## Earth and Ocean Sciences 112

### PELAGIC SEDIMENTS - PART 1

#### **INTRODUCTION:**

The term **pelagic sediments** refers to deposits that have accumulated in the open ocean slowly, from dispersed suspension in the water column, and essentially beyond the influence of processes along the continental margins such as slumps and downslope flow of mud and sand along the continental slope.

Deep-sea sediments fall naturally into two main categories: (a) **terrigenous deposits**, derived via the weathering and erosion of terrestrial rocks and soils and transport to the ocean by rivers, winds and ice; and (b) **biogenic sediments**, which are composed largely of the microscopic remains of planktonic marine plants and animals. Two main compounds, CaCO<sub>3</sub> and opaline silica (SiO<sub>2</sub>·nH<sub>2</sub>O) dominate the chemical composition of biogenic deposits.

Two other minor contributors to pelagic sediments are volcanic ejecta, principally **ash** and dust injected to the atmosphere during eruptions, and extraterrestrial material, principally the remains of meteorites. Volcanic ash can be widely dispersed by winds, before being washed out in precipitation, if it is initially injected high into the atmosphere. Meteoritic debris often occurs in pelagic sediments as iron- and nickel-rich **cosmic spherules** of coarse silt to fine sand size (50-200  $\mu$ m). Such particles were first recovered from pelagic clays during the Challenger Expedition (1872-1876), and were correctly identified by John Murray (one of the "naturalists" aboard the Challenger, later knighted for his efforts) as being of extraterrestrial origin.

### PELAGIC BIOGENIC SEDIMENTS

#### A. CARBONATE SEDIMENTS

The skeletal remains of three groups of organisms constitute the great majority of carbonate-rich pelagic deposits: **coccoliths**, **foraminifera**, and **pteropods**. **Coccolithophores** are calcareous plants that secrete tiny plates of calcite (CaCO<sub>3</sub>), typically <10 in diameter, in their cell walls. These **coccoliths** form a **coccosphere** (see Fig. 7-8(b) in the text), which sheds coccoliths as the cell grows and eventually distintegrates upon the death of the cell; thus, discrete coccoliths only, and not the spheres, are found in the underlying sediments. Calcite is soluble in the deep sea, as discussed below. However, dissolution of coccoliths is inhibited by an organic membrane which covers the calcite and enhances their preservation. **Carbonate oozes** (defined as being composed of >30% CaCO<sub>3</sub> by weight) are often coccolith-rich under central gyres in the oceans. This reflects the fact that coccolithophores are adapted to grow under oligotrophic conditions, rather

than in areas where nutrients are in good supply. Because of their small size, coccoliths are often called **nannofossils** (from the Greek "nanos", meaning dwarf). The Cretaceous white cliffs of Dover are largely composed of coccolith or nannofossil ooze.

**Foraminifera** are cosmopolitan single-celled zooplankton that produce calcareous exoskeletons or tests (see Fig. 7-8 in the text) ranging from about 30  $\mu$ m to upwards of 1 cm, although the typical maximum size found in pelagic sediments is on the order of 400 to 600  $\mu$ m. There are about 40 species of planktonic Foraminifera, all of which live in depths shallower than one km, and up to six thousand species of benthic forams that inhabit marine sediments. Some of the benthic genera are non-calcareous and produce agglutinated tests composed of cemented sand grains. Planktonic foram shells occur in far higher numbers than benthics in marine sediments, and because of their sandy size, they impart a sandy texture to the deposits. Foraminifera increase in number faster than coccolithophores in the photic zone as overall productivity rises; thus, foram oozes are found mainly where productivity is high, and coccolith oozes where productivity is low.

**Pteropods** are planktonic gastropod molluscs that produce thin, conical shells up to a centimetre long composed of **aragonite**, a more soluble structural variant of calcite. These are very elegant animals, which propel themselves by flapping two undulating "wings"; because of this, they have been termed the "butterflies of the sea". Most species in the modern ocean are restricted to tropical and sub-tropical areas, and because aragonite is quite soluble, the shells of pteropods are rarely found in sediments deposited below depths of about 2-3 km where the water is undersaturated with respect to this carbonate phase.

