



# Palaeoenvironmental significance of palustrine carbonates and calcretes in the geological record

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## Abstract

Interest in palustrine carbonates and calcretes has increased over the last 20 years since they contain significant environmental information. Much of the work performed in this area has focused on either of two types of terrestrial carbonate—palustrine carbonates or calcretes (pedogenic and groundwater)—yet their simultaneous study shows there may be a gradual transition from one form to the other, revealing the interplay between pedogenic, sedimentary, and diagenetic processes. Three main factors control the formation of these carbonates: the position of the water table, the host rock, and the period of sub-aerial exposure. In pedogenic calcretes, precipitation of carbonate takes place mostly in the vadose zone above the water table, and within a previous host rock or sediment. In groundwater calcretes, the precipitation of carbonate also occurs within a previous host rock and around the groundwater table. In palustrine carbonates, however, the precipitation of lime mud occurs in a lacustrine water body. Palustrine carbonates necessarily form on previous lacustrine mud, whereas both types of calcretes may form on any type of sediment or soil. The sub-aerial exposure time needed to form palustrine carbonates may be relatively short (even a season), whereas pedogenic calcretes need more time (several years to millions of years). Groundwater calcretes do not form on the topographic surfaces, so there is no need of sub-aerial exposure. However, stable surfaces favour the development of thick groundwater calcretes. Small fluctuations in the water table cause gradual transitions of these three types of terrestrial carbonates and the subsequent mixture of their characteristic features, causing difficulties in the interpretation of these carbonates.

The formation of these carbonates is controlled by palaeoenvironmental factors. Both commonly form in semi-arid climates. Arid climates are also suitable for calcretes, but sub-humid conditions are more suitable for palustrine carbonates. More indications of climatic conditions may be obtained through the analysis of the  $\delta^{18}\text{O}$  content of both calcretes and palustrine carbonates, and from the depth of the horizon containing carbonate nodules in pedogenic calcretes. Vegetation is also important in the formation of these types of carbonates. Data on the prevailing vegetation can be obtained from the analysis of the micro and macrofabric as well as from the  $\delta^{13}\text{C}$  signal of the primary carbonates, which, in pedogenic carbonates, has also been used to estimate atmospheric  $p\text{CO}_2$  during the Phanerozoic. These terrestrial carbonates are widely distributed on floodplains and distal areas of alluvial basins. Their presence and characteristics can be used as indicators of aggradation, subsidence or accommodation rates, and therefore as indicators of different tectonic regimes.

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Even though the study of these carbonates has notably increased in recent years, much less is known about them than about marine carbonates. Presently, there is much emphasis on obtaining a general model for sequence stratigraphy in terrestrial basins, with a need to include the carbonates analysed in this paper.

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## 1. Introduction

Carbonates in terrestrial settings form under a variety of conditions from permanent water bodies such as deep lakes, to permanent sub-aerial conditions (e.g., calcretes and karst), passing by a wide range of environments including shallow lakes and palustrine environments. A continuous transition between permanent lacustrine water bodies to totally sub-aerially exposed environments can be described. Therefore, the boundaries between some environments—or even processes—are not very clear. For example, palustrine carbonates and calcretes are affected by sub-aerial exposure, and therefore not only reflect the sedimentary but also the pedogenic and/or diagenetic environment. Moreover, in the last few years, studies on “groundwater calcretes” have introduced more complications as diagenetic processes unrelated to soil formation also have to be taken into account. Palustrine limestones and calcretes show strong similarities in both microfabrics and the processes involved in their formation. This is the origin of the problem in differentiating between palustrine limestones and calcretes. There is a continuum from the dominance of soil-forming processes in pedogenic calcretes to the interplay between sedimentary and pedogenic processes in palustrine limestones. In addition, the role of shallow groundwater as a controller of surface diagenetic processes must be considered because it is the responsible for the formation of groundwater calcretes.

This work tries to describe and compare carbonates formed in some terrestrial environments, which in some periods have suffered sub-aerial processes. It focuses mainly on palustrine carbonates and calcretes; the karstic carbonates have been excluded since their characteristics differ notably from those of palustrine and soil carbonates. For the same reasons, other terrestrial carbonates such as tufas, travertines and fluvial carbonates are also excluded from this review.

The correct interpretation of these carbonates and their features are important if the environmental conditions in which they formed are to be understood. Their study provides important data that help to interpret the sedimentary record of many terrestrial environments as well as to determine the main controls that took part in their formation. These can be as varied as biogenic influences (type of organisms), climate, the composition of rainwaters, the movements and characteristics of groundwaters, the sedimentary regime, the length of sub-aerial exposure, tectonism, the source area, and many other factors. The simultaneous analysis of both calcretes and palustrine carbonates is the best way to present a general overview of the pedogenic, diagenetic, and sedimentary processes that interplay in their formation.

## 2. Palustrine carbonates

The importance—and difficulty—of the study of these carbonates was clearly envisaged by Freytet (1965, 1971). In these relatively early papers, the idea that palustrine carbonates are palaeosols that formed on lacustrine carbonate substrates was put forward, and their study had therefore to be undertaken from a pedological point of view. These conclusions were clearly presented by Freytet and Plaziat (1982), in what may be considered a classic not only of the study of shallow lake sediments but also of carbonate soils. According to Freytet (1984), a palustrine limestone “must show the characteristics of the primary lacustrine deposit (organisms, sedimentary features) and characteristics due to later transformations (organisms, root traces, desiccation, pedogenic remobilizations)”.

Palustrine carbonates typically occur in lakes with low gradient and low energy margins (Platt and Wright, 1991), and in short-lived ponds isolated

between siliciclastic sediments (Nickel, 1985; Sanz et al., 1995) or even in peritidal settings. In all cases, relatively flat surfaces and low water energy are required (Fig. 1A and B). Under these conditions, the carbonate mud with charophytes, molluscs, and ostracods, etc., is easily sub-aerially exposed after a small fall in the level of the lake (Fig. 1C) or pond. Pedogenic processes therefore modify the lacustrine mud (Fig. 1D) giving place to a variety of palustrine facies and microfabrics, recently reviewed by Freytet and Verrecchia (2002). Recent analogues for these sedimentary environments ought to be widely recognisable, but human behaviour has probably contributed to the loss of many such places. The Florida Everglades have been considered a current analogue of a palustrine freshwater environment (Plat and Wright, 1992). However, around margins they are partially under marine influence, so the geochemistry of their waters and the precipitates formed there may be different from those of fully freshwater palustrine environments. Examples of the latter are some small lakes in the south of Hungary and the margins of Balaton Lake, also in Hungary. Some of these types of environments have been considered seasonal wetlands (Wright and Platt, 1995), although this term is difficult to use in the sedimentary record. In Spain, the so-called “Las Tablas de Daimiel” (Fig. 1 A and B), now a protected National Park, is a wetland area within the relatively dry interior of the Iberian Peninsula. Ecological interest in the area lies in the fact that it serves many types of migratory birds that cross the Iberian Peninsula every year on their journeys between Africa and Europe. Presently, Las Tablas are the subject of much multidisciplinary work (Álvarez-Cobelas and Cirujano, 1996; De Bustamante et al., 1996). Las Tablas are situated in La Mancha plain in Ciudad Real, where mean temperatures ranges between 12 and 14 °C and rainfall between 400 and 500 mm/year. The potential evaporation is 778 mm/year. The wetland area that may be inundated is about 20 km<sup>2</sup> and is fed by surface and groundwaters. The water body is shallow, usually less than 1 m in depth. The water is fresh with carbonate and sulphate as the main ions (Álvarez-Cobelas and Cirujano, 1996; Dorado-Valiño et al., 1999). Some cores have been taken and are being studied. Although a detailed analysis of these cores and their sedimentology is beyond the scope of this review, the author has had access to some samples

in order to describe the appearance of original freshwater lacustrine–palustrine mud.

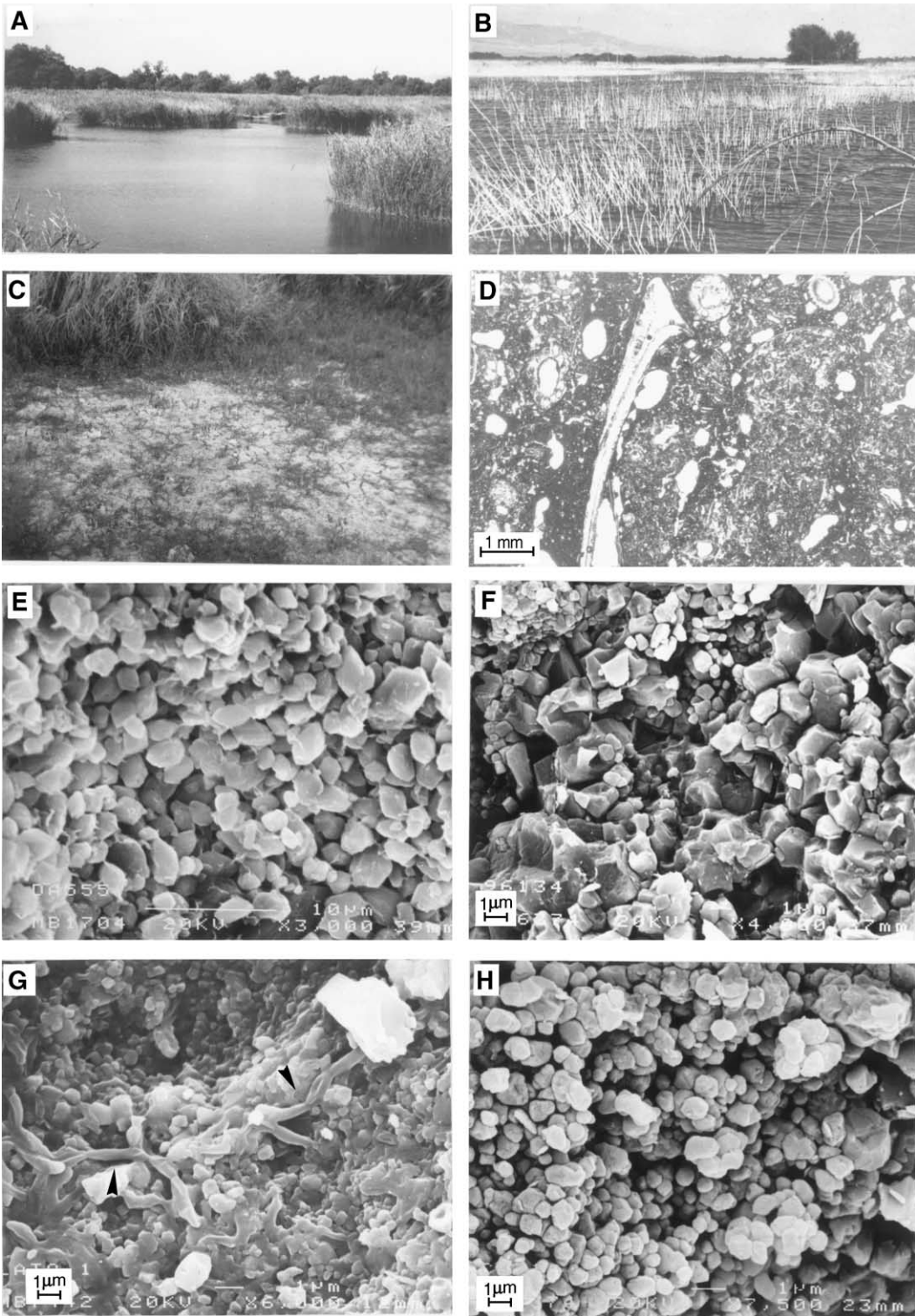
### 2.1. Primary lime mud

Recent sediments deposited in Las Tablas de Daimiel include: organic-rich clays with small oncoids (up to 8 mm long), and white micrite mud with oncoids and fragments of molluscs, ostracods, and calcified charophytes. The micrite mud is composed of relatively euhedral calcite (LMC) crystals 0.3–1.3 μm across (Fig. 1E). These micrite muds are similar to some of the lithified lacustrine micrites of ancient palustrine deposits, where crystal size distribution is also varied; in some samples very homogeneous while in others there is variety (Fig. 1F). Some organic filaments are partially calcified by micrite crystals precipitated on the filament surfaces (Fig. 1G), but in most cases organic influence is difficult to see (Fig. 1H).

Micrite muds similar to those of Las Tablas de Daimiel may be considered examples of primary freshwater lake deposits. As such, they are affected by pedogenic modifications when the level of the lake drops. Pedogenic modifications are due to desiccation processes, root and soil organism activity, and remobilisation of carbonate and iron within the soil and sediments. These processes result in the formation of characteristic palustrine facies or palaeosols, following the criteria of Freytet and Plaziat (1982).

### 2.2. Palustrine facies and features

(1) Nodular and brecciated limestones can occur as single beds or at the top or base of any lacustrine deposit. They consist of centimetre-scale irregular micrite nodules embedded in a softer chalky matrix, or separated by different types of cracks that may remain empty (Fig. 2A) or be filled with microspar and/or sparry calcite. The morphology of the nodules varies from more or less round to angular, forming a breccia. The micrite may contain detrital grains and the debris of charophytes, ostracods, or molluscs. Nodular limestones may be light in colour but mottling (pseudo-gleying) is also common. The nodulisation process has been clearly explained by Freytet (1973), and is mainly due to desiccation and the subsequent formation of planar to curved fissures.



(2) Mottled limestones are micrites with minor amounts of detrital grains. They show a strong yellow–orange–red mottling, which, under the microscope, is seen as very diffuse, darker haloes. Charophytes, gastropods, ostracods, or any other fossil remains are relatively rare in this facies. The mottled areas may be also outlined by desiccation cracks, which show different morphologies such as circumgranular, planar or irregular (Fig. 2B). The cracks are filled by both microsparitic silt and blocky sparry calcite. Several stages of cementation are not uncommon. Root moulds, fenestral and alveolar structures indicating the influence of the vegetation cover are common in these mottled limestones.

Mottled limestones indicate the remobilisation of iron due to changes in the Eh of groundwater when the water table oscillates (Freytet, 1973). Apart from mottling, a number of features can be recognised in palustrine limestones due to the remobilisation of iron. These include the presence of ferruginous nodules, tubular voids, concretions, and iron crusts. Freytet (1973) and Freytet and Plaziat (1982) provided clear descriptions and interpretations of all these features. The mottling is similar to that recognised in poorly drained (gley) palaeosols, as described by PiPujol and Buurman (1997) in the Eocene of the Ebro Basin.

(3) Limestones with vertical root cavities. These are micrites and biomicrites (mudstones to wackestones) with gastropod shells, charophytes, ostracods, desiccation cracks, and fenestral and alveolar structures. Root cavities are large, irregular, vertical cavities several centimetres wide and with lengths up to the decimetre scale (Fig. 2C). They are commonly wider at the top of the beds and taper downwards. These cavities may be empty or partially filled with a looser micrite matrix, microspar peloids, intraclasts, bioclasts and spar cement. Limestones with vertical root cavities occur either as tabular beds or display a wavy, convex-up upper surface, as described by Calvo et al. (1985) in the Madrid Basin. Another character-

istic of these facies is that they are commonly more indurated than any other palustrine or lacustrine deposits, and are therefore very prominent at outcrop scale. A special and very common case of limestone with vertical root cavities is that with columnar structure. These columns, about 10 cm in diameter, are elongated vertically and show some horizontal cracks. The columns may reach 1 m in height. They are thought to form by calcification around vertically penetrating roots. Similar to the prismatic structures recognised in calcretes (Esteban and Klappa, 1983), these columns may be found either in clayey or softer carbonate sediments.

