

**EVOLUTIONARY HISTORY OF THE RAMPUR SHALE:
ITS LITHOLOGY, BIOTA, STRUCTURE AND
GEOCHEMISTRY**



**THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY (SCIENCE)
OF
JADAVPUR UNIVERSITY
(2024)**

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CERTIFICATE FROM THE SUPERVISOR

This is to certify that the thesis entitled as “**Evolutionary history of the Rampur Shale: Its lithology, biota, structure and geochemistry**” submitted by Smt. **Indrani Mondal**, who got her name registered on **20.09.2018** for the award of Ph. D. (Science) degree of **Jadavpur University**, is absolutely based upon her own work under the supervision of **Prof. Subir Sarkar** and that neither this thesis nor any part of it has been submitted for either any degree/diploma or any other academic award anywhere before.

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*Dedicated to,
Source of my inspiration.....*

My Grandfather

Shri Hem Chandra Mondal

Under whose guiding hand, I stepped into the academic world.

ACKNOWLEDGEMENT

Completing a doctoral thesis is often viewed as a solitary journey, but it is, in fact, supported by many individuals. I would like to take this opportunity to express my sincere gratitude to those who have guided and supported me throughout this research endeavour.

First and foremost, I wish to express my profound and heartfelt gratitude to my esteemed supervisor, **Prof. Subir Sarkar**, for graciously accepting me as his Ph.D. scholar. Coming under the guidance of such a distinguished academician has been a true blessing. His invaluable guidance, unwavering support, and constant encouragement have been pivotal throughout the course of my research. His vast knowledge and insightful expertise have not only shaped the direction of this work but have also inspired me to strive for excellence. I am deeply indebted to him for his patience, wisdom, and for providing me with the intellectual freedom to explore new ideas, all of which have been instrumental in bringing this thesis to fruition.

I am deeply grateful to **Prof. Pradip Kumar Bose** for his invaluable mentorship and steadfast support, which have been crucial to the successful completion of this thesis. His insightful guidance, constructive feedback, and rigorous critique have played a pivotal role in refining my research. I am truly appreciative of the significant time and effort he dedicated to my work.

I would like to express my sincere gratitude to the Department of Geological Sciences, particularly to **Prof. Pulak Sengupta** and **Prof. Sanjoy Sanyal**, for their steadfast encouragement and valuable advice, which have significantly contributed to the enhancement of this research. I extend my heartfelt thanks and regards to **Dr. Partha Ghosal** for his encouragement and the invaluable infrastructural support he provided at DRDO.

I would like to convey my heartfelt thanks to my teachers and seniors from JUSEDILAB. **Soumik Sir**, **Sunipa Ma'am**, **Adrita di**, **Tathagata da**, **Amlan da** and **Anudeb da** for their uniform support throughout my research journey. I am especially indebted to **Adrita di**, for her exceptional assistance, not only in providing valuable academic guidance but also in offering financial support for sample analysis. Her constant encouragement, insightful discussions, and dedicated mentorship have been pivotal in the successful completion of my research and I am deeply grateful for her significant contributions.

My sincere appreciation goes to my juniors from JUSEDILAB; **Soumyadip**, **Vivek**, **Arunava**, **Anirban**, and **Shilpa** for their constant assistance, support, and camaraderie, all of which have made this journey more enjoyable and fulfilling. I would like to extend special thanks to **Soumyadip** for his invaluable technical assistance during the editing process, which was crucial in successfully compiling my thesis. Other than Sedi lab, A special thanks goes to **Manna (Anirban)**, my junior who always helped me by giving all types of technological supports throughout this journey.

I am deeply grateful to my friends **Sabyasachi**, **Shilpa**, and **Reeya** for their faithful moral support and cherished friendship throughout this journey. During fieldwork, **Sabyasachi** was my saviour, without whom the completion of this thesis would have been impossible. His dedication and assistance were invaluable. **Shilpa** played a crucial role in continuously

evaluating my progress, pushing me to achieve my best, and her constructive feedback was instrumental in the successful completion of this work. **Reeya**, who is very close to my heart, provided constant moral support, uplifting me during challenging times. I am truly fortunate to have such incredible friends by my side.

Smt. Jayasri Sarkar, our beloved ma'am, deserves a special recognition for her cordial, motherly care and support throughout my journey. I wish to express my sincere and heartfelt thanks to the **Jethima** (late Dr. Sreeradha Bose), **Gopa Pisimoni**, **Boro Pisimoni** and **Prasun Jethu**, **Runai Di** their encouragement and motivation, which have been a constant source of strength for me.

I would like to thank **CSIR** (Council of Scientific and Industrial Research) for providing me the funding to initiate this research work and **Department of Geological Sciences, Jadavpur University** for the infrastructural facilities. I am also thankful to the Department of Earth Sciences, **IIT Kanpur**, **IIT Bombay**, **NCESS** (National Centre for Earth System Science) Kerala, **IISER Kolkata**, **BSIP** (Birbal Sahni Institute of Palaeosciences) Lucknow, **DRML-DRDO** (Defence Metallurgical Research Lab of Defence Research & Development Organisation), Hyderabad and **CSIR-IICB** (Indian Institute for Chemical Biology) for instrumental facilities.

A special thanks to **Binu Da** for helping me out in varied administrative and non-academic work. I am thankful to all non-teaching staff of the Department specially **Koushik Da**, **Sujit Da**, **Arin Da** and **Pranab babu**.

I would like to extend my heartfelt gratitude to my colleagues at Kabi Jagadram Roy Government General Degree College, Mejia, Bankura, for their unwavering support throughout my research journey. A special thanks goes to the Department of Geology, especially to my senior colleagues, **Dr. Aresh Kumar Maji** and **Dr. Nivedita Chakraborty**. Their insightful feedback, encouragement, and steadfast support were crucial in the completion of this research work. **Nivedita Di** is more than just a colleague; she is a senior from JUSEDILAB who has guided and supported me both in the workplace and throughout my research endeavours. I am also deeply appreciative of the Officer-in-Charge of the college, **Mr. Aloke Kumar Das**, for his constant support and assistance. Finally, I would like to express my sincere thanks to **Dr. Avisek Sen**, **Dr. Indrani Hazra**, **Dr. Goutam Dey**, and **Mr. Writtick Bhattacharya** for their persistent motivation and encouragement, which pushed me to complete this thesis in a timely manner.

I would like to express my deepest gratitude and heartfelt appreciation to my family, whose untiring presence and support have been the foundation of my existence. My parents, **Shri. Somnath Mondal** and **Smt. Sandhya Mondal**, have been my pillars of strength. Their boundless love, wisdom, and encouragement have been a guiding light throughout my life. Their sacrifices, constant support, and unshakable belief in my abilities have not only shaped my character but have also been instrumental in my journey towards achieving this milestone. It is through their nurturing care and enduring faith that I have been able to reach this point, and I am profoundly grateful for their invaluable contributions to my personal and academic growth. Especially **Baba**, always helped me to stay focused in every phase of this journey.

I am equally grateful to my parents-in-law, **Bapi** (Shri. Santosh Gorai) and **Mamoni** (Smt. Maya Gorai), whose love and support have made me feel deeply cherished as a member of their family. Their unwavering encouragement, boundless kindness, and genuine warmth have been a source of immense comfort and strength throughout this journey. Their steadfast presence and thoughtful gestures have greatly enriched my life, and I am profoundly thankful for their continuous support and the sense of belonging they have provided.

