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Source of Organic Matter and Paleo-Environmental Reconstruction Using $\delta^{13}C$ Isotope from Mid-Siwalik Sediments of a Late Miocene Himalayan Foreland Basin, Pakistan

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Abstract. This study examined the stable carbon isotope ($\delta^{13}C$) and characterization of sources of organic matter from core samples of sandstones of mid-Siwalik group Dhok Pathan Formation from Surghar-Shingar Range of NW Himalayan foreland Fold-and-Thrust-Belt. These sediments have recorded valuable information regarding the palaeo-vegetation type and paleo-environment/depositional environments. The analytical results of stable carbon isotope range from -24.50 to -28.43% with an average value of -26.56%. These values correspond to C_3 vegetation of cool growing season and support the hypothesis of the dominance of C_3 biomass in the ecosystem during the late-Miocene in this area. The phytoclasts are characterized as huminite/vitrinite, derived from terrestrial plants and referred to as type-III kerogen. The fungal attack, scaring and pitting of bacterial activity, biochemical degradation, replacement/diagenetic development of pyrite suggest that these sandstones of Dhok Pathan Formation were deposited under dyoxic conditions and thus these sandstones are primary reduced sandstones.

Keywords: stable carbon, organic matter, paleo-environment, siwalik, miocene, himalaya, Pakistan

Introduction

The sediments / sedimentary rocks contain important records of paleo-environmental conditions, repeatedly recording local and regional variation in climate. As a result of climate change, vegetation types are usually changed, as most of the land plants are greatly associated with particular temperature and humidity of the environment (Hyun *et al*., 2015). A numerous studies have revealed that local climate variations have direct influence on vegetation (Hyun *et al*., 2015; Lim *et al*., 2013; Takahara *et al*., 2010). The impact of this close relationship between vegetation and climatic variations may extend to global scale (Litwin *et al*., 2013). The changes in palaeo-vegetation and paleo-climate have been traced back and interpreted by using disparities in organic proxies such as stable carbon isotope ($\delta^{13}C$) in diverse geological and ecological environments to reconstruct the paleo-environment (Hyun *et al*., 2015; Zech *et al*., 2012; Zhang *et al*., 2010; Yamamoto *et al*., 2010).

The isotopic studies of organic matter (OM) in sediments and sedimentary rocks demonstrate paleo-environmental changes (Hatem *et al*., 2016; Kohn, 2016; Diefendorf *et al*., 2015; Khan *et al*., 2015; Schubert and Jahren, 2012; Prentice *et al*., 2011; Kohn, 2010; Milligan *et al*., 2010; MA *et al*., 2009; Omura and Hoyanagi, 2004; Kuramoto and Minagawa, 2001). The short term depositional processes and higher sedimentation rates can be well documented in the sediment records (Ahmad and Davis, 2017; Meyers, 2003). The rate of accumulation and composition of OM are affected by both upland and *in-situ* depositional basin conditions (Ahmad and Davis, 2017; Killops and Killops, 2013). The values of $\delta^{13}C$ differentiate source of OM accumulated in the sediments during deposition (Khan *et al*., 2015; Shanahan *et al*., 2013).

The quantity and composition of OM imitate the nature and frequency of biota that survived within the sedimentary basin at the time of deposition of sediments. The isotopic values of the OM reflect information about vegetational types distribution. These isotopic studies are the informative approaches to reconstruct the paleo-environment (Ahmad and Davis, 2017; Wang *et al*., 2003; Lü *et al*., 2000).

The isotopic organic proxies such as stable carbon isotope, organic carbon content (Corg), ratio of C/N

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and organic carbon concentrations are used to recognize the source of OM (Ahmad and Davis, 2017). However, many factors for instance organic matter flux, rate of sedimentation and diagenesis influence the geochemical record of the sediments (Tyson, 1995). The studies of long term variations in environmental record play an important role in forecasting the future global changes (Ahmad and Davis, 2017; Matsumoto *et al*., 2012). The isotopic ($\delta^{13}C$) studies have also been used for the evaluation and correlation of oil source rocks, paleo-oceanography, chemo-stratigraphy and OM characterization (Tyson, 1995; Hollander *et al*., 1993; Fontugne and Calvert, 1992; Hayes *et al*., 1989).