(4) Pseudo-microkarst. Plaziat and Freytet (1978) introduced this term to describe limestones with vertical cavities that resemble a karstic system, in which the cavities are smaller, mostly cylindrical, and vertically elongated. These cavities are only a few centimetres long, but are associated with larger ones on the decimetre scale. The prefix ‘pseudo’ is used because the enlargement of the cavities is mostly mechanical (root activity and desiccation). Dissolution is only a minor process. The cavities show sharp boundaries and are commonly very irregular (Fig. 2D). However, in some cases, the margins are rounded, indicating that some dissolution has also occurred (Platt, 1989). Vertical root cavities are commonly connected to each other horizontally, especially at the top of the beds. Desiccation cracks are common and arranged in an orthogonal network; they may cut root cavities. Cavity fills are complex and include peloids and intraclasts (see description below) as well as different types of cements from vadose to coarse blocky spar. The succession of these cements is a criterion for deciphering the movements of the water table (Freytet and Plaziat, 1982).

(5) Peloidal and/or intraclastic limestones (Fig. 2E) are one of the most characteristic facies of the palustrine environment. These limestones are formed by two different types of carbonate grains: peloids and

Fig. 1. (A) View of Las Tablas de Daimiel in October 1997. The lacustrine system is very shallow, low energy and low gradient. (B) Reeds (up to 1 m tall) living the water bodies of Las Tablas de Daimiel are easily encrusted by carbonate (so they appear white in the picture). (C) A strong dry period during 1990 caused the exposure of parts of the lacustrine system and therefore of the previously deposited micrite mud. (D) Wackestone–packstone with charophytes, ostracods and molluscs from the Tertiary of the Teruel Basin. This may be considered an example of the primary lacustrine deposits before undergoing pedogenesis. (E) SEM image of primary mud from Las Tablas de Daimiel. The micrite crystals are sub-euhedral and about 1–2  $\mu\text{m}$  across. (F) Lacustrine mud from the Upper Miocene of the Madrid Basin showing different crystal sizes. (G) Lacustrine mud from the Upper Miocene of the Teruel Basin, containing organic filaments (arrowed). (H) Highly indurated lacustrine mud from the Madrid Basin, very similar to recent muds from Daimiel (panel E).

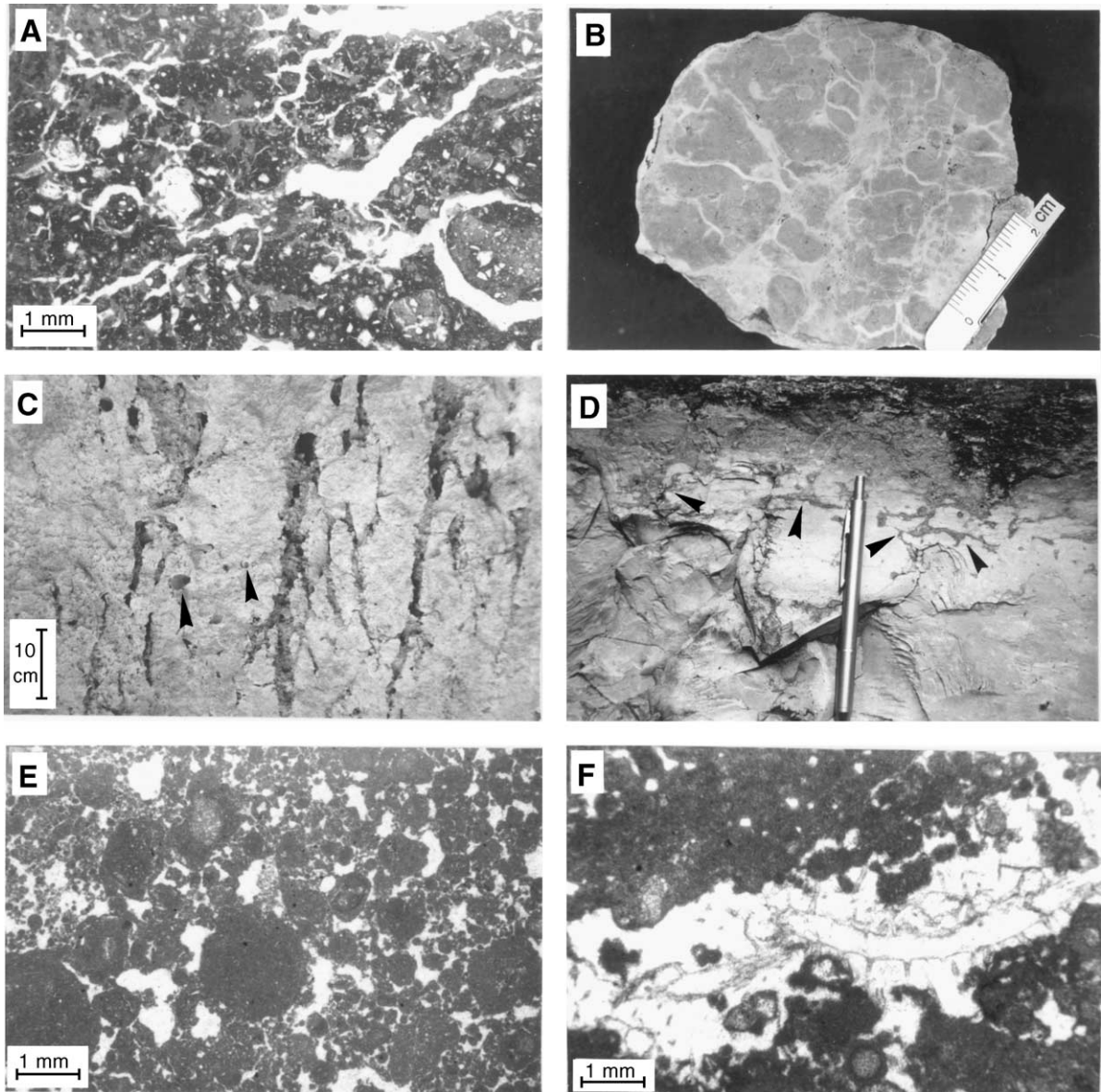


Fig. 2. (A) Thin section of a nodular limestone with irregular and circumgranular desiccation cracks. (B) Slab of a mottled palustrine limestone with a number of desiccation cracks filled with calcite cements. (C) Limestones with vertical root cavities. Some gastropod moulds are indicated by arrows. (D) View of the top of a palustrine limestone bed with pseudo-microkarst. The cavities (arrows) are filled with peloids and intraclasts. Pen is 15 cm long. (E) Peloidal and/or intraclastic limestones are formed by different sized micrite grains embedded in a micrite matrix. The rest of the porosity is filled with spar calcite (white areas). (F) Alveolar septal structure outlined by micrite filaments. The white areas correspond to late calcite spar cement. The material for these photographs comes from the Miocene of the Madrid Basin.

intraclasts. Peloids are more or less rounded grains coated with irregular micritic laminae. They are formed by micrite including some clay, pseudo-spar or compound micritic grains. They may be up to

several millimetres in width. The coatings are formed of irregular, dark micrite laminae alternating with lighter micrite layers that may include smaller peloids. SEM observation of the latter (Alonso-Zarza et al.,

1992a) reveals that a network of fungal filaments arranged within micrite crystals forms the coatings. Intraclasts are more varied in size, ranging from less than a millimetre to several centimetres long. They have different shapes from rounded to angular, and are commonly poorly sorted and may show reverse grading. The intraclasts consist of micrite with scarce fossil debris. Both types of grains are commonly cemented by calcite mosaics whose size vary between that of microspar and coarse crystalline. Root moulds, alveolar septal structures (Fig. 2F) (Wright, 1986), and different types of desiccation cracks are easily recognised within the intraclasts as well as in the intragranular porosity. These different types of cavities form a complex network with the intervening pore space showing a multi-phase history of filling with peloids, internal sediment, microsparitic silt, and blocky calcite. These facies have also been named granular limestones and formed through the process of grainification (Mazzullo and Birdwell, 1989; Wright, 1990a), which also occurs in peritidal settings. These appear as beds, formed totally of this facies, at the top or base of lacustrine and peritidal deposits, or filling different types of cavities.

The facies described here clearly show the different intensity with which lacustrine deposits are affected by pedogenesis and reworking, the variability of processes involved in each palustrine microenvironment (Fig. 3) and the time of sub-aerial exposition or exposure index (Plat and Wright, 1992). A continuum between less pedogenically modified lacustrine limestones to those that are totally modified can be described. This continuity not only affects the degree of pedogenic modification but also the relative influence of physico-chemical versus biogenic processes. Mottled and nodular limestones mostly reveal the influence of physico-chemical processes such as desiccation and iron mobilisation. Both may be considered **less developed palustrine limestones**. Limestones with root cavities, as well as those with prismatic structure, indicate the presence of a well-established vegetation cover. Roots induce the movement of water and chemicals (Clothier and Green, 1997) and act in two different ways: (i) by penetrating the lacustrine mud when the level of the lake descends, and/or (ii) inducing the biochemical precipitation of carbonate around the rhizosphere. In either case, the carbonates formed under these conditions

indicate the influence of more active pedogenic processes or longer sub-aerial periods affecting the lacustrine system. The **more developed palustrine limestones** are the granular limestones (peloidal or intraclastic) and the pseudo-microkarst. In both, the result is an important loss of the primary muddy texture of the deposits. These processes of formation of syngenetic grainstones, or to use a wider term, granular limestones, have been extensively described not only in palustrine environments (Freytet and Plaziat, 1982; Alonso-Zarza et al., 1992a; Armenteros et al., 1997) but also in peritidal settings (Mazzullo and Birdwell, 1989). The formation of these textures is driven by the repeated wetting and drying of the lake mud, meaning root systems had to penetrate the recently deposited micrite mud to reach the water table. This, together with the desiccation of the surface of the sediment, contributes to fragmentation of the lake mud. The intensity and duration of these processes, as well as any later rise in the water table during wetter periods, can cause the reworking, concentration, and coating of the mud fragments. Movements of the grains on the sediment surface give rise to the formation of beds mostly formed by coated (or not) micrite grains that deposited at some distance from the place where the fragmentation originally occurred. On the contrary, pseudo-microkarst and brecciated limestones are formed “in situ”. In both cases, the activity of microorganisms such as fungi and bacteria play a large role in fragmentation and also in the coating of some grains (Alonso-Zarza et al., 1992a).

### 2.3. *Stable isotope geochemistry of palustrine carbonates*

The carbon and oxygen stable isotope composition of palustrine carbonates has been used as a tool for obtaining information on climate, vegetation, hydrology, lake water chemistry and the influence of pedogenic/diagenetic processes, amongst others. However, the interpretation of the data gathered is not easy, as the final figures obtained reflect not only processes occurring within the lake itself, but also the degree of modification that the sediment has undergone. A great number of factors are therefore involved.

Oxygen isotope ( $\delta^{18}\text{O}$ ) values of lacustrine carbonates reflect the composition of the lake water. This depends on the isotopic composition of the

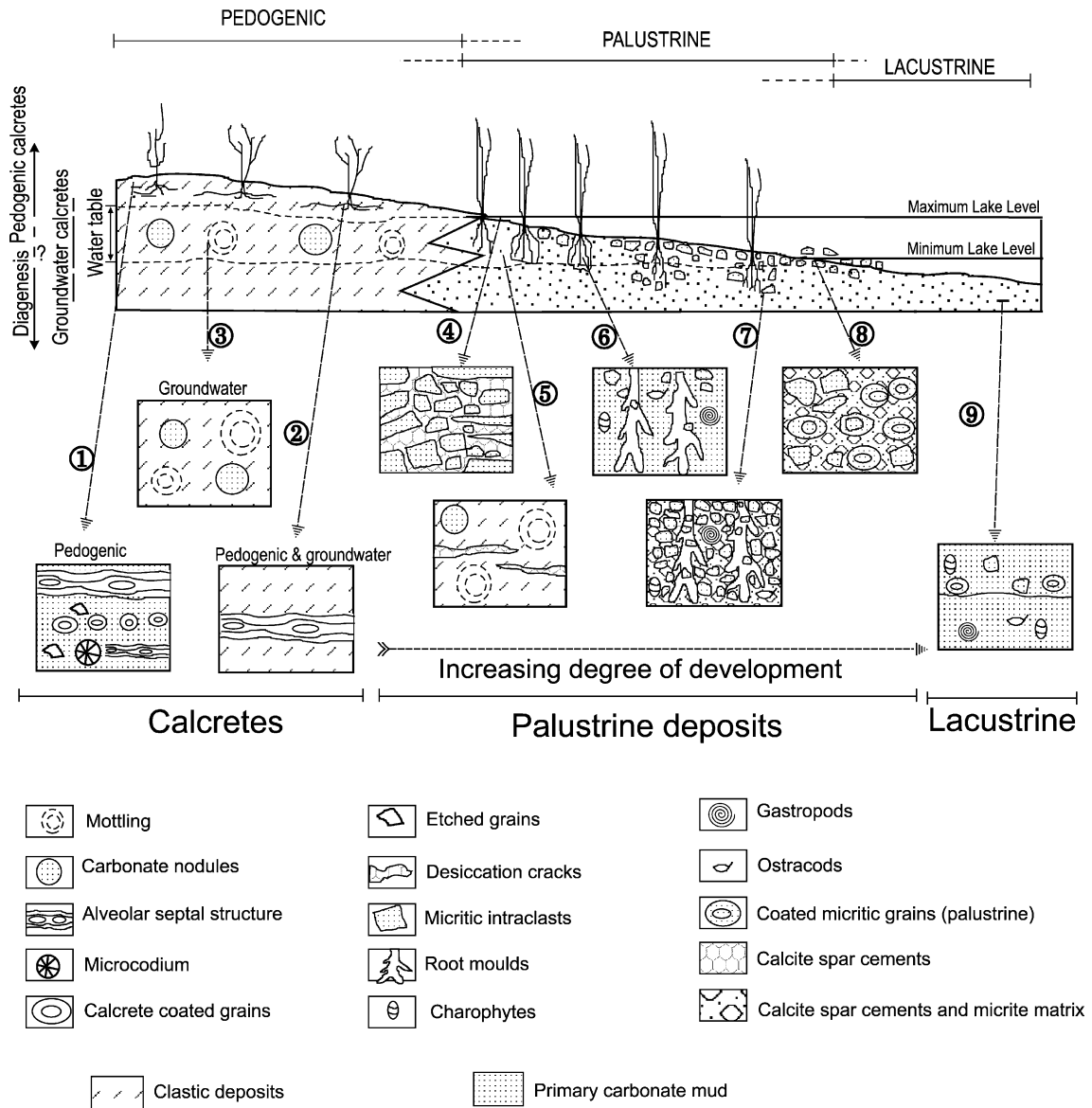


Fig. 3. Sketch of the depositional environments of calcretes and palustrine carbonates. Sketches of the five main palustrine facies (4–8) are included. Most of the characteristic calcrete features are sketched in 1–3.

rainwater in the drainage basin, the potential evaporation, the influence of groundwater flows, and changes in the different water sources. Further, during precipitation of the carbonates there is fractionation owing to the water temperature and the biological processes operating in the lake (Valero Garcés and Kelts, 1997).

