Clay Minerals, Deep Circulation and Climate

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Contents

1. Introduction

The detrital fraction of deep-sea sediments may carry important information about conditions on adjacent continents and about the mechanisms by which material is transported from land to sea (Figure 1). Clay minerals are the main constituents of recent deep-sea or abyssal sediments. Since the late sixties, their role as paleoclimatic and paleoceanographic indicators has been investigated worldwide by X-ray diffraction techniques (Yeroshchev-Shak, 1964; Biscaye, 1965; Berry & Johns, 1966; Chamley, 1967; Griffin, Windom, & Goldberg, 1968; Rateev, Gorbunova,
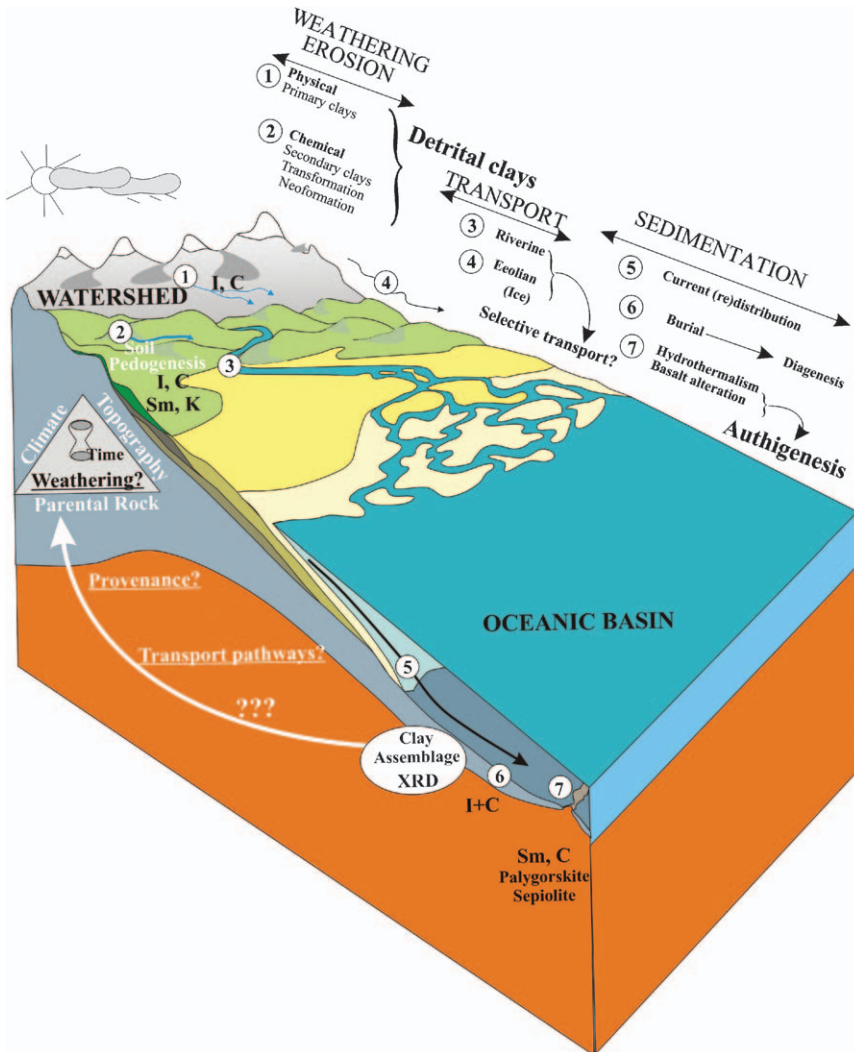
Figure 1 The "clay toolbox". Primary controls on clay assemblage composition of deep-sea sediments. I: illite, C: chlorite, Sm: smectite, K: kaolinite, XRD: X-ray diffraction technique. In marine sediments, only detrital clays can carry *indirect* information regarding weathering conditions within the watershed (clays = climate proxy) or changes in provenance (clays = transport pathway proxy).

Lisitzyn, & Nosov, 1969; Chamley, 1974; Kolla, Kostecki, Robinson, Biscaye, & Ray, 1981; Petschick, Kuhn, & Gingele, 1996; Gingele, Schmieder, Petschick, von Dobeneck, & Rühlemann , 1999; Robert, Diester-Haass, & Paturel, 2005). In marine sediments, clays are mainly detrital (∼90%; Velde, 1995) and their abundances provide abiotic *proxy data*, which may be used to decipher either (1) climate changes in the source area on adjacent landmasses, (2) changes in the intensity of the transport

agent, or (3) changes in the ocean currents that disperse the terrigenous input (Gingele, De Deckker, Girault, & Guichard, 2004).

In essence, clay mineralogy is a useful tool to constrain the provenance of fine-grained terrigenous sediments (Biscaye, 1965). After much discussion in the literature about the usefulness of clay minerals in delineating suspended sediment dispersal routes and constraining the provenance of fine-grained marine deposits (Biscaye, 1965; Hein, Bouma, Hampton, & Ross, 1979), clay mineralogy has been widely used as a *tracer of provenance* in studies of the world's oceans. In these studies, the mineralogy of the fine-grained detrital fraction generally reflects the intensity of continental weathering in the source areas (Biscaye, 1965; Griffin et al., 1968; Rateev et al., 1969). Combining clay mineralogy and radiogenic isotope measurements (Sr, Nd and/or Pb) provides further constraints on the identification of the source area (e.g., Grousset, Biscaye, Zindler, Prospero, & Chester, 1988; Fagel, Innocent, Stevenson, & Hillaire-Marcel, 1999; Walter, Hegner, Diekmann, Kuhn, & Rutgers Van Der Loeff, 2000; Rutberg, Goldstein, Hemming, & Anderson, 2005).

Clays are sensitive indicators of their environment of formation, and their composition may be used to constrain climatic variations which do not affect other size fractions (Moriarty, 1977). The composition of terrestrial clay mineral reflects the prevailing weathering regimes which control the nature and intensity of pedogenetic processes in continental source areas. Weathering depends primarily on climate zonation, which determines the intensity of physical and/or chemical weathering (e.g., Chamley, 1989; Weaver, 1989).

Clay minerals are eroded from soils by rivers, wind or ice and carried into shallow and deep water masses of the surrounding seas. Their modern distribution pattern on the sea floor provides insight into their propagation by ocean currents (Gingele, De Deckker, & Hillenbrand, 2001b): the dispersal of detrital clays constrains the transport pathway of suspended fine-grained particles. As such, clays are *indirect tracers of water masses*. The interpretation of down–core changes in mineral assemblages depends on available information on the modern distribution and sources, as well as independent climate proxy data about the source area. Once the relationship between a specific clay mineral assemblage and a given source, water mass or current system is established, variations of this assemblage in down–core profiles may be used to detect fluctuations in the propagation of the water mass or current system (Diekmann et al., 1996; Gingele et al., 1999).

As the distribution of clay minerals in modern oceans appears to be controlled by contemporaneous climates, marine clays in Cenozoic (and Mesozoic) sediments have been widely used to reconstruct *paleoclimates* (Chamley, 1981). Singer (1984), and later Thiry (2000), questioned the relevance of using marine detrital clays as a continental paleoclimate proxy: indeed, changes in marine clay mineral assemblages do not systematically reflect changes in weathering conditions in the continental source area, but rather changes in source areas or transport media. For older sedimentary sequences, diagenesis can completely erase the paleoenvironmental memory of clay minerals, initially diversified clay assemblages evolving with burial towards an anonymous illite- and chlorite-bearing association with intermediate irregular and regular mixed-layers (e.g., Hower, Eslinger, Hower, & Perry, 1976; Nadeau, Wilson, McHardy, & Tait, 1985; Inoue, 1987). The dominant diagenetic change is the

progressive reaction of smectite to illite, which depends primarily on temperature (Hower et al., 1976; Hoffman & Hower, 1979; Srodon & Eberl, 1984). Other than temperature, the two most important factors are time and fluid chemistry (Eberl & Hower, 1977; Roberson & Lahann, 1981; Ramsayer & Boles, 1986). In sedimentary deposits characterized by a normal geothermal gradient (∼30°C/km), burial diagenesis operates at depths greater than 2,500–3,000 m (i.e., at temperatures >80°C, Chamley, 1989).

In this chapter, we review the literature in order to describe the relationships between (1) clay mineral abundance in deep-sea sediments and deep circulation, and (2) clay variability and short- or long-term climate changes. As the present volume is dedicated to *Proxies in Paleoceanography*, we focus on the interpretation of marine clay mineral data. The identification and quantification of clay minerals using X-ray diffraction methods are described in other methodological textbooks (e.g., Brindley & Brown, 1980; Moore & Reynolds, 1989).

2. Methodology: The Clay Toolbox in Marine Sediments

2.1. Clay Mineral Groups in Deep-Sea Sediments

2.1.1. Definition and identification of clay mineral groups

The mineral component of the "clay-sized" fraction (<2 μm, or even <1 μm) of deep-sea sediments comprises the common clay minerals montmorillonite (or smectite), illite, kaolinite and chlorite, with lesser amounts of quartz and feldspars (Windom, 1976). In addition, the mixed-layer minerals palygorskite and sepiolite have been also identified in this size fraction (Windom, 1976). Clay minerals are identified by their characteristic basal X-ray diffraction maxima (i.e., "reflection" or "peak"; Brindley & Brown, 1980; Moore & Reynolds, 1989). The term "clay minerals" refers to mineral groups rather than specific mineralogical species. "Illite" is used "as a general term for the clay mineral constituent of argillaceous sediments belonging to the mica group" (definition from Grim, Bray, & Bradley, 1937). Illites are characterized by a 10 Å reflection which is affected neither by glycolation nor heating. The term is used in the same general sense as "montmorillonite" or "kaolinite", that is, to refer to a group of minerals. Any material which expands to 17 Å upon glycolation is assigned to the montmorillonite group (Biscaye, 1965). The term "smectite" is often used in more recent works, and encompasses pure smectite but also smectite–illite mixed layers with variable abundances of smectite layers. Chlorites are defined by a 14 Å reflection which is affected neither by solvatation nor, usually, by heating (except if vermiculite is present). Kaolinite is identified by a 7 Å reflection that disappears above 500°C. Minor quantities of non-clay minerals are present in the terrigenous fine-grained component of deep-sea sediments.

2.1.2. Clay mineral classification

Clay minerals belong to the phyllosilicate family (Brindley & Brown, 1980; Caillière, Hénin, & Rautureau, 1982; Moore & Reynolds, 1989). Phyllosilicates are hydrous

silicate minerals essentially composed of two-dimensional Si-bearing tetrahedral, and Al-bearing octahedral sheets stacked in a regular array (White, 1999). The fundamental classification criteria retained by the AIPEA (Association Internationale Pour l'Etude des Argiles) are the tetrahedral–octahedral sheet combination type (layer type, i.e., 1/1, 2/1 or 2/1/1), the cation content of the octahedral sheets (dioctahedral or trioctahedral), the layer charge and the type of interlayer material (Bailey, 1980).

Kaolinite consists of a combination of one tetrahedral layer and one octahedral layer (layer type 1/1). It is a dioctahedral mineral with two-thirds of the octahedral sites filled by a trivalent cation (Al or possibly Fe^{3+}). There is no interlayer material other than H_2O.

Illite comprises a combination of two tetrahedral sheets and one intercalated octahedral sheet (layer type 2/1). It is a dioctahedral mineral characterized by the presence of K cations in the interlayer which compensate the charge deficit resulting from Al^{3+} substitution by Si^{4+} in the tetrahedral sheet.

Smectite is also a 2/1 layer type mineral, but is characterized by variable amounts of the exchangeable cations Na and/or Ca in the interlayer, as well as one or two layers of water. Smectites are divided into two subgroups. Montmorillonites *sensu lato* comprise all dioctahedral smectites, i.e., montmorilllonite *sensu stricto*, characterized by an octahedral Mg^{2+} charge, beidellite, characterized by a tetrahedral Al^{3+} charge, and its Fe-rich end-member nontronite (tetrahedral Fe^{3+} charge). Saponites *sensu lato* consist of a trioctahedral mineral which includes either an octahedral charge (Mg^{2+} in stevensite, Li^+ and F^+ in hectorite) or an octahedral Mg^{2+} charge and a tetrahedral Al^{3+} charge in saponite *sensu stricto*.

Chlorite is also composed of three sheets, two tetrahedral ones and an octahedral one, but its interlayer space is taken up by a hydroxide layer (layer type 2/1/1). In sedimentary environments, although chlorites are mainly trioctahedral with 3/3 octahedral sites filled by bivalent cations such as Fe, Mg, Mn or, more rarely, monovalent cations (Li, Ni), some dioctahedral species are possible (e.g., sudoite). Their chemical composition is complex and varied due to numerous possible substitutions in both the tetrahedral and/or octahedral layers and in the interlayer.

Mixed layers are formed by the regular or irregular stacking of two or more layer types. Not all possible combinations are observed in sedimentary environments (see reported occurrences in Thorez, 1986).

Palygorskite and sepiolite are fibrous clay minerals comprising two discontinuous tetrahedral sheets and one continuous octahedral sheet (modulated 2/1 layer type). They are characterized by a ribbon structure with a large space available for water, hydroxyl and exchangeable cations, more specifically Mg in sepiolite and Al in palygorskite (Caillière et al., 1982).

2.2. Formation of Clay Minerals

Sedimentary clays are divided into two main categories according to their origin (Figure 1). Clay minerals are either formed by *in situ* precipitation from a concentrated solution in closed continental or marine sedimentary basins (authigenic

clays) or by weathering processes on the continent (detrital clays). Authigenesis is a minor process which accounts for less than 10% of clay minerals (Velde, 1995), although it may be important locally. In deep-sea environments, authigenic clays result from the weathering of basaltic oceanic crust or hydrothermal alteration (Chamley, 1989; Weaver, 1989). The nature and chemical composition of clays are strongly controlled by reaction temperatures (Velde, 1992). Authigenic deep-sea clays are mainly Fe- and/or Mg-rich minerals, including various species of smectites (nontronite, saponite), micas (celadonite), chlorites and fibrous clays (palygorskite, sepiolite; Velde, 1995).

