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Reconstructing paleoceanographic oxygen conditions in the Soledad Basin, Mexico

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NONTECHNICAL SUMMARY

The global oceans contain relevant information about past environment. Oceanic sediments retain signatures from variations in productivity, water conditions and temperature making it possible to recreate past environmental conditions in the context of climate change. In Oxygen Deficient Zones (ODZs), oceanic regions with low oxygen concentration, the sediment record is mostly undisturbed creating ideal study sites for paleoceanographic reconstructions. By using organic carbon to mineral surface area ratios and measured differences in nitrogen isotopes, it is possible to estimate the oxygen conditions in the marine environment. This project seeks to reconstruct the oxygen conditions back approximately 600 years in Soledad Basin, a semi-enclosed basin on the continental shelf off Baja California, Mexico from a sediment core collected March 19, 2012. Organic matter preservation in the sediments is approximately four times the ratio seen in typical oxygenated oceanic environments, indicating long term low oxygen concentration in this basin. The ratio of organic carbon to surface area decreases in the sediments deposited more recently, signaling a decrease in the local intensity of oxygen depletion in the basin.

ABSTRACT

The correlation between organic carbon (OC) concentrations and specific mineral surface areas (SA) allow the derivation of oxygen concentrations in past environments. OC:SA ratios in sediments from Soledad Basin, Mexico, were determined utilizing $\delta^{13}C$ and $\delta^{15}N$ isotope analysis in conjunction with the BET N_2 sorption surface area method. Enhanced organic matter preservation between 3.5 mg OC m^{-2} to a high of 5.7 mg OC m^{-2}, well above the typical concentration of 1.1 mg OC m^{-2}, is indicative of an oxygen depleted regime in the basin during the last 600 years. Localized OC:SA ratios in Soledad Basin were similar to previously measured ratios near Mazatlan. Shifts in the Soledad OC:SA ratios can be correlated to global climate shifts, especially the Little Ice Age and recent warming trends. This extended period of anoxia is consistent with larger spatial trends in the open ocean in the Eastern Tropical North Pacific (ETNP) over the same temporal scale. The enhanced organic matter preservation in the coastal ETNP is a key local reservoir for organic carbon.

Understanding the impacts of climatic shifts requires knowledge of oceanic conditions, especially those in Oxygen Deficient Zones (ODZs). Currently, multiple mechanisms have been hypothesized to trigger large scale oceanic environmental shifts including changes in productivity, turnover rates in the nitrogen cycle, and increased carbon flux into the atmosphere (Broecker 1982; Ganeshram et al, 1995, Paulmier et al. 2009). ODZs themselves may be caused by limited circulation and intermediate water flushing, but may be most influenced by high rates of productivity (Paulmier et al. 2009). High productivity can be linked to redox conditions in the water column, biogeochemical cycling and sediment chemistry (Calvert and Pedersen 1993, Muñoz et al. 2011). The ODZ, defined by oxygen levels less than 25 µmol L^{-1}, of the Eastern Tropical North Pacific (ETNP) is a well-documented region changing little since the last glacial maximum (Paulmier et al. 2009; Cartapanis et al. 2011). The ETNP ODZ is an extensive region of decreased oxygen off the western coast of Mexico (Cline and Richards, 1972). ODZs correlate with well-preserved organic matter in sediments providing ideal locations to reconstruct paleoceanographic environments (Keil and Cowie, 1999). The interplay between productivity and organic matter sorption in continental shelf sediments are important influences on the total amount of organic matter sequestration, a key reservoir in the global carbon cycle (Keil and Hedges, 1993).

