MORPHOLOGY, COMPOSITION AND GENESIS OF QUATERNARY CALCRETES FROM THE WESTERN MEDITERRANEAN : A PETROGRAPHIC APPROACH

VOLUME I

by

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TO

MY MOTHER AND FATHER

AND TO

THE MEMORY OF DONALD

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ABSTRACT

Near-surface and surface accumulations of pedodiagenetic calcium carbonate known as calcrete or caliche, are distinctive and widespread terrestial deposits throughout the western Mediterranean regions. Field studies, carried out in the Mediterranean coastal regions of mainland Spain and on the Balearic Island of Ibiza, reveal that Quaternary (Pleistocene to Recent) calcretes form within any host material in the subaerial vadose environment. Quaternary calcretes from the western Mediterranean are the product of pedogenetic and diagenetic processes (pedodiagenesis) which are responsible for the modification or obliteration of precursor fabrics, textures and structures of the host substrate and the production of new, diagnostic fabrics, textures and structures.

Fully developed calcrete profiles comprise, from the uppermost horizon downwards, calcrete hardpan, sheet calcrete, glaebular horizon, chalky calcrete, transitional horizon and unaltered host material. Climate, topography, host material, organisms and time govern the initiation, development and regional distribution of calcrete profiles.

Characteristic macromorphological features, namely, planar laminations, glaebules, rhizoliths, brecciation textures and tepee structures, provide field criteria for the recognition of calcretes. Higher plant root systems are responsible for the formation of rhizoliths, brecciation textures and tepee structures. Some glaebules and planar laminations are related to the physiological and biophysical activities of higher plant roots. Rhizoliths are land plant root-mineral structures which comprise rhizocretions *s.s.*, root casts, root tubules, root moulds and root petrifactions. Biophysical activities of roots form rhizo-breccias and tepee structures. The growth in girth and increase in number of roots exert pressures sufficient to fracture indurated calcrete and force blocks apart. Rhizo-brecciation, together with gravitational instability, are

adequate mechanisms to account for non-tectonic disturbance of indurated calcrete profiles.

Optical and scanning electron microscopical observations indicate that higher and lower plants play an important role in the formation of microfabrics, textures and structures in calcretes. Hyphantic and banded fibrous carbonate plasma form around roots and within root channels to produce alveolar and vesicular textures. Microchemical staining and X-ray diffraction reveal that non-ferroan low magnesian calcite (LMC) is the dominant and usually exclusive carbonate mineral in all studied profiles. Pedodiagenetic calcite exhibits a wide range of shapes and sizes, from submicron-sized to centimicron-sized grains, displaying equant, bladed and fibrous habits. The major component of calcretes is fine crystic LMC plasma.

Biogenetic carbonate structures record evidence of former biophysical and biochemical activity of soil organisms. In addition to rhizoliths, other biogenetic carbonate structures which provide criteria for the recognition of calcretes include calcified filaments, calcified faecal pellets, Microcodium and lichen stromatolites.

Calcified filaments result from calcite encrustations and/or calcite impregnation of filamentous organic structures. Templates for calcified filaments include fungal and actinomycete hyphae, algal filaments and root hairs of higher plants.

Calcified faecal pellets result from the former activities of indigenous mesofauna. Some clotted textures in calcretes result from pedoturbation. Calcified cocoons provide additional evidence to indicate that the enclosing host material acted as a soil.

The new discovery of Microcodium in Recent soils from south eastern Spain extends its stratigraphical range into the Holocene.

Retention of ultrastructural details suggests an hitherto unconsidered origin for this enigmatic structure, namely calcification of mycorrhizal associations (root-fungus symbiosis).

Crustose lichens are important substrate modifiers and sediment producers. Calcification of crustose lichens produces lichen stromatolites which form laminar layers within subaerially exposed calcrete hardpans.

Recognition of biogenetic carbonate structures within calcrete profiles provides valuable criteria for use in palaeoenvironmental, palaeoecological and stratigraphical reconstructions. Pedodiagenetic calcretes are palaeosols and, thus, indicate continental conditions, cessation of sedimentation, subaerial exposure and time-equivalence.

This study illumines the importance of biolithogenesis within calcrete deposits. Biological activities of soil organisms are responsible for the formation of many macromorphological and micromorphological features in calcretes and provide a basic mechanism for calcrete genesis.

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CHAPTER ONE - INTRODUCTION

Until recently, geologists have chosen to neglect or give only fleeting consideration to the study of calcretes. Commonly dismissed as oddities or, at most, classified under miscellanea in early geological reports, the increasing realization of their significance is now proving to be invaluable in contributing towards the reconstruction of past environments. However, this surge of recent interest in calcretes, which has helped incidentally to compensate for past indifference, has been greater than critical inspection. As a consequence, the term 'calcrete', or one of its many synonyms, has been used as a label, in many cases without foundation.

Before calcretes can be used as reliable tools to help interpret environmental and diagenetic histories, they need to be conceptually defined and correctly identified. In other words, the recent impetus of interest needs to be met with by rigorous examination of what calcrete means, of its constitution, of the criteria that can be used to recognize it and of the processes that brought about its formation. This study is directed towards bridging the disparity between groundless postulation and explicit substantiation with regard to the morphology, composition and origin of calcretes.

PURPOSE

The intention of this study is to document macroscopical and microscopical structures, textures and fabrics of calcretes and, thereby, to establish criteria for their recognition in ancient successions. This approach differs from previous investigations in two fundamental aspects. Firstly, emphasis has been placed on the examination of micromorphological features and the relation of these with macromorphological (field) observations; with the exception of a few pioneer studies (e.g. James, 1972; Esteban, 1974; Read, 1974) microscopical fabrics have been overlooked completely by most workers. Secondly, by establishing diagnostic criteria, actualities rather than supposed possibilities are documented with respect to the origin of calcretes; a review of relevant literature has indicated that intuitive proposals greatly exceed substantive evidence.

PROBLEM OUTLINE

Unfortunately, no systematic scheme for the examination of calcretes by petrographic methods exists. Workers with diverging interests have used different terms to describe the same feature and, in many instances, have used the same term to describe different features. This has occurred in different but related disciplines and even within the same discipline. The need to establish a consistent terminology and reliable criteria for the identification of calcretes is a basic requirement. The present position of calcretes in terms of geological understanding is portrayed in the following statement : "Correct recognition of ancient caliche [sic] is an art and, as with most art, the experts often disagree among themselves concerning the criteria to be used in an evaluation" (Blatt, Middleton & Murray, 1972, p.259). This study, by documenting the macromorphological and micromorphological characteristics of calcretes, at least upgrades the present art to the level of observational science.

PROCEDURAL OUTLINE

Field studies have been undertaken in the western Mediterranean (Fig. 1, p.4) to examine Quaternary calcrete profiles. Assessment, on a regional and local scale, has been made of the factors of climate, topography, host material, vegetation and time.

Samples collected for laboratory analysis have been investigated by optical and scanning electron microscopy. Microscopical examination has been supplemented by microchemical techniques. For a fuller discussion of procedures and methods, see Appendix.

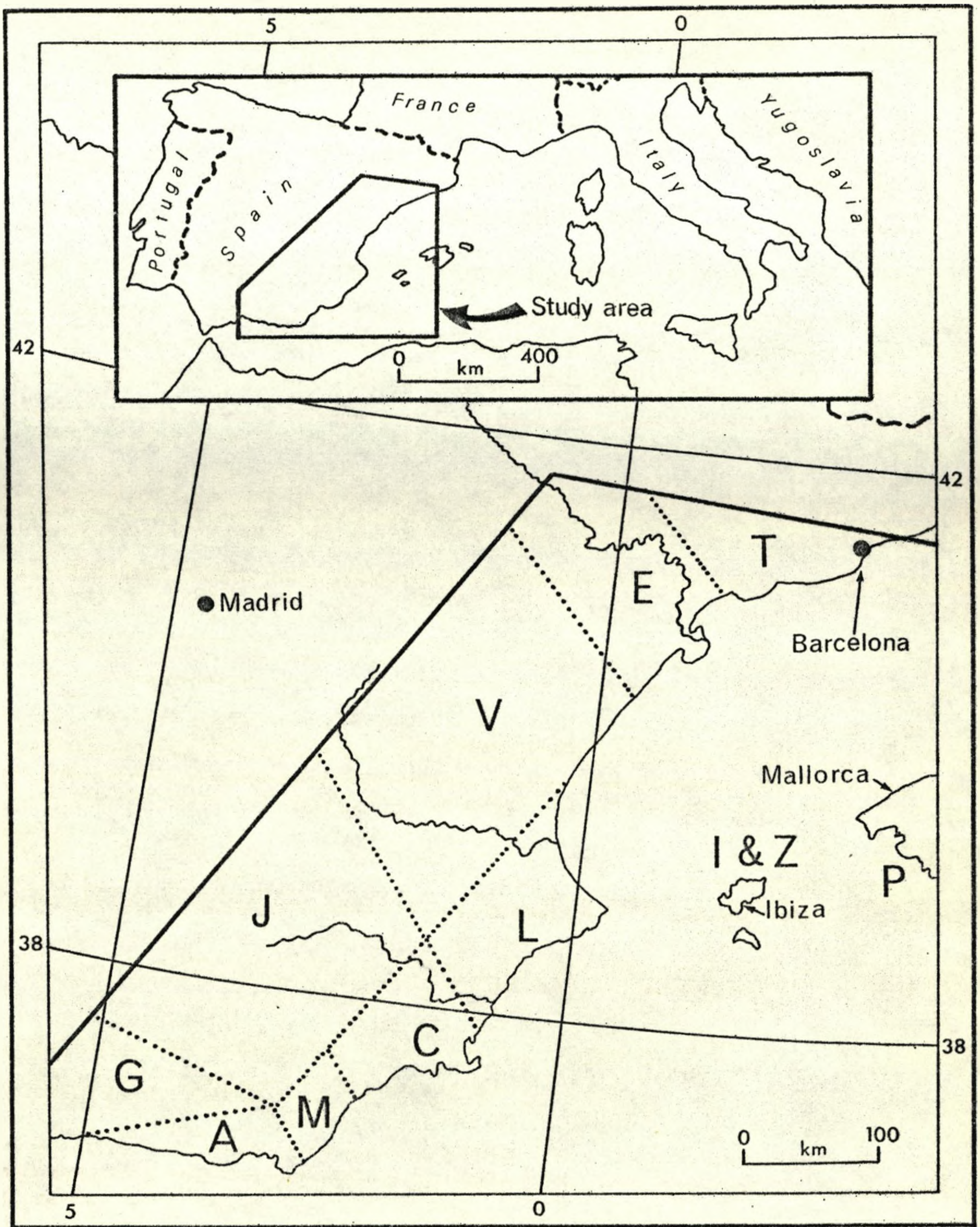
GEOGRAPHICAL LOCATION AND GEOLOGICAL SETTING

The field area can be conveniently divided into two sections: (a) the coastal regions of mainland Spain between Barcelona and Malaga (Fig. 1) and (b) the comparatively small Balearic island of Ibiza (Fig. 1). This natural geographical division bears no relationship to morphological characteristics of calcrete deposits, although some minor distinctions can be made on the basis of substrate differences (Chapter 3).

Mainland Spain

The area of investigation, situated between latitudes 42°N - 86°N and longitudes 3°E - 5°W along the western margin of the Mediterranean Sea, comprises an area of 2.2 x 10^{5} km^{2} (Fig. 1).

Geologically, this area cannot be treated as a single unit. The Iberian Peninsula, as a whole, can be divided into three palaeogeographic zones - the central Meseta block, the epicontinental margins and the geosynclinal depressions (Houston, 1964). Because of diversity of rock types and a complex structural history, generalizations are difficult to make; it will suffice here to divide the geological



Subdivisions of study area

Mainland Spain { T Tarragona
E Ebro Basin
V Valencia

Balearic Islands { P Mallorca

L Alicante
C Cartagena
J Jaén
I & Z Ibiza

M Mojácar
A Almeria
G Granada

Figure 1. Location map of study area - western Mediterranean.

evolution of the Peninsula into three major phases - (1) Hercynian block tectonics, (2) Alpine folding and (3) alternating periods of erosion and sedimentation during the Tertiary.

As with the treatment of geological setting, it is not possible in a few words to give meaningful accounts of climate, vegetation and drainage, and their relationships to the distribution of calcretes. These points are considered in detail later (Chapter 3).

Ibiza

Since this area forms a coherent geographical unit it is treated here in greater detail than mainland Spain as outlined above (p.3).

The island of Ibiza, situated between the latitudes of 39° 6' N - 38° 50' N and longitudes 5° 54' E - 5° 17' E, is an emergent part of the Balearic Platform in the western Mediterranean. The Platform is a shallow submarine topographic feature, elongate NE - SW and approximately 440 km long, which extends from Cape Antonio and the southeastern Spanish Betic margin to the region east of the island of Menorca (Stanley _et_ _al_., 1976). The Balearic archipelago is an extension of the Betic cordillera. Ibiza covers an area of 542 km^2, with a length of 41 km and a width of 21 km. It is composed of three structural units, attributed by Rangheard (1969) to the internal Pre-Baetic. Carbonates (limestones, dolomites, marls) are the dominant lithologies, ranging in age from Muschelkalk (Trias) to Recent. Minor occurrences of igneous rocks (diorites, andesites, trachytes) considered to be Keuper in age (Beauseigneur & Rangheard, 1967), also have been found. All the known terrain between the Muschelkalk and the base of the middle Miocene (Lower Vindobonian) has been involved in an episode of tectonic thrusting. This has given rise to three major thrust sheets aligned NE - SW and dipping to the SE. The topographic expression of the island is a reflection of this tectonic trend, forming NE - SW oriented chains with steep NW slopes and more gently inclined SW slopes. The average altitude is between 200 - 300 m, with the highest point at Atalaya (475 m). Except for the more elevated areas the solid geology is covered by Quaternary sediments and calcareous crusts, including calcrete _s.s._

Towards the centre of the island alluvial depressions can be found, and to the extreme south, a zone of salinas (salt pans). The central depressions and lowlying coastal areas are filled with red silts ('limons rouges'), calcified and calcretized silts, wind deposited calcarenites or aeolianites ('mares') and colluvial (slope) deposits. Exposed limestone surfaces commonly show karstic features such as rillenkarren, kamenitzas and phytokarst. Surface drainage is minimal, Rio de Santa Eulalia being the only perennial river.

Climate and vegetation are of the Mediterranean type. Annual precipitation ranges from 300 - 500 mm. Temperature varies from 33°C (max) in August to 3°C (min) in January (Colom, 1964). Summers are typically hot and dry, while winters are cooler and wetter. Humidity values exceeding 70% are maintained throughout the year.

MAIN ACHIEVEMENTS

Advances made during the course of this work, and discrepancies between this study and previous investigations, have resulted largely because of two basic factors. Firstly, _modern_* calcretes have been studied to gain a better understanding of field relationships, processes and products of formation; it is only these deposits that can

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* Modern = Pleistocene and Recent.

provide reliable criteria for recognition of their ancient counterparts. Secondly, increase in the level of resolution, by using scanning electron microscopy (SEM), has given petrographic insights that are unattainable by other methods of fabric analysis. SEM observations have allowed hypotheses, formulated from observations at lower levels of resolution, to be confirmed or rejected and, moreover, have revealed a bewildering array of formerly unsuspected but significant features within calcrete deposits (Chapters 4 and 5).

Previous investigations, mostly on ancient (fossil) calcretes, have concentrated on physicochemical aspects of calcrete formation. This investigation, by studying modern calcrete from macroscopical to ultramicroscopical levels of observation, demonstrates that biogenetic processes and products are of fundamental importance in determining calcrete morphology. Past neglect of biogenetic aspects may have been due to observation at lower levels of resolution. Alternatively, evidence for biological interference may have been destroyed in ancient calcretes. A cursory examination of ancient calcretes from Spain and the British Isles indicates that biogenetic structures have not been destroyed completely. Thus, the lack of documentation of biogenetic structures within ancient calcretes can be attributed to past oversight rather than absence of evidence.

PLAN OF WORK

Chapter 2 reviews past and prevalent thinking on terminology, definition, classification and genesis of calcrete deposits. This is followed by an outline of my own predilections and recommendations based on the findings of this study.

Chapter 3 is concerned with the morphological field characteristics of calcretes on a regional (100's km^2) and local (m^2) scale.

Chapter 4 provides a microscopical fabric and textural analysis of calcrete deposits, employing both petrographic and soil micromorphological terminology and concepts.

In Chapter 5, microscopical fabric and textural analyses are used to examine calcrete structures, formed by pedogenetic and diagenetic processes, in an attempt to elucidate their origins.

Chapter 6 examines the mineralogy and chemistry of Spanish calcretes by combining petrographic and analytical data gained from laboratory studies.

The first part of Chapter 7 discusses some telogenetic* products which are commonly related to, but not necessarily indicative of, calcrete deposits. The remainder of Chapter 7 describes deposits, superficially similar to calcretes, and provides criteria to help in their recognition.

Chapter 8 synthesizes envisaged processes of calcrete genesis, inferred from observations and data gained from field and laboratory studies, into a conceptual model of calcrete formation.

Finally, Chapter 9 summarizes the results of this study, points out its limitations and makes recommendations for future research.

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* Defined in Glossary, p.445.

CHAPTER TWO - TERMINOLOGY AND CLASSIFICATION

STATEMENT OF PROBLEM

Many attempts have been made to classify calcretes, the number approaching or possibly exceeding the number of terms used to describe them. Classification schemes have been used on a number of considerations such as mode of formation (genesis), parent material, age, composition, morphological characteristics, amount of $CaCO_3$, texture and fabric, degree of induration, geomorphic expression and various combinations of these factors. The geographical widespread distribution of calcretes, the diverging interests of their investigators, the prolific and confusing terminology, and the many theories that have been proposed to account for their origin, all have contributed to the present level of organization - that of chaos. Nevertheless, beneath this camouflage of disorder, various recurring factors of similarity can be recognized. Although synthesis and generalization would ignore outstanding problems of calcrete genesis, composition and morphology, a hint at the level of past and present agreement among workers is given in the résumés that follow.

PREVIOUS INVESTIGATIONS

Terminology

Documentation of calcretes goes back to at least 1840 when Renou described them from Algeria. However, they were not designated as such until 1902 when Lamplugh introduced the term 'calcrete'. The presence of calcretes did not go amiss by such 19th Century celebrities as David Livingston (1857) who described 'calcareous tufa' from south central Africa and Charles Darwin (1890) who described 'tosca' from Argentina. Lamplugh (1902) proposed the term 'calcrete' for sand and gravel beds in the drifts around Dublin, cemented sporadically into hard masses by solution and redeposition of lime through the agency of infiltrating waters. Later, he applied the term to the lime-indurated surficial deposits of Africa (Lamplugh, 1907).

'Caliche', used widely in the Americas and in some Mediterranean countries, is the main rival to the term calcrete. Blake (1902, p.220) reported that the use of caliche in Mexico and southern Arizona referred to calcareous formations "....of considerable thickness and volume found a few inches, or a few feet, beneath the surface-soil, upon the broad, dry, gravelly plains and mesas." Unfortunately, caliche has been used also to describe non-carbonate accumulations. In Chile and Peru, caliche refers to nitrate deposits (W.S.Pitcher, pers. commun.); in California, Hunt & Mabey (1966) used the term caliche to describe gypsiferous deposits. Although Aristarain (1971) advocated the restriction of the term caliche to carbonate accumulations only, the other uses of the term have limited its value. Because of this limitation, Goudie (1972a, 1973) preferred the term calcrete and pointed out its consistency with the parallel terms silcrete, ferricrete, gypcrete, phoscrete, alcrete, magnesicrete and dolocrete, thus providing the basic terminology for duricrusts as suggested by Lamplugh (1902, 1907).

For etymological reasons, calcrete has a slight advantage over the term caliche. Caliche, derived from the Latin calx meaning Lime, is not as informative as the term calcrete, also derived from the Latin calx = lime, together with crescere = to grow. According to Breazeale & Smith (1930), calx was used originally in Spain to designate crusts of lime which flake from plastered walls, or pebbles burned into clay brick.

Phonetically, the term caliche has a 'foreign-air' to many English-speaking geologists and, in addition, frequently is mispronounced. On the other hand, those unfamiliar with the derivation of the term calcrete cannot be blamed for equating calcrete with concrete, implying induration and thereby ignoring soft, powdery forms of calcrete.

For historical reasons, it would be unreasonable to reject previous terminology and establish a new, universally accepted terminology but some terms, listed in Table 1, pp.12-13, are clearly undesirable. For example, 'travertine' and 'tufa' are used in a restrictive, geological sense to describe certain spring deposits. Use of these terms to describe calcrete can only cause further confusion.

Definitions

Calcrete has been defined in various ways; some definitions are usefully restrictive, others are so wide as to become of little value. Some of the more familiar definitions are given below, although their inclusion does not necessarily reflect their worth; they are given to indicate prevalent thinking.

In their study on caliche in southeastern New Mexica, Bretz & Horberg (1949, p.491) reported that ".....the term 'caliche' is applied to calcareous caprocks, soil hardpans, and earthy or porous materials which occur at the surface or at shallow depths below the soil." They advocated a restrictive usage "....to materials of calcareous accumulations......and specifically to those calcareous materials which are formed in the zone of weathering. Subaqueous deposits, spring deposits, and mortar beds thus would be excluded."

TABLE 1. TERMINOLOGY OF CALCRETE

Terms used in various parts of the world as synonyms for calcrete.

TERM	COUNTRY (school of workers in parentheses)	REFERENCE
Akkyrshi	Russia	Strakhov (1970)
Bhata	India	1
Caatinga limestone	Brazil	1
Calcareous crust	Europe; Americas	James (1972)
Calcareous duricrust	Australia; Saudi Arabia	Chapman (1974)
Calcareous laterite	Australia	1
Calcic horizon	USA	Soil Survey Staff (1967)
Calcicrete	England	2
Calcrete	Europe; Africa	Lamplugh (1902)
Calcrust	Morocco	2
Caliche	Americas; Spain	Blake (1902)
Cancar	India	1
Canto blanco	Canary Islands	1
Caprock	USA	Bretz & Horberg (1949)
Carapace calcaire	N Africa (French)	Renou (1840)
Chebi-chebi	Africa	1
Cornstone	UK	Allen (1960)
Costra caliza	Spain	Rangheard (1969)
Croûte zonaire	N Africa (French)	Durand (1963)
Croûte calcaire	N Africa (French)	Durand (1963)
Deckkalk	SW Africa (German)	1
Dhandla	India	1
Duricrust	Australia	1
Encroûtement calcaire	N Africa (French)	Durand (1963)
Gatch	Kuwait	1
Giglin; Jigillin	Nigeria	1
Hardpan	USA; S Africa	Breazeale & Smith (1930)
Havara	Cyprus	Pantazis (1973)
Kafkalla	Cyprus	Pantazis (1973)
Kalkkrusten	Spain (German)	Rutte (1958)
Kancar; Kunker; Kunkur	India	1
Lime crust yerma	Mediterranean	Kubiena (1953)
Lime hardpan	USA	Breazeale & Smith (1930)
Mbuga limestone	E Africa	1
Nari	Israel	Krumbein (1968)
Natural concrete	India	1
Oberflachenbreccie		Johnson (1967)
Paree	Middle East	1
Petrocalcic horizon	USA	Soil Survey Staff (1967)
Reh	India	2
Rimrock	USA	1
Sabath	Egypt	2
Sheet limestone	E Africa	1

- contd -→

TABLE 1. - Continued

TERM	COUNTRY (school of workers in parentheses)	REFERENCE
Soil travertine	Australia	1
Steppenkalk	E Africa (German)	1
Tafezza	Africa	1
Taparas	France	1
Tepetate	USA	2
Tierra blanca	USA	2
Tifkert	N Africa	1
Torba beda	Lybia; Tunisia	1
Tosca; Toska	Argentina; Spain	Darwin (1890)
Trab	N Africa	2
Travertine	Australia	Fairbridge & Teichert (1953)
Travertino	Spain	2
Tufa	Australia; S Africa	1
Vlei limestone	S Africa	Netterberg (1969b)

1 Cited in Goudie (1973)

2 Cited in Reeves (1976)

Gonzalez-Bonorino & Teruggi (1952; cited in Reeves, 1976, p.1) defined tosca as "....a stratiform to irregular deposit formed primarily by calcium carbonate, with earthy, concretional, pisolitic, banded or massive structure that is formed in the soil or subsoil of the arid and semiarid regions. The carbonate is deposited by capillary action or illuviation."

Brown (1956, p.1) followed the usage of Bretz & Horberg (1949) and reiterated that caliche "....applies to the less-indurated form as well as to the hard caprock." James (1972, p.222), on the other hand, gave a different viewpoint, thus: "Indurated portions of caliche deposits are called 'calcrete' (Lamplugh, 1907), while the friable parts are referred to as 'caliche' in Texas (Blank & Tynes, 1965), or 'chalk' (Nelson, 1959) elsewhere."

Johnson (1967, p.151) stated: "caliche is an opaque, reddish brown to buff or white material of secondary accumulation in situ which is commonly but not invariably found as a subsoil deposit in subhumid to arid climates, and which is composed largely of calcium carbonate in addition to such clastics as gravel, sand, silt, and clay, which may be present in various proportions. Other compounds may or may not be present."

Bissell & Chilingar (1967, p.152) defined caliche as "....a lime-rich deposit found in soils and is formed by capillary action drawing the lime-bearing waters to the surface where, by evaporation, the lime is precipitated."

Netterberg (1969a, p.88) defined calcrete as "....almost any terrestial unconsolidated material which has been cemented and/or replaced by dominantly calcium carbonate.....The mechanism of calcification is not restricted and calcretes may be of pedogenic or non-pedogenic origin, or both." However, Netterberg (1969b) indicated his preference for calcrete as a general term for "strongly calcareous soil carbonate deposits", and in another report pointed out that calcrete is a pedogenic material (Netterberg, 1971). His classification into two basic types, pedogenic and non-pedogenic calcretes, is, therefore, puzzling. The confusion arises from the term 'soil' which Netterberg used in a wide, engineering sense.

Aristarain (1971) discussed various definitions and uses of caliche and proposed (p.284) that the term 'caliche deposit' should be defined as ".....a body resulting from the epigenetic accumulation of calcium carbonate (calcite) in unconsolidated sediments derived from soil processes in climates in which moisture is deficient during all seasons."

In his review of the relative merits of the terms caliche and calcrete, Goudie (1972a) pointed out the potential danger of stipulating any mode of origin in any definition and suggested that the definition of Aristarain was too restrictive, the requirements being an initial unconsolidated sediment, accumulation of calcium carbonate by soil-forming processes and a specific climate. As an alternative, Goudie (op.cit., p.466) gave another definition, thus: "Calcrete is a term for terrestial materials composed dominantly but not exclusively of calcium carbonate which occurs in stages ranging from powdery and nodular to highly indurated and involve the cementation of, accumulation in and/or replacement of greater or lesser quantities of soil, rock, or weathered material primarily within the vadose zone. It does not, however, embrace cave deposits (speleothems), spring deposits (for which tufa or travertine are accepted terms), marine deposits (such as beachrock) or lacustrine algal stromatoliths." Unfortunately, this definition, in an attempt to be all-embracing, includes uplifted marine limestones whose metastable skeletal components have been replaced by low magnesian calcite in the meteoric vadose zone, that is to say, virtually all subaerially exposed shelf and marginal marine carbonates.

In a valuable account of Quaternary calcrete deposits from Shark Bay, Australia, Read (1974, p.250) described calcrete simply as ".....accumulations of cryptocrystalline calcite resulting from soil-forming processes." Although this definition ignores Goudie's warning with regard to the danger of incorporating genesis in a definition, it is, nonetheless, usefully restrictive. However, pedogenetic carbonate accumulations include many soils that lack the features of calcrete (for examples of non-calcrete calcareous soils, see Kubiena, 1953). Moreover, passive void-filling calcite cements do not form characteristic calcrete fabrics; the requirement of replacement, as included in the definitions of Netterberg (1969a) and Goudie (1972a, 1975), merit due consideration.

A recent attempt at a comprehensive, non-genetic definition, based on regional setting, profiles and fabrics, has been proposed by Esteban (1976, p.2049) as follows: "Caliche is a vertically zoned, subhorizontal carbonate deposit, normally developed with three main rock types: (1) massive-chalky, (2) nodular-crumbly, and (3) laminated and/or pisolitic compact crust or caprock. The position and development of these rock types in the vertical sequence (profile) and laterally is highly variable. The only rather consistent relation is that the massive-chalky rock grades downward into the original rock or sediment through a transition zone, both with strong evidence for in-place alteration and replacement of the original rock or sediment. Colours are commonly white and light browns, but red and black may be important. The predominant caliche is a clotted, pelloidal micrite with microspar channels and cracks. Accessory fabrics are poorly laminated micrite, karst products, and rhizocretions. Microspar areas usually show evidence of replacement of relict [sic] grains and of other primary and earlier diagenetic microfabrics."

Esteban (op.cit.) pointed out the desirability of restricting the use of the term caliche and stated that "....caliche can be restricted to designate soil products of the vadose freshwater zone in semiarid environments." This use is certainly restrictive, but, unlike his formal descriptive definition stated above, is explicitly genetic, that is to say, he suggested caliche resulted from pedogenesis by being a soil product. This illustrates, perhaps, the difficulty of separating purely descriptive statements from their underlying genetic connotations.

To summarize, most definitions include composition, consensus of opinion being that calcrete (caliche) should be restricted to calcium carbonate deposits. Some workers stipulate certain environmental limits in their definitions, a semi-arid climate being one of the more popular conditions. A terrestial environment is generally implied or stated. The processes involved, the methods of accommodation and the location of carbonate accumulations with respect to the ground-atmosphere interface, however, are subjects of discord. For example, Aristarain (1971) and Read (1974) stipulated soil-forming processes as a basic requirement in their definition. Gonzalez-Bonorino & Teruggi (1952) and Bissell & Chilingar (1967) considered that capillary action had been an important factor in the deposition of calcium carbonate. On the other hand, Goudie (1972a) and Esteban (1976) painstakingly avoided mention of process altogether.

With regard to location of carbonate accumulation, there appears to be little agreement as to whether this has taken place within or below soil (subsoil). Likewise, how calcite accumulates to form calcrete is open to further debate. These points of issue will be examined in detail later (Chapter 8).

In conclusion, it can be stated that a suitable definition for calcrete, of universal acceptance, is wanting. Most workers have formulated or used a definition to suit their own needs. Some workers have attempted to meet the requirements of diverging disciplines, but resolution or synthesis of differing viewpoints has not been entirely satisfactory.

Classification

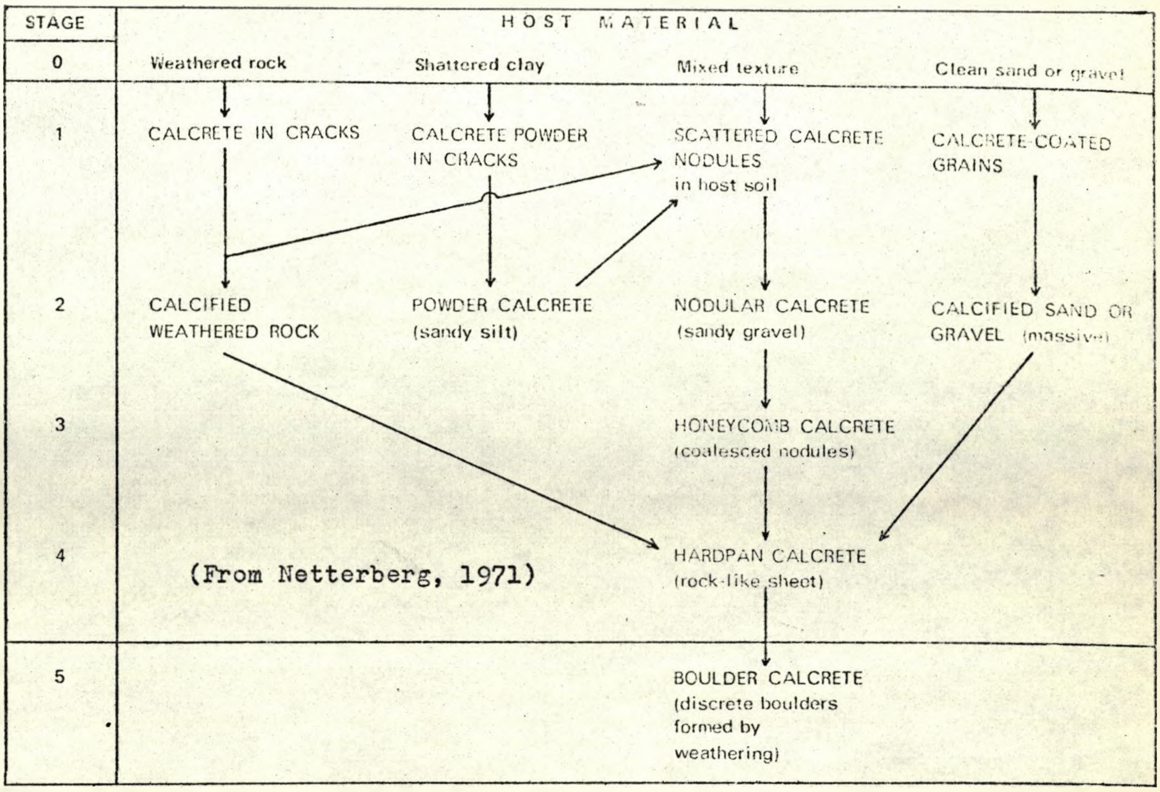
Many classifications for calcrete have been proposed, their utility depending very much on training background and experience of the user. They can be divided broadly into four categories: those based on physical properties (descriptive and quantitative); those based on morphological characteristics (descriptive); those based on progressive development of compositional and fabric changes (evolutionary); and those based on mode of formation (genetic).

Physical characteristics, such as degree of induration, hardness, calcium carbonate content and particle size distribution, have been used in the classification schemes of Brown (1956), Gile, Peterson & Grossman (1965; 1966) and Yaalon & Singer (1974).

Gross morphological characteristics provide the basis for many field classifications. Ruellan (1967), after examining carbonate accumulations in Quaternary deposits from Morocco, established a new nomenclature for field descriptions (*les accumulations diffuses; les amas friables; les granules et les nodules; les encroûtements; les croûtes; la dalle compacte; la pellicle rubanée; les carapaces calcaires*). To some extent, James (1972) used a morphological scheme to describe surficial calcareous crust profiles from Barbados (crusts; chalky carbonate; brecciated profile). Esteban (1976), in his definition of caliche (calcrete), divided a typical profile into three main rock types; (1) massive-chalky; (2) nodular-crumbly, and (3) laminated and/or pisolitic compact crust or caprock. Other investigators who have used morphology as a factor for classification include: Brown (1956), Rutte (1958), Blank & Tynes (1965) and Walls, Harris & Nunan (1975).

A notable classification scheme is that proposed by Netterberg (1969b, 1971). From field observations in southern Africa, Netterberg recognized six basic calcrete types (Table 2,p.20) and placed them in an evolutionary sequence. Although the classification was developed primarily for road construction engineers it is also suitable for geological purposes. Terminology is kept deliberately short and simple and, although transitions invariably exist, the basic types are readily recognizable in the field. In addition, the classification

TABLE 2 CLASSIFICATION SCHEMES OF CALCRETE

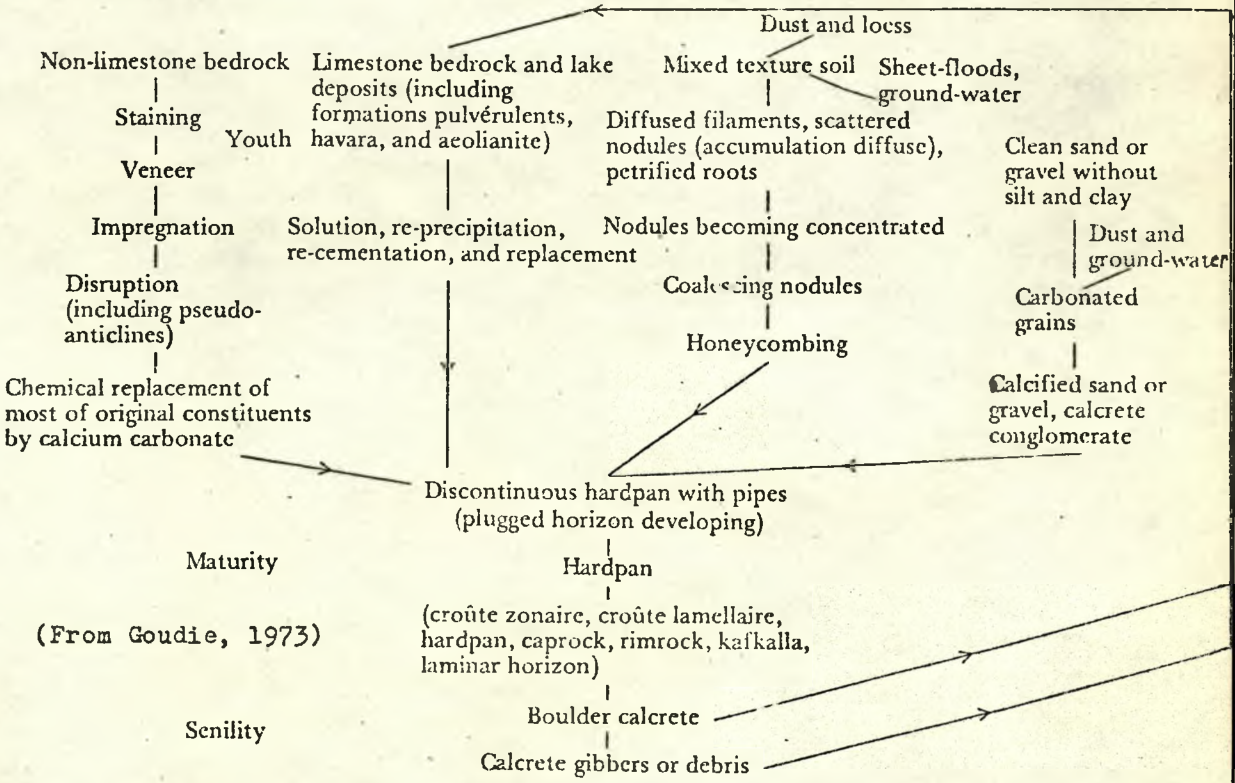


STAGE	HOST MATERIAL			
0	Weathered rock	Shattered clay	Mixed texture	Clean sand or gravel
1	CALCRETE IN CRACKS	CALCRETE POWDER IN CRACKS	SCATTERED CALCRETE NODULES in host soil	CALCRETE-COATED GRAINS
2	CALCIFIED WEATHERED ROCK	POWDER CALCRETE (sandy silt)	NODULAR CALCRETE (sandy gravel)	CALCIFIED SAND OR GRAVEL (massive)
3			HONEYCOMB CALCRETE (coalesced nodules)	
4			HARDPAN CALCRETE (rock-like sheet)	
5			BOULDER CALCRETE (discrete boulders formed by weathering)	

(From Netterberg, 1971)

Any of the developmental stages in Table 1 may be pedogenic in origin, but it is thought that ground water types do not often develop beyond stage 2. The mature calcrete profile is regarded as one which contains a capping of reasonably unbroken hardpan (stage 4). Hardpan thus represents the final stage of development of all calcretes. Boulder calcrete represents the weathered stage.

A descriptive-evolutionary classification of calcrete



(From Goudie, 1973)

is capable of further refinement in the laboratory.

Other classification schemes, based on progressive sequences of development, include those proposed by Price (1933), Reeves (1970) and Stuart, Fosberg & Lewis (1961). These workers used the concept of maturity to describe various calcrete types. Although their classifications share the same terminology - youth, maturity and old age - criteria used by them for identifying young, mature and old calcretes differ. In this context, it is pointed out that age can be used only in a relative sense as the actual rate of calcrete development will depend on the amount of calcium carbonate originally present in the host material, the rate of supply of calcium and carbonate ions, and the kinetics of the system, i.e. the rate of calcite precipitation versus its rate of dissolution. Nevertheless, Stuart _et_ _al_. (1961), Gile _et_ _al_. (1966) and Netterberg (1969a) have noted that there is a reasonable correlation between stage of development (relative age) and absolute age.

Purely genetic classifications have been proposed by some workers. However, their general application relies heavily on correct recognition of certain features and, perhaps more fundamentally, on correct interpretation of the processes responsible for their formation. For example, the _calcaire_ _pulvérulent_ of Durand (1949, 1963) which is a powdery, chalky deposit, is considered by Durand to be lacustrine in origin. His _croûte_ _zonaire_ is interpreted as the result of lime deposition from surface sheet-flood water. However, as pointed out by Goudie (1973), morphologically similar forms may have resulted from different processes.

Of the eight types originally proposed by Durand (1949), his racines petrifiées were omitted from his revised (1963) classification. Ironically, petrified roots are, perhaps more readily identifiable than his other genetic types. Regrettably, Durand considered that petrified roots were insignificant components of calcrete; a viewpoint which is questioned seriously in this study.

A further example of a genetic classification, based on process and location with respect to the water table, is that put forward by Dumas (1969). He distinguished four genetic calcareous crusts: his croûtes zonées, croûtes pédogénétiques, croûtes diagénétiques and croûtes de nappes phréatiquees. Again, correct recognition of these various genetic types presupposes knowledge of the processes involved in their formation.

As with most classifications, no single scheme for classifying calcretes neatly embraces all the recognized types. Some classifications are too rigid; others can be used only for specific areas or for certain host materials. Several schemes have been proposed which require detailed laboratory work before a sample can be assigned to a particular calcrete type. To combat such problems, several classifications have been formulated by combining the previously mentioned categories in an attempt to achieve greater flexibility and utility. The descriptive-evolutionary classification of Goudie (1973) may be cited as illustration (Table 2, p.20). Using existing terminology, Goudie (op.cit.) considered: (1) host material (non-limestone bedrock, limestone bedrock, sediments and soils; (2) sequential textural and fabric changes with increasing calcium carbonate content (diffused filaments, scattered nodules, concentrated nodules, coalesced nodules, honeycomb calcrete, hardpan calcrete); and (3) age (youth, maturity and senility). Basically, this classification synthesizes the schemes of Durand (1963), Gile *et al*. (1966) and Netterberg (1969b).

More recently, Van Zuidam (1975) has proposed a polygenetic classification for calcrete. This scheme is significant in that it recognizes that a particular calcrete type may have resulted from more than one process but suffers from the inherent weakness of any genetic classification, that being the step between observing the product and inferring the process, a step which is not necessarily direct and rarely sign-posted.

In summary, it can be stated that the proposed classifications for calcrete indicate that composition and morphology of calcrete show world-wide similarities, despite use of a varied terminology. Although linguistic and nomenclatural differences mask uniformity of observational characteristics, a set of recognizable and repeatable features allow identification of calcrete stereotypes. On the other hand, whether a classification scheme should consider genesis is a subject of conflict and, in cases where processes are considered, the mechanism or mechanisms responsible for calcrete formation are matters for further argument.

Models of formation - genesis

The origin of calcrete has been, and still is, a subject for much conjectural and intuitive thinking. The large number of theories to account for calcrete formation reflect loose definition and, in many cases, superficial observation, uncritical examination and a poor understanding of the mechanisms that have, or could have, taken place.

Various models for calcrete formation have been discussed by Bretz & Horberg (1949), Brown (1956), Aristarain (1969), Goudie (1973), Van Zuidam (1975) and Reeves (1976). In reviewing relevant literature on the formation of duricrusts in general, Goudie (1973) grouped the various models into six categories: fluvial, lacustrine, in situ, capillary rise from ground water, pedogenic (per descensum) and per ascensum), and detrital models. Unfortunately, such artificial categories are not always clearly separable in reality as Goudie himself, has indicated (p.145): "Although a six-fold classification of formational models has been attempted here, the author [Goudie] recognizes that in many aspects some of the mechanisms may operate concurrently to produce the duricrust form." For example, calcrete formed by in situ alteration of host material is considered to be a distinct group by Goudie but, as I will explain later, soil-forming (pedogenic model) processes may have been responsible for the alteration. Similarly, to give an extreme example, pre-existing calcrete hardpans may be weathered in situ by pedogenic agencies, and the resulting detritus transported by water, deposited, and cemented by calcium carbonate precipitated from rising ground water solutions. The product could be termed an in situ, pedogenic, fluvial, detrital, ground water calcrete (!)

Before the merits and limitations of various models are discussed it is pertinent, at this stage, to pause momentarily and point out some facts. Based on my own field observations and corroborated by earlier workers, the following points require careful consideration when assessing hypotheses regarding genesis. Modern calcretes: (1) express themselves as near-surface and surface accumulations of calcium carbonate; (2) show uniformity and continuity on a megascopic (km) scale; (3) are laterally extensive for tens or even hundreds of kilometres; (4) are common in areas with semi-arid to temperate climates; (5) occur on stable geomorphic surfaces with gentle (less than 25°) slopes; (6) are conformable with present-day topography; (7) are independent of substrate; (8) occur within, not merely on, any host material; show a downward decrease in calcium carbonate content; and (10) rarely exceed 6 m vertical thickness.

As well as reconciliation with field observations, any model must explain adequately the mode of emplacement, the method of transport and the source of calcium carbonate. With regard to source, calcium carbonate may have been derived from the host material or introduced from elsewhere. The first case represents a closed system with respect to calcium carbonate and characteristic calcrete fabrics result from reorganization of the original host material constituents. The second case requires an allochthonous source of calcium carbonate and is clearly essential for calcrete occurring within a non-carbonate substrate. Goudie (1973) has termed these end-members respectively, as *relative* accumulations and *absolute* accumulations of calcium carbonate.

Methods of transport can, likewise, be divided into two basic categories: (1) transport by wind; and (2) transport by water. Aeolian dust is considered to be a major source for calcium carbonate in some areas; marine aerosols (salt spray) are thought to be important locally in coastal regions. Hydrologically, water can be subdivided into several categories: rainfall, surface water (channelled and sheet-flood), vadose water and ground water. Calcium carbonate may be transported by any of these water types as a solid (by bottom traction* or in suspension) or in solution (movement by bulk fluid flow or diffusion).

As with source and methods of transport, mode of emplacement can be treated simplistically by distinguishing two types of deposits: (1) mechanical detritus; and (2) chemical precipitates. Calcium carbonate deposition from solution requires a mechanism for causing precipitation. From physicochemical consideration only, this may be brought about by a change, singly or in combination,of temperature, pressure, partial pressure of carbon dioxide, pH or ionic concentration. Carbon dioxide loss and evaporation are responsible for chemical precipitation at atmospheric pressures and temperatures. However, superimposed on purely physicochemical factors are indirect or direct biogenetic factors such as plant photosynthesis and transpiration, plant and animal respiration, secretion of metabolic products, elemental fractionation and mineral synthesis. These considerations, and their complex interrelationships, provide a formidable list of model variables on which to base various theories of calcrete genesis. The problem, at hand, is to assess the feasibility of each of these in turn.

<u>Fluvial models; lacustrine models</u> - - Without elaboration, I reject both of these models for two fundamental reasons: firstly, passive calcium carbonate precipitation from stationary or surface-flowing waters that takes place on, rather than within, a substrate does not modify or obliterate pre-existing fabrics and structures; and, secondly, the distinct geomorphic expression of river and lake basins,

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* Not applicable to rainwater

and the limited effect of sheet-flooding are incompatible with the great areal extent, topographical correspondence and intra-sedimentary nature of calcretes.

For a fuller discussion of the proponents of fluvial and lacustrine models, the evidence cited to support their arguments and the objections raised by subsequent workers, see Goudie (1973, pp.121-128).

In situ models - - These involve the reorganization of lime-rich substrates by dissolution, replacement and reprecipitation. Thus, original constituents of the parent material are decomposed and transformed. Some elements may be removed completely but relative accumulation and precipitation of calcium carbonate produces a new set of structures and textures. Evidence to support this model include gradual transitions between calcrete and unaltered parent material, inherited (from the parent material) *in situ* relic grains within upper parts of the calcrete profile and gradual obliteration of original bedding and primary textures.

Documented examples that conform to this model include caliche in Texas (Blank & Tynes, 1965), the nari limestone of Israel (Yaalon & Singer, 1974), kafkalla and havara deposits from Cyprus (Pantazis, 1973) and calcareous crusts from Barbados (James, 1972; Harrison, 1977). James (1972) demonstrated that alteration of limestone and precipitation of calcium carbonate produced replacement fabrics, characteristic not only of the crusts of Barbados, but common also to calcareous crusts from Florida and the nari of Israel.

Ground water models - - Calcite precipitation from evaporating ground water has been proposed for the formation of calcrete in some areas (Blake, 1902; Lee, 1905; Theis, 1936; Netterberg, 1969b, 1971). In his discussion on the origin of caliche from southern Arizona, Blake (1902, p.225) stated: "The formation of caliche is clearly the result of upward capillary flow of calcareous water, induced by constant and rapid evaporation at the surface in a comparatively rainless season." He stipulated that a constant supply of calcareous water (source of calcium carbonate) and a continued desiccating atmosphere (evaporitic pump) were essential factors in the formation of caliche.

Although this model cannot be dismissed completely, several major objections severely restrict its general application. According to Baver (1956, p.61; cited in Goudie, 1973) "...The upward rise of water by capillary action under conditions permitting evaporation is not as significant as the older points of view led one to believe." From an assessment of existing experimental data, Goudie (1973) suggested that the rise of capillary water rarely exceeded 2 m. This means that a laterally extensive, near-surface water table would be required for calcrete formation by this model. Moreover, the surface of the water table would need to parallel the topographical surface. Such requirements seldom exist in nature, indeed not on the scale required for extensive calcrete deposits.

In addition, if calcretes formed solely by evaporation one would, not unreasonably, expect to find associated evaporite minerals present. Although halite, dolomite, gypsum and anhydrite have been recorded within calcretes (Netterberg, 1971; this study) such minerals are not typical.

Further objections to this model have been pointed out by

Bretz & Horberg (1949) and Brown (1956). Such objections include: the occurrence of calcrete within impermeable host materials, thereby prohibiting capillary rises from underlying ground water; occurrence of calcrete on slopes and areas of high relief where solutions could never be brought to the surface by capillarity; and gravitational vadose features which suggest downward rather than ascending water movements.

Pedogenic models - - As already mentioned, some workers have stated explicitly in their definitions of calcrete that soil-forming processes are responsible for calcrete formation (Aristarain, 1969, 1971; Read, 1974). In their discussion on the origin of caliche in southeastern New Mexico, Bretz & Horberg (1949, p.509) stated: "Most of the features....clearly indicate that soil-forming processes were of major importance in producing caliche in southeastern New Mexico." They envisaged that solutions containing carbonate moved downwards during rainy periods to be precipitated as rising soil capillary water evaporated in the following dry period. This mechanism was proposed earlier by Price (1933) and is termed the per ascensum pedogenic model by Goudie (1973). However, this model shows an inherent weakness when one considers the amount of carbonate involved. Unless there is an allocthonous source of calcium carbonate, the material overlying the calcrete is generally insufficient to provide enough calcium carbonate for the calcrete. Moreover, the same calcium carbonate will spend its duration moving up and down and, thus, will not show any sequential profile development. On the other hand, if there is an addition of calcium carbonate from elsewhere, its absolute accumulation will reduce gradually porosity of the host material and impede greatly vertical water movements.

The per descensum pedogenic model is similar to the above but invokes downward movement of soil solutions rich in carbonate and accumulation of precipitated calcite at a certain depth in the profile. Some workers (Arkley, 1963; Gile *et al.*, 1965) have suggested that this depth is the level of soil moisture penetration. The source of carbonate may be from the host material, from dissolution of aeolian dust or gastropod tests and other shell debris, from the breakdown of plant litter or from rainfall.

The per descensum and per ascensum models consider only vertically moving waters but Ruellan (1967), Reeves (1970) and Nahon (1976) have stressed the importance of lateral water movements. In addition, the models invoke simple evaporation of soil water as the cause of the precipitation of calcite, a point that Netterberg (1971) questioned. Netterberg suggested that the effect of changes in soil suction pressure (pF) on the solubility of carbonate was possibly the most important mechanism in calcrete formation at all depths.

In addition to CO_2 fluctuations induced by pore water pressure (pF) changes, CO_2 concentrations are affected by soil organisms. CO_2 gradients exist around roots, generally with high CO_2 values at the root surface and decreasing values away from the root. Plants, moreover, increase the concentration of soil solutions by absorbing water through their roots in the process of transpiration. Thus, water losses from transpiration of plants may lead eventually to the precipitation of calcite.

Many soil micro-organisms are capable of affecting carbonate equilibria and some have the ability to synthesize calcite (Krumbein, 1968). The mechanisms for biochemical deposition of calcite are not clearly understood (Arnott & Pautard, 1970) but biochemical products can be identified - if one looks for them (Chapter 5).

In recent years, workers investigating calcrete have shown increasing favour toward models involving soil-forming processes. The reasons are not difficult to see:

- On a megascopic (km) scale, soils are laterally extensive surface materials which occur on stable geomorphic surfaces. Moreover, soils duplicate topographical expression of gently undulating landscapes.

- On a local (cm) scale in a vertical sequence, soils show zonations from the surface, grading downwards into undisturbed host material.

- In considering origin, soils are formed by weathering and transformation of solid rock *in situ* or weathering and/or transformation of transported materials derived from solid rocks (Brewer, 1964).

- In considering mode of formation, soil-forming processes cause modification in sediments or weathered rocks by removal, translocation, transformation and neoformation of mobile constituents. Such changes generally produce horizon differentiation and, thus, the formation of a soil profile.

The above outlined features, characteristic of soils, are common also to calcretes. Surely, this is more than mere coincidence? Soil horizons of carbonate accumulation are common in semi-arid climates. They are referred to as calcic or petrocalcic horizons by soil scientists (Soil Survey Staff, 1967) depending on whether they are friable or indurated respectively. Gile *et al*. (1965) have proposed the term *K-horizon* for such accumulations.

Objections to the pedogenic model are minimal, the outstanding one being the tremendous thickness of some calcrete profiles. Goudie (1973) has recorded a maximum thickness of 60 m for calcrete along the Molopo Valley, South Africa. In Texas, Brown (1956) recorded thicknesses of up to 45 m for the caliche on the Llano Estacado. To account for such thicknesses, Brown (op.cit.) considered that deposition of $CaCO_3$ resulted from subsurface evaporation of soil moisture in an aeolian aggrading soil profile. Alternatively, the quoted thicknesses of some calcretes may represent a multi-sequal succession of superimposed profiles. Brown reported (p.4): "In its thickest expression the caliche is predominantly rudely layered, consisting of two layers of hard caprock....The lower caprock may be divided into two to four thinner, dense caprock layers separated by the relatively unindurated phase." Thus, the objectional thicknesses can be accounted for within a pedogenic model if one allows for multiple profile development.

Summary

This brief historical survey indicates that methodically unsound attempts to solve fundamental problems of calcrete genesis result largely from inadequate definition. This has led to controversial and confused ideas on the properties and composition of calcretes, their characteristic morphologies, and the processes that have operated in producing them. Lacking an accepted framework for observation and description, progress towards a better understanding has been hindered by contradictory statements occurring within a voluminous but scattered literature.

From the foregoing discussion on formational models, fluvial, lacustrine and ground water models do not explain adequately the general characteristics of calcrete. *In situ* and detrital models can be readily accommodated within a broad pedogenic model, the former representing a degrading soil profile, the latter an aggrading one. In both cases, changes that have taken place by addition, removal, translocation and transformation of mobile constituents, can be considered in terms of soil-forming processes. But pedogenesis does not account for the total characteristics of calcrete; induration by physicochemical processes has to take place to produce calcrete hardpans. Thus, pedogenesis and diagenesis require equal consideration with regard to calcrete genesis.

PHILOSOPHY UNDERLYING THIS STUDY

Terminology

Calcrete v caliche - - Although calcrete is a term that is being increasingly misused, I prefer this term to caliche (and other synonyms) for several reasons. Calcrete has been used solely for calcareous accumulations, is a familiar term in most parts of the world, conforms with other types of pedocementation (silcrete, ferricrete, alcrete), is etymologically more informative than caliche and is grammatically easier to handle (can be used singularly or in the plural).

Pedogenetic v pedogenic - - Both terms were used earlier to conform with previous reporting of other investigators. For my own reporting, I use pedogenetic to be consistent with the terms diagenetic, telogenetic, epigenetic, etc. Similarly, biogenetic rather than biogenic is used in this study.

Hardpan, caprock, crust - - All three terms imply induration and have been used to describe well cemented calcrete horizons. Since caprock and crust imply a surface position, I prefer the term hardpan as this horizon does not necessarily occur or form at the surface.

Host material v parent material - - Because the calcium carbonate that formed calcrete may have been derived from bedrock, from the overlying soil, from wind-blown dust or salt spray, or from rain, stream or ground waters, the term host material is preferred. Use of parent material implies that the calcium carbonate has not been introduced to its present position but is the result, solely, of *in situ* reorganization of the original substrate. In effect, parent material is a special case of host material.

Petrographic nomenclature - - An attempt to use existing petrographic concepts led to inadequate description and confusion in terminology. Since calcrete is defined in this study as a term to designate calcareous accumulations which have resulted from soil-forming processes (see below), the pedographic scheme of Brewer (1964) is employed usefully. Nonetheless, many petrographic concepts and terms also have been used in this study.

Additional terms are discussed in relevant sections or in the glossary.

Definitions

Before calcretes can be adequately described, and subsequently interpreted in terms of origin and formation, they need to be clearly defined. Unfortunately, it is practically impossible to define calcrete in such a way as to satisfy all workers. This is due largely to divergent interests and use of independent terminologies which have greatly hindered communication among workers. A review of the literature has indicated that confusion abounds. In order to avoid further misunderstanding it is deemed necessary, at the outset, to discuss the philosophical concepts on which this study is based.

Although a question of semantics, without uniformity of definition and terminology, morphological comparisons, in the same and different areas, become meaningless. From a brief survey on definitions (p.11), it was concluded that a suitable definition of calcrete is wanting. Therefore, the following definition is proposed, not to give yet another alternative, but in an attempt to eradicate the aforementioned confusion and to establish a standard terminology that is, at the same time, usefully restrictive. The definition is based on field and laboratory observations made during this study.

> Calcrete is an accumulation of predominantly fine-grained low magnesian calcite having formed within the meteoric vadose zone by pedodiagenetic* alteration and replacement of any precursor host material.

It follows that:

> Calcretization is the pedodiagenetic* modification or obliteration of primary textures and fabrics, and the production of new textures and fabrics, resulting from the accumulation of low magnesian calcite within the meteoric vadose zone.

*Pedodiagenesis is a new term proposed here to embrace both pedogenesis (soil-forming processes) and diagenesis (processes which occur in sediments or sedimentary rocks between the time of initial deposition and the time - if ever - when the threshold of metamorphism is reached; adapted from Murray & Pray, 1965). The reason for coining this hybrid term is because pedogenesis does not generally include lithification of a soil and diagenesis usually excludes soil-forming processes as well as weathering by inorganic agencies. It is pointed out that new names do not make new processes; the term pedodiagenesis is proposed to embrace demonstrable and inferred processes which have operated during the formation of calcretes.

Soil formation is the result of physical, chemical and biological processes which transform a rock material into a soil (Robinson, 1949). It follows that biological processes have played a role in the formation of calcretes if one accepts the above definition. Therefore, accumulations of calcium carbonate which occur in materials unaffected by biological processes are not calcretes. This prerequisite of biological interference is inherited from the pedogenetic part of the above proposed definition since the definition of soil formation, itself, includes both inorganic processes (e.g. physical and chemical weathering) and organic processes (e.g. biological weathering, biosynthesis of secondary minerals).

By adhering to this concept for calcrete formation, several limestone types, formerly considered to be equivalent to calcrete by previous workers, do not merit such designation. These include 'case-hardened' surficial crusts, speleothem deposits, lacustrine carbonates, beachrock, tufa and coniatolites. However, before we exclude certain types of terrestial and peritidal calcium carbonate accumulations from the definition of calcrete we need to be able to (a) correctly recognize the deposit and (b) demonstrate that distinct differences do exist between such deposits and calcretes. Therefore, 'calcrete-like' deposits are considered (Chapter 7) and criteria are given to allow their distinction from calcretes as defined in this study.