Whereas authigenic clays provide insight into the geochemical environment, detrital clays hold a record of weathering conditions in the adjacent landmass (Velde, 1995). Detrital clays result from the physical breakdown of parental rocks (primary minerals) or from the selective dissolution of pre-existing clay and non-clay minerals and growth of secondary minerals in soils (Allen, 1997). Under normal pH conditions, water attack or *hydrolysis*, is the main chemical weathering process involved (Chamley, 1989). During pedogenesis, secondary clays form by transformation processes or neoformation. Transformed clays are the result of cation loss due to the opening of the sheet structure (degradation) or, conversely, cation addition to repair slightly altered clay (rejuvenation) or to form a new mineral (aggradation; Thorez, 1989). Neoformed clays are formed by recombination and precipitation of ions from a leachate. The intensity of chemical weathering, and hence the nature of the secondary minerals, are primarily controlled by climate conditions. The temperature, water availability and precipitation regimes affect the extent of cation, silica and alumina leaching (Pédro, 1968; Chamley, 1989; Allen, 1997). In cold or arid climate, water availability is too low for chemical weathering to operate. Clays, mainly illite and chlorite, are inherited from parental rocks (*heritage* process). For moderate leaching under temperate conditions, cations released by the breakdown parental minerals promote the formation of cation-bearing clay minerals comprised of two tetrahedral Si-layers and one octahedral Al-layer, such as illite and smectite (*bisiallitisation* process). With increasing hydrolysis under tropical conditions, more silica is released in solution and only one tetrahedral Si-layer and one octahedral Al-layer combine to form kaolinite (*monosiallitisation* process). More intense leaching under warm and humid equatorial climate precludes the formation of clays; the secondary minerals are oxides (gibbsite, *allitisation* process). Although the global weathering pattern shows a zonal or latitudinal control (Allen, 1997), the relationship between climate parameters and clay mineral formation is not always straightforward. For instance, clay mineral products formed under different climate conditions may show mimetism (Singer, 1984). Important factors other than climate include parental material, topography and time (Singer, 1984; Velde, 1992). The acidic or basic nature of parental rocks controls the composition of secondary minerals. Mineral grain size determines specific area, and hence reaction kinetics. Topography controls runoff conditions, making the recombination of ions possible only in depressed areas. Tectonic stability determines the ratio between physical and chemical weathering. Pedogenesis is a relatively slow process the intensity of which increases with time.

2.3. The Origin of Clays in Deep-Sea Sediments

2.3.1. Detrital clays: illite and kaolinite

Studies over large oceanic areas (Biscaye, 1965; Griffin et al., 1968; Rateev et al., 1969; Lisitzin, 1996) show that the interaction of continental sources and ocean distribution mechanisms can account for the major clay mineral abundance patterns (Moriarty, 1977). In particular, for Atlantic Ocean sediments, Biscaye (1965) demonstrated striking geographical distribution patterns for the main clay minerals; more specifically, recent clay distribution in the Atlantic Ocean is controlled by climatic and weathering zonations on adjacent land masses, implying that most clay minerals are terrigenous (Biscaye, 1965; Chamley, 1989). Moriarty (1977) points out that some authors (Berry & Johns, 1966) have proposed that alteration and authigenesis are important mechanisms, but what limited chemical data are available point to no alteration and minimal authigenic inputs, especially in sediments characterized by high terrigenous accumulation rates (McDougall & Harris, 1969; Darby, 1975). In later studies, the occurrence of illite, chlorite and kaolinite in soil-sized eolian dust from the Eastern margins of the Atlantic Ocean is used as evidence for a land–derived origin for these clays (Chester, Elderfield, Griffin, Johnson, & Padgham, 1972). Griffin et al. (1968) claim that clay minerals in the $<2\,\mu m$ fraction of deep-sea sediments are useful indicators of marine sedimentary processes, particularly those involving the transport of land-derived solids to and within the oceans. However, according to Behairy, Chester, Griffiths, Johnson, and Stoner (1975), little is known about the large-scale distribution of major clays in particulate material in the world's oceans. This material represents an intermediate stage between the initial transport of solid components to the ocean and their deposition in bottom sediments. It is during this stage that mixing of various components is expected to begin. Clay mineral concentrations in particulate material from surface ($<5\,m$) waters of the eastern margins of the Atlantic Ocean have been determined (Behairy et al., 1975). Clay minerals in deep-sea sediments and surface particulate matter may be either detrital or authigenic (Behairy et al., 1975). However, clay minerals in eolian dusts have a purely detrital origin. The average concentrations (40% illite, 25% kaolinite) and the latitudinal distribution of illite and kaolinite in surface seawater particulate material between 60°N and 40°S are similar to those of eolian dusts: the relative abundance of illite decreases towards low latitudes, and is compensated by an increase in kaolinite abundance. This observation constitutes strong evidence for the detrital origin of these clays in particulate matter and the underlying deep-sea sediments, which record similar distributional trends (Biscaye, 1965).

As underlined by Biscaye (1965), the strongest evidence yet for the detrital origin of illite is provided by K/Ar measurements from recent North Atlantic deep-sea sediments (Hurley, Heezen, Pinson, & Fairbairn, 1963). Ages on the order of hundreds of millions of years indicate that a major component of the sediments must be derived from old continental rocks and their weathering products. Illite is a widespread mineral in many types of rocks and soils and is quite resistant to chemical weathering (Gradusov, 1974).

Given its elemental composition and the pH conditions required for its formation (Arrhenius, 1963), it is unlikely that kaolinite forms in the oceans (Windom, 1976).

One exception to this is the reported occurrence of kaolinite authigenesis in deep hydrothermal-volcanogenic sediments (Karpoff, Peterschmitt, & Hoffert, 1980).

2.3.2. Mixed detrital and authigenic clays: smectite, chlorite and fibrous clays

Distinguishing authigenic clays from detrital clays can be difficult (Singer, 1984). Because it can be either detrital or authigenic, the origin of smectite in marine sediments was, at one point, a matter of debate (e.g., Biscaye, 1965; Griffin et al., 1968). Authigenic smectites derive mainly from volcanism, hydrothermal activity or diagenetic processes (Chamley, 1989). Submarine alteration of basaltic volcanic glasses and volcanic rock fragments is one of the most important authigenic smectite-forming processes (Windom, 1976; Chamley, 1989; Weaver, 1989). Fe-rich beidellites and nontronites commonly derive from hydrothermal alteration of basalts, and they are particularly abundant in active areas of mid-oceanic ridges (Haggerty & Baker, 1967; McMurthy, Wang, & Yeh, 1983; Parra, Delmont, Ferragne, Latouche, & Puechmaille, 1985, 1986; Parra, Puechmaille, Dumon, Delmont, & Ferragne, 1986). In contrast, detrital smectites are sourced on adjacent continents, and they primarily form by hydrolysis under temperate to semi-arid climate conditions (Pédro, 1968; Chamley, 1989).

   In the North Atlantic, similar smectite abundances in particulate material and deep-sea sediments argue for a primarily detrital origin (Behairy et al., 1975). In the South Altantic, however, the abundance of smectite in particulate matter is too low to account for smectite abundances in deep-sea sediments. This smectite enrichment (by up to a factor of 2) in South Atlantic sediments suggests the presence of authigenically-derived smectites (Behairy et al., 1975). On the whole, however, the lack of correlation between smectite, zeolites and volcanic shards abundances, as well as the low abundance of smectites in Atlantic Ocean surface sediments point to a primarily detrital origin for these clays (Biscaye, 1965).

   The question regarding whether smectite is essentially authigenic or detrital is particularly important when it comes to the Pacific Ocean, where the large extent of oceanic area and the occurrence of sediment-trapping deep-sea trenches seem, a priori, to argue against an important terrigenous input (Chamley, 1986). In such an oceanic environment (low sedimentation rate, strong volcanic-hydrothermal activity, deposition of metalliferous sediments and other exchange processes at the water/sediment interface), synsedimentary and diagenetic processes would be expected, especially in intraplate basins. Griffin and Goldberg (1963) concluded that smectite in recent South Pacific sediments is of volcanic origin: it represents the most abundant clay type within the $<2\,\mu m$ fraction and occurs in close association with zeolites and volcanic shards. However, Deep-Sea Drilling Project (DSDP) data from the Shatsky Rise ($>6,000\,m$ water depth) rather suggest that the pelagic red clays, which are diversified and show no evidence of lithological control, are mainly detrital (Chamley, 1986). Thus, a terrigenous influence is particularly important close to continental margins in the North Pacific Ocean, but may also be a defining factor of clay assemblages in pelagic red clays in the West Pacific Ocean (Shatsky Rise), which is characterized by relatively high sedimentation rates.

Authigenic formation of chlorite in marine sediments requires specific conditions; hence, most chlorites in deep-sea sediments are detrital (Windom, 1976). Chlorite is a widespread primary constituent of low-grade metamorphic, magmatic and terrigenous sedimentary rocks and a secondary weathering product of other clay minerals (illite). Chlorite is relatively uniformly distributed on the continents (Gradusov, 1974). For instance, its detrital origin in the Atlantic Ocean is supported by a higher abundance in the particulate matter (20%) than in the underlying sediments (Behairy et al., 1975). However, authigenic chlorite may form during alteration of oceanic crust or by contact metamorphism of sediments intruded by basaltic lavas (Chamley, 1989).

The fibrous clays palygorskite and sepiolite have been identified in Cenozoic sediments of the Atlantic, Pacific and Indian Oceans (Chamley, 1989 and references therein). Couture (1977) suggested that these clays mainly form authigenically in hydrothermal environments. Although experimental studies suggest the possible *in situ* precipitation of sepiolite from seawater, sepiolite is rare in hydrothermal environments. On the other hand, palygorskite has never been synthesized under such conditions, but it is often associated with metalliferous deposits (Kastner, 1981). Fibrous clays are also formed in calcareous soils or precipitated from concentrated freshwater (lake) or saline water (permarine lagoon) in arid climates (Weaver, 1989; Velde, 1995). The occurrence of abundant palygorskite in oceanic areas adjacent to deserts (Gulf of Aden, Red Sea and Arabian Sea; Kolla et al., 1981; Fagel, Debrabant, De Menocal, & Demoulin, 1992a; Windom, 1976) and the occurrence of sepiolite in dust samples from New Zealand are strong evidence for eolian transport from adjacent continents (Windom, 1976).

In marine sediments, trace element chemistry can be a useful indicator of sedimentary material provenance (e.g., Murray, Buchholtz Ten Brink, Jones, Gerlach, & Russ, 1990; Nath, Roelandts, Sudhakar, & Pluger, 1992; Fagel, André, Chamley, Debrabant, & Jolivet, 1992b, 1997a; Li & Schoonmaker, 2003). In particular, rare earth element (REE) patterns may help in distinguishing between detrital and authigenic clays (Desprairies & Bonnot-Courtois, 1980; Chamley & Bonnot-Courtois, 1981). Indeed, authigenic clays are characterized by a seawater-type REE profile (i.e., negative Ce anomaly and depletion in light REE relative to heavy REE; Piper, 1974). A seawater-like Sr isotopic signature may also constitute an indicator of authigenesis (Clauer, O'Neil, Bonnot-Courtois, & Holtzapffel, 1990; Clauer & Chaudhuri, 1995).

2.4. Clay Particle Transport Mechanisms

Due to their small particle size, clay minerals might be expected to have a long residence time in seawater and, consequently, to get well-mixed (Behairy et al., 1975). This assumption is, however, not valid because clay mineral distributions in deep-sea sediments are, in general, similar to those on surrounding land masses. This implies that the clay minerals present in the upper layers of the seawater column are transported to the bottom relatively rapidly. Sedimentary material initially deposited on continental margins is subsequently transported to deep-sea areas by turbidity currents, and further redistributed by deep currents. As such, clay

distribution in deep-sea sediments must be constrained by seafloor topography. For instance, bathymetry and the abyssal plain outline exert a strong control on the clay mineral abundance contours of the South Indian Basin (Moriarty, 1977). In contrast, the westward decrease in kaolinite abundance observed in the Atlantic Ocean off Africa and across the Mid-Atlantic Ridge is independent of seafloor topography.

The transport of clay particles to the deep sea is controlled by the complex interplay of atmospheric, hydrographic, glaciogenic and topographic conditions (Biscaye, 1965; Petschick et al., 1996). In the arid regions of northern and southwestern Africa, wind transport is the main process which supplies terrigenous matter to the ocean (Prospero, 1981). Along the African coast, the distributions of suspended clayey particles (Behairy et al., 1975) and aerosols (Chester et al., 1972) show a clear relationship with clay mineral provinces in source regions on land. If humid conditions prevail, the nearshore clay input is controlled by river systems (e.g., Amazon River; Gibbs, 1977). At high latitudes, clay minerals are also supplied by glaciomarine processes at the Antarctic continental margin (Windom, 1976; Anderson, Kurtz, Domack, & Balshaw, 1980; Ehrmann, Melles, Kuhn, & Grobe, 1992) and at the Arctic margin (Wahsner et al., 1999).

Different processes exert a control on the transport of sediment from shelves into deep ocean basins (Wahsner et al., 1999): (1) suspension along different current systems which leads to dispersion of clay minerals over large distances within the water column; (2) gravitational flows (turbidity currents and debris flows); (3) at high latitudes, sinking over the continental margin of suspended clay-rich cold and saline water masses formed on the shelf during ice formation (sea-ice or iceberg transport; Figure 2).

