Submarine Groundwater Discharge of phosphorus and iron from carbonate coastlines under rising sea levels, Yucatan Peninsula, Mexico.

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Eutrophication of coastal waters

- P and Fe are key **limiting nutrients** for primary productivity.

- Commonly, an **increase** in limiting nutrients leads to **eutrophication** (under optimal conditions).

- The **retention** of P in carbonate sediments is considered to be the main reason that primary production often **appears** to be P limited in tropical and subtropical coastal waters.
  
  (e.g. Fourquean et al 1992; Lapointe et al 1992)
The Nature of the P-Carbonate Interaction

- The release of phosphate from, and adsorption onto sediments and rocks is calculated as a chemical equilibrium between dissolved orthophosphate (SRP) and two solid phases: iron- and calcium-bound phosphate.

- The shifts in these equilibria have been attributed to changes in pH, oxygen availability, redox and temperature...

\[
\begin{align*}
PO_4^{3-} (aq) & 
\rightleftharpoons \text{calcite/aragonite} \ (s) \\
& \rightleftharpoons \text{apatite} \ (s) \\
& \rightleftharpoons \text{Fe-OOH (P)} \ (s)
\end{align*}
\]

*Fig. 1. Phase Diagram of Fe(OOH)- and CaCO₃ bound ortho-Phosphate.*

(Golterman, 1988)
The source and mechanisms for the elevated TP in the mixing zones GW in Yucatan and Florida are as yet unknown.

Likely mechanisms involve water-rock interactions such as ion exchange and carbonate mineral dissolution.

Experiments on P adsorption-desorption in a Key Largo LS block, showed strong adsorption of SRP in DIW and high release by desorption when exposed to seawater. (Price et al, 2010)

Fig. 1. Experimental apparatus used for adsorption/desorption experiments (Price et al, 2010).
P- storage

P
Biogenic/Geological
Anthropogenic

Re-mineralization
(water pool)
[PO₄³⁻]

Co-precipitation
Calcium phosphate
(Millero, 2001)

P -complexation
(Al, Fe, Mn)
e.g. Fe-OOH
(Golterman, 1998)

P -sorption
On carbonate surfaces
(Mustafa, 2007; Price, 2010)

Diagenetic –HAP
Carbonate hydroxy/
fluoroapatite
(Jensen, 1998)
Yucatan Peninsula: natural laboratory

Coastal aquifers: density stratified
Coastal aquifers: density stratified
Coastal aquifers: sea level changes
Coastal aquifers: sea level changes

“Chromatographic column”

Sea level rise
~200 samples
Cave Diving: 120
Quarries: 80

Described

ICP-OES
Ca, Mg, Sr, Ba, Si
Fe, Al, Mn, P, S

Different cave systems
The ‘average’ rock

Ca (rock) 375.6 g/kg
Mg (rock) 9.26 g/kg

Excluding Ca

P (rock) 2.59 mmol/kg (~80 ppm)
Fe (rock) 1.98 mmol/kg (~110 ppm)

TP (GW) 4.9 µmol/L
TP (ocean) 0.57 µmol/L

Si (rock) 24.24 mmol/kg (~680 ppm)
Si (GW) 128.40 µmol/L
Si (ocean) 2.80 µmol/L
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Excluding Ca, Mg

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Si (GW) 128.40 µmol/L
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Bulk rock composition

- Mg: 379.06
- P: 2.59
- Si: 24.78
- Sr: 13.16
- Fe: 1.98
Bulk rock composition: heterogeneity

High-Mg Calcite / dolomite?

High-Mg Calcite / dolomite?

'Shell'

Paleosol

'Shell'

'Redzina'
How do they look like?

