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Lewis and Clark Fund in Astrobiology
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Redox Variation and Nutrient Controls on Monterey Redox Variation and Nutrient Controls on Monterey Borderland Basins and Proximity Controls

PROJECT REPORT

The Miocene epoch is characterized by a wide range of climatic conditions and is a key interval for understanding Cenozoic global climate evolution. Early-middle Miocene warming (c. 22-16 Ma) of the Miocene Climate Optimum was followed by extreme cooling at ~15 Ma, rendering the Miocene an ideal interval for unraveling the causes and consequences of a transition from a greenhouse to an icehouse world. These climatic swings coincided with dramatic changes in ocean circulation, initiation of upwelling regimes, and subsequent nutrient delivery to surface waters. These factors make the study of Miocene sediments an ideal target for conducting studies of how changes in delivery of nutrients to surface waters affect primary productivity, basin redox, and subsequent delivery of organic matter to sediments. Most importantly, this study meshes perfectly with a stated objective in the Astrobiology Roadmap [to] “Document the ecological impact of changes in climate, habitat complexity, and nutrient availability upon the structure and function of a selected ecosystem, as a guide to understanding changes that might occur over time scales ranging from abrupt events (a few years or less) to millions of years.”

During the Miocene, numerous tectonically induced sedimentary basins developed along the California coast and hosted deposition of the Monterey Formation (17.5 to 5 Ma; Figure 1), which had a paleodepth found within the oxygen minimum zone (OMZ). Today, the Monterey is found in outcrop along the coast from Los Angeles to San Francisco and is of particular economic interest due to its shale-oil reserves. Sedimentation in the various basins was controlled by proximity to tectonic activity, riverine input, and degree of upwelling, resulting in a gradient in primary productivity and associated deposition of organic matter as well as the redox (oxygen) conditions in a given basin. This study seeks to investigate these controls through systematic study of the geochemistry of sediments deposited in basins that capture these gradients with the primary question: *How did basin circulation and nutrient delivery change throughout the climatic events of the Miocene, and what are the subsequent effects—within this backdrop—on primary production and basin redox?* My working hypothesis is that oxygen minimum zones and basin redox are controlled by upwelling and nutrient delivery to primary producers in surface waters.

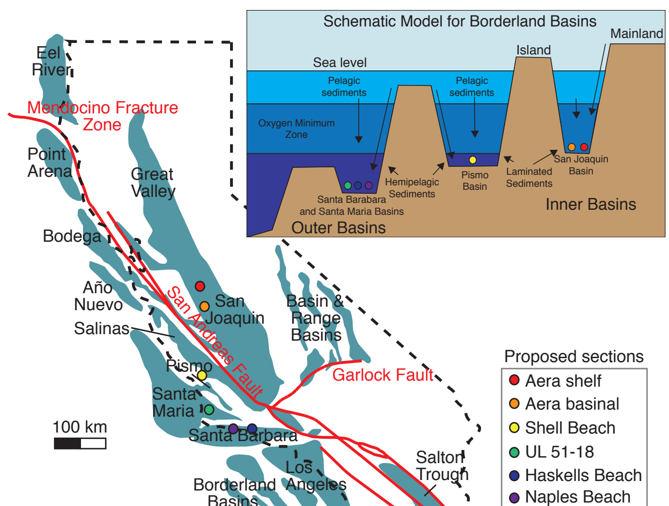

Figure 1: Map of Neogene basins in California. The colored dots represent sections proposed for the entire project. The section collected with the funds received from this grant is from the Santa Maria Basin and is demarked with the green dot. The inset cross-section is a schematic diagram of how these basins might have been connected with the open ocean during Monterey sediment deposition. The Santa Maria basin maintained a relatively decent connection with the open ocean, likely allowing it to capture conditions more common for an OMZ setting.

