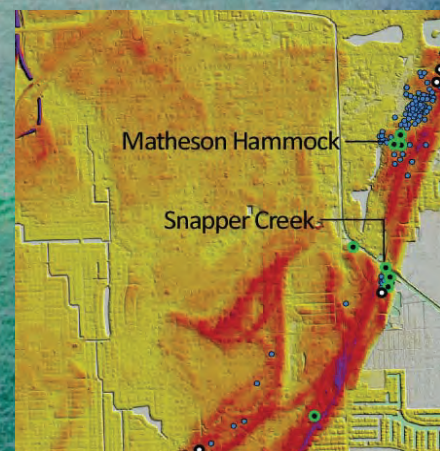
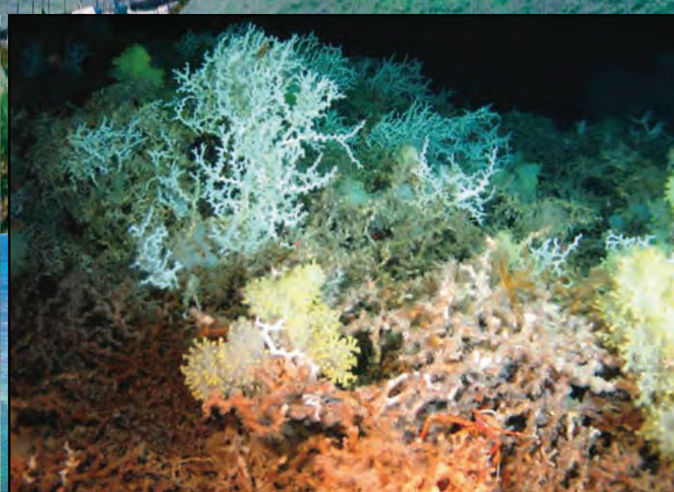
CSL
Center for Carbonate Research
and Education





Prospectus,
2018

UNIVERSITY OF MIAMI
ROSENSTIEL
SCHOOL of MARINE &
ATMOSPHERIC SCIENCE

CSL
CENTER FOR CARBONATE RESEARCH

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Mission of the CSL – Center for Carbonate Research

The mission of the CSL – Center for Carbonate Research is to conduct fundamental research in carbonates for improved reservoir prediction and characterization.

The research conducted within the CSL - Center for Carbonate Research (CSL – CCR) is intended to advance studies in a variety of emerging topics in carbonates. In addition to the fundamental knowledge gained from these studies we aim to inform our industrial associates on the newest research techniques that potentially can be incorporated into the workflow of projects or help to solve longstanding problems in exploration and production.

The 2018 projects integrate geology, geophysics, geo-microbiology, and geochemistry and combine observational, laboratory, and theoretical research, covering four areas:

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

Performing research within these four general research disciplines allows us to address fundamental questions in carbonate research in a comprehensive way. As a consequence, some of the research projects are interdisciplinary while others are designed to advance knowledge in one specific area. The various projects are described in detail in this prospectus and are retrievable on the website www.cslmiami.info.

Knowledge Transfer

The CSL – Center for Carbonate Research transfers the research results to our industry partners through an annual meeting, our website, webinars and publications.

We continue to offer field seminars and short courses.

A Certificate Program in "Applied Carbonate Geology" offers geoscientists the opportunity to become experts in carbonates.

We present the research results described in the prospectus at the **Annual Review Meeting** and provide each company with a digital version of our presentations and publications stemming from CSL sponsored research. On our **website** research results from previous years can be viewed in the archive section, providing a comprehensive database for many topics and geographic areas. Upon request, we also share original data sets with participating companies. Also on request, we offer **webinars** of various aspects of our research to our industrial associates.

PERSONNEL

PRINCIPAL INVESTIGATORS

Gregor P. Eberli, Ph.D. 1985, Geological Institute ETH Zürich, Switzerland
Research Interests: Shallow and deep-water carbonates, seismic facies and sequence stratigraphy, petrophysics of carbonates, 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-, magneto-stratigraphy).

Sam J. Purkis, Ph.D. 2004, Vrije Universiteit Amsterdam, The Netherlands
Research Interests: Carbonate sedimentology, remote sensing, GIS, geomodelling, marine biology, marine spatial planning.

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.

SCIENTISTS

Mara R. Díaz - *geomicrobiology*
Paul (Mitch) Harris - *sedimentology and stratigraphy*
Greta Mackenzie - *carbonate petrography and diagenesis*
Ralf J. Weger - *petrophysics and unconventional plays*

SCIENTIFIC COLLABORATORS

G. Michael Grammer	Oklahoma State University
Christian Betzler, Thomas Lüdmann	University of Hamburg, Germany
Dierk Hebbeln and colleagues	University of Bremen, Germany
Thierry Mulder and colleagues	University of Bordeaux, France
John Higgins	Princeton University

STUDENTS

Sara Bashah, Kimberly C. Galvez, Emma Giddens, Sharmila Giri, Anna H.M. Ling, Sevag S. Mehterian, Evan Moore, Laura Rueda, Jara S.D. Schnyder, Megan Smith, Philip T. Staudigel, Max Tenaglia, Mustafa K. Yuksek

RESEARCH ASSOCIATE

Amel Saied

STAFF

Karen Neher — Manager of Business Operation

2018 RESEARCH FOCUS

The focus of the 2018 projects within the four research areas of the CSL – Center for Carbonate Research are the following.

With a project in Colombia on Oligocene-Miocene reef successions we start a new research direction that focuses on the platforms on volcanic edifices and continental crust in the Caribbean. These relatively small platforms that often start with fringing reefs are typically challenging to distinguish from basement rocks on seismic data. Acoustic measurements on fringing reefs in the Dominican Republic are intended to provide data for pre-stack depth migration models in other areas.

Current-controlled deposits like contourites and drifts have been recognized as major sedimentary bodies in the siliciclastic environment but have received much less attention in carbonates. Several projects in the Carbonate Systems and Reservoir Characterization theme aim to close this gap. A comprehensive review of carbonate contourites and drifts will provide an overview of current processes and their depositional record in carbonates. Criteria for their recognition in seismic data, in cores and logs will be investigated in specific projects on data from the Bahamas, Maldives and Eastern Australia. An outcrop study in the Maiella mountains of Italy will describe in detail the sedimentary structures and dimensions of a coarse-grained carbonate drift fan. Petrophysical analyses in the marine realm and in outcrop examples will evaluate the reservoir quality of these current-controlled deposits.

We continue the quantitative interrogation of the karst features on the LiDAR terrain model of the Miami Oolite. In the deep-water, habitat mapping of benthic communities and associated facies based on high-resolution multibeam bathymetry and video data will elucidate the facies pattern on the slope and basin environments surrounding carbonate platforms.

In the Petrophysics theme the focus is twofold. One direction is the petrophysical characterization of depositional environments such as the coarse-grained carbonate drift fans in the Maldives and the Maiella. The other studies address some fundamental rock physics problems. This year, we test the Extended Biot Theory that potentially relates acoustic properties to permeability on log data from the Maldives. In the laboratory, we investigate how microbially-mediated precipitation of micritic meniscus cement alters the elastic properties of carbonate grainstones.

In the Unconventional theme, we we begin a multi-year project, in collaboration with G. Michael Grammer (Oklahoma State University), in which we establish baseline values and the range of petrophysical characteristics in different carbonate mudrocks as well as characterizing the pore system architecture and permeability of these mudrocks. The extensive dataset from the Vaca Muerta strata in the Neuquén Basin, Argentina, allows us to assess the controlling parameters (mineralogy, TOC, carbonate content, porosity and pore structure) for acoustic and electrical properties of mudstones. The micro-pore structures will be examined in BIM-SEM images of the Vaca Muerta and other mudstones. The outcrop work in the Neuquén Basin will be completed this year by measuring some crucial sections in the Sierra de la Vaca Muerta area. Exploratory sections in the Mendoza Province will follow the organic-rich strata into the northern sub-basin.

The geochemistry group is focusing in three areas in 2018, (i) refining clumped isotopic analyses, (ii) the application of C, S, and B isotopes to the sedimentary record, and (iii) the origin and influence of interstitial water within carbonate skeletons. For the first area, we will continue to investigate the use of the clumped isotope temperature proxy in order to understand, in particular, the diagenesis of dolomitization and early meteoric processes. We have added a new generation clumping instrument which, starting in 2018, will be incorporated into the laboratory. The goal in the coming year is the move to a carbonate based calibration system rather than the heated and equilibrated gases presently used. Our long interest in the use of C isotopes as a stratigraphic tool has stimulated interest in the isotopes of B and S and all three proxies are being studied during well-constrained diagenetic scenarios. In addition, the geochemistry group provides analytical services for many of the projects outlined in this prospectus.

Below is a list of all planned projects. The detailed objectives and deliverables of each project are outlined further in the 2018 research prospectus.

2018 Planned Projects

Carbonate Systems and Reservoir Characterization

- Geostatistical Analysis of Diagenetic Modification of the Miami Oolite
- Reef Development during the Oligo-Miocene Transition: A New Record from the Cocinetas Basin, Colombia
- Carbonate Contourites and Drifts – Sedimentologic Characteristics and Dimensions
- Influence of Ocean Currents on Miocene Carbonate Platform Drowning (Year 2)
- The Maiella Drift Fan – The Cretaceous Analog to the Coarse-Grained Carbonate Drift Fan in the Maldives
- South China Sea Oceanographic Impact on the Luconia Platforms Offshore Sarawak, Malaysia
- Refining Habitat Mapping of Benthic Communities in the Straits of Florida
- The Evolution of the Straits of Florida and the Miami Terrace

Petrophysics

- Petrophysical Calibration of the Coarse-Grained Carbonate Drift Fan, Maldives
- Testing the Extended Biot Theory in Carbonates of the Maldives
- Petrophysical Properties of a Fringing Reef Margin: Pleistocene Dominican Republic
- Rock Physics Observations During Controlled Microbially Induced Precipitation

Unconventional Reservoirs

- Comparing the Petrophysical Characteristics of Unconventional Carbonate Reservoirs (Vaca Muerta, Miss Lime, Bakken, and Eagleford)
- Acoustic and Electrical Calibration of Different Vaca Muerta Facies (Year 3)
- Lithologic and Geochemical Calibration of the Basal Clinoforms in the Sierra the La Vaca Muerta, Neuquén Basin, Argentina
- Concretions as Compaction Proxies in the Vaca Muerta Formation, Neuquén Basin, Argentina

GEOBIOLOGY AND GEOCHEMISTRY

- Global Synchronous Changes in the Carbon Isotopic Composition of Platform-Derived Sediments
- The Influence of Diagenesis on the C, B, and S Isotopic Composition of Carbonate Sediments
- The Behavior of Carbon Isotopes During the Dissolution of Carbonates by Phosphoric Acid
- Towards an Understanding of the Use of Clumped Isotopes to Study Diagenesis
- The Formation and Dissolution of Celestine: A Possible Mechanism for Creating Secondary Porosity in Platform-Derived Sediments

COSTS

The contribution of each Industrial Associate towards the research is **$55,000**. This contribution complements funding the CSL-CCR receives from national funding agencies such as the National Science Foundation (NSF), the International Ocean Discovery Program (IODP) and the Petroleum Research Fund. Contributions from our Industrial Associates are mainly used to support students working within the CSL, while funding for the data acquisition, like from seismic and coring expeditions and the funds for new equipment have been made possible by grants from federal funding agencies.

2018 ANNUAL REVIEW MEETING

ANNUAL REVIEW MEETING AND FIELDTRIP, OCTOBER 15 - 16, 2018

The results of the projects detailed in this prospectus will be presented at the **Annual Review Meeting in Miami, October 15 - 16, 2018**. In conjunction with the meeting we will have a field seminar to the Bahamas on **October 17 - 21, 2018.** We will send out information on the logistics for the meeting and the tentative program in the second quarter of 2018.

REVIEW MEETING FIELD SEMINAR, FACIES OF GREAT BAHAMA BANK, OCTOBER 17 - 21, 2018

We were able to reserve the RV Coral Reef for 5 days after the annual review meeting. Thus, this year's fieldtrip will be to the **Great Bahama Bank**.

Figure 1: A) Satellite image of the Florida Bahamas region with the route of the field seminar in orange and the field stops in green Xs.

This 5-day seminar explores the vertical and lateral facies successions and heterogeneities of Great Bahama Bank.

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. 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.

The objectives are:

1. Illustrate the **depositional characteristics and dimensions of facies belts** across an isolated platform.
2. Relate **variable accommodation space and facies heterogeneities** to reservoir models.
3. Improve the **interpretation of subsurface core, log and seismic data** of carbonate systems.

Cost: Approximately $5,300.-, Transportation to and from the Bahamas, all ground transportation, on-board boat accommodation in the Bahamas, meals and course notes are included.

CERTIFICATE PROGRAM: *APPLIED CARBONATE GEOLOGY*

Department of Marine Geosciences, Rosenstiel School of Marine and Atmospheric Science

PURPOSE AND GOALS OF THE CERTIFICATE PROGRAM

The goal of the Certificate Program is to provide first-rate continuing education to professionals or geology students who want to become experts in carbonate geology. To reach this goal courses are offered in carbonate sedimentology, seismic stratigraphy, petrophysics, and geochemistry for an advanced knowledge and understanding of carbonate systems.

OVERVIEW AND COSTS

A Certificate in *Applied Carbonate Geology* requires the successful completion of 16 course credits assembled from 11 courses in the program (see below). The courses combine classroom teaching, laboratory classes and applied projects. No thesis will be written.

Courses for the Certificate Program will be offered in the Spring Semester and the 1st Summer Session of 2019. The student/geoscientist will be in residence for 6 months. The current tuition fee is $2000/credit.

REQUIREMENTS FOR ADMISSION AND REGISTRATION

A bachelor degree or equivalent degree is required but can be offset by years of working experience. No GRE or TOEFL are required.

Registration for the Certificate Program will start in the summer of 2016 and will be handled by the Graduate Studies Office of RSMAS.

OFFERED COURSES IN THE CERTIFICATE PROGRAM

MGS 611	3 Cr	Earth Surface Systems
MGS 641	2 Cr	Field Evaluation of Fossil Platforms, Margins, and Basins
MGS 678	2 Cr	Field Seminar: Facies Successions on Great Bahama Bank
MGS 688	2 Cr	Field Seminar: Heterogeneity of a Windward Margin
MGS 784	2 Cr	Seismic Interpretation of Carbonate Systems
MGS 785	2 Cr	Petrophysics of Carbonates
MGS 786	2 Cr	Microbial Carbonates
MGS 787	2 Cr	Carbonate Diagenesis and Petrography
MGS 788	2 Cr	Analysis of Carbonate Cores and Logs
MGS 789	2 CR	Petroleum Geology in Carbonates
MGS 601	1 Cr	Seminar in MGS

The syllabus of each course is posted on the CSL and RSMAS websites. The two field seminar courses are identical to the annual Bahamas field seminars that were offered every year.

REGISTRATION

Registration for the Certificate Program will open in June, 2018. Registration is online using the UM-RSMAS graduate program website. Classes will begin in January, 2019.

GEOSTATISTICAL ANALYSIS OF DIAGENETIC MODIFICATION OF THE MIAMI OOLITE

Sam J. Purkis and Paul (Mitch) Harris

PROJECT OBJECTIVES

- Continued investigation of the co-occurrence of surfical karst pits (dolines) and shallow stratiform caves in the Miami oolite.
- Analysis of the relationship between diagenetic modification, stratigraphy, and facies, with respect to potential fluid flow through a Pleistocene sand body.

PROJECT RATIONALE

To date, a LiDAR bare-earth terrain model has been used to explore the preservation potential of various aspects of grainy carbonate systems, including tidal bars and channels (Purkis and Harris, 2017). We further used the LiDAR surface to develop a statistical understanding of the distribution of dolines across the sand body (Purkis et al., 2017). What has not been integrated, however, is the relationship between the dolines and the many shallow cave systems that have been recognized in the Miami oolite (e.g. (Cresseler, 1993; Florea et al, 2015).

SCOPE OF WORK

The project will proceed with an integration of the LiDAR terrain model, our existing maps of doline distribution, and locations of caves as harvested from the literature and our field examination (Fig. 1). An effort will be made to seek congruencies between the surficial karstic overprint (i.e. the dolines) and the better developed cave systems, which, in a subsurface setting would have a meaningful impact on fluid flow. Further effort will be dedicated to examining how both types of karst relate to stratigraphy, facies, and hydrogeography.

SIGNIFICANCE

The Miami oolite is an example of eogenetic karst wherein a dual porosity/permeability system has developed. During the last 125 kyr of meteoric diagenesis, the patterns of porosity and permeability as related to depositional facies have been modified. For instance, core-measured porosity averages 43% but ranges from 17– 67% (Robinson, 1967; Halley and Evans, 1983; Hester and Schmoker, 1985). Facies still clearly influence dissolution pathways, however, within the grainstone deposit to produce a connected vug-cave network preferentially situated in the *Ophiomorpha* ichnofabric (the "burrowed" facies) which mimics a "super'K" zone. Since the Miami oolite is the uppermost portion of the Biscayne Aquifer, a highly transmissive unconfined aquifer, which provides the bulk of potable water for the region, a rich understanding of fluid flow through the deposit already exists and can be integrated into this project.

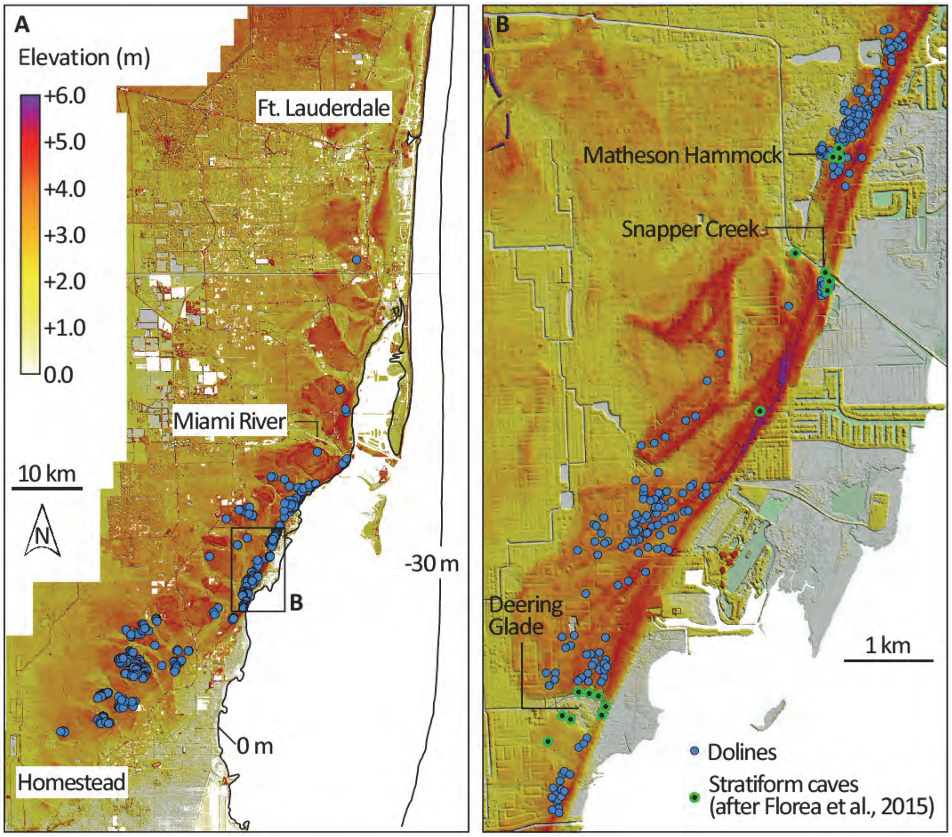

Figure 1. (A) LiDAR topography of the Pleistocene Miami oolite (Purkis and Harris, 2017). Dolines (n = 735) digitized from the LiDAR surface and validated in the field (blue dots) variably develop throughout the deposit. (B) Focuses on an area of the barrier bar spanning Deering Glade through Snapper Creek to Matheson Hammock and highlights locations of dolines and stratiform caves (green circles, as mapped by Florea et al., 2015).