Bhai, (Mr. Indrajit Mondal) also deserves a heart-warming recognition who always been a source of stimulation, standing by my side with genuine support through every challenge and triumph. I am deeply grateful to **Dolon** (Sister), who constantly encouraged and motivated me to complete this thesis in a timely manner. I would also like to extend my inmost love to my little niece **Divisha**, whose joyful presence and playful spirit helped lift my mental fatigue and brought much-needed moments of happiness.

I would like to reiterate my gratitude to my cherished childhood companion, **Thamma** (late Smt. Renuka Mondal). I also extend heartfelt thanks to my maternal grandparents, **Dida** (Smt. Pramila Mondal) and **Dadu** (late Shri Manindra Mondal), **Boromama** (Shri Prasanta Mondal), **Boromami** (Smt. Purnima Mondal), whose blessings have been integral to completing this journey.

Finally, I wish to express my deepest gratitude to my best friend and husband, **Mr. Biswajit Gorai**. He has been my affectionate shelter, handling my each and every tantrum, outburst and moment of anxiety with grace and love. His continuous support has anchored me, providing strength and encouragement during the most challenging times. With endless patience and understanding, he has stood by my side, lifting my spirits and keeping me focused. In addition to being my emotional pillar, his technical expertise in document editing, has been indispensable in the completion of this thesis. I am truly blessed to share my life with someone who not only believes in me but also actively contributes to my success. His love, doubtless support, and belief in me are wonderful gifts which I cherish deeply. I am forever grateful to have him by my side.

Indrani Mondal
(INDRANI MONDAL)

ABSTRACT

The term 'Shale' has been used to describe fine-grained sedimentary rock, largely terrigenous particles with dominance of mud-size particles, containing substantial amount of clay minerals content and fine siltstones. The shales are most important rocks because they constitute by volume almost two-third of the sedimentary rock record, excellent matrix for fossil preservation and may contribute much to a better understanding of earth processes, earth history and evolution of life. The black shales which are rich in organic carbon and present in major part of the studied succession are even more important because they exclusively preserve a wealth of information about the Earth's ancient processes and conditions owing to its unique geochemical signatures. At the outset of the present study a detailed review of the black shales, considering its global distribution and different important aspects (physical, geochemical, biological, biogeochemical etc.) has been done to feel the importance of the present study.

The current study deals with 1.5 billion years-old Rampur Shale (RS) Member of the Rohtas Formation of the Semri Group, Vindhyan Basin of Son valley, Central India and presented a detailed sedimentological, geochemical attribute of the shale and an exceptionally coveted geobiological writ preserved particularly within the black shale part of the Rampur Shale. Eliciting the depositional modes of ancient shale rock is difficult because of its fine grain-size and needs a well-organized classification. A state of art facies analysis has been performed during the present study to gain insight about the palaeoenvironmental dynamics in a Mesoproterozoic basin where the Rampur shale was deposited. The apparent monotony of the finely laminated Rampur shale is broken by the intermittent presence of sandstone/siltstone alternation, mostly present in the lower part of the Rampur shale. Considering the sand: shale ratio, primary sedimentary structures, colour and body geometry of the sand/silt layer present within the shale a lower shoreface to deep marine paleogeography has been suggested for the Rampur Shale. Intermittent presence of laterally persistent sandstone/siltstone layers likely to be deposited by occasional storm intervention. Considering the sand: shale ratio present within the Rampur Shale, it has been subdivided into three segments. The lower segment is sandstone dominated (Facies A), followed by the middle segment consisting of sand-silt interlayering with shale (Facies B, C and D). The upper most segment is almost sand free (Facies E and F). The major part of the RS is forming a transgressive system tract except the uppermost facies F, which show initiation of a highstand system tract (HST). The ca.10-meter-thick black shale (BS) unit (Facies E) suggests a basin-wide marine transgression forming the maximum flooding zone (MFZ). The BS imparts a dark hue due to the preservation of organic matter in

the form of abundant microbial mat growth on the sediment surface. The $\delta^{13}\text{C}_{\text{org}}$ ratio of the BS ranges between -25‰ and -34.4‰ supports this view. Several geochemical proxies suggest that the provenance could be felsic sediments. The weathering intensity was high, and the Rampur shale including the black shale part was deposited under humid climatic conditions. The palaeoredox proxies of BS suggest suboxic to anoxic depositional conditions, possibly resulting from organic matter degradation. The palaeosalinity remains low for the entire Rampur shale, possibly due to the abundant riverine freshwater supply in the epicontinental basin. The trace metal proxies suggest upwelling conditions during the BS deposition. Numerous slide planes at successive intervals bear the signature of basin subsidence and deepening, resulting in black shale formation.

Deep-time microbial record is generally indirect, but some fortuitously preserved microbial remains makes the Rampur Shale interesting and an exceptionally coveted geobiological writ. Amongst the three distinctive segments the lower and the upper one are particularly productive. Field observations are augmented by microscopic and ultramicroscopic studies (SEM and CLSM) and followed by geochemical analyses with help of EDS. The bottommost all sandstone intervals bear numerous cracks, even though the sandstones are matrix-free. At places, the cracks are confined within the ripple troughs resembling *Murchisonophycus*; in a few examples, the cracks are mutually parallel in oblique direction with respect to the ripple crests. Locally the cracks are in multiple sets cross-cutting each other. The fifth interval is, in contrast, almost entirely shale that does not show any fissility plane because of being sewn through by microbial filaments. Three different kinds of microbial mat geometry are present: dark laterally persistent wrinkled mat, darker lenticular mat and darkest spherical mat. All the varieties of mat are carbon-rich. All are penecontemporaneously dolomitized, but their dolomite populations differ little in composition. Cyanobacterial filaments are preserved in form of networks both within black shale and impervious volcanic ash beds; however, patches of organic matter are revealed elsewhere too under confocal microscope. Many forms of other bacteria are also revealed under SEM. Wherever measured these elements reveal high content of carbon.

The glauconite grains occur at the middle segment (more within Facies B and D and in less amount within Facies C) is another important issue have been dealt in the thesis. Their main concentration is, however, where the pyroclastic materials are most conspicuously present. Pyroclasts themselves bear glauconite patches mostly non-pelletal. Nevertheless, free glauconite grains in their close association are mostly perfectly pelletal and green in colour. Numerous stockwork silica veins separate them from each other and fragments of pyroclasts.

Fine chalcedony crystals have grown vertically from the grain surfaces all around them and rest of the grain interstices are filled by colloidal silica. In areas adjacent to the pyroclastic bodies glauconite also occurs as intergranular cement that very often cracks to give rise to the pellet-like form. Further away from the pyroclastic bodies laterally or stratigraphically upward stratified glauconite pellets occur preferably in relatively coarser-grained layers, silty or sandy. Within shales their presence is meagre. However, as a whole glauconite concentration is the highest within facies B and D which decreases to only 10–15% of the rock by volume in facies C. Despite the variation in glauconite pellet morphology and concentration, the compositional spectrum of the glauconite exhibits strongly overlapping K_2O and Fe_2O_3 (total) concentration, representing a highly-evolved maturation stage. The micro-textural study of the green pellets and the mineralogy validate the highly mature state of glauconite. The rare earth and trace elemental geochemistry of the Rampur Shale Member suggests the prevalence of weathering under warm and humid conditions. The glauconites of the Rampur Shale Member are formed by the pseudomorphic replacement of the framework grains, including the pyroclastic fragments, by a substantial intake of iron and manganese at the expense of aluminium and silicon. The low oxygen environment during the Mesoproterozoic time and occasional subsidence during the deposition of the Rampur Shale might have facilitated the mobility of iron, resulting in abundant authigenic glauconite formation. The glauconites from the Lower Vindhyan succession, confined within the Rampur Shale Member and the underlying Chorhat Sandstone, are abnormally rich in MgO , which is not observed for the glauconites within the Upper Vindhyan sediments, suggesting a strong influence of Mg-rich oceans in glauconite composition or the Pyroclastic/microbial source may be responsible for the higher Mg content.

