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Iodine to Calcium Ratios in Marine Carbonates as an Indicator of Oxygen Levels

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Introduction

Oxygen is an essential component of an organism's life. It is the basis for respiration which provides the energy organisms need to function. Due to it's importance, I am indirectly measuring the ocean's oxygen levels from 1,000-120,000 years ago by measuring the iodine to calcium ratio in the shells of marine microfossils, or foraminifera. Iodate concentration directly varies with oxygen concentration in seawater (Lu et al., 2010). If iodate is available, foraminifera have been shown to incorporate it into their shells (Lu et al., 2010). Measuring the I/Ca ratio will indirectly show us how much oxygen was in the ocean in the past. This relatively new method was proposed due to the lack of sensitive proxies in documenting past ocean oxygen levels (Zhou et al., 2014). Given the future estimates of the effect of climate change on the oceans, it is important to measure the oxygen of a warmer past to see how it might influence our future.

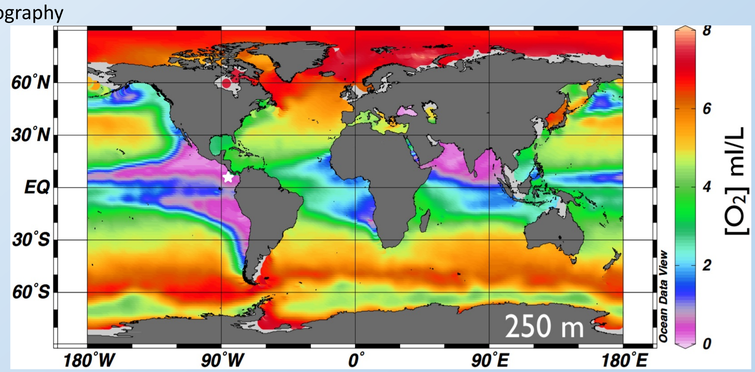


Figure 1: Annual global map of oxygen levels in the subsurface waters, 250 meters deep from World Atlas 2009 plotted with Ocean Data View (Robinson et al., 2014). Ocean Drilling Program research site 1241 indicated by white star

Methods

Reducing background iodine

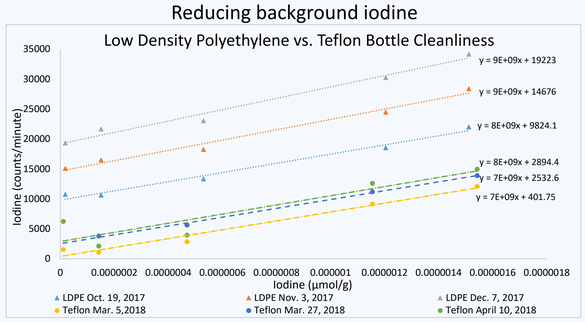
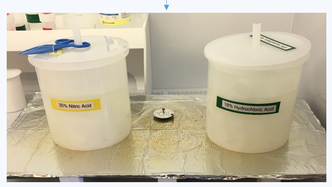


Figure 2: Iodine concentration plotted against iodine counts/minute to show how the LDPE bottles were leeching contaminants into our standards

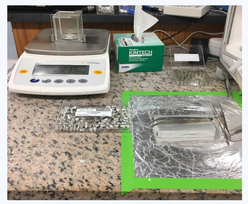


After observing contaminants in our standards, Teflon bottles were cleaned on a 150°C hot plate in 35% nitric acid followed by 18% hydrochloric acid before use

Preparing foraminifera for analysis

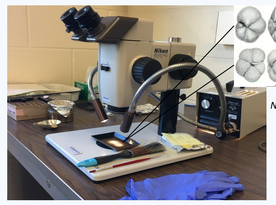
Bulk samples were ground to be measured for ^{15}N

Bulk samples were wet sieved for 150µm and remnants were dried in an oven



Ground samples were weighed and packaged into tin cups for combustion

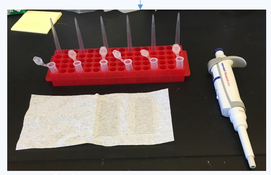
G.menardii



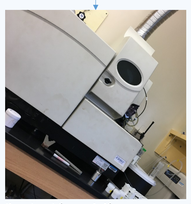
N. pachyderma

Dried samples were dry sieved for 250µm and foraminifera were sorted according to species

Ground, packaged samples were run through a mass spectrometer for analysis



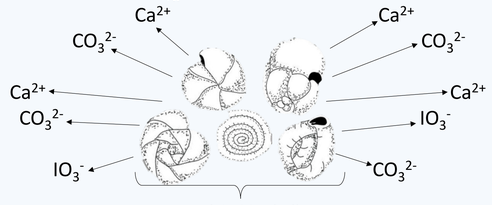
Species specific foraminifera were crushed, put through a multistep cleaning process, and dissolved in acid



Cleaned, dissolved foraminifera were run through an inductively coupled plasma mass spectrometer for analysis

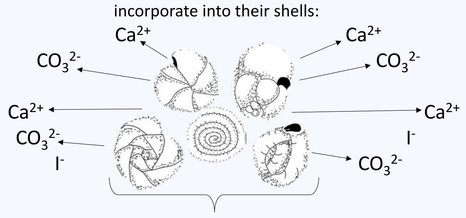
How does iodine get into the shells?