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REEF DEVELOPMENT DURING THE OLIGO-MIOCENE TRANSITION: A NEW RECORD FROM THE COCINETAS BASIN, COLOMBIA

James S. Klaus, Paula A. Zapata-Ramírez

PROJECT OBJECTIVES

- To investigate the changing nature of Oligocene and Miocene reef systems in the southern Caribbean.
- To assess the relative importance of oceanographic factors compared to sea level and tectonics in reef development and coral extinctions.
- Compare the new records from the Cocinetas Basin to a compiled database of Olio-Miocene records from the Caribbean region.

PROJECT RATIONALE

The evolution of Cenozoic shallow marine carbonates has been linked to major perturbations in global climate and environmental conditions (Wilson, 2012). Cenozoic Caribbean reefs appear to be best developed during the Oligocene and Pleistocene, with the record of Cenozoic Caribbean reef diversity punctuated by two intervals of elevated extinction and faunal turnover; the Oligocene-Miocene and Pliocene-Pleistocene transitions. Although the Oliogocene-Miocene faunal transition is broadly recognized, the exact timing and links to climatic and oceanographic changes has yet to be firmly established. The Oligocene has been generally perceived as a time of climate stability, despite Antarctic ice sheet and glacioeustatic sea-level oscillations of up to 50-65 m associated with glacial episodes Oi-2 (29.16 Ma), Oi-2a (27.91 Ma), and Oi-2b (26.76 Ma). Oxygen isotope trends suggest a Late Oligocene Warming Event (LOWE) between 26.5 and 24.0 Ma (Zachos et al., 2001) prior to cooling and the Mi-1 glaciation near the Oligocene/Miocene boundary (Mawbey and Lear, 2013). There is currently a lack of stratigraphic resolution in the record of shallow water reef development that inhibits establishing the link between reef collapse and the specific climate and oceanographic factors outlined above.

Figure 1. Fringing reefs from the Siamaná Formation located at the south flank of Arroyo Uitpa.

SCOPE OF WORK

The goal of this project is to document a new Aquitanian record of Caribbean reef development from the Siamana Formation of the Cocinetas Basin, outcropping within the Guajira Peninsula of Colombia. The Guajira Peninsula, northern Colombia (Fig. 1), provides an extensive and well-exposed Oligocene and Miocene sedimentary and paleontological record for the southern Caribbean. Extensive carbonate deposits within the peninsula offer an exceptional opportunity to study the depositional geometries and the distribution of carbonate facies, and to document the timing and nature of reef development in the Southern Caribbean. A high-resolution biostratigraphic framework of the visited outcrops has been recently conducted (Silva-Tamayo et al., 2017), providing calibrated stratigraphic ranges of the reefal units. Our main objectives are to (1) characterize the faunal composition and nature of reef development in the Cocinetas Basin during the early Miocene, (2) compare the Siamana reef system to other records from the Caribbean region, and (3) refine the temporal and biogeographic records of Caribbean reef coral development in the southern Caribbean to help constrain the response of tropical reef systems to environmental perturbations associated with the Oligocene – Miocene transition.

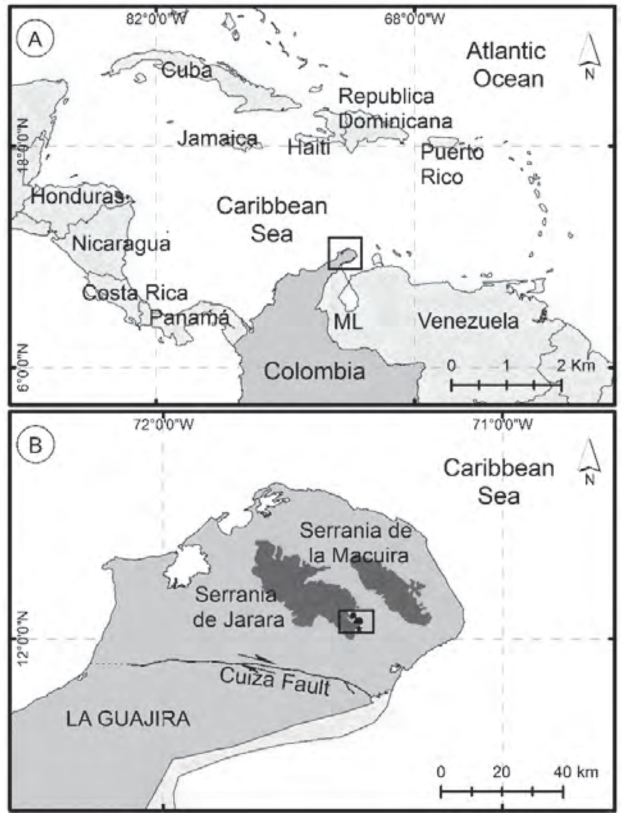

Figure 2. A) Regional Map showing the study area, the Guajira Peninsula of Northern Colombia. ML (Maracaibo Lake). B) Location map of reef sampling localities on the flanks and in the lowlands of Jarara Mountain.

SIGNIFICANCE

Oligo–Miocene platforms and ramps are recognized as good hydrocarbon reservoirs, including the approximately 300 m thick Oligo–Miocene carbonates of the Perla field, offshore Venezuela. These carbonates are predominantly composed of larger benthic Foraminifera and red algae with a minor contribution from shallow water carbonate components (green algae and corals). Comparisons between the Cocinetas and Perla carbonates should provide a broader characterization of facies variability within the carbonate factory of the Oligo-Miocene southern Caribbean.

Carbonate Contourites and Drifts – Sedimentologic Characteristics and Dimensions

Gregor P. Eberli, Christian Betzler[1], Thomas Lüdman[1], and Sara Bashah

[1)] *CEN, University of Hamburg, Germany*

Project Objectives

- Assemble a comprehensive overview of carbonate contourites and drifts from literature and from unpublished examples.
- Relate current dominated sedimentologic processes to their products in particular to contourite/drift body architecture, facies and sedimentary structures.
- Provide dimensions of the various contourite/drift systems.

Project Rationale

The recognition and investigations of contourites and drifts in siliciclastic deep-water systems has been fuelled by the exploration of deep-water clastics. Seismic and core data, and subsequently outcrop analogs have led to the formulation of depositional models for both the large-scale geometries and the bed-size characteristics (Rebesco et al., 2014). Bottom and contour currents are, however, also affecting the deep-water carbonate environment. In fact, isolated carbonate platforms restrict and focus the ocean gyres and thus produce a variety of contourite and drift regimes and bodies (Fig. 1). Yet, the carbonate contourites and drifts have not been studied systematically, mostly because few hydrocarbons are found in deep-water carbonate sequences.

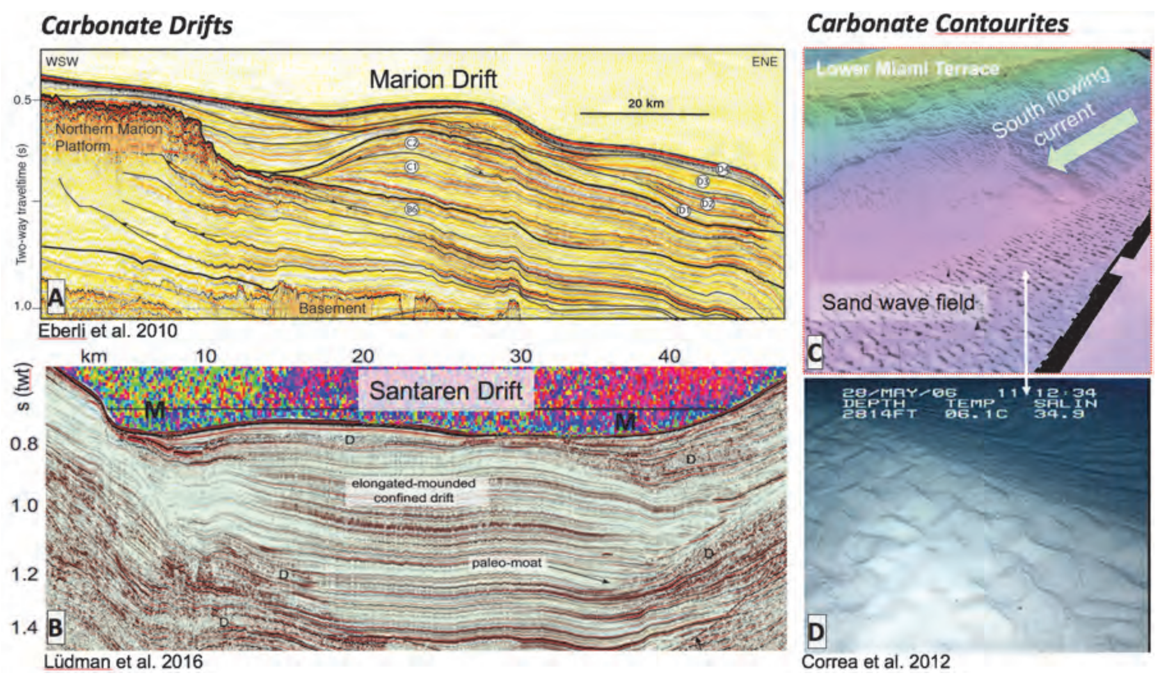

Figure 1: Examples of carbonate drifts and contourites. A) The Marion Drift is a complex separated drift. B) The Santaren Drift is an elongated-mounded confined drift (Lüdmann et al., 2013). C) A sand wave field at the base of the Miami Terrace (865 m water depth) is a contourite deposit. D) The sand waves are ornamented by ripples.

High-resolution seafloor mapping, as well as seismic and oceanographic data, combined with sedimentological sampling from modern deep-water carbonate slopes and basins during the last few years have produced a wealth of data that can document the characteristics of carbonate contourites and drifts. That together with the oceanographic data can provide robust depositional models for the current controlled carbonate deposits.

APPROACH

This study will rely on published and newly acquired data in sites where current controlled sedimentation occurs. The results will be published in a special volume of Sedimentology that aims to present the state of the art of the research in current controlled carbonate strata. One focus of the volume will be on the findings of the recent IODP Expedition 359 to the Maldives (Betzler et al., 2016). Bathymetry and seismic data from the Bahamian archipelago (Bergman, 2005; Lüdmann et al., 2016) and examples from the current swept Marion Plateau (Isern et al., 2004) will make this a comprehensive treatment of these deposits.

SIGNIFICANCE

The deep-water carbonate environments are the emerging but underexplored depositional settings in carbonates. This review study aims to elucidate the role of currents on the slope and basin deposits that are at least as important as gravitational transport mechanisms.

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INFLUENCE OF OCEAN CURRENTS ON THE MIOCENE PLATFORM DEMISE (YEAR 2)

Anna H. M. Ling, Sara Bashah, Gregor P. Eberli, and Christian Betzler[1]

[1) *CEN, University of Hamburg, Germany*

PROJECT OBJECTIVES

- Test if ocean currents affect the demise of Miocene carbonate platforms by:
  - Assessing synchrony of current onset and platform demise by constraining the timing of both events.
  - Identifying similarities between the drowning successions of the Kardiva Platform (Maldives), Marion Plateau (Australia), west-Florida shelf edge, and the Miami Terrace.
  - Providing chemical evidence that nutrient influx did not cause the demise of the carbonate platform.

PROJECT RATIONALE

Carbonate platform drowning is a common phenomenon in the carbonate system for which many theories exist, including global anoxic events, fast sea-level rise, tectonic break-up, and by the negative influence of nutrient excess on reefs (Hallock and Schlager,1986). However, evidence also exists for the close relationship between platform demise and intensification of ocean currents. For example, the platforms on the Marion Plateau stopped growing at the same time as ocean currents started to be diverted along the eastern

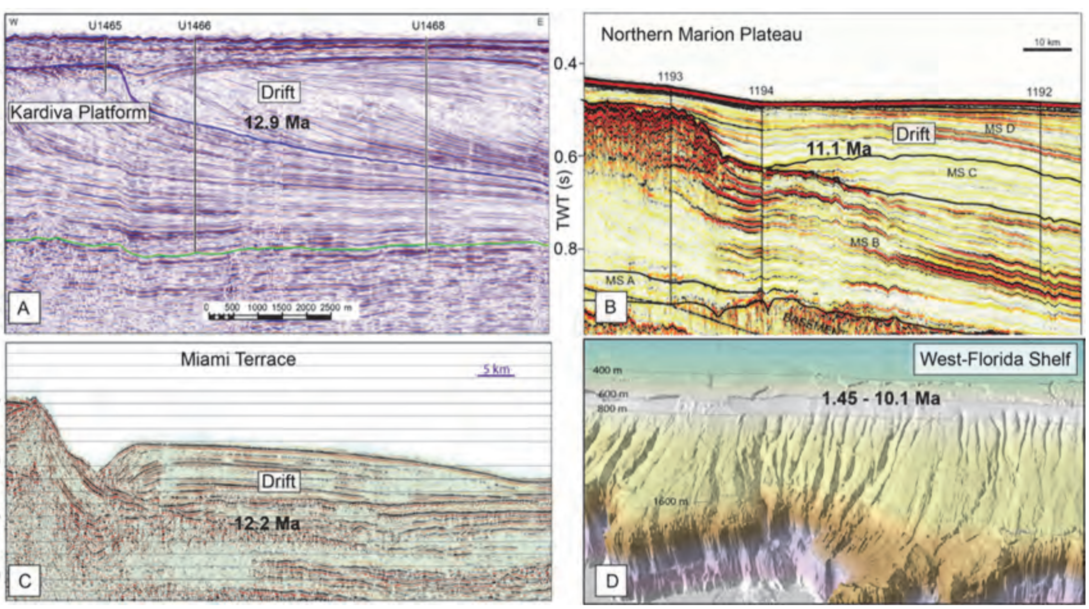

Figure 1: Drowned platforms and drift deposits used to test the influence of currents on platform demise. A) Kardiva Platform Maldives; B) Northern Marion Platform (Australia); C) Miami Terrace (Florida); D) Edge of West Florida Shelf. The ages indicate the onset of the drift deposit in A-C; in D) ages are from hardground samples.

side of Australia (John and Mutti, 2005; Eberli et al., 2010). Likewise, the onset of monsoon-related currents is correlated with the partial drowning of the platforms in the Maldives (Betzler et al. 2009). Mullins and Neumann (1979) proposed that the backstepping of the Florida platform that formed the Miami Terrace was caused by the intensification of the Florida Current. Similarly, the origin of hardgrounds on the West Florida shelf edge is attributed to the Loop Current. In this study, we test if currents alone were responsible for the platform demise or if increased up-welling and, thus, increased nutrient supply during current intensification aided in the process.

APPROACH

To show a causal relationship between platform drowning and current intensification we plan to precisely date the onset of the current and the top of the drowned platform. Biostratigraphic data from IODP Expedition 359 (Maldives) and ODP Legs 101, 166 (Bahamas) and 194 (Marion Plateau) provides the ages for the onset of the drifts (Figure 1). Sr-isotope dating is used to date the drowning successions on the platforms. Synchrony of hardground formation and drift onset would provide evidence of the influence of currents on the demise of these platforms.

Thin section analyses of the platform tops will indicate if the platform was exposed before the demise or if drowning occurred during a sea-level rise. Geochemical signatures (Iron and Phosphorus) and proxies for nutrients (Barium and Cadmium) from XRF analysis will be obtained from both current and platform deposits to evaluate if nutrient supply increased with current intensification. The nitrogen isotope ratio ($\delta N^{15}/\delta N^{14}$) of the Kardiva Platform sediments will also be determined. Any changes in geochemical signature will reveal if there was an influx of nutrients at the time of platform drowning.

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THE MAIELLA DRIFT – THE CRETACEOUS ANALOG TO THE COARSE-GRAINED CARBONATE DRIFT IN THE MALDIVES

Gregor P. Eberli, Emma Giddens, and Mark Grasmueck

PROJECT OBJECTIVES

- Provide a detailed sedimentologic description of the coarse-grained Orfento Formation in the Maiella Mountains that is newly interpreted as a carbonate drift.
- Give dimensions of the drift and the various elements within the drift, including the prograding lobes, slope channels and excavation moat.
- Analyze porosity and permeability of the various drift elements and assess the reservoir potential of these types of current deposits.