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PART I

GENERAL INTRODUCTION AND BACKGROUND STUDY

CHAPTER: 1

GENERAL INTRODUCTION

1.1: Introduction

Earth is the only planet in the solar system where plate tectonics is operative. This plate tectonics help to shape almost all the geological processes (Stern, 2008; Condie, 2021). The understanding of Earth has evolved dramatically with the conceptualization that, its surface is in constant motion, leading to the release of significant energy through earthquakes and volcanic activity. The Earth's structure, formation and destruction of basins, creation of mountain ranges, and sediment deposition and the mineral deposits beneficial to society are all results of the interaction and movement of tectonic plates (Dewey and Bird, 1970; Ingersoll, 1988; Wilson et al., 2019). The history of Earth includes several supercontinents, including Columbia (~2.1–1.8 billion years ago), Rodinia (~1.2–0.9 billion years ago), Gondwana (~500 million–250 million years ago), and Pangea (~250 million–185 million years ago), each shaping the planet's tectonic, climatic, and biogeochemical evolution (Rogers and Santosh, 2002; Zhao et al., 2002; Nance and Murphy, 2013; Condie, 2021). Recent studies (Santosh et al., 2004; Reddy and Evans, 2009; Basu and Bickford, 2015; Meert and Pandit, 2015) have linked the origin of many sedimentary basins to the dispersal or amalgamation of supercontinents, highlighting the need to understand these basins' depositional histories to gain insights into supercontinent configurations. The Indian peninsula, formed by the convergence of five Archean cratonic nuclei (Dharwar, Singhbhum, Bastar, Bundelkhand and Aravalli) has remained relatively stable since the Cambrian period. The geological history spans around 3 billion years, marked by the stabilization of cratons, amalgamation of Archean cratonic nuclei with orogenic belts, and the opening and closing of sedimentary basins on stabilized cratons. During the Proterozoic time development of intracratonic basins on the stabilized shields/cratons started all over the world (Windley 1977; Chakraborty 2006). The sediment deposited in an unvegetated landscape were several km thick and many of them are unmetamorphosed. These sedimentary strata lie unconformably on the Archean–early Proterozoic gneisses, high-grade rocks, granite-greenstones or metasedimentaries of Proterozoic mobile belts. The Vindhyan basin is the 2nd largest Proterozoic sedimentary basin of the world, well known for its unique preservational record and has the scope to resolve many issues concerning the development and evolution of intracratonic basins during the Proterozoic time. The undisturbed and less metamorphosed sedimentary succession of the Vindhyan has recorded a substantial part of Mesoproterozoic and Neoproterozoic and therefore contains crucial information about the evolution of the then biosphere, atmosphere and hydrosphere of our planet.

Mesoproterozoic era is the mystic time zone of the geological history and popularly recognized as “Boring Billion” (1.8-0.8 Ga) (Holland, 2006; Bradley, 2011; Roberts, 2013; Condie, 2021). But this time is equally cryptic for witnessing several global scale events including supercontinent reorganization as well as intercontinental rifting, glaciation and deglaciation events, atmospheric oxygenation and organic evolution (Condie et al., 2001; Holland 2006; Basu et al., 2017). These all-momentous episodes are crucially documented within Meso-Proterozoic sediments.

The Indian Subcontinent is an opulent hub for Proterozoic sedimentologist, diversified with five major cratons, several mobile belts and Proterozoic (Purana) basins. All the cratons along with the purana basins and associated mobile belts describe their own evolutionary history. The present study restricted to the largest purana basin of India, named as Vindhyan Basin. This thesis addresses the history of development of 1.5 Ga old Rampur Shale Member of Vindhyan Basin, Central India (Bose et al., 2001; Rasmussen et al., 2002; Sarkar and Banerjee, 2020). Rampur shale has been chosen for the present dissertation for the following reasons:

1. A large portion of the Rampur shale is black in colour.
2. The black shales are generally rich in organic matter and preserve plenty of information related to ancient earth including palaeogeography and the then climate (Piper & Calvert, 2009).
3. The black shales are the store house of information related to ancient biosphere and ocean's composition (Nesbitt and Young, 1982; Jones and Manning, 1994; Cullers, 2002; Tribovillard et al., 2006; Sheldon and Tabor, 2009; Fathy et al., 2021).
4. The Meso- to Neoproterozoic times are equally cryptic for witnessing several global scale events, including supercontinent break-up and amalgamation (Condie et al., 2001; Rogers and Santosh, 2002; Evans and Mitchell, 2011; Basu et al., 2017).
5. Besides a large part of the Rampur Shale is composed of sandstone/siltstone and shale, the sand being deposited by different episodic events.
6. Plenty of microbial mat related structures (MRS or MISS) are present on the bed surface of the sandstone/siltstone layers present within the Rampur Sale.
7. Green coloured mineral identified as glauconite are abundantly present within some sandstone-siltstone layers which are compositionally unique with respect to magnesium enrichment.
8. Despite the plethora of literature on black shales, the Mesoproterozoic black shales are less discussed.

The work has been carried out over a 120km long stretch roughly parallel to the strike direction. Purpose of this thesis is to address the sediment processes and products in the changing scenario from the shallow shelf to deeper shelf and within a restricted basin at the deepest part sediment origin, palaeoclimate and sequence building scenario for clarifying the unusual chemical composition of the glauconite mineral compare to other glauconites present in this supergroup. The thesis reveals the overall palaeogeography and palaeoenvironmental variations of Mesoproterozoic time.

