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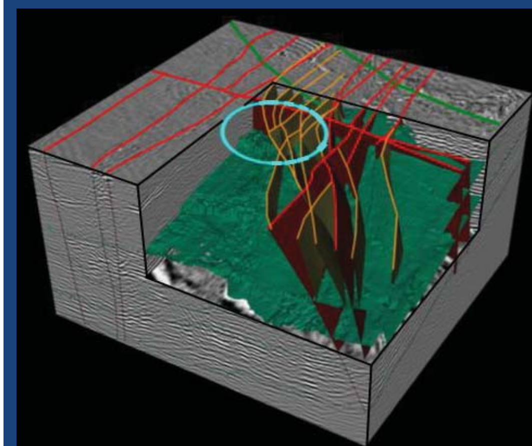
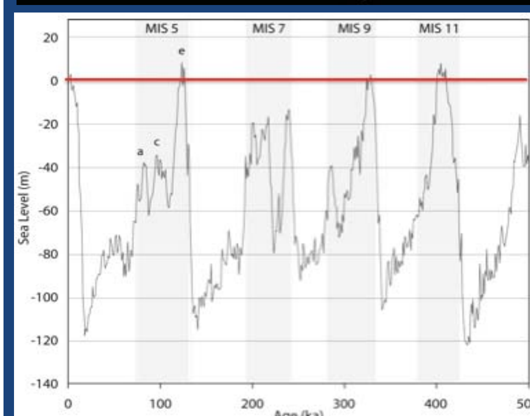
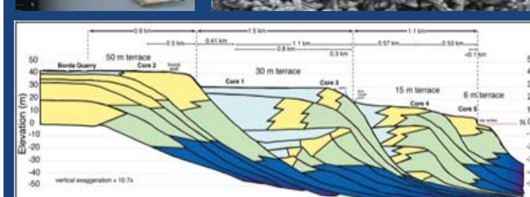
CSL
CENTER FOR CARBONATE RESEARCH







RESEARCH PROGRAM PROSPECTUS 2012

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MISSION OF THE CSL – CENTER FOR CARBONATE RESEARCH

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

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

The projects during 2012 combine observational, laboratory and theoretical data and integrate geology, geophysics, geomicrobiology and geochemistry. These integrated studies are grouped into five areas:

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

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

KNOWLEDGE TRANSFER

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

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

In 2012, we offer two seminars. The first, "Facies Successions on Great Bahama Bank" (June 18 - 23, 2012), is a seminar combined with a seismic and core workshop. The field portion is a platform transect from the leeward to the windward margin of Great Bahama Bank. The second seminar is to the Exumas (June 24-29, 2012) entitled "Heterogeneity of Bank-Margin Ooid Sands Depositional Models and Reservoir Analogs Exuma, Bahamas". The field seminar illustrates facies relationships and heterogeneity of a grainstone dominated, high-energy carbonate platform margin.

PERSONNEL

PRINCIPAL INVESTIGATORS

Gregor P. Eberli, Ph.D. 1985, Geological Institute ETH Zürich, Switzerland
Research Interests: Shallow and deep-water carbonate systems; seismic facies analysis and sequence stratigraphy, petrophysics of carbonates, and mixed carbonate/siliciclastic systems.

Mark P. Grasmueck, Ph.D. 1995, Geophysical Institute ETH Zürich, Switzerland
Research Interests: Applied geophysics, reflection seismic, Ground Penetrating Radar, 3-D and 4-D near surface imaging, reservoir characterization.

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

Donald F. McNeill, Ph.D. 1989, University of Miami/RSMAS
Research Interests: Sedimentology and stratigraphic correlation of carbonate and mixed systems, integrated stratigraphy (bio-, Sr-isotope-, magnetostratigraphy).

Peter K. Swart, Ph.D. 1980, King's College, University of London, England
Research Interests: Sedimentary geochemistry, stable isotope geochemistry, organic geochemistry, global climate change, coral reef sedimentation.

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RESEARCH ASSOCIATE

Amel Saied

STAFF

Karen Neher	Office Manager
Cory Schroeder	Technical Specialist

2012 RESEARCH FOCUS

The projects in **reservoir characterization of carbonate systems** rely on newly acquired cores, seismic and multibeam data covering the depositional environments from the platform top to the basin. The focus in the shallow-water environments is twofold. First, outcrop and core studies of prograding reef successions in the southern coast of the Dominican Republic offered the opportunity to study the heterogeneity created by the combined effects of facies and subsequent pervasive meteoric diagenesis. In the coming year, hydrologic experiments will be conducted to assess the fluid-flow behavior of these reef successions. The second focus is on the sedimentary record of meter-scale sea-level oscillations within highstands. Facies successions in recently drilled cores along the windward margin of the Exumas Sound document the amplitude of these oscillations. Combined with mapping of exposed strata, these cores can now be evaluated in regards to lateral and stratigraphic complexity, which is caused by these oscillations. The findings are important for understanding heterogeneity within carbonate platform cycles that are often flow units in the ancient.

During a seismic, multibeam, and coring cruise (funded by the French Science Foundation) along the slopes of Little and Great Bahama Bank a comprehensive data set was collected to visualize slope morphology and to study sedimentary slope processes. The assessment of slope processes is done in collaboration with French scientists. The distribution of the deep-water coral mounds and their interaction with slope morphology and currents will be spearheaded by the CSL-CCR. To image the Florida slopes and to connect the shallow to the deep environments, we plan to acquire a new regional seismic line across the Straits of Florida.

The connection between the shallow and the deep is also examined in the mixed system in the Neuquén Basin in Argentina where superbly exposed clinoforms allow walking-out of the strata from the shelf break into the basin. The subsurface equivalent of the basinal portion of this system is currently an active exploration target for an unconventional play.

The **petrophysical projects** cover experimental studies of the effects of cementation and dissolution on the porosity, permeability and sonic velocity. The dissolution experiments will provide insight in the development of fluid pathways during acidification. We continue our search for controlling factors of resistivity in carbonates. This year, the focus is on the role of microporosity for electrical conductivity. Petro-acoustic characterization of microbialites and facies of unconventional reservoirs will complement our efforts to increase the database of these important exploration targets.

The **near surface geophysical projects** focus on two aspects. The first is the completion of the quantification of fluid flow in the fractures carbonates using 4D GPR and newly developed processing techniques. This will enable to document the flow behavior in a 10x10 m cube, and is a promising first step in understanding permeability of carbonates on a larger scale. The second project uses diffractions to image discontinuities, in particular fractures. The excellent results in the GPR diffraction analysis for fracture detection prove the validity of the approach of diffraction analysis and fracture detection in seismic data.

Microbialites are an emerging reservoir facies but research has focused either on processes or descriptive petrography. The CSL-CCR will use a combination of geomicrobiology and molecular biology to assess the microbes and bacteria important in geological processes. In addition, efforts are made to place the microbialites in the geological context by relating their distribution and morphometry to the modern depositional environments. These studies are complemented with the petrophysical characterization of ancient microbialites.

In addition to the studies in the Neuquén Basin and on diffractions the **uncoventional reservoirs** are the focus of two projects. Using the CSL-CCR database as a starting point, a petrophyiscal characterization of unconventional reservoir facies is planned. The second project evaluates the distribution of reservoirs in a sequence stratigraphic framework with the goal to enhance the exploration successes.

A new mass spectrometer enables the CSL-CCR to conduct innovative **geochemical projects** in clumped isotopes. These clumped isotopes offer a new look on the temperature of the diagenetic fluids and potentially solve many geochemical controversies like hydrothermal dolomitization. An ongoing project focuses on the relationship between $\delta^{13}C$ and sulfur isotope variations and the global carbon cycle. A large grant from the Department of Energy involves the CSL-CCR in the geochemical monitoring and modeling of carbon capture and storage.

Below is the list of the planned projects. The detailed objectives and deliverables of each project are outlined in the 2012 research prospectus.

2012 PLANNED PROJECTS

CARBONATE SYSTEMS AND RESERVOIR CHARACTERIZATION

A) The Platform Top

- The Sedimentary Record of Sea-Level Oscillations During Highstands: Evidence from the Bahamas and Belize
- Documenting Stratigraphic Heterogeneity Caused By Sea-Level Oscillations During The MIS 5e Highstand: Exumas Margin
- The Record Of Highstand Sea-Level Oscillations in Pleistocene Carbonate Shoals: Florida And Bahamas
- Dating of Quaternary Sea-Level Oscillations in Belize Corals: A Dual Approach
- Hydraulic Conductivity in the Plio-Pleistocene Reefal Deposits of the Southern Dominican Republic

B) The Slope and the Deep

- Distribution & Morphology of Cold-Water Coral Mounds around Little and Great Bahama Bank
- Expedition to the West Atlantic Cold-Water Coral Ecosystems
- Reservoir Potential of Cretaceous-Paleocene Carbonate Turbidite Successions: A Core and Outcrop study, Adriatic Sea, Italy (Year 2)

C) Mixed Systems

- From Outcrop to Basin Scale: Seismic Analysis of the Mixed System in the Neuquén Basin, Argentina

PETROPHYSICS AND (NEAR-SURFACE) GEOPHYSICS

- Rock Fluid Interaction: Velocity Evolution during Controlled Precipitation and/or Dissolution
- Sub-Micron Digital Image Analysis (ESEM-DIA), Pore Geometries, and Electrical Resistivity in Carbonate rocks
- 4D GPR for Quantification and Characterization of Fluid Flow in Fractured Carbonates
- Seismic and GPR Diffractions: Towards the next Generation of Small Scale Discontinuity Imaging

MICROBIALITE PROJECTS

- Assessing the Role of Microbes in the Formation of Ooids and Carbonate Precipitation
- Microbial Facies, Textures, and Porosity Formation on an Isolated Platform: Uplifted Atoll of Mare, Loyalty Islands, New Caledonia
- Petrophysical Properties and Pore Structures in Microbialites

UNCOVENTIONAL RESERVOIR PROJECTS

- Petrophysical Properties of Unconventional Reservoirs: Start of a Database
- Sequence stratigraphic Distribution of unconventional Shale Reservoirs in Three Basins

GEOCHEMICAL PROJECTS

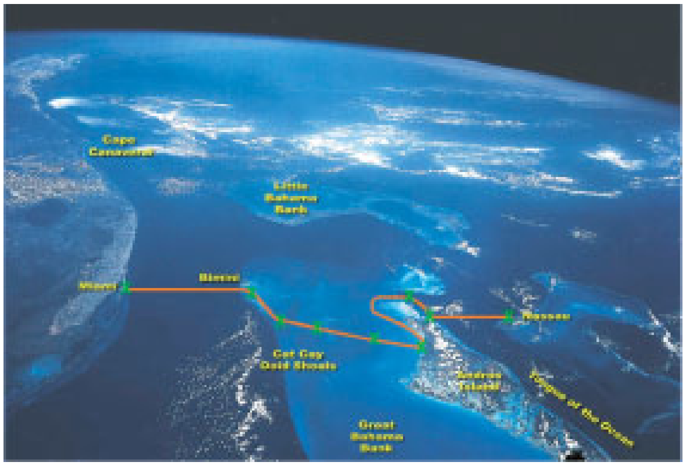
- The Triple Threat: Stable Isotope Studies of Fluid Inclusions, Carbonate, and Clumped Isotopes
- Diagenetic Isotope Signals in Boron, Magnesium, & Calcium Isotopes?
- The Effects of Precipitation Rate on Clumped Isotopes: Re-Evaluating the Accuracy of a New Technique

COSTS

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

REPORTING

The results of the projects will be presented at the **Annual Review Meeting in Miami, October 15-16, 2012**. In conjunction with the meeting, a fieldtrip to the Dominican Republic is tentatively planned for **October 16-20, 2012.**



1. Field Seminar

Offered by the CSL – Center for Carbonate Research

FACIES SUCCESSIONS ON GREAT BAHAMA BANK

Implications for Exploration and Reservoir Characterization

June 18 – 23, 2012

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

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

Objectives:

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

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

Content: This seminar explores the vertical and lateral facies successions and heterogeneities of Great Bahama Bank. The seismic and core workshop on day 1 illustrates the architecture of the prograding western margin of Great Bahama

Bank. Cores across the platform margin provide a unique opportunity to examine the sequence stratigraphic distribution of facies and diagenetic modification in platform carbonate reservoirs. Log and laboratory data from these cores provide insights into porosity/velocity relationships and permeability distribution in platform carbonates.

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

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

In the water at Joulters Cay

In an Andros Island tidal channel

Cost: $4,200.-, Flights to and from the Bahamas, all ground transportation, on-board boat accommodation in the Bahamas, meals, and course notes are included.

Contacts: **Gregor P. Eberli** (305) 421 46 78 geberli@rsmas.miami.edu
Karen Neher (305) 421 46 84 kneher@rsmas.miami.edu

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

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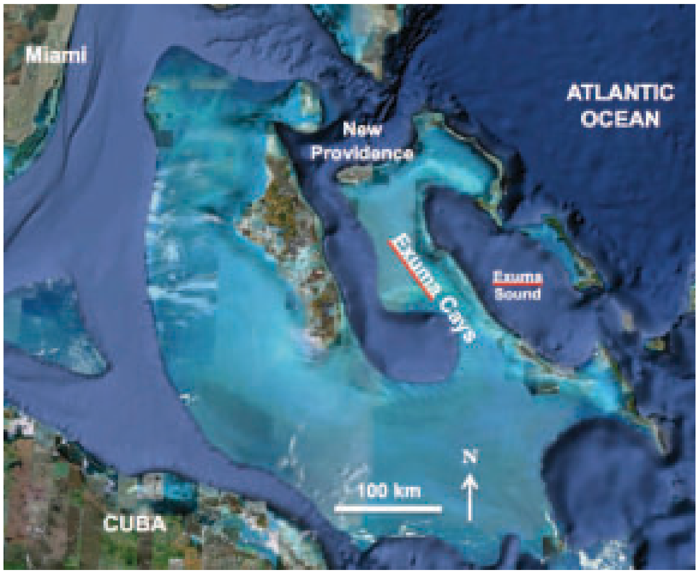

CSL University of Miami

CSL – Center for Carbonate Research

2. Field Seminar

HETEROGENEITY OF BANK-MARGIN OOID SANDS
Depositional Models and Reservoir Analogs
Exumas, Bahamas

June 24 – June 29, 2012

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

Location: Exuma Cays along the western margin of Exuma Sound, Bahamas. This windward margin offers the opportunity to examine the facies relationships and heterogeneity of a grainstone dominated, high-energy carbonate platform margin. We will visit by boat 14 different settings illustrating the various environments. The seminar begins and ends **Nassau** on New Providence Island, **Bahamas**.

Objectives:

1) **illustrate the dimension of the large-scale exploration-scale facies belts** of a windward margin, and
2) **examine the smaller, reservoir-scale heterogeneity** within these grainstone facies.

Who should attend: Exploration and production geoscientists and reservoir engineers working in grainstone reservoirs or on platform margin settings.

Seminar Content: The seminar will illustrate the exploration-scale facies relationships and dimensions as well as reservoir-scale features in a high-energy platform margin including the spatial distribution of the sub-environments, disconformities, sub-aerial exposure horizons.

This windward margin is a complicated arrangement of sediments surrounding the Pleistocene and Holocene islands. Cores through the Pleistocene strata document the vertical juxtaposition of bank-margin lithofacies that is controlled by oscillations of sea level within the latest highstand. We will discuss the implications for reservoir heterogeneity of these sub-orbital sea-level fluctuations. The modern environment displays the sedimentary products that are produced by the physical and biological processes along the bank margin. In particular, we will study the accumulation of sand in tidal channel and tidal deltas and examine the various sub-environments with differing grain-composition and sedimentary structures. Karstified eolian islands, dunes, and Pleistocene outcrops will illustrate the influence of meteoric diagenesis on the bank margin deposits. The islands will also serve as overview points for viewing the dimensions of the various environments. Corals and stromatolites in normal, open marine environments and tidal channels will display the location of the reef building communities in these high-energy environments.

Fowl Cay tidal inlet between Pleistocene islands

Costs: $3,900.-, Includes all ground transportation, boat, meals, and course notes with virtual field seminar CD.

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THE SEDIMENTARY RECORD OF SEA-LEVEL OSCILLATIONS DURING HIGHSTANDS: EVIDENCE FROM THE BAHAMAS AND BELIZE

Gregor P. Eberli, Kelly L. Jackson, Hasan C. Usdun, Noelle J. Van Ee, Donald F. McNeill

PROJECT OBJECTIVES

Recognition that sea level has oscillated several meters during a single highstand has major implications for the duration and origin of shallow-water depositional cycles. Ongoing projects in the Pleistocene strata of the Bahamas and in Belize have produced enough evidence to support a major research effort designed to answer some fundamental questions:

- What is the sedimentary record of inter-highstand sea-level oscillations?
- How much complexity do these oscillations add to the facies and stratigraphic architecture?
- Could these oscillations produce sedimentary cycles that are of short (a few thousand years) duration and thus of suborbital frequency?

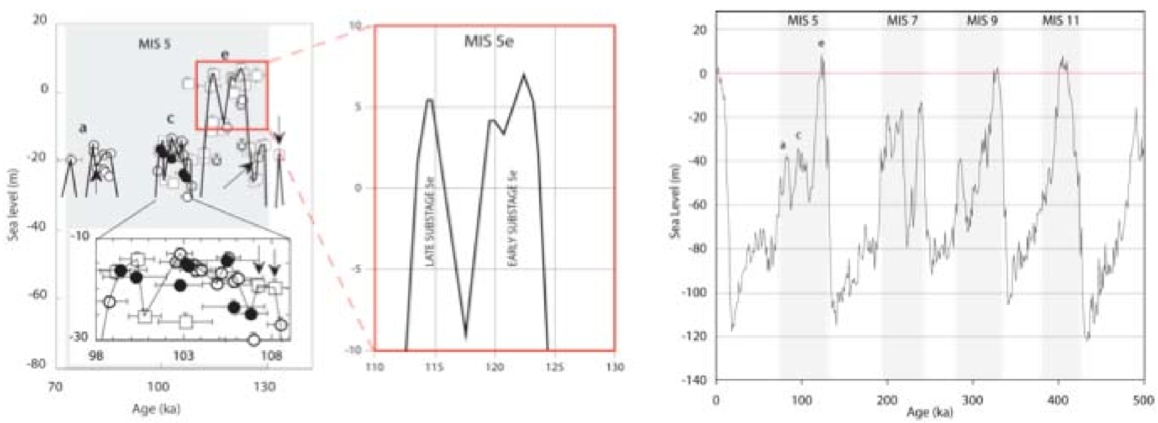

Figure 1. (Left) A high-resolution sea-level curve constructed from Barbados coral data using open system age equations. Arrows identify the eight corals that are not the reef-crest species A. palmata. In general, the sea-level curve is drawn through the highest corals of a given age (Thompson and Goldstein, 2005). (Right) Sea-level curve of the last 500,000 years reconstructed from stable oxygen data (from Lisiecki and Raymo, 2005). Note how each of the sea-level highstands (labeled MIS 5-11) is rugged, indicating oscillations during the highstand.

PROJECT RATIONALE

Carbonate depositional cycles are produced during a high frequency sea-level fluctuation that creates accommodation for deposition. Age dating of Quaternary deposits and frequency spectrum analyses of ancient strata have given strong evidence that these high-frequency sea-level changes are related to the Earth's climate cycles that are linked to the orbital forcing mechanisms with durations of 20, 40 and 100 kyrs (Hinnov and Goldhammer, 1991; Preto et al., 2001). Refined age dating of Quaternary corals within the reef terraces in Barbados and the Bahamas now document sea-level oscillations of several meters within the orbital frequency highstands (Thompson and

Goldstein, 2005; Thompson et al., 2011). Likewise, repetitions of beach-eolian units (Kindler and Hine, 2009) and down-stepping beach terraces (Reid, 2010) within the last sea-level highstand (MIS 5e) are the first documented sedimentologic expressions for these sub-orbital sea-level oscillations. The larger magnitudes of these oscillations are between 15 and 20 m, which is enough to expose and re-flood the shallow-water carbonate platforms and potentially add a complete depositional cycle within a few thousand years. The implications of this process are far reaching not only for understanding short-term climate changes but also because of the stratigraphic complexity added to the sedimentary system. In order to address the latter, the CSL is conducting a large research effort consisting of several projects in various parts of the Bahamas and Belize.

PROJECTS ADDRESSING THE SEA-LEVEL OSCILLATIONS WITHIN HIGHSTANDS

- Documenting Stratigraphic Heterogeneity Caused by Sea-Level Oscillations During The MIS 5e Highstand: Exumas Margin – Jackson et al.
- Dating Of Quaternary Sea-Level Oscillations in Belize Corals: A Dual Approach – Van Ee et al.
- The Record of Highstand Sea-Level Oscillations in Pleistocene Carbonate Shoals: Florida and the Bahamas – Usdun et al.

EXPECTED RESULTS

- Decipher the timing and amplitude of sea-level oscillations within MIS 5e and older highstands.
- Provide a well-constrained documentation of the sedimentologic and stratigraphic record of these oscillations.

REFERENCES

Hinnov, L. A. and R. K. Goldhammer, 1991, Spectral analysis of the Middle Triassic Latemar Limestone. Journal of Sedimentary Petrology, v. 61, p. 1173-1193.

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Lisiecki, L. E. and Raymo, M. E., 2005, A Pliocene-Pleistocene stack of 57 globally distributed benthic $\delta^{18}O$ records. Paleoceanography, v. 20, PA1003, doi:10.1029/2004PA001071.

Preto, N., Hinnov, L. A., Hardie, L. A. and V. De Zanche, 2001, Middle Triassic orbital signature recorded in the shallow-marine Latemar carbonate buildup (Dolomites, Italy). Geology, v. 29, p. 1123-1126.

Reid, S. B., 2010, The complex architecture of New Providence Island (Bahamas) built by multiple Pleistocene sea level highstands. Unpubl. M.S. Thesis. University of Miami, 127 pp.

Thompson, W.G. and Goldstein, S.L. 2005, Open system coral ages reveal persistent suborbital sea-level cycles. Science, v. 308, p. 401-404.