# A.1. Dissolution and preservation of carbonate sediments

Calcium carbonate is an unusual salt - it is more soluble at low temperatures and high pressures, as shown in Table 1. Note that pressure has a much larger effect than temperature: cooling seawater from 25° (average tropical surface water) to 2° (roughly the temperature of all deep water in the ocean) increases the saturation carbonate ion concentration for calcite by about 40% (from 53 to 72 µmol  $L^{-1}$ ), while increasing the pressure from 1 atm at the surface to 500 atm at 5 km depth almost doubles the saturation concentration of CO<sub>3</sub><sup>2-</sup>. Because temperature is essentially constant below about 1 km depth, variation in the solubility of CaCO<sub>3</sub> in the deep ocean is a result of the increase of pressure with depth. **Table 1**. Saturation carbonate ion content of seawater as a function of temperature and pressure for the minerals calcite and aragonite (from Broecker, 1974).

		Saturation Carbonate Ion Content (µmol L <sup>-1</sup> )	
Temperature (°C)	Pressure (atm)	Calcite	Aragonite
24	1	53	90
2	1	72	110
2	250	97	144
2	500	130	190

A second major factor influences the solubility of calcium carbonate in the sea.  $CO_2$  dissolves in seawater and dissociates as described by the following equilibrium reactions:

$$CO_2 + H_2O = H_2CO_3$$
 (1)  
 $H_2CO_3 = H^+ + HCO_3^-$  (2)

The bicarbonate ion produced in (2) will partly dissociate and establish the equilibrium

$$H^+ + CO_3^{2-} = HCO_3^{-}$$
 (3)

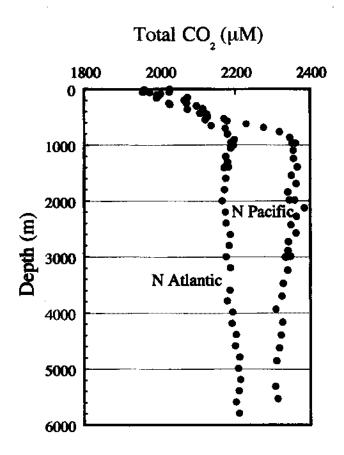
If more  $CO_2$  is added, the protons produced via (2) react with  $CO_3^{2-}$  to drive the equilibrium in (3) to the right.

Thus, the addition of carbon dioxide to deep water increases the bicarbonate ion content and decreases the carbonate ion content, which perturbs the equilibrium

$$Ca^{2+} + CO_3^{2-} = CaCO_3$$
 (4)

resulting in increased undersaturation with respect to  $CaCO_3$ , and therefore more dissolution. Note that very little dissolved inorganic carbon exists as molecules of  $CO_2$  in sea water - only about 3 of every 200 carbon atoms in the deep sea occur as  $CO_2$ ; the rest exist almost entirely as carbonate and bicarbonate ions. In addition,  $Ca^{2+}$  in seawater is abundant, and its concentration varies very little; its contribution to carbonate solubility equilibria in the ocean can effectively be ignored.

The distribution of  $\Sigma CO_2$  (total dissolved inorganic carbon) varies in the ocean as a function of primary production, respiration and thermohaline circulation. The "Total dissolved C" profile in Box Figure 7-1 in the text illustrates these controls. The minimum at the surface is due to the extraction of dissolved inorganic carbon in the euphotic zone by phytoplankton. Degradation of sinking organic matter returns  $CO_2$ to the water column, so that the concentration of  $\Sigma CO_2$  increases at depth, particularly in the top kilometre.  $\Sigma CO_2$  also increases a little in deep water because the source areas for such waters are the cold high latitudes where more atmospheric  $CO_2$ dissolves in the cold surface waters which then sink (remember that gases are more soluble in cold water than warm water). Note that much of the deep-water production happens in winter when little photosynthesis is occurring to consume  $CO_2$  in the surface waters. As shown in Figure 1 below, there is a difference in the  $\Sigma CO_2$ concentrations between the deep Atlantic and the deep Pacific oceans.



This reflects the grand tour of the oceans that bottom waters embark upon when they leave their source areas. Deep waters flow down the Atlantic, make a very brief appearance near or at the surface in the circumpolar current around Antarctica, and then flow north through the Pacific. During this journey, organic matter is constantly raining down into the deep water masses and decomposing , partly in the water column but mostly on the seafloor. The decomposition products include CO<sub>2</sub> and nutrients. Thus, the "older" the bottom water, the greater the  $\Sigma$ CO<sub>2</sub> content. This phenomenon accounts for the significant difference between the Atlantic and Pacific shown in Fig. 1.

