CHAPTER - 4

DURICRUSTS

DURICRUSTS

INTRODUCTION

Among the multifaceted studies on Quaternary geology, soils and laminated crusts, formation of a hard layer of solum enriched in certain chemical/mineralogical assemblages within the profile of weathering, have gained much significance in recent years This hard layer of the solum is termed as the **Duricrust** (Woolnough, 1930). Goudie, (1973) has further refined the definition of duricrusts as

> *"A product of terrestrial processes within the zone of weathering in which either iron and aluminium sesquioxides or silica or calcium carbonate or other compounds like manganese have accumulated in and /or replaced a pre-existing soil, rock or weathered material, to give a substance which may ultimately develop into an indurated mass".*

Depending upon the chemical composition, these duricrusts are classified in to **Calcretes** (comprising predominantly of calcium carbonate); **Ferricretes** (comprising oxides and hydroxides of iron) **Silicretes** (composed dominantly of silica) and **Gypsicretes** (composed of gypsum) Following the definition of Goudie (1973), Watts (1980) has modified the definition of calcretes as

"A terrestrial material composed dominantly, but not exclusively of $CaCO_3$ which occur in states ranging from nodular and powdery to highly indurated and result mainly from the displacive and /or replacive introduction of vadose carbonate into greater or lesser quantities of soil, rock or sediment within a soil profile."

DISTRIBUTION OF DURICRUSTS IN THE THAR DESERT

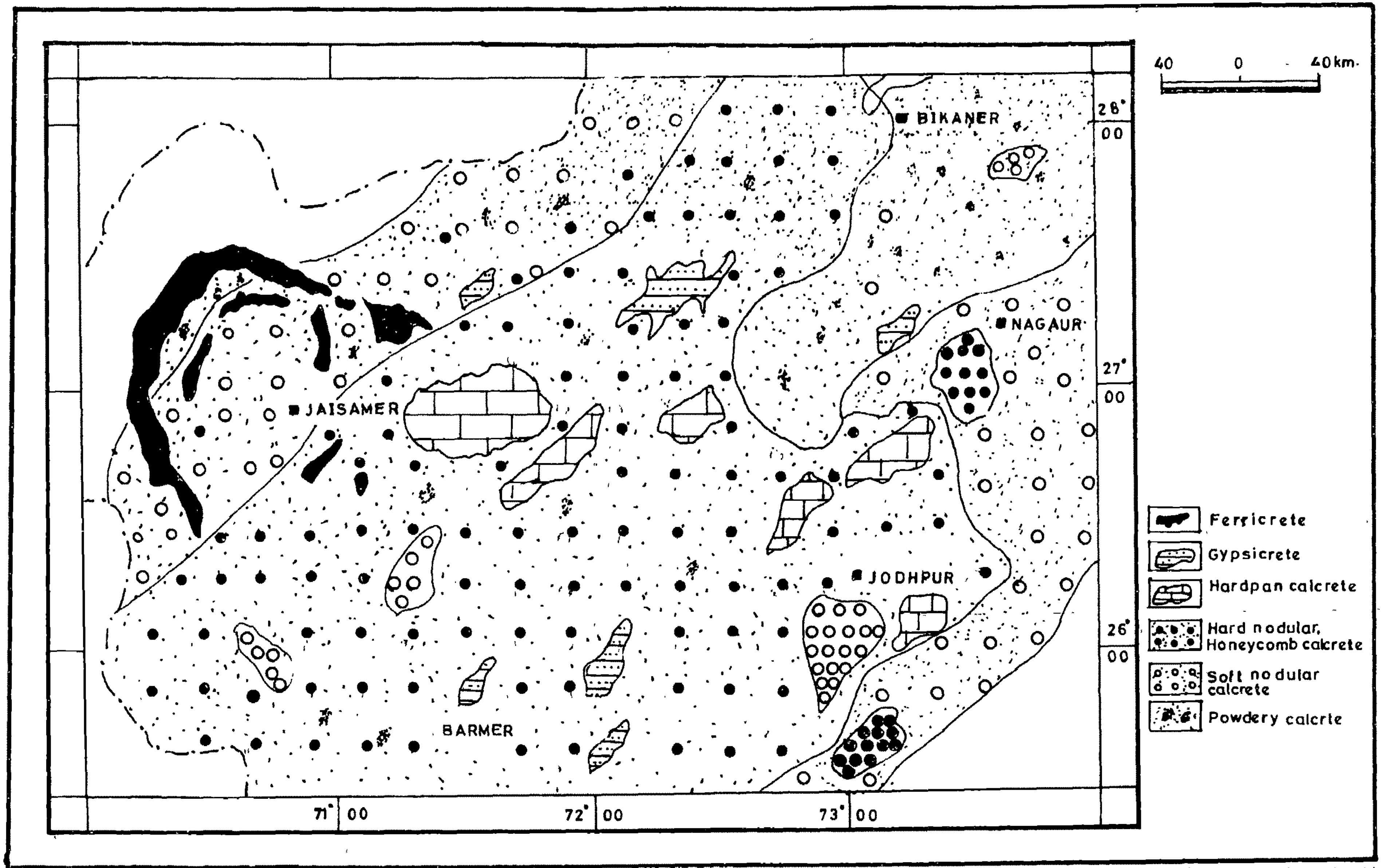
Owing to arid - semi arid climatic regimes, the Thar desert displays a variety of duricrusts viz calcretes, ferricretes and gypsicretes (Figure 4 1).The most widely developed calcretic duricrust is seen associated with wide range of lithology (viz. sandstones, limestones, shales, fluvial and aeolian sediments) and varied geomorphic expressions (dunes,interdunal plains, alluvium, pediments etc.). On the other hand ferricretic duricrust is developed as a narrow strip on the Tertiary rocks of Jaisalmer basin as capping on plateaus, mesas and buttes

The gypsicretes are by and large confined to the present and palaeo playas and salinas.The present study deals with widely developed calcretic and ferricretic duricrusts of the study area

CALCRETES

Among the duricrusts, calcretes have attracted attention throughout the globe from pedologists, geologists, archaeologists and engineers (Gile et al ,1965, Wider and Yaalon 1974, 1982, Yaalon and Wider, 1976; Watts, 1978, 1980, Natterberg, 1980; Warren, 1983; Natterberg and Caiger, 1983; Beier, 1987) by virtue of its applicability in deciphering the past climatic changes and its potentiality as a construction material. Some of the landmark contributions made by various workers are discussed below.

Gile (1965) has defined the position of calcrete within weathering profiles in accordance to soil terminology. Horizons which are strongly impregnated by authigenic carbonates with their morphology determined by carbonates were designated by him as K - horizon, irrespective whether they are powdery or highly indurated forms He also suggested a



Modified after Dhir, R.P.(1992)

Fig.4.1. Distribution of Duricrusts in the study area.

minimum 15 - 45 percent authigenic carbonates for the development of K - fabric Besides the K - horizon the other master horizons for carbonate accumulations are given Ca designations.

Blokhiuis et al , (1969) elucidated the stages of calcretization through micromorphological observations They have identified different forms of pedogenic carbonates viz diffuse nodules, discrete nodules, channel neocalcitans, and iron/manganese impregnations to the profile characteristics, churning, pedoturbations and illuviation.

Aristarain (1970) gave a detailed account on the utility of geochemistry of the calcretic profiles in establishing the mode of genesis of calcretes either due to soil forming processes or groundwater actions.

Wider and Yaalon (1974) has distinguished three kind of carbonate nodules in calcretes viz **orthic nodules**, that have skeleton grains similar to the surrounding soil and a gradual transition to the soil matrix , **disorthic nodules** - that are developed insitu having similar fabric of the soil but with discrete boundary due to pedoturbation and **allothic nodules** that are incorporated to the soil profile due to transportation They also stressed the composition of the matrix, especially the non carbonate clays that control the size and growth of calcite crystals in the nodule.

Watts (1980) explained in detail the various geochemical kinetics (such as displacive / replacive introductions, neoformations) that takes place during the genesis of calcretes and their evolution

Wider and Yaalon (1982) established basic relations between the nodular fabric of calcrete and texture, structure, and carbonate contents of soil material They also elucidated the distinctions between biogenic nodules and accretionary calcitic nodules within the same soil fabric. The mechanisms of calcretization with respect to the texture of soils were also dealt in detail

Braithwaite (1983) explained the distinguishing characteristics between the pedogenic calcretes and vadose water precipitation by way of micromorphological features such as meniscus cement, cement bridges, grain pendants etc and opined that these features could not be possible where evaporation rates are high

Klappa (1983) discussed the formation and evolutionary stages in calcretization beginning from soil formation, horizon differentiation, calcium carbonate accumulation, profile development, and induration to reworking of calcretic profiles. In this, morphology of pedogenic calcretes and extent of profile development were attributed to the role of organic activity. With a view to represent the stages of calcretization, intensity of weathering and geotechnical characteristics, Natterberg and Caiger (1983) classified the calcretes into calcareous soils, calcified soils, powdery calcrète, nodular calcrete, honey comb calcrete, hardpan calcrete and calcrete boulders and cobbles

In India, earlier works (Sehgal and Stoops, 1972; Tandon and Narayan, 1981; Sharma and Tandon, 1983, Desai and Warrier, 1987; Patil and Surana, 1992, Rao and Thamban, 1997) on the calcrete genesis and its applications are available Although, wide and extensive distribution of calcretes in the study area, have attracted various workers (Roy et al , 1969, Courty et al , 1986, Raghavan, 1987, Raghavan and Courty, 1987; Dhir, 1992), the mechanisms of calcretization and its utility in palaeoclimatic interpretations still remains perplexing.

Hence, the author necessitated to take up a regional coverage to elucidate the calcrete genesis vis-a-vis varied geomorphic settings, physico-chemical changes during calcretization, and its utility in interpreting the soil micro environmental changes.

CLASSIFICATION AND DISTRIBUTION OF CALCRETES

Classification of calcretes are two fold viz. genetic and geotechnical (Natterberg,1983, Goudie, 1983) The genetic classification takes into account the parameters related to soil fabric changes and sequence of calcrete development. The geotechnical classification of calcretes are based on the engineering characteristics and their applications The author in this present study has followed the genetic classification since, the calcretic profiles of the study area and the horizons developed within display characteristic genetic attributes

The calcrete profiles are though widely prevalent within the study area, a complete sequence of calcretization beginning from calcified soil to highly indurated varieties (Goudie, 1983) are not ubiquitous However, such sections are also observed in the neighbouring (southern) parts of the study area around Vav and Tharad. Based on the mode of occurrence in the field, the author has classified the calcretes into 5 major types viz

Calcified Soil : Yellowish brown to (10YR 6/3) pale to grey (10 YR 7/1), weakly cemented sands and silty sands with a calcium carbonate content varying between 2 to 6 percentages The calcium carbonates occur predominantly as a clay size fractions. This type is distributed almost every where in the study area.

Powdery Calcretes : They comprise pale brown (10 YR 5/4) to grey (2.5 Y 8/3), fairly compacted and cemented fine grained dunal sands / alluvium with silt sized calcite grains mainly occupying the pore spaces between the detrital grains. However, incipient development of nodules (1 - 2 mm) is widely prevalent. This type of calcrete associated with nodular calcretes and mottling is very commonly observed The calcium carbonate content of these calcretes vary between 8 to 16 percentages.

Nodular Calcretes Comprise soft, diffuse, irregular calcium carbonate cemented sands and silts to hard, discrete, well rounded nodules in a predominantly powdery calcretic matrix The percentage of the matrix vary between 20 and 50 percent The size of the nodules vary from 2 to 4 cm The nodular calcretes are generally white or pinkish in colour and have around 35 percent of calcium carbonates The thickness of the nodular calcrete horizon range from 2 cm to 3 m

Coalesced Nodular / Honeycomb Calcretes : The nodular calcretes by virtue of carbonate accretion and recementation coalesce together there by causing a significant reduction in the matrix content. The presence of the sandy matrix can however be traced along the cavities between the nodules. These varieties of calcretes are predominantly pinkish in colour and are not omnipresent These kind of calcretes though seldom associate with dunes, they are observed commonly in interdunal areas

Hardpan calcretes are hard, pinkish (5 YR 8/4), massive, heavily calcified Their distribution in the field is very scanty and occur as pockets mainly in the interdunal plains and alluviums. They are generally observed lying below the nodular calcrete horizon with a sharp upper boundary or with a transitionary honeycomb varieties The thickness of these types are often to the order of 0.50 - 2 m. The carbonate content in these calcretes vary from 40 to 70 percent Though, calcrete profiles show markable variations both laterally and depth wise, an ideal calcrete profile observed in the field has the following succession

Calcified soil

Powdery calcrete with small nodules,

Soft Nodular calcretes (sand matrix > 50 percent)

Hard Nodular calcrete (sand matrix < 50 percent)

Hardpan calcrete

Powdery calcrete with mottles / nodular calcrete

Un altered source sediment.

The carbonate accumulations (calcretization) in the study area is observed over a wide range of soils from the light textured, homogenous, weakly structured (alluvium) to Torripsamments (well pedogenised dunal soils). However, these loamy fine sands are coarser than the loamy very fine sand prescribed for cambic horizon and hence grouped under Torripsammentic camborthids. Calciorthids and camborthids, the other two common soils of the study area are again distinguished on the basis of presence or absence of calcareousness in the B - horizon.

Based on the above mentioned characteristics the author has studied a large number of calcretic profiles falling within the climatic regimes of present day semi-arid, arid terrains. The section wise details on field characteristics of calcretic profiles are described below The profile designation are after Retllack, (1990)

Dhanola (N 25° 25' ; E 71° 10') :

This dunal profile (Figure 4 2(A), Plate 4 1 A & B) has a soil type resembling Argids The A-horizon is a yellowish brown (10YR 6/4) fine sand with organic matters. The organic content increases at depth (100-160cm). Following this horizon, is the AB horizon with a smooth, wavy boundary comprising illuviated soils of light reddish brown colour (5YR6/4)

The Bt horizon is well illuviated, heavily pedogenised with strongly developed peds loamy sand of greyish hue (5YR6/1) Lime redistribution is also observed This horizon shows sharp contacts with above and below lying horizons.

The bottom most horizon (Bir) is reddish (2.5YR5/8), coarse sand with occasional features of lime distribution and reddish brown clay coatings

Raneri (N 27° 40' ; E 72° 40')

Interdunal, dominantly coarse textured solum with intervening fine textured soils of this profile (Figure 4.2 (B) & Plate 4.2[A]) has calcretes developed in the coarse gravely sand layer The Ac horizon (45-50cm) has pinkish, hard discrete well rounded nodular calcrete that has a sharp distinct boundary with the underlying fine textured yellowish brown (10YR5/4) loamy sand with well developed peds and without any features of lime redistribution (50 -100 cm).

The Bk horizon is a brownish yellow (10YR 6/6) gravely sand impregnated by calcium carbonate (nodular calcretes) The basal part of this horizon however, has a distinct light red (2 5YR 6/8) hue.

Sardarsahar (N 28° 30' ; E 74° 30')

This interdunal, calciorthidic profile (Figure 4 2 (C), Plate 4 2[B]) comprise a well developed nodular calcrete horizon (50-175 cm) of pinkish (5YR 7/4) to pinkish gray

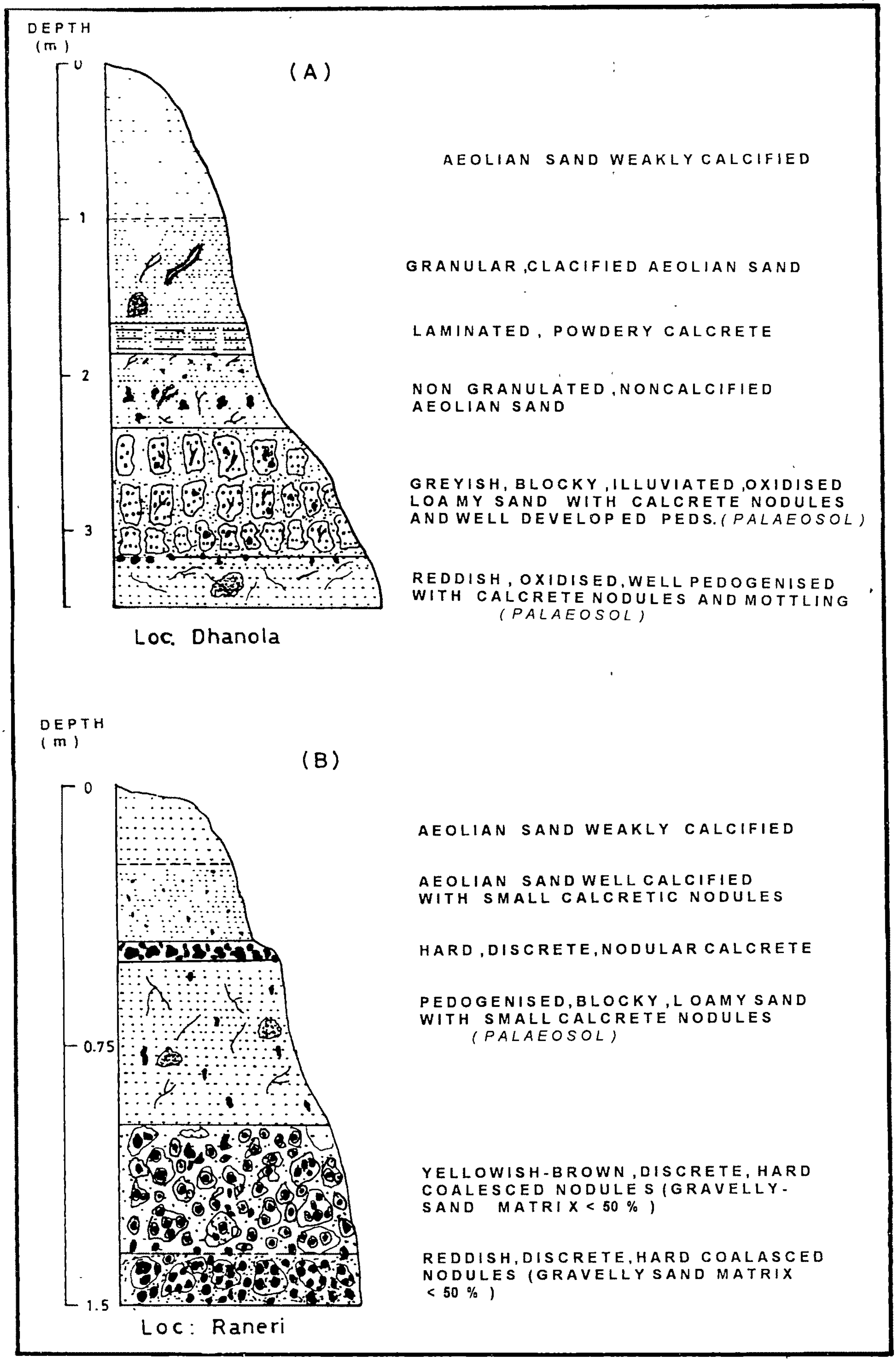


Fig. 4.2 Calcrete profiles of the study area

Plate 4 1

(A) A view of stabilized dunal profile with palaeosol horizons. Loc. Dhanola trijunction.

(B) A close view of above profile showing iron stained second palaeosol horizon lying at the base.

A

B

Plate 4.1

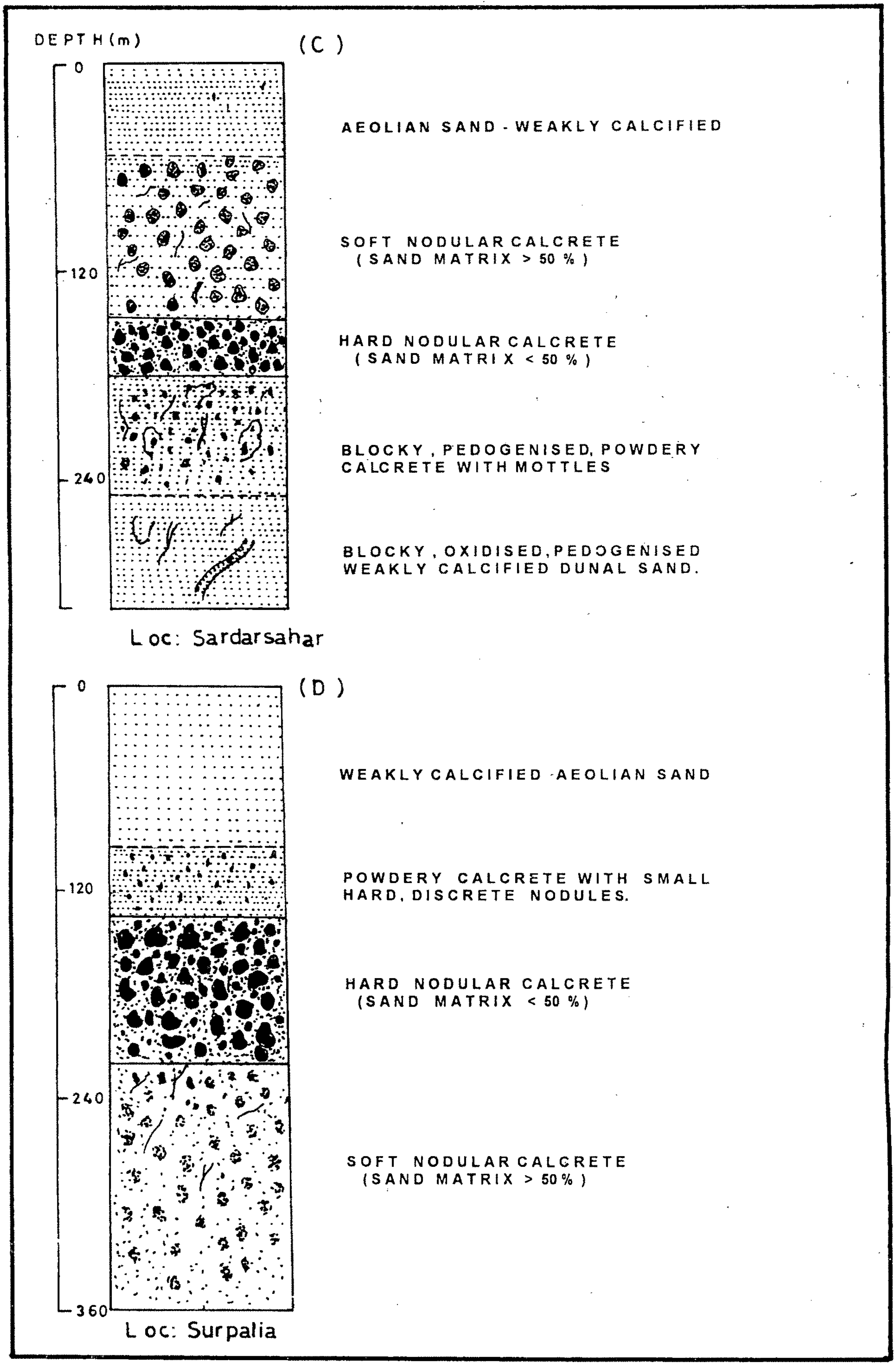


Fig. 4.2 Calcrete profiles of the study area

Plate 4.2

(A) A view of the nodular calcretic profile developed near Raneri.

(B) A view of the calcretic profile with nodular form at the top and massive, powdery form at the base. Loc. Sardarsahar.

A

B

Plate 4.2

(7.5YR 7/2) with fine sandy matrix. While overlying yellowish - brown fine sand has a distinct, sharp boundary with this horizon, however it shows a gradational boundary with the lower pinkish, massive loamy sand with carbonate impregnation (powdery calcretes). The lowest oxidized, reddish yellow (7.5YR 6/6) fine sand exhibit feeble features of lime redistribution.

Surpalia (N 26° 30' ; E 74° 00')

This interdunal calciorthid profile incorporates nodular calcrete formation both at Ac and Bc horizons (Figure 4.2 (D) & Plate 4.3[A]). The A horizon (0-85cm) has a weakly calcified brownish (7.5YR 5/4) that merges with the underlying nodular calcrete (85-135 cm) with a sandy matrix.The enhancement of lime redistribution and reduction of the pale brown (10YR6/3) loamy sand matrix resulted in an another layer of hard nodular calcrete (135-220cm).

The underlying C horizon (320 cm and above) has well pedogenised sand with features of lime redistribution.

Bhaleri (N 28° 25' ; E 74° 45')

Akin to the Dhanola profile, this dunal profile comprise a Bt horizon, besides the development of a prominent Bc horizon (Figure 4.2 (E); Plate 4.3[B]). The top layer is an organic carbon rich horizon brown (10 YR5/3), followed by greyish, loamy sand (5YR6/1) Bt horizon with a sharp boundary. This horizon at the base show considerable features of lime redistribution resulting in the formation of powdery calcrete.

The powdery calcrete has a sharp boundary with the underlying nodular calcrete horizon (160 - 240cm) with a sandy matrix and have reddish yellow (5YR7/6) hue. The bottom most C-horizon (240 and above) is a yellowish brown (10YR 6/4) fine sand showing a gradational boundary with incipient lime redistribution.

Plate 4.3

(A) A view of the calcrete profile with well developed nodular calcrete. Loc. Surpalia.

