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Spatial and temporal distribution of diagenetic alterations in siliciclastic rocks: implications for mass transfer in sedimentary basins

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ABSTRACT

The spatial and temporal distribution of diagenetic alterations in siliciclastic sequences is controlled by a complex array of interrelated parameters that prevail during eodiagenesis, mesodiagenesis and telodiagenesis. The spatial distribution of near-surface eogenetic alteration is controlled by depositional facies, climate, detrital composition and relative changes in sea-level. The most important eogenetic alterations in continental sediments include silicate dissolution and the formation of kaolinite, smectite, calcrete and dolocrete. In marine and transitional sediments, eogenetic alterations include the precipitation of carbonate, opal, microquartz, Fe-silicates (glaucony, berthierine and nontronite), sulphides and zeolite. The eogenetic evolution of marine and transitional sediments can probably be developed within a predictable sequence stratigraphic context. Mesodiagenesis is strongly influenced by the induced eogenetic alterations, as well as by temperature, pressure and the composition of basinal brines. The residence time of sedimentary sequences under certain burial conditions is of key importance in determining the timing, extent and patterns of diagenetic modifications induced. The most important mesogenetic alterations include feldspar albitization, illitization and chloritization of smectite and kaolinite, dickitization of kaolinite, chemical compaction as well as quartz and carbonate cementation. Various aspects of deep-burial mesodiagenesis are still poorly understood, such as: (i) whether reactions are accomplished by active fluid flow or by diffusion; (ii) the pattern and extent of mass transfer between mudrocks and sandstones; (iii) the role of hydrocarbon emplacement on sandstone diagenesis; and (iv) the importance and origin of fluids involved in the formation of secondary inter- and intragranular porosity during mesodiagenesis. Uplift and incursion of meteoric waters induce telogenetic alterations that include kaolinitization and carbonate-cement dissolution down to depths of tens to a few hundred metres below the surface.

Keywords Siliciclastic rocks, distribution pattern, sequence stratigraphy

INTRODUCTION

Siliciclastic diagenesis occurs in multicomponent geochemical systems and is driven by temperature-related thermodynamic and kinetic disequilibrium between the minerals and pore waters. Additionally, changes in lithostatic and hydrostatic pressures put important constraints on the

degree of mechanical and chemical compaction and, consequently, on the porosity and permeability of the sediments and the extent and pattern of fluid flow. Considerable efforts have been made to understand the spatial and temporal distribution of diagenetic alterations in siliciclastic rocks, mainly due to the realization by oil companies that these alterations exert profound

controls on reservoir quality. It is now evident that diagenesis causes a complex deviation from the simple progressive trend of declining porosity and permeability vs. depth. This paper aims to review the state-of-the-art of knowledge on the spatial and temporal distribution of diagenetic alterations and to address key controversies, such as: (i) the extent and patterns of mass transfer between mudrocks and sandstones; (ii) the role of organic acids in diagenetic reactions; and (iii) whether mesogenetic reactions are mediated by advective or diffusive mass transfer.

The boundary between eo- and mesodiagenesis (*sensu* Choquette & Pray, 1970; Schmidt & McDonald, 1979) is not precise in terms of burial depths and temperatures. However, in this review, mesogenetic modifications are considered to occur at depths ≥ 2 km and temperatures ≥ 70 °C, which coincide with the initiation of chemical compaction, clay-mineral transformation reactions, burial quartz cementation and substantial thermal alteration of organic matter. Mesodiagenesis encompasses modifications that occur over a wide range of burial depths and temperatures and is therefore in this paper tentatively subdivided into shallow (2–3 km; $T = 70$ –100 °C) and deep (>3 km; $T > 100$ °C). The burial depths at which mesogenetic reactions occur may vary considerably depending on the burial-thermal history of the sequence. In many basins, burial and mesodiagenesis are succeeded by uplift and telodiagenesis mediated by near-surface waters. It is thus obvious that determining the precise timing and burial depths of diagenetic alterations is often difficult to achieve.

SPATIAL DISTRIBUTION OF EOGENETIC ALTERATIONS IN CONTINENTAL SEDIMENTS

The spatial distribution of diagenetic alterations in continental sediments is strongly influenced by climatic conditions, patterns of regional groundwater flow and depositional facies (Fig. 1). Under warm, subhumid to humid conditions (precipitation > 1000 mm yr⁻¹) and in proximal fluvial sediments, active percolation of undersaturated meteoric waters causes the dissolution of detrital silicates (primarily lithic grains, feldspar and mica) and precipitation of kaolinite. The spatial distribution of kaolinite is influenced by the amounts and distribution of unstable detrital silicates and the hydraulic

conductivity of the sand body. Grain dissolution and formation of kaolinite are thus most prevalent in laterally persistent, permeable sediments, such as proximal, fluvial channel sands, but less important in fine-grained sandstones and siltstones of crevasse splay and distal fluvio-lacustrine facies (Figs 1 and 2).

Conversely, under warm, arid to semiarid conditions (precipitation < 200 mm yr⁻¹) and in distal, fluvio-lacustrine and interdune facies, meteoric-water flux is strongly limited, leading to the formation of smectitic clays, Fe-oxides/oxyhydroxides, sulphates, K-feldspar, zeolites, calcrete, dolocrete and silcrete. The spatial distribution of these cements is related to mineral-water interaction during regional groundwater flow from proximal to distal settings and to evaporative ionic concentration of pore waters (Fig. 1). Groundwater in permeable, proximal fluvial sandstones adjacent to uplifted blocks has elevated $\alpha_{Ca^{2+}}/\alpha_{Mg^{2+}}$ ratios, and hence commonly forms phreatic calcrete (Garcia *et al.*, 1998). Phreatic, concretionary calcrete is frequently elongated in the direction of regional groundwater flow (Johnson, 1989; Mozley & Davis, 1996). In some cases, elongated concretions precipitate from groundwater flowing along faults (Mozley & Goodwin, 1995). Groundwaters in the distal deposits have high $\alpha_{Mg^{2+}}/\alpha_{Ca^{2+}}$ ratios due to calcrete precipitation in the proximal facies and to evaporative concentration of dissolved salts favouring the precipitation of dolocrete (Fig. 1; Arakel *et al.*, 1990; Madé *et al.*, 1994). Precipitation of dolomite or calcite close to the water table may occur due to subtle variations in pore water composition due to various degrees of mixing between phreatic and vadose waters (Watts, 1980). Sandstones rich in magnesian grains are also likely to favour the precipitation

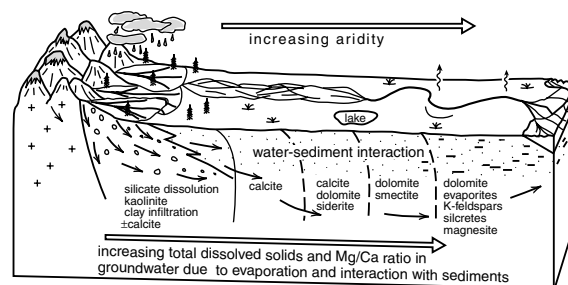


Fig. 1. Block diagram showing the geochemical modifications and flow pattern of regional groundwater as well as the related spatial distribution of eogenetic alterations in proximal-to-distal, continental facies.

of dolocrete (cf. Watts, 1980). In lake-margin environments, phreatic dolocrete forms by the mixing of groundwater with lake brines during periods of strong evaporation and lake-level lowering (Colson & Cojan, 1996). Phreatic calcrete and dolocrete layers may extend over areas of up to 10×100 km, such as in Quaternary sediments in Australia (Arakel, 1986), exerting important controls on reservoir compartmentalization and fluid flow. Siderite is a common, yet often minor, diagenetic cement in siliciclastic lacustrine and fluvial overbank sediments (Figs 1 and 2). Eogenetic meteoric siderite has a chemical composition that ranges from near pure, FeCO_3 end-member composition (Mozley, 1989) to various extents of enrichment in Mg, Ca and Mn (Morad *et al.*, 1998).

In distal sediments and arid climate, vadose silcrete (composed mainly of opal-A and opal-CT) occurs as concretions and as laterally continuous layers that extend over hundreds of metres, such as in Quaternary and Recent sediments in Australia (van de Graaf, 1983). Groundwater (phreatic) silcrete is composed mainly of quartz overgrowths and micro- to megaquartz and can extend laterally up to several kilometres particularly in distal sediments (Thiry & Milnes, 1991). K-feldspar occurs as overgrowths around detrital feldspars, as pseudomorphic replacement of detrital feldspars and as intergranular crystals in distal fluvial sediments (Fig. 1; Morad *et al.*, 1989). The alteration of distal sediments enriched in felsic volcanoclastic fragments causes

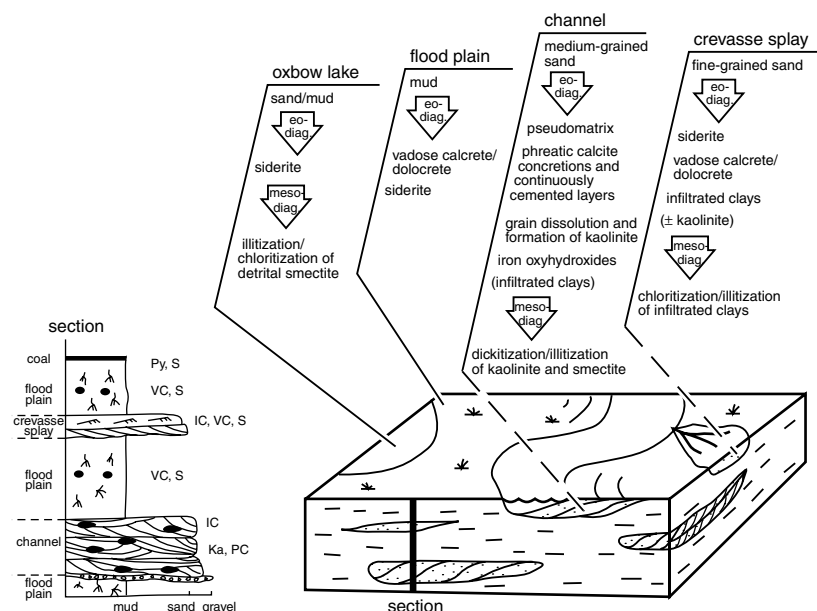
a pervasive cementation by microcrystalline K-feldspar, zeolites (clinoptilolite, phillipsite and analcime) and smectite (Sibley, 1978; Surdam & Boles, 1979; De Ros *et al.*, 1994).

SPATIAL DISTRIBUTION OF EOGENETIC ALTERATIONS IN MARINE AND TRANSITIONAL SEDIMENTS

The spatial distribution of eogenetic alterations in marine and transitional sediments is strongly influenced by sea-level changes, depositional facies and the extent of mixing between marine and meteoric waters (Figs 3–5). The climatic conditions, sediment permeability and availability of proper hydraulic head control the magnitude of alterations induced by meteoric waters into transitional and marine sediments below the seafloor. In coastal settings (peritidal and intertidal zones), pore waters are of mixed marine and meteoric origin. Conversely, the diagenesis of sediments submerged on the shelf, slope and basinal plain is mediated overall by diffusive mass transfer in largely stationary marine pore waters. The most common eogenetic alterations in marine and transitional sediments include:

1 Fe-silicates, including berthierine, glaucony and nontronite. Berthierine and glaucony are closely associated with diagenetic phosphate that

Fig. 2. Block diagram and sedimentary section showing the facies-related, spatial distribution of eogenetic alterations in a fluvial meandering depositional system, and their influence on the mesogenetic evolution of the sediments. S = siderite, IC = infiltrated clays, VC (closed circles) = vadose calcite/dolomite concretions, PC (closed ovals) = phreatic calcite concretions, Py = pyrite and Ka = kaolinite.



