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ORGANIC MATTER-RICH SHALE DEPOSITIONAL ENVIRONMENTS

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2.1 INTRODUCTION

Shale is the most abundant rock type available at the surface of our planet and makes up about two-thirds of the stratigraphic record (Garrels and Mackenzie, 1969). The term "shale"[1] refers to all sedimentary rocks composed predominantly of mud[2] (>4ϕ or <0.0625 mm) particles (cf. Tourtelot, 1960, p. 342). Mud particles may be terrigenous, biogenous, or hydrogenous. Terrigenous—or siliciclastic—mud is always detrital, that is, produced by weathering and erosion of preexisting rocks, and comes into the depositional environment as individual particles and/or as aggregates. Biogenous mud is made by organisms, and includes a skeletal and an organic component. Skeletal mud may be calcareous or siliceous. Some benthic protozoans (agglutinated forams) build their tests by cementing terrigenous and other particles with an organic ligand. Some quartz silt aggregates in shales represent the collapsed or compacted tests of these organisms (Pike and Kemp, 1996; Schieber, 2009). When a shale is characterized by an organic matter content higher than the average marine shale (ca. 0.5%, Arthur, 1979), it is referred to as an organic matter-rich shale or, more commonly, a black shale.[3] Hydrogenous mud precipitates out of solution directly, either from seawater or from interstitial water during diagenesis, and it includes oxides and hydroxides, silicates, for example, zeolites and clay minerals, heavy metal sulfides, sulfates, carbonates, and phosphates. Clay minerals are therefore not only terrigenous, but they may also be hydrogenous, that is, formed *in situ*. Biogenous and hydrogenous mud may be detrital, that is, recycled from older deposits, in which case their origin is biochemical, but their texture will be clastic. The composition of the detrital fraction of a shale depends on the petrology of its source areas and on the intensity and effectiveness of chemical weathering.

[1] Although the original meaning of the word "shale" is "laminated clayey rock," our historical usage of the word has been that of "general class of fine-grained sedimentary rocks" (Tourtelot, 1960). There is no reason why we should restrict our usage of the word shale to laminated and/or fissile fine-grained sedimentary rocks. "Lamination" has a descriptive and a genetic definition with distinct sedimentologic implications (cf. McKee and Weir, 1953; Campbell, 1967), and fissility is a secondary property largely related to weathering (e.g., Ingram, 1953). If we define shale as a fissile fine-grained sedimentary rock, then "there are no shales in the subsurface, only potential shales" (Weaver, 1989, p. 6). Some rocks which are referred to in the literature as shales are actually metasedimentary rocks produced by regional low-grade metamorphism, and should therefore be called slates.

[2] Mud is the name given to particles or collections of particles smaller than sand, that is, smaller than 62.5 μm, that is, silt and clay, which typically occur together. Some authors talk about "mud and silt," perhaps making "mud" a synonym of "clay." Operationally, the mud/sand boundary may be defined based on sieve sizes around this value. Because mud is a term related to grain size, it has no connotations as to composition.

[3] Modern organic matter-lean muds may also be black when their iron sulfide content is high (e.g., Potter et al., 2005); however, they become light-colored on lithification as the sulfide changes into either marcasite or pyrite (Twenhofel, 1939). Black shale is the general term for any dark-colored, fine-grained, organic matter-rich sedimentary rock. In the words of Stow et al. (1996, p. 403): "[m]any black shales are hemipelagites; others, such as black cherts and organic matter-rich limestones, are pelagites; whereas still others are fine-grained turbidites." This *de facto* usage has also been noted by Arthur (1979) who states that "the term 'black shale' is used in a general sense to refer to relatively organic carbon-rich […] mudstone and marlstone which may or may not be 'shale' in the classical sense."

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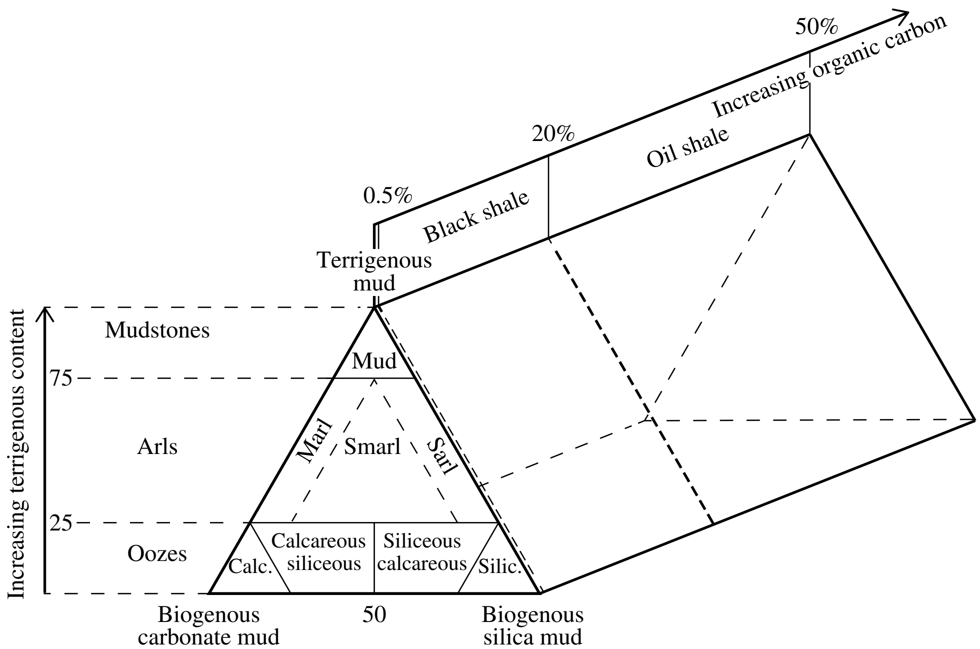

FIGURE 2.1 Classification of shales based on composition. This scheme is based on the classification scheme proposed by Hay et al. (1984, p.14). Shales are fine-grained sedimentary rocks with varying relative proportions of terrigenous mud and mud-sized biogenous components. Shales may also contain up to 25% of terrigenous or biogenous grains coarser than mud (>62.5 μm). A shale with an organic matter content higher than the average marine rock, that is, ca. 0.5%, is referred to as a black shale. Black shale is thus the general term for any dark-colored, fine-grained, organic matter-rich sedimentary rock.

Shales, particularly those deposited in marine environments, are usually combinations of mud from different sources (Fig. 2.1).

Although "black shale" is a useful term when referring to organic matter-rich sedimentary rocks in general, it is a collective noun that groups rocks of various types and origins (Trabucho-Alexandre et al., 2012b). In the petrologic hierarchy of sedimentary rocks, the term "black shale" is equivalent to such terms as "sandstone" or "limestone," rather than to more precise terms such as "lithic arenite" or "oöidal grainstone." However, shales are seldom subdivided based on their composition and texture (Fig. 2.1). For this reason, we are often not able to distinguish subtle compositional and textural differences that would otherwise allow us to subdivide what were once considered monotonous successions of shale and marl (cf. Lewan, 1978).

Shales do not lend themselves well to study in the field or in hand specimen. Sorby (1908, p. 196), who started the microscopic study of rocks, realized that the "examination of […] rocks in a natural condition is enough to indicate that the structure of clays differs enormously, and indicates formation under very different conditions; but there is always some doubt as to their true structure, when not made into thin sections." The study of shales has also been hampered by the ingrained idea that shales always reflect deposition in quiet water. "Aside from this it is hard to say anything definitive about the environment of a shale since most environments have periods and places of quiet water deposition"[4] (cf. Potter et al., 2005, p. 75). Shales have been studied mostly for the unusual geochemical signals they carry, and the composition of shales is often only known in terms of organic matter and elemental content. However, we should not attempt to explain the origin of black shales by focusing solely on explanations for their high organic matter content, which typically constitutes but a few percent of the total rock volume.

It is now widely recognized that black shales show significant compositional and textural variability on a variety of scales (Aplin and Macquaker, 2011; Ghadeer and Macquaker, 2012; Lobza and Schieber, 1999; Macquaker et al., 2007, 2010b; O'Brien, 1996; Plint et al., 2012; Schieber, 1994, 1999; Schieber and Riciputi, 2004; Schieber et al., 2010; Trabucho-Alexandre et al., 2011, 2012a), which reflects the diverse and dynamic nature of the processes and environments behind their formation. The composition, textures (viz. grain size and fabric), structures, and fossil content of shales depend on the physical, chemical, and biological processes responsible for their deposition and on their depositional environments. Patterns of vertical and lateral variability, which can be observed on a variety of scales in shale successions, preserve a record of the evolving

[4] "SEPM Strata, Terminology List," accessed November 2, 2013. http://www.sepmstrata.org/TerminologyList.aspx?search=shale

depositional environments in which they formed. Indeed, shales can be deposited by a variety of processes in almost any environment (e.g., Schieber, 2011; Stow et al., 2001; Trabucho-Alexandre et al., 2012b).

2.2 PROCESSES BEHIND THE DEPOSITION OF ORGANIC MATTER-RICH SHALE

Shales are the end product of the processes that control the production, erosion, transport, deposition, and diagenesis of mud. The composition of shales is a product of the interaction of three key variables: sediment input, removal (or destruction), and mixing (or dilution). Diagenetic processes act on the sediment and result in changes to its composition and/or texture. Although organic enrichment of shales is always a function of the same basic variables, which combinations will yield organic matter-rich sediments depend on depositional environment.

2.2.1 Processes Behind the Transport and Deposition of Mud

Mud may be transported to its final resting place by gravitational settling, by advective processes, that is, mud transport resulting from net horizontal water movement, and by sediment gravity flows, that is, mud transport by density currents for which excess density is produced by the presence of suspended solids.

The deposition of particles smaller than about 10 μm is controlled by gravitational settling, that is, settling from suspension under the force of gravity toward the depositional interface. For particles larger than about 10 μm, depositional processes are dominated by shear stress at the depositional interface, and silt has a bedform succession similar to that of sand finer than ca. 80 μm (Mantz, 1978; Southard, 1971).

In freshwater, mud is mostly present as individual particles, because the excess negative charge present on the surface of fine mud particles keeps them from flocculating. In paralic and marine environments, aggregates are formed due to changes in the chemical environment, namely an increase in salinity, and due to the activity of organisms, and mud tends to be present as flocs, fecal pellets, pseudofeces, and other organomineralic aggregates (e.g., marine snow). Although salt flocculation is an important mechanism, particularly in environments where water masses of different salinities mix, biogenic aggregation is probably the most important process controlling the behavior of mud in paralic and shallow marine environments (Eisma, 1986; Pryor, 1975). Despite their lower density, the behavior of aggregates is comparable to silt- and sand-sized particles. Consequently, mud in paralic and marine environments settles relatively quickly through the water column and can be transported as bedload over a wide range of flow velocities (e.g., Richter, 1926; Schieber et al., 2007; Trusheim, 1929; van Straaten, 1951).

