Sources and Composition of Marine Sediments

4

4.1 The Sediment Cycle

4.1.1 The Concept

Marine sediments consist of deposits accumulating below the sea. They show great variety. There is the debris from the wearing down of continents and volcanic mountains, the shells derived from organisms, organic matter, minerals precipitated from seawater, and there are volcanic products such as ash and pumice. All such matter is transported in various ways, is deposited, and subsequently suffers diagenesis and redeposition to various degrees (Fig. 4.1). Terrigenous muds (with their tremendous fraction of continental erosion products) make up well over one half of the total volume of marine deposits. By area it is deep-sea sediments that are dominant, with roughly one half of the deep seafloor covered by calcareous ooze – largely shell material from coccolithophores and foraminifers, along with some reef debris along many tropical margins. In contrast, extraterrestrial matter, while interesting for its content of information, is negligible when considering abundance.

4.1.2 Notes on Geochemistry

Concerning seafloor geochemistry, reactions of seawater with the hot basalt of the oceanic crust are fundamental. Many of the reactions are conspicuous at the Ridge Crest (*hot vents*). Such reactions may contribute considerable amounts of matter to seawater. Also, they may largely relieve seawater of certain elements, such as magnesium. The types and amounts of elements added or subtracted are the subject of intensive studies, with the origin and evolution of seawater at focus.

As concerns the input to the terrigenous sediment reservoir by erosion, the sea itself takes a toll from the continents: waves and tides can eat into the land, taking debris offshore. Such material, along with the sediment delivered by rivers, by ice, or by winds, may stay on the shelf, or it may bypass the shelf to accumulate on the slope or below that on the rise or the abyssal plain. Sediments that stay on the shelf, of course, essentially stay on the continent. The sediment deposited beyond the shelf eventually is carried back to a continent (e.g., by mountain building) or disappears into the mantle by subduction, as discussed earlier.

4.2 Sources of Sediment

4.2.1 River Input

What rivers carry (the dissolved and particulate load) constitutes the main source of marine sediment making the coalescing fans that build the continental slope off California and elsewhere. The fans are largely riverine mud with an admixture of shell and organic matter. The admixed shell material (largely made of calcium carbonate and opal) also derives to a great extent from river input, that is, from the dissolved load brought by rivers to the sea. We can make a rough estimate of how much material is involved. Slope sediments typically accumulate at a rate of some 100 mm per millennium and deep-sea oozes at rates at one tenth of that, with one half of the deep seafloor ooze-free and accumulating clay at 1 mm/1000 years.

The sediment supply from rivers is reported to be near 12 cubic km per year. If this amount is distributed on the area of seafloor on the planet, we obtain an average sedimentation rate of about 30 mm/1000 years. The erosion rate for continents, at twice that value, would be 60 mm per millennium. The rates of input from reactions of seawater with the basalt of the oceanic crust and from leaching of soils and rocks on land are neglected in this calculation, an input that if considered would decrease the estimate of continental erosion rates somewhat.

E. Seibold, W. Berger, *The Sea Floor*, Springer Textbooks in Earth Sciences, Geography and Environment,
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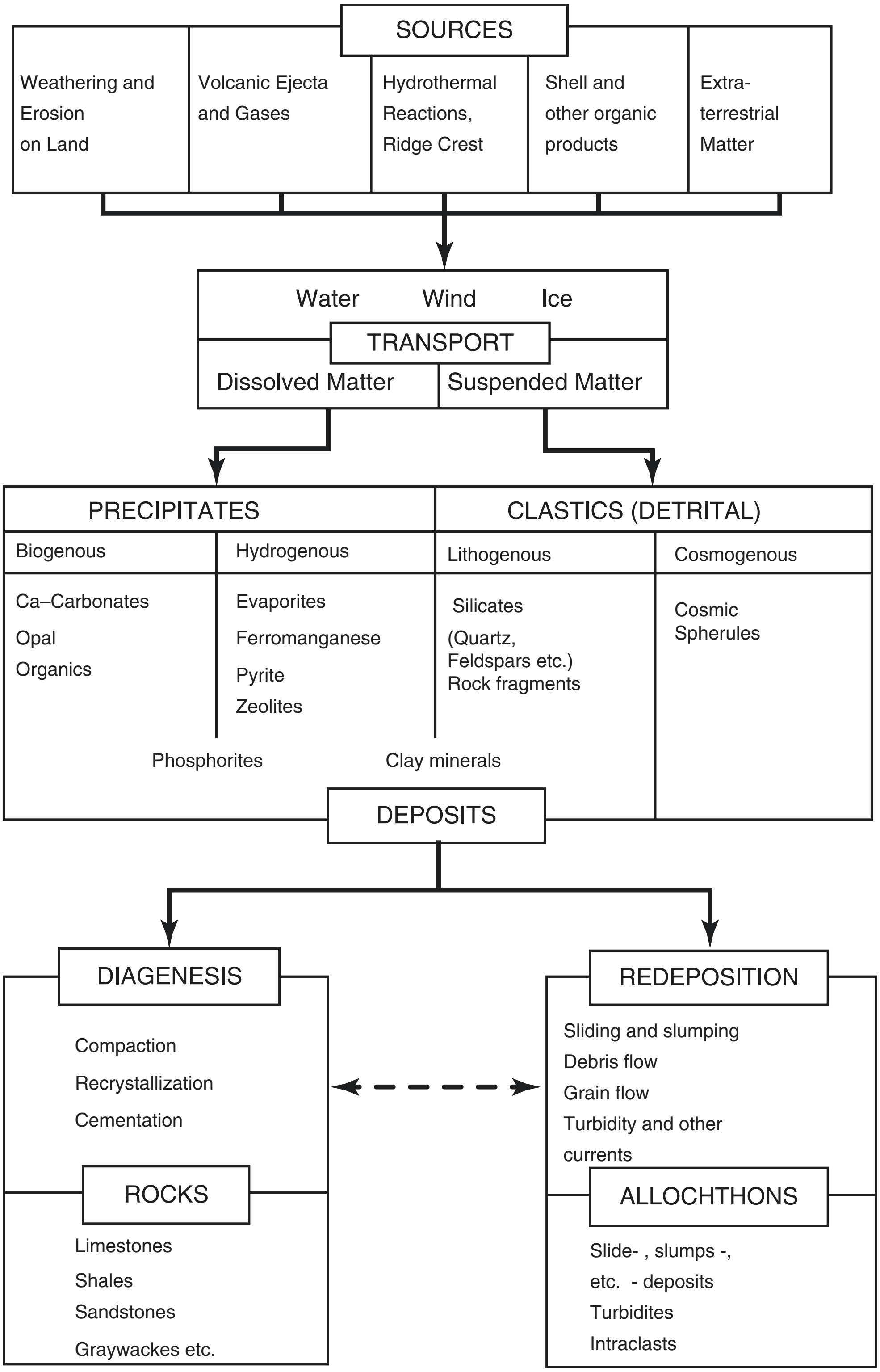

Fig. 4.1 Schematic summary of sources, transport, and destination of marine sediments

In general, mechanical erosion dominates in high latitudes, where much of the water is ice, and in deserts, where water transport is linked to flash floods and other sporadic action unimpeded by vegetation. Chemical weathering (leaching) is favored by rainfall and high temperatures and dominates in tropical areas. In extrapolating these and other present-day patterns into the past, we must remember that we live in a highly unusual period. The growth of mountain ranges and the powerful abrasive action of glaciers have greatly increased mechanical erosion for the last several million years.

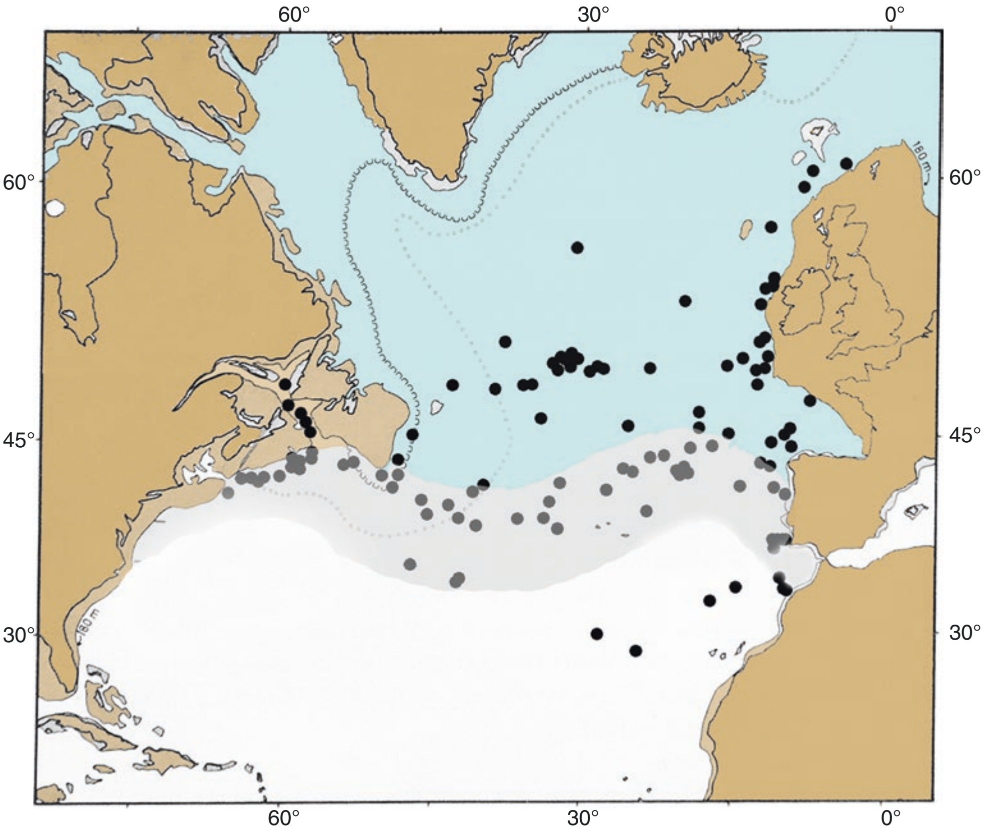

Fig. 4.2 IRD (ice-rafted debris) on the seafloor of the North Atlantic, as recorded by H. R. Kudrass, Bundesanstalt, Hannover. Present limits of drift ice shown schematically (broken lines). Samples of IRD (*black dots*) well toward the south presumably indicate conditions of cold phases of the ice age (suggested southern limit here added: shaded zone) (after H.R. Kudrass, 1973. Meteor Forschungs-ergebnisse Reihe C 13:1, modified). Note the assumed great extent of winter icebergs in the glacial North Atlantic, based on IRD (*blue*). Also note the addition of land as sea level dropped from ice buildup on land

4.2.2 Input from Ice

The great importance of ice in delivering sediment to the sea in high latitudes is readily appreciated when contemplating the immense masses of outwash material glaciers bring to the shores, material that is reworked on the shelves by wave action and by nearshore currents.