1.2: Geology of the Vindhyan Basin

Vindhyan basin is one of the largest epicontinental basin in the world formed during Meso- to Neoproterozoic time. Approx. 4.5-km thick sedimentary succession of the Vindhyan Basin in central India extends over 100000 km² (Ahmad, 1958), widely exposed in parts of Bihar, Jharkhand, Madhya Pradesh, Uttar Pradesh and Rajasthan but not exposed properly as 70,000 Km² area of this basin is veiled under Deccan trap (Fig. 1.1; Auden, 1933; Krishnan and Swaminath, 1959). Vindhyan basin is divided by Archean Buldelkhand Granitic Complex and Cretaceous Deccan Trap into two sectors. One sector is named as Son Valley Sector of Central India, covered Bihar, Jharkhand, eastern part of Madhya Pradesh and the other is Chambal Valley sector of western India, covered Rajasthan and western part of Madhya Pradesh. The basin initiated with the Formation of approximately E-W trending faults (Naqvi and Rogers, 1987). As a result, the sedimentation pattern shows a rapid change in thickness and facies variation within the Lower Vindhyan/Semri Group. This NE-SW elongated and westward opening epeiric rift basin later developed into a sag basin, resulting in the deposition of Upper Vindhyan sediments (Chanda and Bhattacharyya 1982; Bose et al. 1997, 2001; Sarkar et al. 2002). Vindhyan deposit in both the sector looks like they are following a syncline fold trending towards E-W (Fig. 1.2). The older members of the basin are present at the core of the syncline fold and younger are in the flanks. The dip of the younger unit i.e., Upper Vindhyan are very gentle up to 4° whereas dip of the older unit i.e., lower Vindhyan Semri Group vary up to 30°. The alluvial sediments of Ganga, Yamuna and Son River have been covered a vast area of Son Valley Sector of the Vindhyan Basin. The mildly deformed and unmetamorphosed succession is deposited over the Neoproterozoic granitic basement and metasedimentary rocks of the Early Proterozoic Mahakosal Group (Rao and Neelakantam, 1978; Bandyopadhyay et al., 1995; Venkatachala et al., 1996; Bose et al., 2001; Sarkar et al., 2002). Previous workers have suggested a two-fold classification of the Vindhyan Supergroup comprising the Lower Vindhyan/Semri Group (with Deoland, Kajrahat, Porcellenite, Khenjua and Rohtas Formations in ascending order) and the

Upper Vindhyan Group (with Kaimur, Rewa and Bhandar Formations in ascending order) (Bose et al., 2001) (Table 1.1). The dominant lithology of the Vindhyan succession comprises sandstones, shales, and carbonates with rare intraformational conglomerates and thick pile of pyroclastic deposit (Basu and Bickford 2015; Bickford et al. 2017; Mishra et al., 2018). The sedimentary succession of the Vindhyan Basin dominantly represents shallow marine depositional environments; however, terrestrial sedimentation in fluvial and aeolian depositional environments is also not uncommon (Bose et al., 2001).

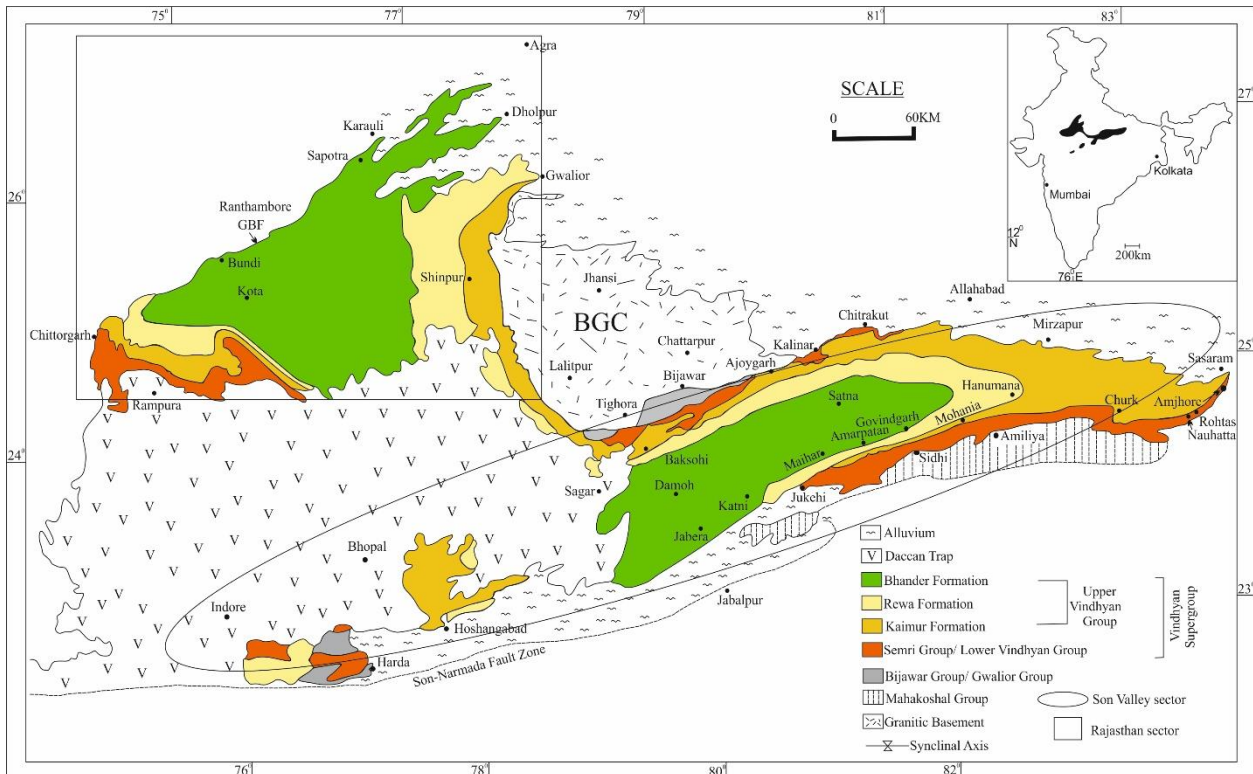


Fig.1.1: Distribution of Vindhyan Rocks (Supergroup, Group and Formations) in Indian Subcontinent (modified after Sarkar and Banerjee, 2020). Son Valley sector comprising parts of Bihar, Madhya Pradesh, Uttar Pradesh and Rajasthan sector is comprising western part of the Madhya Pradesh and Rajasthan.

Table-1.1. Stratigraphy of Vindhyan Supergroup (modified after Sarkar and Banerjee,2020)

Vindhyan Supergroup	Group	Formation	Members
	Upper Vindhyan Group	Bhandar	Upper Bhandar Sandstone
			Sirbu Shale
			Lower Bhandar Sandstone
			Bhandar Limestone
			Ganurgarh Shale
		Rewa	Rewa Sandstone
			Rewa Sandstone
		Kaimur	Dhandraul Quartzite
			Mangesar Sandstone/ Scarp Sandstone
			Bijaigarh Shale
			Upper Quartzite/ Markundi Sandstone
			Silicified Shale/ Bhagwar Shale
		Lower Quartzite/ Sasaram sandstone	
	Unconformity		
	Lower Vindhyan Group	Rohtas	Rohtas Limestone
			Rampur Shale
		Khenjua	Chorhat Sandstone
			Koldaha Shale
		Porcellanite	
		Kajrahat	Kajrahat Limestone
			Arangi Shale
		Deoland Sandstone	
	Basement		

