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SANDSTONE DIAGENESIS:
Recent and Ancient

EDITED BY

Stuart D. Burley and Richard H. Worden

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Sandstone diagenesis: the evolution of sand to stone

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INTRODUCTION TO DIAGENESIS

Diagenesis comprises a broad spectrum of physical, chemical and biological post-depositional processes by which original sedimentary assemblages and their interstitial pore waters react in an attempt to reach textural and geochemical equilibrium with their environment (Curtis, 1977; Burley *et al.*, 1985). These processes are continually active as the ambient environment evolves in terms of temperature, pressure and chemistry during the deposition, burial and uplift cycle of basin history. As such, diagenesis encompasses a broad spectrum of post-depositional modifications to sediments. It ranges from weathering in subaerial environments and oxidation in the water column, includes compaction and lithification of sediments during burial, and eventually grades through a continuum into low-temperature metamorphism. In both humid and arid climates where geochemical reactions approach completion, gibbsite, kaolin group minerals and smectites form from aluminosilicate precursors. In cooler, temperate climates a greater variety of clay minerals occurs in weathering profiles reflecting metastable, intermediate breakdown products of aluminosilicates. Diagenesis is differentiated from metamorphism by a variety of mineral and thermal-history indices (Fig. 1; Frey, 1987; Slater *et al.*, 1994), but broadly a temperature transition of 180–250°C is thought to separate the two regimes. The classic transition from diagenesis to metamorphism was described eloquently in the Salton Sea geothermal field, south-east California, where sandstones of broadly similar composition are present over a temperature interval of 100°C to 350°C (McDowell & Elders, 1980). Here, clearly diagenetic, non-equilibrium mineral assemblages

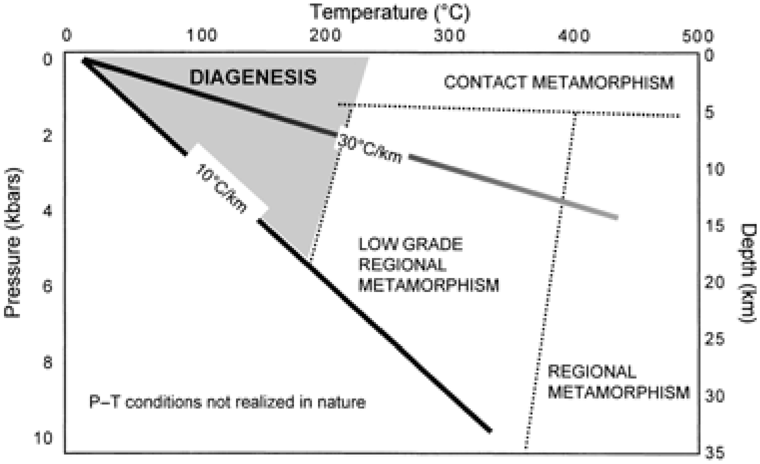


Fig. 1 Pressure–temperature diagram relating diagenesis to metamorphic regimes and typical P–T gradients in Earth's crust. The crustal geotherm of 10°C km^{-1} is representative of stable cratons, whereas a value of 30°C km^{-1} is typical of rifted sedimentary basins. Low-pressure (shallow)–high-temperature conditions are realized only in geothermal systems or in the vicinity of igneous contacts (so-called contact diagenesis: McKinley *et al.*, 2001).

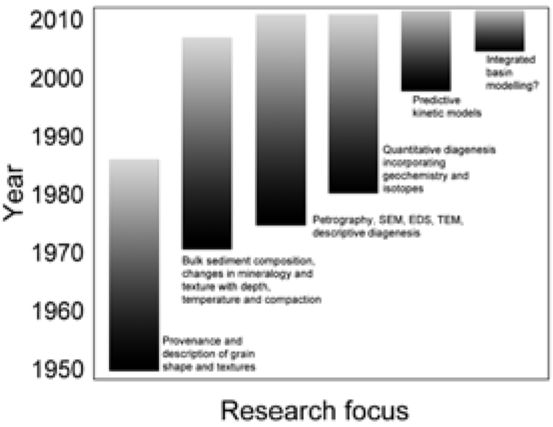


Fig. 2 The history of the study of diagenesis and probable future directions of the subject.

are replaced by an equilibrium metamorphic albite, chlorite and quartz assemblage. In the broadest sense, therefore, diagenesis can be considered as everything that contributes to making a sediment into a sedimentary rock from its weathering through to metamorphism during deep burial.

The study of sandstone diagenesis is relatively new, having grown from the description of grain shapes and textures coupled with the analysis of the evolution of bulk sediment composition with increasing depth and temperature of burial (Fig. 2). The importance of sandstone diagenesis as a subject is evidenced by the explosive growth of both pure and applied research in this subject through the 1980s and 1990s. This was largely driven by the petroleum industry because the amount and distribution of porosity in sandstones controls hydrocarbon migration pathways in the subsurface and, ultimately, the production of oil and gas from reservoirs. Prediction of porosity ‘sweet spots’ became a goal of explorationists world-wide in the 1980s–1990s (Curtis, 1983; Surdam *et al.*, 1984). The construction of predictive reservoir-flow-simulation models required detailed reservoir characterization based on an understanding of detrital and authigenic mineralogy (Hurst, 1987). Furthermore, as the demand for petroleum has increased, enhanced recovery techniques have developed that require the injection of reactive chemicals into the pore space of sandstones and potentially result in damage to reservoir formations (Pittman & King, 1986; Kantorowicz *et al.*, 1992). There is thus a need to understand chemical reactions with the host sandstone through the introduction of steam, surfactants, polymers or acids into reservoirs.

This introductory account provides a framework for the papers included in this compilation, sets the geochemical theme and provides definitions of the terms generally used in diagenesis. Wherever possible we have referred to the papers included in this volume to illustrate the points made. For more comprehensive reviews of characteristics of sandstone diagenesis the reader is referred to Morad (1998), Morad *et al.* (2000) and Worden & Morad (2000).

WHY DO DIAGENETIC REACTIONS TAKE PLACE?

The fundamental driving mechanisms for diagenetic reactions are changes in one or more of ambient pore-fluid chemistry, temperature and pressure. Empirical evidence suggests that this sequence is the order of importance of controlling parameters for diagenetic reactions. Indeed, it has long been recognized in studies of pedogenesis that it is the amount of average rainfall, i.e. the extent of flushing with water, that controls the rate of weathering. In dry temperate climates average saprolite formation rates of 5 mm per 1000 yr are an order of magnitude less than in wet, tropical climates (Tardy, 1969; Nahon, 1991). It is the presence of unstable or metastable mineral components bathed in aqueous pore waters charged with dissolved species that defines the diagenetic system. Without the presence of aqueous pore fluids, diagenesis effectively ceases. The sedimentary mineral assemblage reacts through water–rock interaction via pore fluids towards equilibrium with the ambient geochemical environment. Diagenesis is thus a dynamic suite of processes; as the burial history of a sedimentary basin develops, and pore fluids evolve through time, the diagenetic fabric and mineralogy must change in response.

Time is a critical component in diagenetic reactions. Early diagenetic reactions can be extremely rapid, with marine cementation in carbonates and sandstones taking place over mere decades (Taylor & Illing, 1969; Pye *et al.*, 1990; Al-Agha *et al.*, 1995), although few mineralogical changes take place in most silicates during sediment transport and deposition. More typical is reddening of desert sands, which demonstrably takes place between 5000 and 20 000 yr (Gardener, 1983; Pye, 1983). Mature lateritic soil profiles are known to develop over time-scales of 10 000 to 1 000 000 yr (Valeton, 1983), and calcretes form over comparable time intervals, although possibly much shorter (Wright & Tucker, 1991). Considerably greater time intervals are available during burial, where associated higher temperatures and pressures increase reaction rates and so favour true chemical equilibrium. Even here, some evidence suggests that deep burial diagenetic reactions may be quite rapid, at least in a geological sense, occurring on a scale of tens of thousands of years (Walderhaug, 1994; Duddy *et al.*, 1998; Worden *et al.*, 2000b) to a few million years (Boles, 1987).

Diagenetic assemblages are a function of chemical thermodynamics and kinetics. In this context, phase equilibrium diagrams are useful for predicting the direction of diagenetic mineral reactions (Fig. 3; Garrels & Mackenzie, 1971), but are much less effective at predicting aqueous pore solution compositions in geological systems containing diverse complex minerals. Free energy calculations can be used to identify unstable or metastable systems and predict relative mineral stability (Curtis, 1978). Indeed, it is the bond strength of minerals and free energy of mineral surfaces that define mineral reactivity (Helgeson *et al.*, 1978; Hurst, 1981). However, differential rate phenomena in many systems dominate over thermodynamics, especially in systems at low temperatures in early diagenesis. During diagenesis it is typically the difference between chemical reaction rates and transport rates that is the critical rate-limiting factor in the resultant mineral reaction.