Organic carbon to mineral surface area ratio (OC:SA) measurements might be a valid proxy for paleo oxygenicity, especially in anoxic regions (Hedges and Keil, 1995; Keil and Cowie, 1999). OC:SA studies normalize carbon measurements based on sediment grain surface areas rather than density and grain size. Using mineral surface area allows valid comparisons across spatial and temporal scales despite changes in sediment composition in whole samples (Mayer, 1988; Mayer,1993; Keil et al., 1998). Investigations of OC:SA ratios have demonstrated a linear relationship between sediment surface area and total organic matter with ratios near 0.5 to 1 mg C m^{-2} indicating a monolayer-equivalent coating of organic matter (Suess, 1973; Mayer, 1994a, 1994b; Keil et al., 1997). Ratios in excess signify localized increases in organic carbon preservation or increased sediment grain complexity on the micro scale (Keil et al., 1994; Hedges and Keil, 1995; Bergamaschi et al., 1997). It has been suggested that the oxygen conditions in the depositional environment influence the preservation of organic matter in sediments to a greater degree than the pore spaces in mineral grains, thus correlating a decrease in oxygen content of the overlying water column to excess organic matter in sediments (Keil and Cowie, 1999; Van Der Weijden et al, 1999). It has also been proposed that low oxygen concentrations also decrease the biological degradation of organic matter (Mayer, 1993; Keil et al, 1993).

Isotope analysis (particularly, $\delta^{13}C$ and $\delta^{15}N$) provides information concerning the origin of the OC from terrestrial or marine sources and signals of denitrification via the ^{15}N record. The $\delta^{13}C$ signature of organic matter is bounded by terrestrial signatures from -14 to -27 permil with planktonic OC signature near -20 permil. Shifts in either direction indicate complex organic matter mixing or isotope fractionation driven by phytoplankton (Altabet, 1995; Waser et al., 1998). Denitrification, a metabolic pathway in the nitrogen cycle, occurs in low oxygen conditions (oxygen <10 µmol L^{-1}) such as those seen in ODZs (Knowles, 1982). Since denitrification occurs in low oxygen concentrations, isotopic signatures can increase the accuracy of paleo oxygenicity estimates and historic reconstructions (Groffman et al., 2006). The pairing of $\delta^{15}N$ analysis and OC:SA measurements can provide confirmation of oxygen depletion and the sedimentation setting.

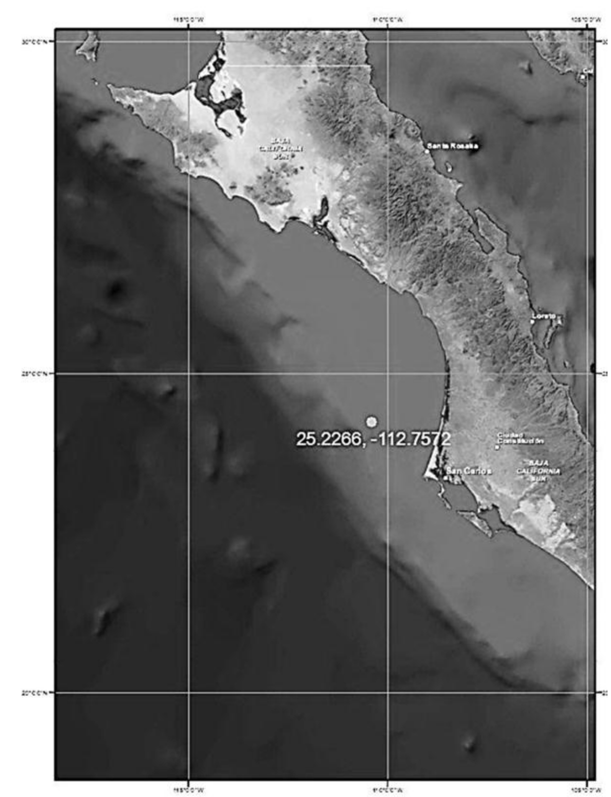

Figure 1: Baja California Sur and the study site

This paper investigates the variation in localized oxygen concentration in Soledad Basin over the last 600+ years in the context of the larger picture in the ETNP and climate change. The Soledad Basin, located on the continental shelf of Baja California, Mexico (25^0 11.99N, 112^0 43.99W), is a 540m deep basin restricted from the ocean by a 290m sill (Fig. 1). Persistent anoxia in Soledad Basin is likely influenced by circulation restrictions by the sill, and low bottom water oxygen (BWO) levels have lead to the formation of dark laminations in Holocene sediments (Van Geen et al., 2003). Low BWO concentrations limit bioturbation and positively influence preservation of laminated sediments. Soledad Basin experiences high sedimentation rates, near 1m kyr^{-1}, creating a high resolution temporal archive of oxygen concentration shifts (Van Geen et al, 2003). This work adds to the understanding of carbon sequestration and localized changes in oxygenation during shifting climate.

