDD) can be used to predict the total pore densities using only a portion of the pore sizes and evaluate how PSDD and other multiscale pore geometric and spatial parameters relate to electrical resistivity.
- Compare Multiscale-DIA to pore size distributions derived from mercury injection (MICP) and magnetic resonance (NMR)

PROJECT RATIONALE

The new method of Multiscale-DIA (Digital Image Analysis) enables quantification of heterogeneity in carbonates across 6 orders of magnitude with up to 20 nm/pixel resolution. The ultra-high resolution imaging is essential as the sub-micron pore structure has a strong effect on electrical resistivity (Norbisrath, 2012). The new technique produces promising results. For example, Pore Size Density Distribution (PSDD) versus pore size reveals a power law, indicating a fractal pattern of pore size distribution (Figure 1). The Nearest Neighbor Connectivity Factor (NNCF) shows good correlation with electrical properties and potentially will help relate pore arrangements to resistivity. The dataset now has to be extended to comprehensively quantify relationships between the digital image parameters and the electrical rock response.



Figure 1. Pore-size Density Distribution (PSDD) vs. size equivalent diameter. PSDD are displayed in exponentially growing pore size bins. Data exhibits linear behavior, i.e. predictability at each resolution with high R^2 values. The regression line is steeper for the more microporous samples. Colors represent different imaging techniques and resolutions.

The Multiscale-DIA that includes sub-micron pore sizes provides the opportunity to relate the imaged pore structure to other methods of pore size analysis, in particular those using mercury injection (MICP) and magnetic resonance (NMR). Comparing and correlating all these techniques is expected to display the strength and limitations of each technique and its relationship to electrical resistivity.

PROJECT DESCRIPTION

The main thrust of this study is to include sub-micron pore geometrical parameters and spatial pore network analyses of various carbonate rock types to better estimate the influence of the pore structure on electrical resistivity. To achieve this goal additional ultra-high resolution imaging of pores using the BIBSEM technique is required. This sub-micron imaging will be done in collaboration with colleagues at the RWTH Aachen, Germany, who have refined this technique.

Analyzing additional BIBSEM mosaics will define whether carbonates show fractal pore size density distributions, and if these patterns can be used to predict pore densities at levels below (or above) the scale of investigation. Specifically, this study will address the question if the amount of microporosity in a rock can be estimated from the distribution of its macropores, identified with conventional DIA from thinsections (using Optical Light Microscopy).

Additionally, the importance of the pore-body to pore-throat ratio (Pb-Pt-ratio) for electrical flow will be determined by combining pore-throat data from MICP and porebody data from NMR or BIBSEM. Likewise, general pore statistics from Multiscale-DIA will be compared to 3-dimensional but indirect analyzing techniques like MICP and NMR. The NMR analysis will be performed in collaboration with Statoil, Norway.

Moreover, by comparing the sub-micron pore geometries of micritic carbonates and shaly siliciclastics, we will try to identify similarities and common features, linking both rock types closer together.

KEY DELIVERABLES

- Comprehensive electrical resistivity database from various locations and depositional settings.
- Key dataset of representative "end-member" samples with characteristic pore geometries, which have been investigated in depth with Multiscale-DIA, MICP and NMR.
- Assessment of accuracy of indirect methods of pore size estimates like MICP and NMR.
- Improved understanding of the electrical flow in microporous rocks.
- Quantification of the importance of "dead" bulk volume of a large pore behind a narrow pore throat.

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VARIABILITY OF ELECTRICAL RESISTIVITY DURING CONTROLLED PRECIPITATION AND/OR DISSOLUTION

Ralf J. Weger, Peter K. Swart, and Gregor P. Eberli

PROJECT OBJECTIVES

- Enhance the understanding of the effects of chemical rock-fluid interaction and its influence on rock properties.
- Capture changes of electrical resistivity during chemically controlled dissolution.
- Assess the correlation between Archie's cementation factor and pore density.

PROJECT RATIONALE

The processes of rock/fluid interaction and diagenetic alteration of carbonate rocks are well understood, but little data exist to quantify the resulting changes and their influence on petrophysical properties. Carbonates are prone to diagenetic alterations that result in changes of the petrophysical properties. Small amounts of newly formed contact cement can stiffen the rock. Similarly, dissolution from slightly acidic formation waters or acid treatment during well completion can produce secondary porosity and increased permeability.

Several laboratory experiments with controlled precipitation and dissolution were performed at the CSL over the last two years. These experiments were designed to enhance the understanding of acoustic behavior during precipitation and dissolution. The results have shown that porosity and acoustic velocity change significantly in an extremely short time, but analysis of CT-scans showed that dissolution only expands existing internal pore geometry by dissolving fine particles with large surface areas (Figure 1). Pores are enlarged, but overall the number of pores remains nearly constant during dissolution.



Figure 1. High-resolution CT-scan before (left) and after (right) the dissolution. The light color is the solid, the gray is the pore space. Pore space increased by $\sim 10\%$ while the overall number of pores remained nearly constant.

