ISOTOPIC AND ELEMENTAL STUDIES OF GONDWANA CARBONATES AND THEIR IMPLICATIONS

A Thesis submitted to

DEVI AHILAYA VISHWA VIDHYALAYA INDORE

For

THE DEGREE OF DOCTOR OF PHILOSOPHY IN PHYSICS

By

PROSENJIT GHOSH

Dedicated To My beloved parents

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.

Prosening lyhoch Author

S.K. Bho Hoch any.

(PROSENJIT GHOSH)

Thesis Supervisor

(Prof. S.K.Bhattachar.ya)

Acknowledgement

9 am indebted to Prof. S.K. Bhattacharya, my cherished guru, for his guidance and encouragement provided throughout the investigation and during the preparation of this thesis. Many of the ideas incorporated in this thesis originated from him. I also express my deep sense of gratitude to him for teaching me the art of stable isotope mass spectrometry. I am beholden to many people, whose inspiration, advice and precious time have helped me considerably in the creation of this thesis. Mr. R.A. Jani and Dr. R. Ramesh of Stable isotope Laboratory, PRL provided me all essential facilities and encouragement for the analyses of samples. I am grateful to Prof. Krishnaswami, Prof. K. Jopalan, Prof. J.N. Goswami, Dr. R. Ramesh Dr. M.M. Sarin, Prof. B.L.K. Somayajulu, Prof. N. Bhandari and Dr. J. Srinivasan for valuable discussions during group seminars and annual review. Dr. A.M. Dayal, Dr. J.R. Trivedi and Dr. M.M. Sarin helped me enormously for analytical works. Many thanks are due to them. REE and Trace elemental analyses of the samples presented in the thesis, would have been impossible without the help of Prof. Ebhihara of Tokys metropolitan University. I am thankful to Prof. Ebhihara and Dr. Anindya Sarkar for timely analyzing the samples and sending me the results.

This study would have been impossible without the generous supply of samples and guidance during field work from Prof. Amitava Chakrabarti of 197 Kharagpur. I gratefully acknowledge his help and cooperation during various stages of this work. His continious support and suggestion helped me improving the guality of this work. My thanks are due to Dr. ParthaSarathi Ghosh of ISI Calcutta for his help in field work and providing me some of the precious samples used during investigation.

9 had a pleasure of working with many members of Earth Science group. PRL. Dr. P.N. Sukhla. Dr. Kanchan Pandey, Dr. Supriya Chakrabarti, Mr. Navin Juyal, Mr. J. 7. Padia, Mr. Despande. Mr. Ravi Ehusan, Dr. Ashish Sarkar, Dr. Sunil Singh, Dr. J.S.Ray, Mr. M.Yadava, Mr. D.K.Rao, Dr. D. Yadav, Mr. Kaushik Dutta, Mr. Rajesh Agnihortri, Mr. Subrata Chakrabarty. Mr. A.D. Sukhla, and Mr. Tarun Dalai. My special thanks are due to Dr. J.S.Ray for guickly analyzing a few thin section samples using CL facility at Ottawa University. 9 am thankful to Prof. K.Gopalan and Dr. A.M. Dayal of N.G.R.9. for their help in analysing large number of samples for Sr isotopes. Dr. Sudipta Sarkar of GS9. Gandhinagar helped me in clay extraction work and taught me the technique. Dr. Simon Prosser of former Europa helped me in Inter-laboratory callibration exersize by analysing a few 3-Cararra and MMB laboratory standards in GE020-20 mass spectrometer at Uthaka University, USA.

9 wish to extend special thanks to Dr. Supriya Chakrabarti and R. Ramesh for reading the manuscript and for their valuable suggestion and criticisms towards the improvement of manuscript.

I learnt many aspects of electronics and software usage from Mr. V. G. Shah. Mr. Pandian. Mr. Pranav, and Mr. Rahul Sharma. I am extremely thankful to all these people, who had the patience to make me understand the subject. I have always enjoyed the favour of Mr. Kurup and Mr. Sivasankaran, for various glass blowing job. I have learnt from them the initial art of glass blowing. I am extremely thankful to both of them for support and encouragement. I am thankful to Mr. J. P. Bhavsar and Mr. N. B. Vaghela for help and assistance.

9 appreciate the help and encouragement provided by Prof. Amitabha Chakrabarti. Prof. Pradip Bose. Prof. V. Rajamani. Prof. K. Balakrishnan, Prof. D.M. Banerjee. Prof. S. Kumar. Prof. S.K. Tandon. Dr. Bhibhuti Ray and Dr. Parthosarathi Ghosh for petrographical studies. Discussion with Prof. S. Kumar and Prof. Pradip Bose were helpful in explaining some of the experimental observations. 9 am thankful to Council of Scientific and Industrial Research (CSIR). PRL and Committee for International conference on Geochronolgy and Cosmochronolgy (ICOG) for providing me travel assistance and oppurtunity for participation in ICOG-9. Beijing. 1998.

The help and cooperation extended by the authorities: PRL's Academic committee. Admistration and Worshop. and Devi Ahilaya Vishwavidyalaya. Indore in particular Prof. K.P. Maheshwari is gratefully acknowledged. I applaud the help provided by PRL Library members. I am thankful to Mrs. Panna Thakkar. Mrs. Rohini Patil. Mrs. Nisitha. Mr. Kewur and Mrs. Giya for support and timely help.

The Inspiration and cheers given by my friends and admirer of my elegant stories. Dr. Ramachandran. Dr. Tarun Pant. Dr. Prashant Rawat. Dr. Siva Kumaran. Dr. Debasish Banerjee. Dr. Debabrata Banerjee were of tremendous value during the course of this work. Biannual field session and PRL sports clubs and members kept my health in good condition through continious involvements in various sports and tournaments.

Special thanks are due to Mr. Dholakia and Mr. P.S. Shah of computer section for assistance. ? am really appreciating the enormous support provided by all colleague and fellow mates during concluding stage of the thesis. ? express special gratitude to Mr. Anirban Das, Mr. Subrata Chakrabarty Mr. Supriya Chakrabarty . Mr. Koushik Dutta, Mr. A.D. Sukhla, Miss Debjani, Hiss Leena, Miss Basu and Miss Kaur .

Abstract

Section-A

Ubiquitous presence of carbonate nodules in glaciogene sediments of various Permo-Carboniferous basins in peninsular India offers promise for delineating the climate and environment of deposition at that time. Isotopic composition of carbon and oxygen have been determined in carbonate nodules collected from the basal formation (Talchir) of three Gondwana basins of East-Central India along with a few samples from contemporaneous Dwyka tillite of South Africa. Petrographic, cathodoluminescence and sedimentary evidences suggest that many of these nodules contain primary carbonate precipitates and therefore their geochemical signatures can be used for palaeoclimatic inference. The mean δ^{10} O, δ^{11} C and 87 Sr/ 86 Sr values of the calcites in the nodules are 10.8 % w.r.t. SMOW, -9.7 % w.r.t. PDB and 0.730 respectively suggesting a freshwater environment (probably lacustrine) for formation of these concretions. The mean oxygen isotopic composition of meteoric water at that time (Early Permian) and location (70 °S palaeolatitude) estimated from δ^{18} O of calcite is -22.5 % and is close to the expected isotopic composition of precipitation (-21.0%) at this latitude. This similarity suggests that (i) assignment of palaeolatitude of this location is reasonably correct and (ii) the global hydrological cycle in Early Permian was operating in a similar way as that of today. There is a slight depletion in value, which can be interpreted either in terms of an amount effect due to enhanced rainfall or an altitude effect if the precipitation occurred at high altitude as expected for development of the Talchir glacier. Nodules are analyzed for Sr isotopic composition and results indicate that samples from Damodar valley region (with Sr ratio ~0.730), received water draining from adjoining granitic terrain of Chotanagpur region as suggested by isotopic ratio of 0.730 for its most weatherable component i.e. plagioclase mineral. Similarly, nodules from Mahanadi valley have ⁸⁷Sr/⁸⁶Sr ratio of 0.720 similar to the ratio observed in mafic granulite of eastern ghat suggesting this region to be water source for Talchir basin in Mahanadi valley. This inference is supported by REE pattern and trace element concentration of carbonate phase of bulk nodule samples.

Section-B

Satpura basin of Central India contains four well-developed soil horizons belonging to Permian (Motur Formation), Triassic (Denwa Formation), Jurassic (Bagra Formation) and Cretaceous (Lameta Formation) periods. These soils contain pedogenic carbonates in the form of rhizocretion and nodules. The oxygen isotopic composition of these carbonates is used for inferring the soil temperature during those periods. The carbon isotopic compositions of the soil carbonate and coexisting soil organic matter are used to infer the δ^{13} C of atmospheric CO₂ and its concentration using the model developed by Cerling. It is seen that the atmospheric CO₂ level increased by a factor of 8 from Permian to Jurassic and declined again during Cretaceous. The nature of the change agrees with the result of the CO₂ evolution model of Berner (GEOCARB II) but the magnitude of the CO₂ increase in Middle Jurassic and Late Cretaceous was higher than the predicted value. The rapid increase in CO₂ concentration is consistent with the observed increase in the maturity of the soil profiles along the stratigraphic column. Degassing of Earth's interior due to rapid break-up of the Gondwana landmass during 'Triassic and Jurassic period could have caused the rapid CO₂ evolution.

Contents

List of figures and Tables	i
Chapter 1 Introduction	
Introduction	1
Purpose of this study	13
The outline of the thesis	14
Chapter 2 Materials & Experimental Techniques	10
2.1 Geology and Stratagraphy of Gondwana basins	10
2.1.1 Damodar valley basin	19
2.1.2 Mananadi Valley basin	20
2.1.5 Godavari valley basin 2.1.4 Development of concretions in siltatons had and their algorithmation	20
2.1.4 Development of concretions in suisione bed and their classification	20
2.1.5 South African hodules	32
2.1.6 Salpura valley basin	55
2.2 Experimental Techniques	44 62
Chapters Results and Discussion	02
Section-A (nodular carbonates from Tatchir)	62
3A.1 Morphology of hodules	65
3A.2 Petrography	65
3A.3 Cathodoluminescence	67
3A.4 Clays in nodules	68
3A.5 Mn, Fe, and Sr concentration in carbonates as diagenetic indicator	73
3A.6 Stable Isolopic study	76
3A.6.2 Carbon isotones in the nodular carbonates	81
34.6.3 Presence of Organic matter in the nodules	82
3A 6.4 Environment during Talchir sedimentation: monsoonal implications	83
3A 6 5 Stable isotopic variation within a nodule	84
3A.6.6 Enigmatic objects in the basal Gondwana of Eastern India	88
3A.6.6a Stable Isotopes	90
3A.6.6b Carbon and Nitrogen in the suspected algae	91
3A.7 Provenance of Talchir Basin sediments	92
3A.7.1 Rare Earth Elements	92
3A.7.2 Trace elements	95
3A.7.3 Strontium isotopic composition	101
3A.7.4 Sr isotopic composition of Mahanadi	
river water and Talchir carbonates	104
Section-B (Palaeosol studies from Satpura basin)	106
3B.1 Results and discussion	106
3B.2 Preservation of Geochemical signature	109
3B.3 Estimation of atmospheric pCO_2	110
3B.4 The pCO_2 determination	119
3B.5 Berner's model of pCO2 and the observed values	121
3B.8 Atmospheric CO2 and Soil Maturity	123
Chapter4 Summary and Conclusion	125
4.1 Environment of Talchir sedimentation	125
4.2 Provenance information	126
Enigmatic objects, in Gondwana sediments:	
fresh water Stromatolites	127
4.4 Suggested future work	128

References

131

List of figures in Chapter 1

Figure 1.1: Schematic representation of Pangean continental configuration during Permo-Carboniferous period

Figure 1.2: Global map showing mean annual precipitation over Pangea. Note high precipitation (6mm/day) in coastal region and widespread aridity in the continental interior (Kutzbach and Gallimore, 1989). Figure 1.3: Global record from late Precambrian to Cainozic. Note presence of glaciers an all the southern continents during Permo_Carboniferous indicating a global scale glacier era (Price, 1999). Figure 1.4: Suggested marine transgression in peninsular India during permian period based on marine fossils found in Mahendragarh, Daltonganj and Umaria shown in the map. A probable trans-Indian seaway is shown by hatched zone (Ghosh, 1954). The Latitude_longitude mark denotes 8 degree interval. Figure 1.5: Present day variation in oxygen isotopic composition of rainfall at various latitudes given by range of colours corresponding to various δ^{18} O values (IAEA data compiled by Rozanski, 1989). Figure 1.6: Atmospheric CO₂ versus time for Phanerozoic (past 550 million year). The parameter RCO₂ is defined as the ratio of concentration of CO_2 in the atmosphere at some time in the past to that at present (i.e. a preindustrial value of 280 ppmV). The heavier black line represents the best estimate from GEOCARBII model. The shaded area denotes the approximate range of uncertainty of the model based on sensitivity analysis. Vertical bars represents estimates of CO2 levels based on study of palaeosols (Mora et al., 1996; Sinha and Scott, 1994; Andrew et al., 1995; Ghosh et al., 1995; Yapp and Poth, 1993; Cerling, 1991)

List of figures in Chapter 2

Figure 2.1: Gondwana basins of Peninsular India.

Figure 2.2: Geological map showing lithological units of the West Bokaro sub-basin, Damodar valley.

Figure 2.3: Bluish grey siltstone containing nodules.

Figure 2.4: Climbing ripple lamination showing oppositely oriented direction of climb.

Figure 2.5: Hummocky cross stratification in bluish grey siltstone bed.

Figure 2.6: Interference ripples in the upper sandy part of the varve like siltstone facies.

Figure 2.7: Suspected trails marking of gastropod preserved in the fine grained silty sediments of rhythmite facies.

Figure 2.8: Schematic diagram showing lateral transition of sedimentary units in Talchir formation around Dudhi Nala area.

Figure 2.9: Geological map showing Talchir sequence, Dhenkanal district, Orissa.

Figure 2.10: Suspected stromatolite with concentric growth laminations, resembling cabbage in structure.

Figure 2.11: Striated Vindhyan pavement at Irai, Godavari basin.

Figure 2.12: Thin section photograph showing calcareous fine grained core of a nodule.

Figure 2.13: Picture showing continuation of lamination from host to interior of nodule.

Figure 2.14: Draping of laminations over and around the nodules.

Figure 2.15: Occurrence of nodules as isolated bodies.

Figure 2.16: Compact cementation of nodule at the core, showing presence of growth ring.

Figure 2.17: Succession of sedimentary rocks of different formations in Satpura basin.

Figure 2.18: The lithological units in Satpura valley, Gondwana basin.

Figure 2.19: Schematic representation showing the morphological pattern of calcrete development in motur formation. A field photograph of palaeosol as inset.

Figure 2.20: Denwa formation with internally cross stratified sediments hosting the soil carbonates. (b) Thin section showing development of glaebules and radial fractures.(c) microphotograph of a glaebule. Figure 2.21: Large cylindrical rhizocretions in the palaeosol profile of Bagra formation, Anjan Nala.

Figure 2.22: Histogram showing the distribution of δ -values(carbon and oxygen), in Z-Carrara laboratory standard measured against working gas. Measurements were made in VG602 updated to 903, conversion to VPDB reference done through working gas calibration (based on Table 2.5).

Figure 2.23: Histogram showing the distribution of δ -values(carbon and oxygen), in MMB laboratory standard measured against working gas. Measurements were made in VG602 updated to 903, conversion to VPDB reference done through working gas calibration.

Figure 2.24: Histogram showing the distribution of δ -values for Z-Carrara standard w.r.t VPDB. Measurements were made w.r.t. working gas CD-197 in order to check the long term reproducibility of laboratory standard (based on data shown in Table 2.7). Figure 2.25: Results of analysis of δ^{13} C of CO₂ obtained by combusting the UCLA glucose (laboratory standard) measured w.r.t. working gas during 197-99 work. Conversion to VPDB reference done through working gas calibration.

List of Tables in Chapter 2

Table 2.1 : Stratigraphic correlation of sediments occurring in four Gondwana basins of peninsular India and their equivalent in South Africa, Antarctica and South America.

Table 2.2: Description of samples collected from Talchir formation of peninsular India.

Table 2.3 :Palaeosol samples from Satpura basins and their descriptions.

Table 2.4: δ^{18} O, δ^{13} C values of carbonate check standard MAKMARB (MMB)* (prepared from Makrana Marble, Rajasthan, India) analysed in VG-903 mass spectrometer (1995-98) (50°C online extraction procedure).

Table 2.5: δ^{18} O, δ^{13} C values of carbonate standard new Z-Carrara* (provided by N.J. Shackleton) analysed in VG-903 mass spectrometer (1995-98) (50°C online extraction procedure).

Table 2.6: Typical examples of δ -Values of standard Z-Carrara carbonate run on single day.

Table 2.7: δ^{18} O, δ^{13} C values of carbonate standard new Z-Carrara[†] (provided by N.J. Shackleton) analysed in GEO20-20 mass spectrometer (80°C online extraction procedure, CAPS).

Table 2.8: Comparison of carbonate standard used during experiment measured at PRL(with VG903 and GEO20-20 mass spectrometer) and two other laboratories (Cambridge Univ., U.K. and Cornell University, New York).

Table 2.9: d13C value of UCLA glucose measured along with samples of CO2 obtained from decomposition of organic matter.

Table 2.10: Observed concentration of Fe, Sr, Mn of Laboratory standard NOVA and MAG-1 compared with expected values.

Table 2.11: Comparison of observed concentration of Fe, Sr, Mn with expected concentration in three laboratory check standards (prepared gravimetrically).

List of figures in Chapter 3

Figure 3.1a: Microphotograph of DN/N7 nodule, comprising angular grains of Quartz (Q) and felspar (F) with calcite occurring in pore spaces.

Figure 3.1b: Microphotograph of DN/N1 nodule, indicating presence of micritic carbonates around detrital quartz and felspar grain denoting percolation of saturated carbonate solution in between detritals.

Figure 3.1c: Microphotograph of nodule showing poikilotopic cements replacing pore spaces.

Figure 3.1d: Microphotograph showing presence of biotite, amphibole, plagioclase and felspar within the nodule sample DN/N/2/95

Figure 3.1e: microphotograph of nodule from Bhunipara locality showing Fe rich smectite clay skin and presence of organic matter in isolated patches.

Figure 3.2: (a) Image of sample DN-7 in plane polarised light.

Figure 3.2: (b) CL image of the same section; blue colour are quartz and darker patches denotes clay and felspars. Bright red CL represents carbonates with high Mn/Fe whereas the dull red represents low Mn/Fe. Figure 3.3: Histogram showing frequency distribution of Mn/Fe ratio in carbonate phase of Talchir nodules. Large number of samples have low Mn/Fe ratio indicating alteration subsequent to their formation. NL denotes zone of non luminescent calcite in CL. An average value of Mn/Fe in modern day lake carbonate is shown by arrow.

Figure 3.4a: Frequency distribution of δ^{18} O values in the unaltered nodule with gaussian fit to the data. The mean value is 11.0‰

Figure 3.4b:Frequency distribution of $\delta^{13}C$ values in the unaltered nodules with gaussian fit to the data. The mean value is -11%

Figure 3.5: Proposed schematic picture of glaciofluvial and glaciolacustrine environment leading to Talchir sedimantation and subsequent nodule formation.

Figure 3.6: Covariation plot of oxygen and carbon isotopic ratios in the micritic calcite from nodules and associated matrix.

Figure 3.7a : Variation of oxygen isotope ratio within nodules collected from West Bokaro basin and Ramgarh dasin. Note depleted core and enriched rim in most of the nodules.

Figure 3.7b : Correlation of carbon and oxygen isotope ratios in samples from nodule sections. Green triangle represents Damodar valley nodules whereas red circles denote data for one nodule from Ramgarh basin, which has anomalously low \Box^{18} O at the center.

Figure 3.8a : Growth of calcite lamination parallel to the bedding surface resembling growth and deposition of algal bodies (bar represents 1 cm).

Figure 3.8b : Juxtaposition of separated hemispherical tussocks of different sizes in a thin section of algal carbonate.

Figure 3.8c : Tussocks structure observed in serizia radians, Southwest Africa for comparison (scale bar =100

Figure 3.9a : Carbon and oxygen isotope ratio in algal carbonates from Nandirjhor Nala section.

Figure 3.9b : Carbon isotope ratio in the organic matter associated with algal carbonate from Nandirjhor Nala section.

Figure 3.10: Chondrite normalized concentrations of eight rare earth elements in the nodules of West Bokaro region (Damodar valley). Red curve shows the pattern of REE in the nearby Singhbhum granite (south of the basin).

Figure 3.11: Chondrite normalized concentrations of eight rare earth elements in the nodules of Ramgarh region (Damodar valley). Blue curve shows the pattern of REE in the nearby Singhbhum granite (south of the basin).

Figure 3.12: Chondrite normalized concentrations of eight rare earth elements in the nodules of Talchir basin (Mahanadi valley). Red curve shows the pattern of REE in the basic granulite occurring in the southern part of the basin.

Figure 3.13a: Schematic diagram showing palaeocurrent direction based on earlier studies on sedimentary structures and heavy mineral assemblage. Note Damodar valley sediments are derived from Chotanagpur granite and Talchir basin sediments are derived from granulite belt of Eastern Ghat.

Figure 3.13: Cartoon showing concentration of trace elements and Sr isotopic ratios in postulated provinces and sediments in corresponding basins.

Fig 3.14: Frequency distribution showing Sr isotopic ratio in carbonate nodule collected from three Talchir basins of peninsular India.

Fig 3.15: δ^{18} O vs δ^{13} C plot of soil carbonates from Motur, Denwa, Bagra and Lameta formation of Satpura Gondwana basin.

Fig 3.16: The Palaeogeographic reconstruction of Gondwana landmasses indicates that the peninsular region of India was situated at 500 during Permian and at 40° to 30° during Middle Triassic and Middle Jurassic respectively.

Fig 3.17: Plot of RCO_2 against soil age (in my) where R represent the ratio of concentration of a given age relative to the preindustrial modern value (280 ppmV) compared with Berner's model prediction. The envelope of uncertainty in the model is shown by dashed lines.

Fig 3.18: Change of soil maturity with pCO₂

List of Tables in Chapter 3

Table 3.1 Clay minerals of a few nodules collected from three Talchir basins.

Table 3.2 Ca, Mg, Fe. Sr and Mn concentrations in carbonate phase[†] of Talchir nodules (% and ppm expressed with respect to bulk).

Table 3.3 Stable isotopic composition of Talchir nodules along with sample description

Table 3.3b Calculated excess precipitation required to explain Talchir Oxygen isotope data

Table 3.4 Stable isotopic composition of Talchir nodules and organic matter present in them along with sample description

Table 3.5 - Carbon and oxygen isotopic compositions of samples from core to rim of nodules A, B, C, D and BP/N1.

Table 3.6 Isotopic composition of stromatolitic carbonates and residual organic matter from Nandirjhor nala section, Mahanadi valley basin.

Table 3.7 REE composition of whole rock samples from three different Talchir basins of Peninsular India (in ppm).

Table 3.8 Trace composition of whole-rock nodule (in unit of ppm).

Table 3.9 Ratios used for discriminating the provenance of sediments.

Table 3.10 Strontium isotopic ratios and concentration in the carbonates.

Table 3.11 Isotopic composition of palaeosol carbonates and residual organic matter in the matrix.

Table 3.12. Determination of soil temperature during Motur (260 m.y.), Denwa (240m.y.), Bagra (200m.y.) and Lameta (65m.y.) periods from measured oxygen isotopic composition of soil carbonates and composition of rain water expected during these periods.

Table 3.13 Estimation of concentration of CO_2 at different times in the past a comparison.

Table 3.14 Estimation of concentration of CO_2 and its isotopic composition in atmosphere at different times in the past.

Chapter 1

1.1 Introduction

Gondwana period represents an important time span in Earth history. During this period continental configuration and distribution of oceans were entirely different from today. For example, towards the end of Permo-Carboniferous (277 m.y.) continents were distributed such that 68% of the land area was in the southern hemisphere (joined as a single continent called Gondwanaland) and 32% of the land area was in the northern hemisphere (joined together as a continent called Laurasia). Combined studies from deepsea drilling, seismic survey and palaeomagnetism have allowed delineation of sea-floor spreading and reconstruction of continental plates in geological past. The distribution of landmasses during the Phanerozoic period is now relatively well understood. During Late Permian (255 m.y.), Early Triassic (237 m.y.) and Early Jurassic (195 m.y.) the percentage of continental landmasses in the southern hemisphere was reduced to 62%, 55% and 44% respectively.

Processes involving convection and radiation operating in the ocean, atmosphere and continental surface control global wind pattern. The thermal heat capacity of continental lithosphere is small compared to that of the ocean which leads to temperature difference between continent and ocean. This differential heating drives convection cells which control the regional climate. Therefore, a natural consequence of continental redistribution across the globe is large scale global climatic change. For example, the global circulation is expected to be widely different during Permo-Carboniferous period when Gondwanaland and Laurasia were combined to form a single super-continent called Pangaea surrounded by a single ocean called Panthalasa (**Figure 1.1**).

The climates of Palaeozoic and Mesozoic periods have been intensively studied by using Global Circulation Models (e.g. Kutzbach and Gallimore, 1989; Chandler et al., 1992; Crowley and Baum, 1993; Fawcett et al., 1994; Valdes et al., 1995; Ree et al., 1999). However, many factors external to the climate system need to be specified in order to run the climate models. These factors, known as boundary conditions or forcing factors



Figure 1.1 Schematic representation of Pangean continental configuration during Permo-Carboniferous period.

include land-sea distribution, topography, extent of land and sea ice, land surface albedo due to vegetation, concentration of CO_2 in the atmosphere, solar radiation, and its modification due to changes in orbital parameters at appropriate time period. Most of the factors except atmospheric CO_2 level and continental configuration are usually kept constant for model simulation. Fawcett et al (1994) used NCAR community climate model to simulate the climatic evolution of India and Australia from Late Permian to Mid-Jurassic. This model predicts major difference in simulated climate for India between high CO_2 (2000 ppm) and low CO_2 (280 ppm) conditions during Late Permian. For low CO_2 simulation, no significant summer monsoonal precipitation is predicted. In contrast, in winter mid-latitude storm tracks are expected to cross this region. Calculations show that this scenario leads to an annually uniform precipitation regime. It is also predicted that summer temperature does not rise above 30°C and winter temperature is just near freezing.