METHODS

Sediment samples for this study were collected March 19, 2012 in Soledad Basin, Mexico (25^0 11.99N, 112^0 43.99W) aboard the R/V Thomas G. Thompson. Eight sediment cores were collected with a multicorer, one of which was selected for this study. The core was sliced into 62 one-centimeter increments, bagged in lab quality Ziploc bags and refrigerated at 4 °C until split in half and then frozen for transport to the University of Washington. Sediment age was calculated from the average sedimentation rate as determined via 14C dating by Van Geen et al. (2003).Utilizing the average sedimentation rate for the basin conservatively estimates the timeframe represented in the core by assuming negligible sediment compaction.

At the University of Washington, samples were prepared for bulk carbon measurements, surface area and nitrogen isotope analysis. All samples were desalted via deionized water rinses and centrifuged for 10 minutes at 10,000rpm. Samples were then frozen at -18 ºC before being freeze dried. Thirty sediment samples were prepared for $\delta^{13}C$ and $\delta^{15}N$ isotope analysis following the Komada et al. (2008) carbonate removal method for coastal sediments. Isotope analysis was conducted at IsoLab at the University of Washington May, 2012 on a Costech Elemental Analyzer. Prior to surface area measurement, organic matter was removed from splits from each sample by slowly heating them to 350 ºC for 12 hours (Keil et al. 1997). Combusted sediment splits were analyzed on a Micromeretics FlowSorb III Surface Area Analyzer following the Brunauer-Emmett-Teller (BET) Single Point method under a 0.3 mole-fraction N_2 in He mixture. Repeated adsorption and desorption measurements of samples had a standard error of ±4%

RESULTS

Specific surface areas were measured in duplicate for each centimeter slice down the core. Sediment age was calculated from the sedimentation rate determined by van Geen et al (2003) as an annual deposition rate. Surface layers exhibit larger surface areas than samples down the core. The youngest two centimeter sections had surface areas of 23 $m^2 g^{-1}$ and 21 $m^2 g^{-1}$ respectively, followed by minimal variation between 14 to19 $m^2 g^{-1}$ down the length of the core (Fig. 2). Sediments in Soledad basin are trending towards more coarse sediments at depth.

