CHAPTER-2

GEOLOGY, MATERIALS AND METHODS

2.1 Introduction

This chapter deals with geological description of various sedimentary bodies from which samples were obtained for geochemical investigations carried out in the present thesis. Relatively young (~11 to 1 Ma old) soil carbonate nodules were collected from palaeosols of various sections of Indian Siwalik Basin. In addition, carbonate

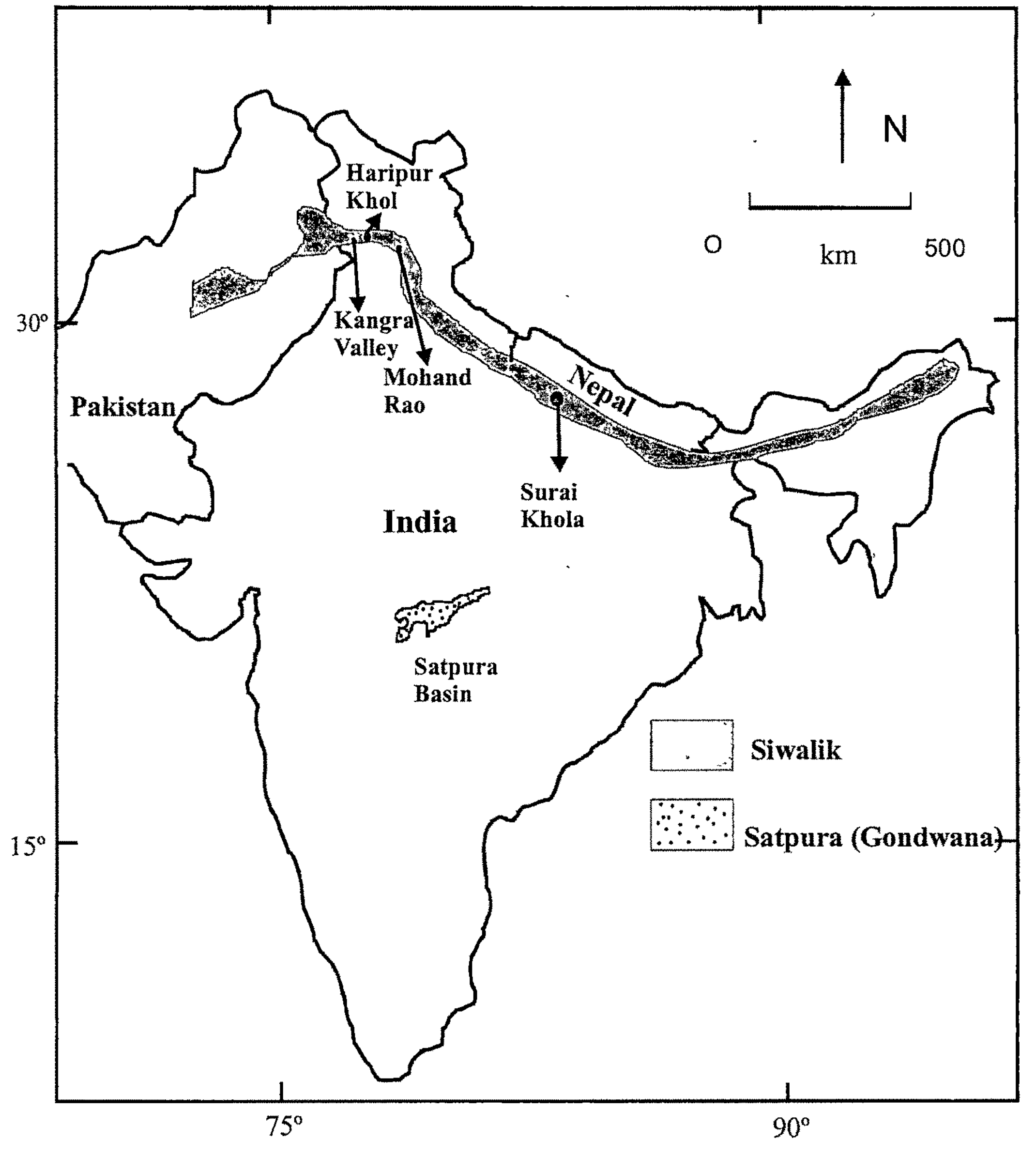


Fig.2.1 *Geographical extension of Siwalik and Satpura (Gondwana) Basins. Locations of different study areas in the Siwalik basin are shown.*

cemented sandstone nodules and sandstone chips (from sheet) were collected. For comparative studies, soil carbonate nodules (~250 to 180 Ma old) from palaeosols of Satpura Basin, Gondwana Supergroup were also collected.

2.1.1 Siwalik Basin

Siwalik sediments were deposited in the foredeep basin created ~20 Ma ago during the last phase of Himalayan orogeny (Johnson et al., 1985). These sediments are dominantly fluvial in nature and are exposed in the southern flank of the Himalaya in a WNW to ESE trending belt (Fig.2.1) in India and Nepal. They are bounded by Main Boundary Thrust (MBT) in north and Himalayan Frontal Thrust (HFT) in south. Near MBT, the Siwalik Group rocks are folded and faulted, but grades southward into flat beds overlain conformably by modern alluvium of the Himalayan Foreland Basin (Karunakaran and Rao, 1979). They are characterized by alternate sandstone and mudstone, and conglomerate and mudstone. The beds generally dip north or northeastward.

The Siwalik basin is divided into a number of sub-basins (Fig.2.2), separated from each other by lineaments (Virdi, 1979; Raiverman et al., 1983). These lineaments are extensions of basement features extending from the Indian shield to the Himalayas. They formed as normal fault during tensional regime and were later reactivated as thrust fault during Tertiary orogeny (Dubey, 1997). These faults not only controlled the thickness of the sedimentary successions but also affected the sedimentation pattern (Raiverman et al., 1983).

The thrust belts are characterized by sinuous traces with alternate re-entrant and salient. For the present study, we chose samples from Ranital and Kotla section of Kangra re-entrant, Haripur Khol section of Subathu salient, Mohand Rao section of Dehra Dun re-entrant (Fig.2.1, 2.2), and Surai Khola section of Nepal Siwalik (Fig.2.1).

2.2 Age of the Siwalik Strata

The ages of the sedimentary succession in different Siwalik sections are determined by magnetostratigraphy in which oriented core samples are obtained from siltstone and mudstone, and directions of remnant magnetization are determined in the laboratory by a magnetometer. Dates are obtained by comparing the composite magnetization direction (normal or reversed) sequence with Standard Geomagnetic

Polarity Scale (GPTS) (Sangode et al., 1996; 1999; 2003, Kumar et al., 1999; 2003a,b; Apple et al., 1991; Gautam and Rösler, 1999). For the Indian Siwalik samples, the dating was done in Wadia Institute of Himalayan Geology. There are several uncertainties associated with the palaeomagnetic dating method (Burbank et al., 1996). The chosen strata may not contain a complete record of magnetic reversal, either due to erosion or sample alteration. It is possible to miss a polarity reversal due to lack of exposure or the

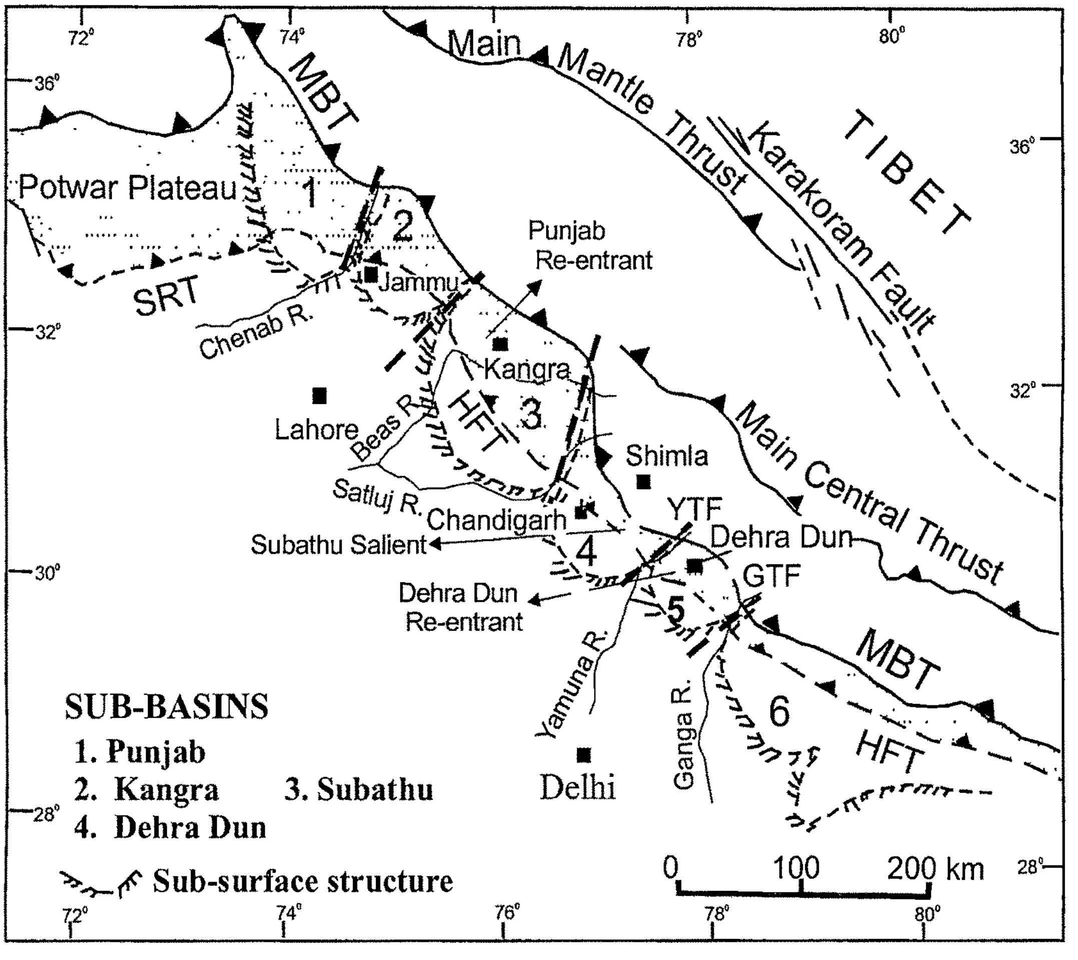


Fig.2.2 *Simplified geological map of Indian sections in the Himalayan Foreland Basin (HFB). HFB is characterized by alternate salient and re-entrant. For the present study samples from Ranital and Kotla section from Kangra re-entrant, Haripur Khol section from Subathu salient, Mohand Rao section from Dehra Dun re-entrant are chosen. (SRT = Salt Range Thrust; HFT= Himalayan Frontal Thrust; GTF= Ganga Tear Fault; YTF= Yamuna Tear Fault).*