Annual precipitation (mm/day)

Figure 1.2 Global map showing mean annual precipitation over Pangaea. Note high precipitation (6 mm/day) in coastal region and widespread aridity in the continental interior (Kutzbach and Gallimore, 1989).

Model calculations for Late Carboniferous (306 m.y.) indicate that extreme summer insolation forcing leads to development of a monsoon that produces a wet pulse penetrating 50° to 60° palaeolatitude (Crowley and Baum, 1993). Kutzbach and Gallimore (1989) demonstrated that the climate of Permian was one of extreme continentality characterized by hot summers, cold winters and large scale summer and winter monsoon circulation for which they coined the term "megamonsoon" (**Figure 1.2**).

An important feature of Gondwana period is the occurrence of an extensive glaciation (**Figure 1.2**) covering most of the southern continents. Late Palaeozoic glacial

rocks of Antarctica, South America, Africa, Australia and India are identified on the basis of lithological features. These include ground moraine, fluvial englacial and subglacial



Figure 1.3 Glacial record from Late Precambrian to Cainozic. Note presence of glaciers in all the southern continents during during Permo-Carboniferous indicating a global scale glacial era (Price, 1999).

deposits, outwash deposits, debris resulting from down slope mass movement of till in a subaqueous environment etc (Frakes, 1992). From global consideration Late Palaeozoic glaciation probably started during Carboniferous and lasted till end of Permian (Price, 1999) but the exact duration of this glaciation is still unknown. Centres of glaciation during Carboniferous were located over Southwest Africa and adjoining parts of South Africa and Brazil. Subsequently, glacial centres migrated towards the eastern continents before the final episode of glaciation in India called Talchir. A great deal is known about this glacial era owing to intensive study undertaken by several workers since its recognition (Hambrey and Harland, 1981; Crowell, 1983; Frakes et al., 1979, 1994). For example, direction of ice movement was studied using striae and grooves, roche mountonnees with stoss and lee features, and friction crescents and cracks. Melting of these glaciers during warm periods released large volume of water and sediments into the respective basins. Early phase of sedimentation in these basins is dominated by glacial boulders and tillites which were subsequently replaced by sand and silty material, higher up in the stratigraphy.

In India, Talchir sediments comprising boulders, sandstone and siltstone are occasionally capped by sediments with marine fossil records (Ghosh, 1954). Considerable information on sedimentological pattern and nature of sediments in Talchir formation have been acquired in the last few decades (Ghosh and Mitra, 1975; Casshyap and Tewari, 1988; Veevers and Tewari, 1995; Bhattacharya et al., 1989; Pandya, 1990). However, many features of Gondwana glaciation in India are yet to be understood and controversy pertaining to their genesis needs to be resolved. In the majority of Gondwana exposures Talchir strata are overlain by coal bearing Barakar formation with intervening deposits bearing signature of continental fresh water regime (Casshyap, 1995). However, in Umaria a marine bed is found sandwitched between Talchir and Barakar formation (Ghosh,1954) assigned Permo-Carboniferous age to this sandwitched marine bed based on fossil assemblage. This marine bed comprises three meter thick limestone containing fossil shells of Productus, Spiriferina, Reticularia etc. Presence of similar marine beds have also been noted in Mahendragarh and Daltonganj locality of central India (Figure 1.4). Exposures containing marine fossils occur in several patches attaining a thickness of up to five meters. The marine fauna identified from these two

sections include *Protoretepora*, *Spirifer*, *Aviculapecten*, *Eurydesma*, *Hyperammina*, *Glomospira* etc. (Bhatia and Singh, 1959). Presence of these marine fossils at Umaria, Mahendragarh and Daltonganj overlying Talchir formation gave rise to the concept of an Inland sea for

Figure 1.4 Suggested marine transgression in Peninsular India during Permian period based on marine fossils found in Mahendragarh, Daltonganj and Umaria shown in the map. A probabble trans-Indian seaway is shown by hatched zone (Ghosh, 1954). The Latitude-Longitude mark denote 8 degree interval.



Talchir sedimentation (Ghosh, 1954). For example, Bose et al (1992) interpreted the morphological (Hummocky cross-stratification) features of the sandstone facies of West Bokaro basin (Dudhinala section) as the product of wave agitated shelf sediments of an open water body (either sea or a



Figure 1.5 Present day variation in oxygen isotopic composition of rainfall at various latitudes given by range of colours corresponding to various δ^{18} O values (IAEA data compiled by Rozanski, 1989)

vast lake). Recently, Sengupta et al (1999) reported presence of external casts of Molluscs from the same place and interpreted this as evidence of marine incursion in West Bokaro. However, absence of marine body fossils in any of the Talchir exposures and question regarding organic origin of external cast raised doubt about the proposed marine environment for sedimentation (Mukhopadhya, 1994; Sen, 1995; Bhattacharya et

al., 1999). On the contrary, association of plant mega-fossils (Rikba horizon) near the top of Talchir, the glacial character of the basal boulder bed and presence of cross bedded sandstone and pebbly conglomerate in the overlying unit are indicative of glacio-fluvial, glacio-lacustrine freshwater milieu (Ghosh and Mitra, 1975). It is now clear that the origin and nature of Talchir sedimentation can not be interpreted unambiguously on the basis of sedimentary structures as these are not always conclusive. For example, hummocky structure is also found associated with sediments from lakes as found in lake Ontario, Canada (Eyles and Clark, 1986). Similarly, herringbone cross stratification commonly associated with tidal waves can also be found in sedimentary records of vast lakes (Sengupta, 1992). Geochemical analysis of Talchir sediments can play an important role in this context. For example, isotopic composition of authigenic carbonates can be used to infer the genesis of the sediments in which they occur. In this work, geochemical composition of carbonate concretions, formed syngenetically along with sediments in Talchir formation have been used in understanding the genesis of the sediments and environment of their deposition.

If carbonate concretions are available in sediments they can be used for resolving the marine/nonmarine controversy for the Gondwana deposits. Geochemical information can also be used for determining the provenance of sediments in the basin. In addition, isotopic analysis of carbonates can be used to derive the composition of meteoric water which, in turn, helps in understanding the hydrological cycle. The isotopic composition of meteoric water is governed by surface air temperature of the location and its altitude, latitude, proximity to the ocean (Rozanskii, 1992). On a global scale, heavy isotopic species ($H_2^{18}O$ and HDO) of rainwater are depleted continuously during transportation from low to high latitudes. Effect of this isotopic fractionation is reflected as a characteristic variation of both δD and $\delta^{18}O$ values of rain water as one moves from equator to pole (Figure 1.5). The rain water composition in the tropics (+1 to -3%) is close to that of ocean water, while the composition gradually decreases (-3 to -12%) in the temperate zones and inside the continent located at high latitudes. The composition of ice in the polar region in winter time is extremely low (up to -62%) (Rozanskii, 1992). This variation must have been present during geological period also as the overall transport mechanism of water vapour from equatorial tropical region to polar region was

similarly operative. However, the composition of rainfall at a given location also depends on the amount of rain in that place. Dansgaard (1964) showed that the isotopic composition of rainfall is inversely correlated with the amount of rainfall. Therefore, isotopic composition of past rainwater at a particular latitude can be compared with contemporary rain in the same latitude and the difference can be quantified in terms of excess or deficiency in amount of precipitation. In this context, ubiquitous presence of carbonate mineral in the sedimentary system is quite useful. The δ^{18} O of carbonate precipitating from a water medium depends on temperature and isotopic composition of the water. In the continental deposits the variation in water composition is usually much more compared to variation in water temperature. Whereas in the oceanic setup variation in temperature mainly governs the isotopic composition of carbonates as the water reservoir is big and relatively constant in composition. If carbonates precipitate in equilibrium condition from water solution (lakes, ocean, river etc.) they can be used to derive the environmental condition (Lord et al., 1988; Faure, 1992; Souchez and Lemmens, 1985; Clark and Fontes, 1990; Gregory et al., 1989; Veizer, 1998). For example, isotopic composition of carbonate in a concretion formed in a lake can help in determination of source of water in the basin. Souchez and Lemmens (1985) measured the isotopic composition of sub-glacially precipitated calcite at the border of a ridge in Swiss Alps (mean δ^{18} O value of -6.77‰) and assuming equilibrium fractionation (1.0347) at 0° C) estimated average value of -10.92‰ for sub-glacial water composition. Hanshaw and Hallet (1978) analysed a few deposits in front of a temperate glacier in the Canadian Rockies to obtain information on the isotopic composition of glacier ice at the time of their formation. Clark and Fontes (1990) measured the isotopic composition of carbonate in travertine and fracture calcite associated with a hyperalkaline spring in Oman. They obtained a wide range of stable isotope ratios. Interestingly large depletions in heavy isotopes (in excess of 10‰ for δ^{18} O and up to 30‰ for 13 C) were obtained in some samples and ascribed to kinetic effects during crystallisation. Carbon and oxygen isotopic compositions were determined in concretions from rocks of Cretaceous age from Australia (Gregory et al., 1989). The carbonate cements have δ^{13} C values between -26.4‰ and 19.6‰ and δ^{18} O values between 3.6‰ and 29.6‰. Assuming that the concretions formed early in the diagenetic history of sediments, the δ^{18} O values were used for determining the isotopic composition of meteoric water in polar region during Cretaceous period. Lord et al (1988) measured δ^{18} O and δ^{13} C in calcites from Pagoda formation in Antarctica and obtained values ranging from -30.7 to -15.5‰ and -1.2 to 2.6‰ respectively indicating strong depletion in ¹⁸O compared to the expected range for modern fresh water carbonates. If equilibrium can be assumed depleted composition of calcites implies that the water from which the calcites precipitated was depleted in ¹⁸O. The depletion is consistent with a non-marine glacial environment when compared to contemporary marine limestone of Permian age whose δ^{18} O values range from -15 to 0.0‰ (Veizer and Hoefs, 1976). Fresh water origin for sediments was established based on carbon and oxygen isotopic composition of sedimentary calcite from Pensacola Mountains in Antarctica (Schmidt and Friedman, 1974). Low δ^{18} O values of 4.9‰ and variable δ^{13} C values of -1.8 to -15.9‰ indicate precipitation of carbonate from glacial melt water. Continental fresh water environment for deposition have also been identified based on isotopic signature (δ^{18} O -7.6‰ and δ^{13} C -9.5 to -4.2‰) of carbonates from Dwyka formation of South Africa (Keith, 1969).

In the marine realm, oxygen isotope data derived from preserved carbonates have been used to infer cool and subfreezing marine condition (Shearman and Smith, 1985, Kemper, 1987). Apart from inferring palaeo-environmental condition these results can be used for determination of rainfall amount and temperature during geological past (Faure, 1992; Gregory, 1988). Some of these information can be useful in providing inputs for the climate models.

Phanerozoic period witnessed large variation in global climate. Most of the time, the Earth was warmer than today and the poles were free of ice. Occasionally the climate reverted to glacial conditions (Fisher, 1984). Occurrence of ice ages in geological past is explained by factors like variation in solar constant, sun earth geometry, continental configuration and amount of green house gases in the atmosphere. Phanerozoic period is also marked by outpouring of huge volume of mantle material into the crust, ocean and atmosphere as evident from identification of two major igeneous activity close to two major geological boundaries: one at Permo-Triassic boundary (Siberian basalt) and the other at Cretaceous-Tertiary boundary (Deccan basalt) (Jablonski, 1996; Raup and Sepkoski, 1986). These events were characterized by expulsion of large volume of water vapor and carbon dioxide into the atmosphere. Release of these gases caused warming of the atmosphere and changed the climate (Manspeizer, 1994). In this context, it is of interest to know the concentration of carbon dioxide in the atmosphere during different geological periods. Geological records indicate several episodes (about 20 clearly recognizable periods) of cooling and glaciation in the Earth history. Interestingly, in a few cases the glacial periods coincide with sudden drop in the pCO₂ level of the atmosphere. A reliable method of estimating the atmospheric CO₂ concentration is by using the isotopic composition of palaeosol carbonate (Cerling, 1991, 1993). Soils present dynamic interface between upper crustal material and atmosphere and record the atmospheric composition through subtle changes in their components. For example, according to the model of Cerling (1991) carbonate nodules formed in situ in a soil have δ^{13} C partly determined by atmospheric pCO₂. Therefore, if these nodules are not changed subsequently by diagenetic process their δ^{13} C can be used to infer pCO₂ in the past.



Figure 1.6 Atmospheric CO₂ versus time for Phanerozoic (past 550 million years). The parameter RCO₂ is defined as the ratio of the concentration of CO₂ in the atmosphere at some time in the past to that at present (i.e. a preindustrial value of 285 ppm). The heavier black line represents the best estimate from GEOCARBII model. The shaded area denotes the approximate range of uncertainty of the model based on sensitivity analysis. Vertical bars represent estimates of CO₂ level based on study of palaeosols (Mora et al., 1996; Sinha and Scott, 1994;Andrew et al., 1995; Ghosh et al., 1995; Yapp and Poth, 1993; Cerling, 1991)

A theoretical model named GEOCARB II describing the CO_2 evolution over the Phanerozoic time has been developed by Berner (1994) (Figure 1.6) and is based on the logical assumption that major source of CO_2 of atmosphere is from volcanic emission and the main removal mechanism is by weathering of continental crust. This model predicts a decline of atmospheric CO_2 level (pCO₂) from Earliest Phanerozoic (550 m.y. ago) value of about 6000 ppmV to the present day value (PDV) of 285 ppmV. The profile of CO_2 changes (**Figure 1.6**) shows a minima (similar to present day value) about 300 m.y. ago, a rapid rise to about 1500 ppmV around 250 m.y. ago and then monotonic decrease to the PDV in Quaternary. This model points to the Palaeozoic era as a period of extreme fluctuation in atmospheric CO_2 level, characterised by 17 fold drop in CO_2 level between Middle and Late Palaeozoic (450 to 280 m.y. ago) and lowest level coinciding with Permo-Carboniferous glaciation (Berner, 1994).

Mora et al (1991, 1996) measured δ^{13} C of pedogenic carbonate from clay rich vertic palaeosols developed in red-bed successions in central Pennsylvania and estimated that the pCO₂ level was 14 times PDV at Silurian. The pCO₂ decrease to 4 time PDV in Devonian and finally touched all time low value of 175 ppm during Permo-Carboniferous (280 m.y.) (**Figure 1.6**). Carbon dioxide concentration in the atmosphere during Miocene and Eocene was ~2 times PDV whereas during Lower Cretaceous, Upper Triassic and Jurassic periods it was 3 to 4 times modern pCO₂ level (**Figure 1.6**). These estimates were made from isotopic ratios of carbon in the carbonate nodules from Africa, Asia, Europe and exposures near Proctor Lake, Texas, USA (Cerling, 1991). The carbon isotope value of the Fe(CO₃)OH in a Late Ordovician Neda formation goethite indicates that CaCO₃ precipitation takes place due to incorporation of CO₂ partly from decomposition of organic matter and partly form atmospheric CO₂ in the medium (Yapp and Poth, 1993). Based on δ^{13} C composition of the carbonate Yapp and Poth (1993) estimated that Late Ordovician pCO₂ level was 17 times PDV consistent with results obtained by Mora et al (1991) (**Figure 1.6**).

In India we have several excellent exposures of fluvial sediments in the central region containing well developed soil profiles arranged stratigraphically providing ideal

sample to study evolution of pCO_2 in Phanerozoic time windows. However, many of these soil profiles are yet to be characterized and explored. Fortunately, many such sequences with soil horizons are capped by thick piles of Deccan lava thus preventing their weathering and loss. These soils can also be used to infer composition of meteoric water in India and thus deduce the rainfall pattern. The shift of Indian Plate from its position in southern hemisphere to its present position is quite large and expected to cause change in wind pattern and climate. These soils provide excellent opportunity to study the environmental changes associated with different position of Indian plate with respect to equator and to validate the prediction of pCO_2 evolution model of Berner (1994).

1.2 Purpose of this study

This thesis undertakes geochemical studies of continental sediments to infer past climatic scenario (in geological time scale) and validate the prediction of present day climate model and CO_2 evolution model. The specific objectives are explained below.

Gondwana sediments were recognised as of fluvial origin, deposited in gradually sinking inland basins forming large river valleys interspersed with lakes. The possibility of marine, esturine, brackish delta front or tidal flat set up was not considered in view of the sediment characters (Sen, 1995). However, higher up in stratigraphy presence of marine beds was noticed first in Umaria and later in Mahendragarh and Daltanganj. These beds lie in between Talchir diamictite and Barakar coal deposits. More recently, marine signatures are suspected even in inland sediments of Talchir period (Sengupta et al., 1999; Mukhopadhyay, 1996; Chandra, 1992) from West Bokaro, Ramgarh, Raniganj and Karanpura coal field. In view of this it is interesting the know the geochemical composition of insitu carbonate bodies in Talchir sediment strata and characterize the depositional environment of these bodies. An attempt is made here to resolve the controversy about marine/nonmarine character of Talchir sediments using oxygen and carbon isotope ratios in the carbonate. In addition, trace elemental and rare earth element (REE) analyses of bulk samples is used to identify the source area of sediments and their provenance.

Soils are important constituents in weathering profile of rock and they represent interface between atmosphere and lithosphere. Soils are made up of detritals and authigenic precipitates and occasionally contain nodular carbonates in arid to semiarid region. These carbonates are ideal materials for pCO₂ estimation by using a model developed by Cerling(1991). Earlier, several workers (Cerling, 1991; Mora et al., 1996; Andrew et al.,1995; Ghosh et al., 1995) have demonstrated the usefulness of soils for atmospheric CO₂ determination. In central part of India sequences of strata are available belonging to the Phanerozoic period where sedimentation is frequently interrupted by development of soils. Several such soil horizons have been analysed to understand the climate and atmospheric CO₂ composition in geological past.

1.3 Outline of the thesis

Chapter I gives the Introduction to the thesis, summarizing the current development and current ideas in the field of carbonate sedimentology in the context of isotope geochemistry. This chapter also describes Gondwana deposits of Peninsular India and their relationship with contemporaneous deposition elsewhere in Southern continents. Nature of deposition, sedimentary structures and previous attempt on geochemical studies of carbonates are also described in this chapter. This chapter draws attention for further investigation of various sedimentary records and emphasizes the need for more critical studies of sedimentary geology from geochemical point of view.

The analytical procedures for stable and Sr isotope measurements of inorganic carbonate are discussed in Chapter II. This chapter also describes technique of separation of organic matter from soil carbonates, experimental procedure for analysis of organic carbon and nitrogen, and procedure of chemical analyses of carbonates using ICP- AES, AAS and neutron activation.

Chapter III is divided into two sections. Section A describes the observation on Talchir carbonates. This section contains tables with results of chemical and isotopic analyses of Talchir carbonates from various Gondawana basins of Peninsular India and describes their implications in determining the environment of deposition. This chapter discusses extent of alteration of carbonates during diagenesis inferred from clay mineralogy and supporting evidence from sedimentological point of view. This chapter also attempts to delineate the effect of megamonsoonal climate on the precipitation hydrology of the basin. Last part of this section describes the discovery of stromatolite like bodies from Talchir basin of Orissa, their resemblence with modern algal deposits and the use of stable isotopes in identifying their genesis.

Section B, describes pedogenic carbonates from three different formation of Satpura basin and results of their isotopic analysis. This chapter also contains description of Cerling's model on soil carbonate and put constraints on CO_2 evolution model of Berner. Chapter IV, summarizes important findings of the dissertation gives suggestions for future work.

Chapter 2

Materials and Experimental Techniques

The primary goal of this thesis, as outlined in Chapter 1, is to obtain information on the environment of deposition of Permo-Carboniferous Talchir sediments and related climate and infer the carbon dioxide concentration during Permian to Cretaceous period. This goal is sought to be achieved by geochemical and isotopic study of carbonates which occur as concretions and pedogenic nodules in the Gondwana sediments of India. These sediments are presently exposed in various parts of central India and have been mapped and stratigraphically classified by Geological Survey of India (Ghosh and Mitra, 1975). Various Gondwana basins of peninsular India hosting these sediments have been identified and named (Veevers and Tewari, 1995). In this chapter, geology of the area of sampling, criteria for sample selection and various experimental methods employed for geochemical analyses are described. At first, a brief description of the geology and stratigraphy of these basins is given.

2.1 Geology and Stratigraphy of Gondwana basins

The sediments overlying the Proterozoic rocks and Precambrian shield of Gondwana countries (South America, Africa, India, Australia, and Antarctica) were deposited during a long period spanning 290 to 65 m.y.. These are collectively designated as Gondwana supergroup. Gondwana sediments are beautifully exposed in four major basins in peninsular India, viz., Damodar valley, Son-Mahanadi, Pranhita-Godavari and Satpura (**Figure 2.1**). Stratigraphic correlation of sediments occurring in these four basins is given in **Table 2.1**. These deposits represent 6000-meter thick succession of glaciolacustrine, glaciofluvial, fluvial and deltaic sediments. However, a complete sequence (comprising all the sedimentary formations from base to top) is not found at any single location and completeness of the stratigraphy is established based on composites from many sections.



Gondwana formations are defined based on lithology, colour, and plant fossils present in them (Ghosh and Mitra, 1975). The basal unit is known as Talchir formation and is composed of glacier derived boulders, tillites, diamictites, varves and green needle shales. Talchir formation is considered to be Permo-Carboniferous in age (Gzellian-Asselian) based on presence of marine fossils (*Eurydesma-Connularia-Productus fauna*) in a bed overlying the Talchir boulder bed at Umaria and Mahendragarh of central India (Ghosh, 1954; Bhatia and Singh, 1959; Sastry and Shah, 1964). Occasionally Talchir formation contains minor amount of plant fossils of seed ferns like *Gangamopteris cyclopterides* and *Glossopteris Indica* and its characteristic stem *Vertebraria Indica* (Tewari, 1999). A rich

Time Damodar valley Mahanadi valley Godavari valley Satpura valley South Africa Antarctica South America m.y. 65 Lameta Formation Chikiala Formation Cretaceous Bagra For No Deposition No Deposition

 Table 2.1 Stratigraphic correlation of sediments occurring in four Gondwana basins of peninsular India and their equivalent basin in South Africa, Antarctica and South America (after Veevers and Tewari, 1995).

assemblage of pollens has also been reported from this formation. In a succession, Talchir formation is overlain by a sequence of coal-shale-sandstone cycle belonging to Karharbari and Barakar formations. Prasad et al (1995) have assigned Early Permian age (Artinskian to Kungurian) to Barakar formation on the basis of pollen assemblage: Scheuringipollenites-Faunipollenites. The formations above Barakar are: non coaliferous Barren measures, coal bearing Raniganj formation, and Panchet formation. Chatterjee and Chowdhury (1974) based on vertebrate fossils (Gondwanosaurus bijoriensis, Rhinosuchus wadiai, Dicynodonts and Detocephalus) assigned a Late Permian age to Raniganj formation. The age of Panchet formation is considered Early Triassic on the basis of Lystrosaurus, Chasmastosaurus, Brachyops leticeps and Amblypteris (Chatterjee and Chowdhury, 1974; Tewari, 1999). Panchet formation is overlain by Supra-Panchet formation whose age ranges from Middle Triassic to Late Triassic based on presence of characteristic pollens (Tewari, 1999). Comparable assemblage has been described from Denwa formation and Tiki formation of Satpura valley (Maheshwari et al., 1978; Nandi, 1996). The faunal assemblage of Denwa formation is dominated by *temnospondyls* (Parotosuchus) belonging to Early Anisian age (Mukherjee and Sengupta, 1998). Bagra formation belonging to Satpura valley is considered to be Late Triassic based on its relationship with underlying Denwa sediments (Singh and Bose, 1977). Bagra formation in sedimentary succession is conformably overlain by Early Cretaceous Jabalpur formation. Late Cretaceous eruption of Deccan basalt covered these sediments in many places and prevented their weathering and removal.

Sediments from Talchir formation in Damodar, Mahanadi, and Godavari valley basins were investigated for deciphering glacial palaeoenvironment while three formations (Motur, Denwa and Bagra) from Satpura valley were searched for palaesols for atmospheric CO_2 studies. Description of each of these basins and nature of samples collected are given below.

2.1.1 Damodar valley Basin

Faure (1992) showed the usefulness of stable isotope composition of carbonates (present in concretions from Permian Pagoda formation in Antarctica) to distinguish between marine and nonmarine sediments (**Table 2.1**). In case of non-marine carbonates the isotopic composition of meteoric water can be derived and information about atmospheric water circulation can be obtained. With similar ideas carbonate concretions from Talchir formation of Damodar valley basin were collected.

Damodar valley basin belonging to Gondwana supergroup is composed of several sub-basins in which Talchir formation is present only in the eastern and western flanks. It is also noticed that complete lithological sequence occurs only in the western margins of these sub-basins (Ghosh and Mitra, 1975). Among these, West Bokaro sub-basin offers an excellent exposure of varied sedimentological units and was chosen for the present study. Presence of carbonates as concretions and lensoidal beds was first noticed in a few exposures of siltstone bed in West Bokaro basin. Afterwards, carbonate nodules were also found in Ramgarh sub-basin (part of Damodar valley basin). Majority of the samples (**Table 2.2**) were obtained from the confluence of Dudhi Nala, Dube Nala and Silai Nala located at about 0.5 km south of the village Jarwa (lat. 85° 27' and long. 23° 49'; **Figure 2.2**). On the basis of lithological assemblages and their sedimentary structures the deposits of Dudhi Nala section can be divided into six major facies or units (presumably these units deposited one after another in response to variation in water depth in a lake):



Unit 1 consists of a basal matrix supported conglomerate bed lying above the granitic basement. The conglomerates contain poorly sorted clasts which are angular and resemble the granitic rocks of the Archaean basement.

Unit 2 consists of a bluish grey siltstone facies containing the calcareous nodules studied in the present work. This unit overlies the basal diamictite with profuse development of ripple drift lamination, oppositely oriented climbing ripple lamination and hummocky cross stratification. Localised pebble beds similar to channel lag deposits were found. Towards the top, this grey siltstone changes to a fine grained yellowish sandstone exhibiting large trough cross bedding. (**Figures 2.3, 2.4 and 2.5**).

