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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 monsoonal winds. Thus the biological, chemical and sedimentological record 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 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 CO_2 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 CO_2 (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 syn-sedimentary 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 CO_2 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 ^{18}O of soil carbonate from Potwar Plateau at around 8 Ma was interpreted as intensification of monsoon in the Indian subcontinent. However, $\delta^{18}O$ 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 $\delta^{18}O$ of the corresponding soil carbonate is governed by geographical configuration of the site during the formation of palaeosol. Thus the interpretation of $\delta^{18}O$ change in soil carbonates is quite complex and it is not clear if $\delta^{18}O$ increase can be explained by an increase in rainfall. Normally, an increase in rainfall is associated with a decrease in $\delta^{18}O$ (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 ^{18}O 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 $\delta^{18}O$ change did not occur concurrently across the Himalayan belt.

The enrichment of ^{18}O 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

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

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

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

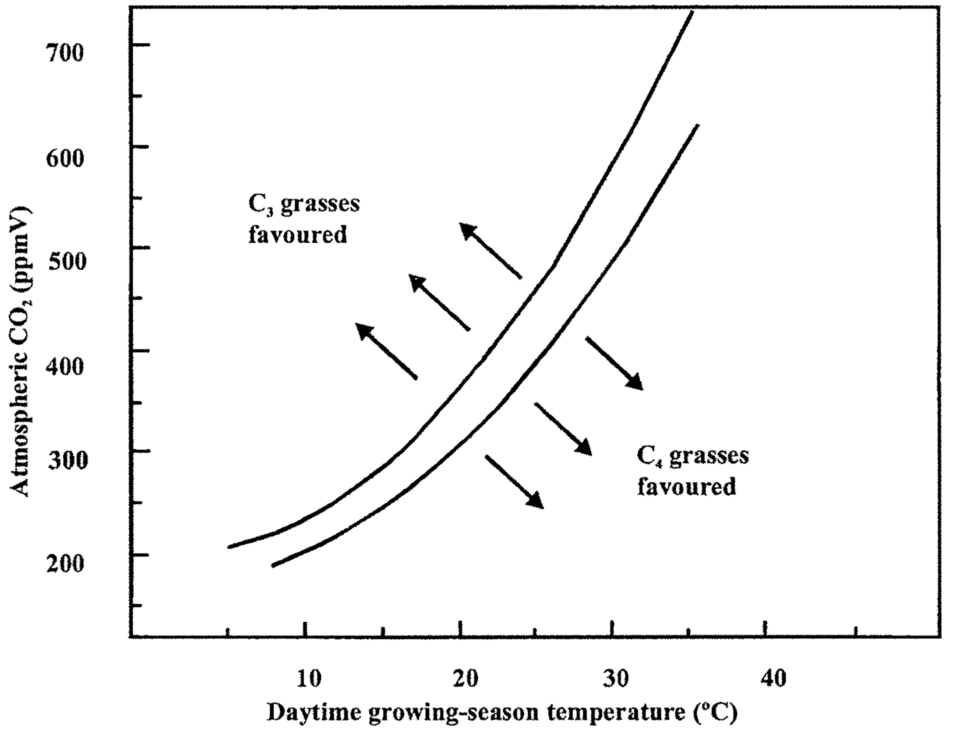

Fig.1.1 *Relation between daytime growing-season temperature and atmospheric CO_2 for grasses. C_4 grasses are favored in high temperature and low CO_2 concentration.*

with both atmospheric CO_2 level and temperature (Fig.1.1). The crossover point favoring C_3 grasses over C_4 grasses is dependent on temperature and partial pressure of CO_2 in such a way that C_4 dominated ecosystems are favored under low pCO_2 conditions when accompanied by elevated temperature. At low CO_2 and high temperature, C_4 plants have physiological advantages over C_3 plants. The CO_2 fixing enzyme Rubisco in C_3 plants has affinity for both CO_2 and O_2 particularly at high temperature. At low CO_2/O_2 ratio the active site of Rubisco reacts with both CO_2 and O_2. Oxygen is undesirable for photosynthesis. To remove oxygen from photosynthetic pathway plants also release CO_2 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 C_4 plants has only affinity for CO_2. As a result, C_4 photosynthesis can occur under very low CO_2 concentration. In addition, high CO_2 concentration in the bundle sheath cells minimizes photorespiration in C_4 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 CO_2 from atmosphere. But high affinity of PEP for CO_2 and absence of photorespiration allow C_4 plants to continue photosynthesis at low CO_2 concentrations. This led Cerling et al. (1997) to propose that lowering of atmospheric CO_2 was the main cause for appearance and expansion of C_4 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 CO_2) due to higher temperature. With progressive decrease in CO_2 concentration in atmosphere, C_4 plants appeared later in higher latitude at relatively lower temperature. Lowering of CO_2 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

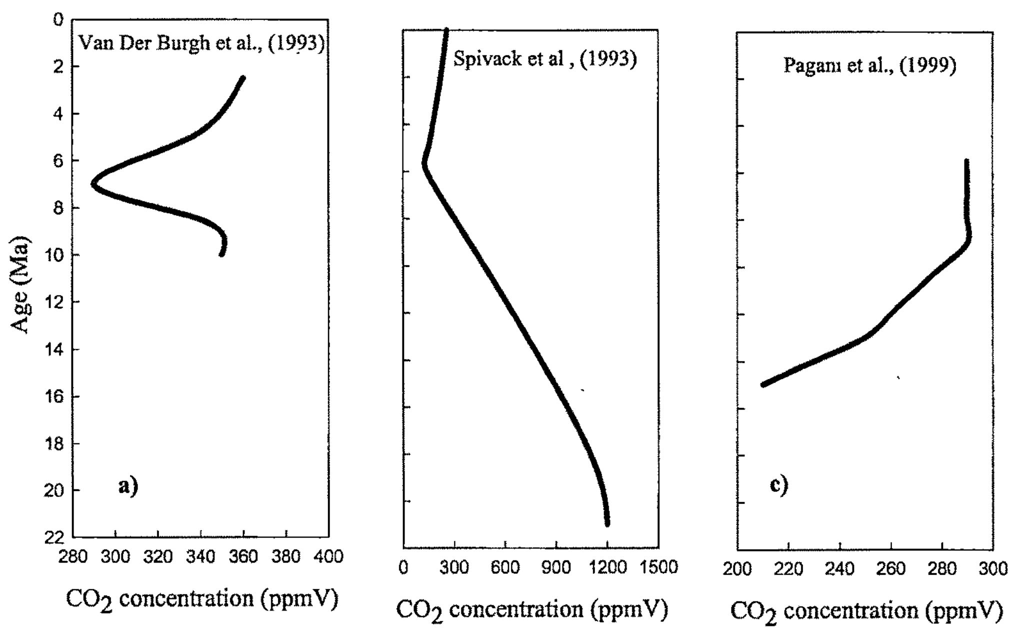

Fig.1.2 *Schematic diagram showing palaeo CO_2 concentration variation obtained from various studies. a) CO_2 estimation from stomatal index variation of leaf shows CO_2 concentration has fluctuated between 370 ppmV to 280 ppmV during last 10 Myr. b) Estimation of palaeo CO_2 from Boron isotope of foraminifera 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.*

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 CO_2 in the growth medium. Studies of carbon isotope ratio of alkenone from sediments showed that CO_2 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 pCO_2 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 C_4 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 C_4 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 CO_2 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.