positions of reversal boundaries may not be known. In some cases, sediments contain reversals that have no apparent counterpart in the magnetic polarity time scale. In addition, field measurements of stratigraphic thickness introduce uncertainties. It is difficult to estimate the combined error due to these factors but past studies have shown that the total error is typically about 10 % (Burbank et al., 1996). The error in age estimate can be minimized if good correlation to Geomagnetic Polarity Time Scale can be made.

The magnetic reversal stratigraphy was made by using mudstones in Haripur Khol, Mohand Rao, Ranital and Kotla sections. In some cases, magnetic property of fine-grained sandstone was also used to make reversal stratigraphy (in Mohand Rao, Ranital and Kotla sections). The magnetic reversal stratigraphy was correlated with the GPTS of Cande and Kent (1995) to obtain ages of the samples. Along with the stratigraphy based on normal-reversal sequence, magnetic fabrics correlation, fossil stratigraphic control, iterative matching, conformable sedimentation rates in adjacent sections were also considered to constrain the ages of the sediments. In addition, absolute age obtained from dating a volcanic ash was used as a benchmark for correlation with GPTS. A 5 cm thick bentonized tuffaceous bed was discovered at 1650 m level within overbank facies in Haripur Khol section. The volcanic nature of the bed was identified by its gray to grayish black color, presence of euhedral biotite, zircon and high magnetic susceptibility. Fission track dating of zircons separated from continuation of this ash bed from an adjacent section gave an age of 2.5 Ma (Ghaggar river section in Punjab Sub-Himalaya, Mehata et al., 1993), which constrained its magnetic polarity to be benchmarked near the Gauss/Matuyama event.

Ages of the sedimentary successions in Kangra sub-basin range from ~11 to ~6 Ma, in Subathu sub-basin ~6 to 0.5 Ma and in Mohand Rao section ~10 to 4.4 Ma (Fig.2.3). Details of magnetic polarity events, method of deriving the ages and sedimentation patterns of various levels are described in several papers and reports of Sangode et al. (1996, 1999,2003).

The age of the Surai Khola section was previously determined by palaeomagnetic method (Apple et al., 1991) based on standard polarity time-scale of Harland et al. (1982) using the magnetic property of sandstone. Later study by Gautam and Rösler (1999) correlated the magnetic polarity of Surai Khola sediments with GPTS of Cande and Kent (1995). For our study we have used Gautam-Rösler magnetic polarity scale. Correlation points for age determination were obtained from *Gomphotherium* sp. at 350 m height of the section which corresponds to ~13 Ma and other fossils (*Arcbidiskodon planiforns, Hexaprotodon siwalensis, stegodon ganesa)* found around 3000 m height corresponding to ~ 5 Ma. Surai Khola section represents an excellent record of Siwalik sediments without any major gap in stratigraphic succession. As a result, the frequency of reversals in the section equals the frequency of reversals in the standard polarity time scale. The entire section (from bottom to top) is found to range from ~13 to 1 Ma).

2.2.1 Sampling in different sections and age of samples

2.2.1a Sampling in Siwalik sections

In Siwalik sections sampling was done along river cuts and road cuts. For samples collection, we have taken traverse along dip direction of the beds, starting from base of the section. The base of the sections were determined by previous workers (Raiverman et al., 1983; Sangode et al., 1996; Kumar and Nanda, 1989). In Ranital and Kotla section of Kangra sub-basin the base is demarcated by Jawalamukhi thrust. In Ranital section, traverse for sample collection started from near Bathu Khad bridge and continued through Bathu Khad-Kangra Road-Dodan Nala-Daulatpur village further on the Kangra Road. The beds in this section dips northeasterly with dip varying from 25° to 45°. In Kotla section, sampling was done along Brail Nala. The dip of beds varies from 30° to 40°.

The base of Mohand Rao section lies 500 m NE of Mohand village in the form of an anticline. The sampling was done on the Mohand Rao River cut, which runs parallel to the Dehra Dun-Saharanpur highway.

In Haripur Khol section, base is marked by Dhanaura anticline. The northern boundary of the section is demarcated by Nahan Thrust. The sampling in this section was done along Somb Nadi and its tributaries (Jamni-Khol). The average strike of the beds is NW-SE with dip varying from 20° to 45°.

In Surai Khola, base of the section was fixed on the basis of fossil and lithology. Presence of *Gomphotherium* sp. indicated lower Siwalik and dominance of mudstone beds helped in identifying the base of the section. Sampling was done along the Mahendra Nagar high way. The road cuts the strike of the beds at right angles the strike being 60° to 75° to the north.

2.2.1b Sampling in Gondwana Section

Exposures in Satpura basin are not continuous. Sampling in the Denwa Formation and Bagra Formation was done on the exposed sections in different villages and river sections. Samples of Denwa Formation were collected from the following locations: Baki Nala crossing near Piparia Chindwara Road, Khirpa village, Taldhana village, Savarbani village. Bagra samples were collected along Anjan Nala.

Soil carbonate nodules were collected from palaeosol horizons and sandstone nodules and sandstone chips collected from sandbodies. The total number of samples collected from different Siwalik sections are:

	Number of Samples		
Section	Soil Carbonate Nodule	Sandstone Nodule	Sandstone Chip
Haripur Khol	31	13	11
Ranital	38		
Kotla	13		
Mohand Rao	9	12	10
Surai Khola	25		156

For calculating age of the samples for Indian Siwalik sections the time duration between two tie points and corresponding thickness of sediments were first used to estimate sedimentation rate. Age of each bed in stratigraphic column was calculated assuming constant sedimentation rate. Samples collected from a bed were assigned the age of the corresponding bed. For Surai Khola section of Nepal Siwalik sampling was carried out from road cuts along the Mahendra Nagar Highway, which has several geologic and geographic markers, allowed us to tie our sample locations with the palaeomagnetic date and stratigraphy provided by Dr. Corvinus who was part of the age determination team of Surai Khola section (personal communication).

2.3 Sedimentological attributes of Siwalik

Traditionally, the Siwalik sediments have been divided into three subgroups: Lower, Middle and Upper based on distinct faunal assemblages (Pilgrim, 1913). Sedimentological characteristics and fluvial architecture also differ in these three subgroups.

The Lower Siwalik subgroup, in general, is characterized by an alternation of sandstone and mudstone (mudstone > 50%). Transition from Lower to Middle Siwalik succession occurs between 11 and 9 Ma and is reflected by a change in sandstone geometry (ribbon type to sheet type) and decrease of mudstone abundance. The changeover from mudstone to sandstone-dominated succession in different Siwalik sections is time transgressive. This changeover occurred at about 11 Ma in Potwar Plateau, Pakistan (Johnson et al., 1985), 10 Ma in the Kangra Sub-basin, India (Kumar et al., 2003a) and 9 Ma in Nepal (DeCelles et al., 1998).

In general, channel body proportion and storey thickness of sandstone beds increase by a factor of 2 to 3 at about 10 Ma. These sandstone bodies can be traced laterally, perpendicular to the palaeoflow direction, for about a kilometer. The mean grain-size gradually increases upsection from fine to medium to coarse-grained, and in places sediments are mostly pebbly.

The Middle Siwalik succession grades upward into thickly bedded conglomerate with lenticular bodies of sandstone. In the lower part of Upper Siwalik subgroup (at around 5 Ma) mudstone is rarely present. It is interesting to note that all the re-entrants such as Dehra Dun and Kangra show relatively coarse-grained facies at 5 Ma but contemporary salients show relatively fine-grained facies. (Kumar et al., 1999; Rao et al., 1988)

2.3a Sedimentology of Kangra Sub-basin

Kangra is the largest depression/sub-basin in the Indian part of NW Himalaya (Raiverman et al., 1983) and its structural style is described as re-entrant (Powers et al., 1998). The Jawalamukhi Thrust is the southernmost limit of the Kangra re-entrant exposing the upper part of the Lower Siwalik mainly in its hanging wall.