Unit 3 is a greenish grey varve-like siltstone with sinusoidal ripples, flame structure, convolute laminations. At the upper part, this unit changes to a sandy facies showing interference ripples (**Figure 2.6**) and straight-crested bifurcating tuning fork type ripples. Climbing ripple lamination is also noticed in sandy facies.

Unit 4 cosists of a bluish grey rhythmite facies comprising a unit with couplets of calcareous siltstone and shale overlain by another unit with alternate brownish yellow

 Table 2.2 List of samples collected from Talchir formation of peninsular India.

Dudhi nala section, West Bokaro sub-basin, Damodar valley				
Sample	Description			
DN/N2/95, DN01, DN1a, DN5a, DNM7, DNM18	5 to 6.5 cm major axis, ellipsoidal nodule, composed of carbonate, Cross section homogeneous, collected from siltstone horizon with ripple drift lamination.			
DN6-1, DN6-a, DNM8, DNM9, DNM11, DNM14	7 to 9 cm diameter irregular shaped nodule, composed of carbonate, Core compact and rim dominated by detrital (clasts), collected from siltstone associated with secondary boulder bed.			
DN-3, DN7, DNM13, DNM12	9 to 12 cm diameter discoidal nodule, composed of carbonate, lying above the horizon of DN-2 nodule associated with compound nodules.			
DN-2, DN7-2	7.1 cm diameter spherical nodule, composed of carbonate, host rock is calcareous siltstone with ripple drift lamination.			
DN-4, DN5b, DN5c	4 to 5 cm diameter spherical nodule with matrix material, collected from a place close to fault zone, chips of shale fragment were found inside the nodule.			
DN/1a/95, DN-1, DNO(2), DN02	7 to 9 cm diameter spherical nodule, composed of carbonate, host rock is calcareous siltstone.			
DN3A-1	Three nodules coalesed together to form compound nodule, elongated and bortroidal in shape, collected from Silahi Nala.			
SN3A	5.8 cm diameter spherical nodule, composed of carbonate, host rock is calcareous siltstone.			
Barkipunu section, Ramgarh sub-basin, Damodar valley				
Sample	Descriptions			
BP/N1	Highly compact, ellipsoidal body, 10cm major axis length, dark grey in colour, presence of concentric growth rings around the centre, compact core and coarser rim.			
BP/N2	Nodular body, spherical shape, 8 cm diameter, megacryst of felspar with corroded rim, bimodal distribution of detrital grains surrounding the core.			
BP/N3A	Discoidal body, 12cm in diameter, concentric growth ring, dislodged from calcareous siltstone where it was firmly attached.			
BP/N3B	20 cm disc shaped concretion, dislodged from the calcareous siltstone bed, several generation of calcite precipitation, presence of neomorphic calcite is noted.			
BP/M1	Matrix, sandstone with calcareous cement			

Talchir sub-basin, Mahanadi valley		
Sample	Description	
BR/N1,	Nodular body, ~5cm in diameter, spherical in shape, host rock is calcareous sandstone, highly altered (collected from Baroghat area).	
BR/N2	5.8 cm diameter spherical nodule with a clay nuclei, composed of carbonate, host rock is calcareous siltstone (collected from Baroghat area)	
BR/N3	Highly compact 7cm size nodular concretion, clay rich core with less carbonate while rim is clast dominated with carbonate (collected from Baroghat area).	
BR/N5	Disc shaped, 10 cm in diameter, compact body, calcareous in nature, surface with solution features indicating alteration (collected from Baroghat area).	
BR/N11	Disc shaped, 14 cm in diameter, less calcareous and more clayey (collected from Baroghat area).	
BH/N6	5 cm size nodular body with signature of recent alteration on the surface, clay dominant (presence of chlorite as green patches). (collected from Boudh locality)	
BH/N3	Lensoidal body, ~5cm major axis length, irregular shape with crenulated boundary, host rock is calcareous sandstone, highly altered(collected from Boudh area)	

BH/N1	Highly compact 6 cm size nodular concretion, clay rich core with less carbonate
	while rim is clast dominated with carbonate (collected from Boudh area)
BH/N5	Carbonate nodule, collected from the Bank of Mahanadi river, alteration features
	like cracks and iron oxide precipitation visible, clayey in composition, 10 cm in
	size.
BR/N4	Spherical Nodule, 5 cm in radii, composed of carbonate cement, clasts are
	pebble sizes, present in the rim (collected from Baroghat area).
BH/N7	5.8 cm diameter spherical nodule with a clay core, carbonate dominant, host
	rock is calcareous siltstone (collected from Boudh area)

Irai river section, Godavari valley				
IR/COM/M1/97	Lime mud (micritic) surrounding the detrital rock fragments, quartz, and feldspar.			
Dwyka tillite, Karoo formation, South Africa Dwyka tillite, Karoo formation, South Africa				
DW-1	Ellipsoidal nodules, 4.3 cm diameter, gery coloured with clay rich interior and			
	carbonate rich outer rim.			
DW-4	Spherical nodular, 7.6 cm diameter, Dark grey carbonate with clay rich outer rim			
	and calcareous core is noted.			
DK/1/95	Spherical body, 8.7 cm diameter, similar in appearance as Talchir nodules,			
-	concentric growth rings present.			
Stromatolite and nodule from Nandir Jhor nala section, Angul, Orissa				
Sample	Description			
NDJ/ST2/95,	spherical body, 50 cm diameter, collected from limestone bed, cabbage shaped,			
NDJ/ST6/95	collected from Nodular shale horizon.			
NDJ/N1/95	Spherical body of limestone, matrix made up of carbonate cement, signature of			
	alteration at the outer rim.			
NDJ/ST1/95	Limestone with layer parallel laminar deposition of carbonate and clay, similar to			
	Travertines or Stromatolitic.			
NDJ/ST4/95	Coarse grained, laminated carbonate, stromatolitic in appearance, associated with			
	Talchir shale substrata as discrete body.			
NDJ/ST3/95	Nodular carbonate, compact and dark grey in colour, stylolites growth observed on			
	the surface of cross section.			
NDJ/ST7/95	Nodular carbonate, dark coloured body, altered carbonate crystal, resembling the			
	stromatolitic structures in the outcrop.			
NDJ/ST8/95	Flaky structures, in between concentric laminations presence of clay material is			
	noticed, grey colour .			
NDJ/ST5/95	Very coarse fibrous samples composition.			
C1, C-3	Lensoidal body of carbonate, associated with calcareous siltstone, reflect effect of			
	precipitation of carbonate from the solution			
NDK-5, NDK-A1	Laminated nodule associated with carbonate band, grey in colour, carbonate rich			
	compact body, ripple drift lamination observed in the hand specimen			
RH/NDJ8/95	Recystallised spars of calcite, probably formed during late diagenesis and re-			
	precipitation process, varve layer in the carbonate body dsitinguishable.			
AN-1	Large body of nodule (10.7 cm), carbonate rich core and detrital rich rim, described			
	as mudball by Seth and Sen, 1998			

sandstone and chocolate brown shale. The sandstone layer pinches laterally. This facies was identified as turbidities by earlier workers (Banerjee, 1966; Ghosh and Mitra, 1975). The calcareous siltstone bed of the lower unit is characterised by wavy laminations,

hummocky structures and occasionally trail-marking of gastropod (**Figure 2.7**). Closer examination of individual layers of the rhythmite unit reveals the development of planer sandstone and chocolate brown shale. The sandstone layer pinches laterally. This facies was identified as turbidities by earlier workers (Banerjee, 1966; Ghosh and Mitra, 1975). The calcareous siltstone bed of the lower unit is characterised by wavy laminations, hummocky structures and occasionally trail-marking of gastropod (**Figure 2.7**). Closer examination of individual layers of the rhythmite unit reveals the development of planer



Figure 2.6 Interference ripples in the upper sandy part of the varve like siltstone facies (diameter of the lens hood 5.5 cm)



Figure 2.7 Suspected trail marking of gastropod preserved in the fine grained silty sediments of rhythmite facies.

lamination or wavy lamination draping over the small ripple lamination. Calcareous nodules are present but are not as profusely developed in these fine-grained sediments as in the earlier facies. Polished section of nodules shows faint development of growth rings cross cutting early-formed structures. In upper part of the rhythmite facies the bluish grey calcareous siltstones are replaced by thick sandstone layers, marked by ripple drift
lamination and planer lamination. Impression of plant leaves (*Gangamopteris sp.*) is occasionally present in these sediments.

Unit 5 lies towards the deeper part of the basin where sandstone predominates over calcareous siltstone and shale. The lower bluish grey calcareous siltstone of the rhythmite facies changes colour to chocolate brown and the upper sandy rhythmite loses its identity as a rhythmite and is replaced by bedded sandstone layers of limited lateral extent. Talchir rocks of Dudhinala section were faulted and folded with the intrusion of a lamprophyric dyke. A schematic diagram of the lateral transition of sedimentary sequences is given in **Figure 2.8**.



Figure 2.8 Schematic diagram showing lateral transition of sedimentary units in Talchir formation around Dudhi Nala area. FF denotes fault. Some of the characteristic sedimentary features observed in different units are also shown (A=Hummocky structure in the sedimentary unit, B=Nodules in the siltstone bed, C=Gloss-opteris leaf fossil in the shale and D= ripple drift lamination in the sandstone).

2.1.2 Mahanadi valley Basin

An exposure of Talchir sediments in Mahanadi valley basin occurs near Angul village of Dhenkanal district, Orissa and has been described by Pandya (1990). Talchir sediments were first discovered at Talchir, Orissa by Blanford et al (1859) and consist of tillites (Boulder bed) succeeded by shale and sandstone. This section is considered as the type area of Talchir formation. The Boulder bed consists of an unsorted mixture of

boulders, pebbles, rock fragments and clay; the boulders often show facets and striations denoting glacial origin. Talchir Boulder bed is overlain by siltstone, sandstone and shale; the shale is greenish in colour and breaks into prismatic (hexagonal cross section) fragments and therefore described as needle shale. Most of the exposures investigated here lie around the southern boundary of the basin, near Bedasar village (lat. 20°52″30′ long. 85°40″; **Figure 2.9**), Dhenkanal district, Orissa. Talchir sequence in this area is divisible into three lithological units: Boulder bed, Fine sandstone, and Blue nodular shale (Pandya, 1990). Pandya discovered striated pebbles in the Boulder bed unit and confirmed the glacial origin for them. Limestone associated with the nodular shale is buff to brown in colour and is composed of coarsely crystalline fibrous carbonate. Nodular concretions occur

sporadically as ellipsoidal bodies and disc shaped objects with concentric rings. Sometimes many of them coalesce together to form lensoidal body of limestones.

While searching for carbonate nodules in Bedasar area we came across a type of objects having carbonate as major mineral but with unusual texture quite unlike the compact nodules. They occur above the strata which contains the nodules. They are about 20 to 30 cm in size and have concentric laminations resembling head of cabbage in structure and texture (**Figure 2.10**) and are similar to stromatolites described from Otavi

series of south west Africa (Kruger, 1968). These were also found by Pandya (1989) who described them as oncolites. Mohanti et al (1998) analyzed their thin section by SEM and showed the presence of bacterial colony resembling cyanobacteria. Interestingly, Srivastava et al (1995) have identified trace fossils of *Cruziana* family from the nodular shale bed in this area. Eight such objects were collected from Nandirjhor Nala section shown in **Figure 2.9**.



Figure 2.10 Suspected stromatolite with concentric growth laminations, resembling cabbage in structure (pen 12 cm in length)

2.1.3 Godavari valley Basin

Among all Gondwana basins Talchir formation Godavari valley basin has received maximum attention (Smith, 1879; Crowell, 1916; Frakes and Crowell, 1976; Smith, 1974) because of the presence of striations in the Vindhyan pavement confirming the hypothesis of glacial origin for overlying boulder beds. Fedden (1874) was the first to identify the striations in the pavement and explain their significance. Smith (1974) studied the



Figure 2.11 striation on Vindhyan limestone at Irai river section, Godavari basin. Note a prominent direction of ice movement.

orientation of the striations (**Figure 2.11**) in the Vindhyan pavement situated near the village of Irai (on the eastern bank of river Penganga about 1 mile to the south of its confluence with the Wardha river) and inferred a northward movement of the glacier ice. This locality is about 10 miles west- southwest of Chanda. Development of nodules was observed in the shale and varve sediments overlying the striated pavement. However, most of the nodules are highly altered and friable due to weathering aided by the river. We have collected a few tillites with carbonate matrix from the underlying beds (**Table 2.2**).

2.2 Development of concretions in siltstone bed and their classification

Selles (1996) visualized the development of concretion as a precipitation process caused by local concentration of mineral species, earlier dispersed as secondary component in the host sediment. The details of this process involving multiple stages will be discussed later. The carbonate nodules investigated here occur mostly in the fine grained siltstone facies overlying the conglomerate bed. They are round to oval in shape and are found scattered randomly in the siltstone bed. Cross section of a nodule shows fine-grained, dense and homogeneous core and coarse grained, porous and heterogeneous rim (a thin section is shown in Figure 2.12). Sometimes they occur as irregular shaped bodies within the siltstone bed. Shape of the concretion is governed by depositional conditions and hydraulic parameters, which are intricately linked. A few attempts have been made earlier to estimate the time required for the growth of a concretion under similar conditions. Pantin (1958) based on ¹⁴C measurements of a 23 cm diameter nodule inferred a range of 7500 yr. to 20,000 yr. for its growth. Boles et al (1985) obtained figures of 140,000 yr. and 4 m.y. for two giant concretions having diameter 36 cm and 190 cm respectively. The concretions in the present study are only 1.5 to 15 cm in diameter (Table 2.2). They are much smaller than the ones studied by Pantin (1958) and Boles et al (1985) and probably took less time for growth. The cement within the concretion is mostly authigenic in nature. This is suggested by several features: i) visible



Figure 2.12 Thin section photograph of a nodule showing core of calcareous fine grained material.

continuation of ripple drift lamination from the bedding plane to the interior of the nodule (**Figure 2.13**), ii) draping of laminations over and around the nodule (**Figure 2.14**), iii) occurrence of the nodules as isolated bodies without any visible disturbance of the underlying layers of the sediments (**Figure 2.15**) and iv) the cement is more dense (i.e. less detrital particles) at the core compared to the rim (**Figure 2.16**). A similar set of criteria was adopted by Selles (1998) for inferring syngenetic character of concretions.

Although there is large variation in the outer appearance of these nodules, broadly three types can be classified based on their shapes.

- 1. Tennis ball shaped, composed of same material as the host rock i.e. arkosic sandstone.
- Discoidal nodules embedded in siltstones, which often display multiple growth giving rise to many bizarre shapes.
- 3. Round to irregularly shaped nodules outcropping as flat plates on the surface of the varve-like siltstone.





2.3 South African nodules

Dwyka tillite of Permo-Carboniferous age lies at the base of Gondwana sequence of Karoo basin of South Africa and has been correlated with Talchir formation of Indian Gondwana (Crowell, 1991) based on similarity of lithology, stucture and fossil record. Interestingly, carbonate concretions are also observed in the sediments of Dwyka formation (Brunn, 1991) similar to the nodules in Talchir sediments in India. Four such concretions were given to us by Prof. Von Brunn of South Africa for isotopic analysis.

2.4 Satpura valley Basin

Gondwana succession of Satpura valley Basin of central India is composed of sedimentary deposits ranging in age from Permo-Carboniferous to Late Cretaceous. The succession is about 5 km thick (**Figure 2.17**) comprising alternate layers of coarse clastics (sandstones along with extrabasinal conglomerates) and fine clastics (red mudstone / carbonaceous shale / white mudstone). The basal unit of this succession is again the glacio-lacustrine Talchir formation comprising boulders, diamictites and sandstone beds.



The series Figure 2.17 Succession of sedimentary rocks of different formations in Satpura basin. odes of alluvial deposition (Crookshank, 1936; Robinson, 1967; Casshyap and Tewari, 1988; Casshyap and Qidwai, 1971; Casshyap et al., 1993; Veevers and Tewari, 1995; Ghosh, 1997). Occurrences of fossil vertebrates (Chatterjee and Roychowdhury, 1974; Mukherjee and Sengupta, 1998; Bandyopadhyay and Sengupta, 1998) and fresh-water bivalves coupled with evidence of pedogenesis like presence of rootlet horizons, palaeosol profiles etc. (Ghosh et al., 1995, 1997, 1998; Ghosh, 1998; Tandon et al., 1995, and 1998) attest to the alluvial origin of these sediments.

As mentioned before, soils and soil carbonates are the objects of investigation in the present study. However, soils in old sediments like Gondwana sequence are rare as soil development requires stable platform, suitable climate, growth of vegetation and time. Soils represent pauses in sedimentation and involve considerable time in a sedimentation history. Preserved calcic palaeosols have been identified in four stratigraphic levels of Satpura valley Basin: Motur, Denwa, Bagra and Lameta formations (Ghosh et al., 1995, 1997, 1998; Tandon et al., 1995, 1998; Andrews et al., 1995). These formations are believed to have formed during Early Middle Permian (260 m.y.), Middle Triassic (240 m.y.), Jurassic (200 m.y.) and Late Cretaceous (65 m.y.) respectively (Raja Rao, 1983; Bandopadhyay and Sengupta, 1998; Casshyap et al., 1993; Satsangi, 1988; Chatterjee and Roychowdhury, 1974). Motur formation in Satpura valley was initially correlated with Barren measures overlying Barakar formation in Damodar valley Basin (Crookshank et al., 1883). However, subsequent studies have shown that Motur formation belongs to middle Permian based on the presence of vertebrate fauna (Raja Rao, 1983; Peters, 1991). Vertebrate fossils recovered from Denwa formation are similar to middle Triassic fossils present in Yerrapalli formation of Pranhita Godavari basin (Satsangi, 1988). Casshyap et al (1993) proposed that Bagra formation should be Late Triassic in age based on its relationship with underlying Denwa formation. Since Deccan basalts capping Lameta formation has been dated at 65 Ma, the formation itself is believed to be Late Cretaceous.

Identification of palaeosols in the field is based on the presence of pedogenic features. Machette (1985) has proposed a comprehensive classification involving six stages of soil development. Based on the observed features in various types of soils Mack et al (1993) showed that highly weathered soils such as Ardisol, Spodosol and Gleysols are more apt to form in humid climate (mean annual precipitation more than 1000 mm), whereas Calcisols are indicative of a dry (mean annual precipitation less than 1000 mm) climate zone. Among these various types of soils pedogenic calcretes can form within Aridisols, Vertisols and Mollisols (Soil Survey Staff, 1975) and usually occur in several discrete horizons. These carbonates or nodules associated with certain class of palaeosols are mostly associated with the root zone of the plant and are formed due to precipitation of carbonate grains from the solution during plant respiration (Cerling, 1991).



Figure 2.18 The lithological units in Satpura valley, Gondwana basin.

A set of criteria was adopted for selection of samples for isotopic analyses. The carbon isotopic composition of the pedogenic nodule is governed by its vertical position in the pedo horizon (Cerling, 1991). In arid soils where carbonate precipitates at soil air interface, the isotopic composition of soil carbonate formed in the upper 10 cm varies considerably (Cerling, 1991). Several studies have shown that isotopic composition of soil carbonate is essentially constant below ~20 cm depth (Quade, Cerling and Bowman, 1989). Therefore, soil carbonates for the present study were collected from depths greater than 20 cm. Description of the sediments from Motur, Denwa and Bagra formations is given below.



2.4.1. Motur formation at Eklahara

An exposure of Motur sediments was found on the bank of Pench river near Eklahara (Lat.22°12'N& Long.78°41'E; Figure 2.18). In this area we could identify two soil profiles. One is only 50 cm thick whereas the other is quite thicker (3 to 4 m) as shown in **figure 2.19**. The thinner palaeosol profile contains an uppermost horizon of platy coalesced glaebules, 3-5 cm thick, overlying a 10 to 30 cm thick horizon containing closely spaced vertically oriented rhizocretions. The rhizocretion zone grades downward to a zone rich in subspherical glaebules that overlies a gleyed zone. The thicker variety of palaeosol profile of Motur formation has 1.2 meter thick upper zone characterized by curved, mutually intersecting subvertical fractures within the claystone host. The horizon underlying this zone of fractures is characterized by small subvertical, dispersed, calcareous rhizocretions. This zone is underlain by a thin (3 to 5 cm thick) zone of subspherical glaebules overlying a gleved horizon (~ 20 cm thick). These palaeosols are similar to modern Vertisols. Vertisols develop mainly on the clayey substratum and are characterized by large cracks in their upper part formed due to expansion and shrinkage of the clays, at the Bk horizon. The fractures allow non-diffusive penetration of atmospheric CO_2 deeper down the soil profile and hence these parts also are not suitable for palaeobarometry work. Samples were collected from the horizon of spherical glaebules and from the basal part of the rhizocretion zone (similar to the Bk horizon of modern arid

soils). A total of 23 samples (Table 2.3) were collected from two soil profiles.

2.4.2. Denwa formation at Taldhana

Denwa formation is 300 to 600 m thick and conformably overlies the coarsegrained fluvial sandstone bodies of Panchmari formation. Its lower half contains alternate beds of medium to fine-grained, thick (3 to 15 m) fluvial channel sandstone and floodplain deposits (**Figure 2.20**). The floodplain deposits are comprised of red mudstones intercalated with centimeter to decimeter thick, fine-grained sandstone layers. In contrast to the lower part of the formation, the upper part is dominated by fine grain sediments. The red mudstones encase 2 to 4 m thick, fine-grained (fine sandstone and siltstones) point bar deposits and cm-dm thick lenticular channel deposits. The channel deposits are



Figure 2.20 (a) Danua formation with internally cross stratified sediments hosting soil carbonates (b)Photo-micrograph of pedogenic gleabules, note the spar-lifted cracks within the calcareous matrix of the gleabules (c) Photo-micrograph of a gleabule. Note the sharp and rounded outline of the gleabule and the spar-filed (glother) circumanular crack. (Lar shown in the photo 0.05 mm in length).

comprised of pet

nally containing

fragments of verteorate rossns. These boules are internary cross summed. The glaebules are subspherical in shape and composed of micrite and minor microspar. Occasionally, sand sized detrital quartz grains, floating in the groundmass of carbonate, can be seen within these glaebules (**Figure 2.20a**). A number of glaebules show radial fractures filled with either blocky spars or barite. Spar-filled, circum-granular cracks have also been noted in some of the glaebules along with pedogenic features like clotted micrite and corroded detrital quartz grains (**Figure 2.20b**). These features provide indirect evidence

of pedogenesis in the fine sandstone and siltstone parts of Denwa sediments. However, only a few such exposures could be identified in the upper part of the formation for which incomplete preservation seems to be responsible. 12 samples of soil carbonate were collected from this formation (**Table 2.3**). The samples are mostly comprised of glaebules from the channel-fill bodies. The rhizocretions from the basal part of the upper pedo-horizon and the underlying glaebules were sampled from exposures near Taldhana village (between lat. 22°38'N&22°35'N and long. 78°20'E&78°38'E, **Figure 2.18**).

2.4.3 Bagra formation at Anjan Nala

Bagra formation overlies unconformably Denwa formation and is overlain by fluvial sandstones and white claystones of Jabalpur formation. Thick units of polymictic conglomerates and pebbly sandstones, interbedded with red claystone units (total thickness varying between 250 to 500 m) characterize Bagra formation. The internal architecture of the clastic bodies indicates that most of them were deposited within the channels of braided streams whereas the claystones were formed in the associated floodplains. The palaeosol profiles are mostly associated with these floodplain deposits and are found in the lower half of the formation. At places, pedogenic modification extends up to the coarse grained abandoned channels and the wings of the main channel bodies. The palaeosol profiles are 70 cm to 2 m thick. They are characterized by a 10 to 50 cm thick well-developed horizon of fused calcareous glaebules at the top. A thick to very thick (50 cm to 1.5 m) horizon of closely spaced, vertically oriented, large cylindrical rhizocretions occurs below the top glaebule horizon (Figure 2.21). The crosssectional diameter of the rhizocretions ranges from 3 to 5 cm and the length ranges from 30 to 100 cm. The rhizocretions internally show two distinct co-axial cylindrical regions with a sharp



Figure 2.21 large cylindrical rhizocretions in the palaeosol profile of Bagra formation,

contact in between. The inner region (1 to 2.5 cm in cross-sectional diameter) comprises large spars and minor carbonaceous clays while the outer region is made up of reddish grey micritic limestone. The field features of the palaeosol profiles of Bagra formation are comparable to the present day aridisols with a well-developed K-horizon at the top and a thick Bk horizon below it. A total of 29 samples were collected from different palaeosol profiles of Bagra formation between lat.22°35′N&22°40′N and long.78°18′E &78°37′30″E (**Table 2.3**).

Chapter 3

Results and Discussion

The present chapter describes the results of the various geochemical analyses done on the samples described in **Chapter 2**. As mentioned in the Introduction (**Chapter 1**) the aim of the present thesis is two folds: (i) determination of climatic and environmental parameters during the Permo-Carboniferous Talchir sedimentation, and (ii) estimation of pCO_2 level in the atmosphere during four periods in the past (from 270 m.y. to 65 m.y.). The discussions on these two aspects are given in **Section A** and **Section B** respectively.

Section A

This section explains the results obtained from analysis of nodular carbonates obtained from various Talchir basins of peninsular India. At the beginning of this section morphological features and petrographic texture of the nodules are described to check if they grew insitu. These nodules were analysed geochemically (**Chapter 2**) and the results obtained from these analyses are used in this section for palaeoenvironmental and palaeoclimatic interpretation. These discussions are presented below under separate headings.