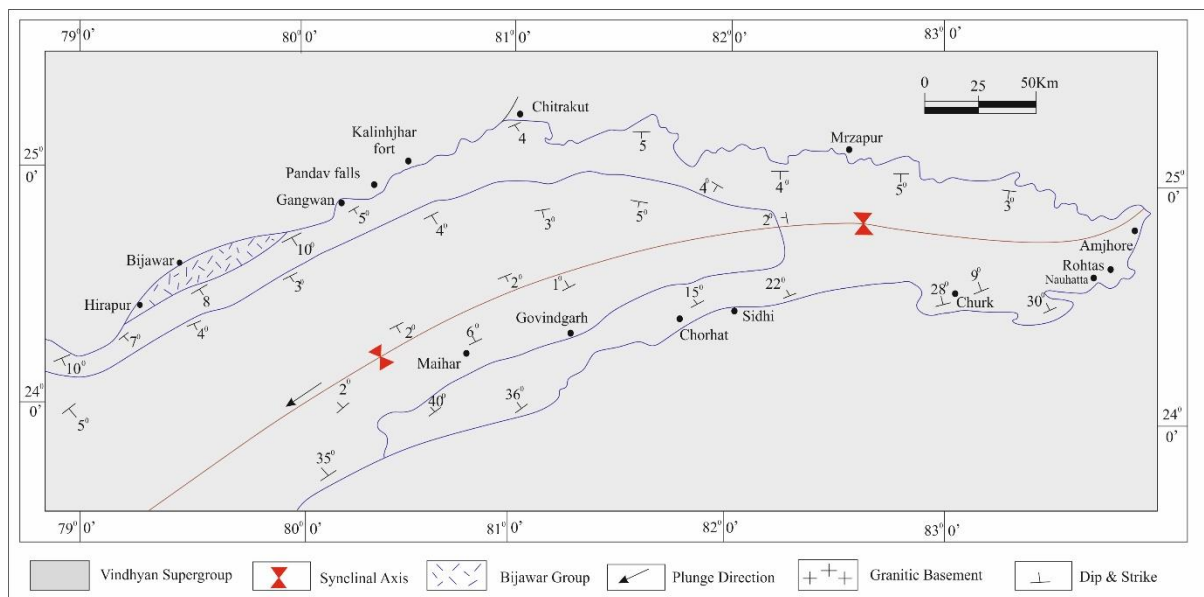


Fig.1.2: Geological map of Vindhyan succession (modified after Sarkar and Banerjee, 2020).

1.2.1: Tectonic Framework of Vindhyan supergroup:

The Vindhyan Basin is the largest Purana Basin of India, mostly occupying the central part of the Indian Subcontinent extended from Bihar at the eastern part to Rajasthan at the western part. Crustal thickness of this Basin varies from 39.5 to 45 km which is cross-cut by several NE–SW and ENE–WSW trending wrench faults that divides the basin into several tectonic blocks (Kaila et al. 1989; Das et al. 1999). Son-Narmada Lineament is a prominent linear feature cut across the Central India with a strike length of 1200 km along NNE-SSW direction; it was active during the Precambrian time period. This lineament prominently divided the Aravalli-Bundelkhand Craton to Dharwar Craton (Fig. 1.3; Choubey 1971; Kaila et al., 1985; Mazumder et al., 2000; Acharyya 2003). About 500 km long northwesterly dipping Great Boundary Fault, a major tectonic lineament consisting of a series of northeast–southwest trending, faults demarcated the western margin of the Vindhyan basin (Tewari 1968; Naqvi and Rogers 1987; Narain 1987; Verma 1991; Srivastava and Sahay 2003). This lineament acted as a thrust boundary along which folded metasediments of the Palaeoproterozoic known as Delhi–Aravalli fold belt, lie against the Vindhyan Supergroup (Fig. 1.3).

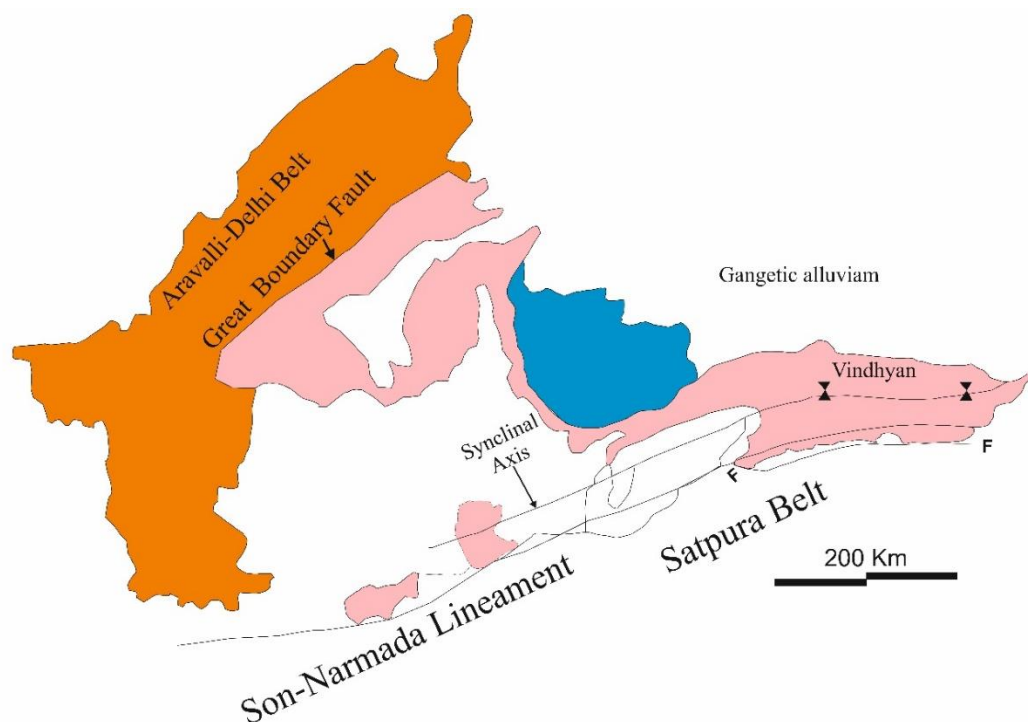


Fig.1.3: Tectonic map and structural boundary of the Vindhyan Basin (modified after Sarkar and Banerjee, 2020)

Vindhyan Basin apparently covered near about 100000 km² area and another 70000 km² area is concealed under the Deccan Trap at the southern part of the basin from the Cretaceous time.

Vindhyan Basin overlies on Mahakoshal group and underlain by Gondwana of Central India. This basin is bordered by Delhi, Aravalli and Satpura mobile belts and it was a southerly dipping and considered as peripheral foreland basin before the collision with the Bhandara Craton (Auden 1933; Chakraborty and Bhattacharyya 1996; Raza and Casshyap 1996). An idea proposed by Verma and Banerjee 1992 and Ram et al., 1996, towards the intracratonic rift origin of the Vindhyan Basin but the grain size, maturity and sedimentary structures does not accord with this setting. Crawford and Compston 1970; and Crawford 1978 proposed that Vindhyan is a strike-slip fault basin. Nd-isotope study of the Clastic and non-clastic sediment supports the idea of foreland basin (Chakrabarti et al. 2007; Chakraborty and Bhattacharyya 1996). Considering all the sedimentological details and overall depositional scenario from lower and Upper Vindhyan sediments Bose et al., (2001) concluded that an initial intra-cratonic rift changed into a sag basin during deposition of the Upper Vindhyan sediments. Extensive field studies on multiple units of this basin reveal that intra-cratonic north–south rifting faced a dextral shear at its initial stage (Bose et al. 1997, 2001) and sag at the later stage (Sarkar et al. 2002b). It is unanimously believed that the Vindhyan Basin is an E-W trending westward opening intra-cratonic basin (Chanda and Bhattacharyya 1982; Chaudhuri and Chanda 1991; Sarkar et al. 2004; Chakraborty et al. 2012).

