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Clay mineralogy of the Late Miocene Baripada Beds (Mayurbhanj District, Orissa): Palaeoclimatic implications

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Abstract
Although the Late Miocene Baripada Beds are well known for their wealth of fossil vertebrates and invertebrates, very little is known about their palaeoclimatic condition of deposition. Here, we present X-Ray Diffraction (XRD) analysis ofnineteen samples collected from a 14 m thick Baripada Bed Section at Mukurmatia. We have used this XRD result to interpret the relationship between clay mineralogy and palaeoclimatic condition prevailed during the deposition of these fossiliferous deposits. The major clay minerals from the study area consist of smectite, kaolinite and illite. However, chlorite is totally absent in all the samples analysed. The abundance of smectite may indicate presence of monsoon type of climate and deposition under relatively low energy condition. The clay mineralogical proxy data and its comparison with other proxy records from different parts of the subcontinent allows us to suggest that the area witnessed a tropical to subtropical climate with an annual precipitation in the range of 50-150 cm, in the Late Miocene time.

Keywords: Clay minerals, Baripada Beds, Paleoclimate, Monsoon, Late Miocene

1. Introduction

Late Miocene represents the time period when marine transgression took place at a global scale [1] and deposits of the fossiliferous Baripada Beds is a consequence of such a transgression [2-6]. Many researchers have carried out palaeontological investigation on this fossiliferous marine deposit and majority of their fossil collection comprises sharks, batoids, mollusks and foraminifers, which are in general well adapted to tropical/subtropical to temperate climate [2-17]. However, till date a very little is known about the palaeoclimatic aspect of Baripada Beds.

Clay minerals are a powerful source for the interpretation of marine depositional processes and their study also helps in understanding weathering conditions [18-19]. The study of clay minerals in marine sediments can facilitate interpretation of oceanic current variations as well [20-23]. The vertical distribution pattern of clay minerals are widely used in identifying the contemporaneous climatic changes prevailing in the continental source area [23-26]. The distribution of clay minerals in recent oceanic sediments reflect weathering process on the adjacent continental areas and climatic based distribution of the soils [27]. Since the clay mineral contents of a particular deposit is controlled by various factors including the type of parent material, weathering regimes, depositional environment and rate of digenetic alteration, they are directly or indirectly applicable for palaeoclimatic reconstruction [28]. When the tectonic, bathymetric and diagenetic controls on the clay mineralogy are sufficiently understood, it is possible to proceed with a palaeoclimatic analysis of the source area [28]. However, provenance holds the major control on variation of clay mineral assemblages in surface sediments [23, 29-31]. The hinterland rocks of the Baripada sediments are considered to be gneiss, granites and migmatites including that of Singhbhum, Bonai, Mayurbhanj plutons of granitic rocks and the Similipal plateaus formed by the massive volcano-sedimentary assemblages. In Similipal, they consist of an alternating sequence of spilitic lava and quartzites lying unconformably above the Singhbhum Granite and intruded by pyroxene granite, granophyres, gabbro and anorthosite [32].

The formation of clays, hydrous aluminum phyllosilicate with variable amounts of iron, magnesium, alkali metal, alkaline earths and other cations, is climatically sensitive. These minerals occupy an important group as they are among the most common products of chemical weathering. Clays are also the main constituents of the fine-grained sedimentary rocks including mudstones, claystones and shales. The study of clay minerals that are climate sensitive in their formation suggests that assessing their abundance will provide information about palaeogeographic and stratigraphic information concerning past climate [28].

The present paper documents the clay mineral content of Baripada Beds which is considered to be deposited during the Late Miocene marine transgression and regression episode [2-4] and attempts to discuss the palaeoclimatic set-up of the study area.