The characterization of OM present in sedimentary rocks also give clues about early diagenetic processes i.e. the biochemical reactivity (bacterial sulphate reduction), redox status of the sediments, depositional environments in terms of oxygenation, salinity, trophic state, fluvial input distance, water column depth, burial and thermal maturation, type and amounts of hydrocarbons that may have been generated (Tyson, 1995). It is also a useful tool to make a differentiation between allochthonous and autochthonous OM which is crucial for carbon cycle modeling.

The Neogene molasse sediments (Siwalik Group) of Himalayan foreland basin have preserved record of Himalayan orogeny in terms of paleo-climate and drainage networks (Najman, 2006). These Siwalik Group rocks are well developed and exposed in different parts of the country such as Kohat-Potwar Plateau, Salt Range, Trans Indus Salt Ranges and the Kirthar – Sulaiman Fold-and Thrust-Belts (Shah and Hafeez, 2009; Ullah *et al*., 2009). The study area lies on the western flank of Surghar-Shingar Range (part of trans Indus Salt Ranges) Fig. 1a. The Siwalik Group rocks of Kohat-Potwar Plateau have extensively been studied by many researchers (Shah and Hafeez, 2009; Ullah *et al*., 2009; Quade *et al*., 1989; Barry *et al*., 1985 etc) in different perspectives, while the Siwalik Group rocks of Trans Indus Salt Ranges are least studied. The previous investigations mainly document the eastern flank of the Surghar-Shingar Range due to their well known coal deposits which had been mined since centuries (Ali *et al*., 2018b). Absolutely, there is no scientific data is available on Mid-Siwalik Dhok Pathan Formation of Surghar-Shingar Range (SSR) regarding the source of organic matter and paleo-environment/ depositional environments. The aim of this pioneering contribution is the utilization of $\delta^{13}C$ data for the characterization of source of OM in the sandstones and to reconstruct the paleo-vegetation type. This will help to draw conclusions concerning the depositional environments of middle Siwalik sandstones of Dhok Pathan Formation in this part of Himalayan foreland basin.

Geology and geotectonic setting. As a consequence of tectonic loading due to continent-continent collision of India-Eurasia a flexural depression was developed in the south of emerging mountain ranges (Rehman *et al*., 2017; Valdiya, 2016; Powell, 1979) known as Himalayan foreland basin. This peripheral basin extends for > 2000 km from Nepal in the east to Pakistan in the west (Ullah *et al*., 2009) Fig. 1d. This foreland basin received a plenty of detritus produced due to India-Eurasia collision during the Neogene time and emerged as unique identity called “Siwaliks” (Najman, 2006). In Pakistan, these Siwalik Group rocks are divided into three sub-groups; Lower, Middle and Upper (Shah, 2009). The Lower Siwaliks include Kamlial and Chinji Formations and are comprised of mudstone dominated facies over sandstone. The Nagri and Dhok Pathan Formations are Mid-Siwalik Formations mainly arenacious in character with typical alternation of sandstone-mudstone facies. The Upper Siwalik Soan Formation is principally conglomeratic in nature.

During the continent-continent collision of India-Eurasia, the continual south ward directed folding and over-thrusting of crustal blocks of Indian plate gave rise to Himalayan foreland Fold-and-Thrust-Belts (Blisniuk *et al*., 1998). An arcuate mountain belt lying west of the Indus River as western extension of the salt Range dislocated by the active strike-slip Kalabagh fault (Fig. 1c) is named as Surghar-Shingar Range (Fig. 1c). The SSR is representing the outer-most Himalayan ranges (Powell, 1979) Fig. 1b. The SSR show an EW configuration along the southern fringes of Kohat Plateau and attain NS structural trend while bordering the Bannu Basin (Fig. 1c) to the west (Rehman *et al*., 2017; Khan and Opdyke, 1987b).

