Diagenetic Controls on Porosity and Permeability in Carbonates

After deposition, carbonates are modified by diagenesis that can markedly alter reservoir properties. As such, studies investigating post-depositional alteration of carbonates can provide novel insights into complex patterns of reservoir quality common in carbonates. Systematic study of diagenetic process and response is necessary. Traditional hydrozone approaches are being reevaluated in the context of new understanding of diagenetic reactions. Examples of some current and pending projects include:
Impact of Diagenesis on Reservoir Properties of Heterozoan Carbonates

Robert H. Goldstein, Evan K. Franseen, Tony Pugliano, Hassan Eltom

SUBSURFACE APPLICATION: Miocene-Pliocene grainy heterozoan systems in Spain are analogs for Oligocene-Miocene heterozoan reservoirs in the Caribbean, such as the Perla giant gas field (offshore Venezuela), and Miocene heterozoan reservoirs in the Indo-Pacific. Lessons from the outcrops can be applied to other heterozoan reservoir systems in the ancient. STATUS: Ongoing research; several projects complete TIMING: Completed and ongoing results available; future projects upon funding FUNDING: KICC

Purpose
Fundamental differences between heterozoan and photozoan carbonates yield contrasting stratigraphic architecture and original mineralogy. With such differences, it would be expected that low-temperature diagenetic alteration of heterozoan carbonates would yield distributions of petrophysical properties that contrast with those of photozoan carbonates. One might hypothesize that, with the calcite-dominated mineralogies of heterozoans, diagenesis might have less overall impact, preserving aspects of petrophysical properties originally generated in the depositional environment.

Project Description
This study examines porosity and permeability from least-altered Pliocene heterozoan carbonates (Carboneras Basin, Spain), and compares them to diagenetically altered Miocene heterozoan carbonates (Ricardillo area, Spain) to evaluate the impact of low-temperature diagenesis on petrophysical properties. Miocene strata have been impacted by dolomitization associated with ascending freshwater-mesohaline mixing (Li et al. 2013; 2014). Dolomite is concentrated in distal regions and decreases updip and upsection. Dolomite content is correlated with moldic porosity. Later alteration in freshwater (Li et al., 2014) led to calcite cementation and moldic porosity that preferentially affected strata in updip locations.

Methods
1. Fieldwork was conducted at the northern end of Playa de Los Muertos, Cala de la Pelirroja in the Carboneras Basin, Spain and at Cerro de Ricardillo and Cala de San Pedro in the Ricardillo Area, Spain. A total of 11 stratigraphic sections were measured and described at centimeter scale, four from the Miocene of the Ricardillo area, and seven from the Pliocene of the southern part of the Carboneras Basin.
2. A total of 333 thin sections are used for transmitted light and UV petrography to point count grain constituents, point count and measure relative grain size, categorize cements, categorize pore type, and to determine and quantify mineralogy. Miocene samples were stained using Alizarin Red-S and Potassium Ferricyanide (Lindholm and Finkelman, 1972) to distinguish calcite from
3. Background extraction micro-imaging analysis is used to quantify dolomite content for Miocene samples. Diagenetic phases and porosity are quantified and the diagenetic alteration is classified into diagenetic facies.

4. Three hundred sixty-one core plugs were taken parallel to bedding for petrophysical analyses. One hundred eighty-six of the plugs were taken from Miocene deposits, and 175 from Pliocene deposits. Helium porosity, air permeability (Kair), and grain density measurements were taken on each core plug.

5. Diagenetic facies models depositional facies models and petrophysical models were created in Petrel™ to be used as analogs for facies prediction and petrophysical distribution in heterozoan carbonate reservoirs. Altogether, a total of 948 distinct models were constructed with the following characteristics: (1) all Miocene deposits along Ricardillo; (2) entire Pliocene clinohem from Carboneras; and (3-8) six end-member, lateral depositional profiles forming clinothems in the Pliocene. Each model includes a facies model, porosity model, permeability model, and predictive distribution models for individual lithofacies.

Results and Deliverables
Strata are classified into six diagenetic facies, using amount of dolomitization, dolomite cement, calcite cement, and dissolution. Diagenesis has lowered petrophysical values in Miocene strata compared to least-altered Pliocene (Figure 1), which is due to dolomite and calcite cement being greater than dissolution. For example, least-altered Miocene rudstones have porosity of 40% and 1,888 md permeability, whereas diagenetically altered rudstones have 34% and 1,307 md. Least-altered Miocene packstones have 43% and 5,131 md, whereas diagenetically altered packstones have 30% and 690 md.

Strata consist of grain-rich fining-updip clinothems and fining-upward cyclothems. The fining is the result of abrasion and sorting during shoaling to form packstones (sea grass beds are an exception). Rudstones form in slightly deeper water where bioclasts are not abraded and sorted. Diagenetically least-altered cyclothems and clinothems show upward increases in porosity and permeability. Sorted packstones have porosity of 51% and permeability of 6,099 md. Rudstones have 42% and 2,537 md. After diagenetic alteration, only 46% of the cycles preserve this petrophysical relationship. Packstone facies capping cycles have been altered the most with some moldic porosity and much cementation. It is hypothesized that this results from originally high permeabilities, which provided preferred conduits for diagenetic fluids.

These data have been developed into 3D Petrel™ reservoir-analog models and facies models to aid in predicting the distribution of reservoir character in similar deposits in the subsurface. They yield reservoir analog models capable of storing 26-166 barrels of fluid, some with stratigraphic trapping mechanisms.

Overall, the data show that low-temperature diagenesis has had a negative impact on petrophysical properties in the heterozoan carbonates studied. In contrast to what might be predicted given the calcitic mineralogy of heterozoans, the petrophysical trends developed in the depositional environment are mostly not preserved after low-temperature diagenesis.
Figure 1. Box and whisker plots of Miocene and Pliocene petrophysical values. DF-1 (diagenetic facies 1) comprises all Pliocene samples and has the least diagenetic alteration. DF-2 in the least altered of the Miocene with less than 30% dolomite and only minor molds and calcite cement. DF-3 has low dolomite content (<30%) and extensive calcite cement that occludes much of the pore space. DF-4 is entirely dolomitized and has >10% moldic porosity. DF-5 grains have been dolomitized or preserved as abundant molds, but some pores are occluded by both dolomite cement and poikilotopic calcite cement. DF-6 is dominated by replacement dolomite and dolomite cement with little moldic porosity.

References
Superhighways for Hydrothermal Fluid Flow in the Midcontinent: Structural and Stratigraphic Controls on Thermal Structure, Flow Rate, and Reservoir Properties

Robert H. Goldstein, Lynn Watney, Tandis Bidgoli.

SUBSURFACE APPLICATION: Ghawar Field, North Field, Ladyfern, presalt Brazil/Angola, Mississippian Lincoln County Colorado, Albion-Scipio, Tengiz, Trenton-Black-River, Arbuckle/Ellenberger and Pennsylvanian Permian Basin and Midcontinent, Mississippian Lime in Kansas, Woodford Chert of the southern USA midcontinent, Shale plays of the Permian Basin, and Bakken/Lower Lodgepole play

STATUS: Beginning stages of project
TIMING: Preliminary results available; project underway
FUNDING: Partial from DOE

Purpose
This project proposes to improve understanding of the effects of hydrothermal fluid flow in regionally advective and fault-pumped systems. This will be accomplished by integrating data from a regional case study from the Midcontinent of North America to be followed by coupled flow and thermal modeling. The workflow for modeling will be tested by using the rock record of a well-studied example that shows density controls on hydrothermal fluid flow leading to predictable alteration with a stratigraphic and structural control. The results will be broadly applicable to improving approaches to modeling thermal history and diagenetic evolution in hydrothermally altered systems in hydrocarbon reservoirs.

Project Description
In many conventional and unconventional carbonate reservoirs, there is strong evidence that hydrothermal fluid flow has had an impact on reservoir quality (Davies and Smith, 2006). Hydrothermal systems require flow of warm fluids into cooler rocks to affect the thermal regime. Hydrothermal porosity enhancement has been incorrectly ascribed to meteoric diagenesis in many cases. For example, in the Midcontinent of North America, it has been suggested that meteoric dissolution associated with unconformities led to much of the reservoir porosity in Midcontinent carbonate reservoirs (e.g. Duren 1960; Euwer 1965; Thomas 1982; Rogers et al. 1995; Montgomery et al. 1998; Franseen, 2000; Watney et al. 2001; Franseen et al. 2004; Mazzullo et al. 2009). New data show that late hydrothermal fluid flow in Ordovician, Mississippian, and Pennsylvanian reservoir rocks of the Midcontinent have had a major impact on porosity in conventional high-permeability reservoirs as well as low-permeability unconventional reservoirs (Goldstein and King, 2014; Ramaker et al. 2014). These fluids also have had an impact on hydrocarbon migration and local thermal maturation in these systems. Although recent publications have challenged the impact of porosity generation at high-diagenetic temperatures in hydrocarbon reservoirs (Ehrenberg et al. 2012), the small Midcontinent reservoirs have clearly been affected. Moreover, this effect is unequivocal at the other end of the size spectrum, including the largest hydrocarbon reservoir in the world,
Ghawar (Cantrell et al, 2004). Thus, understanding the controls and impact on hydrothermal alteration is of broad import for the oil and gas industry.

The Midcontinent USA is ideal to develop the geologic constraints necessary to improve our ability to develop general modeling approaches applicable to various subsurface systems. The hydrothermal fluid flow in the USA Midcontinent occurred in three late stages (King, 2013). Fluid flow was controlled by stratigraphic discontinuities, fault and fracture systems, and temperature-controlled density differences, and had an impact on thermal maturation, porosity, and hydrocarbon migration.

Work to date demonstrates how stratigraphic discontinuities associated with

Figure 1. Summary of fluid inclusion homogenization temperatures and salinities from the Midcontinent.

systems.
unconformities control later hydrothermal fluid flow to create the superficial appearance that porosity originates during low-temperature meteoric diagenesis. It develops a regional data set from reservoirs, shallow cores, and outcrops from the Midcontinent, USA and integrates regional stratigraphic data from the Ordovician through the Pennsylvanian, petrography, fluid inclusions, and stable isotopes to demonstrate the evolution of the hydrothermal system. Petrographic data show that the entire region and stratigraphic succession experienced a similar late time-equivalent paragenesis - with megaquartz, silica dissolution, carbonate dissolution, baroque dolomite, ore minerals, and calcite. Fluid inclusion data in the megaquartz, baroque dolomite, and calcite confirm a complex record of hydrothermal fluid flow, beginning with migration of low salinity connate fluids and gas, and evolving to migration of concentrated brines and oil (Fig. 1).

During the second phase of hydrothermal alteration integrated data indicate advective fluid flow from the basin to the South. A regional dataset shows the Ordovician through Mississippian section was hydrologically connected and that the shale-rich Pennsylvanian section acted as a leaky confining unit (Fig. 2). Temperatures increased upward in the Ordovician-Mississippian section and were lower and decrease upward in the Pennsylvanian section. The data indicate vertical hydrologic connections that allow the warmest, lowest density fluids to float toward the top of the hydrothermal aquifer, concentrating dissolution from hydrothermal solutions below the Mississippian-Pennsylvanian unconformity.

Later, the system evolved from a regionally advective hydrothermal system to a fracture-controlled system. After or during fracturing, hydrothermal solutions precipitated calcite and showed regional geochemical trends indicating vertical fluid flow along fractures, directly from basement or a basal sandstone aquifer (Fig. 3). This late system shows no stratigraphic control and is likely driven by highly localized fault pumping of the hydrothermal fluids.

For the reservoirs studied, the most important system for porosity modification was the regionally advective hydrothermal aquifer, which had warmer fluids at its top, coincident with a stratigraphic discontinuity/unconformity. Porosity enhancement immediately below the unconformity can be ascribed to hydrothermal fluids, which leads to a significantly different model for exploration for the best reservoir quality. This type of fluid flow differs greatly from the highly localized fluid flow interpreted for Trenton-Black River hydrothermal dolomite reservoirs (Davies and Smith, 2006).

This study will focus on developing an improved understanding of predictability of hydrothermal alteration associated with regionally advective hydrothermal flow.

- All Midcontinent reservoir and nonreservoir carbonate diagenetic data (geochemical) and thermal alteration data will be synthesized to develop an improved picture of spatial and stratigraphic impacts of hydrothermal alteration.
- The spatial distribution of these data will be correlated to oil field data (locations of producing wells, water cuts, production history, reservoir quality) and seismic data (provided by consortium members) to improve exploration tools for hydrothermal reservoir enhancement.

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Figure 2. Oxygen isotopic data from baroque dolomite showing evidence for hydrothermal dolomite temperatures increasing upward in the Ordovician-Mississippian section. Lower temperatures are in the Pennsylvanian confining unit.