1.2.2: Vindhyan Stratigraphy: Lithological Distribution of Vindhyan Rocks:

Henry Benedict Medlicott, an Irish geologist proposed the initial stratigraphic classification of ~4500m thick Vindhyan sediments. After Medlicott (1859) the stratigraphy of the Vindhyan supergroup evolved several times; by Mallet (1869), Oldham et al. (1901), Vredenburg (1910), Auden (1933), Banerjee (1974), Rao and Neelakantam (1978), Bhattacharyya (1996), Chakraborty (2006), Chakraborty et al. (2010), Kumar and Sharma (2011) and Sarkar and Banerjee (2020). In both the sector, the Vindhyan Basin is overlain on several Precambrian/ Palaeoproterozoic Basement such as, Bundelkhand Granite, Mahakoshal Group, Bijawar Group, Gwalior Group, Banded Gneissic Complex (BGC) and Chhotanagpur Gneissic Complex (CGC). The Vindhyan exposures of the Son Valley area and the Chambal Valley area are separated by Bundelkhand Granite Complex (Rogers 1986; Bandyopadhyay et al. 1995; Eriksson et al. 1999; Mazumder et al. 2000). For Son valley sector, at the southern and eastern margin, Mahakoshal Group act as a basement rock (2.1–1.6 Ga) (Das et al. 1990; Roy and Bandyopadhyay 1990; Nair et al. 1995), at the northern and northeastern margin, the basement rock is Bijawar Group (2.1 Ga) (Das et al. 1990; Roy and Bandyopadhyay 1990) and most parts of southeastern part Chhotanagpur Gneissic Complex (CGC) forms the basement of

the Vindhyan Basin (Singh et al. 2001). For the Rajasthan sector, Banded Gneissic Complex (BGC) and Gwalior Group form the basement of the Vindhyan Supergroup in (Heron 1953). The major unconformity within the Son Valley sector divided the Vindhyan Succession into two major group known as Lower Vindhyan (Semri Group) and Upper Vindhyan Group (Chanda and Bhattacharyya 1982; Bose et al. 2001, 2015). The Stratigraphy of the Son valley sector will be focused here (Table 1.1).

The Lower Vindhyan /Semri group comprises five formations, Deoland, Kajrahat, Porcellanite, Khenjua and Rohtas. The Deoland Formation is overlying on the basement rock i.e., Mahakoshal group of rock; almost sand dominated and basal part contain a conglomeratic horizon which is glacial originated (Prakash and Dalela 1982). The next overlying formation is known as Kajrahat Formation subdivided into two members; Lower one is Arangi Shale and upper one is Kajrahat Limestone. Arangi Shale has a minimal exposure at places which is carbonaceous dark grey coloured shale with patches of carbonates within. Kajrahat Limestone known for its spectacular preservation of Stromatolitic limestone and dolomites are also a very prominent phase present in between the thin sets of the stromatolites (Rao and Neelakantam 1978; Prakash and Dalela 1982; Banerjee et al. 2007). The sediment deposited over the Kajrahat Limestone is entirely made up with volcanoclastic sedimentation which contain pyroclastic flow, surge deposit, tuffaceous material and salified shale named as Porcellanite formation which is nearly 400m thick. This Porcellanite formation is gradually passes into Khenjua Formations. This formation is again divided into two members; those are black shale dominated Koldaha Shale with intermittent tuff layers at the lower part and microbial mat infested sandstone layers named as Chorhart Sandstone at the upper part (Auden 1933; Rao and Neelakantam 1978; Prakash and Dalela 1982; Bose et al. 1997, 2001; Banerjee 2000; Sarkar et al. 2006). This formation is again overlain by the Rohtas Formation, topmost formation of the Semri group. Rohtas Formation is also divided into two members lower one is black shale dominated Rampur shale and upper one is the carbonate dominated Rohtas Limestone (Chatterjee and Sen 1988). A prominent unconformity is present at the top of the Rohtas limestone which is laterally correlatable with a correlative conformity (Chanda and Bhattacharya, 1982; Chakraborty, 1996; Bose et al., 2001; Mandal et al., 2019).

Like the Lower Vindhyan Semri Group, Upper Vindhyan Group is also subdivided into three formations known as Kaimur, Rewa and Bhandar. Just above the unconformity, the Kaimur Formation started to deposit and it is divisible into five members. The lowermost Sandstone member is Lower Quartzite lies just above the unconformity between Lower and Upper Vindhyan (Mandal et al., 2020). Lower Quartzite followed by Silicified Shale which is also

known as Bhagwar Sahle. After the Bhagwar/ Silicified Shale the lithology grades into Upper Quartzite or Markundi Sandstone followed by a thick Black Shale deposition at its top, named as Bijoygarh Shale. All the four members i.e., Lower Quartzite, Bhagwar Shale, Upper Quartzite and Bijoygarh Shale jointly known as Lower Kaimur member (Chakraborty and Bose 1990; Mandal et al. 2019). This black shale gradually passes to a sandstone deposit named as Scrap Sandstone. The topmost part of this Kaimur Formation is overlain on this Scrap Sandstone recognized as Dhandraul Quartzite. Both the Scrap Sandstone and Dhandraul Quartzite are collectively known as Upper Kaimur (Chakraborty et al. 1996). This Kaimur formation passes into the Rewa formation which has a basin-wide granular blanket like layer known as transgressive lag (Bose et al. 2001). Above this lag, greenish grey coloured Rewa shale has been developed. The Rewa Shale later grades into Rewa Sandstone which has fluvial influence (Bose and Chakraborty 1994; Bose et al. 2001). This Rewa Sandstone overlain by grey coloured Ganurgarh Shale (Sarkar et al. 1996), followed by a stromatolite horizon named as Bhandar Limestone (Sarkar et al. 1996, 1998, 2014a). Bhandar Limestone gradually passes into Lower Bhandar Sandstone and then alternating with shale which is finally ended up with a thick pyritiferous black shale deposition; named as Shirbu Shale (Sarkar et al. 2002b). After the black part of the Shirbu Shale it is again alternate with sandstone and gradationally passes into Upper Bhandar Sandstone which is influence by fluvial and aeolian activity (Bose et al. 1999; Sarkar et al. 2004; Choudhuri et al., 2022).

1.2.3: Geochronology of Vindhyan Supergroup:

Geochronologic description of the Vindhyan Basin is polemical and still the topic is in a debatable stage, perhaps the geochronologic data from radiometric dating and Palaeobiological evidences from microbiota along with trace fossils are conflicting (Venkatachala et al., 1996). However, based on the research work of several Chrono- stratigraphers, the age of the Vindhyan Basin is considered as Meso-Neoproterozoic time. According to Rasmussen et al., 2002, the previous radiometric data based on K-Ar, Rb-Sr and Fission track analysis used for the analysis but these data may represent post depositional or detrital signatures. The triploblastic metazoans reported by Seilacher et al., 1989) left a marvelous impact on chrono-stratigraphy and bio-sedimentology of Vindhyan Basin particularly on Lower Vindhyan (Fig. 1.4).

