CHAPTER-6

CARBON AND OXYGEN ISOTOPE RATIO OF SOIL CARBONATES FROM GONDWANA AND SIWALIK: IMPLICATIONS TO ATMOSPHERIC CO_2, VEGETATION AND RAINFALL

6.1 Introduction

It is well known that CO_2 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 CO_2 concentration changed from a level of 250 ppmV to ten times that level; whereas, the Cenozoic era was characterized by a continuous decrease in CO_2 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 CO_2 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 CO_2 concentration was about 1000 ppmV (Retallack, 2001c). In contrast, carbon isotope ratio of soil carbonate showed that CO_2 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 CO_2 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 CO_2 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 CO_2 concentration during the Triassic and Jurassic time was 1125 ppmV and 2225 ppmV respectively (Ghosh et al., 2001). However, CO_2 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 CO_2 concentration derived from this soil for Early Triassic to Jurassic period was not definitive. We have reinvestigated the issue based on soil 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 C_4 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 C_4 plants till 6 Ma ago (Sanyal et al., 2004a) allowing us derive the CO_2 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 CO_2 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).

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 $\delta^{13}C$ 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 $\delta^{13}C$ with age (see section 2.6 for age of the samples) (Table 6.2). The $\delta^{13}C$ value of oldest sample is –10.7‰ and the value for the youngest sample is –6.4‰. The average $\delta^{13}C$ 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 $\delta^{13}C$ of non-pedogenic carbonate collected from Denwa Formation (n=7, Table 6.2) ranges from – 4.7 to –7.6 ‰.