3A.1 Morphology of nodules

Morphological features of the nodules can provide clues to understand their mode of origin. Some important aspects are: (i) Disposition of laminations inside the concretions relative to the host: Lamination can be used to establish time relationship of concretionary growth relative to host deposition and compaction (Selles, 1996). Pronounced arching of beds above and below the nodules is observed in some cases in the field. This suggests that the concretions grew in partially consolidated sediments and the arching resulted from compaction that deformed the sediments but not the concretion. The individual concretions behaved like elastic bodies while the surrounding hosts were plastic in nature. Internal laminations within the nodules indicating primary features are present in a few nodules collected from West Bokaro basin. Syngenetic character is also suggested by continuation of

ripple drift lamination from sedimentary beds through the concretions. The thickness of the laminations varies inside the nodule and in the host. This variation is caused by differential compaction (Tucker, 1982) and can be used as an index of sediment compaction. (ii) Central clay nuclei: Clay nucleus is found in a few nodules collected from Baroghat and Bhuinpara locality of Mahanadi valley. In this context, Selles (1996) suggested that the clay could not only serve as ion source during concretion growth but also scavenge cations from the medium and provide active centre for nodular growth. (iii) Concentric rings within the nodules: Several nodules collected from Barkipunu locality of Damodar valley basin show the presence of concentric growth rings indicating spherically symmetric growth around a centre. The central portion of the nodule is more calcitic compared to the rim. Outer rim of these nodules shows features like radiating fractures, concentric cracks etc., indicating results of fluid expulsion. The growth of nodules in the sediments requires constant supply of carbonate ions. Any change in the supply of ions creates variation in growth pattern and deficit of ion supply may sometimes result in abrupt termination of nodule development.

Selles (1998) proposed a model to explain the genesis of nodules. According to his model the initiation of nodular growth takes place with nucleation (probably triggered by clayey particles present in the sediments) at sediment water interface. Growth of nodule continues afterwards with slow burial and development of a hydraulic seal. Development of impermeable seal subsequently causes deviation in the trend of sediment compaction, and abnormally pressured cell continues its further evolution. Concretionary bodies grow to larger and larger sizes as long as environmental conditions and brine concentration permit. Terminal phase of nodule formation is characterised by decreasing pore pressures, which may take place at slow or fast rate with separate consequences on nodule growth. This process ultimately leads to transfer of overlying load to the clastic framework and termination of further growth. Growth of nodules in terminal phase may lead to dehydration of core and expulsion of fluid (carbonate rich solution) along cracks and fractures in the outer shell. Nodules with outer cracks and fractures resemble outer skin of a tortoise and are known as Septarian nodules. Similar cracks are seen in a few nodules collected from Barkipunu area of Ramgarh basin. Septarian nodules generally have large size (more than 20 cm), hard outer shell and

concentric growth rings indicating prolonged period of growth, growth during decreasing fluid pressure and multiple episodes of calcite precipitation respectively. Nodules with these



morphological features are not good for palaeoclimatic work because they denote long period of growth at deeper part of the basin where interaction by hydrothermal fluid can obliterate basin water signature. However, majority of the nodules in our collection are composed of micritic calcite cement, relatively smaller in size (<10cm), relatively less compacted, devoid of growth rings or spar filled fractures in the outer rim. These characteristics make them suitable for palaeoclimatic studies.

3A.2 Petrography

XRD analysis of powders from the nodule samples shows that calcite is the dominant carbonate mineral in the matrix. Several lines of petrographic evidence indicate that most of the nodular concretions formed very early in the diagenetic history of the sediments and did not alter significantly afterwards. These can be summarized as:

i) Preservation of the primary depositional features inside the concretions including sorting (poorly sorted), angularity (variable angularity of grains), packing and porosity (loosely packed and pores filled with calcite cement, **Figures 3.1a and 3.1c**), ii) Micrite coating surrounding single and multiple quartz grains with well developed moldic porosity (filled with micritic calcite) indicating meteoric water cementation (**Figure 3.1b**), iii) Preservation of susceptible mineral grains like amphiboles and plagioclase (andesine) in nodules; in contrast, some of these minerals are variably replaced (e.g. andesine replaced by albite) or destroyed in the host rock due to water interaction (**Figure 3.1d**), iv) Absence of secondary diagenetic minerals such as zeolite within the calcite-cemented concretions, v) Presence of Fe-rich smectite clay skins and organic matter within the concretions (**Figure 3.1e**).

3A.3 Cathodoluminescence studies

Cathodoluminescence (CL) technique is useful for studying the extent of diagenetic alteration in carbonates. Viewed under CL, carbonates show varied luminescence signatures ranging from non-luminescent to dull luminescent, to moderately luminescent, to bright luminescent in orange, brick red, and yellow colors. CL studies of calcretes help in recognition of different events and stages of carbonate precipitation. Driese and Mora (1993), based on a study of pedogenic calcites, showed that CL petrographic components define chemically distinct fields corresponding to separate environments. Microprobe data shows that dull red-brown luminescent micrite typically contain Mn concentrations of 500 to 2000 ppm and Fe concentrations below 2000 ppm. Bright yellow orange luminescence in the late calcite spar cement indicates extremely high Mn concentration (upto 34,000 ppm) and low Fe concentration (below detection limit). High concentration of Mn in successively younger calcite spar cements without any significant increase in Fe concentration suggests increasing

mobility of Mn in a reducing environment. Such reducing environment can arise during burial and simultaneous oxidation of organic matter in the sediments.



Figure 3.2 (a) Image of sample DN-7 in plane polarised light. (b) CL image of the same section; blue colour grains are quartz and darker patches denote clays and felspars. Bright red CL represents carbonates with high Mn/Fe whereas dull red represents low Mn/Fe.

Nature of post-depositional cementation was investigated in a few samples with the help of cathodoluminescent (CL) image of thin section. This showed that majority of the nodules are composed of two generation of calcites (**Figures 3.2a and 3.2b**). Calcite cements show two shades of orange colouration: a) bright orange, indicating precipitation from water having high concentration of Mn ion (Veizer et al., 1999; Tobin et al., 1999), and b) dull red CL in the calcite surrounding detrital quartz grains with low Mn abundance.

Based on these characteristics we can distinguish between calcite precipitated at sediment water interface (calcite with less Mn) and calcite formed during burial diagenesis (high Mn). Identification of these two major classes of calcite is helpful in interpretation of isotopic composition of the nodular carbonate. Some of the samples with prominent features of alterations as revealed by CL are discarded during final interpretation.

3A.4 Clays in the nodules

Nodules are admixtures of two sedimentary components: (a) carbonate as calcite cement and (b) detritals. Detritals are mainly composed of quartz, felspar, micas and clays. In

a few cases lump of clay occurs as core of the nodule. It is of interest to know the source of this clay as they can, in some cases, provide information about the genesis of the nodules. Clay minerals in sediments and sedimentary rocks usually have three origins: i) inheritance, ii) neoformation and iii) transformation. In the first, the clays are formed from detrital material in another area, like, for example, in the weathering environment of soil in a neighbouring region, and get transported to the site where they are found. In the second, the clays are formed insitu in the depositional environment of sediment. In the third (transformation) inherited clays are modified by ion exchange or cation rearrangement (diagenesis). In the weathering environment, the type of clay produced depends on the climate, drainage, rock type, vegetation and time involved. We have analysed clay from 8 nodules, 7 from Damodar valley and 1 from Mahanadi valley basin. The clay extracts from Damodar valley samples contain mostly illite while the sample from Mahanadi valley contains smectite (**Table 3.1**). Illite is a weathering product of muscovite whereas biotite is parent mineral for smectite (Grim, 1953; Fordham, 1990; Burkins et al., 1999; Sordon, 1999). Petrographic and SEM photograph

Sample No.	Location	List of clay minerals present		
DN/3A/95	West Bokaro basin,	Illite, Montmorrillonite		
DN6-1	Dudhi nala section	Montmorrilonite, Chlorite, Illite		
DN/N1/95		Montmorillonite, Chlorite, Illite		
BP/N3a/95	Ramgarh basin,	Illite, Chlorite		
BP/N2/95	Barkipunu section	Illite, Chlorite		
BP/N1/95		Illite, Chlorite		
NDK-1	Talchir basin,	Smectite, Montmorillonite, Chlorite		
NDK-A1	Mahanadi Valley.	Smectite, Chlorite, Montmorrilonite		

Table 3.1 Clay minerals of a few nodules collected from three Talchir basins.

of nodules collected from Damodar valley basin and Mahanadi valley basin show the presence of muscovite and biotite respectively. Coexistence of biotite-smectite and illitemuscovite in the powder samples suggests that the clays formed as a result of insitu transformation of parent materials. Cores of a few nodules with central clay nucleus were also analysed and their XRD spectrum indicates presence of smectite. In such cases, the smectite acted as the growth centre for the nodules.

3A.5 Mn, Fe, and Sr concentrations in carbonate as diagenetic indicator

It is known that calcites can be altered by interaction with meteoric water because of their susceptibility to weathering reactions (Tucker and Wright, 1990). During this process Mn, Fe, Mg and Sr can replace Ca in the lattice sites of calcite. Veizer et al (1983) and Lohmann (1988) have used variation of Mn and Sr concentrations in marine carbonates to infer about their alteration by interaction with fresh water. In marine environment precipitation of aragonite in the shell of marine organism (primary carbonate) is associated with incorporation of Mn and Sr from the seawater. Subsequent transformation of aragonite to calcite or dolomite depends on water chemistry and pH-Eh condition in the diagenetic environment. This transformation is also associated with incorporation of Mn from the interacting medium and expulsion of Sr from the primary aragonite.

In the non-marine environment carbonate precipitates as low Magnesium calcite or aragonite in the sediments (Tucker and Wright, 1990). Once precipitated, these carbonates are transformed into stable form of calcite and are difficult to alter in normal water-rock interaction. However, during basin subsidence the environment surrounding the growing calcite can become reducing and as a result concentrations of Mn and Fe can become high in the growing crystal. Concentration of Mn, Fe, Sr and Mg in the calcite phase of the nodules collected from West Bokaro, Ramgarh and Talchir basins was measured in order to understand the extent of burial diagenesis and alteration.

3A.5.1 Manganese concentration in the nodule

Concentration of Mn was measured in the acid leach fraction of the nodules. It is believed that Talchir sedimentation took place in lakes at the margin of glacier and rivers brought sediments from upland located at periphery of the basins (Casshyap and Kumar, 1987; Veevers and Tewari, 1995). Earlier workers have suggested that these rivers were probably flowing along three major fault zones which widened subsequently to form three major rift valleys viz. Narmada, Mahanadi and Godavari (Casshyap and Tewari, 1988; Casshyap et al., 1993). Since then the lithology of the drainage area have not changed much. Therefore, the major and trace element compositions of the present day river water and Talchir nodules derived from glacial melt water are expected to be similar. Krishnaswami (1974) measured the concentration of Mn in the leach fraction of continental lake sediment (taken from Lake Tulsi, Tansa, and Powai near Mumbai) and obtained values ranging from

69

780 ppm to 1560 ppm. These results suggest that if trace elements are released from river borne suspended materials by formation of organo-metallic complexes, considerable amount of Mn can be supplied to the lake by leaching processes. Krishnaswami (1974) also measured the concentration of Mn in the lake sediments (200 ppm and 1150 ppm) of France and Switzerland. Higher Mn concentrations in the tropical lakes are explained by more intense weathering in high rainfall zone. Carignan and Nriagu (1985) in a study of sediment core from Lake Ontario (high northern latitude in Canada) showed that the Mn concentration reaches a maximum of 17,000 ppm at 13 meter depth but is much lower (~5000 ppm) in the sediment layers above and below this zone. This profile is explained by movement of redox front. Lake Vanda is a marginal lake in the Antarctic region and is good for comparison with Talchir basins of peninsular India (because of their location and size). Vanda Lake is characterised by a permanent anoxic deep-water layer where concentration of Mn exceeds that of Fe (Green et al., 1989). Concentration of Mn in the sediment water interface of Lake Vanda ranges from 2500 and 3500 ppm (Green et al., 1989). The behaviour of Mn in a sediment column is governed by the positioning of redox front, which is determined by the competition between supply of oxygen rich water and microbial activity in the sedimentary column. In the Antarctic region, the top surface of lakes is always frozen in winter, which restrict the inflow of air from atmosphere (Green et al., 1989). In addition, microbial activity in the water column can reduce oxides of Fe and Mn. Green et al (1989) show that in such cases the abundance of Mn in the water at the sediment water interface decreases (upto 4000 ppm) and precipitation in this zone contains high Mn concentration.

Mn concentration in the carbonate phase of Talchir nodules ranges from 30 to 3000 ppm (**Table 3.2**); however, the majority of the values are between 100 to 2000 ppm (60%) and they fall within the range observed in the lake sediments of Antarctica (e.g. Vanda Lake). Similarity of Mn concentration in the carbonate nodules and Lake Vanda sediments suggests that the nodules formed from fresh water and did not suffer major alteration afterwards. During the process of burial diagenesis and secondary alteration Mn gets incorporated into the carbonate phase. Therefore, nodule samples with high Mn content (more than 3000 ppm) might have suffered slight alteration by water-rock interaction during late stage diagenesis.

3A.5.2Iron concentration in the nodule

Fe in calcite is responsible for quenching of cathodoluminescence signal. Therefore, it is important to know the concentration of Fe in order to interpret CL signals. It is also known that Fe precipitates along with calcite in oxidizing condition and therefore its presence can be of use to infer the environment of deposition. Out of 50 nodules collected from Talchir basins (Damodar valley and Mahanadi valley) 23 were analysed for trace elements (in carbonate phase). The Fe concentration in the carbonate varies from 130 to 6,500 ppm (**Table 3.2;** an exceptionally high value of 24,150 ppm in sample BP/N1/95 was probably caused by leaching of some iron concretion in the nodule).

Micritic calcite cement of the nodules from West Bokaro basin shows small range of 134 ppm to 850 ppm in Fe concentration (Table 3.2). Fibrous calcite in the nodules from Mahanadi basin has variable and more elevated Fe content (upto 2500 ppm). Concentrations of Mn and Fe are highly variable in the nodules. However, the range of variation is small in case of samples from West Bokaro basin. This may indicate smaller alteration for West Bokaro nodules as during the process of burial diagenesis Mn gets incorporated in the calcite phase and Fe gets removed. The concentration of Fe in the continental sediments is highly variable depending on redox condition during precipitation (Forstner, 1976). Mora et al (1993), based on CL study of pedogenic carbonates of Devonian age showed that dull red luminescence is obtained in calcites containing less than 2000 ppm of Fe. The concentration of Fe in the sediment water interface of lake Vanda ranges from 400 to 1200 ppm (Green et al., 1989) whereas, concentration of Fe in the sediment water interface of Lake Ontario is 5000 ppm (Carignan and Nriagu, 1985). These values are slightly higher than the concentrations observed in the Talchir nodules. Above discussion indicates that majority of the nodules formed in an environment similar to that of Lake Vanda. However, two samples (DN/1a/95 and C-1) showed exceptionally high concentration of Mn (>3000 ppm; late diagenetic alteration?) whereas the concentration of Fe in one sample (BP/N1/95) is unusually high indicating precipitation of iron as concretion.

Table 3.2 Ca, Mg, Fe, Sr and Mn concentrations in carbonate phase[?] of Talchir nodules (% and ppm expressed with respect to bulk).

WEST BOKARO BASIN: DAMODAR VALLEY (DUDHI NALA SECTION)

Sample	Ca(%)	Mg (ppm)	Fe (ppm)	Sr (ppm)	Mn (ppm)

DN/N21/95	19.1	776	638	111	1933
DN6-1	17.3	785	134	45	634
DN-3	23.5	690	470	59	2330
DN-2	19.8	780	468	131	1647
DN-4	23.6	696	490	89	1611
DN/1a/95	24.7	588	848	135	3173
DN3A-1	22.9	1122	461	89	2373
DN/N22/95	20.7	820	281	11	234
SN3A	24.7	604	635	80	1461

RAMGARH BASIN: DAMODAR VALLEY:

Samples	Ca(%)	Mg (ppm)	Fe (ppm)	Sr (ppm)	Mn (ppm)
BP/M1/95	9.0	1137	335	33	648
BP/N1/95	13.8	1236	24150*	7	161
BP/N3b/95	17.0	819	2060	6	255
BP/N3a/95	17.6	1726	6474	7	251
BP/N2/95	17.7	1506	5015	7	290

MAHANADI BASIN: NANDIRJHOR NALA SECTION:

Samples	Ca(%)	Mg (ppm)	Fe (ppm)	Sr (ppm)	Mn (ppm)
RH/NDJ8/95	27.4	395	333	95	2410
NDJ/RC/95	21.1	937	1897	81	2476
NDK-A1 Σ	22.9	739	1795	-	30
NDJ/ST2/952	21.2	941	-	59	2769
C-1Σ	21.5	388	234	131	3386
NDK-A1	19.9	524	1426	9	174
$AR/STR1/95\Sigma$	38.2	904	651	52	2519
RAY/NSt/95	34.6	1437	2526	5	222
NDJ/ST5 Σ	4.9	-	180	84	1852
$NDJ/ST6\Sigma$	21.4	262	194	57	2664

* Suspected presence of iron concretion. $^?$ Leaching of bulk sample powder (80-140 μ size) with 2N HCl. Σ Algal carbonates

3A.5.3 Mn/Fe ratio of the carbonate phase

CL image of the calcite cement of a few nodules reveals two generation of calcite precipitation; one generation of calcite with orange to bright yellow luminescence (high Mn/Fe ratio) is found in the pore spaces and another generation is restricted to the boundary of the grains and emit dull red to brown luminescence (low Mn/Fe ratio). The Mn/Fe ratio of the calcite phase of the nodules (collected from same location) shows large variation. Previous studies on brightness of CL in thin section and microprobe analysis showed that bright CL is associated with high Mn/Fe ratio, usually more than 10 (Driese and Mora, 1993)

whereas dull red-brown luminescent micrite typically contains Mn concentrations of 500-2000 ppm and Fe concentrations below 2000 ppm. The Mn/Fe ratios (in ppm / ppm) of 24 nodules are plotted in **Figure 3.3** as a histogram of frequency distribution. 16 nodules lie within 0 to 4 ratio whereas 8 samples have ratio more than 4 and less than 14. Samples with low ratios (0 to 4) probably represent those where early cement is the dominant component.



Fig 3.3 Histogram showing frequency distribution of Mn/Fe ratio in carbonate phase of Talchir nodules. Large number of samples have low Mn/Fe ratio indicating minimal alteration subsequent to their formation. NL denotes zone of non luminescent calcite in CL. An average value of Mn/Fe in modern day lake carbonate is shown by arrow.

3A.5.4 Strontium and Magnesium in the carbonate phase of nodules

Strontium concentrations in natural waters vary widely, from ppb level in river waters to upto 2000 ppm in subsurface brine (Goldstein and Jacobsen, 1988) and broadly correlate

with salinity. Fluid Sr/Ca ratios exert a fundamental control on the Sr concentration of diagenetic carbonates. The Sr/Ca ratio in carbonate increases with increasing water-rock interaction during burial diagenesis (Veizer, 1983). This relationship holds well for marine aragonite cement and their subsequent transformation into calcite during diagenetic process. However, in the continental setup majority of carbonate precipitation is in the form of stable (low magnesium) calcite where subsequent diagenetic modification is negligible. Moreover, in continental sediments, the concentration of Sr is higher in biogenic aragonite compared to calcite forming from the same medium (Tucker and Wright, 1990; Banner, 1995). During the process of diagenesis the aragonite gets converted to calcite and most of the Sr acquired during precipitation is released into the medium.

Concentration of Sr in the calcite phase of the nodules varies between 6 to 135 ppm and is lower than 300 ppm. This range is expected for a biogenic carbonate precipitating in a continental lake (Forstner, 1976). Most of the analysed carbonates fall under the category of low magnesium calcite (concentration of Mg varies between 250 ppm to 1700 ppm; **Table 3.2**) which are commonly found in modern lake sediments. The low Sr concentrations of Talchir carbonates are similar to those of the low Mg calcites which can accommodate only smaller concentration of Sr (0 to 100 ppm; Tucker, 1990).

3A.6 Stable isotopic study

Fifty nodules were collected from two major Talchir basins (Damodar valley and Mahanadi valley; see **Figure 2.1**) and powder samples (total 59) from inside part of these nodules were analyzed for oxygen and carbon isotopic ratios. In addition, calcareous matrix surrounding some of the nodules (about 11) and one lime mud taken from the rhythmite facies of Irai River section of Godavari valley basin were also analyzed. The measured isotopic ratios are given in **Table 3.3** along with a brief description of the samples. These data are discussed below where oxygen isotopic ratios are taken up first.

Table 3.3	Stable	isotopic	composition	of	Talchir	nodules	along	with	sample	description	

Sample	Description	$\delta^{13}C_{\text{PDB}}$	$\delta^{18}O_{smow}$	Sample	Description	$\delta^{13}C_{\text{PDB}}$	$\delta^{18}O_{smow}$
West Boka	ro Basin			DNM7	Micrite (Nodule)	-7.0	10.4
DN01	Micrite (Nodule)	-12.8	11.4	DNM8	Micrite (Nodule)	-10.5	10.9
DN02	Micrite (Nodule)	-13.8	11.5	DNM9	Micrite (Nodule)	-10.6	11.4

DN3/1	Spar (Nodule core)	-12.2	1.5	DNM10	Micrite (Nodule)	-7.6	14.2
DN3/2	Micrite (Nodule)	-2.5	10.8	DNM11	Micrite (Nodule)	-9.9	10.9
DN3/3	Spar (Nodule core)	-5.5	2.5	DNM12	Micrite (Nodule)	-12.8	4.0
DN3A	Micrite (Nodule)	-8.3	12.2	DNM13	Micrite (Nodule)	-10.9	9.5
DNM 3A	Matrix (Nodule)	-11.4	12.8	DNM14	Micrite (Nodule)	-12.1	7.6
SN 3A	Micrite (Nodule)	-18.9	8.1	DNM15	Micrite (Nodule)	-12.1	9.2
DN3A-1	Spar (Nodule)	-4.7	3.7	DNM16	Micrite (Nodule)	-7.6	12.8
DN1 (T)	Micrite (Nodule)	-11.4	7.6	DNM17	Micrite (Nodule)	-10.5	14.2
DN1 a	Micrite (Nodule)	-10.5	7.6	DNM 3A	Micrite (Nodule)	-11.4	12.8
DNM1 a	Matrix (Nodule)	-12.4	8.1	DNM18	Micrite (Nodule)	-4.9	3.7
DNM1 b	Matrix (Nodule)	-11.4	8.5	Boudh and Ba	aroghat <u>(Mahanadi)</u>		
DN2 (T)	Spar (Nodule core)	-3.2	3.3	BR/N1	Micrite (Nodule)	-13.5	15.3
DN2 (B)	Micrite Nodule	-14.9	10.7	BR/N2	Micrite (Nodule)	-11.3	14.6
DNM 2	Matrix (Nodule)	-10.5	10.2	BR/N3	Micrite (Nodule)	-5.8	7.1
DML	Matrix (Nodule)	-8.7	8.4	BR/N5	Micrite (Nodule)	-12.2	12.6
DMU	Altered (Matrix)	-2.3	20.6	BR/N11	Micrite (Nodule)	-7.9	18.8
DNO(1)	Micrite (Nodule)	-13.5	9.9	BH/N6	Altered (Nodule)	-9.5	26.5
DNO(2)	Micrite (Nodule)	-26.6	12.2	BH/N3	Altered (Nodule)	-13.5	22.7
DNM0	Matrix (Nodule)	-6.7	8.0	BH/N1	Micrite (Nodule)	-9.3	11.6
DN5A(T)	Micrite (Nodule)	-16.0	10.4	BH/N5	Altered (Nodule)	-17.6	21.5
DN5A(B)	Micrite (Nodule)	-11.7	11.5	BR/N4	Micrite (Nodule)	-15.6	15.8
DN5B (T)	Micrite (Nodule)	-12.6	9.3	BH/N7	Altered (Nodule)	17.0	22.0
DN5B (B)	Micrite (Nodule)	-10.5	8.7	<u>Angul (Maha</u>	<u>anadi)</u>		
DN5C(T)	Micrite (Nodule)	-11.4	9.8	C-1	Micrite (Nodule)	-2.8	13.1
DN5C(B)	Micrite (Nodule)	-10.4	11.5	NDK-5	Micrite (Nodule)	-0.5	9.6
DNM5C	Altered (Nodule)	-3.1	27.7	Ramgarh (Da	modar)		
DNM 5C-1	Altered (Nodule)	-0.3	30.3	BP/N1	Micrite (Nodule)	4.3	11.5
DNM 5	Micrite (Nodule)	-9.7	13.9	BP/N2	Spar (Nodule core)	-10.1	-1.8
DNF 5	Micrite (Nodule)	-9.9	11.0	BP/N3A	Micrite (Nodule)	-9.9	-10.1
DN6-a	Spar (Nodule core)	-11.8	-4.7	BP/N3B	Spar (Nodule core)	-13.6	1.5
DNM6	Matrix (Nodule)	-5.0	13.2	BP/M1	Matrix (Nodule)	-9.4	6.0
DN6-1(T)	Micrite (Nodule)	-7.0	10.4	<u>Irai (Godava</u>	<u>ri)</u>		
DN6-1(B)	Micrite (Nodule)	-10.5	10.9	IR/COM//97	Micrite (Nodule)	0.8	9.5
*DN6-1(B)	Micrite (Nodule)	-10.6	11.4				
DNM6-1	Matrix (Nodule)	-7.6	14.2	<u>Ib basin (Ma</u>	<u>hanadi)</u>		
DN6-a	Micrite (Nodule)	-9.9	10.9	AN-1	Spar (Nodule core)	-10.5	-0.5
DN7-a	Spar (Nodule core)	-12.8	4.0	<u>Dwyka tillite</u>	<u>(S.Africa)</u>		
DN7-b	Micrite (Nodule)	-10.9	9.5	DK/1/95	Micrite (Nodule)	-11.4	10.3
DN7-1	Spar (Nodule core)	-12.1	7.6	DW-1	Micrite (Nodule)	-3.5	7.0
DN7-2	Micrite (Nodule)	-12.1	9.2	DW-2	Micrite (Nodule)	-9.8	16.0
DNM-7	Matrix (Nodule)	-7.6	12.8	DW-4	Micrite (Nodule)	-17.1	8.1
BBM-2	(Micrite) Rhythmite	-10.5	14.2				
DFSS-1	Siltstone (Sparitic)	-4.9	3.7				

*= Repeat analysis



74

Figure 3.4a Frequency distribution of δ^{18} O values in the unaltered nodules with gaussian fit to the data. The mean value is 11.0‰

Figure 3.4b Frequency distribution of δ^{13} C values in the unaltered nodules with gaussian fit to the data. The mean value is -11.0‰

3A.6.1 Oxygen isotopes

The oxygen isotopic ratios of the nodules vary over a large range (from 7.6 to 18.8 ‰ w.r.t. SMOW) when all unaltered samples are considered together (neglecting 14 samples,

which show obvious signs of alteration and sparitization). The frequency distribution of the oxygen isotopic ratios of the unaltered nodules follows a Gaussian pattern (**Figure 3.4a**). The mean δ^{18} O is, therefore, well defined and has a value of $11.0\pm 2.5 \%$ w.r.t. SMOW (the standard deviation represents 1σ range around the mean).