When oxygen is abundant in the water:



Hard $CaCO_3$ shells

When there is little to no oxygen in the water, IO_3^- converts to I^- which forams are unable to incorporate into their shells:



Hard $CaCO_3$ shells without IO_3^- signature

Results

Reproducibility of I/Ca in carbonates

Standard	Mean I/Ca within run (cps)	Mean I/Ca between runs (cps)	Literature Value (µmol/mol)
JCP-1	6.67 ± 2.57	4.49 ± 1.11	4.27 ± 0.06
	3.90 ± 0.37		
	6.44 ± 1.70		
EQP8	2.84 ± 1.01	NA	NA

Table 1: Reproducibility of JCP-1 (a standard reference material of homogenous coral) and EQP8 (cleaned, bulk foraminifera) showing mean and standard deviation. JCP-1 was run in three different analysis runs with 6, 20, and 12 replicates per run respectively. 1 outlier was removed from the second run. Runs were conducted 2-3 weeks apart. EQP8 was run 8 times in one run. The data from all runs was corrected for blank and drift deviations. JCP-1 literature value was taken from Lu et al., 2010.

I/Ca in the Eastern Tropical Pacific over a glacial cycle

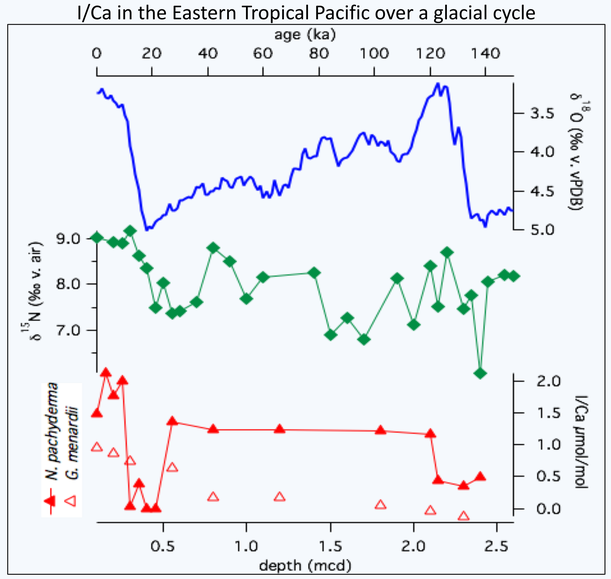


Figure 3: The $\delta^{18}O$ (Lalicata and Lea, 2011), $\delta^{15}N$, and I/Ca ratios plotted against age in thousands of years and depth as meters composite depth. The I/Ca was tested in two different species, *N. pachyderma and G. menardii.*

Discussion

<u>LDPE contamination</u>

Iodine increased in our reagents over time. We found that iodine leeches out of LDPE bottles, but acid cleaned Teflon bottles were appropriate for our work.

<u>Foraminiferal I/Ca record from ODP 1241</u>

The drift and blank corrected data produced does not correlate with the hypothesis initially created. An increasing $\delta^{18}O$ is generally attributed to a colder climate and higher oxygen levels. With higher oxygen levels, the iodine to calcium ratio was expected to increase. However, as shown in Figure 3, the iodine to calcium ratio drops with increasing $\delta^{18}O$ around 20,000 and 130,000 years. This could be due to the fact to the iodine levels in the samples are very close to the detection limit.

In addition, iodine is a very volatile element. The solution used for digestion and dilution both contained TMAH which stabilizes iodine's volatility. However, there were samples that would remain in solution for several days before measurement. It is a possibility that some iodine volatilized out before being analyzed, even with TMAH in solution.

<u>What's next?</u>

As shown in Figure 1, the site of focus for this study is in an area with very low oxygen levels. Because the iodine of these samples is very close to the detection limit of measurement, future studies should look in different areas to possibly find better iodine records.

Referenced Material

Lalicata, Joseph J., and David W. Lea. "Pleistocene Carbonate Dissolution Fluctuations in the Eastern Equatorial Pacific on Glacial Timescales: Evidence from ODP Hole 1241." *Marine Micropaleontology*, vol. 79, no. 1-2, 19 Jan. 2011, pp. 41–51., doi:10.1016/j.marmicro.2011.01.002.

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Acknowledgements

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