Biogenic opal

What is it?

Amorphous silica:

$SiO_2 \cdot nH_2O$ (~ 10% water)

Precipitated in the surface ocean by:

-- phytoplankton

diatoms, silicoflagellates

-- protozoans

radiolaria

A fraction fall of this opal falls to the sea floor

-- it's efficiently recycled, in water column and sediments

-- overall, ~ 3% of opal production is preserved in sediments

The solubility of biogenic opal in seawater

Initial Studies -- Hurd, 1973, GCA 37, 2257-2282

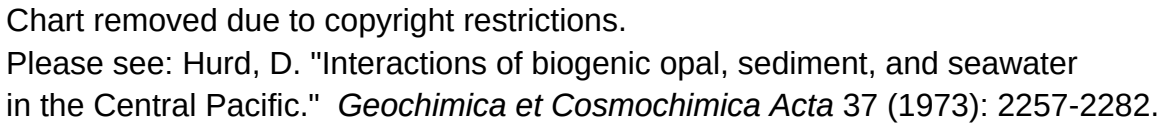
Experiment:

-- separate opal from cores

-- clean with acid

-- place in sw at controlled temp

After ~ days:



$$[SiO_2](aq) \rightarrow [SiO_2]_\infty$$

$$K_{sp}(opal) = [SiO_2]_\infty$$

Note:

T dependence

Solubility ~ 900 µM at 2°C !

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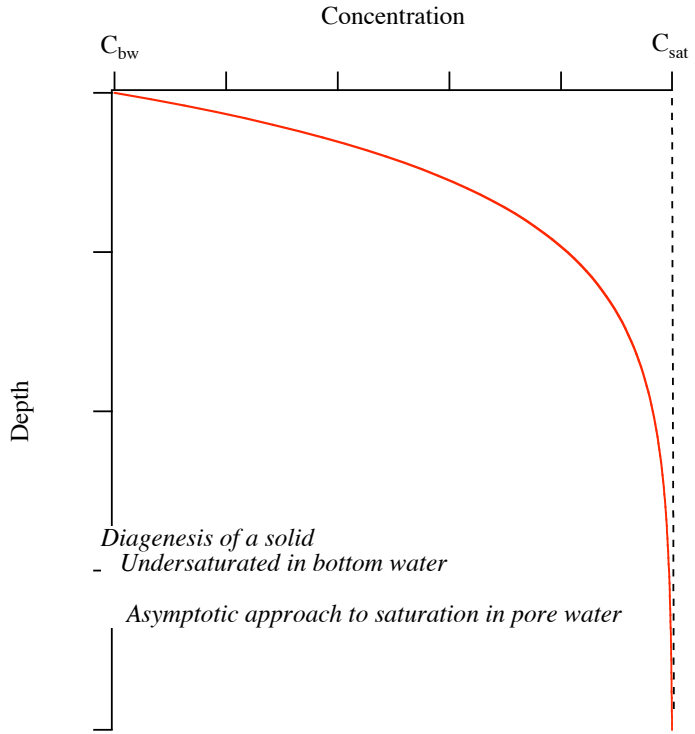
Please see: Hurd, D. "Interactions of biogenic opal, sediment, and seawater in the Central Pacific." *Geochimica et Cosmochimica Acta* 37 (1973): 2257-2282.

A mineral,
undersaturated in seawater
apparently simple dissolution kinetics…

What do we expect $[Si(OH)_4]$ in pore water to look like?