- Thermal history and porosity evolution will be compared spatially to restraining bends on faults, flower structures, and fault orientation to develop predictive models for superhighways for hydrothermal fluid flow, porosity enhancement, oil migration, and thermal maturation of organic matter (Fig. 4)
- The final phase of the project will use coupled modeling approaches incorporating tools such as BASIN2 and TOUGH. The modeling parameters will be constrained by matching the known results from the Midcontinent system to create a broadly applicable simulation model for predicting alteration by advective hydrothermal systems.

Deliverables
The project will explore an important type of hydrothermal alteration in which fluid flow and porosity enhancement had a stratigraphic control. This differs greatly from a common perception of fault pumping as the only applicable model.

The full data set of Midcontinent diagenetic and thermal alteration will be provided as an integrated report focusing on the Ordovician through Pennsylvanian section. This will provide the basis for testing hypotheses of the parameters controlling hydrothermal alteration.

When these data are compared to oil field data, the project will provide a set of conceptual models for reservoir sweet spots in such a system. When they are compared to seismic data, the results will provide seismic signatures that aid in exploration for hydrothermal alteration and porosity enhancement.

Finally, the simulation model set up and parameters that will most effectively be used to predict this type of hydrothermal alteration will be provided to consortium members for application to their exploration and production problems.
Figure 3. Sr isotope data from Stage 3 calcite and Stage 2 baroque dolomite. Baroque dolomite shows values similar to host rock, indicating long distance advective fluid transport and extensive rock-water interaction. Calcite data indicate progressive rock-water interaction from base to top and well-to-well variation suggestive of vertical fluid flow along localized faults and fractures.

Figure 4. Structural contour map on the top of the Mississippian in Kansas with documented and inferred faults. (after Hedke and Watney, 2016)

References
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EHRENBERG, S.N., WALDERHAUG, O. AND BJØRLYKKE, K., 2012, Carbonate porosity


Diagenesis and Porosity Evolution Associated with Unconformities in the Mid-Cretaceous El Abra Formation, Mexico

Paul Enos, Abdul Wahab, Robert Goldstein

SUBSURFACE APPLICATION: Applies broadly to reservoirs where porosity or cementation is associated with unconformities: such as Cretaceous of Mexico, San Andres, Tengiz, Arbuckle/Ellenburger/Tarim, Pennsylvanian/Permian of Permian Basin and Midcontinent, Mississippian Midcontinent, Shuaiba, Lisburne Group of Alaska
STATUS: Focused-term project in progress.
TIMING: Significant results to be reported to membership
FUNDING: Full from KICC, AAPG, GSA, and Fulbright Commission.

Purpose
Depositional facies, origin of early cement, and porosity evolution associated with closely spaced correlative unconformities of short duration and a major pre-Turonian unconformity (up to 17 Ma duration) in the El Abra Formation, Mexico are the foci of this project. The results will provide better understanding of Cretaceous shallow platform-margin carbonate reservoirs and will contribute to models of porosity prediction associated with unconformities of various durations.

Project Description
More than half of carbonate oil fields are closely related to unconformities, according to S.M. Ball (unpublished data). Qualitative and quantitative understanding of the effect of unconformities on porosity, in particular short vs. long duration of exposure, is limited. To explore the unknowns, these hypotheses will be tested: 1) Closely spaced, correlative unconformities in the mid-Cretaceous El Abra Formation exerted significant control on porosity evolution in the shoaling-upward cycles, hence on reservoir heterogeneity. 2) Porosity evolution along these unconformities is a function of facies (grain vs. mud content), mineralogy (calcite and aragonite shell layers of rudists), climate, and distance from the platform margin. 3) Porosity evolution associated with intraformational (short-duration) unconformities is less extensive than with the pre-Turonian unconformity (up to 17 million years duration, Smith, 1986) at the top of El Abra Formation. 4) Repeated exposure, thus early diagenesis in general, affected the rocks of the elevated platform-margin much more extensively than those of the platform-interior lagoon (Minero, 1991).

This project explores porosity evolution associated with unconformities in the mid-Cretaceous shallow platform-margin carbonates of El Abra Formation, Mexican Gulf Coast. A series of shallow-water platforms developed during the mid-Cretaceous (Albian-Cenomanian) in the eastern Mexico, surrounded by vast intracratonic basins (Enos, 1974, 1983). The platforms developed relief of 1000m and slopes as steep as 45° (Enos, 1977). Sierra de El Abra is a low-relief, asymmetric anticline 3-5 km wide and 120 km long (Yurewicz et al, 1997). Extensive quarries provide a nearly continuous cross section of the margin over a distance of ~3km (Figure 1). Previous work by Minero, (1988, 1991) documented three major lithofacies associations in the platform interior: 1) peloid-miliolid, requienid and bioclastic limestone, 2) fenestral, cryptalgal laminate and lime mudstone and 3) laminated grainstone and rudists-skeletal limestone. These facies
associations represent platform lagoon, tidal flat, and shoal depositional environments, respectively (Minero, 1988). Typical cycles in the El Abra Formation start with subtidal lithofacies and terminate in upper intertidal or supratidal units truncated by exposure surfaces (Minero, 1988). The platform margin is comprised of rudist ‘reef’ facies and skeletal sands (Enos, 1986).

Figure 1. A) Generalized Google map of the area showing the location of B) The study area showing multiple quarries. The quarry numbers 2-7 are after Minero, et al, 1983). Quarries 3, 4, 5 & 6 contain platform facies while 2 and 7 are platform margin facies. The distance between quarry 2&6 is ~3 Km.. C) Differential oil stains, quarry 6. D) Quarry 7 into the Abra escarpment in 1991; it is now greatly enlarged, exposing platform-margin as well as slope facies.

Documenting porosity evolution along these unconformities of varying duration should elucidate fundamental controls on both vertical and lateral (elevated rim vs. interior lagoon) early cementation and heterogeneity of porosity in carbonate reservoirs. Unconformities and related subaerial exposure features can also provide useful information about the paleoenvironment. The results of this research can thus serve as a reservoir analogue to understand porosity evolution associated with unconformities of various durations in Cretaceous shallow-platform-margin carbonates, e.g. the Golden Lane, Isthmus, and Campeche reservoirs of the Mexican Gulf Coast (Viniegra and Castillo-Tejero, 1970, Viniegra, 1981, Santiago, 1980), and similar reservoirs of any age.

Deliverables
This project will produce measured stratigraphic sections with diagenetic logs from El Abra Formation; quantitative analyses of porosity, permeability, and cements related to each unconformity at large (Figure 2) and small (Figure 3) scale; analysis of the impact of subaerial exposure on porosity; and analysis of variables of facies, setting, distance from the platform margin, climate, and duration, to develop a predictive model of
porosity and permeability evolution and to evaluate the eventual impact of unconformities on reservoir properties. Results will be presented at the 2016 KICC meeting and details will be available in the MS thesis of Abdul Wahab.

**Figure 2.** (A) Photomosaic showing large-scale vuggy porosity at a discontinuity surface in Valles-Tamuin (CW) quarry section at 31.8 m. (B) Same photomosaic showing the extant porosity in green and cement- and internal-sediment- (IS) occluded porosity in red. Unconformity traced with yellow line. Based on image analysis of the photomosaic, a total of 25% post-exposure porosity, not including matrix porosity is indicated at a 30 cm interval below the unconformity, of which 18% of former pores are reduced by cements and internal sediments.

**Figure 3.** Perm plug analysis of porosity and permeability in small-scale samples. Symbols denote position relative to platform margin.

**References**


Architecture of Lower–Middle Ordovician Stacked Paleokarst in the Nopah Range, California, U.S.A.

Jason Rush, Robert H. Goldstein, Evan K. Franseen, and Eugene C. Rankey

STATUS: Focused-term project in progress
TIMING: Significant results to be reported to membership (year 1 of 3)
FUNDING: none; software donation by Schumberger

Purpose
Paleokarst is likely the most complicated and least predictable style of reservoir architecture. A fundamental goal of this research project is to document paleokarst architecture within a hierarchical stratigraphic framework and use it to understand and predict spatial trends in porosity and permeability. World-class Lower to Middle Ordovician exposures (Figure 1) in the Nopah Range, California, provide an ideal laboratory to analyze the architecture of multiple, vertically stacked paleokarst intervals (Cooper and Keller, 2001). These exposures are an age-equivalent outcrop analog for Ellenburger and Arbuckle paleokarst oil and gas reservoirs.

Project Description
Exposures of ancient paleokarst systems are important because they permit investigation of burial-related processes such as compaction, brittle failure, and late stage porosity modification. The Nopah Range contains one of the most laterally continuous sections (~8 km) of exhumed Ordovician paleokarst in North America (for comparison see Table 1 in Loucks, 1999). The karst of the Pogonip Group straddles the Sauk-Tippecanoe super-sequence boundary, and includes multiple scales of karst, ranging from stratiform breccias to multi-storied collapsed paleocaverns. Collapse features developed in the overlying Eureka Quartzite pass downward into narrow vertical shafts (<3 m) and ultimately open into breccia-filled paleocaverns (~60 m thick) developed within the uppermost Pogonip Group (Figure 2). Stratal geometries, breccias, and fractures show evidence of both top-down (e.g. sinks and vertical shafts) and bottoms-up karst (e.g. silica-cemented fractures). Important questions to be addressed by this research are:

1. Does the Nopah paleokarst reflect surface/vadose processes and/or aggressive subsurface fluids?
2. If exposure-related, does paleokarst architecture record a nested hierarchy driven by relative sea-level?
3. How is porosity distributed across host strata, fractures, breccia-fill, and karst margins?

Stratal geometries and paleokarst features will be recorded onto high-resolution photomosaics and georeferenced within an oblique airborne, LiDAR-based three-dimensional Petrel™ outcrop model. Field observations incorporated into the model include chronostratigraphic surfaces, host strata lithofacies, fracture orientation data, breccia bodies, shafts, sinks, and roof sags. Rock samples will be collected from paleokarst features to analyze fluid inclusions and perform cathodoluminescent microscopy in addition to traditional petrography. This work will allow fingerprinting of
diagenetic fluids (e.g. meteoric vs. burial) and constrain porosity evolution. Porosity and permeability measurements will be taken from a number of representative samples. All data will be integrated into the Petrel™ model to aid interpretation and reconstruction of paleokarst architecture and diagenetic history.

**Deliverables**
Initial field-oriented research indicates that cavern floors opened along a regional water table and sloped upward. Vadose karst features (e.g., breccia-filled shafts) formed via solution enlargement of regularly spaced fractures or joints. Failure and preferential subsidence along the ceiling enhanced surface doline relief. Caverns were filled by breccias derived from ceiling collapse and from the overlying subaerial unconformity via vertical shafts. If confirmed by future petrographic- and laboratory-based research—and further fieldwork—a predictive model for multi-storied composite sequence-scale paleokarst architecture will be presented. A proper marriage of the diagenetic model and architectural framework should provide an accurate model of how porosity in paleokarst reservoirs is redistributed during near-surface and burial processes. Research results and technology transfer can take the form of in-house workshops, fieldtrips, conventions, and publications. Shared data will consist of maps, figures, interpreted photomicrographs, cross sections, conceptual models, lithofacies variography, a Petrel™ geologic model, and reports.

**References**
Figure 1. Digital orthophoto of the Nopah Range showing steeply dipping Pogonip Group contacts. Notice irregular top-Eureka contact illustrating underlying paleocavern collapse.
Figure 2. Photograph of Pogonip Group strata and overlying Eureka Quartzite. Paleokarst is outlined showing a collapse/sag, vertical shaft, and breccia-filled paleocavern.

David A. Fowle

SUBSURFACE APPLICATION: Lacustrine carbonate reservoirs such as the rift basins of the South Atlantic, offshore Brazil and Angola.
STATUS: Proposed project
TIMING: To be completed in the future if recommended by membership, funded, or staffed.
FUNDING: Unfunded.

Purpose
The proposal that carbonate hosted porosity in lacustrine carbonate reservoirs, such as the Barra Velha Formation of the Santos Basin could result from the dissolution of Mg-silicates coupled to the precipitation of Mg-rich carbonates and silica gels (Wright and Barnett, 2015) is both intriguing and speculative, owing to a lack of experimental and modern-environment evidence to support this process. Indeed, the thermodynamic and kinetic behaviors of labile Mg-clays are enigmatic with only a few noteworthy studies in the literature (e.g. Jones, 1986; Galan & Pozo, 2011; and Tosca, 2015). However, recent modeling work by Tosca and Wright (2015) and their accompanying conceptual model is highly suggestive that there are several systems where Mg-rich labile clays have the potential to precipitate (e.g. the rift basins of the South Atlantic). If upon burial these clays are exposed to series of microbially driven metabolic processes that can drive pH lower and alkalinity up, then rapid dissolution of the clays is predicted, followed by precipitation of Mg-rich carbonates.

Unfortunately clay mineral phases, not unlike carbonate phases do not always conform to their predicted thermodynamic behavior, with nano-scale clays and gels initially forming rather than crystalline mineral phases. Generally, the form of these precipitates is under the control of kinetic factors influenced by a variety of geochemical, biological and physical processes that alters the first phase to precipitate and its stability under burial conditions. Therefore major goals of this study are to: 1) Ground truth the geochemical kinetics and broad potential for Mg-rich clay dissolution coupled to carbonate precipitation to develop porosity in carbonate reservoirs; 2) Develop a thermodynamic/reactive transport model that effectively provides boundary conditions for these processes on the reservoir scale over geologic time scales.

