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 2 μ) 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

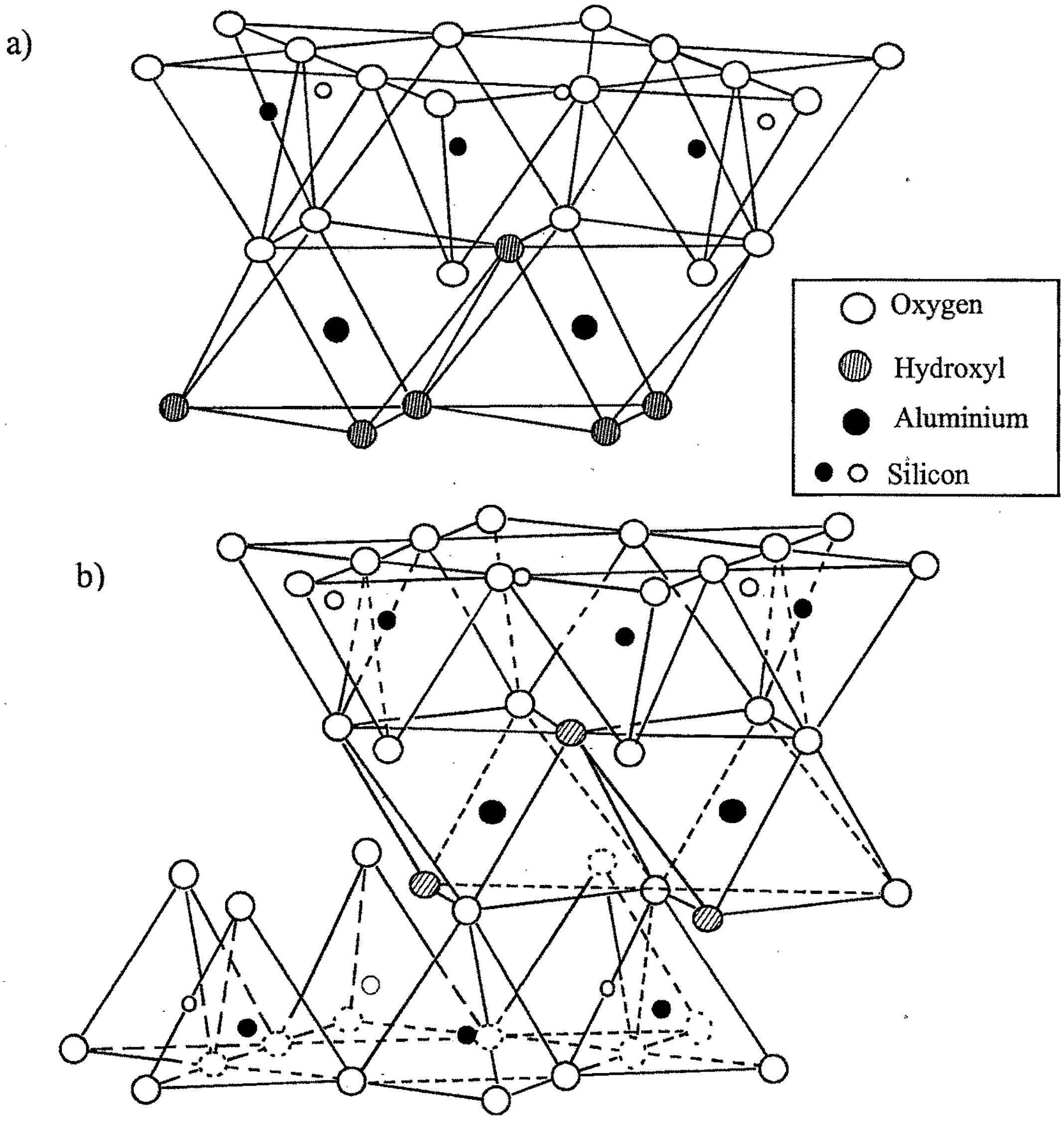

Fig.5.1a. *One octahedral sheet associated with one tetrahedral sheet.* ***b)*** *One octahedral sheet is sandwiched between two tetrahedral sheets.*