Majority of the samples have depleted oxygen isotopic ratio (average = 11‰ w.r.t. SMOW; **Fig. 3.4a**) and therefore, *a fresh water origin for Talchir carbonates can be unequivocally established*. Assuming that the precipitation of carbonates is intimately linked with sedimentation this finding puts to rest the marine/non-marine controversy regarding the origin of Talchir sediments. Additionally, relatively small variation in oxygen isotopic composition suggests a correspondingly small change in meteoric water composition during the period of nodule formation.

As mentioned above, the most characteristic feature of the results (**Table 3.3**) is the extremely depleted oxygen isotopic composition of majority of the nodules.



S Fig 3.5 Proposed schematic picture of glaciofluvial and glaciolacustrine environment $n_{n'}$ leading to Talchir sedimentation and subsequent nodule formation. e tillite of Antarctica (4.9 to 6.1 ‰; Schmidt and Friedman, 1974) and the Permian Beacon Supergroup of the Transantarctic mountains (-0.6 to 10.4 ‰; Lord et al, 1988). However, these studies were done on less number of samples taken from spatially restricted exposures.

In contrast, the present study is based on a large number of samples taken from many exposures of two well-known Gondwana basins in peninsular India and offers a statistically significant data set. Also the samples were selected on the basis of standard criteria to ensure that they represent pristine isotopic composition. As noted before, four similar nodules from Dwyka tillite of Karoo basin comprising micritic calcite were also analysed in the present work. The δ^{18} O and δ^{13} C of these ranges from 7 to 16.0 ‰ (average 10.3) and from –3.5 to – 17.1 ‰ (average -10.4‰) respectively. These values lie within the range of Talchir nodule values and indicate similar environment of formation. **Table 3.3** also lists four nodule samples and two matrix samples, which show signs of alteration and are characterized by enriched oxygen isotopic values (20 to 30 ‰). These values are close to that expected for carbonates forming in waters (lakes or soils) derived from contemporary precipitation in the sample locations (Bhattacharya et al., 1985).

In this study, the analysis was done on bulk powder samples and presence of some minor amount of altered calcites in them can not be ruled out. The dispersion in the oxygen data may, therefore, be partly caused by variable amount of altered calcites with enriched values (as mentioned before, presence of two generation of calcites i.e. original plus altered is revealed by CL studies in some samples). Part of the dispersion could also be due to basinal differences in the water source and temporal variation in water isotopic composition as the analyzed nodules are taken from various units of the Talchir Formation which are not strictly contemporaneous. Despite this dispersion, one can define a meaningful average based on the normal distribution pertaining to the data set (**Fig. 3.4a**) and this average is used here as representative of the isotopic composition of the Talchir carbonates to derive information on the source water.

3A.6.1a Oxygen isotopic composition of meteoric water

As mentioned before, petrographic investigation of the nodular carbonates indicates that most of the nodules represent insitu primary precipitates. Elemental analysis (Figure 3.3) shows that majority of the calcites precipitated from meteoric water characterized by Mn/Fe ratio of 0.1 to 5. This would not be the case if Talchir carbonates were formed in a marine

regime (low Mn/Fe ratio of 0.1 to 1; Tobin et al., 1996). Moreover, occurrence of the nodules in varve like sediments overlying glacial boulder beds suggests freshwater lakes formed by glacier melt-water as probable milieu for sedimentation and carbonate precipitation (schematically described in **Figure 3.5**). The depleted oxygen isotopic composition of the carbonates is strong evidence in support of this proposition. The mode of deposition of the nodules and their isotopic characteristics can be best explained if we assume that they formed inside the sediment bed by supply of ions through pore water around centres of precipitation. These centres might have been provided by localised chemical, microbial or algal carbonate pumps (Reading, 1981; Berner, 1980).

It is well known (Schmidt and Friedman, 1974) that δ^{18} O of sedimentary carbonate depends on: i) isotopic composition of the water from which the carbonate precipitates, ii) the temperature of the carbonate solution during precipitation, and iii) the nature of fractionation i.e. whether the process is in equilibrium or kinetically controlled. One can estimate the mean oxygen isotopic composition of glacier melt-water forming the Talchir lakes assuming slow precipitation of the carbonate cement from pore water under equilibrium condition. However, an estimate of the temperature of precipitation at the lake bottom is required. Palaeogeographic reconstruction shows that Talchir basins were located at about 70°S latitude (Smith et al., 1981; Irving, 1983; Scotese, 1997). Several Antarctic lakes at 70°S near the Shirmacher Range were studied by Varlencar et al (1988) and the mean summer temperature of the bottom waters is about 2.5 °C.



Figure 3.6 Covariation plot of oxygen and carbon isotopic ratios in the micritic calcite from nodules and associated matrix.

Assuming this value as representative temperature of bottom water in Talchir lake one can deduce the value of the fractionation factor between carbonate and water from the Friedman and O'Neil (1977) equation:

$$10^{3} \ln \alpha_{water}^{calcite} = \frac{2.78 \times 10^{6}}{T^{2}} - 2.89.....(3.1)$$

If the temperature of lake bottom water was 2.5°C, then:

$$10^{3} \ln \alpha_{water}^{calcite} = \frac{2.78 \times 10^{6}}{(275.65)^{2}} - 2.89 = 33.7$$

Therefore, $\alpha_{water}^{calcite} = 1.03427$

But
$$\alpha_{water}^{calcite} = \frac{\delta^{18}O_{calcite} + 10^3}{\delta^{18}O_{water} + 10^3}$$

Using the mean $\delta^{18}O_{\text{calcite}}$ value of Talchir carbonate (11.0‰) the estimated isotopic composition of glacier melt water is then –22.5‰ w.r.t. SMOW.

It is of interest to compare this value with that of the present day precipitation at this latitude. Based on the available isotopic data on global precipitation from the compilation of Rozanski et al (1993) the isotopic composition of present day precipitation at 60 to 70 °S latitude is -20 ‰ w.r.t. SMOW. The δ^{18} O of ocean water during Permian period was slightly less and is commonly assumed to be -1‰ (Veizer et al., 1997) which would imply composition of the precipitation to be -21‰ w.r.t SMOW. However, isotopic ratio of

rainwater is modified by evaporation during its conversion to Lake Water through snow, glacier ice, glacier melt-water and fluvial phases. Each of these steps involves isotopic enrichment whose magnitude is difficult to estimate. However, limited data on Antarctic lakes and snows (Bhattacharya and Nijampurkar, 1998) suggest enrichment of a few per mil and we would assume 2 ‰ as a representative value. A similar value is also assumed during conversion of rainwater to ground water in semi-arid zones (Salomons et al., 1978). Under these assumptions the lake water isotopic composition is expected to be -19 ‰ whereas the mean value derived from Talchir carbonate is -22.5 ‰.

Above discussion shows that the inferred isotopic composition is slightly depleted compared to the expected isotopic ratio of rainfall in today's scenario. This depletion can be explained by either an amount effect or altitude effect. One can expect depletion if the intensity of rainfall was higher in the Tethys margin compared to the present day level at this latitude. To explain ~ 3.5 ‰ depletion an annual average rainfall of 640 mm is required instead of 400 mm/yr as observed today (**Table 3.5**; Rozanski et al., 1993). One can also explain the depletion if the altitude was about 400 m higher based on the observed magnitude of the altitude effect in Antarctica (Schimdt and Friedman, 1974). This would be consistent with the proposition of Casshyap and Tewari (1988) that the existing hills of Chotanagpur plateau acted as ice collection centres for the Talchir glacier in the Bokaro area.

Table 3.5 Calculated excess precipitation required to explain Talchir Oxygen isotope data

Mean δ ¹⁸ O of nodule (‰)	Temp. of ppt ^I (°C)	Calc. δ ¹⁸ O [∀] (Lake water) A	Palaeo Lat. [¶]	δ ¹⁸ O of modern precipitation ^η	δ ¹⁸ O of Ocean water ^φ	δ ¹⁸ O of Lake (evaporative enrichment) B	B-A (‰)	Excess precipitation [¶]
11	2.5	-22.5	70°S	-20	-1	-19	3.5	240mm/yr

^IVarlencar et al., 1988. ^δ Friedman and O'Neil, 1977. ^η Scotese, 1998. ^η Rozanski, 1993; Assuming ∂δ/∂P= - 4‰/ 250 mm , ⁹ Veizer, 1986.

3A.6.2 Carbon isotopes in the nodular carbonates

Carbon isotopic ratios of the nodular carbonates are given in **Table 3.3.** Interestingly, the carbon isotope ratios of the Talchir carbonates vary over a much larger range (from –18.9 to 4.3 ‰). This is in contrast to the usual observation where oxygen isotope ratios are more variable due to their susceptibility to alteration (Schidlowski et al., 1992; Aharon and Liew, 1992). We interpret this feature as indicative of primary variation in the carbon isotope ratio caused by the very process of nodule formation as explained below. The values plotted in **Figure 3.4b** shows a positively skewed distribution indicating contribution from two sources in which one is dominant.

It is well known that large kinetic fractionation in carbon isotopes occur during photosynthesis in green plants. The plants and algae are strongly depleted in ¹³C with respect to the source CO₂ resulting in typical δ^{13} C value of –25 ‰ w.r.t. PDB for organic matter (Ehleringer, 1989). If the Talchir carbonates precipitated syngenetically inside the sediment bed as envisaged above (**Figure 3.5**), the local pool of carbon (dissolved CO₂, carbonate and bicarbonate ions) where the nodule started its growth would determine its carbon isotopic composition. If this pool had dominant microbial or organic component the isotopic ratio would shift to negative values. Whereas, if the organic carbon was negligible in the centre of growth and the contribution came mainly from dissolved sedimentary carbon the value would be close to zero or slightly positive as the source of the carbon would be ultimately from neighboring hills containing old marine sediments of Vindhyan origin (Banerjee, 1974) denuded and carried by glacier. Variable proportion of these two sources would govern the isotopic composition of the carbon in the Talchir nodular carbonates.

In conformity with conclusion based on oxygen isotopes, the mean δ^{13} C of the Talchir carbonates (-10.5‰) again strongly suggests precipitation in nonmarine enviorment as the carbon in nonmarine carbonate rocks tends to be depleted in ¹³C and has more variable isotopic composition than marine carbonates. It is to be noted that the carbon isotopic character for deducing sedimentary environment is considered very reliable as numerous studies have shown that post-depositional diagenesis, if any, does not usually modify the carbon isotopic composition of carbonates occurring in geologically old sediments (Schidlowski et al., 1992).

The δ^{18} O and δ^{13} C values are plotted one against the other in **Figure 3.6** showing that these two variables are not correlated. As explained above, the causes of variation in δ^{18} O and δ^{13} C are not related. δ^{18} O change is predominantly due to intrinsic variability in water whereas δ^{13} C vary due to variable admixture of biogenically derived carbon with dissolved marine sedimentary carbon. The non-correlated nature of δ^{18} O- δ^{13} C plot is again a strong indication that alteration did not have a significant role.

3A.6.3 Presence of organic matter in the nodules

As understood from earlier discussions, glacial condition prevailed during the growth of nodules in the Talchir sediments and the process took place in the sediment-water interface in a lake deriving water from glacier melting. The cold climate was unfit for growth of largescale vegetation and microorganism in these basins. However, composition of carbonates in a few nodule shows depleted carbon isotopic ratio. We explained this depletion by contribution from CO_2 derived from decomposition of organic matter during nodule formation. As explained, carbon isotopic composition of nodules depends on source of carbonate ions in the water from which carbonates are precipitated. There are two possible sources of carbonate ions: dissolution of marine carbonates present in the country rock or decomposition of organic matter present in the sediments. In order to verify whether organic matter was indeed present, carbonate matrix was removed from the nodules and remaining material was analysed for carbon. Organic matter was found to be present in all 8 nodules analysed whose isotopic composition was determined. Table 3.4 shows δ^{13} C values of organic matter present in these nodules. Organic matter content in the nodules varies between ~0.5-1% and δ^{13} C ranges between -20% to -25% w.r.t. PDB. This confirms our assumption that the depleted nature of carbon in the carbonates is due to the presence of CO2 derived from microbial activities or from the decomposition of organic matter associated with the sediments. We have also analysed a few samples of coaly matter from a coal seam overlying the nodular bed. The isotopic composition of the coal lies within a range -22 to -23‰ w.r.t. PDB, similar to the range of δ^{13} C of nodular organic matter.

Table 3.4 Stable isotopic composition of Talchir nodules and organic matter present in them along with sample description

Sample No	Description	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C_{\text{org}}$
-----------	-------------	----------------	----------------	-----------------------------

DN/N3	Sparite core	-12.2	1.5	-25.1
SN/3A	Micritic core	-18.9	8.1	-24.9
BP/N3B	Sparitic core	-13.6	1.5	-24.3
BP/M1	Micritic matrix	-9.4	6.0	-23.1
NDK-5	Micitic core	-0.5	9.7	-22.2
NDK-A1	Micritic	-14.3	15.2	-22.1
RH/NDJ8/95	Micritic	2.2	12.5	-21.1

3A.6.4 Environment during Talchir sedimentation: monsoonal implications

Above discussion on the sedimentological aspects and isotopic characteristics of Talchir nodules delineates a chain of events having important bearing on the climatic evolution during Late Carboniferous period in India. Talchir formation is distinguished by the occurrence of a boulder bed at the base derived from glacial moraine, indicating presence of glacier ice near the basin periphery. Subsequent occurrence of sandstone-siltstone facies higher up in the stratigraphy signifies retreat of glacier and beginning of a fluvial regime. The present work suggests that the water supplied by the melting of the glacier formed a vast lake where sediments carried by rivers were deposited (Figure 3.5). This development marks an amelioration in climate which reached a climax when intense storms operated and generated waves in the lake strong enough to create hummocky cross stratification in the sedimentary layers (Eyles and Clark, 1986). This scenario is consistent with the results of climate simulation models which suggest initiation of monsoonal circulation during Late Carboniferous and its culmination in Permian and Triassic with development of a global scale megamonsoonal climate (Parrish, 1993; Fawcett et al., 1994; Kutzbach and Gallimore, 1989). Massive occurrence of coal bearing strata above Talchir formation in India supports the prediction of strong monsoonal rainfall during Permian responsible for widespread vegetation and swampy land conducive for development of coal.

3A.6.5 Stable isotopic variation within a nodule

Some nodules were examined for systematic variation of carbon and oxygen isotopic composition from core to rim (**Table 3.5**). Among the sectioned nodules four were collected from Dudhi nala section of West Bokaro basin. The nodules were of various shapes (ellipsoidal to spherical) and sizes (between 4 to 6 cm). Sections were made by a diamond saw and sampling was done with a diamond drill from five to six points at various distances from centre.

3A.6.5a Variation in oxygen isotopic composition

Nodule A is about 5 cm in size and ellipsoidal in shape. The difference in δ^{18} O between core and rim is 3.6‰. The values (w.r.t. SMOW) are: 5.6‰ (core) and 9.2‰ (rim). Enrichment of oxygen isotopes towards the rim can be explained by two possible scenarios:

- Initial stage of nodule development was driven by supply of carbonate ions from glacial melt water depleted in heavy isotopes. Subsequently, during warm periods (interglacial) melt water discharge was reduced and evaporation of Lake Water was dominant, which caused isotopic enrichment in water. If the rim part formed at that time it would have enriched values.
- 2. Late stage alteration of nodule can take place in presence of water having enriched isotopic composition. In this case, the effect is expected to be more at the rim than at the centre. In order to rule out the possibility of recent alteration, ¹⁴C activity was determined in one of the suspected samples (BP/N1/95). No ¹⁴C was detected in this sample. Absence of ¹⁴C in the nodule rules out possibility of recent alteration in this sample.

 δ^{18} O values (**Table 3.5**) for all samples from core to rim are plotted in **Figure 3.7a** against distance from the centre. Although, there is apparent increase in δ^{18} O with distance (from core to rim) in some nodules, it is not strictly followed in all the nodules. Sample B shows enriched core and depletion in the region surrounding the central portion, followed by enriched values again at the rim. The difference in δ^{18} O between core and rim of sample B is 0.2‰. However, there is significant decrease (3.3‰) at 1 cm away from the centre.

Nodule A Nodule B Distance (cm) $\delta^{18}O_{SMOW}$ $\delta^{13}C_{PDB}$ $\delta^{13}C_{PDB}$ Sample No. Sample No. Distance(cm) $\delta^{18}O_{SMOW}$ D -2.2 3.0 B-7 5.0 -5.5 Е -11.0 9.2 B-6 -8.2 2 8.1 С 0 5.6 -3.5 B-3 7.9 -10.7 0 в 1 3.5 -2.1 B-8 4.9 -5.6 A 2 4.8 -2.6 B-9 2 8.2 -8.0 Н 0.5 2.8 -2.2 **B-4** 1 4.8 -5.3 G 0.5 3.0 1.5 -2.1 B-1 6.8 -6.5 F 7.6 1.3 -6.6 B-2 6.1 -7.8 1 1.5 1.3 6.4 -3.8 7.1 -6.9 B-5

 Table 3.5
 - Carbon and oxygen isotopic compositions of samples from core to rim of nodules A, B, C, D and BP/N1.
| Nodule C | | | | Nodule D | | | | | | |
|------------|---------------|-----------------------|----------------------|------------|---------------|-----------------------|----------------------|--|--|--|
| Sample No. | Distance (cm) | $\delta^{18}O_{SMOW}$ | $\delta^{13}C_{PDB}$ | Sample No. | Distance (cm) | $\delta^{18}O_{SMOW}$ | $\delta^{13}C_{PDB}$ | | | |
| C-3 | 0 | 2.9 | -2.8 | D-1 | 0.25 | 5.7 | -2.2 | | | |
| C-9 | 1.2 | 4.6 | -4.0 | D-2 | 0 | 1.5 | -2.2 | | | |
| C-10 | 2 | 8.8 | -8.3 | D-3 | 1 | 0.4 | -1.1 | | | |
| C-8 | 0.8 | 2.1 | -2.1 | D-4 | 2 | 1.6 | -0.4 | | | |
| C-7 | 1.5 | 8.4 | -7.4 | D-5 | 2.5 | 4.2 | -3.0 | | | |
| C-6 | 2.2 | 10.4 | -11.2 | D-6 | 1 | -1.4 | -1.5 | | | |
| C-4 | 1 | 2.7 | -2.3 | D-7 | 1.5 | 2.7 | -0.9 | | | |
| C-5 | 1.5 | 9.2 | -8.0 | D-8 | 2 | 7.4 | -6.8 | | | |
| C-2 | 1 | 2.8 | -2.8 | | | | | | | |
| C-1 | 2 | 8.7 | -9.2 | | | | | | | |

Nodule BP/N1	l		
Sample No.	Distance (cm)	$\delta^{18}O_{SMOW}$	$\delta^{13}C_{PDB}$
BP-1	3	6.0	-11.3
BP-2	2	8.0	-12.1
BP-3	1	2.0	-11.8
BP-4	0	-10.8	-8.7
BP-5	1	2.5	-12.0
BP-6	2	6.4	-11.5
BP-7	3	12.8	-11.7
BP-9	2	12.5	-11.2
BP-10	1.7	2.2	-11.6
BP-11	2	0.7	-11.3
BP-12	1.7	7.1	-8.9
BP-13	2	5.8	-11.1
BP-15	3	10.0	-10.9
BP-16	4.2	9.3	-11.1
BP-17	4.5	5.9	-12.4

It seems that two enriched zones in this nodule are probably associated with two episodes of deglaciation. Nodule C is 4 cm in length and ellipsoidal in shape. δ^{18} O at the core of the nodule is 3‰ whereas at the rim it is 10.4‰. Nodule D from Dudhi nala is spherical with 4 cm radius; δ^{18} O at the center is 1.5‰ and 4.2‰ at the rim. It is clear that the difference between core and rim is variable in different



Figure 3.7a Variation of oxygen isotope ratio within nodules collected from West Bokaro basin and Ramgarh basin. Note depleted core and enriched rim in most of the nodules.

nodules. The magnitude of variation is large and therefore, seems to be related to variation in water composition during the growth of the nodules. The nodule sample (BP/N1) collected from Barkipunu is 6 cm in dimension and ellipsoidal in shape. This sample has extremely depleted core (-10‰) and enriched rim (8‰). Such highly depleted core region is not observed in any other nodule. Precipitation of calcite from hot aqueous solutions can shift the isotopic composition towards large negative values (Faure et al.,1988). Such negative value can also be explained if the nucleation for nodular growth was provided by a metamorphic carbonate of depleted isotopic composition (Faure et al.,1988). Presence of septarian cracks and compact nature of this nodule may indicate hydrothermal action.

3A.6.5b Variation in carbon isotopic composition

Variability of δ^{13} C is also large across the sections as seen in case of δ^{18} O. However, in contrast to δ^{18} O, carbon isotope ratio shows enrichment at the core and depletion at the rim. Sarkar et al (1998) analysed Proterozoic (Vindhyan) carbonates from adjoining region and showed that δ^{13} C varies between -2% to 3%, similar to the values observed at the core of the nodules. Therefore, it seems that at the initial stage of formation the carbonatebicarbonate ions were derived from marine carbonates. During the later stage of nodule development δ^{13} C showed depletion. This was probably caused by enhanced supply of carbon from decay of organic matter present in the sediments. δ^{13} C of calcite at the core of nodule A is -2∞ and away from the center at a distance of 2 cm the value is -11∞ (w.r.t VPDB).



Figure 3.7b Correlation of carbon and oxygen isotope ratios in samples from nodule sections. Green triangle represents Damodar valley nodules whereas red circles denote data for one nodule from Ramgarh basin, which has anomalously low δ^{18} O at the centre.

Figure 3.7b shows a plot of δ^{18} O- δ^{13} C for these samples. Barring the samples for the Ramgarh nodule (BP/N1/95) other points show an inverse correlation (r^2 =0.81). This can be explained by a simple scenario. Depleted oxygen at the core reflects original glacial melt water while higher values at the rim suggests evaporative enrichment in the lake. Carbon isotope at the core shows dominant contribution from marine carbonate while contribution of CO₂ from decomposition of organic matter is significant towards rim. During interglacial periods when temperature was more conducive for growth of biota their decay may provide depleted carbon to the medium hosting growing nodules. At the same time, due to evaporation the same medium gets isotopically enriched in oxygen. The Barkipunu nodule (BPN1/95) plots away from the regression line. This deviation can probably be related to the suggested interaction of hydrothermal fluid during its early stage as explained before.

3A.6.6 Enigmatic objects in the basal Gondwana of Eastern India

As mentioned in **Chapter 2** during the collection of nodules from different strata of Talchir formation we came across some unusual shaped objects resembling nodules in outer shape but quite different internally. Some of them resemble flattened cabbage heads with concentric laminations indicating growth around a nucleus. They are coarsely crystalline and fibrous in nature occurring in thick beds of shale overlying the nodular bed. Pandya (1987) and Mohanti and Das (1997) described them as oncolites and bacterial colony respectively based on their shapes and micro-fabrics. A total of 8 such algal objects along with 7 nodules were collected from two horizons in a section at Nandirjhor nala, along the southern boundary of Talchir Basin near Angul village in Orissa.

Close examination of polished sections showed growth of calcitic laminations parallel to the bedding surface and around the nucleus. The laminae are separated from each other by thin clay films (**Figure 3.8a**) suggesting growth of calcite as algal mat followed by slow deposition of clayey material on top of it. Similar objects are reported from Antarctic region where ice cover on a lake during winter favours growth of microbial mat while ice free summer is conducive to deposition of silty and clayey layers (Bertrand-Sarfati and Monty, 1994). Detritals in these objects are mainly clays and micaceous. Clay occurs as patches between the laminations and may have acted as repository for organic matter. Flakes of biotite and muscovite are observed as dispersed grains in thin section. Mineralogical studies show that smectite is the major clay mineral. X-ray pattern of bulk powder reveals the presence of calcite and variable amount of quartz, detrital micas and clays.

Morphology of these objects is indicative of their biogenic character (Bertrand-Sarfati and Monty, 1994) as described below:

The objects have tussocky microstructure consisting of regular laminations defined by the juxtaposition of separated hemispherical tussocks of different sizes, sometimes with a concentric growth pattern (Bertrand- Sarfati, 1976). Objects (*Serizia radians*) with similar microstructures have been reported (Fairchild et al., 1990) from Proterozoic basin of Southwest Africa (**Figure 3.8b** and **Figure 3.8c**). Their laminae are composed of bands of



Figure 3.8a Growth of calcitic lamination parallel to thebedding surface resembling growth and deposition of algal bodies. (bar represents 1 cm).

alternating micrite and layers of clay and organic residue. Fibrous microsparite are abundant in most of the samples. The mineralogical and petrographic features of these bodies from upper part of Talchir formation resemble those of nonmarine stromatolites found in other regions (Bertrand-Sarfati and Monty, 1994). Many of these samples are friable in nature, have obvious features of alteration (cracks, veins of secondary calcites, clay rich) and contain high Mn (222 to 2800 ppm) (**Table 3.2**). This indicates significant effect of alteration and re-precipitation of calcite in a reducing environment.

