ISOTOPE GEOCHEMISTRY OF SIWALIK SEDIMENTS AND SIGNATURE OF PAST CLIMATE CHANGE

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Certificate

I hereby declare that the work presented in this thesis is original and has not formed the basis for the award of any degree or diploma by any university or institution.

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Abstract

Uplift of Himalaya in Cenozoic has had a profound effect in regulating climate, vegetation and atmospheric CO_2 . It is now clear that Indian monsoon climate got established only when Himalaya attained a critical height. Weathering in tectonically active Himalaya caused lowering of atmospheric CO_2 . Establishment of monsoon and lowering of CO_2 should have had substantial effect on vegetation. The main emphasis of this thesis is to glean out the monsoonal rainfall variation, quantification of atmospheric CO_2 and build the vegetation scenario for last 11 Myr from Siwalik sediments of Himalayan foothills. The Siwalik sections selected for the present study are Haripur Khol section (Age: 6 to 0.5 Ma) of Subathu sub-basin, Ranital and Kotla section (Age: 11 to 6 Ma) of Kangra Valley, Mohand Rao section (Age: 10 to 5 Ma) of Dehra Dun Valley and Surai Khola section (Age: 13 to 1 Ma) of Western Nepal. For a comparative study Gondwana sediments from Satpura Basin of Central India have also been analyzed.

Carbon and oxygen isotope ratios of soil carbonate nodules and carbon isotope ratio of associated organic matter were measured from Ranital, Kotla and Haripur Khol sections in order to reconstruct vegetational history and change in contemporaneous rainfall. δ^{13} C values of soil carbonate show that from 10.5 Ma to 6 Ma the vegetation was C₃ type and that around ~6 Ma C₄ grasses appeared. The δ^{18} O variations of soil carbonate suggest that the monsoon system intensified, with one probable peak at around 10.5 Ma and a clear onset at 6 Ma, with peak at 5.5 Ma. After 5.5 Ma monsoon strength decreased and attained the modern day condition with minor fluctuations. This finding is supported by marine proxy of upwelling in the Arabian Sea and sedimentary morphology in Siwalik. The covariation between δ^{18} O and δ^{13} C data suggests that a change in precipitation pattern was partly responsible for expansion of C₄ grasses.

It was also noted that in a mixed C_3 - C_4 environment, estimation of abundance of C_3 and C_4 plants using soil carbonate in one case, and residual soil organic matter in another, may differ. This can be explained by assuming that the plant-respired CO_2 is the main contributor of carbon in soil carbonate and may have different isotopic composition from that of residual organic matter in soil. Since plant-respired CO_2 from C_3 or C_4 plants depends on response of each of them on growing season-the net effect

may not be representative of organic matter abundance from their residual in soil. In addition, abundance estimate of C_3 - C_4 plants also shows variation with time, probably caused by change in growing season conditions through time.

Carbon isotope ratio of early diagenetic carbonate cement from sandstone (DCCN) was measured from Mohand Rao and Haripur Khol section to reconstruct palaeovegetation. The δ^{13} C of DCCN from Mohand Rao section varies from –10.5 ‰ to –0.2 ‰ with progressive enrichment in δ^{13} C values from 9 Ma to 7.3 Ma indicating gradual change of C₃ type of vegetation to C₄ type vegetation. Post 7.3 Ma, the δ^{13} C value is anchored around zero per mil indicating mixed C₃-C₄ environment with C₄ plants dominating the ecosystem. In Haripur Khol section (from 6 Ma onwards), the δ^{13} C value of DCCN indicates presence of both C₃ and C₄ type of plants with the dominance of C₄ in ecosystem.

The oxygen isotope ratio of DCCN does not show any systematic variation with time. The δ^{18} O of DCCN from Mohand Rao section ranges from -8.9 to -13.6 ‰ and in Haripur Khol section δ^{18} O ranges from -9.9 to -13.6 ‰. At a given stratigraphic level average δ^{18} O value of DCCN is depleted (maximum depletion up to 4‰) compared to the average δ^{18} O of soil carbonate from the corresponding level. The depletion in δ^{18} O may be due to contribution from river water infiltrating the groundwater system in postmonsoon period.

Carbon and oxygen isotope ratio of soil carbonate nodules and carbon isotope ratio of associated organic matter from the same nodules were also measured from Mohand Rao section in few cases (n=9). From 9 to 8 Ma the carbon isotope ratio of soil carbonate varies from -10.8 to -7.8 ‰ indicating that the vegetation in the flood plain was characterized by C₃ dominated plants and from 5.4 to 4.8 the δ^{13} C ranges from 0.1 to -4.3 ‰ indicating mixed C₃-C₄ plants with C₄ dominating the ecosystem. The carbon isotope ratio of the organic matter from same soil carbonate nodule ranges from -25.2 to -24.4 ‰ (from 9 to 8 Ma) and -17.4 to -24.6 ‰ (from 5.4 to 4.8 Ma) corroborating the above results. The average δ^{18} O value of soil carbonate nodule for the time period 9 to 8 Ma is -8.8 ‰ and for 5.4 to 4.8 Ma the value is -7.9 ‰. These average δ^{18} O values are

comparable with the oxygen isotope data of soil carbonate from Haripur Khol and Kangra valley.

Hydrogen isotope ratio of OH group of pedogenic clays was measured in Siwalik sediment samples from Haripur Khol section. X-ray diffraction analysis of clays separated from pedogenic nodules shows presence of illite as the most dominant species followed by smectite and chlorite. The relative abundance of the three species is nearly constant throughout the section. Hydrogen isotope ratio of the clays (combined illite, smectite and chlorite) varies from -55 % to -90 % (relative to VSMOW). At around 6 Ma and 3 Ma, the hydrogen isotope ratios are characterized by lower δ D values (-80 to -90%), which probably indicates high rainfall; relatively higher δ D (-55%) values occur at around 4 Ma and 2 Ma, which may indicate low rainfall regime. It seems from these data that monsoonal intensity for the last 6 Ma varied with two clear peaks occurring at 6 Ma and 3 Ma punctuated by a decrease at 4 Ma and post 3 Ma. This variation is, in general, consistent with other proxies like vegetation and sediments architecture.

Carbon and oxygen isotope ratio of soil carbonate and carbon isotope ratio of associated organic matter from two stratigraphically superimposed Formations, Denwa and Bagra from Gondwana Supergroup were measured. The δ^{13} C value of the oldest soil carbonate from Denwa Formation is about -10.7 %, the youngest sample is -6.4 % and the average δ^{13} C value of the in-between samples is -8.4 ‰. The mean δ^{13} C value of the associated organic matter from the above samples is about -24.9%. The $\delta^{13}C$ value of soil carbonate from the different exposure of Bagra Formation is almost similar (-6.7‰) and is close to the δ^{13} C value of the youngest sample collected from Denwa Formation (contact of the Bagra Formation). The average δ^{13} C value of associated organic matter from Bagra Formation is -25.9‰. Calculations of atmospheric CO₂ concentration using the carbon isotope ratio of Denwa and Bagra soil carbonate shows that at the beginning of the Denwa Formation CO₂ concentration was about 255 ppmV and it reached a high value of 1520 ppmV at the end of Denwa Formation through an intermediate concentration of 1100 ppmV. During Bagra Formation the concentration was about 2190 ppmV. The progressive increase in CO₂ concentration during the Denwa and constant concentration at Bagra is conformable with the available CO₂ variation record from

other parts of world for the Permo-Triassic boundary to Jurassic time period. The CO₂ concentration during late Miocene (11 to 6 Ma) time was 455 ppmV.

Like carbon isotope ratio, the δ^{18} O value of soil carbonate in individual soil profiles of Gondwana and Siwalik is almost constant though the Siwalik samples show little enrichment toward surface. The average δ^{18} O value of the Siwalik soil carbonate is –9 ‰ and those of the Bagra and Denwa are –6.7 ‰ and –5.2 ‰ respectively. The δ^{18} O values of soil carbonates from the Gondwana and Siwalik probably reflect the difference in the rainfall pattern for these two time periods. In addition, δ^{18} O of Bagra and Denwa indicate that amount effect in rainfall played a major role in determining the oxygen isotope ratio of soil carbonate.

Carbon and oxygen isotope ratios of carbonate cement from Siwalik sandstone were measured from Surai Khola section of western Nepal. The δ^{18} O values of cement show three evolutionary phases. From 12 Ma to ~6 Ma, the average δ^{18} O is around – 13.6±1.9 ‰ (n=114) with a large spread from –10 to –18 ‰. This large spread probably indicates dissolution and re-precipitation of carbonate at various stages during burial. Subsequent to 6 Ma, δ^{18} O shows sudden swing towards enriched values with less scatter in data; the enrichment continues up to 4 Ma with maximum δ^{18} O value around –7 ‰. The average δ^{18} O value for this period is –10.7 ±1.6 ‰ (n=25). From 4 Ma to 2 Ma, δ^{18} O remains fairly uniform with an average value of –8.8±1.2 ‰ (n=17). The increase in oxygen isotope ratio of carbonate cement in sandstone occurs concurrently with that of soil carbonate, indicating a major role of meteoric water in changing oxygen isotope ratio of diagenetic carbonate cement. However, the oxygen isotope ratio of carbonate cement of sandstone is relatively depleted compared to that of soil carbonate in 6 Ma to 4 Ma time range. The depletion probably indicates precipitation of sandstone cement at a temperature higher than that of soil carbonate.

 δ^{13} C values of calcite cement do not show any definite trend with time. From 12 Ma to 7 Ma, the δ^{13} C ranges between -3.3 to -9.9 ‰ with an average of -7.1 ± 1.5‰ (n=91). Subsequent to 7 Ma, the number of relatively enriched ¹³C values increases. From 7 Ma to 2 Ma, the δ^{13} C varies from -2.8 to -9.2 ‰ with an average of -5.7±1.5 ‰ (n=65). Relatively enriched δ^{13} C for post 7 Ma period is due to appearance of C₄ plants,

which have enriched ¹³C, compared to C₃ plants. The large spread in δ^{13} C of the cement probably indicates production of CO₂ at various stages of diagenesis of organic matter. Diagenesis of organic mater at various depths produces CO₂, which could have large range of carbon isotope ratio depending on the depth-level of CO₂ generation.

Mineralogical assemblages show increase in diagenesis with increase in depth. Clay minerals ($<2\mu$) separated from sandstone comprises of smectite, illite, chlorite and kaolinite. Relative increase in the abundance of illite and decrease in the abundance of smectite indicate illitization of smectite with increase in burial, which is compatible with observed absence of K-feldspar in lower stratigraphic succession. Dissolution of Kfeldspar might have supplied potassium for illite formation. In the younger samples Kfeldspar is present but shows corrosive features.

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CHAPTER-1

INTRODUCTION

1.1 Introduction

Asian monsoon is an important climate system of the tropical region. A seasonally reversing wind system with moist oceanic air from southwest during summer and cold, dry continental air from northeast during winter characterizes the monsoon climate. This system is responsible for heavy rains during June, July, August and September in the Indian sub-continent. It is believed that the monsoon system got initiated relatively recently in the geological past (about 20 Myr ago) due to uplift of Himalayas beyond a critical height (Harrison et al., 1992). Heating of land in summer at high elevation intensifies low pressure over the Tibetan plateau creating a powerful pump for moist air from oceans, which results in heavy rainfall during summer months. Reverse circulation of wind occurs during winter; the radiative cooling of elevated landmass is responsible for flow of cold dry continental air towards the ocean.

Experiments with atmospheric general circulation model have shown that changes in elevation of Himalaya-Tibet have large effect on the intensity of monsoon (Prell et al., 1992). Simulation with no mountains or reduced elevation results in significantly weaker or even no monsoon circulation. Monsoon intensity could also be affected by changes in surface boundary conditions, such as the albedo of Africa-Asia, the extent of snow cover over Tibet, the sea surface temperature of the Indian Ocean and the concentration of atmospheric CO_2 (Prell et al., 1992). Information regarding variation of monsoon intensity through time can be obtained from ocean sediments (Kroon et al., 1991; Nigrini, 1991; Prell et al., 1992; Prell and Kutzbach, 1992). During summer monsoon, the wind flow from ocean causes transport of surface water and develops intense centers of upwelling. The upwelling brings cold, nutrient-rich waters from several hundred meters' depth to the surface and trigger high productivity in the photic zone. Duration and intensity of the upwelling reflect the intensity of the upwelling system has a direct link to the structure and intensity of the monsoonal winds.

Monsoon variation record from ocean is well constrained in terms of wind strength. In the Arabian Sea, intense seasonal upwelling is induced by the southwesterly monsoon winds. Sediments in the northwest Arabian Sea exhibit characteristic fauna (radiolarians and foraminifers) that are endemic to areas of upwelling. These biota are Chapter-1

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normally encountered only in cool temperate waters and therefore, their appearance and abundance in sediments should indicate upwelling characteristics. Miocene to recent sediments from the northwest Arabian Sea show distinct geochemical and biological changes, which suggest that monsoonal upwelling conditions were established about 8 Myr ago (Kroon et al., 1991). Pelagic sediments deposited before 10.5 Ma contains nannofossils, which are characteristic of warm water and relatively low productivity. Opal rich sediments, which reflect initiation of strong monsoon circulation, were deposited between 10.5 Ma and 8.0 Ma (Prell et al., 1992). The monsoon intensity variation in ocean should also reflect in continent in terms of variation of rainfall amount. However, only limited information is available about monsoonal rainfall variation from continental archives (Quade et al., 1989).

Uplift of Himalaya and Tibet may also have an indirect but potentially more extensive effect on global climate through the action of carbon cycle (Ruddiman and Prell, 1997). Chemical weathering of silicate rocks on land is the primary long-term sink for atmospheric CO_2 . Carbon dioxide combines with water and forms carbonic acid, which slowly attacks silicate rocks resulting in net subtraction of CO₂ from atmosphere. The tectonic uplift could increase the rate of removal of CO_2 from atmosphere due to combined effect of several factors inherent to regions of uplifted terrain. Some important factors are:(i) active faulting that exposes fresh un-weathered rocks, (ii) vigorous high altitude mechanical weathering due to steep slopes, lack of vegetation, and (iii) strong summer precipitation from monsoon rains (in the Asian context) on the windward margins of high plateaus or from orographic rainfall in summer or winter on the windward slopes of mountain ranges. These factors generate large volume of unweathered bedrock in a highly pulverized form that promotes rapid chemical weathering in the wet environment consuming CO₂ (Raymo and Ruddiman, 1992). However, the uplift-weathering hypothesis for change in CO_2 concentration was challenged by other workers, who contend that CO_2 concentration was controlled mainly by volcanic degassing and metamorphism in subduction zone and thus sea floor spreading and subduction are primary drivers of changes in atmosphere CO_2 level through time (Berner et al., 1983).

 CO_2 decrease in atmosphere and change in rainfall pattern during Miocene time should have had substantial effect on vegetation (Cerling et al., 1997; Pagani et al., 1999). Pre-Miocene epoch was dominated by trees. Evolution of grasses and expansion of grasslands are observed during late Miocene indicating possible atmospheric control on vegetation.

Monsoon rainfall signature during Miocene can be reconstructed from Siwalik sediments, which are derived from higher reaches of Himalaya and deposited by various rivers in the Himalayan foreland basin stretching from Arunachal Pradesh of India in east and Potwar Plateau of Pakistan in the west (Fig.2.1). The Siwalik basin is a synsedimentary basin where sediments were deposited during the last 20 Myr forming a sediment pile as thick as 5 km in some places (Johnson et al., 1985). The lower and middle Siwalik sediments are characterized by intercalation of palaeosols with sandstones while the upper part is characterized by intercalation of conglomerate and palaeosols with occasional lenses of sandstone. These sediments contain a variety of components such as soil carbonate, organic matter, early diagenetic carbonate cement and clay minerals which are sensitive tools for reconstructing vegetation, atmospheric CO₂ concentration and climatic history. Besides, the huge thickness of sediments is ideal for studying geo-chemical changes associated with burial diagenesis.

1.2 Previous studies from Siwalik

The first attempt towards reconstruction of monsoonal rainfall was done based on oxygen isotope ratio of soil carbonate from Potwar Plateau of Pakistan Siwalik (Quade et al., 1989). Enrichment in ¹⁸O of soil carbonate from Potwar Plateau at around 8 Ma was interpreted as intensification of monsoon in the Indian subcontinent. However, δ^{18} O of soil carbonate is a function of several variables, such as temperature of carbonate formation, amount effect in rainfall, source of moisture, shifts in seasonality etc. (Quade et al., 1995; Quade and Cerling, 1995; Stern et al., 1997; Sanyal et al., 2004a). In addition, the amount of precipitation and δ^{18} O of the corresponding soil carbonate is governed by geographical configuration of the site during the formation of palaeosol. Thus the interpretation of δ^{18} O change in soil carbonates is quite complex and it is not clear if δ^{18} O increase can be explained by an increase in rainfall. Normally, an increase in rainfall is associated with a decrease in δ^{18} O (Yurtsever and Gat, 1981) and not an increase as observed by Quade et al. (1989).

Later study by Quade et al (1995) from Surai Khola section of Nepal Siwalik showed that the enrichment in ¹⁸O of soil carbonate took place at 6 Ma i.e. it was delayed by 2 Myr relative to Pakistan Siwalik indicating that climate variation implied by δ^{18} O change did not occur concurrently across the Himalayan belt.

The enrichment of ¹⁸O in soil carbonate in Potwar Plateau was followed by dramatic change in carbon isotope ratio at around 7.8 Ma indicating change in vegetation from pure C_3 type to a mix of C_3 - C_4 . The change in vegetation was thought to be a result of monsoon intensification mentioned above (Quade et al., 1989). Later studies from different sections in low latitude areas showed that the timing and nature of

Area	Time of	Characteristics of C_3 to C_4 plants
	appearance of	transition
	C ₄ plants (Ma)	
East Africa (3°S to 5°N)	8 to 7.5	Very rapid
	7.8 to 6	Slightly more gradual
Pakistan (32°-33°N)		
Southern North	6.8 to 5.5	
America (20°-37°N)		
Central North America	4	
(40°-43°N)		
Western Europe		No indication of C ₄ in mammal diet at
(40°-50°N)		any time

Table 1.1 Timing and nature of C_4 grass expansion in different areas (After Cerling et al., 1997)

 C_4 plant expansion varied from place to place (Table 1.1). Studies on carbon isotope ratio of tooth enamel from East Africa showed that around 8 Ma mammals had a significant fraction of C_4 biomass in their diet. Tooth enamel data from North America show that samples older than 7 Ma indicate a C_3 dominant diet. The modern distribution of C_4 plants in North America, including the south to north gradient from C_4 to C_3 in the Great Plains is recognizable only from about 4 Ma ago (Cerling et al., 1997). Overall, it was found that the appearance of C_4 plants was earlier in tropical region compared to the high latitude belts.

1.3 Causes of vegetational change

A major vegetational change of the type mentioned above must have been caused by change in some component of climate system affecting plant world. Some ideas in this field are discussed below.

 pCO_2 and temperature model: Cerling et al. (1997) proposed that atmospheric CO_2 and temperature have controlled the spatial and temporal distribution of C_4 plants. It has been found that the photosynthetic efficiency of C_3 grasses relative to C_4 grasses varies



Fig.1.1 Relation between daytime growing-season temperature and atmospheric CO_2 for grasses. C_4 grasses are favored in high temperature and low CO_2 concentration.

with both atmospheric CO₂ level and temperature (Fig.1.1). The crossover point

favoring C₃ grasses over C₄ grasses is dependent on temperature and partial pressure of CO_2 in such a way that C₄ dominated ecosystems are favored under low pCO₂ conditions when accompanied by elevated temperature. At low CO₂ and high temperature, C₄ plants have physiological advantages over C₃ plants. The CO₂ fixing enzyme Rubisco in C₃ plants has affinity for both CO₂ and O₂ particularly at high temperature. At low CO₂/O₂ ratio the active site of Rubisco reacts with both CO₂ and O₂. Oxygen is undesirable for photosynthesis. To remove oxygen from photosynthetic pathway plants also release CO₂ by a process known as photorespiration, which causes net decrease in rate of photosynthesis.

On the other hand, CO_2 fixing enzyme Phosphoenol Pyruvate (PEP) in C₄ plants has only affinity for CO₂. As a result, C₄ photosynthesis can occur under very low CO₂ concentration. In addition, high CO₂ concentration in the bundle sheath cells minimizes photorespiration in C₄ plants. This mechanism has advantages in hot and arid environment where plants have to close their stomata to prevent water loss. However, in doing so, they also reduce the ability to take CO₂ from atmosphere. But high affinity of PEP for CO₂ and absence of photorespiration allow C₄ plants to continue photosynthesis at low CO₂ concentrations. This led Cerling et al. (1997) to propose that lowering of atmospheric CO₂ was the main cause for appearance and expansion of C₄ plants.

This model is compatible with earlier appearance of C_4 plants in low latitude areas (Cerling et al., 1997) since the crossover can occur faster (during gradual decrease of CO₂) due to higher temperature. With progressive decrease in CO₂ concentration in atmosphere, C_4 plants appeared later in higher latitude at relatively lower temperature. Lowering of CO₂ in the atmosphere was attributed to increased weathering rate during last 40 Myr in the tectonically active Himalayan belt (Raymo and Ruddiman, 1992).

Quantification of atmospheric CO_2 for the last ~20 Myr has been done using various proxies like stomatal index (ratio of stomata to epidermis cell in leaf) of leaf, boron isotope ratio of foraminifera and carbon isotope ratio of alkenone (Fig. 1.2). The number of stomata in a leaf depends on the atmospheric CO_2 concentration; the number decreases with decrease in CO_2 . The stomatal index variation of fossil *Quercus petraea* leaves indicates that CO_2 concentration fluctuated between 280 to 370 ppmV during the last 10 Myr (Van Der Burgh et al., 1993) (Fig. 1.2a). Boron isotopic composition of foraminifera has also been used to reconstruct CO_2 concentration for the last 21 Myr. The boron isotopic composition of foraminifera depends on the pH of seawater as well as its isotopic composition in seawater and the pH, in turn, depends on atmospheric CO_2 concentration. Assuming that boron isotopic composition of sea water remained constant during last 21 Myr, observed variation of boron isotope ratio in foraminifera indicates that atmospheric partial pressure of CO_2 was 4.5 times the present value at 21 Ma ago and at around 7.5 Ma CO_2 reached the present day concentration (Spivack et al., 1993) (Fig. 1.2b).

Seasonality model: CO_2 estimation based on alkenone (long chain unsaturated ketone produced by haptophyte algae) from Pacific ocean is in contrast with the trend obtained



Fig.1.2 Schematic diagram showing palaeo CO_2 concentration variation obtained from various studies. a) CO_2 estimation from stomatal index variation of leaf shows CO_2 concentration has fluctuated between 370 ppmV to 280 ppmV during last 10 Myr. b) Estimation of palaeo CO_2 from Boron isotope of foraminifera show that at around 21 Ma ago, CO_2 concentration was 4.5 times higher than the present concentration. At about 7.5 Ma ago the CO_2 concentration was at present day level. c) alkenone based CO_2 concentration estimation show CO_2 concentration was lowest around 15 Ma ago; subsequently CO_2 concentration has increased and at about 9 Ma ago reached the present day value.

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from boron isotope and stomatal index study. The alkenone method of estimating pCO_2 depends on carbon isotopic fractionation during photosynthesis in haptophyte algae under nutrient limited condition where the carbon fixation is largely a function of concentration of aqueous CO₂ in the growth medium. Studies of carbon isotope ratio of alkenone from sediments showed that CO₂ in the atmosphere increased from 15 to 9 Ma and stabilized at 9 Ma (Fig.1.2c) (Pagani et al., 1999). If lowering of CO_2 was the main cause for appearance of C_4 plants it should have appeared at 15 Ma, when CO_2 concentration was lowest. This led Pagani et al (1999) to suggest that lowering of pCO₂ in the atmosphere was not the driver of vegetational change; instead, alteration in seasonal patterns of precipitation and changes in growing season condition on a global scale were responsible for appearance and expansion of C_4 plants. Their proposition was based on two arguments: first, every place showing signature of C₄ expansion was associated with change in precipitational pattern. Second, among the environments that favour C_4 plants the most notable one is arid zone with strong seasonal precipitation and high minimum temperature during the growing season for C₄ grasses (Pagani et al., 1999).

1.4 Motivation of present work

Seasonality model supports the proposition of Quade et al (1989) that change in rainfall pattern was the cause for vegetational change observed in Pakistan Siwalik. However, the timings of rainfall variation in Pakistan Siwalik and Nepal Siwalik do not agree. In Pakistan Siwalik, the vegetational change is preceded by rainfall change whereas in Nepal Siwalik, the reverse was observed. Pakistan Siwalik region is situated at the far end of Indian monsoonal rainfall track and as a result, receives only moderate amount of rainfall. It is obvious that rainfall reconstruction can be better done from Siwalik zones situated in monsoon sensitive region. In this context, presence of extensive Siwalik exposures in Himachal Pradesh, India, which experiences high monsoon rainfall in present day condition offers an excellent choice of samples for reconstructing rainfall variation.

Timing of vegetational change in Pakistan Siwalik was also challenged by other workers. Carbon isotope ratio of tooth enamel showed presence of C_4 plants as early as 9 Ma (Morgan et al., 1994). The carbon isotope ratio of long chain alkane from organic

matter also showed that C_4 plants were around at about 9 Ma (Freeman and Colarusso, 2001). Again, existence of different Siwalik sections in Indian Himalayan belt, which are well dated, provides a good opportunity for further study on this topic.

1.5 Objectives of present study

(1) Reconstruction of monsoonal rainfall variation: As mentioned previously, monsoonal climate in Indian subcontinent evolved with the rising of Himalaya. While the onset of monsoon is somewhat clear, the variation of monsoon rainfall in geological past is poorly known. The best way to investigate palaeo-monsoon is to study rainfall proxies from monsoon sensitive regions. Kangra valley and Haripur Khol Siwalik sections in Himachal Pradesh, India are two areas characterized by high seasonal rainfall (mean 550 mm during southwest monsoon; Indian Meteorological Department, 1970) with closely spaced isohyets (Rao, 1976). In this zone, the mean rainfall changes by about 350 mm if one moves over a distance of only 50 km towards north (Rao, 1976). Isotopic studies from such areas could help in deciphering past change in monsoon and assessing their relation with the expansion of C_4 plants. The proxies that offer promises to reconstruct the monsoon are oxygen isotope ratio of soil carbonate and hydrogen isotope ratio of pedogenic clay minerals.

(2) Reconstruction of vegetation from well-dated sections: Since the timing of appearance of C_4 plants in Pakistan Siwalik is debatable well-dated sections from Indian Siwalik could help in clarifying the issue. The proxies that can be used to reconstruct vegetation are carbon isotope ratio of soil carbonate, organic matter associated with soil carbonate nodules and early diagenetic carbonate cement of sandstone nodules.

(3) Estimation of atmospheric CO_2 in geological past: The CO_2 concentration in earth's atmosphere has varied enormously through the geological time (Berner, 1991; Retallack, 2001c; Ekart et al., 1999). The Paleozoic to Mesozoic era was a period of extreme fluctuations when CO_2 concentration changed from a level of 250 ppmV to ten times that level. In contrast, the Cenozoic era was characterized by a decrease in CO_2 with the minimum concentration at the Neogene Period (Ekart et al., 1999; Retallack, 2001c; Ghosh et al., 2001; Pagani et al., 1999). However, there are significant discrepancies between estimates derived from different proxies and the data is not well constrained for some geologically important time periods. Based on carbon isotope ratio in palaeosols and Cerling's model (1991) an attempt has been made in the present thesis to estimate the atmospheric CO_2 concentration for the late Neogene Period. A comparative study on CO_2 concentration for the Mesozoic time was also done based on palaeosols from Denwa and Bagra Formation of central India. There are excellent soil exposures associated with these two Formations containing well-preserved soil carbonate nodules. They provide contrasting picture of a high CO_2 concentration era in the geological history. These studies are particularly important since CO_2 concentration estimation along with monsoonal reconstruction can provide insight about the controlling factors for vegetational change.

(4) Study of diagenesis of sediments: Siwalik basin is a syn-sedimentary basin, which sank continuously by the overburden of depositing sediments. During burial, sediments undergo physical and chemical changes collectively known as diagenesis. An attempt has been made here to study diagenetic processes through isotopic changes in carbonate cement of sandstone, change in the assemblages of clay minerals and feldspar in sandstone. These studies dealing with diagenesis of sediments are necessary for proper interpretation of geochemical data.

1.6 Out line of the thesis

Geology of the field areas and experimental procedures are described in chapter two.

Third chapter deals with studies of vegetational and monsoonal rainfall variation using carbon and oxygen isotope ratio of soil carbonates from Siwalik sediments of Kangra valley and Haripur Khol belonging to Himachal Pradesh, India.

Vegetational reconstruction using carbon isotope ratio of early diagenetic carbonate cement from sandstones of Mohand Rao and Haripur Khol section is discussed in chapter four.

Fifth chapter deals with variation of monsoonal rainfall from hydrogen isotope ratio of pedogenic clay minerals from Haripur Khol section.

Sixth chapter deals with reconstruction of atmospheric CO₂ concentration using carbon isotope ratio of soil carbonate and associated organic matter from Gondwana sediments of Central India and Siwalik sediments of Northern India.

Seventh chapter deals with chemical diagenesis of Siwalik sandstones sampled from Surai Khola section of Nepal

Eighth chapter deals with conclusions and future scope of the present work.

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).

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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 gravish 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.

Surai Khola



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.

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Geology, Materials and Methods

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

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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 coarsegrained 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.

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.
 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

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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 biotubes. 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 \sim 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

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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 CO₂ 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.

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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 CO₂ from powder samples was done by either online extraction or offline 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 CO₂: 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).





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 recrvstallization.

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 $\delta = [(R_{sample}/R_{standard}) -1] \times 1000$ and R=D/H. Typical uncertainty in δ D 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 μ mole of CO₂ 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 CO₂, N₂ and O₂ 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 $-90^{\circ}C$. 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 μ mole 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 CO₂ 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 δ^{13} C and δ^{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.