DOCUMENTING STRATIGRAPHIC HETEROGENEITY CAUSED BY SEA-LEVEL OSCILLATIONS DURING THE MIS 5E HIGHSTAND: EXUMAS MARGIN

Kelly L. Jackson, Gregor P. Eberli, Donald F. McNeill, Paul M. Harris[1], James S. Klaus
1 Chevron Energy Technology Company, San Ramon, CA

PROJECT OBJECTIVES

- Decipher Pleistocene sea-level oscillations recorded in core and outcrop in the Exuma Cays and relate to findings of Reid (2010) to construct a sea-level record for New Providence Platform, Bahamas.
- Document the stratigraphic heterogeneity, which is produced by oscillations within the last sea-level highstand, and assess the significance of this process for heterogeneity within carbonate cycles that are often reservoir flow units.

PROJECT RATIONALE

The Exuma Cays windward margin represents an exploration-scale, stacked succession of carbonate grainstones that include facies deposited over a range of water depths. Similar ancient sedimentary successions are often major hydrocarbon reservoirs. During the last two years we explored the lateral heterogeneity of this grainy margin by documenting the lateral heterogeneity of the marine facies belts and the patterns of Holocene accretion around Pleistocene antecedent topography. An examination of the vertical heterogeneity in cores drilled along the margin identified an oscillating sea level during the last highstand ~125,000 years ago, rather than a single rise and fall. This finding corroborates earlier reports of highstand oscillation in the Bahamas and elsewhere (Thompson and Goldstein, 2005; Kindler and Hine, 2009; Thompson et al., 2011). These meter-scale, sub-orbital sea-level oscillations produce complicated vertical facies successions in cores through these coastal carbonate systems.

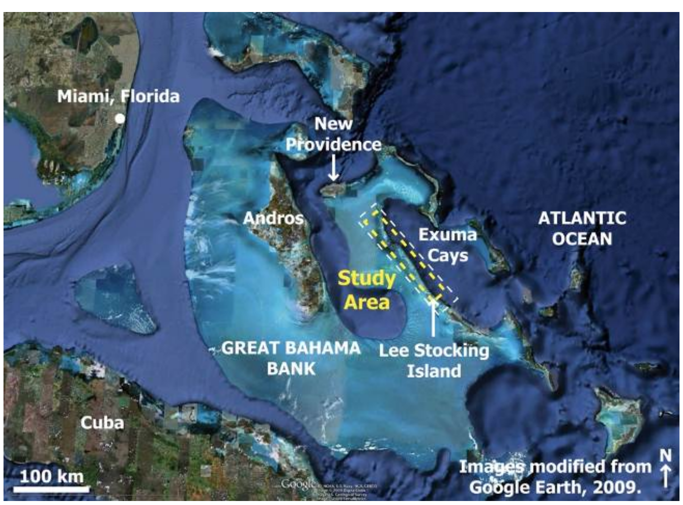

Figure 1. The Exuma Cays are located along the windward margin of Great Bahama Bank forming the eastern margin of New Providence Platform. Image modified from Google Earth, 2009.

One question is whether these oscillations have the ability to produce individual depositional cycles separated by an exposure horizon. If this is the case, it will question the hitherto accepted notion that carbonate cycles are primarily produced by orbitally-controlled sea-level fluctuations (Milankovitch frequencies). On one hand it will complicate modeling of carbonate cycle stacking patterns as the time span for each cycle might vary. On the other hand it might also help explain heterogeneity within carbonate cycles that are often flow units in carbonate reservoirs.

PROJECT SCOPE

To decipher the records of Pleistocene sea-level oscillations in the Exumas, cores were drilled at 14 locations along approximately 100 km of the grain-dominated Exumas windward margin. The maximum depth drilled was 23 m and the cores contain strata from the last interglacial ~125,000 years ago (MIS 5e) as well as 1 - 2 older highstand units (MIS 9 and/or 11). Cores document successions of subtidal, reef, beach, and eolian environments that can be used to document relative sea levels during the Pleistocene. Three criteria are used to document the position of sea level during MIS 5e: 1) the elevation of the transition from beach to eolian dunes, 2) the elevation of reefs plus an assumed water depth of 2 – 5 m, and 3) exposure horizons (calcretes, caliche crusts, and paleosols) within subtidal environments. Evidence from the Exumas combined with work by Reid (2010) indicates that sea level during MIS 5e was not a single rise and fall but oscillated and potentially pulsated at the end of the interglacial. Figure 2 illustrates a possible scenario for a MIS 5e sea-level curve in the Bahamas compared to Thompson and Goldstein (2005). Control points from cores, outcrops, and Reid (2010) were used to construct this working model.

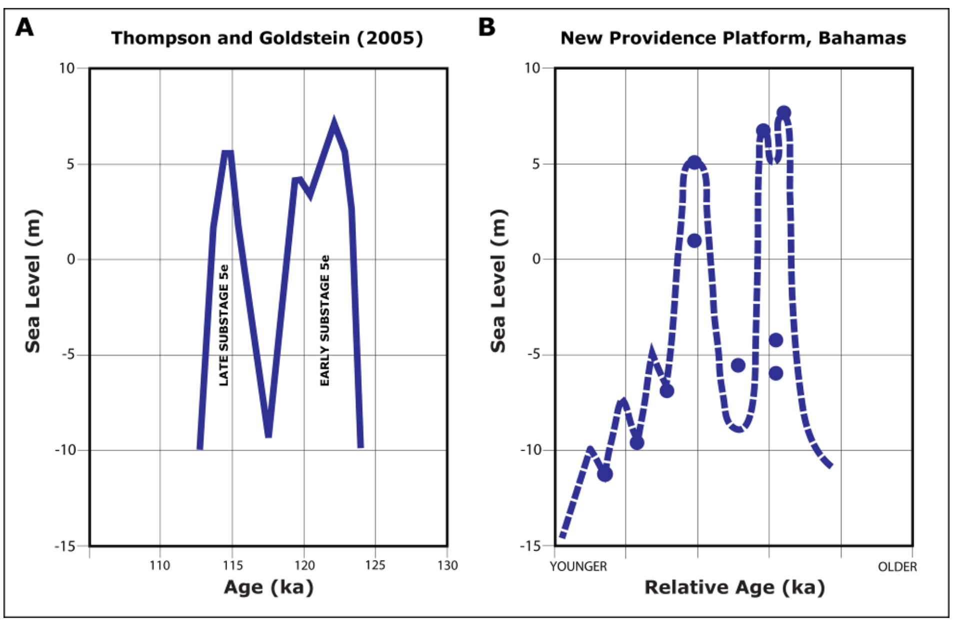

Figure 2. (A) MIS 5e sea level from Thompson and Goldstein, 2005. (B) MIS 5e sea level interpreted from the facies successions in the Exumas and New Providence, Bahamas. Blue dots indicate control points in core and outcrop from this study, Halley et al. (1991), and Aurell et al. (1995). The older peak is interpreted from Exumas subtidal deposits (i.e. Darby 3) and down-stepping beach ridges on New Providence Island. The younger peak is interpreted from Exumas reefs at sea level to +1.5 m above sea level (i.e. Darby 3, Rocky Dundas, and Halley et al., 1991) and New Providence down-stepping beach ridges. The drop between the two peaks is evidenced by the exposure (calcretes and paleosol) in Darby 3 (and other cores) in between the older subtidal unit and younger reef unit as well as a distinct calcrete and paleosol horizon on New Providence. The down-stepping pulses of sea level at the end of MIS 5e are based on downstepping bases of eolian dune ridges in the Exumas.

During 2012, we plan to complete all remaining fieldwork and core analyses. Dating is very important for the reconstruction of the timing of Pleistocene sea-level oscillations but it is not an easy undertaking in these shallow-water carbonates. The approach is to combine the amino acid racemization methodology with U-series dating on core samples. The goal is to at least be able to separate the two sea-level peaks within MIS 5e. If this can be achieved and the corresponding strata are separated by an exposure horizon, it can be postulated that the oscillations within MIS 5e have produced more than one carbonate cycle.

EXPECTED OUTCOME

The expected outcome of this project is to decipher the ages and amplitudes of high-frequency sea-level oscillations during Pleistocene highstands and document facies and stratigraphic heterogeneity resulting from the fluctuations. In particular, we expect to provide evidence for the creation of two carbonate cycles within MIS 5e.

SIGNIFICANCE FOR CYCLOSTRATIGRPAHY AND FLUID FLOW MODELING

The recognition of meter-scale fluctuations of sea level within highstands and the potential that these oscillations produce individual carbonate cycles has far reaching implications for cyclostratigraphy and the driving forces for sea-level changes. Currently, carbonate cycles are mostly related to the frequencies of orbital climate forcing that produce sea-level fluctuations in the 20, 40, and 100 kyr realm. The highstand oscillations with magnitudes of up to 20 m would require another, yet unexplained forcing mechanism of much shorter duration. Carbonate cycles of suborbital durations will add an unwelcomed complication in modeling these cyclic successions.

The oscillating sea level will also influence the lateral and vertical facies architecture within individual shallow-water carbonate cycles. Understanding the resultant facies juxtapositions and heterogeneities will be paramount for understanding the flow behavior in carbonate strata.

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THE RECORD OF HIGHSTAND SEA-LEVEL OSCILLATIONS IN PLEISTOCENE CARBONATE SHOALS: FLORIDA AND BAHAMAS

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

PROJECT OBJECTIVES

- Show how the variable elevations of tidally influenced ooid shoals deposited during the last interglacial document oscillations during the last sea-level highstand.
- Correlate Pleistocene depositional cycles across Great Bahama Bank to illustrate the difficulty of relating cycle thickness to sea level amplitude.

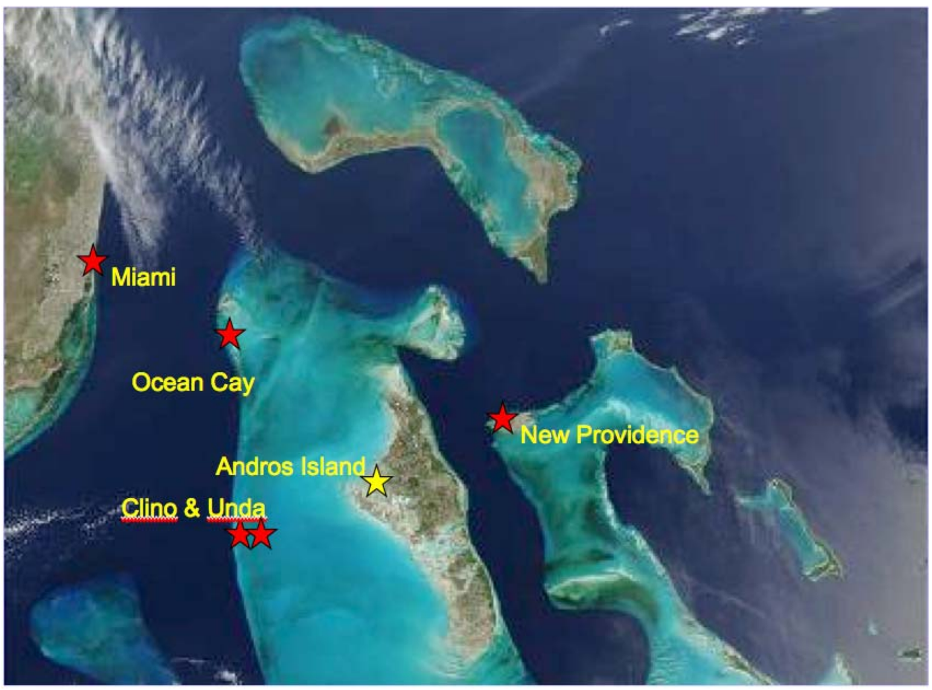

Figure 1: Locations of Pleistocene (MIS 5e) tidal shoals in cores and outcrops that are used in this study. The elevations of Pleistocene ooid shoals vary at each location. This study tests the working hypothesis that these variations are related to oscillations in sea level during MIS 5e.

PROJECT RATIONALE

Sea-level oscillations within highstands have been documented from stacked coral successions and repetitions of beach-eolian units in the Bahamas (Kindler and Hine, 2009; Thompson et al., 2011). There are two reasons why tidally influenced carbonate grainstone shoals potentially record the amplitudes of these oscillations with high precision. 1) The shoal crests are close to mean sea level and are often exposed at low tide. Thus, even small (meter-scale) drops in sea level would produce an exposure horizon. 2) If a sea-level oscillation within a highstand occurs, the tidal range will track it and the ooid shoal will develop at a new position. A small drop in sea level might just restrict the shoal development of the fringes of the existing shoal, thereby promoting lateral accretion. Oscillation-related growth might explain both the lateral extent and lateral heterogeneity in carbonate shoal systems. New Providence Island is a good example of how highstand oscillations expanded the island through lateral accretion (Reid, 2010).

APPROACH AND SCOPE OF WORK

In the Florida-Bahamas region several ooid shoal systems from the last interglacial highstand (MIS 5e) are found at different elevations (Figure 1). These shoal systems are studied in order to estimate the amplitudes of highstand oscillations and their influence on shoal architecture. For example, the Miami Oolite and the ooid shoal at Clifton Pier (New Providence) crest at 6-10 m above modern sea level, whereas at Ocean Cay (Figure 2) and in Andros cores retrieved from the crest of the Pleistocene shoal are about 5 m below modern sea level.

In a first step the elevations of the base and top of these different shoals are estimated with great detail. The vertical successions within each shoal will be logged and compared to the other shoals. Special attention will be given to sedimentologic indications of exposure to ascertain a single or polyphase growth of the shoal. Attempts will be made to date the shoals.

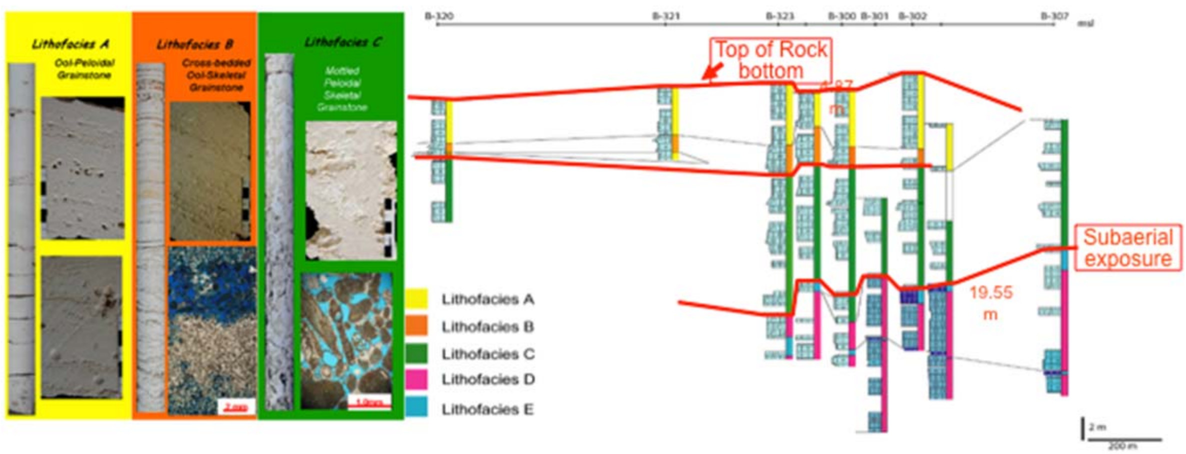

Figure 2: The Pleistocene (MIS 5e) shoal at Ocean Cay has its top about 5 m below modern sea level. Within the shoal a caliche horizon is observed, indicating an intermittent exposure (Cruz, 2008).

Several cores on Great Bahama Bank penetrated several Pleistocene depositional cycles. In borehole Unda and Clino, eight cycles are present within the last 800,000 years, and they are interpreted to be the record of eight orbitally controlled sea-level fluctuations (Kievman, 1998). However, the amplitudes of the sea-level fluctuations during this time period varied and not all of the sea-level highstands flooded the platform. For example, during the last 5,000 years there were only three times when sea level was high enough to flood the platform (Figure 3). This raises the question how five cycles were deposited. It is likely that the short-lived suborbital oscillations during the highstands produce depositional cycles that are identical to orbitally controlled cycles.

To evaluate this possibility, cores from Unda, Clino, Andros, and Clifton Pier are re-visited. Time equivalent cycles are examined for their facies and present elevation. The sedimentologic and diagenetic indicators for exposure vary. These variations might be controlled by the duration of exposure.

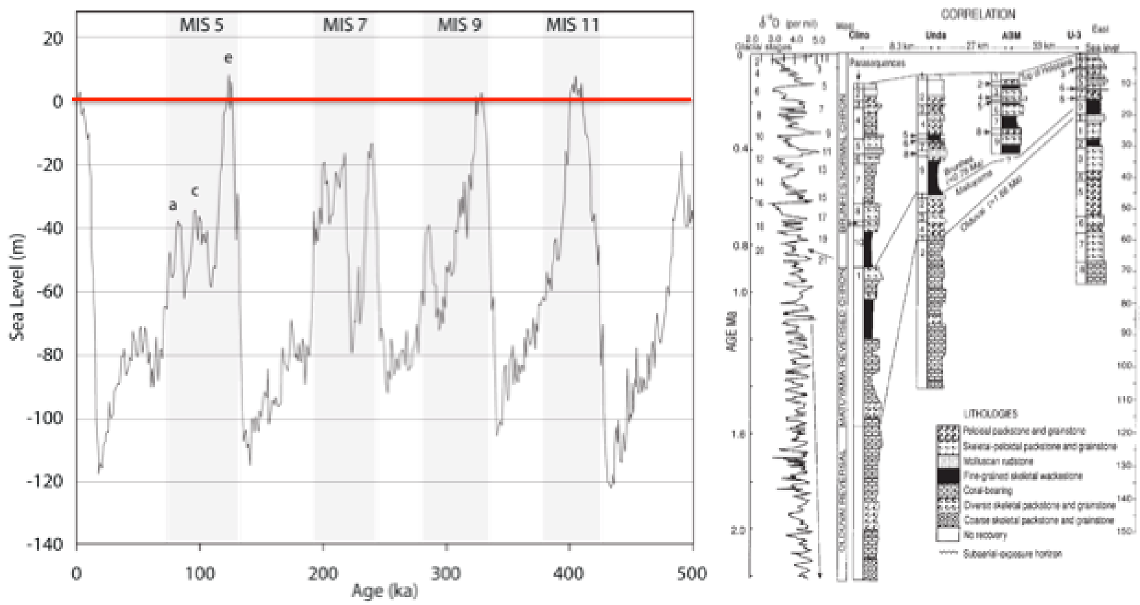

Figure 3: Left) Sea-level curve of the last 500 kyrs. The red line depicts the surface height of the modern Great Bahama Bank. During this time interval only three sea-level highstands reached the platform top. (Right) Correlation of depositional cycles with the stable isotope curve from Kievman (1998). Note how the cycles thin to the east and are at different elevations.

EXPECTED RESULTS

The elevation analysis of the ooid shoals potentially provides a good indicator of the amplitude of highstand oscillations of sea level during the last interglacial. Studying the process of lateral shoal accretion during these oscillations should provide a comprehensive model of oscillation-controlled shoal growth and the generation of stratigraphic complexity.

Analysis of the long cores will shed new light on the formation of orbital and suborbital shallow-water carbonate cycles.

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DATING OF QUATERNARY SEA-LEVEL OSCILLATIONS IN BELIZE CORALS: A DUAL APPROACH

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PROJECT OBJECTIVES

- Produce uranium-series age dates of cored Pleistocene corals with patchy distributions of diagenesis using laser ablation multi-collector inductively coupled plasma mass spectrometry (LA MC-ICPMS).
- Combine U-series dates with best practice methods (reported last year) to calibrate amino acid racemization age models.
- Test hypothesis of MIS 5e sea-level oscillations against age data.

PROJECT RATIONALE

Stacked corals record a 5-15 m sea-level drop within the last interglacial in the Red Sea and elsewhere (Siddall et al., 2003; Thompson & Goldstein, 2005). On Glover's Reef, Belize, an exposure horizon separates the two youngest Pleistocene coral sequences. Both sequences have similar amino acid racemization values suggesting that they are similar in age and possibly sub-stages within Marine Isotope Stage 5e. The earlier studies and our findings generate questions about how platform deposition and reef architecture responds to high-frequency sea-level changes. A pre-requisite before such questions can be answered is to precisely date observed cycles to Marine Isotope Stages (MIS).

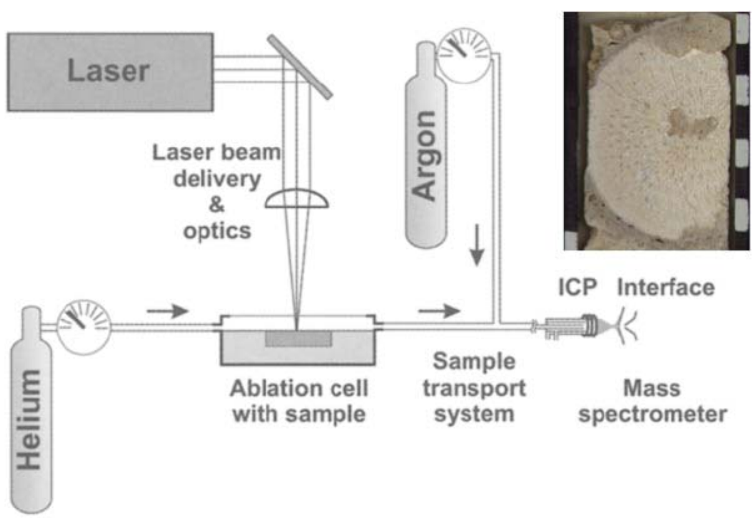

Figure 1. The Laser Ablation ICP-MS system, shown here in schematic, is particularly well suited to targeting areas of primary aragonite when diagenetic alteration is patchy, as shown in the Acropora palmata sample in the upper right corner. Schematic from Kosler, 2007.

