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. Fourqurean 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 *o*-phosphate (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…

$PO_4^{3-}{}_{(aq)}$ ⟷ calcite/aragonite $_{(s)}$
apatite$_{(s)}$
Fe-OOH (P) $_{(s)}$

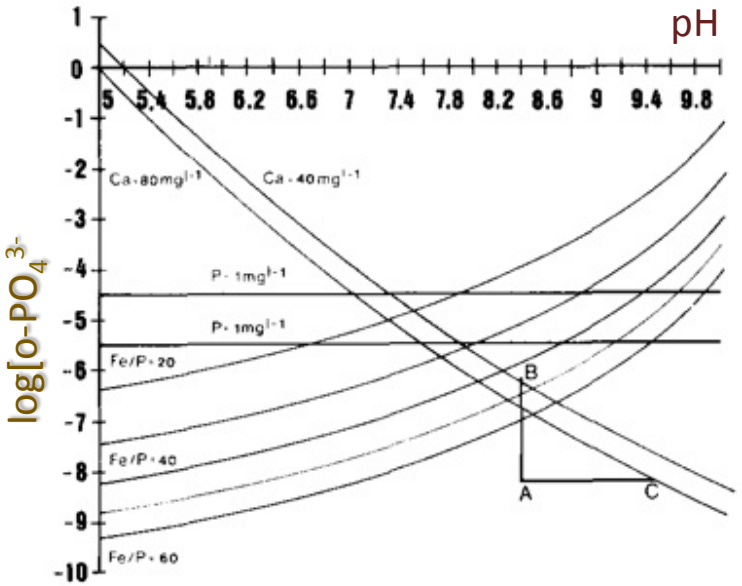


Fig. 1. Phase Diagram of Fe(OOH)- and $CaCO_3$ bound ortho-Phosphate.

(Golterman, 1988)

P-Carbonate absorption-desorption

- 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)

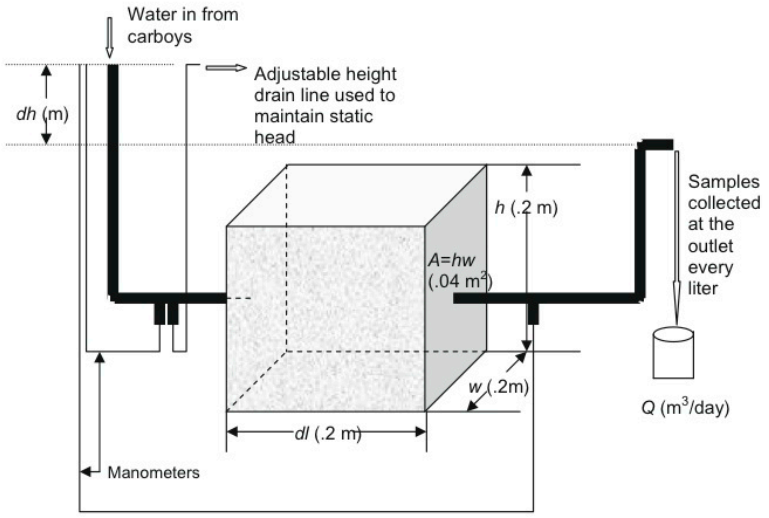
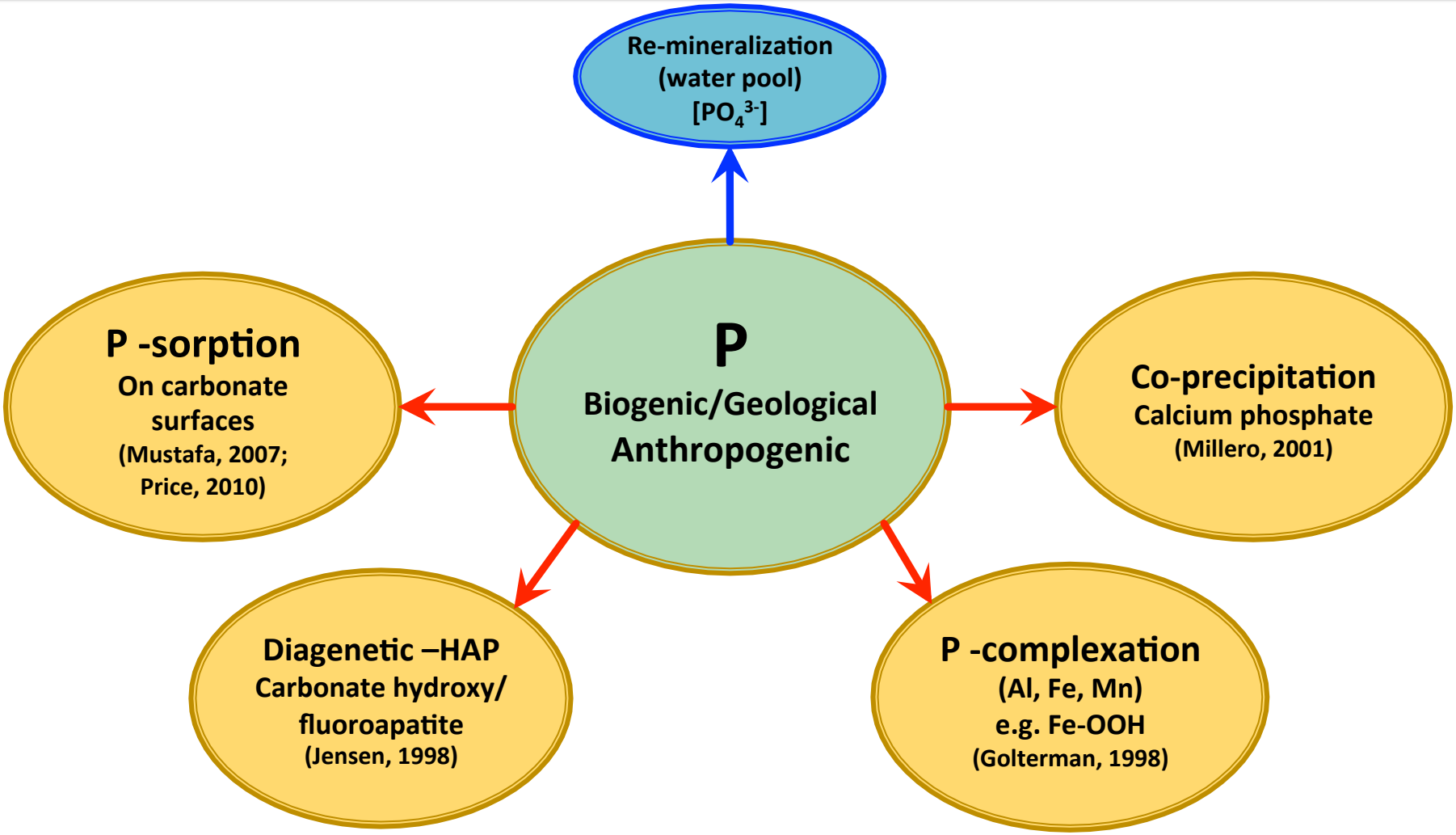
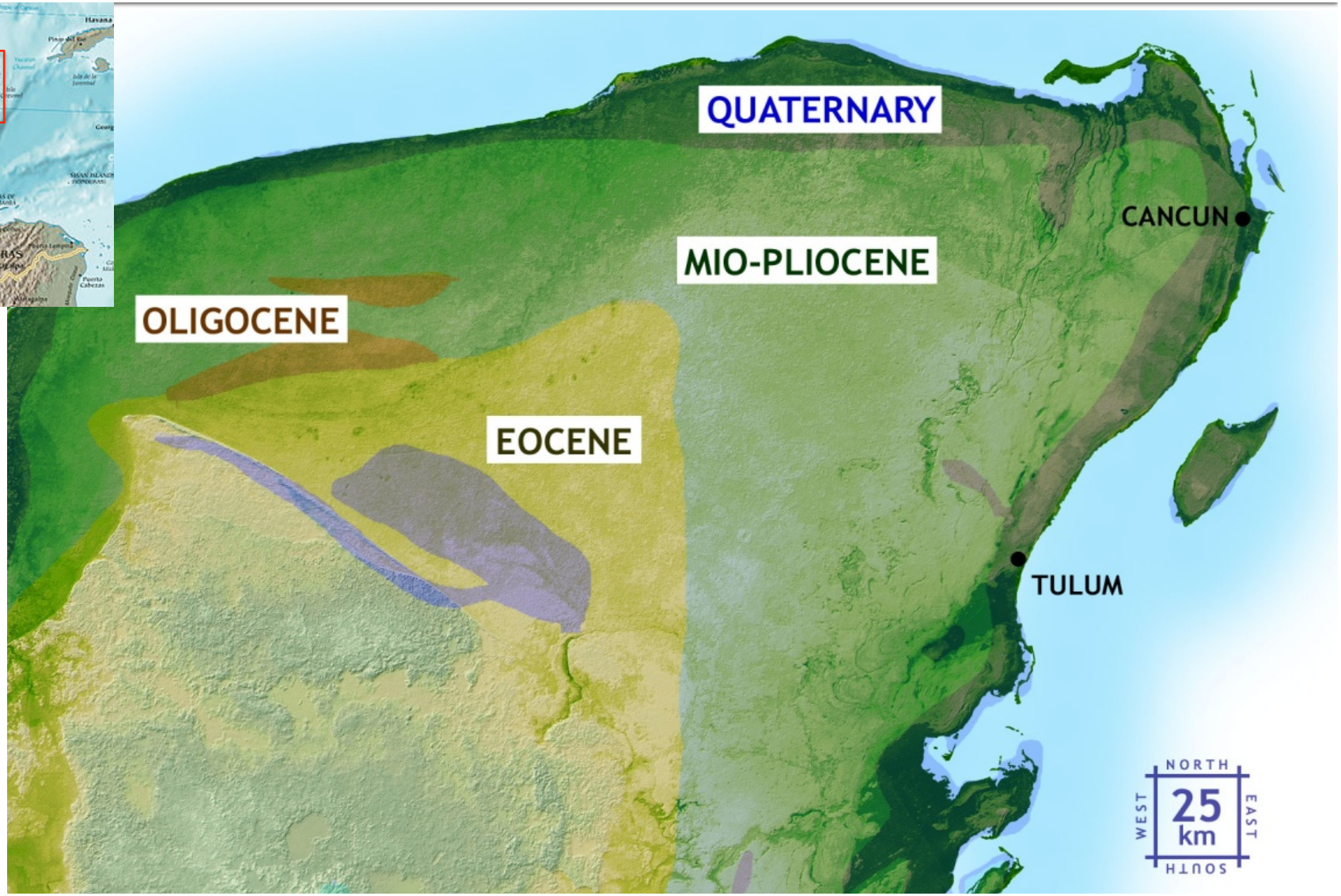