Mud can also accumulate in the presence of current velocities that exceed the threshold of mud erosion if suspended sediment concentrations exceed 1 g l^{-1}. Fluid mud, which is a highly concentrated aqueous suspension of mud in which settling is hindered by particle proximity, forms when the amount of mud entering the near-bed layer is greater than the dewatering rate of the high density suspension (McAnally et al., 2007). Fluid mud is a common feature of river, lake, estuarine, and shelf environments in which water is laden with fine-grained sediment. Along coastlines with abundant mud supply, fluid mud dampens waves (Wells and Coleman, 1978) and allows mud deposition in relatively high energy environments (Rine and Ginsburg, 1985). Mud drapes can therefore be formed over significant portions of the tidal cycle, rather than just at slack water; if fluid mud layers persist, mud can accumulate continuously over multiple tidal cycles (MacKay and Dalrymple, 2011). Large volumes of fluid mud can be transported downslope advectively by high energy events across low-gradient shallow marine environments as wave-enhanced sediment gravity flows (e.g., Macquaker et al., 2010b).

The fabric of freshly deposited mud that resulted from the gravitational settling of individual mud particles has a stable subparallel structure with comparatively little water; whereas, the fabric of aggregated mud deposited in the same way is open with a water content in excess of 90% by volume (Hedberg, 1936; Migniot, 1968; Terwindt and Breusers, 1972). The density and shear strength of aggregated mud deposits are therefore lower. However, if aggregated mud is transported as bedload to its final resting place, the deposits are denser, less porous, and contain less water than the deposits produced by gravitational settling of aggregated mud (J. Schieber, personal communication). The fabric of settling mud particles and of freshly deposited mud is difficult to observe directly, and burial of mud tends to obscure initial sedimentary fabrics (Allen, 1985, p. 144, fig. 8.5) unless there is early cementation of the sediment. Flocs are crushed and rearranged by the accumulating overburden (Migniot, 1968), while water loss and compactional processes normally destroy the pelletal character of fecal pellet mud (Pryor, 1975). For this reason, fine-grained sediments sampled from recent or fossil deposits and analyzed in the laboratory may show a textural composition quite different from the original or *in situ* material (e.g., de Boer, 1998).

2.2.2 Production, Destruction, and Dilution: The Many Roads to *Black* Shale

Production is the synthesis of organic compounds from nutrients, carbon dioxide, and water by terrestrial and aquatic organisms through photo- and chemosynthesis, that is, using (sun) light or the oxidation of inorganic molecules as an energy source, respectively. Primary organic production from photo- and/or chemosynthesis is the first and foremost prerequisite to generate an organic matter-rich sediment. In its broader sense, production also refers to the biomineralization processes by which aquatic organisms produce their skeletons. The relationship between organic productivity and biomineral productivity is typically nonlinear; a possible reason for this may be the effect of dissolution.

Organic matter in continental environments is terrigenous, that is, produced by land-dwelling organisms, whereas in marine sediments organic matter may be either of marine or terrestrial origin. On land, almost all primary production since the Devonian is by vascular plants. Land-derived organic matter, highly degraded and nitrogen poor, is brought into the ocean by rivers in dissolved and particulate forms. Most terrestrial particulate organic matter, for example, pollen, plant debris, and charcoal, is deposited in nearshore environments, whereas the dissolved component escapes removal and is carried out into the ocean. The bulk of dissolved organic carbon in seawater is marine. Land-derived dissolved organic matter entering the open ocean must therefore be extensively oxidized back to CO_2 (Emerson and Hedges, 1988; Hedges and Keil, 1995; Hedges et al., 1997). Marine organic matter is produced largely by phytoplankton, for example, cyanobacteria, diatoms, and dinoflagellates, in the photic zone. Productivity on the continental margin is favored by a combination of fluvial, eolian, and offshore nutrient supplies. Nutrients carried by rivers to the ocean are consumed quickly within and immediately off river mouths (Piper and Calvert, 2009). Nutrients supplied from the base of the thermocline by mixing and by upwelling are the main source of nutrients in highly productive areas of the ocean, and fuel about three-quarters of the new production in the ocean (Eppley and Peterson, 1979). Although coastal regions have higher rates of photosynthesis than the open ocean, most (ca. 80%) of the total photosynthetic production occurs in the open ocean (Emerson and Hedges, 1988), which accounts for about 90% of the total sea surface. However, export production, that is, the amount of organic matter that is not remineralized before it leaves the photic zone and sinks to the seafloor, is lower in the open ocean. At present, for example, most export production is concentrated along the relatively shallow continental margins (Laws et al., 2000; Walsh, 1991), where up to 90% of organic carbon burial takes place (Berner, 1982; Hedges and Keil, 1995).

Although primary productivity is important (e.g., Pedersen and Calvert, 1990), it is not sufficient by itself. In the modern Southern Ocean, for example, areas associated with oceanic divergence are characterized by high primary productivity; yet, sediments below these fertile surface waters are organic matter lean (Demaison, 1991). This is because the water column is well oxygenated, largely due to very low water temperatures, and because silica-secreting zoöplankton produce large amounts of skeletal debris, viz. frustules, which results in significant dilution of organic matter. To generate an organic matter-rich sediment, the destruction of organic matter must be minimized. Destruction refers to the remineralization of organic matter by organisms (mainly bacteria) and oxidation in the water column. These processes can continue at the sediment–water interface and to some depth within the sediment column. Destruction also includes the dissolution of skeletal material in the water column. Dissolution of calcareous skeletal material increases with water depth and with an increase in supply of organic matter (Emerson and Archer, 1990), which lowers the pH of sediment interstitial waters unless sulfate-reducing conditions in the sediment prevail (Morse and Mackenzie, 1990). Dissolution of siliceous skeletal material occurs throughout the water column, but is more intense in the warmer surface layers of the ocean and shortly after deposition (Berger, 1974). A minimization of the destruction of organic matter can be achieved by lowering dissolved oxygen content in the water column, by making the export path and/or transit times shorter, and/or by reducing sediment exposure time to bottom water after reaching the sediment–water interface.

Oxygen levels in seawater depend on how much oxygen seawater can hold and on oxygen supply and demand. Oxygen levels are lower in warm climates due to the reduced solubility of oxygen in warmer water. This is the case in a geographic sense, that is, sea surface water at lower latitudes contains less oxygen, and in a geologic sense, that is, seawater during hot/greenhouse intervals contained less oxygen than at present. Dysoxia, and—depending on the frequency, intensity, and depth of mixing—anoxia, is favored in basins whose physiography (e.g., oxbow lakes and silled marine basins) and/or water column thermohaline structure (e.g., lakes) result in the stagnation of (part of) its water column. Dysoxia develops in response to runoff of nutrient-rich water from rivers to lakes and oceans, and upwelling of nutrients and consequent enhanced surface productivity in lakes (overturning) and oceans. Oxygen depletion is more dynamic than commonly assumed and depends on the interaction between lake/ocean circulation, biological activity, and nutrient distribution (Meyer and Kump, 2008). Biochemical processes are ultimately responsible for the consumption of oxygen, but ocean circulation is responsible for the distribution of dysoxic and anoxic water masses in the ocean (Wyrtki, 1962). Oxygen depletion may be either local or regional, and it may be seasonal or permanent (e.g., Lake Tanganyika). It has been suggested that the preservation of organic matter in mid-Cretaceous marine sediments was favored by decreased oxygen supply to deep water as a consequence of sluggish ocean circulation (e.g., Bralower and Thierstein, 1984; Erbacher et al., 2001). In a stagnant ocean, the supply of nutrients to the photic zone would not be sufficient to sustain the elevated primary productivity required to support high oxygen demand in deep water (e.g., Hotinski et al., 2001). Whereas a sluggish ocean would result in a significantly decreased oxygen supply to deep water, that reduction would be balanced by a reduction in oxygen demand (Meyer and Kump, 2008). Other studies have suggested that a more vigorous circulation resulted in a more productive mid-Cretaceous ocean (Hay and Floegel, 2012; Southam et al., 1982; Topper et al., 2011; Trabucho-Alexandre et al., 2010; Wilson and Norris, 2001).

The Black Sea is often used as a model for ancient sluggish or stagnant oceans. However, evidence suggests that this enclosed basin is not properly described as stagnant. Radiocarbon dating indicates a mean residence time of 935 years for deep Black Sea water, whereas mass balance calculations indicate a shorter residence time of 475 years (Östlund, 1974). Brewer and Spencer (1974) calculated a present-day upward advective velocity of $0.5\,m\,a^{-1}$ in the interior of the Black Sea (in Degens and Ross, 1974). These results suggest that the rates of vertical exchange in the Black Sea are of the same order of magnitude as those in the modern open ocean, and that euxinia, which refers to the presence of free hydrogen sulfide in the water column, in the Black Sea represents a dynamic balance (Southam et al., 1982).

In the open ocean, the fraction of the organic matter produced in surface waters that reaches the seafloor is inversely proportional to water depth (Hedges and Keil, 1995; Müller and Suess, 1979; Suess, 1980). All other variables being equal, the preservation of organic matter is favored where the seafloor is relatively shallow, namely, on the continental shelf and upper slope and on the top and flanks of seamounts. Long transit times through mildly oxidizing water (e.g., ca. $3\,ml\,l^{-1}\,O_2$ in the deep modern North Pacific, Southam et al., 1982) and slow sedimentation rates (ca. $2\,m\,Myr^{-1}$) are sufficient to result in the deposition of organic matter lean, red/brown pelagic clay on the deep ocean floor. A significant part of the vertical flux of particulate organic matter from the photic zone is in the form of organomineralic aggregates. Because they are larger than their constituent mud particles, these aggregates settle much faster through the water column, and transit times to the seafloor are within weeks. The preservation of organic matter is thus greatly favored.

Dilution is a consequence of the mixing of siliciclastic, skeletal, and organic material, because the composition of a sediment is a zero-sum game; an increase in one component must be accompanied by a relative decrease in the others. The input of siliciclastic material, which is a key control in the composition of a shale, may be included in dilution. Up to a certain point, an increase in the input of siliciclastic and/or skeletal material, that is, an increase in sediment accumulation rates which leads to relatively rapid burial, favors the preservation of organic matter. Indeed, the preservation of organic matter, particularly in oxidizing environments, is favored by sedimentation processes that deliver large quantities of sediment to the seafloor, including metabolizable organic material, in a short period of time (e.g., Degens et al., 1986; Ghadeer and Macquaker, 2012; Macquaker et al., 2010a). Moreover, large fluxes of metabolizable organic matter favor processes of natural vulcanization, which lead to the creation of resistant geobiopolymers (Lallier-Vergès et al., 1997; Sinninghe Damsté et al., 1989). However, too much of any component will "mask" others, especially if they are present in low absolute amounts in the sediment, as is typically the case for organic matter. Dilution of organic matter by inorganic material, terrigenous and/or biogenous (skeletal), is an important control in the accumulation of organic matter in sediments (Bohacs et al., 2005; Tyson, 2001). High dilution rates can result in organic matter-lean sediments even under regions of high surface productivity. In deltaic settings, for example, organic carbon contents are feeble where elevated sedimentation rates of terrigenous sediment dilute the organic component of sediments (Dow, 1978).

Along continental margins, the calcite compensation depth (CCD) is raised due to higher primary productivity and consequent respiration of organic matter in sediments, which releases metabolic CO_2 and thus increases carbonate dissolution (Berger, 1974; Seibold and Berger, 1996). As a result, dilution of organic matter by calcareous skeletal debris is minimized. On the other hand, dilution can also be too low. The fraction of organic carbon that reaches the basin floor is a function of water depth and of bulk sedimentation rate (Müller and Suess, 1979), but more than 90% of the organic matter that does reach the seafloor is nonetheless remineralized (Emerson and Hedges, 1988). Where sedimentation rates are low, the preservation of organic matter is reduced because the sediments are kept within the mixed sediment layer for too long, where they are exposed to active microbial reworking and oxidants in pore waters, as well as erosion and transport (Bohacs et al., 2005, and references therein). In condensed sequences in the Mesozoic of Alabama, United States, for example, organic matter was not preserved probably due to low sedimentation rates (Mancini et al., 1993). In conclusion, there is not just a single combination of variables that will yield organic matter-rich sediments, but optimum organic enrichment occurs where production is maximized, destruction minimized, and dilution optimized (Bohacs et al., 2000; Tyson, 2001).