The SSR is an overfolded-asymmetrical anticline exposing Mesozoic and Paleocene rocks in the core which are under laid by Permian rocks (Akhtar, 1983). The Siwaliks are well exposed on western limb of the anticline (present study area) while older rock units are exposed on the eastern limb. The Surghar Thrust which is an equivalent of the Salt Range Thrust probably persistent along the axis of Surghar anticline that has

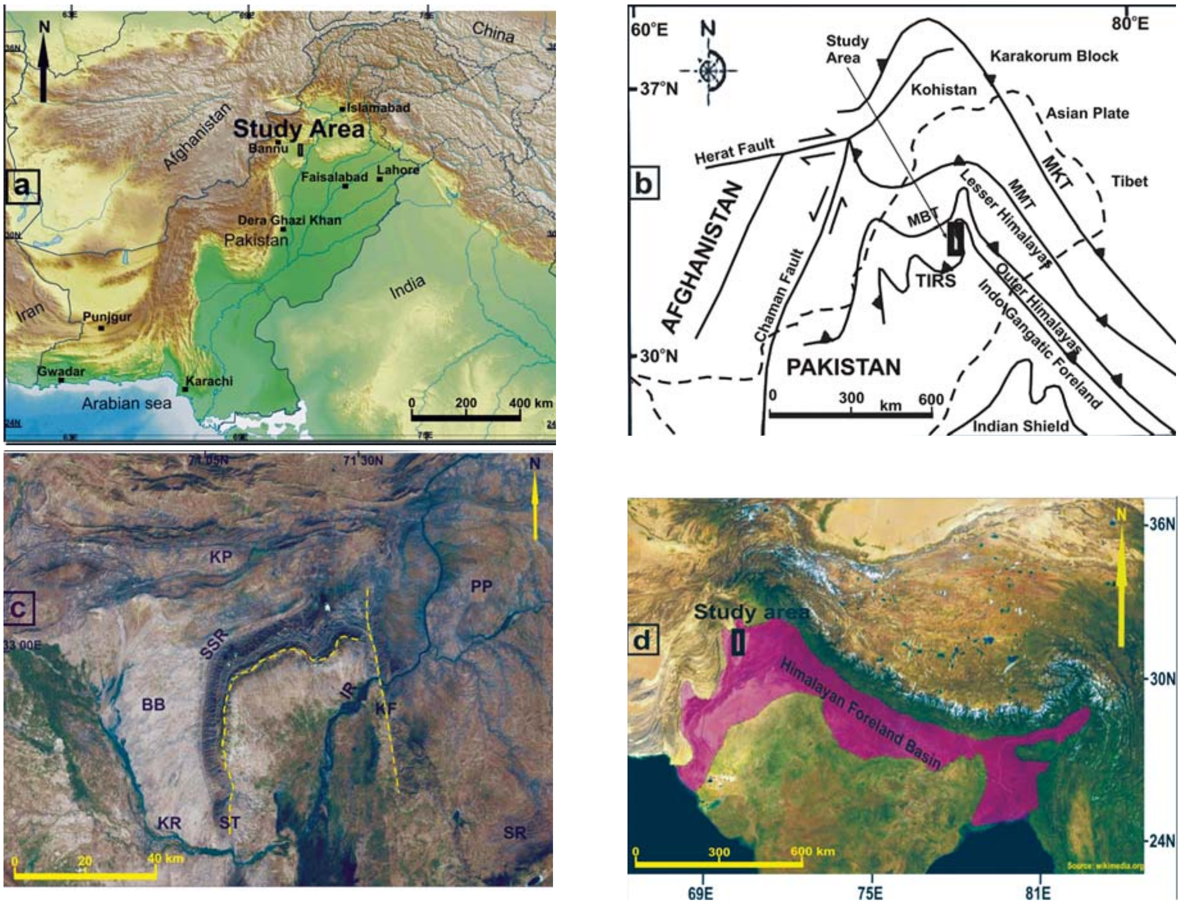

Fig. 1(a-d). Regional map of Pakistan depicting location of study area, b) Tectonic map of NW Pakistan, c) Zoom earth satellite image of SSR and surrounding areas. BB: Bannu Basin, PP: Potwar Plateau, KP: Kohat Plateau, KF: Kalabagh Fault, IR: Indus River, KR: Kurram River, SR: Salt Range, ST/SF: Surghar Thrust/Fault, SSR: Surghar Shingar Range, MKT: Main Karakoram Thrust, MMT: Main Mantle Thrust, MBT: Main Boundry Thrust, MFT: Main Frontal Thrust, TIRT: Trans Indus Range Thrust, d) Himalayan foreland basin (purple colour) (after Ali *et al*., 2019)

brought Punjab foreland alluvium in contact with the Neogene rocks to the south and Permian and Mesozoic rocks in the north (Gee, 1989).