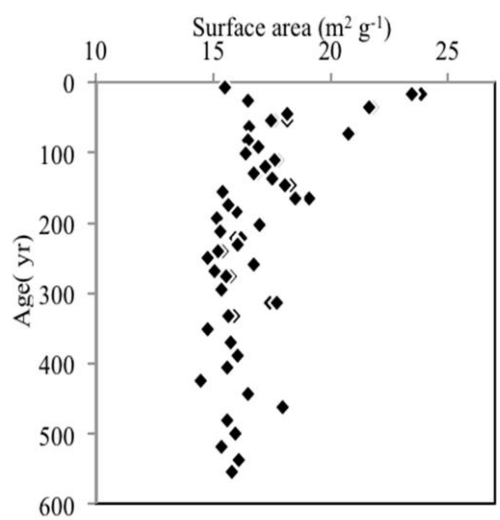

Figure 2: Down core specific mineral surface areas in Soledad Basin

Thirty samples were analyzed for $\delta^{13}C$ and $\delta^{15}N$ isotopic signatures for application in OC:SA ratios. Carbon and nitrogen peak areas were positively correlated, allowing the calculation of organic content in the 30 analyzed samples. The $\delta^{13}C$ in the sediment was typically between -20‰ and -21‰, indicating a marine source. Weight percent carbon (Wt% C) was consistently above 7 Wt% C for each sample, ranging from 7.1 Wt % C to 8.9 Wt% C. Down core the Wt% C generally decreases (Fig. 3). When these weight percent values are converted to amount per sample of carbon, the sediment contained portion of carbon between 71 mg C g^{-1} and 89 mg C g^{-1}. In these samples, $\delta^{15}N$ is approximately 10‰, possibly indicating denitrification and nutrient stress (Altabet, 1995). The nitrogen percent of each sample was consistent through the core near 0.6 Wt% N, resulting in approximately 6 mg N g^{-1} in each section.

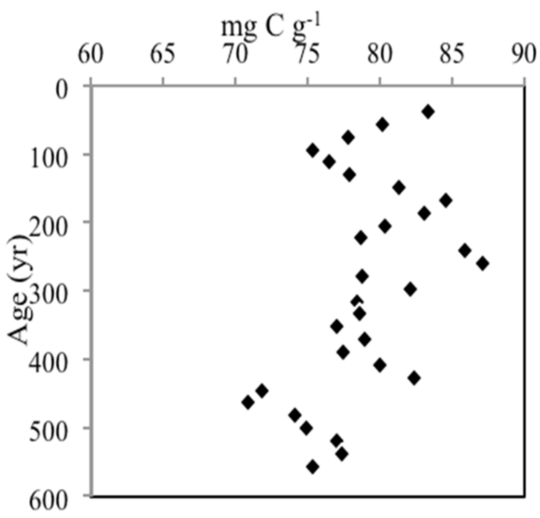

Figure 3: Down core carbon loading in Soledad Basin.

The most telling environmental proxy is recorded in the OC:SA ratio profile. Soledad Basin has been consistently anoxic for the last 600 years, recording a OC:SA ratios above 3.5 mg OC m^{-2} to a high of 5.7 mg C m^{-2}. The OC:SA ratios increase down core, with a large peak approximately 430 years ago following a decrease in the ratio approximately 460 years ago. The decadal OC:SA ratios have been decreasing since the Industrial Revolution of the 1850's, after a stable period from 150 years ago to 420 years ago (Fig. 4).

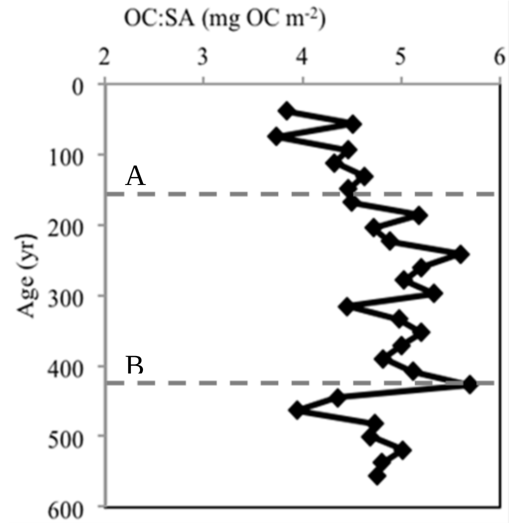

Figure 4: OC:SA ratios from present to 600 years ago. The ratio values from 1850(A) and 1580 (B) are noted for their correlations to the Industrial Revolution and intensification of the Little Ice Age, respectively.

DISCUSSION

Surface Areas

The range of mineral surface areas has interesting implications for the environmental history of the region. The coarsening of sediment grains down core can imply a greater terrestrial input in relation to marine originating sediments in the past. The average surface area measured lower in the core indicates high degrees of surface roughness and silt sized particles, in the range of 8 to 64 µm (Keil and Cowie, 1999). The decrease in larger sediment grains in the last few decades may be attributed to the developmental boom of agricultural irrigation projects and dams on the Baja Peninsula and west coast of Mexico during the 1960's to 1970's, which would restrict the transport of larger clasts to the ocean in an already arid environment (Vorosmarty et al, 1997). Natural sediment traps in the form of mangrove forests would also restrict sediment transport, with the smallest grains escaping the system (Wolanski, 1995). The positive surface areas shift in more recent decades could be due to the long shore transport of fine grained sediments northward in the coastal currents. Energetic currents would transport small grains long distances from restricted rivers, reservoir systems and local mangrove forests.

