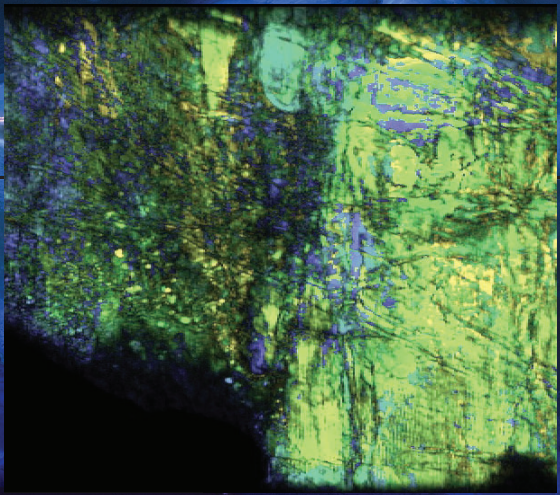
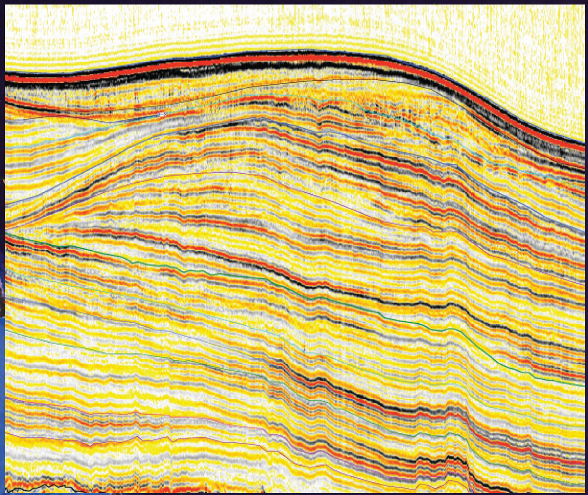
CSL
Center for Carbonate Research *and Education*

Prospectus

2023





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MISSION OF THE CSL – CENTER FOR CARBONATE RESEARCH

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

Our research program aims to comprehensively cover carbonates exploring new approaches and techniques in a variety of emerging topics. To reach this goal, the research projects integrate geology, geophysics, geobiology, and geochemistry and combine observational, laboratory, and theoretical research. Most research projects are interdisciplinary, but some are designed to advance knowledge in one specific area. This year the 22 projects are divided into five main topics:

- Shallow-water Carbonates
- Carbonate Contourite Depositional Systems
- Unconventional and Conventional Reservoir Characterization
- Geochemistry and Geobiology
- Carbon Capture Utilizations and Storage (CCUS)

In addition to the fundamental knowledge gained from these studies we aim to inform our industrial associates regarding the newest research techniques that potentially can be incorporated into the workflow of projects or help to solve longstanding problems in exploration and production. The various projects are described in detail in this prospectus and are retrievable on the website www.cslmiami.info.

KNOWLEDGE TRANSFER

The CSL – Center for Carbonate Research transfers the research results to our partners through semi-annual meetings, our website, and publications.

In addition, we offer field seminars and in-house short courses.

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

We present the research results of the projects described in the prospectus in a Progress Report in the form of an executive meeting in early summer and at the Annual Review Meeting in the fall. We provide each industrial partner with a digital version of our presentations and publications stemming from CSL sponsored research. On our website, research results from previous years can be viewed in the archive section, providing a comprehensive database for many topics and geographic areas. Upon request, we also share original data sets with participating companies.

PERSONNEL

PRINCIPAL INVESTIGATORS

Gregor P. Eberli	Professor, Seismic Stratigraphy, Sedimentology
Sam Purkis	Professor, Sedimentology
Peter K. Swart	Professor, Geochemistry
James S. Klaus	Associate Professor, Paleontology
Amanda M. Oehlert	Assistant Professor, Geochemistry
Ralf J. Weger	Assistant Professor, Petrophysics
Donald F. McNeill	Scientist, Sedimentology, Stratigraphy
Mara R. Diaz	Scientist, Geobiology
Mark Grasmueck	Adjunct Professor, Subsurface Imaging
Paul (Mitch) Harris	Adjunct Professor, Applied Sedimentology

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G. Michael Grammer	Oklahoma State University

2023 RESEARCH FOCUS

We are excited that for our research in **shallow and deep-water carbonates** we have and will receive very **unique core material** with which we can investigate depositional environments that are rarely recovered in cores. The first set of cores was retrieved in 2020 from a rift setting in the northern Red Sea from a brine pool and from **abyssal microbialites** during the course of the OceanX 'Deep Blue' cruise. The second set of cores is from the windward margin in the Exumas, where cuttings from two disposal wells contain the **deepest record** of this complex windward margin. This latter material, in conjunction with shallow cores, will help to decipher the heterogeneity of the high-energy platform margin. A precious set of **cores from offshore Mozambique,** drilled through a fringing reef that grew during the Last Glacial Maximum (LGM) and drowned during the first meltwater pulse, will be shipped to the CSL for a multiyear study. The international ocean discovery program (IODP) has with large costs retrieved cores through such **lowstand reefs** offshore the Great Barrier Reef and in Tahiti and soon in Hawaii. The core recovery from offshore Mozambique is better than their efforts and thus allows us to address a whole series of scientific questions, many of which are relevant for exploration efforts.

Besides core analysis, a second approach in our research in understanding carbonate depositional systems is **modeling**. This year, we have two projects; one addresses the processes of off-bank transport and the other self-organization of the depositional environment.

Carbonate contourite depositional systems. As a result of our multiyear research effort we can now assemble an **atlas** of carbonate contourite drifts, which is a data base of modern and ancient drift systems. Two other projects explore the relationship between slope curvature and evolution as a result of current activity along the slope.

Projects in **Unconventional and conventional reservoir characterization** combine petrophysical and geophysical data with stratigraphy and sedimentology. In the potential unconventional strata in the Agrio Formation in the Neuquén Basin we will be measuring the acoustic velocity and resistivity within the context of stratigraphic succession. The assessment of petrophysical properties of ramp carbonates in Apulia is another project. A study of the velocity in dolostones is intended to document the importance of pore structure for velocity variations. Testing and applying a new method for increasing the visualization of lithoclasts, fractures and faults is an attempt to increase the reliability of seismic interpretation from 3D cubes.

In the **geochemistry and geobiology** theme, the focus is twofold. The first is to maintain a leading role amongst scientific laboratories using the **clumped isotope method.** The stable isotope laboratory (SIL) is one of only two laboratories that can measure the Δ_{48} proxy and apply it to various aspects of carbonate geochemistry. The second focus is understanding **microbial carriers and biosignatures in microbialites**. Both are important for identifying microbial origin of ancient carbonates.

Carbon Capture Utilization and Storage (CCUS). Testing the **seal capacity** of rocks with experiments run for weeks on end is the main laboratory effort. Although results are forthcoming, we plan to add more pressure chambers and advanced monitoring of changes in velocity and chemical composition of the pore fluids that will improve the experimental setup and output. Long overlooked and thus underestimated is the production of carbonate by fish. Because this precipitation occurs within the fish, it is removing carbon from the seawater – permanently if not all is dissolved before it reaches the seafloor. Determining the **dissolution rate of ichthyocarbonates** is therefore important and will be studied this year.

Below we provide a detailed description of each project planned for 2023.

2023 Reporting

We will report on our research findings during the year. In a virtual meeting in June we will give a **Mid-Year Progress Report** to inform the Industrial Associates of the status of the projects and the results in hand.

The detailed results of the individual projects will be presented at the **Annual Review Meeting in Miami** in mid-October. Hopefully we will be able to meet in person. The dates for these two meetings are tentatively set at:

June, 2023 – Mid-Year Progress Report

Executive style presentation of the projects and results in hand followed by a discussion. The meeting will be online starting at 9 o'clock in the morning (USA-EST) and 3 pm (UTC+01:00) in continental Europe. The meeting is expected to last about 2 – 3 hours. We will send out a program and other details by early May.

October, 2023 - Annual Review Meeting

The results of the projects detailed in this prospectus will be presented at the **Annual Review Meeting in Miami**. We will send out information on the logistics for the meeting in the second quarter of 2023.

Costs

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

2023 Planned Projects

Shallow and Deep-Water Carbonates

- Rift Carbonates, Brine Pools, and Deep Sea Microbialites in the Red Sea – Part II
- Over the Edge: Linking On-Platform Processes to Off-Platform Deposition on Great Bahama Bank
- Stratigraphy and Diagenesis of the Exumas Windward Margin at Bell Island, Bahamas
- South Joulter Cay, Great Bahama Bank - A Geo-Archive of Climate Change and Sea-level Variation?
- Mozambique Shelf Cores – Research Initiative
- Self-Organization in Carbonate Depositional Systems

Carbonate Drift Deposits

- Atlas of Carbonate Contourites
- Testing Current Control on Slope Curvature
- Timing of the Distally Steepening West Florida Shelf

Unconventional and Conventional Reservoir Characterization

- Acoustic Velocity and Resistivity of The Agrio Formation, Neuquén Basin, Argentina
- Reservoir Properties of the Apulia Carbonate Platform (Gargano Promontory, Italy)
- StratiPondView: Fabric Visualization inside Dipping Stratigraphic Units
- The Importance of Pore Structure on the Velocity of Dolostones

Geochemistry

- The Carbon Isotopic Composition of Proximal and Distal Sediments in the Vaca Muerta
- The Delineation of the Mixing Zone Using Clumped Isotopes
- The Use of Δ_{47} and Δ_{48} Disequilibrium in Understanding Dolomite Formation
- Origin of Δ_{47} and Δ_{48} Disequilibrium in Carbonate Minerals
- Clumped Isotope Evidence on the Origin of the Marinoan Cap Dolostone
- Impacts of the Microbialite Evolution History on Chemical Biosignatures
- Peloids as Microbial Carriers for Organomineralization in Ooids

Carbon Capture Utilization and Storage

- Testing Seal Capacity for Carbon Storage - an Experimental Approach – (Part II)
- Exploring Organic Carbon Sequestration Potential in Ichthyocarbonate

UNIVERSITY OF MIAMI
ROSENSTIEL SCHOOL of MARINE & ATMOSPHERIC SCIENCE

Department of Marine Geosciences
University of Miami

CSL
CENTER FOR CARBONATE RESEARCH

CERTIFICATE PROGRAM
APPLIED CARBONATE GEOLOGY

PURPOSE AND GOALS OF THE CERTIFICATE PROGRAM

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

OVERVIEW AND COSTS

A Certificate in Applied Carbonate Geology requires the successful completion of 16 course credits assembled from 10 courses in the program. The courses combine classroom teaching, laboratory classes and applied projects. No thesis will be written.
Courses for the Certificate Program will be offered in the Spring Semester and the 1st Summer Session of 2023. The student/geoscientist will be in residence for 6 months. The current tuition fee is $2,301/credit.

REQUIREMENTS FOR ADMISSION AND REGISTRATION

A bachelor degree or equivalent degree is required but can be offset by years of working experience. No GRE or TOEFL are required. Registration for the Certificate Program started in the summer of 2016 and is handled by the Graduate Studies Office of RSMAS.
Registration for the Certificate Program opens each year in June for classes in the following year. Registration is online using the UM-RSMAS graduate program website.

LEARNING OUTCOMES OF THE CERTIFICATE PROGRAM

Learning Outcome 1:

Geoscientists/students will gain a broad knowledge of carbonate geology and geophysics.

Learning Outcome 2:

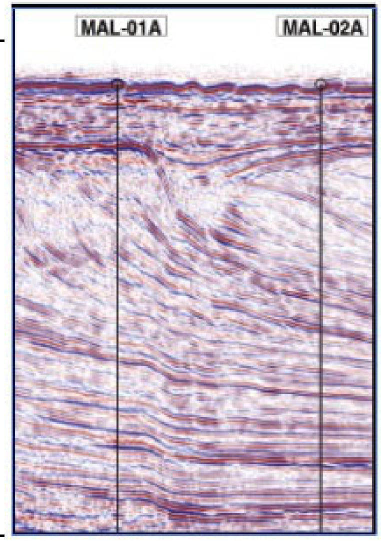
Geoscientists/students will learn to incorporate the acquired knowledge and available data and tools into the workflow of applied projects.

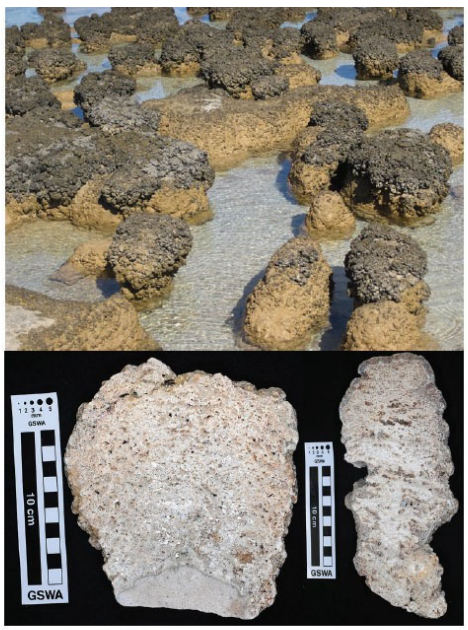
Learning Outcome 3:

Geoscientists/students will learn oral and written communication skills and will be able to communicate their ideas and findings to peers, managers, and administrators.

INSTRUCTORS IN THE PROGRAM

Gregor P. Eberli	Seismic Sequence Stratigraphy
Peter K. Swart	Carbonate Geochemistry, Petrography
Donald F. McNeill	Sedimentology, Stratigraphy
Mara R. Diaz	Molecular and Geomicrobiology
Ralf J. Weger	Petrophysics
John Dolson	Carbonate Petroleum Geology
Paul M. (Mitch) Harris	Carbonate Geology





OFFERED COURSES

MGS 611 3 Cr Earth Surface Systems
MGS 641 2 Cr Field Evaluation of Fossil Platforms, Margins, and Basins
MGS 601 1 Cr Seminar in MGS
MGS 678 2 Cr Field Seminar: Facies Successions on Great Bahama Bank
MGS 688 2 Cr Field Seminar: Heterogeneity of a Windward Margin
MGS 624 3 Cr Seismic Interpretation of Carbonate Systems
MGS 626 3 Cr Petrophysics of Carbonates
MGS 628 2 Cr Carbonate Diagenesis and Petrography
MGS 627 2 Cr Analysis in Carbonate Cores
MGS 689 2 Cr Petroleum Geology in Carbonates

For additional information about the Certificate Program in Applied Carbonate Geology please contact:

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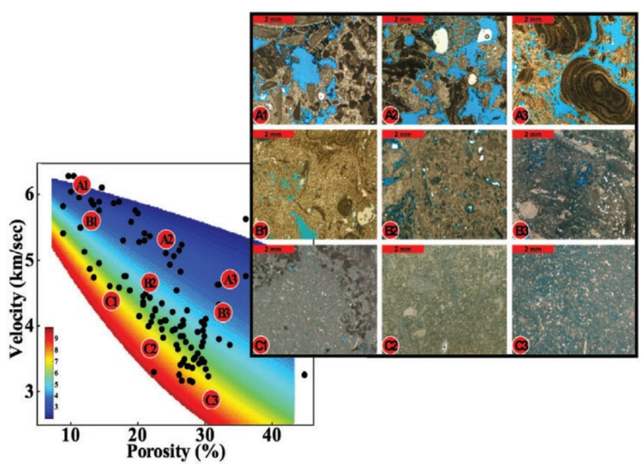

SHALLOW AND DEEP-WATER CARBONATES

RIFT CARBONATES, BRINE POOLS, AND DEEP SEA MICROBIALITES IN THE RED SEA – PART II

Sam J. Purkis, Morgan Chakraborty, Amanda Oehlert, and Peter K. Swart

PROJECT OBJECTIVES

- To characterize rift basin carbonates in an active maritime rift setting.
- To analyze a new suit of cores acquired in 2022 from the NEOM Brine Pool (Gulf of Aqaba) to evaluate the formation of deep-sea extremophile microbial mat-forming communities.

PROJECT RATIONALE

The Red Sea and Gulf of Aqaba sedimentary basins are developed along the African and Arabian conjugate margins and are characterized by Late Tertiary rifts filled with siliciclastic, carbonate, and thick evaporite successions. In collaboration with OceanX, we have now conducted two research cruises to explore these basins, the first in 2020 and the second in 2022. Both cruises used the R/V OceanXplorer and had the common objective of exploring and further detailing the deep seabed offshore Saudi Arabia.

This project assembles a unique dataset spanning swath multibeam bathymetry, sub-bottom profiles, sample collections from submersible and ROV, and deep-sea coring. Work to date has focused on margin stability of the rift shoulders (Purkis et al., 2022a) and description of a complex of brine pools that we discovered at a depth of 1770 m in the Gulf of Aqaba (Purkis et al., 2022b). Having had the opportunity to collect more cores in these pools, we are now using geochemical and genetic analyses to understand the sedimentary record preserved in these anoxic (and therefore not-bioturbated) settings and the geological relevance of the diverse and expansive extremophile microbial communities that they host.