PROJECT RATIONALE

The nature of a large-scale prograding wedge of coarse-grained carbonate sands and breccias that reaches from the Upper Cretaceous Maiella platform margin for some 20 km into the basin had been variably interpreted as "sea-level controlled platform progradation" (Mutti et al., 1996) or as "lobes that combine characteristics of unidirectional sandwaves and alternating point-sources of the depositional deltas" (Vecsei, 1998). IODP Expedition 359 to the

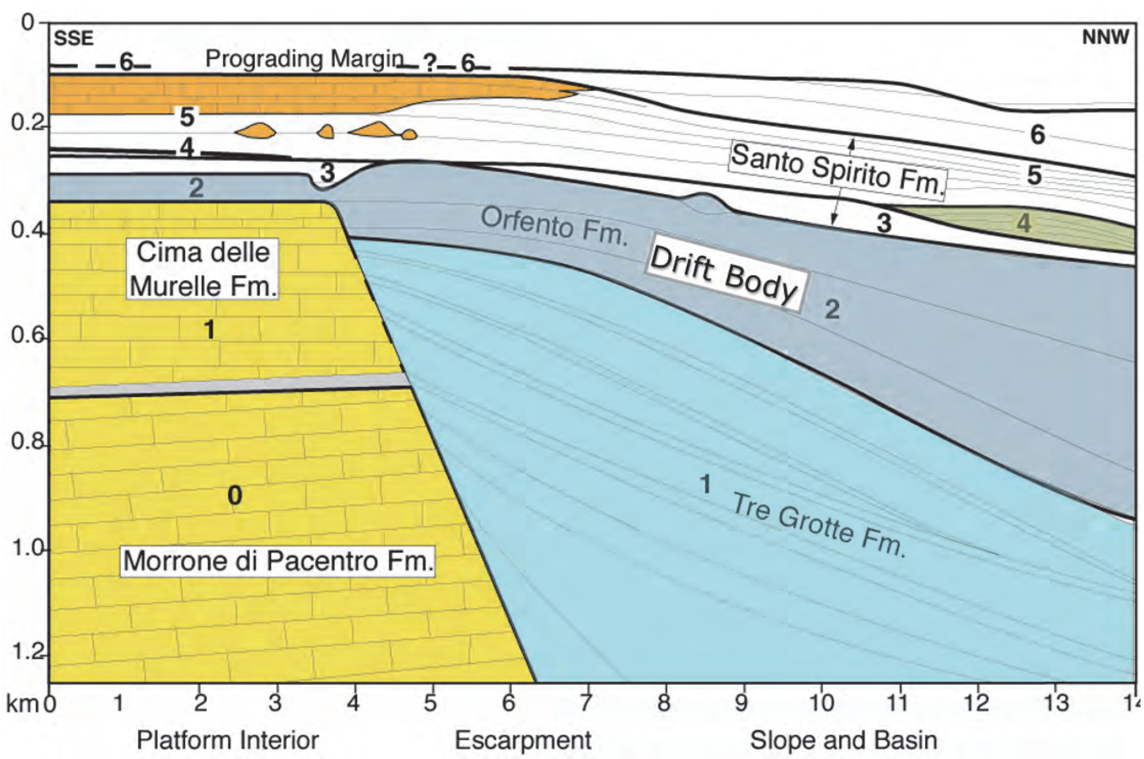

Figure 1: The prograding wedge of the Orfento Formation (2) is a coarse-grained bioclastic wedge that is deposited by currents flowing in a channel across the Upper Cretaceous platform. This type of drift deposit has similarities to a deep-water delta.

Maldives discovered two channel-related drift fans that have very similar geometries and facies distribution. These include depositional lobes, slope channels, and an excavation moat where the channel feeding the prograding wedge reaches the platform edge (Lüdmann et al., in press). As in the Maldives the facies consist of coarse-bioclastic debris with both coarsening and fining-upwards successions. The superb outcrops in the Maiella drift offer the opportunity assemble in detail the characteristics of such drift deposits that aid in interpreting the seismic and log facies of these potentially excellent reservoirs.

APPROACH

Extensive fieldwork has already been conducted in this formation when the sequence stratigraphic framework of the Maiella platform margin was documented (Eberli et al., 1993; Vecsei et al., 1998). We plan to visit key locations for additional petrophysical sampling and document large-scale depositional geometries with gigapan photography, and document in detail the sedimentary structures of these deposits from the proximal portion to the distal reaches of the lobes that are exposed for approximately 20 km.

Based on past petrophysical analyses, the coarse-grained bioclastic wedge is of high-porosity and high permeability. We plan to add a systematic petrophysical analysis of all the architectural elements of the drift body to assess the variability in reservoir quality within the drift.

SIGNIFICANCE

The Maiella drift potentially serves as the outcrop example of a newly recognized contourite drift system in carbonates. The description of the facies, sedimentary structures and dimensions of all architectural elements will be a guide for correctly interpreting such deposits in outcrop and in the subsurface. Their excellent reservoir quality makes such deposits potential exploration targets in deep-water carbonate environments.

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South China Sea Oceanographic Impact on the Luconia Platforms Offshore Sarawak, Malaysia

Sara Bashah and Gregor P. Eberli

Project Objectives

- To investigate whether the demise of the carbonate platforms in the Luconia province was influenced by the strengthening of currents sweeping across the province.
- To assess the relative importance of oceanographic factors compared to sea level and tectonics, influencing the geometry and dolomite distribution of the platforms in the Luconia province.

Project Rationale

For the past three decades, the morphology and reservoir distribution of the carbonates in the Luconia province has been discussed in terms of eustasy, tectonics and clastic input (e.g. Vahrenkamp et al, 2004; Menier et al., 2014). The impact of oceanographic changes in the South China Sea (SCS), in particular the changes in atmospheric and ocean circulation, is much less studied. Although it has been hypothesized that waves, winds and ocean currents impacted carbonate platform growth, and ultimately their

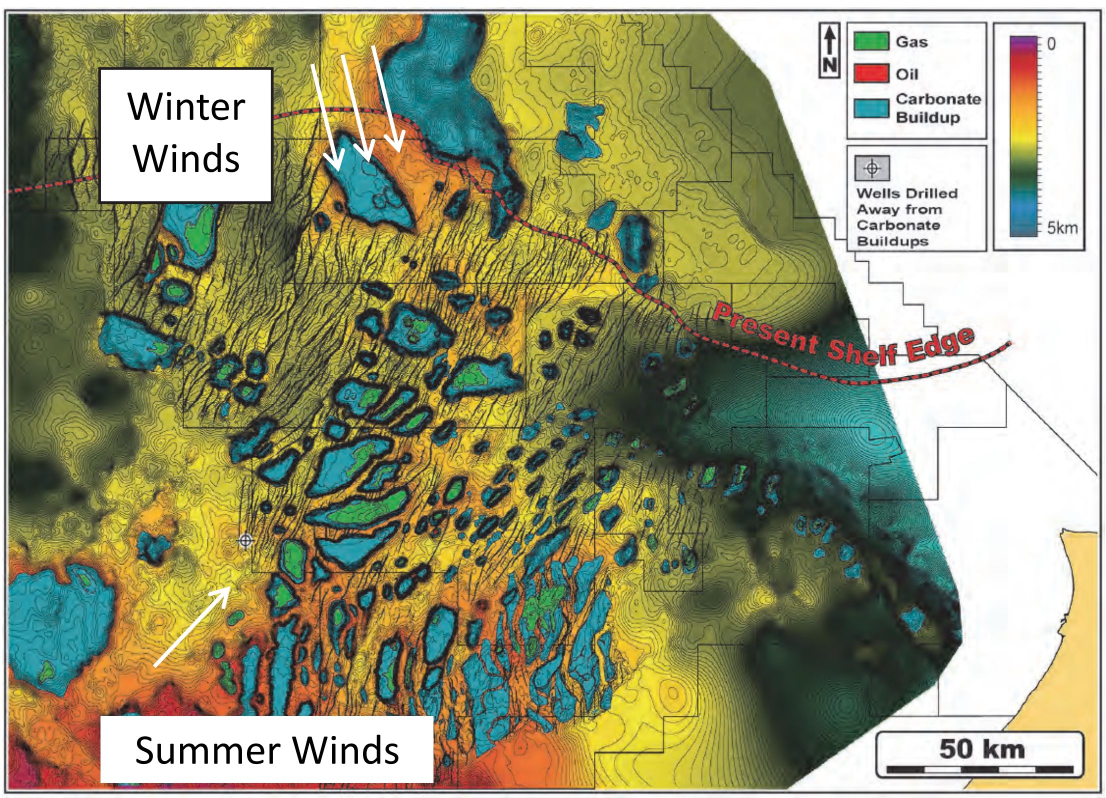

Figure 1. The Luconia carbonate province, offshore Sarawak, Borneo, in the South China Sea. The white arrows show the East Asian Monsoon wind patterns (Modified after Kosa, 2015).

demise, no precise mechanism was proposed (e.g. Bracco Gartner et al., 2004). There is increasing evidence that oceanographic changes, in particular the onset of strong ocean currents, have caused or at least contributed to the drowning of platforms on the Marion plateau and parts of the Maldives. Thus, we evaluate if the oceanographic changes influenced the platform demise in the Luconia province.

DATA SETS AND SCOPE OF WORK

A large 2D and 3D seismic data set, provided by PETRONAS, that also includes core and log information, will be systematically searched for geometries indicative of current deposits, such as moats or mounded features in the off-platform areas that have been documented in the Luconia Province (e.g. Koša et al., 2015). The onset of the current system and the platform demise will be studied by comparing the age of the platform drowning with the base of the basinal (drift) deposits. The age will be constrained using available well and biostratigraphic data. We will also investigate if changes in platform architecture correlate with the oceanographic events and if the dolomite distribution is indicative of changes in upwelling currents.

SIGNIFICANCE

Understanding the impact of the SCS paleoceanographic changes on the evolution of the Luconia carbonate platform will provide new insights regarding the influence of currents on the platform architecture and platform demise. Findings from this research can be applied to other carbonate platforms in the SCS region and potentially to many drowned isolated platforms. Furthermore, trends recognized in the sedimentary record of the Luconia province will shed light on the history of both the East Asian monsoon and the Western Pacific Warm Pool.

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Refining Habitat Mapping of Benthic Communities in the Straits of Florida

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Project Objectives

- Produce habitat maps in the Straits of Florida along Great Bahama Bank using high-resolution bathymetry, backscatter, and sidescan sonar (SSS) in conjunction with images/videos from remotely operated vehicles (ROV).
- Calibrate high-resolution backscatter data with visual data and grab samples to classify facies of the seafloor.
- Calculate area of coral growth sites relative to shape and orientation of seafloor morphology.

Project Rationale

High-resolution bathymetry, backscatter, and sidescan sonar (SSS) data in conjunction with images/videos from remotely operated vehicles (ROV) were collected on several research cruises along the western side of Great Bahama Bank (RSMAS AUV Florida Straits 2005, CARAMABAR Bordeaux 2010, MARUM Bremen MSM20/4 2012). These data allow for extensive habitat mapping that includes both the cold-water coral mounds and the sedimentary facies. The slope and adjacent basin is a complex arrangement of slope sediments dissected by slope scars, mass transport complexes and unconsolidated fine and coarse carbonate sediments (Correa et al., 2012; Mulder et al., 2012; Betzler et al., 2014). In addition, various cold-water coral (CWC) mound fields have been discovered (Grasmeuck et al., 2006; Hebbeln et al., 2012, Lüdmann et al., 2016). A previous habitat map model was created from classification attributes based on morphological features (Fig. 1; Schynder et al., 2014). Additional data and new techniques now allow a comprehensive and aerially extensive habitat map to be created for the toe-of-slope environment that will capture the dimensions and lateral juxtaposition of facies and cold-water coral reefs.

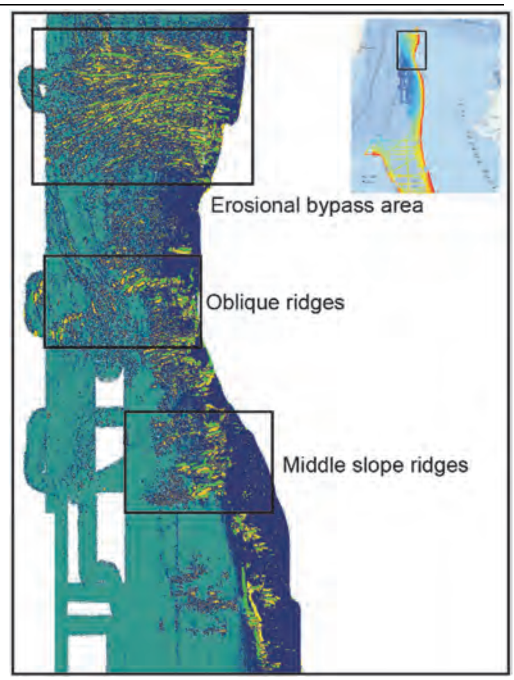

Figure 1. Habitat map of GBB slope. (Schnyder et al., 2014)

METHODS

We will be following the methodology outlined in Correa et al. (2013) that relies on ground-truthing images from submersible (submersible and ROV) transects to create sea-floor categories based on coral coverage and particle grain size. In our data set, five habitat classes are distinguishable. Using the corresponding color coding, the habitat classes are used to classify the entire acoustic values through a supervised classification algorithm (ENVI; Mahalanobis distance classifier). The acoustic images are identified through pixel by pixel classification, whereby each pixel represents a specified acoustic property assigned to distinguish it from other classes. Pixels are then converted to a vector-based classification (i.e. polygon) and then polygons are assigned the classifications and subsequently exported as a shapefile to be overlain on the bathymetry data in ArcGIS, thus forming a habitat map.

SIGNIFICANCE

Incorporation of the high-resolution backscatter data will further refine the habitat classification maps of the seafloor of the western GBB. The planned high-resolution habitat map provides the necessary cataloguing of spatial distribution of facies and CWCs in relation to the physical features of the seabed. The habitat map will document the dimensions and diversity of sedimentologic and biologic features in the Straits of Florida and shed light on the importance of benthic communities as carbonate sediment producers.

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THE EVOLUTION OF THE STRAITS OF FLORIDA AND THE MIAMI TERRACE

Sara Bashah, Gregor P. Eberli, Anna Ling, and CARAMBAR scientists

PROJECT OBJECTIVES

- To revise the age model for Oligocene to Pliocene deposits throughout the Straits of Florida.
- To investigate whether the partial drowning of the Florida platform was influenced by the strengthening of the Gulf Stream.
- To assess the relative importance of oceanographic factors relative to sea level and tectonics on the evolution of the Straits of Florida.

PROJECT RATIONALE

The Straits of Florida is a major seaway between carbonate platforms of the Bahamas-Florida region. The origin and the evolution of the seaway have been discussed for years. There are two main competing ideas with regards to origin; one postulating that the seaway is an unfilled graben that formed during the extension of the continental crust when the Atlantic opened in the late Jurassic (Mullins and Lynts, 1977). Others proposed a shallower and younger origin of the seaway, attributing genesis to a partial drowning of a megabank that existed in the early Cretaceous in the Florida Bahamas region (Sheridan et al., 1981; Schlager and Ginsburg, 1981). Based on a large data set of regional seismic lines, Massaferro and Eberli (1999) postulated that tectonic loading during the Cuban-American collision caused reactivation of Jurassic faults and drowning of the once larger platform. Since the late Middle Miocene the Straits of Florida has also been the main getaway of the Florida Current, which influences the sediment distribution in the Straits (Bergmann, 2005). The partial drowning of the Florida Platform that created the Miami and

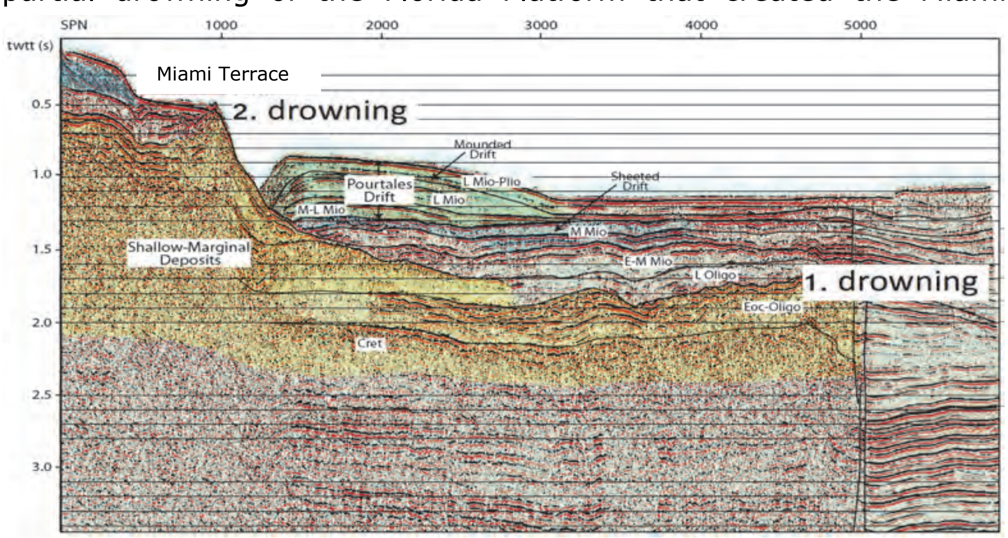

Figure 1. Seismic section across the Miami Terrace and the buried older platform in the Straits of Florida. The two partial drowning events are the focus of this study (modified from Bergman, 2005).

Pourtales Terrace occurred around the time of the onset of the Florida Current. There is increasing evidence in other carbonate platform systems that the onset of strong ocean currents may have contributed to the drowning of platforms, for example, the Marion platforms (Eberli et al., 2010) and parts of the Maldives (Betzler et al., 2009). Here, we evaluate if the oceanographic changes or tectonics caused the platform demise that formed the Miami Terrace.

SCOPE OF WORK

This research will focus on the Neogene environmental impact on the Florida Platform in the Straits of Florida. To estimate the timing and causes of the drowning we will focus on the pre-, syn, and post-drowning sediments by determining their ages and composition. New seismic data collected during the CARAMBAR 1 cruise allow the drill sites of ODP Leg 101 and 166 to be correlated to the seismic data for the first time. Seismic-core correlation of the ODP Sites 626 and 1007 will provide the data for the precise dating of the seismic horizon, including the onset of drift deposition. Dating of hardgrounds on the Pourtales Terrace will produce independent timing of the partial drowning of the Terrace. A causal relationship between partial drowning and current onset is likely if the two dates are similar.

SIGNIFICANCE

The impact of paleoceanographic changes, in particular currents, on the evolution of carbonate platforms is still not fully understood. This study likely shows how these oceanographic changes, together with tectonic and eustatic histories, need to be taken into account in order to correctly reconstruct the depositional architecture of a carbonate platform.

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PETROPHYSICAL CALIBRATION OF THE COARSE-GRAINED CARBONATE DRIFT FAN, MALDIVES (YEAR 2)

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PROJECT OBJECTIVES

- Comprehensively describe the carbonate drift fan in the Kardiva Channel that includes the sedimentologic characteristics, petrophysical properties, and the seismic signature.
- To reach these goals we will perform the following tasks:
  - Laboratory measurements of porosity, permeability, velocity, and resistivity and relate these properties to the facies, diagenesis, and pore structure of each plug.
  - Measure pore geometries through thin section and SEM analysis.
  - Correlate lithology to logs and seismic data for a thorough calibration of the seismic and log facies of the drift fan.

PROJECT RATIONALE

One of the discoveries of IODP Expedition 359 to the Maldives was that the current deposits in the Kardiva Channel form a drift fan (Fig. 1). The drift origin of the deposits was recognized on the seismic data based on the geometries (Lüdmann et al., 2013), but the cores revealed a facies that has far-reaching implications for interpretations of neritic carbonates. No such system has been reported for carbonates before. Thus, a comprehensive documentation of the lithology, seismic and log facies, as well as diagenesis and petrophysical properties of the drift fan is needed. This documentation will be achieved in a collaborative effort that started with the documentation of the sedimentology and seismic facies by Thomas Lüdmann on behalf of the entire scientific party.