2. Stratigraphy of the Study area

The Baripada Beds in Orissa shows a sedimentary sequence consisting of limestone and shales which is overlain by lateritic soils at the top (fig. 1). The generalized stratigraphy of Baripada Beds along the river Burbhalang shows a fossiliferous sedimentary horizon of shale which is below the water table. The shales are arenaceous toward the top. This bed has yielded certain microfossils, vertebrate remains including mammalian teeth; teeth, vertebrae, spines of shark, rays and teleost [2-17]. This bed is overlain by fossiliferous limestone bed of thickness of 1.5 m. The limestone bed is hard and compacted. Certain invertebrate fossils including bivalves were collected from this bed. This bed has yielded a large number of oysters and so the name “oyster bed” has been assigned to this bed. Certain shark teeth and unidentified bone fragments were also collected from this bed. The bone fragments were collected from the top of this bed. This bed is overlain by grey shale having a thickness of about 7-8m. This shale bed is more arenaceous than the previous one. The shale is finely laminated and has yielded abundant foraminifers. The occurrence of bivalve, gastropods was also reported from this bed [7-12]. Above this grayish shale bed lies a thick yellowish shale deposit. This shale deposit is coarser and arenaceous than any other shale below. Above this bed lies a thick, hard, compacted deposit of conglomerate bed of approximately 1.5 m thickness.

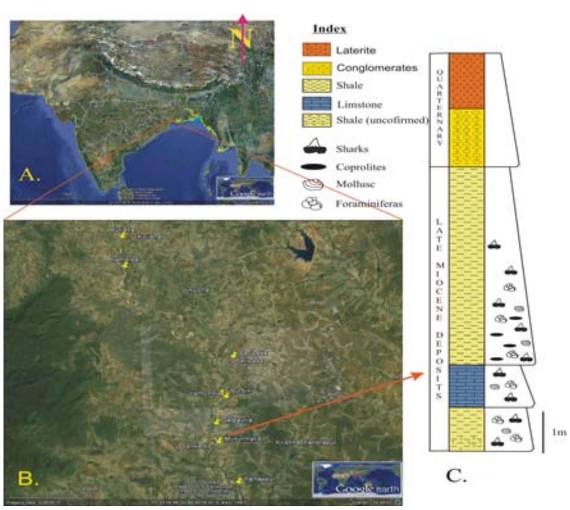

Fig 1: A. Physical map of India (Source, Google earth image, 2012), B. Location map of Study area (Source, Google earth image, 2012), C. Generalised litho-section of Baripada Beds exposed along Burbhalang River [2-5].

3. Material and Methodology

A total of 35 Samples were collected from the shale bed of the exposed section at the bank of BurbhalangRiver near Mukurmatia (Fig. 2). The exposure has a total thickness of 12 meter above the water level of the river. Sampling was done with an interval of 0.34 meters. The samples were weighed before and after drying for water content. Out of these 19 samples were separated and logged for the analysis of clay mineralogy.

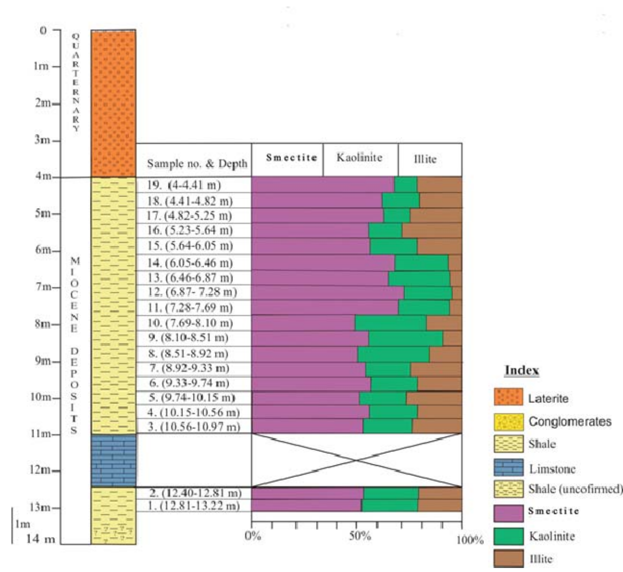

Fig 2: Variation in the distribution of relative percentages of clay minerals at different depth of Mukurmatia litho- section, Baripada Beds.