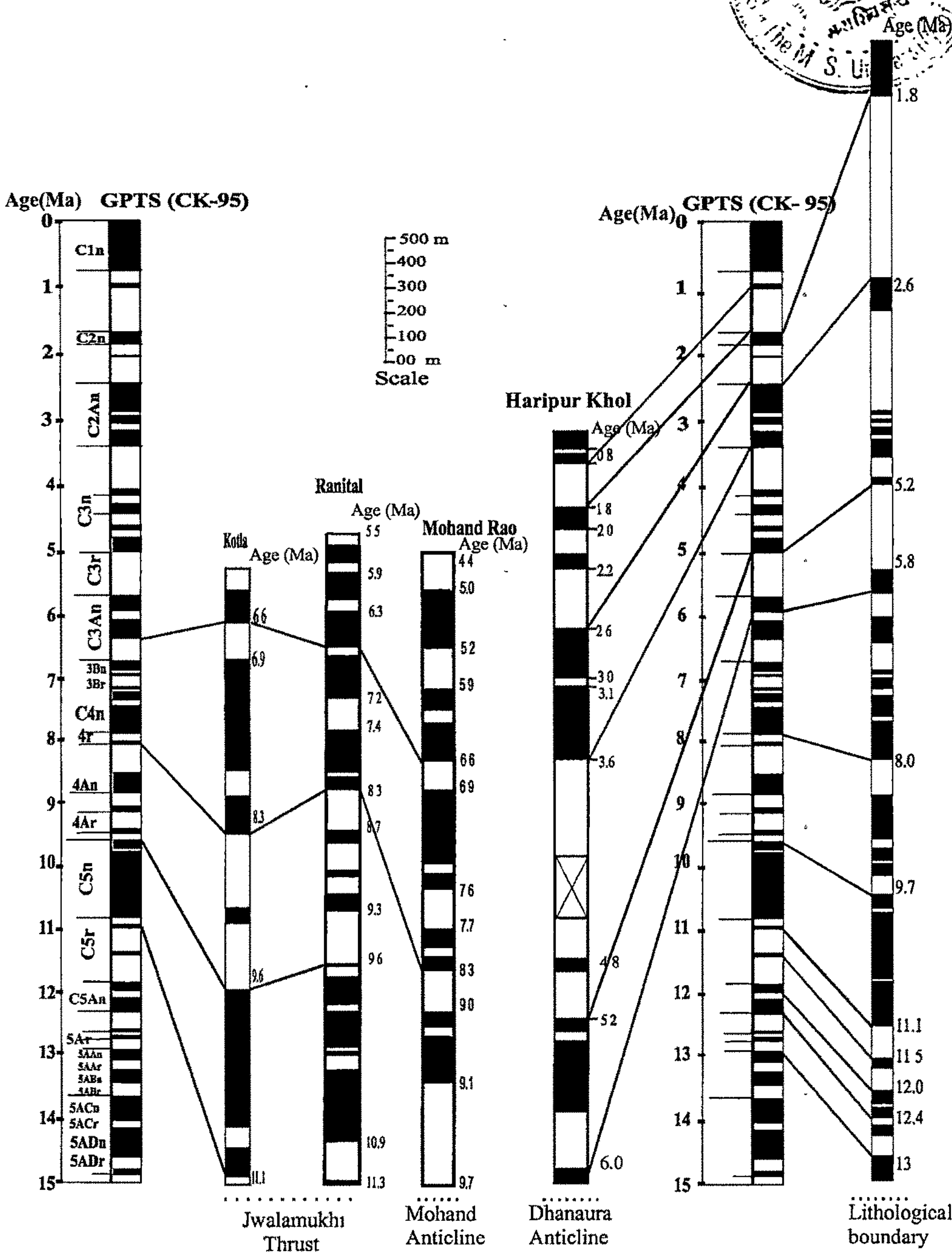


Fig.2.3 *Correlation of magnetic stratigraphy of Kotla and Ranital (Kangra), Mohand Rao (Dehra Dun), Haripur Khol (Subathu) and Surai Khola section with modified GPTS of Cande and Kent (1995). The age ranges (in Ma) for the sections are: Kotla + Ranital ~11 to ~6, Mohand Rao ~10 to 5, Haripur Khol ~6 to ~0.5, Surai Khola ~13 to 1. The base of Ranital and Kotla section is demarcated by Jwalamukhi Thurst, Mohand anticline for Mohand section, Dhanaura anticline for Haripur Khol section. The base of Surai Khola section was determined based on lithological characteristics. The scale refers to the thickness of all the five stratigraphic successions.*

In the Kangra sub-basin, Ranital and Kotla sections are situated on the southern limb of Lambargaon syncline. The sediments in the Ranital section encompasses Lower (partly) Middle and Upper Siwalik subgroups (Raiverman et al., 1983; Karunakaran and Rao, 1979). Lower 2000 m sediments are characterized by alternate sandstone and mudstone whereas rest of the section is dominated by massive conglomerates. The abundance of mudstone facies in lower part varies from 20 to 80 % within individual fluvial cycles.

Channel sedimentation in the Kangra sections is represented by fine to coarse grained, gray, light gray and buff colored sandstone along with a variety of conglomerates. Individual sand bodies are characterized by fining upward while the whole sequence shows coarsening upward merging into massive conglomerate sequence after ~2000 m level. The sand bodies are typically 1 to 10 m in thickness. However, 50 to 100 m thick sand bodies dominated by gray sandstones are also present occasionally. The sandstones commonly occur in multistory fashion varying from two to nine storeys, each separated by erosional surfaces. These erosional surfaces are generally planar or concave upward and locally exhibit decimeter to meter scale relief. The thickness of cross strata in the trough cross-stratified sandstones decreases upward with concomitant decrease in grain size. Apart from thick sheet sandstone, single storey ribbon sandstone bodies are also present. They are generally fine to very fine grained and buff colored. Small scale cross-stratification and ripple drift lamination are the other common sedimentary features observed in these sandstones.

The fluvial architecture at around 10 Ma shows gradual change from minor to major sandstone bodies and indicates increase in channel dimension and discharge. The sedimentary succession in this time period is characterized by multistoried sandstone with abundant erosional surfaces, no lateral accretionary surfaces and low palaeoflow variability. These features indicate that deposition took place in frequently avulsing large braided river system. Between 8.7 and 7 Ma, initiation of conglomerate accumulation started in the Kangra sub-basin. This event may indicate a shift of the basin margin near Dhauladhar granite massif and/or activation of Manali-Roper mega-lineament in the east and Ravi lineament in the west.

2.3b Sedimentology of Mohand Rao section

Mohand Rao section lies in the southern flank of Dehra Dun valley lying between Mohand Rao River in the east and Yamuna River in the west (Fig.2.2). In Mohand Rao section, only Middle and Upper Siwalik subgroups are exposed. The Middle Siwalik sediments are 1500-1800 m thick, with lower 300-450 m characterized by sandstone couplets. Multistory sandstone complex along with few pebbly beds and mudstone horizons characterizes the upper part. The mudstone percentage is 20% in the basal part and <5% in the upper part. This sequence passes upward into thickly bedded conglomerate of the Upper Siwalik subgroup (Kumar, 1993).

A variety of features like sheet geometry of sand body, low mudstone content, frequent erosional surfaces, consistency of palaeoflow and presence of unconfined sandstone bodies suggests deposition of sediments by sheet floods in a braided channel environment. Vertical stacking of thick multistory sandstone complexes indicates predominance of channel bar migration with the depositional sites remaining as channel belts for long periods with only minor flood plain deposits. Conglomerate facies in the lower part of the Upper Siwalik is characterized by oriented clast and intercalated with stratified sandstone and massive mudstone, indicating deposition under high energy conditions during persistent stream flow. Irregular or flat lower bounding surfaces and sheet geometry of conglomerate beds suggest that channel were broad and unconfined. The association of trough cross-stratified conglomerate facies suggests lateral migration of longitudinal gravel bars. Massive, nonpedogenic mudstone facies indicates rapid deposition during times of widespread overbank flooding. The geometry of conglomerate facies changes up section. Poorly sorted, disorganized and poorly imbricated conglomerates suggest rapid deposition from overloaded high-energy traction current flow. Thick amalgamated sheet conglomerate beds having several sedimentation units reveal deposition during more than one flood event.

2.3c Sedimentology of Haripur Khol section

The Haripur Khol section is approximately 2.4 km thick and is bounded by Yamuna River in the east and Markanda River in the west (Fig.2.2). The basal 400 m multistoried gray sheet sandstone beds are characterized by abundant erosional surface, low palaeocurrent variability and absence of lateral accretionary surface indicating deposition in a braided river system. Presence of cross beds up to 2 m size and bank derived intraclast lags indicate a major river system. Though mudstone facies are rarely preserved in the basal 400 m of the section, abundance of mudstone increases and the size of the sandstone bodies decreases between 400 and 600 m. Lateral accretion surfaces and channel plug deposits in the sandstone bodies and abundance of overbank mudstone in this interval suggest a meandering river environment. Relatively small trough cross-strata and mud cracks suggest a low flow magnitude river system. Above 600 m, increased size of gray sand bodies, absence of internal lateral accretionary surfaces and decrease in mudstone content indicate a braided river environment. Buff ribbon sandstone bodies, which first appear at 760 m, show no evidence of lateral accretion. Smaller size of these sandstone bodies indicates low magnitude rivers that have laterally fixed channels. The frequency and size of buff sandstone bodies increase above 1450 m, which suggests a gradual increase in magnitude of piedmont drainage. Palaeoflow directions in the piedmont drainage were almost perpendicular to the transverse trunk drainage.

At 1375 m (3.36 Ma), pre-Tertiary clast bearing conglomerates appear within multistoried gray sandstone bodies. The conglomerate deposits increase upsections after 2100 m and are found to be intercalated with gray and buff sandstones. This interval probably represent interfingering of gravelly braided transverse trunk stream and piedmont streams.

Further upwards, conglomerates become massive, mud-matrix supported, and are composed only of reworked lower Tertiary sandstone clasts. This suggests rapid deposition in proximal part of alluvial-fan debris flows.