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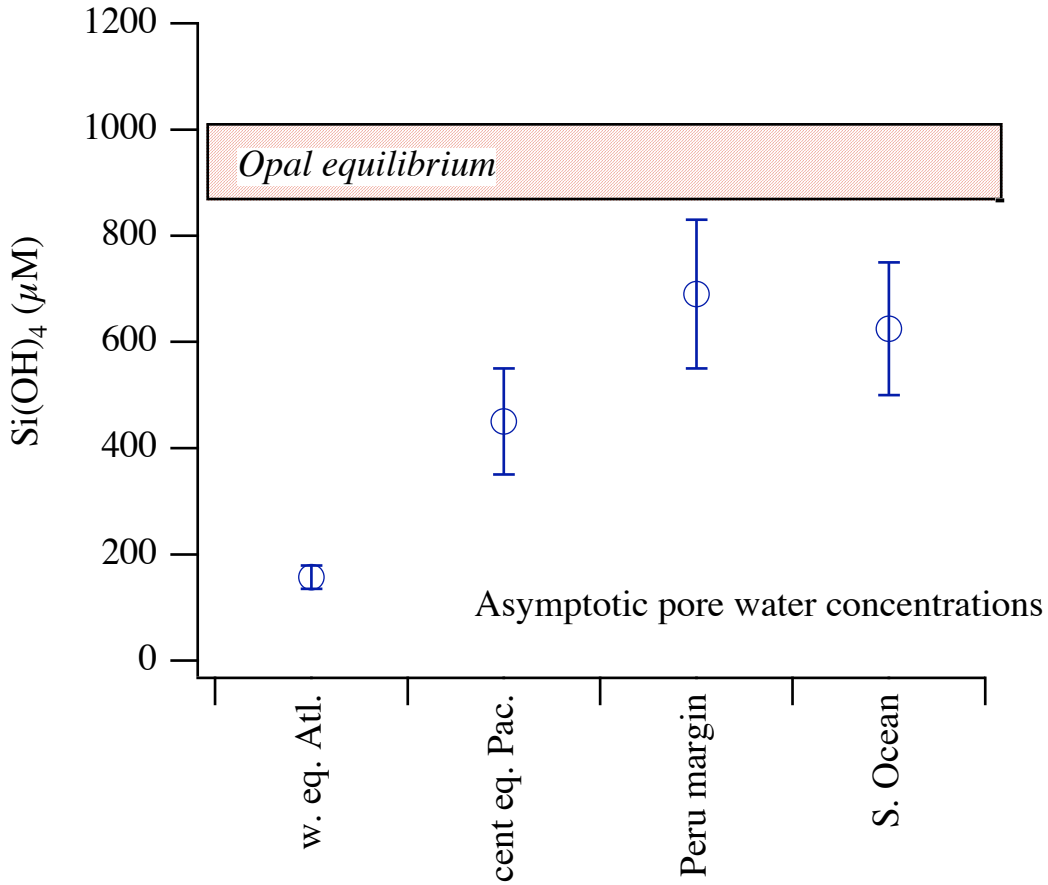
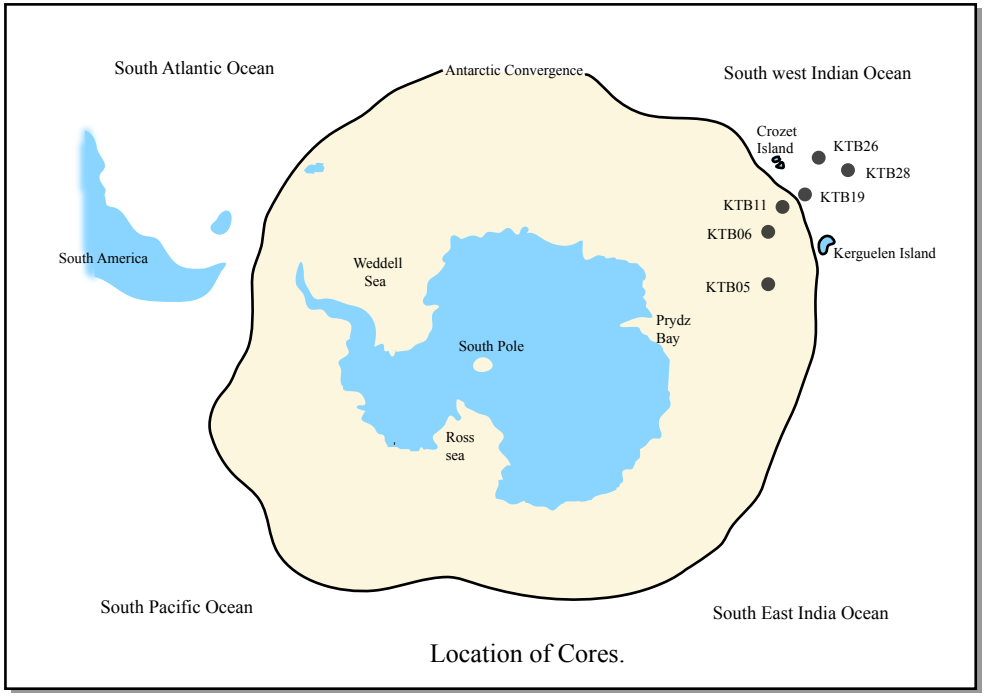
Comparing asymptotic pore water [$Si(OH)_4$] to the “equilibrium” value





Location of Cores.

Figure by MIT OCW.