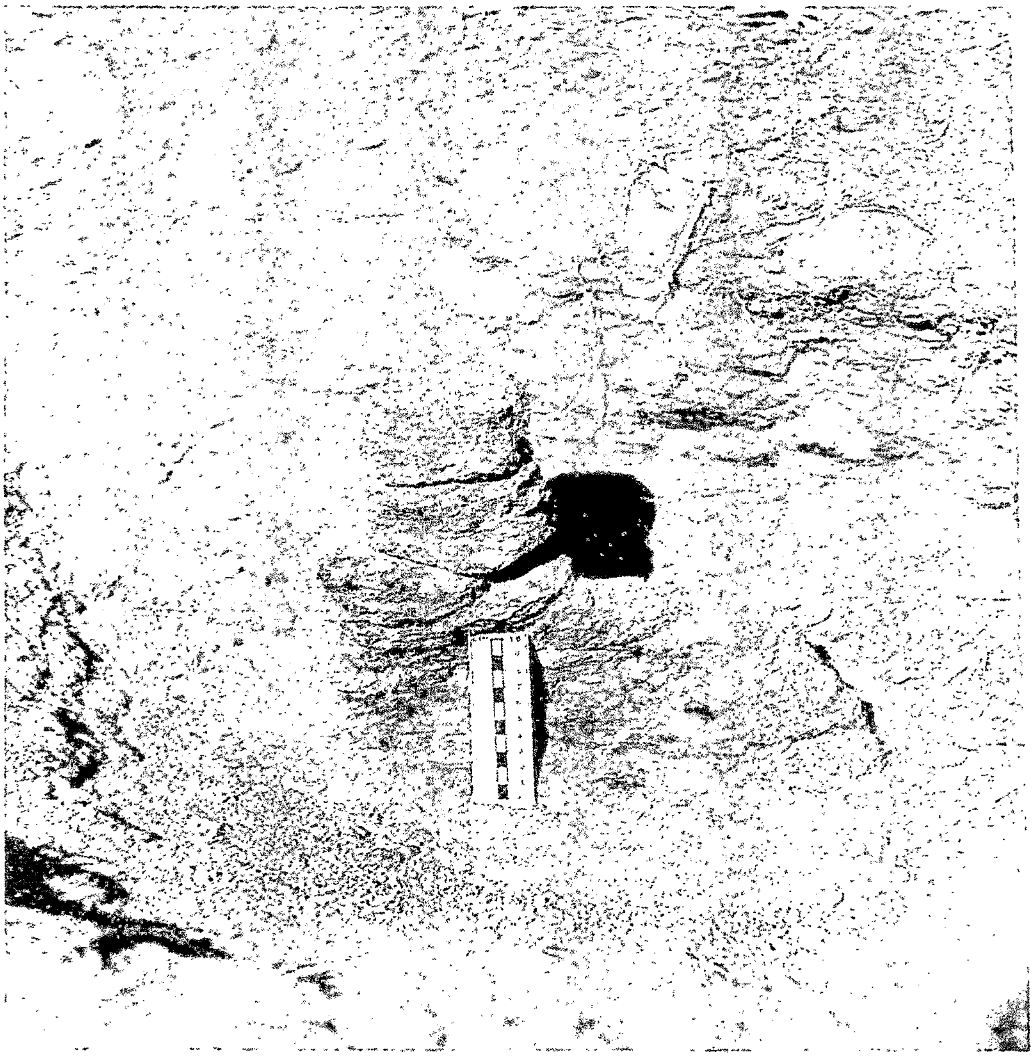

Fig.6.1b *Preserved root mold at Denwa Formation. The root is almost 30 cm in length.*

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

From Bagra Formation, most of the samples were collected along soil profile. The $\delta^{13}C$ 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 $\delta^{13}C$ 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 $\delta^{13}C$ of recycled carbonate is –7.3±0.6‰ (n=3,Table 6.2).

The mean $\delta^{13}C$ value of soil carbonate nodules from six individual soil profiles from Ranital are –11.1 ± 0.3 ‰, –10.9 ± 0.5 ‰, –10.4 ± 1.0 ‰, –10.4 ± 1‰, –11.0 ±

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±0.4‰ (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 $\delta^{18}O$ value of sample collected from clay dyke contact is –4.7 ‰ and that of fracture filled carbonate is –2.1 ‰. Calcrudites have $\delta^{18}O$ value –3.8 ± 1.5‰ (Table 6.1). Like carbon isotopic ratio, oxygen isotope ratio of soil carbonate from the Bagra

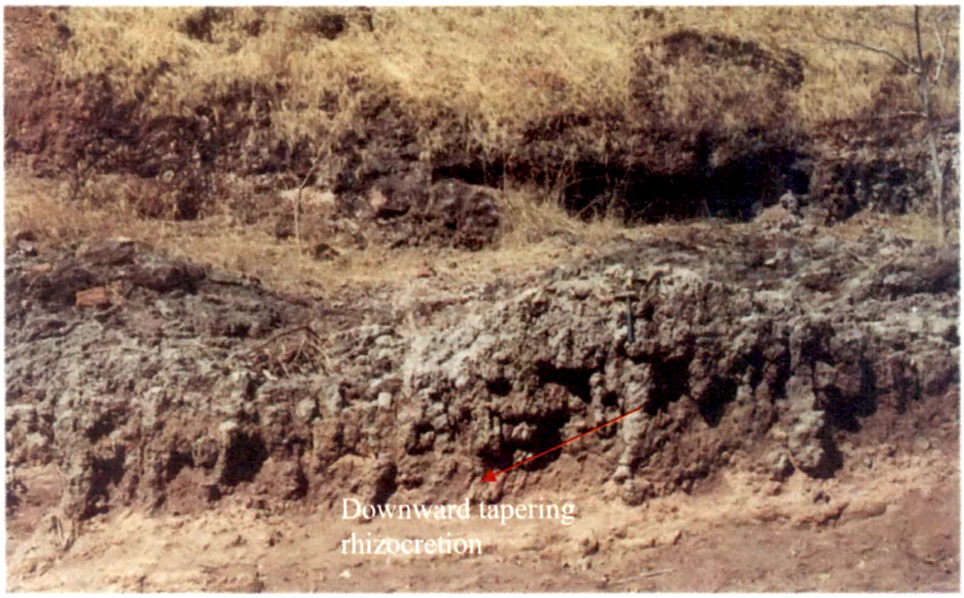

Fig.6.3b *Frontal view of the palaeosol bed from Bagra Formation. The bed is characterized by thick to very thick horizons of closely spaced, vertically oriented large cylindrical rhizocretions with tapering in downward direction.*