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 Si^{4+} 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 K-rich 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

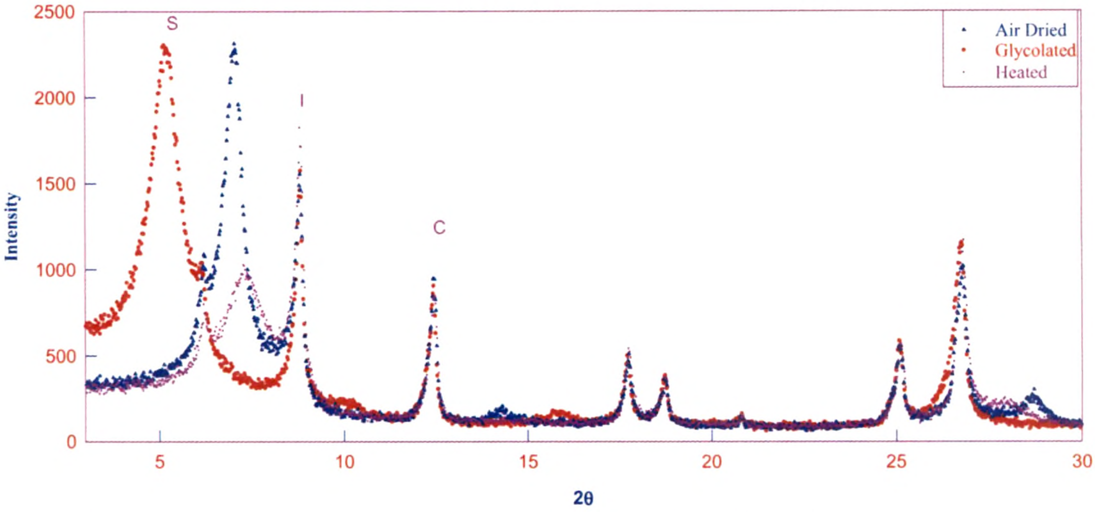

Fig.5.2 *X-ray diffractograms of clays made from oriented samples of less than 2-micron size. X-ray diffraction patterns have been made from air-dried, glycolated and heated samples. Clay species identified are smectite (S), illite (I) and chlorite (C).*

(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 different clay 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