APPROACH

The Red Sea is the youngest actively rifting marine basin in the world and it is also one of the few giant salt basins that is still evolving. Our overarching goal of this project is to use the Red Sea rift as a present-day analogue for rifted continental margins with adjacent "Atlantic-type" sedimentary basins. The Red Sea facilitates an examination of

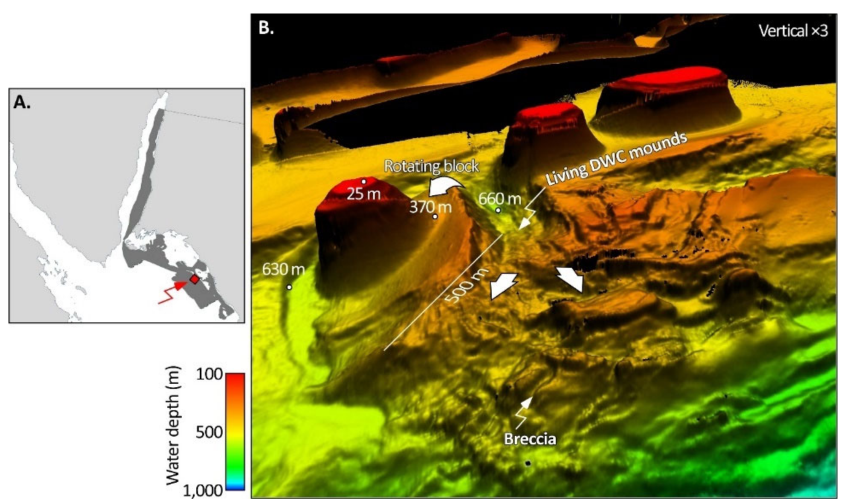

Figure 1: Rotated and tilted fault blocks hosting isolated carbonate platforms in the northeastern Red Sea as imaged from multibeam.

carbonate deposition in an active rift setting. In particular, the basin allows the interaction of shallow-water carbonates atop fault–bounded syn-rift highs to be examined. The analog is of broad interest because syn-rift carbonate platform strata can form important petroleum reservoirs within rift-basin systems.

Our dataset allows the interaction between flowing sub-seabed Miocene evaporites and shallow-water carbonates to be examined in a nascent oceanic basin. At the present time, the Miocene evaporites of the Red Sea are covered by 200-300 m of hemipelagic Pliocene-Quaternary (PQ) overburden sediments, which appear to do a good job of preventing the halite within the evaporites from re-dissolving, except where exposed by faults or slumps. The PQ overburden would, however, have been much thinner or absent in the early Pliocene. Our dataset is interesting as it hints at the likely seabed environment that occurred in the early Pliocene Red Sea and in early stages of other salt giants shortly after reflooding of their basins by seawater. Presumably, they were floored by patchy brine pools accompanied by exotic fauna, as seen at the NEOM brine pools. This kind of detail is hard to work out for the older margins such as off Brazil, although our observations hint at things to look for in those areas, such as evidence of undisturbed sediments within brine pools immediately or closely above the salt deposits. Why did those salt deposits not simply re-dissolve once those basins become reflooded with seawater after the desiccation phase? Seemingly the answer to that might be partly in the stability of brine pools if diffusion loss is slow.

SIGNIFICANCE

The multibeam data assembled for this project allow for the direct imaging of the seabed structures generated by evaporite flowage, displacement, and withdrawal (Fig. 1). Submersible and ROV dives have allowed direct sampling of the seabed structures associated with this movement. Discovery of the NEOM brine pools shows how sub-seabed evaporites can be dissolved by water penetrating along faults combined with hydrothermal circulation. Geologists commonly study microbialites but rarely in a deep-sea context as they are generally thought to be a shallow-marine phenomenon (Sprachta et al., 2001). The microbial fauna of the NEOM brine pool, however, implicates the potential formation of microbialites in bathyal-to-abyssal environments too. Further analyses will seek to determine if this microbial assemblage is actively trapping and binding sediments. Preliminary genomic analyses reveal that the sediments surrounding the brine pool are just as diverse as the brine pool itself, while also harboring a distinctly different microbial assemblage. Thus, the biodiversity present in brine pool communities is even higher than previously thought, potentially opening the door for new research avenues in these extremophile environments.

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OVER THE EDGE: LINKING ON-PLATFORM PROCESSES TO OFF-PLATFORM DEPOSITION ON GREAT BAHAMA BANK

Cecilia Lopez-Gamundi, Amanda Oehlert, Paul (Mitch) Harris,
Gregor P. Eberli, and Sam Purkis

PROJECT OBJECTIVES

- Conduct a sediment budget analysis of the Great Bahama Bank (GBB).
- Sesimically quantify volumes of Holocene sediment along GBB's slopes.
- Reconcile off-platform deposits with platform-top sediment production and resuspension volumes to estimate sediment export.

PROJECT RATIONALE

Roughly 25 billion kg of sediment is produced annually atop the Great Bahama Bank (GBB), with up to 250% of it remobilized on the platform top alone (Lopez-Gamundi et al., *in prep*). While the quantity of sediment that is delivered over the platform margin and onto the slopes is unknown, cascading density currents are understood to be the dominant mode of transport (Wilson and Roberts, 1995). These hyperpycnal flows are challenging to observe in the field or through remote sensing. Fortunately, seismic data (Fig. 1) offers a way by which the volume of sediment shed by the platform can be quantified. The resulting sediment budget has three plausible permutations: (1) the volume of sediment on the GBB's flanks exceeds that which is being produced atop the platform, (2) these volumes are balanced, or (3) off-platform volumes fall short of the ability of the platform to shed sediment over its margin. Each possibility elucidates a different, yet non-unique, dynamic for GBB in the last 6 kyr since it last flooded. If (2) is true, then the GBB is a self-contained isolated platform, self-regulating and stable. However, if (1) is true, then either off-platform deposits are receiving additional sedimentary contributions from more distant sources, or sediment production was much higher in the geological past. But, if (3) is true, sediment is exported far beyond the margin itself, else modern production rates are greater than those experienced at the onset of the last sea-level transgression. The sedimentary surplus or deficit proposed by (1) or (3) could also

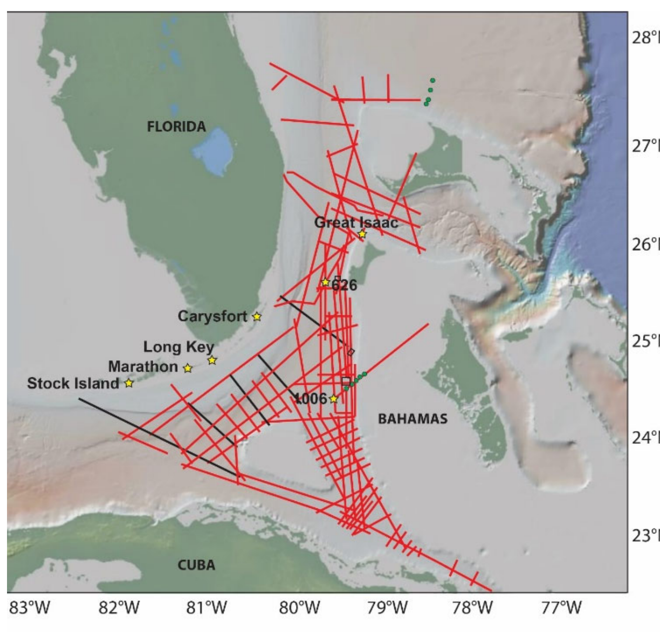

Figure 1. Available 2D seismic surveys on the western margin of the Great Bahama Bank. Datasets will be used to assess off-platform sediment volumes and facies.

intimate either the existence of an unaccounted-for production mechanism, such as seawater precipitation of carbonate, or substantial dissolution, neither of which have yet been quantified in a budget before.

Seismic analysis of slope deposits not only sheds light on the overall balance between on- and off-platform processes, but also hints at the inner workings behind fine-scale facies heterogeneity. Along strike variability of slope sedimentary facies often reflects the different export pathways transited by exiting platform-derived sediments (Mulder et al., 2012). Previous hydrodynamic modeling suggests that fine sediment can travel substantial distances (>1000 km) from sources within the platform interior before escaping through different "leak points" along the GBB's margins (Lopez-Gamundi et al., 2022). Upon reaching the slope, sediments of differing shapes and sizes, once only reflecting their initial sources, are subject to winnowing and redistribution by deeper contouring currents. Analysis of these slope seismic facies coupled with hydrodynamic modeling elevates our understanding of the drivers responsible for facies heterogeneity on the flanks of carbonate platforms.

APPROACH

High-resolution seismic data on the GBB's flanks and adjacent contourite drifts will be analyzed in order to: (1) assess total Holocene sediment volumes in order to audit the GBB's sediment budget, and (2) decipher the causes behind slope facies heterogeneity. This new facet in our research will leverage previous work on sediment production estimates, total suspended sediment analysis, and hydrodynamic modeling; thereby offering a more integrated and complete view of platform top and slope evolution.

SIGNIFICANCE

Understanding the accumulation of sediment beyond the GBB's margin is the final step of our comprehensive sediment budget analysis. Such budgetary audits are key to understanding the fundamental dynamics of source-to-sink relationships, contourite formation, and the overall evolution of carbonate platforms over time.

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STRATIGRAPHY AND DIAGENESIS OF THE EXUMAS WINDWARD MARGIN AT BELL ISLAND, BAHAMAS

Brandon Navarro, Gregor P. Eberli, Donald F. McNeil, and Kelly L. Jackson[1]
1) Ransom Everglades School

PROJECT OBJECTIVES

- To decipher the stratigraphy of the windward margin along the Exuma Sound from cuttings of two disposal wells.
- Determine the facies and the ages of the sediments deposited during the last interglacial (MIS 5e; 128 – 115 kyrs).
- Investigate diagenetic and mineralogical changes of dolomite-limestone alternations observed in the deep wells.

PROJECT RATIONALE

Windward platform margins are often excellent reservoirs of grainy, high energy facies successions. This complex transition zone from the platform to the slope is built by stacked successions of highstand deposits that are typically very heterogenous alternating between marine and eolian deposits (McNeill et al., 2013). In addition to the vertical complexity, lateral heterogeneity is produced by the antecedent topography that focuses tidal energy, resulting in a complex shoal and channel morphology. The modern Bell Island (Fig. 1) is situated on the windward

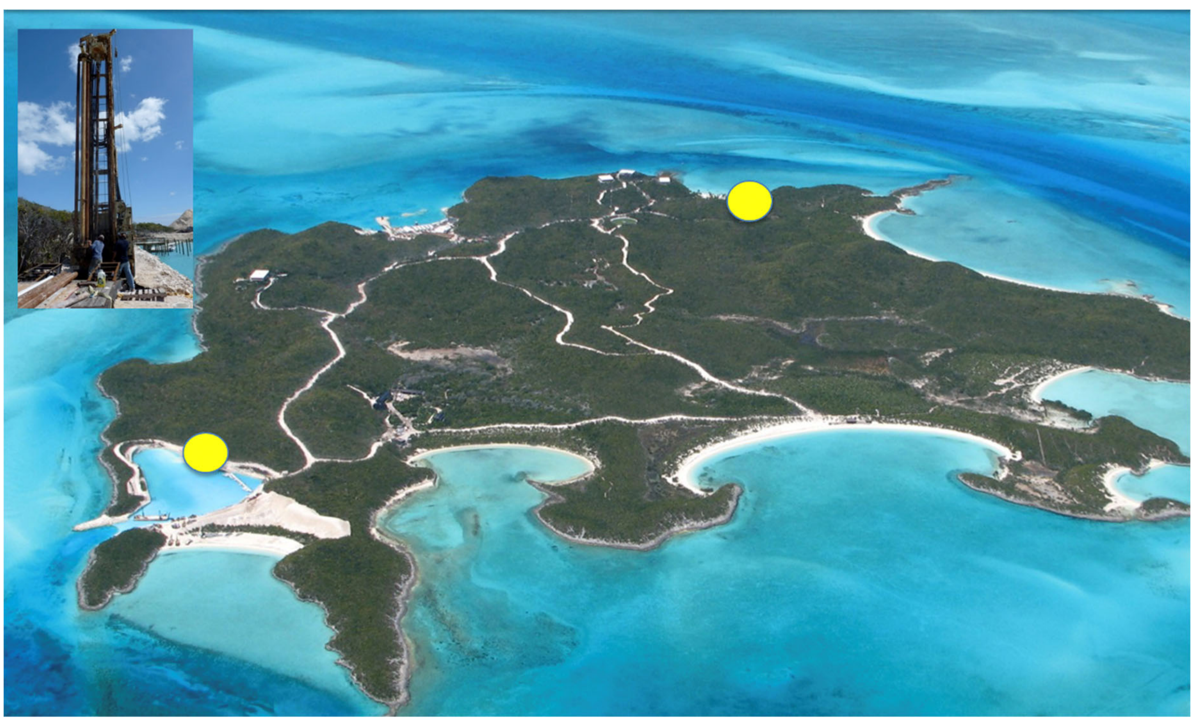

Figure 1: Bell Island with the location of the two disposal wells that were drilled down to 183 m (600') thereby providing the deepest record of the Exumas windward margin. Inset: Drill rig used to drill the disposal wells.

margin along Exuma Sound and consists mostly of eolianites from the last interglacial (MIS 5e). Cores drilled to various depths and at various locations allow us to investigate the vertical and lateral heterogeneity of the bank-margin succession and small-scale features. The deepest cores reach 183 m (not dated yet) and might penetrate the entire Pleistocene succession. Preliminary XRD analyses document the transition from aragonite to calcite with dolomite appearing at about -40 m, subsequently alternating with limestone, illustrating a complex diagenetic overprint on the heterogeneous facies succession.

DATA SETS

Bell Island and its surrounding area was mapped by Jackson (2017), illustrating the influence of the Pleistocene aeolian topography on the modern marine facies distribution. In the course of planning the construction of a yacht harbor the owner asked the CSL to drill several short cores (1m) together with a longer 11 m core on the island. In addition, two disposal wells (Fig. 1) to 183 m were drilled. The CSL collected the cuttings that now provide the deepest record of the windward margin in the Exumas chain.

WORKPLAN

The planned work consists of a detailed analysis of the core and cutting material, starting with description, thin section analysis and facies reconstruction. The preliminary XRD measurements will be complemented with additional data points. Other geochemical analyses will include stable isotope measurements. Porosity measurements will be performed on the shorter cores where core plugs can be cut.

The results will subsequently be compared to the results of two cores drilled to -36 m on Normans Cay and Lee Stocking, situated about 80 km further south on the Exuma margin (McNeill and Hearty, 2008, 2009).

SIGNIFICANCE

Grainy platform margins in the transition between platform interior and platform flank is a complex zone where correlation of sequences and facies connectivity is hard to establish. The results of this study will provide an example of the potential scale of heterogeneity both in facies and diagenesis. Such data is important as input in modeling but also in training of AI guided models.

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South Joulter Cay, Great Bahama Bank - A Geo-Archive of Climate Change and Sea-level Variation?

Paul (Mitch) Harris and Juan Carlos Laya[1]

2) Texas A&M University

Project Objectives

- Further calibrate the timing of key depositional events within the history of SJC with radiometric dating of select beach ridges.
- Thereby test to what extent island growth is the result of variations in storm frequency and/or sea level during the Holocene.

Project Rationale

Our ongoing examination of South Joulter Cay (SJC), a key part of the modern Joulters ooid sand body on Great Bahama bank, targets a better delineation of the timing and processes that formed the island. High resolution imagery and a DEM constructed from a drone survey helped to formulate a scenario for island beach ridge development (Harris and Laya, 2022). We continue testing the hypothesis that the island ridges are the result of storm deposition and resulting changes to the local hydrodynamic setting (Fig. 1).

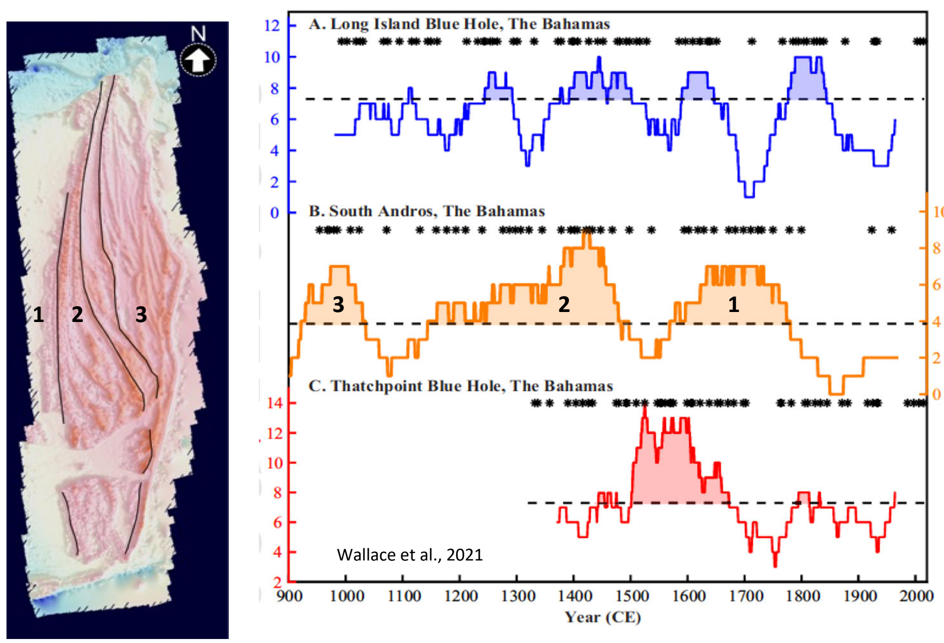

Figure 1: Left - DEM from high-resolution drone imagery (Harris and Laya, 2022) annotated to show interpreted morphological stages of island growth. Stage 1 Linear Ridges represent initial island formation; Stage 2 Arcuate Ridges formed as part of an ebb tidal delta lobe related to a channel cutting the island; and Stage 3 Cuspate Ridges were deposited as multiple prograding beach ridge sets driven by longshore currents. Right - Results from sediment coring by Wallace et al. (2019, 2021) in blue holes at three Bahamian sites to assess timing of storm deposits and therefore storm frequency. Data delineates periods of intense storm activity, numbered 1-3, that may relate to stages of island growth of SJC.

Approach

From observing the impacts of recent hurricanes, we believe that major storms delivering east to west energy and sediment transport are most likely to have played a role in island development, but that a single storm by itself may be insufficient to cause change (Laya and Harris, 2022). Instead, it is more likely that periods of intense storm activity as determined for the last 1100-1500 years by recent sediment coring and dating from several blue hole sites on GBB (Wallace et al., 2019, 2021) provide the type of collective storm activity that can relate to the initiation and growth change variability observed at SJC. We intend to calibrate the timing of key depositional events within the history of SJC with radiometric dating of select beach ridges to facilitate a more rigorous comparison with storm activity as well as possible sea-level change. Preliminary ^{14}C ages provided by the Keck Carbon Cycle AMS Facility of UC Irvine, which are still being evaluated, indicate ages 1775 YBP and younger. Note the timing of the oldest (1) period of intense storm activity on Figure 1.