2.3 STRATIGRAPHIC DISTRIBUTION OF ORGANIC MATTER-RICH SHALES

Although shales are a ubiquitous component of the stratigraphic record, the distribution of black shales in the Phanerozoic is predominantly limited to six stratigraphic intervals (Fig. 2.2), which together represent about one-third of Phanerozoic time (e.g., Bois et al., 1982; Klemme and Ulmishek, 1991; North, 1979; Tissot, 1979). The petroleum source rocks in these

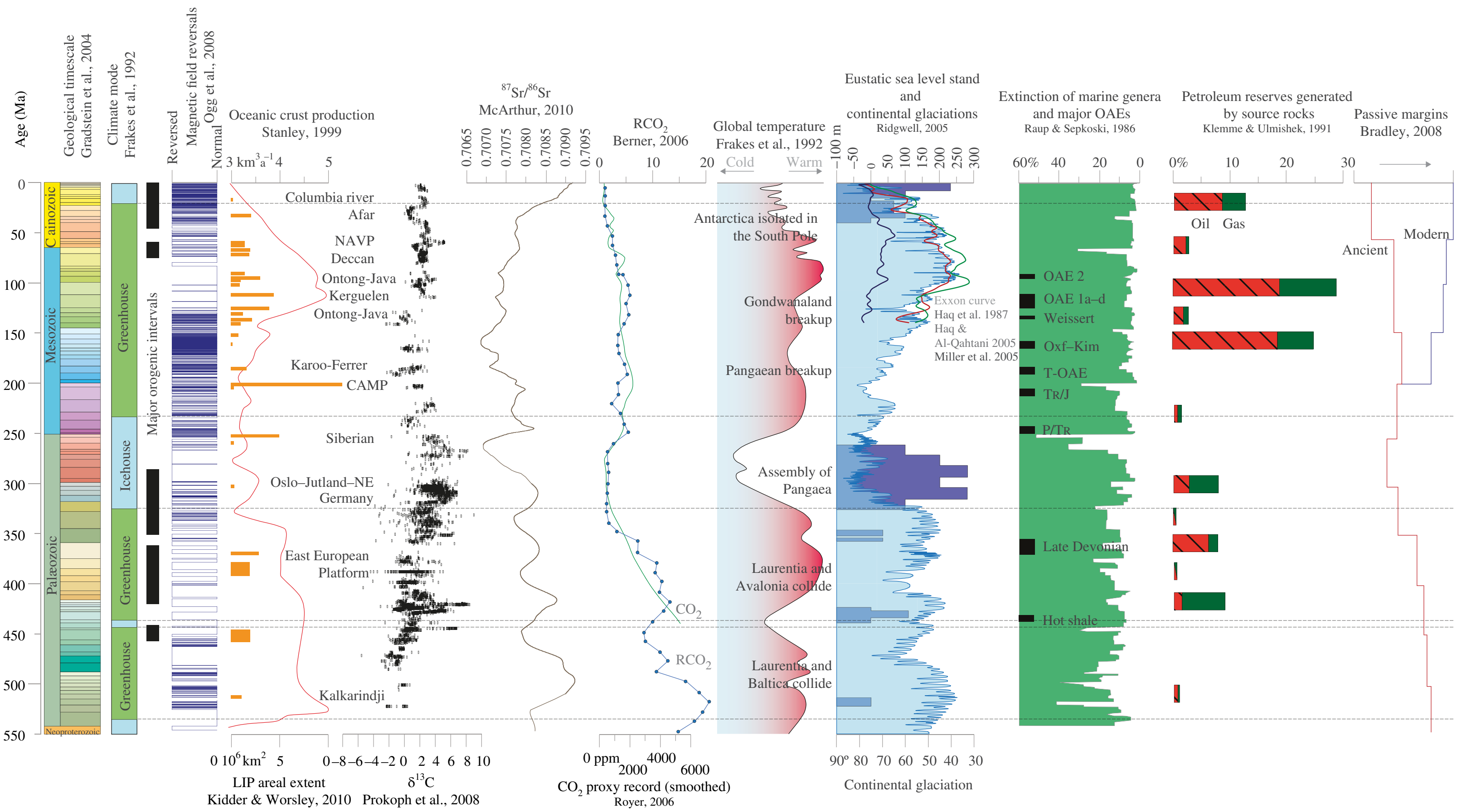

FIGURE 2.2 Phanerozoic patterns of various indicators of global change. From left to right: Phanerozoic geological timescale (Gradstein et al., 2004), climate mode (Frakes et al., 1992), major orogenic intervals, magnetic field reversals (Gradstein et al., 2004), oceanic crust production (Stanley, 1999), and large igneous province areal extent (Kidder and Worsley, 2010), carbon isotope curve (Prokoph et al., 2008), strontium isotope curve (McArthur, 2010), RCO_2 and CO_2 proxy record (Berner, 2006; Royer, 2006), global temperature, eustatic sea-level stand (Haq and Al-Qahtani, 2005; Haq et al., 1987; Miller et al., 2005), continental glaciations (Ridgwell, 2005), extinction of marine genera and major oceanic anoxic events (OAEs) (Raup and Sepkoski, 1986), petroleum reserves generated by source rocks (Klemme and Ulmishek, 1991), and passive margin extent (Bradley, 2008).

intervals have provided more than 90% of the world's known conventional hydrocarbon reserves (Klemme and Ulmishek, 1991; Tissot, 1979). Overmature oil-prone source rocks[5] deposited during these six stratigraphic intervals also function as reservoirs in the increasingly explored and exploited unconventional shale gas plays.

Correlations between geologic anomalies and black shale deposition (Condie, 2004; Kerr, 1998; Larson, 1991; Sheridan, 1987; Sinton and Duncan, 1997) may explain the stratigraphic clustering of black shales in specific stratigraphic intervals of the Phanerozoic (Klemme and Ulmishek, 1991; Tissot, 1979; Trabucho-Alexandre et al., 2012b). Phanerozoic intervals characterized by enhanced tectonic activity, namely, supercontinent breakup, ocean basin formation, and large igneous province emplacement, are associated with greenhouse climates, eustatic highstands, vigorous ocean circulation, and abundant nutrients in seawater (Fig. 2.2). Warm and humid greenhouse climates support abundant life, such as highly productive tropical rain forests on land, reef communities on the shelf, whose area is greatly expanded during eustatic highstands, and abundant plankton in the ocean. Abundant nutrients in seawater are a product of intense seafloor spreading activity and large igneous province emplacement, increased circulation of deep, nutrient-rich water, and an enhanced hydrologic cycle (e.g., Larson, 1991; Sinton and Duncan, 1997; Trabucho-Alexandre et al., 2010).

Tectonic processes lead to changes in the geography of the earth and to the evolution of depositional environments through time (Chamberlin, 1909; Scotese, 2004; Wilson, 1968). The geographic distribution of Phanerozoic black shales is largely independent of latitude but instead related to the distribution of continental masses (Irving et al., 1974; Klemme and Ulmishek, 1991). The distribution of continents (and ocean basins) controls the position of landmasses relative to climate belts, the opening and closure of gateways (i.e., basin connectivity), and hence ocean circulation. Ocean circulation affects seawater temperature, oxygenation, and nutrient content. The preservation of organic matter on the seafloor of marine basins appears to be aided by a latitudinal position of continents that obstructs meridional ocean circulation. This position, typical of the Mesozoic, inhibits the formation and spread of cold, oxygenated, high-latitude deep water which promotes the destruction of organic matter in deeper water. Global climate also exerts an important control in this regard, because bottom water cannot be colder than the coldest surface water; bottom water during greenhouse climates will therefore contain lower initial oxygen content than present-day bottom water (Berger, 1974).

It has long been recognized that tectonic processes have the potential to affect global climate (Chamberlin, 1897), over both extremely short (e.g., Storey et al., 2007) and long (e.g., Raymo and Ruddiman, 1992) timescales. Climate, which is also forced by subtle cyclic variations in the earth's axis and orbit (de Boer and Smith, 1994), plays a fundamental role in the evolution of sedimentary environments on earth. Seafloor spreading and mountain building, both driven by tectonic processes, control earth's climate over long timescales. These two processes lead to changes in CO_2 input by volcanism and dissociation of subducted limestones, and to changes in CO_2 removal by weathering of silicates and organic matter burial (Berner, 1991). Volcanism related to plate tectonic processes can also drive rapid climate change both directly due to faster seafloor spreading rates (Berner et al., 1983), increasing length of oceanic ridges, and extrusion of large igneous provinces (e.g., Kerr, 1998; Sinton and Duncan, 1997), and indirectly due to greenhouse gas generation as a consequence of increased seawater temperatures (e.g., Dickens et al., 1995; Hesselbo et al., 2000) and contact metamorphism (e.g., McElwain et al., 2005; Storey et al., 2007).

Relative sea level, which depends both on global and local tectonics and on climate, controls the size and distribution of paralic and shallow marine environments, where most ancient black shales were deposited (Arthur and Sageman, 2005; Hedges and Keil, 1995; Laws et al., 2000; Walsh, 1991; Wignall, 1991). It is therefore unsurprising that intervals of relatively widespread black shale deposition should coincide with eustatic highstands. High sea levels favor the deposition of black shales (Duval et al., 1998) by expanding sunlit shallow marine environments where primary productivity is high and export paths short. Moreover, during transgressions and early highstands, coarser grained siliciclastic material is trapped in nearshore environments, such as, estuaries, reducing excessive dilution of organic matter on the shelf. The composition, including organic matter type and content, and texture of marine sediments are thus a function of depositional environment and of allogenic forcing mechanisms acting on them.

2.4 GEOGRAPHIC DISTRIBUTION OF ORGANIC MATTER-RICH SHALES

2.4.1 Background

In the early scientific literature, the main debate concerning the origin of black shales focused on whether they had been deposited in shallow or deep water (Cluff, 1981). Hard (1931), for example, interpreted the Devonian black shales of New York as having been deposited in shallow water under toxic and saline conditions, whereas Clarke (1904)

[5] Oil-prone kerogens have higher capacities for hydrocarbon generation per unit organic carbon than gas-prone kerogens. Although gas-prone source rocks generate large amounts of gas at high maturity, late stage gas generation and cracking of residual oil/bitumen in oil-prone source rocks can account for more gas generation than gas-prone source rocks (Dembicki, 2013).