I proposed to collect samples from four localities (though this has now expanded to six sections; Figure 1) that represent the gradient from proximal to distal sites of deposition and use a combination of organic and inorganic geochemical tracers to unravel the feedbacks associated with increasing surface productivity. These laboratory methods include standard trace metal extractions and iron speciation for redox reconstructions; biomarker analyses; carbon, oxygen, sulfur, and nitrogen isotopic analysis; and metal isotope work. This combination of classic and novel lab techniques enables the first ever comprehensive study of local and global redox variation as coupled to nutrient input and primary producer populations in the Monterey Formation—and by analogy illuminates the processes and feedbacks in all organic- and typically methane-rich settings throughout Earth history and in our near future.

Though originally intended for collection of outcrop samples in the field, this grant ultimately allowed me to collect from an excellently preserved core at the Bureau for Economic Geology in Houston, Texas. This core has not been studied in detail from an inorganic geochemical perspective, and it was an ideal core for a study of the Miocene Santa Maria Basin. The outcrop sampling had to be delayed due to issues with access through private property, and that sampling will take place using a different field grant in the fall of this year. The Lewis and Clark grant provided me the means of airfare, lodging, accomodation, and equipment necessary for sampling this core. I travelled to Houston in June of 2015 to collect the samples, and upon arrival realized that the core facility did not have any means by which I could cut smaller samples. I was able to purchase a small tile saw from Home Depot to solve this problem, however.

Here I present the results of the analysis of the core collected using this grant money. The core itself is comprised of the two upper members of the Monterey Formation (Figure 2)—an extremely organic rich phosphatic facies and a siliceous upper member. We applied both iron speciation measurements and trace metal concentration measurements to reconstruct redox regimes through the deposition of this core. The distribution of iron mineral phases in fine-grained siliciclastic sediments has emerged as a powerful approach to delineating local water column redox conditions in ancient marine settings. Elevated concentrations of reactive Fe, phases that react with H_2S on short diagenetic time scales, are characteristic of anoxic conditions. Euxinia, a condition where waters are both anoxic and

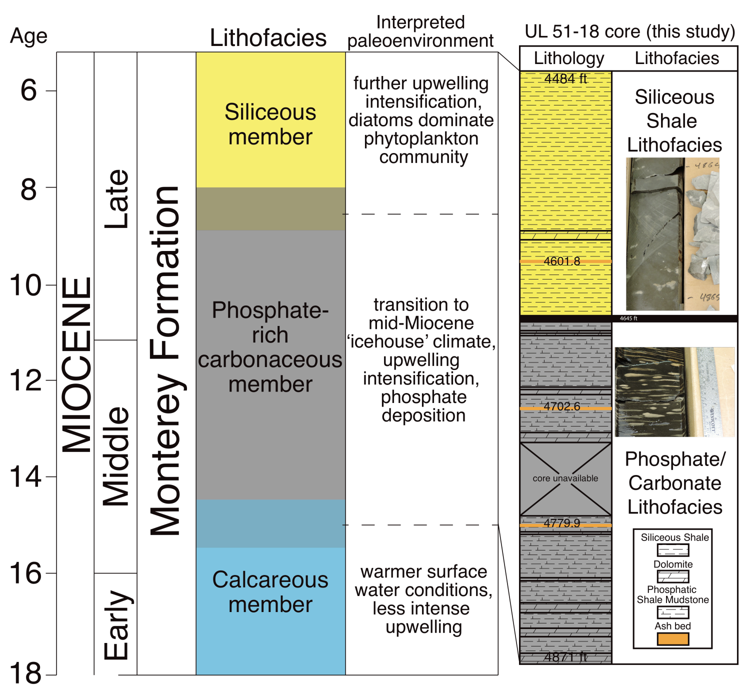

Figure 2: Generalized units of the Monterey Formation on the left side, with ages of lithofacies transitions provided, as well as the interpreted paleoenvironmental changes associated with the deposition of that lithofacies. On the right is a stratigraphic section of the core that was collected, with photos of the two major facies.

sulfidic, is fingerprinted by high degrees of pyritization of those reactive minerals. The related pathways of Fe cycling and corresponding Fe enrichment are well known from studies in the modern ocean and applications to the geologic record.