Amino acid racemization (AAR) is a Quaternary dating technique that has the ability to attain a resolution of 5-10 ka in Pleistocene strata from tropical sites without the sensitivity to aragonite preservation of U-series dating (Miller & Brigham-Grette, 1989). It is also inexpensive, rapid, and requires very little fossil material for analysis. However, AAR is not an independent dating technique. For Pleistocene cores with abundant coral material but a high degree of mineral recrystallization, calibrating an AAR age model to U-series ages obtained by laser ablation will allow for a more continuous, accurate record than could be obtained by either method on its own.

PROJECT DESCRIPTION

This project attempts to improve the age dating of Quaternary sea level using corals obtained from cores taken at six sites on Glover's Reef, Belize. Although coral material is abundant, meteoric diagenesis has made dating the Pleistocene portions of the cores difficult. Several bulk Pleistocene coral samples have >98% aragonite preservation, but attempts to derive U-series from these samples have failed because of odd initial uranium isotopes and other indications of open system behavior. However, the ability of a LA MC-IPCMS to target individual spots on the scale of microns means that patchy distributions of secondary aragonite and other diagenetic products could be avoided (Figure 1) (McGregor et al., 2011).

This project will also take advantage of developing technology and methodology in the field of amino acid stratigraphy. Previous work has demonstrated that the extent of AAR increases monotonically down core and can be used to establish relative age with high resolution provided best practices for sample selection and preparation are followed. Even with laser ablation techniques available, suitable samples for U-series dating are only present in 1-2 intervals in the two cores from the windward cayes and no cores from the patch reefs of the atoll lagoon. In contrast, Pleistocene samples from five different drill sites and all described intervals are suitable for AAR analysis. By using LA MC-ICPMS U-series dates, where available, to calibrate the strong down core trends in AAR values, we hope to generate an age model for the development of Glover's Reef that is both accurate and robust against which to test our hypothesis of sub-orbital sea-level oscillations within MIS 5e.

EXPECTED RESULTS

Expected results include an effective method for constructing reliable Quaternary age models in coral-rich deposits that have been subjected to meteoric diagenesis, an enhanced understanding of how offshore atolls respond to sea-level change on the scale of thousands to hundreds of thousands of years, and a possible insight into how carbonate heterogeneity can be induced within sea-level highstands.

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Hydraulic Conductivity in the Plio-Pleistocene Reefal Deposits of the Southern Dominican Republic

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Project Objectives

- Determine how depositional facies and progressive diagenetic alteration influence the hydraulic conductivity and early porosity evolution of reefal carbonates.
- Integrate stratigraphic and hydrogeologic data into a reservoir model that can be used to test the effects of depositional and diagenetic heterogeneities on reservoir-scale transport and flow.

Project Rationale

Depositional and diagenetic heterogeneities within carbonate rocks can influence flow and transport parameters, and it is increasingly recognized that sedimentological and stratigraphic models can provide a method of incorporating geologic variability into models of fluid flow in both sedimentary aquifers (Fraser and Davis, 1998) and petroleum reservoirs (Fogg and Lucia, 1990). In carbonates, the porosity and permeability structure is dependent on both matrix porosity and the development of larger scale secondary porosity. The resulting complex porosity distribution in carbonates is reflected in the hydraulic-conductivity. If one views dissolution zones as discrete heterogeneities, the challenge of predicting transport in carbonate rocks is one of characterizing the hydraulic-conductivity distribution at a scale that captures the variability of these heterogeneities.

This study will integrate surface and subsurface stratigraphic, depositional, diagenetic and petrophyscial data with hydrogeologic data in order to characterize the hydraulic properties of Plio-Pleistocene reefal limestones of the Dominican Republic (Figure 1). Vertical profiles of hydraulic conductivity, obtained from short-interval packer tests will be conducted in a transect of six wells drilled perpendicular to the prograding depositional packages. Previous stratigraphic analyses of depositional and

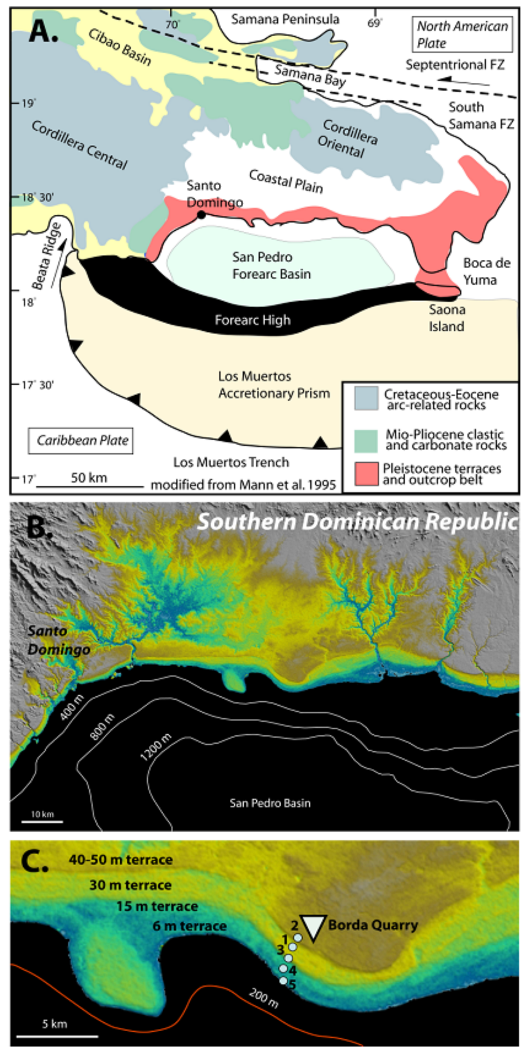

Figure 1. Southern Dominican Republic with core locations.

diagenetic facies, combined with detailed petrophysical characterizations will be combined with the short-interval (<1m) packer tests. These packer tests provide hydraulic conductivity data on both matrix and dissolution zones. The goal of the project is to obtain hydrostratigraphic data from the Plio-Pleistocene carbonates that can ultimately be incorporated into a reservoir model.

PROJECT DESCRIPTION

The Dominican Republic Drilling Project (DRDP) was initiated with support of the Industrial Associates in the summer of 2010. The project has focused efforts on defining lithofacies, delineating diagenetic zones, characterizing petrophysical properties and establishing the chronostratigraphic framework within five drilled boreholes from the southern coast of the Dominican Republic (Figure 1). In the absence of shallow seismic and borehole log data we have concentrated on generating the highest resolution age constraints possible for correlation. These new age data, combined with depositional lithofacies and faunal indicators has allowed us to better define the internal anatomy and stratal geometry of the individual sigmoids and sigmoid sets (Figure 2).

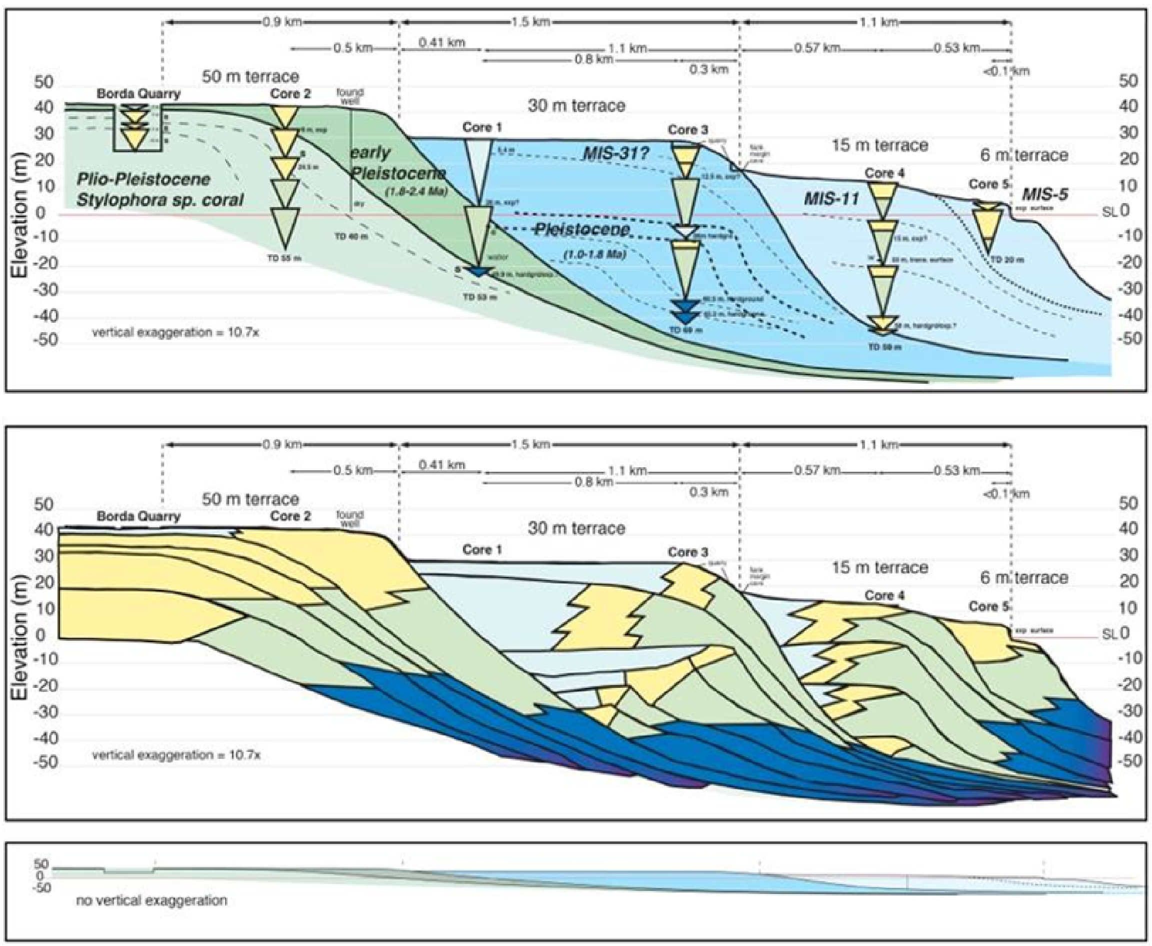

Figure 2. Cross-sectional model of Pleistocene reef sigmoids on the southern coast of the Dominican Republic east of Las Americas Int. Airport based on five recently drilled boreholes (Figure 1). Vertical and lateral variations in hydrologic conductivity will be determined by stratal packer tests and compared to depositional and diagenetic facies patterns (lower).

Vertical and lateral variability in hydraulic conductivity will be determined from constant-head injection tests performed in six different wells varying in depth from 25 m to 70 m. A straddle-packer assemblage with an open interval of 0.3-0.9 m will be used to perform constant-head injection tests at 1.0 m intervals in the six wells. Hvorslev (1951) developed an equation for analyzing steady-state, constant-head injection tests. Although designed for saturated zones, the method has applications in unsaturated zones. If L is greater than $5r$, as is the case in all testing proposed here, the equation simplifies to:

$$K = \frac{\left(Qln\left(\frac{L}{r}\right)\right)}{2\pi HL}$$

where K is hydraulic conductivity, r is the radius of the well, L is the length of the test interval, H is the injection head, and Q is the injection rate. Detailed descriptions of the constant-head injection test procedure are provided in Harlow and Lecain (1993).

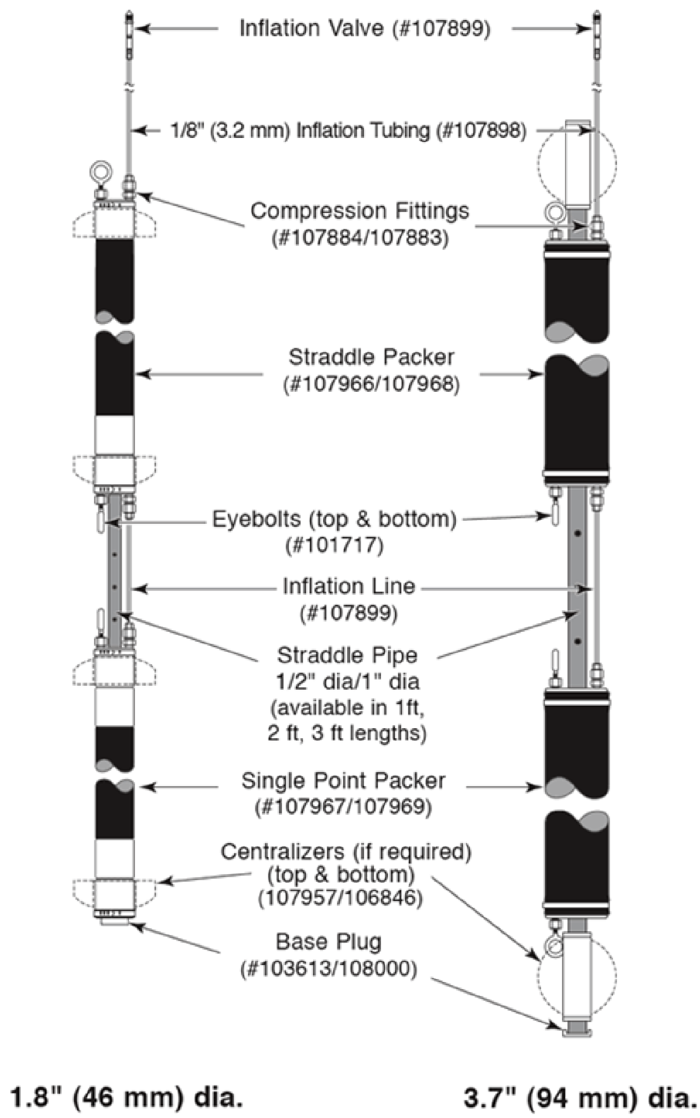

Figure 3. Schematic diagram of Solinst stratal packer system that will be used to determine the hydrologic conductivity from the southern DR wells.

While the short measurement interval was designed to minimize the averaging inherent with most packer tests, this methodology has limitations. Resulting hydraulic conductivities are still averaged over the length of the test interval; for matrix dominated test intervals this is probably appropriate. For dissolution (or fracture) dominated test intervals, the bulk of the flow is carried through the moldic porosity (or fracture) despite representing a minor percentage of the overall test-interval length. In order to calculate realistic cavity transmissivities, it would be necessary to know the number and apertures of these structures. These data are not currently available.

KEY DELIVERABLES

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

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DISTRIBUTION & MORPHOLOGY OF COLD-WATER CORAL MOUNDS AROUND LITTLE AND GREAT BAHAMA BANK

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PROJECT OBJECTIVES

- Determine the number and distribution of cold-water coral (CWC) mounds on the slopes and basinal areas of Little and Great Bahama Bank.
- Relate mound morphology and distribution to the slope morphology and current pattern.
- Assess the growth process of CWC mounds by: 1) visualizing and quantifying the sediment and coral framework in the Matterhorn mound, and 2) determining the growth rate of the Matterhorn mound by dating the corals in the core.
- Describe the nature of the sediments in the and off the mounds for an assessment of sedimentary processes on the seafloor.

PROJECT RATIONALE

Large cold-water coral mounds are thought to form in areas that experience strong bottom currents, since these currents: (1) concentrate and transport nutrients to corals; (2) facilitate coral settlement by minimizing sediment accumulation on hardgrounds; and (3) deliver fine-particles that are baffled into the coral framework (*e.g.* Mullins et al. 1981; Van Rooij et al., 2003). In many areas along the slopes of Great Bahama Bank hydrodynamic conditions are not related to either the orientation or the height of the mounds (Eberli et al., 2007, Correa et al., 2012). Thus, other factors such as antecedent topography, slope morphology created by sedimentary processes and accumulation rates processes might also be important for mound location and development.

Two large data sets of multibeam bathymetry that cover 5500 km^2 along the slopes of GBB and 5000 km^2 along Little Bahama Bank (LBB), collected during the CARAMBAR cruise, provide the opportunity to examine the variations of the CWC mounds on the slope and relate these variations to changes in sloe morphology and current pattern. In particular, it allows assessing if slope canyons and mass gravity flow deposits are preferred sites of mound growth. Two piston cores taken during the cruise, one into a 120 m high mound (Matterhorn) and one into the adjacent sediment, offer the opportunity to examine the distribution of the corals within the mound and to shed light on the growth rate of the mound. Together these data sets provide a comprehensive overview of the distribution, growth and morphology of CWC mounds in the Straits of Florida.

ASSESSING THE DISTRIBUTION AND MORPHOLOGIES OF THE MOUNDS

The new data sets have a resolution of about 6m and thus image the mounds with great detail. The number and morphologies of the mounds vary along strike (Figure 1). In some areas the mounds are very abundant and aligned along ridges and canyons. In

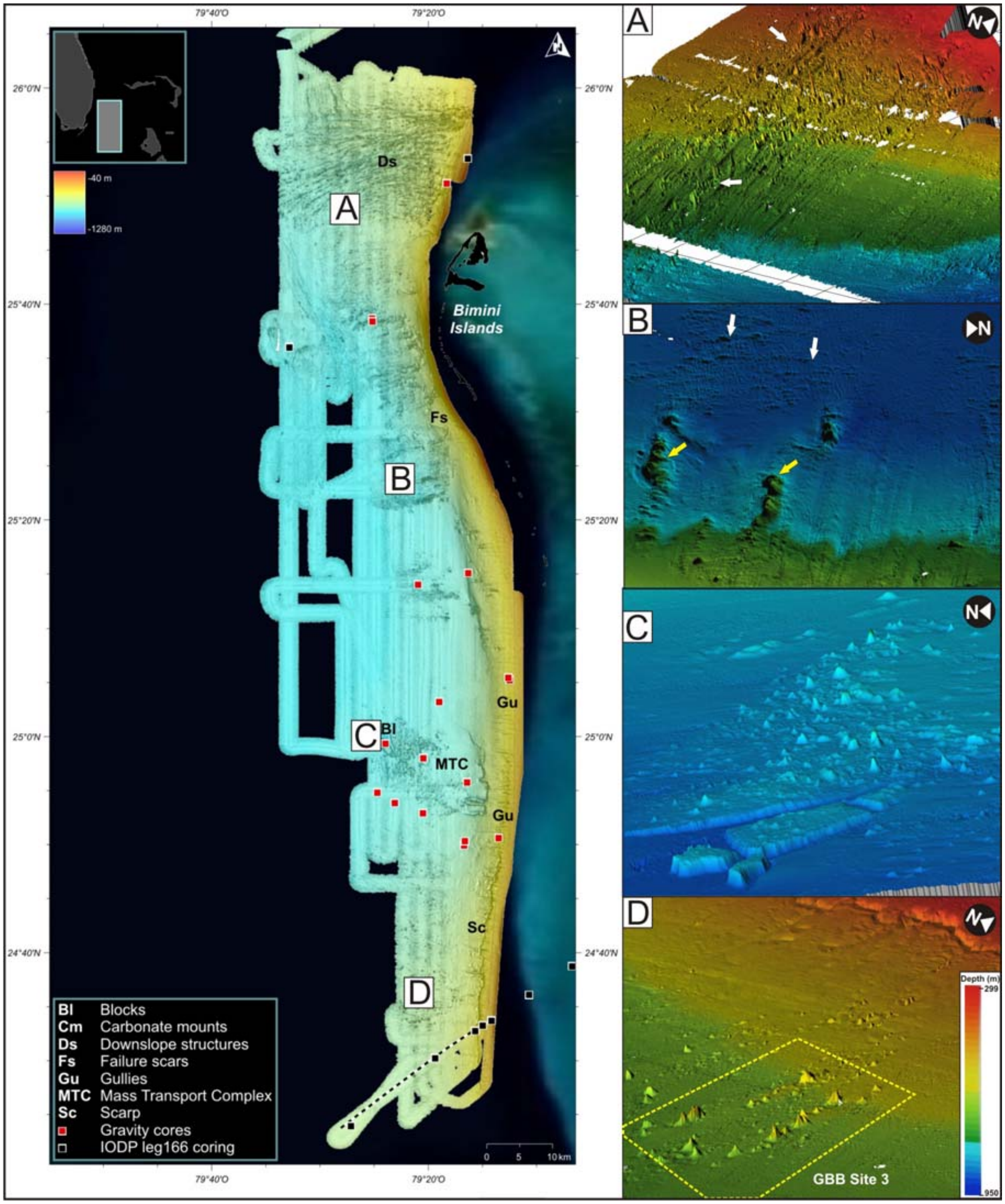

Figure 1. Left) Multi-beam bathymetry image of the western slope of Great Bahama Bank displaying the slope morphology including the cold-water coral mounds along the slope. Right) Close-up of bathymetry maps with examples of the various mound fields. A. North of Bimini, the mounds are arranged along ridges next to canyons and gullies. They are often tens of meters high. B. Further south, the mounds also arranged in two ways; on the slope they cover or form downslope ridges (yellow arrows) while in the adjacent basinal area they are knobby and smaller and have a NNW-SSE orientation (white arrows). C. In the scar and mass transport complex area (MTC), they sit on spur formed by the slope failure and cover the mass wasting deposits, including large slabs. D. In the southernmost part of the investigated area, large mounds are scattered over a large area but the mounds are generally arranged downslope, perpendicular to the platform margin. (from Sianipar et al., 2011)

other areas they are irregularly distributed or likely situated on mass gravity flow deposits. In the more distal areas, the mounds are smaller and generally elongated following the contour lines of the slope. We will test the hypothesis that these contrasting mound morphologies are the result of different controls. The large irregular mounds are mostly controlled by irregular antecedent topography while hydrodynamic processes primarily control the smaller mounds.

To quantify the number and the variable morphologies, the digital elevation model (DEM) from the multibeam bathymetry map will be analyzed using the workflow developed by Correa et al. 2012). For this quantitative analysis each mound needs to be defined, which is not an easy task because mounds can coalesce and are often on an inclined slope. A reproducible, automated method for extracting mound features from the DEMs was developed using Petrel™ software. This method relies on the change of slope angle between mound and surrounding area. Based on dip angle maps closed polygons are generated surrounding each mound. A Matlab™ routine calculates the maximum thickness (i.e., mound height) within each mound polygon (Correa et al., 2012).