Less important as concerns sediment mass, but very useful in the reconstruction of paleoclimate, is the fact that icebergs from calving glaciers can transport both fine and very coarse materials far out to the sea. Upon melting, an iceberg drops its load (as *ice-rafted debris* or *IRD*). Around Antarctica iceberg transport reaches to about 40°S, well off the continent. At present, about 20% of the seafloor receives at least some ice-transported sediment. During the *last glacial maximum* (*LGM*), as expected, the dropstone limit extended much farther toward the equator than today (Fig. 4.2).

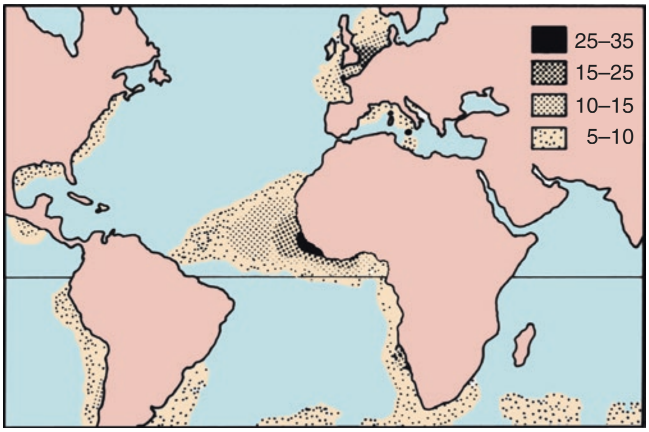

Fig. 4.3 Abundance of haze from dust over the Atlantic (G.O.S. Arrhenius, 1963. In M.N. Hill (ed.) The Sea vol. 3: 695; color here added)

4.2.3 Input from Wind

In striking contrast to ice, wind only moves fine material. Medieval Arabian scientists already noted the dust coming out of the Sahara into the "dark sea" of the Atlantic (Fig. 4.3). In the nineteenth century, Charles Darwin assumed (correctly) that the dust blown offshore off NW Africa must end up on the seafloor. Particles in a large Saharan dust storm in 1901 had an average size of about 0.012 mm in Palermo. Sizes of particles were about half of that in Hamburg (i.e., Hamburg was reached by extremely fine silt, the rest having settled out on the way). During this same storm up to 11 g of dust per cubic meter were measured over the Mediterranean. Some Saharan dust ends up in the Caribbean, as noted in satellite images. In the Pacific,

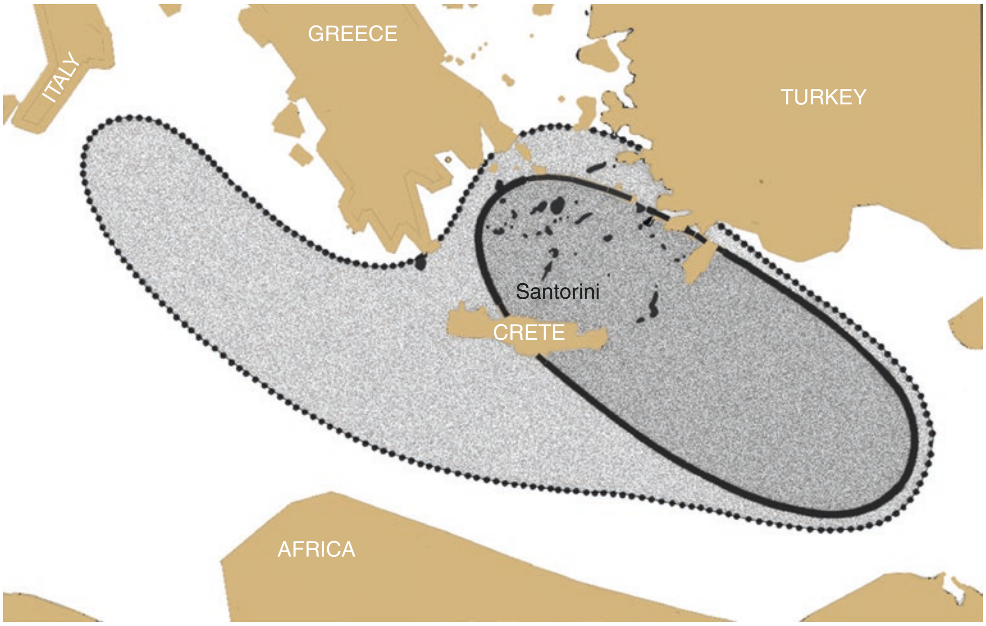

Fig. 4.4 Distribution of volcanic ash on the seafloor of the Mediterranean near Crete; ash is produced by two large explosions in the Aegean Sea (presumably Thera and Santorini). The lower ash layer marks a prehistoric event (>25,000 years). The upper layer is less than 5000 years old and possibly reflects an eruption that ended the Minoan culture (After D. Ninkovich and B.C. Heezen, from K.K. Turekian, 1968. Oceans. Prentice-Hall, New Jersey. Simplified topography; color here added)

we have the example of quartz on and around Hawaii, fine grains apparently blown in from sources in China, thousands of km away.

4.2.4 Input from Volcanism

Volcanoes supply a substantial amount of marine sediment, especially in the vicinity of active margins, such as the ones around much of the Pacific basin. While much of the "*volcanic ash"* carried by winds is widely dispersed and makes thin layers, layers several cm thick are not uncommon in deep-sea sediments. Some of these, marking periods of major eruptions, *correlat*e over large distances (i.e., they originate from the same event and are of equal age, therefore). A well-known example is the Toba super-eruption in Sumatra (Indonesia) 73,500 years ago. Volcanic products that reach the stratosphere result in strong cooling. In the Toba case, the effect presumably was severe and lasted for several years. It has been suggested that such cooling may have contributed to the fast re-glaciation at the end of the last interglacial. While we may indeed be looking at tectonic feedback in climate change (re-glaciation may have changed the distribution of gravitational forces on the planet and thereby helped trigger eruptions), suggestions of a link between volcanism and re-glaciation are somewhat ad hoc and superfluous in a Milankovitch setting.

Near island arcs, volcanic ash layers (*tephras*) can build sediment aprons several thousand meters thick from tens of thousands of eruptions. The composition of deep-sea clay (Chap. 10) suggests that in the time before ten million years ago, before vigorous mountain building and glaciation changed the planetary environment in drastic fashion, the main source of deep-sea clay in the Pacific was the decomposition of volcanic ash. Not all volcanogenic sediment is brought by wind. *Pumice*, highly porous volcanogenic rock with plenty of air within, can float and move with ocean currents for long distances, even carrying gooseneck barnacles and other organisms. Of course, volcanic material also is eroded on land and is then brought into the sea as terrigenous sediment. Differences in color, mineral composition, glass properties, as well as subtle differences in chemistry hold the clues as to the source of a given volcanogenic deposit.

Geologically, volcanoes have a short life, with single eruptions marking flash-like events. Ash layers, therefore, are very useful in much of regional stratigraphy (as *tephrochronology*), for example, in the Mediterranean realm (Fig. 4.4) or in the vicinity of Iceland. Volcanic activity also adds gases and hydrothermal solutions to the sea. These fluxes have an important bearing on the evolution of the chemistry of seawater and of the atmosphere. As mentioned earlier, they are the subject of intense study.

4.3 Sediments and Seawater Chemistry

4.3.1 Acid-Base Titration

To a first approximation, seawater is a solution of sodium chloride (with a bit of Epsom salt thrown in). Sodium and chloride make up 86% of the ions present by weight. The other major ions are magnesium, calcium, and potassium (alkaline and earth alkaline metals) and the acid radicals sulfate and bicarbonate. The major cations form strong bases that are balanced, on the whole, by the acid radicals. However, bicarbonate forms a weak acid, and seawater is slightly alkaline, therefore, with a "pH" near 8, slightly basic (neutral: pH = 7). On the whole, the salty ocean may be understood as the end product of emission of acid gases from volcanoes (hydrochloric, sulfuric, and carbonic acid) and the leaching of common silicate rocks of oceanic and continental crust, the rocks having minerals of the form [Me Si_a Al_b O_c], where Me stands for the metals Na, K, Mg, and Ca and the remainder makes insoluble silica-aluminum oxides, that is, clay minerals.

How stable was the composition of seawater through geologic time? If we use the above concept of acid-base titration and assume that seawater is a solution in equilibrium with the sediments on the seafloor, the result is that the composition was rather stable. Paleontologic evidence certainly agrees with this assessment. Already in the early Paleozoic, there are organisms in various groups whose closest modern relatives have rather narrow salt tolerances: radiolarians, corals, brachiopods, cephalopods, and echinoderms. Naturally, we cannot rule out adaptation of the organisms in question to a changing salt content of the sea. There is no guarantee that the ratios of leached rocks did not change considerably through time. Thus, it is quite likely that the composition of seawater did change, contrary to the equilibrium argument, which implicitly assumes that present conditions are a permanent feature of the sea.