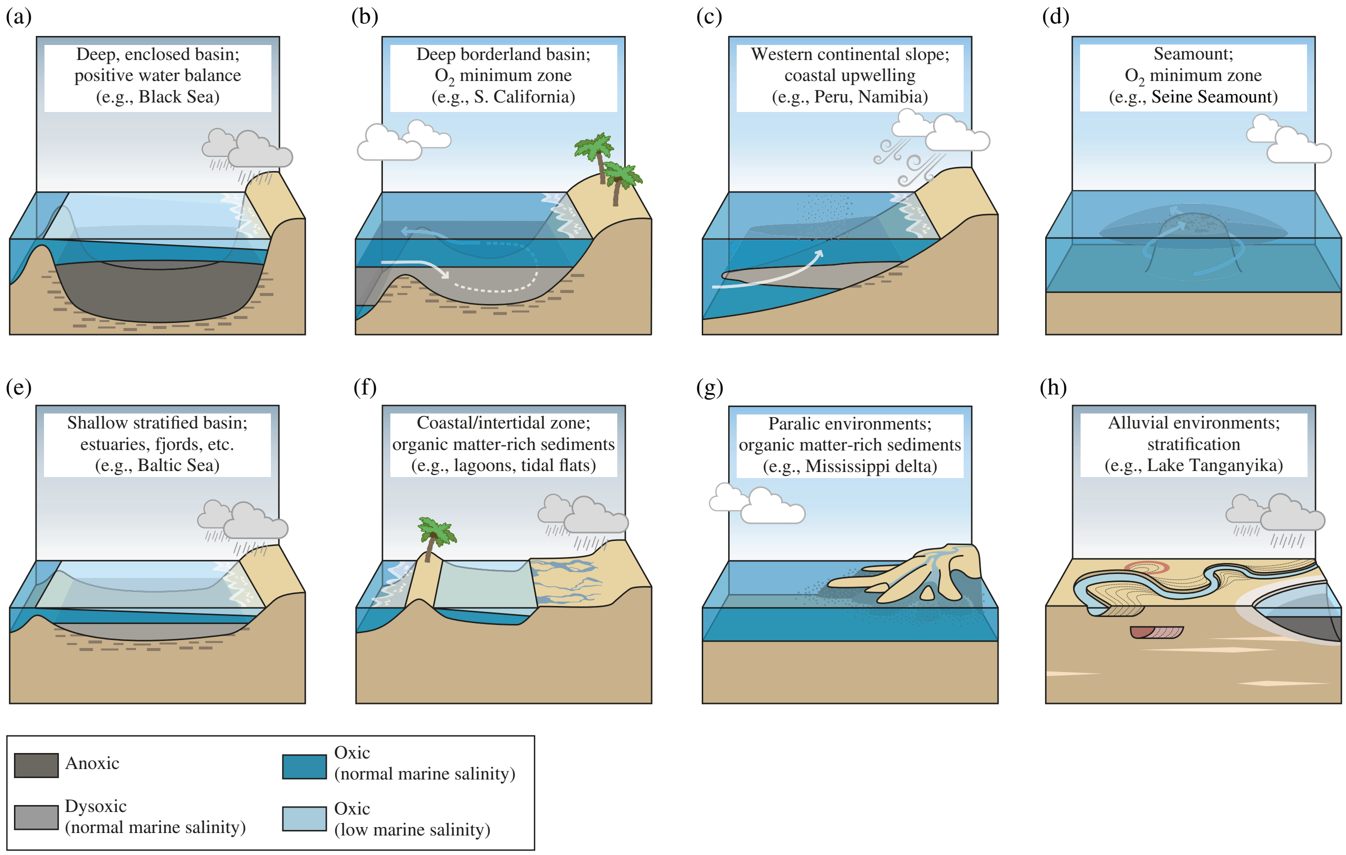

FIGURE 2.3 Summary of the environments of accumulation of organic matter showing an idealized basin physiography, water mass distribution and properties, and prevalent climate (rain cloud indicates positive water balance, cloud streamers indicate offshore winds). This figure is an adaptation and expansion of figure 1 in Arthur and Sageman (1994, p. 507).

favored a deepwater environment similar to the bottom of the modern Black Sea. Pettijohn (1975, p. 284) summarized this debate as follows: "[t]he origin of black shales has been much debated. *Certainly they were deposited under anaerobic conditions.* [emphasis added] How such conditions were achieved is less certain. […] Some writers contend that black shales were deep-marine (geosynclinal) sediments; others have postulated comparatively shallow waters, either lagoonal or marine."

It is obvious from Pettijohn's remark that reducing environments, whether shallow or deep, were considered the key control behind the deposition of black, organic matter-rich mud. The idea that black shales are the product of sedimentation in reducing environments was reinforced early on by the study of black muds in the Black Sea (Pompeckj, 1901; Schuchert, 1915) and in Norwegian fjords (Strøm, 1939). The Black Sea (Fig. 2.3a) has been used extensively as a model for the deposition of ancient epicontinental and open ocean black shales. However, the presence of a halocline in the Holocene Black Sea and the fact that it is significantly deeper (ca. 2000 m) than ancient epicontinental seas (ca. 100 m), and therefore characterized by a different depth-to-width ratio, preclude its use as an analog for shelf or open ocean sedimentation in the geologic record. Tyson (2005, p. 29) summed up this idea by stating that the "Black Sea is […] a freak of paleogeography and has very specific circumstances that are unlikely to be common in the geological record." Although some authors argued for an open marine origin for black shales, the view that black shales were deposited in restricted basins conducive to strongly reducing conditions, and for which the Black Sea may be a good analog, was largely prevalent. Twenhofel (1939), for example, argued for an open marine origin for ancient black shales in general, but favored the Black Sea as an analog for the Paleozoic shales of northwest Europe and the Appalachian basins of North America. Fleming and Revelle (1939), who discussed the role of oceanographic processes on dissolved oxygen distribution in the water column, also gave the Black Sea and the borderland basins of Southern California as examples of modern environments of black mud deposition (Fig. 2.3a and b), and thus emphasized the role of sill depth in controlling the rate of renewal of bottom water and oxygen replenishment.

While early authors placed great emphasis on the role of anoxia, some noted the importance of primary productivity in generating organic matter-rich sediments. Goldman

(1924), for example, suggested that the rate of supply of organic matter was important in oxygenated settings. Trask (1932) analyzed a very large amount of samples and concluded that upwelling zones were favorable settings for the deposition of organic matter-rich sediments. Brongersma-Sanders (1971) also discussed in detail the effects of upwelling on sediment composition. Importantly, Brongersma-Sanders noted that upwelling is a countercurrent system that creates a nutrient trap. This trap leads to high fertility of a basin or coast and, where the subsurface water ascends toward the photic zone, to high productivity. Parrish (1987) predicted the geographic distribution of ancient upwelling zones and compared that distribution with the distribution of organic matter-rich rocks. She concluded that as many as half the world's black shales may have been deposited in upwelling zones.

In addition to the debate concerning the physiography of ancient environments of black mud accumulation, which is probably one of the longest running controversies in geology, another intense debate arose, this time concerned whether unusually high primary productivity in the photic zone or unusual chemical conditions in the water column, namely, anoxia, provide the first-order control on the accumulation of organic matter-rich sediments in the ocean (Demaison, 1991; Pedersen and Calvert, 1990). As a result of this debate, models of black shale deposition are traditionally divided into two end-member types: one of enhanced supply and the other of enhanced preservation of organic matter. More recently, however, some authors recognized the interdependent roles of primary productivity, microbial metabolism, and sedimentation rates (e.g., Bohacs et al., 2000, 2005; Sageman et al., 2003; Tyson, 2005).

Although Van Waterschoot van der Gracht (1931) proposed a link between changes in ocean circulation on a global scale and the deposition of black shales (cf. Chamberlin, 1906), most early authors thought of black shales as the product of local processes. Indeed, it was not until Cretaceous black shales were recovered in a number of Deep Sea Drilling Project (DSDP) sites in the 1970s that it became widely recognized that basin physiography was not a sufficient explanation for some ancient black shale successions. The discovery of widespread organic matter-rich horizons in the deep sea represented a breakup with the notion that ancient black shales were the product of local conditions in marginal, restricted basins. Bernoulli (1972) recognized the similarities between Tethyan Cretaceous sediments exposed on land in the Mediterranean region and sediments recovered by drilling in the North Atlantic, and suggested that black shale horizons now exposed on land and horizons recovered by drilling are coeval. The discovery of Cretaceous black shales of the same age in the Pacific greatly extended the geographic range of those horizons, and led to the suggestion that the deposition of black shales during the Early Cretaceous might have been a worldwide oceanographic phenomenon (Jackson and Schlanger, 1976, p. 925). As a result, Schlanger and Jenkyns (1976) proposed that the occurrence of black shale horizons globally was due to the expansion of the oxygen minimum layer in the ocean as a consequence of the Late Cretaceous transgression and a reduced supply of oxygen to deep water due to an equable climate (Fig. 2.4), the so-called oceanic anoxic events (OAEs). The term OAE is unfortunate because it implies ocean-wide anoxia, although it has been noted that this is not the spirit of the term (Arthur et al., 1990). Indeed, the original concept (Fig. 2.4) included several environments of black shale deposition. At first, the idea that the deep sea could become anoxic was rejected by geochemists

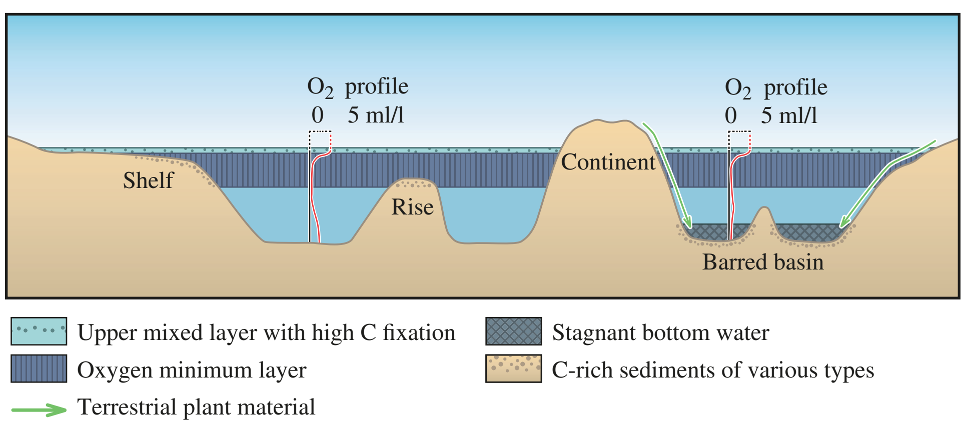

FIGURE 2.4 Ocean stratification during an oceanic anoxic event as proposed by Schlanger and Jenkyns in 1976 (their figure 2). The oxygen minimum layer is expanded and intensified. The shoaling of the upper boundary of the oxygen minimum layer translates into a geographic expansion of shallow seafloor impinged on by the oxygen minimum. The sinking of its lower boundary results in the seafloor at the top and flanks of oceanic rises being impinged by the oxygen minimum layer. The concept included a barred basin setting in which abundant terrestrial plant debris accumulated "in their early opening stages by rivers and turbidity currents."

(Broecker, 1969). However, the presence of "widespread" organic matter-rich horizons in the deep sea is sometimes invoked as evidence for episodes of ocean-wide stagnation and/or anoxia, and much modeling effort has been put into creating increasingly complex models that attempt to recreate global conditions that explain all occurrences of organic matter-rich sediments in ancient oceans. While certain stratigraphic intervals are characterized by frequent and/or widespread black shale horizons, the correlation of individual layers is almost always questionable and the petrologic characteristics of the black shales varied. This suggests that multiple processes are behind the deposition of not exactly coeval organic matter-rich sediments during OAEs (Hay, 1988; Trabucho-Alexandre et al., 2011); black shales are the product of both local and global conditions (cf. Trabucho-Alexandre, 2011). The danger in creating "fully detailed models of complex systems is ending up with two things you don't understand—the system you started with, and your model of it" (Paola and Leeder, 2011).