The steep cliffs and rugged topographic expression of SSR has been developed due to head-ward erosion of streams as the range experienced tectonic uplift phases. The eroded material has lain down in the adjoining Indus and Bannu plains (Danilchik and Shah, 1987). In SSR the marine sedimentation has been ended by the deposition of Siwalik Group rocks. The base of Lower Siwalik can be distinguished by the existence of thick, distinct conglomeratic bed primarily consists of pebbles and boulders of Eocene formations (Azizullah and Khan, 1997). The Siwalik Group rocks exposed on the western limb of SSR are 5300 m thick, while the thickness of Dhok Pathan Formation varies from 807-1540 m showing the character of repeated sandstone-shale sequences in fining upward rhythm (Ali *et al*., 2019). Khan and Opdyke (1987b) have assigned 7.5-2.5 Ma age to Dhok Pathan Formation of this area based on magneto-stratigraphic studies.

Materials and Methods

The method used for this study can be summarized as below:-

- 10 samples of sandstone were collected from positions marked as A, B, C on Fig. 2. The OM was separated from these sandstone samples using novel techniques. The OM was treated with 0.5 M HCl solution without heating to remove the carbonates. After 24 h the samples were picked and rinsed with distilled water and again treated with the HCl solution to confirm the complete removal of carbonates. Samples were rinsed with distilled water and oven dried. The samples were grinded to 200 µm with non-iron manual mortar and pestle to avoid any contamination:

- The stable carbon isotopic data was obtained by analyzing these OM samples on elemental analyzer isotope mass spectrometer (EA-IRMS).
- The polished slides of OM were studied under reflected light microscope and scanning electron microscope (SEM, Nova Scan 450) for its morphological characteristics and characterization/ classification. The samples were gold coated before analyzing on the SEM. Massoud and Kinghorn (1982) and Hart (1986) classifications were used as reference.

These analyses were carried out at "State key Laboratory Breeding Base of Nuclear Resources and Environment" and "Jiangxi Province Key Laboratory of the Causes and Control of Atmospheric Pollution, East China University of Technology, Nanchang".

Results and Discussion

Characterization of Organic Matter. The OM which is grey, light-brown to blackish in colour is coaly material or woody tissues show typical cellular structure (Fig. 3a and 3b). Their morphology obtained through SEM imaging revealed that these organic materials are angular in outline with good structural framework. The cell walls are moderately disrupted by fungal attack (Fig. 3c and 3d). Bacterial pitting, scaring and replacement features such as pyritization are also observed (Fig. 3e, 3f, 3g and 3h). These phytoclasts can be characterized as poorly preserved to amorphous structural phytoclasts (Hart, 1986) or as huminite/vitrinite (Ercegovac and Kostic, 2006; Massoud and Kinghorn, 1982). These phytoclasts are mainly derived from land plants and referred to as Type-III kerogen (Massoud and Kinghorn, 1982). Plants exhibit three different carbon isotopic categories. Nearly all trees (climate independent), shrubs, herbs and grasses which are favoured by a cool growing season are included in C3 plant category (Quade *et al*., 1989). Their $\delta^{13}C$ value range from -35 to -20% with an average value of -27% depending upon light intensity, plant species and longevity, moisture stress and other variables (Ehleringer, 1989). A few shrubs of