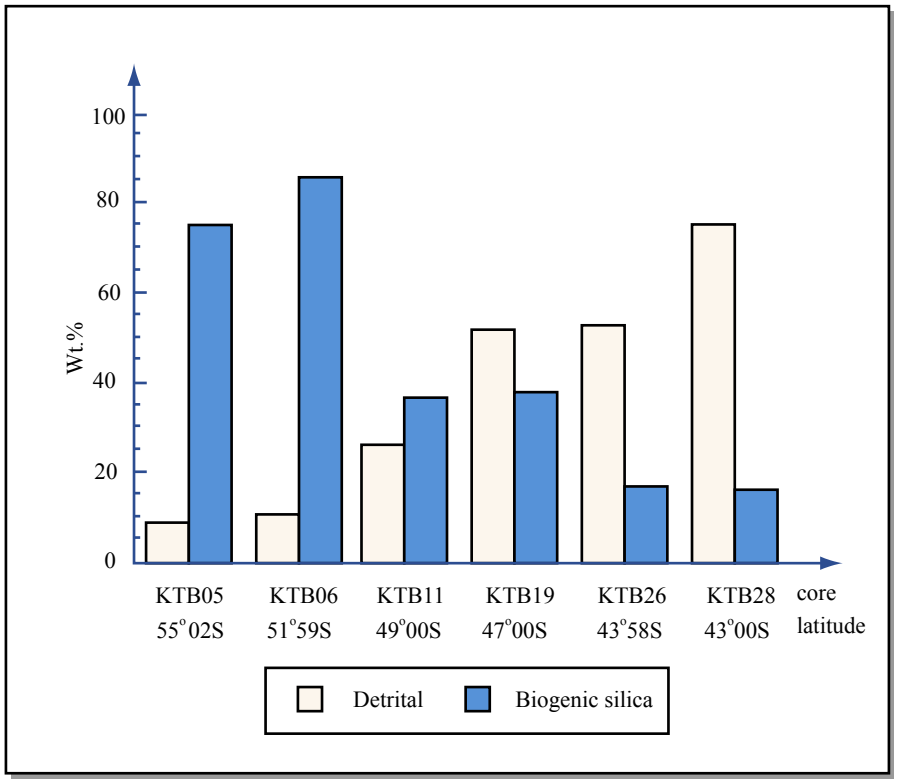


Figure by MIT OCW.

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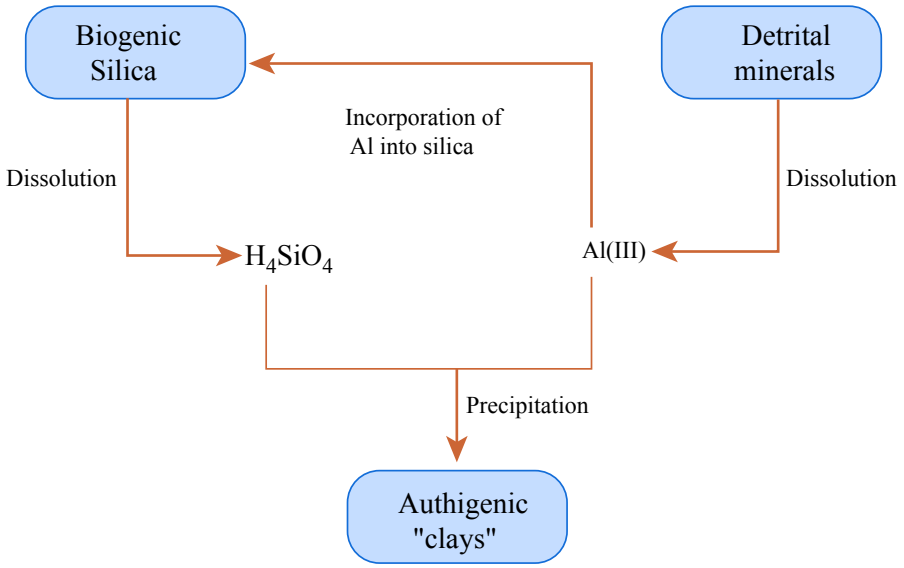
Please see: Cappellen, Philippe Van, and Linqing Qiu. "Biogenic silica dissolution in sediments of the Southern Ocean." *I Solubility*, 1109-1128.



Schematic representation of Al(III)-mediated interactions between detrital matter and biogenic silica in sediments. The interactions depicted are those for which evidence was obtained in this study. (Note: this does not exclude additional processes involved in controlling the build-up of silicic acid in marine sediments.)

Studies of the Preservation Rate of Opal in deep-sea sediments

Components of the studies:

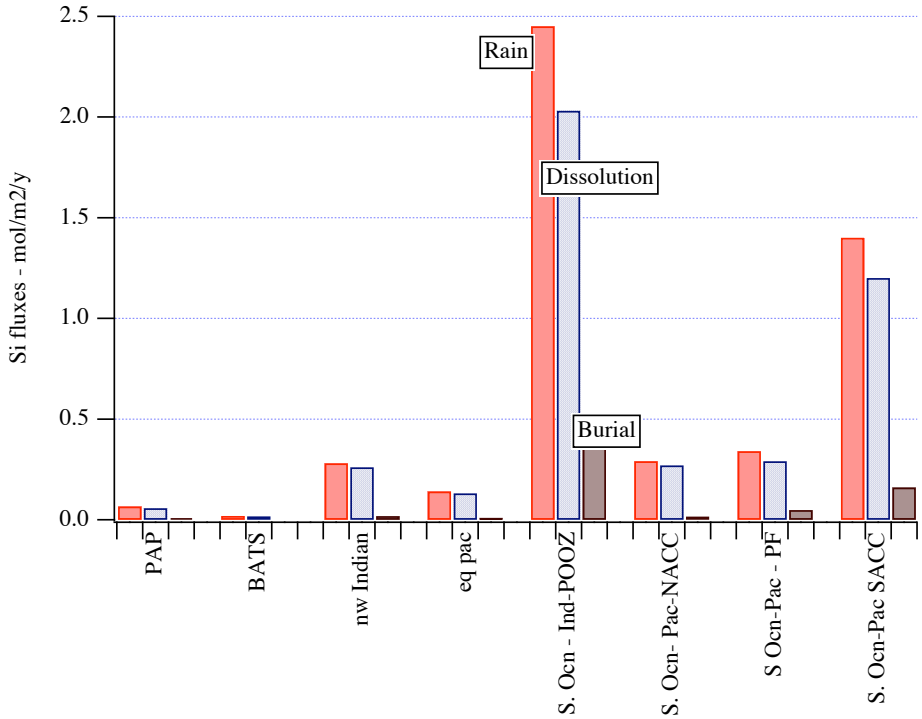
Rain rate to sea floor : time-series sediment traps