Project Description
If funded our team will systematically investigate the linkages between Mg-rich carbonate formation and Mg-rich labile clay dissolution through the use of laboratory synthesized Mg-clay (directly related and a close proxy for Stevensite) based on the work of Tosca and Masterson (2014) who demonstrated that this phase was favored at pH values > 9.4, high salinity and Mg/Si ratios >1. This synthesis will be followed in parallel with a biotic synthesis approach (similar to Kenward et al., 2013) to investigate the effects of heterogeneous nucleation on clay formation and subsequent stability. Specifically, this work will directly address our first and second hypotheses: H1: The
presence of organic matter in saline lacustrine settings promotes the formation of Mg-rich labile clays at lower pH values and salinities. H2: Mg-rich clays formed in the presence of organic matter will be nanoscale in size with high reactive surface areas making them more susceptible to dissolution.

This work alone will be of interest to the KICC members as it will provide initial boundary conditions for this conceptual model. Models from Tosca and Wright (2015) (Figure 1) suggest that enhanced pCO₂ and bicarbonate lead to the destabilization and congruent dissolution of the Mg-silicate phases followed by the precipitation of carbonates.

This leads to our third hypothesis H3: Microbial metabolisms that lead to organic matter oxidation will promote dissolution of Mg-rich clay phases and the formation of carbonates through lowering of pH, increasing alkalinity and destruction of the biological matrix supporting nanoscale clays. This hypothesis can be directly explored through abiotic and geomicrobiology experiments with the clays synthesized previously. Aqueous geochemistry and mineralogy will be followed throughout the experiments which will bracket conditions where carbonates are undersaturated (to study straight clay dissolution), saturated and supersaturated. Finally, we will investigate our final hypothesis H4: Increased temperature and pressure will have differential effects on biogenic- and abiotic-formed clay phases and in turn the types of carbonates formed through microbiologically mediated diagenetic processes, such as organic carbon oxidation and methanogenesis. This hypothesis will be addressed through a series of controlled temperature and pressure treatments of the initial starting clay materials and by conducting the similar experiments to H3 but at higher temperatures.

**Deliverables**

Specific deliverables include: 1) Development of a new experimental based conceptual and reactive transport model of the role of Mg-rich clays on lacustrine carbonate formation; 2) Preliminary mechanistic, morphological and kinetic data on Mg-rich clay formation, dissolution and carbonate formation in these conditions; 3) Multiple publications; and 4) Full participation of PI and student in KICC Annual Meeting.
References

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Carbonate and Clay Formation in Deep Lacustrine Sediments: Answers from an Ancient Lake System and an ICDP core initiative.

*David Fowle*

SUBSURFACE APPLICATION: Ancient lakes formed in particular tectonic settings, especially those with low width/depth ratios, represent strong candidates for organic matter preservation. These Lacustrine Source Rocks represent 80% of the petroleum reserves of Brazil, China and Indonesia and nearly half the reserves of India (Katz, 1995). Furthermore, these settings represent potential for hydrocarbon production from oil shales.

STATUS: Project Proposed and core acquired

TIMING: To be completed in the future if recommended by membership, funded, or staffed

FUNDING: $1,200,000 ICDP

**Purpose**

The Malili Lakes are situated on Sulawesi Island and constitute a morphologically diverse group that includes Lake Matano, Lake Mahalona, Lake Towuti, Lake Lawontoa, and Lake Masapi. To date, Lake Matano is the most extensively characterized (e.g. Crowe et al. 2008). Lake Matano is tectonic in origin and is hosted by a cryptodepression with a graben structure. More than 590 m deep, Lake Matano is among the 10 deepest lakes in the world. It has been suggested, based on geological and biological information, that Lake Matano is between one and four million years old. Due the unique nature of theses lakes (stratified and mixed, ancient, organic carbon delivery to anoxic iron rich sediments, authigenic mineral formation, high methane production) our goals are to use the lakes as a living laboratory to evaluate carbon preservation and authigenic mineral formation in a tectonically formed ancient lake system.

**Project Description**

Petroleum source rocks that have been deposited in lakes have become an area of enhanced interest in recent years in particular in regard to passive margin sequences (e.g. Brice et al., 1980) and the rift basins of Africa (Schull, 1984). However, the broad variety and complexity of lacustrine sediments has led to comparatively minimal study of these systems. Here we provide the opportunity to study the mechanisms of preservation of lacustrine organic sediments in both a stratified and well mixed, deep (> 590 m) ancient lakes in Sulawesi, Indonesia. We will address such questions as:

- How is organic matter accumulating in these potentially oil prone sediments?
- Under what paleoenvironment conditions do authigenic mineral phases such as siderite and clay minerals form in both the lake and its sediments?

These questions will be tested using field-based studies of the mineralogy, microbiology and geochemistry (inorganic and organic) of the sediments and water column. Sediment samples will also be used to seed studies of how the assemblages respond to increases in temperature and pressure experimentally. This field work has been completed, in collaboration with NSF and the International Continental Drilling Program (ICDP) and we have retrieved over ~800,000 years of core from these lakes, which are now in long
term storage and are available to participating partners for correlating changes in paleo-environment to organic matter accumulation as well studying the early diagenetic changes of these iron rich sediments.

Deliverables
Specific deliverables include: 1) Quantitative data of mechanisms of carbon preservation as a function of sedimentation and productivity in a deep tectonically formed lake; 2) Models for authigenic mineral formation in these sediments and others of interest based on pore water chemistry, stable isotopes; and temperature proxies 3) Information regarding changes in organic matter preservation as a function of paleoenvironment (e.g. climate, weathering rate, productivity) from an ICDP core 4) a conceptual model of all of these processes for use in interpreting other paleo-lacustrine sediment environments such as those in the south Atlantic.

References

![Figure 1. Map of location and bathymetry of Lake Matano, Indonesia. Shaded area represents anoxic region of the lake (after Crowe et al., 2008)](image)
Effects of Seepage-Reflux Diagenesis on Porosity Modification in Carbonate Reservoirs

Robert H. Goldstein, David Fowle, and students

SUBSURFACE APPLICATION: Smackover reservoirs, Midcontinent Pennsylvanian, Mississippian, Arbuckle, Grayburg/San Andres of Permian Basin, Mississippian Williston Basin, Arab-D
STATUS: Long-term project in progress
TIMING: Significant results to be reported – Results currently available to membership
FUNDING: Partial

Purpose
Evaporative concentration of seawater at the surface leads to chemical evolution of the fluids, increased reactivity, and density inversion that leads to sinking of brines downward through less dense fluids. The process, which was originally introduced as seepage-reflux, a mechanism of dolomitization proposed by Adams and Rhodes (1960), is now known as a widespread process with major effects on oil and gas reservoir rocks.

The purpose of this research is to systematically evaluate the effects and distribution of refluxing systems in carbonate reservoir rocks, as a means for predicting porosity distribution.

Project Description
For many years, reflux was one of those undersubscribed diagenetic processes. It is now known that very little evaporative concentration is required to have refluxing fluids penetrate deeply into carbonate platforms. Now, we know that reflux is common, a major diagenetic process, and that it requires very little evaporation. It leads to dolomitization, anhydrite precipitation, and calcite cementation. This process has had a major effect on many large and small carbonate reservoirs around the world.

On the Great Bahama Bank, for example, it is well known that during certain times of the year, salinity becomes slightly elevated above that of normal seawater (Traverse and Ginsburg, 1966). Reflux of this bank water is taking place today, and has taken place in the past. In their study of karst of the eastern part of the bank, Whitaker and Smart (1990) demonstrated that saline waters of the lagoon sink to depths of about 150 m and discharge eastward into the Tongue of the Ocean. In the subsurface from 60 to 1100 m depth, west of the bank margin, salinity is high (up to 62 ppt; Kramer et al., 2000). Calcite cement from the Pliocene section of the Clino core contains saline fluid inclusions indicating an origin from reflux (Goldstein et al., 1998). It is interpreted that refluxing fluids dolomitized sediment updip leading to calcite cementation downdip.

Some of the dolomite from deep core of Enewetak Atoll is best explained by deeply sinking moderate salinity refluxing brines (Goldstein, 1996). Enewetak consists of 1400 m of carbonate overlying volcanic basement. Two cores have been taken and sample all the way down to basement. There is porous dolomite near the base of the section that owes its origin to deeply refluxing, relatively recent fluids, on the basis of dolomite Sr
isotopic compositions, oxygen isotopic compositions, and fluid inclusions ranging from 44-85 ppt.

If surface waters on a carbonate platform reach high salinities, initially, it is expected that refluxing brines would dolomitize the host sediment. Downdip, however, reactive transport models suggest that anhydrite should precipitate and plug significant amounts of pore space (Jones and Xiao, 2005). This process appears to be an excellent explanation for early anhydrite plugging in some systems. In repeated examples of ancient systems, however, reflux appears to result in updip dolomitization and downdip calcite cementation, which exerts major controls on reservoir porosity. In the Permian and Pennsylvanian rocks of western Kansas, for example, brine reflux led to dolomite reservoirs close to the source of refluxing brines (Luczaj and Goldstein, 2000), but down section, about half of the reservoir porosity was occluded by the same brines farther along their flow path (Goldstein et al., 1991). This process, resulting from reflux, dolomitization, and microbial sulfate reduction, appears to be among the most important diagenetic processes in large-scale reduction of porosity by calcite cementation.

The project proposes to systematically examine regionally extensive reflux systems from the surface and subsurface. It will reconstruct the flow path using cathodoluminescence cement stratigraphy, stable isotope geochemistry, and fluid inclusion microthermometry. These data will be used to calibrate reactive transport models for diagenetic alteration of carbonate systems.

**Deliverables**

This project will provide quantitative data on the effect of reflux processes on carbonate reservoir rocks. It will concentrate first on developing conceptual models for porosity modification, such as top-down and bottom-up patterns related to fluid flow. It will provide ground truth for manipulation of reactive transport models to quantitatively predict distribution of dolomite, anhydrite, and calcite cement related to this process.

**References**


Jones, G.D. and Xiao, Y., 2005, Dolomitization, anhydrite cementation, and porosity evolution in a reflux system: Insights from reactive transport models: American


Figure 1. Regional fluid flow model for dolomitization and calcite cementation in Permian and Pennsylvanian reservoirs, Kansas.
Figure 2. Example of bottom-up diagenetic pattern of dolomitization related to flow of dense fluids along base of aquifer system.
Database - Effect of Sequence Boundaries on Meteoric Cementation: A Tool For Subsurface Modeling

Robert H. Goldstein and students

SUBSURFACE APPLICATION: Important for all carbonate reservoirs that have experienced subaerial exposure such as Tengiz, Arbuckle/Ellenburger/Tarim, Pennsylvanian/Permian of Permian Basin and Midcontinent, Mississippian Midcontinent, Shuaiba, Lisburne Group of Alaska
STATUS: Long-term project in progress
TIMING: Significant results to be reported – Results currently available to membership
FUNDING: Partial

Purpose
It is well known that meteoric diagenesis associated with subaerial exposure may enhance or reduce porosity. The controls on cementation and dissolution during events of subaerial exposure are not simple. This research constructs a database quantifying the effect of various processes of meteoric diagenesis on porosity. Many research groups have shown complex patterns of low-Mg calcite cementation that can be mapped in two or three dimensions, associated with events of subaerial exposure (e.g., Meyers, 1978; Meyers and Lohmann, 1985; Goldstein, 1988; Saller et al., 1994; Carlson et al., 2003; Buijs and Goldstein, 2012). The database includes a catalog of approximately 100 case histories. These case histories can be used as training images or quantitative relationships in subsurface models, and can populate a geomodel using each sequence boundary to predict the control of meteoric diagenesis on distribution of reservoir porosity.

Project Description
Typical subsurface limestones have less than 5% porosity, whereas carbonate sediments at time of deposition commonly have more than 30% porosity. Among the most important factors in porosity decrease is calcite cementation. Thus, many carbonate reservoirs are those that preserve porosity where calcite cementation has not been prevalent. Predicting the distribution of calcite cementation is among the most important factors in predicting the distribution of reservoir porosity. This project will focus on building a database of controls on meteoric calcite cementation from known ancient examples.

