PRF# 57545-ND2

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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Year two of our ongoing New Directions Grant from the American Chemical Society Petroleum Research Fund (PRF-57545-ND2) has been focused on publication of data and setting up future work and collaborations that have been supported by this grant. The overarching goals of this study were to constrain 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 in particular is ideal for these types of studies because it was an interval characterized by global temperatures higher than those of today, and these climatic changes were accompanied by shifts in global stable isotope patterns, surface and deep water circulation patterns, changes in sea-level, and major turnovers in marine and terrestrial biota. The Monterey Formation spans many of these transitions, and this grant has funded the collection of high-resolution sample sets from three sub-basins of the Monterey Formation spanning gradients in sedimentological history, which likely impacted both the burial of organic carbon in these sub-basins and the ability of these basins to capture global signals.

In January of 2019, the part of this work that laid the groundwork for future products was published in the journal of Palaeogeography, Palaeoclimatology, Palaeoecology (details below). These data and the interpretations that arose from them set up a redox framework that provided essential context for how local sediment and nutrient dynamics affected organic carbon burial rates and organic carbon preservation. Importantly, this work demonstrated that the Miocene basins of the California margin were more reducing than their modern equivalents along the California borderlands. This suggests that either the entire ocean was more reducing or that oxygen minimum zones could have been more intense at least along the California coastline. These finding led to a second study, which explored using molybdenum (Mo) and thallium (Tl) isotopes to determine whether these reducing conditions were found worldwide. Despite a wide range of paleo-depositional conditions inferred from the first study, Mo and Tl isotope records have limited variability both within and among the three basins, despite large swing in the concentrations of Mo and Tl. The Mo isotope values are offset from the modern seawater value of 2.3‰, and the most restricted basin has the lightest isotopic values, contrary to the expectations. Limited stratigraphic variability in these records in all three basins suggests that sulfide levels in these basins were relatively consistent, and that we cannot confidently reconstruct seawater values from these records. Thallium isotope data yielded an average ε^{205}Tl of -6.4. This closely matches the expected coeval seawater values based on Pacific and Indian Ocean ferromanganese crusts, providing independent evidence that the Monterey basins are capturing a true seawater value, and indicating that we can reconstruct Miocene global seawater using the Tl isotope signals.

The results of this second study are important and exciting, because Mo and Tl isotopes have been used frequently to reconstruct global marine redox landscapes, and the Monterey provided an excellent example of a place where these proxies may have differences in their application and utility. This study will act as a cautionary tale for the application of Mo isotopes to reconstruct global signals. This study additionally marks the very first Miocene Tl isotopes records ever published, and a combination of Mo and Tl isotopes that is unprecedented. Another major finding of this work is that although there is evidence that the California margin experienced locally anoxic and sulfidic conditions during the Miocene, Tl isotope records suggest that anoxic conditions were globally rare during this interval. Using a simple mass balance model guided by this Tl isotope record, we estimate a maximum anoxic area of no more than 1.2% of the global seafloor. In summary, our results suggest that global changes in temperature and ocean circulation do not necessarily result in wholesale changes in the marine redox landscape, in strong contrast to the effects of rapid warming events. This highlights that perhaps rates of change must be accounted for to predict the magnitude of marine deoxygenation events. This study is nearing submission to *Earth and Planetary Science Letters* (details below).

Because of the varied climate, sedimentological, and depositional environments represented by the Monterey Formation, this grant has also supported the development of the U isotope (δ^{238}U) proxy. U isotopes are growing in popularity for providing quantitative information about the redox conditions of past oceans. Uranium accumulation and isotopic fractionation are modulated by local variations in productivity, basin connectivity, sedimentation rate, and bottom-water redox conditions—conditions that are captured in the Monterey Formation. To isolate the processes that control δ^{238}U and U accumulation in reducing sediments, the support that the grant provided allowed a postdoc to perform two complementary studies. First, the sensitivity of authigenic U isotopic fractionation and accumulation to depositional conditions was explored using a reactive transport model that couples biogeochemical reactions to diffusive transport and the burial of solutes and minerals. The results of this model make new predictions about the controls on U fractionation, and specifically organic carbon burial rate, and provides a framework for understanding how the isotopic signature of the overlying water column is altered by diagenetic U processes. This work has been revised and resubmitted to *Geochimica et Cosmochimica Acta*.