3A.6.6a Stable Isotopes

These algal carbonates were also analyzed for stable isotope composition and carbonate-free residual material was examined for presence of organic matter. The δ^{18} O and δ^{13} C values range from 5‰ to 25‰ and 3‰ to -15‰ respectively (**Table 3.6**). In case of altered samples, δ^{18} O values are similar to those of local freshwater (pedogenic) carbonates with values around 25‰. However, samples with less alteration have mean δ^{18} O values 11‰ and mean δ^{13} C value -6.5‰. The δ^{18} O- δ^{13} C covariation plot (**Figure 3.9a**) shows that these two variables are, in general, anti-correlated if altered samples are neglected. The low δ^{18} O and δ^{13} C values in them confirm that they were precipitated in a freshwater lake having water

temperature conducive for growth of bacteria and algae. Interestingly, higher ratio of ¹⁸O/¹⁶O compared to nodules and depleted carbon in majority of samples are consistent with a scenario involving warm water and availability of biogenic carbon dioxide.

	1 (011011	J		i tunej et	
Sample	$\delta^{13}C$	$\delta^{18}O_{smow}$	%org.C	$\delta^{13}C_{org}$.	C/N ratio
NDJ/ST1/950	-11.1	25.3	1.24	-25.5	12.1
NDJ/ST2/951	-10.2	13.2			
NDJ/ST2/952	-9.3	13.9	1.01	-22.1	
NDJ/ST2/953	-9.9	13.1			
NDJ/ST2/954	-9.9	13.1			
NDJ/ST2/955	-10.1	13.3			
NDJ/ST3/95	-3.5	5.2			
NDJ/ST4/95	-3.4	14.5	0.45	-22.8	8.5
NDJ/ST5/95	-12.1	8.8	1.29	-24.4	
NDJ/ST6/95	-8.2	14.3	1.07	-24.5	
NDJ/ST7/95	-1.7	13.4			
NDJ/ST8/95	-2.7	13.5			
NDJ/N1/95	-3.2	14.7			
C-1	-2.8	13.2	0.04	-20.6	10.4
C	1	1	1	1	3
	30			-	

 Table 3.6 Isotopic composition of stromatolitic carbonates and residual organic matter from

 Nandirihor nala section. Mahanadi vallev basin.



Figure 3.9a Carbon and oxygen isotope ratio in algal carbonates from Nandirjhor Nala section.



Figure **3.9b** Carbon isotope ratio in the organic matter associated with algal carbonate from Nandirjhor Nala section.

3A.6.6b Carbon and Nitrogen in the suspected algae

Field observations, petrographic features and δ^{13} C of inorganic carbonate suggest that these bodies are probably biogenic. It is therefore, of interest to know if the carbonate-free residual matter is organically derived. Average δ^{13} C value of residual matter obtained from seven samples is -22.8 ± 1.6 ‰ w.r.t. VPDB (**Figure 3.9b**). In addition, carbon to nitrogen ratio of the residual matter was also analysed. It is known that C/N ratio in the terrestrial vegetation is considerably higher (>20) than the ratio observed in microorganism like bacteria, algae etc (Tyson, 1995). Interestingly, the C/N ratio of the carbonate residues lies between 2.8 to 10 (**Table 3.6**) as expected in case of microbial matter (Tyson, 1995). Depleted carbon in the calcite, highly negative δ^{13} C of residual matter and their low C/N ratio strongly suggest presence of microbes in these samples.

3A.7 Provenance of Talchir Basin sediments

Mineralogical and geochemical composition of sediments have widely been used to determine the provenance of detrital matter (Wronkowicz and Condie, 1987; Condie et al., 1991; Hiyashi et al., 1997). Owing to the fine grained nature the mineralogical make up of siltstone and shale is commonly established through its major element composition. The trace elements like REEs, Th, Sc, LILEs (Sr, Ba, Rb) and HFSEs (Cr, Zr, Ni) are commonly used to characterize the source area. Several factors affect the chemical composition of sedimentary rocks viz., grain size, adsorption of ions by clays, mobilisation of elements during diagenesis, degree of chemical weathering of the source rocks, climate and rate of tectonic uplift, bulk composition of the source terrain, tectonic settings etc. (Wronckowicz and Condie, 1987; Cullers, 1988). Being relatively insoluble in most natural waters these

elements are transported with detritals from the source rocks to the site of deposition (McLennan et al., 1980; Taylor and Mclennan, 1985; Condie, 1991). The detritals are also stable under diagenetic and low-grade metamorphic conditions (Argast and Donnelly, 1986; Bhatia, 1985; Feng and Kerrich, 1990). REE concentration in pelitic rocks is believed to reflect the REE distribution pattern of the source material (Ronov et al., 1974; Taylor and McLennan, 1985; Cullers et al, 1988; and Condie et al., 1991). The cratonic sediments are known to have uniform chondrite normalised REE distribution and negative Eu anomaly. Such uniformity is generally due to efficient mixing of continental sources during erosion and deposition (Taylor and McLennan, 1985; McLennan, 1980). Strontium isotopes of carbonate phase of these nodules further strengthen the provenance interpretation based on geochemical data.

3A.7.1 Rare Earth Elements

Lanthanum (Z=57) and the following fourteen elements from cerium (Z=58) to lutetium (Z=71) are usually classified as rare-earth elements. Although the REE exist predominantly as 3+ cations in the environment, there are two important exceptions, namely Ce which exists as Ce^{4+} and Eu which exists as Eu^{2+} . Thus, these two elements may fractionate from the 3+ cations as a function of redox potential. The REE of the bulk sediments were analysed to determine the catchment area of the river and thereby delineate the provenance of sediments in different basins. REE geochemistry of lake sediments is strongly controlled by dissolved and detrital components (Tricca,1999). Culler (1987,1988) found that bulk of REEs resides in the clay and silt-size fractions of the rock. However, silt fraction contains much less REE than clay fraction. Sand fraction is poorest in REE. Clays and micas are very good host for REEs. The heavy mineral suite in the silt and sand fraction is enriched in HREE (Gd to Lu) as compared to the clay fraction. Relative abundance of the heavy minerals and the clays appears to affect ratio of LREE (La to Sm) to HREE (Gd to Lu) and La/Yb ratios of the rocks.

Bulk samples (total 23 in number) from three basins (West Bokaro, Talchir and Ramgarh) were analysed for REE using non destructive neutron activation technique (**Table 3.7**). The Chondrite normalised REE distribution patterns of samples are plotted for West Bokaro, Ramgarh and Talchir basin in **Figure 3.10**, **3.11** and **3.12** respectively. The REE concentrations of surrounding country rocks are also plotted for comparison. All three figures

show LREE enrichment and negative Eu anamoly. The (La/Yb)_{chn} ratio for West Bokaro, Ramgarh basin and Mahanadi valley varies from 2.6 to 8.2 (Average= 5.7), 6.8 to 9.3 (Average= 8.0) and 7 to 17 (Average =11.1) respectively. One sample from Mahanadi valley and another from Ramgarh basin (NDJ/ST5 and BP/N3b) show exceptionally high (La/Yb)_{chn} ratio of 45.2 and 43.8 respectively. The reason for such anomalous values is not clear. However, majority of samples is composed of sediments more or less similar in composition to post-Archaean shale (9 to 9.2) (Taylor and McLennan, 1985).

Eu anamoly is defined as ratio of measured concentration of Eu in the sample and estimated Eu concentration obtained from linear interpolation of normalised concentration of preceding and succeeding elements (Sm and Tb). It is computed using the formula of McLennan et al (1980) modified by later workers (Taylor and McLennan, 1985):

$$Eu^* = \frac{2}{3}[Sm]_N + \frac{1}{3}[Tb]_N$$

The $(Eu/Eu^*)_{chn}$ varies from 0.739 to 0.489 (Avg: 0.628), 0.47 to 0.697 (Avg: 0.564) and 0.47 to 0.663 (Avg:0.569) for West Bokaro, Ramgarh and Talchir basin respectively. Such negative Eu anomaly is commonly observed in sedimentary rocks derived from old continental crusts (Nance and Taylor, 1977; Taylor and McLennan, 1985; Gormet et al., 1984).

Sample No	La	Ce	Nd	Sm	Eu	Tb ng/gm	Yb	Lu ng/gm
	W	est Boka	ro basi	n, Dan	odar	valley		
SN/3A	76.1	172.4	83.0	22.5	5.0	2811.0	11.2	2210.0
DN/1A/95	54.8	121.0	57.8	13.4	3.3	2279.0	8.1	978.2
DN/N4	74.2	138.4	71.4	23.9	5.6	5108.8	19.6	3035.9
DN 3A-1	67.0	128.0	68.0	14.4	2.6	1859.6	6.3	885.5
DN6-1	77.1	113.2	70.1	16.1	2.7	1827.6	6.6	1000.6
DN/N3/95	90.7	206.1	114.3	37.8	7.1	1817.8	7.5	903.2
DN/N2/95	58.9	118.1	59.6	12.8	2.6	1656.6	6.1	848.7
DN-2	42.7	100.9	47.8	10.6	2.0	1403.4	5.3	713.6
DN/3A/95	73.2	124.3	70.8	21.3	3.3	2867.9	12.1	1480.4
Mean	68.3	135.8	71.4	19.2	3.8	2403.5	9.2	1339.6
]	Ramgarł	ı basin,	Damo	dar va	lley		
BP/N3a/95	49.6	114.3	49.5	9.9	2.2	1251.3	5.0	579.0
BP/N3b/95	195.2	302.4	121.1	20.0	2.7	1546.2	3.0	331.7
BP/N1/95	63.2	95.7	53.6	9.2	1.5	1176.3	5.0	682.1
BP/N2/95	86.2	143.3	76.1	16.4	2.7	1797.7	6.3	800.9

Table 3.7 REE composition of whole rock samples from threedifferent Talchir basins of Peninsular India (in ppm).

BP/M1/95	73.8	151.9	76.7	15.3	2.9	1984.3	6.7	885.2		
Mean	93.6	161.5	75.4	14.2	2.4	1551.2	5.2	655.8		
Talchir basin, Mahanadi valley										
NDK-A1	161.3	339.6	160.3	32.0	6.3	3049.8	6.4	1243.2		
NDK-5	48.6	112.4	64.5	11.6	2.1	1631.2	4.5	589.0		
NDK-1	62.4	144.2	77.1	14.1	2.5	1894.3	5.6	717.0		
NDJ/ST5/95	41.1	66.5	24.9	4.2	0.6	431.0	0.6	72.8		
NDJ/ST2/95	56.7	103.8	58.9	10.4	1.8	1143.3	3.0	379.2		
Mean	74.0	153.3	77.1	14.5	2.7	1629.9	4.0	600.2		

As mentioned before, Talchir sediments are believed to have been derived from the southern periphery of the basins. Southern periphery of Damodar valley basin is composed of granites and gneisses of Chotanagpur region (shown by cross fill in **Figure 3.13**) whereas for Mahanadi valley basin southern part is composed of basic igneous and metamorphic rocks of Eastern Ghat. REE compositions of Singhbhum granite (Chotanagpur region) and granulite (Eastern Ghat region) were determined by Mazumder (1988) and Paul et al (1990) respectively and are used here for comparison with concentrations in the corresponding nodules. The REE composition of Chotanagpur gneisses though unknown may possibly be similar to that of the granitic rocks of Singhbhum belt (Saha, 1994; Mazumder, 1988). The rare earth distribution in samples from West Bokaro and Ramgarh basins is similar to the pattern observed in Singhbhum granite except for a larger negative Eu anamoly in granite (**Figure 3.10 and Figure 3.11**). The enrichment of Eu in bulk sediments compared to that of granite can be explained by preferential uptake of Eu in calcite lattice sites during precipitation, as calcites constitute a major part of bulk samples.

Rapid decreases with Z for LREE and flat pattern for HREE are seen for both Singhbhum granite and nodules from Damodar valley (West Bokaro and Ramgarh) region. The similarity is consistent with the proposition that the source for West Bokaro basin sediments was the granitic rocks of Chotanagpur region. This is also supported by analysis of palaeocurrent direction from sedimentary structures and study of heavy mineral composition in the sediments (Tiwari and Casshyap, 1978; Tewari, 1990) (shown schematically in **Figure 3.13**). The REE distribution of samples from Talchir basin, Mahanadi valley is similar to the pattern observed in mafic granulites occurring in the south of the basin. In addition, the individual values show good agreement. In fact, the agreement is much better than that of Damodar valley. A rapid decrease with Z for LREE and gentle decrease in HREE is observed

in case of samples from Mahanadi valley. Result obtained from this investigation is consistent with the observation made earlier based on heavy mineral composition of sediments (sandstone underlying nodule bed) and rocks of Eastern Ghat granulite belt (Das and Pandya, 1997).

3A.7.2 Trace elements

Trace element composition of nodules is measured to confirm the inferences drawn based on REE distribution. Simultaneous use of trace elements and REE concentration is valuable in deriving the source of sediments deposited in a basin (McLennan et al., 1980; Taylor and McLennan, 1985). As discussed in the previous section, REE analysis in the nodules suggests that granite and gneissic rocks of Chotanagpur plateau and mafic granulites of Eastern Ghat belt are source rocks for the sediments in Damodar and Mahanadi valley basins respectively. Several samples of nodules were also analysed for a few provenance sensitive elements to obtain corroborative evidence.



Fig 3.10 Chondrite normalized concentrations of eight rare earth elements in the nodules of West Bokaro region (Damodar valley).Red curve shows the pattern of REE in the nearby Singhbhum granite (south of the basin).

Fig 3.11 Chondrite normalized concentrations of eight rare earth elements in the nodules of Ramgarh region (Damodar valley).Blue curve shows the pattern of REE in the nearby singhbhum granite(south of the basin).

95

Fig 3.12 Chondrite normalized concentrations

These elements are Mo, U, Th, Cr, Hf, Ba, Sr, Ni, Sc, Rb, Zn, and Co. The concentrations of these elements are highly variable in different rock types and can be used as tracers to understand the provenance of grains constituting a sedimentary rock.

Sample No./	Ba	Sr	Ni	Rb	Zn	Sc	Со	U	Th	Cr	Hf	Мо
West Bokaro basin, Damodar valley												
SN/3A	582.2	188.0	47.2	134.1	58.7	12.1	10.4	6.2	21.8	84.5	7.1	8.7
DN/1A/95	381.0	nd	nd	112.7	39.7	10.1	8.8	0.8	11.6	61.8	5.8	1.4
DN/N4	589.2	182.2	32.2	129.7	58.4	8.1	5.4	7.6	16.7	71.7	6.8	9.5
DN 3A-1	378.4	187.2	32.8	103.4	72.0	10.4	12.5	1.7	16.1	83.9	7.0	1.9
DN6-1	822.4	231.1	18.8	116.9	40.7	6.8	5.5	2.5	13.4	52.6	8.2	2.9
DN/N3/95	962.8	65.4*	nd	152.6	59.7	10.8	10.8	22.0*	19.7	67.3	6.2	28.2*
DN/N2/95	425.9	232.9	22.0	122.1	34.2	9.5	6.1	1.7	12.0	117.8	5.8	2.2
DN-2	643.3	188.0	12.8	144.2	30.5	9.5	6.1	1.3	17.5	195.1	6.9	2.3
DN/3A/95	483.2	340.2	18.5	101.0	43.9	9.7	6.8	2.7	17.1	102.1	9.5	Nd
Mean	585.4	221.9	26.3	124.1	48.7	9.7	8.0	3.1	16.2	93.0	7.0	4.1
	•	•	R	amgarh b	asin, Dan	odar vall	ey					
BP/N3a/95	nd	nd	346.7*	97.2	83.1	10.1	11.7	0.9	12.1	69.7	4.8	Nd
BP/N3b/95	300.3	1126.8*	nd	81.7	85.6	5.8	12.8	0.5	23.6	55.5	0.7	Nd
BP/N1/95	550.0	284.7	nd	128.1	28.4	7.1	5.9	1.0	13.2	99.4	6.6	Nd
BP/N2/95	662.5	252.3	22.5	110.4	47.2	11.5	10.2	1.5	nd	158.9	5.4	Nd
BP/M1/95	640.0	173.4	26.5	111.9	45.7	12.3	11.0	1.0	15.9	134.9	7.4	Nd
Mean	538.2	236.7	24.5	105.9	58	9.4	10.3	1.0	16.2	103.7	4.98	Nd
	•	•]	Falchir bas	sin, Maha	nadi valle	ey					
NDK-A1	782.8	496.5	32.9	132.4	67.8	13.7	11.6	2.5	24.1	125.0	6.0	3.5
NDK-5	735.9	151.6	58.2	134.0	67.1	11.6	13.3	0.6	14.6	98.1	3.4	1.0
NDK-1	639.0	283.4	44.3	141.7	78.8	13.5	12.8	0.7	17.6	124.7	6.3	0.9

Table 3.8 Trace composition of whole-rock nodule (in unit of ppm).

												9	17
NDJ/ST5/95	59.9	197.1	n.d	19.8*	12.3	1.3	2.7	0.1	5.2	12.5	0.2	Nd	1
NDJ/ST2/95	434.1	163.1	41.4	107.9	50.2	9.3	11.3	0.5	12.1	80.7	2.2	0.6	
Mean	648	258.3	44.2	129	52.2	9.9	10.3	0.9	14.7	88.2	3.6	1.5	
												-	-

* Exceptionally high and low values neglected during mean calculation.

Concentrations of these 12 elements which belong to the category of Large Ion Lithophile Elements (LILEs) and High Field Strength Elements (HFS) are given in **Table 3.8.** These elements are incompatible during most igneous processes; therefore, they tend to be enriched in felsic relative to mafic rocks. According to Taylor and McLennan, (1985) and Bhatia and Crook (1986), Th is generally resistant to change during weathering and alteration processes and in majority of mafic rocks concentration is less than 1.3 ppm whereas in the felsic sediments it has higher abundance. Th and U are geochemically coherent during most magmatic processes.





The average concentrations (in ppm) of U, Th, Ni, Ba and Sr in the granite from Chotanagpur region are: 6.2, 20.5, 9, 483 and 342 respectively (Saha 1994). **Table 3.8** shows reasonable agreement for these elements (except Ni) between the nodules from West Bokaro and the granite. Uniform Th/U ratios in the samples indicate that they were unfractionated during secondary processes.

Higher concentrations of Ni (mean value is 44 ppm) in the samples from Mahanadi valley (**Table 3.8**) may reflect contribution from source rocks intrinsically rich in Ni, such as ultramafics and mafic granulites of Eastern Ghat region. The Proterozoic belt of Eastern Ghat constitutes the southern limit of Talchir basin in Mahanadi valley and is mainly composed of granulites with minor component of charnockites and migmatites. The average concentrations of U, Th, Ni, Ba and Sr (in ppm) measured in a few samples of granulites from Eastern Ghat region are: 0.61, 1.3, 80, 91, and 92 respectively (Paul et al., 1990). Composition of charnockite rocks is not known. However, it is expected to be similar to the charnockites from Southern Indian craton. The average concentrations of Th, Ni, Sr, and Ba (in ppm) in the Southern Indian charnockites are: 14, 10, 96, and 315 respectively (Windley and Naqvi, 1978). The migmatite, a minor component of Eastern Ghat belt, is not well studied except for U and Th whose concentrations are: 1.5 ppm and 22 ppm respectively. These values are similar to those of nodule samples collected from Mahanadi valley basin whereas samples from Ramgarh basin probably represent an admixture of sediments originating from granite and granulite rocks (**Figure 3.13**).

Cullers et al. (1988) showed that immobile elements La, Th are more abundant in felsic than in basic rocks, but that the opposite is true for Sc and Co. Ratios such as La/Sc, Th/Sc, Th/Co, Ba/Sc and Ba/Co, (Table **3.9**) in sediments, therefore can, in favourable circumstances, allow a distinction to be made between a felsic and a mafic source. However, no significant difference is found among the samples from the three basins (**Table 3.9**).



Sample	La/Sc	Th/Sc	La/Co	Ba/Sc	Ba/Co
	We	est Bokaro, Da	modar valley	basin	
SN/3A	6.3	1.8	7.3	48.0	55.8
DN/1A/95	5.4	1.1	6.2	37.6	43.3
DN/N4	9.1	2.1	13.8	72.6	109.6
DN 3A-1	6.5	1.5	5.4	36.5	30.3
DN6-1	11.4	2.0	14.0	121.5	149.7
DN/N3/95	8.4	1.8	8.4	89.1	89.0
DN/N2/95	6.2	1.3	9.6	45.0	69.5
DN-2	4.5	1.8	7.0	67.8	105.7
DN/3A/95	7.6	1.8	10.8	50.0	71.0
-	F	Ramgarh basin,	Damodar Va	lley	
BP/N3a/95	4.9	1.2	4.2		
BP/N3b/95		4.0	15.2	51.6	23.4
BP/N1/95	8.8	1.9	10.7	77.0	93.5
BP/N2/95	7.5		8.4	57.4	64.8
BP/M1/95	6.0	1.3	6.7	52.1	58.0
	,	Talchir basin, l	Mahanadi Val	ley	
NDK-A1	11.8	1.8	13.9	57.3	67.5
NDK-5	4.2	1.3	3.7	63.7	55.5
NDK-1	4.6	1.3	4.9	47.3	49.8
NDJ/ST5/95	31.7	4.0	15.4	46.3	22.4
NDJ/ST2/95	6.1	1.3	5.0	46.6	38.4

Table 3.9 Ratios used for discriminating the provenance of sediments.

3A.7.3 Strontium isotopic composition

Chemical composition of river water depends on the geochemistry of the rock types in the drainage area of the basin. Carbonates precipitating at sediment water interface in a lake incorporate and preserve the signature of Sr isotopic composition of the water medium. It is also known that the concentration of Sr in such carbonates is related to the Sr/Ca ratio of the basin water and the ⁸⁷Sr/⁸⁶Sr ratio of the carbonates is equal to that of the water due to insignificant fractionation during precipitation. Therefore, Sr isotopic ratio of the water is traceable to that of the rocks and minerals in the drainage area.

In this study, ⁸⁷Sr/⁸⁶Sr ratio of the carbonate nodules from Talchir formation of peninsular India was used to understand the intensity of glacial weathering in the catchment area. Weathering of silicates contributes high radiogenic strontium to the river water. In addition, marine influence in Talchir sedimentation can also be inferred by the ratios obtained from the carbonates. Marine Sr isotopic ratio has evolved with time in the geological past. Large variation in Sr isotopic composition in carbonates during Phanerozoic has been correlated with major mountain building processes and ice sheet expansion. Veizer et al (1999) argued that increase in ⁸⁷Sr/⁸⁶Sr (i.e. radiogenic Sr) in the ocean was due to major tectonic activities in the past, which resulted in higher erosion rate and supply of radiogenic Sr. He also pointed out that decrease in Sr ratio could be related to major episodes of glaciation when discharge of radiogenic Sr was low. As discussed before, Permo-Carboniferous record of marine and continental sediments suggests an extensive glaciation covering all the Southern continents including India. Subsequent melting of glacier where Talchir sediments represent the melting episode resulted in high river water discharge and caused an increase in marine Sr isotopic ratio (Veizer et al., 1999; Faure et al., 1988) due to enhanced weathering in the continental regions (Archaean shields). Talchir carbonates, deposited in basins located around the eastern periphery of Gondwanaland in the Southern Hemisphere (Scotese, 1998), would then represent average composition of regional river water during deglaciation.



Figure 3.14 Frequency distribution showing Sr isotopic ratios in carbonate nodule collected from three Talchir basins of peninsular India.

In this study carbonate nodules grown insitu in the siltstone bed of Talchir formation are used to trace the composition of rocks present in the catchment area of the basin. These carbonates are composed of detritals along with calcite as diagenetic cement. Sr concentration of the carbonate phase is low ranging from 10-60 ng/g with mean of 40 ng/g. Earlier workers have shown that carbonates deposited in fresh water environment have low concentration of Sr compared to marine carbonates (Faure, 1992). Low Sr concentration along with depleted oxygen isotopic composition of the carbonates indicates that these sediments were precipitated in water derived from glacial melt stream (Bhattacharya et al., 1999).

Sr analysis of carbonates shows that a narrow range of isotopic ratio characterizes carbonates from each basin (**Table 3.10**). The ⁸⁷Sr/⁸⁶Sr ratios of the samples from West Bokaro basin and Ramgarh basin are clustered around 0.738 and 0.730 respectively (**Figure 3.14**). As explained below, these values are consistent with expected ⁸⁷Sr/⁸⁶Sr ratio of source water if the drainage was through the granitic rocks of Chotanagpur craton. The mineralogical composition of these granites showed that they are predominantly made up of plagioclase, quartz, K-felspar and biotite. Earlier analyses of a suite of these rocks from Chotanagpur belt showed age of 1590 Ma with initial ⁸⁷Sr/⁸⁶Sr ratios of 0.715 (Pandey et al.1986). Analyses also show ⁸⁷Sr/⁸⁶Sr ratios of 1.13, 1.98 and 8.96 for plagioclase, K-felspar and biotite respectively with whole rock ratio of 1.37 (Pandey et al., 1986). The contribution of plagioclase to the Sr isotopic ratio is significantly more than the others due to higher abundance of Sr in plagioclase and its susceptibility to weathering (Brantley et al., 1998).

Assuming that Talchir sediments deposited at time t=290 Ma and the plagioclase within granite formed at 1590 Ma (along with the whole rock), the 87 Sr/ 86 Sr ratio in the plagioclase at 290 Ma can be derived using the equation given below.

$$\left(\frac{{}^{87}Sr}{{}^{86}Sr}\right)_{290Ma} = \left(\frac{{}^{87}Sr}{{}^{86}Sr}\right)_{Initial} + \left(\frac{{}^{87}Rb}{{}^{86}Sr}\right)_{290m.y.} (e^{\lambda t} - 1)$$

The time t denotes the time after its formation till deposition i.e. t = 1590-290 m.y. i.e. 1300 m.y. and the initial ⁸⁷Sr/⁸⁶Sr ratio is taken as 0.715. In order to determine the ⁸⁷Sr/⁸⁶Sr ratio at 290 Ma the ⁸⁷Rb/⁸⁶Sr is obtained using the equation:

$$\left(\frac{{}^{87}Rb}{{}^{86}Sr}\right)_{290Ma} = \left(\frac{{}^{87}Rb}{{}^{86}Sr}\right)_{today} \left[e^{\lambda.290.10^6}\right]$$

 ${}^{87}\text{Rb}/{}^{86}\text{Sr}$ of plagioclase at 290 Ma can be obtained from present day measured concentration and using the value of λ the decay constant (1.42 x 10⁻¹¹ y⁻¹). The age-corrected value of ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ (i.e. Sr isotope ratio 290 m.y. ago) is 0.7304 in the plagioclase mineral, similar to the ratio observed in the carbonates from Damodar valley region.