Given that carbonate buildup has taken place within - not on - a pre-existing material, there are three possible modes of carbonate accumulation within calcrete profiles: (1) as a passive void-filling cement or sediment; (2) by replacement of original constituents by calcite; and (3) by displacement as a result of calcite growth.

Scattered but well documented evidence exists in the literature which suggests that partial or total replacement of the host material by calcite is a common feature in calcretes. This is supported by my own findings recorded elsewhere in this study. Displacement, on the other hand, together with a resulting expansion of the calcrete profile, are phenomena that have been inferred by some workers but never unequivocably demonstrated. Thus, it is pertinent to note here that the concept of replacement is incorporated in my definition of calcrete but the requirement for displacive growth is deliberately omitted.

Classification

From my field observations, I have classified horizons within a given profile on the basis of gross morphological characteristics.

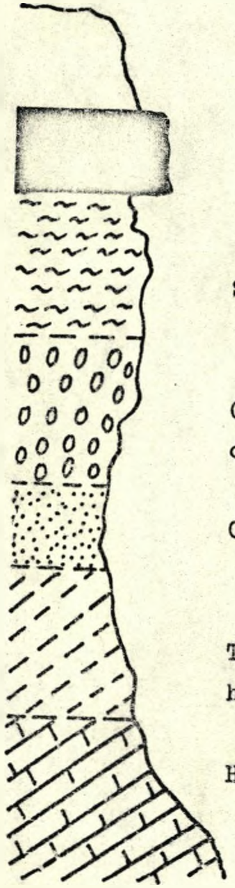
The classification requires the presence and recognition of host material for a complete profile description but, nonetheless, can be applied equally well if only part of the calcrete profile is available for study.

Although calcrete profiles commonly show rapid vertical and lateral variations within a few metres, it is possible to recognize certain patterns with sufficient repetition to allow at least some generalization. Thus, an idealized vertical calcrete profile can be drawn up (Fig. 2, p.39). This purely morphological field classification provides a framework for more detailed descriptions, both in the field and in the laboratory. The sequence illustrated in Fig. 2 is only one of many possible variations, albeit the commonest. In addition, it is pointed out that boundaries between designated horizons tend to be irregular and diffuse, and the horizons themselves may be repeated several times or be absent altogether (see Appendix Figs. A-1 to A-5).

Equivalent terms used in previous classifications also are given in Fig. 2 to facilitate correlation of already published descriptions of calcrete profiles.

Genesis - Preliminary Statement

It would be premature to discuss the origin and mode of formation of Spanish calcretes without, firstly, presenting the evidence on which my interpretations are based. Therefore, such discussion is deferred until my findings have been presented. At this stage, it will suffice to say that the effects of biological interference on calcrete formation have not been given the attention they merit.



Horizon no.	This study	Durand (1949)	Ruellan (1967)	Netterberg (1969b)	Others
0	Soil				
1	Hardpan	Croûte zonaire; Croûte lamellaire	Carapace	Hardpan	Caprock; Rimrock; Kafkalla; Nari; Laminar horizon
2	Sheet calcrete		Un horizon à amas friables	Honeycomb calcrete	
3	Glaebular calcrete	Nodules concretionés	Un horizon à concrétions	Nodular calcrete	
4	Chalky calcrete	Calcaire pulvérulent	Accumulation diffuse	Powder calcrete	Havara
5	Transitional horizon				
6	Host material				

Figure 2. Idealized calcrete profile and horizon nomenclature.

CHAPTER THREE - MACROMORPHOLOGY

INTRODUCTION

The term macromorphology is used here for the analysis of forms or features which are readily observable in the field. In the first part of this chapter, the distribution of present-day surface and near-surface calcrete deposits in western Mediterranean regions are examined. The regional distribution of calcretes is discussed in relation to the five basic soil-forming factors of climate, host material (substrate), topography, organisms and time.

The second part of this chapter is concerned with the descriptions at outcrop of the vertical succession of horizons, that is to say, with the description of calcrete profiles. The physical properties of calcrete profiles, namely thickness, hardness and macroscopical porosity are evaluated from field data. Since calcium carbonate content is related to these physical properties, an indication of the amount and distribution of calcium carbonate within selected calcrete profiles is also included.

The final part of this chapter deals with several characteristic macromorphological features. These features include planar laminations, glaebules, rhizoliths, brecciation textures and tepee structures. Classification, description and interpretation of these features are presented in turn. Finally, the significance of these features is pointed out with respect to the recognition and genesis of calcrete deposits in general.

REGIONAL DISTRIBUTION

Calcretes are widespread in many semi-arid areas of the world today. Many attempts have been made at correlating their distribution with present-day factors, especially climatic factors. This may be valid in some areas but calcretes are relic features in many parts of the world and, thus, present-day conditions have little bearing on present-day distribution. Moreover, the exact distribution of calcrete is difficult to determine, both on a regional (100's km) and on a local (km) scale. With regard to Spain, several maps have been published to show the distribution of calcrete but, even in the comparatively well surveyed Mediterranean, the prepared maps show significant differences in distribution patterns (Fig. 3, p.42). The problems to contend with are manifold: concept and definition of calcrete; correct recognition of the designated material; differentiation between active, relic and exhumed profiles; destruction of calcrete as a result of natural erosion; removal of calcrete as a result of agricultural practices; coverage by man-made constructions; masking by vegetation cover or recent sedimentation; and inaccessibility. Because of such problems, delimitation of calcrete tends to be somewhat subjective. Distribution maps may be accurate with respect to the assumptions made in fixing boundaries but, unless these assumptions are stated explicitly, the maps are of limited value. It is requisite to know the criteria that have been used in producing calcrete distribution maps since they provide the basis for making correlations with such factors as past and present climatic patterns, vegetation patterns and different types of host materials.

For the purposes of this study, I have drawn up a calcrete distribution map for Spain (Fig. 4, p.43) based on (1) my own

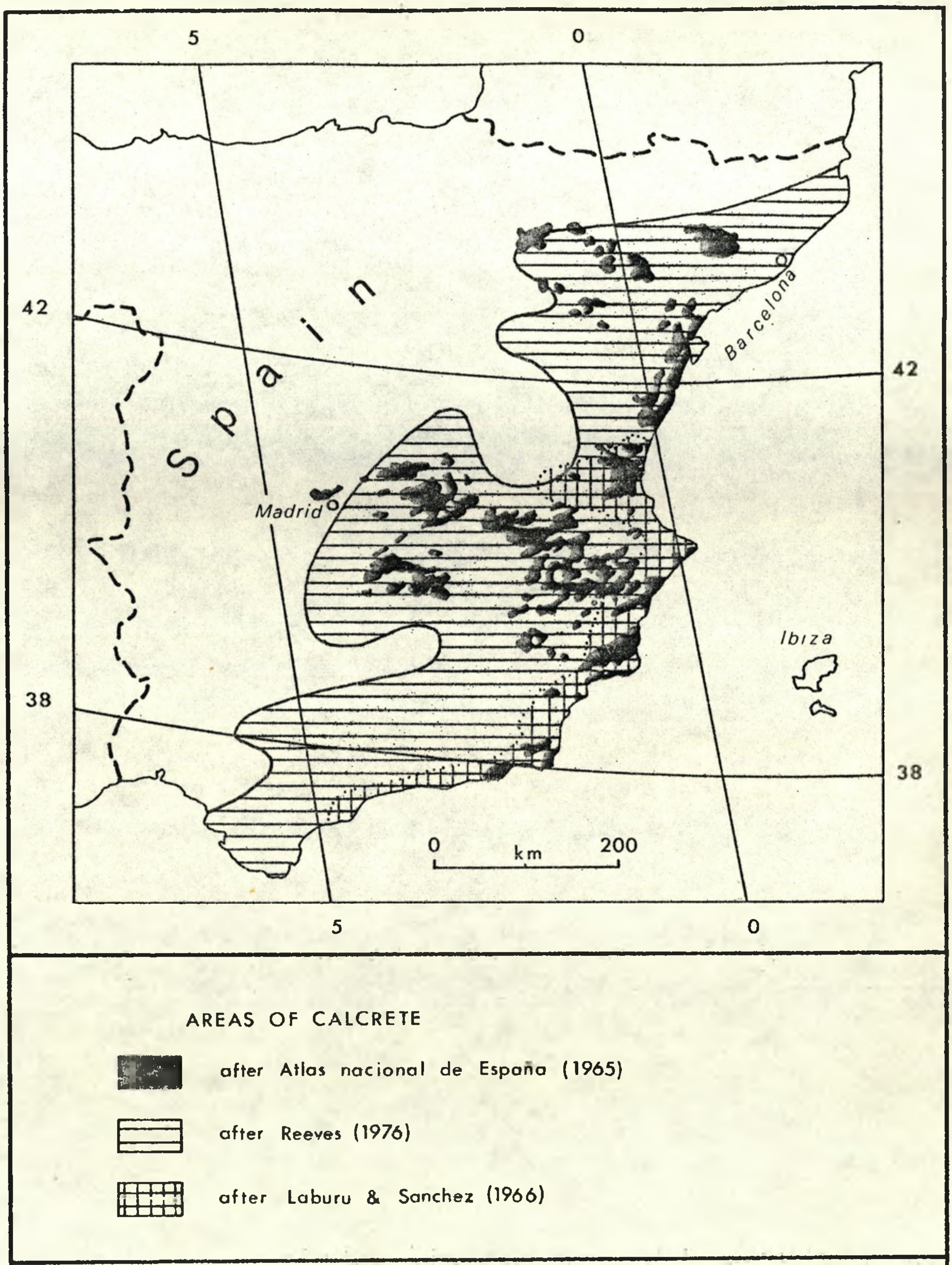


Figure 3. Calcrete distribution in Spain based on published maps.

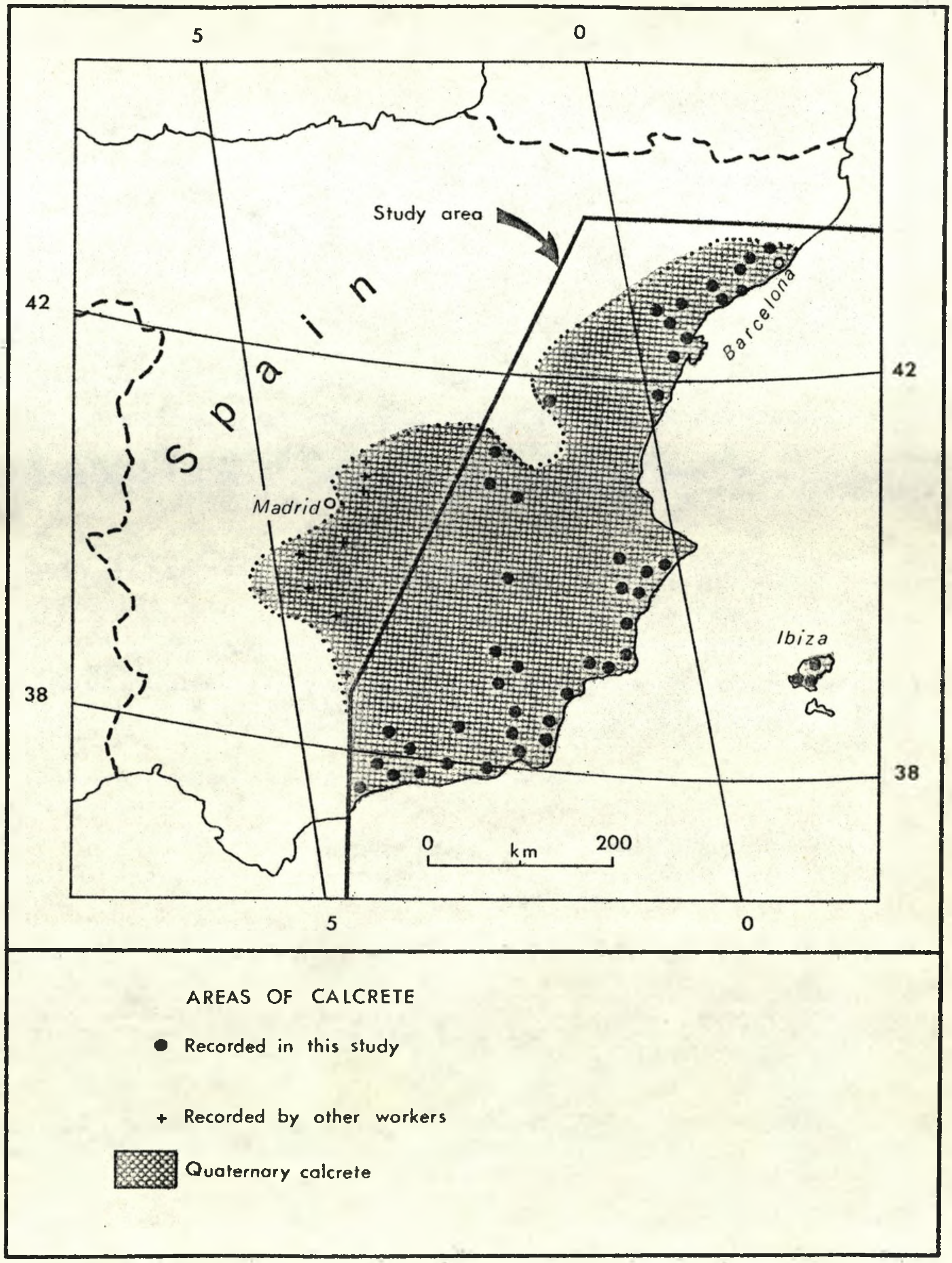


Figure 4. Calcrete distribution map presented in this study.

field observations, and (2) inspection of published field descriptions and photographs of calcrete profiles (Rutte, 1958; Laburu & Sanchez, 1967; Gladfelter, 1971; Dumas, 1969, 1975; Nagtegaal, 1969; Esteban, 1972, 1974; Vaudour, 1975). I have included published descriptions only if there is evidence to indicate that the described calcareous deposits have a pedodiagenetic origin. In other words, I have included only those 'calcretes' that comply with my definition of calcrete (p.35). No distinction has been made between active and fossil calcrete profiles and, because chronological age is difficult if not impossible to determine, all _in situ_ calcrete deposits have been included if they occur at or immediately below the land surface. In areas where industrial and agricultural practices have removed extensive (km^2) areas of calcrete, former presence of calcrete has been inferred from fragments contained within stone walls - calcrete is useful economically for its building properties. Allowance for natural erosion has been made only in areas where truncated calcrete profiles are clearly recognizable, as occur along abandoned river valleys.

It is emphasised here that my own calcrete distribution map for Spain is not necessarily more accurate or less accurate than those of other workers. However, the assumptions on which my map is based have been stated explicitly so that the reader may draw his own conclusions with regard to its usefulness.

SOIL-FORMING FACTORS

Since calcretes have a pedodiagenetic origin (p. 36), the effects of five basic soil-forming factors on the distribution of

Spanish calcretes have been examined to find out if any causal relationships exist. The factors chosen are essentially those outlined in the equation put forward by Jenny (1941), that is to say, the factors of climate, host material, topography, organisms and time. The basic factors define the state of the soil; they are not soil-forming processes. Soil-forming processes lead to horizon differentiation. They have been divided into four groups by Simonson (1959) - additions, removals, translocations and transformations. Such soil-forming or pedogenetic processes are dealt with in Chapter 8. Soil factors, in contrast, are independent variables which affect soil properties such as pH, porosity, non-carbonate clay content and $CaCO_3$ content.

Several criticisms have been made of the use of equation factors in soil studies (Crocker, 1952). One major criticism is that the equation of Jenny (1941) has never been solved. This can be attributed partly to the qualitative nature of some of the data; of the five basic factors, host material and organisms (biotic factor) are not readily amenable to quantification. Moreover, Birkeland (1974, p.126) remarked "...if an equation cannot be solved we have not gained much by merely listing the factors." Another criticism is that one learns a lot about soil-forming factors, but little about the soil itself (Bunting, 1965). But perhaps the greatest objection and of direct relevance to pedodiagenetic calcretes is that soils are generally polygenetic, that is to say, that they have formed under more than one set of factors. Thus strictly, present-day conditions should not be used to define the state of polygenetic soils.

Despite the above mentioned drawbacks, the five basic factors - climate, host material, topography, organisms and time - provide a convenient framework in which to examine the regional distribution and characteristics of Spanish calcretes. Possible relationships between calcrete distribution and the five basic soil-forming factors are evaluated but it is emphasized here that the limitations of this approach should be borne in mind.

Climate

Precipitation (rainfall) and temperature are important aspects of climate that influence soil properties. Many workers have noted that a relationship exists between macroclimate and calcrete distribution (Price, 1933; Netterberg, 1969b; Goudie, 1972b, 1973). Goudie (1973, p.101) stated: "In Spain....there is a very fair correlation between crust distribution and the 400 mm annual precipitation. Thornwaite's -20 index* gives another moderate fit. Calcretes are rare where precipitation is more than 400 mm." Figure 5 shows these relationships (p.47).

Some workers have suggested that there is a relationship between the amount of precipitation and the distance from the surface to the $CaCO_3$-bearing horizon (Jenny, 1941; Arkley, 1963). Viewed simplistically, if rainfall is so low that infiltration of calcareous solutions is negligible, only surface crusts can form. Surface-forming crusts have been documented in areas receiving less than about 300 mm rainfall per

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* Thornwaite moisture index $Im = 100\ (S-D)/PE \simeq 100\ (r/PE - 1)$
where S = monthly water surplus; D = monthly water deficit;
PE = potential evapotranspiration; r = annual precipitation
(From Barry & Chorley, 1971).

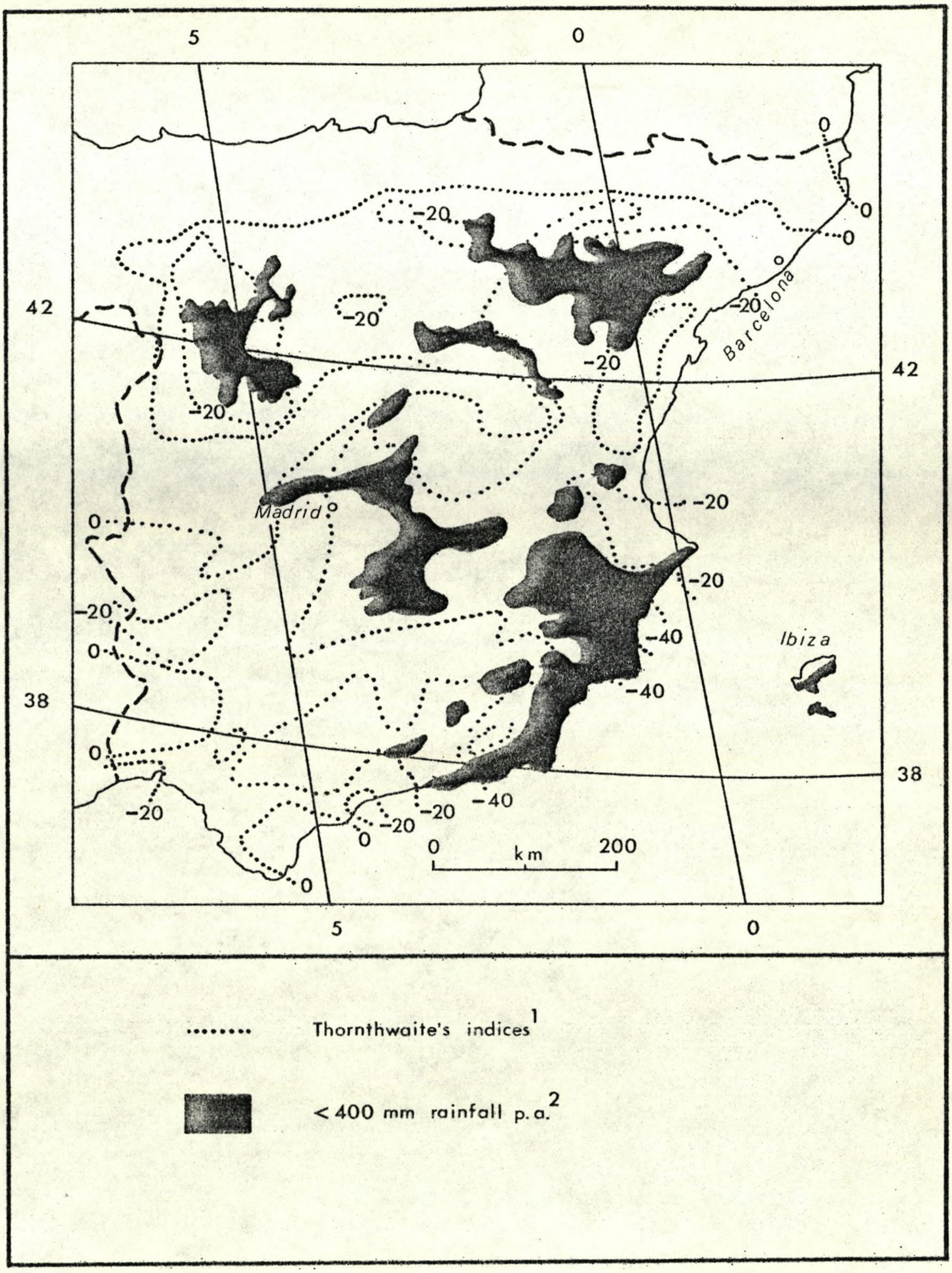

Figure 5. Climatic indices of Spain.

annum although amounts and rates of infiltration depend also on temperature (function of evaporation). On the other hand, if rainfall is sufficiently high to cause complete leaching, no $CaCO_3$ can accumulate. To allow subsurface calcrete development to proceed, hydrological conditions need to be between these two extremes.

In a steady state system (dynamic equilibrium), inputs balance outputs. However, the formation of calcrete profiles generally indicates that gains (in $CaCO_3$) have exceeded losses. Yaalon (1971) has termed such development as an 'irreversible self-terminating process'. Thus, a calcrete hardpan can be considered as a climax horizon whereby calcium carbonate has accumulated progressively and effectively sealed the layer. The term 'climax' is used here to describe the maximum attainable end phase of a developmental sequence, governed by prevailing environmental conditions (adapted from definition of 'climax soil' by Kubiena, 1970). However, such development depends also on climatic stability; if the climate changes there may be a retrogressive stage instead of a sequential, progressive development. For example, solution of calcrete hardpans (Plate 5c) leading eventually to the formation of 'boulder calcrete' (cf. Netterberg, 1969b) is a retrogressive stage in calcrete development. Mechanical and biochemical destruction of calcrete hardpans by present-day vegetation is a further example illustrating retrogressive development (Plates 10c, 22). These changes have taken place in response to environmental and, in particular, to climatic changes.

A characteristic feature of the Mediterranean climate is a marked seasonal change between hot (greater than 28°C), rainless summers and cooler, humid winters. However, the regularity, duration and intensity of seasons in a given region vary with latitude, altitude, topographical aspect and degree of continentality. Bunting (1965), in his discussion on Mediterranean soils, recognized four soil subtypes related to length of the dry season and general aridity: humid (less than 6 weeks drought), subhumid (6-12 weeks drought), semi-arid (13-22 weeks drought) and arid (greater than 22 weeks drought). I have taken these values as a basis for dividing the loosely defined and somewhat stereotyped 'Mediterranean-type climate'. Thus, the regional distributions of climatic subtypes based on duration of the dry season, are illustrated in Fig. 6, p.50. No discernible relationship exists between present-day aridity and distribution of calcrete deposits in Spain (compare Fig. 4, p.43 with Fig. 6, p.50).

Because of significant fluctuations in various past climates during the Quaternary, the present distribution of calcretes may not be related to the present climate. Thus, the distribution of Spanish calcretes may have been controlled, partly at least, by an earlier climatic regime. However, in view of the confusion with regard to chronostratigraphical and lithostratigraphical associations in Quaternary sediments of the Mediterranean (for discussion see Houston, 1964; Biberson, 1970), I have made no attempt at palaeoclimatic reconstructions. Indeed, it would be irresponsible to conclude that calcrete deposits indicate a certain set of climatic conditions on such limited and generalized information. A great deal of work is required to substantiate or refute the often quoted presumptive statement that calcrete deposits indicate an arid or semi-arid climate. For the time being, I have refrained from making conclusions on possible climate-calcrete relationships.

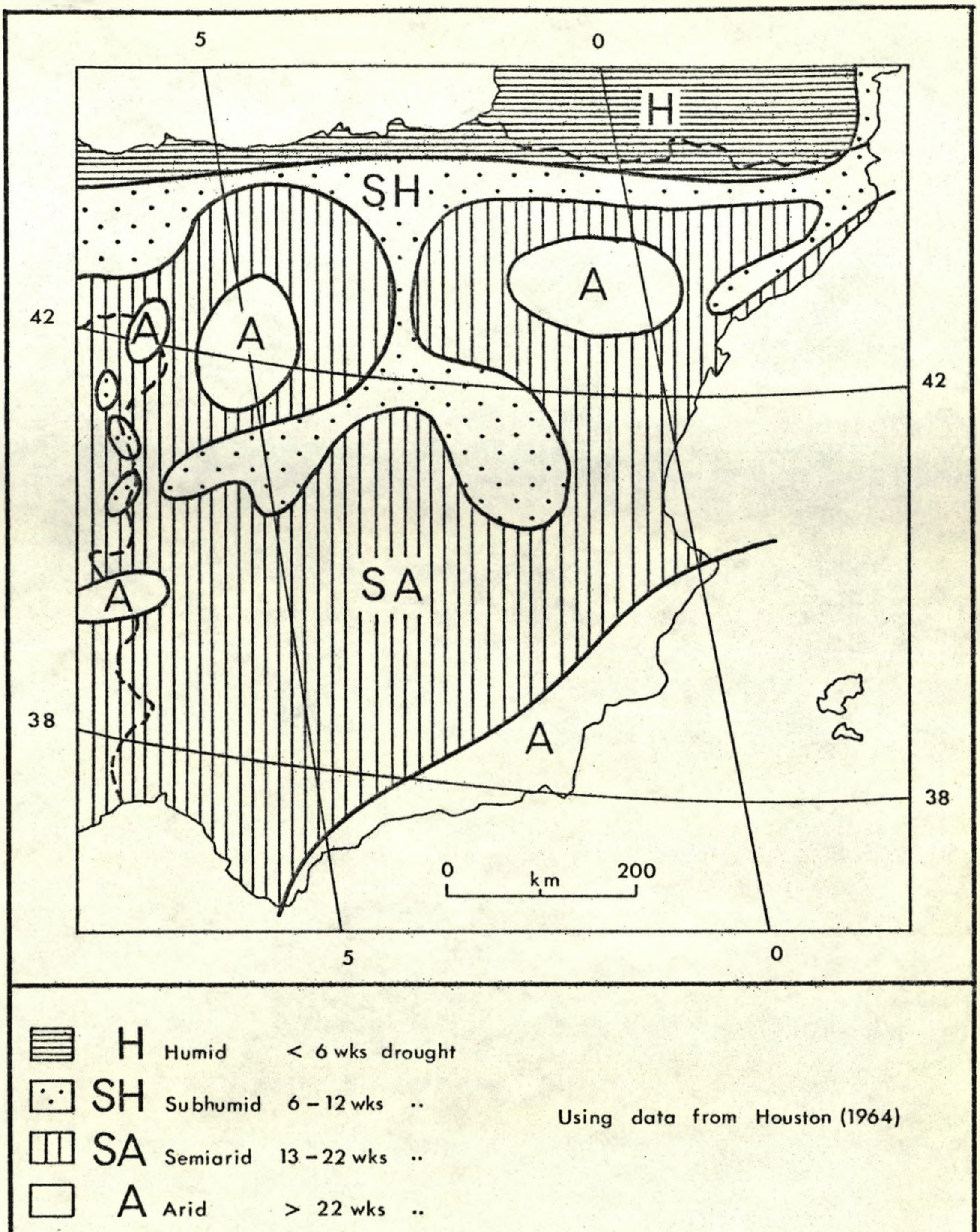

Figure 6. Climatic divisions in Spain based on the duration of the dry season.

Host Material

In this study, I am concerned primarily, not with the age, history or geological relationships of rocks as such, but with their physical and chemical properties that control or influence calcrete formation. The properties of greatest relevance include original texture, porosity, permeability, hardness, induration, composition and mineral stability of the host material. To find out if calcrete forms or has formed preferentially within a particular host material, special attention was given to the characteristics of the underlying unaltered host substrate.

During my field studies, calcretes were recognized within sedimentary, igneous (intrusive and extrusive) and metamorphic rocks, unconsolidated sediments and pre-existing soils. Calcretes *s.s.* were identified within carbonate rocks (limestones and dolomites), coarse-grained to fine-grained fluvial siliciclastics, alluvial fan deposits, colluvial deposits, wind-blown or aeolian sands, vitric tuffs, andesites, diorites and palaeosols (red *terra rossa* soils, brown *terra fusca* soils). Thus, it might be concluded that calcrete formation is independent of lithology. As long as a source of calcium carbonate exists, whether it is autochthonous or allochthonous in origin, calcrete does not appear to be restricted to a particular lithological type. However, it was noted that calcrete profile development tended to be poor within well consolidated carbonate rocks. Whereas silicate minerals are susceptible to weathering in an environment conducive to calcrete formation, low magnesian calcite and, to a lesser extent, dolomite tend to be stable. Thus, it is inferred that weathering of carbonate rocks coincides with the destruction of calcrete profiles whereas when the environment is conducive to calcrete formation, indurated carbonate rocks are not readily weathered.

My field observations indicate that the main factor which appears to govern the distribution of calcretes in Spain is not the composition but the geomorphic stability of the host material. Whereas the formation of calcrete within bedrock is initiated by in situ weathering, calcrete can form only within unconsolidated sediments or soils that are morphodynamically stable. For example, in the province of Almeria, active fan deposits have not been calcretized, whereas Recent abandoned (stable) river terraces show signs of calcretization.

On the island of Ibiza, coastal cliff sections are composed of alternating unconsolidated and non-calcretized colluvial silts and calcretized aeolian deposits of Pleistocene age (Plate 1). It has been suggested (Butzer, 1964; Rohdenburg & Sabelberg, 1973) that slope erosion during periods of morphodynamic activity led to the accumulation of colluvial calcareous and siliclastic silt deposits in basinal areas. Rapid sedimentation precluded soil formation. In contrast, calcretization is considered to have taken place during periods of morphodynamic stability, that is to say, when displacement of slope deposits and aeolian sands had ceased.

Plates 3, 4 and 17 show the development of calcretes within andesite, diorite and aeolianite (wind-blown calcareous sands) host material respectively. In these three examples from Ibiza, much of the $CaCO_3$ within the calcrete profile has been derived from the host material. In other words, the host material is the parent material for the constituents of the calcrete profile in these examples. It is not mere coincidence that roots or evidence of former roots are prominent features of these profiles; roots are largely responsible for substrate modification and the formation of several diagnostic features and textures within calcretes, regardless of initial lithology.

Topography

A prominent feature of calcrete distribution in Spain is its correspondence to present-day topography (Plates 1, 2). This topographical correspondence appears to be common in many other parts of the world (James, 1972; Goudie, 1973; Read, 1974). Dunham (1969b) has suggested that recognition of ancient calcretes within geological successions can be used to identify palaeotopography.

Calcretes are widespread throughout the western Mediterranean on gentle slopes, with slope angles of 25° or less. Calcretes were observed on steeper slopes but profile development is poorer on these surfaces compared with those developed in lowlying, basinal areas. On inclined surfaces with slope angles greater than 25° from the horizontal, mechanical and chemical erosion, has largely removed weathered detritus, exposing bedrock surfaces. In areas where the bedrock is limestone or dolomite, karstic features characterize the surface expression. Further downslope, the transported material is dominantly fluvial and alluvial deposits. This phenomenon is illustrated simplistically in Fig. 7, p. 54.

In northeastern Spain, major slope erosion and basinal deposition have virtually ceased; the Pleistocene alluvial fan deposits on the Plain of Tarragona, for example, are now stable surfaces which have been calcretized. Further south, however, in the provinces of Murcia and Almeria, alluvial fans are active today (indicated by sediment-covered roads) and calcrete formation

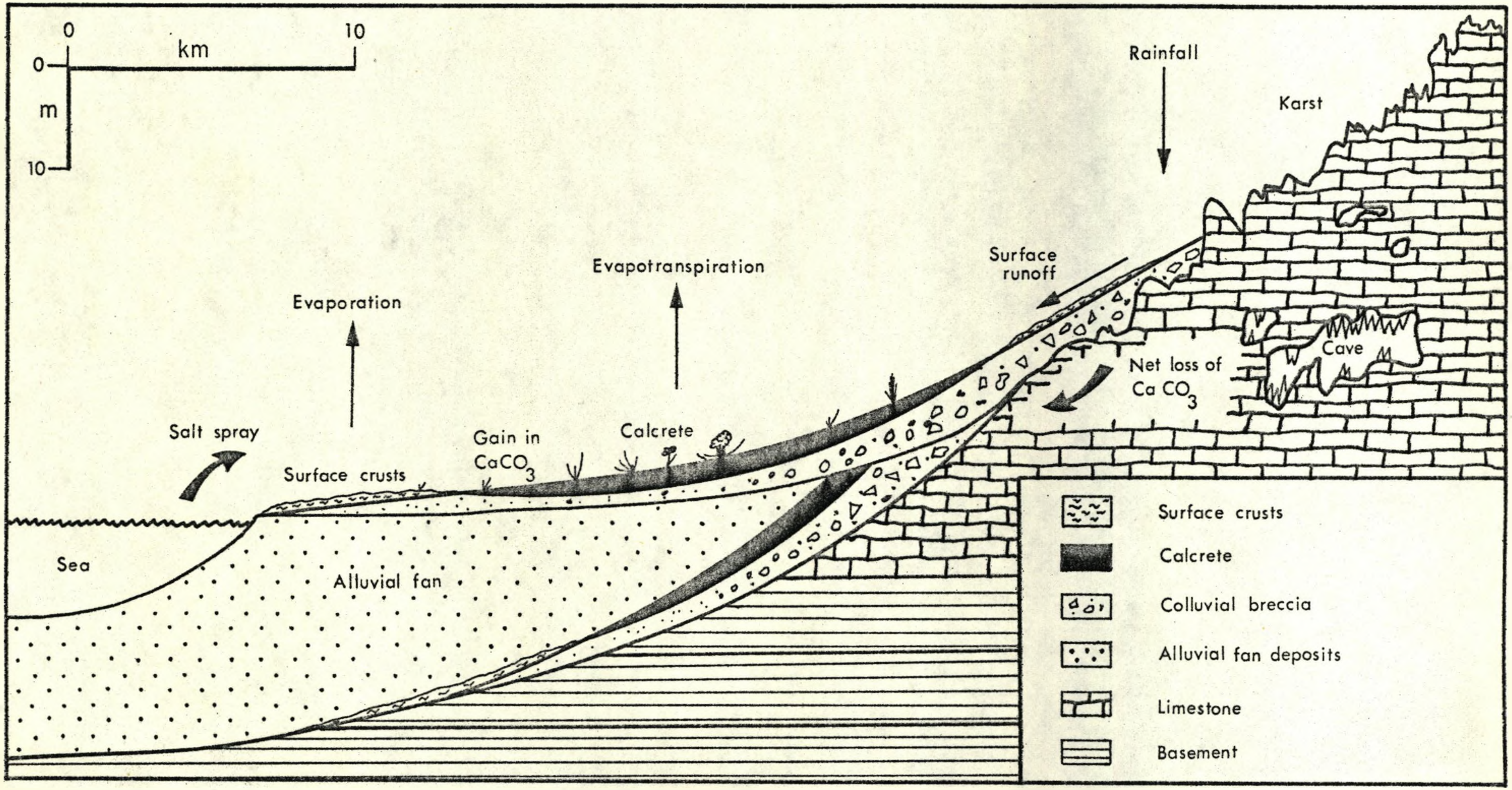

Figure 7. Schematic representation of an idealized toposequence of the western Mediterranean coastal regions.

is minimal or absent in these deposits. It is inferred that present-day slope instability has restricted or inhibited calcretization in these deposits since calcretes are common on neighbouring, stable slopes.

In addition to affecting erosion and sedimentation, the topographical slope influences runoff and infiltration rates. Topography, together with geology, climate and vegetation, also determines the position of the water table. Nevertheless, my own field observations, together with those of numerous other investigators (e.g. James, 1972; Goudie, 1973; Ward, 1975; Harrison, 1977), indicate that the land-atmosphere interface has determined the position of calcrete profiles, regardless of depth to the water table (Plates 1, 2).

Biotic Factor

The vegetation cover is intimately related to climatic and soil conditions of the past as well as the present environment. Because of complex interactions among soils, climate and vegetation, the biotic factor is difficult to assess with regard to the distribution, morphology and formation of calcretes. For a comprehensive appraisal, information is required on the types, patterns and effects of vegetation before, during and after calcrete formation. Unfortunately, such information is not available. Whereas it is possible to map present patterns and types of vegetation, evidence of earlier vegetation within calcretes generally lacks sufficient detail to allow identification of plant species. This does not mean to say that evidence of former vegetation within calcretes is lacking completely. On the contrary, sufficient evidence of former plant activity is preserved in most calcrete samples collected during the course of this work to suggest that plants, particularly their rooting systems, play a fundamental role in calcrete formation. In the glaebular zone of many profiles, the nuclei of vertically elongate nodules* were found to contain partially decayed roots (Plates 16a, 19). Moreover, petrified and cemented root structures or <u>rhizoliths</u> (p. 90) are major components in many calcrete profiles (Plates 7, 17, 18). In some observed profiles, rhizoliths occur in such profusion at certain horizons that the horizon itself can be designated a <u>rhizolite</u> (p. 93) or root rock.

In addition to vertically elongate root systems, horizontal layers of root mats were recorded in many calcrete profiles examined throughout the western Mediterranean (Plate 12a). The thickness (generally between 2 - 10 cm), position (commonly occur within sheet calcrete horizons) and undulatory nature (low amplitudes with wavelengths in metres) of these root mats were noted for their likeness to subsurface micritic sheets. Indeed, several transitional stages between horizontal root mats and subsurface micritic sheets were recognized, indicating that the end-members are related genetically as well as morphologically (Plates 12, 13). In other words, the micritic sheets are calcified root mats. Harrison (1977) recorded 'subsurface micritic stringers' within Pleistocene calcrete profiles from Barbados; their origin may, likewise, be attributed to horizontal root mats.

Any soil, by definition, supports biological ecosystems (Russell, 1973). In addition to higher (vascular) plants there is invariably a host of associated micro-organisms present in the soil. In calcretes, which are products of pedodiagenesis, evidence of a former microflora has been observed by optical and scanning electron microscopy (Chapter 5).

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*A nodule = a glaebule lacking an internal concentric fabric. See p. 84 for details.

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Briefly, evidence includes: calcified (calcite impregnated and encrusted) filaments of algae, fungi, actinomycetes; rod-shaped bacterial (?) structures; calcified spores; and unidentifiable organic mucilaginous substances.

The above mentioned plant life provides a source of food for the soil fauna. Evidence of faunal activity within calcretes at the time of their formation has been inferred from: (1) the sizes, shapes and patterns of certain channels which are interpreted as former burrowing systems of soil organisms (p.135); (2) the fabric of certain kinds of peloids which are interpreted as calcified faecal pellets (p.190); and (3) certain kinds of spherical structures which are interpreted as calcified insect puparia (p.191).

In conclusion, it can be asserted that evidence of former biological activity exists within Spanish calcretes. However, I have not been able to identify recognizable organic constituents beyond Division name, mainly because of inadequate preservation of diagnostic details. Nevertheless, even without taxonomic refinement, documentation of the existence of the above outlined organic constituents is, in itself, evidence to support the contention that calcretes are products of pedodiagenesis.

Time

The time factor in calcrete formation can be assessed in several ways: (1) by absolute dating using carbon isotopes (Netterberg, 1969a; Williams & Polach, 1971); (2) by the relative stage of calcrete development from time zero (Gile et al., 1966); (3) by using empirical formulae (Arkley, 1963; Gardner, 1972; Goudie, 1973); (4) by correlation with datable geomorphic surfaces on which calcretes have developed (Ruhe, 1967), and (5) by dating contained artifacts and fossils to give a maximum age of the encasing calcrete (Netterberg, 1969a).

Despite the several possible methods of dating, the time factor in calcrete formation is difficult to evaluate with accuracy. There are numerous problems that undermine the validity of both absolute and relative dating methods. For example, it is generally assumed that the thickness of a calcrete profile increases with time. However, the rate of $CaCO_3$ accumulation depends also on: original $CaCO_3$ content, porosity, permeability and grain size of the host material; rates of rock and mineral weathering; sedimentation and erosion rates; amount and availability of additional $CaCO_3$; amount, movement and chemistry of infiltrating solutions; and rates of calcite precipitation and solution. If the $CaCO_3$ source has been derived from *in situ* mineral weathering of the host material, calcrete formation is controlled largely by the rate of weathering of calcium-bearing minerals. If, on the other hand, aeolian dust has been the major $CaCO_3$ source, buildup is governed by rates of influx, translocation and precipitation of $CaCO_3$. Thus, although calcrete development is a function of the duration of pedodiagenetic processes, the intensity and continuity of such processes are of equal importance.

The chronostratigraphy of the Quaternary in the western Mediterranean is not known with precision. In particular, reliable dates for Spanish calcretes are not available. Some workers believe that they can distinguish geomorphic levels which reflect past sea levels during the Pleistocene (Solé Sabarís, 1961; Butzer & Cuerda, 1962). Although I have recognized distinct surfaces on the island at Ibiza, I am not convinced that these levels can be used with certainty for stratigraphical correlation. Therefore, I have refrained from using such criteria for relative dating.

Terrestial fossils, mostly gastropods, were recorded within many calcrete profiles throughout the study area. It was hoped that these fossils could be used to establish a relative chronology. Unfortunately, subsequent identification (carried out by Dr. C.R.C. Paul, Department of Geology, University of Liverpool) indicated the stratigraphical range of most sampled species extended throughout the whole of the Pleistocene to the present day. Thus, they are unsuitable as index fossils for distinguishing stages of the Quaternary.

Because the interacting factors that control the rate of $CaCO_3$ buildup are difficult to separate, I have not attempted to date calcrete profiles by stage of development. Likewise, calculations of ages using empirical formulae have not been attempted. Most models are based on assumptions far removed from reality and, thus, I am sceptical of ages derived from such empirical models.

To my knowledge, no radiocarbon datings of Spanish calcretes have been made. Therefore, I have relied on the 'law of superposition' for gross dating, that is, calcretes are assumed to be younger than the host material in which they have intruded. Hence, I have relied largely on published geological maps to deduce the maximum age of calcretes throughout the study area.

CALCRETE PROFILES

The term calcrete profile is used here to describe the complete vertical succession of morphologically distinct layers or horizons, from the outcropping surface down into unaltered host material. Like soil profiles, the physical and chemical properties of calcrete profiles show a vertical anisotropy which can be assessed by qualitative and quantitative methods. However, boundaries between horizons tend to show gradual transitions rather than abrupt changes. Thus, it is difficult to define boundaries with accuracy and objectivity. Although quantitative analyses can be carried out with precision, dependable results rely on representative sampling. To minimize sampling bias, materials for laboratory analyses were collected from the central parts of designated horizons after removal of surficial weathered detritus.

In addition to a typical vertical anisotropy which characterizes a calcrete profile, calcretes commonly show lateral variations in sequences and thicknesses of horizons on a scale of a few metres. Wherever traceable, the lateral continuity of horizons was measured in an attempt to quantify lateral variations in thickness. The distinctness of boundaries between horizons was described using the intervals given in Table 3, p.61.

The nomenclature used in this study to designate morphologically distinct horizons has been outlined (Fig. 2, p.39). To recapitulate, these horizons are, from the top surface downwards in a fully developed profile: active soil; hardpan; sheet calcrete, glaebular calcrete; chalky calcrete; transitional horizon; and unaltered host material. For every profile description, the numbers and types of horizons were recorded in a two-dimensional log (see Appendix Figs. A-1 to A-5). The thicknesses of individual horizons, distinctness of boundaries, qualitative assessments of colour and colour variation of constituents, hardness, visible porosity (fractures, vugs) and consistencies of horizons were recorded in the field. Contained macroscopical features within individual horizons were noted. Overlying soils, if present, were described in terms of their thickness, colour, texture and contained organic matter.

TABLE 3. TERMINOLOGY FOR THE DESCRIPTION OF CALCRETE PROFILES

A. HORIZONS	DIVISIONS
1. Hardpan	Massive; laminar; glaebular; brecciated
2. Sheet calcrete	
3. Glaebular horizon	Soft chalky; indurated
4. Chalky horizon	
5. Transitional horizon	
6. Host material	Unconsolidated; consolidated carbonate; consolidated non-carbonate

B. HORIZON BOUNDARIES@

Very abrupt	< 0.1 cm
Abrupt	0.1 - 2.5 cm
Clear	2.5 - 6.0 cm
Gradual	6.0 - 12.5 cm
Diffuse	> 12.5 cm

C. CEMENTATION@

1. Cementing agent
2. Continuous or discontinuous cementation
3. Strength of cementation

a. Weak	material is brittle and can be broken with the hands
b. Strong	material is brittle and easily broken with a hammer
c. Indurated	material is brittle and broken only with a sharp hammer blow

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@After Birkeland 1974

Description of Horizons

Hardpan calcrete

In a typical profile, the hardpan occurs as the uppermost indurated horizon. The hardpan has been termed 'caprock' by some workers (e.g. Price, 1933; Bretz & Horberg, 1949) when the hardpan occurs at the surface. Being well indurated and lacking visible porosity, the hardpan is generally more resistant to weathering than underlying horizons and, thus, stands out in sections as a prominent feature (Plates 1, 2, 5a). Vertical thicknesses vary from 1 mm laminar layers to massive horizons, 1.5 m thick. The horizon is made up dominantly of well cemented microcrystalline or cryptocrystalline calcite. The thicker horizons commonly show evidence of fracturing, non-tectonic brecciation, solution and recementation (Plates 5b, c, 27a-d). Colours are generally white or cream, although pale orange to brown are not uncommon. The horizon may be macroscopically structureless or massive (Plate 5), laminated (Plate 11), brecciated (Plates 21, 22, 24, 25) or glaebular (Plate 27d, e). Upper boundaries between hardpan and unconsolidated breccia calcrete or soil cover vary from abrupt (Plate 5a) to diffuse (Plate 5b).

Sheet calcrete

The sheet calcrete horizon invariably occurs immediately below the hardpan horizon or, in profiles lacking a hardpan, occurs as the uppermost calcareous horizon (Plates 3a, b, 6a, b) or below a soil cover (Plate 4a). Sheet calcrete is distinguished from hardpan calcrete by its horizontal to subhorizontal platy or thinly bedded habit, its planar fracture porosity and greater friability (Plate 5a, b). Whereas a hardpan can be broken only with a sharp hammer blow, sheet calcrete can be dug out with a rigid knife blade or trowel. Boundaries between sheet calcrete and hardpan horizons tend to be diffuse.

Recognizable transitional stages suggest that hardpans represent advanced stages of sheet calcrete development. Maximum and average thicknesses of sheet calcrete horizons are greater than those of hardpans, the maximum thickness recorded for sheet calcrete being 3.1 m. Sheet calcrete generally grades downwards into glaebular calcrete. The boundary separating these horizons tends to be diffuse (Plate 6a, b).

Glaebular calcrete

The term glaebule is used here as defined by Brewer (1964). Derived from the Latin glaebula meaning a small clod or lump of earth, Brewer defined a glaebule as: "a three-dimensional unit within the s-matrix* of the soil material, and usually approximately prolate to equant in shape; its morphology (especially size, shape and/or internal fabric) is incompatible with its present occurrence being within a single void in the present soil material. It is recognized as a unit either because of a greater concentration of some constituent and/or difference in fabric compared with the enclosing soil material or because it has a distinct boundary with the enclosing soil material."

With regard to calcrete profiles, glaebules consist of discrete, powdery to indurated concentrations of calcium carbonate embedded in a less carbonate-rich s-matrix. Individual glaebules range from decimicron-sized[x] to centimetre-sized particles. They may be spherical to subspherical (Plate 15), irregular (Plate 14b) or cylindrical in shape (Plate 6b, c). Most cylindrical forms are vertically elongate in orientation (Plates 6b, c, 14a). Some, however, show branching patterns (Plate 16b).

Glaebules occur either as isolated particles (Plate 15b, c)

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* s-matrix is broadly equivalent to matrix of sedimentologists but for a precise definition, see p. 112.

x See p. 113 for size classification scheme. This scheme is followed because of current usage but is etymologically inconsistent with formal definition of 'deci' meaning one tenth. Here decimicron means tens of microns rather than a tenth of a micron.

or as coalesced masses (Plates 4e, f, 7). Coalesced masses of indurated glaebules tend to stand out in relief whereas the generally less well consolidated s-matrix tends to be eroded more easily. This differential weathering within glaebular horizons (Plates 9c, 18b) gives rise to 'honeycomb calcrete' (cf. Netterberg, 1969b, 1971).

In addition to greater concentrations of calcium carbonate and greater cohesion, glaebules usually can be distinguished from the surrounding s-matrix by colour differences (Plates 14b, 15c, 16c). Glaebules are commonly white to cream, whereas the s-matrix tends to be red or red-brown. Higher concentrations of acid-insoluble residues, such as layer lattice minerals and ferric hydroxides, are responsible for red to red-brown colours of the s-matrix. However, some glaebules, especially millimetre-sized glaebules with internal concentric fabrics, are dark red-brown whereas the s-matrix is pale brown or cream. Iron salt impregnation within these darker glaebules was found to be responsible for this colour difference.

Glaebular horizons invariably show diffuse upper and lower boundaries. In many profiles, the boundary between glaebular and chalky-powdery horizons is so indistinct that I have designated this 'boundary' as a separate horizon, that is, the glaebular-chalky horizon.

The glaebular horizon is, volumetrically, the major horizon in a complete profile. Average vertical thickness for 263 measured glaebular horizons is 1.2 m. The maximum recorded thickness of 6 m occurs at San Vicente de Calders, province of Tarragona (Plates 6a, 14a). At this locality, glaebules grade upwards from large (10 cm), vertically elongate, isolated glaebules at the base to smaller (3-4 cm) but more numerous, subspherical to irregular coalesced glaebules towards the top (Plate 14a). This fining-upwards sequence is a common feature of glaebular calcretes throughout the western Mediterranean.

Chalky horizon

The chalky horizon is characterized by white to cream, unconsolidated decimicron-sized calcite grains. Cementation between grains is absent so that the material has the consistency of a powder (Plates 4a, 5a). Apart from minor siliciclastics and organic matter, the chalky horizon is composed almost exclusively of calcium carbonate. The horizon tends to be homogeneous structurally and texturally, although scattered, isolated glaebules are sometimes present. Areas around plant root systems appear to be favoured sites for $CaCO_3$ accumulations (Plates 16a, 19c). This phenomenon gives rise to incipient glaebular development. The reasons for preferential concentrations of $CaCO_3$ around roots are discussed elsewhere in this study (p.167).

Maximum thicknesses of this horizon rarely exceed 1 m and are generally less than 50 cm. Chalky horizons are poorly developed or absent in most profiles with aeolianite as host material. When present, the chalky horizon is noticeable because of its brilliant white colour and powdery consistency. However, the horizon is difficult to define because upper and lower boundaries are invariably diffuse. The chalky horizon generally grades upwards into glaebular calcrete and downwards into the transitional horizon.

Transitional horizon

The term transitional horizon refers to the transition zone between unaltered host material and overlying calcrete horizons that lack macroscopically discernible features inherited from the host material. The transitional horizon, itself, contains macroscopically discernible evidence of in situ alteration and partial replacement of the original host material (Plate 8). This evidence includes: (1) relic sedimentary structures such as bedding (Plate 8c); (2) in situ relic fossils embedded in otherwise calcretized host material; (3) in situ relic siliciclastic grains with distribution patterns inherited from the host material; and (4) relic mineral veins traceable from the underlying host material into the calcrete profile without deviation or disruption. Plate 3b shows quartz veins traceable from slightly weathered diorite at the base into the overlying calcrete profile. This profile also illustrates the gradual obliteration of igneous textures with progressive increase in $CaCO_3$ accumulation upwards into a calcrete hardpan (consisting of virtually 100% calcium carbonate).

In profiles developed within bedded sedimentary deposits, dipping beds of unaltered host material can be traced upwards into transitional and chalky horizons (Plate 8c). Alteration has taken place preferentially along bedding and joint planes. These planes of access allow water to move through the host material more easily and are, thus, sites susceptible to diagenetic alteration. Such places are also susceptible to penetration by roots (Plate 23).

Because this horizon is essentially an in situ weathered zone, consisting of partially degraded host material, it is difficult to fix boundary limits with objectivity. However, the thickness of this product of partial substrate alteration generally exceeds 50 cm, the computed average for 326 particles being 142 cm. Thus, because of its volumetric and genetic significance, I prefer to distinguish this transitional zone as a distinctive horizon. Unfortunately, although it is easy to define conceptually, this horizon is not so readily defined with precision in the field.

Host material

As already indicated, the host material may be of any composition, texture, age and origin (p. 51). The only significant factor of host material that influences calcrete formation is its mechanical stability; development of a calcrete profile, with replacement of the host material by calcium carbonate and cementation, requires a stable substrate sufficiently long for pedodiagenetic processes to operate.

The host material is distinguished from the overlying calcrete profile by the absence of typical features which characterize calcrete deposits. Original structures, textures and fabrics of the host material are clearly recognizable; they have not been modified or obliterated by subsequent calcretization, in contrast to the transitional, chalky, glaebular, sheet and hardpan horizons which do show such alterations.

Soils

Present-day active soils of the western Mediterranean may, or may not, be related genetically to subjacent calcrete profiles. Because it is rarely possible to prove or disprove whether a relationship exists between the present active soil and the underlying calcrete horizon, soils were included in field descriptions of calcrete profiles.

Active soils, overlying hardpans in northeastern Spain and Ibiza contain roots which are, today, playing an important role in the brecciation of the underlying calcrete (p.97). Thus, successive sequences of soil formation, carbonate accumulation and induration, followed by brecciation of the indurated part of the profile, may lead to the formation of reworked, in situ, calcrete breccias (Plate 23a). Active and relic (hardpan) soils, thus, are mixed together and, if they become cemented, form breccia-conglomerate calcrete hardpans (Plate 27a, b).

Physical and Chemical Properties of Calcrete Profiles

Thickness

Based on 326 measured calcrete profiles, Table 4, p.69 summarizes the computed average and recorded maximum thicknesses for individual horizons. It is pointed out that the idealized calcrete profile of Table 4 includes actual profiles that do not follow the sequence of horizons as illustrated. For example, some measured profiles have two or more glaebular horizons, whereas other profiles show no glaebular development (see Appendix, Figs. A-1 to A-5).

Total thicknesses of calcrete profiles were plotted in relation to their geographical positions. However, no systematic changes were recognized, suggesting that profile thicknesses are not a simple function of latitude or climate. Complex interacting factors which may have influenced total thicknesses of calcrete profiles, include the composition, porosity and permeability of the host material, original amount of $CaCO_3$ present, availability of additional $CaCO_3$, topographical

TABLE 4 PHYSICAL PROPERTIES OF CALCRETE PROFILES (BASED ON 326 MEASURED PROFILES)

HORIZON	AVERAGE THICKNESS (cm)	BOUNDARY	POROSITY			CEMENTATION		
			TYPE	% FIELD ESTIMATE	% POINT COUNTING	CEMENTING AGENT	CONTINUITY	STRENGTH
0. Soil	32.5		Channel	30		Minor calcite	discontinuous	weak
		---very abrupt to clear						
1. Hardpan	20.6		-	-	0-13	calcite ± silica	continuous	indurated
		---clear to diffuse						
2. Sheet calcrete	62.6		fracture; mouldic	10	3-17	calcite	continuous	strong
		---diffuse						
3. Glaebular calcrete	118.2		inter-particle	10-15	3-23	calcite	discontinuous	strong to weak
		---diffuse						
3.4. Glaebular-chalky horizon	89.0		inter-particle	15-20		calcite	discontinuous	weak
		---gradual to diffuse						
4. Chalky horizon	54.5		inter-particle	15-20	9-35	calcite	discontinuous	weak
		---gradual to diffuse						
5. Transitional horizon	142.0		fracture; vug	15-25	3-31	calcite	discontinuous	weak to strong

slope and its mechanical stability, amount and type of vegetation cover, sedimentation, erosion and time. It has not been possible to isolate these factors and, thus, I have been unable to assess their relative importance in determining thicknesses of calcrete profiles.

Calcium carbonate content

Samples from 7 complete profiles were treated with acid to determine the $CaCO_3$ equivalent (see Appendix for procedure). In addition, 7 laminar hardpans and subjacent aeolianite host materials were digested in acid. For all samples, it was assumed that the weight loss resulted from solution of calcium carbonate. The computed values are shown graphically in Fig. 8, p.71.

Hardness

In the field, the hardness and degree of induration were assessed qualitatively using the scheme presented by Birkeland (1974; see Table 3, p.61). The cementing agent, the continuity and strength of cementation were recorded for all profiles. The results are summarized in Table 4, p.69.

Porosity

Macroscopical porosity (visible with the naked eye) was noted qualitatively in terms of presence or absence, or semi-quantitatively with the aid of visual estimation charts from Yaalon (1966). Porosity type was recorded using a scheme (see p. 129 for details) adapted from those presented by Brewer (1964) and Choquette & Pray (1970).

Laminar and massive hardpans generally lack macroscopical porosity unless solutional vugs and channels, post-dating hardpan

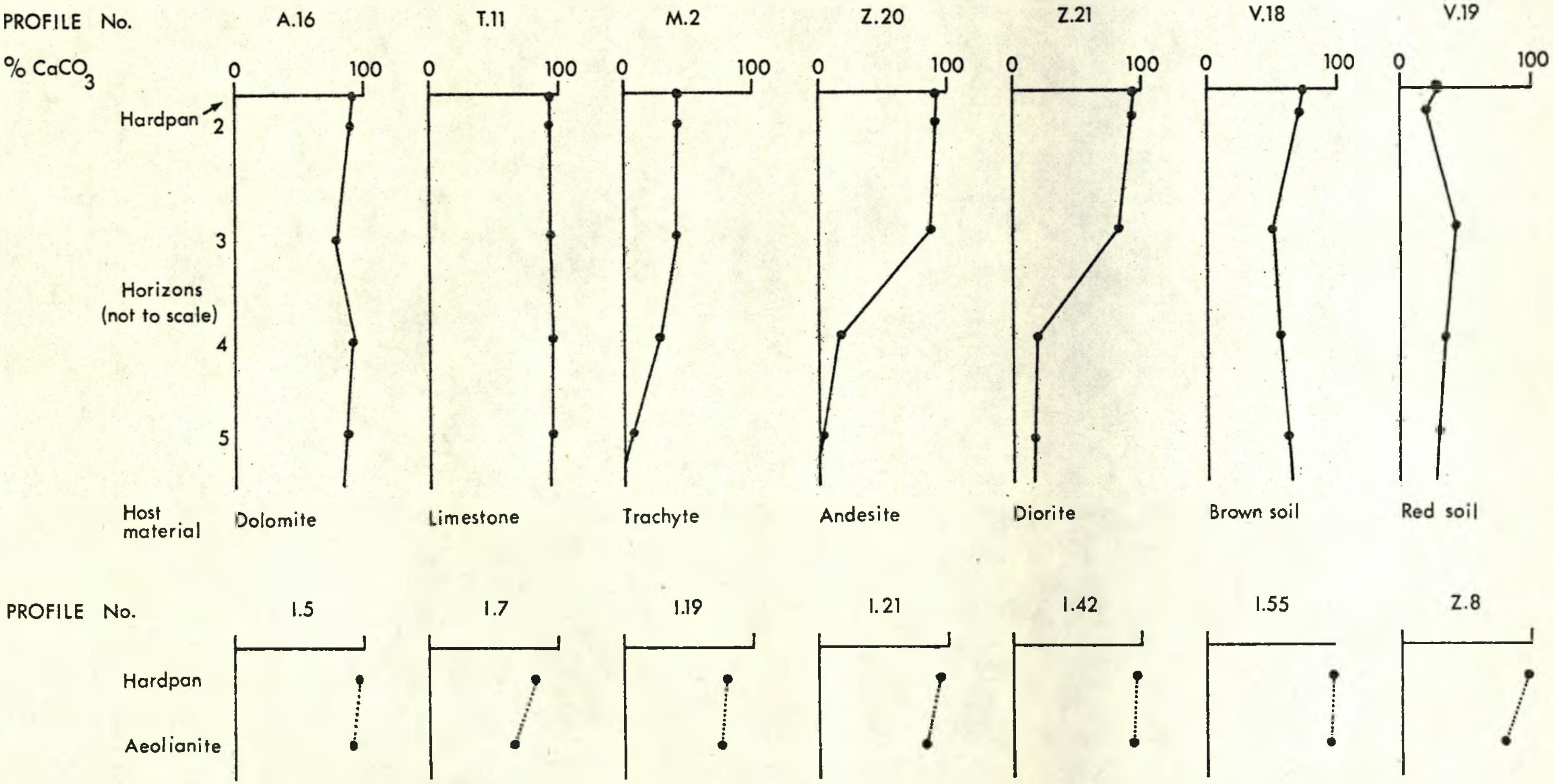

Figure 8. Distribution and amount of calcium carbonate in calcrete profiles.

formation, are present (Plate 5c). Sheet calcrete horizons are characterized by horizontal to subhorizontal planar fracture porosity (Plate 5b). Nodular and chalky horizons generally have a visible interparticle porosity. The porosity of transitional horizons varies considerably, being a function of the original host material porosity and susceptibility of minerals, derived from the host material, to weathering processes.