Near continental slopes, abundant clayey material can be derived from turbidity currents and local dense thermohaline underflows (Kuhn & Weber, 1993). With increasing distance from the source areas, advection of fine-grained particles by deep-water currents becomes the most important mode of detrital sediment transport to the deep sea (Biscaye, 1965; Petschick et al., 1996). For instance, in the North
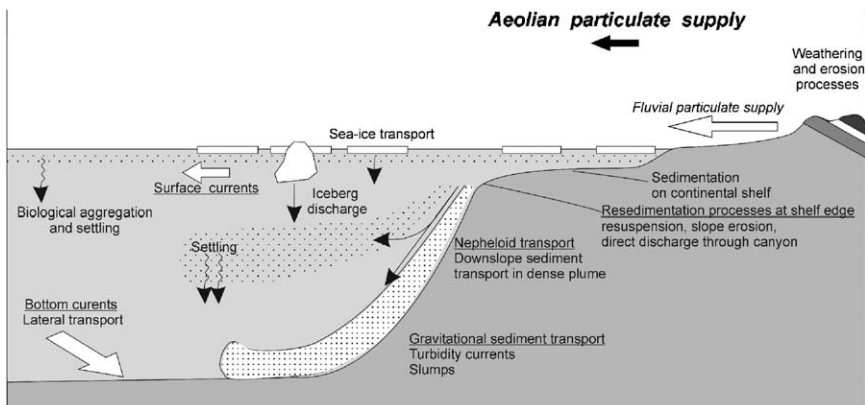
Figure 2 Mechanisms of transport of detrital clays into the deep sea. Modified with permission from Stow (1994) and Wahsner et al. (1999).

Atlantic, erosion products from Iceland are transported into basins by gravity currents, then cut off by Norwegian Bottom Current (NWBC) and transported southwards as a fine-grained suspension (Grousset, Latouche, & Maillet, 1983). Southwest of the Grand Banks of Newfoundland, Alaf (1987) showed evidence for large amounts of detrital clay being injected into the system by turbidity currents through (Laurentian) channels, canyons and surface sediment plumes, the latter being, in turn, strongly affected by surface circulation (i.e., locally, the Labrador Current). Fine-grained sediments injected into the system by turbidity currents through the Laurentian Channel are probably trapped by deep circulation. In the Weddell Sea, it is likely that high proportions of silt and clay are mainly carried within permanent or temporary bottom currents prior to deposition, whereas sand is transported by ice rafting (Diekmann & Kuhn, 1999).

   Bottom current activity causes resuspension of these minerals to form nepheloid layers as well as horizontal drift on the scale of several thousands of miles (Biscaye, 1965). The resuspended particulate loads in the nepheloid layer of basins west of the Mid-Atlantic Ridge, which result from the interaction of abyssal currents with the bottom, range from $\sim 2 \times 10^6$ tons in the equatorial Guyana basin, to $\sim 50 \times 10^6$ tons in the North American basin (Biscaye & Eittreim, 1977). Offshore of Africa, the weight of clays accounts on average for almost 81% of suspended particulate matter in the near-bottom layer (McMaster, Betzer, Carder, Miller, & Eggimann, 1977). The total resuspended particulate load in the western basins (111×10^6 tons) is almost an order of magnitude greater than those in the basins located east of the Mid-Atlantic Ridge (13×10^6 tons). The net northward flux of resuspended particles carried in Antarctic bottom waters (AABW) drops from $\sim 8 \times 10^6$ tons/yr between the southern and northern ends of the Brazil basin and remains at $\sim 1 \times 10^6$ tons/yr across the Guyana basin. The extension of the nepheloid layer in the North Atlantic was constrained by comparing mineralogical analyses of subsurface sediments from different cores (Bout-Roumazeilles, Cortijo, Labeyrie, & Debrabant, 1999). The nepheloid is enriched in peculiar illite–vermiculite mixed layers. Those clays are not commonly observed in sediments, and hence constitute a good indicator of particle sources. They are primarily derived from moderate pedogenic processes in the Appalachian Mountains of Canada and transported by run-off to the Labrador shelf area. The nepheloid layer forms in shallow areas where it is enriched in illite–vermiculite mixed layers by erosion of the shelf. It flows eastwards along the slope and into the basin at intermediate water depths, to the mid-oceanic ridge, which prevents its propagation into the northeastern Atlantic basin. The current flows primarily southwards, following the main pattern of deep-water circulation (Bout-Roumazeilles et al., 1999) and carrying illite–vermiculite mixed layers at least as far south as New Jersey (Deconinck & Vanderaveroet, 1996). A dense nepheloid layer flowing at intermediate water depth and following the general pattern of intermediate and deep-water circulation is seasonally documented in the modern Labrador Sea (Biscaye & Eittreim, 1977).

   During transport, detrital clay assemblages may undergo differentiation processes (e.g., selective erosion of the soil source) by size sorting or differential flocculation (Singer, 1984). The dispersal pathways of clay minerals during transport from source to deposition site are dependent on the transport agent (wind, ice or river; Singer, 1984).

There has been much debate in the literature about the lateral evolution of clay mineral assemblages from river mouths to shelf and slope sediments (Chamley, 1989). The alteration of clay minerals due to chemical disequilibrium in seawater was the first hypothesis put forth (Grim & Johns, 1954). In a study of clay minerals on the Brazilian continental shelf, Gibbs (1977) demonstrated that the dominant mechanism accounting for lateral changes in clay mineral composition is the physical sorting of sediments by grain size. Mineral composition changes from the mouth of the Amazon River over a distance of 1,400 km along the shelf, the proportion of montmorillonite increasing from 27% to 40%, as those of kaolinite and micas decrease from 36% to 32% and 28% to 18%, respectively. Gibbs (1977) pointed out that all these clays are characterized by similar flocculating properties due to organic and metallic coatings.

2.5. Clay Mineral Distribution in the World Ocean Basins

2.5.1. Literature review of clay distribution patterns in the world oceans

With the expansion of oceanographic programmes in the late sixties, the distribution of clay minerals in recent deep-sea sediments from the world oceans was studied by X-ray diffraction (Table 1, Figure 3). Biscaye (1965) determined the relative abundance of the four main clay mineral groups (i.e., montmorillonite, illite, kaolinite and chlorite) within the carbonate-free, <2 μm fraction of 500 sediments of the Atlantic Ocean and adjacent seas. For this author, the "clay fraction" refers to the silicate fraction of deep-sea sediments. The term is to be distinguished from "clay minerals", which refers to specific mineral constituents of "clay", and from "clay-size", which is a particle size range (Windom, 1976; Weaver, 1989). Using contour maps, Biscaye (1965) reported the relative mineral composition of the <2 μm size fraction assuming that montmorillonite, illite, kaolinite and chlorite account for 100% of the mineralogical composition in that size fraction. Using Biscaye's quantification method to obtain comparative values, Griffin et al. (1968) presented some 350 new analyses, primarily from the Pacific and Indian Oceans. Incorporating Biscaye's (1965) database for the Atlantic Ocean, Griffin et al. (1968) and Rateev et al. (1969) reported quite similar distributions of clay minerals in the world oceans, in spite of the fact that they did not analyse the same size fraction. Rateev et al. (1969) analysed the <1 μm fraction of some 380 additional surface samples from the Pacific, Antarctic and Indian Oceans. Compiling new and available (Biscaye, 1965) data, they published the distribution patterns of clay minerals in surface sediments in all of the world oceans, with the exception of the Arctic Ocean. Later, Windom (1976) integrated all those data to produce average mineral assemblages (Table 2) and maps of the distribution of the four main clay mineral groups in the world oceans. Lisitzin (1972) presented a compilation of the numerous Russian investigations of deep-sea clay minerals, but this work, initially published in Russian, was only translated in 1996. The contour maps drawn by Russian scientific teams (Yeroshchev-Shak, 1964; Rateev et al., 1969; Lisitzin, 1996) have the advantage of presenting clay mineral distributions in both deep-sea sediments and potential source areas on land (see simplified Figure 4a–d, which show the distributions of illite, chlorite, smectite and kaolinite,

Table 1 Literature Review of Clay Minerals from Surface Sediments in Basins of the World Oceans.

Ocean	Oceanic Area	References
	World ocean	Griffin et al. (1968); Rateev et al. (1969); Windom (1976); Lisitzin (1996)
Pacific Ocean	All basins	Griffin et al. (1968)
	Central Arctic	Darby (1975); Stein, Grobe, and Washner (1994); Wahsner et al. (1999) and references therein
	Alaska, Chukchi Sea and East Siberian seas	Hein et al. (1979); Naidu et al. (1982); Naidu and Mowatt (1983); Moser and Hein (1984)
	Barents and Kara seas	Elverhøi, Pfirman, Solheim, and Larssen (1989); Nürnberg, Levitan, Pavlidis, and Shelkhova (1995); Gorbunova (1997)
	Laptev Sea	Serova and Gorbunova (1997)
	North East Pacific	Carson and Arcaro (1983)
	West Pacific basins	Chamley (1981)
Atlantic Ocean	All basins	Biscaye (1965)
	Labrador, Irminger and Iceland basins	Zimmerman (1982); Grousset et al.,(1983); Bout-Roumazeilles (1995); Fagel et al. (1996)
	Western North Atlantic margin	Zimmerman (1972); Piper and Slatt (1977)
	Eastern North and South Atlantic margin	Behairy et al. (1975)
	Equatorial Atlantic	Bremner and Willis (1993)
	South Atlantic	Petschick et al. (1996); Diekmann et al. (2000, 2003)
	Antarctic shelf	Ehrmann et al. (1992); Ehrmann et al. (2005); Hillenbrand and Ehrmann (2005)
	Mediterranean Sea	Venkatarathnam and Ryan (1971)
Indian Ocean	North Indian	Bouquillon et al. (1989)
	Arabian Sea	Kolla et al. (1981)
	Central Indian Basin	Rao and Nath (1988)
	South East Indian Ocean	Kolla and Biscaye (1973); Moriarty (1977); Kolla, Henderson, Sullivan et al. (1978); Gingele et al. (2001b)
	West Indian Ocean	Kolla et al. (1976)

respectively). As underlined by Chamley (1989), these maps are for "large-scale reference" purposes only.

2.5.2. Clay distribution in Atlantic Ocean surface sediments

Like gibbsite, kaolinite abundance decreases both northwards and southwards from the equatorial Atlantic region (Biscaye, 1965). The strong correlation between
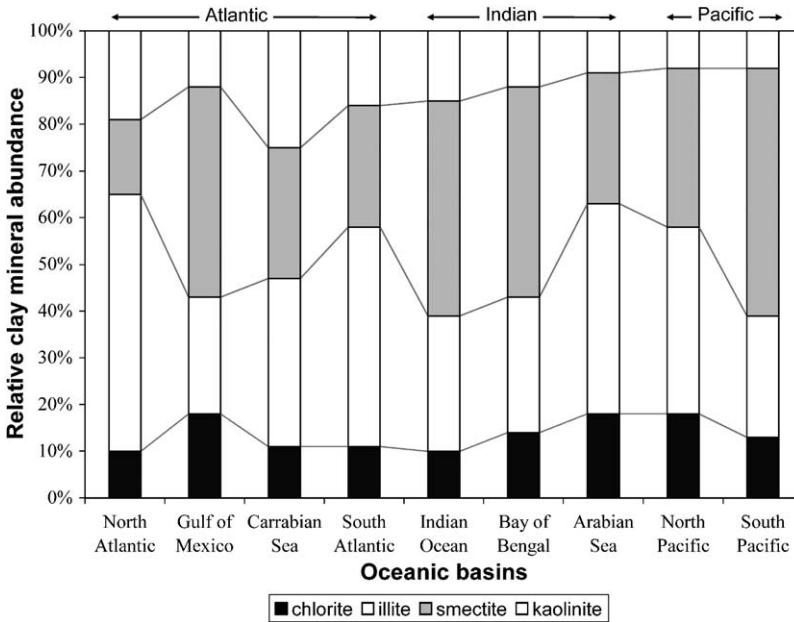
Figure 3 Mean clay mineral assemblages in the <2 μm fraction of surface sediments from basins of the world oceans compiled by Windom (1976) (Table 1). Illite and smectite are the two most variable clays. Inherited from continental landmasses, illite tends to decrease southwards, consistent with the asymmetrical distribution of landmasses. The climate-derived (or zonal) distribution of smectite is locally masked by the presence of additional authigenetic clays produced by alteration of volcanic material (including basaltic oceanic crust) and/or hydothermalism. In addition, major fluviatile inputs locally dilute deep-sea clay assemblages (e.g., smectite-rich inputs from the Mississippi River into the Gulf of Mexico; illite- and chlorite-rich inputs from the Indus into the Arabian Sea).

Table 2 Mean Clay Mineral Assemblages in the <2 μm Fraction of Surface Sediments from Basins of the World Oceans.

Ocean area	Illite	Chlorite	Smectite	Kaolinite	Nb. samples
North Atlantic	55	10	16	19	181–193
Gulf of Mexico	25	18	45	12	38
Carrabian Sea	36	11	28	25	49–56
South Atlantic	47	11	26	16	196–214
North Pacific	40	18	34	8	170
South Pacific	26	13	53	8	140–151
Indian Ocean	29	10	46	15	129–245
Bay of Bengal	29	14	45	12	25–51
Arabian Sea	45	18	28	9	29