Deliverables
The database will include the following:

- Lithofacies-specific effect of meteoric cementation on porosity and permeability (e.g. Figure 1, 2)
- Lithologic controls on calcite cementation (e.g. Figure 3)
- Duration of subaerial exposure and climate factors that affected the flux of meteoric water (e.g. Figure 4)
- Three-dimensional distribution of cements (e.g. Figure 5)
- Approximately 100 examples quantifying patterns of cementation below exposure surfaces and relating those patterns to paleotopographic position and hydrogeology (e.g. Figure 6)
References


Figure 1. Models illustrating the two hypothetical relationships between the decrease in porosity vs. the increase in calcite cement: (A) simple one-to-one relationship, the amount of porosity decrease equals the amount of calcite cement increase; (B) less than 45 degree correlations, dissolution after or coeval with calcite cementation. (after Li et al., 2014)

Figure 2. Plots of calcite cement content vs. porosity and permeability measured from core plugs (A and B, respectively). Plot of calcite cement content vs. PIA porosity (C). Increasing percent of calcite cement leads to predictable decrease in porosity and permeability. The relationships are lithofacies dependent. (after Li et al., 2014)
Figure 3. (A) Original porosity determined from non-compacted areas in the grainstone lithofacies. (B) Original porosity (%), porosity remaining (%) after intermediate-stage cementation, porosity remaining (%) after compaction and rock volume removed (%) by compaction (mean original porosity minus % cement). Data presented are for grainstone lithofacies. (C) Cross plot comparing % crinoids and % intermediate-stage cement in grainstones. (after Ritter and Goldstein, 2012)
<table>
<thead>
<tr>
<th>Surfaces</th>
<th>Duration</th>
<th>Climate</th>
<th>Mineralogy</th>
<th>Meteoric dissolution</th>
<th>Meteoric cementation</th>
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<td></td>
<td></td>
<td></td>
<td>Extent</td>
<td>Amount</td>
</tr>
<tr>
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<td>120-130 kyrs</td>
<td>Arid</td>
<td>primarily calcitic</td>
<td>upper 1.5 m</td>
<td>Less than 1%</td>
</tr>
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<td>150-400 kyrs</td>
<td>More humid</td>
<td>calcitic and aragonitic</td>
<td>upper 2 m</td>
<td>up to 20%, averaging 5%</td>
</tr>
<tr>
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<td>120-350 kyrs</td>
<td>Arid</td>
<td>primarily aragonitic</td>
<td>upper 1.2 m in updip areas</td>
<td>4 to 6%</td>
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<td>Less than 25-100 kyrs</td>
<td>Arid</td>
<td>primarily aragonitic</td>
<td>localized in the upper 1 m</td>
<td>2%</td>
</tr>
<tr>
<td>5</td>
<td>Less than 25-100 kyrs</td>
<td>Less arid</td>
<td>primarily aragonitic</td>
<td>upper 1 m</td>
<td>less than 3%</td>
</tr>
<tr>
<td>6</td>
<td>Less than 25-100 kyrs</td>
<td>More humid</td>
<td>primarily aragonitic</td>
<td>upper 2 m in updip areas</td>
<td>7%</td>
</tr>
<tr>
<td>7</td>
<td>Greater than 5.3 myrs</td>
<td>Both arid and humid</td>
<td>primarily dolomite</td>
<td>the entire carbonate complex</td>
<td>1 to 18%, averaging 12%</td>
</tr>
</tbody>
</table>

**Figure 4.** Summary of diagenetic alteration associated with seven subaerial exposure surfaces in the Miocene of Spain (after Li, 2012; Li et al. 2014)

**Figure 5.** Contour maps represent the basal surface of the upper cemented zone (A), top surface of the lower cemented zone (B), and basal surface of the lower cemented zone (C). (after Li et al., in submission)
Figure 6. Distribution of A1 and B1 calcite in the Wahoo Limestone, northeastern Brooks Range, Alaska. Cements are graphed as estimated percent of total cement. Oldest cements are on the left, and younger cements are added cumulatively to the right. Gray areas to the right represent later cements. All early cements shown formed before or during intra Lisburne events of subaerial exposure. The depth of penetration of calcite cements associated with each surface of subaerial exposure is shown by an arrow at the right margin. Horizons with demonstrated paleotopographic relief are indicated by dashed lines. (after Carlson et al. 2003)
Structural Control on Diagenesis Through Time: The Impact of Setting and Prior Diagenetic Variation on Stepwise Shifts in Reservoir Location

Robert H. Goldstein and students

SUBSURFACE APPLICATION: Important for all carbonate reservoirs experiencing a complex diagenetic history, especially applicable where reservoir sweet spots can be tied to structural position or paleotopographic position such as Tengiz, Pennsylvanian-Permian of Midcontinent and Permian Basin, Jurassic Middle East
STATUS: Long-term project in progress
TIMING: Significant results to be reported – Results currently available to membership
FUNDING: Partial

Purpose
Early stages of diagenesis have a clear impact on later diagenesis by affecting mineral stability, porosity and permeability, and response to compaction. This project seeks to study reservoir rocks and reservoir analogs in the context of original setting to evaluate the evolution of pore systems through time. The focus of this research concentrates on the diagenetic feedback that exists between earlier events and later events, in order to improve understanding of what workflows are important for predicting the location of the best reservoir at multiple stages of pore-fluid history. Given similar setting and history, these case studies will serve as qualitative predictive models for carbonate reservoir porosity. They formulate the conceptual understanding required for eventual application of reactive transport models to aid in reservoir prediction.

Project Description
The project will be divided into several phases, with the first concentrating on the selection of extant carbonate reservoirs that vary in quality over structural or paleotopographic relief. This phase is followed by evaluation of cores to determine impact of depositional setting on original porosity and permeability. Thin section petrography follows, and includes transmitted light and cathodoluminescence. Cements and porosity will be quantified with image analysis techniques. Each diagenetic phase will be analyzed using fluid inclusions and stable isotopes to evaluate cement origin. Finally, reservoir evolution will be integrated with the interpreted diagenetic history to interpret the impact of setting and diagenetic feedback on reservoir distribution through time.

A preliminary study was completed in the Pennsylvanian Lansing-Kansas City group oolitic reservoir rocks on the flank of the Central Kansas Uplift (Poteet, University of Kansas Masters Thesis). This project illustrates the utility of this approach. (1) Initially, Lansing-Kansas City Reservoirs are deposited on flank of Central Kansas Uplift (Figure 1). (2) During early events of subaerial exposure, meteoric cements form best on paleohighs, reducing porosity updip and migrating best reservoir downdip (Figure 2). (3) During burial compaction, brittle compaction is more prevalent downdip because of the lack of early meteoric cements. This leads to higher permeabilities but lower porosity downdip. Best reservoir porosity shifts updip (Figure 3). (4) During the initial phases of
Permian seepage reflux, dolomite forms up section and calcite forms down section. The initial phases of calcite cementation formed preferentially downdip due to higher permeabilities created by the prior stage (Figure 4). (5) During continuation of reflux cementation, preferred zone of cementation shifts to updip areas due to prior preferred cementation downdip (Figure 5). Best reservoir remains updip. (6) After Laramide deformation, hydrothermal fluid flow leads to major alteration of the pore system. Preferred cementation occurs updip due to outgassing, and this leads to shift in better reservoir properties to downdip locations (Figure 6).

**Deliverables**
The work will focus on reservoir studies conducted for KICC companies on their reservoirs. Results will evaluate the controls on evolution of pore systems in different areas with different structural or paleotopographic settings. The work will produce an evaluation of the complex interaction of pore systems through time. Each major diagenetic event will be documented to develop a conceptual understanding of what feedbacks led to the best reservoir locations through time.

**References**

**Figure 1.** Location of cores sampled.
Figure 2. Calcite cement forms preferentially updip during meteoric diagenesis. Star illustrates location of best reservoir porosity.

Figure 3. Highest post-compaction permeability downdip because of preferred mechanical compaction leads to higher porosity updip. Star illustrates location of best reservoir porosity.

Figure 4. Calcite cement precipitates during Permian seepage reflux cementation and downslope wells initially received more cement due to higher permeability after compaction. Star illustrates location of best reservoir porosity.
**Figure 5.** During continuation of seepage reflux calcite cementation, preferred cementation shifts to updip areas because of pore throat reduction by prior stage of cementation, which preferentially reduced pores in downdip areas. This shifts best reservoir permeability away from downdip area. Best reservoir porosity remains updip. Star illustrates location of best reservoir porosity.

**Figure 6.** Laramide leads to structural rejuvenation and hydrothermal fluid flow. Updip settings received more cement than downdip settings because of shallower depth and degassing of active fluid. This shifts best reservoir properties to downdip locations. Star illustrates location of best reservoir porosity.
Predicting Diagenetic Alteration in Carbonate Reservoirs from Sea-level History and Modeling

Robert H. Goldstein, Fiona Whitaker, David Fowle, Anita Csoma, and students

SUBSURFACE APPLICATION: Important for all carbonate reservoirs that have experienced subaerial exposure such as Tengiz, Arbuckle/Ellenburger/Tarim, Pennsylvanian/Permian of Permian Basin and Midcontinent, Mississippian Midcontinent, Shuaiba, Lisburne Group of Alaska, Shuaiba

STATUS: Long-term project in progress

TIMING: Significant results to be reported – Results currently available to membership

FUNDING: Partial

Purpose

Given popular models of low-temperature diagenetic alteration, it would be helpful if diagenetic alteration could be accurately predicted from knowing the history of sea-level change and modeling hydrogeologic data, known rates from extant systems, or chemical equilibria. This is an important direction, and well worth continuing its pursuit (see Whitaker and Smart, 2007; Jones et al., 2003), but still, there remains much to learn about the variables that control diagenesis in such low-temperature systems for effective predictive modeling.

Most researchers focus on freshwater vadose, freshwater phreatic, mixing zone, and marine diagenesis at low temperature (Figure 1). Views of these systems have commonly held that if you get one of these salinity realms, then you get a particular diagenetic product in the rock - whether it is dissolution, cementation, or replacement. The idea that predictable salinity realms should lead to a predictable diagenetic record has been pervasive, but the rock record and modern systems tell another story that should lead us to rethink this model. The purpose of this project is to systematically study the rock record as ground truth in refining conceptual and quantitative models for predicting diagenetic alteration in carbonate reservoirs, given a history of sea-level rise and fall.

Project Description

Given a cycle of sea level fall and rise, one should be able to predict the diagenetic record at a given point in the rock because of the predictable fluids that pass any given point in the rock (Figure 2). Known sea-level history can result in a predictable pattern of cementation (Figure 3). This fluid history would be predicted to form a diagenetic salinity cycle associated with each cycle of sea level change (Csoma et al., 2004). If diagenetic systems are predictable, with each salinity realm leading to a predictable diagenetic product, then each diagenetic salinity cycle should be somewhat symmetrical in terms of diagenetic product, and successive diagenetic salinity cycles should yield repetition in diagenetic products.

In a study of diagenesis associated with a single paleokarst surface, Csoma et al. (2004) recognized a complex paragenesis consisting of no less than 22 paragenetic events, which led to the designation of four diagenetic salinity cycles. The diagenetic products of each were not symmetrical and each of the four resulted in different products. Thus, simple
diagenetic models relating to groundwater salinity realms do not seem to predict diagenetic product faithfully. This research asks the question: why not?

The answer may lie in our understanding of processes in the meteoric realm. Most analyses of early meteoric carbonate diagenesis interpret dissolution, low-Mg calcite cementation, or mineral stabilization as the dominant processes. Few deal with all, and questions remain as to which will dominate in any given ancient system. Even in very young or extant meteoric systems, researchers continue to debate the relative importance of rate of fluid flow, CO₂ degassing near the water table, mixing at the water table, microbially controlled chemistry, and rates related to alteration of unstable minerals (e.g., Budd and Land, 1990; Budd, 1994; 1998; McClain et al., 1992). Some groups focus on dissolution in such systems because of observations in some modern aquifers (Whitaker and Smart, 2007). On the other hand, numerous researchers dealing with reservoir rocks and outcrop analogs have shown a complex record of low-Mg calcite cementation, the distribution of which is related to aquifer configuration, climate, and duration of subaerial exposure (e.g., Goldstein, 1988; Saller et al., 1994; Carlson et al., 2003; and Buijs and Goldstein, 2006)

This project will focus on quantifying the diagenetic processes and products of known sea-level change to refine predictive models of early diagenetic alteration associated with events of subaerial exposure in the stratigraphic record. It will systematically evaluate the formation and reduction of porosity associated with subaerial unconformities on marine carbonates. Techniques include cathodoluminescence cement stratigraphy, fluid inclusion geothermometry and stable isotope geochemistry.

**Deliverables**

The work will provide quantitative models of porosity evolution given various systems of subaerial exposure in carbonate reservoir systems. The long-term goal is collaboration with others to produce refined models for quantitatively predicting porosity distribution in ancient systems.

**References**


CSOMA, A.E., GOLDSTEIN, R.H., MINDSZENTY, A. AND SIMONE, L., 2004, Diagenetic salinity cycles and sea level along a major unconformity, Monte Camposauro, Italy: Journal of Sedimentary Research, v. 74, no. 6, p. 889-903


Figure 1. Traditional hydrozone approach to carbonate diagenesis.
Figure 2. Diagenetic salinity cycle predicted from an event of sea level fall and rise (after Csoma et al., 2004). Yellow spot is fixed point in a carbonate reservoir rock experiencing cycle of different diagenetic environments.