Only 10 gm of each of the unconsolidated samples were disintegrated in distilled water and the same was treated with H_2O_2 from time to time to remove the organic matter. The suspensions were kept until the pH is checked. The decarbonated suspensions were washed successively with distilled water to remove excess ions and to help the deflocculation of clays. The particles less than 2 um were separated following the Stoke’s law [33] and were concentrated using a centrifuge. The resulting paste was spread onto glass slides. Two slides for each sample were made and air dried to get ready for the XRD analysis. The analyses of the samples were conducted using Xpart Pro, Pan Analytical housed at the Wadia Institute of Himalayan Geology, Dehradun. The analyses of all the samples were done under the voltage of 40 kV and an intensity of 25 m A. The samples were scanned between 2 and 60° 2θ. One of the slides is measured directly as air-dried sample. Then the slide was measured again after ethylene-glycol salvation as glycosylated sample. Then the other slide was heated at 550°C for 2 hrs and was measured as heated sample. The preparation and measurement of the clay mineral analysis were performed at the sedimentological laboratory and XRD laboratory of Wadia Institute of Himalayan Geology, Dehradun. The relative percentage of clay minerals was calculated by using the following relation [34]: -

Relative percentage = I_{001} clay minerals/ $\sum I_{001}$ all clay minerals X 100

Where, I_{001} is the intensity of the 001 peak.

For proper identification of the clay minerals present in the samples, the following properties of the clay minerals in the diffractograms are discussed: -

3.1 Kaolinite: Clay minerals of kaolinite group consists minerals with unchanged dioctahedral unit with 1:1 layer structure [35]. In general the determination of kaolinite group of minerals by X-ray diffraction is simple, but the identification of a particular member of the group is more difficult [36]. Kaolinite group of minerals are distinguished by their basal reflection at about 7.15 (100) and 3.57 A^o (002) which are usually adequate for their identification. However, chloritic clay mineral may be confused with kaolinite as the 14 A^o reflection of chlorite is not pronounced and it also show its reflection at 7.1 A^o(002) and 3.57 A^o (004). Thus, the slight difference in the C-axis dimension of the two minerals can cause doublet at 3.5 A^o to 3.57 A^o which required further techniques to identify these two separately. There is no effect of ethylene glycol solvation in the reflections. It is, therefore, necessary to distinguish the reflections between the two by carrying out some other procedures.The sample was heated at 550^{0}C for 2 hr. Chlorite is thermally stable above at 550^{0}C and its reflection intensified, however, kaolinite tends to lose its crystalline character at this temperature and there its reflection in the diffractograph is collapsed to an X-ray amorphous mineral metakaolin.

3.2 Illite: Illite is the most dominant clay mineral in the argillaceous rocks [37]. It has a dioctahedral or trioctahedral 2: 1 layer structure. The illite minerals can easily be identified on the basis of X-ray diffraction by their (100) spacing, with the first order at about 10 A^o (9.95-10.1 A^o)and with integral series of basal reflections at about 5 A^o (4.98-5.01 A^o), 3.3 A^o, 1.98-1.99 A^o. The peaks of illite minerals are not affected by glycolation. On heating the sample upto 550^{0}C its peaks are more intensified. The peaks of illite minerals are not affected by glycolation. On heating the sample upto 550^{0}C its peaks are more intensified.

3.3 Smectites: Smectite have reflection (001) variable from 6.80 to 5.89 (°2Theta) with spacing from 13-15 A^o. It expands upto 17 A^o upon ethylene glycolation and its peak is also used as a measure of the relative abundance of the mineral. When heated upto 550^{0}C, the peak is again collapsed between 9 A^o and 10 A^o with corresponding integral series of higher order reflection. It differs from chlorite which gives reflection at 14 A^o.