2.3d Sedimentology of Surai Khola section

No formal stratigraphic nomenclature is available for the Siwalik units in Surai Khola section. For the present work we shall use the informal Formation names proposed by Corvinus (1990), namely Bankas, Chor Khola, Surai Khola, Dobata and Dhan Khola Formation in the ascending order. The Bankas Formation is composed of pigmented mudstone and medium to very fine-grained sandstone. The Chor Khola Formation is characterized by an almost equal proportion of mudstone and coarse to fine grained sandstones. The Surai Khola Formation consists mainly of coarse to very coarse-grained sandstones. A typical character of this Formation is "pepper and salt" appearance due to presence of significant amount of biotite and quartz grains. The Dobata Formation comprises massive mudstone beds and medium to coarse-grained sandstone. The Dhan Khola Formation is made up of conglomerates, which are composed of pebble to cobble sized quartzite.

From Surai Khola section eight lithofacies associations have been recognized by Nakayama and Ulak (1999) on the basis of lithology, assemblages of sedimentary structure and sediment body architectures. These are

1) Lithofacies 1: This facies is the finest grained amongst all. It is characterized by pigmented and bio-turbated mudstones, and very fine to medium grained sandstones. The thicknesses of individual mudstone and sandstone beds vary between 0.5 to 3 m and 0.5 to 2 m respectively. The bases of sandstone beds are generally flat to slightly erosional. Lateral accretion of sandstones is frequently recognized in thicker sandstone beds. Ripple lamination is well preserved in thinner sandstones. This facies is represented as fine grain flood plain deposit of a meandering river system. The rippled and sheet like geometry of sandstone beds interbedded within mudstone implies crevasse splay deposits. Predominance of bio-turbated, pigmented and calcareous palaeosols indicate long exposure of extensive flood plain deposit.

2) Lithofacies 2: This facies is characterized by coarser sandstone with lateral accretion deposits and amalgamation of muddy sandstone beds. The former reflects bed load of meandering channels; the latter is formed by frequent flood flows. Climbing ripple laminations within a bed represent gradual velocity change of flood flow. This facies can be interpreted as the product of a flood-flow dominated fine-grained meandering system.

3) Lithofacies 3: This facies is characterized by medium to coarse-grained sandstone with laterally accreted cross-stratification which is product of sandy meandering system. Amalgamation of muddy sandstone beds again indicates major role of flood flow. Variegated mudstone beds were formed on flood plains and muddy sandstone beds represent flooding or crevasse splay deposit. Overall, this facies represents flood flow dominated sandy meandering system.

4) Lithofacies 4: In this case great volume of bed load in the form of coarse to very coarse sandstone in downstream and lateral accretionary architecture and strong unimodal flow are indicative of braided river. In addition, thick and upward-fining

successions and thick units of sandstone and pebbly sandstone beds with deep erosional bases imply deep channel flow. In a nutshell, this facies represents deep sandy braided systems.

5) Lithofacies 5: This facies is very similar to facies 4. Sheet like geometry of sandstones and pebbly sandstones, development of planar cross-stratification, and less clear upward fining successions are characteristics of the classic 'Platte-type' braided river deposits. Generally, minor upward-fining cycles are not recognized within any major upward fining successions. Thus it represents deposits of sandy braided systems shallower than those of lithofacies 4. The combination of ripple lamination and planar stratification may reflect rapid fluctuations in palaeoflow discharge and velocity, such as flash flood events.

6) Lithofacies 6: This facies is characterized by abundance of mudstone, which indicates flooding and long periods of standing water development. Irregular directional relations between erosional surfaces and palaeoflows suggest that lateral and downward developments of channels were weak. Ribbon shaped sandstone bodies and a comparatively finer grain size indicate development of standing water in a fluvial system with low gradient and low stream power. Fine to medium grained sheet like sandstone beds within mudstone beds are interpreted as crevasse splay deposits. According to these features, this facies could be considered as the product of anastomosing river system.

7) Lithofacies 7: This facies is dominated by gravel clasts in bed load. Palaeocurrent directions are uniform within individual upward fining succession. This is interpreted as the deposits of a gravelly braided system. Numerous erosional surfaces and predominance of conglomerate imply that the system was characterized by relatively shallow and/or unstable channels.

8) Lithofacies 8: This facies is characterized by poorly sorted boulder conglomerates, a product of debris flow. The well-sorted pebbles to cobble conglomerate signify bed load of gravelly river. Thus this facies could be considered as the product of braided system dominated by debris flow.

The facies associations and their corresponding depositional processes are directly related to the evolution of fluvial style through time. Fine-grained sediments, dominance of flood flow and crevasse splay deposit at the beginning of the section indicates meandering river system. Fluvial style changed from meandering system to braided river as revealed by lithofacies 4 and 5. Lithofacies 7 is a product of gravelly braided river.

2.4 Palaeosol Facies

As discussed so far, Siwalik sediments are fluvial deposits and characterized by alternate coarse grained (sandstone/conglomerate) and fine grained (mudstone) sediments (Fig.6.2). In a fluvial system, coarse-grained sediments represent channel deposit while fine-grained sediments (mudstone) are the product of overbank deposit. During pause in sedimentation in case of overbank deposit vegetation can grow in mudstone beds and form soil (Fig.2.4).

Palaeosols in Siwalik were mostly developed in overbank facies. Thickness of palaeosols varies from a few tens of centimeters to several meters. In exposed sections, palaeosols appear reddish, reddish-brown, grayish and greenish and are invariably mottled. Rhizoliths and rhizocretions are also common. Soil structure is extensive in the B-horizons. Majority of palaeosols contain carbonate in disseminated and nodular form (Fig.2.5). For the present study nodular soil carbonates have been analyzed.

Nodular soil carbonate can form either by pervasive growth or by concentric growth (Raiswell and Fisher, 2000) (Fig.2.6). In case of pervasive growth (Fig.2.6a), nodules first form by precipitation of crystallites throughout the body and then solidify by continued crystal growth onto these nuclei.

In case of concentric growth (Fig.2.6b) successive layers of cement are added to the outer surface and as a result the radius increases with time. The nodule size varies from 1 to 5 cm. During sampling, nodules were identified in the field and carefully collected from palaeosols after monitoring their vertical position in the profile. Composite lithologs of all sections studied in the present work were made and positions of palaeosols ascertained in each lithologs for ascribing the age as described earlier.

2.4a Palaeosol facies of Kangra sub-basin

In Kangra sub-basin, overbank facies are characterized by gray, brown and yellow palaeosols which are arranged in variegated multiple horizons. Palaeosols with

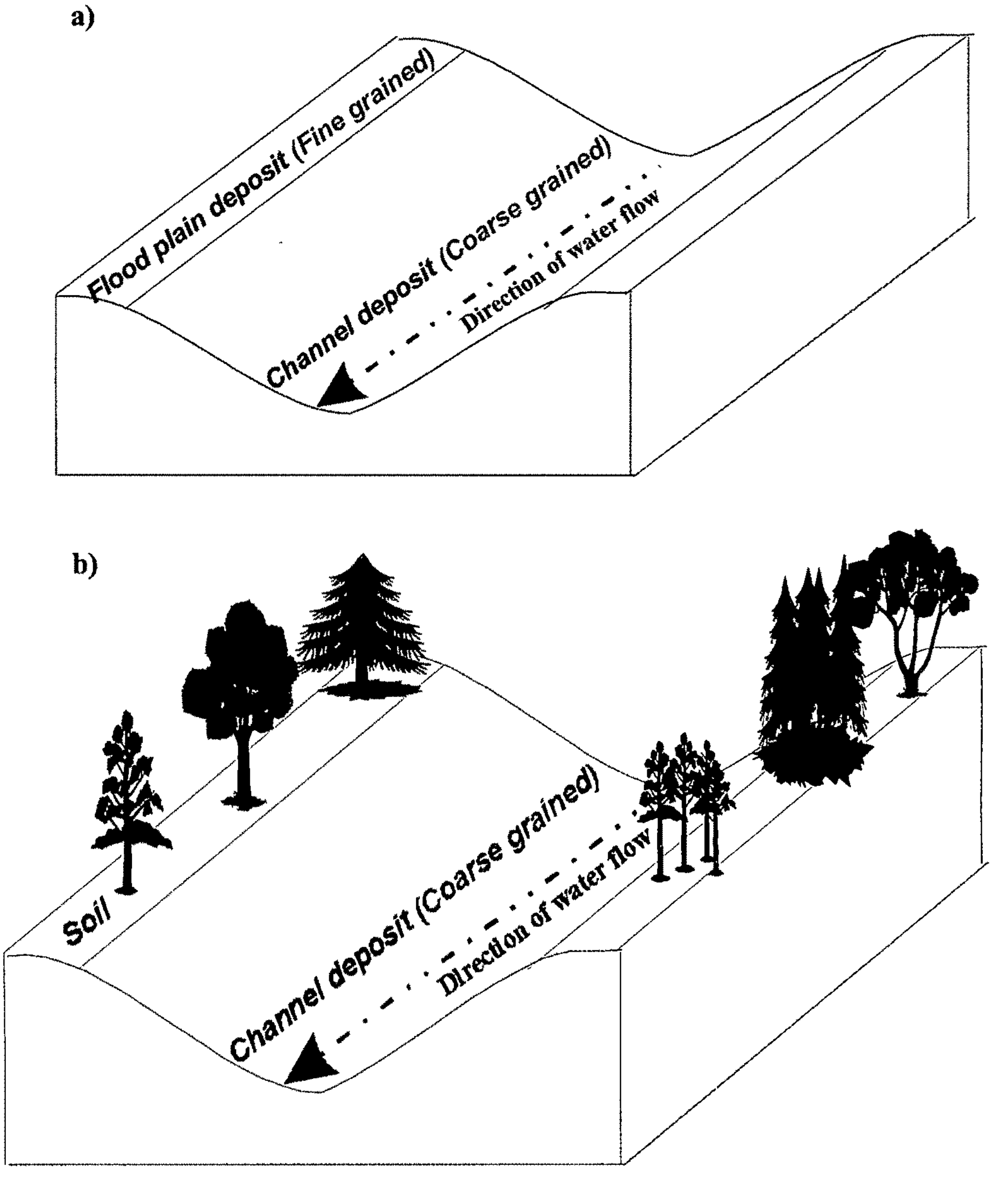


Fig.2.4 *Sedimentation in fluvial system and formation of soil: a) Coarse-grained sediments represent channel deposit and relatively fine-grained sediments flood plain deposit. b) During pause in sedimentation, vegetation grows in flood plain and transforms the mudstone into soil.*

