4 Erosion, Sedimentation and Sedimentary Origin of Clays

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4.1 Introduction

Of all the various types of sediment, fine-grained sediments with a high proportion of clay minerals are by far the most abundant. In the marine environment, terrigenous (land-derived) muds cover about 60% of the continental shelves, and almost 40% of the deep ocean basins, amounting in total to about a third of the Earth's surface (Fig. 4.1). Similarly, although proportionally much smaller in area, continental aquatic environments are often dominated by fine-grained sediments, and these environments include many of the rivers, lakes, deltas and estuaries used extensively by man.

However, their wide distribution is not the only feature that makes fine-grained sediments an important component of the environment, it is also the properties that their fine grain size and chemistry impart to them. Large surface areas (up to $800 m^2 g^{-1}$) and surface properties such as adsorbtion, make them important transporters and sinks for pollutants. Surface properties also contribute to many engineering problems, such as the silting up of harbours, and landslides.

In addition to their modern-day environmental importance, the sedimentology of clay minerals can be used to learn about past environments on both historic and geological time scales. Frequently, clay minerals are used to infer sediment dispersal patterns, palaeoclimatic variations, and stratigraphic correlations, all with varying degrees of success. Their importance is further emphasised by the fact that mudstones and shales account for about 70% of the sedimentary geological record (Blatt et al. 1980) and they have an outcrop area of about 33% of the worlds land surface (Meybeck 1987), twice as much as any other rock type, on both counts.

Clay sedimentology is concerned with the interpretation of clays and clay minerals in terms of sedimentary environments, provenance and tracers of sediment dispersal, palaeoclimatology, palaeocirculation, and even geotectonics (Chamley 1989; Weaver 1989). All of these aspects are based on how reliably we can determine the processes that have resulted in the observed assemblages and distribution of clay minerals in sediments. This brief account of the sedimentology of clays is mainly concerned with the processes that affect their sources and fluxes to aquatic environments, mechanisms of

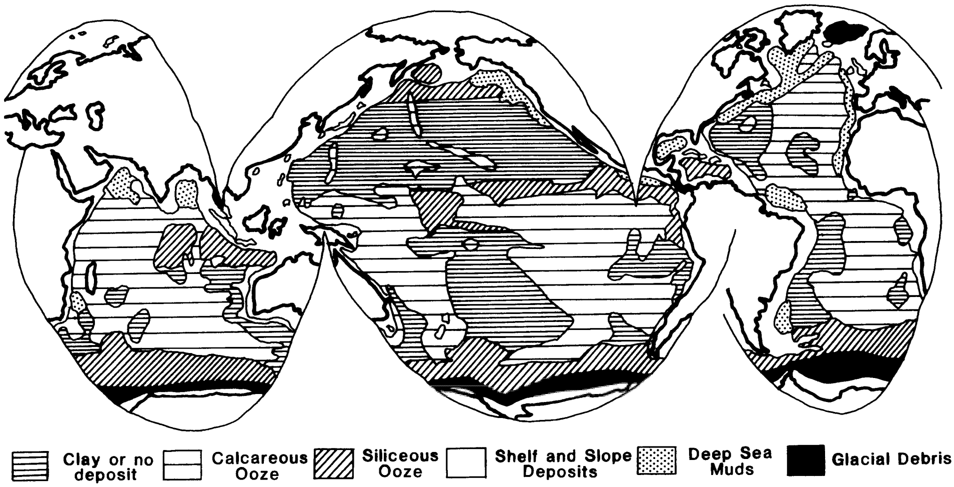

Fig. 4.1. Distribution of recent sediment types in the world ocean. Modified from figures in Berger (1974) and Davies and Gorsline (1976)

erosion, transport and deposition, and the mechanisms and products of transformation and in situ formation of clay minerals in sediments. Some processes are common to many environments while others are often, but not always, environmentally specific. A final part of this account considers the environmental information that can be obtained from clays and clay minerals if we are able to establish their origins, and some of the problems that may confront an investigator attempting to do this.

Much of what concerns the sedimentology of clays as fine-grained minerals (largely phyllosilicates) also concerns the sedimentology of clays as fine-grained (<2 μm) materials, as well as that of muds and shales, as fine-grained sediments containing a high proportion of clay-sized material. As a consequence of such close connections and overlap, no attempt is made to stick to a precise terminology, but instead to try to convey what is meant by its context.

4.2 Origins, Sources and Yields, and Global Fluxes of Clay Minerals

4.2.1 Origins of Clay Minerals in Sediments

The clay minerals present in a sediment or sedimentary rock may have one of two main origins; they may be detrital or they may be authigenic (Fig. 4.2). Detrital clays are inherited from another environment to the one in which they are now found. Authigenic clays are formed in situ, and this may occur by one,

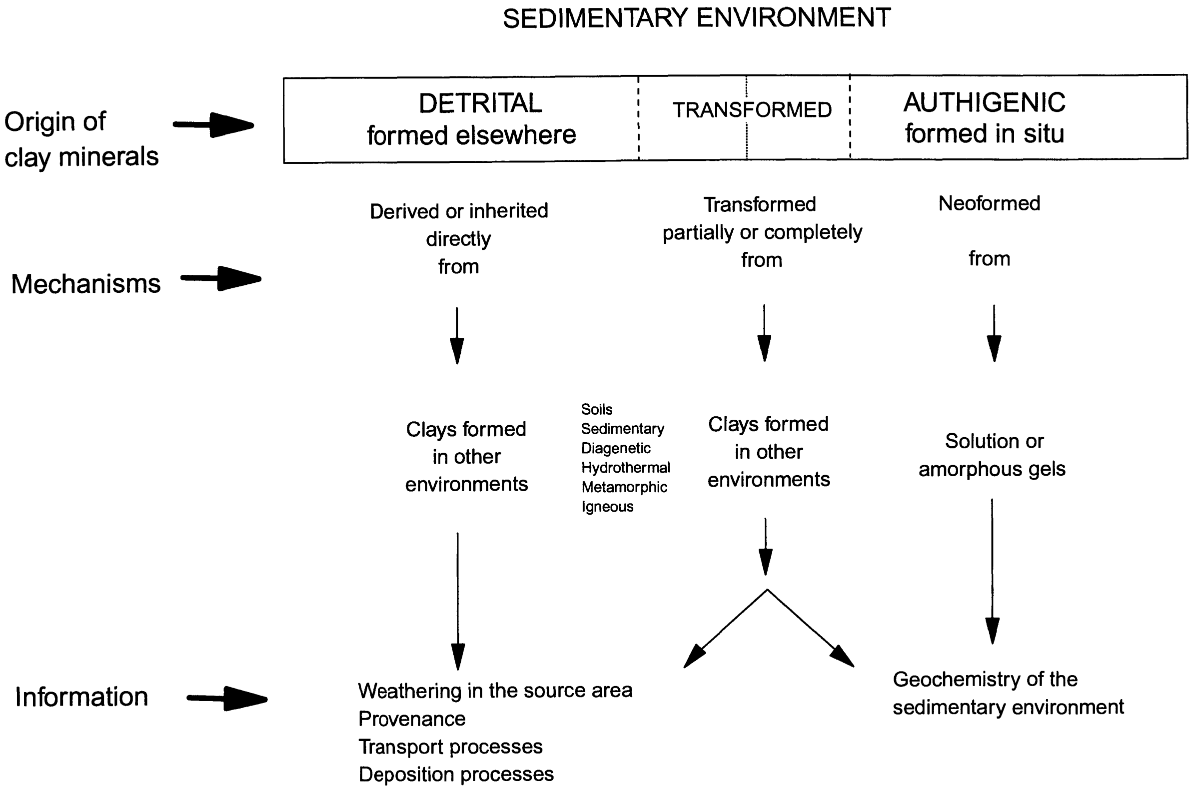

Fig. 4.2. The various origins of clay minerals in the sedimentary environment and the information that may be obtained from them. Most clay minerals, probably more than 90%, are detrital. In areas starved of detrital inputs authigenic clays may make an important contribution to the clay fraction. Clays formed by transformation are intermediate in character. In much of the early literature on clays in sediments, transformation processes were believed to be more important than they are generally considered to be now

or some combination, of three different processes; direct precipitation from solution (a process known as neoformation.), reaction or ageing of amorphous materials, and transformation of some precursor mineral, i.e. where some structural elements are retained. Clay minerals themselves are usually the precursor minerals for transformation processes, so that a third origin known as transformed lies between the poles of detrital and authigenic origins and has characteristics attributable to both (Fig. 4.2).

Transformation processes may be degradative or aggradative (Millot 1970, 1978). According to Millot (1970), the majority of transformation processes in the sedimentary environment involve aggradative transformations of clay minerals formed by previous degradative transformations in soil environments. Although there is evidence for some forms of transformation processes, such as the aggradation of soil vermiculites back to more micaceous clays on exposure to the marine environment (Weaver 1989), many of the mineral trends attributed in the early literature (Millot 1970) to transformations in the sedimentary realm, particularly the more dramatic ones, such as chlorite formation in estuaries and in hypersaline basins, have since been shown to be the result of other processes. Estuarine clay patterns are now largely attributed to mixing of different detrital sources (Chamley 1989), and the chlorites in ancient hypersaline facies are probably formed by authigenic processes during deep-burial diagenesis (Hillier 1993). Nevertheless, transformation processes in the sedimentary realm may be widespread, but difficult to document clearly because they are easily masked by more dramatic changes due to other processes.

One of the major problems involved in studying the sedimentology of clays is that of trying to distinguish between detrital and authigenic clay minerals. The problem arises because of the fine grain size of clay minerals and because clay minerals are often recycled from one environment to another (Eberl 1984). Fine grain size makes direct, origin-diagnostic, observations of clay minerals difficult, while recycling of clay minerals between the weathering, sedimentary, diagenetic and hydrothermal environments, means that a clay mineral observed in the sedimentary realm may well have formed in another. Although authigenic clays do not normally form in great abundance in the sedimentary environment, they tend to become increasingly abundant during burial diagenesis. Consequently, where ancient sediments are concerned, the distinction between authigenic and detrital clay minerals becomes an even more important issue. Often firm evidence for the origin of a clay mineral can only be obtained by combining data from a variety of sources and techniques. Even then the evidence is often circumstantial.

4.2.2 Sources and Yields

Most clay minerals, probably more than 90%, are detrital and they are supplied to the sedimentary system from two main sources; one is rocks, the other is the soils that develop on them by weathering. According to Potter et al. (1980) most mud (clay minerals) comes from the erosion of pre-existing mudstones. On the other hand, Curtis (1990) asserts that most muds are derived from the erosion of soils. Such apparently different statements are no doubt due to the boundary problems of precisely defining what constitutes a rock source and what constitutes a soil source. For instance, clay minerals derived from a rock, frequently pass through a soil with little or no obvious modification by soil processes. Others are only partly modified (transformed) so that they have features of both a rock and a soil source (see Sects. 3.2.2.2, 3.2.2.4, 3.2.3). The difficulties of such definitions are largely avoided if the problem is restated in terms of whether most clay minerals are derived by physical weathering, in which precursor minerals and aggregates are simply reduced in size, or chemical weathering, in which clay minerals may be transformed and new ones neoformed.

In absolute terms, the production of mud is greatest from areas of both high relief and high rainfall, especially where bedrocks are dominated by mudstones and shales. Low-lying arid regions, regardless of bedrock, and carbonate regions, produce the least. Considering that only about one fifth of the Earth's land surface is subjected to intense chemical weathering, that the conditions conducive to the greatest mud production are not conducive to well-developed soil formation, that erosion typically samples whole soil profiles not just the potentially most altered surface horizons, and that mudstones and shales cover 33% of the land surface, then it is probable that most mud (clay minerals) is derived by physical weathering of pre-existing mudstones and shales. This, however, is the present-day situation, but with changes in the distribution of climatic belts and the presence or absence of mountain ranges in the geological past, it may not always have been the case. Similarly, vegetation strongly affects sediment yield, by both sheltering and binding soil constituents together. Clearly, changes in vegetation through time, such as the evolution of grasses during the Cretaceous, or the development of agriculture, must have had substantial effects on soil development and erosion, and therefore the relative importance of physical versus chemical weathering, and hence rocks versus soils as sources of clay minerals.

Sediment yield depends on a complex interplay of many factors, amongst the most important of which are climate, relief, vegetation and lithology. On a local and on a basin scale, sediment yields vary greatly and there is little correlation between drainage basin size and yield (Fig. 4.3). Nor is there any general statistical relationship between single variables such as runoff and yield (Selby 1994). Variation of sediment yield in the Amazon basin (Fig. 4.4) was studied by Gibbs (1967) who showed that 80% of the sediment is derived from only 12% of the basin area comprising the mountainous Andean regions. Land use by man has also greatly affected sediment yields, which in many regions have probably increased two to three times since late Pleistocene times (Gorsline 1984).

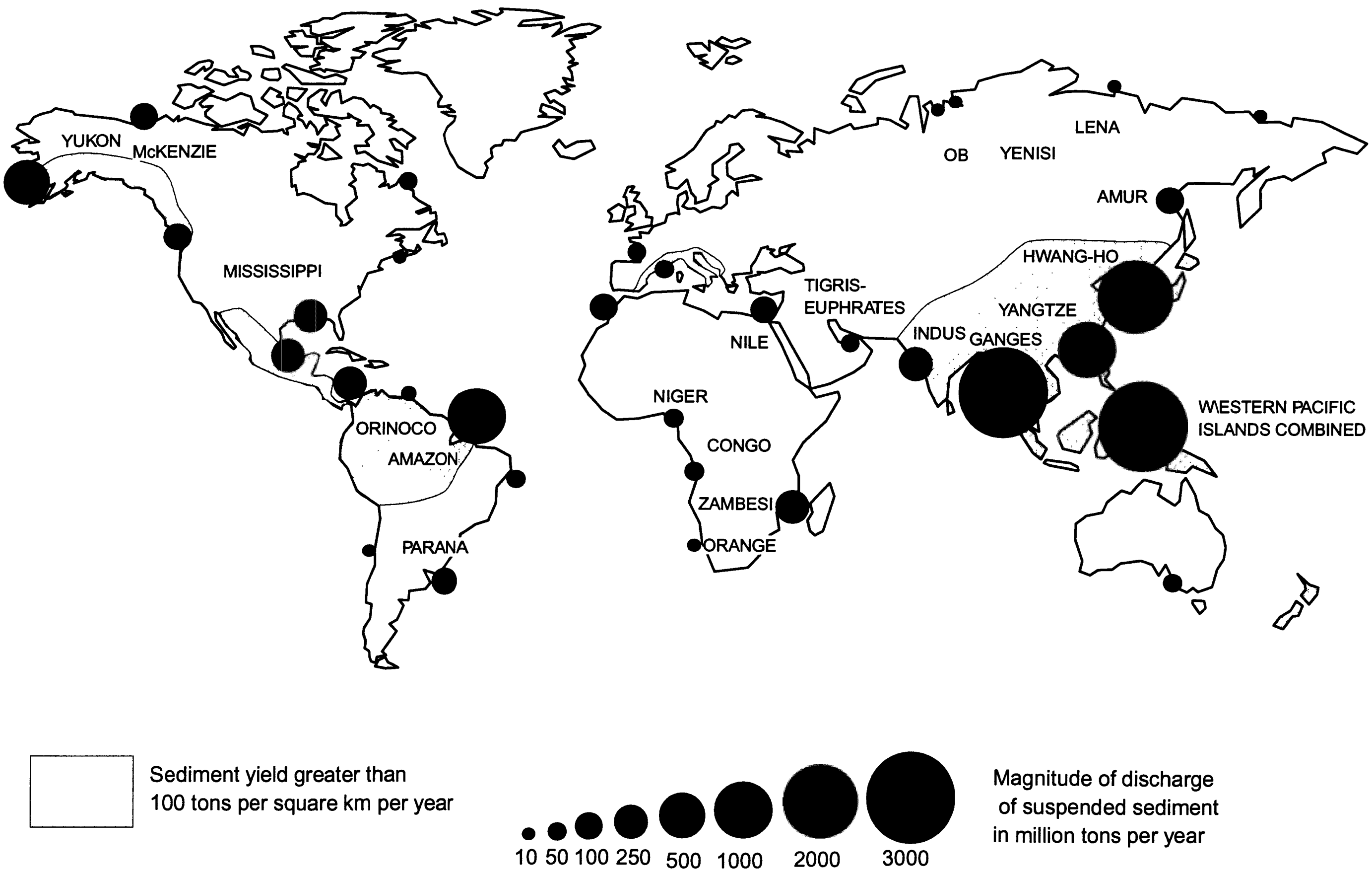

Fig. 4.3. The magnitude of annual sediment discharge of the world's major rivers and the worldwide distribution of regions with the highest sediment yields. Note the huge amounts of sediment erosion in southeast Asia and the western Pacific islands due the combination of high relief and high rainfall in these regions. Based on data and figures from Strakhov (1967), Stoddart (1971), Milliman and Meade (1983) and Jannson (1988)

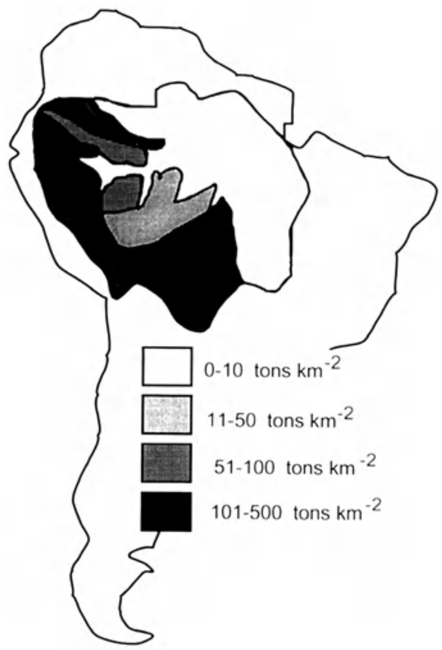

Fig. 4.4. Variation in sediment yield in the Amazon basin. For the basin as a whole, sediment yield is clearly dominated by that from areas of high relief in the Andes and their foothills. (Modified from Gibbs 1967)

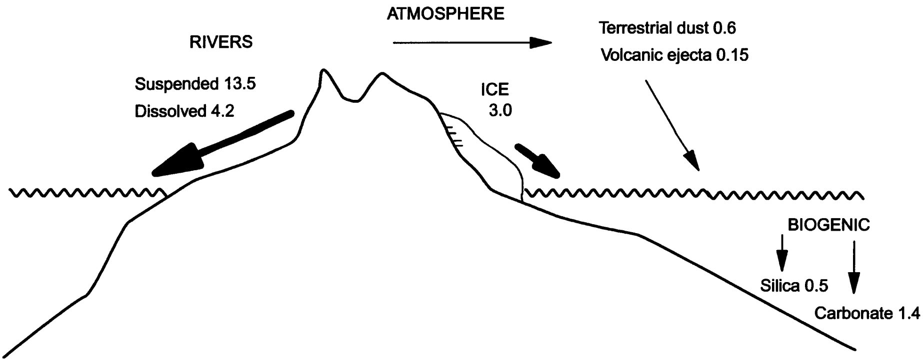

Fig. 4.5. Masses of sedimentary materials transported to the oceans annually. Most of this sedimentary material is both clay sized and dominated by clay minerals. Modified from Garrels and Mackenzie (1971) with updated estimates of fluxes from Milliman and Meade (1983) and Gorsline (1984)

4.2.3 Global Fluxes

Whatever the source of clay minerals, through the agents of erosion they are transported away from their sources to be deposited elsewhere, and eventually may find their way to the oceans. The bulk of the mud supplied to the oceans comes from the worlds twenty largest rivers (Milliman and Meade 1983). Estimates of the annual global fluxes of materials to the ocean indicate that rivers supply about 13.5 billion tons yr^{-1} of suspended load. Ice transport is second in importance supplying about 3 billion tons yr^{-1}, while supply from atmospheric transport is estimated at about 0.75 billion tons yr^{-1}, mainly from dusts of terrigenous origin (Fig. 4.5). Assuming, as did Weaver (1989), that about 60% of all this material is phyllosilicates, then about 10 billion tons yr^{-1} of phyllosilicates are delivered to the oceans. Of this amount, Weaver (1989) suggests that about half is in the <2 µm clay-size fraction. For completeness, mention must also be made of the fine-grained biogenic contribution that comes from the remains of planktonic carbonate and siliceous micro-organisms. Together these contribute about 2 billion tons yr^{-1} to oceanic sediments, mainly in areas of high biological productivity, and their accumulated deposits cover large areas of the ocean floor (Fig. 4.1).