In the laboratory, porosity values were obtained for each horizon by point-counting microscopical porosity in standard petrographic thin sections. The results obtained from field and laboratory observations are summarized in Table 4, p. 69.

Discussion of Observed and Measured Properties of Calcrete Profiles

The computed average thicknesses of horizons show no systematic change from top to base of the idealized profile (Table 4). Individual measured profiles, likewise, show no systematic increase or decrease of horizon thicknesses with depth. Volumetrically, the glaebular horizon is the most important part of the profile. However, the indurated hardpan is the most noticeable horizon in the field because of its relative resistance to weathering and its near-surface or surface position. Because of its low porosity, high calcium carbonate content and high degree of induration (Table 4), the calcrete hardpan is also the easiest part of the profile to examine petrographically. As a result, most workers have, if at all, made thin sections only of the hardpan. The hardpan is the thinnest (21 cm) horizon in a complete profile (Table 4) and, thus, sampling by many workers is, to say the least, somewhat biased.

Hardnesses are proportional to calcium carbonate content and inversely proportional to porosity. This result has been determined by quantitative methods for the nari profiles of Israel (Yaalon & Singer, 1974). Increased hardnesses of some hardpans studied here result also from silica impregnations within the s-matrix.

Induration is a function of the amount of cementation. Although the glaebular and chalky horizons generally have high calcium carbonate contents, the paucity of cementation among calcite grains leaves these horizons in a friable state.

The correlation between estimated macroscopical porosity, using visual charts, and microscopical porosity, determined by point-counting petrographic thin sections, is proportionally reasonable, although actual values tend to be about a third greater for microscopical porosity. Fracture and mouldic porosity characterize the hardpan and sheet calcrete horizons, whereas interparticle porosity is commoner within the glaebular and chalky horizons. The type of porosity in the transitional horizon is dependent largely on the inherited textures of the host material.

Despite the lateral discontinuities or change in thicknesses of horizons on a local (metres) scale, the vertical successions of calcretes on a regional (kilometres) scale show sufficient repetitions to allow a useful model calcrete profile to be constructed (Fig. 2, p.39).

MACROMORPHOLOGICAL FEATURES

Planar Laminations

Most well developed calcrete profiles show some degree of planar lamination, the individual laminae ranging from a sub-millimetre scale to several centimetres in thickness. The laminar aspect also is generally recognizable in hand specimens and petrographic thin sections by colour, textural and compositional variations. In addition to their widespread occurrence throughout the western Mediterranean, laminar calcretes have been documented in many other parts of the world, including Algeria (Durand,1963), Morocco (Ruellan, 1967), Botswana (Watts, 1977), Australia (Read, 1974), Texas and Mexico (Reeves, 1970) and Barbados (James, 1972; Harrison, 1977).

Many theories to account for the formation of laminar calcretes have been put forward but there is little agreement among workers regarding their formation. Greatest divergence of opinion concerns the place of origin; some workers attribute planar laminations to surface phenomena, others favour subsurface formation. Field observations made during the course of this study indicate that both surface and subsurface laminar calcretes exist. However, whether surface laminar layers formed actually at the surface, or formed at depth and were subsequently exposed, requires careful consideration before attempting to infer processes of formation. To help better understand the processes and place of formation, the various types of laminae recorded throughout the western Mediterranean have been classified and grouped within a simplistic framework or model. For each laminar type, characteristic features have been documented below. Mechanisms to account for the formation of laminar layers have been inferred from the available evidence. Criteria for distinguishing the basic types of laminar calcrete are presented and the reliability of the established criteria is discussed.

Model - - I have chosen to restrict the model variables to four, namely texture and consistency of the host material, position of the water table, position of the laminar layers with respect to the substrate-atmosphere interface and mode of emplacement of the carbonate (accretion, replacement, displacement). Other factors of importance include stability and composition of the host material, surface topography, amount of mechanical and chemical erosion and rates of sedimentation. For the purposes of this discussion it will be assumed that there is a readily available source of $CaCO_3$ and that land surfaces are morpho-dynamically stable.

Surface accretion

Some workers include buildup of carbonate on subaerially exposed surfaces as a form of calcrete. For example, the croûte zonaire of Durand (1963) is a calcareous travertine deposit with a zoned structure. Scholz (1971) discussed 'sintric deposits' in his seven-fold classification of calcretes from South West Africa. However, these examples are essentially physicochemical precipitates on an exposed surface; pedodiagenetic processes are not necessarily involved in their formation. Similarly, biochemical buildups in the form of cryptalgal laminates and algal stromatolites are non-pedogenetic in origin. Moreover, the above mentioned carbonate buildups do not typically affect textures and fabrics of the subjacent substrate. Thus, such surface accretionary deposits should not be equated with pedodiagenetic calcretes. Criteria for distinguishing between laminar calcretes and non-pedogenetic laminar structures are given later (Chapter 7).

Surface alteration

Surface laminar layers may form on a calcium-bearing substrate by solution and reprecipitation of calcium carbonate. Non-carbonate substrates may be weathered by surface processes and calcium carbonate, derived from elsewhere, may replace weathered minerals and occlude primary and secondary pore spaces. 'Case-hardening', used in the sense given by Lattman & Simonberg (1971; see p.277 of this study) rather than in its strict metallurgical meaning, is an example of surface dissolution-reprecipitation of carbonate deposits. However, unless pedodiagenetic processes have been responsible for the alteration of the host material, such deposits are, by the same reasoning as outlined above for surface accretions, not strictly calcrete deposits.

Lower plants, especially bacteria, fungi, algae and lichens, are pioneer colonizers on subaerially exposed surfaces of virtually any substrate. They are important initiators of soil formation (p.261). The presence of soil micro-organisms within laminar calcretes provides evidence to indicate that soil-forming processes have been active in the formation of these surface laminations. To identify such laminae it is necessary to show: (1) that the laminations actually formed at the surface; and (2) that pedogenetic processes have played an active, not merely an incidental role in their formation.

Mud cracks and other features of surface desiccation, light dependent plants, intercalated mechanically deposited detritus, intercalated surface chemical accretions such as travertine or flowstone crusts, and unconformities between laminar layers resulting from alternating dissolution and deposition of calcite are criteria that can be used to identify surface conditions. Elongate grains showing a preferred directional fabric parallel with individual laminae further suggest surface rather than subsurface formation. Grain size differences between juxtaposed laminae may have resulted from successive increments of sediment and, thus, provide an additional criterion for surface aggradation.

Evidence of causal pedodiagenetic processes resulting in the formation of surface laminar layers is more difficult to find. Light dependent non-vascular and vascular plant materials have been recorded in many laminar calcretes examined in this study but whether this biological evidence was related directly, or merely incidental, to calcrete formation is not readily resolved.

Surface alteration, in contrast to surface accretion, is indicated by relic or 'ghost' structures within the laminae, fractured and partially replaced in situ fragments of the subjacent substrate between laminae, and a transition or alteration zone between the surface laminae and the subjacent unaltered substrate. Recognizable in situ cellular structures of higher plant roots, calcified lichens, fungi and algae, and amorphous organic matter are common features within these laminae which suggest, but do not prove, that biogenetic processes have played a role in their formation. Kahle (1977), in his valuable discussion on Holocene calcareous crusts from Florida, demonstrated that terrestial algae and fungi play an important role in the alteration of subaerially exposed Pleistocene marine limestones. Krumbein (1968) identified a well developed microflora consisting of large amounts of autotrophic and heterotrophic bacteria, fungi, actinomycetes, green algae and blue-green algae within samples of a 'nari-lime-crust' from Israel. Other accounts that mention the occurrence of biogenetic structures within subaerially formed laminar carbonates include those of Kornicker (1958), Multer & Hoffmeister (1968), James (1972) and Ward (1975). Thus, biogenetic structures are not peculiar to surface crusts of the western Mediterranean regions but appear to be geographically widespread.

At present, it has not been possible to establish a cause and effect relationship between biological processes and the formation of all surface laminar layers but, because of the ubiquity of biogenetic structures within these laminae, it is suggested elsewhere in this study (p. 273) that a causal relationship does exist for some laminae.

Some workers (e.g. Gile *et al.*, 1966; Goudie, 1973; Reeves, 1976) state or imply that laminar calcretes can form only on an impermeable substrate. However, I have observed many examples of surface (and also subsurface) laminar calcrete hardpans occurring at the top of a porous, poorly cemented host material (Plates 9a, 10a, b, 11, 13c). Therefore, composition, texture, porosity and consistency of the host material are not controlling factors of laminar formation in samples examined during this study.

With regard to mode of emplacement, I have found no evidence to suggest that laminar calcrete hardpans have formed by displacement of the host or overlying material by calcite. Observations made during this study, together with additional evidence presented in many published reports, indicate that replacement of the host material by calcite has led to the formation of micritic laminar layers.

Subsurface accretion

Passive subsurface void-filling calcite cement and/or calcareous sediment within channels and fractures do not produce typical calcrete textures and fabrics. Therefore, these subsurface accretions of calcium carbonate are excluded from my definition of calcrete for the same reasons that surface accretions are excluded, namely, that there has been no replacement of the host material and pedogenetic processes are not involved in such accretion.

Subsurface alteration

Subsurface laminar hardpans are commonly associated with millimetre-sized glaebules (Plate 12b, c). These glaebules are usually well indurated and occur in layers, generally less than 5 cm thick, which overlie the laminar hardpan (Plate 12b, c). Glaebules of similar sizes and shapes also occur within and around horizontal to subhorizontal root mats (Plate 13c). Roots maintain structural pores within these layers, thus enhancing porosity and permeability of these subsurface sheet-like layers. The arrangement of horizontal to subhorizontal root mats (Plates 12a, 13a) allows a greater movement of pore solutions through these layers. These conditions favour the formation of concentric glaebules; the movement of solutions maintains a supply of calcium carbonate and ensures agitation, if only intermittent, of particles. The structural voids created and maintained by roots provide spaces in which the glaebules can grow. Periodic rainfall followed by intense evaporation and transpiration in these root mat layers provide mechanisms which are conducive to calcite precipitation, thus allowing millimetre-sized, spherical glaebules to form by chemical accretion.

Immediately subjacent to these horizontal to subhorizontal root mats and/or glaebular layers, calcrete hardpans consisting of millimetre thick laminations of cryptocrystalline calcite are generally present (Plates 12, 13a, c). In thin section, these laminae show evidence of dissolution and redeposition of calcite. In a few samples, decimicron-sized detrital grains show a preferred planar fabric with long axes parallel to the laminae. This planar fabric suggests that there may have been mechanical transportation of particles by laterally flowing waters. Precipitation of calcium carbonate, as a result of water removal by roots, may lead to the formation of a thin (mm) calcite cement layer which would act as an aquiclude. Thus, subsequent calcite precipitation would take place on this cement layer, leading to the formation of planar laminae. It is interesting to note that these laminar hardpans occur at the base of root mats; I have not observed laminar hardpans immediately above root mats, unless a subjacent laminar layer also is present.

Subsurface micritic laminae, showing no visible evidence of roots in the field (Plates 9b, 12c), reveal their origin when samples immediately above these layers are examined by optical microscopy. Tubular pores, alveolar textures (p. 138) and rhizoliths (p.158) are characteristic features of these samples. Such features suggest that these laminae are related to calcified root mats which occur above the laminae themselves. Moreover, a transitional stage has been recognized between root mats (Plate 12a) and subsurface micritic layers (Plate 12c). The transitional stage is illustrated in Plate 12b. The glaebular layer overlying the laminar hardpan contains abundant partially decayed root debris.

Similar observations have been documented by Stuart & Dixon (1973). They reported (p. 323) that: "Roots play a major role in the formation of caliche near a layer of sand and/or gravel in the upper part of the soil. The concentration of roots at the top of a physical barrier, such as a coarse layer, bedrock, or an impermeable carbonate accumulation, would lead to rapid water removal and consequent precipitation of carbonate and silica. Such a concentration of roots would hasten the accumulation of carbonate at the top of the coarse layer. Often a root may be traced by a well-defined zone or incrustation of pure calcium carbonate. Remains of roots have been found in the center of crusts or tubular crusts that were formed when water was removed."

Individual subsurface micritic laminar layers are generally less than 20 mm thick (Plate 9b). However, these horizontal or subhorizontal sheet-like layers commonly occur in groups, sometimes in such profusion to form a sheet calcrete horizon, up to 1.5 m thick (Plates 3d, 5a, b). Individual layers tend to be undulatory and show cross-cutting relationships with neighbouring layers (Plate 9b). The irregular or undulatory form of laminar layers (Plates 9a, b, 11a-c) precludes an origin located at the surface of a ground water table. Pendulous or gravitational cements within these laminar hardpans indicate that they formed, partly at least, within the vadose zone. The location and distribution of the roots of xeric vegetation are consistent with an inferred meteoric vadose environment for the laminar hardpan - root mat layers. Plant roots obtain water directly from vertically oriented taproots which extend downwards to the capillary fringe above the ground water table and/or from vadose soil water taken up by horizontal root systems. Plants with laterally extensive, shallow root systems maximize their uptake of water by forming dense, horizontal root mats (Evenari et al., 1971). Thus, the positions of subsurface micritic layers, which I interpret as former root mats, are governed by the depth of penetration of infiltrating vadose soil water and not by the position of the ground water table.

With regard to the effect of various host materials, the only stringent requirement is that materials above root mats need to be permeable; material subjacent to root mats may be permeable or impermeable. Plate 13a shows a micritic lamina, 2 mm thick, beneath a root mat. The underlying substrate is a porous, weakly cemented aeolianite. Solutional features in the overlying soil (Plate 13b) suggest that calcium carbonate has been moved downwards in solution and been reprecipitated immediately subjacent to the root mat. Water removal by plants is suggested here as a mechanism to induce precipitation of calcite at the level of the horizontal root mat.

Gile _et_ _al_., (1966) suggested that laminar calcretes formed at the base of a soil overlying an impermeable or plugged horizon. However, my field observations indicate that plugging, as a result of progressive accumulation of calcium carbonate, is not necessary for the formation of laminar calcretes. Subsurface laminar calcretes have been recorded overlying both impermeable (Plate 12c) and permeable (Plates 12b, 13a, c) materials.

In areas where the formerly overlying materials have been removed, there is usually sufficient remaining evidence to recognize that now exposed, subsurface laminar calcretes actually formed at depth. Sinuous channels with dendritic patterns occur on the surfaces of many exposed calcretes (Plate 20a). I interpret these as moulds of former roots. In addition, some exposed hardpan surfaces contained _in situ_ horizontally aligned root casts and root petrifactions (Plate 20b, c, d). These biogenetic structures provide further evidence of subsurface calcrete formation.

Summary and reliability of criteria for the recognition of the basic types of laminar calcretes in the field

The characteristic features of the basic types of laminar calcretes have been documented and their mechanisms of formation have been inferred in the above sections. Surface and subsurface accretions without any effect on the subjacent substrate have been excluded for the reasons given in relevant sections. The criteria used for distinguishing surface from subsurface laminar calcretes are summarized in Table 5, p. 83. The reliability of criteria can be assessed by noting similarities and differences between surface and subsurface criteria, together with the relative frequency of the recorded criteria.

TABLE 5. CRITERIA FOR DISTINGUISHING SURFACE FROM SUBSURFACE LAMINAR CALCRETES

SURFACE ALTERATION	SUBSURFACE ALTERATION
1. Laminae follow surface topography (c)	Laminae independent of surface topography (c)
2. Laminae thicken in depressions (c)	Soil-filled depressions (c)
3. Laminae have sharp upper boundaries (c)	Laminae have diffuse upper and lower boundaries (c)
4. Unconformities between laminae (a)	Unconformities between laminae (u)
5. Light dependent organisms (c)	Horizontal root mats (c)
6. Fenestral voids (c)	Fenestral voids (r)
7. Desiccation features (u)	Desiccation features (-)
8. Detrital grains with preferred orientation (c)	Detrital grains with preferred orientation (u)
9. Glaebules (u)	Glaebules (a)
10. Colour variations of laminae (c)	Colour variations of laminae (c)
11. Textural variations (c)	Textural variations (c)
12. Organic-rich laminae (a)	Organic-rich laminae (c)

(a)	abundant	more than 50%
(c)	common	26 - 50%
(u)	uncommon	10 - 25%
(r)	rare	less than 10%
(-)	absent	0%

Glaebules

Introduction

As already defined (p.63) following Brewer (1964), glaebules are units which are distinguished from the enclosing s-matrix by a greater concentration of some constituent and/or difference in fabric. The term glaebule embraces various terms used to describe concentric and undifferentiated to irregular structures recorded in calcretes from many parts of the world. These include: calcrete oöids (Siesser, 1973; Read, 1974); 'oölites' (Ward, 1975); 'pseudooöids' (Rutte, 1958), pisolites (Swineford et al., 1958; Dunham, 1969b; Read, 1974); peloids and pellets (Harrison, 1977); pelletoids and coated particles (James, 1972; Walls et al., 1975); nodules (Wieder & Yaalon, 1974); concentric structures (Goudie, 1975) and concretions (Ruellan,1967; Scholz, 1971).

Because of confusing terminology, I prefer glaebule and use it as an inclusive term for the above listed groups. By adhering to Brewer's concept of glaebules, such structures can be described and classified with precision. In particular, his major division of nodules (undifferentiated glaebules) and concretions (differentiated glaebules) is extremely useful for describing the main types of glaebules that occur within calcretes.

Occurrence of glaebules

Glaebules vary considerably in position and abundance within calcrete profiles. On the one hand, they are so abundant that certain horizons are characterized by glaebular development (Plates 6, 7, 14). On the other hand, glaebules are accessory features or absent altogether in some horizons. Calcrete hardpans generally contain indurated glaebules but are rarely dominated by them. Sheet calcrete horizons are not characterized by glaebules but, not uncommonly, interstratified layers composed almost entirely of contact-packed glaebules are present within the sheet calcrete horizon (Plate 12b, c).

As the name indicates, glaebules dominate the glaebular horizon. They differ from glaebules occurring in other horizons in size, shape and degree of induration. Whereas glaebules occurring in the hardpan and sheet calcrete hardpans tend to be spherical, generally less than 5 mm in diameter and have internal concentric fabrics, glaebules of the glaebular horizon tend to be irregular in shape, have diameters greater than 5 mm and lack discernible internal fabrics. Moreover, glaebules tend to be well indurated and easily removed by hand from the enclosing s-matrix when they occur in sheet and glaebular horizons. Below the glaebular horizon, in a complete calcrete profile, glaebules are absent altogether.

Although it is possible to record the present position of glaebules in calcrete profiles, this does not provide any substantive evidence for elucidating their origin. Glaebules may have been inherited from the host material, may have resulted from in situ growth or may have been transported from elsewhere and deposited in their present positions. In order to solve the problems of inheritance (place of formation), the processes that were responsible for these features (genesis) and the conditions under which they formed (environment), it is first necessary to describe the morphological characteristics of glaebules.

Description

In the field, glaebules were described in terms of internal fabric, composition, distinctness and ease of removal with respect to the enclosing s-matrix, shape, size, distribution, orientation patterns, packing, association with other features and degree of induration. These observations are described below.

Internal fabric - - Fresh fracture surfaces of glaebules were examined and salient features were noted. Undifferentiated (random) and concentric internal fabrics were found to be common. Concentric laminations, less than 1 mm thick have well defined (distinct) to diffuse boundaries. It was noted that spherical glaebules tend to have a well defined concentric internal fabric, whereas irregular and tuberose* glaebules tend to be structureless, that is to say, they have an undifferentiated internal fabric. Macroscopical voids were found to be uncommon in glaebules.

Composition - - Treatment with 1.5% hydrochloric acid indicated that most glaebules are composed of fine-grained calcium carbonate with minor amounts of other minerals and organic matter. However, some glaebules, especially cylindrical and tuberose forms, were found to have nuclei consisting of partially decomposed organic matter. Closer inspection revealed that root systems have been encased in concentrations of calcium carbonate (Plate 16a).

Distinctness - - Sharpness of external boundaries was found to be difficult to assess. In some profiles, abrupt changes in colour or density helped to distinguish glaebules from the surrounding s-matrix (Plates 6, 14). As a generalization, based on field observations, indurated (hardened) glaebules tend to have sharp boundaries on a millimetre scale, whereas friable (soft) glaebules tend to have diffuse boundaries.

Shape - - The shapes of glaebules were recorded in terms of sphericity and roundness. Most glaebules were observed to be subround to round in outline. Glaebules less than 4 mm diameter were found to

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* Tuberose - having very irregular rounded surfaces, often giving rise to gnarled, root-like shapes (Brewer, 1964, p.264).

be spherical in form; larger glaebules were observed to be cylindrical or elliptical, with long axes oriented vertically (Plate 6). Irregular, botryoidal and tuberose forms were found in abundance in several profiles (Plates 4e, f, 7, 14b, 16b) but, regionally, were found to be volumetrically insignificant.

Size - - A complete size range from decimicron-sized to centimetre-sized glaebules was recorded during field studies.

Distribution - - In all profiles examined in detail (326 profiles), only three examples of clearly recognizable coarsening upward sequences were observed. Fining upward sequences were found to be commoner, with 54 profiles containing glaebules with a fining upward size distribution. The remaining profiles containing glaebules showed no systematic variation in size of glaebules.

Orientation patterns - Vertically elongate (prolate) glaebules characterize many glaebular horizons (Plates 6, 14). However, horizontally elongate (oblate) glaebules were observed in the upper parts of glaebular horizons, commonly grading into sheet calcrete (Plate 14a, c, d). Thus, the vertical anisotropy characterizing glaebular horizons, changes into one of horizontal anisotropy higher up the profile within sheet, and finally, hardpan horizons.

Packing - - With the exception of thinly bedded, horizontal layers composed largely of 1 - 2 mm diameter, grain-supported spherical glaebules (Plate 12b, c), most glaebules were found to be matrix-supported (Plate 15c), giving a wackestone texture (cf. Dunham, 1962).

Association with other features - - Plant root structures were noted as being the most striking and perhaps the most significant feature associated with glaebules (Plate 7). As already mentioned, many vertically elongate and branching glaebules contain partially decomposed roots (Plates 16a, 19). In addition, horizontal glaebular-rich layers within sheet calcrete horizons commonly contain root mats (Plate 12a). The significance of this association has been discussed elsewhere in this study (p.79).

Degree of induration - - A complete range from soft, powdery to hard, well indurated glaebules was recorded in the field. Soft glaebules can be crushed between thumb and forefinger, whereas indurated glaebules can be broken only with a hammer. Indurated glaebules commonly showed conchoidal fractures when broken with a hammer. Using a steel penknife, some glaebules were found to contain minerals with hardnesses of greater than 5 on the Mohs' hardness scale. Subsequent laboratory analysis show that amorphous silica was responsible for this hardness.

Discussion

Before possible processes of glaebular formation can be evaluated, it is first necessary to decide on the place of origin of glaebules. Glaebules may have been: (1) inherited from the host material and, thus, be relic features; (2) formed in situ; (3) disturbed and moved from their place of formation but not transported; or (4) transported from elsewhere. Wieder & Yaalon (1974) have tackled this problem by classifying various types of glaebules (nodules) according to their origin and morphology. 'Orthic nodules' are composed of material similar to that of the enclosing s-matrix, show diffuse boundaries and are interpreted as having formed in situ. 'Disorthic nodules' are similar to orthic nodules but have sharp rather than diffuse boundaries. The sharp boundaries are considered to be the result of pedoturbation or churning. However, the composition and fabric of the nodules are the same as the surrounding s-matrix, suggesting to Wieder & Yaalon (1974) that translocation has not taken place. On the other hand, 'allothic nodules' have compositions and fabrics unlike the surrounding s-matrix; their present positions are attributed to transportation from a nearby horizon or introduction into the soil from elsewhere. Therefore, to understand the mechanisms of glaebular formation, it is necessary to identify and exclude allothic glaebules since their present positions reveal little information regarding their formation. Similarly, relic glaebules of the host material can be excluded by identifying these forms in the subjacent, unaltered substrate. Thus, attention is confined here to the formation of orthic and disorthic glaebules.

Treated simplistically, glaebules result from concentrations of authigenic minerals about a point, line or plane. In the field, removal of part of vertically elongate glaebules commonly revealed nuclei of plant root material (Plate 16a). Spherical and irregular glaebules also were found to contain plant debris. These observations suggest that plant materials may have induced calcite precipitation by modifying the ambient microenvironment during and/or after life of the plant.

Spherical glaebules with internal concentric laminations may have resulted from several processes - by diffusion (including Liesegang ring formation), by crystallization from a solution (chemical accretion), by mechanical accretion of colloidal and/or clastic particles in suspension, or by rearrangement of the s-matrix as a result of wetting and drying cycles. Recrystallization and replacement of precursor fabrics within the s-matrix may further complicate the diagenetic evolution of glaebular formation. Unfortunately, these possibilities cannot be evaluated by field observations alone; a fuller discussion on the possible and most likely mechanisms for the formation of glaebules is given later, following documentation of their microscopical characteristics carried out in the laboratory (p.147).

Rhizoliths

Terminology and classification

Since calcretes result from pedodiagenetic processes (p.35) one would, not unreasonably, expect to find evidence of former plant activity within such deposits. Rhizoliths, herein defined as organo-sedimentary structures produced by roots, provide evidence of former higher plant colonization within calcretes. These structures, termed in various ways by other workers (Table 6, p. 92), have been recognized and reported widely. However, few accounts have documented their microscopical fabrics and textures as present in this study (p. 158). Indeed, most citations go no further than merely listing their presence in the field. Sarjeant (1975, p.173) remarked: "Despite the abundance of preserved records, fossil root marks and casts have received little attention from geologists, and their paleoecological potential has scarcely even begun to be examined." In addition, although published field descriptions of rhizoliths are numerous, they are riddled with loose and misleading terms (Table 6). Thus, imprecision in terminology limits the scientific validity and usefulness of such macromorphological descriptions.

With the notable exceptions of Ruth (1927) and Calvet *et al.*,(1975), there has been little or no attempt made to differentiate clearly between the possible forms of root preservation that exist. For example, whether these biogenetic structures have resulted from mineral encrustation, impregnation or replacement of the root, or as a void-filling sediment or cement is not indicated in most reports. Moreover, whether part, or all, of the plant root is present or absent is rarely stated. It is considered pertinent, therefore, to point out this inadequacy. In order to understand and unravel their pedogenetic and diagenetic histories, it is necessary to be able to recognize the different types of rhizoliths. This task of differentiating among the several preservational types can be achieved only by use of a consistent and unequivocable terminology. In so doing, it will ensure that prevalent confusion and ambiguity are not perpetuated.

Northrop (1890) used the term 'rhizomorph' to describe root-like structures from the Bahamas. Derived from the Greek <u>rhizo</u> = root + <u>morphe</u> = form, this term would be useful as a basic field description but, unfortunately, has a strict biological meaning which is defined and adhered to elsewhere in this study (p. 219). Thus, its use in this context for higher plant root structures is not advocated.

The term 'rhizoconcretion', considered synonymous with Northrop's 'rhizomorph' (American Geological Institute, 1972), was used by Kindle (1923) to describe cylindrical concretions of calcium carbonate and quartz sand which had formed around decayed roots. In a later communication, Kindle (1925) reported that 'rhizocretions' or root-shaped concretions occurred also around living roots and suggested (1925, p.744) that "some, and probably all, rhizocretions must therefore be recognized as phenomena associated with growth, instead of the decay of roots."

The term rhizocretion or rhizoconcretion has been used increasingly in recent years to describe various forms of root structures that occur in calcretes and subaerially exposed marine carbonates (e.g. Johnson, 1967; Steinen, 1974; Ward, 1975; Calvet <u>et al</u>., 1975; Esteban, 1976; Read, 1974; Harrison, 1977). The use of the term rhizocretion to describe pedodiagenetic accumulations around roots is valid. However, when the root itself has been partially or totally replaced by calcite, the concept of concretionary growth is inappropriate

TABLE 6 TERMINOLOGY OF RHIZOLITHS

AUTHOR/YEAR	TERM
Northrop (1890)	Rhizomorph
Kindle (1923, 1925)	Rhizoconcretion; rhizocretion; root-shaped concretion
Ruth (1927)	Petrified wood (replacement and impregnation)
Teichert (1950)	Root structures
Durand(1949)	Racines petrifiées
Fairbridge & Teichert (1953)	Travertinized roots
Sherman & Ikawa (1958)	Calcareous concretions; rhizoconcretions; calcareous rhizo-concretions
Brewer (1964)	Pedotubule
Hoffmeister & Multer (1965)	Fossil mangrove
Johnson (1967)	Rhizoconcretions
Glennie & Evamy (1968)	Dikaka
Strakhov (1970)	Akkyrshi
Valeton (1971)	Tubular fossils
Read (1974)	Root casts
Steinen (1974)	Rhizocretions
Bal (1975b)	Carbonate crystal tube (carbonate root-pseudomorph)
Calvet *et al*., (1975)	Rhizocretion
Braithwaite (1975)	Pedotubules
Ward (1975)	Rhizocretions; root hair sheaths
Amiel (1975)	Root-like structures
Esteban (1976)	Rhizocretions
Harrison (1977)	Rhizocretions
Perkins (1977)	Land plant root structures

for description of plant root preservation by mineral replacement. Replacement of organic matter by mineral matter is better termed petrifaction or petrification (American Geological Institute, 1972), and to be more specific, calcification and silicification for replacement by calcite and silica respectively.

In the field, it is rarely possible to discern petrifaction, especially in samples where concretionary growth also has taken place around roots. Thus, designation of all plant root structures as rhizocretions or rhizoconcretions (preferential cementation around roots) does not strictly consider preservation of plant anatomical features. Because of this conceptual omission, I propose the general term rhizolith to include accumulation and/or cementation around, cementation within, or replacement of, higher plant roots by mineral matter. In addition, and at the risk of neologistic excessiveness, I propose also the term rhizolite for a rock showing structural, textural and fabric details determined largely by the activity, or former activity, of plant roots. The term rhizolite would appear to be equivalent to 'root rock', an informal term used by Perkins (1977) to describe Pleistocene rocks of south Florida composed almost exclusively of 'root tube calcifications'.

It is pointed out here that the terms rhizolith and rhizolite are necessarily genetic; their use and usefulness depend on availability and reliability of criteria for their recognition and, more fundamentally, on the identification of such criteria which allow reasonable interpretations to be made. The purpose of this section is to provide field criteria for the recognition of pre-existing higher plant activity contained within calcrete profiles. Criteria for the recognition of rhizoliths at microscopical levels of observation are provided elsewhere in this study (p. 158).

Boyd (1975), in referring to the problems of distinguishing between burrow and root traces stated (p. 77): "The time seems propitious for a major study, from a geological point of view, of modern root systems and their characteristics....Until such work provides trustworthy criteria for recognition of fossil roots, authors should include descriptions of the features they interpret as roots....rather than be content merely to announce their presence." Although such a major task is not the purpose of this study, modern rhizospheres* have been examined from macroscopical (field) to ultramicroscopical (SEM) levels of observation to help interpret features recorded within calcretes which appear to be related to roots. Thus, this study is at least a step forward in the direction suggested by Boyd (op.cit.). If I had been content with the mere noting of the presence of 'root-like' structures, the origin of many petrographic features recorded during the course of this study (Chapters 4 and 5) would have remained unresolved completely.

Preservational types of rhizoliths

Five basic preservational types of rhizoliths exist: root moulds, root casts, root tubules, rhizocretions s.s. and root petrifactions. These genetic forms may occur individually or in various combinations. In addition, unaltered or decayed plant root material may occur essentially intact within sediment and/or be cemented to form composite rhizoliths. Figure 9, p. 95 summarizes the common forms of rhizoliths recorded in Quaternary calcretes from the western Mediterranean.

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* Rhizosphere - zone of soil immediately surrounding a root which is modified by its activity (Abercrombie et al., 1973).

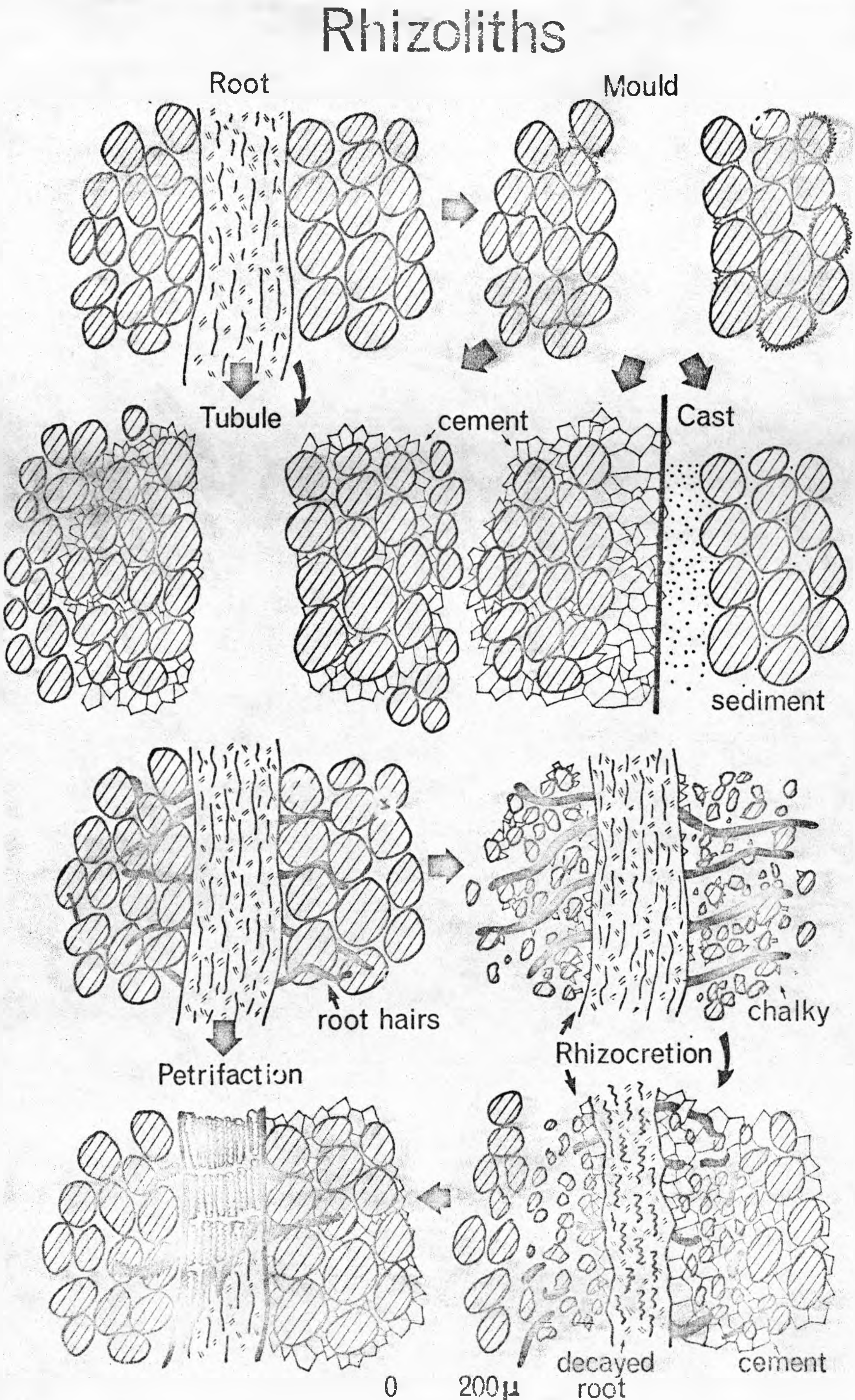

Figure 9. Schematic representation of types of rhizoliths and their relationships (see text for explanation).

The possible diagenetic pathways of the basic types of rhizoliths and their relationships to each other are also indicated in Fig. 9. Plates 17 - 20 illustrate various types of rhizoliths.

Field criteria for the recognition of rhizoliths

The most obvious characteristic feature of rhizoliths is their cylindrical shape, being either solid rods (Plates 17e, g, 20b-f) or hollow tubes (Plate 17f). Lengths vary from a few centimetres (Plate 20e) to several metres (Plate 17a, g), the longest recorded in this study being 4 m long. The diameters of rhizoliths range from 0.1 mm to about 20 cm. Downward bifurcations with decreasing diameters of second, third and fourth order branches (Plate 18c) distinguish rhizoliths from animal burrows (Plaziat, 1971a). Rhizoliths show many orientations although the commonest forms occur as vertical, isolated or branching structures (Plates 17a-d, e, f, 19, 20f) and as ramifying horizontal networks (Plate 20b-d).

Although roots prefer to grow in unconsolidated sediments, they can, if necessary, bore through indurated rock (Plates 21a, b, 27c). Roots are primarily concerned with the activities of absorbing water and mineral nutrients from soil solutions, storage of reserve food supplies and anchorage (Russell, 1973). There is no reason why roots cannot live within indurated rock if these activities can be carried out normally in such substrates. Thus, the occurrence of borings in rocks (Plate 27c) does not militate against an origin related to former plant activity. On the contrary, branching borings with decreasing bore diameters downwards strongly suggest an origin associated with root systems.

Rhizoliths and associated features of the rhizosphere such as soil fungi indicate terrestial conditions and subaerial exposure of marine sediments. Rhizoliths can be used to help recognize pedogenetically modified substrates, an example of which is illustrated in Plate 18. Plate 18a shows an unaltered, cross-bedded aeolianite. Plates 18b and c show aeolianites of the same age (Upper Pleistocene) which have been subjected to pedoturbation and subsequent cementation. The formation of rhizoliths has destroyed pre-existing bedding structures of the aeolianites shown in Plates 18b and c, whereas the cross-bedding structures of the aeolianite shown in Plate 18a have not been affected by pedogenesis.

The presence of contained root material within rhizoliths (Plate 19) provides unequivocable criteria for their recognition. In samples lacking plant material, the anatomical features of roots can sometimes be recognized (Plates 49e, f, 50e, f). Although some animal burrows contain internal structures (e.g. spreite), they are usually distinguishable from root anatomical features.

Additional criteria for the recognition of rhizoliths at microscopical levels of observation are given elsewhere in this study (p. 158).

Brecciation Textures and Tepee Structures: the Plant Factor as a Role in their Formation

Introduction

Although many investigators have documented brecciation textures (Bretz & Horberg, 1949; Aristarain, 1969; James, 1972) and tepee or pseudo-anticline structures (Price, 1925; Jennings & Sweeting, 1961; Blank & Tynes, 1965; Watts, 1977), few attempts have been made to elucidate their origin. At the outset, it is admitted that there may be several related or independent mechanisms to account for brecciation and the formation of tepees within calcrete profiles. After studying modern calcretes from the western Mediterranean, the intention here is to point out a single and possibly underestimated factor responsible for these features, namely, the modifying effect of plant roots.

Terminology and classification

According to the *Glossary of Geology* published by the American Geological Institute (1972), a *tepee structure* is "...a disharmonic sedimentary structure consisting of a fold which in cross section resembles a chevron or an 'inverted depressed V' or a profile of a peaked dwelling of the North American Indians (Newell *et al.*, 1953, p.126). It is believed to be a diagenetic structure formed during the hydration of anhydrite." The term *pseudo-anticline* is omitted from the 1972 edition, but Jennings & Sweeting (1961) noted that the *American Dictionary of Geological Terms* (American Geological Institute, 1957) defined pseudo-anticline as "an arrangement of rock strata simulating the arch of an anticline. Used with reference to sand bodies which have a convex top (Ver Wiebe, W.A. *How Oil is Found*, 1951)." Jennings & Sweeting (1961) pointed out that reference to Price's prior usage is not given. In addition, because pseudo-anticlines are not restricted to sand bodies, they suggested that the definition should embrace only the first, general part.

The term *tepee* was introduced by Adams & Frenzel (1950) to describe buckling zones in the Capitan Barrier Reef, Texas and New Mexico. Referring to these zones, they stated (p. 308): "The cause of the buckling is not apparent, but the accompanying deformation is clearly contemporaneous with reef growth. In the field, for the lack of a better name, the structures were referred to as 'tepee structures'."

Assereto & Kendall (1977) have proposed a new scheme of classification and terminology for carbonate antiform structures, relating their genesis to the location of the expansion process with respect to sea level (subtidal, peritidal, continental) and increasing time of exposure (embryo, mature, senile). Thus, the following genetic terms have been re-defined by Assereto & Kendall as follows:

> Pseudo-anticline - any antiform structure formed by the expansion of indurated carbonate beds where the process and environment responsible for expansion cannot be established.
>
> Tepee - antiform structures that can be established to form the margins of near-marine megapolygons developed by contemporaneous expansion of peritidal crusts; embryo, mature and senile.
>
> Caliche-pseudoanticlines (Price, 1925) - the saucer-like structures that form by expansion of calcareous crusts within a fresh-water soil profile.
>
> Submarine-pseudoanticlines - anticlines found at the edges of expanded subtidal megapolygons formed in carbonate beds during early submarine cementation.

As can be seen from their proposed classification, Assereto & Kendall have given the morphological term tepee a genetic connotation by stipulating a peritidal environment of formation. Furthermore, their use of the terms pseudo-anticline, caliche-pseudoanticline and submarine-pseudoanticline require evidence, or at least, acceptance, of expansion of carbonate beds or calcareous crusts. Therefore, if this classification is adhered to, the structures described and illustrated in this section cannot be called tepees or pseudo-anticlines, since a peritidal environment cannot be established and expansion of carbonate beds cannot be demonstrated (or indeed accepted!). The main contention of this contribution is that expansion of the profile has taken place, not by any postulated mechanisms such as the force of calcite crystallization, but by the physical exertion of growing tree roots. In other words, the calcareous crusts or hardpans themselves have not expanded but have been disrupted mechanically by biogenetic disturbance.

Previous investigations

In his assessment of disturbed structures in caliche from central Tamaulipas, Mexico, Price (1925) concluded that "....the growth of caliche takes a prominent part in the process of weathering in certain areas of semi-arid lands. Its effect is two-fold: on the one hand, it moves and disrupts rock beds at shallow depths, facilitating the entry of plant roots; on the other hand, it cements the broken rock fragments, retarding erosion." The word 'caliche' is used by Price (1925, p. 1012) to describe a porous calcium carbonate. Given this, his conclusion quoted above can be paraphrased, viz: "the growth of porous calcium carbonate moves and disrupts rock beds." How this takes place is left apparently to the ingenuity of the reader. Similarly, Dunham (1972), according to Assereto & Kendall (1977, p. 192), thought that tepees resulted from "expansion of caliche soil." Jennings & Sweeting (1961) believed that high temperatures were necessary for the formation of pseudo-anticlines and mentioned that climatic conditions of semi-aridity favoured their development, as emphasized earlier by Price (1925). Again, such opinions only explain away rather than explain how expansion has taken place.

Blank & Tynes (1965), after examining caliche in Texas, stated that "....small anticlines having filled arches with caliche, resemble the 'pseudo-anticlines' in Mexico described by Price, but evidence of the in situ formation of the caliche suggests that the folding may have been caused by the expansion accompanying hydration of anhydrite associated with the Kirschberg Evaporite of Barnes, and that the caliche is the result rather than the cause of the distortion and folding of the limestone."

Aristarain (1969), in his discussion on the characteristics and genesis of caliche deposits of New Mexico, stated (p. 128): "another characteristic structure of these deposits is that of auto-brecciation.. ...This structure is attributed to self-breaking due to the force of crystalization [sic] of calcite during its deposition."

Reeves (1970) considered that caliche anticlines, or expansion structures, form only in mature caliche or pre-existing carbonates because of expansion of the entire zone caused by filling of horizontal and vertical desiccation cracks by vadose silt and calcareous dripstone. He suggested (p.358) that there are several different types of structures found in thick caliche profiles, some formed by solution and settling, some even being structures which antedate formation of caliche.

Envisaged mechanisms discussed by previous investigators to account for non-tectonic expansion and disruption of calcretes include force of crystallization, salt hydration and/or removal, thermal expansion and contraction, wetting and drying cycles and biological activities. Reeves (1970, 1976) suggested that expansion of the entire caliche profile resulted from severe climatic conditions which cause drying, fracturing, buckling and subsequent filling of resulting voids with calcite, thus leading to a volumetric increase in sediment. Assereto & Kendall (1977) suggested that the force of crystallization of calcium carbonate in the plugged horizons of mature caliche is the most important mechanism involved with expansion and fracturing. However, the currently favourable hypothesis that the force of calcite crystallization has caused expansion of calcrete profiles owes its widespread acceptance to indoctrination rather than objective proof.

Thermal expansion and moisture swelling may be contributory mechanisms which lead to the disruption of calcretes but singly, as many workers have demonstrated (e.g. Blackwelder, 1925, 1933; Griggs, 1936; Roth, 1965), the magnitude of volumetric changes as a result of these mechanisms is insufficient to cause extensive disruption and brecciation.

Expansion of salt minerals following their hydration exerts a disruptive stress (Chatterji & Jefferys, 1963; Goudie et al., 1970). However, the importance of this expansion process in tepee development is unknown (Assereto & Kendall, 1977). Moreover, hydrated salts are volumetrically insignificant in most calcrete deposits (Goudie, 1973; Watts, 1977; this study, p. 237). The possibility exists that complete solution of salts has taken place but I have found no evidence which suggests the former presence of such minerals.

In a recent paper by Watts (1977), additional driving mechanisms which may have been responsible for disturbance and folding of calcrete profiles are discussed. Removal of soluble salts, tectonic deformation, frost action, biogenic activity, the influence of swelling clays, volumetric increase with inversion of aragonite to calcite and displacive growth of calcite are considered and evaluated. All but the last are rejected or considered to be inadequate. However, the opinion that displacive growth is responsible for disturbance and folding of calcrete profiles requires substantive evidence which is not given. This omission is openly portrayed in his concluding paragraph (p.73) as follows: "Why calcite crystallization should not be merely a void filling process but have the displacive effect is difficult to explain. There is a marked lack of literature in this field and further investigation seems necessary."

Assereto & Kendall (1977), in assessing earlier investigations on tepee structures, stated that: "...there is a general agreement between previous authors on an origin related to carbonate precipitation and expansion for 'submarine and caliche-pseudoanticlines." In view of the preceding comments outlined above, this statement of Assereto & Kendall is hardly justified. Therefore, it seems to me that a critical re-evaluation of tepee structures, in situ brecciation and other features of disturbance in calcrete profiles is deemed necessary. This will not be attempted here in this short contribution but it is reiterated that the role of vegetation, the subject of this section, should be given due consideration in such assessment.

Suggested mechanism from observations made during this study

Any theoretical consideration must explain adequately the observational characteristics of non-tectonic disturbance in calcrete profiles. The most notable characteristic of in situ brecciation and tepee formation in calcretes is one of superficiality. Disruption is restricted largely to the uppermost horizons immediately below the land surface (Plates 21a, 24a, 25a, b). As mentioned earlier, calcretes are widespread on surfaces with gentle slopes where lateral transport of sediments is minimal (p.53). The angular shapes of brecciated calcrete (Plates 21a, 23a, 25, 27a-c), the juxtapositions of formerly fitting fractured particles and hardpans (Plates 21c, 25d) and the lack of preferred orientation of brecciated fragments (Plates 21a, b, 25c, 27a, b) indicate that transportation of weathered calcrete has not taken place. Thus, in situ processes have operated only and these have been restricted to the upper, near-surface layers of calcrete profiles (Plates 22, 23a, 24, 25, 26a, b, 27a).

Field observations indicated that present-day vegetation has had a marked effect within the uppermost horizons of indurated calcrete profiles (Plates 21a, b, 22, 23). Present-day roots have penetrated not only pre-existing planes of weakness but have caused mechanical disruption of indurated layers (Plates 21a, 22, 23a, b).

That roots have the ability to disrupt mechanically indurated material has been documented in other settings. For example, it is well known that the physical exertion of growing roots is sufficient to cause cracking and buckling of roads and street pavements (Dunham, 1972; Birkeland, 1974). In a soil, growing roots mechanically push grains apart, and, if the density of roots is great enough, volumetric expansion of the soil profile may occur (Russell, 1973; Birkeland, 1974).

In addition to their mechanical effect, roots can have a substantial effect on the ambient chemical environment. On the surfaces of exhumed calcrete hardpans, anastomosing and dendritic channels mark the former positions of root systems (Plates 20a, 21c, 25c). These corroded surfaces indicate that roots, at some stage during their growth, are capable of dissolving calcium carbonate.

Further evidence of biochemical dissolution has been recorded within calcrete profiles where roots have bored chemically through indurated hardpans (Plates 21b, 27c). These observations indicate that roots do not merely occupy pre-existing voids within soils (s.l.) but create spaces by their own biochemical and biophysical activities.

The combined effects of mechanical disruption and chemical dissolution on calcrete profiles lead to the formation of in situ calcrete breccias (Plates 23a, b, 25, 27). I have informally termed this type of non-tectonic disturbance as rhizo-brecciation (Gk. rhizo = root). Calcrete rhizo-breccias consist of angular to subround fragments of indurated calcrete embedded in an undifferentiated s-matrix. The s-matrix contains abundant root systems or evidence of former roots (Plates 23, 24, 25, 26, 27). The s-matrices of profiles illustrated in Plates 7, 24, 25, 26, 27, which encase disrupted hardpan fragments, contains abundant calcified root structures or rhizoliths.

The brecciated lenses of calcrete hardpan illustrated in Plates 24, 25a, b are arranged to form tepee structures of low amplitude. This disrupted unit, which has a maximum thickness of 1.2 m, is underlain by a 20 cm thick, continuous planar calcrete hardpan (Plate 24b). Thus, it is unlikely that tectonic deformation could have been responsible for such shallow, localized disruption and folding of the uppermost layers without disturbing the lower part of the profile. Similarly, Plate 7a shows only localized disturbance of a calcrete hardpan. It is necessary to look for an alternative mechanism to account for the observed features.

From the field evidence, I have not been able to resolve whether deformation took place during or after calcretization. Even so, it is perhaps more important to know how, rather than when, disruption took place. The possible processes that may have caused disruption can be separated into three categories - physical, chemical and biological - although, in reality, such processes are likely to have operated together. Purely physical and chemical processes have been outlined already in the discussion of previous investigations (p. 100). Disruption and expansion of calcrete profiles as a result of biological activity have been mentioned briefly by some workers (Read, 1974; Watts, 1977). However, the effects of biological disturbance are thought, by these workers, to be insignificant.

Hitherto, the biological influence on calcrete formation in general has been suspected but not considered in detail. This lack of serious consideration is surprising; most workers agree that soil-forming processes are of fundamental importance for calcrete formation (Bretz & Horberg, 1949; Aristarain, 1969, 1970; Reeves, 1970, 1976; Read, 1974, Esteban, 1976; this study) but the role of vegetation is rarely discussed. Vegetation, after all, maintains soil viability. More specifically, present-day vegetation penetrates indurated calcretes, giving rise to *in situ* rhizo-breccias (Plates 22, 23). The physical exertion of roots causes expansion of the profile. The direction of least resistance is upwards; brecciated fragments are forced upwards as growing roots increase in size and number.

Plate 22a shows a pine tree (*Pinus halepensis*) which has managed to survive and grow in a calcrete hardpan. The supporting soil consists of little more than brecciated fragments of indurated calcrete and plant litter. The branching root system is laterally extensive for several metres but limited vertically to the top 40 cm below the land surface. Plates 22b and c, which show slabs of brecciated calcrete hardpan enmeshed in the root systems of fallen pines, indicate that taproots are absent. Thus, disruption has been limited to the depth of rooting which, in these examples, is less than 50 cm below the present land surface. The calcrete hardpan has remained intact below the root layers; the boundary is marked by a planar, horizontal surface (Plate 22a), comparable with the planar surface illustrated in Plate 24a and b. It is suggested here that the undisturbed calcrete hardpan acts as an aquiclude. In other words, the hardpan has a sufficiently low permeability to form a perched water table. Thus, vegetation can obtain water without penetrating downwards as far as the hydrostatic level of the regional water table.

Plates 7, 25a, b, 26b, c are examples of brecciated horizons within calcrete profiles. Vertically elongate glaebules are present below these disrupted horizons (Plates 7d, e, 25a, 26b, c). Field and laboratory studies of these profiles indicate that rhizoliths are present within the glaebular and brecciated horizons. Although a genetic relationship cannot be established unequivocably, the morphological similarity among the profiles illustrated in Plates 22a, 24, 25, 26b, c and the evidence of former plant life in Plates 7, 25a, b, 26, 27 strongly suggest that brecciation by roots (rhizo-brecciation) has caused mechanical disruption of these calcrete profiles.

Summary and conclusions

In summary it can be stated, from field observations, that roots modify calcrete profiles by biophysical and biochemical weathering. Mechanical disintegration of indurated calcrete hardpans is due, partly at least, to the pressures exerted by growing roots which are sufficient to rupture rock and force blocks apart. In addition, brecciated fragments may be dissolved peripherally and in situ hardpans may be etched or bored as a result of changes in the chemical environment, the chemical changes being attributable to the physiological processes of penetrating roots.

It is admitted that root activities are not necessarily the only factor responsible for disturbance and disruption of calcrete profiles. As mentioned earlier, the purpose of this contribution is to point out that the modifying effect of higher plants on calcrete profiles is an important, though hitherto, neglected phenomenon. Many workers have documented brecciation textures in calcretes but little or no attempt has been made to explain the cause of brecciation. Physical disruption by roots within near-surface materials provides one mechanism and, when considering brecciated calcretes, perhaps the most important mechanism to account for in situ brecciation. Expansion of calcrete profiles, as a result of the volumetric increase of growing roots, leads to the formation of rhizo-breccias and tepee structures. This phenomenon also may be responsible for the formation of some intraformational breccias and tepee structures recorded in ancient calcretes. Evidence of former rhizospheres may be present in these ancient successions which show non-tectonic disturbance; it remains for us to look for them.

CHAPTER FOUR - MICROMORPHOLOGY PART I

INTRODUCTION

The term micromorphology is used here for the analysis of forms or features which can be observed only with the aid of a microscope. Micromorphology is intrinsically observational, whereas interpretation of the observable forms is based on knowledge of the properties and behaviour of the constituents involved in the formation of such forms. This Chapter is concerned with: (1) the identification of the constituents; and (2) fabric analyses of the identified constituents in terms of their sizes, shapes and arrangements. However, as pointed out by Brewer (1964), fabric analyses solve no problems unless the properties of the constituents, their behaviour under various conditions and the conditions and processes involved in producing the various kinds of arrangements are known. Chapter 6 is concerned with the physicochemical properties of the constituents. By combining compositional studies (Chapter 6) and fabric studies (this Chapter and Chapter 5), we are in a better position to examine the conditions and processes involved in producing calcretes, that is, in their genesis which is the subject of Chapter 8.

Following the concept of Brewer (1964), soils and, likewise calcretes, are formed by weathering and transformation of solid rock in situ or weathering and/or transformation of transported materials derived ultimately from solid rock. Thus, calcrete-forming constituents comprise: (1) primary rock-forming minerals, weathering products, authigenic minerals and derived rock fragments which constitute the inorganic fraction; together with (2) higher and lower plant remains and their humified products, faunal remains (bioclasts) and products of faunal activity (e.g. faecal pellets) which constitute materials of organic origin. Kubiena (1938) divided these constituents into two broad groups on the basis of their relative stabilities. Brewer (1964) used this concept to define <u>skeleton grains</u> which are relatively stable and not readily translocated, concentrated or reorganized by soil-forming processes, and <u>plasma</u> (Gk. <u>plasma</u> = formed) which includes all soil particles less than 2 microns in diameter, together with soil materials capable of being moved, reorganized and/or concentrated by soil-forming processes. Brewer pointed out that the material need not be in a suitable state for translocation or concentration at present to be termed plasma. Skeleton grains are stable, not only in their physicochemical properties but also in their positions in the soil profile; extreme conditions are required to change significantly their properties and/or positions. The plasma, in contrast, is relatively unstable because of the ease with which it can be translocated through the soil profile and because its physical and chemical properties can be modified by relatively small changes in conditions. In other words, the plasma comprises the mobile part of soil constituents. The difference in stability or activity between the constituents of the two groups were attributed, by Brewer (1964, p.11), to three factors: (1) particle size, (2) particle shape and (3) composition. Low magnesian calcite is the dominant constituent in calcretes and occurs in various shapes and sizes. This calcite may be stable at present, yet because of its relatively high solubility at normal pressures and temperatures, it is susceptible to: (1) modification <u>in situ</u> of its grain size and shape, (2) translocation from one part of the profile to another part and (3) complete removal. Therefore, pedodiagenetic calcite is considered here as part of the plasma. Additional plasma constituents which are commonly found in calcretes include amorphous silica, hydrous oxides, organic matter and micron-sized particles of rock-forming minerals. These additional plasma constituents are discussed in Chapter 6.

Skeleton grains include skeletal grains (hard parts of organisms, some of which are composed of carbonate plasma) and detrital terrigenoclastic grains of silt size or larger.

In addition to the solid constituents, calcretes, like most sedimentary rocks, have a porosity. The fabric of porosity is considered after fabric analyses of the carbonate plasma and skeleton grains have been given. These three major components - plasma, skeleton grains and porosity - are considered together in the last section of this Chapter on calcrete microtextures.

S-MATRIX

Sedimentary rocks can be conveniently considered as comprising four components - grains, matrix (mechanically deposited material between grains), cement and voids. Distinction between grains and matrix is based on an arbitrarily based upper size limit for the matrix. This upper size limit varies among workers, being generally between 4 to 30 microns. However, as pointed out by Brewer (1964, p.147), the grain size of the matrix is defined in relationship to the size of the members of the framework. The grain-matrix concept is difficult to apply in pedography because of the continuous particle size distribution in the majority of soil materials. The grain-matrix concept is equally difficult to apply to the petrography of calcretes. Viewed in petrographic thin sections, the 'micritic' component of calcretes is unresolvable. The 'micrite', or 'calcrete matrix' of some workers, may consist of fine-grained cement, mechanical detritus, neomorphic calcite or metasomatic calcite. This material is commonly interspersed with micron-sized voids. In addition, the characteristic lack of a recognizable self-supporting framework of grains provides further problems when describing textures in calcretes. For example, matrix-supported or 'floating' textures may have been depositional or diagenetic (p. 143).

In order to overcome some of the above mentioned problems, I have made use of the s-matrix concept of Brewer (1964). The s-matrix consists of plasma, skeleton grains and voids which do not occur as pedodiagenetic structures (Chapter 5). In other words, the s-matrix of calcretes consists of: (1) materials and voids which are not recognizable as three dimensional entities by optical microscopy; (2) pedodiagenetic calcite plasma which is susceptible to alteration in form or position; and (3) terrigenoclastic grains which are relatively stable components.