OC:SA

The OC:SA ratios from Soledad Basin are consistently enriched in organic matter comparatively to the typical OC:SA ratios for monolayer-equivalent sorption in oxygenated marine settings. The Soledad Basin OC:SA are four times greater than literature values of monolayer-equivalent OC sorption, ratio values between 0.5 mg OC m^{-2} and 1.1 mg OC m^{-2} (Fig. 5). The elevated OC:SA ratio indicates a persistent anoxic region in the basin, but intensity of the anoxia has been decreasing since the 1850s as the OC:SA ratio decreases. The decrease in the intensity of anoxia as recorded in the OC:SA ratio can be attributed to the beginning of climate change after the Industrial Revolution. Notably, there is a strong increase in the OC:SA ratio approximately 430 years before present. This localized ratio increase correlates with the continuation and intensification of the Little Ice Age during the late 1500s and may be a sign of increased surface productivity (Paytan et al., 1996; Paulmier et al. 2009, Miller et al., 2012).

The high sedimentation rate in Soledad Basin offers a high temporal resolution archive not seen in the better-known ETNP study sites near Mazatlan. In cores from Mazatlan, Mexico collected by Keil and Devol (unpublished data, 1997), sediments recorded regional anoxia back 9,700 years after a long period of oxygenation. Recent sediments from Mazatlan, over the last 1,000 years, have similar OC:SA ratios to Soledad Basin, indicating similar oxygenation history in the larger region of the ETNP. Longer cores are needed to determine if a similar period of oxygenation occurred on the same timescale in Soledad Basin as in open ocean environments.

$\delta^{15}N$

In Soledad Basin the $\delta^{15}N$ composition and OC:SA ratio increase relatively linearly. Generally, $\delta^{15}N$ increases as OC:SA increases, indicating coupled processes occurring and increases in nutrient stress in this anoxic basin (Fig. 6a). The biological conversion of nitrate into nitrogen gas preferentially utilizes lighter nitrogen isotopes, concentrating the heavy isotopes in the nutrient reservoir of the marine system (Altabet et al., 1995). There are two outlying points from the general positive trend which coincide with noticeable shifts in the OC:SA ratio (Fig. 6b). In short periods of increased oxygenation in a localized system, the OC:SA ratio will respond faster and to a greater degree than $\delta^{15}N$, whose isotopic fractionation is driven by biologic processes and independent of oxygen concentration. This relationship is apparent 450 years ago in the sediment record, when the OC:SA ratio had a net increase of 2.6 mg OC m^{-2} and the $\delta^{15}N$ only increased 0.6‰ over the same timeframe. Overall, the $\delta^{15}N$ in Soledad Basin sediment contains a relatively stable denitrification signal during the time-span studied. More isotopic analyses would make the temporal resolution of nitrogen use more robust.

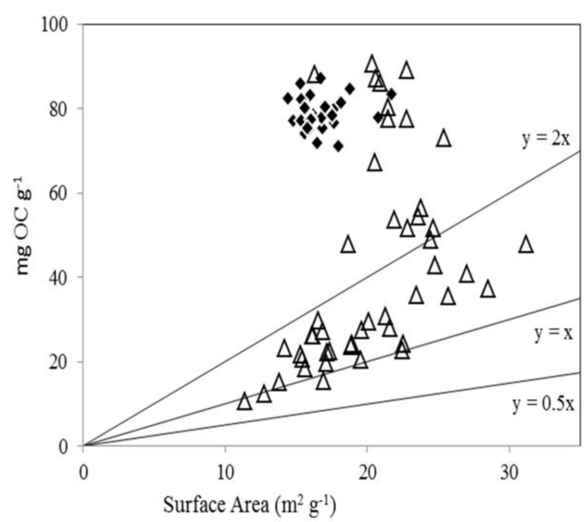

Figure 5: OC content and surface area from Soledad Basin (diamonds) and Mazatlan(Triangles). Mazatlan sediments from the last glacial maximum fall within the OC:SA ratio range of monolayer equivalent sorption of carbon.

