Lecture 14 - Marine Sediments – Formation and Distribution

"*When I think of the floor of the deep sea, the single, overwhelming fact that possesses my imagination is the accumulation of sediments. I see always the steady, unremitting, downward drift of materials from above, flake upon flake, layer upon layer – a drift that has continued for hundreds of millions of years, that will go on as long as there are seas and continents..... For the sediments are the materials of most stupendous snowfall the Earth has ever seen...*"

Rachel Carson, The Sea Around Us.

The sediments deposited in the ocean are an archive of historical information about the Earth and, specifically, they provide information about global biogeochemical cycles. The distribution of sediments in the ocean is determined by biological and chemical processes and therefore should be discussed in the context of marine chemistry.

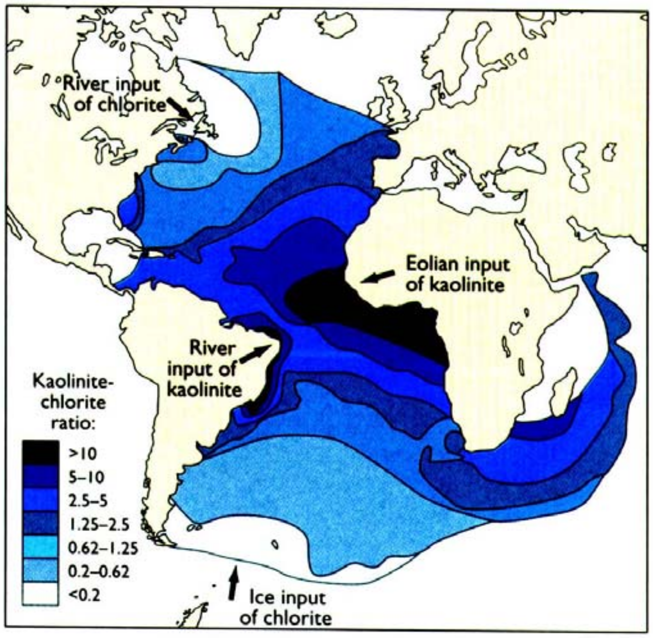
The first detailed study of marine sediments was done in the 1870's. An expedition called the "Challenger expedition" led by Sir Murray and Renard dredged the bottom of the ocean systematically and described the sediments. They classified their findings into 5 major groups: red clays, carbonate ooze, silicic ooze, nodules and volcanic material. This is quite similar to what we do today. We categorize the type of sediments mostly by their source and composition. In the late 1940's, the first recovery of a long core was achieved and that introduced the possibility of investigating sediments over time. Shortly afterward, a global ocean drilling program was designed and sediment cores are now continuously collected from different oceanic locations.

The sediments in the ocean consist of 3 major components: **detrital, biogenic** and **authigenic** based on their origin. They are classified using the 30% rule, if there is more than 30% of any type of component in the sediment it will be classified as such. However, it must be kept in mind that there are no pure detrital, authigenic or biogenic sediments; sediments are always mixtures of different components.

Detrital: brought into the ocean from outside, consists of terrigenous, volcanic, and cosmogenic material.

Terrigenous sediments are those where the ultimate source is weathering and erosion of rocks on land. The materials composing these sediments are introduced to the ocean by water, wind or ice. Terrigenous sediments are more abundant close to the continents, specifically near river mouths and in the very deep areas of the oceans.

The composition of terrigenous sediments thus depends on the climate and weathering at the source region, and the distribution of these sediments by the geographic deposition of rivers and the prevailing winds. Rivers and glaciers carry large particles and deposit 10^{10} tons annually, while the winds deposit 10^{8} tons of much smaller particles.

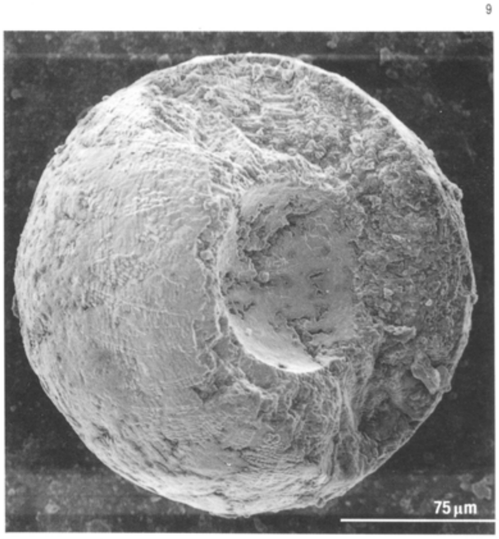


These sediments are most abundant on continental margins where rivers come in (Atlantic > Pacific). The smaller, wind blown terrigenous particles, are present everywhere in the oceans and they are the major component of a large fraction of the sediment in the deep Pacific basin, mostly because the biogenic components are not preserved there. Thus, terrigenous and hydrogenous minerals are the dominant components of red clays. This does not mean that the input of this material is larger there but rather that there is nothing else to dilute it with.

Terrigenous sediments enclose information about river fluxes, sources of the weathered material (provenance), weathering processes on land, wind stress and direction, as well as glacial extent and glaciers location (ice rafted debris).

Volcanic sediments are composed of minerals brought into the ocean mostly by wind, as dust and ash from volcanic eruptions. They are typically in the size range of 1µm. Their abundance gives information about periods and locations of intensive volcanic activity. These sediments are more abundant close to volcanic islands but also globally distributed after big eruptions. These deposits are easy to date by radioactive age determination and because of their global and instantaneous distribution can be used for global correlation.