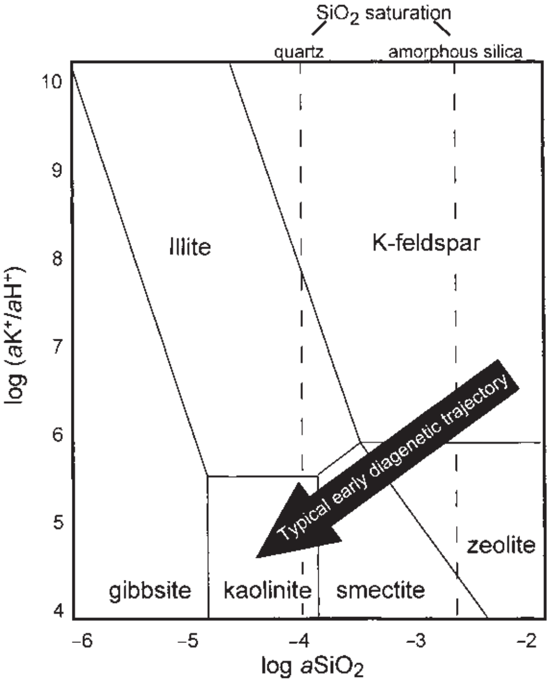


Fig. 3 Phase diagram for the system $\log(aK^+/aH^+)$–$\log aSiO_2$ (where 'a' indicates chemical activity of species) illustrating how changing isothermal water geochemistry can lead to diagenetic reactions. For example, if water in contact with feldspathic sandstones is flushed with fresh water (e.g. meteoric water) then the water will progressively evolve to lower aqueous potassium and silica concentrations. This explains why advanced eogenesis (and telogenesis) leads to kaolinite growth at the expense of feldspar minerals.

DEFINING DIAGENESIS

A variety of terms are used to describe diagenetic processes that have acquired a specific meaning. Important terms used in this text, and commonly applied to diagenesis, are defined in Table 1 and a brief commentary on their meanings is given below.

Authigenesis literally means 'generation *in situ*' and is usually applied to describe all diagenetic mineral formation in sediments.

Table 1 Common terms used in diagenesis.

Term	Definition
Authigenesis	*In situ* mineral growth
Cementation	Growth or precipitation of minerals in pore spaces
Compaction	Suite of processes resulting in the collapse of pore space in a sandstone
Decarboxylation	Loss of CO_2 from organic matter in response to increased temperature
Dehydration	Loss of H_2O from minerals and organic matter as a result of increased temperature
Dissolution	Process whereby a mineral is destroyed by interaction with a fluid leaving behind a cavity
Lithification	The process of indurating a loose or friable sediment through compactional and cementation processes
Neoformation	New growth of minerals during diagenesis
Neomorphism	Transformation of a mineral typically involving changes in crystal chemistry
Paragenetic sequence	The order in which diagenetic processes occur in sediments as recorded or inferred by petrographic, geochemical or isotopic methods
Precipitation	Crystallization of a mineral from solution
Recrystallization	Dissolution followed by precipitation involving changes in crystal size or habit of a given specific mineral
Replacement	Growth of a chemically different authigenic mineral within the body of a pre-existing mineral

Authigenic minerals are thus distinct from detrital (transported) minerals and formed *in situ* within the host sediment in which they now occur.

Cementation is the diagenetic process by which authigenic minerals are precipitated in the pore space of sediments which thereby become lithified. Compaction typically includes simple grain rearrangement during shallow burial as well as the ductile deformation of soft sand grains and intergranular matrix. This is quite different from the process known as chemical compaction, which involves the chemically induced dissolution of grains at intergranular contacts and reprecipitation of the dissolved material on grain surfaces facing open pores. Dissolution is the diagenetic process by which a solid component in the host sediment is dissolved by an aqueous pore solution leaving behind a space or cavity within the host sediment (see Schmidt & MacDonald, 1979; Burley & Kantorowicz, 1986).

Neomorphism describes the processes of replacement and recrystallization of one mineral by a related mineral but involving changes in the details of the mineral chemistry, excluding simple pore filling processes (Folk, 1965). The term has been applied widely to limestones and dolostones in which it is commonly used to describe the coarsening of aragonitic micrite into calcite microspar and is equally applicable to sandstones. Examples of neomorphism in sandstones are the conversion of aragonite to low Mg calcite cement or the evolution of sand-grain-coating green clays (e.g. Odin, 1990) into chlorite (e.g. Ehrenberg, 1993). Neomorphism commonly preserves textural evidence (ghost fabrics) of the previous phase.

Recrystallization, in contrast, is the change in crystal size or shape resulting from thermodynamic instability (such as the reprecipitation of finely grained calcite by coarse grained calcite cement; Hendry *et al.*, 1996; or kaolinite by dickite; Ehrenberg *et al.*, 1993) when kinetic barriers are exceeded to allow the reaction to proceed. In the diagenetic realm both recrystallization and neomorphism always require and involve the presence of an aqueous medium. These processes are distinct from replacement whereby an authigenic mineral occupies the place of another former mineral (either detrital or authigenic) via a dissolution–precipitation process (e.g. carbonate cements replacing detrital quartz; Hesse, 1987; or the albitization of detrital K-feldspar grains; Ramseyer *et al.*, 1992). It has been suggested replacement must take place via a ‘thin film’ mechanism (Pettijohn *et al.*, 1972).

A paragenetic sequence is the interpreted order in which diagenetic processes occurred.

The sequence is constructed on the basis of observations about the order of mineral growth and, typically, some degree of interpretation. Thus, for example, if quartz cement encloses illite crystals, the quartz is interpreted to have grown after the illite. A paragenetic sequence includes all the processes listed above as well as compaction, dissolution, recrystallization and precipitation. So very high 'minus cement volumes' (the sum of pore space and the space occupied by cements) in carbonate cemented sandstones, for example, is commonly taken to indicate that the carbonate cementation took place before compaction, and thus before significant burial. A paragenetic sequence is a simple way of relating a potentially complex series of events in a time series. However, it always should be remembered that a paragenetic sequence constructed for any sandstone is largely an interpretation of textural data. In some instances, a paragenetic sequence can be constrained by the use of absolute age determinations from radiometric dating of minerals (such as the K–Ar technique for illite) or via a burial curve using an independent temperature (or pressure) determination (such as apatite fission-track dating or fluid-inclusion microthermometry).

REGIMES OF DIAGENESIS

The concept of diagenetic regimes is a broad framework that relates diagenetic processes to the evolution of sedimentary basins (Fig. 4). Three conceptual regimes are commonly recognized: early diagenesis (eogenesis), burial diagenesis (mesogenesis) and uplift-related diagenesis (telogenesis). This terminology was adopted from a scheme developed initially by Choquette & Pray (1970) to describe limestone diagenetic processes, but is now more generally applied: correctly so, as the same fundamental processes and controls operate in clastic diagenesis and in carbonate diagenesis. Alternative schemes (e.g. the Russian system including

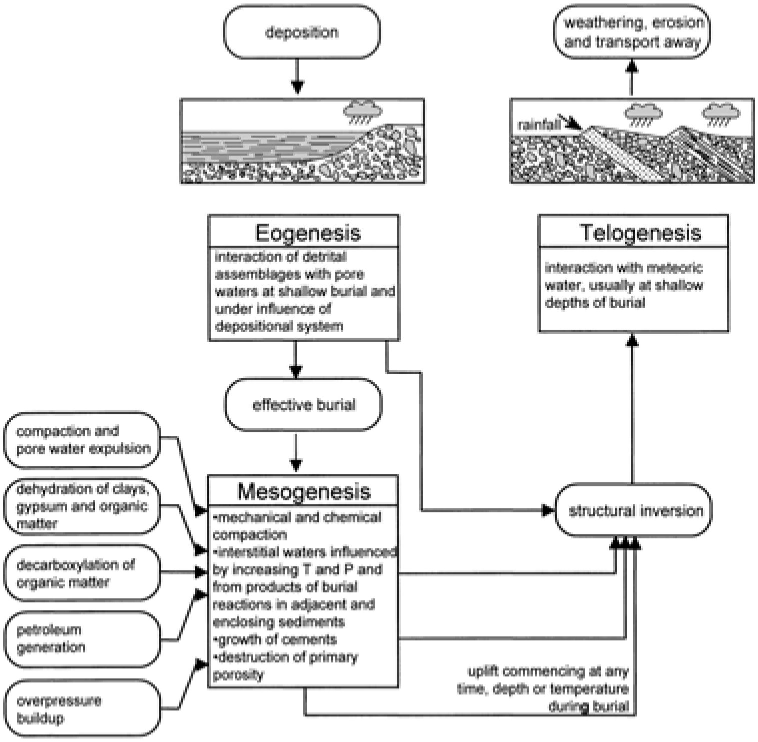


Fig. 4 Flow chart showing the links between the regimes of diagenesis. The change from mesogenesis (burial diagenesis) to telogenesis can occur at any stage during burial. Telogenesis (uplift-related processes) only happens when surface waters penetrate into the inverted basin and cause mineral reactions.

such terms as catagenesis and epigenesis; see Prozorovich, 1970, for example) have been used but are less commonly applied now. This is because systems and classifications defined by the maximum temperature of burial run into the difficulty of the effect of varying time spent at a given temperature—a direct consequence of the kinetic control on the rate of diagenetic reactions. Moreover, classifications defined by the equivalent stage of petroleum generation in source rocks are not useful for sandstones because these contain only sparse organic matter and their different thermal and poro-mechanical properties compared with fine grained, organic-matter-rich sediments results in quite different responses to ambient geochemical environments. Recognition must be made of the arbitrary nature of any diagenetic classification, but the three-fold scheme adopted here is simple and inclusive.