Carbon isotope ( $\delta^{13}\text{C}$ ) levels for lakes are mostly controlled by biogenic factors (McKenzie, 1985). High rates of organic productivity in lakes cause a decrease in dissolved  $^{12}\text{C}$  in the lake water, whereas the carbonates precipitated are  $^{12}\text{C}$ -enriched (Kelts and Talbot, 1990; Talbot and Kelts, 1990). The type of vegetation cover of the surrounding lake area may



also be reflected in the  $\delta^{13}\text{C}$  values. If  $\text{C}_3$  plants are dominant in the area, the waters of the drainage basin will be enriched in  $^{12}\text{C}$ , and this will be reflected in the carbonates precipitated in the lake (Valero Garcés et al., 1995).

The covariance between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  has been used as a criterion to distinguish between carbonates precipitated in closed or open lakes. Each closed lake has its own covariant trend, whereas hydrologically open lakes lack covariance and show a limited spread of  $\delta^{18}\text{O}$  values (Talbot, 1990; Valero Garcés et al., 1997; Alonso-Zarza and Calvo, 2000). Marl lakes may show covariance during a given year and also secular covariance associated with long-term climatic variations (Drummond et al., 1995).

These general parameters that govern the isotopic values of lacustrine carbonates become more complex when analysing palustrine carbonates. Soil processes and early meteoric diagenesis (either phreatic or vadose) contribute to the modification of the primary isotope values. Further, the influence of the vegetation cover is more important than in any other lacustrine setting. Macrophytes and microbes contribute to the precipitation of carbonates and may lead to isotopic fractionation (Andrews et al., 1997). The influence of  $\text{CO}_2$ , derived from the soil or the atmosphere, controls the enrichment of  $^{16}\text{O}$  and  $^{12}\text{C}$  in shallow lakes and interstitial waters. Very commonly palustrine carbonates show lower  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values than non-pedogenically modified lacustrine carbonates (Platt, 1989; Arenas et al., 1997), and greater values than adjacent carbonate soils (Wright and Alonso-Zarza, 1992; Dunagan and Driese, 1999; Tanner, 2000). However, evaporation processes and lakes fed by groundwater that have drained marine carbonates results in isotopic values greater than those expected. In addition, the influence of meteoric diagenesis may account for the loss of the primary signatures, the loss of a covariant trend, or a homogenisation of values. This mostly reflects the influence of light meteoric diagenetic waters (Wright et al., 1997).

#### 2.4. Environmental control of the development of palustrine carbonates

Tectonism, climate and eustasy are the three main controls operating on any depositional environment. Eustasy is only important in peritidal deposits and

coastal lakes, but these are uncommon compared with the terrestrial palustrine deposits that have formed far from any marine influence.

##### 2.4.1. Climate

Palustrine carbonates are sensitive to climate. There must be sufficient rainfall to carry the carbonate-rich solutions either in the surface or in groundwaters (De Wet et al., 1998). Very arid or very humid climates do not favour carbonate deposition in lakes (Cecil, 1990), whereas semi-arid to sub-humid climates with marked seasonality are more appropriate (Platt and Wright, 1991; Sanz et al., 1995; Gierlowski-Kordesch, 1998). Palustrine carbonates are sensitive to variations in humidity. Therefore, palustrine facies and sequences may vary according to the climate regime (Platt and Wright, 1992). In sub-humid climates, palustrine deposits include more organic matter—such as in the Miocene of the Teruel Graben (Alonso-Zarza et al., 2000)—which may develop into coals as in the Oligocene of the Ebro Basin (Cabrera and Sáez, 1987). On the contrary, semi-arid climates are characterised by wide pseudo-microkarst development on top of the sequences, and organic matter is hardly preserved. More arid climates favour the presence of evaporite nodules within the palustrine carbonates, or palustrine carbonates dominated by dolomite (Sanz et al., 1999).

Climate also affects the carbonate precipitation rate since most of the carbonate precipitated within the lakes is biogenically produced. This is commonly associated with algal and microbial photosynthesis (Platt and Wright, 1991). Temperature plays a role in biogenic carbonate production. Some carbonate may be inorganically precipitated as a result of seasonal and diurnal temperature fluctuations (Kelts and Hsü, 1978).

Climate not only controls the palustrine environment itself but also the activity of the adjacent, usually siliciclastic, depositional environments (rivers, alluvial fan, etc.), and therefore the arrangement of palustrine sequences. However, in many cases it is difficult to evaluate the relative roles of climate and tectonism separately.

##### 2.4.2. Tectonism and climate

In lacustrine basins, tectonism seems to be the main agent responsible for generating accommodation

space for deposition (De Wet et al., 1998), whereas sediment plus water supply, which is mostly climatically controlled, is the critical factor in defining the main features of both recent and ancient lake fills (Carroll and Bohacs, 1999; Bohacs et al., 2000). The interplay between these two factors has been used to establish a complete framework of lacustrine basins using a sequence-stratigraphy approach. This framework establishes three types of lake basins: overfilled basins characterised by the association of fluvial–lacustrine facies, balance-fill basins dominated by the association of fluctuating–profundal facies, and underfill basins characterised by evaporite facies association (Bohacs et al., 2000). Palustrine carbonates may be present in any of the three types, but are more prominent in overfilled basins and in the highstand depositional systems of balanced-fill and underfill basins.

Palustrine deposition requires shallow water bodies within relatively flat depressions. In addition, the activity of the adjacent alluvial systems within the alluvial basin controls the stability and permanence of the water body. In terms of accommodation space and/or sequence stratigraphy, two major situations are possible:

(1) Low activity alluvial/fluvial systems allowing long periods of water body permanence, and favouring the development of vertically stacked palustrine sequences. Examples include the Cretaceous Rupelo Formation of the Cameros Basin (Platt, 1989) and the Late Cretaceous–Early Tertiary of southern France (Freytet and Plaziat, 1982). This situation usually occurs at the final stages of the infilling of closed basins where very often the carbonates overlap the basin margins (Alonso-Zarza et al., 1992a). This reflects either a progressive decrease of tectonic activity along the basin margins or the change of the topography from a steeper to less steep gradient due to basin infilling or the reduced activity of alluvial systems, during periods of low subsidence rate. The palustrine deposits may represent stages of reduced accommodation space, and, tentatively, highstand depositional systems. In the stratigraphic framework proposed by Carroll and Bohacs (1999) and Bohacs et al. (2000), this situation may be relatively common in overfilled basins.

(2) In cases where alluvial–fluvial systems occasionally reach the shallow water body, pond systems

interbedded with clastic alluvial deposits develop. The pond deposits of the Eocene Guarga Formation in the Pyrenees (Nickel, 1982), as well as some Miocene sequences from the Madrid Basin (Sanz et al., 1995), are good examples of this. In both cases, palustrine carbonate lenses occur interbedded with red alluvial mudstones. The latter represent distal fan facies and/or floodplain deposits while the carbonate lenses were deposited in periods or areas of reduced clastic sedimentation. This is common in stages of high accommodation space that favour high levels of storage of floodplain sediments, resulting in isolated channels, weakly developed soils (Wright and Marriott, 1993) and ponds. Together, these characterise transgressive depositional systems. Balance-fill basins (Carroll and Bohacs, 1999) are the more favourable to contain these pond deposits.

On a smaller scale (decimetres to a few metres), the development of palustrine sequences responds to the relationship between the subsidence rate and the vertical aggradation of the basin. In alluvial basins, pulses of subsidence due to the tilting of the basin floor may cause the redistribution of the lake water resulting in the emergence of the water table and the rapid formation of a shallow lake. Subsequent infill of the lake favours the exposure of lacustrine carbonates and their pedogenic modification. These sequences are common in the Cretaceous of the Serranía de Cuenca (Gierlowski-Kordesch et al., 1991) and in the Teruel Graben (Alonso-Zarza and Calvo, 2000). In contrast, the equilibrium between tectonic subsidence and sedimentation favours a slow, but continuous aggradation of the floodplain areas and a gradual rise of the water table. Under this regime, a gradual vertical transition from palaeosols developed in floodplain mudstones to palustrine carbonates are commonly seen, as in carbonate pond deposits of the Madrid Basin (Sanz et al., 1995).

#### 2.4.3. Sources of carbonates

Many of the better-illustrated sequences of palustrine carbonates developed in basins surrounded by highlands in which carbonate rocks dominate. There are a number of examples in the Iberian Peninsula (Platt, 1989; Alonso-Zarza et al., 1992a, amongst many others) and in the Triassic of Pennsylvania (De Wet et al., 1998). However, this is not always a prerequisite for lacustrine–palustrine carbonate sedi-

mentation. For example, in the Late Hercynian of the Pyrenees, carbonate lacustrine series are interbedded with pyroclastic layers (Valero Garcés, 1993). The weathering of calc-alkaline volcanic rocks in the catchment area favours low to moderate calcite production in adjacent lakes. Nevertheless, the presence of carbonates underlying lakes or in the basin margins notably contributes to carbonate precipitation within them because it favours high carbonate concentrations in the surface and groundwaters (Gierlowski-Kordesch, 1998), and low siliciclastic input, both controlling the carbonate production within the lake (Cohen, 1989).

#### 2.4.4. Hydrology (mechanism of water supply)

The origin of the water accumulated within the lake plays an important role in determining the lake chemistry and therefore the mineralogy of the lacustrine sediments and latter transformations during early diagenesis. There are two main sources of water, surface and groundwater, although it is often difficult to establish which is the more important (Gierlowski-Kordesch, 1998). Both can operate simultaneously in the same lake.

A purely meteoric supply gives rise to lake water relatively fresh. If there is any chemical precipitate in the lake it is usually mainly calcite. However, chemical precipitation may be inhibited, as surface water will also carry clastic material that may constitute the main infill of the lake. If the lake is mainly fed by groundwaters directly or via springs, more complex lake geochemistry can be expected. The mineralogy of the palustrine deposits will depend on the composition of the groundwaters reaching the lake. Factors such as the distance that the groundwater has flowed, the composition of the catchment areas, and the ratio of rock–water interaction and evaporation rates, all control groundwater composition and therefore the mineralogy of the primary precipitates and their possible transformation during early diagenesis (Ara- kel and McConchie, 1982).

Low-Mg calcite is a common precipitate if groundwater flows only relatively short distances or if the catchment area is dominated by low-Mg calcite and little evaporation occurs. Dolomite and gypsum may form from more evolved groundwaters due to evaporation during flow towards the lake or within the lake itself (Wright and Sandler, 1994; Calvo et al., 1995a).

However, the evolution of groundwaters and the formation of other precipitates such as dolomite, gypsum or Mg clays depends not only on hydrology but also on climate and/or the presence of source rocks containing evaporites.

Commonly, as in the Late Eocene of South Dakota, palustrine limestones are found in fault zones, spatially associated with palaeo-groundwater or spring deposits. Some of these carbonates formed behind the tufa barrages (Evans, 1999) and their occurrence in the geological record proves the importance of groundwater supply in shallow lacustrine environments, where the entrance of water through seepage may cause the expansion of the lacustrine environments as in the Miocene of Spain or in the Pliocene of the Amargosa Desert (Calvo et al., 1995b).

#### 2.5. Diagenesis

The exact boundaries of diagenesis are commonly difficult to separate from sedimentation processes in many depositional environments, but in palustrine environments it is almost impossible. Many questions arise. When does sedimentation end and pedogenesis start? What is the boundary between pedogenesis, sedimentation, and diagenesis in these terrestrial environments? These questions are most difficult to answer since in palustrine environments there is a continuity in this sequence of processes (Fig. 3). It might be more suitable to consider diagenesis as those processes controlled by the chemistry and position of the groundwater. Therefore, diagenetic processes in palustrine environments will be those that result from the interaction of pedogenically modified carbonates with groundwaters. The more common processes are:

(1) Cementation. Cementation is normally meteoric (both phreatic and vadose). Very commonly, different phases of low-Mg calcite cements alternate, indicating the oscillation of the groundwater. CL studies have notably aided the identification of these alternations (Valero Garcés and Gisbert, 1992). Vadose cements are commonly acicular and both pendant and meniscus, whereas phreatic cements are of coarse calcite spar (Freytet and Plaziat, 1982).

(2) Mineralogical stabilisation and recrystallisation. Palustrine sediments are commonly very indurated in spite of the fact that they have not undergone

significant burial or cementation. The induration of these deposits is interpreted to be the result of the mineralogical stabilization and aggrading neomorphism (Wright et al., 1997; Anadón et al., 2000) of the initial lacustrine muds. However, due to the small crystal size of these rocks, it is difficult to completely understand the real processes that lead to the induration of these muds. Pseudo-sparitic and microsparitic textures are common, forming irregular patches with sharp to gradual boundaries with the micrite host (Valero Garcés and Gisbert, 1992).

(3) Karstification may be an early or late diagenetic process occurring when the meteoric waters that infiltrate the lacustrine carbonates are undersaturated with respect to calcite. Processes of karstification are well illustrated in marine carbonates (see for example Esteban and Klappa, 1983), but less known in the case of lacustrine host rocks. Cañaveras et al. (1996) have shown that the results of karst-related processes on terrestrial carbonates are similar to those developed in marine environments. However, the geochemical and textural changes may be different, since the initial chemistry, mineralogy and texture of the rocks were also different. Karstification processes in these environments cause, apart from common dissolution and collapse features, extensive recrystallisation, dissolution of intrasedimentary evaporites and dedolomitisation.

(4) Dolomitization is commonly an early diagenetic process, which results in the formation of dolomicrites in which the primary fabric is well preserved. In these shallow lake environments, dolomitization is the result of intense evaporation by the pumping of water through the mudflats or lake margins during periods of exposure, allowing an increase in the Mg/Ca ratio. This would favour both the intrasedimentary growth of evaporites, primary dolomites and dolomitization. Good examples of these processes have been illustrated by Wells (1983) in the Palaeogene of Central Utah or by Arenas et al. (1999) in the Miocene of the Ebro Basin in Spain.

### 2.6. Other palustrine deposits

Palustrine features are not restricted to carbonates but also occur in other sediments such as clays and evaporites. They should also be considered palustrine if they have been precipitated within a shallow water

body and show features related to later emersion and pedogenesis.

In evaporites, palustrine features can occur and are similar to those often seen in carbonates, including pseudo-microkarst, nodulisation, root traces, and bioturbation (Rodríguez-Aranda and Calvo, 1998). In this case, slight differences in climate have interacted with source rocks to favour evaporite instead of carbonate deposition.

Siliceous source rocks favour clay sedimentation in the lake and also regulate carbonate deposition. In the Eocene continental deposits of the Paris Basin where siliciclastic input is high, clays are relatively abundant in the evaporite sequences. The available Mg is therefore incorporated into the clay lattice to form aluminomagnesian clays with calcite the only carbonate precipitated. If the clay input is lowered, the magnesium content rises and dolomite can form (Thiry, 1989).

