# MORPHOLOGY AND GENESIS OF CALCRETE IN SOUTH AUSTRALIA WITH SPECIAL REFERENCE TO THE SOUTHERN MURRAY BASIN AND YORKE PENINSULA

John Charles Dixon, B.A.Hons. (N.S.W.)

Submitted in fulfilment of the requirements
for the degree of Master of Arts
The University of Adelaide

1978

Awarded September [illegible]

# STATEMENT OF ORIGINALITY

This thesis is based on original research carried out in the Department of Geography, University of Adelaide. It contains no material previously published or written by another author, except where due reference is made in the text of the thesis.

John C. Dixon

# ACKNOWLEDGEMENTS

The completion of this thesis would not have been possible without the assistance of a number of people to whom I am most grateful.

In particular I would like to thank:

- Dr. C. R. Twidale, my supervisor, for his interest, advice and invaluable criticism.
- Mr. J. Hutton from C.S.I.R.O. Division of Soils for his assistance and advice with X-ray fluorescence analyses.
- Mr. J. Pickering from C.S.I.R.O. Division of Soils for his assistance and advice on the preparation of samples for X-ray diffraction and for interpreting X-ray powder photographs.
- Miss C. Barrington, cartographic assistant in the Department of Geography, for printing photographs so speedily and efficiently.
- Mr. F. Hilton, education section, South Australian Museum, for identifying the molluscs.

# CONTENTS

## LIST OF TABLES

# LIST OF FIGURES

PAGE

# SUMMARY

The aim of this thesis is to describe and account for the calcrete which occurs extensively throughout the Murray Basin and Yorke Peninsula in southern South Australia and to see what light, if any, their investigation throws on similar features developed elsewhere. Calcrete is widely distributed in South Australia. It is of considerable geomorphological significance and is in some quarters used as a stratigraphic marker. Yet there has been little work done on the morphology and genesis of these deposits. Unless we understand the ways in which calcrete forms it is obviously fruitless to draw conclusions from it about the age of the land-surfaces on which it is developed.

In order to come to some understanding of the processes responsible for the formation of calcrete the chemistry and mineralogy of calcrete from various sites in the two selected study areas were examined using X-ray fluorescence spectrometry and X-ray diffraction techniques. The gross morphology and geomorphological setting of the calcretes also provided information on the processes of formation.

Field observations and laboratory analyses show that the calcretes of the Murray Basin and Yorke Peninsula form in various ways. In the Murray Basin the occurrence of considerable quantities of palygorskite, sepiolite and dolomite strongly suggest that many of the calcretes developed there are of lacustrine origin. The dominant

clay minerals in the calcrete from the western margin of the Murray Basin are illite and kaolinite which suggests that the carbonates are of a pedogenic origin. On Yorke Peninsula also, where the dominant clay minerals in the calcrete are illite and kaolinite and where dolomite contents are very low, pedogenic processes are responsible for the formation of the extensive calcrete hardpans.

Calcretes of the southern Murray Basin appear to have been formed in shallow saltwater lakes related to Pleistocene marine regressions. The calcretes of Yorke Peninsula have been derived from the solution and subsequent redeposition of carbonates in the Pleistocene aeolian dunes and sand sheets which cover large areas of the landscape and from the Tertiary and Cambrian limestones on which the younger sediments are developed.

# CHAPTER I

# INTRODUCTION

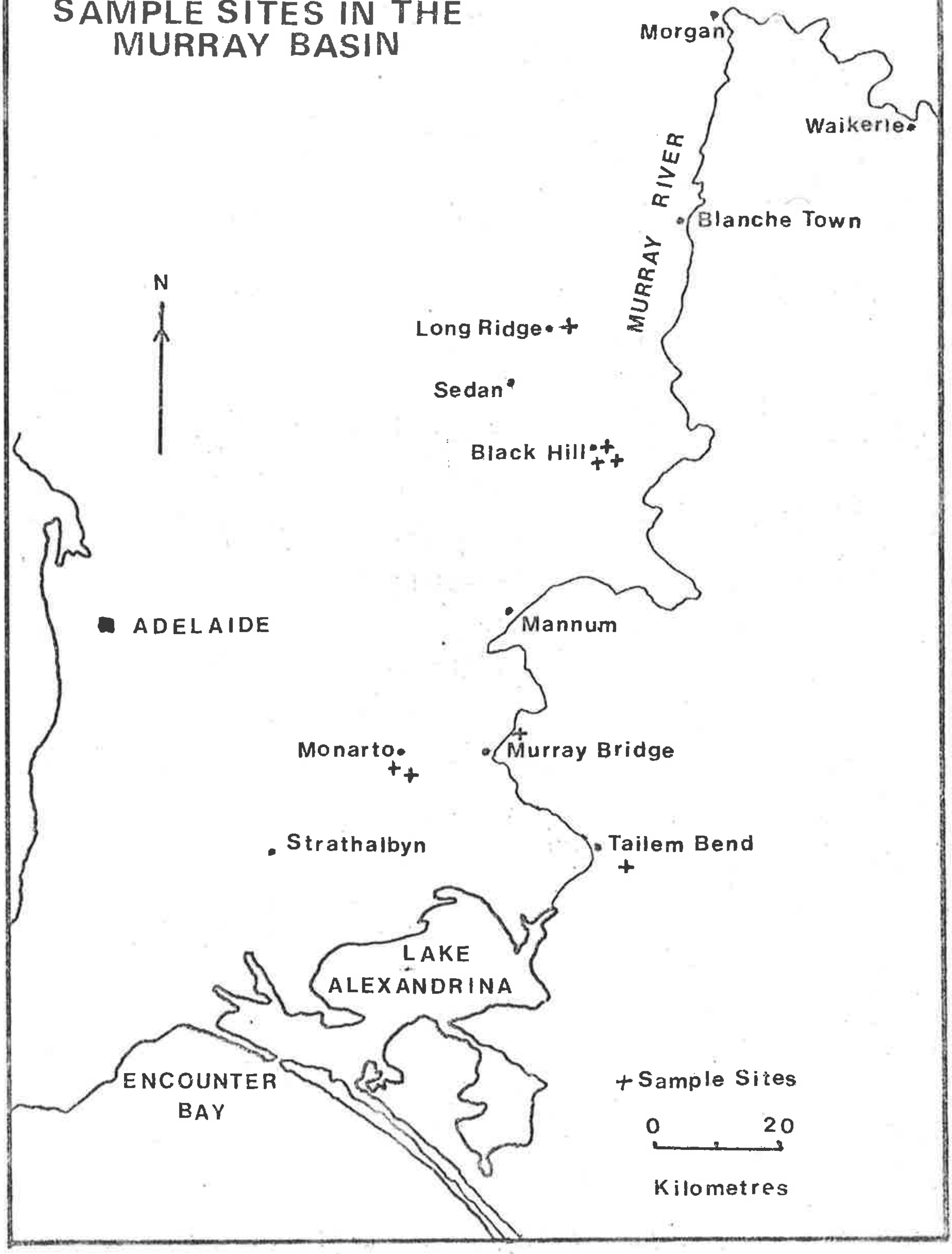
Much of the South Australian landscape is characterized by the development of an extensive surficial covering of indurated calcrete. This material has been described by a number of South Australian geologists, and possible modes of origin have been discussed by many early workers including Howchin (1901), Jack (1914) and Prescott (1931). Perhaps the most significant and enduring work on calcrete is that of Crocker (1946) who discussed its origin in considerable detail. Recent workers, and notably Crawford (1965) and Firman (1966, 1969, 1971, 1973), have accepted Crocker's theory of origin almost without question.

## Aim of the Thesis

The first aim of the thesis is to outline the morphology of calcrete from a number of selected sites in southern South Australia, primarily from the Murray Basin (figure 1.1) and Yorke Peninsula (figure 1.2). Field observations have shown that there is considerable variation in the physical appearance of calcrete and in the relationship between the various calcrete types in specific profiles. Unlike other semiarid areas of the world from which calcrete has been described, notably South Africa (Netterberg 1967, 1969a, 1969b, 1971) and the United States (Bretz and Horberg 1949; Brown 1956; Aristarain 1970, 1971; Reeves 1970; Gardner 1972), there have been

FIGURE I.I

LOCATION OF TOWNS AND SAMPLE SITES IN THE MURRAY BASIN



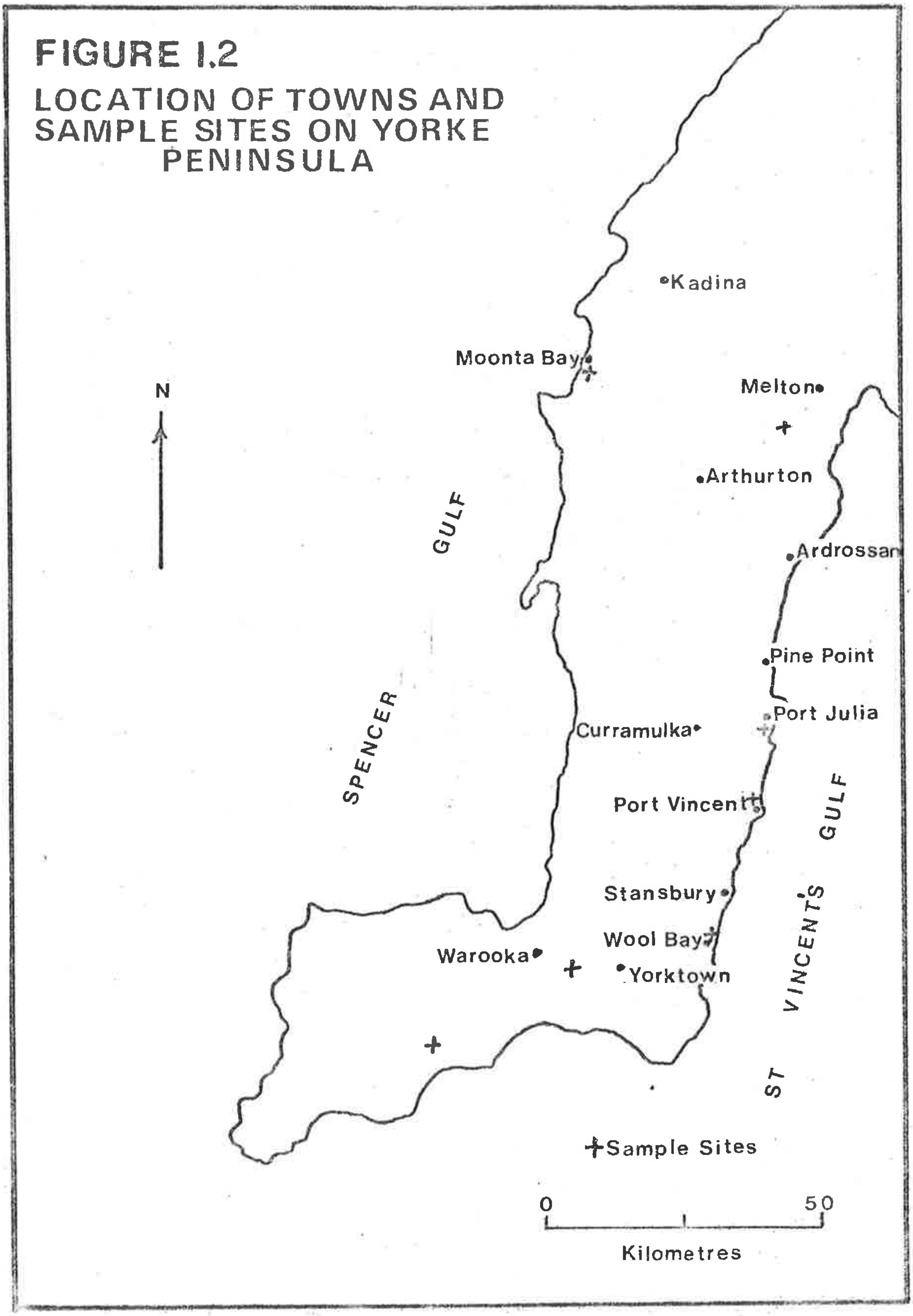


FIGURE I.2

LOCATION OF TOWNS AND SAMPLE SITES ON YORKE PENINSULA very few morphological descriptions of calcrete from South Australia except for brief descriptions of some sites on Yorke Peninsula by Crawford (1965).

Secondly, the genesis of the calcrete at the selected sites in the Murray Basin and on Yorke Peninsula is discussed. Chemical analysis by X-ray fluorescence spectrometry, mineral identification by X-ray diffraction and thin section studies as well as field observations are used as the basis for conclusions as to the origin of the calcrete at the sites examined. No attempt is made to present a theory which accounts for the origin of all calcretes in South Australia, for the origin of this material may vary from one locality to another; no single process necessarily accounts for all calcrete deposits. Rather, each locality must be examined in the context of its geomorphological and geological environment.

## Definition of Calcrete

The term calcrete was originally coined by Lamplugh (1902) to refer to lime-cemented Pleistocene gravels near Dublin, and later used to refer to lime-rich surface materials in the catchment of the Zambezi River (Lamplugh 1907). In the same year that the term calcrete was coined, Blake (1902) introduced the equivalent term caliche which is still frequently found in the North American literature.

> "In southern Arizona and Mexico caliche is in general use to denote a calcareous formation 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." (Blake 1902 p. 220)

Of the two terms, however, Lamplugh's term calcrete appears to be the most precise for describing the surface and near-surface accumulations of calcium carbonate which occur extensively throughout the semiarid areas of the world. The term calcrete is preferred to caliche as it is consistent with the other two duricrusts named by Lamplugh (1902); silcrete for materials cemented by silica and ferricrete for iron oxide cemented materials.

Moreover, despite the common application of the term caliche in North America to indurated carbonate deposits, it has also been used to refer to nitrate on the west coast deserts of South America (Goudie 1973) and to gypsum deposits in Death Valley, California (Hunt and Mabey 1966). Thus the term calcrete is much to be preferred.

Perhaps one of the earliest and most widely accepted definitions of calcrete is that proposed by Bretz and Horberg (1949).

> "Throughout the Southwest and southern High Plains the term caliche is applied to calcareous caprock, soil hardpans and earthy or porous materials which occur at the surface or at shallow depths below the soil ... it is desirable, if possible to restrict the term to materials of calcareous composition ... as indicated by the derivation of the word and especially to those calcareous materials which are found in the zone of weathering. Sub-aqueous deposits, spring deposits and mortar beds would thus be excluded." (Bretz and Horberg 1949 p. 491)

This definition has been improved upon by Netterberg (1969):

> "A calcrete may be defined as almost any terrestrial material which has been cemented and/or replaced by dominantly calcium carbonate ... cave deposits are excluded ... the mechanism

> of calcification is not restricted and calcretes
> may be of pedogenic or non-pedogenic origin
> or both." (Netterberg 1969 p. 88)

Of the definitions which are to be found in the literature this is perhaps the most satisfactory as it clearly conveys the secondary nature of calcification thus distinguishing calcrete from primary sedimentary limestone. Furthermore unlike most earlier definitions it clearly implies that calcrete is not necessarily a soil phenomena.

Throughout this thesis the term calcrete is used in the sense which Netterberg defined and will be used in preference to the terms kunkar, travertine and travertine limestone which have frequently been used in the geological literature on South Australia in the past.

With respect to Kunkar (or Kankar) Saini (1966) has shown that this Hindi term means gravel and is used in that sense in England for nodules in alluvium (Goudie 1973). For this reason the term should preferably not be used to refer to the continuous sheets of massive calcrete found in South Australia, although arguments could justifiably be presented to use this term when referring to nodular calcrete. Such double usage would however lead to unnecessary confusion.

Travertine has also been used extensively in Australia (Woolnough 1930; Crocker 1946), but it is unsatisfactory in the present context as it has been properly applied to stream, spring or cave deposits of calcium carbonate. In much of the pedological literature calcrete has been referred to simply as limestone or lime (Northcote 1951) or as calcareous marl (Crocker 1946).

# CHAPTER II

# GEOLOGICAL SETTING

As much of the later discussion on the origin of the calcretes, particularly with regard to the source of calcium ions, centres on the geological environments of the Murray Basin and Yorke Peninsula, a detailed account of the geology of the two areas is included here.

## The Murray Basin

The Murray Basin is a Tertiary sedimentary basin which covers an area in excess of 76,000 $km^2$ in south-eastern South Australia. It is characteristically an area of plains underlain by Cainozoic, Mesozoic, Lower Palaeozoic and Precambrian sediments and rocks (Firman 1973) (Table 2.1).

The western and north-western boundaries of the Murray Basin are delineated by the folded sediments of the Adelaide Geosyncline, metasediments of the Kanmantoo trough and various intrusive granites. Cainozoic sediments transgress all of the Palaeozoic and Proterozoic basement rocks of the Basin.

During the Permian, when ice covered many parts of the State, the Murray Basin appears to have been relatively ice-free. Permian glacial deposits are to be found only in the south-eastern part of the basin in the vicinity of the Coorong and Lake Alexandrina where boulder clays have been found in bores (Ludbrook 1961). Glaciogene sediments have not been reported from the north of the Murray Basin.

TABLE 2.1

Stratigraphy of the Murray Basin

| Age | | | | Description | |
|---|---|---|---|---|---|
| QUATERNARY | RECENT | | | Recent sand dunes | |
| | | | | Coonambidgal Formation - clays, silts and sands | |
| | | | | Bunyip Sands<br>red sands | Molineaux Sand<br>yellow sand |
| | | | | Monoman Formation - alluvial clays, silts and coarse sands | |
| | PLEISTOCENE | UPPER | | Callabonna Clay | |
| | | | | Pooraka Formation - clayey sands, sands and gravels | |
| | | | | Woorinnen Formation - red brown quartz sand with carbonate silt (Loveday Soil) | |
| | | MIDDLE | | Bakara Soil - { | Bakara Calcrete<br>Ripon Calcrete |
| | | LOWER | | Bungunnia Limestone - dolomitic micrite | |
| | | | | Blanchetown Clay - fluvio-lacustrine sandy clays and limestone | |
| TERTIARY | PLIOCENE | | | Norwest Bend Formation<br>sandy limestones and calcareous sand | Parilla Sand<br>clayey and micaceous quartz sand |
| | | | | Loxton Sands - cross-bedded yellow micaceous sands | |
| | | | | Bookpurnong Beds - glauconitic marls | |
| | MIOCENE | | Group | Pata Limestone | |
| | | | MURRAY | Morgan Limestone - cream coloured, richly fossiliferous bryozoal limestone | |
| | | | | Finnis Clay - blue-green, green and brown mottled clay | |
| | | | | Mannum Formation - calcareous sandstones and sandy limestones | |
| | OLIGOCENE | | GLENELG | Ettrick Formation - glauconitic sandy marl | |
| | | | | Compton Conglomerate | |
| | EOCENE | | BUCCLEUCH | Buccleuch Beds - limestones, marls, sands, clays | |
| | | | KNIGHT | Renmark Beds - silty sands, gravels, clays and carbonaceous silts | |
| CRETACEOUS | | | | non-marine quartz sandstones, marine mudstones, siltstones and shales | |
| PERMIAN | | | | boulder clays, claystones and sandstones | |
| CAMBRIAN | | | | Kanmantoo Group - metasediments and granites | |

After Ludbrook 1958, 1961 and Firman 1969, 1973

Permian glacial sediments, which consist of claystones and sandstones are overlain unconformably by Lower Cretaceous sediments. The Cretaceous sediments consist of non-marine quartz sandstones overlain by marine siltstones and shales.

Early in the Tertiary, accompanying the uplift of the Mount Lofty Ranges to the west, there was subsidence of the present Murray Basin. Accompanying this subsidence was a marine transgression and the deposition of paralic carbonaceous sands, silts, lignitic beds and low-rank coals. Late in the Eocene normal marine limestones and marls were deposited.

At the base of this sequence is a relatively thick accumulation of paralic silty sands, gravels, clays and carbonaceous silts which are Middle to Upper Eocene in age (Ludbrook 1958). These strata cover most of the Murray Basin and are known as the Renmark Beds.

Overlying the Renmark Beds is a marine sequence known as the Buccleuch Beds, representing an upper Eocene marine transgression which extended as far north as Waikerie (Firman 1973), and consisting of a thin series of lenticular limestones, clays and bryozoal limestones (Ludbrook 1958).

Early in the Oligocene there was a marine transgression which resulted in the deposition of the Compton conglomerate. Associated with this was the deposition of the Ettrick Formation consisting of glauconitic marls and sandy marls.