- High-Mg Calcite / dolomite?
- Paleosol
- 'Shell'
- 'Redzina'
**Quarry 6**

<table>
<thead>
<tr>
<th>SCALE (m)</th>
<th>LIMESTONES</th>
<th>LITHOLOGY</th>
<th>STRUCTURES/FOSSILS</th>
<th>NOTES</th>
</tr>
</thead>
<tbody>
<tr>
<td>U0</td>
<td>mud</td>
<td></td>
<td></td>
<td>Hard 'caliche' crust. Soil scarce, vegetation</td>
</tr>
<tr>
<td></td>
<td>pack</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>grain</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>rud. &amp; bound</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U1</td>
<td></td>
<td></td>
<td></td>
<td>Well indurated tan light wackstone</td>
</tr>
<tr>
<td>U2</td>
<td></td>
<td></td>
<td></td>
<td>MGr packstone interbedded with planar laminated FGr tan mudstone</td>
</tr>
<tr>
<td>U3</td>
<td></td>
<td></td>
<td></td>
<td>Light tan, v-well indurated mudstone</td>
</tr>
<tr>
<td>U4</td>
<td></td>
<td></td>
<td></td>
<td>Friable wackstone composed of 5-10cm thick well consolidated planar beds</td>
</tr>
<tr>
<td>U5</td>
<td></td>
<td></td>
<td></td>
<td>Light tan, v-well indurated mudstone</td>
</tr>
<tr>
<td>U6</td>
<td></td>
<td></td>
<td></td>
<td>Packages of interbedding dark tan and light reddish wackstone</td>
</tr>
<tr>
<td>U6G</td>
<td></td>
<td></td>
<td></td>
<td>Trace fossils, gastropods</td>
</tr>
</tbody>
</table>
Q1: Is there a geographical decrease inland?
Q2: Is there a decrease with depth?

Q2a: Is there any relationship to the hydro-chemical mixing zone (halocline)?
Q3: Chemostratigraphic correlation?

**Quarry 04**

<table>
<thead>
<tr>
<th>Scale</th>
<th>Unit</th>
<th>Limestones</th>
<th>Structures/Fossils</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>U1</td>
<td>mud</td>
<td></td>
<td>V-well indurated impermeable caliche; root marks</td>
</tr>
<tr>
<td>2</td>
<td>U2</td>
<td>mud</td>
<td></td>
<td>Light tan thinly bedded mudstone. Infiltration of reddish clay 'redzina' is common</td>
</tr>
<tr>
<td>3</td>
<td>U3A</td>
<td>grain</td>
<td>friable wackestone</td>
<td>Friable wackestone. Some secondary deposition in cavities. Coral heads fossils (montastrea sp.)</td>
</tr>
<tr>
<td>4</td>
<td>U3B</td>
<td>grain</td>
<td>friable wackestone</td>
<td>Friable wackestone. Articulated bivalves not imbricated and gastropod fossils.</td>
</tr>
<tr>
<td>5</td>
<td>U4</td>
<td>grain</td>
<td></td>
<td>FGr light pink wackestone, friable</td>
</tr>
<tr>
<td>6</td>
<td>U5</td>
<td>grain</td>
<td></td>
<td>Articulated bivalves</td>
</tr>
<tr>
<td>7</td>
<td>U6</td>
<td>grain</td>
<td></td>
<td>Cavities, conduits and caves are common</td>
</tr>
<tr>
<td>8</td>
<td>U7A</td>
<td>grain</td>
<td></td>
<td>VGr friable mudstone; absence of large clast and shell fragments</td>
</tr>
<tr>
<td>9</td>
<td>U7B</td>
<td>grain</td>
<td></td>
<td>Planar bedding</td>
</tr>
<tr>
<td>10</td>
<td>U8</td>
<td>grain</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>U9</td>
<td>grain</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>U10</td>
<td>grain</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>U11</td>
<td>grain</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>U12</td>
<td>grain</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Graph**

- log Ca/Mg vs Depth (m)

- mmol/kg

- Al, Ba, Fe, Mn, P, S, Si, Sr, -logCa/Mg
Growing dataset

Seeking data on post-Paleozoic carbonate environments

Yucatan Peninsula sedimentology and stratigraphy data

Additional characterizations and analyses...
(Thin sections, Raman, stable isotopes, etc.)
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