PRF# 57824 ND8

Redox-Sensitive Chemical Elements of Upwelling Ramp Systems: A Comparative Study of Modern and Ancient Carbonates

Dr. Eugene C. Rankey, University of Kansas

Describe briefly the progress of the research.... Heterozoan carbonate and biosiliceous facies can contain large hydrocarbon reserves (Rogers and Longman 2001; Gates et al. 2004), including Lower Carboniferous biosiliceous accumulations in North America (Mazzullo et al. 2009). In the modern, heterozoan and biosiliceous facies are common in temperate or cold climate settings, but these types of deposits also can be found in tropical and subtropical shelves, with upwelling playing a primary role in creating conditions favorable for these associations (e.g., Gammon et al. 2000; Gammon and James 2001; Westphal et al., 2010). Although the influences of water temperature and nutrients can be clear in modern heterozoan and biosiliceous sediment, the processes responsible for the deposition of these facies in ancient carbonate ramp successions can be less evident based on physical or biological sedimentary structures or faunal composition alone (Klicpera et al. 2015). To provide an additional arrow in the quiver of interpretive tools for understanding the origin and dynamics of carbonate systems, this project tests the hypothesis that ***carbonate (heterozoan) and biosiliceous sediments in areas impacted by upwelled waters (at least seasonally dysoxic to anoxic settings) are enriched in redox sensitive elements.*** The value of such a study lies in assessing geochemical proxies for oceanic productivity variations that impact (and thus could be used to predict) carbonate, biosilicious, and organic-rich deposits.

The objectives of this study are to compare geochemical signals (redox sensitive elemental composition) of heterozoan and biosiliceous sediments in modern (Yucatan) and ancient (Jurassic Hanifa Formation, Saudi Arabia) ramps to help to assess the role of upwelling on their sedimentation. For this purpose, this study will investigate modern ramp sediments (Yucatan Peninsula), and relate those data to water-chemistry data to develop a conceptual model. The results will be compared to sedimentological, geochemical, and ichnological character of ancient strata of an ancient ramp system (the Hanifa Formation, Jurassic, Saudi Arabia) to explicitly test the model.

With funds from this grant, we completed two field campaigns to Yucatan in Spring and Summer 2018. These campaigns collected sediment on 6 transects up to 30 km offshore and deployed chemical oceanographic sensors. We also collected and synthesized regional oceanographic data, to provide a more regional perspective on the *in situ* measurements. Sediment samples are currently being freeze-dried, and their sedimentology is being characterized. Upon completion of those efforts, we will send the samples for rare-Earth element analysis. These will be compared with the measurements and estimates of pH, DO, temperature, conductance, salinity, turbidity/total suspended solids. These oceanographic data provide a range of conditions, collected during the ~3 months total deployment, from "winter" and "summer" seasons. Collectively, these efforts will provide insights into sediment geochemistry, and how REE vary with the chemical oceanographic character of the shoreface system.

On this ramp, subtle shifts in the sediment and geochemical data are evident, and can be linked to oceanographic changes along and across the ramp. Specifically, the nearshore parts of the ramp system include a mixed photozoan-heterozoan assemblage, with biosilicious components. Molluscs and forams are the dominant sediment type, with locally common *Halimeda*. Corals are rare, peloids are generally absent. Small lithoclasts and relict ooids occur infrequently offshore near Sisal and Celestun. Likewise, fines (vfs and mud) are more common nearshore Celestun and Isla Arena, and in lagoons; areas with dunes tend to be better sorted.

This 'cool water' association is consistent with chemical oceanographic sensors and remote-sensing data that indicate the sporadic presence of cooler, low dissolved-oxygen water that includes elevated sediment in suspension (during both calm periods and in association with passage of fronts). Sensors deployed offshore Sisal from April through June 2018 captured chemical oceanographic variability, trends consistent with regional MODIS satellite data: a) salinity increased (by up to 1.5 ppt) and was more variable nearshore; b) temperature was less variable and decreased (up to 5°C) offshore and into the summer; c) dissolved oxygen (DO) was lower nearshore and into the summer, reaching less than 5 mg/l at times; d) suspended sediment increased during the passage of fronts and in association with lower temperature/lower DO periods.