The maximum marine transgression in the Murray Basin occurred early in the Miocene when sediments up to 100 m thick and collectively known as the Murray Group were deposited in warm shallow seas (Firman

1973). Because this group is a major source of calcium for calcrete formation in the Murray Basin the members of the Murray Group will be discussed in some detail.

The Mannum Formation, which is extensively exposed in the cliffs of the Murray River, is composed of calcareous sandstones and sandy limestones some 10 m thick. The unit can be traced along the banks of the Murray River south past Murray Bridge and westward to Strathalbyn and Monarto where it is transgressive on Kanmantoo Group sediments and Monarto Granite respectively (Ludbrook 1961).

In some areas the Mannum Formation is overlain by the Finnis Clay which consists of 5 m of blue-grey, green and brown mottled clay. This unit represents a break in sedimentation as a result of a localized marine regression, but where limestone deposition was continuous the Mannum Formation is conformably overlain by the Morgan Limestone.

This unit which is lithologically indistinguishable from the Mannum Formation, is exposed in the cliffs of the Murray River south of Morgan. It consists of a cream-coloured, richly fossiliferous bryozoal limestone. Like the Mannum Formation, this unit comprises two members (Ludbrook 1958), the lower member soft and even grained, the upper member hard and banded. At the type locality four miles downstream from Morgan the combined thickness of the two members is 23 m (Ludbrook 1957). In some places the two members of the Morgan Limestone are separated by a 7 m thick lens of richly fossiliferous blue-grey sandy marl known as the Cadell Marl Lens.

Between Loxton and Pineroo another limestone unit occurs at depth, where there is 30 m of a grey to yellow bryozoal limestone above the Morgan Limestone (Ludbrook 1958). This unit is known as the Pata Limestone and according to Firman (1973) represents the uppermost Miocene marine unit in the Murray Basin. Like the Mannum Formation and Morgan Limestone this unit also consists of hard bands and is in places marly.

In early Pliocene times there was a further marine ingression soon after which the Bookpurnong Beds were deposited. These beds consist of a series of red-green and green micaceous and glauconitic shelly marls as well as buff coloured calcareous limestone (Firman 1973). These beds lie between the Pata Limestone and the Loxton Sands, which consist of a shallow, partly brackish water deposit characterized by bright yellow to cream cross-bedded, coarse, gritty, very micaceous sands and silty sands with shelly beds (Ludbrook 1958). This formation exhibits considerable facies change and includes calcareous equivalents in the Waikerie and Cadell areas.

Following the deposition of the Loxton Sands there was a marine regression until the upper Pliocene when the sea again inundated the Basin in the form of a broad estuary which probably followed the present course of the Murray River. In the estuary a thick and extensive oyster bank known as the Norwest Bend Formation was deposited (Ludbrook 1958). It consists of 9 m of sandy limestones and calcareous sand (Firman 1973).

Equivalent in part to the Norwest Bend Formation is the Parilla Sand which grades into the former near Kingston-on-Murray.

It is a slightly clayey and micaceous sand which is believed to have been deposited in a fluvio-lacustrine environment upstream from the Norwest Bend estuary (Firman 1973).

The basal Pleistocene unit in the Murray Basin is a widespread, thin fluvio-lacustrine sandy clay and limestone sequence known as the Blanchetown Clay. Overlying this is a fossiliferous dolomitic micrite called the Bungunnia Limestone. In some places these two units are separated by loess. The Bungunnia Limestone has according to Firman (1965) been deposited in a system of Middle Pleistocene valley lakes which he has collectively termed Lake Bungunnia.

Overlying the Bungunnia Limestone is the Bakara Soil which Firman (1963) defined as a soil stratigraphic unit and which he suggests is an old brown soil characterized by an indurated limy fossil "B" horizon. This calcrete is referred to as Ripon Calcrete which is predominantly a massive calcrete consisting of cemented calcium carbonate nodules. Distinguishable from the Ripon Calcrete, but still part of the Bakara Soil is what Firman (1971) refers to as younger calcrete or Bakara Calcrete. This younger calcrete is distinguishable from the Ripon Calcrete, Firman argues, in that it is essentially nodular in form and unlike the former is not cemented into a massive sheet.

Widespread aeolian deposition began in the Upper Pleistocene and is represented in the stratigraphic sequence by the Woorinen Formation which consists of a pale red-brown quartz sand mixed with the carbonate silt. This carbonate silt, which Firman (1973) considers to be stratigraphically associated with the Woorinen

Formation, has been called the Loveday Soil or Loveday Calcrete (Firman 1971), a chalky white calcite with no cementation between the carbonate grains and the parent material.

The uppermost Pleistocene deposits of the Murray Basin are the colluvial and alluvial materials which are found on the western and north-western margins of the Basin. These deposits consist of clayey sands, sands and gravels of the Pooraka Formation, which are overlain by the Callabonna Clay (Firman 1970).

Recent sediments consist primarily of valley fill deposits, the oldest of which are referred to as the Monoman Formation. This formation consists of alluvial clays, silts and coarse sands. The reworking of this formation and older Tertiary deposits has contributed to the formation of the red Bunyip Sand and yellow Molineaux Sand. These two deposits have in turn been overlain by later phases of valley fill to which the name Coonambidgal Formation has been assigned. The sand dunes which cover large areas of the Murray Basin consist of red or yellow sands depending on whether their source has been the Bunyip or Molineaux sands respectively (Firman 1973).

## Yorke Peninsula

Yorke Peninsula is a leg-shaped peninsula which extends into the Southern Ocean, separating Spencer Gulf from St. Vincents Gulf on the west coast of South Australia. The Peninsula covers an area of some 6,800 km$^2$, is 240 km in length and varies in width from about 30 km at Stansbury to 50 km at Arthurton. Like the Murray Basin, Yorke Peninsula is an area characterized by plains and underlain by limestone sequences thus making it essentially a karst plain lacking permanent streams. The only complete geological survey of the Peninsula was carried out by Crawford (1965) and this summary of the geology of the Peninsula is based on that survey (Table 2.2).

Yorke Peninsula is a fault-bounded ridge of Archean rocks overlain by a thin covering of younger deposits. The Archean basement consists primarily of metasediments, amphibolites, schists, gneisses and intrusives.

Lying unconformably on the Archean basement are two Proterozoic Formations. Crawford distinguishes them as a shelf sequence which consists of quartzose sandstones, quartzites, conglomerates and arkose sandstones with shaly beds at the top. This sequence is best developed in the central and northern parts of Yorke Peninsula. The second sequence of Proterozoic rocks, which Crawford refers to as geosynclinal are similar to those of the Mount Lofty Ranges. This sequence outcrops in the uplands to the north of the Peninsula.

Cambrian rocks cover a large area of the Peninsula and are represented by a series of limestones with interbedded clastics. This sequence consists of a Lower Cambrian unit called the Kulpara Limestone. It consists of grey limestones and yellow dolomitic limestones which are silicified in their upper sections. Intraformational limestone breccias also occur within the unit. This limestone unit is exposed in a number of localities, including

TABLE 2.2

Stratigraphy of Yorke Peninsula

| Age | | Description |
|---|---|---|
| QUATERNARY | RECENT-PLEISTOCENE | modern beach sand and dunes |
| | | saline lakes, salt flats and gypsum lakes |
| | | longitudinal sand dunes |
| | | older beach ridges |
| | | massive, nodular and laminar calcrete |
| | | aeolianite in cliffs |
| | PLEISTOCENE | Ardrossan Clays - mottled sandrock with angular gravels |
| TERTIARY | PLIOCENE | Hallett Cove Sandstone - sandy and gritty fossiliferous limestones |
| | LOWER MIOCENE | Melton Limestone - conglomeratic, sandy bryozoal limestone |
| | OLIGO-MIOCENE | Port Willunga Beds - soft bryozoal sandy limestone |
| | | Port Julia Greensand - glauconitic clayey sandstone, overlies limestone at Urania |
| | | Point Turton Limestone - soft bryozoal limestone |
| | EOCENE | Blanche Point Marl - shelly clays, silicified sandstone, sandrock and marl |
| | | Muloowurtie Clays - sandy clays and shelly limestone |
| | | coarse, cross-bedded lignitic sands |
| PERMIAN | | glacial till, siltstones and sandstones |
| CAMBRIAN | MIDDLE | arkose, greywacke and shale |
| | | Coobowie Limestone |
| | | unnamed clastics |
| | | Stansbury Limestone |
| | | arkose, feldspathic sandstones, silts and shales |
| | | Ramsay Limestone - crystalline limestone, dolomite and interbedded shales |
| | LOWER | unnamed red beds - clastics, conglomerates and shales |
| | | Minlaton Conglomerate |
| | | Parara Limestone - crystalline limestone and dolomite |
| | | limestone member unnamed |
| | | Kulpara Limestone - limestone, dolomite, siliceous limestone and limestone breccia |
| PROTEROZOIC | | quartz conglomerates, feldspathic sandstones, shales and quartzites |
| ARCHEAN | | gneisses, schists, granites and pegmatite |

After Crawford 1965 and Daily 1967.

the Ardrossan dolomite quarry.

Overlying the Kulpara Limestone is an unnamed limestone unit, recognized from bores by Daily (1967), which passes into the Parara Limestone, a dark blue-grey crystalline nodular limestone with soft dolomitic bands at depth. Daily (1956) reports a thickness of approximately 25 m at the type section and 33 m at Curramulka. Crawford (1965) however suggests that it may be closer to 300 m, a figure supported by Daily in recent investigations (Daily 1967).

The limestone sequence is interrupted by the recurrence of the Minlaton Conglomerate and unnamed red beds of clastics, conglomerates and shales, which are up to 150 m thick, and which are calcareous in the upper 15 m of the unit. Underlying the red beds is a 10 m thick bed of limestone conglomerate which in turn is underlain by 20 m of shale. This unit has only been recognized in bores and is believed to be of similar age to the red beds and sedimentary breccias and limestone conglomerates of the Pine Point and Rocky Point areas.

In the Middle Cambrian, shallow water limestone deposition resumed and the Ramsay Limestone was laid down. This is a dark blue-grey crystalline nodular limestone with buff coloured dolomitic shaly interstitial material. Lithologically, the Ramsay Limestone resembles the Parara Limestone.

Remnants of red feldspathic sandstones, and shales have been reported overlying the Ramsay Limestone by Crawford (1965) and Daily (1967). Whether these remnants represent the deposition of the red and green clastics of the Lake Frome Group on Yorke Peninsula in the Middle to Late Cambrian is uncertain, they may simply be related to the red beds which underly the Ramsay Limestone.

Overlying the red feldspathic sandstones is the Stansbury Limestone which reaches a thickness of 54 m and is succeeded by another unit of unnamed clastics. The Coobowie Limestone was then deposited and reaches a thickness of 12 m. The top of the Cambrian sequence is represented by a further unnamed unit of arkose, greywacke and shales. All of these Middle Cambrian units, except the Ramsey Limestone, have only been reported from bores.

Permian sediments on Yorke Peninsula are extensively distributed especially in the south. They consist of tills, siltstones, sandstones and granite erratics, though some are obviously of glacial origin. Crawford (1965) has also suggested that there may be marine Permian sediments in some parts of the Peninsula.

Unlike the Murray Basin, Tertiary rocks cover only a relatively small area of Yorke Peninsula. They range in age from Eocene to Pliocene. The base of the Eocene is characterized by a coarse cross-bedded lignitic sand unit which is relatively thick and quite extensive. Overlying these lignitic sands are the Muloowurtie Clays and associated limestone and sandy clay beds.

Succeeding the Muloowurtie Clays and associated beds is a marley unit consisting of shelly clays with bands of nodular silicified sandstone passing up into sand rock. Bands and nodules of alunite also occur within the marl beds.

At the close of the Oligocene there was a marine transgression and the deposition of calcareous sediments including bryozoal limestone, sandy limestones and calcareous sands. The lowermost member of these calcareous deposits is the Point Turton Limestone which, like other members of the sequence, is a soft bryozoal limestone and is similar to the overlying limestone found in the Urania district.

Equivalents of the Port Willunga Beds on the eastern side of St. Vincents Gulf overlie the bryozoal limestones. These beds are essentially a sequence of bryozoal limestones similar palaeontologically and lithologically to those mentioned above. Also included in this unit is the Port Julia Greensand, a glauconitic clayey sandstone.

Shallow, warm water marine conditions continued into the Lower Miocene with the deposition of the Melton Limestone, consisting of a conglomeratic sandy bryozoal limestone which displays strong cross-bedding. Outcrops of this limestone are to be found to the north and west of Melton as far north as Kadina and south to Port Hughes. The thickness of this unit varies considerably but at Myponga Point reaches 5 m.

Favourable conditions for carbonate sedimentation continued into the Pliocene with the deposition of limestone units of limited extent. This unit was called Hallett Cove Sandstone by Crespin (1954, cited in Crawford 1965) because of its similarity in appearance to the unit of that name in the Adelaide area. It is a very thin unit consisting of sandy and gritty richly fossiliferous limestone which has in places been considerably altered to calcrete.

At the end of the Pliocene there was a marine regression and associated development of a more humid climate. Accompanying this humid climate was the deposition of the Ardrossan Clays and sandrock which Crawford (1965) suggests are colluvial deposits. Overlying the Ardrossan Clays and sandrock are red sandy clays with alunite seams.

The Upper Pleistocene/Recent boundary is far from clear and as a result it is difficult to determine the exact age relationships between the many surficial deposits which cover the pre-Pleistocene deposits. It is clear however that during the Pleistocene there was a world-wide reduction in sea-level and subsequent exposure of the continental shelf which made available vast quantities of calcareous sand. Much of this was blown on-shore with the result being the development of considerable thicknesses of aeolianite on the southern coasts of Yorke Peninsula and Eyre Peninsula (Crocker 1946). This aeolian activity was however clearly not a continuous process as calcrete horizons are to be observed in the aeolianite cliffs thus indicating periods of soil formation.

Other Pleistocene/Recent deposits on the Peninsula include sand sheets, transverse coastal dunes and longitudinal dunes. However the most areally extensive Pleistocene material is the calcrete.

# CHAPTER III

# MORPHOLOGY OF CALCRETE IN THE MURRAY BASIN AND ON YORKE PENINSULA

## Terminology of Calcrete Varieties

The terminology used in this chapter is based primarily on that of Netterberg (1967, 1969b, 1971). However this terminology has shortcomings with respect to the South Australian calcretes observed for Netterberg's terminology relates to a system in which the different varieties of calcrete are believed to evolve in sequence through time (Figure 3.1).

Netterberg recognizes five principal types of calcrete: powder, nodular, honeycomb, hardpan and boulder. Powder calcrete, which according to Netterberg represents the initial stage of calcrete development consists of carbonate silt or sand in which there is no discernible carbonate nodule development. Nodular calcrete consists of carbonate nodules or concretions in a host material. Honeycomb calcrete is an intermediate stage of calcrete formation between nodular and massive hardpan calcretes and forms when calcrete nodules coalesce leaving voids filled with lime-free soil. The final stage of calcrete development suggested by Netterberg is hardpan calcrete which is a "hard sheet-like crust which ... overlies less well-cemented material of a lower stage of development" (Netterberg 1971 p. 4). As the hardpan calcretes are eroded they break down into rounded boulders and

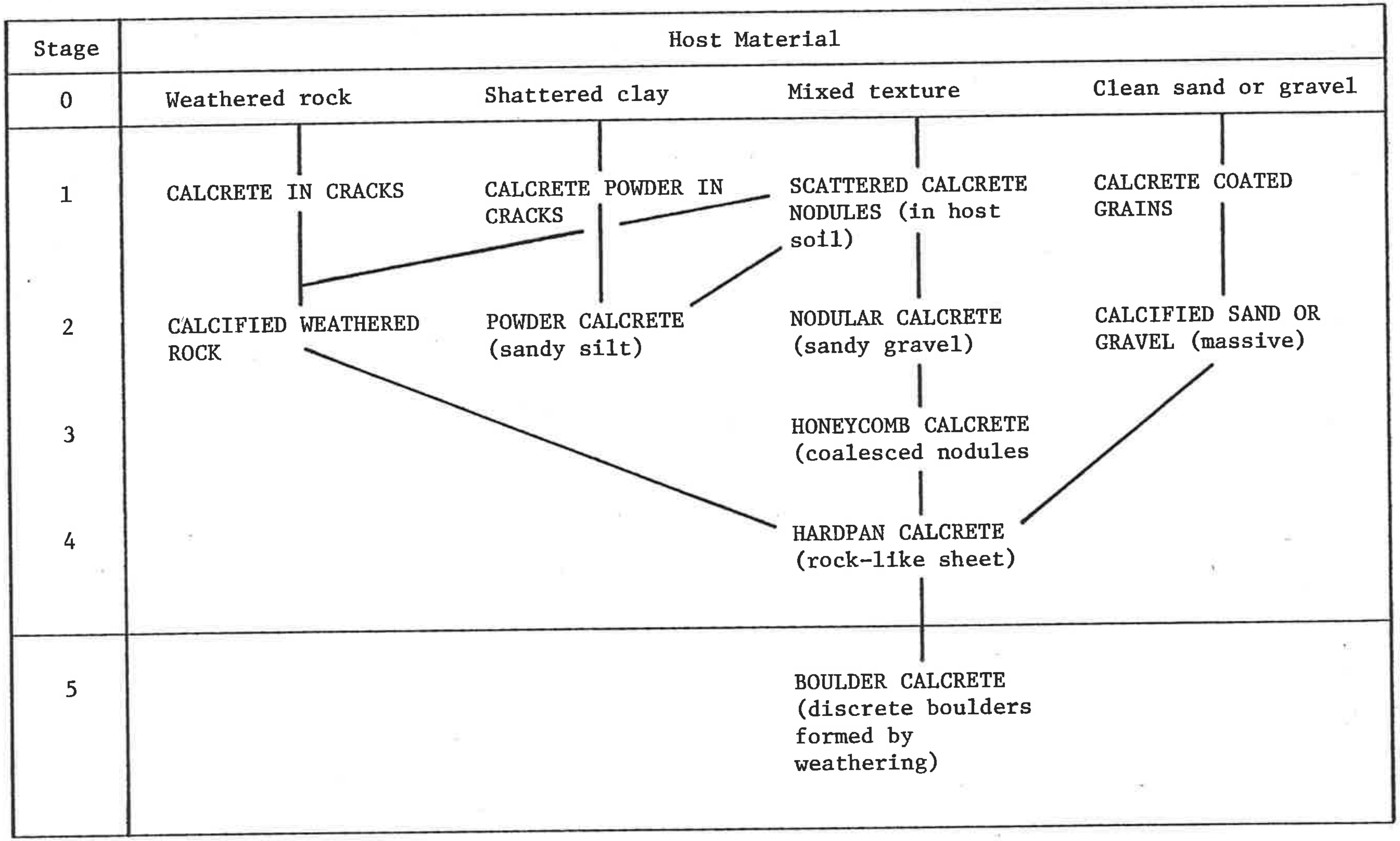


Figure 3.1. Netterberg's Stages of Calcrete Development

Source: Netterberg 1971

form boulder calcrete which exhibits solution cavities filled with lime-free soil.

Netterberg's is not the only scheme of calcrete terminology, but is used in this thesis in preference to Durand's (1949) as the terminology in that system has generally not been used in the English speaking world. Also, in Durand's system each calcrete type carries specific genetic connotations which are not widely applicable (Goudie 1973).

## Calcrete Varieties in the Murray Basin and on Yorke Peninsula

All of the major calcrete varieties, with the exception of honeycomb calcrete occur in the Murray Basin and on Yorke Peninsula. The broad morphological groups display considerable internal variation, a characteristic which Netterberg's system of classification and terminology largely overlooks.

Powder calcrete, more correctly termed carbonate silt as there is no evidence of induration, commonly occurs at the base of the calcrete profile. However, thin lenses of powder calcrete have been reported occurring in massive calcrete horizons in bore logs of the South Australian Highways Department. The powder calcrete is an off-white (10YR8/2),[1] soft friable silty clay composed of grains of carbonate and quartz.

Nodular calcrete occurs as distinct horizons within the calcrete

---

[1] Colours are those of the Munsell Colour Chart and refer to the dominant colour of the dry material being described.

profile or the nodules may be embedded in powder calcrete horizons. Two forms of nodular calcrete can be distinguished. The first consists of rounded indurated particles of carbonate with an essentially uniform matrix in which there is no evidence of successive phases of carbonate accretion. The second is concretionary and displays a series of concentric carbonate rinds. These concentric layers of carbonate may extend to the centre of the nodule or may be developed around a nucleus of either non-calcareous materials or morphologically different and apparently older calcrete. For example the nucleus of the nodule frequently consists of rounded to sub-angular particles of blackened calcrete. The degree of induration of the nodules also varies considerably within the profiles.