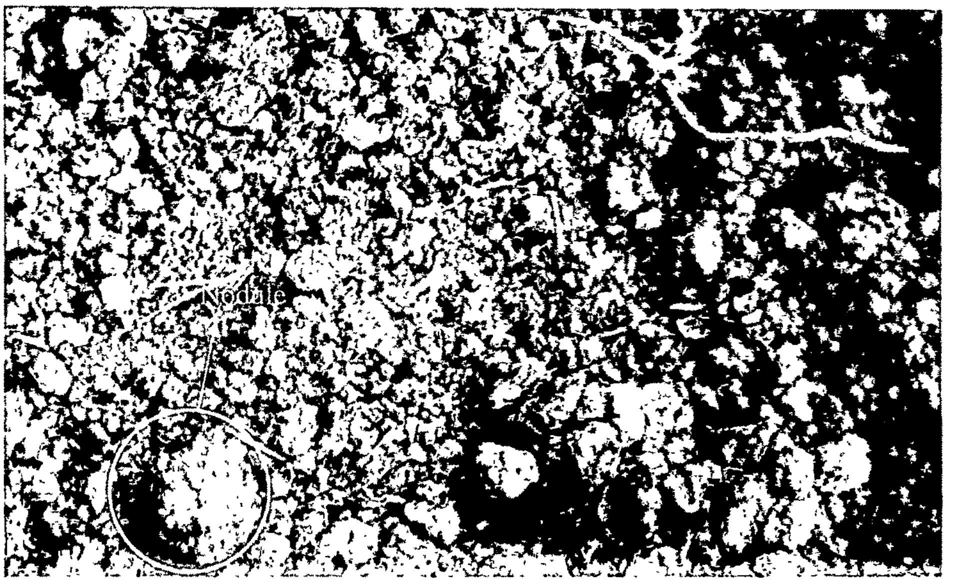


Fig. 2.5a *Soil carbonate nodules in palaeosol bed.*

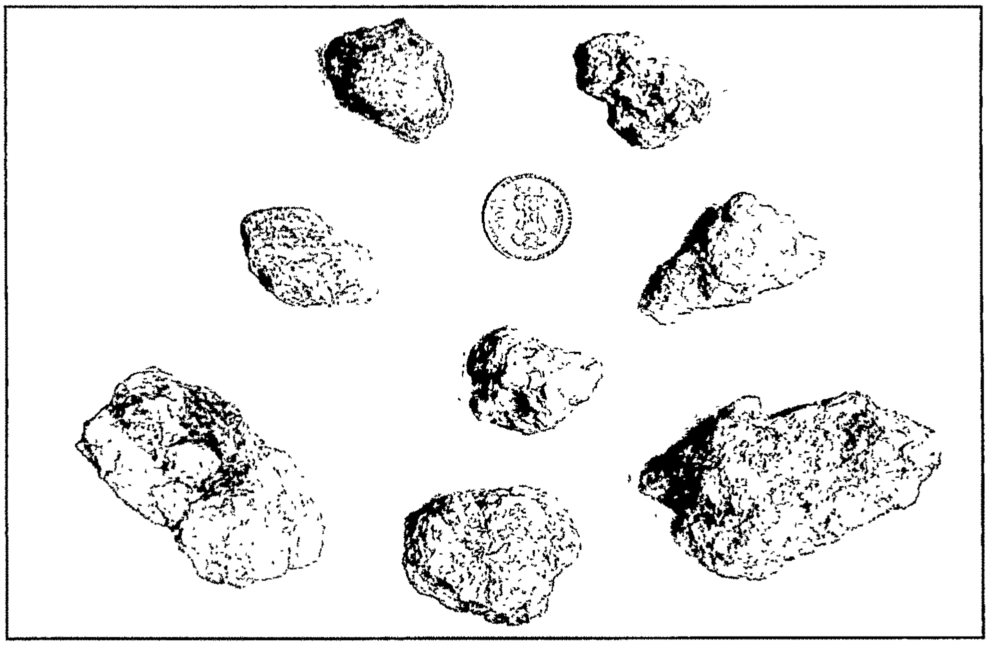


Fig.2.5b *Soil carbonate nodules separated from palaeosol bed.*

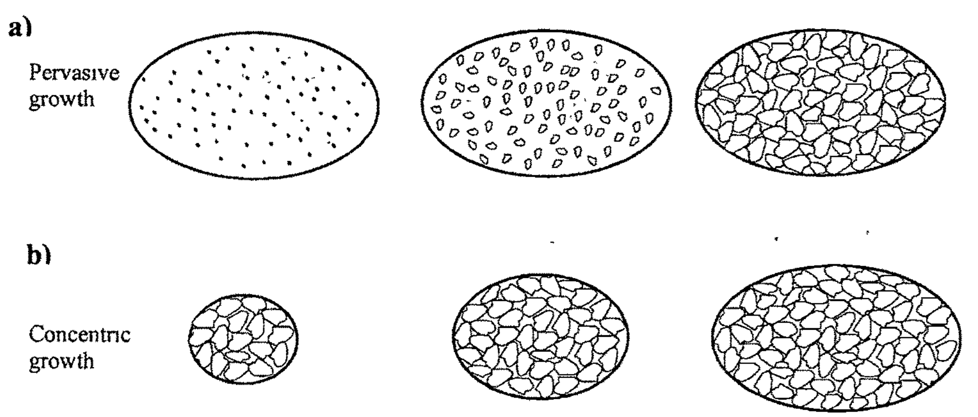


Fig.2.6 *Schematic diagram showing mechanism of nodule formation (After Raiswell and Fisher, 2000). a) During pervasive growth an isolated patch of crystals evolves towards a mass of zoned crystallites. b) During concentric growth the patch of crystals become well cemented itself, before further concentric addition of texturally similar cements. The grey area represents residual porosity.*

green mottling are common and contain iron and calcareous nodules, root traces and bio-tubes. From 11 to 7 Ma, brown, purple and red palaeosols are common and yellow palaeosols dominate in the time range 7 to 6 Ma. Palaeosols are not observed after ~6 Ma.

2.4b Palaeosol facies of Mohand Rao section

Palaeosol occurrence is quite low in Mohand Rao section. Where available, they occur as discontinuous lenticular body within multistoried sandstone (between 350 and 1400 m). The palaeosols are mostly gray in color but occasionally could be brown. Green mottling is common. Palaeosols show evidences of biological activities in the form of vertical, unlined burrows (skolithos) and surface traces (sinusitis). The soil carbonate nodules are common and locally mudstones show immature soil profile (Kumar et al., 2004).

2.4c Palaeosol facies of Haripur Khol section

Palaeosol facies of Haripur Khol section has been studied in detail by Thomas et al. (2002). They showed that maturity and carbonate content in the palaeosols change from bottom to top of the section. From 0 to 270 m the palaeosols are moderate to strongly developed. The interval 270 to 870 m is characterized by moderate development of pedo-facies, which are mostly non calcareous. The palaeosols occurring from 870 to 1750 m are also moderately developed but weakly developed palaeosols are more common in this interval than 270 to 870 m. Both Fe-Mn and soil carbonate nodules are observed in moderately developed palaeosols of 270 to 1750 m interval. The lower 200 m of 1750 to 2288 m interval has well-developed yellow palaeosols, but above this level palaeosols are mostly weakly developed. About 70% of the palaeosols are calcareous in nature and contain significant amount of calcite in the form of nodules or fine calcareous matter disseminated in the groundmass.

Color and maturity of palaeosols change from the bottom to top of the section (Thomas et al., 2002). Red, moderate to strongly developed palaeosols grade into less-developed yellow palaeosols starting at about 2.6 Ma. In the lower part of the section strong illuviation of clay forms well-developed Bt horizons in the palaeosols.

2.5 Gondwana Supergroup

The Gondwana Supergroup represents a unique sequence of fluviatile sediments deposited during Permo-Carboniferous and Mesozoic times. They occur in several scattered basins in India. Satpura basin in central India contains one of the best exposures of Gondwana sediments where excellently preserved palaeosols are available over a wide range of time scales. Gondwana sediments in Satpura basin (Fig.2.1) ranges in age from Permo-Carboniferous to the late Cretaceous (Ghosh et al., 2001). The thickness of the whole sedimentary succession is about 5 km. The Satpura Group has been divided into four lithoformations: Motur, Denwa, Bagra and Lameta. The respective ages of these Formations are Early Middle Permian (269 to 260 Ma), Middle Triassic (240 to 220 Ma), Jurassic (200 to 145 Ma) and Late Cretaceous (65 Ma) based on fossil assemblages. Overall, the sediments are characterized by alternate layers of sandstone and mudstone/carbonaceous shale; occasionally extrabasinal conglomerates also alternate with mudstone/carbonaceous shale. In several places, the mudstone beds underwent pedogenesis during break in sedimentation. Soil carbonate is common in these palaeosols. In our present work, soil carbonates of Denwa and Bagra Formation have been analyzed to reconstruct atmospheric CO_2 concentration for the Triassic and Jurassic Period. Some details of these two Formations are given below:

2.5a Denwa Formation

Fluvial architecture of Denwa Formation was studied in detail by Maulik et al., (2000). Denwa Formation is 300 to 600 m thick. Lower part of the Denwa Formation is characterized by fine to medium grained thick sandstone (3 to 15 m) interbedded with red color mudstone. Sand bodies occur as sheets with width to thickness ratio greater than 100. The sand bodies comprise of storeys stacked one upon another. The storeys internally consist of small lenticles of mud-pebble conglomerates and 30 to 70 cm thick sets of compound cross strata at the top. Basal surface of the sandstone bodies are locally concave up, sharply defined and has erosive relationship with underlying mudstone.