Fig. 1. Experimental apparatus used for adsorption/ desorption experiments (Price et al, 2010).

P- storage

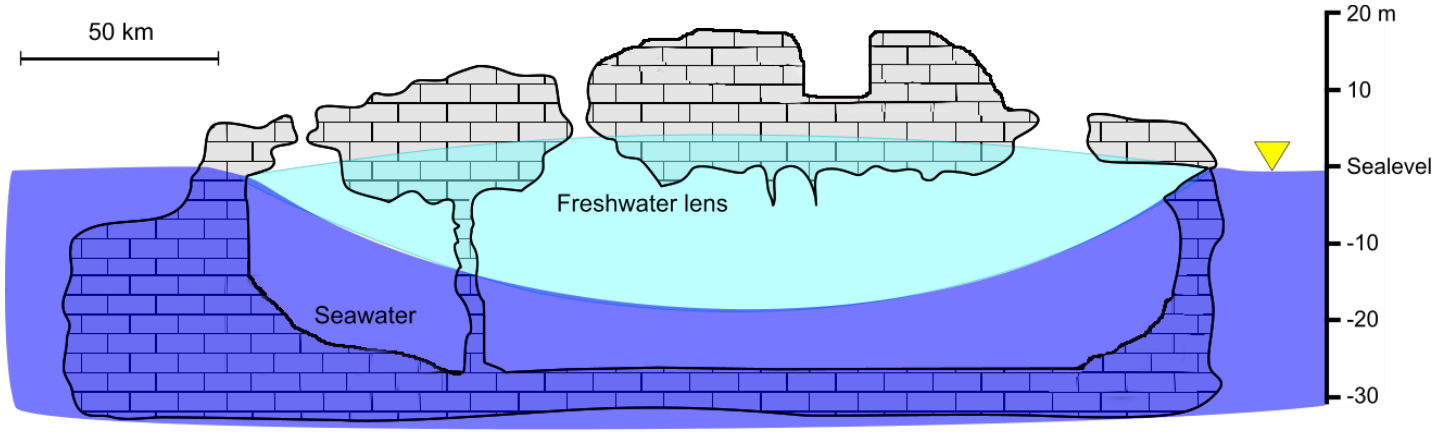

Re-mineralization
(water pool)
[PO_4^{3-}]
P
Biogenic/Geological
Anthropogenic
P -sorption
On carbonate surfaces
(Mustafa, 2007; Price, 2010)
Co-precipitation
Calcium phosphate
(Millero, 2001)
Diagenetic –HAP
Carbonate hydroxy/ fluoroapatite
(Jensen, 1998)
P -complexation
(Al, Fe, Mn)
e.g. Fe-OOH
(Golterman, 1998)

Yucatan Peninsula: natural laboratory



Compiled from Weidie, 1985 and Ward, 1985.

Coastal aquifers: density stratified



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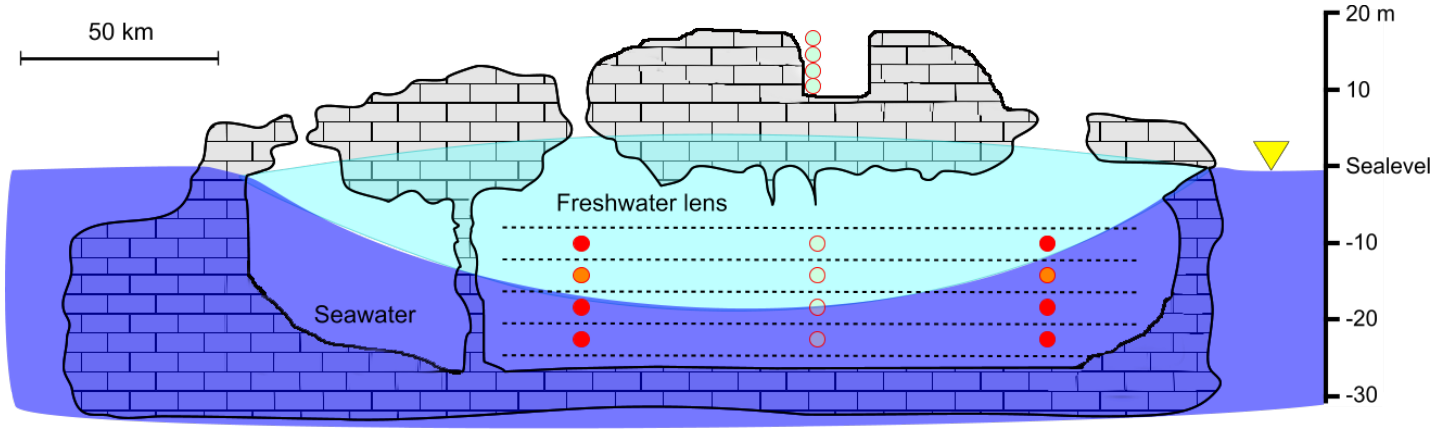
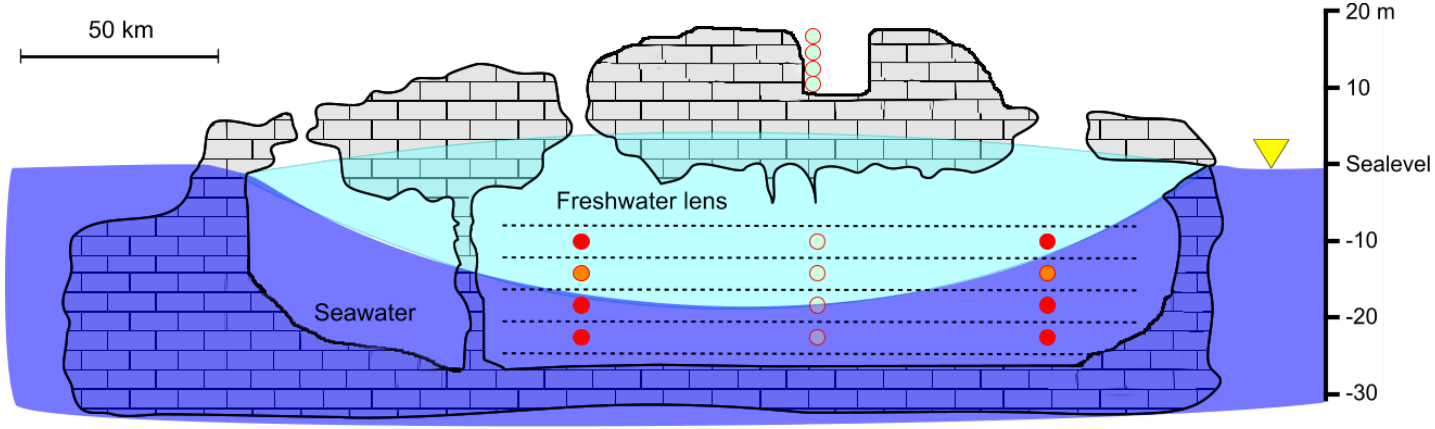
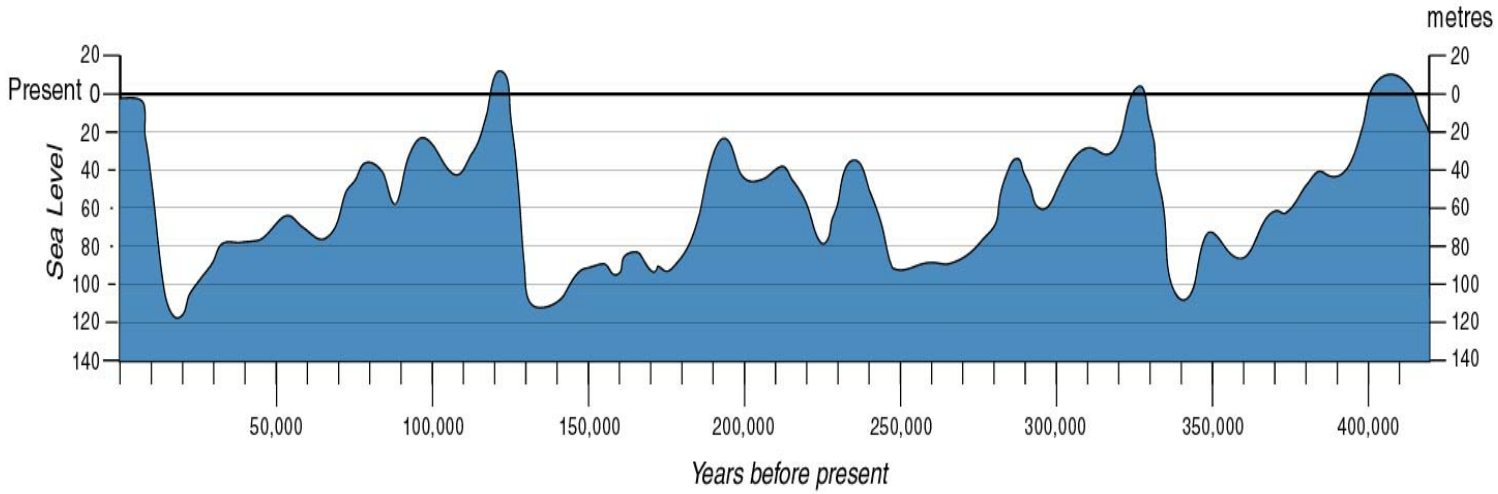