ARCHITECTURE OF THE MATTERHORN MOUND

A gravity core taken through the Matterhorn penetrated 7.03 m and bottomed out in indurated wackestone. Corals are distributed throughout the core, indicating that the mound is not a lithoherm, but built by soft layers coral boundstone and floatstone with wackestone interruptions (Figure 2).

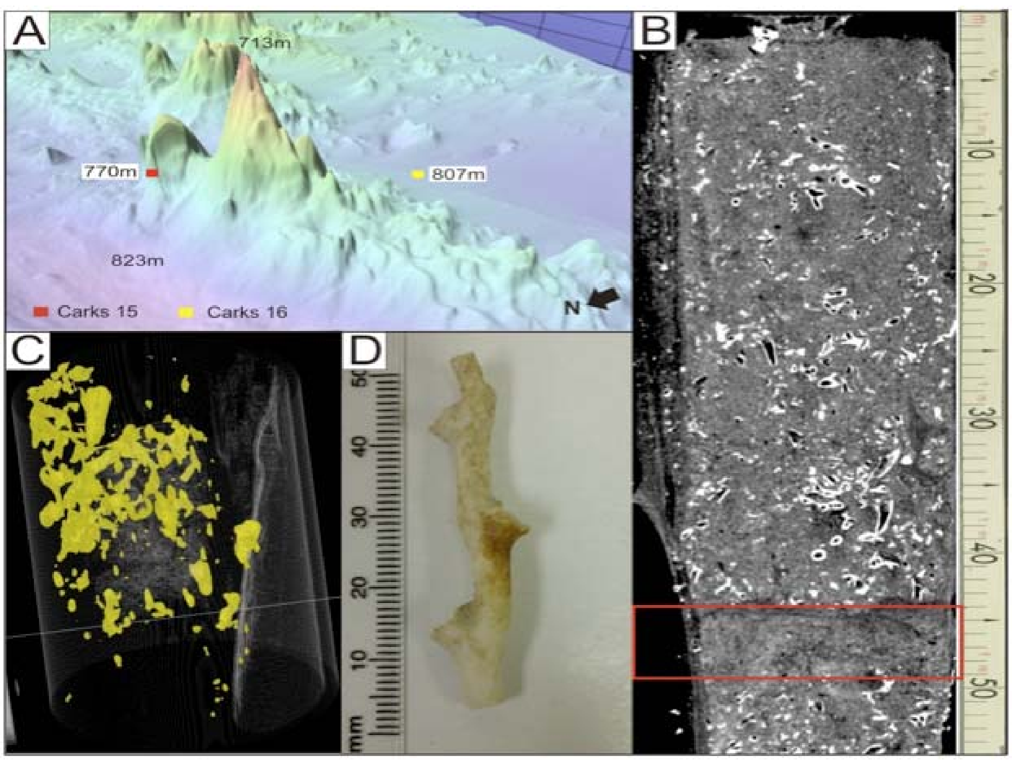

Figure 2: A) The Matterhorn mound with the location of the two gravity cores. B) CT scan of the part of the mound core displaying coral floatstone and a thin interruption of fine-grained sediment. C) 3D display of the coral boundstone within the core. D) example of coral from the inside of the mound that will be used for dating.

The cores from the Matterhon mound allow examining the internal architecture of the top portion of the mound. The mound core was scanned with CT scanner. The 3D scan display the distribution of coral, their growth direction, and the amount of corals. We will visualize and quantify the corals and the trapped sediment by uploading the Seg-y files of the scans into Geoprobe for attribute analysis and bodychecking.

Coral species will be determined to assess the biodiversity in the mound. Age dating of corals will help establish the growth rate of the mound.

Sedimentologic analysis of the trapped sediment and sediment adjacent to the mound will include x-ray diffraction, grain size analysis, modal composition and assessment of the provenance of the grains. These data will be compared to the findings of Correa et al. (2008) who found that variable mound heights in the Straits of Florida correlate to variable input of periplatform sediment into the mound structure and that the large mounds on the slope of GBB contain higher percentages of peloids and aragonite content than smaller mounds in the middle of the Straits.

The induration at the base of the core indicates some early diagenetic alteration within the mounds. These diagenetic changes are assessed by petrographic and geochemical analyses. These include: carbon and oxygen isotope of coral fragments from the Matterhorn and the mud-sized fraction of the matrix , X-Ray diffraction to determine the mineralogy, chemical analyses of the pore water chemistry.

EXPECTED RESULTS

The morphometric analyses of the mounds fields along both Little and Great Bahama Bank is placed within the context of the slope processes and hydrodynamic regime. As such this study offers the opportunity to relate growth, distribution and abundance of coral mounds to topographic, sedimentologic and hydrodynamic conditions.

The cores from the Matterhorn mound will provide a documentation of mound growth and early diagenesis that can be compared to the findings from cores into the mounds located in the Porcupine Basin.

Together these data sets will provide a comprehensive model for CWC mound initiation and morphologic evolution in the vicinity of carbonate platforms.

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EXPEDITION TO THE WEST ATLANTIC COLD-WATER CORAL ECOSYSTEMS

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PROJECT OBJECTIVES

- Collect a comprehensive data set from the deep-water environments of the Gulf of Mexico and Florida Bahamas region that can be exploited for the geological characterization of the seabed and its cold-water coral (CWC) habitat.
- Correlate in each site mound size, height, shape and spatial density of cold-water coral mounds in the Gulf of Mexico and the Straits of Florida to current strength and direction.
- Describe and quantify the facies of the CWC habitats for a better understanding of the spatial pattern of facies in deep-water environments.

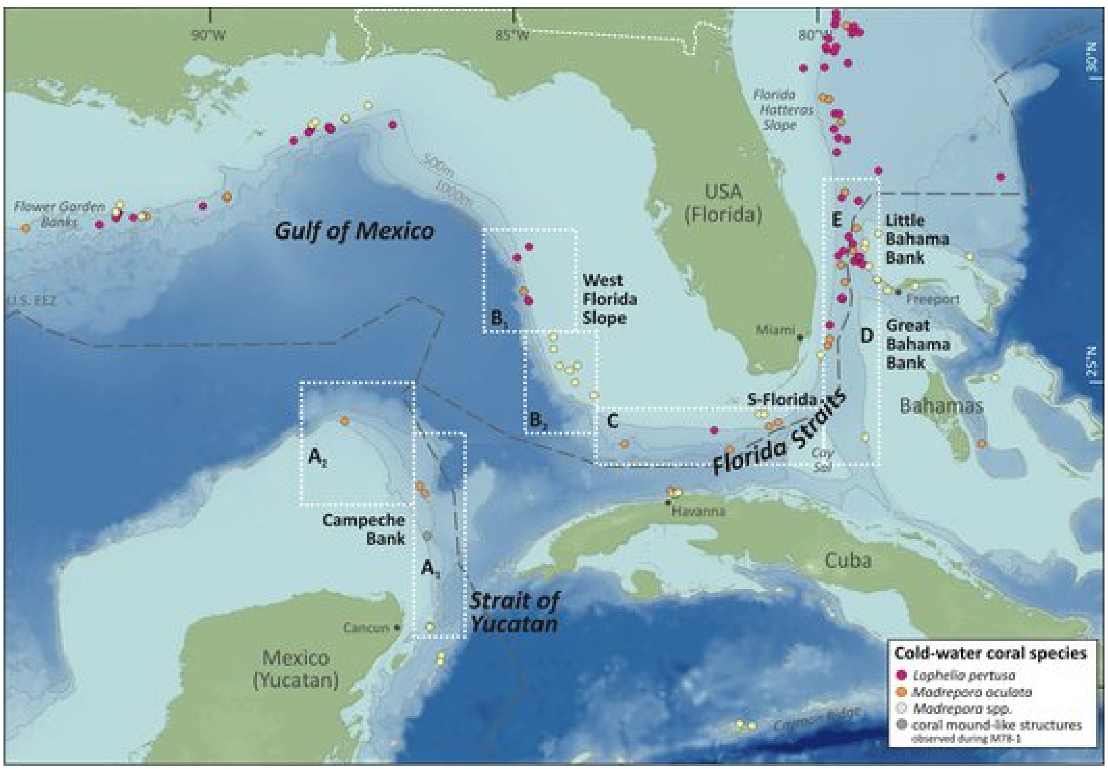

Figure 1. Location map of the working areas during the expedition.

PROJECT FOCUS AND GOALS

The expedition with RV MARIA S. MERIAN will investigate cold-water coral (CWC) ecosystems in the West Atlantic Ocean (Florida Straits, Gulf of Mexico). Occurring in water depths of 300 m to 900 m these cousins of the more famous shallow-water corals are still poorly known. The overall focus of the expedition will be on the assessment of the CWC ecosystem distribution, appearance and biodiversity under present and past glacial conditions. The overall aim is to compare the CWC ecosystems of the West Atlantic (Gulf of Mexico and Florida-Bahamas region) with the CWC sites of the East Atlantic and to the sites in the Straits of Florida that have been extensively studied by the CSL-CCR (Grasmueck et al., 2006; Correa 2011).

CSL-CCR participation in this international research expedition under the leadership of Dierk Hebblen and Claudia Wienberg from the University of Bremen will complement the ongoing investigations of CWC mounds in the Straits of Florida. The additional bathymetry and core and sediment material will add important information to answer fundamental questions surrounding the CWC mounds and the associated facies.

APPROACH

The sampling targets during the cruise to the NW Atlantic Ocean comprise "potential" CWC mounds along the N- and E-Campeche Bank (working areas A1 & A2, Yucatan Peninsula) and the West Florida Slope (working areas B1 & B2) within the Gulf of Mexico, and reported CWC occurrences in the Florida Straits (working area C: south off Florida, working area D: Great Bahama Bank, working area E: Little Bahama Bank). For all selected sites station work will start with detailed bathymetric mapping (multibeam echosounder) and ROV video surveys to characterize the facies and fauna, and to identify the most suitable coring sites. We will apply the Bremen ROV Cherokee to conduct a detailed characterization of the existing facies and fauna (video mapping) supplemented by surface sediment sampling (box corer, grab sampler) as well as the measurement of water mass properties (CTD/Rosette, deployment of satellite lander systems). Moreover, it is intended to collect a series of sediment cores to study the development of the west Atlantic cold-water coral ecosystems under changing environmental conditions. Based on this information, positions will be defined to conduct a dedicated sampling (gravity cores, box cores, grabs, water samples) and monitoring (CTD, lander) program within, or in the direct vicinity of, the observed CWC sites. During previous expeditions this strategy (mapping -> video observation -> targeted sampling) has proved to be very successful in sampling CWC material and providing data on their surrounding environment.

KEY DELIVERABLES OR EXPECTED RESULTS

The samples and data to be obtained during the expedition will allow (1) reconstruction of the spatial and temporal distribution patterns of CWCs in the Straits of Florida and the Gulf of Mexico during the last glacial-interglacial cycle and (2) the resulting data to be placed in a North Atlantic-wide context by linking them with the available extensive NE Atlantic dataset, and finally (3) identification of the major environmental forcing factors that control CWC growth and development in the North Atlantic realm (Marum website).

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Reservoir Potential of Cretaceous-Paleocene Carbonate Turbidite Successions: A Core and Outcrop study, Adriatic Sea, Italy (year 2)

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Project Goal

The main goal is of this project is to assess the reservoir potential of Cretaceous–Tertiary carbonate turbidite successions through a sedimentological, diagenetic, and petrophysical characterization of the strata in the basin adjacent to Adriatic carbonate platforms. The main tasks for this year are:

- Petrophysical characterization of the re-deposited carbonates that includes permeability, porosity, sonic velocity, and resistivity measurements from the core plugs.
- Comparative study of coeval onshore strata at Monte Conero and the Maiella Mountains, and coeval strata in the Bahamas.

Project Rationale

Porosity and permeability measurements of carbonate turbidite successions, including large megabreccias found in outcrops along the Maiella platform margin documented that such turbidites have a reservoir potential. Interestingly, the underlying Cretaceous strata have significantly more porosity than the overlying Tertiary strata (Eberli et al., 2006). A 286 m core taken by ENI offshore in the Adriatic Sea from coeval slope and basinal facies shows similarly a better reservoir quality in the Cretaceous strata. The better reservoir quality is most likely related to the original mineralogy of Cretaceous re-deposited carbonate, which is calcite, compared to the Tertiary sections with aragonite that are prone to remobilization and recrystallization (Maura et al., 2011). To test this hypothesis a thorough petrographic and petrophysical analysis of the carbonate turbidite successions and the associated background sedimentation is needed.

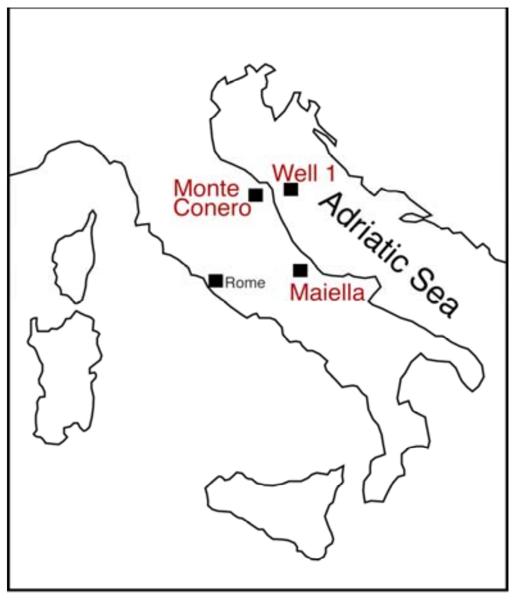

Figure 1. Locations of the two main outcrop areas at Maiella and Monte Conero, and the position of Well 1 in the Adriatic Sea. The core of Well 1 is provided by ENI for this study.

Approach and Scope of Work

For the assessment of the reservoir potential of re-deposited carbonates a comprehensive petrophysical characterization will be conducted, which includes sonic velocity, porosity, permeability, and some resistivity measurements on samples from various outcrops and the core material from Well 1. A thin section will be cut from each sample for analysis of texture, pore structure, and diagenetic overprint. Digital image analysis of the pore structure will allow this feature to be related to both the acoustic and hydraulic properties.

The diagenetic alteration of both the turbidite successions and the background sediment will be investigated in order to test the hypothesis that the difference between calcite (Cretaceous) and aragonite (Tertiary) seas influences the reservoir potential. Both thin sections and extensive SEM imagery will document the differences (Figure 2). We plan to study samples from several outcrop localities to assess potential local effects. In addition, a comparison will be made with the diagenetic state of coeval carbonate successions in the Bahamas that were cored during DSDP Leg 11 (Bernoulli, 1972) and during ODP Legs 101 and 166.

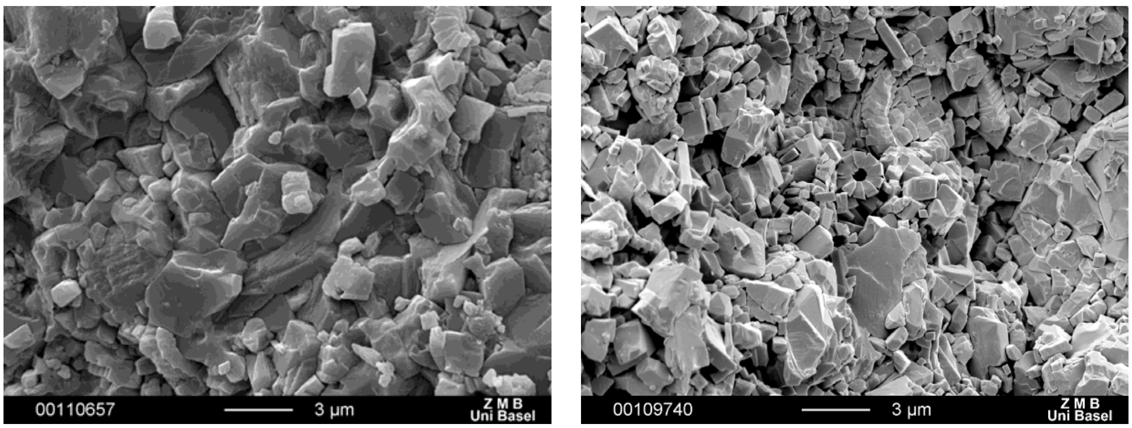

Figure 2. SEM photomicrographs of the background sediments in Well 1 (Left) Recrystallized coccolith-rich matrix of Upper Paleocene background sediment. (Right) Coccolith chalk with abundant micro-porosity in the Cretaceous portion of Well 1. (Photos provided by University of Basel). The difference in crystallization indicates a variable diagenetic overprint related to the stratigraphic position.

KEY DELIVERABLES

This project will provide a comprehensive sedimentological, petrophysical and diagenetic characterization of Cretaceous and Tertiary mass gravity flow deposits along some Adriatic carbonate platforms. Together these results will help assess the reservoir potential of re-deposited carbonates and quantify the differences that variations in the original mineralogy might have on the petrophysical properties.

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FROM OUTCROP TO BASIN SCALE: SEISMIC ANALYSIS OF THE MIXED SYSTEM IN THE NEUQUÉN BASIN, ARGENTINA

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PROJECT OBJECTIVES

- Refine the sequence stratigraphic framework in the mixed system of the Neuquén Basin based on regional cross sections.
- Correlate the detailed outcrop descriptions to the producing fields using seismic data.
- Analyze the seismic architecture and their changes based on the sequence stratigraphic framework.

PROJECT RATIONALE

The Quintuco-Vaca Muerta System is a highly heterogeneous mixed carbonate siliciclastic succession. Over the last three years we have described two field-scale outcrop analogs in both distal and proximal settings in great detail. This fieldwork yielded insights into the field-scale architecture, (reservoir) facies distribution and the processes controlling the mixing of carbonate and clastics. However, the next step should be to aquire an understanding of the regional relationships and develop a large-scale seismic stratigraphic framework based on regional 2D seismic lines.

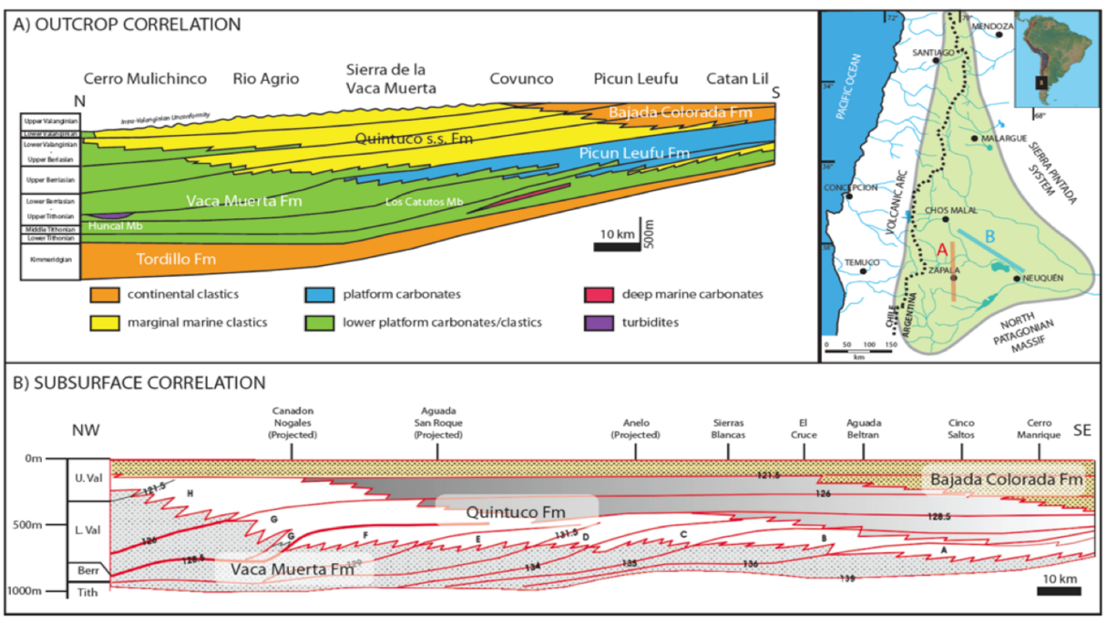

Figure 1: Existing outcrop and subsurface correlations of the Upper Jurassic – Lower Cretaceous Mixed System. A: Outcrop correlation with the observed depositional environments (modified from Leanza et al., 2011). B: Subsurface correlation along the producing fields (modified from Mitchum and Uliana, 1985). Approximate locations of lines A and B are given in the map (modified after Howell et al., 2005).

Moreover, the correlation between the outcrop sections in the west and the producing fields in the east using regional 2D lines will allow the knowledge gained from the outcrop analogues to be applied to the subsurface and will simultaneously test its accuracy (Fig. 1).

Finally, using the same seismic stratigraphic framework, the extensive 3D seismic dataset can be used to interpret and map geometries along dip and strike and will help us understand the basin wide depositional processes during Late Jurassic to Early Cretaceous times in the Neuquén Basin.

SCOPE OF WORK

The Neuquén Basin is a traditional petroleum province that has been explored for many decades and where large datasets of 2D and 3D seismic data have been acquired over the years. These combined data sets offer a unique opportunity for a detailed seismic stratigraphic analysis that with its comprehensive nature and higher resolution potentially add new insights to the studies of the 1980s (Mitchum and Uliana, 1985). In a first step, we will collect several large-scale (>200km) seismic lines and develop a sequence stratigraphic scheme following Mitchum and Uliana (1985) nomenclature. This will act as the regional framework (Fig. 1B).

In a second step, this framework will be connected to the outcrops at the Sierra de la Vaca Muerta (Fig. 1A) by mapping several main sequence boundaries along 2D lines from east to west. The well-established biostratigraphic subdivision (Fig. 1A) at the outcrop sections can be used to place other sections (e.g. Picun Leufu Anticline) within the large-scale framework.

Finally, the extensive 3D seismic dataset (> 10 000 km^2) can be interpreted and key reflectors can be mapped over several seismic volumes in order to analyze architecture, changes along dip and strike and get better insights into the developments of the basin over time. This adds a new scale and another dimension, which cannot be obtained from outcrops alone.

EXPECTED RESULTS

Seismic stratigraphy:

The high quality seismic data available for the seismic stratigraphic interpretation (Fig. 2) will allow for an unprecedented detailed interpretation, which will make it possible to extend interpretation from the sequence into the system tract scale. This will add substantial new information and will serve as the new benchmark for seismic stratigraphic interpretations in the highly active exploration and development area.