Figure 3. Hydrogeological model for calcite cement precipitation in two cemented zones. (A) Precipitation of calcite in the upper cemented zone along a paleo-water table. (B) After formation of the upper cemented zone, water table dropped from the combined effect of eustatic sea-level fall, tectonic uplift and landscape incision. After the water table fell, the locus of cementation shifted downward, and formed the lower cemented zone. (see Li dissertation for details)
Quantifying Processes of Diagenetic Alteration in Mixing Zones: Cementation, Dissolution, and Dolomitization in Special Settings

Robert H. Goldstein, ExxonMobil team, Anita Csoma, and Zhaoqi Li

SUBSURFACE APPLICATION: Important for all carbonate reservoirs that have experienced subaerial exposure such as Tengiz, Arbuckle/Ellenburger/Tarim, Pennsylvanian/Permian of Permian Basin and Midcontinent, Mississippian Midcontinent, Shuaiba, Lisburne Group of Alaska
STATUS: Long-term project in progress
TIMING: Significant results to be reported – Results currently available to membership
FUNDING: Partial

Purpose
In the context of carbonate diagenesis, mixing zones commonly describe groundwaters that are mixtures between seawater and freshwater, and thus have compositions intermediate between the two. The goal of this project is to systematically evaluate the effect of mixing ratio and end-member fluid composition on diagenetic processes in mixing zones to evaluate the effects on porosity in carbonate systems.

Project Description
Given mixing of seawater and meteoric waters, in the past, most researchers would call on dolomitization and perhaps dissolution in carbonates (Runnels, 1969; Badiozamani, 1972; Land, 1972; Plummer, 1975). Researchers would expect that mixing ratio would be the primary control on the diagenetic product, as that is supported by thermodynamics. Many recent studies of mixing zones, however, fail to show dolomite, or the interpretation of the dolomite’s origin is debated (e.g., Csoma et al., 2006; Figure 1). On the contrary, mixing zones seem to produce a wide variety of cement mineralogies from low-Mg calcite, to high-Mg calcite, to aragonite, and dissolution (Frank and Lohmann, 1995; Melim et al., 2004; Csoma et al., 2004). Moreover, fluid inclusion data show no predictable control of mixing ratio on mineralogy of precipitate or dissolution (Csoma et al., 2006). It appears that dynamic processes, such as outgassing at the water table and microbial activity, may dominate predictability in these systems, and this interpretation calls for geochemists to take a new approach toward modeling such systems.

Moreover, the state of the end member saline fluid may exert a significant effect. It is known that there have been times when tropical surface seawater was precipitating aragonite and high-Mg calcite, as it does today; but it is also well known that at other times, dominant mineralogies of tropical seawater precipitates were calcite (Sandberg, 1983). During some of those times, it appeared that aragonite in tropical surface seawater dissolved right on or just below the seafloor (Johnson and Goldstein, 1993; Wright and Cherns, 2007). Some reasons for these shifts have been changes in atmospheric pCO₂ and marine Mg/Ca over time (e.g., Demicco et al., 2005; Berner and Kothavala, 2001), demonstrating that modern seawater may not be the best model for ancient seawater.

This project concentrates on fluid inclusion and stable isotopic analysis of purported mixing zone diagenetic phases to characterize processes and products through time and in various hydrologic settings. It evaluates the effect of mixing ratio, proximity to water
table, hydrogeology of the system, and composition of saline end member as controls on processes and products in mixing zones.

**Deliverables**
Recent results have indicated that the mixing zone dolomite model is not dead, as suspected by many. The research already has provided quantitative data on dolomite distribution by this (Figure 2) process and discovered a new hydrologic mechanism controlling dolomitization called ascending freshwater-mesohaline mixing (Figure 3). This type of dolomitization by ascending mixing leads to porosity enhancement (Figure 4). All other mixing zones appear to lead to cementation and dissolution depending on proximity to water table, and microbial activity. Mixing ratio is less important than originally proposed on diageneric product.

Deliverables will be a series of case studies in various settings. These projects define the parameters that are needed to be modeled for quantitative prediction of mixing zone systems in reactive transport models. Reactive transport modeling will be applied to evaluate parameters useful in predicting dolomitization by ascending freshwater-mesohaline mixing.

**References**


Figure 1. Fluid inclusion data (from Csoma et al. 2006) illustrating that water table dynamics appear to be a more important control on diagenetic process than mixing ratio.

Figure 2. Cross section of La Molata Platform with contours of percent dolomite superimposed to illustrate the distribution of dolomite. Dolomite abundance increases basinward and stratigraphically downward. In general, this carbonate platform has been extensively dolomitized. The rocks of greater than 90% dolomite comprise at least 80% of this platform (Li et al., 2013)
Figure 3. Dolomitization from ascending freshwater-mesohaline mixing. Fractures in the volcanic rocks provide fluid pathways for freshwater flux. Hydraulic head from hinterland and density contrast force freshwater upward when discharging into carbonate platform. This creates extensive fluid mixing. Upward flow of fluids leads to decrease of pressure, which results in degassing of CO₂. Fluid mixing of freshwater and mesohaline seawater, and degassing of CO₂ may all be responsible for extensive dolomitization (modified from Li et al. 2013).

Figure 4. Correlation between dolomitization from ascending mixing and enhancement of moldic porosity (thesis by Tony Pugliano).
Modification of Reservoir Porosity by Hydrothermal Fluids: Recognition and Setting

Robert H. Goldstein and students

SUBSURFACE APPLICATION: Ghawar Field, North Field, Devonian of Western Canada, presalt Brazil/Angola, Mississippian Lincoln County Colorado, Albion-Scipio, Tengiz, Trenton-Black-River, Arbuckle/Ellenberger and Pennsylvanian Permian Basin and Midcontinent, Mississippian Lime in Kansas, Woodford Chert of the southern USA midcontinent, Shale plays of the Permian Basin, and Bakken/Lower Lodgepole play

STATUS: Long-term project in progress
TIMING: Significant results to be reported – Results currently available to membership
FUNDING: Partial

Purpose
It is now well known that warm fluids injected into cooler rocks have an effect on thermal maturation and porosity distribution. In some cases, such hydrothermal systems enhance porosity and in others they reduce it. The goal of this long-term project is to develop techniques for recognition of hydrothermal systems, and evaluate how geologic setting controls porosity modification to begin to form predictive conceptual models useful in the oil and gas industry.

Project Description
Carbonate specialists are just now identifying the hallmarks of hydrothermal processes (e.g., Smith and Davies, 2006) and recognizing that many pore systems thought to have formed by meteoric waters were likely to have formed from hydrothermal fluids (Esteban and Taberner, 2007). Some of the largest oil (e.g., Ghawar) and gas (e.g., North) fields have been affected by hydrothermal alteration. Hydrothermal processes in reservoirs are known to lead to moldic porosity (e.g., Newell et al., 2003), cavernous pores (Carlson, 1995), vugs (Hiemstra and Goldstein, 2005) and solution enlargement of fractures. Ultimately, the explanation for hydrothermal porosity enhancement may simply be the cooling of hydrothermal fluids, which leads to undersaturation with respect to carbonate minerals (Rossi et al., 2002), but mixing and other processes are possible (Mazzullo and Harris, 1991; Salas et al., 2007).

To understand many hydrothermally enhanced reservoirs, it appears necessary to understand early as well as late paragenesis. For example, using data from the Indian Basin Field, New Mexico, Hiemstra and Goldstein (2005) showed that the distribution of hydrothermal dolomite and secondary porosity were controlled by depositional setting, preferentially forming where facies were deposited deep enough to escape early meteoric diagenesis, as well as proximity to fault and fracture systems in the presence of a fluid drive (Figure 1). This complex group of controls led to the best reservoirs forming only in downdip positions, and would not have been predictable without understanding the earlier paragenesis.

This project will systematically study reservoir carbonates and use fluid inclusion and other geothermometers to develop methodologies for the identification of ancient
hydrothermal systems. Models for fluid flow will be developed for implementation of predictive models based on geologic setting.

**Deliverables**

Hydrothermal alteration is clearly important in the localization of sandstone and carbonate oil and gas reservoirs as well as MVT ore deposits (e.g. Leach and Sangster, 1993; Wojcik et al., 1997; Rossi et al., 2002; Cantrell et al., 2004; Smith and Davies, 2006; Davies and Smith, 2006). Fluid inclusions and other geothermometers are essential in recognizing ancient hydrothermal fluid flow. Geothermometers, such as fluid inclusions, are useful in identifying when and where the normal burial system has been perturbed by hydrothermal fluid flow and flow of cool waters into warmer rocks.

New results show that hydrothermal systems typically require a mechanism to move fluids upward from deeper parts of the basin, a setting in which warmer fluids exist and are capable of being transmitted into cooler rocks, and conduits such as fractures or permeable horizons that provide a focus for rapid fluid flow.

There has been much discussion of the criteria necessary to identify ancient hydrothermal heating (e.g., Machel and Lonnee, 2002; Esteban and Taberner, 2003; Davies and Smith, 2006). It has been suggested that measured paleotemperature higher than predicted from burial history modeling is an appropriate indication. On the other hand, it must be pointed out that the many assumptions of such modeling and the nature of the thermal maturity data typically available (i.e., vitrinite reflectance, pyrolysis data from Rockeval) normally make it impossible to unequivocally distinguish between a hydrothermal system, higher heat flow than modeled, or deeper burial than interpreted.

New models, developed in this research, for identification of hydrothermal systems include evidence for: (1) fluctuating paleotemperature; (2) geothermometers higher than possible from burial history models; (3) gradients and pressure data inconsistent with normal thermal regime; (4) variation in paleotemperature at same depth; and (5) higher paleotemperatures in conduits (Figure 2).

Detailed case histories of hydrothermal alteration will be used to constrain geologic models of localization of porosity enhancement and reduction.

**References**


Figure 1. Core images from the Indian Basin field, studied by Erik Hiemstra. Hydrothermal processes have both enhanced and reduced porosity.

Figure 2. A. Carbon and Oxygen stable isotope data from Indian Basin field of New Mexico. Data come from dolomite cement, correlated with cement stratigraphy and shown to be approximately time equivalent throughout the area. Circled data are from fault zones and other data come from the same dolomite phase away from fault zones. The more negative oxygen isotopic data indicate that the dolomite from the fault zones formed from warmer fluids than the dolomite outside of the fault zones. This character confirms a hydrothermal origin in which the fault zones were preferred conduits for fluid flow (Hiemstra and Goldstein, 2005) B. Stratigraphic variation in vitrinite reflectance values from Pennsylvanian strata of southeastern Kansas. Locally, anomalously high vitrinite values are located in close stratigraphic proximity to the sub-Pennsylvanian unconformity. The diagram shows schematically that the sub-Pennsylvanian unconformity is a regional paleokarst, and that it acts as a regional stratigraphic conduit for hydrothermal fluid flow. The Pennsylvanian section, however, acts as a leaky confining unit. This pattern confirms hydrothermal fluid flow for the system. Data from Barker et al. (1992). Modified from Walton et al. (1995).
Fracture, Fluid Flow and Diagenetic History of the Arbuckle Group

Robert H. Goldstein, Evan K. Franseen, W. Lynn Watney, Bradley King

SUBSURFACE APPLICATION: Arbuckle/Ellenberger/Tarim reservoirs
STATUS: Newly completed
TIMING: Significant results available to membership; project complete
FUNDING: Partial funding from DOE

Purpose
Complex fractured and dolomitized reservoirs are some of the prime targets for geologic CO₂ sequestration and oil and gas production. The Ordovician Arbuckle Group, and its equivalents, comprise an extensive system (Figures 1, 2) with an exceptional history of oil production from porosity modified by dolomitization, karst, fracturing, and hydrothermal alteration. This research is part of a larger study to characterize the Arbuckle Group reservoir to improve understanding of the effect of diagenesis on reservoir rocks. The project’s focus is to understand the geologic fundamentals behind the internal stratal architecture, structural deformation, and diagenesis and to evaluate their role on flow units, cap rock integrity, aquifer storage, and identification of reservoir compartments and barriers to flow. This part of the project concentrates on the late fracturing, fluid flow, and diagenetic alteration as a model for reservoir evolution.

Project Description
Fractured carbonates are important oil and gas reservoirs, as well as sites for geologic CO₂ sequestration. Understanding the fundamental controls on fluid flow in such systems have wide-ranging implications.

In this study, core samples have been examined by petrographic and geochemical tools to determine diagenetic environment and history so that its influence in creation of impermeable and permeable zones can be ascertained. Cathodoluminescence, SEM-BSE, and transmitted-light petrography will establish a cement stratigraphy and the extent and nature of fracture-fill sequences. Fluid-inclusion microthermometry, supplemented by Raman microprobe analysis, will provide temperatures, salinities, and compositions of fluids precipitating and recrystallizing mineral phases. UV epifluorescence microscopy will identify petroleum fluid inclusions so that oil migration can be placed into the diagenetic history. Growth zones in fracture fills will be microsampled for stable isotopes (C, O, Sr) to help interpret the processes of dolomitization and cementation and to determine their timing and influence in permeability.