- For CO₂ 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.
- Powder contamination in the line was checked periodically and the extraction line was cleaned at least once in two months.
- The machine performance was tracked routinely i) with check standard (made from Z-Carrara, ii) by checking the zero enrichment.
- 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 CO2

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 ($\delta^{13}C = 2.2 \pm 0.1$; $\delta^{18}O = -1.2 \pm 0.1$ ‰, Table 2.2). Later on, a new batch of Z-Carrara powder was made and freshly calibrated (called ZC-2002). The ZC-2002 has $\delta^{13}C = 2.0 \pm 0.1$, $\delta^{18}O = -2.1 \pm 0.2$ (Table 2.1) and was treated as laboratory carbonate standard and always analyzed along with the samples. Long-term

Date	$\delta^{13}C$	$\delta^{18}O$	Date	δ 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 2.1 *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	$\delta^{13}C$	$\delta^{18}O$
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 2.2 Carbon and oxygen isotope ratio values of old Z-Carrara. The average values of $\delta^{I_3}C$ and $\delta^{I_8}O$ are 2.2±0.1 and -1.2±0.1 respectively (relative to VPDB in ‰).

Table 2.3 Carbon and oxygen isotope ratio values of MMB. The average values of $\delta^{43}C$ and $\delta^{48}O$ 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 expressedrelative 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.

CHAPTER-3

SIGNATURE OF MONSOON VARIATION AND VEGETATIONAL CHANGE IN SIWALIK

3.1 Introduction

Carbon isotope ratio of soil carbonate is determined mainly by the type of vegetation sustained by the soil since the carbon derived from plant respiration and vegetation decay (soil respiration) is the dominant source of soil-CO₂, which leads to soil carbonate. Based on the carbon isotope ratio of soil carbonates from Pakistan and Nepal Siwaliks, it was shown that a major shift in vegetation (from a pure C₃ regime to C₄ dominant environment) occurred around 7 Ma ago (Quade et al., 1989; 1995). Later, the timing of shift in vegetation in Pakistan Siwalik was questioned by Morgan et al. (1994) who showed presence of C₄ grasses as early as 10 Ma based on carbon isotope ratio of tooth enamel. Carbon isotope ratio of alkanes extracted from soil organic matter also showed presence of C₄ plants at around 9 Ma (Freeman and Colarusso, 2001).

In Pakistan Siwalik, the above-mentioned C₃ to C₄ transition coincides with ¹⁸O enrichment in soil carbonate, which was attributed to an increase in summer monsoon strength (Quade et al., 1989). However, δ^{18} O of soil carbonate is a function of several variables, such as temperature of carbonate formation, amount effect in rainfall, source of moisture, shifts in seasonality etc. (Quade et al., 1995; Quade and Cerling, 1995; Stern et al., 1997). In addition, the amount of rainfall over a soil regime and δ^{18} O of the corresponding soil carbonate is governed by the geographical configuration of the site during the formation of palaeosol. Thus, interpretation of δ^{18} O changes in soil carbonates is quite complex and it is not clear if the δ^{18} O increase in Pakistan Siwalik can be immediately explained by an increase in rainfall. In a later paper, Quade and Cerling (1995) also pointed that out increase in monsoon rainfall should cause depletion in oxygen isotope ratio and not enrichment as observed.

The presence of extensive Siwalik exposures in many parts of present-day India provides an opportunity for further studies on this topic. The present work was aimed to document the timing and nature of C_4 grass expansion in the Indian Siwaliks and its possible relationship to changes in rainfall. We present an investigation carried out on three Siwalik sections, two from the Kangra sub-basin (Ranital and Kotla) and one from the Subathu sub-basin (Haripur Khol) in Himachal Pradesh, India (Fig 2.1). These two areas are located in a region expected to be sensitive to changes in monsoon pattern because the seasonal rainfall in this part is very high (550 mm during SW monsoon; Indian Meteorological Department, 1970) with closely spaced isohyets (Rao, 1976). Therefore, a small shift in monsoon pattern is expected to result in major change in rainfall here. Isotopic studies from such an area can help in deciphering past changes in monsoon circulation and in assessing their relation with the expansion of C_4 grasses.

3.2 Results

We identified six palaeosols in Ranital with easily discernible top and bottom parts where they are in contact with sandstone beds (see Fig.6.2); all these soils contain nodular soil carbonate. This allowed us to study the isotopic variation as a function of depth in a *single* soil profile.

The mean δ^{13} C values of soil carbonate nodules from six individual soil profiles from Ranital are $-11.1 \pm 0.3 \%$, $-10.9 \pm 0.5 \%$, $-10.4 \pm 1.0 \%$, $-11.1 \pm 0.6\%$, $-11.0 \pm 0.4\%$, -11.1 ± 0.6 , (n=2 to 4). The values are tightly clustered except one deviant sample with unusual enrichment (-5‰) (Table 3.1; Fig.3.1).

 δ^{13} C of soil carbonate nodules in the Ranital section (corresponding to 11 Ma to 6 Ma) ranges from -11.5 ‰ to -7.8 ‰ (Table 3.2), whereas in the Kotla section (corresponding to 11 Ma to 6.5 Ma) it ranges from -12.2 ‰ to -9.3 ‰ (Table 3.2; Fig.3.2a). Correspondingly, δ^{13} C values of organic matter range from -24.7 ‰ to -26.3 ‰ in the Ranital section and -23.7 ‰ to -25.6 ‰ in the Kotla section (Table 3.2; Fig.3.2c). In these sections, the difference between δ^{13} C of organic matter and the soil carbonate, $\Delta(\delta^{13}$ C), lies within 14.9 ± 1 ‰. In the Haripur Khol section (corresponding to 6 Ma to 0.5 Ma) δ^{13} C of soil carbonate ranges from -4.8 ‰ to +2.4 ‰ (Table 3.2; Fig.3.2a). The corresponding δ^{13} C of the soil organic matter lies between -18.2 ‰ and -24.3 ‰ (Table 3.2; Fig.3.2c); the mean $\Delta(\delta^{13}$ C) in the Haripur Khol section is 19.7 ± 1.9 ‰.

The variability in δ^{13} C values of soil carbonate and organic matter is higher in Haripur Khol (post 6 Ma) compared to Kangra valley (Ranital and Kotla; pre-6 Ma). In Haripur Khol, the average δ^{13} C is $-2.3 \pm 1.7 \%$ (n=28), whereas for Kangra valley the mean value is $-10.3 \pm 1.3 \%$ (n=50). The average δ^{13} C of organic matter from Kangra valley, is $-25 \pm 0.7 \%$ (n=21) and for Haripur Khol it is $-21.9 \pm 1.9 \%$ (n=30) (Table 3.3). Chapter-3

Monsoon and Vegetation

As in the case of carbon isotopic ratio, oxygen isotope ratio of soil carbonate from a soil profile does not vary significantly with depth, except for marginal enrichment near the surface (Fig.3.1). The mean δ^{18} O values of nodules from six individual soil profiles from Ranital are $-9.2 \pm 0.6 \%$, $-8.9 \pm 0.5 \%$, $-8.0 \pm 1.3 \%$, $-8.8 \pm 0.8 \%$, $-8.9 \pm 0.2\%$, $-10.7 \pm 0.8 \%$.

The isotopic data from the three sections (Haripur Khol, Ranital and Kotla) along with the age of the samples (see section 2.2 for discussion on age) can be combined to make a composite plot representing regional time variation of carbon and oxygen isotope ratios (Fig.3.2a, b, c). The composite plot for δ^{13} C shows a major change at about 6 Ma when the values become more positive by about 8 ‰. In the composite plot, the oxygen isotope ratio shows three evolutionary phases (indicated by three solid lines in Fig 3.2b). At around 10.5 Ma, δ^{18} O is characterized by highly depleted value of about –10 ‰; it tends towards more positive side with decrease in age, reaching –6.6 ‰ at around 6.5 Ma. Subsequently, the isotope ratio is characterized by a sharp depletion going up to –9 ‰ at 6.0 Ma and then a second phase of enrichment reaching –6.5 ‰ at around 2 Ma. These indicate two phases of depletion occurring around 10.5 Ma and 6.0 Ma punctuated by a period of maximum enrichment at around 6.5 Ma. Though the δ^{18} O values show definite trend with time, they are also characterized by scatter at the same stratigraphic depth, which complicates the interpretation.

3.3 Discussion

3.3.1 Information on vegetation change from carbon isotope ratio of soil carbonate and associated organic matter

Based on carbon isotope ratio, plants can be divided into two main photosynthetic pathways, C_3 and C_4 , whose isotopic ratios are quite different. The majority of plants, comprising trees, shrubs, cool–season grasses, etc., follow C_3 pathway. The $\delta^{13}C$ of C_3 plants vary over a large range: -20 ‰ to -35 ‰ but the average is well constrained at -26.7 ‰. For C_4 type of plants (grasses), $\delta^{13}C$ values range from -6 ‰ to -19 ‰, with an average of about -13 ‰ (Cerling et al., 1997). Plant debris and associated bio-organic residues get incorporated in the soil (especially after death of the plants) and constitute the soil organic matter, which preserves the mean carbon isotopic composition of the contemporary vegetation with little or no fractionation. The soil carbonate forms from soil solution that uses soil CO₂ derived from oxidation of soil organic matter and plant respiration. In this step, the carbonate gets enriched in ¹³C with respect to the source carbon (Cerling, 1984) due to two processes, namely, diffusion of CO₂ and equilibrium fractionation associated with carbonate precipitation from solution. The diffusion causes an enrichment of 4.4 ‰ in ¹³C in soil CO₂ compared to the soil-respired CO₂. The equilibrium fractionation causes a further isotopic enrichment in soil carbonate depending on the temperature (for example, enrichment of 12.7‰ occurs at 0 °C and 9.8 ‰ at 25 °C). Assuming average soil temperature between 0 to 25 °C, the net increase in carbon isotopic ratio in transition from soil organic matter to soil carbonate [$\Delta(\delta^{13}C)$] should be in the range of about 14 ‰ to 17 ‰ if soil pCO₂ is high enough to prevent infiltration of atmospheric CO₂ (Cerling et al., 1989). However, occasionally $\Delta(\delta^{13}C)$ values lie beyond 14 ‰ to 17 ‰ limits even when the temperature is within 0 to 25 °C (Pendall and Amundson, 1990;

Table 3.1 Carbon and oxygen isotope ratio of soil carbonate and carbon isotope ratio of associated organic matter from individual soil profile from Ranital Section of Kangra Valley. $\delta^{I3}C$ and $\delta^{I8}O$ are given relative to PDB in ‰ with errors of analysis: ±0.05 ‰ for carbonates and ±0.1‰ for organic carbon. Depth is measured from the top of each soil profile identified in the field by sharp transition to mudstone above.

Sample No	Depth (cm)	δ ¹³ C (‰)	δ ¹⁸ Ο (‰)	δ ¹³ C _{Org} (‰)	Sample No	Depth (cm)	δ ¹³ C (‰)	δ ¹⁸ Ο (‰)	δ ¹³ C _{Org} (‰)
Profile-1					Profile-4				
PRL-010A1	30	-11.3	-8.7	-24.6	PRL-013A3	70	-10.6	-9.3	
PRL-010A2	55	-11	-8.7		PRL-013A1	30	-11.5	-8.2	
PRL-010A3	90	-11.5	-10	-25.3	Profile-5				
PRL-010A4	120	-10.7	-9.2	-25.2	PRL-019A	30	-11.0	-8.6	
Profile-2					PRL-019A1	45	-10.4	-9.0	-24.7
PRL-02B1	5	-4.9	-8.2		PRL-019A2	60	-11.4	-9.0	
PRL-02B2	30	-11.4	-9.2		PRL-019A3	90	-10.4	-8.8	-24.7
PRL-02B3	55	-10.9	-8.8		Profile-6				
PRL-02B4	95	-11.4	-9.4		PRL-017A	30	-11.3	-11.1	
Profile-3					PRL-017C	50	-10.5	-11.2	
PRL-03A01	30	-9.5	-6.6		PRL-017D	80	-11.1	-9.8	
PRL-03A0	35	-9.5	-7.1						
PRL-03A4	70	-11.2	-8.8						

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Table 3.2 Carbon and oxygen isotope ratio of soil carbonate and carbon isotope ratio of associated organic matter from Ranital, Kotla and Haripur Khol section. Age of each sample is determined by interpolation between palaeomagnetically dated horizons.

Ranital Section											
Sample No.	Age $\delta^{13}C$	δ ¹⁸ Ο	$\delta^{13}C$	Sample No.	Age	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$			
	(Ma) Carb	Carb.	Org.	DDI 11	(Ma) _.	Carb.	Carb.	Org.			
PKL-02B2	10.9 -11.4	-9.2	na	PRL-11	6.2	-8.2	-0.0	-26.3			
PRL-02B3	10.9 -10.9	-8.8	nd	PRL-12	6.2	-8.5	-/.1	-25.9			
PRL-02B4	10.9 –11.4	-9.4	nd	PRL-047	6.1	-7.8	-7.5	-25.9			
PRL-01	10.9 –11.4	-8.8	nd	PRL-048	6.1	-10.6	-8.7	nd			
PRL-1	10.9 –10.8	-8.7	-25.0	PRL-050	6.0	-10.7	-7.5	nd			
PRL-010A1	10.0 -11.3	-8.7	nd	Kotla Sect	tion						
PRL-010A2	10.0 -11.0	-8.7	nd	Sample	Age	δ ¹³ C	δ ¹⁸ Ο	$\delta^{13}C$			
PRL-010A3	10.0 -11.5	-10.0	nd	No.	(Ma)	Carb.	Carb	Org.			
PRL-010A4	10.0 -10.7	-9.2	nd	KRL-2	10.5	-9.6	-9.7	nd			
PRL-04A	9.7 -10.9	-7.8	nd	KRL-7	10.3	-9.3	-9.8	-23.7			
PRL-011	9.5 -11.2	-8.1	nd	KRL-11	9.2	nd	nd	-24.5			
PRL-2	9.5 -10.7	-7.9	-25.3	KRL-10	9.2	-10.8	-8.7	nd			
PRL-013A1	9.4 -11.5	-8.2	nd	KRL-13	8.8	-9.7	-9.4	-24.0			
PRL-013A3	9.4 -10.6	-9.3	nd	KRL-14	8.7	-10.8	-8.9	-25.0			
PRL-022	9.4 -11.5	-8.1	nd	KRL-17	8.5	-11.1	-9.4	-24.0			
PRL-017A	9.3 -11.3	-11.1	nd	KRL-20	8.4	-12.2	-7.9	-24.0			
PRL-017C	9.3 -10.5	-11.2	nd	KRL-21	7.9	-10.9	-7.9	-24.5			
PRL-017D	9.3 -11.1	-9.8	nd	KRL-22	7.9	-10.7	-7.3	nd			
PRL-06	9.1 -10.7	-8.7	-24.8	KRL-24	7.1	-10.7	-7.4	-24.8			
PRL-019A	9.0 -11.0	-8.6	nd	KRL-28	6.3	-9.4	-6.9	-24.2			
PRL-019A1	9.0 -10.4	-9.0	nd	KRL-29	6.2	-9.4	-6.8	-25.6			
PRL-019A2	9.0 -11.4	-9.0	nd	Haripur K	Chol sec	ction					
PRL-019A3	9.0 -10.4	-8.8	nd								
PRL-3	8.8 –9.9	-7.2	-25.1	Sample	Age	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$			
PRL-024	8.8 -10.8	-9.3	nd	No.	(Ma)	Carb	Carb	Org			
PRL-026	8.7 -10.0	-7.8	nd	HP-2(c)	5.9	-4.8	-8.7	-24.3			
PRL-029	8.7 -10.7	-7.6	nd	HP-3(c)	5.9	-4.2	-8.5	-23.9			
PRL-032	8.1 -10.2	-8.7	-25.5	HP-6(c)	6.0	-4.6	-8.8	-24.0			
PRL-5	8.0 -10.1	-6.8	-25.2	HP-8(c)	5.6	-2.6	-9.1	-23.3			
PRL-037	7.4 –9.1	-8.0	nd	HP-13(c)	5.4	-2.8	-9.5	-18.2			
PRL-9	7.3 -8.3	-8.3	-24.7	HP-15(c)	5.2	-2.8	-8.4	-21.1			
PRL-042	7.1 -10.3	-7.7	nd	HP-18(c)	5.0	nd	nd	-23.5			
PRL-10	6.9 –9.5	-7.3	-25.9	HP-A20(c)	4.8	-1.3	-8.2	-20.6			

Haripur Khol Section													
Sample No.	Age	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	Sample No.	Age	$\delta^{13}C$	δ^{18} O	$\delta^{13}C$				
	(Ma)	Carb.	Org.	Org.		(Ma)	Carb.	Carb	Org				
HP-A23(c)	4.7	-4.5	-9.8	-23.8	HP-42(c)	2.7	nd	nd	-23.4				
HP-21(c)	4.1	-3.2	-8.2	-22.3	HP-53(c)	2.6	0.4	-7.1	-22.3				
HP-24(c)	3.9	-1.9	-7.6	-23.1	HP-54(c)	2.6	-2.6	-7.5	-21.3				
HP-26(c)	3.8	-0.5	-6.6	-21.7	HP-55(c)	2.5	0.2	-7.6	-22.3				
HP-30(c)	3.8	0.4	-7.0	-20.7	HP-57(c)	2.5	-2.6	-7.5	-22.6				
HP-31(c)	3.7	-2.7	-8.2	-22.4	HP-61(c)	2.3	-2.2	-7.2	-22.4				
HP-33(c)	3.6	-1.6	-8.6	-23.4	HP-64(c)	2.3	-2.3	-6.6	-23.0				
HP-36(c)	3.3	-2.6	-7.2	-20.3	HP-65(c)	2.3	-3.5	-7.5	-23.0				
HP-37(c)	3.3	-3.4	-7.2	-19.8	HP-66(c)	2.2	-3.3	-7.3	-18.2				
HP-38(c)	3.2	-4.3	-8.3	-23.0	HP-70(c)	1.9	2.4	-6.8	-18.3				
HP-39(c)	3.2	nd	nd	-18.2	HP-73(c)	1.9	1.4	-7.4	nd				
HP-40(c)	3.0	0.9	-7.6	-23.5									

nd = not determined

In the Kangra valley, the carbon isotope ratio of individual palaeosols shows little variability with depth, except for one sample in soil Profile # 2 at depth ~5 cm (Table (3.1) (Fig.3.1)). The enriched value is probably due to contribution from atmospheric CO₂ ($\delta^{13}C = -7 \%$) since the sample has a depth less than 25 cm (Cerling, 1984). The mean $\delta^{13}C$ (-10.9 ‰) obtained from the six profiles indicates that the source of carbon in the nodules is exclusively from plant-respired CO₂ (C₃ plant) if the samples are taken from a depth greater than ~25 cm (Fig.3.1) in a soil profile.

Data from the Kangra valley show that between ~10.5 to 6 Ma the floodplain was dominated by C_3 plants. Surprisingly, previous studies from neighboring Siwalik regions of Pakistan and Nepal showed that around 7 Ma, C_4 plants were already a major part of the ecosystem in the flood plain (Quade et al., 1989; 1995; Quade and Cerling, 1995). Unfortunately, paucity of pollen and fossil anatomy data from the Kangra valley prevents us from comparing isotopic data with vegetational record. For the interval between 6 Ma to 1.9 Ma the soil carbonate data from Haripur Khol show that the ecosystem was a mixture of C_3 and C_4 plants. The variability in $\delta^{13}C$ of soil carbonate Chapter-3

and organic matter in Haripur Khol may be a reflection of the change in growing season conditions in a mixed C_3 - C_4 environment, (see section 3.3.2 for further discussion).

The abundance of C₄ plants in Haripur Khol section can be estimated by isotopic mass balance from the data of either soil carbonate or organic matter by assuming that the mean δ^{13} C of C₄ plants is -13 % and the mean δ^{13} C of C₃ plants is -25 % (mean values of δ^{13} C_{org} measured from Ranital and Kotla sections). Such calculations show that the abundance of C₄ plants varied from 33 % to 78 % with an average of 53 ± 12 % (n=26) from soil carbonate data. In contrast, from soil organic matter of the same set of samples, estimate of C₄ plant abundance ranges from 5 % to 54 % with an average of $31 \pm 12 \%$ (n=26) (Fig.3.3). Ideally the two estimates should agree, but Fig.3.3 shows that for a given estimate of C₄ plant abundance from inorganic carbonate (take for example 50 %) the estimate from organic matter varies over a large range (from 10% to 55%). This indicates that in a mixed C₃–C₄ environment the δ^{13} C of residual organic matter cannot be taken as a proxy for the δ^{13} C of plant-respired CO₂. This is also clear from a plot of $\Delta(\delta^{13}$ C) (Fig.3.4a, derived from the composite plot: Fig.3.2.a, c) as a function of time which shows that the mean $\Delta(\delta^{13}$ C) for pre-6 Ma period is $14.9\pm1 \%$ whereas the value is $19.7\pm1.9\%$ for post-6 Ma period. Possible causes of this variation are explored below.

3.3.2 Relationship between $\delta^{13}C$ values of soil carbonate and soil organic matter

The difference between abundance of C₄ plants calculated from data of soil carbonate and soil organic matter can be explained by the source-controlled model proposed by Wang and Follmer (1998), which modifies the assumption of Cerling regarding source of CO₂ (1984). According to the Wang-Follmer model, plant residue biomass contributes to soil organic matter whereas plant-respired CO₂ provides carbon source for soil carbonate, the respiration being vigorously active during the growing season. Thus the carbon isotope ratio of soil organic matter represents annual-average C₃/C₄ biomass content, whereas soil carbonate is more representative of growing-season plant respiration.

In a mixed C₃-C₄ environment if the growing season favors C₄ plant respiration, relatively more CO₂ would be produced from C₄ plants compared to that expected from the C₃-C₄ ratio in the residual organic matter. Therefore, the δ^{13} C value of soil CO₂ will be higher than the δ^{13} C value of the residual organic matter, and soil carbonate from

such enriched soil CO₂ would make $\Delta(\delta^{13}C)$ larger than 14 ‰. Reverse case would occur if the growing season favours C₃ plant respiration.

In the Haripur Khol section, even though C_3 plants were dominant contributors of the soil organic matter, C_4 plant respiration was probably more active in the growing season compared to that of coexisting C_3 plants, which resulted in $\Delta(\delta^{13}C) > 14 \%$ (Fig. 3.4a). It is of interest to note that the $\Delta(\delta^{13}C)$ in the Haripur Khol section show wide fluctuations (16.4 to 24.4 ‰) with age. There are two major swings towards higher value- at around 4 Ma and 2.6 Ma, thus indicating higher C_4 respiration. Lower values of $\Delta(\delta^{13}C)$ at around 3.2 Ma and 2.2 Ma may reflect the reverse condition. It is apparent that accurate estimates of these changes may have climatic implications. We note that each data point refers to a single soil profile, which represents time-averaged record over ~ 1,000 to 10,000 yr (Retallack, 2001a).

Table 3.3 *Carbon isotope ratio difference between soil carbonate and associated soil organic matter* $[\Delta (\delta^{13}C) = \delta^{13}C_{S,C} - \delta^{13}C_{Org}].$

Ranital S	ection		Kotla Secti	on		Haripur Khol Section			
Sample No	Age (Ma)	$\Delta(\delta^{13}C)$	Sample No	ple Age $\Delta(\delta^{13}C)$ Sample (Ma) No.		Age (Ma)	$\Delta(\delta^{13}C)$		
FKL-1	10.9	13.9	KKL-/	10.5	14.4	$\Pi F - 2(C)$	5.9	19.5	
PKL-2	9.5	14.3	KKL-10	9.2	14.0	HP-3(C)	5.9	19.7	
PRL-06	9.1	14.1	KRL-13	8.8	14.3	HP-6(c)	6.0	19.4	
PRL-3	8.8	14.9	KRL-14	8.7	14.2	HP-8(c)	5.6	20.7	
PRL-032	8.1	15.3	KRL-21	7.9	14.0	HP-15(c)	5.2	18.3	
PRL-5	8.0	15.1	KRL-24	7.1	14.1	HP-A20(c)	4.8	19.3	
PRL-042	7.1	15.6	KRL-28	6.3	16.2	HP-A23(c)	4.7	19.3	
PRL-10	6.9	15.5	KRL-29	6.2	14.8	HP-21(c)	4.1	19.1	
PRL-11	6.2	16.9				HP-24(c)	3.9	21.2	
PRL-12	6.2	16.9				HP-26(c)	3.8	21.2	
Haripur l	Khol sec	tion							
Sample No HP-30(c)	Age (Ma) 3.8	$\Delta(\delta^{13}C))$ 22.4	Sample No HP-38(c)	Age (Ma) 3.2	$\Delta(\delta^{13}C)$ 18.7	Sample No HP-61(c)	Age (Ma) 2.3	$\frac{\Delta(\delta^{13}C)}{20.2}$	
HP-31(c)	3.7	19.7	HP-40(c)	3.0	24.4	HP-64(c)	2.3	20.7	
HP-33(c)	3.6	21.8	HP-53(c)	2.6	22.7	HP-65(c)	2.3	19.5	
HP-36(c)	3.3	17.7	HP-54(c)	2.6	18.7	HP-66(c)	2.2	14.9	
HP-37(c)	3.3	16.4	HP-55(c)	2.5	22.5	HP-70(c)	1.9	20.7	

Therefore, any inference regarding variations in growing season conditions would refer to average climatic fluctuations over this interval.

In this context it may be mentioned that climatic fluctuations have also been inferred from variation of oxidation, hydroxylation and humification index of



Fig.3.1 Carbon and oxygen isotope ratio variation in soil carbonate taken from various depths within individual soil profiles (total 6) from Ranital section, Kangra valley. The carbon isotope ratio shows little variation with depth except one point ($\delta^{I_3}C = -5\%$), which may represent dominant atmospheric CO₂ contribution in soil CO₂. $\delta^{I_3}C$ values are consistent with C₃ type of plants in the soil. Oxygen isotope ratio shows enrichment as one moves towards the surface which may be due to evaporation of water from the top surface of the soil.

Haripur Khol palaeosols. The indices are based on selective saturation levels of induced magnetic field, inorganic and organic carbon content, and Rb/Sr ratios. Variations in the indices indicate large-scale climate changes within the Pliocene-Pleistocene time span,
with warm-humid climate during early Pliocene and intermediate phase during the early mid-Pliocene and warm oxidative phase during the mid to late Pliocene. The early-mid Pleistocene was characterized by a cold phase (Sangode et al., 2001).

Color and maturity of palaeosols also show evidence of climate change during the Pliocene-Pleistocene time period. Between 5.3 and 2.6 Ma, warm and humid climate



Fig.3.2 Composite plot of isotope ratios against age of soil carbonate nodules from three sections (Ranital, Kotla and Haripur Khol) a) Carbon b) Oxygen and c) Organic matter from the same nodules. Carbon isotope ratio of soil carbonate and associated organic matter indicates that vegetation was entirely of C_3 type from 11 to 6 Ma. Post 6 Ma time is marked by appearance and expansion of C_4 grass. Oxygen isotope composition shows stepwise variation with probable peak at ~10.5 Ma and a clear peak at ~6 Ma. These variations are attributed to change in monsoon rainfall. The solid lines are drawn to guide the eye.

is inferred from the formation of red Alfisols with soil carbonate and Fe nodule and strong illuviation of clay forming well-developed Bt horizons. After 2.6 Ma, formation of poorly developed yellow soils with commonly occurring nodular soil carbonate and calcite material disseminated in the ground mass indicate slightly cooler and drier climate (Thomas et al., 2002).

Fortunately a different record of monsoon variation in Plio-Pleistocene period is available from sea sediments, which gives us an opportunity to compare our results. The relative abundance variation of radiolarian species *Actinomma* in the Arabian Sea, a marine proxy for upwelling caused by monsoon winds, shows variation after 6 Ma with peaks around 4.7, 3.8, 3 and 2.2 Ma (Prell et al., 1992). Although there is no one to one correlation between the abundance peak of radiolarian species and higher value of $\Delta(\delta^{13}C)$, but overall, a monsoon change interpretation seems to agree with the observed



Fig.3.3 Cross plot of estimates of C_4 plant abundance from two phases, soil carbonate and soil organic matter from Haripur Khol section. Calculations were done by isotopic mass balance and using the data of soil carbonate and soil organic matter, taking mean $\delta^{13}C$ of C_4 plant as – 13 ‰ and that of C_3 plants as –25 ‰. The figure shows that for a given estimate of C_4 plant from soil carbonate (take for example 50 %) the estimate from soil organic matter varies over a large range (from 10% to 55%).

 $\Delta(\delta^{13}C)$ change for the post-6 Ma period (Fig.3.4a and Fig. 3.4b.). In case of Kangra valley, despite changes in climatic condition from 10.5 Ma to 6.5 Ma, as discussed later, the $\Delta(\delta^{13}C)$ value is nearly constant at 14 ‰ because only C₃ type of plants dominated the region at that time (Fig.3.4). This is consistent with Cerling's model (Cerling, 1984), which shows that for a single type of plants (in this case C₃) the change in soil respiration rate does not affect $\delta^{13}C$ significantly provided soil respiration rate is high.



Fig. 3.4 a) Variation of $\Delta(\delta^{I3}C)$ ($\delta^{I3}C$ soil carbonate $-\delta^{I3}C$ organic matter) through time. In Ranital and Kotla $\Delta(\delta^{I3}C)$ is 14.9±1‰ which is well within the prediction of diffusionproduction model (Cerling, 1984). However, in Haripur Khol mean $\Delta(\delta^{I3}C)$ is 19.7±1.9‰, which is beyond the predicted value of diffusion-production model. The variation of $\Delta(\delta^{I3}C)$ in Haripur Khol is probably caused by growing season variation induced by climatic change. Variation is absent in pre 6 Ma period since only C_3 type of plants were present at that time. **b**) Abundance variation of endemic upwelling radiolarian species Actinomma in the Arabian Sea indicating variation in monsoonal strength. Comparison between the variation of $\Delta(\delta^{I3}C)$ and abundance of radiolarian species shows reasonable agreement during the last 5 Ma, but not exact correlation.

3.3.3 Supporting evidence of growing season change in Haripur Khol

The pollen record from Haripur Khol section supports the interpretation of variation of growing season condition with time. Considering the relative frequency of

ecologically significant taxa, four major stages of vegetation has been recognized in Haripur Khol (Phadtare et al., 1994). The stages are: I) 4 to 3.5 Ma, II) 3.5 to 2.7 Ma, III) 2.7 to 2.5 Ma, and IV) 2.5 to 1 Ma. During stage I, the vegetation was dominated by dry grassland. The variety of monoporate, psilate and distinctly microreticulate pollen morphotypes indicates that at least four prominent genera of Poaceae were thriving in this area. The presence of Amaranth/Chenopodiaceae along with members of Polypodiaceae and other ferns further shows that at a few places, these plants were thriving during rainy to early summer times. During stage II, there was significant drop in percentage of grass pollens associated with sudden rise of the spores of Lycopodium and polypodiaceous ferns. During the later half of this stage, significant rise in Amaranth/Chenopodiaceae and large concentration of Ceratopteris pores indicates a marshy or muddy condition. During stage III, consistent increase in the spores of Lycopodium along with regular presence of algal cysts as well as dicot pollens collectively suggest the existence of well-developed ponding conditions. Presence of Nymphaeaceae indicates shallow-water or seasonal lacustrine habitat. A large population of *Pinus* pollen, restricted only to this stage, also indicates a temperate to sub-tropical climate. During stage IV, which is marked by the presence of volcanic ash bed, the leaf tissues are found to be abnormally thick. The abnormal cell wall thickness at this stage is intriguing but could be due to response of the leaves to a cool and dry climate (Phadtare et al., 1994). Also, effect of a possible CO₂ concentration change cannot be ruled out (Retallack, 2001b).