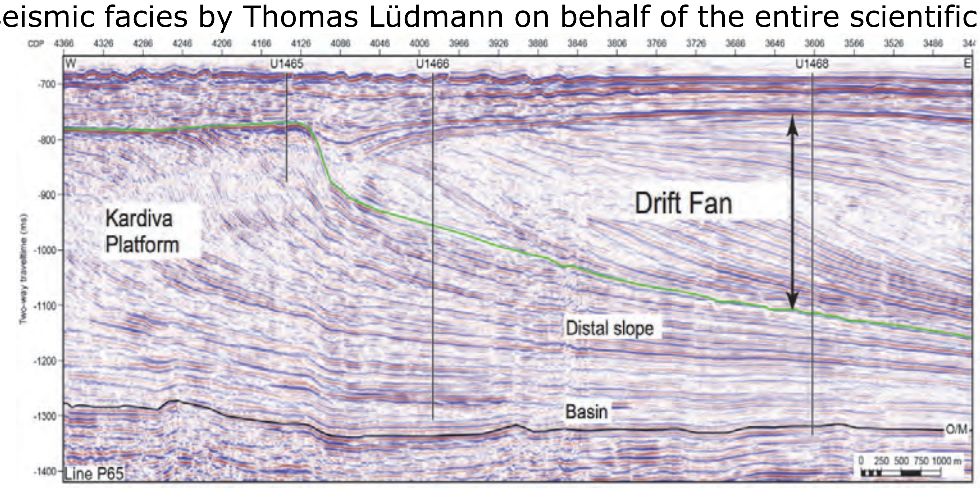

Figure 1. Seismic image of the drift fan in the Kardiva Channel. This unique current-deposited system is a succession of coarse-grained carbonates with high porosity with excellent reservoir qualities.

SCOPE OF WORK

The sedimentologic description of the drift fan will rely on core descriptions made by the shipboard scientific party. Laboratory measurements made on core plug samples from these cores will be used to calibrate the petrophysical properties. The core-log correlation will be made in collaboration with Angela Slagle and the seismic correlations with Thomas Lüdmann and Christian Betzler.

For the petrophysical characterization of the contourite fan, we will measure porosity, permeability, velocity, and resistivity. Velocity and resistivity measurements will be conducted under variable pressure conditions to simulate the burial depth of the samples. This data set will be compared to the log data and both will be correlated to the lithologic and seismic facies.

In addition to the laboratory measurements, we will investigate the pore structure with digital image analysis (DIA). The DIA is able to quantify the pore structure that influences both velocity and resistivity variations at any given porosity.

The high porosity of up to 60% in these deposits indicates secondary porosity development. In a related study, the role of celestine formation and dissolution will be investigated as an important process affecting the occlusion and preservation of porosity (see Swart et al., this volume).

The data set will also be compared to the petrophysical characteristics of the drift deposits on the Marion Plateau and the Cretaceous Orfento Formation in the Maiella Mountains. Both laboratory measurements and log data already exist (Ehrenberg et al., 2004; Eberli et al., 2010; Maura, 2013).

SIGNIFICANCE

The documentation of this coarse-grained drift fan in carbonates will have major implications for carbonate sedimentology. It is a new sedimentary system that has not been described before. The comprehensive documentation of this carbonate contourite fan will prompt the re-interpretation of deposits with these characteristics, such as neritic shoals or prograding delta lobes. The coarse nature and the high porosity make these deposits potentially an important reservoir facies.

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TESTING THE EXTENDED BIOT THEORY IN CARBONATES OF THE MALDIVES

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PROJECT OBJECTIVES

- Test the Extended Biot Theory on core and logs from IODP Site U1467 by:
  - Calculating the pore shape parameter γ_k from laboratory measurements of porosity and p-wave and shear wave velocity.
  - Assessing the pore structure with digital image analysis and relating it to the theoretical pore shape parameter γ_k.
  - Correlating γ_k to permeability.

PROJECT RATIONALE

The Extended Biot Theory captures theoretical pore structure variations in a term called γ_k, which uniquely quantifies velocity variations at a given porosity (Fig. 1; Sun, 1994; Weger, 2006). Other theoretical equations of poro-elasticity do not account for pore structure and thus produce large uncertainties when relating porosity to velocity in carbonates. Because the pore shape factor is directly linked to the pore structure, it links sonic velocity to permeability. Laboratory measurements of discrete samples have shown that γ_k indeed relates to the pore structure (Weger, 2006). The next step is to test the Extended Biot Theory with core and log data. During IODP Expedition 359 in the Maldives, the necessary data set was acquired for such a test. At Site U1467, a continuous core through highly porous carbonates was recovered and the

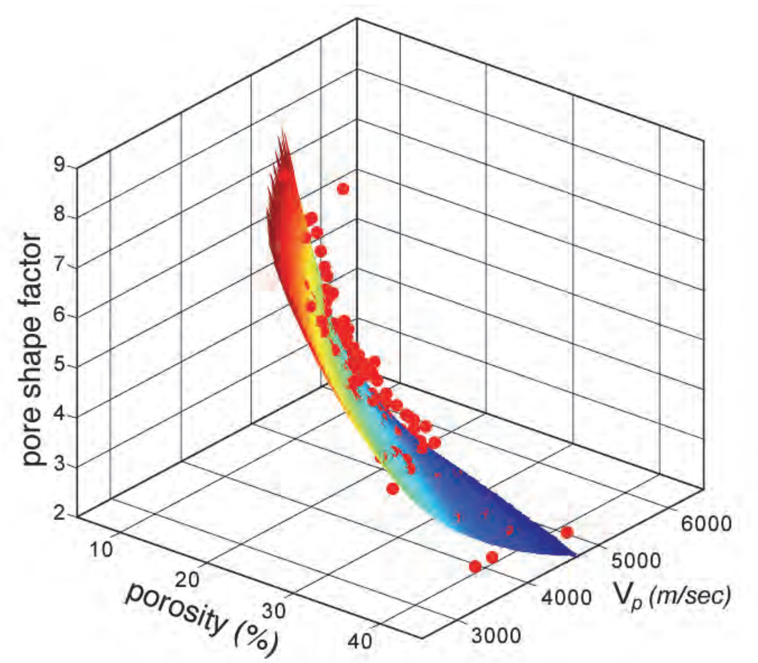

Figure 1. 3-D plot of velocity-porosity and γ_K. Red dots are measured samples. The colored surface is a theoretical surface of γ_K values formed by all possible velocity-porosity combinations for water saturated calcite at a given Vp-Vs ratio.

logs included a DSI (dipole shear imager) sonic log that measures both compressional and shear waves as needed to test the Extended Biot Theory in core and logs.

Scope of Work

At Site U1467 all the data are in hand to test the Extended Biot Theory (Fig. 2). The log data (P and S-waves, density, and porosity) will be used to calculate the theoretical pore shape parameter γ_k. We will measure the acoustic properties in the laboratory on discrete samples and calculate γ_k. Thin sections from the plug samples will be used to determine the pore structure with digital image analysis (DIA) in a workflow described by Weger et al. (2009). The test will be positive if γ_k correlates to permeability.

Significance

The Extended Biot Theory captures the pore structure using acoustic properties and therefore relates acoustic to hydraulic properties, which can potentially help to estimate permeability from seismic data. Because γ_k is derived from theoretical equations it can be calculated from acoustic data like a seismic attribute.

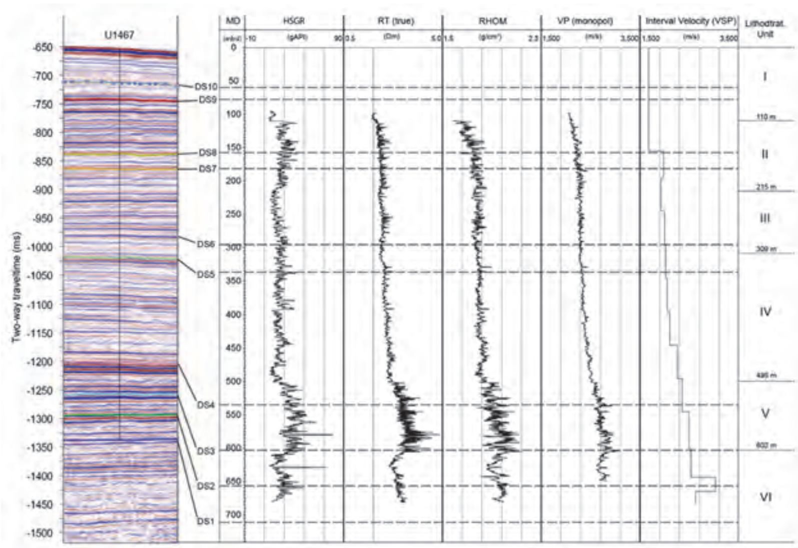

Figure 2. Seismic data of IODP Site U1467 and the corresponding logs allowing the Extended Biot Theory to be tested in carbonates (from Betzler et al., 2016).

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Petrophysical Properties of a Fringing Reef Margin: Pleistocene Dominican Republic

Robert Goodin, James S. Klaus, Donald F. McNeill,
Ralf J. Weger, and Gregor P. Eberli

Project Objectives

- Determine the petrophysical properties (electrical resistivity, ultrasonic velocity, porosity, permeability, and density) of Pleistocene reefal carbonates within DRDP drilling phase II (cores 1, 6, 4, and 5) to expand the petrophysical survey by Ditya (2012) into previously unsampled slope and lowstand reef facies.
- Assess the relative influence of primary depositional facies and subsequent diagenetic alteration as determined by Diaz (2017) on the measured mechanical and petrophysical properties.

Project Rationale

Understanding controls on the petrophysical properties of carbonates is often key to proper interpretation of reservoir properties (porosity, permeability) from either seismic or well-log data (Anselmetti and Eberli, 1993). Petrophysical properties of carbonate sediments exhibit considerable spatial heterogeneity based on grain size, texture, and packing. Furthermore, diagenesis alters the original fabric and rock properties shortly after deposition due to changes in mineralogy and inversion of pore distribution.

The objective of this project is to complete a comprehensive characterization of the mechanical and petrophysical properties of the Pleistocene reefal carbonates of the southern Dominican Republic. Following the initial drilling phase of the Dominican Republic Drilling Project in 2010, a total of 170 plug samples were analyzed for mechanical and petrophysical properties (Ditya, 2012). These samples were collected at a maximum depth of ~60 m, and represented primarily by shallow water depositional facies heavily impacted by meteoric diagenesis. In 2012 a second phase of drilling added new deep wells in both younger and older strata, and extended existing wells to recover the deeper water forereef facies.

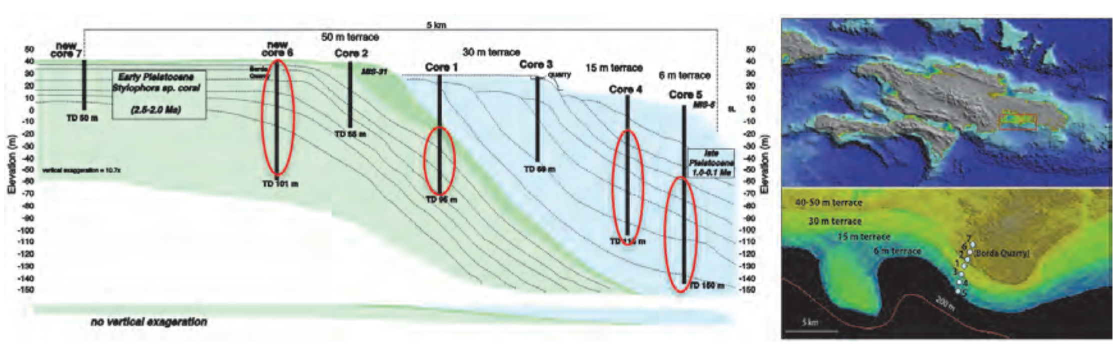


Figure 1. Cross-sectional model of Pliocene to Pleistocene reef sigmoids on the southern coast of the Dominican Republic based on seven drilled boreholes

SCOPE OF WORK

Since the initial drilling of the DR cores we have been working to develop a temporally constrained sequence stratigraphic model for the seven core transect through the Pleistocene reef deposits. Age determinations were based on biostratigraphic markers, strontium isotopes, magnetostratigraphy, and radiometric dating. A revised depositional model constrains the prograding reef system of the southern Dominican Republic to between 1.6 and 0.125 Ma. Once dated, these cores were used to assess accretion and progradation, and reconstruct fringing reef zonation and facies geometries both vertically and perpendicular to the coast.

In addition to the previously sampled cores (Ditya, 2012), an additional 87 one-inch diameter cylindrical plugs with variable lengths were drilled for petrophysical measurements. Plugs were sampled from the cores using a water-cooled diamond drill bit with vertical and horizontal orientation. The ends of the plugs were cut off and then polished within 0.01 mm precision (measured with a micrometer gauge) to create a flat surface for optimizing contact area between sample and sonic or electric transducers. Samples were dried at 60C for 48 hours and then stored in a desiccator box for approximately 24 hours. The dry-mass of the samples were measured to the microgram using a Thomas Scientific T200S electronic scale. Chips from one end of each plug were sent to the University of Iowa's Geology Department for thin section preparation.

Petrophysical measurements will include electrical resistivity, ultrasonic velocity, porosity, permeability, and density. The petrophysical properties will be compared to assess their relationship to each other and for external comparison, for instance: porosity-permeability, porosity-acoustic velocity. The petrophysical properties are then analyzed based on petrographic observations in order to assess a correlation between petrophysical properties and depositional / diagenetic environments.

EXPECTED RESULTS

The Dataset of petrophysical properties will be coupled to geologic parameters:

- Age
- Platform morphology (isolated, shelf, and ramp)
- Climate zone (tropical, cool-water, temperate)
- Depositional environment (top, shoal, slope, basin)
- Type of information (outcrop, subsurface)
- Texture (Dunham)
- Dominant pore type and microporosity
- Sequence stratigraphic position
- Mineralogy

The resulting dataset will be compiled with other well-studied projects to provide an unprecedented catalogue of sample set information with interconnected relationships.

ROCK PHYSICS OBSERVATIONS DURING CONTROLLED MICROBIALLY INDUCED PRECIPITATION

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

PROJECT OBJECTIVES

- To elucidate the involvement of microbes in ooid cementation processes and their potential effect on the acoustic properties of un-cemented ooid sandstone at low pressures.
- Compare the influence of microbially mediated versus inorganic precipitated cements on acoustic velocity and rock strengths of carbonates.

PROJECT RATIONALE

Carbonates are prone to diagenetic alterations that sometimes result in drastic alteration of petrophysical properties. Small amounts of newly formed contact cement can create enormous changes in rock stiffness if deposited precisely at grain contacts, and can act to dramatically increase the stiffness of a particulate aggregate (Dvorkin and Nur, 1996). There is strong evidence that early microbial micritic bridging cements are the start of cementation processes that include fringing cements (Eberli et al., 2017). These cements are influential in determining the rock strengths both with regards to compaction and bulk and shear modulus. The question is whether these early microbial cements produce a significant increase in rock strength that increases velocity and is able to resist compaction.

In previous inorganic precipitation studies at the CSL we have shown that clean ooids can be cemented together by calcium carbonate crystal precipitation in only a few weeks (Fig. 1). Precipitation occurs preferentially at the ooid-to-ooid grain contacts, but sometimes overgrows the entire ooid surface with needle structures. The contact cements are responsible for increasing rock stiffness and thus acoustic velocity. Needle structured crystals on the other hand reduce porosity with very little increase in velocity. The rock undergoes apparent weakening creating a rock framework of lower stiffness for its lower porosity. This study aims to induce microbially mediated cements and test their influence on the elastic properties.

PROJECT OBJECTIVES

In this project, experiments that quantify both the chemical changes in the fluids and the diagenetic and petrophysical changes in the rocks are designed to enhance our understanding of the effects of chemical rock-fluid interaction specifically focusing on the differences between microbial and inorganic precipitation. In particular, the study will capture changes in acoustic velocity and permeability during chemically controlled rock-fluid interaction that causes precipitation in experiments that deliberately enhance or inhibit microbial activity.

SCOPE OF WORK

In this project, experiments will be performed in order to:

Quantify the chemical changes in the fluids and the diagenetic and petrophysical changes in the rocks during different types of precipitation, including inorganic and microbially mediated precipitation. While inorganic precipitation experiments will be undertaken in incubation chambers inoculated with sterilized ooids – to discard any potential microbial involvement in calcification processes –, microbially mediated carbonate precipitation experiments will use an inoculum of freshly collected ooids supplemented with glucose for bacterial growth.

Determine the presence and potential involvement of biofilm extracellular polymeric substances (EPS) in carbonate precipitation at grain-to-grain contact loci and non-contact areas of the grains. The presence and development of EPS will be determined using fluorophore-conjugated lectins. This analysis, which uses confocal laser scanning microscopy (CLSM), will allow the visualization of EPS distribution in the grains via specific binding of lectins to EPS-carbohydrates.

Determine if ACC nanograins can act as precursors of cementation processes in ooids. Detection of ACC will use morphological attributes based on SEM image analyses

KEY DELIVERABLES

A data set will be generated that captures changes in acoustic velocity and fluid flow permeability generated by microbially induced precipitation. High-resolution images using SEM will provide insights regarding the precipitated material and its preferential location within the rock framework.

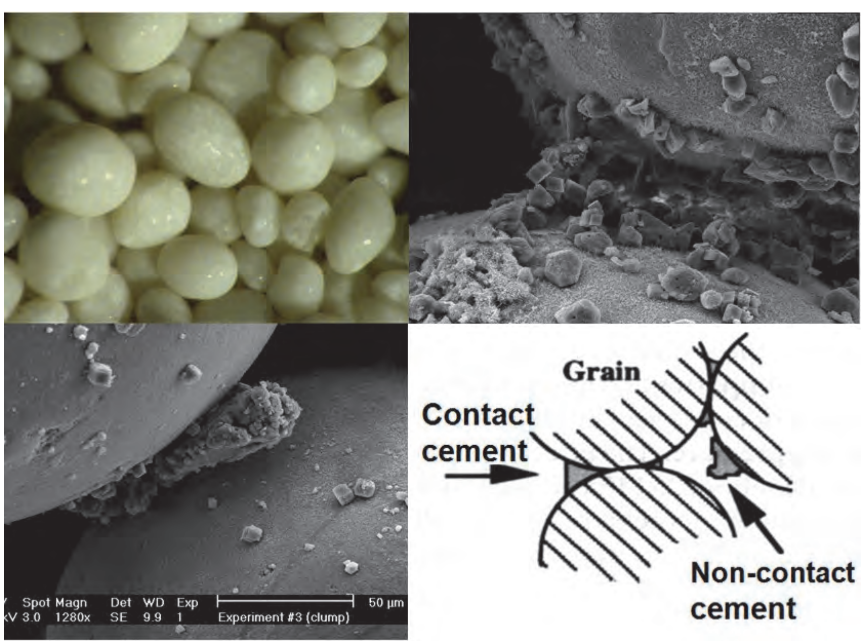


Figure 1: Results of precipitation study. Top right, clean ooids before experiment. Top right and bottom left, calcium carbonate crystals precipitated during the experiment. Precipitation occurs preferentially at the ooid-to-ooid grain contacts. Bottom right, illustration of contact vs. non-contact cement (from Dvorkin and Nur, 1996).