4. Results

The XRD analysis of the samples collected from the Baripada Beds suggest that the dominant clay minerals found in these Late Miocene deposits include those of the smectite group, kaolinite and illite. The identification of clay minerals was made according to the comprehensive comparison of the X-Ray diffractogrammes obtained from the air dried, glycosylated and heated samples, respectively. Kaolinite is identified by its (001) reflection at 7.15 A^0 peak and (002) at 3.57 A^0. These peaks are not changed in glycosylated samples but disappeared on heating at 550^{o}c. Smectite is identified by 15 A^0 peak which is shifted to 17 A^0 on glycolation. Illite is identified by its 10 A^0 peak at (001) (See, Fig. 3).

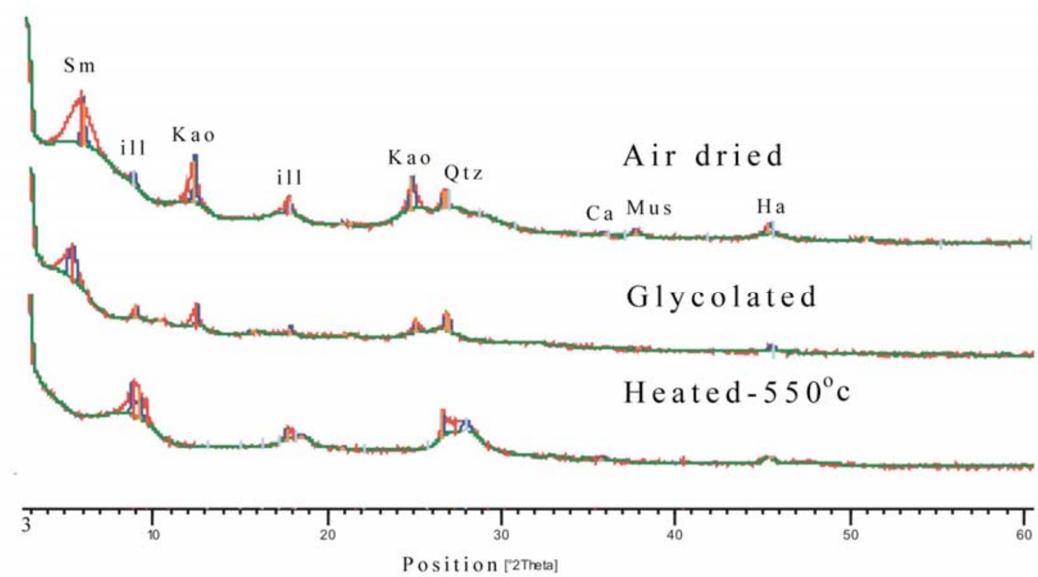

Fig 3: X-ray diffraction pattern of sample no. 9 having a significant quantity of Smectite, illite, Kaolinite.

All the nineteen samples which were analyzed consist of smectite, kaolinite and illite. However, Chlorite is not found in any of the samples. Smectite is the most abundant of the three clay minerals comprising of 49.52-68.3% of the total clay mineral content which is followed by illite with the abundance ranging from 6.65-29.32%, which in turn may be due to dominant dry climate. This is followed by kaolinite constituting as much as 10.5-34.3%. Its variation towards the litho-section can be interpreted to be the result of climate changes/depositional condition at shallow water or erosional rate and composition of the initial provenance of the rock. Kaolinite in the study area is the product of weathering of aluminosilicate minerals. Thus, rocks rich in feldspar e.g. granitic rocks, commonly served as the source of kaolinite.In order to form, ions like Na, K, Ca. Mg, and Fe must be first leached away by the weathering or alteration process which is favored by acidic conditions [38]. The semi quantitative percentage of the clay mineral composition of Baripada Beds is given in the table no. 1.

The present study reveals that clay mineral distribution in Baripada Beds is variable from bottom (Fig. 3) to the top of the litholog. The graphical representation of illite (Fig. 4), kaolinite (Fig. 5) and smectite (Fig. 6) from the study area clearly depict a minor fluctuation in relative percentage of these clay minerals which might be due to minor change in the intensity of climatic factors.