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

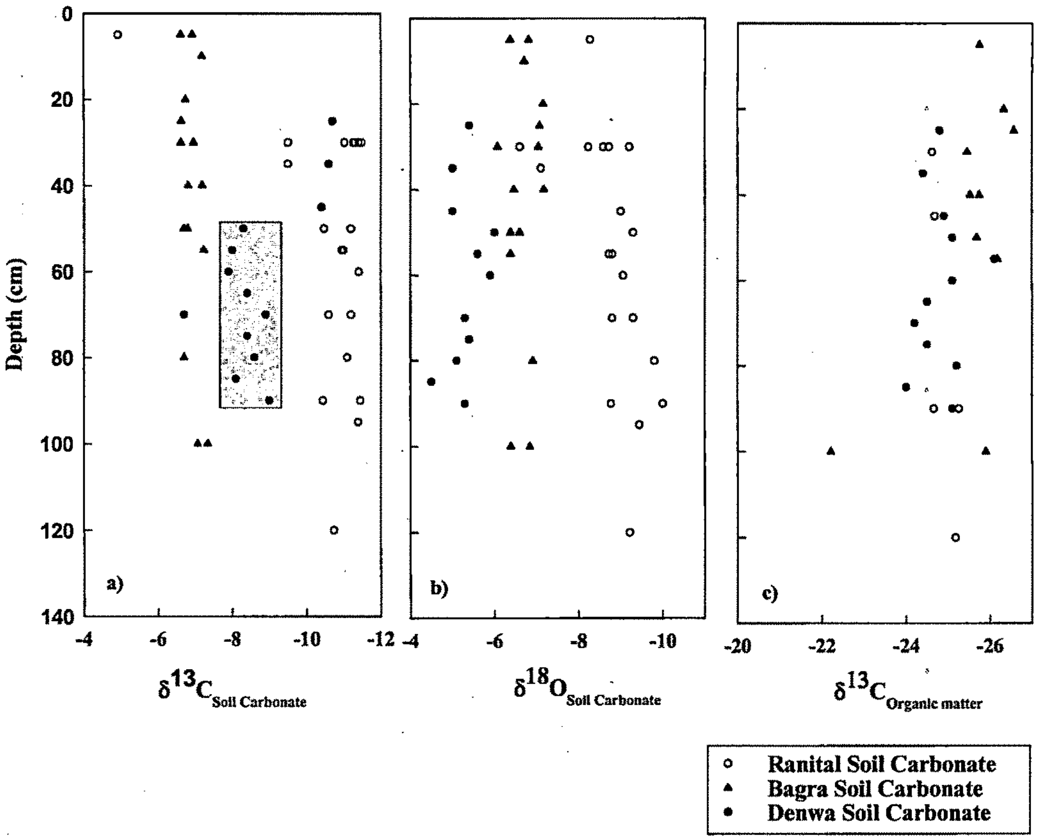

Fig.6.4 *Isotope ratio variation in soil profile. a) $\delta^{13}C$ of the Ranital soil carbonates show source of carbon is exclusively from C_3 plants. The average $\delta^{13}C$ of the Bagra samples are 4 ‰ enriched compared to Ranital samples indicating contribution of atmospheric CO_2 in soil CO_2. In contrast, $\delta^{13}C$ of samples from Denwa Formation shows continuous increase in atmospheric CO_2 from lower Denwa to Upper Denwa. The shaded region indicates $\delta^{13}C$ 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 $\delta^{18}O$ values of two profiles are –6.4 ± 0.2 ‰ and –6.9 ± 0.3 ‰ and from the other two exposures the mean

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value is –6.7 ‰ (Table 6.1). The mean $\delta^{18}O$ of recycled soil carbonate from the Bagra Formation is –6.4±0.2 ‰. The $\delta^{18}O$ of soil carbonate nodules in Ranital soil profile does not vary significantly with depth, except for marginal enrichment near the surface. The mean $\delta^{18}O$ 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 $\delta^{13}C$ value of the organic matter associated with soil carbonate nodules from the Siwalik soil profiles, Bagra and Denwa Formation are –24.9 ± 0.3 ‰ (n=5), –25.9 ± 0.4 ‰ (n=10) and –24.8 ±0.5 ‰ (n=13) respectively (Table 6.1 and 6.2). The $\delta^{13}C$ of the organic matter associated with non-pedogenic carbonate is –24.0 ± 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 CO_2. In addition, atmospheric CO_2 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 ^{13}C enriched atmospheric CO_2. At greater depth it tends to approach a constant value depending on the ratio of plant-respired CO_2 and atmospheric CO_2 (Cerling, 1991). Porosity of soil affects pCO_2 in soil atmosphere as CO_2 diffusion coefficient depends on porosity and consequently penetration of atmospheric CO_2 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 $mmol/m^2/hr$ 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.*