Comparison of solutes in river water and in seawater suggests that siliceous acid is removed from river water as it enters the sea. Diatom production is especially high at river mouths. This is one aspect of the observation that the ratios in the river influx of dissolved matter to the sea tend to be irrelevant to the makeup of sea salt. In the simplest terms, very soluble salts are abundant in seawater and the others are not. For example, iron is removed rapidly and efficiently, keeping concentrations very low. The implication is that the common iron compounds (hydroxides and sulfides) are not very soluble.

4.3.2 Interstitial Water and Diagenesis

Fine-grained sediments (clays and silts) have porosities (i.e., water content) of 70–90% by volume when first deposited on the seafloor, while sands have around 50%. As the sediments are buried, pore space is reduced by compression. The water expelled does not necessarily have the same composition as the water trapped originally. Instead, the expelled water has contents reflecting reactions within the sediment, reactions that correspondingly change the chemistry of the solids accumulating. Compaction and chemical reactions involving pore fluids (or solids only, as in recrystallization) constitute *diagenesis*, the process that ultimately transforms sediment into rocks.

Typically, diagenesis is most active in the uppermost meter or so of freshly deposited sediments, and the chemical reactions within the sediment are commonly driven by the reactions of organic matter. In fact, *redox* reactions usually dominate the process (called "early diagenesis"). They depend greatly on the organic carbon present. The oxidation of organic carbon leads to removal of dissolved oxygen from pore waters. Additional oxygen demand, after such removal, is satisfied by stripping oxygen from dissolved nitrate and from solid iron oxides and hydroxides (e.g., coatings on grains). If the demand is strong enough, sulfate also is stripped of its oxygen, resulting in an abundance of hydrogen sulfide (which produces the foul-smelling hydrogen sulfide, as well as the ubiquitous gold-colored iron sulfide or "fool's gold"). The redox reactions within sediments are mediated by bacteria and archaea, which are in evidence even deeply below the surface (Fig. 1.11), especially in the organic-rich deposits below the coastal ocean.

Once the sediment is buried, concentrations within the interstitial waters can increase to the point where re-precipitation must occur. This leads to *cementation* of remaining grains by carbonate and silica cements (most commonly calcium carbonate and also quartz with microscopic grains). These various processes, including recrystallization (crystal growth within preexisting solids), can be reconstructed by studying the distribution of the elements and compounds involved, within the solids and the interstitial waters. The distribution of certain isotopes (oxygen, carbon, strontium, and others) is of special interest in this context, because dissolution, migration, and re-precipitation under various conditions can result in altered ratios of the isotopes. Diagenetic processes are extremely important for making hydrocarbon source rocks, of course, and for migration and for reservoir rock porosity and permeability (see Chap. 14).

4.3.3 Methane

Escaping pore waters carry information from the redox reactions: they are enriched in gases such as methane (from fermentation of organic compounds), carbon dioxide (from plain oxidation of organic matter), ammonia (from reaction of water with oxygen-stripped nitrate). *Methane* (*Earth gas*) can react with water (given low temperature and high pressure) to make *methane clathrates* (Fig. 4.5).

The stability of methane clathrate depends on temperature and pressure; hence the temperature below the seafloor is of enormous importance in defining the depth at which the hydrate becomes unstable. Correspondingly, the relevant graph (Fig. 4.5, right panel) emphasizes that hydrates will not be found at great depth within certain sediment stacks, owing to the rising temperature below the seafloor. Since methane implies the presence of large amounts of organic matter for fermentation, the marine methane is likely to be found fairly close to continents (in the coastal ocean); that is,

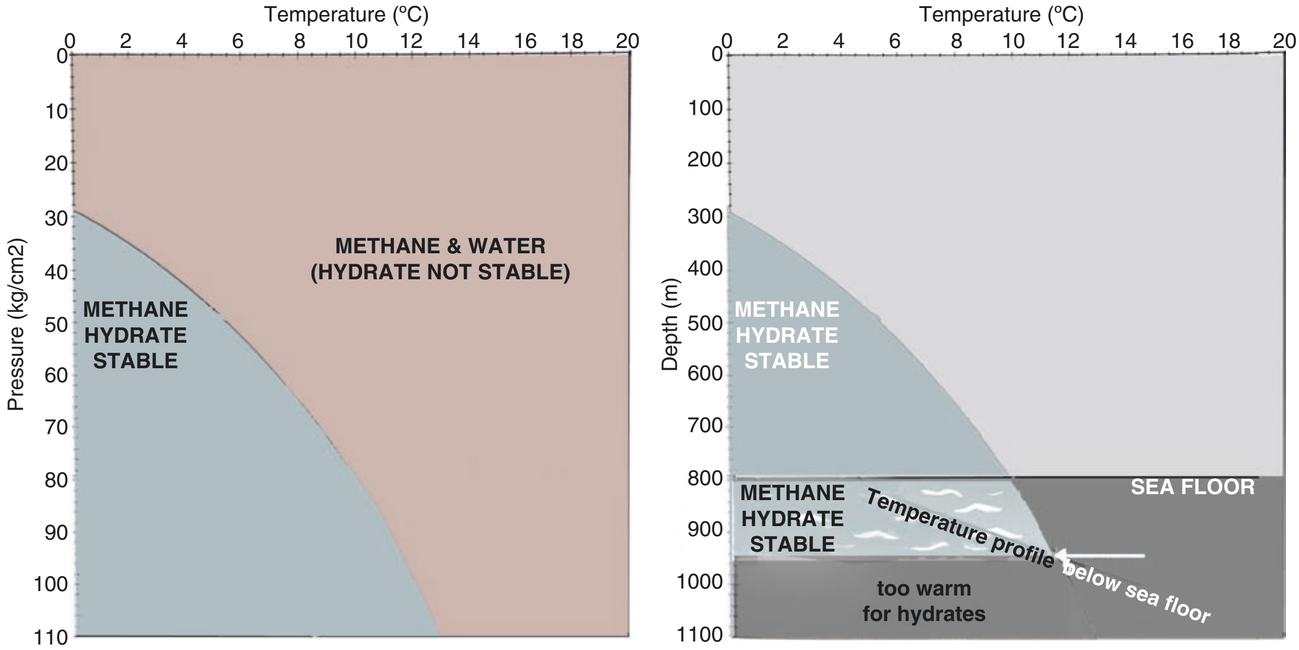

Fig. 4.5 Stability field of methane ice (*left panel*, **a**) and application to sedimentary deposits (*right panel*, **b**). A bottom-simulating reflector (BSR) can occur at the bottom of the layer bearing methane hydrate. At the BSR sound is strongly reflected. The distribution of clathrate is restricted; its presence requires appropriate temperature and pressure to ensure survival if clathrate is present, in addition to a source of methane (stability field and example of occurrence after Erwin Suess (Kiel and Corvallis) and Gerhard Bohrmann (erstwhile Kiel, now Bremen) in G. Wefer and F. Schmieder (eds.) 2010. Expedition Erde (3rd ed.), MARUM, Bremen Univ. Here modified for clarity). A high supply of organic matter is necessary to make methane. For clarity, the clathrate presumably forms within slope sediments, not in water

much of the seafloor likely does not have it. Nevertheless, the amounts of carbon fixed in methane ice are thought to be enormous, exceeding the carbon in the world's estimated coal reserves.

The evidence for methane storage within sediments includes pieces of *methane ice* (burning when lit, in spite of its icy nature; Fig. 1.10), *cold seeps* with its unusual fauna and microbes, *bottom-simulating reflectors* (*BSRs*), and chlorine-poor water from melting, occasionally obtained during drilling. In addition, escaping methane can produce *mud volcanoes* on the seafloor (Fig. 4.6), features that are identified in seismic profiles or by acoustic side scanning. Sizes of the gas-produced mud volcanoes vary; smaller ones are known as *pock marks*.

Besides redox reactions, the dissolution (and also the re-precipitation) of carbonate and of opal is of prime importance in diagenesis. During *early diagenesis* much of the dissolved matter can leave with the escaping pore water or depart simply by diffusion out of the sediment into the overlying water.

4.3.4 Residence Time

For steady state conditions, output must equal input of a geochemical system. Thus, if seawater composition is to stay constant, seawater has to rid itself of all new salts coming in, in a "sink." Where then are the *sinks* for this material? We might first look to the sediments for maintaining the balance, but this is not the whole story. In fact, the quantitative assessment of sinks is a major geochemical problem. For calcium carbonate the sink indeed is largely calcareous shells and skeletons built by organisms, and for silica it apparently is opaline skeletons. Metals presumably leave the ocean largely in newly formed minerals such as authigenic clay (produced in place), oxides, sulfides, and zeolites, as well as in products resulting from reactions between hot basalt and seawater near the crest of the mid-ocean ridge. Sulfur is precipitated in heavy metal sulfides in anaerobic sediments near the land and as gypsum in restricted basins. Some salt leaves with pore waters in sediment. Under the assumption that seawater maintains its composition, we can calculate the average time a seawater component remains in the sea before going out. This time is called *residence time.*