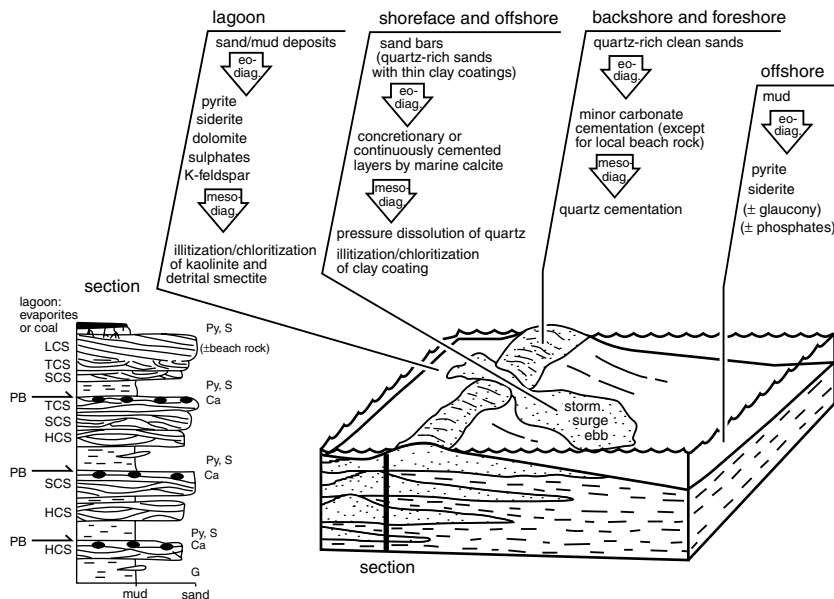


Fig. 3. Block diagram and sedimentary section showing the facies-related, spatial distribution of eogenetic alterations in a wave- and storm-dominated shelf, and their influence on the mesogenetic evolution of the sediments. LCS = low-angle cross-stratification, TCS = trough cross-stratification, SCS = swaley cross-stratification, HCS = hummocky cross-stratification, PB = parasequence boundary, Py = pyrite, S = siderite, Ca (closed ovals) = calcite concretions, and G = glaucony. Calcite cement may also occur in the interbedded, organic-rich mudstones.

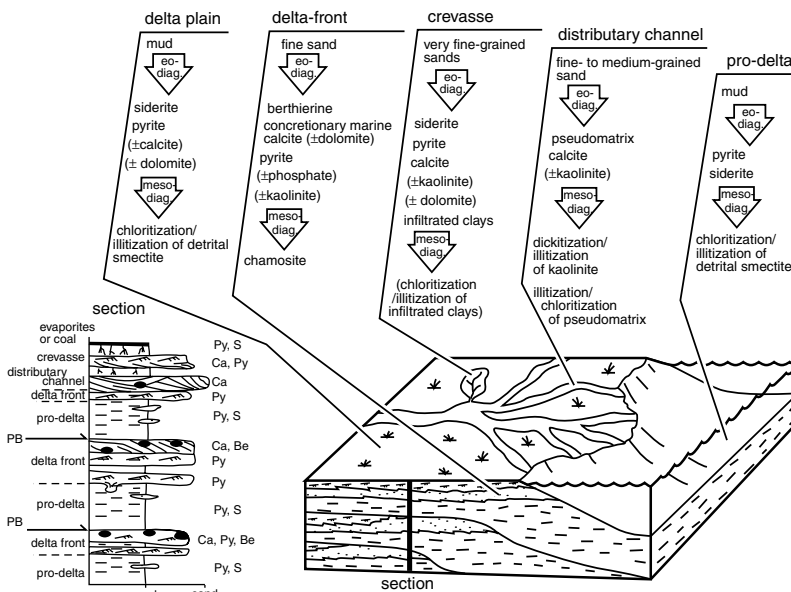
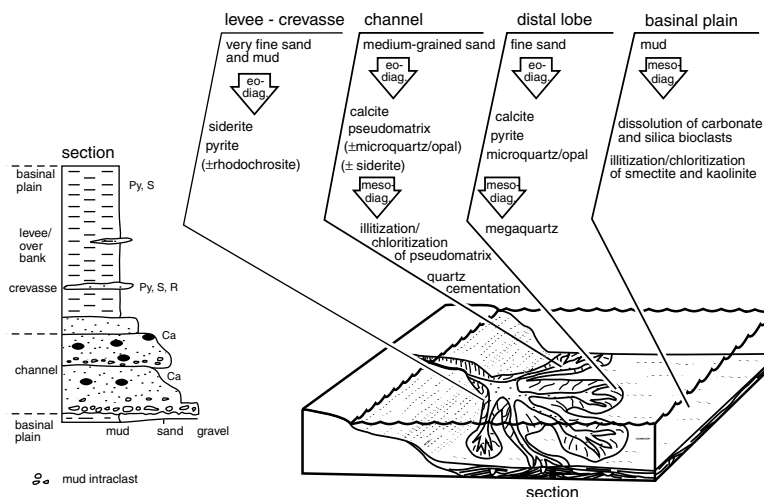


Fig. 4. Block diagram and sedimentary section showing the facies-related distribution of eogenetic alterations in a deltaic depositional system, and their influence on the mesogenetic evolution of the sediments. PB = parasequence boundary, Be = berthierine, Ca (closed ovals) = calcite concretions. Pyrite (Py) occurs throughout most of the sequence.

occurs as concretions in mudrocks and, less commonly, as cement in sandstones. Berthierine (1:1 clay mineral; $Fe^{2+}:Fe^{3+} \geq 4:1$; e.g. Hornibrook & Longstaffe, 1996) forms in shallow-water, marine and deltaic sediments (Figs 3 and 4), such as in the Niger and Mississippi deltas. Berthierine forms from suboxic, Fe-reducing, marine and brackish pore waters in sediments that are enriched in Fe-oxides/oxyhydroxides and organic matter. Glaucony forms in the outer shelf from suboxic marine

pore waters that undergo nitrate reduction immediately below the seafloor (Fig. 3). Low sedimentation rates and slight enrichment in organic matter in this setting prevent a rapid consumption of dissolved oxygen and build up of Fe^{2+} in pore water. In some cases, the formation of glaucony and berthierine is closely linked to the alteration of volcanic-ash layers (Sturesson, 1992), as these layers release considerable amounts of Fe, Mg, K, Si and Al ions upon interaction with seawater. Upwelling of hot

Fig. 5. Block diagram and sedimentary section showing the facies-related, spatial distribution of eogenetic alterations in a marine turbidite depositional system, and their influence on the mesogenetic evolution of the sediments. Py = pyrite, S = siderite, Ca (closed ovals) = calcite/dolomite, R = rhodochrosite.



hydrothermal fluids to the shallow seafloor can lead to the formation of abundant Fe-oxide ooids, such as those found today in the vicinity of volcanic islands in Indonesia (Heikoop *et al.*, 1996). In these areas, a 1-m-thick layer composed of ooidal Fe-oxide formed during the Recent. Upon shallow burial of these ooids in the suboxic zone, the dissolution of Fe-oxyhydroxides may lead to the formation of berthierine (Sturesson *et al.*, 1999). Nontronite [$\text{Fe}^{3+}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$], which is closely associated with Mn-oxyhydroxides, forms in oxic porewaters (dissolved oxygen $\geq 2 \text{ mg kg}^{-1}$) of pelagic, deep-sea sediments that are poor in organic matter. In these deep-sea settings, abundant Fe and Mn are derived from hydrothermal vents near mid-ocean ridges.

2 Sulphides are conspicuous cements in marine and transitional sediments with anoxic, sulphidic pore waters. The amounts of sulphides are greatest in organic matter-rich near-shore sediments and in shelfal settings influenced by upwelling of nutrient-rich marine waters. The sulphides occur as microcrystalline and framboidal pyrite that is disseminated within eogenetic cements and clay matrix and replace micas, rock fragments, bioclasts and intraclasts. The Fe-sulphides in Recent sediments occur as framboidal mackinawite ($\text{FeS}_{0.9}$) and greigite (Fe_3S_4). These minerals are metastable and transform rapidly into pyrite during shallow eodiagenesis. The amounts of Fe-sulphides formed are related to diffusibility of sulphate ions from seawater and to the amounts and reactivity of detrital Fe minerals and organic matter (Raiswell, 1982). Slow supply rates of dissolved iron and/or sulphide ions, such

as in abyssal-plain sediments, lead to the formation of discrete euhedral pyrite. In some basins, such as the Baltic Sea, microcrystalline alabandite (MnS) and gamma-MnS precipitate in Recent sediments in areas characterized by a smaller degree of input of reactive, detrital Fe- than Mn-oxyhydroxides (Boettcher & Huckriede, 1997).

3 Carbonate cements in marine and transitional sediments are dominated by calcite. Intertidal and lower peritidal sands in tropical and subtropical regions (latitude between $\approx 30^\circ\text{S}$ and 30°N) are cemented extremely rapidly and extensively by microcrystalline calcite and aragonite leading to the formation of tight beach rocks (Fig. 3). Carbonate precipitation in these coastal settings occurs from seawater due to evaporation and CO_2 degassing (Hanor, 1978). Seawater is moved into beach sands by tidal waves and storm-generated currents.

Carbonate cement in marine and deltaic sandstones occurs as scattered and stratabound concretions at the bottom or top of the bed (Figs 3–5). The coalescence of concretions develops continuously cemented siliciclastic layers that persist over considerable lateral distances ($\geq 1.5 \text{ km}$; Prosser *et al.*, 1993; Klein *et al.*, 1999) which may induce reservoir compartmentalization. According to Bjørkum & Walderhaug (1990), the original distribution of the carbonate bioclasts, which they consider to be the main cement source, and the number of nucleation sites are the primary controls on the spatial distribution and geometry of calcite cement. However, this has not always been found to be the case (e.g. McBride *et al.*, 1995). Concretions are spheroidal, ovoidal or flattened parallel to the bedding

planes. Compared with spheroidal concretions, flattened concretions may form due to: (i) permeability anisotropy, with maximum growth occurring parallel to the bedding plane; (ii) growth in the direction of fluid flow (McBride *et al.*, 1994); (iii) greatest flux of ions, due to greater concentration of bioclasts along the bedding plane (Walderhaug & Bjørkum, 1998); or (iv) concretion growth during compaction of the layer (Raiswell, 1971).