Note: Data expressed as relative abundance in the clay-size fraction (i.e., values are summed to 100%). Data from Windom (1976).
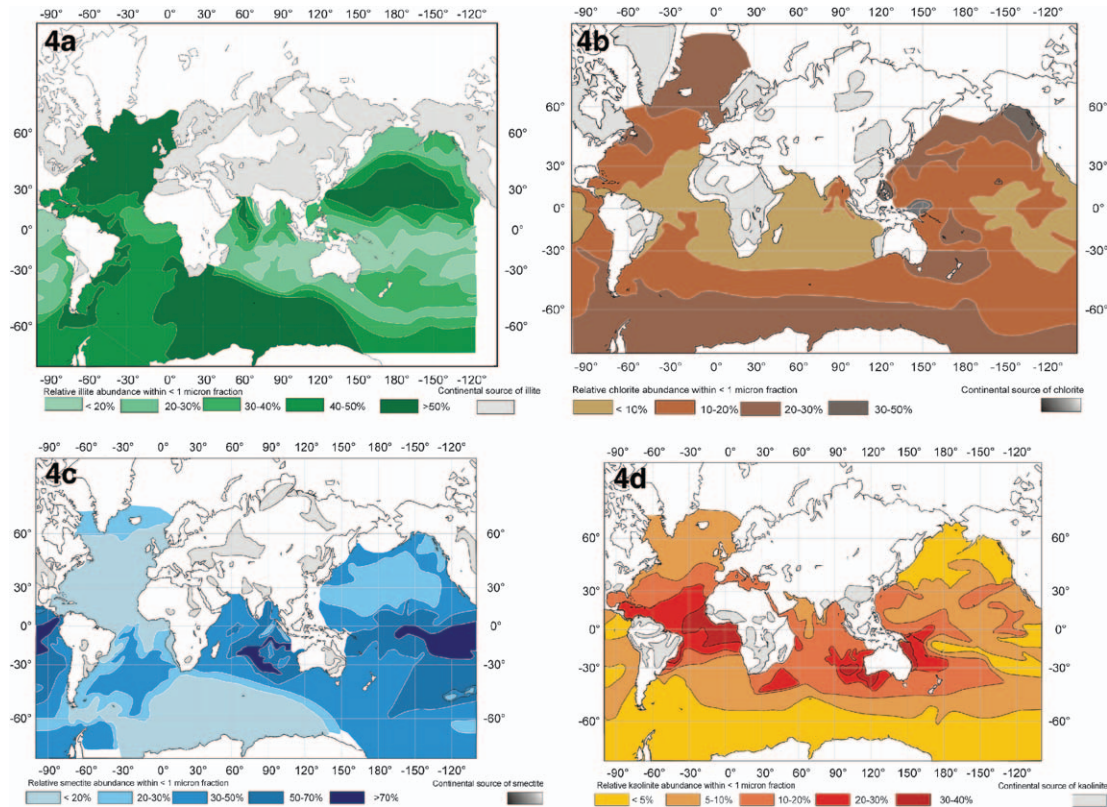
Figure 4 (A) Distribution of illite in the "clay" (<1 μm) fraction of surface marine sediments. Continental areas characterized by high abundance of illite (i.e., >50%) in soils are also reported. (B) Distribution of chlorite in the "clay" (<1 μm) fraction of surface marine sediments. Major continental sources of chlorite are reported. (C) Distribution of smectite in the "clay" (<1 μm) fraction of surface marine sediments. Major continental areas characterized by high abundances of smectite (i.e., >50%) in soils are also reported. (D) Distribution of kaolinite in the "clay" (<1 μm) fraction of surface marine sediments. Continental areas characterized by occurrence of kaolinite or kaolinite and gibbsite in soils are also reported. Simplified from Lisitzin (1996), with permission.

kaolinite and gibbsite abundances and proximity to continental areas undergoing intense tropical weathering seems to constitute conclusive evidence for their continental origin (Biscaye, 1965). Kaolinite constitutes 20–30% of the clay fraction in the eastern sector of the equatorial Atlantic but, due to input from the Niger River draining kaolinite-rich African equatorial soils and to wind transport from North African deserts, it reaches up to 50% in the western sector (Windom, 1976).

In Atlantic sediments, chlorite abundances increase towards the polar regions (Windom, 1976). This mineral is more prevalent in soils at higher latitudes where chemical weathering is less intense (Gradusov, 1974). The strong correlation between the continental and deep-sea abundances of chlorite supports a detrital origin for this mineral (Biscaye, 1965).

Illite is the dominant clay mineral in the $<2\,\mu m$ fraction of Atlantic Ocean sediments, showing minor variations compared to other clay minerals (Biscaye, 1965). Rivers play a major role in the asymmetrical distribution of illites in deep-sea Atlantic sediments (Rateev et al., 1969). There is an obvious illite zonation in the North Atlantic, which is supplied by large drainage areas within temperate and cold zones (Windom, 1976). In the South Atlantic, drainage areas are small or non-existent (Windom, 1976). The concentration of continental masses in the northern hemisphere supports a detrital origin for illites, a conclusion which is confirmed by the old K/Ar ages of these clays minerals (see above, Biscaye, 1965). Additional illite-rich inputs are transported by wind from desert soils of southwest Africa to the South Atlantic (Windom, 1976). For instance, the high concentration of illite measured in the suspended load of rivers draining South America contributes to the high illite content in South Atlantic sediments at the mouths of the Amazon, the Parana, the Orinoco, etc. In contrast, smectite-rich particulate inputs from the Mississippi dilute the illite content in the Gulf of Mexico. The lack of correlation between smectite, zeolites and volcanic shards, as well as the low abundance of smectites in surface Atlantic Ocean sediments point to a primarily detrital origin for smectite (Biscaye, 1965). Smectite abundance is low in the North Atlantic, where it is diluted by high inputs of illite and chlorite (Windom, 1976). The Mississippi River supplies smectite-rich particulate matter to the Gulf of Mexico and the Caribbean Sea. The Amazon River also supplies smectites to the southern North Atlantic which are mainly detrital, except in the vicinity of the Lesser Antilles Arc. The high smectite contents in the South Atlantic have been attributed to eolian inputs or alteration of Mid-Atlantic Ridge (MAR) material (Windom, 1976).

The resulting clay mineral distribution patterns highlight the fact that most recent deep-sea clays are derived from surrounding continents (Biscaye, 1965). The mineralogical analysis of the fine-grained fraction of Atlantic deep-sea sediments is therefore a useful indicator of sediment provenance. In the North Atlantic, the topographic control exerted by the MAR contributes to the importance of bottom current transport. In the equatorial Atlantic Ocean, detrital clays are transported by rivers draining South America and Africa, and by winds from Africa. Biscaye (1965) emphasizes the importance of AABW in the northward transport of clays in the South Atlantic.

2.5.3. Clay distribution in Pacific Ocean surface sediments

Griffin et al. (1968) related the relative amounts of chlorite, montmorillonite or smectite, kaolinite and illite in pelagic sediments to the sources and transport paths of solid particles from the continents to the oceans and to injections of volcanic materials into marine environments, especially in the South Pacific Ocean. According to Rateev et al. (1969), wind is the primary transport agent in the North and South Pacific.

Windom (1976) provides a detailed discussion of the maps presented by Griffin et al. (1968). Kaolinite is abundant in low latitude marine sediments. Pacific Ocean sediments have low kaolinite contents due to minimal terrigenous supply from river discharge, especially in the South Central and East Pacific. Along the eastern Pacific coast, relatively arid source areas with low run-off supply very little kaolinite. Regions of intense chemical weathering and high run-off along the western coast act as important sources of kaolinite. In the South Pacific, kaolinite-rich particles are supplied by wind from the Australian desert.

Although more uniform, the distribution of chlorite in deep-sea Pacific sediments is inversely related to that of kaolinite. The highest chlorite abundances occur in sediments adjacent to the Alasakan and Canadian coasts, reflecting suspended particle compositions in major rivers draining into this area. The Asian continent also supplies chlorite to the northwestern Pacific, which is subsequently redistributed by surface current. The high abundance of chlorite in the south-western Pacific has been attributed to eolian transport from Australian soils.

An illite-rich belt observed in North Pacific sediments has been attributed to eolian inputs. It is likely that illite enrichment in the South Pacific results from dust supplied from Australia deserts. It is interesting to note that sepiolite has been observed in a few samples from the South Pacific, including dust from New Zealand (Windom, 1976).

The highest smectite abundances observed are from the Pacific Ocean. Smectite is uniformly distributed and undergoes local dilution by continental run-off or wind-transported, continentally-derived material. In the South Pacific, high abundances of smectite are observed in the vicinity of volcanically active areas (Windom, 1976). The high abundance of smectite and its close association with zeolites and volcanic glasses are evidences for its volcanogenic origin (Griffin & Goldberg, 1963).

2.5.4. Clay distribution in Indian Ocean surface sediments

The kaolinite contents of recent Indian Ocean sediments are intermediate between those of the Atlantic and Pacific Oceans (Windom, 1976). A clear trend of increasing kaolinite abundance towards Western Australia, which is attributable to wind transport, is observed.

Indian Ocean sediments are depleted in chlorite, except in the Arabian Sea, where chlorite is supplied by rivers (e.g., the Indus) or wind (Windom, 1976). Illite contents are also low, decreasing towards the Indian coast as a result of dilution by smectite-rich fluvial detrital inputs from the Deccan traps. The exceptionally high illite abundance in the Bay of Bengal is related to Ganges run-off (Bouquillon, Chamley, & Frolich, 1989; Fagel, Debrabant, & André, 1994), whereas the high

smectite content of the Indian Ocean is linked to river discharge (Windom, 1976). In addition, abundant authigenic smectites are observed locally in the eastern and southwestern Indian Ocean (Biscaye, 1965; Windom, 1976). Palygorskite has been observed in the Gulf of Aden, the Red Sea and the Arabian Sea (Windom, 1976; Kolla et al., 1981; Fagel et al., 1992a).

2.5.5. General trends in recent clay distributions in the world oceans

As previously highlighted for the Atlantic Ocean (Biscaye, 1965), the spatial distribution of clay minerals in the world oceans shows some significant regular patterns (Rateev et al., 1969). The relative abundances of the different clay minerals in bottom sediments show a pronounced latitudinal control. In bottom sediments of the world oceans, two groups of clay minerals can be distinguished based on their distribution patterns:

(1) kaolinite, gibbsite and smectite are concentrated in the tropical–humid zone, and their abundances decrease to both the north and south; this is called the equatorial-type distribution;

(2) chlorite and illite are concentrated at moderate and high latitudes, mainly within the cold, moderately humid and glacial zones; this is called the bipolar-type distribution.

To explain the latitudinal distribution of clay minerals, Rateev et al. (1969) called upon several factors related to the nature of the continental catchment basins (climatic zonation, type of continental weathering, and intensity of denudation), ocean hydrodynamics (current directions and the overall movement of water masses), the influence of volcanism, etc. It is possible to assess the influence of catchment basins on the distribution of clay minerals by comparing the distribution of clay minerals with the distribution of the different types of weathering and the intensity of mechanical denudation on the continents (Strakhov, 1960). The location of the kaolinite- and smectite-rich belt coincides with an area of intense chemical weathering in the tropics (35°N–35°S). The northern concentration maxima of illite (60–80%) and chlorite (>30%) are associated with the belt of normal weathering which encompasses the cold, moderately humid zones of Siberia and Canada. The distribution of clay minerals in world ocean sediments is closely related to latitude or climate. Kaolinite, smectite and gibbsite are formed in areas of tropical lateritic soil development. Illite and chlorite are mainly formed in soils of moderate and high latitudes. A gradual decrease in the abundance of equatorial minerals towards the poles and in the abundance of bipolar minerals towards the equator is the results of hydrodynamic scattering.

Deviations from the normal picture are associated with the asymmetry of catchment basins (e.g., the southern hemisphere), the effect of vertical climatic zonation on the delivery of clayey particles (India), and/or irregular patterns of ocean currents. A relationship between the distribution of minerals and hydrodynamics may be established by comparing compiled maps of clay mineral distributions with maps of currents in the world oceans. Rateev et al. (1969) noted the relationship between an area of high kaolinite abundances (40–60%) in the Indian and Pacific Oceans and the south trade wind currents, and the fact that the area characterized by 20–40%

kaolinite in the Atlantic Ocean is limited by the north trade wind and North Atlantic currents. In the southern hemisphere, westerly winds affect clay mineral distribution. Ocean currents which usually display a latitudinal direction play an important role in promoting the latitudinal zonation of clay minerals in ocean sediments by retaining them within their latitudinal belts. The influence of volcanism on the distribution of clay minerals in ocean sediments is evidenced by the occurrence of aclimatic and azonal areas of high smectite contents which are superposed on latitudinal climatic belts, thus creating a more complex zonal distribution.

   Clay mineral patterns in deep-sea sediments match the overall latitudinal distribution of clay minerals in soils worldwide (600 samples; Gradusov, 1974). Regions with soils characterized by high concentrations of illites (>70%) in the C horizon primarily occur in the northern hemisphere, with minor regions occurring in the southern hemisphere. These areas include morainic deposits in mountainous regions, shields in cold and temperate humid climates, as well as low altitude areas covered by alluvial and glacial deposits. All these areas are characterized by a cold climate. In the southern hemisphere, high illite contents are mainly observed in soils of mountainous regions. In parental material of the equatorial belt and bordering regions, illite abundance is minimal (<30%). The illite content is usually lower in upper eluvial horizon A. Smectite and mixed-layers abundance maxima are observed in soils formed from alteration products of basic parental rocks in subtropical and tropical, arid and semi-arid climates. Smectite abundances tend to increase from the upper to the lower horizons of soil profiles. Soils with low smectite contents predominate in mountainous areas and shields characterized by free drainage and cold or temperate climates.

   Later regional studies have mainly served to confirm the overall distribution patterns of clays in the world oceans (see Table 1). For instance, Naidu and Mowatt (1983) compiled clay mineral assemblage data from 700 sediment samples from the Gulf of Alaska and the South Bering Sea in the North Pacific Ocean. Although the data compiled were obtained by various investigators using different sample preparation, analytical and quantification techniques, which increases uncertainties (Naidu, Creager, & Mowatt, 1982), the results are consistent with the general latitudinal trends, controlled by climate and associated pedogenic processes, previously identified for clay mineral distribution in the world oceans (Biscaye, 1965; Griffin et al., 1968; Rateev et al., 1969). The distribution patterns of clay minerals in all of the marginal seas of Alaska (except the Beaufort Sea) are related to the various contemporaneous terrigenous sources of clay minerals and subsequent clay mineral dispersal by prevailing currents. Conversely, clay mineral distribution may be used to infer net current patterns. Naidu and Mowatt (1983) do, however, point to the higher kaolinite abundances and kaolinite/chlorite ratios in the north Bering, Chukchi and Beaufort Seas. This local kaolinite enrichment is attributed to reworking of kaolinite-bearing sedimentary rocks of northern Alaska, and subsequent transport to the adjacent Arctic seas. In the outer continental shelf region of the Beaufort Sea, the lack of recognizable dispersal patterns in clay distribution may be due to peculiarities of the sedimentary regime resulting from ice sediment transport (Naidu & Mowatt, 1983).

Exceptions to the latitudinal zonation of clay minerals in the oceans suggest that climate is not the only factor responsible for the distribution of terrigenous clay minerals (Thiry, 2000). Around continental masses, marine clay patterns are clearly controlled by terrigenous inputs, but the presence of abundant smectite in the centre of ocean basins must result from other processes, among which authigenesis and/or differential settling along advective marine currents are the most commonly mentioned (Thiry, 2000).