4.3 Erosion, Transport and Deposition of Clay Minerals

As with all other sedimentary materials the agents of erosion, transport and deposition of clay minerals are water, wind, and ice. On the continents rivers are the principal agents of transport and deposition of clays. Then, through estuaries and deltas, the suspended clay-mineral loads of rivers reach the ocean where they are further dispersed by currents, and in many instances also by mass flows after a period of temporary deposition. Wind also erodes, transports and deposits large quantities of clay-sized material from many areas. Of the three agents, water, wind and ice, processes involving water are by far the most important (Fig. 4.5). However, there are significant areas of the oceans where the majority of the clay minerals in the sediments have been transported there by wind or by ice.

4.3.1 Transport by Rivers

By far the majority of clay mineral transport in fluvial systems occurs in suspension, and suspended loads, and therefore clay minerals, account for by far the largest proportion of sediment moved by rivers. At the mouths of large rivers such as the Mississippi, the Amazon and the Congo, typically more than 90% of the total sediment transport is suspended load. The suspended load is defined as those grains whose settling velocity is greatly exceeded by the upward component of turbulence, and although this is obviously a loose definition, suspended loads generally consist of particles finer than coarse silt (about 30 µm). In deep rivers, because of the greater settling velocity of larger and denser particles, a concentration gradient may develop where the mass of sediment per unit volume decreases with height above the bed. These changes in mass are often also accompanied by changes in the composition of the

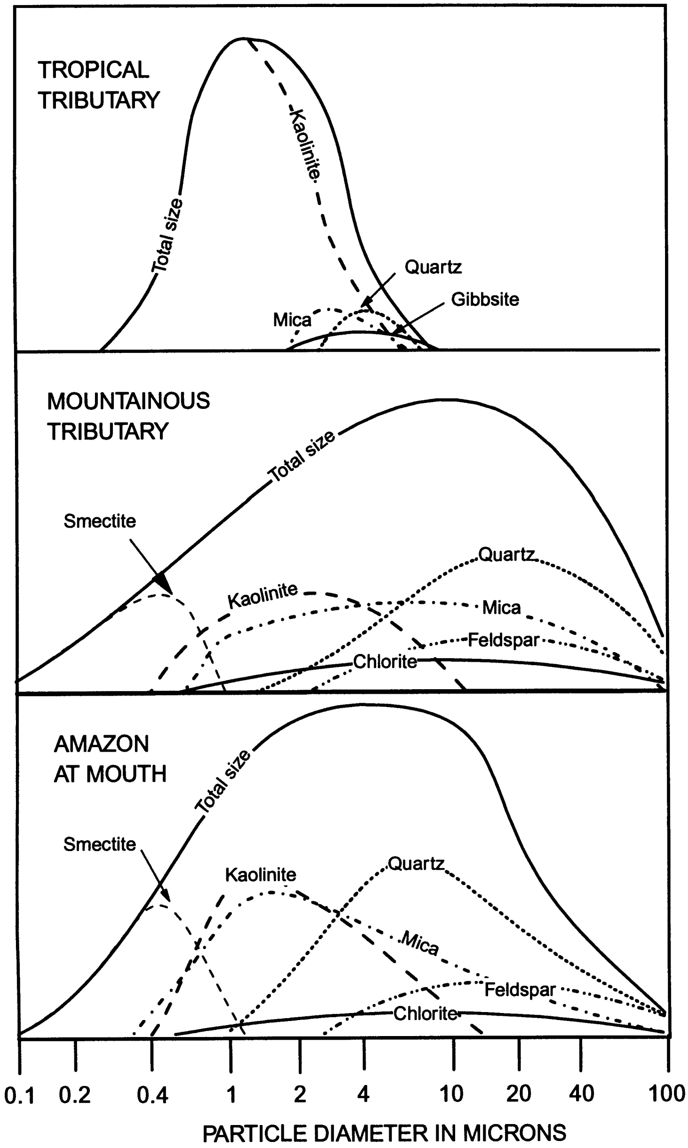

Fig. 4.6. Comparison between mineralogy and grain-size distribution of suspended sediments from a lowland tropical tributary and a mountainous region tributary to the Amazon river, and at the mouth of the Amazon. (Modified from Gibbs 1967)

suspended load. Furthermore, particles which are carried in suspension in one part of the flow may be carried as bed load in another part due to changes in the turbulence of the flow, i.e. more turbulent flows can carry more and larger particles.

The way in which the suspended sediments in the Amazon river vary between tributaries which rise in tropical regions compared to mountainous regions is shown in Fig. 4.6. Tributaries which rise in low-relief tropical areas carry predominantly kaolinite, and the vast majority of the suspended load is <2 μm in size. In contrast, tributaries which rise in mountainous regions carry more varied loads, and a much wider grain-size distribution concentrated in the silt-size fraction. The abundant mica, chlorite, quartz and feldspar reflect the dominant origin by physical weathering. Because of the dominance of the mountainous regions in terms of sediment yield (Fig. 4.4) the composition of the suspended sediment at the mouth of the Amazon (Fig. 4.6) is also dominated by the minerals derived from the rocks and soils of the mountainous regions (Gibbs 1967; Meade 1988).

Much of the suspended load carried by rivers originates outside the river channel and is supplied as wash load from overland flow on hill slopes. However, erosion of the river banks can also be a very important, often the dominant, source of sediment (Reid and Frostick 1994). Concentrations of suspended sediment typically range from a few tens to several thousand mg l^{-1}, although values as high as six hundred thousand mg l^{-1} (60% sediment by weight) have been observed (Reid and Frostick 1994).

Generally, suspended sediment concentration increases with increasing water discharge so that most clay is transported during times of flood. However, the relationship is only a very general one that varies both from one river to another and with time in the same river. This is due to the many factors which affect the availability of sediment, including the length of time since the previous flood. Furthermore, sediment concentrations are normally higher, by one or two orders of magnitude, on the rising limb of a flood hydrograph than at corresponding levels of discharge on the falling limb. This is due to the flushing of most of the available sediment from hill slopes and channel banks during the early stages of a storm. The importance of floods to the transport of clay-sized material is emphasised by the fact that many rivers transport more than half of their annual sediment load in only 5–10 days of the year (Meade and Parker 1985).

4.3.2 Transport in the Sea and Ocean

Most of the fine-grained sediment that reaches the open sea is supplied by rivers, and initially most of this is transported no further than the shallow shelf environments of the continental margins. Locally, this fluvial supply often results in the formation of mud belts on the shelf, their location being controlled by the dynamics of supply and dispersal. Generally, the concentration of suspended sediments in shelf waters shows an exponential decreases from values of 10–100 mg l^{-1} in coastal areas to values of 0.1–1 mg l^{-1} over the outer shelf. McCave (1972, 1985) described the sites of shelf mud belts in terms of five different types, namely muddy coasts, nearshore, mid- and outer-shelf mud belts, and shelf mud blankets (Fig. 4.7). Notionally, their location is explained by the relationship between the general exponential decrease in

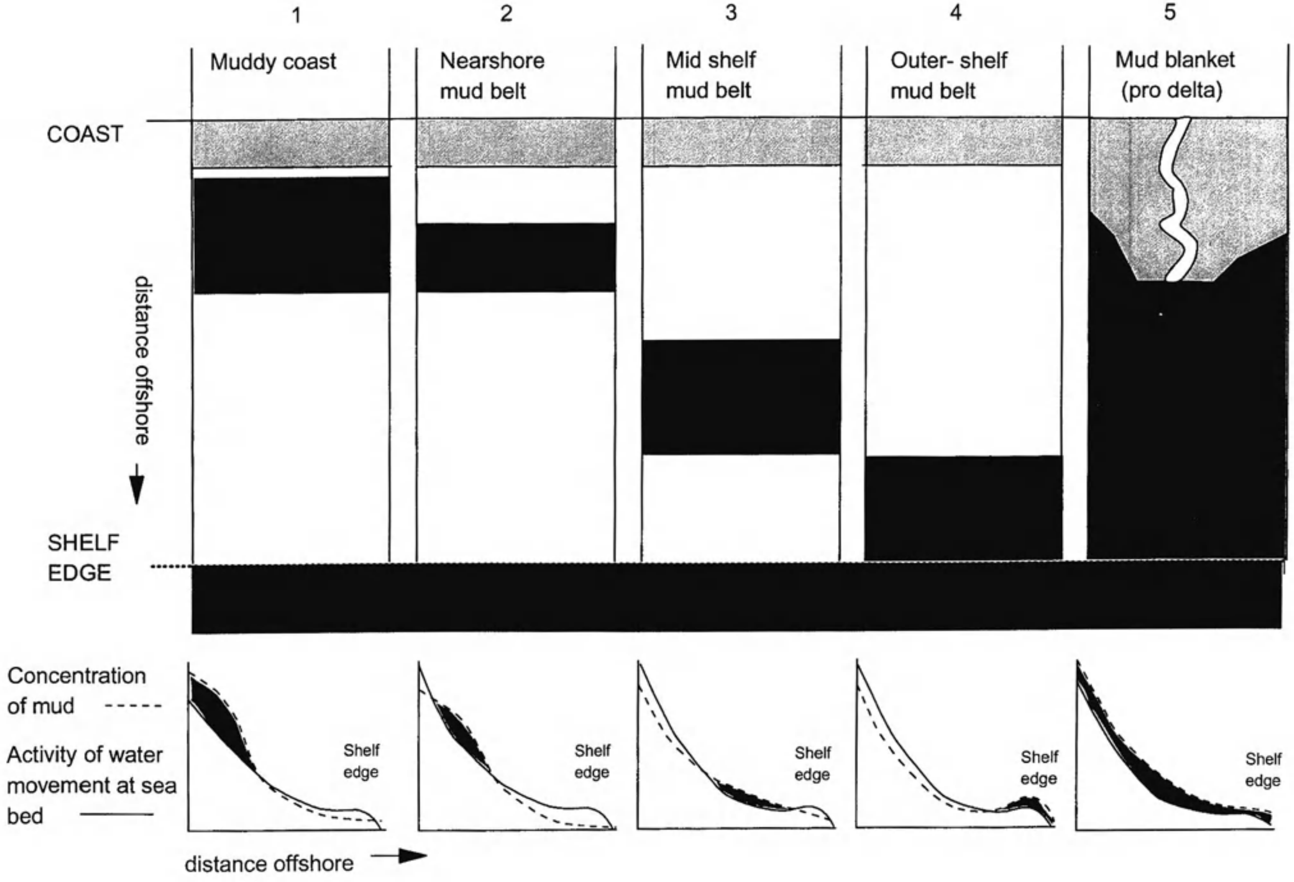

Fig. 4.7. The different locations of mud belts on continental shelves and their schematic explanation in terms of changes in mud concentration and a notional parameter combining wave and tidal activity. (Modified from figures in McCave 1972)

suspended sediment concentration in an offshore direction and the pattern of wave and current activity at the sea bed. Muddy coasts form in areas adjacent to major fluvial inputs, as do nearshore mud belts where supply is less, while mid-shelf mud belts characterise areas of higher wave energy which displaces mud deposition seawards. In areas offshore from major deltas, especially those in the tropics, muds often blanket the whole shelf. Muddy coasts and blanket deposits are essentially due to very high supplies of mud, and demonstrate that muds can be actively deposited in areas of high energy simply if there is enough of it about. An impressive example of this contradiction to long-held assumptions that mud only accumulates slowly in quiet wave-free conditions is provided by the 1600 km of muddy coastline between the Amazon and Orinoco rivers. Here suspended sediment concentrations are typically up to 1000 mg l^{-1}: about 150×10^6 m^3 yr^{-1} of mud is transported to the northwest in suspension and another $100 \times 10^6 m^3 yr^{-1}$ as migrating mud banks, largely as a result of wave action (Wells and Coleman 1981).

According to McCave (1972) the transport of mud across the shelf is achieved by both diffusion and by advection. Advective plumes associated with fluvial supply points and with areas of convergent tidal currents are the most important, but there is also a gradual seaward diffusive transport of material suspended by wave and current activity. Examples of advective transport are the Rhine mudstream northwards along the Dutch coast, and the Amazon mudstream northwards along the Guinea coast as mentioned above.

In addition to the supply of suspended sediments from rivers to the continental shelves, Meade (1972) emphasised the potential importance of other sources and the assumption that river suspended loads are naturally transported out onto the shelf. For example, on most outer shelves organic material from marine organisms may make up the bulk of suspended matter, and resuspension of relict sediments by wave and current activity may represent an important source. Concerning rivers as sources, on the Atlantic coastal plain of the United States, Meade estimated that about 90% of the fine-grained suspended sediment supplied by rivers is deposited in the estuaries and in wetlands fringing the coast. Based on studies of the clay mineral assemblages it has also been shown that some fine-grained sediments in the estuaries of the eastern United States have been transported into them from the sea (Hathaway 1972; Peaver 1972). The role of coasts in northwest Europe as either sources or sinks of sediments to the marine environment has been discussed by Kirby (1987). In several areas there is evidence that human activity has resulted in estuaries changing from sinks, for both fluvial and marine sediments, to sources of sediments to the shelves (Avoine 1987; Irion et al. 1987). The contribution of clay minerals from the rivers Ems, Weser and Elbe to the mud deposits of the German Bight in the southern North Sea is confirmed by the associated high levels of pollution, and it appears that mean sedimentation rates of between 1–4 m for the last hundred years are also much higher than for older deposits as a result of human activity (Irion et al. 1987).

Further availability of shelf muds to the deep sea depends on sea level and shelf width. High sea levels and wide shelves promote deposition on the shelf, whereas low sea levels and narrow shelves promote the transport into, and deposition of mud in the deep sea environment. According to Stow (1994), the processes that transport and deposit fine-grained sediments in the deep sea are resedimentation processes that involve some form of mass flow, bottom currents, and surface currents in combination with pelagic settling (Fig. 4.8).

Resedimentation processes are event processes driven by gravity, and as far as clays and muds are concerned the most important are turbidity currents. Turbidity currents are mixtures of sediment and water propelled downslope as a result of their density contrast with the surrounding waters. They develop as a result of events that include slumps, debris flows, storms, and river floods, and they may travel up to a few thousand kilometres across the sea floor. Waning turbidity currents that have already deposited the bulk of their sediment may become more buoyant than the deep cold ocean waters they have penetrated. Frequently, this results in the discharge of the remaining fine-grained material into a plume rising up to 1000m above the ocean floor, a process known as flow lofting. By this means fine-grained sediments may be dispersed well beyond the turbidity current deposit itself (Stow 1994).

Bottom, or contour, currents are driven episodically by wind, tides and waves, and more continuously by thermohaline circulation (Faugères and Stow 1993). Unlike turbidity currents they are not driven by gravity and so they may flow along, and even up, slopes as well as down them. The major pattern of deep water circulation in the world ocean is driven by the cooling and sinking of saline surface waters at high latitudes and their slow movement away to lower latitudes. As result of the Coriolis force these water masses are banked up on the western sides of the oceans to form the Western Boundary Undercurrents. Water from these currents spreads slowly eastwards and upwells to the surface layers. Associated with these currents are concentrations of suspended matter forming bottom nepheloid layers, usually extending up to about 1 km above the ocean floor. They are formed by the resuspension of bottom sediment by the current motions of the abyssal circulation. The suspended particles in these layers are on average less than 12 μm in size, and concentrations are only about $0.01-0.3\,\mathrm{mg\,l^{-1}}$. Net particulate loads of nepheloid layers in the Atlantic were calculated by Biscaye and Eittreim (1977) and were shown to be almost an order of magnitude lower in the eastern Atlantic, at 13×10^6 tons, compared to the western Atlantic, at 111×10^6 tons. This difference is due to the strong western boundary currents. These layers are also well developed in areas where surface kinetic energy may propagate downwards to produce "deep sea storms" (McCave 1986).

