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Local and Regional Controls on Organic Carbon Burial: Insights from an Integrated, Novel Nitrogen Isotope Application to the Miocene Monterey Formation

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The focus of our ongoing New Directions Grant from the American Chemical Society Petroleum Research Fund (PRF-57545-ND2) has been on constraining local and regional controls on organic carbon burial, with the Miocene Monterey Formation representing an excellent test bed for unravelling the various feedbacks and controls on carbon burial including nutrient delivery to surface waters, basin redox, and basin connection with the global ocean. The Miocene was a time of intensified upwelling regimes and enhanced nutrient availability caused in part by dramatic climate transitions that led to and coincided with major ocean circulation changes. The Monterey Formation spans a major transition from greenhouse to icehouse conditions and represents a significant locus of organic carbon burial deposited under an oxygen-minimum zone in several sediment-starved basins with varying sedimentological histories. Despite the Monterey's vital economic and paleoceanographic importance, relatively little is known about the local and ocean-scale controls that modulated organic carbon burial across time and space.

This grant primarily supported the work of one graduate student and allowed her to focus full-time on this project. Over the past year, she performed over 300 trace metal, total organic/inorganic carbon, and iron speciation analyses on samples from three sub-basins of the Monterey Formation: The Santa Barbara, Santa Maria, and San Joaquin Basins. These basins represent a gradient from proximal and restricted to distal and connected with the open ocean. These basins experienced a wide range of depositional conditions and were ideal for understanding the impacts of local hydrodynamics on global signals. The results of this study highlight the impact of these different depositional histories on overall basin redox conditions. In general, all three basins sustained anoxic conditions throughout deposition, but while the Santa Barbara and Santa Maria Basins likely only intermittently achieved water column euxinia, the San Joaquin Basin was likely continuously euxinic throughout the entirety of the studied section. In contrast, similar oxygen minimum zones in the modern are rarely characterized by euxinic redox conditions. The Santa Maria and Santa Barbara Basins were likely most similar to the modern Peru Margin, an area of intense upwelling where euxinic conditions are achieved seasonally, while the San Joaquin Basin was similar to more restricted basins such as the Cariaco Basin. Importantly, all three of these basins were fundamentally more reducing than those of their modern equivalents, suggesting that either the global ocean was more reducing, or that oxygen minimum zones had the potential to be more intense during the Miocene, at least along the California coastline.

Two of these sections were the focus of nitrogen isotope work, and ~50 samples were analyzed for bulk $\delta^{15}N$. The section from the more outboard Santa Maria Basin yielded $\delta^{15}N_{bulk}$ that ranged from +2.5 to +11.3 ‰, but the majority of samples were greater than the modern ocean nitrate value of +5 ‰ (>80% of samples). These results, supported by the redox proxy results, suggest this basin was similar to the modern Peru Margin, which has $\delta^{15}N_{bulk}$ values ranging from +6 to + 11 ‰ (Junium et al., 2015, *Geochim. Cosmochim. Acta*). In contrast, the samples from the more restricted and more anoxic San Joaquin Basin yielded less variable $\delta^{15}N_{bulk}$ values that ranged from +5.6 to +7.6 ‰. Additionally, we have successfully identified the presence of porphyrins in two of the sections, and $\delta^{15}N_{porphyrin}$ results range from +0.4 to +5.06 ‰. In general, these collective results are indicative of periods of organic carbon burial under conditions of extreme water column denitrification, illuminating the importance of and potential limitation of nitrogen in the photic zone of these paleobasins.

The support this grant provided allowed the graduate student three quarters of research assistantship and summer stipend to focus on the field collection and analysis of these samples. She has also received training in Dr. Ann Pearson's laboratory on the extraction and chromatographic separation of porphyrins. Parts of this work has recently been published in the journal of *Palaeogeography, Palaeoclimatology, Palaeoecology* (details below), and these data are also published in the dissertation. This redox framework provided important context for understanding both how nutrient dynamics may have impacted organic carbon burial and also how these basins may have been different in the warmer Miocene world than their modern equivalents. Two other manuscripts are in preparation and build on the results of this study using novel isotopes of Mo, Tl, and U to extrapolate the conclusions of this study to the global Miocene ocean. This isotope research focuses on using different basins of the Monterey Formation, as a well-constrained analog for reducing environments that are not represented in the modern ocean, to advance interpretations of these novel and non-traditional proxies for pale oceanographic conditions. For example, comparisons of U isotopes in the Santa Barbara and San Joaquin Basins are helping to elucidate the mechanistic underpinnings for trace metal accumulation and isotopic fractionation in different depositional environments.

Products:

Hancock, L.G. (2018) Proxy applications for reconstructing carbon and sulfur cycling in ancient marine environments: Unpublished Dissertation, UC Riverside.

Hardisty, D.S., Lyons, T.W., et al. (2018) An evaluation of sedimentary molybdenum and iron as proxies for pore fluid paleoredox conditions: *American Journal of Science* **318**, 527-556.

Raiswell, R., Hardisty, D.S., Lyons, T.W., et al. (2018) The iron paleoredox proxies: A guide to the pitfalls, problems and proper practice: *American Journal of Science* **318**, 491-526.

Hancock, L.G., Hardisty, D.S., Behl, R.J., Lyons, T.W. (2019) A multi-basin redox reconstruction for the Miocene Monterey Formation, California: *Palaeogeography, Palaeoclimatology, Palaeoecology* **520**, 114-127.

Two other manuscripts are in preparation discussing our use of novel isotopes of Mo, Tl, and U to extrapolate the data and conclusions of this study to the global Miocene ocean.

The student also presented results at two international conferences: the Goldschmidt Conference in 2017 and the Society for Sedimentary Geology's Garrison Monterey Research Conference in 2018.