Calculating this time is analogous to figuring out how long people are staying in a museum from counting the people present and the number of people entering per unit time. The ratio is the average viewing time (commonly between half an hour and somewhat greater than an hour, within a museum):

$$t = A / r, \tag{4.1}$$

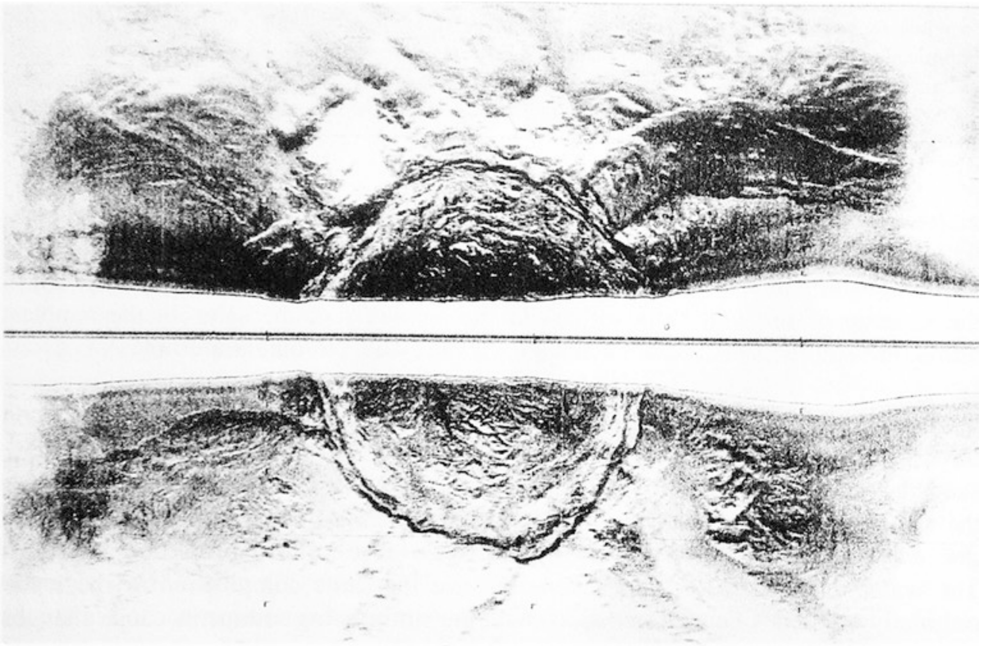

Fig. 4.6 Mud volcano in an acoustic side-scan image. Side-scan record is from the bottom of the Black Sea (Courtesy Dr. Glunow, Moscow; see UNESCO-IMS Newsletter 61, Paris)

where A is the number present and r is the rate of input. A successful exhibit has a large t. In the sea, the residence time is, in essence, a measure of geochemical reactivity. Sodium and chloride have a very long residence time, while silica has a short one. Sodium, having found its partner chloride, tends to stay in solution, while silica is readily precipitated and becomes close to inert as a consequence of diagenesis. Equation (4.1) was once used to calculate a *salt age* for the ocean, assuming that the ocean started out as a freshwater body and retained the sodium added. It was then a useful concept as an estimate for the scale of geologic time. The result came out near 100 million years, much longer than many other estimates and closer to the truth, therefore. However, it was still very short of reality: the calculation was flawed. (Earth is more than 40 times older than 100 million years; the age of the ocean remains unknown, but presumably exceeds a factor of 30 over the salt-age guess, based on various clues.)

4.4 Major Sediment Types

4.4.1 General

There are essentially three types of marine sediments: those that come into the ocean as particles, are dispersed, and settle to the seafloor, those that are precipitated out of solution inorganically, and those that are precipitated by organisms. We call the first type *lithogenous*, the second hydrogenous, and the third biogenous (see Box 4.1: Classification of Marine Sediments).

Around the ocean margins, lithogenous sediments are predominant, their source being largely mechanical weathering of continental rocks. Also, there are salt deposits here (hydrogenous) and biogenous sediments, but in relatively low abundance. On the deep seafloor, on the other hand, biogenous sediments ("oozes") dominate (Fig. 4.7), with *calcareous ooze* being much more common than *siliceous ooze*. In fact, calcareous ooze covers roughly one half of the seafloor. Defining components are (silt-sized) coccoliths and (sand-sized) foraminifers and very small mollusks for the calcareous ooze and (silt- to sand-sized) diatoms and radiolarians for the siliceous ooze. The organisms involved are eukaryotic microbes, with coccoliths and diatoms photosynthesizing (i.e., these are microbial algae).

4.4.2 Sand

Marine sediment particles mainly come in three sizes: sand, silt, and clay (Box 4.1, Fig. 5.4; Appendix A5). To geologists "sand" denotes solid particles between 0.064 and 2 mm in diameter, no matter what it is. Under the microscope, we can see that beach sand in Southern California (Fig. 4.8) and in most places elsewhere mostly consists of mineral grains, small pieces of rock, and shell fragments. We have known for more than half a century that sand grains are readily transported far offshore into the realm of continental fans and continental rises by turbidity currents running down submarine canyons, as discussed in the previous chapter. The same process works with sediments of the deep sea, of course, as long as the seafloor is sloped, as along the flanks of the MOR, except that we largely deal with oozes here that are being displaced. Foraminifers are largely sand (the smallest ones are silt size).

Beach sediments are mainly mixed lithogenous and biogenous.

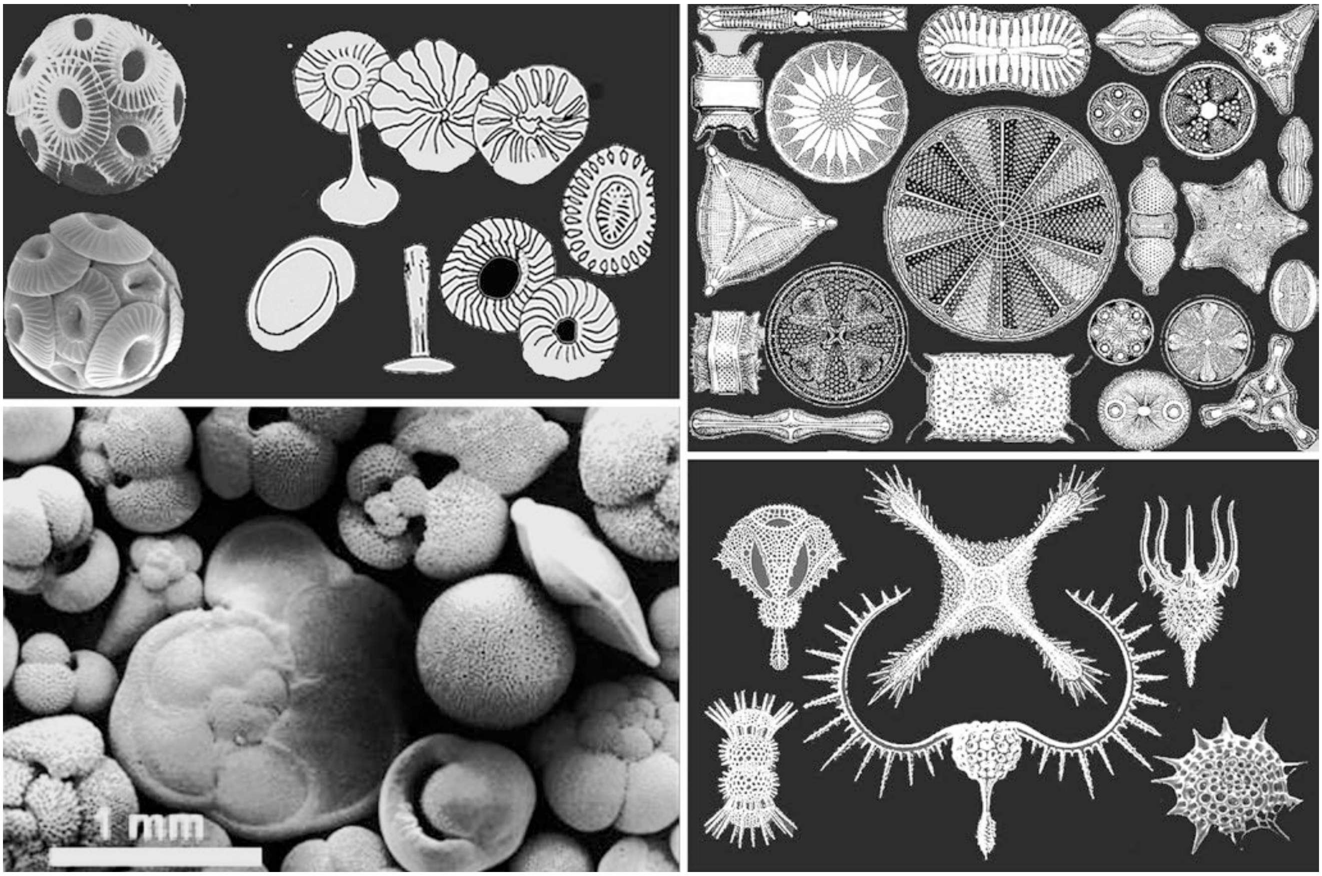

Fig. 4.7 Components of "ooze." (*Left side*; calcareous ooze; *upper panel*: coccolithophores and coccoliths (The former courtesy G. Wefer, and R. Norris; the latter mainly after A. McIntyre, Lamont); *lower panel*: foraminifers (SEM by M. Yasuda, S.I.O.). *Right*: components of siliceous ooze (diatoms and radiolarians; from E. Haeckel, 1904). Colors: calc. particles buff to very *light gray*; diatoms *greenish brown*; radiolarians glassy. Sizes: silt, except the foraminifers, many of which are sand. Coccoliths commonly are extremely fine silt

Fig. 4.8 Beach off S.I.O., in La Jolla. *Left*: pebbles. *Right*: sand grains. The beach sand has an abundance of (glassy) quartz grains (proportionally many more than produced by erosion). Quartz is resistant to chemical attack and to abrasion, other common minerals less so. The pebbles are igneous rocks from the cliffs (Photo of pebbles W.H.B.; microphoto courtesy of P.A. Anderson, S.I. O)

4.4.3 Classification

Box 4.1 Classification of Marine Sediment Types *Lithogenous sediments*. Particles derived from preexisting rocks and volcanic ejecta. Nomenclature based on grain size and various properties including composition, structure, and color. Typical examples, with most common environment in parentheses:

- Organic-rich *clayey silt* with root fragments (marsh)
- Finely laminated *sandy silt* with small shells (delta-top)
- Laminated quartzose *sand*, well sorted (beach)
- Olive-green homogeneous *mud* rich in diatom debris (upper continental slope)

(*Mud* is the same as *terrigenous clayey silt* or *silty clay*, commonly with some sand.)