2.6. The Significance of Clays in Cenozoic Marine Sediments

Only the detrital clay component of marine sediments is indicative of weathering conditions in the continental formation environment. Detrital clays also provide insight into provenance and transport processes (Velde, 1995). Many papers dealing with the mineralogy of present-day marine environments have shown that clay minerals are, in general, continentally-derived (Biscaye, 1965; Griffin et al., 1968; Rateev et al., 1969). This also appears to be the case for older deposits. For instance, Chamley (1981) studied the long term Cenozoic clay deposition trends in DSDP material from different marine environments of the Mediterranean Sea, the North and South Atlantic and the northwestern Pacific, and concluded that the clay assemblages of recent deep-sea deposits are largely derived from the terrigenous supply of rocks and soil materials (Biscaye, 1965; Griffin et al., 1968). This is evidenced by comparing the average latitudinal zonation of clay mineral abundance in continental soils and in marine sediments, and by demonstrating a relationship between the principal geological provinces and clay sedimentary provinces. Mineralogical and geochemical studies point to the existence of similar conditions during past geological times in the same areas. The dominant nature of the terrigenous component in most Cenozoic deep-sea clays is suggested by: (1) the absence of continuous changes in clay content related to diagenetic modifications with the depth of burial; (2) the occurrence of a variety of clay assemblages, as in present-day deposits, including species derived from surficial and thermodynamically immature environments (e.g., poorly crystallized chlorite, irregular mixed-layers) which are not genetically associated with diagenetic minerals like clinoptilolite or opal CT; (3) the overall lack of a relationship between clay mineralogy and lithology; (4) the lack of a relationship between smectite abundance and volcanic activity, except in oceanic basalts and volcanogenic sediments; and (5) the occurrence of fragile fibrous clay minerals in reworked sediments. Long-term marine clay sequences are therefore potential tools in deciphering continental paleoenvironments expressed by changing pedogenesis, marginal sedimentation, erosion, transport and sedimentation.

Because of their continental provenance, clays have been used to reconstruct oceanic paleoenvironments over the Cenozoic period. The interpretation of down-core changes in mineral concentrations depends on the best possible information on the modern distribution and sources, as well as independent climate *proxy data* about the source area (Gingele et al., 2004). The significance of clay minerals for paleoenvironmental reconstructions varies with site location as well as sediment age. For instance, Ehrmann et al. (1992) studied different geological settings in the Antarctic Ocean to assess the significance of clay mineral assemblages in

reconstructing the glacial history of the Antarctica Peninsula, the paleoceanographic history of the Antarctic Ocean, and the sedimentary processes operating at the Antarctic continental margin. They concluded that clay mineral assemblages in late Mesozoic to Paleogene sediments are sensitive tools for reconstructing climatic conditions. For example, the shift from smectite-rich to illite- and chlorite-dominated assemblages in the earliest Oligocene reflects the transition from chemical weathering conditions under a warm and humid climate to physical weathering under cooler conditions. Submarine plateaus (e.g., Maud Rise, Kerguelen Plateau) provide the best record for direct paleoclimatic studies. On proximal sites of the continental slope and shelf, as well as in the deep sea, paleoclimatic information is often masked by a variety of processes resulting in sediment redistribution. At those sites, however, clay mineral assemblages carry a wealth of information on different sedimentary processes. Following the establishment of the continental East Antarctic ice sheet, physical weathering prevailed and variations in the clay mineral record predominantly reflect the influence of different sediment sources controlled by different glacial, hydrographic or gravitational transport processes. Because these sedimentary processes are generally linked to climatic variations, clay mineral assemblages in most of Neogene and Quaternary sediments in Antarctic deposits provide indirect paleoclimatic information (also see Robert, 1982; Robert, Caulet, & Maillot, 1988). These processes are best documented by clay mineral composition in those areas where changes in source regions with distinct petrographic properties are expected and where distances from the source region are short.

Clay mineral assemblages in the approximately 1,600 m thick Cenozoic sedimentary succession off of Cape Roberts on the McMurdo Sound shelf in Antarctica were analysed in order to reconstruct the paleoclimate and glacial history of this part of Antarctica (Ehrmann, Setti, & Marinoni, 2005). The Cenozoic sediments exhibit a large number of unconformity-bound, fining-upwards cycles attributed to sea level variations or changes in the proximity of the ice masses. The lack of correlation between sedimentary facies and clay mineral assemblages, and the absence of systematic differences in clay signature between proximal and distal glaciomarine sediments suggest that the clay mineral distribution pattern is not influenced by transport, sedimentation and reworking processes, but that it is rather primarily controlled by climate conditions and changes in source area.

In the North Atlantic, this approach has enabled paleohydrological reconstructions based on clays from different periods, including the Quaternary (Latouche & Parra, 1979), the Cenozoic (Latouche, 1978) and the Mesozoic (Chamley, 1981). In some environments, the use of clay data for sedimentological reconstruction purposes may be difficult. For instance, in volcanic environments, volcanic products and their by-products (i.e., authigenic minerals from aerial and sub-marine environments) mix with terrigenous inputs, making it difficult to differentiate the two types of materials (Grousset et al., 1983). Moreover, in the North Atlantic, source rocks yield relatively constant clay mineral assemblages through time with minimum variability between glacial and interglacial stages (Fagel & Hillaire-Marcel, 2006). Elsewhere, processes such as rapid tectonic uplift, as in the Himalayas, may result in progressive changes through time (e.g., Bouquillon et al., 1989; and other references in Chamley, 1989).

2.7. Provenance of Detrital Inputs

Detrital clay mineral assemblages in deep-sea sediments have been widely used to determine the provenance of detrital inputs. Clay mineralogy has been used as a tracer of provenance and transport mechanisms in studies of the world oceans in which the mineralogy of the fine detrital fraction ($<20\,\mu m$) generally reflects the intensity of continental weathering in the source areas (Biscaye, 1965; Griffin et al., 1968). The effectiveness of clay proxies is best documented in areas characterized by distinct mineralogical provinces (e.g., the southwest Pacific, Gingele, De Deckker, & Hillenbrand, 2001a; the southeast Indian Ocean, Moriarty, 1977; the Arabian Sea, Fagel et al., 1992a; the South China Sea, Liu et al., 2003; the eastern Mediterranean Sea, Venkatarathnam & Ryan, 1971). For instance, clay mineral assemblages in 166 surface sediments from the southwest Pacific, between Indonesia and NW Australia, show a strong relationship with the geology and weathering regime of the adjacent hinterland and allow the distinction of four clay mineral provinces (Gingele et al., 2001a). Likewise, the study of 245 surface sediments from the southeast Indian Ocean and southwest Pacific allows the delineation of four geographical provinces (Moriarty, 1977).

The alternation of two distinct clay mineral assemblages as expressed by their clay mineral ratios has been used to trace seasonal transport direction changes related to monsoon circulation in the South China Sea (Liu et al., 2003) and the Arabian Sea (Fagel et al., 1992a), for instance. In the northern South China Sea, present-day illite and chlorite mainly come from northern source areas (Taiwan and the Yangtze River), and are carried by the surface currents which prevail during the winter monsoon. In contrast, smectites are mainly derived from southern volcanic source areas (Luzon and the Indonesian islands) and are transported by summer monsoon circulation (Liu et al., 2003). In the Arabian Sea, southwesterly summer monsoon winds carry palygorskite-rich clay assemblages from the Somalian and Arabian desert regions whereas the winter northeasterly monsoon winds bring illite-rich material from the Indus River (Fagel et al., 1992a). It should be pointed out that comparing two clay mineral components using their ratio reduces the effect of dilution by other components, and hence facilitates interpretation (Gingele et al., 2001b).

In general, the presence of multiple sources and transport processes makes it difficult to assign one main source area to a given clay mineral assemblage. For instance, Carson and Arcaro (1983) emphasized the fact that constraining the areal distribution patterns of clay minerals is not sufficient to define their provenance. Clay mineral studies require analysis of mineralogy-size variables to assess the relative contribution of provenance and selective transport. Carson and Arcaro (1983) studied Late Pleistocene and Holocene sediments from the Cascadia Basin and Juan de Fuca abyssal plain in the northeast Pacific Ocean. They noted that clay mineralogy is size-dependent, with a grain-size mineralogy relationship similar to that reported by Gibbs (1977) for sediments along the Amazon shelf, namely that the fine fraction is enriched in montmorillonite. The increase in montmorillonite in Holocene sediments cannot be explained by a change of source. For the American continental shelf, Nittrouer (1978) established that selective transport resulted in the preferential deposition of sands in nearshore waters and silts to silty clays on the

middle to outer continental shelf. If the shoreline and associated river mouths are immediate sources of clays, a change in the position of the shoreline would result in a change in the distance to any deposition site. Moreover, selective transport is a function of current velocity: a decrease in bottom velocity could lead to progressively smaller particles being deposited. Given the size dependency of the clay mineralogical content, less vigorous currents than those that were active during the Pleistocene could produce smectite-rich Holocene deposits without any change in provenance.

Further constraints on sediment sources may be provided by complementary analyses. In some cases, detailed studies of X-ray patterns and cation saturations can yield additional information. For instance, the link between smectite composition in sediments from the northern North Atlantic and the Labrador Sea and deep circulation allows a clear distinction between the various dominant terrigenous sources associated with the main components of the modern Western Boundary Undercurrent (Fagel, Robert, Preda, & Thorez, 2001).

The radiogenic isotopic signature of the detrital sedimentary fraction has been used to trace sediment provenance. Huon, Jantschik, Kubler, and Fontignie (1991) measured the isotopic K/Ar signature of the clay-size fraction of NE Atlantic sediments to constrain the sources of detrital material. In ice-rafted layers, K/Ar ages reflect an enrichment in old detrital material which is consistent with erosion of Precambrian rocks. Because the contribution of radiogenic ^{40}Ar in recent rocks is negligible, it was difficult to pin down the influence of recent volcanically derived material. Sm/Nd systematics provide better insight into the mixing of crustal and volcanically derived material. Goldstein and O'Nions (1981) have shown that detrital clays in marine sediments retain their Nd isotopic signature throughout the sedimentary cycle, that is, from continental weathering, through sediment transport to diagenesis. Nd isotopic analyses of these terrigenous fractions can therefore provide direct and quantitative information on sediment provenance (McCulloch & Wasserburg, 1978; Jones, Halliday, Rea, & Owen, 1994). In order to constrain complex sedimentary mixing, Nd isotopic analysis may be coupled with other radiogenic isotope measurements. For instance, Nd and Pb isotopes have proven to be powerful tracers of the origin and provenance of deep-sea sediments in subduction areas (e.g., White, Dupré, & Vidal, 1985; White & Dupré, 1986; Vroon, Van Bergen, Klaver, & White, 1995), in worldwide turbidites (McLennan, McCulloch, Taylor, & Maynard, 1989) or, more regionally, in the Indian (Dia, Dupré, & Allègre, 1992), the Pacific (Jones et al., 1994) and the South Atlantic Oceans (Bayon, German, Nesbitt, Bertrand, & Schneider, 2003). In particular, these isotopes constitute suitable tracers of the origin of fine-grained deep-sea sediments of the northwestern North Atlantic (Labrador Sea), where, at present, mid-Atlantic mantle sources interact with old crustal North American inputs (Innocent, Fagel, Stevenson, & Hillaire-Marcel, 1997; Fagel, Innocent, Gariépy, & Hillaire-Marcel, 2002; Fagel et al., 2004). Nd and Pb isotopes have been measured in the clay-size fraction of Late Glacial and Holocene deep-sea sediments recovered from two Labrador Sea piston cores. These data provide better constraints on the different source areas that supplied clay-size material into the Labrador Sea. Changes in their relative contribution through time further constrain the deep circulation pattern from the last deglaciation until 8.6 ka (Fagel et al., 2002).

Although Sr isotopes are less conservative than Nd isotopes during weathering processes (Goldstein, 1988; Allègre, Dupré, & Négrel, 1996), sedimentary Sr isotope signatures have been successfully related to continental sources of the detrital fraction in the North Atlantic (Dasch, 1969; Biscaye, Chesselet, & Prospero, 1974), the equatorial Atlantic (Hemming et al., 1998) and the northern (Asahara, Tanaka, Kamioka, & Nishimura, 1999) and western Pacific (Mahoney, 2005). Nd and Sr have been widely used to trace detrital provenance in the North Atlantic (Grousset et al., 1988; Revel, Sinko, Grousset, & Biscaye, 1996a), in the South Atlantic (Walter et al., 2000; Bayon et al., 2003) and in the Arctic Oceans (Tütken, Eisenhauer, Wiegand, & Hansen, 2002).

Although such multiproxy methods remain scarce in the literature, coupling radiogenic isotope analyses and clay mineralogy is a powerful approach. The interpretation of isotopic data is made easier with prior knowledge of the main potential sources of detrital particles obtained from recent clay distribution, especially in complex environments involving multiple transport agents. For instance, Bayon et al. (2003) have analysed the Nd isotopic composition of the entire detrital fractions (mainly $<20\,\mu m$) of four sediment cores from the SE Atlantic Ocean to investigate variations in the accumulation of particles transported by Circumpolar Deep Water (CDW) and North Atlantic Deep Water (NADW) to this region during the Late Quaternary. Their data reproduce the complex modern-day hydrography of the SE Atlantic Ocean and confirm the relative variations in NADW and CDW at the Last Glacial Maximum (LGM). On the basis of Nd concentrations and isotopic compositions of terrigenous sediment in the Cape Basin, Bayon et al. (2003) demonstrated that the supply of terrigenous material derived from the southwest Atlantic region was greater during glacial periods than during interglacials. These authors suggested that the increase in the flux of clays from the southwest Atlantic region was the result of increased transport into the Cape Basin by CDW. The glacial–related change in deep circulation was questioned by Rutberg et al. (2005) who called instead upon higher glacial inputs from Patagonia (Diekmann et al., 2000; Walter et al., 2000). Indeed, clay mineralogy records from Cape Basin sediments at ODP 1089 show systematic climate-related changes (Rutberg et al., 2005). Kuhn and Diekmann (2002) showed that kaolinite/chlorite ratios varied by more than a factor of two, low values corresponding to glacial periods. They determined that Patagonia was the principal source of chlorite input into Cape Basin sediments. In fact, chlorite enrichment (Kuhn & Diekmann, 2002) and the shift in Nd isotopic signature (Bayon et al., 2003) suggest a greater contribution from South America or other western sources during the LGM rather than any change in the deep current regime (Rutberg et al., 2005).