Eogenesis equates broadly to early diagenesis but is defined as including all processes that occur at or near the surface of the sediments where the chemistry of the interstitial waters is controlled mainly by the depositional environment (Fig. 4; Berner, 1980; Chapelle, 1993). Strictly speaking, this is the regime where the influence of the original depositional pore water dominates, and so includes weathering and soil development in continental depositional settings, and bacterially mediated redox reactions in marine environments. In some cases this is the regime in which meteoric water penetrates into the subsurface, although coastal sediments with a reflux of marine waters would also be classed as eogenetic. In reality, the eogenetic realm may extend to only a few metres below the sediment surface (in low permeability mudstones for example) or several thousand metres (as in coarse porous continental sandstones flushed by active recharge) depending on the geometric arrangement of aquifers, aquitards, synsedimentary faults and aquifer permeability. Eogenesis has also been defined in terms of depth of burial (and by inference, temperature) instead of the nature of the pore waters, where the maximum depth limit of eogenesis is about 1–2 km. Most basins of the world have a geothermal gradient between 20 and 30°C km^{-1} so that the limit of eogenesis (for a mean surface temperature of 10°C) lies between 30 and 70°C according to this scheme (Morad *et al.*, 2000).

Mesogenesis occurs during burial and is defined as those diagenetic processes occurring once the sediment has passed from the influence of the depositional environment through to the earliest stages of low-grade metamorphism. Boundaries may not be sharp, and may be difficult to define by textural, mineralogical or isotopic means. In many cases, this regime therefore includes sediments of between about 100–1000 m burial and those at depths with equivalent temperatures of up to 200–250°C. Mesogenesis is often termed burial diagenesis because it happens during burial. However, mesogenesis can continue following burial in inverted sedimentary basins that have experienced a degree of uplift and cooling. The main factors that influence mesogenesis include the time–temperature history, the primary mineralogy and fabric, loss and gain of material to neighbouring lithologies (so-called 'mass-transfer'), the geochemistry of the pore water and the presence of petroleum-related fluids (including oil, hydrocarbon gas, organic-derived CO_2 and H_2S). The boundary between eogenesis and mesogenesis can be defined in depth and temperature terms instead of the connectivity of pore water with surface waters (Morad *et al.*, 2000; and see above). In this case mesogenesis begins at 1–2 km burial (temperatures of between 30 and 70°C).

Telogenesis occurs in uplifted and exhumed rocks that have been exposed to the influx of surface (meteoric) water that is not related to the depositional environment of the host sediment. It differs from mesogenesis during moderate inversion and uplift simply because the rocks are in contact with flowing, low salinity, highly oxidized, CO_2-charged waters. Such water has the capacity to cause significant geochemical changes, including feldspar alteration to clay minerals (usually kaolinite) and ferric mineral oxidation (including alteration of ferroan calcite and dolomite), even though these waters are typically of low ionic strength. Many early studies of diagenesis were on outcrop samples that had inevitably undergone variable degrees of telogenetic alteration.

DIAGENETIC MINERAL CEMENTS IN SANDSTONES

A host of minerals occur as cements in sandstones. The most common mineral cements are quartz (and related chalcedonic silica varieties), the carbonate minerals, and a variety of aluminosilicate clay minerals. Less common, although locally important, cements include anhydrite (and gypsum), pyrite, feldspars, zeolites, haematite, apatite and Ti-rich minerals (such as sphene).

Quartz cement (Figs 5 & 6) is mineralogically the most simple of cements but occurs in a variety of forms. Quartz overgrowths are approximately equal thickness rinds that form on detrital quartz grains (Waugh, 1971). These are usually optically continuous with the substrate minerals (forming a syntaxial fabric) revealing that the two types of quartz are in perfect crystal continuity. In the case of detrital polycrystalline quartz grains, or strained quartz, the overgrowths typically adopt the crystallographic orientation of the detrital quartz immediately adjacent to the cement. Microcrystalline

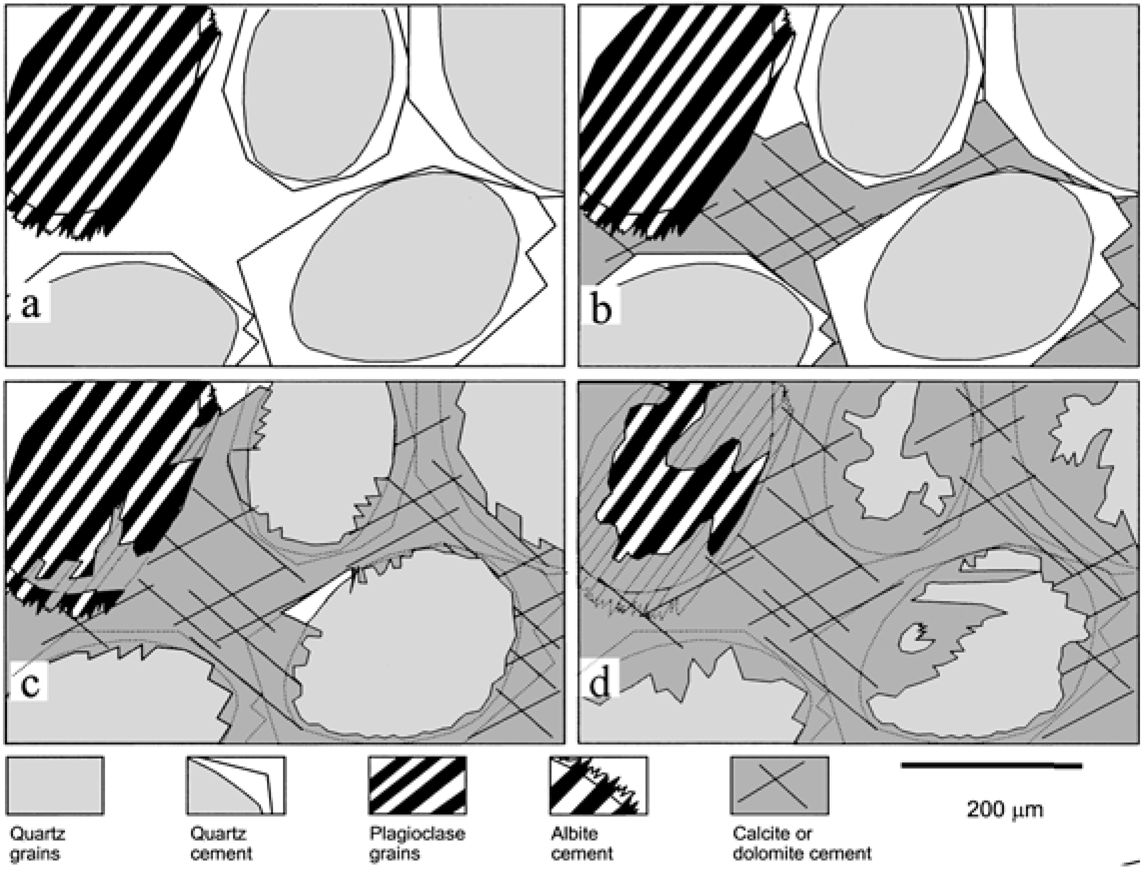


Fig. 5 Schematic cartoon illustrating types of pore-filling cementation in a paragenetic sequence. (a) syntaxial overgrowth cements, (b) passive pore-filling cements post-dating overgrowths, (c) peripherally grain-replacive cements post-overgrowths and (d) extensive grain replacement cements.