In the Madrid Basin, whose northern and north-eastern basin margins are formed by low-grade metamorphic rocks and granites, the palustrine sequences include green and pink clays alternating with bioturbated dolostones (Calvo et al., 1989). Within the clays, the change from green to pink has been interpreted as an indicator of sub-aerial exposure. Other palustrine features are the nodulisation of dolostones, mainly at the top of the sequences, and the wide occurrence of root traces throughout the sequence. In this context, Mg-rich clays (tri-octahedral smectites, sepiolite and palygorskite) are the most typical palustrine facies (Ordoñez et al., 1991; Calvo et al., 1995a).

### 3. Calcretes

Calcretes are one of the sedimentary materials that have received the most attention from a variety of scientists including geomorphologists, sedimentologists, pedologists, and others. This interest in calcretes is owed to their widespread occurrence in recent and ancient arid and semiarid settings. Moreover, calcretes contain important information that help interpret ancient ecosystems, their palaeogeography, and the tectonic, climatic and sedimentary regimes in which they formed. A good definition of a calcrete is that proposed by Watts (1980) after modifying that of Goudie (1973): “pedogenic calcretes are terrestrial

materials composed dominantly, but not exclusively, of  $\text{CaCO}_3$ , which occur in states ranging from nodular and powdery to highly indurated and result mainly from the displacive and/or replacive introduction of vadose carbonate into greater or lesser quantities of soil, rock or sediment within a soil profile". This definition only refers to pedogenic calcretes, however Wright and Tucker (1991) later proposed a wider use of the term calcrete to include, according to the initial ideas of Netterberg (1980), the effects of shallow groundwaters.

Exhaustive and very clear reviews on calcretes have been provided by Esteban and Klappa (1983) and Wright and Tucker (1991), and it is difficult to improve upon them without being repetitive. The most important aspects of calcretes are clearly developed in these papers. The present review tries, however, to briefly put forward the most important aspects of calcretes such as classification, morphology, micromorphology, and geochemistry, but focuses mainly on the palaeo-environmental significance of these soils.

Despite the wide use of the term calcrete and its synonyms cornstone (Allen, 1960) and caliche, none are included in any soil classification, either as a soil name or as a horizon. Within a soil, the horizon of prominent carbonate accumulation has been named the K horizon (Gile et al., 1965), and has a diagnostic K-fabric. Pedogenic calcretes form within soil profiles where they constitute several discrete horizons of carbonate accumulation, which forms a sub-profile within the main soil profile (Wright and Tucker, 1991). Aridisols, vertisols, mollisols and alfisols (Soil Survey Staff, 1975) are the more typical soils containing calcretes (Wright and Tucker, 1991). In palaeosol classifications, calcretes are considered aridisols (Retallack, 1993), calcisols (Mack et al., 1993), or palaeoaridisols (Nettleton et al., 2000).

The classification of calcretes is complex since some different criteria may be used. Purely descriptive classifications consider mineralogy and morphology. With the dominant carbonate mineral and the amount of dolomite in mind, a simple classification was proposed by Netterberg (1980) who distinguished between calcretes, magnesian calcretes, dolomitic calcretes, and dolocretes. The morphology of calcretes and their different horizons has given rise to a large number of names (Netterberg, 1980; Goudie, 1983),

which have been summarised by Wright and Tucker (1991). These include calcareous soil, calcified soil, powder calcrete, pedotubule calcrete, nodular calcrete, honeycomb, hardpan, laminar calcrete and boulder/cobble calcrete.

The morphology of calcretes is not only a descriptive criterion for classification. Gile et al. (1966) proposed that the morphology of calcic soils could be seen as a sequence of morphological stages that reflect the different degrees of development (relative time of development) of the soil. Gile et al. (1966) proposed four different stages. Within stages I–III the gravel contents are important and are different in fine and coarse clastic deposits, with calcrete development more rapid in coarse-sized substrates. In gravel-rich calcic soils, Stage I is characterised by thin discontinuous coatings on pebbles. In Stage II, the coatings are continuous and vary in thickness. Massive accumulations between clasts and fully cemented gravels are included in Stage III. In gravel-poor soils, Stage I shows few filaments or faint coatings on ped surfaces. Soft nodules, 5–40 mm in diameter are indicative of Stage II, whereas coalescent nodules are indicators of Stage III. Machette (1985) established six stages (Fig. 4A), the first three similar to those previously established by Gile et al. (1966). Stage IV is characterised by carbonate-rich laminae less than 1 cm thick. Thicker laminae and pisoliths are indicators of Stage V. Stage VI includes multiple phases of brecciation, pisolith formation, and recementation.

The calcretes that commonly form within soil profiles, and therefore in very superficial settings above the groundwater table, are pedogenic calcretes and commonly show well-developed profiles (Fig. 4B). However, groundwater (Arakel and McConchie, 1982) may induce carbonate precipitation around the capillary fringe in less surficial settings, on occasion under the influence of phreatophytic plants (Semeniuk and Meagher, 1981). These are termed phreatic or groundwater calcretes and their formation is owed to the presence of a relatively shallow water table. Groundwater calcretes may be difficult to distinguish from those formed under pedogenic environments (Pimentel et al., 1996; Mack et al., 2000; Tandon and Andrews, 2001). In some cases it may also be difficult to separate groundwater calcretes or dolocretes from the effects of non-exclusively meteoric diagenesis (Williams and Krause, 1998).

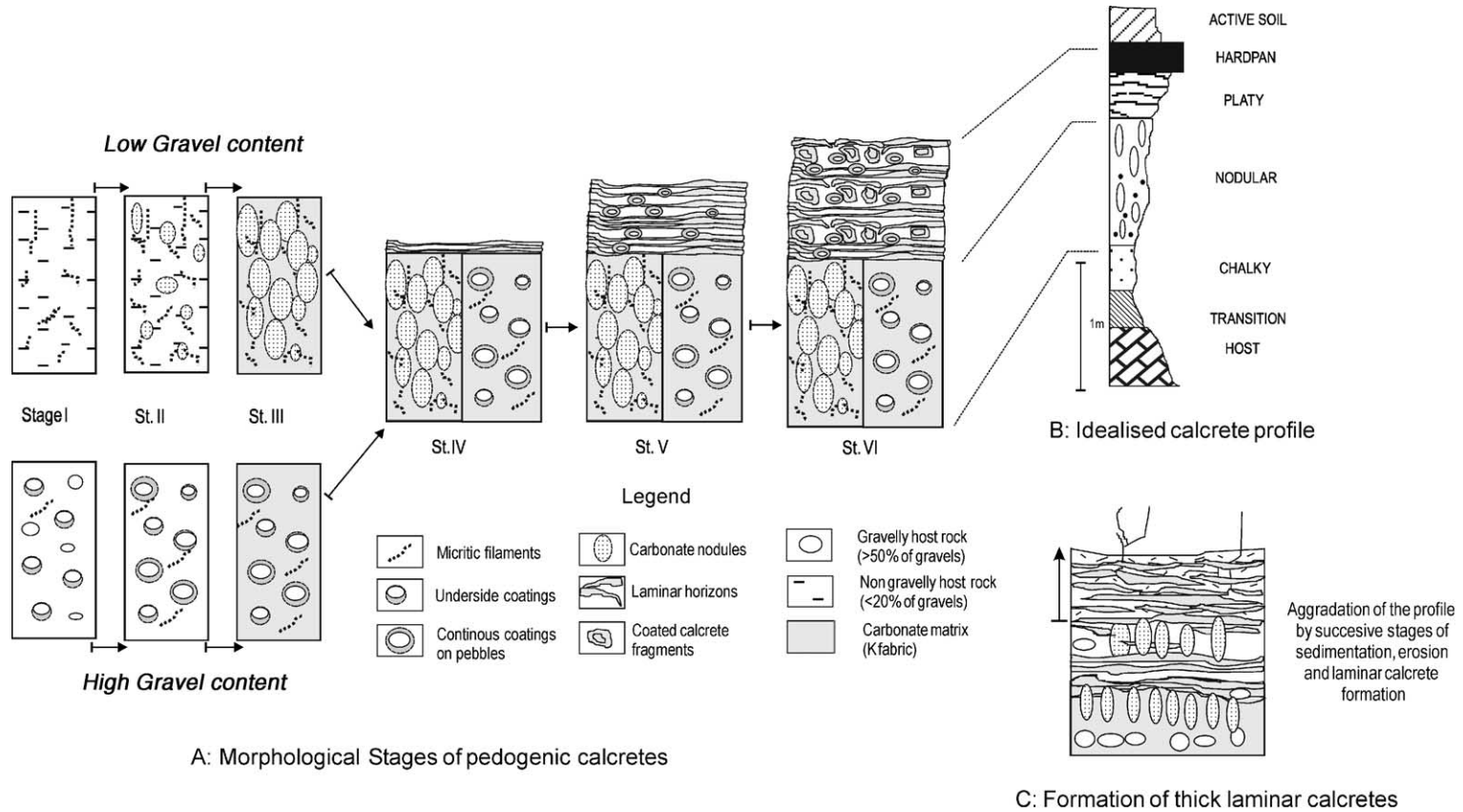


Fig. 4. (A) Stages of development of pedogenic calcretes. Based on Machette (1985). (B) Idealised calcrete profile. Modified from Esteban and Klappa (1983). Relationship between panels (A) and (B) is also shown. (C) Thick laminar calcrete profiles require equilibrium between sedimentation and soil formation processes, which allows the aggradation of the profile. Example taken from the Canary Islands (based on Alonso-Zarza and Silva, 2002).

### 3.1. Pedogenic calcretes: calcrete profiles

Pedogenic calcretes are formed of well-differentiated horizons of carbonate accumulation at the macro- (Fig. 5A and B) and micro-scales. Calcrete profiles may be relatively complex as similar horizons may occur at different positions within the calcrete, indicating composite profiles. In contrast, significant horizons may be lacking due to truncations within the profile development (Alonso-Zarza et al., 1998a). Based on a number of observations, Esteban and Klappa (1983) have described an idealised calcrete profile (Fig. 4B), which consists (from base to top and including the host) of the following horizons.

#### 3.1.1. Host material

This may be of any type of composition, texture, and degree of compaction. Permeability and calcium carbonate content may affect the degree of calcrete development (Wright, 1990b). The host material lacks any calcrete features and is so distinguished from the overlying calcrete horizons.

#### 3.1.2. Transitional horizon

This is the zone of “in situ” weathering of the host. Its lower boundary is difficult to outline. It lies between the host material and the well-defined uppermost calcrete horizons. It has features of “in situ” weathering as well as partial replacement of the host. Relic primary structures of the host are commonly preserved.

#### 3.1.3. Chalky horizon

This is a soft horizon consisting of a micrite and/or microspar matrix that contains etched detrital grains and peloids. It tends to be homogeneous texturally and structurally, although some nodules formed in relation to roots are present. It is commonly located between the transitional and nodular horizons, but it may occupy any other position within the profile.

#### 3.1.4. Nodular horizon

This horizon is formed by powdery to indurated nodules of calcium carbonate embedded in a less carbonate-rich matrix. The nodules vary in morphology between vertical, horizontal, irregular or even branching. In cases when the nodules are vertically elongated (Fig. 5A), the horizon has also been called

the *prismatic horizon*. Nodular horizons tend to show diffuse lower and upper boundaries. Microscopically, the nodules are composed of micrite rich in etched grains, relics from the host material. Coated grains in which the nucleus is an etched grain are also common.

#### 3.1.5. Platy horizon

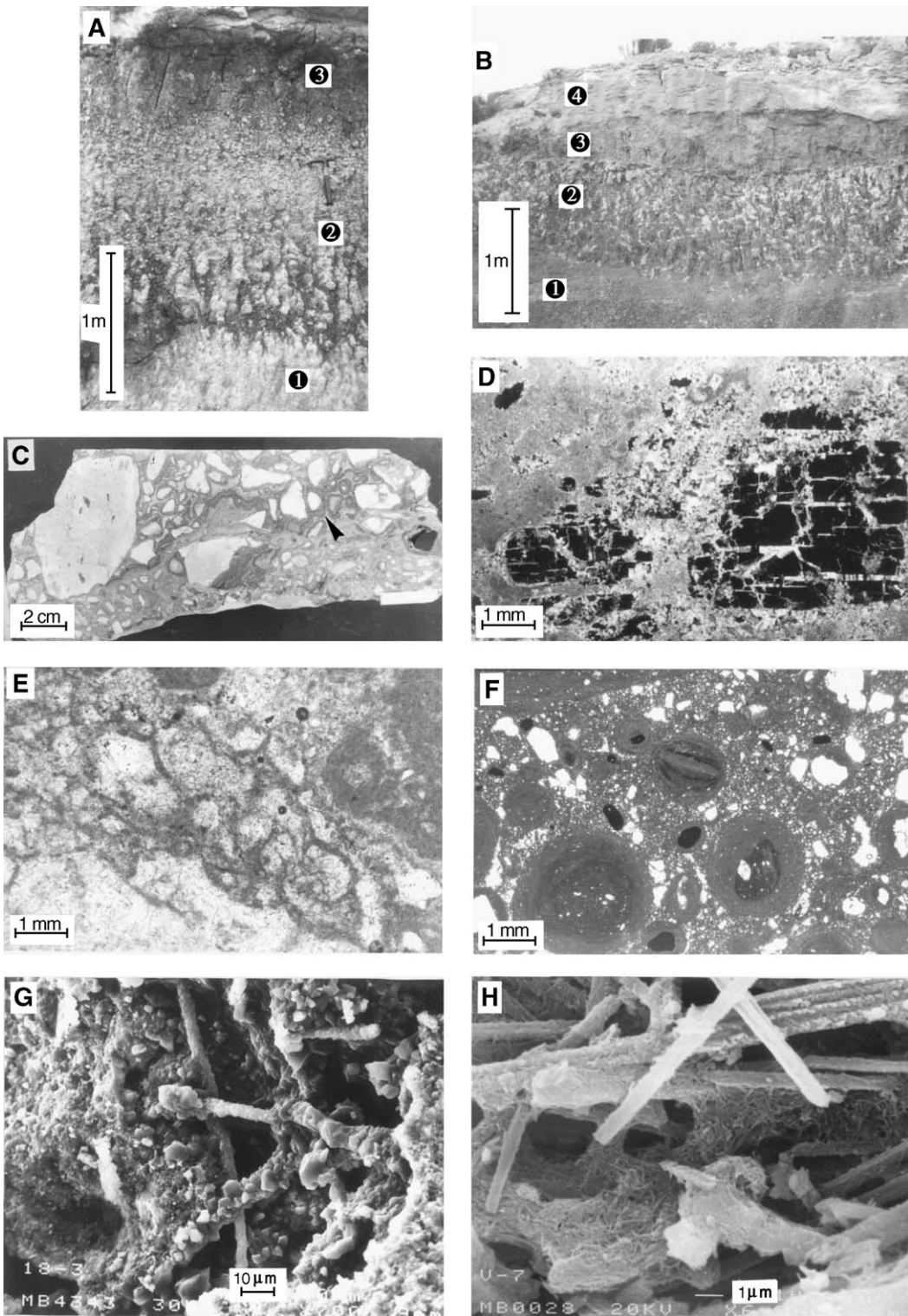
This commonly occurs overlying the nodular horizon. When a hardpan is present at the top of the profile, the platy horizon underlies it. However, if a hardpan is lacking, the platy horizon is the topmost horizon of the calcrete profile. This horizon has also been called the *laminar horizon*. Some calcretes composed almost exclusively of the laminar horizon are named *laminar calcretes*. These are later discussed in more detail. The platy or laminar horizon has a wavy to thinly bedded habit, planar fracture porosity, and an abundance of alveolar textures, rhizoliths and needle fibre calcite. Internally, the different laminae show varied microfabrics that include micritic layers, micritic layers with tubiform pores, laminae very rich in alveolar septal structures, and laminae including micrite coated grains.