The compound cross strata in the storeys are records of migration and/or growth of macro forms like bars which accreted mostly along local flow direction. A storey thus represents deposit of bars adjacent to channels. Since the sandstone bodies are made up of a number of superposed groups of storeys, it is inferred that they formed in braided channels, which were part of a large alluvial tract containing number of channel belts. The lateral switching and shifting of individual channel belts within the tract resulted in superposition of different storey groups to form thick sandstone bodies.

The upper unit of the Denwa Formation is mudstone dominated and devoid of thick multistorey sandstone bodies. The high mud-sand ratio indicates suspended-load fluvial system. Ribbon-shaped sand bodies encased within pedoturbated mudstone represent the basic architecture of the succession. They contain inclined heterolithic stratification, resembling laterally accreting point bar deposits. The presence of point bar deposits and variable palaeocurrent direction indicate high sinuosity meander channels.

2.5b Bagra Formation

Bagra Formation consists of conglomerate in the lower and middle parts and sandstones with intercalated lenses of shale in the upper part (Casshyap et al., 1993). The conglomerate assemblages crop out in discontinuous patches along the northern margin of the basin. The conglomerates are both clast and matrix-supported. The clast supported conglomerate facies occurs mostly in the lower part. The finer clastic assemblage of interbdded sandstone and shale (red and gray color) occur in the southern end of the study area. Thickness of the individual sand bodies ranges from 2 to 8 m.

The coarse-grained nature of the sediments, upward-fining distribution and lateral variation in lithology and stratification type together with palaeo-current data suggest that Bagra conglomeratic sequence was deposited by an alluvial fan system that prograded southward from a highland source area. The characteristics of massive conglomerate facies in lower part of the Formation strongly support an active bed load system in which sediments deposited as broad sheet-like bodies. Intercalated matrix supported conglomerate facies containing subangular to subrounded outsize clasts may represent local lobes of high viscosity debris flow of alluvial fans. Clast and matrix supported conglomerate in middle part of the Formation are relatively fine grained, better sorted and interbedded with cross-bedded channel sandstone indicating high energy fluvial system in mid-alluvial fan.

The palaeosol profiles are associated with floodplain deposits and are mostly found in lower half of the Formation. The palaeosols have been described in detail in section 6.2.

2.5c Age of Denwa and Bagra Formation

The age of Denwa Formation was initially regarded as Upper Triassic based on the presence of *Mastodonosaurus* (Lydekker, 1877). Later on, identification of *Parotosaurus,* which is of Middle Triassic age indicate that Denwa Formation is of late Lower Triassic to Middle Triassic age (Chatterjee and Roychowdhury, 1974).

The Bagra Formation has not yielded any faunal remains except two imperfect casts of gastropod shells. Field relationship with Denwa and other Formations have been used for assigning age of Bagra Formation (Casshyap et al., 1993). Bagra Formation lies unconformably on Archean metamorphics and Early Permian Talchir/Barakar rocks along the northern margin of the basin. In southwest, it lies on late Lower to Middle Triassic Denwa with angular unconformity. The varied relationship of Bagra with underlying strata may imply uplift followed by erosion after deposition of Denwa producing uneven surfaces over the basin, which indicates a prolonged time interval of non-deposition. A break in sedimentation is further supported by marked contrast in the lithofacies and reversal of palaeoslope of Bagra with respect to underlying Denwa. So it is likely that the Bagra Formation is younger than late Triassic. Additionally, Bagra is conformably overlain by Jabalpur Formation which has been assigned an early

Cretaceous age and the Jabalpur, in turn, is directly overlain by the Deccan basalt having erupted at about 66 Ma (Jaeger et al., 1989). The sediment transport and palaeoslope of the Jabalpur Formation, like the Bagra, are southward directed suggesting a northerly provenance and a broad similarity of depositional setting. The Jabalpur assemblage characterized dominantly by sandy facies may well represent the distal and uppermost facies of the braided river alluvial fan system of the Bagra Formation.

Thus, various lines of stratigraphic, tectonic and sedimentologic evidence cited above would tend to suggest that Bagra Formation of the Satpura Basin should be younger than the late Triassic but older than or equivalent to late Jurassic-early Cretaceous (Casshyap et al., 1993).

2.6 Materials and Methods

2.6.1 Analysis of soil carbonate nodules

For isotopic analysis of the carbonate phase, soil carbonate nodules were first washed in mild HCl to remove any modern carbonate sticking to the outer surface. Thin sections of the nodules showed that the calcium carbonate is mostly micritic (Fig.2.7a, b and c). Absence of sparry calcite rules out any major recrystallization subsequent to the precipitation of original carbonate.

2.6.2 Analysis of sandstone nodules

Microscopic study of thin sections of sandstone nodules showed that the carbonate cement are of three types: a) a pore-filling variety with a patchy distribution b) massive cloudy distribution that forms a ground mass and contains relict quartz grains c) replacement of quartz and feldspar grains by calcite (Fig. 5.1).

2.7 Experimental Techniques

For the present work, carbon and oxygen isotope ratios of soil carbonates, carbon isotope ratio of organic matter associated with soil carbonates, hydrogen isotope ratio of pedogenic clay minerals and, carbon and oxygen isotope ratios of carbonate cement from sandstone nodules and sandstone chips were analyzed. Procedure for measurement of the above mentioned isotope ratios is described below:

2.7.1 Carbon and oxygen isotope ratio of carbonate

For carbon and oxygen isotopic analysis of carbonate, powdered samples were obtained from fresh surfaces of soil carbonates, sandstone nodules and pieces of sandstone by use of a dental drill while viewed under a microscope to avoid any fracture filling carbonate. The powder was treated with 100% phosphoric acid under vacuum for generating CO_2 for analysis in a Europa Geo 20-20 Stable Isotope Ratio Mass Spectrometer. Preparation of phosphoric acid is an important step.

100% phosphoric acid was prepared following the procedure described by Coplen et al., (1983). 1400g AR grade 85 orthophosphoric was added to 600g AR grade phosphorous pentaoxide in a 3 L beaker. 10 mg of AR chromium tri-oxide was added to the solution. The solution was heated in the beaker for seven hours at around 200°C with loose covering of aluminum foil. 6 ml of 35% AR grade hydrogen peroxide was added to the solution and heating was continued at 220°C for another 4 hours. The specific gravity of the final acid was measured to be 1.91 in confirming with the recommended specific gravity (1.90 to 1.95).

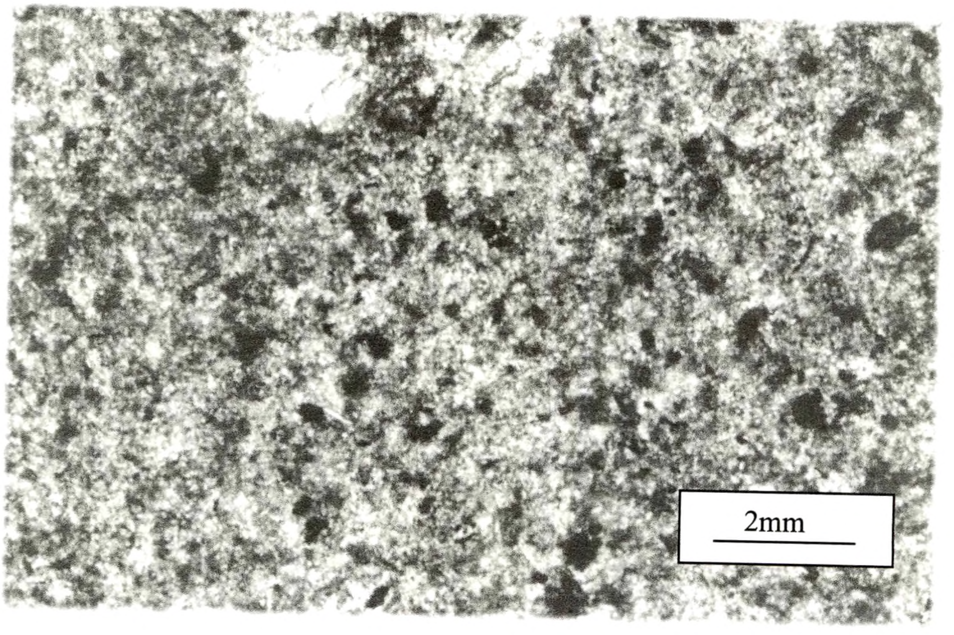
Production of CO_2 from powder samples was done by either online extraction or off-line extraction.

Online extraction of CO_2: The on line carbonate acid preparation system (CAPS) which is a unit of Europa Geo 20-20 stable isotope ratio mass spectrometer was used for treating the samples. The CAPS consists of a sample carousel containing 26 glass vials where powder samples are loaded and housed in an oven kept at 80°C. Each vial is lifted in its turn to mate with the acid-dosing device and evacuated before acid is dropped in it. The evolved gases are taken out of the oven through stainless steel pipe line and water is retained in an alcohol trap cooled to –90°C by a cryocool unit.