SIGNIFICANCE

This study has relevance to facies interpretation and correlation within subsurface grainstone reservoirs. Islands like SJC add significantly to complexity and potential localized heterogeneity within a broader development of reservoir quality grainstone (Harris and Laya, 2022). Assessing the impact of storms in forming the island and changing ridge morphology will continue to help refine our understanding of the broad suite of controls over shallow carbonate platform facies patterns. And beach ridge systems like SJC are potentially important geo-archives for the study of climate change and sea-level variations over the Holocene.

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Mozambique Shelf Cores – Research Initiative

Gregor P. Eberli, Ricardo Argiolis[1], Iva Tomchovska, Ralf T. Weger, James Klaus, Peter K. Swart, Amanda Oehlert and others.

1) EniProgetti SpA

Goals of Project

- To decipher the initiation, growth and drowning of the fringing reef during the last glacial maximum.
- To assess the composition of the reef and the contribution of microbial crusts in stabilizing the reef.
- To thoroughly analyze the diagenetic alteration in this reef that was never exposed to fresh water.
- To produce a comprehensive petrophysical data set of the core material that includes porosity, acoustic velocity, and resistivity.

Introduction And Rationale

The slopes above the newly discovered giant gas fields offshore Mozambique (Fonnesu et al., 2020) revealed a long, approximately 40 m thick fringing reef that crested at -95 m water depth. The reef started to grow during the Last Glacial Maximum (LGM) at approximately 20 kyrs and drowned during the subsequent deglaciation. Such lowstand reefs have been cored in a few places around the world, including offshore the modern Barrier Reef and Tahiti (Camoin et al., 2006; Heindel et al., 2012). However, these earlier borings have not achieved the level of core recovery as those of Mozambique. The shareholders have released these cores to the CSL – Center for Carbonate Research- for scientific study.

We are expecting the official release from the government of Mozambique. A 2 m section had been made available to us a couple of years ago. It showed a diverse coral community with several species but also thick crusts of greyish microbialites and microbial pellets inside the coral frame (Tomchovska et al., 2022). Two samples collected for C-14 dating from this section

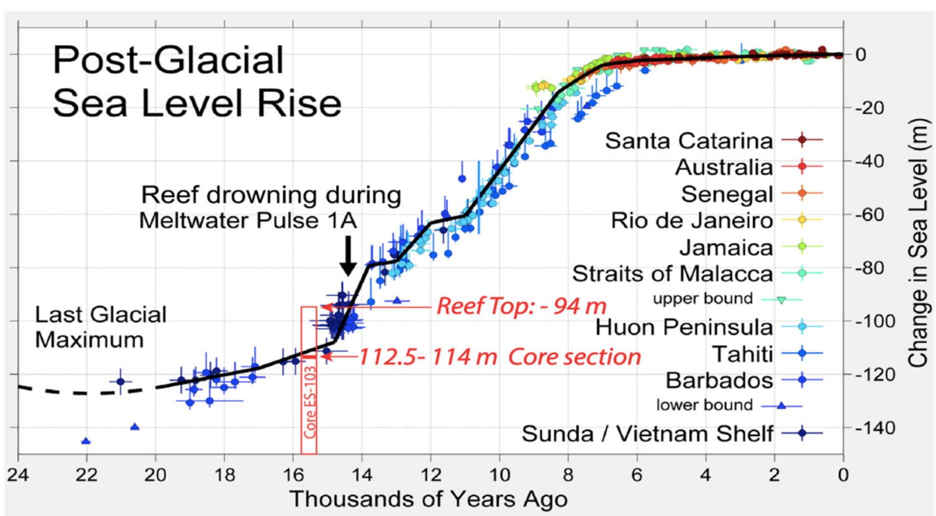

Figure 1: Core position within the post glacial sea-level rise. This lowstand reef that crested at -94 m has a diverse coral community and encrustations of microbialite (M) as well as calcareous red algae (CR).

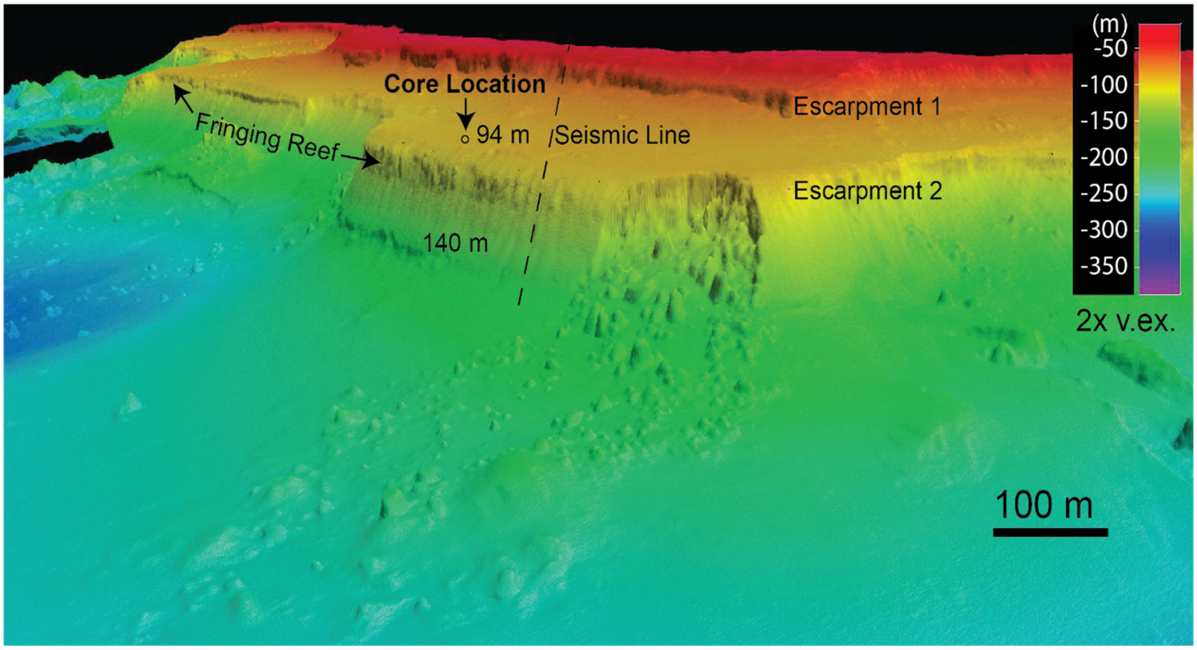

Figure 2: Core location on the fringing reef.

yielded ages of 13400 and 13600 kyrs, documenting reef growth shortly after the Last Glacial Maximum during the deglaciation and the accelerated sea-level rise event called Meltwater Pulse 1A (Fig. 1).

The Mozambique cores (Fig. 2) will provide a unique opportunity to study lowstand reef complexes that have never been exposed to freshwater diagenesis. Given the high level of preservation, these cores are of intrinsic value as they represent an unaltered geological record.

Analyses of these cores will address several fundamental topics.

These include: 1) the evaluation of seawater composition and temperature during the LGM, 2) the timing and rate of sea-level rise during the early deglaciation, 3) early marine diagenetic processes, 4) the identification of the coral species and their changes from the LGM through the early stages of the deglaciation, 5) the role of microbial crusts that have been documented as important components of reef environments during the LGM, and 6) relate the pore structures to the petrophysical properties of these carbonate rocks cemented solely in the marine realm.

PLANNED TASKS

1) Curation of core: The cores will be cut longitudinally into two halves. One half will be the archive core, which will be photographed and preserved, while the other will be used as a "working" half for a myriad of analyses, including petrographic, geochemical and petrophysical analyses.
2) Detailed core description on the archive half of the core will use Dunham classification.
3) Coral ecology: Identification of the coral species will be undertaken using morphological attributes; in addition, changes in coral community structure will be assessed as sea water composition changes during the onset of the deglaciation.

Component	Percentage of Surface Area
Coral	53.6%
Microbialite crust	14.1%
Calcareous coralline algae (CCA)	3.8%
Skeletal rudstone to grainstone	28.5%

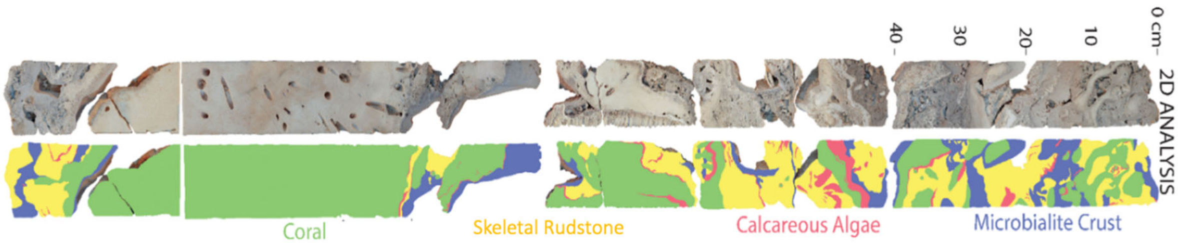

Figure 3: Quantitative analysis of the 2 m core section, displaying the four elements present and their respective abundance.

4) Quantitative analysis of core components will be undertaken by identifying textures (i.e. microbial crusts, corals, sediment grains) (Fig. 3) in core and on stitched images. The quantification will be done on adjusted images using Image J's "analyze particles" function.
5) Thin section analysis of petrographic fabrics, diagenetic alterations and grains will be conducted.
6) SEM (scanning electron microscopy) analysis of the microbial crusts and marine diagenetic cements will be undertaken.
7) Age determination using the C-14 method on reef material and crusts will be employed to determine if they grew coevally.
8) Petrophysical studies will be done on 1 inch core plugs that are drilled vertically and horizontally into the working half of the core. Porosity will be measured with a Micromeritics AccuPyc 1330 Helium pycnometer utilizing Boyle's law. Laboratory measurements of acoustic velocity and electrical resistivity measurements will be performed on brine-saturated core plugs under variable pressures using a New England Research Autolab1000 system.
9) Geochemical analyses will consist of: 1) stable isotope analysis on regularly spaced samples in each core, 2) XRD of the same samples to determine mineralogy and 3) clumped isotopes to determine the water temperature during reef growth.
10) Results from this research will be compared to previous studies conducted in Tahiti and offshore the Great Barrier Reef. The comparison will include reef composition, coral species ecology and geochemical signature.

Workplan

The study of this extensive core material and the large scope of the project will require three to four years to complete. The proposed tasks are arranged in the workplan below; roughly in chronologic order, but once sampling is completed, several investigations will be done simultaneously by different scientists.

Work Plan

Activities	Year 1	Year 2	Year 3	Year 4
	Transportation of cores to Miami			
	Curation core, cutting, sampling			
	Description of Core	Description of Core		
	Thin section analysis	Thin section analysis	Thin section analysis	
		Quantitative component analysis	Quantitative component analysis	
		Age determination	Age determination	
		Coral ecology	Coral ecology	
		Geochemical analysis	Geochemical analysis	Geochemical analysis
		Petrophysical studies	Petrophysical studies	Petrophysical studies
			SEM analysis	SEM analysis
				Comparison to other studies
				Final Report/Papers

Significance

The cores from offshore Mozambique will add a much-anticipated data set for establishing the environmental conditions during the Last Glacial Maximum and the early sea-level rise. In addition, these microbially encrusted coral reefs seem to preferentially grow during deglacial periods. They typically contain large intraframe porosity yet display an extraordinary strength, thus maintaining this porosity to large burial depth. If such microbialite/coral reefs form in a lowstand setting they could be identified as lowstand reefs on seismic data and are potentially excellent reservoirs.

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Self-Organization in Carbonate Depositional Systems

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Project Objectives

- To simulate reefal buildup morphogenesis using a spatially-explicit mathematical model based on partial differential equations (PDEs).
- To track self-organized processes through time and distinguish among alternative mechanisms of reef morphogenesis.
- To use modern shallow-water scleractinian reefs as a model biome for investigating biotic self-organization as a structuring force in carbonate depsitional systems.

Project Rationale

Reefs, whether built by scleractinian corals or their more ancient predecessors, have frequently been shown to simultaneously display two important hallmarks of spatial self-organization—scale-invariant patchiness and coherent spatial patterning. Alacranes Reef, situated in the Gulf of Mexico, demonstrates such 'morphogenesis' in exemplary fashion. Importantly, this pattern manifests at scales of tens of meters, to kilometers, which can easily be resolved from orbit (Purkis et al., 2015; Schlager and Purkis, 2015). A hallmark of the emergent patterning induced by self-organization is that it lacks a characteristic scale, as the fractal (power-law) size-frequency distribution of the Alacranes platform-interior reefs demonstrate. Power-law scaling implies one dominant process of reef growth at all scales (Brown et al., 2002). Scale invariance is not only observed within individual reefs, but also for entire archipelagos (Schlager and Purkis, 2013). Emergent patterning is not rare; preliminary results emphasize that 30% of atolls globally show a degree of spatial coherence of their lagoonal reefs and 15% show pronounced regular patterning. Based on the conceptual model proposed by Purkis et al. (2016), frame-building carbonate systems undergo a predictable sequence of emerging self-organized patchiness as ecological stress accumulates.

Approach

This project will deliver a mechanistic understanding of the triggers for self-organized patterning in carbonate depositional environments by integrating remote sensing, spatial patterning analysis, numerical morphogenesis modeling and comparisons of modern reefs that inhabit diverse environmental settings. Preliminary results suggest globally observed reef patterns can be clustered into nine groups and correspond to at least two different evolutionary paths in response to different local environmental conditions (Fig. 1). To test this hypothesis and further explore the underlying mechanisms, a mathematical model is developed, driven by four governing equations to describe the dynamics of four state variables: [i] reef biomass

(B; kg/m^2), [ii] sediment accumulation (S; mm), [iii] water depth (w; mm), and [iv] flow velocity (v; m/s).

Significance

This project has the potential to advance scientific knowledge by a) quantifying a reef morphology that has only been described qualitatively, b) identifying relationships between sea surface temperature (SST), community structure, and reef reticulation, as the cellular nature of a highly developed reticulate reef suggests that the reefs therein may be subject to shallower and warmer waters, c) identifying the key processes driving the formation of reticulate reefs using numerical models, and (d) exploring the possibility of SSO in reticulated reefs and the geological significance of their patterning.

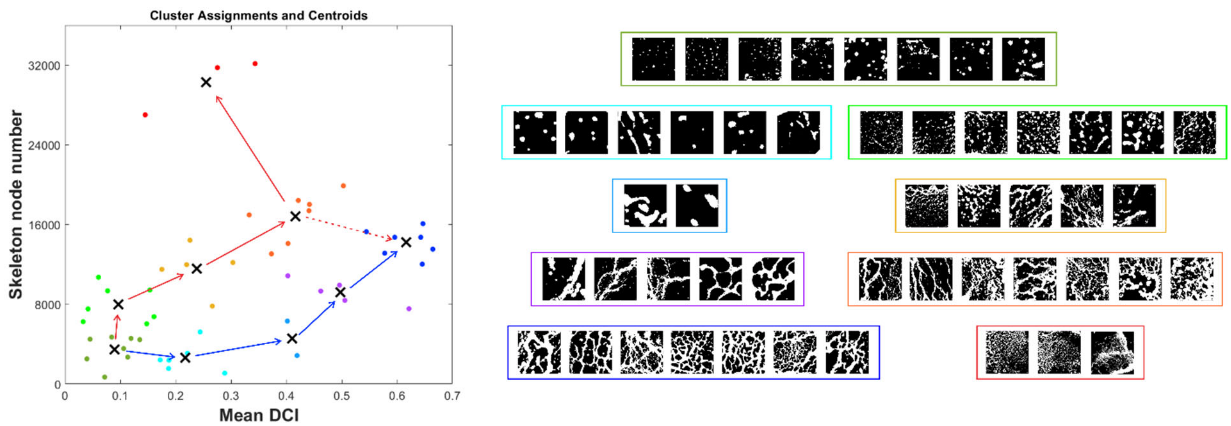

Figure 1: Clustering results of 50 global coral reef patterns showing nine groups and at least two evolution paths.

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CARBONATE DRIFT DEPOSITS

Atlas of Carbonate Contourites

Sara Bashah and Gregor P. Eberli

Project Objectives

- Provide a database of global carbonate contourite depositional systems.
- Analyze the geometry and dimensions of the various contourite depositional systems.

Project Rationale

120 major contourite areas have been recognized worldwide (Rebesco et al., 2014). Recognition of these contourite systems has influenced not only paleoclimatology and paleoceanography studies but also geological hazard assessment and hydrocarbon exploration. In carbonate environments, platforms are substantial barriers in the way of ocean currents; hence drifts are a frequent component of carbonate platform depositional systems. In addition, sizable carbonate contourites have been recognized in various settings (such as continental platforms and seaways) and ages (Eberli and Betzler, 2019). We aim to provide a catalog of global carbonate contourites depositional systems based on existing studies presented in a user-friendly Google Maps format.

Approach

Each carbonate contourite depositional system location will be pinned on Google Maps with specific coordinates. For each location, a description of the carbonate contourite system and a link to the scientific articles will be provided. Users can choose to view information on either the Miocene and/or Cretaceous carbonate contourites depositional systems.