The size and shape of calcrete nodules also varies considerably. Calcrete nodules range from 1 or 2 mm in diameter to 10 cm. Most are essentially round in shape and some are elongate, but none of the nodules observed in the field show any sign of thickening of the carbonate in their lower sides such as described by Bretz and Horberg (1949), and Swineford et al. (1958). As well as varying morphologically, calcrete nodules exhibit considerable variation in colour. Generally calcrete nodules and concretions are off-white to pink (7.5YR8/4) in colour but in the more indurated varieties the nodules are frequently brown to orange in colour.

Hardpan calcrete occurs in three basic forms: strongly indurated, moderately indurated and laminar.

The strongly indurated form occurs as discontinuous horizons at the top of the calcrete profiles. Generally it is darker than the other forms being reddish yellow (5YR6/6) in colour. It is commonly surrounded by a layer of laminar calcrete up to 2 cm in thickness. The matrix of this material varies considerably from locality to locality. Some has an essentially massive matrix with relatively few calcrete nodules (Figure 3.2) but elsewhere consists of large numbers of nodules (Figure 3.3).

Moderately indurated hardpan calcrete forms a continuous capping to many of the calcrete profiles (Figure 3.4). The top of the horizon commonly has a layer of laminar calcrete developed on it but it is generally much thinner than that found surrounding the strongly indurated calcrete. The moderately indurated calcrete is generally lighter in colour, commonly off-white to pinkish. Some examples are massive in form while others consist of coalescing nodules.

Laminar calcrete commonly consists of a series of laminae which either parallel the surface of the calcrete or form domes and depressions which resemble algal stromatolites (Logan et al. 1964) (Figure 3.5). The boundaries between the laminae are generally wavy in form.

The strongly indurated calcrete described earlier can be considered as boulder calcrete. Its origin must be interpreted as an erosional one for it represents remnants of a once more extensive hardpan horizon. This suggestion finds support in the occurrence of the thicker laminar calcrete layer on the surface of these boulders and the extension of the laminar zone around the boulders. The occurrence of similar material in Nevada has been interpreted by Gardner (1972) as being boulder calcrete.

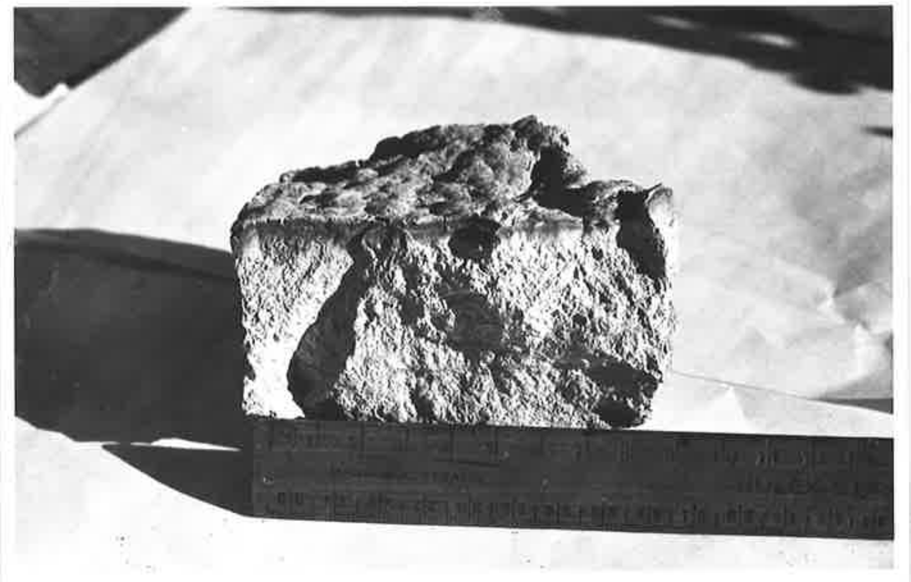


Figure 3.2 Massive hardpan calcrete with a thin horizon of laminar calcrete developed on the upper surface.

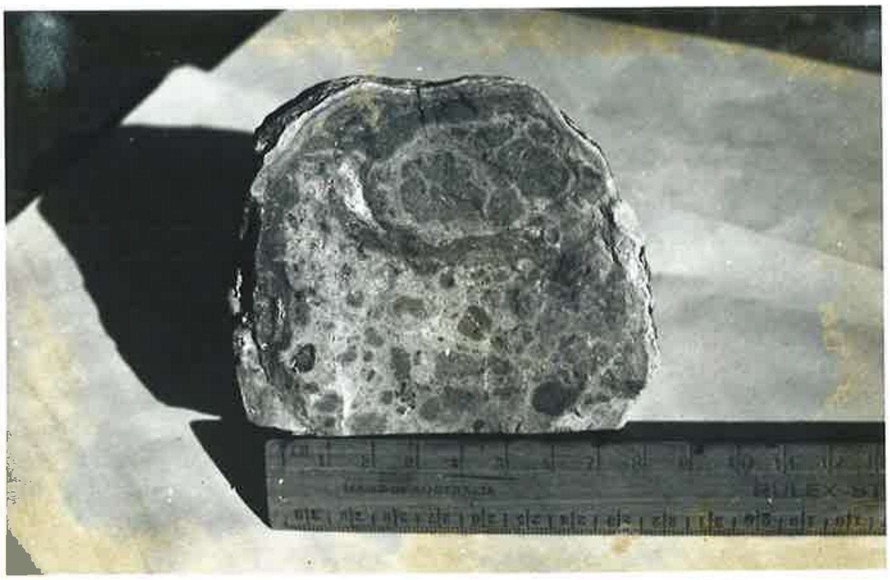


Figure 3.3 Strongly indurated hardpan calcrete showing nodules floating in the matrix. A thin zone of laminar calcrete occurs on the upper surface.

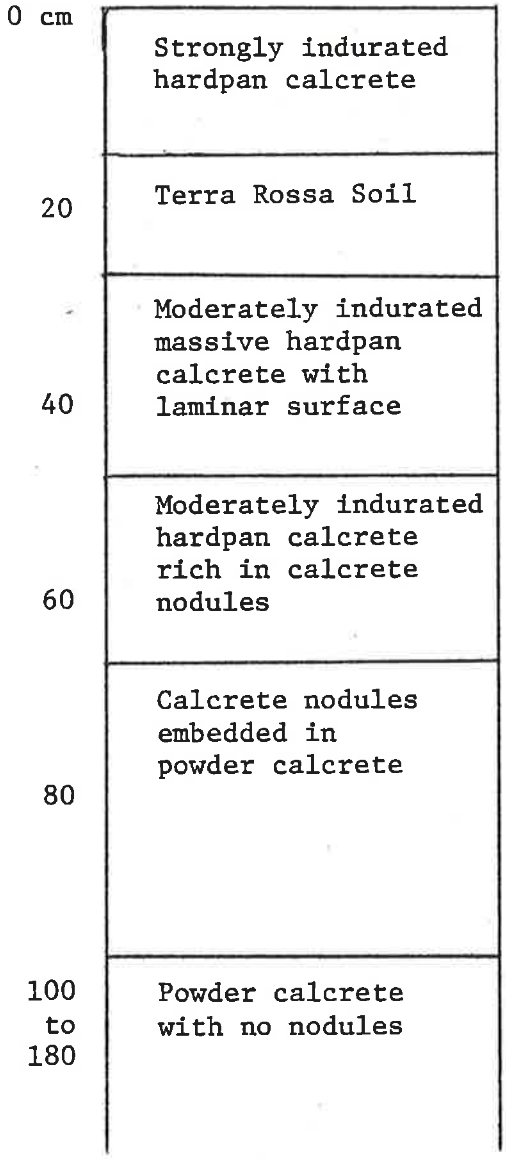
Figure 3.4 Continuous hardpan calcrete horizon near Virginia, northern Adelaide Plains.

Figure 3.5 Outer surface of strongly indurated hardpan calcrete showing the stromatolitic appearance of the laminar calcrete which surrounds the boulder.

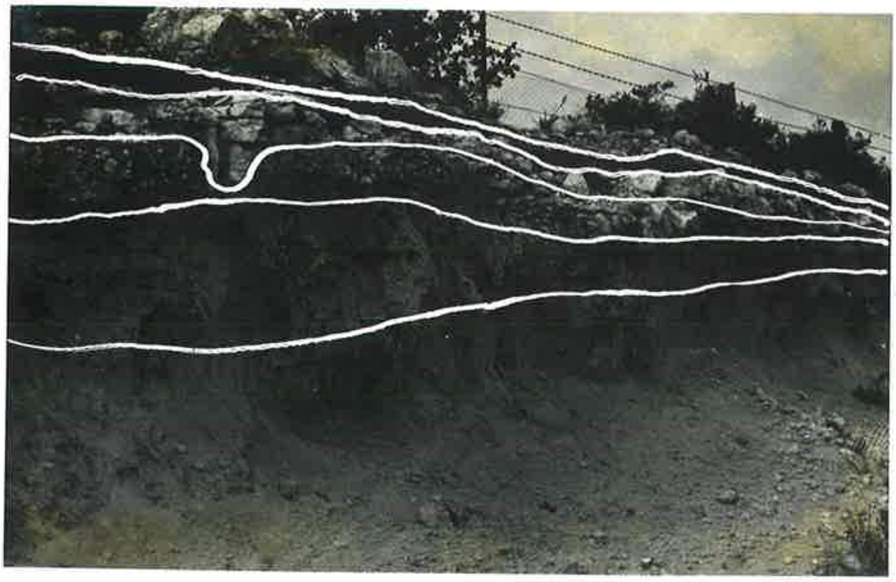
## Murray Basin and Yorke Peninsula Calcrete Profiles

Whilst there is considerable discussion of the various calcrete types in the literature, notably by Netterberg (1967, 1969b, 1971) and Goudie (1973), little has been written on the distribution of the various forms within calcrete profiles.

The following profile descriptions at the sites of samples collected for chemical and mineralogical analyses illustrate the diversity of profile forms:



<u>Figure 3.6</u>. Calcrete profile, Monteith Quarry I 8.5 km east of Murray Bridge.



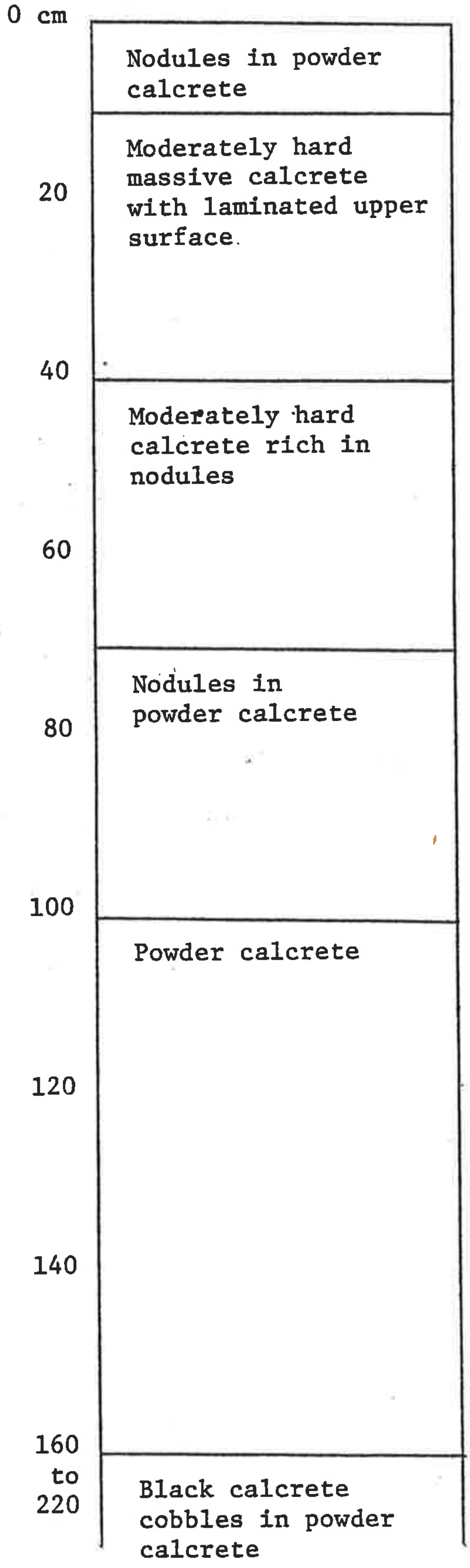


Figure 3.7. Calcrete profile, Monteith Quarry II, 8.5 km east of Murray Bridge opposite Monteith Quarry I.

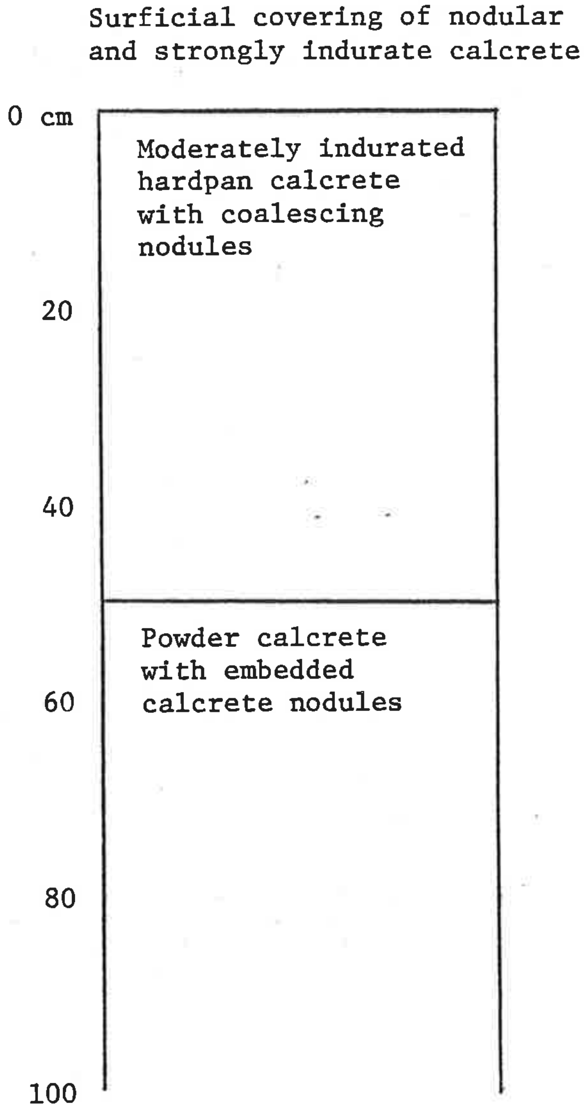
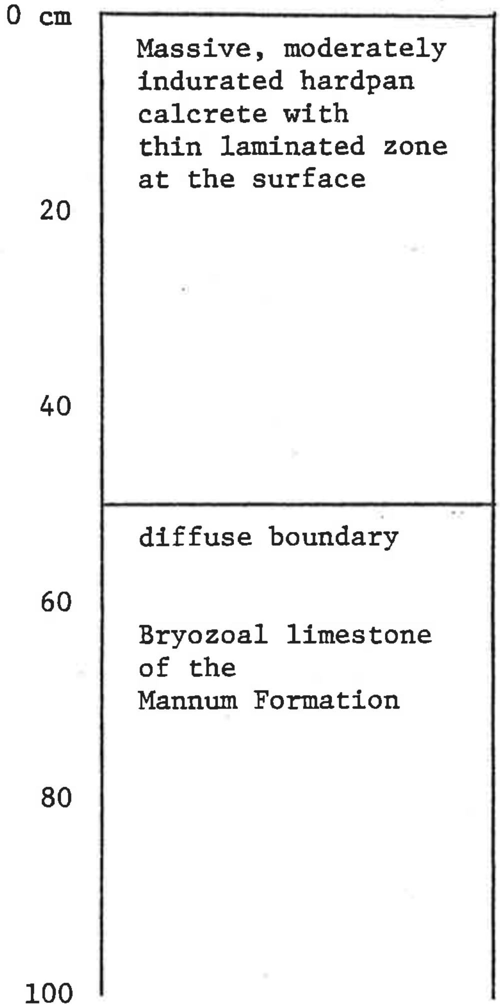


Figure 3.8. Calcrete profile in quarry on Dukes Highway 5 km S.E. of Tailem Bend.



<u>Figure 3.9</u>. Calcrete horizon developed on Limestone of the Mannum Formation, Murray Bridge.

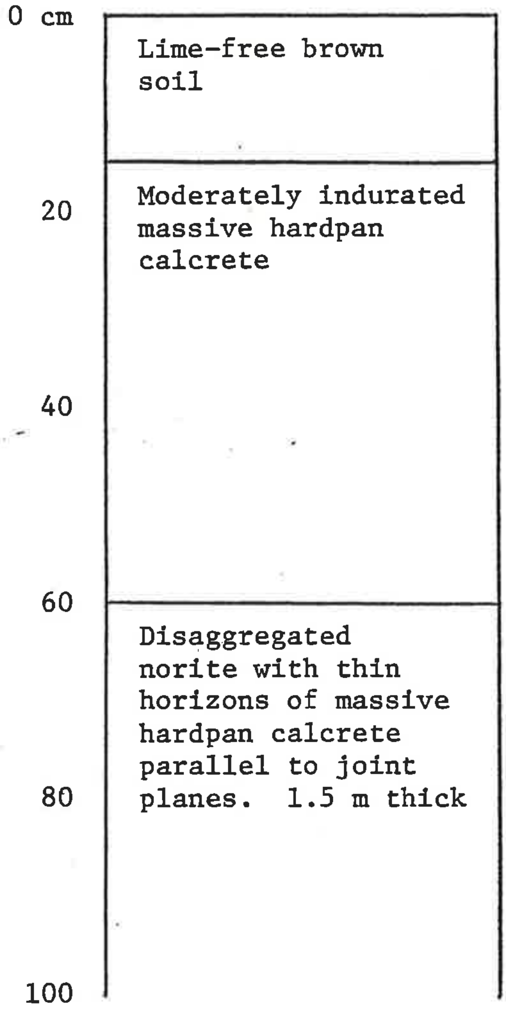


Figure 3.10. Calcrete profile developed on top of disaggregated norite, Old Martins Quarry, Black Hill.

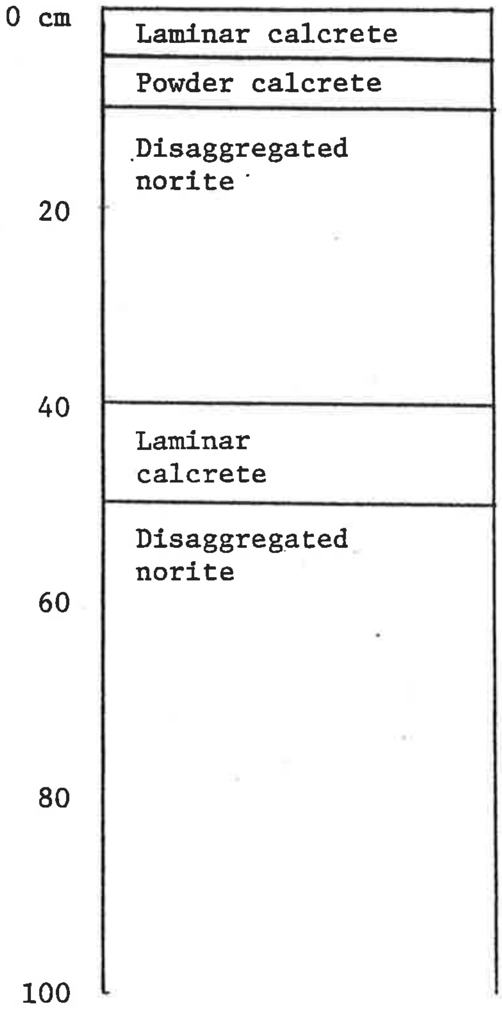
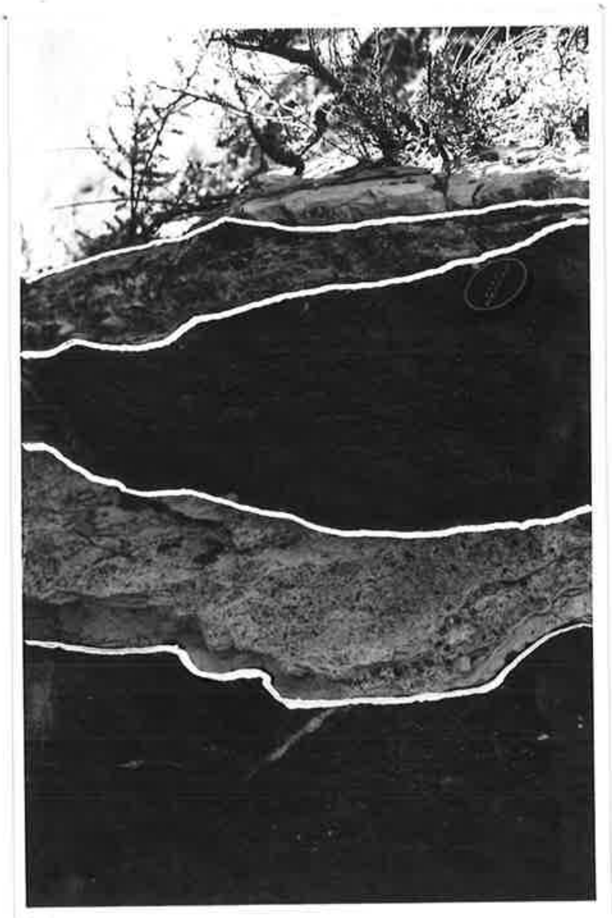


Figure 3.11. Laminar calcrete lenses developed in the disaggregated norite at Martins Quarry, Black Hill.