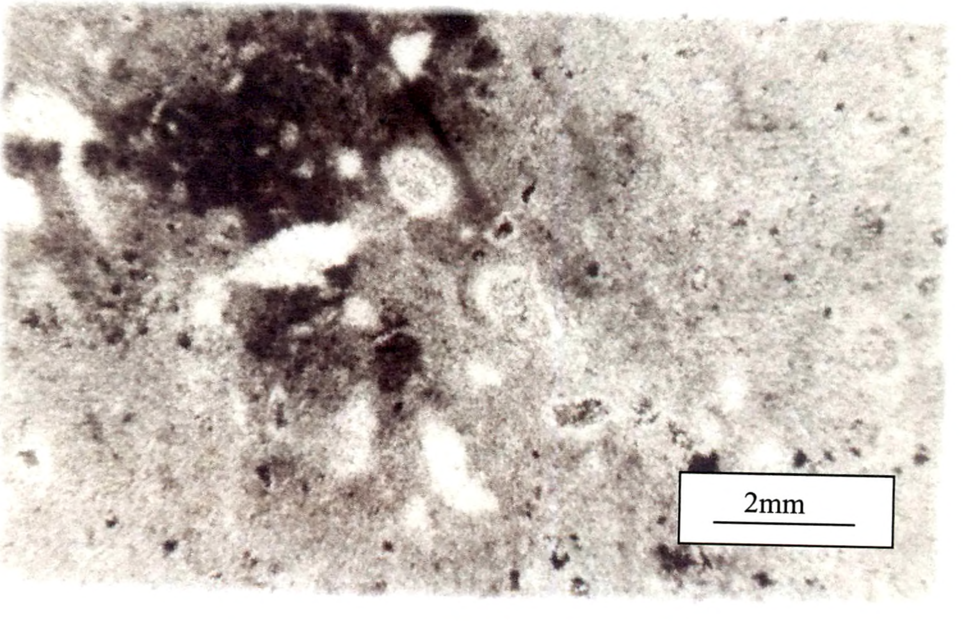
Off-line extraction of CO_2: Samples were taken in bottles with side arm containing acid. After evacuation, acid from the side arm was poured into the samples by tilting the bottle for reaction. Then the bottle was kept in water bath at 25°C for 12 hours. The evolved gas was purified by passing it through three cold traps kept at –90°C in the extraction line.

In a single batch, along with samples calibrated internal carbonate standards were also measured. The internal standards are ZC-2002 ($\delta^{13}C$= 2.1‰, $\delta^{18}O$= –2.1‰), Z-Carrara (old) ($\delta^{13}C$= 2.2‰, $\delta^{18}O$= –1.3‰), Makrana Marble (MMB) ($\delta^{13}C$= 3.9‰, $\delta^{18}O$= –10.5‰) (values are expressed relative to PDB).

a)



b)



c)

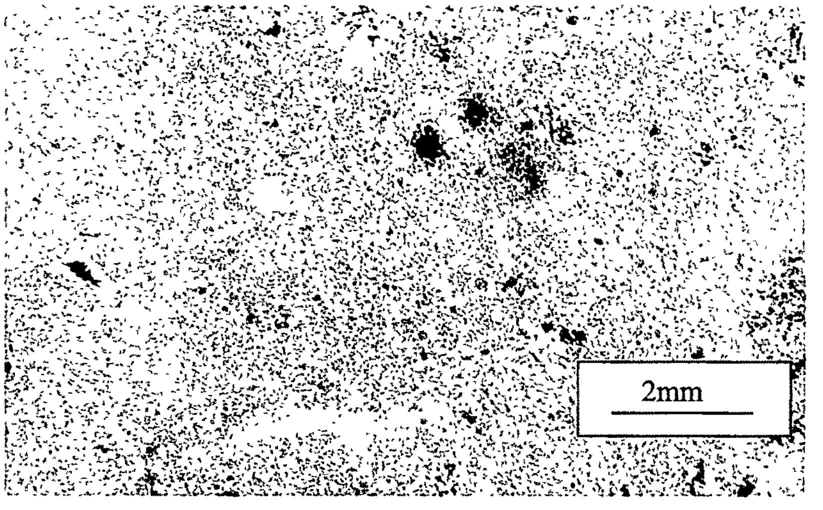


Fig.2.7 *Thin section of soil carbonate under microscope. Micritic nature of: a) soil carbonate from Ranital section, b) Bagra soil carbonate and c) Denwa soil carbonate indicates absence of recrystallization.*

2.7.2 Carbon isotope ratio of organic matter

The nodules were first treated with mild HCl to remove any modern component sticking to the surface of the nodule. The cleaned nodules were pulverized using mortar and pestle, and the powder was treated with 0.5 N HCl for 6 hours to remove associated carbonate carbonate. To check complete removal of carbonate the samples were again treated with 0.5N HCl. The residue was cleaned several times with distilled water till a neutral pH was obtained. Finally, the residue was kept for drying in an oven at 60°C. About 100 mg of powder was combusted at 800°C with purified CuO and a small silver strip in an evacuated and sealed quartz tube. The CuO was previously purified by heating in 300°C for 2 hours to remove traces of carbon. In a single batch, 12 samples along with one aliquot of internal glucose standard (UCLA Glucose $\delta^{13}C = -9.7‰$) were processed. For final calibration, IAEA C-3 ($\delta^{13}C = -24.5‰$) standard was used. Combusted sample in S-sealed quartz tube was placed inside a bigger diameter tube connected to the vacuum line and cracked by lifting and dropping an iron piece guided by two magnets. The CO_2 obtained from each sample was purified using three water traps at –90°C, collected in a 20 cc sample bottle and introduced to the mass spectrometer through inlet system for isotopic measurement. Reproducibility of the measurement was checked by measuring UCLA glucose standard and IAEA C-3 standard.

2.7.3 Hydrogen isotope ratio of pedogenic Clay minerals

2.7.3a Dissolution of calcium carbonate from nodules

Carbonate cement from soil carbonate (pedogenic) nodules was removed following the method described by Jackson (1969). First, the big nodules were crushed into small pieces. The small pieces were put into a buffer solution made by dissolving 82 g of sodium acetate in 900 mL of distilled water and 27 mL of glacial acetic acid. 10 g of crushed sample was put in 250 mL of buffer solution and kept for 6 hrs. The acid treatment was repeated to check any carbonate residue. The samples were then rinsed with distilled water 5 times to get rid of acid.

2.7.3b CBD treatment in clay

The residue was treated with citrate-bicarbonate-dithionite (CBD) solution at 40°C for four hours to remove oxides of iron (Mehra and Jackson, 1960). The solution was made using following procedure:

0.3M sodium citrate solution was made by putting 88 gm of sodium citrate in 1000 mL of distilled water. 1M sodium bicarbonate solution was made by dissolving 84 gm sodium bicarbonate in 1000 mL distilled water. One gram of sample was put into a mixture of 45 mL of sodium citrate solution, 5 mL of sodium bicarbonate solution and one gram of sodium dithionite. The solution was kept at 40°C for four hours. The whole solution was then rinsed 5 times with distilled water. The residue was then put into one liter cylinder filled with distilled water and less than 2 micron sized clay minerals were separated out by gravitational settling method. Identification and quantification of clay minerals will be discussed in detail in section 5.3 and 7.6.

2.7.3c Production of hydrogen from pedogenic Clay

Hydrogen isotope analysis was done on twenty samples. The clay samples were heated in vacuum at 250°C for five hours to remove the adsorbed water. Subsequently, they were heated to 900°C for 6 hours in presence of CuO (Savin and Epstein, 1970).

The water produced was then passed through hot uranium for conversion into hydrogen gas. Isotope ratio of the hydrogen gas was measured in the same Europa Geo 20-20 stable isotope ratio mass spectrometer in the low mass mode. Results are presented in the usual δ notation as per mil (‰) deviation of the sample hydrogen from SMOW standard, where $\delta=[(R_{sample}/R_{standard})-1]\times1000$ and R=D/H. Typical uncertainty in δD analysis of clay is about $\pm$ 2‰.

2.7.4 Stable isotope ratio measurement

The GEO 20-20 dual inlet mass spectrometer made by Europa Scientific, UK is computer controlled and designed for easy operation. The mass spectrometer is capable of measuring 1 μmole of CO_2 gas with internal precision of 0.01‰. It has two collector configurations: i) a simple triple collector configuration designed for measurement of isotopic ratios of CO_2, N_2 and O_2 and ii) an additional collector in combination with one of the triple-collector assembly (for mass 2 in a side lobe) for measuring hydrogen isotopic ratio.

Measurement of stable isotope ratios in CO_2 involves preparation of working gas and its calibration. A CO_2 working gas is needed for regular use in mass spectrometer on the reference side. This was prepared by reacting large amount (50 gm) of carbonate obtained from mixed foraminiferal assemblage (separated from a sediment core from Arabian Sea) with phosphoric acid. The reaction was carried out at room temperature in an evacuated flask having a side arm filled with phosphoric acid. The evolved gas was purified several times by passing through water trap having alcohol slurry kept at –90°C. The working gas was designated as CD 197 (as the core was raised in a cruise of RV Charles Darwin in the Arabian Sea and the standard was prepared in January 1997) and stored in a 5 liter flask; the initial pressure in the flask was 40 cm.