2.4.2 Controls on the Geographic Distribution of Black Shales

The petrologic characteristics and widespread geographic distribution of black shales suggest that processes rather than environments control their accumulation.[6] For this reason, a discussion concerning their geographic distribution should focus on the processes that result in the deposition of organic matter-rich mud in each environment. In particular, we are interested in linking the petrologic characteristics of shales, that is, their varying composition and texture, with depositional process and environment. This is important because regional changes in shale composition and texture due to paleoöceanographic and paleogeographic controls affect, among other things, the economic potential of a rock. Changes in organic matter content *and* in its nature affect the hydrocarbon generation potential of a shale, while changes in the relative amounts of siliciclastic mud and skeletal biogenous material, calcareous and siliceous, affect the mechanical properties of a rock and consequently its behavior when subjected to, for example, hydraulic stress. The nature of the phases that compose the rock is also important. Carbonate, for example, may be present as porous biogenous particles or as porosity-filling diagenetic crystals (e.g., dolomite). Likewise, silica may be present as detrital or authigenic quartz or as porous biogenous silica. The nature of the phases present in a rock depends on the processes and environments behind its formation.

[6]An environment has been defined as "the complex of physical, chemical, and biological conditions under which a sediment accumulates," (Krumbein and Sloss, 1963, p. 234) and as "a spatial unit in which external physical, chemical, and biological conditions and influences affecting the development of a sediment are sufficiently constant to form a characteristic deposit" (Shepard and Moore, 1955, p. 1488).

In continental environments, the composition of shales is largely dominated by terrigenous material. In terms of composition and texture, shales deposited in continental environments are typically shales *sensu stricto*, that is, laminated and/or fissile organic matter-rich *siliciclastic* mudstones, and their organic matter is terrigenous. In the marine environment, however, sediments only rarely come from a single source (Fig. 2.1). Most marine sediments are a mixture of biogenous and terrigenous particles of various grain sizes, with an additional hydrogenous (authigenic) and/or (very minor) cosmogenous component. Biogenous debris, which may be either calcareous or siliceous, may form a significant proportion, if not the majority, of the inorganic fraction of a shale. The composition of marine shales follows a general pattern that is related to basin physiography, namely, water depth, and ocean circulation (Fig. 2.5).

The relationship between depositional setting and the texture of shales is more complicated. For example, although we often think that sediment grain size is a function of distance to shore, this is typically not the case, and there are many examples of fine-grained shores and relatively coarse-grained deepwater deposits (e.g., Rine and Ginsburg, 1985; Stow, 1985b). In neritic environments below effective wave base, which are most affected by variations in terrigenous input and in relative sea level, the variation in seafloor texture is the most unpredictable, because a significant fraction of the seafloor is covered in either relict or palimpsest sediment (Emery, 1968a; Shepard, 1932). The texture of shales is largely independent of environment and therefore more difficult to predict in terms of its geographic distribution than composition.

The sediments of continental margins are different both in quantity and quality from those on deeper seafloor. Almost 90% of the total volume of all marine sediment is associated with continental margins, that is, shelves, slopes, and rises, which constitute only about 20% of the ocean's area. Neritic sediments, that is, those deposited on the continental shelf, consist primarily of terrigenous material. Terrigenous material is always ultimately derived from the continent, and it is brought to the ocean by rivers, coastal erosion, and, to a lesser extent, wind. The immediate source of the terrigenous component of a marine sediment, however, is often within the marine environment (Meade, 1972). Most terrigenous sediment brought into the ocean by rivers is deposited where rivers meet the coastal ocean (e.g., Walsh and Nittrouer, 2009). Sediment that escapes paralic sediment traps and sediment from coastal erosion tend to travel along the shore within a few kilometers of the coast rather than moving seaward (e.g., Manheim et al., 1970; McCave, 1972). Sediment resuspended from the shelf bottom and sediment transported laterally from offshore constitute the main source of suspended matter on the shelf away from the mouths of large rivers. Many ancient black shales were deposited on broad continental shelves at times when sea levels were much

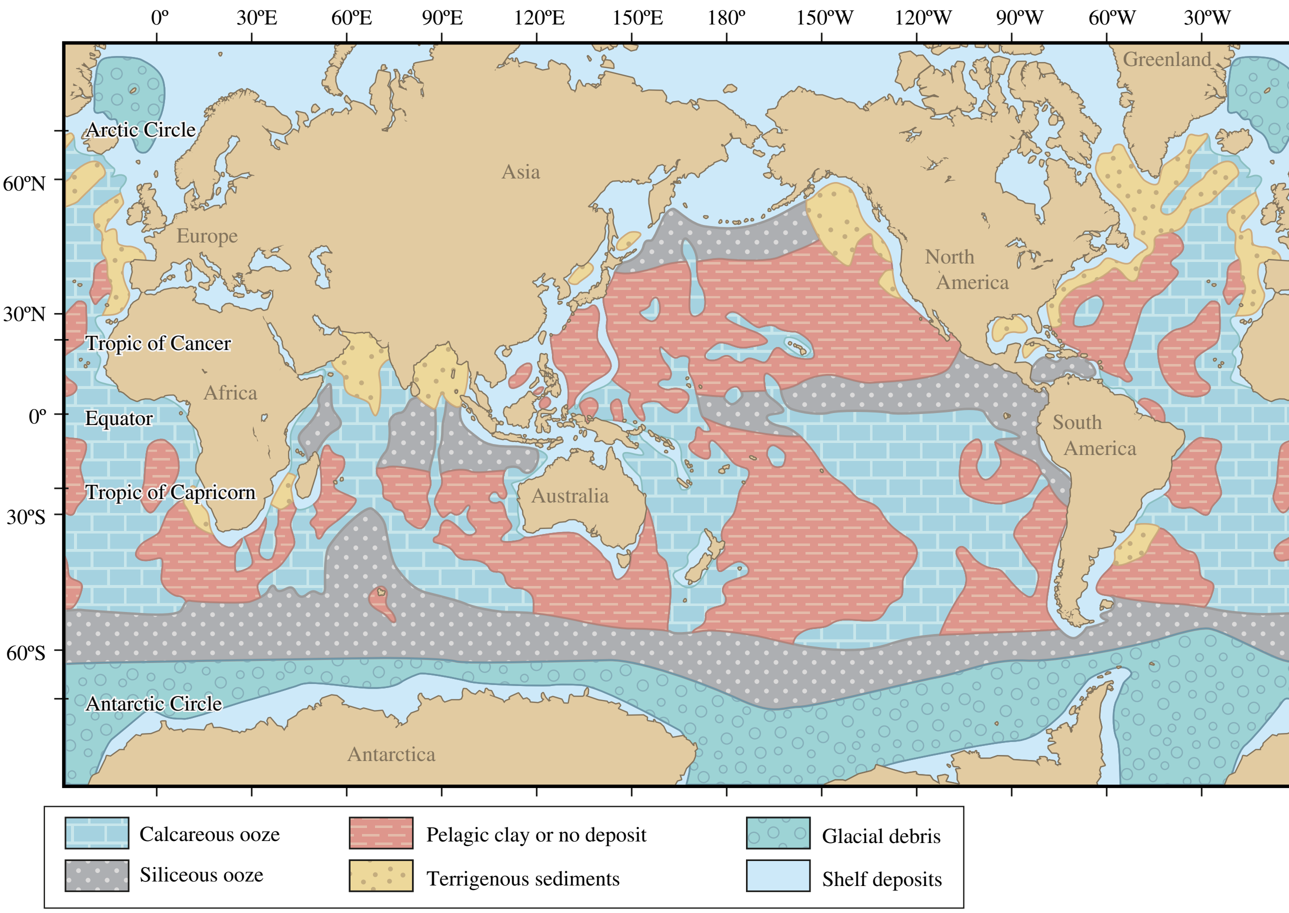

FIGURE 2.5 The general pattern of sediment cover of the seafloor. This pattern has been known more or less in its present state since the work of Murray and Renard (1891) following the voyage of H.M.S. *Challenger*. The main sediment facies are pelagic clay and calcareous ooze. Pelagic clay, also known as red clay, is typical for the deep seafloor, whereas the calcareous facies outlines oceanic rises and platforms. Biosiliceous deposits, characteristic for the seafloor beneath areas of high fertility, are superimposed on the previously mentioned topographically controlled dichotomy. The sediment that results in pelagic clay deposits, which is mostly eolian and cosmogenous dust associated with hydrogenous minerals, is present everywhere in the ocean, but it is masked whenever another component is present, because its mass accumulation rates are so low. Terrigenous sediment is present along the continental margins. In front of large rivers and submarine canyons, terrigenous sediment can penetrate the ocean basin to a considerable distance from the shelf. Even though this map shows sharp boundaries between well-defined facies, the seafloor is actually covered by a complex pattern of overlapping mixtures of the various components of fine-grained marine sediments (Fig. 2.1).

higher than today (Fig. 2.2). Terrigenous sediment is efficiently trapped in nearshore environments during highstands, and thus large areas of those shelves must have been starved of new terrigenous sediment input; their terrigenous mud was probably largely derived from longshore and relict offshore sources. Nevertheless, unlike black shales recovered in the deep sea by ocean drilling, which are never more than tens of centimeters in thickness, epicontinental black shales are usually meters to tens of meters thick, for example, the Devonian Chattanooga Shale (ca. 9 m in central Tennessee) and the Pliensbachian–Toarcian shales of northwest Europe (>100 m in northeast England). The thickness of these successions does not necessarily equate to high terrigenous input, because the successions often represent very long periods of time represented in the rock record by gaps and by mud beds that were deposited relatively quickly (e.g., Baird, 1976; Macquaker and Howell, 1999; Schieber, 1994, 2003; Trabucho-Alexandre, 2014). The gaps reflect periods during which no sediment accumulated, either because there was no sediment to accumulate, or because sediment was being removed from one area of the shelf to be deposited elsewhere on the shelf or in deeper water.

In addition to terrigenous material, neritic sediments almost always contain biogenous material (Fig. 2.1), which is a product of high fertility of surface water along continental margins. This is due to a high position or breakdown of the thermocline, which normally functions as a barrier to nutrient transport between deep and shallow, sunlit water. Upward mixing of nutrient-rich water containing dissolved silica leads to high productivity in the photic zone and to a high proportion of silica-secreting plankton in the upwelling biota. The production of siliceous skeletal material is maximal in coastal regions, where productivities can exceed by a factor of 10 the values in the subtropical gyres (Berger, 1974). These oceanographic conditions are also favorable for the deposition of organic matter and the intensification of the oxygen minimum layer, which may impinge on the seafloor and enhance the preservation of hydrogen-rich organic matter-rich sediments (Fig. 2.4). It is important to note here that anoxia is not a requirement for the preservation of organic matter in marine sediments; rather, under such conditions, more hydrogen is associated with carbon in the organic matter (Demaison, 1991; Pedersen and Calvert, 1990), which means that the shales thus produced have an enhanced hydrocarbon-generating potential. On the other hand, these conditions are adverse for the preservation of calcite, which minimizes the importance of carbonate as a diluent in high fertility settings. Dilution in such settings depends on the proximity of terrigenous sediment sources and pathways, and on biogenous silica input and dissolution.