COMPARING THE PETROPHYSICAL CHARACTERISTICS OF UNCONVENTIONAL CARBONATE RESERVOIRS (VACA MUERTA, MISS LIME, BAKKEN, AND EAGLEFORD)

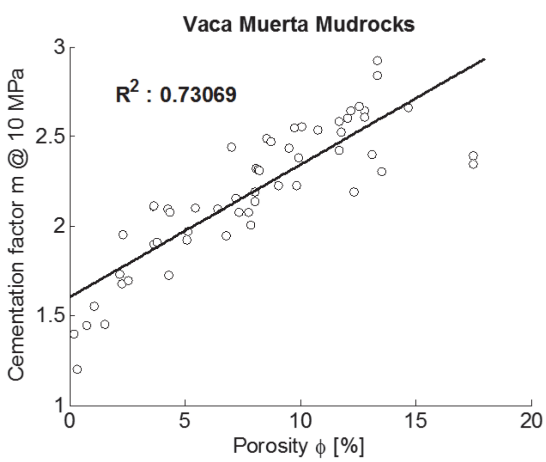
Ralf J. Weger, G. Michael Grammer[1], and Gregor P. Eberli and students
[1)] *Boone Pickens School of Geology, Oklahoma State University*

PROJECT OBJECTIVES

- Determine baseline values and the range of petrophysical characteristics (sonic velocity, resistivity, and nuclear magnetic resonance) in different carbonate mudrocks and tie these parameters to pore system architecture and permeability of various carbonate mudrocks.
- Continue to evaluate and characterize the sonic, resistivity and NMR response of the Vaca Muerta and Miss Lime and add samples from the Bakken and Eagleford Shale reservoirs in attempt to establish patterns that can be utilized in these and other mudrock reservoirs.
- Tie rock and mechanical properties to varying facies types and position within a sequence stratigraphic framework to evaluate the potential to maximize predictability of reservoir facies from wireline logs.

PROJECT RATIONALE AND GOALS

Unconventional carbonate reservoirs such as the Vaca Muerta, Miss Lime, Bakken, and Eagleford are characterized by generally low porosity with extremely low permeability values, often in the 0.01 to 0.001MD range (or lower). Due to the small size (micro- to nano-meter scale) and complex spatial distribution of the pores and pore throats in carbonate-rich mudrock reservoirs, evaluating and predicting the controls of pore structure and associated petrophysical properties such as porosity, permeability and fluid saturation is problematic. The goal of this study is to characterize pore types



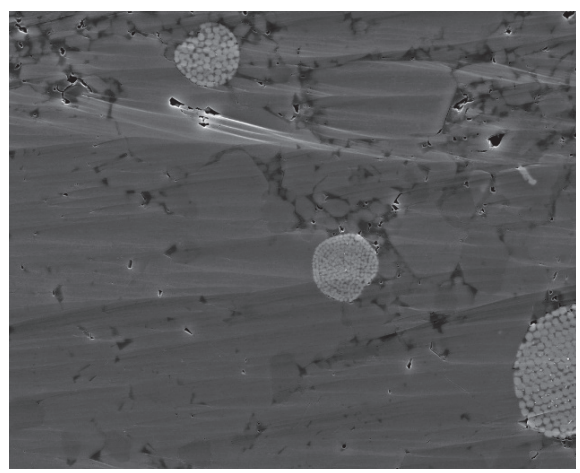


Figure 1. Left: Porosity vs cementation factor (m) cross-plot for 56 mudrock samples from the Vaca Muerta Formation with high correlation coefficient of R^2 = 0.73. Right: BIB-SEM image of Pyrite framboids in sample P03_1A with a low cementation factor of m = 1.27. (modified from Norbisrath, 2017).

and the pore system architecture of carbonate mudrocks and to tie these pore systems to key petrophysical responses to establish baseline characteristics and ranges of values that can be utilized in maximizing production in these unconventional reservoirs.

The systematic comparison of the petrophysical properties of the various mudstones in the above-mentioned reservoirs will likely result in similarities in some properties, while other petrophysical parameters may be different due to compositional, textural and/or diagenetic variations. The proposed study will establish the key controls on varying petrophysical responses and provide insight into how reservoir quality may be better predicted not only in the studied rocks, but also in newly discovered unconventional reservoirs.

APPROACH

Previous studies have tied petrophysical properties to pore architectural parameters, i.e., size, shape, and overall geometry, to macroporosity (Anselmetti et al., 1998; Weger et al., 2009) and microporosity in conventional carbonate reservoirs (Norbisrath et al., 2016). The small size (micro- to nano-meter scale) and complexity of the pore types and associated pore throats in unconventional reservoirs, however, are a challenge for correlating sonic velocity, resistivity, and other petrophysical responses to pore structure. Recent studies (Vanden Berg and Grammer, 2016) on carbonate mudrocks have found that expected petrophysical relationships between pore structure and laboratory-measured parameters such as sonic velocity and permeability, which are well-defined in conventional carbonate reservoirs, may not be readily apparent in carbonate mudrocks with predominantly micro- to nano-meter scale pores. Vanden Berg and Grammer (2016) suggest that mixed mineralogical compositions and post-depositional diagenesis such as mineralization along pore throats may be a major process that yields complex pore systems which complicate flow and affects petrophysical response. In addition, the composition (carbonate content, TOC and clay volume) influences the variability of acoustic properties on both log and seismic scale (Singleton, 2015).

Composition of the samples will be evaluated the following way: Carbonate content is determined by crushing part of the sample and dissolving the carbonate portion using 10% hydrochloric acid. The remaining non-carbonate portion is then used to determine %TOC on a Costech Elemental Analyzer coupled to a Delta V Advantage Mass Spectrometer. XRD analysis on crushed bulk materials of the plug established the main mineral constituents of the samples and broad-ion-beam milled SEM images will used to qualitatively determine some of the clay and other components (Fig. 1). Broad-ion-beam milled SEM images will also be used to characterize the micro- and nano-pore structure in the mudrocks.

In addition to continuing the characterization of the samples from the standpoint of the sonic velocity response and the associated complex resistivity parameters associated with these rocks (e.g. Norbisrath et al., 2017), we also plan an analysis of the NMR response in these complex and low permeability systems. Recent work has shown that the NMR response of very low permeability carbonate reservoirs are also variable from conventional carbonate reservoirs. Data from NMR provides crucial information on pore-size distributions, porosity and permeability to saturation and fluid(s) mobility. In combination with petrographic methods, the qualitative analysis of NMR data has also been utilized to infer rock fabric and dominant pore types in carbonate rocks. Successful applications of NMR in unconventional reservoirs include pore network analysis, permeability estimations, and differentiation between mineral- and organic matter-hosted porosity (e.g. Rylander et al. 2013). Incorporating quantitative pore structure data and petrographic descriptions with NMR data will provide a tie between rock fabric, the prevailing pore system, and the petrophysical response in carbonate mudrocks.

Variations in composition, in particular carbonate content and TOC, in any given field are to a large extent related to the position of the sample within the sequence stratigraphic framework. As a result, the petrophysical and mechanical properties of the formation will vary vertically, dividing the succession into zones of different reservoir quality. To address this

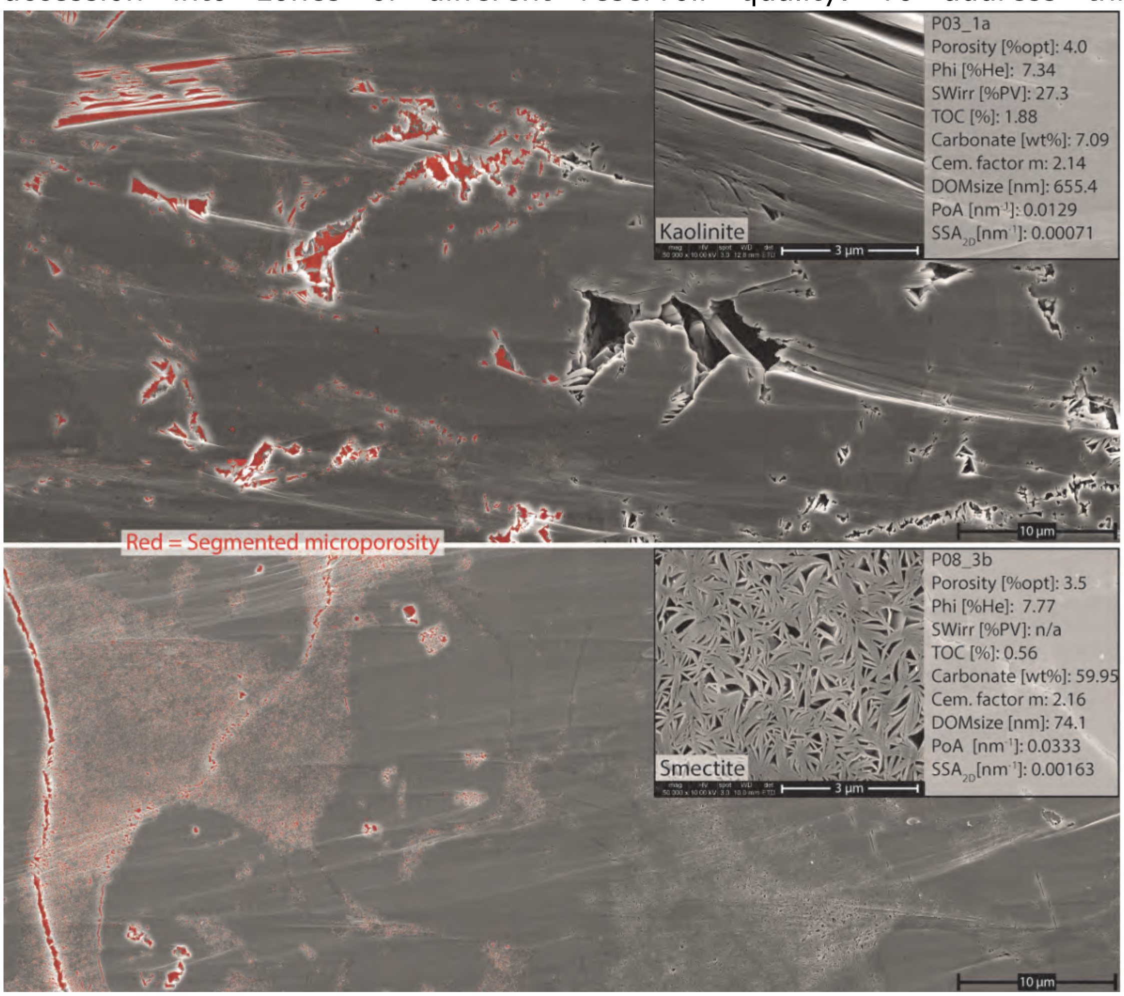


Figure 2. Example of broad-ion-beam milling SEM mosaics consisting of 50 images each at 15,000x magnification and 9.6 nm pixel side length that image the micro and nano-porosity. Segmented microporosity in red. Inserts show petrophysical and mineralogical data and a zoom into different clay pore structures at 50,000x magnification.

stratigraphic compartmentalization, we will place the rock properties into a sequence stratigraphic framework and we will calculate mechanical rock properties using a rock physics model. This analysis will be performed in the Vaca Muerta and the Miss Lime Formations where a sequence stratigraphic analysis has already been made.

SIGNIFICANCE

The assemblage of comprehensive petrophysical data sets from different organic-rich mudrock formations is expected to produce patterns of similarity and differences. The simultaneously assembled geologic information for each plug sample, such as pore structure, composition and TOC content, will aid in explaining the causes for both the similarities and differences. Taken together the results will provide information on which of the rock and mechanical properties are constant in all investigated mudrock formations and which are unique or more local in nature. As such the baseline characteristics and ranges of values can be utilized in maximizing production in these and other unconventional carbonate mudrock reservoirs.

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ACOUSTIC AND ELECTRICAL CALIBRATION OF DIFFERENT VACA MUERTA FACIES (YEAR 3)

Mustafa K. Yüksek, Ralf J. Weger, and Gregor P. Eberli

PROJECT OBJECTIVES

- Produce a comprehensive petrophysical data set (porosity, acoustic velocity, resistivity, permeability, and pore structure) of the facies in the Vaca Muerta Formation.
- Establish an acoustic and electrical data set for each of the Vaca Muerta facies in order to facilitate well log interpretation.
- Define the control of mineralogy and clay content on the petrophysical properties and, in particular, the acoustic anisotropy.
- Examine the relationship between clay content, acoustic velocity, and resistivity to find differences between ductile and brittle behavior of the mudstones of the Vaca Muerta Formation.

PROJECT RATIONALE

Unconventional resource plays rely primarily on seismic data to recognize target intervals suitable for hydraulic fracturing. Successful exploitation of such plays requires reservoir zones to be brittle, porous, and rich in hydrocarbons. These properties are largely dependent on the composition of the background rock, and TOC and carbonate content. In addition, these properties have to be identifiable from the seismic signature. Some efforts have been made to calibrate different seismic and acoustic impedance facies in the Vaca Muerta with core data, but few laboratory calibrations have been published. Thus, this study aims to generate laboratory measurements of horizontal and vertical acoustic velocities as an aid to assess the mechanical properties of different facies within the Vaca Muerta Formation.

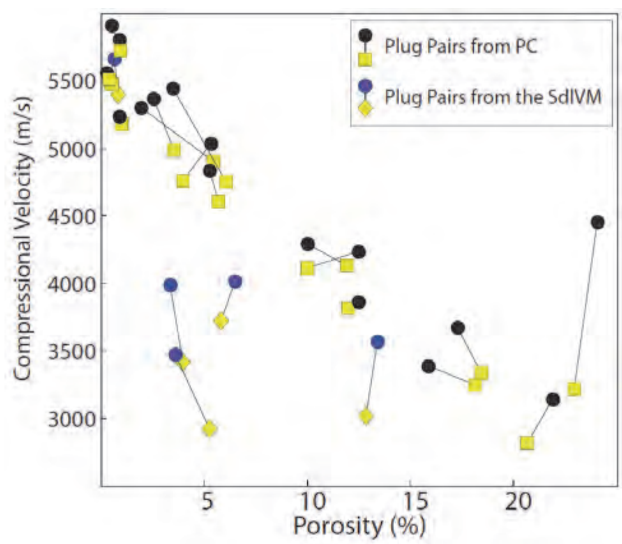

Figure 1. Anisotropy measurements performed until early 2017. Large differences between horizontal and vertical velocities emphasizes the importance of accurate anisotropy determination in Vaca Muerta mudstones.

SCOPE OF WORK

Unaltered plug samples (little to no surface exposure) of representative facies and rock types within the Vaca Muerta Formation were retrieved from different outcrop locations by drilling over 100 m of short cores (3” diameter). Over 40 m of recovered core, strategically distributed throughout the Puerta Curaco reference section, allowed all dominant facies of the Vaca Muerta Formation to be sampled.

We plan to measure acoustic velocity, porosity and resistivity of all samples and determine the mineralogy using XRD (X-ray diffraction). Chemical methods will be used to determine the carbonate content and the amount of Total Organic Carbon (TOC) will be measured on an Elemental Analyzer. Acoustic velocities will be measured on over 150 plug samples from both short core and sub-surface samples, while porosity will be measured for all plug samples under a variety of pressure conditions and saturation states. Furthermore, we will extract core plugs at three different angles to assess the anisotropy within the samples. The measured acoustic data is compared to data from mudstones of different ages and locations. Some of these measurements have already been completed and provide the first results (Figs 1 and 2).

FIRST RESULTS

Porosity varies between 1-29%, while compressional velocities vary between 3 and 5.5 km/sec and their Poisson's-ratio ranges from 0.19 to 0.33. Carbonate content is between 1% and 89%, while TOC varies between 1-10%. The Vaca Muerta mudstones show substantially lower compressional and shear velocities than most other datasets. In addition, Vaca Muerta mudstones display a very high degree of anisotropy (VTI) with an average ε of 0.06, ranging from 1-15%.

Figure 2. Example of core plug extraction at several different angles at almost the same sampling location.

SIGNIFICANCE

Well documented acoustic properties of the different facies in the Vaca Muerta Formation will not only improve well log interpretation, but enhance understanding and the ability to interpret seismic data and its attributes. The study will produce a comprehensive data set of mineralogical and petrophysical properties currently unavailable for organic-rich fissile mudstones and will aid and improve seismic processing and result in better imaging.

LITHOLOGIC AND GEOCHEMICAL CALIBRATION OF THE BASAL CLINOFORMS IN THE SIERRA THE LA VACA MUERTA, NEUQUÉN BASIN, ARGENTINA

Laura E. Rueda, Gregor P. Eberli, Max Tenaglia, Ralf J. Weger,
Donald F. McNeill, Larry Peterson, and Peter K. Swart

PROJECT OBJECTIVE

- Document the facies distribution of the early to late Tithonian prograding clinoforms that contain the first high TOC interval in the Neuquén Basin.
- Correlate high-resolution geochemical logs with lithological logs in the different depositional sub-environments to produce a geochemical calibration of the various facies in the southern, proximal portion of the basin located in the Sierra de la Vaca Muerta (SdlVM).
- Produce a detailed model of the depositional processes within the sequence stratigraphic subdivisions.

PROJECT RATIONALE

The Tithonian- Valanginian Vaca Muerta Formation contains the sediments of the foresets and bottomsets of the prograding clinoforms that fill the Neuquén Basin. Facies and cycles change vertically and laterally within the clinoforms. The high-resolution geochemical and lithological study of stratigraphic sections in outcrops complemented with detailed analysis of short cores is required in order to quantify the vertical and lateral variations of the facies and cycles across the clinoforms and to correlate them to log data.

Figure 1. Location map of the Neuquén Basin and areas of study: Sierra de la Vaca Muerta (SdlVM), and Puerta Curaco (PC) section.