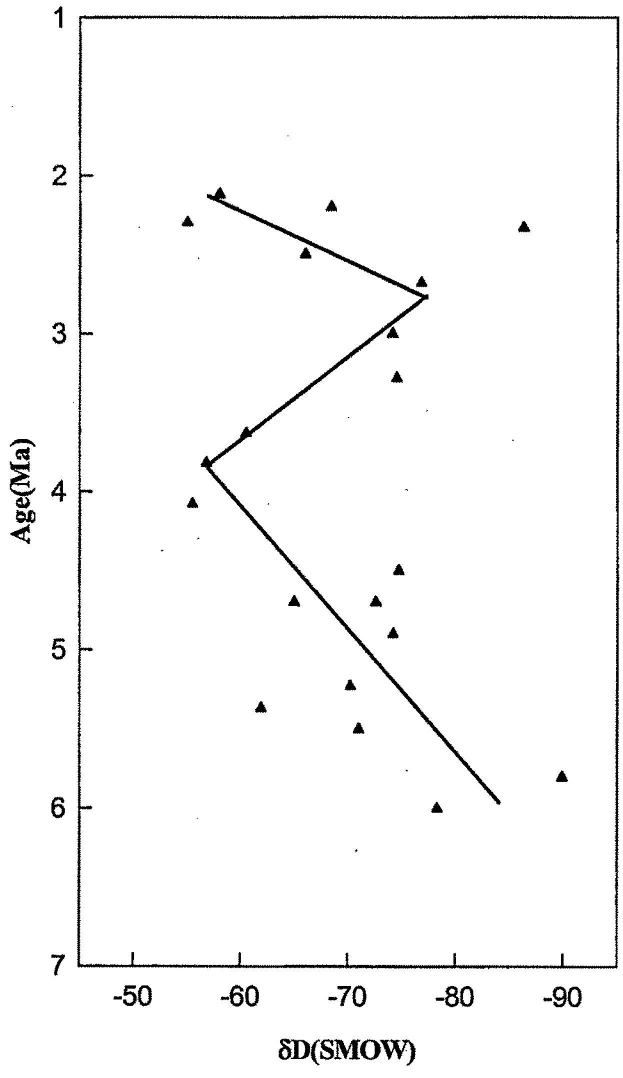

Fig.5.3 *Hydrogen isotope ratio of pedogenic clays from Haripur Khol section. The profile is characterized by lower values at around 6 Ma and 3 Ma punctuated by higher value at around 4 Ma. The two phases of lower δD probably indicate intensified monsoonal rainfall. It could be mentioned that oxygen 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

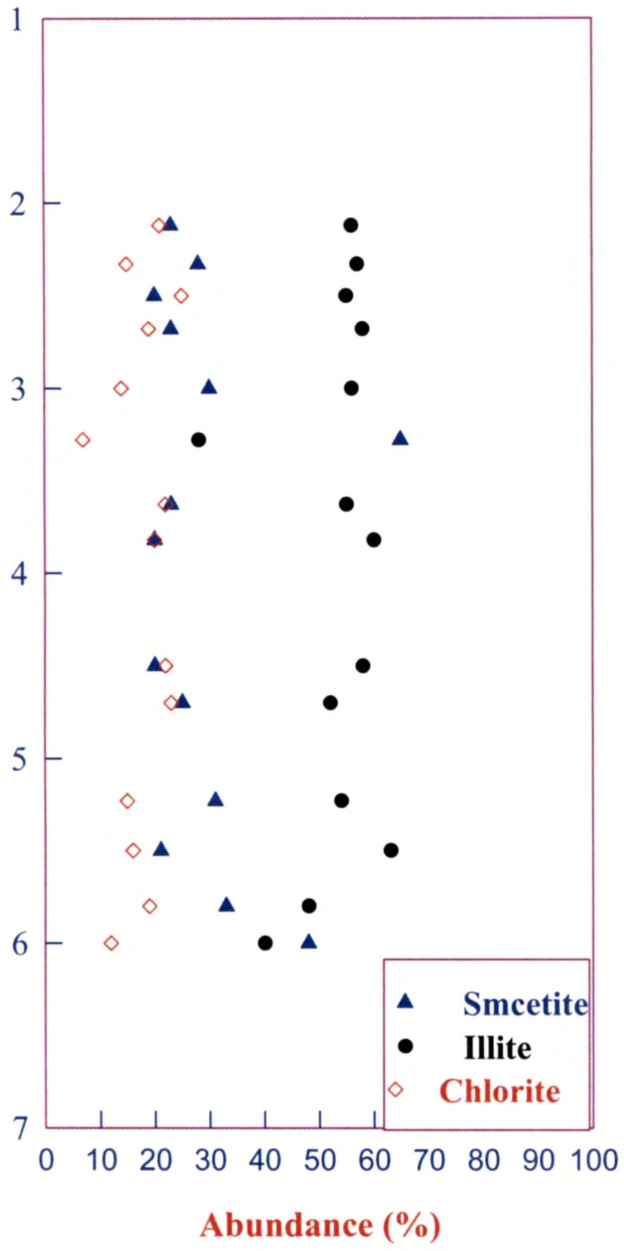

Fig.5.4 *Semi-quantitative analysis of clay minerals shows that relative abundances of smectite, illite and chlorite are almost constant throughout the succession. Illite is the most dominant (~56%) species followed by smectite (25%) and chlorite (15%).*

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 δD 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 δD value of Haripur Khol pedogenic clay is about –67.5 ‰. This value is only slightly depleted (~9‰) compared to the observed mean δD 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 sub-continent. 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 $\delta^{18}O$ are also negatively correlated, such that an increase of 100 mm of precipitation is associated with a decrease in $\delta^{18}O$ 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 $\delta^{18}O$ 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 CO_2 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