Calcite cementation in shallow-marine and deltaic sediments (Figs 3 and 4) occurs by marine and mixed marine–meteoric waters (Simpson & Hutcheon, 1995). Cementation in subtidal and deeper-water environments occurs largely by marine pore water that is slightly modified in composition by increased carbonate alkalinity due to suboxic to anoxic degradation of organic matter. Carbon and calcium ions can also be transferred directly from the seawater by diffusion subsequent to the establishment of chemical potential gradients with low ionic concentrations in pore waters due to calcite precipitation. In addition to seawater, other sources of carbonate cement include the dissolution of biogenic carbonates, micritic carbonate intraclasts and volcanic material (Morad & De Ros, 1994). Bioclastic carbonates, and hence calcite cement, are common in wave- and storm-dominated sands (Fig. 3), turbiditic sediments (Fig. 5) and in tidal channels and point bars. The time required to develop a continuously cemented sandstone layer decreases with an increase in: (i) the number of nucleation sites available for concretion growth and (ii) the ratio of percentage of cement in concretion to percentage of cement source (Wilkinson, 1989). The number of nucleation sites depends, in turn, on the number of sites where selective supersaturation (e.g. bioturbation) occurs and/or the distribution pattern of substrates (i.e. carbonate grains) for calcite precipitation and concretion growth.

Other eogenetic carbonate cements include dolomite, siderite, rhodochrosite and magnesite, which are most common in shelfal and deep-sea muds (Figs 3–5). The precipitation of eogenetic dolomite in marine sediments occurs by mixing between seawater and freshwater, and in anoxic pore waters in which the dissolved sulphate ions were removed by bacterial reduction to sulphides (Baker & Kastner, 1981); this is often referred to as organogenic dolomite, and forms in the bacterial sulphate-reduction and methanogenesis zones. Microcrystalline

siderite cement precipitates as concretions in mudrocks and sandstones. Siderite in shallow-water marine sediments is enriched in Ca and Mg (Mozley, 1989) whereas in deep-sea sediments it is enriched in Mn (Chow *et al.*, 1996), due to the derivation of Mn-oxyhydroxide particles from the discharge sites of hydrothermal waters in the vicinity of mid-ocean ridges. Enrichment of deep-sea sediments with Mn-oxyhydroxide also accounts for the formation of authigenic rhodochrosite (Chow *et al.*, 1996). Magnesite that occurs in deep-sea sediments is enriched in Fe and Mn, and forms either by direct precipitation or through the transformation of landfordite (hydrous Mg-carbonate) during shallow-burial and slight increase in temperature ($T \approx 40^\circ\text{C}$; Matsumoto, 1992).

In some cases, the localized precipitation of marine carbonate cements with extremely low $\delta^{13}\text{C}$ values at or immediately below the seafloor is related to an increase in carbonate alkalinity due to the oxidation of methane at sites of gas seepage (Hovland *et al.*, 1987; von Rad *et al.*, 1996). In deep-sea sediments, the dissociation of methane hydrates (clathrates) causes a strong enrichment of authigenic carbonates (e.g. siderite) in ^{12}C and ^{18}O isotopes (Matsumoto, 1990).

4 Precipitation of zeolite, K-feldspar, albite, smectite (commonly Mg- and Fe-rich), opal-A, opal-CT, chalcedony and microquartz as rims in marine sediments that are strongly enriched in volcanic fragments and biogenic silica, such as in deep-water, marine turbidites of arc basins. The dissolution of opaline skeletons of radiolaria, diatoms and sponge spicules results in the formation of grain-coating microquartz (Carvalho *et al.*, 1995; Hendry & Trewin, 1995). Microquartz coatings inhibit the nucleation and growth of syntaxial quartz overgrowths, and hence influence the spatial distribution of porosity and permeability in deep reservoirs (Aase *et al.*, 1996). Eogenetic alteration of volcanic fragments to zeolite induces a rapid loss of permeability. The zeolites are typically phillipsite and clinoptilolite, being formed as a result of a high $\alpha_{\text{H}_4\text{SiO}_4}$ in the pore waters at temperatures $\leq 35^\circ\text{C}$ (Boles, 1977).

5 In coastal sabkha settings, siliciclastic sediments are cemented by anhydrite, gypsum, barite, calcite, dolomite and, in a few cases, halite. However, the amount of halite cement in the sedimentary record is probably underestimated due to its dissolution during thin-section preparation. Other cements in coastal sabkha settings

include magnesite and quartzine (length-slow fibrous quartz); the latter forms by the replacement of sulphate cements.

RELATIONSHIPS BETWEEN THE SPATIAL DISTRIBUTION OF EOGENETIC ALTERATIONS AND SEQUENCE STRATIGRAPHY

Relative changes in sea-level and rates of sediment supply are the main factors controlling transgression and regression events, which can be predicted within the context of sequence stratigraphy. These events control the position and dynamics of the meteoric, mixed marine/meteoric and marine pore-water zones. Changes in pore-water composition driven by transgression and regression promote various diagenetic reactions. The intensity of these reactions in a specific pore-water zone depends on the duration of cycles of relative sea-level changes. Typically, diagenetic reactions are related to third- and fourth-order sea-level changes (McKay *et al.*, 1995; Taylor *et al.*, 1995; Loomis & Crossey, 1996; Rossi & Cañaveras, 1999), i.e. between 10 Myr and 200 kyr

(Vail *et al.*, 1977). Nevertheless, fifth-order cycles are long enough to create recognizable diagenetic alterations, such as cementation of carbonate platforms (Read & Horbury, 1993) and of beach and probably offshore sediments.

Transgression and regression also influence the detrital composition of sandstones in terms of the proportion and spatial distribution of intra- and extrabasinal grains (Zuffa *et al.*, 1995). Noncarbonate intrabasinal grains are volumetrically important only during times of reduced supply of extrabasinal sediments, such as during transgression. Otherwise, these intrabasinal grains would be diluted by extrabasinal sediments (Garzanti, 1991; MacQuaker *et al.*, 1996). During transgression and highstand times, sea water covers the shelf and carbonate production is at a maximum. Re-sedimentation of shallow-water carbonate sediments into deep-water sites immediately after its deposition on the shelf (allodapic, *sensu* Dolan, 1989) produces pure limestones or hybrid arenites rich in carbonate fragments in transgressive and highstand system tracts (TST and HST; Fig. 6; Dolan, 1989; Fontana *et al.*, 1989). Therefore, such TST and HST deposits have a great potential to be cemented by carbonates. Intraclasts are usually ductile, and can thus cause a rapid destruction of porosity and permeability of hybrid sandstones upon mechanical compaction. Conversely, during exposure of the shelf due to relative sea-level fall or progradation during late HST, carbonate production is at a minimum, chemical weathering dominates over erosion and thus sediments reaching basinal settings are dominantly siliciclastic. These conditions result in cementation and karstification of limestones and possible bauxite formation in the shelf (Bardossy & Combes, 1999). Consequently, there will be little or no intrabasinal carbonate sediment in lowstand systems tract (LST) deposits (Fig. 6), and hence lower potential for carbonate cementation and/or for rapid porosity-permeability loss as a result of mechanical compaction.

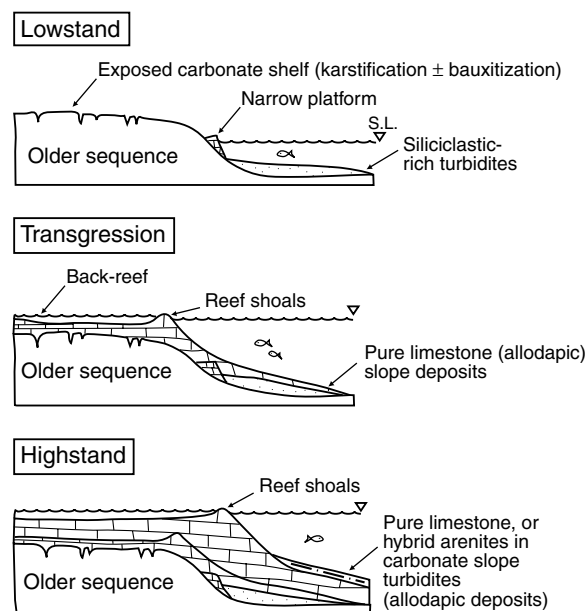


Fig. 6. Schematic relationships between relative sea-level changes and the composition of sediments in deep-water turbidites. Note that transgressive and highstand, deep-water deposits are enriched in carbonate intraclasts (i.e. hybrid arenites), and thus have a greater potential to be tightly cemented by calcite than lowstand, siliciclastic turbidites.

Regression and sequence boundaries

Regression is produced by relative sea-level fall (forced regressions; Posamentier *et al.*, 1992) and/or by excessive sediment supply (normal regression). In both cases, the meteoric and mixed marine-meteoric zones migrate basinward. The eogenetic alterations due to forced and normal regressions are similar, but those induced due to forced regressions tend to be localized below the

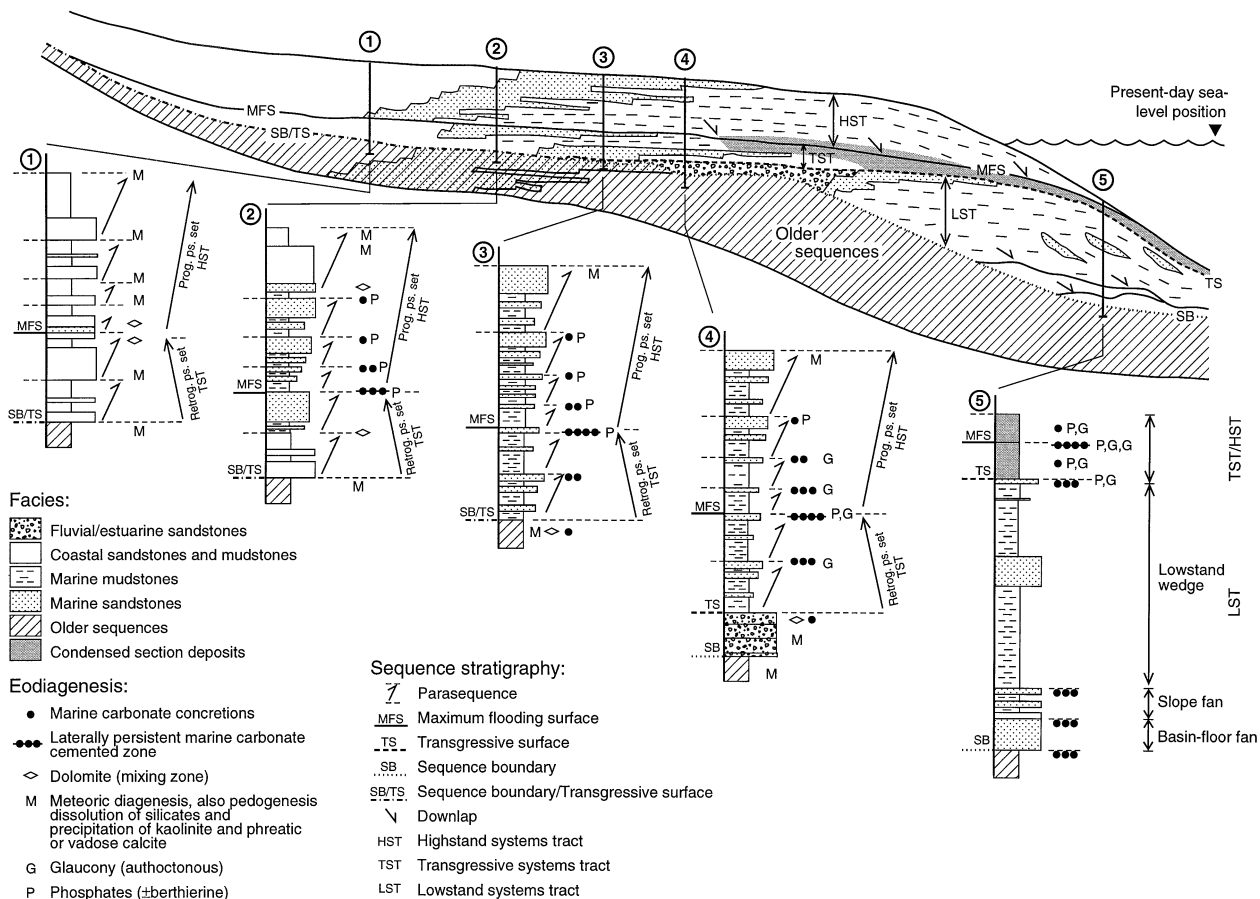


Fig. 7. Examples of the spatial distribution of eogenetic alterations that occur along key sequence stratigraphic surfaces and system tracts. Sequence stratigraphy framework modified from van Wagoner *et al.* (1990).

subaerial exposure surfaces, i.e. unconformities (Fig. 7; van Wagoner *et al.*, 1990). Conversely, eogenetic alterations during normal regression are localized in zones of high sediment supply or relatively low sediment accommodation space, such as during late stages of the HST.