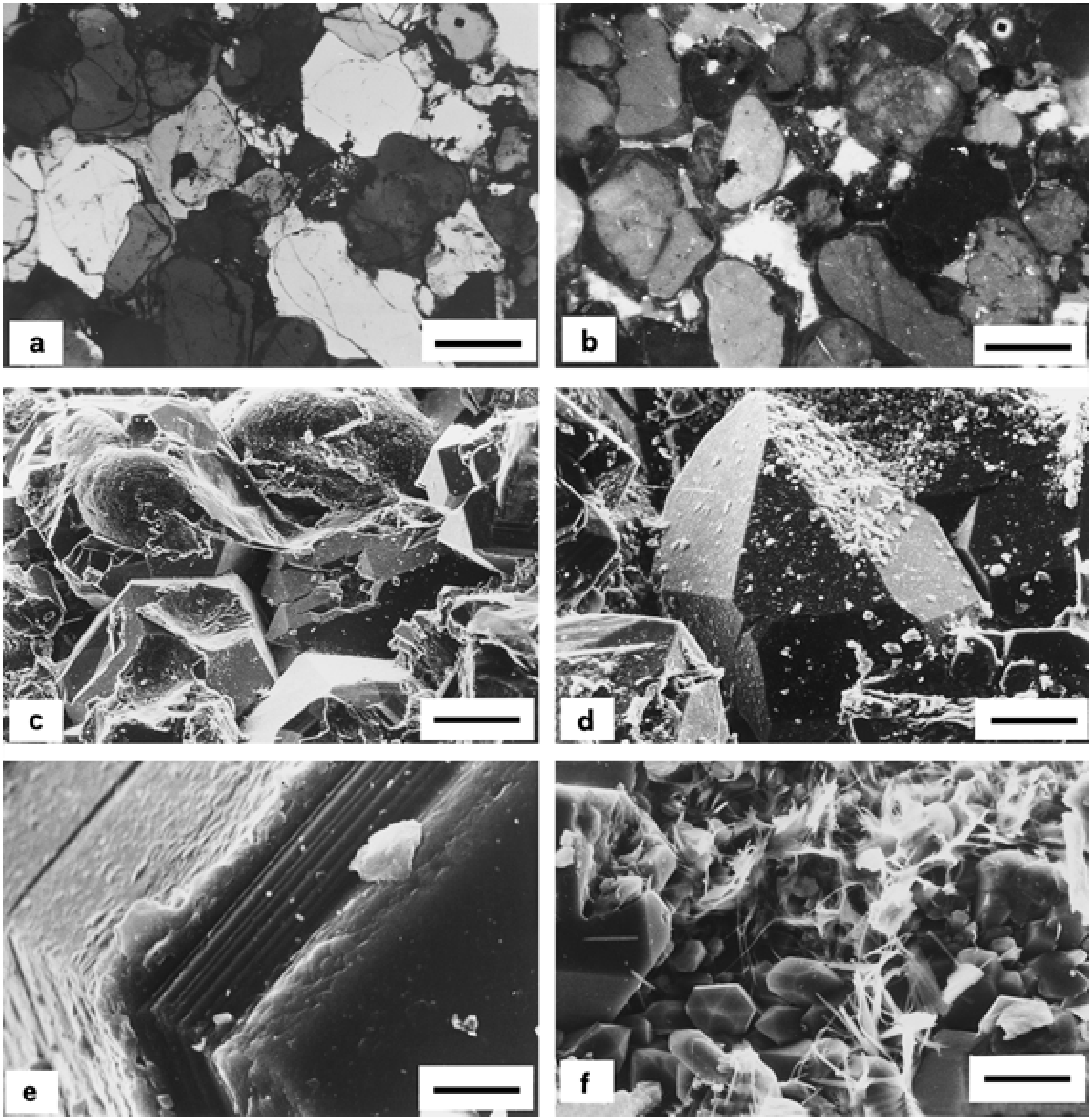


Fig. 6 Quartz cement in sandstones. (a) Optical micrograph of sandstone with large quartz overgrowths (crossed polars). (b) Same field of view under cathodoluminescence showing extent of quartz overgrowths (scale 300 μm). (c) A scanning election microscopy (SEM) image of the same sample showing well-rounded detrital grains enclosed in quartz overgrowths (scale 180 μm). (d) Detail of large euhedral overgrowth, SEM (scale 60 μm). (e) Close-up of edge of overgrowth showing successive growth zones (scale 10 μm). (f) Microquartz crystals lining intergranular pores, SEM (scale 20 μm).

quartz cement grows as a multitude of crystals of less than 10 μm length. These are often in optical continuity with detrital quartz but can also grow on detrital or diagenetic clay minerals. Quartz not in optical continuity with its host is termed epitaxial. Microcrystalline quartz is often observed to have replaced siliceous fossils (such as *Rhaxella*; Vagle *et al.*, 1994),

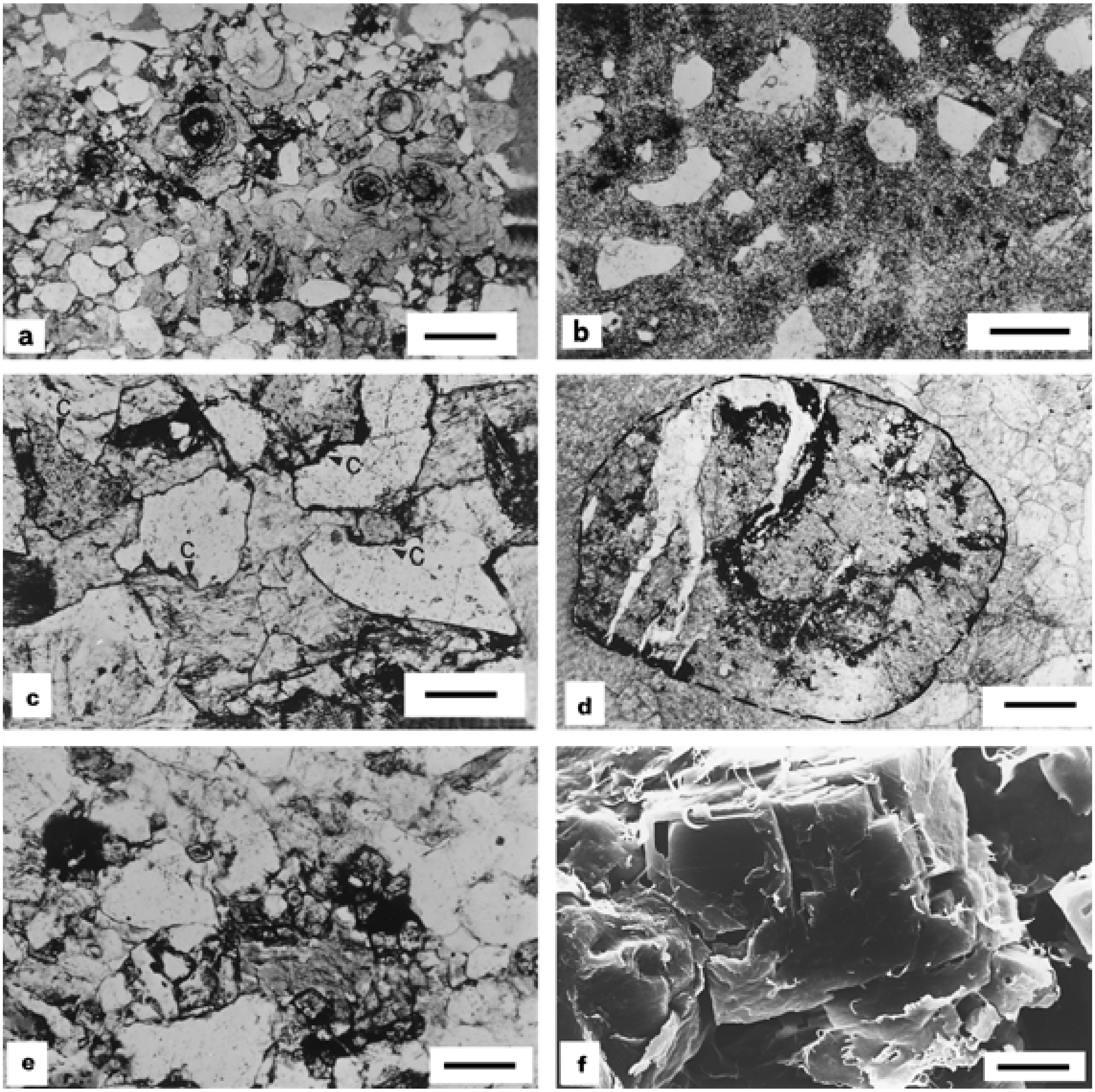


Fig. 7 Carbonate cements in sandstones. All optical micrographs in plane polars. (a) Displacive pedogenic calcite with root structures, optical micrograph (scale 900 μm). (b) Highly grain replacive microspar calcite from a mature calcrete, optical micrograph (scale 500 μm). (c) Pore-filling calcite spar cement that is peripherally replacive to quartz grains (arrowed, c) (scale 300 μm). (d) Detail of detrital rock fragment grain that has been extensively replaced by calcite spar, optical micrograph (scale 500 μm). (e) Rhombic dolomite cement, optical micrograph (scale 200 μm). (f) Comparable SEM view of rhombic dolomite (scale 60 μm).

which it is generally inferred to have replaced former biogenic Opal A (Williams *et al.*, 1980). Quartz cement tends to occur during burial diagenesis at temperatures above 70°C (Bjørlykke and Egeberg, 1993) although silcrete formation can also result in quartz overgrowths (Thiry *et al.*, 1988).