The above discussion indicates that the post-4 Ma vegetational regime in this part of the Indian Siwalik carries signature of major climatic changes, which could have prompted variations in the C₃:C₄ ratio, the type of C₃/C₄ plants and growing season condition which was finally recorded in the $\Delta(\delta^{13}C)$ variation observed here (Fig.3.4).

3.4 Oxygen isotope ratios of soil carbonate

3.4a Source of scatter in data

Oxygen isotope ratio of soil carbonate depends upon the isotopic ratio of soil water derived from local precipitation. Hence the δ^{18} O of soil carbonate can be used to decipher the average isotopic composition of precipitation (Quade et al., 1989). However, in the near-surface zone, the isotopic ratio of soil water can be significantly

enriched in ¹⁸O due to evaporation (Amundson et al., 1989; Quade et al., 1989). The δ^{18} O analysis of nodules at different depths from six individual soil profiles from Kangra valley (Fig.3.1) shows such enrichment towards the top. Therefore, the ¹⁸O-depleted values deeper in the profile would better represent the soil water.

In individual soil profiles, higher variability in oxygen isotope ratio compared to that of carbon isotope ratio may reflect differential infiltration of seasonal precipitation. Precipitation may penetrate differentially into a soil, with deeper infiltration during one season, and more run-off during another. Because seasonal differences can cause changes in isotopic composition of meteoric water, a preferential infiltration may result in soil water delta value different from that of the average local meteoric water (Mora et al., 1993). Similar explanation can be offered for variation of δ^{18} O observed at a given depth in the composite profile. However, the variation in the composite δ^{13} C profile is not due to this reason. The scatter in the pre-6 Ma period is due to combination of data from two locations (Ranital and Kotla) each having slightly different C₃ population with different delta values (-25.4‰ for Ranital and -24.4 ‰ for Kotla). The post-6 Ma period is characterized by a mixed C₃-C₄ regime with two sources of scatter: variation in the relative proportion of C₃ and C₄ plants in different soils and the growing season variability. Despite the scatter, signals of distinct change (in both δ^{18} O and δ^{13} C) are easily discernible in these records.

3.4b Implication of δ^{18} O variation

A major assumption in the interpretation of δ^{18} O of soil carbonate is that it forms in isotopic equilibrium with the soil water. This can be tested if the soil temperature is known. As a first-order approximation, the soil temperature can be taken as the mean annual air temperature (T) of the location. The fractionation factor between calcium carbonate and water is given by (Friedman and O'Neil, 1977): 1000ln $\alpha_{water}^{calcite} = 2.78 \times 10^6$ / T² - 2.89 where $\alpha_{water}^{calcite} = (1000 + \delta^{18}O_{calcite})/(1000 + \delta^{18}O_{water})$. The δ^{18} O of rainwater in Kangra and Haripur Khol has not been measured but can be estimated from data pertaining to the Delhi region (IAEA, 2003). The mean annual weighted average δ^{18} O in Delhi rain is about -6 ‰ (relative to SMOW). Correcting for the continental effect (a decrease of about 0.4‰; Krishnamurthy and Bhattacharya, 1991) and enrichment effect (about 1 ‰) due to evaporation during recharge (Salomons et al., 1978) the δ^{18} O of soil water in Kangra can be estimated to be –5.4 ‰. Taking the mean annual temperature of Kangra and Haripur Khol to be about 23 °C (based on the meteorological data of Pathankot, which is 60 km from Kangra valley) Kangra soil carbonate is expected to have a δ^{18} O value of –7 ‰ (PDB), which is close to the observed mean value of the younger soil carbonates from both Kangra and Haripur Khol. The close agreement lends validity to the equilibrium assumption for the soil carbonate as well as the temperature estimate. The situation is complex when one wants to interpret the isotope data for the old soils since the past soil temperature has to be known or estimated.

Taking modern δ^{18} O value of the Kangra soil water (-5.4 ‰) as representative, a δ^{18} O value of ~ -10 ‰ (PDB) for soil carbonate (at 10.5 Ma) would require mean annual temperature of about 39 °C (using Friedman and O'Neil equation). This value is unrealistically high for the region and, therefore, temperature cannot be the cause for ¹⁸O depletion at 10.5 Ma; the same argument holds for depletion observed at 6.0 Ma. Additionally, the geographical location of the site was not significantly different from that of today (Harrison et al., 1998) and, therefore, the mean temperature was probably similar to that of today.

We propose that the above-mentioned two phases of depletion in ¹⁸O, which occurred around 10.5 Ma and 6.0 Ma, (Fig 3.2b) reflect an increase in the intensity of summer monsoon rainfall. The summer monsoon in North India is characterized by heavy rains during June, July, August and September and is caused by convective vortex of west-northwest moving depressions originating from the Bay of Bengal operating on moist oceanic air moving in the same direction. In contrast, during winter, dry continental air blows from the northeast, resulting in little rains except occasional precipitation in Kangra region due to western disturbances bringing moisture from the Mediterranean region. The winter rains are usually more enriched compared to summer rains as observed from the seasonal variation data of Delhi rains (IAEA, 2003). Furthermore, δ^{18} O of rainwater decreases with an increase in the amount of precipitation (IAEA, 2003). At low latitudes, the average monthly rainfall and the mean monthly δ^{18} O are usually negatively correlated, showing that an increase of 100 mm of precipitation is associated with a decrease in δ^{18} O by 1.5 ‰ (Yurtsever and Gat, 1981). Therefore, it can

be argued that the two phases of depletion in oxygen isotopic composition of soil carbonate (i.e. during 10.5 Ma and 6.0 Ma) were the result of contemporary intensification of the summer monsoon, because intensified monsoonal wind system would generate more intense and frequent depressions (storms) and result in more rains. It is to be noted that Quade et al. (1989) also obtained depleted δ^{18} O values at about 10.5 Ma and in their composite profile, the maximum depletion occurs at about 9 Ma. Subsequently, the value increases and the scatter becomes too large to detect any signal. We obtained an increasing trend up to 6.5 Ma with an attendant swing after 5.5 Ma. This sharp change is probably present but not clearly recorded in the profile of Quade et al. (1989). One reason could be that, the Pakistan Siwalik is located at the farthest end of the Indian monsoon system and consequently may not be able to record minor oscillations, which may show up in Indian Siwalik.

3.5 Comparison of monsoon evolution with other proxies

It is natural to enquire if there are other proxies showing monsoon intensification signals in this time scale. In the marine regime, there are foraminiferas (e.g. *G. bulloides*), which are sensitive indicators of upwelling, whose strength is influenced by monsoon winds. Interestingly, a quantitative frequency analysis of *G. bulloides* from the Arabian sea shows high abundance values around 8 Ma, followed by gradual diminution around 5.5 Ma. This is succeeded by an increase at around 4.5 Ma that continued until today, with minor oscillations (Kroon et al., 1991) (Fig.3.5). Radiolarian assemblages also show onset of monsoon at 11.9 Ma (followed by weakening at 9.6 Ma) and an upwelling peak at around 4.7 Ma (Nigrini, 1991). The ~4.5 to 4.7 Ma monsoon intensification peak in ocean data is close to our proposed monsoon increase at ~6 Ma. Though *bulloides* data are somewhat different, the radiolarian increase during 11.9 to 9.6 Ma is close to the 10.5 Ma Siwalik peak. The time difference of about 1 Myr or less between the two systems could be due to dating errors inherent in the age control of the two systems.

Sedimentological evidences from Siwalik support our observation regarding changes in the Indian summer monsoon. The fluviatile sedimentation of the Himalayan Foreland Basin (HFB) was controlled by tectonics and weathering with a strong influence of climate. Kumar et al. (2003a) observed two major changes of sedimentation



Fig.3.5 Comparison between abundance variation of G. bulloides in Arabian Sea and oxygen isotope ratio variation of soil carbonates from Siwalik through time. Arrows show correlation of monsoon intensity between the two records.

pattern and drainage organization at 10 Ma and 5 Ma and several minor interspersed events, reflecting environment of sedimentation during the entire 10 to 0.5 Ma period. The succession around 10 Ma is characterized by multistory sandstone with abundant erosional surfaces but no lateral accretionary surfaces, and low palaeoflow variability. These features indicate deposition in frequently avulsing large braided river system. Net sediment accumulation rate also increased by a factor of 2 to 3 at 10 Ma. This change may be due to uplift of source area coupled with intensified rainfall regime. Although increase in tectonism can produce high relief, more detritus transportation of sediment across the foreland basin requires enhanced discharge by large river systems, which can be brought about only by intense rainfall (Kumar, et al., 2003a). The evidence for increase in tectonism is provided by mineralogical studies, which show that the Central Crystalline zone suffered a major uplift in response to reactivation of the Main Central

Chapter-3

Monsoon and Vegetation

Thrust (MCT) at around 10 Ma (Zaleha, 1997; Hisatomi, 1990; Ghosh and Kumar, 2000; White et al., 2001). In addition to the tectonic controls on basin fill, climate also exerted an influence on the overall distribution of grain size and rate of sediment supply to the basin. Formation of purple and brown colored palaeosols with calcareous nodules around 10 Ma suggests a humid warm climate. Fluvial architecture during this time also suggests a gradual increase in river size and its discharge. For example, mass accumulation rate in the Ganga basin shows rapid increase around 10 Ma (Metivier et al., 1999). From a host of such sedimentary features, it appears that precipitation in the Himalayan region increased at around 10 Ma.

Presence of gypsum needles in the Ranital section at around 6.5 Ma, noted during the present field excursion, indicates extreme aridity marking a weakened phase of the monsoon. This was quickly followed by widespread distribution and stacking of conglomerate and progradation of alluvial fans between 6 and 5 Ma, suggesting a broad catchment area with high basin relief (Kumar et al., 2003b) heralding the second phase of monsoon intensification. It provided a high volume of sediment resulting in distribution of coarse-grained sediments in the proximal part, and fine sediments in the distal part of the alluvial fan system.

In Siwalik sections of Pakistan and India, strata older than 8 Ma are characterized by thick amalgamated sandstone with minor occurrence of overbank deposits. The overbank deposits are characterized by deeply leached palaeosols lacking humic horizons. In contrast, the lithofacies younger than 8 Ma are characterized by abundant overbank deposits with shallowly leached palaeosols having significant humic horizons. This lithofacies contrast suggests that flooding and effective rainfall were considerably greater before 8 Ma (Burbank et al., 1993).

It is known that uplift of the Tibetan plateau had profound influence in the initiation of Asian monsoon system. However, there exists a great deal of uncertainty regarding the time of attainment of present day elevation of Tibetan plateau. Harrison et al. (1992) suggested that much of the elevation was attained ~8 Ma ago. In contrast, Coleman and Hodges (1995) argued that the Tibetan plateau was uplifted to its present elevation ~14 Ma ago. Supporting evidences for the latter are provided by studies of Edward et al. (1996) and Yin et al. (1994) suggesting uplift of High and Tethyan

Himalaya during the middle Miocene (17–11 Ma). Recent paleo-botanical evidence from the Namling basin (West of Lhasa) also indicates that the plateau had already attained its present elevation at around 15 Ma (Spicer et al., 2003). The bulk of the evidences thus favour an earlier timing for uplift of the Tibetan plateau.

Although the above studies provide a time constraint for plateau upliftment and consequent initiation of Monsoon, they do not necessarily imply *intensification* of the southwest monsoon. Burbank et al. (1996) showed that almost all the Siwalik sections from Pakistan to Nepal recorded acceleration in sedimentation and increase in subsidence at around 11 Ma. This increase in sediment flux to the Himalayan foreland basin was probably due to the combined action of intensified monsoonal precipitation and tectonic activity. In this context, our study provides support for enhanced precipitation at around 10.5 Ma.

3.6 Causes of C₄ plant appearance

It is well known that physiology of C_4 plants provides them with competitive advantage over C_3 plants when the ratio of atmospheric CO_2/O_2 concentration is low. Moreover, the ability to increase internal CO_2 concentrations allows C_4 plants to decrease their stomatal conductance, which effectively increases their water-use efficiency. Such adaptations provide advantages under hot, high-irradiance, water stressed conditions, where plants must close their stomata to prevent water loss, and in doing so they also reduce the ability to take CO_2 from the atmosphere. However, as they can concentrate CO_2 within the leaf they can continue photosynthesis without any hindrance. The above physiological considerations led Cerling et al. (1997) to propose that a lower concentration of atmospheric CO_2 operating in typical low latitude temperatures was the main cause of expansion of C_4 plants.

This proposition is compatible with observed lowering of the atmospheric CO_2 concentration in the Neogene period. Boron isotope ratios of foraminifera act as a proxy for surface ocean pH and indicate that atmospheric partial pressure of CO_2 was 4.5 times the present value at 21 Myr ago (Fig.1.2) (Spivack et al., 1993). Stomatal index variation of fossil leaves also shows a Late Miocene CO_2 decline in atmosphere (Fig.1.2) (Van Der Burg et al., 1993; Retallack, 2002). However, there are some recent studies, which are at variance with this proposition (Fig.1.2). As mentioned in the introduction,

reconstruction of paleo-CO₂ concentrations from alkenones led Pagani et al. (1999) to rule out CO₂ change as the cause for C₄ expansion. Instead, they attributed this event to increasing seasonality and aridity (Pagani et al., 1999). Their model is based on the fact that C₄ expansion was always associated with changes in seasonal pattern of precipitation during late Miocene time. For example, evolutionary trends in mammals and floras from middle to late Miocene suggest a pattern of increasing seasonality and aridity in North America, Europe, Africa, Pakistan and Australia. Increase in δ^{18} O values of soil carbonates from Pakistan, Nepal, East Africa, Argentina and the eastern Mediterranean, as well as in δ^{18} O values of tooth enamel from Argentina and North America, suggest increasing evaporation and aridity preceding and accompanying the expansion of C₄ flora (Pagani et al., 1999).

Our study from the Indian Siwalik shows that hydrological change is not always accompanied by vegetational change. Around 10.5 Ma, monsoon was intensified and contemporary vegetation was characterized by C_3 type of plants. After 10.5 Ma, monsoon strength started diminishing and by 6.5 Ma it reached the weakest phase. But during this entire period (10.5 Ma to 6.5 Ma) the vegetation was exclusively of C_3 type. The intensification of monsoon after 6 Ma was accompanied by appearance of C_4 plants (Fig.3.3a, 3.3b). An intense monsoon implies not only high rainfall but also strong seasonality, and we think that this latter property could have helped in the invasion of C_4 plants.

It is, therefore, clear that monsoon was intensified first at 10.5 Ma and then at 6 Ma, but C_4 plants appeared only at around 6 Ma. This indicates that although a change in seasonality associated with strong monsoon was probably a controlling factor for the appearance of C_4 plants, this factor must have operated in tandem with CO_2 decline discussed above. It is likely that initial lowering of CO_2 created an environment for C_4 grasses that was facilitated by change in precipitational pattern and the expansion of C_4 plants in Indian Siwalik followed this combined change.

3.7 Conclusions

The evolution of southwest monsoon, which is the main source of precipitation in the Indian subcontinent, was not gradual. The monsoon system intensified with one probable peak at around 10.5 Ma and a clear onset at 6 Ma with peak at 5.5 Ma; after 5.5 Ma monsoon strength decreased and attained the modern–day condition with minor fluctuations. From 10.5 Ma to 6 Ma, the floodplain was exclusively dominated by C_3 plants. C_4 plants appeared after 6 Ma and this coincides with monsoon intensification. From 6 Ma to 1.8 Ma the vegetation was characterized by a mixture of C_3 and C_4 types of plants. The sudden appearance of C_4 plants at ~ 6 Ma probably reflects the compound effect of intensified monsoon and lowering of pCO₂ in the atmosphere.

Our studies demonstrate that in a mixed C_3 - C_4 environment, estimates of abundance of C_3 and C_4 plants from soil carbonate and associated soil organic matter may differ. Because soil carbonate is derived exclusively from plant-respiration, this difference may be due to differential response of respiration by these two types of plants (C_3 and C_4) to growing season. The abundance estimate based on $\delta^{13}C$ of soil carbonate would, therefore, change if the growing season differs from time to time in response to climate fluctuations. Consequently, the difference in $\delta^{13}C$ values of soil carbonate and organic matter may provide a unique way to decipher past climatic change.

CHAPTER-4

PALAEOVEGETATIONAL RECONSTRUCTION BASED ON EARLY DIAGENETIC CARBONATE CEMENT OF SANDSTONE NODULES

4.1 Introduction

It is now well established that a remarkable transition in vegetation took place in the Indian subcontinent during late Miocene. Based on carbon isotope ratio of soil carbonates from palaeosol beds of Siwalik sections in Pakistan and Nepal Quade et al (1989, 1995) showed that around 7 Ma ago there was a sudden invasion of C₄ plants. Subsequent analysis showed that the timing of transition from pure C₃ to mixed C₃-C₄ era was different in different Siwalik sections. For example, in the Pakistan Siwalik, expansion of C₄ plants started rapidly at around 7.7 Ma (Quade et al., 1989) whereas in the Surai Khola section of Nepal Siwalik it was 0.7 Myr later (Quade et al., 1995). Our study from the Kangra valley, India, showed absence of C₄ plants before 6 Ma (Sanyal et al., 2004a).

As mentioned before, the presence of extensive Siwalik exposures in many parts of present-day India provides an opportunity for further studies on this topic. However, scarcity of soil carbonate nodules in Indian Siwalik sections prevents accurate reconstruction of the timing and nature of C_3 to C_4 transition in these sections. In this context, it is worthwhile to explore if the carbon isotope ratio of early diagenetic carbonate cement in sandstone nodules can be used to reconstruct a picture of palaeovegetation. Since the cement is primarily derived from dissolved carbonate in shallow ground water, which is in isotopic equilibrium with local plant-derived CO_2 . Signature of vegetation change can have some reflection in $\delta^{13}C$ of the cement. However, a precondition for signal preservation in cement is negligible post depositional changes (Quade and Roe, 1999).

Here we present an investigation carried out in two Siwalik sections: Mohand Rao of Dehra Dun sub-basin (DSB) in Uttaranchal and Haripur Khol of Subathu sub-basin (SSB) in Himachal Pradesh (Fig.2.1). In the Mohand Rao section, early diagenetic sandstone nodules are continuously present between 9 to 5 Ma whereas only a few nodule bearing soil horizons are seen. In the Haripur Khol section (age 6 to 1 Ma) both soil carbonate nodules as well as early diagenetic sandstone nodules are present throughout the section thus providing an opportunity for intercomparison and validation of cement data. In this chapter early diagenetic carbonate cement of sandstone nodules

has been referred to as "DCCN", soil carbonate nodules as "SCN" and carbonate cement of sandstones as "CCS" for simplicity.

4.2 Evidence for early diagenetic character of the cement

Quade and Roe (1999) were the first to use carbon isotope ratio of DCCN from Siwalik sections of Pakistan to reconstruct palaeovegetation. The early diagenetic sandstones occur in the field as densely cemented nodules that stand out in relief in outcrops upon weathering. For the present study, rounded nodules (Fig.4.1) and ellipsoidal nodules with long axis parallel to bedding planes (Fig.4.2) were chosen. In this type of nodules, calcite cement constitutes 35-60 % of matter by volume, which is consistent with the porosity of slightly compacted or uncompacted sands (Fig.4.3) (Quade and Roe; 1999).

The carbon and oxygen isotope ratios at various points in the section of a nodule were determined to check isotopic homogeneity (Fig.4.4). Carbon isotope values at different points vary from -0.5 to -1.1 ‰ with an average of -0.8±0.2‰ and the corresponding oxygen isotope ratio varies from -11.6 to -11.9 ‰ with an average of - $11.8\pm 0.1\%$ (n=14). The dispersion in δ^{13} C and δ^{18} O values is quite small. This shows that the nodules are isotopically un-zoned and do not contain significant amount of later generation cements which may complicate the issue by having different and possibly variable composition.

4.3 Mudstone facies with concretions in Mohand Rao Section

As mentioned in section 2.4b, abundance of mudstone facies is low in Mohand Rao section. The mudstone occurs as discontinuous lenticular body within the multistoried sandstone beds (between 350 and 1400 m). In the lower and upper part, these beds are 0.5 to 8 m thick and gray (rarely brown) in color. Green mottling is common in the mudstone and palaeosols. Mudstone shows evidence of biological activities and comprises vertical, unlined burrows (skolithos) and surface traces (sinusitis). Pedogenic concretions are common locally and mudstones show immature soil profile (Kumar, 2004)

4.4 Results

Isotopic analysis of DCCN from Mohand Rao section shows that at around 9 Ma DCCN δ^{13} C is about –10.5 ‰ and then progressively becomes enriched with time. At

around 7.5 Ma, the δ^{13} C is -3.2 ‰. From 7.5 to 6 Ma the δ^{13} C is almost constant at about zero per mil. In Haripur Khol section (6 to 1 Ma), δ^{13} C of DCCN varies from -3.5 ‰ to 0.4 ‰ (Fig.4.5a, Table 4.1).

The corresponding δ^{18} O value of DCCN in Mohand Rao section varies from – 8.9‰ to –13.6 ‰ and in Haripur Khol section from –9.9 ‰ to –13.6 ‰ (Fig.4.5b, Table 4.1).

DCCN from Mohand Rao Section			DCCN form Haripur Khol section				
Sample No	Age (Ma)	δ ¹³ C (‰)	δ ¹⁸ Ο (‰)	Sample No	Age (Ma)	δ ¹³ C (‰)	δ ¹⁸ Ο (‰)
MD-1s-N	9.0	-10.5	-10.8	HP-12S	5.4	-2.0	-9.9
MD-3S-N	8.9	-6.1	-12.1	HP-A24S	4.7	-2.8	-12.4
MD-4S-N	8.7	-6.6	-11.7	HP-23S	3.9	-0.9	-13.6
MD-5S-N	8.6	-8.4	-13.6	HP-32S	3.6	-3.5	-11.7
MD-7S-N	8.2	-6.0	-8.9	HP-33S	3.3	0.4	-12.3
MD-8S-N	8.0	-4.0	-12.0	HP-38S	3.2	-0.2	-12.5
MD-10S-N	7.5	-3.2	-11.2	HP-39S	3.0	-0.7	-12.7
MD-19S-N	6.5	-0.3	-12.6	HP-40S	2.8	-3.2	-12.6
MD-20S-N	6.5	-0.7	-11.2	HP-41S	2.8	-0.4	-12.4
MD-21S-N	6.4	-0.3	-10.5	HP-50S	2.6	-2.3	-11.8
MD-22S-N	6.3	-0.2	-12.1	HP-51S	2.6	-0.6	-11.4
MD-24S-N	6.0	-2.0	-12.1	HP-53S	2.5	-0.4	-10.7
				HP-58S	2.4	-2.8	-10.7

Table 4.1 *Carbon and oxygen isotope ratio of DCCN from Mohand Rao and Haripur Khol sections. Values are relative to VPDB in ‰.*

Table 4.2 $\delta^{13}C$ and $\delta^{18}O$ of SCN and $\delta^{13}C$ of organic matter associated with SCN from Mohand Rao. Values are relative to VPD in ∞ .

Sample No	Age (Ma)	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C_{\text{Org.}}$	Sample No	Age (Ma)	$\delta^{13}C$	$\delta^{18}\!O$	$\delta^{13} C_{\text{Org.}}$
MD-1C	9.0	-10.8	-8.8	-24.4	MD-2(C)	5.4	-4.3	-8.9	
MD-2C	8.5	-9.2	-7.4	-24.5	MD-4(C)	5.3	-1.6	-7.1	-19.0
MD-2C1	8.5	-9.5	-9.6	-24.4	MD-5(C)	5.3	-2.7	-7.8	-22.6
MD-7C(N)	8.2	-7.8	-9.0	-25.2	MD-6(C)	5.3	-3.3	-8.5	-24.3
					MD-7(C)	4.8	0.1	-6.8	-17.4

Mohand Rao section and Haripur Khol section are about 100 km apart and both the places are located in a monsoon sensitive region. As the geographical configuration of India has not changed much from the Siwalik time, the isotopic data from Mohand Rao and Haripur Khol sections can be combined to make two composite plots representing regional time variation of carbon and oxygen isotope ratios of DCCN (Fig.4.5) respectively. In such composite plot carbon isotope ratio shows enrichment starting from 9 Ma and reaches its maximum value at around 7.0 Ma. Subsequently, till about 1.8 Ma the δ^{13} C is reasonably constant with some scatter in data (within ± 1‰) (Fig.4.5a). The δ^{18} O of sandstone nodules in composite plot does not show any systematic variation with time (Fig.4.5b).

The δ^{13} C of the SCN (n=9) in Mohand Rao section ranges from -10.8 ‰ to -7.8 ‰ between the time period 9 to 8 Ma and from 5.4 to 4.8 Ma, the δ^{13} C ranges from -4.3 to 0.1‰ (Fig.4.6a, Table 4.2) and the δ^{13} C of associated organic mater ranges from -25.2 to -24.4 ‰ and -17.4 ‰ to -22.6 ‰ respectively (Fig.4.6c, Table 4.2). The δ^{18} O value of SCN in the time range 9 to 8 Ma varies from -9.6 ‰ to -7.4 ‰ and in between 5.4 to 4.8 Ma the value varies from -8.9 ‰ to -6.8 ‰ (Fig.4.6b, Table 4.2).

4.5 Discussion

4.5.1 Carbon isotope ratio of soil carbonate and early diagenetic carbonate cement of sandstone

In section 3.3.1 it was argued that carbon isotope ratio of soil carbonate could be used to reconstruct vegetation scenario as the soil carbonate forms in isotopic equilibrium with soil CO₂, which, in turn, represents local vegetation. Carbon isotope ratio in shallow ground water just below the soil zone is also in or near isotopic equilibrium with plant-derived CO₂ as demonstrated by ¹⁴C and stable isotope studies (Pearson and Hanshaw, 1970; Fritz et al., 1978; Bath et al., 1979; Deak, 1979; Andrews et al., 1984; Wassennar et al., 1992; Leaney and Herczeg, 1995; Clark et al., 1997). Ground water calcite cement should also form in equilibrium with this reservoir, as long as it forms shortly after burial without any interaction with carbon sources other than plant-CO₂. Hence, carbon isotope ratio of early diagenetic carbonate cement could also be used to reconstruct the type of vegetation (Quade and Roe, 1999).



Fig. 4.1 a) Occurrence of rounded nodules in sandstone bed b) Close view of the same Rounded sand nodule.



Fig.4.2 Ellipsoidal sandstone nodules with long axis parallel to bedding.



Fig.4.3 Thin section shows two quartz grains separated by calcite cement indicating that cementation of sediments occurred before significant burial. The calcite cement constitutes 35-60 % of the nodule which is consistent with the porosity of slightly compacted or uncompacted sand (Q=Quartz; C= carbonate cement) (Quade and Roe, 1999).

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The carbon isotope ratio of DCCN from Mohand Rao section indicates that around 9 Ma the vegetation was exclusively of C_3 type and subsequently it shows the appearance of C_4 plants. Gradually, the C_4 plants started dominating the ecosystem and reached its acme at around 7.0 Ma and continued to dominate the vegetation in a mixed C_3 - C_4 environment. The carbon isotope ratio of SCN from the same section also shows the presence of C_3 type of plants between 9-8 Ma (except one sample possibly indicating isolated appearance of C_4 plants, Fig.4.6a). Around 5 Ma, the vegetation was characterized by both C_3 and C_4 types of plants with the dominance of C_4 type of plants in the ecosystem.



Fig.4.4 Carbon and oxygen isotope ratio of carbonate cement in a DCCN. The uniformity in carbon (-0.8 ± 0.2) and oxygen isotope ratios (-11.8 ± 0.1) throughout the nodule section indicates that the nodule is isotopically un-zoned and does not contain significant amount of later generation cements.



Fig.4.5 Composite plot of isotope ratios against age for sandstone nodules from Mohand Rao and Haripur Khol sections. a) Carbon isotope ratios of DCCN show that at around 9 Ma the vegetation was mainly C_3 type and subsequently C_4 plants started appearing. By 6 Ma abundance of C_4 plants reaches a high value and remains so thereafter. b) Oxygen isotope ratios of DCCN do not show any systematic variation. The dispersion in $\delta^{18}O$ may be due to variable contribution of river water into shallow groundwater.





Fig.4.6 Time variation of carbon isotope ratio of soil carbonate nodules (a) and associated organic matter (c) from Mohand Rao section indicates that around 9 Ma the vegetation was purely C_3 type, whereas a mixed C_3 - C_4 environment existed around 5 Ma. b) Oxygen isotope ratio of soil carbonate from Mohand Rao section at about 9 Ma and 5 Ma are almost similar and comparable to the oxygen isotope ratio of soil carbonate from Kangra valley and Haripur Khol section for the same time period. These oxygen isotope values are depleted compared to the values obtained in other section for different time periods (Chapter3). The depletion has been attributed to an intensification of the monsoon.

Studies based on carbon isotope ratio of SCN from Siwalik showed that the transition from C_3 to mixed C_3 - C_4 type was abrupt with distinct difference in time of appearance of C_4 plants in different sections (Quade et al., 1989; 1995; Quade and Cerling, 1995; Sanyal et al., 2004a). The carbon isotope ratio variation of DCCN from Mohand Rao section offers a relatively continuous picture and indicates that the appearance of C_4 plants was earlier compared to other sections and the transition from C_3 to mixed C_3 - C_4 plant regime was gradual in this area. C_4 plants appeared just after 9 Ma and took around 2 Myr to reach its maximum abundance.



Fig.4.7a Detrital carbonate (DC) in sandstone. The abundance of the detrital carbonate varies from 5-20%.



Fig.4.7b Thin section showing blocky micritic grains (SC) possibly representing intrabasinal soil carbonate. Q = Quartz.