Oceanic sediments, that is, those deposited beyond the shelf break, on the continental margin generally consist of an increasing proportion of biogenous material away from land due to decreasing dilution by siliciclastic material, which is mostly trapped nearshore. Indeed, about half of the deep seafloor area is covered by oozes, that is, by planktonic debris. The general outlines of sediment distribution on the seafloor are relatively simple. The main facies boundary in the ocean is the CCD, that is, the boundary between calcareous and noncalcareous sediments. Calcareous facies characterize shallower

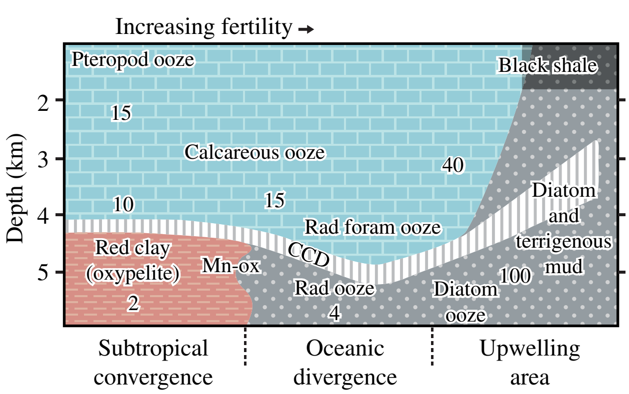

FIGURE 2.6 Distribution of major facies in a depth–fertility frame based on sediment patterns in the Eastern Central Pacific (Berger, 1974). Numbers are typical sedimentation rates in m Ma^{-1}. The CCD is the main facies boundary in deep-sea deposits. The composition of oozes varies according to water depth, fertility, and latitude, and depends on whether surface ocean currents have a tropical or polar origin. Black shales, or sapropelites, according to other authors, occur in high fertility settings on the relatively shallow seafloor of continental margins (shelf and upper slope). Other black shale occurrences are related to oceanic topographic highs (viz. seamounts, rises, etc.) and to sediment gravity flows transporting fine-grained material toward deeper water.

oceanic environments and submarine highs, whereas the "red clay" facies is typical for the deep ocean (Fig. 2.5). Red clays, derived mainly from eolian, volcanic, and cosmic sources accumulate by default in distal, barren regions of the seafloor below the CCD. Siliceous ooze accumulates under surface waters of high fertility, that is, along the margins of continents, along a periequatorial belt, and along the polar front regions (Fig. 2.5). The composition of marine sediments is normally a mixture of these components (Fig. 2.1). The main controls on sediment composition on the seafloor are thus distance to shore, water depth, and fertility of surface water (Fig. 2.6).

As mentioned before, the flux of biogenous sediment through the water column is mainly determined by two variables: productivity and destruction. Together with processes that redistribute sediment on the seafloor, these two variables also control the nature and distribution of sediments on the seafloor away from point sources of terrigenous sediment. The destruction of planktonic organic matter by bacterial oxidation during its transit through the water column dominates at depths of 300–1500 m. The supply of organic matter depresses oxygen content due to decay in deep water and on the seafloor and an oxygen minimum layer develops. The position of the oxygen minimum layer in the water column depends on ocean circulation (Wyrtki, 1962). The oxygen minimum layer is further characterized by a maximum in CO_2 and nutrients. Upwelling of this water leads to high primary productivity in surface waters and, therefore, to an abundant supply of biogenous sediment to the seafloor, namely, siliceous skeletal debris and organic matter. The oxygen minimum below upwelling zones is also more intense. If the rates of organic matter supply are sufficiently high and oxygen levels sufficiently low, the preservation of organic matter in the sediment is favored. Upwelling occurs at divergent oceanic fronts, over submarine topographic highs, and adjacent to continental margins, particularly on the western sides of continental masses. The distribution of ancient open marine black shales has been shown to correspond closely to the distribution of predicted upwelling zones (Parrish, 1982, 1987; Parrish and Curtis, 1982), and the deposition of black shales on the pericontinental shelves of the North Atlantic during OAEs has also been shown to be related to upwelling of nutrient-rich water (e.g., Trabucho-Alexandre et al., 2010).

Nutrient-rich surface waters have sufficient silica available to support the production of siliceous skeletal material. Siliceous ooze is an often forgotten component of marine fine-grained sedimentary rocks, and biogenous silica is typically not differentiated but grouped with clastic silica (e.g., quartz and feldspar) in ternary diagrams reflecting shale composition (e.g., Boak, 2012; Gamero-Diaz et al., 2013; Passey et al., 2010). Because silica-secreting plankton tends to proliferate in settings conducive to high organic productivity, organic matter-rich sediments are often siliceous (Hay, 1988). Many Mesozoic black shales that occur around the former Tethys and North Atlantic Oceans and on Indo-Pacific seamounts that occupied a periequatorial position at the time of deposition are actually black cherts. Black, organic matter-rich cherts are not always laminated.

Most of the skeletal debris produced by planktonic organisms never reaches the seafloor, and most of the debris that does reach the seafloor is nonetheless dissolved. This is particularly the case for siliceous skeletal material, because seawater is undersaturated with respect to biogenous silica at all water depths. Silica corrosion is greatest in surface waters due to elevated temperature, whereas carbonate dissolution is greatest at depth (Berger, 1974). There is a negative correlation between silica and carbonate distribution patterns on the seafloor (Fig. 2.5), which has been attributed to opposing chemical requirements for preservation (Correns, 1939): increasing productivity leads to decreasing preservation of calcite and to increasing accumulation of silica.

Seawater is also undersaturated with respect to all forms of calcium carbonate. At a critical level of undersaturation, dissolution rates of calcium carbonate increase rapidly and, below the CCD, which is the level at which the rate of supply of carbonate is balanced by its rate of dissolution, calcium carbonate does not accumulate on the seafloor. High fertility along the equator in the Pacific leads to a depression of the CCD by some 500 m (Seibold and Berger, 1996). Increased fertility leads to an increased supply of calcareous skeletal debris to the seafloor in excess of the increased supply of organic matter, because while the calcareous debris transits to the seafloor, organic matter tends to be destroyed on its way down. Along continental margins, however, high productivity raises the CCD (Seibold and Berger, 1996). In fertile areas along continental margins, the high supply of organic matter to the relatively shallow seafloor leads to increased benthic activity and to the development of much CO_2 in sediment pore waters, which produces carbonic acid. For this reason, carbonate debris is dissolved even at depths of a few hundred meters on continental slopes, and pericontinental black shales tend to contain little carbonate.

In the ocean, most biogenous material is produced in the top layers of the water column and arrives at the seafloor as a rain of particles. These particles are mostly aggregates, and a large fraction of these consists of fecal pellets of various sizes and in various stages of disintegration. Aggregates sink faster through the water column than their constituent particles, which would take years to settle to the average depth of the seafloor. Because all biogenous particles are subject to dissolution and/or remineralization in the water column, if it were not for the aggregation mechanism, most would never reach the seafloor. Despite this mechanism, the proportion of primary production that leaves the photic zone (export production) is small. Along the continental margin, higher export factors and shorter distances to the seafloor enhance the burial of organic matter.

Sediment trap studies indicate that for every 100 gC that is produced in the sunlit layer of the ocean, about 30 gC reach the seafloor on the shelf and upper slope, but only 1 gC reaches the deep seafloor (Berger et al., 1989). Most of the sinking material is oxidized and remineralized. Deep-sea sediments have low concentrations (C_{org} < 0.25%) of organic matter. Below the equator, the concentrations increase slightly, because upwelling along the equator results in a greater supply of organic matter to the seafloor. The highest concentrations of organic matter, however, are linked to coastal upwelling along continental margins (Fig. 2.6). The large supply of organic matter along the continental margin, as well as the physiography of the basin, generates an oxygen minimum zone as a consequence of high oxygen demand and, in the case of restricted basins, low oxygen replenishment (Fig. 2.3), and this may result in anoxic conditions on the seafloor. Under such conditions, the preservation of organic matter is enhanced because anaerobic bacteria are less efficient in destroying organic matter.

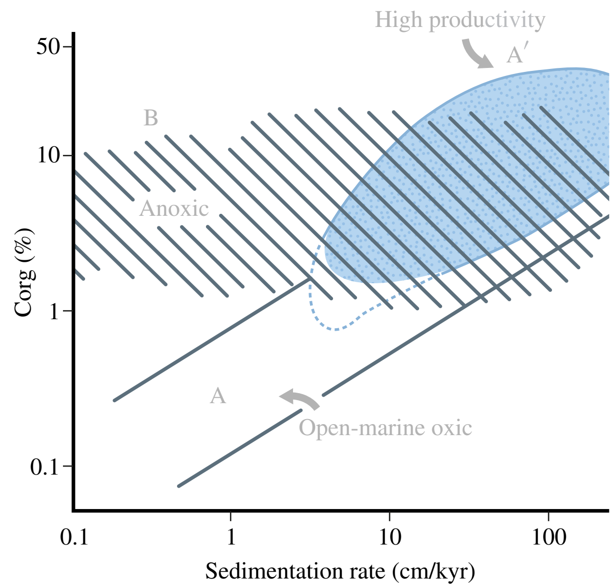

FIGURE 2.7 Correlation between marine organic carbon and sedimentation rates. The three fields, A, A′, and B are based on data derived from Neogene and Quaternary sediments deposited in open ocean environments (A), upwelling zones (A′), and anoxic environments (Black Sea and Mediterranean sapropels and modern Black Sea sediments). The stippled area in field A′ indicates coastal upwelling and the open area at the lower end of the field indicates equatorial upwelling. Based on figures 2 and 3 in Stein (1986).

The relationship between organic matter content and sedimentation rates in oxic and anoxic Neogene marine sediments gives insight into the processes that control the organic carbon content of marine sediments (Fig. 2.7). There is a lack of correlation between sedimentation rate and C_{org} in anoxic conditions, and a good correlation in oxic conditions (Stein, 1990). In the case of anoxic sediments, if there is sufficient input of organic matter, the organic matter is preserved even when sedimentation rates are low. In the case of oxic sediments, relatively rapid burial is required to preserve a significant portion of the organic matter delivered to the seafloor. Rapid burial removes the organic matter from the oxygen-rich sediment–water interface, thereby enhancing preservation. This mechanism appears to be particularly important for deep-sea black shales. Sediment gravity flows triggered by tectonic activity along the continental shelf, storms, and destabilization of organic matter-rich sediment as a consequence of gas generation in pore water transport large amounts of sediment toward deeper water. Sediment gravity flows are probably the most important mechanism for moving large quantities of mud to distal parts of deep basins. The quick burial of remobilized shallower water organic matter-rich sediment enhances the preservation of the organic matter in fine-grained turbidites.

Carbonate is also often preserved in fine-grained turbidites despite having been deposited below the CCD (Stow, 1985a; Trabucho-Alexandre et al., 2011). At the present time, organic matter-rich sediments are not accumulating in the central parts of major ocean basins. In the geologic past, however, this did occur. Although part of the sediment is of biogenic derivation and settled vertically through the water column, much material is redeposited (e.g., Degens et al., 1986; Stow et al., 2001; Trabucho-Alexandre et al., 2011; van Andel et al., 1977).