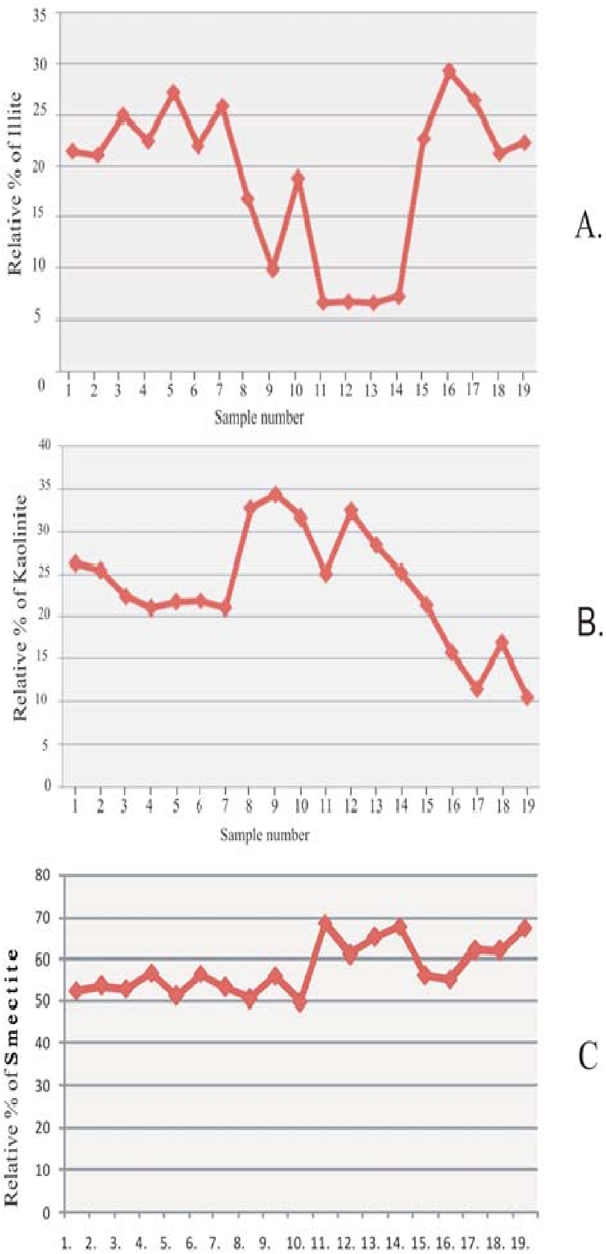

Fig 4: A. Graphical representation of relative percentages of illite in Baripada shale; B. Graphical representation of relative percentages of Kaolinite in Baripada shale; C. Graphical representation of relative percentages of Smectite in Baripada shale.

5. Discussion

In the Indian Ocean, the Asian summer (southwest) and winter (northeast) monsoons, characterized by a seasonally reversing wind system, have a profound effect on the rainfall, runoffand vegetation in South Asia, as well as on the biota [39]. The intense, wet, southwesterly winds of the summer monsoon cause extensive upwelling and high surface productivity in the Indian Ocean, particularly in the Arabian Sea [40]. Conversely, during the prevalence of dry northwesterly winds of the winter monsoon, surface productivity is relatively low [40]. The study of palynological data from the Oligocene-Miocene subsurface sediments of West Bengal tropical–subtropical, humid climate prevailing during that time, being more humid than the present day [41].

Table 1: Distribution of relative percentage of clay minerals from different stratigraphic units with their depths from the litho-section of Mukurmatia, Baripada Beds.