4.5.2 Comparison between δ^{13} C of early diagenetic carbonate and soil carbonate

The main source of carbon in SCN and DCCN is plant-derived CO₂. In addition, minor (5-20 %) amount of detrital carbonate is also present as seen from thin section analysis of sandstone nodules. Our observation of low detrital amount is consistent with the earlier published data (Quade and Roe, 1999). The detrital carbonate in the sandstone is probably marine carbonate, derived from Himalayan sediments (Fig.4.7a). In some cases, fragments of SCN are also seen (Fig.4.7b). Since the Himalayan carbonates have δ^{13} C close to zero which is quite different from SCN values ranging from -10 to +2% (depending on vegetation cover on soil) contribution of detrital carbonate may change the original δ^{13} C signature of groundwater cement. Fig.4.8 shows the correlation between δ^{13} C values of SCN and DCCN where samples of DCCN and SCN represent adjacent beds. The scatter of the points and deviation from 1:1 line probably points towards variable but minor contribution of detrital carbonates in sandstone nodules. It is also possible is that δ^{13} C values of DCCN reflect vegetation over a broader area than one represented by average SCN (Quade and Roe, 1999). In the Himalayan foothills, the active floodplain is dominated by C₄ plants in post- 6 Ma period (Quade et al., 1995; Sanyal et al., 2004a) whereas C₃ forest covers higher abandoned terraces and adjacent frontal Himalayan foothills. Therefore, the δ^{13} C of SCN and DCCN from adjacent beds may differ due to variable contribution from water draining C₃ sources and influencing DCCN.

4.5.3 Oxygen isotope ratio of soil carbonate and early diagenetic carbonate cement of sandstone

The oxygen isotope ratio of SCN and DCCN depends on several factors such as oxygen isotope ratio of ambient water, the temperature at which the carbonate precipitates, post depositional (late) diagenetic changes etc. If diagenetic effect is not significant it is possible to derive information about rainfall variation in the past from δ^{18} O data. It was discussed in section 3.4 that oxygen isotope ratio variation in SCN from the Kangra Valley and Haripur Khol section of Indian Siwalik reflects a change in amount of rainfall in the past (Sanyal et al., 2004a). It is seen that the oxygen isotope ratio variation from the above sections is characterized by two phases of depletion, which occurred around 10.5 Ma and 5.5 Ma reflecting increase in the intensity of

summer monsoon rainfall (Sanyal et al., 2004a). In contrast, the oxygen isotope ratio of DCCN does not show any systematic variation with time (Fig.4.5b). It is noted that, at a given stratigraphic level, the average δ^{18} O value of DCCN is depleted (maximum depletion being about 4‰) compared to the average δ^{18} O of SCN from the same level (Fig.4.5b). The cause of this depletion may be related to the difference in the source of water. In case of SCN the source of water is local rainfall whereas, shallow ground water



Fig.4.8 Correlation between the carbon isotope ratios of soil carbonates and early diagenetic carbonate cements of sandstones. The plot represents samples taken from adjacent beds. The scatter of the points and deviation from 1:1 line points towards variable but minor contribution of detrital carbonates in sandstone nodules.

from which carbonate cement in sandstones precipitates could have contribution from other sources. In the Indo-Gangetic plain, during the post monsoon period the river water feeds the groundwater. The average δ^{18} O of water from tributaries of Yamuna river (which is close to the sampling sections) for the period just after monsoon is – 9.7‰ (SMOW) (Dalai et al., 2002). If we take this as representative value of Dehra Dun

sub-basin and Subathu sub-basin groundwater, the δ^{18} O of the corresponding carbonate would be around -11.6 % [considering the annual average temperature of the area ~25°C and using the fractionation factor between calcium carbonate and water: $1000 \ln \alpha \frac{\text{carbonate}}{\text{water}} = 2.78 \text{ x} 10^6 / \text{T}^2 - 2.89$ (Friedman and O'Neil, 1977) where $\alpha \frac{\text{carbonate}}{\text{water}} =$ $(1000 + \delta^{18}O_{carbonate})/(1000 + \delta^{18}O_{water})]$ which is close to the observed average $\delta^{18}O$ (-11.7‰) value of DCCN. The close agreement supports our suggestion regarding depleted ¹⁸O values of the cement. It is also of interest to know the δ^{18} O of carbonate cements from sand bodies (CCS) other than DCCN. The δ^{18} O value of CCS sheets ranges from -10.3 % to -15.3 % with an average of -13.6 ± 2 % (n=21), which is depleted compared to the average δ^{18} O value of DCCN (-11.7±1.1‰). This can be explained by precipitation/re-equilibration of cement in sandstone sheets at higher burial temperature since an increase in temperature causes depletion in the δ^{18} O of carbonate. In addition, water-rock ratio (W/R) also affects the final δ^{18} O of carbonate during precipitation/re-equilibration. W/R The ratio can be expressed as: W/R = $(\delta^{18}O_{carbonate}^{final} - \delta^{18}O_{carbonate}^{initial})/(\delta^{18}O_{water}^{initial} - \delta^{18}O_{water}^{final})$ (Quade et al., 1995) where superscript 'initial' and 'final' refer to the δ^{18} O values of carbonate and water before and after equilibrium isotopic exchange. Using above equations it can be shown that at infinite water-rock ratio the observed depletion in the carbonate cement of sandstone sheet (~2‰) would require a temperature of about 33 °C which could be reached within 400 m of burial assuming geothermal gradient to be 20°C/km.

Oxygen isotope ratio of DCCN from Pakistan Siwalik ranges from -11.6 to -6.6 ‰ (Quade and Roe, 1999). Overall, the δ^{18} O increases upsection but it has an excursion toward lower values at around 7 Ma. However, the composite section, which has been made from Mohand Rao and Haripur Khol section (Fig.4.5b) does not show any such excursion around 7 Ma. There is a clear swing toward enriched values at ~3 Ma in both the Indian and Pakistan sections. In Pakistan section the δ^{18} O at around 3 Ma is -10% and subsequently it increases to -7%. In the Indian section, the δ^{18} O of sandstone nodule around 3 Ma is -12.7% and subsequently it reaches the value ~ -10.7 ‰ (Fig. 4.9).



Fig.4.9 Comparison between oxygen isotope ratio of DCCN from Pakistan and Indian sections. In Pakistan section overall $\delta^{18}O$ increases up-section with an excursion toward lower values at around 7 Ma. This excursion is missing in Indian sections. There is a clear swing toward enriched values at ~3 Ma in both the Indian and Pakistan sections.

bracket. This difference in δ^{18} O ranges up to about 3.5‰. One probable cause for the depleted δ^{18} O in Indian section is depleted value of local rainwater. Mohand Rao and Haripur Khol sections are located in a region, which receives very high rainfall (550 mm during SW monsoon, JJAS; Indian Meteorological Department, 1970). On the other hand, the Pakistan Siwalik is located at the farthest end of the Indian monsoon system and receives only 170 mm (average of SW monsoon, Rao, 1981) rain. At low latitudes, the average monthly rainfall and the mean monthly δ^{18} O are usually negatively

correlated; an increase of 100 mm of precipitation is associated with a decrease in δ^{18} O by 1.5 ‰ (Yurtsever and Gat, 1981). Hence, the δ^{18} O of rainwater in Mohand Rao and Haripur Khol area could be depleted by ~4 ‰ compared to the δ^{18} O of rainwater in Potwar plateau in Pakistan. This is close to the observed δ^{18} O difference between the two carbonates.

It is also noted that the trend of oxygen isotope ratio of SCN from Kangra valley and Haripur Khol section differ from the oxygen isotope ratio trend in Pakistan (Quade et al., 1989; Sanyal et al., 2004a). As mentioned earlier, the oxygen isotope ratio of SCN from Kangra valley and Haripur Khol section is characterized by two phases of depletion at around 10.5 Ma and 5.5 Ma. The oxygen isotope ratio of SCN from Potwar Plateau is characterized by enrichment starting from 8 Ma and reaching a maximum at around 5 Ma (Quade et al., 1989).

Though based on limited samples (n=9), the oxygen isotope ratio of SCN of Mohand Rao section is consistent with the results of Kangra valley and Haripur Khol section. The average oxygen isotope ratio at about 9 Ma and 5 Ma is around -9% and -8% (Fig.4.6b). Previous study from the Kangra and Haripur Khol section showed similar oxygen isotope ratios for these two time periods. These values are depleted compared to other time periods of the section (Sanyal et al., 2004a) and have been attributed to an intensification of monsoon. The present data lends support to the same conclusion.

4.6 Timing and nature of change in vegetation in various Siwalik sections of Pakistan and India

Carbon isotope ratio of SCN from Potwar Plateau of Pakistan Siwalik showed appearance of C₄ plants at around 7.7 Ma; the abundance of C₄ plants reached a maximum by 6.5 Ma. The appearance of C₄ plants was preceded by a change in rainfall pattern (Table 4.3). In Nepal Siwalik, the appearance of C₄ plants was about 0.7 Myr later compared to Pakistan Siwalik while change in rainfall pattern was observed at around 6 Ma. In Kangra Valley-Haripur Khol section of Indian Siwalik, C3 plants dominated vegetation up to 6 Ma. Abrupt change in vegetation from pure C₃ to mixed C₃-C₄ occurred after 6 Ma. In Kangra Valley-Haripur Khol section intensification of rainfall (monsoon) was observed at around 10.5 Ma and 6 Ma. Appearance and expansion of C_4 plants coincided with the second phase of monsoon intensification. In Mohand Rao section, appearance of C_4 plant was observed at around 9 Ma and it took nearly 2 Myr to reach maximum abundance of C_4 plants.

Present day rainfall data in these sections (where available) show variation in rainfall amount during southwest monsoon. The mean rainfall during southwest monsoon in Potwar Plateau is 170 mm (average of SW monsoon, Rao, 1981), in Kangra valley 550 mm and in Mohand Rao section 440 mm (taken from Dehra Dun rainfall

Table 4.3 Timing and nature of change in vegetation and timing of rainfall pattern change in different Siwalik sections.

Section	Timing of appearance	Nature of change in	Timing of rainfall	
	of C ₄ plants	pure C_3 to mix C_4 -	change	
		C ₃ vegetation		
Potwar Plateau,	7.5 Ma	Rapid, took 1.5 Myr	8 Ma	
Pakistan		to reach maximum		
		abundance of C ₄		
Surai Khola,	6.8 Ma	Rapid, took 1.5 Myr	6 Ma	
Nepal		to reach maximum		
		abundance of C ₄		
Kangra Valley -	6 Ma	Abrupt	10.5 Ma and 6 Ma	
Haripur Khol,				
India				
Mohand Rao,	9 Ma	Gradual, took 2 Myr	Data scanty, but	
India		to reach maximum	comparable with	
		abundance of C ₄	Kangra Valley-	
			Haripur Khol data	

data). The difference in the amount of rainfall in these areas suggests that climatic conditions were probably different in them. This might have played an important role in controlling the timing and nature of change in vegetation. However, direct correlation between rainfall amount and vegetation cannot be clearly established.

4.7 Conclusions

Carbon isotope ratio of early diagenetic carbonate from sandstone nodules shows that C_4 plants started to appear in Mohand Rao section at around 9 Ma, which is somewhat earlier compared to the other Indian sections. Also, the transition from pure C_3 type of plants to mixed C_3 - C_4 plant regime was gradual. The carbon isotope ratio of sandstone nodules from Haripur Khol section showed presence of mixed C_3 - C_4 vegetation with C_4 dominating the ecosystem for the time period 6 to 1 Ma. The vegetational transition is, therefore, now established from four Indian sections albeit with temporal difference in their onset. Oxygen isotope ratio of early diagenetic carbonate cement shows variable contribution of river water into shallow groundwater. The oxygen isotope ratio of soil carbonate indicates intensified monsoon at around 9 Ma and 5 Ma.

CHAPTER-5

MONSOON VARIATION FROM HYDROGEN ISOTOPE RATIO OF PEDOGENIC CLAY MINERALS

5.1 Introduction

Oxygen isotope ratio of soil carbonates from the Neogene sedimentary succession of Himalayas has been used extensively to reconstruct past monsoonal rainfall variation (Quade et al., 1989,1995, Quade and Cerling, 1995; Sanyal et al., 2004a). Normally, the soil carbonate forms in isotopic equilibrium with soil water, which is derived mainly from local rainfall. However, the oxygen of soil carbonate is relatively enriched compared to that expected from annual average oxygen isotope ratio of local rainfall as soil carbonate precipitates mostly in dry season (Salomons et al., 1978; Stern et al., 1997). Also, the oxygen isotope ratio of water can change through exchange with silicate minerals. It is known that to form soil carbonate the rainfall should be normally below 75 cm per year (Cerling, 1984). Such condition was not always present in the geological past. We find that soil carbonates are often absent in parts of Siwalik sections corresponding to high rainfall regimes in the past, thereby, disallowing continuous monsoon reconstruction. In this context, hydrogen isotope ratio of hydroxyl group of pedogenic clay minerals offers an alternative choice as clay minerals form throughout the year in isotopic equilibrium with soil water (Savin and Hsieh, 1998). In addition, hydrogen isotopes of water do not exchange with silicate minerals since most silicate minerals are devoid of hydrogen in crystal structure.

Hydrogen isotope ratio of water from bulk clays separated from mudstones of Haripur Khol section of Himachal Siwalik was used to reconstruct rainfall by Ghosh et al. (2004). Their study was based on a limited number of samples and isotope analysis was done on bulk clays from mudstone without quantification of clay species. It is important to have quantitative analysis of clay species to evaluate the effect of concentration variation of clay species on the bulk isotope ratio. Abundance variation of species can change the bulk hydrogen isotope ratio as the hydrogen-water fractionation factor for individual species is different (Graham et al., 1984; Capuano, 1992; Gilg and Shepard, 1996; Yeh, 1980). In addition, in the above study, organic matter associated with clay was not removed. Combustion of clay-associated organic matter can contribute significant amount of water, which can complicate the interpretation of hydrogen isotope ratio of hydroxyl group of clay minerals.

An attempt has been made here to study the hydrogen isotope ratio of pedogenic clay minerals (less than 2μ) from the same Haripur Khol section of Himachal Pradesh. Oxygen isotope ratio of soil carbonate (when available) from this section has already been used to reconstruct monsoon rainfall variation (Sanyal et al., 2004a). Analysis of hydrogen isotope ratio of clay minerals from the same section provides a well-constrained and independent reference data set for comparison.

5.2 Structure of Clay minerals

The term clay is generally used in textural and mineralogical sense. Any grain



Fig.5.1a. One octahedral sheet associated with one tetrahedral sheet. **b**) One octahedral sheet is sandwiched between two tetrahedral sheets.

size less than 4 micron is usually referred to as clay. On the other hand, hydrous aluminum silicate is also referred to as clay minerals. Clay minerals are phylosilicates consisting of alternating layers of two types. One type consists of Al^{3+} , O^{2-} and OH^{-} ions in which the negative ions form octahedra around Al^{3+} and the adjacent octahedra are shared with O^{2-} and OH^{-} to make the structure continuous in two dimensions. This type of layer is known as octahedral layer. The second type of layer is made up of Si^{4+} , O^{2-} and OH⁻ ions with Si⁴⁺ in the center of tetrahedron of oxygen ions. The tetrahedra are all face the same direction (Fig. 5.1a, b) and the oxygen atoms at their bases are linked so as to form hexagonal rings. This type is known as tetrahedral layer. In nature, a given clay structure consists of one of several possible combinations of the octahedral and tetrahedral layers. The simplest combination is an octahedral layer linked to a tetrahedral layer by sharing some of the oxygen ions (Fig.5.1a). The double layer extends indefinitely in two dimensions and the clay crystal forms by succession of these layers one on top of other. In another variety, an octahedral layer is sandwiched between two tetrahedral layers (Fig.5.1b). Successive unit layers of the clay structure are stacked one on top of another to build the crystal structure.

The clay minerals are formed by alteration of aluminum silicates in weathering and/or low temperature hydrothermal processes. However, the mechanism of alteration process is still obscure. During the formation of clay, initial chemical composition is determined by parent rock composition, but in the long run the clay reflects local climatic condition. For example, initial weathering of granitic rock produces illite (a Krich clay), but in a humid climate and well-drained condition illite transforms into kaolinite (cation free clay).

5.3 Identification of clays

Clays in Siwalik sediments are weathering product of Himalayan rocks (See section 5.5.1). To identify the clay minerals and determine their abundance a set of thirteen samples was analyzed by X-ray diffraction method (for separation of clay minerals see 2.8.1.3). The species identified are illite, smectite and chlorite (Fig.5.2). Identification of clay minerals was based on X-ray diffractogram from air-dried, glycolated and heated (at 375°C) glass slide (Fig.5.2). Semi-quantitative estimation of the relative abundance of clay minerals was done based on the peak area method

(Biscaye, 1965). The peak areas of glycolated samples were first computed under 17Å peak for smectite, 10 Å peak for illite and 7 Å peak for chlorite. These values were multiplied by the weighting factors 1, 4 and 2 respectively for smectite, illite, chlorite



Fig.5.2 *X-ray diffractograms of clays made from oriented samples of less than 2-micron size. X-ray diffraction patterns have been made from air-dried, glycolated and heated samples. Clay species identified are smectite (S), illite (I) and chlorite (C).*

(Biscaye, 1965).

5.4 Results

The hydrogen isotope ratio of clays varies from -55 to -90 ‰ (Fig.5.3) over the section. Around 6 Ma, the hydrogen isotope ratio is characterized by lower values (from -80 ‰ to -89 ‰). Subsequently, the isotopic ratio shows enrichment, reaching a maximum of -55 ‰ around 4 Ma. From 4 Ma to 3 Ma, the hydrogen isotope ratio gets depleted again. After 3 Ma, the isotopic ratio shows a second phase of enrichment, with maximum enrichment (-55 %) being reached at around 2 Ma.

5.5 Discussion

5.5.1 Pedogenic origin of Clays

Sediments in the Himalayan foreland basin are derived from weathering of Himalayan rocks. Weathering is accompanied by dissolution and re-precipitation of new minerals of which clays constitute a major component. Higher Himalayan rocks, composed of granites and metamorphic rocks, are prone to produce illite and chlorite rich clays whereas lesser Himalayan hinterland volcanic rocks can only produce smectite. Kaolinite can also form from lesser Himalayan rocks during chemical weathering in warm temperature, but develops principally in climate that have wet and dry seasons and have more water percolation than that needed for smectite formation (Suresh et al., 2004). For the last 18 Myr, weathering debris of Himalayan rocks are continuously being transported by various rivers and deposited into the foreland basin (Johnson et al., 1985). Mudstone beds in the basin are products of sedimentation by river in flood plain where clays are the major fraction of sediments. During pause in sedimentation, sediments on the floodplain undergo pedogenesis and new generation of

Table 5.1 Hydrogen isotope ratio of bulk pedogenic clays and abundance of differentclay species.

Sample No	δD (SMOW) ‰	Age(Ma)	Illite (%)	Smectite(%)	Chlorite(%)
HP-3C	-78	6	48	40	12
HP-04C	-90	5.8	33	48	19
HP-6C	-71	5.5	21	63	16
HP-13C	-62	5.37			
HP-15C	-70	5.23	31	54	15
HP-24C	-74	4.9			
HPA-23C	-73	4.7	25	52	23
HP-45C	-65	4.7			
HP-22C	-75	4.5	20	58	22
HP-21C	-56	4.08			
HP-26C	-57	3.82	20	60	20
HP-33C	-61	3.63	23	55	22
HP-30C	-75	3.28	65	28	7
HP-40C	-74	3	30	56	14
HP-42C	-77	2.68	23	58	19
HP-55C	-66	2.5	20	55	25
HP-54C	-55	2.3			
HP-61C	-86	2.33	28	57	15
HP-66C	-68	2.2			
HP-70C	-58	2.12	23	56	21
clay minerals forms. Hence any clay sample from pedogenic beds probably represents mixture of clays transported from higher mountain reaches and clays formed during pedogenesis. Previous study from Siwalik section of Potwar Plateau in Pakistan showed higher abundance of clay species in pedogenic beds compared to unweathered mudstone



Fig.5.3 Hydrogen isotope ratio of pedogenic clays from Haripur Khol section. The profile is characterized by lower values at around 6 Ma and 3 Ma punctuated by higher value at around 4 Ma. The two phases of lower δD probably indicate intensified monsoonal rainfall. It could be mentioned that oxygen isotope ratio of soil carbonate from Haripur Khol section also shows intensification of monsoon at around 5.5 Ma but the peak at 3 Ma was not observed from oxygen isotope ratio of soil carbonate. Solid lines are drawn to guide the eye.

(Stern et al., 1997) indicating clay formation during pedogenesis. In another study, depleted hydrogen isotope ratio of clays from Bengal Fan indicates interaction of clays with meteoric water in soil (Lanord et al., 1994) during pedogenesis. As mentioned earlier, for the present study clays were separated from pedogenic nodules, which implies that analyzed samples contain predominantly pedogenic clays.

5.5.2 Pristine character of hydrogen isotope ratio

For proper interpretation of data it is important to enquire whether the measured hydrogen isotope ratios reflect a pristine signal or are mere artifacts resulting from secondary processes. The question is particularly worrying due to abundant evidence of hydrogen isotope exchange in clays (Yeh and Epstein, 1978; Wilson, 1987; Bird and Chivas, 1988; Longstaffe and Ayalon, 1990; Kotzer and Kyser, 1991). However, Sheppard and Gilg (1996) showed that high temperature isotope exchange data cannot be extrapolated unambiguously to ambient temperature. In particular, they established that exchange of hydrogen isotopes in clay, especially for kaolinite with water, is not significant below temperature 50°C.

Siwalik rocks represent a near continuous pile of sediments deposited in the Himalayan Foreland Basin by ancient mighty rivers originating in Himalayas. The rivers carried the sediments produced from the mountain faces by chemical and physical weathering. As the sediments deposited the basin started sinking due to overburden and diagenetic changes could have ensued at progressively higher temperatures. The maximum temperature attained by Haripur Khol sediments can be estimated from the geothermal gradient of the basin. Haripur Khol section represents the top part of Upper Siwalik. So the total thickness of the sediments here (~2 km) can be considered as the maximum burial depth. Assuming the geothermal gradient of foreland basin as 20°C/ km, the maximum temperature to which the sediments were exposed was ~63°C (Assuming temperature of surface to be 23°C). Therefore, it is reasonable to assume that exchange of hydrogen isotopes between clay and water was not significant.

Hydrogen peroxide treatment to remove the organic matter can also, in principle, change the hydrogen isotope ratio of smectite (Hyeong and Capuano, 2000). It has been shown that H_2O_2 treatment can change the hydrogen isotope ratio of smectite up to about

8 ‰. In our samples, the maximum variation in hydrogen isotope ratio is found to be around 40 ‰, which is much larger than any possible H_2O_2 treatment effect.

5.5.3 Hydrogen isotope ratio of pedogenic clays

Hydrogen isotope ratio of bulk clays depend on (i) abundance of clay species (ii) temperature of clay formation and (iii) amount of rainfall. With this background, one can investigate the pattern of δD variation with depth (age) observed in Haripur Khol samples.

(i) Abundance of species: Semi-quantitative analysis of clays showed that in individual samples illite is the most dominant species followed by smectite and chlorite. The relative abundance of species is almost constant throughout the section (Fig.5.4). In general, variation in abundance of species can change hydrogen isotope ratio in bulk samples, as the hydrogen-water fractionation factor is different for different species (Yeh, 1980). The fractionation factor of a clay mineral depends on the octahedral cation chemistry of the clay. Since both illite and smectite have the same octahedral cation the fractionation factor for illite-water and smectite-water can be assumed to be equal (Yeh, 1980). The fractionation factor for chlorite-water depends on the Fe/(Fe+Mg) ratio in the octahedral site (Marumo et al., 1980). X-ray diffraction pattern of chlorite (which depends on the Fe content) shows similar trace for all samples indicating similar Fe content in the chlorite phase. At low temperatures, the fractionation for illite-water (or smectite-water) differs only by 1‰ from chlorite-water fractionation. Near constant abundance of the three clay species throughout the section and similar values of their fractionation factor implies that the observed large variation in hydrogen isotope ratio is not due to abundance variation of clay species.

(ii) **Temperature of clay formation:** A major assumption in interpreting the isotope data of pedogenic clay is that it forms in isotopic equilibrium with soil water. This can be tested if the temperature of clay formation and hydrogen isotope ratio of soil water are known. To a first approximation, the annual average air temperature could be taken as the temperature of clay formation and the hydrogen isotope ratio of soil water as the δD of local rainwater. Unfortunately, The δD of Haripur Khol rainwater is



Fig.5.4 Semi-quantitative analysis of clay minerals shows that relative abundances of smectite, illite and chlorite are almost constant throughout the succession. Illite is the most dominant (~56%) species followed by smectite (25%) and chlorite (15%).

not available. However, it can be estimated from data pertaining to the Delhi region (IAEA, 2003). The mean annual weighted average δD in Delhi rain is about -33 ‰.

Correcting for the continental effect (a decrease of about 3.2‰) as obtained by Krishnamurthy and Bhattacharya (1991) and enrichment effect (about 8 ‰) due to evaporation during recharge (Salomons et al., 1978), the δ D of soil water in Haripur Khol can be taken as –28.2 ‰. Taking the mean annual temperature of Haripur Khol to be 23°C, smectite-illite abundance 80% and chlorite abundance 20%, published fractionation factors for smectite-illite (Yeh, 1980) and chlorite and water (Ziegler and Longstaffe, 2000), the expected δ D value of Haripur Khol pedogenic clay is about –67.5 ‰. This value is only slightly depleted (~9‰) compared to the observed mean δ D value of the youngest pedogenic clays. The close agreement lends validity to the equilibrium assumption for Siwalik pedogenic clays as well as the temperature estimate. We note that the most depleted value (–90 ‰) observed in Haripur Khol samples cannot be explained by a higher temperature as increase in temperature results in increase of hydrogen isotope ratio of clay.

(iii) Amount of rainfall: Since clay mineral abundance or temperature variation of diagenesis cannot explain the δD variation in totality, the two phases of depletion observed in Haripur Khol samples (around 6 Ma and 3 Ma) probably represent increased amount of rainfall due to monsoon intensification. A seasonally reversing wind system with moist oceanic air from southwest during summer and cold, dry continental air from northeast during winter characterizes the Indian monsoon climate. This system is responsible for heavy rains during June, July, August and September in the Indian subcontinent. It has been shown that increase in rainfall is usually associated with lower δD , the phenomenon being known as "amount effect". Hence the periods with lowered δD values probably represent intervals with high rainfall; contrastingly, higher δD values should represent relatively dry seasons.

Variation of Indian monsoon has also been reconstructed from the same section using oxygen isotope ratio of soil carbonate (Sanyal et al., 2004a) through its dependence on isotopic ratio of soil water, derived from local precipitation (Quade et al., 1989). At around ~6 Ma, the average oxygen isotope ratio of soil carbonate was ~ -9 ‰ and subsequently, the ratio became enriched and reached a value of -6.5 ‰ at around 2 Ma. At low latitudes, like hydrogen isotope ratio, the average monthly rainfall and the mean monthly δ^{18} O are also negatively correlated, such that an increase of 100 mm of precipitation is associated with a decrease in δ^{18} O by 1.5 ‰ (Yurtsever and Gat, 1981). It was argued that, the depletion in oxygen isotope ratio around 6 Ma is due to intensification of monsoon rainfall and correspondingly, subsequent higher δ^{18} O reflects decrease in amount of rainfall. It should be mentioned that though the oxygen isotope ratio of soil carbonate corroborated the intensification of rain (monsoon) at around 6 Ma, monsoon intensification at ~3 Ma could not be identified due to several interfering effects in case of oxygen isotopes.

5.5.4 Supportive evidence of climate change during last 6 Ma

5.5.4.1 Proxies from Haripur Khol section

Climatic fluctuations have also been inferred from variation of oxidation, hydroxylation and humification index from the Haripur Khol palaeosols (Fig.5.5). The indexes are based on selective saturation levels of induced magnetic field, inorganic and organic carbon content, and Rb/Sr ratios. Variations in the indexes indicate large-scale climate changes within the Pliocene-Pleistocene time span, with warm-humid climate during Early Pliocene and intermediate phase during the early Mid-Pliocene and warm oxidative phase during the Mid to Late Pliocene. The early-mid Pleistocene was characterized by a cold phase (Sangode et al., 2001).

Color and maturity of paleosols also show evidence for climatic change during the last 6 Myr. Between 5.3 Ma to 2.6 Ma warm and humid climate is inferred from the formation of red Alfisols with pedogenic carbonate and Fe nodule and strong illuviation of clay forming well-developed Bt horizons. After 2.6 Ma, formation of poorly developed yellow soils with commonly occurring nodular pedogenic carbonate and calcite material disseminated in the ground mass indicate slightly cooler and drier climate (Thomas et al., 2002) which is consistent with the hydrogen isotope ratio data of pedogenic clays.

The pollen record from Haripur Khol section supports the interpretation of variation of rainfall with time. Considering the relative frequency of ecologically significant taxa, four major stages of vegetation has been recognized in Haripur Khol (Phadtare et al., 1994). The stages are: I) 4 to 3.5 Ma, II) 3.5 to 2.7 Ma, III) 2.7 to 2.5 Ma, and IV) 2.5 to 1 Ma. During stage I, the vegetation was dominated by dry grassland. During stage II, there was significant drop in percentage of grass pollens associated with

sudden rise of the spores of *Lycopodium* and polypodiaceous ferns. During the later half of this stage, significant rise in Amaranth/Chenopodiaceae and large concentration of *Ceratopteris* pores indicate a marshy or muddy condition. During stage III, consistent increase in the spores of *Lycopodium* along with presence of algal cysts as well as dicot pollens collectively suggest the existence of well developed ponding conditions which may indicate high rainfall. Presence of Nymphaeaceae indicates shallow-water or seasonal lacustrine habitat. A large population of *Pinus* pollen, restricted only to this stage, also indicates a temperate to sub-tropical climate. During stage IV, which is marked by the presence of a volcanic ash bed, the leaf tissues are found to be abnormally thick. The abnormal cell wall thickness at this stage is intriguing but could be due to response of the leaves to a cool and dry climate (Phadtare et al., 1994). Also effect of a possible CO₂ concentration change cannot be ruled out (Retallack, 2002).

The above discussion indicates that the post-4 Ma vegetational regime in this part of the Indian Siwalik carries signatures of variation of rainfall.