2.5 ORGANIC MATTER-RICH SHALE DEPOSITIONAL ENVIRONMENTS

Mud is everywhere, and life ubiquitous. Therefore, it is not surprising that black shales may be deposited in a wide range of sedimentary environments from the bottom of lakes to the abyssal plains of the ocean. The interpretation of ancient environments of black shale deposition has been influenced by studies of modern environments where organic matter-rich sediments are currently accumulating (Fig. 2.3 and Table 2.1). However, most ancient black shales appear to have been deposited in shallow marine epicontinental environments for which we have no modern analogs (cf. Arthur and Sageman, 1994).

2.5.1 Continental Depositional Environments

Organic matter-rich rocks deposited in continental environments account for more than 20% of current worldwide hydrocarbon production (Bohacs et al., 2000; Potter et al., 2005). Following the colonization of land by plants in the Devonian, organic matter becomes an important component in continental sediments. Mud in fluvial sequences mainly accumulates by vertical accretion as overbank deposits, which are produced when mud is deposited during floods in ephemeral ponds marginal to the main channel, and in oxbow lakes, which are persistent lakes formed by abandonment of meander loops.

Mud deposited in lakes often has organic matter contents that are significantly above the average for sediments in general. This organic matter comprises reworked terrestrial vegetation, from riparian environments, marginal macrophyte swamps, and phytoplankton (Talbot and Allen, 1996). Large lakes can contain a range of depositional environments including deltaic, coastal, and deepwater environments. Lakes are extremely sensitive to changes in climate and consequent changes in accommodation space (Bohacs, 1998). The ratio of accommodation space creation, that is, basin subsidence, to sediment/water input, which is controlled by climate, is the fundamental control on the stratigraphy of lakes (Carroll and Bohacs, 1999). Accommodation space determines water depth, which is a factor behind oxygen deficiency, depositional environments, and facies; climate determines the biota, temperature, and salinity of a lake (Potter et al., 2005).

The processes that favor enrichment in organic matter of lacustrine sediments depend on several factors that are ultimately linked to the type of lake in which the sediments are deposited (cf. Bohacs et al., 2000). A key factor is the availability of nutrients, which support primary production. Nutrients are brought in by land surface flow from the lake catchment area and by eolian transport. In many lakes, seasonal overturn recycles nutrients into surface waters. Permanently stratified lakes require an external nutrient source to support primary productivity. In alkaline lakes, such as lakes in tropical Africa, productivity is enhanced due to the abundance of carbonate ions that are available for incorporation by primary producers in addition to atmospheric CO_2 (Kelts, 1988).

The oxygenation of lake waters occurs primarily via exchange with the atmosphere, although some oxygen is a byproduct of photosynthesis. When a lake is thermally or chemically stratified, oxygen in bottom waters cannot be replenished (Fig. 2.3h). Oxygen is depleted by oxidation of sinking organic matter and the waters become anoxic, thereby favoring the preservation of organic matter. The extent and duration of bottom water anoxia in a lake depend on the frequency and intensity of mixing. In highly productive lakes, neither stratification nor permanently anoxic conditions are needed for the preservation of organic matter (Talbot, 1988). Bohacs et al. (2000) and Carroll and Bohacs (1999, 2001) discuss the processes and environments of organic matter-rich sedimentation in different types of lakes in great detail.

Lake deposits occur in several settings, but are most common in rift, intramontane, and foreland basins. Lake deposits of rift basins with rapid subsidence are more likely to be thick and well preserved (Potter et al., 2005). The lower Permian Whitehill Formation, South Africa, contains lacustrine black shales that are thought to originate from the accumulation of freshwater algae under anoxic, fresh-to-brackish-water conditions in a protorift basin in southwestern Gondwana (Faure and Cole, 1999). Lake Tanganyika in the East African Rift is a good example of a modern lacustrine environment of black shale deposition (Demaison and Moore, 1980). It is a large, deep lake with sedimentary environments ranging from deltas and narrow carbonate platforms in shallow water to deepwater fans. The equatorial location of the lake and its great depth result in high surface productivity

TABLE 2.1 Characteristics of shales and of major shale depositional environments (after Bohacs, 1998, table 1 and Potter et al., 2005, Table 5.1)

	Fluvial/ floodplain	Lake: Underfilled	Lake: Balanced	Lake: Overfilled	Coastal	Deltaic	Shelf	Continental slope/ basin
Lithology	Siliciclastic	Chemical (evaporites) biogenous	Biogenous chemical	Siliciclastic coal	Coal siliciclastic	Siliciclastic coal	Siliciclastic biogenous	Biogenous (siliciclastic)
TOC (%)	2 (1.8–50)	1.5 (0.2–15)	15 (2–30)	7 (0.5–45)	9.2 (4–17)	6 (3–34)	4.6 (1.1–20)	7 (1–27)
Type of organic matter	III HI = 150 (230–445)	I HI = 400 (10–600)	I HI = 900 (600–1100)	I/III HI = 600 (50–700)	III, III–II HI = 188 (35–599)	III, III–I HI = 280 (170–520)	I/II HI = 530 (165–825)	II ± sulfur HI = 500 (150–800)
Typical thickness (m)	10–70	1–5	5–15	10–30	5–50	20–200	3–40	10–130
Major controls	Ratio of load to discharge; gradient	Supply + H_2O << accommodation Very climate sensitive	Supply + H_2O = accommodation	Supply + H_2O >> accommodation; minor role for climate	Ratio of inshore wave/tidal power to supply		Water depth, bottom energy, and supply	Supply, slope stability, and bottom currents
Current systems	Overbank flows/shifting channels/ floods; suspension in strongly turbulent, unidirectional flows	Stable shoreline Mostly wind-driven, but also flood plumes, storms, turbidity currents (deep lakes), stratification, and overturning	Stable shoreline	Oscillating, but prograding shoreline	Longshore currents, tides, and storms; mud deposition behind barriers except for fluid mud along open coastlines	Diverse depending on type but includes overbank flows, shifting channels, longshore currents, tides, and storms	Distal riverine plumes, oceanic currents, storms, and tides; surface, midwater flows, and bottom currents	Resedimentation and contour currents on slope and proximal basin; some midwater suspensions
Organic matter input	Land plants, algae	Algae, bacteria	Algae (±land plants)	Land plants, algae			Marine algae (±some plants)	Marine algae, bacterial mats(?)
Fossils	Plant debris, spores, pollen, and rare vertebrates and invertebrates	Sparse, restricted fauna (high salinity or deep water)	Great diversity of pelagic and bottom fauna; water depth and climate permitting	Modest diversity; plant debris and rare vertebrates	As in alluvial, but also some brackish marine invertebrates		Open marine benthic and pelagic; some fine plant debris; spore abundance provides distance to shoreline	Open marine pelagics and limited benthics
Lateral continuity	Limited by channel cutouts and valley width	Carbonates, evaporites, and black shales most widespread	Carbonates and black shales most widespread	Sheets with channel cutouts on prograding shorelines	Limited except for some large lagoons and for open coastlines	Similar to alluvial except for widespread delta front deposits and some bay fills	Widespread lobes and sheets at highstands	Restricted on slope, but widespread in basin

and in the stratification of the water column. The waters of the lake are therefore increasingly dysoxic below 100 m, and the sediments have up to 12% organic matter and hydrogen index values up to 600 (Potter et al., 2005).

2.5.2 Paralic Depositional Environments

Paralic environments are transitional environments on the landward side of a coastline that are shaped by a complex interaction of processes; they form an intricate mosaic of closely associated facies between land and ocean. The morphology of a coast, which controls what sedimentary environments are present, is a function of wave energy, tidal power/range, and relative sea level change (Boyd et al., 1992; Dalrymple et al., 1992). The quantity and type of sediment supplied from land, alongshore, and offshore are also important.

Much, if not most, terrigenous mud is trapped in paralic environments; deltas, estuaries, lagoons, tidal flats, and so on, form the depocenters of many ancient shale successions. Grabau (1913, pp. 483–484) thought that ancient marine black shales (his sapropelargillytes) with a wide geographic distribution, namely the early Toarcian black shales of northwest Europe, had been deposited in coastal lagoons and/or on extensive mudflats on marginal epicontinental seas exposed to some extent at low tide (cf. French et al., 2014). The abundance of mud in a paralic environment depends on the relative magnitude of fine-grained fluvial sediment input versus sediment reworking by nearshore currents. The distribution of organic matter-rich sediments in paralic environments is typically patchy, and the organic matter content is variable and often dominated by terrestrial components. The preservation of organic matter depends on local water column oxygen deficiency and on relatively rapid burial. Excessive dilution by siliciclastic materials works against organic enrichment in paralic environments.

Mud-rich deltas form where the work carried out by waves, tides, and associated nearshore current systems is insufficient to winnow mud. Although tide-dominated deltas can also trap some of the mud brought by the rivers associated with them, mud-rich deltas are typically river-dominated. Mud in a delta is deposited in its subaerial environments, namely, lakes, swamps, and abandoned distributaries, and as interdistributary bay fills. Mud in tide-dominated deltas and in estuaries is trapped in broad mudflats that grade into marshes or evaporative flats depending on regional climate. In the upper delta plain, interdistributary areas may contain coals or carbonaceous shales deposited in swamp and marsh environments. For example, in the Mahakam Delta, Indonesia, plant debris from palms and mangroves, supported by the tropical climate, accumulates alongside mud in tidally influenced interdistributary areas (Reading and Collinson, 1996).

Mud that escapes these sediment traps is transported offshore and deposited on the subaqueous prodelta, which is the main site of mud accumulation in deltaic systems. When lower density river water flows out over saltwater (hypopycnal flow), suspended mud flocculates and is deposited on the subaqueous prodelta. Flocculation and biogenic pelletization result in mud aggregates that settle rapidly and proximally. During periods of high discharge, sediment-laden water may be denser than saltwater and the river becomes hyperpycnal (Bhattacharya, 2010). Prodelta hyperpycnites, the deposits of these bottom-hugging flows, may represent more than half of shelf mud (Bhattacharya, 2009).

Mud deposited in the prodelta is prone to resuspension during storms, but also by fair-weather waves and tides. This resuspended mud may migrate along the shelf forming dilute, hyperpycnal geostrophic fluid mud belts (Bhattacharya, 2010) and wave-enhanced sediment gravity flows (Macquaker et al., 2010b). In saltwater basins, rapid sedimentation of flocculated mud and methane formation in organic matter-rich sediments can result in high pore pressure and reduced mud density, which favor slope failures and resedimentation processes. Such failures occur at slopes as shallow as 0.2° (Potter et al., 2005).

Mud is deposited behind barriers in wave-dominated estuaries and lagoons, and on the bottom of fjords and other shallow-silled basins (Fig. 2.3e and f). Mud also accumulates in coastal swamps and mudflats along the sides of estuaries. Estuaries act as mud traps because filter-feeders remove suspended organic and inorganic particles greater than 3 μm from the water column, and convert them into dense, mucus-bound fecal pellets and pseudofeces (Eisma, 1986; Newell, 1988; Pryor, 1975).

Climate is an important control on sedimentation in shallow, barred basins (Fig. 2.3e and f). In humid and temperate climates, mud will be dark colored and rich in organic matter, including plant debris washed in by rivers. In arid climates, mud will be lighter in color, organic matter lean, and alternate with evaporite beds.