Pelagic settling is the slow and continuous vertical settling of fine-grained materials in the open sea. Most material settles at rates of between $1\,\mathrm{cm\,sec^{-1}}$ to $1\,\mathrm{cm\,min^{-1}}$ as aggregates that may be flocs, or pellets produced by filter feeders. In the open sea, biological debris, such as the skeletons of calcareous and siliceous microfossils, are often the dominant component of various

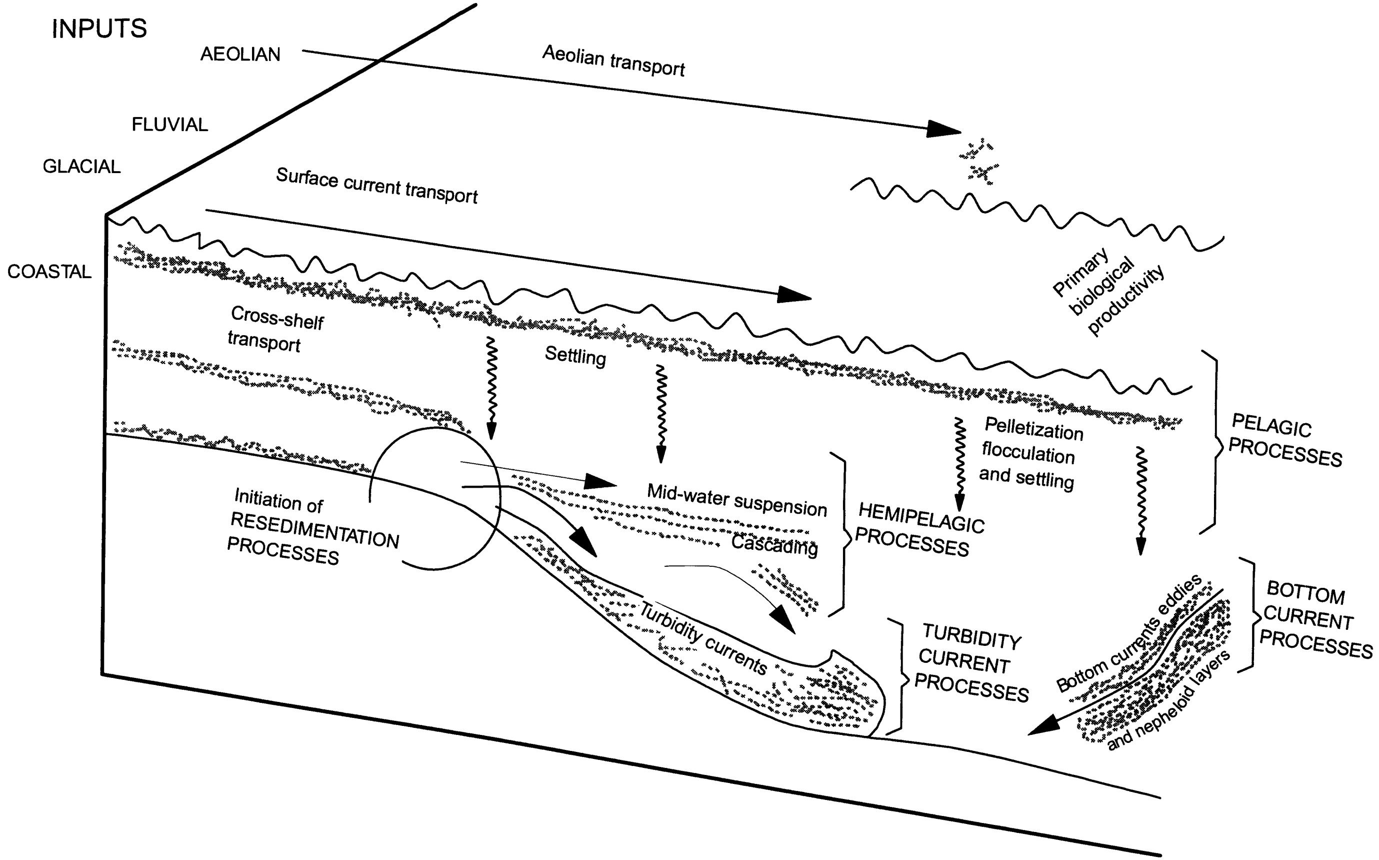

Fig. 4.8. Fine-grained sediment transport and deposition processes in the ocean. (Modified after Stow 1994)

pelagic deposits known as oozes (Fig. 4.1). The accumulation of these deposits is controlled by biological productivity in surface waters and by the carbonate compensation depth (CCD). The CCD is the depth at which the rate of carbonate supply is balanced by the rate of dissolution; thus carbonate does not accumulate below this depth which is typically at about 4km. Siliceous oozes are found in peri-equatorial zones, the subarctic and Antarctic, and along the margins of some continents. All are areas of important upwelling of waters enriched in nutrients due to the bacterial oxidation of dead planktonic organic matter that has sunk from the surface layers. The deep-sea sediments which accumulate below the CCD, in areas of low biological productivity and away from important terrigenous supply, are known as red clays. The deepest-sea red clays are a combination of mostly aeolian, but also volcanic and cosmic sources (Glasby 1991). Somewhere between pelagic settling and the deposits of low-density turbidity currents there is a range of overlap of processes and deposits that are conveniently termed hemipelagic (Fig. 4.8). A typical distri-

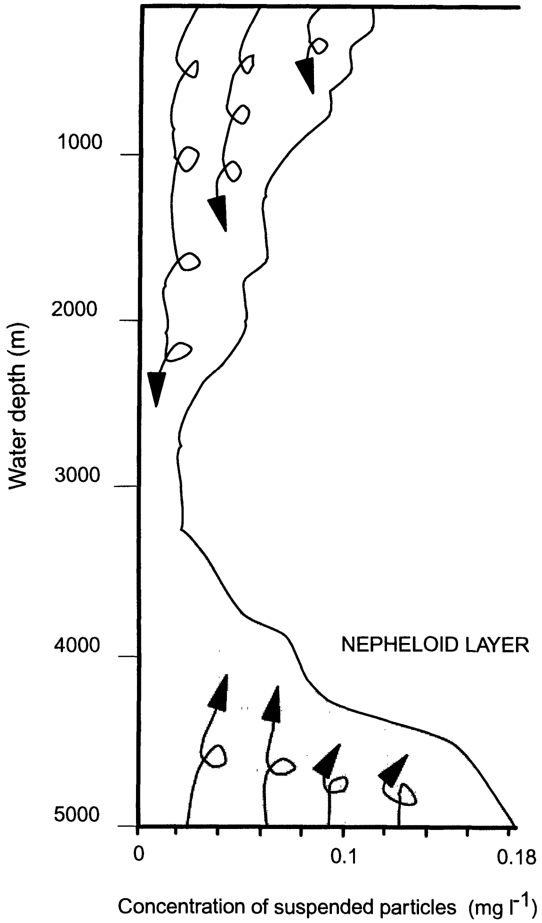

Fig. 4.9. Typical profile of suspended particulate matter in the ocean from an area with a well-developed nepheloid layer. The surface waters contain more biogenic particles than bottom waters and the decreasing concentration depth profile is due to a combination of large-scale equilibrium processes including vertical settling, dissolution and decomposition of biogenic particles, and lateral injection of particles from shelf areas. The increasing concentration in deeper waters towards the ocean floor, known as the nepheloid layer, contains material suspended and mixed vertically or laterally injected by bottom contour currents and turbidity currents. (Modified from Biscaye and Eittreim 1977)

bution of suspended particulate matter in the ocean resulting from the interaction of pelagic settling and all of the various transport processes is shown in Fig. 4.9.

4.3.3 Deposition of Clay Minerals by Settling

The deposition of clay-sized particles from all kinds of water bodies occurs, principally, by settling from suspension. In static water the rate of settling is governed mainly by particle size, and with various assumptions, e.g. that the particles are spheres, it can be estimated from Stokes' law. The effect of different particle shapes has been treated by Lerman (1979). Basically, non-spherical particles settle more slowly than their volume equivalent sphere, especially platy shapes like those of many clay minerals (see Sect. 2.2.1). Under many sedimentary conditions the water in which the particles are suspended is not static but flowing, and this will further determine whether particles remain suspended, or if they are deposited. For clay particles less than $1\,\mu m$ in size settling times are extremely slow, of the order of about $3\,h\,cm^{-1}$ or longer. In effect, the bulk of sedimentation of fine-grained particles only occurs because of processes of aggregation which increase particle size by one or two orders of magnitude (McCave 1984). Up to concentrations of about several tens of thousands of $mg\,l^{-1}$ settling rates tend to increase because of the greater chance of particle–particle collisions leading to the formation of aggregates. Above these concentrations setting rates begin to decrease due to mutual particle hindrance. The terms, aggregation, agglomeration, flocculation and coagulation are sometimes used interchangeably, and sometimes more specifically to refer to a certain type of process of particle association (van Olphen 1977; Yariv and Cross 1979). From a sedimentological viewpoint, aggregation is probably the best general term.

In order for aggregation to occur, two things must happen: particles must approach each other close enough to interact and they must sometimes stick together as a result. Three physical processes are responsible for bringing the particles together; Brownian motion, velocity gradients due to laminar and turbulent shear, and differential settling, also known as scavenging. The operation of these three different mechanisms is discussed in some detail by Lerman (1979). In estuaries and in coastal waters turbulent shear is dominant, whereas in the deep ocean basins Brownian motion may dominate for particles of $< 1\,\mu m$ in size and is succeeded by scavenging and then by shear for increasingly large particle sizes (McCave 1984). The second step of aggregation, that of sticking particles together, depends on the surface properties of the particles. The sticking together part of aggregation may have various causes such as electrochemical flocculation by salts, or biological processes that produce "glues" such as the biopolymers exuded by bacteria (McCave 1984). The obvious aggregation of particles which occurs in estuaries has often been attributed to salt flocculation, but there is a substantial body of evidence which indicates to some workers that biological processes may be much more important than changes in salinity.

4.3.3.1 Salt Flocculation

The process of salt flocculation occurs between fine-grained particles that are charged. The charge may originate in two ways, one is from substitutions within the mineral structure, and the other from surface reactions. Most clay minerals carry a permanent net negative charge due to the substitution of cations of higher valence by cations of lower valence in the crystal structure. In contrast, charge originating at the surface is pH dependent; it is usually positive at low pH and negative at high pH. For a clay particle in suspension its charge is balanced by ions of opposite charge which are loosely held in a "cloud" surrounding the particle. In this cloud the concentration of the so-called counter ions is in excess of that in the electrically neutral bulk solution, and there is a deficiency of ions of similar charge to the particle (Fig. 4.10). In water of low ionic strength this disturbance in electrical neutrality extends

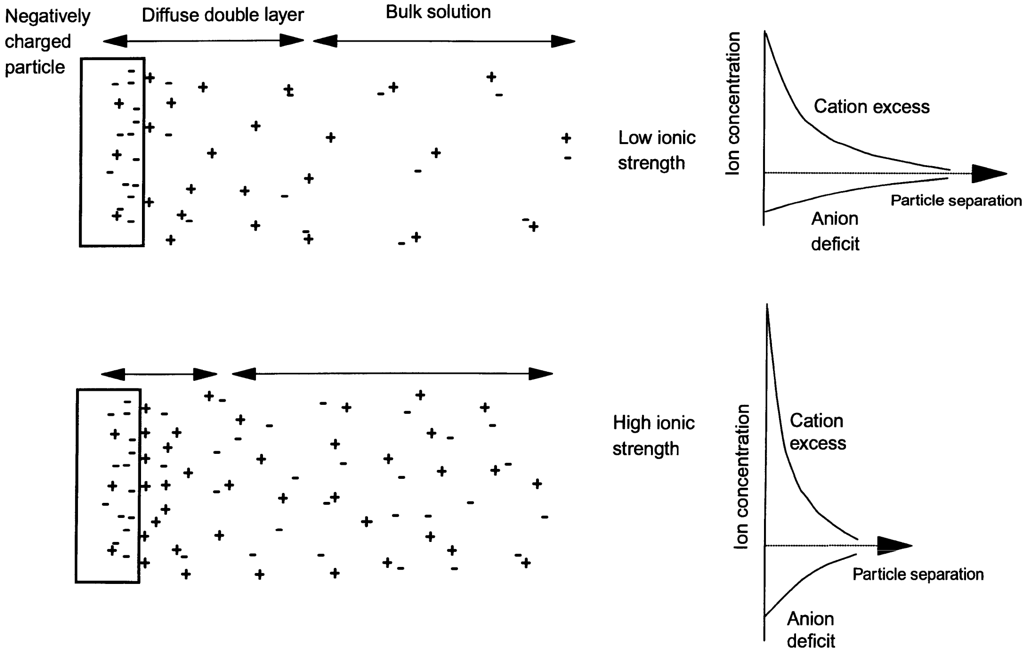

Fig. 4.10. Changes in the diffuse double layer thickness with changes in ionic strength. The net negative charge on a particle in suspension is shown to be balanced by an excess of cations (+) in the solution surrounding the particle. Together, this balanced region of charge is known as the diffuse double layer. In a solution of low ionic strength the diffuse double layer extends out much further from the particle surface than in a solution of higher ionic strength. The distribution of cations (+) and anions (–) in the solution is also shown graphically. (Modified from Arnold 1978)

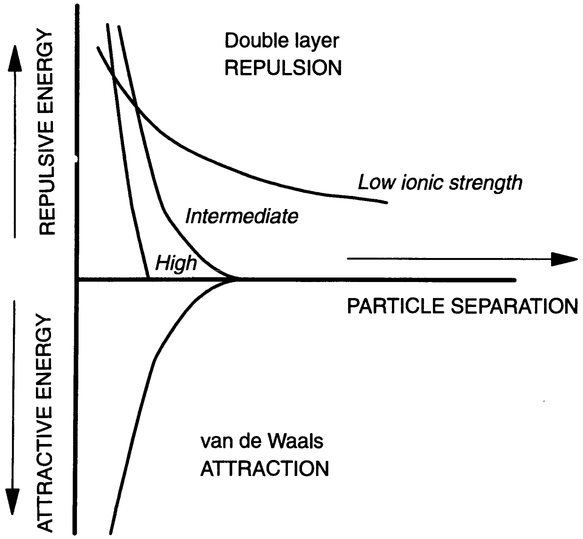

Fig. 4.11. Changes in repulsive energy as a function of particle separation for three different ionic strengths. Attractive energy due to van de Waals attraction remains constant so that at low ionic strength repulsive energy is greater than attractive energy, whereas at high ionic strength attractive energy is greater. (Modified from van Olphen 1977)

much further into the solution than is the case in a solution of high ionic strength (Fig. 4.10). As particles approach each other in suspension their clouds of counter ions interact and cause them to repel each other. In addition to this repulsive force, the particles have an attractive force due the van de Waals attraction. In solutions of high ionic strength the cloud of counter ions becomes so compressed (Fig. 4.11) that the particles may approach each other close enough for the van de Waals attraction between them to stick them together. This process is known as flocculation, or more specifically salt flocculation. The idealised distribution of charge from the clay particle and the cloud of counter ions surrounding it are often referred to as the "double layer", and the dynamic interactions between surfaces, ions in the surrounding "cloud", and the bulk solution are described by various diffuse double layer models (van Olphen 1977; Stumm 1992).

Salt flocculation occurs most obviously when there is a change in salinity, such as at the contact between fresh water and sea water in estuaries, or when fresh water flows into a saline lake. Changes in pH from river water (pH 5–6) to sea water (pH 8) will also affect pH-dependent surface charge and therefore may also influence the flocculation process. The rate at which flocculation occurs depends on the concentration of particles in suspension, the amount of agitation, i.e. the processes that may bring the particles together, and salinity which is the most important variable. Gibbs (1983) found that salt flocculation occurs already at salinities of 0.05 to 0.1%. Different cations also have different flocculating powers related to their hydrated ionic radii and their valence. For monovalent cations flocculating power decreases in the order Cs > Rb > NH_4 >K > Na > Li. The effect of valence means that the flocculating power of divalent cations may be 5–200 times, and that of trivalent cations 250–15 000 times, the power of monovalent cations (van Olphen 1977). In the absence of complicating factors, such as specific adsorption of certain ions, the critical concentrations of an ion required for flocculation are in the ratio 1 / (valency)^6.

In river waters, which typically have ionic strengths of <0.01 mol kg $^{-1}$, the diffuse double layer might extend over a thickness of about 100 Å for a monovalent cation as opposed to 50 Å for a divalent cation. In sea water with an ionic strength of 0.7 mol kg^{-1} the double layer for both monovalent and divalent cations would be less than a few Ångstroms thick.

4.3.3.2 Differential Flocculation and Settling

From theoretical considerations and laboratory experiments with saline solutions, it is well known that some minerals flocculate more readily than others (Hahn and Stumm 1970; Gibbs 1983). This is known as differential flocculation. The flocculation behaviour of a mineral depends on its surface charge density, such that smectites with their typically low charge density (high surface area/low charge) will flocculate less readily than illites and kaolinites which have higher surface charge densities (small surface area and/or high charge). However, the results of various experiments with natural clays are often contradictory. Most probably, this reflects the complex nature of the natural materials, including the presence or absence of surface coatings of organics and hydrous oxides which modify surface properties. Although it can be observed in the laboratory, it is doubtful whether differential flocculation is important in nature. Furhtermore, it is not certain whether salt flocculation is an important process in nature, as it may be overwhelmed by the aggregation effects of biological processes (Meade 1972; Eisma 1986). On the other hand, differential settling, due simply to differences in particle size, does appear to be a mechanism capable of sorting clay minerals in natural environments (Gibbs 1977). In particular, fine-grained smectites often appear to be preserved in suspension longer than other clay minerals (Chamley 1989).

4.3.3.3 Bio- and Organic Flocculation

Eisma (1986) reviewed a large number of studies on flocculation in estuaries and emphasized the paramount importance of biological processes. He concluded that the formation of flocs in estuaries is controlled by the origin of the organic matter present, the organisms producing it, and the (temporary) conditions of deposition and resuspension. According to Eisma (1986) salt flocculation plays only a minor role, if any, affecting only the very fined-grained materials <1 µm in size. Biological processes act to both bring the particles together, often as faeces, and keep them together as a result of the sticky properties of various mucopolysacharides produced by bacteria, algae and higher plants. The size of flocs is controlled by the binding strength of the organic matter, and they may also be broken up by organisms that consume the organic "glues". Furthermore, many natural clay particles are coated with organic, principally humic, substances. Much of the negative charge of such organic-coated clay particles may be due to the organic coatings themselves, which are weak polyelectrolytes. Just as the extent of the electric double layer varies with pH and ionic strength, so too does the extent and the configuration of the organic layer (known as the macromolecular absorbed layer). The stability, i.e. flocculation or dispersion, of much particulate matter may therefore be largely controlled by the interactions between such organic layers as the coated particles collide with one another (O'Melia and Tiller 1993). The nature of the coatings are themselves related to the origins of the clay particles, such as soil versus rock origins. Changes in clay-mineral distributions in estuarine sediments have been attributed to differential salt flocculation, but, given the likely minor role of this process, Eisma (1986) argues that they are more likely to be related to different sources, and to the mixing and dispersal patterns from various sources in the estuary and in the sea. Mixing of different continental and marine sources, rather than selective flocculation, now appears to be the consensus of most studies concerning the origin of estuarine clay mineral trends (Chamley 1989; Weaver 1989). A recent example is provided by the study of Algan et al. (1994) of the Solent region in southern England.

4.3.3.4 Properties of Aggregates and Flocs

Flocs and aggregates of particles are typically made from all of the diverse materials that occur in suspension, and as such they may have a wide variety of properties. However, almost all aggregates or flocs have substantial proportions of organic matter. Because of the aggregate structures, densities are lower than the component materials, while sizes may be up to one or two orders of magnitude larger than the components. The flocs found in estuaries are typically between a few to a hundred microns in size, although larger more loosely bonded aggregates known as macroflocs (Eisma 1986) have sizes up to 3–4mm. In the oceanic environment the largest aggregates are known as "marine snow" and these also may have sizes of up several millimetres in diameter. The larger flocs often trap silt and fine sand grains between clay particles, increasing their settling velocities.