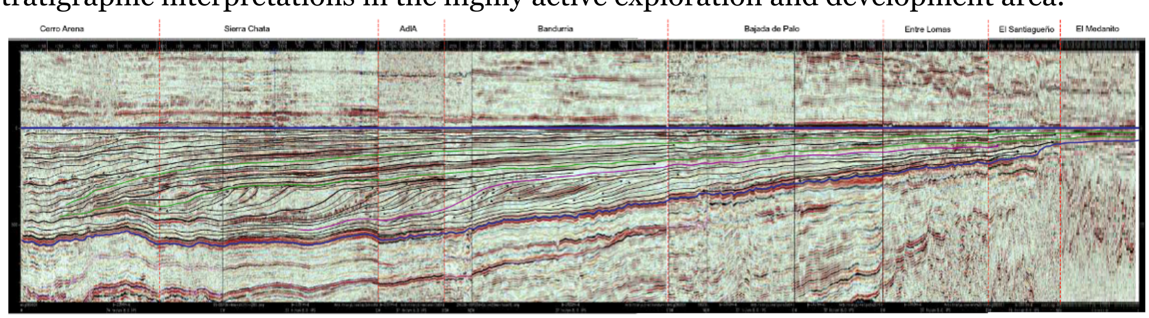

Figure 2: Regional 2D Seismic Cross Section (from Leanza et al., 2011). Example of a published line, similar to the available data. Note the variability in dip angles and reflection strength. This type of data will allow detailed seismic stratigraphic analysis.

Outcrop Subsurface Correlation:

The correlation of detailed outcrop sections with the regional 2D seismic stratigraphic framework holds two very valuable implications. First, placing the outcrop information in this very heterogeneous system at the correct stratigraphic position will help to interpret the specific interval and thereby enhance the subsurface reservoir characterization.

Second, correlating the main sequence boundaries with the well-established biostratigraphic framework will enable us to test Mitchum and Uliana's (1985) age model. Since this model was mainly based on the global eustatic curves it carries some uncertainty in the tectonically very active back-arc basin where synsedimentary deformation has been proven to have a strong influence on the sedimentary system (Grimaldi and Dorobek, 2011).

3D Seismic Analysis:

The 3D seismic analysis will offer insights into the large-scale architecture of the mixed carbonate siliciclastic system. Changes in geometries, reflection strength etc., already observed in 2D sections (Fig. 2), can be related to alternations along dip and strike. Together with the 2D seismic stratigraphy framework, these developments can be linked to both tectonic and eustatic variations during time of deposition. Finally, we plan to establish an atlas of seismic geomorphologies representing the typical seismic geometries characteristic for the particular seismic systems tract.

The expansion of the study from the outcrop to the basinal scale will provide an exceptional framework in order to implement the detailed outcrop descriptions into the subsurface reservoir characterization workflow and will significantly support interpretations for conventional and unconventional hydrocarbon exploration in the Neuquén Basin.

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ROCK FLUID INTERACTION: VELOCITY EVOLUTION DURING CONTROLLED PRECIPITATION AND/OR DISSOLUTION

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

PROJECT OBJECTIVES (OR PURPOSE)

The processes of rock/fluid interaction and diagenetic alteration of carbonate rocks are well understood, but little data exist to quantify the resulting changes and their influence on petrophysical properties. 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
- Enhance our understanding of the effects of chemical rock-fluid interaction
- Capture changes of acoustic velocity and permeability during chemically controlled rock-fluid interaction

PROJECT RATIONALE

Carbonates are prone to diagenetic alterations that result in changes of the petrophysical properties. Small amounts of newly formed contact cement can stiffen the rock. Similarly, dissolution from slightly acidic formation waters or acid treatment during well completion can produce secondary porosity and increased permeability.

Laboratory experiments with controlled precipitation and dissolution are needed to better understand the acoustic behavior of carbonates during such processes. During these experiments the petrophysical properties of the sample need to be observed before, during, and after altering the rock. This experimental design will allow answering questions in regards to the stiffening of the rock frame by newly formed crystals at grain-grain contacts, and the evolution of fluid pathways, porosity and permeability as well as the softening of the rock framework during dissolution

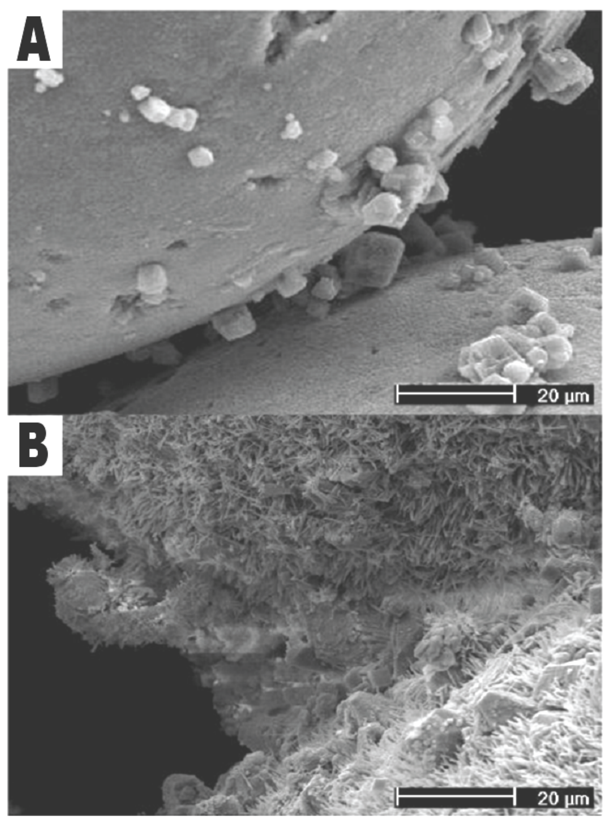

Figure 1: Precipitation occurs preferentially at the ooid-to-ooid grain contacts (top), but sometimes overgrows the entire ooid surface with needle structures (bottom).

PROJECT DESCRIPTION

Rock evolution and changes will be documented, particularly with respect to acoustic velocity. One aspect will be to evaluate the effects of observed crystallization at grain-to-grain contacts on measured acoustic velocity. Another aspect will concentrate on the effect of dissolution in ooid grainstones on both acoustic velocity and fluid flow permeability.

Results of phase 1 precipitation study have shown that clean ooids are cemented together by calcium carbonate crystal precipitation in only a few weeks (Figure 1). Precipitation occurs preferentially at the ooid-to-ooid grain contacts (Figure 1A), but sometimes overgrows the entire ooid surface with needle structures (Figure 1B). 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 rockframe of lower stiffnes for its lower porosity.

In the second phase of this project, the focus will be more on dissolution. Under-saturated solution will be circulated though the samples for several days. Fluid composition, acoustic velocity, and fluid flow permeability will be measured during the experiment. Changes in the rocks pore structure will be captured by high-resolution CT scans before and after the experiment. Changes in pore geometry will be analyzed in the context of changes in petrophysical parameters.

DISSOLUTION WORKFLOW

- Perform high-resolution CT scan of several samples of variable texture (grainstone, packstone, etc.) but similar porosity.
- Measure acoustic velocities and permeability.
- Expose these samples to long-term infiltration with an under-saturated solution.
- Measure velocity and permeability at set intervals during infiltration experiment.
- Sample and analyze downstream fluid line for chemical changes.
- Perform high-resolution CT scan and compare pore structure changes.

EXPECTED RESULTS

A data set will be generated that captures chemical changes of the pore fluid and the resulting changes in acoustic velocity and fluid flow permeability in the rock. High-resolution images using SEM and high-resolution CT scans will provide estimates of crystallization or dissolution during chemical rock-fluid interaction.

In particular, we will focus on determining the differences in acoustic velocity changes due to growth of different crystal structures. Preliminary results have shown that larger blocky crystals growing on grain-grain contacts create apparent stiffening while smaller needle like crystal growth creates apparent weakening. Additional experiments are design to confirm these findings.

SUB-MICRON DIGITAL IMAGE ANALYSIS (ESEM-DIA), PORE GEOMETRIES AND ELECTRICAL RESISTIVITY IN CARBONATE ROCKS

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

PROJECT OBJECTIVES

- Assess the controls of the sub-micron pore structure on electrical resistivity.
- Expand the resistivity dataset to dolomites and combine with existing datasets.
- Develop methods to apply Digital Image Analysis (DIA) to Environmental Scanning Electron Microscopy (ESEM) imagery; combine and compare with Mercury Injection Capillary Pressure (MICP) and/or µ-CT measurements.

PROJECT RATIONALE

Verwer et al. (2011) postulate that electrical resistivity and Archie's cementation factor *m* are directly related to the number of pores and pore throats. This hypothesis is based on digital image analysis (DIA) of thin sections. Successive tests of this hypothesis with a) imaging the pore structure with high-resolution CT scans and subsequent modeling and b) by relating MICP in rocks to electrical resistivity corroborated Verwer's findings (Figure 1). Finite element modeling of resistivity of the µ-CT tomographs, however, revealed the importance of the microporous regions that often lie in the sub-micron range. To understand and predict the effect of the pore structure on the electrical behavior of a rock, it is paramount to analyze both macro- and microstructure of the pore system in both limestones and dolomites.

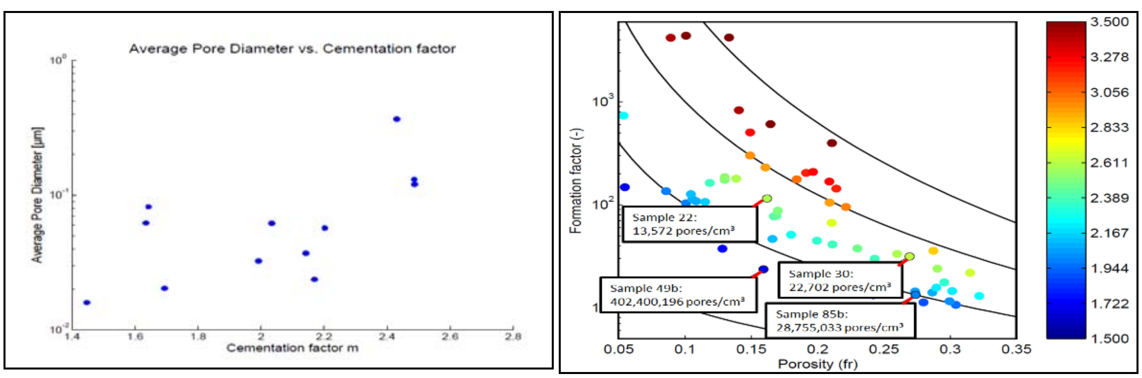

Figure 1. Left: Graph of pore diameter vs. cementation factor based on MICP measurements. The cementation factor increases with average pore size. Right: Number of pores per cm³ (in boxes) derived from µ-CT measurements at equal porosities vs. cementation factor in color. The cementation factor decreases as the amount of pores increases (modified from Norbisrath et al., 2011).

AIM AND APPROACH

This study aims to document that a small and intricate pore network is favorable for the flow of electrical charge due to its increased pore count, whereas simpler networks with larger pores but less pore connections attenuate electrical flow in comparison. To reach this goal, high-resolution 2-D ESEM imagery for DIA and MICP measurements are used to investigate the rock's microstructure and its effects on the rock's electrical behavior.

DIA of thin sections produces quantitative parameters of various aspects of a pore system that can be related to physical properties (Weger et al., 2009). We plan to apply the DIA technique on ESEM images to similarly characterize and quantify the sub-micron pore structure. Combining the results from DIA on OLM (Optical Light Microscopy) imagery and ESEM imagery will quantify the rock's geometrical properties over several orders of magnitude. ESEM images of an extensive array of rock samples with differing petrophysical properties will be acquired and quantitatively analyzed on the geometric parameters of their pore structure. The main difficulty with ESEM-DIA is sample preparation, because a nanometer-scale, perfectly flat 2-dimensional surface is needed for this method to work. Core plugs will get resin-impregnated and their surfaces treated with ultra-fine polishes, in order to get appropriately flat surfaces for truly 2-dimensional images.

A second independent approach to investigate the microstructure of the rock is with MICP, which is a widely used, reliable methodology for assessing the number and size of pore throats. We plan to measure the cap curves on a variety of lithologies and correlate the measurements with resistivity, velocity and permeability. In addition to various limestones, the lithologies will include a set of pure Mississippian dolomites for which the porosity, velocity and a good analysis of the crystal structure are available (Figure 2). Shen et al. (2000) showed that deviations in velocity at similar porosity can be explained by the occurrence of different rock and pore types but also crystal shapes and crystal size. This data set offers the opportunity to evaluate the influence of the crystal structure on electrical resistivity.

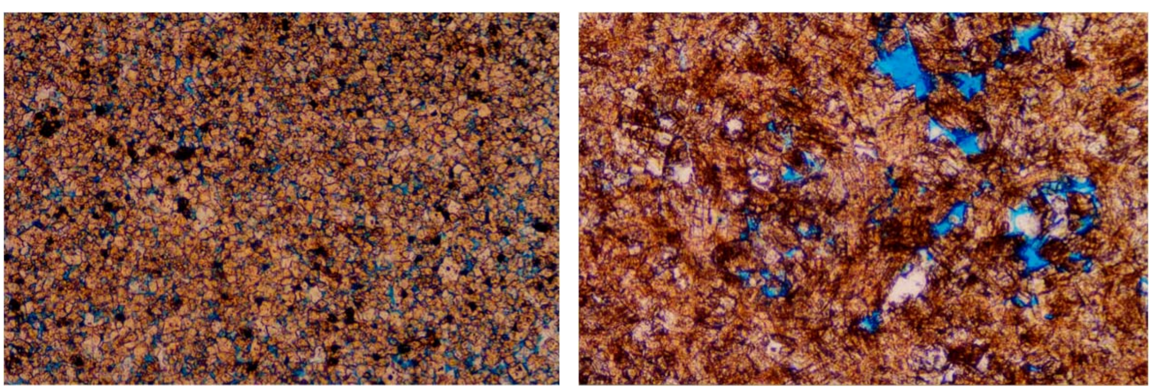

Figure 2. Examples of differences in pore and crystal structure in the Mississippian dolomites. Left: The rock is dominated by intercrystalline porosity and euhedral crystal shape. Right: Moldic porosity and anhedral crystal shapes (modified from Shen et al., 2000).

PROJECT TASKS

- Micro-structural analyses on representative samples from a broad variety of rock facies.
- Perform MICP (Mercury Injection Capillary Pressure) measurements.
- Acquire ESEM (Environmental Scanning Electron Microscopy) imagery and analyze with DIA (Digital Image Analysis).
- Where available, compare to μ-CT imagery and modeled results.
- Evaluate scatter in resistivity measurements as function of pore throat diameters (from MICP), pore size and numbers, and other geometric parameters (from ESEM-DIA).
- Measure electrical resistivity on Mississippian dolomite samples and correlate results with pore and crystal structure.

KEY DELIVERABLES AND EXPECTED RESULTS

This study will add to the comprehensive data set being assembled at the CSL – Center for Carbonate Research that correlates resistivity to porosity, permeability and pore structure, size and number (using MICP and ESEM-DIA). Specifically, the study will address the influence of the sub-micron pore structure on electrical resistivity by means of analyzing both OLM imagery and high-resolution ESEM imagery with DIA, interpreting cap curves from accompanying MICP measurements, and comparing the combined results to measured resistivities of the samples. The results will help to further improve the inversion of carbonate pore structure from down-hole log resistivity data and the thereby improve the calculation of water saturation in carbonate reservoirs, eventually leading to improved oil estimates. Additionally, the outcome will indicate which method of quantification of the pore structure, either with ESEM-DIA or MICP, is the most accurate and/or feasible for following studies of rock microstructures.

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4D GPR FOR QUANTIFICATION AND CHARACTERIZATION OF FLUID FLOW IN FRACTURED CARBONATES

Pierpaolo Marchesini, Mark Grasmueck, and Gregor P. Eberli

PROJECT OBJECTIVES

- Calculate volumetric water content changes and visualize wetting/draining zones as the response to a controlled infiltration experiment in fractured carbonates.
- Compute flow rates within porous matrix and quantify influence of faults and deformation bands on flow.
- Relate flow parameters to geology: faults, deformation bands, stratigraphy, petrophysics of rock matrix.
- Compare results with Miami Oolite infiltration experiment.

PROJECT RATIONALE

Characterization of the parameters controlling fluid flow mostly relies on 0.01-0.1 m scale laboratory measurements, upscaling and modeling. To visualize and quantify fluid flow at a more realistic scale of 1 to 10 m we monitor in-situ fluid flow in response to a controlled water infiltration experiment at an outcropping fractured carbonate reservoir analog. 4D GPR is used in this study to quantify local water content changes, delineate wetting and drainage zones and determine the influence of faults and deformation bands and stratigraphy on fluid flow (Figure 1). Characterizing the dynamics of fluid flow in a porous matrix is possible because of variations detected in the GPR response between time-lapse data (Truss et al., 2007). Quantification of fluid flow within a network of faults and deformation bands helps in perfecting flow models and residual fluid recovery.

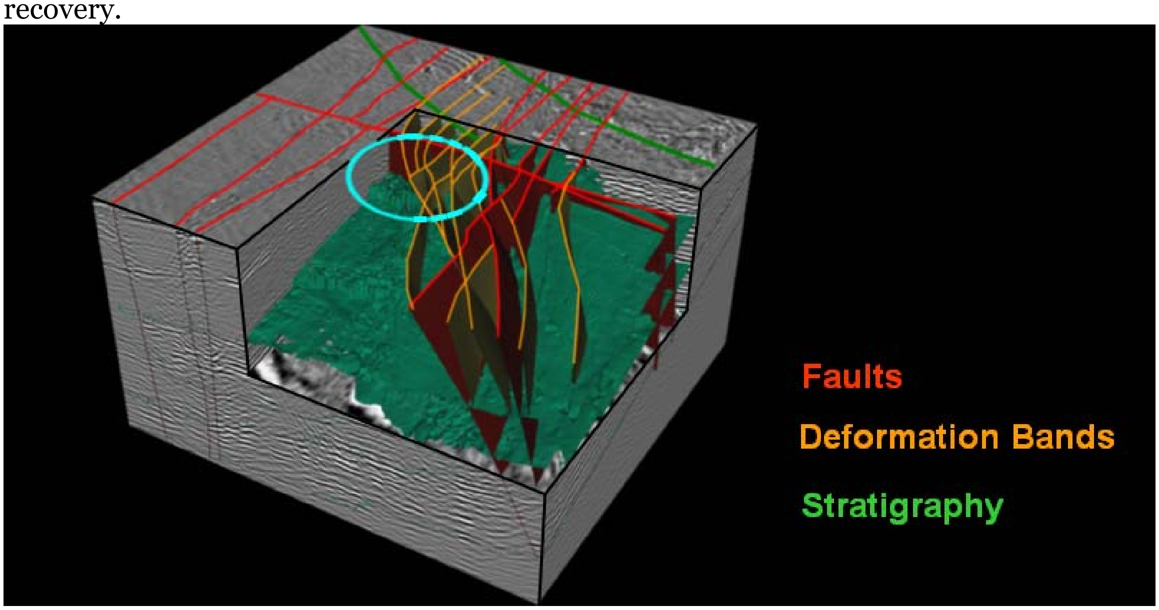

Figure 1. Three dimensional interpretation of the main geological features within the 3D GPR volume. The blue circle indicates the area where a 4 m diameter pond was installed.

4D GPR field data acquisition

Data were acquired at the Madonna della Mazza quarry. This quarry is cut into a sequence of Upper Cretaceous rudist grainstones (Orfento Formation) located in the Majella anticline in southern Italy. We chose the infiltration area where previously acquired 3D GPR surveys revealed the coexistence of dipping layers, faults, and deformation bands in a high porosity matrix. Average porosity and permeability are 30% and 300 mD respectively. 3000 l of water were infiltrated over 30 hours from a temporary pond with 4 m diameter installed on the quarry floor. The timelapse dataset consists of 16 repeated 3D GPR surveys (2 before and 14 after the infiltration) monitoring a 20x20x10 meter rock volume over 5 days. A 3D rotary laser positioning and guidance system coupled with a 200 MHz GPR system achieved high resolution 3D data quality and centimeter precise repeatability between surveys.

4D GPR processing method for quantification of in-situ water content changes

Event time shifts and amplitude differences between repeated surveys are related to subsurface water content changes. Figure 2 shows how GPR reflection travel timeshifts are extracted from survey pairs with a 3D warp algorithm, followed by quantification of volumetric water content changes with the Topp petrophysical transfer function (Topp et al., 1980). For a selection of infiltration stages, volumetric water content changes have already been computed with an accuracy of 1%. Results show that the momentary wetting and drainage progress faster in undisturbed host rock, compared to strata containing deformation bands (Fossen et al., 2007). We also observe how gravity driven transport of water, occurring in the initial stages of the experiment, shifts to a capillary driven transport mechanism within 12 hours.