Dissolved inorganic carbon is added to seawater not only via the decomposition of organic matter, but also (and, in fact, mostly) by the delivery by rivers of carbonate and bicarbonate ions derived from the weathering of rocks on the continents.  $HCO_3^-$  is the major anion in river waters. However, the rate of extraction of dissolved inorganic carbon species from seawater by organisms exceeds the supply by rivers and exchange with the atmosphere, so that the ocean is undersaturated with respect to aragonite and calcite. **Surface waters, however, are supersaturated**. This is because organisms also extract  $CO_2$  when synthesizing organic matter, so that bicarbonate ion dissociates to produce more  $CO_3^{2^-}$  (reaction 6, which is derived by combining (1) to (4) above), via

$$CO_2 + CO_3^{2-} + H_2O = 2HCO_3^{-}$$
 (5).

At depth, the progressive addition of  $CO_2$  consumes carbonate ion and produces bicarbonate (via reaction (5)). This, combined with the pressure effect (which increases solubility in deeper water), makes deep deep water undersaturated with respect to solid carbonate phases.

The  $\Sigma CO_2$  content in the deep north Pacific is about 10% higher than in the deep North Atlantic (Fig. 1), and the  $CO_3^{2-}$  concentration is about one-third lower. Thus, North Pacific deep water is considerably more corrosive with respect to CaCO<sub>3</sub> than North Atlantic deep water. The net result is that calcite is readily dissolved on the seafloor of the North Pacific but is more likely to be preserved in North Atlantic sediments.

The depth at which the calcite concentration in the sediments falls to very low values is called the Calcite Compensation Depth (CCD). **This is defined as the horizon where the rate of supply of calcite raining down to the sea floor equals the rate of dissolution**. The CCD can be thought of as being a "snowline" in the ocean, below which no snow (read calcite) accumulates. John Murray (of Challenger fame) first recognized the existence of such a compensation depth in the sea. He also showed that an Aragonite Compensation Depth, above which pteropods accumulate in the sediments, occurred at a much shallower level. Although John Murray suggested that the compensation depth should be placed at the level in the ocean where the calcite content of the sediments falls below 20% by weight, most modern investigators define the CCD as being the depth at which the calcite concentration falls to "a few per cent".

Note that on a broad scale the CCD must shoal progressively between the North Atlantic and North Pacific to reflect the gradual addition of  $CO_2$  as deep water makes its grand tour.

Because the CCD is a kinetic boundary (**rate** of supply = **rate** of dissolution), it has relief superimposed on the gradual tilt between the Atlantic and Pacific. This topography is most easily seen in the equatorial regions, where high productivity along the equatorial divergences increases the rain rate of calcite and causes a regional depression of the CCD. This is particularly obvious in the Pacific, where the CCD deepens by more than 500 m below the equator (Fig. 2).

The combination of deep-sea circulation and the increasing solubility of  $CaCO_3$  as a function of pressure (thus depth) explains the abundance of calcite on topographic highs in the ocean, as can clearly be seen by the distribution on the relatively shallow Mid-Atlantic Ridge, and the virtual absence of calcite in sediments underlying corrosive north Pacific bottom waters (Fig. 2).

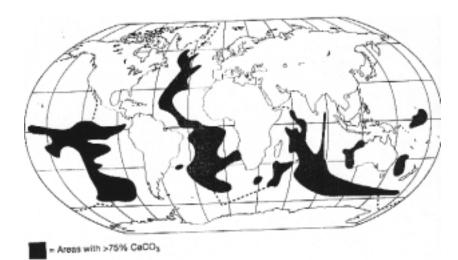


FIGURE 2. The concentration of CaCO<sub>3</sub> in marine sediments.

Note that sedimentary carbonate concentrations are low around most continental margins. This reflects two processes: (a) dilution by higher inputs of terrigenous detritus, and to some extent, opal (see below) near the continents; and (b) increased dissolution of  $CaCO_3$  (i.e. a very shallow CCD) because the high productivity of margin settings is associated with a increased settling flux of organic matter to the sea floor and a change in the proportion of carbonate-shelled plankton to organic tissue. This is because siliceous diatoms (see below) become relatively more important in upwelling areas such as on continental margin, while the proportion of total production represented by coccolithophorids declines. Thus, the "rain rate ratio" of  $CaCO_3$  to total organic C in settling particulate matter decreases. The bacterial degradation of the organic moiety at the sea floor or in shallowly-buried sediments supplies abundant  $CO_2$  to pore and bottom waters on these productive margins, which is not matched by a commensurate deposition of  $CaCO_3$ . The

overall result is that much if not all of the CaCO<sub>3</sub> dissolves at or very near the sediment surface.