Verwer et al. (2011) correlate the electrical resistivity and Archie's cementation factor to the number of pores and the pore density. They propose that the number of pores is more important than their size. Subsequent tests by analyzing high-resolution CT scans and MICP data corroborate Verwer's findings (Norbisrath et al., 2011, 2012). In our controlled dissolution experiments pore size increased but the number of pores remained nearly constant. If Verwer et al. (2011) are correct; the electrical resistivity during laboratory-induced dissolution should not change much.

In contrast, laboratory-induced precipitation is occurring either as contact cement or as fine needle cement. With regards to resistivity, the contact cement is decreasing the pore throat and the needle cement is increasing pores. Both processes are important for electrical resistivity. Thus the following experiments are planned.

DISSOLUTION WORKFLOW

Select several different carbonate grainstones of different grain sizes and permeabilities. Measure acoustic velocity and electrical resistivity at different confining pressures using the NER1000. Subsequently, infiltrate the samples with a slightly undersaturated solution and circulate the solution through the rocks for several days. Measure electrical resistivity, at set intervals during the infiltration experiment and record the changes over time. Sample and analyze the downstream fluid line for chemical changes that occurred during the experiment.

EXPECTED RESULTS

Rock evolution and changes will be documented, particularly with respect to electrical resistivity and fluid flow permeability. We will focus on analyzing electrical resistivity at different stages of dissolution, testing the Verwer principle. Highresolution images using SEM will provide estimates of dissolution during chemical rock-fluid interaction.

Precipitation experiments will address the influence of restricted pore throats and the increased pore complexity by fine needle cement.

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PETROPHYSICAL PROPERTIES AND PORE STRUCTURES OF MICROBIALITES (STROMATOLITES, TRAVERTINE AND TUFA)

Gregor P. Eberli, Ralf J. Weger, Jan Norbisrath, Giovanna della Porta¹, and Pedro Robledo²

¹ University if Milano, Italy, ² Geological Survey of Spain, Palma de Mallorca. Baleares

PROJECT OBJECTIVES

- Produce a comprehensive data set of the petrophysical properties of microbialites including:
 - Porosity and permeability
 - Acoustic velocity
 - Resistivity
- Quantitatively assess pore structure and correlate it to the physical properties

PROJECT RATIONALE

Microbialites are one of the major reservoir facies in the pre-salt offshore Brazil and stromatolites are an important reservoir facies in some Proterozoic carbonate reservoirs. In these reservoirs, the microbialites maintain good reservoir quality and a remarkable amount of preserved primary porosity to a great burial depth, indicating that the microbially fused grains or microbial precipitation produce a stiff framework.

This study investigates the porosity, permeability, sonic velocity and resistivity in conjunction with the pore structure to identify the petrophysical characteristics of the different microbialites. The comprehensive data set is intended to help explain the petrophysical signature of various microbialites in log and seismic data. Examination of the modern microbialites should shed light on the microbial processes that produce the characteristic petrophysical properties in microbialites.



Figure 1. The microbialites measured in this study consist of tufa from lakes in the US (left), modern stromatolites in the Bahamas and from the Miocene in Mallorca (middle) and travertine from Italy (right).

DATA SETS

A first data set (86 samples) consisting of modern stromatolites, travertine and microbially cemented hardgrounds will be expanded by additional travertine samples and tufa samples from lakes in the western US. Both sets of samples were collected

by Giovanna della Porta who will also collaborate on the digital image analysis of these samples. In addition, Miocene stromatolite samples were collected in collaboration with Pedro Robledo. We will add more samples when they become available in order to build a large comprehensive data set.

PROJECT DESCRIPTION

In order to petrophysically characterize the microbialites the following properties are measured: porosity, permeability, sonic velocity and resistivity. The latter two properties are acquired under variable confining pressures to assess the influence of burial depth on these properties. In the samples measured so far, although the influence of the pressure is relatively small, significant differences in velocity still exist between these three sample sets (Figure 2). Velocity is also measured dry and wet to capture the influence of saturation on the velocity in microbialites.



Figure 2. Velocity evolution of modern hardgrounds (TOTO), stromatolites and travertine samples with increasing pressure.

Most hardgrounds and stromatolites do not display a velocity increase with increasing confining pressure. Travertine samples have а high acoustic velocity and display a small increase with increasing pressure.

A horizontal thin section is cut from each plug for a quantitative assessment of the pore structure with digital image analysis (DIA). Travertine samples display strong velocity anisotropy. Therefore the plug is also cut vertically for an examination of the pore structure perpendicular to wave propagation. Initial results on the horizontal plugs indicate that the microbialites generally have a simple pore structure but a highly variable pore size.

KEY DELIVERABLES AND EXPECTED RESULTS

The comprehensive data sets (available to CSL associates) will evaluate the spectrum of physical properties in the different microbialites. It is expected that the different microbialites will produce characteristic petrophysical classes that can help discriminate them using geophysical tools.

The correlation of the petrophysical properties to the pore structure will potentially answer the question why these rocks are such good reservoir rocks. Furthermore, the study of the modern stromatolites and tufa will provide insight on the microbial processes that are important for the petrophysical behavior of the different microbialites.