Sedimentological evidences from Siwalik support our observation regarding changes in the Indian monsoon. The fluviatile sedimentation of the Himalayan Foreland Basin (HFB) was controlled by tectonics and weathering, with a strong influence of climate. Kumar et al. (2003a) observed major changes of sedimentation pattern and drainage organization at 6 Ma. Widespread distribution and stacking of conglomerate along with progradation of alluvial fans between 6 and 5 Ma, suggesting a broad catchment area with high basin relief (Kumar et al., 2003b) indicating monsoon intensification. The fluvial regime provided a high volume of sediment resulting in distribution of coarse-grained sediments in the proximal part and fine sediments in the distal part of the alluvial fan system.

5.5.4.2 Marine proxies in support of deduced climate change for Siwalik soils

Arabian Sea record for past monsoon also shows variation in intensity during Plio-Pleistocene time. The relative abundance variation of radiolarian species *Actinomma* in the Arabian Sea, a marine proxy for upwelling caused by monsoon winds, shows variation after 6 Ma with peaks around 4.7, 3.8, 3 and 2.2 Ma (Prell et al., 1992). Although there is no one-to-one correlation between the abundance peak of radiolarian



Fig.5.5 Comparison of various climate proxies with hydrogen isotope ratio of clay minerals obtained from Siwalik soils. Though oneto-one correlation among different proxies is not observed, there is overall agreement among them over last 6 Ma. They jointly indicate two warm phases with increased rainfall \sim 6 Ma and \sim 3 Ma.

species and depleted values of δD , on the whole a monsoon change interpretation seems to agree with the observed δD change in Siwalik clays for the post 6-Ma period.

Similarly, abundance of foraminiferal species *G. bulloides*, which are sensitive indicators of upwelling caused by monsoon winds, also shows variation for the last 6 Ma. Quantitative frequency analysis of *G. bulloides* from the Arabian Sea sediments shows high abundance around 6 Ma, followed by gradual diminution till 5.5 Ma. This is succeeded by an increase at around 4.5 Ma that continued until today, with minor oscillations (Kroon et al., 1991). The time difference in monsoon intensification in the various proxies could be either due to dating errors inherent in the age control of the systems, or due to the different response times of them to climate change.

5.6 Conclusions

Abundance of pedogenic clay minerals is almost constant throughout the Haripur Khol section in Indian Siwalik with illite as the most dominant species followed by smectite and chlorite. Reconstruction of rainfall (induced by monsoon) from δD values of bulk pedogenic clay showed that monsoon strength has varied through time with two peaks around 6 Ma and 3 Ma punctuated by a weak phase at around 4 Ma. This pattern of variation in monsoon strength is in broad agreement with the record reported by earlier workers using non geochemical proxies like pollen abundance, sediment architecture or abundance of marine organism like radiolaria, foraminifera.

CHAPTER-6

CARBON AND OXYGEN ISOTOPE RATIO OF SOIL CARBONATES FROM GONDWANA AND SIWALIK: IMPLICATIONS TO ATMOSPHERIC CO₂, vegetation AND RAINFALL

6.1 Introduction

It is well known that CO₂ concentration in the earth's atmosphere varied enormously in the geological past (Berner, 1991; Retallack, 2001c, 2002, Ekart et al., 1999). In particular, the Paleozoic to Mesozoic era was a period of extreme fluctuation when CO₂ concentration changed from a level of 250 ppmV to ten times that level, whereas, the Cenozoic era was characterized by a continuous decrease in CO₂ with the lowest concentration at the Neogene period (Ekart et al., 1999; Retallack, 2001c, 2002; Ghosh et al., 2001; Pagani et al., 1999). However, the estimates of these changes are not universally accepted and there are significant discrepancies among values derived from different proxies. For example, the CO₂ estimation based on variation of stomatal index in leaves for the Triassic and Jurassic period (from ~250 Ma to 150 Ma) showed that during this time CO₂ concentration was about 1000 ppmV (Retallack, 2001c). In contrast, carbon isotope ratio of soil carbonate showed that CO₂ level increased from a low value (~250 ppmV) at the Permo-Triassic boundary (~250 Ma) to approximately 3000 ppmV at the end of Triassic (~200 Ma) and remained high throughout the Jurassic period (Ekart et al., 1999). Identifying the real change in CO_2 in this time bracket has great significance in constraining the CO₂ budget model involving degassing from sea floor spreading (Berner, 1991; Berner and Kothavala, 2001). In this context, palaeosols discovered in central India straddling the Triassic and Jurassic periods offer an excellent opportunity to study the CO₂ variation in this time range.

Palaeosols of Mesozoic era containing soil carbonates are present in the sediments of Gondwana Supergroup in central India. pCO_2 estimation based on carbon isotope ratio of soil carbonate and organic matter from Denwa and Bagra Formation of the Gondwana Supergroup from Satpura basin (Fig.2.1) (Madhya Pradesh) showed that average atmospheric CO₂ concentration during the Triassic and Jurassic time was 1125 ppmV and 2225 ppmV respectively (Ghosh et al., 2001). However, CO₂ estimation for the Triassic period from Denwa Formation was based on a limited set of samples. Additionally, the samples were not taken from any identified soil horizon but obtained from detrital glaebules with pedogenic micro-fabric as indirect evidence of pedogenesis. Hence, the change of CO₂ concentration derived from this soil for Early Triassic to Jurassic period was not definitive. We have reinvestigated the issue based on soil

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samples taken from new exposures in this area to calculate CO_2 concentrations in this period and compare them with earlier results from time equivalent (but geographically separated) palaeosols in other regions (Ekart et al., 1999).

As mentioned before, the CO_2 concentration in the Neogene period was quite low and estimation by Cerling (1991) from the Pakistan Siwalik for the time range 8-16 Ma showed concentration levels less than 700 ppmV. This estimation could be done only up to 8 Ma because C₄ plants appeared in that region at around that time and complicated the issue. Our study from Ranital Siwalik section in Himachal Pradesh, India showed absence of C₄ plants till 6 Ma ago (Sanyal et al., 2004a) allowing us derive the CO₂ concentration from carbon isotope ratio of soil carbonate for the period 11 to 6 Ma. This is geologically recent and is of enormous interest since this bears on the issue of Himalayan uplift and weathering and their effect on CO₂ concentration and climate.

6.2 Soil carbonate from Denwa and Bagra Formation and Ranital section

As mentioned, previous study from Denwa Formation (see section 2.6 for age) of Satpura Basin was based on a few samples of detrital palaeosols where micro fabric provided indirect evidence of pedogenesis (Ghosh et al., 2001). Since that report, we have undertaken several field trips to discover new exposures of palaeosols belonging to Denwa Formation. These soils contain soil carbonate nodules and root molds indicating intense pedogenic activity during the Denwa time. Samples were collected from nine different exposures and one of them was found to be in contact with younger Bagra Formation. These exposures were sequentially arranged based on dip direction of the associated sandstone beds. Denwa soil carbonate nodules are fairly large (~4 cm in diameter Fig.6.1a) and in one palaeosol bed a well preserved and almost complete root mold was found (Fig.6.1b).

In addition, soil carbonates in the form of rhizocretion were collected from four different exposures of palaeosols from Bagra Formation (see section 2.6 for age). Here the thickness of palaeosols varies from a few cm to meter and contains well-developed horizons of fused gleabules. The field features of palaeosol profiles are comparable to present day aridisols with well-developed K-horizons at the top and thick Bk horizons below (Ghosh et al., 2001).

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The palaeosols in the exposed section of Ranital (see section 2.2 for age) are gray, brown and yellow in color. Palaeosols with green mottling are common and contain iron and calcareous nodules, root traces and bio-tubes.

6.3 Identification of top surface of soil profile

To study the variation of carbon and oxygen isotope ratio of soil carbonate with depth it is necessary to identify the top surface of soil. In the Siwalik Group, one palaeosol bed is usually sandwiched within two sandstone beds (Fig.6.2). Therefore, based on the dip direction of the sandstone beds the top surface of the soil profile can be easily fixed. In case of Bagra, one palaeosol profile in the exposed section was closely packed between sandstone/conglomerate beds (Fig.6.3a) but this was not so for the other (Fig.6.3b). The latter profile is characterized by thick to very thick horizons of closely spaced, vertically oriented large cylindrical rhizocretions with diameter ranging from 3 to 5 cm and length ranging from 30 to 150 cm. Frontal view of this soil profile shows tapering of the rhizocretion in downward direction (Fig.6.3b). The top view shows circular appearance of rhizocretion, which mimics the cross section of a root (Fig.6.3c). These two features identify the present top as the top surface of the soil bed.



Fig6.1a Soil carbonate nodules in Denwa Formation.

6.4 Results

The δ^{13} C of small root molds and soil carbonate nodules from the Denwa Formation ranges from -6.4 to -10.7 ‰ with an average of -8.5 ±1.4 ‰ (n=14, Table 6.2). There is systematic change in δ^{13} C with age (see section 2.6 for age of the samples) (Table 6.2). The δ^{13} C value of oldest sample is -10.7‰ and the value for the youngest sample is -6.4‰. The average δ^{13} C value for the intermediate samples is -8.4‰. The carbon isotope ratio in completely preserved root (Fig.6.1b, 30 cm) ranges from -10.7 to -10.4 ‰ (n=3). The δ^{13} C of non-pedogenic carbonate collected from Denwa Formation (n=7, Table 6.2) ranges from -4.7 to -7.6 ‰.



Fig.6.1b Preserved root mold at Denwa Formation. The root is almost 30 cm in length.

Non-pedogenic carbonate samples collected from near contact of a dyke have δ^{13} C values of -6.9 and -6.5 ‰; the fracture filled carbonate in vertisol have δ^{13} C value of - 5.7 ‰ and calcrudites have δ^{13} C value -6.8 ±1.4‰ (n=4, Table 6.2)

From Bagra Formation, most of the samples were collected along soil profile. The δ^{13} C values of the Bagra rhizocretion from two soil profiles are independent of depth and the average values are -7.0 ± 0.2 ‰ (n=6) and -6.8 ± 0.3 ‰ (n=9) (Fig.6.4, Table 6.1). The δ^{13} C of soil carbonate from other two exposures are -6.3 ‰ and -6.9 ‰. Recycled soil carbonates associated with the conglomerate bed in Bagra Formation have also been analyzed. The average δ^{13} C of recycled carbonate is -7.3 ± 0.6 ‰ (n=3,Table 6.2).

The mean δ^{13} C value of soil carbonate nodules from six individual soil profiles from Ranital are $-11.1 \pm 0.3 \%$, $-10.9 \pm 0.5 \%$, $-10.4 \pm 1.0 \%$, $-10.4 \pm 1\%$, $-11.0 \pm$



Fig.6.2 *Mudstone bed on which palaeosol formed is sandwiched between two sandstone beds (from Siwalik section of Ranital).*



Fig.6.3a Palaeosol bed between sandstone and conglomerate from Bagra Formation

0.6%, $-11.1\pm0.4\%$ (n=2 to 4); one deviant sample had very enriched value (-5‰).

In Denwa Formation, the mean oxygen isotope ratio of soil carbonate is -5.2 ± 0.6 ‰. The δ^{18} O value of sample collected from clay dyke contact is -4.7 ‰ and that of fracture filled carbonate is -2.1 ‰. Calcrudites have δ^{18} O value -3.8 ± 1.5 ‰ (Table 6.1). Like carbon isotopic ratio, oxygen isotope ratio of soil carbonate from the Bagra



Fig.6.3b Frontal view of the palaeosol bed from Bagra Formation. The bed is characterized by thick to very thick horizons of closely spaced, vertically oriented large cylindrical rhizocretions with tapering in downward direction.



Fig.6.3c Top view of the rhizocretion, the circular appearance mimics the cross section of root.



Fig.6.4 Isotope ratio variation in soil profile. a) $\delta^{I_3}C$ of the Ranital soil carbonates show source of carbon is exclusively from C_3 plants. The average $\delta^{I_3}C$ of the Bagra samples are 4 ‰ enriched compared to Ranital samples indicating contribution of atmospheric CO_2 in soil CO_2 . In contrast, $\delta^{I_3}C$ of samples from Denwa Formation shows continuous increase in atmospheric CO_2 from lower Denwa to Upper Denwa. The shaded region indicates $\delta^{I_3}C$ of samples from middle Denwa. The depth of the samples from Denwa has been plotted assuming they have formed below 50 cm depth. **b**) Oxygen isotope ratio of the soil carbonates show enriched value both for Bagra and Ranital toward the top of the profile, indicating evaporation from the top of the soil. The oxygen isotope ratio of Ranital samples is depleted compared to the Bagra and Denwa samples showing difference in the rainfall pattern during the Gondwana and Siwalik time. **c**) Carbon isotope ratios of organic matter associated with pedogenic carbonates from Ranital, Denwa and Bagra indicate exclusive presence of C_3 plants in all the three areas.

Formation is nearly constant throughout the soil. The average δ^{18} O values of two profiles are -6.4 ± 0.2 ‰ and -6.9 ± 0.3 ‰ and from the other two exposures the mean

value is -6.7 ‰ (Table 6.1). The mean δ^{18} O of recycled soil carbonate from the Bagra Formation is -6.4±0.2 ‰. The δ^{18} O of soil carbonate nodules in Ranital soil profile does not vary significantly with depth, except for marginal enrichment near the surface. The mean δ^{18} O values of nodules from six individual soil profiles from Ranital are -9.1 ± 0.3 ‰, -9.2 ± 0.5 ‰, -8.9 ± 0.2 ‰, -8 ± 1.3‰ -10.7±0.8‰ and -8.9 ± 0.5 ‰ (Table 6.1).

The δ^{13} C value of the organic matter associated with soil carbonate nodules from the Siwalik soil profiles, Bagra and Denwa Formation are $-24.9 \pm 0.3 \%$ (n=5), $-25.9 \pm$ 0.4 ‰ (n=10) and $-24.8 \pm 0.5 \%$ (n=13) respectively (Table 6.1 and 6.2). The δ^{13} C of the organic matter associated with non-pedogenic carbonate is $-24.0 \pm 0.4\%$ from Denwa Formation (Table 6.2).

6.5 Discussion

6.5.1 Comparison between carbon isotope ratio of soil carbonates from Siwalik and Gondwana

As discussed in section 3.3.1, carbon isotope ratio of soil carbonate is primarily controlled by plant-respired CO₂. In addition, atmospheric CO₂ concentration, porosity of soil and respiration rate also play important role in determining carbon isotope ratio of soil carbonate. Studies from modern soils indicate that $\delta^{13}C$ value of shallow soil carbonate increases upwards in response to mixing with ¹³C enriched atmospheric CO₂. At greater depth it tends to approach a constant value depending on the ratio of plantrespired CO₂ and atmospheric CO₂ (Cerling, 1991). Porosity of soil affects pCO₂ in soil atmosphere as CO₂ diffusion coefficient depends on porosity and consequently penetration of atmospheric CO₂ into soil. It is difficult to estimate porosity of palaeosols but soil carbonates generally form in well-drained soils whose porosity varies from 0.3 to 0.4 (Cerling, 1991). In poorly drained soils water fills much of the pore space leading to gleying in palaeosol (Cerling, 1991). Since gleying is absent in both Siwalik and Gondwana samples, similar range of porosity could be assumed for both soils. The respiration rate of plants in temperate and subtropical ecosystem including grassland and woodland is similar and typically ranges between 4 to 10 mmol/m²/hr during the growing season (Dörr and Munich, 1987; Gaudry et al., 1990). The respiration rate could **Table.6.1** Carbon and oxygen isotope ratio of soil carbonate and carbon isotope ratio of associated organic matter from individual soil profile of Siwalik and Gondwana.

<u>Ranital S</u>	ection, Siwalik G	<u>roup</u>									
Profile-1	Sample No	Depth (cm)	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C_{Org}$		<u>Bagra s</u>	ection, Satpura	Basin, G	Gondwa	<u>na Supergroup</u>
	PRL-010A1	30	-11.3	-8.7	-24.6	Profile-1	Sample No	Depth (cm)	$\delta^{13}C$	δ^{18} O	$\delta^{13}C_{Org}$
	PRL-010A2	55	-11	-8.7			BG-5	5	-6.9	-6.4	
	PRL-010A3	90	-11.5	-10	-25.3		BG-8	10	-7.2	-6.7	
	PRL-010A4	120	-10.7	-9.2	-25.2		BG-9	30	-6.9	-6.1	-25.5
Profile-2	PRL-02B1	5	-4.9	-8.2			BG-11	40	-7.2	-6.5	
	PRL-02B2	30	-11.4	-9.2			BG-12	50	-6.7	-6.4	-25.7
	PRL-02B3	55	-10.9	-8.8			BG-14	100	-7.1	-6.4	-25.9
	PRL-02B4	95	-11.4	-9.4		Profile-2	BG-5A2	5	-6.6	-6.8	-25.7
Profile-3	PRL-03A01	30	-9.5	-6.6			BG-5A4	20	-6.7	-7.2	-26.3
	PRL-03A0	35	-9.5	-7.1			BG-5A6	25	-6.6	-7.1	-26.6
	PRL-03A4	70	-11.2	-8.8			BG-5A7	30	-6.6	-7.0	25.6
Profile-4	PRL-013A3	70	-10.6	-9.3			BG-5A8	40	-6.8	-7.2	-25.7
	PRL-013A1	30	-11.5	-8.2			BG-5A10	55	-7.2	-6.4	-26.2
Profile-5	PRL-019	30	-11.0	-8.6			BG-5A11	80	-6.7	-6.9	
	PRL-019A1	45	-10.4	-9	-24.7		BG-5A14	100	-7.3	-6.8	-22.2
	PRL-019A2	60	-11.4	-9.1			BG-5A9	50	-6.8	-6.6	
	PRL-019A3	90	-10.4	-8.8	-24.7	Denwa sec	tion, Satpura Ba	isin, Gondwana			
Profile-6	PRL-017A	30	-11.3	-11.1		Profile-1	Sample No	Depth (cm)	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C_{Org}$
	PRL-017C	50	-10.5	-11.2			DN-C-2	25	-10.7	-5.4	-24.8
	PRL-017D	80	-11.1	-9.8			DN-C-2A1	35	-10.6	-5.0	-24.4
							DN-C-2B	45	-10.4	-5.0	-24.9

Location	Sample No	δ ¹³ C _{Carb} ‰	δ ¹⁸ Ο _{Carb} ‰	δ ¹³ C org. (‰)	Description
Lower Denwa	DN-C-2	-10.7	-5.4	-24.5	root mold
	DN-C-2A1	-10.6	-5.0	-24.9	root mold
	DN-C-2B	-10.4	-5.0	-24.9	root mold
Middle Denwa	DN-ND-8A1	-8.3	-6.0	-25.1	root mold
	DN-ND-8A2	-8.0	-5.6	-26.1	root mold
	DN-ND-8A3	-7.9	-5.9	-25.1	root mold
	DN-ND-8A4	-9.0	-5.3	-25.1	root mold
	DN-ND-8A5	-8.9	-5.3	-24.2	root mold
	DN-ND-8A6	-8.4	-5.4	-24.5	root mold
	DN-ND-8A9	-8.6	-5.1	-25.2	root mold
	DN-ND-8A10	-8.1	-4.5	-25.2	root mold
Upper Denwa	DN-C-6A3	-6.4	-3.9	-24.4	Nodule, contact of Denwa and Bagra
	DN-C-6A	-6.9	-5.9		soil carbonate nodule
	DN-C-7A1	-6.7	-4.5	-24.4	soil carbonate nodule
Non Pedogenic	Carbonate, Der	iwa			
	DN-C-3A	-6.9	-4.9	-23.7	Clay dyke contact
	DN-C-3A3	-6.5	-4.4	-23.6	Clay dyke contact
	DN-C-4A2	-7.5	-4.1	-24.1	calcrudite
	DN-C-4A1	-7.5	-5.4		calcrudite
	DN-C-5A2	-5.7	-2.1		fracture filled
	DN-C-6A2	-4.7	-1.7	-24.5	calcrudite
	DN-C-8A	-7.6	-4.1	-24.3	calcrudite
Bagra	BG-ND-4A1	-6.3	-6.7	-25.9	soil carbonate nodule
	BG-H-2	-6.9	-6.7	-25.7	soil carbonate nodule
Recycled soil ca	arbonate, Bagra				
	BG-CNG-2	-7.4	-6.3		
	BG-CNG-3	-7.8	-6.3		
	BG-CNG-4	-6.7	-6.7		

Table 6.2. Carbon and oxygen isotope ratio of soil carbonate and carbon isotope ratio of ratio of organic mater from different sections of Denwa and Bagra Formation.

also be taken to be same for Denwa, Bagra and Siwalik soils as the palaeoposition of the first two was in temperate region (Ghosh et al. 2001) and Siwalik was in subtropical region (Harrison et al., 1998).

Formation	Mean $\delta^{13}C$	$\delta^{13}C$	Mean δ^{13} C org	δ^{13} C air	S_Z (ppmV)	CO ₂ (ppmV)	Mean CO ₂	Age (Ma)
	carbonate	CO_2	(‰)	(/00)	(PP)	(FF)	(ppmV)	()
	(700)	(/00)						
Lower	-10.6	-19.4	-24.7	-3.7	3000	190	255 ±65	240
Denwa					4000	255		
					5000	320		
Middle	-8.4	-17.2	-25.1	-4.1	3000	825	1100 ±275	220
Denwa					4000	1100		
					5000	1375		
Upper	-6.7	-15.5	-24.4	-3.4	3000	1140	1520 ±380	206
Denwa					4000	1520		
					5000	1900		
Bagra-1	-6.8	-15.6	-25.7	-4.7	3000	1600	2110 ±500	180
					4000	2130		
					5000	2610		
Bagra-2	-6.8	-15.6	-26	-5	3000	1730	2275 ±535	145
					4000	2300		
					5000	2880		
Siwalik	-10.4	-19.2	-25.2	-4.2	3000	340	455 ±115	6–11
					4000	455		
					5000	550		

Table 6.3 *Estimated CO*₂ *from Gondwana and Siwalik palaeosols.*

The δ^{13} C of soil carbonate and organic matter from Ranital soil profiles indicate that for most of the samples the source of carbon was C₃ plant. One sample collected from 5 cm below the present surface has substantial contribution of CO₂ from atmosphere (Sanyal et al., 2004a). In lower Denwa Formation, the δ^{13} C of soil carbonate and organic matter associated with root mold suggest that here also the source of CO₂ is from C₃ plant. In Bagra Formation, the mean δ^{13} C of rhizocretion is enriched by ~4 ‰ compared to the mean δ^{13} C of soil carbonate from Ranital and lower Denwa but the carbon isotope ratio of organic matter shows that vegetation comprised of C₃ plants. If the source of soil CO₂ is only from oxidation of organic matter and plant respiration, the δ^{13} C of soil carbonate from Ranital should have been same. Considering the absence of C_4 plants during Gondwana, the enriched carbon isotope ratio of soil carbonates in Bagra and Denwa palaeosols (except lower Denwa) indicate substantial input of atmospheric CO_2 in soil atmosphere. Usually the p CO_2 in soil atmosphere is much higher than the partial pressure of atmospheric CO_2 ; this results in minor contribution of atmospheric CO_2 in soil atmosphere. However, during upper Denwa and Bagra time substantial input of atmospheric CO_2 indicates relatively higher atmospheric CO_2 concentration. The concentration of atmospheric CO_2 could be calculated using Cerlings' palaeobarometric equation (1991).

6.5.2 Estimation of atmospheric CO₂

The concentration of soil CO_2 in a soil profile is determined by contribution of soil-respired CO_2 and diffusion of atmospheric CO_2 into soil. The steady state condition for CO_2 in soil can be described by the diffusion-production equation:

$$\frac{\partial C_s^*}{\partial t} = D_s^* \frac{\partial^2 C_s^*}{\partial z^2} + \varphi_s^*(z)....(1)$$

where C_s^* is the concentration of CO₂ in the soil (moles/cm³), D_s^* is the diffusion coefficient (cm²/s) for CO₂ in soil, z is depth (cm) and $\varphi_s^*(z)$ is the production rate of CO₂ (moles/cm³/s) in the soil at of depth z. The general solution of this equation with no flux boundary at depth z=0 and C_s^* equal to atmospheric CO₂ is:

$$C_{s}^{*}(z) = S(z) + C_{a}^{*}$$
(2)

where C_a^* is the CO₂ concentration in the atmosphere and S(z) is CO₂ contributed by soil respiration. Cerling (1984,1991) solved this equation for ¹²C and ¹³C and showed that isotopic composition of soil CO₂ is controlled by diffusional mass transfer and production. The solution to the soil CO₂ equation can be rearranged in the following form

$$C_{a}^{*} = S(z) \frac{\delta^{13}C_{s}^{*} - 1.004\delta^{13}C_{\phi}^{*} - 4.4}{\delta^{13}C_{a}^{*} - \delta^{13}C_{s}^{*}} \dots (3)$$

by using the assumption of ${}^{12}C/{}^{13}C \approx C_s^*/C_a^*$ (Davidson, 1995) where $\delta^{13}C_s^*$, $\delta^{13}C_{\phi}^*$ and $\delta^{13}C_a^*$ are the isotopic composition of soil CO₂, soil-respired CO₂ and atmospheric CO₂ respectively. Equation (3) shows that concentration of atmospheric CO₂ can be

calculated if the $\delta^{13}C$ of soil CO₂, the $\delta^{13}C$ of atmospheric CO₂, $\delta^{13}C$ of soil-respired CO₂ and the difference between the soil pCO₂ and the atmospheric pCO₂ which is known as S_Z are known. These parameters for the contemporaneous time period are estimated in the following way:

1) δ^{13} C of soil CO₂: Carbon isotope ratio of soil CO₂ can be estimated from three inputs: carbon isotope ratio of soil carbonate, fractionation factor between CO₂carbonate and temperature of carbonate precipitation. Generally mean annual air temperature of a region could be taken as the temperature for carbonate precipitation in soil. Palaeo global temperature estimation by Scotese (1998) showed that during Triassic to Middle Jurassic global temperature was 30°C. However, the temperature of soil carbonate precipitation for Denwa and Bagra Formation was inferred based on a comparison between the character of palaeosols and modern soil (Ghosh et al. 2001). A plot of maximum monthly temperature suitable for soil carbonate precipitation reveals that for modern condition 25°C is a typical temperature at 45°S and 25°S, which are the palaeo-position of Satpura basin during Bagra and Denwa times respectively. At 25°C the carbon isotopic enrichment during the transformation of CO₂ to CaCO₃ is about 9‰ (Romanek et al., 1992).

2) Carbon isotope ratio of soil-respired CO₂ and atmospheric CO₂: The carbon isotope ratio of plant-respired CO₂ is same as average δ^{13} C of whole plant body. The δ^{13} C of soil-respired CO₂ could be taken as the mean δ^{13} C of organic matter associated with soil carbonate assuming that plant-respired CO₂ and oxidation of plant debris are the sources of soil-respired CO₂.

During photosynthesis plants take CO₂ from atmosphere to form metabolites through a chain of reactions by which the initial carbon isotope ratio of CO₂ gets depleted by about 21 ‰ (Mora et al. 1996). Hence, the δ^{13} C of the atmospheric CO₂ could be estimated by subtracting 21 ‰ from the mean δ^{13} C of organic matter (Mora et al. 1996; Grocke et al., 1999).

3) S_Z parameter: The S_Z parameter can vary widely depending on soil respiration rate. Observations made on the modern soils show that for desert soil S_Z is less than 3000 ppmV and for well-drained temperate and tropical soil S_Z ranges between 5000 and 10,000 ppmV (Mora et al., 1996; Ghosh et al., 1995; Tandon et al., 1995). However, considering the latitudinal position of the soils, mean annual temperature of soil formation and condition of soil formation, the range of the S_Z value is taken between 3000 and 5000 ppmV following arguments given in Ghosh et al. (2001).



Fig.6.5 Atmospheric CO_2 concentration variation through time based on $\delta^{13}C$ of paleosols from Gondwana deposit of Satpura basin. Lower Triassic CO_2 concentration was about 255 ppmV and it reached a maximum of 1520 ppmV during upper Triassic through an intermediate concentration of 1100 ppmV. During the Jurassic period the average concentration was about 2190 ppmV. During Siwalik time (11-6 Ma) CO_2 concentration was 455 ppmV.

The average carbon isotope ratio of Denwa soil carbonate is depleted compared to the Bagra samples. The δ^{13} C value of Denwa soil carbonate shows progressive enrichment from bottom to top of the stratigraphic succession and the most enriched value is found at the contact with the Bagra Formation. On the other hand, the δ^{13} C value of the Bagra soil carbonate from different exposures is almost similar. The CO₂ estimation based on Cerling formalism show that during lower Denwa time, atmospheric CO₂ concentration was almost equal to the recent pre-industrial value. In the upper Denwa time it reached a high value of 1520 ppmV through an intermediate concentration of 1100 ppmV (middle Denwa) and during Bagra time the CO₂ concentration ranged from 2110 to 2275 ppmV. A plot of these values against the inferred ages of the samples show continuous increase of CO₂ concentration with time (Fig.6.5). The CO₂ concentration of 455 ppmV for the late Neogene Period (6-11 Ma) (Table 6.3).

Though the nature of CO₂ concentration change from Triassic to Jurassic is similar to that given by Ekart et al. (1999), our estimation is lower by about 1000 ppmV. This difference is very large and ought to be accounted for. Ekart et al (1999) estimated the carbon isotope ratio of atmospheric CO₂ from fossil record of marine carbonates (Ekart et al., 1999) whereas in the present work the estimation was done directly from the organic matter of palaeosols. Consequently, Ekart et al obtained a larger difference between δ^{13} C of atmospheric CO₂ and that of soil carbonate which translates to a larger atmospheric CO₂ abundance. This issue needs to be resolved in future.

6.5.3 Oxygen isotope ratio of soil carbonate

It has been established earlier that Ranital, Denwa and Bagra soil carbonates formed in equilibrium with soil water and oxygen isotope ratio of soil carbonate would be representative of local rainfall (Sanyal et al., 2004a; Ghosh et al. 2001). The δ^{18} O of local rainfall mainly depend on the following factors 1) Latitudinal effect 2) Temperature and 3) Amount effect.

1) Latitudinal effect: Moisture in moving atmospheric air masses tends to become progressively depleted in heavy isotopes during their progressive condensation and removal by precipitation. As a result, the δ^{18} O values of rain in the tropics is close to that

of ocean water, but the values become systematically lower in temperate zones, and even lower in continental interiors at high latitude. Extremely low values are obtained in winter ice at the Poles (Criss, 1999). This depletion in isotope ratio of rainwater is known as latitudinal effect. The net depletion can be explained as the combined effect of rainout and temperature gradient from equator to pole.