Terminology

Before petrographic descriptions are given, it is necessary to clarify several terms used in this section. Briefly, these are as follows:

Unit - - the individual under study. This may be a crystal, a void, a grain, a compound particle, a horizon or even a complete profile.

Unit fabric - - the size, shape and arrangement of units.

Size - - following the classification of Friedman (1965) with the addition of a lower limit class, namely 'submicron-sized' and without the restriction to crystals only. Thus, for the measurement of unit diameters (or if not equant, of the longest dimension) the following classification is used:

Submicron-sized	less than 1.0 micron
Micron-sized	1 - 10 microns
Decimicron-sized	10 - 100 microns
Centimicron-sized	100 - 1,000 microns
Millimetre-sized	1 - 10 mm
Centimetre-sized	10 - 100 mm

Shape - - following Folk (1965) and Friedman (1965).

Arrangement - - as defined by Brewer (1964) for his soil fabric, namely, the physical constitution of a material as expressed by the spatial arrangement (random, radial, concentric, etc.) of solid particles and associated voids.

Texture - - the size, shape and arrangement of units and the degree of crystallinity of the solid components.

Carbonate Plasma

The commonest plasmic fabrics occurring in calcretes are portrayed diagrammatically in Fig. 10, p. 116. Terminology of plasmic fabrics follows that of Brewer (1964) and Bal (1975a, 1975b). Possible relationships among the various types of plasmic fabrics are indicated in Fig. 10.

Fine crystic plasmic fabric

Definition: the distance between fine-grained (less than 10 microns) more or less isodiametric calcite crystals is less than the diameter of the crystals (Bal, 1975a). Brewer (1964) used the term 'crystic' to describe soil materials composed almost completely of a dense mass of crystals.

Fine crystic calcite plasma is the major constituent of calcretes. It is commonly referred to as the 'calcrete or caliche matrix'. Because of the fine grain size (generally less than 4 microns), fine crystic plasma appears as an amorphous material when viewed in petrographic thin sections (Plates 28a-d, 29a). Fine crystic plasma appears as a white, or less commonly, as a red-brown micritic s-matrix in reflected light. Using SEM, the fabrics of this plasma can be more readily discerned (Plates 28e, 35, 36e, f). The s-matrix shown in Plate 28e consists of submicron-sized calcite crystals and submicron-sized intergranular voids. The walls of centimicron-sized voids shown in Plates 28e, f and 35 are lined with scalenohedral, micron-sized to decimicron-sized calcite crystals. The long axes of these crystals are normal or inclined to the substrate (Plates 28a, b, e, f, 35). Aggregates of crystals commonly form rosettes (Plates 28e, 29d, e) on the surfaces of clots consisting of submicron-sized calcite grains (Plate 28b). This arrangement gives a characteristic clotted texture (Plate 29a) to the s-matrix, a texture that is typical of calcretes and of some marine cements (Alexandersson, 1969).

Submicron-sized calcite grains, whose fabrics are not readily resolvable - even by SEM - are volumetrically the most important component of calcrete hardpans. Microchemical staining and powder X-ray diffraction indicate that this material is non-ferroan low magnesian calcite.

Calcic^{x} plasmic fabric

Definition: single calcite crystals or clusters of calcite crystals less than x microns in grain diameter occur close to each other throughout the s-matrix but without forming a crystic plasmic fabric (Bal, 1975a).

The upper size limit (x microns) chosen depends on the grain size distribution of the sample but is generally between 10 - 100 microns in samples examined in this study. The distance between crystals or crystal clusters is greater than in crystic fabric. The space between decimicron-sized calcite crystals is generally occupied by micron-sized and submicron-sized calcite grains (fine crystic calcite plasma), submicron-sized clay minerals and amorphous materials. This fabric grades into crystic plasmic fabric in samples where the space between decimicron-sized calcite crystals is almost absent (Fig. 10, p. 116). Where the calcite crystals, which are poikilotopic (cf. Friedman, 1965) are greater than 100 microns in diameter and the space between them is much greater than the diameters of poikilotopic crystals, they are better termed 'intercalary carbonate crystals' (p. 118).

Although calcic^{100} plasmic fabric is not characteristic of calcretes in general, it is common within calcrete hardpans of Pleistocene age from Ibiza (Plate 74a). This fabric is uncommon in other horizons from the

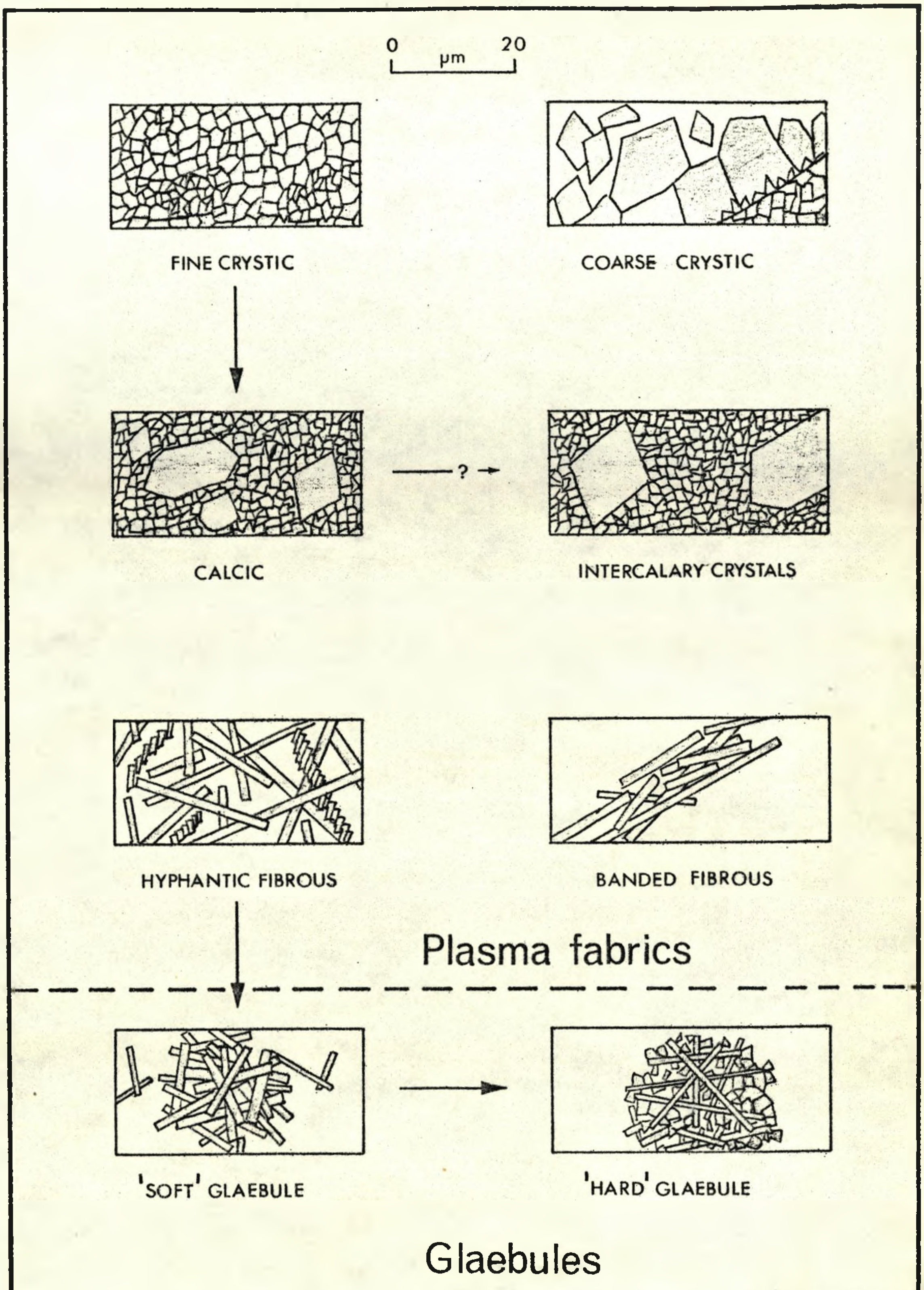

Figure 10. Diagrammatic representation of carbonate plasma fabrics and their relationship to glaebules.

same area and, moreover is rare in all horizons (including hardpans) from mainland Spain. A proliferation of detrital Microcodium grains (p.194) floating in a cryptocrystalline or fine crystic calcite plasma is responsible for the restricted occurrence of calcic plasmic fabrics in Pleistocene calcites from Ibiza.

Coarse crystic plasmic fabric

Definition: the distance between coarse-grained (more than 10 microns grain diameter) more or less equant (isodiametric) calcite crystals is less than the diameter of the crystals (Bal, 1975a).

This fabric is characteristic of calcite which lines primary and secondary voids. It is perhaps better known as sparry calcite cement when it occurs in such voids. It also occurs as a gravitational or microstalactitic cement (Plate 30). The chalky or powdery horizon of a typical calcrete profile consists of masses of decimicron-sized calcite grains (Plate 31) having a coarse crystic plasmic fabric. The grains tend to be lozenge-shaped with no preferred orientation of long axes (Plates 31a, b). SEM reveals that the surfaces of grains are irregular (Plate 31c, d), possibly because of natural etching but more likely to have resulted from rapid precipitation (E. T. Alexandersson, Univ. of Uppsala; J. Schroeder, Oceanographic Institute, Sudan; pers. commun.). These grains, which act as single crystals when viewed by optical microscopy, are generally 10 - 30 microns in length and 10 - 20 microns in width (Plate 31). They have all the characteristics of a microsparry or sparry calcite cement, except for one factor, they are not attached to a substrate and are rarely cemented to each other. They are an accumulation of isolated grain-supported calcite crystals showing no lattice fit among themselves (Plate 31a, b). Thus, a coarse crystic calcite plasma is a better description for this material. The reason for calcite precipitation without cementation is unknown. A tentative suggestion put forward here is that the crystals are free to jostle and, thus, continued disturbance as a result of biogenetic activity and through-flowing waters, prevents crystals from becoming firmly attached to a physically inert substrate.

If downward water movements have sufficient energy to transport these grains and deposit them within voids in subjacent material, the upper part of the profile will become gravitationally unstable. _If_ this process operates in nature, the effect is two-fold: firstly, gravitational instability as a result of loss of material from the chalky horizon may lead to _in situ_ brecciation of the overlying hardpan and; secondly, translocation of these calcite crystals and their deposition within voids will form geopetal sediments. Thus, the chalky horizon of calcrete profiles could be a potential source for 'crystal vadose silt' (_cf_. Dunham, 1969a). These suggestions are admittedly speculative but, in my opinion, worthy of serious consideration. Further investigations are needed to examine rigorously these hypotheses.

Intercalary crystals and crystallaria (cement)

Definitions: (a) Intercalary crystals - crystallaria that consist of single large crystals or groups of a few large crystals set in a soil material and apparently not associated with voids of equivalent size or shape to that of the crystallaria as a whole; the crystals are enhedral to subhedral having at least some crystal faces (Brewer, 1964).

(b) Crystallaria - crystalline fillings of intergranular voids, vugs, fractures and other open spaces (Brewer, 1964).

The term crystallaria is included here for completeness and consistency with the classification of Brewer. However, following the reasoning of Braithwaite (1975), the petrographic term cement is preferred to crystallaria since precipitation in voids plays no role in a functional soil (Plate 30).

Intercalary crystals, on the other hand, are not associated with voids (see definition above). They may have formed *in situ*, been inherited from the host material (relics), or formed by disturbance of carbonate crystals (*cf.* Brewer, 1964; Bal, 1975b) such as rhizoliths (p.158) and *Microcodium* aggregates (p. 203).

Plates 49e, f, 74a, b, d and 78d illustrate examples of carbonate intercalary crystals within calcrete deposits. These examples are examined in detail in relevant sections.

Non-carbonate intercalary crystals are rare in calcretes but they do occur. Plate 34a shows what is possibly an authigenic or intercalary quartz crystal. Distinction between intercalary crystals and skeleton grains is sometimes difficult but the shape of grains is a useful guideline in making such distinctions. Skeleton grains tend to be anhedral as a result of abrasion during transport, whereas intercalary crystals are euhedral to subhedral and have crystal faces. However, corrosion of grains *in situ* makes it difficult to determine their origin (Plate 34b-d).

Hyphantic* fibrous plasmic fabric

Definition: the basic distribution of fibrous (acicular or needle-shaped) calcite crystals is arranged in a random, loosely woven pattern within voids (Bal, 1975a).

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* Gk. *hyphantos* = woven

Ramifying, self-supporting but loosely woven or hyphantic calcite needles are common in the upper parts of calcrete profiles. This fabric is common in voids within hardpans and sheet calcrete horizons (Plates 32a, b, 33a-c). Hyphantic and banded (p.119) plasmic fabrics are characteristic of sheet calcrete horizons (Plates 32, 33). They also form soft, powdery glaebules within and below the sheet calcrete horizon (Plate 44). Figure 10, p. 116 shows diagrammatically the relationship between fibrous plasmic fabrics and the formation of some types of glaebules. Fibrous plasmic fabrics also constitute vesicular (p.141) and alveolar (p.138) textures.

Staining and X-ray diffraction indicate that the mineralogy of these needle fibres is non-ferroan low magnesian calcite (LMC). Folk (1974, p.41) stated that LMC was "seldom if ever finely fibrous." In addition to this relatively uncommon habit for LMC, some needles show an apparent oblique extinction of 30 - 45°. The reason for this apparent non-parallel extinction can be seen when such crystals are viewed under SEM; each needle is composed of rod-shaped crystallites, 3.0 microns long and 0.3 - 0.5 microns wide, stacked obliquely with respect to the length of the needle (Plate 32d-f). This phenomenon was noted independently by Stoops (1976).

Needle-shaped calcite has been referred to as 'lublinite' by many soil scientists (e.g. Kubiena, 1938; Seghal & Stoops, 1972; Stoops, 1976). Needles of calcite commonly occur in tubular voids of root moulds and form 'pseudomycelia' (Kubiena, 1938; Ruellan, 1967). According to Kowalinski *et al.*,(1972), lublinite or needle-shaped calcite is preserved only in xeromorphic soils.

Hyphantic fibrous calcite plasma is synonymous with the random needle fibres of James (1972). This fabric is common within Pleistocene and Holocene calcareous crusts from Barbados (James, 1972; Harrison, 1977). Ward (1975) documented identical fabrics subjacent to ancient and present-day weathering surfaces and within soil zones developed in and upon Pleistocene aeolianites from Yucatán. Steinen (1974) demonstrated that needles of calcite found in cores of Pleistocene age from the subsurface of Barbados were confined to those sediments which had been subjected only to subaerial vadose diagenesis.

The above outlined reports of needle-shaped calcite occurring near the land surface are consistent with my own observations. Needles of low magnesian calcite, having a hyphantic fibrous plasmic fabric (Plates 32, 33a-d), are characteristic of the near-surface subaerial vadose diagenetic environment. Hyphantic fibrous plasma composed of halite (Plate 37d-f) also is indicative of subaerial vadose conditions. However, it is unlikely that halite needles will be preserved in the fossil record, whereas needles of low magnesian calcite are not only stable but are volumetrically abundant in calcrete profiles. A cursory examination of thin sections of Carboniferous calcrete hardpans within Dinantian limestones from Wales (thin sections lent by I. Somerville, Univ. of Belfast and G. Spalton, Univ. of Reading) reveal that calcite needles are indeed preserved in the fossil record.

Banded fibrous plasmic fabric

Definition: the basic distribution of fibrous (acicular or needle-shaped) calcite crystals is arranged in a band with long axes of needles parallel to the band (Bal, 1975a).

Bundles of calcite needles may be attached to a substrate (Plate 37c) or form self-supporting bridges across voids (Plates 33e, f, 36d). The bridges are composed of low magnesian calcite needle fibres (mineralogy determined by staining and X-ray diffraction), 0.5 - 2.0 microns wide and from 3 - 120 microns in length (Plate 33e). Length : width ratios are generally between 6 to 8 : 1 although some needles have been recorded with L : W ratios of 100 : 1 (Plate 33a). Needle-shaped crystals appear to be aligned tangentially with respect to the surface of a void or lie parallel with the self-supporting bridge frameworks when viewed in thin section (Plate 36d). However, SEM observations indicate that long axes, and presumably crystallographic orientations are more complex than this apparent tangential alignment (Plate 32f). The reasons for this disparity at different levels of magnification are unclear; it may be that there is an 'averaging' effect when the needles are viewed in transmitted light at relatively low power with the polarizing microscope.

Position and abundance of carbonate plasma within an idealized profile

The fabric descriptions given in earlier sections provide morphological criteria for the identification of carbonate plasma fabrics within calcrete deposits. However, viewed in isolation, such fabric descriptions reveal no information with regard to the distributions, spatial relationships and volumes of the identified units throughout a profile. Therefore, based on petrographic (optical and SEM) observations and point-counting of thin sections, the type and relative abundance of the aforementioned carbonate plasmic fabrics were identified and evaluated for designated horizons (Fig. 11, p. 123). The information was gained from

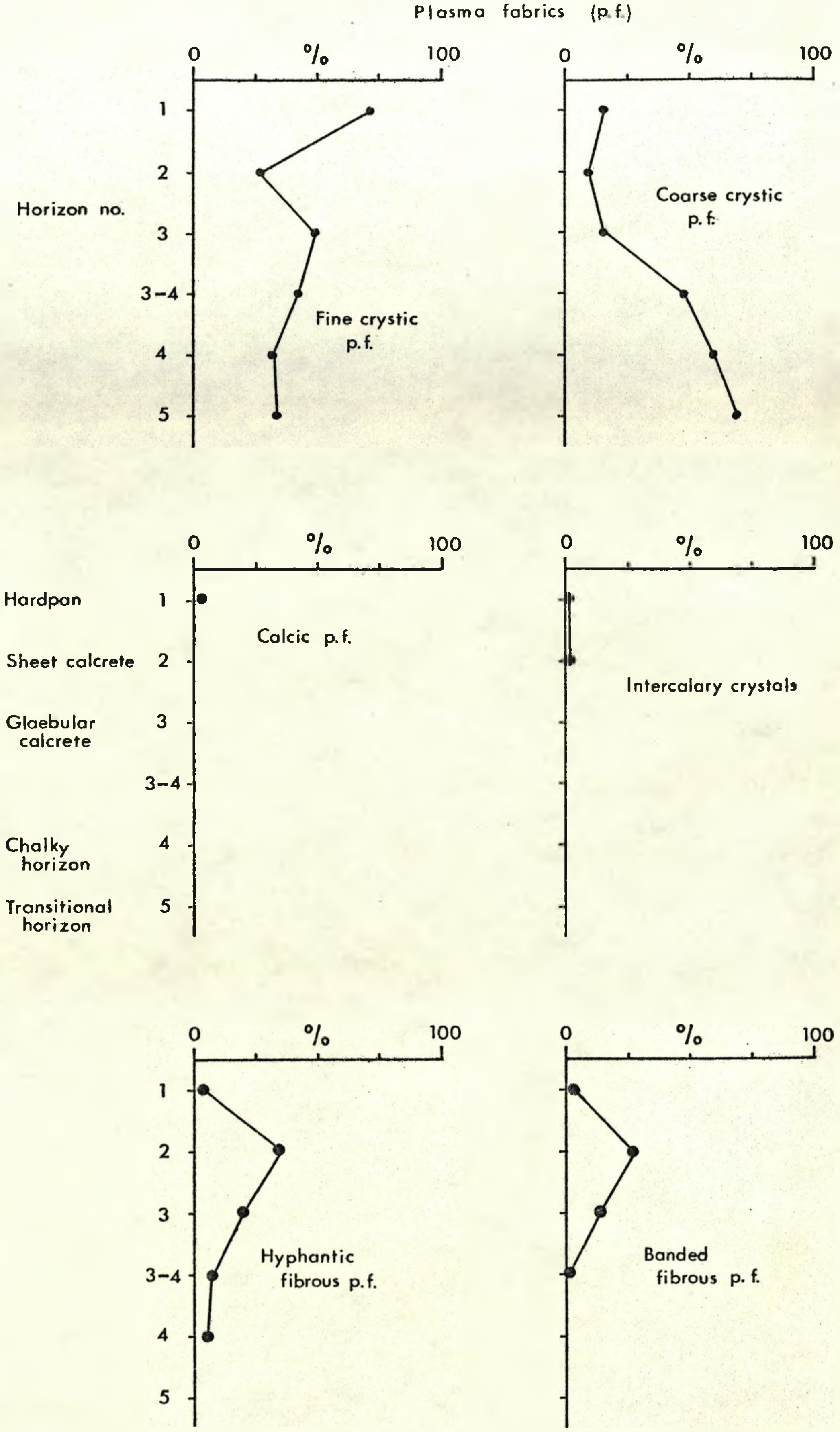


Figure 11. Position and abundance of carbonate plasma within an idealized calcrete profile.

examination of over 300 samples from profiles of widely differing geographical locations in the study area. The relative abundance of the defined types of carbonate plasma have been calculated as a percentage of the total carbonate plasma within a single horizon. The positions of characteristic carbonate plasma fabrics for a fully developed, idealized calcrete profile, are shown in Fig. 12, p. 125.

Skeleton Grains

The fabric and abundance of skeleton grains are related intimately to the fabric and composition of the host material and the amount of pedodiagenetic alteration which has taken place. Skeleton grains are incidental to the characteristic fabrics which can be recognized in calcrete profiles. Nonetheless, the study of such grains serves a purpose; the degree of alteration or modification of skeleton grains allows a qualitative assessment to be made of the intensity and duration of pedodiagenesis.

Skeleton grains range from single, decimicron-sized detrital grains to lithoclasts of centimetre size. Primary shapes (pre-calcretization) are related to earlier transportation regimes or, in the case of skeletal (bioclast) grains, to organic growth. Present shapes, however, are a function of mineralogical stability and amount of pedodiagenetic alteration of the skeleton grains. Although skeleton grains are defined as stable constituents (p. 110), in a calcrete-inducing environment all minerals other than low magnesian calcite are unstable.

Most non-carbonate skeleton grains are composed of quartz. Minor minerals include micas, feldspars and ore minerals. Spherical grains of framboidal pyrite were observed in a few samples by SEM.

The distribution and arrangement of skeleton grains is, as with

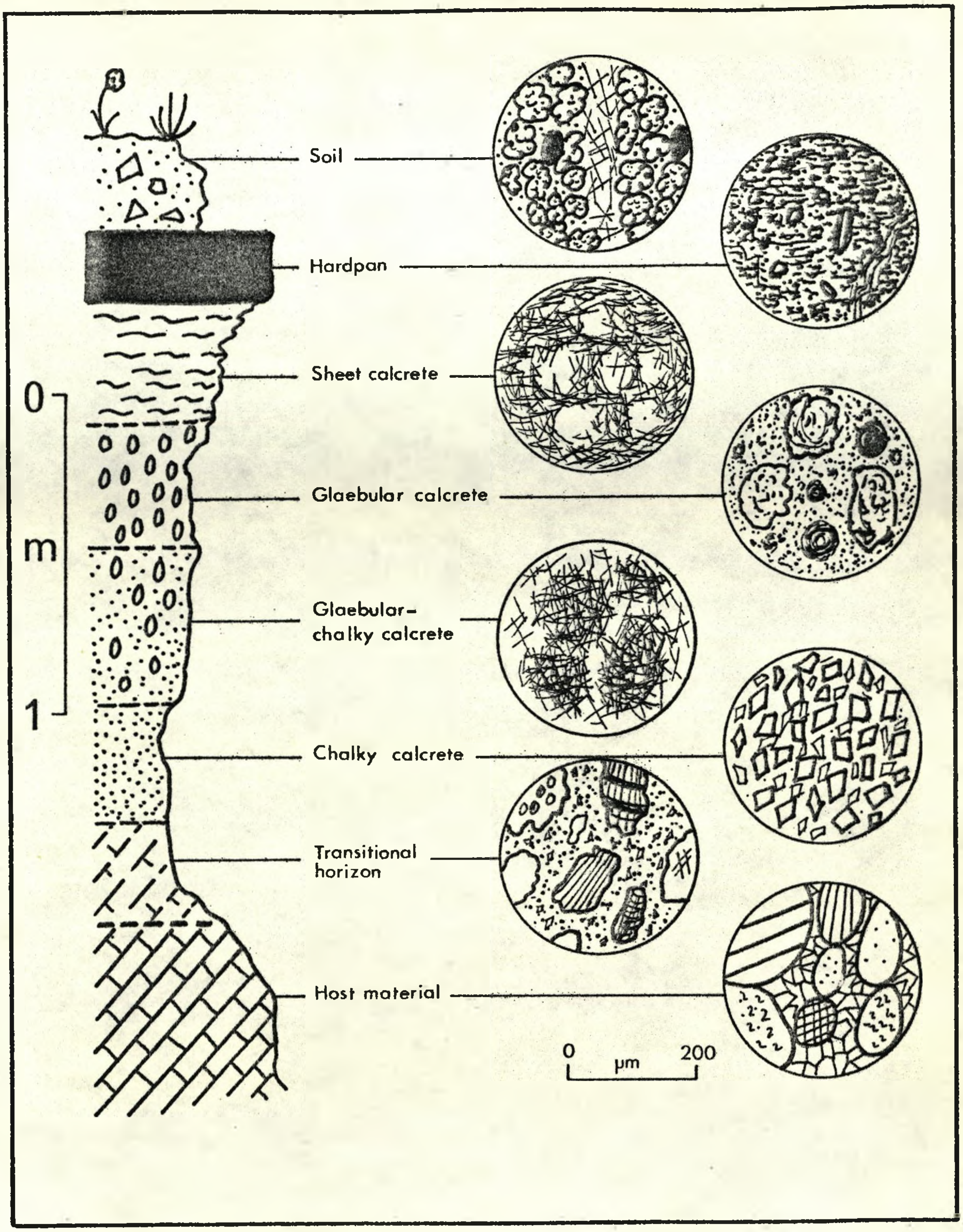


Figure 12. Characteristic plasma types in an idealized calcrete profile.

their original shapes and sizes, a function of their original distribution and arrangement within the host material. Wackestone or floating textures are common in my samples but many of these textures are secondary rather than primary textures (p.142).

Black pebbles

Black skeleton grains, more generally referred to as black pebbles (Ward *et al.*, 1970), are a noticeable feature in some calcrete hardpans examined in this study. Ward *et al.*, (1970), after examining blackened aeolianite and caliche rubble from Yucatán, attributed the blackening to the preservation of trapped organic matter within calcite crystals. They suggested (p. 548) that layers of fragmented dark-coloured limestone may indicate subaerial exposure adjacent to hypersaline water.

During my field studies in the western Mediterranean region, black pebbles, which had been cemented in calcrete hardpans, were recorded within several kilometres of the present-day coastline. They were not recognized further inland, although apparently they do occur (M. Esteban, Univ. of Barcelona, pers. commun.). In addition, some black freshwater or brackish water limestones occur inland; again organic matter is responsible for their blackening. These deposits usually can be distinguished from blackened calcrete by their lithofacies associations and textural characteristics.

In thin section, black pebbles show typical calcrete textures and fabrics, including alveolar and brecciated textures, fine and coarse crystic plasmic fabrics, fractures and channel porosity. The origin of the blackening is unresolvable by optical microscopy; it appears as an amorphous substance. However, partly blackened pebbles show filamentous networks, consisting of micron-sized threads encrusted by ferric and/or manganese oxides, arranged around the grain perimeter.

Following removal of the carbonate fraction by acid digestion, the insoluble residues were examined by SEM. Branching filaments, 1 - 2 microns in diameter, were recognized within the residues. Temporary mounts were viewed also under the petrographic microscope, revealing that some of the filaments are septate. The size, branching and internal structure of these filaments suggested a fungal origin. Examination of this material by Barbara Javor, University of Oregon, supported this interpretation.

Black-rimmed and totally black pebbles were boiled in 30% hydrogen peroxide or sodium hypochlorite for 30 mins. No colour changes were observed, suggesting that the colour was not because of contained organic matter. Likewise, Ward _et al._, (1970) reported that their samples showed no colour change when powdered samples of untreated black pebbles were stirred in full-strength Clorox. However, after they had removed the calcite present in the pebbles by acid treatment, the black residuum was bleached and dissolved in a Clorox solution. This finding led them to the conclusion that finely-disseminated organic matter was preserved in calcite crystals.

The procedure of Ward _et al._, (1970) as outlined above was followed for my samples but, still, the black residuum remained. These findings, combined with the information gained from light and scanning electron microscopical observations, led me to the conclusion that the blackened filamentous networks resulted from metal encrustation on fungal hyphae. Following fungal infestation of free pebbles, indurated or soft, the fungal hyphae were encrusted during or after life by ferric and manganese oxides.

It is known that several types of bacteria are capable of causing precipitation of metallic oxides (Krumbein, 1971; Buchanan & Gibbons, 1974). *Metallogenium* and *Pedomicrobium* are examples of such bacteria; they may have colonized the penetrative fungal hyphae and used the organic matter of the fungi as a source of energy. However, this is a hypothesis which requires further study before definite conclusions can be made with confidence.

POROSITY

Terminology and Classification

Brewer (1964) has provided a useful morphological classification of voids in soils; Choquette & Pray (1970) have established a morpho-genetic classification with the additional consideration of time for sediments and sedimentary rocks. If plotted on a soil-sediment-rock triangular diagram, calcretes would occupy a central position. The problem of how best to classify porosity in calcretes is great; neither Brewer's nor Choquette & Pray's classifications are completely suitable for this purpose. Therefore, I have formulated a morpho-genetic classification which categorizes the basic porosity types found in calcretes. Table 7, p.130 summarizes this classification. It is pointed out that this classification differs from others because of its consideration of three physical constituents - solid inorganic, solid organic and liquid - the volumes of which are inversely proportional to air porosity. In addition, porosity types are considered within two major categories, one where constituents have been removed, the other where constituents have been retained or added (Table 7). Porosity types are described morphologically, whereas porosity evolution is examined by considering the processes of porosity modification, that is, by considering the genesis of porosity.

Porosity Types

Intergranular porosity (fabric selective)

Simple packing voids among skeleton grains vary in their sizes, shapes and arrangements because of the variations in grain shapes and the grain size variation within a given material. Intergranular porosity is difficult to observe directly in calcretes because of the fine grain size (micron-sized or submicron-sized) of the plasma. Intergranular porosity is volumetrically insignificant in the upper horizons of calcrete profiles but may be the dominant porosity type in the

TABLE 7. POROSITY TYPES IN CALCRETE (FS fabric selective; NF not fabric selective)

CONSTITUENTS REMOVED			CONSTITUENTS ADDED	CONSTITUENTS RETAINED	
SOLID INORGANIC	SOLID ORGANIC	LIQUID	EXPANSION		ISOVOLUMETRIC
Physicochemical dissolution	Biochemical decay	Physical wetting and drying	Biophysical rhizo-brecciation	Physical gravity	Physical packing
VUGS NF	ORGANIC MOULDS FS	SHRINKAGE CRACKS NF CIRCUM-GRANULAR CRACKS FS	FRACTURES NF	CRACKS NF FRACTURES NF	INTERGRANULAR FS
Biochemical corrosion		Biophysical desiccation		Physical expansion by heat	Biophysical inheritance
BORINGS NF VUGS NF		FENESTRAE FS		CRACKS NF FRACTURES NF	INTRAGRANULAR FS
Biophysical excavation				Physical expansion and movement of fluid bubbles	Physicochemical
CHAMBERS NF CHANNELS NF				VESICLES NF	INTERCRYSTAL FS

transitional horizon if the underlying host material consists of grain-supported sand grains. Intergranular voids are volumetrically significant in aeoliantes from Ibiza, for example. Skeleton grains tend to be in point contact or have long contacts as a result of grain-grain dissolution. Grain-grain dissolution gives an overpacked fabric (cf. Knox, 1977).

Intragranular porosity (fabric selective)

Like intergranular voids, intragranular porosity is a function of the characteristics of the host material. This type of porosity is important in the lower parts of calcretized aeolianites (Plate 30c) where skeleton grains consist of skeletal grains (forams, gastropods, echinoderms, bryozoans and coralline algae). Intragranular porosity also is important locally within heavily corroded siliciclastic skeleton grains.

Intercrystal porosity (fabric selective)

Because the plasma of calcretes is typically micron-sized or submicron-sized, this type of porosity can best be assessed by SEM. SEM examination reveals that the intercrystal and intergranular microporosity of calcrete hardpans, composed of 'dense' highly indurated microcrystalline or cryptocrystalline calcite, may be in excess of 40%. The same sample examined in thin section would show an apparent porosity of 0%! In other words, the dense, dark appearance of the fine crystic plasma (micrite) is due largely to internal reflection in a highly porous material, resulting in a high incidence of Becke lines.

Brittle fracture porosity (not fabric selective)

In situ brecciation of indurated calcrete has been documented by many workers (Bretz & Horberg, 1949; James, 1972; Goudie, 1975). The resulting cracks and fractures are commonly filled with calcite cement, thus re-establishing the rigidity of hardpans. Plates 27e and 39 illustrate examples of calcite-filled fractures in calcrete deposits.

The origin of fracture porosity is rarely given serious consideration. I have already suggested one mechanism to account for in situ brecciation of calcrete hardpans - rhizo-brecciation, that is, the biophysicochemical forces exerted by penetrating plant roots (p.105). An additional mechanism that I consider for brecciation of hardpans is the differential stresses that are set up within indurated horizons which overlie unstable foundations. This suggestion is, unfortunately, based on intuition rather than objective proof. Briefly, the envisaged mechanism is explained as follows:

- A complete calcrete hardpan contains an upper indurated portion and a lower, poorly consolidated or unconsolidated portion. The chalky and transitional horizons do not provide solid foundations for overlying indurated horizons. Because of small-scale topographical changes, varying thicknesses of individual horizons, non-uniform porosity distribution and structural instability of unconsolidated horizons, any given profile is unlikely to maintain gravitational equilibrium. Thus, as a result of gravity instability, the continuous, indurated hardpan in the upper part of the profile is likely to be subjected to differential stresses. With an increase in overburden (top soils, vegetation) and alternating rainy and dry periods (which result in volumetric changes in the water content within calcrete profiles), the hardpan may fracture in an attempt to re-establish uniform stress conditions. Thus, in situ brecciation may take place within the hardpan. Calcite may grow in the open spaces and recement the brecciated calcrete, thus forming another solid hardpan. The process may be repeated many times, leading to the formation of a hardpan with a complex cross-cutting fracture system (Plates 27b, 39).

Although I have no experimental data to support the validity of this proposal, the same phenomenon in nature can be seen in concrete roads which are underlain by unsound foundations. The only difference is that once the road has broken up as a result of foundation collapse, the brecciated fragments remain free in contrast to brecciated hardpans which are commonly in an environment conducive to cementation by calcite and, thus, likely to be recemented.

Gravitational fracturing leads to the creation of porosity without addition or subtraction of constituents. Rhizo-brecciation, on the other hand, leads to the creation of porosity by addition of organic constituents, namely, the addition of growing and penetrating roots. Both envisaged mechanisms, gravity-induced fracturing and rhizo-brecciation, lead to expansion of the profile and the creation of porosity.

Vesicles (not fabric selective)

The term vesicle is used here to describe spherical pores which have formed by rearrangement or crystallization of plasma around fluid bubbles in an unconsolidated material. Vesicles are larger than grain-supported voids and differ from vugs principally in that the walls consist of smooth, simple curves (Brewer, 1964).

Vesicles have been described in cultivated soils (Miller, 1971) and in desert soils (Evenari et al., 1974). Braithwaite (1975) included vesicular structures and 'birds-eyes' in his eight-fold grouping of textures identified in palaesols from the atoll of Aldabra, Western Indian Ocean. Braithwaite stated (p. 7) that"'vesicular' structures are formed by thin micritic sheaths surrounding polygonal 'bubbles'."

Vesicles have been recognized in samples collected during this study. Although widespread geographically, vesicles are volumetrically insignificant contributors to porosity in calcretes. Vesicles have a restricted distribution within the profile, occurring only in the sheet calcrete horizon and in macroscopical voids within hardpans. The vesicular voids left by fruiting bodies of endolithic lichens (Plate 81a) are, likewise, restricted to the top few millimetres below a land surface.

In thin section, vesicles are delineated by self-supporting framework or walls (Plate 28b) as described by Braithwaite (1975). The framework consists of calcite needles with banded to hyphantic plasmic fabrics (Plate 37a-c). Intercrystal pores among needles may or may not be filled with microcrystalline calcite. Thickening of calcite needle walls results from precipitation of micron-sized calcite crystals on the surfaces of needles.

Vugs (not fabric selective)

Adhering to the definitions of Brewer (1964) and Choquette & Pray (1970), a vug is essentially a macroscopically visible, irregular or equant, normally isolated, non-fabric selective void. Vugs are larger than intergranular packing voids; in calcretes they result from removal of plasma by physicochemical dissolution or biochemical corrosion (Plate 35). Secretion of organic acids by plants and products of organic decay are mainly responsible for such corrosion.

Vugs can be recognized easily when they occur in otherwise non-porous indurated hardpans. They have irregular shapes and random arrangements. Maximum dimensions are measured in millimetres or tens of millimetres; larger vugs are rare, except in profiles that have undergone or are undergoing destruction by karstification (Plate 5c). Such vugs post-date calcretization.

Channels (not fabric selective)

Channels are cylindrical voids with relatively uniform cross-sectional size. Individual channels have circular cross-sections with diameters typically of 0.1 - 0.5 mm but may be up to 2 cm. Channels may be isolated or joined to form branching patterns. Brewer & Sleeman (1963) recognized and described four types of channels - single, dendroid, anastomosing and trellised. The first two types are common morphological forms in calcretes.

From their sizes, shapes and branching patterns, together with contained organic material in some channels, the origin of many single and branching channels can be attributed to burrowing organisms or root activities. The roots of many plants grow by forcing a root tip, only a few tenths of a millimetre in diameter, into soil pores of about the same size, and the young root then swells making the pore larger (Russell, 1973). As a result of growth, roots exert pressures on the channel walls leading to a denser packing near the wall surfaces as compared with the normal soil material. Calvet _et al_., (1975) recorded this phenomenon in Pleistocene aeolianites containing rhizocretions from Mallorca.

Evidence of former root systems also is indicated by partially decayed or, frequently, petrified root material in channels. In some samples, decayed organic material has diffused into the outer margins of the walls and surrounding s-matrix giving rise to a dark, diffuse stain around the channel (Plates 16c, 66a, b, e, f). A greater concentration of soil micro-organisms has been recorded within root channels by SEM (Plates 55, 56).

Organic moulds (fabric selective) and borings (not fabric selective)

If the s-matrix is sufficiently rigid, organic moulds are left when organic constituents decompose. Root channels are specific examples of this type of porosity. Other embedded organic constituents that may leave moulds include soil micro-organisms (fungi, algae) and calcareous skeletal grains (molluscs, coralline algae and other bioclasts with metastable hard parts). In situ organic moulds are readily recognizable in the lower parts of calcretized aeolianites. The identification of organic moulds in fine-grained deposits is more difficult because of the problems of distinguishing between boring and embedment structures (cf. Bromley, 1970). Examples of organic moulds and borings are shown in Plates 20a, 27c, 36, 37e, 42d, 57a).

Desiccation cracks (fabric and not fabric selective)

Alternating wetting and drying cycles may lead to 'pore-cracking' and circum-granular cracking' (Ward, 1975), irregular desiccation cracking or the formation of fenestral fabrics (Tebbutt et al., 1965).

In an unconsolidated s-matrix, wetting may cause expansion (addition of H_2O), whereas loss of water as a result of evaporation or evapotranspiration may cause shrinkage. It is worth pausing for a moment to consider what exactly is expanding and shrinking. Increase in volume may result from adsorption of water on micron-sized and submicron-sized particles or amorphous organic matter, or by hydration of certain minerals. In calcretes, hydrated minerals are rare. Since calcite is an anhydrous mineral, expansion and shrinkage must be restricted largely to the organic and expandable clay fraction of calcretes.

Simple experiments were set up in the laboratory to observe the effects of drying moistened insoluble residues from calcrete hardpans. Irregular shrinkage cracks developed in residues which were left to dry out at room temperatures in 5 cm diameter watch glasses. The fabrics of these cracks were identical to those recorded in petrographic thin sections of calcrete hardpans.

'Circumgranular-cracking', unlike irregular desiccation fracturing, is fabric selective. Alternating expansion and shrinkage around skeleton grains, followed by filling of voids by calcite, leads to the formation of concentric glaebules (Plates 40, 41d, f).

Fenestral porosity is common within the laminar layers of many calcrete hardpans (Plate 11d), It already has been noted that the laminar layers are composed of alternating organic-rich and organic-poor layers (p.83). Shrinkage of organic-rich layers may be the main factor responsible for crinkling and doming, thus forming fenestral pores. Shrinkage during drying may be supplemented by doming as a result of gas accumulation in isolated pockets, the gas resulting from organic decay. This type of porosity is characteristic of lichen stromatolites (p.270) and is indicative of surface rather than subsurface buildups of $CaCO_3$.

TEXTURES

Clotted and microglaebular textures

The dominant component of indurated calcrete horizons is microcrystalline or cryptocrystalline calcite. It occurs as irregular aggregates of submicron-sized crystals surrounded by patches of micron-sized, or less commonly, decimicron-sized crystals. This gives the rock a clotted texture (structure grumeleuse, Cayeux, 1935; crumb aggregates, Braithwaite, 1975; caliche matrix, Harrison, 1977) when viewed in thin section (Plate 43c, d). SEM examination of this texture provides additional information. Aggregates of cryptocrystalline material form vague spheres, 20 - 80 microns in diameter, which are encrusted by bladed and equant micrite cement with long axes of 1 - 4 microns (Plate 29a-e). A few samples examined in this study have coarser cement fabrics composed of randomly oriented blades up to 10 microns long (Plate 29f). It should be noted that the intercrystal porosity is high in these samples. When viewed in thin section, this type of porosity gives a dark, dense-looking appearance to the s-matrix which hinders identification of individual crystals and gives the impression of zero porosity.

Alveolar texture

The first mention of alveolar texture found in the literature is by Esteban (1974). He stated (p.111) that "Alveolar texture is a peculiar feature in 'mature' caliche, but not very common....Alveolar texture, like clotted and channeled micrite, is thought to be exclusive of caliche." Unfortunately, he only illustrated this texture with two photomicrographs and did not attempt to define, describe or interpret alveolar texture in any way.

According to the FAO (1972), alveolization is defined as "....pitting of a rock surface, often into hexagonal shapes produced by aggressive water, plant roots, or by wind-blown sand." However, from an examination of calcrete samples collected during this study, it is evident that alveolization and alveolar texture are not equatable. Alveolar texture is not restricted to exposed rock surfaces but occurs within calcrete hardpans and sheet calcrete horizons (Plates 36a, 39b). Alveolar texture consists basically of a number of cylindrical to irregular pores, which may or may not be filled with calcite cement, separated by a network of anastomosing micritic walls (Plate 36b, c). For the time being, this will serve as a crude definition; any formal designation will be delayed until this texture has been described more stringently.

Petrography - - As indicated already, alveolar texture is composed of an irregular network of micritic walls with unfilled, partially filled or totally occluded pore spaces. Pore diameters commonly range from 100-500 microns, but a few may reach 1.0 mm. The micritic walls are composed of LMC needle fibres, 0.5-2.0 microns wide and from 3-120 microns in length (Plate 36d-f). Some pore spaces are partially or totally occluded with equant, anhedral to subhedral decimicron-sized calcite mosaics (coarse crystic plasmic fabric), other pores are unfilled or have been occluded partially with a ramifying network of random needle fibres (hyphantic fibrous plasmic fabric).

Although the shape of pore spaces (as defined by the ramifying micritic wall network) is variable, oval or subspherical walls tend to be common (Plate 36b, c). When viewed by SEM, the walls can be seen to be tubular or cylindrical (Plate 36e, f). In some samples, two distinct tube diameters can be recognized (Plate 62c, d).

Distribution - - The distribution of alveolar texture is related to the porosity distribution and porosity type within a given calcrete profile. Alveolar texture occurs dominantly in porous but, nonetheless, coherent or lithified parts of sheet calcrete horizons and within fractures in hardpans (Plate 39b).

Origin - - The origin of alveolar texture has been suggested by several recent authors. Steinen (1974) has recorded alveolar texture in core samples of Pleistocene limestones from Barbados. He noted that ramified networks of micritic walls enclosing pore spaces which contain needle fibres were found only in localized areas within near-surface voids. He suggested that they may represent discrete channelways within sediment which had been penetrated by rootlets. He noted further that the walls were composed of tangentially oriented lath-shaped crystals and that the structures may have accumulated as sheaths around rootlets. This arrangement produces a ramified structure which would stand by itself after decay of the rootlet.

Harrison (1977), in his discussion on caliche profiles of Pleistocene age from Barbados described and illustrated "sponge-like networks of root voids partially occluded by an irregular internal mat of randomly oriented needle-fibre crystals." Calvet et al., (1975) recorded alveolar texture within Pleistocene rhizocretions from Mallorca.

Evidence to support the idea that the micritic walls represent encrustation of calcite needles around decomposed roots was gained by SEM examination of calcite fabrics around living and partially decayed roots in actively forming calcretes. Plate 63e shows a partially decayed root surrounded by a loosely packed fabric of random needle fibres. Plate 63f shows brittle, sloughed off root hairs supported by hyphantic fibrous calcite plasma. Living roots lack this calcite encrustation. It is likely that calcite precipitation took place during decay of the roots. Partial collapse of decaying roots, followed by needle calcite encrustation, would lead to irregularly shaped tubes rather than regular cylinders. This may account for the irregular arrangement of some micritic walls (Plate 36b). It is suggested here that decaying roots influence their surrounding chemical micro-environment in such a way as to favour precipitation of calcite needles on their surfaces.

Vesicular texture

In thin section, vesicular texture and alveolar texture are not readily differentiated, except that the latter may show tubular longitudinal sections, whereas vesicular texture has only spherical shapes. SEM examination reveals that vesicular texture is composed of spherical pores (vesicles), 50-100 microns in diameter, surrounded by needle calcite walls, 10-40 microns thick (Plate 37a, b).

Whereas alveolar texture results from precipitation around decaying roots, the formation of vesicular texture is more difficult to resolve with certainty. The meniscus effect of trapped water around gas bubbles may be responsible for vesicular texture. Precipitation of needle calcite following evaporation of meniscus-held solutions would give this arrangement. This texture has been observed only in porous, poorly consolidated material within the uppermost (1 m from the subaerially exposed surface) part of a given profile.

Vermicular texture

Dense networks of micritic tubes and/or rods set in a fine crystic plasma give vermicular ('spaghetti-like' or 'worm-like') textures when viewed in the thin section (Plate 50f). SEM examination shows that the micritic tubes and/or rods are composed of calcite encrusted or calcite impregnated filaments, generally 5-20 microns outer diameter and up to 1 mm long (Plate 59a). The origin of these filaments are discussed later (p.169). It will suffice here to say that the filaments are biogenetic carbonate structures formed by the calcification of fungal hyphae, algal filaments or land plant root hairs.

Floating texture and corroded skeleton grains

Embedded, centimicron-sized skeleton grains showing no point contacts in a fine-grained calcite plasma give an arrangement that is commonly referred to as 'floating' texture (Brown, 1956; Goudie, 1975) or 'sea and island' texture (Aristarain, 1969, 1970). Read (1974) referred to this texture as a secondary or diagenetic wackestone. Plate 38 illustrates this texture. Terrigenoclastic grains of corroded quartzes and micas float in a fine crystic calcite plasma (microspar). Quartz grains have been heavily corroded around their perimeters and replaced by calcite (Plate 38f). Cracks within grains also have been preferential sites for calcite replacement. This gives individual grains an exploded jig-saw appearance (Plate 38e). However, individual fragments are in optical continuity, the exploded appearance is a result of replacement of quartz by calcite - not displacement as widely postulated. Plate 38f shows the contact between quartz and replacement calcite. It should be noted that the boundary is irregular; calcite crystals have grown at the expense of quartz.

Goudie (1975, p.5) stated that carbonate disperses original clastic grains so that they do not occur point contact as they would in the parent sediment. He noted further that many calcretes contain more carbonate that can be accommodated by the original void space in the parent sediment. In an earlier work, Goudie (1973, p.25) suggested that there had been a volumetric expansion of calcrete as a result of the displacive growth of calcite. This conclusion was reached earlier by Gardner (1972) on empirical grounds and by petrographic observation. He maintained that the lack of dissolution of detrital grains ruled out peripheral replacement as being the cause of floating textures. Because there was approximately 2.5 times more $CaCO_3$ in the calcite than could be accommodated by the original void space in the parent material, he concluded that the process of calichification involved expansion of the detrital framework of the parent material. He admitted that the mechanism of expansion was not clearly understood but suggested that crystal growth of calcite and the action of expandable clays may have played important roles.

In all samples collected during the course of this study, floating textures can be explained adequately in one of three ways: (1) by partial replacement of original constituents by calcite; (2) by expansion of the profile as a result of penetration and mechanical dislocation by roots and root hairs; and (3) by normal sedimentary processes, i.e. some floating textures are depositional wackestone textures (*cf*. Dunham, 1962).

By way of example, Plate 38d is a thin section photomicrograph of an exploded 'book' of mica plates. This arrangement can be explained by surficial weathering and disaggregation of micas in an unconsolidated chalky s-matrix, followed by passive calcite cementation in voids. Weathered micas have been observed in the chalky horizons overlying igneous and metamorphic host materials from southeastern Spain.

I have found no evidence to indicate that displacive calcite is responsible for floating textures in my samples.

Figure 13, p. 145 illustrates diagrammatically possible origins for floating textures and calcite-fringed skeleton grains recorded in this study by optical and scanning electron microscopy.

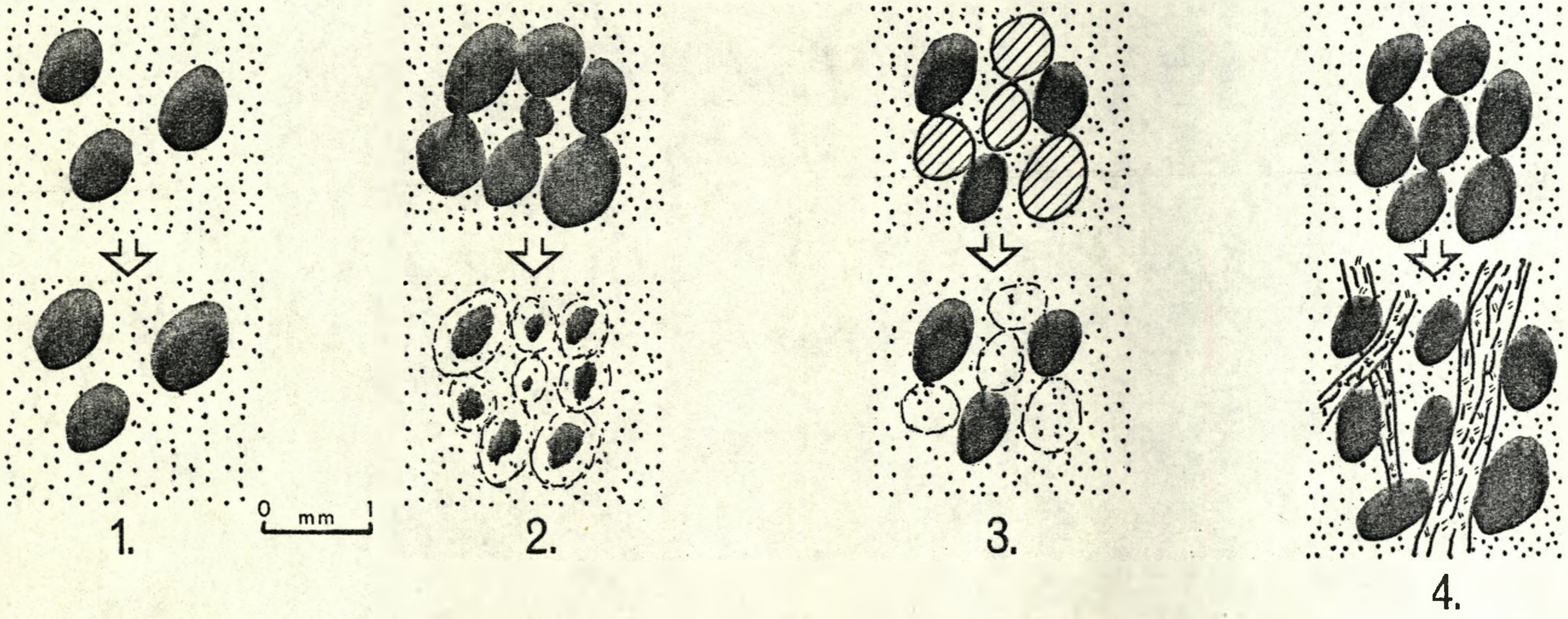
Brecciation texture

In situ non-tectonic brecciation occurs on macroscopical (Plates 22-27) and microscopical scales (Plate 39b-d). Bretz & Horberg (1949) reported that a complex history of brecciation, precipitation and cementation had occurred in caprocks from the High Plains, New Mexico. James (1972) recorded brecciation textures in Pleistocene marine limestones of Barbados. However, the origin of the brecciation was not discussed by these workers.

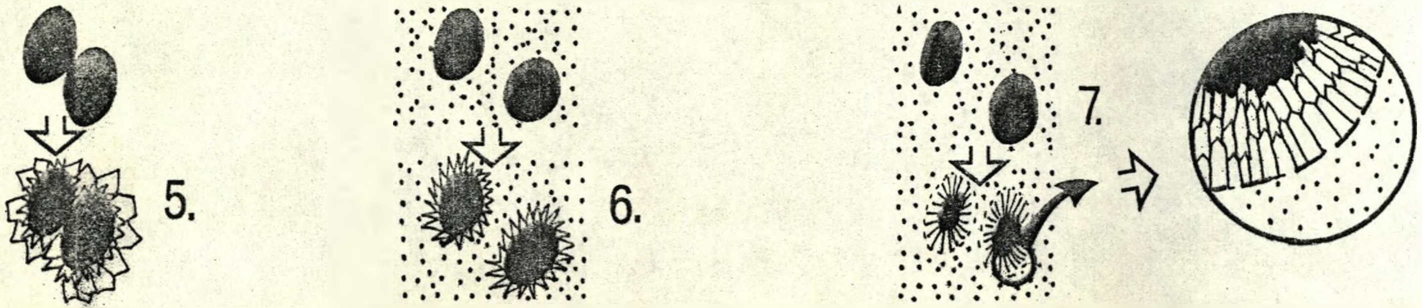
Plate 39a shows a brecciated hardpan underlain by a transitional horizon. The transitional horizon consists of fractured and weathered (spheroidal weathering) dolomite with fractures filled with microcrystalline calcite. Plate 39b is a polished slab taken from the uppermost part of the brecciated hardpan shown in Plate 39a. The dark-coloured fragmented clasts are dolomite host materials. The light-coloured fractures are filled with microcrystalline calcite. The submillimetre-sized pores in these calcite-filled fractures are root moulds. The relationship between the calcite s-matrix and the root mouldic porosity gives an alveolar texture. The *in situ* brecciated part of the hardpan is overlain by a laminar calcrete layer.

In thin section, the boundary between the relic dolomite host material and the calcite s-matrix is highly irregular (Plate 39c). The s-matrix has a fine crystic calcite plasmic fabric and contains root moulds and relic dolomite grains.

Floating texture



Calcite-fringed grains



Several channels, which cut through dolomite grains, show lateral extensions penetrating from the channel surface into the dolomite (Plate 39d). The sizes, shapes and distribution of these lateral extensions are consistent with a root hair origin. Thus, Plate 39 is interpreted as an example of rhizo-brecciation, the significance of which has been pointed out elsewhere in this study (p. 108).

Glaebular texture

As already indicated (p. 87), glaebules vary from decimicron-sized to centimetre-sized structures. This section considers only samples containing glaebules with diameters of 10 mm or less.

Glaebular texture is readily recognizable when sharply defined concentric glaebules are embedded in an otherwise homogeneous s-matrix (Plate 40). However, glaebules show transitions from diffuse aggregates (clotted or microglaebular textures) to well defined contact-supported glaebules (pisolites) cemented by sparry calcite (Plates 29, 41, 42, 43). The genetic relationships between poorly defined plasma concentrations and well-defined, coherent glaebules are discussed later (p. 152), together with an outline of the mechanisms involved in their formation.

CHAPTER FIVE - MICROMORPHOLOGY PART II

PEDODIAGENETIC STRUCTURES

INTRODUCTION

Brewer (1964) introduced the concept of pedological features to describe "recognizable units within a soil material which are distinguishable from the enclosing material for any reason, such as origin (deposition as an entity), differences in concentration of some fraction of the plasma, or differences in arrangement of the constituents (fabric)." This concept is extended here to describe units in calcretes which have formed as a result of both soil-forming (pedogenetic) and diagenetic processes. I have termed such products of pedodiagenesis pedodiagenetic structures.

Pedodiagenetic structures can be divided into two major groups, physicochemical structures and biogenetic structures. In the first group, I will concentrate on two characteristic pedodiagenetic structures of calcretes, carbonate glaebules and cutans. In the second group, biogenetic structures which are characteristic of samples examined in this study include rhizoliths, mineralized organic filaments, calcified faecal pellets, calcified cocoons, palynomorphs and *Microcodium*. These structures will be described in turn, their origins and modes of formation will be discussed and their significance pointed out in relation to the genesis of calcretes.

ABIOGENETIC STRUCTURES

Carbonate Glaebules

Introduction

In an earlier section (p.84), glaebules were described and possible mechanisms to account for their origin were presented. This section is concerned with examining possible mechanisms of formation in detail with the help of information gained by optical and scanning electron microscopical observations.

Description

Glaebules considered here are divided into two basic types, concretions (concentric internal fabric) and nodules (random internal fabric). Glaebules studied here are calcitic unless stated otherwise.

Concretions are characterized by isopachous, concentric coats of fine crystic calcite plasma (Plates 40, 41). The number of coats or concentric laminae varies but is generally less than ten. The laminae themselves are visible in thin section by changes in grain size from submicron-sized crystals to micron-sized or decimicron-sized crystals (Plate 40). In addition to these textural changes, concentric laminations are sometimes recognizable in polished slabs as colour bands when viewed in reflected light.

Sizes of concentric glaebules range from about 30 microns to 20 mm in diameter, although most are between 0.1-2.0 mm in diameter. Concentric glaebules (concretions) tend to be spherical to subspherical in shape (Plates 40, 41). Glaebules with an elongate-shaped nucleus, such as a molluscan bivalve shell, commonly have thick (20 - 30 microns) coats parallel to the long axis of the nucleus and thinner (5 - 10 microns) coats normal to the long axis. This phenomenon also has been recorded by other workers (James, 1972; Goudie, 1975). However, some glaebules studied here have asymmetric coats showing downward elongations as a result of gravitational thickening at the base (Plate 42c). Swineford *et al.* (1958) noted that there was a tendency for the growth of the outer layers to be downward. In the vadose zone, after the bulk of mobile water has drained out of the pores, thicker solution films would tend to remain on the lower surfaces of grains and at grain contacts.

If precipitation of calcite takes place in these solutions, gravitational cements (cf. Müller, 1971) and meniscus cements (cf. Dunham, 1971) will form respectively. Thus, asymmetric concretions showing downward thickening indicate formation, at least of their downward thickened laminae, in the vadose zone. Similarly, meniscus bridging cements among glaebules (Plates 42b, 44) and other grains indicate that these particles were cemented together in the vadose zone.

Glaebules in grain contact are relatively uncommon; matrix-supported glaebules are far more numerous. Glaebules that are in contact with their neighbours do not show polygonal fitting as in the Permian pisolitic facies of the Capitan reef complex of New Mexico illustrated by Dunham (1969b). Glaebules in point contact with adjacent glaebules or other grains suggest that the packing is a depositional rather than a diagenetic feature since there is no reason why growth of glaebules should cease as soon as adjacent glaebules touch each other.