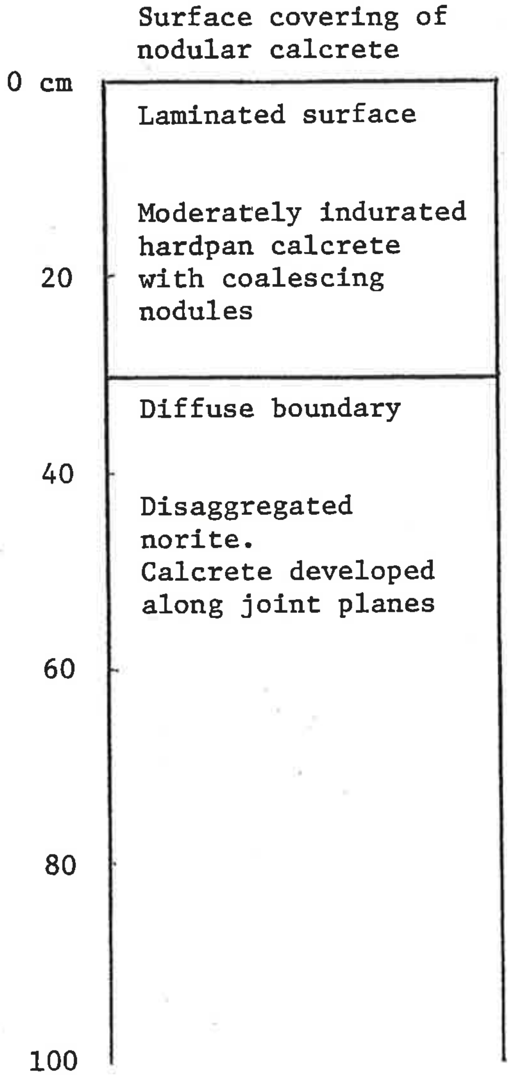
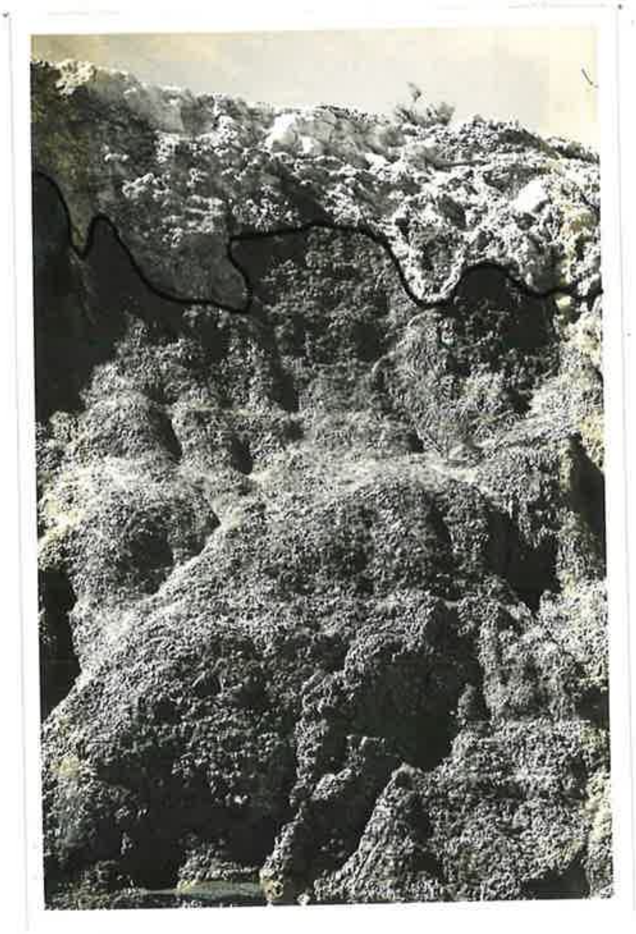


Figure 3.12. Calcrete horizon at the top of the Council Quarry, Black Hill.



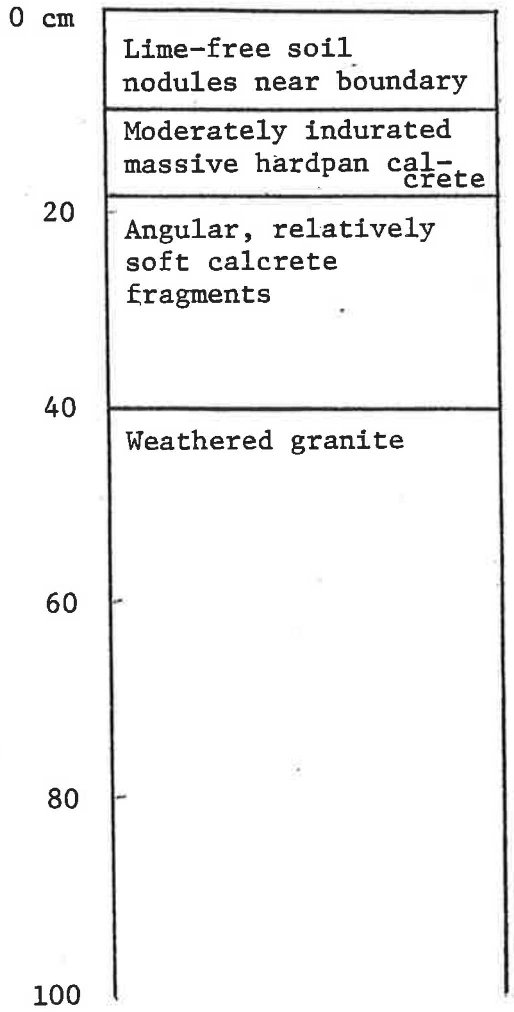


Figure 3.13. Calcrete developed on top of granite weathering profile Long Ridge.

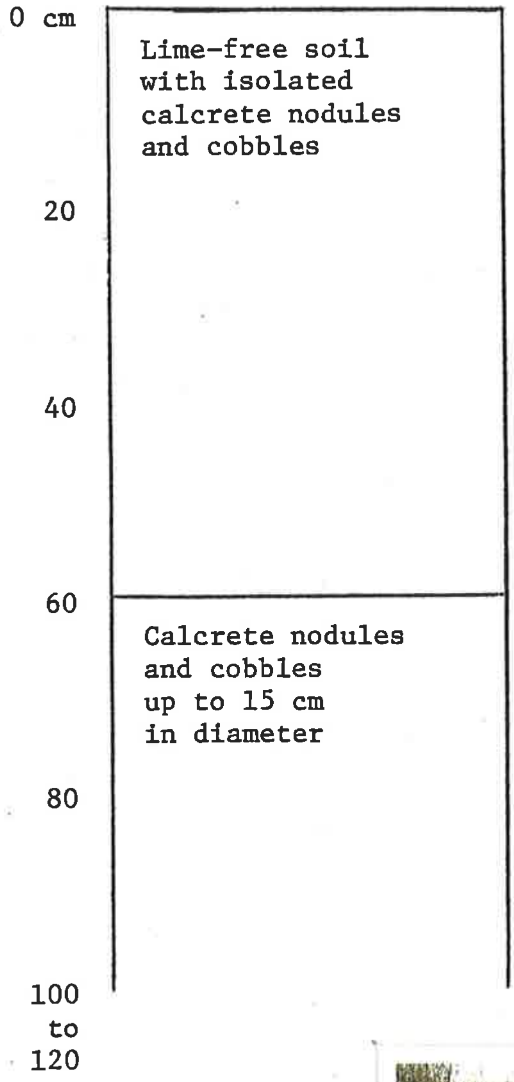
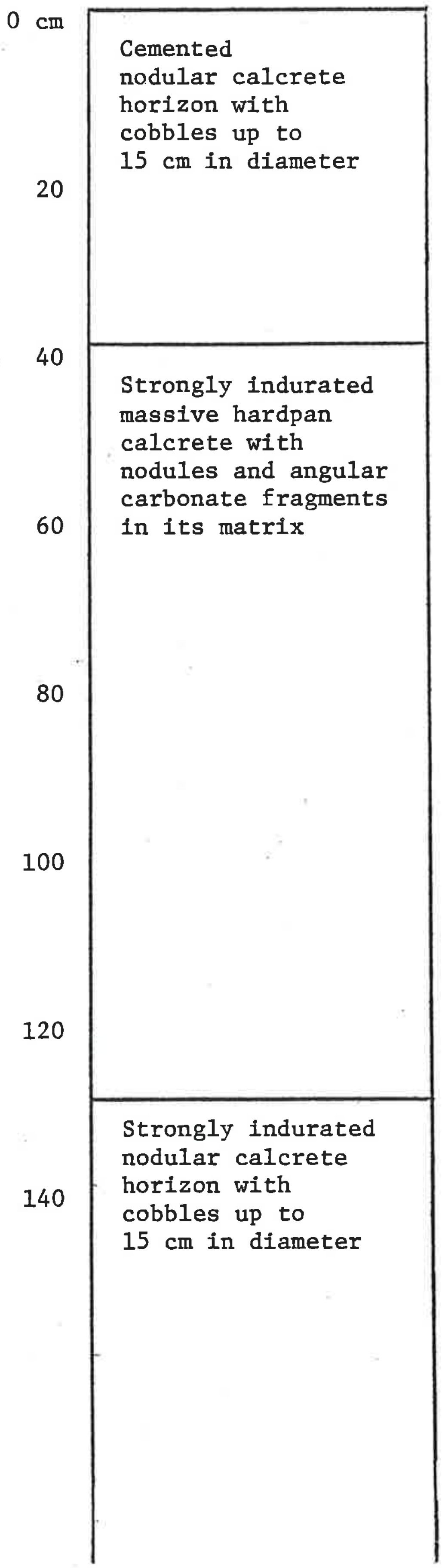


Figure 3.14. Horizon of calcrete nodules and cobbles developed beneath a lime-free soil 20 km north of Ardrossan, Yorke Peninsula.

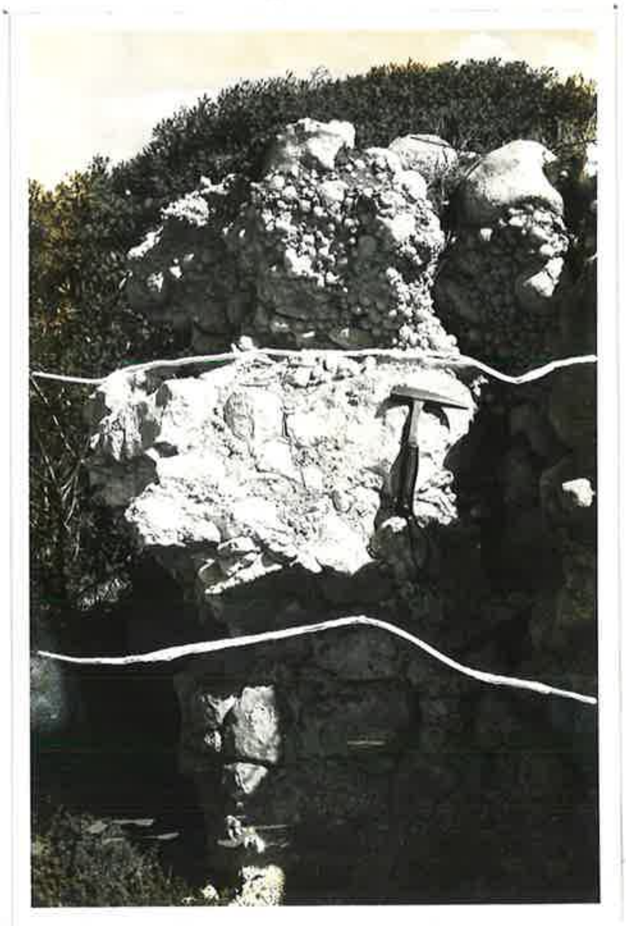


Cemented nodular calcrete horizon with cobbles up to 15 cm in diameter

Strongly indurated massive hardpan calcrete with nodules and angular carbonate fragments in its matrix

Strongly indurated nodular calcrete horizon with cobbles up to 15 cm in diameter

Figure 3.15. Calcrete profile in coastal cliffs, Port Julia.



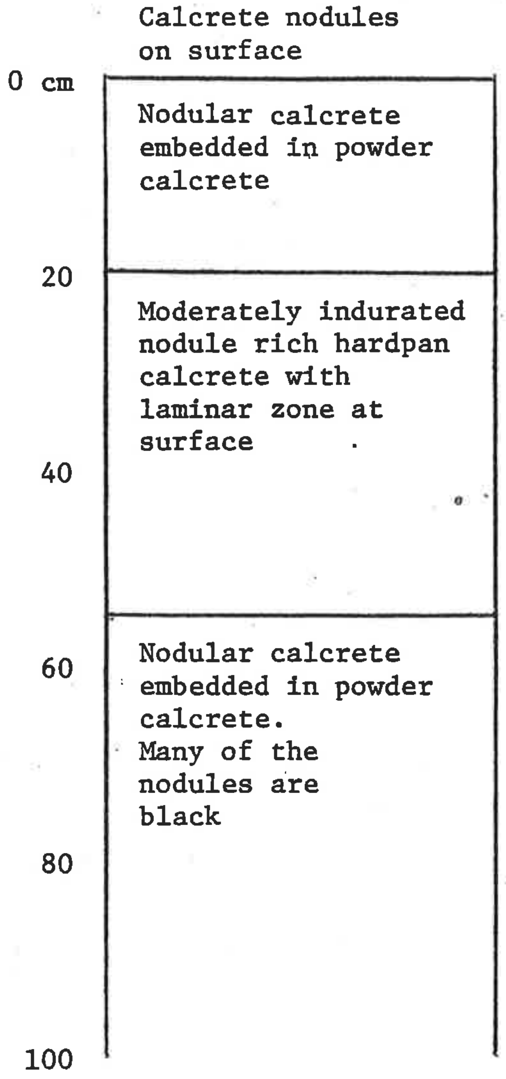
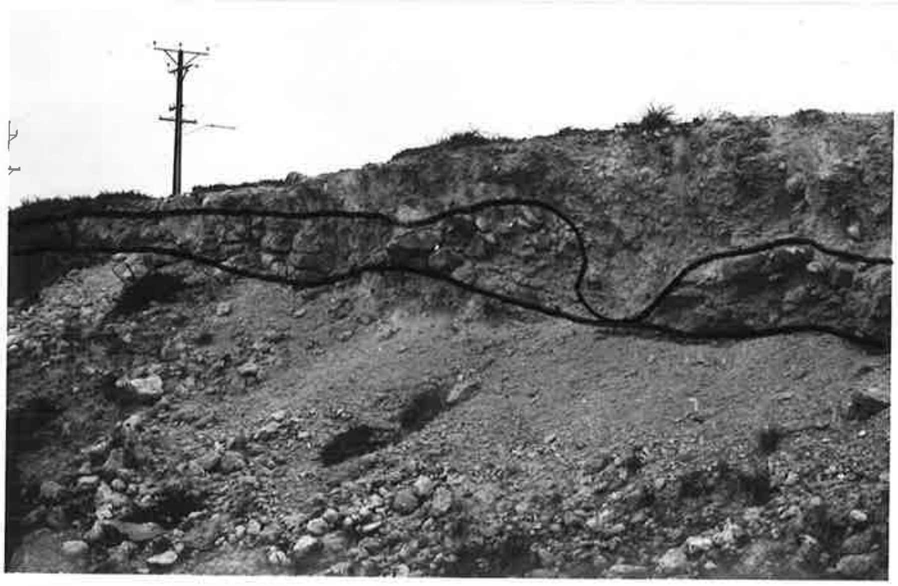


Figure 3.16. Calcrete profile at Wool Bay.



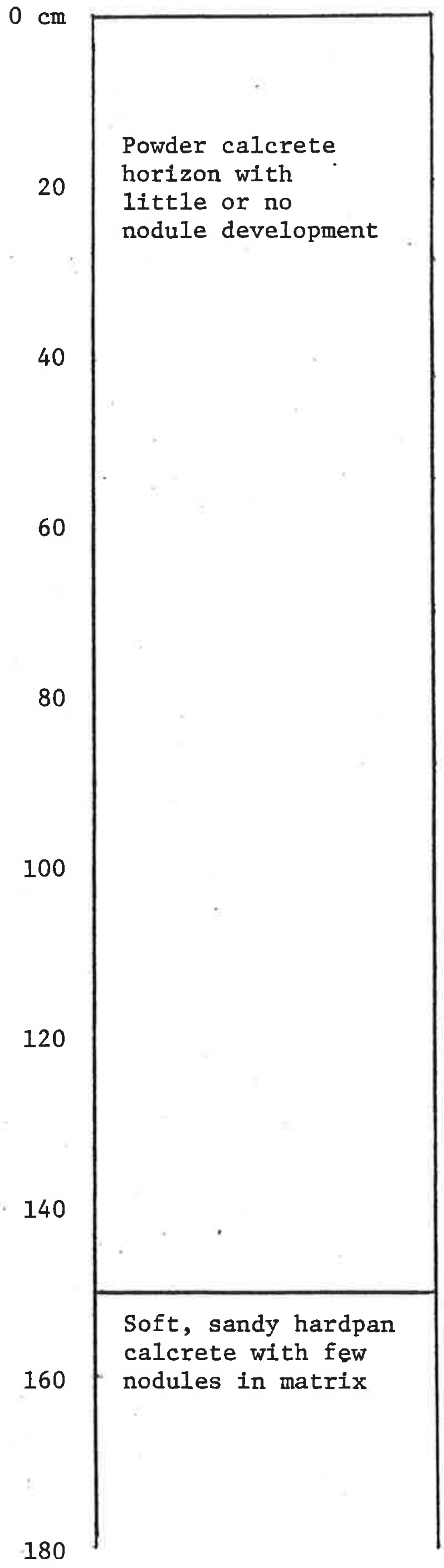


Figure 3.17. Calcrete profile at Port Vincent.

Continued on following page.