For platy clay-mineral particles, flocs may be formed by several modes of particle interaction (van Olphen 1977). Adhesion between the oxygen planes of basal surfaces is known as face-to-face (FF) association; adhesion between broken-bond surfaces at the sides of the plates is known as edge-to-edge (EE) association; and adhesion between broken bonds surfaces at the edges of the plates and the oxygen planes of the basal surfaces is known as edge-to-face (EF) association (Fig. 4.12). The ease of formation of the different types of associations depends on the balance of repulsive and attractive forces which are controlled by the chemistry of the solution and the van de Waals interac-

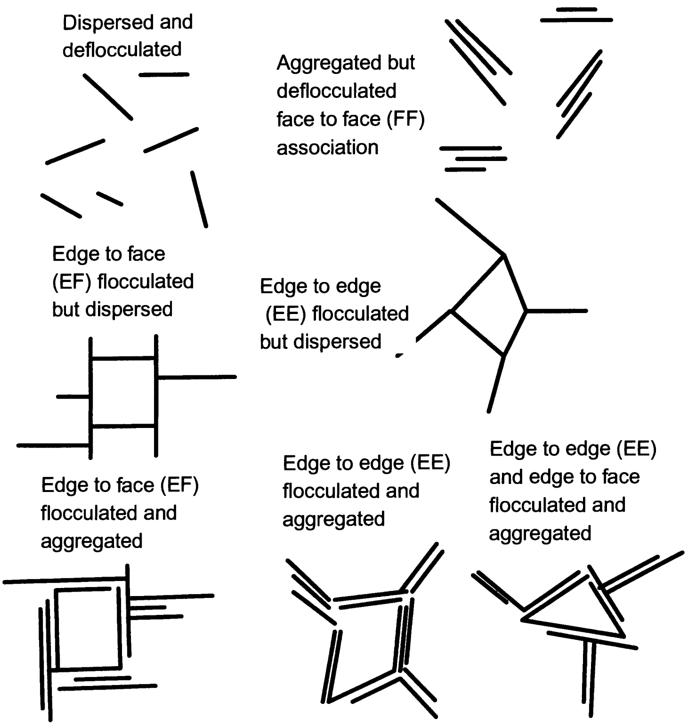

Fig. 4.12. Modes of platy clay particle associations in suspension and clay flocs according to the terminology of van Olphen (1977). (Modified from van Olphen 1977)

tion energy of the particles. The van der Waals interaction energy is different for the three types of association being highest for FF. Associations of the FF type give thicker particles whereas associations of EF and EE lead to much lower density, larger volume aggregates (Fig. 4.12). For the phyllosilicate clay minerals, F (face) surfaces carry permanent net negative charges due to substitutions within the mineral structure, whereas charges at edge sites are due to broken bonds and are pH dependent. Such charges become increasingly positive at low pH due to adsorption of H^+ ions and more negative at high pH due to adsorption of OH^- ions. EF interactions between particles are therefore more probable at low pH. The FF associations are sometimes referred to as tactoids. However, it should be pointed out that in natural materials, modes of association may be more closely controlled by any surface coatings on the particles rather than by the intrinsic properties of the particles themselves.

4.3.4 Erosion, Transport and Deposition by Wind

Although not as important globally as water, in certain areas of the world wind is an important agent of erosion, transport and deposition of clay minerals, and can contribute the dominant source of material to some deep-sea sediments.

Erosion and entrainment of clay particles by wind occurs principally in the worlds deserts and semi-arid areas where soil moisture content is most deficient. However, regions in more temperate areas can also be affected, especially where agricultural practices expose large areas of soil for part of the year. For example, Coote et al. (1981) have estimated that 160×10^6 tons of soil is lost annually by wind erosion of the Canadian Prairies, compared to an annual lost of 117×10^6 tons by water erosion. Apart from the degradation of soils, other environmental effects include the health hazards of dust and deterioration of air quality; in many parts of the world dust storms reduce visibility to less than 1000 m for 20 to 30 days a year (Nickling 1994). On the other hand, vast areas of the world are covered by wind-blown clay and silt, known as loess (Catt 1988), and the soils formed on these deposits can be very fertile.

Fine-grained aeolian sediments do not form important deposits in desert areas because the desert conditions ensure that they act principally as a source of material to other environments. Other types of terrain that may be important sources include glacial outwash plains, dried up lake beds, wadies, and alluvial fans.

The direct entrainment by wind, of particles smaller than about 80 μm in diameter is inherently difficult (Fig. 4.13) because at these small grain sizes sediment surfaces become aerodynamically smooth and interparticle forces increase in importance. As a result, most small particles, including clay minerals, are usually entrained by the impact of larger sand-sized grains and also by abrasion and break-up of larger particles during transport (Nickling 1994). Particles >20 μm in diameter are usually transported only within a few meters of the surface, but smaller particles may be transported to great heights (Fig. 4.14) and great distances. In arid regions dust storms typically transport material up to 3000 m height, and cover areas up to 500000 km^2 (Goudie 1983).

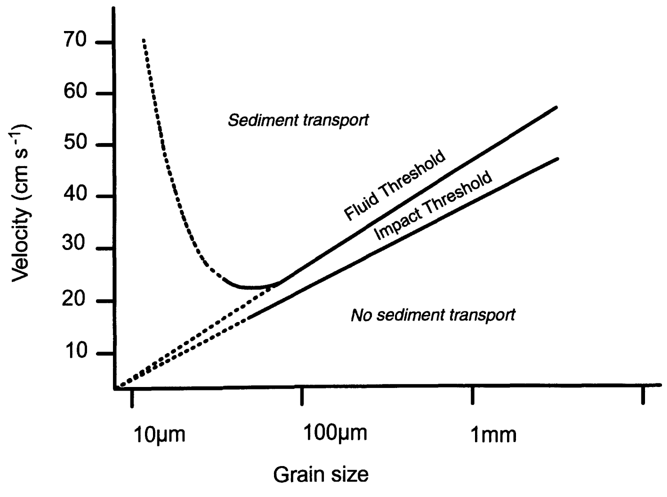

Fig. 4.13. Wind velocity required to entrain particles of various sizes. (Redrawn from Bagnold 1941)

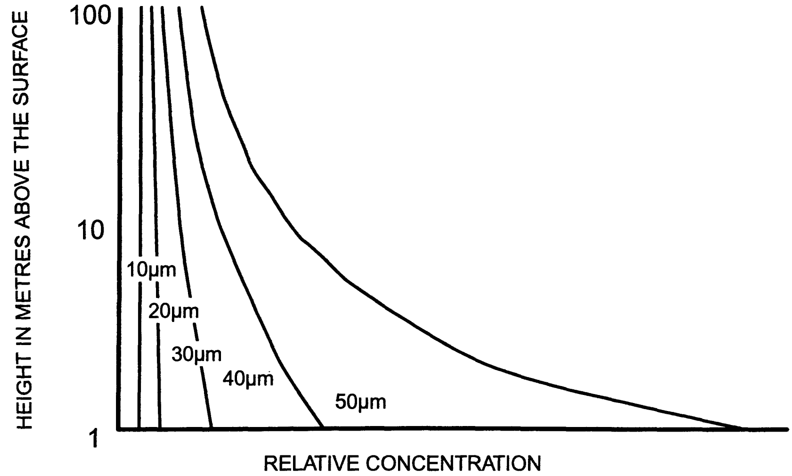

Fig. 4.14. Predicted changes in relative concentration of particles of different sizes with height in a severe wind storm. (Redrawn from Tsoar and Pye 1987)

Long-distance transport depends on many related factors including the texture of the eroding surface, ejection rate into the air stream, particle size and shape, and the turbulent structure of the wind (Nickling 1994). The maximum distance that particles of various sizes could be transported in suspension during a moderate storm was calculated by Tsoar and Pye (1987). For clay-size material, their calculations show that even moderate storms are capable of transporting particles over thousands of kilometres, whereas particles >20 μm in diameter are not likely to travel more than 30 km.

To a large extent the deposition of aeolian dusts depends on dampness and roughness of surfaces (Nickling 1994). Deposition increases over damp surfaces because of cohesion, and over open water there is no longer any further source of particles for entrainment. Changes in roughness, such as from unvegetated to vegetated ground, cause trapping of particles. Just as in sedimentation from water, fine-grained clay particles suspended in the atmosphere may become aggregated which increases their settling velocities. In the atmosphere, aggregation by scavenging and by shear become more efficient than aggregation due to Brownian motion, for particles >3 μm in size (Lerman 1979). The potential for long-distance aeolian transport is nowhere more evident than in the sediments of the deep ocean basins where, because of the paucity of other sediment sources, aeolian supply may become the dominant source of sediment. According to Windom (1969, 1975) dust transported by wind from deserts contributes from 10 up to 75% of the non-biogenic fraction of deep ocean sediments. The great variety of anthropogenic aerosol also suggests that there is likely to be a growing number of anthropogenic components in deep-sea sediments.

The major source areas for wind blown dust and dust trajectories are shown in Fig. 4.15. The most important meteorological conditions for dust

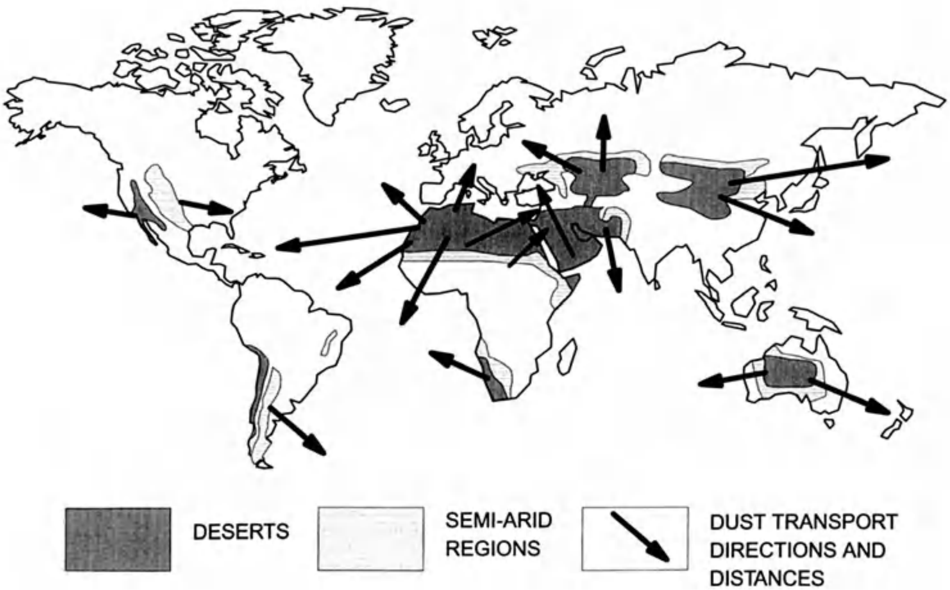

Fig. 4.15. Aeolian dust trajectories and transport distances from the world's desert areas. Long-distance transport involves particles with grain sizes of <20 μm. (Modified from diagrams in Péwé 1981; Pye 1987)

transport occur when low pressure fronts cross these regions, although locally many other weather patterns are capable of producing winds strong enough to entrain large amounts of dust. The composition of aeolian dusts varies greatly because it is determined by the minerals in the source area, although the influence of local sources diminishes with distance.

4.3.5 Erosion, Transport and Deposition by Ice

Ice can be an important agent of erosion, transport and deposition of clay minerals in two settings; glacial environments, and high-latitude oceans where the climate is seasonally cold enough for sea ice to develop (Fig. 4.16). At the present time glaciers cover about 10% of the Earth's surface, but during the Quaternary, maximum coverage was about 30% (Edwards 1986). As a result direct glacial deposits known as "tills", together with various sediments formed or fed by glacial outwash, form important deposits in many present-day temperate regions. There are many kinds of tills (Edwards 1986), but all are typically poorly sorted and often contain large amounts of fine-grained sediment forming a matrix for the coarser-grained material. Much of the fine-grained material is formed as "rock flour" generated by glacial grinding of rock against rock. Glacial meltwater or outwash also forms many kinds of sedimentary deposits (Edwards 1986), but as far as fine-grained sediments are

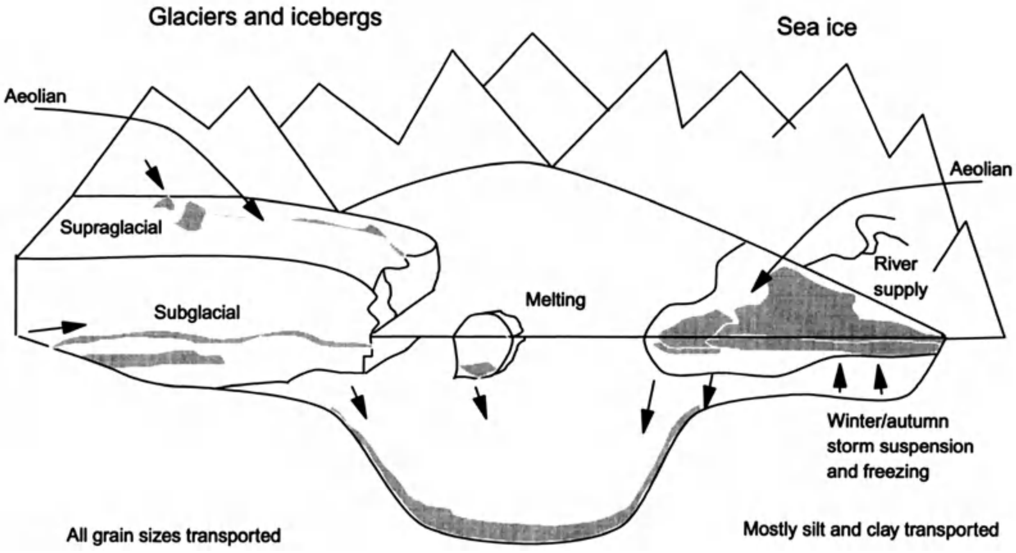

Fig. 4.16. Mechanisms of sediment incorporation into, and transport by, ice. One of the most significant processes for clay minerals is suspension freezing in shallow-shelf waters. Sediments transported by sea ice may be distinguished from those transported by icebergs by their grain-size distribution

concerned, the contributions of outwash deposits to wind blown loess (Catt 1988) and to glacio-lacustrine and glacio-marine sediments are probably the most important. Strong seasonal variations often result in changes in sediment load of glacial meltwater, resulting in the deposition of laminated deposits of silt and clay, which, when they are composed of annual couplets of silt and clay-rich layers, are known as varves.

Generally, temperate and subpolar glaciers produce more meltwater and release the largest quantities of suspended sediment which may form underflows or overflows depending on whether the receiving water body is marine or fresh, and on the concentration of material in suspension.

In addition to acting as fine-grained sediment sources to lacustrine and marine environments via meltwater, ice may accomplish direct sediment entrainment and transport in lakes and in the ocean by the process known as ice rafting. Where glaciers are concerned, ice rafting by icebergs is best known for its ability to transport and deposit coarse sediments in regions that normally receive only fine-grained pelagic sediment. As the ice drifts away from its source and begins to melt, coarse material incorporated within it is released and drops into the sediments below forming so called "drop stones". However, large quantities of fine-grained sediment may also be transported in this way by icebergs, and in sea ice it is typically the major sedimentary component (Barnes et al. 1982; Nürnberg et al. 1994).

Sediment distribution in sea ice is very variable but tends to be concentrated near the surface or in the interior of the ice in distinct layers, in some instances up to 5m thick (Nürnberg et al. 1994). Sediment concentrations are also very variable. Typically, they range from a few mg l^{-1} to several hundred mg l^{-1} but they may be as high as several thousand mg l^{-1}. Near surface accumulations may become more concentrated by cycles of melting and freezing of surface ice. The processes by which sediment may be incorporated into sea ice include aeolian transport to the ice, bottom freezing in shallows, slumping of cliffs, flooding by sediment laden river water, and bottom dragging by ice keels, but all to these processes are of minor importance compared to suspension freezing (Fig. 4.16; Barnes et al. 1982; Nürnberg et al. 1994). Suspension freezing occurs when strong winds and intense turbulence in combination with extreme subfreezing temperatures, cause shallow-shelf waters to become slightly supercooled, resulting in the underwater growth of ice crystals which interlock with clay and silt sediment particles suspended in the water by the turbulence due to the storm. With time, the crystals accumulate at the surface as a layer of slush ice which gradually congeals into a continuous layer of turbid ice. The process of suspension freezing is confined to shallow shelves, and then only occurs seasonally during the autumn and winter freeze up. It is also most effective on the widest shelves where the progressive seaward extension of freezing is most prolonged, and where the prevailing winds blow offshore, promoting the continuous advection of newly formed ice seawards. By these processes sea ice and icebergs may transport clay minerals over hundreds of kilometres (Ehrmann et al. 1992; Kuhlemann et al. 1993).

For both icebergs and sea ice, cycles of freezing and melting can cause sediment to become aggregated into pellets which remain intact and are deposited as pellets onto the sea bed in areas where the ice melts (Goldschmidt et al. 1992). Pellets from icebergs appear to be larger, up to 2 cm diameter, than those from sea ice, which are at most a few millimetres in diameter. Sea-ice pellets can also be distinguished from those of iceberg origin by the finer grain size of the component grains.

4.3.6 Modifications and Transformations During Transport and Deposition

During transport, and during cycles of transport and temporary deposition, by any number of the processes discussed in the previous sections, clay minerals may undergo both physical and chemical modifications and transformations. Principal among these modifications are those that occur by the processes of ion exchange and fixation, indeed many modern-day environmental pollution problems are determined by the way in which pollutants interact with the surfaces of clay-sized materials. A useful summary of the kinds of interaction that may occur is given by Yariv and Cross (1979).

4.3.6.1 Ion Exchange and Fixation

One important process that affects clay minerals during transport is ion exchange. Most clay minerals are negatively charged so that most ion exchange

Table 4.1. Typical ranges of cation exchange capacity (mEq/100 g) of various clay minerals and river-suspended sediment. Values for clay minerals are from Grim (1968), values for suspended sediment are from Kennedy (1965)

Kaolinite	3–15
Chlorite	10–40
Illite	10–40
Smectite	80–150
USA river-suspended sediment	6–48

involves cations which balance these negative charges. The amount of exchangeable cations required to balance the net negative charge is known as the cation exchange capacity (CEC). CEC is traditionally quoted in units of milliequivalents per 100 g of dry clay. An equivalent of an ion is its molecular weight divided by its valence. The net negative charge of the clay mineral may originate from substitutions within the mineral structure, and from surface reactions such as those with "broken" bonds. The proportions of charges of different origin vary from one mineral to another, for example broken bonds at the edges of crystals are the major cause of CEC for kaolinite, whereas substitution in the mineral structure is the major cause of CEC for smectites. Surface related charge is pH dependent, and by convention the CEC is normally measured at neutral pH. Typical CECs of the common clay minerals are given in Table 4.1. along with a range of CECs for suspended river sediments.