(B) A view of calcretic profile showing a cap of active dunal sand followed by palaeosol (greyish) horizon and massive calcrete. Loc. Bhaleri.

A

B

Plate 4.3

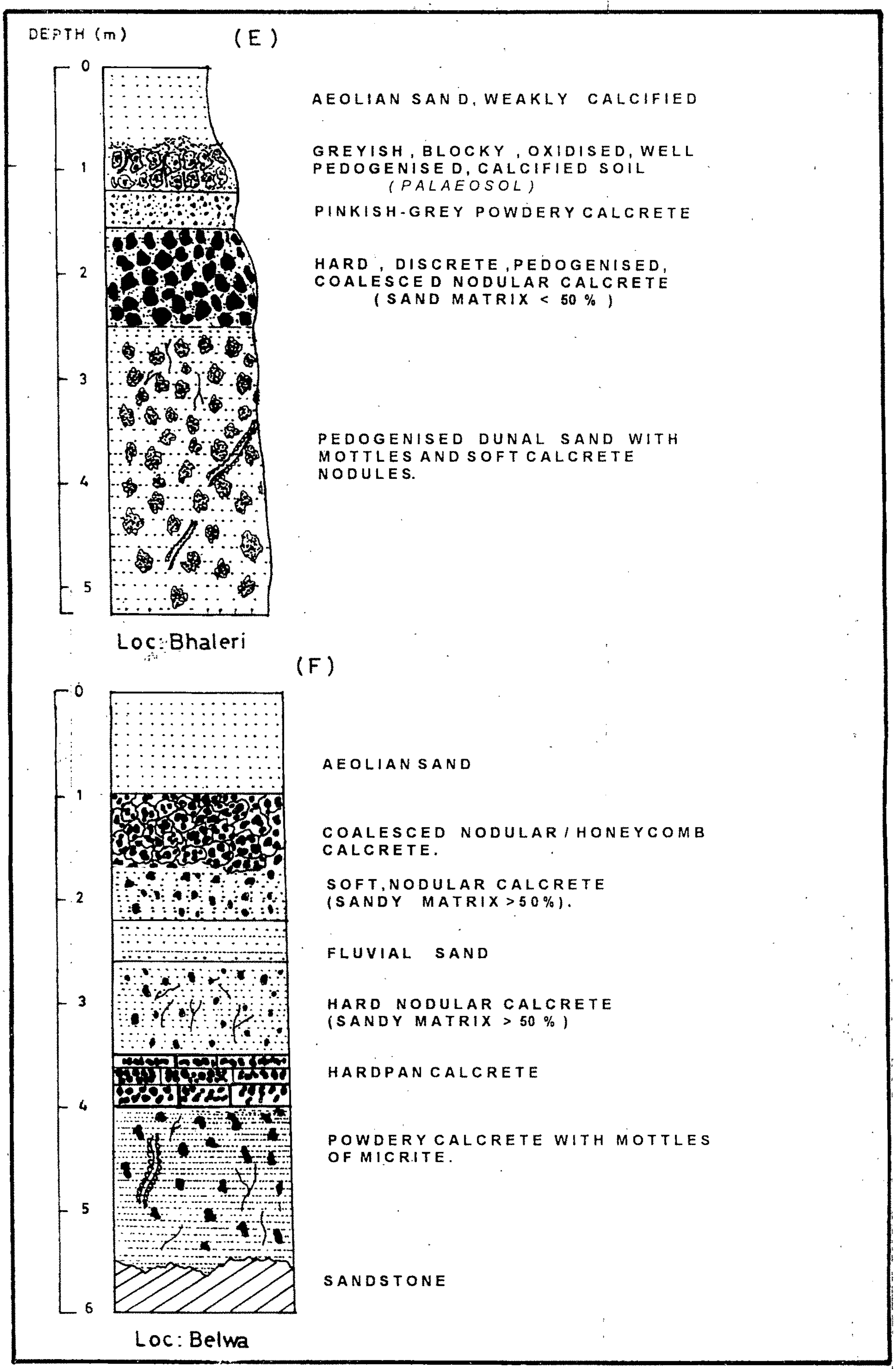


Fig. 4·2 Calcrete profiles of the study area

Belwa (N 26° 28' ; E 72° 50')

This interdunal profile comprise (Figure 4.2 (F), Plate 4.4[A]) calcium carbonate accumulations at various levels in a predominantly fine textured soil (Calciorthids). The A horizon (0-100cm) is a non calcified dunal sand followed by a coalesced nodular (Ac) horizon (100-170cm) of pinkish colour (7.5 YR 8/4) with sharp upper boundary.

The underlying AB horizon (170-220) is a coarse textured pale brown sand (10YR 6/3) with features of illuviation and carbonate redistribution. The Bc horizon (260-350cm) comprise nodular calcretes in a pale brown (10YR 7/4) loamy sand. The underlying K horizon (350-400) is a massive, compact hardpan calcrete of pinkish colour that merge progressively with the underlying nodular calcrete (C) horizon

Nimbijodhan (N 27° 37' ; E 74° 10' E)

Here, calcretes (calcified soils and powdery calcretes) are developed in a pediment zone with a matrix of aeolian sand (Figure 4.2 (G), Plate 4.4[B]). Due to monolithic development of calcretes, no horizon could be recognized within the profile.

Ramgarh (N 27° 22' ; E 70° 32')

This calcretic profile in the buried pedimentary flat comprise a top structure less yellowish brown fine sand with humus (50cm). With a sharp boundary this unit passes down to small (2-3cm), hard, nodular calcrete layer (50-120cm),in a loamy sand matrix (Figure 4.2 (H),). This layer with a gradational boundary passes down into a well lime impregnated, coarse (5-7cm), soft nodular calcrete with a coarse sandy matrix.

Tejsingh Ki Dhani (N 25° 50' ; E 71° 15')

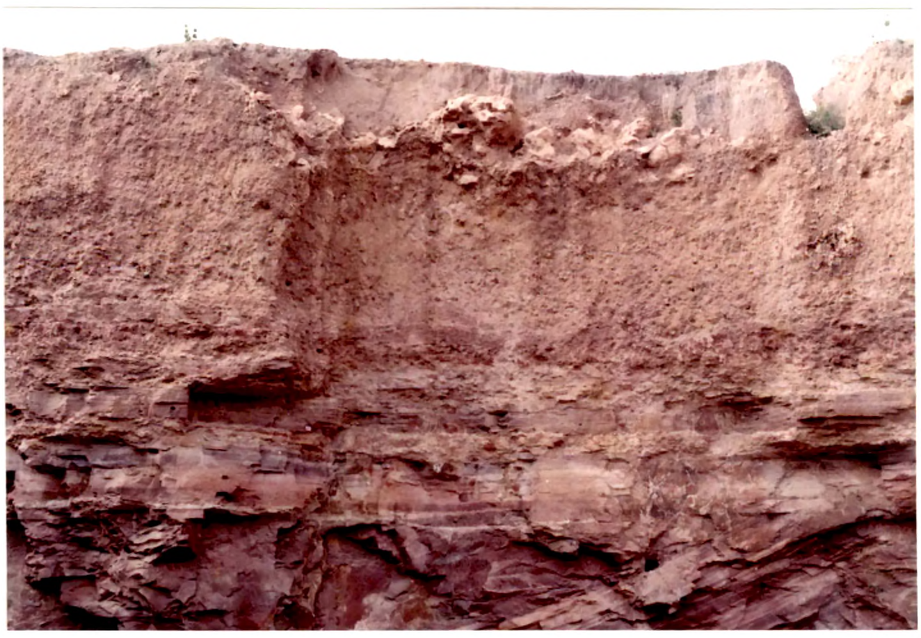
The top 50 cm of this dunal profile (Figure 4.2 (I), Plate 4.5[A]) comprise yellowish brown (10YR5/3) dunal sand showing a gradational boundary with the underlying nodular calcrete horizon within a loamy sand matrix. This nodular calcretic horizon with further

Plate 4.4

(A) A view of calcretic profile showing coalesced nodular calcrete at the top and hardpan calcrete at the bottom. Loc. Belwa.

(B) A view of quarry section showing development of nodular calcrete over weathered pediments of Jodhpur sandstone. Loc. Nimbijodhan.

A



B

Plate 4.4

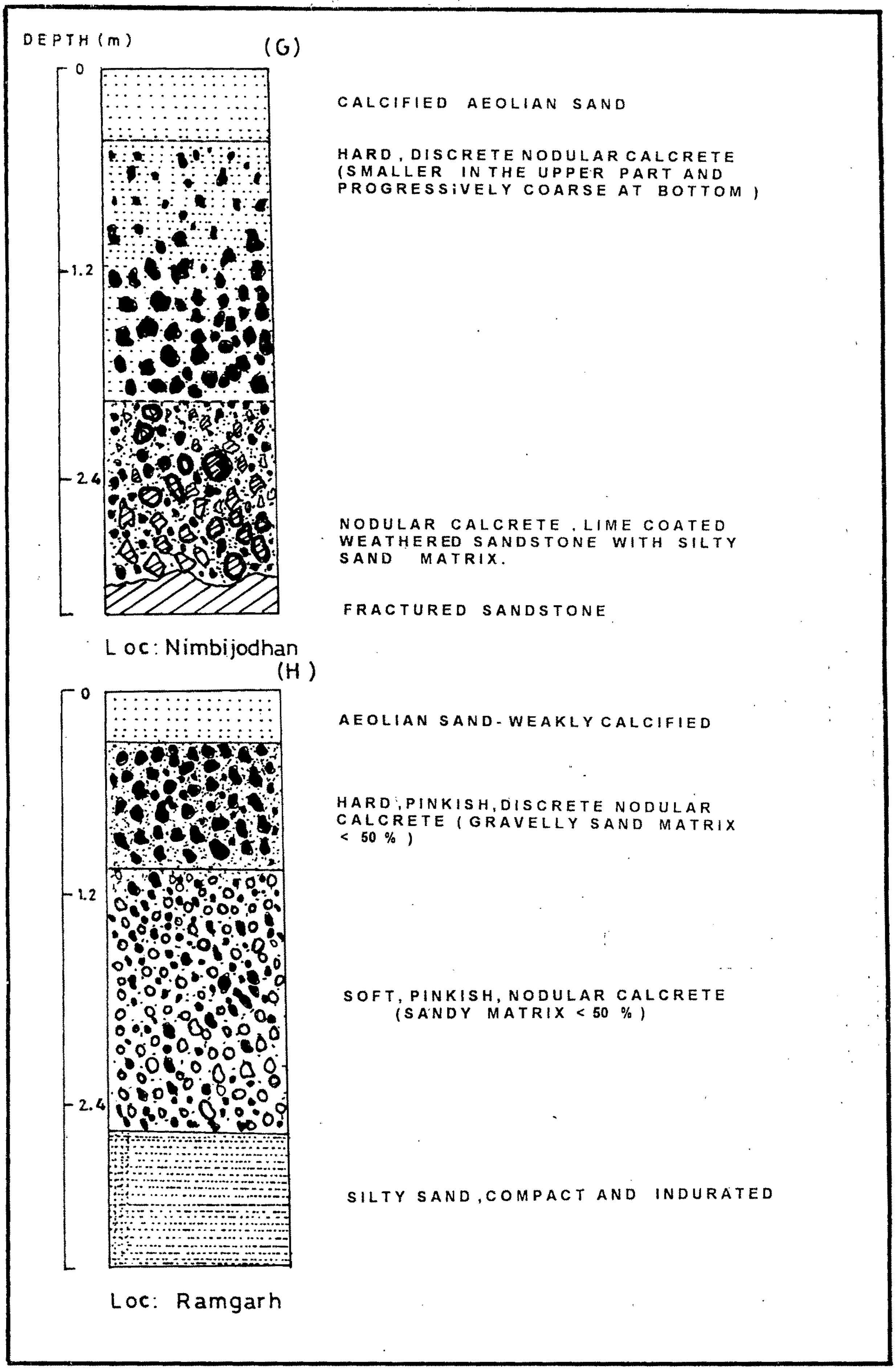


Fig. 4.2 Calcrete profiles of the study area

impregnation by lime and fusion of the nodules have resulted in a dense, pinkish, honeycomb variety of calcretes (200cm and above) probably, representing the Bk - horizon.

Girab (N 26° 08' ; E 70° 40')

The interdunal flat located on the western fringe of Miyajalar comprising calciorthids of about 3 m thick (Figure 4.2 (J), Plate 4.5[B]). The A horizon consist of yellowish brown (10YR 5/6), structure less fine sand, followed by a 10-15cm thick Ac-horizon characterized by soft nodular calcrete. The Bc horizon is totally lime impregnated with the formation of a hard,pinkish coalesced compact honeycomb calcretes within a loamy sand matrix.

C-horizon is a pale yellowish-red fine sand, pedogenised, with mottles of lime and clear features of lime redistribution within the horizon.

Bhukan (N 25° 50' ; E 72° 00')

Development of calcretes in a fine textured interdunal solum (calciorthids) comprise yellowish brown, structure less (10YR5/4) calcified soil (0-75cm) followed by soft, pale brownish nodular calcretes (75 -150cm) with fines and matrix (Figure 4.2 (K)). Clear lime redistribution is evidenced with a more compact and hard nodular calcretes at the basal part The lowest part of this profile (150-300 cm) is a compact, well carbonate impregnated pinkish coalesced nodular / honeycomb type of calcrete.

Derasar (N 25° 50' ; E 71° 06')

This calciorthid dunal profile comprise alternations of lime coated rhyolitic pediments and dunal sands in the upper part and lime impregnated Bk horizon and C -horizon in the lower parts (Figure 4.2 (L)).

The A-horizon comprise yellowish brown (10YR 5/4) fine sand with intercalated layers of rhyolitic pediments (30-60 cm; 190-250 cm).The Ac horizon is characterized by a 10cm thick nodular calcrete layer with no features of lime redistribution .

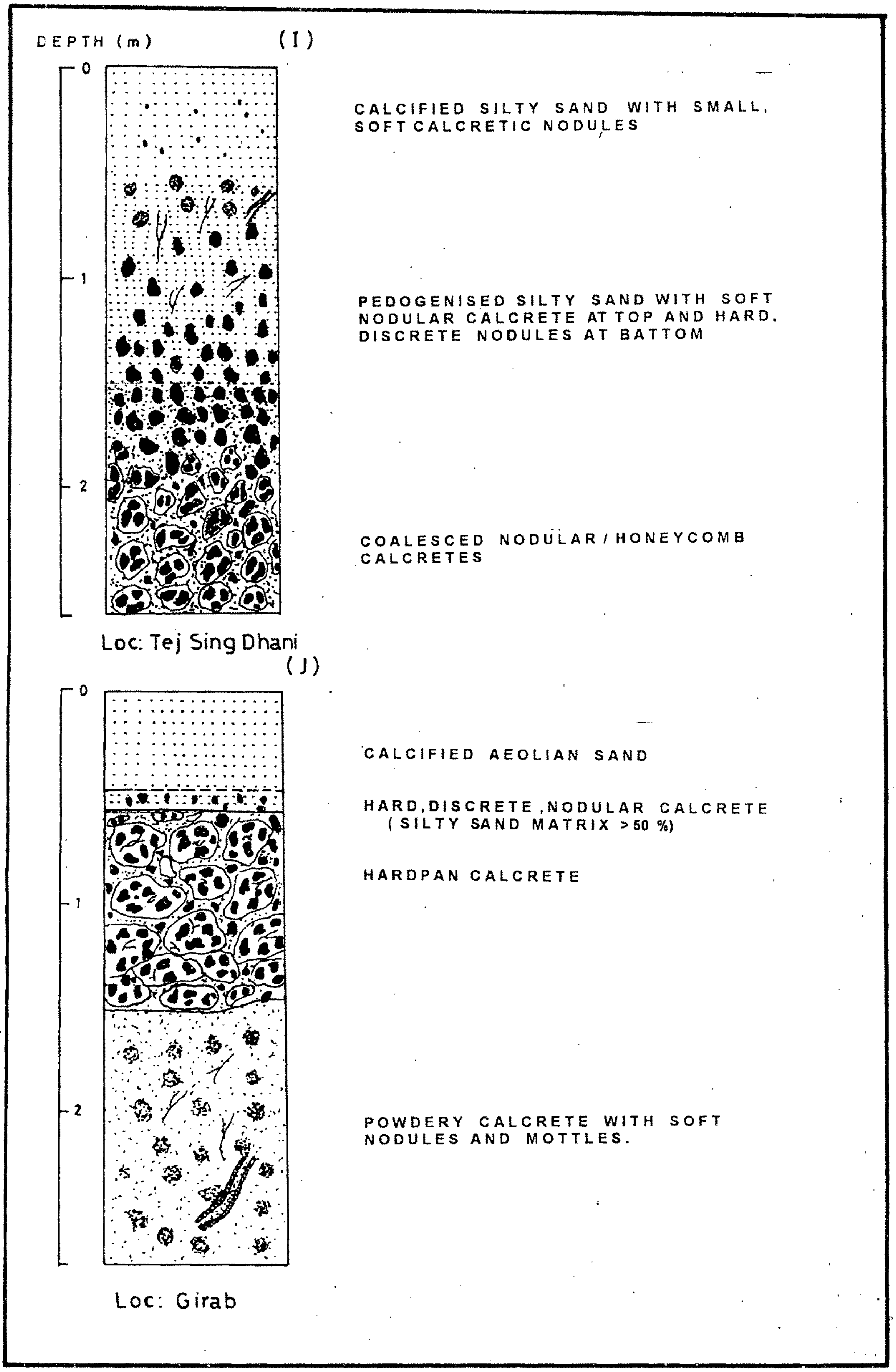


Fig. 4.2 Calcrete profiles of the study area

Plate 4.5

(A) A view of dunal profile showing nodular calcretes, lime coated rhyolitic colluvium. Loc. Tejsingh ki dhani.

(B) A view of quarry section showing the development of honeycomb calcrete in a sandy plain. Loc. Girab.

A

B

Plate 4.5

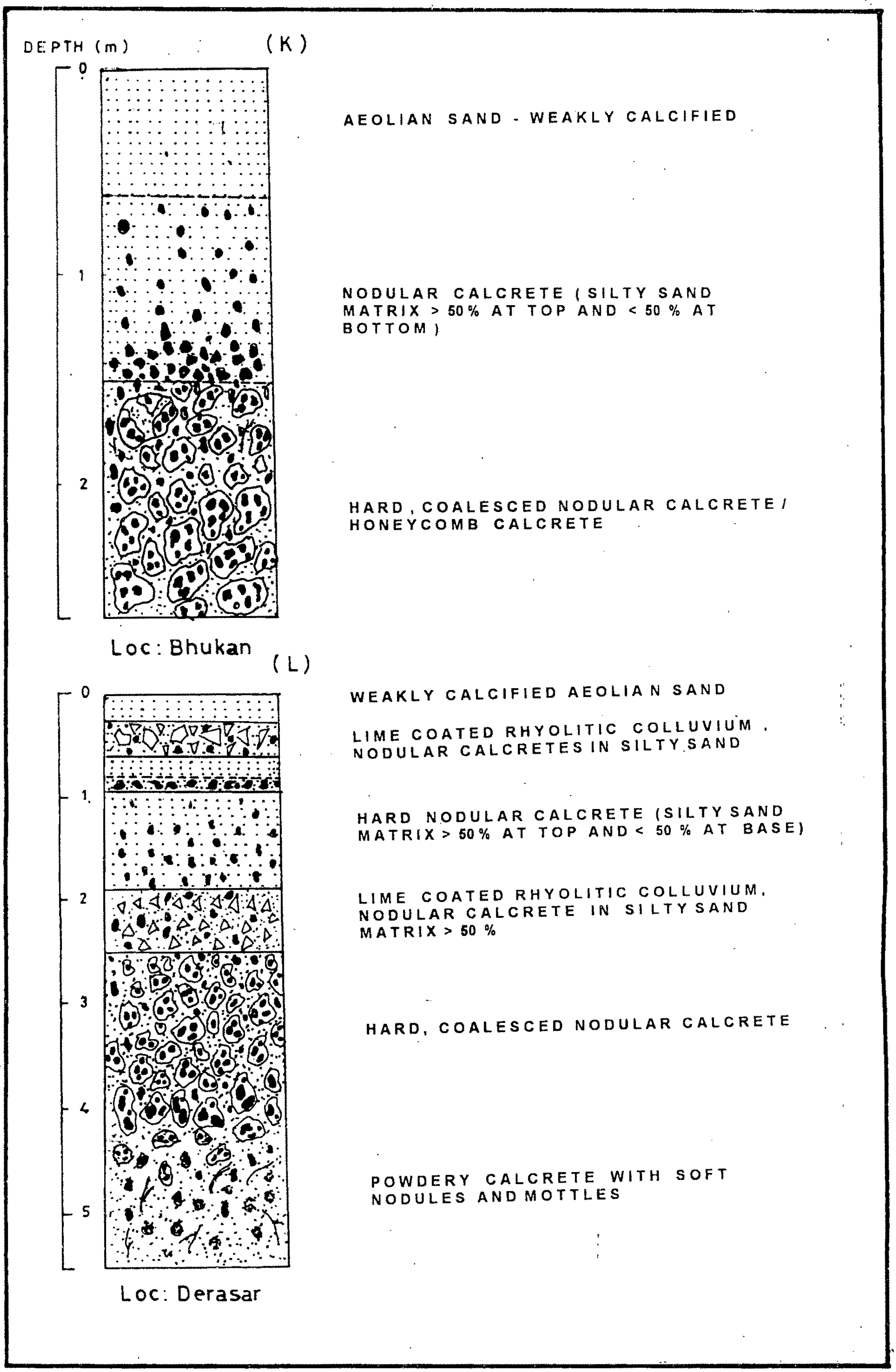


Fig. 4.2 Calcrete profiles of the study area

The Bk horizon (250-400cm) is pinkish, well lime impregnated, coalesced nodular calcrete horizon that have a sharp boundary with the overlying pediments and gradational boundary with the lower lying yellowish brown fine sand (C-horizon) showing weak features of pedogenic lime redistribution.

Thob (N 26° 03' ; E 72° 20')

The stratigraphy of this interdunal calciorthid soil profile (Figure 4.2 (M)) comprise a well developed Ac, Bc and K horizons developed on fine textured aeolian sand. The A-horizon is a brownish (10YR 5/3), structure less fine sand that has a progressive, gradational boundary with the underlying soft,white powdery-nodular calcrete horizon. This powdery-nodular calcrete horizon is followed by a hard, discrete nodular calcrete horizon (with a sharp,distinct boundary) which is strongly lime impregnated and redistributed (100-140cm). The K horizon has a gradational upper and lower boundary and is characterized by totally lime impregnated,pinkish hardpan variety of calcrete that inturn transits down to C horizon comprising lime coated sandstone fragments and massive sandstones.

Dechchu (N 26° 77' ; E 72° 20')

It is a dunal profile of 3.5 m thick with weakly developed horizons and structure less, brown fine sand in the upper part (0 - 100cm) that grades into the underlying pale brown layer of small (1-2 cm) nodular calcrete in a predominantly (>50%) pedogenised, fine sand matrix (Figure 4.2 (N)). The lowest horizon (250cm and above) shows increase in lime impregnation by way of reduction in matrix content and bigger size nodules (2.5-4 cm).

Vav (N 24° 45' ; E 71° 40')

This exemplary calciorthid interdunal profile has carbonate accumulations in Ac, Bc and K horizons (Plate 4.6[A]). The organic carbon rich A horizon (0-55cm) is a yellowish brown (10YR 5/4) fine sand. The sharp underlying Bc horizon (55-125cm) is a nodular calcrete with olive brown (2.5Y 5.4) loamy sand.