Diagenetic analyses will place pore-producing and cementation events in a stratigraphic, temporal, tectonic and conceptual framework. We will establish cross-cutting relationships between diagenetic growth zones, fractures, stratigraphic surfaces, and karst to establish a cement stratigraphy (e.g., Voss et al., 1989; Farr, 1989; Gregg et al., 2001). Primary fluid inclusions will provide the record of temperature and salinity of fracture healing, dolomite precipitation and recrystallization (Goldstein and Reynolds, 1994).
Deliverables
The project will provide a characterization of the late diagenetic history of the Arbuckle Group placed in the context of tectonics and regional fluid flow. It will evaluate history of leakage through the Arbuckle in the context of characterization of possible leakage pathways, modeling of fluid flow, regional CO₂ sequestration potential, and regional source-sink relationships. Preliminary work shows complexly zoned late dolomite (Figure 3) with high fluid inclusion homogenization temperatures (Figure 4) and Tm ice indicating decreasing salinity of brine (Figure 4). Data suggest hydrothermal fluids affected porosity and permeability through initial flow of connate fluids and gas separation. Later, hydrothermal basinal brines were transported advectively with warmer, lower density fluids flowing along the top of the Arbuckle (Figure 5). Later fracture-flow dominated the hydrothermal system. A relationship between hydrothermal flow and porosity suggests that strategies for exploration and production in the Arbuckle could incorporate concepts of structurally controlled hydrothermal circulation (e.g., Devonian of Western Canada and Trenton-Black River; Qing and Mountjoy, 1992, 1994; Allan and Wiggins, 1993)

References
WATNEY, W.L. AND BATTACHARYYA, S., 2009, Modeling CO₂ sequestration in saline aquifer and depleted oil reservoir to evaluate regional CO₂ sequestration potential of Ozark Plateau aquifer system, south-central Kansas, DOE Grant Proposal 076248616
**Figure 1.** Setting of study area for the Arbuckle Group strata (base Simpson to Precambrian) in the Midcontinent of North America.

**Figure 2** (left). Java-based color imaging well profile of deep cored Arbuckle injection well #10 at the Occidental Chemical brine injection site near Wichita, Kansas. (From Watney and Battacharya, 2009)
Figure 3. Arbuckle Group paragenesis was established using cross-cutting relationships observed in core, transmitted light, and UV-epiﬂuorescence.

Figure 4. Summary of homogenization temperature measurements (Th) and salinity data.
Figure 5. Cross-plot of $\delta^{18}O$ values and depth of samples. $\delta^{18}O$ values clearly become more depleted with decreasing depth, likely illustrating higher temperatures, potentially caused by preferential fluid flow or temperature-controlled density stratification in the Arbuckle Group. The gradual depletion of $\delta^{18}O$ with decreasing depth, especially within Scheffer’s (2012) low porosity/permeability zone, supports a temperature-controlled density gradient affecting the entire unit at the time of baroque dolomite precipitation. Blue boxes represent modern zones of higher porosity/permeability due to solution enhanced fractures and brecciated zones (Scheffer 2012). The data appears to follow a trend of increasingly depleted values towards the top of the unit, regardless of modern reservoir conditions.
Early Diagenesis and Petrophysical Evolution of Reef-Associated Carbonates

Michelle Mary and Gene Rankey

SUBSURFACE APPLICATION: Isolated carbonate platform reservoirs, especially Cenozoic examples; quantitative data on spatial patterns in diagenesis that can be used for modeling subsurface systems
STATUS: Focused-term project in nearing completion
TIMING: Significant and final results to be reported to membership this year
FUNDING: AAPG, AWG, ExxonMobil, GSA and KICC

Purpose
Diagenesis can be a fundamental control on porosity and permeability, modifying original depositional textures. In many carbonate systems, diagenesis starts as early sediment modification in the marine realm, where it can be essentially syndepositional and rapid (see Grammer et al., 1993, and discussion within). This syndepositional diagenesis can include early marine cementation as well as sediment modification by the processes of bioerosion. Although previous work has shown that reef margin carbonates tend to be better cemented than platform interior sediments (James et al., 1976; Macintyre, 1977; Marshall, 1985), studies quantifying changes in abundance or type of cement across platforms are rare. In addition to aiding grain diminution, boring organisms create macro- and micro-porosity. This porosity can be preserved, occluded, or facilitate the subsequent wholesale diagenetic alteration of grains. Studies of bioerosion rates across entire platforms are absent from the literature. The main purposes of this project are to 1) evaluate and quantify the nature and controls of early porosity creation by bioerosion and 2) explore spatial variability in the character and extent of early cementation, by examining a well-constrained and well-exposed Holocene system in the equatorial Pacific.

Project Description
Examining trends in early diagenesis among well-exposed and well-constrained Holocene atolls provides quantitative information on spatial variability and potential controls on both bioerosion and cementation. Coupled with petrophysical data (porosity, permeability, and acoustic velocity), these spatial trends and information on potential controls provide quantitative information that are essential for modeling the effects of early diagenesis in analogous ancient reservoir systems.

Three atolls (Tarawa, Aranuka, and Beru) in the western equatorial Pacific (Gilbert Island Chain, Kiribati) were included in the study. Prominent around all three atolls are mid-Holocene (3,500 to 1,500 years B.P.) strata from previous sea-level high(s), that now outcrop above present-day sea level. These Holocene deposits are mainly barforms of coral rubble, and are oriented normal to the platform margin.

Ichnologically-produced porosity via bioerosion
To better understand the nature and controls of bioerosion in atoll settings, this study utilizes several strategies including \textit{in situ} block experiments, collection of coral rubble, and petrographic and scanning electron microscopy (SEM) analysis. Blocks were placed on transects from platform margin to interior on both windward and leeward margins of Aranuka Atoll. Rates of bioerosion are calculated for the duration of the experiment by combining the depth of penetration of bioeroding organisms with the surface area expression of boreholes. Results indicate that rates of bioerosion vary predictably with relation to the platform margin in this atoll system, and that although rates of removal seem low, on geological time scales, bioerosion can play an important role in the modification of carbonate sediment.

\textit{Early Cementation and Porosity Evolution}

Variability in Holocene rock outcrops of the three atolls is captured through systematic sampling of several transects from the margins to the lagoon on each atoll on both windward and leeward margins. Petrographic thin sections, SEM observations (including energy dispersive x-ray spectrometry), and image analysis (JMicroVision) allow for quantification of relative amounts of cement, macroporosity, and sediment characteristics. Petrophysical parameters, including velocity, porosity, and permeability, were measured on a subset of 1-inch diameter core plugs from all three atolls.

Depositional porosities across all atolls range from 7.5 – 64%. Early cementation is complex and includes spatially variable pores. Up to six cement phases can reduce porosity between 0.1 and 27%. Variability in both depositional porosity and cementation results in petrophysical heterogeneity. Measured total plug porosity varies from 3–36%, permeability varies from 61–19,500 mD, and compressional velocity varies from 4,000 to almost 6,000 m/sec. Multivariate regressions provide insights into possible relationships between potential controls and metrics of depositional porosity, cement, and velocity.

\textbf{Deliverables}

To explore diagenetic pathways and links between depositional and diagenetic processes, this project examines the earliest stages of diagenesis of a young, well-constrained system. Results will relate spatial changes in rates of bioerosion and will demonstrate how over geologic time periods, bioeroding organisms can modify large amounts of reef-derived material. Other results will relate geographic location relative to the platform margin, grain size and type, and pore size and type with complex and includes spatially variable cementation patterns. Collectively, these processes could create pronounced interwell-scale diagenetic and petrophysical heterogeneity that would not be predicted by simple conceptual diagenetic models. These results will be captured in the dissertation chapters of Michelle Mary, and presented in final form to sponsors by end 2016.

\textbf{References}


Figure 1. Representative textures, Holocene of Aranuka. A) sample with highest velocity has the lowest porosity, with a more complex pore system made of relatively small pores. B) sample with relatively low velocity, note that cement is concentrated predominantly at grain contacts. C) large interparticle pores remain open with almost complete pore-filling cement in smaller interparticle pores. D) sample is dominated by intraframe porosity rather than interparticle porosity; velocity is similar to C.
Sedimentology and Diagenesis of the Miocene-Pliocene Mona Reef Complex

Luis Gonzalez and Wilson Ramirez (UPRM)

SUBSURFACE APPLICATIONS: Dolomitized and karstified carbonate reservoir in isolated platforms. Such as Malampaya field, Philippines; Luconia province, Malaysia; Banyu Urip Field, Indonesia
STATUS: Long-term project in progress
TIMING: Significant results to be reported – results on dolomitization and stratigraphy currently available to membership
FUNDING: None

Purpose
Isla de Mona (Figure 1) and Isla Monito are uplifted and faulted carbonate plateaus that expose sections of the only known Miocene-Pliocene reef complex in the Caribbean. The excellent 3D exposures on these two islands allow for detailed facies mapping and sampling of this unique reef complex. The upper units of the reef complex have been extensively karstified (Figure 2) and the lowermost units densely dolomitized (Figure 3). Dolomitization and karstification are early and appear to be controlled by sea-level oscillations (Gonzalez et al., 1997).

This study focuses on the generation of detailed facies maps of the reef complex, structure, and strontium isotope “dating” of exposure surfaces, limestone units, and dolomitized units. The goals are to produce a model of reef development linked to glacio-eustatic (global) or tectono-eustatic (local) oscillations. The model will serve as the foundation for diagenetic studies delineating mega-porosity (caves), macro- and micro-porosity distribution and evolution and dolomitization.

Project Description
The Isla de Mona plateau is composed of two Neogene lithostratigraphic units originally defined and named by Kaye (1959) and later redefined by Briggs and Seiders (1972) to the current units Lirio Limestone (Figure 2) and Isla de Mona Dolomite (Figure 3). Whereas Caribbean coral reef diversity and abundance increases in the late Miocene, no major shelf edge (i.e., barrier) system had been recognized prior to the 1990’s. The Mona Reef Complex in Isla de Mona is the first discovered and described Miocene-Pliocene (10 to 4 Ma) barrier reef complex in the Caribbean (Gonzalez et al., 1997). It is during the Miocene to Pliocene that the gradual (step-wise) closure of the Central American Seaway (CAS) occurred, and coupled with sea-level oscillations, controlled oceanic circulation from the Pacific to the Atlantic oceans (Burton et al., 1997). Furthermore, during the Miocene to Pliocene, this region was undergoing collision with the Bahamas platform resulting in clockwise rotation of Puerto Rico and the opening of the Mona Passage (Dolan et al., 1998). Thus, the Mona reef complex affords us a unique opportunity to gain understanding on the relative roles of global (glacio-eustatic), regional (closure of the CAS), and local (faulting) controls on reef development.
The reef complex exposed on Isla de Mona and Isla Monito bear many similarities in terms of facies and stratal geometries to subsurface reef reservoir systems reported from the Philippines, Malaysia, Australia and Indonesia (Wilson and Bosence, 1997; Kusumastuti et al., 2002; Neuhaus et al., 2004; Vahrenkamp et al., 2004; Ehrenberg et al., 2006) (Figure 1).

Recent observations by our research team reveal that the Mona Reef Complex had two distinct phases of growth (Figure 4). A Miocene (Stage 1) phase is characterized by a \textit{Stylophora} reef framework, and is terminated by major exposure and development of an erosional surface (Stage II) in the late Miocene. Growth resumed in the Pliocene (Stage III) with a reef core dominated by \textit{Acropora cerviconis} and \textit{Caulastrea portoricensis}. Laboratory work ($^{87}\text{Sr}/^{86}\text{Sr}$ determinations, petrography) will help produce more accurate timing (ages) of deposition, faulting, calcitization, and dolomitization. As the reef complex has not been deeply buried, nor are there volcanic activity at this late stage of the arc, dolomitization must have been effected by marine or mixed freshwater - marine fluids.

**Deliverables**

- Conceptual model for evolution of barrier reef in a post-volcanic phase island arc collisional system.
- Predictive model for early karstification and dolomitization, porosity evolution and distribution.
- Rate estimate and rate law for massive dolomitization

**References**


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**Figure 1.** (left) View of Isla de Mona from approximately 20,000 ft. North side of island is toward bottom of picture. (right, upper) A Subsurface Middle Miocene carbonate platform at Luconia Province, offshore Sarawak, Malaysia. This Miocene Platform is located in a regional fault-bounded structural high, first aggraded and then backstepped during a series of third-order sea-level fluctuations (Vahrenkamp et al., 2004). (right, lower) Bathymetry of the Mona Passage: Modified from UGS: New Bathymetric Map of Mona Passage, Northeastern Caribbean, Aids in Earthquake-and Tsunami-Hazard Mitigation (http://soundwaves.usgs.gov/2007/05/).
Figure 2. Karstified reef facies of the Isla de Mona Reef Complex (Lirio Limestone) along the cliffs on the southern side of the island.