Walter et al. (2000) have also combined clay mineralogy and Sr-Nd isotopic data for Late Quaternary surface sediment and sediment cores from the South Atlantic and southeast Pacific to reconstruct past circulation changes in the Austral Ocean. The glacial/interglacial shift in sources may be due to either the decreasing influence of NADW during glacial times or a larger contribution of glaciogenic detritus from southern South America. Hemming et al. (1998) combined clay mineralogy and Sr isotopic data of the detrital bulk sedimentary fraction of western equatorial Atlantic sediments to constrain particle provenance. The geographic gradients in clay

mineralogy and Sr isotopic composition of the detrital bulk fraction suggest mixing between Andean and Brazilian shield-derived sediments transported by the nepheloid layer from more kaolinite-rich sources, probably located in the Brazil Basin.
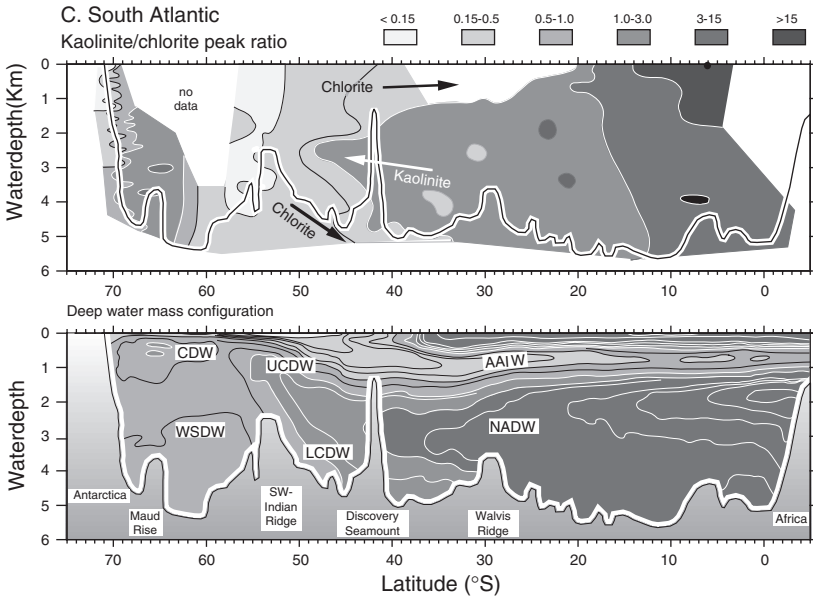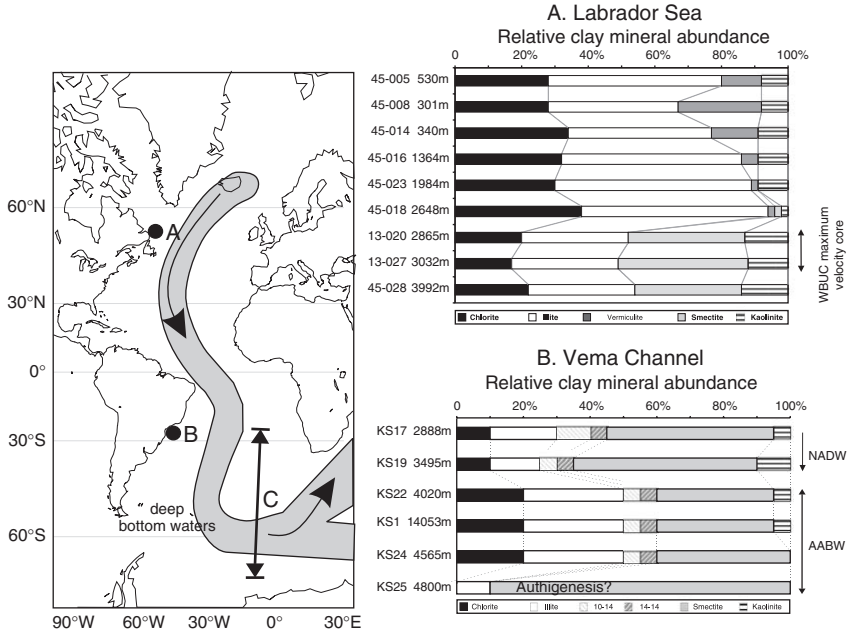
Isotopic measurements can be performed on the bulk detrital fraction (e.g., Walter et al., 2000; Bayon et al., 2003) or on specific size fractions ($<63\,\mu m$, Hemming et al., 1998; $10–63\,\mu m$ and $<10\,\mu m$, Revel, Cremer, Grousset, & Labeyrie, 1996b; $<2\,\mu m$, Innocent et al., 1997; Fagel et al., 1999). Walter et al. (2000) analysed the Sr isotopic compositions of bulk, silt and clay fractions and pointed out that this approach allows additional constraints to be placed on transport processes. Innocent, Fagel, and Hillaire-Marcel (2000) showed that the clay-size fractions ($<2\,\mu m$) yielded different Sm-Nd signatures than the cohesive silt fraction ($2–10\,\mu m$). Of these different size fractions, the clay-size fraction appears to be of particular interest for tracing sedimentary inputs transported by deep currents (Fagel et al., 2002). Silt fractions mainly record the influence of proximal supplies, whereas clay-size fractions are more sensitive to sedimentary input advected by deep currents (Innocent et al., 2000). Clay-size particles may be transported by deep currents then deposited when current strength decreases. However, because of their cohesive behaviour, they are less sensitive to further current winnowing following deposition (McCave, Manighetti, & Beveridge, 1995). More investigations of grain-size dependence are required, because Tütken et al. (2002) provided evidence for the grain-size-dependent fractionation of Sr isotopes, a behaviour which Nd isotopes do not appear to display.

2.8. Relationship between Clay Mineralogy and Ocean Circulation

2.8.1. General statement

Clay mineral assemblages have been used to trace ocean currents at the ocean scale (e.g., the Atlantic Ocean) since the sixties (Biscaye, 1965) and, more recently, at the regional scale as, for instance, in the North Atlantic (Grousset & Latouche, 1983), the South Atlantic (Gingele, 1996; Petschick et al., 1996; Figure 5), the East Indian Ocean (Gingele et al., 2001a), the southeast Indian Ocean and the southwest Pacific Basin (Moriarty, 1977). In given water mass, fine-grained clay minerals can be advected over considerable distances to finally settle far away from their original source. There has been much discussion in the literature about the usefulness of clay minerals in delineating suspended sediment dispersal routes and in indicating the provenance of marine fine-grained deposits (e.g., Biscaye, 1965; Knebel, Conomos, & Commeau, 1977). Hein et al. (1979) showed that clay minerals in estuarine and shelf deposits in south central Alaska provide a record of their source areas and patterns of dispersal. Surface clay mineral distributions have allowed the reconstruction of a mean regional oceanic circulation pattern which is consistent with independent current, salinity and temperature data.

A prerequisite for the reconstruction of transport pathways is the identification of specific source areas on the adjacent landmasses (Hillenbrand & Ehrmann, 2005). Clay mineral assemblages in surface ocean sediments, which differ significantly from those in local sources, have already been used successfully to outline the extent and propagation of water masses (e.g., Petschick et al., 1996, for the South

A. Labrador Sea
Relative clay mineral abundance

B. Vema Channel
Relative clay mineral abundance

C. South Atlantic
Kaolinite/chlorite peak ratio

Deep water mass configuration

Atlantic; Gingele et al., 1999, for the eastern subtropical Atlantic; Fagel, Robert, & Hillaire-Marcel, 1996, for the northern North Atlantic; Gingele et al., 2001a, for the southeast Indian Ocean). Over glacial/interglacial cycles, changes in marine clay mineral assemblages usually record changes in source areas or transport media (Gingele et al., 2001a). Once the relationship between a specific clay mineral suite and a certain source, water mass or current system is established, variations of this suite in down–core profiles may be used to constrain fluctuations in the propagation of the water mass or the current system (Diekmann et al., 1996; Gingele, Schmieder et al., 1999; Gingele et al., 2004).

2.8.2. Surface sediments

Many studies have demonstrated a relationship between clay mineral assemblages in surface sediments and water depth. Venkatarathnam and Ryan (1971) mapped the distribution of clay minerals in surface sediments in the deep-water basins of the eastern Mediterranean Sea to trace the sources and understand the mechanisms of sediment dispersal in this body of water by correlating the distribution of clay minerals with water circulation patterns. These authors concluded that bottom currents are important in transporting illite and chlorite-rich sediments into the deep parts of the Ionian Basin.

In the South Atlantic, advection of chlorite with southern AABW was already suggested by Biscaye (1965). For the southwest Pacific, Moriarty (1977) interpreted the high chlorite content in the South Tasmanian Basin to have resulted from the

Figure 5   The relationship between clay mineral assemblages and deep oceanic circulation. Evidence for clay mineral evolution with water depth reported for three areas (labelled A, B, C) located along the present-day general circulation path of cold deep bottom water generated in the northern North Atlantic. (A) SW-NE transect across the Canadian margin, Labrador Sea, northern North Atlantic. The clay mineral assemblage changes with increasing water depth (data from Fagel et al., 1996, with permission). Note the sharp change in clay mineral composition and abundances between 2,648 and 2,865 m. Abundant vermiculite-like clays are only reported in sediments from the continental shelf. The disappearance of vermiculite coincides with massive amounts of smectite in the deepest sediment cores. The highest smectite abundance occurs at depths consistent with the maximum velocity core of the WBUC. (B) NW-SE transect along the western flank of the Rio Grande Rise, Vema channel, Equatorial Atlantic (data from Melguen et al., 1978, with permission). A significant change in clay mineral assemblage is observed between 3,495 and 4,020 m, i.e., at the lower limit of NADW and the upper limit of AABW. Chlorite abundance in sediments collected between 4,000 and 4,565 m is twice as high as that observed in shallower sediments (<3,495 m). Chlorite was widely used as a proxy for AABW-transported inputs. The significant change in chlorite abundance in the deepest sediments is striking; such smectite-dominated clay assemblages may reflect the presence of authigenetic clays, although this is not confirmed by any geochemical anomaly in the bulk sediments (Melguen et al., 1978). (C) Latitudinal transect through the South Atlantic, from Antarctica to the equator including data collected from 20°W to 20°E and projected along the Greenwich meridian. Data from Petschick et al. (1996), with permission. Upper panel: relationship between the kaolinite/chlorite ratio (3.58 Å/3.54 Å) and water depth. Lower panel: water mass distribution. This figure, simplified from Petschick et al. (1996), clearly demonstrates the strong link between clay mineral assemblage and the nature of the intermediate or deep water mass: at present, kaolinite-rich inputs are transported by NADW, whereas chlorite-enriched inputs are carried by Antarctic Intermediate Water and Lower Circum Antarctic Deep Water (LCDW, i.e., previously AABW).

reworking of sediment from the Tasman Fracture zone by AABW bottom current. In the southeast Indian Ocean, dispersal of both the clay and quartz components in deep basins is also largely controlled by AABW circulation (Kolla, Henderson, Sullivan, & Biscaye, 1978). Quartz is primarily continent-derived, whereas clay abundances may reflect both continental derivation and the alteration of submarine basalts. Not only are clay abundances high in zones of high quartz abundances, but clays also extend farther into deeper, more seaward areas than quartz. Clays are also more readily dispersed than the coarse-grained quartz and are characterized by more extensive, uniform distribution of high abundances. Clay abundances cannot be used as a reliable indicator of the extent of influx of continental detritus. To do this, data on clay mineralogy and clay accumulation rates are required (Kolla et al., 1978).

The use of deep-sea clay mineral assemblages as indicators of water mass fluctuations (i.e., NADW versus AABW) was well documented for the Vema Channel in the southeast Atlantic (Petschick et al., 1996). Based on their strong latitudinal and opposite distribution patterns in surface sediments of the South Atlantic, kaolinite and chlorite were inferred to be useful tracers of the major deep water masses in the vicinity of the Rio Grande Rise. Advection of chlorite with southern AABW deep water was already suggested by Biscaye (1965). Melguen et al. (1978) demonstrated that the clay mineralogy of six cores from the Vema Channel largely depends on the provenance of the water masses (AABW or NADW) that transported the inherited products of continental weathering. They concluded that AABW transports chlorite and crystalline illite northwards. In contrast, the distribution of kaolinite and poorly crystallized illite is related to southwards flowing NADW (Figure 5).

More recently, the advection of kaolinite with NADW was documented from numerous cores (>900 samples) from the South Atlantic (Diekmann et al., 1996; Petschick et al., 1996). Alternatively, assuming that the suspended load of NADW in the western South Atlantic is too small to account for significant kaolinite enrichment, Jones (1984) proposed that kaolinite is advected along isopycnals from resuspended kaolinite-rich deposits of the Sao Paulo Plateau. Kaolinite/chlorite ratios of surface sediment samples provide evidence for both the advection and isopycnal transport models (Gingele et al., 1999). On the one hand, the symmetrical nature of the kaolinite enrichment at mid-depths on either side of the Rio Grande Rise is consistent with advective transport from low latitude. Consequently, similar kaolinite/chlorite ratios should be observed at comparable depths along the Middle Atlantic Ridge. However, only a slight increase in kaolinite/chlorite values is recorded near the surface, which may result from minor advection of kaolinite from low latitude. On the other hand, the transport of kaolinite to the western slope of the Rio Grande Rise along isopycnals, from the Sao Paulo Plateau may explain the kaolinite enrichment on the western side of the Rio Grande Rise, but not on its eastern side. To explain the symmetrical nature of the kaolinite enrichment on the Rio Grande Rise, Gingele et al. (1999) suggested the injection of suspended kaolinite at intermediate depths of the NADW off the mouth of the Rio Doce, and short-distance transport southwards instead of long-distance advection from lower latitude.