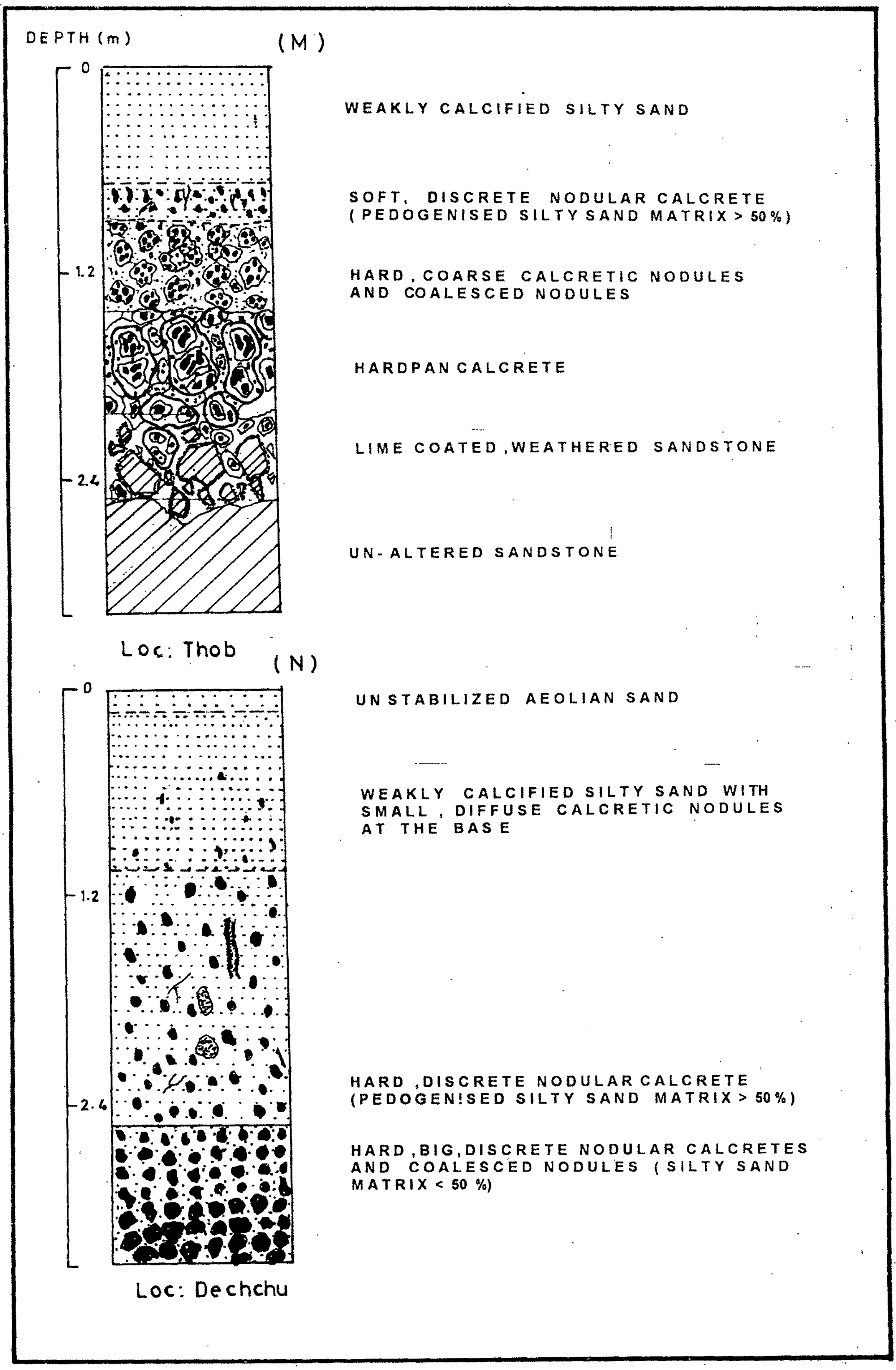


Fig. 4.2 Calcrete profiles of the study area

Underlying K-horizon (125-215cm) has a sharp upper boundary and gradual lower boundary. This incorporates coalesced and hardpan varieties of calcretes.

The lowermost C - horizon (215 and above) is a oxidized fine sand of yellowish brown colour (10YR 5/6) with features of lime insignificant lime redistribution.

Bikaner (N 28° 10' ; E 73° 20')

This 10 - 12 m thick profile within an alluvial flat comprise coarse textured solum (gravel, coarse sand and fine sand sequences) under a aeolian sandy cover and incorporate heavy carbonate impregnations in the upper part (Plate 4.6[B]). Because of the massive nature and poor profile development, horizon designation remains perplexing. The central silty sand layer (270-350cm) is plugged by the soft, calcium carbonate impregnations (powdery calcrete) that is underlain by a poorly calcified gritty sand layer (350 - 650 cm).

Kuri (N 26° 38' ;E 70° 42')

This alluvial flat calcrete profile comprise solum of fine texture (aeolian sand) in the upper part and coarse texture (coarse sand) in the lower part (Figure 4.2 (R), Plate 4.7[A]). The pinkish nodular calcrete layer (40-70 cm) has distinct, sharp boundaries with overlying and underlying units. The coarse textured soil has poor lime distribution and merges with the underlying silty-sand. Nodular calcretes and honeycomb type of calcretes developed in buried pediment flats, associated with ferricrete lags and fine sands are observed at **Sultana (N 27° 25'; E 70° 56')** [Figure 4.2 (P), Plate 4.7[B]] **Mohangarh** (Plate 4.8[B] and **Bersi (N 26° 25'; E 70° 35')** [Figure 4.2(Q)), calcretic profiles. Near **Sadewala (N 27° 27' ; E 70° 07')** calcretic profiles developed over the fine textured calciorthidic soil (Figure 4.2(O),Plate 4.8[A]) comprise a nodular calcretic horizon (120-275cm) with gradational upper boundary to a powdery calcretic horizon and sharp lower boundary that separates the Tertiary clays.

Plate 4.6

(A) A view of calcrete profile in a sandy plain. Loc. Vav.

(B) A view of intensely calcretized gravelly sand.
Loc. Chetak, Bikaner.

A

B

Plate 4.6

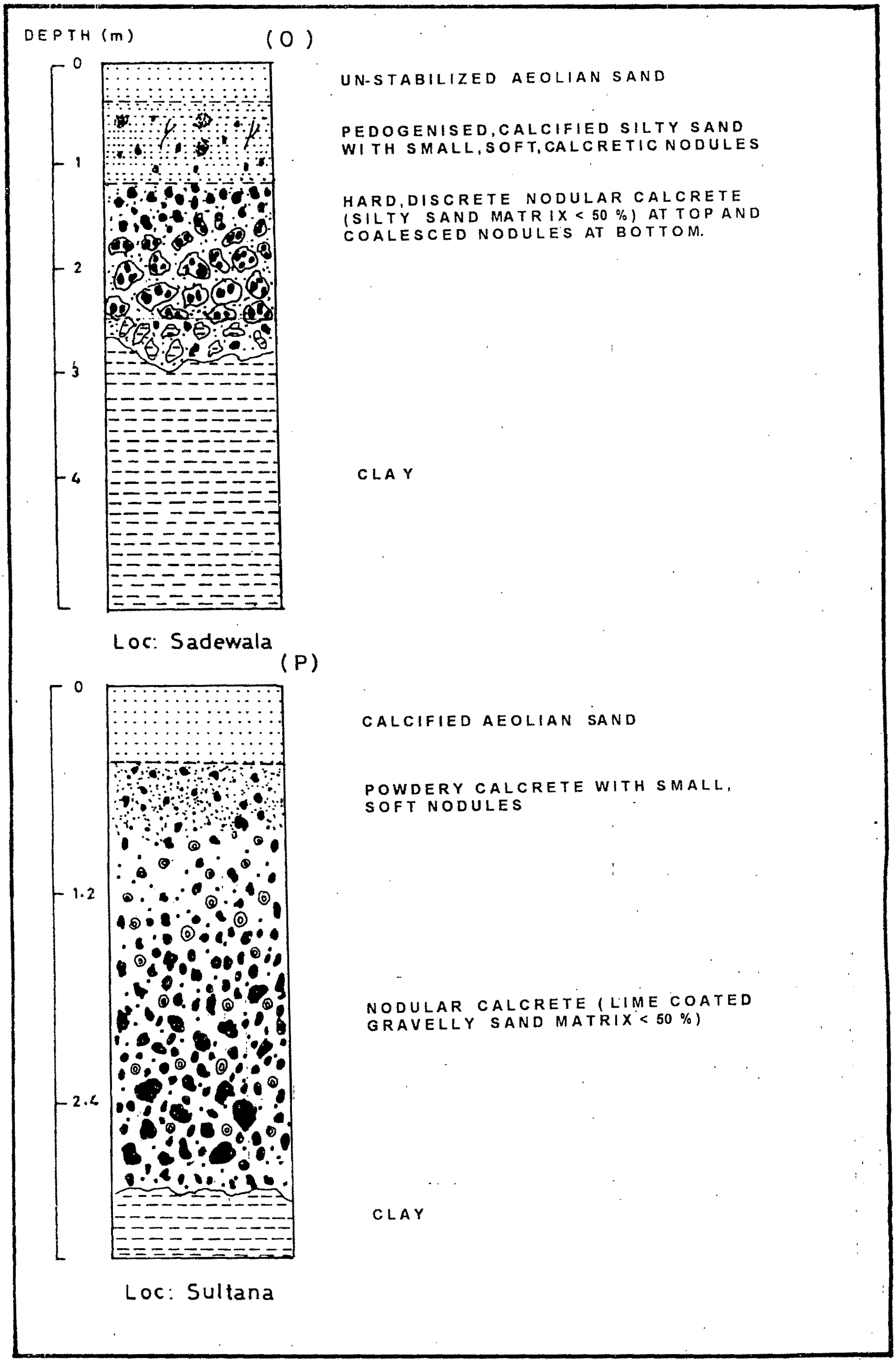


Fig. 4.2 Calcrete profiles of the study area

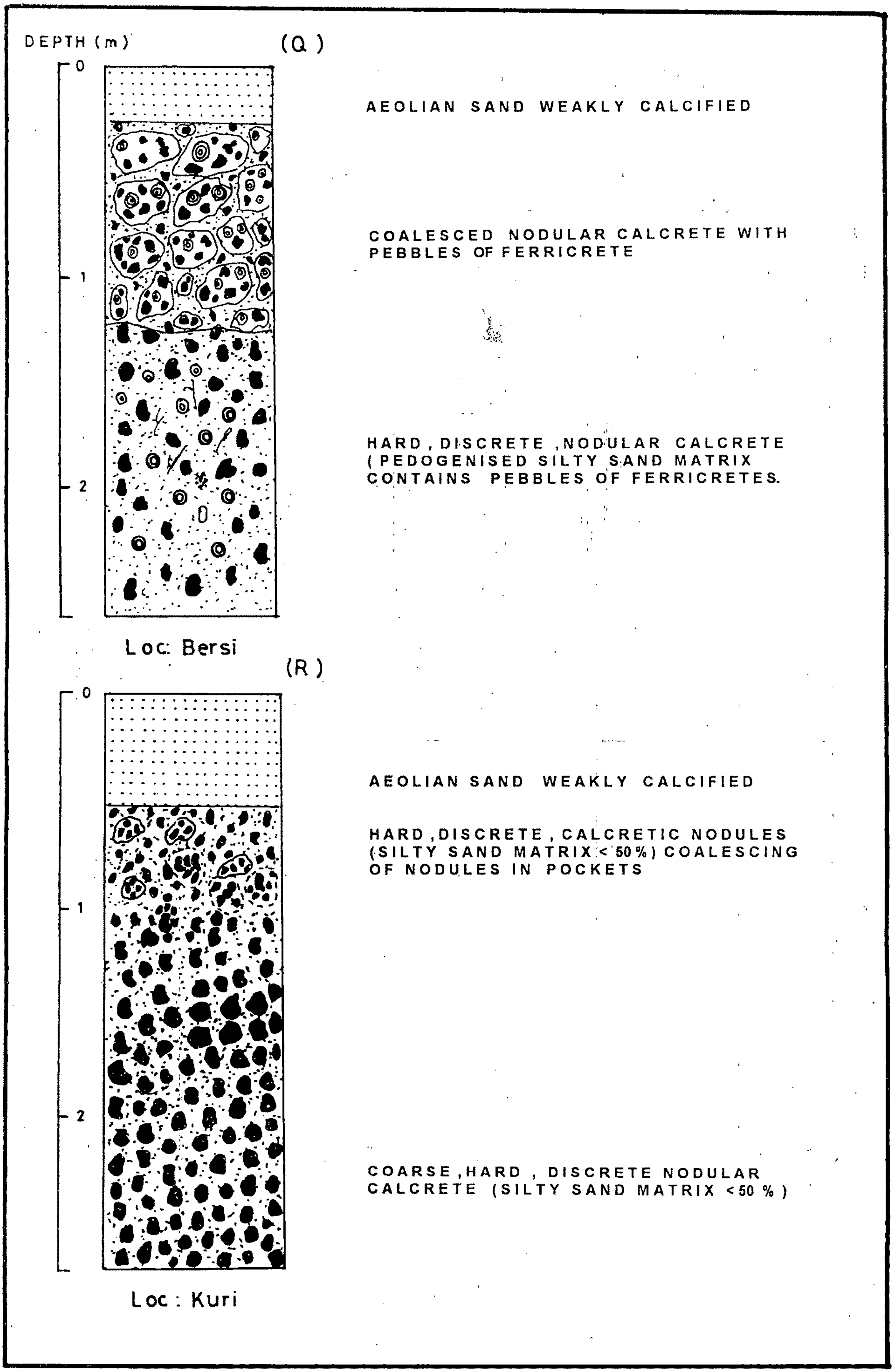


Fig. 4.2 Calcrete profiles of the study area

Plate 4.7

(A) A view of calcretic profile within the interdunal flat comprising nodular calcrete at top and honeycomb calcrete at bottom. Loc. Kuri.

(B) A view of hard honeycomb calcrete developed in an interdunal area. Loc. Sultana.

A

B

Plate 4.7

Plate 4.8

(A) A view of quarry section showing the development of nodular calcrete and honeycomb calcrete over Shumar formation. Loc. Sadewala.

(B) A view of nodular calcrete incorporating ferricrete breccias. Loc. Mohangarh.

A

B

Plate 4.8

MICROMORPHOLOGY OF CALCRETES

The thin section observations of calcrete profiles (calcretes and associated solum) have supplied copious information pertaining to the pedogenic and non pedogenic carbonate accumulation, accretion, and neoformation during the various stages of calcrete formation. Based on detailed micromorphological studies, the micromorphological features of the calcretes are grouped under three broad categories viz. calcitic features, biogenic features and fabric pedofeatures. The terminologies used here are after Brewer, (1964); Blokhuis et al., (1969); Wider and Yaalon, (1982); and Bullock et al., (1985).

I. CALCITIC FEATURES

Calcitic features of the calcretes include both pedogenic and non pedogenic features viz. coatings, glaebules, calcitans, intercalary crystals, meniscus cement, pendants, displacive / replacive spars, etc. Based on the micromorphological studies, the author has identified varied nature of the pedogenic carbonate accumulations. Accordingly they are grouped in to seven types (Table 4.1). But for the type I, IV and VII, the pedogenic carbonate accumulations are mainly calcitic glaebules either adhesive and diffusive or discrete and normal. Apart form the inclusions of soil plasma and skeleton grains, these glaebules apparently consist entirely of calcites. All diffused and most of the normal glaebules are nodules, however septarian type is seldom observed. Several variations and transitions occur between the different types, which are described as below.

Type I Comprise dusty micritic or microsparitic cement without any differentiation of b - fabric.(Plate 4.9 A).

Type I (A) *Al*though similar to type I, it includes slightly differentiated b- fabric and neocalcitans (Plate 4.9 B).

Type II Comprises of adhesive, diffusive, yellowish - whitish calcitic nodules without any impregnations. These nodules commonly include part of the soil plasma and skeleton grains of the original fabric (Plate 4.9 C). However glaebules

Types	Sub - types	Description
Type - I		undifferentiated b - fabric with dusty micrites and clay
	A	Undifferentiated b - fabric with clear microsparitic neocalcitans
Type - I I (Glaebules)		Diffusive, adhesive nodules with or without skeletal grains.
Type - I I I (Glaebules)	A	Discrete, normal nodules without any impregnations.
	B	Discrete, normal nodules with a neo / quasi ferran or a central or total iron impregnation.
	C	Discrete, normal nodules with iron impregnations, but in addition to that dendritic or manganese impregnations are also present.
Type - IV (Glaebules)		Discrete iron nodules with or without skeletal grains and neo - ferrans and manganans.
Type - V		Discrete / diffusive compound nodules incorporating type - II and / or type - III nodules.
Type - VI		Channel neocalcitans and grain neocalcitans.
Type - VII		Crystallaria - occurring mainly as included pedofeatures in nodules

* The nodules can be orthic, disorthic and allothic of Wider and Yaalon , 1982.

TABLE 4.1 MICROMORPHOLOGICAL CLASSIFICATION OF PEDOGENIC CARBONATES IN CALCRETES OF THE STUDY AREA

Type III Characterized by discrete, normal, calcitic glaebules (normally nodules but occasionally septaria), generally well rounded with high sphericity, sometimes subangular with low sphericity (Plates 4.9 E & F, 4.10 A). The size of the nodules are commonly between 0.2 to 15mm, however larger and smaller ones also occur. Included skeletal grains are less distinct than that of type II.

They are subdivided further into different subtypes viz A, B, C on the basis of included pedofeatures and sesquioxide impregnations.

Type III (A) They are nodules without any impregnations and cutans. (Plate 4.9 E). The nodules include undifferentiated b-fabric with micritic or microsparitic carbonate accumulations.

Type III (B) Comprise nodules that have distinct ferrugenous impregnations that have imparted yellowish to reddish brown colouration to the nodule (Plate 4.9 F) however the colour varies in accordance to the intensity of impregnation. The impregnations may be either homogeneous or heterogeneous or peripheral or as ferricutans. However, the neoformed sparites and microsparites are found to be clearly free from the impregnations.

Type III (C) In addition to the ferrugenous impregnations as that of type III B, these nodules have opaque dendritic manganese impregnations either throughout the nodule or restricted to the central part or forming along the periphery (Plate 4.10 A). The black, opaque manganese dendrites are clearly distinguished from the brownish ferrugenous impregnations under the plane polarized light.

Type IV These glaebules include discrete to diffusive, rounded to angular compound nodules. The nodules generally have sesquioxide impregnations and neocalcitans as included pedofeatures. Micro laminations and sparitic to microsparitic mosaics are most prevalent.

Type V This type incorporates discrete, well rounded, opaque to translucent ferrugenous nodules with or without skeletal grains. Neoferrans and manganans are seldom observed (Plate 4.10 B).

Plate 4.9 Photomicrograph of calcretes showing

(A)	Type I	Pedogenic carbonate and vesicular structure.
(B)	Type I-A	Pedogenic carbonate with neoclacitans around detrital.
(C)	Type II	Diffused nodules with a clear s - fabric.
(D)	Type II-A	Pedogenic carbonate with a diffusive boundary.
(E)	Type III-A	Pedogenic nodules without any impregnation.
(F)	Type III-B	Pedogenic nodules with uniform iron impregnation.

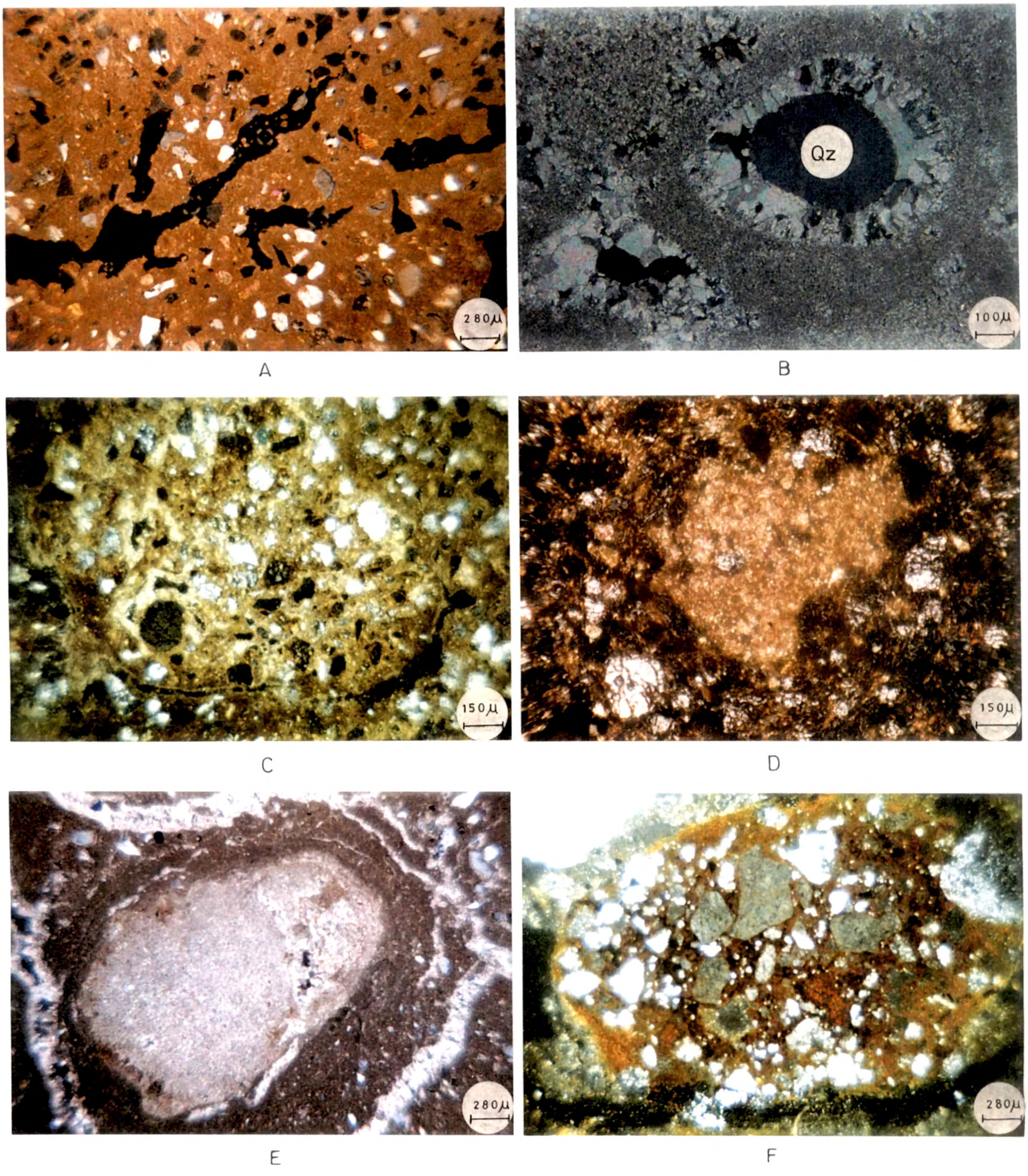


PLATE 4.9

Type VI	This pedogenic carbonate is a channel neocalcitan formed around fine channels (Plate 4.10 C). The outer boundaries of the channels are diffusive and the neocalcitans are strongly adhesive to the S- matrix. Sometimes, the channels include micro laminations and sparitic infillings from the outer walls towards the center. Calcitans, besides their occurrence as included pedofeatures, are also observed around glaebules and skeletal grains. The calcitans differ from the S - matrix and glaebules by virtue of their bigger crystal size and free from any impregnations.

Type VII	These pedogenic carbonate are intercalary crystals or crystallaria (Brewer, 1964) found as single crystals embedded in the soil matrix, a feature most commonly observed in the calcified soils and occasionally in type II nodules.

The most common non pedogenic carbonate accumulation includes meniscus cement, a micritic or microsparitic wedge that bridge the detrital grains is the most common form of non pedogenic carbonate accumulation generally observed in the early stages of calcretization. The meniscus cement (Plate 4.10 D) is formed due to the retention of a film of water around the skeletal grains, that dissolves the carbonates of the matrix and reprecipitate as a bridge (Knox,1977).

Besides the meniscus cement, the needle fibers (Warren,1983) (Plate 4.10E), micritic envelopes around skeletal grains and micritic pore fillings-floating texture [Plate 4.10 F] (Goudie,1975) are the different types of non-pedogenic carbonate accumulations.

The author has also observed the differences in carbonate accumulations between the fine textured soils (stabilized dunes and interdunal flats) and coarse textured soils (alluvial flats, dunal plains, pediment surfaces) by way of micro morphological studies of representative calcrete profiles (Tables 4.2 A & B). The exemplary profiles representing each type of soils are discussed as under.

Plate 4.10 Photo micrographs depicting

(A) Type III-C Nodules with manganans.

(B) Type IV Glaebules with dissolution feature along the boundary.

(C) Type VI Pedogenic carbonate - channel neocalcitan indicative of pedogenic carbonate accretion.

(D) Meniscus cement around detrital grain indicative of high soil moisture regime.

(E) Poorly developed needle fibers, a feature of quick precipitation with partial transformation into sparites.

(F) Typical floating texture, characteristic feature of groundwater precipitations.