Cosmogenic particles are those that arrive from outer space and survive the Earth's atmosphere to enter the sedimentary record. About 4-6 x10^4 tons of these particles accumulate each year, they range in size from 0.1 to 1mm and have a typical spherule shape. They have distinct geochemical signatures (high ^{3}He, Ir, Os and Os isotopes and organic compounds not typical to Earth) and provide information about possible changes in the rate of cosmogenic bombardment as well as catastrophic impacts (K-T). They could also be a mean of estimating sedimentation rate if we assume constant accumulation.



Authigenic components are oceanic inorganic minerals that precipitate directly from the seawater, either in the water column or in the sediment after burial. These minerals make up only a small fraction of deep-sea sediments today, but in special environments and certain geological times, they comprise the bulk of the sedimentary sequence.

These include *evaporites*, which are sediments that are deposited as a result of evaporation of water and usually occur in restricted basins and lagoons on the shelf where evaporation exceeds precipitation and flushing in of water. This includes the minerals anhydrite, gypsum, halite, dolomite and more. These sediments enclose information about the climate and basin configuration conditions at the location and time of their formation and also carry valuable information about the chemical makeup of seawater. For example, when anhydrite precipitates, the sulfate forming this mineral comes from seawater and has the same isotopic composition as seawater sulfate, so we get a record of the seawater S isotopic composition.

Another group of important authigenic components are *Hydrogenous Fe-Mn oxy-hydroxides*: These minerals usually form as coating on existing minerals, but also occur as nodules and crusts. The Fe-Mn oxides and hydroxides co-precipitate and scavenge trace metals from seawater and thus could reveal chemical information of the ocean.

Figure 5.7 Drawing of a section cut through a small manganese nodule, about 2cm across. The nodule has grown round a shark's tooth (top centre) and a volcanic fragment (bottom centre), and has incorporated other particles as it grew. This was recovered by the *Challenger* expedition from a depth of 2375 fathoms (*c.* 4350m) in the South Pacific.

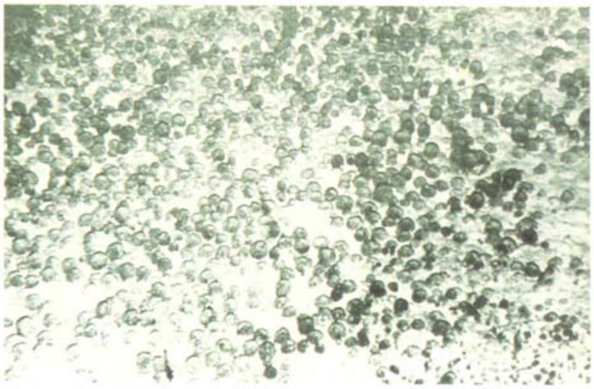


Figure 5.8 Typical appearance of a rich manganese nodule field in the deep ocean.

Manganese nodules in the South Pacific

Hydrothermal deposits are also Authigenic; they precipitate around active ridges where hydrothermal circulation leaches transition metals from the basalt and carries the dissolved material to the seafloor. Oxidizing conditions and cooling of these hydrothermal solutions results in precipitation of Fe and Mn oxides and hydroxides in the form of crusts or metal rich ooze, as well as sulfides ($(Zn,Fe)S$, $CuFeS_2$, FeS_2) and sulfates ($BaSO_4$, $CaSO_4$). The existence of these minerals can indicate locations of previous hydrothermal activity and carry information about the temperature and nature of the reactions with the basalt.

Other authigenic minerals like zeolite, pyrite, Cd and U minerals form in the sediment and provide information about the conditions in the sediment and water column. For example authigenic U will only precipitate in anoxic conditions.

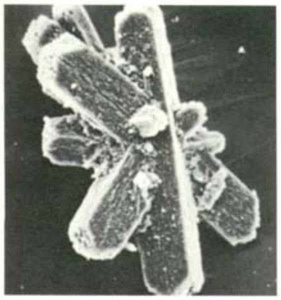
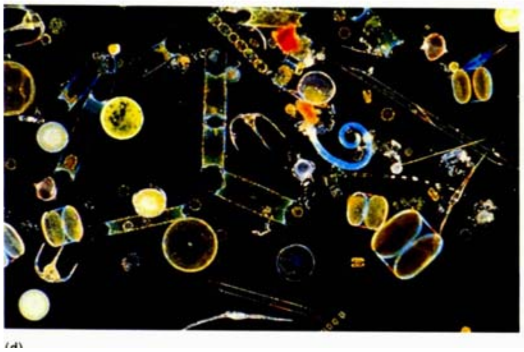
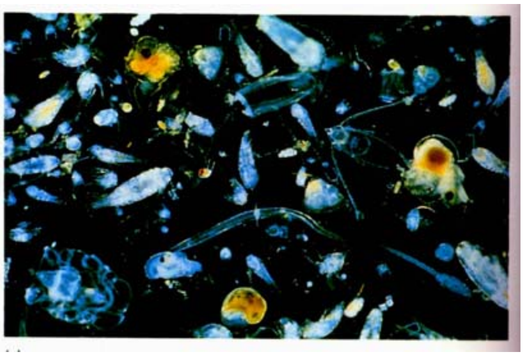


Figure 5.6 Electron micrograph of a cluster of phillipsite crystals recovered from Pacific deep-sea sediments. Scale bar 25µm. The formula of phillipsite is $(K,Na,Ca)_3(Al_3Si_5O_{16}).6H_2O$.

<u>Biogenic Sediments</u> are one of the most important constituents of marine sediments. As the name implies, these form directly or indirectly through biological activity. They are made of a variety of delicate and intricate structures mostly of skeletal remains of marine phytoplankton and zooplankton. The life span of most of these organisms is on the order of weeks, so there is a slow continuous "rain" of their remains down through the water column to build successive layers of sediment. The distribution of these sediments would depend on the abundance of organisms precipitating these phases and dissolution at depth (e.g. preseration).