PROJECT DESCRIPTION

In this study, the lithological and geochemical characteristics of sections and cores from the sections in the SdlVM (Fig. 1) will be examined to generate a composite transect across the oldest clinoforms in the basin that contain the first interval of high total organic carbon (TOC). The high-resolution characterization of stratigraphic sections and 1 m cores from outcrops exposed in the SdlVM (Fig. 1) will be completed using detailed lithological descriptions in situ and by performing geochemical analyses in the laboratory that include: isotopic $\delta^{13}C$ and $\delta^{15}N$ analysis; mineral and components identification using thin sections, X-ray Diffraction (XRD) and Near-Infrared Spectroscopy (NIR). Also, ultra-high-resolution elemental analysis (0.5 mm) in short cores will be conducted in order to find a series of elemental proxies. Correlations between the detailed logs and core descriptions and the geochemical findings will aid in the definition and interpretation of facies and cycles.

PRELIMINARY FINDINGS AND EXPECTED RESULTS

In the proximal position, in the SdlVM (Fig. 1), six stratigraphic sections were measured and described in detail and 27 1 m cores were taken in the sections for this study. The composite transect, with a thickness of around 650 m, covers the deposits of the Middle to Upper Tithonian. The studied outcrops in the SdlVM (Fig. 1) expose sedimentary structures like cross-bedding, faint and fine-plane and inclined parallel-lamination, and small-scale ripples but also a large mass transport complex (Fig. 2).

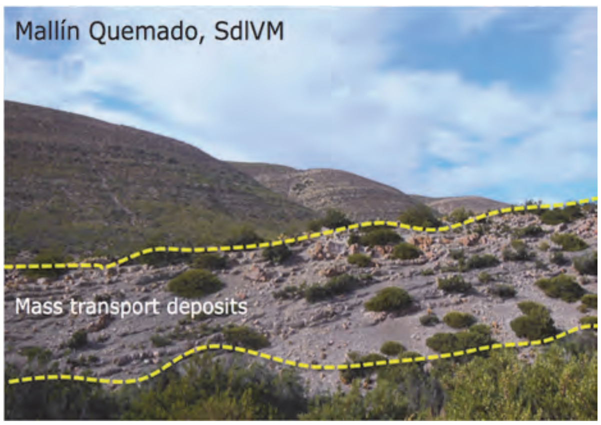

Figure 2. Large mass transport complex in the basal Vaca Muerta Formation was traced along the foothills of the SdlVM for around 2 km in the Mallín Quemado area.

The studied transect at the base of the Vaca Muerta will complement the stratigraphic framework assembled by Zeller (2013). The findings of this study, a composite proximal transect section, will be correlated to a more distal section, the Puerta Curaco (PC) reference section, measured near the town of Chos Malal (Fig. 1). The PC section in the basin center is about 800 m thick and has already been measured and used to define 11 stratigraphic sequences. The PC section and the new section obtained from this study will be correlated in order to study the lateral variations in facies and cycles and to compare sequence thicknesses variations within the clinoforms. This correlation from proximal to distal will give insights into facies, cycles and sequences variability in the Neuquén Basin.

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CONCRETIONS AS COMPACTION PROXIES IN THE VACA MUERTA (NEUQUÉN BASIN, ARGENTINA)

Donald F. McNeill, Jara S.D. Schnyder, Ralf Weger, and Gregor P. Eberli

PROJECT OBJECTIVES

- To measure the compaction in lime-rich mudrock using early cemented concretions as a pre-compaction reference.

PROJECT RATIONALE

Concretions retain original (or close to original) sediment thickness due to their early, rapid, and pervasive pre-burial cementation near the sediment-water interface. This preservation of original sediment thickness is confirmed by petrographic studies that show a lack of compaction in mud peloids and very delicate skeletal grains (Fig. 1A). In addition, stable isotope data from concretion cements suggest early, pre-compaction seafloor cementation driven by bacterial sulfate reduction through diffusion with normal seawater (sulfate, Ca^{2+} supply).

PROJECT DESCRIPTION

The compaction of the surrounding host sediment, in this case the fissile mudstones around the concretions, is very clearly visible in strain shadows around the nodular concretions recovered in core (Fig. 1B) and seen in outcrop (Fig. 2). From the initial sediment thickness (T_0) compared to the compacted sediment in the host sediment (T_c) we can calculate compaction strain using the following relationship:

$$\frac{T_0 - T_c}{T_0} = \varepsilon \qquad (1)$$

This was done in a preliminary attempt for the concretion shown in Figure 1, where a compaction strain of -0.914 (91.4%) was calculated. Obviously, since this has only been done so far on one single concretion it is hardly

Figure 1. (left) Example of the early, pervasive calcite cementation in Vaca Muerta concretions. Delicate large radiolaria (center, center right) are preserved with extensive ornamentation. (right) Initial sediment thickness T_0 and sediment thickness after compaction T_c can be used to calculate compaction strain ε. Puerta Curaco section short core SC-PC3-129.

representative. Based on the extensive dataset available from the Vaca Muerta and especially basinal outcrops, we should be able to obtain more results in order to assess a statistically representative compaction strain parameter.

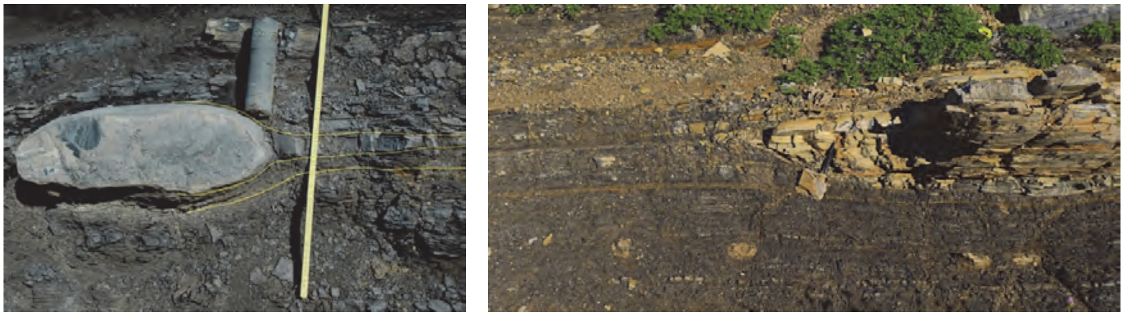

Figure 2. Typical isolated concretions in the Vaca Muerta Formation that can be used to measure the compaction strain between the concretions and the adjacent mudrock.

Compaction strain can be used to approximate paleoporosity using the following relationship (Jacob, 1949):

$$\phi_{palaeo} = \frac{\phi_0 + 100\varepsilon}{\varepsilon + 1} \qquad (2)$$

Porosity is expressed in volume percent. The results depend on reasonable estimates of Φ_0, which is porosity at the onset of compaction. Such a value could be approximated based on textural analysis of the concretions (diagenetic carbonate in void spaces, volume percent of carbonate cement in pores at time of concretion growth, Raiswell, 1971). We have estimated a value of >40% in fine sand concretions, a very general estimate. However, higher original porosity values (~70-80%) can be expected for modern marine clay deposits (lime mud and clay minerals) close to the water-sediment interface (Velde, 1996). An initial porosity value of 40%, is likely conservative, as many Vaca Muerta concretion thin section estimates are >60% cement. SEM images from strain shadows could also give us clearer evidence about porosity values at the onset of compaction. Obviously, this is only valid if we can expect a negligible amount of compaction in the strain shadow of the concretion.

Expected Results

This project will assemble a dataset on the compaction properties of lime-rich mudrock in deposits that contain variable amounts of organic matter.

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GLOBAL SYNCHRONOUS CHANGES IN THE CARBON ISOTOPIC COMPOSITION OF PLATFORM-DERIVED SEDIMENTS

Peter K. Swart and Amanda M. Oehlert

PROJECT OBJECTIVES

- To correlate the carbon isotopic composition of periplatform sediments from globally disparate locations.
- To ascertain the veracity of carbon isotopic archives in the ancient record using Modern and Neogene strata.

PROJECT RATIONALE

Platform-derived sediments are the major sedimentary archive of the early history of the Earth (> 200 Ma). Many studies have used the carbon isotopic composition ($\delta^{13}C$) of such sediments for correlative purposes as well as a means of understanding the global carbon cycle (Halverson et al., 2007; Husson et al., 2015; Swanson-Hysell et al., 2010). However, in order to understand the mechanisms operating to affect such variations, studies are necessary on Modern and Neogene sediments so that any changes related to processes such as diagenesis and source can be properly understood (Swart and Eberli, 2005; Swart et al., 2009). Such studies have suggested that periplatform sediments over the past 10 Myrs do not record the $\delta^{13}C$ values of open oceanic dissolved inorganic carbon (DIC), but rather reflect the varying input from platform-derived sediments relative to oceanic sediments. In this study, we intend to investigate $\delta^{13}C$ values in carbonates from widely separated carbonate platforms in order to ascertain whether the patterns documented in sediments over the past 10 Myr are also present in older portions of the record.

SCOPE OF WORK

Leg 166 of the Ocean Drilling Program drilled seven sites along two transects along the western margin of the Bahamas. The geochemical records in these cores have already been investigated in a number of studies (Higgins et al., 2018; Swart, 2008; Swart and Eberli, 2005). In addition to the Bahamas, we have material from the Nicaraguan Rise (ODP Site 1000)(Sigurdsson et al., 1997) and from the Maldives (IODP Sites U1466-U1471) (Betzler et al., 2016). We have already analyzed Sites 1000 and U1467 at high resolution and made a tentative correlation with Site 1006. This correlation, shown in Figure 1, appears to show striking similarities between the isotopic profile at each site. The upper 5 Myrs of each record shows a trend towards more positive values, a pattern previously interpreted as reflecting the influence of sedimentation from adjacent shallow-water carbonate platforms (Swart, 2008; Swart and Eberli, 2005). In the older portion of the record (> 5 Ma), the sediments may be more influenced by pelagic sedimentation, perhaps recording global changes in the $\delta^{13}C$ values of oceanic DIC. Evidence for this interpretation is given by the remarkably similar variations in the $\delta^{13}C$ values between the three

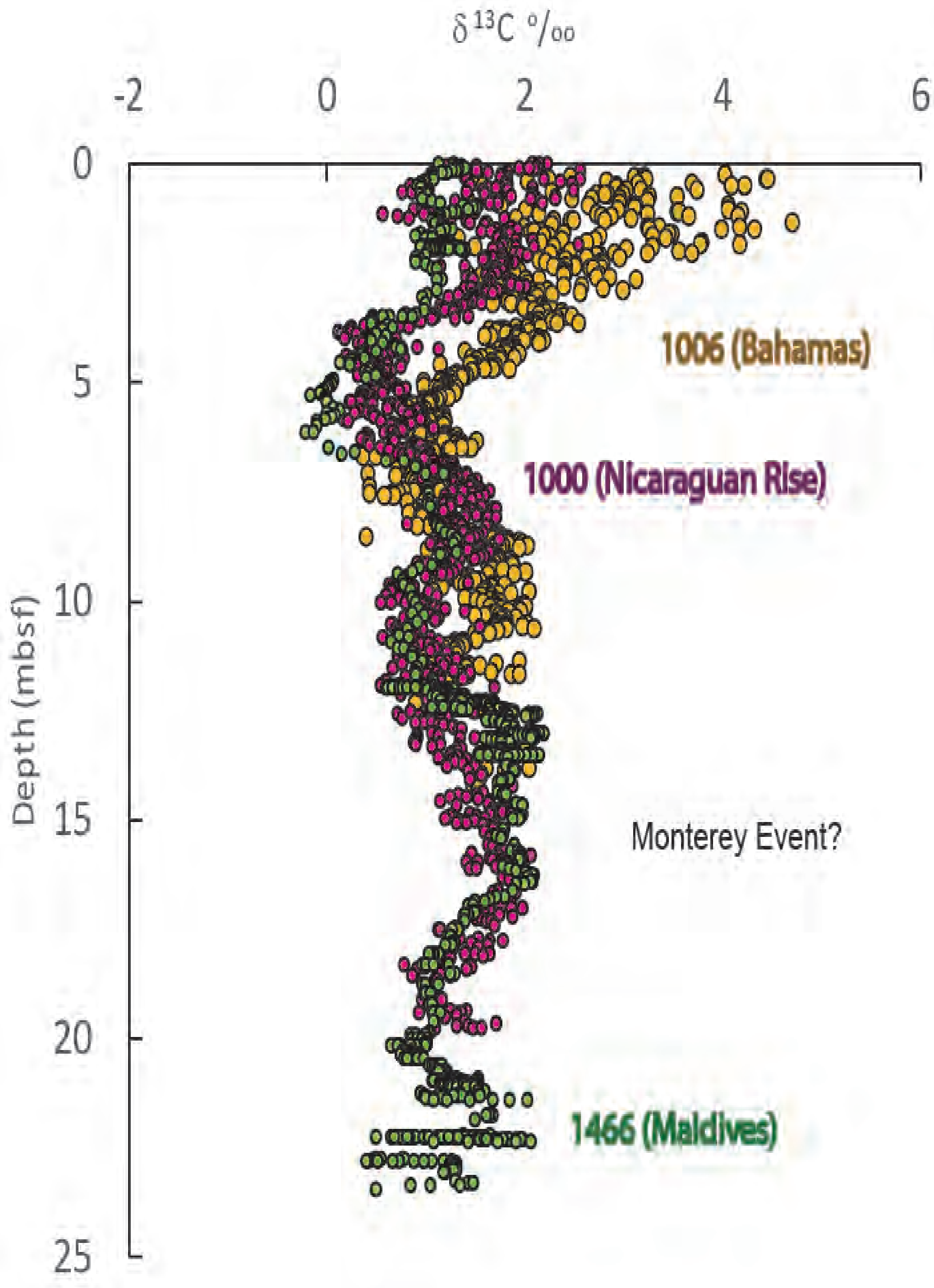

Figure 1: Changes in the $\delta^{13}C$ of the carbonate component in three cores from Bahamas, Maldives, and Nicaraguan Rise. The Monterey event (Berger and Vincent, 1986; Woodruff and Savin, 1991), an increase in the $\delta^{13}C$ values between 13 and 17Ma, is seen in Site 1000 and U1466.

sites despite their wide geographical separation. Slight differences between the records may be a result of inconsistencies in the sedimentation rate at each site and these discrepancies will be investigated during the course of this study.

We will also analyze the $\delta^{13}C$ values of the organic material from these cores and correlate these values with the values of the carbonates and between cores. One early indication that there may be a global signal in the older portions of these records is the observation of what appears to be a broad increase in the $\delta^{13}C$ values in all three cores between 13 and 17 Ma which may represent the Monterey carbon anomaly. The Monterey carbon isotopic anomaly is a series of six maxima in the $\delta^{13}C$ values between approximately 13 and 17 Ma, first recognized by Woodruff and Savin (1991). While Mutti (2000) has previously suggested that this anomaly could be recognized in Site 1000, it has not been seen in either the Bahamas or the Indian Ocean. Figure 2 shows a close up of the C isotopic record from U1466 between 10 and 20 Ma and possibly the six cycles in the $\delta^{13}C$ values can be seen in the record.

SIGNIFICANCE

The record of $\delta^{13}C$ values from periplatform sediments has been widely used, both for stratigraphic purposes and to reconstruct the global carbon cycle (Hayes et al., 1999). The proposed work will help ascertain the veracity of such archives in the ancient record.

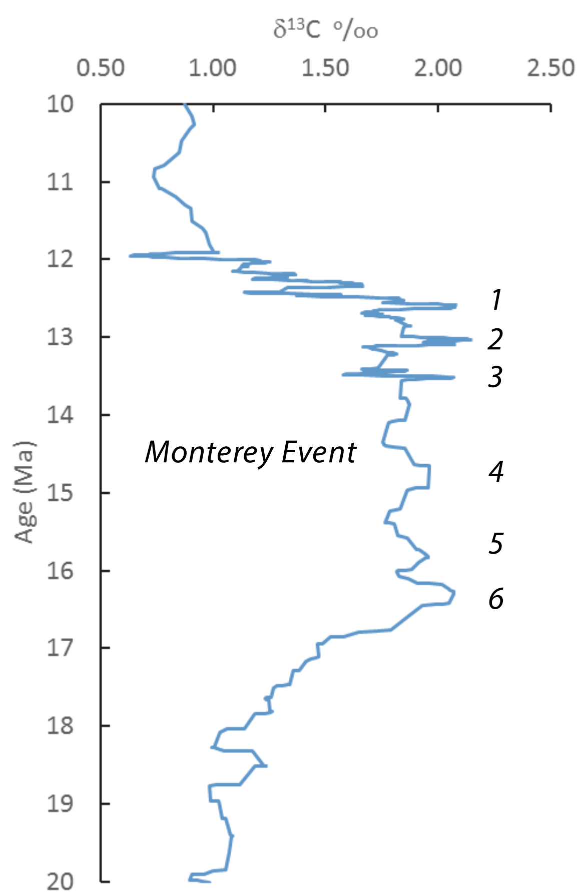

Figure 2: Carbon isotopic composition of sediments from Site U1466 between 10 and 20 Ma. The broad increase in $\delta^{13}C$ values denotes the position of the Monterey anomaly. Within the anomaly there have been six C isotopic anomalies identified.

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THE INFLUENCE OF DIAGENESIS ON THE C, B, AND S ISOTOPIC COMPOSITION OF CARBONATE SEDIMENTS

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PROJECT OBJECTIVES

- To rigorously calibrate the stable isotopes of B, C, and S so that these chemical proxies can be used to study both the paleoenvironment and the diagenesis of carbonates in older time periods.
- To use compound specific C isotopic analysis to confirm interpretations made using bulk organic $\delta^{13}C$ values during freshwater diagenesis.
- To investigate the behavior of B and S stable isotopes during meteoric and marine diagenesis.

PROJECT RATIONALE

Chemical proxies such as C ($\delta^{13}C$), B ($\delta^{11}B$), and S ($\delta^{34}S$) isotopes measured within carbonate rocks and organic material have been widely used to understand changes in the Earth's environment through time. For example, changes in $\delta^{13}C$ values have been suggested to indicate changes in the burial of organic material (Hayes et al., 1999; Saltzman et al., 2004), changes in $\delta^{11}B$ values indicate variations in the pH of the oceans (Kasemann et al., 2010; Ohnemueller et al., 2014), and variations in $\delta^{34}S$ indicate changes in the anoxic state of the oceans and the concentration of O_2 in the atmosphere (Jenkyns, 2010; Lyons and Gill, 2010). However, recent work by various authors has cast some doubt on some of these interpretations.

Carbon: While carbonate sediments deposited in the deep marine environment are immune to meteoric diagenesis, they do not necessarily record changes in the $\delta^{13}C$ values of the dissolved inorganic carbon in the oceans. In particular, sediments deposited adjacent to carbonate platforms or in epeiric seas, the type of record preserved in the deep geological record, can be composed of different skeletal allochems all with varying $\delta^{13}C$ values (Swart and Eberli, 2005). Within the meteoric realm the $\delta^{13}C$ values of the carbonates are heavily affected by dissolution and precipitation reactions, yielding very negative $\delta^{13}C$ values (Melim et al., 2001). As meteoric diagenesis occurs on a global scale, similar negative signals can be seen in globally disparate settings, a phenomenon often cited as indicating original signals (Swart and Kennedy, 2012).