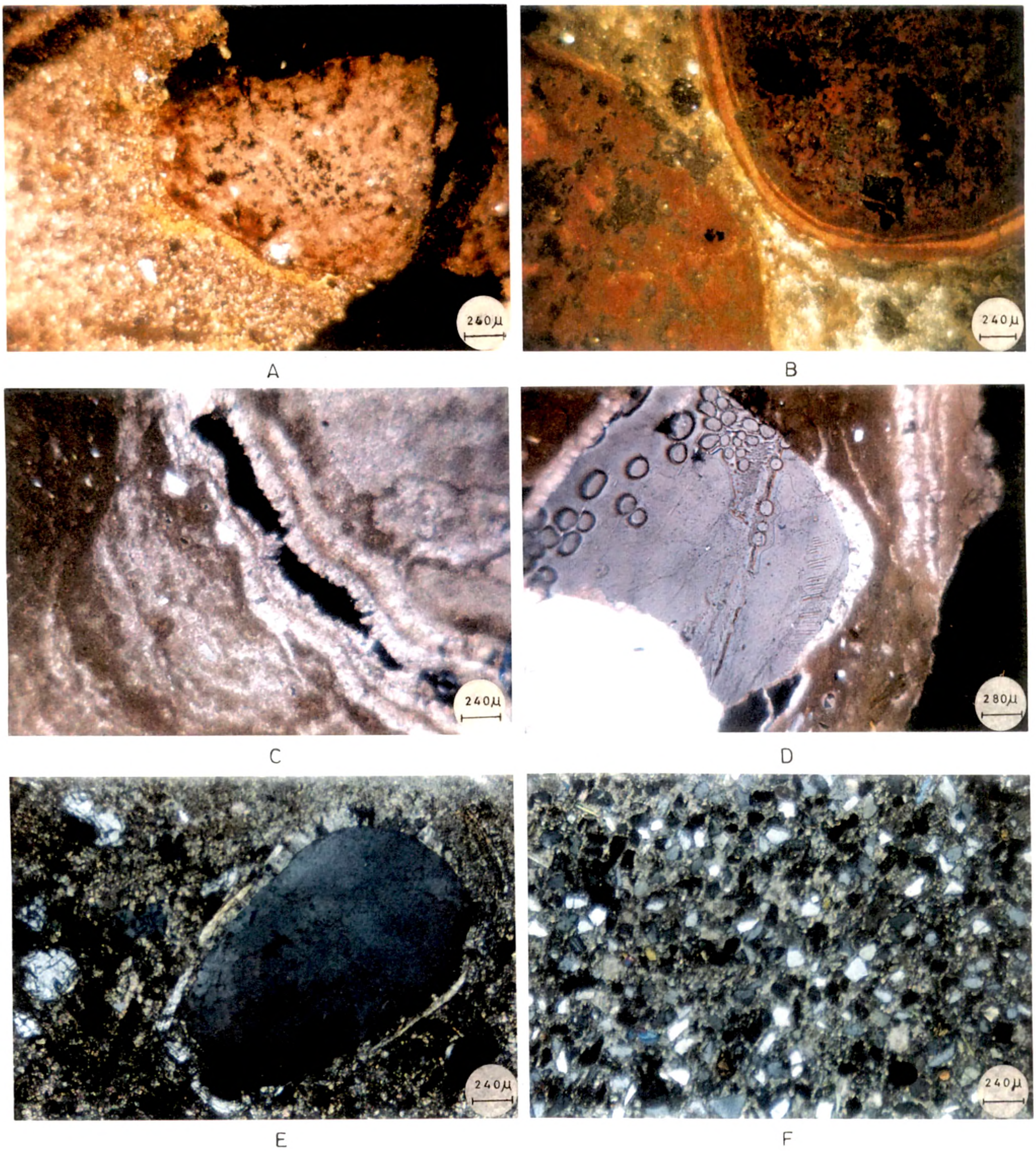


PLATE 4.10

Location	Geomorphic association	Horizon & Depth (cm)	Fabric	Mineralogy of skeletal grains*	Micro features
Dhanola	Dune	A (100 - 160)	Single - grain	Qz - 45 % F - 35 % M - 8 % P & A - 5 % C - 4 %	Neo - calcitans at lower parts, dissolution of detrital calcites.
		Bt (220 - 320)	Intergrain micro aggregate	- do -	Cutans, Coated peds, neo - calcitans, type -II nodules, type-III allothic nodules, Insitu altered micas, pyroxenes.
		Bir (> 320)	Pelicular grain.	Q - 65 % F - 30 %	Sesquans, oriented argillans, type-III (A) allothic nodules.
Sardarsa- - har	Dune	Bc (50 - 150)	Crystic	Q - 55 % F - 45 % M - 3 %	Neocalcitans , Argillic cutans , type II nodules.
		Bk (150 - 175)	Crystic	- do -	Sesquans,cutans,neocalcitans, type - II , III orthic nodules , corroded skeletal grains.
		Cc (175 - 320)	Complex	- do -	Crystic in the upper part with sesquans, type - III orthic nodules. ferricutans, allothic type - V nodules, uncoated fractures at the lower parts.
Bhaleri	Dunal	Bt (50 -100)	Intergrain micro aggregate	Q - 75 % F - 20 %	Cutans, channel neocalcitans, type - II, III (A) orthic & III B allothic nodules, coated peds.
		Bc (100 - 200)	Crystic	- do -	Cutans, sesquans, neocalcitans, crystallaria, glaebular halo, translocated detritals, type - V nodules.
Vav	Inter dunal	Bc (55 - 125)	Crystic	Q - 60 % F - 30 % RF - 3 % M - 2 %	Crystallaria, channel neo calcitans, cutans, type - II, III (orthic) nodules
		K (125 - 200)	Complex	Q - 75 % RF - 15 % F - 8 %	Channel neo calcitans, ferrans, manganans, meniscus cement, needle fibres and iron halo around diagested micas.

TABLE 4 . 2 (A) MICROMORPHOLOGY OF CALCRETE PROFILES - FINE TEXTURED SOILS.

Location	Geomorphic association	Horizon & Depth (cm)	Fabric	Mineralogy of skeletal grains *	Micro features
Raneri	Inter dunal	Ac (45 - 50)	Crystic	Q - 80 % F - 15 % M - 2 %	Channel neo-calcitans, type - II nodules.
		Bt (50 - 100)	Intergrain micro aggregate	Q - 45 % F - 40 % M - 13 % P & A - 2 %	Cutans, crystallaria, coated channels, type - III (A) allothic nodules, Insitu weathering of micas, pyroxenes.
		Cc (100 - 175)	Crystic	As Ac - horizon.	Calcic cutans, neo-calcitans, sesquans, type-II orthic & type III allothic nodules.
Belwa	Alluvial plain	Ac (100 - 150)	Crystic	Q - 40 % F - 45 % M - 5 % P - 3 %	Channel neo - calcitans, argillans, sesquan, type - II, III (A) nodules.
		Bc (260 - 340)	Intergrain micro aggregate	- do -	Argillic cutans, neo-calcitans, crystallaria, type II, III (A & B) nodules.
		K (350 - 400)	Crystic	Q - 65 % F - 25 % M - 2 %	Calcitans, ferri calcitans, needle crystals, sesquans, manganans, corroded skeletal grains.

Q - Quartz, F - Feldspars, M - Micas (Biotite & Muscovite),
P & A - Pyroxenes and Amphiboles, RF - Rock fragments.
* Mineralogy Inclusives of opaques

TABLE 4.2 (B) MICROMORPHOLOGY OF CALCRETE PROFILES - COARSE TEXTURED SOILS

FINE TEXTURED SOILS

The micromorphology of four exemplary calcretic profiles are :

Dhanola - It is a stabilized dunal profile with palaeosols and well developed Bt horizon and weakly developed Bir horizon.

Sardarsahar - This is a dunal profile with a strongly developed Bc, Bk and C horizons.

Bhaleri - A dunal profile comprising of palaeosol and well developed Bt and Bc horizons.

Vav - An interdunal profile with very well developed petrocalcic horizons (Bc&K).

Dhanola

The micro morphological description of this profile is discussed in accordance to the stratigraphic sequence viz. lithounit-I (0-160cm), lithounit-II (160-320cm) and lithounit III (320cm and above).

Lithounit I (0 - 160 cm)

The top 100 - 160 cm of the solum have undifferentiated, non oriented b-fabric with micritic clay. The skeletal grains comprise well sorted, angular to subrounded fine sand (quartz 45%; 35% feldspars; 8% micas; 5% and pyroxenes and amphiboles, C 4% and the rest being opaque) with a single grain microstructure. Uncoated channels and voids are also common. The basal part of this lithounit however, have drussy crystallaria and micritic calcitans with a slightly differentiated b - fabric.

Lithounit II (160 - 320 cm) comprises skeletal grains similar to lithounit I, but with a differentiated b - fabric. Insitu weathering and bleaching of iron bearing minerals (biotite, hornblende etc.) and cutanic features are also common. Though, calcitic features are not observed in the upper part (160 - 80 cm) of this unit, neocalcitans, type II & II (A) nodules are common at depth (180 - 220 cm). The lowest part of this unit (220 - 320 cm) is heavily illuviated, and the b-fabric is well differentiated. The solum is highly compact and dense with a strongly developed micrite coated peds. Iron impregnations, oriented, birefringent clay coatings around channels and oxidized, etched skeletal grains are ubiquitous. Insitu weathering of mica detritals and migration of iron to the soil plasma is characteristic of this layer (Plate 4.11 A). The most common calcitic features are type II, III (A, B) nodules, channel neocalcitans, and intercalary crystals. Type III nodules are orthic, allothic and disorthic in nature.

Lithounit III (320 cm and above) comprises skeletal grains akin to lithounit I & II but are relatively coarser.The b-fabric is well differentiated with skeletal grains having thick coating of (2 - 5) birefringent, oriented reddish-brown clay. The calcitic features are of type III (B) allothic nodules.

Bhaleri

Horizon A (depth 15 - 50 cm) have skeletal grains in a weakly differentiated b-fabric with channel neocalcitans and micritic envelops. Appearance of neoformed microsparites and sparites have resulted in the development of impregnation and cutan free crystic fabric. The salient pedogenic carbonates are type II nodules.

Horizon Bt (depth 50 -100 cm)

This is a dense, illuviated, oxidized, compact layer with considerable reduction in microporosity. The b-fabric is well differentiated and have birefringent, oriented clay in the upper part and calcic cutans in the lower part. The fabric is crystic with coarse neocalcitans.The nodules are of type II and type III (A, B). Type III (A) nodules are both orthic and disorthic, whereas type III (B) nodules are allothic. The oxidized skeletal grains incorporate displacive spars.The well developed peds have micritic coatings.

Bc & C Horizons (depth 100 - 200 cm) have thick birefringent, oriented clay coatings within a strongly differentiated crystic b-fabric. The calcitic features are orthic and disorthic, iron impregnated nodules (type III, B), crystallaria, and neocalcitans . Glaebular halo around the nodules are also widely prevalent.

Sardarsahar

Horizon A (depth 0 -50 cm) have undifferentiated soil fabric with detrital grains comprising (40 -50% quartz, 40 - 48% feldspars, 2 - 3% micas, amphiboles and pyroxenes and the rest being opaques) have a loose packing with a typical vuggy or vesicular structure.

Bc Horizon (depth 50 - 150 cm) The S - matrix of this horizon is compact and dense with a reduction in microporosity. By way of neoformed calcitans, the fabric of the soil changes from calciacepic to crystic. Argillic cutans and type II nodules are widely prevalent features of this horizon.

Horizon - Bk (depth 150 -175 cm)

The skeletal grains of the dense and compact S-matrix are well oxidized, etched and corroded. The fabric is crystic with channels having sparry neocalcitan and argillans. The drussy micritic groundmass is iron impregnated while the neoformed microsparites and sparites are free from any impregnations. Evolution of orthic, type III nodules with glaebular halo from Type II nodules is the most salient feature observed pointing to the clear churning actions with in the horizon.

Horizon - Cc (depth 175 - 250 cm)

The b-fabric is well differentiated with small segregations and crystic with strong sesquioxidic impregnations. The well developed pedosurfaces have clear microsparitic calcitans. The transformations of orthic type III nodules to disorthic type III nodules point to the continuous carbonate accumulation and nodules development.

Horizon - C (depth 250 - 320 cm)

The fabric of the soil is complex (Bullock et al, 1985) with b-fabric having strongly birefringent, oriented reddish brown clays with ferricalcitans. The discrete, well rounded opaque to translucent allothic (type V) nodules with uncoated fractures and depletion pedofeatures (dissolution of plasma along nodule surfaces) are most salient.Ferricutans are seldom observed in b-fabric with uncoated fractures running across the nodules and soil plasma.

Vav

Horizon Bt (depth 30 - 55 cm)

The skeletal grains are loosely packed in a non differentiated siliceous and carbonate clay plasma. The fabric is calciacepic without any neocalcitans and channels, voids remaining uncoated.

Horizon Bc (depth 55 - 125 cm)

The S-matrix is dense, compact with crystic fabric. Neocalcitans and intercalary crystals are widely prevalent within a well differentiated soil plasma. Channels have micritic / micro sparitic neocalcitans and argillans laminations and associated bow shaped features (Plate 4.12 F) (Bullock et al. 1985). Occasionally channels do also have translocated detrital infillings (Plate 4.11E) in addition to sparry channel neocalcitans. The glaebules are type II nodules and type III (A) orthic nodules.

Horizon K (depth 125 - 215 cm)

The S-matrix is very dense and heavily impregnated by carbonate accumulations. The fabric is typically crystic with channels having sparitic infillings and channel neocalcitans. The b-fabric is highly impregnated with ferrans and dendritic manganans. Glaebules are of type III (A, B,C) and type IV (orthic, disorthic, and allothic) (Plate - 4.11 B, C & D)

Plate 4.11 Photomicrographs of calcretes illustrating

(A) Insitu weathered biotite with a ferrugenous halo - a feature of pedogenesis and neoformations.

(B) An orthic nodule with glaebular halo, pointing to insitu development of nodules.

(C) An allothic nodule, an indicator of palaeo erosional surfaces.

(D) A disorthic nodule - a feature pointing to pedoturbated soils.

(E) Translocated skeletal grains along the channel, supporting the pedoturbations.

(F) Intergrain micro aggregate structure, caused due to segregation of b - fabric.

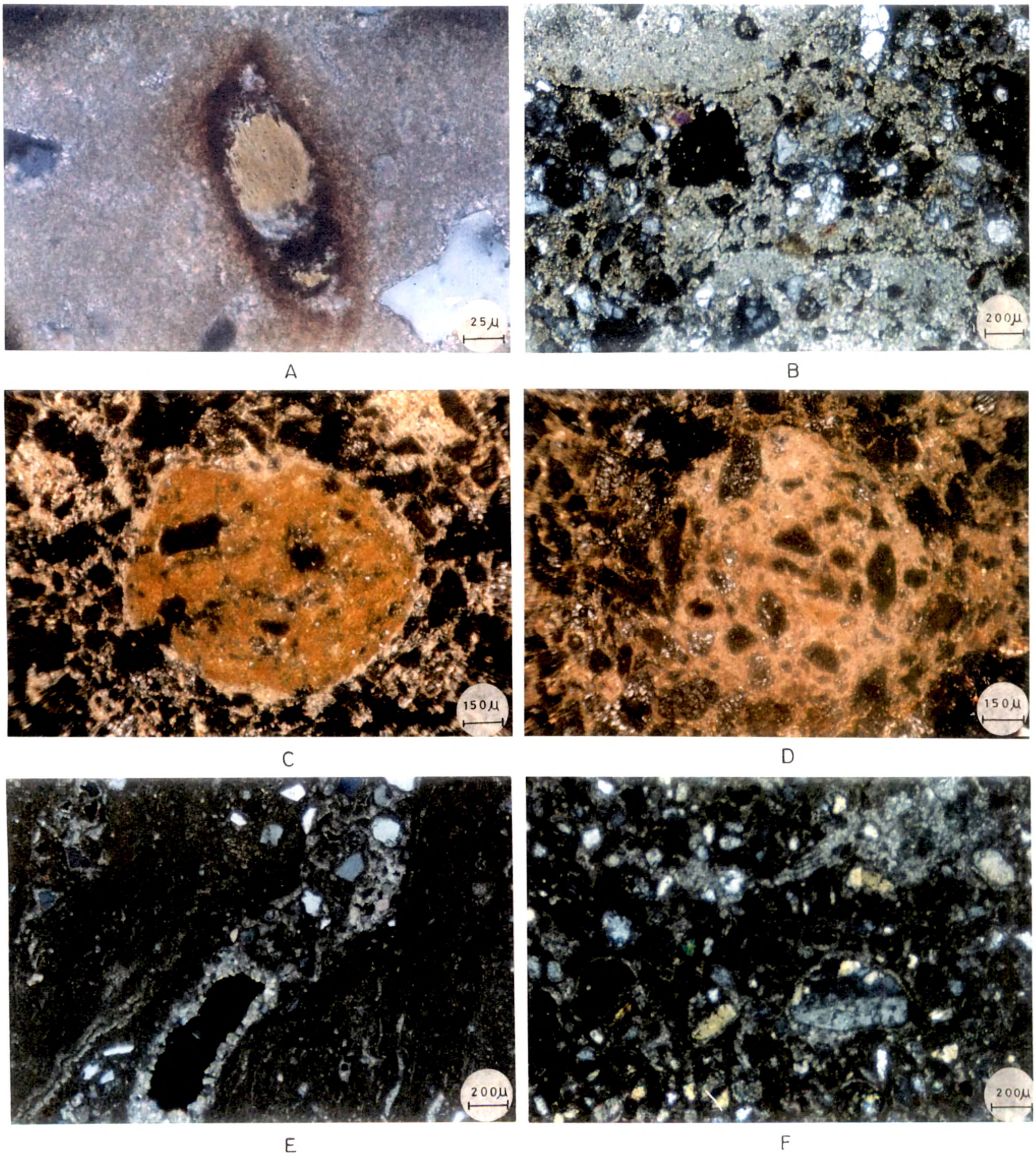


PLATE 4.11

with included calcans. Prevalence of meniscus cement and needle fibers along with sesquioxidic impregnations point to the nonpedogenic mode of carbonates in addition to pedogenic carbonate accumulations The iron bearing minerals underwent strong, insitu weathering with the release of iron that form a ferrugenous halo around the altered detritals The quartz detritals are fractured, etched and corroded with displacive spars

Horizon C (depth 215 cm onwards)

The skeletal grains are loosely packed with micritic cement Channels and voids are absent Sesquioxidic impregnations and meniscus cements are the dominant micromorphic features

MEDIUM - COARSE TEXTURED SOILS

Ideal calcretic profiles developed in these soils are observed in the following locations :

Raneri	This profile is developed over an alluvial (gravelly-sand) plain, is concealed under an aeolian cover
Bikaner	This calcretic profile, forms a part of an alluvial plain
Belwa	It represents predominantly fine textured interdunal calcretic profile
Nimbijodhan	Here calcretes developed over weathered pediments, covered under a aeolian sand.

Raneri

Horizon Ac (depth 45 - 50 cm)

This horizon comprises calcium carbonate impregnated S-matrix with coarse skeletal grains (coarse sand) dominantly of quartzitic and feldspathic composition. The b- fabric has drussy microsparites and sparites and clear neoformed sparites The channels have coatings of argillans and sparites which are exclusively of type II. Insitu fracturing of the detrital grains (quartz) are also evidenced.

Horizon - Bt (depth 50 - 100 cm)

The b-fabric is well differentiated and have intergrain microaggregate structures (Plate 4 11F) The skeletal grains (silt size) comprise 45% quartz; 40% feldspars and 13% micas and occasional well rounded sparitic crystals. The calcitic features are mainly type III (A) allothic nodules, type II nodules and intercalary crystals The allothic type III nodules resembles by means of fabric and included pedofeatures to the underlying horizon

Cc - horizon (depth 100 -175 cm)

The characteristic micromorphological features of this horizon are :

Compact, dense and crystic with coarse sand-gravelly, highly altered, etched skeletal grains The sparites and microsparites of the b-fabric and glaebules have sesquioxidic impregnations. The glaebules are orthic type II, orthic and disorthic of type III (A, B) Allothic nodules are of type III (A, B and C) Occurrence of allothic nodules with a fine textured soil fabric (argid soils) with dendritic manganans point to a possible occurrence of older fine textured soils below this horizon (Bullock et al., 1985). Occurrence of needle fibers and displacive spars are also evidenced.

Belwa

Horizon - Ac (depth 120 - 180 cm)

The crystic b-fabric have dense, compact, well differentiated, circular striated carbonate and non carbonate clays The channels have coatings of argillans and microsparitic channel neocalcitans Glaebules are mostly of type II nodules, however orthic type III (A) nodules are seldom observed. Bio relics with neoformed microspars and iron impregnations are also evidenced

Horizon Bc (depth 260 - 340 cm)

The micro morphological features show intergrain microaggregate structure with well differentiated b-fabric and oriented argillans around the detritals, argillic cutans The channels and skeletal grains show coating of neoformed sparites and microsparites The calcic features dominantly comprise type II nodules, orthic type III (A) nodules and intercalary crystals

Horizon - K (depth 350 -400 cm)

This horizon displays highly compact, dense, carbonate impregnated S-matrix with weathered, etched, corroded skeletal grains in a floating texture. The crystic fabric has calcicutans, ferricalcitans, meniscus cement, needle crystals with iron impregnations and dendritic manganans

Nimbijodhan

Micromorphology of this horizon depicts a loose vuggy microstructure incorporating coarse, angular rockfragments (sandstones) with interstitial fine textured soil The b-fabric in the fine textured soil is undifferentiated with occasional neoformed microsparites and the skeletal grains have neoformed microsparitic envelopes.

Bikaner

The top 200 cm of the solum is strongly carbonate impregnated with a crystic, dense, well compact S-matrix with quartzitic skeletal grains (gravelly sands) The fabric incorporates drussy microsparites and sparites with ferrugenous impregnations The neoformed sparites along the cavities and grain boundaries are free of any impregnations Diffuse, adhesive, type II nodules are commonly observed. However, at depth on account of the fine textured skeletal grains, S-matrix is micritic and exhibit a typical floating texture and needle fibers.

CHEMISTRY AND MINERALOGY OF THE CALCRETES

In order to understand the chemical kinetics of soil formations, calcretization, alteration of mineral phases and neoformations, the author has carried out detailed analytical studies on geochemical [major oxides, trace elements (by AAS-GBC, Australia, 1990 model) and REE (by ICP-MS, VG plasma Quad model, U.K)] and mineralogical (by XRD, Philips PW 1720, Cu Kα) characters of individual horizons of the characteristic calcrete profiles For this the author has selected Dhanola, Raneri, Surpalia, Sardarsahar, Belwa, and Bhaleri profiles for detailed discussion For rare earth element studies, the REE concentrations along with commonly used ratios to illustrate REE fractionation (Balashov et al , 1964) are normalized to upper crust (Rollinson,1992) The major oxide, trace element chemistry and mineralogy of the six exemplary calcrete profiles are discussed in Table 4 3, 4 4, 4.8 and in Figures 4.3 (A - F), 4. 4 (A - F) and 4 5 (A - D)

Dhanola

The A - horizon is by and large silica dominant (79 9%). The CaO concentration is progressive downwards and is maximum at the Bt horizon (18.2%). Higher MgO (8.9%) and Al_2O_3 (10 5%) concentrations, and less CaO / MgO ratio are characteristic features of this horizon The iron concentration is orbitarily high (1.5%) at Bt horizon. Within this profile Mn is showing enhancement at two levels i e. at A horizon and Bt horizon

The Bir-horizon shows general depletion in all elements except the silica (Figure 4 3-A) The REE abundance pattern of this profile (Figure 4 4 - A) shows significant variations in the concentration of REE's in general and LREE in particular from top to bottom Both LREE, MREE and HREE are strongly depleted in the Bt-horizon with immediate increment in the underlying Bir- horizon La/Lu, La/Sm and Nd/Sm clearly confirms the REE fractionations, especially between LREE and HREE. Though, La/Sm, Nd/Dy shows fractionation in B - horizon they are not very pronounced as seen between LREE & HREE The Removal Index (ρ), where ρ = [Cρ - Cm] / Cρ [Cρ - REE concentration in unaltered materials, Cm - REE concentrations in altered materials] (Ronov et al , 1967) helps in comparing the concentrations of individual REE elements in the source and altered materials Negative ρ indicates the enrichment relative to parental material, while positive ρ indicates depletion The positive ρ values of REE's but for Lu in B horizon and strong negative ρ values are the manifestations of REE fractionation and their mobility from Bt to Bir horizons.

The semi-quantitaive analyses of the mineralogy of different horizons by X-ray diffractometry (Table 4 8) reveal the presence of illite, chlorite, montmorillonite among the clay minerals besides calcite, dolomite and quartz The increase in the percentage of dolomite at the Bt - horizon is also significant.

Raneri

The salient geochemical characteristics of this profile (Figure 4.3-B, 4 4-B) are as under .

CaO enhancement at Ac horizon (14 9%) and Cc horizon (35 1%) with a low concentration of CaO in B-horizon (9 7%). MgO concentration though low throughout the profile, slight increment is visualized in B-horizon Alumina and Mn behaves similarly with enhancement at the Bt-horizon Iron and other trace elements do not show significant mobility within the profile The anomalous silica - alumina; iron - alumina and calcium - magnesium ratios indicate an abrupt change in the chemistry of the solum at a depth of 50 cm This abrupt change in alumina / silica ratio could be attributed to a non homogenous solum. A distinct change in the REE pattern (Figure 4 4 (B)) of the underlying gravelly sand horizon (depleted in Ce) and the overlying dunal sand layer (slightly enhanced Ce) is observed Clear fractionation of REE is evidenced at least in the dunal sand Mineralogy of the profile indicates dominance of calcite, quartz and feldspar in the upper parts, however, dolomite and montmorillonite appear in the B horizon

Bhaleri

This profile like the Dhanola profile show enrichment in CaO, and Fe_2O_3 in the Bc horizon, which is located just below the Bt - horizon (palaeosol). The high magnesian nature of this horizon is reflected both by the increment in MgO and net decrease in the CaO / MgO ratio comparing to the upper and lower horizons (Figure 4 3 - E). While Fe_2O_3 and Mn shows a depletion in A & C horizons with respect to B the $Al_2 O_3$ is slightly enriched in upper part of the C - horizon

Behavioural pattern of Cu and Zn is similar to that of silica i e , depletion in B -horizon Clear REE fractionation within the profile (Figure 4 4-E) is observed from low La / Lu ratio (8 3) in Bhorizon and sharp increase in C horizon (53 3) MREE and HREE fractionation though noticed, is insignificant comparing to LREE.

