## Tracing continental input and organic matter export using the long-lived thorium isotopes

Antarctic Science Bursary granted in 2015, Final Report (Submitted Oct. 2017) Dr. Christopher T. Hayes, University of Southern Mississippi

## I. Summary

This bursary supported the analysis of the long-lived thorium and uranium isotopes (<sup>232</sup>Th, <sup>230</sup>Th, <sup>238</sup>U and <sup>234</sup>U) in seawater samples collected during the austral summer, January 2015, Palmer Long Term Ecological Research (LTER) time-series grid on the West Antarctic Peninsula (WAP, Fig. 1.). The bursary supported material supplies and analytical costs for Inductively-Couple Plasma Mass Spectrometry (Nu Plasma II) in the laboratory of David McGee during my postdoctoral research at MIT. We also received samples from the following year, January 2016, and thorium isotopes were analyzed by ICP-MS (Element XR) in my new lab at the University of Southern Mississippi, supported by faculty start-up funds. Published methods were used for these analyses (Hayes et al., 2015; 2017).

Our scientific goal with these analyses was to use  $^{232}$ Th as a tracer of continental material, and furthermore as an indicator of supply of the micronutrient Fe, which can limit primary productivity in the WAP seas. Having two sampling campaigns to compare allowed us to determine how  $^{232}$ Th distributions changed in relation to other biogeochemical fields (such as chlorophyll or dissolved silicon, as in Figs. 1-3). Both years indicate a strong source of  $^{232}$ Th coming from Antarctic shelf sediments, likely also supplying Fe, being advected offshore at ~100-150 m depth.

Additionally, we used <sup>230</sup>Th to provide a quantitative estimate of the export flux of organic matter. This is done by multiplying the integrated production of <sup>230</sup>Th by <sup>234</sup>U decay by the ratio of organic carbon to <sup>230</sup>Th in particulate material. For particulate organic carbon estimates, we used available time-series measurements (http://dx.doi.org/10.6073/pasta/d2de255ff3e7c6538c9d49c69c0ad377). Collected at the site of long-term moored sediment traps, our Th results produce reasonable estimates of organic matter export in comparison to the sediment trap time-series (Fig. 4-5). This result contrasts findings from <sup>234</sup>Th fluxes that suggested extensive under-collection of the sediment traps (Buesseler et al., 2010). A useful check on this result will be measurement of <sup>230</sup>Th on sediment trap material, as our particulate <sup>230</sup>Th estimates are based on the difference between unfiltered and filtered seawater samples which produces a relatively imprecise estimate.

Finally, in the 2015 dataset, we also measured dissolved uranium concentration (<sup>238</sup>U) and isotopic composition (<sup>234</sup>U/<sup>238</sup>U). These parameters are critical in the use of thorium isotopes (both <sup>230</sup>Th and the shorter-lived <sup>234</sup>Th) to determine organic matter export. It was found that the isotopic composition was indistinguishable from the global average. The U concentration had a linear relationship with salinity that was consistent with that in global average seawater within the uncertainty of the regression (Owens et al., 2011) (Fig. 6). These uranium results were included in an undergraduate thesis (Rosen, 2016).

All our results will be published in peer-reviewed literature within the next 2 years, in coordination with our collaborators Jessica Fitzsimmons (Texas A&M University) and Robert Sherrell (Rutgers University) who collected the samples for us and made measurements of Fe and other trace metals, with which we will compare results.