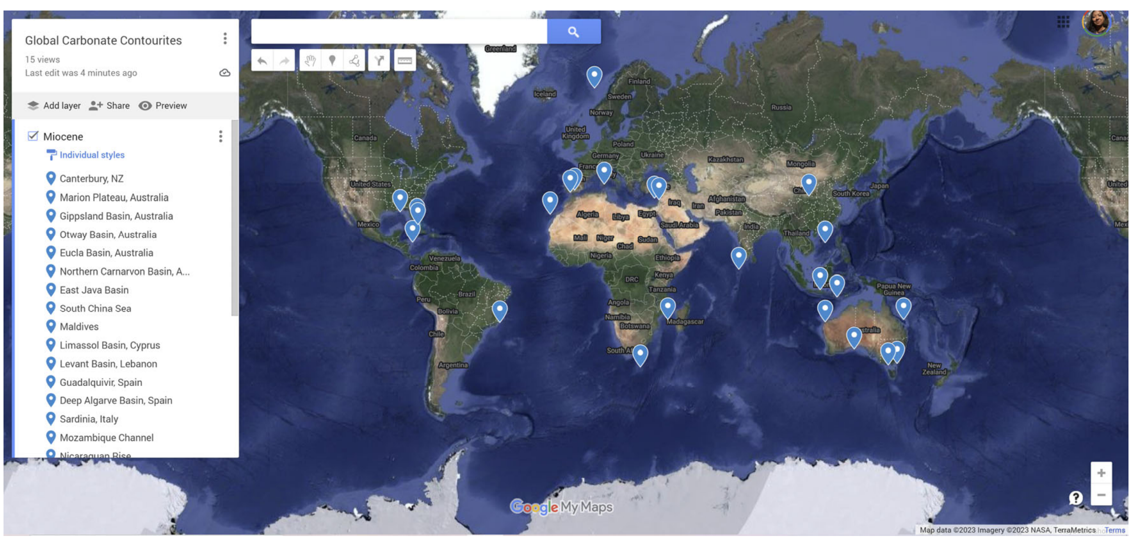

Figure 1: Google Maps showing the location of Miocene carbonate platforms with existing contourites studies.

SIGNIFICANCE

The carbonate contourite database will provide easy access to information on the available literature, geometry, and dimensions of carbonate contourites around the world to aid exploration involving carbonate depositional systems.

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TESTING CURRENT CONTROL ON SLOPE CURVATURE

Sara Bashah and Gregor P. Eberli

PROJECT OBJECTIVES

- Test the hypothesis that contour currents influence carbonate slope curvature.
- Propose evolutionary trends of carbonate slope morphology with increasing and decreasing current strength.
- Investigate the role of bottom currents on the distribution of carbonate slope facies.

PROJECT RATIONALE

Carbonate slopes display a variety of curvatures (Adams and Schlager, 2000). Analyses of the morphology of the East Florida Shelf, the Northern Marion Platform, the Kardiva Platform, the Maiella Platform, and the Wolcampian Platform of the Delaware Basin give evidence that contour currents strongly influence carbonate slope curvature. In particular, contrary to the model proposed by Schlager and Ginsburg (1981), we found that currents influenced both the accretionary and escarpment margins and that neither age nor height of the slope is directly related to the slope morphology. Likewise, incorporating currents into slope models will require refining and altering existing carbonate slope models compiled by Playton et al., 2011.

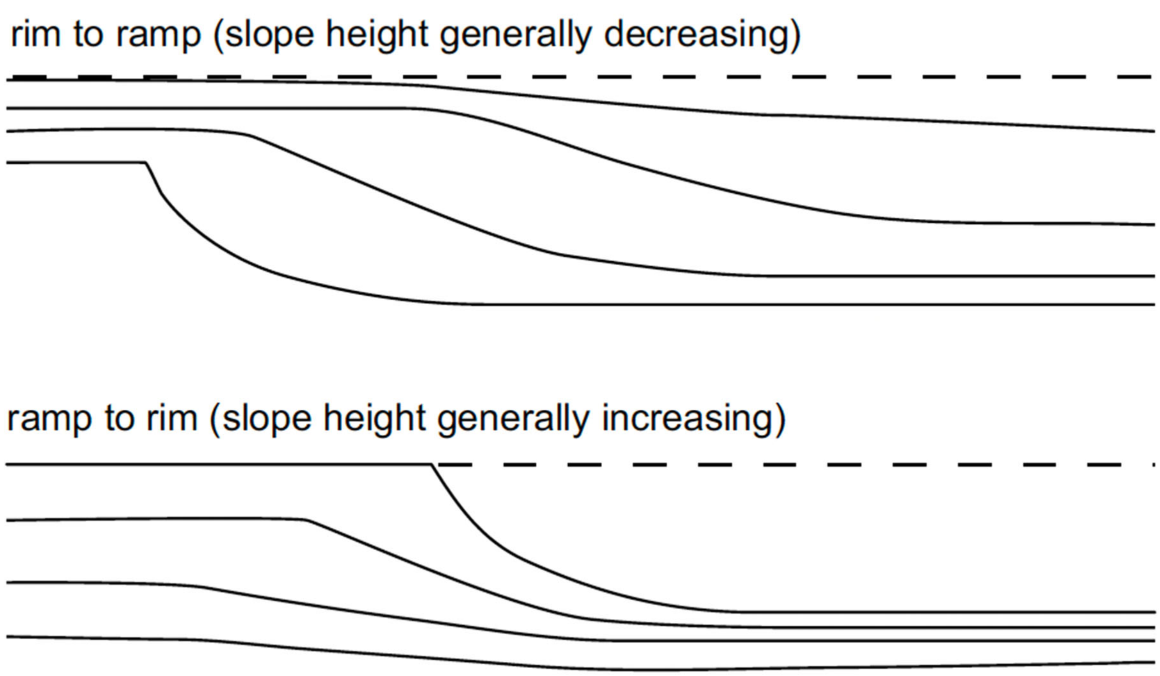

Figure 1: Slope profile evolution explained with slope height (Schlager, 2005). This project tests whether increased sedimentation to the slope by currents or decreased sedimentation can produce these two differing slope profiles.

Consequently, the role of currents in slope evolution needs to be investigated. This project tests the hypothesis that slope curvature is controlled by the slope's sedimentation, which is strongly controlled by contour currents.

WORKING HYPOTHESIS

This project tests the following hypothesis:

a) Erosion and nondeposition by currents form escarpment margins, while current-derived contribution to the slopes produces the accretionary slope.
b) Plastered and periplatform drifts decrease slope angles and might transform steep margins to more ramp-like margins, enabling the platform to change from aggradation to progradation.
c) The morphology changes from the ramp to the rimmed shelf are related to the onset of currents.

APPROACH AND DATA SETS

Investigate carbonate slope profiles that are exposed to currents with variable strength. An ideal place to pursue such an investigation is the Bahamian archipelago, as all the platforms are of the same age and composition but have different exposure to currents. In the Straits of Florida, slopes experience the strong Florida Current, the northern slope of Little Bahama Bank is exposed to the less vigorous Antilles Current, and in Exuma Sound, ocean currents are absent. Seismic, core, and log data that can be investigated exist for all three locations from ODP Leg 101. In addition, seismic and core data from ODP Leg 194 and IODP Expedition 359 will be revisited to investigate the carbonate slope facies and their associated drift deposits. Investigations into ancient carbonate slopes will concentrate on 1) the Cretaceous platforms in Abruzzi, Italy, that were exposed to currents flowing from east to west in the Tethys Ocean, and 2) the Permian platform system of West Texas, where current influence has been documented (Price et al., 2022).

SIGNIFICANCE

Contour currents have proven to be important agents in slope sedimentation but, hitherto, current influence has not been incorporated in slope models. Incorporating these processes into the models will provide a new outlook to characterize the carbonate slopes.

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TIMING OF THE DISTALLY STEEPENING WEST FLORIDA SHELF

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PROJECT OBJECTIVES

- Evaluate when the distally steepened ramp morphology formed and if a time difference exists between the north and south.
- Assess if the evolution of the distally steepened ramp of the West Florida shelf is related to the onset of the Loop Current.
- Search if a fault exists that separates the northern from the southern portion of the shelf.

BACKGROUND

The West Florida Platform is often taken as a modern example of a distally steepened ramp (Read, 1985; Mullins et al., 1988). The steepening occurs in two steps, one at around 100 m and the more pronounced one at 400 m water depth when the distal ramp transitions into an approximately 20 km wide ramp slope with a declivity that ends abruptly at the Florida Escarpment. The slope that stretches from the inclination break to the top of the escarpment has average slope angles of 5- 7°with steeper, irregular slope failure scars 50 – 70 m in height and abundant canyons (Fig. 1). There are, however, differences in the morphology of the Florida slope and the escarpment from north to south. In the central part, the slope is convex in profile, while in the southern part it is concave. The change from convex to concave occurs across a narrow canyon that cuts into the slope about halfway between our study sites. Most studies attribute a major role to the Loop Current as a mechanism

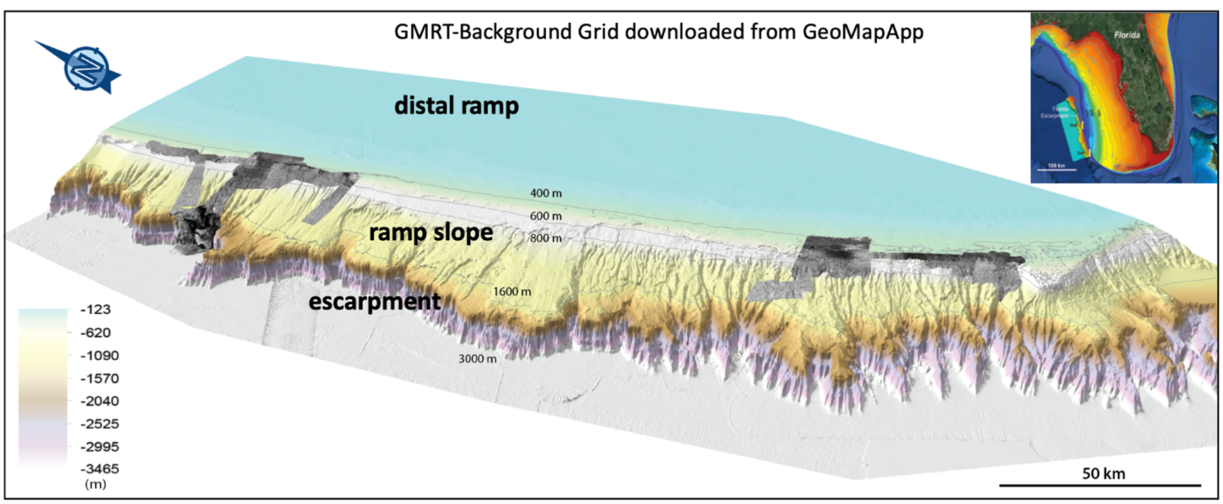

Figure 1: 3D view of the distal portion of the southwestern Florida Shelf, displaying the distal ramp, ramp slope and the Florida Escarpment. Canyons and slope failure scars in the slope connecting the outer ramp with the escarpment. Grey areas are backscatter images in two study areas.

for distributing sediment along the West Florida ramp (e.g. Mullins et al., 1988) but the slide scars and canyons document large-scale gravity flows on the ramp slope while current activity manifests itself in nondeposition and the formation of hardgrounds (Ling et al., 2021).

PROJECT RATIONALE

The modern distally steepened ramp is subjected to both mass gravity flows and the Loop Current. The Loop Current invades the distal ramp more frequently in the south and is likely responsible for the concave slope curvature by preventing deposition of pelagic material. Based on several lines of evidence, the Loop Current started to flow sometime in the late Middle Miocene when the modern global ocean circulation system appeared (Mullins et al., 1988). It is therefore possible that the onset of the current system transformed the Florida ramp into a distally steepened ramp. This possibility makes the West Florida shelf an ideal place to test if this process of preferential non-deposition due to contour currents is transforming a homoclinal ramp to a distally steepened ramp.

APPROACH AND DATA SETS

To investigate the influence of the modern current activity on the slope profile along the West Florida shelf we rely on multibeam bathymetry maps acquired during the RV Maria S. Merian (MSM 20-4) cruises and combine these with the large-scale bathymetry data GMRT-Background Grid downloaded from GeoMapApp (Ryan et al., 2009). Slope angles from north to south will be compared with oceanographic data.

In order to investigate the long term evolution of the Florida ramp we used seismic data that are publically available in the National Archive of Marine Seismic Surveys and that were also used by Poag (2017) to investigate the effect of the Chicxulub impact on the West Florida Shelf.

SIGNIFICANCE

The influence of contour currents on the slope curvature needs to be investigated for two main reasons. First, the interplay of mass-gravity flows and currents determines the facies of distally steepened ramps. Second, if currents can change the progradation-aggradation ratio of prograding systems, sequence stratigraphic methods that use this ratio to discriminate sea level-controlled sedimentation need to be critically re-evaluated.

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UNCONVENTIONAL AND CONVENTIONAL RESERVOIR CHARACTERIZATION

ACOUSTIC VELOCITY AND RESISTIVITY OF THE AGRIO FORMATION, NEUQUÉN BASIN, ARGENTINA

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

PROJECT OBJECTIVES

- Produce a comprehensive petrophysical data set consisting of porosity, velocity and resistivity for calibration of various lithologic facies of the Agrio Formation.
- Establish an acoustic velocity-porosity data set for each facies.
- Compare these data with the existing data set in the Vaca Muerta Formation to assess similarities and differences in these two marine stages of the basin.

PROJECT RATIONALE

Although the economic viability of unconventional reservoirs is primarily due to advances in horizontal drilling and hydraulic fracture stimulation technologies, properly acquired and processed 3D seismic data and correctly interpreted log data still plays a significant role in the success of development. Laboratory acoustic measurements quantifying vertical sonic velocity in different facies can be used to minimize, or eliminate, errors in processing and interpreting geophysical data.

Throughout the last decade we measured over 20 different sections of the late Jurassic and early Cretaceous, Vaca Muerta Formation in the Neuquén Basin in Argentina. Outcrop and short core samples are strategically distributed throughout the entire Vaca Muerta Formation at the Puerta Curaco reference section between Tordillo and Mulichinco (Weger et al., 2016). The results are comparable to the subsurface data obtained from the El Trapial Block (Weger et al., 2015). This new project attempts to produce a similar data set in the overlying Agrio Formation. The Agrio Formation records the next sedimentary cycle of continental to marine succession in the basin (Schwarz et al., 2006). After this marine flooding event organic-rich strata, similar to that seen in the Vaca Muerta Formation, was deposited. However, the Vaca Muerta Formation is more enriched in TOC than the younger Agrio Formation with the latter containing 2-5% TOC in a 50-400 m thick section (Legarreta and Villar, 2011).

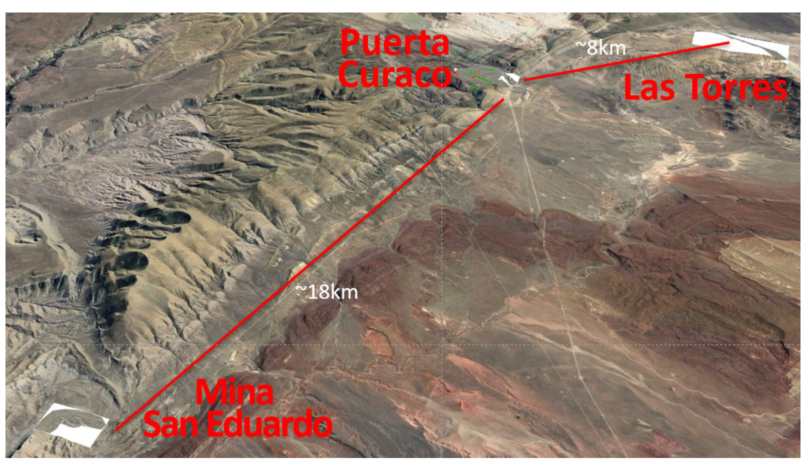

Figure 1: Location Map of the measured sections covering the Mendoza Group in the Neuquén Basin at Puerta Curaco, Mina de San Eduardo, and Las Torres.

APPROACH

To produce usable acoustic measurements, unaltered plug samples with little to no surface exposure are required of the representative facies or rock types within the Agrio Formation. Such samples are retrieved with short cores (1- 1.5 m) from the outcrop. The sample locations will be along last year's measured sections of the Mulichinco Formation and the entire Agrio Formation. At Puerta Curaco we measured the lower portion of the Pilmatue Member and at las Torres the rest of the Agrio Formation. To analyze the acoustic properties of the different facies in the Agrio Formation we will drill short cores from the outcrops in both areas.

SIGNIFICANCE

Better knowledge of well documented acoustic and electrical properties of some of the facies in the Agrio Formation will help in log interpretation. Furthermore, successful extraction of core plugs at three different angles, will provide insights into anisotropy parameters and will potentially aid and improve seismic processing and result in better imaging. Improved 3D seismic images will add value through optimizing drilling operations and hydraulic fracturing efforts.

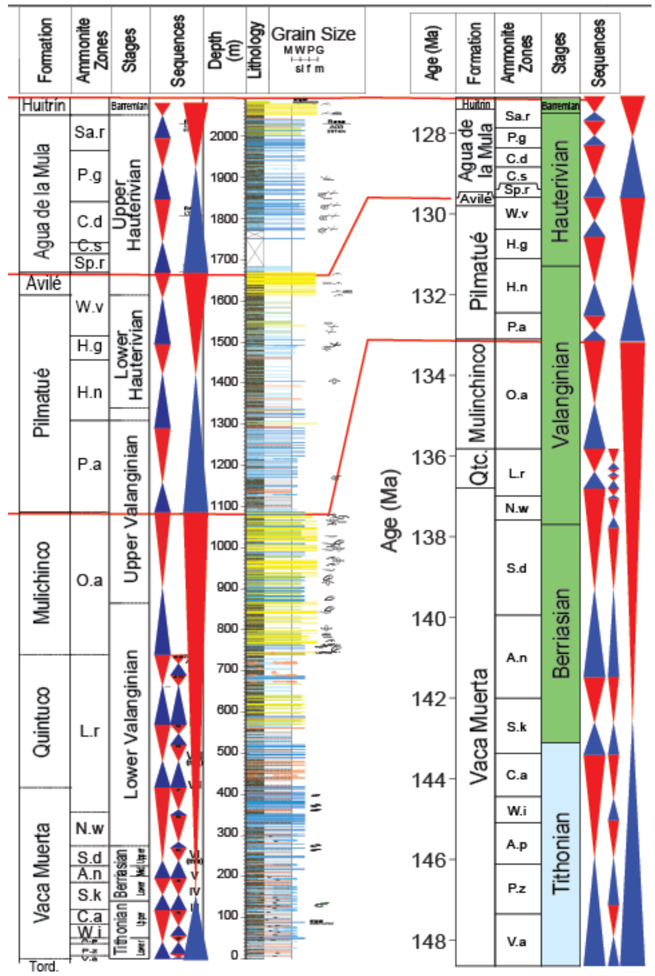

Figure 2: Measured section in the PC area covering over 2000 m (left) of sedimentation over 20 Myr (right). The three distinct flooding events associated with deposition of organic rich sediments form the basis of short core selection.