The clay mineralogy (chlorite and montmorillonite) show definite enhancement in the Bt horizon The dolomite content of the profile is progressive in Bk horizon (20 5 % to 42 2%) and is altogether absent in the C - horizon Goethite content is also observed along with the zones of dolomite increment (Table 4.8).

Belwa

The distinct lime accumulations at Ac and K horizons are reflected by the sudden spurt in the CaO content The mobility pattern of magnesia and alumina show a close affinity to the mobility pattern of the calcium Zn and Cu also behave almost similar to CaO However, Mn shows sharp increment in the K horizon only

LREE and MREE fractionation and mobility is evidenced within the profile (Figure 4.4-F). It is reflected by La/Lu, La/Sm and Nd / Dy ratios The increment of La, Ce, Tb and Lu at depth is also evidenced by the negative ρLa, ρCe, ρTb and ρLu values.

Mineralogy of the profile indicates dominance of calcite and quartz Chlorite, montmorillonite and dolomite appearance are confined to the b - horizon only. The major oxide chemistry of **Surpalia** (Figure 4.3-C) and **Sardarsahar** (Figure 4 3-D) profiles are self explanatory. REE geochemistry of these profiles (Figure 4.4 - C & D) points to the intra profile fractionation and mobility of LREE than HREE The mineralogy of the profiles show presence of chlorite, montmorillonite, biotite, dolomite besides calcites and feldspars

Sa.No	Location	Depth (cm)	LOI Wt.%	SiO_2 Wt %	Al_2O_3 Wt %	Fe_2O_3 Wt.%	CaO Wt.%	MgO Wt.%	Pb ppm	Zn ppm	Cu ppm	Mn ppm	SiO_2 / Al_2O_3	Al_2O_3 / Fe_2O_3	CaO / MgO
1	Dhanola	110	35.8	79.9	6.3	1.3	9.2	3.2	17	19	13	197	12.7	4.8	2.9
2		205	40.8	79.2	6.5	1.4	10.0	2.8	18	17	20	182	12.2	4.6	3.5
3		300	45.9	60.9	10.5	1.5	18.2	8.9	14	19	14	213	12.0	3.7	2.0
4		350	19.6	88.1	5.1	1.0	5.0	0.9	16	23	14	150	17.3	5.1	5.3
5	Raneri	20	40.3	84.9	7.0	1.4	5.6	0.9	15	28	36	148	18.4	2.0	53.0
6		50	43.8	76.2	6.2	1.5	14.9	1.1	18	19	31	119	26.4	1.6	70.2
7		75	42.5	74.4	8.9	1.5	9.7	1.2	17	17	21	211	8.4	5.9	8.1
8		100	42.5	60.7	2.3	1.4	35.1	0.5	18	10	12	119	12.3	4.1	13.5
9		150	49.4	62.5	3.4	1.7	31.8	0.6	16	23	14	150	12.1	5.0	6.2
10	Surpalia	110	36.9	75.3	5.0	1.1	16.9	1.6	11	8	10	77	15.1	4.5	10.5
11		210	78.1	9.8	15.3	3.1	68.8	2.9	14	6	10	60	0.6	4.9	23.7
12		300	65.7	54.1	10.4	2.4	21.4	11.7	14	11	13	125	5.2	4.3	1.8
13	Sardarsahar	100	49.2	77.4	8.6	1.7	8.3	4.0	14	13	19	227	9.0	5.1	2.1
14		175	79.3	17.2	15.7	4.1	40.7	22.7	18	10	15	145	1.0	3.8	1.8
15		220	47.4	72.9	7.1	1.6	10.1	8.4	17	17	25	190	10.3	4.4	1.2
16		300	27.6	93.5	3.9	1.0	1.1	0.6	16	7	15	52	24.6	3.8	1.8
17	Bhaleri	120	27.9	87.1	6.0	1.2	4.6	1.0	17	14	18	168	14.5	5.0	4.6
18		220	64.3	53.6	8.8	2.4	24.4	10.8	14	11	16	300	6.1	3.7	2.3
19		350	46.7	80.7	8.5	1.6	8.2	1.2	17	24	39	97	9.5	5.3	6.7
20	Belwa	220	71.8	33.2	7.8	2.6	55.1	1.5	14	12	18	81	4.3	3.0	36.6
21		300	33.3	87.3	6.8	1.2	4.1	0.6	18	8	13	138	12.8	5.7	6.8
22		380	55.9	58.0	6.1	1.8	33.2	1.0	17	10	14	164	9.5	3.4	33.2
23		500	21.1	86.7	6.0	1.1	5.6	0.7	15	10	14	120	14.6	5.5	8.0

TABLE 4.3 MAJOR OXIDES AND TRACE ELEMENT CHEMISTRY OF CALCRETE PROFILES

Sa. No	Location	Dep-th (cm)	La	Ce	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Er	Lu	La/ Lu	La/ Sm	Nd/ Dy	ρLa	ρCe	ρTb	ρLu
1	Dhanola	100	3400	8400	920	3600	420	440	100	340	60	180	180	18 9	8.1	10 6	----	----	----	----
2		205	3200	7600	820	3200	460	460	100	340	60	180	220	14.5	7 0	9.4	+0 1	+0 1	0 0	-0.2
3		300	2200	5200	580	2400	340	300	60	260	60	140	180	12 2	6.5	9.2	+0.4	+0 4	+0 4	0.0
4		350	3600	9400	960	4000	540	760	120	380	80	180	680	5.3	6.7	10.5	-0 1	-0 1	-0 2	-2 8
5	Raneri	20	2000	3800	500	2000	320	300	80	280	60	160	260	7.7	6.3	7.1	----	----	----	----
6		50	2000	2600	520	1800	380	380	80	340	80	160	240	8.3	5.3	5.3	-0 1	-0 1	0 0	+0 8
7		75	3000	7400	820	3200	500	540	120	380	80	220	360	8 3	6.0	8.4	0 0	0 0	-0 2	-0.3
8		100	3200	7800	820	3200	460	520	100	380	60	200	60	53.3	7.0	8.4	+0.3	+0.6	+0 2	+0.1
9		150	3000	7200	740	3200	500	540	100	400	80	200	280	10.7	6.0	8.0	+0.3	+0 5	+0 2	+0.1
10	Surpalia	110	3000	6800	740	3000	500	520	120	380	80	180	240	12.5	6 0	7.9	----	----	----	----
11		210	2000	3400	480	1800	320	320	80	280	60	140	200	10.0	6 3	6.4	+0.3	+0 5	+0 3	+0 2
12		300	2400	4800	620	2400	360	380	80	280	60	140	260	9.2	6 7	8.6	+0.2	+0.3	+0.3	-0.1
13	Sardar .	100	2000	4800	480	2000	380	420	100	300	60	160	220	9.1	5.3	6.7	-----	-----	-----	-----
14		175	2000	4200	480	1800	340	340	80	240	60	140	260	7.7	5 9	7.5	0 0	+0 1	+0 2	-0.2
15		220	2600	6400	660	2800	340	424	80	300	60	160	260	10.0	7.6	6.0	-0 3	-0 3	+0 2	-0 2
16		300	3000	8000	760	3000	420	480	100	320	60	180	240	12.5	7.1	9.4	-0 5	-0.7	0.0	-0.1
17	Bhaleri	120	2000	4200	460	1800	380	360	80	280	60	140	240	8 3	5.3	6.4	-----	-----	-----	-----
18		160	1800	3800	440	1600	280	300	60	240	40	120	220	8.2	6.4	6.7	+0 1	+0.1	+0.1	+0.
19		220	3400	8400	860	3200	460	400	100	380	80	200	240	14.2	7.4	8.4	-0 7	-1.0	-0 3	0.0
20		350	3400	8400	860	3400	480	440	100	380	80	180	300	11.3	7.1	8.9	-0 7	-1.0	-0.3	-0.3
21	Belwa	120	1200	2600	260	1200	240	160	60	240	60	160	300	4.0	5.0	5 0	----	----	----	----
22		300	4000	9800	1000	4200	560	480	100	400	80	240	360	11 1	7 1	10.5	-2.3	-2 8	-0.7	-0.2
23		400	3200	6800	740	2800	440	340	100	360	80	220	320	10.0	7 3	7.8	-1 7	-1.6	-0 7	-0 1
24		500	1600	3800	380	1600	300	240	80	240	60	160	280	5.7	5.3	6.7	-0 3	-0 5	-0 3	+0 7

REE concentrations are in ppb

TABLE 4.4 RARE EARTH ELEMENT CHEMISTRY OF CALCRETE PROFILES.

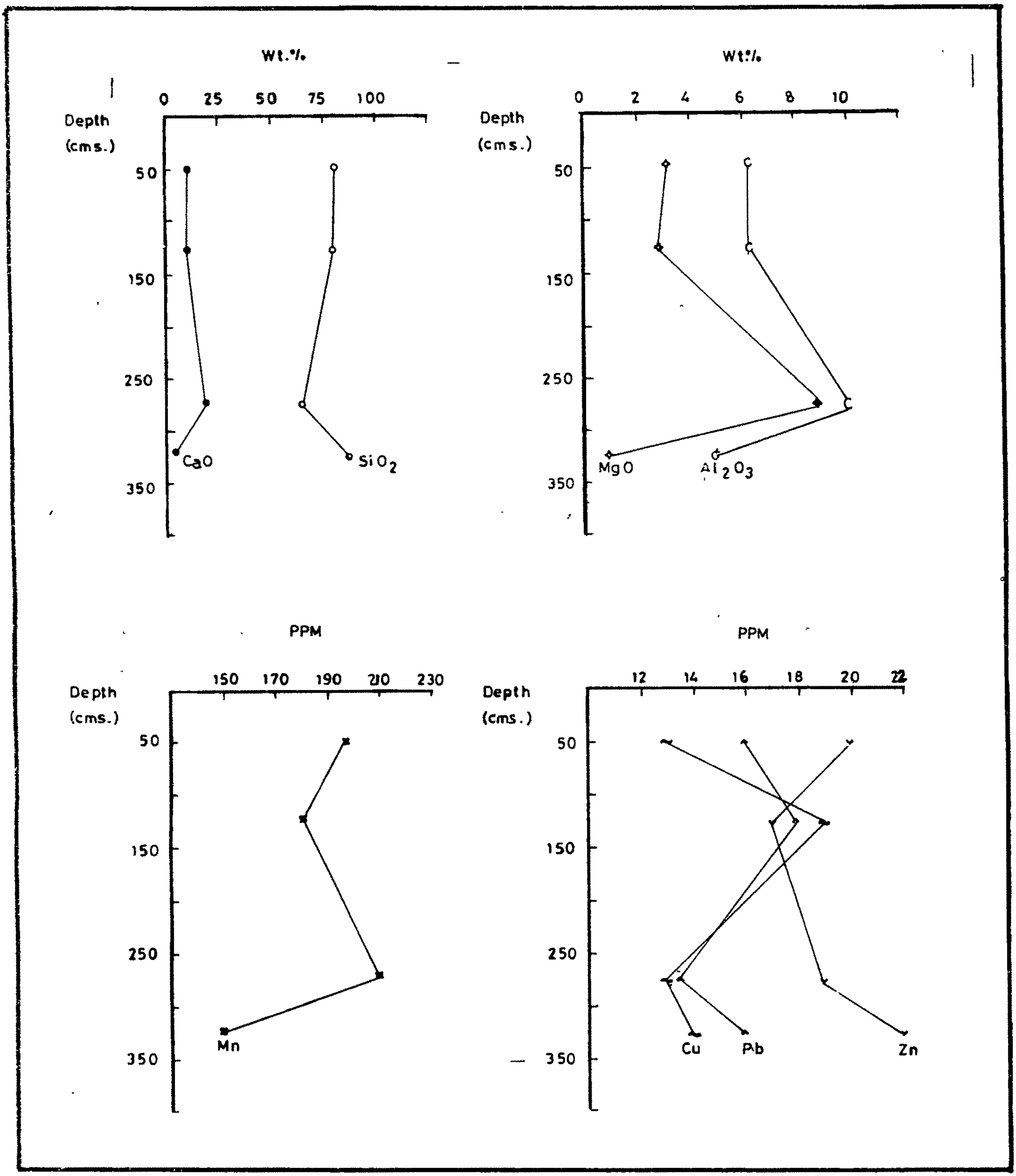


Fig. 4.3.- Major oxide, trace element chemistry of Dhanola profile.

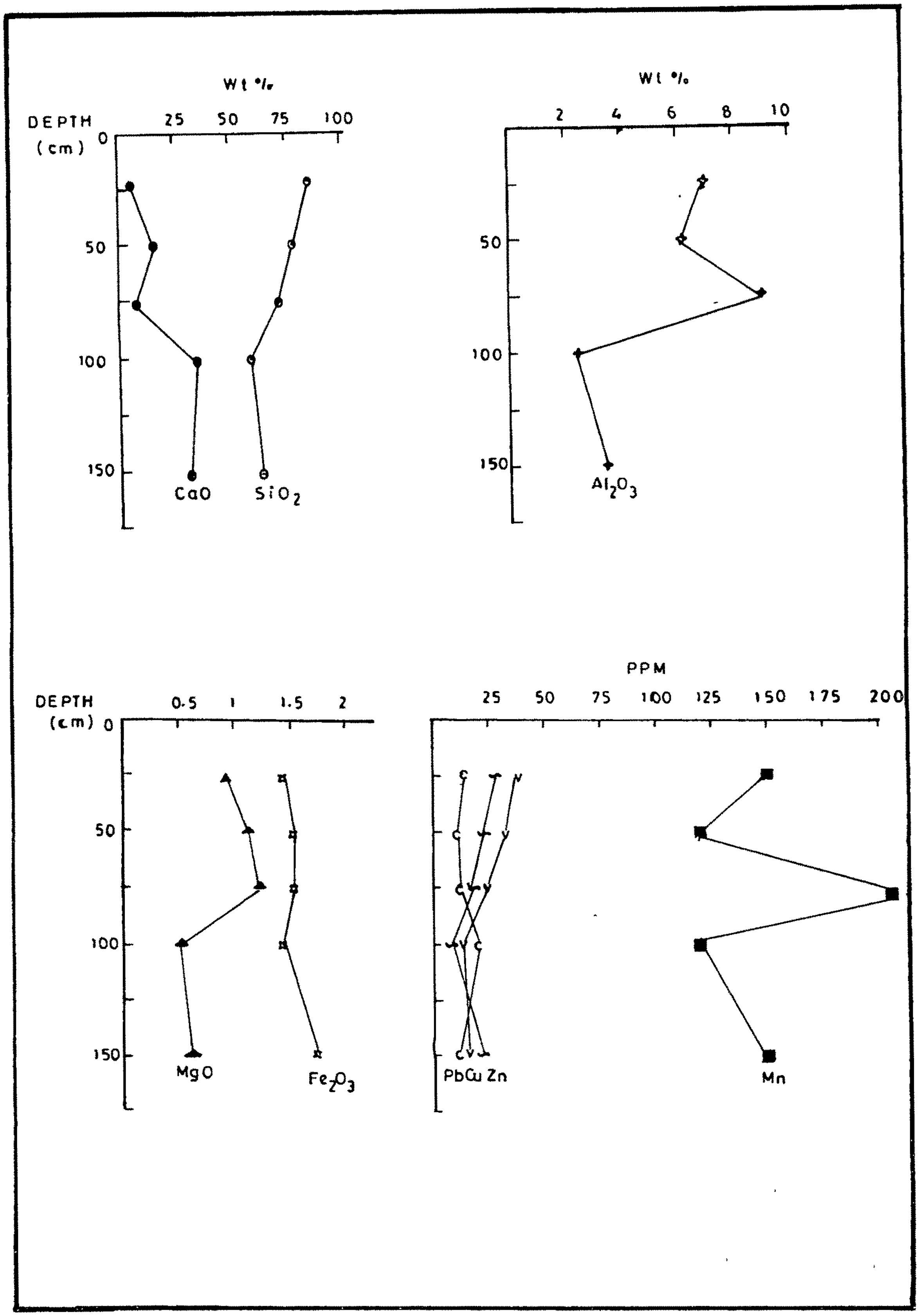


Fig. 4.3-B. Major oxide, trace element chemistry – Raneri profile.

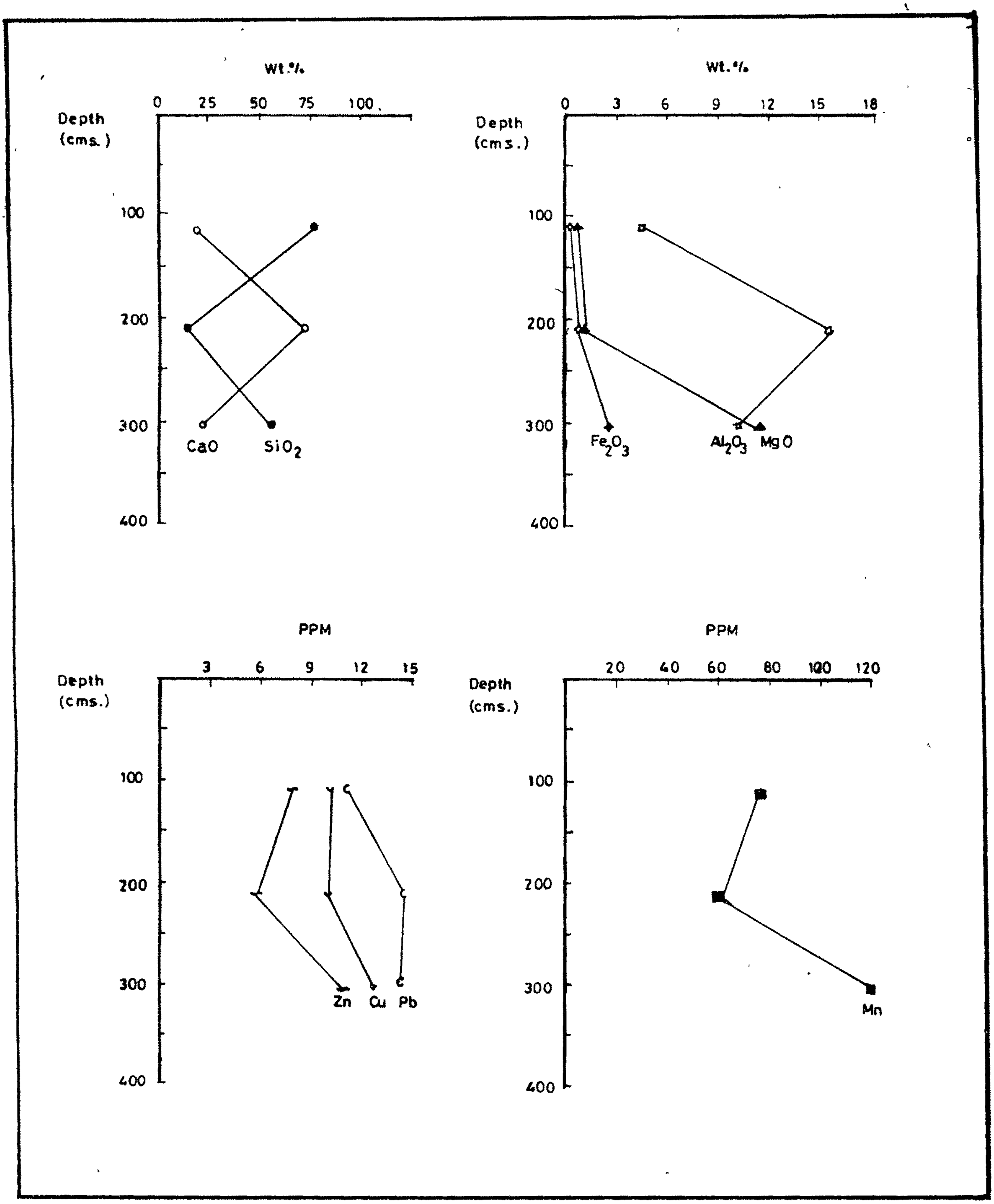


Fig.4.3-C. Major oxides, trace element chemistry – Surpalia profile.

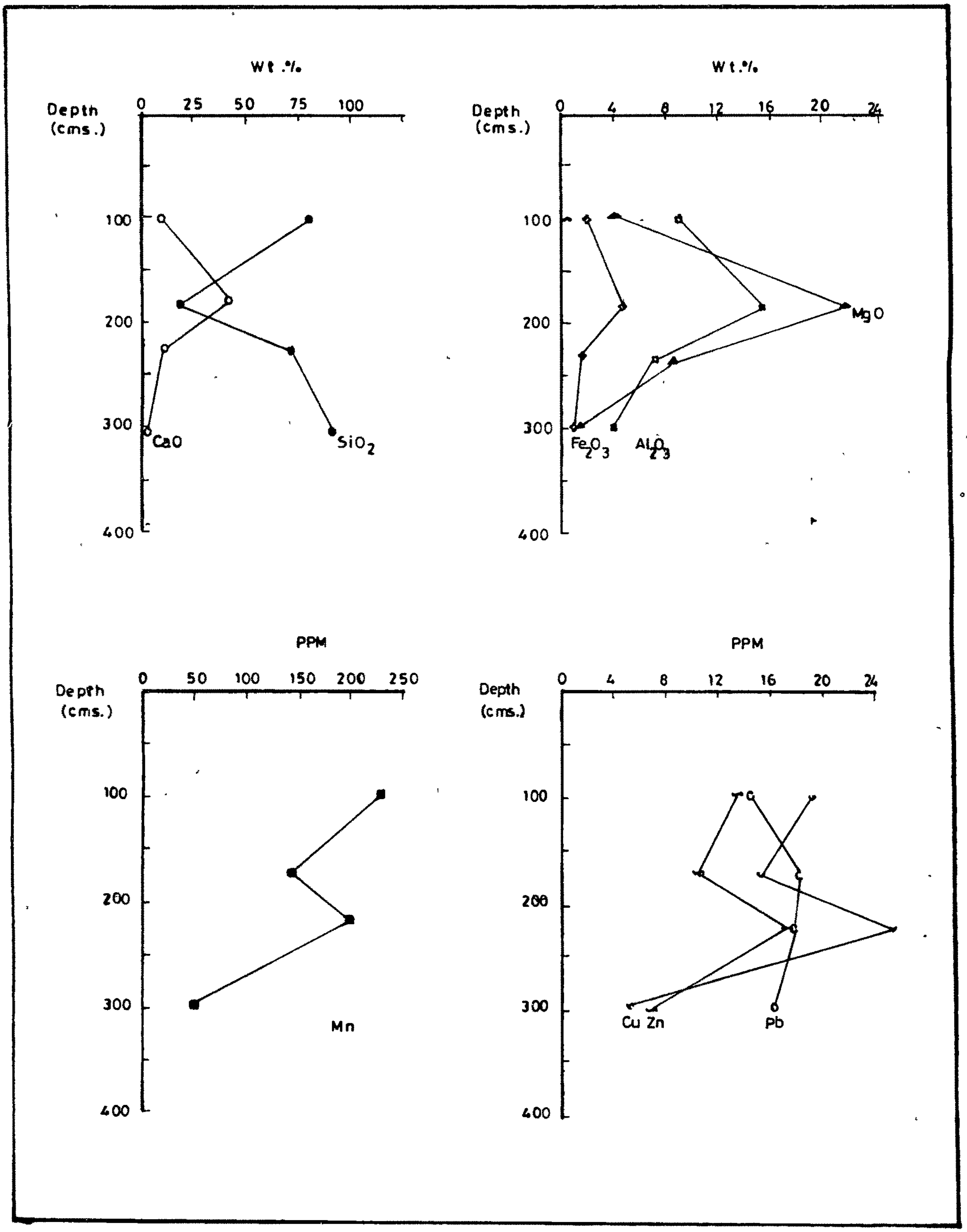


Fig. 4.3-D Major oxide, trace element chemistry – Sardarsahar profile.