2) Temperature: Mean annual air temperature can affect the δ^{18} O of rainwater in two ways. It has been seen that every degree Celsius rise in air temperature causes enrichment in δ^{18} O of rain by 0.7 ‰. This is explained by a complex temperature effect on the rainout sequence and rainfall mechanism (Criss, 1999). In addition, during the recharge of water into the soil, higher temperature increases evaporation, enriching the δ^{18} O value of residual water. Part of this is compensated during carbonate formation since a rise in temperature causes depletion of ¹⁸O in carbonate (0.2‰/°C).

3) Amount effect: The δ^{18} O of rainwater decreases with an increase in the amount of precipitation (IAEA, 2003). At low latitudes, the average monthly rainfall and the mean monthly δ^{18} O are usually negatively correlated where an increase in 100 mm of rainfall is associated with a decrease in δ^{18} O by 1.5 ‰ (Yurtsever and Gat, 1981).

During Gondwana time the present landmass of India was at Southern Hemisphere. Palaeo-latitude reconstruction of Satpura basin of Gondwana Supergroup (which was located at the southern part of the mega-continent Pangea) showed that during Denwa time it was at 45°S and during the Bagra time at 25°S. If latitudinal effect were to operate, the δ^{18} O of the Denwa soil carbonate should have been depleted compared to the Bagra samples. However, the average δ^{18} O of samples collected from Denwa Formation is -5.0 ‰ in contrast to -6.3‰ for Bagra samples. This indicates absence of latitudinal effect in rainfall at that time. It has been summarized by many workers that during Gondwana time the equator-pole temperature contrast was much less (only 20° to 30°C). This may explain the above unusual δ^{18} O contrast.

Since the palaeo temperature of the Denwa and Bagra times was not radically different, a temperature effect can be ruled out to explain the difference in δ^{18} O of the samples from two formations. In Gondwana time, the amount of rainfall varied enormously through time as the configuration of the landscape changed. The

supercontinent Pangea started forming at the beginning of the Triassic (corresponding to Denwa) and by early Jurassic the formation was complete resulting in decrease in the amount of shoreline, formation of mountains and a dry, desert-like terrain in the interior of the supercontinent. These factors could have caused enrichment of ¹⁸O in soil carbonate in Denwa. However, during the Bagra time, the supercontinent started breaking up and polar ice started melting which made the δ^{18} O of ocean water lower than before. The rainwater forming at that time would be characterized by depleted δ^{18} O value, which is probably reflected in the oxygen isotope ratio of soil carbonate of Bagra time. We propose that climate effect during these two periods could have been the principal factor for the observed δ^{18} O contrast.

In Ranital Siwalik, the oxygen isotope ratio of soil carbonate in a complete stratigraphic succession shows continuous enrichment with decrease in age (Sanyal et al., 2004a). At around 10.5 Ma, the δ^{18} O is characterized by highly depleted value of about -10 %; it reaches higher value of -6.6 % at around 6.5 Ma. As explained in Chapter 3, the relatively depleted δ^{18} O value of soil carbonate at around 10 Ma compared to the younger samples represent intensified monsoonal rainfall (Sanyal et al., 2004a). The age of the six-soil profiles, which has been considered for the present study, ranges around 10 Ma and hence the relatively depleted oxygen isotope ratio is representative of the proposed intensified monsoonal rainfall.

6.6 Conclusions

Among many variables that can determine the carbon isotopic ratio of soil carbonate in a soil profile, the ratio of soil-respired CO₂ and atmospheric CO₂ in soil atmosphere is the most important. During Gondwana time when the atmospheric CO₂ concentration was high the δ^{13} C of soil carbonate demonstrate contribution from both soil-respired CO₂ and atmospheric CO₂. On the other hand, during Siwalik time, due to relatively lower concentration of CO₂ in atmosphere the carbon isotope ratio of plant-respired CO₂ was the sole determinant below depth of a few centimeters.

Atmospheric CO₂ concentration during Denwa time was characterized by a continuous increase from 255 ppmV and reaching a maximum during the upper Denwa at 1520 ppmV through an intermediate concentration of 1100 ppmV. During the Bagra time, the concentration was 2190 ppmV. In contrast, during the Siwalik time,

atmospheric CO_2 concentration was 455 ppmV. Since the soil samples for the Triassic Period was taken from a single Formation (Denwa) the relative variation of CO_2 concentration in the form of continuous increase is well constrained.

The oxygen isotope ratio of soil carbonate of individual soil profiles from both Gondwana and Siwalik sediments shows enrichment toward the surface, which may be the effect of evaporation of soil water in near surface zone. The δ^{18} O value of the Denwa and Bagra samples suggest that the latitudinal effect was not operative during the Gondwana time and climate was the main cause for depleted δ^{18} O of Bagra compared to Denwa. On the other hand, we demonstrate that the depleted δ^{18} O value of the Siwalik samples at 10.5 Ma represent intensified monsoonal rainfall.

CHAPTER-7

DIAGENESIS OF SIWALIK SEDIMENTS AND ITS EFFECT ON STABLE ISOTOPES

Diagenesis and Isotopes

7.1 Introduction

Freshly deposited sediments are commonly unconsolidated, with relatively low bulk density and high permeability and if accumulated under water, contain substantial amount of water. Subsequently, while being buried under younger sediments, the older sediments progressively lose water and become denser and lithified. All the changes involved in such a process is collectively termed diagenesis (Gerhard, 2000). Diagenesis can be of two types: mechanical and chemical. Mechanical diagenesis results from vertical stresses caused by overburden of younger sediments and, in some cases, by additional stresses due to tectonic movements. It expels pore water and leads to a rearrangement of the sediment particles. Chemical diagenesis involves dissolution and re-crystallization of primary sediment particles as well as precipitation of cement in pore space. Dissolution and cementation may take place at different depth levels within the sediments. The effects of mechanical and chemical diagenesis in various sediment types are quite complex but some issues can be investigated using a variety of proxies.

Siwalik sediments of Himalayan foothills were deposited continuously by various rivers in the foothills of Himalaya for last 20 Myr (Johnson et al., 1985) and provide an excellent opportunity to study diagenetic changes in fluvial sediments over a specified time. As a whole, the Siwalik sediments are characterized by coarsening upwards reflecting increase in energy levels for sediment transport with time. The lower and middle Siwalik sediments consist of alternation of sandstone and mudstone beds while upper Siwalik is mostly characterized by alternation of conglomerate and mudstone beds with occasional lenses of sandstone in-between. Compositionally, the sandstone is lithic arenite with calcite as the main cementing material.

An attempt has been made here to study diagenetic imprints through isotopic changes in calcite cement, assemblage of clay minerals and abundance of K-feldspar in sandstones from Surai Khola section of Nepal Siwalik (Fig.2.1). Previous study from Surai Khola section showed interesting variation of carbon and oxygen isotope ratios of soil carbonate with implication of change in vegetation and climate during Miocene. It would be of interest to know how late diagenesis changed the pristine isotopic signature of sandstone cements and the mineralogy of sandstones. Such analysis is possible in case of Surai Khola due to availability of isotopic results from soil carbonates, which are less

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susceptible to change and provide a well-constrained contemporary reference data set for comparison.

7.2 Cement morphology of sandstone

The primary cementing material of Siwalik sandstone is calcite. According to Tandon and Varshney (1991) calcite precipitated in sub-aerial vadoze zone due to capillary action under wet and dry climatic condition. Calcite in sandstone generally occurs as pore-filling variety with a patchy distribution (Fig.7.1a). Corrosion of quartz and feldspar grains by cementing action is common (Fig.7.1b, 1c). Calcite spar frequently shows complex variations in the birefringence colors indicating partial dissolution of crystals.

7.3 Isotopic Results

The δ^{18} O values of sandstone cement samples show three evolutionary phases (Fig.7.2a). From 12 Ma to ~6 Ma, the average δ^{18} O is around $-13.6\pm1.9 \%$ (n=114) with a large spread from -10 to -18 %. Subsequent to 6 Ma, δ^{18} O shows sudden swing toward enriched values with less scatter in data; this enrichment continues up to 4 Ma. The average δ^{18} O value for this time range is $-10.7 \pm 1.6 \%$ (n=25). Around 4 Ma, the δ^{18} O reaches a maximum value of -7 %. From 4 Ma to 2 Ma, δ^{18} O value is fairly uniform with an average of $-8.8\pm1.2 \%$ (n=17) (Table 7.1).

Unlike δ^{18} O, the δ^{13} C of calcite cement does not show any definite trend with time (Fig.7.3) but varies randomly from -2.8 ‰ to -9.9 ‰. From 12 Ma to 7 Ma, the δ^{13} C ranges between -3.3 ‰ to -9.9 ‰ with an average of -7.1 ± 1.5 ‰ (n=91). Subsequent to 7 Ma, the number of relatively enriched values increases. From 7 Ma to 2 Ma, the δ^{13} C varies from -2.8 ‰ to -9.2 ‰ with an average of -5.7±1.5 ‰ (n=65) (Table 7.1).

7.4 Discussion

7.4.1 Oxygen isotope ratio of carbonate cement

Oxygen isotope ratio of calcium carbonate depends on temperature of crystallization and oxygen isotope ratio of ambient water. Calcium carbonate precipitating at shallow level reflects the oxygen isotope ratio of local ground water initially but subsequent burial of the carbonate can modify this ratio. δ^{18} O of carbonate associated with the sandstone bears the imprints of burial as discussed below.

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Temperature during burial: Isotopic exchange between carbonate and fluid is not significant at temperatures typical of sedimentary environment except during dissolution and re-precipitation (Anderson, 1969; Land, 1980). Oxygen isotope exchange resulting from re-crystallization becomes more important as temperature rises. Since rise in temperature results in more negative δ^{18} O, the most depleted value in a set of samples should represent the highest temperature acquired during burial. To calculate temperature of diagenesis from δ^{18} O value of carbonate cement, oxygen isotopic composition of solution from which calcium carbonate has precipitated needs to be known. A critical but reasonable assumption about the δ^{18} O value of formation water can be made from two inputs: δ^{18} O of soil carbonate of same time period and modern day δ^{18} O of meteoric water (ground water). The average oxygen isotope ratio of soil carbonate from Surai Khola section showed that pre-6 Ma (12 Ma to 6 Ma) meteoric water was depleted by ~3.5 % compared to the present day δ^{18} O (Quade et al., 1995). Assuming that δ^{18} O of shallow ground water is governed mostly by meteoric water (Krishnamurthy and Bhattacharya, 1991) and present day mean δ^{18} O value of ground water on the piedmont of Nepal is -6.5 % (SMOW), (Quade et al., 1995) the δ^{18} O of ground water for the time range 12 to 6 Ma can be approximately taken as -10 %(SMOW). Using this value of water δ^{18} O and the Friedman-O'Neil (1977) equation of carbonate-water fractionation $1000 \ln \alpha_{water}^{calcite} = 2.78 \times 10^6 / T^2 - 2.89$ where $\alpha_{water}^{calcite} =$ $(1000 + \delta^{18}O_{calcite})/(1000 + \delta^{18}O_{water})$ it can be shown that the required temperature to achieve the most negative δ^{18} O (-18 ‰) is around 57°C. Such high value was possibly attained during deep burial of sediments (3 to 5 km).

Large scatter in δ^{18} O values (from -10% to -18%) at the bottom (12 to 10 Ma) of the stratigraphic succession may be due to dissolution and re-precipitation of calcites at different temperatures corresponding to various depths and generations during burial. As mentioned before, at a given level, the most negative δ^{18} O probably represents calcite samples which precipitated at the highest available burial temperature; similarly, the most enriched ¹⁸O probably represents calcite precipitated at lowest



Fig.7.1a Thin section showing calcite cement filling the pore space of sandstone samples from Surai Khola. Dissolution of grain boundary (marked by white line) of K-feldspar grain by calcite cement is also shown.



Fig.7.1b Remnant of quartz grain after corrosion by calcite cement in medium grained sandstone



Fig.7.1c Corrosion of K-feldspar grain by calcite cement.



descent, isotopic ratio of cement could have changed due to dissolution/re-precipitation of calcite. However, some samples suffered minimal change and some probably retained the original isotopic signature. This implies that the depleted value is most altered and the enriched value is least altered when samples are compared at the same stratigraphic
Sample No	Age(Ma	a) $\delta^{13}C$	$\delta^{18}O$	Sample No	Age (Ma)	$\delta^{13}C$	δ ¹⁸ Ο
PS2K-BNK-02-S1	12.0	-7.2	-17.6	PS2K-BNK-48-S14	10.5	-8.2	-11.8
PS2K-BNK-04-S2	12.0	-9.2	-16.5	PS2K-BNK-48-S15	10.5	-8.2	-16.3
PS2K-BNK-07-S2	11.9	-9.8	-11.1	PS2K-BNK-48-S19	10.5	-6.7	-14.6
PS2K-BNK-08-S2	11.9	-7.6	-15.7	PS2K-BNK-49-S2	10.5	-7.8	-11.7
PS2K-BNK-10-S1	11.9	-7.2	-15.5	PS2K-BNK-50-S1	10.5	-8.2	-12.1
PS2K-BNK-012S1	11.9	-8.5	-15.0	PS2K-BNK-51-S1	10.4	-5.7	-14.5
PS2K-BNK-012S2	11.7	-6.7	-15.7	PS2K-BNK-51-S3	10.4	-5.3	-15.3
PS2K-BNK-15-S3	11.7	-7.5	-11.4	PS2K-BNK-52-S2	10.4	-6.9	-13.4
PS2K-BNK-15-S4	11.7	-7.7	-11.7	PS2K-BNK-54-S2	10.4	-5.3	-13.2
PS2K-BNK-20-S2	11.7	-8.1	-14.0	PS2K-BNK-55-S1	10.4	-5.7	-13.3
PS2K-BNK-22-S1	11.7	-9.6	-10.4	PS2K-BNK-59-S2	10.3	-6.8	-12.6
PS2K-BNK-22-S2	11.7	-8.7	-10.0	PS2K-BNK-61-S1	10.3	-6.0	-15.9
PS2K-BNK-25S2	11.6	-5.6	-15.7	PS2K-BNK-62-S1	10.3	-8.3	-10.7
PS2K-BNK-26-S2	11.6	-5.3	-13.5	PS2K-BNK-66-S2	10.1	-6.9	-12.6
PS2K-BNK-27-S2	11.6	-5.3	-13.3	PS2K-BNK-67-S2	10.0	-8.6	-17.5
PS2K-BNK-27S2(R)	11.5	-6.3	-14.9	PS2K-BNK-68-S1	9.9	-8.3	-16.3
PS2K-BNK-28-S2	11.2	-6.6	-12.1	PS2K-BNK-68-S2	9.8	-8.4	-18.0
PS2K-BNK-30-S2	11.2	-6.7	-12.2	PS2K-BNK-69-S1	9.7	-8.6	-17.3
PS2K-BNK-32-S1	11.1	-8.3	-15.2	PS2K-BNK-69-S2	9.6	-7.5	-15.1
PS2K-BNK-34-S2	11.1	-8.1	-11.5	PS2K-BNK-70-S2	9.5	-5.4	-13.7
PS2K-BNK-36-S2	11.0	-6.5	-16.2	PS2K-BNK-71-S1	9.4	-9.2	-10.7
PS2K-BNK-37-S1	10.7	-5.5	-12.7	PS2K-BNK-72-S2	9.2	-8.6	-12.5
PS2K-BNK-42-S2	10.7	-5.8	-13.8	PS2K-BNK-77-S2	9.1	-5.0	-15.7
PS2K-BNK-44-S1	10.7	-9.6	-11.0	PS2K-BNK-80-S2	9.1	-5.9	-10.7
PS2K-BNK-45-S1	10.7	-9.5	-11.7	PS2K-BNK-81-S2	9.1	-5.6	-12.5
PS2K-BNK-45-S2	10.6	-9.0	-17.7	PS2K-BNK-86-S1	9.0	-6.6	-14.7
PS2K-BNK-48-S1	10.6	-5.5	-12.6	PS2K-BNK-86-S2	9.0	-8.7	-10.3
PS2K-BNK-48-S2	10.6	-5.7	-14.4	PS2K-BNK-87-S1	8.5	-8.6	-11.3
PS2K-BNK-48-S4	10.6	-6.8	-15.4	PS2K-BNK-92-S2	8.2	-6.1	-16.5
PS2K-BNK-48-S6	10.6	-7.2	-16.1	PS2K-SK-114-S	8.0	-6.0	-16.4
PS2K-BNK-48-S10	10.6	-5.3	-11.7	PS2K-SK-114-S	8.0	-6.8	-12.4
PS2K-BNK-48-S11	10.5	-6.0	-12.9	PS2K-SK-117-S1	8.0	-7.7	-11.4
PS2K-BNK-48-S13	10.5	-9.3	-10.1	PS2K-SK-121-S1	7.9	-6.9	-15.5

 Table.7.1 Carbon and oxygen isotope ratio of carbonate cement from sandstone

Sample No	Age(Ma)	$\delta^{13}C$	$\delta^{18}O$	•	Sample No	Age(Ma)	$\delta^{13}C$	$\delta^{18}O$
PS2K-SK-122-S2	7.9	-7.3	-13.3	•	PS2K-SK-210-S1	6.2	-4.6	-14.8
PS2K-SK-123-S2	7.9	-8.8	-11.1		PS2K-SK-215-S1	6.2	-4.7	-14.5
PS2K-SK-123-S1	7.9	-6.9	-14.7		PS2K-SK-216-S1	6.2	-4.9	-13.1
PS2K-SK-125-S1	7.8	-7.9	-12.5		PS2K-SK-217-S1	6.2	-7.1	-16.8
PS2K-SK-129-S1	7.8	-5.0	-15.6		PS2K-SK-218-S1	6.1	-4.7	-13.8
PS2K-SK-133-S1	7.8	-8.9	-11.9		PS2K-SK-219-S1	6.1	-3.8	-13.8
PS2K-SK-133-S2	7.7	-8.4	-11.3		PS2K-SK-222-S1	6.1	-4.8	-12.4
PS2K-SK-134-S2	7.7	-6.1	-12.3		PS2K-SK-223-S1	6.1	-3.7	-13.6
PS2K-SK-137-S1	7.7	-6.1	-12.9		PS2K-SK-224-S1	6.1	-4.4	-12.0
PS2K-SK-137-S1	7.6	-7.8	-12.6		PS2K-SK-224-S2	6.1	-3.9	-12.0
PS2K-SK-138-S1	7.6	-7.7	-13.4		PS2K-SK-225-S1	6.0	-4.2	-12.9
PS2K-SK-138-S2	7.6	-9.2	-11.6		PS2K-SK-229-S1	6.0	-4.4	-11.4
PS2K-SK-139-S1	7.5	-3.3	-13.3		PS2K-SK-229-S2	5.4	-4.6	-10.6
PS2K-SK-142-S1	7.4	-5.7	-14.5		PS2K-SK-242-S1	5.4	-7.8	-11.5
PS2K-SK-153-S2	7.3	-8.8	-13.9		PS2K-SK-242-S2	5.3	-4.4	-12.8
PS2K-SK-154-S2	7.3	-4.0	-15.5		PS2K-SK-244-S1	5.3	-3.0	-13.6
PS2K-SK-155-S2	7.3	-7.1	-12.3		PS2K-SK-245-S1	5.2	-8.9	-10.9
PS2K-SK-156-S1	7.3	-6.5	-13.1		PS2K-SK-247-S1	5.1	-5.6	-10.6
PS2K-SK-156-S2	7.2	-5.6	-12.9		PS2K-SK-253-S1	5.1	-6.2	-10.7
PS2K-SK-159-S2	7.2	-6.6	-11.9		PS2K-SK-255-S1	4.9	-3.6	-13.4
PS2K-SK-159-S1	7.1	-9.4	-12.7		PS2K-DB-270-S1	4.8	-6.3	-10.4
PS2K-SK-160-S1	7.1	-8.9	-12.2		PS2K-DB-271-S1	4.7	-8.1	-10.9
PS2K-SK-160-S2	7.1	-6.4	-12.3		PS2K-DB-275-S1	4.7	-7.9	-10.9
PS2K-SK-163-S2	7.1	-8.3	-15.4		PS2K-DB-275-S2	4.7	-8.8	-10.8
PS2K-SK-163-S4	7.0	-3.5	-15.4		PS2K-DB-276-S2	4.7	-6.5	-8.8
PS2K-SK-166-S1	6.5	-5.0	-14.4		PS2K-DB-280-S1	4.7	-7.5	-8.1
PS2K-SK-172-S1	6.4	-5.1	-12.2		PS2K-DB-280-S2	4.7	-7.8	-10.1
PS2K-SK-183-S1	6.4	-7.2	-14.5		PS2K-DB-280-S4	4.6	-5.3	-11.1
PS2K-SK-194-S1	6.4	-5.4	-13.6		PS2K-DB-285-S1	4.6	-9.2	-9.2
PS2K-SK-196-S1	6.4	-5.9	-14.6		PS2K-DB-285-S2	4.5	-5.9	-8.5
PS2K-SK-199-S1	6.4	-5.5	-13.2		PS2K-DB-287-S1	4.5	-5.5	-9.6
PS2K-SK-199-S2	6.4	-5.2	-13.7		PS2K-DB-287-S2	4.5	-3.9	-12.5
PS2K-SK-199-S2	6.3	-5.1	-12.7		PS2K-DB-288-S1	4.5	-5.2	-7.9
PS2K-SK-203-S1	6.3	-3.9	-12.2		PS2K-DB-289-S1	4.4	-5.1	-8.0
PS2K-SK-204-S1	6.3	-6.0	-13.6		PS2K-DB-290-S1	4.4	-7.6	-12.1
PS2K-SK-206-S1	6.3	-5.8	-12.2		PS2K-DB-295-S1	3.9	-5.3	-10.9
PS2K-SK-209-S1	6.2	-4.7	-14.2		PS2K-DB-320-S1	3.9	-6.3	-8.7

Sample No	Age	$\delta^{13}C$	$\delta^{18}O$	Sample No Age δ^{13} C δ^{18} O
	(Ma)			(Ma)
PS2K-DB-320-S2	3.86	-2.8	-10.9	PS2K-DB-329-S2 3.7 -5.8 -8.5
PS2K-DB-321-S1	3.85	-8.6	-7.8	PS2K-DB-331-S1 3.7 -6.7 -7.7
PS2K-DB-322-S1	3.83	-7.7	-9.2	PS2K-DB-334-S1 3.0 -6.3 -7.8
PS2K-DB-323-S1	3.83	-7.4	-8.9	PS2K-DB-373-S1 3.0 -6.5 -7.9
PS2K-DB-323-S2	3.79	-4.5	-10.9	PS2K-DB-373-S2 2.9 -5.3 -7.5
PS2K-DB-326-S1	3.79	-5.4	-8.3	PS2K-DB-377-S1 2.5 -5.4 -8.6
PS2K-DB-326-S2	3.73	-4.5	-9.3	PS2K-DN-389-S1 2.5 -6.8 -7.7
PS2K-DB-329-S1	3.73	-2.6	-8.1	

level. We further assume that the least altered value corresponds to calcite deposition near the surface level of the sediment column. Using this assumption, the maximum depth up to which re-precipitation of cement could have taken place can be estimated from the temperature difference between the most enriched and most depleted values from same stratigraphic level. Using the observed geothermal gradient of the Siwalik basin ~20°C/km (Mugnier et al., 1995) and assuming that the initial δ^{18} O was same for both the samples 40°C difference in temperature requires at least 2 km subsidence.

With decrease in depth, the scatter in δ^{18} O decreases. At around 7.5 Ma, the most depleted value is -15.6% and the most enriched value is -10%. The temperature difference of precipitation for these two samples is 28°C (44°C for -15.6% and 16°C for -10%) which implies a burial of ~ 1.5 km. The decrease in temperature difference with decrease in stratigraphic depth supports our assumption that temperature was the main controlling factor for oxygen isotope alteration in calcite cement.

The maximum depth up to which re-precipitation and re-crystallization has occurred can also be calculated from the most depleted value at a given stratigraphic level (S.L.) as it corresponds to maximum temperature acquired during burial. The maximum temperatures estimated in this way for 11.6 Ma (S.L.=4.9 km) and 7.5 Ma (S.L.=3.5 km) are 57°C and 44°C respectively corresponding to burial depths of nearly 2 km and 1.5 km (taking surface temperature as 16°C corresponding to -10% value obtained near the sediment surface as discussed above.). Near agreement of calculated depths for re-precipitation of calcite from horizontal spread of δ^{18} O and from most

depleted values at a given S.L. supports our contention that re-precipitation of calcite below 2 km was not significant.

This estimate of depth may represent a lower limit as re-precipitation of calcite is also possible during the uplift. The Siwalik basin was about 5.5 km deep and as



Fig.7.2 *a)* Oxygen isotope ratio of diagenetic calcite cement from sandstone samples of Surai Khola showing three evolutionary phases. From 12 Ma to 6 Ma, oxygen isotope ratio is characterized by large spread: -10 to -18 ‰. The large spread is probably due to dissolution and re-precipitation of carbonate at different stages of burial. At around 6 Ma, the ¹⁸O shows sudden swing towards enriched values and the maximum enrichment is attained near 4 Ma. The sudden swing is in tandem with enrichment of oxygen isotope ratio in soil carbonate (**Fig. 2b; Data from Quade et al., 1995**) from the same section, which indicates change in precipitational pattern. The similar trend of isotope ratio for cement and soil carbonate (for post 6 Ma period) suggests meteoric water has played an important role in determining the ratio during diagenesis. However, the ratio of sandstone cement is depleted compared to the ratio of soil carbonate (b). The depletion may be due to precipitation of cement at higher temperature compared to that of soil carbonate. Subsequent to 4 Ma, the δ^{18} O is nearly constant.

mentioned before, this depth was achieved due to continuous sinking during sedimentation. Later, as a result of tectonic activity, sediment in the foreland basin got uplifted. New generation of calcite could have precipitated during the upliftment at relatively lower temperature. The δ^{18} O of this generation of calcite would be enriched

compared to the calcite precipitated at higher depth. Thus, it is possible that the calculated depth of re-precipitation underestimates the actual depth of burial for samples which experienced subsidence followed by uplift.



Fig.7.3 Carbon isotope ratio of carbonate cement from sandstone shows large spread throughout the section. From 12 Ma to 7 Ma the $\delta^{13}C$ ranges between -3.3 to -9.9 ‰ with an average of $-7.1 \pm 1.5\%$ (n=91) and the post 7 Ma time the $\delta^{13}C$ ranges from -2.8 to -9.2 ‰ with an average of -5.7 ± 1.5 ‰ (n=65). CO₂ produced from decomposition of organic matter at various stages of burial and dissolution and re-precipitation of carbonate could be the cause of large spread in the carbon isotope ratio of carbonate. The enrichment in the carbon isotope ratio subsequent to 7 Ma probably reflects appearance of C₄ plants in the flood plain, which has enriched carbon isotope ratio compared to the C₃ plants.

During diagenesis, with increase in depth, dissolution and re-precipitation of minerals prone to diagenesis increase. Several workers suggested that alkali feldspar

undergoes extensive dissolution during burial diagenesis of sandstone (Milliken, 1989; Harris, 1992; Wilkinson and Haszeldine, 1996). Thin section analysis of Surai Khola sandstone shows absence of K-feldspars in the older samples in most cases while in the younger samples, K-feldspar is present with corrosive features (Fig.7.1a, 1c). Dissolution of K-feldspar is probably the result of interaction with weakly acidic pore fluid formed by decomposition of organic matter. Dissolution of K-feldspar results in increasing concentration of K, Al and SiO₂ in the diagenetic fluid, which can cause precipitation of quartz and illite. The semi-quantitative analysis of clays shows increase in abundance of illite with increase in stratigraphic depth, consistent with above observation.

Role of diagenetic fluid: Calcite cementation in fluvial sandstone probably occurs in shallow ground water regime due to capillary evaporation. It has been shown that oxygen isotope ratio of early diagenetic carbonate cement in sandstone represents ground water oxygen isotope ratio (Sanyal et al., 2004b) which, in turn, is mainly determined by the oxygen isotope ratio of meteoric water as it recharges the ground water with little or no fractionation. Any carbonate precipitating in equilibrium with ground water would reflect the oxygen isotope ratio of ground water as long as the carbonate does not interact with other sources. As discussed earlier, scattered $\delta^{18}O$ values of carbonate cement in lower part of the stratigraphic section at Surai Khola (pre-6 Ma period) indicate dissolution and re-precipitation of carbonate during deep burial. At around 6 Ma, the scatter in δ^{18} O decreases on either side (both enriched and depleted side) resulting in a conical shape of depth variation. The increase in depleted side values indicates lowering of temperature of re-precipitation while decrease in the enriched side may indicate change in the isotopic composition of water. Subsequent to 6 Ma, the δ^{18} O of carbonate cement increases rapidly, which is in accordance with the observed enrichment of ¹⁸O of soil carbonate in Surai Khola section (Fig.7.2b) (Quade et al., 1995) and other sections of Indian Siwalik (Sanyal et al., 2004a). The profile of $\delta^{18}O$ variation by considering only the most enriched values shows a minimum at around 6 Ma, which compares well with the proposed intensification of monsoon in Indian subcontinent based on pedogenic carbonate (Sanyal et al., 2004a). This indicates that despite alteration and consequent scatter, signature of a rapid δ^{18} O change is still

preserved in the sandstone. Additionally, it establishes that the δ^{18} O signal is definitely induced by meteoric water and represents a significant regional change in the rainfall pattern.

It is to be noted that ¹⁸O/¹⁶O ratio in sandstone cement is generally depleted compared to that of soil carbonate at the same stratigraphic depth despite having a similar trend in depth variation. This probably indicates higher formation temperature of sandstone calcite. Depleted oxygen isotope ratio in sandstone cement can also be caused by mixing of river water with shallow ground water by lateral flow. In the Himalayan region, river water flowing from highlands has lower δ^{18} O values than the water from low land. Mixing between groundwater and the local river water would, therefore, make the δ^{18} O value of formation water more depleted.

Detrital carbonates can, in principle, contribute to the bulk carbonate. The Siwalik sediments are weathering products of Himalayan rocks, which have many limestone formations. The δ^{18} O value of Himalavan marine limestones ranges from -8.9 to -14.5% (Quade et al., 1995). Contribution from such carbonates can make δ^{18} O of bulk carbonate more negative compared to carbonates precipitated from groundwater. However, modal abundance of carbonate grains shows only 2% to 15% of the carbonate as detrital. The contribution of detrital carbonate to the bulk δ^{18} O in various time brackets can be calculated by isotopic mass balance using the following inputs: (i) average bulk δ^{18} O values: for 12 to 6 Ma, -13.6%; for 6 to 4 Ma, -10.7%; and for 4 to 2 Ma, -8.8% (ii) average δ^{18} O of detrital carbonate as: -11.7% from the observed range – 8.9 to -14.5% (Quade et al., 1995) (iii) abundance of the detrital carbonate from 2 to 15%. Such calculation shows that maximum correction from detrital carbonate contribution is -0.3 % for 12 to 6 Ma; for 6 to 4 Ma +0.2%; and for 4 to 2 Ma +0.5%. This calculation indicates that the contribution of the detrital carbonate is not significant in changing the bulk δ^{18} O, especially in view of the large scatter introduced by several other factors discussed before.