Sample no.	Depth(m)	Layer	Clay mineral assemblages with relative percentage		
			Illite	Kaolinite	Smectite
1.	12.81-13.22	4	21.51%	26.24%	52.25%
2.	12.40-12.81	4	21.1%	25.4%	53.5%
3.	10.56-10.97	2	25%	22.3%	52.7%
4.	10.15-10.56	2	22.5%	21%	56.5%
5.	9.74-10.15	2	27.28%	21.7%	51.02%
6.	9.33-9.77	2	22%	21.8%	56.2%
7.	8.92-9.33	2	25.9%	21%	53.1%
8.	8.51-8.92	2	16.85%	32.64%	50.51%
9.	8.10-8.51	2	9.97%	34.3%	55.8%
10.	7.69-8.10	2	18.89%	31.59%	49.52%
11.	7.28-7.69	2	6.7%	25%	68.3%
12.	6.87-7.28	2	6.76%	32.39%	60.85%
13.	6.46-6.87	2	6.65%	28.37%	64.98%
14.	6.05-6.46	2	7.28%	25.17%	67.55%
15.	5.64-6.05	2	22.74%	21.3%	55.96%
16.	5.23-5.64	2	29.32%	15.76%	54.92%
17.	4.82-5.25	2	26.5%	11.5%	62%
18.	4.41-4.82	2	21.26%	16.95%	61.79%
19.	4-4.41	2	22.35%	10.5%	67.15%

Analysis of the clay mineralogical data (Table 1) indicates the presence of smectite, illite and kaolinite in Baripada shale. Acid igneous rocks containing considerable quantity of potassium and magnesium on weathering yield illite and smectite [24]. Kaolinite can be an indicator of moist and tropical to temperate weathering condition. Smectite, which is the most abundant clay mineral of Baripada Beds, is the product of weathering and transportation from non-marine/terrestrial conditions. Clay minerals such as Chlorite are a typical product of physical weathering in arid cold climate, whereas illites and kaolinites are produced under humid conditions [42-43]. Illite is essentially detrital [44], most stable and it is also a significant indicator of paleoclimate and diagenesis [45]. An overall dominant presence of smectite in all the shale samples of Baripada Beds is a good indicator of paleoclimate as it indicates a broad precipitation range of 25-150 cm with the seasonality in the source region [46]. The general dominance of smectite over kaolinite reflects strong fluctuation in seasonal humidity [27]. Distribution of Al-Fe rich smectite is good indicator of warm hydrolyzing climate [24]. A relatively less abundance of illite and complete absence of Chlorites may indicate high weathering intensity and warm climatic conditions. In case of Baripada Beds, predominance of smectite over illite and chlorite is due to the combined effect of high weathering in the catchment area and post depositional weathering in association with the function of ambient climate. Smectite group of minerals may indicate monsoonal climate, which, with their alternative wet and dry seasons promote the formation of this alternately expanding and contracting mineral [24-47]. The increase of the chlorite/illite ratio will therefore result from arid climatic conditions and kaolinite/chlorite ratios will signify a prevalence of humid phase [48]. However, the absence of chlorite reveals that there was no harsh climate during the deposition of the Baripada Beds as its presence in sediment as a detrital clay is a good indicator of cool/or dry climate [49]. Chemical weathering condition leads to the formation of illite and chlorites, moderate leaching leads to formation of smectite and intense leaching yields kaolinite. In the area where after burial clay transformation is expected to be minimal the clay mineralogy may be used as a valuable tool for understanding the environmental conditions coeval with deposition [50]. Kaolinite is used as an example of a suitable clay mineral in the approximation of paleoclimate [28, 51]. If the geology and relief of the area has not altered significantly, the variation in the clay suite produced from a source will be climatic dependent [43] i.e. formation of kaolinite takes place under a very humid climate, illite and smectite during moderate-humid climate [42, 52-52]. The presence of significant amount of kaolinite in the clay assemblages normally interpreted as presence of warm and wet conditions associated with high leaching rate. The large percentage of smectite, illite and kaolinite in all the samples indicates the prevalence of humid phase which might have been associated with the intensification of early monsoon in the region. Variation in the percentage of these clay minerals along the stratigraphic column (Fig. 3) may indicate cyclic fluctuation in the intensity of monsoon associated with the tectonic upheaval of the Himalaya during this period. The presence of higher percentage of smectite in this area also suggests either because of its volcano-sedimentary provenance or the sea water was less active and relatively calm. High agitating action of waves could have easily dispersed fine particle such as those of smectite. The relatively higher percentage of smectite in marine sediments of Baripada Beds may also suggest differential settling and influence of pH. It has also been determined that kaolinite forms when the mean annual precipitation (MAP) is above 50 cms [34, 54-55]. Smectite is suggested to form during the weathering in seasonally wet and dry climate [24]. It is inferred from the coprolite data that the palaeo temperature of this site might have ranged from warm subtropical to tropical with a minimum temperature of not less than 15^{0}C [5] which is further supported by the diverse assemblages of sharks, turtle, oysters and foraminifers that prefer a warm condition [13, 17]. The reconstructions of Tortonian vegetation for theIndian subcontinent also suggested vegetation composed of tropical forests and savanna suggests an increase in precipitation relative to today [56-57].