#### 3.1.6. Hardpan

In very mature profiles this is commonly the topmost horizon (Fig. 5B). It is well indurated and porosity is very low. Macroscopically it may be structureless or massive or laminated or nodular. This horizon is commonly formed by micrite containing corroded grains, rarely coated. Laminated micritic layers may also be present. Thick hardpans are commonly fractured and brecciated, allowing the identification of the *brecciated horizon*.

#### 3.1.7. Pisolithic horizons

These consist of sand or gravel-sized clasts coated by laminated micrite (Fig. 5C) and are very common in calcretes developed on coarse-grained host rocks. In many cases the horizons follow the geometry of the coarse deposit on which they developed (Alonso-Zarza et al., 1998a). The micrite laminae may coat all the clasts or only their undersides. The laminae are composed of dense micrite, micrite with alveolar septal structures, and/or microspar. The coated clasts are embedded in a dense matrix of irregular masses of microspar including some detrital grains, and micrite with alveolar septal structures. Pisolithic horizons are





common at the top of the calcrete profile when intense brecciation favours the formation of calcrete-sourced clasts.

The formation of thick calcrete profiles is the result of different stages of development, which, in many cases, are repeated over time. In some situations, one single stage may include several phases of erosion, soil formation and even sedimentary processes. [Esteban and Klappa \(1983\)](#) have defined five stages for the development of a mature calcrete profile. These authors also include the weathering of the host. More specifically, [Machette \(1985\)](#) considers six stages according to morphological features. It is not easy, therefore, to establish a single sequence of stages for calcrete profile development, mainly because, in some cases, the profiles may be truncated or composed. A simple sequence includes the following phases:

(1) Preparation of the host material through mechanical, physicochemical, and biological processes to form a regolith or weathered detritus.

(2) Initial soil development through changes produced by the action of organisms and by movement of water through the host material.

(3) Accumulation of calcium carbonate forming the nodular and/or chalky horizons. At this stage carbonate precipitation takes place only in discontinuous areas in close association with roots and related microorganisms. Run-off water can easily infiltrate and little water is retained in the soil. Plants have to extend their roots vertically to look for local water tables and so contribute to the disintegration of the substrate and the formation of the transitional horizon. Precipitation of carbonate without significant induration leads to the formation of the chalky horizon that consists mostly of peloids and coated grains formed in close association with roots and root hairs ([Calvet and Juliá, 1983](#); [Jones and Squair, 1989](#)). The biological components of the soil become calcified forming

rhizoliths, calcified filaments, and nodules. Vertical water movements and vertical root systems favour the formation of vertically oriented carbonate nodules. Initially they are very dispersed, but with time they coalesce to form the nodular horizon. These processes lead to the formation of morphological Stages I–III of [Machette \(1985\)](#).

(4) Formation of the platy or laminar horizon. Once the nodules coalesce, root systems cannot easily penetrate the nodular horizon. In addition, water is mainly confined to the uppermost part of the profile in the still-unconsolidated zone above the nodular horizon. The morphology of the root systems therefore changes. Roots trying to get the maximum amount of water tend to extend laterally, promoting the development of sub-horizontal networks. The laminar horizon starts to form in the still-unconsolidated zone. The degree of development as well as the characteristics and thickness of this horizon depend on the time the root systems can be supported in the upper soil horizon by new detrital deposits that favour the activity of the topmost soil. This stage includes Stages IV and V of [Machette \(1985\)](#). A wider discussion on the origin of laminar calcretes is provided in Section 3.3.

(5) Calcrete formation can follow different paths depending on the relationship among calcrete formation, erosion, and sedimentary and diagenetic processes. Three possibilities are envisaged:

- Stage 5A. Erosion and sedimentation at the top of the profile are very reduced or close to zero. Accumulation of calcium carbonate is continuously increasing. A point is reached when soil organisms can no longer live in the soil and so calcrete development stops. Diagenetic processes lead to the lithification of the soil profile and to the formation of the hardpan. This is subjected to processes that weather the profile (the activities of both lower and higher plants, fracturation, dissolution, etc.), causing the

Fig. 5. (A) Calcrete profiles developed on red mudstones (Miocene of the Teruel Basin). The lower profile (1) is overlain by the upper profile (2), which consists mostly of a nodular–prismatic horizon, which progressively grades towards the top to red mudstones (3). (B) Well-developed calcrete profile from Carboneras (SE Spain): 1. Red mudstones (host rock), 2. Nodular horizon, 3. Laminar horizon, 4. Hardpan with laminar structure. (C) Slab of part of a horizon of coated gravels. The micrite coating is best developed on the undersides of the clasts (arrowed) (Miocene of the Madrid Basin). (D) Feldspar grain etched and corroded by carbonate from the Palaeogene of the Sado Basin in Portugal. (E) Alveolar septal structure. The porosity left by the micrite filaments is filled by calcite spar, Neogene of the Teruel Basin, Spain. (F) Coated micrite grains. The envelopes are dark and irregular and in some cases include silt-size detrital grains. Pleistocene of Cabo de Gata (SE Spain). (G) Calcified filaments under the SEM from Pleistocene calcretes from Murcia, Spain. (H) SEM view of needle fibre calcite crystals with two different sizes. The larger (more than 10  $\mu\text{m}$  long) are coated by the smaller (1  $\mu\text{m}$ ). Miocene of the Duero Basin, Spain.

brecciation of the uppermost part. This is stage VI of Machette (1985) and stage 6A of (Alonso-Zarza et al., 1998a).

- Stage 5B. Deposition is low and episodic but exceeds the erosion rate, contributing to new surface sediments for soil organisms and the subsequent development or maintenance of root systems. This favours the formation of very thick laminar horizons, which are not single events but the addition of multiple phases of sedimentation and soil formation processes (Fig. 4C) (Stage 6B of Alonso-Zarza et al., 1998a).

- Stage 5C. The erosion rate is low but exceeds the sedimentation rate. The upper part of the calcrete profile (B horizon) is removed and the laminar horizon is exposed directly to the atmosphere. Lichens (Klappa, 1979) and spherulites may grow in these superficial conditions. Karstic microforms may be also present.

### 3.2. Micromorphology and microscopic features of calcretes

The microscopic features of calcretes are so varied and sometimes so spectacular that the literature on this topic is perhaps almost too extensive. Comprehensive reviews can be found in Braithwaite (1983), Esteban and Klappa, (1983), Wright and Tucker (1991), and Wright (1994). It is not this paper's aim to extensively review all this literature, but to outline the main aspects of calcrete micromorphology.

Wright (1990c) proposed two end-member microfabrics for calcretes. *Beta* microfabrics show varied biogenic features, whereas they are absent in *Alpha* microfabrics, which are dominated by non-biogenic features. These types are the end-members, but most calcretes show both biogenic and non-biogenic features. Moreover, in some cases, the ultimate origin of a specific feature may not be completely clear.

Non-biogenic features include crystalline carbonate groundmasses and the cristic plasmic fabrics of Brewer (1964), with crystal sizes from micrite to spar. The presence of patches with coarse crystals distributed irregularly amongst the micrite/microspar is common. Floating grains of mostly silicates, but which can be varied depending on the composition of the host, are commonly etched (Fig. 5D) and show evidence of grain expansion or fracturing. Together,

these features provide evidence of the displacement and replacement of the host rock (Braithwaite, 1989) and multiple phases of calcite growth (Wright and Peeters, 1989). Different types of desiccation and shrinking cracks, which may be filled with calcite cements are also interpreted as non-biogenic, as are calcite rhombs (whose origin is not fully clear). Nodules are common in alpha calcrete, but their origin is difficult to establish. The sharpness of the nodules may be an indicator of their genesis. Nodules with diffuse margins may indicate that they formed inorganically from meteoric waters (Khadkikar et al., 1998), whereas sharper nodules are commonly associated with vertical root structures. However, it not easy to distinguish between nodules formed biogenically from those formed inorganically.

The amount and type of biogenic features in calcretes is enormous and include alveolar septal structures (Fig. 5E) formed by arcuate micritic septae of variable length appearing within pores (Adams, 1980) that border root traces (Klappa, 1980), or which appear intercalated between micritic laminae (Alonso-Zarza, 1999). The septa are formed either by equidimensional micritic crystals or by acicular needle-fibre calcite. Alveolar septal structures are basically interpreted as calcified fungal filaments associated with roots (Wright, 1986). Fungi and cyanobacteria are also responsible for the formation of the irregular micritic envelopes of coated grains (Fig. 5F) (Knox, 1977; Calvet and Juliá, 1983), and also for calcified filaments often present in any type of calcretes (James, 1972; Kahle, 1977). Calcified filaments are straight or sinuous (Fig. 5G), and either single or with Y-shaped branching. The filaments are connected to each other and may appear collapsed and be coated in calcite crystals. In other cases, only their porosity is preserved. Coated grains are very variable in size (Hay and Wiggins, 1980). The nucleus of the grains varies among relics of the host rock, micrite, or even parts of alveolar septal structures. The formation of these grains requires the individualisation of the nuclei, either by desiccation or root activity, and the formation of the coating, which is controlled by roots and associated microorganisms, especially fungal filaments (Calvet and Juliá, 1983; Alonso-Zarza et al., 1992a). Needle-fibre calcite crystals are up to 10 µm wide and up to 50 µm in length, but generally very variable in size (Fig. 5H). An ample description and

detailed classification of needle fibre calcite crystals was published by Verrecchia and Verrecchia (1994). Their formation is due either to high levels of supersaturation or to microbial activity, especially that of fungi (Callot et al., 1985; Phillips and Self, 1987).

Rhizoliths are organo-sedimentary structures produced by roots (Klappa, 1980). The diameter varies between a few millimetres and a few centimetres; length is commonly on the centimetre to decimetre scale (Fig. 6A). The internal structure of rhizoliths varies from massive, more or less sandy micrite that represents the infill of the root mould, to very complex textures including calcified cells, cements, alveolar septal fabrics, needle-fibre calcite, microbial coatings and calcified tubes (Calvet et al., 1975; Wright and Tucker, 1991). The micromorphology and structure of calcified roots depends on the position in which the calcification occurred in the rhizosphere, on the organisms involved, and whether the plant was alive or dead when calcification occurred (Jaillard et al., 1991; Alonso-Zarza, 1999). Calcification may occur in the medulla, in the root cortex, or both (Fig. 6B). Calcification of the cells of the root-medulla indicates that the plant was alive and needed  $\text{Ca}^{+2}$  to stabilise its cell walls. In this case, there is no need for the interplay of other organisms. Calcification of the root cortex through the replacement of the cell walls (Fig. 6C) and intracellular spaces, leaving a central pore corresponding to the medulla, indicates the interplay of roots and fungi, and that calcification started while the plant was still alive. In contrast, the lack of preservation of detailed root microstructures may indicate that the formation of the rhizolith occurred after the decay of the root (Alonso-Zarza, 1999) (Fig. 7). The organization of calcified root cells within rhizoliths resembles problematic features known as *Microcodium* (Fig. 6D) (Klappa, 1978), especially *Microcodium* (b) of Esteban (1972) or type 3 of Plaziat (1984). Experimental studies on recent roots (Jaillard, 1987; Jaillard et al., 1991) and examples from the sedimentary record (Alonso-Zarza et al., 1998b) indicate that, very probably, this type of *Microcodium* is formed by the calcification of root structures with or without the influence of other microorganisms. The origin of the other types of *Microcodium* is not so well known and is currently under study.

Other biogenic structures in calcretes are those related to the activity of soil organisms, especially

insects such as bees, wasps, termites and ants, amongst others. These are included as the ichnofacies-type *Coprisnisphaera* (Genise et al., 2000) and include, for example, insect cocoons (Read, 1974). Trace fossils are of undoubted interest since they are very good palaeoecological indicators.

### 3.3. Laminae calcretes

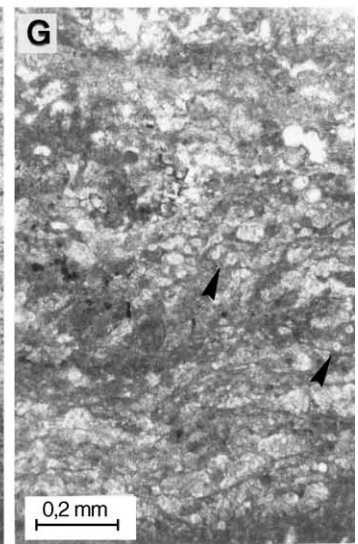
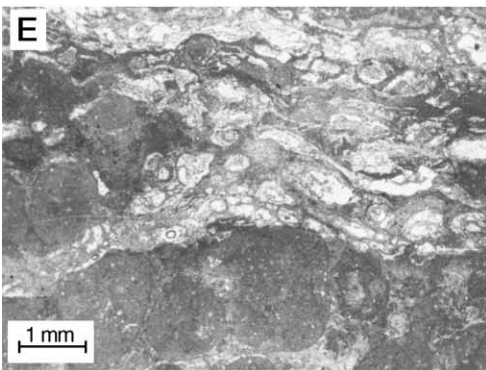
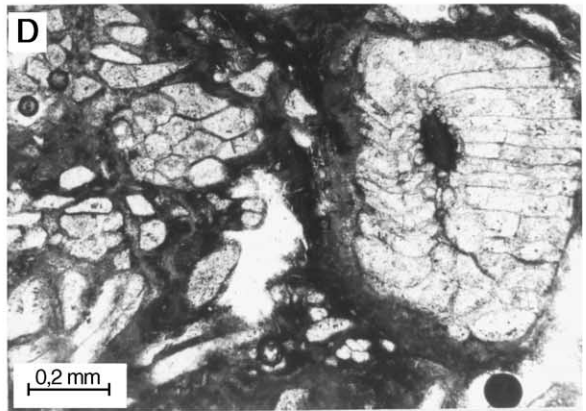
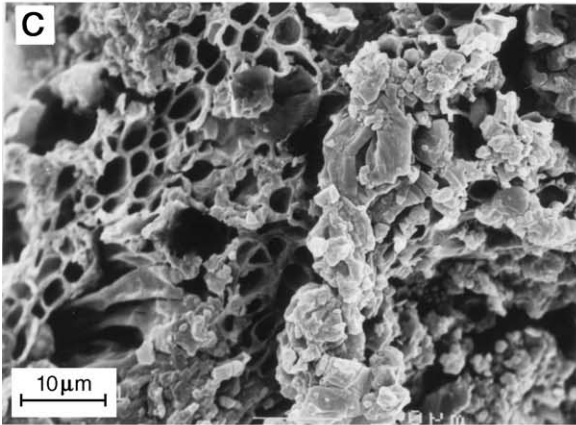
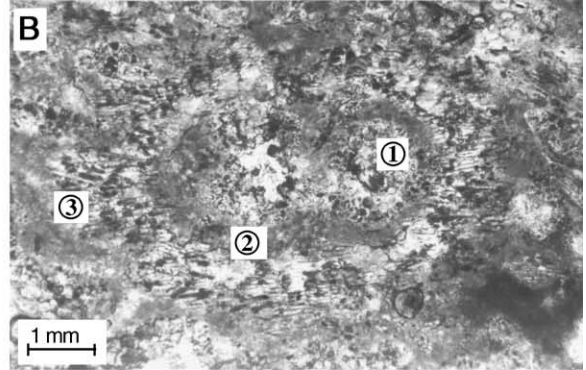
Laminar carbonate horizons may occur in three different situations: (1) at the top of thick calcrete profiles but below the top soil (Fig. 5B), (2) interbedded within sedimentary deposits (Fig. 6A), or (3) at the top of any bedrock. Sometimes it may be difficult to distinguish these horizons from stromatolites (Wright, 1989). The main features of calcretes that allow their differentiation from stromatolites are: the different laminae are very irregular and show micro-unconformities attributable to phases of dissolution (Wright, 1989); the laminae include etched grains, ooids and clays; rhizoliths and alveolar septal structures (Fig. 6E) are very common in laminar calcrete horizons (in some cases they may form the whole horizon) (Wright et al., 1988); and alternations between micrite laminae and others rich in detrital sediments, ooids or coated micritic grains are common (Fig. 6F) (Sanz and Wright, 1994; Fedoroff et al., 1994). Calcified filaments are common in both laminar calcretes and stromatolites, but in the latter they are commonly oriented perpendicular to the lamination, whereas in calcretes they show no preferred orientation.