Boron: The $\delta^{11}B$ value of Modern marine carbonates has been widely used as a paleo-pH proxy (Honisch et al., 2004). Several studies have applied the method to important geological transitions, characterized by large $\delta^{13}C$ values such as the Permian-Triassic boundary and the Marinoan glacial event (Kasemann et al., 2010; Ohnemueller et al., 2014) and claimed pH drops associated with these boundaries. However, studies documenting the behavior of $\delta^{11}B$ are lacking although a recent study did show that large changes in $\delta^{11}B$ values can be associated with freshwater diagenesis (Stewart et al., 2015).

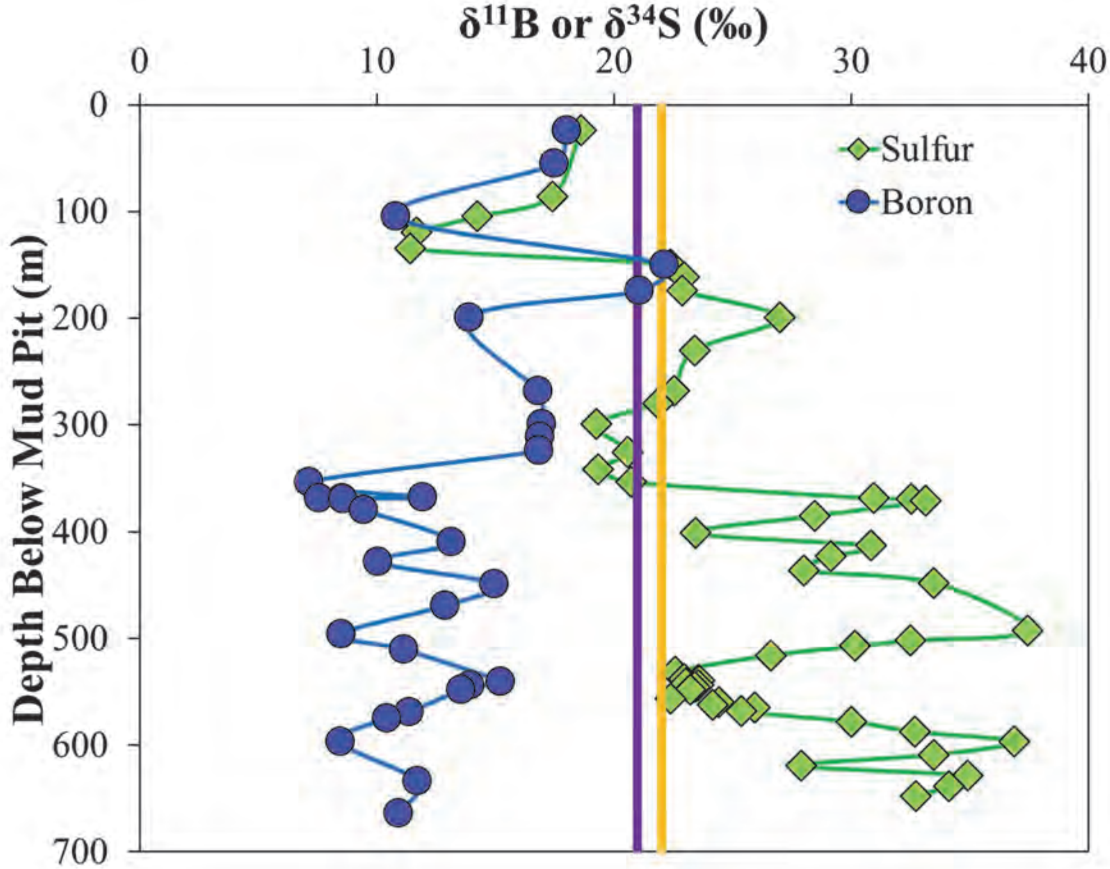

Figure 1: Variations in the B (34 samples) and S (63 samples) isotopes from the Clino core. The two vertical lines reflect the $\delta^{34}S$ values of the Modern (purple) and Pliocene (yellow) oceans.

Sulfur: Although it has been suggested that the $\delta^{34}S$ values of carbonate associated sulfate (CAS) are relatively immune to diagenesis (Gill et al., 2008), it is safe to assume that because of the predominance of bacterial sulfate reduction (BSR) and the large fractionation associated with this process, that the $\delta^{34}S$ values of pore fluids, and consequently any diagenetic calcite formed in association with BSR, will likely be different than the original carbonate value.

SCOPE OF WORK

Sulfur and Boron

Meteoric Diagenesis: We have started to investigate the changes in the $\delta^{11}B$ and $\delta^{34}S$ values from sections of the Clino core which have unequivocally been altered by meteoric fluids. The sampling for $\delta^{11}B$ values was designed not only to replicate the samples measured previously (Stewart et al., 2015), but also to encompass the entire core (Fig. 1). These values will also be measured on other cores from the Bahamas in our collection. Although our initial $\delta^{11}B$ values within the zone of meteoric diagenesis are similar to those measured previously (Stewart et al., 2015), these data record a large drop in pH within the top portion of the freshwater phreatic lens as defined by Swart and Oehlert (2018).

Marine Diagenesis: Carbonate sediments are normally recrystallized/neomorphosed as they are buried in the marine realm. During burial, the timing of BSR relative to recrystallization controls whether the original $\delta^{34}S$ values of the sediments are preserved. For example, if BSR reduces the concentration of sulfate in the pore fluids to zero before the initiation of sediment recrystallization, then the $\delta^{34}S$ values of the recrystallized sediment should be similar to the values in the original sediment. However, if BSR is not complete, then the residual sulfate will have a very positive $\delta^{34}S$ value and as recrystallization starts the new carbonate will incorporate S with more positive $\delta^{34}S$ values. The changes in the $\delta^{34}S$ value of the CAS from the Clino core reflect these scenarios (Fig. 1). The pH values of the pore waters in both of these previous scenarios will probably be lower than those prevailing during sediment deposition. In fact, in the section of the Clino core dominated by marine diagenesis, the $\delta^{11}B$ values are substantially lower, reflecting the low pH throughout. Although the sampling interval of B and S isotopes is different, the $\delta^{11}B$ values do not seem to correlate with the zones in which the $\delta^{34}S$ values are elevated, reflecting enhanced BSR.

Carbon Isotopes: The work of Oehlert and Swart (2014) clearly show that within the zone of meteoric diagenesis there is strong positive covariance between the $\delta^{13}C$ values of the carbonate and the $\delta^{13}C$ values of the organic material. In order to explain these data, it was proposed that during sub-aerial exposure terrestrial C-3 vegetation colonized the islands masking the original $\delta^{13}C$ values of the local marine organic material. In order to test this hypothesis, we will (i) measure the $\delta^{13}C$ values of the organic material in other cores from the Bahamas and Pacific, (ii) extract distinct organic compounds from the cores, which might reflect the original shallow marine biota, and measure their $\delta^{13}C$ values using compound specific isotopic techniques.

SIGNIFICANCE

The application of geochemical proxies towards understanding the ancient need to be rooted in rigorous calibration studies, in which the Recent is the key to the past. This is true not only for the stable isotopes of B, C, and S, but also for a myriad of other hopeful isotopic proxies. In this regard it is useful to quote from a recent paper (Swart, 2015) '*So that we do not 'Throw the Baby out with the Bath Water' (Marshall, 1992), such proxies should be cautiously applied to older materials. Only then can the potential of geochemical indices be made available to correctly study both the paleoenvironment and the diagenesis of carbonates in older time periods.'*

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THE BEHAVIOR OF ISOTOPES DURING THE DISSOLUTION OF CARBONATES BY PHOSPHORIC ACID

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PROJECT OBJECTIVES

- To understand the behavior of the clumped isotope proxy (Δ_{47} values) during the dissolution of carbonates by phosphoric acid and consequently improve the understanding of the application of the clumped isotope proxy.

PROJECT RATIONALE

The stable C and O isotopic analysis of CO_2 released from carbonates has become a standard tool in the study of numerous geological and biological processes since the early 1950s. The experimental method involves the release of CO_2 through the dissolution of carbonate in ortho-phosphoric acid (McCrea, 1950) (equation 1).

$$CaCO_3 + H_3PO_4 \rightarrow CO_2 + H_2O + CaHPO_4 \quad (1)$$

This acid was chosen by McCrea, in preference to others such as nitric acid or sulfuric acid, for a variety of reasons, including its low vapor pressure and consistent isotopic exchange between the oxygen in the acid and the CO_2 produced in the reaction with carbonate. Despite these properties which have seen its use persist for over 50 years, phosphoric acid contains oxygen in its structure and the reaction itself produces three compounds, all with oxygen. As a consequence, there is significant oxygen isotopic fractionation associated with the reaction (Sharma and Clayton, 1965). This study will reexamine the oxygen and clumped isotopic exchange between CO_2 and phosphoric acid by means of a series of experiments in which stochastic and non-stochastic CO_2 will be equilibrated with phosphoric acid over periods of weeks as well as over times that are more representative of times used in carbonate reactions.

BACKGROUND

Phosphoric acid (H_3PO4) is normally supplied at a nominal concentration of 88 %. In order to lower the vapor pressure, reduce the amount of H_2O in the acid, and thus make it suitable for reacting with carbonates, P_2O_5 can be added and/or the acid can be heated. However, as the process proceeds the acid undergoes polymerization reactions forming various forms of poly-phosphoric acid and water (Fig. 1).

In considering the possibility of isotopic exchange of ^{18}O and the $^{13}C^{18}O$ species during the exposure of phosphoric acid to CO_2 there are several possible points at which fractionation could take place. First, isotopic exchange could take place between the CO_2 and the H_2O already present in the acid. During the polymerization reactions water is produced and this water is then utilized to produce additional phosphoric acid. Water equilibrated in this last step would then re-exchange with the CO_2. Equilibrium established at this point would be dependent upon the temperature. During excessive heating of the phosphoric acid, P_2O_5 and excess H_2O are produced, also possible points of isotopic exchange.

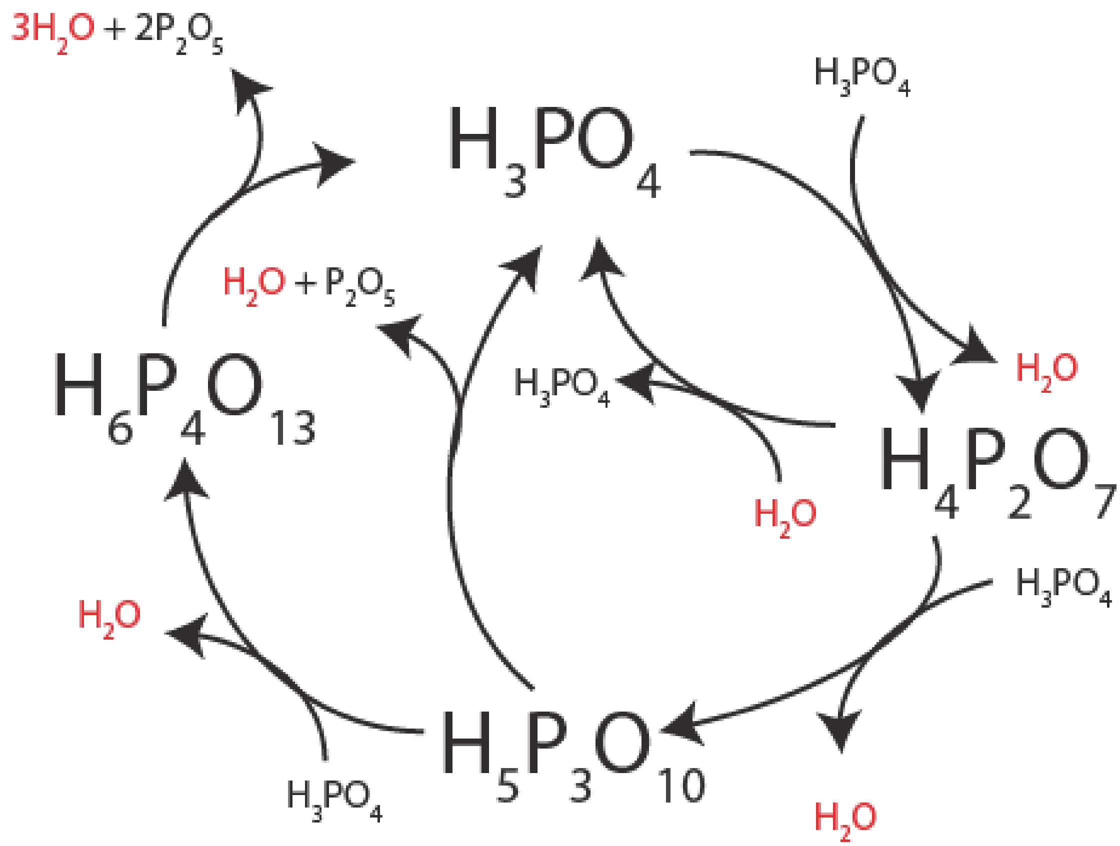

Figure 1: Possible pathways of for the production of poly phosphoric acid and the creation of water during the preparation of 'strong' phosphoric acid.

SCOPE OF WORK

Three experiments are proposed.

Experiment 1: In this experiment phosphoric acid, with a specific gravity (sg) of either 1.98 or 1.88, will be placed in Pyrex tubes with an aliquot (~1 μM) of one of three different CO_2 gases. At predetermined times the tubes will be removed and the CO_2 extracted and cleaned using the standard procedures in our laboratory (Murray et al., 2016).

Experiment 2: Aliquots of CO_2 from the three tank gases will be allowed to equilibrate in our normal reaction area over acid at 90°C with a sg of 1.98 for periods of between 5 and 120 minutes. A limited number of experiments will be also carried out using an acid temperature of 25°C. In addition, aliquots of Tank A and C that are heated to 1000°C will also be equilibrated with the 1.98 acid for varying lengths of time. Normally during this equilibration period, the acid is stirred using our usual protocol for the reaction of carbonate samples. Some of the experiments will not be stirred. In some experiments, a blank reaction vessel without acid will be substituted. After the equilibration is complete, the CO_2 will be cleaned in the normal manner.

Experiment 3: Calcite samples precipitated at temperatures between 5 and 75°C, and therefore possessing a range of Δ_{47} values between 0.57 and 0.80‰, will be reacted at 25°C using the normal protocol as outlined by Murray et al. (2016). The procedure at 25°C will be identical to that carried out at 90°C with the exception that ~180 minutes will be used for each reaction, as opposed to 30 minutes at 90°C. These last experiments are designed to examine the difference in exchange as a function of temperature.

SIGNIFICANCE

It is our contention that the processes outlined above will lead to important variations in the Δ_{47} values measured in carbonates. At 90°C, which is the common reaction temperature, the Δ_{47} value of CO_2 in equilibrium with water in the acid will be 0.619‰. Hence samples with inherently lower Δ_{47} values, carbonates produced at high temperatures, will exchange with the water producing a lower temperature than they should. Conversely, carbonates with higher Δ_{47} values, colder carbonates, will tend to manifest higher temperatures. We further contend that these differences will vary between laboratories based on the design of the carbonate extraction systems as well as the method of preparing the phosphoric acid.

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TOWARDS AN UNDERSTANDING OF THE USE OF CLUMPED ISOTOPES TO STUDY DIAGENESIS

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PROJECT OBJECTIVES

- To understand the behavior of the clumped isotope proxy (Δ_{47} values) during meteoric and early marine burial diagenesis.
- To examine the calibration between the Δ_{47} value of aragonite and temperature.

PROJECT RATIONALE

The clumped isotope proxy (Δ_{47} value) has enabled temperatures to be obtained directly from carbonates through a single analysis. The clumped isotope proxy has the potential to revolutionize the study of diagenesis, as it is now possible to obtain both the temperature and the $\delta^{18}O$ of the fluid without using other proxies such as fluid inclusions. However, like many geochemical tools there are many uncertainties which need to be resolved before the full potential of the technique can be realized. The work proposed here will address one of these issues and build on papers published by current and past PhD students and visiting scientists, Monica Arienzo, Sean Murray, Florian Smit, and Philip Staudigel (Murray, 2016; Murray et al., 2016, Staudigel and Swart, 2014; Staudigel and Swart, 2016).

SCOPE OF WORK

Deep Marine Sites: We have already extensively examined two sites from the Leg 166 Bahamas transect. In ODP Sites 1006 and 1003, the uppermost sediments record a general down core cooling trend at both sites, averaging ~14°C (Figs 1A & 1B). In addition to adding two more sites from Leg 166, Sites 1005 and 1007 (Fig. 1), we will examine sites from other DSDP/ODP/IODP expeditions as appropriate.

Shallow Cores: We propose to examine the clumped isotope behavior in a series of shallow-water cores drilled from sequences which have been exposed to well constrained meteoric diagenetic conditions. These cores include the Clino and Unda cores on Great Bahama Bank, as well as other cores from the Bahamas. We will make use of our new model (Swart and Oehlert, 2018), which reinterprets variations in the stable C and O isotopic composition of these cores.