Coastal aquifers: sea level changes





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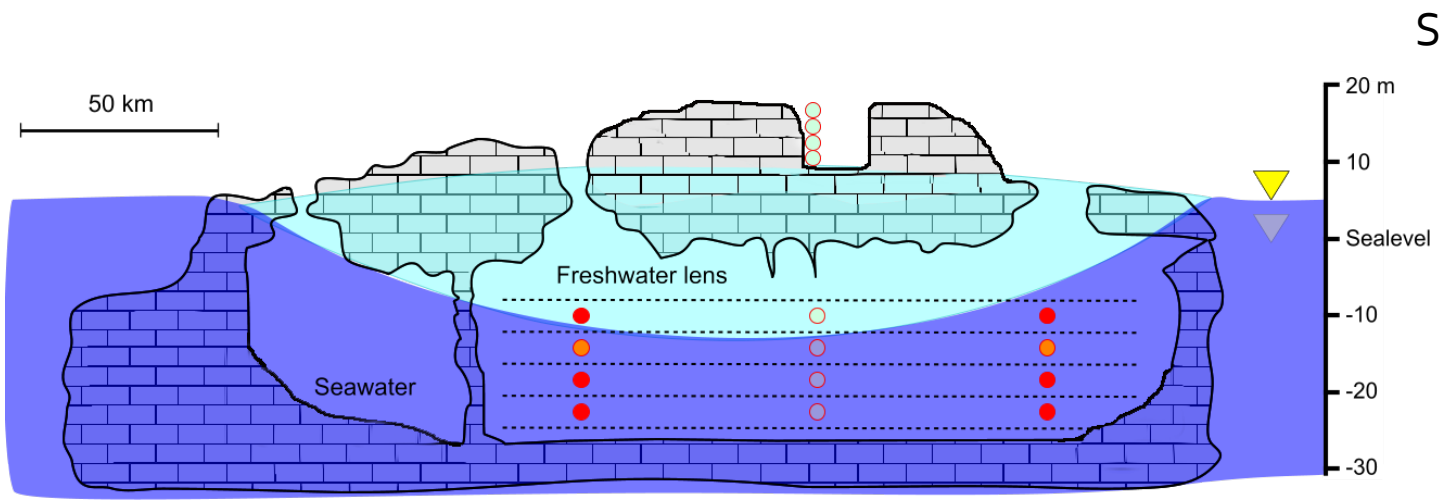
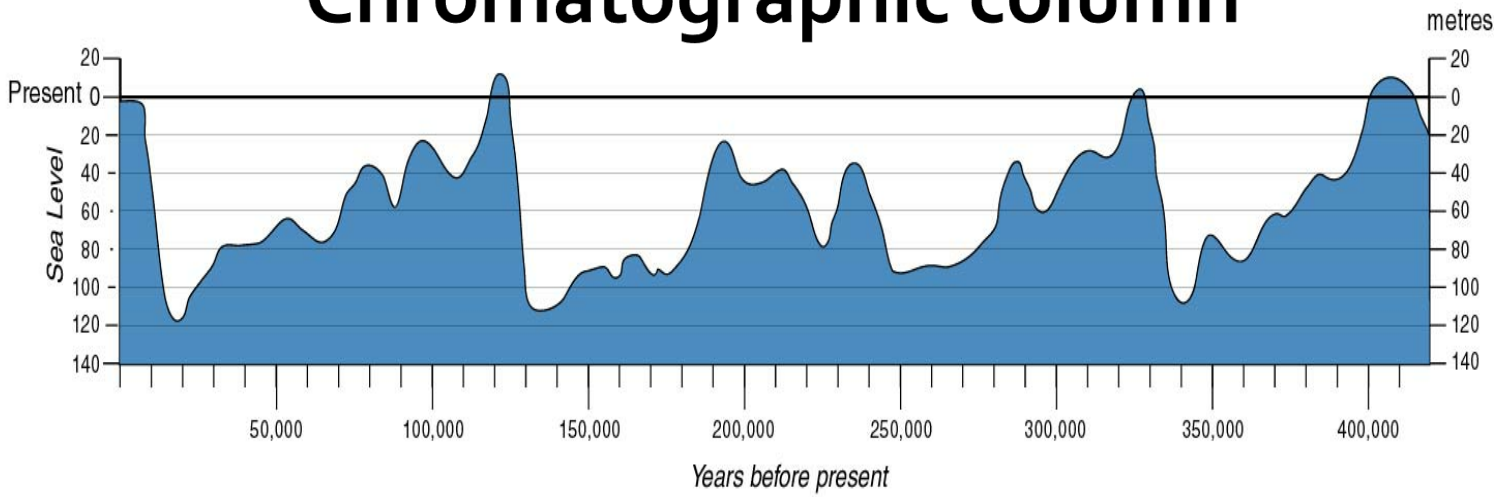


"Chromatographic column"



What do we know so far?