Fine-grained lithogenous sediments are the most abundant by volume of all marine sediment types (about two thirds), largely because of the great thickness of sediment in continental margins.

Biogenous sediments. Remains of organisms, mainly skeletal parts (calcium carbonate from mollusks, calcareous algae, coral, foraminifers, coccolithophorids, etc.), hydrated silica from diatoms and radiolarians, and calcium phosphate from arthropods and vertebrates. *Organic* sediments, while strictly speaking biogenous, are commonly considered separately. Arrival is as particles (some precipitated in situ) or in aggregates, dispersal by waves and currents. Redissolution is common, both on the seafloor and within the sediment. Appellation is by organism source and by chemical composition and by other properties. Examples:

- Oyster bank (lagoon or embayment)
- Shell sand (tropical beach)
- Coral reef breccia (fragments, reefal debris)
- Oolite sand, well sorted (strand zone, Bahamas)
- Light gray to buff calcareous ooze, bioturbated (deep seafloor)
- Greenish-gray siliceous ooze (deep seafloor)

Biogenous sediments are widespread on the seafloor, covering about one half of the shelves and more than one half of the deep ocean bottom, for a total of around 55%. About 30% of the volume of marine sediments being deposited at the present time may be labeled biogenous, although there may be considerable admixture of lithogenous material, in part volcanogenic.

Hydrogenous sediments. Precipitates from seawater or from interstitial water, especially within freshly deposited sediments (*early diagenesis*). Redissolution is common. Nomenclature is based on origin and chemical composition, as well as some other obvious properties. Examples:

- Laminated translucent halite (salt flat)
- Finely bedded anhydrite {i.e., calcium sulfate} (Mediterranean basin, subsurface)
- Nodular grayish white anhydrite (ditto)
- Manganese nodule, black, mammilated, 5-cm diameter (deep seafloor, Pacific)
- Phosphatic concretion, irregular slab, 5-cm thick, 15-cm diam., light brown to greenish, and granular (upwelling area, upper continental slope)

Hydrogenous sediments are widespread but not important by volume at present.

4.5 Lithogenous Sediments

4.5.1 Grain Size

The bulk of sediment around the continents consists of debris washed off the elevated areas of the continents. The debris results from mechanical breakup with or without chemical attack on continental igneous and sedimentary rocks. Transportation of the resulting rock fragments and minerals is by rivers. Thus, the process is part of the hydrological cycle (Fig. 4.9).

Grain size is extremely important for assessing source and transport processes. One distinguishes *gravel, sand, silt,* and *clay* (see Hjulström Diagram; Fig. 4.3). *Sand*, as mentioned, is all solid material of a size between 0.063 and 2 mm, regardless of composition or origin. Silt is the next smaller size category, at sizes between 0.063 and 0.004 mm (see Appendix A5). The next smaller category, clay, has particles smaller than 0.004 mm (or 4 μm). In some scales 2 μm is taken as the upper clay limit. The term "clay" is somewhat confusing, *clay minerals* being sheetlike minerals of a certain type regardless of size (albeit being common within the size category of "clay"). For clarity, "pebble," "sand," "silt," and "clay" are *size* categories to a geologist. The material needs naming if it is to be specified.

Overall there is a gradation of grain size from source to place of deposition, with coarser particles (including boulders) closer to the source and clay-sized material far away, commonly carried off by water and wind. *Gravel-size* (2–256 mm) and *boulder*-size (>256 mm) material does not commonly travel far, except when taken along by ice (which is hardly sensitive to the size of the load and thus gives rise to *erratics*, that is, boulders without an obvious source in

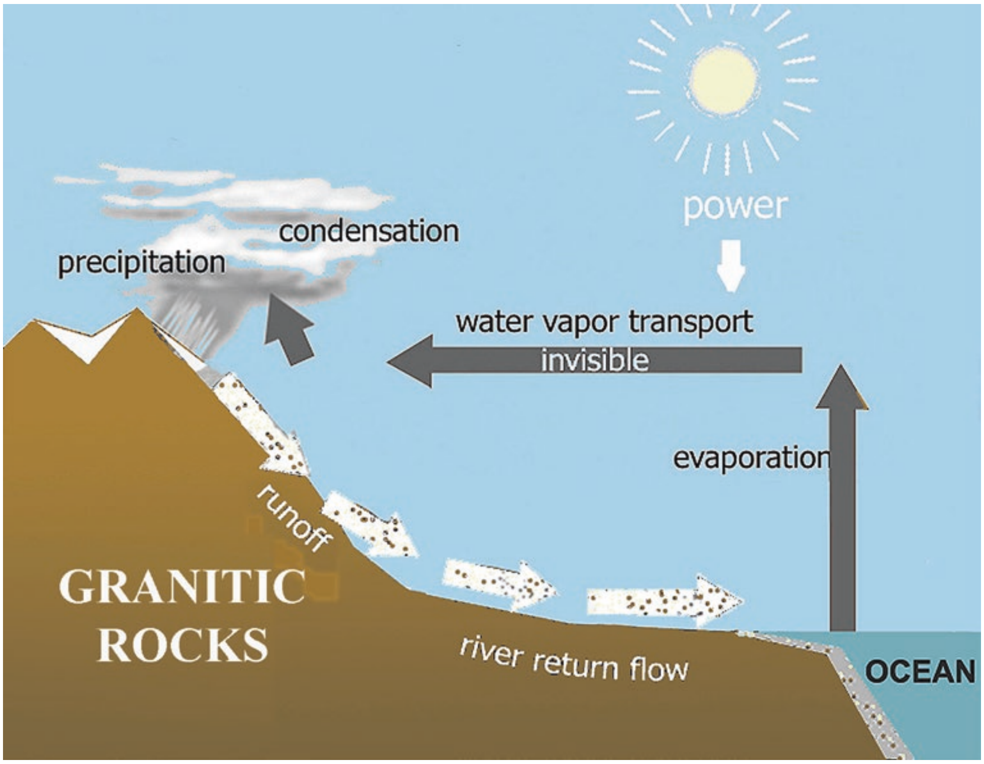

Fig. 4.9 Origin of lithogenous sediments. Weathering of source rock and river transport as part of the hydrologic cycle. The situation schematically depicted is typical for the western coast in North America, as well as for many other places where erosion of mountains delivers sediments to the sea (W.H.B., 2013. San Elijo Lagoon, UCSD, modified)

strange surroundings. Except around reefs and in high latitudes, boulders and gravel are not common in marine sediments.

4.5.2 Lithic Sand

Lithogenous sands are typical of certain beach and shelf deposits, as in Southern California, for example (Fig. 4.8). The sand may consist of minerals (commonly dominated by the resistant quartz) or of rock fragments, as is the case for volcanic material. A striking example of the latter is provided by black beach sands in the Hawaiian Islands (Fig. 4.10). Also, green mineral sand of volcanic derivation can be found on occasion. Other volcanic islands such as Iceland and the Galapagos Islands also have dark gray lithogenous beaches – light brown beaches are largely of continental origin, while white beaches are typical for carbonate environments.

The source areas and dispersal history of sands can be explored by noting the compositional types of *heavy minerals* (densities >2.8 g/cm^3; examples are the silicates hornblende, pyroxene, and olivine; also the iron-rich compounds magnetite and hematite; and the titanium-bearing ilmenite and rutile (see Appendix A4)). The heavy mineral association allows the mapping of depositional provinces. In turn, such mapping provides clues to the action of shelf current wave climate and other factors.

The *shape* of sand grains has been used to obtain clues about their origins. For example, sharp edges have been linked to recent mechanical action, while rounding has been ascribed to reworking. Problems arise with recycled sand grains (i.e., *polycyclic sand*) and with post-depositional etching of grains within sediments.

Fig. 4.10 Lithogenic volcanic dark gray beach sand on Hawaii. Note volcanogenic gravel and boulders in background. The young coconut tree presumably brought in by waves as seedling (foreground) is unlikely to survive on the shifting sand (Photo W.H. B)

4.5.3 Lithic Silt

Lithogenous silt is common on the continental slope and rise, although largely mixed with coccoliths and other biogenous particles (Fig. 4.11). The composition of the silt is eas-

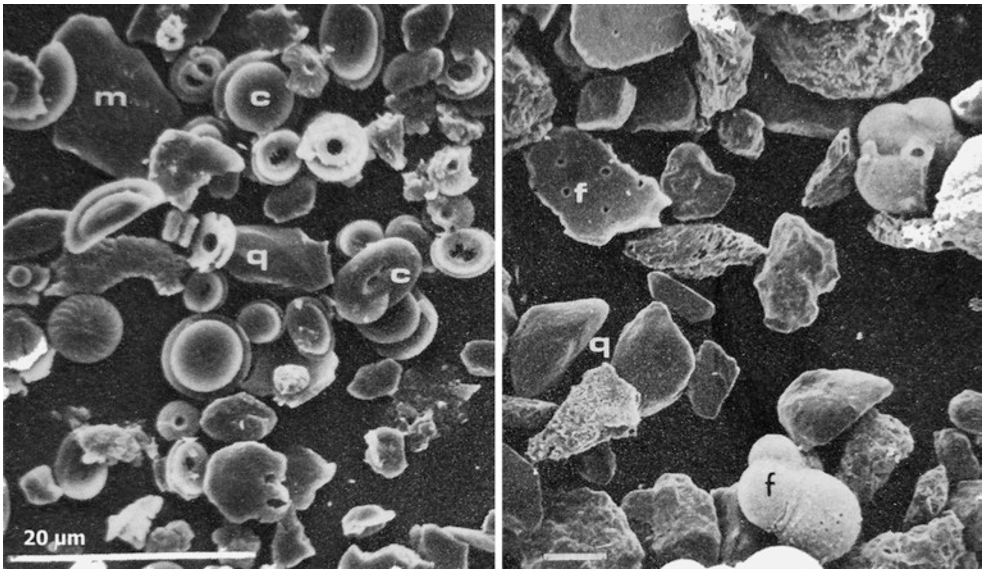

Fig. 4.11 Mixed terrigenous and biogenous sediment makes up the fine silt fraction (2–6 µm) on the continental rise off Cape Verde (NW Africa). The medium-size silt (*right panel*) likewise consists of a mixture. *c* coccoliths, *f* foram shell, *m* mica, *q* quartz (SEM photos courtesy D. Fötterer, then Kiel)

ily rationalized by comparing with adjacent sand deposits and with associated clay. Mica, a platy terrestrial mineral delivered both by igneous and ancient sedimentary rocks, is commonly especially well represented.