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Reservoir Properties of the Apulia Carbonate Platform (Gargano Promontory, Italy)

Claudia Morabito, Michele Morsilli, Ralf J. Weger, and Gregor P. Eberli

Project Objectives

- Analyze the middle to late Eocene carbonate system of the Apulia Carbonate Platform.
- Conduct Acoustic velocity, Resistivity and Digital image analysis for a reservoir characterization.
- Identify the mineralogy to better understand variations in the petrophysical properties of the measured samples.

Project Rationale

Collapse structures and their associated slope gravity deposits are common features of platform margins imaged in seismic sections and multibeam geophysical data as well as in outcrops (e.g. Eberli et al., 1993). Carbonate margin and slope are increasingly being recognized as significant conventional hydrocarbon reservoirs as well (Verwer et al.,2014). Nevertheless, outcrop studies are needed because the details of architecture and textural details of associated gravity deposits are near or below the limit of resolution of geophysical imaging (Lehrmann et al., 2020). The present research project aims to analyze the base-of -slope resedimented gravity flow carbonates belonging to the middle to upper Eocene carbonate system of the Apulia Carbonate Platform, located in the Gargano Promontory, in terms of facies, spatial distribution and depositional architecture.

The carbonate base-of-slope deposits, divided into two main sedimentary models such as apron and carbonate conoids, are little known from the sedimentological point of view, although they are important economically because they can contain large amount of hydrocarbons (Mullins and Cook, 1986). The few systems studied still leave many unanswered questions about what may be the control factors that affect the depositional architecture and the transport mechanisms (Payros and Pujalte, 2008). These still open questions can find answers in detailed

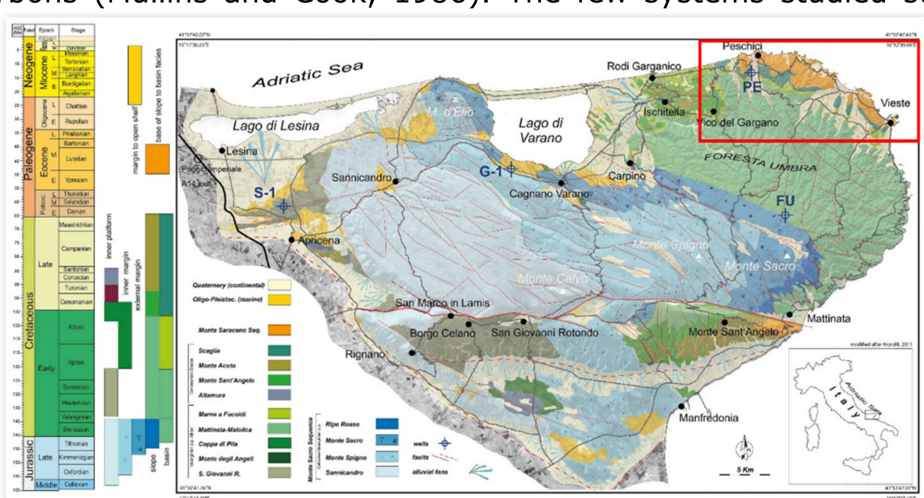

Figure 1: Geological map of the Gargano Promontory (Morsilli et al., 2017). The red box highlights the studied area.

sedimentological studies, improving scientific knowledge about such systems in terms of identification and characterization of carbonate reservoirs, since submarine fans form important oil and gas reservoirs around the world.

In addition, slope environments also provide an extensive stratigraphic record that, although it is preserved differently than platform-top or basinal strata, can be utilized to unravel the growth evolution, sediment factories, and intrinsic to extrinsic parameters that control carbonate platform systems (e.g. Verwer et al., 2014). Thus, the focus of this study is to reconstruct the depositional geometries useful to understand resedimentation processes, analyze and map the facies present in order to improve the scarce knowledge about these depositional systems, implement the facies models and understand the controlling factors that act during deposition. Finally, the results will be compared with other coeval carbonate systems.

WORK PROPOSED

In order to reach the stated objectives, 54 carbonate rocks from the Gargano Promontory, belonging to the Vieste and Peschici area and from Lutetian-Bartonian in age, will be analyzed. Acoustic velocity and resistivity properties will be measured using the Autolab 1000 system at the CSL. Digital Image Analysis will be performed on thin sections using the method described by Weger et al. (2009) to quantify the pore structures. Mineralogical analysis will be fundamental to better understand the petrophysical properties (sonic velocity, resistivity, porosity) response to the different mineralogies.

SIGNIFICANCE

The analysis of the petrophysical properties (sonic velocity, resistivity, porosity) combined with the mineralogical analysis, will be extremely useful for the reservoir characterization of the Gargano Promontory samples and the further comparison with coeval systems.

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STRATIPONDVIEW: FABRIC VISUALIZATION INSIDE DIPPING STRATIGRAPHIC UNITS

Mark Grasmueck and Gregor P. Eberli

PROJECT OBJECTIVES

- Apply the PondView Method to visualize sedimentologic and structural features in high-resolution 3D GPR cube in the Madonna della Mazza quarry.
- Visualize facture network in quarry using the StratiPondView method.
- Compare the results with outcrop and the short cores drilled in the quarry.

PROJECT RATIONALE

Interpretation of high-resolution 3D GPR and seismic data relies on the continuity of subsurface features between adjacent vertical and horizontal slices. However, 3D information is often lost because cross sections and time slices are opaque and only show information contained in the very thin layer of a single sample. 3D volume rendering can capture the 3D nature of fracture networks but low amplitude features are lost. The limitations of single sample slice animation, interpretation and 3D volume rendering can be overcome by the PondView Method (PV) that adds 3D information about the zone above and below the GPR or seismic horizontal slice (Grasmueck and Viggiano, 2018).

This project applies and tests this method on a high-resolution 3D-GPR data set from the Madonna della Mazza quarry near Pretoro, Italy (Fig. 1). Here we explore

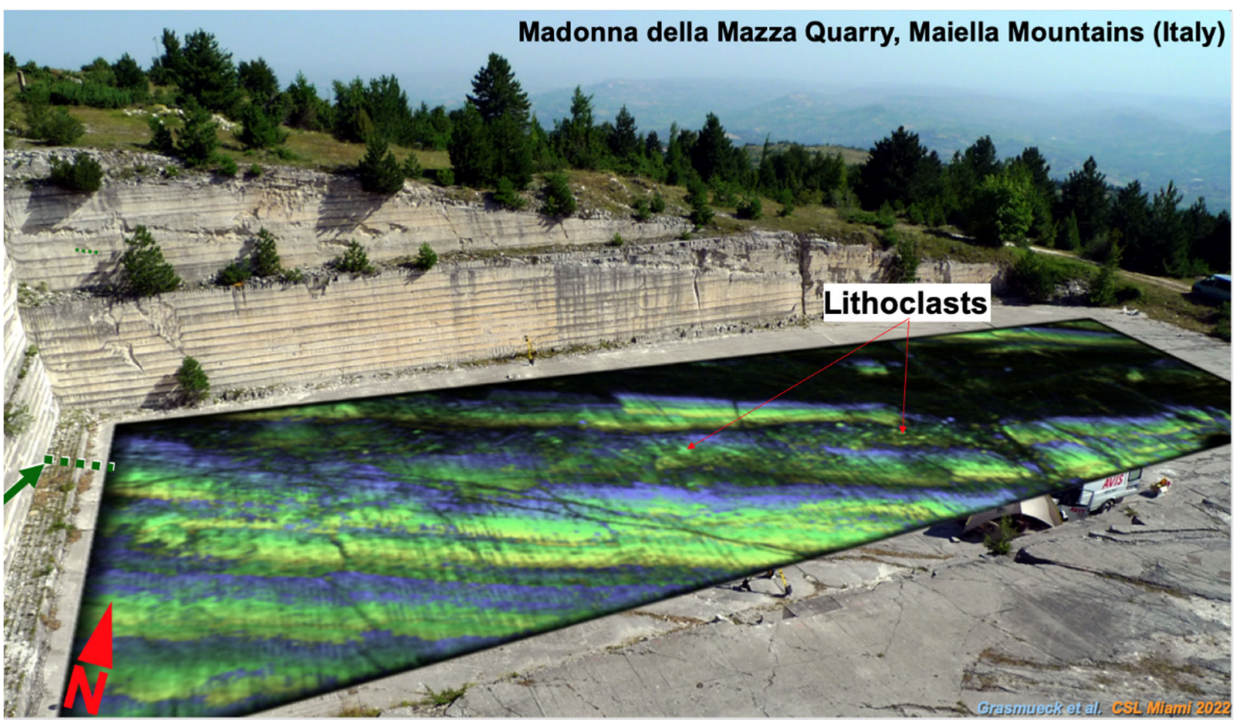

Figure 1: Madonna della Mazza quarry with stratal slice of dipping beds using the pond view technology applied in the high-resolution 3D GPR cube that was acquired in the quarry.

how far this method can achieve better visualization of both the sedimentologic and structural complexities in the strata.

NEXT STEP IN VISUALIZATION AND INTERPRETATION

So far, we have processed the 200 MHz 3D-GPR data including a 3D migration with a constant velocity of 0.09 m/ns, and constructed a Geomodel using Paleoscan, which resolves the individual horizons of the quarry succession (Grasmueck et al., 2021). Blended spectral decomposition attributes revealed the prograding sand-waves in the distal portion of the delta drift and was moderately successful in imaging of graded beds, layers with lithoclasts and reworked horizons (Fig. 2).

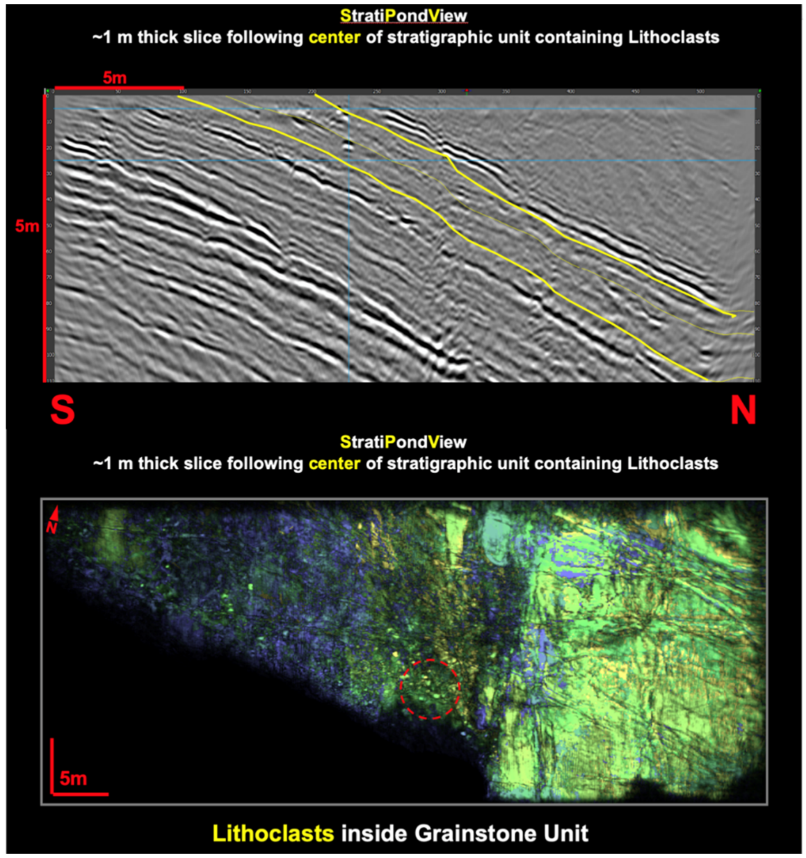

Figure 2: Top: 2D in line of the GPR cube of the Madonna della Mazza quarry with a 1 m thick horizon that contains lithoclasts is outlined with yellow boundaries. Short high-amplitude reflections indicate the presence of lithoclasts. Below: Stratal slice in the middle of the stratigraphic unit that contains the lithoclasts using the StratiPondView method.

To improve the visualization of all features including the fractures in the quarry we will 1) refine the Geomodel with a denser fault network and 2) do another 3D migration with noise reduction. We will then compare the interpretation with the outcrop and the cores we drilled in the quarry.

SIGNIFICANCE

This study visualizes, for the first time, sedimentary structures in the rock record in three dimensions. This third dimension offers a better quantification of the sedimentary product from the flow processes in this carbonate contourite drift.

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The Importance of Pore Structure on the Velocity of Dolostones

Ralf J. Weger, Gregor Baechle, Shouwen Shen, and Gregor P. Eberli

Project Objectives

- Contrast and compare the sonic velocity and permeability of dolomite and calcite samples.
- Quantify pore structures of the measured samples using Digital Image Analysis (DIA) parameters and theoretically-derived parameters from the Extended Biot Theory.
- Assess the respective impact of mineralogy and pore geometry on acoustic velocity of carbonate rocks predominantly composed of dolomite and calcite.

Project Rationale

Dolomite is acoustically faster than calcite but dolostones have a wide range of sonic velocities related to the different dolomite types that form during the transformation from limestone to dolostone (Ehrenberg et al., 2006). The purpose of this project is to quantitatively assess the internal pore geometry of various samples composed of both dolomite and calcite, together with their sonic velocity to evaluate the impact of geometry compared to that of mineralogy.

Transforming calcite to dolomite during diagenesis occurs either in a fabric-preserving or fabric-destructive manner. During this transformation a variety of crystal sizes, textures, and geometries are produced. Fabric-preserving dolomitization maintains to a large degree the limestone rock texture and pore types.

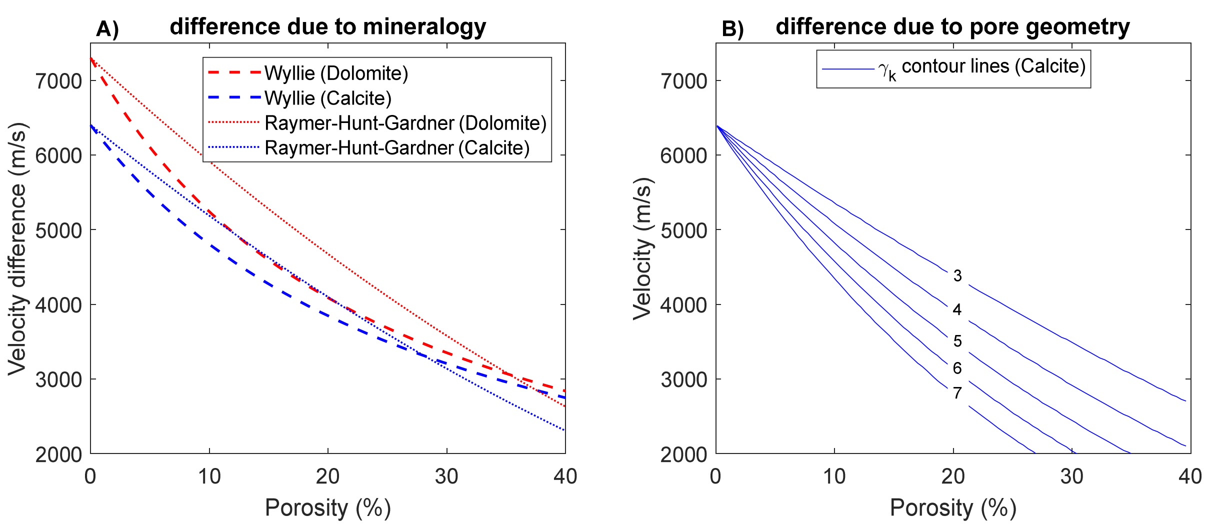

Figure 1: (A) Difference in acoustic velocity caused by variations in mineralogy (dolomite vs. calcite) as predicted by Wyllie time-average-equation and Raymer-Hunt-Gardner relationships (Wyllie et al., 1958; Raymer et al., 1980). (B) Variation in acoustic velocity caused changes in internal pore geometry at any given porosity as predicted by the Extended Biot Theory (Sun, 2001).

Original rock textures are largely destroyed and replaced by an intercrystalline rock fabric in fabric-destructive dolomites but the matrix velocity of dolomite remains faster than that of calcite.

With increasing porosity, the importance of mineralogical differences diminishes (Wyllie et al., 1958; Raymer et al., 1980) and the influence of internal pore geometry on acoustic velocity increases (Sun, 2001; Weger et al., 2009). Understanding these variations requires an assessment of sample mineralogy and the different rock fabrics with respect to their petrophysical properties.

WORK PROPOSED

For this study, we compiled 77 carbonate rocks (38 limestone core plugs and 39 dolomite core plugs) from two different locations, one from the Aptian (Shu'aiba Formation), and one from the Mississippian outcrops of the Madison Formation in Wyoming. Petrophysical properties (porosity, velocity, permeability) used for comparison of the samples have been measured at the CSL in the past. Digital image analysis of thin sections was performed using the method described by Weger et al. (2009) and geometrical parameters from the Extended Biot Theory are derived directly from the measured petrophysical properties.

We will compare the differences and similarities of dolostones and limestones to illustrate and quantify the impact of variations in mineralogy and internal pore geometry at different porosities. Our working hypothesis is that the pore structure is more important than (the calcite - dolomite) mineralogy for determining the velocity of carbonate rocks.

SIGNIFICANCE

The combined analysis of velocity, porosity, and permeability of samples from the Madison Formation and the Shu'aiba Formation with petrographic, digital image and mineralogical analyses will help to identify the controls each parameter exerts on the petrophysical behavior. This study will likely provide evidence that mineralogy is a minor factor on sonic velocity of dolostones.