- ~200 samples

Cave Diving: 120

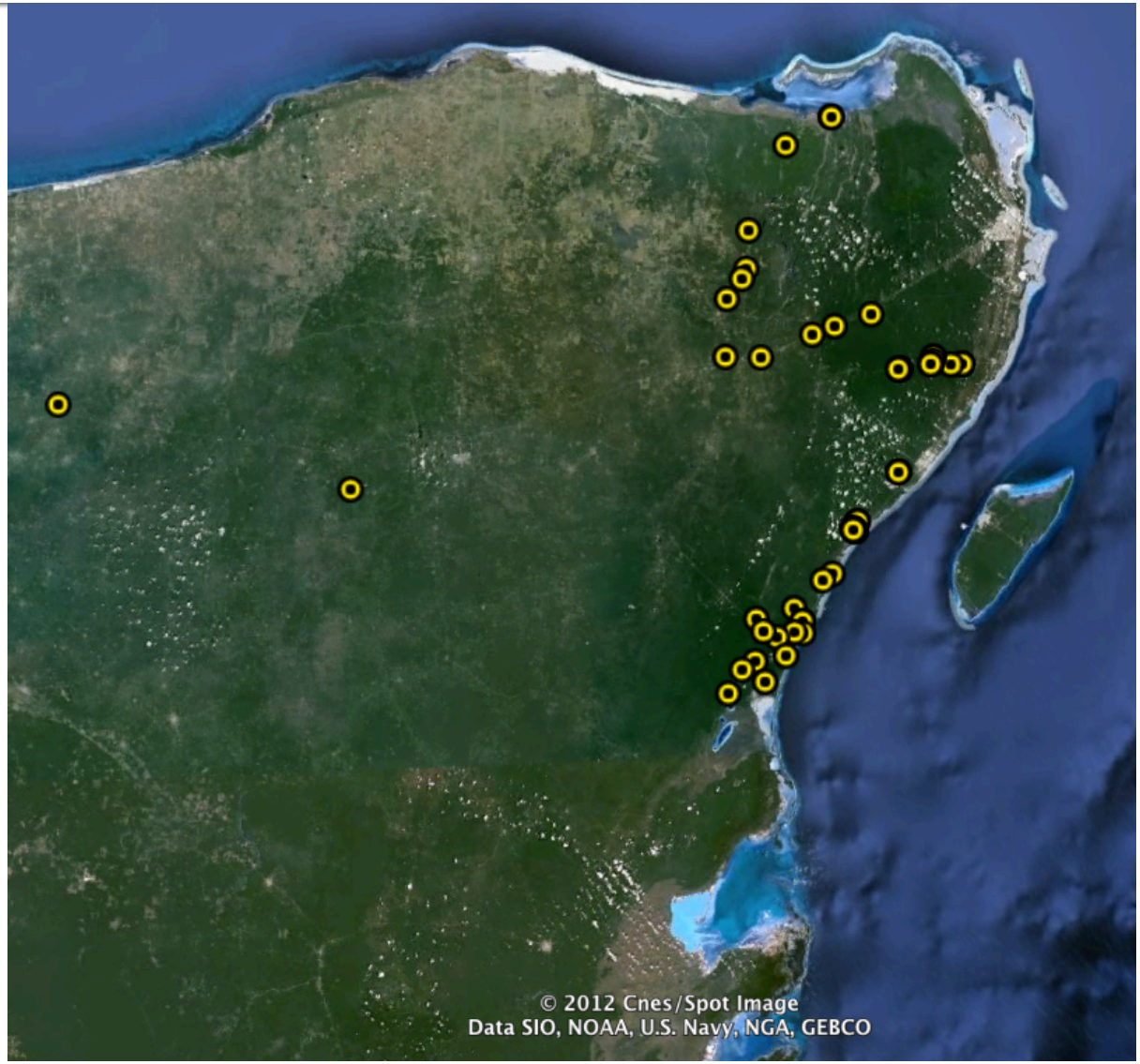
Quarries: 80

- Described
- ICP-OES

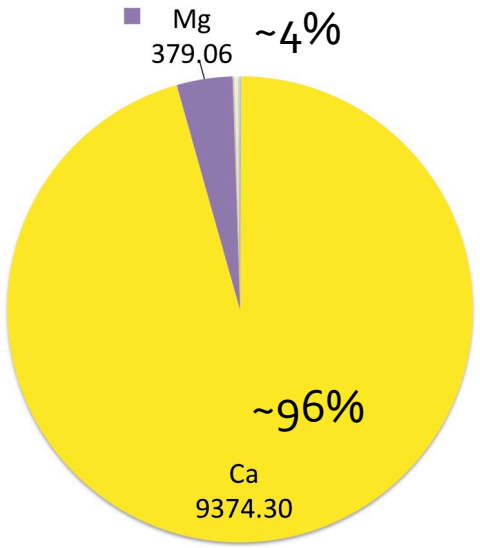
Ca, Mg, Sr, Ba, Si

Fe, Al, Mn, P, S

- Different cave systems

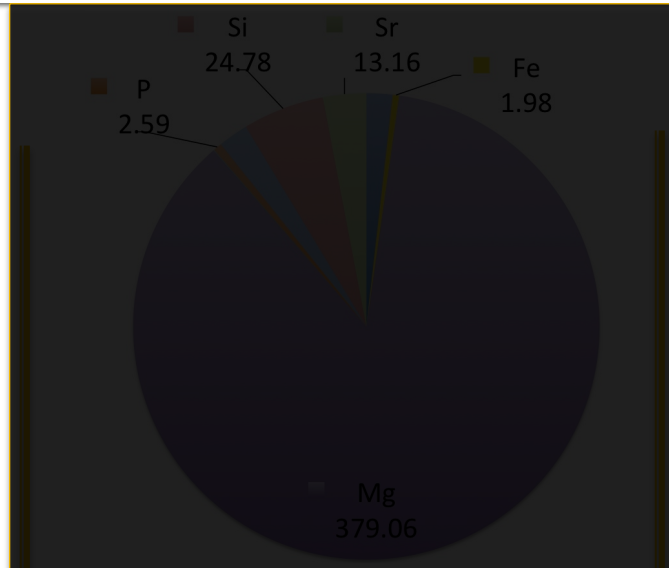


The 'average' rock



Ca (rock) **375.6** g/kg

Mg (rock) **9.26** g/kg

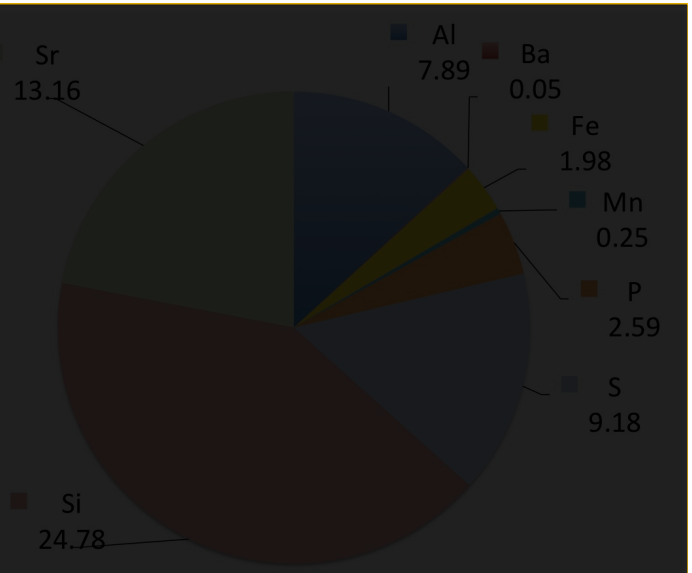


Excluding Ca

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



Excluding Ca, Mg

Si (rock) **24.24** mmol/kg (~680 ppm)

Si (GW) **128.40** µmol/L
Si (ocean) **2.80** µmol/L

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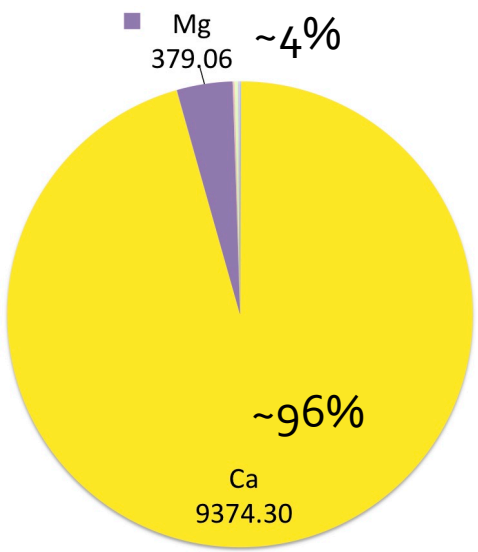

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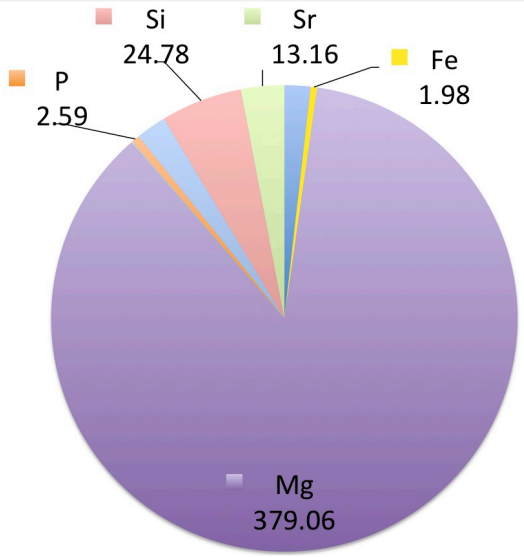

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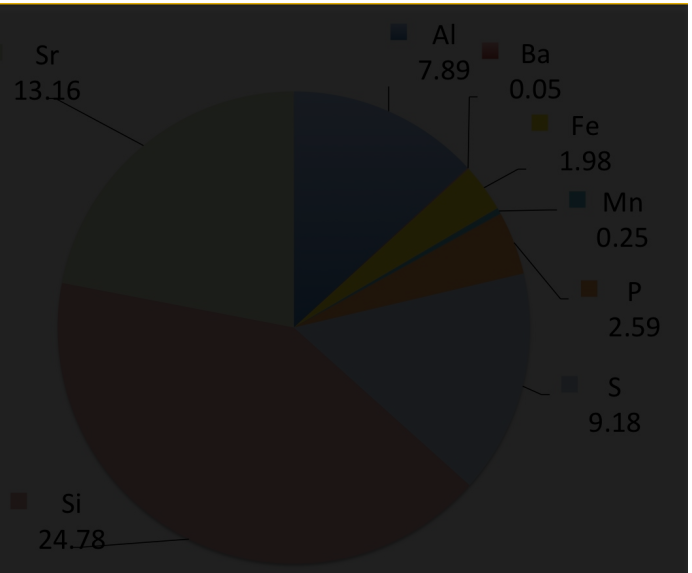

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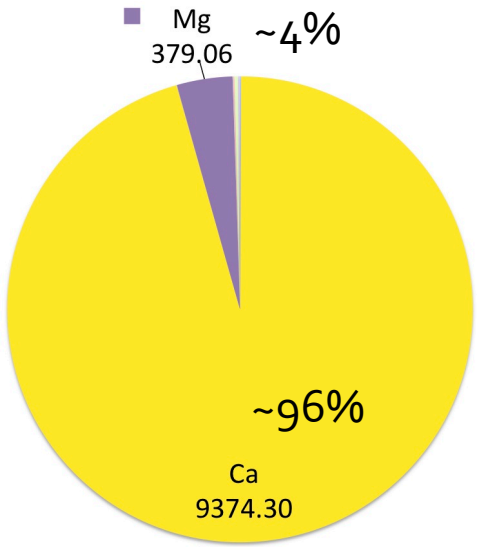