Nodule samples from Mahanadi valley (**Figure 3.15**) show clustering of data points around 0.720. The ⁸⁷Sr/⁸⁶Sr ratios of adjoining country rocks (near Puri, Orissa), comprising pyroxene granulite, khondalites and charnockites are estimated to be 0.7053, 0.753 and 0.781 respectively after correcting the ratios for their ages i.e. 816 Ma, 3090 Ma, and 2695 Ma respectively obtained from Perraju et al (1979) and Paul et al (1990). Close similarity in Sr isotopic composition between carbonate nodule and adjoining rocks can only be explained if the water responsible for precipitation of carbonates in Mahanadi valley basin derived its Sr from granulite, khondalites and charnockites of Eastern Ghat belt. However, the country rocks comprising basic granulites and metasediments are made up of minerals like pyroxene, amphiboles and plagioclase which are prone to weathering and can contribute significant amount of Sr to river water during weathering. Unfortunately, Sr isotopic ratios from these individual minerals are not available for comparison.

3A.7.4 Sr isotopic composition of Mahanadi river water and Talchir carbonates

Mahanadi river basin is one of the eight major drainage systems in India. Its water composition reflects weathering of the carbonate, the most abundant lithology in the drainage area (Chakrapani and Subramanian, 1990). The Mahanadi annually delivers 15.74. 10^6 t of sediments to the Bay of Bengal, which is high, compared to its basin size (Chakrapani and Subramanian, 1990). The dissolved load dominates over physical load by a factor of 4, with 95% of the transport taking place in the monsoon season. The catchment area of Mahanadi river, covering central and eastern India receives large volume of material from Cratonic region. The cratonic region is composed of Archean basement and Phanerozoic sediments

Sample Number	⁸⁷ Sr/ ⁸⁶ Sr	Sr(ppm)
Dudhi N	ala section ,West Bokaro (Damoda	r Valley)
DN/N3/95	0.739	34.4
DN3A-1	0.739	40.1
DN/N4	0.739	40.3
DN/1A/95	0.735	43.1
DN-2	0.738	56.1
SN/3A	0.738	50.4
DN/N2/95	0.737	47.0
DN/3A/95	0.735	42.1
DN6-1	0.738	24.4
Barkipu	u section, Ramgarh basin (Damoda	ar Valley)
BP/ N2/95	0.726	33.7
BP/M1/95	0.731	22.2
BP/N1/95	0.728	33.4
BP/N3a/95	0.733	55.3
BP/N3b/95	0.733	50.3
Angu	l section, Talchir basin (Mahanadi y	valley)
NDJST295	0.718	24.8
NDK-5	0.719	30.8
NDJST595	0.719	24.6
NDK-1	0.718	32.4
NDK-A1	0.723	29.0
Chotanagpur granit	te, end member component of nodules	s in Damodar valley
AMD/GC/G-15/Plag	0.738 (corrected for 1590 Ma.)	28.2
Basic granulites from Ea	astern Ghat, end member component f	for Mahanadi carbonates
Basic granulite	0.7115	126
Khondalite Orissa	0.7206(corrected for 816 Ma.)	244

 Table 3.10
 Strontium isotopic ratios and concentration in the carbonates.

(granite suite= 34%, khondalite=7%, charnockite=15%, limestone, shale of lower Gondwana=17%, sandstone and shale of upper Gondwana=22% and coastal alluvium=5%). Sedimentary rocks are more prone to weathering than igneous and metamorphic rocks occurring as patches on top of Archean basement. Talchir sediments lying on the basement rocks are made up of boulders, sandstone and siltstone beds and constitute major source of ions and detrital components in the Mahanadi river water (Chakrapani and Subramanium, 1990). Isotopic composition of ⁸⁷Sr/⁸⁶Sr in the Mahanadi river water sample collected from Cuttack, Orissa is 0.719 (Trivedi et al., 1995) similar to isotopic composition in the nodular carbonates (0.718 to 0.723 in 5 samples) from Talchir basin in Orissa. Similarity of isotopic composition of carbonates and river water suggests that major source of Sr in the river water is carbonates from Gondwana sedimentary sequence confirming the earlier claim made by Chakrapani and Subramanium, (1990) based on major ion composition of river.

Section B

Palaeosol studies from Satpura basin

Satpura basin of Central India is one of the important Gondwana basins of peninsular India and contains four well-developed soil horizons belonging to Permian (Motur formation), Triassic (Denwa formation), Jurassic (Bagra formation) and Cretaceous (Lameta formation) periods. These palaeosols preserve valuable records of atmospheric variation in Permian and Cretaceous periods. The soils contain pedogenic carbonates in the form of rhizocretion and nodules. The δ^{13} C analyses of these soil carbonates are used in this work to estimate the past pCO₂ using the method of Cerling (1991). In addition, the carbon isotopic composition of the organic matter associated with these soils is used to estimate the isotopic composition of the atmospheric CO₂ and the plant-respired CO₂ during periods when these soils were formed.

3B.1 Results and discussion

The results of isotopic analysis of pedogenic carbonates from soil samples of Satpura basin are given in **Table 3.11** and the δ^{18} O vs δ^{13} C values are plotted in **Figure 3.15**. The mean δ^{18} O values (w.r.t. VSMOW) of the samples from Motur, Denwa and Bagra

formations (excluding the outliers which deviate by more than 2σ) are: 18.1 ‰ ($\sigma = 1.1$ ‰), 24.4 ‰ ($\sigma = 0.9$ ‰) and 24.1 ‰ ($\sigma = 0.8$ ‰) respectively. The corresponding mean δ^{13} C values (w.r.t. VPDB) are: -6.7 ‰ ($\sigma = 0.9$ ‰), -6.5 ‰ ($\sigma = 0.8$ ‰) and -6.1 ‰ ($\sigma = 0.8$ ‰). The corresponding values for pedogenic carbonate samples from Lameta formation (Ghosh et al., 1995) are: 24.7 ‰ for δ^{18} O and -9 ‰ for δ^{13} C.The mean δ^{13} C values of organic matter associated with the palaeosols are: -23.3 ‰ ($\sigma = 1.1$ ‰) for Motur formation, -24.5 ‰ ($\sigma = 1.0$ ‰) for Denwa formation and -26.1 ‰ ($\sigma = 1.2$ ‰) for Bagra formation.

SAMPLE	$\delta^{13}C$	$\delta^{18}O$	$\delta^{18}O$	$\delta^{18}O$	$\delta^{13}C_{PDB}$	δ^{13} C(org)				
			(sw)	(mw)	(plantco2)					
		MOTU	<u>R (260 m.y.</u>)						
M-1(Micrite)	-6.3	19.8	-11.0	-13.0	-21.4	-23.3				
M-2-1/rizhtrunk(M)	-6.2	18.2	-12.5	-14.5	-21.2					
M-2-2/rizhcore (M)	-5.1	18.5	-12.2	-14.2	-20.2	-23.1				
M-2-3(Micrite)	-6.2	(16.0)	-14.6	-16.6	-21.2	-23.6				
M-2-4(Micrite)	-7.0	17.7	-13.0	-15.0	-22.1	-23.0				
M-2-5(Micrite)	-5.7	18.3	-12.4	-14.4	-20.7	-21.9				
M-2-6 (Micrite)	-5.4	19.1	-11.6	-13.6	-20.4					
M-3 (Micrite)	-6.6	17.2	-13.4	-15.4	-21.6					
M-6 (Micrite)	-7.7	16.5	-14.1	-16.1	-22.7					
M-7 (Micrite+spar)	-7.7	(22.2)			-22.7					
M-10(Micrite)	-7.9	17.8	-12.9	-14.9	-22.9					
M-12 (Micrite)	-5.7	18.7	-12.0	-14.0	-20.7	-24.1				
M-13 (Micrite)	-6.9	18.4	-12.2	-14.2	-21.9					
M-14 (Micrite)	-6.7	18.0	-12.6	-14.6	-21.7	-21.4				
M-15 (Micrite)	-6.2	20.2	-10.5	-12.5	-21.3					
M-16(Micrite+Spar)	-7.4	(21.5)			-22.4					
Average	-6.7	18.1	-12.5	-14.5	-21.7	-23.3				
S.D.	0.9	1.1	1.1	1.1	0.90	1.1				
M-2/spar	-13.3**	[4.0]								
M-5/spar	-4.6**	[20.1]								
M-6-chkdia	-8.1	[12.4]			-23.1					
M-8/spar	-13.9**	[6.8]				-25.1				
M-9/spar	-11.1**	[18.4]				-24.0				
M-11/spar	-4.8**	[20.2]								
	DENWA (240 m.v.)									
D-2 (Micrite)	-7.2	25.2	-3.5	-5.5	-21.2	2				
D-3 (Micrite)	-6.4	25.2	-3.5	-5.5	-20.5	i				
D5-2 (Micrite)	-6.6	24.0	-4.7	-6.7	-20.7	-24.7				

Table 3.11 Isotopic composition of palaeosol carbonates and residual organic matter in the matrix.

D5-3 (Micrite)	-6.3	23.6	-5.0	-7.0	-20.4	-23.1
D5-4 (Micrite)	-7.0	24.0	-4.6	-6.6	-21.1	
D5-5 (Micrite)	-6.7	24.9	-3.8	-5.8	-20.8	
D5-6 (Micrite)	-7.2	24.0	-4.7	-6.7	-21.3	
D5-8 (Micrite)	-7.2	(19.6)			-21.3	
D5-11 (Micrite)	-5.8	26.1	-2.6	-4.6	-19.9	
D5-12 (Micrite)	-6.0	24.6	-4.1	-6.1	-20.1	-24.2
D5-16 (Micrite)	-6.4	(19.6)			-20.5	-25.2
D-8 (Micrite)	-7.0	23.5	-5.1	-7.1	-21.1	
D-9 (Micrite)	-6.7	23.3	-5.4	-7.4	-20.7	
Average	-6.6	24.4	-4.0	-6.2	-20.6	-24.5
S.D.	0.8	0.9	0.8	0.8	0.8	1.0
D5-15(Micrite+sp)						-24.0
D-1(Micrite+sp.)	-4.0	-2.7				
D5-1(spar)	-5.9**	[16.4]				

D5-7(spar)	-4.0*	** [27.9]				
D5-9(spar)	-8.6*	** [24.6]				
D5-10(spar)	-3.6*	** [28.5]				-25.9
	•	BAGRA	(200 m.y.	.)		
B-1 (Micrite)	-5.4	24.4	-4.3	-6.3	-19.5	
B-1-1(Micrite)	-6.0	25.5	-3.2	-5.2	-20.1	
B-1-4(Micrite)	-6.6	24.4	-4.3	-6.3	-20.7	
B-1-5(Micrite)	-5.7	23.4	-5.2	-7.2	-19.8	
B-1-6/L(Micrite)	-5.1	25.3	-3.4	-5.4	-19.2	
B-1-6/U(Micrite)	-6.1	23.9	-4.8	-6.8	-20.2	-27.5
B-2 (Micrite)	-6.4	24.0	-4.6	-6.6	-20.5	-27.3
B-2-5 (Micrite)	-4.0	23.3	-5.3	-7.3	-18.1	
B-2-6 (Micrite)	-6.3	23.4	-5.2	-7.2	-20.4	
B-2-8 (Micrite)	-6.2	24.4	-4.2	-6.2	-20.2	
B-2-9 (Micrite)	-5.9	22.3	-6.3	-8.3	-20.0	-23.0
B-2-10 (Micrite)	-4.7	24.0	-4.6	-6.6	-18.8	
B-3 (Micrite)	-6.4	24.3	-4.4	-6.4	-20.4	
B-4 (Micrite)	-6.0	25.1	-3.6	-5.6	-20.1	
B-5 (Micrite)	-7.3	22.7	-6.0	-8.0	-21.3	
B5-1 (Micrite)	-5.8	23.8	-4.8	-6.8	-19.9	
B5-2 (Micrite)	-5.1	25.0	-3.7	-5.7	-19.2	
B5-3 (Micrite)	-6.7	24.1	-4.5	-6.5	-20.8	
B5-4 (Micrite)	-6.1	24.6	-4.1	-6.1	-20.2	
B5-5 (Micrite)	-7.3	23.3	-5.4	-7.4	-21.4	-24.7
B5-6 (Micrite)	-6.8	24.1	-4.6	-6.6	-20.9	
B5-7 (Micrite)	-7.0	24.1	-4.5	-6.5	-21.1	
B-6 (Micrite)	-6.1	25.0	-3.6	-5.6	-20.2	-25.5
B-7 (Micrite)	-6.0	24.9	-3.8	-5.8	-20.1	
B-8 (Micrite)	-7.7	23.7	-5.0	-7.0	-21.8	
Average	-6.1	24.1	-4.5	-6.5	-20.2	-26.1
S.D.	0.8	0.8	0.8	0.8	0.8	1.2
B-1-2/spar	-6.0	[19.7]				
B-1-3/spar	-6.1	[18.4]				

B-2-3/spar	-4.9**	[19.8]							
B-2-4/spar	-6.2	[21.6]				-25.6			
LAMETA (65 m.y.)									
L1(Micritic)	-9.5	21.1	-7.5	-9.5	-23.6				
329/M/P*	-9.2	24.7	-6.0	-8.0	-23.3	-27.6			
Recent Concretion	-3.8	-2.9	-2.9	-4.9					

** () and []Outlier (values more than 2 sigma from the average) neglected during calculation. sw = soil water, mw = meteoric water

Organic matter from a single sample of Lameta soil yielded a value of -27.6 ‰. Andrews et al (1995) reported δ^{13} C values of -22.1‰ and -17.1‰ for two samples of organic matter from Lameta formation. These latter values are somewhat inconsistent with the normal range of C₃ plants and therefore, not considered here.

3B.2 Preservation of Geochemical signature

In order to derive palaeoclimatic information from the stable isotopic composition of palaeosol carbonate and organic matter, it is necessary to establish that the samples have not undergone any post-depositional alteration. The dominance of pedogenic micrites and finegrained fabrics in the samples and the absence of sparry calcites rule out major recrystallization subsequent to the precipitation of original carbonates. The isotopic data also show only minor spread in carbon and oxygen isotopic composition among various samples from the same formation (except in a few outlier cases which are neglected in calculation of mean). The consistency in isotopic composition within 1 ‰ would be unlikely if major alteration affected the samples. Additionally, our results are comparable with the published data of other workers on soil carbonates of similar ages and environments (Cerling, 1991; Yapp and Poth,1992; Mora et al., 1996).

The observed δ^{13} C values of the organic matter associated with the pedogenic carbonates lie within a range which closely matches with that of the C₃ vegetative biomass. As all the samples are from horizons older than Miocene (when C₄ plants were absent), these values provide additional evidence regarding the absence of any late diagenetic modifications. Moreover, the difference in δ^{13} C between coexisting organic matter and carbonate have a range (14 ‰ to 20 ‰) similar to that obtained for other palaeosol samples of similar age (Mora et al., 1996).

3B.3 Estimation of atmospheric pCO₂

Cerling's (1991) palaeobarometer is basically an isotope mixing model where the soil-CO₂ is made up of atmospheric CO₂ (through diffusion) and plant-respired CO₂ from vegetative sources. The signature of soil CO₂ is reflected in the δ^{13} C composition of soil carbonate which is governed by the δ^{13} C value of the soil-CO₂ and fractionation during precipitation which is temperature dependent (Deines et al., 1974). The δ^{13} C values of the two sources of soil-CO₂ are quite different. Whereas the δ^{13} C values of atmospheric CO₂ is – 6.5 ‰, the CO₂ respired by C₃ type vegetation can have value between –20 ‰ and –35 ‰, with a mean around –27 ‰ (Ehleringer, 1989). The degree of infiltration of the atmospheric CO₂ in the soil matrix (which is dependent on the atmospheric pCO₂) thus influences the δ^{13} C value of the soil-CO₂ and consequently the δ^{13} C value of the pedogenic carbonate. The details about Cerling's model and its mathamatical formulations are described below.

Model for pCO₂ in palaeo atmosphere(Cerling, 1991):

Pedogenic carbonates precipitate by combined processes of plant respiration and microbial activity in the soil. The concentration of soil CO_2 in a soil profile is controlled by the production rate of CO_2 and diffusion through the soil to its upper boundary, the atmosphere (Cerling, 1984). The concentration of soil CO_2 is governed by diffusion-reaction equation:

$$\frac{\partial C_s^*}{\partial t} = D*\frac{\partial^2 C_s^*}{\partial z^2} + \varphi_s^*(z)\dots(1) \text{ where } C*s \text{ is the concentration of } CO_2 \text{ in the soil } ($$

moles/cm²),

D* is the diffusion coefficient (cm²/s) for CO₂ in soil, z is depth (cm) and $\partial C/\partial z$ is the production rate of CO₂ in the soil as a function of depth. The subscript s refer to soil and * as bulk CO₂ without isotopic distinction. One boundary condition is the equality of the CO₂ concentration at the soil-air interface and that of atmosphere:

$$C_{s}^{*}=C_{a}^{*}$$
 for z=0.....(2)

Where C_a^* is the concentration of CO₂ in the atmosphere. The lower boundary condition is a no-flux state at an impermeable barrier (e.g. z = L, at the depth of ground water table) :

$$\frac{\partial C_s^*}{\partial z} = 0 \text{ at } z = L \dots (3)$$

The general solution to this equation is:

 $C_s^*(z) = S(z) + C_a^*$ (4) where S(z) is the specific solution to the eq (1) for a particular production function $\phi_s^*(z) = \phi_s^*(0) e^{-(z/\tilde{z})}$:

$$S(z) = \frac{\varphi_s^*(0)\hat{z}^2}{D_s^*} (1 - e^{-(z/\hat{z})}) \dots (5)$$

Same equation applies for ¹²CO₂ and ¹³CO₂ with appropriate diffusion coefficients D_s^{12} and D_s^{13} rather than bulk diffusion coefficient for CO₂. Using a standard δ notation, it is possible to derive the equation describing the variation of $\delta^{13}C(CO_2)$ in a soil with depth. The general solution as given by Cerling (1991) is:

$$\delta_{s}(z) = \left[\frac{1}{R_{PDB}}\left\{\frac{S(z)\frac{D_{s}^{*}}{D_{s}^{13}}\hat{\delta}_{\varphi} + C_{a}^{*}\hat{\delta}_{a}}{S(z)\left(1 - \frac{D_{s}^{*}}{D_{s}^{13}}\hat{\delta}_{\varphi}\right) + C_{a}^{*}\left(1 - \hat{\delta}_{a}\right)}\right\} - 1\right] \times 1000 \dots (6)$$

where

$$\widehat{\delta} = \left[\frac{R_{PDB} \left(\frac{\widehat{\delta}_i}{1000} + 1 \right)}{1 + R_{PDB} \left(\frac{\widehat{\delta}_i}{1000} + 1 \right)} \right] \text{ where } \delta_s, \ \delta_a, \ \delta_\phi \text{ are the permit (\%) values for soil CO2, the}$$

atmospheric CO₂, and soil respired CO₂, respectively, and R_{PDB} is the ratio ${}^{13}C/{}^{12}C$ in the isotopic reference standard PDB.

Therefore, this model allows us to estimate the pCO₂ values of the ancient atmosphere from the δ^{13} C values of the pedogenic carbonates if the following parameters are known:

1) The temperature of calcite precipitation in the soil.

- 2) The δ^{13} C value of the plant -respired CO₂
- 3) The δ^{13} C value of the atmospheric CO₂
- 4) The difference between the soil pCO_2 and the atmospheric pCO_2

The procedure for estimating each of these parameters is discussed below.

3B.3.1 Temperature of calcite precipitation

The temperature of the calcite precipitation in the soil is close to the mean soil surface temperature. Scotese (1998) surmised that Permian was a period during which large global temperature changes took place. In Early Permian global temperature was low with a mean around 10°C and at the end of Permian the temperature was extremely high near about 35°C (Scotese,1998). The global temperature was maintained at a slightly reduced value of 30°C till middle Jurassic. The wide spread glacial deposits at Permo-Carboniferous boundary (Talchir formation) followed by thick coal deposits of the overlying Barakar formation, the occurrence of red beds and calcic palaeosols in Motur, Denwa and Bagra formations and the

presence of thick deposits of carbonaceous claystones in Bijori formation (late Permian) together corroborate the suggested trend of the global temperature. However, the surface temperature of a locality is also influenced by its altitude and its latitudinal position. The palaeogeographic reconstruction of Gondwana landmasses indicates that the study area was situated at 50°S during Permian and at around 40° S to 30°S in middle Triassic and middle Jurassic (**Figure 3.16**). During this period the altitude seems to have remained consistently low and probably close to the sea level (Scotese, 1998). From the coupled ocean-atmosphere models and from the palaeoclimatic reconstructions it has been suggested that during summer the average surface temperature of the study area was 15°C in middle Permian and 25°C during middle Triassic and Jurassic (Kutzbach and Gallimore, 1989; Parrish et al., 1982), similar to the average summer temperature observed today at 50° and 35°S latitudes (Rudloff, 1981).

These estimates of the surface temperatures can be indirectly verified with the help of the δ^{18} O values of the pedogenic carbonates. The δ^{18} O value of carbonate precipitating in equilibrium with its water solution depends on: 1) δ^{18} O of water and 2) the temperature of precipitation. Therefore, if δ^{18} O of carbonate and δ^{18} O of soil water is known, the soil temperature can be derived. Reconstruction of continental configuration during the Phanerozoic period is available in map of Scotese (1998) which shows migration of Indian plate from Southern Hemisphere such that the study area moved from 60°S latitude (Permian) to 20°S latitude (Cretaceous). It is known that δ^{18} O of precipitation depend on the latitude where precipitation occurs. Based on IAEA compilation Rozanski et al (1993) showed systematic depletion of heavy isotopes in rainfall as one move from equator to pole and attributed the process to Rayleigh fractionation in the transportation of water vapour from equatorial region to polar region. This trend is supported by a few data points from Southern Hemisphere. The average δ^{18} O of rainfall at different meteorological stations situated at 60° and 35° latitudes in Southern Hemisphere are -10.0‰ and -4.5‰ (w.r.t. VSMOW) respectively. However, isotopic composition of rainfall at a given latitude depends on two factors: a) δ^{18} O of ocean water and b) Amount of rainfall.

3B.3.1.a δ^{18} O of ocean water

Veizer et al (1997) tried to establish the secular trend of ocean water δ^{18} O from isotopic composition of marine carbonates during Phanerozoic period. Dispersion of data points introduces genuine uncertainty in determining the ocean water isotopic composition at a particular time period. An apparent shift in isotopic ratio is observed at around 65 Ma (-1‰) and prior to that it seems to have fluctuated between -3 to -1‰ between 260 Ma to 65 Ma. A composition of -1‰ for ocean water between 260 to 65 Ma seems to be good approximation for our purpose. It means that the precipitation was lighter by 1‰ for the period 260 to 65 m.y.



113

3B.3.1.b Amount of rainfall

Amount of precipitation at a given latitude is governed by several factors like, distribution of land and sea, latitudinal distribution of landmasses and pCO_2 level in the atmosphere etc. Kutzbach et al (1989), using a global climate model predicted high rainfall during Permian to Jurassic period. Parrish et al (1993) and Crowell et al (1995) also postulated a high rainfall in giving rise to deposits of coal bed during this period in both the hemispheres. Assuming that the predicted increase in rainfall amount is correct the isotopic composition of rain water can be deduced.

Table 3.12 . Determination of soil temperature during Motur (260 m.y.), Denwa (240m.y.)
Bagra (200m.y.) and Lameta (65m.y.) periods from measured oxygen isotopic composition o
soil carbonates and composition of rain water expected during these periods.

Formation	Latt. $^{\Pi}$	δ^{18} O	δ^{18} O ow ^{Ω}	δ^{18} O of rain	δ^{18} O of sw	δ^{18} O of	Soil
	(°S)	(present		(expected)	(expected) [⊕]	carb.	Temp.
	. ,	day) ^{<}				(Measured)	(°C).≁
Motur							
260my	60	-10.5	-1	-14 ^{&}	-12	18.2	17
Denwa							
240my	45	-7	-1	-8	-6	24.4	17
Bagra							
200my	25	-6	-1	-7	-5	24.1	23
Lameta							
65my	20	-4	-1	-8^{ω}	-6	22.6	25
			0				

^{Π} from Scotese(1990). [<] from Rozanski et al (1993). ^{Ω} from Veizer (1986).

[&] Assuming extra depletion due to amount effect calculated from the difference between today's rainfall at 60°S latitude and rainfall amount during Permian time from Kutzbach and Gallimore, (1989). ⁽⁶⁾ Assuming extra depletion due to continental effect explained in Ghosh et al (1995). ⁽⁷⁾ Assuming 2‰ enrichment during conversion of meteoric water to soil water (see text). ⁽⁴⁾ Obtained from 10³ln α = (2.78 x 10⁶)/ T² –2.89 (Friedman and O' Neil, 1977)

The average δ^{18} O values of present day rainfall at 50° and 35°S latitudes are -10%and -4.5% respectively (Rozanski et al., 1993) when ocean water is 0‰. The isotopic composition of ancient precipitation can then be derived based on -1% ocean water and the increase in amount of rainfall at these latitudes from Kutzbach et al (1989) and variation in δ^{18} O of the rainwater with amount of precipitation obtained from Rozanski et al (1993). Rozanski et al (1993) have shown long term monthly and annual mean δ^{18} O values for an island station in tropical region as a function of mean monthly precipitation. The regression coefficient obtained from such plot suggests decrease in δ^{18} O value by 7‰ corresponding to 450 mm increase in precipitation amount. Assuming evaporative enrichment of 2‰ (Salomons et al., 1978) for Motur, Denwa, Bagra and Lameta time soil water compositions of -12, -6, -5 and -6‰ can be estimated. These values are used along with δ^{18} O of carbonates for estimating soil temperature. The soil temperature estimated for Motur, Denwa, Bagra and Lameta formations are 17° , 17° , 23° , and 25° C (shown in **Table 3.12**) respectively. These values are in broad agreement with the values adopted earlier.