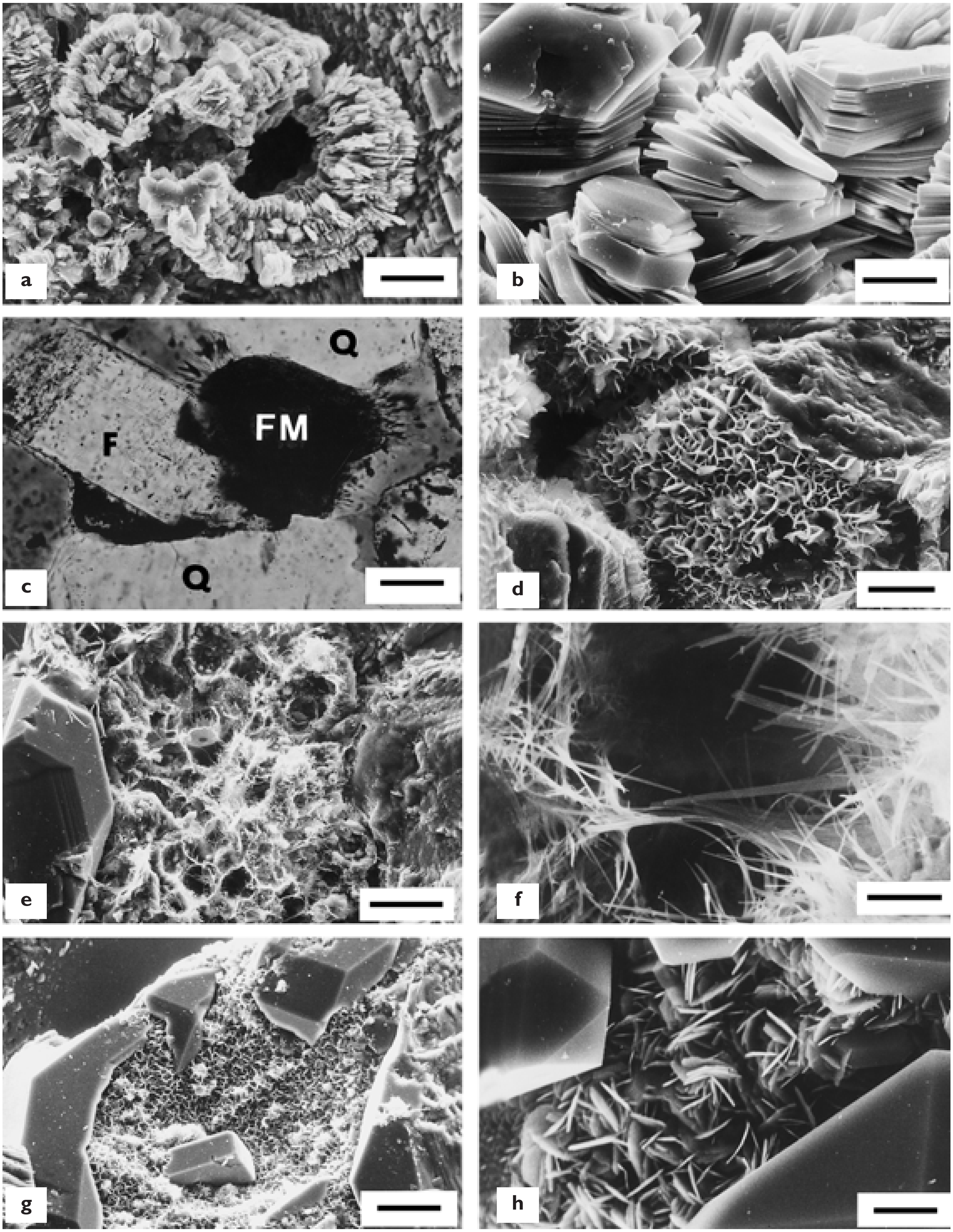
Carbonate cements (Figs 5 & 7) include calcite ($CaCO_3$), dolomite ($MgCa(CO_3)_2$) and siderite ($FeCO_3$). Calcite and dolomite cements occur as both ferroan and non-ferroan compositions. This is clearly revealed by the sensitivity of the mineral to Fe-detecting stains (Dickson, 1965). All three main carbonate mineral cements found in clastic rocks can develop during eogenesis as well as mesogenesis. Eogenetic cementation results in pore-filling cement fabrics composed of fine microspar crystals in quantities ≤ 40%.

Pedogenesis in arid continental environments leads to non-ferroan calcrete and dolocrete with an abundance of biogenic calcite and dolomite cement fabrics (Purvis & Wright, 1991; Spötl & Wright, 1992). The presence of calcrete intraclasts results in carbonate recementation at the bases of fluvial channels in red bed and other arid or semi-arid successions (Burley, 1984). Shallow marine sandstones are often cemented with nodules or discrete layers of eogenetic calcite (Wilkinson, 1991) owing to the dissolution and reprecipitation of shell detritus (Hendry *et al.*, 1996) as non-ferroan calcite. Marine sandstones develop a wide range of carbonate cements through reaction between detrital aluminosilicate minerals and the products of the breakdown of organic matter (Hein *et al.*, 1979). Eogenetic siderite develops in iron-rich, partially reduced systems with a minimal marine influence (Baker *et al.*, 1996; compare with Pye *et al.*, 1990). Complete reduction in natural systems with a significant marine influence leads to sulphide (initially greigite, ageing to pyrite) growth owing to the reduction of sulphate as well as ferric iron (Love, 1967). Such early cements commonly form at sequence boundaries and flooding surfaces in response to increased residence time at periods of low sedimentation rate (Taylor *et al.*, 2000).

Burial diagenesis is characterized by the recrystallization of pre-existing carbonate minerals (calcite and dolomite) in a ferroan form and results in cement typically at the 2–10% level. Burial diagenesis also results in a coarser grained fabric of locally pore-filling rhombohedral crystals of ferroan dolomite (and less often ferroan calcite). Many crystals exhibit zoning, with an increasing Fe content evident during diagenesis. Late diagenetic carbonate crystals (usually ferroan dolomite) can also develop in the apparent absence of pre-existing carbonate minerals. These probably result from an influx of source-rock-derived CO_2 and alkaline earth elements (and iron) from reactive-sand grain decomposition processes and from neighbouring mudstones or evaporites. Eogenetic and burial diagenetic carbonate cements frequently have an exaggerated effect upon the flow properties of sandstone because they locally fill pores or preferentially block pore throats.

Clay mineral cements (Figs 8 & 9) are volumetrically small but important components of sandstones because of the enormous effect they have on permeability. Clay minerals are thus a vital consideration in studies involving the movement of fluids through pore spaces. The most common clay minerals are kaolinite ($Al_2Si_2O_5(OH)_4$), illite ($KAl_3Si_3O_{10}(OH)_2$) and chlorite ($[Fe–Mg]_5Al_2Si_3O_{10}(OH)_8$). The smectite (typical dioctohedral clay; montmorillonite, typical trioctahedral clay; saponite) family of clays also occur as cements but these are generally less well documented than the others. All types of clay can occur as detrital components although hydrodynamic sorting tends to prevent co-deposition of sand grains and clays. Bioturbation, mass flow and soft-sediment deformation are the most likely mechanisms for introducing detrital clays into the fabric of marine sandstones, whereas mechanical infiltration is the dominant mechanism in continental sandstones (Walker *et al.*, 1979). Detrital

Fig. 8 (*opposite*) Clay cements in sandstones. (a) Eogenetic vermiform kaolinite, SEM (scale 40 μm). (b) Blocky, euhedral dickite, the high-temperature polymorph of kaolinite, SEM (scale 5 μm). (c) Grain-coating smectite preferentially nucleated on a detrital ferromagnesian (FM) grain, but absent on quartz (Q) and feldspar (F) grains, optical micrograph (scale 80 μm). (d) Comparable SEM view of grain-coating radial smectite, SEM (scale 20 μm). (e) Post-quartz overgrowth pore bridging ‘hairy’ illite, SEM (scale 80 μm). (f) Detail of authigenic illite showing the lath-shaped nature of the illite crystals, SEM (scale 4 μm). (g) Pre-quartz overgrowth grain-coating chlorite cement, SEM (scale 60 μm). (h) Detail of authigenic chlorite enclosed by but partially inhibiting quartz overgrowths, SEM (scale 4 μm).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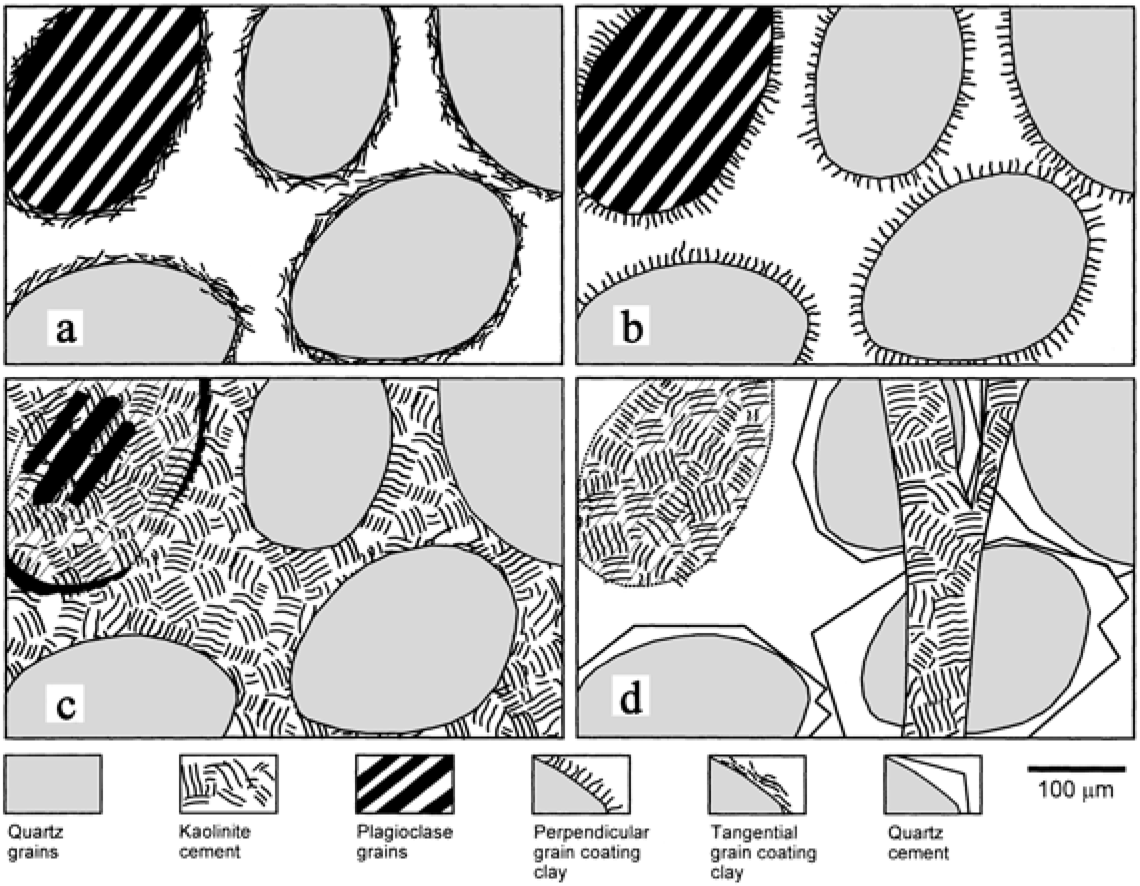