Suspended sediments usually contain a range of clay minerals along with various oxides, hydroxides and organic matter derived from soils, all of which may have important CECs. Bulk CEC measurements of such materials obviously depend on both the proportions and the properties of the various different components.

The kinds and proportions of different exchangeable ions associated with a clay-mineral particle depend on the kinds and proportions of different ions in the surrounding solution. If the composition of the solution changes, the exchangeable cations also change in a related fashion. Such cation exchange reactions are effectively instantaneous. Hence, changes in river water chemistry, either spatially or through time, will cause concomitant changes in the exchangeable ions associated with clay particles. Such changes in water chemistry may occur as a result of significant changes in the geology, soils, and weathering in different parts of a river's catchment, or they may occur due to human influences such as the drastic chemical changes that characterize acid mine drainage. However, the most obvious and dramatic change in water chemistry occurs when river waters eventually meet and mix with the ocean.

Typically, the exchangeable cation suites of clay minerals in fresh waters are dominated by Ca^{2+} ions. On entering sea water Ca^{2+} ions are exchanged principally for Na^{+} ions (Sayles and Manglesdorf 1977). To a lesser extent there is usually some increase in exchangeable Mg^{2+} and K^+ ions. Data from many early studies often showed that clay minerals took up Mg^{2+} from seawater in preference to Na^+, and this was sometimes suggested as indicating the formation of interlayer brucite and hence chlorite layers. However, these data are now known to be erroneous due to a flaw in the experimental procedure, namely the rinsing of samples with distilled water (Sayles and Manglesdorf 1977). Essentially, the dilution effect of rinsing sea water from the sample leads to the selective uptake of cations of higher valence as predicted qualitatively by Donnan equilibrium concepts. Experiments by Sayles and Manglesdorf (1977) showed that clay minerals in equilibrium with sea water contain a suite of exchangeable cations consisting of about 50% Na^+, 20–40% Mg^{2+}, up to 20% Ca^{2+} and around 5% K^+. The main variation appears to be in the relative proportions of the divalent cations Ca^{2+} and Mg^{2+}, but together their sum is usually constant at around 40%. The dominant change from Ca^{2+} to Na^+ is related to the change in relative abundance of these ions in fresh waters and sea water, respectively. However, the exchangeable cation populations of different clay minerals are not identical, because changes in concentrations of cations in solution are not the only factor involved in cation exchange. Certain cations may be selectively sorbed at various different exchange sites.

There are some data that suggest that the CEC of certain clay minerals may decreases on passing from river to marine waters. Processes such as K^+ fixation by vermiculitic clay minerals formed in soil environments may often be responsible for such observations (Weaver 1989). In this respect, Weaver (1989) notes that vermiculitic clay minerals are common in East and Gulf Coast rivers in the United States, but are not observed in the estuaries and marine bays. Weaver (1989) suggests that K^+ fixation may have resulted in much vermiculite reverting back to a more micaceous or illitic nature. Potassium fixation, and the resulting formation of illite layers, may also occur for smectites, particularly when they are subjected to cycles of wetting and drying (Srodon and Eberl 1984; Eberl et al. 1986). This process is most effective for smectites with high layer charge and may result in the formation of randomly interstratified illite/smectite with up to 50% of illite layers.

4.3.6.2 Pollutant Transport and Regulation

As a result of the same properties which give rise to cation exchange and fixation, clay minerals may also act as important transporters and regulators of environmental pollutants (Malle 1990; Förstner et al. 1990; Kühnel 1992). Many pollutants or contaminants such as heavy metals, like lead, zinc, cadmium and copper, tend to be quite insoluble in most surface waters and are strongly sorbed to surfaces. Consequently, both the amounts of many contaminants in the environment and their transport pathways, cycling, and ultimate removal, are not controlled by solubility, but by sorption–desorption reactions on sedimentary particulate matter (Schindler 1991).

The nature of sedimentary particulate matter is diverse, but in general it is the finest grain-size material, including clay minerals, with which most pollutants become associated (Baker 1980; Helios Rybicka 1992). This is because the finest size fractions have the largest surface areas and therefore dominate the surface properties of most sediments. It follows that the dispersal of pollutants in the environment depends on the processes which control the dispersal and accumulation of fine-grained sediments. In addition, the potentially toxic effects of pollutants and their bio-availability, depend on how the pollutants are sorbed to the clay-sized material, and how this may be altered by changes in the chemical environment such as pH and Eh, either during transport, or after deposition. The transport of pollutants by clay materials is not only important in surface environments, but also in the subsurface through the porous media of soils and aquifers by the process known as colloidal transport (McCarthy and Degueldre 1993).

An impressive example of the potential importance of clay minerals in regulating the effects of contamination is provided by the fate of radioactive caesium in the type of upland soils of Scotland that were contaminated following fallout from the Chernobyl nuclear disaster in 1986 (Cheshire and Shand 1991; Shand et al. 1994). Most upland soils in Scotland are high in organic matter, but immobilisation of caesium is related to the small amounts of mineral matter present within them, particularly the micaceous clay minerals because of their ability to fix caesium. This is an example of selective fixation. Fixation of caesium occurs in much the same manner as potassium, so that one might speculate that cycles of wetting and drying of the clay material, as might occur under natural conditions depending on the weather, may also be of some importance in governing the effect that the clay minerals have on the fate of caesium in particular environments.

Pollutants may be introduced to the environment from both point or diffuse sources. An example of a diffuse source, where its wider dispersal and later concentration is probably controlled by clays, is phosphorus applied to agricultural lands as fertilizer (Oglesby and Bouldin 1984). Movement of phosphorous in the environment may have disastrous ecological consequences by promoting the eutrophication of lakes and estuaries. The principal mechanism of phosphorus movement is by erosion and transport of clay particles to which phosphorus is sorbed (Froelich 1988).

4.4 Authigenic (in situ) Formation of Clay Minerals in Sediments

In many different sedimentary environments the new formation of clay minerals at surface or near surface temperatures is common place. Such in situ formation of a clay mineral in any environment, be it soil, sedimentary, diagenetic, hydrothermal or metamorphic, is known as authigenic formation.

Typically, in sedimentary environments such authigenic clay minerals are not abundant, but they have often been studied extensively because they contain much information about specific geochemical processes that are occurring there. Among the most common authigenic clays are various minerals of the smectite group, such as nontronite and stevensite, minerals of the mica group including glauconite and celadonite, various minerals related to the chlorites, and two fibrous clay minerals sepiolite and palygorskite. As a very general rule, in continental and evaporitic environments the most common clay minerals that form are usually Mg-rich, whereas in shallow marine environments they are Fe-rich, and in deep marine environments both Fe and Mg-rich varieties are common. This is illustrated in Fig. 4.17. Clearly, the geochemistry of both Mg and Fe must play a major role in the formation of authigenic clay minerals in surface and near surface environments.

4.4.1 Continental Authigenic Smectite

In continental environments, smectite formation by authigenesis and transformation processes is undoubtedly dominated by smectites formed in the soils that are an integral part of many sedimentary systems. Such smectite formation is dealt with in Chapter 3. Here, we deal only with authigenic smectites that form in continental aqueous sedimentary environments, either during or shortly after deposition, as a direct result of the chemistry of the depositional waters. Such smectite authigenesis is essentially restricted to saline alkaline lakes (Fig. 4.17), and is related to the unusual water chemistries that may develop in these settings. However, it should be emphasised that the conditions that give rise to clay mineral formation in alkaline lakes appear to be the exception, rather than the rule (Chamley 1989), although without detailed chemical and mineralogical data (e.g. Jones and Weir 1983) minor amounts of authigenic smectites might be difficult to detect amongst large amounts of detrital clays. In fact, the clay-mineral assemblages found in most saline, alkaline lakes are detrital (Droste 1961). Furthermore, where volcanic inputs coincide with high alkalinity, zeolite formation is often the prevalent type of silicate authigenesis.

The most commonly reported authigenic smectites in alkaline lakes are trioctahedral Mg-smectites, including stevensite, hectorite, and saponite (Dyni 1976; Trauth 1977; Jones 1986). In addition stevensite may occur interstratified with layers of kerolite, a disordered relative of the mineral talc (Eberl et al. 1982; Martin de Vidales et al. 1991). These clays often occur in carbonate lithologies disseminated throughout the sediment, but stevensite has also been reported in oolitic form from the Green River Formation (Tettenhorst and Moore 1978). Occurrences of peloidal and oolitic nontronite, a dioctahederal smectite, rich in Fe and Si, and poor in Al, are also known from recent sediments in lake Chad (Lemoalle and Dupont 1973) and lake Malawi (Müller and Förstner 1973).

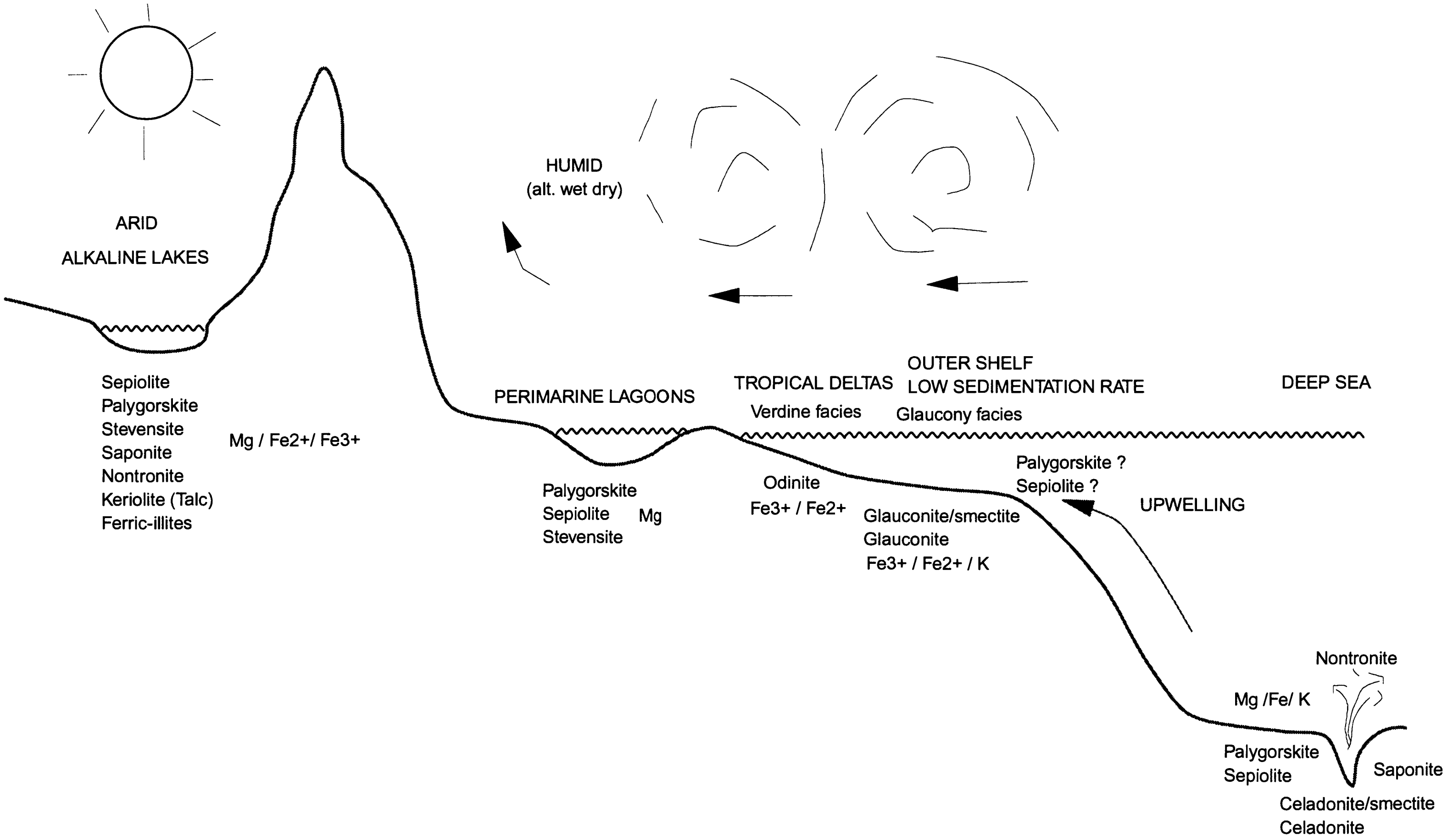

Fig. 4.17. Environmental situations in which many authigenic Mg-rich and Fe-rich clay minerals form. (Modified from Weaver 1989)

Often it appears that there is a transition from dioctahederal Al and Fe-rich smectites in lake marginal sediments, to more Mg-rich trioctahedral varieties in the lake-centre sediments (Trauth 1977; Darragi and Tardy 1987). Such sequences represent transitions from detrital-dominated sequences, supplied to the lake from the surrounding catchments, to authigenic dominated sequences in the basin centre. Because of the potential for mixing of detrital and authigenic smectites, the identification of authigenic varieties can be ambiguous and requires careful mineralogical characterisation. The problem is complicated because detrital inputs of reactive colloidal material, including smectite, probably serve as nuclei or templates for authigenic clay formation by some form of transformation mechanism, as emphasised by Jones (1986). Several of the most extensive deposits of lacustrine Mg-smectites are characterised by thick beds of these clays, often in close association with deposits of the fibrous clay minerals sepiolite and palygorskite. Such occurrences have much in common with those in peri-marine lagoonal environments in coastal locations (Fig. 4.17), where Mg is supplied periodically from sea water (Weaver and Beck 1977). According to Jones (1986), smectites such as stevensite precipitate under conditions of higher salinities and lower aqueous silica contents compared to the conditions that favor sepiolite and kerolite formation.

In many ancient continental evaporite basins, especially of Permo-Triassic age, Mg-rich chlorites and corrensite are very common clay minerals. Although many workers have interpreted these minerals as syn-sedimentary, they do not occur in any modern evaporitic environments, marine or non-marine. It seems more likely that they are the result of diagenetic alteration, either of the kinds of Mg-rich smectites described above, or of other early formed Mg-rich minerals, originally present in such sediments (Hillier 1993).

4.4.2 Marine Authigenic Smectites

In the marine environment, the formation of authigenic smectites can be divided essentially into three different categories. The first includes smectites associated with the alteration of volcanics and associated material, especially the hydrous alteration of volcanic glass known as palagonitisation. The second includes smectites formed in the mixing zones of ocean waters and plumes of hydrothermal fluids issuing from vents in the ocean floor. And the third category includes the so-called hydrogenous formation of smectite on the sea floor, by mechanisms that do not depend directly on volcanic and hydrothermal input but involve halmyrolysis (submarine weathering) and direct precipitation. The identification of authigenic smectites in marine settings is often a difficult task because of the potential for mixing with very similar detrital material of both allochthonous and autochthonous origin. This is particularly the case for the category referred to hydrogenous formation where the amount of authigenic smectite is often small. In most cases, where the authigenic formation of smectite is unequivocal, the smectites formed are nontronites. This contrasts with detrital terrigenous smectites which usually belong to the aluminous montmorillonite–beidellite series.

The palagonitisation of basaltic volcanic glass occurs by hydration and, among other minerals, results in the formation of nontronitic smectites. The process begins when the basalts are still hot, and this probably explains why many of the early formed smectites are trioctahedral Mg-saponites similar to those found where true hydrothermal alteration of basalts occurs deeper in the ocean crust. Later formed smectites are usually dioctahedral nontronitic varieties. In fact, considerable amounts of potassium are added in the process and many of the authigenic clay minerals are probably mixed-layer celadonite/smectites (Weaver 1989).

Fine-grained glassy volcanic material is also dispersed across large areas of the ocean floor, but there is no general agreement on whether or not it is an essential prerequisite for smectite formation in this environment. Weaver (1989) discusses numerous studies that have shown that there are a lot of fresh volcanic ash layers in buried Tertiary sediments, which have not altered to smectite. Such ash layers are the precursors of bentonite beds and indicate that most marine bentonites must be diagenetic in origin, rather than sedimentary.

One of the best-documented and spectacular sites of authigenic smectite formation are the hydrothermal discharge deposits found at many locations above the mid-ocean ridge system. Well-known examples are from the Galapagos spreading centre (McMurtry et al. 1983) and from the Red Sea. The authigenic clay minerals are typically true nontronites, and precipitate during the mixing and cooling of hydrothermal brines with ocean water. However, with time many appear to have altered to celadonite/smectite or glauconite/smectite by fixation of K^+ ions from sea water. Significant deposits of clay minerals are usually found only very close to the vents in the local depressions of the ridge system. However, dispersal of smectites from the plumes and transportation by ocean currents has been suggested to explain some occurrences of authigenic smectite in areas of the south-east Pacific and Indian Oceans that are far removed from the ridge systems. Indeed, hydrous-oxides of Fe and Mn are known to disperse laterally away from the ocean ridge vents to distances up to 2000 km, and there is every reason to believe that smectites will be similarly dispersed. Nonetheless, the distinction between transported hydrothermal clays and so-called hydrogenous clays is often obscure because it is difficult to find criteria with which to distinguish them.

Mechanisms envisaged for the hydrogenous formation of smectites include the halmyrolysis (submarine weathering) of volcanic glass, reactions between biogenic silica and Fe-oxy-hydroxide precursors, or possibly the ageing of amorphous ferrous-silicic complexes. Although there is plenty of evidence that the alteration of volcanic glass is not the only, or indeed the dominant, mechanism of smectite formation, the potential contribution of smectites from allochthonous sources often makes it difficult to identify mechanisms and origins with certainty. In this respect, smectites attributed to an hydrogenous formation often appear to be appreciably richer in Al and Mg compared with clearly authigenic nontronites, such as those at hydrothermal discharge sites: in many cases, this may be due to mixing of authigenic smectite with allochthonous Al-rich smectites derived from the continents.

4.4.3 Marine Glauconite and Glauconite/Smectite

One of the most extensively studied groups of authigenic clay minerals is that of glauconite and glauconite/smectite (Odom 1984; Odin 1988). These names refer to specific minerals and because of past confusion between the use of the term glauconite to refer both to a mineral and a facies, the term glaucony was recommended (Odin and Matter 1981) for use when reference is made to the aggregate green-grains and to uncharacterised minerals belonging to this group. This usage is followed here.