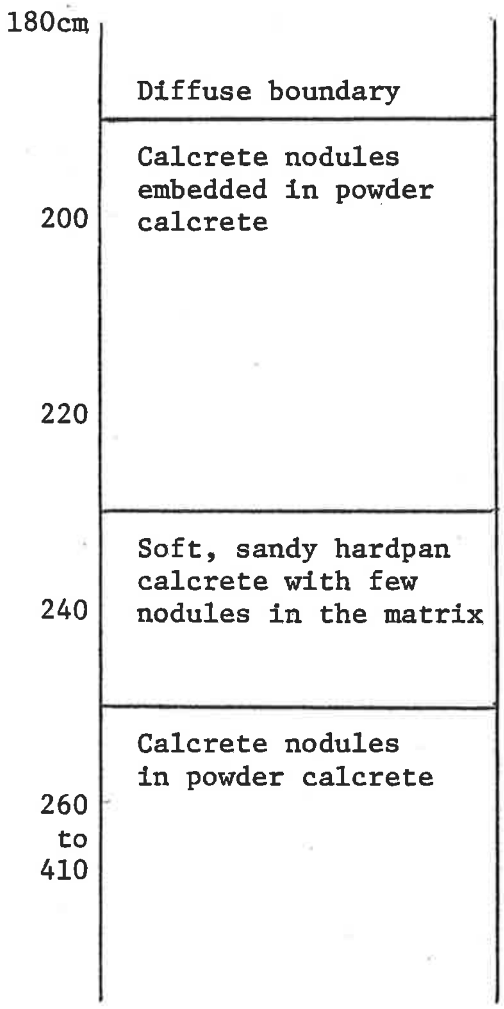
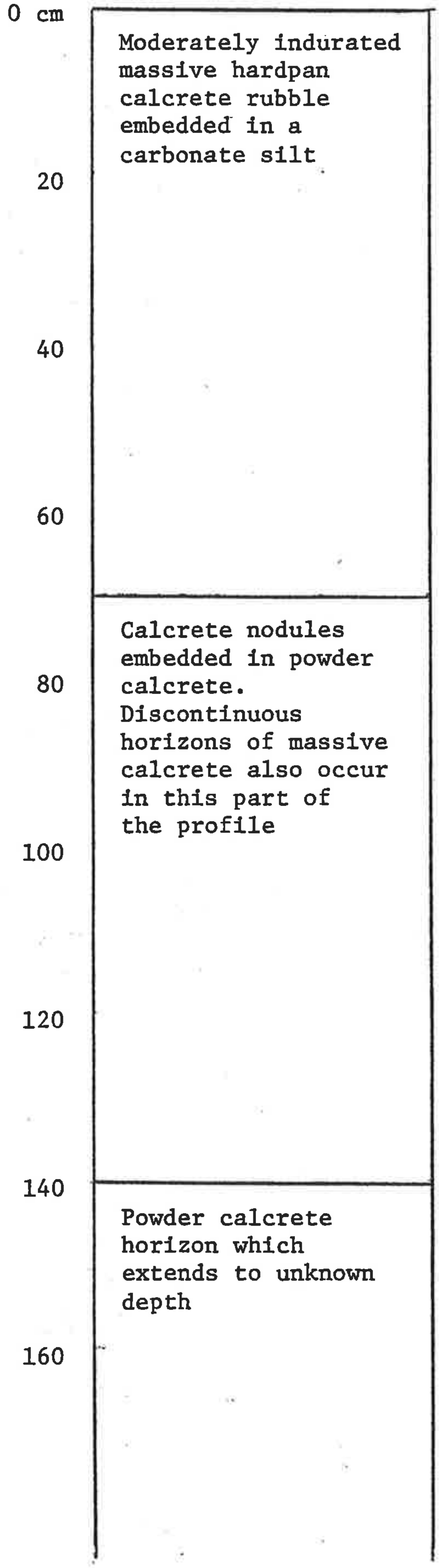


Figure 3.17 continued



Moderately indurated massive hardpan calcrete rubble embedded in a carbonate silt

Calcrete nodules embedded in powder calcrete. Discontinuous horizons of massive calcrete also occur in this part of the profile

Powder calcrete horizon which extends to unknown depth

Figure 3.18. Calcrete profile 15 km west of Yorketown.

Laminar calcrete surface

0 cm

Strongly indurated massive hardpan calcrete, with brecciated horizon 5cm from surface

20

Shell bed consisting of *Katelysia Scalorina*, *Zeacumontus corithium*, *Austrocochla torri*, and *Quibbula tenuissima* embedded in partially indurated carbonate silt. At the top of the shell bed there is a thin laminar calcrete zone

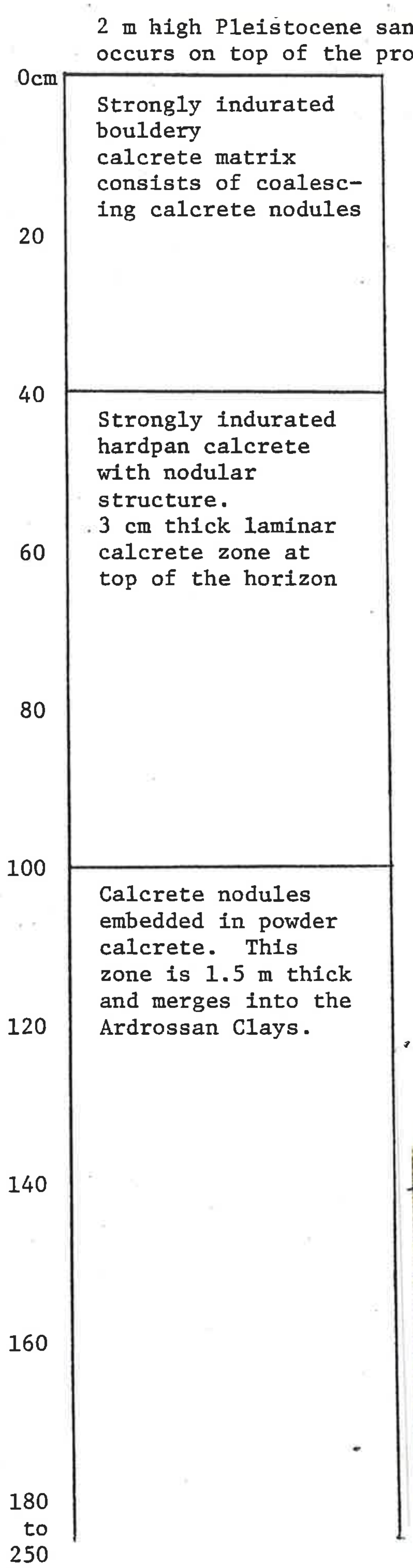
40

60

80

100 to 110

Figure 3.19. Calcreted Pleistocene shell bed 30 km south west of Warooka.



2 m high Pleistocene sand dune occurs on top of the profile.

Strongly indurated bouldery calcrete matrix consists of coalescing calcrete nodules

Strongly indurated hardpan calcrete with nodular structure. 3 cm thick laminar calcrete zone at top of the horizon

Calcrete nodules embedded in powder calcrete. This zone is 1.5 m thick and merges into the Ardrossan Clays.

Figure 3.20. Calcrete profile, Moonta Bay, developed on the Ardrossan Clays. The thin white bands at the base of the profile are alunite.

# CHAPTER IV

# THE CHEMISTRY AND MINERALOGY OF CALCRETE IN THE MURRAY BASIN AND ON YORKE PENINSULA

## Calcrete Chemistry - Introduction

There is a considerable volume of literature on the chemistry of world calcrete deposits (Goudie 1971, 1972a, 1973; Aristarain 1970) but there are few published analyses of Australian calcretes. Goudie (1972a) cites a set of analyses for Australian calcretes but does not acknowledge the source of the data. He also refers to the high magnesium calcretes reported by Johns 1963.

This chapter discusses the chemical characteristics of the calcretes in the Murray Basin and on Yorke Peninsula.

## Gross Chemistry

Using the X-ray spectographic techniques of Norrish and Hutton (1969) chemical analyses of calcretes from the Murray Basin and Yorke Peninsula are discussed below, Tables 4.1 and 4.2.

The most abundant oxide in the calcrete is calcium oxide (CaO). In the Murray Basin it ranges from 12.6% in powder calcrete to 40.9% in hardpan calcrete. The mean CaO percentage is 34.3% which is some 8% lower than the world mean (Goudie 1972a).

In the calcretes from Yorke Peninsula however the mean calcium oxide percentages are some 7% higher than that of the Murray Basin.

TABLE 4.1

## Chemical Analyses of Calcrete Samples from the Murray Basin (Oxide %)

| SAMPLE NUMBER | CALCRETE TYPE* | CaO | $SiO_2$ | MgO | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | $K_2O$ | $P_2O_5$ | LOSS ON IGNITION | TOTAL |
|---|---|---|---|---|---|---|---|---|---|---|---|
| TBS1 | P | 22.8 | 30.5 | 8.5 | 2.7 | 1.3 | 0.20 | 0.31 | 0.04 | 32.8 | 99.2 |
| TB1 | M | 40.4 | 9.4 | 6.8 | 1.2 | 0.6 | 0.08 | 0.22 | 0.04 | 41.3 | 100.04 |
| TB5 | M | 40.9 | 15.7 | 3.8 | 2.0 | 0.9 | 0.20 | 0.67 | 0.07 | 37.3 | 101.5 |
| TB6 | M | 35.8 | 18.7 | 7.0 | 2.1 | 0.9 | 0.20 | 0.40 | 0.04 | 36.4 | 101.5 |
| TB7 | N | 40.0 | 12.3 | 6.8 | 1.7 | 0.8 | 0.14 | 0.41 | 0.05 | 39.2 | 101.5 |
| TB8 | N | 34.2 | 10.8 | 13.3 | 1.3 | 0.6 | 0.12 | 0.40 | 0.04 | 41.1 | 101.9 |
| TB9 | M | 38.1 | 10.4 | 9.6 | 1.4 | 0.6 | 0.10 | 0.35 | 0.04 | 40.5 | 101.1 |
| TB11 | M | 37.9 | 14.8 | 9.3 | 1.4 | 0.7 | 0.20 | 0.22 | 0.04 | 38.7 | 103.3 |
| TB12 | N | 33.2 | 13.4 | 12.4 | 1.5 | 0.8 | 0.15 | 0.40 | 0.05 | 39.7 | 101.6 |
| MQ001 | M | 33.9 | 26.4 | 3.4 | 1.9 | 0.7 | 0.14 | 0.46 | 0.05 | 33.0 | 99.9 |
| MQS2 | P | 12.6 | 48.0 | 8.3 | 4.1 | 1.5 | 0.31 | 0.61 | 0.02 | 23.4 | 101.0 |
| MQ3 | M | 36.5 | 20.7 | 4.2 | 1.9 | 0.7 | 0.13 | 0.46 | 0.07 | 35.4 | 100.1 |
| MQ4 | M | 29.0 | 32.2 | 5.0 | 2.7 | 1.0 | 0.21 | 0.84 | 0.05 | 29.3 | 100.3 |
| MQ5 | N | 33.5 | 24.0 | 5.8 | 2.1 | 0.9 | 0.20 | 0.56 | 0.05 | 33.5 | 100.6 |
| MQ6 | N | 31.2 | 24.3 | 8.0 | 2.4 | 0.9 | 0.20 | 0.54 | 0.04 | 33.4 | 101.0 |
| MQ7 | N | 31.9 | 20.3 | 9.1 | 2.0 | 0.8 | 0.20 | 0.56 | 0.04 | 35.5 | 100.5 |

*P - powder calcrete

M - massive calcrete

N - nodular calcrete

Cont.

TABLE 4.1 Continued

| SAMPLE NUMBER | CALCRETE TYPE* | CaO | $SiO_2$ | MgO | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | $K_2O$ | $P_2O_5$ | LOSS ON IGNITION | TOTAL |
|---|---|---|---|---|---|---|---|---|---|---|---|
| OMQ1 | N | 36.1 | 23.6 | 3.6 | 2.2 | 1.0 | 0.17 | 0.50 | 0.05 | 33.8 32·3 | 101.0 |
| OMQ2 | M | 35.7 | 24.3 | 4.3 | 1.8 | 0.8 | 0.15 | 0.49 | 0.04 | 33.7 32·7 | 101.3 |
| OMQ3 | M | 28.8 | 17.7 | 13.2 | 2.1 | 0.8 | 0.16 | 0.58 | 0.04 | 37.5 [illegible] | 100.9 |
| MB1 | M | 39.4 | 17.8 | 4.6 | 1.3 | 1.2 | 0.12 | 0.54 | 0.08 | 36.2 35·9 | 101.2 |
| MB2 | M | 36.3 | 27.3 | 2.5 | 1.6 | 1.3 | 0.20 | 0.54 | 0.08 | 31.1 31·2 | 100.9 |
| BHC1 | N | 37.3 | 16.8 | 4.1 | 2.7 | 1.3 | 0.22 | 0.35 | 0.08 | 36.7 33·7 | 99.6 |
| BHC2 | M | 37.6 | 17.0 | 4.1 | 2.7 | 1.3 | 0.22 | 0.26 | 0.07 | 36.4 34·5 | 99.7 |

*P - powder calcrete
M - massive calcrete
N - nodular calcrete

TABLE 4.2

## Chemical Analyses of Calcrete Samples from Yorke Peninsula (Oxide %)

| SAMPLE NUMBER | CALCRETE TYPE* | CaO | $SiO_2$ | MgO | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | $K_2O$ | $P_2O_5$ | LOSS ON IGNITION | TOTAL |
|---|---|---|---|---|---|---|---|---|---|---|---|
| YT1 | M | 40.4 | 15.1 | 3.0 | 2.7 | 1.1 | 0.14 | 0.83 | 0.06 | 36.8 | 100.1 |
| YT2 | N | 40.3 | 16.0 | 3.1 | 3.2 | 1.1 | 0.16 | 0.75 | 0.08 | 36.8 | 101.5 |
| YP1 | M | 51.1 | 4.4 | 1.1 | 1.0 | 0.4 | 0.06 | 0.51 | 0.12 | 43.2 | 101.9 |
| YP2 | M | 53.0 | 2.5 | 1.1 | 0.7 | 0.3 | 0.04 | 0.19 | 0.07 | 43.3 | 101.2 |
| YP3 | P | 22.8 | 30.5 | 8.5 | 2.7 | 1.3 | 0.20 | 0.31 | 0.04 | 32.8 | 99.2 |
| PV1 | M | 31.5 | 32.3 | 2.4 | 1.7 | 0.8 | 0.09 | 0.42 | 0.11 | 29.8 | 99.1 |
| PV2 | N | 31.4 | 33.2 | 2.5 | 2.2 | 0.9 | 0.11 | 0.35 | 0.13 | 29.8 | 100.6 |
| MB3 | M | 39.3 | 20.9 | 2.1 | 2.3 | 0.8 | 0.13 | 0.44 | 0.08 | 35.0 | 101.1 |
| MB4 | N | 27.3 | 36.0 | 5.0 | 1.2 | 0.5 | 0.06 | 0.40 | 0.07 | 29.2 | 99.7 |
| PJ1 | N | 43.5 | 12.8 | 2.0 | 2.0 | 0.7 | 0.10 | 0.47 | 0.10 | 39.3 | 101.0 |
| PJ2 | M | 42.8 | 11.5 | 3.6 | 1.5 | 0.5 | 0.07 | 0.35 | 0.05 | 40.1 | 100.5 |
| WB1 | M | 42.0 | 14.8 | 3.5 | 2.4 | 0.9 | 0.12 | 0.32 | 0.08 | 38.4 | 102.5 |
| WB2 | N | 44.9 | 8.8 | 4.8 | 1.9 | 0.7 | 0.07 | 0.34 | 0.07 | 41.5 | 103.1 |

*P - powder calcrete
M - massive calcrete
N - nodular calcrete

Percentages range from 27.3% CaO in powder calcrete up to 53.0% in massive laminated calcrete. The mean CaO% in the Yorke Peninsula calcretes is comparable to the world mean of 42.62% (Goudie 1972a).

The second most abundant oxide in the calcrete is silicon dioxide ($SiO_2$) which in the Murray Basin ranges from 9.4% in massive calcrete to 38.0% in powder calcrete. The mean $SiO_2$ content is 20.6% which is some 8.3% higher than the world mean of 12.3% (Goudie 1972a).

On Yorke Peninsula the $SiO_2$ values range from 2.5% in massive calcrete up to 30% in the powder calcrete. The mean $SiO_2$ content of the Yorke Peninsula calcretes is 18% which is some 3% lower than that in the Murray Basin calcretes but still greater than the world average.

Magnesium oxide (MgO) is the third most abundant oxide in the calcretes although in most cases considerably less abundant than the other two oxides. In the calcretes from the Murray Basin it ranges from 2.5% in massive calcrete up to 23.4% in powder calcrete. The mean MgO content is 7.4% which is slightly more than double the world average of 3.05%.

On Yorke Peninsula the magnesium oxide percentages range from 1.1% to 5.03% with a mean MgO content of 2.9%. This mean is some 4.5% lower than the mean of the magnesium oxide contents of the Murray Basin calcretes but only slightly below the world average.

The three oxides discussed above together with carbon dioxide are the most abundant constituents of the calcrete. Together they account for some 95% of the bulk chemistry of the calcrete. Minor oxides detected in the calcrete include those of aluminium, iron, titanium, potassium, sulphur and phosphorus.

Of the minor oxides, aluminium oxide ($Al_2O_3$) is the most abundant. In the Murray Basin it ranges from 1.2% to 4.1% with a mean of 2.03%. On Yorke Peninsula it ranges from 0.7% to 3.2% with a mean of 1.9%. These means are comparable to the world mean of 2.12% (Goudie 1972a).

Iron oxide ($Fe_2O_3$) is the second most abundant of the minor oxides. It ranges from 0.6% to 1.5% in the Murray Basin calcretes with a mean of 0.9%. Similar percentages are obtained for Yorke Peninsula where $Fe_2O_3$ contents range from 0.3% to 1.1% with a mean of 0.7% which is below the world mean of 2.03% (Goudie 1972a).

The remaining constituents of the calcretes are quantitatively insignificant. Titanium oxide ($TiO_2$) percentages in the calcretes from the Murray Basin range from 0.08% up to 0.3% with a mean of 0.2%. On Yorke Peninsula $TiO_2$ ranges from 0.01% to 0.2% with a mean of 0.1% or approximately half the mean of the Murray Basin.

Potassium oxide ($K_2O$) percentages in the Murray Basin calcretes ranges from 0.1% to 0.8% with a mean of 0.5%. Very similar contents of potassium are found in the Yorke Peninsula calcretes where $K_2O$ percentages range from 0.2% to 0.8% with a mean of 0.5%.

The last of the minor oxides is phosphorus pentoxide ($P_2O_5$) which is commonly present in very small quantities. The low phosphorus contents in most Australian soils and weathering profiles shows that phosphorus is very rapidly lost from the system. In the calcretes of the Murray Basin $P_2O_5$ ranges from 0.02% to 0.08% with a mean of 0.05% while on Yorke Peninsula it ranges from 0.05% to 0.1% with a mean of 0.1%.

## Discussion

The results of the chemical analyses shown in Tables 4.1 and 4.2 and the differences observed between the two areas show that the South Australian calcretes in general show great variability in their chemistry. It has also been shown that in general the chemistry of the calcretes studied differs considerably from those described from other parts of the world. These differences suggest that the nature of the environment or environments in which the southern South Australian calcretes have formed and are forming may differ significantly from those which obtain in other semiarid regions of the world.

One notable chemical characteristic of the calcretes is their impurity. Compared to most of the world calcretes (Goudie 1972a) most of them are considerably lower in calcium and higher in silica and magnesium. Crawford (1965) has commented that the calcretes on Yorke Peninsula are too impure to be of any use as an economic source of lime.

The high silica content of the calcretes appears to be consistent with some observations overseas. Silica, in the form of opal, chalcedony and quartz has been reported to occur extensively in calcretes from southern Africa by Lamplugh (1907), McGregor (1930) and Rogers (1934, 1936). It has also been reported in considerable quantities in a variety of forms from caliche deposits in High Plains of Texas and New Mexico by Price (1933), Sidwell (1943), Brown (1956), Swineford and Franks (1959) and Reeves (1970).

Calcareous deposits which contain abundant quantities of silica have also been reported from Central Australia by Mabbutt (1967) and from the Canning Basin of Western Australia by Casey and Wells (1964). In hand specimen quartz can also be observed in hardpan and laminar calcretes from the Murray Basin and Yorke Peninsula.

In the calcretes from the Murray Basin and Yorke Peninsula silica occurs principally in the form of quartz, alumino-silicate clay minerals and only very minor amounts of amorphous silica.

For the South Australian calcretes it must be concluded that the relatively high silica contents reflect the quartzose character of parent material and nearby sand dunes.

Magnesium contents of the South Australian calcretes analysed are higher than most of those reported from other parts of the world. Goudie (1972a) cites a number of calcretes from south west Africa and Hawaii where high magnesium contents have been reported. As the calcretes of the Murray Basin and Yorke Peninsula contain large quantities of magnesium it must be concluded that there is something distinctive about the environments under which they have formed, as under free draining soil conditions magnesium is generally rapidly removed from the profile.

## Chemistry of Principal Calcrete Types

The mean percentages of the oxides were calculated for the principal calcrete types. From tables 4.3 and 4.4 it can be seen that there is considerable difference between the chemistry of the indurated and powder calcretes. The powder calcretes are generally much lower in calcium oxide and much higher in silica, magnesium and aluminium oxides.