Figure 3. Back reef to lagoon dolomitized facies (Isla de Mona Dolomite) exposed on cliffs of the southeastern tip of Isla de Mona (Pta. Este).
Figure 4. The evolution of the reef complex is divided in three stages that are attributed to episodes of relative fluctuations in sea level. The first stage comprises the deposition of a Miocene reef complex (Unit I) that is characterized by a *Stylophora* reef framework. The second stage represents a period of subaerial exposure that is associated with local tectonism. The third stage encompasses the deposition of the Pliocene reef complex (Unit II) that is characterized by an *Acropora cervicornis* and *Caulastrea portoricensis* reef framework. The platform was uplifted during the Late Pliocene to Early Pleistocene followed by the deposition of Pleistocene reef terraces.
Carbonate Cementation in Meteoric Phreatic Systems: Morphology, Distribution, and Rates

Luis A. Gonzalez, Jennifer Roberts, Robert H. Goldstein

SUBSURFACE APPLICATIONS: Broad application to systems that have undergone early cementation in meteoric phreatic systems. Results can constrain predictive modeling.
STATUS: Long-term project in progress
TIMING: Significant results to be reported – Results currently available to membership
FUNDING: Currently none, earlier work funded by Shell.

Purpose
This project simulates precipitation of carbonates (i.e., cementation) under phreatic conditions and seeks to:

- Quantify rates of carbonate cement precipitation
- Quantify the impact of microorganism on carbonate cementation
- Quantify the relative role of flow rates vs. saturation (e.g. fluid chemistry) on cementation
- Quantify the impact of diminishing permeability as cementation progresses.
- Establish petrographic and geochemical diagnostic criteria for the identification of inorganic vs. microbially mediated cementation

To date, very little experimentation has been conducted to simulate and quantify carbonate cementation processes in shallow or deep phreatic systems. Yet, such data is crucial to the modeling of porosity/permeability evolution in carbonate and other systems in which carbonate cements play key roles. The lack of such data limits the accuracy and utility of predictive models for cementation and is imperative that rate laws and appropriate algorithm for cement distribution be integrated with reactive transport and porosity evolution models.

Project Description
During much of the second half of the 20th century carbonate geologists embarked in extensive documentation of carbonate diagenetic features in modern and ancient systems while geochemist conducted numerous experiments aimed at determining the physicochemistry of carbonate precipitation. While much progress was made in the understanding of carbonate dissolution processes, many uncertainties regarding carbonate precipitation remain. Surprisingly, empirical data have rarely been integrated in experimental design, and few experimental designs have actually simulated natural systems. Our recent work (DeChoudens-Sanchez, 2007; DeChoudens-Sanchez and González, 2009) on the simulation of speleothem precipitation has shown that experimental design integrating empirical observations is key to replication of mineralogy and textures in natural systems. Furthermore, few studies have systematically carried out comparative experiments of inorganic and microbially mediated or assisted precipitation.
Our team has applied the lessons learned from simulation of vadose carbonate precipitation to create a flow-cell design that simulates phreatic cementation. After extensive trouble-shooting of the experimental apparatus the system is ready for intensive simulations of cementation in phreatic systems. Initial experiments have produced cementation fabrics that are nearly identical to those observed in nature (Figure 1). Two surprising findings in the early stages of experimentation are: 1) the formation of putative meniscus cements (Figure 2), and 2) the observation that cementation rates appear to be greater under slower flow conditions. If reproducible, the former observation questions the validity of the paradigm of meniscus cements as indicators of vadose environments. The latter is counterintuitive as other experimental and empirical work suggested that increased reactant delivery rates, as controlled by increased fluid flow, would result in faster carbonate cementation. Our experimental simulations of vadose systems have also shown that inorganic processes can produce many textures and fabrics that have been utilized as diagnostic of microbially mediated precipitation (DeChouden-Sanchez et al., 2007).

Our current and future work focuses on simulation on carbonate cementation under a range of flow rates, fluid chemistry, and temperature in which parallel simulations of inorganic and microbially influenced systems are run. Both the impact of living and dead microbial biomass is being explored. Whereas spheres and ooids are the substrate of choice in early experimentation, the experiments can utilize a variety of carbonate substrates (sands) from modern environments or reservoirs. The experiments are designed to allow quantification of cementation rates, distribution of cements, and temporal and spatial evolution of cements and their impact on permeability. Long-term experimentation (i.e.- running experiments for over a year) is expected to allow study of replacement processes and resulting fabrics.

**Deliverables**
The outcome of these simulations will be kinetic rate laws that can be integrated into predictive models and simulation. These will: 1) include fluid chemistry dependence; 2) quantify impact of biomass on cement mineralogy, morphology, and fabrics; and 3) describe models, equations, or algorithms of the temporal evolution and spatial distribution of cements and their impact on permeability.

**References**
DECHOUDENS-SÁNCHEZ, V., 2007, Calcium carbonate polymorphism: new insights into the role of solution saturation state and composition (Mg/Ca) on calcium carbonate mineralogy, morphology, and fabrics: [unpublished Ph.D. dissertation], University of Kansas, 203 p.


Figure 1. High-Mg calcite cemented silica spheres (0.5 mm diameter). Isopachous fibrous calcite with binding of spheres along grain-to-grain contacts has produced aggregates that resemble grapestone. Fluid Mg/Ca 1:1.

Figure 2. Apparent high-Mg calcite meniscus cement (?) developed along silica sphere contacts.
Carbonate Cementation in Meteoric-Marine Shoreline Systems: Revisiting Beachrock Cementation Processes

Luis A. Gonzalez, Jennifer Roberts, George Tsoflias, Chi Zhang, Isabel Villaneda van Vloten

SUBSURFACE APPLICATION: Broad based application to early marine phreatic, marine vadose, and mixed meteoric-marine early diagenetic processes. Specific reservoirs with identified beachrock cementation include the Eocene upper Wilcox in southern Louisiana and the Albain Macae Formation of the Campos Basin in Brazil,

STATUS: Focused-term project in progress

TIMING: Significant results to be reported

FUNDING: KICC.

Purpose
This project is investigating cementation on carbonate and mixed carbonate sands along northern and western shorelines of Puerto Rico focusing on active beachrock formation. The study seeks to

• Determine the relative role of physical factors (wave energy, wind velocity and persistence, beach/coast line geometry, etc.) on beachrock distribution.
• Determine the interplay, if any, between meteoric-water and seawater and relative importance of phreatic vs. vadose systems.
• Conduct a rigorous mapping of the beachrock system including geometries of deposits and distribution of associated phreatic systems and their mixing zone.
• Evaluate biotic processes, in particular microbial processes, and their possible impact on beachrock cementation.
• Carry out rigorous geochemical analysis of fluids associated with beachrock deposits and adjacent non-cemented sands.

Project Description
Beachrock deposits are most abundant along high-energy tropical coasts although they can be found in subtropical and even high latitude shorelines. In current literature there is no concurrence over the process that result in sand cementation and generation of beachrock. It is unclear whether these processes occurs as a result of marine water and meteoric water mixing, solely in the unsaturated water zone (vadose), or in the presence of marine water alone. It is also unclear if cementation is a result of a unique process or a result of diverse set of conditions. There is also very little data and no consensus on the role of microbial activity in cementation.

This research has applications to the study of reservoir and aquifer properties, particularly porosity and permeability distribution. Beachrock deposits retard erosion, it allows preservation of sand deposits that can become future reservoirs. Beachrock also provides a relatively impervious layer of protection from cementation for underlying units. These layers limit cementation to proximal sand units and preserve primary porosity and permeability.
Three study areas in Puerto Rico (2 sites in northern and 1 in western Puerto Rico) will showcase different energy levels, rainfall amounts, and microbial communities. Selected deposits in Puerto Rico are readily accessible allowing for deployment of the instrument intensive study arrays. GPR, coring, and sampling for microbial and geochemical analysis have been conducted. Resistivity surveys will be conducted in the near future. Age of sampled beachrock deposits has been constrained by the presence of artifacts that can be dated to early Spanish occupation, and to key events controlling first or last occurrence of artifacts found on beach rock (e.g. last appearance of tar deposits from offshore tanker cleaning operations; occurrence of dateable glass and metal artifacts, etc.).

**Deliverables**

The major deliverable of this project will be

- A quantitative data set that will allow us to better understand porosity and permeability distribution in areas of beachrock cementation.
- A rigorously collected physical and biogeochemical data set that will can used in developing a cementation predictive model.

**References**


KENDALL, C. G.SST C., SADD, J. L., AND ALSHARHAN, A., 1994, Holocene Marine Cement Coatings on Beach-rocks of the Abu Dhabi Coastline (UAE); Analogs for Cement Fabrics in Ancient Limestones: Carbonates and Evaporites:, v. 9, p. 119-31.

Experimental Approaches to Primary Low-Temperature Dolomite Formation in Carbonate and Mixed-Siliciclastic Systems

Jennifer Roberts, Luis González, Randy Stotler

SUBSURFACE APPLICATION: Applicable to modeling microbialite and carbonate reservoir diagenesis and lacustrine carbonate reservoirs.

STATUS: Project Proposed

TIMING: Proposed experiments June 2016-December 2017

FUNDING: KICC seed funding.

Purpose

Our proposed research will focus on low-temperature dolomite formation in evaporative and lacustrine environments. The role of microbial surfaces in enhancing kinetics of low temperature dolomite (Kenward et al., 2013; Roberts et al., 2013) in a variety of environments and our recent work has suggested (Voegerl, 2014; Edwards et al., 2016) that microbial biomass may play a substantial role in dolomite formation in hypersaline and variable salinity environments. Mechanisms of dolomite formation are further clouded by the presence Mg-bearing clays (e.g. Bontognali et al, 2010), which can also nucleate via microbial biomass (e.g. Burne et al., 2014). Mg-bearing clay formation and subsequent dissolution in lacustrine microbialites underpin models for reservoir porosity formation and preservation (e.g. Tosca and Wright, 2015; Kenward et al., 2012) as well as dolomitization of calcium carbonate phases.

Our recent work in the alkaline lakes of the Sand Hills, Nebraska presents a natural analogue for lacustrine carbonate reservoir formation (e.g., Alonso-Zarza and Warme, 1990; Wright, 2012) as well as a rare location in which low temperature dolomite is currently forming. These lakes also host putative stevensite ((Ca0.5,Na)0.33(Mg,Fe++)3Si4O10(OH)2•n(H2O)) formation in organic-rich, alkaline, saline fluids. Despite variation in salinity and concentrations of Mg and silica, yet persistently high pH and alkalinity in lakes, stevensite, calcite and aragonite are ubiquitous, while dolomite is only present in a single lake.

We will use experimental approaches that address the availability of Mg$^{2+}$ in dolomite nucleation and precipitation in high pH, organic-rich, alkaline fluids. Our goal is to further investigate the role of organic matter in Mg$^{2+}$availability and dolomite nucleation, but investigating a range of fluid geochemistry that span lacustrine to sabkha. Results from this work will support a conceptual model for low temperature dolomite formation and produce quantitative data that can be incorporated into diagenetic models for dolomite reservoirs, including those that form in carbonate and mixed carbonate/siliciclastic evaporative and lacustrine systems.

Preliminary Results

We have devised an experimental protocol that produces disordered and ordered dolomite at 30°C in as few as five days. The protocol utilizes synthetic or dead organic matter.
with high carboxyl group densities that we hypothesize are responsible for the dehydration of Mg$^{2+}$, which is the rate-limiting step in dolomite nucleation at low-temperature (e.g. Roberts et al., 2013). These efforts provide a sound basis for experiments that will quantify rates and capture the heterogeneity of natural systems. We know have the opportunity to apply these successful protocols to natural systems that are relevant to carbonate reservoir formation. Our preliminary results from alkaline, saline lacustrine environments in the Sand Hills of Nebraska, indicate extensive carbonate mineral formation, including dolomite, coincident with the clay mineral, stevensite (Figure 1). Because these lakes are saline (I=0.1-9M), they are also ideal locations to field test hypotheses about conditions that promote highly carboxylated organic matter, responsible for dolomite nucleation at low temperature (e.g. Roberts et al., 2013). Our results also show that microbial surfaces respond to increased salinity by increasing density of surface function groups, including carboxyl groups that dewater Mg$^{2+}$ ions and promote dolomite formation. These results tie microbial physiology to environmental conditions and give insight into microbial controls on low-temperature dolomite precipitation in sabkha and lacustrine environments, yet the dataset still requires measurement of natural microbial consortia. We propose to utilize fluids and natural consortia from the Sand Hills lakes to further refine our organogenic model for low temperature dolomite formation and expand the model to include clay mineral phases, which may compete with carbonates for Mg$^{2+}$.

Proposed Project Description

The aim of the proposed research is use fluids and native microbial consortia from saline, alkaline lake systems to test our previous results that indicate carboxylated organic matter is responsible for the nucleation and precipitation of low temperature dolomite. While the results of the proposed work will refine this broad hypothesis, the use of geochemistry and microbial consortia from a modern alkaline lake system applies elucidated early diagenetic processes to lacustrine carbonate reservoirs.