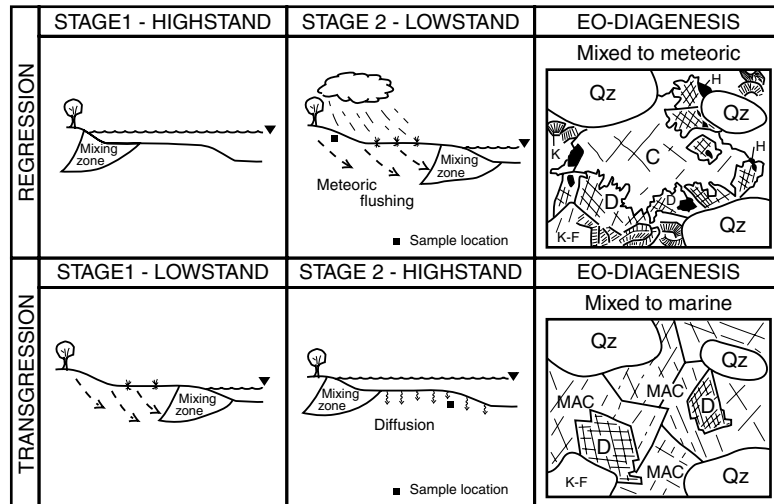
During forced regression and lowstand times, large areas are subaerially exposed on the shelf, leading to an enlargement of the areas of meteoric recharge. The basinward migration of the meteoric zone promotes the flushing of shallow-marine sediments and, in some cases, even deep-water turbidites by meteoric waters (Hayes & Boles, 1992; Carvalho *et al.*, 1995). Meteoric-water flushing during regression results in the dissolution of framework silicates and early marine and mixing-zone cements and in the precipitation of kaolinite and meteoric carbonate cements (Fig. 8; Rossi & Cañaveras, 1999). Carbonate cements that precipitated during regression display a decrease in the Sr, Na and Mg content, as well as lower $\delta^{18}\text{O}$ and higher $^{87}\text{Sr}/^{86}\text{Sr}$ values towards the centre of

the pores, indicating progressive geochemical modification of pore-waters towards a meteoric composition (Kaldi & Gidman, 1982; Glasmann *et al.*, 1989; Hart *et al.*, 1992; Morad *et al.*, 1992). Alterations resulting from the incursion of meteoric water are expected to be progressively more intensive towards HST due to the occurrence of a distinct progradation. In the interfluvial areas along sequence boundaries or subaerially exposed areas during normal regression, pedogenesis may result in the formation of clay cutans and precipitation of calcretes, dolocretes and silcrettes.

Transgression, parasequence boundaries and condensed sections

A relative sea-level rise and increase in accommodation space promotes transgression and, consequently, marine flooding of subaerially exposed sediments with landward shifting of the mixed and marine pore-water zones, and restriction of meteoric-water recharge areas.

Fig. 8. Diagenetic alterations in siliciclastic sediments during regression and transgression. During regression, earlier formed mixing-zone dolomite cement (D) is dissolved or calcitized through interaction with meteoric water; this process is associated with the formation of meteoric calcite cement (C), iron oxides/oxyhydroxides (H) and kaolinite (K). During transgression, earlier formed mixing-zone dolomite is post-dated by marine calcite cement (MAC) formed by ionic diffusion from the overlying seawater.



When the transgressive surface coincides with the sequence boundary, marine water will infiltrate below flooding surfaces, mixing with meteoric waters and promoting the precipitation of dolomite (Yin & Surdam, 1985; Taylor *et al.*, 1995; Dixon & Davis, 1997). Dolomitization or calcite cementation is also likely to occur close to the MFS in continental sediments when the fluvial bars on top of the TST are reworked by coastal processes (e.g. tides) and in the TS at top of the incised valley deposits (Fig. 7; Taylor *et al.*, 1995).

In the marine pore-water zone, typical diagenetic processes include the precipitation of carbonate concretions at shallow depths below the seafloor (Fig. 8). Ions needed for this cementation are derived by diffusion from the overlying sea water and from the dissolution of aragonitic and high-Mg calcite grains. As ionic diffusion is most efficient over distances ≤ 10 m, marine carbonate cementation is expected to be most common during a long 'residence time' at shallow depths below the seafloor (Kantorowicz *et al.*, 1987; Wilkinson, 1989). Hence, cementation would occur along surfaces of low sedimentation rates, such as parasequence boundaries or MFS and within condensed sections (Fig. 7; Taylor *et al.*, 1995; Loomis & Crossey, 1996). As the 'residence time' is longest along the MFS, it has the highest potential to develop laterally persistent cemented horizons by coalescence of concretions. Considering deep-water turbidites, a rise in relative sea-level induces modifications in the architecture of turbidites, whereby basin-floor fan deposits evolve into slope-fan deposits. This facies transition, which is possibly marked by a down-lap surface, represents a major break in sedimentation, and is thus a potential site for

marine carbonate cementation, particularly in sediments enriched in carbonate grains.

Stratigraphic levels corresponding to low sedimentation rates in marine environments also favour the formation of glaucony and phosphates (Fig. 7), which thus occur along parasequence boundaries, TST and lower HST deposits and within condensed section deposits (Loutit *et al.*, 1988; Amorosi, 1995). Glaucony displays an upward increase (from TST) and then decrease (towards HST) in both abundance and maturity (Fig. 7; Amorosi, 1995). The maturation of glaucony, i.e. an increase in K_2O (derived from seawater) and development of a mica-like structure, is thus enhanced by long residence time at shallow depths below the seafloor. Glaucony and phosphate-rich sediments may also occur without a clear association with transgressions. In such sediments, glaucony is typically allochthonous, derived by erosion and reworking of autochthonous glaucony (Baum & Vail, 1988; Amorosi, 1995). Additionally, the formation of glaucony may also be closely linked to the alteration of volcanic-ash layers (Sturesson, 1992). Compared with glaucony, berthierine forms during somewhat higher sedimentation rates in sediments with greater organic-matter content, and hence closer to the strandline. Berthierine and siderite commonly form ooids in ironstones, which mark intervals of low sedimentation rates (e.g. parasequence boundaries and MFS) and condensed sections (Burkhalter, 1995; MacQuaker *et al.*, 1996). The frequency and abundance of glaucony and berthierine are higher in ancient than in Recent sediments, probably due to the

relatively low present-day sea-level. A transgression and rise in sea-level induce conditions of upwelling of nutrient-rich seawater into the shelf and formation of organic-rich sediments.

SPATIAL AND TEMPORAL DISTRIBUTION OF MESOGENETIC ALTERATIONS

Subsequent to the main phase of mechanical compaction and the initiation of chemical compaction (burial depths ≥ 2 km; $T \geq 70$ °C), temperature and basinal brines increasingly control not only the spatial but also the temporal distribution of diagenetic alterations. Basinal brines evolve chemically and isotopically during progressive burial. In addition to the continued, but less important, brittle grain fracturing and plastic deformation of ductile grains, a wide variety of chemical, physical and biochemical mesogenetic modifications are induced in the sediments, including cementation, mineral transformation, dissolution of grains and cements, chemical compaction and overpressuring (Fig. 9).

Mineral transformation affects mainly clay minerals and detrital feldspars due to their sensitivity to changes in temperature and pore-water composition. Additionally, the spatial and temporal distribution of mesogenetic alterations is strongly influenced by: (i) the extent and distribution of eogenetic alterations (Figs 1–5); (ii) the residence time at certain P – T conditions, indicating that mesogenetic reactions are kinetically controlled; and (iii) alterations in mudrocks, such as thermal maturation of organic matter and formation of organic acids, the dissolution of K-feldspar, biogenic silica and carbonates, as well as the illitization and chloritization of smectite and kaolinite.

Flow patterns and geochemical evolution of formation waters

A subject of long-standing debate and controversy is whether fluids are stagnant, moving sluggishly or actively (by advection and convection) in the deep subsurface. Thus, whether the spatial and temporal distribution of mesogenetic reactions are mediated by advective fluid flow or by

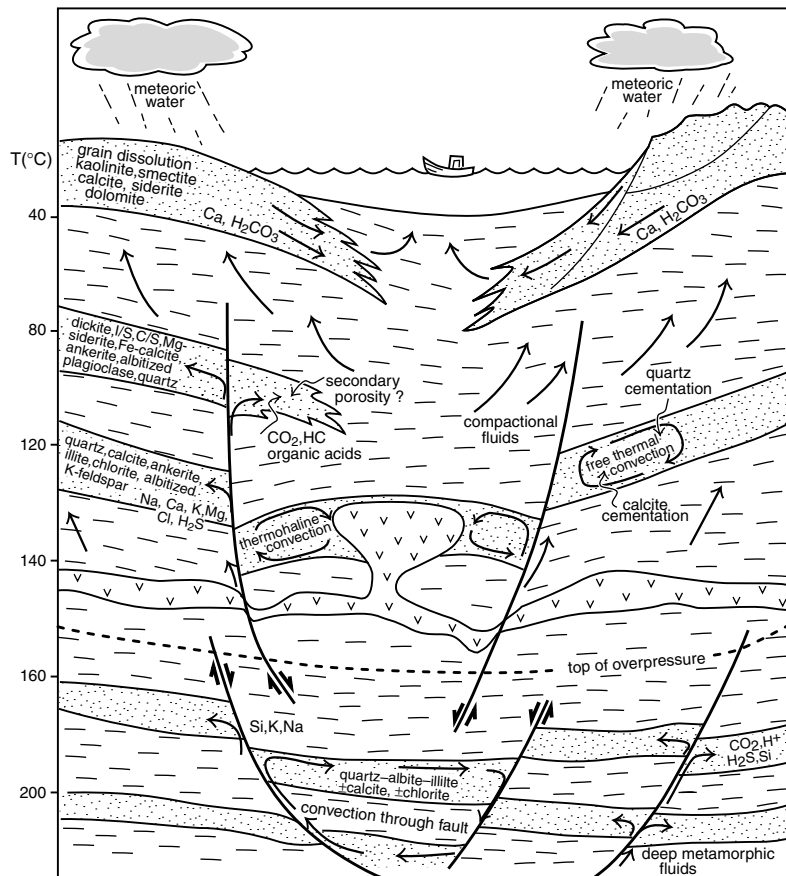


Fig. 9. Spatial and temporal distribution of diagenetic alterations and patterns of fluid flow and mass transfer in a hypothetical basin.