Fig. 9 Schematic cartoon illustrating types of clay morphologies in sandstones. (a) Grain coating, tangential clays typified by detrital and mechanically infiltrated clays, (b) grain coating, perpendicular clays typified by smectite, illite and chlorite, (c) pore-filling and feldspar-replacive clays typified by kaolinite, (d) grain replacive and fracture filling cements (typically kaolinite).

clay, of whatever mineral chemistry, occurs as tiny, ragged, abraded crystals and naturally accumulates in pore spaces forming tangential grain-coating and pore-bridging fabrics. Formerly, it was widely held that clay mineral neoformation took place when detrital clays, derived from continental weathering, entered the marine environment (see Millot, 1970). However, it is now documented that detrital clays do not undergo significant chemical or structural alteration during transport or deposition. Flocculation leads to a sedimentary fractionation of clays in passing from the fluvial into an estuarine or open marine environment (Jeans, 1989). Only cation exchange reactions with the surface of clays take place during transport and deposition. In the late 1960s one of the great debates of the time centred on whether the clay matrix characteristic of argillaceous Palaeozoic sandstones (so-called greywackes) was detrital or diagenetic in origin. This debate was resolved as diagenetic by Whetten & Hawkins (1970) in one of the first detailed petrographic and mineralogical studies of diagenesis.

Smectites, kaolinite, and chlorite all occur as eogenetic cements dependent on the composition of the detrital sediment supply, rate of *in situ* weathering of detrital minerals versus subsequent sediment supply, climate and the composition of eogenetic pore waters. Smectites and related minerals (such as palygorskite) form in Na–K-rich, alkaline brines under oxidizing conditions (Jeans, 1978). By contrast, kaolinite and the kaolin family of aluminosilicates require low pH, low ionic strength waters and so are typical of weathering profiles and early diagenesis in fluvial and deltaic environments. Chlorite often occurs in reduced, marine waters whereas glauconite cement develops in Fe-rich, oxidized shallow marine environments (Odin & Matter, 1981). The habit of eogenetic clays varies with their mineralogy and chemistry (Wilson & Pittman, 1979) but has not been investigated systematically. Smectites tend to occur as very small crystals that line intergranular pores and replace grains that contain Mg and Fe required for their development, resulting in the so-called 'grain localization' effect of Burley (1984). Kaolinite usually occurs as pore-filling aggregates (termed 'books') of euhedral hexagonal crystals.

Kaolinite, illite and chlorite all occur as burial diagenetic cements. Kaolinite forms vermiform masses that occupy, and locally fill, pores. It can also occur as a pseudomorphic replacement of altered detrital feldspar minerals. Much of what is described as kaolinite in mesogenetic clay assemblages is most probably the polymorph dickite, which forms as a replacement of kaolinite as temperature increases (Ehrenberg *et al.*, 1993; McAulay *et al.*, 1994). Illite is an exclusively burial authigenic clay that forms at temperatures exceeding approximately 70°C in potassium-bearing formation waters and has been shown to be of phengitic composition (Warren & Curtis, 1989). It typically grows as fine, ribbon-like filaments on the surface of detrital grains and on the surface of earlier burial cements and replaces kaolinite at depth (Hancock & Taylor, 1978). Chlorite cement typically grows as radial detrital grain coatings composed of euhedral, interlocking plates that typically shield detrital grains from subsequent diagenetic processes.

Feldspar mineral cements are common although typically much less abundant than quartz, carbonates and clays. Early diagenetic K-feldspar (Morad *et al.*, 1989; Fig. 10) and burial diagenetic albite (Waugh, 1978; Ramseyer *et al.*, 1992) routinely are found in sandstone. Both minerals can form as overgrowths on detrital grains or as pore-filling cements. The diagenetic minerals typically have subtly different mineral chemistry and crystallography from the substrate grains often leading to an absence of optical continuity (i.e. non-uniform optical extinction positions). These differences also lead to differential diagenetic reactivity. Diagenetic feldspar minerals are more thermodynamically stable in the diagenetic environment than detrital feldspars. A consequence of this is that in some cases detrital feldspars are dissolved away leaving a rind of the earlier diagenetic feldspar overgrowth. Such reactions are temperature dependant and so depth-defined decrease in detrital feldspar abundance is common in many sedimentary basins (e.g. Harris, 1989). Albitization occurs when detrital K-feldspar or calcic plagioclase are replaced by albite (Ramseyer *et al.*, 1992). The first of these can occur during increasing salinity of formation water (usually dominated by Na in terms of the aqueous cation population). The second can occur at any stage during diagenesis because the anorthite feldspar end-member is unstable at all conditions found in sedimentary basins. The second stage releases Al and thus leads to clay mineral growth as well as feldspar replacement.

Pyrite cement (FeS_2) occurs as both eogenetic and burial diagenetic cements and is common although often at the $\leq 1\%$ bulk sandstone volume level. The eogenetic form is typically microcrystalline framboids (like submicrometre sized raspberries) and results from the microbial reduction of detrital ferric iron and typically the presence of seawater sulphate during earliest burial (Love, 1967). The burial diagenetic form of pyrite is somewhat coarser than the framboids and is usually at least subhedral. It is often found to be one of the last cements to form and is especially associated with the reduction of haematite in the presence of hydrocarbons (Elmore *et al.* 1987).

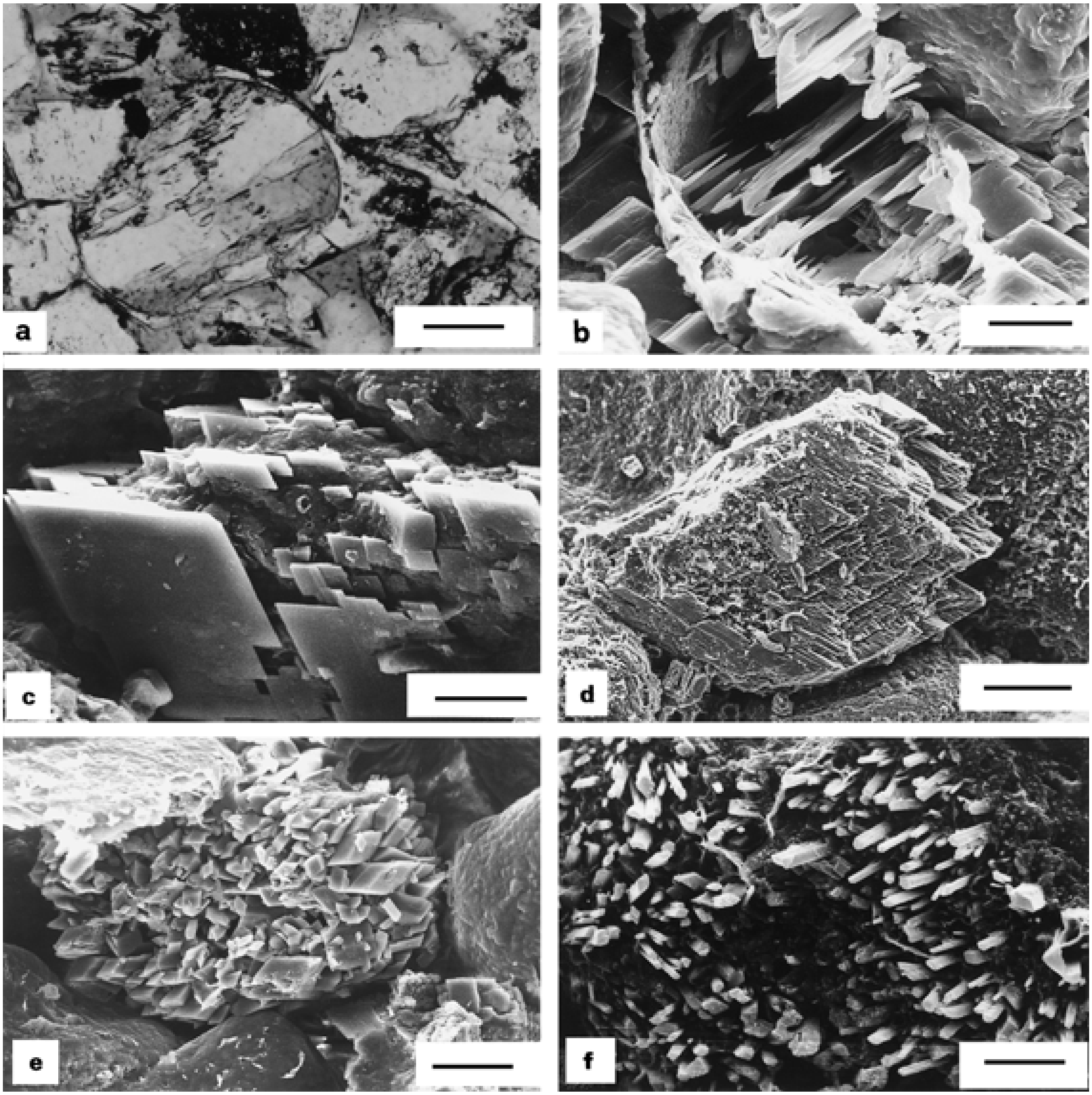

Fig. 10 Feldspar cement in sandstones. (a) Partially dissolved detrital feldspar grain with overgrowth, optical micrograph, plane polars (scale 60 μm). (b) Comparable view with the SEM showing dissolved grain interior and euhedral overgrowths (scale 40 μm). (c) Early stage of K-feldspar overgrowth development, SEM (scale 60 μm). (d) Complete, euhedral K-feldspar overgrowth, SEM (scale 120 μm). (e) Cluster of euhdral pore filling authigenic K-feldspar crystals, SEM (scale 60 μm). (f) Epitaxial K-feldspar overgrowth on detrital grain, SEM (scale 40 μm).