The specific aims of this research are:

1. Measure the carboxyl group densities on native microbial consortia inhabiting a lacustrine environments in which fluids have high alkalinities and pH, with a range of salinities (0.1-9M).
2. Determine mechanistic controls on low temperature dolomite formation as a function of organic matter character, Mg/Ca ratios and silica concentration in fluids that represent alkaline, saline lakes and native and artificial organic matter.

These objectives will be accomplished using controlled laboratory experiments (e.g. Roberts et al., 2013) using native microbial consortia, carboxylated organic matter, native fluids as well as artificial fluids that mimic field conditions.

Deliverables

These experiments will validate previous success precipitating low temperature dolomite experimentally by extending the work to include conditions thought to form lacustrine carbonate reservoirs. These experiments underpin conceptual models for the formation of low-temperature dolomite via primary and replacement mechanisms and have implications for early diagenetic reactions in other dolomite reservoirs as well.
Specific deliverables include: 1) Validation and refinement of quantitative model in which salinity primes microbial biomass for dolomite precipitation; 2.) Quantitative relationships between salinity, dolomite formation, and Mg-bearing clay formation that will further elucidate early diagenetic processes in lacustrine carbonate reservoirs; 3.) An MS thesis completed by Adam Yoerg; 4.) Presentations at the 2017/18 KICC Annual Meetings.

References
Figure 1. XRD spectra of sediments from three alkaline, saline. All lakes contain calcite, aragonite, and putative stevensite. Dolomite and Mg-calcite only occur in one lake (Wilkinson).
The Role of Carboxylated Organic Matter in Low-Temperature Dolomite Precipitation

Jennifer Roberts, David Fowle, Robert H. Goldstein and Luis González

SUBSURFACE APPLICATION: Applicable to a variety of dolomite reservoirs; critical to modeling reservoir diagenesis.
STATUS: Project Proposed
TIMING: To be completed in the future if recommended by membership, funded, or staffed
FUNDING: None

Purpose
Recent work by our group has established that carboxylated organic carbon surfaces are necessary for achieving low-temperature dolomite precipitation (Roberts et al., in revision in dolomite-supersaturated solutions. Our success in synthesizing ordered, stoichiometric dolomite in less than 20 days at 30°C opens the possibility for easily performing controlled laboratory experiments that address the kinetics and thermodynamics of dolomite formation as well as stable isotope fractionation. Because the of the importance of dolomite as a reservoir rock, our goals are to use controlled laboratory experimentation to elucidate details of early dolomitization as a function of different types and abundances of carboxylated organic matter, and to evaluate how initial microbial phases seed systems for large scale precipitation.

Project Description
Dolomite and limestone are effective hydrocarbon reservoirs, with 80% of North America’s carbonate reserves accumulating in dolostones (Zenger et. al., 1980) due, in part, to their typically elevated porosity and permeability (Halley and Schmoker, 1983). Despite being abundant throughout the rock record, dolomite is uncommon in modern settings. Because dolostones are excellent reservoirs and abiotic synthesis of dolomite at low temperature has been difficult, research into the origin of massive dolomites is of interest to those in the petroleum industry. We hypothesize that:

- Organic matter with high densities of carboxyl group nucleate dolomite in dolomite supersaturated solutions by overcoming kinetic barriers;
- These dolomites may have distinct textural and morphological characteristics identifying this mode of formation in ancient rocks (Figure 1); and
- These early dolomite phases may serve as “seed” crystals for larger dolomite precipitation events in the presence of Mg-rich fluids.

These hypotheses will be tested using controlled laboratory batch experiments containing marine-type fluids with varying Mg:Ca ratios and a different types and quantities of organic matter. These reactors will be run until precipitation occurs at which time they will be: 1) characterized for rates of precipitation; 2) characterized for mineralogy, mineral chemistry and crystallinity, as a function of solution chemistry and the presence/absence of organic matter; and 3) analyzed petrographically to discern textural and morphological information to distinguish a “biological” signature.
Deliverables
We expect precipitation of low-temperature dolomite to be initiated by the presence of organic matter with a high density of carboxyl groups. Due to the ability of carboxyl to dewater the Mg ion, these organic surfaces lower activation energy of nucleation, facilitating precipitation, forming highly crystalline phases that are more resist to recrystallization, thereby persisting through geologic time in order to serve as seed crystals for mass dolomite events.

Specific deliverables include: 1) Quantitative data to be implemented into kinetic models regarding the amount of biomass and specific geochemical parameters needed for precipitation; 2) petrographic information on distinctive “biological” signatures associated with carboxylated organic matter, 3) Information regarding isotope fractionation, particularly δ18O, and refinement of dolomite paleothermometers at low temperature, and 4) a conceptual model regarding this pathway of dolomite formation and subsequent seeding of dolomite precipitating system.

References

Figure 1. Scanning electron photomicrographs of dolomite formed in freshwater in the presence of methanogenic microorganisms. A) A cell embedded in EPS and encrusted with dolomite. Arrow indicates one well-formed crystal. B) A more developed platy crystal of dolomite. Oval denotes boundary between EPS and crystal edge. Note nanoglobules in EPS. Images courtesy of Paul A. Kenward with special thanks to the University of Kansas MAI.
Kinetics of Microbial Dolomite Precipitation and Incorporation of Kinetics into Porewater/Basin Evolution Models

Jennifer Roberts, David Fowle, and Robert H. Goldstein

SUBSURFACE APPLICATION: Applicable to a variety of dolomite reservoirs; critical to modeling reservoir diagenesis.
STATUS: Project Proposed
TIMING: To be completed in the future if recommended by membership, funded, or staffed
FUNDING: None

Purpose
This project will determine how microbes and associated organic matter control rates of carbonate dissolution, dolomitization, and cementation applicable to predictive models of porosity in carbonate reservoir and non-reservoir rocks. We will: 1) develop a quantitative model to describe the activity of Mg$^{2+}$, Ca$^{2+}$, HCO$_3^-$, and H$^+$ in association with the cell wall and other types of organic matter; 2) measure rates of carbonate precipitation as a function of cell wall and organic matter properties and fluid geochemistry; and 3) incorporate kinetic parameters into porewater/basin evolution models.

Project Description
The need for improved data on conceptual process and quantitative response is apparent in low-temperature meteoric systems. Even in very young meteoric systems, researchers continue to debate the relative importance of rate of fluid flow, CO$_2$ degassing near the water table, mixing at the water table, microbially controlled chemistry, and alteration of unstable minerals (e.g., Budd and Land, 1990). In this study, we investigate the role of microbial biomass and organic matter in enhancing rates of carbonate precipitation.

We hypothesize that:
- Charge density and functionality of organic matter and specifically microbial cells is the mechanism by which ions are dehydrated, often the rate limiting step for carbonate nucleation; and
- Microbial cell walls and some types of organic matter facilitate carbonate mineral precipitation and the kinetics of this reaction can be measured.

We will use controlled laboratory experimentation to test our hypotheses and quantify relationships between microbial cell walls and carbonate precipitation rates. We will: 1) characterize cell wall functional groups and charge density, defining reactivity with charged ions such as Mg$^{2+}$, using acid-base titration, and metal sorption experiments; 2) using these data, develop a surface complexation model (SCM) to describe the activity of Mg$^{2+}$, Ca$^{2+}$, HCO$_3^-$, and H$^+$ in association with the cell wall; 3) use flow-through experimental reactors to measure precipitation rates as a function of fluid geochemistry and biomass density; and 4) all kinetic parameters will then be integrated into porewater/basin evolution models (Figure 1), for example Geochemist’s Workbench (Bethke, 2007) and reactive transport models such as TOUGHREACT (Xu et al., 2004).
Deliverables
We expect that microbial cell walls and some types of organic matter lower the activation energy of carbonate precipitation through the dehydration of ions on cell wall functional groups and that kinetic parameters that can be incorporated into geochemical and reactive transport models, allowing more precise modeling of early diagenetic relationships and prediction of the evolution of porosity in carbonate reservoirs.

- Define the bulk relationship between carbonate production and microbial biomass (or organic matter content) and functionality as a function of fluid geochemistry.
- Using these data, develop a surface complexation model (SCM) to describe the activity of Mg$^{2+}$, Ca$^{2+}$, HCO$_3^-$, and H$^+$ in association with organic surfaces.
- Quantify rates of carbonate formation and incorporate kinetic parameters into porewater/basin evolution models, providing a more robust treatment of microbial influences on precipitation kinetics.

References
Salinity Controls on Microbial Cell Wall Character and Impacts on Microbially Mediated Precipitation of Carbonates

Jennifer Roberts and David Fowle

SUBSURFACE APPLICATION: Applicable to modeling carbonate reservoir diagenesis or testing hypotheses of “production-induced” diagenesis in produced carbonate reservoirs.
STATUS: Project Proposed
TIMING: Experiments June 2015-May 2016
FUNDING: Seed funding from KICC proposed

Purpose
Recent microbial models and experimentation have demonstrated that dolomite precipitation is possible at low temperatures (<50°C) in laboratory settings, by microbial influence and mediation (e.g., Roberts et al., 2004; Mastandrea et al., 2006; Sánchez-Román et al., 2008). Many of these studies have observed dolomite precipitates that are intimately associated with microbial surfaces (Warthmann et al., 2000; van Lith et al., 2003) and recent studies have implicated microbial exopolymeric substances (Rivadeneyra et al., 1996; Dupraz et al., 2004; Sánchez-Román et al., 2007) in its formation (Krause et al. 2012). These recent studies demonstrate low temperature dolomite precipitation via nucleation on microbial surfaces that have high (>0.06 groups ångstrom^-2) carboxyl-group densities (Roberts et al., 2013). Carboxyl-groups complex and dewater Mg^{2+}, favoring carbonation and subsequent nucleation and precipitation of dolomite. Our previous study demonstrated compelling evidence that carboxyl group density of microbial cell walls was determined by the salinity of growth solutions, with higher solution salinity correlated to higher carboxyl group density. These results suggest that environmental controls on salinity and changing salinity may be a primary control on microbial biomass surface character and therefore, microbially mediated carbonate mineral nucleation and precipitation.

Our goals in this proposal are to verify if solution salinity correlates to microbial carboxyl group density, the mechanism for low-temperature dolomite nucleation, utilizing additional organisms, focusing on seawater microorganisms and native consortia.

Project Description
Previous work with dolomite-forming and non-dolomite forming microorganisms demonstrate that carboxyl group densities increased by 275%, when doubling salinity concentrations for Desulfovibrio brasiliensis; increased by 170% when increasing salinity concentrations (16x) for Shewanella putrefaciens, and decreased by 47.5% when decreasing salinities by 75% for Haloferax sulfurifontis. The noted increases of carboxyl group density serve as evidence for environmental control on microbes.

The high-density values for D. brasiliensis and H. sulfurifontis are consistent with previous research that suggests that carboxyl group density (>0.6 sites Å^-2) is necessary for dolomite nucleation. These results, however, tie microbial physiology to
environmental conditions and give insight into microbial controls on low-temperature dolomite precipitation in mixing zones, sabkha and hypersaline lagoon environments, yet the dataset is incomplete and does not encompass the wide range of seawater-type salinities found in marine environments.

The aim of the proposed research is to quantify the carboxyl group density of microbes that inhabit and are grown in salinity/ionic strength ranges similar to that of seawater to complete the data set that relates carboxyl group site density to ionic strength of growth medium shown in Figure 1, relate these data to our broader dataset and refine our conceptual model of where and when organic-matter-driven dolomite formation occurs. The specific aims of this research are:

3. Measure the carboxyl group densities on microbial cell surfaces for a collection of microbes that inhabit environments with seawater salinities.

4. Determine whether the concentration of carboxyl groups on microbial surfaces change as a function of growth medium ionic strength, and in cases where this occurs determine the rate at which density changes.

These objectives will be accomplished using controlled laboratory experiments with pure cultures grown at varying salinities and carboxyl group density will be quantified via quantification of proton adsorption to the site (e.g. surface titrations) (e.g. Fein et al., 2001). We have chosen a variety of organisms (Table 2) from a range of environments typical of carbonate formation, from freshwater lacustrine, to normal marine, and more evaporative marine settings.

**Deliverables**

If changes in salinity actively promote higher concentrations of carboxyl group density then we can define specific quantities of biomass necessary to nucleate carbonates and predict the timing and location of these nucleation events based on salinity distribution. These experiments underpin conceptual models for the formation of low-temperature dolomite via primary and replacement and therefore have implications for early diagenetic reactions in dolomite reservoirs.

Specific deliverables include: 1) Validation and refinement of quantitative model in which salinity primes microbial biomass for dolomite precipitation; 2.) Quantitative relationships between salinity and carboxyl site density can be established and added to reactive transport models for early diagenesis; 3.) An MS thesis completed by Mathew Edwards.

**References**


Figure 1. Fitting a power function to the data shows the predictable relationship between functional group density and growth media ionic strength. Data in the red box are for 3 generations of growth of H. salinarum.