diffusion is uncertain, and depends, among other things, on the burial diagenetic evolution and tectonic setting of the basin. In basins that are tectonically inactive, overpressured or compartmentalized by low-permeability rocks or structural barriers, fluids become stagnant for prolonged times. However, the episodic release of overpressure from mudrocks causes pulses of focused fluid flow along major faults (Fig. 9; Cartwright, 1994). Owing to the low compressibility of water, flow is probably enhanced by simultaneous vertical and lateral stresses. Concrete geochemical and palaeogeothermal evidence for the occurrence of vertical and lateral mass and heat flux along a large, fairly shallow (≈ 2 km) growth fault has been provided by Losh *et al.* (1999). Slow (less than a few mm yr^{-1}) fluid flow occurs by compactional expulsion of waters from mudrocks and by convection. Convection is driven by buoyancy forces associated with temperature- and salinity gradients (Hanor, 1987; Evans & Nunn, 1989). However, so far, there are no unequivocal data supporting the role of fluid convection within a sandstone unit on the spatial and temporal distribution of diagenetic minerals in sedimentary basins. Nevertheless, fluid convection may occur along fault planes, particularly when the basin experiences high heat flux, such as resulting from extensional tectonics. In the absence of fluid convection, mass transfer from mudrocks into sandstones occurs along faults and by cross-formational ionic diffusion. The latter process suggests that the spatial distribution of mesogenetic alterations in sandstones occurs over distances of metres or tens of metres from the mudrocks. At burial depths > 3 km, an important factor that favours diffusive mass transfer is the limited amount of pore water available compared with the volume needed to explain common mesogenetic alterations. The spatial distribution of diagenetic reactions is also strongly controlled by the degree of hydrocarbon saturation in the reservoir and by the concentration of dissolved and exsolved gases, such as CO_2 . A high degree of hydrocarbon supersaturation impedes fluid flow in reservoirs. In such reservoirs, diagenetic reactions may slow and proceed mainly by diffusion (Worden *et al.*, 1998).

Shallow mesogenetic alterations

The most typical mesogenetic alterations that occur at burial depths of 2–3 km and temperatures of 70–100 °C include (Fig. 9):

1 Precipitation of carbonate cements, including calcite, ankerite, magnesian siderite and ferroan magnesite. In sandstones in which pore-water pH is buffered by aluminosilicate equilibrium or by organic acids, excess CO_2 derived from thermal oxidation of organic matter is eliminated by carbonate precipitation (Smith & Ehrenberg, 1989) in the vicinity of associated organic-rich mudrocks. Increased carbonate alkalinity and consequent carbonate cementation may occur due to the anaerobic or, less commonly, aerobic degradation of oil by deeply infiltrating meteoric waters (Smith, 1996). Hence, the spatial distribution of carbonate cements is closely related to the position of the oil–water interface. Important sources of carbonate ions include associated mudrocks and marls (Souza & Silva, 1998), mainly through the dissolution of biogenic and micritic calcite. Calcium supply from, and hence the intimate spatial distribution of carbonate cement with, these lithologies occurs simultaneously with smectite illitization (Wintsch & Kvale, 1994) and the generation of organic acids. The latter process lowers the pH values of pore waters, and thus enhances biogenic-carbonate dissolution in marls and mudrocks.

2 The precipitation of small amounts of dickite as well as increasing crystal-structural ordering and incipient to pervasive dickitization of kaolinite. Dickitization is a dissolution–precipitation process that occurs in pore waters with low $\alpha_{\text{K}^+}/\alpha_{\text{H}^+}$ ratio; otherwise illite forms (Ehrenberg *et al.*, 1993; Morad *et al.*, 1994). Low $\alpha_{\text{K}^+}/\alpha_{\text{H}^+}$ ratio in pore fluids can be achieved through input of acids (Morad *et al.*, 1994) and through absence or retardation of K^+ release from minerals (Ehrenberg, 1991). Acidic fluids in the temperature ranges considered can be derived from the thermal maturation of kerogen. Hence, dickitization is expected to be most pervasive in sandstones that are poor in detrital K-feldspars (e.g. in aeolian facies or due to eogenetic dissolution) and/or in the vicinity of sites of influx of acidic waters such as along faults or adjacent to organic-rich mudrocks.

3 Progressive, burial transformation of detrital and eogenetic smectite, first into poorly, and then at greater depths into well-ordered, mixed-layer illite/smectite (I/S) or chlorite/smectite (C/S), respectively, and of berthierine into chamosite. These alterations, which proceed via dissolution/precipitation, rather than by solid-state, layer-conserving reactions (Rask *et al.*, 1997), are volumetrically more important in mudrocks than

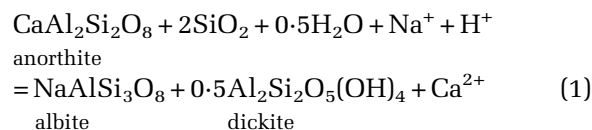
in sandstones. In sandstones, I/S and C/S form by replacement of mechanically infiltrated, grain-coating smectite, mud intraclasts and volcanic fragments. Infiltrated clays, and hence grain coating chloritic and illitic clay minerals, are common in point-bar and delta-plain sandstone facies.

Thus, illitization of smectite in mudstones consumes K^+ but releases considerable amounts of Si, Mg, Fe, Na and Ca ions that can be used in diagenetic reactions in adjacent sandstones (Boles & Franks, 1979). The release of interlayer water influences the spatial distribution of diagenetic reactions by shifting mineral-water equilibrium by diluting the total solid concentrations in formation waters. Although K^+ can be supplied locally from the concomitant dissolution of K-feldspar (i.e. closed-system diagenesis; Hower *et al.*, 1976), an increasing number of studies suggest that the illitization of smectite in mudrocks may occur in an open system in which an external source of K^+ , such as interbedded sandstones, is required (e.g. Furlan *et al.*, 1996; Land *et al.*, 1997). In contrast to illitization, the spatial distribution of mesogenetic alterations in siliciclastic sequences, as a consequence of smectite chloritization in mudrocks, is poorly explored in the literature. Chloritization occurs in sediments that are rich in biotite and intermediate to mafic volcanic rock fragments, as these materials act as sources of Fe and Mg required for the reaction. Hence, diagenetic chlorite in sandstones should be spatially associated with basaltic dykes and sills. Iron is also commonly derived from the reduction of goethite and hematite. Therefore, chlorite formation is often related spatially and temporally to the formation and migration of hydrocarbons, such as in bleached zones close to faults along which such reducing fluids have migrated (Surdam *et al.*, 1993). As illitization and chloritization are processes that involve ionic flux, they are expected to occur more readily as well as at shallower depths in permeable sandstones than in mudrocks. Chang *et al.* (1986) found that corrensite formation begins at a burial depth of 1500 m (60 °C) in sandstones and 2000 m (70 °C) in mudrocks. K-Na-rich smectite is potentially prone to illitization whereas Mg-rich smectite, which forms in sandstones rich in intermediate to mafic volcanoclastic sediments, is prone to chloritization (Chang *et al.*, 1986).

The transformation of berthierine into chamosite, which occurs in shallow-water marine siliciclastic facies, begins at temperatures of $\approx 70^\circ\text{C}$, but becomes extensive at temperatures

exceeding $\approx 100^\circ\text{C}$ (Odin, 1985; Jahren & Aagaard, 1989; Hillier & Velde, 1992). The spatial and temporal distribution of mesogenetic alteration of smectitic glaucony is poorly understood. However, smectitic glaucony should be potentially subjected to illitization and chloritization (Wilson & Stanton, 1994).

4 Incipient to extensive replacement of detrital plagioclase by nearly pure, albite end-member, i.e. albitization (Boles, 1982; Morad *et al.*, 1990) releases excess Al^{3+} and Ca^{2+} as by-products. The immobile Al^{3+} ions precipitate as minor dickite, laumontite or mixed-layer clays in the vicinity of albitized grains, whereas Ca^{2+} ions either dissolve in pore waters or precipitate as calcite or laumontite (Boles, 1982; Helmold & Kamp, 1984; Morad *et al.*, 1990). The overall albitization reaction can thus be tentatively written as follows:



This reaction denotes that albitization influences the anorthite solid solution in plagioclase and is controlled by pH (i.e. $-\log \alpha_{H^+}$) and $\alpha_{Na^+}/\alpha_{Ca^{2+}}$ of the formation waters rather than by the absolute

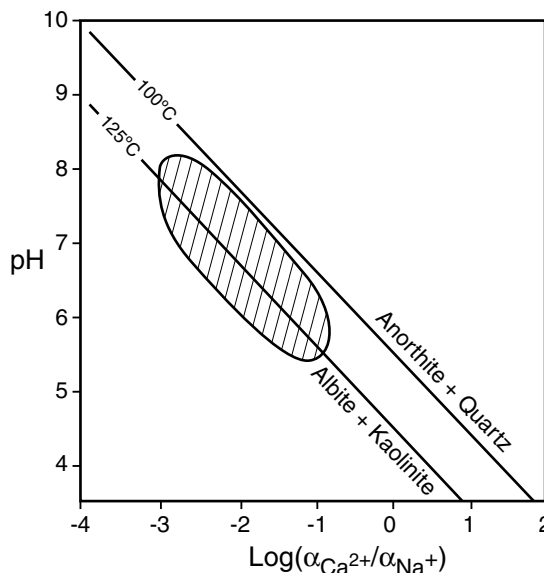


Fig. 10. Equilibrium diagram showing the temperature-related albitization of detrital calcic plagioclase (anorthite) and formation of kaolinite as a by-product. Hatched area represents the composition of most formation waters from North Sea reservoirs (data from Egeberg & Aagaard, 1989; Warren & Smalley, 1994).

Na content (Fig. 10). In North Sea reservoirs, the formation waters are in equilibrium with albite + kaolin rather than with anorthite + quartz at a temperature of 100 °C (Morad *et al.*, 1990; Fig. 10). However, albitization may commence at temperatures as low as ≈ 65 °C (Saigal *et al.*, 1988). A high $\alpha_{\text{Na}^+}/\alpha_{\text{Ca}^{2+}}$ in the water would be enhanced by the input of Na^+ and/or the precipitation of Ca^{2+} as calcite, which occurs in the presence of very low CO_2 fugacities (Wood, 1994). Illitization of smectite in mudrocks was suggested to be a viable source of Na^+ (Boles, 1982; Aagaard *et al.*, 1990). However, an external source of Na^+ is probably not required as the detrital plagioclase contains significant amounts of sodium (Morad *et al.*, 1990). Plagioclase albitization may thus occur in a closed diagenetic system. Nevertheless, a number of studies have shown that albitization is most pervasive in permeable sandstones (Boles & Ramseyer, 1988; Saigal *et al.*, 1988; Milliken, 1989), indicating that it occurs in open diagenetic systems as well (Aagaard *et al.*, 1990).

