HISTORICAL TRENDS IN HYPOXIA OF THE SOUTHEASTERN GULF OF CALIFORNIA: 18,000 YEAR RECORD WITHIN PESCADERO BASIN SEDIMENTS

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The Holocene and Pleistocene have the most trustworthy, complete and detailed paleoceanographic record of the Earth history which makes it a perfect time period for novel proxy validation.

However, several questions remain unsolved due to logistical complications during sampling, preservation issues, core dating difficulties, among many others. Marine basins that are suitable for this kind of research are rare through the oceans.

Also the separation between human-influenced alterations and naturally driven cycles is often complicated or even impossible.

International programs exist:

- PAGES (Past Global Changes)
- IODP (International Ocean Discovery Program)
- GEOTRACES

But often the need of collecting new sedimentary material arise.
Reducing conditions

- Modern suboxia, anoxia and euxinia
Relative sea level fluctuations changed bottom dissolved oxygen concentrations of certain basins (for example OMZ depths), affecting nutrient inputs, biological activity and diagenetic transformations.
- **Climate:**
  - semi-arid
  - low precipitation, mostly during summer (< 200 mm/yr)

- **Other features:**
  - Seasonal wind pattern reversal (NE/SW): “Mexican monsoon”
  - River input
  - Tropical cyclones
  - ENSO and PDO
  - Upwellings

- Pacific Ocean (global variability) meets the Gulf of California (semi-restricted processes)
- **Water column:**
  - Strongly defined OMZ at depths from 500 to 1100 m (Alvarez-Borrego and Lara-Lara, 1991)
  - Seasonal $O_2$ variability is still unknown (only sparse data)
- **DIPAL-III T2 gravity core**
  - Collected: during DIPAL-III campaign
  - Water column depth: 577 m (upper OMZ)
  - Recovered sediment length: 263 cm
  - Sub-sampling interval: 1 cm
**Materials and Methods**

**Analyses**

- **Core dating by $^{14}$C AMS method**
  - Rafter Laboratory at GNS Science (New Zealand) and Beta Analytic Lab (USA)
  - Reservoir effect correction (dilution and delay)

- **Determinations (Lyons Lab, UCR):**
  - Total carbon (C), total inorganic carbon ($C_{inorg}$) and total sulfur ($S$) measured on an ELTRA CS-500. **Total organic carbon ($C_{org}$)** was calculated.
  - Major and trace elements using the Agilent 7500 series ICP-MS
  - Iron speciation by sequential extraction (Poulton and Canfield, 2005):

<table>
<thead>
<tr>
<th>Target Fe mineral phases</th>
<th>Extraction reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{\text{carb}}$</td>
<td>carbonate-associated: siderite, ankerite / ferroan dolomite</td>
</tr>
<tr>
<td>Fe$_{\text{ox}}$</td>
<td>(oxyhydr)oxides: goethite, hematite</td>
</tr>
<tr>
<td>Fe$_{\text{mag}}$</td>
<td>magnetite</td>
</tr>
</tbody>
</table>
**SEDIMENTOLOGICAL CHANGES**

**DIPAL-III T2 Core**

<table>
<thead>
<tr>
<th>Core depth (cm)</th>
<th>Core description</th>
<th>Age (cal kyr B.P.)</th>
<th>Sedimentation rate (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Clear and visible lamination</td>
<td>0.760</td>
<td>0.29</td>
</tr>
<tr>
<td>100</td>
<td>Thin lamination, barely visible</td>
<td>1.255</td>
<td>0.29</td>
</tr>
<tr>
<td>200</td>
<td>Homogeneous sediments, no lamination</td>
<td>3.580</td>
<td>0.19</td>
</tr>
<tr>
<td>300</td>
<td>Wavy lamination</td>
<td>5.000</td>
<td>0.16</td>
</tr>
<tr>
<td>400</td>
<td>Homogeneous sediments, no lamination</td>
<td>5.890</td>
<td>0.14</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td>7.350</td>
<td>0.14</td>
</tr>
<tr>
<td>600</td>
<td></td>
<td>10.000</td>
<td>0.05</td>
</tr>
<tr>
<td>700</td>
<td></td>
<td>11.140</td>
<td>13.631</td>
</tr>
<tr>
<td>800</td>
<td></td>
<td>15.000</td>
<td>17.625</td>
</tr>
</tbody>
</table>