**Figure 1.** Surface water distribution of dissolved <sup>232</sup>Th (top) and chlorophyll a (bottom) for Palmer LTER sampling years 2015 (left) and 2016 (right). Chlorophyll data is from <a href="http://dx.doi.org/10.6073/pasta/250c33b6ae7325102f0c06686f063971">http://dx.doi.org/10.6073/pasta/250c33b6ae7325102f0c06686f063971</a>



**Figure 2.** Section data for dissolved <sup>232</sup>Th (left) and silicic acid (right) for Palmer LTER sampling years 2015 (top) and 2016 (bottom) along the 200 line of the sampling grid. Nutrient data is from <a href="http://dx.doi.org/10.6073/pasta/9894dad135256558445e61d1956ff6a6">http://dx.doi.org/10.6073/pasta/9894dad135256558445e61d1956ff6a6</a>



**Figure 3.** Section data for dissolved <sup>232</sup>Th (left) and silicic acid (right) for Palmer LTER sampling years 2015 (top) and 2016 (bottom) along the 600 line of the sampling grid. Nutrient data is from <a href="http://dx.doi.org/10.6073/pasta/9894dad135256558445e61d1956ff6a6">http://dx.doi.org/10.6073/pasta/9894dad135256558445e61d1956ff6a6</a>



**Figure 4.** Water column <sup>230</sup>Th data collected at the Palmer LTER sediment trap site (Station 580.130) for collection years 2015 (left) and 2016 (right). Total represent analysis of unfiltered seawater, dissolved represents filtered seawater, and particulate is the difference between total and dissolved. In some cases dissolved concentrations were indistinguishable from total concentrations, making the particulate concentration below detection. In general, <sup>230</sup>Th concentrations increase with depth, in concordance with a model of reversible scavenging of thorium on to a uniform class of sinking particles.



Particulate Organic Carbon Export (mmol/m<sup>2</sup>/day) at Palmer LTER sediment trap site

**Figure 5.** Comparison of particulate organic matter export estimates from summers 2015 and 2016 based on <sup>230</sup>Th data collected in this study with that estimated from the Palmer LTER sediment trap time-series of recent years (station 580.130 in the Palmer sampling grid). Sediment trap data from <a href="http://dx.doi.org/10.6073/pasta/c0a2d3a87876ff3baddad20343b6483d">http://dx.doi.org/10.6073/pasta/c0a2d3a87876ff3baddad20343b6483d</a>



**Figure 6.** Uranium analyses of the same 2015 sampling year water samples for which Th concentrations are reported in Figs. 1-3. A linear regression between the Palmer LTER U concentrations and salinity (dotted line in blue, top plot) was consistent with the global average (black lines) regression reported by Owens et al. (2011), within uncertainties. The <sup>234</sup>U/<sup>238</sup>U ratio of these samples (bottom plot, reported as per mil deviation of the activity ratio from secular equilibrium) was also consistent with the global average reported by Andersen et al., (2011), black lines, given the uncertainty in our analysis shown in the error bars.

## 2. References

Andersen, M. B., C. H. Stirling, B. Zimmermann, and A. N. Halliday (2010), Precise determination of the open ocean <sup>234</sup>U/<sup>238</sup>U composition. *Geochemistry, Geophysics, Geosystems* 11, Q12003.

Buesseler, K. O., A. M. P. McDonnell, O. M. E. Schofield, D. K. Steinberg, and H. W. Ducklow (2010), High particle export over the continental shelf of the west Antarctic Peninsula. *Geophysical Research Letters* 37, L22606.

Hayes, C. T., J. Rosen, D. McGee, E. A. Boyle (2017), <u>Thorium distributions in high and low dust</u> regions and the significance for iron supply, *Global Biogeochemical Cycles* 31, 328–347.

Hayes, C. T., J. N. Fitzsimmons, E. A. Boyle, D. McGee, R. F. Anderson, R. Weisend, P. L Morton (2015), <u>Thorium isotopes tracing the iron cycle at the Hawaii Ocean Time-Series Station ALOHA</u>, *Geochimica et Cosmochimica Acta* 169, 1–16.

Owens, S. A., K. O. Buesseler, and K. W. W. Simms (2011), Re-evaluating the <sup>238</sup>U-salinity relationship in seawater: implications for the U-2<sup>34</sup>Th disequilibrium method. *Marine Chemistry* 127, 1-4.

Rosen, J., (2016), Constraining <sup>238</sup>U-<sup>234</sup>Th isotope systematics in the northwest Atlantic and Southern Oceans. *Senior Integrative Exercise*. Carleton College.