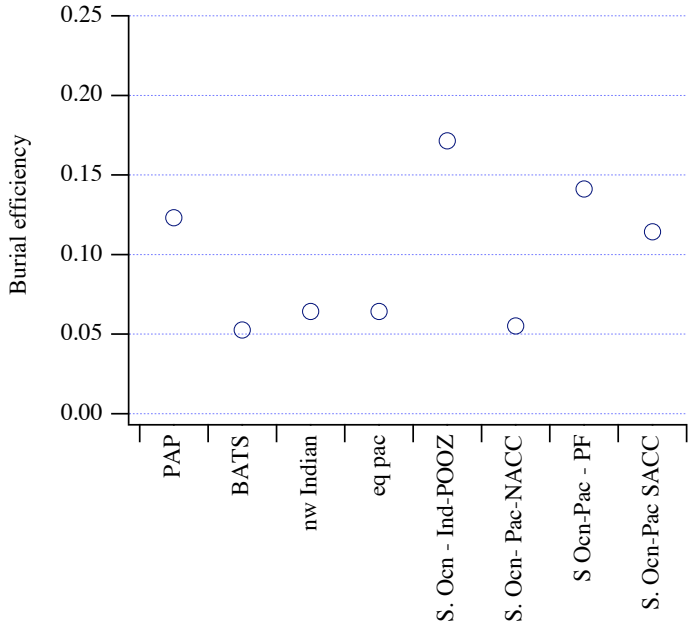
Benthic remineralization rates : flux chambers ; pore waters

Burial rates : solid phase measurements

Opal preservation efficiency in sediments : summary

Sources: Ragueneau et al., 2001
Nelson et al., 2002, DSRII 49, 1645-1674





% opal in sediments -- from Gruber and Sarmiento

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Please see: Gruber, and Sarmiento. *Ocean Biogeochemical Dynamics*. Princton, NJ: Princeton University Press, 2006. ISBN: 9780691017075.

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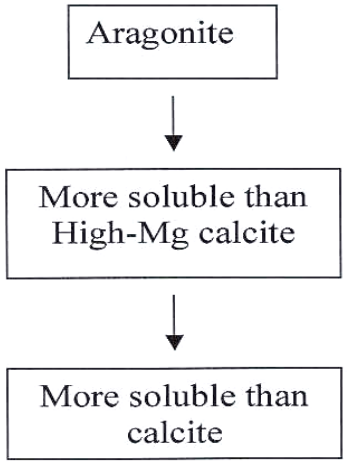
Mechanism for $CaCO_3$ Dissolution in Sediments:

Dissolution in pore waters that are undersaturated w.r.t. the abundant mineral phase

1. Which mineral?



….. CALCITE is the predominant mineral in the deep sea.

2. Quantifying solubility <u>in seawater</u>

<u>Conditional</u> Solubility product,

$$K_{sp} = [Ca^{2+}][CO_3^{2-}]$$

T=25°C, P=1atm, S=35 psu:

Ingle (1975)	$4.60 \pm 0.10 \times 10^{-7}$
Mucci (1983)	$4.30 \pm 0.20 \times 10^{-7}$

i.e., $\pm \sim 5\%$

The pore water based estimate (Sayles 1985)

① Measure Alk, ΣCO_2, Ca^{+} vs. depth in pore waters of sediments underlying water columns of varying depth

② Calculate $[CO_3^{2-}] \times [Ca^{2+}]$
: Most often is constant below a few cm.

③ If the pore waters have reached saturation with respect to calcite, $\left([CO_3^{2-}][Ca^{2+}]\right)_{meas} = K_{sp}^{sw}$

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Please see: Sayles, J. "CaCO3 solubility in marine sediments: Evidence for equilibrium and non-equilibrium behavior." *Geochim Cosmochim Acta* 49 (1985): 877-888.

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Temperature dependence of calcite solubility: Experimentally determined:

As T *decreases*, K_{sp} *increases*

Pressure dependence of calcite solubility: Both experimentally determined and calculated:

As P *increases*, K_{sp} *increases*

SO: CALCITE BECOMES MORE SOLUBLE WITH INCREASING DEPTH IN THE OCEAN.