Typically, glaucony occurs as bright green rounded to subrounded pellets in the silt to sand size range. The pellets form near the sea water sediment interface by replacement of the fine-grained sediment/biogenic aggregates that comprise faecal pellets or, more commonly, the carbonate tests and contents of foraminifera and other microfossils. In detail, many types of substrates such as quartz, feldspar, phosphate or mica grains may also be replaced or serve as templates for glaucony growth, but faecal pellets and especially various carbonate grains are the most common. Glaucony may also occur as a film coating various types of substrate.

The distribution of glaucony in modern sediments is largely concentrated in continental shelf areas at water depths between 100 and 300 m (Fig. 4.18). Tropical latitudes appear to be especially favourable areas for glaucony development, but unlike the verdine facies (see below) glaucony is not restricted to tropical latitudes and is known to occur from latitudes 50 °S to 65 °N (Fig. 4.18). Deep-water occurrences down to 3000 m have also been documented, but it is not clear to what extent these may represent relict occurrences that formed originally at much shallower water depths. Generally, glaucony is characteristic of shallow, fully marine, shelf settings, especially where sedimentation rates are very low, such as towards the shelf edge away from areas of terrigenous input and active sediment transport. Indeed, slow sedimentation rates appear to be one of the factors necessary for glaucony formation. Often during periods of sea-level transgression successive substrates of biogenic and terrigenous origin, each characteristic of different water depths, may be glauconitised in turn.

The predominate granular form of glaucony as a replacement of grains, the preferential glauconitisation of silt and sand sized material rather than smaller particles, and the more advanced glauconitisation of the interiors of grains compared to their peripheries, all indicate that the genesis of glaucony

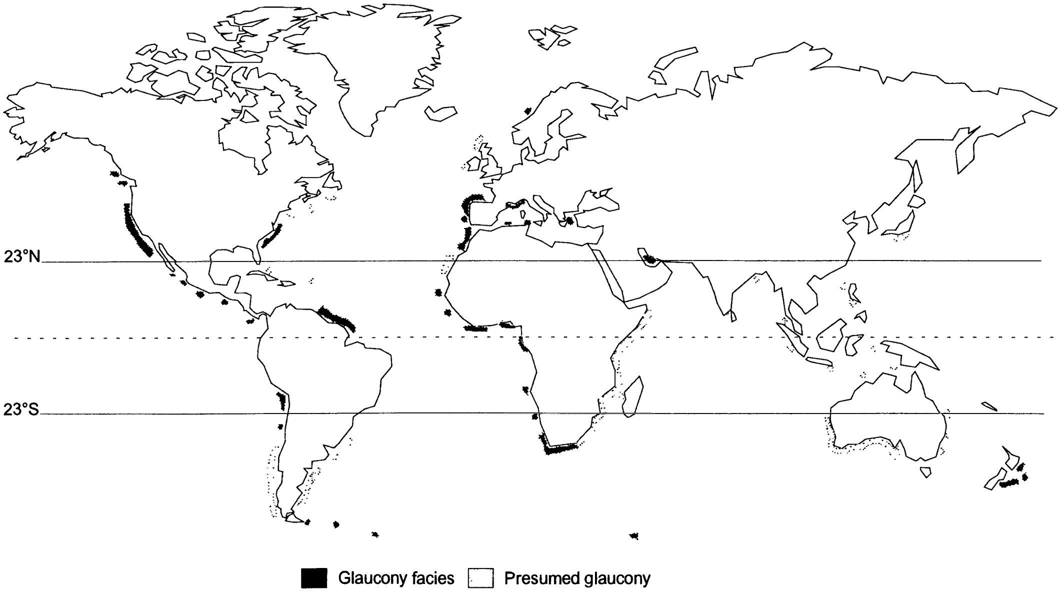

Fig. 4.18. Distribution of glaucony on the modern shelf. (Modified from Odin 1988)

is favoured by a semi-confined micro-environment (Odin and Matter 1981). Semi-confined means the environment is partially isolated from sea water via the microporous substrate. Initially, the first phase to form in the glauconitisation process is an Fe-rich smectite with about 20 wt% Fe_2O_3. With time, the potassium content increases and the structure of the mineral changes from smectite, through mixed-layer glauconite/smectite, towards the micaceous end member glauconite. This process occurs at the sea floor with most of the K^+ ions apparently supplied from sea water, because if the grains are buried the process is stopped at whatever stage it may have reached, presumably because the ready supply of K^+ ions is cut off. X-ray diffraction patterns of glaucony grains from the present-day continental shelf, illustrated by Odin (1988), demonstrate that the process of glauconitisation may proceed all the way to the micaceous end member glauconite at the sea floor. The enrichment in Fe occurs before K, and the amount of Fe shows little or no change from smectite to glauconite. Odin and Matter (1981) described the continuous progress of the glauconitisation process in terms of four stages (Fig. 4.19). The first (nascent) stage is characterised by the relatively rapid alteration of the support material, and the establishment of the microporous semi-confined environment. At the second (slightly evolved) stage the porosity allows ionic exchange with both sea water and the interstitial water of the underlying sediment. The grain becomes green and begins to loose most of the structures of the original support material. In the third (evolved stage) the structure of the support has disappeared entirely and preferential clay growth in the centre of the grain causes the grain to grow bigger, and the exterior of the grain to develop cracks. By this stage K_2O content has reached 6–8%. The final (highly evolved) stage corresponds to grains that have been completely replaced by minerals near the glauconite end member, and the surface cracks have been filled by less-evolved glaucony to form a more rounded outline. Potassium contents of glauconitic minerals are directly related to the proportion of expandable layers present. Other chemical changes which accompany the obvious increase in K^+ are more difficult to discern because of the heterogeneous nature of most glaucony samples (Odom 1984).

Various theories regarding the origin of glaucony have been advanced over the years (Odin 1988). Currently, most workers favor the neoformation theory. Much of the evidence that supports this theory has been gained by use of the scanning electron microscope to demonstrate the obvious neoformed morphologies of glaucony. Other pertinent observations that support the neoformation theory are: (a) glauconitization of biotites occurs by growth between sheets; (b) non-micaceous substrates may be entirely replaced; and (c) glaucony growth may be displacive, leading to the break up of shell substrates.

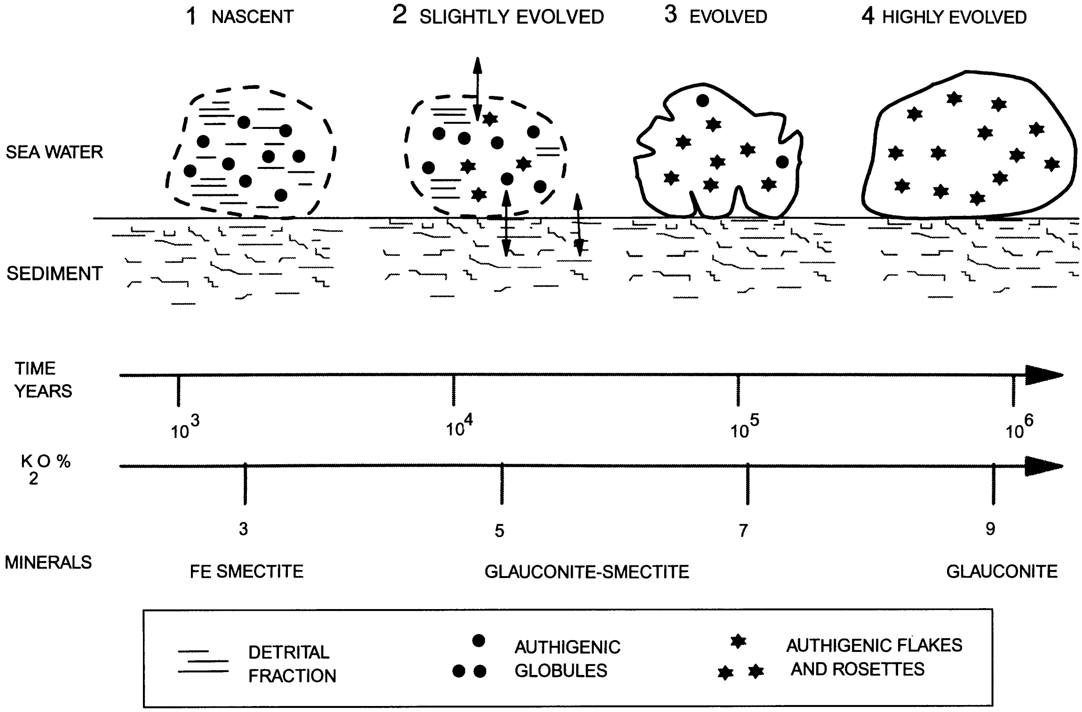

Fig. 4.19. The four stages in the development of pelloidal glaucony

4.4.4 Celadonite and Celadonite/Smectite

Celadonite is a mineral very similar to glauconite in composition, especially in its Fe content, the main chemical differences being that celadonite is usually richer in Si and Mg and poorer in Al than glauconite (Odom 1984; Odin 1988). The principal difference concerns their occurrences, in that unlike glauconite, celadonite never occurs in granular form and is characteristically a product of the submarine weathering of volcanics. However, mode of origin is not a criterion for the identification of glauconite or celadonite. Typically, celadonite forms by the alteration of basalts under oxidising conditions, probably at temperatures above those of ambient ocean waters. Mg and K are provided from sea water and Fe and Al from the rock.

Morphologically, celadonite usually occurs as well-shaped laths, in contrast to the more anhedral globules, box-work and irregular lamellar structures of glaucony. These differences may be related to the fact that a lot of glaucony is glauconite/smectite, whereas celadonite/smectite is less frequently reported with most material being close to end member celadonite. This may be due in part to the higher temperatures associated with celadonite formation, the more concentrated solutions involved, and the greater availability of pore space allowing the growth of euhedral crystals.

4.4.5 Non-Marine Glauconite and Ferric Illite

Glauconite-like clay minerals and clay minerals known as ferric illites have been reported from a number of lacustrine environments. Early data on these minerals were summarised by Porrenga (1968). Characteristically, these minerals are found in green clays often associated with carbonates and gypsum, and are thought to form by the alteration of smectite. Their contents of ferric iron (around 10 wt% Fe_2O_3) are intermediate between marine glaucony, and ordinary illites which are also more aluminous. Like marine glauconite, they are believed to form at surface temperatures. More recently, they have been reported by Norrish and Pickering (1983) from Oligocene sediments of lake Eyre and from desert soils in Australia, and by Deconinck et al. (1988) from the Purbeckian of the Swiss and French Jura. Deconinck et al. (1988) suggested that the Purbeck illites may have formed by cycles of wetting and drying, which is certain to be a common process in many lacustrine settings because of frequent changes in lake level. However, experimental work on wetting and drying cycles has shown that this process can only form randomly interstratified illite/smectite with up to 50% illite layers (Eberl et al. 1986). Typically, ferric illites and/or non-marine glauconites, including the Purbeck examples, are much more illitic than this, so that another process such as neoformation, as documented for marine glaucony, may be involved. More recently, Jeans et al. (1994) has shown that much of the illite in the Permo-

Triassic continental facies of western Europe has characteristics like those of ferric illite, and it is suggested that it may have formed in coeval desert soils before being eroded into the adjacent sedimentary basins.

4.4.6 Minerals Related to Chlorites and the Verdine Facies

The formation of a true chlorite (14 Å, 2:1 + 1 mineral) in recent sediments has never been demonstrated. Early reports in the literature of sedimentary chlorite formation, which usually refer to only minor amounts of 'chlorite', are often equivocal in their identifications, or use the term 'chlorite' in a different sense to that which is understood today. However, Fe-rich minerals with a 7 Å basal spacing, closely related in composition to chlorites, are relatively common components of green-grains in recent sediments at water depths of 10 to 60 m off the coast of many deltas in tropical regions, such as the Niger delta. Formerly, many of these occurrences where described as chamosite (e.g. Porrenga 1967), and then subsequently as berthierine (e.g. Odin and Matter 1981) when the name chamosite was reserved for a true (14 Å) Fe-rich chlorite. Like chlorites, the Fe in berthierine is mainly Fe^{2+} and it is a trioctahedral mineral. However, extensive study of these recent and subrecent green-grains by Odin (1988) showed that in almost all cases the 7 Å mineral in these grains contains predominantly Fe^{3+}, and is richer in Si and Mg, and poorer in Al compared to the berthierines described from sedimentary rocks. This led Odin (1988) to suggest that this mineral was a new type of phyllosilicate to which he gave the provisional name phyllite V. Subsequently, Bailey (1988) proposed the new name odinite. Odin (1988) has studied the minerals in these green-grains very extensively and has shown that in addition to odinite, the green-grains are sometimes dominated by a chemically similar mineral which more closely resembles chlorite in structure but contains a swelling component. In older green-grains, of 1000 to 20000 years, the chemistry in still similar, but minerals with other structures are present including a 7–14 Å mixed layer, a ferric chlorite, and a pyrophyllite-like clay mineral. Collectively, all of these minerals comprise the verdine facies.

As mentioned above, the verdine facies occurs in relatively shallow marine waters and appears to be confined to tropical latitudes (Fig. 4.20), in contrast to the glaucony facies which occurs at greater water depths and is not confined to the tropics (Fig. 4.18). However, like glaucony, the substrates that are replaced are similar, the minerals of the verdine facies forming in the semi-confined micro-environments of faecal pellets, foraminifera tests, and porous mineral grains.

The latitudinal restriction of the verdine facies is curious. Offshore from the Niger delta, Porrenga (1967) noted that the seaward boundary to the verdine (chamosite) facies coincided with the thermocline. From this he inferred that a water temperature >20 °C was necessary for verdine (chamosite)

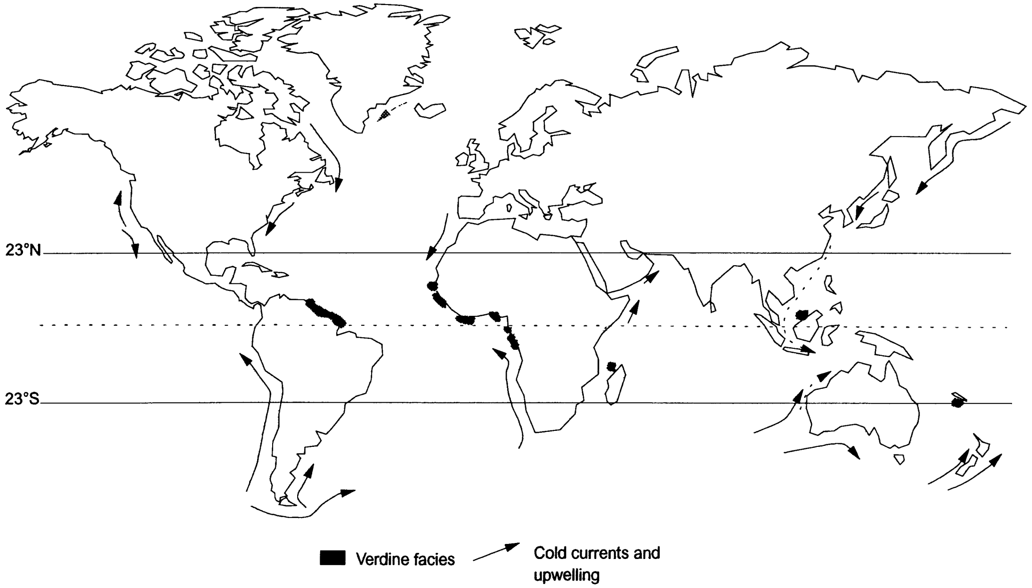

Fig. 4.20. The distribution of the verdine facies on the modern shelf. Modified from Odin and Matter (1981) and Odin (1988). The verdine facies appears to be confined to tropical areas mostly in association with fluvial inputs (which may provide a source of reactive colloidal Fe) and appears to be absent from shelf areas crossed by cold currents associated with upwelling, suggesting some temperature control

to form. An effect of temperature is also suggested by the observation of Odin and Matter (1981) that verdine (berthierine) is absent on continental shelves crossed by the cold oceanic currents that are frequently associated with areas of upwelling (Fig. 4.20). Another important factor may be the supply of Fe. Rivers draining tropical regions frequently carry high loads of dissolved and colloidal forms of Fe that would be reactive and available for clay formation in near shore sediments.

Although the verdine facies does not contain iron-oolites, many ancient marine sedimentary oolitic ironstones contain minerals which may have formed under similar conditions to those of the verdine facies. This hypothesis supposes that the minerals berthierine and chamosite found in oolitic ironstones, and which contain dominantly ferrous iron, formed from minerals such as odinite with dominantly ferric iron, as a result of burial diagenetic processes. Its attraction is that it is no longer necessary to try to explain the formation of minerals which require both reducing conditions and agitated waters at one and the same time. Instead, the minerals can be formed in essentially oxidizing conditions, and the Fe present reduced after burial along with other structural modification to produce berthierine and, with increasing temperature, chlorite (Hillier 1994).

The relationship of the verdine facies to other authigenic Fe-rich minerals in the marine environment is shown schematically in Fig. 4.21. In the deep ocean basins, various types of true chlorites, corrensite, and mixed-layer chlorites are commonly described as alteration products of submarine basalts, but the fluids involved in the formation of these minerals are undoubtedly hydrothermal.

4.4.7 Sepiolite and Palygorskite

The fibrous clay minerals palygorskite and sepiolite are relatively rare minerals, but locally, in certain lacustrine and peri-marine basins, they may occur in abundance. Palygorskite may also be found in many deep-sea deposits, while sepiolite is more rarely reported and usually less abundant. Both minerals are Mg-rich, especially sepiolite, but they are also very high in Si, and so their formation is favoured in environments where amorphous Si is abundant. There is some question as to whether they are formed by transformation of pre-existing phyllosilicates, or neoformed by direct precipitation from solution. According to Jones and Galan (1988) both sepiolite and palygorskite commonly form by a dissolution–precipitation mechanism which incorporates components of pre-existing detrital material.