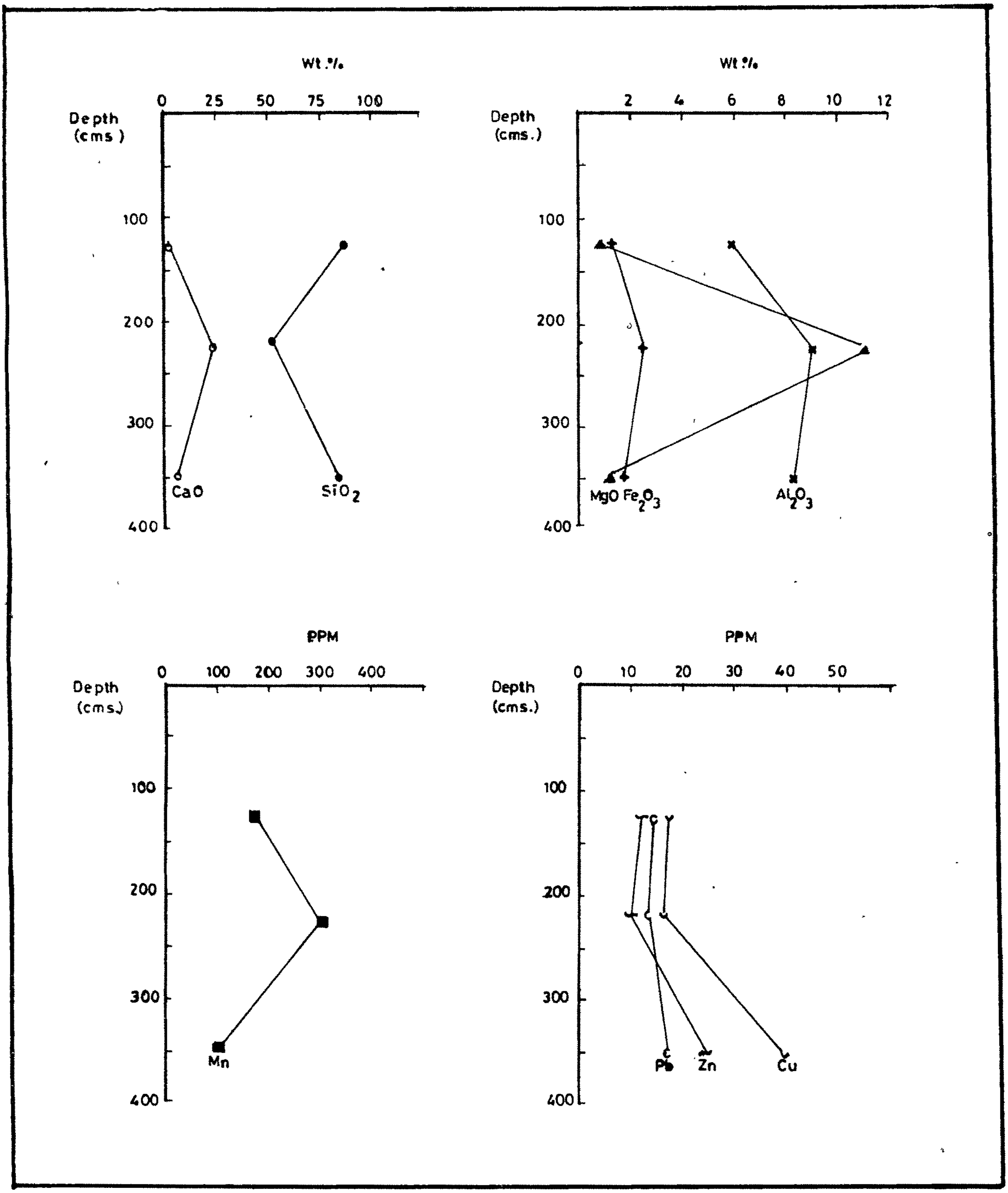


Fig. 4.3-E. Major oxide, trace element chemistry — Bhaleri profile.

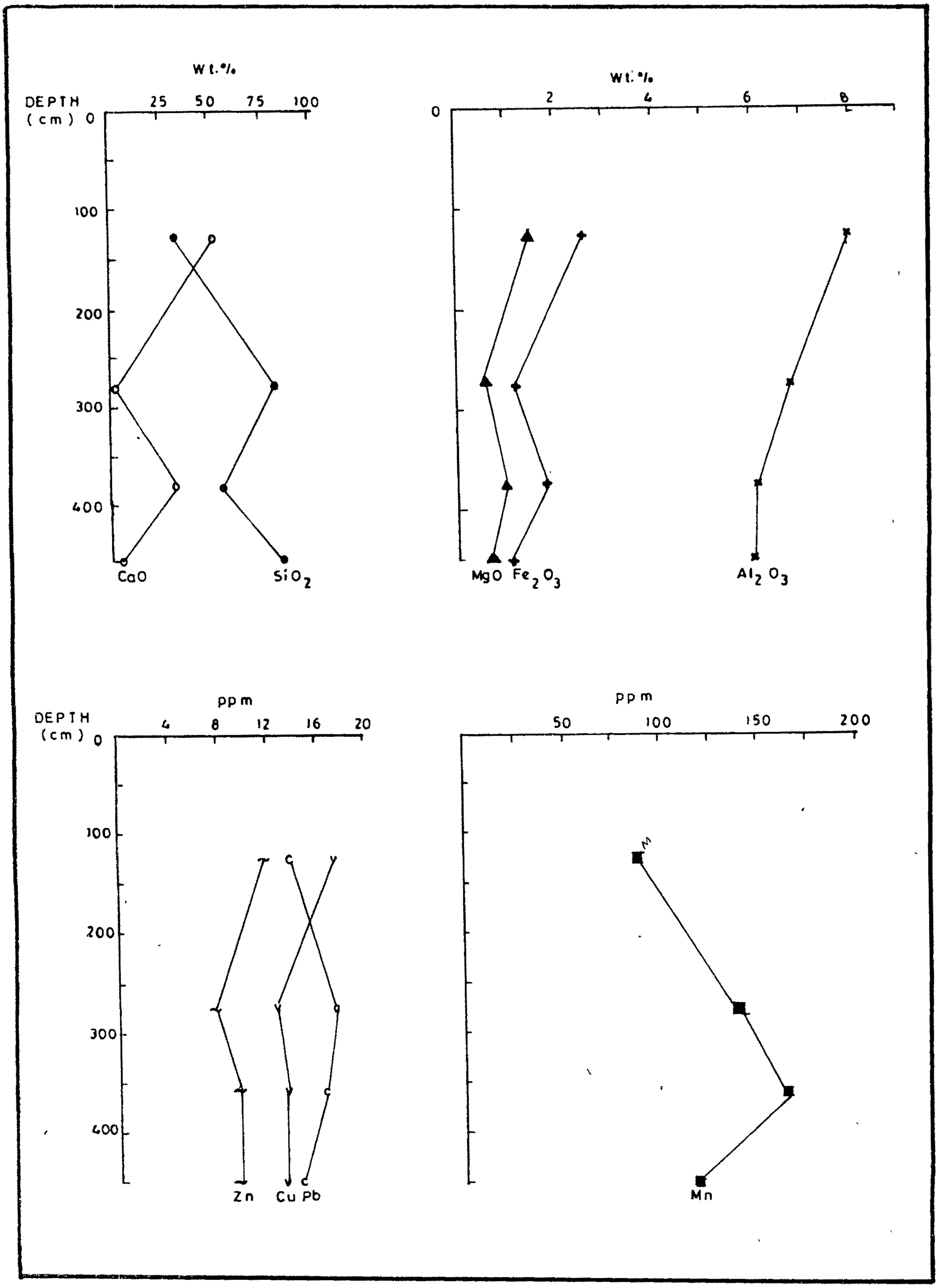


Fig. 4·3-F. Major oxides, trace element chemistry – Belwa profile.

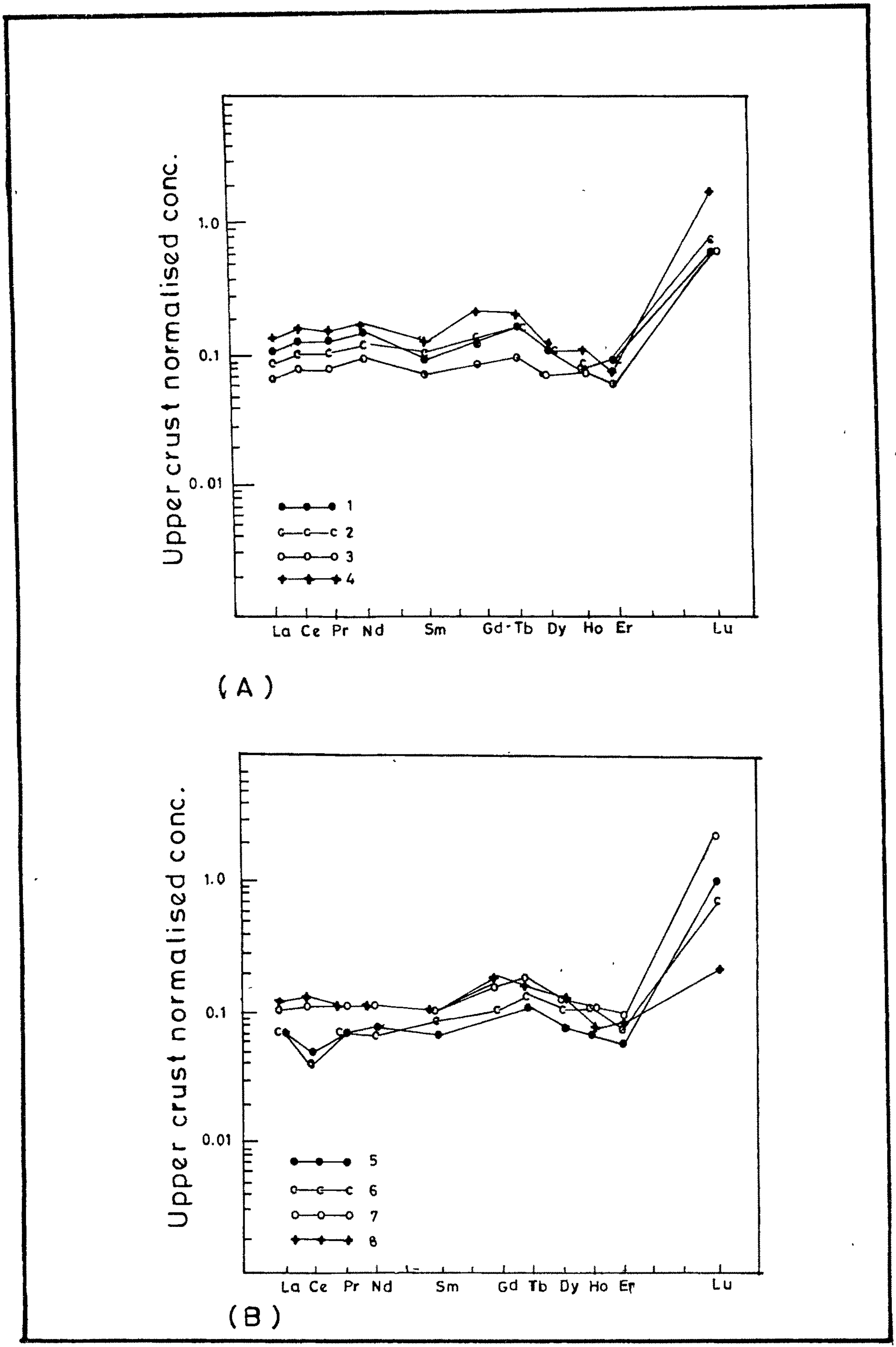
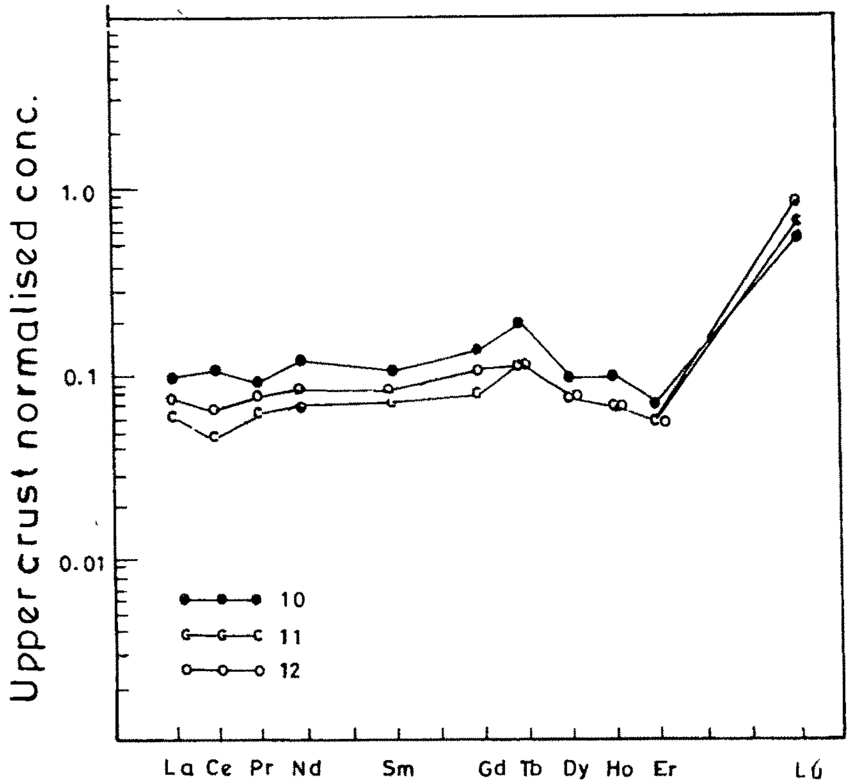
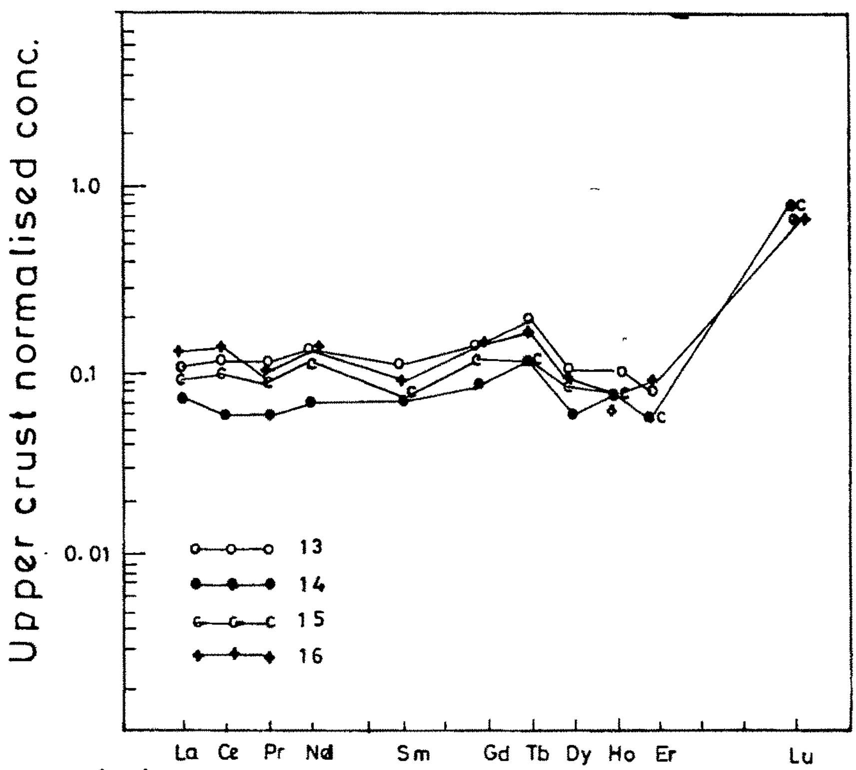


Fig. 4.4. REE Geochemistry. A - Dhanola profile, B - Raneri profile.



(C)



(D)

Fig. 4.4. REE Geochemistry C – Surpalia profile, D – Sardarsahar profile.

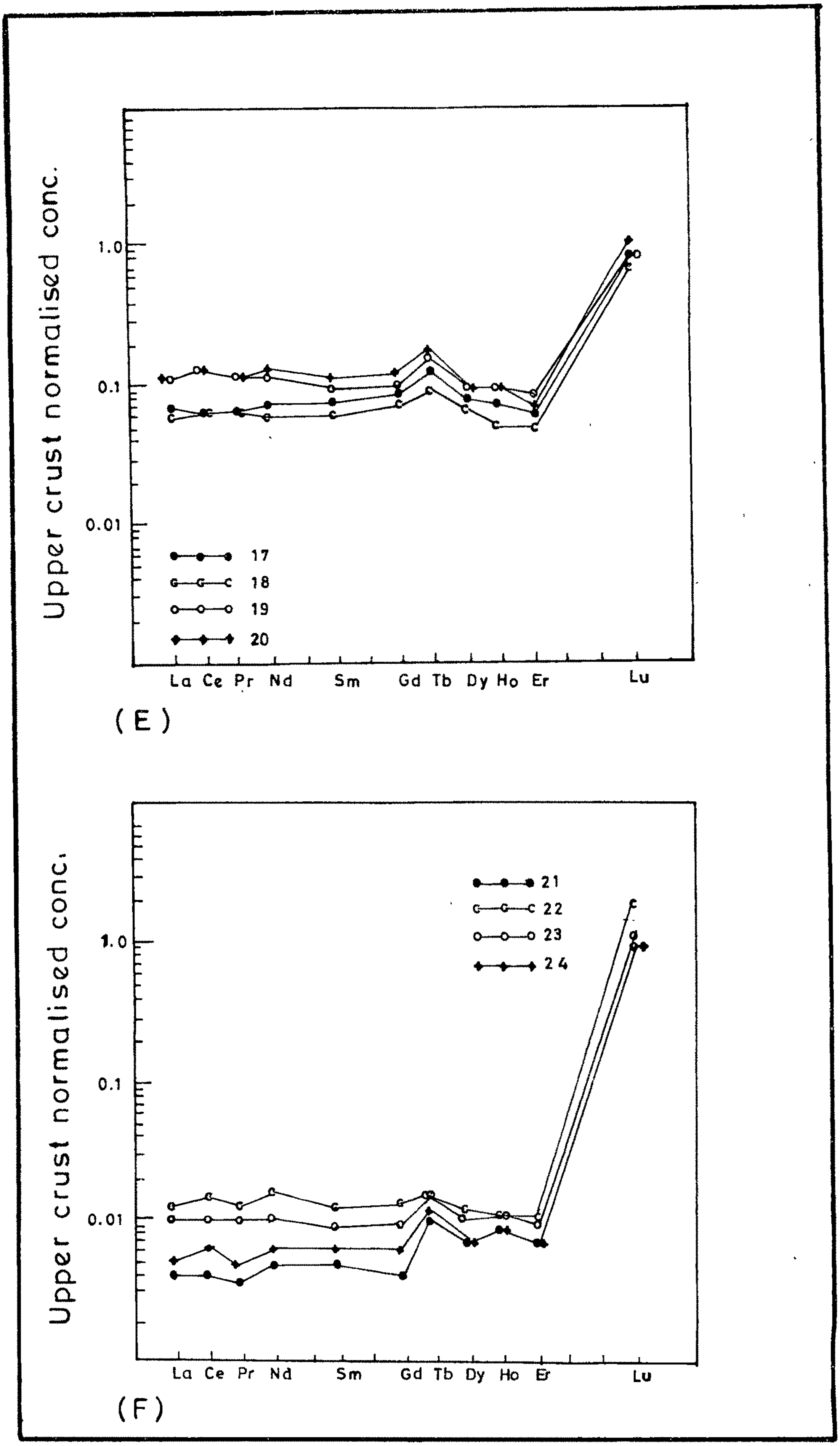


Fig. 4.4. REE Geochemistry, E-Bhaleri profile, F-Belwa profile.

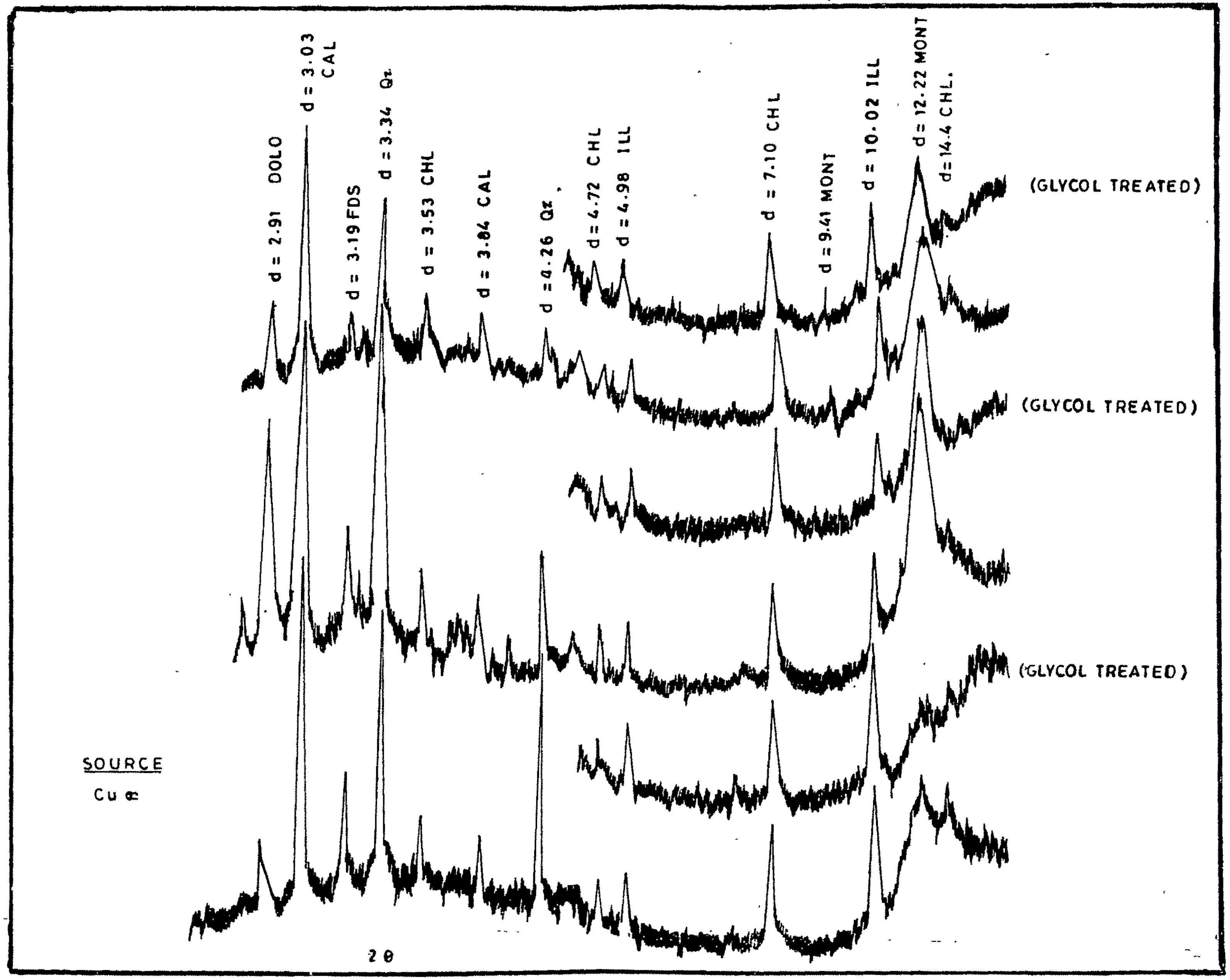


Fig.4.5-A X-Ray diffractogram – Dhanola profile.

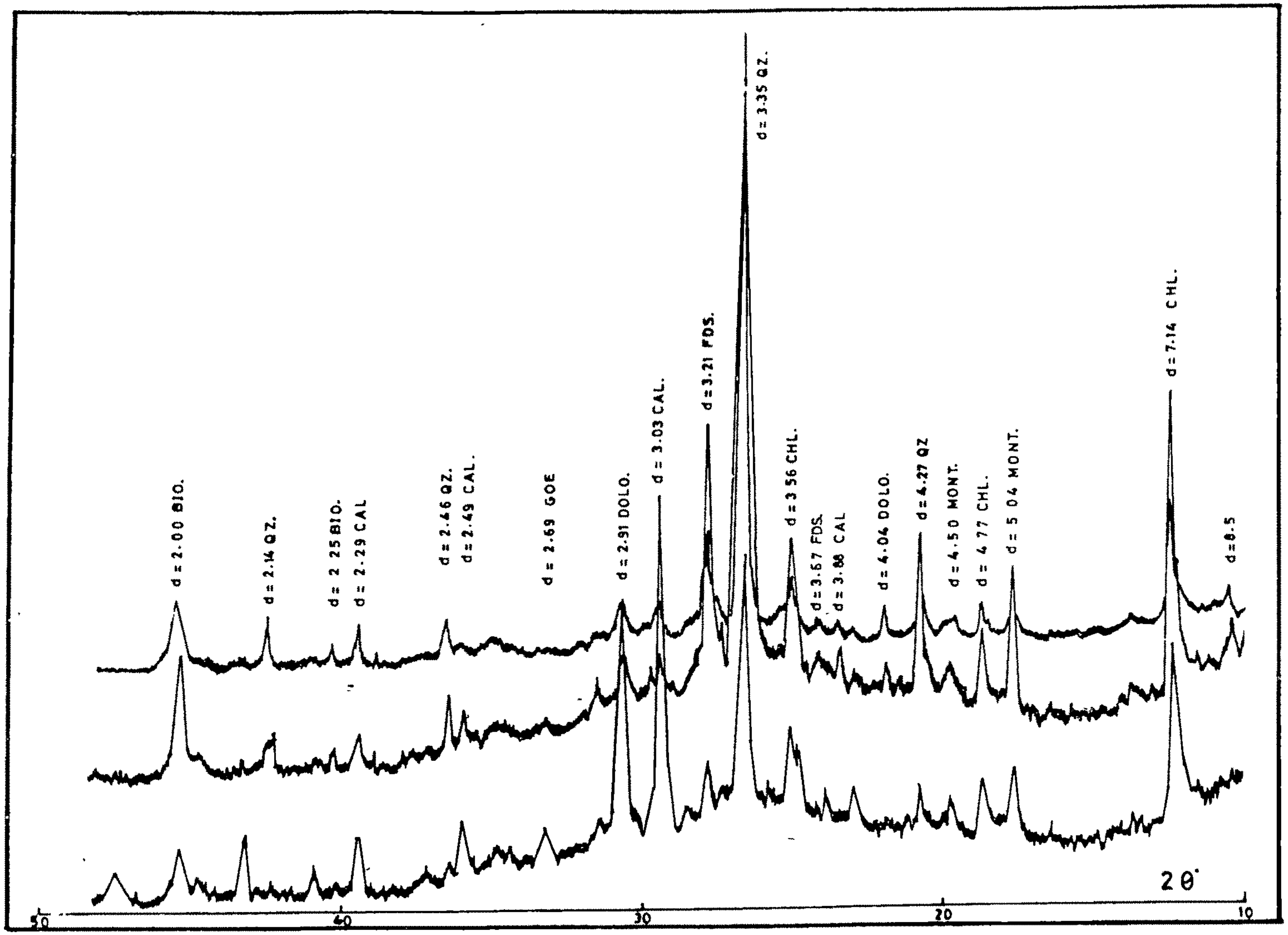


Fig. 4·5-B. X-Ray diffractagram.-Sardarsahar profile.