Sand is commonly studied with a binocular microscope, while the composition of clay is investigated by X-ray diffraction and other sophisticated methods. The study of silt used to fall into the crack between the methods. It has had a rather low popularity rating. For the last several decades, the scanning electron microscope (SEM) has made it possible and attractive to investigate this size fraction in some detail. Not surprisingly, it turned out that the composition of the silts is commonly closely related to that of the associated fine sand fraction. Biogenous contributions (plankton remains of the coastal ocean) can be dominant in places (including diatoms and radiolarians), rather than continental debris (Fig. 4.11).

4.5.4 Clay-Sized Sediment

Clay-sized particles are ubiquitous both on the continental margins and on the deep seafloor. Much like fine silt, the presence of clay, where abundant, indicates *low-energy environments*. Clay is easily transported, although, in places, pickup is hindered by a bacterial mat covering the sediment. In well-oxygenated environments, however, such mats are commonly disturbed by the churning of sediment (*bioturbation*) by larger organisms, if they form at all.

Common *clay minerals* are montmorillonite (or smectite), illite, chlorite, and kaolinite. When mapping their distributions on the deep seafloor, patterns emerge that are readily interpreted in terms of origin and paleoclimate, with links to volcanic activity, metamorphic processes, and physical erosion as well as deep chemical weathering on land (Chap. 10).

The high surface areas of clay particles that come with their minute size give clayey sediments special chemical properties. For example, clays readily absorb a large variety of substances, and many react easily with the ions in seawater and in interstitial waters, establishing chemical equilibrium with their surroundings. During diagenesis within buried sediments, new clay minerals can form at elevated temperature and pressure. Ultimately such reactions have important implications for the chemistry of seawater and for geochemical processes in general.

Clayey sediments in regions of high sedimentation rate are commonly rich in organic matter, partly because organics cling to the clay during deposition and partly because where conditions are quiet enough for the deposition of clay, they also are favorable for the deposition of fluffy organic particles. Much of the clayey matter actually may be brought to the seafloor within fecal pellets of organisms filtering the water. Such clay is associated with food particles. Experience with sediment-trapping equipment (in the Baltic and off California, among other places in the sea) suggests that the *fecal pellet transport* mechanism is a significant agent of sedimentation.

4.6 Biogenous Sediments

4.6.1 Types of Components

Organisms produce sediments in the form of shells and other skeletal materials and organic matter. The label "biogenous" is generally applied only to the hard parts, that is, to calcareous, siliceous, and phosphatic matter. The organisms involved actually include bacteria and archaea (e.g., in producing metal oxides, hydroxides, and sulfides). Easily recognized as fossils are diatoms, radiolarians, silicoflagellates, and primitive multicellular forms such as sponges (hydrated silicon oxide). Coccolithophores, foraminifers, various kinds of algae, mollusks, corals, bryozoans, certain

Fig. 4.12 Biogenous sediments on the beaches in the Hawaiian Islands. *Left*, pebble-size material; *middle*, coarse sand; *right*, beach, dark gray: volcanogenic pebbles among coral-derived pebbles thrown up by storm waves (Photos W.H. B)

brachiopods, arthropods, echinoderms, annelid worms, calcareous sponges, and vertebrate remains (i.e., solids made of calcite, aragonite, Mg-calcite, and those made of calcium phosphate minerals) are especially common.

Perhaps the most abundant and certainly the most conspicuous biogenous types of sediment are delivered by calcareous skeletal parts of organisms. In shallow tropical waters, there are abundant remains of coral and associated materials, depending on location (Fig. 4.12). On the deep seafloor, there are the remains of coccolithophores and of pelagic foraminifers (Fig. 4.7). The shells of benthic foraminifers and coccoliths are ubiquitous and are especially abundant in shallow water. The benthic "forams" show great variety (Fig. 4.13) and are useful therefore in stratigraphy and in environmental studies. We have already pointed out the strong biogenic aspect of low-latitude silt in slope sediments and on the continental rise. In places, the biogenic component can be truly striking, as in certain shell pavement deposits in the "wadden" of the North Sea and in similar tidal flats.

One source of carbonate that is ubiquitous, involving both shelves and the deep seafloor, is a tremendous variety of foraminifers, with hundreds of common species in the benthic types (Fig. 4.13). Pelagic forms, with relatively modest diversity (tens of species), may have arisen several times during geologic history from benthic stock.

For siliceous (opaline) hard parts, the gradient pattern from shallow to deep is similar to the carbonate pattern: remains of benthic organisms dominate in shallow water (sponges, benthic diatoms) and pelagic materials dominate in sediments of deep water (diatoms, radiolarians). Pelagic diatoms are typical for the coastal ocean (overlying shelf and upper slope) and especially for upwelling areas. Likewise, river mouths are prime areas of diatom deposition, especially benthic ones.

In addition to carbonate and silica, phosphatic particles are produced by organisms (including phosphatic fecal pellets). The sedimentation of such particles plays an important role in the phosphorus budget of the biosphere and is of great interest geochemically, therefore. The various other types of hard parts – strontium sulfate, manganese, iron, and aluminum compounds – are intriguing in the context of evolutionary studies but do not materially contribute to marine sediments. Organogenic sediment is important in the context of the productivity of the sea (Chap. 7) and of hydrocarbons (Chap. 14).

4.6.2 Sediment Contributions by Benthic Organisms

The great importance of carbonate-secreting benthos in producing sediment is apparent all through the Phanerozoic record, that is, more than the last half billion years. There is some indication that the less stable carbonate minerals aragonite and Mg-calcite are more abundant during cool and cold conditions (latest Precambrian, latest Paleozoic, Neogene) than during warm time periods such as much of the Cretaceous. At present, the most conspicuous biogenic edifice in the sea is the Great Barrier Reef. It is largely composed of the remains of benthic organisms: corals, calcareous algae, mollusks, and benthic foraminifers. Among the calcareous matter, both calcite and aragonite (same chemical composition, different arrangement of elements) are found. Aragonite is much more soluble than calcite. Also, there is a tendency for higher Mg content in the calcite precipitated in warm water, compared with pure calcite.

Mesozoic and later Cenozoic platform carbonates once were deposited all around the *Tethys,* the ancient tropical seaway that once linked the western Pacific with the central Atlantic. The shallow-water limestone rocks of the geologic record, which originated in the shelf environments of ancient oceans, commonly contain an admixture of siliceous rocks, as

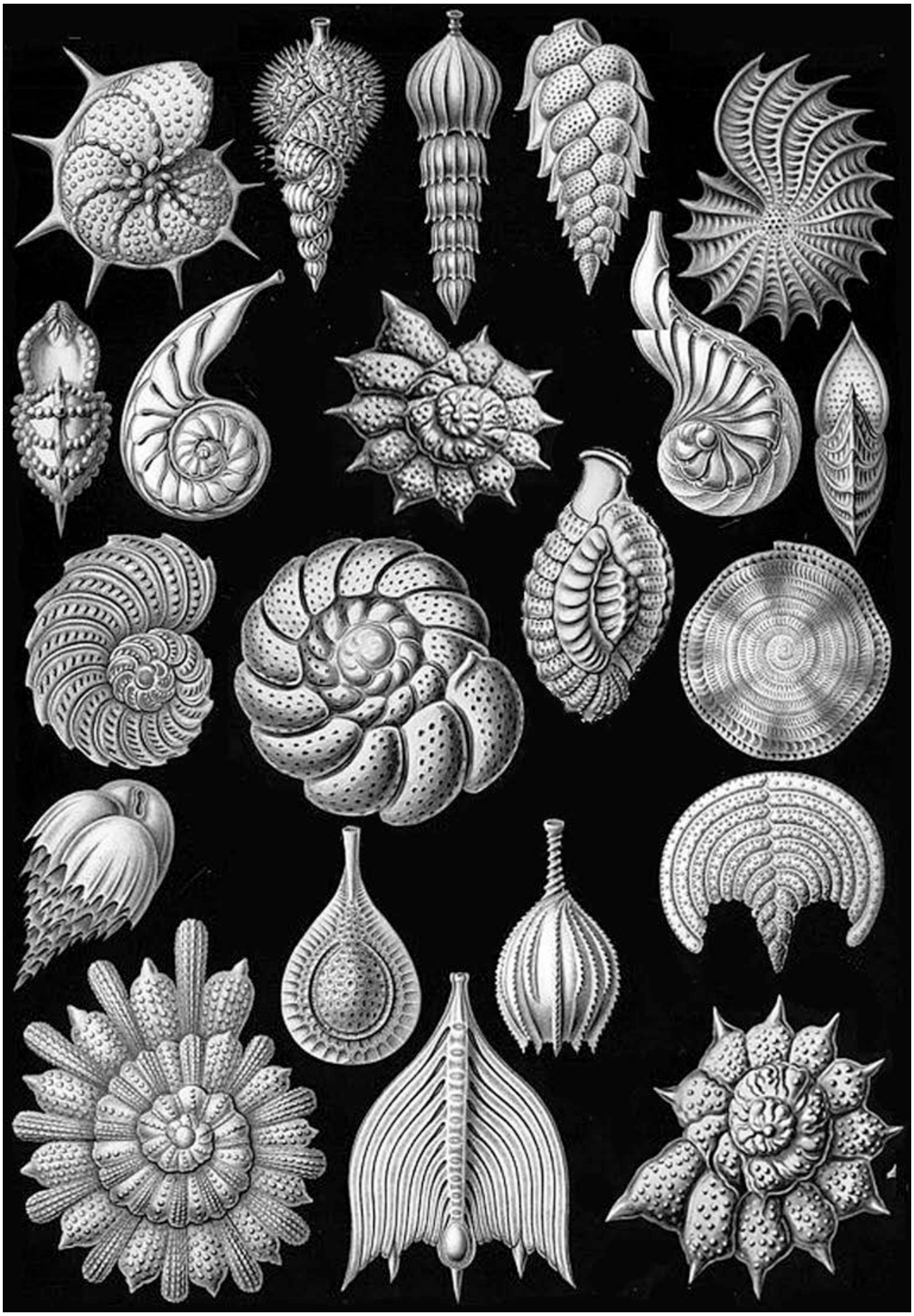

Fig. 4.13 Shells from benthic foraminifers, illustrating the great variety in these forms (From E. Haeckel, 1904. Kunstformen der Natur. Leipzig)

layers of *chert* arranged along horizons parallel to the bedding. The "chert" usually appears as microcrystalline quartz lumps and beds and originated from recrystallization after expulsion of the water from the opal. Any of the silica-producing organisms can be responsible for the origin of a given piece of chert, even though some fossils (e.g., sponge remains, radiolarians) may be more conspicuous within it than other fossils.