Anhydrite cement ($CaSO_4$) and other sulphates (e.g. barite $BaSO_4$) also occur as burial cements in typically minor but locally important quantities (Sullivan *et al.*, 1990; Baines *et al.*, 1991). They result from circulation of evaporite-related pore waters and occur as subhedral laths and poikilotopic crystals in similar amounts as the burial carbonate cements.

EOGENESIS (DEPOSITIONAL-ENVIRONMENT RELATED DIAGENESIS)

Diagenetic processes that fall into the eogenetic realm (dominated by interstitial waters that are connected to the surface of the sediment pile) are controlled by the overall physical, biological and geochemical characteristics of the depositional system. The gross depositional environment of the sand controls most eogenetic processes and imparts a distinctive diagenetic 'fingerprint', or assemblage, on the sandstone. Complex diagenetic assemblages and paragenetic sequences can result if the depositional environment changes as a result of relative sea-level fluctuations prior to burial and isolation of the sand unit (Curtis & Coleman, 1986).

On deposition, the primary sand comprises a mixture of minerals formed under a wide range of conditions of temperature, pressure, oxidation state, water composition and pH. Much depositional sand contains unstable grains that have not had the opportunity to react during initial weathering, erosion and transport before deposition. Therefore, a detrital mineral assemblage is typically inherently unstable and during eogenesis will tend to react with the ambient water and atmosphere. In many cases (especially in non-marine environments), these processes are simply a continuation of processes initiated during weathering.

The inherent instability of detrital sand during eogenesis results in the subsequent sandstones being 'fingerprinted' by the nature of the interstitial waters. These waters, directly influenced by the environment of deposition, leave their mark on the sandstone if any of the eogenetic minerals are preserved into the mesogenetic or telogenetic regimes. Although there are few index minerals that uniquely define a particular environment of deposition, this is often evidenced by the assemblage and specific chemistry of mineral suites. There are three broad subdivisions that frequently result in distinct eogenetic assemblages.

1 Subaerial, arid, hot (tropical to subtropical) environments where sediment hinterlands often undergo little chemical weathering because of the reduced rainfall. The resulting interstitial waters are alkaline and concentrated and dominated by Ca^{2+}, Mg^{2+} and HCO_3^- species.

2 Subaerial, humid, warm (subtropical to temperate) verdant environments where sediment hinterlands are subject to intense weathering in the presence of very dilute (less than a few 100 ppm) interstitial waters. These pore waters are dominated by aqueous Na^+ and HCO_3^- and are slightly to moderately acidic owing to the presence of decaying organic material.

3 Marine environments characterized by slightly alkaline waters (pH of seawater 8.3) and dominated by aqueous Na^+ and Cl^- (with subordinate SO_4^{2-}, HCO_3^-, Ca^{2+} and Mg^{2+}) with a salinity of 35‰.

Hot, dry, continental environments (Fig. 11) are highly oxidizing and have a paucity of reducing organic matter and low water tables. All iron remains in the ferric state and coats minerals in a hydroxide or sesquioxide form leading to a characteristic red coloration of continental sediments (and hence the term: red beds). These oxides age with time and increasing temperature to the mineral haematite (Walker *et al.*, 1979). Carbonate minerals that precipitate in these environments are thus iron-free. Evaporation often exceeds meteoric influx, leading to an upward flux of groundwater, evaporation and the consequent development of caliche (mostly calcrete, dolocrete or gypcrete). Diagenetic alunite ($KAl_3(SO_4)_2(OH)_6$) also develops under these conditions (Khalaf, 1990). The minimal weathering in the hinterland and minimal flux of water in the eogenetic zone leads to the common accumulation or growth of various smectite clays (e.g. montmorillonite, saponite, palygorskite), because these typically represent the results of the earliest stages of aluminosilicate mineral weathering and reaction in pore waters with high Ca and Mg activity. Eogenetic silica cement is not uncommon in arid environments and can occur in silcrete nodules on bedding surfaces on the distal parts of braid plains (Leckie & Cheel, 1990).

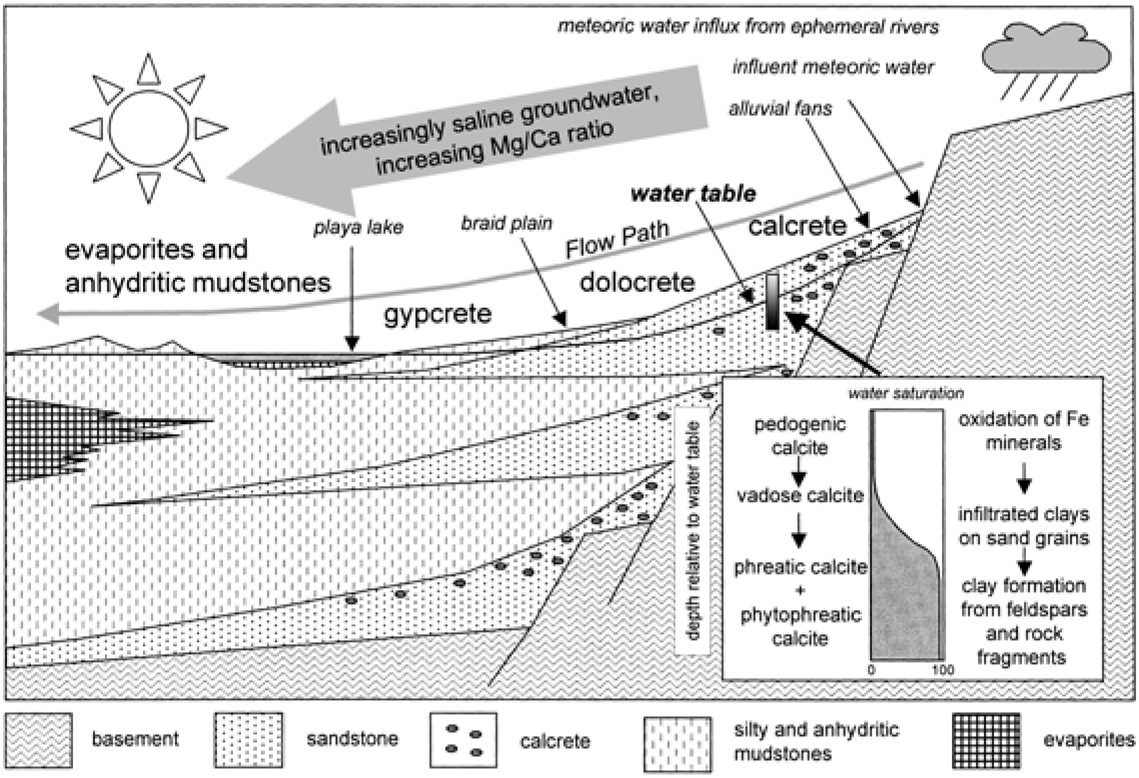

Fig. 11 Schematic diagram summarizing reactions in the fluvial–alluvial, hot and dry eogenetic regime. Calcretes develop closest to the rift shoulder, dolocretes form some distance down the flow path and gypcrete only forms in the vicinity of playa lakes. Waters have increasing Mg/Ca ratios down the flow path as calcite growth leaves Mg in the water. The groundwaters become increasingly saline owing to evaporation and weathering/alteration of detrital grains. Pedogenic calcretes form near to the surface although groundwater calcretes (phreatic) form deeper in the section. Plant activity can raise local HCO_3^- levels and cause localized phytophreatic calcrete formation. Dolocretes can also form in soils and in groundwaters.