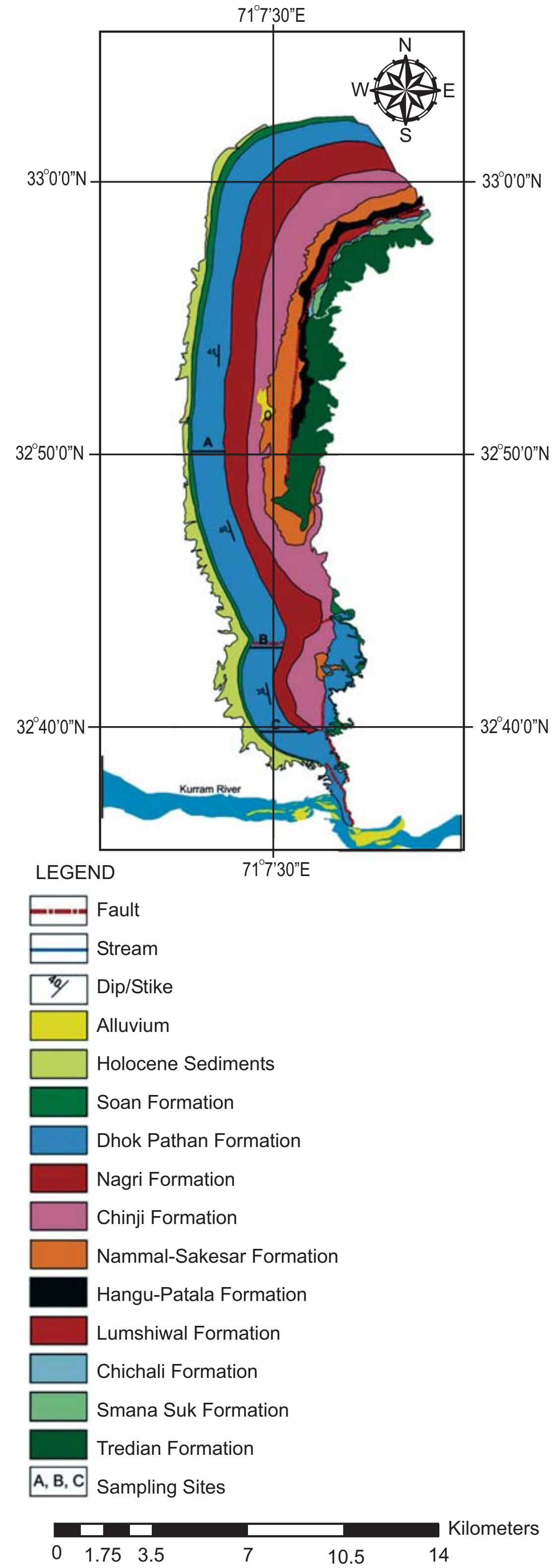

Fig. 2. Detailed geological map of NS segment of SSR showing location of sampling sites (after Ali *et al*., 2019)