Data from South China Sea, Arabian Sea and Bay of Bengal shows that, monsoon driven erosion intensified in the Miocene reaching its peak by ~15 Ma ago and remained high till 10.5 Ma. The presence of diverse tropical to subtropical species of sharks, batoids, mollusk and foraminers [2, 13-18] from Baripada Beds might have been resulted simultaneously in association with monsoon intensification. By the Late Miocene global cooling, spread of arid conditions and possibly monsoon intensification brought change in the vegetation marked by fragmentation of forests and spreading of grasslands [58-59]. Analogous Late Miocene (10-8 Ma) monsoon intensification is well documented in the marine record [60-61].

In Asia, the Miocene period marks the peak time for Himalayan exhumation combined with of the enhancement of Asian monsoon, palaeoclimate models suggest that Asian monsoon is directly linked to the uplift of the Himalayas and the Tibetan Plateau [62]. Various proxies including oceanic microfossils, land flora, stable isotopes and sedimentary records suggested that the monsoon system initiated or increased in intensity at 10–8 Ma as a consequence of this uplift 58, 60, 63-64. Earlier records of micro-vertebrates from the Eastern coast of Baripada Beds [2-4] and the Miocene deposits of Kutch [65] also suggested a warm tropical climate which is very similar to the present day climate. The prior results of numerical climate-model experiment, using idealized stepwise increase of mountain plateau elevation, supports the argument that the stages in evolution of Asian monsoon are linked to phases of Himalayan-Tibetan Plateau uplift and to Northern Hemisphere glaciations [66].

6. Conclusions

(i) The clay minerals contents of the Baripada Beds is partly controlled by its provenance of massive volcano-sedimentary and metamorphic assemblages and climatic condition as well as the intensification of weathering of its parent rocks under warm, tropical humid climatic condition.

(ii) Clay minerals are useful indicator of past climate. The results from the XRD data of the samples suggest that the major clay minerals from Baripada Beds consist of smectite (49.52-68.3%), kaolinite (6.65-29.32%) and illite (10.5-34.3%).

(iii) Abundance of smectite indicates presence of low energy environment of deposition as smectite is usually found to be associated with the finer clays and salinity condition [24]. Our finding is in conformity to earlier report of coprolite matters from these beds which are indicator of low energy condition [5].

(iv) The relatively greater abundance of smectite over illite and kaolinite is due to the combination of weathering in the catchment area and post depositional weathering in association with the function of ambient climate. Smectite is a broad indicator of warm hydrolyzing climate with a precipitation ranging between 25-150 cm with the seasonality in the source region. Kaolinite forms when the Mean Annual Precipitation (MAP) is above 50 cm. Thus, the clay mineralogical proxy of the area in correlation with other proxy records from different parts of the world indicates that the area might have received an annual precipitation in the range of 50-150 cm.

(v) The complete absence of clay chlorite from the study area may probably be either due to extreme humid condition under which chlorite can't survive or lack of arid and cold climatic conditions.

(vi) Thus the current climatic proxy from the study area is in conformity with the other regional and global climatic data indicating presence of a warm, humid and seasonally wet-dry climate in the Late Miocene, such as an intensification of Indian monsoon system, which in turn could have caused faunal diversification as well.

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