Warm, wet, typically verdant, subaerial eogenetic environments (Fig. 12) have an abundance of reducing organic matter that undergoes bacterially mediated decay (Curtis *et al.*, 1986). Any ferric iron in the solid sediment is soon reduced to the Fe^{2+} form by the redox processes and is often available for incorporation in siderite. Siderite-dominated eogenetic carbonates occur owing to local enrichment of iron in the system, resulting from the alteration of Fe-rich detrital clays (Baker *et al.*, 1996; Browne & Kingston, 1993). However, the relative absence of SO_4^{2-} and Mg^{2+} leads to a different suite of minerals than found in the marine eogenetic realm. Sulphide minerals are relatively scarce; carbonate minerals include the nearly universal eogenetic mineral calcite but also ferroan dolomites and siderite, including the iron-rich dolomite pistomesite. In the relative absence of sulphur (in the form of sulphide), any iron is free to associate with carbonate or aluminosilicate clay minerals. The clays in this environment are typified by kaolinite as this mineral represents the last (i.e. advanced) stage of silicate weathering prior to the development of oxides and hydroxides (e.g. bauxite and goethite, as in laterites). Andrews & Turner (1991) documented a case of dolomite cement forming during non-marine eogenesis, assigning the abundance of Mg to sporadic temporary inundations by seawater,

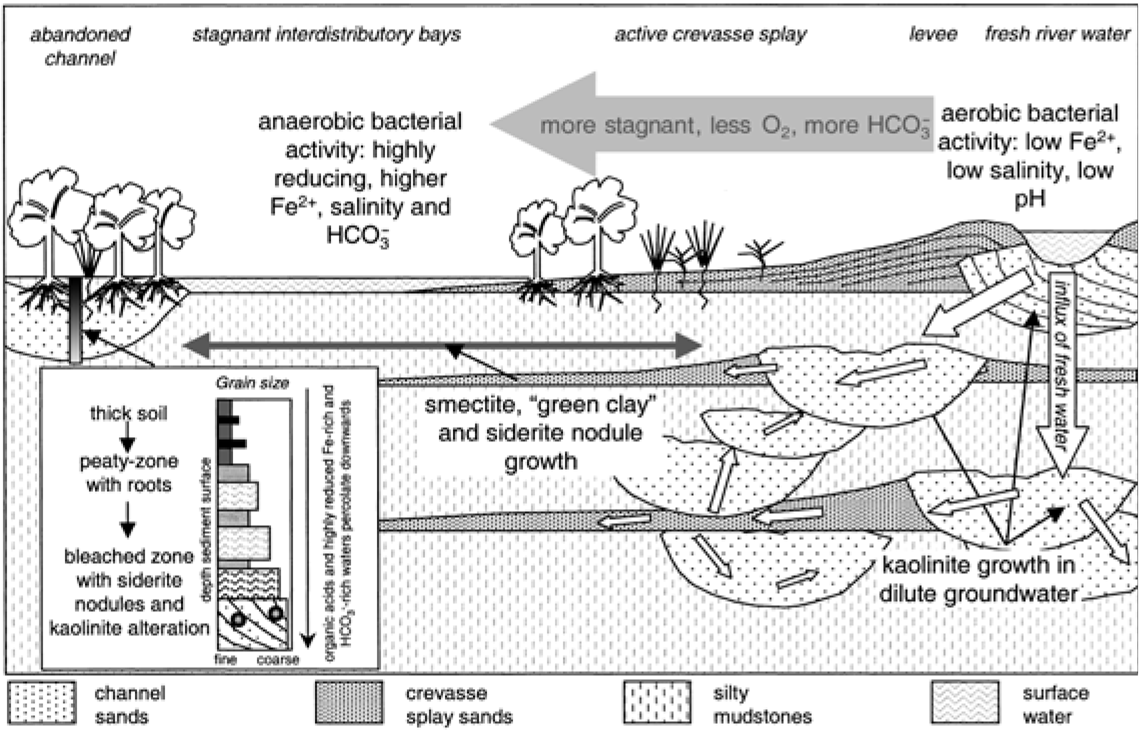

Fig. 12 Schematic diagram summarizing reactions in the fluvial, humid eogenetic regime. Influent, fresh, oxidized water from the river will lead to low salinity, low pH and low Fe-waters in the underlying sands and thus kaolinite growth with minimal carbonate mineral formation. Flow from rivers (magnitude represented by size of arrow) decreases away from the main river axis, with flow rates depending on connectivity of sandbodies. Distal to the main channel axis, groundwaters become stagnant, and in the presence of decaying organic matter, promote the activity of anaerobic bacteria, leading to elevated aqueous Fe, HCO_3^- and higher pH values. Stagnant waters result in higher aqueous potassium and silica concentrations and thus result in smectite growth (instead of kaolinite growth as under the main channel) or the growth of various 'green clays' (Fe-rich smectites). Vegetated abandoned channels are filled with organic-rich silt and detrital clay that promote anaerobic conditions. The abundance of humic acids from resulting peat development lead to bleaching of sands (so-called 'seat-earths', effectively advanced 'weathering') and kaolinite growth and the development of siderite nodules deeper in the section.

weathering of a local source of Mg in the hinterland, or even contemporary volcanism.

Bacterially catalysed processes characterize marine eogenesis (Fig. 13). The interaction of reducing organic matter and oxidizing inorganic solutes (e.g. SO_4^{2-}) and minerals (e.g. Fe^{3+} minerals) causes rapid eogenetic alteration of shallow buried sediments (Irwin *et al.*, 1977; Hesse, 1986). The bacteria and a potent mix of oxidizing and reducing material leads to an authigenic suite of minerals, including pyrite (and other sulphides), various carbonate cements and a range of typically green sheet-silicates ('glaucony') including glauconite, illite and smectite. The unusual glauconite–phosphate assemblage is typical of suboxic zones and may be related to sulphide oxidation (Coleman, 1985). Colonization of shallow-marine sandstones by shelly invertebrates (especially during breaks in sedimentation) can lead to an abundant supply of the components needed for carbonate authigenesis. The development of calcite nodules and sheets is often characteristic of (especially shallow) marine eogenesis. Eogenetic dolomite cements can develop (see the carbonate literature, e.g. Tucker & Bathurst,

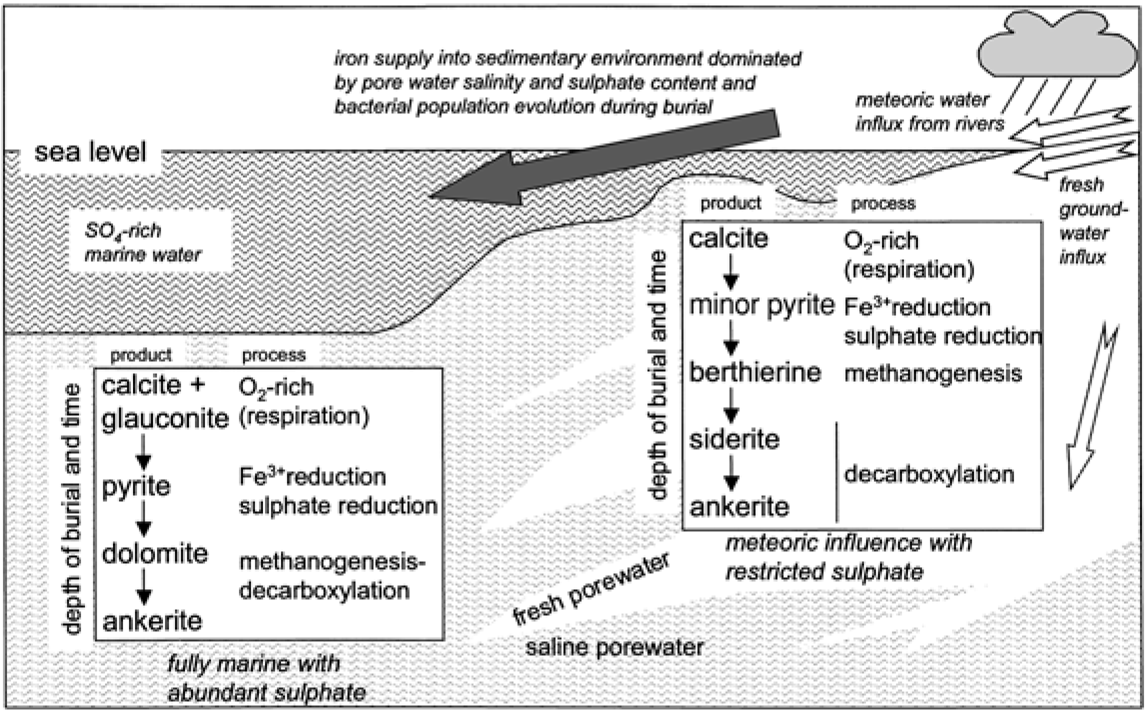

Fig. 13 Schematic diagram summarizing reactions in the marine eogenetic regime. Seawater-saturated sediments undergo a series of bacterially mediated processes: respiration, Fe and then sulphate reduction, methanogenesis and decarboxylation. These lead to a series of depth-related eogenetic facies: calcite +/– glauconite, pyrite and dolomite (+/–ankerite). Deltaic, fresh or brackish water eogenetic facies are different mainly because there is much less sulphate available (leading to less sulphide and thus less pyrite). The Fe that remains, owing to the lack of pyrite growth, instead forms 'green clays' such as berthierine because methanogenesis destroys CO_2 and prevents Fe-carbonate mineral growth. Decarboxylation reactions take over from methanogenesis with further burial, and result in siderite growth.

1990) although they are less abundant than calcite.

COMPACTION

This is the process of volume reduction and consequential pore-water expulsion within sediments. Normally this takes place in response to vertical shear–compressional stresses owing to increasing weight of overburden, but the same processes operate under tectonic compressional forces. Compaction can be expressed as a percentage of the original porosity of the sediment or by specific compressibility values based on strength or rigidity. All of these parameters are influenced by the lithology of the sandstone (Pittman & Larese, 1991) and relative porosity values commonly used by sedimentologists are a useful way of expressing compaction during burial (Fig. 14).

Moderately sorted, coarse-grained clastic sediments have depositional porosity values of about 40% (Beard & Weyl, 1973), which corresponds to a random packing fabric of uniform spheres. In fact initial porosity values are strongly dependent on grain packing arrangements and so are much more affected by sorting than grain size. Compaction takes place as the sediment package is gradually buried by younger sediment and the overburden load increases. The overburden load operates as an effective stress, defined as the difference between the lithostatic pressure and fluid pres-