Describing the saturation state of seawater & pore water with respect to calcite:

"Degree of saturation"

$$\Omega = \frac{\left(\left[Ca^{2=}\right]\left[CO_3^{2-}\right]\right)_{meas}}{K_{sp}} \approx \frac{\left[CO_3^{2-}\right]_{meas}}{\left[CO_3^{2-}\right]_{equil}}$$

"Delta-carbonate"

$$\Delta CO_3^{2-} = \left[CO_3^{2-}\right]_{meas} - \left[CO_3^{2-}\right]_{equil} \quad \text{in } \mu\text{mol/kg}$$


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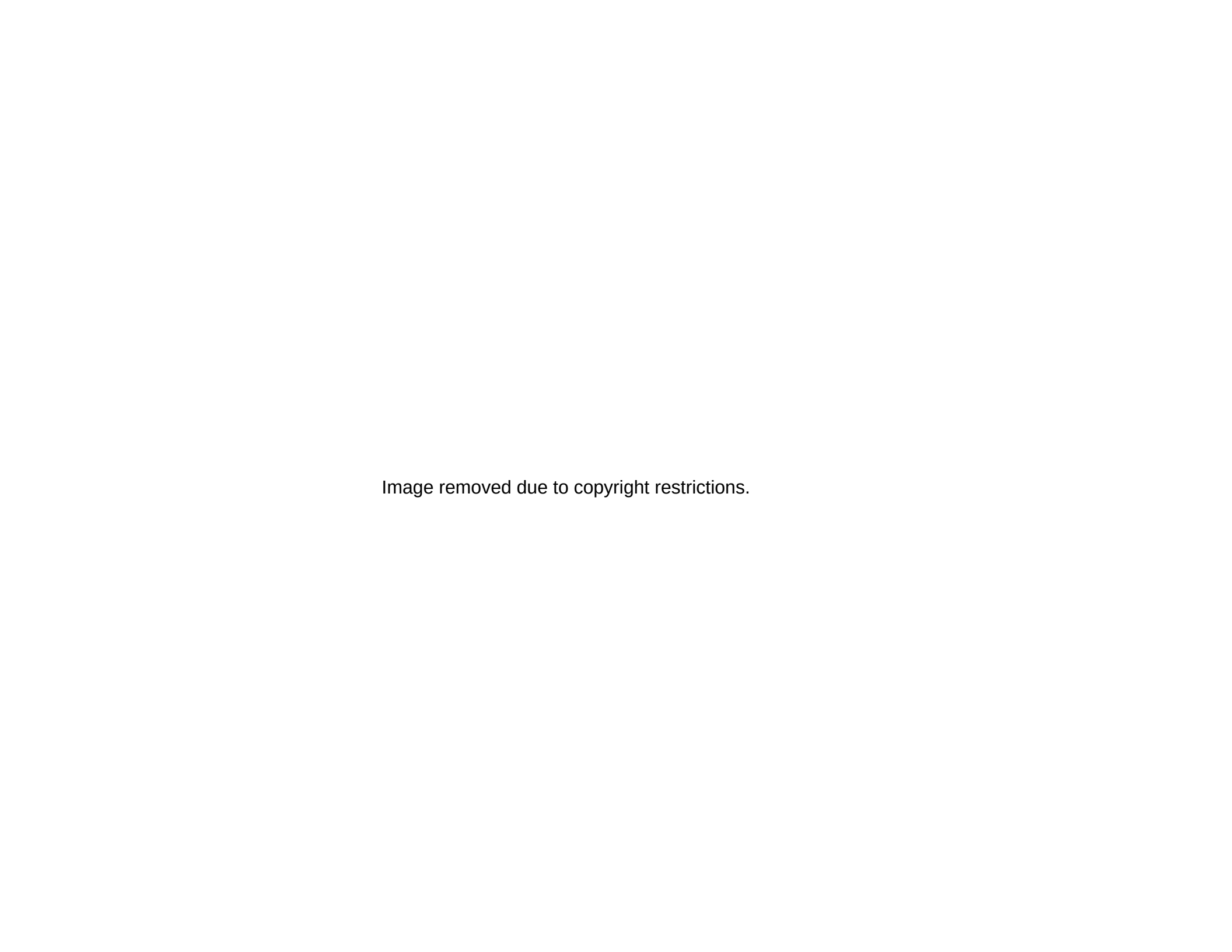
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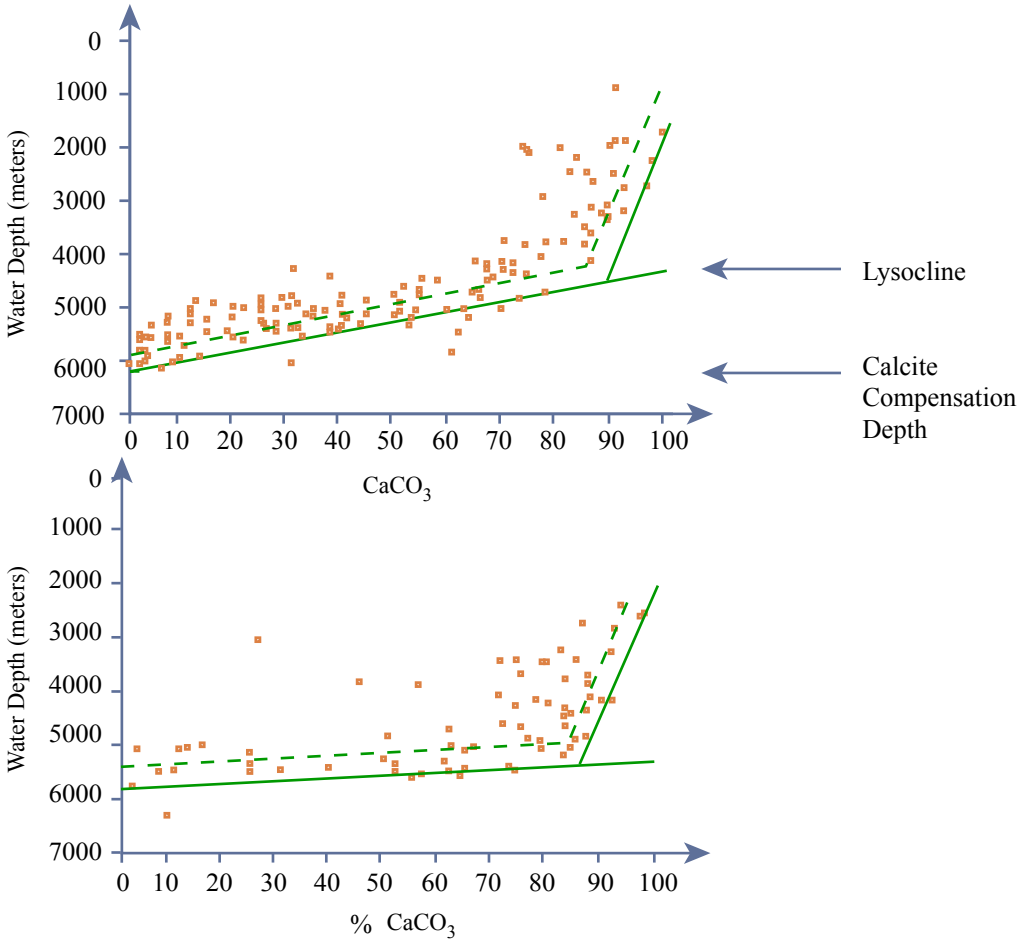