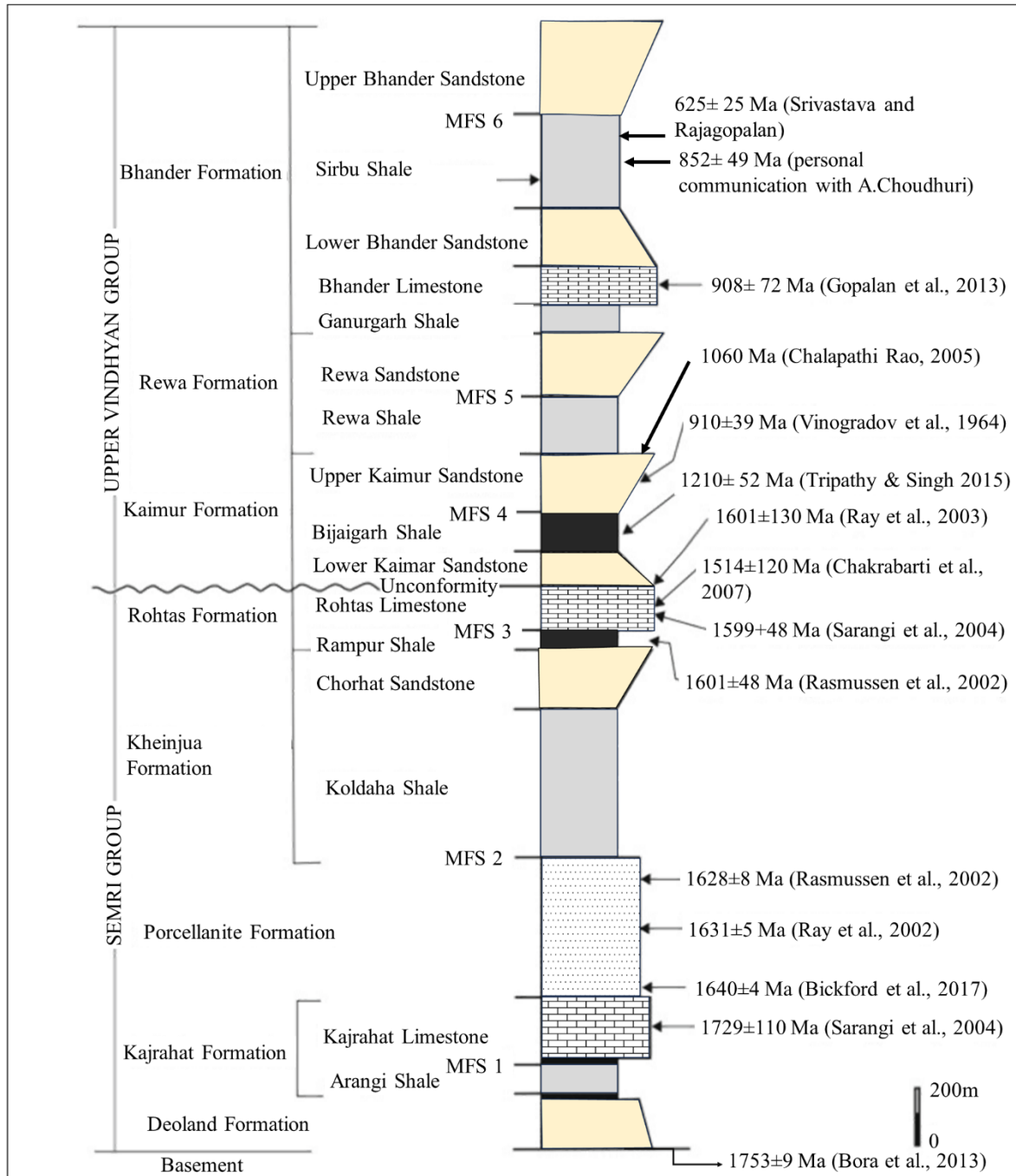


Fig. 1.4: Geochronology of the Vindhyan stratigraphic succession (modified after Sarkar and Banerjee, 2020). Note the pronounced depositional age for this suitable sedimentary unit.

The age of the Lower Vindhyan, is based on Pb-Pb isochron method, Sarangi et al. 2004 worked on underlying Kajrahat Limestone and derived the age about 1729±110 Ma. Using SHRIMP U-Pb ages from the magmatic zircon, derived from the volcanoclastic layers and Rhyolite flows of the Porcellanite formation. several research groups work on this same formation and calculated broadly similar ages 1628 ± 8 Ma, 1630.7 ± 0.8 Ma, 1640 ± 4 Ma and

1647 ± 18 Ma (Rasmussen et al. 2002; Ray et al., 2002; Bickford et al. 2017) from this same formation. Combining all the radiometric ages it can be envisaged that the Vindhyan basin was opened around ~1800 Ma (Basu and Bickford 2015). Rasmussen et al., 2002, also worked on ash layers of the Rampur Shale of Rohtas Formation and using U-Pb zircon method they showed the age of the ash layer within Rampur shale is near about 1599±8 Ma. Using Pb-Pb isochron method, Sarangi et al. 2004 also showed an age of about 1599 ± 48 Ma. Another research group worked on overlying Rohtas Limestone and also used the Pb-Pb isochron method they derived an age of 1514 ± 120 Ma (Chakrabarti et al. 2007) (Table 1.2).

Table 1.2. Depositional age of different stratigraphic unit in order of stratigraphic succession of the Vindhyan Supergroup, Son valley (modified after Sarkar and Banerjee, 2020)			
Stratigraphic Unit	Authors	Age	Methods
Upper Bhandar Sandstone	Crawford and Compston, 1970	550 Ma	K/ Ar
Sirbu shale	Srivastava and Rajagopalan, 1988	625±25 Ma	F-T
Lower Bhandar sandstone	Ray et al. 2002	600 Ma	⁸⁷ Sr/ ⁸⁶ Sr
Bhandar Limestone	Ray et al. 2002	908±72 Ma	Pb-Pb
	Ray et al. 2003	750-650 Ma	⁸⁷ Sr/ ⁸⁶ Sr
	Gopalan et al. 2013	1075-900 Ma	Pb-Pb
Upper Kaimur (from Majhgawan kimberlite)	Laura et al. 2006	1073.5±13.7 Ma	Ar-Ar
Bijoygarh Shale	Tripathy and Singh, 2015	1210±51 Ma	Re-Os
Rohtas Limestone	Sarangi et al. 2004	1599±8 Ma	Pb-Pb
	Ray et al. 2002	1631±1 Ma	U-Pb
	Chakraborti et al. 2007	1514±120 Ma	Pb-Pb
Rampur Shale	Rasmussen et al. 2002	1593±12 Ma	SHRIMP
	Rasmussen et al. 2002	1602±10 Ma	SHRIMP
Porcellanite	Rasmussen et al. 2002	1628±8Ma	SHRIMP
	Ray et al. 2002	1631.2±5.4 Ma	SHRIMP
	Ray et al. 2002	1630.7±0.4 Ma	U-Pb
	Bickford et al. 2017	1640±4 Ma	²⁰⁷ Pb/ ²⁰⁶ Pb
	Mishra et al. 2018	1647±18 Ma	²⁰⁷ Pb/ ²⁰⁶ Pb
Kajrahat Limestone	Ray et al. 2002	1631±5 Ma	U-Pb
	Sarangi et al., 2004	1729±110 Ma	Pb-Pb
Basement-Mahakoshal (Jhiragadandi Granite)	Bora et al. 2013	1753±9 Ma	U-Pb