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GEOCHEMISTRY AND GEOBIOLOGY

The Carbon Isotopic Composition of Proximal and Distal Sediments in the Vaca Muerta

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

Project Objectives

- Evaluate the ability to use $\delta^{13}C$ values from organic material to correlate between different sections within the basin, located kilometers apart, in both proximal and distal positions.
- Re-validate that the $\delta^{13}C$ values of organic material ($\delta^{13}C_{org}$) are unrelated to changes in the total organic content.
- Confirm that $\delta^{13}C$ values of organic material can be used to correlate coeval sections within a basin more accurately than the $\delta^{13}C$ values of carbonate.

Project Rationale

The $\delta^{13}C$ values of carbonate and organic material within sedimentary deposits have been studied extensively and variations have been interpreted principally as changes in the rates of organic carbon production relative to burial and preservation (Hayes et al., 1999). Previously we studied the $\delta^{13}C$ values of organics and carbonates from 800 m of continuous, Late Jurassic to Early Cretaceous strata (~ 15 Myrs) exposed in the Neuquén Basin, Argentina (Rodriguez Blanco et al., 2019; Rodriguez Blanco et al., 2020; Tenaglia et al., 2020). The data provided a unique opportunity to compare this high-resolution $\delta^{13}C_{org}$ record to other published organic carbon isotope records from the same time period sourced in Atlantic, Arctic, and Tethyan sections. The data from the Vaca Muerta showed correlation to several globally distributed locations that show a large negative isotopic excursion of organic carbon ($\delta^{13}C_{org}$) of over 4‰ (V-PDB) and to a minimum of −30.3‰; an anomaly that has been named the 'Volgian Isotopic Carbon Excursion' (VOICE).

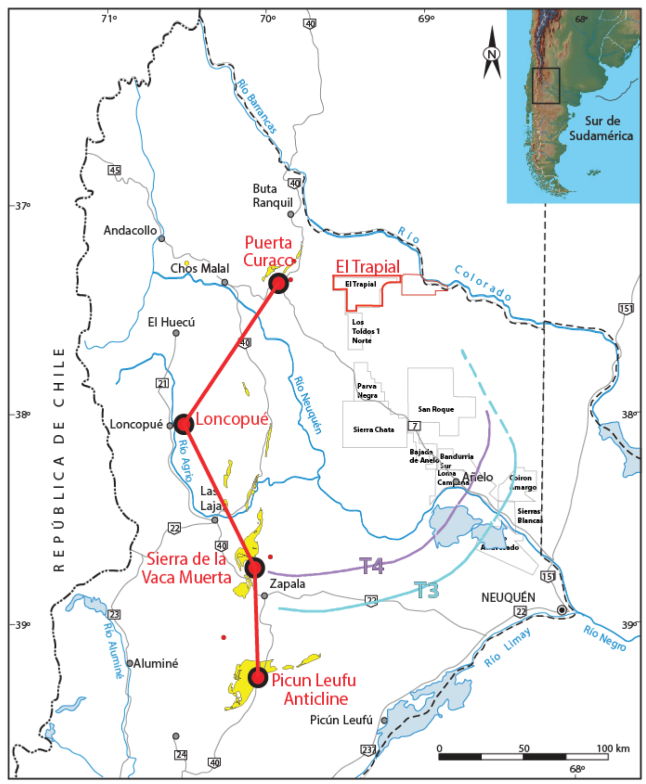

Figure 1: Location of outcrops in the Neuquén Basin, indicating location of outcrops, producing fields, and interpreted shelf breaks during the early Tithonian.

WORK PROPOSED

We have obtained samples from ~350 m of measured section of outcrops at the Picun Léufú anticline, the Tithonian portion of the Vaca Muerta Formation in a proximal setting. We have already carried out several studies of the variation of $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ values on the cores and measured sections in the basinal portions of the Vaca Muerta Formation (Rodriguez Blanco et al., 2022; Weger et al., in press) and plan to perform the same analysis on these newly obtained proximal, time correlative samples.

SIGNIFICANCE

This investigation represents a combined study of the $\delta^{13}C$ values of organic and inorganic material found within the Neuquén Basin in Argentina. The $\delta^{13}C_{org}$ values appear to be unrelated to the global patterns in $\delta^{13}C_{carb}$ values, but they show similarity to patterns seen in $\delta^{13}C_{org}$ values at several boreal localities. This study will provide a detailed comparison of $\delta^{13}C$ values of carbonate and organic carbon and their variations between coeval distal and proximal locations. A key question to be answered is if changes in $\delta^{13}C$ values from proximal and/or distal locations correlate within the Neuquén Basin.

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THE DELINEATION OF THE MIXING ZONE USING CLUMPED ISOTOPES

Peter K. Swart and Chaojin Lu

KEY FINDINGS

- The Δ_{47} values of carbonates, affected by freshwater and marine fluids, can be used in conjunction with the $\delta^{18}O$ values of the carbonates ($\delta^{18}O_{carb}$) to determine the $\delta^{18}O_{fluid}$ values of the diagenetic fluids.
- These data show that the zone of covariance between $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values, previously interpreted as representing diagenesis within the zone of mixing between fresh and marine fluids, takes place largely within the freshwater phreatic zone. The purpose of this work is to refine the hypotheses previously suggested.

INTRODUCTION

The interpretation of changes in the $\delta^{13}C$ and $\delta^{18}O$ values of marine carbonates ($\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$) during early diagenesis is one of the most often used applications of stable C and O isotopes. Allan and Matthews (1982) outlined a series of changes in $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values expected to be visible within carbonates exposed to freshwater diagenesis and these trends have been used by numerous workers to interpret their isotopic records. Of relevance to this study is that a zone of strong covariance (ZOC) between the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values is suggested to represent diagenesis within the mixing zone. The goal of this study will be to test the principal assumption made in the model of freshwater diagenesis of Allan and Matthews (1982) that variations in the $\delta^{18}O_{carb}$ values within the ZOC reflects differences in the $\delta^{18}O$ values of the fluids ($\delta^{18}O_{fluid}$).

THE MIXING ZONE

The mixing zone is a region in the subsurface in which meteoric waters mix with marine fluids producing a gradient in salinity as well as in both the $\delta^{13}C$ values of the dissolved inorganic carbon (DIC) and the $\delta^{18}O$ values of the fluids ($\delta^{18}O_{fluid}$). As such, Allan and Matthews (1982) proposed that carbonate diagenesis taking place along this gradient would result in diagenetically altered materials with $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values reflecting the gradients in the $\delta^{13}C_{DIC}$ and $\delta^{18}O_{fluid}$ values, producing a covarying trend between the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values. This mixing trend is found in all recently altered carbonates from coastal locations and is documented in numerous papers on both Quaternary and more ancient carbonates. The mixing-zone also found fame for the production of solutions which were undersaturated with respect to various carbonate minerals (Badiozamani, 1973), even though the original end member solutions would have been saturated with respect to these minerals.

Does the Zone of Covariance Really Represent the Mixing Zone?

For a number of years, it has been noted that the position of the zone in which the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values are strongly correlated (zone of covariance; ZOC) was inconsistent with the location of the mixing zone based on known sea-level history. For example, it is well established that global sea level was approximately 130 m lower than at present during the last glacial period. Assuming that the water table was 2-3 m higher than sea level (similar to the position of the water table in South Florida relative to sea level) this would have positioned the mixing-zone about 80-120 m lower, so at around 200 m below current sea level and well below the ZOC. The ZOC, therefore, cannot be a result of diagenesis in the mixing-zone. Instead Swart and Oehlert (2019) suggested that the covarying trends resulted from greater amounts of freshwater diagenesis in the upper portion of the ZOC when compared to the lower portion. Furthermore, it was suggested that the majority of the fresh water phreatic zone is rather geochemically inactive as it is already supersaturated with respect to carbonate minerals. Swart and Oehlert (2019) proposed that the carbonate sequence became cemented as the water table is dragged up and down by tidal variation and long-term sea-level changes.

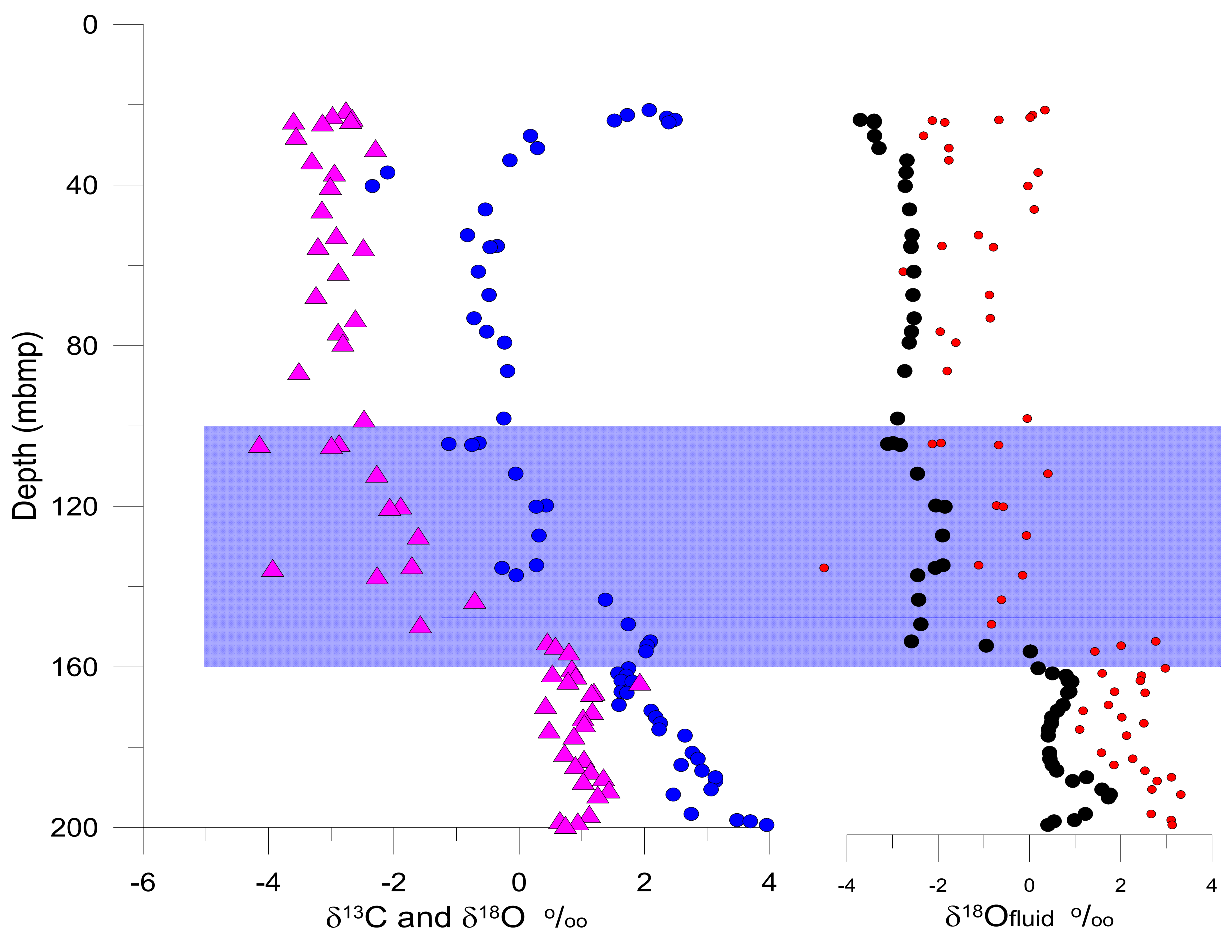

Figure 1: Comparison of the $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values of carbonates compared to the calculated $\delta^{18}O_{fluid}$ values. The data shown in black circles, represent the end of a covarying trend between temperature and the $\delta^{18}O_{fluid}$ values calculated using a five point moving correlation, while the red points are simply the raw $\delta^{18}O_{fluid}$ values.

RESULTS AND INTERPRETATIONS

The Allan and Matthews (1982) model predicts a steady increase in the $\delta^{18}O_{fluid}$ values through the ZOC as a result of salinity gradients due to the mixture of freshwater and seawater in the mixing zone. The Swart and Oehlert (2019) model suggests that the ZOC does not represent the mixing zone, but rather alteration at the boundary between the vadose and phreatic zone (water table). It therefore predicts a binary response of the $\delta^{18}O_{fluid}$ values with the values through the majority of the ZOC, reflecting meteoric $\delta^{18}O_{fluid}$ values. The difference between these two models can be tested using a similar approach to that applied to the Inverted 'J'. Preliminary data from this approach are shown in Figure 1. The average $\delta^{18}O_{fluid}$ value (~ -2‰) is slightly more positive than rainfall in Miami, but consistent with rainwater expected during the last glacial when these rocks were altered. The $\delta^{18}O_{fluid}$ values in the ZOC are like those measured in the freshwater portion. Diagenesis in the marine zone produces $\delta^{18}O_{fluid}$ values of ~ +2 to +3‰, in agreement with values measured on Great Bahama Bank (Lowenstam and Epstein, 1957; Shinn et al., 1989; Swart et al., 2009). The data indicate a constant fluid composition throughout the ZOC, in support of the Swart and Oehlert (2019) model.

SIGNIFICANCE

This study shows how the clumped isotope values can be used in innovative ways to refine the interpretation of diagenetic alteration in carbonates.

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The Use of Δ_{47} and Δ_{48} Disequilibrium in Understanding Dolomite Formation

Chaojin Lu and Peter K. Swart

Project Objectives

- To investigate the utility of dual clumped isotope thermometry (Δ_{47} and Δ_{48}) to understand the processes of dolomitization.
- To use Δ_{47} and Δ_{48} values to decipher the kinetic isotopic effects during microbial induced dolomitization.

Project Rationale

Dual clumped isotope thermometry can not only be used to reconstruct the temperature of the reactive fluid, but also allows us to decipher kinetic effects present during the formation of carbonate minerals (Swart et al., 2021a). While recent studies have examined the disequilibrium in the behavior of Δ_{47} and Δ_{48} values during the formation of biogenic and inorganic carbonates such as corals and speleothems, the kinetic behavior of Δ_{47} and Δ_{48} values in dolomite has not been well explored.

In this investigation, we have applied the dual clumped approach to Cenozoic dolomites from the Bahamas (Clino and San Salvador cores) (Fig. 1) and other dolomites standards. The San Salvador dolomites formed within a seawater-buffered open system, which is reflected in the invariable $\delta^{34}S$ values and Sr concentrations. In contrast, Clino dolomites formed in a semi-closed environment and have elevated $\delta^{34}S$ values, suggestive of bacterial sulfate reduction (BSR), and high Sr concentrations indicating closed system recrystallization (Fig. 1).

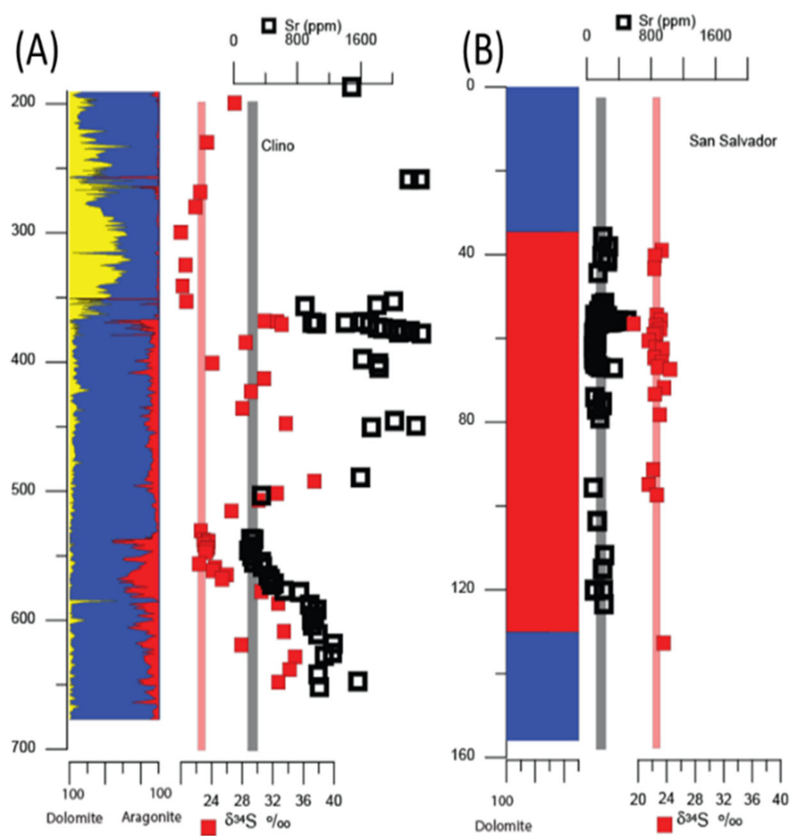

Figure 1: The profiles of sulfur isotopes and Sr concentrations in Clino and San Salvador cores (Murray et al., 2021). (A) Sulfur isotopes and Sr concentrations in Clino dolomites. (B) Sulfur isotopes and Sr concentrations in San Salvador dolomites.

APPROACH

The ISoDIC model has been developed by Guo (2020) in order to investigate changes in the Δ_{47} and Δ_{48} values of dissolved inorganic carbonate (DIC) during such processes as DIC-H_2O exchange, CO_2 degassing, and absorption (Fig. 2). During the formation of dolomite, the change of bicarbonate concentrations (HCO_3^-) via CO_2 hydration in the dolomitizing fluid is a critical factor in breaking the hydration of Mg ions with water and overcoming the kinetic barrier. Therefore, it is believed that this model is applicable to offer the quantitative constraints on the Δ_{47} and Δ_{48} values depending on the changes of pH and DIC concentrations (Fig. 2). We will apply this model to recent dolomites formed by various different mechanisms, including normal marine fluids (San Salvador), closed system marine fluids under the influence of BSR (Clino), and hypersaline reflux (Qatar), possibly affected by microbial processes. A second phase of this project will apply the model to ancient dolomites throughout the Proterozoic and Phanerozoic.