Lysocline : depth at which there is evidence of dissolution

CCD : depth at which % $CaCO_3$ = 0 i.e, at which dissolution rate = supply rate.

CCD is straightforward; but what does lysocline indicate?

Figure by MIT OCW.

Is %$CaCO_3$ a sensitive indicator of dissolution?

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Please see: Broecker, W. S., and T.-H. Peng. *Tracers in the Sea*. Palisades, NY: Lamont-Doherty Geological Observatory, 1982.

“Metabolic” calcite dissolution

Oxic respiration results in the release of acids to solution :

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$
$$NH_3 + 2O_2 \rightarrow NO_3^- + H_2O + H^+$$

Acids are neutralized by

$$CO_2 + H_2O + CO_3^{2-} \rightarrow 2HCO_3^-$$
$$CO_2 + B(OH)_4^- \rightarrow B(OH)_3 + HCO_3^-$$
$$CO_2 + H_2O + CaCO_3(s) \rightarrow Ca^{2+} + 2HCO_3^-$$

(and similar reactions for neutralizing H^+)

Graphs removed due to copyright restrictions.
Please see: Hales, B., et al. "Respiration and dissolution in the sediments of the western North Atlantic: Estimates from models of in situ microelectrode measurements of porewater oxygen and pH." *DEEP-SEA RES (A OCEANOGR RES PAP)* 41, no. 4 (1994): 695-719.

2nd in situ wcs result --
Cape Verde Plateau, E. tropical Atlantic
well above CSH

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Lines = fits of model to data to quantify dissolution rate

Counter evidence?
In situ benthic flux chambers
Jahnke & Jahnke, 2004, GCA 68, 47-59