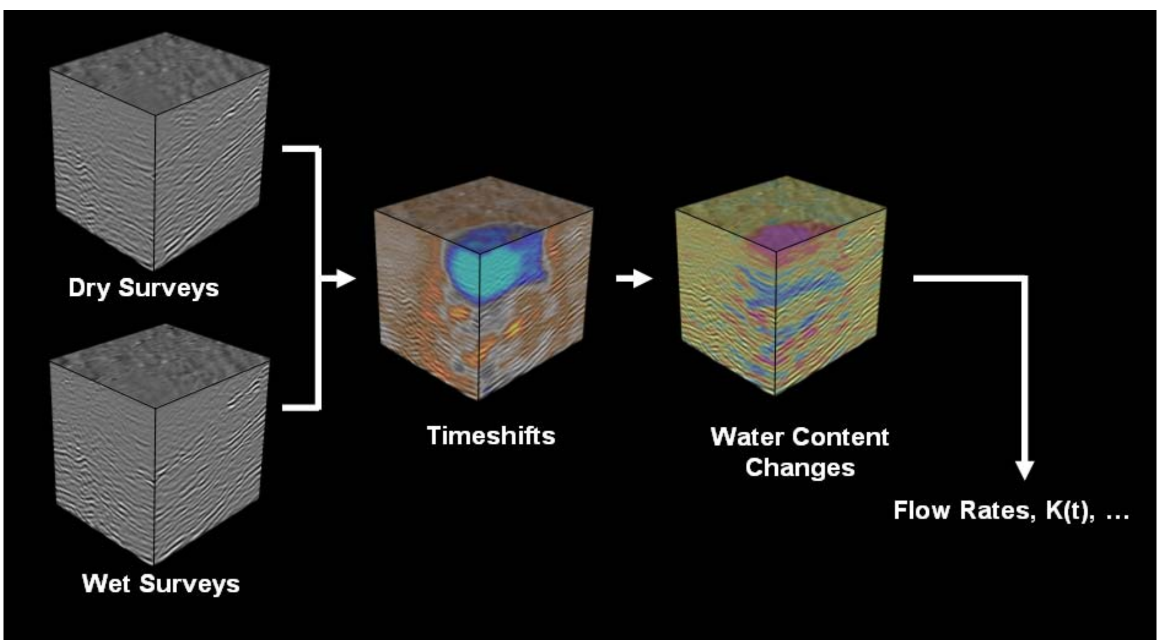

Figure 2. 4D GPR Processing workflow: Warping extracts the time shifts between pairs of time-lapse volumes. Application of the Topp petrophysical transfer function yields volumetric water content changes over time.

KEY DELIVERABLES

- *Computation of water content changes over time intervals ranging from 2 hours to 5 days after start of infiltration:* Preliminary results of water content changes suggest that such data allows the behavior of the infiltrated water mass to be described over time and space. This unique dataset will be used to reach a comprehensive visualization and quantification of fluid flow dynamics with unparalleled accuracy.
- *Comparison of flow behavior in the fractured carbonates of the Madonna della Mazza quarry with results from a similar infiltration experiment in undisturbed oolitic grainstone.* A previous GPR time-lapse experiment was performed in Pleistocene Miami Limestone. 3200 liters of water infiltrated strata with porosities ranging from 20-50% and permeabilities up to 1 Darcy (Grasmueck et al., 2007). Water propagated preferentially along dipping cemented shell hash layers, causing an asymmetric wetting bulb. There are also indications of local breakthroughs across stratigraphic boundaries likely caused by dissolution features. The comparison of the two infiltration experiments allows an assessment of the role of sedimentary structures versus structural deformation features on fluid flow.
- *Comparison of 4D GPR derived flow parameters with petrophysical plug measurements and thin sections.* In order to comprehensively capture the flow behavior of the rudist grainstone facies from the plug to the meter scale, plugs from various stratigraphic intervals will be analyzed for their porosity, permeability, velocity, and electrical resistivity.
- *Integrate Geophysical, Geological and Petrophysical Results.* The water content change volumes, propagation rates, quantification of fluid mass balance, conventional 3D GPR data and rock sample measurements characterize the stratigraphic-structural-hydraulic relationships at the Madonna della Mazza Quarry. This pilot project develops tools and workflows applicable to other outcropping reservoir analogues where a precise understanding of flow processes is needed.

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SEISMIC AND GPR DIFFRACTIONS: TOWARDS THE NEXT GENERATION OF SMALL SCALE DISCONTINUITY IMAGING

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PROJECT OBJECTIVES

- Determine the basic geological features capable of generating measurable diffractions in the near surface and at reservoir depth.
- High-resolution 3D Ground Penetrating Radar (GPR) cubes and outcrop observations serve as a bridge between synthetic models and real seismic data.
- Assemble a catalog of typical diffraction signatures to identify and quantify sub-wavelength discontinuities in complex geology such as fracture corridors and salt flanks.

PROJECT RATIONALE

Production of carbonate reservoirs, unconventional shales and deformed reservoir units near salt diapirs is often controlled by discontinuities such as fractures or voids. The reflection seismic method is optimized towards imaging of continuous reflectors to delineate stratigraphic boundaries. As a consequence, reflection seismic is of limited use for characterization of small scale fractures and voids. Sub-wavelength discontinuities cause diffractions and generate scattered energy on seismic records. For decades diffractions have been noticed as chaotic criss-cross patterns on seismic profiles in fractured and deformed geology (e.g. Rieber 1937). Commonly such scatter is considered as noise and suppressed as much as possible during acquisition and processing. Diffractions present an opportunity to expand the resolution limit of subsurface imaging to the sub-wavelength scale.

SCOPE OF WORK

Diffractions are best visible on densely acquired unmigrated data. The first step towards the use of diffractions for characterization of small scale discontinuities in reservoirs is to understand the origin and nature of the diffraction signals recorded in seismic data. The analysis of diffractions has already started in collaboration with Tijmen Jan Moser and Michael Pelissier and is progressing along three main thrusts:

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

Synthetic modeling is performed with the Ray-Born method (Moser 2012) which is a very efficient tool to model both diffractions and reflections in 3D. Classic ray tracing can not be used due to a lack of omni-directional radiation of scatterers. Finite difference modeling is computationally prohibitive for the fine grids needed to represent small scale discontinuities. In the Ray-Born approach models are built from regular grids of elementary point scatters. For a direct as possible verification of the modeled diffractions we use high-resolution 3D GPR data. GPR uses electromagnetic waves but has very similar kinematics in terms of reflection, refraction and diffractions. We have already acquired and processed several 3D GPR data sets in fractured and karstified outcropping reservoir analogues. With outcrop control the diffractions in the GPR data can be directly linked to geological features enabling the design of realistic models for synthetic data generation. The models are scaled in units of wavelengths making the synthetic data universally applicable to both the GPR-outcrop and the seismic scales. Hence the GPR cubes serve as a bridge between synthetic and real seismic data to decipher the origin of diffractions.

2) Determine the Geological Origin of Diffractions:

Geological scattering mechanisms and diffraction detection limits are not well understood. To date the majority of synthetic models of diffractions has encompassed perfectly flat planes and long straight lines. A typical example of such an overly simplistic model is shown in Figure 1. The corresponding linear diffraction pattern does not exist in field data which are dominated by arrangements of point diffractions with circular cross-sections on timeslices. The key question is what geological features generate point diffractions. Natural fractures are far from planar features, have limited extent and have significant roughness. Brittle rock deformation results in conjugate fracture systems and partitions the rock into blocks with sizes above and below the wavelength with many corners and edges. On well developed fractures small conjugate fractures cause steps and corners acting as wave scatterers. The alignment of such diffractions defines the main fracture trend. From our 3D GPR data we see that zones consisting of fractures with one millimeter or less aperture cause abundant diffractions. Such thin fractures with openings on the order of 1/500 wavelength are well below the 1/40 thin bed detection limit commonly known from reflection seismic imaging (Widess 1973). True amplitude Ray-Born models of basic fracture intersection geometries allow us for the first time to determine how fracture extent, width and roughness control the generation of diffractions recorded in GPR and seismic data. Once we can determine the basic geological features capable of generating measurable diffractions we can use them as basic building blocks for modeling of complex geometries such as fracture corridors in carbonates or deformed reservoir units near salt diapirs.

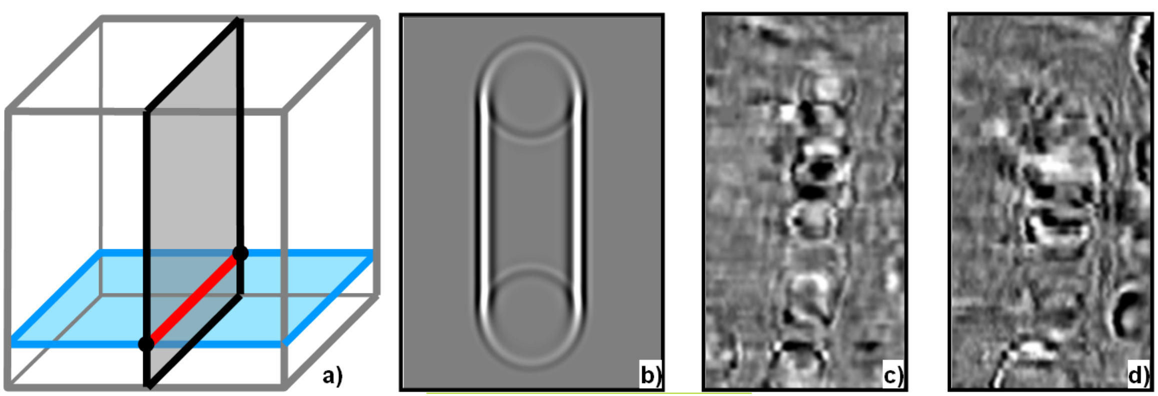

Figure 1. a,b) Intersection of a vertical and horizontal fracture causes a linear diffraction with two circular tipwaves as seen on a 3D synthetic data timeslice c) Conversely, strings of closely spaced circular diffraction are observed in 3D GPR field data. d) A deeper time slice of the same diffraction cluster shows mirrored half circles with a lower amplitude corridor in between.

3) Expand Diffraction Signature Catalogue

Currently availability of high resolution seismic data acquired with dense enough grid spacings to fully sample the steeply dipping diffraction tails is very limited. On the other hand full-resolution 3DGPR data including non-aliased diffractions can be acquired within a few days. For example as seen in Figure 2 the Cassis 3D GPR data contains hundreds of diffractions in different configurations (Grasmueck et al. 2011). Characteristic diffraction patterns from unmigrated 3D GPR data cube, combined with the interpretation of 3D migrated data and typical outcrop images are compiled in the Diffraction Signature Catalogue. These typical configurations can then be used like a dictionary to read and interpret diffraction patterns observed in seismic data. Until now our main focus has been on 200 MHz GPR data which we will extend to the 100 and 500 MHz center frequencies in order to gain insights on resolution and scaling behavior of diffractions.

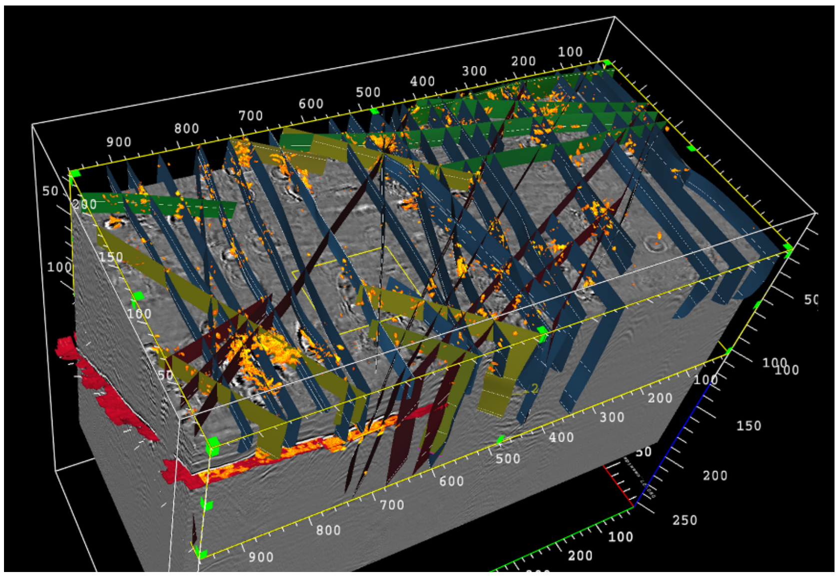

Figure 2. 3D view of the unmigrated Cassis 3D GPR data cube with steep fracture interpretations based on migrated data. Orange colored are volume rendered high amplitude clusters of focused diffractions indicating zones of intense fracturing and karstification.

EXPECTED OUTCOME

With the new knowledge about diffractions gained from True Amplitude Ray-Born Modeling, 3D GPR and outcropping reservoir units, seismic diffractions are promoted from noise to valuable signal. Diffractions make sub-wavelength discontinuities in complex reservoirs such as fracture corridors and salt flanks visible and quantifiable.

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ASSESSING THE ROLE OF MICROBES IN THE FORMATION OF OOIDS AND CARBONATE PRECIPITATION

Mara R. Diaz, Alan Piggot, and James S. Klaus

PROJECT OBJECTIVES

This project investigates the role of sediment-associated microbial biofilms on calcium carbonate precipitation with the goal of better understanding the physical, chemical and microbiological conditions involved in the formation of large-scale ooid shoals. Towards this end we seek to:

- Quantify the amount of biofilm coating carbonate grain surfaces and assess the stability/adherence of sediment biofilms through column flow-through and agitation experiments.
- Characterize metabolic processes associated with carbonate precipitation through metabolic gene profiling of active, non active, and mat stabilized sediments.
- In vitro precipitation experiments to assess the roles of microbial metabolism and biofilm/EPS in carbonate precipitation.

PROJECT RATIONALE

Microbial communities are abundant components of the sedimentary environment where their metabolisms alter the surrounding geochemical environment. The vast metabolic diversity and complex interactions within these communities efficiently cycle nutrients and mediate levels of carbonate saturation (González-Muñoz et al., 2010; Dupraz et al., 2009). Moreover, microbes typically exist in interdependent cooperative communities referred to as a biofilms. Extracellular polymeric substances (EPS) facilitate the aggregation and attachment of microbes within biofilms in order to remain in optimal conditions for growth. Three different types of EPS alteration have been proposed to lead to $CaCO_3$ precipitation: 1) microbially mediated decomposition of EPS, liberating HCO_3^- and Ca^{2+}; 2) organomineralization in which the EPS matrix is altered by chemical or biological activity, creating a template for $CaCO_3$ binding and precipitation; and 3) precipitation regulated by the balance of the external cation concentration and binding capacity of EPS (Dupraz and Visscher et al., 2005).

Despite the presumed importance of microbial processes in shallow water carbonates, there is scant information about microbial community composition and associated metabolism. This knowledge gap in carbonates is nowhere more evident than in the formation of oolitic sand bodies. In spite of the importance of ooilitic grainstones as potential carbonate reservoirs, the genesis of ooids remains controversial. Some researchers support abiotic processes (Duguid et al., 2010), while others have attributed ooid genesis to biogenic factors (Gerdes et al., 1994).

The first stage of this project focused on the molecular characterization of surface sediment microbial communities based on 16S rRNA gene sequencing and TRFLP community profiling. This preliminary work showed that sediments from active, non active and mat stabilized depositional facies all harbor complex microbial communities, some of which have been intrinsically linked to mineralization processes. Furthermore, preliminary studies suggest the amount of EPS coating varied in the three depositional environments. Although all three environments contained EPS coatings, the amount of coating decreased from the mat stabilized to the active environment (Figure 1). Ongoing research over the coming year will give special attention to three areas: 1) characterization of sediment biofilm/eps; 2) metabolic gene profiling of sediment biofilms; and 3) controlled in vitro precipitation studies.

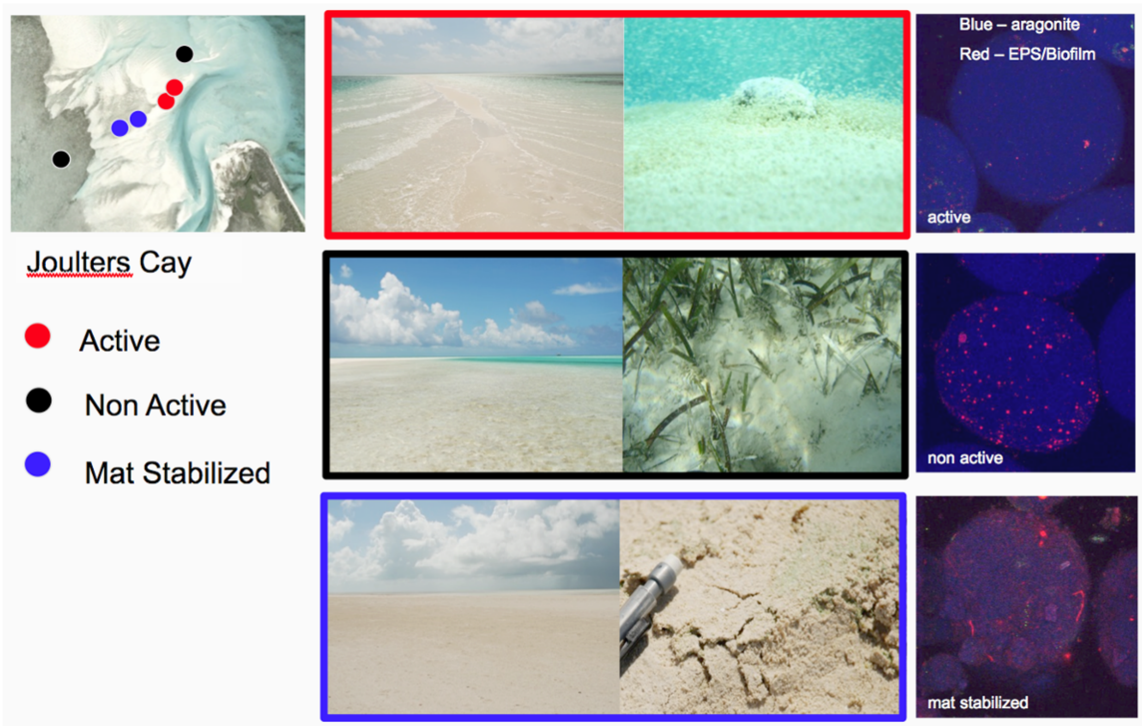

Figure 1. Transect from the active to the mat stabilized environments of the Joulters Cay ooid shoal and confocal laser scanning microscopy images of the grains and their EPS coating. The confocal images depict a progression of the amount of EPS coating from active to the mat stabilized environment.

CHARACTERIZATION OF SEDIMENT BIOFILM/EPS

We will conduct quantitative analysis of EPS coatings on sediment samples from various hydrodynamic settings. EPS analysis will follow the sulfuric acid assay. In addition, some of the samples will be preserved in 70% formaldehyde to microscopically analyze the microspatial distribution of attached microbes within biofilms. Confocal laser scanning microscopy (CLSM) provides the ability to acquire in-focus images from selected depths, a process known as optical sectioning or tomography. Images are acquired point-by-point allowing for three-dimensional surface reconstructions of topologically-complex objects like sand grains. Sediments observed with CLSM are stained with a cyanine die-conjugated lectin, wheat germ agglutinin (WGA). The WGA lectin binds to extracellular polysaccharide secretions (EPS) associated with the biofilms (Neu et al., 2001). Environmental scanning electron microscopy (ESEM) will also be used to obtain high-resolution images of natural sediment biofilms. Together, these analyses will allow quantification and visualization of the spatial distribution of EPS and microbes on sediment grains and the relationship of these two components in sediment biofilms.

In addition, we will also test the adherence/stability of EPS within various hydrodynamic conditions. Toward this end, we will perform an agitation assay that emulates various hydrologic conditions found within oolitic shoals. Treatment 1 and treatment 2 will simulate low and high groundwater flow within the pore space and will be undertaken in flow-through columns. Published reports for groundwater flow range from 0.025 – 4.3 L m^{-2} min^{-1} (Shellenbarger et al., 2006). Core sediments exposed to treatment 3 will be emptied into a large glass baking dish along with 2 liters of filtered seawater and placed on a laboratory rocker/shaker table set at 10 rpms for a duration equal to the pumping times of treatments 1 and 2. Treatment 4 sediments will be placed into a sterile 4 L polyethylene bottle and vigorously shaken on a reciprocating shaker for the same duration. In treatment 5 we will attempt to remove all associated microbes from the sediment grains by subjecting them to pulsed ultrasonic treatment (150 s incubation time, 30% of this time pulsed, Bandelin M72 probe, 3mm diameter, 20 kHz, 70W, vials on ice) following an optimized protocol for sandy sediments (Ferguson et al., 2005, Rusch et al., 2006). After the sand grains have settled and the supernatant removed, the remaining sediment will be washed 6 times with filtered seawater and all supernatants combined. Ultrasonic treatments followed by 6 washings each will be carried out until no additional microbes can be removed from the sediment. For each treatment the removed EPS will be quantified using the sulfuric acid assay.

BIOFILM GENE PROFILING

Profiling of microbial functional genes will provide insight on the intrinsic enzymatic capacity of key genes associated to carbonate precipitation. To achieve this goal, we will use GeoChip, a robust high-throughput functional gene array that comprises over 24,243 oligonucleotide probes with the potential capability to target 150 functional gene groups involved in nitrogen, carbon and sulfur cycling (He et al., 2007). Special attention will be given to microbial genes that are key players in metabolic processes (e.g. denitrification, sulfate reduction, photosynthesis) known to create an alkaline environment with conditions that promote calcium carbonate precipitation. Some genes of interest will include: a) carbon fixation (RbCL); b) sulfate reduction (dSr); c) nitrogen reduction (narG, nasA, niRs, niRk, norB, nosZ); d) ammonia monooxygenase (amoA); e) methane oxidation (mmO, pmO; and f) urea hydrolysis (ureC). Gene profiles will be compared between sub-environments of the Joulters Cay ooid shoal.

PRECIPITATION EXPERIMENTS

To test the effect of microbes and EPS on calcification, a series of precipitation experiments will be performed in small flow-through sediment columns. The column experiments will be performed on three sediment treatments. Treatment 1 will represent the control treatment in which all microbes and EPS will be removed from the sediment surface. In treatment 2, all active microbes will be killed through UV and antibiotic treatment, but the sediment-associated biofilm will remain in place. In treatment 3 sediments with active biofilms will be loaded into the precipitation columns and supplemented with seawater growth media. Precipitation in the three treatments will be compared using the buoyant weight method and will be visually inspected under SEM.

KEY DELIVERABLES OR EXPECTED RESULTS

- Quantitative data on sediment Biofilm/EPS concentrations across different depositional facies based on the sulfuric acid assay and CLSM.
- A quantitative assessment of the stability/adherence of biofilm/EPS to sediment surfaces under varying hydrodynamic regimes.

- Preliminary assessment of the variation in sediment microbial metabolisms operating in a range of depositional settings based on functional gene profiles.
- Assessment of the role of active microbes and associated EPS coatings in controlled ooids precipitation studies.