It is also possible, with respect to some oxides to distinguish between the chemistry of massive and nodular calcretes. In the calcretes from both the Murray Basin and Yorke Peninsula the calcium oxide content of the massive hardpan calcrete is higher than that of the nodular calcrete. In the case of the Murray Basin calcretes it is 1.5% higher, and on Yorke Peninsula 5.5% higher. However, the change in the CaO/MgO ratio from powder through nodular to massive calcretes is more significant. In the Murray Basin calcretes this changes from 2.10 - 4.38 - 6.03 while on Yorke Peninsula the ratio changes from 2.70 - 10.7 - 17.95. The change in the ratio reflects the greater concentration of MgO in the less indurated calcrete types. As the calcrete becomes progressively more indurated there is an addition of calcium and hence a decrease in the relative quantity of magnesium present.

In the Murray Basin calcretes there is relatively little difference in the silica content of the hardpan and nodular calcretes. However on Yorke Peninsula silica is 7% higher in the nodular calcrete.

## TABLE 4.3

Mean Oxide Percentages for Calcrete Types in the Murray Basin

| OXIDE | MASSIVE CALCRETE $(\bar{X}\%)$ | NODULAR CALCRETE $(\bar{X}\%)$ | POWDER CALCRETE $(\bar{X}\%)$ |
|---|---|---|---|
| $CaO$ | 36.2 | 34.7 | 17.7 |
| $SiO_2$ | 19.4 | 18.2 | 39.3 |
| $MgO$ | 6.0 | 7.9 | $\boxed{8.4}$ |
| $Fe_2O_3$ | 0.9 | 0.9 | 1.4 |
| $TiO_2$ | 0.2 | 0.2 | 0.3 |
| $K_2O$ | 0.5 | 0.5 | 0.5 |
| $Al_2O_3$ | 1.9 | 2.0 | 3.4 |
| $P_2O_5$ | 0.1 | 0.1 | 0.03 |

TABLE 4.4

Mean Oxide Percentages for Calcrete Types Yorke Peninsula

| OXIDE | MASSIVE CALCRETE ($\overline{X}$%) | NODULAR CALCRETE ($\overline{X}$%) | POWDER CALCRETE ($\overline{X}$%) |
|---|---|---|---|
| CaO | 43.0 | 37.5 | 22.8 |
| $SiO_2$ | 14.5 | 21.4 | 30.5 |
| MgO | 2.4 | 3.5 | 8.5 |
| $Fe_2O_3$ | 0.7 | 0.8 | 1.3 |
| $TiO_2$ | 0.1 | 0.1 | 0.2 |
| $K_2O$ | 0.4 | 0.5 | 0.3 |
| $Al_2O_3$ | 1.8 | 2.0 | 2.7 |
| $P_2O_5$ | 0.1 | 0.1 | 0.04 |

The other minor chemical constituents of the calcretes tend to show uniformity of concentration in the hardpan and nodular calcretes. These minor constituents remain fairly constant after the formation of the indurated calcretes as they generally represent the presence of clay minerals which in indurated calcrete are minimal compared to the powder calcretes. Hence the indurated calcrete differs from other forms by addition of pure calcite which dilutes other minerals present in powder calcrete.

## Spatial Variations of Calcrete Chemistry

In the Murray Basin there is a very strong relationship between the chemistry of the calcretes and their parent-rock environment as is shown by the ratios of the principal elements of the calcrete, Table 4.5.

As can be seen from Table 4.5 there is a pronounced grouping of ratios of elements from the different rock environments. There are some exceptions however, the ratios of aluminium to titanium (Al/Ti) and calcium to magnesium (Ca/Mg) remain fairly constant in all environments except on limestones in the case of the latter ratio.

The ratio of silica to titanium (Si/Ti) is much higher in calcretes developed in the granitic terrain of the Monteith area and on the limestones of the Mannum Formation than in areas of basic igneous rocks where silica contents are relatively low and titanium relatively higher.

TABLE 4.5

Elemental Ratios of Calcrete in Different Rock Environments

| ELEMENTAL RATIO | GRANITIC ENVIRONMENT $\overline{X}$ | AMPHIBOLITE ENVIRONMENT $\overline{X}$ | NORITE ENVIRONMENT $\overline{X}$ | LIMESTONE ENVIRONMENT $\overline{X}$ |
|---|---|---|---|---|
| Al/Ti | 11.3 | 11.3 | 10.7 | 8.5 |
| Al/K | 2.8 | 4.2 | 5.5 | 1.7 |
| Si/Ti | 120.8 | 88.3 | 59.2 | 114.0 |
| Ca/P | 1443.8 | 1883.9 | 1246.0 | 784.0 |
| Al/P | 93.0 | 66.4 | 65.5 | 22.05 |
| Ca/Mg | 7.0 | 6.6 | 9.9 | 13.7 |

Calcium/phosphorus ratios are relatively high in the granitic, amphibolite and norite environments but quite low in the calcretes overlying the limestones. This low Ca/P ratio of the calcretes on the Mannum Formation may be accounted for by the presence of phosphorus in the fossil shells present in the Mannum Limestone.

The ratio of aluminium to phosphorus (Al/P) is higher in the calcretes of the granitic environment than any of the other environments and lowest in the calcrete of the limestone environment with that of the two basic igneous rocks lying in between the two extremes. Although acid igneous rocks and basic igneous rocks contain approximately the same amount of aluminium the content of phosphorus in basic rocks is approximately double that of acid rocks. This no doubt accounts for the differences in the Al/P ratios in the calcretes developed in the two different terrains. The Al/P ratio of the calcretes developed on the limestones of the Mannum Formation reflects the lack of aluminium silicates in the limestones and the higher phosphorus associated with the shells.

Calcretes developed on the basic igneous rocks have relatively higher aluminium to potassium ratios than those developed in the granitic environment and on the limestone. The abundance of alumino-silicates in the norite and amphibolite account for their higher aluminium content and hence their higher Al/K ratio. The low Al/K ratios of the calcretes of the granitic and limestone environments can be accounted for by the fact that in the granitic areas potassium contents are higher as a result of the presence of micaceous minerals and potassium feldspar. In the limestone environment the quantity of aluminium is low because of the lack of alumino-silicates and hence the Al/K ratio is low.

The calcium to magnesium ratio is fairly constant in the granite and amphibolite environments but shows a slight increase in the calcretes developed on the norite and then rises sharply in the calcretes developed on the limestone. This noticeably higher Ca/Mg ratio of the calcrete developed on the Mannum Limestone reflects the high calcium content of the limestone. Whilst the relatively higher ratio of these elements in the calcretes developed on the norite would appear to reflect the higher calcium content associated with the calcium plagioclase of the norite.

No such relationship has been observed with respect to the calcretes on Yorke Peninsula. Like the Murray Basin there are considerable variations in the ratios of constituent elements but these variations tend not to be related to particular rock type environments. For example most of the calcretes on Yorke Peninsula are developed in essentially limestone terrain yet there are marked fluctuations from one locality to another. These variations in elemental ratios on Yorke Peninsula are shown in Table 4.6.

## Mineralogy of Calcretes

Mineralogical examination of the calcretes from the Murray Basin and Yorke Peninsula was carried out using a number of techniques. Thin sections of calcrete were examined under a petrographic microscope using plane polarized light. X-ray diffraction powder photographs were obtained using a Debye-Scherrer camera and

TABLE 4.6

Ratios of Major Elements in the Yorke Peninsula Calcretes

| SAMPLE NUMBER | Al/Ti | Al/K | Si/Ti | Ca/P | Al/P | Ca/Mg |
|---|---|---|---|---|---|---|
| YT1 | 17.1 | 2.1 | 83.9 | 1068.7 | 53.3 | 15.9 |
| YT2 | 17.6 | 2.7 | 77.7 | 872.0 | 51.2 | 15.2 |
| YP1 | 16.2 | 1.3 | 60.8 | 689.7 | 10.1 | 57.4 |
| YP2 | 14.0 | 2.2 | 47.3 | 1305.6 | 12.1 | 56.9 |
| YP3 | 11.7 | 5.4 | 119.0 | 1253.0 | 108.0 | 3.2 |
| PV1 | 17.4 | 2.6 | 290.7 | 469.7 | 18.9 | 15.7 |
| PV2 | 17.9 | 3.2 | 284.5 | 273.0 | 16.8 | 14.9 |
| MB3 | 16.3 | 3.4 | 130.3 | 803.3 | 34.9 | 22.2 |
| MB4 | 17.4 | 1.9 | 467.5 | 629.4 | 20.3 | 6.4 |
| PJ1 | 17.4 | 2.7 | 96.2 | 712.5 | 23.9 | 25.1 |
| PJ2 | 18.1 | 2.7 | 125.2 | 1275.2 | 32.5 | 14.1 |
| WB1 | 17.8 | 4.8 | 96.4 | 834.7 | 32.5 | 14.4 |
| WB2 | 24.3 | 3.7 | 97.5 | 1106.5 | 35.1 | 11.1 |

CoKα radiation in order to determine the mineralogy of the clay fraction of the insoluble residue of the calcretes.

Thin-section examination of the calcrete showed that the principal minerals present were micro-crystalline calcite, quartz and in some cases small angular pieces of plagioclase feldspar. Finely disseminated clay minerals could also be observed.

X-ray spectograph analyses revealed very high magnesium oxide contents in the calcrete. In order to determine whether any of this magnesium was in the form of dolomite, samples of calcrete were finely crushed by hand in a mortar and pestle and mounted in an aluminium holder for X-ray diffraction analysis using a Philips X-ray diffractometer. Diffractometer analyses showed that many of the calcretes contained considerable quantities of dolomite, Tables 4.7 and 4.8. Because of the considerable variation in the degree of induration of the calcretes and hence the degree of crystallinity of the carbonate minerals it was not possible to accurately calculate the percentages of dolomite and calcite from the X-ray diffractometer traces so they were calculated from the oxide percentages.

From Tables 4.7 and 4.8 it can be seen that calcite is the most abundant carbonate mineral in most of the Murray Basin calcretes and in all of the Yorke Peninsula calcretes. In the Murray Basin calcretes the mean calcite percentage is 44.0 and on Yorke Peninsula is 61.9.

The mean dolomite contents of the Yorke Peninsula calcretes are considerably lower than those of the Murray Basin with mean percentages

## TABLE 4.7

### Calcite and Dolomite Percentages in Calcretes of the Murray Basin

| SAMPLE NUMBER | CALCITE % | DOLOMITE % |
|---|---|---|
| TBS1 | 19.4 | 39.3 |
| TB1 | 55.1 | 31.4 |
| TB5 | 63.5 | 17.4 |
| TB6 | 46.6 | 32.0 |
| TB7 | 54.4 | 31.2 |
| TB8 | 27.8 | 61.3 |
| TB9 | 44.0 | 44.3 |
| TB11 | 44.3 | 42.9 |
| TB12 | 28.3 | 56.9 |
| MQ001 | 52.1 | 15.5 |
| MQS2 | 10.0 | 36.0 |
| MQ3 | 54.6 | 19.5 |
| MQ4 | 39.3 | 23.2 |
| MQ5 | 45.2 | 26.8 |
| MQ6 | 35.5 | 37.0 |
| MQ7 | 34.3 | 41.8 |
| OMQ1 | 55.3 | 16.8 |
| OMQ2 | 53.0 | 19.9 |
| OMQ3 | 18.4 | 60.8 |
| MB1 | 58.9 | 21.1 |
| MB2 | 58.4 | 11.6 |
| BHC1 | 56.9 | 19.1 |
| BHC2 | 56.2 | 19.0 |

## TABLE 4.8

## Calcite and Dolomite Percentages in Yorke Peninsula Calcretes

| SAMPLE NUMBER | CALCITE % | DOLOMITE % |
|---|---|---|
| YT1 | 64.6 | 13.8 |
| YT2 | 64.0 | 14.4 |
| YP1 | 88.7 | 4.9 |
| YP2 | 91.8 | 5.1 |
| YP3 | 19.4 | 39.3 |
| PV1 | 50.4 | 10.9 |
| PV2 | 50.3 | 11.6 |
| MB3 | 65.0 | 9.7 |
| MB4 | 36.2 | 23.1 |
| PJ1 | 72.5 | 9.4 |
| PJ2 | 67.4 | 16.6 |
| WB1 | 66.4 | 15.9 |
| WB2 | 68.2 | 22.1 |

of 15 and 30.6 respectively. In a number of samples dolomite is dominant over calcite. Failure to recognize the presence of dolomite in thin section was possibly due to the very micro-crystalline nature of the carbonates.

The second most abundant mineral in the calcretes of the Murray Basin and Yorke Peninsula is quartz. It accounts for some 20% on average of the mineralogy of the calcrete and constitutes the principal mineral of the insoluble residue of the calcretes. Minor quantities of plagioclase feldspar and clay minerals are also present. The quartz is generally angular in shape and approximately 1 mm in diameter. Quartz grains float in the carbonate matrix as phenocrysts.

### Clay Mineralogy

The less than 2μ m fraction of the insoluble residue of the calcrete was separated from the coarser fractions by settling. After eight hours settling in a 500 ml cylinder 35 ml of the clay fraction was drawn from a depth of 20 cm using a pipette. The sampled clay suspension was centrifuged until all the clay had settled to the bottom of the centrifuge tubes. The water was decanted and the clay dried in an oven at 105°C. After drying the clay was crushed in a small mortar and pestle and loaded into plastic containers for X-ray powder photography. X-ray powder photographs were taken of the clays using a 5.73 cm diameter Debye-Scherrer camera and CoKα radiation.

Examination of the powder photographs showed that the clay minerals present in the insoluble residues of the calcretes consist of palygorskite, sepiolite, illite, kaolinite, quartz, goethite and/or hematite. This assemblage of clay minerals is similar to that reported in calcretes from other parts of the world. Van den Heuvel (1966) and Gile (1967) report the presence of palygorskite in the calcretes of New Mexico, whilst Litchfield (1969) has found palygorskite in calcretes in the Northern Territory. More recently Gardner (1972) has reported palygorskite from the caliche of Mormon Mesa in Nevada.

Illite and kaolinite have been reported from New Mexico by Aristarain (1970) and Gardner (1972) found traces of these minerals in the Mormon Mesa caliche in addition to the palygorskite.

Like the chemical characteristics of the Murray Basin calcretes, there is a pronounced regional distribution of the clay minerals of the insoluble residue. In the Black Hill and Murray Bridge areas the dominant clay mineral was found to be palygorskite with only minor amounts of kaolin. The clays in the calcretes from the Monteith area of the Murray Basin consist of palygorskite and sepiolite with minor amounts of kaolin. Near Tailem Bend the dominant clay mineral was found to be sepiolite with minor amounts of illite and kaolinite. The environmental significance of this pattern of distribution is discussed in detail in Chapter 5.

The calcretes from the Long Ridge area of the Murray Basin consist primarily of illite with minor amounts of kaolinite. The dominance of illite is most likely related to the presence of potassium derived from the weathering of granites in the Long Ridge area and granitic intrusions in the eastern Mount Lofty Ranges.

On Yorke Peninsula the clay mineralogy of the insoluble residue of the calcretes is considerably different to most of those in the Murray Basin. Illite is the dominant clay mineral ranging from 65 to 80% with minor amounts of kaolinite, 20-30% of the clay fraction. There are also traces of quartz, 1 to 5% in all the samples. In some of the photographs the illite line is quite broad, suggesting that much of the clay may be interstratified with some vermiculite and chlorite. In one of the samples a trace of hematite and/or goethite was found (Pickering pers. comm.). Similar mineral assemblages have been found in calcretes from the Adelaide area (Norrish and Rogers 1956).

The uniformity of the clay mineralogy of the calcretes from Yorke Peninsula reflects the uniformity of the materials on which the calcrete has developed and the processes responsible for its formation.

From the chemistry and the mineralogy of the calcretes in the Murray Basin and on Yorke Peninsula it is possible to draw some conclusions on the nature of the environments under which the calcretes formed and the processes responsible for their formation.

# CHAPTER V

# GENESIS OF CALCRETE

## Previous Investigations

Relatively little has been written on the genesis of calcrete in South Australia. Some of the early geologists (Howchin 1901, Jack 1914, Woolnough 1927) looked briefly at the problem and suggested that the calcrete resulted from the evaporation of lime-rich waters brought to the surface by the capillary movement of ground waters.

It was not until the work of Prescott (1931) on Australian soils that the ideas of Howchin and Jack were questioned. Prescott suggested that there was a need to consider an external source for the calcium carbonate in order to account for the large quantities of lime required for the formation of the thick calcrete layers observed in many parts of the State.

Crocker (1946) suggested that the source of the calcareous material for the formation of calcrete in South Australia was the continental shelf exposed during Pleistocene marine regressions. He argued that the carbonate in the calcretes represents the fine particles of the exposed dunes and sand-sheets which had been carried in suspension due to the constant wind-winnowing of these deposits. This fine calcareous material was carried inland under prevailing southerly and south westerly winds before being deposited over the land surface and on vegetation. Once the calcareous loess was deposited it was taken into solution and washed into the soil and precipitated within the soil profile as a calcium carbonate horizon.

Subsequent work on the nature of the surficial geological deposits in the Murray Basin, notably that of Firman (1963, 1965, 1969, 1973) and on Yorke Peninsula (Crawford 1965) has largely accepted and perpetuated the ideas of Crocker (1946). Crawford (1965) however acknowledges that in addition to exposed continental shelf deposits some of the calcium may be derived from the Cambrian limestones of Yorke Peninsula.

## Origin of the Murray Basin Calcretes

From field observations and laboratory analyses of calcretes from various localities within the Murray Basin it can be concluded that calcretes are the result of a number of processes. They are not, as Crocker (1946) and more recent workers have suggested, all the result of the translocation and subsequent deposition of carbonates in lower parts of the soil profile.

Morphological characteristics of the calcrete profiles observed in the Murray Basin in fact meet the criteria for pedogenic formations outlined in the literature. One of the most striking features of the calcrete hardpans is their continuity over large areas of the landscape. Frequently the upper surface of the hardpan parallels the land surface and over wide areas is the land surface. The calcrete is commonly overlain by varying thicknesses of brown carbonate-free soil thus strongly suggesting a pedogenic origin for the calcrete.

Other morphological characteristics observed in the Murray Basin and which have been advanced in the literature as evidence for a pedogenic origin are related to the nature of the calcrete profile. Calcrete profiles commonly display a sequence which shows progressively stronger induration, from carbonate silt and scattered to diffuse nodules low in the profile through to thick calcrete hardpans near the top, (Hawker 1927, Netterberg 1967). The mixing of the clastics in the calcrete has been suggested by Brown (1956) to be the result of activity by soil animals and plants and soil dessication as a result of the alternate wetting and drying. Goudie (1972b) has suggested that the correlation observed between the depth of soil above the calcrete hardpan with rainfall reflects the importance of leaching processes and hence pedogenic processes.

Despite these morphological observations which can be taken to support a pedogenic origin for calcrete, the mineralogical and chemical characteristics do not support such a general conclusion. The morphological characteristics can all be accounted for by other processes. In particular, the occurrence of considerable quantities of dolomite in association with sepiolite, palygorskite or both appears to support a non-pedogenic origin for many of the calcretes of the southern Murray Basin.

Palygorskite has been reported from a variety of physical environments. Bradley (1929), Heysteck and Schmidt (1954), Rogers et al. (1954), Bonython (1956) and Millot (1970) have reported and described palygorskite of lacustrine origin. Callen and Tedford (1976) and Callen (1977) have suggested an alkaline lake environment for the precipitation of palygorskite found in the Miocene Namba Formation in the Lake Frome area of South Australia. Muir (1951), Millot (1953), Grim (1953), Barshad et al. (1956) and Weaver and Beck (1977) all suggest that it can form in lagoons, playas and evaporation basins. Millot (1970) has also suggested that it may be marine, a conclusion which Weaver and Beck (1977) very strongly refute. The common association of palygorskite with dolomite strongly supports a non-marine origin for palygorskite for reasons discussed later in this chapter.

Palygorskite has also been reported in soils. Yaalon (1955), Barshad et al. (1956), Ravikovitch et al. (1960) and Singer (1971) have reported palygorskite from calcareous soils in Israel. Whilst Elgabaly (1962) has reported it from soil profiles in Egypt. In most of these cases however the palygorskite appeared to have been derived from the underlying parent material of lacustrine or brackish water origin (Singer and Norrish 1974).