Some features present in calcretes, such as the so-called spherulites (Fig. 6G), have been the cause of lengthy discussion, not only about their own origin but also how they relate to the origin of laminar calcretes. Spherulites are about 100  $\mu\text{m}$  in diameter and show fibro-radial textures (example in Fig. 6G). They tend to occur at the very top of calcretes (Alonso-Zarza et al., 1998b) or in very superficial carbonate crusts (Verrecchia et al., 1995). Spherulites have been grown experimentally and their formation seems to be related to cyanobacterial mats often requiring direct light exposure, meaning they have to form at the calcrete–atmosphere interface.

The formation of these laminar calcrete horizons has been widely discussed in recent years (Verrecchia et al., 1995; Wright et al., 1996; Freytet et al., 1997; Alonso-Zarza, 1999), and there is a large consensus that they be

interpreted as rootcretes (Jones, 1992) or rhizogenic calcretes (Wright et al., 1995) since it is commonly accepted that the main agents responsible for their

formation are horizontal root systems (Mack and James, 1992; Wright, 1994). However, cyanophyceae (Vogt, 1984) or cyanobacteria, (Verrecchia et al.,



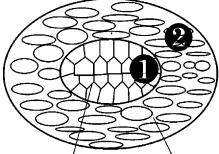
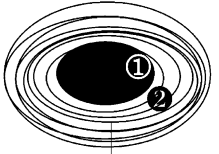



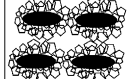


Location	Paracuellos	Villacadima	Viñegra
Calcified Zones	Medulla & Cortex	Cortex	Mucilaginous sheets in roots
Root Structure			
Cell structure	 		
 <b>Increasing root decay &amp; fungal activity</b>			

Fig. 7. Sketch of the different types of calcification in roots. Black areas represent the porosity. 1. Medulla of the root, 2. Root cortex. Reprinted from Alonso-Zarza (1999).

1995), bacteria, fungi (Verrecchia and Verrecchia, 1994) and lichens (Klappa, 1979) may also be important in their formation. In most cases, these laminar calcretes are formed by centimetre scale alternations in which the different laminae may consist of: micritic layers, micritic layers with fine tubiform pores, ooids, detrital grains and clays, and micrite with alveolar septal structure. These alternations reflect the small-scale periods of sedimentation, erosion, and soil formation (Fedoroff et al., 1994) in the upper part of a relatively stable surface, and may indicate climate-vegetation changes (Alonso-Zarza and Silva, 2002). The occurrence of these laminae interbedded with

detrital sediments characterises environments in which sedimentation was low and episodic. Therefore, after detrital sediment input, the surfaces became stable and root mats developed. Renewed sedimentation accounted for the death of the root mats and the development of new laminae on the new surfaces. The result is the occurrence of thin calcrete laminae interbedded within detrital deposits (Alonso-Zarza, 1999). Where sedimentation rates were lower, the laminae tended to amalgamate, and thicker laminae calcrete profiles (Fig. 4C) formed as those described from the western USA (Machette, 1985) or the Pleistocene of the Canary Islands (Alonso-Zarza and Silva, 2002).

Fig. 6. (A) Vertical rhizoliths (arrows) developed in vulcaniclastic deposits from La Palma (Canary Islands). Horizontal calcrete laminae grew between the deposits. (B) Rhizolith with a clear concentric structure, 1. Medulla of the root with complete calcification of the cells, 2. The endodermis is represented by a micritic ring, 3. Cortex of the root; only the cell walls are calcified. The sample comes from the Miocene of the Madrid Basin. (C) SEM image of part of a root in which only the cell walls are calcified (Miocene of the Madrid Basin). (D) Part of a *Microcodium* aggregate (Palaeogene of the Teruel Basin). (E) Root mat formed by alveolar septal structures, which in this case are developed on peloidal microfabrics (Neogene of the Teruel Basin). (F) Laminar calcrete consisting of an alternation of different layers with ooids and silt-size detrital grains (Pleistocene, Canary Islands). (G) Laminar calcrete containing a number of spherulites (arrows). Most of the rounded white structures of this calcrete correspond to spherulites, either isolated or amalgamated (Quaternary, Teruel Basin).

The formation of laminar calcretes by root mats may be favoured by the presence of shallow waterables and thin pondwater films on top of the soil surface. Both can contribute to the lithification of the laminae and to the formation of non-pedogenic structures such as coarse spar calcite cements, to the precipitation of micrite by increased carbonate concentration of the ponded or capillary rise water, and to the calcification of algae and/or cyanobacteria. All these features may obliterate the primary pedogenic features of the laminar calcrete or form carbonate laminae not related to soil processes.

### 3.4. Groundwater calcretes

Groundwater calcretes are non-pedogenic carbonates whose formation is related to shallow aquifer systems (Netterberg, 1969; Mann and Horwitz, 1979). They were initially referred to as “valley calcretes” (Butt et al., 1977) to describe the massive carbonate bodies associated with drainage channels. However, this term may include both pedogenic and non-pedogenic types, so the terms groundwater or phreatic calcretes are generally preferred. These calcretes delineate the trunk valleys of palaeodrainage channels (Arakel, 1986; Nash and Smith, 1998) and are also common in mudflat environments of playa lakes that act as outlets for discharge of regional groundwater (Arakel, 1991), as well as near the toes of large alluvial fans (Mack et al., 2000). In all cases, groundwater calcretes occur in arid to semiarid climates. Climate control their formation for three reasons (Mann and Horwitz, 1979): (1) conditions of continual moisture favours carbonate dissolution, (2) intermittent heavy rain tends to develop better groundwater systems (due to more effective infiltration) than the equivalent rainfall spread over a long period of time and, (3) high evaporation and evapotranspiration rates are essential for chemical precipitation of carbonate. In Western Australia, the active zone of groundwater formation occurs where the water table lies at depths of 2–5 m. In such arid environments, evaporation and evapotranspiration from the water table is insignificant below 5 m.

Groundwater calcretes vary in thickness from several centimetres (Tandon and Gibling, 1997) to several metres (Arakel, 1986). However, the existence of very thick (>10 m) groundwater calcretes (Pimentel et al.,

1996) is unclear since more recently, for example in the Sado Basin, they are considered to be palustrine carbonates (Pimentel and Alonso-Zarza, 1999). The lateral extent of groundwater calcretes is from about a square kilometre to areas more than 100 km long and 10 km wide. Shape is controlled by the drainage topography (Mann and Horwitz, 1979). Groundwater calcretes or dolocretes form as the result of the interplay between cementation, replacement and displacement by calcite or dolomite in these very surficial environments. The mechanisms of carbonate precipitation are mostly evaporation, evapotranspiration, CO<sub>2</sub> degassing and the common ion effect (Wright and Tucker, 1991).

The morphology and characteristics of groundwater calcretes are varied. The most common are the following:

1. Soft carbonate nodules with diffuse boundaries that occur in layers which conform to the stratification of the sediment body, or which even follow stratal planes of channels and mimic the convex geometry of the channel-fill deposits (Khadkikar et al., 1998).
2. Cemented layers forming lenses up to 20 cm thick and 3 m long, locally with vertically elongated nodules (Tandon and Gibling, 1997).
3. Proximal and medial alluvial fan facies as well as fluvial channel deposits cemented by different types of carbonates (Tandon and Narayan, 1981; Nash and Smith, 1998).
4. Thin (30–50 cm) massive beds with an upper fringe of nodules and tubules precipitated at the water table and in the capillary fringe (Mack et al., 2000).
5. Thick (1.5–3 m) massive beds of carbonate deposited by the lateral flow of groundwater or at springs (Mack et al., 2000).
6. Thin calcified root mats have also been included as groundwater carbonates as they may have been developed by phreatophytes in relation to very surficial, perched groundwater tables (Semeniuk and Meagher, 1981).
7. Thin sheets (10–50 cm) in the subsurface of barrier dunes (Purvis and Wright, 1989). These sheets consist of aggregates of CaCO<sub>3</sub> developed just above the water table, so they may transect stratigraphic boundaries and unconformities (Semeniuk and Meagher, 1981).

Several attempts have been made to identify criteria to differentiate between groundwater and pedogenic calcretes (Wright, 1995; Pimentel et al., 1996). In addition, groundwater calcretes may also be confused with palustrine carbonates (Fig. 8). Groundwater calcretes commonly show sharp basal and top contacts. In general, the features they lack—more than the features they have—allow the distinction of groundwater calcretes from these two types of carbonate. Groundwater calcretes are mostly massive bodies lacking any horizonation. No profiles are distinguished. They commonly lack vertical root traces and peds (Mack et al., 2000) and they are not overlain by horizons of translocated clays (Mack and James, 1992). They also lack lacustrine fauna or any indication of carbonate precipitation within a free water body. In marginal lacustrine, distal alluvial and floodplain environments, the distinction between palustrine carbonates, groundwater calcretes and pedogenic calcretes may be very difficult since small changes in the water table cause significant environmental changes. Fig. 8 illustrates how a gradual rise of the water table results first in the modification of previously formed pedogenic carbonates by groundwater pore fluids, and later in the emergence of a free water body on the surface. A further lowering of the water table causes the lacustrine sediments to be situated either in the vadose or phreatic zone. They are modified by either pedogenic or groundwater processes.

The micromorphology of groundwater calcretes is characterised by the absence of biogenic features. They are therefore encased in the so-called “alpha” microfabrics (Wright and Tucker, 1991). Very commonly they consist of crystalline mosaics, with crystals varying in size from microns to millimetres, etched and floating grains, nodules, and variety of desiccation features. The chemistry of phreatic water controls the mineralogy of the groundwater precipitates. In the proximity of the catchment areas, groundwater is commonly fresh and calcite is the main precipitate, but groundwater movement from the catchment down to the playa-lake marginal discharge areas favours their progressive concentration in the water of these near-surface environments (Arakel, 1986). Changes in groundwater chemistry explain the formation of groundwater dolocretes and silcretes towards the inner part of closed basins (Arakel,

1986; Armenteros et al., 1995). Groundwater dolocretes show a wide range of crystal size and include spheroidal (Spötl and Wright, 1992) and zoned dolomite crystals, as well as dolomite with cloudy nuclei (Pimentel et al., 1996). Groundwater dolocrete formation may also be favoured by the mixing of groundwaters and lake brines (Colson and Cojan, 1996) or with sea water (Williams and Krause, 1998).

### 3.5. *Stable isotope geochemistry of calcretes*

The analysis of the stable isotopes of oxygen and carbon in pedogenic carbonates has proven to be a useful tool in the interpretation of terrestrial palaeoenvironments, especially in the reconstruction of palaeoclimates (Talma and Netterberg, 1983; Cerling, 1984), palaeovegetation (Cerling et al., 1989, 1997), and the atmospheric concentration of CO<sub>2</sub> (Cerling, 1991; Cole and Monger, 1994). The recording of stable isotope data in calcretes can be found dating from more than 20 years ago (Salomons et al., 1978; Talma and Netterberg, 1983; Salomons and Mook, 1986), with the range of data still valuable despite the quantity available in more recent literature. In these compilations, calcrete  $\delta^{13}\text{C}$  values vary between  $-12\text{‰}$  to  $+4\text{‰}$ , whereas the  $\delta^{18}\text{O}$  values ranges from  $-9\text{‰}$  to  $+3\text{‰}$ . In general, variations in  $\delta^{13}\text{C}$  are much wider than those of  $\delta^{18}\text{O}$  (Talma and Netterberg, 1983; Ding and Yang, 2000). Both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  are strongly dependent on the depth in the profile at which the samples are obtained, decreasing rapidly with depth to become almost constant at 10–50 cm below the soil–air interface (Quade et al., 1989).