Deep mesodiagenesis

As sandstones enter the window of deep mesodiagenesis (≥ 3 km; $T > 100$ °C), they may dramatically lose their porosity and permeability, unless the sediments are, for example, subjected to overpressuring or to shallow-burial emplacement of hydrocarbon. In some sequences, considerable secondary porosity develops due to the dissolution of framework grains and intergranular cement. The most important mesogenetic alterations include (Fig. 9):

- 1 Chemical compaction and quartz cementation are the most important porosity-reducing alterations in deeply buried sandstones. Quartz cementation commonly occurs near stylolites and sites of intergranular dissolution. Dissolved silica is transferred by diffusion due to the establishment of a dissolved-silica concentration gradient between the sites of quartz dissolution and precipitation. These sandstones are referred to as silica exporters and importers, respectively (Houseknecht, 1988). Clean, coarse-grained quartz-cemented sandstones (e.g. foreshore sands) are thus expected to be spatially associated with silica-exporting, micaceous, fine-grained sands and sands rich in clay-coated quartz grains (e.g. shoreface sand bar; Wescott, 1983). Oelkers *et al.* (1996) found that the spatial distribution of quartz cement about stylolitic surfaces depends on temperature and on the interstylolite distance.

In cores, taken from a depth of 3.6 km, the distribution of quartz cement is independent of distance from the stylolite. Conversely, sandstones at depths of 5 km show a greater concentration of quartz cement near stylolitic surfaces only if the surfaces are closely spaced (about 50 cm).

Additional sources of silica include illitization of kaolinite and smectite reactions and the dissolution of detrital feldspars. Quartz cementation of sandstones may occur due to the transfer of silica released from adjacent mudrocks by the illitization of smectite and kaolinite and by the dissolution of quartz, siliceous bioclasts and volcanic ash (Moncure *et al.*, 1984; Hendry & Trewin, 1995; Gluyas *et al.*, 2000). Quartz cementation may also occur as a result of a decrease in quartz solubility during cooling and mixing of brines with low-salinity pore waters in sandstones near major faults (cf. Hanor, 1996). The frequent zonation of quartz overgrowths observed under cathodoluminescence is, in some cases, due to variations in Al and transitional metal contents (Hogg *et al.*, 1992; Kraishan *et al.*, 2000). This zonation may result from multiple cementation episodes, interrupted by episodes of non-cementation (Hogg *et al.*, 1992). It is, however, uncertain whether or not the cementation episodes are related to pulses of brine upwelling and cooling or reflect geochemical evolution of formation waters due to water-sediment interaction during progressive burial of the sandstones. An

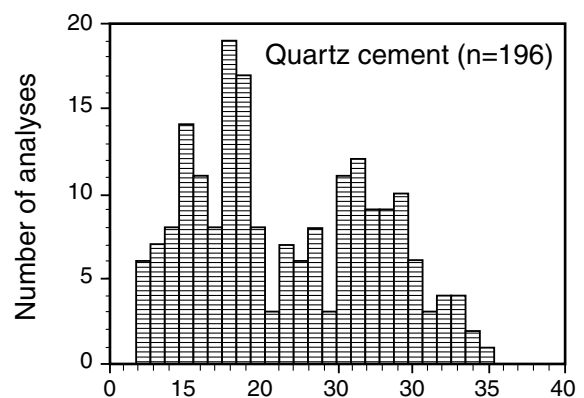


Fig. 11. Histogram showing the ranges and frequency of $\delta^{18}\text{O}_{\text{SMOW}}$ values of quartz cement (based on data from Lee *et al.*, 1985; McBride *et al.*, 1987; Tilley & Longstaffe, 1989; Brint *et al.*, 1991; Girard & Deynoux, 1991; Aplin *et al.*, 1993; Girard & Barnes, 1995; Hervig *et al.*, 1995; Hogg *et al.*, 1995; Summer *et al.*, 1995; Graham *et al.*, 1996; Macaulay *et al.*, 1997; Sullivan *et al.*, 1997; William *et al.*, 1997) in sandstones.

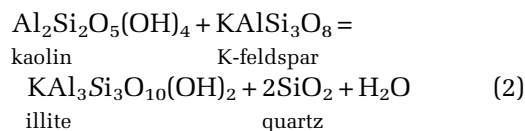
example of the latter is the dissolution of aluminosilicates and increase in Al^{3+} concentrations of formation waters due to complexation by organic acids.

The $\delta^{18}\text{O}_{\text{SMOW}}$ values of quartz cement reported in the literature vary widely (+12 to +35‰; Fig. 11), and apparently reflect the wide range of precipitation temperatures and/or of oxygen isotopic compositions of the fluids involved. Indeed, fluid-inclusion analyses in quartz overgrowths reveal a wide range of salinities and precipitation temperatures. Quartz with high $\delta^{18}\text{O}$ values may have precipitated at low temperatures as ground-water silcretes.

2 Precipitation of finely crystalline, discrete quartz or blocky carbonate cements (e.g. ferroan dolomite, ankerite and calcite in pores that remain after quartz cementation (Boles, 1978; Land & Fisher, 1987). Indeed, carbonate cements that post-date quartz overgrowths are a global phenomena, which may be related to the different temperature-related solubility of the two minerals. With an increase in temperature, carbonate minerals have retrogressive solubility whereas quartz has a progressive solubility. Therefore, during progressive burial, quartz becomes more soluble, whereas carbonates tend to precipitate. Petrographic evidence substantiating this includes the partial replacement of quartz overgrowths by abutting carbonate cement. The precipitation of mesogenetic carbonate cements may also occur due to a decrease of p_{CO_2} during release of overpressure, such as during faulting and hydrofracturing in mudrocks, or due to cross-formational fluid flow (Caritat & Baker, 1992; Schulz-Rojahn, 1993). Healing of hydrofractures is followed by another period of pressure build up due to clay dehydration and thermal alteration of organic matter.

3 Illitization of I/S and kaolin. In sandstones, illite occurs mainly as mat-like and fibrous or lath-like rims around framework grains, and as a pore-filling cement. Illite rims form by precipitation from pore waters and by transformation of I/S. The mat-like illite may inherit the habit of precursor clay, such as palygorskite. When illite has originated by transformation of eogenetic infiltrated smectitic coatings, it implies that: (i) its distribution is facies related, and (ii) coatings occur along grain contacts. Conversely, late authigenic illite is absent from such contacts. Thus, intergranular pressure dissolution is enhanced by illitized, originally eogenetic, smectitic coatings rather than by authigenic (neoformed) illite. Oversized illite patches form by mesogenetic illitization of kaolin

and argillaceous fragments. The typical book-like stacking crystal habit of kaolin may be preserved during illitization (De Ros, 1998). The illitization of kaolinite also induces a considerable damage to reservoir permeability due to its position in pore throats and to the formation of abundant, discrete quartz cement as a by-product:



Illite becomes the dominant clay mineral at temperatures $\geq 130^\circ\text{C}$ (Ehrenberg & Nadeau, 1989; Giles *et al.*, 1992). However, Darby *et al.* (1997) concluded, based on illite dating in reservoir sandstones from the North Sea, that temperature is not the most important factor controlling illite precipitation. Theoretically, illite may form at temperatures as low as $\approx 50^\circ\text{C}$ (Bjørkum & Gjelsvik, 1988) under prolonged conditions of low water-to-rock ratio (Huang *et al.*, 1986), high $\alpha_{\text{K}^+}/\alpha_{\text{H}^+}$ ratio and relatively low degree of quartz supersaturation in formation waters. Hence, illite formation is kinetically controlled.

Dickite is less susceptible to illitization than kaolinite due to its better-ordered crystal lattice

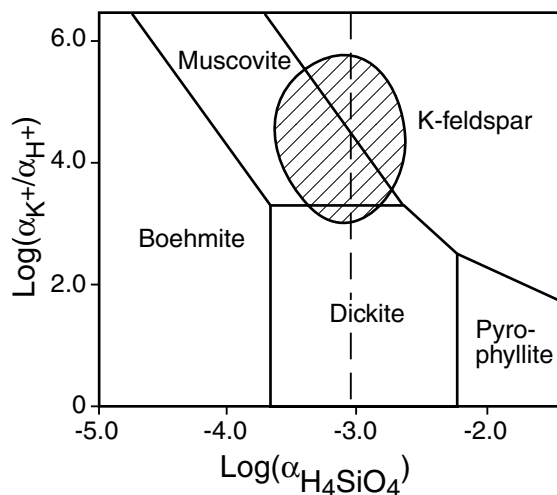
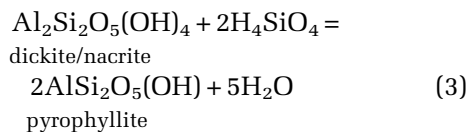


Fig. 12. Stability diagram of the system $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ at 100°C and 170 bar based on thermodynamic data of SUPCRT; the stability field of dickite is calculated based on data from Zotov *et al.* (1998). Quartz saturation is represented by the dashed line. Hatched area represents the composition of most formation waters from the North Sea reservoirs (data from Egeberg & Aagaard, 1989; Warren & Smalley, 1994).

(Morad *et al.*, 1994). Accordingly, dickite has a wider stability field than kaolinite as revealed by thermodynamic data presented by Zotov *et al.* (1998; Fig. 12). Therefore, extensive dickitization during shallow mesodiagenesis enhances the preservation of reservoir quality as it retards illite formation. Pervasive or complete dickitization of kaolinite occurs at $\approx 110^\circ\text{C}$ (Ehrenberg *et al.*, 1993). Hence, during mesodiagenesis, illite and dickite compete in the replacement of kaolinite. Illitization is favoured over dickitization under conditions of low water-to-rock ratio and high $\alpha_{\text{K}^+}/\alpha_{\text{H}^+}$ ratio. The $\alpha_{\text{K}^+}/\alpha_{\text{H}^+}$ ratio required to stabilize illite at quartz saturation decreases with increasing temperature (Fig. 13). K^+ is most often believed to be derived internally on the scale of sandstone bed (Ehrenberg, 1991), or from juxtaposed evaporites (Gaupp *et al.*, 1993). As evaporites contain very little or no intercrystalline porosity (i.e. little connate waters), they may supply K^+ due to their dissolution by formation waters (Fig. 9). During a closed-system diagenesis of K-feldspar-poor sandstones, dickite will survive, to be later transformed into nacrite or pyrophyllite when pore waters are characterized by high activity of dissolved silica (Figs 12 and 14) at the boundary between diagenesis and low-grade metamorphism ($\approx 200^\circ\text{C}$; Schulz-Rojahn & Phillips, 1989), as follows:



This reaction is fairly uncommon, as most kaolinite and dickite are apparently pervasively transformed into chlorite and illite during mesodiagenesis.

4 Fe-chlorite, which occurs as rims of pseudo-hexagonal crystals that are arranged perpendicular to the surfaces of framework grains. Such chlorite has a spatial distribution that is opposite to that of quartz cement, as it inhibits the precipitation of quartz overgrowths. Hence, chlorite coatings contribute to porosity and permeability preservation in deep sandstone reservoirs (Pittman *et al.*, 1992; Ehrenberg, 1993). Such reservoirs are, however, characterized by high amounts of irreducible water due to the presence of abundant microporosity in the chlorite, which poses a serious reservoir evaluation problem. It is, so far, poorly understood why chlorite is more efficient in inhibiting the precipitation of quartz overgrowths than illitic clays; the latter clays are commonly partially to completely engulfed by

quartz overgrowths (Bonnell *et al.*, 1999). It is possible that the chemistry of fluids that are in equilibrium with chlorite, and not the chlorite itself, somehow retards the nucleation and growth of quartz.