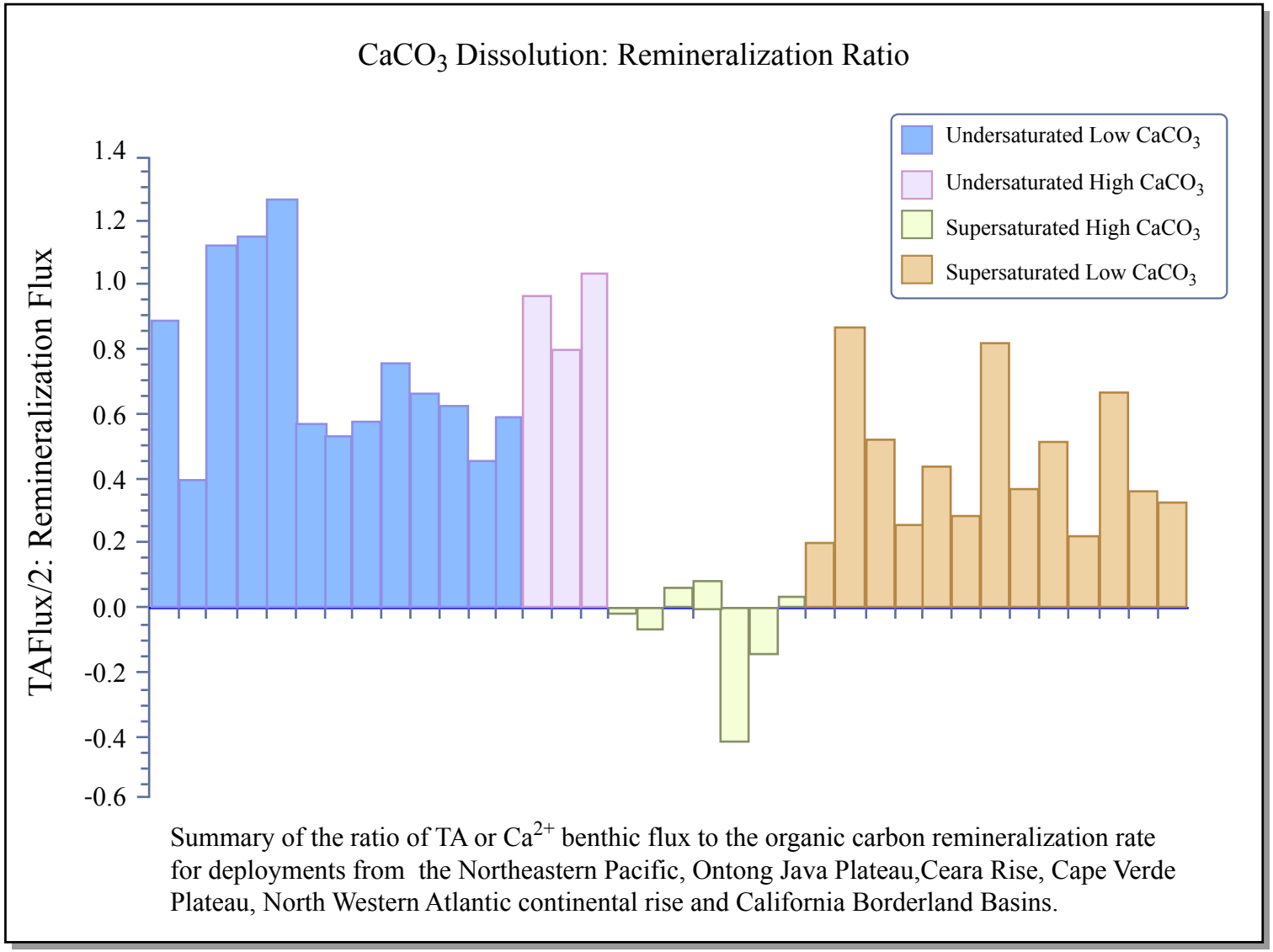
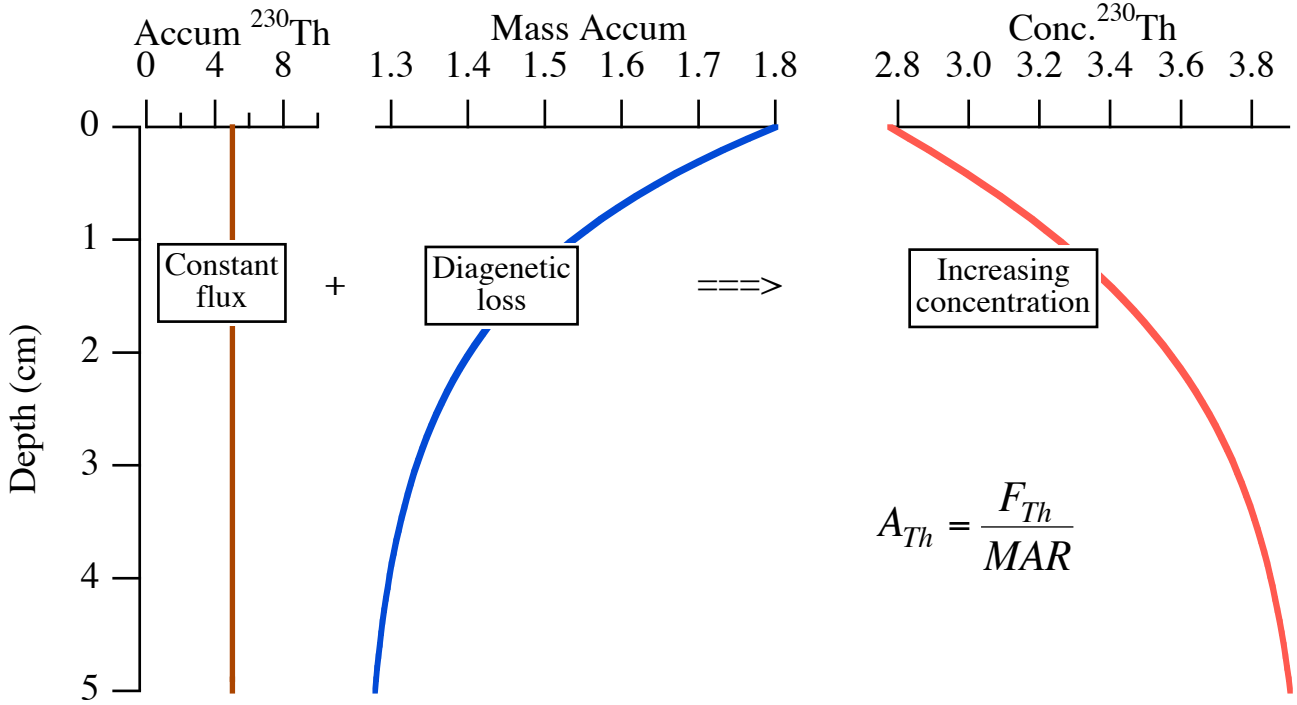
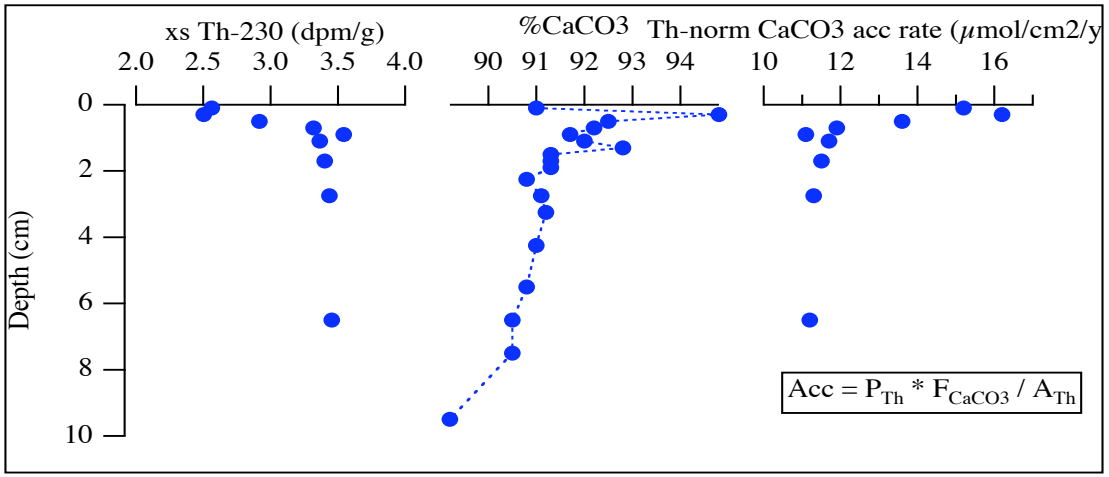