Why is there little or no evidence for incipient chert formation in modern shelf carbonates?

The answer is not clear. The reason may be that silicate concentrations are comparatively low in present tropical waters. Seawater (especially shallow seawater making shelf carbonates) commonly is highly undersaturated, presumably stripped of its silicate by diatoms in upwelling regions. In fact, a general rarity of chert (as is evident after the Eocene) may be an inevitable consequence of planetary cooling and associated upwelling. In any case, the once popular idea that waning volcanism is to blame for the post-Eocene rarity of chert has been largely abandoned. Eocene chert in deep-sea sediments attracted much attention by deep-sea geologists when deep-sea drilling started, its presence being rather inimical to any drilling.

4.6.3 The Remains of Planktonic Organisms

Remains of pelagic species are much in evidence in slope sediments, as we pointed out earlier when discussing silt and Fig. 4.11. The bulk of deep-sea sediments, to be sure, is rich in planktonic skeletal matter. Shelf sediments as well can contain considerable amounts of planktonic remains. Thus, for example, the English chalk of Cretaceous age is extremely rich in *coccoliths,* that is, particles produced by *coccolithophores* (more commonly addressed as *nannofossils* by geologists*).* Siliceous remains of diatoms, radiolarians, and silicoflagellates (all planktonic and opaline) are characteristic of offshore high-production areas, as mentioned. This general pattern must be added as a clue to distance from the shore to the gradient in the benthic-planktonic ratio in foraminifers that parallels distance from the shore. In deep-sea sediments, planktonic remains (specimens, not species) tend to outnumber benthic ones by ratios of 10:1 to 100:1, the higher values being typical in areas of good preservation.

4.7 Nonskeletal Carbonates

4.7.1 Carbonate Saturation and Precipitation

In the present ocean, carbonate precipitation occurs either within organisms (shells, skeletons, "internal precipitation") or in association with their metabolic activity (e.g., algal crusts, "bacterially mediated precipitation," "external precipitation"). This need not always have been the case: at very high levels of saturation, there might have been inorganic precipitation, which may have produced certain types of limestone seen in the geologic record. Where would one look for possible inorganic precipitation today? One would need to look in regions of unusually high carbonate saturation. Seawater that spontaneously precipitates a mineral is said to be *supersaturated* with this mineral phase. In contrast, seawater that dissolves the mineral is *undersaturated. Saturation* obtains at the point of balance between precipitation and dissolution in a solution. For two-ion compounds (such as calcium carbonate), the degree of saturation is expressed as the ratio between the products of observed concentration of the two ions involved and the product of concentrations at saturation. This criterion defines much shallow tropical seawater as being supersaturated with calcium carbonate. Yet spontaneous inorganic precipitation is not observed. Presumably the expected reaction does not occur because of interfering factors, that is, the presence of a blocking agent or several such agents.

In the presence of interference, if inorganic precipitation is to be observed, especially high levels of supersaturation need to be extant (and any blocking agent is to be removed), assuming that appropriate nuclei for crystal formation are sufficiently abundant. Naturally, when saturation is lowered substantially, for example, by the addition of carbon dioxide (in modern times from human energy use), it becomes more difficult to make carbonate sediment or shell. This is, in a nutshell, the effect from the *acidification* of seawater. When carbonate is dissolved, carbon dioxide is used up in the reaction. Conversely, when precipitating carbonate, carbon dioxide is released and any undissolved excess is at least partially expelled from the sea to the atmosphere. Evidently, then, the reactions involving carbonate are of prime importance when discussing changes in the atmospheric concentration of carbon dioxide and associated greenhouse effects on various time scales.

4.7.2 The Bahamas

One place that seemed ideally suited for finding out whether inorganic precipitation is now occurring or not is the archipelago known as "the Bahamas."

The islands are surrounded by some of the warmest and most alkaline waters in the ocean. There is hardly any terrigenous input, so that pure carbonates can accumulate. The Great Bahama Bank is very flat and very shallow over large areas (Fig. 4.14). Evaporation and warming by the sun combine to increase saturation. Ubiquitous benthic algae remove carbon dioxide when growing. Thus, conditions would seem very favorable indeed for the precipitation of carbonate directly from seawater.

Fig. 4.14 Carbonate oolite deposits on the Bahama Banks, seen from the air (Air photo courtesy D.L. Eicher, Boulder, Colorado)

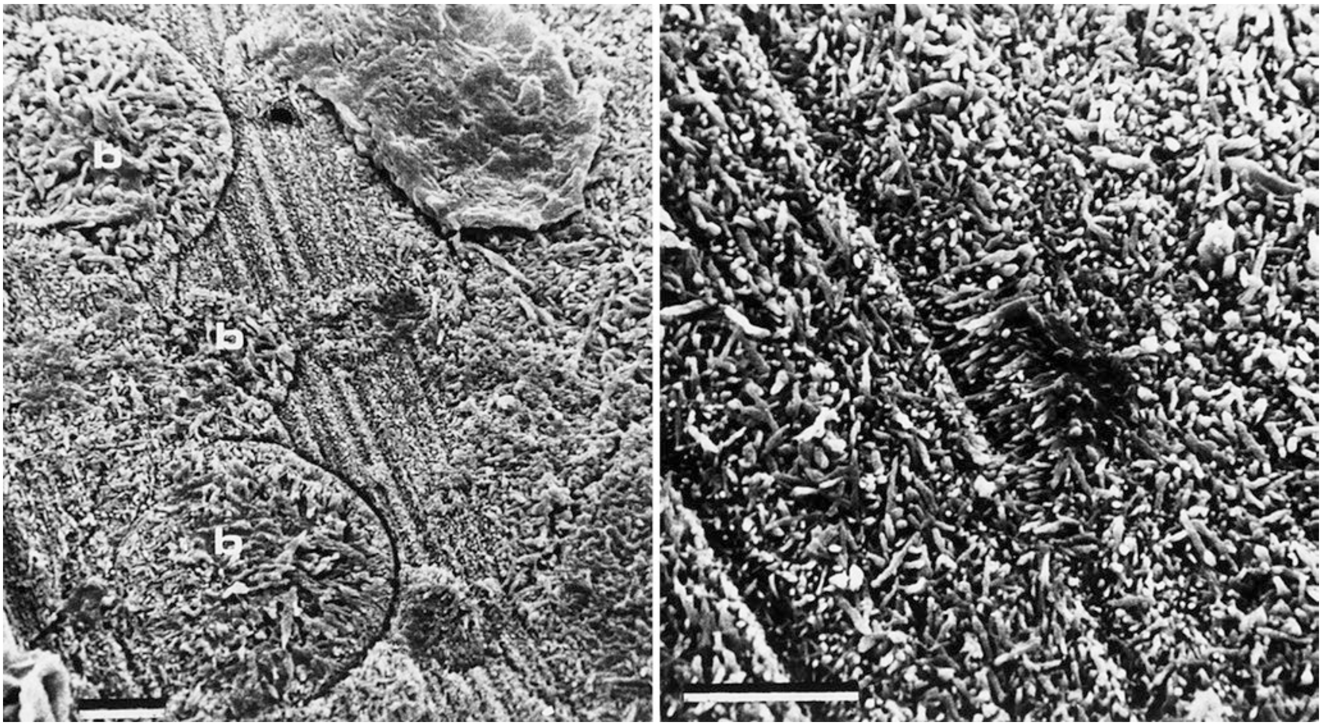

Fig. 4.15 SEM images of ooids, scale bar 5 µm. *Left*, slightly etched section. Three secondarily filled borings (marked "b") intersect the concentric laminae of primary oolitic coating. *Right*, close-up of oolite laminae showing acicular aragonite needles (Images courtesy of D. Fütterer, Kiel)

Two types of calcareous particles on the seafloor of the Great Bank have been considered as possible products of inorganic precipitation*: aragonite needles* (length of a few micrometers) and *oolites* (consisting of spherically layered particles (*ooids)* with a diameter near one third of a millimeter) (Fig. 4.15). The origin of the aragonite needles has puzzled geologists for some time; apparently they form within certain algae. Oolites are a favorite object of geologic discussion, famous for being mentioned by Mark Twain (in an ironic remark on the quality of geologic reasoning). Oolites are abundant in the geologic record, especially in subtropical shelf sediments. In the Bahamas they occur especially on the outer rim of the Great Bank in the shallowest water, suggesting a strong influence of tidal currents and breaking waves in their origin. Apparently the ooids only form in the presence of sufficient organic matter. This is not good as support for the action of inorganic precipitation. In fact, observations now suggest that precipitation is largely through biocalcification by unicellular algae. It appears, then, that even here in the Bahamas precipitation directly from seawater is negligible in present-day conditions.