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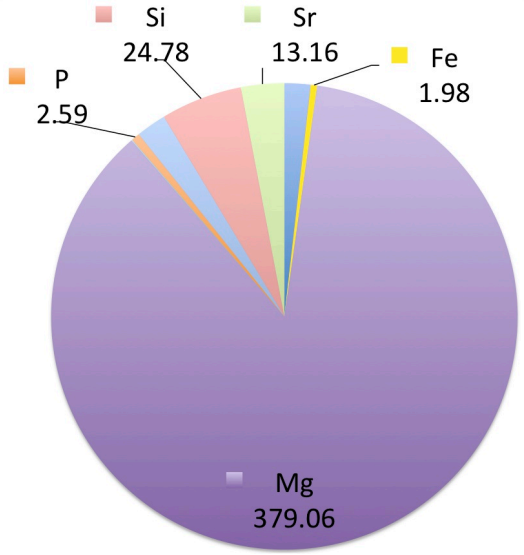

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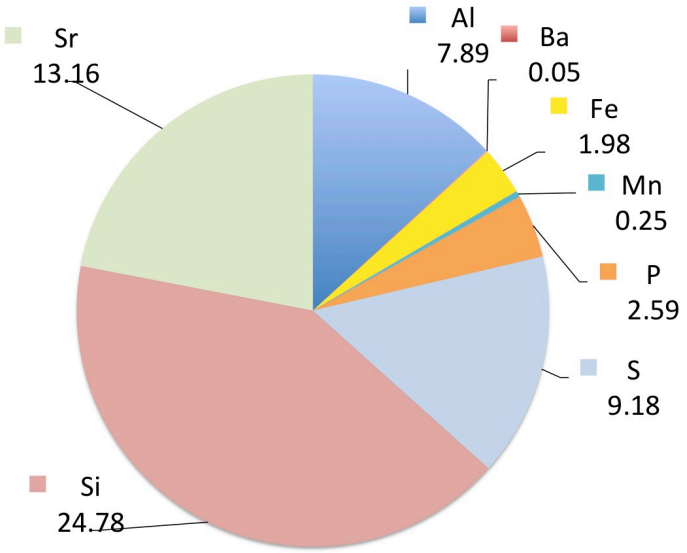

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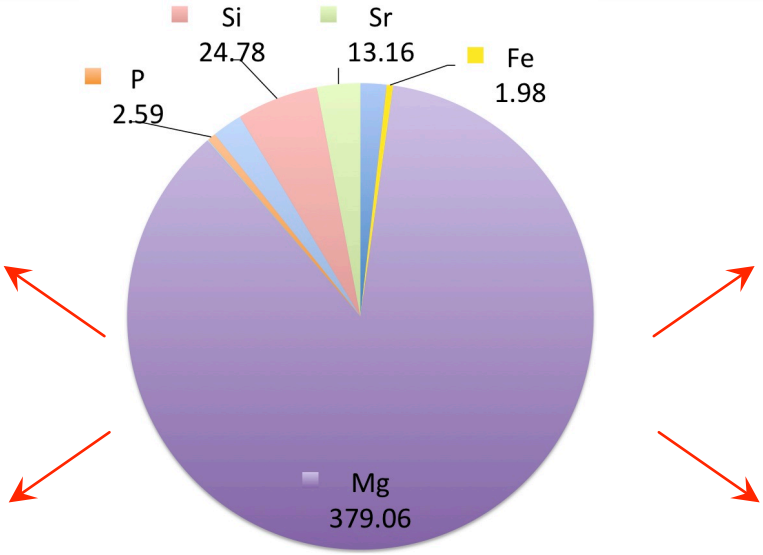
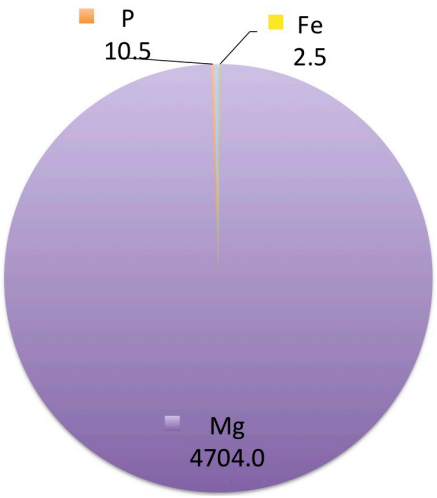
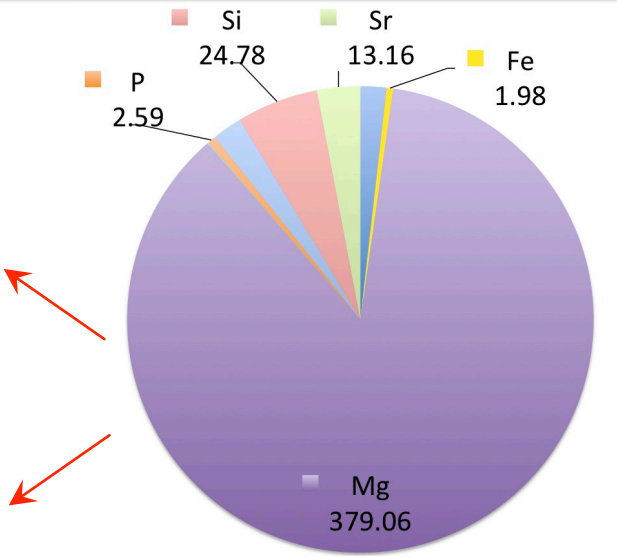
Bulk rock composition

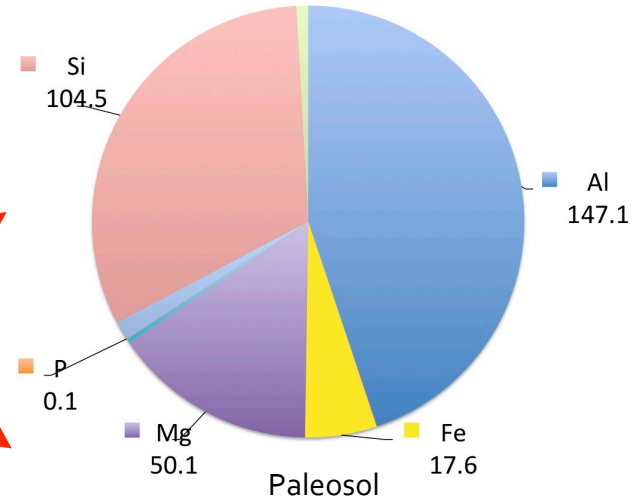


Bulk rock composition: heterogeneity

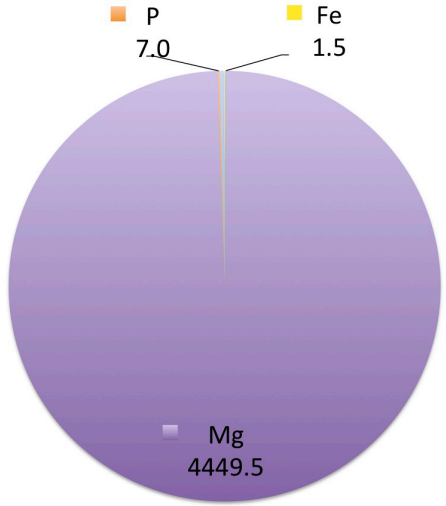


High-Mg Calcite / dolomite?





Paleosol



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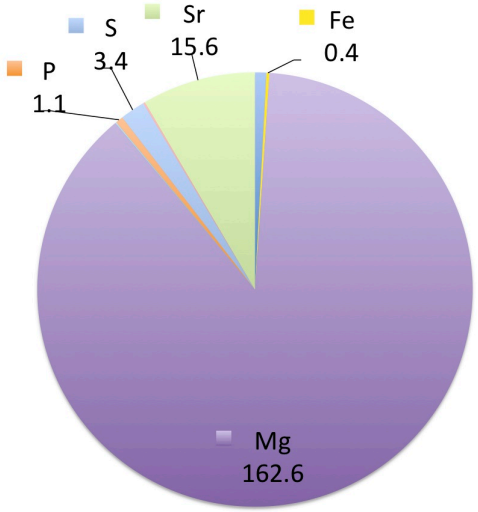
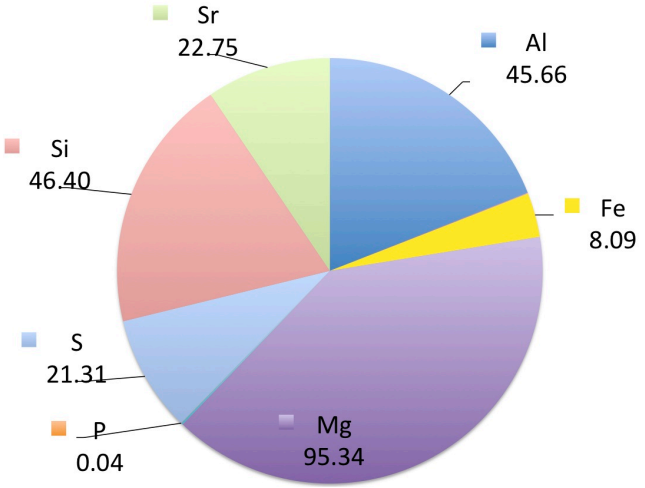
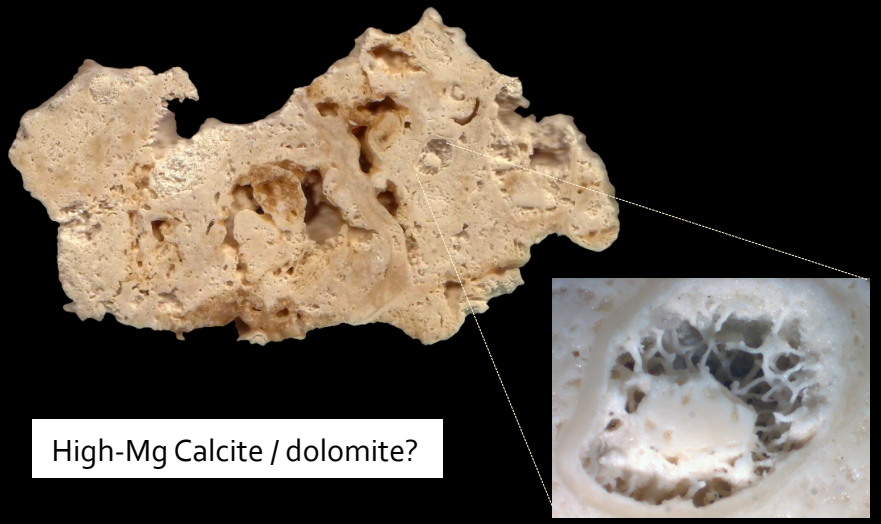