Glaebules with no preferred internal fabric (nodules) have similar sizes and arrangements to concretions but tend to be more irregular in shape (Plate 43a, b). Concretions and nodules differ also in their distribution patterns. Whereas concretions are commonly embedded in a s-matrix, nodules tend to occur within voids (Plates 42a, 44). In addition, whereas concretions rarely can be separated from the encasing s-matrix, nodules tend to be weakly adhesive and easily removed. The nodules themselves may be soft (easily crushed between forefinger and thumb) or hard (indurated). Nodules are commonly white in reflected light in contrast to many concretions which are red-brown or, less frequently, black. Iron and manganese oxides impregnations were found to be responsible for these colours.

The s-matrix of embedded concretions is usually the same as the s-matrix of the remainder of the sample. Elongate skeleton grains within concretions, such as micas, tend to be oriented tangentially to the laminae, whereas in the surrounding s-matrix they usually have a random basic distribution. Concentric fractures which strongly resemble concentric shrinkage cracks (cf. Swineford et al., 1958) are recognizable in some concretions (Plate 40c). Cracks around the outer perimeter (circum-granular cracking) also are recognizable in some samples. Fractures showing no relationship to the fabric of the glaebules (Plate 40b) occur less frequently. These non-fabric selective fractures, together with borings and solutional vugs (Plate 42d, e), are features which post-date the formation and induration of glaebules.

The internal fabric of soft, white glaebules consists of hyphantic fibrous plasma which is recognizable in petrographic thin sections (Plate 44) and by SEM (Plate 45b, d). Needles of calcite, 0.1 - 2.0 microns wide and up to 100 microns long, form a loosely woven framework. Intercrystal porosity may exceed 70% (Plate 45b, d). These glaebules have an undifferentiated internal fabric.

Some nodules are composed of fine crystic plasma (Plate 45c). Microvoids within this plasma are commonly lined with scalenohedral calcite crystals 4 - 8 microns in length (Plate 45c). Glaebules with an internal concentric fabric are composed of alternating fine crystic plasma laminae, 5 - 10 microns in thickness, and concentrically arranged cracks lined with micron-sized calcite crystals (Plates 41b, d, f). These voids, lined or totally filled with calcite cement, correspond to shrinkage cracks when viewed in thin section (Plate 40).

Although most glaebules have a fine crystic or hyphantic fibrous plasmic fabric (Plates 40, 41, 42), a few glaebules were recorded during this study with coarse crystic plasmic fabrics (Plate 43c, d).

Mechanisms of formation

In situ formation of carbonate glaebules in soils has been discussed by many workers (Gile, 1961; Wilbert, 1962; Brewer, 1964; Gile *et al*., 1965, 1966; Ruellan, 1967; Blokhuis *et al*., 1968-1969; Seghal & Stoops, 1972; Siesser, 1973; Wieder & Yaalon, 1974; Bal, 1975a; Bal & Buursink, 1976). Brewer (1964, p.276) suggested that some glaebules formed *in situ* by accretion of soluble constituents which accumulated by diffusion or crystallization from solution in the numerous, very small voids in the s-matrix because of suitable local chemical conditions. Siesser (1973) suggested that calcrete oöids from South Africa formed by a diagenetic dissolution-precipitation process. Wieder & Yaalon (1974), after studying orthic nodules in a loessial serozem from the northern Negev, Israel, concluded that the nodules form from gradual precipitation of carbonate in microvoids of the s-matrix. As a result of gradual calcite precipitation, non-carbonate clay was concentrated at the fringes or expelled from the nodules.

Boulaine (1966) suggested that hard nodules form as a result of carbonate precipitation around a privileged point, namely a pore or the meeting point of several pores. It is interesting to note that Boulaine mentioned that such pores are common in the vicinity of roots and that some pores result from displacement of such roots. Similar observations have been made during this study and are discussed elsewhere (p. 79).

Wilbert (1962) suggested that hard nodules could form in any cavity in the soil. However, Blokhuis *et al.*, (1968-1969) found discrete, hard nodules embedded in, but unrelated to, the soil mass. From observations of their material, they were unable to establish whether their nodules formed *in situ* or were transported to their present position.

After studying *in situ* carbonate nodules formed in a calcareous loess from North Afghanistan, Bal & Buursink (1976) suggested that formation may start with an accumulation of lublinite (needle fibre calcite in a soil). Such diffuse, loosely packed accumulations form soft, white glaebules which may change into firm glaebules following precipitation of calcite within intercrystal voids between and on calcite needles. The fine crystic calcite plasma of the glaebules shown in Plate 45a may represent cement-filled areas of needle fibre calcite, or the needles themselves may have recrystallized to form a fine crystic calcite plasmic fabric. Thus, Plates 44 and 45b, which illustrate soft nodules, may represent an early stage of glaebular formation, whereas Plate 45a, which illustrates hard glaebules, may represent a later stage of glaebular development. This scheme of development is shown diagrammatically in Fig. 10, p.116). Such an evolutionary sequence was assumed by Wilbert (1962). He considered that hard glaebules formed *in situ* from soft, powdery forms.

Thus far, the precipitation of calcite in microvoids within the s-matrix or within root channels is one mechanism to account for the formation of glaebules. From the above comments, it is evident that many workers believe that this mechanism is an important one. However, before accepting this without question, it is worth examining other possible processes which may produce morphologically similar structures.

Coloured diffusion bands, known as Liesegang rings, form when an electrolyte is allowed to diffuse into a gel (Krauskopf, 1967). Although the processes involved in the formation of Liesegang rings are not entirely understood, slow movement of calcium ions and a depletion of carbonate ions in some parts of the gel would lead to supersaturation in other parts. As calcium carbonate is precipitated on a nucleus, a concentration gradient is established. Calcium and carbonate ions move toward areas where precipitation has lowered the concentration of such ions within the gel. Thus, the glaebules grow in size by an amount determined by the rate of supply and rate of precipitation of calcium carbonate. However, the microporosity of glaebules, as seen by SEM (Plates 41c, e, 45a-d), does not favour an origin akin to Liesegang ring formation for the carbonate glaebules discussed here.

Mechanical accretion, either of colloidal particles or of clastic particles, or both, is a further possible mechanism which may lead to concentrations of carbonate plasma. Glaebules, with or without a visible nucleus, commonly contain skeleton grains arranged concentrically within the laminae (Plate 40c). This arrangement may have resulted from mechanical accretion from a suspension or from rearrangement of skeleton grains within the s-matrix without significant transport.

In his discussion on glaebular textures in terrestial sediments from Aldabra, Braithwaite (1975) considered that the general appearance of concentric bodies and the inclusion of 'foreign' bioclasts and other grains were sufficient to suggest a purely mechanical accretion of clastic particles for the formation of his glaebules. However, mechanical accretion, by itself, does not necessarily form structures with concentric fabrics and does not account for the microporosity of glaebules since the spaces are not simple packing voids. Braithwaite (1975) overcame this problem by accepting the widely held view that concentric glaebules result from a climatically controlled seasonal alteration of wetting and drying (Swineford et al., 1958; Brewer, 1964; Reeves, 1970). Brewer (1964, p.278) suggested that thin, distinct laminae indicated formation in waves during alternating wet and dry periods with desiccation following formation of each lamina. Swineford et al., (1958) suggested that a generally arid climate with occasional wet periods favoured the formation of caliche pisolites in a seasonal climate. Thus, accretion may take place, by mechanical or chemical processes or both, within cracks caused by desiccation. It is considered likely that both processes have operated to form glaebules examined in this study.

The fundamental question to raise, if wetting and drying is accepted as a likely mechanism to account for concentric laminae, is - what is actually expanding? It cannot be pure calcite since it is anhydrous; other constituents must be present. Montmorillonitic clays absorb water between their layer lattices and swell during wetting. Such clays may be responsible for the formation of concentric cracks around nuclei during periods of drying. Desiccation of organic matter, disseminated or concentrated in the s-matrix, also may create shrinkage cracks. Both montmorillonitic clays and unidentifiable organic matter have been detected in many glaebular-rich samples studied here. However, the quantities of such constituents are low, generally less than 2% by weight in total for a given sample. Whether this is sufficient to cause the necessary volumetric changes is unknown.

Chemical accretion by movement of ions in solution and precipitation within voids is the most adequate explanation to account for the formation of glaebules. As a tentative proposal, I suggest that the size of voids is a controlling or contributory factor which determines whether glaebules have a concentric or undifferentiated internal fabric. Precipitation of calcite needles, having a hyphantic fibrous plasmic fabric, will tend to form loose aggregates and eventually undifferentiated glaebules. The maximum size of the calcite needles and the resulting glaebules themselves will be governed by the size of the containing voids, whereas the sizes of glaebules formed by precipitation of micron-sized calcite crystals within concentric shrinkage cracks will depend on the amount, frequency and duration of wetting and drying cycles.

Additional evidence to help interpret mechanisms of formation may be found in the distinctness of boundaries around and within glaebules. Drosnoff & Nikiforoff (1940), in their discussion of iron-manganese concretions in Dayton soils from Oregon, noted that accretionary glaebules with sharp external boundaries commonly occurred in A_2 horizons which were subject to periodic desiccation, while those in lower horizons, which were not affected by wetting and drying to the same extent, tended to have diffuse boundaries. Brewer (1964) suggested that sharp boundaries may be due to irreversible chemical desiccation, while diffuse boundaries may be due simply to the absence of this process. On the other hand, sharp boundaries may indicate movement, with or without transport (Blokhuis _et al._, 1968-1969; Wieder & Yaalon, 1974).

This study does not provide a single, all embracing theory to account for the formation of glaebules in calcretes. It is more likely, because of the complexity of recognizable textures which have been revealed by optical and scanning electron microscopy, that several possible mechanisms as outlined above have operated concurrently or sequentially to produce glaebules.

Cutans*

Plasma concentrations or plasma separations associated spatially with natural surfaces within the soil material are known as cutans (Brewer, 1964). They have been designated 'clay skins' or 'tonhautchen' by some workers but Brewer pointed out the inadequacy of these terms. Brewer defined a cutan as "a modification of the texture, structure, or fabric at natural surfaces in soil materials due to the concentration of particular soil constituents or _in situ_ modification of the plasma."

Brewer recognized several groups of cutans, distinguishable by the characteristics of the surfaces affected, mineralogy of the cutanic material and internal fabric of the cutans. Cutans are, by definition, pedological features and are, thus, products of soil-forming processes. While many pedological features such as glaebules, faecal pellets and animal burrows are not uncommon in sedimentary rocks, cutans are thought to be exclusive of soils (Teruggi & Andreis, 1971).

Several types of cutans are common in calcrete deposits. They can

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* Latin _cutis_ = a coating, rind

be divided conveniently into two groups, grain cutans and void cutans. Grain cutans may be free grain cutans or embedded grain cutans. They have been termed coated particles by some workers (e.g. James, 1972) but this nomenclature camouflages their pedological significance. Grain cutans with thick coats (greater than the the diameter of the coated grain) grade into glaebules.

Most cutans in calcrete deposits are composed of calcite. In a few of my samples, void cutans of ferric-rich, layer lattice minerals also were recognized (Plate 45e). These void cutans have a planar internal fabric consisting of plate-shaped, micron-sized grains lying parallel to the void wall. Their origin may have resulted from illuviation, that is, by movement of argillaceous material in suspension followed by subsequent deposition on the wall of voids. Brewer has termed cutans composed of non-carbonate clay minerals as argillans and those composed of calcium carbonate as calcitans. Calcitans may have formed as a result of illuviation or diffusion. It is possible that some free grain cutans and void cutans formed by deposition of suspended particles on free surfaces. However, embedded grain calcitans, and probably most calcitans associated with void walls, are more likely to have formed by deposition of calcium carbonate from solution or by diffusion of calcium carbonate through the s-matrix and concentration at a natural surface.

Palygorskans (cutans composed of the fibrous clay mineral, palygorskite) were recognized as grain coatings by SEM (Plate 45f). Because of the hyphantic arrangement of fine (500 - 1,000 Å wide) fibres, it is considered highly unlikely that these cutans are mechanical deposits. They are better interpreted as authigenic fibrous clay precipitates from magnesium-rich pore solutions. It is interesting to note that the coated grain is a dolomite rhomb; partial dissolution of dolomite provides a potential source of magnesium for the formation of palygorskite (Weaver & Beck, 1977; N.L.Watts, Shell, Rijswijk, pers. commun.).

BIOGENETIC STRUCTURES

Rhizoliths

Introduction

Terminology, classification and macromorphological features of rhizoliths have been discussed elsewhere (p. 90). Of the five commonest types of rhizoliths, attention will be confined in this section to rhizocretions and root petrifactions. Rhizocretions and root petrifactions are the most important types of rhizoliths recorded in this study. Apart from several notable exceptions (Kindle, 1923, 1925; Ruth, 1927; Johnson, 1967; Calvet et al., 1975), rhizocretions and root petrifactions have not received the attention that they deserve. This section provides further documentation and presents new information on the morphology and genesis of these biogenetic structures.

Rhizocretions

The term rhizocretion is used here to describe pedodiagenetic accumulations of mineral matter around roots. Accumulation, usually accompanied by cementation, may occur during life or after death of plant roots. Rhizocretions are abundant in Pleistocene aeolianites of the Mediterranean coastal regions (Amiel, 1975; Calvet et al., 1975; this study). They have been reported within aeolianites from other parts of the world, including Yucatán, Mexico (Ward, 1975), California (Johnson, 1967), Barbados (Harrison, 1977), Florida (Northrop, 1890; Perkins, 1977) and Australia (Fairbridge & Teichert, 1953; Read, 1974). My field observations reveal that rhizocretions also occur in other host materials. Some Recent river gravels and silts (calcareous and non-calcareous) in south eastern Spain contain isolated, vertically elongate rhizocretions (Plate 19d). Calcrete profiles developed within igneous and metamorphic rocks also contain rhizocretions (Plates 3,4).

Rhizocretions (and root petrifactions) examined in this study are composed dominantly of low magnesian calcite although silicified roots have been recorded (Plate 34e, f). Other workers have reported rhizocretions containing dolomite (Sherman & Ikawa, 1958), gibbsite (Valeton, 1971) and gypsum (Calvet et al., 1975).

Whereas modern rhizocretions can be recognized easily in the field, especially when the surrounding, less well consolidated materials have been removed by erosion and root materials are still present, they are more difficult to recognize in older rocks which have undergone a long history of diagenesis. To help identification of rhizocretions in the geological record, the petrographic characteristics of modern rhizocretions have been studied in detail to document their fabrics and textures.

Description - - Plate 46a shows a fibrous root system surrounded by a cemented sheath of aeolianite material. The aeolianite host material is capped by a micritic crust. Plate 10a is a general view of the surrounding area. Rhizoliths are abundant in this material which, at first glance, is surprising since there are no visible signs of vegetation on the land surface (Plate 10a). Yet the rhizocretion shown in Plate 46a contains intact or only partially decayed roots (Plate 46b-f). Thus, the aerial parts of former dune vegetation have decomposed or have been eroded, whereas their subterranean root systems still remain.

Plate 46b is a transverse section through the rhizocretion shown in Plate 46a. The calcareous sheath or envelope (cf. Calvet et al., 1975) is about 1 mm thick and consists of micritized and micrite-cemented carbonate grains. Fibrous roots, together with weakly cemented centimicron-sized grains of forams, molluscs, coralline algae and lithoclasts, occupy the central or axial part of the rhizocretion. The inner wall of the calcareous sheath in Plate 46b is irregular in form, the embayments marking the positions of earlier roots which have now decayed. The younger roots, which are still preserved, have occupied root moulds of earlier roots.

Transverse sections through roots (Plate 46c, d, e) show some interesting features. The cylinder shown in Plate 46d is not a typical feature of vascular plants. Dr. J. C. Collins (personal commun. Univ. of Liverpool) suggests that it may be a heterotrophic alga which lived within the living root symbiotically or parasitically, or infested the dead root as a saprophyte. The centre of this root consists of partially decomposed xylem vessels. The dark, clotted, amorphous material of the outer root cortex (Plate 46d, f), which contains lignin (determined by staining following Gurr, 1965; see Appendix for procedure), is partially humified. Plate 46f shows sloughed off, humified root cortex debris and root hairs. Plate 46e is a section through a root meristem. Differentiation of the root is slight here; the three larger groups of cells (lighter areas) are initial stages of differentiation. The triradiate symmetry, which is just discernible in Plate 46e, is better developed further up the root (not illustrated).

SEM examination of the fibrous roots shown in Plate 46 indicates that saprophytic micro-organisms are present in the humified, cortical layers (Plate 55). Hyphae and spore chains of the actinomycete Streptomyces (identified by Dr. S. T. Williams, Univ. of Liverpool) are abundant on surfaces of dead roots encased in aeolianite (Plate 55c-f).

In Plates 47 and 48, rhizocretions from Pleistocene aeolianites, Ibiza, show further interesting features. Original root materials are absent from both these samples. However, evidence of the former existence of roots is indicated by root moulds (Plate 47a, b, d) and root petrifactions (Plate 48e, f). The rhizoliths shown in Plates 47 and 48 have similar fabrics and textures to calcrete profiles. The unaltered host material is an aeolianite or biosparite (Plate 47c). The transitional horizon of calcrete profiles is comparable with the calcareous sheaths of rhizoliths which consist of micritized and corroded grains, floating in a cryptocrystalline matrix (Plates 47e, 48a, c). The chalky zone consists of micron-sized calcite grains and rare centimicron-sized grains of corroded bioclasts (Plate 48d). The sheet calcrete and hardpan zones share common features with the central parts of rhizocretions, including root moulds (Plates 46b, d, 48e), alveolar textures (Plates 47d, 48e), clotted textures and rhizoliths (Plate 48e, f). The clots in Plate 48e are believed to be coalesced calcified faecal pellets of soil mesofauna.

Transitional stages between the calcareous sheath and chalky interior of rhizocretions show a gradual obliteration of primary textures and a marked change from a fine crystic to a coarse crystic plasmic fabric (Plates 47e, 48b). Some samples show irregular channels extending into calcareous sheaths from the central axial parts of rhizocretions (Plate 47e, f). That these calcite-filled channels were definitely voids at one time, is indicated by a first generation isopachous fringe cement lining the walls of these channels (Plate 47f). Thus, apart from a difference of scale, the fabrics and textures in a calcrete profile from top to base are similar to the zonal changes from the central part of the rhizocretion outwards into unaltered host material. This point has been made by Calvet *et al.*, (1975); they noted that a marked lithological and genetic similarity existed between the vertical caliche profile and the transverse section of a rhizocretion.

Root petrifactions

The American Geological Institute (1972) defined petrifaction as "a process of fossilization whereby organic matter is converted into a stony substance by the infiltration of water containing dissolved inorganic matter (e.g. calcium carbonate, silica) which replaces the original organic materials, sometimes retaining the original structure." For the purposes of this section, the term *petrifaction* will be extended here to include mineral precipitation within voids of organic structures and deposition of minerals on (encrustation) and within (impregnation) living and dead tissues. Thus, root petrifaction is a process which involves replacement, impregnation, encrustation and void-filling of organic matter by mineral matter without total loss of root anatomical features. In calcrete deposits, calcite is the dominant mineral which preserves plant morphology.

Description - - Plate 49a shows collapsed cells of a root cortex. The sample was collected from the transitional horizon of a Pleistocene calcrete developed in an alluvial fan from north-eastern Spain (locality T.3). Cell contents of the root have decomposed but the cell walls, which have been attacked by saprophytic fungi, are still present. Plate 49b is part of a root from the same sample but showing a different form of preservation. Here, lignified ground tissue of the outer part of the cortex and epidermis have remained intact, whereas the cell walls have decayed. The state of root preservation at the time of petrifaction determines the morphology of the resulting rhizolith. In Plate 49c-f, the cortical cells have been replaced by calcite. Viewed by light and scanning electron microscopy, these rhizoliths consist of isodiametric calcite crystals, 20 - 30 microns in diameter. The vascular system in these examples has not been preserved (Plate 49f). Similar forms of preservation are shown in Plate 50e, f. Oblique sections show central voids which mark the positions of former vascular systems. The cortex and dermal layers have been replaced by calcite. Root hairs, which are extensions of epidermal cells, also have been preserved in this sample (Plate 50f).

Petrifaction of cortical cells by calcite is a common, but by no means the commonest, form of preservation. Petrification of cell walls is of greater importance in samples studied here (Plates 50a-d, 51, 52, 53). In Plate 50a and b, xylem vessels of a ?Recent root within a Pleistocene aeolianite have not decayed completely, whereas the cortex has been sloughed off. In Plate 50c and d, the morphology of elongate xylem vessels has been preserved by submicron-sized calcite crystals. It is impossible to determine whether the cell walls have been replaced by calcite or whether the cementing substance between juxtaposed cell walls (middle lamella) has been petrified. Examination of other samples in differing states of preservation provides information which suggests that the middle lamella between adjacent cells acts as a template for calcification (Plates 51, 52, 53). These samples are discussed below.

In Plate 51, the rhizolith consists of a petrified epidermis. Root hairs radiate outwards from the root (Plate 51a). Calcified root hairs occur as tubes in the surrounding s-matrix, giving a vermicular or spaghetti-like texture when viewed in thin section (Plate 52e, f). Closer inspection of the rhizolith shown in Plate 51a reveals that micron-sized plates of calcite are present in the position of the middle lamella between adjacent cells (Plate 51c, d). Similar fabrics have been found in other rhizoliths (Plate 53). The rhizolith of Plate 53a is composed of calcified parenchymatous cells and xylem vessels which have been preserved in plate-shaped and rhombic micrite (Plate 53b-f). The protoplast or cell contents have not been calcified in this sample. The cells are now voids (Plate 53d, e) or partially filled with needle fibres of calcite (Plate 53c). Thus, it appears that the middle lamella, originally composed of or containing calcium pectate, is a preferential site for calcification. Thus, the cell morphology of the roots are maintained.

In thin section, calcite impregnated or replaced middle lamellae replicate the cellular pattern of root cells (Plate 52a). In Plate 52b and c, root anatomy has not been preserved in detail but the concentric layering of cells can be discerned. This form of preservation is especially characteristic of rhizoliths which occur within the sheet calcrete horizon.

SEM examination of what was considered initially as a typical rhizocretion, that is, accumulation and cementation of calcium carbonate around a root, reveals further interesting features (Plate 54). The root itself is partially decomposed; the epidermis has been sloughed off or has decayed, thus revealing cortical cells (Plate 54a-c). Some walls show a wrinkling pattern (Plate 54a, b) which may be simply a result of desiccation. On the other hand, it is known that some fungi live symbiotically within cells or cell walls (p. 211). The vermicular pattern in Plate 54b may be a result of fungal penetration. While the cell walls have collapsed, the chitinous fungal hyphae which lived within the cell walls have maintained their form. Thus, the relief of the cell walls shown in Plate 54a and b may be the product of fungal infestation. During life, the root-fungus association would have formed a composite structure known as an ectendomycorrhiza (p. 212).

Additional features recorded from the decayed root illustrated in Plate 54 include ellipsoid-shaped structures, 0.5 microns long attached to cell walls (Plate 54c, d) and crystals embedded in and nucleated on the cell wall material (Plate 54e, f). Because of the fine scale and small quantities, these crystals have not been determined mineralogically. Dr. J. H. Schroeder (personal commun. Oceanographic Institute, Sudan) expresses doubt regarding a calcite mineralogy. As a tentative proposal, I offer two alternative explanations. Firstly, the crystals are ?calcium oxalate which precipitated within the plant during its life and, secondly, the ellipsoidal structures (Plate 54c, d) are rod bacteria which acted as passive templates for subsequent precipitation of the micron-sized crystals shown in Plate 54e and f. Without the facility of EDAX, the mineralogy of these crystals remains unresolved. Nevertheless, this sample illustrates a likely path of calcification, one of inorganic precipitation of minerals on and within decomposing organic templates. The resulting form of preservation will reflect the relative resistance to decay of these templates as opposed to the less stable components of the root.

The discovery of these crystals in this decayed root means that it cannot be termed simply a rhizocretion as originally designated; incipient petrifaction has taken place. For such a reason I use the term 'rhizolith'.

Genesis of rhizoliths

As an introductory statement on the occurrence of rhizoliths in calcrete profiles, it is reiterated from earlier discussions that roots of higher plants are partly or totally responsible for numerous and characteristic features of calcrete deposits studied here. Apart from rhizoliths themselves, roots are primarily responsible for the formation of vertically elongate glaebules (p.87), sheet calcrete layers (p.79), brecciation textures and the formation of tepee structures (p. 97), brittle fracture, channel and mouldic porosity (p.131) and alveolar textures (p. 138). Roots, together with symbiotic fungi, are also responsible for the hitherto enigmatic structure *Microcodium* (p. 194).

Calcretization involves modification or obliteration of precursor fabrics, textures and structures in a given host material and the production of new fabrics, textures and structures. Roots modify and destroy rocks. Roots also become calcified. Thus, roots are contributors to the pedodiagenetic processes of calcretization.

The role of plants in biological weathering is well known (Keller & Frederickson, 1952). Plant roots accelerate weathering of rocks by exchanging H^+ ions from the roots for Ca^{2+}, Mg^{2+}, K^+, etc. ions in the rocks. Keller & Frederickson (1952) suggested that the surface chemistry of a plant root could be explained by the Debye-Hückel double layer system. The root and adhering water film is surrounded by an ionic double layer of which the root has a strong negative charge which is balanced by a surrounding area of positive ions (typically H^+). Thus, the high concentration of H^+ ions in the diffuse ionic double layer around roots will accelerate weathering of surrounding minerals if the released metal cations are removed from the system.

The above outlined mechanisms of biological weathering may account for root borings and the breakdown of host materials, but the production of cemented cylinders of calcium carbonate around roots to form rhizocretions and the calcification of root tissues to form root petrifactions require further explanation. Ca^{2+} ions are not removed from the system in environments conducive to the formation of rhizoliths. On the contrary, calcium carbonate is the stable mineral phase in such environments. The problem is to explain why this should be so.

Gray and Williams (1971) have questioned the assumption that roots increase acidity in the surrounding soil as a result of excretion of CO_2 and H^+ ions. Some roots take up more anions than cations. Such roots maintain electrical neutrality by passing out HCO_3^- ions rather than H^+ ions. In so doing, the pH of the surrounding soil is raised, rather than lowered. Plant uptake of water during transpiration and carbon dioxide loss during photosynthesis may trigger precipitation of calcium carbonate around roots, thus leading to the formation of rhizocretions.

Johnson (1967) listed further possible ways of forming rhizocretions. He stated (p. 154): "Root sheaths apparently form in one or more of five biochemical ways, dependent upon (1) the presence of organic acids exuded by living plant roots; (2) symbiotic relations between roots and certain soil bacteria; (3) symbiotic relations between roots and certain soil fungi; (4) the presence of some blue-green soil algae which have calcium carbonate-precipitating bacteria housed in their slime sheaths; (5) calcium exclusion properties of some plants which promote the precipitation of calcium carbonate outside the root." Although Johnson admitted the possibility that the formation of rhizocretions may result from a combination of these processes, he favoured the first one.

Calvet _et al._, (1975) suggested that rhizocretions, occurring in Pleistocene aeolianites from Mallorca formed by (1) progressive root penetration, producing a closer packing of sand grains around the roots; (2) formation of a calcareous envelope (sheath), resulting mainly from the activity of micro-organisms, the effects of organic acids and evapotranspiration; and (3) centripetal filling of chalky material following death and decay of the root.

Kindle (1925, p.744) suggested that the presence of certain bacteria, or of fungi, on living roots may constitute the initial factor in the development of root concretions. That micro-organisms are present in and around roots has been documented in this study (Plates 55, 56) and elsewhere (Burges, 1958; Alexander, 1961; Gray & Williams, 1971; Russell, 1973). Whether they play an active role in, or are incidental to, the formation of rhizoliths is another question. The suggestions of Kindle (1925), Johnson (1967) and Calvet et al., (1975) are reasonable but not readily amenable to substantiation. I have offered further suggestions which also involve the activities of rhizosphere microflora (p.220) but these proposals, likewise, cannot be substantiated at the present time. Clearly more information is necessary before definite conclusions can be made.

As a concluding remark, it seems to be more than coincidental that sites for calcification in root petrifactions correspond to naturally occurring calcium-rich layers within plant tissues, notably the middle lamella and the outer layer of calcium pectate in root hairs. A substrate (template) control appears to govern the form of preservation in samples examined in this study.

Calcified Filaments

Introduction

Organic filaments are common in Quaternary calcretes from the western Mediterranean. Calcification of a filament produces a tubiform fossil (cf. Riding, 1977) or a solid rod, depending on the type of preservation and timing of calcification. Calcified filaments observed in samples collected during this study are described (below) in terms of their sizes, shapes, mode of branching, presence or absence of a central hollow and contained or trapped organic matter within or between calcite crystals. The calcite, itself, is described in terms of its fabric, mineralogy and composition. Additional information, gained by decalcification of calcified filaments and examination of the insoluble residues by optical microscopy, also is documented.

Calcified filaments are recognizable in calcrete samples with a hand lens or under a binocular microscope using reflected light. They are recognizable also in petrographic thin sections (Plates 28c, 62e, f) but, because of the fineness of scale (micron-sized), are best studied by SEM (Plates 57 - 62).

Possible filamentous templates for calcification in this study include fungal and actinomycete hyphae, algal filaments and root hairs of vascular plants. In order to better understand the processes of calcification, uncalcified organic filaments as well as calcified filaments from Recent calcretes were studied by optical and scanning electron microscopy. This approach facilitated morphological comparisons among the various forms of filaments and provided criteria for determining the origin of the possible organic templates.

Terminology and classification

The term calcification is used here in a general way to include encrustation on, impregnation within and replacement of, organic constituents by calcium carbonate. Arnott & Pautard (1970) have provided a useful review on calcification in plants. Figure 14a, p.172, taken from the work of Arnott & Pautard (1970), summarizes the location of calcium carbonate in plant cells. Although mucilaginous sheaths are not present around all plant cells, this diagram serves as a useful framework for a general discussion on calcification.

The term filament is used here to describe any tubular or rod-shaped organic structure which lacks calcification. It follows that a calcified filament is, in agreement with the usage of Kahle (1977), a biogenetic carbonate structure wherein $CaCO_3$ has replaced the filament or has been precipitated on (encrustation) or within (impregnation) the filament.

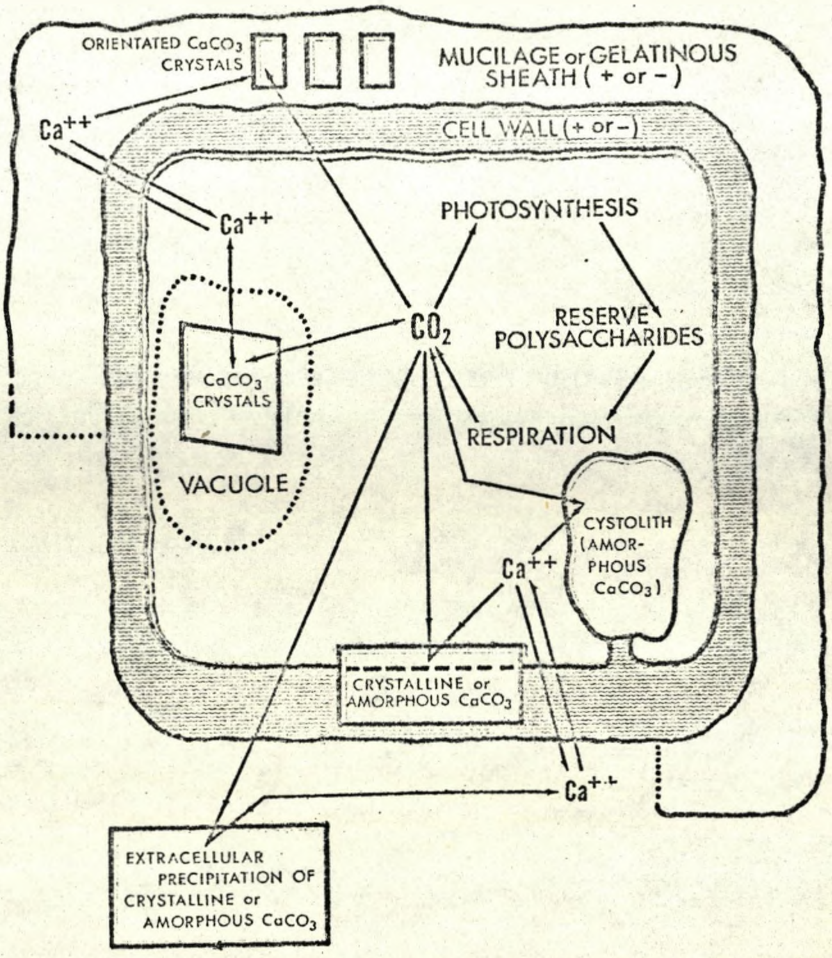
The relation between the filament and the s-matrix can be used to define three basic groups of filaments, epiliths, endoliths and chasmoliths. An epilith is located on the surface of the substrate (Golubić, 1969). An endolith is a compound structure composed of a filament found in a bore of its own making (adapted from Lukas, 1973). A chasmolith is a filament within a pore space not created by the organisms responsible for the filament (adapted from Lukas, 1973). Numerous workers (e.g. Alexandersson, 1972; Schroeder, 1972; Golubić *et al*., 1975; Kahle, 1977; Kobluk & Risk, 1977) have pointed out that a single filament can be epilithic, endolithic and chasmolithic along its entire length.

Templates for calcification

Calcium in plants - - Arnott & Pautard (1970) stated that a substantial proportion of calcium in a plant is concentrated in the cell wall. Figure 14b, p.172, is a diagrammatic representation of the calcium distribution in a typical plant cell wall as seen by Arnott & Pautard (1970).

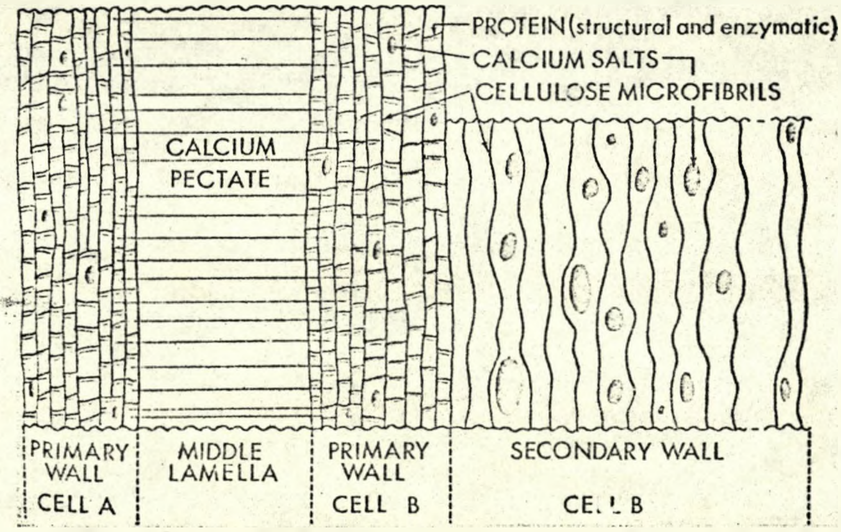
Plant cells are enclosed by a solid structure composed dominantly of layers of cellulose with different quantities of hemicelluloses, lignin, suberin, cutin and pectic substances (Fahn, 1974). The cell wall consists of a primary wall composed mainly of cellulose and usually a secondary wall which often consists of three layers composed of cellulose and other polysaccharides (Fahn, 1974; Cutter, 1969). Juxtaposed cell walls are joined or cemented together by the middle lamella which is composed of calcium pectate (but see below).

Figure 14a. CALCIUM CARBONATE IN PLANTS



Diagrammatic view of calcium carbonate in plants. Both unicellular and multicellular plants are represented.

Figure 14b.CALCIUM IN THE CELL WALL



Calcium distribution in the cell wall of plants. Many components (e.g., hemicelluloses) are not illustrated in order to show a generalized picture of calcium.

(From Arnott & Pautard, 1970)

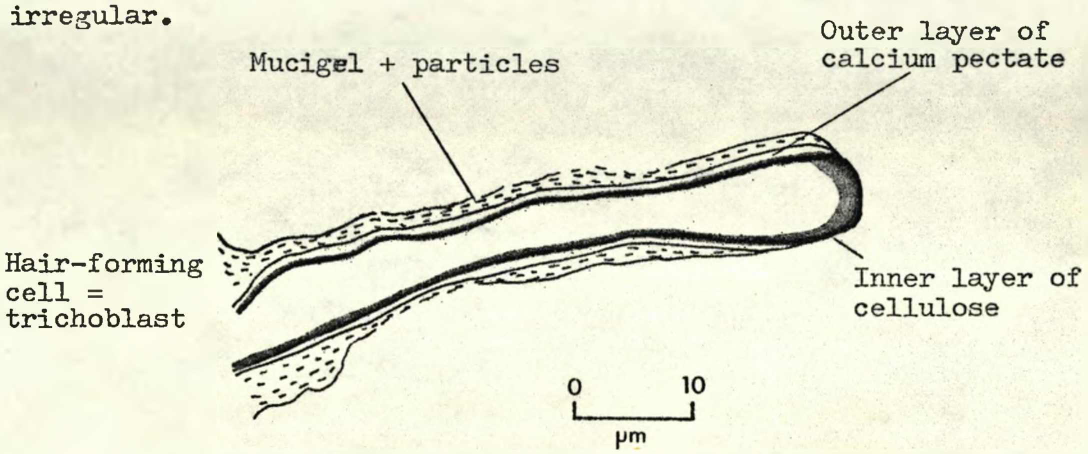
Bailey (1957) found that the cell wall is built up of a system of microscopic threads (submicron-sized), known as fibrils. It has been shown that the wall consists of two continuous interpenetrating systems, one of which consists of cellulose fibrils and the other which consists of a continuous system of microcapillary spaces (Lopez Gonzalez & Jenny, 1958). These spaces may be filled with lignin, suberin, cutin, pectic substances and other organic materials, and even mineral crystals.

The problem of the state of calcium in the cell wall is far from resolved (Arnott & Pautard, 1970). Some calcium appears to be bound as calcium pectate but, as pointed out by Arnott & Pautard, there is no conclusive proof that this substance alone is essential for the integrity of the cell wall. Although it has long been accepted that calcium pectate is the principal complex present in the middle lamella, in recent years some doubts have been raised concerning the precise organic association of the calcium, both in the process of growth and in the nature of the salt.

In addition to calcium pectate, other calcium salts occur in cell walls and within cells. Calcium oxalate has been detected in many plant cells (Cutter, 1969). Calcium carbonate has been claimed as a widespread phenomenon in the secondary walls of deciduous angiosperms (Pobeguin, 1954a). Other plants known to contain calcium carbonate in their cells, and perhaps more familiar to carbonate sedimentologists and palaeontologists, are the calcareous algae (Wray, 1977).

Root hairs - - Root hairs are tubular extensions of epidermal cells (Fahn, 1974). Each root hair is merely part of one epidermal cell. Hair-producing cells are known as trichoblasts. The root-forming cell is made up of two parts, an inner layer of axially oriented cellulose microfibrils and an outer layer of calcium pectate (Fig.15,p.174).

Dittmer (1949) measured diameters and lengths of root hairs in 37 species. He found that within any one species the size was relatively constant but for all species there was a range from 5 to 17 microns in diameter and 80 to 1500 microns in length. Dittmer (*op.cit.*) noted that the morphology of most hairs were straight, uniform in thickness and non-septate. Only a few were found to be crooked and irregular.



(After Greaves & Darbyshire, 1972)

Figure 15. Diagrammatic sketch of longitudinal section through a root hair.

According to Cormack (1949), root hair morphology is related to the amount of calcium in the soil. Long, straight and exceedingly narrow hairs form when calcium is plentiful. When calcium is not readily available, the hairs become inflated, bulbous at the base and branched. Cormack (*op.cit.*) reported that, in general, root hairs are short-lived, collapsing and withering after a few days, but are replaced continually by new plant tissue. He also noted that the formation of root hairs is markedly dependent on external conditions which modify the hardening of the epidermal cells, the hardening resulting from the gradual incorporation of calcium in the outer wall of the growing hair. Cormack _et al_., (1963), by tracing labelled calcium by radioautography, suggested that gradual calcification is essential for the normal growth and formation of root hairs.

Algal filaments - - In his discussion of calcified _Plectonema_ from Aldabra as a Recent representative of the tubiform fossil _Girvanella_, Riding (1977) distinguished between calcification of the sheath and massive encrustation of the filament. Precipitation of $CaCO_3$ within the mucilaginous sheath is considered to be biochemically controlled, whereas encrustation on the sheaths is viewed as the result of physicochemical control. Following decay of the alga, the resulting cavity may be left unfilled or filled with calcite crystals. Schroeder (1972) illustrates excellent examples of calcite-encrusted filaments with solid cores from Recent Bermuda reefs. The sites of $CaCO_3$ deposition in relation to the cell wall and sheath determine the size and morphology of the algal filament. Figure 16, p. 176 illustrates diagrammatically the forms of biogenetic carbonate structures that result from calcification of filaments, with and without an extracellular mucilaginous sheath.

Actinomycete and fungal hyphae - - Elongate, strand-like cells which are joined together form a thread of cells or hypha (Moore-Landecker, 1972). Cell walls of fungi and actinomycetes consist of microfibrils of chitin or cellulose distributed within an amorphous matrix. Most fungi have chitinous walls but, occasionally, both chitin and cellulose may occur together. Cellulose and chitin are complex polysaccharides whose structures are not completely known (Moore-Landecker, 1972).

Criteria for the recognition of the origin of calcified filaments - - It is difficult to distinguish between calcified fungal hyphae,

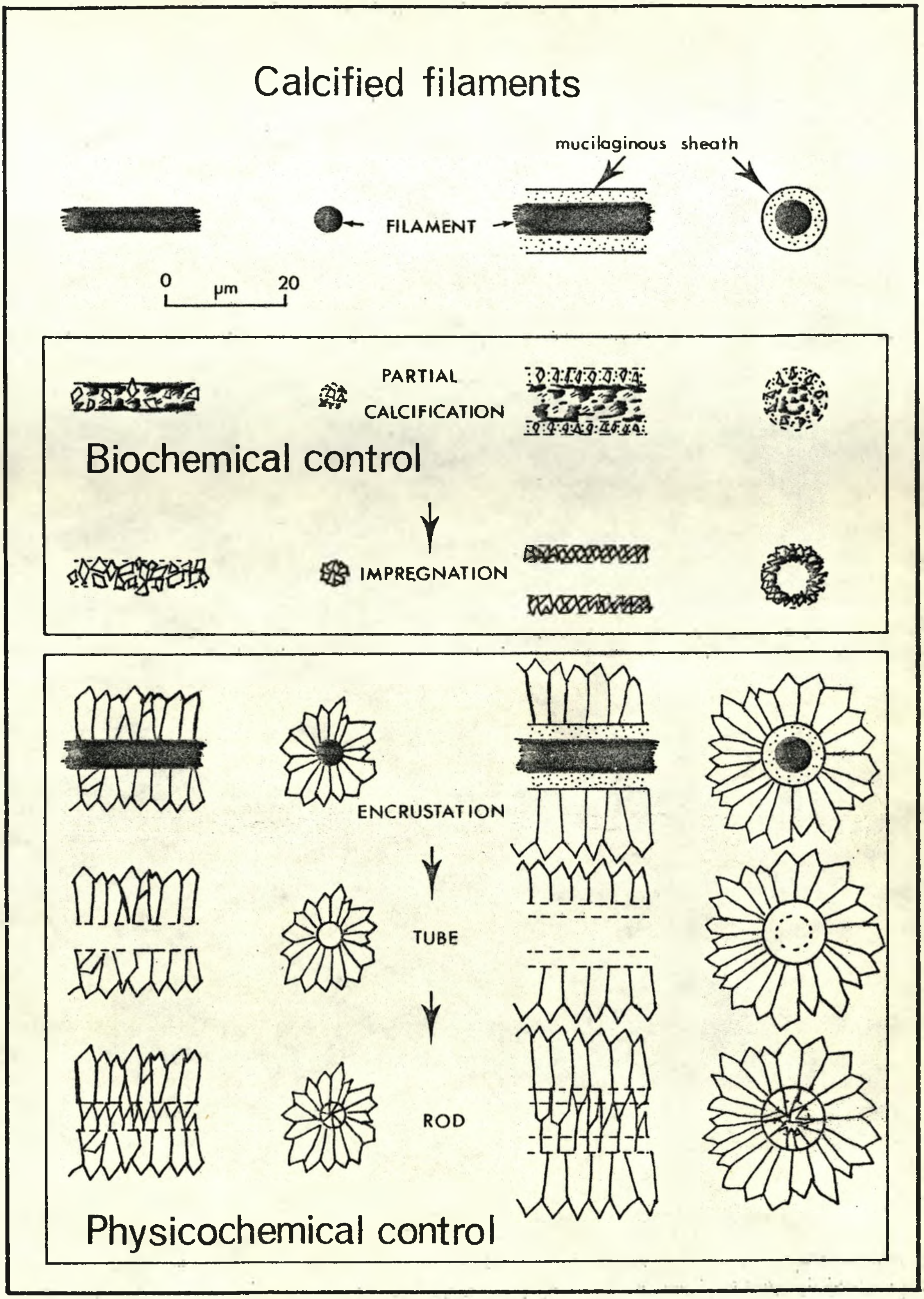


Figure 16. Diagrammatic representation of possible diagenetic pathways of calcified filaments.

actinomycete hyphae, algal filaments and root hairs when structural details of the cell walls have been lost. As a generalization, but subject to many exceptions, Table 8, p. 178 summarizes diagnostic features to help interpret the origin of calcified filaments. The listed criteria also help interpretation of microborings created by these organisms. Microborings are widespread through material examined in this study.

Present investigation

This study reveals that calcified filaments are abundant in Pleistocene and Recent calcretes throughout the western Mediterranean. Calcified filaments studied here show morphological and spatial differences which provide clues as to their origin. Some filaments are root hairs, others are fungal or actinomycete in origin. Definitely recognizable algal filaments have been recorded in this study but they are rare compared with fungal hyphae and root hairs. Calcified filaments are, thus, polygenetic in origin. The remainder of this section will examine these calcified filaments in detail.

Morphology - - Calcified filaments, up to 2 cm in length, were observed under a binocular microscope in fractured samples of semi-indurated and indurated calcrete. Most filaments in calcrete samples studied here are chasmolithic (Plates 57 - 61) but some can be seen to be both chasmolithic and endolithic (Plates 62a, d, 64a). Calcified filaments may be solid rods (Plates 57a, b, 58e, 61c, 64c-f) or tubes with hollow centres (Plates 57c, d, 58a, b, d, 59b, d, 62d). Tubiform calcified filaments have differing wall thicknesses (0.5 - 5 microns) but most have wall thicknesses of considerably less than the diameters of the central hollow cores (Plates 58b, d, 59b, d-f). The inner surface of the tubes are generally smooth (Plate 59b, d), whereas

TABLE 8 FILAMENTOUS TEMPLATES

	BLUE-GREEN AND GREEN ALGAE[1]	FUNGI[2]	ACTINOMYCETES[3]	ROOT HAIRS[4]	BACTERIA[3]
FILAMENT DIAMETER					
microns Average	8	2	0.5	10	0.5
Range	6-20 (green) 0.1-2 (blue-green)	0.5-20	0.1-2	5 - 17	0.1-10
VARIATION IN DIAMETER OF SINGLE FILAMENT	Variable	Constant	Constant	Constant	Constant
MODE OF BRANCHING	False ramification	Dichotomous branching	Dichotomous branching	Rare	-
ANGLE OF BRANCHING	Variable	60°-90°		-	-
SHAPE	Irregular	Straight	Straight Coiled	Straight Curved	Straight
ENVIRONMENT	Marine Freshwater Subaerial Light independent	Aerobic Light independent	Aerobic Light independent	Subaerial Aerobic Light independent	Aerobic Anaerobic Light independent

SOURCES : 1 Krumbein (pers. commun. Univ. of Oldenburg)
2 Bathurst (1975)
3 Russell (1973)
4 Dittmer (1949)

the outer surface has a rough topography determined largely by the fabric of the calcite crystals (Plates 57d-f. 58, 59, 61c).

Most calcified filaments are straight or gently curved (Plates 57-59). Branching patterns are not determined easily by SEM but, when recognized, show simple 'Y'-type (Plates 57c, d, 58d, 60e) or dichotomous branching patterns (Plate 61a).

Location of calcite in calcified filaments is variable. In a single sample, some filaments may be encrusted by calcite, some are impregnated with calcite while others are uncalcified completely (Plates 58c, 59a). This may reflect a specificity for $CaCO_3$ deposition on or within certain filaments or, and perhaps more likely, may reflect different ages of filaments. Uncalcified filaments may be relatively recent intruders in contrast to older, now calcified filaments.

Structure - - Calcified filaments are composed dominantly of micron-sized and submicron-sized low magnesian calcite crystals (mineralogy determined by microchemical staining and interpretation of crystal morphology as seen in SEM). Only two samples were found which contained petrified filaments with other mineralogies, dolomite and silica (p.188). Calcified filaments are composed of equant calcite rhombs, 1 - 2 microns in diameter (Plates 58b, f, 61c, 64c-f), micron-sized calcite crystals with platy habits (Plates 58a, 59b, 63d) or needles 1 - 2 microns long and less than 0.1 microns in width (Plate 57d-f). Decalcification of calcified filaments by acid digestion left insoluble residues which were mounted on glass slides and examined by optical microscopy. Thin sections containing calcified filaments also were decalcified and stained with Gentian Violet.

Unfortunately, insufficient structural details of the original organic constituents remained to allow identification.

It was found that SEM examination of untreated samples was the best method of obtaining information on the original organic template. SEM examination revealed that non-calcified filaments may be smooth (Plates 58c, 59a, 61a, b), warty (Plate 60a, b) or hairy (Plate 59c). Some filaments show partial or total collapse (Plates 60a, 61a, b), others have maintained their original shapes and surface ornaments (Plates 59a, c, 60a, b). Some, however, have decomposed, leaving behind only resistant components of their cell walls (Plates 60c-f; 64e-f).

Between the completely calcified and non-calcified end-members as outlined above, partially calcified filaments have been recognized (Plate 60c-f). These transitional stages of calcification provide valuable information regarding the processes and timing of calcification. Using information gained from SEM observations, the timing, rates, location and processes of calcification will now be discussed.

Calcification

Introduction - - In his discussion of carbonate construction and decomposition by epilithic and endolithic micro-organisms in salt and freshwater, Schneider (1977) reported (p. 249): "The physiologic processes, which lead to the precipitation of micritic calcite on algal filaments and fungal hyphae, are not yet known in detail." Similarly, in their review on calcification of plants, Arnott & Pautard (1970) reported (p. 431): "Most authorities agree that the carbonate arises by the interaction of carbonate, or bicarbonate, with calcium under alkaline conditions, but the process by which CO_2 is released or absorbed to achieve this end is obscure."

Although not stated explicitly, the above quoted comments refer to calcification of living plants. The questions to ask when examining calcified filaments are - when, where and how did the processes of calcification operate?

Timing and rates of calcification - - In general, calcified filaments studied here have constant diameters and cross-sectional shapes along their entire length (Plates 57a-d, 58, 59). A few may have bulbous terminations (Plate 57e) but the original morphology of the filaments are maintained. These observations indicate that calcification took place prior to collapse of the organic filaments. Hardening of root hairs results from incorporation of calcium within the calcium pectate layer whilst the hairs are still alive (Cormack, 1949; Cormack et al., 1963). Secretion of calcite crystals within the mucilaginous sheaths of non-calcareous blue-green algae is biochemically controlled (Riding, 1977) and, thus, takes place during the life-span of these algae. Organic microfibrils of partially decomposed cell walls are recognizable among calcite crystals in some calcified filaments (plates 57b, 60f, 64f). Admixtures of plant fibrillar material and calcite grains (Plate 60d, f) suggest that decomposition of organic material in cell walls and deposition of $CaCO_3$ in the voids created by organic decay occur simultaneously. Thus, calcification is, diagenetically, an early process which may take place during life, or during decay of the organism following its death.

Kobluk & Risk (1977) placed iceland spar (calcite) crystals, infested with the filamentous boring alga Ostreobium sp., in seawater. Within 25 days after the crystals were placed in the sea, filaments were observed to project from the substrate into the sea. Between 65 and 95 days the exposed filaments had become completely calcified by low magnesian calcite. They pointed out that submarine precipitation of calcite occurred only on and within dead filaments at a geologically very rapid rate. Before their work, the consensus of opinion maintained that the non-skeletogenic precipitation of carbonate required time of the order of years or decades (Alexandersson, 1972). The studies of Kobluk & Risk (1977) indicate that rates of calcification in shallow submarine tropical waters can be measured in days rather than years. Such rapid rates of calcification also may be applicable to calcification of filaments in calcrete profiles. As already noted, Cormack (1949) reported that root hairs are short-lived, collapsing and withering after a few days. Root hairs in calcrete samples studied here (Plate 63) have not collapsed, suggesting that rapid rates of calcification have prevented their collapse. The same reasoning can be applied to calcified fungal actinomycete and algal filaments; calcification took place before complete decay and breakdown of organic material. Thus, the gross morphology of the filaments has been preserved.

Location of $Ca\ CO_3$ with respect to cell walls - - Calcified filaments with hollow cores (Plates 57c, d, 58a, b, d, 59b, d, 62d) indicate that calcification of cell constituents or filling of vacuoles has not taken place. Nevertheless, the morphology of the filament is preserved by calcite encrustation or impregnation of cell walls prior to organic decay. Tubiform calcified filaments may be later filled with calcite in the void of the original filament. Thus, solid rods may be accounted for by calcite precipitation within voids created after decay of the encrusted organic template. However, calcification of cells cannot be discounted but, because of the ultramicroscopic (TEM) scales of observation required to examine this possibility, cannot be demonstrated in this study.

Because of the structural control of cell wall constituents, it would be reasonable to expect to find calcite oriented in an organized manner determined by cell wall structure. Bailey & Bisalputra (1970) suggested that Golgi-derived vesicles in the cell of articulated coralline algae initiated calcification in the outer part of the wall and subsequently extended inwards leaving an uncalcified lamella surrounding the protoplast. In both intracellular and intercellular areas, internal ordering of organic constituents is likely to control the sizes, shapes and orientations of precipitated calcite crystals. This control also may exist in the mucilaginous sheaths of blue-green algae (Riding, 1977). However, Pobeguin (1954b) suggested that the cells provide only the chemical environment in which the crystalline phase develops, and that the physical shape of the mineral product may be controlled by other factors such as rates of crystallization, composition of contained fluids and shapes of pore spaces within and between cells.

Precipitation of calcite within areas formerly occupied by cell wall material has preserved gross morphology of some filaments (Plates 57a, 59d, 60e, f). Calcite crystals have invested resistant cell wall materials. The fibrils illustrated in Plate 60c-f may be chitinous in composition but, because of the fineness of scale and small quantities, have not been identified chemically. Similarly, the fibrillar mats shown in Plate 61 may be composed of chitin or they may be cellulosic. Unfortunately, I have not been able to isolate these materials and, thus, their compositions are unknown. Nevertheless, the arrangement of calcite crystals within partially decomposed fibrillar wall materials suggests that pore spaces for crystal growth have been created by decomposition of relatively unstable organic constituents. If this is accepted, it will be realized that replacement of organic filaments by calcite crystals takes place piece-meal. The envisaged diagenetic pathway for calcification runs thus:

At first, relatively unstable cell wall constituents (such as cellulose and the hellicelluloses) will decompose and leave voids within the wall. Relatively stable organic materials, such as chitin and lignin, provide templates on which calcite crystals can grow. It is possible that the decay of unstable organic materials modifies the chemical micro-environment in and around filaments in a way that is favourable to the precipitation of calcite. At a later stage, the calcite crystals themselves form rigid structures which act as substrates for further inorganic deposition of $CaCO_3$. At this stage, even if chitin and lignin have been lost, the morphologies of the replaced filaments are ensured. Plate 60 shows the envisaged stages of calcification and Fig. 16, p. 176 illustrates diagrammatically this scheme of development.

Piece-meal replacement of cell walls by calcite is only one of many possible pathways for calcification of filaments. It is a likely process for the calcification of fungal and actinomycete hyphae. Calcification of root hairs, however, probably takes place during growth (Cormack, 1949; Cormack _et al._, 1963) and not during decay of the hair. Calcified root hairs are examples of calcification by impregnation. Calcite encrustation may take place after the death and collapse of root hairs but, because of their relatively constant outer diameters (Plates 62c-f, 63), it seems that this does not occur.

Calcification of living blue-green algal filaments is well documented (Riding, 1977; Schneider, 1977) and takes place extracellularly within mucilaginous sheaths. Calcification of dead algal filaments by calcite encrustation is also known (Kobluk & Risk, 1977). Encrustation on a filament forms a calcite cement crust whose diameter is controlled by physicochemical factors (uncontrolled calcification of Riding, 1977). The calcified filaments of endolithic algae described by Schroeder (1972) from Recent Bermuda reefs are examples of physicochemical calcification. However, although calcification may not be related directly to the life activities of the algae, precipitation may have been influenced biochemically or controlled by organic constituents in the thalli or by saprophytic micro-organisms living on and breaking down the algal filaments. The micron-sized structures in Plate 61d may be examples of such saprophytic micro-organisms.

Schroeder (1972, p.27) pointed out: "It is a matter of culture experiments to provide the basis for an understanding of this calcification mechanism." With only a few such culture experiments to help guide us, I will now discuss possible mechanisms of calcification.

Mechanisms of calcification - - More is known about the nature and location of skeletal carbonates than is understood about their function and precipitation mechanisms (Wray, 1977). Although directed specifically at the calcareous algae, Wray's comment is relevant to the problems of calcification in general. Riding (1977) noted that the mechanism of calcification in blue-green algae has still to be elucidated. Even in the well studied Bivalvia, the exact mechanisms of calcification have yet to be worked out in detail (Taylor et al., 1969).

During the experiments of Kobluk & Risk (1977), they observed that precipitation of carbonate was commoner on algal filaments than on the surface of Iceland spar crystals which were infested with Ostreobium sp. and immersed in seawater. This observation suggested to Kobluk & Risk that organic compounds played an important role in calcite precipitation. Mucilaginous coatings on dead filaments, organic matter bound in the algal thalli and associated activities of bacteria during decay of the filaments were put forward as factors that may have created a micro-environment suitable for the precipitation of calcite.

The role of bacteria in calcite precipitation is unclear. Krumbein (1974) reported that although precipitation of $CaCO_3$ via microbial activity has been demonstrated for terrestial and marine environments, it was not known whether precipitation took place inside the cell, on the cell surface or in the immediate environment of bacteria. Experiments by Krumbein (1974) showed that precipitation of aragonite on the cell surfaces of bacteria produced 'Weizenkorntype' or wheat-grain type crystal aggregates. Coccoid bacterial colonies have been recorded on surfaces of fungal hyphae in this study (Plate 60a, b) but mixed crystal-bacteria aggregates have not been clearly recognized. Calcification of filaments may well have been initiated at the sites of bacterial cells, as in the experiments of

Krumbein (1974), but I have found no evidence to support this possibility.

Surficial or external precipitation (encrustation) of $CaCO_3$ on organic filaments may be related to the extraction of CO_2 by plants during photosynthesis. However, because not all photosynthetic plants are coated with $CaCO_3$, and a given species may calcify in one habitat but not necessarily elsewhere, external controls such as chemistry of the surrounding waters, partial pressure of CO_2 and temperature may be of greater importance.

Regrettably, this study has not made fundamental progress towards a better understanding of mechanisms of calcification. However, a few comments on the envisaged battle between calcification and decomposition of plant material may provide stimulus and direction for further study.

- Plant constituents can be divided conveniently into three groups of material: (1) the cell contents; (2) the reserve food supply; and (3) the cell wall and structural material (Russell, 1973). The first group is rich in proteins and sugars; the second in starches, fats and proteins. The skeletal framework consists of cellulose and lesser amounts of other substances. The cementing and encrusting materials consist of polymerized sugar units and the lignins. During initial stages of plant decomposition, proteins and sugars may be released, creating a micro-environment conducive to the precipitation of calcite. Deposition of calcite is likely to occur near the sites of released catabolic substances. These sites will be within or close to the remaining, more resistant plant constituents which act as a substrate for the deposition of calcite. Thus, the structural framework maintains the gross morphology of the organic template which eventually becomes calcified, giving rise to a calcified filament.