In the Labrador Sea, the clay mineralogy of deep-sea sediments has been used to trace the outflow of the Western Boundary Undercurrent (WBUC), the dominant lateral transport agent of suspended load in the North Atlantic (Eittreim & Ewing, 1974). Surface sediments from both margins of the Labrador Sea provide evidence for a link between smectite abundance in the clay fraction and the depth of the high velocity axis of the WBUC (Fagel et al., 1996; Figure 5). Based on a significant shift in the Nd isotope signature (Innocent et al., 1997), the WBUC is thought to be responsible for erosion and transport of clay particles from the smectite-rich western North Atlantic Iceland and Irminger basins, followed by redeposition in the Labrador Sea.

2.8.3. Late Cenozoic sediments

Grousset and Latouche (1983) have suggested that smectite-rich advective inputs in northwest Atlantic basins derived from erosion of Icelandic products were probably transported by Norwegian bottom currents. In the northeast Atlantic, changes in the smectite/illite ratio and variations in smectite and illite fluxes have been used to monitor variations of the WBUC outflow and, consequently, to constrain the NADW evolution during the last glacial/interglacial transition (Fagel et al., 1997b). This interpretation derived from clay mineralogy was later confirmed by estimating the relative contribution of proximal and distal current-driven clayey inputs, which are characterized by distinct Nd isotopic signatures (Fagel et al., 1999).

The clay mineral record in South Atlantic sediments (ODP Site 1089) has been used to reconstruct regional current systems in response to climate variability over the last 590 ka (Kuhn & Diekmann, 2002). Clay minerals indicate the source of terrigeous mud and trace the dispersal of fine-grained suspensions by water-mass advection within oceanic currents (Diekmann et al., 2003). Terrigenous sediments mainly originate from African sources with minor contributions from distal southern sources, and are supplied by circumpolar water masses, NADW, and surface currents of the Agulhas Current (Kuhn & Diekmann, 2002). Surface distribution maps and depth transects clearly indicate that kaolinite is especially abundant in the deep waters of the South Atlantic basins, and closely associated with NADW circulation (Petschick et al., 1996). Changes in clay mineralogy are best displayed by the quartz/feldspar and kaolinite/chlorite ratios of the clay-size fraction. Mineralogical variations reflect both the northward displacement of NADW injection into the Antarctic Circumpolar Current and a weakening of the Agulhas Current during glacial stages, sub-stages and stadials. During glacial stages, the influence of NADW decreases and allows the spreading of southern-source water masses in the area. The LGM map shows that low kaolinite/chlorite ratios in the northeast migrate towards lower latitudes and shallower water depths on topographic highs because of the larger extent of chlorite-bearing southern-source water masses and the reduced influx of kaolinite-bearing NADW (Diekmann et al., 2003).

In the southeast Indian Ocean, three cores taken below the path of the present day Leeuwin Current in the Timor Passage, offshore of the Australian Northwest Shelf and of the North West Cape of Western Australia, provide a Late Quaternary record of environmental changes (Gingele et al., 2001b). Today, kaolinite and

chlorite are transported into the Timor Passage by the Indonesian Throughflow, while illite is locally derived from Timor. Where the Leeuwin Current leaves the Timor Passage, it bears a characteristic clay mineral signature acquired in the Indonesian Archipelago (kaolinite, chlorite and illite). The uptake of clay minerals along its path through the Timor Sea (e.g., illite from the Kimberley area) changes this signature. South of North West Cape, chlorite injected by rivers of the Pilbara region into the path of the Leeuwin Current is a prominent constituent of surface sediments at water depths less than 1,000 m and delineates the present-day flow of the current. During the last glacial period, the volume of the Indonesian Through-flow decreased, and less kaolinite and chlorite reached the Timor Passage. Offshore from North West Cape, a reduction in the amount of chlorite during the last glacial may indicate a decrease in the intensity of the Leeuwin Current or its absence, and/or a lower chlorite input due to drier conditions on land. An illite maximum in Holocene and recent sediments offshore of North West Cape is the result of ma-terial input from rivers which periodically drain the adjacent hinterland. Lower illite abundances point to a drier climate in the area during the last glacial stage.

Recently, Barker and Thomas (2004) highlighted the fact that their "knowledge of the development and palaeoclimatic significance of the ACC will be best served by (…) mineralogical studies of clays as a way of examining provenance and therefore surface and bottom current directions and the existence of interocean connections".

2.9. Relationship between Clay Minerals and Climate

2.9.1. General statement

The paleoclimatic interpretation of clay mineral data requires knowledge of the potential source areas (Moriarty, 1977), as well as of the mode and strength of transport processes (Diekmann et al., 1996; Gingele et al., 1999). Variations in down-core clay mineral distribution in deep-sea sediments have been interpreted in terms of changes in the climatic conditions prevailing in the continental source area (Chamley, 1967, 1989; Robert & Maillot, 1983; Clayton, Pearce, & Pzeterson, 1999; Foucault & Mélières, 2000) and, potentially, subsequent changes in sea level (Robert et al., 2005). The paleoclimatic interpretation of clays is based on the assumptions that they are detrital and have not been significantly altered by diagenesis, that their source areas can be identified, and that they represent secondary products of continental weathering (Singer, 1984). Based on the latitudinal climate-driven clay-mineral distribution trends in recent deep-sea sediments (Biscaye, 1965; Griffin et al., 1968; Rateev et al., 1969), variations in vertical marine clay mineral distribution patterns have been interpreted in terms of shifts in the climatic conditions prevailing in the continental source areas of the detrital clay minerals (Singer, 1984) and have been widely used to reconstruct paleoclimates.

However, the interpretation of past climate change based on clay mineralogy is complicated by several factors described below (Moriarty, 1977; Singer, 1984; Chamley, 1989; Thiry, 2000):

(1) Clay minerals go through several stages between their development in soils and their final deposition in an ocean basin. For instance, clay minerals may persist

in soils through climate changes (Caroll, 1970), especially in regions where humid and arid weathering conditions alternate.

(2) The signal may be obliterated by erosion and transport processes as erosion products from bedrock and different soil horizons undergo mixing. Soils formed during interglacial periods in the Arctic can be eroded during the following glacial period, and become mixed with glacial "rock flour" and loess (Darby, 1975; Caroll, 1970).

(3) Marine sediment may also contain ancient recycled clay minerals which hold no paleoclimatic information regarding the period of interest (Singer, 1984). Unexpectedly high amounts of kaolinite at high latitudes in the Arctic Ocean are the result of reworking of kaolinite-bearing Mesozoic sedimentary rocks from surrounding continental masses (Singer, 1984). Although the deposition of kaolinite in recent sediments of the world oceans is consistent with proximity to wet climatic zones, this is partly due to the fact that kaolinitic paleosurfaces coincide with tropical areas where kaolinite is still developing at present (Thiry, 2000).

(4) There is a lag time between the formation of the soil-derived clay assemblages on the continents and their arrival in ocean basins. Clay sedimentation may occur several thousands of years and more after the formation of soils on the continent, and climate may have considerably changed during that time. The resolution of the paleoclimatic record in marine clays is therefore limited by soil formation rates, which are sometimes on the order of 1 or 2 Ma (Moriarty, 1977; Thiry, 2000).

Although clay assemblages in Cenozoic DSDP sedimentary records are primarily controlled by climate, other factors, such as selective distribution of clay minerals during erosion and transport (Singer, 1984), may readily modify them. Rivers are the principal carriers of fine-grained sediments from continental areas into the ocean. With increasing distance from the source areas, the sediment load decreases, but the extent of this decrease is a function of clay mineral type. Later deposition of fine-grained marine sediments is controlled by current flow strength and direction, and seasonal meteorological and oceanic factors (winter storm, periodic river discharge, seasonal upwelling, etc.). Although these factors are related to climate, their relationship to it is complex (Singer, 1984). The relationships between climate and paleoceanography will be illustrated in the last section of this chapter (see Section 3, "Applications").

According to Thiry (2000), clay mineral assemblages provide an integrated record of overall climatic impacts. Paleoclimatic interpretations of marine clay assemblages are "yielding nothing more than rather broad paleoclimatic information". However, short-term changes in clay mineral assemblages have been observed in many oceanic basins. These were not directly related to climate-induced changes in the adjacent landmasses, but were interpreted as resulting from either changing pathways and/or strength of transport processes (Latouche & Parra, 1979; Kissel, Laj, Lehman, Labeyrie, & Bout-Roumazeilles, 1997; Liu et al., 2003), local changes in glacial erosion related to ice sheet advance and retreat and in the supply of source rocks (Vanderaveroet, Averbuch, Deconinck, & Chamley, 1999; Hillenbrand & Ehrmann, 2005), fluctuations in river discharge between humid and arid phases

(Gingele et al., 1999) or sea level change and the related variation in shoreline position (Carson & Arcaro, 1983). These processes are direct or indirect consequences of climate change. According to Gingele et al. (1999), multiple sources and transport processes as well as the dilution of different clay minerals make it difficult to relate changes in the down-core record of any one component to changes in specific paleoclimatic parameters. In general, comparing two clay mineral components using the ratio of one to the other reduces the effect of dilution by other clays, which facilitates interpretation (Gingele et al., 1999).

2.9.2. Glacial/interglacial fluctuations of clay mineral assemblages

Short-term clay mineralogical (and geochemical) changes (i.e., over glacial/interglacial periods) were observed in four cores of Quaternary sediments from the Northwest Atlantic Mid-Ocean Canyon (Latouche & Parra, 1979). The mineralogical evolution over the last climate cycle was explained "both by climatic changes and the nature of the sedimentary sources which successively contributed to the deposits". During the glacial period, illite- and chlorite-rich sediments are autochthonous, carried from the nearby continental platform by turbidity currents. The lack of other inputs is explained by the shutdown of the main circulation of North Atlantic water masses during the glacial period. During the interglacials, sedimentary material inputs were more complex, the variability of sedimentary materials reflecting the establishment of circulation patterns similar to present-day patterns. Detrital deposits are mixed with smectite-rich material which may have originated from volcanic areas such as Iceland, the Reykjanes Ridge or the Gibbs fracture and have been carried by Norwegian deep-sea waters. Furthermore, the Gulf Stream seems to account for the transport of montmorillonitic clay mineral inputs from southern areas towards the north. Thus, clay mineral assemblages provide indirect information about hydrological features of the study area over the last 120,000 yr. Parra (1982) attributed mineralogical differences between glacial and interglacial periods primarily to changes in erosion and alteration conditions on the continent, while recognizing that hydrological changes may also play a role. The distribution of clay minerals in Late Quaternary sediments between the Gibbs fracture and the Greenland basin is attributed to glacial/interglacial cycles (Grousset et al., 1982), although this relationship does not result from climate-induced clay formation in the continental source areas, but from the relative influence of different transport and deposition agents, such as bottom currents in warm periods and ice rafting during cold periods (Singer, 1984). Also in the northeast Atlantic basins, Kissel et al. (1997) combined the study of clay minerals, and magnetic anisotropy and susceptibility for one core (SU90-33) from 2,400 m water depth along the Iceland–Scotland overflow water (ISOW), a branch of NADW. The magnetic susceptibility record indicates down-core variations in the amount of magnetite which co-vary with changes in the proportion of smectite in the clay fraction (Bout-Roumazeilles, 1995). Both parameters are "climatically" controlled, glacial periods being associated with lower values than interglacial periods. Down-core changes in the degree of anisotropy have been interpreted to be due to changes in the strength of bottom water circulation. Indeed, the strength of the contour current associated with transport in the ISOW appears to have been significantly greater during climatic stages 5, 3 and 1 than during stages 6, 4 and 2.

Gingele et al. (1999) analysed sedimentary clay mineral assemblages from the eastern terrace of the Vema Channel, the western flank of the Rio Grande Rise and the Brazilian continental slope in the South Atlantic. Variations in kaolinite/chlorite ratios are believed to record variations in the Rio Doce discharge and to reflect humidity conditions on the adjacent South American hinterland. The long-term decrease in smectite content and kaolinite/chlorite ratios from 1,500 ka to the present is believed to document a trend towards more arid and cooler climate conditions for subtropical southern latitudes of South America.

Regarding the southwest Indian Ocean, Gingele et al. (2004) studied a sediment core from a submarine rise on the continental slope offshore of southern Sumatra in order to reconstruct the paleoceanographic evolution of the South Java Current over the past 80 ka. This core shows variations in clay mineral assemblages over glacial/interglacial cycles related to alternating changes in atmospheric and oceanographic circulation dominated by the Northern Hemisphere East Asian Monsoon system and the Southern Hemisphere Australian Monsoon system. During low sea level glacial periods, the Sunda Strait was closed and kaolinite-rich terrigenous supply from that source ceased. The SE Winter Monsoon reached its maximum between 20 and 12 ka and intensified the westward-flowing South Java Current which carries smectite-rich particles originating south of Java. A similar, albeit much weaker, regime prevailed from 74 to 70 ka. During most of the glacial period from 70 to 20 ka, strong northeasterly winds associated with the East Asian Winter Monsoon intensified the Indian Monsoon Current and the eastward-flowing South Java Current, and may also have carried dust. The monsoonal system as we know it today, with its distinct dry and wet seasons, may not have been active before ~12 ka.

As for the Pacific Ocean, Liu et al. (2003) also provided evidence for strong glacial/interglacial cyclicity, northern South China Sea sediments showing high illite, chlorite and kaolinite abundances associated with glacial periods and high smectite and mixed-layers mineral abundances associated with interglacials. Liu et al. (2003) interpreted fluctuations in glacial/interglacial clay mineral assemblages at Site 1146 to have resulted from variations in the intensity of transport processes. In the South China Sea, the intensity of ocean surface currents is controlled by seasonal monsoon variability. Based on these present-day regional mineralogical provinces, (smectite +mixed-layers)/(illite+chlorite) ratios were used to constrain alternating summer and winter surface circulation patterns. Higher smectite abundances at Site 1146 reflect stronger southwesterly currents. Therefore, higher (smectite+mixed-layers)/(illite+chlorite) ratios during interglacials indicate enhanced summer monsoon and weakened winter monsoon circulation. In contrast, lower clay ratios indicate strongly intensified winter monsoon and weakened summer monsoon during glacial periods.