The  $\delta^{13}\text{C}$  values of carbonates formed within soil horizons at depths below 30 cm depend on the isotopic composition of the soil CO<sub>2</sub> (Quade et al., 1989). In turn, this is controlled by the relative proportion of plants that use the C<sub>4</sub>+CAM and C<sub>3</sub> photosynthetic pathways, the density of vegetation cover and consequent soil-respiration rate, and the amount of atmospheric CO<sub>2</sub> that penetrates the soil (Cerling, 1984; Amundson et al., 1988; Mack et al., 2000). C<sub>3</sub> plants (trees, most shrubs and cool-season grasses) supply more <sup>12</sup>C than C<sub>4</sub>+CAM, giving rise to lower  $\delta^{13}\text{C}$  values than when vegetation covers are dominated by C<sub>4</sub> plants. Dense vegetation covers also contribute to lower  $\delta^{13}\text{C}$  values by increasing the respiration rate and decreasing the amount of atmos-

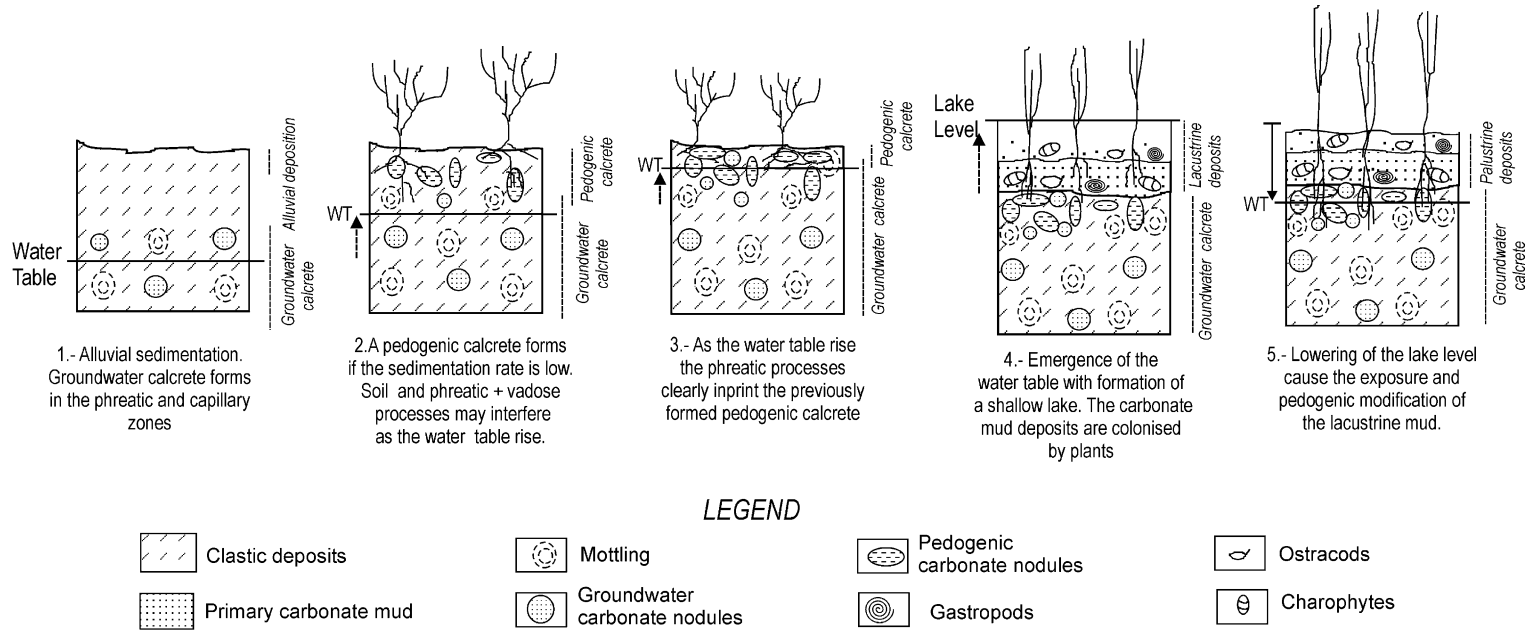


Fig. 8. Sketch of a complete cycle of rise-lowering of the water table in a distal alluvial and/or floodplain environment. Superposition of groundwater and pedogenic calcretes is common. Both may modify the lacustrine deposits.



pheric CO<sub>2</sub> that penetrates the soil (Quade et al., 1989). This, together with the presence of more C<sub>4</sub>+CAM plants at lower elevations, explains the systematic decrease in the  $\delta^{13}\text{C}$  of pedogenic carbonates with increasing altitude in the Great Basin of the United States (Quade et al., 1989).

The oxygen isotope composition of calcretes is directly related to that of the meteoric (rain) water from which they formed, with some alteration caused by selective infiltration and evaporation, plus a small temperature effect (Talma and Netterberg, 1983; Cerling, 1984). The  $\delta^{18}\text{O}$  values are sensitive to climatic conditions. In arid zones (annual rainfall <250 mm), values of  $\delta^{18}\text{O}$  lower than  $-5\text{‰}$  do not occur, and areas receiving less than 350 mm have  $\delta^{18}\text{O}$  values greater than  $-2\text{‰}$  (Talma and Netterberg, 1983). Monsoon climates may account for especially light rainwaters with the resulting pedogenic carbonates showing values up to 6‰ lower than carbonates of non-monsoon climates in the same areas (Andrews et al., 1998). The  $\delta^{18}\text{O}$  of rainwater and pedogenic carbonates systematically decreases with increasing altitude (Quade et al., 1989).

A positive covariation of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  is common, but is not always observed. This may be explained by the consequences of climatically induced changes. In climates with fluctuating aridity, the most arid conditions favour an increase of C<sub>4</sub> plants, together with a decrease of soil respiration rates, which in turn allows the input of greater amounts atmospheric CO<sub>2</sub> into soil profiles (Cerling, 1984; Alam et al., 1997; Andrews et al., 1998).

Stable isotope data of pedogenic carbonates are undoubtedly valid in the reconstruction of ancient environments. Kleinert and Strecker (2001) have indicated that changes in isotopic values of pedogenic carbonates respond to changes in regional climate caused by the uplift of the Eastern Cordilleras in Argentina. This progressive uplift occurred during the late Neogene and caused a rain-shadow effect, inducing stages of aridification in which C<sub>4</sub> plants were dominant. Nevertheless, isotopic data must be interpreted with care, since many factors interplay with one another. For example, isotope data of groundwater calcretes also can give information about the degree of modification that meteoric waters have undergone, and on the possible mixing with marine or burial fluids (Talma and Netterberg, 1983). Some-

times, for the same area, pedogenic and groundwater carbonates may show similar isotope values (Mack et al., 2000). Further, changes in vegetation may not only be related to climate. Variations in atmospheric CO<sub>2</sub> levels may also induce changes in the relative amount of C<sub>3</sub>/C<sub>4</sub> plants (Cole and Monger, 1994), with C<sub>3</sub> plants favoured under higher levels of atmospheric CO<sub>2</sub>. Special care must also be taken to avoid contamination with detrital carbonate components of the host rock, the “limestone dilution effect”, and the possible influence of diagenesis. Depth within the profile must also be considered (Talma and Netterberg, 1983; Cerling, 1984; Quade et al., 1989). When these factors are taken into account, stable isotope analysis is undoubtedly valid, especially for the study of specific areas where all geological data are well constrained (see the work performed by Wright and Alonso-Zarza (1992) in the Miocene of the Madrid Basin, by Mack et al. (2000) in the Pliocene–Pleistocene of the Palomas Basin, or by Tandon and Andrews (2001) in the Maastrichtian of India). In these and many other studies, the overall geological and geochemical data has been a good approach towards understanding ancient environments.

The carbon isotope composition of palaeosols has also been used to estimate atmospheric  $p\text{CO}_2$  values, the initial model being proposed by Cerling (1991). Later studies have concentrated on different geological times from the Palaeozoic (Mora et al., 1991, 1996) to the Tertiary (Sinha and Stott, 1994), or have tried to envisage the overall development of  $p\text{CO}_2$  values from as far back as 400 million years ago (Cerling, 1999; Ekart et al., 1999). The general trend shows high values (2000–4000 ppm approximately) during the late Palaeozoic, low values in the Permian (about 1000 ppm), high again during most of the Mesozoic (2500–5000 ppm approximately), and low once more during the Tertiary (less than 1000 ppm).

### 3.6. Environmental control on the development of calcretes

Most calcretes are pedogenic, therefore the environmental factors that operate in their formation are the same as that for any soil. Jenny (1941), in his classic study, considered five main factors controlling soil development: climate, parent material, organisms, topographic relief, and time. The evaluation of the

effects of any of these factors in a soil requires its isolation by analysing those cases where the other factors are constant and independent of one other. This approach has many problems. For example, it may be difficult to find situations in different climates showing uniform vegetation (Retallack, 2001). Nevertheless, each of these factors has a recognisable effect on the soil, so it is possible to understand the complex and multiple processes that operate in soil formation (Yaalon, 1975; Retallack, 1998). The soil formation processes approach proposed for the study of modern soils provides useful information and a solid framework for understanding the palaeoenvironmental controls that operated in ancient soils. However, it cannot be applied directly to palaeosols for several reasons: information about ancient palaeoenvironments may not be good enough, many ecosystems have changed over geological time, the preservation of the soil's properties may have been deleted by diagenesis or erosion, information of the absolute time of soil formation or climate is difficult to obtain, and even factors such as relief and time may be clearly dependent in fossil soils. Taking these considerations into account, the main factors controlling calcrete formation, and therefore how calcretes and the features they present can be used as palaeoenvironmental indicators, are discussed below.

### 3.6.1. Climate

Classically, a close relationship between climate and calcrete formation has been recognised (Goudie, 1973; Birkeland, 1984), despite the fact that climate is not the only forming factor. The accumulation of calcium carbonate in the B horizon of soils leading to the production of calcretes is the main pedogenic process that occurs in the dry subtropical zone (Mack and James, 1994), which is characterised by an annual precipitation of less than 100 cm/year, and by seasonal differences in temperature (Strahler and Strahler, 1992). Calcrete distribution seems to be favoured by rainfall averages below 500–600 mm/year (Goudie, 1973; Birkeland, 1984), although they may form under less dry conditions (Strong et al., 1992). In Tanzania, for example, calcretes occur up to the 750 mm isohyet, while in the Pampas and Chaco of South America, calcretes extend into zones of over 1200 mm/year (Goudie, 1973). In short, the upper boundary mean annual precipitation for calcrete formation can

span values from 600 to 1000 mm/year (Mack and James, 1994). The lower boundary may be as low as 50 mm/year (Goudie, 1973; Retallack, 1994).

Data on average rainfall may be obtained from calcretes by studying the specific features they present and the mineralogy of the clays they contain. According to Khadkikar et al. (2000), calcretes associated with sepiolite/palygorskite are indicative of an arid climate (mean annual rainfall of about 50–100 mm). When associated with soils containing oxidised iron, montmorillonite and illite they probably indicate semiarid climates (100–500 mm/year). If associated with vertisols containing montmorillonite and illite, they probably formed under sub-humid climates (500–700 mm/year).

Quantitative data on mean rainfall can be obtained by analysing the depth to the calcic horizon, since this reflects the depth of wetting of the soil by available water. In drier regions, the calcic horizon is closer to the surface than in wetter regions. Different relationships have been obtained since the early studies of Jenny (1941). More recently, Retallack (1994) compiled data from 317 Quaternary soils to obtain the following equation:

$$P = 139.6 - 6.388D - 0.01303D^2$$

$P$  is the mean annual precipitation in mm and  $D$  the depth to the soil carbonate horizon. The equation has a correlation coefficient of 0.79 and a standard error of  $\pm 141$  mm. This relationship is only valid for soils of moderate development (nodules of carbonate rather than layers) in unconsolidated parent materials. It is also applicable to soils and palaeosols of seasonal warm climates. The depth is measured to the horizon with abundant nodules and within the low points of gilgai microrelief (Driese et al., 2000; Retallack, 2001). It is not valid for well developed calcretes or dolocretes (Retallack, 2000). The equation has three main problems: (1) erosion at the top of the soil may induce incorrect measurements; (2) there may be compaction, which may be solved by using standard equations from geological estimates of burial (Caudill et al., 1997); and (3) the higher past levels of  $\text{CO}_2$  in the atmosphere seem to create deeper calcic horizons (McFadden et al., 1991). This last problem, however, is important only in periods of extreme greenhouse effect such as the Jurassic–Cretaceous, Ordovician–

Silurian and perhaps the early Precambrian (Ekart et al., 1999).

There is no general agreement on the validity of this equation. Recent work on 1168 modern soil profiles has found no correlation between mean annual precipitation and the depth to the top of the carbonate horizon. However, a significant correlation has been found between the presence of carbonate horizons and mean annual precipitation below 760 mm (Royer, 1999).

When analysing sedimentary sequences containing calcretes, periods of calcrete formation have very often been considered relatively more arid, with clastic sedimentation tending to occur in wetter periods. Nevertheless, there are many examples in which calcretes represent the relatively more humid periods within an arid to semiarid climate. The Negev contains examples where horizons containing carbonate nodules formed during the warmer and wetter periods of the last glaciation (Goodfriend and Magaritz, 1988). Calcretes of the Pleistocene of the Ebro basin (Sancho and Meléndez, 1992), and Lanzarote and Fuerteventura in the Canary Islands, also represent relatively wetter periods during which some vegetation was able to develop (Alonso-Zarza and Silva, 2002).

### 3.6.2. Parent material and source of carbonate

Calcretes can form on any type of host rock. However, it seems that its chemical composition can favour and accelerate calcrete formation processes. The host rock is important since it may be a source for  $\text{Ca}^{+2}$ . Many calcretes are developed on top of highly calcareous rocks and sediments, such as in the Carboniferous of England (Adams, 1980) or the Pleistocene to Holocene calcretes from Barbados (James, 1972). There are also many examples of calcretes developing on basic volcanic rocks; some minerals they contain are very rich in calcium (Goudie, 1973). However, the carbonate necessary for calcrete formation often comes from far away as  $\text{CaCO}_3$  dust, water-soluble Ca in that dust, or Ca dissolved in the rain (McFadden and Tinsley, 1985; Monger and Gallegos, 2000). These sources of carbonate have been considered atmogenic soil carbonate, and include the  $\text{Ca}^{+2}$  derived from non-carbonate rocks. Carbonates formed by dissolution and reprecipitation of primary carbonate rock fragments are included in the lithogenic soil carbonates (Monger and

Gallegos, 2000). In short, the type of host rock is not a pre-requisite for calcrete formation, but the formation of calcretes seems to be faster when  $\text{Ca}^{+2}$  availability is higher (Wright, 1990b).

The parent material is not only important as a source of  $\text{Ca}^{+2}$ . Apart from composition, grain size may also be important. For example, in detrital host rocks, all stages of calcrete development form more rapidly on gravel host rocks than on non-gravelly sediments (Gile et al., 1966).

### 3.6.3. Vegetation and soil organisms

Vegetation and soil organisms control calcrete development but, at the same time, calcrete also has an important effect on soil ecosystems. The relative impermeability of the hardpan, the presence of very shallow soft soil layers, and the carbonate composition of the calcrete lead to distinctive vegetation patterns and types (Goudie, 1973). Calcretes commonly support a sparse vegetation cover including a wide variety of plants such as grasses, trees and shrubs. A wide list of species characteristics of calcretes has been compiled by Goudie (1973). Many are xerophytic, but not all, and root development may vary from horizontal (Wright et al., 1988) to more vertical and penetrative (Rossinsky et al., 1992). Large plants are the most obvious contributors to soil formation, but microflora and soil fauna must also be considered when analysing this factor of soil formation.

Soil vegetation and fauna provide organic matter to the soil. Microbial decomposition releases  $\text{CO}_2$  that controls the dissolution and precipitation of carbonate. Pedogenic carbonate is easily precipitated through the activity of living organisms (Lal and Kimble, 2000). This is shown by the biogenic microfabrics commonly recognised in calcretes (see above), which are formed in relation to soil microbes such as fungi, bacteria, lichens (see, for example, Klappa, 1979; Verrecchia and Verrecchia, 1994), and plants (Semeniuk and Meagher, 1981; Alonso-Zarza, 1999; amongst many others). The fauna may also contribute to carbonate precipitation in soils, e.g., termites build mounds that contain more  $\text{Ca}^{+2}$  than adjacent soils (Monger and Gallegos, 2000). In short, both soil flora and fauna notably contribute to calcium precipitation within the soil, accelerating the rate of calcrete formation.