We, therefore, conclude that in the lower part of the stratigraphic section the large scatter is due to re-precipitation of calcite at different stages during burial and uplift and subsequent to 6 Ma, the oxygen isotope ratio of calcite is mainly controlled by meteoric water.

7.5 Carbon isotope ratio of carbonate cement of sandstone

In general, the dissolved inorganic carbon in shallow groundwater below the soil zone is in isotopic equilibrium with plant-derived CO_2 if the soil has substantial vegetation (Pearson and Hanshaw, 1970; Fritz et al., 1978; Bath et al., 1979; Deak, 1979; Andrews et al., 1984; Wassennar et al., 1992; Leaney and Herczeg, 1995; Clark et al., 1997). Ground water calcite should also form in equilibrium with this reservoir as long as it forms shortly after burial and does not undergo extensive interaction with carbon sources other than plant-derived CO_2 .

Plant-derived CO₂ can have different δ^{13} C values depending on the type of plant since different plants have different photosynthetic pathway. The majority of plants, comprising trees, shrubs, cool-season grasses etc., follow the C₃ pathway. The δ^{13} C of C₃ plants vary over a large range: -20 to -35 ‰ but the average is well constrained at -26.7 ‰. For the C₄ type of plants (grasses), δ^{13} C values range from -6 ‰ to -19 ‰, with an average of about -13 ‰ (Cerling et al., 1997). When calcium carbonate forms in equilibrium with plant-derived CO₂, the δ^{13} C of calcium carbonate become enriched by 14 to17 ‰ compared to the plant-derived CO₂ depending on temperature (Cerling, 1984).

Vegetational reconstruction based on carbon isotope ratio of soil carbonate from Surai Khola section showed that the flood plain in pre-7 Ma time was dominated by C_3 type of plants (Quade et al., 1995). Therefore, sandstone carbonates older than 7 Ma and precipitating from shallow ground water should have values around -10 to -13%depending on the temperature of precipitation. However, this is not observed in the data set. Instead, there is a large scatter from -10 to -5% indicating other sources of carbon. As discussed earlier, the scatter in oxygen isotope ratio of the cement indicates dissolution and re-precipitation of carbonate during burial and uplift. The same effects can lead to carbon isotope ratio variation. During progress of diagenesis associated with burial, organic matter contained in sandstone undergoes several decarbonation reactions and CO_2 produced from these reactions can have different isotopic ratios. With progress in burial, organic matter gets modified by processes like fermentation, thermally induced decarboxylation etc. operating at different depths (Irwin et al., 1977). Carbon isotope ratio of CO_2 produced during these reactions can vary from -25% to +15%. At the

highest level of diagenesis, thermal decomposition of organic matter can produce very depleted CO_2 (-25 ‰) whereas fermentation can produce very enriched CO_2 (+15 ‰). Large spread of carbon isotope ratio at the same stratigraphic level probably indicates precipitation of carbonate in equilibrium with CO_2 derived from plant organic matter but at various stages of decarbonation.

Subsequent to 7 Ma, the spread in δ^{13} C values increases. Interestingly, enriched carbon isotope ratios (up to -2.5%) also appear (Fig.7.3). The enriched values are possibly due to appearance and expansion of C₄ plants in the flood plain, a fact known from earlier studies (Quade et al., 1995). Carbon isotope ratio of soil carbonate from Surai Khola section showed decrease in abundance of C₃ plants and expansion of C₄ plants in the flood plain at around 7 Ma (Quade et al., 1995). Larger spread in carbon isotope ratio for post-7 Ma period may be due to incorporation of organic matter from upper reaches by lateral flow of river water into ground water. In such circumstances, carbon isotope ratio of cement represents not only the vegetation of flood plain but also the vegetation of the catchment area. Organic matter brought from higher reaches would have C₃ type δ^{13} C value. Depending on the mixing between the in-situ CO₂ and CO₂ produced from oxidation of transported organic matter the carbon isotope ratio of the cement would vary. For pre-7 Ma time period, this factor did not play significant role as both in the flood plain and higher reaches the vegetation was of C₃ type.

7.6 Clay mineral assemblage in sandstone

Sediments in the Siwalik foreland basin are weathering products of rocks derived from one of the most tectonically active areas in the world i.e. the Himalaya. Weathered materials are being transported to the foreland basin from the Higher, Lesser and Sub-Himalaya (Kumar et al., 1999; Ghosh et al., 2003) for last 18 Myr. Weathering of these rocks is accompanied by varying degrees of dissolution and in-situ precipitation of authigenic products, of which clay minerals are a major component. Higher Himalayan rocks have large percentage of granitic rocks, which are prone to produce illite and chlorite rich clays, whereas lesser Himalayan hinterland volcanic rocks mainly produce smectite. Kaolinite can also form from lesser Himalayan rocks during chemical weathering in warm temperature, but develops principally in climate that have wet and

dry seasons and have more water percolation than that needed for smectite formation (Suresh et al., 2004).

Less than 2-*micron* grains separated from sandstone show presence of smectite, kaolinite, chlorite and illite clay minerals (Fig.7.4). Semi-quantitative estimation of the



Fig.7.4 X-ray diffraction pattern of less than 2 micron size clay minerals separated from Surai Khola sandstone. Glycolation of oriented slide shows shifting of air-dried $6.2^{\circ} 2\theta$ peak to $5.1^{\circ} 2\theta$ confirming the presence of smectite. 8.8° and $12.4^{\circ} 2\theta$ peaks confirm the presence of illite and chlorite. 24.9° and 25.1° peaks confirm the presence of chlorite and kaolinite. Heating of clay slide up to 550° C shows disappearance of smectite, chlorite and kaolinite peaks

relative abundance of clay minerals was done based on the peak area method (Biscaye, 1965). The peak areas of glycolated samples were first computed under 17Å peak for smectite, 10 Å peak for illite and 7 Å peak for chlorite and kaolinite. These



Fig.7.5 Time variation of smectite and illite abundances from Surai Khola sandstone. The maximum abundance (63%) of illite is found in the lower part of the stratigraphic succession and minimum abundance (12%) is seen in the upper part. In contrast, the maximum abundance (70%) of smectite is found near the top of the section and the minimum abundance (10%) is found at lower part. Increase in the abundance of illite with increase in depth probably represents progressive illitization of smectite.

values were multiplied by the weighting factors 1, 4, 2 and 2 respectively, for smectite, illite, chlorite and kaolinite (Biscaye, 1965). The relative proportions of chlorite and kaolinite were determined from the ratio of peak heights (3.53 Å and 3.58 Å respectively) when this ratio is 1, the amount of chlorite is assumed to be twice that of kaolinite.

Semi-quantitative analysis of clays shows increase in abundance of illite and

decrease in smectite with increase in depth (Fig.7.5). In the lower part of the stratigraphic succession the abundance of illite rose to a maximum of 63%, whereas, minimum abundance (12%) was found in the upper part. On the other hand, the maximum abundance (70%) of smectite was found near the top of the section and the minimum abundance (10%) was found at lower part. The difference in these abundances could be the result of progressive transformation of smectite into illite with increase in depth. During burial diagenesis, smectite transforms into illite due to loss of water molecules from crystal lattice (Keller, 1970). Progressive transformation of smectite to illite depends on time, potassium availability, water/rock ratio, fluid and rock composition, starting composition of mixed layer illite-smectite and pressure. Although clay distribution appears to be a function of depth, it is controlled primarily by temperature (Pollastro, 1989). On the whole, the clay mineral analysis supports the explanation regarding isotope changes caused by burial diagenesis.

7.7 Conclusions

Isotopic imprints on diagenetic calcite cement shows that temperature and meteoric water played major role during diagenesis of Surai Khola sandstone. In the lower part of the succession (12 to 6 Ma) re-precipitation of successive generation of calcite at different temperatures was possibly responsible for variation of oxygen isotope ratio. The dissolution/re-precipitation seems to have been active up to depth of 2 km. With decrease in burial depth, the variation in oxygen isotope ratio decreases due to decrease in temperature. During the post-6 Ma period, along with temperature, meteoric water also played a major role in controlling the oxygen isotope ratio. The oxygen isotope ratio variation in cement of the post-6 Ma period shows that despite the complicating presence of diagenetic change it can still be used to decipher alteration in meteoric water isotopic composition due to monsoon variation.

Mineralogical abundance also shows significant change during diagenesis. The smectite abundance decreases with depth whereas illite abundance increases. With increase in depth, K-feldspar abundance also decreases along with illitization of smectite. Dissolution of K-feldspar might have supplied the potassium during illitization of smectite.

CHAPTER-8

CONCLUSIONS AND FUTURE STUDIES

8.1 Conclusions

A major climatic change occurred in the Indian subcontinent during Miocene time as a consequence of uplift of Himalaya and Tibetan plateau resulting in alteration of air circulation (Ruddiman and Kutzbach, 1989). It is believed that this change in circulation of air established the monsoon system in Asia. However, the monsoon intensified only after Himalaya attained a critical height. There was another important consequence. Uplift of Himalaya caused increase in chemical weathering, which, in turn, reduced CO₂ concentration in the atmosphere since weathering takes place through CO₂ consumption. Change in climate along with CO₂ concentration in atmosphere also resulted in vegetational change in the Himalayan foothills.

In the present study, we attempted to understand the details of monsoonal rainfall variation, contemporary CO₂ concentration in the atmosphere and associated vegetational change based on analysis of sediments from Himalayan foothills, which are collectively known as Siwalik Group. Siwalik sedimentary sequence comprises of weathered materials from Himalayan rocks carried by various rivers and deposited in foreland basins more or less continuously for the last 20 Myr. In India, the Siwalik sediments are exposed in a WNW and ESE direction, which is almost parallel to the summer monsoonal track. The effect of rainfall variation was imprinted on Siwalik sediments in various modes. Two important proxies, viz. oxygen isotope ratio of soil carbonate and hydrogen isotope ratio of pedogenic clay minerals (both bearing the signature of rainfall) were used to detect if there was any variation in the monsoonal rainfall.

Our results on rainfall variation for the last 11 Myr show that the evolution of monsoon in Indian sub-continent was not smooth. The rainfall was intense at around 10, 6 and 3 Ma. During these periods, the rainfall was at least 3 times higher than the present day amount. Other proxies from Siwalik basin investigated before support these inferences. Net sediment accumulation rate in Siwalik basin at around 10 Ma and 6 Ma increased by factor of 2 to 3. This can be interpreted as increased transportation of weathered material from tectonically active Himalaya by large river systems supported by intense rainfall. Soil characteristics also changed with rainfall variation. Formation of purple and brown color palaeosols with calcareous nodules at around 10 Ma suggests

a warm humid climate. The monsoonal rainfall variation record from Siwalik is consistent with record from ocean sediments but the timing does not match exactly with the ocean record probably due to limitation of age determination by palaeomagnetic method.

Weathering in Himalaya caused lowering of CO₂ in atmosphere. Estimation of atmospheric CO₂ from Siwalik palaeosols showed that the CO₂ concentration was about 455 ppmV from 10 to 6 Ma. Before the Himalayan orogeny, the CO₂ concentration fluctuated widely in geological past. For a comparative analysis, CO₂ concentration was also determined from geologically older palaeosols of Gondwana period. CO₂ concentration estimation from Gondwana palaeosols showed that lower Triassic CO₂ concentration was about 255 ppmV and increased up to 1520 ppmV during upper Triassic through an intermediate concentration of 1100 ppmV. During the Jurassic time, the concentration was between 2110 and 2275 ppmV.

Lowering of CO₂ concentration in Mid Siwalik era along with change in rainfall pattern had important impact on vegetation. Pre-Miocene era was dominated by C₃ type of plants. It is seen from Siwalik data that C₄ plants appeared in Late Miocene time. The timing of C₄ plant appearance ranges from 9 to 6 Ma in Indian Siwalik. The nature of vegetational transition from pure C₃ type plants to mixed C₃-C₄ type varies from section to section. In Kangra valley-Haripur Khol section abrupt expansion of C₄ plant was observed at around 6 Ma. In Mohand Rao section, appearance of C₄ plants was observed at around 9 Ma and the transition from pure C₃ to mixed C₃-C₄ was gradual. To reach the maximum abundance of C₄ plants it took around 2 Myr in Mohand Rao section. In all these studies, the age values were determined by palaeomagnetic method with its inherent limitations as discussed before.

In Kangra valley-Haripur Khol section, appearance of C_4 plants at 6 Ma nearly coincides with period of monsoon intensification. This may indicate that appearance of C_4 plants is probably related to joint effects of increase in monsoonal strength (monsoon induced seasonality) and lowering of CO_2 in atmosphere. This follows from the observation that C_4 plants are favored in strongly seasonal climate and it has some physiological advantages over C_3 plants in low CO_2 concentration. Before the appearance of C_4 plants, the CO_2 concentration (estimated from Siwalik palaeosols) was about 455 ppmV. This may imply that, for appearance of C_4 plants, the CO_2 concentration should probably be less than 455 ppmV.

Vegetational reconstruction from Pakistan Siwalik by earlier workers (Quade et al., 1989) showed appearance of C₄ plants at around 7.7 Ma; the abundance of C₄ plants reached a maximum by 6.5 Ma. The appearance of C₄ plants was preceded by a change in rainfall pattern. In Nepal Siwalik, the appearance of C₄ plants was about 0.7 Myr later compared to Pakistan Siwalik while change in rainfall pattern was observed at around 6 Ma. In Kangra Valley-Haripur Khol section of Indian Siwalik vegetation was dominated by C_3 plants up to 6 Ma. Abrupt change in vegetation from pure C_3 to mixed C_3 - C_4 vegetation occurred after 6 Ma. In Kangra Valley-Haripur Khol section intensification of rainfall (monsoon) was observed at around 10.5 Ma and 5.5 Ma. Appearance and expansion of C₄ plants coincided with the second phase of monsoon intensification. In Mohand Rao section, appearance of C₄ plants was observed at around 9 Ma and it took nearly 2 Myr to reach the maximum abundance of C_4 plants. Present day rainfall data (where available) show variations in rainfall amount during southwest monsoon in these sections. The difference in the amount of rainfall in these sections suggest that climatic conditions were probably different in them and this might have played an important role in controlling the timing and nature of change in vegetation.

In a mixed C_3-C_4 environment, one can estimate the relative abundance of C_4 plants based on $\delta^{13}C$ of soil carbonate as well as $\delta^{13}C$ of residual organic matter in soil. Our study shows that these two estimates may differ. Assuming that soil carbonate is derived exclusively from plant-respiration, this difference may be due to different respiration rates of these two types of plants (C_3 and C_4) during the growing season. The abundance estimate based on $\delta^{13}C$ of soil carbonate would, therefore, change if the growing season differs from time to time in response to climate fluctuations. Consequently, the difference in $\delta^{13}C$ of soil carbonate and organic matter provide a unique way to decipher climatic change.

Study of chemical diagenesis of sandstones showed that meteoric water has played a major role in determining the oxygen isotope ratio of calcite cement in sandstone. Clay mineral assemblages show illitization of smectite with increase in depth due to diagenesis. Abundance of K-feldspar also decreases with depth, which is consistent with the illitization of smectite. The K-feldspar might have acted as a supplier of potassium during illitization process.

8.2 Future Studies

8.2a Reconstruction of relative abundance of C₃ and C₄ grasses

Reconstruction of vegetational change from pure C_3 to mixed C_3 - C_4 plants has been done from the carbon isotope ratios of soil carbonates, tooth enamel, leaf waxes and early diagenetic carbonate cement of sandstone (Quade et al., 1989, 1995; Freeman and Colarusso, 2001; Quade and Roe, 1999; Sanyal et al., 2004a,b). However, carbon isotope ratio of these proxies cannot differentiate C_3 grasses from trees and shrubs. As a result the abundance of C_3 versus C_4 grasses in Siwalik is not known. Understanding of evolution of both the grasses is important as the relative proportions of C_3 and C_4 grasses growing at a site is determined by climatic condition. For example, minimum summer temperature and lower moisture favors C_4 grass (Kelly et al., 1991b).

Reconstruction of grasses can be done from the carbon isotope ratio of organic matter occluded within phytoliths. Phytoliths are microscopic opaline bodies that occur in stems, leaves and roots of plants. During transpiration, along with ground water plants carry silica as monosilicic acid and deposit it in plant cell wall, eventually forming bodies composed of opaline silica. Following the decay or burning of organic tissues, phytoliths are released back into the soil, preserving record of vegetation. Grasses produce large quantities of very distinctive, densely silicified, short-celled phytoliths. Trees and shrubs on the other hand produce significantly fewer, less densely silicified phytoliths in a variety of shapes that are more susceptible to breakage and dissolution (Knoepp et al., 1998).

To quantify the abundance of C_3 and C_4 grasses from phytolith, it is important to characterize the $\delta^{13}C$ value of phytoliths from C_3 and C_4 grasses. It is seen that in the process of phytolith formation and its incorporation into soil, the carbon isotope ratio of phytolith organic matter can be modified in the following ways (Kelly et al., 1991b):

1) Modification of carbon isotope ratio during formation of phytoliths: Phytoliths from modern C_3 and C_4 grasses exhibit different carbon isotope ratio relative to that of whole plant tissue (Fig.8.1). This difference may be due to incorporation of ¹³C-depleted components such as lipid or lignin in phytolith organic matter. The depletion of heavy isotope in phytolith is more in C_4 plants (9‰) than in C_3 plants (5.3‰), indicating higher concentration of lipids and lignin in C_4 plants relative to those in C_3 plants (Kelly et al., 1991b).

2) Modification of carbon isotope ratio during pedogenesis: Carbon isotope ratio of fresh phytoliths is not same as that of soil phytoliths, which are enriched compared to their fresh counterparts. The enrichment could be due to removal of some lipid fraction during pedogenesis (Kelly et al., 1991b). However, calculation showed that to make the observed enrichment, 90% of the organic matter should be removed which is quite unrealistic. Another possibility is preferential preservation of phytoliths that originate in tissues that are lipid poor relative to lipid rich phytoliths extracted from fresh leaves. The carbon isotope ratio of fresh phytoliths from C_3 and C_4 plants are fixed at -26.8% and -15.3% respectively. After doing corrections for the above enrichment factor, phytolith isotope data can be used to determine the abundance of C_3 and C_4 grasses through mass



Fig.8.1 Relation between carbon isotope ratio of fresh phytoliths and plant tissue. The figure shows that carbon isotope ratio of phytoliths is depleted compared to the plant tissue.

balance.

8.2b Sr isotope ratio in soil carbonate

Sr isotope ratio record from ocean sediments show steady increase in ⁸⁷Sr/⁸⁶Sr ratio during late Cenozoic period. The rise in Sr ratio was attributed to draining of weathered material from Himalaya, which contains both radiogenic ⁸⁷Sr/⁸⁶Sr ratios and high Sr (Hodell et al., 1989; Richter et al., 1992). Weathering of sediments, in turn, is controlled by several factors like climate and source rock composition.

Oxygen isotope ratio of soil carbonates from different Siwalik sections shows climatic change in the form of intensification of monsoon at around 10.5, 6 and 3 Ma (Sanyal et al., 2004a). If climate had played a major role in weathering, ⁸⁷Sr/⁸⁶Sr ratio in contemporaneous river water for the above mentioned periods should be elevated as wet summer (monsoonal) conditions enhances weathering. On the other hand, if Sr isotope ratio is controlled by source rock composition then the variation of ⁸⁷Sr/⁸⁶Sr in the weathering product will be independent of timing of climate change. This issue could be checked from Sr isotope ratio of soil carbonate, early diagenetic carbonate cement and clay minerals as these bear the signature of river water.

8.2c Ar-Ar dating of ash bed

Age of Siwalik sediments was determined by palaeomagnetic method. In this dating technique magnetic polarity events were constructed from iron oxides, which preserve in situ records of contemporary depositional/crystallization remanence magnetization caused by earth's magnetic field. The magnetic polarity events obtained from sequentially arranged rock succession were correlated with standard geomagnetic polarity time scale (GPTS) and conversion to absolute age was done through tie points. The tie points that have been used for dating Indian Siwalik sequences are age of fossils, matching of the reversal patterns with GPTS. However, best correlation with the GPTS can only be made with tie points of known "absolute age". Presence of ash bed in stratigraphic succession can serve this purpose. Ash bed contains mica, which are considered to be cogenetic with ash falls and should, therefore, date the eruptive events and contemporaneous sedimentation.

Three ash bed samples have been discovered from Indian Siwalik by earlier workers (Sangode et al., 1995; Tandan and Kumar, 1984); one from Haripur Khol

section of Himachal Pradesh and two from Ghaggar section of Punjab. Stratigraphic positions of these ash beds show approximate age between 2 to 3 Ma (Tandon and Kumar, 1984; Sangode et al., 1996). Fission track dating of Zircon separated from Ghaggar section ash bed showed that the age of corresponding bed is around 2.5 Ma (Mehta et al., 1993). However, the age obtained in this method was associated with large error (± 0.5 Ma,). Ar-Ar dating of mica associated with this ash bed will provide a strong control to constrain the depositional age of the Siwalik sediments.

REFERENCES

References

- Anderson, T.F., 1969. Self-diffusion of carbon and oxygen in calcite by isotope exchange with carbon dioxide. J. Geophysical Research, 74: 3918-3932.
- Andrews, J.N., Balderer, W., Bath, A.H., Calusen, H.B., Evans, G.V., Florkowski, T., Goldbrunner, J.E., Ivanovich, M., Lossli, H. and Zojer, H., 1984.
 Environmental isotope studies in two aquifer systems, in Isotope Hydrology 1983 (Proceedings of the International Symposium): Vienna, International Atomic Energy Agency, pp. 535-576.
- Amundson, R.G., Chadwick, O.A., Sowers, J.M.and Doner, H.E., 1989. The stable isotope chemistry of pedogenic carbonates at Kyle Canyon, Nevada. Soil Science, 53:201-210.
- Apple, E., Rosler, W. and Corvinus, G., 1991. Magnetostratigraphy of the Miocene-Pleistocene Surai Khola, Siwaliks in West Nepal. Journal of Geophysical International, 105: 191-198.
- Bath, A.H., Edmunds, W.M. and Andrews, J.N., 1979. Paleoclimatic trends deduced from the hydrochemistry of a Triassic sandstone aquifer, United Kingdom, in Isotope Hydrology 1978 (Proceedings of the Symposium, Neuherberg, 1978), 1: Vienna, International Atomic Energy Agency, pp. 545-568.
- Berner, R. A., Lasaga, A. C. and Garrels, R. M., 1983. The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. American Journal of Science, 283: 641-683.
- Berner, R.A., 1991. A model for atmospheric CO₂ over Phanerozoic time. American Journal of Science, 291:339-376.
- Berner, R.A. and Kothavala, Z., 2001. GEOCARB III: A revised model of atmospheric CO₂ over Phanerozoic time. American Journal of Science, 301: 182-204.
- Biscaye, P.E., 1965. Mineralogy and sedimentation of recent deep sea clay in the Atlantic Ocean and adjacent seas and oceans. Geological Society of American Bulletin, 76: 803-832.
- Bird, M.I. and Chivas, A.R., 1988. Stable isotope evidence for low temperature kaolinitic weathering and post-formational hydrogen-isotope exchange in Permian kaolinites. Chemical Geology, 72:249-265.
- Burbank, D.W., Derry, L.A. and Lanord, C.F., 1993. Reduced Himalayan sediment production 8 Myr ago despite an intensified monsoon. Nature, 364:48-50.

- Burbank, D.W., Beck, A.R. and Mulder, T., 1996. The Himalayan foreland basin. In: An Yin and Mark Harrison (Eds.), The tectonic evolution of Asia. Cambridge University Press, USA. pp. 149-188.
- Cande, S.C. and Kent, D.V., 1995. Revised calibration of the geomagnetic polarity timescale for the late Cretaceous and Cenozoic. Journal of Geophysical Research, 100: 6093-6095.
- Capuano, R.M., 1992. The temperature dependence of hydrogen isotope fractionation between clay minerals and water: evidence from a geopressured system. Geochimica et Cosmochimica Acta, 56:2547-2554.
- Casshyap, S.M., Tewari, R.C. and Khan, A., 1993. Alluvial fan origin of the Bagra Formation (Mesozoic Gondwana) and tectono-stratigraphic implications. Journal Geological Society of India, 42:269-279.
- Cerling, T.E., 1984. The stable isotopic composition of modern soil carbonate and its relationship to climate. Earth and Planetary Science Letters, 71: 229-240.
- Cerling , T.E., 1991. Carbon dioxide in the atmosphere: Evidence from Cenozoic and Mesozoic paleosols. American Journal of Science, 291:377-400.
- Cerling, T.E., Quade, J., Wang, Y. and Bowman, J.R., 1989. Carbon isotopes in soils and paleosols as ecology and paleoecology indicators. Nature, 341: 138-139.
- Cerling, T.E., Harris, M. J., MacFadden J.B., Leakey, G. M., Quade, J., Eisenmann, V. and Ehleringer, R. J., 1997, Global vegetational change through the Miocene/Pliocene boundary. Nature, 389: 153-158.
- Chatterjee, S. and Roychowdhury, T., 1974. Triassic Gondwana vertebrates from India. Indian Jour. Earth Sciences, 1: 96-112.
- Clark, J.F., Stute, M., Schlosser, P., Drenkard, S. and Bonani, G., 1997. A tracer study of the Floridian aquifer in southeastern Georgia: implications for groundwater flow and paleoclimate. Water Resources Research, 33:281-289.
- Coleman, M. and Hodges, K.,1995. Evidence for the Tibetan plateau uplift before 14 Myr ago from a new minimum age for east-west extension. Nature, 374:49-52.
- Coplen, T.B., Kendall, C. and Hopple, J., 1983. Comparison of stable isotope reference samples. Nature, 302: 236-238.
- Corvinus, G., 1990. Litho and biostratigraphy of the Siwalik succession in Surai Khola area, Nepal. In Jain, K.P. and Tiwari, R.S. (eds.), Proc. Symp. 'Vistas in Indian Palaeobotany', Palaeobotanist, 38: 293-297.

- Criss, R.E., 1999. Principles of stable isotopic distribution. Oxford University Press, New York.
- Dalai, T.K., Bhattacharya, S.K. and Krishnaswami, S., 2002. Stable isotopes in the source waters of the Yamuna and its tributaries: Seasonal and altitudinal variations and relation to major cations. Hydrological Processes, 16: 3345-3364.
- Davidson, G.R., 1995. The stable isotopic composition and measurement of carbon in soil CO₂. Geochimica et Cosmochimica Acta, 59:2485-2489.
- Deak, J., 1979. Environmental isotopes and water chemical studies for groundwater research in Hungary. In Isotope Hydrology 1978 (Proceedings of the Symposium, Neuherberg, 1978), 1: Vienna, International Atomic Energy Agency, pp. 221-249.
- Decelles, P.G., Gehrels, G.E., Quade, J., Ojha, T.P., Kapp, P.A. and Upreti, B.N., 1998. Neogene foreland basin deposits, erosional unroofing and kinematic history of the Himalayan fold-thrust belt, western Nepal. Geological Society of American Bulletin, 110: 2-21.
- Dörr, H. and Munnich , K.O., 1987. Annual variation in soil respiration in selected areas of the temperate zone. Tellus, 39B: 114-121.
- Dubey, A.K., 1997. Simultaneous development of noncylindrical folds, frontal ramps and transfer faults in a compressional regime-experimental investigations of Himalayan examples. Tectonics, 16: 336-346.
- Edwards, M. A., Kidd, W.S.F., Li, J., Yue, Y. and Clark, M., 1996. Multi stage development of the southern Tibet detachment system near Khula Kangri. New data from Gonto La. Tectonophysics, 260: 1-20.
- Ekart, D.D., Cerling, T.E., Montanez, I.P. and Tabor, N.J., 1999. A 400 million year carbon isotope record of pedogenic carbonate: implications for paleoatmospheric carbon dioxide. American Journal of Science, 299: 805-827.
- Freeman, K.H. and Colarusso, L.A., 2001. Molecular and isotopic records of C₄ grassland expansion in the late Miocene. Geochimica et Cosmochimica Acta, 65:1439-1454.
- Friedman, I. and O'Neil, J.R., 1977. Compilation of stable isotopic fractionation factors of geochemical interest. In: M. Fleischer (Editor), Data of Geochemistry. U.S. Geol. Surv. Prof. Pap., 440-K, pp-12.

- Fritz, P., Reardon, E.J., Barker, J., Brown, R.M., Cherry, J. A., Killey, R. W. D. and Mc-Naughton, D., 1978. The carbon isotope geochemistry of a small groundwater system in northern Ontario. Water Resources Research, 14: 1059-1067.
- Gautam, P., and Rösler, W., 1999. Depositional chronology and fabric of Siwalik group sediments in Central Nepal from magnetostratigraphy and magnetic anisotropy. Journal of Asian Earth Science, 17: 659-682.
- Gaudry, A., Polian, G., Ardouin, B. and Lambert, G., 1990. Radon-calibrated emission of CO₂ from South Africa. Tellus, 42B: 9-19.
- Gerhard, E., 2000. Sedimentary Basins- Evolution, Facies and Sediment budget. Springer-Verlag, New York.
- Ghosh, S.K. and Kumar, R., 2000. Petrography of Neogene Siwalik sandstone of the Himalayan foreland basin, Garhwal Himalaya: Implications for source area tectonics and climate. Journal Geological Society of India, 55: 1-15.
- Ghosh, S.K., Kumar, R. and Suresh, N., 2003. Influence of Mio-Pliocene drainage re-organization in the detrital modes of sandstone, Subathu sub-basin, Himalayan foreland basin. Journal of Himalayan Geology, 24: 35-46.
- Ghosh, P., Bhattacharya, S.K. and Jani, R.A., 1995. Palaeoclimate and palaeovegetation in central India during the Upper Cretaceous based on stable isotope composition of the palaeosol carbonates. Palaeogeography, Palaeoclimatology, Palaeoecology, 114: 285-296.
- Ghosh, P., Ghosh, P. and Bhattacharya, S.K., 2001. CO₂ levels in the Late Palaeozoic and Mesozoic atmosphere from soil carbonate and organic matter, Satpura basin, Central India. Palaeogeography, Palaeoclimatology, Palaeoecology, 170:219-236.
- Ghosh, P., Padia, J.T. and Mohindra, R., 2004. Stable isotopic studies of palaeosol sediment from Upper Siwalik of Himachal Himalaya: evidence for high monsoonal intensity during late Miocene? Palaeogeography, Palaeoclimatology, Palaeoecology, 206:103-114.
- Gilg, H.A. and Sheppard, S.M.F., 1996. Hydrogen isotope fractionation between kaolinite and water revisited. Geochimica et Cosmochimica Acta, 60:529-533.