Ranital Section, Siwalik Group

Profile-1	Sample No	Depth (cm)	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C_{Org}$
	PRL-010A1	30	–11.3	–8.7	–24.6
	PRL-010A2	55	–11	–8.7	
	PRL-010A3	90	–11.5	–10	–25.3
	PRL-010A4	120	–10.7	–9.2	–25.2
Profile-2	PRL-02B1	5	–4.9	–8.2	
	PRL-02B2	30	–11.4	–9.2	
	PRL-02B3	55	–10.9	–8.8	
	PRL-02B4	95	–11.4	–9.4	
Profile-3	PRL-03A01	30	–9.5	–6.6	
	PRL-03A0	35	–9.5	–7.1	
	PRL-03A4	70	–11.2	–8.8	
Profile-4	PRL-013A3	70	–10.6	–9.3	
	PRL-013A1	30	–11.5	–8.2	
Profile-5	PRL-019	30	–11.0	–8.6	
	PRL-019A1	45	–10.4	–9	–24.7
	PRL-019A2	60	–11.4	–9.1	
	PRL-019A3	90	–10.4	–8.8	–24.7
Profile-6	PRL-017A	30	–11.3	–11.1	
	PRL-017C	50	–10.5	–11.2	
	PRL-017D	80	–11.1	–9.8	

Bagra section, Satpura Basin, Gondwana Supergroup

Profile-1	Sample No	Depth (cm)	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C_{Org}$
	BG-5	5	–6.9	–6.4	
	BG-8	10	–7.2	–6.7	
	BG-9	30	–6.9	–6.1	–25.5
	BG-11	40	–7.2	–6.5	
	BG-12	50	–6.7	–6.4	–25.7
	BG-14	100	–7.1	–6.4	–25.9
Profile-2	BG-5A2	5	–6.6	–6.8	–25.7
	BG-5A4	20	–6.7	–7.2	–26.3
	BG-5A6	25	–6.6	–7.1	–26.6
	BG-5A7	30	–6.6	–7.0	25.6
	BG-5A8	40	–6.8	–7.2	–25.7
	BG-5A10	55	–7.2	–6.4	–26.2
	BG-5A11	80	–6.7	–6.9	
	BG-5A14	100	–7.3	–6.8	–22.2
	BG-5A9	50	–6.8	–6.6	

Denwa section, Satpura Basin, Gondwana

Profile-1	Sample No	Depth (cm)	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C_{Org}$
	DN-C-2	25	–10.7	–5.4	–24.8
	DN-C-2A1	35	–10.6	–5.0	–24.4
	DN-C-2B	45	–10.4	–5.0	–24.9

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.*

Location	Sample No	$\delta^{13}C_{Carb}$ ‰	$\delta^{18}O_{Carb}$ ‰	$\delta^{13}C$ 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, Denwa					
	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 carbonate, Bagra					
	BG-CNG-2	–7.4	–6.3		
	BG-CNG-3	–7.8	–6.3		
	BG-CNG-4	–6.7	–6.7		

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).

Table 6.3 *Estimated CO_2 from Gondwana and Siwalik palaeosols.*

Formation	Mean $\delta^{13}C$ of carbonate (‰)	$\delta^{13}C$ of soil CO_2 (‰)	Mean $\delta^{13}C$ org. (‰)	$\delta^{13}C$ air (‰)	Sz (ppmV)	CO_2 (ppmV)	Mean CO_2 (ppmV)	Age (Ma)
Lower Denwa	−10.6	−19.4	−24.7	−3.7	3000	190	255 ±65	240
					4000	255		
					5000	320		
Middle Denwa	−8.4	−17.2	−25.1	−4.1	3000	825	1100 ±275	220
					4000	1100		
					5000	1375		
Upper Denwa	−6.7	−15.5	−24.4	−3.4	3000	1140	1520 ±380	206
					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		

The $\delta^{13}C$ of soil carbonate and organic matter from Ranital soil profiles indicate that for most of the samples the source of carbon was C_3 plant. One sample collected from 5 cm below the present surface has substantial contribution of CO_2 from atmosphere (Sanyal et al., 2004a). In lower Denwa Formation, the $\delta^{13}C$ of soil carbonate and organic matter associated with root mold suggest that here also the source of CO_2 is from C_3 plant. In Bagra Formation, the mean $\delta^{13}C$ of rhizocretion is enriched by ~4 ‰ compared to the mean $\delta^{13}C$ of soil carbonate from Ranital and lower Denwa but the carbon isotope ratio of organic matter shows that vegetation comprised of C_3 plants. If the source of soil CO_2 is only from oxidation of organic matter and plant respiration, the $\delta^{13}C$ of soil carbonate from Denwa, Bagra and 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 pCO_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 CO_2

