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

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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.

We expect the modern system to display systematic trends in major, trace, and rare-earth elements, and that these changes will be related to types and size of sediment. These trends will be compared lateral and vertical change on redox-sensitive trace elements and rare-earth elements that correspond to changes in facies and total organic content (TOC) of Oxfordian-Kimmeridgian strata (Hanifa Formation) from Saudi Arabia.

The Hanifa Formation represents strata deposited in a relatively shallow intrashelf basin, formed within an extensive broad epeiric sea. This basin was flanked by marginal shallow shelf oceanward (to the east), which provided isolation from open marine waters and restriction within the basin, and resulted in a slow rate of sedimentation. Two outcrop sections (WN and DQ) of shelf settings in the Hanifa Formation on the west of the basin illustrate lithological characteristics and stratigraphic stacking patterns, and are the focus of our analyses.

To characterize major, trace and rare earth elements, 73 samples from the outcrop were analyzed by ALS Minerals Service (Vancouver, Canada) using X-ray fluorescence spectroscopy for major elements (precision is > 0.01 %), and inductively coupled plasma mass spectrometry for trace and rare earth elements (precision is > 0.01 ppm). Enrichment factors for trace elements (EF)X were calculated as: XEF = (X/Al)sample/(X/Al)AUCC, where X is the trace elements of interest and AUCC is average upper continental crust from McLennan (2001). TOC was calculated using C% in the noncarbonate portion of these samples. C% was determined by reacting an aliquot of the insoluble residue of the analyzed samples in a Costech ECS 4010 Elemental Combustion System (EA) in Keck

Paleoenvironmental and Environmental Stable Isotope Laboratory at the University of Kansas (KPESIL) following methods of Eltom et al. (2017, 2018).

A convergence of several independent lines of evidence suggests that this system was characterized by changes in water chemistry through space and time, and that these changes influenced lithofacies. Specifically, the abundance of concentration and enrichment of the redox-sensitive elements from intrashelf basin to shelfal facies in the Hawtah Member suggest anoxic conditions prevalent in the intrashelf basin passed updip to more oxic conditions in shelfal areas (suboxic to oxic) (*Figure 1*). This interpretation is consistent with the progressive decrease of biosiliceous deposits from downdip to updip, and the decrease in TOC on the same transect.

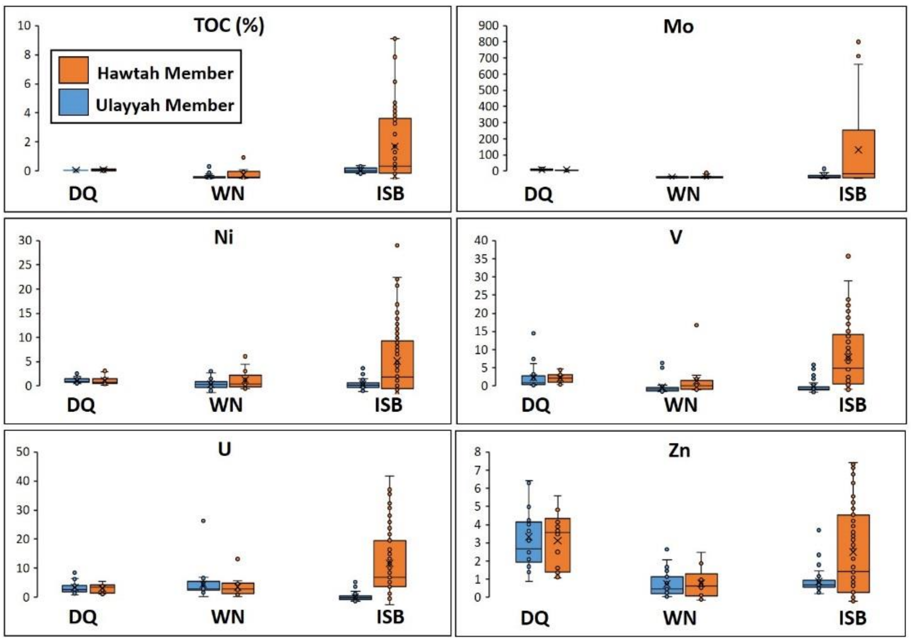

Figure 1: Box-whisker plots showing lateral variation in TOC and enrichment factors for Mo, Ni, V, U and Zn in the Hawtah and Ulayyah members across downdip (intrashelf basin, ISB)–updip (WN to DQ sections) transect. Note the systematic lateral decrease in TOC and trace elements in shelf strata compared to intrashelf strata, and vertical decrease in TOC and trace elements in the Ulayyah Member compared to Hawtah Member.

....the impact of the research on your career and that of the students. Rankey comment: This project has opened new doors as far as the way I view the world, now from a more geochemical perspective. Although I'd be the first to admit that the learning curve has been steep (and at times difficult) for me, I am optimistic that coupling these new data and perspectives with my previous biases will provide new and novel insights into the way the world works! Having said that, we are still collecting and analyzing the data, much less synthesizing between the modern and ancient.

Post-doc Eltom comment: This project provides several unique opportunities for me as a postdoctoral researcher. First, the project introduced me to modern ramp system. 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 system and their potential resources. Second, the project provide opportunity to work under the supervision of Professor Eugene Rankey who provided a comprehensive guidance in understanding both ancient and modern depositional system. Third, the fund in the project provides financial stability and allows me to focus on my research.