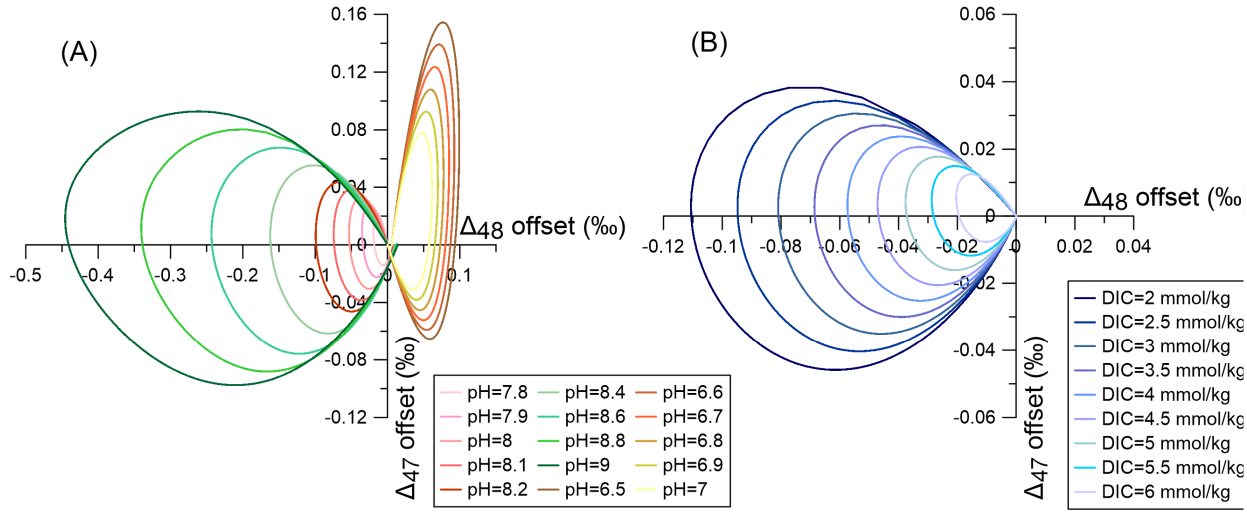

Figure 2: Comparison between measured and modeled offsets of Δ_{47} and Δ_{48} between the measured and expected values (Guo, 2020). (A) The modeled patterns of the Δ_{47} and Δ_{48} offsets in a range of pH values compared with the measured data. (B) The modeled patterns of the Δ_{47} and Δ_{48} offsets in a range of DIC concentrations compared with the measured data.

SIGNIFICANCE

This study will show for the first time the potential of the dual clumped isotope technique as an aid to understanding the formation of dolomite.

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ORIGIN OF Δ_{47} AND Δ_{48} DISEQUILIBRIUM IN CARBONATE MINERALS

Peter K. Swart and Chaojin Lu

KEY FINDINGS

- The combination of Δ_{47} and Δ_{48} proxies can be used to ascertain whether carbonates are deposited close to equilibrium or if they are affected by kinetic influences.

INTRODUCTION

The Δ_{47} proxy has caused a revolution in the study of the stable oxygen isotopes in carbonate rocks. By examining the difference between the measured and the theoretical 47/44 ratios, the Δ_{47} value can be determined. This in turn is related to the temperature of formation, both theoretically and experimentally (Wang et al., 2004; Ghosh et al., 2006). Recently, measurement of the Δ_{48} values has also been added (Fiebig et al., 2019; Bajnai et al., 2020; Bajnai et al., 2021; Swart et al., 2021b) to the clumped isotope arsenal, although its application is still in the early stages. As a result of the potential of the Δ_{47} proxy, particularly during Earth's early history (Bergmann et al., 2018) as well as uncertainties regarding the meaning of variations in $\delta^{13}C$ and $\delta^{18}O$ values of these rocks (Swart

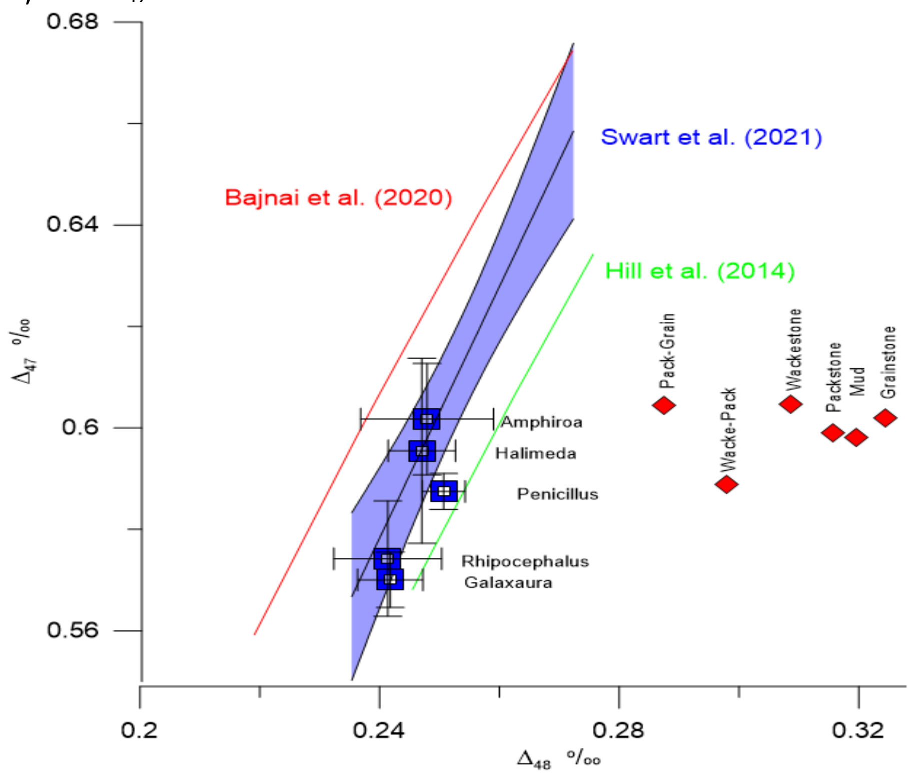

Figure 1: The two calibration lines (Bajnai et al., 2020; Swart et al., 2021b) together with the theoretical line (Hill et al., 2014). The Swart et al. (2021) line is shown together with the 95% confidence limits. Also shown are data from between 5-6 replicates of various calcareous algae: Halimeda sp., Penicillus sp., and Rhipocephalus sp. are green algae and form aragonite, while Amphiroa sp. and Galaxaura sp. are red algae and have HMC skeletons. All the algae data fall close to the equilibrium line based on the calibration of Swart et al. (2021). Also shown are values for non-skeletal material from GBB which show elevated Δ_{48} values, but no relationship between either Δ_{48} or Δ_{47} values and grain size.

and Kennedy, 2012; Hoffman et al., 2021), it is more important than ever to understand how early diagenetic processes affect both the conventional and clumped isotope proxies.

THE NON-EQUILIBRIUM PROBLEM

It is well established that numerous systems precipitate carbonates with Δ_{47} values 'out of equilibrium' (Saenger et al., 2012; Affek and Zaarur, 2014; Davies and John, 2018). Systems in which CO_2 degassing causes the precipitation of carbonates, such as in a speleothem environment (Affek et al., 2008), produce Δ_{47} values which are too negative yielding warmer than expected temperatures, while systems such as corals (Saenger et al., 2012; Spooner et al., 2016) give cooler temperatures. Although both types of non-equilibrium behaviors can be modeled and hence explained (Guo and Zhou, 2019b), it is necessary to use an additional geochemical proxy such as the Δ_{48} value which shows a different type of non-equilibrium behavior to enable the Δ_{47} value to provide temperature information (Guo and Zhou, 2019a; Bajnai et al., 2020). Using the modeled behavior of the Δ_{47} and Δ_{48} values it is theoretically possible to correct both values to equilibrium.

PROPOSED WORK

In order to obtain a better understanding of the behavior of disequilibrium of Δ_{47} and Δ_{48} during early diagenesis, it is necessary to establish base line values for the sedimentary allochems. Here follows some preliminary data on this aspect. We propose to extend this work over the next 12 months.

Calcareous Algae: We show Δ_{47} and Δ_{48} values from algae (red and green) from the Bahamas relative to the calibration lines for Δ_{47} Swart et al. (2019) and Δ_{48} (Swart et al., 2021b) values. Also shown on this figure are the calibrations from Bajnai et al. (2021) and Hill et al. (2014) (Fig. 1). These three lines fall within error of each other. These values plot close to the expected lines of Swart et al. (2021).

Great Bahama Bank Sediments: The origin of sediments on Great Bahama Bank (GBB) are still controversial. The sediments are considered to be mainly non-skeletal in origin, although there is still controversy as to whether the mud is derived from the breakdown of green algae or is a direct precipitate (Shinn et al., 1989) perhaps induced by cyanobacteria (Robbins et al., 1997) and fertilized by dust (Swart et al., 2014). The majority of the sediments on GBB are peloids, which based on their $\delta^{13}C$ and $\delta^{18}O$ values, are similar to the muds therefore suggesting a common origin (Swart et al., 2009). The Δ_{47} values of the sediments are close to equilibrium (Atasoy, 2014), while the Δ_{48} values appear to be slightly elevated (Fig.1).

Speleothems: Previous students at UM have studied the $\delta^{13}C$ and $\delta^{18}O$ values of speleothems through the use of precipitation plates placed under stalagmites (Arienzo et al., 2016). During the precipitation periods water samples and temperature measurements were collected. The calcites precipitated on these plates within several months and yielded calcite with a wide range of $\delta^{13}C$ and $\delta^{18}O$ values with the central axis of the stalagmite clearly being out of equilibrium. We also measured the Δ_{47} and Δ_{48} values of some of these materials and determined that the Δ_{47} values were too negative and the Δ_{48} values too positive in the central region.

Corals: Corals are known to precipitate skeletons with respect to $\delta^{13}C$, $\delta^{18}O$, and Δ_{47} values (Saenger et al., 2012). In order to study this in more detail we examined an eight-year record from the skeleton of *Copophyllia* sp., collected from the island of Tobago. Sampling the coral at a resolution of four samples a year we measured an annual cycle in the Δ_{47} values and showed the offset documented by Saenger et al. (2012). As a test of the Δ_{48} proxy we measured the same coral again over one year and not only reproduced the values measured previously but showed lower than expected Δ_{48} values.

SIGNIFICANCE

This study will establish base line values for the Δ_{47} and Δ_{48} values of Modern sediments as well as casting light on the origin on some of the more controversial sediments, such as the muds from the surface sediments of Great Bahama Bank.

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CLUMPED ISOTOPE EVIDENCE ON THE ORIGIN OF THE MARINOAN CAP DOLOSTONE

Chaojin Lu, Jiuyuan Wang, Matthew Hurtgen, and Peter K. Swart

PROJECT OBJECTIVES

- Examine whether reordered dolomite and calcite can preserve the primary oxygen isotopic composition of formation fluids.
- Decipher the formation process of the Marinoan cap dolostone (primary versus diagenetic origins).

PROJECT RATIONALE

The Marinoan cap dolostone (~635 Ma), directly overlying the glacial sediments, is thought to be globally distributed preserving critical climatic and oceanographic information on one of the most extreme climate events in Earth history. In terms of hydrological processes, there are two proposed models, "plumeworld" (Shields, 2005) and "early diagenetic systems" (Ahm et al., 2019). The key distinctions between these two models are the nature of formation fluids and their hydrological processes through the proximal to distal platform. The proposed "plumeworld" model witnesses the mixing of meltwater and seawater following the deglacial period. (Fig. 1A). In contrast, the cap dolostone in the platform margin and upper slope is characterized by fluid-buffered behavior approaching glacial seawater chemistry, while the diagenetic system gradually transfers to the sediment-buffered system preserving the meltwater signal in the inner platform. Correspondingly, the spatial perturbation of geochemical compositions (e.g., carbon, magnesium and calcium isotopes) is observed as a product of interactions by these binary diagenetic systems (fluid- and sediment-buffered) (Fig. 1B).

APPROACH

Natural samples: Samples were collected from five outcrops of cap carbonates located in South China and Namibia. In order to examine the two existing models, the distribution of collected samples ranges from the platform interior to the

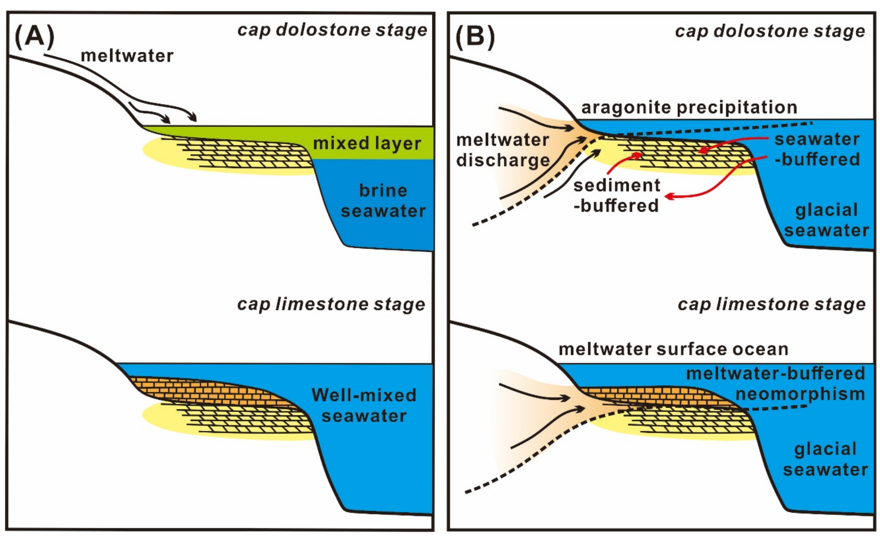

Figure 1: The cartoon graphs for two formation models of cap carbonates. (A) Mixing water-mass model. (B) Binary diagenetic system model.

platform margin. The cap carbonate includes calcite and dolomite minerals, which can be used to decipher whether the alteration is attributed to recrystallization or to solid-state reordering (Lu et al., 2023).

Heating experiments: In order to decipher the solid-state reordering process of clumped isotopes, we performed heating experiments with two dolomites, Bahamas marine dolomite and a dolomite standard (NIST-88b), and compared these data with published data from a hydrothermal dolomite (Lloyd et al., 2018) (Fig. 2). The measured Δ_{47}-temperatures and $\delta^{18}O_{fluid}$ values (calculated by Δ_{47}-temperatures and $\delta^{18}O_{carb}$ values) can illustrate the evolving process deviating from the original composition during solid-state reordering. The comparison of these evolving patterns between natural and heated samples can examine the origin of alteration in cap carbonates as well as tracing the nature of dolomitizing fluids.

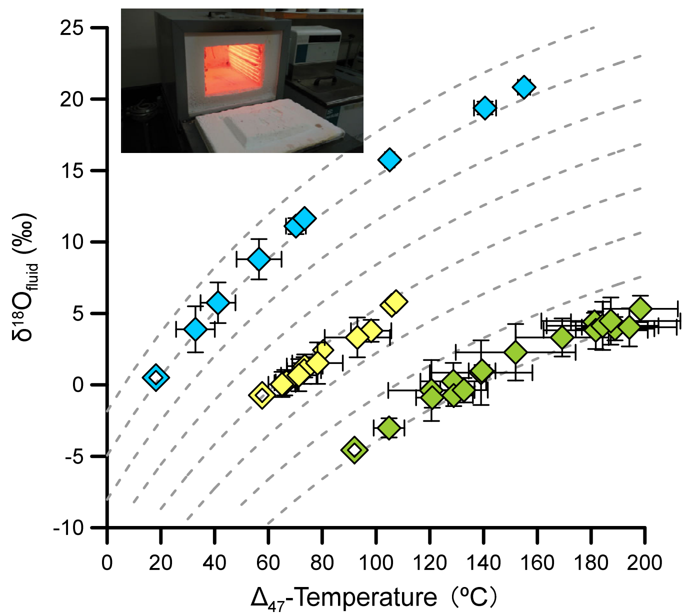

Figure 2: The reordering trajectories simulated by heating experiments for three dolomites. Bahamian dolomites shown in blue. The dolomite standard (NIST-88b in yellow) is from the National Institute of Standards and Technology. The hydrothermal dolomite (green) as reported by Lloyd et al. (2018). The hollow and solid rhombs represent the unheated and heated dolomites, respectively.

SIGNIFICANCE

Our findings will demonstrate the usefulness of the reordered clumped isotopes as a fluid tracer in deep time successions and offers an insight into the enigmatic origin of cap carbonates.

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IMPACTS OF TAPHONOMIC EVOLUTION ON CHEMICAL BIOSIGNATURES IN MICROBIALITES

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PROJECT OBJECTIVES

- Determine which elements are transferred from microbial organic matter into carbonate minerals during early taphonomy.
- Develop a workflow to constrain the preservation mechanism of chemical biosignatures within microbialite systems.

PROJECT RATIONALE

Microbialites dominate the fossil record for over 80% of Earth history and represent significant components of carbonate reservoirs around the world. Various microbial metabolisms contribute to microbialite lithification, each of which can be based on biogeochemical cycling of elements capable of supporting life. These metabolisms can leave evidence of their existence in the geochemistry of accreted microbialites. Under certain conditions, these geochemical biosignatures can be preserved in the geological record and serve as archives of the dynamic interplay between microbes, minerals, and their environment (Sforna et al., 2014). However, because significant changes in the geochemical composition of microbialites occur during early taphonomic modification and later diagenetic alteration (Sforna et al., 2017), establishing the mechanisms driving the geochemistry of ancient microbialites can be challenging.