'Shell'



'Redzina'

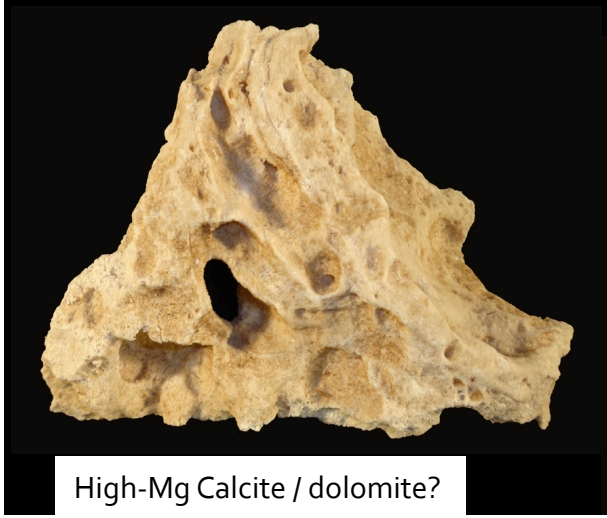
How do they look like?



High-Mg Calcite / dolomite?

2.5 mm

Paleosol



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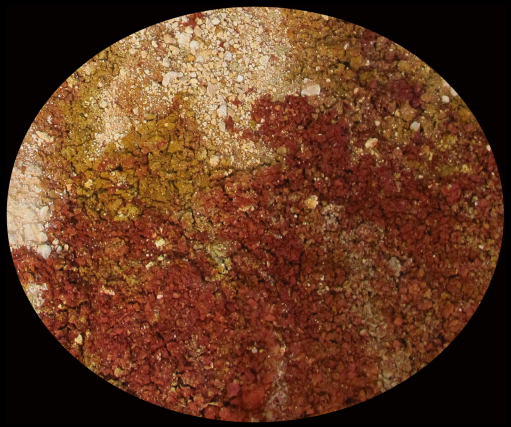
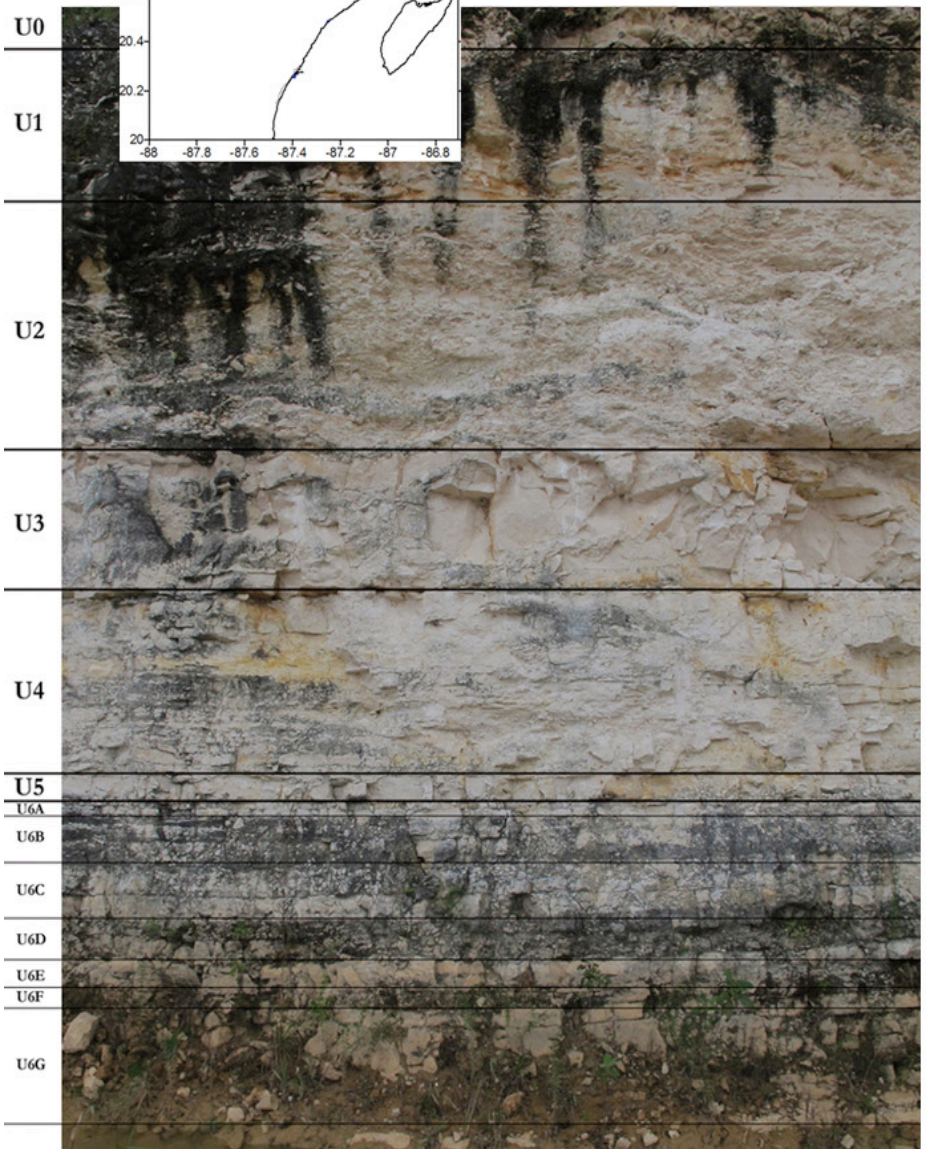
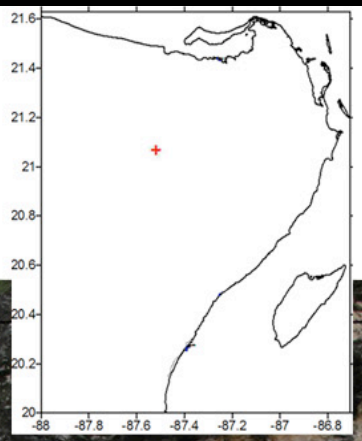