Living Phytoplankton



Living Zooplankton

The most important biogenic minerals are carbonates and biogenic silica (opal)

Carbonate Sediments are composed principally of skeletal remains of calcite or aragonite secreting organisms.

Coccolithophores are phytoplankton covered with a test made of plates of calcite, 10µm in size that are called coccoliths; the organisms shed these plates throughout their life time. An organic membrane covers the coccoliths and this inhibits their dissolution. The coccoliths are also referred to as "nano fossils"; nano means dwarf in Greek. Coccolithophores are abundant in central gyres where productivity is relatively low.

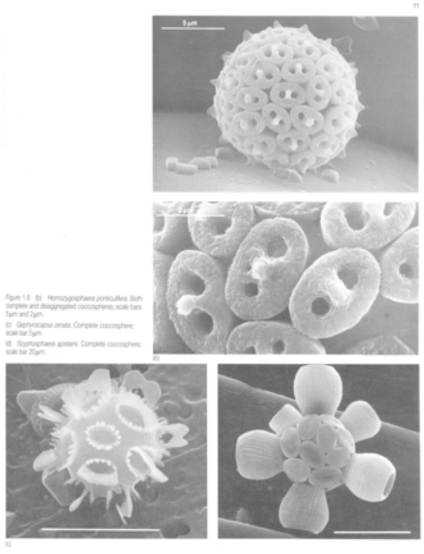
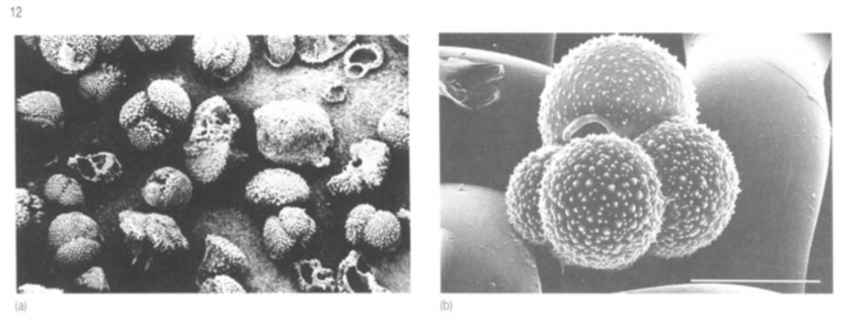
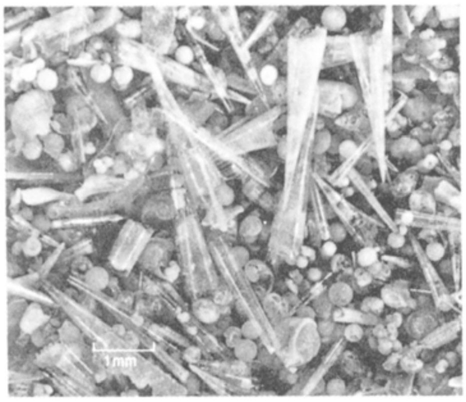


Figure 1.8 (b) *Homozygosphaera ponticulifera.* Both complete and disaggregated coccospheres; scale bars 5µm and 2µm.
(c) *Gephyrocapsa ornata.* Complete coccosphere; scale bar 5µm.
(d) *Scyphosphaera apsteinii.* Complete coccosphere; scale bar 20µm.

Foraminifera are protists that produce calcite exoskeletons, or tests. They can be planktonic (float on the surface) or benthic (live at the bottom) and range in size from ~ 30μm to 1mm. The spiny ones have symbionts and live in the photic zone where light is available; these spiny species are very delicate and more soluble. Non-spiny forms are better preserved in sediments.



Pteropods are planktonic gastropods, mollusks that are restricted to the tropics and subtropics and have aragonitic shells. Usually not preserved well and cannot be found in sediments deeper than ~2000m.

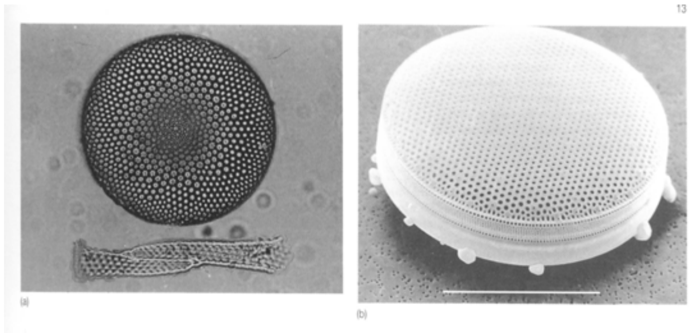


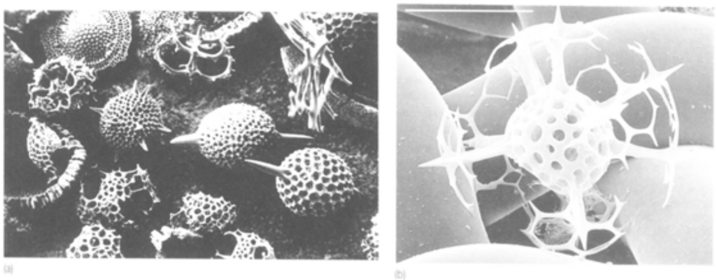
Corals are colonial organisms that form aragonitic reef structures that are common in shallow coastal environments of the tropics. As they grow concentric layers, they provide a vast array of information – in particular for the short-term high resolution SST, sea level changes, precipitation, run off, upwelling and more.

Some other carbonate secreting organisms include alga, mollusks, and echinoderms.