These model results and predictions are coupled to measurements of δ^{238}U in the Monterey Formation deposits in the San Joaquin and Santa Barbara Basins, which represent end-member environments for U cycling that differ by their sedimentation rate, strength of upwelling and local redox conditions, productivity, and degree of basin restriction. Distinct patterns in U enrichment and δ^{238}U values between basins indicate that local depositional controls impart a strong influence on sedimentary records. We determine that sedimentation rate and potential water column U reduction in the Santa Barbara Basin drive a diagnostic inverse relationship between U enrichment and δ^{238}U. In the San Joaquin Basin, we propose that basin hydrography results in apparent stratigraphic excursions, despite the lack of evidence for global shifts in seawater δ^{238}U. These interpretations are supported by predictions from the early diagenetic model described earlier for U enrichment and isotopic fractionation under these conditions. Our results help establish a more robust framework for the δ^{238}U proxy by elucidating conditions under which fractionation will vary, carrying implications for uranium archives in organic-rich shales as well as refining past U isotopic budgets as captured, for example, in the δ^{238}U records of carbonate rocks. In particular, it is likely that the fractionation of U into reducing sinks has varied through Earth history and in different paleogeographic locations as a result of local productivity and basin restriction. This paper is in preparation to be submitted to *Geochimica et Cosmochimca Acta* shortly.

Products:

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.

Hancock, L.G., Planavsky N.J., Nielsen S.G., Owens, J.D., Isson, T.T., Behl, R.J., Lyons, T.W. A coupled molybdenum and thallium isotope assessment of regional and global paleoredox in the Monterey Formation: Implications for relative proxy fidelity. To be submitted to *Earth and Planetary Science Letters*.

Lau, K.V., Lyons, T.W., Maher, K. Uranium reduction and isotopic fractionation in reducing sediments: Insights from reactive transport modeling. Revision submitted at *Geochimica et Cosmochimica Acta*.

Lau, K.V., Hancock, L.G., Severmann, S., Kuzminov, A., Planavsky, N.J., Cole, D.B., Behl, R.J., Lyons, T.W. Uranium isotope fractionation and implications for reconstructing past marine anoxia: Insights from the Miocene Monterey Formation. To be submitted to *Geochimica et Cosmochimica Acta*.

Presentations:

Lau, K.V. (2019) Reconstructing anoxia in Phanerozoic oceans: insights from paleoredox proxies. Geobiology Society Conference, Banff, Alberta.

Lau, K., Lyons, T., Maher, K. (2018) Early diagenetic reactive transport modeling of uranium concentrations and 'stable' isotopes. AGU Fall Meeting.

Lau, K., Lyons, T., Maher, K. (2018) Modeling insights and a case study of uranium accumulation and isotopic fractionation during early diagenesis of marine sediments. Uranium Biogeochemistry conference, Ascona, Switzerland.

Lau, K., Lyons, T., Maher, K. (2018) Modeling insights into uranium accumulation and isotopic fractionation during early diagenesis of marine sediments. Goldschmidt Meeting, Boston.

Lau, K.V., Hancock, L.G., Maher, K., Severmann, S., Kuzminov, A., Behl, R., Lyons, T.W. (2018) Uranium Isotopes in Organic-Rich Shales as a Proxy for Oxygen in the Ancient Oceans: A Case Study from the Miocene Monterey Formation. SEPM Garrison Monterey Research Conference, Santa Cruz, CA.

Lau, K.V., Hancock, L.G., Maher, K., Severmann, S., Kuzminov, A., Behl, R.J., & Lyons, T.W. (2017) Constraints on uranium isotope fractionation and reconstruction of past marine redox conditions from the Miocene Monterey Formation. GSA Annual Meeting, Seattle WA.

Hancock, L.G., Planavsky N.J., Nielsen S.G., Owens, J.D., Behl, R.J., Lyons, T.W. (2019) Thallium and Molybdenum Isotopes as Archives of Miocene Seawater Paleoredox. Invited talk, Michigan State University Distinguished Speaker Series.