- Graham, C.M., Atkinson, J. and Harmon, R.S., 1984. Hydrogen isotope fractionation in the system chlorite-water. NERC 6th Progress Report of Research 1981-1984, NERC Publication Series D, No. 25: p139.
- Grocke, D.R., Hesselbo, S.P. and Jenkyns, H.C., 1999. Carbon isotope composition of lower Cretaceous fossil wood: Ocean atmosphere chemistry and relation to sea-level changes. Geology, 27: 155-158.
- Harland, W.B., Cox, A.V., Llewellyn, P.G., Pickton, C.A.G. and Smith, A.G., 1982.A geological Time Scale, Cambridge University Press, Cambridge, UK.
- Harris, N.B., 1992. Burial diagenesis of Brent sandstone: a study of statford, hutton and Lyell fields. In: Morton, A.C., Haszeldine, R.S., Giles, M.R. and Brown, S. (eds) Geology of the Brent Group. Geological Society, London. Special Publications, 61: 351-376.
- Harrison, T.M., Copeland, P., Kidd, W.S.F. and Yin, A., 1992. Raising Tibet. Science, 255:1663-1670.
- Harrison, T.M., Yin, A. and Ryerson, J.F., 1998. Orographic evolution of the Himalaya and Tibetan Plateau. In: Crowley J.T., Burke C.K., Tectonic boundary condition for climate resolution. Oxford monograph on Geology and Geophysics. No.39: 39-72.
- Hisamoti, K., 1990. The sandstone petrography of the Churia (Siwalik) Group in the Arung Khola-Binai Khola Area, West Central Nepal. Bull. Fac. Edu. Wakayama Univ., Nat. Sci., 39: 5-29.
- Hodell, D.A., Mueller, P.A, McKenzie, J.A and Mead, G.A., 1989.Strontium isotope stratigraphy and geochemistry of the late Neogene ocean. Earth and Planetary Science Letters, 92:165-178.
- Humphrey, J.D. and Ferring, C.R., 1994. Stable isotopic evidence for latest Pleistocene and Holocene climatic change in north-central Texas. Quaterney Research, 41: 200-213.
- Hyeong, K. and Capuano, R.M., 2000. The effect of organic matter and the H_2O_2 organic matter removal method on the δD of smectite-rich samples. Geochimica et Cosmochimica Acta, 64, no 22: 3829-3837.
- IAEA, 2003. http://isohis.iaea.org
- Indian Meteorological Department, 1970. Printed by Manager, Govt. of India Press (P.L. Wing), Nasik. pp.195-196.

- Irwin, H., Curtis, C. and Coleman, M., 1977. Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments. Nature, 269: 209-213.
- Jackson, M.L., 1969. Soil chemical analysis-advance course: 2nd edition, published by the author, Madison, Wis., pp 895.
- Jaeger, J.J., Courtillot, V. and Tapponier, P., 1989. Paleontological view of the ages of Deccan Traps, the Cretaceous/Tertiary boundary, and the India-Asia collision. Geology, 17:463-469.
- Johnson, M.N., Stix, J., Tauxe, L., Cerveny, P.F. and Tahirkheli, R. A. K., 1985. Paleomagnetic chronology, fluvial process and tectonic implications of the Siwalik deposits near Chinji Village, Pakistan. J. Geol., 93:27-40.
- Karunakaran, C. and Rao, R.A., 1979. Status of exploration for hydrocarbons in the Himalayan region - contributions to stratigraphy and structure. In Himalayan Geology Seminar-1976, Geological Survey of India, Miscellaneous publications 41:1-66.
- Kelly, E.F., Amundson, R.G., Marino, B.D. and DeNiro, M.J., 1991a. Stable carbon isotopic composition of carbonate in Holocene grassland soils. Soil Science. Society of American Journal. 55: 1651-1658.
- Kelly, E.F., Amundson, R.G., Marino, B.D. and Deniro, M.J., 1991b. Stable isotope ratios of carbon in Phytoliths as a quatatitative method of monitoring vegetation and climate change. Quateranry Research, 35:222-233.
- Keller, W.D., 1970. Environmental aspects of clay minerals. Journal Sedimentary Petrology, 40: 785-813.
- Knoepp, J.D., Tieszen, L.L. and Fredlund, G.G., 1998. Assessing the vegetation history of three southern Appalachian Balds through soil organic matter analysis. Research Paper, SRS-13. U.S department of Agriculture, Forest service, Southern Research Station. 1-12.
- Kotzer, T.G. and Kyser, T.K., 1991.Retrograde alteration of clay minerals in uranium deposits: radiation catalyzed or simply low-temperature exchange? Chemical Geology, 86: 307-321.
- Krishnamuthy, S.V. and Bhattacharya, S.K., 1991. Stable oxygen and hydrogen isotope ratio in shallow ground waters from India and a study of the role of evapotranspiration in the Indian Monsoon. Isotope Geochemistry: A tribute to

Samuel Epstein; Special publication No.3 of The Geochemical Society (ed.H.P.Taylor, J.R.O'Neil and I.R. Kaplan) pp.1-7.

- Kumar, R.,1993. Coalescence megafan: multistorey sandstone complex of the lateorogenic (Mio-Pliocene) sub-Himalayan belt, Dehra Dun, India. Sedimentary Geology, 85: 327-337.
- Kumar, R. and Nanda, A.C., 1989. Sedimentology of the Middle Siwalik Subgroup of Mohand Area, Dehra Dun Valley, India. Journal Geological Society of India, 34: 597-616.
- Kumar, R., Ghosh, S.K. and Sangode, S.J., 1999. Evolution of a Neogene fluvial system in a Himalayan foreland basin, India. Himalaya and Tibet: Mountain Roots to Mountain Tops: Boulder, Colorado, Geological Society of America Special Paper. Edited by Macfarlane A., Sorkhabi, R. B., Quade J. pp 239-256.
- Kumar, R., Ghosh, S.K. and Sangode, S. J., 2003a. Mio-Pliocene sedimentation history in the northwestern part of the Himalayan foreland basin, India. Current Science, 84, no 8: 1006-1013.
- Kumar, R., Ghosh, S. K., Mazari, R. K. and Sangode, S. J., 2003b. Tectonic impact on fluvial deposits of Plio-Pleistocene Himalayan foreland basin, India. Sedimentary Geology, 158: 209-234.
- Kumar, R., Sangode, S.J. and Ghosh, S.K., 2004. A Multistory sandstone complex of the Himalayan foreland basin, NW Himalaya, India. Jour. Asian Earth Sci., In Press.
- Kroon, D., Steens, T. and Troelstra, S.R., 1991. Onset of monsoonal related upwelling in the western Arabian Sea as revealed by planktonic foraminifers.In: Prell, W.L., Niitsuma, N et al., (Eds.) Proceedings of the Ocean Drilling Program, Scientific Results, 117: 257-263.
- Land, L.S., 1980. The isotopic and trace element geochemistry of dolomite: the state of art, in Zenger, D.H., Dunham, J.B. and Ethington, R.A., eds., Concepts and Models of dolomitization: Soc. Econ. Paleontologists, Special Paper 28: 87-110.
- Lanord, C.F., Derry, L. and Michard, A., 1994. Evolution of the Himalaya since Miocene time: isotopic and sedimentological evidence from Bengal Fan.

From Treloar, P.J and Searle, M.P. (eds.), Himalayan Tectonics. Geological Society Special Publication, London. No.74: 603-621.

- Leaney, F.W. and Herczeg, A.L., 1995. Regional recharge of a karst aquifer estimated from chemical and isotopic composition of diffuse and localized recharge, South Australia. Journal of Hydrology, 164: 363-387.
- Longstaffe, F.J. and Ayalon, A., 1990. Hydrogen-isotope geochemistry of diagenetic clay minerals from Cretaceous sandstones, Alberta, Canada: evidence of exchange. Applied Geochemistry, 5: 657-668.
- Lydekker, R., 1877. Vertebrata from Indian Tertiary and Secondary rocks. Rec. Geol. Surv. India., 10, no.1: 34.
- Maulik, P.K., Chakraborty, C., Ghosh, P. and Rudra, D., 2000. Meso and Macro-Scale Architecture of a Triassic Fluvial Succession: Denwa Formation, Satpura Gondwana Basin, Madhya Pradesh. Journal Geological Society of India, 56: 489-504.
- Marumo, K., Nagasawa, K. and Kuroda, Y., 1980. Mineralogy and hydrogen isotope of clay minerals in the Ohnuma geothermal area, Northeastern Japan. Earth and Planetary Science Letters, 47:255-262.
- Mehra, O.P. and Jackson, M.L., 1960. Fe oxide removal from soils and clays by dithionite-citrate system buffered with sodium bicarbonate. In Proceeding of the 7th National conference on Clays and Clay minerals (ed. A.Swineford. Pergamon Press) pp. 317-327.
- Mehta, Y.P., Thakur, A.K., Lal, N., Shukla, B. and Tandon S.K., 1993. Fission track age of zircon separates of tuffaceous mudstones of the Upper Siwalik subgroup of Jammu-Chandigarh sector of the Panjab Sub-Himalaya. Current Science, 64, no.7: 519-521.
- Metivier, F., Gaudemer, Y., Tapponnier, P. and Klein, M., 1999. Mass accumulation rates in Asia during the Cenozoic. Geophysical Journal International, 137: 280-318.
- Milliken, K.L., 1989. Petrography and composition of authigenic feldspars, Oligocene Frio formation, South Texas. Journal of Sedimentary Petrology, 59: 361-374.
- Mora, C.I., Driese, S.G. and Fastovsky, D.E., 1993. Geochemistry and stable isotopes of paleosols. A geological society of America continuing education short course. Knoxville Publication, University of Tennessee.

- Mora, C.I., Driese, S.G. and Colarusso, L.A., 1996. Middle to Late Paleozoic atmospheric CO₂ levels from soil carbonate and organic matter. Science, 271:1105-1107.
- Morgan, M.E., Kingston, J.D. and Marino, B.D., 1994. Carbon isotopic evidence for the emergence of C₄ plants in the Neogene from Pakistan and Kenya. Nature, 367: 162-165.
- Mugnier, J.L., Charlaron, E., Mascle, G., Pradier, B. and Herail, G., 1995. Structural and thermal evolution of the Siwaliks of western Nepal. Bulletin of the Geological Society, Nepal, 11: 171-179.
- Nakayama, K. and Ulak, P.D., 1999. Evolution of fluvial style in the Siwalik Group in the foothills of the Nepal Himalaya. Sedimentary Geology, 125: 205-224.
- Nigrini C., 1991. Composition and biostratigraphy of radiolarian assemblages from an area of upwelling (Northwestern Arabian Sea, Leg 117). Proceeding of the Ocean Drilling Program, Scientific Results, 117: 89-101.
- Pagani, M., Freeman, K.H. and Arthur, M.A., 1999.Late Miocene atmospheric CO₂ concentrations and the expansion of C₄ grasses. Science, 285: 876-879.
- Pearson, F.J., Jr. and Hanshaw, B.B., 1970. Source of dissolve carbonate species in groundwater and their effects on ¹⁴C dating, in Isotope Hydrology 1970: Vienna, International Atomic Energy Agency, pp. 271-286.
- Pendall, E. and Amundson, R., 1990. The stable isotope chemistry of pedogenic carbonate in an alluvial soil from the Punjab. Soil Science, 149: 199-211.
- Phadtare, N.R., Kumar, R. and Ghosh, S.K., 1994. Stratigraphic palynology, floristic succession and the Tatrot/Pinjor boundary in upper Siwalik sediments of Haripur Khol area, district Sirmaur(H.P), India. Himalayan Geology, 15:69-82.
- Pilgrim, G.E., 1913. The correlation of the Siwaliks with mammal horizones of Europe. Rec.Geo.surv.India, 43:264-236.
- Pollastro, R.M., 1989. Clay minerals as geothermometers and indicators of thermal maturity-application to basin history and hydrocarbon generation. Am Assoc Petrol Geol Bull., 73: 1171.
- Powers, P.M., Lillie, R.J. and Yeats, R.S., 1998. Structure and shortening of the Kangra and Dehradun re-entrants, sub-Himalaya, India. Geological Society of America Bulletin, 110, no.8: 1010-1027.

- Prell, L.W., Murray, W.D., Clemens, C.S. and Anderson, D.M., 1992. Evolution and variability of the Indian Ocean Summer Monsoon: Evidence from the Western Arabian Sea drilling program. Synthesis of results from scientific drilling in Indian Ocean. Geophysical Monograph, 70:447-469.
- Prell, L.W. and Kutzbach, J.E., 1992. Sensitivity of the Indian Monsoon to forcing parameters and implications for its evolution. Nature, 360: 647-652.
- Quade, J., Cerling, T.E. and Bowman, J.R., 1989. Development of Asian monsoon revealed by marked ecological shift during the latest Miocene in the northern Pakistan. Nature, 342:163-166.
- Quade, J., Cater, M.L.J., Ojha, P.T., Adam, J. and Harrison, M.T., 1995. Late Miocene environmental change in Nepal and the northern Indian subcontinent: Stable isotopic evidence from paleosols. Geological Society of America Bulletin, 107, no. 12:1381-1397.
- Quade, J. and Cerling, T. E., 1995. Expansion of C₄ grasses in the Late Miocene of Northern Pakistan: evidence from stable isotopes in paleosols. Palaeogeography, Palaeoclimatology, Palaeoecology, 115: 91-116.
- Quade, J. and Roe, J.L., 1999. The stable isotope composition of early ground water cements from sandstone in paleoecological reconstruction. Journal of Sedimentary Research, 69, no.3: 667-674.
- Rabenhorst, M.C., Wilding, L.P. and West, L.T., 1984, Identification of pedogenic carbonates using stable carbon isotope and microfacies analyses. Soil Science, 48:125-132.
- Raiverman, V., Kunte, S.V. and Mukherjee, A., 1983. Basin geometry, Cenozoic sedimentation and hydrocarbon prospects in north-western Himalaya and Indog-Gangetic plains. Pet. Asia J, 6 (IV): 67-92.
- Raiswell, R. and Fisher, Q.J., 2000. Mudrock-hosted carbonate concretions: a review of growth mechanisms and their influence on chemical and isotopic composition. Journal of the Geological Society, London, 157:239-251.
- Rao, Y.P., 1976. South West monsoon. Meteorological Monograph Synoptic. Meteorology No 1/1976. Published by Indian Meteorological Department. Pp.8.
- Rao, Y.P., 1981. The climate of the Indian subcontinent. In climates of southern and western Asia (ed. K.Takahshi and H. Aarakawa): World survey of climatology 9: 67-182.

- Rao, R.A., Agarwal, R.P., Sharma, U.N., Bhalla, M.S. and Nanda, A.C., 1988. Magnetic polarity stratigraphy and vertebrate palaeontology of the Upper Siwalik Subgroup of Jammu Hills, India. Journal of Geological Society of India, 31: 361-385.
- Raymo, M.E. and Ruddiman, W.F., 1992. Tectonic forcing of late Cenozoic climate. Nature, 359: 117-122.
- Retallack, G.J., 2001a. Soils of the Past. Blackwell Science. USA. pp-185.
- Retallack, G.J., 2001b. Cenozoic expansion of grasslands and climate cooling. The Journal of Geology, 109:407-426.
- Retallack, G.J., 2001c. A 300-million-year record of atmospheric carbon dioxide from fossil plant cuticles. Nature, 411:287-290.
- Retallack, G.J., 2002. Carbon dioxide and climate over 300 Myr. Philosophical Transactions: Mathematical, Physical and Engineering Sciences, 360:659-673.
- Richter, F.M., Rowley, D.B. and DePaolo, D.J., 1992. Sr isotope evolution of seawater: the role of tectonics. Earth and Planetary Science Letters, 109: 11-23.
- Romanek, C.S., Grossman, E.L. and Morse, J.W., 1992. Carbon isotopic fractionation in synthetic aragonite and calcite: Effects of temperature and precipitation rate. Geochimica et Cosmochimica Acta, 56: 419-430.
- Ruddiman, W.F. and Prell, W.L., 1997. Introduction to the uplift-climate connection. In: W.F. Ruddiman (Editor), Tectonic Uplift and Climate Change. Plenum, New York, pp. 3-19.
- Ruddiman, W.F. and Kutzbach, J.E. 1989. Forcing of late Cenozoic northern hemisphere climate by plateau uplift in Southern Asia and the American West. Journal of Geophysical Research 94(D15): 18, 409-18,427.
- Salomons, W., Goudie, A. and Mook, W.G., 1978. Isotopic composition of calcrete deposit from Europe, Africa and India. Earth Surface Process, 3: 43-57.
- Sangode, S.J., Kumar, R. and Ghosh, S.K., 1996. Magnetic polarity stratigraphy of the Siwalik sequence Haripur area (H.P.), NW Himalaya. Journal of Geological Society of India, 47: 683-704.
- Sangode, S.J., Kumar, R. and Ghosh, S.K., 1999. Palaeomagnetic and rock magnetic perspectives on the post-collisional continental sediments of the Himalaya,

India. In: Radhakrishna, T., Piper J.D.A. (Eds.), The Indian Subcontinent and Gondwana: A Palaeomagnetic and Rock Magnetic Perspective. Geol. Soc. India Mem., 44:221-248.

- Sangode, S.J., Bloemendal, J., Kumar, R. and Ghosh, S.K., 2001. Plio-Pleistocene pedogenic change in the Siwalik Palaeosols: A rock magnetic approach. Current Science, 81,no.4: 387-392.
- Sangode, S.J., Kumar, R. and Ghosh, S.K., 2003. Magnetic Polarity Stratigraphy of the Late Miocene Siwalik Group sediments from Kangra Re-entrant, H.P., India. Himalayan Geology, 24, no 1: 47-61.
- Sanyal, P., Bhattacharya, S.K., Kumar, R., Ghosh, S.K. and Sangode, S.J., 2004a. Mio -Pliocene monsoonal record from Himalayan Foreland basin (Indian Siwalik) and its relation to the vegetational change. Palaeogeography, Palaeoclimatology, Palaeoecology, 205:23-41.
- Sanyal, P., Bhattacharya, S.K., Kumar, R., Ghosh, S.K. and Sangode, S.J., 2004b. Palaeovegetational reconstruction in Late Miocene: a case study based on early diagenetic carbonate cement from Indian Siwalik. Under revision in Palaeogeography, Palaeoclimatology, Palaeoecology.
- Savin, S.M. and Epstein, S., 1970. The oxygen and hydrogen isotope geochemistry of clay minerals. Geochimica et Cosmochimica Acta, 34:25-42.
- Savin, S.M. and Hsieh, J.C.C., 1998. The hydrogen and oxygen isotope geochemistry of pedogenic clay minerals: principles and theoretical background. Geoderma, 82: 227-253.
- Scotese, C.R., 1998. Gondwana's climate changes. J. Afr. Earth Science, 27:172-173.
- Sheppard, S.M.F. and Gilg, H.A., 1996. Stable isotope geochemistry of clay minerals. Clay Minerals, 31:1-24.
- Spicer, A.R., Harris, B.W.N., Widdowson, M., Herman, B.A., Guo, S., Valdes, J.P., Wolfe, A.J. and Kelley, P.S., 2003. Constant elevation of Southern Tibet over the past 15 million years. Nature, 421:622-624.
- Spivac, A. J., You, C.F., Smith, J.H., 1993. Foraminiferal boron isotope ratios as a proxy for surface ocean pH over the past 21 Ma. Nature, 363: 149-151.
- Stern, A.L., Chamberlain, R.C., Reylonds, C.R. and Johnson, D.J., 1997. Oxygen isotope evidence of climate change from pedogenic clay minerals in the Himalayan molasse. Geochimica et Cosmochimica Acta, 61 no.4: 731-744.

- Suresh, N., Ghosh, S.K., Kumar, R. and Sangode, S.J., 2004. Clay-mineral distribution patterns in late Neogene fluvial sediments of the Subathu subbasin, central sector of Himalayan foreland basin: implications for provenance and climate. Sedimentary Geology, 163: 265-278.
- Tandon, S.K. and Kumar, R., 1984. Discovery of tuffaceous mudstones in the Pinjor Formation of Panjab sub-Himalaya, India. Current Science, 53:982-984.
- Tandon, S.K. and Varshney, S.K., 1991. Origin of selective carbonate cemented (concretionary) layers within multistoried sandstone bodies of the Neogene Middle Siwalik Subgroup, NW Himalaya, India. Abstract, Birbal Sahni Birth Centenary Symposium on the Siwalik Basin, WIHG, Dehra Dun, India, p.45.
- Tandon, S.K., Sood, A., Andrews, J.E. and Dennis, P.F., 1995. Palaeoenvironments of the dinosaur-bearing Lameta Beds (Maastrichtian), Narmada Valley, Central India. Palaeogeography, Palaeoclimatology, Palaeoecology, 117:123-154.
- Thomas, J.V., Prakash, B. and Mahindra, R., 2002. Lithofacies and paleosol analysis of the Middle and Upper Siwalik Groups (Plio-Pleistocene), Haripur-Kolar section, Himachal Pradesh, India. Sedimentary Geology, 150:343-366.
- Van Der Burgh, J., Visscher, H., Dilcher, L.D. and Kurschner, M. W., 1993. Paleoatmospheric signatures in Neogene fossil leaves. Science, 260:1788-1790.
- Virdi, N.S., 1979. On the geodynamic significance of mega-lineaments in the Outer and Lesser regions of western Himalaya. Himalayan Geology, 9, no 1:79-99.
- Wang, H. and Follmer, R. L., 1998. Proxy of monsoon seasonality in carbon isotopes from paleosols of the southern Chinese Loess Plateau. Geology, 26, no. 11: 987-990.
- Wassenaar, L.I., Aravena, R., and Fritz, P., 1992. Radiocarbon contents of dissolved organic carbon in shallow groundwater systems. In Isotope Techniques in Water Resources Development 1991 (Proceedings of the international Symposium): Vienna, International Atomic Energy Agency, pp. 143-151.
- White, N.M., Parrish, R.R., Bickle, M.J., Najman, M.R., Burbank, D. and Maithani, A., 2001. Metamorphism and exhumation of the NW Himalaya constrained by U-Th-Pb analyses of detrital monazite grains from early foreland basin sediments. Journal Geological Society London, 158: 625-635.

- Wilkinson, M. and Haszeldine, R.S., 1996. Aluminum loss from arkoses produces diagenetic quartzites and secondary porosity: Fulmar Formation, North Sea. Journal of the Geological Society, London, 154: 747-751.
- Wilson, M.J., 1987. A Handbook of Determinative Methods in Clay Mineralogy. Blackie, Glasgow. pp 308.
- Yeh, H., 1980. D/H ratios and late-stage dehydration of shales during burial. Geochimica et Cosmochimica Acta, 44: 341-352.
- Yeh, H. and Epstein, S., 1978. Hydrogen isotope exchange between clay minerals and sea water. Geochimica et Cosmochimica Acta, 42:140-143.
- Yin, A., Harrison, T.M., Ryerson, F.J., Chen, W., Kidd, W.S.F. and Copeland, P., 1994. Tertiary structural evolution of Gangdese thrust system, South eastern Tibet. J. Geophys. Res., 99: 18,175-18,201.
- Yurtsever, Y. and Gat, J.R., 1981. Atmospheric waters. In stable isotope hydrology: Deuterium and Oxygen-18 in the Water cycle. In: J.R. Gat and R. Gonfiantini (Eds.). Technical Report Series 210, IAEA, Vienna. pp. 103-142.
- Zaleha, M.J., 1997. Intra- and extra-basinal controls on fluvial deposition in the Miocene Indo-Gangetic foreland basin, northern Pakistan. Sedimentology, 44: 369-390.
- Ziegler, K. and Longstaffe, F.J., 2000. Clay mineral authigenesis along a midcontinental scale fluid conduit in Palaeozoic sedimentary rocks from southern Ontario, Canada. Clay Minerals, 35: 239-260.

LIST OF PUBLICATIONS
Research papers in referred journals

1) Isotopic and Sedimentological clues to productivity change in Late Riphean Sea: A case study from two intracratonic basins of India.

P.P.Chakraborty, A.Sarkar, S.K.Bhattacharya, <u>**P.Sanyal**</u> .*Proc. Indian Acad. Sci. (Earth Planet Sci.)* v. 111 No.4 December 2002, pp 379-390.

2) Mio-Pliocene monsoonal record from Indian Himalayan Foreland basin (Siwalik) and its relation to vegetational change. **Prasanta Sanyal,** S.K.Bhattacharya, Rohtash Kumar, Sumit K. Ghosh, S.J. Sangode. *Palaeogeography, Palaeoclimatology, Palaeoecology*. v.205, 2004, pp 23-41.

Manuscript under revision

1) Paleovegetational reconstruction in Late Miocene: a case study based on early diagenetic carbonate cement from Indian Siwalik. <u>Prasanta Sanyal</u>, S.K.Bhattacharya, Rohtash Kumar, Sumit K. Ghosh, S.J. Sangode. Under revision in *Palaeogeography, Palaeoclimatology, Palaeoecology*.

Manuscript under review

 ¹³C enrichment in the Palaeoproterozoic carbonate rocks of northwest India: influence of microenvironment. Ritesh Purohit, <u>Prasanta Sanyal</u>, S.K.Bhattacharya, A.B Roy. Manuscript under review in *Precambrian Research*.

 Chemical diagenesis of Siwalik sandstone: Isotopic and mineralogical proxies from Surai Khola section, Nepal. <u>Prasanta Sanyal</u>, S.K.Bhattacharya, Mahesh Prasad. Manuscript under review in *Sedimentary Geology*.

Manuscript under preparation

1) Carbon and Oxygen isotope ratio of pedogenic carbonate from Siwalik and Gondwana: Implications to the atmospheric CO₂, vegetation and precipitation. <u>Prasanta</u> <u>Sanyal</u>, S.K.Bhattacharya, Rohtash Kumar, Partho Ghosh. Manuscript under preparation for *Geology*.

2) Origin of graphitic carbon in Precambrian migmatites of Eastern Ghats, Orissa, India. **Prasanta Sanyal**, S.K.Acharya, S.K.Bhattacharya. Manuscript under preparation for *Geology*.

3)Palaeovegetation and palaeoprecipitation reconstruction for late Miocene period from Kangra valley, Himachal Pradesh, India. S. Sinha, <u>**Prasanta Sanyal**</u>, S.K.Bhattacharya,

Rohtash Kumar, Sumit K. Ghosh, S.J. Sangode. Manuscript under preparation for *Journal of Asian Earth Sciences*.

 Monsoon reconstruction from hydrogen isotope ratio of pedogenic clay minerals from Indian Siwalik. <u>Prasanta Sanyal</u>, S.K.Bhattacharya, Rohtash Kumar, Sumit K. Ghosh, S.J. Sangode. Manuscript under preparation for *Geology*.

5) Origin and age of graphite from Dharwar Craton. Maibam Bidyananda, <u>Prasanta</u> <u>Sanyal</u>, S.K. Bhattacharya, J.N.Goswami. Manuscript under preparation for *Current Science*.

6) **Precambrian-Cambrian boundary at Cuddapah Basin.** <u>Prasanta Sanyal</u>, S.K. Bhattacharya, A.Moitra, Ashok Kumar. Manuscript under preparation for *Precambrian Research*.

Abstracts in conferences

(1) Carbon and Oxygen isotope of Surai Khola section of Siwalik of Nepal Himalaya. <u>Prasanta Sanyal</u> and S.K.Bhattacharya in 9th ISMAS workshop on Mass Spectrometry, National Institute of Oceanography, Goa, India, December 12-16,2000.

(2) Carbon and oxygen isotope ratios of Siwalik soils from Kangra valley, Himachal Pradesh and their implications. **Prasanta Sanyal**, S.K. Bhattacharya, Rohtash Kumar, Sumit K. Ghosh and Satish J. Sangode in International conference on Quaternary Climate, Tectonics and Environment of the Himalaya: Comparison with other regions. Organized by Department of Geology, Faculty of Science, Kumaun University, Ninital, India, March 11-15, 2002.

(3) C₄ grass expansion record from Siwalik soils, Kangra valley, Himachal Pradesh, India. <u>Prasanta Sanyal</u>, S.K. Bhattacharya, Rohtash Kumar, Sumit K. Ghosh and Satish J. Sangode⁻ In Paleo-Grassland Research 2002: A conference on the reconstruction and modeling of grass-dominated biomes, St. Cloud, Minnesota, June 13-15,2002.

(4) Oxygen isotope composition of carbonate cement in sandstones from Siwalik sediments of western Nepal: implication to the evolution of meteoric water. <u>Prasanta</u> <u>Sanyal</u>, S.K.Bhattacharya, Mahesh Prasad. Presented to 12th Bathurst Meeting of Carbonate Sedimentologists Durham, England from 8th-10th July 2003. (5) Paleovegetational reconstruction in Late Miocene: a case study based on early diagenetic carbonate cement from Indian Siwalik. <u>**Prasanta Sanyal**</u>, S.K.Bhattacharya, Rohtash Kumar, Sumit K. Ghosh, S.J. Sangode. Presented to 12th Bathurst Meeting of Carbonate Sedimentologists, Durham, England from 8th-10th July 2003.

(6) Late Miocene Monsoonal record from oxygen isotope ratio of Siwalik soil carbonate. <u>Prasanta Sanyal</u>, S.K. Bhattacharya, Rohtash Kumar, Sumit K. Ghosh and Satish J. Sangode. Submitted in IAEA isotope Hydrology Symposium, Vienna, 19th -23rd May 2003.

(7) Monsoon reconstruction from hydrogen isotope ratio of pedogenic clay minerals from Indian Siwalik. <u>Prasanta Sanyal</u>, S.K. Bhattacharya, Rohtash Kumar, Sumit K. Ghosh and Satish J. Sangode in 11th ISMAS workshop, held on Shimla during 7th to 12th October, 2004.

(8) Origin of graphitic carbon in Precambrian migmatites of Eastern Ghats, Orissa, India. S.K.Bhattacharya, <u>Prasanta Sanyal</u>, B.C.Acharya in 11th ISMAS workshop, held on Shimla during 7th to 12th October, 2004.