Silica Secreting Organisms include:

Diatoms which are unicellular alga a few micron to 200 micron in size. They secrete frustules from amorphous hydrated silica (opal). They are abundant in high productivity areas such as coastal upwelling, equatorial regions and high latitude areas. There are some benthic diatoms that are restricted to shallow waters.





Radiolarians are large zooplankton in the range of 50-300 micron. They secrete very intricate shells structures. They are usually abundant in low latitudes.

Sponges and *silicoflagellates* also leave siliceous remains, but are less common today.

Other biogenic minerals include *apatite*, which is a phosphatic mineral that mostly makes the bones and teeth of fish and marine mammals. *Celestite* is an $SrSO_4$ mineral that forms the shells of acantharian zooplanktons that are quite abundant, but their shells are so soluble and are not preserved in most sediments. *Barite* is another biogenic mineral that, although does not form directly within organisms, it is precipitated when organic matter or the soft tissue of organisms decompose; this enriches the closed environment with Ba and SO_4 thus, promoting barite saturation and precipitation.

Although not a mineral, *organic matter* is an important component of sediments. There are a lot of organisms that do not form hard parts and what is preserved from them is the organic matter. On average in the ocean only about 1% of the organic matter that sinks to the bottom of the ocean is preserved. The amount of organic matter preserved in the sediment depends on how much is produced and the preservation efficiency.

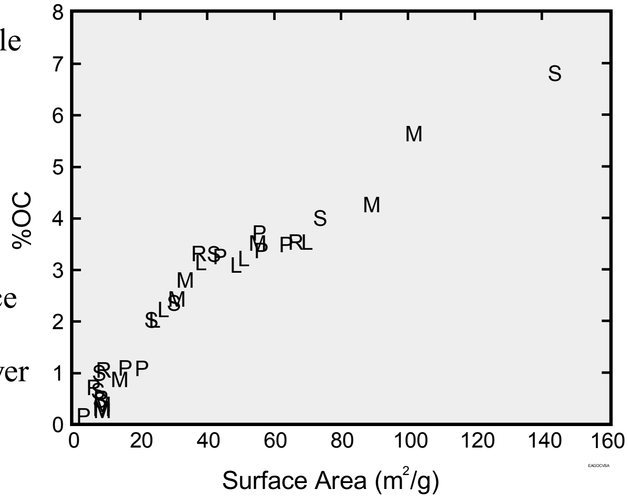
Sedimentary Organic Carbon Preservation

There are several controls that affect the org C distribution in in sediments.

Accumulation in sediments depends on:
Flux of org C from surface (productivity), water depth, and sedimentation rate

1. Overlying productivity	High prod	High org C
2. Water depth	Deep	Lower org C
3. Sedimentation rate	High sed rate	High org C

Some people think that **Surface area** of the particle is important in controlling preservation. This is based on empirical correlations between surface area and % organic C. The "loading" of OC onto mineral surfaces is typically ~0.5-1.0 mgOC/m^2, which has been referred to as "monolayer-equivalent" because it corresponds to ~one-molecule deep, full-coverage of the mineral surface with a protein-like molecule. The organic component associated with the organic C monolayer is highly resistant to degradation.



Laboratory experiments subjecting organic matter desorbed from “old” marine sediments to seawater found that this organic matter is extensively re-mineralized within a week, indicating the sorbed organic matter is protected by its "environment” and not by an intrinsically un-reactive chemical structure.

Previous theories on the processes that control organic matter preservation were all based on correlations of organic C to productivity, sedimentation rate, O_2 content and organic matter source. The idea was that OM preservation heavily depends on oxygen content. This hypothesis is based more on an attempt to understand the **mechanism** involved in organic C preservation rather than simply correlative information. However, this does not seem to hold in many places. There are multiple parameters controlling organic C preservation, including the exposure time to oxygen.

Summary

The abundance and distribution of sediments on the oceans depends on the

(a) **amount of material delivered** to the seafloor, which in turn depends on proximity to the source (for terrigenous and hydrothermal sediments) and the abundance and distribution of the organism forming the mineral (for biogenic minerals).

(b) Because the type of sediment is defined in a relative manner the degree of **dilution** by other components is important; although productivity is very high in coastal environments, there is so much river deposition that the sediment is classified as terrigenous.

(c) The **preservation** of the sedimentary components is a major issue. This is a function of the solubility of the minerals and the chemistry of the ocean. Some of the deep sea is supersaturated with respect to the minerals that form the tests and some is under-saturated. Thus, ocean chemistry plays an important role in the preservation of certain minerals in marine sediments.

Distribution of different types of sediment on the seafloor and their relation with water depth and location.