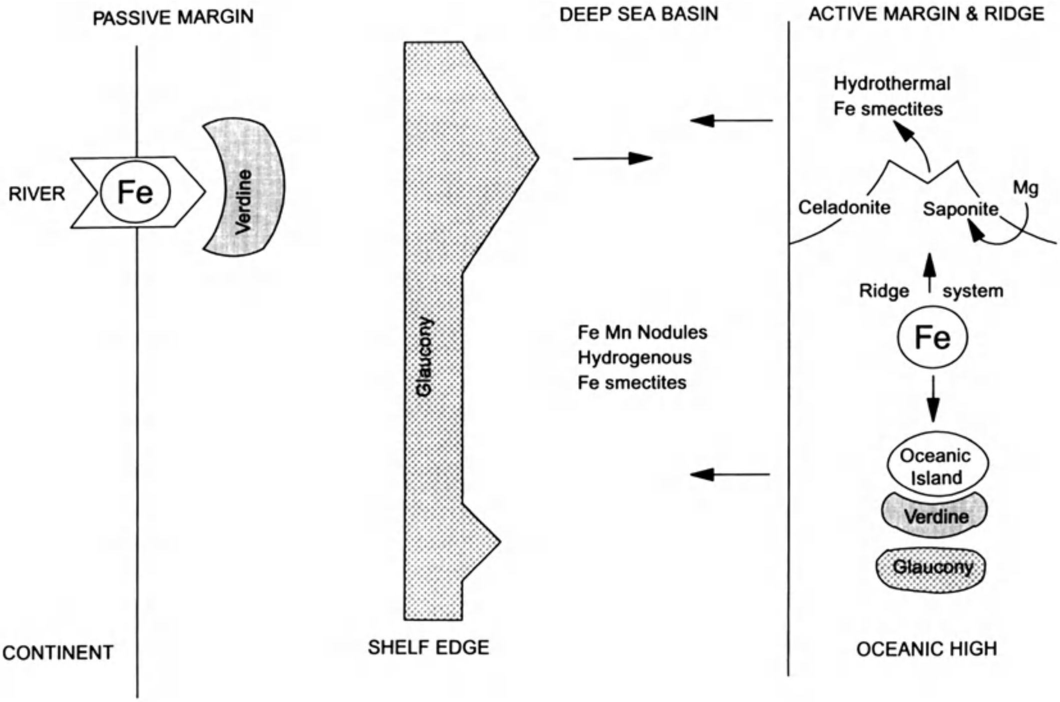

Fig. 4.21. The distribution of the verdine facies in relation to the glaucony facies and other iron-bearing marine clays. Fe is supplied to the marine environment from two main sources; rivers, and hydrothermal processes at active margin and ridge systems. (Modified from Odin 1988)

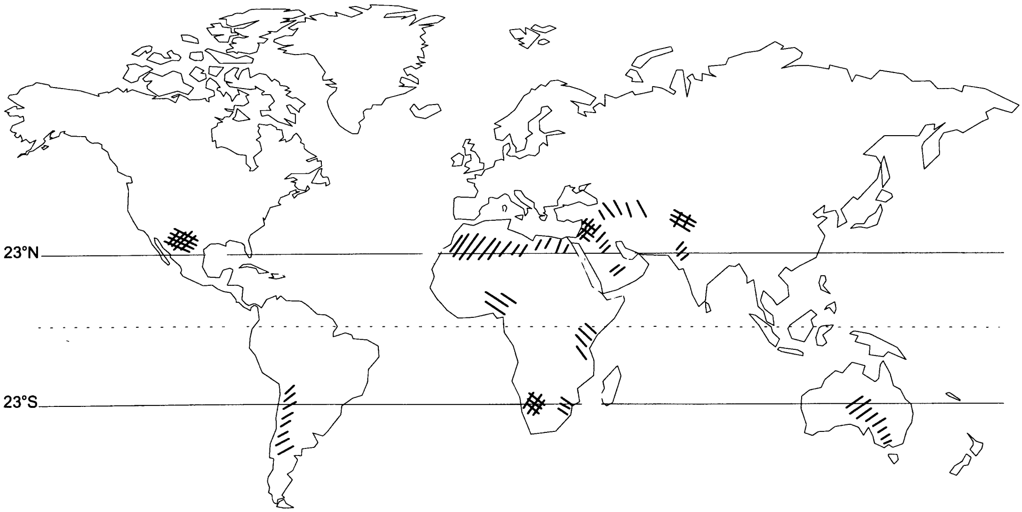

Fig. 4.22. The distribution of both continental and marine occurrences of palygorskites and sepiolite for the late Pliocene to Holocene. Oceanic occurrences are shown by the *dotted shading* and continental soil data by *diagonal shading*. *Cross-hatching* indicates occurrences where soils are superposed on sedimentary basins with palygorskite. (Modified from Callen 1984)

The distribution of both continental and marine occurrences of palygorskites and sepiolite for the late Pliocene to Holocene is shown in Fig. 4.22. Shallow water lacustrine and peri-marine occurrences are found only in arid to semi-arid climatic settings adjacent to areas of intensive chemical weathering and subjected to strong evaporation but also characterised by frequent mixing with supplies of fresh water. A supply of fresh water is necessary to maintain the brackish conditions and pH range 8 to 9 favourable for these minerals. Restricted detrital terrigenous input is also a characteristic feature, and various carbonates and cherts are typical associated deposits. Often there is a zonation of minerals from sepiolite in the basin centre to palygorskite in more marginal locations where the influence of detrital materials entering the basin becomes evident. This may reflect the fact that palygorskite formation requires a supply of Al, a fact which seems to be corroborated by observations that sepiolite is usually favoured over palygorskite in cases where fresh water supplies are replenished by ground waters rather than surface run off that is certain to be richer in aluminous colloidal material.

In deep sea deposits there is general agreement that some palygorskite and sepiolite may be formed in situ as a result of hydrothermal activity combined with the influence of sea water. Authigenic origins have been suggested for the more widely dispersed occurrences over large areas of the ocean floor, but in their reviews of these occurrences both Weaver (1989) and Chamley (1989) favor an origin by inheritance from sources on the continents via aeolian and marine transport, although they do not rule out authigenic occurrences. Indeed, it is now clear that the delicate fibres of these minerals tolerate transport more easily than was once thought to be the case (Chamley 1989). Observations in support of an inherited origin for many occurrences include the following; present and past occurrences in the deep sea correspond with the distribution of tropical to subtropical climatic belts suggesting a supply from contemporaneous continental deposits confined to these climatic zones (Fig. 4.22); past concentrations in the deep sea correspond to times of greatest abundance (potential source) on land; there is no correlation of occurrences to any particular sediment type, as there should be given that particular geochemical conditions are required; and electron micrographs show the mineral fibres to be short and broken giving the appearance of having been transported and redeposited. Cases where delicate fibre morphologies are preserved are often attributed to transport by wind. Note that, as well as lacustrine and peri-marine deposits, many calcareous soils in arid zones represent potential sources of palygorskite and sepiolite; the dry arid conditions often promoting aeolian transport of clay material.

However, the question of the more widespread authigenic formation of palygorskite and sepiolite in deep marine sediments is still unresolved. For example, in Miocene marine sediments from the North Carolina continental margin, palygorskite and sepiolite appear to be demonstrably authigenic because of their pore-bridging arrangement (Allison and Riggs 1994). They occur in association with authigenic dolomite, abundant siliceous microfossils, and phosphate and organic-rich sediments. This association is believed to be related to upwelling of nutrient-rich waters. Dolomite and Mg-rich clays are suggested to have formed from the early interstitial pore waters under anaerobic conditions. An association of palygorskite and sepiolite with phosphorites has been mentioned previously by Bentor (1980) and it is interesting to note that several of the deep sea occurrences shown in Fig. 4.22 coincide with areas of upwelling as shown in Fig. 4.20. As pointed out by Jones and Galan (1988), opinions on the origin of deep sea occurrences of the fibrous clays have ranged between the extremes of asserting that all are detrital, to asserting that all are authigenic. According to Chamley (1993), like smectites, certain occurrences of palygorskite and sepiolite can pose difficult problems in determining which side of the autochthonous–allochthonous boundary they lie on. Thus it appears that more investigation of marine occurrences is required.

4.5 Mineralogical Patterns in the World Ocean

Several workers have compiled data on the distribution of the major clay minerals in the oceans. Notable contributions include the work of Biscaye (1965), Griffin et al. (1968) and Rateev et al. (1969); the most recent compilation is that of Windom (1976). Such compilations show that the largest-scale feature of the distribution is a broad latitudinal zonation of the different clay minerals (Figs. 4.23, 4.24, 4.25, 4.26). This feature is related to the different latitudinal climatic zones that cross the continents and the consequent weathering regimes, and is testimony to the dominant detrital origin of oceanic clay-mineral assemblages from terrigenous sources. This dominant detrital origin is also attested by many other observations including; the absence of isotopic re-adjustments with respect to the composition of sea water; the radiometric age of the clay minerals which typically corresponds to the average age of rocks on the adjacent continents, and which is often older than the age of sedimentation or even the ocean basin itself; the flux of terrigenous clay particles to the ocean

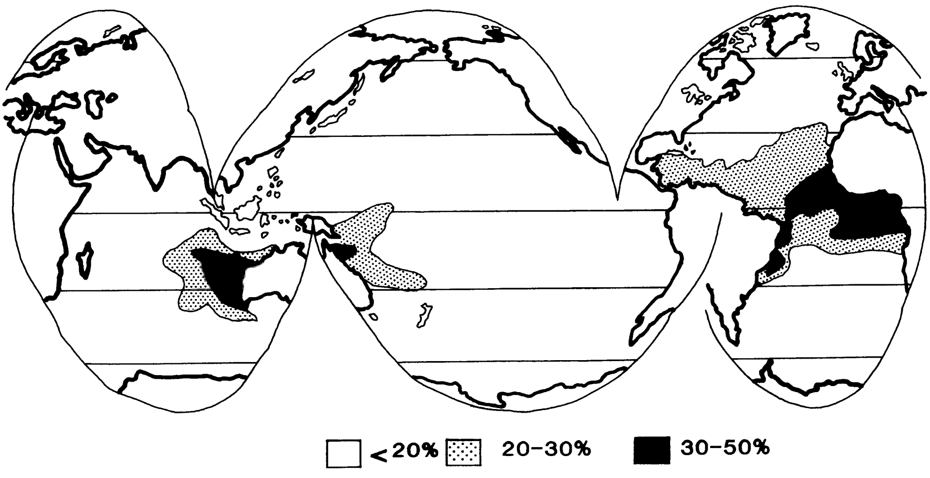

Fig. 4.23. The distribution of kaolinite in the world ocean. (Modified from Windom 1976)

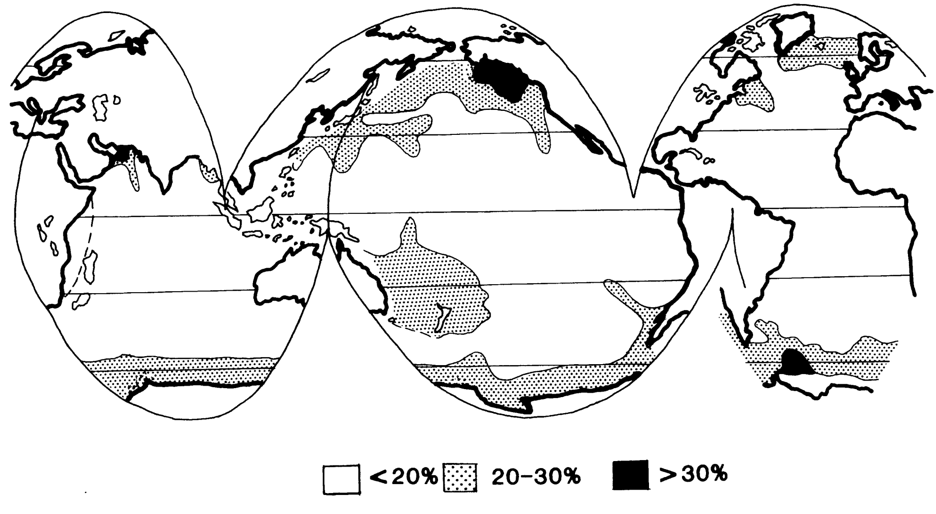

Fig. 4.24. The distribution of chlorite in the world ocean. (Modified from Windom 1976)

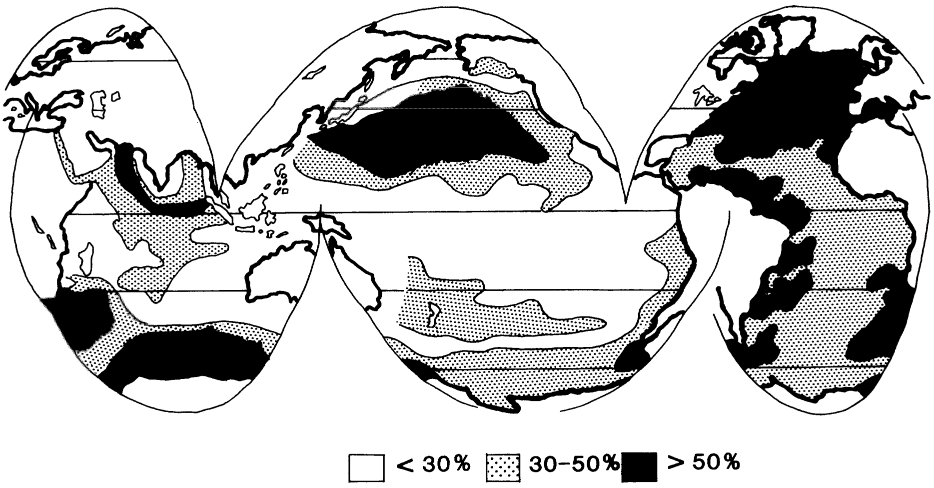

Fig. 4.25. The distribution of illite in the world ocean. (Modified from Windom 1976)

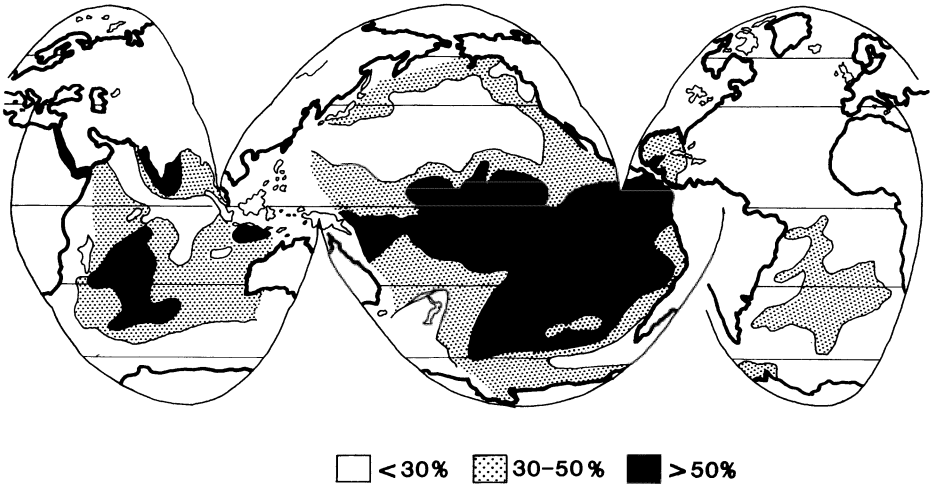

Fig. 4.26. The distribution of smectite in the world ocean. (Modified from Windom 1976)

(Fig. 4.5) which is much greater than the flux of dissolved material; the absence or extremely weak character of mineralogical transformations at the continent ocean boundary; the essentially physical nature of sorting and sedimentation during marine transport; and the constant similarity in any particular region between the clay mineral composition of rocks and soils and that of fluvial sediments, marine suspensions, aeolian dusts and the sediments from the ocean bottoms (Chamley 1989, 1993; Weaver 1989).

The two minerals that illustrate this latitudinal zonation best are kaolinite and chlorite. The distribution of kaolinite (Fig. 4.23) shows that it is concentrated in low latitudes where it is largely derived from kaolinite-rich soils developed by chemical weathering in humid climates. In contrast, chlorite is one of the most easily weatherable phyllosilicates and is one of the first minerals to be destroyed where soils are well-developed and chemical weathering intense. Consequently, it is usually minor or absent in low latitudes, but abundant and concentrated at high latitudes where physical weathering predominates (Fig. 4.24). In the southern oceans the increase in chlorite abundance below 50 °S coincides almost exactly with the northern limit of material transported by ice from Antarctica (Fig. 4.24)

The distributions of illite (Fig. 4.25) and smectite (Fig. 4.26) also show broad latitudinal patterns, but these are not as well defined as those of kaolinite and chlorite. Like chlorite, illite tends to increase towards the polar regions due to the decrease in chemical weathering, but it is also more abundant in northern than in southern oceans. This appears to be related to the concentration of the continental landmasses, and therefore terrigenous sources, in northern latitudes. The largest-scale features of the distribution of illite are similar to those for quartz. The grain-size characteristics of quartz indicate a dominantly aeolian supply and the illite is also thought to be dominantly aeolian, but with river inputs becoming more important toward the continental margins. (Chamley 1989; Weaver 1989).

Smectite abundance (Fig. 4.26) also shows a distribution that is quasi-parallel to the continental climatic zones, but it is much more abundant in the southern oceans than in northern oceans. Again this may reflect the distribution of the continents in that large areas of the southern oceans receive comparatively little terrigenous supply. Volcanic contributions, both subaerial and submarine, which may alter to smectite, are likely to be proportionally more important, as are smectites formed by other authigenic processes at the sea bed.

The average clay mineral composition of the world ocean has been estimated by Windom (1976). Illite and smectite are the most abundant minerals accounting for about 35% each, whilst chlorite and kaolinite account for about 15% each. Weaver (1989) estimates that about half of the smectite is authigenic. In detail, much of what is termed smectite or illite is often intermediate mixed-layer material (Weaver 1989). Other, but less common, clay minerals that may also be locally important include palygorskite and sepiolite which are characteristic of low latitudes (Fig. 4.22) and talc which is often thought to be entirely from anthropogenic sources, but may also have some authigenic input.

Still at a global scale, other features of the distribution of clay minerals in the oceans serve to emphasize that the latitudinal climatic control via weathering is only a very general pattern. These include: physical weathering dominated regimes related to mountain ranges at low latitudes; the minerals that are available where physical weathering is concerned; and the processes of transport and deposition that are responsible for the wider dispersal of the minerals in the oceanic environment. All of these can produce clay-mineral distribution patterns that are in total contradiction to the general latitudinal pattern described above. Furthermore, even at the scale of a depositional system like a delta, such variables may leave clay-mineral signatures that are totally unrelated to the contemporaneous latitudinal climatic zones. Examples, of large-scale discrepancies include abundant kaolinite and smectite in some polar regions simply due to their abundance in Mesozoic rocks of the sediment source area, and abundant kaolinite in the ocean sediments adjacent to modern-day desert regions because it has been stored for some considerable length of time in soils formed under wetter, more humid conditions (Singer 1984).

4.6 Environmental Interpretation of Clay Minerals

All environmental interpretations of sedimentary clay minerals are fundamentally based on determining the origin of the clay minerals present. Without doubt, this is a difficult and challenging task, because the origins of clay minerals are diverse, and because of the very nature of the sedimentary realm where clay minerals, of many different origins, are normally mixed together by various sedimentary processes. Nonetheless, clay minerals do contain information on many aspects of their origin, related to sources and provenance, dispersal patterns, depositional environment, climate, and even tectonics and eustasy (Chamley 1989). The previous sections of this chapter were devoted to the origins of clay minerals in sediments from the standpoint of the fundamental processes that determine them. Environmental interpretations are built upon our understanding of these processes and our ability to recognise the results and products of them in the sedimentary record. The purpose of this final section is to illustrate the kinds of studies that can be made and the sort of information that may be obtained, but with emphasis always on the problems of environmental interpretation that the careful investigator must try to tackle. More details of various aspects of environmental clay mineralogy, and compilations of many case studies, can be found in the detailed books of Chamley (1989) and Weaver (1989).