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Microbial Facies, Textures, and Porosity Formation on an Isolated Platform: Uplifted Atoll of Mare, Loyalty Islands, New Caledonia

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

Project Objectives

- Characterize the Late Pliocene (2.5-3 Ma) bedded pisolitic-oncolitic deposits that cap the coralline facies of an isolated atoll platform.
- Provide field, petrographic, and geochemical data to determine the origin of carbonate micro-textures that are hypothesized to be microbial in origin.
- Assess the influence of the microbial (?) carbonate on the unconventional paragenetic sequence, especially the preservation of aragonitic allochems during subaerial exposure and delayed moldic porosity formation during exposure.
- Provide samples amenable to petrophysical characterization as part of the microbial sonic velocity database project.

Project Rationale

Microbial influence on carbonate textures and facies has been increasingly recognized for their importance in the formulation of geological and reservoir models. This study will characterize how cyanobacterial-formed grains form with the transition from marine deposition to the onset of uplift-driven subaerial exposure. Of special interest is the unusual preservation of nuclear aragonitic allochems encased by a fine-grained, microbial rind, and their resistance to early dissolution and moldic porosity development. By characterizing the chemical and physical attributes of these microbial carbonates we can provide a better understanding of their formation, their occurrence, and their physical properties.

Project Setting and Scope of Work

We propose a field sampling campaign to collect a series of short cores (~80 cm long) from the outcrops on the island of Maré, New Caledonia (Figure 1). D. McNeill has conducted several studies from samples collected on Maré in the mid-1990's (Guyomard et al., 1996; McNeill and Pisera, 2010). Fieldwork will be conducted in July 2012 to collect cores that will form the basis of this project.

The samples of interest occur as a series of bedded pisolitic-oncolitic units that cap several of the small faroes that form part of the Pliocene atoll rim (see Figure 1). The presumed microbial deposits appear to have formed during the final stages of marine deposition as the atoll was progressively uplifted in the late Pliocene (Figure 1).

The island of Maré is located on a submarine volcanic ridge eastward of the island of New Caledonia in the Loyalty Island chain, 40 km west of the New Hebrides trench; the convergence of the Pacific and Australian plates. Volcanism on the island is thought to have occurred up until the middle-late Miocene (9-11 Ma), but has since been dominated by phases of carbonate deposition and diagenesis, with final atoll deposition projected to the mid-late Pliocene (Baubron et al., 1976, Guyomard et al., 1996). Maré is dominated by partially dolomitized, shallow-water limestone. Carriere (1987) suggests that a small fringing reef, intertwined with rhodolith beds ~40km wide, formed and back stepped as sea-level rose, surrounding the central volcanic rock during the Miocene. During the early Pliocene an atoll rim developed on the rhodolith platform. For this study we focus on the bedded pisolite-oncolite beds that cap the reefal rim of the atoll (McNeill and Pisera, 2010).

KEY DELIVERABLES AND PRELIMINARY RESULTS

The results of this fieldwork and analysis will be used to document the potential contribution of microbial influence on depositional facies and the disruption of conventional (moldic) porosity development. These pisolitic-oncolitic rocks will also contribute to the larger CSL-Center for Carbonate Research effort to characterize the petrophysical properties of microbial rocks.

We have begun petrographic and geochemical analysis of existing samples (collected during the study of Guyomard et al. 1996). A summary of the initial results is presented below from an abstract submitted to the AAPG Hedberg Research Conference on Microbial Carbonate Reservoir Characterization (June 2012).

Initial Results: PETROGRAPHIC CHARACTERIZATION

The diameter of the oncolite grains range from 1-10mm (Figure 2). The grains contain a massive to crudely layered, fine-grained (mud) coating or rind, and are classified as oncolites, defined as having diameters <10cm. The general composition of the oncolites consists of a minimum of three distinct units (Figure 2). The innermost unit is the nuclei, made of aragonitic skeletal fragments and intraclasts. Aragonitic mollusc shell fragments, some with their original nacre (mother-of-pearl) are sometimes found. Nuclei thickness ranges from 0.60-4mm. The second unit is a microbial coating (rind) surrounding the nuclei. Rind thickness ranges from 1.5-6 mm, representing 12-49% of the total oncoid diameter. While most nuclei are not well rounded, the encircling rind generally displays a more circular shape. The microbial rinds consist of 1-10 micron crystals, tightly packed, with low-permeability. These crystals form an effective seal around the skeletal or composite nuclear grains. Possible microbial fibers in the rind indicate *in situ* biological formation. The rind unit has some evidence of crude layering, usually discontinuous around the nuclear fragment. A third unit of blocky calcite spar crystals encases these oval- to circular-shaped grains. These fringing calcite spar rims are typical of meteoric cements. The boundary between the rind-coated grain and these calcite cements suggest a distinctly different environment of formation. The microbial rind appears to preserve the aragonite skeletal nuclei.

Initial Results: STABLE ISOTOPIC CHARACTERIZATION

One key feature of the microbial rind is its resistance to meteoric diagenesis. Unlike oolitic grainstones, the microbial rind inhibits nuclei dissolution and the formation of associated moldic porosity. Fine-scale isotope sampling enabled the analysis of the minute layering within each oncolite. The average $\delta^{18}O$ signal for the nuclei, rind, and cement layers were -4.7, -4.9, and -5.6, respectively. The average $\delta^{12}C$ signal for the nuclei, rind, and cement layers were -6.7, -7.6, and -10.1, respectively. These stable isotopic results show a general trend toward lighter carbon and oxygen isotopes from the nuclei to the cement. This trend records the transition from marine to freshwater conditions with progressive uplift. The permeability of the microbial rinds was sufficiently low at this early stage to preclude freshwater access to the aragonitic fragments in both the nuclei and rinds. This exception to the usual diagenetic sequence is well illustrated in thin section and SEM images and has important implications for the dissolution of aragonitic grains. Furthermore, the recognition of microbial textures, their formation, and distribution within existing facies models may challenge the typical diagenetic paradigm of early moldic porosity formation during subaerial exposure.

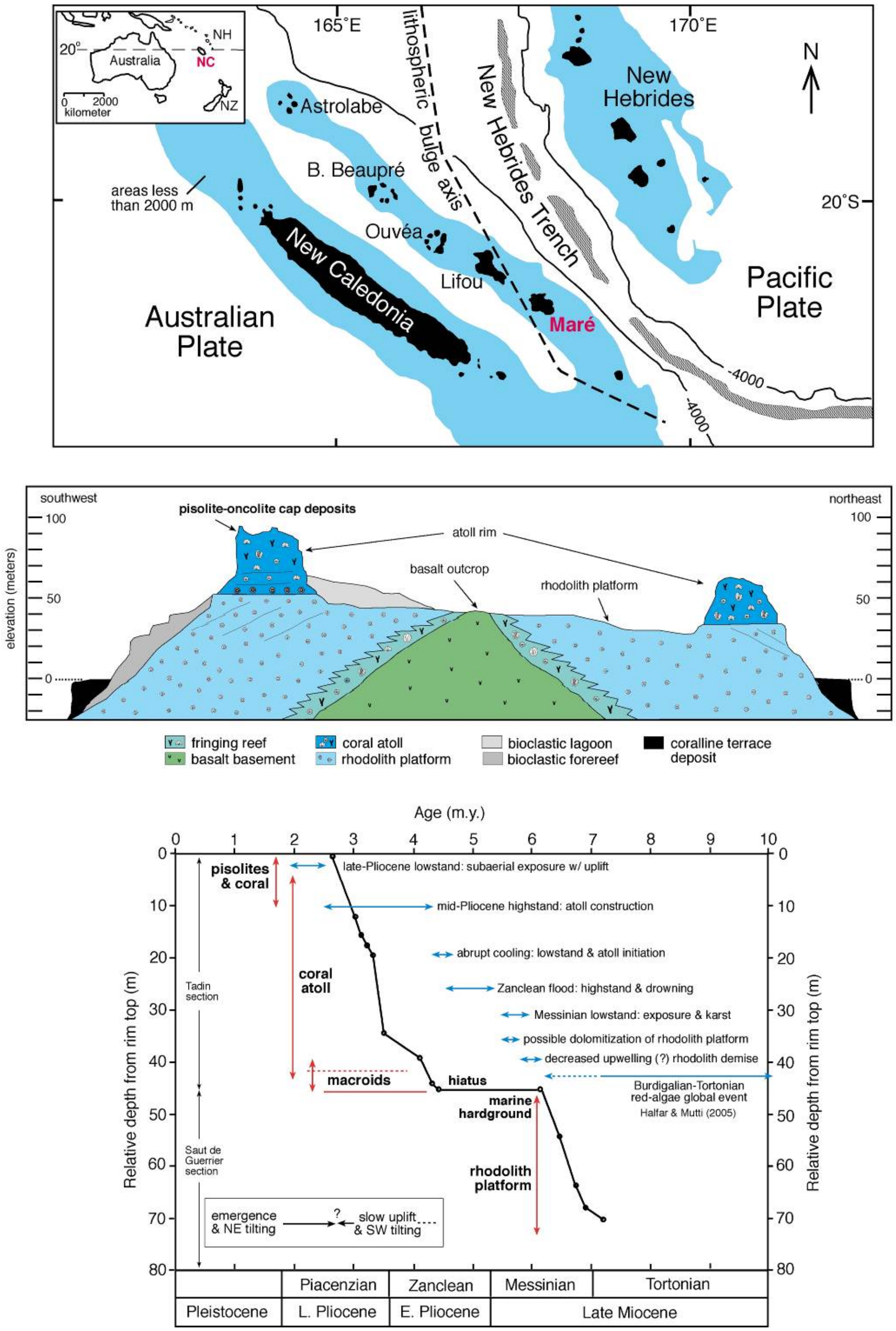

Figure 1. Location of the uplifted atoll of Maré, New Caledonia (upper). Cross-section of the Maré atoll redrawn from Carriere (1987) showing the location of the pisolite-oncolite deposits that cap the Pliocene atoll sequence (middle). Age-depth relation of the rhodolith platform and the atoll section (from Guyomard et al. 1996) (lower). The pisolite-oncolite facies is 2.5-3.0 Ma.

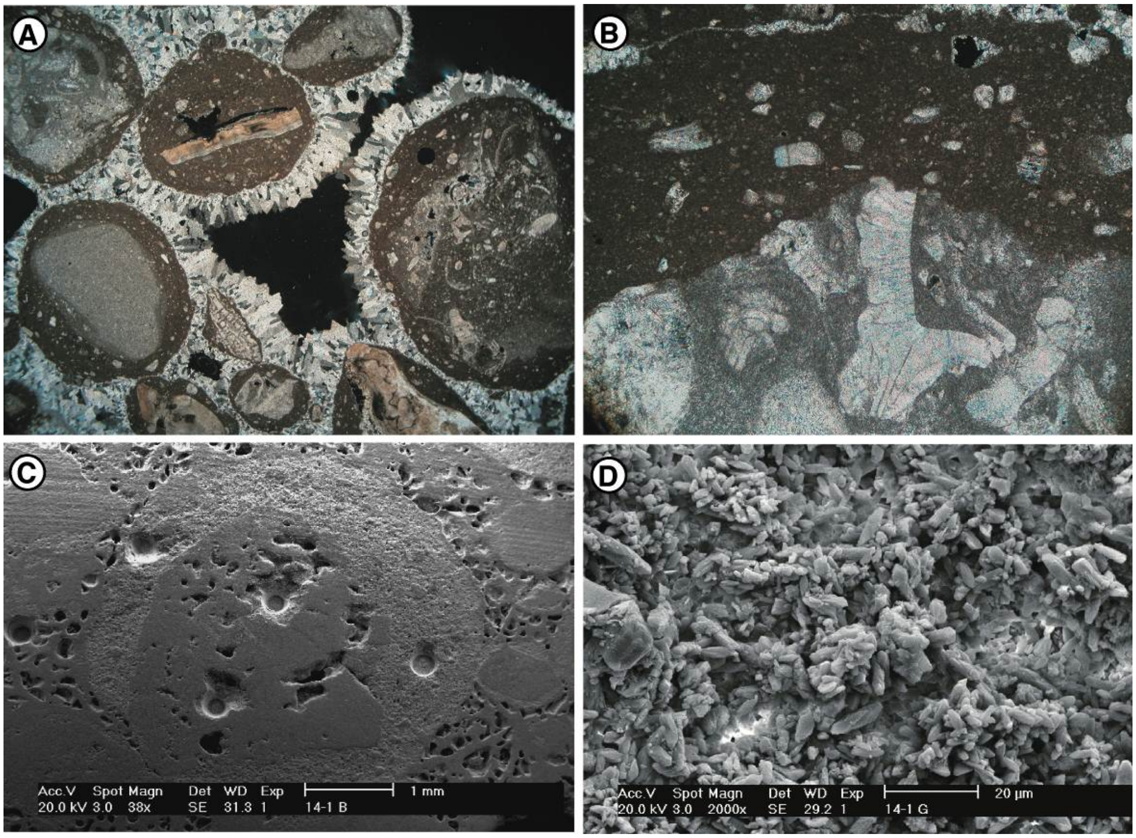

Figure 2. (a) Thin-section photomicrograph of pisolite-oncolite unit on Maré. Horizontal dimension of the photo is ~1.7 cm. (b) close-up photomicrograph of the transition from the nucleus (gray) of the pisolite-oncolite to the fine-grained, microbial(?) rind (dark brown). Note the aragonite composition of the skeletal fragments in the nucleus, as well as skeletal fragments within the microbial rind. Horizontal dimension of the photo is ~2 mm. (c) SEM photomicrograph of the pisolite-oncolite showing the nuclear fragment, the rind, and the sparry calcite cement. The five circular holes are from a microdrill that sampled for stable isotope composition.

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PETROPHYSICAL PROPERTIES AND PORE STRUCTURES IN MICROBIALITES

Gregor P. Eberli, Giovanna della Porta[1], Ralf J. Weger, and Jan Norbisrath

PROJECT OBJECTIVES

1. Assemble a comprehensive petrophysical database of microbialites, including stromatolites, travertine, and tufa.
2. Quantify pore structures of microbialites.
3. Correlate pore structures to petrophysical properties and classes of microbialites.

PROJECT RATIONALE

Microbial carbonates are the major reservoir facies in the pre-salt strata of the South Atlantic. No modern setting contains all the varieties of microbialites found in the pre-salt but each modern environment might produce a microbialite with characteristics found in some of the pre-salt population. In addition, microbialites occur throughout the stratigraphic record and several of them can be analogs to the pre-salt varieties. By measuring a variety of modern and ancient microbialites a data set will be created that can be compared to the pre-salt microbialites in regards to their petrophysical behavior and their pore- and frame structures.

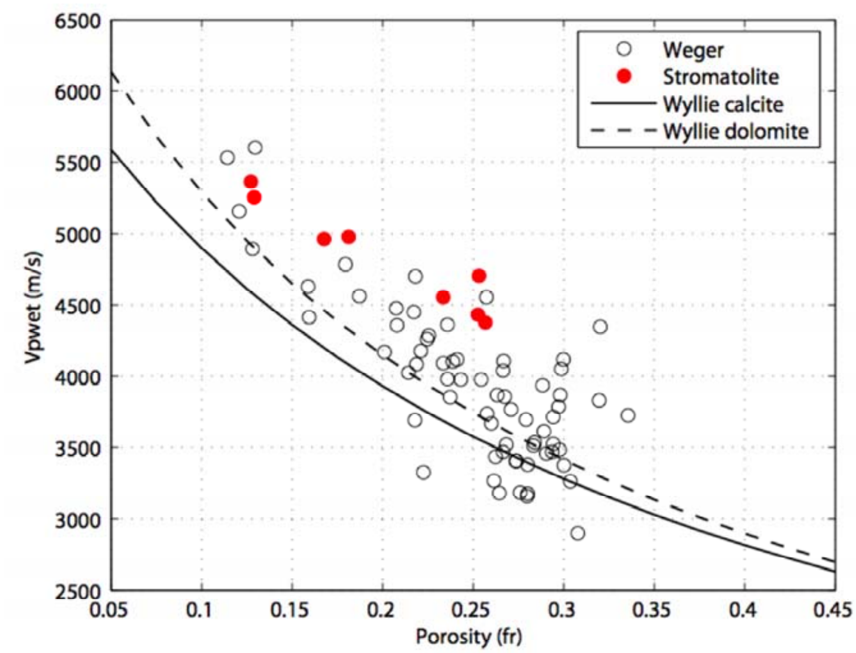

Figure 1. Microbialites, like modern stromatolites, have a great stiffness that is created by microbial processes that weld grains together into a pressure resistant framework. This stiffness is reflected in the high acoustic velocity at a given porosity. In this project we test if the stiffness variations are related to pore structure and grain coupling.

PROJECT DESCRIPTION

This project is a collaboration between the University of Miami and the University of Milano, with both providing samples to the project. The samples consist of travertine, tufa from modern lakes, and modern and ancient stromatolites and other microbialites. The petrophysical measurements include porosity, permeability, acoustic velocity (both dry and brine saturated) and resistivity. The latter will be measured under varying confining pressure. From each sample, a horizontal and a vertical thin section will be cut after the measurements have been made. Petrographic analysis will be used for documenting the texture and the diagenetic overprint, such as cementation and microbial binding. Digital image analysis will provide the quantitative parameters of the pore structures. Together, they are used to explain the physical behavior of the sample.

EXPECTED RESULTS

The correlation between the petrophysical properties and the rock frame and pore structure parameters will shed light on 1) the processes that cause the high stiffness in microbialites, and 2) their behavior under changing pressure and saturation. We expect that different microbialites will show different relationships and consequently some general rules can be formulated for the different varieties of microbialites.

PETROPHYSICAL PROPERTIES OF UNCONVENTIONAL RESERVOIRS: START OF A DATABASE

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

PROJECT OBJECTIVES

- Assemble a database that covers many of the varieties of shales found in unconventional reservoirs.
- Correlate petrophysical properties to carbonate content and TOC to better understand the enhanced fracability of carbonate-bearing shales.

Figure 1. Main shale plays in the United States that occur in a variety of stratigraphic horizons and different lithologic expression. (eia website)

PROJECT RATIONALE

Unconventional plays rely, to a large extent, on the success on fracturing the low porosity shale intervals in order to exploit as much volume as possible. Therefore mechanical properties are of key importance to define the most economic well locations. Unconventional reservoirs occur in shales in different stratigraphic levels each with their own petrophysical characteristics (Figure 1). Fracability is largely enhanced by carbonate content. In order to improve the understanding of carbonate/shale distribution and acoustic behavior we plan to measure shales with variable carbonate and TOC content. The ultimate goal is to produce a data and knowledge base that enhance production in these plays.

Scope of Work

Starting with existing samples from the Devonian (Perdix Formation), Paradox Basin (Chimney Rock Shale) and the Neuquen Basin (Vaca Muerta) we intend to measure porosity, permeability, and velocity and resistivity under variable pressure. For each sample the carbonate content will be determined. In each of these formations the carbonate content varies and we expect to have a first indication of the relationship between carbonate content and physical behavior from these samples.

Expected Results

The proposed study is a first step towards a larger database covering the petrophysical properties of carbonate/shale variations. The results are expected to produce a better understanding of the physical behavior of shales and to be a guide for delineating carbonate/shale ratios from logs.

SEQUENCE STRATIGRAPHIC DISTRIBUTION OF UNCONVENTIONAL SHALE RESERVOIRS IN THREE BASINS

Gregor P. Eberli and Michael Zeller

PROJECT OBJECTIVES

- Examine the sequence stratigraphic distribution of organic-rich shales in the Devonian of Canada, the Paradox Basin and the Neuquén Basin from the large second order to the third-order sequences and into higher frequency cycles.
- Test the hypothesis that both the accumulation of the organic matter and the influx of clay and carbonates are tied to certain conditions during transgressive events and variations in the organic/shale ratio are related to a combination of changes in sea level and current regimes.

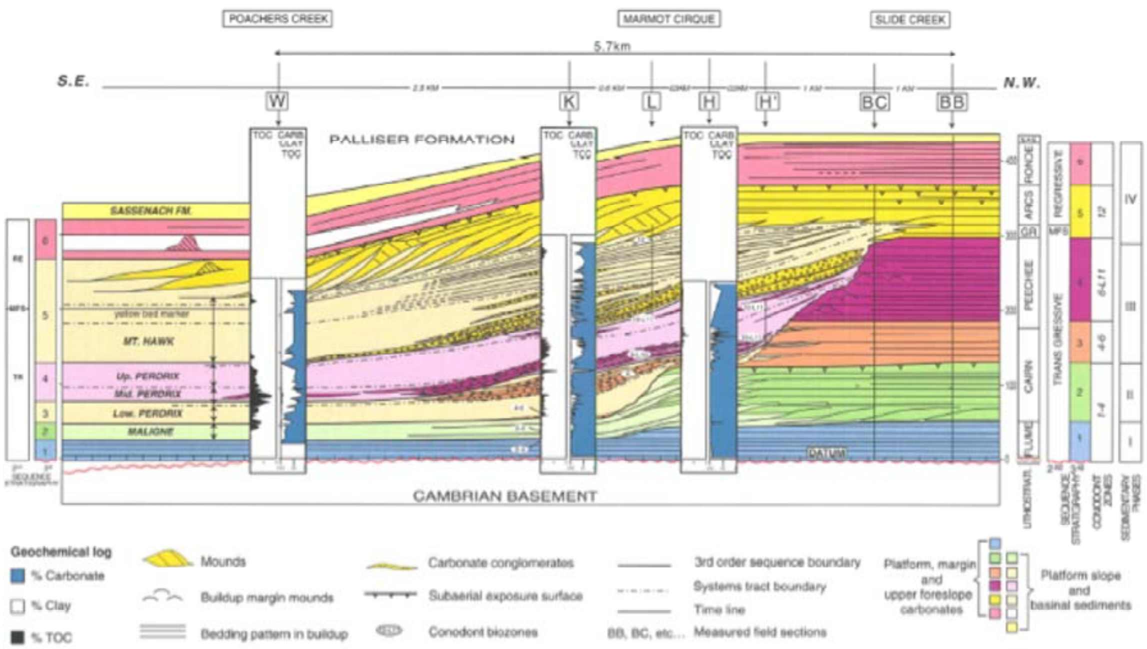

Figure 1. Sequence stratigraphic correlation scheme of the Miette buildup margin with the distribution of six color-coded 3rd order sequences. The basinal portions of sequences 2 and 3 contain a higher amount of TOC and clay (from Van Buchem et al., 2000)

PROJECT RATIONALE

The shales in unconventional reservoirs cover vast areas often with little change in thickness. This large extent is testimony of the uniform conditions during deposition. Nevertheless vertical variations exist in the respective amounts of TOC, clay and carbonate and result in variations in fracability. It is our working hypothesis that these variations are not random but intimately tied to the sea-level changes and associated changes in the sediment flux and current regime. If this proposed hypothesis is correct the variations are predictable within a sequence stratigraphic framework, which could help target horizons for fracking. To test this hypothesis we examine the sequence stratigraphic distribution of organic-rich shale in three basins.