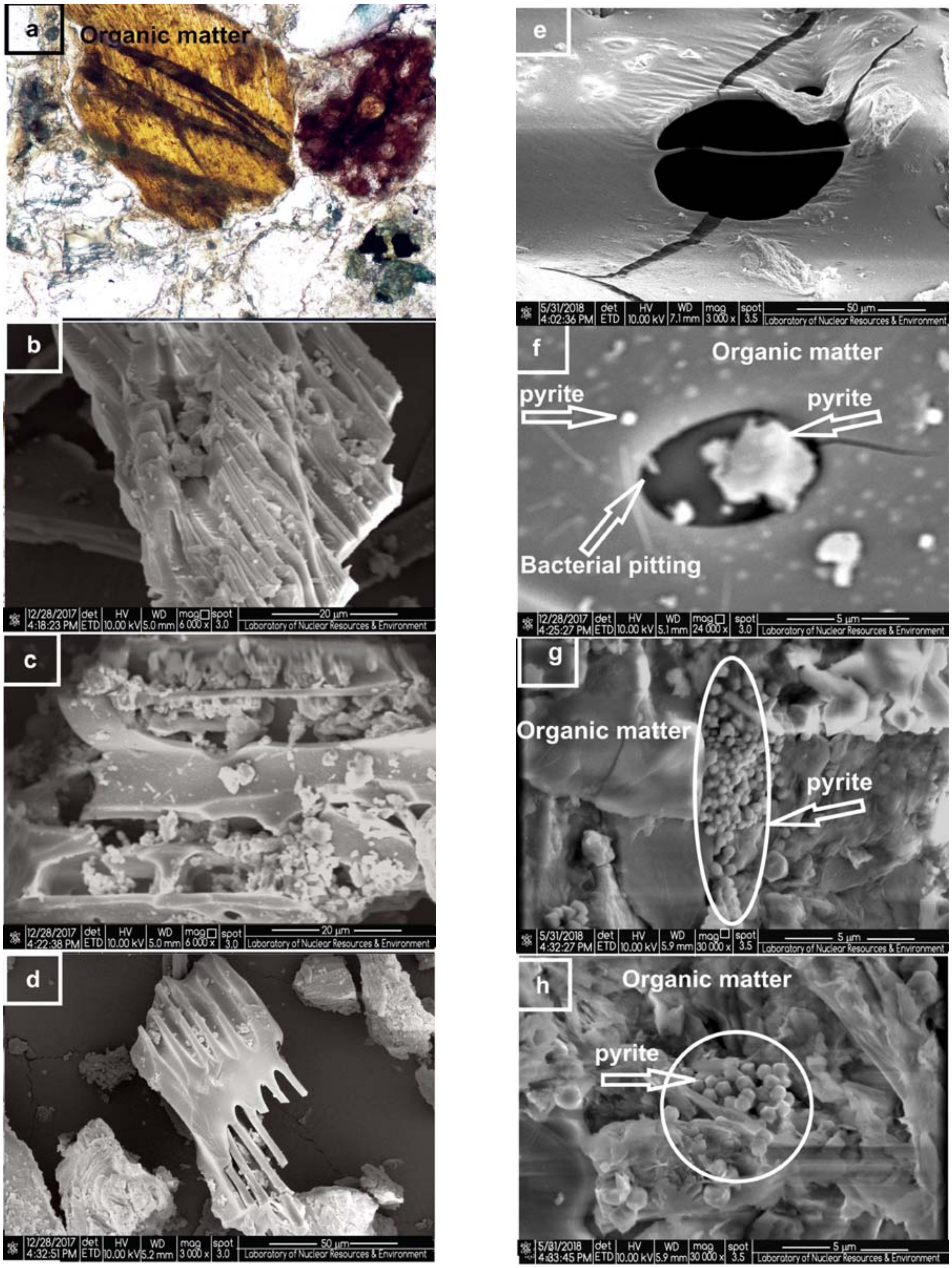

Fig. 3. Photomicrograph and SEM back scattered images of organic matter, a) coaly phytoclast in reflected light, b) back scattered image of phytoclast, c & d) fungal and bacterial attack on phytoclast, e) bacterial pitting and scaring on organic matter, f) replacement of organic matter with pyrite, g & h) development of pyrite crystals in interstitial spaces of organic matter.

Euphorbiaceae and Chenopodiaceae families those like to grow under warm conditions fall in the category of C_4 plants. Their average $\delta^{13}C$ values ca. -13%. The luscious cactus and yuccas which are not significant part of the ecosystem beyond desert environment are fall under the category of crassulacean acid metabolism (CAM) (Quade *et al*., 1989).

The earth's biota had experienced intense/diverse effects during the Neogene time due to climatic changes, continental and oceanic position movements (Barry *et al*., 1985). Nearly before 7.4-7.0 MYr pure or nearly pure C_3 biomass was dominated (Quade *et al*., 1989). According to the microwear and isotopic data of Morgan *et al*. (1994), the major part of vegetation during Mid-to-late-Miocene was C_3 grasses in Pakistan. A considerable growth of C_4 biomass was recorded between 8 and 6 MYr from four diverse and broadly distributed areas "East Africa, low latitude North America, south America and Pakistan" (Cerling *et al*., 1997). The $\delta^{13}C$ results from Dhok Pathan Formation clearly specify that the C_3 vegetation was dominated during the Late-Miocene to Early-Pliocene time in this part of Himalayan foreland basin.