The above comments are, admittedly, highly speculative. Controlled laboratory experiments are required to substantiate or refute these ideas. This study is purely observational. Progress has been made, however, by documentation of fabric relationships between organic constituents (fibrillar materials) and ?inorganically precipitated calcite. But much work remains to be done.

Silicified and Dolomitized Filaments

All but two samples containing mineralized filaments were found to have calcite mineralogies. However, one sample contained tubular voids surrounded by silicified filaments (Plate 65). One other sample was found to contain dolomitized filaments (Plate 64a, b). The filaments in the latter sample are restricted to fenestral voids within laminar calcrete hardpans. The walls of the fenestral voids have a dolomite lining. There is no evidence to suggest that the dolomite is replacive; it has all the characteristics of a normal sparry cement and is interpreted as a dolomite cement. J. Gidman (personal commun. Univ. of Liverpool) agrees with this interpretation and suggests that the dolomite cement represents cementation from a localized flow of magnesian-rich solutions through these pores. It is interesting to note that Triassic dolomites occur immediately upslope of the sample locality. Partial dissolution of Triassic dolomites may have been the source of Mg^{2+} for the dolomitized filaments of Plate 64a, b.

The origin of the silicified filaments presents more of a problem. From their arrangement, size and morphology, they are interpreted as former root hairs around a root mould. Why these hairs should have been silicified rather than calcified is unknown. The surrounding s-matrix is composed of low magnesian calcite.

Authigenic silica is restricted to rhizolith areas. Some plants accumulate silica within their cells and cell walls. It is possible that this restricted formation of silicified filaments is related to a particular plant species. Jones & Handreck (1967; cited in Goudie, 1973) noted that gramineous species are especially active in silica uptake and generally contain 10 - 20 times the silica found in leguminous species.

Calcified Faecal Pellets

Description

Routine examination, using a binocular microscope and reflected light, indicated that peloids are common in channels and irregular chambers within weakly consolidated or friable calcretes. For a given pore, the sizes and shapes of contained peloids are roughly the same. The long dimension of the peloids was measured and found to be between 100 - 200 microns. Most peloids have cylindrical, ellipsoidal or spherical shapes. Their colours range from black, brown-grey to pure white. Most are arranged randomly. The packing is loose, although some peloids were found to be cemented together and form irregularly shaped aggregates. They were found to be abundant locally within root channels. These channels commonly contain decayed material.

Peloids were recognized also in petrographic thin sections. The distribution and arrangement of groups of peloids are illustrated in Plate 66. Plate 66a, b, e, f shows spherical to ellipsoidal peloids within channels. A characteristic feature of these channels is a dark layer along the surface of the wall. Plate 66c and d shows decayed (and digested?) plant root material surrounded by dark, cryptocrystalline peloids.

Examination of white and black peloids by SEM revealed some interesting features. Penetrative and aerial fungal hyphae are abundant in and around these peloids (Plates 67c, d, e, f). Some peloids are encrusted with needle calcite fibres (Plate 67a, b). Plata 67a shows that the needles are tangential to the surface of cylindrical peloids. Self-supporting needle frameworks among peloids have meniscus outlines. These calcite encrustations occur only on white cryptocrystalline peloids. Black peloids (Plate 67d) show no crystalline form; they are composed of amorphous material.

Interpretation

The sizes, shapes, arrangements and distributions of the peloids are consistent with them being faecal in origin. Thus, the peloids described above are interpreted as faecal pellets. Fitzpatrick (1971), in his discussion of organisms ingesting organic material, noted (p.38) that the soil mesofauna (worms, millipedes, mites, ants, etc.) avoid the outer lignified tissues of dead roots and stems but burrow into the softer, central part. The presence and progress of such organisms is usually shown by the occurrence of small ovoid faecal pellets. Fitzpatrick also noted that mites consume large amounts of fungal mycelium, fragments of which are found in their faecal pellets.

Kowalinski *et al.*, (1972), in their micromorphological comparison of three soils derived from loess in different climatic regions, illustrated faecal pellets impregnated with lublinite (needle fibre calcite).

In all samples studied here, no evidence was found to indicate that compression or collapse of faecal pellets has taken place. This suggests that cementation was early; transitional stages between white calcified faecal pellets and black organic-rich faecal pellets suggests that calcification occurred concomitantly with organic decay.

Significance

Correct recognition of calcified faecal pellets indicates former faunal activity. When faecal pellets occur in association with land plant root systems it is reasonable to suppose that the sediment functioned as a soil. The presence of needle fibre calcite suggests that calcification took place in the subaerial vadose zone, that is to say, above the ground water table. Thus, calcified faecal pellets and associated fabrics can be used to identify a subaerial vadose pedodiagenetic environment where calcite is the most stable mineral. In other words, calcified faecal pellets can be used to help identify pedodiagenetic calcretes.

Calcified Cocoons

Spherical structures of 1.0 - 1.5 cm diameter were found within Pleistocene aeolianites and Recent wind-deposited littoral sands from Ibiza (Plate 68). The spherical structures have outer walls consisting of well cemented aeolianite, 1.0 - 2.0 mm thick. The walls commonly have a hole, 2.0 - 4.0 mm in diameter, which leads into an internal chamber. Thin sections of these structures reveal that elongate centimicron-sized skeleton grains are aligned tangentially to the wall surfaces. The interior is either a hollow chamber or, more commonly, contains loosely packed peloids, 200 - 500 microns in diameter. Calcified filaments also were observed cemented on the internal surfaces of walls.

Similar structures were described by Lea (1925) from palaeosols of Western Australia. He identified ovoid cases as calcified puparia of soil-dwelling insects and attributed many of the cocoons to the weevil, Leptops duponti.

Read (1974) recorded the same structures in Quaternary calcretes from Western Australia, as did Ward (1975) in Pleistocene palaeosols from Yucatán, Mexico. The spherical structures discovered on Ibiza probably have the same origin as those described by Lea (1925). The holes in the well cemented walls are probably the entrances to the insect cases and the peloids within the structures are likely to be faecal pellets. The outer well cemented walls may have been cemented initially by a slime secreted by the host soil organisms. Abundant calcified filaments within the chambers suggest that a rich supply or organic matter, available to filamentous micro-organisms, existed at an earlier stage.

These structures, if the above interpretation is correct, indicate a former period of soil fauna colonization of pedodiagenetically altered aeolianites. Thus, calcified cocoons provide additional evidence to help identify periods of soil formation.

Palynomorphs

In several freshly fractured samples examined by SEM, decimicron-sized and centimicron-sized non-carbonate spherical structures with distinctive surface sculpturings were recognized (Plate 69). R. Thomas (Univ. of Liverpool) identified these structures as palynomorphs or plant spores of higher plants.

Following the suggestions of Andrews (1961), I have termed spores with diameters of less than 200 microns as miospores. Spores and pollen grains with diameters greater than 200 microns are termed polyspores. Plate 69 illustrates examples of miospores of vascular plants. They were found in samples collected from sheet calcretes, glaebular horizons and chalky calcrete horizons. They also may be present in other horizons but a systematic palynological analysis was not attempted to assess the total distribution of spores and pollen grains. The distinctive sculpturing of these palynomorphs allows the specialist to identify plant species and, therefore, such a study also would provide valuable clues concerning the type of vegetation present during calcretization. My ignorance in this field precludes the undertaking of a detailed palynological analysis; here, I can make only recommendations.

Miospores of algae, fungi, lichens, actinomycetes and possibly bacteria also were recorded by SEM. Spore chains of the actinomycete Streptomyces (Plates 55c, e, f, 56e, f) were identified by Dr. S. T. Williams (Univ. of Liverpool). These spore chains were found on partially decayed roots within Pleistocene and Holocene aeolianites from Ibiza. Many workers have suggested that a rhizosphere microflora may exist in and around roots; Plates 55 and 56 record visual evidence to confirm these suggestions.

Microcodium *

Introduction

The term *Microcodium* was used by Glück (1912) to describe unusual calcite crystals from the marine Miocene of southern Germany (Baden). From their shape and arrangement, evoking 'cells' in palisades around small nuclei, Glück created the genus *Microcodium elegans* to designate these calcite crystals, which he considered to be organic in origin. He attributed them to Siphonaceous algae and, hence, placed *Microcodium* in the Codiaceae of the Chlorophyta.

Later workers (e.g. Jodot, 1935; Moret, 1952a), doubted their organic origin, considering them to be purely physicochemical precipitates. Interest in *Microcodium* was directed mostly towards an organic versus inorganic debate until Johnson (1953) argued convincingly in favour for an organic origin.

Curved faces and presence of certain internal structures are criteria commonly put forward to argue against a purely inorganic crystallization. In addition, Bodergat (1974) has demonstrated, using isotopic ratios, that the carbon within the calcite is organic in origin, having been metabolised by *Microcodium* in the meteoric environment. Thus, the analytical results of Bodergat (1974) corroborate the morphological evidence. Further details on ultrastructure, presented herein, establishes the organic nature of *Microcodium* beyond doubt.

Apart from the mere noting of its presence, and recording its facies associations, our understanding of *Microcodium* was not advanced until Lucas & Montenat (1967) described and interpreted

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*The information in this section is presented in the form of a paper, entitled 'Biolithogenesis of *Microcodium* : elucidation' which has been accepted for publication in SEDIMENTOLOGY.

its internal structure. More recently, Bodergat (1974) has given a detailed petrographic and geochemical analysis of *Microcodium*. This work, together with that of Esteban (1972, 1974), also provides an excellent literature review on this, hitherto, enigmatic organism. Esteban states that the genus *Microcodium* refers to elongate, petal-like calcite prisms about 1 mm long and hexagonal in basal section. The prisms are grouped in spherical, elliptical, sheet or bell-like clusters (Esteban, 1974). This description refers to his *Microcodium* (a) form and appears to embrace types 1 (épis de maïs) and 2 (colonies en laminae) described by Bodergat (1974). Esteban (1972) also defines a new form as *Microcodium* (b), which is distinguished by its smaller size and quadrangular section of its prisms. Nevertheless, because a complete range of sizes exists between (a) and (b) forms, Esteban (1972, 1974) considered it unnecessary to define another genus. Furthermore, he gives additional ground for not establishing taxonomic refinement (and/or confusion!) as follows ..... "Another reason is that we do not know what *Microcodium* is."

Microcodium has been discussed in several studies concerned with caliche (Esteban, 1972, 1974; Truc, 1975a, 1975b). Similarly, my interest in *Microcodium* was initiated from an examination of calcrete samples of Pleistocene age collected in the western Mediterranean (Fig. 17, p. 196; mainland of Spain and the Balearic Islands). In addition, the new discovery of *Microcodium* within soil samples collected from the province of Murcia (southeast Spain) extends its stratigraphical range into the Holocene. Truc (1975b,p.51) states "...Or les microcodiums, qui jouent un rôle primordial dans ces systèmes, n'ont jamais été signalés encore dans les encroûtements actifs actuels." The discovery

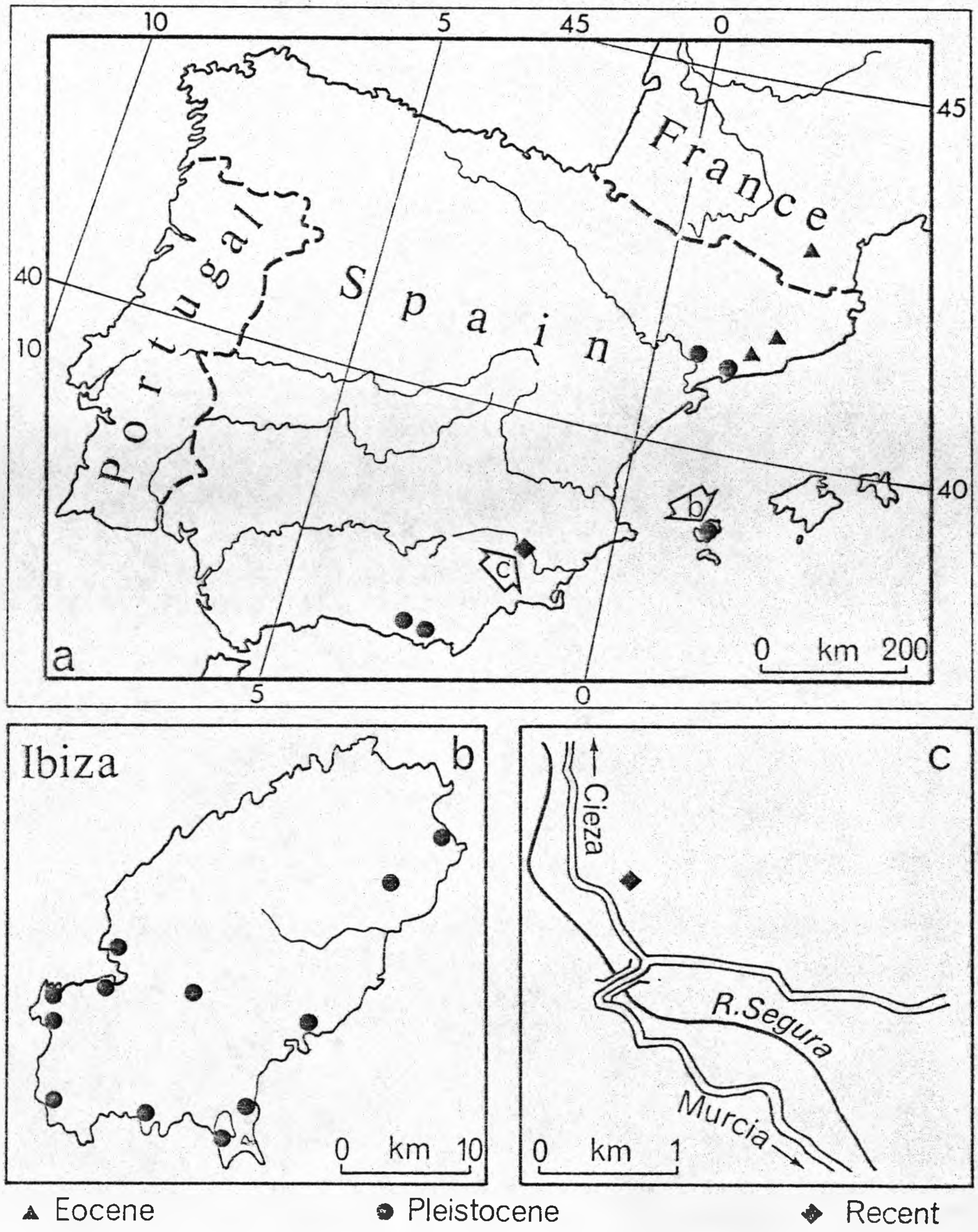

Figure 17. Recorded localities of calcrete profiles containing Microcodium.

of *Microcodium* in the Recent necessitates a revision of this quotation.

Because *Microcodium* forms a significant component of many of these samples it was considered unscientific to pass off *Microcodium* as a 'whim of nature' (an attitude mentioned, although not necessarily followed, by Cuvillier & Sacal, 1961). As a consequence, a detailed examination of this material has led to new findings on *Microcodium* which are presented herein.

Purpose

The intention of this section is:

(1) to document, for the first time, the presence of *Microcodium* in samples collected from the Pleistocene of Ibiza (Balearic Islands).

(2) to demonstrate the existence of *Microcodium* in the Recent.

(3) to provide further details on the microfabrics of *Microcodium*.

(4) to demonstrate that Ancient and Recent *Microcodium* structures are the product of the same phenomenon. Sufficient details are retained in Ancient *Microcodium* sampled from the Eocene of northeast Spain and Southern France to allow such direct comparisons.

(5) to point out the environmental significance of *Microcodium*.

(6) to stimulate a search for *Microcodium* whose presence may have been overlooked or misinterpreted.

(7) to suggest an, hitherto, unconsidered origin for *Microcodium*.

Previous Investigations

Well documented specimens of *Microcodium* have been recorded by French geologists in lacustrine, paludal (swamp), alluvial, and fluvial deposits, at palaeokarstic horizons, and as 'contaminants' in marine facies. Microcodium occurs dominantly in Tertiary rocks, being particularly conspicuous at the Cretaceous-Eocene boundary. The stratigraphical levels at which Microcodium occurs share several common characteristics: a carbonate-rich substratum, indications of subaerial exposure, and frequently the presence of an overlying palaeosol. Microcodium appears to be associated with continental conditions during periods of negligible sedimentation, i.e. with sedimentation rates being insufficient to preclude pedogenetic processes. The Garumnian and Vitrollian of French stratigraphy are examples of such facies.

Most recorded in situ colonies of Microcodium are from rocks of Eocene age. In younger rocks they may be detrital but evidence for in situ growth within Pleistocene rocks has been documented (Bodergat, 1974; Ward, 1975). Visual evidence that Microcodium has grown in situ is indicated by grain truncations within the host rock. This relationship with the enclosing substrate has led to the suggestion that Microcodium actively dissolves carbonate in search of trapped organic matter (Lucas and Montenat, 1967; Esteban, 1972, 1974; Bodergat, 1974; Bodergat, Triat & Truc, 1975; Truc, 1975a, 1975b). Insoluble residues (e.g. layer lattice silicates, quartz grains) are pushed aside and the dissolved carbonate is reprecipitated to form the calcite prisms of Microcodium.

However, this scheme of development does not explain fully the observed microfabrics and raises questions of actual processes. For instance, Bodergat (1974) has pointed out that although there may be many micro-organisms capable of dissolving carbonate (e.g.

certain algae, fungi, lichens, actinomycetes, bacteria) the same organisms cannot also bring about a reprecipitation. This line of reasoning led Bodergat (1974) to the hypothesis that two organisms (at least) have played a role in producing the structure of Microcodium. She suggested that actinomycetes were responsible for the destructive component of her 'biocorrosion-biosynthesis' system. However, the mechanisms of biosynthesis and the type of organism responsible for such a process are not discussed.

Although the study of Microcodium has been largely confined to France, its presence has not been overlooked completely in other parts of the world. For example, Microcodium has been reported from the Miocene in Germany (Glück, 1912), the Eocene and Pleistocene in Spain (Esteban, 1972, 1974), the Permian in Russia (Maslov, 1956), the Eocene in Switzerland (Kamptner, 1960), the Devonian and Carboniferous in North America (Wood & Basson, 1972), the Eocene of Turkey (Richard, 1967), the Pleistocene in Mexico (Ward, 1975) and in the Miocene from the Pacific Islands of Bikini and Saipan (Johnson, 1953, 1957).

The single reference found (from an extensive, though not exhaustive literature survey) of Microcodium occurring in the Recent is by Marie (1957). According to this worker, Microcodium is present in littoral deposits from the Bay of Along, Indochina. However, the presence of Microcodium is explained as being due to reworking rather than in situ growth.

Problems of terminology

Early attempts to describe Microcodium directed me to problems of terminology. The term Microcodium has been used in various ways. Some workers refer to Microcodium as the actual (hypothetical) organism, while others have used it to describe the observed calcite structure. Two important considerations may have contributed to this semantic problem: firstly, whether Microcodium is organic or inorganic and; secondly, whether the calcite is part of the skeleton (as in calcareous algae) or a later precipitate within a vacated or original chamber. Terms frequently used such as 'thallus', 'cell', 'vacuole', 'filament' have genetic overtones. Because of potential confusion in terminology, the morphological term 'Microcodium grain' is used in this section to describe individual prisms or units. In instances where a number of Microcodium grains form an organized arrangement the term 'aggregate' is employed.

Geographical location and geological setting

Ibiza

Microcodium has been recorded in calcretized bedrock (dominantly carbonates but also in profiles with igneous substrates) of Tertiary and Mesozoic age, and in aeolianites and colluvial silts of Pleistocene age (Fig. 17b).

Southeast Spain - occurrence of Recent Microcodium

Recent Microcodium was discovered in southeast Spain, 8 km south of Cieza (30 km NNW of Murcia). The site occurs along an unmetalled forest track (38° 11' N, 2° 18' W) on the east side of the road Mula-Cieza (Fig. 17c).

The bedrock of upland areas is composed of Upper Triassic dolomites, whereas the lower slopes and valleys consist of Lower Eocene lime muds and unconsolidated or poorly consolidated marls. Conglomeratic slope deposits, which overlie the solid geology, also lack consolidation apart from their uppermost layers. At or near the surface, subaerial vadose pedogenetic and diagenetic processes have led to the formation of calcrete profiles in various stages of development, from nodular to thin laminated crusts. However, present-day pedogenetic processes are causing modification and/or destruction of these indurated layers, mainly by the mechanical penetration of root systems (Plate 70b).

Samples containing Microcodium were located 25 cm below the present day surface in a rubbly calcareous soil (Plate 70a). Anastomosing channels, 1.0 mm wide, were noticed on the surfaces of many pebble-sized clasts (Plate 73a). The arrangement of the channel networks suggests that roots have caused peripheral dissolution of these pebbles. Evenari, Shanan & Tadmor (1971) have noted that the surfaces of pebble-sized grains, in otherwise fine-grained soils, tend to be sites of greater moisture content and, therefore, provide readily available water for the indigenous flora. While many channels were devoid of any material, some contained rows of white to translucent, ellipsoidal grains (Plate 73b). Their morphology and ordered arrangement initiated the idea that they may be the same as Microcodium grains recorded from the Pleistocene of Ibiza. Subsequent laboratory examination substantiated this preliminary field observation (Plates 71, 72, 73).

The possibility that these Microcodium grains are detrital, having been reworked from older geological successions, can be discounted for several reasons. Firstly, organized aggregates occur within the present-day soil profile. Secondly, the soil-matrix surrounding and supporting undisturbed aggregates is friable; the aggregates could not maintain form if mechanically churned or transported. Thirdly, aggregates unaffected by chemical corrosion, are extremely delicate; even the slightest pressure of a steel needle is sufficient to cause disaggregation. Fourthly, moribund fungal mycelia (masses of hyphae) surround and penetrate *Microcodium* grains (Plate 72a, b). Fifthly, partially decayed vascular plant material surrounds *Microcodium* aggregates. Similar plant debris, and also fungal hyphae, are present throughout the soil-matrix. Finally, some of the fine details of *Microcodium* grain ultrastructure, as revealed by SEM (Plates 71e, 72, 73e, f) are considered unlikely to be preserved completely in the Ancient.

Laboratory Analysis of *Microcodium*

Petrography

Abundance. Point-count analysis of 50 thin sections containing *Microcodium* of Pleistocene age indicated that this component ranges from less than 0.5% to 43% of the total rock by volume, with an average of 17%.

Size. The sizes of individual *Microcodium* grains were measured for loose sediment mounts and thin sections which contained them. Apparent dimensions (measurement on grains with various orientations in thin section) showed a range from 100 - 200 microns, averaging 120 microns for long axes, and from 30 - 100 microns, averaging 70 microns for grain widths (diameters of isodiametric grains and/or transverse sections). The maximum observed length for loose grain mounts was 375 microns, considerably less than the typical 1.00 mm prisms of Eocene Microcodium described by Esteban (1974).

Shape. The shape of individual Microcodium grains varies from well defined prisms with length:width ratios of 2:1 to 3:1 (Plates 73b, 74a,d, 75c), to vague ellipsoidal or sub-spherical outlines (Plates 71a,c, 74f). Transverse sections show hexagonal, quadrangular or sub-spherical outlines (Plate 74a). Curved faces, both convex and concave, tend to be commoner than straight (Plates 71, 72e, 74f). Many Microcodium grains display re-entrants or embayments (Plate 74f) giving shapes that cannot be attributed simply to mechanical abrasion or fracture during transport.

Arrangement. The arrangement of individual grains with each other and the enclosing substrate varies from single, isolated crystals, to organized aggregates. The latter may occur as rosettes ('épis de maïs' of François & Sigal, 1957) with prisms radiating from a central nucleus (Plate 76a) or as groups of prismatic to isodiametric grains lacking any discernible radial or concentric pattern (Plate 75a,b). Another type of arrangement, although rare in Pleistocene samples from Ibiza but common in the Eocene of northeast Spain and south France, is a laminar or sheet-like layering of prismatic grains (long axes normal to layers). However, in general, because of reworking, isolated detrital grains of Microcodium or fragmented *Microcodium* aggregates are far more numerous than *in situ* growth forms.

Optical properties. Optical properties suggest a calcite mineralogy for the *Microcodium* grains. In plane polarized light, grains are colourless or pale brown, but contain dark radial-fibrous inclusions. The filamentous inclusions appear white using reflected light. SEM examination of *Microcodium* grains reveals that non-carbonate filaments may be present (Plate 75c,f) but in many cases, selective leaching has produced pits which give an optical effect analogous to the porous 'shell-residue micrite' described by Alexandersson (1972). Some *Microcodium* grains have a rhombohedral cleavage but many show only an irregular pattern of cracks (Plates 74b, 75d).

Extinction patterns vary between grains and within the same grain. Uniform (relatively uncommon) to aggregate (suggesting a number of sub-crystals) extinction may be observed in one part, while a sweeping extinction may be present in the remainder of an individual grain. Some grains show a complete radial-fibrous structure with fibres radiating from a point on the perimeter of an individual grain and not from the centre as in typical spherulites (Plates 72d, 74b). Adjacent grains show also a radial-fibrous structure radiating from the same point (Plate 74e). As a result, a pseudo-uniaxial cross is formed when the juxtaposed grains are seen under crossed nicols. Because of this extinction pattern, combined with overlapping sub-crystals, optical interference figures were not readily obtained. In cases where interference figures could be recognized,a uniaxial-negative figure corroborated the evidence in favour of calcite.

Ultrastructure. In several *Microcodium* aggregates the calcite was removed by etching in dilute hydrochloric acid (1.5%). Total dissolution revealed the presence of a network of branching filaments 1.0 - 2.0 microns in diameter. The filaments may have been originally transparent (common in fungi, for example) but the presence of iron and/or natural organic staining rendered them visible in reflected and transmitted light.

SEM examination of *Microcodium* from the Pleistocene of Ibiza shows several interesting features that have not, to my knowledge, been documented elsewhere. Linear patterns of tubular cavities 0.5 - 2.0 microns cross-section can be seen in grains (Plate 75e). These may radiate from a larger tubular cavity 5.0 microns in diameter (Plate 75d) or from a point on the grain perimeter. Similar tubular patterns can be seen within Recent *Microcodium* grains mounted in immersion oil and viewed under the petrographic microscope (Plate 72e, f). Some tubes have a hexagonal cross-section which perhaps suggest that these cavities are moulds of aragonite needles. However, two points of observation do not favour such an interpretation. Firstly, the tubes are not necessarily straight but show curved or wiggly shapes (Plates 71e, 72e, f, 74f), whereas aragonite needles have planar crystal faces. Secondly, gentle etching of the calcite prior to SEM coating, revealed the presence of residual structures less than 1.0 micron diameter within some of the tubes (Plate 75f). These structures seem to have been unaffected by acid etching, a point which further argues against them being aragonite. Because of the fineness of scale it has not been possible to isolate these filaments for further tests.

Viewed with SEM, the tubular pores can be equated in petrographic thin sections with the so-called dark, filamentous inclusions that show a radial pattern (Plate 74d-f). It is significant that these filaments radiate from a point on the periphery of the *Microcodium* grain and not from the centre. Furthermore, the calcite within the *Microcodium* grain also shows a radial-fibrous fabric (Plates 72d, 74b). The crystallites that make up this radial-fibrous fabric similarly radiate from the grain perimeter, unlike spherulites which radiate from a central point. This indicates growth from a 'wall' into a cavity. Moreover, the radial arrangement for the vacated or tubular pores, likewise, suggests penetration from the walls of *Microcodium* grains. The question now arises as to what constitutes this 'wall' and its relationship, if any, to the tubular pores.

In thin section, *Microcodium* grains from the Eocene of northern Spain show walls between, and cross-walls within, petal-shaped grains (Plate 76c, e, f). The walls consist of dusty, pale to dark brown microcrystalline calcite (staining and etching in dilute hydrochloric acid indicates that at least part of the wall has a calcite mineralogy). SEM observations of fractured surfaces show that these walls are made up of equant, subhedral to anhedral submicron-sized grains with a high intergranular porosity(Plate 76f). The fine grain size and high porosity is probably responsible for the dusty appearance of the walls. No organized fabric was recognized within these walls; the micrite has an apparently random fabric.

However, SEM studies of Recent *Microcodium* grains from southern Spain provide further surface and internal features that have relevance to the above outlined details, and perhaps more fundamentally, provide evidence for overall interpretation (p.215).

The surfaces of Recent Microcodium grains show a granular appearance with bordered pits and cylindrical pores 0.4 - 1.0 microns in diameter (Plates 71b, 72c). The pores appear to be connected to a subsurface anastomosing network of tubes (Plates 71b,e). Indeed, some Microcodium grains with the surface layer removed by fracturing or natural flaking, reveal the presence of a fine network of tightly bound, branching or coiled tubes 0.4 - 0.8 microns in diameter (Plate 73f). This network does not appear to be continuous throughout the grain but restricted to a thin superficial layer less than 5.0 microns thick. This layer corresponds to the 'wall' of Ancient Microcodium grains. The ultrastructure of the remainder of the grain, both in the Recent and Ancient, consists of foliate calcite (Plates 71d, 76e). Bodergat (1974) stated that the 'platy' calcite was oriented perpendicular to the long axes of elongate Microcodium grains. Although this orientation was recorded in many grains examined in this study, calcite plates were observed also with a sub-parallel alignment with respect to grain long axes.

The complex ultrastructure of Microcodium grains, as revealed by SEM examination, perhaps helps to explain the reasons for anomalous optical properties and staining patterns of the same grains when viewed under a petrographic microscope.

Mineralogy

In order to substantiate the petrographic data several microchemical tests were carried out to evaluate the mineralogy of Microcodium grains. Staining thin sections with a filtered solution containing Alizarin red S and potassium ferricyanide combined (Dickson, 1966), revealed certain anomalous features. Staining colours were weak or absent in many Microcodium grains, or present within irregular cracks (possibly because of the difficulty of thorough washing within micro-pores). In grains with composite extinction patterns a red stain (non-ferroan calcite or aragonite) was commonly taken up only by the fibrous part of the grain (Plate 74b) whereas the clear spar, with uniform extinction, remained unstained. According to Dickson (1966) the intensity of the combined stain depends on the amount of iron present, the orientation of the c-axis with respect to the plane of the thin section, and the concentration of the acid in solution. Additional factors considered in the course of this work that may have affected the staining pattern and colour intensity include the presence of organic matter, particularly mucilaginous films, the presence of non-carbonate micron-sized grains, the micro-porosity of individual crystals (Plates 71b,f, 75d-f) and the presence of other foreign ions (in addition to iron).

Because of the atypical staining patterns as outlined above, some Microcodium grains were suspected of having a mineralogical composition other than pure calcite. Further microchemical tests were carried out for the presence of: aragonite (Feigl's solution, Feigl, 1943); high magnesian calcite (Clayton yellow, Winland, 1971); dolomite (Alizarine cyanide green, Davies & Till, 1968). The presence of these minerals was not detected using these methods.

Because Microcodium is considered to be organic in origin, several microbiological tests were carried out. It is well known that certain plants secret crystals (cystoliths) within their cells (Cutter, 1969; Arnott & Pautard, 1970). Most contain calcium; calcium oxalate is the commonest organic compound found within plant tissues, although calcium carbonate also occurs. Such crystalline deposits are generally considered to constitute deposits of waste products. Examples of oxalate crystals - whewellite ($CaC_2O_4H_2O$), and weddellite ($CaC_2O_4.2H_2O$) - are organic salts of inorganic cations (calcium) and organic acids.

Following the procedure of Gurr (1965), a test was carried out to detect calcium oxalate. Observation of the chemical reactions, both under the binocular and petrographic light microscopes, suggested the presence of calcium oxalate within part of the Microcodium grains tested, but not throughout. However, the reliability of the method is unknown and further geochemical tests were undertaken.

Hand-picked Microcodium grains were ground to a fine powder and prepared for X-ray diffraction analysis. A Guinier camera was employed, using CuKα radiation, for mineral identification. The results showed that only calcite was present in these samples. If other compounds were present, as earlier tests seemed to indicate, then their trace amounts were masked by calcite.

Comparative Approach - Microcodium and terrestial vegetation

Preliminary observations

This section examines cumulative data gained from field and laboratory studies on Eocene to Recent Microcodium, giving due - and in my opinion, long overdue - consideration to present-day soil systems.

Up till now, Microcodium has disguised itself so well that it has not been recognized in the Recent. After studying Pleistocene samples from Ibiza containing abundant Microcodium grains, this discrepancy seemed somewhat puzzling. Did Microcodium really become extinct at the end of Pleistocene, or has the environment of its formation not been studied by geologists?

The presence of Microcodium near or within rhizocretions has been recorded by Calvet et al., (1975) in Pleistocene aeolianites from Mallorca. Dr. W. C. Ward (written communication) suggests that Microcodium from the Pleistocene of Yucatán may, in some way, be related to roots. Moreover, the conviction that roots are of paramount importance in determining many textures in calcretes, and are related to the formation of Microcodium, has been amplified in valuable discussions with Dr. M. Esteban, of the University of Barcelona.

From my field observations, cumulative evidence indicated that roots play an important role in determining macro-morphological features of calcrete profiles (p.90;p.97). This realization led to a search for rhizospheres (Gk. rhiza = root) on a microscopical scale.

Biogenetic aspects

In the previous section (p.202), several features were described but left unexplained, namely, the occurrence of walls, radial-fibrous calcite and filaments radiating from discrete points on the grain perimeter, preservation of grain morphology and possible presence of calcium oxalate. In order to account for these observed features a new model is proposed in this section (p.215) which contends that Microcodium is the result of calcification of mycorrhizae.

However, before the morphological observations can be interpreted in the light of this proposal, it is deemed necessary to clarify terminology and introduce basic concepts of plant anatomy and physiology.

Great variability exists in the shape and structure of roots (Fahn, 1974). This is related mainly to root function, i.e. whether they are storage roots, succulent roots, aerial roots, pneumatophores, prop roots, or whether they contain symbiotic fungi (to form mycorrhizae). Nevertheless, the general anatomy of young roots shows several common characteristics which can be conveniently divided into the following zones: (1) the root cap (situated at the tip of the root); (2) the epidermis (outermost layer of cells), including root hairs which are projections or tubular outgrowths of the epidermal cells; (3) the root cortex (parenchyma tissue surrounding the vascular cylinder and bounded on the outskirts by the epidermis); and (4) the vascular or central cylinder (consisting of xylem and phloem).

It is well known that roots provide habitats for many soil micro-organisms (Burges, 1958). Fungi may form a union with roots to make composite structures known as mycorrhizae. However, it should be made clear that not all fungal attacks on roots are necessarily mycorrhizal; many fungi are parasitic or saprophytic, whereas a mycorrhiza is defined as "a symbiotic association between a non-pathogenic (or weakly pathogenic) fungus and living, primary cortical cells of a root" (Marks & Kozlowski, 1973).

Mycorrhizae can be divided into two main categories (ecto- and endo-), although a transitional stage has also been recognized (ectendomycorrhizae). Marks & Kozlowski (1973) define these as follows: Ectomycorrhizae ... fungus is confined exclusively to the intercellular spaces of cortical cells of the host root; Endomycorrhizae ... fungus is confined exclusively to the intracellular spaces of cortical cells of the host root; and Ectendomycorrhiza .... fungus occupies the intercellular spaces of the root and penetrates some (or all) of the adjacent cortical cells.

As a result of fungal infection, the plant cell may be structurally modified in a characteristic way. A particular type of mycorrhiza, known as vesicular-arbuscular, usually applies to an endomycorrhiza where the fungal hyphae inside the cortical cells are either coiled or divided into haustorial branches (Plate 73d). Haustoria (Latin : haustor = drinker) are generally regarded as specialized absorbing organs. They may be knob-like in shape, elongate, or branched like a miniature root system (Alexopoulous, 1962).

Although the role fungi play in mycorrhizal associations is unclear, the general consensus of opinion is that mycorrhizal infections assist in the absorption of mineral salts, particularly in soils where the levels of available minerals are low (Burges,1958). This point may be of particular relevance to calcrete profiles which are poor in many essential mineral salts for normal plant growth.

The actual mechanisms for uptake of nutrients into mycorrhizae are imperfectly understood as the following statement by Kelley (1950, p.12) indicates ".....whether materials get from the soil into the plant by mechanical means or black magic is left to the imagination of the reader." However, recent work on mechanisms subsequent to Kelley's cynicism is reviewed by Bowen (1973). His discussion may have some relevance to the problem of calcification of *Microcodium*, but much remains to be learned before actual processes are understood. For the time being, the above quotation from the work of Kelley (1950) can also be applied to this problem, even though several possible mechanisms for calcification have been outlined (p. 220).

The possibility that *Microcodium* is related to a fungus-root association is consistent with previously noted associations recorded on a macroscale. For example, Ancient *Microcodium* has been found within palaeosols, particularly calcareous soils (Bodergat, 1974), at unconformities indicating subaerial exposure of marine successions (Lapparent, 1966; Esteban, 1972), and at palaeokarstic horizons (Freytet, 1969). With respect to the latter, the presence of *Microcodium* within deep fractures and solution hollows has raised doubt as regards an algal origin for *Microcodium*; algae generally require light for their vital life processes. Because of this factor, Gottis (1963) suggested that *Microcodium* was an obligatory heterotroph. Lucas & Montenat (1967) overcame this problem by considering *Microcodium* to be the result of the activities of colonial bacteria. Wood & Basson (1972) state that the occurrence of their specimens and presence of chitin suggest that the organism could be a fungus. They note (p.212) that "...if this organism is a fungus, the question as to how *M. elegans* was able to live in the absence of light .... would be answered." Similarly, mycorrhizae (fungal-root symbiosis) occur generally in a subterranean environment and, thus, do not require direct light.

Several pertinent general comments regarding plant roots may help to convey the reasons for emphasizing their importance with respect to the occurrence of Microcodium. Roots are responsible for acid reactions that may stimulate rock decomposition. Roots add CO_2 to soil-air and soil-water, thus increasing the production of carbonic acid which lowers the pH of circulating waters. This may lead to dissolution of carbonate minerals. Roots provide channels which allow easier circulation of water and air. Roots penetrate joints and cracks, causing mechanical disintegration. Roots are surrounded by a concentration of micro-organisms within the rhizosphere, or may provide habitats for micro-organisms on the root surface (rhizoplane), or actually within root tissues (intracellular infection). Such micro-organisms contribute to changes in the chemical micro-environment by respiration, secretion of acids, organic decomposition and other complex interacting processes.

However, because of this biogeochemical complexity of soil formation and modification, it is not always possible to substantiate such generalities as outlined above. For example, the assumption that roots increase acidity in soil around them by excretion of carbon dioxide, and possibly H^+ ions, may not be valid. It has been suggested that roots take up on average more anions than cations and would therefore tend to pass out HCO_3^- ions, rather than H^+ ions to preserve electrical neutrality (Gray & Williams, 1971). This would increase the pH of the soil around the roots and possibly counteract the effect of carbon dioxide which would diffuse away from the root region more rapidly than the carbonate ions.

Nevertheless, whatever the complex processes may be, field observations indicate that roots can both dissolve solid rock (Plate 21b) and act as nuclei for cementation (Plate 16a). Calcification of roots leads to the formation of rhizoliths (p. 93). Dissolution by roots, on the other hand, provides the biochemical-corrosion component for Microcodium, i.e. the attack by Microcodium on the substrate may be a function of rhizo-solution. However, the preservation of plant form (biosynthesis component) still requires explanation; it is suggested herein that penetrative fungal hyphae within plant cells and walls provide a template for such preservation.

Synthesis of model

Following the above rudimentary introduction on plant physiology and anatomy, it is now possible to present evidence to substantiate the claim that observed morphological features of Pleistocene and Recent Microcodium are the result of mycorrhizal associations. This will be presented in two sections, viz: (i) evidence for the presence of roots; and (ii) evidence for fungal presence and modification.

Unfortunately, because the biological systems are no longer living it is impossible to demonstrate that the root-fungal association is definitely a symbiotic one. Nevertheless, the morphological similarity between the material studied here and actual mycorrhizal associations is considered sufficient to suggest that this was the case.

(i) Evidence for the presence of plant roots

1. Size of Microcodium grains. Grains (Microcodium) from Ibiza

and southeast Spain have similar dimensions to plant cells.

2. Shape of *Microcodium* grains. Grain shapes are similar to parenchymatous and collenchymatous plant cells.
3. Non-planar grain boundaries (Plates 71d,e, 74f, 75d). Convex, concave and re-entrant faces are common for *Microcodium* grains; curved faces are not typical of inorganically precipitated calcite.
4. Arrangement of *Microcodium* aggregates. The cylindrical arrangement (Plate 71c) in many aggregates is like that of the cortical layer of a plant root.
5. Occurrence of *in situ* *Microcodium* aggregates within channels (Plate 73b). Channels in calcrete (millimetre scale) are common. Many owe their origin to root channels.
6. Insoluble residues from indurated calcrete profiles. Xylem vessel members (specialized vascular plant cells used for transporting water) and other plant remains have been extracted from Pleistocene calcrete (Plate 77c). Microchemical tests indicate that these residues contain lignin.
7. Presence of calcium oxalate. Plants may secrete crystals within their cells. However, according to Kelley (1950), a general opinion held maintains that fungal hyphae do not penetrate raphide cells (cells containing bundles of acicular needles). On the other hand, Kelley (1950) also mentioned the work of Busich (1913) who said that a fungus is not warded off by calcium oxalate but on the contrary forms it. Thus the minor amounts of calcium oxalate detected in *Microcodium* grains may be the product of fungal activity rather than of vascular plant secretion.

8. *Surface features of Microcodium grains*. Bordered pits on grain surfaces (Plate 72c) correspond to positions of connection between cells of thin cytoplasmic strands (plasmodesmata).

9. *Presence of fine strands or fibrils* (Plate 73e). Fungal (?) bores (1.0 micron diameter) which penetrate *Microcodium* walls are surrounded by fine fibres (less than 0.05 microns diameter). The latter are interpreted as macrofibrils that constitute plant cell walls.

10. *Subterranean habitat of Microcodium*. *Microcodium* is encountered dominantly within a subterranean environment that shows pedological features, i.e. within a soil which by definition, supports a biological ecosystem.

(ii) *Evidence for the presence of fungi*.

1. *Filaments (1.0 micron diameter) radiating from the grain perimeter* (Plate 74c-f).

   In thin section, radiating filaments show a radial arrangement with respect to *Microcodium* walls. These are interpreted as intracellular fungal hyphae, possibly haustoria (special absorptive hyphae that invade living cells). In endo- and ectendomycorrhizae these hyphae radiate out from the cell wall into the cell lumen.

2. *Presence of filamentous networks*. Following acid etching of *Microcodium* grains, rod- or needle-shaped structures (0.4 - 1.0 microns diameter) were revealed by examination under the SEM (Plate 75f). Their size and shape are compatible with them being of fungal origin.

In some Microcodium aggregates the arrangement cf filaments forms an organized pattern. The total structure resembles a sclerotium which is a firm, rounded, often hard, mass of hyphae devoid of spores that forms a resting stage (Marks & Kozlowski, 1973). Trappe (1971) shows a photomicrograph (his fig. 5, p.25) of a microtomed section of the surface of a sclerotium of Cenococcum graniforme. The hyphal arrangement in Microcodium resembles that of the mycorrhizal mantles formed by this fungus. Trappe (1971) illustrates such a mycorrhizal mantle (his fig. 4, p.24) which is similar in shape and size to Microcodium aggregates sampled from the Eocene of northern Spain.

3. Coiled filaments or finely divided branches within Microcodium walls (Plate 73f).

These are considered to be fine networks of closely packed fungal hyphae within cell walls. Fungi are composed dominantly of chitin, whereas cellulose constitutes most of the cell wall in higher plants with minor amounts of lignin, tannins and pectic substances. Cellulose is rapidly broken down by microbial decomposition but chitin, when associated with polyphenols contained within the hyphal wall, resists decay for much longer (Potgieter & Alexander, 1966). Therefore, it is possible that the presence of fungi within cell walls preserves the cell form. A tentative proposal made here is that such a template is the reason for preservation of plant morphology.

4. Bores within Microcodium grains (Plates 72e,f, 73e). Tubular pores (0.4 - 1.0 microns diameter) within Microcodium grains are thought to be moulds of intracellular fungal hyphae. The hyphae have been later embedded in calcite so that the 'bores' are, strictly speaking, embedment structures (Bromley, 1970).

5. Protuberances in naturally etched Microcodium grains (Plates 71f, 73c,d).

   Rod-shaped protuberances (0.5 microns diameter) within naturally etched grains have been observed by SEM. Such intragranular (intracellular) structures, whose dimensions and forms are similar to haustoria, are interpreted as the fungal component of vesicular-arbuscular mycorrhizae.

6. Hypertrophied Microcodium grains (Plate 71a, c). Hypertrophy (Gk. hyper = over + trophe = food) is an excessive enlargement of cell size without an increase in cell number (Alexopoulous, 1962). Hyphal infection (intracellular) exerts a physical pressure on adjacent cortical cells (fungi forming mycorrhizal associations do not generally penetrate beyond the cortical layer). Enlargement of cells, because of this fungal infection, leads to interference during growth between adjacent cells. Concavities and bizarre cell shapes (Plates 71e, 72a-d) are considered to be the result of this phenomenon.

7. Presence of peritrophic (surrounding surfaces of roots) mycelia. Viewed under a binocular or petrographic microscope, Recent Microcodium from southeast Spain were observed to be surrounded by networks of fungal hyphae (Plate 72a). These form a mycelium (mass of fungal hyphae) or a rhizomorph (densely packed mass of fungal hyphae that resembles a tree-root). SEM examination shows that these hyphae are slightly larger than the previously mentioned filaments. Hence, a dimorphism exists in the diameter of relatively thick aerial hyphae (2.0 - 5.0 microns diameter) around Recent Microcodium grains, and finer hyphae (1.0 micron or less) on and within these grains (Plate 72b). A similar example of hyphal dimorphism has been recorded by Nicolson (1967).

Thus, by documenting the fabric (size, shape and arrangement) of *Microcodium* grains by light and scanning electron microscopical observations and comparing the results with known biological features, *Microcodium* is interpreted as a product of mycorrhizal activity.

Mechanisms for calcification within plant cells - calcification

This section is an attempt to indicate possible mechanisms that may lead to the accumulation of calcite within plant cells, and conclusions reached are to be regarded as highly tentative.

The term calcification is used here to include preservation of plant form by calcite precipitation within vacated or original pore spaces (vacuoles) and metasomatic replacements of organic compounds by calcium carbonate. Treatment of this subject can be conveniently divided into several categories, viz:

I. Phenomena associated with plant growth

  (i) Direct biochemical

    a. metabolic products of plants during normal growth.
    b. metabolic products of symbiotic or parasitic micro-organisms.
    c. secretion of substances in an attempt to flush out foreign intruders.
    d. selective uptake or rejection of ions by sorption (Lovering, 1959), ion exchange, or contact exchange (Keller & Frederickson, 1952).

  (ii) Indirect biochemical

    a. change in partial pressure CO_2 because of synthesis and respiration of plant and associated microflora.
    b. change in solute concentration because of evapo-transpiration.
    c. change in pH because of plant and microbial activity.

  - d. exudation of organic acids and the sloughing off of plant debris, leading to changes in the chemical micro-environment of the rhizosphere.
- (iii) Physicochemical
  - a. accumulation of H_2O in the proximity of the root because of surface tension effects.
  - b. diurnal and seasonal changes in temperature which affect the solubility of calcium carbonate.

II. Phenomena associated with plant decay

- (i) Microbial decomposition
  - a. decay of plant organic material.
  - b. decay of micro-organisms associated with plants during life (symbiotic or parasitic) or after death (saprophytic).
- (ii) Metabolic products of saprophytic organisms

Documented isotopic analyses on Ancient (Eocene) *Microcodium* are given by Bodergat (1974). With respect of $^{13}C/^{12}C$ ratios, the conclusion reached by J. C. Fontes (who carried out the isotopic work) is quoted by Bodergat (*op.cit.*, p.209) as follows: "...pratiquement tout le carbone qui s'intègre au carbonate a été préalablement métabolisé." Bodergat points out that this analytical evidence confirms the organic nature of *Microcodium* and that the carbon is photosynthetic in origin.

By tacitly assuming that a $^{13}C/^{12}C$ isotopic analysis on Recent *Microcodium* would give similar results, only the above mentioned mechanisms for inducing calcification that involve metabolic processes will be considered in greater detail.

Metabolic products of plants during normal growth - As a result of metabolic activity in the cell, some plants form ergastic substances as cell inclusions (Cutter, 1969). Such substances include proteins, starch, fats, oils and crystals. Some of these may be waste products, others are stored food material. Crystalline deposits in various forms occur in the cells of certain plants and are generally considered to be waste products (Cutter, 1969).

The size, shape and arrangement of isodiametric *Microcodium* grains are consistent with those of certain types of plant cells (particularly the parenchymatous cells of vascular plants). At first, this led to the idea that *Microcodium* grains were secretory crystals within plant cells. However, the observation that *Microcodium* has destroyed or at least modified the substrate (Plate 73a) by dissolution and reprecipitation indicates that the product cannot be attributed simply to passive cavity filling of cell lumina.

Metabolic products of symbiotic, parasitic and saprophytic soil-plant micro-organisms - Little is known regarding the ability of microbes to precipitate calcium carbonate (Alexandersson, 1974) but the culture experiments of Krumbein (1968) may have some relevance in this context. He demonstrated that the microflora from a nari lime-crust (calcrete) could produce large quantities of calcite. Likewise, Adolphe & Billy (1974) have observed the precipitation of calcite by bacteria *in vitro*, but it is unclear whether the phenomenon is the result of a direct or indirect biochemical control.

Metabolic secretion in response to foreign bodies - This idea may be treated with the greatest scepticism as I am unable to substantiate whether such mechanisms occur in nature for this given situation.

Reasoning by analogy with pearl formation in oysters, the suggestion is put forward here that the penetration of plant cells by micro-organisms may induce the secretion of substances in order to flush out intruders. Although mycorrhizae involve symbiotic rather than parasitic associations, the physical presence of fungal hyphae within the cytoplasm, or even restricted to the cell wall, may cause the release of certain substances. Alternatively, there may be a chemotactic response, stimulated by substances diffusing from the fungal hyphae.

Whatever the exact mechanisms are, it is evident from consideration of the above possibilities that higher and lower plants have the ability to exert direct or indirect biochemical controls which may culminate in calcification of plant tissues.

It is not denied that the above comments are speculative and should be treated with caution. The chemical complexities of the soil micro-environment are beyond the scope of this study. Nevertheless, as a concluding remark in this section, it can be stated unequivocally from direct observation that calcification has taken place.

Ancient Microcodium

It is not the intention of this section to give a complete petrographic analysis of Ancient Microcodium. This has been covered by the study of Bodergat (1974). After reviewing this work, together with the studies of Esteban (1972, 1974), Freytet (1969, 1971a, 1971b, 1973), Lucas & Montenat (1967) and Truc (1975a, 1975b), and using my own findings on the same material, it has been possible to make comparisons between Ancient and Recent *Microcodium*.

Description

The illustrations and descriptions of Bodergat (1974) and Esteban (1972, 1974), generally agree with observations made in the course of this work. Viewed with the light and scanning electron microscopes, *Microcodium* grains include the following features: - the calcite that makes up the grains is non-limpid. Grains are dominantly prismatic in shape. Inclusions are commonly aligned parallel or sub-parallel to the length of the prisms. Grain boundaries typically display curved faces, both concave and convex, and show re-entrant outlines. Lines of insoluble residues occur between prisms and at the boundary between the *Microcodium* aggregate and the attacked rock. Some transverse sections perpendicular to the long axes of prisms have a central tubular hollow. Fractured grains show that the ultrastructure of the calcite that makes up the solid part of the prism is composed of a pile of thin plates, commonly although not invariably, oriented perpendicularly to the long axes of the prism.

However, some differences and additional features have been noted in the material examined in this section. For example, some samples show that the calcite plates that constitute the individual prisms are aligned sub-parallel to the long axes of elongate *Microcodium* grains.

Another point at variance with previous studies concerns the insoluble residues. The presence of insoluble clay residues at the contact between the *Microcodium* grain and the enclosing substrate was not recognized in all samples (Plate 76a,c). Instead, in some cases, a micro-honeycombed structure (hitherto undocumented) with pore diameters of 1.0 micron was observed (Plate 76d).

An additional feature, not previously recorded in Ancient (Eocene) *Microcodium*, is the presence of disc-shaped constrictions along rod-shaped aggregates (Plate 76b).

Interpretation of new features recorded in Ancient *Microcodium*.

A micro-honeycombed structure within *Microcodium* grains has apparently been found in Eocene samples studied by Dr. L. Pomar (Esteban, written communication). Esteban thinks the units may be bacterial precipitates. However, in line with observations of Recent and Ancient *Microcodium* made during this study, it is considered that the walls forming the honeycombed structure are the result of calcite precipitation on intracellular fungal hyphae. Following decay of the hyphae, the resulting pores mark their former positions.

The origin of the constrictions is not clearly understood, but as a tentative proposal it is suggested that they may represent the nodes of a plant (parts of a plant stem where one or more leaves arise). If this proves correct, then calcification of plant cells penetrated by fungal hyphae may not be restricted only to the root zone as emphasized earlier. Thus, preservation may be simply a function of environment; structures already enclosed within a sediment (roots) have a better chance of survival than aerial parts of a plant which tend to be rapidly oxidized (Barghoorn, 1952). The sample illustrated in Plate 76b may reflect a case of unusual preservation.

Comparisons between Ancient and Recent Microcodium

On a megascopic scale, the occurrence of Microcodium at specific lithostratigraphic levels, namely at surfaces indicating subaerial exposure and within dominantly continental facies, is perpetuated throughout the geological record. The presence of Microcodium within calcareous sediments affected by pedogenesis suggests that a genetic relationship exists between Microcodium and the rhizosphere of lime-rich soils.

Observation at microscopic level indicates the presence of radiating filamentous structures within single Microcodium grains. Pitted surfaces, and tubular pores of 1.0 micron diameter or less, are characteristic of Ancient and Recent Microcodium. (Plates 71b, f, 72c, 76d). Shapes of grains typically show curved faces (Plates 71a, c, d, 74f, 76a) a features which militates against a purely inorganic origin. However, some Ancient Microcodium aggregates contain prisms with straight faces. Monocrystalline calcite with uniform extinction is characteristic of Ancient Microcodium, whereas Pleistocene and Recent Microcodium grains tend to be composed of a number of sub-crystals, commonly displaying a radial-fibrous fabric. The latter gives aggregate or sweeping extinction patterns. These differences are thought to result from subsequent diagenetic modification of Ancient Microcodium.

Following the classification of Bodergat (1974), type 1 ('épis de maïs' = corn on the cob) and type 2 ('colonies en laminae' = laminar colonies) are common habits shown by Ancient Microcodium. Type 3 (isodiametric grains forming a cortical layer that surrounds a central canal; Plate 75a) is apparently rare in the Ancient, whereas samples of Pleistocene and Recent age are dominantly of this form. The size-range for type 3 grains is similar for Ancient and Recent Microcodium but types 1 and 2 tend to be composed of somewhat larger, elongate prisms up to 1.0 mm in length. However, such monocrystalline, elongate grains of Ancient Microcodium commonly have cross-walls normal to the length of the prism (Plate 76e,f). Cross-walls within single Microcodium grains have not been recorded in Quaternary samples. The widths of Ancient and Recent Microcodium grains are similar; the greater lengths of the former may be due simply to recrystallization of a number of isodiametric grains. Thus, the 'cross-walls' may, in reality, mark the sites of former outer walls of juxtaposed, more or less isodiametric, single grains.

With regard to the smaller Microcodium (b) forms of Esteban (1972) which are possibly equivalent to the 'seed-plots' of Lucas & Montenat (1967) and Microcodium described by Montenat & Échallier (1977), their occurrence at the perimeter of rhizocretions or subjacent to root channel walls, displaying either a concentric arrangement in transverse sections or palisade rows in longitudinal sections, suggests an intimate relationship with plant root systems. They occur both in the Ancient and Recent. Their origin may be the result of calcite encrustation on fungal hyphae. Fungi commonly form a peritrophic mantle around root surfaces, utilizing sloughed off debris and exudates of the root as sources of food. Both calcite encrusted fungal hyphae and detached calcified root hairs have been recorded by SEM around rhizocretions and root moulds.

Microcodium (b) form grains typically have a central tube (unfilled) or channel, or a central rod (filled), which is surrounded by a layer of calcite 5 - 20 microns thick. This arrangement gives Microcodium (b) grains an overall diameter of between 10 - 40 microns. The diameter and shape of the central tube or rod allows distinction between the two suggested origins: root hairs have diameters of 5 - 17 microns according to Dittmer (1949) and tend to be straight unless penetrated by fungi, whereas fungal hyphae tend to be somewhat narrower (0.5 - 10 microns) depending on species (personal observations) and are commonly sinuous. This morphology, combined with the cut-effect, gives a spaghetti-like appearance in thin section (Plate 52e).

Microcodium is considered to be, on the basis of this study, the product of calcification of plant cells whose forms have been maintained by fungi which show mycorrhizal associations. Since mycorrhizae are not restricted to a particular species of plant, variations in form may exist between different plant species. Moreover, given a time-span from the Eocene to the present day, morphological differences between Ancient and Recent Microcodium are to be expected. As well as the involvement of completely different species, sufficient time is also available for variation to result from evolutionary change within a single plant species.

As a concluding remark in this section, it is pointed out that variations between Ancient and Recent Microcodium may also be explained (away), in part, by the 'cinderella' of carbonate sedimentology, that is, by diagenesis.

Consequences and Implications

Misinterpretations, oversights (?)

In reviewing the literature, in an attempt to elucidate the origin of Microcodium, several petrographic descriptions were found that show affinities with those of Microcodium. For example, Seghal & Stoops (1972, pp. 67-68) state that "... a puzzling form of calcite accumulation is the occasional occurrence of sand-sized, single, rounded calcite grains with wavy extinction." They suggest that abrasion during transport was responsible for the rounded shapes, and the wavy extinction is attributed to their derivation from metamorphic rocks. They also note that similar kinds of calcite crystals have been observed by other authors (Al Rawi, Sys & Laruelle, 1968; Altaie, Sys & Stoops, 1969) who could not categorically state their origin.

Schlanger (1964, p.D11) states "...small radiating and sheaf-like clusters of stubby, acicular and rhombohedral crystals have formed in some mosaics. These crystals are coffee coloured and show weak pleochroism or absorption in shades of light yellow brown. Absorption is greater parallel to the long axis of the crystals. These crystals show high birefringence and indices of refraction greater than calcite; they have not been identified."

Unfortunately, neither of the above descriptions are furnished with any illustrations; thus, direct comparisons are difficult to make. Nonetheless, some points in their descriptions may be applied to Microcodium and perhaps should be interpreted with this consideration in mind.

Folk (1971), in discussing unusual neomorphic fabrics illustrates an example of: "neomorphic bladed calcite forming a very crudely oriented (N.B_4.C) crust on an intraclast" (his fig.84B, p.165). He mentions a "...microspar matrix of blades L/W 2:1 to 4:1, often circular in cross-section. Some of these particles taper at their end, others splay out like a worn toothbrush. They have slightly undulose extinction, and appear to be made of poorly defined fibres." Folk's illustration (his fig. 84B) shows a remarkable similarity with Plate V, figs. 21, 22 and 23 of Calvet et al. (1975). The latter figure illustrates rhizocretions surrounded by structures considered analogous to Microcodium (b).

Harbaugh (1961), in a discussion on calcite fabrics in late Paleozoic limestones from Kansas, Texas and New Mexico, established four specific types of visibly crystalline calcite. He suggests that his 'blade calcite', characterized by tapered, blade-shaped crystals bunched in flowerlike aggregates, probably formed by recrystallization under mild shearing stresses. The photomicrograph illustrating blade calcite (his Plate 1B, p.99) is alarmingly similar to Ancient Microcodium. No plausible explanation is given as to how mild shearing stresses could produce this form; perhaps a closer examination at the stratigraphic horizon from which this sample was taken might lead to the discovery of a former Microcodium-attacked subaerial exposure surface. The observation that Harbaugh's (op.cit) blade calcite shows a close resemblance to Microcodium was noted independently by Mišík (1968).