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:

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

where C_s^* is the concentration of CO_2 in the soil (moles/cm^3), D_s^* is the diffusion coefficient (cm^2/s) for CO_2 in soil, z is depth (cm) and $\varphi_s^*(z)$ is the production rate of CO_2 (moles/cm^3/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 CO_2 is:

$$C_s^*(z) = S(z) + C_a^* \text{......................}(2)$$

where C_a^* is the CO_2 concentration in the atmosphere and S(z) is CO_2 contributed by soil respiration. Cerling (1984,1991) solved this equation for ^{12}C and ^{13}C and showed that isotopic composition of soil CO_2 is controlled by diffusional mass transfer and production. The solution to the soil CO_2 equation can be rearranged in the following form

$$C_a^* = S(z)\frac{\delta^{13}C_S^* - 1.004\delta^{13}C_\varphi^* - 4.4}{\delta^{13}C_a^* - \delta^{13}C_S^*} \text{................}(3)$$

by using the assumption of $^{12}C/^{13}C \approx C_S^* / C_a^*$ (Davidson, 1995) where $\delta^{13}C_S^*$, $\delta^{13}C_\varphi^*$ and $\delta^{13}C_a^*$ are the isotopic composition of soil CO_2, soil-respired CO_2 and atmospheric CO_2 respectively. Equation (3) shows that concentration of atmospheric CO_2 can be calculated if the $\delta^{13}C$ of soil CO_2, the $\delta^{13}C$ of atmospheric CO_2, $\delta^{13}C$ of soil-respired CO_2 and the difference between the soil pCO_2 and the atmospheric pCO_2 which is known as S_Z are known. These parameters for the contemporaneous time period are estimated in the following way:

1) $\delta^{13}C$ of soil CO_2: Carbon isotope ratio of soil CO_2 can be estimated from three inputs: carbon isotope ratio of soil carbonate, fractionation factor between CO_2-carbonate 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 CO_2 to $CaCO_3$ is about 9‰ (Romanek et al., 1992).

2) Carbon isotope ratio of soil-respired CO_2 and atmospheric CO_2: The carbon isotope ratio of plant-respired CO_2 is same as average $\delta^{13}C$ of whole plant body. The $\delta^{13}C$ of soil-respired CO_2 could be taken as the mean $\delta^{13}C$ of organic matter associated with soil carbonate assuming that plant-respired CO_2 and oxidation of plant debris are the sources of soil-respired CO_2.

During photosynthesis plants take CO_2 from atmosphere to form metabolites through a chain of reactions by which the initial carbon isotope ratio of CO_2 gets depleted by about 21 ‰ (Mora et al. 1996). Hence, the $\delta^{13}C$ of the atmospheric CO_2 could be estimated by subtracting 21 ‰ from the mean $\delta^{13}C$ 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).