The degree of alteration of OM depends on its exposure to surface environments. The prolonged exposure can augment the decay rate of OM. According to Ehrlich (1981), the complete process of organic material degradation took place in two ways, in anaerobic conditions it broke down into H_2S, CH_4, CO_2, and NH_3 while in aerobic conditions it converted into H_2O, CO_2, SO_4^{-2}, and NO^{-3} etc. If these degradational processes were completed, the OM remained as part of the dissolved chemical cycle within the water column, conversely, it deposited at sediment water interface (Hart, 1986). Once the OM deposited at sediment water interface it has to experience different changes such as biological, physical and chemical which are independent of its origin. From geological view point, the depositional environments do not exist neither in superficial nor at sediment-water interface, these can be interpreted from sub-surface where Eh goes negative i.e. the redox-potential discontinuity occur (Hart, 1986). The light-brown, grey-to-blackish coaly material/woody tissues (phytoclasts) from sandstones of Dhok Pathan Formation which are typical characterized as huminite/vitrinite are generally preserved in low oxic-to-low anoxic fresh water conditions (Ercegovac and kostic, 2006) within the active river channel of fairly high energy conditions. The phytoclasts with angular in outline and good structural framework may be resistant lingo cellulosic materials undergo biodegradation in oxic environments. The fungal attack and bacterial pitting and scarring are evidences of biodegradation. This degradation can take place under both aerobic and anaerobic conditions (Hart, 1986). The presences of bacterial pitting indicate degradation under anoxic conditions. Under relatively high-to-normal temperature and oxidizing conditions, this woody material may alter to form inertinite which are indicative of specific environments within the sediments (Ercegovac and Kostic, 2006).

$\delta^{13}C$ isotope. The values of $\delta^{13}C$ we measured range from -24.50% to -28.43‰ with a mean value of -26.56% (n=10). The total carbon content of analyzed phytoclasts range from 15.9% to 49.55% with a mean value of 33.87% (n=10). These measured values of Δ13C correspond to C_3 terrestrial plants (Ehleringer, 1989). The $\delta^{18}O$ (oxygen) and ^{13}N (nitrogen) values were below the detectable limits. The results are shown in Table 1.

Sometimes the diagenetic products are different not only to interpret but also to relate them with their parent materials due to the diagenetic processes complexities. The early diagenetic alteration processes are more diverse to understand because of diagenetic and depositional controls are perhaps extremely diverse without definite trends and reactions are rarely at equilibrium (Swart, 1984; Ragland *et al*., 1979). The hydrologic character of stream, solubility of OM and sediment-water interface may provide minor but distinctive signals of the degree of alteration. Under certain diagenetic conditions, partial replacement of

Table 1. EA-IRMS analytical results of organic matter from sandstone samples of Dhok Pathan Formation

Sample no.	Δ13C %	Total C %	Sample type
211	-26.15	35.42	sandstone
212	-25.23	45.95	sandstone
215	-26.64	15.82	sandstone
216	-28.43	31.80	sandstone
217	-28.26	37.75	sandstone
218	-27.28	36.19	sandstone
219	-24.50	33.41	sandstone
220	-27.85	36.44	sandstone
2122	-24.70	49.55	sandstone
2152	-28.80	15.96	sandstone

Average Δ13C = -26.56%, Average total carbon = 33.87%

OM occurs with the formation of frambiodal and other types of pyrite. There is a direct relationship between metabolizable organic matter flux and sulphate reduction, the pyritization process is dependant on sediment accumulation rate (Fisher and Hudson, 1987). This pyritization process can take place in the presence of sulphate reducing bacteria which is a diagnostic maker of some particular environments/postdepositional conditions (Brand, 1994). It indicates that the micro-organisms were still alive, required elements of iron and sulpher (Fe and S) were available and redox conditions were prevailed within the superficial burial conditions of the sediments containing OM (Raiswell and Berner, 1985; Howarth, 1979). The preservation of this pyrite-OM replacement process required dyoxic conditions to be prevailed. The SEM images of OM from sandstones of Dhok Pathan Formation clearly indicate this replacement / diagenetic formation of frambiodal and other types of pyrite. It revealed that the deposition of this part of Dhok Pathan Formation took place under dyoxic conditions. Under normal conditions this environment is considered to be favourable for the precipitation of uranium from aqueous solutions.

Conclusion

The study of OM confirms that the C_3 vegetation prevailed at the time of deposition of this part of Neogene Molasse sediments in the NW Himalayan foreland basin. The phytoclasts are characterized as huminite/vitrinite, derived from terrestrial land plants and referred to as Type-III kerogen. The fungal attack, scaring and pitting of bacterial activity, biochemical degradation, replacement/diagenetic development of pyrite suggest that these sandstones of Dhok Pathan Formation were deposited under dyoxic conditions. These sandstones are primary reduced sandstones which are considered favourable to host sandstone-type uranium deposits.

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Conflict of Interest. The authors declare no conflict of interest

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