As with the Fe methods, we have calibrated our paleo-applications of redox-sensitive trace metals in modern anoxic basins such as the Black Sea and Cariaco Basin. Molybdenum is of particular value because of the requirement for appreciable free sulfide (H_2S) in the water column to establish the signature enrichments in organic-rich sediments and shales. Furthermore, sites independently identified as anoxic or euxinic via the Fe proxies provide constraints on local and global inventories of the various metals through their magnitudes of enrichment—which then speak to global extents of oxygen deficiency, basin morphology and connectivity to the open ocean, and bioavailability of essential trace metal cofactors.

Figure 3 shows the results of the work done so far. Interestingly, the highly reactive to total iron ratios are above that of crustal values, indicating anoxic conditions, but the pyrite iron to highly reactive iron ratios are not within the diagnostically euxinic window. This suggests that background conditions were ferruginous throughout deposition (no oxygen, but free iron), a condition that is not achieved in the modern ocean. Further, the molybdenum concentrations are highly variable, suggesting that redox was relatively unstable, like some other modern anoxic basins such as the Baltic Sea. We conclude that in this environment, organic carbon burial was controlled primarily by the availability and stability of oxygen content in this paleo-OMZ. Interestingly, despite being commonly compared to modern upwelling and OMZ systems such as the Peru Margin, this work demonstrates that the Monterey basins were much more reducing than any of the present day upwelling areas, and continued work on this project will aid in elucidating the cause of this.

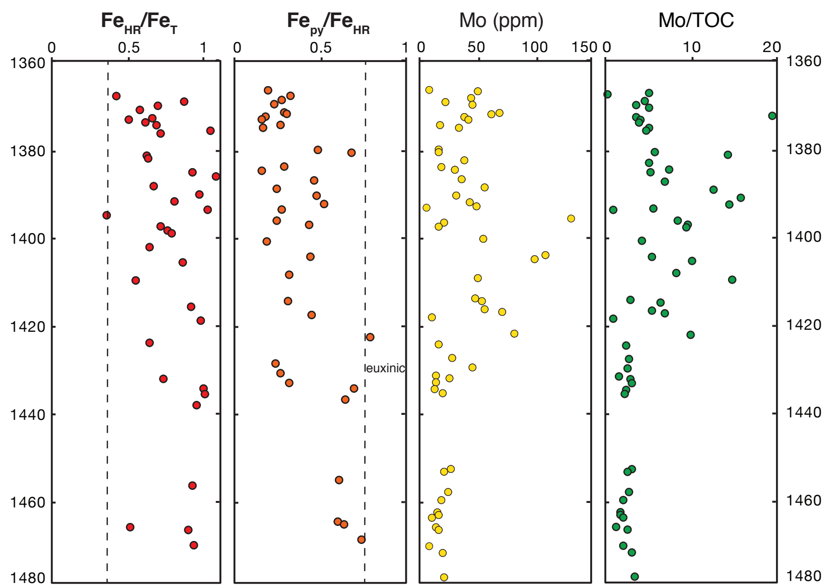

Figure 3: Data from core UL 51-18, collected in this study. The first panel shows the ratio of highly reactive iron to total iron in the samples- dotted line is the threshold above which anoxic conditions are interpreted. The second panel is pyrite iron to highly reactive iron, and this ratio remains low throughout the section- suggesting insuffient sulfide for pyrite formation, and therefore non-euxinic conditions. Mo concentrations above ~25 ppm (panel 3) are indicative of unstable redox regimes, with episodic euxinia.

Ongoing and future work on this project entails the analysis of other sections from other basins shown in Figure 1, that may have had different controls on organic carbon burial due to the basin paleogeography. For example, a more restricted basin, such as the San Joaquin Basin, has limits on the availability of upwelled nutrients due to its limited connection with the open ocean. A comprehensive deconstruction of Monterey carbon and nutrient cycling demands independent constraints on the local and global conditions of marine oxygenation, and to truly unravel the causes and effects of the climatic variation during the Miocene, we must continue to unmix global versus local drivers on organic carbon deposition. The Monterey has and will continue to prove an important and interesting locality for such a study. These data will be published within the next year, alongside similar analyses on cores and outcrop sections from other basins, allowing a full reconstruction of carbon cycling along the California coast during the Mid- to Late Miocene.