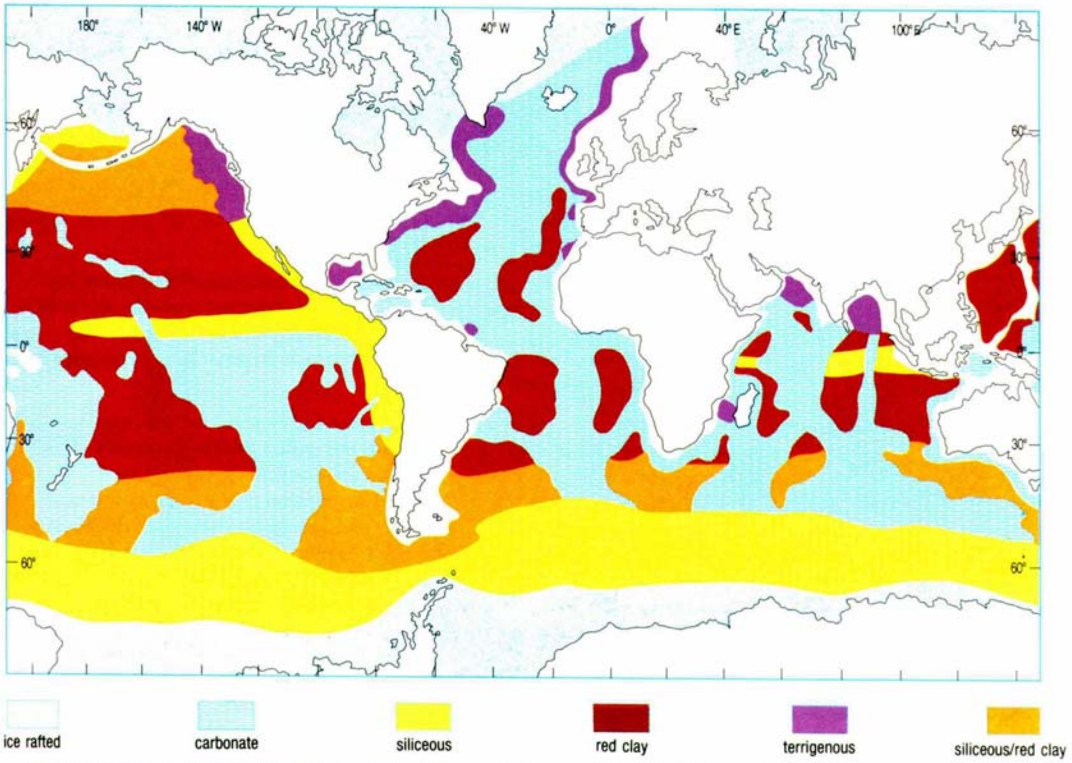


Figure 1.4 Distribution of dominant sediment types on the floor of the present-day oceans. Note that red clays are also terrigenous sediments.

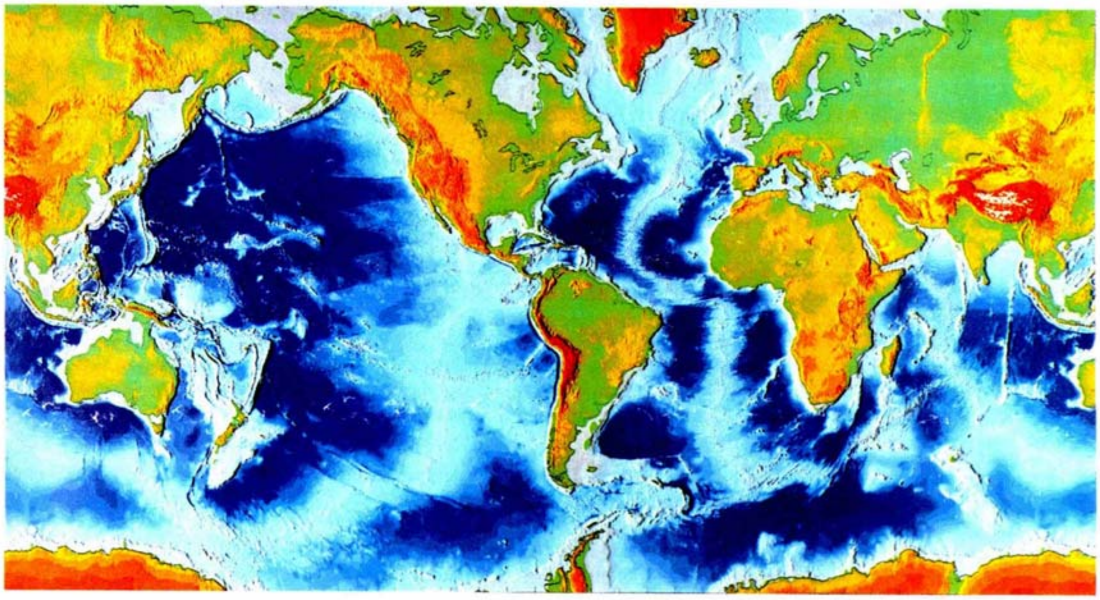


Figure 1.5 Shaded relief map of the Earth's solid surface. In oceanic areas, the deeper the blue, the deeper the water.

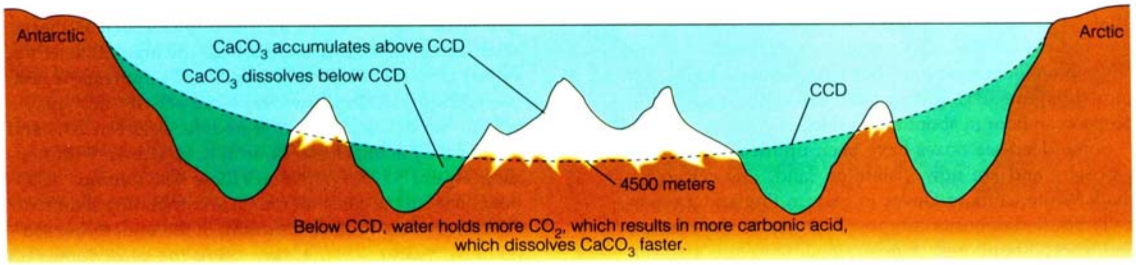
Carbonate Distribution and Preservation In the Ocean

$CaCO_3$ is the main mineral in marine sediments. About ¼ of the ocean basins contains sediment that is >30 % $CaCO_3$ (mostly calcite). In addition, $CaCO_3$ production, burial, and dissolution effects ocean alkalinity. About 20 % of the particulate $CaCO_3$ rain is buried, and the percent burial depends on seawater chemistry. Variations in the concentration of $CaCO_3$ in sediments over time reveal changing ocean chemistry.