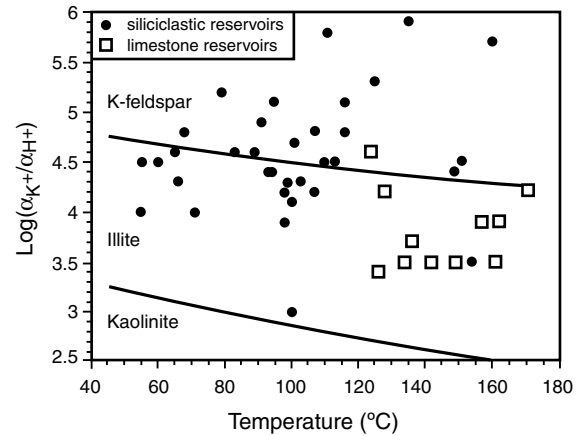


Fig. 13. Diagram showing the equilibrium relationship between North Sea formation waters (data from Egeberg & Aagaard, 1989; Warren & Smalley, 1994) and kaolinite, illite and K-feldspar related to $\log(\alpha_{\text{K}^+}/\alpha_{\text{H}^+})$ ratio and temperature. Note that the $\log(\alpha_{\text{K}^+}/\alpha_{\text{H}^+})$ ratios for the siliciclastic reservoirs increase with increasing temperature due to dissolution and albitization of K-feldspars. The $\log(\alpha_{\text{K}^+}/\alpha_{\text{H}^+})$ ratio needed to illitize kaolinite decreases with increasing temperature.

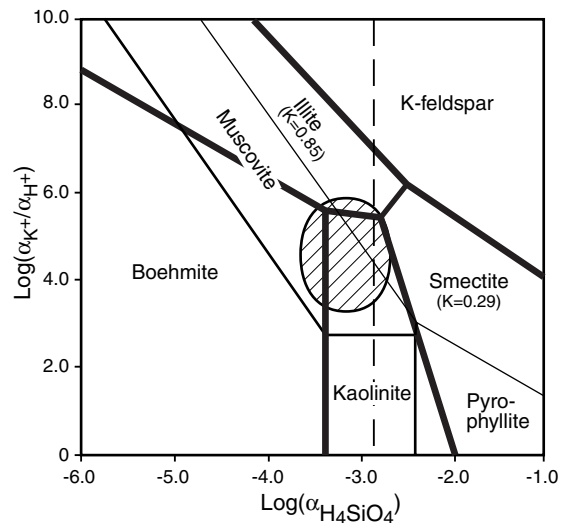


Fig. 14. Stability diagram in the system $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ at 110°C based on thermodynamic data of SUPCRT (thin lines; Helgeson *et al.*, 1979) and on data from Aja *et al.* (1991; bold lines). The latter data suggest a dramatic increase in the stability field of kaolinite. Quartz saturation is represented by the dashed line. Hatched area represents the composition of most formation waters from the North Sea reservoirs (data from Egeberg & Aagaard, 1989; Warren & Smalley, 1994).

Chlorite fringes form by precipitation from pore waters, by grain replacement and by the progressive transformation of eogenetic berthierine or S/C coatings (Moraes & De Ros, 1990; Longstaffe *et al.*, 1992; Ehrenberg, 1993; Humphreys *et al.*, 1994). Thus, although chlorite rims reveal an early diagenetic, precompactational habit, it is a deep-burial, high-temperature mineral (Jahren & Aagaard, 1989). In contrast to mesogenetic neoformed chlorite, chloritized smectite or berthierine coatings are continuous along the intergranular grain contact. Nevertheless, the fringe-like habit of chlorite develops only on grain surfaces that face an open pore space, and not at grain contacts. At such contacts, the precursor smectite preserves its tangential alignment around the grains.

In sandstones containing pore-lining chlorite, the biotite, mud intraclast, volcanic rock fragments and, less commonly, feldspars are replaced by chlorite too (Morad, 1990; Pittman *et al.*, 1992; Hillier, 1994; Humphreys *et al.*, 1994). Biotite chloritization is accompanied by the consumption of H^+ from pore waters and release of K^+ and Si^{4+} , leading to the creation of a microenvironment characterized by elevated pH, $\alpha_{K^+}/\alpha_{H^+}$ and $\alpha_{H_4SiO_4}$ in water films within the biotite. This microenvironment enhances the precipitation of numerous authigenic minerals, such as K-feldspar and carbonates (Boles & Johnson, 1984). Micro-crystalline, mesogenetic K-feldspar is also closely associated with illite and chlorite that replace mud intraclasts (Morad *et al.*, 1994). Grain-rimming and replacive chlorites thus form within a similar depth-temperature interval to illite, and are most abundant at temperatures $\geq 100^\circ C$ (Jahren & Aagaard, 1989). However, illite usually covers, and hence post-dates, chlorite, probably reflecting an increase in $\alpha_{K^+}/\alpha_{H^+}$ with increasing temperatures of formation waters (Fig. 13).

5 Albitization of detrital K-feldspars is a dissolution-precipitation process rather than a simple, solid-state diffusional exchange of K by Na. At this burial stage, the remaining less-calcic plagioclase grains will be albitized too. The albitization of K-feldspar is spatially and temporally linked with and provides K^+ needed for illitization of kaolinite in sandstones (Morad *et al.*, 1990). Indeed, the dissolution and albitization of K-feldspar are governed kinetically by the consumption of K^+ in the illitization of kaolinite (Aagaard *et al.*, 1990). Upon fixation of K^+ in illite, albitization is thus controlled by pH, activity of Na^+ in formation waters and temperature (Fig. 15). The α_{Na^+} and $\alpha_{Na^+}/\alpha_{H^+}$ required to

stabilize albite-illite-quartz at the expense of K-feldspar and kaolinite decreases considerably with increase in burial depth and temperature (Fig. 15). Pervasive to complete illitization of kaolinite and albitization of K-feldspars in North Sea sandstones occurs at temperatures $\geq 130^\circ C$ (Bjørlykke *et al.*, 1986).

In some deeply buried sandstones ($T \geq 110^\circ C$), albitization is accompanied by cementation and replacement of the feldspar by coarse laumontite (Helmold & Kamp, 1984; Merino *et al.*, 1997). In order to stabilize laumontite, the formation waters in these sandstones should be characterized by extremely low p_{CO_2} (Crossey *et al.*, 1984). In volcanoclastic sandstones, both albitization and laumontite formation occur at relatively shallow depths and low temperatures ($\approx 50^\circ C$; Surdam & Boles, 1979; Wopfner *et al.*, 1991; Remy, 1994). This implies that laumontite forms in a wide temperature range (≈ 50 – $200^\circ C$; Boles & Coombs, 1977).

6 Precipitation of pyrite and, less commonly, Cu-Pb-Zn sulphides occurs during thermal sulphate reduction and invasion of the reservoirs by metal-rich brines (Siebert, 1985; Metcalfe *et al.*, 1994). Variable amounts of barite and ankerite are associated with these sulphides. Diagenetic ores composed of this mineral assemblage are referred to as Mississippi Valley-type ores which form by large-scale, tectonically driven fluid flow, such as in foreland basins. As fluid flow is mostly focused, these minerals are distributed mainly along fractures and faults.

Spatial and temporal distribution of mesogenetic secondary porosity

Various patterns of spatial and temporal distribution of secondary porosity that result from the dissolution of framework grains (mainly feldspars

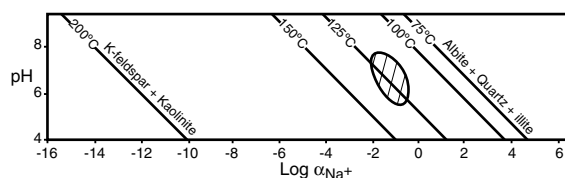


Fig. 15. Stability diagram for the reaction $2K\text{-feldspar} + 2.5\text{kaolinite} + Na^+ = \text{albite} + 2\text{illite} + 2\text{quartz} + 2.5H_2O + H^+$, showing that the stability field of K-feldspar+kaolinite decreases successively with increasing temperature. Hatched area represents the composition of most formation waters from the North Sea reservoirs (data from Egeberg & Aagaard, 1989; Warren & Smalley, 1994).

and rock fragments) and cements (mainly calcite) are reported in deeply buried sandstones. However, determination of the timing and burial depths at which mineral dissolution occurs is difficult. This is particularly true for siliciclastic sequences that have undergone complex burial–uplift histories. Additionally, the degree of preservation vs. destruction of eogenetic secondary porosity during mesodiagenesis is poorly understood, and the distinction between primary and secondary intergranular porosity is fraught with uncertainty. It appears that the presence of relatively small amounts of rigid, evenly distributed, intergranular eogenetic cement, such as dolomite rhombs and quartz overgrowths, can limit or prevent mechanical compaction during deep burial, even in sandstones that are rich in ductile lithic grains (Souza *et al.*, 1995). Indeed, mouldic pores outlined by, for example, clay minerals and feldspar overgrowths are common over a wide range of burial depths. However, primary and secondary porosities decline fairly sharply with depth, except for hydrocarbon-saturated (Swarbrick, 1994) and overpressured sandstones (Hall, 1994). Other conditions that favour porosity preservation include a short period of deep burial (Sombra & Chang, 1997) and mechanically stable framework-grains (e.g. quartz, chert and feldspars).

Despite the uncertainties, it is argued in the literature that secondary porosity can account for many high-quality, deep reservoirs such as those in the US Gulf Coast (e.g. Taylor & Land, 1996). As undersaturated meteoric waters are unlikely to penetrate siliciclastic sequences to depths greater than 3 km, particularly in overpressured and actively subsiding basins, mineral dissolution has been suggested to be accomplished mainly by organic acids and CO₂ released during thermal maturation of organic matter and oil generation in source mudrock (Fig. 9). Organic acids (mainly carboxylic) form also by the interaction of water with hydrocarbons, mineral oxidation of organic matter and by bacterial degradation of organic matter and hydrocarbons (MacGowan & Surdam, 1988). Generation of CO₂ also occurs by thermal reduction of sulphate ions which are derived from the dissolution of evaporite deposits.

Organic acid anions, which occur in variable concentration in formation waters depending on temperature, type of organic matter in the source rocks, lithology and redox reactions (Carothers & Kharaka, 1978; MacGowan & Surdam, 1988; Shock, 1988), may enhance the solubility of carbonates and aluminosilicates by complexing

Si, Al, Ca and Mg (Surdam *et al.*, 1984, 1989). Maximum concentrations of organic acid anion occur at ≈ 80–120 °C. Over this temperature range, the pH of formation waters is buffered by carboxylic acid anions. At temperatures ≥ 100 °C, the carboxylic acids begin to progressively decarboxylate, resulting in an increase in pCO₂. If pH is buffered by silicates, the increase in pCO₂ at temperatures of 100–120 °C will cause dissolution of carbonate cements.