**Anoxic bottom waters?**

**Anoxic bottom waters? Transition?**

**Oxygenated bottom waters?**
Similar trends:
- Cariaco Basin core (Lyons et al., 2003; Haug et al., 2001)
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- Cariaco Basin core (Lyons et al., 2003)
- GISP2 Greenland ice core: temperature reconstruction (Alley, 2004)
Iron chemistry

\[
\text{Fe}_{\text{carb}}: \text{carbonate associated}
\]
\[
\text{Fe}_{\text{ox}}: \text{(oxyhydr)oxides}
\]
\[
\text{Fe}_{\text{mag}}: \text{magnetite}
\]
- Biological records
- GISP2 Greenland ice core: temperature reconstruction (Alley, 2004)

Similar trends:

- Paleoproductivity indicators
  - DIPAL-III T2 core
  - Cu, Cd, Ba/Ca

Upper Crust: 2.5 mg/kg
Comparison of DIPAL-III T2 core with other records
- Global trends
- Local variability
- 4 cal kyr B.P. event
- **Pescadero (DIPAL-III T2 core)**
  - Low: biogenic, terrigenous, redox sensitive elements
  - High: Fe_{carb}, Fe_{ox} and Fe_{mag}

- **Soledad Basin, Pacific Ocean**
  - Foram Mg/Ca (Marchitto et al., 2010)

- **Guaymas Basin, Gulf of California**
  - Bio-silica, CaCO_{3}, diatom and silicoflagellates (Barron et al., 2005)
EVOLUTION OF OXYGENATION

<table>
<thead>
<tr>
<th></th>
<th>12 cal kyr</th>
<th>Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Sea Level</td>
<td>-100 m</td>
<td>0 m</td>
</tr>
<tr>
<td>Oxygenation</td>
<td>oxic</td>
<td>anoxic</td>
</tr>
<tr>
<td>Terrigenous input</td>
<td>higher</td>
<td>lower</td>
</tr>
</tbody>
</table>

Pescadero Basin

Note: based on corals and corrected for uplift
1) Low sedimentation rate, bathymetric setting with bottom anoxia, connection to the Pacific Ocean while being part of the Gulf of California allows Pescadero Basin to preserve longer and complete undisturbed geochemical records

2) Organic carbon, sulfur and trace element trends followed the sea-level transition around 11 cal kyr B.P., as well as global climatic variability and even important features such as the southward migration of the Intertropical Convergence Zone

3) A prominent event reported for the Gulf of California and adjacent Pacific occurred around 4 cal kyr B.P. was also found for other proxies/records of the region
Reconstructing paleoceanography and paleoredox of the Gulf of California and Pacific ocean during the LGM

- Dry subsamples of a 47.76 m long core (MD02-2510) from Alfonso Basin
  - Collected in 2002 with the giant CALYPSO coring system only operable from R/V Marion Dufresne
  - Preliminary dating suggest the oldest sediments to be at least 80,000 years
  - Carbon and sulfur chemistry, major and trace elements, Fe chemistry

New paleoredox proxy validation

- Uranium isotopes as a novel paleoredox proxy
  - DIPAL-III T2 core (Pescadero Basin) and MD02-2510 core (Alfonso Basin)
  - Fresh sedimentary material from Alfonso Basin (December, 2014)
R/V El Puma crew (UNAM) and DIPAL-III expedition participants
GRACIAS!

Mazatlan, Sinaloa