3. Applications: Clays as a Proxy for Paleocirculation

3.1. Clay Distribution in Arctic Ocean Surface Sediments

The identification of source areas and transport pathways of terrigenous material was illustrated by an extensive study of clay minerals from the Arctic Ocean and

adjacent Eurasian shelf areas (Wahsner et al., 1999). Detailed distribution maps of clay minerals were derived from the study of the fine fraction (<2 m) of a large number (∼470) of surface sediment samples, including new analyses and data from the literature. All semi-quantitative estimates were obtained using the same quanti-fication method or were recalculated. Results for other size fraction (e.g., Russian data on clays from the <1 μm fraction) were excluded from this compilation.

In the Arctic Ocean, clay minerals in surface sediments are purely detrital, reflecting the mineralogical composition of surrounding landmasses. Illite (>50%) and chlorite are the main clay minerals. Except in some parts of the Kara Sea, illite is the dominant clay mineral. The highest concentrations of illite (>70%) are observed in the East Siberian Sea and around Svalbard. Chlorite abundances show the least variations in the Eastern Arctic, ranging from 10% to 25%. Smectite and kaolinite occur in minor amounts (<20%) in the Central Arctic, but show strong variations in shelf areas. Wahsner et al. (1999) emphasized the fact that "these differences can be used to reconstruct pathways of terrigenous matter and circulation patterns in Arctic Ocean". Indeed, the Kara Sea and the western part of the Laptev Sea are enriched in smectite, the highest values (upto 70%) being observed in the Ob and Yenisey deltas. Using a triangular diagram, it is therefore possible to distinguish Kara Sea (highest smectite values) from East Siberian Sea clay mineral assemblages (lowest smectite and kaolinite values and highest illite content).

Clay mineral data also yield information on the transport mechanisms of fine particulate material. According to Wahsner et al. (1999), the high smectite content of the Kara and Laptev Seas surface sediments is related to sea-ice formation and surface current transport. In contrast, smectite-poor sediments in the Eurasian Arctic Ocean are related to turbidity and deep oceanic currents. The high kaolinite content of Nansen Basin sediments is related to sediment transport by turbidity currents. Chlorite abundance is relatively uniform in the Eurasian Arctic Ocean and therefore does not constitute a useful source indicator. Wahsner et al. (1999) con-cluded that clay mineral abundances do not seem to be a reliable indicator of the extent of sediment supply by sea-ice in Arctic Ocean surface sediments.

3.2. Clay Distribution in Holocene and Last Glacial Sediments in the North Atlantic

Following Biscaye's (1965) seminal paper, the distribution of clay minerals in the North Atlantic and their evolution through glacial/interglacial cycles have been the subject of numerous studies (e.g., Zimmerman, 1972; Parra, 1982; Parra et al., 1985; Grousset et al., 1983; Bout-Roumazeilles, 1995; Fagel, Robert et al., 1996; Fagel et al., 1997b; Kissel et al., 1997; Bout-Roumazeilles et al., 1999). Among these studies, Zimmerman (1982) analysed the clay mineral composition of sediments from 88 sites in the North Atlantic and compared the distribution of the different clays for both the Holocene and the Last Glacial (Figure 6). This study illustrated the spatial variability of clay mineral distribution at the oceanic basin scale and provided significant insight into the relationship between regional deep circulation patterns and NADW.
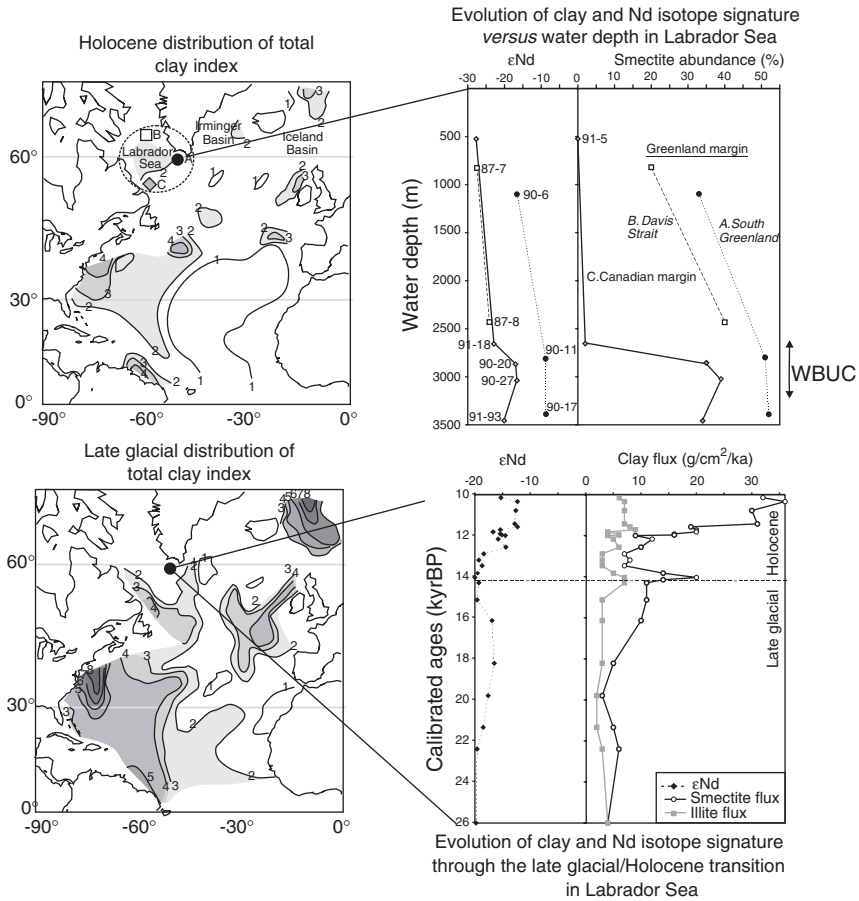
Figure 6 Comparison of Holocene (upper left panel) and Last Glacial (lower left panel) Total Clay Index distributions in the North Atlantic. Data from Zimmerman (1982), with permission. Upper right panel --- The influence of WBUC on clay transport in recent sediments from the Labrador Sea is highlighted. A significant increase in relative smectite abundance is systematically observed in WBUC-bathed surface sediments. The most pronounced shift is recorded in sediments from the Canadian margin. Mineralogical data for transects A and C are from Fagel et al. (1996), transect B data are from Fagel et al. (2001). The influence of eastern inputs at WBUC depth is also marked by contrasting Nd isotope signatures as a function of water depth (data from Innocent et al., 1997, with permission). Lower right panel --- Clay mineralogical evolution through the Last Glacial/Holocene was used as a proxy for WBUC intensity (Fagel et al., 1997b). The smectite flux evolved significantly through the Last Glacial/Holocene transition, whereas the illite flux remained more or less constant. The evolution of the Nd isotope signature of the clay fraction (data from Fagel et al., 1999) is consistent with higher inputs from the eastern basins into the Labrador Sea, which is consistent with the WBUC pathway.

According to Zimmerman's (1982) distribution maps, both the Iceland and Irminger basins show low present-day illite abundances. However, the evolution of clay mineral assemblages in these basins during glacial periods differs, illite abundance decreasing in the Irminger basin, whereas it increases in the Iceland basin.

Zimmerman (1982) speculated that large amounts of illite were brought into the glacial Iceland basin by bottom current transport from the Norwegian Sea. The influence of WBUC on clay fraction transport from the Eastern basins into the western North Atlantic is further evidenced by specific clay mineral and Nd isotopic signatures recorded from a depth corresponding to the WBUC maximum velocity axis in the Labrador Sea (Fagel et al., 1996; Innocent et al., 1997; see Figure 6).

In addition to clay distribution maps, Zimmerman (1982) also estimated the abundance of clay minerals within bulk sediments. He defined a "Total Clay Index" (TCI) based on the sum of the areas above background under the curve for the 17, 10 and 7 Å peaks on solvated XRD patterns, after multiplying by Biscaye's (1965) factors. According to Zimmerman (1982), the TCI defines mineral provinces that are dependent on source, current transport, basin topography and clay deposition rate. In the North Atlantic, three areas are characterized by TCI values greater than three (Figure 6, upper panel). A high Holocene TCI characterizes the continental rise off of the east coast of North America. It is explained by an important depocenter of clay minerals transported southwards by WBUC (Zimmerman, 1972). The locally high TCI at the base of the Great Banks in the Newfoundland basin suggests a high clay deposition rate behind the Newfoundland barrier, which obstructs the south-flowing WBUC. A third area of locally high TCI off of northeastern South America reflects Orinoco River related deposition.

During the Last Glacial, the areas of high TCI were much wider, including the entire North American basin, the TCI reaching values of up to eight off of the east American margin (Figure 6, lower panel). This pattern suggests a more active dispersal system resulting from important continental erosion and active currents. For instance, a latitudinal pattern with high quartz content and dilution of total clay contents occurred along the 45°N parallel. Coinciding with the position of the polar front, this pattern reflects the ice-rafted origin of marine sediments in this area, an interpretation consistent with more recent studies of clay minerals (Bout-Roumazeilles et al., 1999). In contrast, for the finer fraction, Zimmerman (1982) suggested that sediments are injected into WBUC by active turbidity currents, enhanced by glacial low sea-level stands. This transport mechanism is consistent with the proposed sediment dispersal mode (Heezen, Hollister, & Ruddiman, 1966). The relatively high abundance of smectite in Last Glacial sediments along the northwest Atlantic margin (e.g., off the Grand Banks, Piper & Slatt, 1977; or in the Labrador Sea, Fagel et al., 1997b) have been interpreted to result from the persistent, albeit sluggish, influence of WBUC on clay transport during the Last Glacial. At the southern tip of Greenland, variations with time of clay mineral assemblages suggest gradually increasing sedimentary fluxes and WBUC intensity since the Late Glacial Maximum. The smectite flux increases throughout the 2/1 transition whereas the illite flux remains approximately constant (Figure 6). The increasing WBUC trans-port through the Last Glacial/Holocene transition is further confirmed by a closely related significant change in the Nd isotope signature of the clay fraction (Fagel et al., 1999).

3.3. Clay Distribution since the Last Glacial in the Southeast Indian Ocean

Gingele et al. (2001a) analysed the clay mineral distribution in 166 core-top samples from between Indonesia and NW Australia to trace modern current pathways. In addition, the recent distribution of clay minerals was used to reconstruct the evolution of the Leeuwin Current through the Late Quaternary (Gingele et al., 2001b). The Indonesian Island Arc and Australia, which are characterized by contrasting geology and climates, constitute an ideal provenance case study. Gingele et al. (2001a) identified four clay mineral provinces closely related to the geology of the adjacent hinterland. Although they are all subjected to tropical conditions, the samples from the Indonesian Island Arc display significant differences which allowing three clay mineral provinces to be distinguished. Illite is the major clay mineral of the Western and Eastern Provinces, whereas the Central Province abounds with smectite. The fourth province comprises the northwest and west Australian shelf, slope and offshore plateaus and is dominated by kaolinite. Unlike the latitudinal zonation of clay mineral assemblages observed in other parts of the world oceans, samples from offshore of northwestern Australia show little variation in clay mineral composition (Windom, 1976; see Figure 4). Gingele et al. (2001a) emphasized the fact that the observed clay mineral assemblages do not reflect changes in weathering conditions of the terrigenous source, because weathering profiles develop over long periods of time (Thiry, 2000), particularly in Australia. Rather, the clay assemblages record changes in source areas or transport media. Transport of clays by surface and subsurface ocean currents is observed within the provinces (e.g., with the Leeuwin and West Australian Currents in the NW Australian Province, and with the outflow of low-salinity water through the Sunda and Lombok straits in the Central Province). Kaolinite and chlorite are transported into the Timor Passage by the Indonesian Throughflow, while illite is brought in locally from Timor. The Leeuwin Current leaves the Timor Passage with a characteristic clay mineral signature acquired in the Indonesian Archipelago (kaolinite, chlorite and illite). The uptake of clay minerals along its path through the Timor Sea (e.g., illite from the Kimberley area) changes this signature. South of North West Cape, chlorite injected by rivers of the Pilbara region into the path of the Leeuwin Current is a major constituent of surface sediments in water depths of less than 1,000 m and delineates the present-day flow of the current. The transport of clays across province boundaries is inhibited by strong salinity fronts, with the exception of the boundary between the Central and Eastern Province. It should be pointed out that the relationship between clay assemblage and current is not always obvious. For instance, Gingele et al. (2001a) emphasized the fact that clay mineral patterns do not provide decisive information regarding the transport of suspended matter from the Timor Passage along the path of the northern branch of the Leeuwin Current. Although high illite contents around Timor provide a distinct signal, the main Indonesian Throughflow through the Timor Passage cannot be traced by clay mineral distribution alone. Northeasterly current directions during the major runoff periods prevent the development of an expected illite-rich tongue of sediment to the southwest.

Clay mineral evolution from three cores taken from beneath the path of the present day Leeuwin Current in the Timor Passage was studied in order to constrain

changes in the strength and/or path of the current system since the Last Glacial (Gingele et al., 2001b). Based on the lower amounts of kaolinite and chlorite that reached the Timor Passage, Gingele et al. (2001b) inferred a decrease in the volume of the Indonesian Throughflow during the Last Glacial. Offshore, a reduction in the amount of chlorite during the Last Glacial is interpreted to have resulted either from a decrease in the intensity of the Leeuwin Current or its absence, and/or a lower chlorite input due to drier conditions on land. The latter hypothesis is consistent with the synchronous decrease in illite abundance. An illite maximum in Holocene and recent sediments offshore of North West Cape is the result of material input from rivers which periodically drain the adjacent hinterland. Lower illite abundances point to a drier climate in the area during the last glacial stage.

4. Some Perspectives

Most marine sediments comprise a complex mix of clay minerals derived from different source areas and/or formed by different processes. The interpretation of marine clay mineral data could be facilitated by a multiproxy approach. For instance, combining radiogenic isotopic analysis and clay mineralogy would help to distinguish between variations in particulate inputs and variations in paleoclimate and/or paleoenvironmental conditions in the hinterland.

In addition, the clay mineralogy approach is hindered by non-uniform sample preparation methods (pre treatments, clay-size fraction extraction methods) and interpretation of X-ray diffraction patterns, such that comparison of clay data sets produced by different labs or countries remains tricky. Intercalibrations must be developed. Ongoing developments in computer-assisted clay quantification methods could contribute to improving this delicate step in the interpretation of the significance of clay minerals.

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