Carboxylic and carbonic acids may account for secondary porosity, particularly in sandstones adjacent to hydrocarbon source rocks due to the dissolution of calcite cement and, less commonly, of aluminosilicates (Moncure *et al.*, 1984; Surdam *et al.*, 1984; Surdam & Yin, 1995). It was shown experimentally that ionic solubility is enhanced substantially through complexation by carboxylic compounds. For instance, acetate complexes with Ca, Mg and Al and oxalate complexes with Si (Bennett & Siegel, 1987). However, mass-balance calculations and the usually low measured concentrations of organic acids in formation waters, as well as the absence of a marked increase in Al and Si concentrations, raise some doubts about the efficiency of these acids in creating secondary porosity in sandstone reservoirs (Giles *et al.*, 1995). Nevertheless, relatively high concentrations of Al (up to 6 mg L⁻¹) have been reported in formation waters from Tertiary sediments in the San Joaquin basin, USA (Fisher & Boles, 1990) and Palaeozoic–Cenozoic sediments in the Tarim Basin, China (Chufuang *et al.*, 1997). Acetate, which is a dominant species, may reach concentrations of up to 1000–3000 mg L⁻¹ in some oil-field brines (Carothers & Kharaka, 1978; Fisher, 1987), whereas oxalate concentrations only reach 100 mg L⁻¹, probably due to the precipitation of Ca-oxalate (Manning *et al.*, 1992). Additionally, organic acids may react with clay minerals and carbonates, and thus be neutralized while still in the source mudrock. Obviously, despite the importance of organic acids deduced based on theory and experimental work, their influence on the spatial and temporal distribution of diagenetic alterations is still a controversial topic. However, the formation-water samples so far analysed reflect compositions that post-date the peak of thermal maturation of organic matter and hydrocarbon formation. Consequently, the peak of maximum organic-acid concentrations in formation waters and direct evidence for their active role in influencing the spatial distribution of mesogenetic alterations have not been observed.

Other sources of acidic fluid during mesodiagenesis include low-grade metamorphic reactions (so-called reverse weathering) in deep regimes of sedimentary basins (Taylor & Land, 1996). As these fluids are believed to move by focused flow, the spatial distribution of resulting secondary porosity is strongly associated with major, deep fault zones. In some rare cases, large amounts of CO₂, which can be derived from the contact metamorphism of carbonate rocks, can be emplaced in sandstone reservoirs, such as in the Norphlet Formation, Pisgah Anticline, Mississippi, USA (Studlick *et al.*, 1990).

SPATIAL AND TEMPORAL DISTRIBUTION OF TELOGENETIC ALTERATIONS

Telodiagenesis occurs when sedimentary sequences that have undergone eo- and mesogenetic modifications are uplifted and subjected to pressure rebound and the influence of meteoric waters. Factors controlling the spatial and temporal distribution and the extent of meteoric telodiagenesis below unconformity surfaces include: (i) hydraulic head, which depends on the degree of uplift above sea-level; (ii) climate; (iii) degree of porosity and permeability loss during eo- and mesodiagenesis; (iv) presence vs. absence of thick, impermeable mudrock layers which would halt the infiltration of meteoric water; (v) presence of faults, which extend to the surface and act as conduits for meteoric water; (vi) duration of the exposure; and (vii) the mineral composition (Fig. 16). Although meteoric waters were suggested to penetrate to depths of 2 km or more in sedimentary basins, the thickness of pervasive telogenetic alterations varies, often from tens to hundreds of metres (Emery *et al.*, 1990; Shanmugam, 1990).

Therefore, spatially and temporally extensive telogenetic meteoric alterations are expected to occur around uplifted blocks in humid climates and in mineralogically immature sandstones with good hydraulic conductivity. Telogenetic alterations are better preserved if the rate of uplift/erosion is lower than the rate of meteoric alteration (Bjørkum *et al.*, 1990, 1993), and are expected to increase systematically upwards when the sandstones are exposed at the unconformity surfaces (Fig. 17). As the incursion of meteoric water along faults bounding

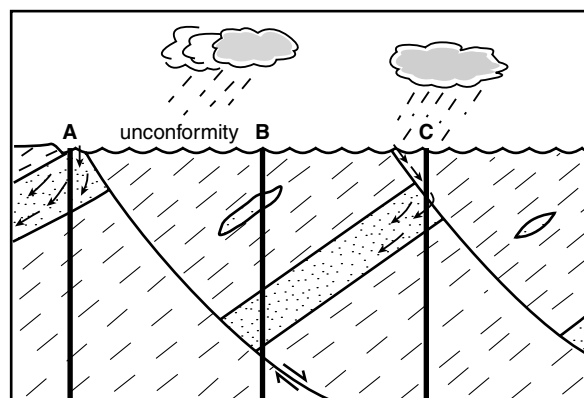


Fig. 16. Hypothetical diagram showing the possible ways by which meteoric telodiagenesis occurs below an unconformity surface. Different distribution patterns of telogenetic alterations (e.g. kaolinite content) occur below the surface in each of the wells A, B and C. Telogenetic alterations in well A are systematically related to the unconformity surface. Alterations are halted in well B due to the occurrence of a thick mudstone layer, but meteoric water flow may occur along the tilted sandstone layer. In well C, alterations occur near a fault.

uplifted blocks occur to depths of a few hundreds of metres, the spatial and temporal distribution of telogenetic modifications are not necessarily systematically related to unconformity surfaces (Fig. 16).

The most important telogenetic modifications promoted by meteoric flushing in siliciclastic sequences include:

- 1 Dissolution of unstable framework grains, such as feldspars, mica, rock fragments, mud intraclasts and heavy minerals (Smale, 1989; Emery *et al.*, 1990). Under humid conditions, the dissolution of detrital aluminosilicates is typically accompanied by the precipitation of kaolinite. Unlike eogenetic kaolinite, telogenetic kaolinite post-dates quartz overgrowths and is closely associated with dissolved eo- and mesogenetic carbonate cement. The dissolution of K-feldspars and removal of K below unconformities are evidenced by the progressive increase in the Th/K ratio in natural gamma-ray logs (Emery *et al.*, 1990).

It is generally agreed that telodiagenesis enhances the porosity and permeability of sandstones at shallow depths below the unconformity surface due to the dissolution of framework grains and cements (Fig. 17; Giles & De Boer, 1990; Ghosh, 1997). This enhancement is most evident under humid climatic conditions even when

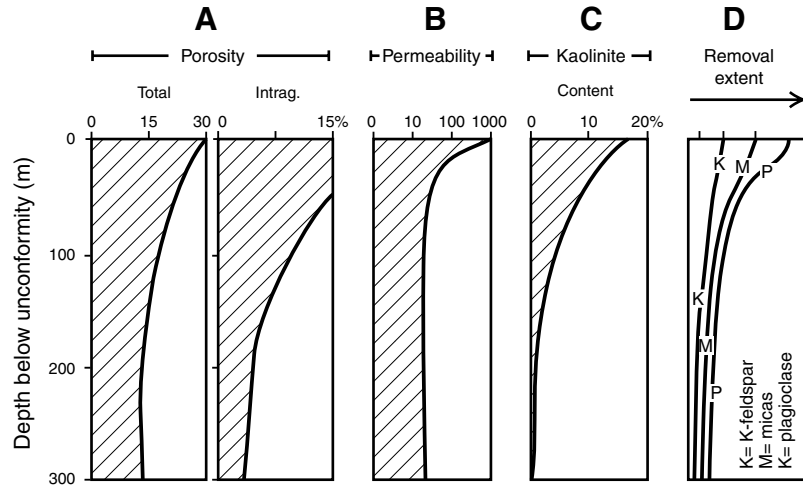


Fig. 17. Distribution patterns of porosity–permeability (e.g. Shanmugam, 1990) and kaolinite contents due to telodiagenesis below an unconformity surface under a humid climate. An increasing order of dissolution of plagioclase, micas and K-feldspar occurs towards the unconformity surface.

silicate dissolution is accompanied by precipitation of kaolinite (Garcia *et al.*, 1998). Sandstones with normal porosity of <10% and permeability of <10 mD can reach porosity and permeability values up to 25% and 1000 mD, respectively, close to unconformities (Fig. 17; Shanmugam, 1990).

2 Alteration of eo- and mesogenetic cements, such as the dissolution of calcite, dolomite, sulphate and feldspar overgrowths and the oxidation of ferroan carbonates, chlorite and pyrite (Stanton, 1986; Morad *et al.*, 1995; Garcia *et al.*, 1998). Sequential mineral dissolution by meteoric waters occurs in the upper 200 m below the unconformity surface (Fig. 17; Thrailkill, 1968; Shanmugam, 1988; Shanmugam, 1990; Hayes & Boles, 1992). Dissolution of calcite cement is most important in humid climates. Conversely, calcite dissolution under semi-arid conditions is followed by supersaturation and precipitation. Tightly cemented sandstones, particularly with ferroan carbonates, are not normally subjected to significant dissolution.

3 Pedogenesis and clay infiltration along the unconformity surface occur under semi-arid climatic conditions, in some cases accompanied by the formation of duricrusts like calcrete, silcrete and ferricrete (Shanmugam, 1988). Telogenetically infiltrated clays cover mesogenetic cements, such as quartz overgrowths.

CONCLUDING REMARKS

The complex array of parameters that control the spatial and temporal distribution of diagenetic

alterations in siliciclastic sequences include: (a) tectonic setting and thermal–burial history of the basin; (b) origin and geochemical evolution of formation waters; (c) depositional environment and facies; (d) climatic conditions; (e) the physical and chemical properties of framework grains; (f) relative changes in sea-level; (g) amounts and reactivity of organic matter; and (h) timing of hydrocarbon emplacement and the degree of hydrocarbon saturation. Despite the complexity and wide variations of the diagenetic systems, attempts have been made to develop global models for the diagenetic evolution of siliciclastic sequences. This paper has demonstrated that the spatial distribution of eogenetic alterations can be constrained based on variations in depositional facies and climatic conditions, and within a predictive, sequence stratigraphic context. Many of the conceptual and numerical diagenetic models so far developed are biased, as they rely heavily on the huge amounts of data collected from two extensively studied hydrocarbon provinces, namely the US Gulf Coast and the North Sea. The challenge ahead is to develop reliable, predictive, three-dimensional conceptual and numerical models that consider, on a world-wide basis, as much surface and subsurface data about the spatial and temporal distribution of diagenetic alterations as possible. Furthermore, successful models should be developed based on: (1) improved thermodynamic and kinetic databases on organic and inorganic phases and reactions; (2) a combination of ‘microscopic’ observations (paragenetic relationships and fluid-inclusion data) and larger, basin-wide observations of the distribution of diagenetic alterations; and (3) if diagenetic models are to be useful in hydrocarbon

exploration and exploitation, multidisciplinary research involving seismic interpreters, petrophysicists and reservoir engineers should be carried out.

Among the key questions that have to be answered before successful models can be developed are: (1) How can we distinguish between mesogenetic alterations that are mediated by diffusion from those mediated by active fluid flow? In others words, do mesogenetic reactions occur in open or closed systems in terms of mass and heat transfer? What are the scales of mass transfer? And what is the precise role of faults in mass and heat transfer? (2) What is the relationship between the thermal maturation of organic matter and the timing of formation and emplacement of hydrocarbons in reservoirs and the spatial and temporal distribution of mesogenetic alterations? (3) Can the formation-water samples so far collected from sedimentary basins be used as the basis for a global understanding of the spatial and temporal distribution of mesogenetic alterations? In other words, is the present a key to the past?

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