There are two mineralogical forms of calcium carbonate that have very different solubility:

solubility:	Aragonite	–	hexagonal crystallographic structure
	Calcite	–	rhombihedral crystallographic structure

Aragonite is deposited in shallow water as coral and coraline algae; calcite is deposited mostly in the deep ocean as tests of microscopic algae that grow in surface waters. Milliman and Droxler estimate that roughly half of the $CaCO_3$ presently being deposited in the ocean is in coral reefs and coraline algae and half in deep-sea sediments, however the estimates vary quite a bit. There is a very clear depth dependence of the $CaCO_3$ content of marine sediments. If water were removed from the ocean, the ocean floor would look like snow-capped mountains. The "snow line", the level below which there is no calcium carbonate preserved in the sediment is called the **Calcite Compensation Depth (CCD)**. At the CCD, the rate of $CaCO_3$ input equals the rate of dissolution. Below the CCD is where the red/brown clay (and in places, silica) accumulates.



The CCD is kinetically controlled. Carbonate dissolution begins at shallower depths than the CCD. It is difficult to define the depth where dissolution begins because of the non-linear relationship between weight % calcite and the amount of the rain that has dissolved. Imagine a situation where 90 calcite tests and 10 clay mineral grains of equal weight fall to every square cm of sediment surface. If nothing dissolves, the weight percent $CaCO_3$ is 90 %. If 20 % (18 tests) dissolve, the sediment has now 90-18= 72 tests, and 72 / (72 + 10) = 0.87 or 87 % $CaCO_3$. If half dissolves (45 tests left), it is, 45 / (45 + 10) = 0.82, 82 % $CaCO_3$. Weight percent is very insensitive to the amount of dissolved material. The depth where dissolution starts can be determined by

(a) Thermodynamic calculations of solubility e.g. at what depth does seawater become under-saturated with respect to a certain mineral.
(b) Empirically by suspending calcite spheres of known weight at different depths in the ocean and evaluation weight of loss of these spheres.

Thermodynamics

The relationship between sedimentary $CaCO_3$ and the carbonate chemistry of seawater.

(1) Equilibrium reaction: $CaCO_3(s) \Leftrightarrow Ca^{2+} + CO_3^{2-}$

(2) Solubility product: $K_{sp} = a_{Ca}\, a_{CO3} / a_{CaCO3} = a_{Ca}\, a_{CO3}$

Apparent solubility product $K_{sp}' = [Ca^{2+}]\,[CO_3^{2-}]$

(3) Saturation state $\Omega = [Ca^{2+}]\,[CO_3^{2-}] / K_{sp}'$

$\Omega > 1$, waters are supersaturated: the mineral will not dissolve, should precipitate

$\Omega < 1$, waters are under-saturated: the mineral should dissolve

The depth where $\Omega = 1$ is called the Saturation Depth. At this depth the *in situ* carbonate ion concentration is equal to the saturation carbonate ion concentration.

$[CO_3^{=}]_{\text{in situ}} = [CO_3^{=}]_{\text{sat}}$

Since $[Ca^{2+}]$ varies by only a few percent in the ocean, factors influencing Ω are K_{sp}' and $[CO_3^{2-}]$ and not $[Ca^{2+}]$. Therefore, $\Omega = [CO_3^{2-}]$ seawater / $[CO_3^{2-}]$ at saturation

The solubility product. K_{sp}' in seawater depends on pressure, salinity, and temperature. *K_{sp}'* has been determined in the laboratory five times over a period of 20 years (at one atmosphere, 25°C and S = 35):

SOURCE	$K'_{sp,calcite}$	$K'_{sp\ aragonite}$,
	$(\text{moles kg}^{-1})^2 \times 10^7$	
MacIntire (19965)	4.57 (±0.36)	
Ingle et al.(1973)	4.50 (±0.10)	
Plath et al.(1980)	4.70 (±0.10)	
Morse et al. (1980)	4.36 (±0.20)	6.65 (±0.12)
Mucci (1983)	4.30 (±0.20)	6.65 (±0.12)
Mean	4.50 (±0.17)	6.65 (±0.12)

Pressure and temperature effects on solubility

		Saturation $[CO_3^{2-}]$ (10^{-6} mole/kg)	
Temperature °C	Pressure, atm*	Calcite	Aragonite
24	1	46	66
2	1	48	69
2	250	71	101
2	500	106	152

* a pressure of 100 atm ≈ 1000 meters water depth

Temperature Dependence of K_{sp}': $CaCO_3$ is an unusual mineral in that it is more soluble at lower temperatures (K_{sp}' increases with decreasing temperature); the effect is only about 4% over a temperature range of 20°C. Since the temperature range in the deep sea is only a few degrees, this is not important.

Salinity Dependence of K_{sp}': The apparent solubility product increases about 3% per 1 salinity unit increase. Since salinity changes in the deep sea are typically much less than this, this is insignificant.

Pressure Dependence of K_{sp}': The effect of pressure is the most important environmental variable affecting the solubility product of $CaCO_3$. K_{sp}' increases with increasing pressure. Thermodynamically, the pressure effect is related to the partial molar volumes of Ca^{2+}, CO_3^{2-} and $CaCO_3$. Like free energies, the partial molar change for the reaction is calculated from the sum of the products minus the sum of the reactants:

$$\Delta V_r = V_{Ca} + V_{CO3} - V_{CaCO3}$$

The ΔVr for calcite is negative meaning that the volume occupied by $CaCO_3$ is greater than the combined volume of Ca^{2+} and CO_3^{2-} in solution and $CaCO_3$ becomes more soluble with depth.