4.6.1 Sedimentary Environments and Provenance

Principally there are two ways in which studies of clay minerals may contribute to the analysis of sedimentary environments: firstly, the presence of certain authigenic clay minerals may be indicative of a particular depositional regime, and secondly, detrital clay minerals can be used as tracers of sediment transport processes, dispersal, and provenance. A classic example of the use of authigenic minerals is the inference that the presence of glaucony indicates a shallow marine environment of deposition. Another example is the presence of authigenic smectites or the fibrous clay minerals sepiolite and palygorskite, in lacustrine sediments from which inferences can be made concerning the chemistry of the lake waters from which they were deposited. Much of the background to these sorts of interpretations has been given previously in the section on authigenic clays. However, the point that must be made here is that there are exceptions of which the investigator must be aware, such as non-marine glaucony, for example. The formation of glaucony occurs under a specific set of geochemical conditions, and although these conditions are common in shallow marine environments, they are not restricted to them. Additionally, there is often more than one plausible explanation for the origin of a clay mineral, such as when palygorskite could form authigenically in lake sediments or form in arid soils surrounding the lake and subsequently be reworked into it by wind.

Both of these examples emphasise that there is often more than one possible origin for a clay mineral in a sediment. Although the examples concern authigenic clay minerals, this fact is even more true of detrital clays, which, as we have seen, are by far the most abundant. This important point is illustrated in Fig 4.27 which shows the potential for sedimentary smectite to be derived from six different sources (Chamley 1989), and to which can be added the authigenic formation of smectite in situ in the sedimentary basin. It is this diverse spectrum of origins which complicates the use of clay minerals as tracers of sediment sources and dispersal. Nevertheless, the use of clay minerals as tracers is the main sedimentological use to which they have been put.

The kinds of information that can be obtained can be illustrated by the study of Kolla et al. (1981) of the surface sediments of the Arabian Sea (Fig. 4.28). To the west and north the Arabian Sea is surrounded by arid lands, with no significant fluvial inputs. To the northeast the river Indus drains the Himalayas and forms the major fluvial source to the area; up until recent dam construction it delivered up to 400 million tons per year of suspended sediment to the region. In the east the main fluvial sources are the Namada and Tapai rivers which drain soils developed on the Deccan trap basalts. The Arabian Sea is an area where the distribution of clay minerals in the surface sediments reflects the nature of the surrounding land masses and a variety of different sediment transport processes. Smectite-rich clays, which extend all along the Indian margin, are related to their derivation from smectite-rich soils developed on Deccan trap basalts, and their subsequent southerly transport by the prevailing ocean surface currents. In the far south some smectite may also have been transported around the tip of India by surface currents from the Bay of Bengal. Over most of the rest of the region illite-rich sediments dominate and are derived from several sources. In the east the main source is the Indus river, from which illite-rich sediments are dispersed westwards and southwards by surface currents and turbidity currents across the Indus deep-sea sediment fan. Other sources of illite are from the arid lands of Iran, and

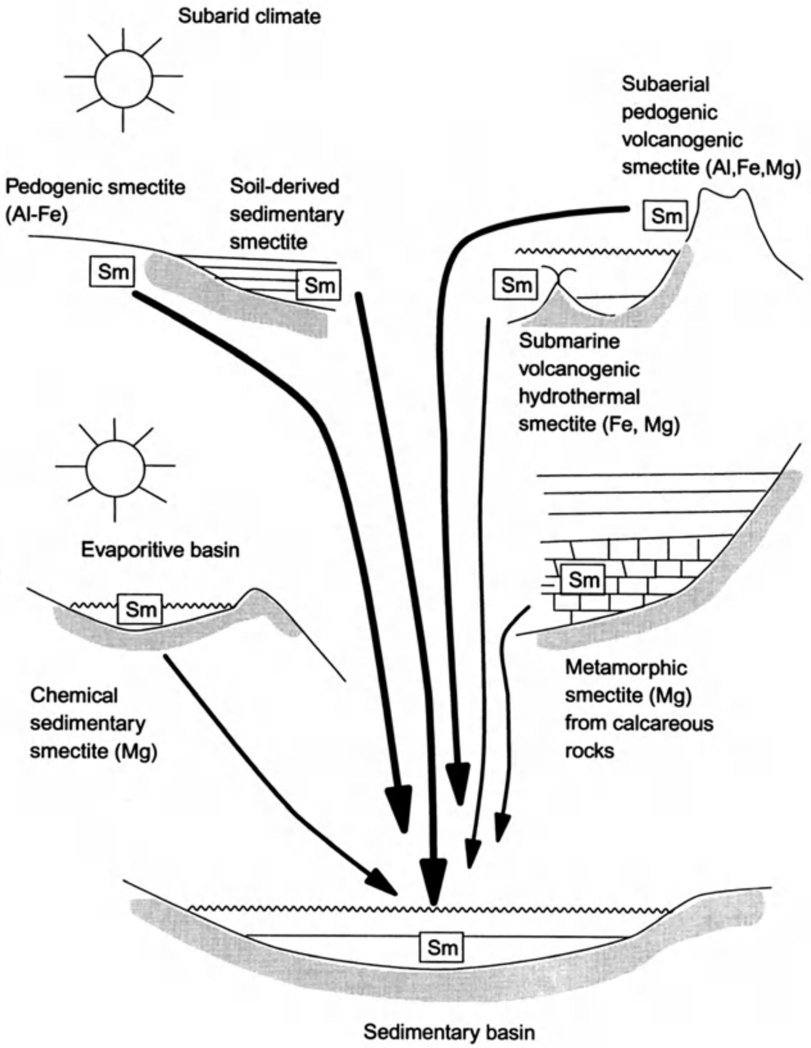

Fig. 4.27. The potential for the same type of clay mineral, in this case smectite, to be derived from very different sources. The *thickness of the arrows* is meant to be schematically proportional to the probable global importance of different sources of smectite to sediments, but in any one instance, one or other of these sources, including the more exotic ones such as metamorphic smectite, may be dominant. (Modified from Chamley 1989)

Makran in the north, and Arabia and Somalia in the west. The illite-rich sources from the west are associated with palygorskite and have been transported by wind as far as the Indian margin. Although some chlorite is introduced from the Indus, most of it appears to be derived by aeolian transport from northerly sources. The sediments of the deep-sea Indus fan appear to be a mixture of all of these sources. Kaolinite-rich sediments are restricted to a small area off southern India and to a belt across the very south of the region.

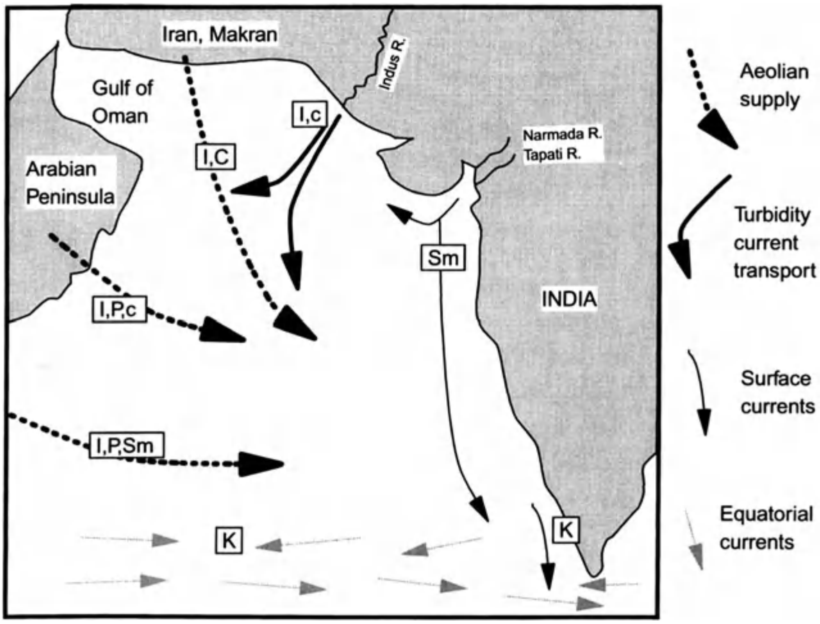

Fig. 4.28. Sedimentary dispersal processes and provenance of recent clay deposits in the Arabian Sea. Based on interpretation of Kolla et al. (1981) as illustrated by Chamley (1989)

It appears that they are derived from tropical soils in Africa and Madagascar and from southern India, their dispersal being related to the prevailing equatorial ocean circulation.

4.6.2 Palaeoclimatic Interpretation of Clay Minerals

The palaeoclimatic interpretation of sedimentary clay-mineral assemblages is based on the correlation of climate with weathering and soil formation, and hence with the clay minerals which these processes produce. This correlation is clearly shown by the changing clay mineralogy of the worlds zonal soils (Chap. 3; Sect. 3.2.3), and evidence of its affect on sedimentary clay-mineral assemblages is found in the broad latitudinal distribution of clay minerals in the world ocean. However, as emphasised by Singer (1984) the palaeoclimatic interpretation of clay minerals in sediments is anything but straight forward and needs to be undertaken with the utmost care. This is because in addition to climate there are many other factors which affect the clay mineralogy of sediments and, acting in isolation, or in combination, they may completely obliterate any climatic signal (Fig. 4.29).

As indicated in Chapter 3, weathering, soil formation, and the resulting clay minerals are not simply dependent on climate. The time that is available for weathering to proceed, parent materials, and topography, may all affect the kinds of soil profiles and clay minerals that may be produced (Fig. 4.29). The length of time over which weathering may occur, depends on tectonic and geomorphologic stability, and these periods may be shorter or longer than periods of climatic change. Furthermore, in certain climatic regimes weathering may be too weak or too strong to register certain climatic changes. Secondly, the clay minerals released to the sedimentary system are not only a function of weathering and soil formation, but of parent materials (Fig. 4.29). This is important in terms of the parent material's response to weathering, but even more so because of the possibility that the parent materials themselves may act as significant sources of clay minerals to the sedimentary system. Such clay minerals bear no relation to the prevailing climate. Thirdly, between the formation and the final deposition of clay minerals in a sediment, the processes of erosion and transport intervene (Fig. 4.29). Both erosion and transport may be selective, and furthermore transport distances may be so large that clay minerals are transported from one climatic regime to another. Lastly, after clay minerals have been deposited, they may be subjected to post-depositional changes, amongst the most important of which are those that occur during burial diagenesis. Indeed, burial diagenetic change may completely obliterate any palaeoclimatic signal. All of these aspects must be considered when trying to determine if clay-mineral assemblages preserve signals of palaeoclimate and/or palaeoclimatic change. Nevertheless, large sedimentary basins inte-

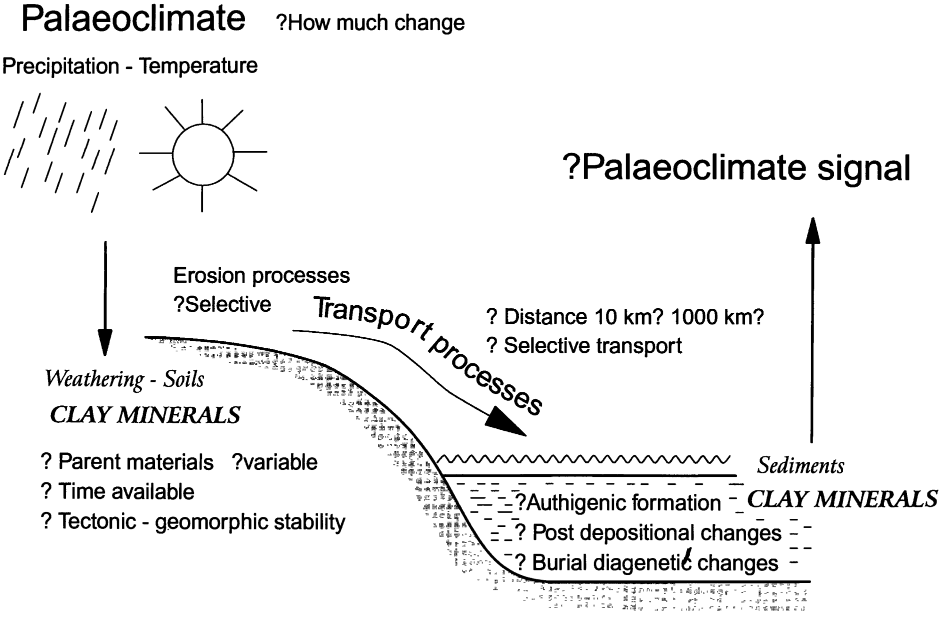

Fig. 4.29. The many processes and factors that must be considered when attempting to extract palaeoclimatic information from the analysis of clay minerals

grate the clay-mineral response of their source areas to climate change, so that in favourable cases climatic signals do appear to be preserved.

According to Chamley (1989), palaeoclimatic investigations in oceanic sediments are likely to be more favourable with increasing distance from land, and in sequences that have not been buried more than 2.5km. These are favourable due to the integration effect of distance on different sources, and to the need to avoid the effects of burial diagenesis, respectively. Furthermore, the effects of climate change are typically more pronounced in mid-latitudes. To combat the problem of diverse origins of clay minerals, Chamley (1989) advocates the use of changes in relative abundance of clay minerals rather than absolute abundances. As well as direct effects of climate on clay assemblages, climate changes may also be recorded indirectly through the affects that changes in the intensity of rainfall, ice cover, sea level, and marine currents, all may have on clay-mineral source areas and dispersal. Clay minerals alone rarely provide primary evidence of climate change and the best approach is the interdisciplinary one where evidence from clays is compared and correlated with that from the likes of microfossils and geochemical data, such as oxygen isotopes (Singer 1984; Chamley 1989).

Clearly, the application of clay mineralogy to palaeoclimate analysis must be based on a thorough understanding of weathering and its clay-mineral products. So far, in practice, most studies use very simplified schemes wherein abundant illite, and chlorite are taken to relate to cold or arid climates, kaolinite to more humid climates, and smectite to seasonal climates with a pronounced dry season. Indeed, more detailed schemes may not be warranted given the many factors which may swamp any climatic information (Fig. 4.29). However, even if climatic information is obscured, clay minerals can be characterised in considerable detail by modern mineralogical techniques, and such characterisation may provide much more data concerning their origin than the above generalisations. An early attempt at such an approach is the use of crystallinity data in Quaternary hemipelagic muds of the Mediterranean sea by Chamley (1971). Cold dry periods corresponding to glacial intervals are characterised by relatively more abundant and better crystallised illite and chlorite. Warmer and wetter periods, corresponding to interglacials, are characterised by more abundant and better crystallised smectite and more abundant kaolinite. A more recent example is the work of Fagel et al. (1992) where the palygorskite/illite ratio in sediments from the Arabian Sea has been investigated by various signal processing methods and related to periods in the Earth's orbital cycles. Increasingly, there have also been many attempts to better characterise minerals such as smectites which show a wide range of chemical composition that may be related to specific origins. However, work on oceanic smectites shows that there can be many causes of apparently significant compositional variation, including what might be dismissed by some as 'minor' contamination, and it is clear that a careful approach to characterisation of these kinds of materials is necessary (Vali et al. 1993).

Various studies of Cainozoic sediments from the western Atlantic region appear to provide an impressive example of the widespread nature of climate induced changes in clay-mineral assemblages. Studies from the North Sea (Karlsson et al. 1978), the northern Bay of Biscay (Chamley 1979; Debrabant et al. 1979), the Sierra Leone Rise (Robert 1982), and the Goban Spur (Chennaux et al. 1985), although different in detail, all show the same general trends in their clay-mineral assemblages. Essentially, Palaeocene and Eocene sediments are dominated by smectite, while chlorite appears in the Oligocene or Miocene and persists through Pliocene to recent sediments, accompanied by ever increasing amounts of illite. These trends are thought to correspond to the general cooling of world climate throughout the Cainozoic, and to increased relief in the source areas due to Alpine tectonics, whereby the importance of chemical weathering diminished and that of physical weathering increased. However, the changes may in fact reflect some combination of climatic control and of tectonics on oceanic circulation. From mid-Miocene times onwards, subsidence of the Iceland Faroe ridge allowed increased southerly flow of cold bottom water from the Norwegian Sea to the North Atlantic, and these waters may have been responsible for some of the observed increase in illite and chlorite (Chennaux et al. 1985). Nonetheless, comparable trends in Tertiary clay mineralogy are also observed in areas of other oceans, such as the Antarctic (Ehrmann et al. 1992), and most investigators seem to agree that the overriding control is climate change, even though it may frequently be expressed indirectly by related changes in sediment-transport processes.

Palaeoclimate appears also to have left its record in certain marine Mesozoic rocks. For example, generally speaking, Cretaceous sediments of the Atlantic and Tethyan domains are relatively rich in smectite. This is believed to be due to the warm seasonal climates and general tectonic stability of this period, smectite being supplied from the continents (Chamley 1989). However, an alternative hypothesis has been put forward by Thiry and Jaquin (1993) which involves transformation of other minerals into smectite at the sediment–water interface and during early diagenesis while there is still free exchange of pore water with sea water. In addition, Jurassic sediments from the same region are frequently enriched in kaolinite which is related to the more humid climatic conditions of this period (Chamley 1989). Palaeoclimatic interpretations of older rocks become increasing difficult because of the greater chance that they have been altered by burial diagenesis.

Besides climate, changes in palaeocirculation and tectonics are amongst the most common factors that may produce changes in the clay-mineral assemblages of marine sediments. According to Chamley (1989), changes in circulation of ocean currents affect clay-mineral assemblages to the same order of magnitude as those resulting from climate change. In contrast, changes due to tectonic effects on clay-mineral supply are potentially much more significant and longer lived than either the effects of climate or circulation. Tectonic rejuvenation causes soil sources of clay minerals to be replaced by rock sources. Therefore, the effects are most pronounced when tectonics affects regions where soils have developed under conditions of intense chemical weathering such as in humid tropical climates.

A detailed compilation of changes in clay mineralogy through geological time is given by Weaver (1989). The main trend is an increase in smectite and decrease in illite from Cambrian to Recent times. Weaver (1989) discusses how this trend may be related to changes in weathering through time, or to the increased chance that older sediments have been affected by burial diagenesis. Weaver (1989) also discusses the interpretation of the data for various geological periods in terms of changes in climate and global tectonics.

It is evident, as will be seen in the following chapter, that as sediment becomes rock during burial, mineral changes occur which have a tendency to obscure the chemical and environmental orgin of sedimentary clays. If diagenesis occurs, it must strongly affect the mineral assemblages of clays in sedimentary rocks. Hence, the signature of sedimentary provenance will be restricted to superfical and young areas of the sedimentary pile.

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