One aliquot of this gas (about 10 cc at 40 cm pressure corresponding to 200 μmole gas) was enough for getting major beam current of 7×10^{-9} A (at mass 44) with the variable reservoir fully open. Usually one aliquot of reference gas was used for 3 to 4 days. Routine check of mass spectrometric performance was made using a check standard of CO_2 made from Z-Carrara powder (obtained through the courtesy of Prof. R.Gonfiantini). The calibration of the Z-Carrara (calcite) w.r.t VPDB (calcite) was done via carbonate standard NBS-19 (obtained from IAEA) which has $\delta^{13}C$ and $\delta^{18}O$ value 1.95 ‰ and –2.2 ‰ (relative to VPDB).

Hydrogen isotope ratio measurements were made relative to hydrogen gas (designated as SAB) prepared from water collected from Sabarmati River, Ahmedabad. Hydrogen from water was made by passing the water over hot uranium at 800°C. The hydrogen standard was periodically calibrated with hydrogen prepared from IAEA OH-6 (–38.3‰ relative to VSMOW). One aliquot of SAB used to give 6×10^{-9}A (at mass 2) with the variable reservoir fully open. Each aliquot of reference gas was used for 2 days.

As routine precaution, following steps were adopted achieving good precision and accuracy in analysis.

1. For CO_2 measurement ZC-2002, Z-Carrara (old) and MMB standards were run regularly. ZC-2002 was used along with every set of 15-20 samples. For hydrogen isotope ratio measurement one IAEA OH-6 sample was run regularly for every two samples.
2. Repeat measurements were made for some samples.
3. Powder contamination in the line was checked periodically and the extraction line was cleaned at least once in two months.
4. The machine performance was tracked routinely i) with check standard (made from Z-Carrara, ii) by checking the zero enrichment.
5. The source housing was cleaned while changing the filament and after filament changing the source containing part of mass spectrometer was baked at 80°C overnight.

2.7.4a Reproducibility of standards and inter-laboratory comparison for CO_2

The reproducibility of the total system was determined by periodic measurement of international and laboratory standards e.g. NBS-19, Makrana Marble and Z-Carrara (old) and ZC-2002 whose δ values w.r.t. VPDB are known or established in Physical Research Laboratory. An old batch of Z-Carrara was used for internal calibration during the early phase of the work ($\delta^{13}C$ = 2.2± 0.1; $\delta^{18}O$ = – 1.2±0.1 ‰, Table 2.2). Later on, a new batch of Z-Carrara powder was made and freshly calibrated (called ZC-2002). The ZC-2002 has $\delta^{13}C$ = 2.0±0.1, $\delta^{18}O$= –2.1 ±0.2 (Table 2.1) and was treated as laboratory carbonate standard and always analyzed along with the samples. Long-term

Table 2.1 *Carbon and oxygen isotope ratio values of Z-Carrara (ZC-2002) during thesis period. All values are expressed relative to VPDB in ‰.*

Date	$\delta^{13}C$	$\delta^{18}O$	Date	$\delta^{13}C$	$\delta^{18}O$	Date	$\delta^{13}C$	$\delta^{18}O$
20/4/02	2.0	−2.3	3/1/03	2.0	−1.8	17/6/03	2.0	−2.1
	2.0	−2.5		2.0	−2.1		2.0	−2.2
21/4/02	1.9	−2.2	4/1/03	2.0	−1.9	24/6/03	2.0	−1.9
	1.8	−2.2		1.9	−2.3		2.1	−1.9
25/4/02	1.9	−2.4	5/1/03	2.1	−1.8	25/6/03	2.0	−2.1
27/4/02	2.0	−2.1		2.0	−1.8		1.9	−2.3
28/4/02	2.0	−2.1	6/1/03	2.0	−2.0	26/6/03	2.1	−1.8
4/6/02	2.0	−2.1		2.0	−2.1		1.9	−2.0
15/8/02	2.1	−1.9	7/1/03	2.0	−2.1	5/9/03	2.1	−1.8
	1.9	−2.0		2.0	−1.9		2.1	−2.1
16/8/02	2.0	−2.3	8/1/03	2.1	−1.9	19/9/03	2.1	−2.0
	2.0	−2.0		1.8	−2.3		2.1	−1.9
17/8/02	1.9	−2.0	9/1/03	2.1	−1.9	20/9/03	2.1	−2.2
	2.1	−2.0		1.8	−2.5		1.9	−2.2
18/8/02	2.0	−2.0		1.9	−1.9	21/9/03	2.1	−1.8
19/8/02	2.0	−1.9	13/3/03	1.9	−2.3		1.9	−2.0
20/8/02	2.0	−1.9		2.0	−2.1	22/9/03	2.0	−2.3
21/8/02	2.0	−1.8	15/3/03	1.8	−2.2		2.0	−2.2
	2.0	−1.8	16/3/03	1.9	−2.0	23/9/03	2.0	−2.2
22/8/02	2.0	−1.9		2.0	−1.9		2.0	−2.5
23/8/02	1.9	−2.1	17/3/03	1.9	−2.2	24/9/03	2.0	−2.2
24/8/02	1.9	−2.1		1.9	−2.0	25/9/03	2.0	−2.4
	2.0	−1.9	13/6/03	2.0	−2.1		2.0	−2.4
31/12/02	2.0	−1.9		2.1	−2.0	26/9/03	2.0	−2.4
	2.0	−1.9	14/6/03	2.0	−2.0	27/9/03	2.1	−2.3
1/1/03	1.8	−2.5		2.0	−2.1		2.0	−2.5
	1.8	−2.3	15/6/03	2.0	−2.0	8/10/03	2.0	−2.3
1/1/03	2.0	−2.0		2.1	−1.9		2.0	−2.2
	1.8	−2.3	16/6/03	2.0	−2.1	28/10/03	2.1	−2.2
				2.0	−2.2		2.1	−2.1
						29/10/03	2.0	−2.1

Table 2.2 *Carbon and oxygen isotope ratio values of old Z-Carrara. The average values of $\delta^{13}C$ and $\delta^{18}O$ are 2.2±0.1 and –1.2±0.1 respectively (relative to VPDB in ‰).*

Date	$\delta^{13}C$	$\delta^{18}O$	Date	$\delta^{13}C$	$\delta^{18}O$	Date	$\delta^{13}C$	$\delta^{18}O$
2/3/01	2.2	–1.4	8/3/01	2.2	–1.3	13/4/01	2.3	–1.2
	2.2	–1.3		2.2	–1.3		2.2	–1.2
3/3/01	2.2	–1.2	9/3/01	2.2	–1.3	14/4/01	2.3	–1.2
	2.2	–1.1		2.2	–1.2	15/4/01	2.3	–1.1
4/3/01	2.2	–1.2	27/3/01	2.3	–1.1		2.2	–1.4
	2.2	–1.2		2.2	–1.2	21/4/01	2.2	–1.3
5/3/01	2.2	–1.3	29/3/01	2.2	–1.2		2.1	–1.5
	2.2	–1.2		2.2	–1.2	22/4/01	2.1	–1.4
6/3/01	2.2	–1.1	12/4/01	2.3	–1.1		2.1	–1.5
7/3/01	2.2	–1.3				22/4/01	2.1	–1.4

Table 2.3 *Carbon and oxygen isotope ratio values of MMB. The average values of $\delta^{13}C$ and $\delta^{18}O$ are 3.9±0.1 and –10.6±0.1 respectively (relative to VPDB in ‰)*

Date	$\delta^{13}C$	$\delta^{18}O$	Date	$\delta^{13}C$	$\delta^{18}O$	Date	$\delta^{13}C$	$\delta^{18}O$
21/07/01	3.9	–10.7	27/07/01	3.9	–10.5	27/12/01	3.8	–10.7
	3.8	–10.7	29/07/01	3.9	–10.6		3.9	–10.6
26/07/01	3.9	–10.7		3.8	–10.5	28/12/01	3.9	–10.7
	3.9	–10.6	9/11/01	3.6	–10.7			
27/07/01	3.9	–10.5		3.9	–10.6			

Table 2.4 *Hydrogen isotope ratio IAEA OH-6 and Kaolinite standard. Data are expressed relative to VSMOW in ‰.*

Date	Sample No	δD	Date	Sample No	δD
22/01/04	OH-6	–33	12/4/04	Kaolinite	–70
	OH-6	–32	12/4/04	OH-6	–35
23/01/04	Kaolinite	–68		OH-6	–35
23/01/04	OH-6	–37	20/04/04	OH-6	–30
	OH-6	–36		OH-6	–30
10/4/04	OH-6	–35	23/04/04	OH-6	–33
	OH-6	–32		OH-6	–32
	OH-6	–33			

reproducibility of the carbonate analysis was also checked with our second laboratory standard Makrana Marble (MMB) (Table 2.3).

For checking the reproducibility of hydrogen isotope ratio measurement IAEA OH-6 and kaolinite clay standard (courtesy Prof. H.A.Gilg) was used (Table 2.4).

2.7.5 Calibration of isotope data

The carbon and oxygen isotope ratios of each set of samples were calibrated based on the isotope data of laboratory standard measured in that set. The tables (Table 2.1, 2.2 and 2.3) reporting the routine analysis of the standards show the analytycal variation in isotope data. The maximum variation of carbon isotope ratio of different standards are: 1.8 to 2.1‰, 2.2 to 2.3‰ and 3.8 to 3.9‰ for ZC-2002, Z-Carrara (old) and MMB respectively. The variation in oxygen isotope ratio are: –1.8 to –2.5 ‰, –1.1 to –1.5 ‰ and –10.5 to –10.7 ‰ respectively. The hydrogen isotope ratio of IAEA OH-6 varies from –30 to –37‰. The deviation of laboratory standard's value from its calibrated value in a particular day was considered as an off set and used for calculating final delta values of the samples analyzed on that day.