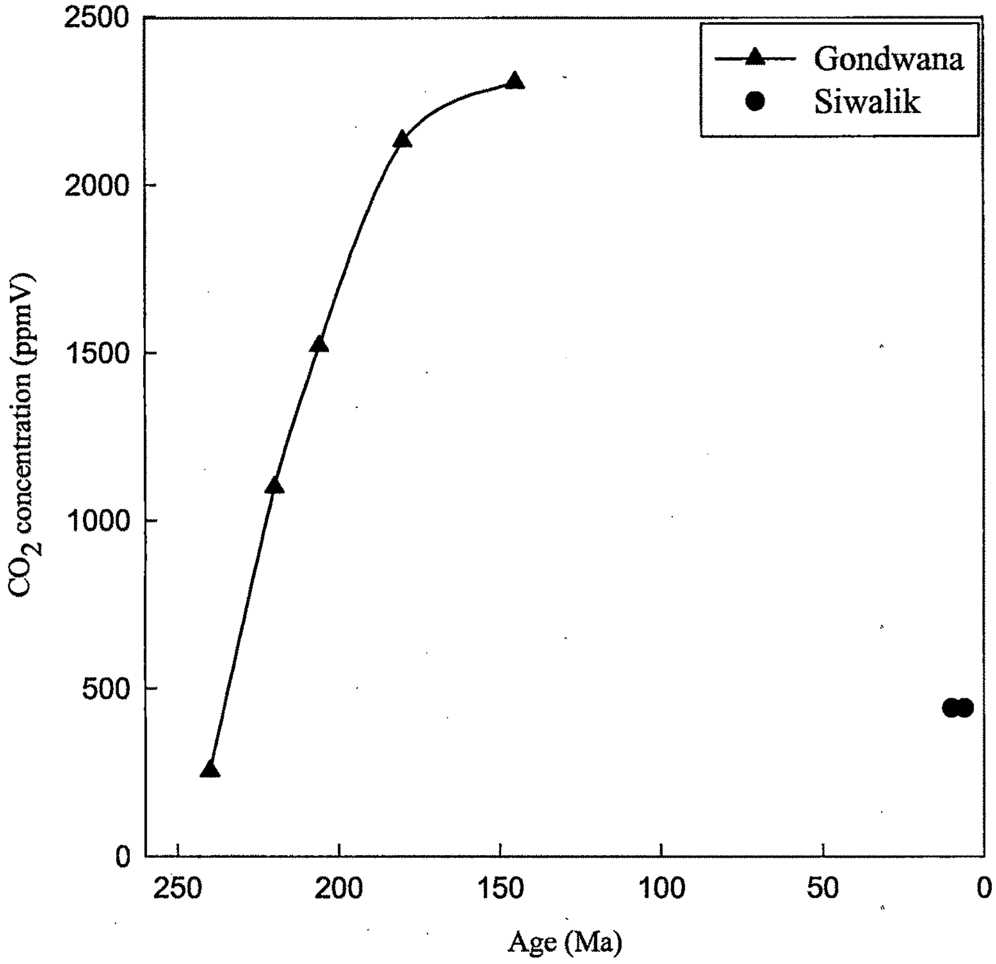

Fig.6.5 *Atmospheric CO_2 concentration variation through time based on $\delta^{13}C$ of paleosols from Gondwana deposit of Satpura basin. Lower Triassic CO_2 concentration was about 255 ppmV and it reached a maximum of 1520 ppmV during upper Triassic through an intermediate concentration of 1100 ppmV. 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 $\delta^{13}C$ 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 $\delta^{13}C$ value of the Bagra soil carbonate from different exposures is almost similar. The CO_2 estimation based on Cerling formalism show that during lower Denwa time, atmospheric CO_2 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 CO_2 concentration ranged from 2110 to 2275 ppmV. A plot of these values against the inferred ages of the samples show continuous increase of CO_2 concentration with time (Fig.6.5). The CO_2 concentration estimated from the Ranital Siwalik samples show an atmospheric CO_2 concentration of 455 ppmV for the late Neogene Period (6-11 Ma) (Table 6.3).

Though the nature of CO_2 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 CO_2 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 $\delta^{13}C$ of atmospheric CO_2 and that of soil carbonate which translates to a larger atmospheric CO_2 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ of rainwater in two ways. It has been seen that every degree Celsius rise in air temperature causes enrichment in $\delta^{18}O$ 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 $\delta^{18}O$ value of residual water. Part of this is compensated during carbonate formation since a rise in temperature causes depletion of ^{18}O in carbonate (0.2‰/°C).

3) Amount effect: The $\delta^{18}O$ of rainwater decreases with an increase in the amount of precipitation (IAEA, 2003). At low latitudes, the average monthly rainfall and the mean monthly $\delta^{18}O$ are usually negatively correlated where an increase in 100 mm of rainfall is associated with a decrease in $\delta^{18}O$ 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 $\delta^{18}O$ of the Denwa soil carbonate should have been depleted compared to the Bagra samples. However, the average $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 ^{18}O in soil carbonate in Denwa. However, during the Bagra time, the supercontinent started breaking up and polar ice started melting which made the $\delta^{18}O$ of ocean water lower than before. The rainwater forming at that time would be characterized by depleted $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 CO_2 and atmospheric CO_2 in soil atmosphere is the most important. During Gondwana time when the atmospheric CO_2 concentration was high the $\delta^{13}C$ of soil carbonate demonstrate contribution from both soil-respired CO_2 and atmospheric CO_2. On the other hand, during Siwalik time, due to relatively lower concentration of CO_2 in atmosphere the carbon isotope ratio of plant-respired CO_2 was the sole determinant below depth of a few centimeters.

Atmospheric CO_2 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 $\delta^{18}O$ 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 $\delta^{18}O$ of Bagra compared to Denwa. On the other hand, we demonstrate that the depleted $\delta^{18}O$ value of the Siwalik samples at 10.5 Ma represent intensified monsoonal rainfall.