Key insights from our previous work indicated that Arsenic (As), involved in the microbialite-building communities of the Hamelin Pool, Australia, is initially incorporated into microbial organic matter before being transferred to the carbonate fraction of the microbialites during early taphonomic evolution (Pollier et al., 2022). Our new data suggest that additional elements, such as S, Mg, and Sr, experience a similar taphonomic transfer as As, while others exhibit the opposite behavior (Fig. 1). Taphonomic transfer likely impacts preservation of elemental concentration, and thus their interpretation as chemical biosignatures. A key implication is that some biosignatures will be enhanced by taphonomy, while others may result from non-biological geochemical

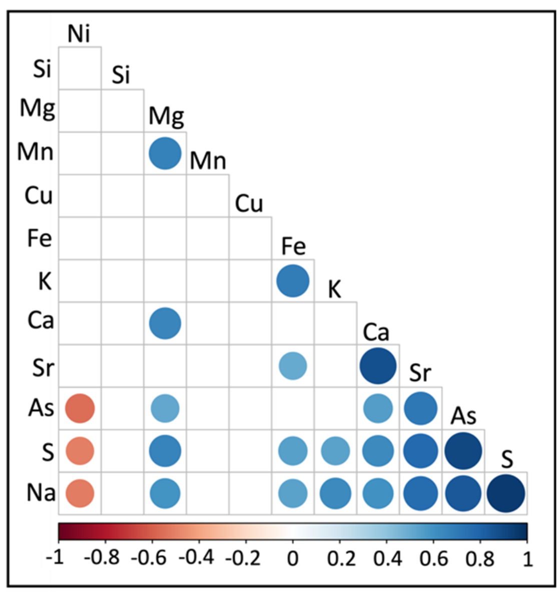

Figure 1: Correlogram showing significant correlation coefficients (R) of bulk elemental composition of Hamelin Pool microbialites. Circle size indicates correlation strength.

artifacts incorporated after accretion of initial architecture. Further, some biosignatures may also be lost during early taphonomy. Consequently, improved characterization of the origin, timing, and rate of taphonomic transfer between organic matter and carbonate mineral fractions, as well as the ultimate fate of a biosignature, is needed to better understand the geological record.

APPROACH

Hamelin Pool, Western Australia is an ideal living laboratory to address the challenge of defining the impacts of taphonomic alteration on chemical biosignatures. Taphonomic modification of microbialites has already been characterized petrographically (Vitek et al., in review) and subdivided into two successive stages: (1) precipitation of micrite along laminations and around clots; and (2) precipitation of aragonitic marine cement infill. Thus, Hamelin Pool microbialite fabrics provide a stepwise window into microbialite accretion and evolution. We will conduct a sequential leaching experiment to chemically isolate the organic matter and carbonate fractions within each stage of the taphonomic evolution. Their elemental composition will be measured using an Agilent 8900 ICP-QQQ. Statistical analyses, such as correlograms and principal component analyses will be presented. Distribution coefficients will be calculated for each element presented.

SIGNIFICANCE

Characterization of the taphonomic exchange of elements during the evolution of microbialites will provide new insight into the processes influencing the preservation of chemical biosignatures. Results from Hamelin Pool microbialites are anticipated to differentiate between 1) true chemical biosignatures, 2) chemical biosignatures that were potentially lost during taphonomic transfer, and 3) geochemical artifacts unrelated to microbial activity that were derived from the environment and incorporated during early taphonomy. This step is required to disentangle the impacts of early taphonomy from the effects of further diagenetic alteration on microbialite geochemistry. The results of this study will provide critical insights for the interpretation of biogenicity in the geological record of early Earth, including carbonate reservoirs such as the pre-salt deposits of Brazil (Wright & Barnett, 2017).

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Peloids as Microbial Carriers for Organomineralization in Ooids

Mara R. Diaz and Gregor P. Eberli

Project Objectives

- To test the hypothesis that peloids, which form the majority of nuclei in ooids, carry the microbial communities for organomineralization in ooids.
- To compare the organic and mineral composition within peloidal nuclei of ooids and fecal pellets by integrating RAMAN spectroscopy for the characterization of biomolecules (e.g. lipids and carbohydrates) and SEM/EDX for the mineral phases.

Project Rationale

Ooids are very important non-skeletal carbonate grains whose accumulations produce prolific and large carbonate reservoirs. Recent studies have shown that they form via organomineralization from a highly diverse microbial community that inhabits the ooids (Diaz et al., 2017). The origin of the microbial community is unknown. Nobody has documented such a large species diversity in sea water as is observed in ooids and thus seawater can be excluded as the source. It is more likely that the nucleus of the ooid is the carrier of microbes. In the modern ooid shoals of the Bahamas, the nuclei of the ooids are predominantly peloids (Diaz et al., 2022). SEM images of peloids from Great Bahama Bank document abundant decaying EPS (Extracellular Polymeric Substances) lined with nanograins, in a similar manner to that observed in the accreting cortices of ooids, where nanograins have been identified as ACC (amorphous calcium carbonates), the precursor to aragonite needles (Diaz et al., 2017). Likewise, nanograin clusters in peloids are also likely of biological origin. Together, these observations indicate that fecal pellets harbor a

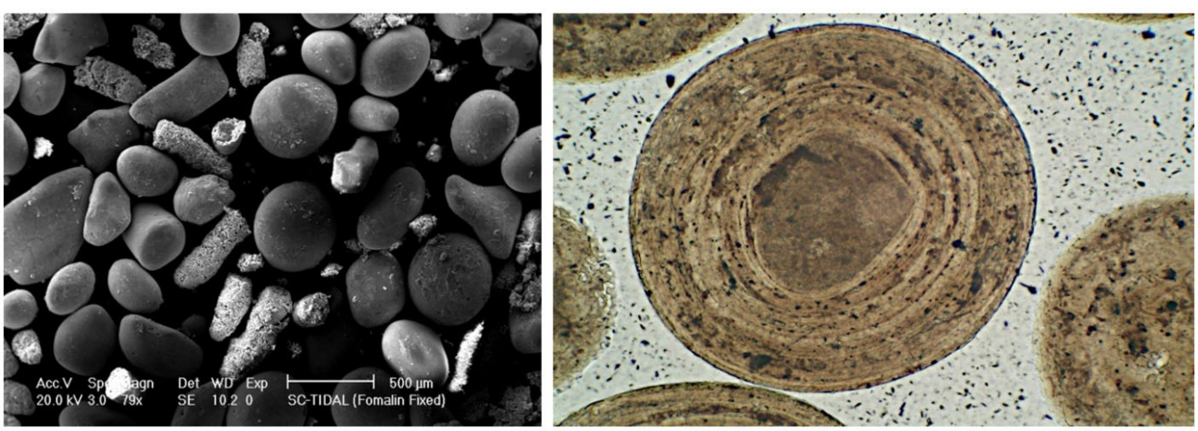

Figure 1: Left; SEM image of soft fecal pellets and hardened peloids. Right; Photomicrograph of an ooid with a peloidal nucleus and aragonitic cortices. SEM images display similar microbially induced precipitation in peloids as are observed in ooids, indicating that the microbes responsible for organomineralization in ooids are carried by the fecal pellets.

microbial community that is likely introduced into the fecal pellet via the digestive system of the burrowing shrimp. This microbial community transfer from organisms to ooids has been documented in ooids in the Great Salt Lake (Paradis, 2019). This project aims to test this potential microbial transfer in the marine environment by analyzing both fecal pellets and ooids with regards to their microbial composition and mineral phases.

APPROACH AND METHODOLOGY

We will collect samples of mud, newly formed fecal pellets, hardened peloids and ooids from the same area with an established protocol that preserves the indigenous microbial communities in each sample set.

To establish the source of peloidal nuclei and the role of fecal pellets as seeds for the first nucleation step in ooid formation, microbial and biogeochemical analyses will be undertaken. These analyses will elucidate any commonalities among fecal pellets and ooids. Any relatedness in genetic-make up or microbial composition will be assessed through sequencing of 16S rRNA, the gene that encodes the rRNA component of the smaller subunit of the bacterial ribosome. In addition, we will integrate petrographic analysis, RAMAN spectroscopy–a powerful tool for the characterization of biomolecules (e.g. lipids and carbohydrates) – and SEM/EDX analyses to characterize the organic and mineral phase composition within peloidal nuclei of ooids and mud fecal pellets.

In order to gain further insights into the nucleation process that leads to the initiation and hardening of fecal pellets, we will use SEM and elemental mapping analysis via wavelength-dispersive x-ray spectroscopy - coupled with an electron microprobe. This analysis will enable us to understand early diagenetic precipitation of minerals and whether initial crystallization on unhardened and hardened fecal pellets occurs through a pre-nucleation cluster pathway involving a metastable mineral phase.

Characterization of the sedimentary grains will be done on epoxy-impregnated thin sections. Snapshots of up to five different random areas – per thin section – will be taken with an Olympus BH2 petrographic camera. The grains, and the composition of ooid nuclei, will be quantified and classified (ie. ooid, peloids, skeletal grains) using Image J. Plugin/ Manual Counting.

SIGNIFICANCE

This project addresses a fundamental question regarding the source and transfer of microbial communities in the carbonate system to determine those responsible for organomineralization in carbonates. Here the pathway of the microbial vector for the formation of ooids is explored.

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CARBON CAPTURE UTILIZATION AND STORAGE

TESTING SEAL CAPACITY FOR CARBON STORAGE - AN EXPERIMENTAL APPROACH – (PART II)

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PROJECT OBJECTIVES

- Re-Design an experimental set-up that allows for CO_2-Brine saturation prior to CO_2 injection.
- Evaluate how the pre saturated CO_2-Brine mixture alters the seal capacity of mixed carbonate-siliciclastic samples.
- Run experiments to assess the amount of dissolution and possible breach of samples.

PROJECT RATIONALE

Carbon Capture Utilization and Storage (CCUS) will be a crucial component in reducing global CO_2 emissions in the coming years. Although the utilization of the captured CO_2 is an important component, it is likely that carbon capture with permanent storage will play a more important role in achieving faster, large-scale reduction of CO_2 emissions. Permanent storage requires natural reservoirs with a seal that resists dissolution by CO_2 saturated fluids. Many theoretical modeling studies dealing with such rock-fluid interactions have been published in recent years (André et al., 2007; Gaus et al., 2005; Yuan et al., 2019; amongst many others) but actual laboratory experiments are rare. Luquot and Gouze (2009) have shown that CO_2 injection triggered dissolution increased permeability, while inducing only minimal modification of porosity.

Changes in elastic properties resulting from the removal of the smaller particles (i.e., those with highest surface area), the creation of pits of dissolution on the grain surfaces, and changes at grain contacts such as grain welding caused by injection of CO_2 saturated solution have been reported by Vialle and Vanorio (2011).

This project aims to contribute to the experimental side of rock fluid interaction for carbon storage by building on our past precipitation/dissolution experiments in carbonate rocks (Weger et al., 2012), addressing the potential changes in the seal rocks resulting from CO_2 injections.

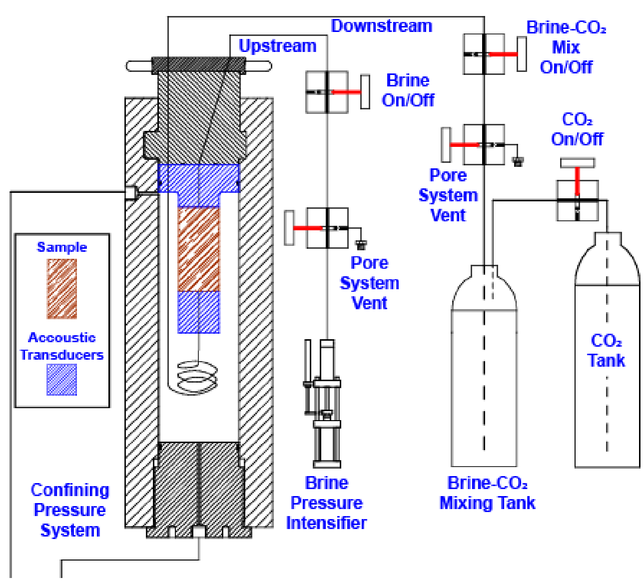

Figure 1: Set-up of proposed dissolution experiments using the Autolab 1000 which allows for pre-CO_2-Brine saturation.

WORK PROPOSED

Phase 2 of the project is the design and testing of the experimental setup. The following workflow will be tested first on various rock samples in our New England Research Autolab 1000 system. We will be using a semi-closed system where pore fluid with a predetermined geochemical composition is emplaced in the sample, CO_2 pressure is then established, and only the existing fluid volume within the intensifiers (~5-10 pore volumes of the sample) will be used to create fluid flow within the sample. This limited fluid injection will ensure that any chemical reaction of the fluid with the rock proceeds before the system reaches equilibrium with the host and the chemical reaction halts.

Monitoring of possible reactions that result in dissolution or mineralogy changes is a crucial element of the experiment. We plan to monitor physical changes with time series measurements of velocity. For this, the upstream pore fluid connection is closed. Five MPa pore pressure is installed at 60 MPa confining pressure, resulting in 55 MPa Ep. Time series measurement of VP and VS will be conducted for 72 hours (3 days) taking an acoustic measurement each hour.

After each three-day reaction time, the pore fluid will be extracted and chemically analyzed. In addition, all samples will be documented using SEM and CT scans before and after the experiment.

SIGNIFICANCE

This work will improve our understanding of how rock-fluid interaction changes microstructure and its elastic properties when CO_2 enriched fluids are injected in rocks with seal capacity. The proposed equipment re-design is expected to produce better results than the previously used method. The quantification and high resolution image documentation of the resulting rock alterations will further enhance our understanding of the rate of changes resulting from CO_2 injection.

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EXPLORING ORGANIC CARBON SEQUESTRATION POTENTIAL IN ICHTHYOCARBONATE

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PROJECT OBJECTIVES

- Determine amount and distribution of organic matter in carbonate produced by marine fish.
- Quantify the overlooked contribution of ichthyocarbonate-associated organic matter in the biological pump, which sequesters CO_2 in the ocean.
- Test the hypothesis that organic matter content plays a role in ichthyocarbonate dissolution.

PROJECT RATIONALE

Marine carbonate mineral and organic matter production in the ocean are important biogeochemical processes that drive the global carbon cycle, and thus Earth's climate and CO_2 through time. Marine fish were recognized as important carbonate producers in 2009, when global marine bony fish biomass (0.812-2.05 Gt) was estimated to produce 3-15% of new carbonate production in the oceans each year (0.34 to 0.95 Pg $CaCO_3$ yr^{-1}; Wilson et al., 2009). Since this initial estimate, substantial upwards (2.5-10× greater) revisions of global fish biomass have been reported, suggesting that carbonate production by marine fish may be significantly greater than previously appreciated (Jennings et al., 2015; Bianchi et al., 2021). However, it is currently unknown how embedded organic matter within ichthyocarbonate contributes to the biological pump, the activity of which reduces atmospheric concentrations of carbon dioxide. Assuming a conservative factor of 5× increase in fish biomass and presuming that this is linearly reflected in carbonate production by marine fish (hereafter called ichthyocarbonate), extrapolation of production rates from Wilson et al. (2009) suggests that marine fish could plausibly produce as much as 1.7 to 4.7 Pg $CaCO_3$ yr^{-1}, comparable to or even exceeding

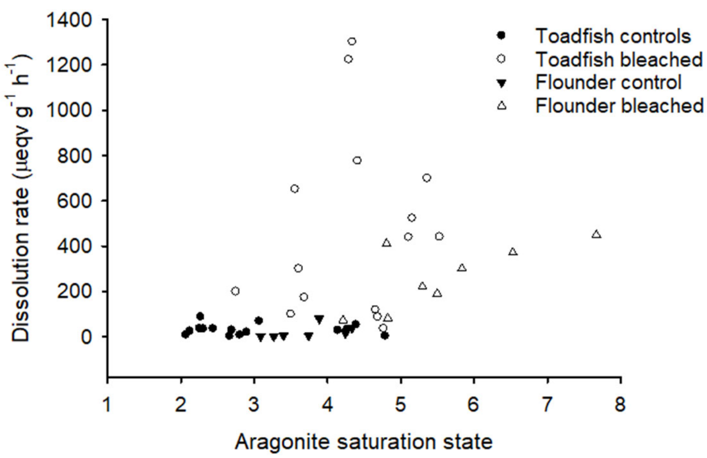

Figure 1: Comparison of dissolution rates for bleached (open symbols) and untreated (black symbols) ichthyocarbonate produced by the Gulf toadfish (circles) and the Olive Flounder (triangles). Aragonite saturation states were calculated from in situ measurements of pH and TA using CO_2sys.

contributions of coccolithophores and foraminifera (both ~1.0 Pg $CaCO_3$ yr^{-1} (Broecker and Clark, 2009; Langer et al., 2008). We hypothesize that ichthyocarbonate associated organic matter occurs in high quantities and plays a key role in ichthyocarbonate dissolution rate.

APPROACH

We will assess the quantity and distribution of organic matter in ichthyocarbonate produced by two species of marine fish using geochemical and microCT approaches. Initial results from geochemical analyses of total organic carbon (TOC) content indicate that ichthyocarbonate produced by both species contains significant TOC, with toadfish ichthyocarbonate containing 5.5 ± 1.9% (n=6) and flounder ichthyocarbonate containing 6.3 ± 1.6% (n=3). Dissolution rate will be assessed on natural ichthyocarbonate, and samples treated with bleach to oxidize the outer coating of organic matter on ichthyocarbonate. Preliminary results indicate that dissolution rates are significantly ($p<0.05$) faster for bleach treated samples than natural ichthyocarbonate (Fig. 1). Multiple linear regression indicates that dissolution rates for toadfish ichthyocarbonate (n=15) were not dependent on aragonite saturation index ($p=0.613$), while initial experiments conducted on flounder ichthyocarbonate (n=8) suggest that dissolution rate is significantly impacted by aragonite saturation index ($p<0.001$).

SIGNIFICANCE

Marine fish are prodigious producers of carbonate in the oceans, and our initial results suggest that the ichthyocarbonate they produce also contains significant quantities of organic carbon. Rapidly sinking ichthyocarbonate likely increases the probability that this organic matter will evade shallow ocean remineralization and be sequestered in the deep sea or in marine sediments.

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