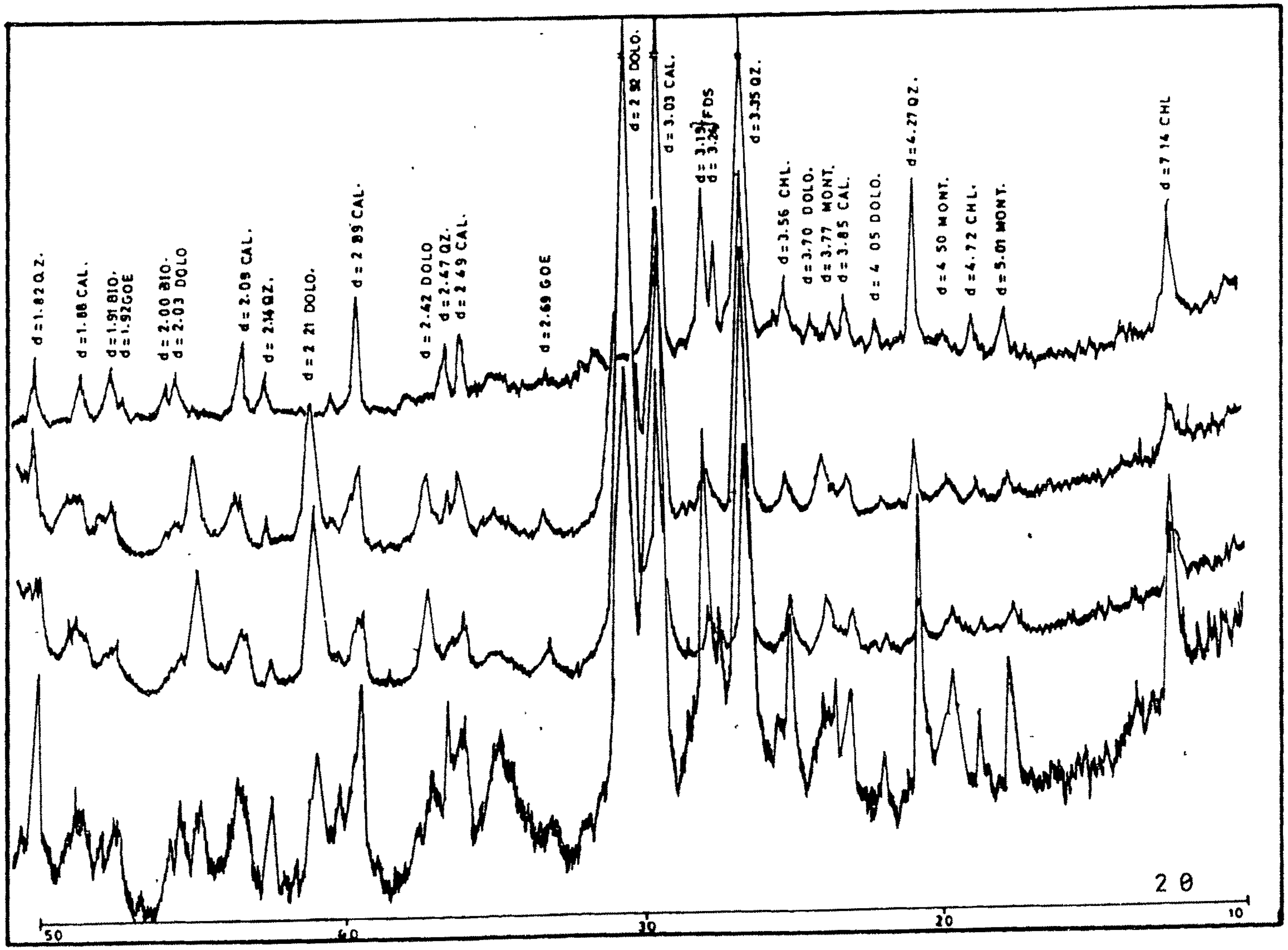


Fig. 4·5-C. X-Ray diffractogram – Bhaleri profile.

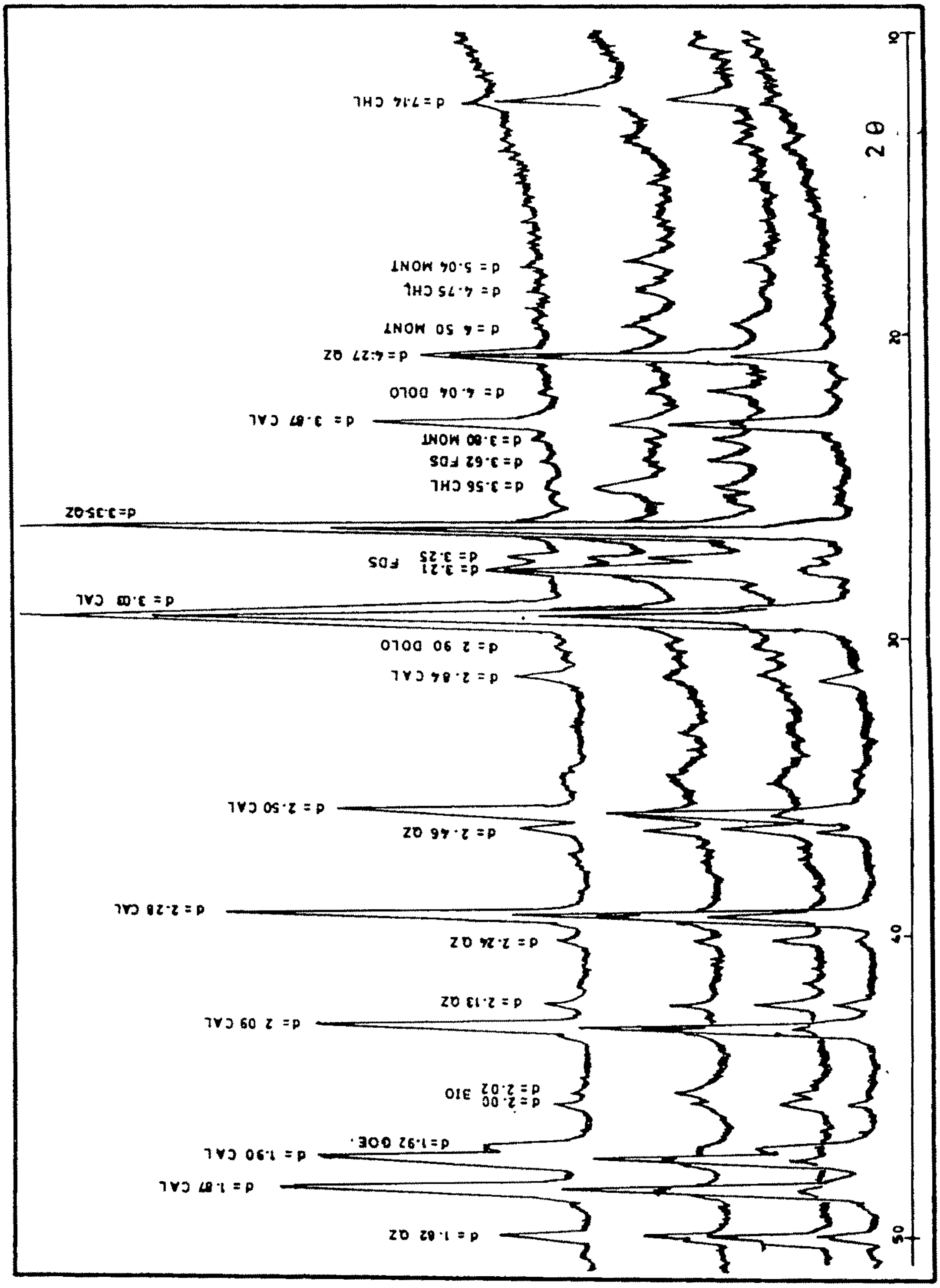


Fig. 4.5-D. X-Ray diffractogram - Belwa profile.

Location	Horizon	Mineralogy (%)								
		Ch	**Mont.**	**Ill.**	**Q.**	**F**	**Cal.**	**Dol.**	**Bio**	**Goe.**
Dhanola	Bt	15 3	11.8	10 9	21 4	5.26	23 6	6.1	----	-----
	Bc	18 2	11 2	9.6	30.4	9.9	30.4	13.8	-----	-----
	C	19 2	4 2	11.8	30 5	6.7	23 2	4.2	-----	-----
Sardarsahar	Bk	18 9	6.4	-----	22.9	2 7	29.0	14 4	4 5	1 6
	Cc	21.4	9.8	-----	39.0	14 0	5.4	4.0	6.7	-----
	C	15.5	5.8	-----	54.0	0.2	5.5	5.5	6.0	-----
Bhaleri	Bt	9 2	10.2	----	25.0	10.0	20.8	20.5	3.7	-----
	Bc	5 3	4.6	----	22.0	2.5	20 8	40 7	3 6	1 2
	K	5 2	5.2	----	19 7	1 8	20.5	42.2	3 6	1.5
	C	10 0	6 3	----	39 8	11 6	30.0	-----	4 2	-----
Belwa	Ac	-----	-----	-----	22.8	2 4	70 5	-----	4.3	-----
	B	4 3	6.0	-----	51 3	14.8	14.6	4.6	2.9	-----
	Bc	8.8	3 3	-----	37 2	8 2	38.3	1.2	3.0	-----
	K	1.3	-----	-----	28.2	3.4	63.9	-----	3.3	-----

Ch. - Chlorite, Mont - Montmorillonite, Ill - Illite, Q - Quartz
F - Feldspar, Cal. - Calcite, Dol - Dolomite, Bio. - Biotite
Goe - Goethite.

TABLE 4.8 SEMI - QUANTITATIVE MINERALOGY OF CALCRETE PROFILES

OXIDATION STATES OF IRON IN CALCRETE PROFILE

Since, the state of iron is found to be varying widely within the calcretic profiles, Mossbauer analysis of the calcretic profiles have been carried out. The Mossbauer spectra reveal two doublets, there by indicating the existence of two states of iron However, the observed Isomer Shift for all the samples ranges from -0 3 to -0 6, indicating that the iron is present either in ferric (Fe^{+3}) form or a higher charge state Further, the absence of magnetic hyperfine spectrum in the samples point to the occurrence of iron as hydroxide or as carbonate than that of oxide state The percentage absorption of gamma rays is approximately 1%, a feature pointing that Fe is not tightly bound and doesn't enter into the lattice of crystal structure Comparison of electrical field gradient for the two quadruple splittings of the calcretes to the calculated electric field of Al_2O_3 (Trigonal and Hexagonal forms) ensures that if iron is of the Fe^{+3} form then it shows affinity to Al^{+3} and if higher charge state of Fe is avaliable then it goes to Si^{+4} site. The implications and relative affinity of Fe^{-3} vis-a-vis microenvironment regime are discussed in the following pages

WEATHERING AND NEOFORMATIONS

The detailed micromorphological studies of calcretes clearly indicates the different stages of mineral weathering (micas, pyroxenes, amphiboles, feldspars, quartz) and neoformations with the maturity of calcretes from simple calcified soil to the hardpan calcrete Weathering of iron bearing minerals (micas, pyroxenes, amphiboles) begin with a simple bleaching of colour in the early stages of calcretization

The next stage of weathering is manifested by the migration of reddish-brown ferrugenous clay into the fractures and cleavage planes of the pale coloured detritals In the final stages of weathering, the reddish-brown clay form an halo around the completely altered grains (Plates 4 9 A, 4 12 A) Migration of these reddish clays in to the soil and their incorporation into b - fabric is also evidenced.

Electron probe micro analysis (Cameca, XL50, France) of the core and periphery of such an insitu weathered biotite grain (Figure 4.6) revealed the enhancement of Si, Al, Ca, Mg, Na and K in the periphery of the grain in contrast to the central altered part.

In feldspars, alteration starts along the cleavage planes resulting in the formation of pale white clay Further stages of weathering are observed by means of etching, dissolution (Plate 4 12 B) and the introduction of displacive spars. Weathering of quartz detritals are manifested primarily through etching , corrosion , dissolution (Plate 4 12 C) and by displacive spars along the grain boundary or fractures.The author also observed the catalytic action of the ferrugenous clays in the dissolution of quartz.

GENESIS OF CALCRETES

The detailed micromorphological studies coupled with the field observations enabled the author to sequentialize the various developmental stages of calcretes. Influence of geomorphology i.e by way of changes in the textures of the solum are evidenced to have great bearing in overall mechanism of calcretization Periodic water logging or role of groundwater are also evidenced to have an impact on the accumulation of carbonates in some cases. Hence, taking into account these two criteria, the author has differentiated the calcretization processes under two categories viz.

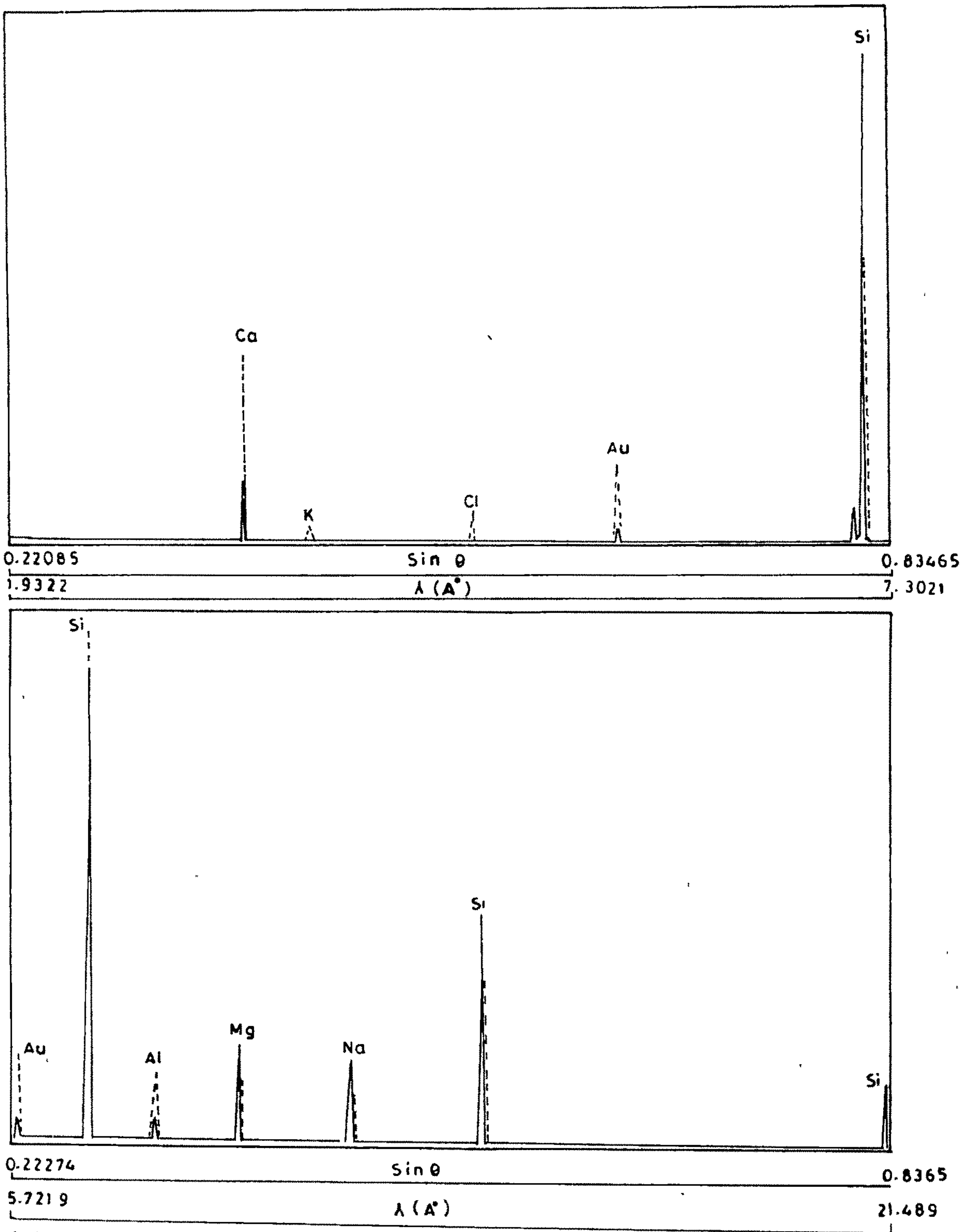
I Calcretization in dunes and interdunal plains characterized by fine textured soils.

II Calcretization in alluvial plains, buried pediments, interdunal plains characterized by coarse textured soils.

I. CALCRETIZATION IN FINE TEXTURED SOILS

The schematic diagrams (Figure 4.7) explaining the different stages of calcretization of fine soils can be explained by following stages.

Stage 1 Marked by a predominantly structureless dune sand with biogenic activities and feebly developed, A - horizon



Peak Intensity

Elements	Core	Periphery	Ratio
Si	340	667	1:1.96
Al	16	93	1:5.81
Ca	45	171	1:3.80
Mg	70	96	1:1.37
Na	62	72	1:1.16
K	—	13	—

——— Core of the grain
----- Periphery of the grain

Fig.4.6. EPMA Spectra of an insitu weathered biotite.

Plate 4 12 Photomicrographs of calcretes depicting

(A) Insitu weathering of mica and incorporation of neoformations into the b- fabric A common feature in the early stages of pedogenesis.

(B) Altered, dissolved feldspar detrital with retention of twin lamellae - a feature of insitu weathering

(C) Etched, corroded and dissolved quartz detrital in a micritic groundmass indicating high alkaline soil- microenvironment

(D) Argillic cutans, an ideal feature of clay illuviation

(E) Bow shaped features (Bullock et al , 1985) suggestive of intense pedoturbation.

(F) Insitu fractured quartz detrital caused due to high soil temperature gradient.

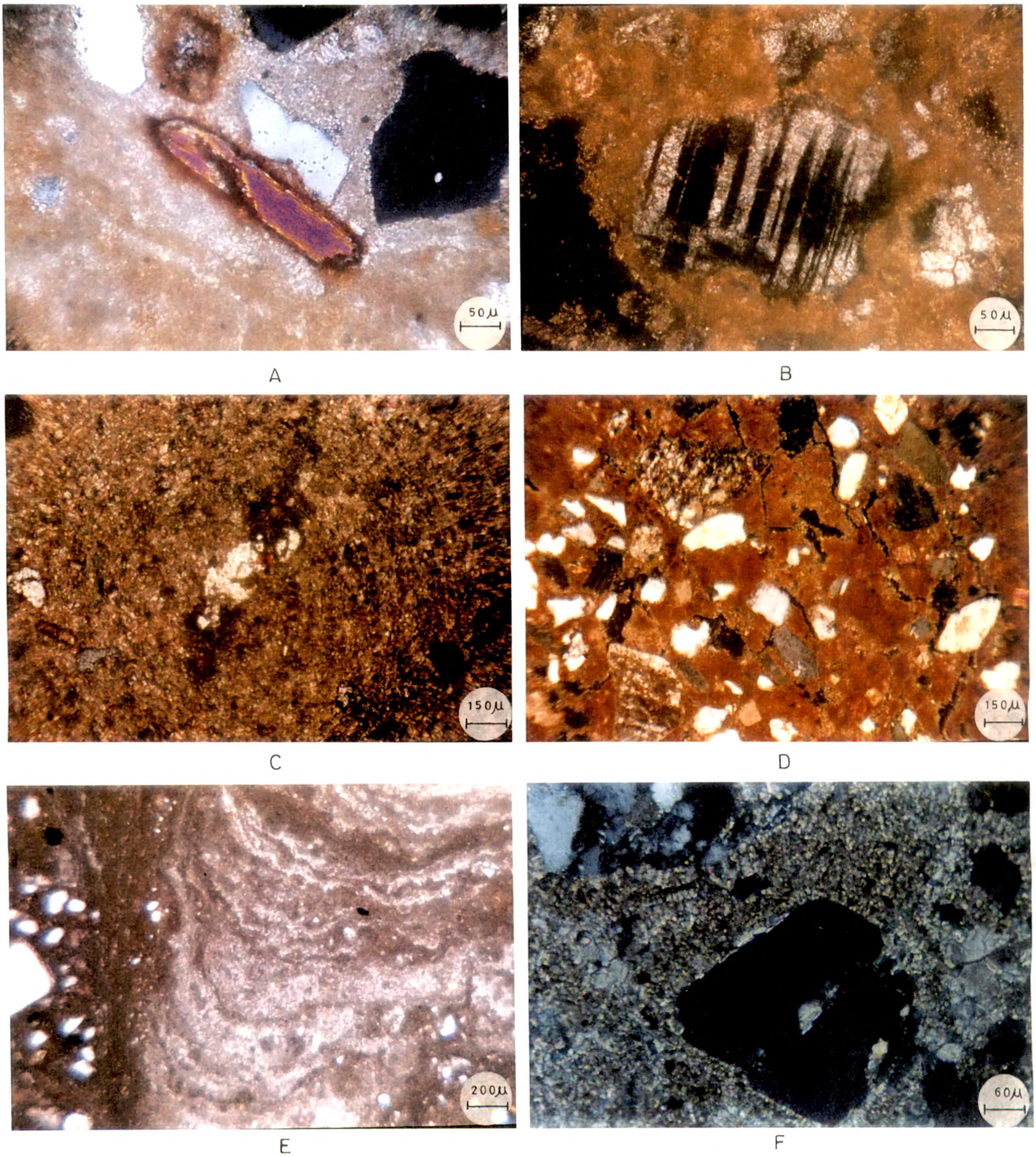


PLATE 4.12

Stage 2 In this stage lime precipitations as drussy micrites is observed as coatings along the biogenic channels, voids and pore spaces just below the A- horizon. The fabric of the solum is entirely calciacepic. Thus, micritic channel coatings and calciacepic fabric are the representative of the first stage of calcretization in a horizon occurring just below the A-horizon, designated as Bc horizon (Wider and Yaalon, 1982, Courty and Federoff,1985).

Stage 3 By way of carbonate accretion and neoformations (Sehgal and Stoops, 1972), coatings and hypocoatings fuses to form a dense diffuse seggregations The fabric of the soil is heading towards crystic with the developments of intercalary crystals The microporosity of the Bc horizon is reduced further by way of carbonate impregnations

Stage 4 Further due to neoformations and addition of lime from the upper horizons, the lower parts of the Bc horizon develop into a dense, discrete nodules with the original soil fabric (orthic nodules). However, in the upper parts of the Bc horizon, the diffuse nodules dominate With further biogenic activities, one more horizon with calcitic features resembling stage I develop in between A and Bc horizons designated as Ac horizon

Stage 5 is marked by the coalescing of the nodules in the basal parts of Bc horizon This horizon is characterized by type IV nodules and in accordance to pedological terms can be designated as Bk horizon The Bc horizon is strongly crystic with the development of dense, discrete nodules. Ac horizon is characterized by the development of soft, diffusive nodules.

Stage 6 comprises well lime impregnated K-horizon (Gile, 1965) with strongly crystic fabric Calcicutans and type IV nodules are also common In the interdunal areas, occasional water logging is evidenced by the iron impregnations and type V orthic and disorthic nodules. The other horizons include Bk, Bc and Ac (with dense discrete nodules) At this stage feeble calcification is also evidenced in the C horizon by way of high soil moisture regimes at depth.