With such limited data it is not the intention here to reinterpret the above citations. They are pointed out only to give Microcodium a hearing before sentence is passed or deferred regarding unusual calcite fabrics.

Geological Importance

The chronological and stratigraphical importance of Microcodium is well established in the French geological literature. Correct recognition allows precision of correlation and is equally effective in application to sedimentological studies. As already indicated, Microcodium is intimately related to a land surface, which, by definition is a disconformity and represents a time-equivalent horizon marker. Thus, the presence of in situ Microcodium indicates terrestial conditions, and may provide evidence for subaerial exposure in essentially marine lithofacies.

An origin associated with root systems necessitates the presence of a soil cover. Therefore, Microcodium may be used as a criterion for recognition of palaeosols. Soil formation, itself, requires a cessation or pause in sedimentation sufficiently long to allow pedogenetic processes to act on a given substrate. A prerequisite for the development of Microcodium appears to be a lime-rich soil.

Petrographic analysis demonstrates that Microcodium not only modifies or obliterates pre-existing textures but provides a potential source for centimicron-sized detrital calcite grains in reworked sediments. Thus, the cumulative effect of Microcodium on substrate may provide valuable clues that assist in palaeoenvironmental reconstructions.

Summary and Conclusions

From samples of calcrete collected in the western Mediterranean, calcite grains showing atypical fabrics have been recorded. A review of the literature indicates that such grains have been designated Microcodium, a hypothetical organism considered by early investigators to be possibly algal in origin. More recently, several workers have presented models which, although considering *Microcodium* to be the result of microbial activity, favour fungal, actinomycete, or bacterial interference. This study presents a new model based on petrographic examination of Eocene to Recent samples of *Microcodium*. Cumulative evidence, interpreted in the light of modern plant-soil ecosystems, suggests a mycorrhizal origin for *Microcodium*. The significant points resulting from this study are summarized as follows:

(1) *Occurrence*. Calcrete samples collected from mainland Spain and the island of Ibiza, Balearics, reveal the presence of *Microcodium* grains constituting up to 43% of the rock by volume. The occurrence of *Microcodium* on Ibiza has not been previously documented.

(2) *Age*. Stratigraphical, palaeontological and lithological relationships indicate the presence of significant quantities of *Microcodium* in the Eocene and Pleistocene. The existence of *Microcodium* in the Recent is reported here for the first time.

(3) *Unusual fabrics*. Preservation of fine detail in Pleistocene and Recent samples, as revealed by SEM, portrays an exceedingly complex ultrastructure. The presence and subsequent calcification of microtubules, filamentous structures, radiating pore systems within grains, and protuberances, pits and raised borders on grain surfaces give a somewhat bewildering array of calcite fabrics when viewed in thin section.

(4) *Ancient versus Recent Microcodium*. Sufficient details are retained in Ancient *Microcodium* to allow fruitful comparisons with Recent samples. Their origins are considered to be homologous.

(5) Origin. Previous investigations regarding the origin of Microcodium are outlined. New field and petrographic data are at variance with earlier studies and have led to the formulation of a new model of formation. Microcodium is reinterpreted as being the result of calcification of mycorrhizae, a symbiotic association between fungi and cortical cells of roots.

(6) Geological importance. Correct recognition of Microcodium has wide application in terms of environmental, stratigraphical and palaeoecological studies. Emphasis is placed on Microcodium being a pedological feature and, thus, a valuable criterion for the recognition of the existence of a palaeosol.

(7) Scope and limitations. It is hoped that this study will at least provide an introduction to those unfamiliar with this potentially useful diagenetic 'whim of nature' and lead to a search for a better understanding of distribution, environmental parameters and diagenetic processes. Refinement is required to clarify many poorly understood but fundamental details resulting from this study. Such progress can be achieved only by an interdisciplinary approach.

CHAPTER SIX - COMPOSITION

INTRODUCTION

General Statement

Calcretes are composed dominantly of calcium carbonate with a world mean value of 79.2 %wt $CaCO_3$ (Goudie, 1972b). The second most important constituent of calcrete is silica, which averages 12.3 %wt for over 300 published and unpublished analyses (Goudie, 1972b, 1973). Silica, occurring as amorphous silica and detrital grains, comprises the bulk of the insoluble residues after digestion of the acid-soluble fraction. Additional but minor components in calcretes include terrigenoclastic grains other than quartz, clay (layer lattice) minerals, hydrous oxides and organic matter. Laboratory analyses of material collected for this study were carried out to evaluate the composition of Quaternary calcretes from the western Mediterranean.

MINERALOGY

Methods

Using optical microscopy, artificial staining techniques and powder X-ray diffraction, the distribution and mineral composition of the carbonate and non-carbonate fractions were determined. Additional information was gained on the basis of crystal habit as seen by SEM.

For details of techniques and methods used, see Appendix.

Non-Silicates

Carbonates

Artificial staining techniques (Feigl, 1943; Dickson, 1966; Davies & Till, 1968; Winland, 1971) proved to be the quickest and most reliable way of determining the mineralogy and relative distributions of the carbonate minerals in a given sample. Low magnesian calcite (LMC) was found to be volumetrically the most important carbonate. Indeed, LMC forms 100% of the carbonate fraction in most samples studied here. Other carbonate minerals were found to be minor, except in Pleistocene and Holocene aeolianites from Ibiza where aragonite and high magnesian calcite (HMC) assumed some importance. However, carbonate minerals such as aragonite, HMC and dolomite, were found to be volumetrically significant only in the detrital fraction. For most samples studied here, LMC was found to be the only authigenic carbonate mineral. The relative percentages of LMC, HMC, aragonite were found to be dependent on the composition and type of host material. No meaningful results could be obtained by quantifying the amount of various carbonate minerals present in a given profile because of the mineral heterogeneity of host materials.

Bulk mineralogy of 22 powdered calcrete samples was determined qualitatively by X-ray diffraction. Again, LMC was found to be the major carbonate mineral present. Dolomite and aragonite were detected in some samples but petrographic thin sections of the same sample showed that these minerals occurred as detrital grains. No shift in the d-spacing was recorded on powder X-ray diffraction films, indicating that HMC was absent from these samples.

Staining, using Alizarin red S and potassium ferricyanide combined (Dickson, 1966), indicated that over 90% of the calcite is non-ferroan. This suggests that precipitation took place under aerobic conditions (Evamy, 1969). Such aerobic conditions occur in subaerial vadose diagenetic environments. Ferroan calcite, on the other hand, is indicative of alkaline but reducing conditions. The minor quantities of ferroan calcite were detected mostly within glaebules, indicating that local anaerobic conditions occurred during their formation.

Braithwaite (1975), in his discussion on the mineralogy of terrestial sediments from Aldabra, stated (p. 28) that "virtually all of the cements are calcitic and the greatest interest lies in the allochemical components." This statement has some relevance to materials studied here, although minor non-calcitic authigenic minerals also have been recognized. It is to these minerals, together with detrital and inherited minerals of interest, that the remainder of this section will be directed.

Halides

Halite crystals were observed in several samples using a hand lens or binocular microscope and reflected light. Halite needles, 1 - 5 microns diameter and up to 200 microns long were recorded also by SEM (Plate 37d-f). The mineralogy of these needles was determined by flame photometry, by immersing samples in distilled water and by their saline taste. Some samples were collected near the present coastline; the halite in these samples was thought to have precipitated from evaporating seawater trapped in pores. However, a few samples containing halite were collected tens of kilometres from the present coastline. Unless salt spray was carried such distances, evaporating seawater was not the source for halite in these inland samples. It is known that concentration and precipitation of highly soluble salts occur in semi-arid areas where evaporation rates are high (Runnells, 1969;

Goudie, 1973; Cooke & Warren, 1974). Netterberg (1971) indicated that highly soluble salts were important in the early stages of calcrete development. Hunt (1972) suggested that soil profiles showing increasingly soluble salts in their upper parts indicate evaporitic conditions. The observed needle crystal habit lends support to the idea put forward here that the precipitation of halite needles in calcrete samples indicates precipitation from evaporitic soil waters.

Calcium sulphates

Only three samples were found to contain traces of calcium sulphate minerals. Isolated gypsum crystals and anhydrite were found in profiles underlain by Triassic evaporites. The presence of anhydrite and gypsum owe their origin to inheritance, that is, they are relic minerals. Authigenic calcium sulphates were not detected in any of the samples examined in this study.

Lattman & Lauffenberger (1974) suggested that locally very thick or rapidly deposited calcretes in Nevada may have been derived, in part, from gypsum which reacted with organic matter and bacteria to produce larger amounts of calcite than would have been otherwise carried in solution. These deposits lie downwind of extensive outcrops of gypsiferous rocks. Even if the mechanism proposed by Lattman & Lauffenberger (1974) proves to be correct for the materials which they have studied, I believe that it is only of local importance. Gypsum is not a characteristic mineral of calcretes in general (Goudie, 1973; Watts, 1977; this study).

Calcium oxalates

Calcium oxalate is an organic compound which is commonly found within plants (Arnott & Pautard, 1970). Oxalate crystals have been found in a wide variety of sites, including roots and shoots, leaves, wood and bark of vascular plants and within lichen thalli and fungal hyphae. For a review, see Arnott & Pautard (1970).

Crystals showing unusual optical properties were recognized within many Pleistocene and Holocene calcretes examined in this study. With the exception of two samples (p. 209), it was not possible to extract sufficient material for X-ray diffraction mineral determinations. However, following the procedure of Gurr (1965), spot tests were carried out on uncovered thin sections and polished slabs to detect calcium oxalate. Observation of the chemical reactions, by incident and transmitted light microscopy, indicated that calcium oxalate occurred in these samples. Petrofabric analyses of thin sections showed that calcium oxalate crystals occurred as Microcodium grains (p.209) and within lichen stromatolites as products of lichen synthesis (p. 267). The presence of in situ calcium oxalate is indicative of plant life and, thus, provides valuable evidence to suggest that the enclosing sediment acted as a biological soil.

Hydrous oxides

Russell (1973) used the term hydrous oxides to include hydroxides, hydrous oxides and oxides of iron, aluminium and manganese when no particular form is specified. This usage is retained here for brevity. It is also used here as a convenient umbrella term of ignorance since hydrous oxides are difficult to identify by X-ray diffraction or optical methods. Individual crystals are generally too small to analyze and larger aggregates are usually composed of admixtures of various compounds.

The problems of identifying hydrous oxides were overcome, in part, by making replicas of thin sections etched with acetic acid as carried out by Lees (1958). This method leaves insoluble residues standing in their original positions so that their distributions are readily seen. Various microchemical stains and solvents were used on prepared thin sections to help identify the *in situ* residues.

Thin sections, prepared according to the method of Lees, were boiled in 30% NaCH for 20 min. The red-brown natural staining, which is characteristic of the insoluble residues in collected samples, showed no colour change with this treatment. It was deduced that ferric oxides and/or hydroxides were responsible for the red-brown pigmentation rather than organic matter. Russell (1973) reported that ferric hydroxide is not a normal constituent of aerated soils. Most calcrete profiles examined in this study are well aerated today but whether they have always maintained this condition cannot be determined. It has been suggested that ferrous ions were mobilized during wetter periods and deposited as ferric oxides in drier conditions (Ruellan, 1967).

In a pilot experiment carried out in this study, hand specimens were immersed in distilled water and then dried and heated on a hotplate to 350°C. Some of the samples were initially pure white but turned red-brown or patchily black on heating. The colour changes from white to red-brown were attributed to oxidation of iron; the patchy blackening suggested that charring of organic matter had taken place.

Black dendritic impregnations were recognized in many hand specimens and thin sections. Petrographic observations suggested that these impregnations were iron and/or manganese oxide encrustations on organic filaments rather than being simply inorganic mineral stains. Addition of 30% H_2O_2 to these dendrites caused an immediate reaction which continued until the dendrites had disappeared. Observation of this reaction under a petrographic microscope revealed that the organic filaments were translucent but they, too, were chemically reactive in hydrogen peroxide and were oxidized within a few minutes. Organic matter and manganese oxides are soluble in hydrogen peroxide (Brewer, 1964; Blokhuis *et al*., 1968). The above observations suggest that the black dendrites are manganese oxide-encrusted organic filaments.

Silicates

Silica minerals

Silica was recorded in three forms, detrital quartz grains (skeleton grains), amorphous silica within the s-matrix and authigenic crystalline quartz (chalcedony and microcrystalline quartz). The relative abundance of these forms is difficult to assess for several reasons. Detrital centimicron-sized and decimicron-sized quartz grains show varying degrees of corrosion and replacement by calcite. Detrital micron-sized grains and relic fragments of quartz are difficult to identify by petrographic methods when they occur embedded in a fine crystic calcite plasma. Similarly, amorphous silica cannot be detected by petrographic observation alone. Authigenic silica cements were difficult to recognize, not only because of their poorly resolvable optical properties but because of their rarity in samples studied here.

In order to overcome the difficulties of recognizing the various forms of silica, other than detrital centimicron-sized quartz grains, several simple techniques were adopted to help identify the type and distribution of silica minerals present. One method, modified from Schmidt (1965) makes use of the shift in birefringence colours by using optic plates inserted in the petrographic microscope. Standard petrographic thin sections were viewed between crossed nicols with a gypsum plate inserted below the analyzer and a mica plate inserted above the polarizer. The fast directions of the plates were oriented parallel with each other, giving an additive effect. Whereas first order minerals show second and third order colours, the colours of carbonate minerals remain unchanged because of their high birefringence. This technique also facilitated recognition of the porosity distribution in thin sections.

Another method employed to map the distribution of silica and other acid-insoluble constituents was one suggested by Lees (1958) and has been discussed elsewhere in this study (p. 239).

Because amorphous silica is not readily identified optically, spot tests for silica were carried out following the procedure of Feigl (1943). Samples showing hardnesses greater than 4 on the Mohs' scale were selected to determine whether the hardness was due to impregnated amorphous silica in the s-matrix. Hardnesses were determined by scratching samples with minerals of known hardnesses. Using this crude method, results revealed that a correlation existed between increasing hardness and increasing silica content. It was interesting to note that samples containing amorphous silica were restricted to hardpan horizons and that, if present, macrocrystalline quartz grains had been severely corroded. It is considered likely that released silica from corroded grains had been mobilized and reprecipitated in a disseminated amorphous form throughout the s-matrix, thus giving samples hardnesses greater than pure calcium carbonate.

Füchtbauer (1974), in his discussion on silificiation of sedimentary rocks, considered three groups of silicification, namely surface, early diagenetic and late diagenetic silicification. He noted that many examples of surface silicification had been reported from deserts. Chalcedony commonly occurs in areas subjected to frequent and intensive evaporation. Thus, the presence of silica in calcrete hardpans may be indicative of conditions of increasing aridity. In this connection, one hardpan sample of Pleistocene age from Ibiza was found to contain pores lined with quartzine which Folk & Pittman (1971) interpreted as being indicative of evaporitic conditions. However, as a concluding remark in this section, it is pointed out that authigenic silica minerals are noteworthy because of their rarity, not because of their abundance.

Clay minerals

Goudie (1973, p.25) reported that little work has been done on clay minerals in calcretes. However, recent work by Nahon (1976) has increased our knowledge in this field considerably. Nahon has confirmed the findings of earlier workers (Vanden Heuvel, 1966; Gile, 1967; Millot, Paquet & Ruellan, 1969; Gardner, 1972) by indicating the importance of the palygorskite clay mineral group (palygorskite, attapulgite and sepiolite) in calcretes.

Other clay minerals recorded in calcretes include illite, montmorillonite, kaolinite and chlorite (Aristarain, 1970). However, the presence or absence of these minerals is dependent on the mineralogy of the host material, the hydrological regime, the age and stage of development of the calcrete and the intensity of diagenetic processes. Gardner (1972), for example, found that attapulgite is the dominant clay mineral throughout calcrete profiles developed on the Mormon Mesa, Nevada. Minor amounts of kaolinite and illite also were found. However, montmorillonite was not detected in the calcrete even though the unaltered host material contains appreciable quantities of this mineral. Aristarain (1970) found that montmorillonite and kaolinite increased systematically downwards from the calcrete surface into unaltered host material, whereas illite showed an increase upwards.

Clay minerals in Quaternary calcretes from the western Mediterranean are volumetrically insignificant. Ten samples of calcrete hardpan were decalcified by acid digestion. Insoluble residues were sieved, dried and weighed. The clay-sized fraction was found to be less than 5% by weight of the total rock for all samples. Because of the small amounts (generally less than 1 g), identification of the constituents proved extremely difficult. However, sufficient material was obtained for X-ray diffraction determinations. The results indicated that illitic and montmorillonitic* clays were present. These determinations corroborated the results obtained by artificial staining techniques for the identification of clay minerals (following a method given by Allman & Lawrence, 1972). Palygorskite was not detected in these samples but other samples examined by SEM contained fibrous clay minerals which are interpreted as palygorskite (Plate 45f). The orientation and loose packing of the fibres suggest that they are authigenic cutans rather than mechanically deposited clay cutans. Plate 45f shows fibrous palygorskite (?) on the surfaces of euhedral and subhedral dolomite grains. Weaver & Beck (1977) have recorded

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*Montmorillonitic clays swell and shrink on wetting and drying respectively. This phenomenon may be responsible for circum-granular cracking porosity.

a similar clay-dolomite configuration in samples from Miocene peri-marine sediments from southeastern USA. They noted that if Mg/Ca>1, the ratio in the solution would increase as dolomite grows (assuming direct replacement of calcite is not a major factor). If the ratio becomes high enough, and sufficient dissolved silica is present, the formation of palygorskite would be favoured.

N. L. Watts (oral presentation, Leeds, 1977; Shell, Risjwijk) suggested that high magnesian calcite (HMC) was an important, early diagenetic cement in Quaternary calcretes from Botswana. He suggested that the release of Mg^{2+} during the transformation from HMC to LMC may give rise to the formation of magnesian-rich clays such as palygorskite and sepiolite. Unfortunately, my studies lend no support to this hypothesis. Early HMC cements have not been recognized and precursor fabrics which suggest a former HMC cement cannot be used with confidence in view of the latitude in crystal habits of LMC vadose cements within calcretes.

CHEMISTRY OF THE ACID-SOLUBLE FRACTION

Introduction

Since calcretes are composed dominantly of low magnesian calcite and are thus mineralogically homogeneous, wet chemical analyses were undertaken to detect possible changes in the amount and distribution of major and minor elements within the acid-soluble fraction (carbonates and minor amounts of halites and calcium sulphates).

The conditions and processes that control the composition of carbonates are complex (see Wolf, Chilingar & Beales, 1967 for a review). Physicochemical factors that influence or control the composition of carbonate minerals include composition of the solution, concentration of ions present in the solution, temperature and pressure, Eh and pH conditions and rates of reactions. Superimposed on these factors may be a host of, as yet poorly understood, organic influences.

The purpose of this section is to present data on the composition of the authigenic component of calcretes, that is, the composition of pedodiagenetic calcite. However, because the inherited components of the host material cannot be separated from authigenic components, the following analytical results also indicate the composition of the acid-soluble fraction of the original host materials.

Materials and Methods

Materials

Five calcrete profiles, developed in host materials of widely differing compositions, were chosen for chemical analyses. In addition, a single rhizolith (sample Z.1/2) was selected for a detailed chemical analysis. Brief descriptions of the selected samples are given as follows:

Profile T.11 Segur de Calafell, NE Spain. Host material : Pleistocene alluvial fan sediments consisting dominantly of Mesozoic limestone lithoclasts.
T.11/1 laminar hardpan
T.11/2 sheet calcrete
T.11/3 glaebular calcrete. White, chalky, vertically elongate nodules in a red-brown silt s-matrix
T.11/6 alluvial fan gravel with a chalky s-matrix.

Profile M.2 Garrucha SE Spain (Plate 8b).
M.2/1 laminar hardpan
M.2/4 chalky horizon
M.2/5 transitional horizon
M.2/6 vitric tuff host material.

Profile A.16 Berja - Adra, SE Spain.

A.16/1 recemented laminar calcrete breccia

A.16/2 sheet calcrete

A.16/5 transitional horizon consisting of fanglomerate in a chalky s-matrix

A.16/6 alluvial fanglomerate.

Profile Z.20 Santa Eulalia del Rio, Ibiza (Plate 4).

Z.20/2 sheet calcrete

Z.20/3-4 glaebular-chalky calcrete

Z.20/5 transitional horizon

Z.20/6 andesite host material of Triassic age.

Profile Z.21 Calo d'es Pou d'es Lleo, Ibiza (Plate 3).

Z.21/2 sheet calcrete

Z.21/3-4 glaebular-chalky calcrete

Z.21/5 transitional horizon

Z.21/6 diorite host material of Triassic age.

Rhizolith Z.1 Punta de Ses Briades, Ibiza (Plate 47).

Z.1/A centre of rhizolith

Z.1/B chalky zone

Z.1/C outer cemented sheath

Z.1/D aeolianite host material of Upper Pleistocene (Tyrrhenian III) age.

Although sample Z.1 is not a calcrete profile, it has the characteristics of one. The centre of the rhizolith can be compared with a sheet calcrete horizon which contains abundant calcified roots; the chalky zone of the rhizolith is directly comparable with the chalky horizon; and the cemented sheath of rhizo-micritized aeolianite is analogous to a transitional horizon. The unaltered aeolianite is the host material. Thus, apart from a difference in scale, rhizoliths and calcrete profiles share many similarities, both in fabric and genesis. This point has been made previously by

Calvet _et al._, (1975). For the purposes of this section, rhizolith Z.1 is considered as representative of a calcrete profile developed in an aeolianite host material.

Methods

Determination of the elements in the acid-soluble fraction - - Major and minor elements in the rock solutions were determined by atomic absorption spectrophotometry (AAS) for CaO, MgO, SrO and MnO using a Pye Unicam SP 90 spectrophotometer. For a detailed discussion on operation, calibration and accuracy, see Raiswell (1973).

Total iron was determined by visible spectrophotometry using a Pye Unicam SP 600 series 2 instrument. Sodium was determined using an Evans Electroselenium Limited (EEL) flame photometer. Carbon dioxide was determined by weight loss on ignition (Dean, 1974) and measurement of liberated CO_2 following reaction with phosphoric acid (Bush, 1970).

Mean standard deviations for calcium and carbon dioxide determinations are ±4%. For magnesium, strontium, iron, manganese and sodium, errors are ±8% because of their smaller amounts. Data were recalculated on a residue-free basis (i.e. total soluble fraction = 100%). Further details of the methods are given in the Appendix.

Results

Calcium

By far the most important cation present in the acid-soluble fraction is calcium (Table 10, p.250). The maximum recorded here of 53.3 %wt CaO agrees closely with the figure quoted by Graf (1960) for caliche from Mexico. Goudie (1972b) quoted a world mean value of 42.62% (based on 345 analyses). However, because of the heterogeneity of host materials and the change in amount of calcium carbonate within a single profile (Table 9, p. 249), mean values have not been calculated for this study.

As to be expected, there is a high positive correlation between CaO and CO_2 values. Calculated $CaCO_3$ values are inversely proportional to the amount of insoluble residues. Carbonate values of indurated parts of sampled profiles vary from 44 - 99 %wt. (Table 9). Calcrete profiles which have developed within non-carbonate host materials (profiles M.2, Z.20 and Z.21) show a systematic decrease downwards in their $CaCO_3$ values. Profiles T.11 and A.16, which have limestone-rich and dolomite host materials respectively, show no systematic change in carbonate content, that is to say, they have complex $CaCO_3$ and $MgCO_3$ gradients. The minimum carbonate value for profiles T.11 and A.16 is greater than 80%; for the rhizolith Z.1, carbonate contents exceed 94% (Table 9). The high carbonate content of 90.8 wt% carbonate for sample A.16/6 is a reflection of the mineralogy of the host material; the host material was found to be almost pure dolomite by petrographic methods.

Magnesium

The magnesium content of the acetic acid-soluble fraction varies from 0.19 - 11.39 wt% Mg^{2+}. High magnesian calcite (greater than 10% $MgCO_3$) was found only within marine allochems in aeolianite materials by petrographic methods (Winland, 1971; see Appendix). The relatively high value of 11.4 wt% Mg^{2+} in sample A.16/6 is because the mineralogy of the host material is dolomite. Dolomite is minor or

TABLE 9

ANALYSES OF CARBONATE AND ORGANIC CARBON BY LOSS ON IGNITION (DEAN, 1974)

Sample no.	Depth m	Carbonate[x]	Organic[*] carbon wt%	(Dean,1974) carbon dioxide wt%	(Bush,1970) carbon dioxide wt%	Insoluble residue %
Profile T.11						
1	0.20	95.9	0.1	42.2	42.6	3.5
2	0.45	96.5	0.2	38.0	37.9	3.4
3	1.75	98.4	0.6	42.6	41.6	1.6
6	2.00	97.1	0.1	41.9	40.8	2.8
Profile M.2						
1.	0.15	44.2	0.7	16.1		57.8
4	0.70	43.6	0.7	16.4		56.4
5	1.00	30.7	0.5	12.8		69.3
6	18.00	8.0	0.5	2.6		91.1
Profile A.16						
1	0.20	85.7	0.2	37.5	35.8	14.3
2	0.30	81.6	0.1	35.8	34.7	18.0
5	1.20	92.2	0.1	43.3	43.1	7.6
6	1.60	90.8	0.1	44.1	44.2	8.1
Profile Z.20						
2	0.50	91.0	0.3	38.8	40.0	8.0
3-4	1.50	82.7	0.2	35.3	33.5	17.2
5	2.20	19.2	0.3	8.7	9.4	80.7
6	3.50	5.3	0.1	2.9	3.2	94.7
Profile Z.21						
1	0.15	94.8	0.4	40.3		5.2
3-4	1.00	88.0	0.4	37.1		12.1
5	10.00	20.6	0.3	5.8		79.5
6	15.00	19.0	0.3	6.8		81.1
Rhizolith Z.1						
A	Centre	99.6	0.2	n.d.		-
B	0.01	99.7	0.1	n.d.		-
C	0.02	99.1	0.1	n.d.		-
D	0.03	94.3	0.1	n.d.		4.0

n.d. not detected

x Assuming all of the 550 - 1,000°C loss was due to CO_2 evolved from carbonate

* Assuming all of the 0 - 550°C loss was due to ignition of organic carbon.

TABLE 10

ANALYSES OF THE ACETIC ACID-SOLUBLE FRACTION

Sample no.	%CaO	%MgO	%SrO	%FeO	%MnO	$\%Na_2O$	$\%CO_2$	% Insoluble residues	% Total
Profile T.11									
1	52.7	0.30	0.01	0.01	0.01	0.13	42.2	3.5	98.8
2	52.4	0.31	0.01	0.02	n.d.	0.15	42.0	3.4	98.3
3	53.1	0.39	0.02	0.01	0.01	0.13	42.6	1.6	97.8
6	52.3	0.28	0.01	0.01	0.01	0.15	41.9	2.9	97.6
Profile M.2									
1	21.8	0.59	0.04	0.01	0.01	0.18	16.2	58.8	97.6
4	21.8	0.60	0.03	0.91	0.01	0.23	16.4	59.4	99.4
5	15.6	0.41	0.02	0.92	0.01	0.12	12.8	69.2	99.3
6	2.3	0.17	0.01	0.03	0.02	0.13	2.3	93.8	98.7
Profile A.16									
1	43.4	3.08	0.02	0.06	0.03	0.15	37.5	14.3	98.4
2	38.9	4.91	0.04	0.01	0.02	0.13	35.8	18.0	97.8
5	49.6	3.00	0.03	0.03	0.01	0.17	40.4	7.6	100.7
6	29.4	17.19	0.05	0.29	0.05	0.15	44.1	9.0	100.3
Profile Z.20									
2	47.6	0.66	0.04	0.02	0.01	0.27	38.8	11.9	99.1
3-4	45.0	0.52	0.01	0.01	0.02	0.15	35.3	17.2	98.2
5	9.7	0.22	0.01	0.01	0.03	0.13	8.8	80.7	99.5
6	2.3	0.12	0.02	0.98	0.05	0.13	2.9	93.8	100.2
Profile Z.21									
2	49.9	0.76	0.05	0.03	0.01	0.39	40.3	8.1	99.6
3-4	46.9	0.91	0.05	0.02	0.01	0.26	37.1	13.0	98.2
5	9.0	0.21	0.01	0.04	0.01	0.21	8.8	80.4	98.7
6	8.6	0.23	0.01	0.01	0.04	0.53	6.8	83.0	99.5
Rhizolith Z.1									
A	52.2	1.19	0.18	0.03	n.d.	0.21	47.6	0.4	99.8
B	53.3	1.10	0.10	0.02	n.d.	0.19	44.7	0.3	99.2
C	52.2	1.66	0.12	0.03	0.01	0.04	43.9	0.9	98.8
D	50.6	1.32	0.01	0.02	0.01	0.02	44.4	5.7	97.2

absent in other profiles which have magnesium values of generally less than 2.0 wt% Mg^{2+}.

Strontium

Strontium values vary from 100 - 1,500 ppm for the acetic acid-soluble fraction (Table 11, p. 252). The higher values (greater than 1,000 ppm) occur in sample A.16/6 which is a Triassic dolomite and in sample Z.1 which is a rhizolith in aeolianite material of Pleistocene age. In other samples, known to be LMC by petrographic examination, Sr^{2+} contents vary from 100 - 910 ppm. These relatively low Sr^{2+} values and correspondingly low Sr/Ca ratios are typical of calcites precipitated in the meteoric phreatic or vadose diagenetic environment. In such environments, calcite typically has Sr^{2+} values of 400 ppm or less (Bathurst, 1975).

Total iron

In samples studied here, iron contents vary from 75-7,130 ppm. Values quoted by Graf (1960) for total iron in caliche from Mexico and for 'average limestone' are 0.85 wt% and 0.54 wt% respectively. Computed values in samples analyzed in this study vary from 0.009 wt% to 0.975 wt% total iron. In a single profile, the plotted gradient for total iron is complex, that is, the gradient shows no systematic increase or decrease in one direction. However, the iron content shows a positive correlation with the amount of insoluble residues. As the insoluble residue content increases, there is an increase in the iron content within the acetic acid-soluble fraction. A similar relationship exists between the insoluble residue content and the manganese content. Irion & Müller (1968), from their analyses of calcareous tufa deposits from the Schwabische Alb, Germany, found the

TABLE 11

CATION CONTENT IN THE ACETIC ACID-SOLUBLE FRACTION

Sample no.	%Ca	%Mg	Sr ppm	Na ppm	Fe ppm	Mn ppm
Profile T.11						
1	39.1	0.19	120	1,320	110	60
2	38.8	0.20	130	1,490	220	n.d.
3	38.5	0.24	320	1,270	80	30
6	38.5	0.21	200	1,370	110	70
Profile M.2						
1	35.2	0.36	690	4,000	290	220
4	35.7	0.83	670	5,180	90	230
5	36.2	0.81	490	4,280	490	250
6	20.4	1.25	100	16,060	3,780	1,870
Profile A.16						
1	36.2	2.18	380	1,710	730	350
2	33.9	3.61	820	1,550	170	250
5	38.4	1.96	630	1,830	310	90
6	23.1	11.39	1,000	1,200	3,490	580
Profile Z.20						
2	37.0	0.43	680	2,910	270	150
3-4	38.8	0.38	230	1,790	160	270
5	35.8	0.68	100	6,520	770	1,480
6	30.7	1.36	380	24,640	7,130	9,530
Profile Z.21						
2	37.6	1.36	910	4,170	330	40
3-4	38.1	1.03	910	2,980	270	70
5	20.7	0.6	650	4,030	1,060	280
6	32.1	0.14	90	28,050	720	2,100
Rhizolith Z.1						
A	37.5	0.72	1,500	2,070	350	n.d.
B	38.2	0.66	900	1,990	280	n.d.
C	37.6	1.00	1,060	400	360	60
D	38.3	0.87	490	190	280	90

same relationships. Their suggestion that the iron and manganese were derived primarily from oxide and hydroxide compounds may have relevance to this study.

Manganese

Manganese contents vary from undectable to 9,500 ppm (Table 11, p. 252). Manganese contents are extremely low, 100 ppm or less, in profiles developed in limestone host materials. Profile A.16, developed in a dolomite host material, shows slightly higher values (90 - 580 ppm). In profiles developed in non-carbonate host materials, there is a systematic and substantial increase in the manganese content downwards. Profile M.2, developed in vitric tuff, shows an increase downwards from 220 ppm to 1,870 ppm; profile Z.20 developed in andesite, shows an increase downwards from 150 ppm to 9,530 ppm; and profile Z.21, developed in diorite, shows an increase downwards from 40 ppm to 2,100 ppm. However, even these relatively high values are low compared with published data. For example, using MnO wt% values in the total sample (Table 10, p. 250) instead of Mn ppm values of the acetic acid-soluble fraction, the maximum recorded value recorded in this study of 0.05 wt% MnO is lower than the 0.14 MnO wt% mean value quoted by Goudie (1972b) for 13 calcrete samples.

Sodium

From electrical conductivity measurements, (Goudie, 1973) concluded that water-soluble salt levels in calcretes are usually low. However, Goudie recorded anamolously high values in samples collected from coastal sites and around margins of saline depressions. Sodium values in excess of 10,000 ppm were measured by flame photometry in some of my samples collected from coastal sites. It is likely that precipitation of halite from salt spray is responsible for these high values in some of these samples, but not necessarily all of them. In this respect, the sodium values measured in samples Z.1/A-D are worth closer inspection.

The centre of the rhizolith, sample Z.1/A, has a sodium content of 2,070 ppm. The sodium content decreases outwards to a value of 190 ppm in the unaltered aeolianite host material. The sample was collected within 50 m of the present-day coastline. If evaporation of seawater trapped in pore spaces is responsible for the sodium present, then one would expect to find sodium values in the aeolianite equal to those of the rhizolith. This is not the case, however. The difference in porosity is not an adequate explanation to account for the difference in sodium values; the porosity of the aeolianite is greater than the porosity of the rhizolith. If porosity differences were responsible for the difference in sodium content, sodium values should be higher, not lower, in the surrounding aeolianite.

Profile M.2 shows a high (16,000 ppm) sodium content. The profile is over 10 km from the present coastline. Profile T.11 is within 1 km of the present coastline; sodium values in this profile are less than 1,500 ppm. It might be argued that wind direction may account for these differences in sodium contents; marine aerosols may be carried many kilometres inland in some areas, whereas offshore winds may predominate in other areas. Alternatively, profile M.2 may be near a saline depression or salt pan.

The above explanations to account for anomalous values are considered unlikely. No evidence was found to suggest nearby salt pan accumulations in the area of M.2. In the area of T.11, strong land-sea breezes change direction daily. For sample Z.1, salt spray does not account for the relatively low sodium values in the coastal aeolianite and higher values in the rhizolith. Similarly, fluctuations in the sea level during earlier periods of the Quaternary cannot account for these differences. Marine aerosols may have been the original source of the sodium but additional factors need to be considered to explain varying concentrations of sodium in a given profile. I suggest that relatively high (greater than 1,000 ppm) sodium values indicate precipitation of halite and/or sodium-rich calcite induced by evaporation or evapotranspiration. Profiles M.2, Z.20 and Z.21 have downward increasing sodium contents. This gradient suggests that downward moving sodium-rich solutions lost water at depth by evapotranspiration or upward moving capillary waters from sodium-rich ground water were evaporated. Both mechanisms would lead to the precipitation of halite and/or sodium-rich carbonates. Similarly, concentration of sodium as a result of evapotranspiration is a suggested mechanism to account for the higher sodium content in the centre of the rhizolith than in the surrounding aeolianite. If this last suggestion proves to be correct, it indicates that the formation of the rhizolith took place during the life of the plant which was responsible for this biogenetic carbonate structure.

Summary and Conclusions

The values obtained for CaO and MgO are related directly to the amount of carbonate present in the sample. MgO wt% values are less than 1.0 for all samples, except those of profiles A.16 and Z.1.

In A.16, values of 3 - 17 wt% MgO are related to the amount of dolomite derived from the host material. In Z.1, magnesium is contained within HMC coralline algae and foraminifera. Strontium, total iron and manganese values are low (less than 10,000 ppm) and measured values are typical of meteoric carbonate cements. Sodium values are higher than normal marine and meteoric phreatic carbonates. I suggest that values greater than 2,000 ppm for sodium in the acid-soluble fraction indicate precipitation of halite and/or sodium-rich calcite from evapotranspiring meteoric or marine vadose waters.

The results obtained are characteristic of calcite which precipitated in the subaerial vadose diagenetic environment.

ORGANIC MATTER

Introduction

If calcretes are considered to be disintegrated rock and accumulation of calcium carbonate within pore spaces, then physicochemical weathering and calcite precipitation are the only requirements for the formation of calcrete deposits. However, the concept that physicochemical weathering alone is an adequate explanation for soil formation is no longer upheld. Russian soil scientists (see Jacks, 1953 for a review) were the first to emphasize that soil genesis should be considered as a combination of weathering and certain additional changes resulting from interactions between living organisms and weathered rock. Similarly, my concept of calcrete genesis concerns not only weathering and lithification of regolith but includes also the interactions between living and dead organisms and weathered host materials. Thus, it would not be unreasonable to find evidence which indicates former organic activity within calcrete deposits. Biogenetic structures within calcretes indicate such activity and have been discussed elsewhere (p. 158). In addition, non-skeletal plant remains and unidentifiable organic residues also have been found in calcrete deposits and are documented below.

Methods

In standard petrographic thin sections, organic matter is difficult to identify unless it is particularly abundant. Decalcification of uncovered thin sections and examination of the acid-insoluble residues under the petrographic microscope were employed to help overcome difficulties of identification. Insoluble residues also were examined from acidified powdered rock samples. Organic residues were separated from inorganic residues by centrifuging and filtering (see Appendix for details). In samples containing insufficient material for recovery by centrifuging and filtering, organic constituents were identified in the acidified solution under the binocular microscope. Organic constituents were removed with a steel needle, washed, dried and mounted on a glass slide with molten glycerine jelly containing Gentian Violet. Some organic residues were tested for lignin, cellulose and chitin following procedures outlined by Gurr (1965). In addition, etched and decalcified petrographic thin sections and etched polished slabs were treated with various stains and dyes to map out the distribution of organo-mineral complexes _in situ_ (see Appendix for details).

Results

Vascular plant remains were recognized in decalcified samples taken from profiles showing no signs of higher plant activity today. Maximum dry weight of organic carbon was found to be 0.7% by the ignition loss method (Table 9, p. 249). As can be seen from Table 9, there does not appear to be a relationship between depth or type of horizon and the amount of organic matter.

Recognizable organic constituents included lignified plant fibres (Plate 77a), parenchymatous cell walls (Plate 77b), xylem vessels (Plate 77c, d) and root hairs (Plate 63). Palynomorphs (Plate 69) and calcified roots (Plates 49 - 53) also were recognized. Non-vascular plant constituents were found to consist dominantly of chitinous fungal hyphae (Plates 60a, 61a, 77e). Possible coccoid and algal remains also were found but loss of their internal structures prevented definite identification.

In samples collected from calcretized aeolianites of Pleistocene age from Ibiza, the freshwater diatom Asterionella was found to be abundant in the insoluble residues. Because their living environment is usually a lake or river, they are considered to be allocthonous components of the aeoliantes. Nevertheless, two points of interest are worthy of comment. Firstly, many appear to have suffered microbial attack (Plate 77f). Round (1965) gives a similar illustration of Asterionella infected by chytridaceous fungi. Secondly, whereas quartz grains in the enclosing aeolianite have been etched or corroded, the siliceous tests of Asterionella remain unaffected. I put forward the suggestion that the presence of an organic coating has protected Asterionella from chemical corrosion.

Other identifiable structures were recognized by SEM. Fungal and actinomycete hyphae were found to be particularly abundant in many samples. The possibility that some of these organic structures are later contaminants is not denied but is considered unlikely since most of them show signs of calcification. Similarly, rhizoliths (p. 158) and calcified faecal pellets (p.189) show complex organo-mineral associations. Because of the tendency to calcification, biogenetic carbonate structures are formed.

Discussion

Recent marine carbonate mineral surfaces are coated with 0.1 - 1.5 mg C/m^2 which is the amount of organic matter needed to form a monomolecular layer (Suess, 1970). SEM observations of fractured samples collected for this study indicated the presence of carbonate threads, less than 0.01 microns wide, in many samples. Such small particles, assuming they are calcite, should recrystallize or go back into solution within a few minutes of their formation (Chave & Schmalz, 1966). The presence of a monomolecular organic layer on the surfaces of these particles may be responsible for their stability. If so, organic matter within calcretes may have a significant influence on diagenetic processes. In this connection, it is worth reiterating that organisms are of paramount importance in the formation of calcretes; the resulting biogenetic carbonate structures provide valuable criteria to help recognize calcrete deposits.

CHAPTER SEVEN

RELATED PHENOMENA AND SUPERFICIALLY SIMILAR DEPOSITS

INTRODUCTION

As with most classifications, the black and white divisions are, in reality, lighter shades of darker pale. When does pedogenesis begin and when does diagenesis end? Where does one draw the line between pedogenesis and diagenesis? In the first part of this chapter, products which commonly occur in association with calcretes are discussed. Lichen stromatolites, herein defined for the first time, are common within many calcrete hardpans examined in this study. Lichen stromatolites form at the subaerial surface and mark the initial stages of pedogenesis. 'Case-hardened' carbonate crusts, likewise, form at the land surface but without the influence of biological interference. Lichen stromatolites and 'case-hardened' carbonate crusts are categorized as phenomena related, but not requisite, to calcrete formation.

In the second part of this chapter, prevalent misconceptions are exposed regarding deposits which show superficial similarities to calcretes. Criteria are given to help distinguish coniatolites, speleothems, travertine, freshwater tufa and algal stromatolites from pedodiagenetic calcretes. Finally, lacustrine carbonates are discussed briefly and an indication of outstanding problems of finding reliable criteria for environmental interpretations is given.

LICHEN STROMATOLITES

Introduction

The object of this section is to document the effect of lichens on subaerially exposed substrates, with particular reference to calcrete (caliche) hardpans, and to bring to the attention of geologists the potential usefulness of using lichen structures in making palaeoenvironmental reconstructions.

Many calcrete hardpans contain, or are composed of, microcrystalline calcite with a planar laminar fabric (Plate 82b). The origin of the laminae has been discussed widely (Kornicker, 1958; Gile et al., 1966; Hoffmeister, 1968; James, 1972; Goudie, 1973; Walkden, 1974; Read, 1974, 1976; Braithwaite, 1975; Harrison, 1977) but mechanisms of formation remain poorly understood. Opinions differ with regard to place of origin; some workers attribute planar laminations to surface phenomena, others favour precipitation of calcite at the base of a soil overlying a plugged horizon. However, no single mechanism accounts for all laminations within calcrete profiles (p.74); several unrelated processes can produce identical fabrics.

The common occurrence of lichens on exposed hardpan surfaces (Plate 78a, b) would, at first, seem to be incidental and of no significance to calcrete formation. However, a closer examination of the distribution of lichens and their effect on the colonized substrate in terms of textural and fabric changes has revealed several features which have some relevance to the formation and recognition of calcretes. Before these changes are documented a few comments on the general nature of lichens are given to provide a basis for subsequent discussion.

Biogenetic Aspects

Biological weathering

The concept that lichens play a fundamental role in the initial breakdown of rocks by mechanical disintegration and chemical decomposition is well established (Keller & Frederickson, 1952; Jacks, 1953, 1965; Krumbein, 1969, 1972; Jackson & Keller, 1970; Williams & Rudolph, 1974). Moreover, Robinson (1949) considered that accumulation of organic matter and other effects of biological activity initiate soil formation. Thus, lichens are important in two respects: firstly, they cause biophysical and biochemical transformations which generally accelerate the decomposition of minerals, although elemental uptake and synthesis of secondary minerals may prevent removal of some of the more mobile elements of the system. (Syers, 1964) and; secondly, accumulations of lichen and associated microbial organic matter become incorporated into the weathered detritus which leads to the formation of a primitive soil (protosoil or microsoil of some workers). These two processes, biological weathering and initiation of soil formation, proceed concurrently.

Outline of lichen structure (adapted from Hale, 1974)

Lichens are symbiotic associations of algae and fungi. The body of a lichen, or thallus, consists of a fungal component (mycobiont) which belongs to either the Ascomycetes or Basidiomycetes and an algal component (phycobiont) which may belong to any of the free-living algal groups. The fungal component, consisting of elongate cellular threads called hyphae, forms a vegetative thallus or mycelium. Algae are usually limited to a thin layer (gonidial layer) just below the surface of the thallus. The bulk of a lichen thallus consists of medullary tissue which is made up of loosely interwoven hyphae in a periclinal arrangement. Many lichen substances are deposited extracellularly in the medulla and on the upper surface of the thallus. The thallus also may be interspersed with calcium oxalate and/or calcium carbonate crystals deposited on the surface of the hyphae (Plate 78f).

Lichens which consist only of medulla and an algal layer have a granular or powdery appearance (Plate 78b). Most lichens are protected by a cortical layer which is sometimes pigmented. The surface of the cortex is commonly covered with a very thin (less than 100 microns) homogeneous cuticle. Some lichens have a whitish pruina (chalky powder) that may have a morphological origin as necrotic hyphal layers or may be an accumulation of carbonates and oxalates (Plates 79a, 80c).

Crustose lichens are attached to the substrate by the hyphae of the medulla and the contact is so intimate that lichen and substrate are virtually inseparable. The hyphae of endolithic lichens secrete lichen substances which dissolve minerals and, thus, hyphae have the ability to penetrate several millimetres into the rock. In many lichens, the thallus is anchored to the substrate by compacted strands of colourless or blackened hyphae that originate from the lower cortex. These structures are known as rhizines and may be unbranched (simple) or branched (squarrose, dichotomous). Hale (1974, p.22) noted "...to what extent rhizines are capable of transporting dissolved mineral or organic metabolites from the substrate to the thallus has yet to be established."

Fruiting bodies of lichens are known as ascocarps. Mature ascocarps are classified either as apothecia or perithecia on the basis of shape. Apothecia typically are open disc- or club-shaped structures with diameters generally between 0.5 mm and 10 mm (Plate 78b). Perithecia are flask-shaped structures contained within the lichen thallus (Plates 78c, 81a, c, d), usually less than 1 mm in diameter. The presence of endolithic lichens is indicated by the ascocarps which are visible at the surface (Plate 78a), the remainder being buried within the rock (Plates 78c, 81a). These reproductive structures contain spores (Plate 81c, d) which are classified according to their shapes and cell configuration. Spore sizes range from 1 - 10 microns, measured for the longest dimension.

Lichen physiology and substrate ecology

Although some subaqueous fungal-algal symbiotic associations have been recognized (Schneider, 1976), lichens are dominantly terrestial organisms. Most lichens occur at, or immediately below, the subaerial surface. The lichen-substrate relationship, itself, is extremely complex. Factors responsible for this complexity include macroclimate, water relations, texture and composition of the substrate, lichen physiology, structure and nature of attachment to the substrate and the presence or absence of other organisms. Krumbein (1969) claims that in humid climates lichens usually protect rocks from weathering, whereas in arid climates they are one of the most effective agents in rock decay and deterioration.

Physiologically, water absorption and water loss in lichens are entirely physical processes (Friedmann & Galun, 1974). Their water content is, therefore, subject to fluctuations governed by environmental conditions. Textural modifications of the substrate result from partial or total dissolution of minerals as a result of secretion of chelating agents and disintegration as a result of physical forces exerted during lichen growth. Penetrative boring by fungal hyphae further modifies pre-existing textures and increases porosity of the original substrate (Plates 78c, e, 79e, 80d, 81e, f). In this connection, Pomar _et al._, (1975) noted that penetration of lichen-fungal hyphae tended to follow planes of weakness, such as crystal boundaries and cleavage planes, indicating that modification is to some extent fabric selective. Fry (1922) and more recent workers (e.g. Syers, 1964) have noted that limestone immediately below lichen thalli frequently appears to be slightly laminated, more fractured and darker in colour than limestone at depth. Fry (1922) suggested that the expansion and contraction of gelatinous tissue of lichens causes mechanical disintegration of the substrate, the detachment of particles being accomplished by the contraction of the upper surface of the thallus on drying.

In addition to the endolithic and epilithic lichens which are termed saxicolous (rock substrate), some lichens grow on tree bark (corticolous), leaves (foliocolous) or directly on soil (terricolous). In this study, only saxicolous lichens are considered in detail since other forms do not affect directly calcrete profiles.

Materials and Methods

Samples of Pleistocene and Recent calcretes were collected from the study area. Samples collected at the present-day land surface invariably were found to be colonized by micro-organisms (fungi, algae and lichens).

Direct observations of lichens and underlying host substrates, using binocular (reflected light), petrographic (transmitted and reflected light) and scanning electron microscopes, provided the basic sources of information. These visual studies were supplemented by microchemical tests to determine mineralogy and chemical composition of lichen substances and their products.

Rock samples colonized by crustose (endolithic and epilithic) and chasmolithic (living in pre-existing cavities) lichens were prepared for thin sectioning by standard techniques. Some samples required prior impregnation with epoxy resin (see Appendix for details) because of the high porosity and friability of the host material which had been modified by lichen colonization. Prepared petrographic thin sections were stained for carbonate identification using the methods of Feigl (1943), Dickson (1966) and Winland (1971). Staining tests for organic matter also were carried out using aqueous solutions containing Gentian Violet, Toluidine Blue or Methylene Blue (Gurr, 1965; Suess, 1968). Tests for the presence of calcium oxalate were undertaken following the method of Gurr (1965).

Petrography

Purpose

The purpose of this examination was to obtain petrographic information on (1) the mode of attachment of the lichen thallus to its substrate; (2) the depth of fungal penetration; (3) the extent and effect of textural modification of the lichen layer compared with the underlying unaffected substrate; and (4) the preservational potential of the resulting fabrics within calcrete profiles.

Petrography of Recent crustose lichens

The lichen thallus, 0.5 - 5 mm vertical thickness, appears as a more or less unstratified amorphous layer (Plater 79a), that merges gradationally with the rock substrate. The thallus contains spherical green algal cells 20 - 30 microns in diameter (Plate 79b) and algal filaments 8 - 15 microns in diameter which are interspersed with a network of fungal hyphae (Plate 79a). The hyphae tend to be straight and branch dichotomously (Plate 79c). Hyphae and fungal borings are between 0.5 - 2 microns in diameter (Plates 79c, e, 81e, f). Surface ornament on fungal hyphae and algal filaments is generally absent and fungal borings, likewise, have smooth walls (Plates 78e, 81f). The density of fungal hyphae within the substrate decreased rapidly (Plate 81b) from a thick mycelium in the upper 5 mm to isolated penetrative hyphae extending down to a maximum recorded depth of 12 mm from the top surface. SEM examination shows that crystals are present on many fungal hyphae (Plates 78f, 81c). Microchemical staining indicates that these crystals are composed of calcium carbonate (low magnesian calcite) and calcium oxalate. Hydrated calcium oxalate occurs in two forms, weddellite (tetragonal) and whewellite (monoclinic). Tetragonal bipyramidal crystals (Plate 78f) indicate that weddellite rather than whewellite is the oxalate form present. Irregular fissures within some of the crystals (Plate 78f) are interpreted as dehydration phenomena. In addition, some crystals and grains (surfaces are not defined by crystal faces) contain tubular pores (Plate 80e) which are considered to be moulds or borings of fungal hyphae on the basis of their sizes (1 - 3 microns cross-section) and smooth walls.

Calcium oxalate and calcite crystals occur also on the upper surface of the thallus. These crystals are recognizable in hand specimens as a white, chalky powder or pruina. Prepared slides of epilithic lichens, when examined between crossed nicols, show a thin crystalline anisotropic layer, 50 microns or less in thickness (Plate 79a). This layer overlies amorphous organic matter (Plate 79a). SEM examination indicates the presence of euhedral, decimicron-sized crystals on this surface (Plate 80c). Microchemical staining for mineral identification reveals that these crystals consist of low magnesian calcite and calcium oxalate, as occur within the medulla.

Petrography of exposed calcrete hardpan surfaces colonized by crustose lichens

Exposed calcrete hardpans are commonly colonized by crustose lichens (Plate 78a, b). Binocular microscope examination of these surfaces shows an irregular microtopography with pits, 100 - 200 microns in diameter, either empty or occupied by blue-green and green algae, and anastomosing surface grooves, 0.5 - 2mm wide. These grooves, which join to form a jig-saw pattern, demarcate the junctions of juxtaposed lichen colonies. The microtopographical expression is, thus, a product of microbial weathering and may be termed phytokarst (Folk et al., 1973) or biokarst (Schneider, 1976, 1977).

In thin section, cavities with spherical shapes, and sizes between 100 - 200 microns diameter, mark the former position of perithecia (fruiting bodies) of endolithic lichens (Plates 78c, 81a). This enhanced porosity, as a result of biochemical dissolution, decreases rapidly from the surface downwards into unaltered host material within a vertical thickness of 5 mm or less. A network of straight, dichotomously branching microborings, 1 - 2 microns in cross-section, is present below this porous layer (Plates 78c, 79c, e, 81b). Unfortunately, the presence of brown amorphous organic matter and iron hydroxides in the top 5 mm hinders identification in thin section of textural and fabric details. However, SEM examination of this layer reveals that it is composed of anhedral, submicron-sized calcite (?) grains intimately mixed with organic matter. The substrate below this layer, even though it is typically micrite, is composed dominantly of coarser grains (greater than 2 microns diameter) with readily discernible grain boundaries (Plate 81e).

Although calcite within the thallus is dominantly cryptocrystalline, decimicron-sized and centimicron-sized calcite grains occur sporadically throughout the thallus. They have been identified in petrographic thin sections (Plate 78d) and in SEM preparations (Plate 78f). When viewed in thin section, these grains show curved outlines and, not uncommonly, appear to contain vertically oriented tubes, 1 - 4 microns in cross-section (Plate 78d). SEM shows that these tubes are cylindrical pores (Plate 80e) which I interpret as moulds or microborings of fungal hyphae.

Thus, to summarize the textural and fabric changes that have been observed, the following points have been recorded -

From the lichen-colonized surface downwards there is: (1) a decrease in porosity; (2) a decrease in amount of organic matter and iron hydroxides; (3) an increase in grain size; and (4) an increase in cohesiveness of the host substrate. Similar textural and fabric changes have been documented by Pomar et al., (1975) from exposed carbonate surfaces of NE Spain. Additional features recorded in this study include the presence of calcite grains with curved faces and tubular pores (Plate 78d) and spherical aggregates of radial-fibrous calcite (Plate 79d), both of which are present just below the lichen thallus. These changes produce a complex but recognizable structure expressed as a thin layer (5 mm or less) at the subaerial surface (Plate 82a). Leading on from these observations, it is pertinent to ask to what extent this structure is preserved and what its significance is with regard to the formation and recognition of certain types of laminar calcrete. Thus, examination of surface and subsurface indurated calcrete hardpans were carried out with the intention of providing answers to these questions.

Petrography of laminar calcrete hardpans

On the upper surfaces of many calcrete hardpans (Plate 82a) and within indurated hardpans (Plate 82b), a laminar layer is recognizable in hand specimens. Individual laminae, 1 mm thickness or less, are recognizable using a hand lens. The alternating laminae are distinguished by colour differences, textural (grain size and porosity) variations and/or organic matter content discernible as dark organic-rich and organic-poor couplets. Boundaries between laminae tend to be diffuse and the laminae themselves are laterally discontinuous on a centimetre scale. Although the laminae appear planar in hand specimens, petrographic thin sections show that the laminae tend to be crinkled or even convolute (Plate 80a). The complete laminar unit is composed dominantly of microcrystalline and cryptocrystalline calcite with a clotted texture. The laminae are commonly interrupted by subhorizontal lenticular (fenestral) and subvertical channel voids. Passive void-filling calcite cement has reduced this original porosity to less than 20% in the majority of samples examined.

The above outlined features are not only common in material sampled from the western Mediterranean but, from reviewing the literature, appear to be characteristic of laminar calcretes and crusts in general (Kornicker, 1958; Swineford et al., 1958; James, 1972; Read, 1974, 1976; Walkden, 1974; Goudie, 1975; Ward, 1975; Walls et al., 1975; Harrison, 1977). In addition to these features several, hitherto, undocumented features have been recognized in the material studied here. These include the presence of decimicron-sized calcite grains with curved outlines and central tubular pores (Plates 78d, 80a, e), spherical calcite structures (100 - 200 microns in diameter) with thin (2 - 5 microns) partitions and outer walls (Plate 81c, d), and micritic filaments (10 microns or less in diameter) within fenestral voids (Plate 79c). Calcite spherulites, up to 40 microns in diameter, were recorded by Ward (1975, p.562). He did not give any illustrations of these spherulites or discuss their origin but his description suggests that they may be similar to the slightly smaller (10 - 20 microns) calcite spherulites recorded in this study (Plate 79d).

The features listed above have been recorded within Pleistocene and sub-Recent laminar calcretes from many areas of mainland Spain and from the Balearic Islands. They do not appear to be restricted to a particular region and show no relationship with composition or texture of the host substrate. The features are absent from lower parts of the calcrete profile and have not been recognized in unaltered host material beneath the calcrete profile. Thus, it is unlikely that these features have been inherited from the original substrate and their distributions and orientation patterns do not favour a detrital origin. It is concluded, therefore, that these features owe their origin to formation in situ. It now remains to explain how these features originated.

Petrogenesis - Lichen Stromatolites

The factors responsible for textural, fabric, colour and compositional changes, together with the appearance of unusual structures in laminar calcretes, are difficult to explain adequately. Some workers have attempted to explain isolated features but, as pointed out by Braithwaite (1975, p.10): "...solutions seem to have been intuitive rather than observational." For example, Multer & Hoffmeister (1968, p.188) stated "...the banding in laminated crusts is due chiefly to organic staining and concentration of minute organic particles. One explanation of the origin of such bands could be the washing down of such minute soil particles (product of microbial decomposition) during excessively long wet periods. Light bands would represent merely the normal accumulation of fine-grained, chiefly inorganic detritus during intervening dry periods when bacterial decay activity is minimized." Taken singly, this theory is plausible but not readily amenable to substantiation, although Multer & Hoffmeister (1968) mentioned briefly a laboratory experiment which duplicated their theoretical explanation of the observed phenomena. On the other hand, by considering all the observational data we at least have more foundation on which to base interpretation. Adequate explanation is required for organic-rich and organic-poor laminae, fine (cryptocrystalline) and coarser (decimicron-sized) calcite laminae, lenticular or fenestral voids, filaments and microborings of 10 microns or less, calcite spherulites (10 - 20 microns in diameter), larger (100 microns) spherical structures containing and bordered by thin (5 microns) calcite walls, and decimicron-sized calcite grains with tubular pores. More fundamentally, the ubiquity of such features suggests that there is a common and widespread mechanism to account for their formation.

As previously mentioned, not all laminar calcretes necessarily have the same origin. However, those that contain the features listed above may be used together, to suggest an hitherto unconsidered origin for laminar calcretes, namely, that successive colonization of crustose lichens produced them. Thus, the organic-rich, dark brown cryptocrystalline laminae are interpreted as calcified lichen thalli; colour variations reflect the distributions of organic matter and iron hydroxides; the wrinkled nature of the humus-rich laminae and the fenestral voids are attributed to desiccation and shrinkage of lichen tissues; the smooth, straight and branching microborings (1 - 2 microns in diameter) indicate the former presence of penetrative fungal hyphae, the larger (10 microns in diameter) microborings and calcified filaments are considered to be algal in origin; the calcite spherulites and clotted micrite textures are believed to be calcified cells of coccoid algal bodies and aggregates of decomposed organic detritus respectively; larger (100 microns in diameter) calcite spheres are interpreted as calcified perithecia (fruiting bodies); and finally, the interspersed decimicron-sized calcite grains are thought to be crystals resulting from lichen synthesis. These explanations are based on the morphological similarities, distributions and associations of features recorded within modern crustose lichens (p.267).