THE THREE BASINS

In the **Devonian of the Western Canadian Basin** the organic-rich shales are confined mostly to the Duvernay (subsurface) and Perdrix (outcrop) Formation. They are deposited during the transgressive intervals of sequence 3 and 4 (Figure 1) and a peak accumulation is observed at the base of high frequency cycles (Van Buchem et al., 2000). In the **Paradox Basin** thick organic-rich shales (Hovenweep, Gothic, Chimney Rock) of Pennsylvanian age are deposited during transgressive intervals of 4th order sequences but many of the depositional cycles contain black laminated shales in the transgressive hemicycle (Grammer et al., 2000). In the **Neuquén Basin** the Vaca Muerta shales represent the time-equivalent downslope deposits of the mixed carbonate-siliciclastic Quintuco Formation developed during the Upper Jurassic to Lower Cretaceous, following a major transgression, which converted the Neuquén Basin from continental to marine depositional settings (Zeller et al., 2011). Carbonate enrichment in the Vaca Muerta shale is coeval with carbonate production on the shelf, which also is related to sea level.

SCOPE OF WORK

In all three basins the basinal sections will be tied into the detailed sequence stratigraphic framework established in the more proximal portions. This correlation is done on all stratigraphic levels down to the individual depositional cycles. A particular focus will be to relate time-equivalent shelfal and basinal strata to establish the lateral facies variations.

EXPECTED RESULTS

The sequence stratigraphic analysis of the distribution of shales will enhance the understanding of the vertical and lateral variations in these basinal settings. These facies variations will influence the petrophysical properties and thus the mechanical behavior of the strata. Thus, the results bear important implications, which can potentially explain production and mechanical behavior in the producing fields.

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THE TRIPLE THREAT: STABLE ISOTOPE STUDIES OF FLUID INCLUSIONS, CARBONATE AND CLUMPED ISOTOPES

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

PROJECT OBJECTIVES

- Applying multiple geochemical proxies to stalagmites from the Bahamas offers the opportunity to better understand the paleoclimate of the region.
- Initial results support the idea that cold periods in the North Atlantic during the last glacial period (Heinrich events) are intervals of aridity followed by a shift to a much wetter climate in the sub-tropics. Additionally, these periods were extremely dusty, a phenomenon which could have actually induced climate change.
- The methods proposed here are additionally applicable for a range of studies including diagenetic histories in all types of carbonates.

PROJECT RATIONALE

During the last glacial period there is substantial evidence for global variability in climate dominated by Heinrich events. Heinrich events are categorized in the North Atlantic by the deposition of ice rafted debris (IRD) and have been shown to correlate with rapid climate change such as cooling in the North Atlantic, precipitation decrease in Africa and Asia and warming in Antarctica. While a comprehensive picture of climate patterns is emerging, the climate in the tropical Atlantic is still not as well understood.

In order to better understand the paleoclimate of the Bahamas during the last glacial period, a variety of geochemical proxies from stalagmites collected from flooded caves will be utilized (Figure 1). In the subtropics, it has been demonstrated that higher volume rainfall events generally leads to a depleted $\delta^{18}O$ and $\delta^{13}C$ signal, whereas heavier $\delta^{18}O$ and $\delta^{13}C$ values are attributed to lower amounts of rainfall. However, oxygen isotopes of the carbonate are not only reflective of the $\delta^{18}O$ of the water, the $\delta^{18}O$ is also influenced by the temperature at the time of formation of the carbonate mineral, therefore making it difficult to elucidate between these competing influences. These problems can be overcome by combining the $\delta^{18}O$ analyses of fluid inclusions with clumped isotopes.

Fluid inclusions are small voids within the calcite crystal that trap water at the time of formation. The trapped water can then be extracted and the water is measured for oxygen and hydrogen isotopes. This allows for the direct measurement of the isotopic composition of the fluid from which the calcite precipitates. This information combined with the $\delta^{18}O$ of the carbonate allows us to calculate the formation temperature.

The temperature at the time of formation can also be determined through the analysis of multiply substituted ‘clumped’ isotopologues since temperature and the proportion of clumped isotopologues are directly related (Ghosh et al., 2006). At low temperatures, the carbonate mineral is more stable and therefore an increased number of rare isotopes are multiply substituted into a single molecule. As the temperature increases, there is a decrease in the number of clumped isotopes. To measure clumped isotopes, the proportion of doubly substituted isotopologues (predominately $^{13}C^{18}O^{16}O$) of the sample gas is compared to CO_2 gas that has a stochastic isotopic value (Eiler, 2007; Ghosh et al., 2006). This relationship is expressed as the Δ47 value of the sample gas. The linear relationship between temperature and Δ47 has been demonstrated by Ghosh et al. (2006) and Dennis and Schrag (2010). Clumped isotopes have been utilized for a wide range of paleoclimate and paleotemperature studies (Eiler, 2011). In one study conducted on speleothems from Soreq cave it was demonstrated that the derived temperatures were similar to those in the literature, however, there was an observed offset in the modern temperature values (Affek et al., 2008). This suggests that there is a need for a separate calibration line for speleothems. The observed offset is thought to be due to the mechanism of calcite precipitation in a speleothem. Calcite precipitation occurs through the rapid degassing of CO_2 from a thin film of solution. During this process, the DIC does not undergo full oxygen isotope exchange with the water leading to an additional fractionation and a calcite which is enriched in Δ_{47} (Affek *et al.*, 2008, 2010). Through the application of stable isotope analysis of calcite, fluid inclusions and clumped isotopes, we can develop a better understanding of the paleoclimate in the Bahamas.

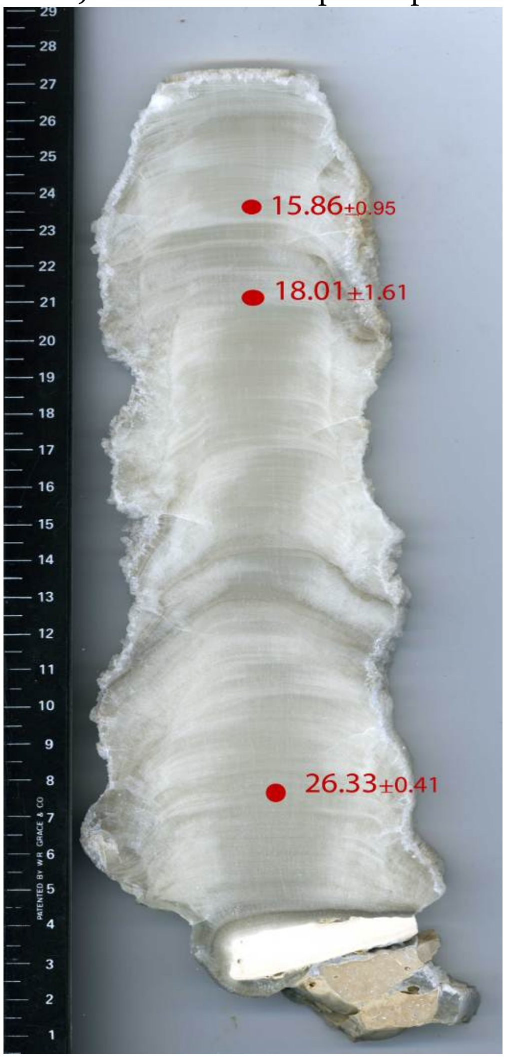

Figure 1. Cross section of stalagmite from the Bahamas showing the position of U-Th dates (kyrs). This stalagmite samples Heinrich event 1-3.

SCOPE OF WORK

Preliminary results support a significant shift in the stable carbon and oxygen isotopes of the calcite across Heinrich events. These changes were initially interpreted as a drier climate leading into the events followed by a shift to wetter climates after. However, in the summer of 2011, fluid inclusion isotopes were analyzed at Vrije Universiteit, Amsterdam, utilizing the "Amsterdam Device", an instrument built specifically for crushing carbonates in order to extract water from fluid inclusions (Vonhof *et al.*, 2006). These results support the idea that most Heinrich events are associated with cooler temperatures and a more arid climate. Initial clumped isotope results also show a decrease in temperatures across Heinrich events, however, there is an observed offset similar to other caves (Affek et al., 2008).

Recently acquired at the University of Miami Stable Isotope Laboratory is a new Picarro Cavity Ring-Down Spectrometer. The Picarro will allow for measurement of oxygen and hydrogen isotopes of water at a much higher precision than previous studies. Future plans are to construct a fluid inclusion extraction device to work in conjunction with the Picarro to conduct fluid inclusion isotopic analyses in house. Additional future work will include a cave analogue precipitation experiment where calcite will be precipitated in environments reflective of cave conditions. The experimental design will allow for various cave environments where calcite can be precipitated. For example, calcite will be precipitated in varying humidity, precipitation rates, and pCO_2 environments to better understand how these factors influence isotopic ratios. This work will help develop a clumped isotope calibration equation for speleothems.

EXPECTED RESULTS

The results of this project have important implications both for the study of speleothems and climates as well as for the study of diagenetic carbonates. The paleoenvironment of the Bahamas over the last glacial period is unknown and important for better understanding the climate system. As regards diagenetic carbonates, the fluid inclusion and clumped isotope methods are both applicable to a wide range of geochemical problems, such as understanding the paragenetic sequence of hydrocarbon bearing reservoirs.

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DIAGENETIC ISOTOPE SIGNALS IN BORON, MAGNESIUM, & CALCIUM ISOTOPES?

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PROJECT PURPOSE

A fundamental argument used to support the idea that large changes in the C isotopic record during specific periods of time are related to changes in the global carbon cycle is that similar changes in the C isotopic signals are seen on a global basis during ancient time periods. However, we have shown in a recently published paper that this is not the case (Swart and Kennedy, 2012). In fact similar changes in the C isotopic composition were evident in Pleistocene carbonates collected from both the Pacific and the Atlantic which are related to freshwater diagenesis connected to sea-level changes and not global changes in the carbon cycle. They appear to be similar in nature to C isotope patterns observed in the Neoproterozoic which have been interpreted as being original in nature. Within the Neoproterozoic sections other isotope systems (B, Mg, and Ca) have also been investigated and suggested to be original in nature. The purpose of the project outlined here will be to investigate how changes in other isotopic systems (Ca, Mg, and B-isotopes) in the well-known diagenetic zones are documented in comparatively recent rocks (Pleistocene-Miocene) and ascertain whether these systems can be usefully applied to the other geological time periods. The results of this study will be of use in applying these new isotope systems towards the understanding of diagenesis in carbonates.

PROJECT RATIONALE

We have already analyzed the stable C and O isotopic composition of shallow water carbonates from several cores in the Bahamas. These show a characteristic change in stable C and O isotopic composition from isotopically negative values associated with meteoric diagenesis to heavy values associated with marine processes (Melim et al., 2002). We also have extensively studied processes of dolomitization in what we consider to be relatively well constrained environments (Swart and Melim, 2000). The goal will be to resample these materials and analyze variation in B-isotope (Foster), Ca-isotopes (Holmden), and Mg-isotopes (Higgins) within the context of the observed C and O isotope changes. The results of this work would then be applied to ancient geological sections not only including the Neoproterozoic, but also younger geological materials.

PROJECT DESCRIPTION

Large carbon isotope excursions occur stratigraphically beneath erosion/exposure surfaces throughout the geological record. In the Neoproterozoic these changes are widely believed to record changes in the global carbon cycle even though they are commonly associated with evidence of diagenetic alteration including, textural evidence of karst and carbonate neomorphism, dolomitization and covariation between $\delta^{13}C$ and $\delta^{18}O$ within some data sets. In spite of such evidence, a marine origin for C isotope values remains the consensus view based on 1) the recurrence of excursions in lithologically similar successions in multiple basins, 2) replication of the C isotopic values in some sections within basins (where others do not conform, they have been

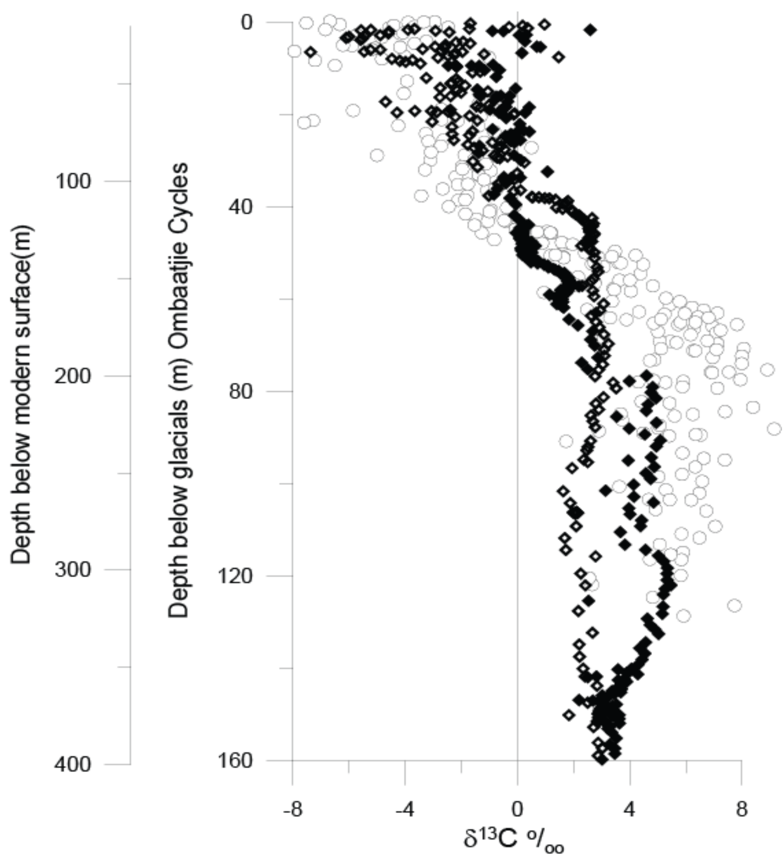

Figure 1. Comparison of the C isotopic profile from Clino (closed diamonds) and Unda (solid diamonds) with data from the Ombaatije formation (circles) in Namibia. Note the similarity of the profile and the range (Swart and Kennedy, 2012).

assumed to be incomplete as a result of erosion, 3) the distinctive magnitude (both positive and negative) of the values perceived to be limited to this period of Earth history, 4) step-wise development of values to define peaks, and 5) a perception that $\delta^{13}C$ values are robust to diagenetic change because pore fluids and interbedded organic carbon do not contain sufficient carbon to affect a mass balance dominated by marine material. By comparing the pattern of changes seen in the Pleistocene, where the diagenetic history is well constrained, we have been able to draw similarities to the Neoproterozoic (Figure 1). By inference we proposed that the Neoproterozoic changes are also diagenetic in origin. Within these same Neoproterozoic sections, various workers have started to utilize other isotope systems (Ca, Mg, and B) to make interpretations regarding changes in the chemistry of the Neoproterozoic oceans. Are these changes original or do they also reflect diagenesis? In the proposed work we intend examine the behavior of these isotopes under well constrained diagenetic systems.

<u>B Isotopes</u>: The two stable isotopes of boron occur in seawater as either borate ion, $B(OH)_4^-$ (enriched in ^{10}B) or boric acid, $B(OH)_3$ (enriched in ^{11}B). At low pH levels, all dissolved boron is in the form of $B(OH)_3$; at high pH levels, both ^{10}B and ^{11}B are in the form of $B(OH)_4^-$. The ratio of the two isotopes has been proposed as a paleo pH proxy and been applied to recent and modern carbonates (Hemming and Hanson, 1992) as well as very old examples (Neoproterozoic) (Kasemann et al., 2010; Sansjofre et al., 2011).

<u>Mg Isotopes</u>: Magnesium has three stable isotopes (24, 25, and 26). Although there has not been a great amount of work in this area there are suggestion from preliminary data that the ratio of 26/24 may be characteristic of the type of dolomitization (Carder et al., 2005)(Higgins and Swart, unpublished).

<u>Ca Isotopes</u>: Calcium has multiple stable isotopes (40, 42, 43, 44, 46, and 48). The ratio of 44/40 has recently been used in a number of studies to ascertain temperature (Hippler et al., 2006)and the diagenetic process (Holmden, 2009).

ANTICIPATED FINDINGS

In the case of these isotope systems, the behavior of the isotopes during early diagenesis is poorly constrained and the interpretation controversial. However, they all have the potential to reveal new information about diagenetic systems. Our work will take materials from well characterized diagenetic environments and examine the changes that take place in the calcium and boron isotopic systems.

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THE EFFECTS OF PRECIPITATION RATE ON CLUMPED ISOTOPES: RE-EVALUATING THE ACCURACY OF A NEW TECHNIQUE

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

PROJECT OBJECTIVES

- Manually precipitate calcium carbonate under varying environmental conditions with a control on all factors that have a role in the final composition.
- To quantify the variation in Δ_{47} CO_2 with changes in precipitation rate in order to evaluate the effect on clumped isotope measurements.

PROJECT RATIONALE

The variation of multiply substituted "clumped" isotopologues in calcium-carbonate, measured as the Δ_{47} of CO_2, has been found to be a precise and easily accessible paleothermometer. The use of this technique has a major advantage because it does not require any knowledge of the original solution from which the carbonate precipitated. This is because the multiple substitution of isotopes into a molecule is strongly dependent on temperature and is not reliant upon the oxygen or carbon composition within the solution. The use of clumped isotopes as a paleothermometer opens up a new realm of possibilities in the variety and age of samples that can be measured.

The ability to accurately measure clumped isotopes is a relatively new and unexplored field of geochemistry. When the paleothermometer based on clumped isotopes was first discovered by Ghosh et al. (2006), it was explained as a simple and elegant approach that could measure any carbonate, biological or inorganic, at any temperature. Consequently many laboratories quickly adopted the technique and utilized it for a multitude of applications without further exploring the development and proper measuring of clumped isotopes. With further research, it was found that clumped isotopes suffer from a few problems characteristic of measurements in most isotope systems:

- The calibration between Δ47 and temperature is only applicable to a small range of temperatures and had to be adjusted to suit more extreme ranges.
- Some carbonates (e.g. deep water corals, speleothems) showed fractionation in their clumped isotope measurements relative to other carbonates.
- The accurate measurement of clumped isotopes is susceptible to many contaminations and drift within the machines that varies with each machine.

In order to explain some of these patterns we will examine the behavior of the Δ_{47} of CO_2 produced from the dissolution of carbonates. For example the effect of precipitation rate on the isotopic composition of carbonates was shown in Romanek et al. (1992) to have a measurable enrichment factor (ε) of 2.7% in aragonite and 1.0% in calcite. While this effect is minimal in $\delta^{13}C$ and $\delta^{18}O$ measurements, its impact on Δ_{47} of CO_2 is magnified many times over and needs to be quantified to increase the accuracy of clumped isotope measurements.

PROJECT DESCRIPTION

The Stable Isotope Laboratory at RSMAS has acquired a Thermo MAT-253 mass spectrometer which is capable of measuring clumped isotopes, making our lab one of less than twenty world-wide. This project entails precipitation of carbonate samples in an apparatus that is capable of controlling the temperature, precipitation rate, precipitate mineralogy, and solution chemistry. The project will follow the methods of Romanek et al. (1992) using a water-jacketed reaction vessel (±0.1 °C).

Each precipitation experiment will be performed at a range of Earth temperatures and in a suite of precipitation rates. The experiment starts with making a stock solution of $NaHCO_3$ dissolved in deionized water plus the addition of CaCl. At this point, an equilibrium between the gaseous and aqueous phases must be reached by the continuous pumping of CO_2/N_2 gas until the solution is supersaturated. To encourage the precipitation of calcite, a known quantity of a seed material of pure $CaCO_3$ will be added to the solution. The presence of the seed will dictate the crystalline structure that is precipitated out ensuring a pure calcite. As the calcite is precipitated out, the solution chemistry will be constantly changing. To control this and keep the environment constant, a computer-controlled system will analyze the environment using pH probes and then add in an equivalent amount of chemical solution to readjust the environment back to the original saturation state. By doing this, each molecule within the precipitated calcite will be formed from the same environmental conditions and the rate of precipitation can be controlled by increasing or decreasing the saturation.

After each experiment, the precipitate will be dried, weighed, and analyzed by x-ray diffraction to check the composition of the sample. These samples will then be processed on our extraction line. They will be digested in a 90 °C phosphoric acid bath, releasing CO_2 gas which will be cleaned using a series of traps and vacuums. The sample will then be measured for its multiply substituted isotopologues on the Thermo MAT-253.

ANTICIPATED FINDINGS

We expect to be able to determine what the variation of precipitation rate has on the carbonate molecular structure. This will be shown if it is found that Δ_{47} values vary at the same temperature when the precipitation rate is different. If it is found that Δ_{47} values are independent of precipitation rate, then further focus on saturation state and the varying forms of high-Mg calcite, low-Mg calcite, and aragonite will be looked at. The overall impact of the experiment will be based on whether a discernible pattern can be found and applied to real life carbonate samples. Because of the possible impacts of the clumped isotope technique on the field of geochemistry, we believe it is well worth the effort to better understand what impacts the measuring of it in samples.

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