Truely pedogenic palygorskite has been reported from only relatively few localities. Van den Heuvel (1966) reports the presence of the mineral in soils near Las Cruces, New Mexico, Al-Rami et al. (1967) from soils in Iraq, and Millot et al. (1969) and Paquet et al. (1969) from Morocco. In these occurrences the palygorskite has not been observed to occur in the parent materials of the soils. Palygorskite has also been reported occurring as crusts around soil peds in some Australian soils by Beatie and Haldane (1958), Beatie (1970) and more recently by Singer and

Norrish (1974).

The clay fraction of the insoluble residue of the calcretes overlying the limestones of the Mannum Formation at Murray Bridge and the weathered norite in the council quarry at Black Hill consist of palygorskite with no other mineral being identified. At both of these localities the parent materials do not contain palygorskite and it is therefore impossible for the palygorskite in the calcrete to have been inherited from them. It must therefore be concluded that the palygorskite is primary or neoform in origin.

It is also most unlikely, if not impossible, for the palygorskite and hence the calcrete to be of marine origin for two principal reasons. Palygorskite has been shown to grow only in environments where the salinity is less than normal sea water (Weaver and Beck 1977). The common association of palygorskite with dolomite also precludes a marine origin for the palygorskite. Dolomite formation has been shown to be inhibited, if not completely prohibited under marine conditions (Falk and Land 1975). Such an origin for the palygorskite and hence the calcrete in the above localities would also be at odds with the geological history of the Murray Basin outlined earlier.

However at least two possible origins for the palygorskite and hence the calcrete at the above localities can be suggested. Despite the disagreements in the literature on the nature of the physical environment or environments under which palygorskite forms, there appears to be a general agreement on the nature of the chemical environment. All workers agree that palygorskite is a product of alkaline chemical sedimentation. Such an environment had been believed to exist only under lacustrine type conditions until very recently. Singer and Norrish (1974) showed from laboratory studies that such a chemical environment is feasible under pedogenic conditions. Thus either of these environments can be invoked to account for the formation of the calcretes at the two sites.

The occurrence of dolomite in association with palygorskite in the calcretes from Murray Bridge and Black Hill strongly supports a lacustrine rather than pedogenic environment of formation. Dolomite has been shown to form almost exclusively in lacustrine, lagoonal or brackish water environments (Folk and Siedlecka 1974; Folk and Land 1975; von der Borch et al. 1975). It is most unlikely that the dolomite and hence the calcrete is of a pedogenic origin. The few references to dolomite in soils in the literature have been concerned with soil formation on lacustrine sediments and hence the dolomite is a secondary phenomena (Alway and Zetterberg 1935; Sherman et al. 1962). In both of the localities described here dolomite does not occur in the parent material. At Black Hill evidence for a lacustrine environment of formation is further supported by the occurrence of amorphous silica (Hutton et al. 1977).

In the Monteith area of the Murray Basin, between Murray Bridge and Tailem Bend, the clays of the insoluble residue of the calcrete consist of a combination of palygorskite and sepiolite. The calcretes to the north east of Tailem Bend consist almost entirely of sepiolite with the presence of minor amounts of illite.

The presence of sepiolite as the dominant clay mineral in the insoluble residue of the calcretes in the southern Murray Basin and its association with dolomite also strongly suggests a lacustrine type of environment for the formation of the calcrete. Like palygorskite, sepiolite has commonly been reported occurring in alkaline lacustrine environments (Millot 1949; Parry and Reeves 1968; Wallas et al. 1968). Recently Weaver and Beck (1977) stated that:

> "Sedimentary sepiolite is most commonly formed, along with dolomite, in highly alkaline and schizohaline evaporitic environments. Sepiolite apparently forms under more alkaline conditions than does palygorskite and where Si and Mg concentrations are high and Al low." (Weaver and Beck 1977 p. 3)

Sepiolite has not been reported in the literature to form in soils (Van den Heuvel 1966). Whether the highly alkaline conditions favourable for its formation occur within soil profiles is uncertain. The work of Singer and Norrish (1974) makes only brief mention of sepiolite noting that sedimentary deposits of lacustrine environments contain sepiolite. They do not state whether or not it can be pedogenic. Despite the lack of reference to pedogenic sepiolite it is considered that in the Murray Basin it is lacustrine because of the occurrence of dolomite with the sepiolite, for the reasons outlined earlier.

The chemical relationship between sepiolite and palygorskite has been noted earlier. Spatially however they represent part of a basin edge sequence with the sediments at the outer edge showing a lakeward progression from kaolinite to montmorillonite to palygorskite to sepiolite. Thus where sepiolite is the dominant clay mineral in the calcretes it would be reasonable to expect that it was formed close to the centre of the basin whilst in those calcretes dominated by palygorskite are envisaged to have formed toward the margins of the basin. Where the two minerals occur together a zone intermediate to the two must necessarily be envisaged.

In the preceeding discussion an essentially neoform or primary origin for the palygorskite, sepiolite and dolomite has been advanced. The unlikely formation of these three minerals in a soil profile has been demonstrated. These conclusions however are apparently at odds with the original definition of calcrete outlined in the introductory chapter. By definition (cf. Netterberg 1969b) calcrete is a secondary material involving the cementation or replacement of a pre-existing material by predominantly calcium carbonate. In the case of the Murray Basin calcretes it would appear from geochemical and mineralogical evidence that they are the result of the cementation of a pre-existing lacustrine sequence of magnesium rich carbonate rocks. That is to say the calcrete is of the *in situ* type (Blank and Tynes 1965).

Despite the fact that the calcrete in the Black Hill, Tailem Bend and Murray Bridge areas is all envisaged to have formed from lake sediments it is unlikely that its formation is related to the same sequence of lakes. At Black Hill the calcrete stands some 45 m above the Murray Plains and the calcrete is most probably related to a residual lake or lakes associated with the Miocene marine transgression (Hutton et al. 1977). It is unlikely that the higher stands of the sea during the Pleistocene would have been high enough to inundate the Black Hill area.

Where the calcrete occurs closer to the tract of the Murray River such as those deposits at Murray Bridge and Tailem Bend it is suggested that the lacustrine environment in which the calcrete formed was related to higher stands of the sea during the Pleistocene. It appears likely that the calcretes of the lower Murray Valley represent part of a sequence of lakes which extended down the Murray Valley as the sea regressed towards the end of the Pleistocene. Whilst it is not envisaged that the calcretes of the Lower Murray represent a southerly extension of Lake Bungunnia (Firman 1965) they no doubt represent members of the same series of lakes. It would however be misleading to suggest that all calcrete in the Murray Basin is lacustrine in origin. It is clear from the chemical and mineralogical analyses of calcretes from the Sedan area of the Basin that in some localities the calcrete is pedogenic in origin. The dominant clay mineral in the insoluble residue of the calcrete is illite which is the dominant clay mineral in soils (Pickering pers. comm.) and the dominant carbonate mineral in the calcrete is calcite with little or no dolomite being present.

A similar mineralogical sequence was found in the calcretes developed at Long Ridge in the central Murray Basin just to the north of Black Hill. The dominant clay mineral in the insoluble residue is illite whilst the principal carbonate mineral was calcite. Long Ridge is an inlier of grandiorite and stands some 40 m above the Murray Plains. Here the calcium carbonate has no doubt been derived from the deflation of the surrounding plains and subsequently transported as wind born particles to be deposited on Long Ridge or it may be relict from Tertiary calcium carbonate.

## Source of Calcium and Magnesium Ions in the Murray Basin

Crocker (1946) suggested that the principal source of calcium for the formation of the calcretes of the Murray Basin, in fact for South Australia generally, was the exposed continental shelf at times of lower stands of the sea during the Pleistocene. The need to seek an external source of calcium was based on two observations. First that there were insufficient calcareous parent materials to provide the quantities of calcium required to account for the considerable thicknesses of calcrete hardpans. Secondly the occurrence of calcretes over non-calcareous parent materials lead him to believe that the calcium could not be derived from underlying parent materials.

In the Murray Basin there are a considerable number of limestone and other calcareous sedimentary units which are capable of supplying calcium for calcrete formation. Some of these units have an average calcium carbonate content of 85% and extend to depths of 30 m as is the case with the Mannum and Morgan Limestones.

Work by Miller (1952) on the solubility of calcium carbonate under varying conditions of temperature and carbon dioxide partial pressures suggested that:

> "Assuming the rain to be in equilibrium with an atmospheric partial pressure of $CO_2$ ($3.5 \times 10^{-4}$ bars)

> and to contain no impurities, rain water could dissolve 0.044 g $CaCO_3$ per litre at 25°C. This would mean that 3.1 tons of $CaCO_3$ per square mile per inch of rain could be removed from the limestone area provided equilibrium in the system was attained ..." (Miller 1952 p. 195)

Given these rates of solution and accompanying release of calcium from the large quantities of limestone and other calcareous sediments in the Murray Basin a local source of calcium would appear to be more likely than earlier workers suggested.

Whilst the bulk of the calcium which has gone into calcrete formation has been derived from the calcareous sediments of the Murray Basin evidence locally also suggests that the weathering of calcium rich igneous and metamorphic rocks contribute some calcium to the system. At Black Hill the norite, dominated by calcium rich plagioclase, has a fresh rock calcium oxide content of some 9% (Soult 1973). Studies of the weathering of the Black Hill norite by Soult (1973) have shown that on weathering there is up to a 60.5% loss of calcium oxide. It is suggested that much of this calcium is rapidly re-deposited within the weathering profile as discontinuous horizons of massive calcrete and as thin horizons of laminar calcrete.

To the south east of Tailem Bend there is an outcrop of amphibolite and associated calc-silicate meta-sediments. Chemical analyses show that the amphibolite contains up to 15% calcium oxide (Morris and [illegible] et al. 1974). Whilst there is no data available on the percentage loss of calcium on weathering of the amphibolite the high calcium content strongly suggests that the amphibolite on weathering has contributed to the formation of the calcrete.

The source of much of the magnesium for the formation of the palygorskite and sepiolite is undoubtedly the calcareous sediments of the Murray Basin. Johns (1963) has shown that many of the Tertiary limestones contain up to 14% magnesium. As outlined earlier, magnesium is considerably more soluble than calcium and hence would be rapidly taken into solution and subsequently re-deposited in the shallow depressions in which the Pleistocene lakes formed.

A second major source of magnesium are the basic igneous rocks which occur in parts of the Basin. At Black Hill the norite contains some 5% magnesium oxide in the fresh rock up to 50% of which is lost on weathering (Soult 1973). This magnesium was no doubt removed from the weathering profile and transported down the valley in ground water and deposited in the shallow water saline lakes.

At Tailem Bend the amphibolite contains up to 7% magnesium oxide in the unweathered rock. Again no loss on weathering figures are available but with the relatively high magnesium content it is most likely that it was also a significant source of magnesium for dolomite and clay mineral formation. It is also likely that magnesium was derived from the lake waters.

## Genetic Implications of Calcrete Morphology in the Murray Basin

Many of the morphological characteristics of calcrete profiles have been cited as supportive evidence for a pedogenic origin. It is believed however that the morphological characteristics may also be indicative of a lacustrine environment of formation.

The classification of calcretes developed by Netterberg (1967, 1969b) is an evolutionary one which suggests that hardpan calcrete is the ultimate product of formation whilst powder calcrete or calcified soil is the initial. Such an evolutionary scheme for calcrete formed within soil horizons is most useful and certainly the evidence from the morphology of hardpan calcretes supports such a sequence of formation. However difficulties arise in interpretation when all three calcretes occur in a single profile. Where nodular calcrete horizons occur beneath massive hardpan horizons it is difficult to explain how calcium carbonate can be transported through the massive calcrete in order to complete cementation. Likewise if the source of the calcium, magnesium and silicon is from the ground water why massive calcrete should already have formed over the nodular calcrete, unless cementation is accompanied by a progressively lowering water table. The commonly observed pattern of profile development could more satisfactorily be explained in terms of calcrete weathering than stages of calcrete formation.

It has been shown in an earlier chapter that there is a relationship between the degree of calcrete induration and concentration of the major oxides. Calcium oxide contents are generally higher in the massive calcrete than they are in nodular and powder calcretes, magnesium oxide is generally higher in massive calcretes than lesser indurated varieties whilst silica is much higher in powder calcrete than the indurated forms.

From the pattern of distribution of the oxides within the calcrete profiles with a tendency for calcite to occur in massive calcretes at or near the top of the profile and dolomite to occur lower in the profile it would appear that the pattern of chemical sedimentation in lacustrine environments is being reflected in the calcrete profile. The degree of induration of the calcrete horizons within calcrete profiles would therefore appear to be in large part a response to chemical composition rather than stage of development. Where there is a series of alternating massive and essentially nodular horizons, breaks in the processes of chemical sedimentation must necessarily be invoked to account for them. Under such lacustrine environmental conditions the characteristics of the calcrete profiles outlined earlier such as horizontality of horizons etc. would still occur (cf. Von der Borch et al. 1975).

## Origin of Yorke Peninsula Calcretes

The geological and geomorphological setting of Yorke Peninsula is considerably different to that of the Murray Basin and as a result the origin of the calcretes is different. Much of the Peninsula is covered by Quaternary deposits which consist of fixed longitudinal sand dunes and associated sand sheets, aeolianite, beach dune ridges and recent dunes. Large areas of these Quaternary deposits have been calcreted thus concealing much of the stratigraphy of the Peninsula. Unlike the Murray Basin, Yorke Peninsula consists of much more extensive calcareous aeolian deposits associated with Pleistocene eustatic sea level fluctuations. These larger quantities of essentially marine derived aeolian sediments result from the exposed nature of the Peninsula to the marine environment.

Calcrete formation on Yorke Peninsula is intimately associated with these Pleistocene calcareous deposits. The processes which have given rise to the extensive calcrete horizons would appear to be essentially pedogenic. That is to say the calcretes represent indurated carbonate horizons which owe their origin to the downward movement of calcium carbonate as a result of the percolation of meteoric water through the calcareous aeolian Pleistocene deposits. Such a pedogenic origin is supported by the chemistry and clay mineralogy of the calcretes.

As has been shown in Chapter 4 the calcretes of Yorke Peninsula are chemically purer than those in the Murray Basin. Silicon percentages are lower, calcium percentages are considerably higher and there is a much lower magnesium content than in the Murray Basin calcretes. Other minor oxides are of comparable concentrations to the calcretes of the Murray. The considerably higher calcium carbonate contents are a reflection of the nature of the chemically pure carbonate parent materials on which the calcrete has formed and is forming. Accompanying this higher calcium carbonate content is a correspondingly lower silica content.

The presence of some dolomite in the Yorke Peninsula calcretes can be accounted for by the nature of the parent materials of the calcretes. As the calcareous parent materials consist in large part of the disintegrated skeletons of marine invertebrates it is reasonable to expect that the magnesium has been derived from the solution of magnesium rich calcite which makes up the tests of many marine invertebrates. It is therefore a secondary feature.

X-ray diffraction examination of the clay fraction of the insoluble residue has shown that the dominant clay mineral of the Yorke Peninsula calcretes is illite with minor amounts of kaolin. This assemblage of clay minerals further supports the pedogenic origin of the Yorke Peninsula calcretes. Both of these minerals are found to be the most dominant clay minerals in contemporary soil profiles.

## Source of Calcium and Magnesium Ions on Yorke Peninsula

The Cainozoic deposits of Yorke Peninsula consist predominantly of calcareous sediments. The Pleistocene deposits which mantle much of the Peninsula consist almost exclusively of calcium carbonate in the form of disintegrated tests of marine invertebrates. It is from the solution of these deposits that much of the calcium in the calcrete has been derived.

From the discussion of the geology of Yorke Peninsula in Chapter 2 it has been shown that much of the Tertiary is dominated by bryozoal limestones. Analyses of these limestones have shown that calcium carbonate contents commonly exceed 90% with only 1% or 2% magnesium (Johns 1963). As many of these limestones show evidence of considerable solution it is clear that at least locally they contribute or have contributed significantly to the supply of calcium for the formation of the calcrete which overlies them.

Further supplies of calcium for calcrete formation are almost certainly derived from the Cambrian limestone deposits which occur extensively under the Pleistocene mantle. These limestones also commonly contain greater than 90% calcium carbonate (Johns 1963).

As was suggested earlier much of the magnesium in the calcretes of the Peninsula would appear to have been derived from the solution of the magnesium rich calcite tests of marine organisms. Analyses of similar materials from the south east of South Australia (Firman 1973) have shown that the calcareous sands commonly contain up to 2.5% magnesium. It would appear unlikely that the Tertiary and Cambrian limestones have contributed much magnesium to the system as they commonly contain less than 1% magnesium (Johns 1963).

Locally however magnesium is contributed from dolomitic limestones such as those in the Ardrossan and Clinton areas where the magnesium contents of the dolomites reaches approximately 40% (Johns 1963). It is also likely that these localities have contributed in part to the magnesium of calcretes in the north-eastern part of the Peninsula.

## Genetic Implications of Calcrete Morphology on Yorke Peninsula

Field observations of calcrete profiles and massive hardpan calcretes support a number of phases of calcrete formation rather than one single phase. It is suggested that calcrete formation occurred during periods of landscape stability which occurred during interglacial periods. Separating each period of calcrete formation was a period of landscape instability during which time there was local dune building and alluviation (Williams 1971). It is during glacial periods that dissection of earlier formed calcrete hardpan occurred.

The earliest phase of calcrete formation on Yorke Peninsula is preserved in the calcrete profiles in the form of black calcrete nodules. At the conclusion of this phase there appears to have been a major break in calcrete formation. From the presence of the black calcrete two conclusions are possible, either the early black calcrete hardpans were extensively eroded leaving only nodules and cobbles behind or the environment of depostion was such that only nodular black calcrete was formed. This latter possibility is however unlikely as in some of the massive hardpan calcretes into which the black calcrete has become incorporated angular fragments of black calcrete can be observed. The occurrence of angular fragments supports the contention that an earlier extensive covering of massive black calcretes has been eroded and remnants subsequently became re-incorporated in later stages of calcrete formation.

Following the period of erosion which removed much of the massive black calcrete there was a period or periods of landscape stability during which the extensive calcrete profiles observed on Yorke Peninsula were developed. These phases of calcrete formation were complex, as the variety and complexity of structures observed in many of the massive hardpan calcretes illustrates. It would appear that even during a single major period of calcrete formation there were phases of carbonate solution and re-deposition consequent upon minor changes in the nature of the geochemical environment at the soil/calcrete interface.

It is unlikely that the complex history of calcrete formation reflected in the structure of the massive hardpan calcretes reflects an environment of continuous soil cover. Rather there appears to have been periods during the Pleistocene when there was removal of the soil covering the landscape and destruction of the massive calcrete hardpans.

The eroded calcrete fragments have subsequently become re-cemented and incorporated into the contemporary calcrete profiles. Whether this re-cementation took place prior to the development of the thin horizons of carbonate free soil which occurs on top of the hardpan calcretes or whether the debris was re-cemented as a result of the movement of calcium carbonate down through the soil profile is uncertain. However from the evidence in the Murray Basin it would appear that the former situation is the most likely.

The uppermost surface of the massive hardpan calcretes commonly displays a thin horizon of laminated calcrete. This laminated calcrete horizon suggests that the uppermost part of the calcrete is constantly undergoing solution and re-deposition of the near surface carbonate. This laminated horizon represents carbonate accretion as the laminations are confined to the surface of the calcrete while the interstices of the hardpan layer is massive in form.

Profile form presents many problems in interpretation. Many profiles exhibit an overall tendency for the degree of calcrete induration to decrease with depth such that the uppermost part of the profile consists of a horizon of massive calcrete while the lowermost horizon of the profile consists of carbonate silt, the two being separated by a horizon of carbonate nodules embedded in the silt. At a number of localities, described in Chapter 3 there is evidence of alternating horizons of massive and nodular calcretes, thus further complicating genetic interpretation.

If the ideas of Netterberg (1969b, 1971) and Goudie (1973) on the evolutionary relationships that exist between calcrete forms are correct then it must be accepted that within any calcrete profile the massive hardpan calcretes consisting of nodule in nodule structures represent the penultimate stage of calcrete formation whilst the carbonate silt represents the initial stage of development. Therefore where there occurs within any calcrete profile a number of alternating horizons of the three basic forms of calcrete it must be interpreted that each horizon represents a period of calcrete formation and the stage of development indicates the relative length of time during which conditions favourable for calcrete formation prevailed.