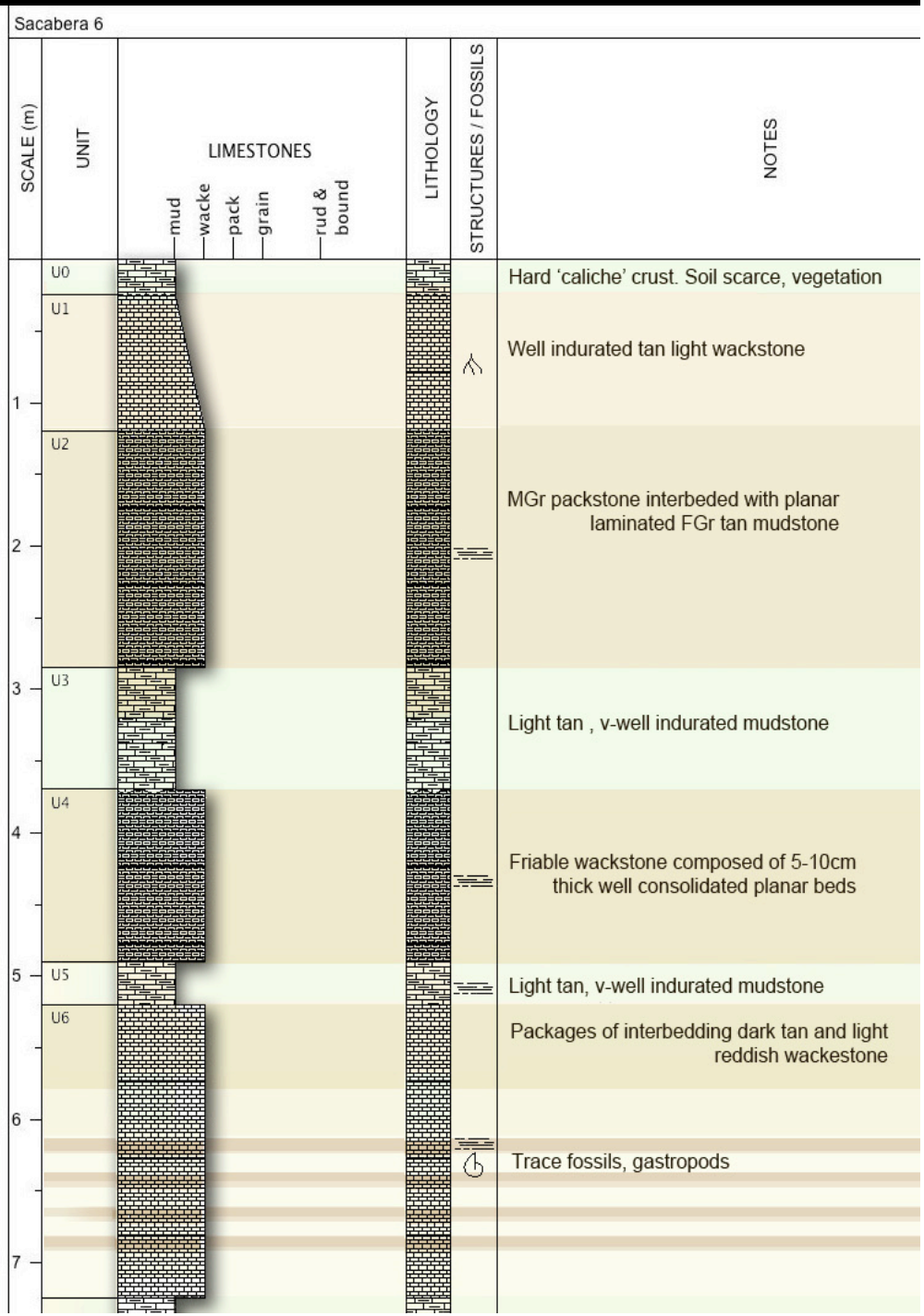
'Redzina'

