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!
Please see: Hurd, D. "Interactions of biogenic opal, sediment, and seawater in the Central Pacific."
A mineral, undersaturated in seawater apparently simple dissolution kinetics…

What do we expect $[\text{Si(OH)}_4]$ in pore water to look like?
Image removed due to copyright restrictions.
Comparing asymptotic pore water $[\text{Si(OH)}_4]$ to the “equilibrium” value

Asymptotic pore water concentrations

$\text{Si(OH)}_4$ (µM)

w. eq. Atl.
cent eq. Pac.
Peru margin
S. Ocean

Opal equilibrium
Location of Cores.

Figure by MIT OCW.
Image removed due to copyright restrictions.

Incorporation of Al into silica

Dissolution

Precipitation

Biogenic Silica

Detrital minerals

H₄SiO₄

Al(III)

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.)

Figure by MIT OCW.
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

Image removed due to copyright restrictions.
Graphs removed due to copyright restrictions.
Mechanism for CaCO₃ Dissolution in Sediments:

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

1. Which mineral?

   Aragonite

   More soluble than High-Mg calcite

   More soluble than calcite

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

2. Quantifying solubility in seawater

   Conditional Solubility product,

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

   \[ T=25^\circ C, P=1\text{ atm}, S=35\text{ psu}: \]
   Ingle (1975) \quad 4.60 \pm 0.10 \times 10^{-7}
   Mucci (1983) \quad 4.30 \pm 0.20 \times 10^{-7}
   i.e., \pm \sim 5\%
The pore water based estimate (Sayles 1985)

1. Measure Alk, \( \Sigma CO_2 \), vs. depth in pore waters of sediments underlying water columns of varying depth.

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

3. If the pore waters have reached saturation with respect to calcite, \( ([CO_3^{2-}][Ca^{2+}])_{\text{med}} = K_{sp}^{sw} \).
Image removed due to copyright restriction.

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”

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

“Delta-carbonate”

\[
\Delta CO_3^{2-} = \left[ CO_3^{2-} \right]_{\text{meas}} - \left[ CO_3^{2-} \right]_{\text{equil}} \text{ in } \mu \text{mol/kg}
\]
Image removed due to copyright restrictions.
Graphs removed due to copyright restrictions.

Image removed due to copyright restrictions.
Image removed due to copyright restrictions.
Lysocline: depth at which there is evidence of dissolution

CCD: depth at which \( \% \text{ CaCO}_3 = 0 \) i.e., at which dissolution rate = supply rate.

CCD is straightforward; but what does lysocline indicate?
Is $\%\text{CaCO}_3$ a sensitive indicator of dissolution?

Figure removed due to copyright restrictions.
“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

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

(and similar reactions for neutralizing H\(^+\))
Graphs removed due to copyright restrictions.
2nd in situ wcs result --
Cape Verde Plateau, E. tropical Atlantic
well above CSH

Figure removed due to copyright restrictions

Lines = fits of model to data to quantify dissolution rate
Counter evidence?
In situ benthic flux chambers
Jahnke & Jahnke, 2004, GCA 68, 47-59

Summary of the ratio of TA or Ca\(^{2+}\) benthic flux to the organic carbon remineralization rate for deployments from the Northeastern Pacific, Ontong Java Plateau, Ceara Rise, Cape Verde Plateau, North Western Atlantic continental rise and California Borderland Basins.

Figure by MIT OCW.
One more approach --

$^{230}$Th activity changes near swi

Martin, 2004

\[ A_{Th} = \frac{F_{Th}}{MAR} \]
Results:

Depth = 1614m

BW ΔCO3 = + 11 µmol/kg
Conclusions -- CaCO$_3$

1) Dissolution is driven by undersaturation -- calcite is the most important CaCO$_3$ mineral in the deep sea.

2) Calcite solubility + biogeochemical cycles $\Rightarrow$ 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.