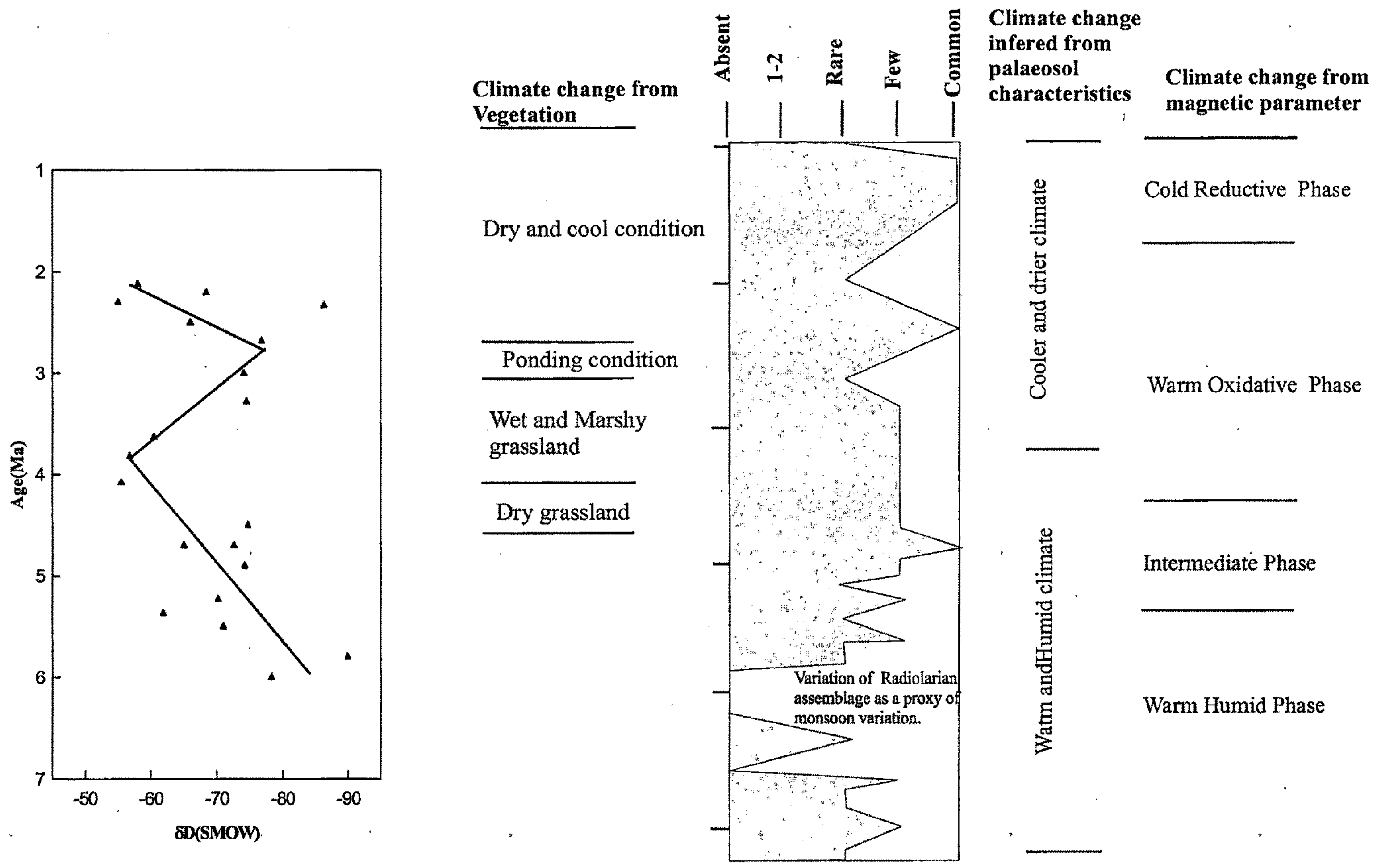

Fig.5.5 *Comparison of various climate proxies with hydrogen isotope ratio of clay minerals obtained from Siwalik soils. Though one-to-one correlation among different proxies is not observed, there is overall agreement among them over last 6 Ma. They jointly indicate two warm phases with increased rainfall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