These observations implicate primary production, related to the upwelled waters. Spatial changes in oxygen stable isotopes, Ce/Ce* ratios, and HREE/LREE ratios are consistent with the interpretation that these signals are influenced by this nearshore, westward movement of cooler, upwelled water.

Collectively, these data and interpretations provide a conceptual model for relations among sediment, chemical oceanography, and sediment geochemistry on the modern ramp system. These results emphasize the role of along-strike movement of upwelled waters in the upper shoreface, influencing the carbonate factory several 100 km away from the source. Similarly, in terms of interpretation of the ancient, the results illustrate constraints on use of geochemical metrics to interpret chemical oceanographic controls on the nature of the carbonate factory.

The Yucatan results illustrate carbonate geochemical shifts that reflect represent subtle changes in bottom water character. If comparable shifts are preserved thru diagenesis, geochemical data may be used to constrain paleoceanography, including influences on carbonate factories, biosilicious material, and organic matter. Analysis of REE from the Hanifa Formation provide a means to test these implications.

Previous work (Eltom et al., 2018) implicated the influence of upwelled waters on sedimentological character of this intrashelf basin. This model predicts the spatial distribution of depositional style (organic-rich, biosiliceous, heterozoan, and protozoans system) based on the spatial change of water chemistry across the shelf. A Ce-anomaly (redox condition indicator) coupled with loss-on-ignition data (TOC, and thus primary productivity indicator) of samples from the Hanifa Formation show trends consistent with the predictions of the conceptual model.

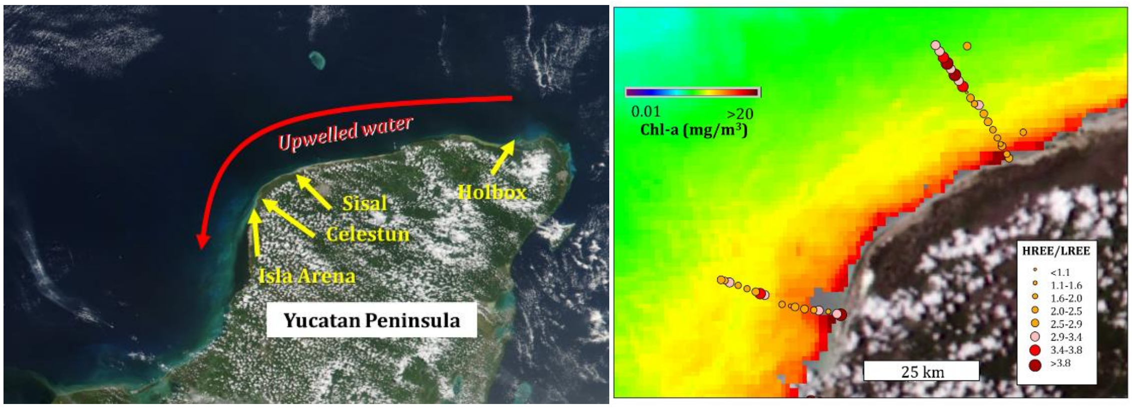

Figure 1. (left) Regional MODIS image of Yucatan Peninsula and the adjacent oceans. The four study areas describe in the text are highlighted, and westward movement of upwelled water is schematically noted by the red arrow. (right) Plot of spatial variability in HREE/LREE superimposed on Chl-a concentrations from a typical June day. Note the higher Chl-a concentrations nearshore.

....the impact of the research on your career and that of the students. Rankey comment: This project has changed the way I view the world, now from a more geochemical perspective. Although I'd be the first to admit that I am still not a geochemist, I these new data and perspectives provide new and novel insights into the way I understand the world to work! I already have a wealth of ideas for significant follow-up questions, to be addressed using these new (to me) tools.

Post-doc Eltom comment: This project provides several unique opportunities for me as a postdoctoral researcher. First, the project has introduced me to modern ramp systems. All my previous research included only investigation of carbonate strata from ancient ramp system. Thus, the integration of modern and ancient ramp system will arm me with a strong background to understand depositional and stratigraphic controls of carbonates in ramp systems and their potential resources. Second, the project provides opportunity to work under the supervision of Professor Eugene Rankey who provided a comprehensive guidance in understanding both ancient and modern depositional system.