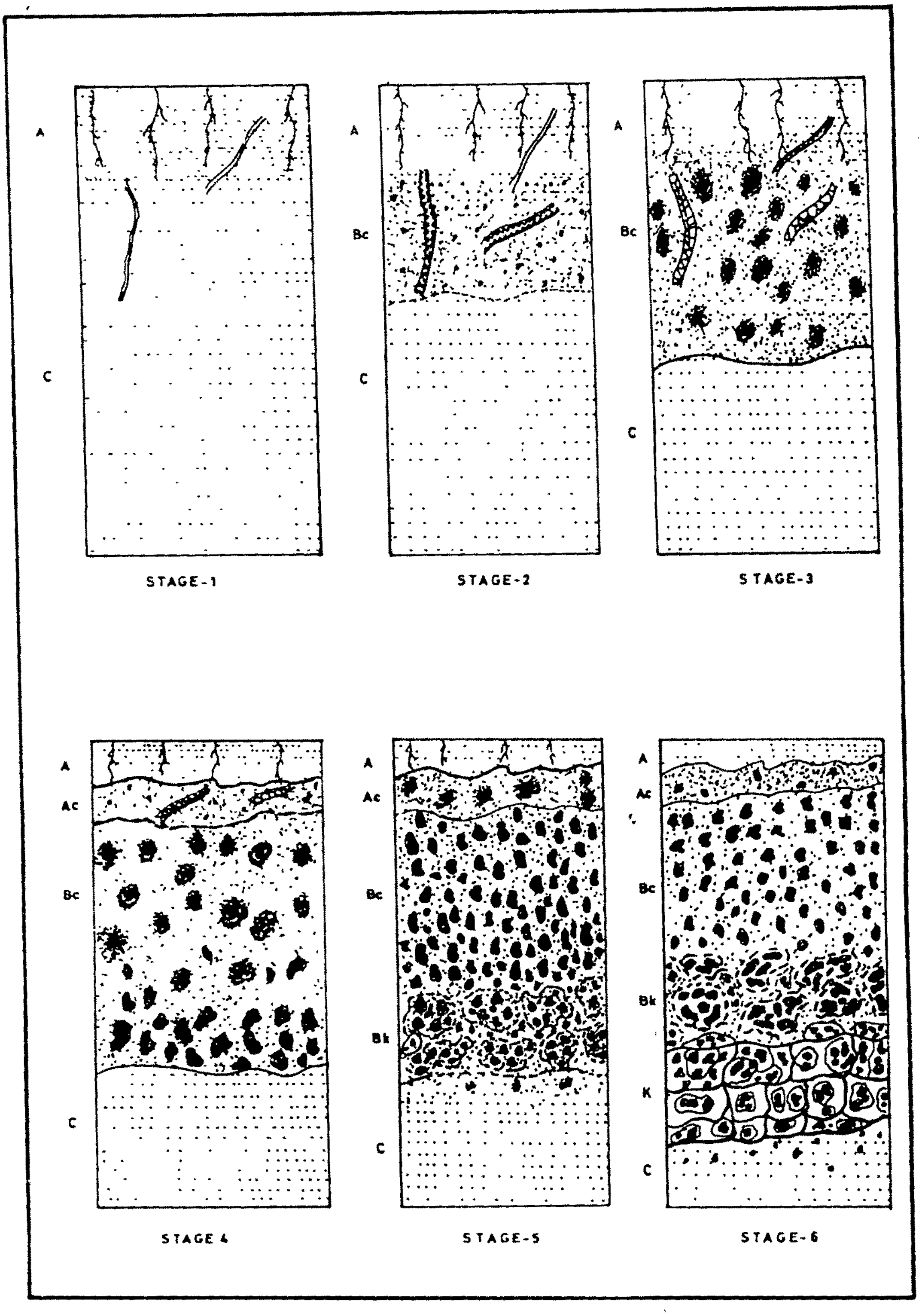


Fig.4.7 Stages of calcretization—Fine textured soils.

II. CALCRETIZATION IN COARSE TEXTURED SOILS (FIGURE 4.8)

Stage 1 Invariable presence of thin aeolian cover forms in most of the coarse textured soils as A - horizon with the underlying coarse gravel or gravelly sand or coarse sand representing the C - horizon

Stage 2 Akin to the fine textured soils, the first stage of development of calcitic features are micritic coatings of channels and calciacepic fabric. However in the coarse textured soils microsparites and occasionally sparites marks the beginning of calcretization in contrast to the fine textured soils owing to the availability of space for the growth of crystals

Stage 3 This stage is marked by the development of poor Ac horizon with a diffuse nodules in the fine textured soil. The coarse textured soil with further lime impregnation decrease in porosity and segregation of fabric is observed, i.e Bc horizon In the C horizon neoformed calcites are mostly microsparites in contrast to the sparites of the first stage of lime accumulations. Lime contribution from groundwater in low lying areas is evidenced by way of clear maturates, needle fibers and meniscus cements.

Stage 4 is marked by development of discrete, dense nodules in Ac horizon. Bk horizon is characterized by compound nodules comprising small dense nodules similar to fine textured soils within a crystic fabric. This stage comprise two generations of sparite i.e the relics of the first stage and neoformed sparites of this stage The K - horizon comprises the pedogenic lime accumulations along with groundwater precipitations.

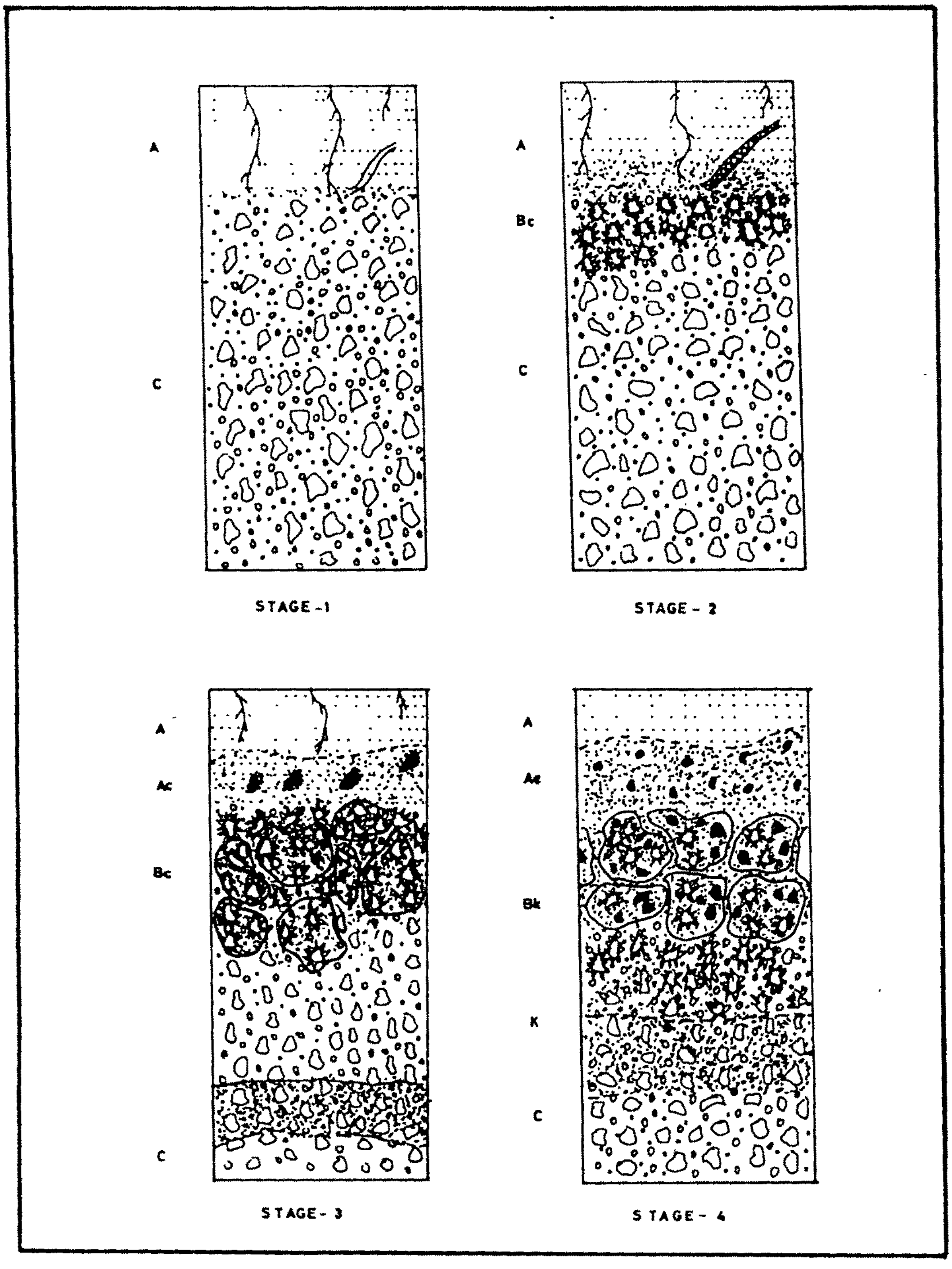


Fig. 4·8· Stages of calcretization – Coarse textured soils.

DISCUSSION

From the foregoing account on the distribution pattern, nature of calcrete profiles, compositional parameters, mobility and enrichment patterns the following conclusions can be made

1 In contrast to the prevailing views on the calcretization processes (Raghavan, 1987a) the author attributes the control of geomorphology, solum and role of ground water during the calcretization. The pedogenic processes are dominated in the fine textured soils of dunes and interdunal plains, akin to the observations of Wider and Yaalon (1982) However, the coarse textured soils of the buried pediments, interdunal flats and alluvial plains besides pedogenesis, the role of groundwater is also clearly evidenced by the presence of needle fibers, meniscus cement, floating textures (Braithwaite, 1983)

2 Presence of colluvial, fluviatile layers in the dunal sequences (at Tej singh Dhani, Shergarh Trijunction and Belwa) are clear indications of break in the dune accretion. Even within the complete aeolian sequences, the author has established (Ramakrishnan and Tiwari, 1996b) at least three phases of dune building activities and subsequent stabilization by way of the occurrence of allothic nodular calcretes at different layers of calcrete profiles

3 While in the fine textured soils drussy micrite marks the beginning of calcretization, in coarse textured soils sparites and microsparites which appear at the initial stages of calcretization due to high porosity Sehgal and Stoop's (1972) generalization for the appearance of sparites in the final stages of calcretization can thus be applicable to the fine textured soils only On the contrary in the coarse textured soils sparites appear first, with the micrites and microsparites and again sparites at the final stages

4 Presence of ferrugenous clay as coatings around the skeletal grains and channels in the B - horizons can be attributed to clay illuviation (Plate 4 12 D) (Yaalon, 1971) . Insitu weathering of iron bearing minerals, (a feature commonly observed in nodular calcretes) and the incorporation of resultant neo - formations into the b-fabric strongly suggest pedoturbations (Federoff, 1969). The authigenic nature of the clays and iron pigments are further evidenced from

a) Iron impregnations in b-fabric, and orthic nodules

b) Ferrugenous clayey halo around weathered detritals.

Etching, corrosion, dissolution and displacive introduction of calcite into the skeletal grains can be attributable to either high alkaline (Brantely et al , 1986) or by complex organic acids (Huang, 1972) under an elevated soil moisture regime (Sharma and Tandon, 1983).

5 Occurrence of wide variety of pedogenic carbonates in contrast to a few non pedogenic carbonate forms point to the dominance of pedogenic mode of calcretization in the coarse and fine textured soils.

6 In general, the geochemical analyses of calcrete profiles (Figures 4 3 A - F) indicate the accumulation of CaO at the Ac, Bc and K horizons with a sharp decrease in the percentages of silica. The correlation matrix of the major oxide chemistry (Table 4.5) also point to a negative correlation of silica with alumina, iron, calcium and magnesium within the calcrete profiles. This feature can best be correlated to pronounce displacive and /or replacive actions of calcites during the matured stages of calcretization (Aristarain, 1970) The clear increasing behavior of alumina, magnesia and manganese in the palaeosol horizons (at Dhanola, Raneri and Bhaleri) are the evidences of a possible reducing environment caused due to the increase in humic acids or a poorly drained conditions or high alkalinity (pH > 8) (Watts, 1980, Braithwaite, 1983, Meyer and Guillet,1980; Meyer,1997)

Meyer, (1997) attributed enhancement of Mn within the soil profile as Mn^{+3} in the upper oxidizing environment or as Mn^{+2} state in the lower reducing, acidic or poorly drained parts. Such enhancement of Mn is also observed in Dhanola and Sardarsahar profiles Microscopic evidences also support the accumulation of Mn at these horizons as an opaque dendrites within these profiles

The Mossbauer spectra clearly point to the existence of iron in the profile as Fe^{+3} and in higher energy states. Hence, the minor variations in iron content in the upper parts of the calcretic profiles owe principally to clay illuviation as an adsorbed ion. However, micromorphic observations have revealed occurrence of iron in soluble ferrous forms by means of ferroan calcites, translucent iron impregnations, and incorporation of mobile reddish-brown iron (by b-fabric) released from the weathered biotites. Thus in the palaeosol horizons (Dhanola, Raneri and Bhaleri) and lower horizons of Surpalia, Belwa profiles their existence in ferrous forms could be attributed to reversal of ferric iron to ferrous forms caused by the low pH values generated by organic acids or due to reducing conditions during short periods of water logging or both (Watts, 1980; Sharma and Tandon, 1983; McFarlane, 1983; Meyor, 1997). Mobility of other trace elements viz Pb, Zn and Cu within the calcrete profiles still remain perplexing and in general (but for Zn) have a negative correlation to the mobility of Mn.

The author has also evidenced the fractionation and mobilization of different Rare Earth Elements (REE) with in the calcrete profiles (Ramakrishnan and Tiwari, 1996d). Before going into the details of REE fractionation and mobilization during calcretization, an understanding of their concentration in the source sediments is necessary. As the dunal sediments are of local provenance (Chaudhry and Khan, 1981; Wasson et al., 1983; Raghavan , 1987), the REE composition of the source sediments are homogenous even in the case of multiphase dune building processes The common provenance of the sediments within the profiles are also evidenced from the similar upper crust normalized REE patterns. It is now apparent from the foregoing results (Figures 4.4 A - F; Table 4.4) that REE shows fractionation and mobilization within calcrete profiles. From the detailed analysis of above mentioned results, mineralogy, and micromorphology three major factors are found to have bearing on the fractionation and mobilization of these elements.

(A) Pedogenesis (soil forming processes) liberates element from their parent minerals

(B) Transport of water soluble / suspended REE compounds at low concentrations during short periods of wetting and water logging (Smedley,1991).

(C) The clay minerals that change in response to pH and Eh determines the accumulation and retention of REE elements by way of adsorption (Duddy,1980)

Weathering of hornblende, biotite and feldspars in these profiles varies from simple bleaching in colour to complete alteration to clay (mainly montmorillonite, Illite). Generation of Fe-Mn oxyhydrates (after biotite, hornblende) and their mobility within the profile is also well established (Ramakrishnan and Tiwari, 1996b), REE in general have greater affinity for adsorption with the colloidal materials, in particular Fe-Mn hydroxides (Haskin et al., 1968; Varshal et al., 1975).

The clay minerals especially, vermiculite and montmorillonite, Fe-Mn hydroxides, relics hornblende and biotite have sites preferentially to take HREE while kaolinite and illite better accommodate the light LREE (Nesbit 1979). High proportions of illite at Dhanola and Montmorillonite at Raneri, Belwa, Surpalia and Sardarsahar confirm the above view. Regarding the mechanism of REE fixation in clays it is considered that the REE first adsorb with the clay which is, subsequently fixed and absorbed in the clay structure in acidic conditions (Bolt et al., 1976). Seasonal wetting and drying of clay minerals, which is well documented in the study area (Joshi et al., 1982) also aid in REE fixation in clays (McKenzie, 1963). REE solubility is also strongly controlled by pH and Eh. In solution, they tend to be more a complex ions than free ions. In near neutral and alkaline conditions they predominantly complex with carbonate and bicarbonate anions. In acidic and reducing conditions they complex with sulphate anions (Goldstein et al., 1988;

Wood, 1990) Thus the REE depletion observed in the palaeosol horizons of Dhanola and Belwa could be ascribed to the removal of REE in solutions under the influence of reducing, acidic conditions caused by organic acids The enrichment of REE in the bottom layers (below palaeosol) may be due to the change in the pH heading towards near neutral or alkaline conditions (Sklyarenku,1953)

The correlation matrix (Tables 4.6, 4.7) of both fine textured and coarse textured soils point a strong statistically significant relations among the LREEs viz. La, Ce, Pr However, MREE and HREE doesn't show any significant interrelationships Similar trends are observed between dunal and interdunal profiles with a difference that negative correlation is observed between Lu and Er Multivariate regression analyses of the REE's with depth by profile revealed stastically insignificant relationship among the individual elements. However, as a whole, the mobility of REE's within the different calcrete profiles have statistically significant relation (F = 0 003 to 0 004)

Thus the present study clearly demonstrates the fractionation of REE in general and LREE in particular within calcretic profiles In most of the cases LREE is more enriched than HREE The concentration and depletion of REE in calcretic profiles seems to be influenced by pH, Eh, primary and secondary mineral abundances.

Occurrence or concentration of dolomite is further evidenced with the palaeosol horizons or in B - horizons of dunal profiles or with the K horizons of the interdunal profiles The enhancement of dolomite concentration at these horizons could be due to the incorporation of Mg ion by calcite under a reducing and high alkaline conditions (Watts, 1980, Braithwaite, 1983) Staining by Alizarin Red (Dickson, 1966) of some calcretes (from Bhaleri, Raneri, Belwa profiles) revealed the presence of neoformed calcites within a high magnesium calcitic soil fabric Similar features are also observed by Raghavan (1987b) in some of the calcrete

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
SiO_2	1 0000				
Al_2O_3	- 0 .7059	1 0000			
Fe_2O_3	- 0. 9225	0 8418	1 0000		
CaO	- 0 9380	0 4802	0.7537	1.0000	
MgO	- 0. 5421	0 6287	0.7357	0.2449	1 0000

TABLE 4.5 CORRELATION MATRIX OF MAJOR OXIDES

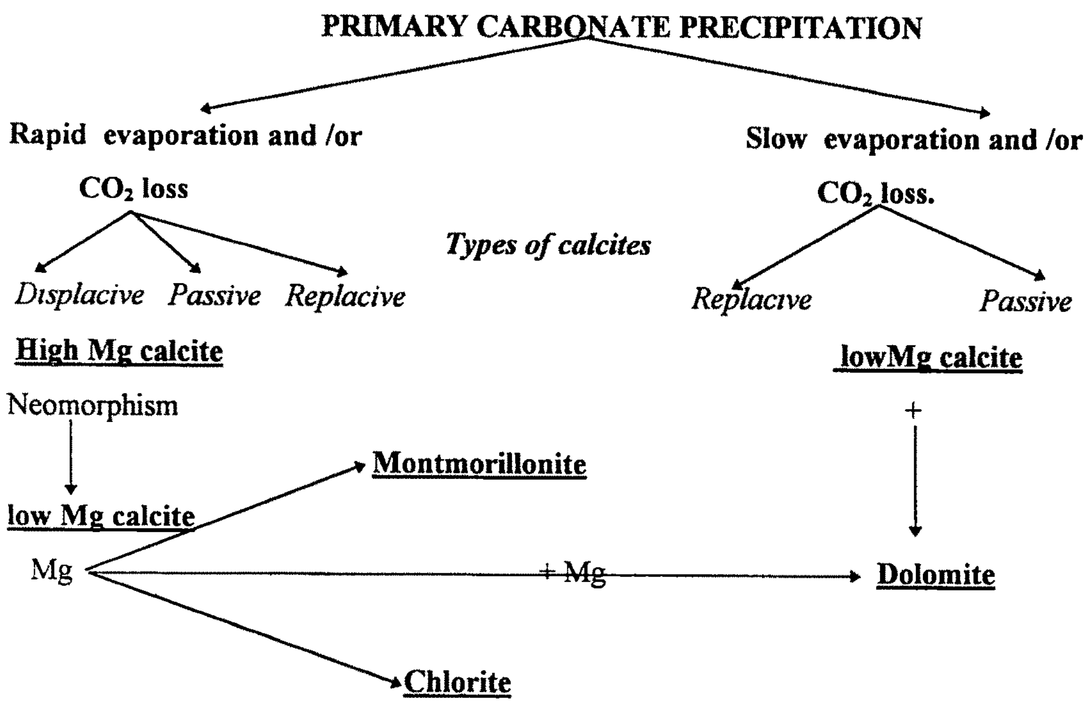
	Pb	Zn	Cu	Mn	La	Ce	Sm	Gd	Tb	Lu
Pb	1 000									
Zn	0 139	1 000								
Cu	0.285	0 610	1.000							
Mn	- 0 010	0 455	- 0.815	1 000						
La	0 405	0.263	0 264	- 0.054	1.000					
Ce	0 437	0.303	0 331	- 0.406	0.960	1.000				
Sm	0 417	0.248	0.285	- 0.056	0.900	0.860	1.000			
Gd	0.336	0.329	0.238	- 0.023	0.740	0.750	0.851	1 000		
Tb	0 394	0.180	0 186	- 0.063	0.750	0.740	0.863	0.834	1.000	
Lu	0 030	0 153	- 0.117	0.185	0.260	0.290	0 364	0 465	0 365	1 000

TABLE 4.6 CORRELATION MATRIX OF REE AND TRACE ELEMENTS

	La	Ce	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Er	Lu
La	1.000										
Ce	0.960	1 000									
Pr	0.999	0 970	1.000								
Nd	0.980	0.970	0.990	1 000							
Sm	0 910	0.880	0.900	0 900	1 000						
Gd	0.760	0 760	0.790	0 800	0.850	1 000					
Tb	0 770	0 760	0.770	0.760	0.880	0.830	1.000				
Dy	0 880	0 810	0 860	0.850	0.940	0 770	0.830	1.000			
Ho	0.600	0.500	0.570	0 570	0.750	0.510	0 670	0.800	1.000		
Er	0.770	0 740	0.740	0.750	0 790	0.500	0.720	0 830	0.720	1.000	
Lu	0 290	0.300	0 290	0 340	0 370	0 480	0 370	0.252	0 470	0 240	1 000

TABLE 4 .7 CORRELATION MATRIX OF REE OF CALCRETE PROFILES

profiles around Nagaur. This feature again point to the release of Mg to the system by dolomite upon recrystallization under an oxidizing, near neutral environment (Watts,1980). Among the clay minerals illite is seldom observed, where as chlorite and montmorillonite, are ubiquitous Sehgal (1972) postulated the possibility of chlorites and montmorillonite derivation from illites under ustic soil moisture regimes. Persistence of illite in the palaeosol horizon (Bt-horizon) of Dhanola profile point to a poorly drained microenvironmental conditions under a possible temperate climatic condition (Meyer, 1997). Choudhari and Dhir (1982) reported the occurrence of inherited smectite, kaolinite and illite within the dunes of the study area. However authors observation points to the predominance of neoformed montmorillonite and chlorite within the soil profiles, probably formed under a near neutral or alkaline environment with the abundance of Ca and Mg. Under similar conditions, presence of K lead to the formation of illites (Grim, 1968). The neomorphic changes within the calcretic profiles of the interdunal areas (where, periods of waterlogging are observed) are summarized in a flow chart as below.



Though different stages of calcretization mark the relative age of soil maturity (Gile 1965), it is often the associated pedofeatures and chronology of weathering of the solum yield better criteria for pedostratigraphic correlations (Finkl, 1984, Birkeland, 1974, Retllack; 1990, Meyer, 1997). Hence, the author has attempted to correlate pedostratigraphic features of soil profiles with similar profiles worked out by others (Courty et al 1986, Raghavan, 1987a; Dhir, 1992,1994; Singhvi et al. 1994). The details of the correlations are dealt separately in chapter 6.

Uncorrected U/Th dates of nodular calcretes from 16R dunal section [ranging from 26 Ka to 390 Ka B.P] (Raghavan, 1987a) and radiocarbon dates from Shergarh trijunction (Dhir,1994) are highly debatable on account of a open soil forming system.

Based on the micromorphological, geochemical and mineralogical studies the microclimatic changes within various soil profiles are attempted and are dealt in detail in Chapter 6, on palaeoclimatic implications. However, the foresaid evidences strongly point to a prevalence of arid, semi-arid climatic regime with minor fluctuations in the climate from temperate (as evidenced by the presence of illite in Bt horizon) to very hot and arid conditions (as evidenced by the insitu fracturing of quartz detritals (Plate 4.12 F) due change in thermal gradients (Verheye,1976) during the development of different soil profiles.

7. The principle source of calcium carbonate for the pedogenic carbonates are attributable to the aeolian sands, that incorporate detrital calcites, calcium rich primary minerals viz feldspars and amphiboles. The limestones of Tertiary age forms one of the major sources of detrital carbonates in dune sediments. The calcium carbonate accumulation in the low lying areas by capillary water can be attributable to water charged with lime or due to lime redistribution caused by dissolution, reprecipitation and recementation.

Based on above studies following conclusions can be derived

1 Two distinct types of calcrete genesis are noticed viz.

a) Pedogenic calcretes associated with dunes and interdunal plains

b) Vadose water calcretes associated with alluvial flats and interdunal plains.

2 Presence of allothic nodules with in the calcrete profiles indicate palaeo surfaces.

3 REE fractionation and mobilization is evidenced within calcrete profiles.

4 Multiphase dune building and stabilization is evidenced.

5 Role of meteoric water or episodes of water logging is observed especially in the alluvial and interdunal flats

6 Besides the pedogenic features REE depletion is also proposed as a chemical criterion for the recognition of palaeosols

7 Mechanism /process of calcretization in coarse textured soils are different from that of fine textured soils.

8 Mineralogy, pedofeatures and geochemistry of calcretic profiles point to a dominant oxidizing alkaline micro-environmental conditions. However, reducing micro environments is also evidenced at depth in the interdunal flats and palaeo Bt horizons.