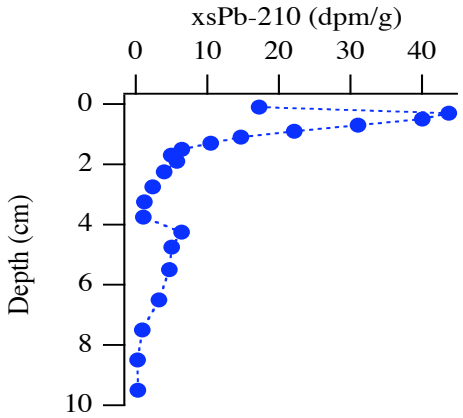
Figure by MIT OCW.

One more approach --
^{230}Th activity changes near swi

Martin, 2004







Results:
Depth = 1614m
BW ΔCO3 = + 11 μmol/kg

Conclusions -- $CaCO_3$

1) Dissolution is driven by undersaturation -- callcite is the most important CaCO3 minerall in the deep sea.

2) Calcite solubility + biogeochemical cycles ===> the degree of saturation of seawater with respect to calcite decreases with increasing depth AND decreases going from the deep Atlantic to the deep Pacific

3) Calcite solubility -- that is, its preservation efficiency -- drives the major features of the oceanic calcite distribution

4) BUT : oxic metabolism can drive dissolution of calcite in sediments lying above the calcite saturation horizon. This “metabolic dissolution” may play an important role in the marine carbonate cycle -- but its occurrence in high %$CaCO_3$ sediments is debated.