Calcretes contain a wide record of the activity of fauna and flora within the soil. This is important for

the reconstruction of ancient landscapes, even though many times only trace fossils and specific structures rather than whole organisms are preserved. The study of these trace fossils, such as those of insect associations now included in the *Coprinisphaera* ichnofacies (Genise et al., 2000), or the morphology and characteristics of root traces (McCarthy et al., 1998), undoubtedly offer important data on ancient soil ecosystems. In the case of microbes and plants, it is often difficult to know exactly the type of plants that lived in the calcrete. Nevertheless, important data can be obtained from the study of different features: (1) the relative amount of C<sub>3</sub> versus C<sub>4</sub> plants may be known through the  $\delta^{13}\text{C}$  composition of the soil carbonate (Cerling, 1991); (2) the location of ancient water tables may be indicated by the presence of thin sheets of laminar calcretes resulting from the development of horizontal root-mats (Semeniuk and Meagher, 1981; Mack et al., 2000); (3) the presence of a mollic epipedon is deduced by the granular ped structure and fine root networks (Retallack, 1991); and (4) data on seasonality can even be obtained through the analysis of the distribution of root traces (dense near-surface networks of fine roots are active during the wet period, whereas in drier times, few but deeply penetrating roots develop) (Retallack, 1991).

#### 3.6.4. Relief

As with most soils, the development and characteristics of calcretes vary depending on the topography and drainage conditions. Catenas are group of soils with similar parent materials, developed under similar climates but with different characteristics related to variations in relief and drainage.

Topography controls the morphology and stage of development of calcretes (Milnes, 1992). In Israel (Dan, 1977), calcretes that have developed on hillcrests and slopes lack the laminar horizon, whereas downslope the calcretes are thicker and show this feature (Yaalon and Singer, 1974). In the southern area of the Madrid Basin, the Miocene–Pliocene boundary is marked by a wide exposure surface affecting folded Miocene limestones on which different types of sub-aerial exposure profiles developed, depending on the inherited topography. Karstic processes operated on the anticline crests, whereas different types of calcretes (from laminar to brecciated) formed on the synclines (Sanz, 1996). The catenary

relationships are especially important in floodplains where there are differences in topography and hydrology between the alluvial ridges and floodplain areas. The ridges are slightly above the water table, and relatively well-drained immature soils may form. In contrast, in the topographically lower areas of the floodplain, drainage is poor and soils are typically poorly drained (Wright, 1992). This catenary relationship in floodplains commonly results in an increase of gleying (Fastovsky and McSweeney, 1987) and/or a decrease in leaching (Arndorff, 1993) with distance from the channels.

Lateral variations in the low-relief plain of the Maastrichtian of India (Tandon and Andrews, 2001) are also the result of small-scale topographic differences. Palustrine limestones were deposited in shallow lakes of topographic lows, whereas brecciation and shrinkage resulting in calcrete formation occurred on the highs. Groundwater calcretes formed in sandy facies where the water table was in the shallow subsurface.

#### 3.6.5. Time

The degree of development of calcretes is clearly controlled by the time they have had to develop, which is recorded in the morphological stages previously described. Several attempts have been made to determine the absolute time of formation of calcretes, but currently most figures are relative and have to be used with care. The rate of formation of calcretes varies depending on factors other than time (Wright, 1990b). Some estimations of calcrete formation time are given by Gile et al. (1966) and Machette (1985), although there are many others. Unfortunately, these “numbers” have often been applied to other basins without taking into account the possible differences in specific geological settings. Although not dealing specifically with the real time of formation of calcretes, good data for dating sedimentary sequences and geomorphic processes can be obtained through the U/Th ratios of nodular and massive calcretes (Kelly et al., 2000), or the U/Pb of mud-rich carbonate palaeosols (Rasbury et al., 2000).

Calcrete formation depends on the relationship between sedimentation and erosion rates, and the actual calcrete formation rate (Alonso-Zarza et al., 1998a). Like any other type of soil, calcretes form—though particularly easily—in weakly degradational

or weakly aggradational regimes (Allen, 1989). Floodplains are the sites where most studies have been performed on calcrete development as a response to variations in the rate of flood sediment accretion. In areas or periods in which the sedimentation rate is low, the residence time of the sediment in the active zone of soil formation is high (Wright, 1992), and relatively well developed calcrete profiles form. Higher sedimentation rates favour weak or no calcrete development. The presence or absence of a particular genetic stage of calcrete may be used as a rough estimate of ancient flood basin accretion rates (Leeder, 1975). Kraus (1999) also indicates that when erosion is insignificant, the variation in palaeosol types is a response to the type and rate of sedimentation versus the rate of pedogenesis. If sedimentation is rapid and unsteady, weakly developed and vertically stacked profiles separated by minimally weathered sediment (compound palaeosols) form. Vertically successive profiles may partially overlap (composite palaeosols) if the rate of pedogenesis exceeds the rate of sedimentation. If sedimentation is steady, thick cumulative soils can form (Kraus, 1999); thick laminar calcretes are a good example of this situation (Alonso-Zarza et al., 1998a). Wright and Marriott (1996) have elaborated a quantitative and more sophisticated model to estimate the rates of floodplain aggradation using calcretes. These authors consider that the residence time of the sediments in the zone of active pedogenesis is controlled by the frequency of the depositional events and by the thickness of sediment deposited in each event. Both can be represented in a plot to obtain different stages of pedogenic development. The plots do not allow absolute estimation of sedimentation rates but crude ranges of likely deposition rates, which can be used to interpret ancient floodplain sequences.

In alluvial basins, the sedimentation rate, which is an autogenic process, decreases across the floodplain with distance from the channel. The sedimentation rate may, however, also vary in relation with allogenic causes such as the accommodation space available or the tectonic regime of the basin. Both types of process are reflected in the soil type and the degree of development within a specific sedimentary basin (Wright and Alonso-Zarza, 1990; Alonso-Zarza et al., 1992b).

Autogenic processes are those responsible for the pedofacies relationship. Pedofacies refers to “laterally

contiguous bodies of sedimentary rocks that differ in their contained laterally contiguous palaeosols as a result of their distance (during formation) from areas of relatively high sediment accumulation” (Bown and Kraus, 1987). The pedofacies relationship explains why areas near the alluvial ridges have thick poorly developed palaeosol profiles, whereas more distal floodplain areas commonly exhibit different types and better developed soil. Pedofacies relationships have been recognised in many ancient alluvial sequences (Bown and Kraus, 1987; Smith, 1990) and seem to be appropriate for overbank deposits (Kraus, 1997). However, they have not been seen in all floodplain palaeosol successions (Wright, 1992). Three main causes may explain the lack of pedofacies relationships in floodplain settings: (1) very low sedimentation rates may favour soils reaching the steady state, thus erasing pedofacies variations (Kraus, 1999); (2) floodplain aggradation may not only be formed by real overbank deposits but also by deposition of laterally extensive crevasse-splay lobes (Behrensmeyer et al., 1995) or by the deposition of significant fine-grained sediments (Smith, 1990) or even by sheet-floods containing pedogenic mud aggregates; and (3) in poorly drained soils, the intensity of soil development may mask the lateral variations in maturity (Kraus, 1997), and soil properties are more directly controlled by hydrology than by the duration of development, which is more a catenary than a pedofacies relationship.

The palaeosol characteristics within a specific alluvial basin may also reflect changes in the accommodation space that are a response to updip changes in the subsidence rate, possible down dip eustatic effects (McCarthy et al., 1999), and climate (Shanley and McCabe, 1994). The interplay of these three factors (tectonism, climate and eustasy) makes the establishment of unique models of sequence stratigraphy in terrestrial basins very difficult. Wright and Marriott (1993) proposed a simple architectural/pedogenic model for a fluvial sequence deposited during a third order scale base-level fall–rise, in which the only autogenic control is eustasy. During lowstands, well-developed and well-drained soils form on the terraces produced by channel incision. In the initial stages of the transgressive system tract, the rate of creation of accommodation space is low, which favours the development of hydromorphic soils. A

later rise in sea level accounts for the formation of weakly developed soils, but which are well-drained since the increased accommodation rate leads to high levels of storage of floodplain sediments. During the highstand, phase accommodation is reduced and floodplain accretion rates drop, favouring better developed soils. This model may be considered a first approach to the establishment of detailed sequence stratigraphy in terrestrial basins, but has to be improved by taking into account the position of the system tracts in the basin, and testing it in areas where there are coeval marine and nonmarine strata (Shanley and McCabe, 1994). A realistic application of palaeosols to the understanding of sequence stratigraphy and floodplain development is the McCarthy et al. (1999) study of the Cenomanian of British Columbia. Here, the higher frequency sequence boundaries are represented by valleys and interfluves. The lower and middle parts of the valley sequences are characterised by coals and lake deposits that probably reflect the highest rates of accommodation, representing “late transgressive” and early highstand systems tracts. Lower accommodation rates in the “late highstand” system tract favours pedogenic modification of the upper part of the sequences. Interfluve surfaces record sediment bypass and erosion during “falling stage”, “lowstand” and “early transgressive” systems tract times.

When it is possible to isolate other allogenic factors, tectonism also controls palaeosol characteristics by its influence on the sedimentation rate and by generating different geomorphic settings. In the study of the Capella Formation in the Spanish Pyrenees, Atkinson (1986) showed that variations in the subsidence rate along the basin caused important differences in the rate of floodplain aggradation, and therefore in the maturity of the palaeosols. The morphology of the basin may also be reflected in the palaeosols. In the southern Rio Grande, rift symmetrical basins contain stage II and III palaeosols that are laterally continuous, and about five times more abundant than in asymmetrical basins, where palaeosols lack well-developed horizons and consists mostly of spaced rhizoliths (Mack and James, 1993). In the Triassic of the Iberian Ranges in Spain (Alonso-Zarza et al., 1999), carbonate palaeosols developed on the footwall are scarce and well developed (Stage V), whereas in the hanging wall the number of palaeosols

is higher though they are less mature (up to Stage III). Differences in the characteristics of palaeosols developed on the footwall or hanging wall not only concern maturity. Mack et al. (2000) found that authigenic carbonates in general—and carbonate palaeosols in particular—formed in footwall-derived alluvial fans, show higher  $\delta^{13}\text{C}$  values than those formed in hanging walls. This may reflect differences in vegetation types and/or density.

Calcretes, and indeed any other type of palaeosols, are also commonly associated with unconformities. Therefore, they can often be used as sequence boundaries (McCarthy and Plint, 1998) in nonmarine deposits. The maturity of the palaeosols may give an idea of the type and range of the sedimentary discontinuity. Etthenson et al. (1988) described mature and thick caliche profiles on disconformities related to times of important tectonic activity or regional regressions, and less mature profiles related to local regressions, in the Mississippian of the Appalachian. In the southern Madrid Basin, a thick laminar calcrete profile represents the boundary between the Pliocene and the Quaternary (Sanz, 1996). The calcrete formed in different stages of erosion, sedimentation, and calcretisation represents an important period of relative stability within the basin previous to the entrenching of the Quaternary river systems.

#### 4. Summary and conclusions

##### 4.1. Main differences between pedogenic calcretes, groundwater calcretes and palustrine carbonates

The terrestrial carbonates analysed in this paper are a unique example of the interplay between sedimentary, pedogenic, and diagenetic processes. These processes often may occur so close together in time and space that it is difficult to establish boundaries between them. The result is a continuum between pedogenic and groundwater calcretes and palustrine carbonates. Three main factors have to be analysed when trying to distinguish among these terrestrial carbonates:

(1) The position of the water table. Pedogenic calcretes are commonly well-drained soils. They may be affected by the capillary rise from the water table, but they form most clearly above the water table. Groundwater calcretes form in the area of influence

of the water table, either in the vadose or phreatic zones. Palustrine carbonates form when the water table emerges to constitute a water body subjected to intermittent desiccation. This sequence of carbonates—pedogenic calcretes → groundwater calcretes → palustrine carbonates—represents the sequence of elevations of the water table. In many cases the textures are very clear and there is no problem in interpretation. However, when the rise in the water table is progressive (as commonly occurs in floodplains and distal mudflats), it may be difficult to establish the exact boundaries and to know when the precipitation of carbonate was pedogenic (in pedogenic calcretes) or diagenetic (mostly in groundwater calcretes), or took place in a water body (palustrine carbonates). All three cases deal with surficial groundwaters close to the topographic surface and not with deeper waters. These carbonates are therefore very surficial: either sedimentary, pedogenic or diagenetic products.

(2) The host rock clearly controls the formation of these carbonates. Palustrine carbonates necessarily form on previously lacustrine host rocks. Calcretes, either pedogenic or groundwater, may form on any type of host rock, although they develop faster on carbonate host rocks.

(3) Sub-aerial exposure is needed to form pedogenic calcretes and palustrine carbonates. The duration of sub-aerial exposure for palustrine carbonates may be as short as a season, since it is only needed to modify the previously deposited lacustrine carbonate. However, more time (years to millions of years) is needed for the formation of pedogenic calcretes. An index of sub-aerial exposure has been proposed for terrestrial carbonates (Plat and Wright, 1992). Calcretes form when the index is 100%, whereas palustrine carbonates may form at indices lower than 50%. Groundwater calcretes do not really need any exposure as they form in the subsurface. However, thick groundwater calcretes are easily formed on stable surfaces as the water table may occupy the same position for long periods of time.

#### 4.2. Palaeoenvironmental significance

Palustrine carbonates and calcretes are good records of the palaeoenvironments in which they formed. Climate and vegetation are important controls in the formation of both calcretes and palustrine

carbonates. Semi-arid climates are favourable to both; more arid climates are more favourable for calcretes, whereas sub-humid climates are also suitable for palustrine carbonates. In primary carbonates,  $\delta^{18}\text{O}$  values, and the depth of the pedogenic carbonate horizon may be good indicators of climatic conditions. Vegetation controls the formation of both palustrine carbonates and calcretes at macro- and micro-scales. Data on vegetation may be obtained through the study of the macro- and micro-fabrics, but it is also recorded in the  $\delta^{13}\text{C}$  values of these carbonates. Low  $\delta^{13}\text{C}$  indicates the dominance of  $\text{C}_3$  plants, whereas heavier values indicate environments dominated by  $\text{C}_4 + \text{CAM}$  communities. The carbon isotope composition of palaeosols has also been used to estimate atmospheric  $p\text{CO}_2$  values dating from the Phanerozoic, and therefore may provide data on the development of the atmosphere.

Both calcretes and palustrine carbonates are widely spread over floodplains and the distal areas of alluvial basins. Their presence is a good indicator of periods and/or areas of reduced clastic input, and they may be used as indicators of the rate of aggradation of the floodplain. This is especially important in the case of calcretes. Sedimentary sequences containing both calcretes and palustrine carbonate also record different tectonic regimes in the basin. Gradual transitions from calcretes to palustrine carbonates indicate a progressive rise of the water table, whereas sharp contacts of palustrine carbonates with the underlying floodplain sediments may suggest destabilisation of the base level due to tectonic pulses. At basin scale, the arrangement of these carbonates in the overall infill of the basin has been used for stratigraphic analysis, either because they (especially calcretes) may be indicators of sequence boundaries or because their characteristics reflect different accommodation rates during basin infill.

In summary, calcretes and palustrine carbonates are two types of terrestrial carbonate whose formation is controlled by so many factors that their correct study, plus that of the features they contain, offers invaluable data on ancient terrestrial palaeoenvironments. In recent years, interest in them has increased notably, but more work is needed to reach the degree of understanding already attained with marine carbonates. Recently, it has become of special interest to reach a general model for sequence stratigraphy in

terrestrial basins, and this must necessarily include these types of carbonates.

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