However, this comparative reconstruction does not account for the vertical succession of alternating laminae which, in this study, have a maximum recorded total thickness of 4 cm. The explanation to account for such successions of laminae which display the documented fabric, textural, colour and composition changes is as follows:

Crustose lichens are typically pioneercolonizers in plant succession on limestone surfaces (Fry, 1922; Syers, 1964, Jones, 1965; Krumbein, 1969, 1972). Once established, lichens form a protosoil by breaking down the indurated substrate, trapping detrital constituents within their thalli and adding organic matter to the accumulating sediment. The modified substrate, as a result of organic telogenesis, is capable of supporting a wider range of soil flora and fauna if moisture conditions permit. However, whereas lichens are capable of remaining viable in environmentally restrictive conditions, most other organisms do not possess the necessary morphological and physiological adaptions for survival. In particular, calcretes are widespread in semi-arid environments with intermittent and low rainfall separated by long, dry periods of intense evaporation (Goudie, 1973). Moreover, because carbonates tend to be chemically stable in such environments, the intermittent supply of water rapidly becomes supersaturated with respect to calcium carbonate, eventually leading to precipitation of calcite and cementation of both mineral and organic constituents. Therefore, the early stages of soil formation are prevented from further development because of the tendency towards calcification. In other words, early stages of pedogenesis are terminated by diagenesis. Thus, the resulting calcified lichen thallus acts as a substrate for further colonization by crustose lichens. This scheme of development produces a vertical succession of surface parallel laminae (Plate 82a) and, as a result of calcification, the laminae retain evidence of lichen colonization in the form of the features outlined above.

This simplistic sequential development may be interrupted by mechanical and/or chemical erosion of some or all laminar increments before the next colonization takes place. An example of this type of modification is illustrated in Plates 80b, d, f, 81e). Plate 82b shows a silicified layer within a calcrete hardpan. In thin section, this chalcedonic layer contains vertical to subvertical tubular structures with diameters of 10 microns or less (Plate 81e). SEM examination reveals that these tubular structures are microborings (Plate 80d) and silicified filaments (Plate 80f). The upper boundary of the chalcedonic layer is sharp (Plates 80b, d, 81e). Truncation and silicification presumably took place at the subaerial surface and, therefore, the upper surface may be termed a subaerial discontinuity surface.

To summarize, the sequence can be delineated into three separate but related process-stages: (1) organic telogenesis; (2) pedogenesis; and (3) diagenesis. Organic telogenesis results in the modification of an indurated substrate as a result of lichen colonization. Pedogenesis leads to the formation of a protosoil. Diagenesis involves cementation and replacement of soil constituents by calcite. Successive repetition of this sequence, thus, produces a characteristic laminar structure. In samples where this type of laminar structure can be demonstrated to have resulted from lichen colonization, I propose that the term <u>lichen</u> <u>stromatolite</u> be used to denote this form of preservation. Use of the term <u>stromatolite</u> in this context is not at variance with the definition given by Walter (1976, p.1): "Stromatolites are organosedimentary structures produced by sediment trapping, binding and/or precipitation as a result of the growth and metabolic activity of micro-organisms, principally cyanophytes." In the samples studied here, the micro-organisms happen to be a symbiotic association of algae and fungi, that is, lichens. The philosophical concept of stromatolites remains unchanged.

Summary and Conclusions

As a result of biophysical and biochemical weathering, epilithic and endolithic lichens modify indurated substrates and initiate soil formation. Fossilization of newly formed textures and fabrics produces millimetre-sized laminae at the substrate-atmosphere interface. Successive buildup of these laminae produces lichen stromatolites. Recognition of lichen stromatolites has far reaching implications in terms of palaeoenvironmental reconstructions. Correct identification of lichen stromatolites provides evidence of subaerial vadose conditions. More specifically, lichen stromatolites demarcate subaerial discontinuity surfaces.

Recognition of lichen stromatolites within calcrete hardpans allows distinction between surface and subsurface calcrete formation. Calcretes containing evidence of lichen colonization must have been exposed directly to surface organic processes at some stage during their evolution. Moreover, lichens provide a source of organic matter, dissolve rock-forming minerals, synthesize calcium carbonate and calcium oxalate, produce fenestral voids and accumulate residual minerals derived from the altered substrate within their thalli. The lichen thallus, consisting of algal and fungal organic matter, is overlain and underlain by synthesized calcium carbonate and calcium oxalate. Detrital and residual minerals supplement these mineral-rich layers. Thus, compositional differences give rise to organic-rich and mineral-rich laminae. These laminae are accentuated by textural (grain size and porosity) and colour differences. Laminae showing similar textural, fabric and compositional differences within laminar calcretes have been reported by numerous workers. However, up till now, little or no attempt has been made to explain their genesis. This study provides one explanation, namely that epilithic and endolithic lichens modify rock substrates in a characteristic way to form lichen stromatolites.

'CASE-HARDENED' CARBONATE CRUSTS

Non-pedogenetic surface dissolution of calcite and subsequent surface cementation has been termed 'case-hardening' by Lattman & Simonberg (1971). According to these workers, case-hardening of carbonate alluvium and colluvium from Spring Mountains, Nevada, begins within 1 - 2 years on freshly exposed surfaces and forms crusts, 2.5 - 10 cm in thickness. They carefully pointed out that case-hardening should not be considered as caliche but their comments have been ignored by some workers (e.g. Reeves, 1976). Case-hardening (as used here and not in its metallurgical context) is a physicochemical process resulting from surface dissolution and subsequent deposition of calcite. Case-hardening may take place on vertical surfaces as well as on gently sloping or horizontal surfaces. Lattman & Simonberg (1971) noted that in their study area the case-hardening cement is dark grey, whereas soil caliche is light buff to white. The calcite cement of case-hardened crusts consists of decimicron-sized rhombic crystals in contrast to the typical micron-sized and submicron-sized crystals of calcrete. The mechanism of formation envisaged for case-hardening is identical to that proposed for the *croûte zonée* of Durand (1963). Such physicochemical processes may take place during calcretization but they are not essential and, by themselves, are inadequate for the formation of calcrete profiles.

'CALCRETE-LIKE' DEPOSITS

Coniatolites

The term coniatolite (Gk. koniatos = lime encrusted) is used here as defined by Purser & Loreau (1973) to describe aragonitic supratidal encrustations. The strontium-rich aragonite crusts described by Purser & Loreau (1973) from the Persian Gulf, coat grains and form smooth (pelagosite) to highly irregular sheets. Micro-dripstone or gravitational cements are common on the undersurfaces of the sheets. Purser & Loreau noted that although many of these aragonitic encrustations resemble algal stromatolites and some cave deposits, the dripstone morphologies, nannostructures and invariably lithified character of coniatolites strongly suggest that they formed by physicochemical precipitation from seawater. They concluded that their discovery of marine vadose encrustations indicates that vadose fabrics should not be equated automatically with a non-marine environment.

Scholle & Kinsman (1974) went one step further and suggested that aragonite and high magnesian calcite laminated, lacy and pisolitic crusts from the Persian Gulf formed "...by the same processes which act in other caliches but with different mineralogies." They suggested that Holocene-Quaternary pisolitic crusts with their 'unusual' mineralogies were analogous to the pisolitic facies of the Permian reef complex of Texas and New Mexico and provided a comparative model for their formation and genesis. However, Esteban (1976) warned of the dangers of equating caliche deposits with those developed primarily by precipitation in marginal marine intertidal to supratidal evaporitic flats as described by Scholle & Kinsman (1974).

Although Esteban (1976) did not object formally to the analogy drawn between Persian Gulf pisolites and the 'vadose pisolites' of the Permian reef complex of Texas and New Mexico, he did question the generally accepted interpretation of the 'vadose pisolite' (caliche) origin. Pioneered by Dunham (1969b), it is the 'vadose pisolite' caliche origin which has been the source of confusion. Esteban (1976) compared 'vadose pisolite' with modern caliche and concluded, after exposing prevalent misconceptions, that the interpretations of the pisolitic facies of the Permian (Capitan) reef complex of New Mexico, of the Italian Calcare Massiccio and of the Saskatchewan Winnipegosis were incompatible with a caliche origin. He suggested that 'vadose pisolite' could be better interpreted as a depositional facies close to an intertidal setting in hypersaline environments similar, although not entirely adequate as a model, to those found in the Persian Gulf coniatolite belt today.

Speleothems and Travertine

Calcareous speleothems (Gk. spelaion = cave; thema = deposit) and travertine or calcareous sinter crusts are considered together here since their mechanisms of formation are similar, namely, inorganic precipitation of calcite* from meteoric waters.

Speleothems can be divided conveniently into attached and unattached types (Thrailkill, 1976). Attached speleothems include flowstone (Plate 82c, d), stalagmites, stalactites, cave popcorn and moonmilk. Unattached speleothems include cave pearls which have smooth outer surfaces, and pool accretions which are crudely spherical or ellipsoidal and have rough surfaces (Thrailkill, 1976).

The term travertine is used here for sheet-like inorganic precipitation of calcite from surface meteoric waters. Travertine

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*Only calcite is considered here although the number of recorded minerals in speleothems is vast (see Hill, 1976).

is the same as flowstone except that the latter forms in a subterranean environment. Both may be deposited from moving or stationary meteoric waters.

The gross morphology and internal structures of speleothems and travertine may mimic superficially calcrete deposits. Some calcrete deposits have even been called travertines (Fairbridge & Teichert, 1953). However, although similarities undoubtedly exist, sufficient differences allow distinction between inorganic calcite precipitates and calcretes. These similarities and differences are listed in Table 12.

TABLE 12 SPELEOTHEMS *VERSUS* CALCRETES

SPELEOTHEMS	CALCRETES
SUPERFICIAL SIMILARITIES	
Moonmilk	Chalk
Pool accretions	Glaebules
Flowstone, travertine	Laminar calcrete
DIFFERENCES	
Abiogenetic (inorganic)	Abiogenetic and biogenetic
Telogenetic	Pedodiagenetic
No alteration of substrate	Alteration of substrate
Decimicron to centimetre-sized calcite crystals	Micron - sized calcite crystals
Preferred crystal fabrics	Random crystal fabrics
Internal sediments common	Internal sediments rare
Irregular solution vugs and caverns	Root mouldic porosity
Numerous authigenic minerals	Dominantly calcitic

Algal Stromatolites

Structures and fabrics of many calcrete deposits resemble superficially some stromatolitic structures (Read, 1976). In particular, planar cryptalgal laminates may be confused with laminar calcretes and unattached stromatolites (oncolites) may be confused with calcrete glaebules. For correct palaeoenvironmental reconstructions, it is fundamental to differentiate between algal stromatolites which are supratidal, intertidal or subtidal organo-sedimentary structures and calcretes which are products of subaerial vadose soil-forming processes. Multer & Hoffmeister (1968) made this point in their discussion on Holocene subaerial laminated crusts of the Florida Keys. They stated (p. 183) that "....these crusts have locally been identified as indurated marine algal stromatolites similar to the soft, marine, living algal stromatitic mats of the Florida Keys, which border and occasionally even coat the encrusted bedrock; such juxtaposition is now considered merely coincidental." They listed criteria for distinguishing between algal stromatolites and subaerial laminated crusts, some of which have been included in Table 13. Table 13 lists differences between algal stromatolites and laminar calcretes.

TABLE 13 ALGAL STROMATOLITES VERSUS LAMINAR CALCRETES

ALGAL STROMATOLITES	LAMINAR CALCRETES
Antigravitational thickening; thickening over highs	Fill of depressions; follow microtopography
Sharp laminae	Diffuse laminae
Alternating grain size	Laminae due to staining
Organic-rich and organic-poor	Organic-rich and organic-poor
Abundant algae	Abundant fungi and lichens
Desiccation features common	Desiccation features rare
Associated marine sediments and organisms	Associated vadose diagenetic phenomena

Read (1976) gives an excellent review on calcretes and their distinction from stromatolites, despite his adherence to the interpretation of the Capitan pisolitic facies as an example of ancient calcrete (cf. Dunham, 1969b; Esteban, 1976).

Freshwater Tufa

The term tufa is used here to describe encrustations of plant fragments by calcium carbonate. Tufas are common in freshwater (meteoric) lakes and rivers with calcareous-rich waters. Subaqueous algae and mosses are the commonest plants found in tufas (Irion & Müller, 1968). Assimilation of carbon dioxide and bicarbonate by these plants during photosynthesis raises the level of $CaCO_3$ saturation. If the level is raised sufficiently, $CaCO_3$ may be precipitated on plant fragments. Schneider (1977) has emphasized that this phenomenon is an example of inorganic precipitation of $CaCO_3$, which is brought about by the physiological activities of organisms. However, some algae are capable of biochemically controlling the precipitation of $CaCO_3$ within their mucilaginous sheaths (Riding, 1977).

Freshwater tufas have simple mineralogies; most tufas consist of calcite (Irion & Müller, 1968). The fabrics of tufas depend on the morphology of the encrusted plants. Tufas commonly have a high framework porosity. Calcite cements tend to be coarsely crystalline, showing equant, bladed and, occasionally, fibrous habits. Most crystals are euhedral or subhedral but some crystals have feathery outlines. Long axes of crystals are generally normal to the substrate from which the crystals grew. The calcite is often limpid (clear). It may, however, contain organic matter, clay particles or fluid inclusions.

Some calcretes have been called, inexcusably, tufa deposits (Table 1, pp.12-13). Calcretes have sufficient differences from tufas to warrant their separation. Table 14 lists these differences and, at the same time, provides criteria for the recognition of tufa deposits.

TABLE 14 FRESHWATER TUFAS VERSUS CALCRETES

TUFAS	FEATURE	CALCRETES
Meteoric phreatic	Environment	Meteoric vadose
Non-ferroan and ferroan LMC	Mineralogy	Non-ferroan LMC
Decimicron- to centimicron-sized	Crystal size	Micron-sized
Framework, intraparticle	Porosity	Fracture, channel, vug
Rare	Replacement fabrics	Common
Rare	Terrigenoclastic grains	Variable
Lake, river	Facies	Independent
Hydrophilic plant remains of mosses, algae (esp. Chara) ostracods, freshwater gastropods	Fossils	Terrestial gastropods

Lacustrine Carbonates

Accumulations of calcium carbonate in lake environments may result from: (1) fixation in skeletal grains (e.g. molluscs, ostracods, charophytes); (2) inorganic precipitation caused by extraction of CO_2 and HCO_3^- during plant photosynthesis; (3) inorganic precipitation caused by favourable changes in environmental conditions (e.g. increase in temperature, decrease in pressure); or (4) inorganic precipitation caused by mixing of waters of differing composition (Runnells, 1969).

In his monumental contribution, Cayeux (1935; translated and updated by A.C.Carrozzi, 1970) noted that "the structures and textures of freshwater limestones are extremely varied, in spite of their very uniform mineralogical composition and the small number of organic groups which participate in their constitution. Besides dense, cryptocrystalline, sublithographic or microgranular limestones, corresponding to the average type, vermicular, vuggy, clotted, pseudobrecciated, pseudoolitic, concretionary, oolitic, brecciated and conglomeratic varieties also occur, some of which are of great importance for the understanding of the past freshwater environment."

Some of the above terms used by Cayeux for describing freshwater limestones have been used widely in studies of calcretes. Indeed, the subsequent descriptions that Cayeux gave (1970, pp. 287 - 295) are so embarrassingly similar to descriptions of calcrete fabrics that one wonders if he was, inadvertently, mistaking his material for something entirely different. Was Cayeux, unknowingly, the first person to document the micromorphological characteristics of calcrete? I raise the question but lack the knowledge to answer it.

Illustrations of lacustrine and paludal (swamp) carbonates given by Freytet (1973) provide further embarrassments for students of calcretes. Lacustrine limestones may be homogeneous or show brecciation and burrowing. Paludal limestones, which have resulted from emersion of lacustrine muds, may be affected by soil-forming processes. Such deposits, described by Freytet (1973), show signs of reworking - penetration of roots, formation of nodules, fissuration and remobilization of iron.

The pisolitic limestone from the upper part of the late Tertiary Ogallala Formation in Kansas, Oklahoma and Texas has been interpreted as a lacustrine deposit by Elias (1931) and Frye (1945). Swineford et al., (1958) reinterpreted this limestone as a calcrete. They noted that the only evidence favouring a lacustrine origin was the reported presence of the alga Chlorellopsis bradleyi. Objections to a lacustrine origin are not so difficult to find. Swineford *et al.*, (1958) listed eight objections of which the evidence for downward growth of the rock was considered to be the most important.

Criteria for recognizing lacustrine carbonates which differ sufficiently from criteria for recognizing calcretes are few. Picard & Hugh (1972) provide valuable information to help recognize lacustrine rocks in general. The local to regional size, circular shape, basinal configuration with fining clastics toward the centre, lateral continuity of beds, varves, freshwater biota and sedimentary structures such as ripple marks, cross-stratification and polygonal shrinkage mud cracks are perhaps the most useful criteria for recognizing lacustrine rocks. Dolomitization and silicification of lacustrine rocks also are fairly common in ancient successions. However, reliable petrographic criteria are not so readily listed. In view of the descriptions of Cayeux (1935, 1970) and the illustrations and comments of Freytet (1973), I leave the problem of distinguishing between lacustrine carbonates and calcrete deposits with unsatisfactory resolution.

CHAPTER EIGHT - PEDODIAGENESIS: CAUSE AND EFFECT

INTRODUCTION

Calcretes are the products of pedogenetic and diagenetic processes which have acted within the meteoric vadose zone (p. 35). As pointed out by Murray & Pray (1965), adequate interpretation of the diagenesis of carbonate rocks depends on knowledge of the rocks themselves, the physical and chemical processes involved, the method of transporting materials into and out of the volume of rock under consideration and the nature of the starting materials. For the study of calcretes, I find it necessary to add to this list by including biological processes which are of fundamental importance to the processes of calcretization.

To give meaningful interpretations of the genesis of calcretes, it is requisite to know where the calcium carbonate came from, how it was transported and for what reasons it was deposited. It is also useful to know of the intensity and duration of the processes which determine the morphology of calcretes. Thus, this Chapter is concerned with possible sources of calcium carbonate, processes of pedodiagenesis, the nature and movement of pore fluids and the mechanisms of calcite precipitation. These topics will be discussed in turn. All the information gained thus far will be used to build conceptually a process-response model for the formation of calcretes. Before this is attempted, a few general comments will be made on the cyclicity of telogenetic environments which I have termed, to be consistent with the philosophy of this study, the pedodiagenetic cycle.

THE PEDODIAGENETIC CYCLE

Soils are derived from the decomposition of the mineral particles they contain and from the plant and animal remains added to them (Russell, 1973). Soils form by the breakdown of rock into unconsolidated sediments and the incorporation of organic materials. Soils generally show a vertical anisotropy as a result of biological and physicochemical soil-forming processes. Unconsolidated calcretes are active or relic calcareous-rich soils. Indurated calcretes are consolidated, relic calcareous-rich soils. Thus, rocks of any composition or origin may be broken down into weathered detritus and organisms may transform this sediment into a soil. If environmental conditions are conducive to the accumulation of calcium carbonate, powdery or unconsolidated calcretes will form. Continued soil-forming processes will modify the underlying host material (parent rock) until the resulting regolith eventually forms a protective blanket over the unaltered substrate. Induration of the calcrete will lead to the formation of a near-surface pedodiagenetic rock. The indurated calcrete may be subjected to further pedodiagenetic processes, leading to its modification or destruction. The cycle, thus, is repeated. This idealized cycle is illustrated schematically in Fig. 18, p. 288.

The above simplistic cycle assumes that the system is volumetrically constant, that is to say, that gains and losses of materials are zero. The cycle becomes more complicated, and more difficult to model, if net erosion or net deposition becomes significant. Erosion may result in degrading profiles or, if erosion is sufficient, may remove all weathered detritus. If on the other hand, sedimentation rates are sufficiently great, there may be insufficient time for profile development. In areas where erosion predominates, soils will tend to be thin or may be absent altogether. In areas where weathering predominates, soils will tend

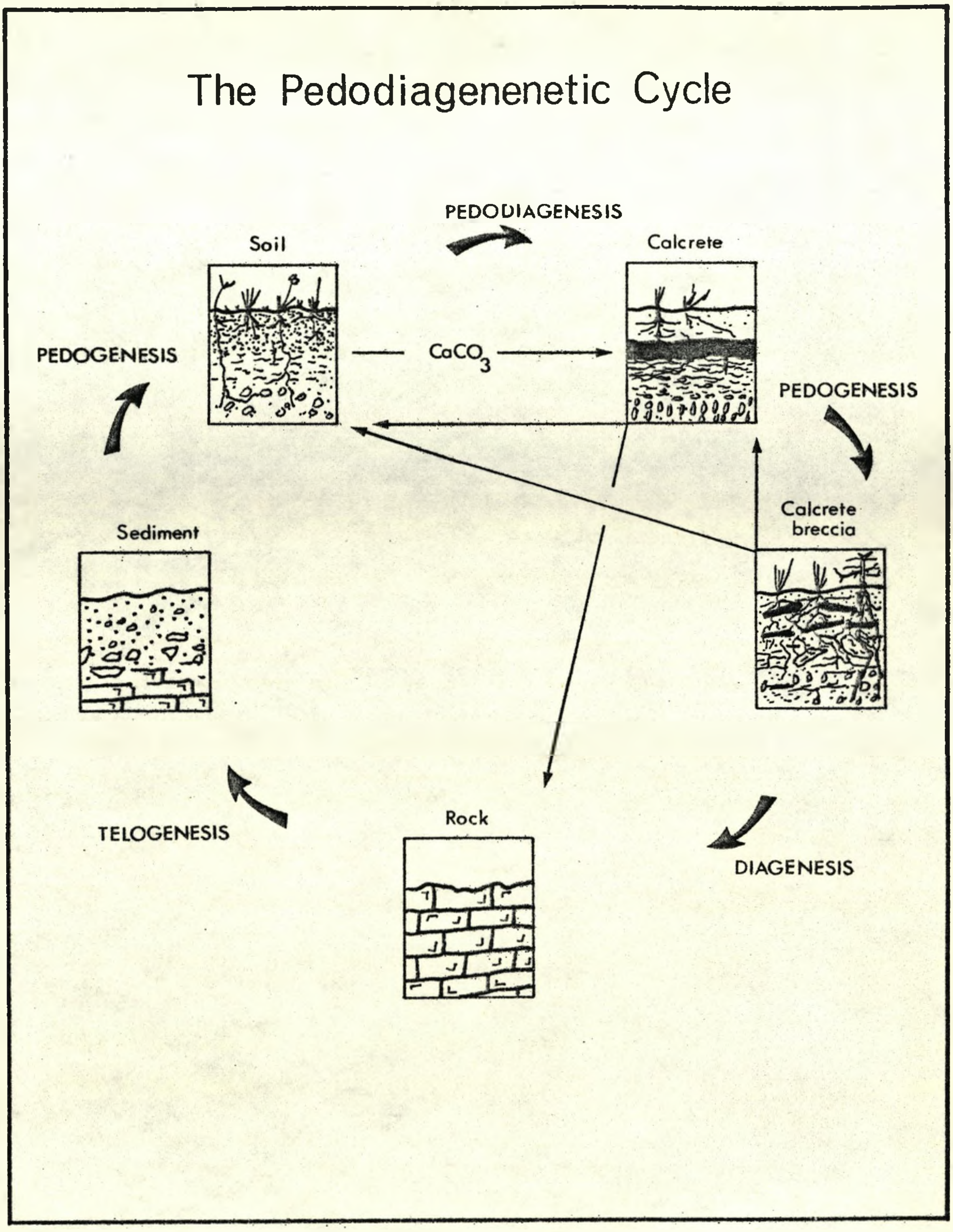

Figure 18. The pedodiagenetic cycle.

to be thick. Soils will tend to be thick also if material is being introduced from elsewhere by aeolian or fluvial transport.

Harrison (1977), in his discussion on Pleistocene caliche profiles from Barbados, suggested that climate, nature of the soil cover, moisture balance, availability of calcium carbonate, time, and fabric of both substrate and caliche were important controls of the formation, evolution and destruction of caliche. With respect to a favourable moisture balance, Harrison suggested that insufficient water would lead to the formation of a superficial 'case-hardened' surface, whereas too much moisture would result in net solution and leaching, giving rise to a karst topography. However, although the amount of available water is important, the fate of this water is of equal importance. If slopes are too steep, or if permeabilities of exposed rocks are too low, then surface runoff will tend to be more important than surface infiltration. Rates of evaporation and evapotranspiration merit further consideration. Thus, even though Harrison noted that the development of caliche coincided with the most arid regions of Barbados whereas the most humid portions of the island are characterized by a karst terrain, I contend that the relationship between moisture balance and calcrete distribution is not necessarily direct. To begin with, Harrison correlated the distribution of Pleistocene caliche with the present-day climate. Secondly, the karst-like terrain of Barbados is composed largely of well cemented Tertiary and Pleistocene rocks of low permeabilities. These rocks form mountainous terrains with steep slopes. In such terrains, as in parts of the Mediterranean coastal regions, karstification is more important than calcretization, regardless of whether the climate is humid or arid. In these areas, removal of material, mechanically and in solution, prevents the buildup of regolith. Thus, soil formation and, likewise, calcrete formation do not have opportunity to proceed.

SOURCES OF CALCIUM CARBONATE

Possible sources of calcium carbonate have been discussed by many workers (Brown, 1956; Motts, 1958; Coque, 1962; Gile et al., 1966; Gardner, 1972; James, 1972; Yaalon & Ganor, 1973). Goudie (1973) and Reeves (1976) provide useful reviews on this problem. In addition, Goudie has brought together information not concerned directly with studies of calcrete formation but, nonetheless, of relevance to this topic. A similar review will not be repeated or extended here. Instead, the possible sources of calcium carbonate will be evaluated and summarized in a general discussion, relying largely on information given in the above mentioned references. Examples used for illustrating points raised in this discussion are taken from materials examined during the course of this study.

Breakdown of components and redistribution of calcium within soils may initiate the formation of calcretes in essentially non-calcareous host materials. Such components may include calcium-rich primary minerals derived from the host material, certain plants which contain calcium within their tissues, detrital carbonate grains incorporated into the soil by colluvial or fluvial processes and calcareous skeletal grains of soil organisms such as terrestial gastropods. The land snails Helicella sp. and Rumina sp. were found on exposed surfaces throughout the western Mediterranean, with densities of up to 150/m^2 in some places.

Calcium carbonate may be carried in solutions of rain water and ground water. Using published data, Goudie (1973) calculated that the average calcium content of rainfall came to 6 - 7 ppm. However, he pointed out that this relatively low figure may be increased two-fold after rainfall has passed through the canopy of trees or bushes. Plants also may increase the amount of calcium in the soil by removing calcium ions at depth from ground water and depositing calcium carbonate or calcium oxalate as plant residues in the litter layer. Taproots with lengths of up to 5 m were observed in this study. Goudie (1973) stated that some common tree species from southern Africa put taproots down to as much as 50 m to ground water.

Some plants accumulate carbonate within their tissues. This study has shown that lichens are capable of synthesising calcium-bearing minerals. Other biogenetic carbonate structures, including rhizoliths and *Microcodium*, contribute to the buildup of calcium carbonate in calcretes studied here.

Atmospheric dust, derived from volcanic ash or desert loess, provides an external source of calcium carbonate in some areas. It is conceivable that fallout of wind-blown dust from the Sahara may have supplied Mediterranean soils with additional calcium carbonate.

In coastal areas, an important source of calcium carbonate may be derived from marine aerosols. James (1972, p. 829) noted that the effect of wind-blown salt spray is two-fold: firstly, high salinity inhibits growth of vegetation which leaves soils susceptible to erosion; and secondly, calcium carbonate is added to the surface and increases the $CaCO_3$ content of near-surface waters.

Throughout the western Mediterranean coastal regions there are extensive outcrops of Mesozoic and Tertiary limestones and dolomites. Whether transported as alluvium, colluvium, atmospheric dust or in solution, the supply of calcium carbonate to calcrete-forming areas is not a limiting factor in these regions. Calcretes occur within any host material.

PEDODIAGENETIC PROCESSES

Pedogenetic and diagenetic processes determine the morphology and composition of calcretes. Pedogenetic or soil-forming processes form pedological features and modify plasma (Brewer, 1964). In calcrete profiles, diagenetic processes are superimposed on features formed by pedogenetic processes, resulting in the formation of pedodiagenetic structures (Chapter 5). In addition, diagenetic processes modify the fabrics of the soil s-matrix, resulting in the formation specific fabrics which are diagnostic of the near-surface subaerial diagenetic environment (Chapter 4). Diagenetic processes tend to post-date pedogenetic processes, although the two processes may operate simultaneously.

Although the distinction is made here between pedogenetic and diagenetic processes, in nature they cannot be separated entirely. For example, the processes of dissolution, precipitation, compaction, brecciation and neoformation are common to both pedogenesis and diagenesis. Moreover, because calcretes are both pedogenetic and diagenetic in origin, the two basic processes are treated here under the same heading.

Pedodiagenetic processes operate in an attempt to restore and maintain equilibrium or steady state. Treated simplistically, these processes lead to changes which involve additions, removals, translocations and transformations of materials. The driving mechanisms behind these changes, which are physical, chemical or biological in origin, may proceed independently or together. One of the main attributes of calcrete is its complexity of types, patterns and mutual relationships of processes. A similar viewpoint has been made by Harrison (1977) in his discussion of complex cementation patterns in caliche profiles from Barbados. Accepting the complexity of processes, the more fundamental questions - of what are the processes in detail and what causes the complexity - require answering.

Cementation, dissolution, recrystallization, brecciation and metasomatic replacements are characteristic processes of calcrete deposits (Bretz & Horberg, 1949; James, 1972; Esteban, 1974; Goudie, 1975; this study). However, such processes are diagnostic not only of calcretes; they have determined fabrics, textures and structures of many types of sedimentary rocks. Even so, these widespread processes have not been worked out in detail for calcrete deposits. This statement reiterates the comment of Esteban (1976) who noted (p. 2049): "...processes that produce caliche are not understood well."

One of the main problems is that, with the exception of several experimental studies (Breazeale & Smith, 1930; Thorstenson *et al.*, 1972; McCauley & Roy, 1974; Dumont, 1975; Badiozamani *et al.*, 1977) processes can be inferred only from observations of the products. This method of study is both difficult and dangerous. It is difficult because of the complexity and interaction of processes; it is dangerous because we do not consider processes which leave no evidence of their former activity. In addition, even processes which leave clues may be overlooked if we have little understanding of them. The biological processes involved in calcretization are relevant examples. Up till now, biological processes have been mentioned only briefly or not at all by workers interested in calcrete genesis. This study emphasizes the importance of such processes and helps to compensate for past neglect. Comments such as "....it has been suspected that organic processes also may influence the accumulation of subaerial crusts" (Ward, 1975) and "...the organic influence in calcretization is thought to be greater than previously realized" (Watts, unpubl. abstract) indicate recent intuitive ideas regarding the formation of calcretes. Esteban (1974) suggested that we should look for biologically determined caliche fabrics similar to those described by Krumbein (1968). Knox (1977) suggested (p. 673) that "a careful study of semi-indurated parts of profiles may bring biogenic structures to light in areas where caliche formation is considered only due to mechanical and inorganic processes." By studying actively forming calcretes from the western Mediterranean, whose pedodiagenetic histories have yet to be completed, I have followed recent suggestions and confirmed recent suspicions. By bringing to light biogenetic structures, formed by pedodiagenetic processes, I have indicated the significance of biological activity in calcrete profiles. Biogenetic processes directly influence calcrete morphology. Recognition of biogenetic structures is fundamental for making reasonable interpretations regarding the processes of calcrete formation. Biogenetic processes include: the dissolution of minerals as a result of secretion of organic acids and chelating compounds; plant photosynthesis and respiration which affect CO_2 and O_2 levels in the ambient micro-environment; the formation of organo-mineral complexes; selective uptake of ions by plants; burrowing and boring by plants and animals; brecciation and disruption of indurated hardpans by roots; calcification of organic matter to form biogenetic carbonate structures and; biosynthesis of new minerals. Discussions of biogenetic processes have been given in relevant sections and will not be repeated here. The processes are listed to indicate the complexity of biogenetic processes which influence and are themselves influenced by physicochemical soil-forming and diagenetic processes.

Physicochemical soil-forming processes include: physical disintegration and chemical decomposition of rocks and minerals; dissolution; precipitation; recrystallization and; metasomatic replacements. Grains may be translocated by illuviation, leached, dissolved, recrystallized or reorganized to form new minerals from the residues of leached minerals (neoformation). The near-surface subaerial pedodiagenetic environment is subjected to wetting and drying cycles which lead to the formation of shrinkage cracks and channels. This Pandora's box may be loosely termed subaerial weathering. The line between the above listed pedogenetic processes and diagenetic processes is arbitrary. In the study of calcretes, this line is unnecessary. Pedogenetic processes and diagenetic processes are so intimately related that they cannot be justifiably separated.

NATURE AND MOVEMENT OF PORE FLUIDS

In his study of chemical weathering, soil development and geochemical fractionation in bedrock of the White Mountains, California, Marchard (1974, p. 379) stated: "it is impossible..... to clearly comprehend the transformation of bedrock into soil by studying changes in the mineral phases alone, for weathering involves important alteration of liquid and gas phases in contact with the minerals as well." Thus, to better understand how bedrock can be transformed into calcrete, a few comments on the nature and movement of pore fluids is in order.

The moisture condition of calcretes close to or at the land surface is subject to large variations. Similarly, the composition and temperature of pore fluids fluctuate rapidly as a result of alternating periods of short, intense rainfall followed by longer periods of evaporation in a Mediterranean climate. Transpiration by plants, percolation into ground water and capillary rises from ground water cause changes in the amount, composition and temperature of the remaining held water within the calcrete profile. In the vadose zone (zone of aeration), the pore water pressure is less than atmospheric pressure. Above the water table, water is held at less than one atmosphere because of surface tension and adsorptive forces (Croney, 1952). The intensity with which water is held by a soil can be measured in units based on the concept of soil suction. When dealing with negative pressures (soil suction), the pF scale is commonly used, where $pF = \log_{10}$ (height above the water table, h in cm). Netterberg (1971) suggested that one of the most important mechanisms in calcrete formation is the dissolution and precipitation of calcium carbonate during changes in soil solution.

Transpiration by plants and evaporation of held water are important processes which bring about suction gradients. Water movements take place by bulk liquid flow in plants, as rising capillary water and as descending water under the influence of gravity. After gravitational water has drained completely into ground water, stationary water is held in the vadose zone. The geometry of this immobile, held water determines the morphology of plasmic fabrics of calcite crystals which precipitate within pore spaces of host materials. Occasionally, if the pores are small enough, isopachous fringes precipitate on grain surfaces rather than gravitational and meniscus cements. Thus, care is needed when interpreting isopachous, phreatic-type cements which have precipitated in the vadose zone.

In addition to calcite cements, which are by definition firmly attached to a substrate, some hyphantic fibrous and rhombic calcite crystals precipitate in the vadose zone without any substrate attachment. Hyphantic and coarse crystic plasmic fabrics which lack cementation are indicative of vadose diagenesis; their origin is attributed to rapid precipitation from evaporating pore solutions.

Apart from volumetrically insignificant but genetically important held water, a notable property of soil vadose water is its mobility. Water movements (mostly bulk liquid flow and movement as water vapour), together with the composition of these moving waters, determine the direction and intensity of pedodiagenetic processes.

MECHANISMS OF CALCITE PRECIPITATION

Possible Mechanisms

To say that calcrete formation results from processes in the vadose zone which culminate in the accumulation, mainly by precipitation, of calcium carbonate tells us nothing of the mechanisms involved. To better understand the possible mechanisms of calcite precipitation, and to be in a better position to suggest the most likely mechanisms, the chemistry of the CO_2 - H_2O - $CaCO_3$ system will be discussed briefly. This system is discussed in detail by Sweeting (1972) and Bathurst (1975).

The reactions involved in the CO_2 - H_2O - $CaCO_3$ system can be summarized by the general equation:

$$CO_2 + H_2O + CaCO_3 \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

The solubility of calcium carbonate is affected by five independent variables. The solubility product $[Ca^{2-}] . [CO_3^-]$ decreases with increasing temperature, increases by adding salts lacking common ions, decreases by adding salts with common ions, decreases with increasing pH and decreases with rising partial pressures of CO_2.

The equations which relate to the formation of calcium bicarbonate are as follows:

(1) Equation of hydration $CO_2 + H_2O \rightleftharpoons H_2CO_3$

(2) Dissociation of carbonic acid $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

(3) Combination of hydrogen and carbonic ions $H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$

(4) Dissociation of calcium carbonate $CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$

(5) Ionic dissociation of water $H_2O \rightleftharpoons H^+ + OH^-$

All these reactions are reversible. If reactions move to the right, both CO_2 and $CaCO_3$ are dissolved. If CO_2 or H_2O are removed, as a result of agitation, aeration, photosynthesis or evaporation, $CaCO_3$ is precipitated. Loss of CO_2 may result simply from solutions coming into contact with air at lower partial pressures of CO_2.

Netterberg (1971) reported that the mechanisms postulated by most authors to account for calcium carbonate crystallization from the soil solution during calcrete formation is simply evaporation. However, Netterberg pointed out that evaporation is important only in the upper metre or so of the soil profile. He suggested that the effect of changes in soil suction on the solubility of carbonate is possibly the most important mechanism in calcrete formation at all depths. Transpiration and, to a lesser extent, evaporation are considered to be responsible for bringing about increases in suction pressures.

Precipitation of calcite may occur at some point in a calcrete profile which has a downward increasing pH gradient. Multer & Hoffmeister (1968) measured a minimum pH of 5.6 in soils from Florida, increasing downwards to a maximum of 8.2 in underlying host materials.

Precipitation of calcite can be influenced or controlled by biological activities. Culture experiments by Krumbein (1968) showed that microfloras, consisting of autotrophic and heterotrophic bacteria, fungi, actinomycetes, green algae and blue-green algae, were able to cause precipitation of calcite by changing pH conditions and possibly by transmission of Ca^{2+} by chelating substances generated by these micro-organisms.

With the removal of H_2O, as a result of evaporation or water uptake via plant roots, the concentration of solutions may be increased sufficiently to cause precipitation of calcite. Similarly, increasing temperatures favour calcite precipitation since the amount of CO_2 in solution decreases with increasing temperature. Removal of CO_2 also takes place during plant photosynthesis. By assimilation of CO_2 and HCO_3^-, plants may bring about the precipitation of calcite. As emphasized by Schneider (1977), this process is an inorganic precipitation of $CaCO_3$, which is promoted by the physiological activities of organisms.

In contrast to the removal of CO_2, which favours the precipitation of calcite, increasing CO_2 partial pressure leads to the dissolution of $CaCO_3$. Partial pressures of CO_2 in the soil are commonly many times greater than in the atmosphere or in the underlying bedrock (Bathurst, 1975). High CO_2 partial pressures in soils result mainly from respiration of higher plants and micro-organisms. Dissolution of calcite is promoted also by secretion of organic acids from growing plants or the release of substances during the decay of organic matter. However, Berner (1968) pointed out that proteinaceous organisms, upon decay, release not only carbonic and other acids but also give off basic substances such as ammonia and amines. Thus, decomposition of organic matter may result in a rise in pH instead of a decrease. This may lead to the precipitation of $CaCO_3$, thus:

$$NH_3 + Ca^{2+} + HCO_3^- \rightleftharpoons CaCO_3 + NH_4^+$$

Berner (1968) showed experimentally that bacterial decomposition of fish led to an increase in pH and the precipitation of Ca^{2+} from solution as a mixture of calcium fatty acid salts or soaps. Berner suggested that some ancient $CaCO_3$ concretions, especially those enclosing fossils of soft-bodied organisms, may have formed initially as calcium soap (adipocere) which was later converted to $CaCO_3$. Without going into further detail, I leave discussion of calcite precipitation as a result of bacterial decomposition with a provocative thought, namely, what the importance of this process is with regard to the formation of biogenetic carbonate structures recorded in this study.

Another source of CO_2 which may be important, both on the surface and underground, is that produced by the mixing of chemically differing natural waters (Runnells, 1969). Extending the work of Bögli (1964) who introduced the term 'Mischungkorrosion' (mixture corrosion), Runnells showed experimentally that mixing of solutions which differ only in their content of dissolved electrolytes may cause either precipitation or dissolution of rock-forming minerals.

Likely Mechanisms

Following the above discussion on possible mechanisms of calcite precipitation, attention will now be directed to observations made during this study which may provide clues as to the most likely mechanism or mechanisms for the formation of Quaternary calcretes in coastal regions of the western Mediterranean.

Irregular cracks and channels, suggesting that periods of wetting and drying have occurred, are common porosity types in calcretes studied here. Hyphantic and banded needle calcite precipitates (fibrous calcite plasma) are characteristic of the upper parts of calcrete profiles. Crystal morphology is highly variable. Crystal sizes tend to be micron-sized or submicron-sized. Development of calcite cements tends to be irregular in distribution, type and amount. Cementation is preferential around roots of higher plants. The chalky horizon is characterized by precipitates of uncemented or weakly cemented micron-sized and decimicron-sized calcite crystals.

Evaporation is the simplest explanation for the formation of shrinkage cracks. Rapid and intense periods of evaporation following rainfall also may have been responsible for the precipitation of hyphantic and banded needle calcite crystals. James (1972) suggested that the small size of calcite needles and rhombic micrite in calcareous crust profiles from Barbados were formed from a rapidly evaporating solution. He noted further that intense evaporation of fluids in narrow pore spaces at or near the ground surface may bring solutions to very high degrees of supersaturation quite rapidly. Crystals precipitated from highly supersaturated solutions are known to exhibit special growth forms such as dendrites, spherulites and whisker crystals s.s. (Buckley, 1951; Walton, 1967).

Preferential cementation of calcite around roots has been discussed in detail elsewhere in this study (p.158). Removal of water during life of the plants by transpiration is one possible and likely mechanism to account for the precipitation of calcite around roots. Alternatively or in addition, organic decay of dead roots may induce calcite precipitation. The location of the precipitate will be determined largely by the distribution and amount of moisture within pore spaces of the rhizosphere. Precipitation will tend to occur on surfaces which retain moisture as held water films on and between skeletal grains, root surfaces, fungal hyphae and already precipitated calcite crystals.

The Mediterranean climate today is characterized by high temperatures which favour evaporation. Admittedly, the climatic regime may have differed considerably during earlier periods of the Quaternary but, combining the observations and interpretations made above, it is considered most likely that evaporation and transpiration have been and still are the most important mechanisms which culminate in the precipitation of calcrete-forming pedodiagenetic calcite.

COMPOSITIONAL AND FABRIC EVOLUTION: A PROCESS-RESPONSE MODEL

The complex interrelationships among the factors of climate, host material, topography, hydrology, organisms and time render the construction of a generalized model exceedingly difficult. Harrison (1977), following his proposed model for caliche formation on subaerially exposed marine carbonate sediments, noted (p. 146): "the model...is of necessity an oversimplification of a very complex process....To take into account every possible variation that might be introduced into the model by changes in the relative influence of climate, soil, substrate, and time would negate the whole exercise." Bearing in mind the above comments of Harrison, the model presented here also is, of necessity, a blanket assessment of the intricacies of reality.

Stages of the Model

Stage 1. Preparation of host material

The formation of regolith or weathered detritus from an initially consolidated bedrock involves mechanical and biophysical disintegration, physicochemical dissolution and biochemical weathering. Whether this material accumulates *in situ* or is eroded and deposited elsewhere depends on the rate of sediment production *versus* its rate of removal. For calcrete formation to take place within a weathered host material, sediment production must equal or exceed the rate of removal.

Stage 2. Soil formation

Unconsolidated sediment or weathered detritus is transformed into a soil by changes produced by the action of organisms and by changes due to the movement of water through the sediment. Vertical movements of moisture tend to reinforce the changes produced by organisms, the general result being a vertical anisotropy shown by layers or horizons parallel to the land surface.

Stage 3. Accumulation of calcium carbonate

The soil becomes progressively enriched with calcium carbonate. Pore spaces become lined or filled with calcite whereas relic quartz grains and other minerals inherited from the host material become progressively replaced by calcite. Characteristic structures composed of concentrations of pedodiagenetic calcite, such as glaebules and calcitans (free and embedded grain cutans), are formed. Biological constituents of the soil may become calcified, thus forming biogenetic carbonate structures such as rhizoliths, calcified filaments, calcified faecal pellets, calcified cocoons and *Microcodium* aggregates. The thickness and depth of carbonate accumulation will depend on: the amount of available calcium and carbonate ions; the depth to which calcium-bearing waters can penetrate; the relative and absolute amounts of precipitation and dissolution of calcium carbonate within the soil profile; and the porosity and permeability of the host material.

Stage 4. Profile development

In the early stages of calcrete development, the profile is composed of weathered materials with high porosities and permeabilities. Vertical movements of meteoric vadose water can take place relatively easily. The amount of water retained within the soil profile is insufficient to supply the requirements of all plant species. Some plants extend taproots vertically downwards to the capillary fringe above the water table or to a perched water table overlying an impermeable substrate. Accumulations of calcium carbonate form vertically elongate glaebules and vertically oriented rhizoliths as a result of vertical water movements and the presence of taproots respectively. Roots extend downwards into fractures and joints within the host material, thereby modifying original fabrics, textures and structures. This biological modification is assisted by physicochemical alteration of the host material, culminating in the formation of the transitional horizon.

Precipitation of calcium carbonate, without significant cementation because of mechanical and chemical instability of the profile, forms the chalky horizon. The chalky horizon is subjected to frequent periods of wetting and drying. Precipitation and dissolution of calcium carbonate take place concurrently. Pedoturbation (physical, chemical and biological disturbance of soil materials) precludes the formation of indurated layers.

As the accumulation of calcium carbonate increases, porosity and permeability of the profile decreases. Original constituents of the host material are progressively replaced with increasing amounts of calcite. At some point in profile development, it becomes easier for soil water to move laterally rather than vertically. By this stage, most plants form lateral root systems. The change from vertical to horizontal root systems may reflect a change of plant species as the calcrete profile evolves. Interroot distances in woody species are large compared with herbaceous species (Bowen, 1973). Large (5 - 20 cm), isolated, vertically oriented rhizoliths are common in glaebular horizons, whereas smaller (1 - 2 mm), branching, horizontally oriented rhizoliths form the bulk of sheet calcrete horizons. Thus, the development of the sheet calcrete horizon from the glaebular horizon may be a reflection of plant succession in a developing calcrete profile.

Stage 5. Induration

As accumulation of calcium carbonate increases, a point will be reached when the soil organisms can no longer maintain viability. The intensity of soil-forming processes diminish and eventually cease to be important. Diagenetic processes, mainly cementation and replacement, lead to the fossilization and induration of the soil profile.

Stage 6. Reworking

The indurated profile, if it remains at the land surface, is subjected to further processes which will alter or destroy the profile. Soil-forming processes, governed initially by lower plant activities (lichens, algae, fungi, bacteria) will form a protosoil. The prepared substrate allows colonization of other plants such as mosses and grasses. Eventually, the soil profile is able to support higher plants. The root systems of these plants penetrate, dissolve and fracture the indurated hardpan. Disturbance of the calcrete profile by vegetation may form tepee structures and rhizo-breccias. Further pedoturbation, carbonate dissolution and reprecipitation, lead to the formation of a reworked, recemented, breccia-conglomeratic calcrete hardpan.

Summary

As already indicated, the model presented here is simplistic. The processes involved in the rock-sediment-soil-rock cycle are exceedingly complex. The model is an outline only of sequence of possible events. Some stages may be repeated or reversed; others may be omitted. Emphasis has been given to the role of organic activity which determines largely the morphology of calcrete profiles and which controls the direction of profile development. Little is known in detail of the exact processes of bioerosion and biolithogenesis in calcrete formation. At the present time, even less is known of the importance and ubiquity of these processes in determining fabrics, textures and structures of calcrete deposits. Physicochemical considerations alone do not explain satisfactorily the natural phenomena associated with the growth and decay of calcrete deposits. Biological considerations provide many answers to, hitherto, perplexing and unresolved problems of calcrete genesis. This study recognizes the importance of biological interference in calcrete formation and has documented the products of biolithogenesis.

CHAPTER NINE - SUMMARY AND CONCLUSIONS

METHODOLOGY

Quaternary calcretes from western Mediterranean regions have been examined to document their morphological characteristics and chemical properties. By combining field and laboratory observations and analyses, information has been gained which provides a greater understanding of the origin of calcretes. Although this study lacks spatial and temporal precision, morphological characteristics of calcretes have documented in detail at several scales of observation. In so doing, a number of significant advances have been made regarding the mechanisms of calcrete formation. This study does not provide full answers; it does, however, give insights into many formerly unresolved problems of calcrete genesis and, at the same time, has exposed misconceptions and erroneous interpretations in this peripheral, though increasingly important, branch of geology.

TERMINOLOGY AND CLASSIFICATION

A review of pertinent literature reveals that calcrete terminology and classification are in a state of confusion. This has hindered communication among workers of differing interests and backgrounds. Proposed mechanisms of calcrete formation have been based largely on intuition and circumstantial evidence. The prevailing view that calcretes are pedogenetic in origin finds favour with most workers interested in calcrete genesis. This study provides substantive evidence to support the contention made here that calcretes are pedogenetic and diagenetic in mode of formation. The newly proposed term pedodiagenesis is used here to embrace all processes involved in calcrete formation. New definitions of calcrete and calcretization are presented which summarize the philosophical concepts of this study. To recapitulate, calcretes are the result of pedodiagenetic alteration or obliteration of precursor fabrics, textures and structures and the production of new fabrics, textures and structures which take place as a result of accumulation of low magnesian calcite within the meteoric vadose zone.

Thus, calcretes are distinctive terrestial accumulations of calcium carbonate which have diagnostic fabrics, textures and structures that allow of their recognition. Nonetheless, as noted by Dunham (1969b), there has been a scarcity of identified calcretes in ancient rocks. Dunham suggested that some calcretes may have been mistaken for algal stromatolites. James (1972) in his valuable contribution on Holocene and Pleistocene calcareous crusts from Barbados, concluded (p. 834): "Although these calcareous crust profiles may be good criteria for subaerial exposure, by mimicking other structures they guard their secret well." Both Dunham (1969b) and James (1972) thought that calcretes were likely to be preserved in the fossil record.

With the words of Dunham (1969b) and James (1972) echoing in the ears of geologists, the number of recent documented reports of ancient 'calcretes' has risen dramatically. However, great care is needed; many workers have based their identifications of calcrete on criteria given by Dunham (1969b). Dunham suggested that the pisolitic facies of the Permian Capitan reef complex may be pisolitic caliche. This suggestion has been seriously questioned by Esteban (1976) and, as a consequence, has undermined the validity of interpretations made by those workers who accepted Dunham's interpretations as facts. Accepting features of ancient deposits as being representative of modern counterparts without studying the latter is an inherently dangerous and unscientific procedure.

In this study, I have examined modern (Pleistocene and Recent) calcretes to gain a better understanding of relationships, processes and products of calcrete formation. By this approach, I feel that I am in a better position to evaluate available criteria for the recognition of calcretes and to assess the usefulness of such criteria for recognizing ancient counterparts.

From my definition of calcrete, evidence is required to substantiate that: (1) the environment of calcrete formation was the meteoric vadose zone; (2) pedogenetic and diagenetic processes were responsible for calcrete formation; and (3) formation took place within a host material, causing modification or obliteration of original fabrics, textures and structures and the production of new fabrics, textures and structures. Criteria to satisfy these requirements are summarized below. As a cautionary note, it is pointed out that all information needs to be evaluated before any interpretations can be made. Mere recognition of a few features characteristic of calcretes is not sufficient to designate deposits as such. Criteria listed below, taken in isolation, may be found in distinctive but completely unrelated sedimentary and diagenetic environments. But, as stated so succinctly by Bathurst (1975, p.417): "safety is in numbers and a satisfactory decision can generally be reached if several criteria are combined." At the same time, it should be borne in mind that many calcretes may not contain characteristic features; absence of these features does not necessarily mean that the deposit is not a calcrete, a point made previously by Esteban (1974).

FIELD ASSESSMENT

Regional Distribution

Factors controlling the regional distribution of calcretes throughout the western Mediterranean have been examined. The five soil-forming factors of (1) climate, (2) host material, (3) topography, (4) organisms and (5) time have been considered and evaluated as follows:

(1) Climate - - The popular view that calcretes form in semi-arid environments is not refuted but no reliable evidence has been found in this study to lend support to this contention. It seems, however, that alternating wet and dry periods are conducive to calcrete development.

(2) Host material - - Calcretes are independent of lithology. Calcretes occur within indurated rocks, unconsolidated sediments and pre-existing active or relic soils. Host materials may be carbonate or non-carbonate in composition. On gentle (less than 25°) slopes, morphodynamic activity (erosion and sedimentation) is the only factor which precludes calcrete development in the study area, assuming that sources of calcium carbonate are available.

(3) Topography - - Quaternary calcretes are best developed on stable, gentle slopes in lowlying areas surrounded by older limestones or dolomites. Mesozoic and Tertiary limestones and dolomites are volumetrically significant components of western Mediterranean landscapes. Calcretes are laterally extensive over several hundred square kilometres.

(4) Organisms - - The type and distribution of present-day vegetation cannot be related to the distribution of Recent or Pleistocene calcretes. Regardless of what types of vegetation are or were present during calcrete formation, higher and lower plants play a fundamental role in terms of substrate modification and the production of new fabrics, textures and structures (listed below). Soil mesofauna also play an important role by producing channels and faecal pellets.

(5) Time - - The time factor in calcrete formation is difficult to assess for several reasons. While quantitative datings are few and those that have been determined are unreliable, relative dating methods lack precision. I have relied largely on the 'law of superposition' for gross dating.

Calcrete Profiles

Field observations indicate that, regardless of composition and texture of host materials, calcretes have a vertical anisotropy which forms a profile with recognizable horizons. A complete calcrete profile consists of, from the top downwards, a calcrete hardpan, a sheet calcrete horizon, a glaebular horizon, a chalky or powdery horizon, a transitional horizon and unaltered host material. Calcretes develop in, not merely on, pre-existing substrates. The sequence of horizons may be repeated or may be incomplete for a given profile. Present-day soils may or may not be related to the underlying calcrete profile.

Macromorphological Features

Calcretes contain macromorphological features including rhizoliths, glaebules, laminar structures, tepee structures and brecciation textures. Rhizoliths are land plant root-mineral structures which comprise five main preservational types, namely, rhizocretions s.s., root casts, root moulds, root tubules and root petrifactions. Carbonate glaebules are concretionary structures which grow as concentrated accumulations of calcium carbonate about a point or line, giving rise to roughly spherical or ellipsoidal bodies respectively. Laminar structures result from incremental growth of calcium carbonate and organic layering on a free surface. Crustose lichens are responsible for the formation of some laminar calcretes which form at the rock-atmosphere interface. Subsurface laminar calcretes form at the base, and accasionally on the roof, of horizontal to subhorizontal root mats.

Root penetration is responsible for the production of tepee structures and in situ brecciation textures. Rhizo-breccias result from the biophysical activities of growing roots. Living roots force open pre-existing planes of weakness. In addition, roots bore biochemically into indurated calcrete. The growth in girth and increase in number of roots exert pressures which are sufficient to fracture and force blocks apart. Rhizo-brecciation is an adequate mechanism to account for non-tectonic disturbance of indurated calcrete profiles.

LABORATORY ASSESSMENT

Micromorphology

Drawing heavily on the pedological classification scheme of Brewer (1964), microfabrics, textures and structures have been documented by optical and scanning electron microscopy. The basic unit of study, termed the s-matrix, is divided into three components - plasma, skeleton grains and voids. Fine crystic and fibrous calcite are important plasma types of Spanish calcretes. The chalky horizon consists of uncemented fine to coarse crystic calcite which may be equivalent to the vadose silt of Dunham (1969a). Hyphantic and banded fibrous calcite plasmic fabrics form alveolar and vesicular textures within the sheet calcrete horizon. The overlying hardpan is dominated by fine crystic calcite plasma.

Partial replacement of skeleton grains by pedodiagenetic calcite and displacement of s-matrices by biophysical root penetration produce floating textures. Vermicular textures are associated with rhizoliths and result from calcification of vascular plant root hairs.

Rearrangement of the s-matrix during calcrete development produces pedodiagenetic structures which may be abiogenetic or biogenetic in origin. Abiogenetic structures include glaebules and cutans which are useful indicators of soil formation. Glaebules may form initially as friable aggregates composed of hyphantic and banded fibrous calcite plasma. Cutans form on free or embedded surfaces by chemical accretions of neoformed plasma. Biogenetic structures include rhizoliths, calcified filaments, calcified cocoons, palynomorphs of higher and lower plants, calcified faecal pellets and Microcodium.

Calcified filaments result from calcite encrustation and/or calcite impregnation of filamentous organic structures. Templates for calcified filaments include soil fungi, actinomycetes, filamentous algae and root hairs.

Calcified faecal pellets and calcified cocoons result from the former activities of indigenous mesofauna. Some clotted textures in calcretes result from pedoturbation.

The new discovery of Microcodium in Recent soils from southeastern Spain extends its stratigraphical range into the Holocene. Retention of ultrastructural details suggests an hitherto unconsidered origin for this enigmatic structure, namely, calcification of mycorrhizal associations (fungus-root symbiosis).

Composition

Micromorphological and analytical determinations for mineralogical and compositional determinations reveal that calcretes studied here are composed dominantly of low magnesian calcite. Depending on the composition and extent of alteration, quartz, micas, clay minerals, dolomite and other detrital or inherited minerals occur in variable but lesser amounts. Minor quantities of authigenic silica and halite may be present; both form within the subaerial vadose diagenetic environment. Hardnesses of up to 6 on the Mohs' scale are the result of silica impregnation of the s-matrix. Released silica from corroded quartz grains provides a potential source for the silicification of calcretes.

The composition of the acid-soluble fraction suggests that pedodiagenetic calcite is precipitated within the subaerial vadose environment. Evaporation, carbon dioxide loss during photosynthesis and transpiration are considered to be likely mechanisms which induce the precipitation of calcite.

Related Phenomena and 'Calcrete-like' Deposits

Phenomena commonly related to, but not necessary for, calcrete formation include lichen stromatolites and 'case-hardened' carbonate crusts. Epilithic and endolithic lichens are important substrate modifiers and sediment producers. Calcification of crustose lichens produces lichen stromatolites which are significant components of many laminar calcretes.

Deposits superficially similar to calcretes include coniatolites, speleothems, travertine, algal stromatolites, freshwater tufa and lacustrine carbonates. With the exception of lacustrine carbonates, these deposits can be distinguished relatively easily from calcretes by field and petrographic criteria. Lacustrine carbonates, on the other hand, have many fabrics, textures and structures which are typical of calcretes. Lacustrine carbonates and calcretes can be differentiated from each other by examining regional settings and field relationships rather than by using petrofabric information.

CALCRETE MODEL

By combining macromorphological and micromorphological observations, the processes of calcrete formation and destruction have been placed within a conceptually defined pedodiagenetic cycle. From a consideration of potential sources of calcium carbonate, pedodiagenetic processes, nature and movement of pore fluids within calcrete profiles and possible mechanisms of calcite precipitation, the compositional and fabric evolution of calcrete deposits have been summarized within a process-response model by using all available information and data gained during the course of this work.

RECOMMENDATIONS FOR FURTHER STUDY

This study does not pretend to be definitive. Many questions raised during the course of this work still require answering; some avenues of research have yet to be explored. A more rigorous approach to the timing and duration of calcrete formation is necessary before the climatic conditions during formation can be assessed with confidence. More information is required on the biotic factor, particularly the type of vegetation and the effect of organic matter on the precipitation and dissolution of calcite. A detailed pollen analysis might provide the necessary evidence for the identification of plant species.

An interdisciplinary approach is required to resolve outstanding problems of calcrete formation. This study has made use of the knowledge and methods of several specialist fields within the earth and life sciences. Advances made during the course of this work need to be refined by collaboration with botanists, microbiologists, organic chemists and soil scientists, whose sympathies lie with the problems of a geologist——trying to make sense of the morphology, composition and genesis of calcrete deposits.

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