It would be difficult to account for the observed profile forms in any one stage of calcrete development. To do this it would be necessary to explain how carbonate laden water moves through the massive hardpan calcrete to form the transitional powder and nodular horizons. The above interpretation overcomes this difficulty. Having suggested that each horizon in the calcrete profile essentially represents a period of calcrete formation it is now necessary to suggest the nature of the pedogenic environment under which the deposition of the carbonate took place.

The characteristics of the calcrete profiles and the structures within the massive calcretes briefly outlined above and discussed in greater detail in Chapter 3 would suggest a more or less continually aggrading aeolian environment in which carbonate was continually being contributed to the land surface (Crocker 1946). As has already been discussed the presence of angular debris and the formation of an essentially brecciated hardpan calcrete record breaks in the process of aggradation but such conditions were followed by further aggradation. Such an interpretation is consistent with that suggested by Brown (1956) for the caliche in Texas and Gardner (1972) for caliche in Nevada where similar calcrete morphologies have been observed. Further such an explanation would also account for the absence on many occasions of the A and B soil horizons (Gardner 1972) and the absence of extensive solution cavities and cupped nodules (Bretz and Horberg 1949, Gile et al. 1966) commonly cited as evidence for degrading calcrete profiles.

# CHAPTER VI

# SUMMARY AND CONCLUSIONS

Field observations have shown that in the Murray Basin and on Yorke Peninsula three basic types of calcrete occur over much of the landscape: powder, nodular and hardpan calcretes. Each form shows variation in thickness, structure, colour and degree of induration.

Hardpan calcrete may be either massive or laminar in form. The laminations may be parallel to the surface of the calcrete or form small domes and depressions. The matrix of the hardpan calcrete in some areas may consist exclusively of carbonate cemented nodules. Nodular calcrete may also be massive or concretionary in form consisting of numerous envelopes of white carbonate surrounding a core of black or grey calcrete.

Chemical and mineralogical analyses indicate that the calcretes of the Murray Basin are the result of two processes. In the southern Murray Basin the occurrence of dolomite, sepiolite and palygorskite suggest that the calcretes have formed in a lacustrine environment or are the result of the replacement of lacustrine sediments by calcite and dolomite. In the western part of the Basin the calcretes are the result of pedogenic processes involving the deposition of calcium carbonate by evaporative precipitation as a result of wetting and drying and seasonal loss of $CO_2$ due to seasonal vegetation changes. Such pedogenic processes are supported by the dominance of illite in the clay fraction of the insoluble residue.

On Yorke Peninsula, the dominant carbonate mineral in the calcretes is calcite and the principal clay minerals are illite and kaolinite. This mineral assemblage suggests that the calcretes are primarily the result of pedogenic processes involving the solution and subsequent redeposition of dominantly calcium carbonate in the calcareous aeolian deposits of the Peninsula.

The source of calcium for the formation of the calcretes in the Murray Basin appears to be the calcareous Tertiary sediments and calcium rich basic igneous and metamorphic rocks which constitute much of the Murray Basin. Given the richly calcareous nature of the sediments of the Basin there is no need to invoke an external source for the carbonate. Magnesium ions for the formation of dolomite, palygorskite and sepiolite also appear to have been derived from the calcareous sediments and the weathering of basic igneous and metamorphic rocks of the Murray Basin.

On Yorke Peninsula, where the calcrete has developed principally in the Pleistocene calcareous dunes and sand sheets which cover large areas of the Peninsula the calcium for the calcrete formation has been derived from the solution of the shell tests which constitute the dunes. Calcium is also no doubt derived from the solution of the Tertiary and Cambrian limestones which form the bulk of the pre-Quarternary sediments of Yorke Peninsula.

Calcrete formation in the Murray Basin and on Yorke Peninsula appears to have occurred during interglacial periods when rainfall was higher than at present and when seasonal drought was common. Such conditions appear to have occurred on at least three occasions during the Late Quaternary; 30,000 - 24,000 yrs B.P., 16,000 - 12,000 yrs B.P. and 5,000 - 3,500 yrs B.P. (Williams and Polach 1971). It is suggested that the massive, nodular and powder calcretes represent each of these phases of calcrete development respectively.

# REFERENCES CITED

Al-Rawi, C. J. and Sys, C., 1967, A comparative study between Euphrates and Tigris sediments in the Mesopotamia Flood Plain, Pedologie Grand, 17, 187-211.

Alway, F. J. and Zetterberg, J. M., 1935, Relative amounts of calcium carbonate and magnesium carbonate in some Minnesota subsoils, Soil Sci., 39, 7-14.

Aristarain, L. F., 1970, Chemical analyses of caliche profiles from the High Plains, New Mexico, J. Geol., 78, 201-212.

Aristarain, L. F., 1971, On the definition of caliche deposits, Z. Geomorph., 15, 274-289.

Barshad, E., Halevy, E., Gold, H. A., and Hagin, J., 1956, Clay minerals in some limestone soils of Israel, Soil Sci., 81, 423-437.

Beattie, J. A., 1970, Peculiar features of soil development in parna deposits in the eastern Riverina, New South Wales, Aust. J. Soil Res., 8, 145-156.

Beattie, J. A. and Haldane, A. D., 1958, The occurrence of palygorskite and barytes in certain parna soils of the Murrumbidgee region, New South Wales, Aust. J. Sci., 20, 274-275.

Blake, W. P., 1902, The caliche of southern Arizona : an example of deposition by the vadose circulation, Trans. Am. Inst. Mining and Metallurgical Eng., 31, 220-226.

Blank, H. R. and Tynes, E. W., 1965, Formation of caliche in situ, Bull. Geol. Soc. Am., 76, 1387-1392.

Bonython, C. W., 1956, The salt of Lake Eyre. Its occurrence in Madigan Gulf and its possible origin, Trans. Roy. Soc. S. Aust., 79, 66-92.

Bradley, W. H., 1929, The occurrence and origin of analcite and meerrschaum beds in the Green River formation of Utah, Colorado and Wyoming, U.S.G.S. Prof. Paper, 158A, 1-9.

Bretz, J. H. and Horberg, L., 1949, Caliche in south-east New Mexico, J. Geol., 57, 491-511.

Brown, C. N., 1956, The origin of caliche in the north-east Llano Estacado, Texas, J. Geol., 64, 1-15.

Callen, R. A., 1977, Late Cainozoic environments of part of north-eastern South Australia, J. Geol. Soc. Aust., 24, 151-169.

Callen, R. A. and Tedford, R. H., 1976, New Late Cainozoic rock units and depositional environments, Lake Frome Area, South Australia, Trans. Roy. Soc. S. Aust., 100, 125-168.

Casey, J. N. and Wells, A. T., 1964, The geology of the northeast Canning Basin, Western Australia, Rept. Aust. Bur. Min. Res., Geol. and Geophys., 49, 61 pp.

Crawford, A. R., 1965, The geology of Yorke Peninsula, Bull. Geol. Surv. S. Aust., 39, 96 pp.

Crespin, I., 1958, Permian foraminifera of Australia, Bur. Min. Res. Geol. Geoph. Bull., 48, 1-207.

Crocker, R. L., 1946, Post Miocene climatic and geologic history and its significance in relation to the genesis of the major soil types of South Australia, Bull. Coun. Sci. Industr. Res. Aust., 193, 56 pp.

Daily, B., 1956, The Cambrian in South Australia, Rep. Int. Geol. Congr. Mexico, 2, 91-147.

Daily, B., 1967, Surface stratigraphy and palaeontology of the Cambrian Sequence, Unpublished report to Beach Petroleum N.L.

Durand, J. H., 1949, Essai de nomenclature des croutes, Bulletin Societe des sciences Nautrelles de Tunisie, 3-4, 141-142.

Elgabaly, M. M., 1962, The presence of attapulgite in some soils of the western desert of Egypt, Soil Sci., 93, 387-390.

Firman, J. B., 1963, Quaternary geological events near Swan Reach in the Murray Basin, South Australia, Quart. Geol. Notes, Geol. Surv. S. Aust., 5.

Firman, J. B., 1965, Late Cainozoic lacustrine deposits in the Murray Basin, South Australia, Quart. Geol. Notes, Geol. Surv. S. Aust., 16.

Firman, J. B., 1966, Kunkar in Bakara Soil.  Pinaroo-Karoonda map sheet, Geological Atlas of South Australia, Special series, 1:250,000, Geol. Surv. S. Aust.

Firman, J. B., 1969, Quaternary Period, in L. W. Parkin (ed.), *Handbook of South Australian Geology*, Geol. Surv. S. Aust., 204-233.

Firman, J. B., 1970, Late Cainozoic stratigraphic units in the Great Artesian Basin, South Australia, *Quart. Geol. Notes, Geol. Surv. S. Aust*., 36.

Firman, J. B., 1971, Calcrete and related materials in the Murray Basin and Gambier Embayment, South Australia, ANZAAS, 43rd Congress, Brisbane.

Firman, J. B., 1973, Regional stratigraphy and surficial deposits in the Murray Basin and Gambier Embayment, *Rept. Invest*., *Geol. Surv. S. Aust*., 39, 68 pp.

Folk, R. L. and Land, L. S., 1975, Mg/Ca ratio and salinity : two controls over crystallization of dolomite, *Am. Assoc. Pet. Geol*., 59, 60-68.

Folk, R. L. and Siedlecka, A., 1974, The "schizohaline" environment : Its sedimentary and diagenetic fabrics as exemplified by the Late Paleozoic rocks, Bear Island, Svalbard, *Sed. Geol*., 11, 1-15.

Gardner, L. R., 1972, Origin of the Mormon Mesa caliche, Clark County, Nevada, *Bull. Geol. Soc. Am*., 83, 143-156.

Gile, L. H., 1967, Soils of an ancient basin floor near Las Cruces, New Mexico, *Soil Sci*., 103, 265-276.

Gile, L. H., Peterson, F. F., and Grossman, R. B., 1966, Morphological and genetic sequences of carbonate accumulation in desert soils, *Soil Sci*., 101, 347-360.

Goudie, A., 1971, A regional bibliography of calcrete, in W. G. McGuinnies, B. J. Goldman, and P. Paylor (eds.), *Food, Fiber and the Arid Lands*, Tuscon, 421-437.

Goudie, A., 1972a, The chemistry of world calcretes, *J. Geol*., 80, 449-463.

Goudie, A., 1972b, Processes of limestone deposition in deserts, Unpublished paper presented to B.G.R.G. Conference, Oxford, 24 pp.

Goudie, A., 1973, *Duricrusts in tropical and subtropical landscapes*, Clarendon Press, Oxford.

Grim, R. E., 1953, *Clay Mineralogy*, McGraw-Hill, New York.

Hawker, H. W., 1927, Soils of Hidalgo County, Texas, Soil Sci., 23, 475-485.

Heysteck, H. and Schmidt, E. R., 1954, The mineralogy of the attapulgite montmorillenite deposit in the Springbok Flats, Transvaal, Trans. Geol. Soc. Sth. Afr., 56, 99-115.

Howchin, W., 1901, Suggestions on the origin of the salt lagoons on southern Yorke Peninsula, Trans. Roy. Soc. S. Aust., 25, 1-9.

Hunt, C. B. and Mabey, D. R., 1966, Stratigraphy and structure, Death Valley, California, U.S.G.S. Prof. Paper, 494A.

Hutton, J. T., Lindsay, D. S., and Twidale, C. R., 1977, The weathering of norite at Black Hill, South Australia, J. Geol. Soc. Aust., 24, 37-50.

Jack, R. L., 1914, The geology of the County of Jervois, and portions of the counties of Buxton and York, with special reference to underground water supplies, Bull. Geol. Surv. S. Aust., 3, 47 pp.

Johns, R. K., 1963, Limestone, dolomite and magnesite resources of South Australia, Bull. Geol. Surv. S. Aust., 38, 100 pp.

Lamplugh, G. W., 1902, Calcrete, Geol. Mag., 9, 575.

Lamplugh, G. W., 1907, Geology of the Zambezi Basin around Batoka Gorge, Quart. J. Geol. Soc. London, 63, 162-216.

Litchfield, W. H., 1969, Soil surfaces and sedimentary history near the MacDonnell Ranges, Northern Territory, CSIRO Aust. Soil Publication, 25.

Logan, B. W., Rezak, R., and Ginsburg, R. N., 1964, Classification and environmental significance of algal stromatolites, J. Geol., 72, 68-83.

Ludbrook, N., 1957, A reference column for the Tertiary sediments of the South Australian portion of the Murray Basin, Proc. Roy. Soc. N.S.W., 90, 174-180.

Ludbrook, N., 1958, The Murray Basin in South Australia, in M. F. Glaessner and L. W. Parkin (eds.), The Geology of South Australia, J. Geol. Soc. Aust., 5, 102-114.

Ludbrook, N., 1961, Stratigraphy of the Murray Basin in South Australia, Bull. Geol. Surv. S. Aust., 36, 96 pp.

Mabbutt, J. A., 1967, Denudation chronology in central Australia, in J. N. Jennings and J. A. Mabbutt (eds.), Landform Studies from Australia and New Guinea, A.N.U. Press, Canberra, 144-181.

McGregor, A. M., 1930, Geological notes on a circuit of the Great Makarikari Salt Pan, Union Sth. Afr. Geol. Soc. Trans., 33, 89.

Miller, J. P., 1952, A portion of the system calcium carbonate - carbon dioxide - water, with geological implications, Am. J. Sci., 250, 161-203.

Millot, G., 1949, Relations entre la constitution et al genese des roches sedimentaires argileuses, These Sci. Nancy et Geol. Appl. Prospec. Min., 2, 1-352. Cited in Millot, G., 1970, Geology of Clays, New York, 429 pp.

Millot, G., 1953, Mineraux argileux et leurs relations avec la geologie, Rev. Inst. Fr. Petrole., 8, 75-86.

Millot, G., 1970, Geology of clays, (trans. W. R. Farrand and H. Paquet), Springer, New York, 429 pp.

Millot, G., Paquet, H., and Ruellan, A., 1969, Neoformation de l'attapulgite dan le sols a carapaces calcaires de la Basse Moulouya (Maroc oriental), C. R. Acad. Sci. Paris, 268, 2771-2774.

Morris, B. F. and Nichol, D., 1974, Basic rocks of the Kanmantoo Group at Tailem Bend, Quart. Geol. Notes, Geol. Surv. S. Aust., 51.

Muir, A., 1951, Notes on Syrian soils, J. Soil Sci., 2, 163-181.

Netterberg, F., 1967, Some road-making properties of South African calcretes, Proc. 4th Regional Conf. for Afr. on Soil Mechanics and Foundn. Eng., Cape Town, 77-81.

Netterberg, F., 1969a, Ages of calcretes in Southern Africa, S. Afr. Archaeol. Bull., 24, 88-92.

Netterberg, F., 1969b, The interpretation of some basic calcrete types, S. Afr. Archaeol. Bull., 24, 117-122.

Netterberg, F., 1971, Calcrete in road construction, Nat. Inst. Road Res. Bull., 10, 73 pp.

Norrish, K. and Hutton, J. T., 1969, An accurate X-ray spectrographic method for the analysis of a wide range of geological samples, Geochim. cosmochim Acta., 33, 431-453.

Norrish, K. and Rogers, L. E., 1956, The mineralogy of some Terra Rossas and Rendzinas of South Australia, J. Soil Sci., 7, 294-301.

Northcote, K. H., 1951, A pedological study of the soils occurring at Coomeolla, New South Wales, C.S.I.R.O. Bull 264.

Paquet, H., Ruellan, Y., Tardy, Y., and Millot, G., 1969, Geochimie d'un bassin versant au Maroc oriental. Evolution des argiles dans les sols des montagnes et des plaines de la Basse Moulouya, C. R. Acad. Sci. Paris, 269, 1839-1842.

Parry, W. T. and Reeves, C. C., 1968, Sepiolite from Pluvial Mound Lake, Lynn and Terry Counties, Texas, Am. Mineral., 53, 984-993.

Prescott, J. A., 1931, The soils of Australia in relation to vegetation and climate, Bull. Coun. Sci. Industr. Res. Aust., 52, 82 pp.

Price, W. A., 1933, The Reynosa problem of South Texas and the origin of caliche, Bull. Am. Assoc. Petroleum Geol., 17, 488-522.

Ravikovitch, S., Pines, F., and Ben-Yair, M., 1960, Composition of the colloids in the soils of Israel, J. Soil Sci., 11, 82-91.

Reeves, C. C., 1970, Origin, classification and geologic history of caliche on the southern High Plains, Texas and Eastern New Mexico, J. Geol., 78, 352-362.

Reeves, C. C., 1976, Caliche - Origin, classification, morphology and uses, Estacado Books, Texas.

Rogers, A. W., 1934, The build of the Kalahari, Sth. Afr. Geog. J., 17, 3-12.

Rogers, A. W., 1936, Surface geology of the Kalahari, Trans. Roy. Soc. Sth. Afr., 24, 57-80.

Rogers, L. E., Martin, A. E., and Norrish, K., 1954, The occurrence of palygorskite near Ipswich, Queensland, Min. Mag., 30, 534-540.

Saini, G. R., 1966, Discussion of the nomenclature of soil carbonates, Aust. J. Sci., 29, 225.

Sherman, G. D., Schultz, F., and Alway, F. J., 1962, Dolomitization in soils of the Red River Valley, Minnesota, Soil Sci., 94, 304-313.

Sherman, G. D. and Thiel, G. A., 1939, Dolomitization of glacio-lacustrine silts of Lake Agissiz, Bull. Geol. Soc. Am., 50, 1535-1552.

Sidwell, R., 1943, Caliche deposits of the southern High Plains, Texas, Am. J. Sci., 241, 257-261.

Singer, A., 1971, Clay minerals in the soils of the southern Ramat Hagalan, Israel J. Earth Sci., 20, 105-112.

Singer, A. and Norrish, K., 1974, Pedogenic palygorskite occurrences in Australia, Am. Min., 59, 508-517.

Soult, D. S., 1973, Weathering and landforms at Black Hill, Murray Valley, South Australia, Unpublished B.A. Hons. thesis, University of Adelaide, 69 pp.

Stace, H. C. T., 1956, Chemical characteristics of Terra Rossas and Rendzinas of South Australia, J. Soil Sci., 7, 280-293.

Swineford, A. and Franks, P. C., 1959, Opal in the Ogallala Formation in Kansas, Soc. Econ. Palaeontologist and Mineralogists Spec. Pub., 7 111-120.

Swineford, D. A., Leonard, A. B., and Frye, J. C., 1958, Petrology of the Pliocene pisolitic limestone in the Great Plains, Bull. State Geol. Surv. Kansas, 130, 97-116.

Van den Heuvel, R. C., 1966, The occurrence of sepiolite and attapulgite in the calcareous zone of a soil in near Las Cruces, New Mexico, Proc. 13th Nat. Conf. Clay and Clay Mineralogy, 193-207.

Von der Borch, C. C., Lock, D. E., and Schwebel, D., 1975, Ground-water formation of dolomite in the Coorong Region of South Australia, Geology, 3, 283-285.

Ward, W. C., Folk, R. L., and Wilson, J. L., 1970, Blackening of eolianite and caliche adjacent to saline lakes, Isla Mujeres, Quintana Roo, Mexico, J. Sed. Pet., 40, 548-555.

Weaver, C. E. and Beck, K. C., 1977, Miocene of the south-east United States. A model for chemical sedimentation in a peri-marine environment, Sed. Geol., 17, 1-234.

Williams, G. E., 1973, Late Quaternary piedmont sedimentation, soil formation and paleoclimates in arid South Australia, Z. Geomorph., 17, 101-125.

Williams, G. E. and Polach, H. A., 1971, Radio-carbon dating of arid-zone calcareous paleosals, Geol. Soc. Am. Bull., 82, 3069-3086.

Wollast, R., Mackenzie, F.T., and Bricker, O.P., 1968, Experimental precipitation and genesis of sepiolite at earth-surface conditions, Am. Mineral., 53, 1645-1662.

Woolnough, W.G., 1927, The duricrust of Australia, Proc. Roy. Soc. N.S.W., 61, 25-53.

Woolnough, W.G., 1930, Influence of climate and topography in the formation and distribution of products of weathering, Geol. Mag., 67, 123-132.

Yaalon, D.H., 1955, Notes on the clay mineralogy of the major soil types in Israel, Bull. Res. Counc. Israel, 58, 168-173.