Fred Sayles (1985) from WHOI designed an instrument to recover pore waters from marine sediments *in situ*. He deployed this instrument in calcite rich sediments at different depths and determined the calcium and carbonate concentrations.
If one assumes the pore water environment is at equilibrium with respect to calcite then this is an *in situ* measurement of K_{sp}'. The solubility increases by about a factor of 2 for a change of 4 km.

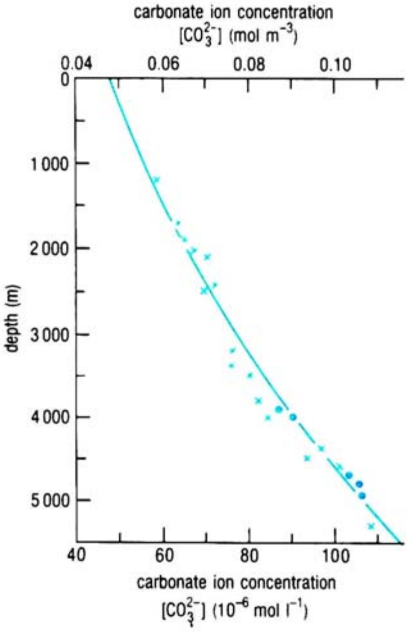
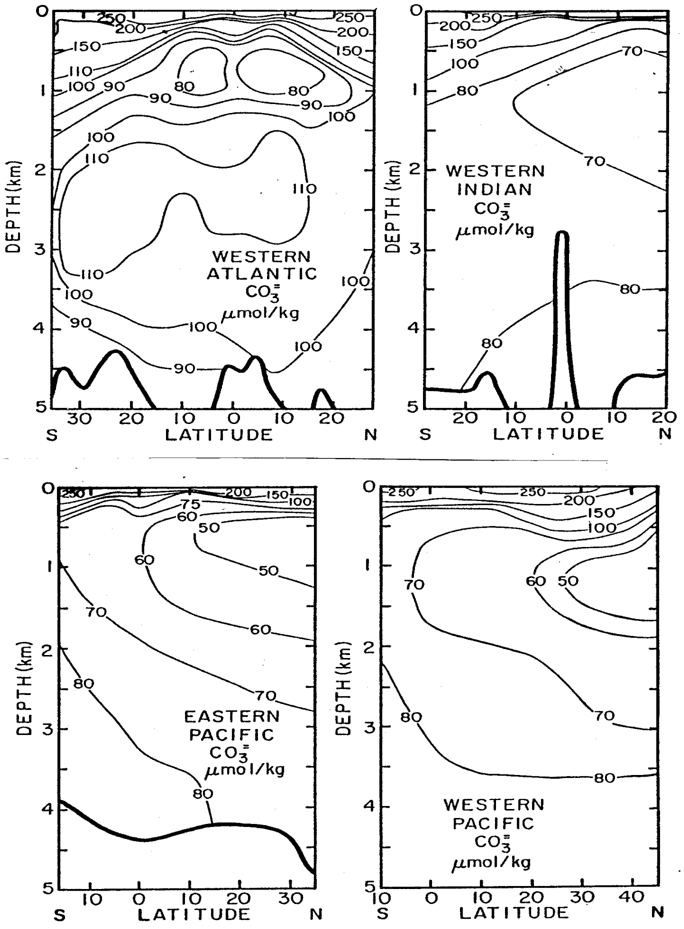


Figure 3.2 The saturation curve of CO_3^{2-} concentration versus depth for calcite, $CaCO_3$. The theoretical relationship is given by the solid line; crosses are experimentally determined points; dots represent actual observations of calcite dissolution in the oceans.



CO_3^{2-} Concentrations in the Ocean.

What makes [CO_3^{2-}] change? As deep water "ages" during its trip through the Atlantic, Indian, and Pacific Oceans, the degradation of organic matter and dissolution of $CaCO_3$, in a 4:1 ratio, cause seawater to become slightly more acidic, thus lowering in CO_3^{2-} content. The concentration ranges form 110 µmol/ kg in the deep North Atlantic (below 2 km) to 70-80 µmol/ kg in the North Pacific. A change of about 30 % (Broecker and Peng, 1982).

Remember the four variables in the carbonate system: pH, pCO_2, TCO_2, and Alkalinity.

(1) Alkalinity $\approx [HCO_3^-] + 2[CO_3^{2-}]$
(2) $TCO_2 \approx [HCO_3^-] + [CO_3^{2-}]$

subtract (1) from (2) to get carbonate ion concentration:

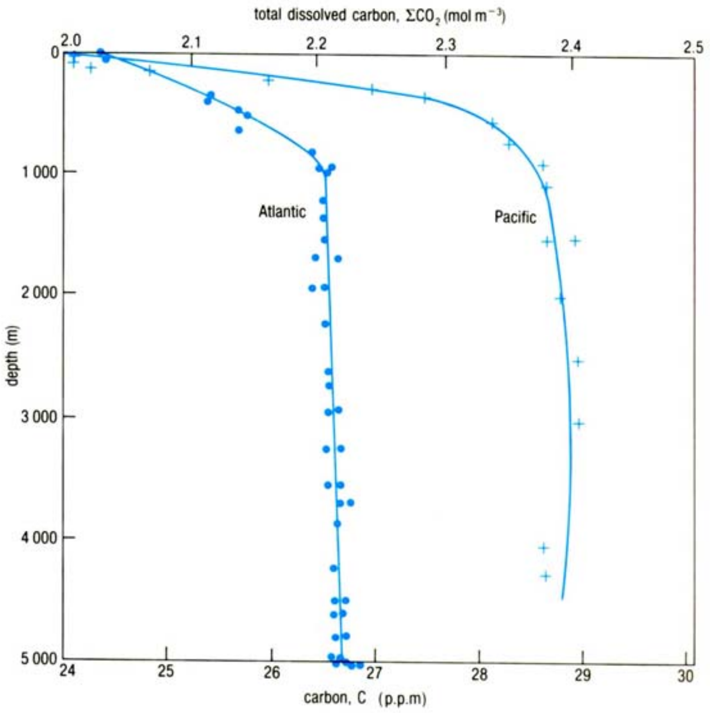
$$[CO_3^{2-}] = \text{alkalinity} - TCO_2$$
$$[HCO_3^-] = 2\,TCO_2 - \text{alkalinity}$$

*** Any two of the carbonate system variables: Alk, TCO_2, pH or pCO_2 will suffice to determine the other two if the equilibrium constants are known. ***

So the parameters that make seawater [CO_3^{2-}] change are those determining Alk, TCO_2, pH or pCO_2.