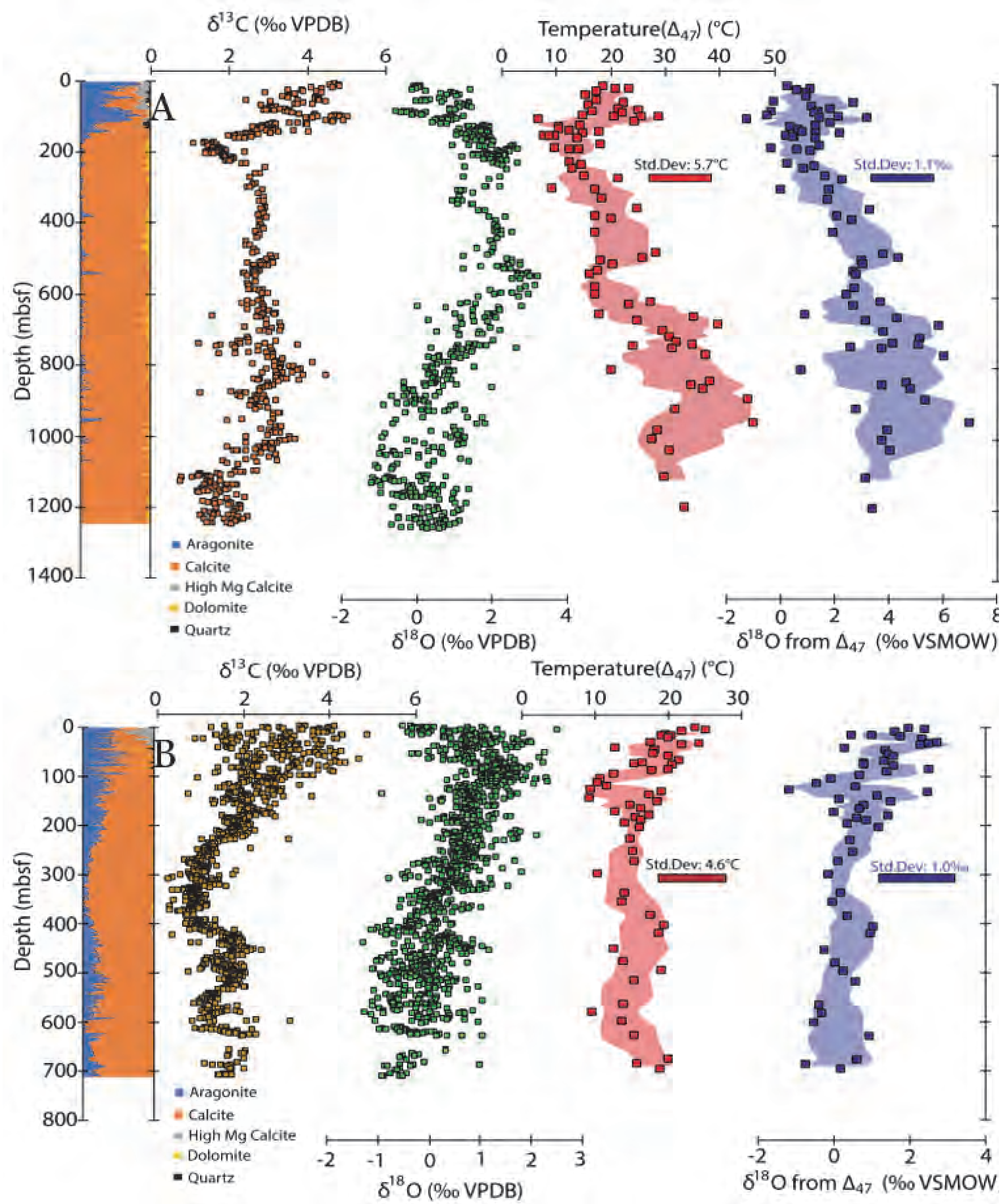

Figure 1: Mineralogy and isotopic composition of ODP Site 1003 (top) and 1006 (bottom).

Ancient Samples: As the first application of our studies to older materials we will examine the diagenesis of the European chalk using outcrop and core material. Some of this work was presented at the 2017 sponsors meeting, but we have already initiated new projects utilizing samples of macrofossils and bulk rocks from the chalk in the U.K. and the U.S. A second area of research will utilize samples from the Carboniferous, collected on the Isle of Man in the Irish Sea (Dickson and Coleman, 1980). These samples were some of the first in which individual generations of cements were separated and analyzed for their $\delta^{13}C$ and $\delta^{18}O$ values. Utilizing the small sample capability of the Kiel device, we have cross-calibrated the University of Miami and Cambridge laboratories and started to analyze samples as small as 130 μg (compared to 8 mg in Miami).

Synthetic carbonate calibration: We have experimentally precipitated calcite and aragonite over a range of temperatures (5 to 75°C). These samples have resulted in a temperature calibration unique to the University of Miami (Staudigel et al., In Review) (Fig. 2). We propose to extend the range of this calibration to lower (-10°C) and higher temperatures (95°C) and investigate differences in the calibration when precipitating aragonite compared to calcite.

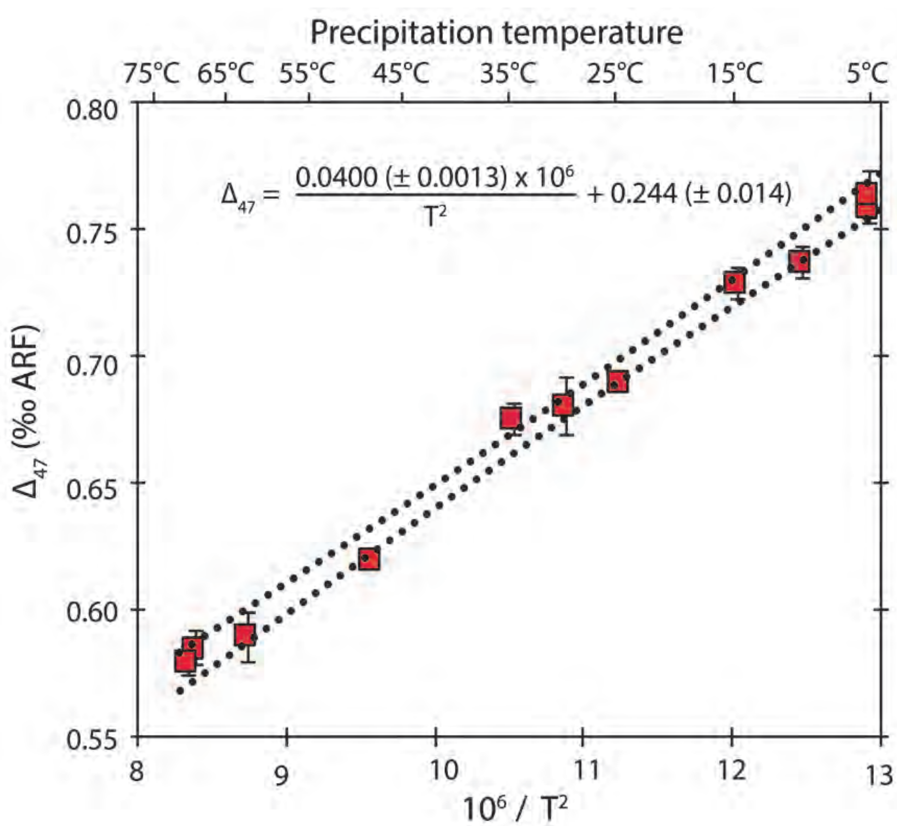

Figure 2: Relationship between Δ_{47} and temperature for samples precipitated in Miami.

SIGNIFICANCE

As the clumped isotopic proxy is applied to progressively older materials, it will become important to ascertain the extent of the influence of early diagenesis upon the eventual signature. At the present time, many such studies have skipped this fundamental step when interpreting their data. The work completed to date clearly illustrates the utility of clumped isotopes for studying early and late stages of diagenesis, enabling more nuanced interpretations of other isotope systems.

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THE FORMATION AND DISSOLUTION OF CELESTINE: A POSSIBLE MECHANISM FOR CREATING SECONDARY POROSITY IN PLATFORM-DERIVED SEDIMENTS

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PROJECT OBJECTIVES

- To understand the importance of celestine formation on the occlusion and preservation of porosity.
- To understand the influence of celestine upon the pore water geochemistry during and subsequent to its formation.

PROJECT RATIONALE

The formation and occlusion of porosity in sediments deposited along the margins of carbonate platforms is an important process in controlling the hydrocarbon potential of a reservoir. However, the processes which govern the development of porosity in carbonate reservoirs are poorly understood and frequently large variations occur, the reasons for which are not immediately obvious. In the proposed work, we will investigate a new process related to celestine formation and later dissolution, which we believe is important in controlling porosity development in marginal sediments deposited adjacent to carbonate platforms.

BACKGROUND

Celestine ($SrSo_4$; often referred to as celestite) is a common mineral forming during the marine burial diagenesis of platform-derived sediments as the Sr, which is more abundant in biogenic carbonates, is excluded during neomorphism and recrystallization (Swart, 2016). Celestine saturation is common in the deep-sea record and about 10% of all sediments cored by the DSDP-ODP-IODP show saturation with respect to this mineral (Hoareau et al., 2010). Celestine is also common throughout the geological record (Hanor, 2004) and in some instances forms large concretions, up to one meter in diameter, that are often replaced by calcite (Yan and Carlson, 2003). While the origin of celestine in deep sea environments is well

Fig. 1: Specimen of celestine in sample from Site U1467.

understood, its occurrence in coastal and evaporitic settings is more problematic (Hanor, 2004; Taberner et al., 2002).

SCOPE OF WORK

We will analyze samples collected during IODP Expedition 359 (Betzler et al., 2016) and from ODP Site 1005 (Leg 166 in the Bahamas) (Eberli et al., 1997). Expedition 359 drilled eight sites adjacent to the Maldives and penetrated up to 1000 m of strata below the sea floor (mbsf) reaching sediments of Late-Oligocene age. These sites are located close to ODP Site 716 drilled during Leg 115 where celestine was also detected (Fig. 1). In the cores from Exp. 359, celestine was detected using X-ray diffraction (XRD) at four of the sites; U1466, 1467, 1468, and 1471 (Fig. 1). The greatest abundance of celestine was measured at Site U1471, although it should be emphasized that samples were only analyzed every ~ 9 m and therefore celestine may be more prevalent than recorded. Coincident with the pore waters attaining supersaturation with

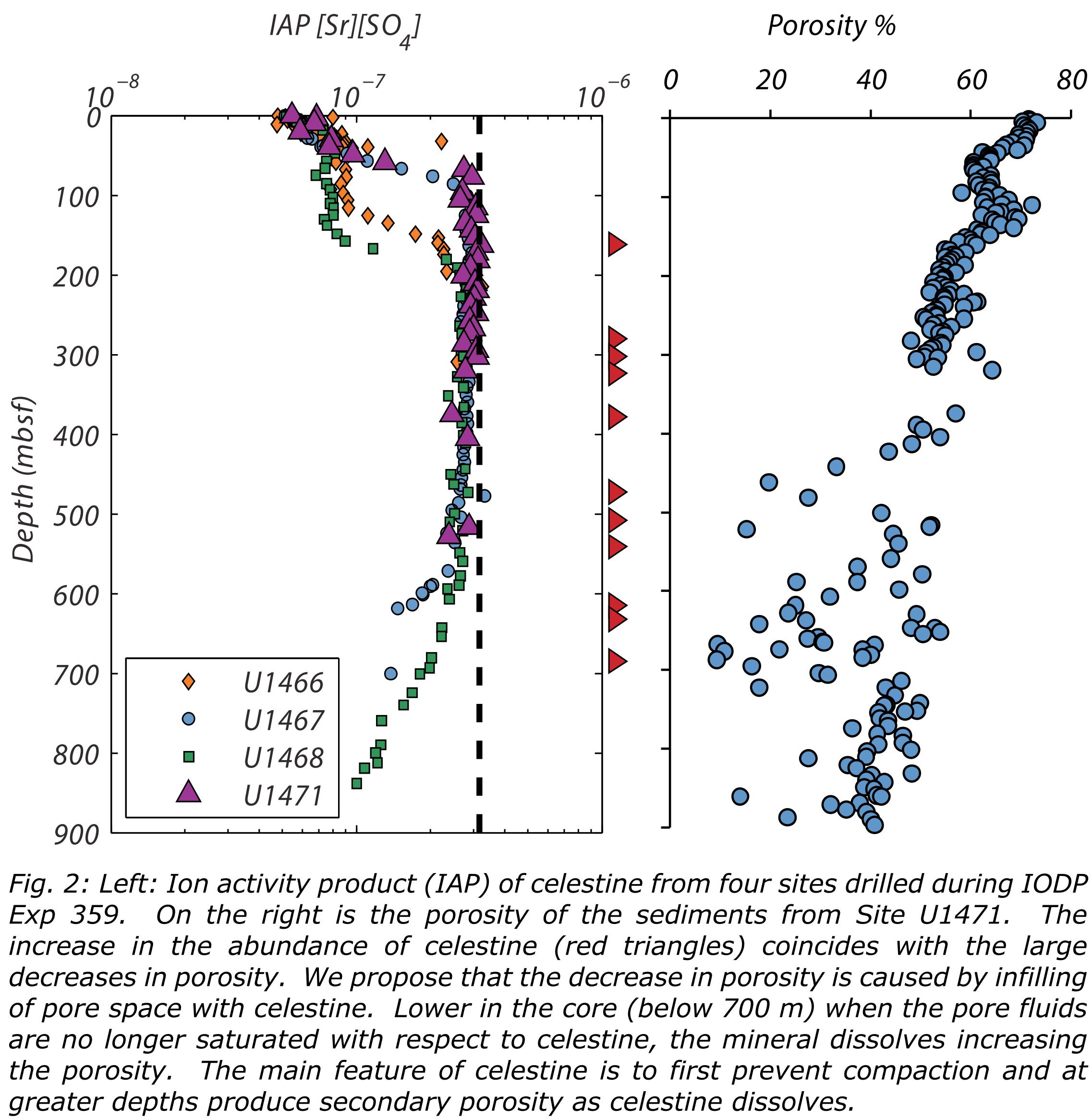

Fig. 2: Left: Ion activity product (IAP) of celestine from four sites drilled during IODP Exp 359. On the right is the porosity of the sediments from Site U1471. The increase in the abundance of celestine (red triangles) coincides with the large decreases in porosity. We propose that the decrease in porosity is caused by infilling of pore space with celestine. Lower in the core (below 700 m) when the pore fluids are no longer saturated with respect to celestine, the mineral dissolves increasing the porosity. The main feature of celestine is to first prevent compaction and at greater depths produce secondary porosity as celestine dissolves.

respect to celestine at this site, the nature of the change in porosity as a function of depth alters from one in which porosity is gradually decreasing as a result of compaction and cementation, to one in which the porosity shows large erratic drops (Fig. 2). We suspect that these decreases in porosity are a result of localized celestine precipitation filling the pore space. Similar behavior was observed at some of the Leg 166 sites drilled adjacent to the Great Bahama Bank. At Site U1467 in the Maldives the hole was logged using a formation microscanner (FMS) and the presence of numerous nodules was noted and interpreted as being celestine. A detailed analysis of the FMS log should be able to quantify how much celestine is present at this site.

Ancient Occurrences: As part of this study we will investigate the formation of celestine nodules from geological sections in the Permian of China (Yan and Carlson, 2003). A geochemical comparison of nodules from the Bahamas and China will be accomplished using methods such as the isotopic analysis of S and Sr (Fig. 3).

Fig. 3a: A celestine sample from core Clino in the Bahamas. The $\delta^{34}S$ value is ~10 ‰ more positive than ambient seawater indicating bacterial sulfur reduction (BSR).

Fig. 3b: A celestine nodule from the Permian in China with drill holes for $\delta^{34}S$ analyses. Values are elevated relative to Permian seawater also indicating BSR.

SIGNIFICANCE

The occurrence of celestine, while well known, has been mainly regarded as a curiosity. The proposed study will be the first to recognize its potential as a major and important creator of secondary porosity. We propose that this mineral forms early in the paragenetic sequence, filling porosity and thus preventing sediments from becoming compacted and filled with carbonate cement. Once the surrounding carbonate sediments become lithified and the sediment is buried below the zone in which the pore waters are super saturated, the celestine dissolves and the porosity of the rock becomes available once more. Furthermore, this process occurs preferentially in sediments derived from aragonite precursors and therefore should be more prevalent in sediments that formed during periods of the Earth's history which had higher Mg/Ca ratios in so-called aragonite seas (Lowenstein et al., 2001; Sandberg, 1983).

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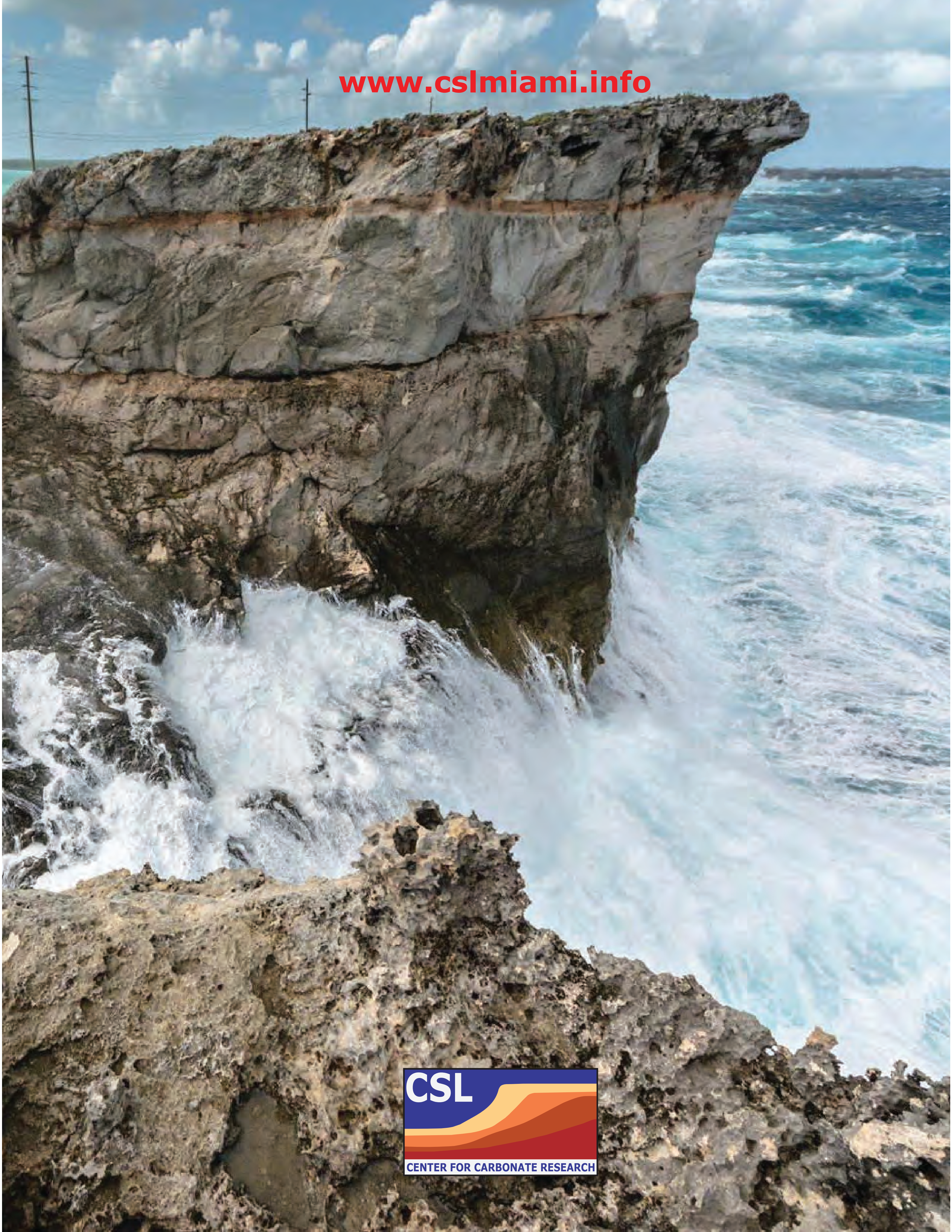
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