Where nearshore wave power and associated nearshore current systems are high, mud is transported away from the river mouth along the shelf. Downdrift many modern large rivers, where the supply of mud is sufficient to dampen wave power and tidal currents, mud is deposited on open coastlines. The Chenier Plain of southwestern Louisiana is a sediment wedge formed by the westward moving mud stream of the Mississippi and Atchafalaya deltas (Gould and McFarlan, 1959). Variations in mud supply related to distributary channel activity (avulsions) cause shifts in the shoreline: the shoreline migrates seaward when supply is abundant and landward when supply is reduced. The longest nearshore Holocene mud belt is located along the open, high-energy northeastern coast of South America. The Amazon brings more than 10^9 tons of sediment to the Atlantic per year (Milliman and Meade, 1983). Most of this sediment is mud and a large fraction moves along the South American coast (Meade, 1994), part in suspension and part as large migrating mud banks (Rine and Ginsburg, 1985). Despite several modern examples (e.g., Anthony, 2008; Frey et al., 1989; Nair, 1976; Rine and Ginsburg, 1985), ancient equivalents of muddy open coastlines are not well documented in the literature. Walker (1971) studied Devonian marine mudstones in Pennsylvania that pass upward into mudstones with rootlets and mud cracks without a sand body at the paleoshore.

2.5.3 Shallow Marine Depositional Environments

Mud-dominated facies are the most abundant of all ancient shallow marine deposits (Johnson and Baldwin, 1996). On the shelf, siliciclastic sediment is supplied from adjacent land and, away from the mouths of large rivers, by reworking of seafloor sediment. Skeletal debris is an additional sediment source on shallow marine environments, but it only becomes dominant when siliciclastic sediment supply is low and biogenous sediment supply high. In the geologic record, shallow marine mudstones covered large epicontinental areas in response to sea-level rise. Examples of this type of setting include Paleozoic sequences of Africa, Europe, and North America, the upper Jurassic Kimmeridge Clay, and the Mesozoic of the Western Interior Seaway of North America (Johnson and Baldwin, 1996, and references therein).

Shallow marine, neritic, or shelf environments are those in which the seafloor is within the photic zone and periodically reworked by storms, that is, shallower than ca. 200 m. Most Neogene continental shelf sediments are relict in composition but modern in texture (Emery, 1968b; Milliman et al., 1972); the sediments were brought to the shelf during lowered sea levels associated with glacial episodes but have been reworked by present-day currents. The seafloor of the pericontinental shelf dips seaward from the shoreface to the shelf break at low angles of 0.1–1°, and the width of the shelf varies from tens to hundreds of kilometers. Because of their gentle slope, shelves are greatly influenced by changes in sea level.

A large proportion of preserved ancient marine sediments, including many black shales, was deposited in epicontinental marine environments. Epicontinental black shales are the typical subjects of shallow versus deepwater origin debates. At present, most shallow marine environments consist of relatively narrow pericontinental shelves, and there is a strong relation between water depth and distance to land. Shallower deposits thus show stronger terrigenous signatures than deeper deposits. During times of higher sea level in the geologic past, however, wide epicontinental shelves were common and covered vast areas of the continental crust. In epicontinental shelves, the relation between water depth and distance to land breaks down, and shallow water deposits remote from river input of terrigenous material and freshwater may have sedimentological, geochemical, and paleobiological signatures more characteristic of "deep" water (Hallam, 1967).

The organic matter content of sediments on the shelf seafloor is typically higher than in the deep sea (about three times higher, at present). Indeed, organic matter-rich deep-sea sediments are usually redeposited organic matter-rich shelf sediments (e.g., Dean et al., 1984; Degens et al., 1986). The water column of the shelf receives nutrients from runoff and coastal upwelling and thus is thus very fertile. Because water depths are relatively shallow, the export path for organic matter is much shorter and organic particles are less likely to be extensively oxidized en route to the seafloor. Sedimentation rates on the shelf are high in comparison to those of the deep ocean, which aids in the preservation of organic matter in relatively well-oxygenated environments, but retrogradation of clastic systems and trapping of terrigenous sediment in nearshore environments during transgressions and early relative sea level highstands minimize excessive dilution of organic matter settling to the seafloor of the shelf.

Shelf sediments below areas with strong upwelling are typically rich in organic matter and opal. For example, sediments on the SW African shelf, particularly off Walvis Bay, Namibia, have up to 20% organic carbon and up to 70% opal from the frustules of diatoms (Seibold and Berger, 1996). Fish debris and other vertebrate phosphate remains are also abundant. Upwelling is due to a combination of the cold, coastal Benguela Current with persistent offshore winds blowing in a northwest direction (Fig. 2.3c). Oxygen-poor, nutrient-rich water ascends from a depth of about 200 m and mixes in the photic zone with oxygenated water causing high productivity along a narrow coastal strip (Demaison and Moore, 1980). A zone of oxygen depletion, parallel and close to the coastline, is created on the shelf by the high oxygen demand due to the decomposition of large quantities of planktonic organic matter resulting from the Benguela Current upwelling.

However, not all areas of upwelling and high productivity in the ocean are associated with the intensification of oxygen minima and with the deposition and preservation of organic matter on the seafloor. This is the case in areas where oxygen supply exceeds the biochemical oxygen demand, for example, offshore Antarctica, offshore southeastern Brazil, and offshore Japan and the Kuril Islands (Summerhayes et al., 1976).

Shelf bathymetry can favor the preservation of organic matter-rich sediments. Bottom waters can become isolated from the well-mixed surface layer in bathymetric lows and may become oxygen-deficient through aerobic oxidation of organic matter. Moreover, topographic lows are traps for low-density organic matter. During winter, however, effective wave base is deeper and the water column is better mixed than in summer. Indeed, oxygen-deficiency in Phanerozoic shallow epi- and pericontinental shelves must have been seasonal.

Organic matter-rich shales may also form in epicontinental carbonate platforms. There are no modern examples, but these carbonate platforms were widespread in the geologic past. Some of these platforms may represent the interior of carbonate shelves or ramps, while others were truly epeiric platforms covering areas in the order of millions of square kilometers (Wright and Burchette, 1996). Intraplatform basins in such settings are rimmed by low gradient, ramp-like margins, and water depths in these basins were shallow (<150 m). During transgressive and/or highstand phases, intraplatform basins became stratified and cyclic suboxic or anoxic sediments developed in the basin center. Organic matter-rich sediments may form in these settings, and a number of examples of black shales deposited in intraplatform basins are known, particularly in the Jurassic and Cretaceous of the Middle East (Burchette, 1993; Droste, 1990).

2.5.4 Deep Marine Depositional Environments

Deep marine environments extend from the shelf break to the abyssal seafloor. The deep marine continental margin, that is, the slope and rise, consists of thick accumulations of terrigenous sediment mixed with marine biogenous material; beyond the continental margin, the deep ocean is characterized by extensive facies belts dominated by biogenous sediment (Fig. 2.5), and little terrigenous sediment reaches the deep sea under modern conditions (e.g., Meade, 1994, his figure 2.8).

In terms of depositional processes, there are three different facies in the deep sea: pelagites, turbidites, and contourites (Stow, 1985a); the processes that are responsible for the enrichment in organic matter and its preservation in deep-sea sediments vary according to facies. Black pelagites form under regions of high surface productivity, where the rate of supply of organic matter exceeds aerobic oxidation in the water column. Rapid downslope resedimentation of organic matter-rich shelf sediments favors the preservation of organic matter in black turbidites on the deep ocean floor (e.g., Dean et al., 1984). High sedimentation rates associated with sediment gravity flows lead to a rapid burial of organic matter and therefore to its removal from the upper oxygenated part of the sediment column where degradation of organic matter is particularly aggressive (Stow et al., 2001). Low oxygen levels in pore water and low predator pressure in deep marine environments result in the absence of deep burrowing, characteristic of the *Nereites* ichnofacies, which also favors the preservation of organic matter in black turbidites.

The consumption of oxygen by biochemical processes in a layer of relatively small replenishment of oxygen by advective movement results in an oxygen minimum layer (Wyrtki, 1962). Where this layer comes into contact with the seafloor, the sediments are typically organic matter-rich, because the preservation of organic matter is favored (Fig. 2.4).

The occurrence of low oxygen water masses in the modern ocean appears to be much less widespread than during the Mesozoic. There are probably many reasons behind this, but two are likely to be the most important: seawater temperature and paleogeography. The modern Atlantic Ocean, for example, is a corridor for meridional circulation of cold, oxygen-rich water formed in the polar regions; this thermohaline circulation counters the expansion and intensification of the oxygen minimum layer. In comparison, the northwest Indian Ocean contains very little oxygen at depths between 200 and 1200 m (Southam et al., 1982). Where oxygen concentrations in the oxygen minimum layer fall below 0.5 ml l^{-1} and the layer impinges on the continental slope, sediments on the seafloor are typically rich in organic matter ($2\% \leq C_{org} \leq 20\%$).

The California continental borderland consists of a series of basins of varied sizes, separated by submarine ridges, sills, and islands (Gorsline, 1978). High nutrient levels in surface waters due to the combined effect of climate and oceanography support high, but variable, primary productivity. An oxygen minimum zone, which partly results from the oxidation of sinking pelagic organic matter, impinges upon this structurally complex continental margin. The basins are silled below a depth of about 500 m and contain predominantly dysoxic water due to the interplay of oxygen-deficient deepwater flow and bottom topography (Savrda et al., 1984). The preservation of significant thicknesses of organic matter-rich sediments in these basins is favored by the impingement of their seafloor by the oxygen minimum layer (Fig. 2.3b). The Miocene Monterey Formation of southwestern California comprises a large volume of organic matter-rich siliceous and phosphatic (hemi)pelagic sediments. The sediments were deposited under similar conditions in relatively quiet deep water in a fault-bounded complex of borderland basins separated by islands and banks (Pisciotto and Garrison, 1981). Basins adjacent to shore received abundant terrigenous sediment, whereas basins farther offshore are sediment starved.

Seamounts and other oceanic rises affect ocean circulation patterns and result in local high fertility of seawater and consequent high productivity (e.g., Boehlert and Genin, 1987). The preservation of organic matter is generally favored on the seafloor of seamounts because the length of the export path is reduced (Fig. 2.3d). The preservation of organic matter is also favored where the oxygen minimum layer intersects the flanks of seamounts and other submarine topographic highs (Fig. 2.4). Cretaceous black shales in the Pacific were deposited on seamounts, oceanic plateaus, and other submarine topographic highs as a consequence of local high productivity. Other black shales were deposited as a result of high productivity associated with the passage of the submarine highs beneath the equatorial belt of high fertility (Waples, 1983).

2.6 CONCLUSION

Black shales are mixtures of terrigenous, biogenous, and hydrogenous sediment in which organic matter constitutes at least 0.5% of the material. The composition, texture, structures, and fossil content of a shale depend on depositional environment, that is, on a complex interplay of physical, chemical, and biological variables and processes that control the production, erosion, transport, deposition, and diagenesis of mud. Diagenetic processes act on the sediment and result in changes to its composition and/or texture. Patterns of vertical and lateral variability, which can be observed on a variety of scales in shale successions, are an expression of the dynamic nature of the processes behind their development, and preserve a record of the evolving depositional environments in which they formed.

Although shales are the most ubiquitous component of the stratigraphic record, the distribution of black shales in the Phanerozoic is predominantly limited to six stratigraphic intervals.

Black shales may be deposited in a wide range of sedimentary environments from the bottom of lakes to the abyssal plains of the ocean; however, most ancient black shales appear to have been deposited in shallow marine epicontinental environments for which we have no modern analogs.

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