3B.3.2 δ^{13} C value of the soil respired CO₂

The δ^{13} C of the organic matter associated with the pedogenic carbonates has been determined in this study and can be considered as proxy for δ^{13} C of the corresponding soil-CO₂. Prior to the Miocene C₄ plants were not present in the ecosystem and C₃ plants were the dominant vegetative biomass. The δ^{13} C values of the soil-respired CO₂ of the modern C₃ plants range from -20‰ to -35‰ (w.r.t. PDB) with an average of -27‰ (Ehleringer, 1989). The mean δ^{13} C values of organic matter associated with pedogenic carbonates from Motur, Denwa, Bagra and Lameta formations are -23.3‰, -24.5‰, -26.1‰ and -27.6‰ respectively (**Table 3.11**) and lie well within the range of the modern C₃ plants. These values provide robust estimates of δ^{13} C of the soil CO₂ at those times.

3B.3.3 δ^{13} C value of the atmospheric CO₂

The δ^{13} C of atmospheric CO₂ is also an input in Cerling's model and needs to be estimated independently. In earlier studies (Cerling, 1991, Andrews, 1995, Ghosh, 1995) this was assumed to be constant and its value was taken to be -6.5‰, the pre-industrial atmospheric CO₂ value. However, since then several studies (Mora et al., 1996; Thackeray et al., 1990) have shown the possibility of δ^{13} C variation in the past. There are two ways of estimating the δ^{13} C of atmospheric CO₂ in the past as described below:

3B.3.3.a Method based on marine brachiopods

Oceans contain 50 times more CO₂ (as bicarbonate and carbonate ions) than the atmosphere and maintain isotopic equilibrium with it (Watson et al., 1991). It is also known that the δ^{13} C of oceanic inorganic carbon is close to that of the marine limestone. Therefore, the δ^{13} C value of marine limestone can be used to estimate the δ^{13} C atmospheric CO₂ after correcting for isotopic fractionation. A number of studies indicate that the δ^{13} C value of the marine limestone (based on brachiopods) and marine organic matter have varied in the past (Veizer et al., 1997; Veizer et al., 1986; Weissert and Breheret 1991; Weissert et al., 1998). Therefore, it follows that the δ^{13} C value of the marine carbonates are estimated as 6‰, 0.9‰, 1.2‰ and 1.8‰ for 260 Ma, 240Ma, 200Ma and 65 Ma which are the respective ages corresponding to the four soils studied here (Veizer et al., 1986). Using the modern (pre-industrial) value of δ^{13} C_{atm-marine} as -6.5 ‰ (Cerling,1991) the δ^{13} C of atmospheric CO₂ for these periods would then be -0.5‰, -5.6‰, -5.3‰ and -4.7‰.

3B.3.3.b Method based on soil organic matter

The mean δ^{13} C of the C₃ organic matter is depleted by about 21‰ compared to the δ^{13} C of the atmospheric CO₂. A similar relationship has been noted for late Palaeozoic and lower Cretaceous samples (Mora et al., 1996; Grocke et al., 1999). Therefore, it is possible to arrive at alternative estimate of the δ^{13} C of the atmospheric CO₂ from the carbon isotopic ratio of organic matter. Using the mean δ^{13} C of the organic matter from Motur, Denwa, Bagra and Lameta formations (-23.3‰, -24.5‰, -26.1‰ and -27.6‰ respectively) the δ^{13} C values of the atmospheric CO₂ in those periods are estimated to be -2.3‰, -3.5‰, -5.1‰ and - 6.6‰ respectively.

It is interesting to note that there is systematic decrease in the δ^{13} C of organic matter from 260 to 65 m.y. Terrestial biota incorporate atmospheric carbon dioxide during photosynthesis reaction and therefore any change in δ^{13} C composition of atmospheric CO₂ is reflected in the composition of organic matter in the sediments (Thackeray et al., 1990).

The above estimates based on two methods are not in firm agreement. However, we believe that the estimates based on soil organic matter (OM) are more reliable due to the following reasons:

In contrast to marine limestone, soil OM represents composite mixture of plant derived materials which are photosynthetic products from atmospheric CO_2 and is expected to be sensitive to the composition of CO_2 in the atmosphere (Farquhar et al., 1989).

There are large spreads in the δ^{13} C values of marine brachiopod at any given geological time (Veizer, 1986) the origin of which is not clear. This spread makes it difficult to arrive at firm estimate of the mean marine limestone δ^{13} C value. Moreover, there are very few samples corresponding to 240 Ma time range. Our data set shows that the samples of OM from a given strata are characterised by tight cluster of δ^{13} C values ($\sigma = 0.8\%$, **Table 3.11**). This makes it possible to define a robust mean, which can be used to derive the δ^{13} C of atmosphere at that time.

3B.3.4 Difference between the soil pCO_2 and the atmospheric pCO_2 : S_Z parameter

The difference in concentration between the soil CO_2 and the atmospheric CO_2 depends on soil porosity, soil respiration rate and depth of CO_2 production. This difference (S_z) plays an important role in Cerling's mixing model and needs to be assessed independently. Approximate value of the soil porosity can be obtained from observations made on recent soils of the same type. However, the mean CO_2 production depth and the soil respiration rate for geologically ancient soils can not be estimated with certainty. The rooting depth, the dimensions of the rhizoliths and their density of occurrence in the palaeosol profiles may probably be used for such estimation but no such model is available at present. Observations made on the modern soils show that for the desert soils S_z is less than 3000 ppmV and for well drained temperate and tropical soils S_z ranges between 5000 and 10,000 ppmV. Mora et al. (1996) assumed a value between 3000 and 7000 ppmV for the middle to

late Palaeozoic semi-arid tropical to temperate vertic palaeosols. Some of these palaeosols (of Silurian age) indicate a very shallow rooting depth. On the other hand, Ghosh et al. (1995) adopted a range between 3000 and 5000 ppmV for the well-drained semi-arid late Cretaceous palaeosols with higher rooting depths than Silurian soils (Ghosh et al., 1995; Tandon et al., 1995; Ghosh et al., 1998; Tandon et al., 1998). We note that the gleyed pedohorizons (signature of clay rich component with less permeability) are, in general, absent in the profiles of Denwa, Bagra and Lameta formations. Some amount of gleying is present below the Bk pedohorizons of Motur formation which may suggest a higher value of S_z . However, high latitudinal position (50°S) of the study area along with low mean annual temperature (17°C) during the Motur time implies reduced plant productivity and consequently low S_z . All the palaeosols analyzed in this work show characteristics of well-drained, semi-arid soils. In view of the above considerations, a range of S_z values between 3000 and 5000 ppmV is adopted for these palaeosols.

3B.4 The pCO₂ determination

Using the mean δ^{13} C values of the palaeosol carbonates along with above mentioned values of the required parameters and estimated δ^{13} C of the atmospheric CO₂ based on marine carbonates in the model of Cerling (1991) we obtain following range of pCO₂ values (in ppmV): 325 to 540 for Motur period, 1100 to 1800 for Denwa period, 1700 to 2850 for Bagra period and 975 to 1650 for the Lameta period (**Table 3.13**). However, if δ^{13} C of atmospheric CO₂ estimated from the organic matter is used, the obtained ranges are: 460 to 780, 700 to 1180, 1610 to 2660 and 1110 to 1850 respectively (**Table 3.14**). The given ranges cover the uncertainties in the model parameters.

Table 3.13 Estimation of concentration of CO_2 at different times in thepast a comparison.

Formation (Age in m.y.)	δ ¹³ C* (carb.)	$\delta^{13}C$ (atmospheric CO_2) [@]	pCO ₂ =		Mean CO ₂ (ppm V)	R
			А	В		
MOTUR (260)	-6.5	-2.3	325	540	433	1.5
DENWA (240)	-6.7	-5.6	1100	1800	1450	5.1

BAGRA	-6.1	-5.3	1700	2850	2275	8.0
(200)						
LAMETA	-9.1	-4.7	975	1650	1313	4.6
(65)						

[≅] from Table 3.11.

[@] δ^{13} C of atmospheric CO₂ obtained from marine carbonate (Veizer et al., 1986).

⁼Column A and B refer to S(z) values of 3000 and 5000 ppm in Cerling's model (see text)

R= CO2 in past / CO2 at pre-industrial time

In view of our earlier discussion the second set of values are adopted for further discussion. These values represent the first independent estimates of CO_2 level in the atmosphere during the period 260 to 200 Ma. Additionally, the soil samples belong to the same basin and therefore, provide a more reliable measure of relative CO_2 variation. An increase in CO_2 level after early Permian low (310-285 Ma) is an interesting aspect of Berner's model prediction and arises due to enhanced rate of degassing. Cretaceous period is again characterised by low value. These two predictions are verified by our results but the detailed nature of variation is found to be slightly different from Berner's model. **Figure 3.17**, shows a plot of $R(CO_2)$ against soil age (in m.y.) where 'R' represents ratio of CO_2 concentration at a given age relative to pre-industrial modern value (280 ppmV).

Table 3.14 Estimation of concentration of CO_2 and its isotopic composition in atmosphere at different times in the past.

Formation (Age in m.y.)	$\delta^{13}C^*$ (carb.)	δ ¹³ C* (OM)	Temperat ure [≅] (°C)	$\delta^{13}C$ (atmospheric CO_2) [@]	pCO ₂ =		Mean CO ₂ (ppm V)	R
					А	В		
MOTUR (260)	-6.5	-23.3	17	-2.3	460	780	620	2.2
DENWA (240)	-6.7	-24.5	17	-3.5	700	1180	940	3.4
BAGRA (200)	-6.1	-26.1	23	-5.1	1610	2660	2135	7.6
LAMETA (65)	-9.1	-27.6	25	-6.6	1110	1850	1480	5.3

 \cong from Table 3.11.

^(a) δ^{13} C of atmospheric CO₂ obtained by subtracting 21‰ from δ^{13} C (OM) (see text).

⁼Column A and B refer to S(z) values of 3000 and 5000 ppm in Cerling's model (see text)

 $R = CO_2$ in past / CO_2 at pre-industrial time

It is seen that there is excellent agreement of derived R values with Berner's prediction for Motur and Denwa time but the derived R value for Bagra (200 my) and Lameta time are 7.2 and 5.5 respectively, in contrast to Berner model value of about 5 and 2 respectively. The disagreement persists even at the lower limit of our estimate. The parameters involved in the calculation of pCO₂ during the Bagra and lameta time are well constrained and the high CO₂ level seems to be genuine. Uncertainities in average δ^{13} C (OM) have not been accounted for in the CO₂ calculations. If taken into account, these uncertainities would increase or decrease calculated mean CO₂ concentration by about 15% for Motur and Denwa formations while in case of Bagra formation the change would be atleast 25%.

3B.5 Berner's model of pCO₂ and the observed values

Berner (1994) has proposed a model for calculating the level of atmospheric CO_2 over Phanerozoic time. This model is based on long term carbon cycle which involves the transfer of carbon between rocks and the ocean/atmosphere/biosphere system. This includes: (1) the weathering of Ca and Mg silicates and carbonates and sedimentary organic matter on the continents; (2) burial of organic matter and Ca-Mg carbonates in sediments, and (3) the thermal breakdown of carbonates and organic matter at depth with resultant CO_2 degassing to the atmosphere. **Figure 3.17** shows the plot of estimated pCO₂ values over time along with the model curve of Berner (1994, 1997). The derived values lie within the error envelope of the model curve except in Late Cretaceous but the profile of pCO₂ variation is different. There could be several reasons for this difference. The model results are sensitive to various assumptions used in the calculation. For example, it is assumed that the CO_2 concentration during the Palaeozoic era was governed in large measure by variation in solar constant and biological activity compared to tectonic effects. Some of these assumptions can be constrained by the CO_2 values obtained in this work.

At 260 m.y.

The amount of CO_2 estimated for Early Permian (260 Ma) is 620 ppmV which is little higher than expected value of 430 ppmV from model prediction. However, the estimate fell
within the error envelope of model prediction curve. During Early Permian Southern Hemisphere, experienced extensive glaciation which results in large drop in CO_2 level in the atmosphere. The prediction of low CO_2 level for Permo-Carboniferous fits with the estimate based on soil carbonate records (Mora et al., 1996, Berner, 1997). This work added one more point, ahead in time and the estimated value higher than predicted value is slightly for Early Permian.

At 240 m.y.

The amount of CO_2 in Early Triassic (240 Ma) is 940 ppmV, found to be lower than the model result of 1425 ppmV. This estimate rests on a large number of samples with small standard deviation. High abundance of CO_2 predicted by the model may be due to high estimate of sea floor subduction rate at 240 m.y. obtained by extrapolation from sea floor subduction rate over the past 150 m.y.

At 200 m.y.

For Late Triassic pCO₂ value is much higher (2135 ppmV) than the predicted value of 1140 ppm V. High value of CO₂ in the atmosphere is likely to be related to enhanced degassing from Earth's interior during Triassic period. High rate of degassing may be due to Siberian volcanism, which occurred in continental platform in the Northern Hemisphere. The Late Cretaceous (65 Ma) pCO₂ value of 1480 ppmV, estimated from this work is higher than the simulated pCO₂ value (1140 ppm V) of Berner (1991,1997). Earlier workers have suggested average pCO₂ value of 1000 ppmV and more than about 1300 ppmV for Late Cretaceous (Andrews et al., 1995; Ghosh et al., 1995) atmosphere. Enhanced emission of CO₂ could be due to Deccan flood basalt eruption which started around ~71 m.y. and continued till ~65 m.y. (Venkatesan et al., 1986)



3B.8 Atmospheric CO₂ and Soil Maturity

Atmospheric CO_2 plays an important role in development of soil and growth of calcrete in sedimentray strata. Mature soils are composed of abundant clayey materials and charecterised by development of laterite bed. Such soils are difficult to find because of their susceptibility to weathering. Extremely mature soils are formed in well drained tropical regions and are related to high rainfall. However, in semiarid to arid regions, where little moisture moves through the soil, translocation of calcareous material occurs in lower horizons as pedogenic nodules and calcretes. Dominance of pedogenic clay layer in the B and C horizon are indicative of

Bagra Soil More stable platform, complete development of soil profile, intact rhizocretion and glaebular horizon, 2240 prolific microbial acitivit aterally widespread. PCO₂ level (ppm) Denwa Soil Incipient soil development, incomplete soil profile, K-horizon absent, smaller glaebules,negligible 1500 microbial activity, unstable platform. Motur Soil Hardpan carbonates, incomplete soil profile, 430 glaebules absent, rhizocretion less frequent, microbial activity absent, and unstable platform. enhanced maturity and is related to high productivity and bioturbation. Carbon dioxide level in the atmosphere has impact on soil maturity through biotic growth and calcrete formation. High CO₂ level (620 ppm V) in Early Permian and subsequent increase during Early Triassic (940 ppm V) and very high level in Late Triassic (2135 ppmV) must have severely affected rainfall and soil productivity. The net effect is observed in the soils studied here through increase in the zone of gley horizon, bioturbation, rizhocretion occurrence and nodule formation. **Figure 3.18** shows a comparative picture of the three soils studied here against the pCO₂ level prevalent at that time. Motur formation has a calcrete horizon and 2-3 cm zone of rhizocretion, less clay content and is covered by a bed containing non pedogenic carbonate. Soil of Denwa formation is incipient in character; clay content is small and occurs in small patches. Bagra formation is characterised by the presence of high percentage of iron oxide, reflecting increasing oxidation of ferromagnesium minerals in the host country rock. These changes in soil micromorphology and composition seem to be linked with increasing CO_2 level in the atmosphere.

Chapter 4

Summary and conclusion

This chapter summarizes the salient results of this thesis and presents the conclusion drawn from them. Primary focus of this thesis, presented in section-A is to understand the environment of precipitation for nodular carbonates grown syngenetically with Talchir sediments in three sedimentary basins of Peninsular India and to identify the provenance of water and bulk sediments. In section-B the stable isotopic study of soils and associated organic matters from different sedimentary formations of Gondwana time periods are used to derive atmospheric CO_2 concentration in the past. These two aspects are summarized below.

4.1 Environment of Talchir sedimentation

The Section-A of this thesis deals with isotopic analyses of nodular carbonates from Talchir formation of Peninsular India. Occurrence of nodular bodies in the Talchir sediments has not been reported in geological literature and geochemical study of Talchir sediments for determination of palaeo-environment was never attempted prior to this work. Nodules from Talchir sediments of West Bokaro, Ramgarh and Talchir basins were analysed isotopically. Results show that they have depleted values of δ^{18} O and δ^{13} C (mean 10.8 ‰ wrt SMOW and -9.7 ‰ wrt PDB respectively) corresponding to the marine limestones. These values are indicative of lacustrine environment of deposition where the water was supplied by melting of glacier formed in nearby hills. The mean δ^{18} O value is used for estimation of average isotopic composition of the lake water and its ultimate source i.e. the meteoric water. The estimated composition of the meteoric water is found to be slightly depleted compared to today's rainfall at the palaeo-latitude of these Talchir basins (about 70 °S). This can be explained partly by an amount effect (640 mm rainfall compared to today's 400 mm) or minor altitude effect (glacier formed in higher altitudes covering the hill top). In addition, the carbon isotopic composition of the nodular carbonates indicates presence of biota in the lake which could supply pool of organically derived carbon dioxide for facilitating nodule formation.

Widespread occurrence of nodules in the Talchir strata of Peninsular India and coeval strata in other Gondwana continents (South Africa, Antractica) and the similarity in isotopic composition in their carbonate phase suggest their coexistence during PermoCarboniferous. Petrography and Isotopic composition (both carbon and oxygen) of carbonates suggest fresh water/ lacustrine environment for the deposition of Talchir sediments, contradicting the proposition of marine origin based on earlier sedimentological and palaeontological studies (Bose et al., 1989; Sengupta et al., 1999; Mukhopadhya and Bhattacharya, 1994).

4.2 **Provenance information**

Sr isotopic ratios of the carbonate nodules were used to understand the source of water in Talchir basin. The possible sources of Sr for these sediments are mainly granitic basement rocks (Bundelkhand granite) and susceptible granulites and Vindhyan limestone underlying these sediments. The 87 Sr 86 Sr ratios of the samples from West Bokaro basin and Ramgarh basin are clustered around 0.738 and 0.730, respectively. Such high values are expected it the carbonates formed by precipitation from water draining granitic rocks of Chotanagpur region. Chotanagpur granite is composed of highly susceptible plagioclase feldspar whose Sr/Sr ratio at the time of Permo-Carboniferous time is estimated to be 0.739, similar to the composition of nodules from Damodar valley basin. This proposition is consistent with the palaeo-current records and heavy mineral composition of Gondwana sediments of West Bokaro region (Ghosh and Mitra, 1975; Veevers and Tewari., 1995). Sr isotope ratio of Nodules found in Talchir basin of Orissa clustered around 0.720, indicating that the source of Sr in the water is mafic granulites of Eastern ghat region. Sr isotopic composition of the carbonates from Talchir basins of Mahanadi valley suggests the dominance of weathering of mafic granulites, present in the southern portion of the basin. REE and trace elemental composition of bulk nodules were also determined to further help in characterising provenance of sediments deposited in various Talchir basins.

4.3 Enigmatic objects, in Gondwana sediments : freshwater Stromatolites?

During the course of investigation in the various basins a large number of unusual shaped enigmatic objects were found in the type locality of Talchir formation. These bodies are described as algal carbonates based on their similarity with algal stromatolites from Otavi Series, Southwest Africa described by Kruger (1994). These bodies are found on top of beds containing nodules and may represent environmental amelioration at the end of glacial era. The stable isotopic analyses of these carbonates indicate large

dispersion in the isotopic ratio with δ^{18} O values ranging from -30‰ to -15‰ and δ^{13} C ranging from 5‰ to -25‰. These two variables are in general anticorrelated if altered samples are neglected. This pattern of anticorrelation has been used to infer the end member composition of the samples. The low δ values confirm that these bodies were precipitated in fresh water lakes. However, it is impossible to verify the genesis of these bodies with stable isotopic composition of carbonates alone especially due to large spread in the isotopic composition. However, organic matter was detected in these bodies whose δ^{13} C values indicate characteristic composition of biota present in the Talchir lake. The δ^{13} C value of -23‰ w.r.t. PDB obtained from the analyses of a few selected samples are analogous to contemporary algal and bacterial composition. A few samples were analysed for C/N ratios and the result lies between 5-10. Presence of nitrogen in the samples and depleted δ^{13} C composition of residual organic confirm the existence of microbial life in the glacial melt water.

4.4 Carbon dioxide evolution from Permian to Jurassic period:

A number of soil horizons have been discovered in the Gondwana strata of central India which developed in Motur, Denwa, Bagra and Lameta Formations of Satpura basin. All these soils have well formed pedogenic carbonates. Field relationship and microscopic features indicate that calcification in the soil zone was contemporaneous with overbank sedimentation adjoining the ancient river valley. Soil carbonates from several horizons of these formations were analysed for oxygen and carbon isotopic ratios to infer about the environment of precipitation and estimate the concentration of CO₂ in the atmosphere using Cerling's model. The concentration of CO₂ was low (~620 ppmV) during the Early Permian (260 my) followed by continuous rise during middle Triassic (~940 ppmV at 240 my) and middle Jurassic(~2135 ppmV at 200 my). This period was followed by a decline to ~1480 ppmV during Cretaceous. The general feature of the variation in CO₂ level found in this study is consistent with Berner's model prediction. Mora et al., (1996) studied palaeosols from Newport, Pennsylvania in similar way and found that the pCO2 in the atmosphere during Early Permian and Late Carboniferous periods were low : 150 to 200 ppm and 450 to 800 ppm respectively (Figure 3.26). The pCO2 level in mid-Jurassic and Cretaceous obtained from the present study seem to be much higher than the predicted concentration. The rapid increase in CO₂ is also

consistent with field observation of the soil maturity from the three stratigraphic levels. Since this study is based on soils developed in the same basin representing same geochemical milieu the relative variation over time is well constrained. The δ^{13} C of the atmospheric CO₂ is inversely related to the concentration in this period suggesting enhanced role of degassing from Earth's interior. Such increased degassing is expected from rapid break-up of Gondwana land mass during this time. Mora et al (1996) have pointed out that the isotopic fractionation between atmospheric CO₂ and soil organic matter remained relatively constant at 21‰ through Middle to Late Palaeozoic, despite 6‰ change inferred for δ^{13} C of atmospheric CO₂ over this time period. Thus bulk organic matter composition in the soil directly tracked secular changes in the isotopic composition of atmospheric CO₂.

4.4 Future work:

4.4.1 Carbon isotopic ratio in the Coaly matter:

A worldwide synchronous shift of organic and atmospheric δ^{13} C values at the end of the Permian has been proposed, on the basis of δ^{13} C measurements of fossil tooth apatite of *Diictodon*, a terrestial mammallike reptile (Thackeray et al., 1990). The magnitude and timing of a 6‰ decrease in δ^{13} C reflect the rapid changing isotopic composition of the Southern hemisphere plants on which these animals fed. Similar inference was drawn based on the study of coal occurring in Late Carboniferous and Early Middle Permian sedimentary rocks (Faure et al., 1995). It has to be noted that diagenesis of organic matter into coal does not result in any isotopic fractionation (Degens, 1969). In this work, variation in δ^{13} C of organic matter preserved in the soil record of Permian to Jurassic period indicates that the biosphere was affected by significant decrease in δ^{13} C values during the Palaeozoic-Mesozoic transition on a global scale (Ghosh et al., 1999). This transition also witnessed global extinction of marine and terrestrial fauna considered to reflect the most severe crisis in Phanerozoic biosphere (Erwin, 1993).

In India coals of various ages are disposed in the Gondwana sedimentary succession in continuous fashion. The sequence of coals with intermittent sedimentary units are arranged in the exposures along four major river valleys (Damodar valley, Son-Mahanadi valley, Narmada valley and Godavari valley). Faure et al (1995) have pointed out that the general decrease in the δ^{13} C values of Gondwana coals across the Permian-Triassic boundary is consistent with an overall decrease in the δ^{13} C value of the ambient atmospheric CO₂ over a period of 10 m.y., from Late Permian up to Middle Triassic. The principal factor controlling ¹³C depletion in plants is photosynthesis (Smith and Epstein, 1971). Terrestrial plants are found to be most sensitive to any shift in the carbon dioxide level in the atmosphere (Compston, 1960; Popp et al., 1989; Magaritz et al., 1992; Faure et al., 1995; Veto et al., 1999). Therefore coals representing the composite mixture of terrestrial biota and forming at different time periods are expected to have variable carbon isotopic ratios (-22.7‰ to -24.4‰) (Faure et al., 1995). It will be of interest to study isotopic composition of coals occurring in different strata and representing different ages to reconstruct the variation in δ^{13} C of atmospheric CO₂ which will help understanding the secular variation of atmospheric CO₂ concentration.

4.4.2 Sr isotopic studies in the palaeosol carbonates

Isotopic composition of Sr in water mainly depends on source rock composition over which the water flows. The isotopic composition of calcite in the nodules is governed by the isotopic ratio of water medium and in a sedimentary succession reflects variation in water chemistry with time. Based on sedimentological studies of Casshyap et al (1991) it is expected that the sediments in the Narmada valley basin have changed their Provenance with time and this may be reflected in variation of Sr isotopic composition of carbonates precipitating from soil water. A combined study of stable isotopic composition along with Sr, Nd and REE in the carbonate and bulk samples may help in characterizing their source region.

4.4.3 Stable isotopic studies of nodules in Talchir sediments from other basins

Although impressions of marine fossils is reported from the Dudhinala section of West Bokaro Talchir basin (Sengupta, 1999; Bose et al., 1989), a marine geochemical signature is absent in these sediments. It is clear that deposits of Dudhinala section could not have formed in a marine setting. This finding immediately puts constraint on the extent of marine incursion during Talchir time. In view of this it would be interesting to investigate the geochemical records in the successive sedimentary units overlying and underlying the Umaria, Mahendragarh and Daltonganj marine beds. This work can be undertaken in future to understand the time span and event of this suspected marine incursion.