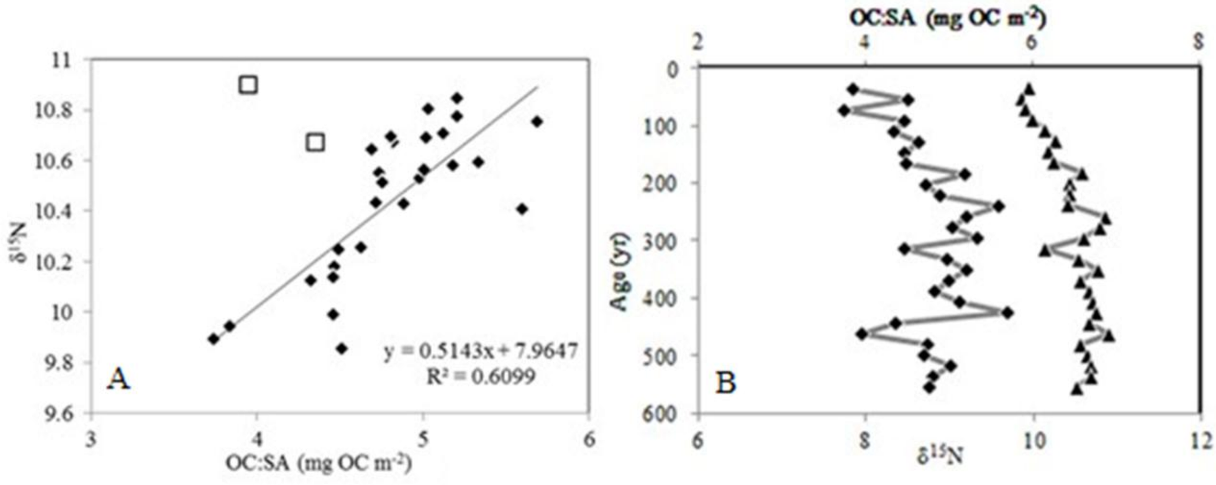

Figure 6: A)) δ15N and OC:SA ratios increase linearly. Black diamonds represent values consistent with increases in denitrification and carbon preservation. White squares are sections where carbon preservation was less than expected in relation to the recorded dentrification. B) OC:SA(diamonds) and δ15N (triangles) down core trends from Soledad Basin.

The implications of decreasing carbon preservation in sediments with rising temperatures are important factors in understanding the carbon cycle under changing climate. Reduced carbon sequestration in continental margins and anoxic basins would reduce one of the largest global carbon reservoirs (Hedges and Keil, 1995). Future research will need to investigate the role of excess carbon in the marine system if carbon sequestration in sediment is depressed.

CONCLUSIONS

Soledad Basin is undergoing environmental influences from anthropogenic landscape alteration and climate change. The surface areas of sediment grains coarsen down core, indicating a decrease in terrestrial sediment deposition in recent decades, which can be attributed to a decrease in coastal runoff. Overall, Soledad Basin has remained anoxic during the last 600 years, with variation in the ratio of carbon preservation. The OC:SA ratio shifts correlate with global temperature changes, including an increased ratio of carbon preservation during the Little Ice Age (450 years ago) and decreases in carbon preservation ratios since the Industrial Revolution (1850's to present). Signals from the $\delta^{15}N$ record, indicate consistent denitrification and lags between large OC:SA ratio shifts and increased nutrient stress. The lags between these two proxies are driven by rapid oxygen changes and consistent isotope fractionation. Identifying changes in carbon preservation are important for global carbon cycle estimates.

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