4.7.3 Dolomite

Calcite may contain magnesium in different concentrations (*magnesium calcite*). In the present shelf environment, as mentioned, magnesium-rich calcites are found in greater abundance than pure calcite. *Dolomite,* a carbonate mineral with equal amounts (by atom numbers) of magnesium and calcium, is a different story. It does not precipitate in shells or other biogenic products. Its presence in the geologic record poses many unsolved questions. Thus one might expect that dolomite would precipitate from seawater because it is much less soluble than aragonite. There is, after all, plenty of magnesium in seawater. However, such precipitation has not been observed. Instead, dolomite apparently forms *within* sediments, either through partial replacement of calcium with magnesium in preformed carbonate or possibly also by precipitation from pore waters. Either process would be referred to as "diagenesis." Much of "diagenesis" is about postdepositional geochemical problems. Thus, geochemists have done much fundamental work on dolomitization (Scripps examples: M. Kastner, P. Baker). In recent years, petroleum and methane geologists and chemists have shown much interest in the topic.

A classic area for the study of incipient dolomite formation is the southern margin of the Persian/Arabian Gulf. Here the intertidal flats lie behind barrier islands within lagoons with warm and very saline water. In the pore waters of sediments above low tide, magnesium is greatly enriched with respect to calcium, while sulfate (which apparently hinders dolomite formation in many surroundings) is reduced in abundance owing to the precipitation of gypsum (calcium sulfate) in adjoining evaporite pans (which are common in the *sabkha* environment). Microbial sulfate reduction in the uppermost few tens of meters of continental margin sediments similarly seems to favor "dolomitization." One problem interfering with solving the dolomitization question is that unknown conditions of the geologic past and in a warm ocean may have played a large role in some of the dolomite formation.

4.8 Hydrogenous Sediments

4.8.1 Marine Evaporites

Evaporites form when seawater evaporates. Desert belts – high ratios of evaporation rates over those of precipitation – are located near 25° of latitude, on both hemispheres. Unsurprisingly, these also are the latitudes of the highest salinity in the surface waters of the open ocean. For precipitation of salt, however, concentrations have to exceed saturation values, and this happens only upon restriction of exchange of shelf-water bodies with the open ocean, commonly in a semi-enclosed basin on the shelf (the one widely quoted exception being the Mediterranean basin at the end of the Miocene, as documented by deep-sea drilling during DSDP Leg 13.

How much salt can be produced by evaporating a 1000-m-high 1-m^2 column of seawater? Salt is 3.5% (or 35 per mil) of the weight of the column; thus the answer is 35 tons or 14 m at the common density of 2.5 tons per cubic meter. Most of the readily recognized salt obtained would be kitchen salt ("halite"). The salts precipitating first would not include halite, though, but have abundant carbonates and sulfates.

To precipitate halite the brine would need to be concentrated about tenfold. Many evaporites only contain carbonate and gypsum (or "anhydrite"), whereas others have thick deposits of halite or (even more rarely) final layers of the valuable (and very soluble) potassium salts. In marine sediments, to get any one salt without the others, "fractionation" in linked basins is necessary or periodic removal of certain salts by dissolution, while preserving others.

4.8.2 Phosphorites

Phosphatic deposits presumably are largely of biogenic origin. Phosphorites are of prime importance in the cycling of phosphorus and hence in the productivity of the ocean (Chap. 7). Also, they constitute an important marine resource, used predominantly in the fertilizer industry. Thus, phosphorites are encountered again in the chapter on resources (Chap. 14).

4.8.3 Iron Compounds

Microbes are notably involved in the origin of both iron sulfides and iron hydroxides, as has been known for more than a century. Iron apparently is of prime importance in the productivity of the ocean, with at least some of it mobilized from the seafloor upon loss of oxygen. Sulfides and hydroxides are important items in the geochemical cycling of temporarily free oxygen, the abundance of which changes in Earth history, with consequences for marine sedimentation (black mud, clay, and shale and greenish deposits versus brown, reddish, and yellowish deposits).

An iron-bearing mineral that has attracted much attention by marine geologists is *glauconite*. It is a greenish silicate common in shallow marine areas and is commonly found in association with phosphatic sediments in high-productivity regions along certain continental margins, as, for example, off Angola.

The origin of iron oolites, common in Mesozoic marine sediments (e.g., "minette" ores of Alsace-Lorraine), is not known. Apparently minette ores are not forming in the present ocean in noticeable abundance.

4.9 Sedimentation Rates

The idea of *geologic time*, so fundamental in all of geology, is in fact quite young, compared with the age of various branches of science. It was early discussed by James Hutton (1726–1797), and its chief protagonists were Charles Lyell (1797–1875) and Charles Darwin (1809–1882). Lyell, like Hutton, invoked geologic time to create Earth's morphology and the geologic record. Darwin made use of geologic time in his explanation of evolution. However, before the discovery of radioactive decay at the end of the nineteenth century and the application of this discovery to the geologic record, there was no reliable way of telling just how much the geologic time scale differs from the chronology derived from multimillennial human time, that is, the account in Genesis, summarized by Bishop Sam Wilberforce, FRS. Wilberforce's clever but derogatory pronouncements on Darwin's ancestry were forcefully attacked by T.H. Huxley, in 1860. The disputations reflected different belief systems, not certain knowledge.

We now know that the guesses proposing millions of years of Earth history were closer to the truth than those postulating thousands of years. Modern determinations of sedimentation rates span the gamut between 1 m per million years and many km per million years, depending on the environment (see Fig. 4.16). A million years is a useful time interval to work with, for geologists contemplating pre-ice age processes. To apply the rates listed to ancient sediments, one has to consider compaction and loss of porosity – about 40% in sands and about 70% in muds. On the whole, high rates of sedimentation (say 100 m per million years) occur at the edges of the continents. Exceptionally high rates are found off many glaciers. The lowest rates occur on the deep seafloor far away from continents.

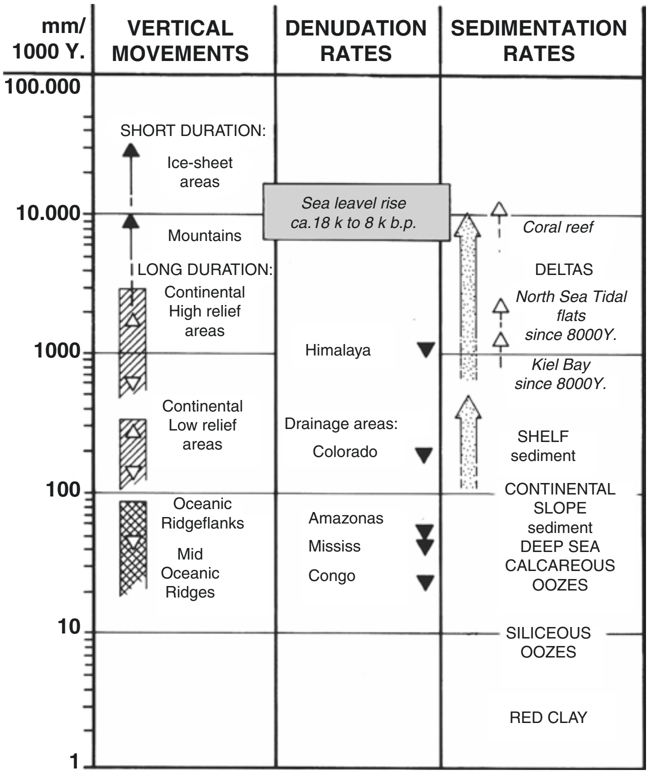

Fig. 4.16 Typical rates of vertical crustal motion, of denudation, and of sedimentation rates. Scale in mm per thousand years (meters per million years). Postglacial sea-level rise shaded (average of some 100 m in 10 thousand years; *k* kilo years). Logarithmic scale. The values are approximate and for comparison (E. Seibold, 1975. Naturwissenschaften 62: 62; modified)

Characteristic values of sedimentation rates on continental slopes are 40–200 mm per thousand years, with a typical value near 100 mm per millennium or 100 m per million years. Theoretically, coral reefs can build up at rates near 1 cm per year, that is, 10 m per millennium or 10 km per million years! More commonly, one finds values somewhat less than half of that in reef growth. In any case, such high rates make the sinking of the seafloor irrelevant to the growth of stony reefs. Such findings throw doubt therefore on the commonly quoted Darwinian origin of atolls.

Reliable estimates of high sedimentation rates are possible in the case of *annual layers* or *varves*. Counting varves in the Black Sea have yielded rates near 400 mm per millennium. In a bay off the Adriatic Island Mljet, 250 mm per millennium was found. In Santa Barbara basin off Southern California, counts of varves yielded values near 1 mm per year, that is, 1 m per millennium. Such high rates of sedimentation are favorable for the detailed reconstruction of environmental changes over the last few millennia and centuries (Chap. 15).

In concluding this chapter about the composition of marine sediments, some of the more esoteric components may be mentioned. So-called cosmic spherules were first described by John Murray of the *Challenger E*xpedition. Black magnetic spherical objects up to 0.2 mm in diameter, commonly rich in Fe and Ni, can be found in pelagic sediments, typically several spherules per gram of pelagic clay. Because it was thought that they represent a steady influx of matter from space, their abundance was used on occasion as an indicator for accumulation rates.

Glassy objects, normally up to 1 mm in diameter, may be produced by the impact of meteorites on rocks. They are called *microtectites* or simply *tectites*. Tectites were found in deep-sea sediments in strewn fields around Australia (dated at 0.7 million years), off the Ivory Coast (1.1 million years), and in the Caribbean (33–35 million years), for example. Where abundant, they can be used as a time marker and serve for correlation of sedimentary rocks by ev*ent stratigraphy*. Tectites commonly serve as evidence for impact events.

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