2.5 cm

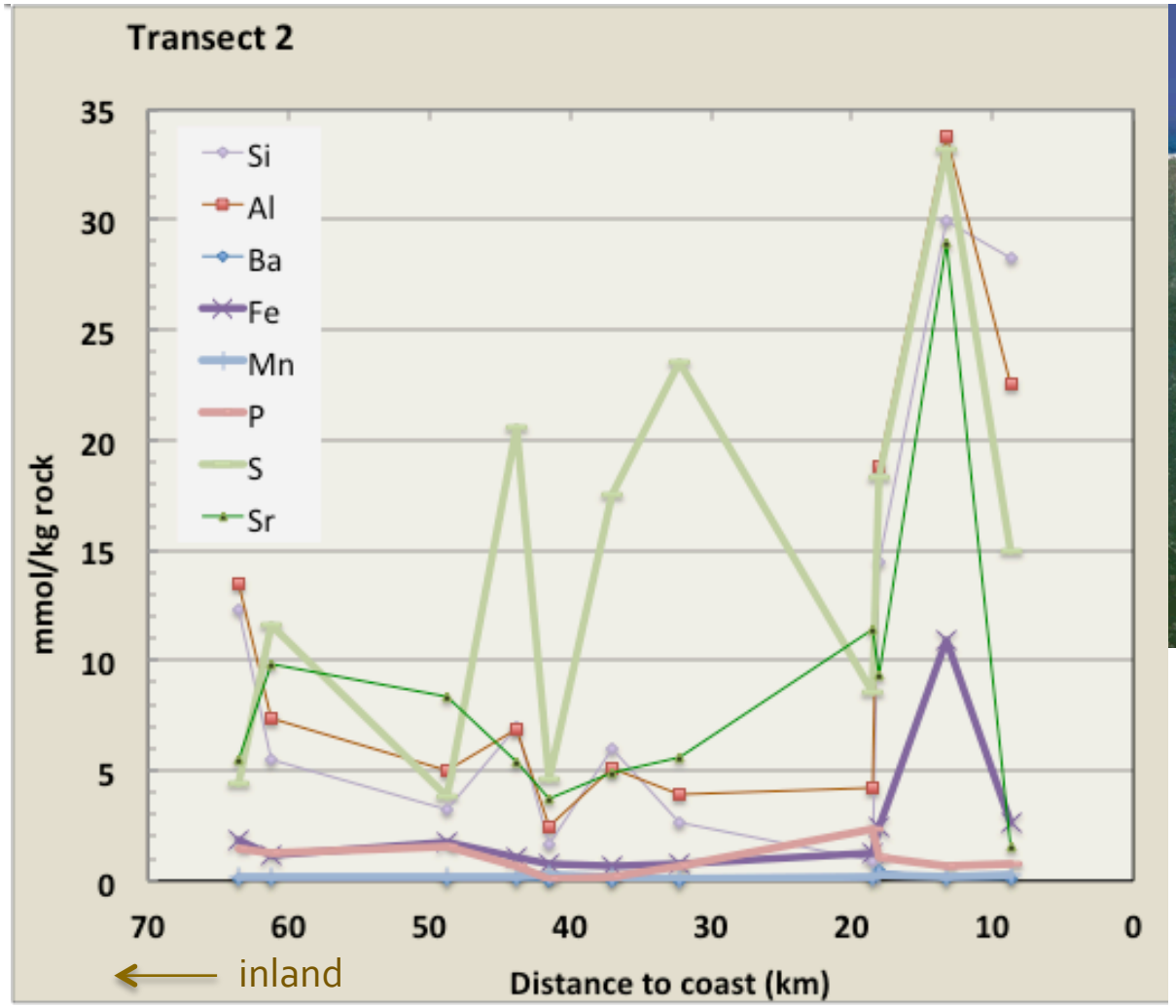
Quarry 6

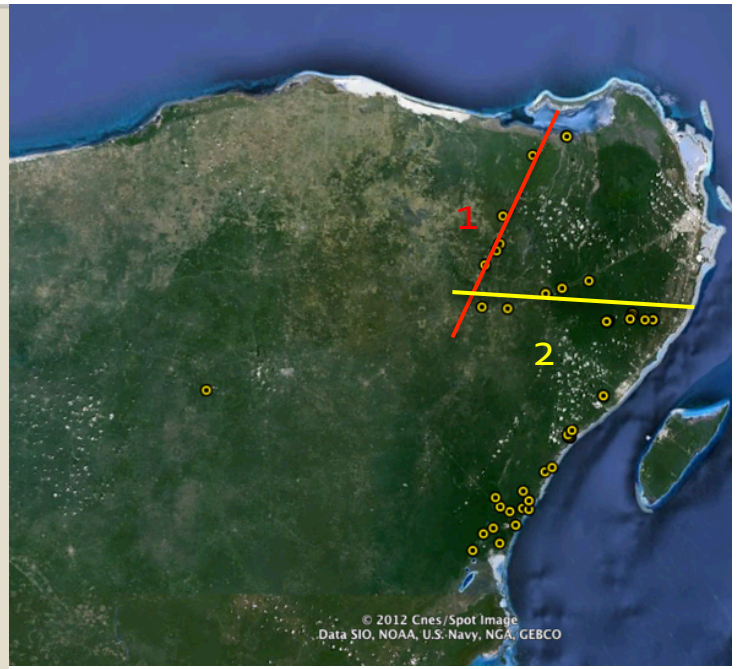

U0
U1
U2
U3
U4
U5
U6A
U6B
U6C
U6D
U6E
U6F
U6G


21.6
21.4
21.2
21
20.8
20.6
20.4
20.2
20
-88
-87.8
-87.6
-87.4
-87.2
-87
-86.8

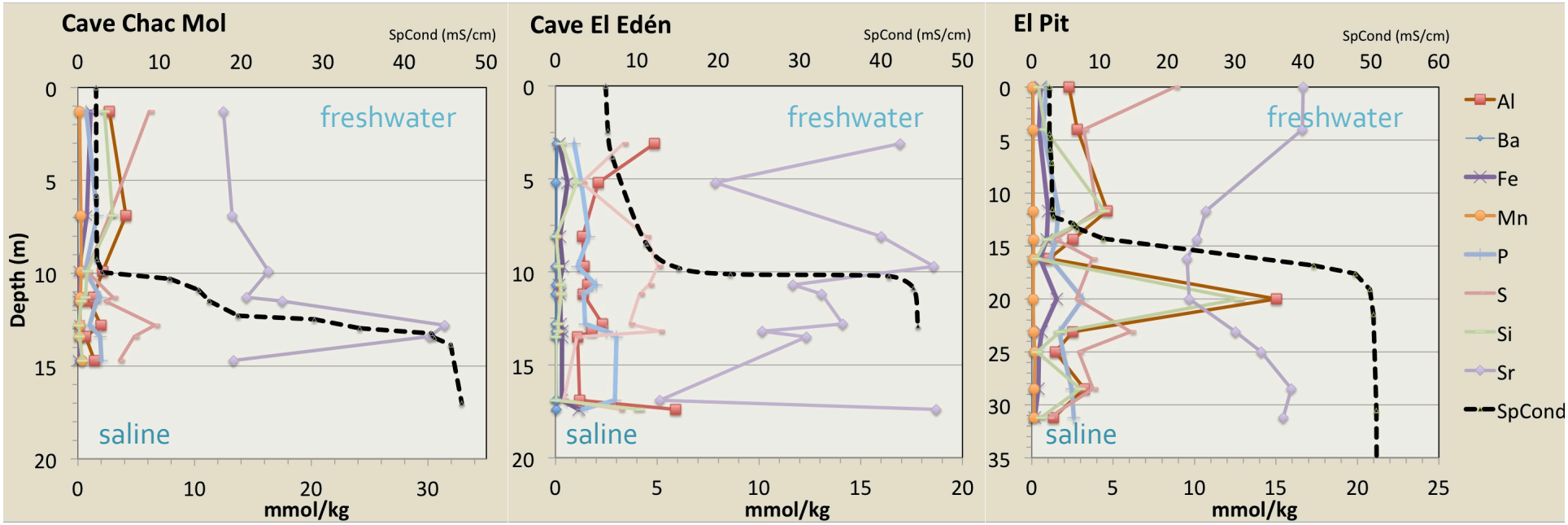

Sacabera 6
SCALE (m)
UNIT
LIMESTONES
mud
wacke
pack
grain
rud &
bound
LITHOLOGY
STRUCTURES / FOSSILS
NOTES
1
2
3
4
5
6
7
U0
U1
U2
U3
U4
U5
U6
Hard 'caliche' crust. Soil scarce, vegetation
Well indurated tan light wackstone
MGr packstone interbeded with planar laminated FGr tan mudstone
Light tan , v-well indurated mudstone
Friable wackstone composed of 5-10cm thick well consolidated planar beds
Light tan, v-well indurated mudstone
Packages of interbedding dark tan and light reddish wackestone
Trace fossils, gastropods

Q1: Is there a geographical decrease inland?



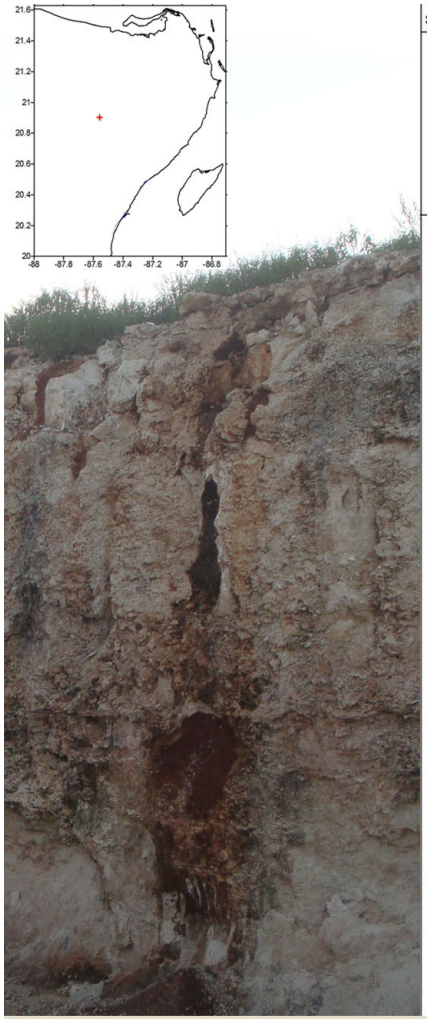


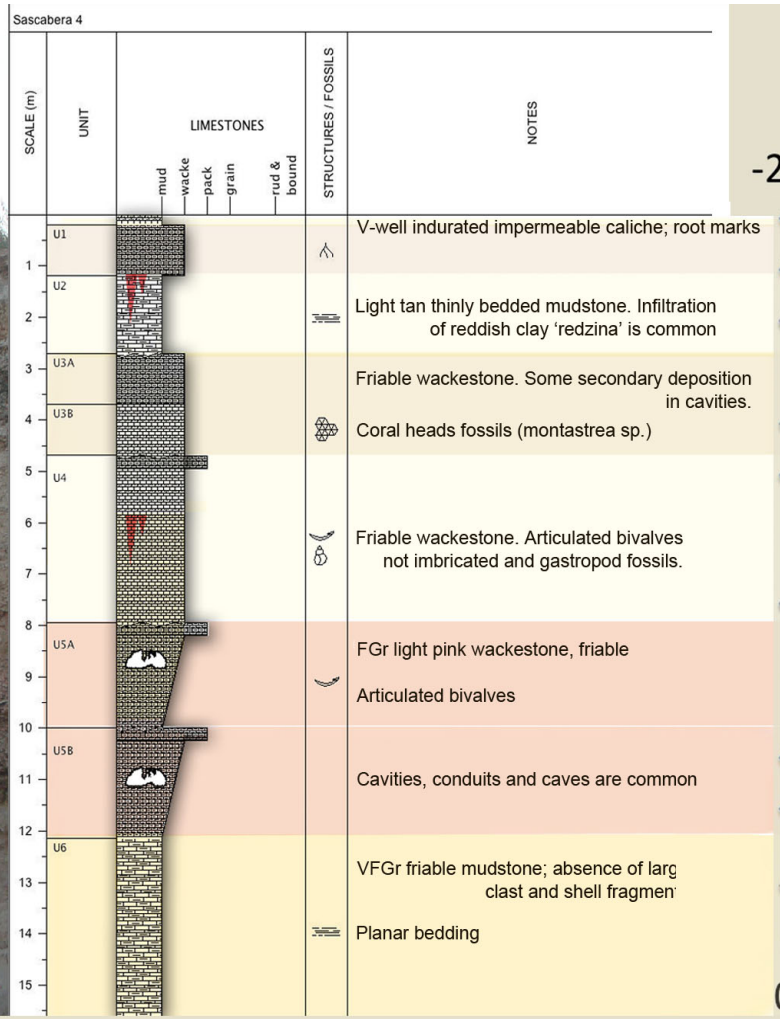
Q2: Is there a decrease with depth?

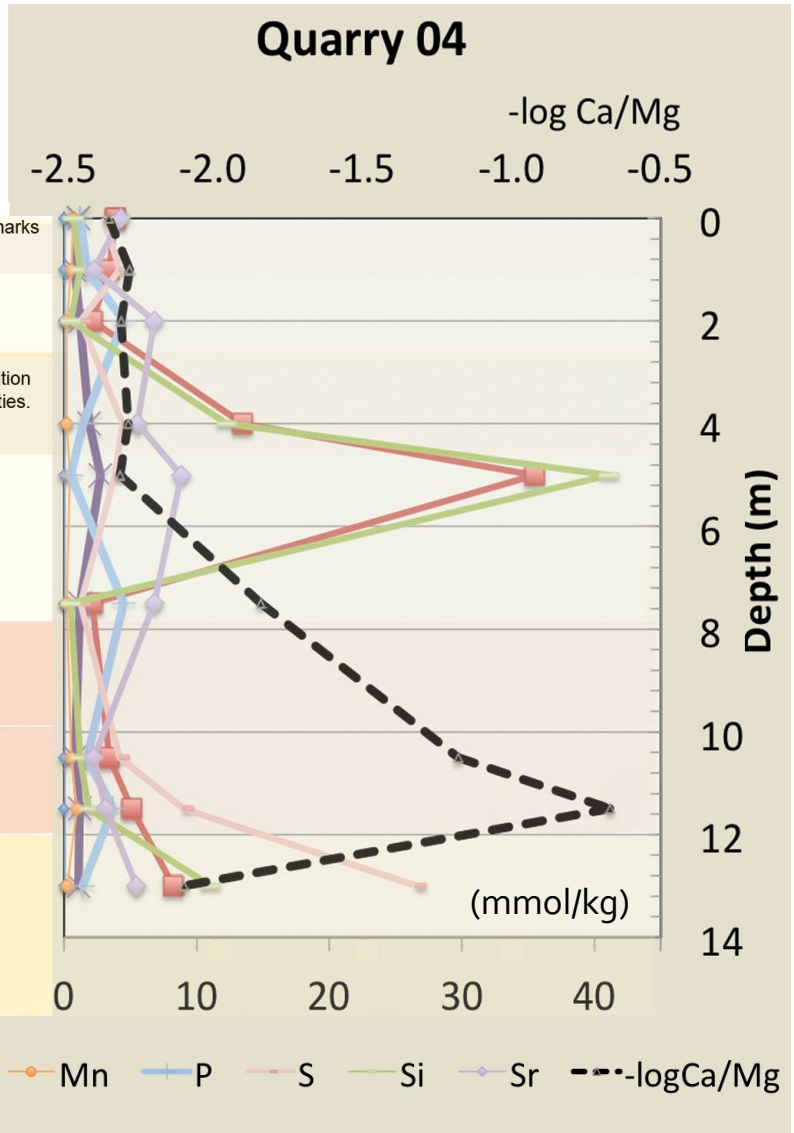


Q2a: Is there any relationship to the hydro-chemical mixing zone (halocline)?

Q3: Chemostratigraphic correlation?







Continuing forward

- 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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