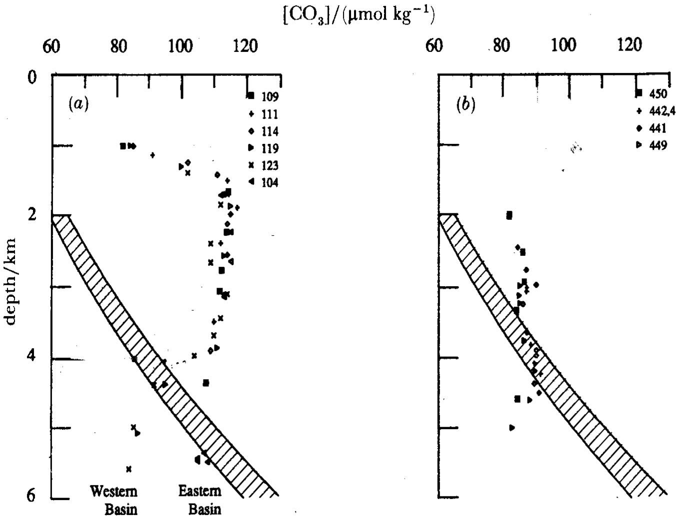
1. In surface waters: biological photosynthesis **increases** [CO_3^{2-}]
    - Plants extract CO_2 from surface waters (thus reducing TCO_2)
    - CO_2 is utilized by plants during photosynthesis, so: $CO_2\downarrow$, $[H^+]\downarrow$, pH↑ thus [CO_3^{2-}] ↑ and [HCO_3^-] ↓and more CO_2 is pulled from the atmosphere.
2. In intermediate waters: respiration of organic matter **decreases** [CO_3^{2-}]
    - Respiration produces CO_2 which is rapidly converted to H_2CO_3 (acid)
    - Because H^+ is produced, pH ↓, [CO_3^{2-}] ↓ ([HCO_3^-] ↑, TCO_2 ↑.
3. In deepwater, aging of water mass **decreases** [CO_3^{2-}] due to lowering of pH.
    - Increasing accumulation of remineralization products including (CO_2):

      $TCO_2\uparrow$, $[HCO_3^-]\uparrow$, pH↓ and $[CO_3^{2-}]\downarrow$.



These processes control the spatial variations in the $[CO_3^{2-}]$ of seawater.

If we know how the measured seawater $[CO_3^{2-}]$ varies from place to place, then we can compare the *in situ* $[CO_3^{2-}]$ saturation to the measured values to determine if calcite will dissolve or not (e.g. the saturation level). The saturation horizon is deepest in the Atlantic Ocean (~4500 m) relative to the Indian Ocean (~3500 m) and shallowest in the Pacific (<3000 m). Aragonite is more soluble than calcite therefore the saturation depth is shallower than calcite in the Atlantic it is ≅2 km.



The wide lines in the figure are the predicted carbonate saturation concentration, using the K_{sp}' from Sayles (1985) and a Ca concentration of 10.28×10^{-3} mol / kg. The hatched area assumes an error of ± 10% in determining the saturation value. Symbols are $[CO_3^{2-}]$ from measurements of Alk and DIC. (a) is in the Atlantic and (b) in the Pacific oceans.

The water depth where calcite dissolution begins to increase markedly as reflected by where the calcite content of the surface sediments begins to decrease abruptly is defined as the **lysocline.** This depth, like the saturation depth, is different for calcite and aragonite and is different in the different ocean.

Note that some dissolution occurs above the saturation depth due to pH lowering as a result of organic matter decomposition within the sediment.

Silica Preservation in the Ocean

A fundamental difference between carbonate and silicate sediments is that seawater is everywhere under-saturated with respect to silica (silica secreting organisms have to spend energy to metabolize and produce the shells). The solubility of silica decreases with decreasing temperature by about 30% from 25-5 ºC, with less silica dissolving when the waters are colder. The solubility increases slightly with pressure, providing some offset to the temperature effect. Most of the dissolution occurs at the seabed and only 1-10% of the flux survives dissolution. Siliceous sediments are therefore found in zones of high productivity and high sedimentation rates but only below the CCD where less carbonate dilution occurs and specifically at high latitudes where the water is colder; in such reasons, diatom productivity is typically high.

Other factors that effect the preservation of shell material are the size and shape of the shells; the smaller and thinner they are the more surface area to volume they have and the faster they dissolve. Some times, the assemblage of organisms may change due to differential dissolution (**dissolution index, used for reconstruction of lysocline depth and carbonate chemistry**). The settling rate of the small particles is expected to be very slow (stocks law); thus, few micron size coccoliths are expected to dissolve while still in the water column. The reason we find them in the sediment is that they take the “elevator” down. Most of the particles arrive to the sea floor as aggregates, which are bio-packaged as fecal pellets and marine snow. The speedy transfer allows burial and preservation.

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