For the Upper Vindhyan rocks, age determination from these Upper Vindhyan formations is more conflicting as well as controversial. The kimberlite pipes within Rewa Formation produced the ages about 974 Ma to 1067 ± 31 Ma, 1170 ± 46 Ma and phlogopite Ar–Ar age of 1073.5 ± 13.7 Ma (Chalapathi Rao 2006; Gregory et al. 2006). Providing a K–Ar age of 910 ± 39 Ma derived from glauconites of the Kaimur Formation (Vinogradov et al. 1964). Another date derived from Upper Rewa Formation by fission-track method with the date of 710 ± 120 Ma (Srivastava and Rajagopalan 1988). Based on Sr-isotope stratigraphy, Ray et al. (2003) suggested the ages of ~650 and 750 Ma for the Bhandar Limestone (Son Valley). Palaeobiological traces like Ediacaran-type fossils, large-diameter, burrow-like structures from the Bhandar Group strongly create controversies (Chakrabarti 1990; De 2003, 2006; Seilacher 2007; Banerjee et al. 2010; Kumar 2016). Similarities found between the ages derived from palaeomagnetic data of Bhandar Formation and Kimberlite pipe from Rewa Formation which is about 20 Ma (Malone et al., 2008; Turner et al. 2014). However, the Vindhyan Basin was closed tentatively around 900–1000 Ma (Malone et al. 2008; Gopalan et al. 2013; Basu and Bickford 2015) based on Re–Os age of 1210 ± 52 Ma from the Bijoygarh Shale in the Kaimur Group and recent palaeomagnetic and detrital zircon data (Tripathy and Singh 2015) (Table 1.2, Table 1.3).

Table 1.3: Tectonic models proposed by previous workers (Modified after Sarkar and Banerjee, 2020)

Authors	Tectonic models
Auden (1933); Chakraborty and Bhattacharyya (1996); Raza and Casshyap (1996); Chakraborti et al. (2007)	Foreland basin
Crawford (1978)	Strike-slip basin
Chanda and Bhattacharya (1991); Chaudhuri and Chanda (1991); Prakash and Dalela (1982)	Syncline
Choubey (1971); Naqvi and Rogers (1987); Kaila et al. (1989); Verma and Banerjee (1992); Ram et al. (1996)	Rift basin
Valdiya (1982)	Intracontinental platform
Bose et al. (2001)	Rift to sag basin
Sarkar et al. (2002)	Sag Basin (Upper Vindhyan)

1.2.4: Palaeogeography and Palaeoclimate of the Vindhyan Rocks:

The Vindhyan basin was opened for ~ 400Ma (Tripathy and Singh, 2015). Near about 4500m thick sediment was deposited under a wide variety of sedimentary environment but

mostly the whole sedimentation took place in a shallow marine (epeiric sea) condition (Singh, 1980, 1985; Chanda and Bhattacharya, 1982; Sarkar et al., 1996; Bose et al., 1999, 2001). Along with the shallow marine condition, the sedimentary units of the Vindhyan Supergroup shows the signature of barrier bar, lagoon, tidal flat, beach deposition along with few fluvial and aeolian inputs (Banerjee, 1964; Rao and Neelakantam, 1978; Chanda and Bhattacharya, 1982; Prakash and Dalela, 1982; Singh 1985; Soni et al., 1987; Prasad and Verma, 1991; Bose and Chakraborty, 1994; Akhtar, 1996; Sarkar et al., 1996, 2011; Bose et al., 1999, 2001; Sarkar et al., 2002a, b, 2004).

The entire Vindhyan basin is subdivided into two groups; Lower Vindhyan Semri group and Upper Vindhyan Group. Each group is again subdivided into several members which contain a definite sedimentation pattern. Lower Vindhyan is composed with a variety of lithology like sandstone, shale, carbonate and occasional intervening of volcanoclastic sediments. For Upper Vindhyan this variation is confined to sandstone, shale and carbonate. Comparing the lithological characteristics of Lower and Upper Vindhyan, one can get a reflection that the Lower Vindhyan is carbonate rich than the Upper Vindhyan. Lower Vindhyan has a thick deposition of Pyroclastic deposit named as Porcellanite and few interposed tuffaceous layers are present in between clastic sedimentary layers. Compare to Upper Vindhyan, Lower Vindhyan is less studied.

As discussed in the section 1.2.2, the Lower Vindhyan succession is made up with five Formations named as Deoland, Kajrahat, Porcellanite, Khenjua and Rohtas. Deoland Sandstone have conglomerate horizon at its base. Dubey and Chaudhury, 1952; Ahmad, 1955; 1958; Mathur, 1954, 1960, 1981, inferred that this conglomerate influenced by some glacial deposit. Some other group proposed that these conglomerates are originated from high gradient coastal river deposit or by mainland beach (Singh 1973; Banerjee 1974). The recent work of Bose et al., 2001 and Banerjee et al., 2008 concluded that the stratigraphic succession of Deoland Sandstone is solely influenced by shelf environment (Table 1.4). Gradually this sandstone grades into Arangi shale of Kajrahat Formation which is again a product of shelf environment (Bose et al., 2001). Some other groups claimed that Arangi shale is a product of lagoon or shallow marginal lagoon (Table 1.4; Singh, 1973; Banerjee, 1974). Arangi shale is overlain by Kajrahat Limestone which is made with calcium carbonate and dolomite with a well-known stromatolite horizon. The depositional environment is tidal flat or may be shallow marine product (Singh 1973; Banerjee 1974; Banerjee 1997; Bose et al. 2001; Sarkar and Banerjee, 2020). This limestone is showing a shallowing up trend from its bottom to top. The Porcellanite formation deposited over the Kajrahat Limestone and compact with pyroclastic flow, silicified shale, surge deposit,

elucidated as shallow marine deposit (Table 1.4) (Bose et al., 2001; Srivastava 1997; Banerjee 1997). This Pyroclastic layer gradually replaced a dark coloured shale which is the basal part of the Khenjua Formation. This sand free dark shale is contained some tuff layer alternating with this dark shale which are reworked from the previously deposited underlying Porcellanite Formation (Bose et al., 2001; Banerjee and Jeevankumar, 2005). Koldaha Shale is inferred as a product of shelf environment with some deltaic input. The Koldaha Shale gradually passes into a prominent sandstone deposition which contain few cycles of Sandstone -siltstone and shale deposition along with few storm features are also preserved within, reflecting a characteristic of Shallow marine deposition (Table 1.4) (Bose et al., 2001) but according to Sarkar et al., 2006 & 2014 the depositional environment of Chorhat sandstone has been interpreted that there is subtidal-intertidal to supratidal influence is definitely present. This Chorhat sandstone again overlain by a black shale deposition named as Rampur shale Member of Rohtas Formation, which have a sand-shale alternation at base and shale-limestone (siliciclastic-carbonate) intercalation at the top. The depositional environment specially identified as shelf environment (Table 1.4) (Bose et al., 2001 Sarkar et al., 2002a) but controversies are still there, Singh, 1973 and Banerjee, 1974 interpreted that Rampur shale is deposited under tidal flat dominated environment. The topmost succession of Rohtas Formation and last member of the Lower Vindhyan is the Rohtas Limestone, again interpreted as shelf environment where as Banerjee et al., 2009 and Sarkar et al., 2019, suggested that presence of flat pebble and edgewise conglomerate indicate presence of gas degradation and storm surge.

Table 1.4: Depositional environment and sequence stratigraphic tract of Vindhyan Super group (modified after Bose et al., 2001 & Sarkar and Banerjee 2020)					
Group	Formation	Members	Lithology	Depositional Environment	System Track
Upper Vindhyan Group	Bhander Formation	Upper Bhander Sandstone	Well sorted sandstone with wave features, current crescents at the lower part and the upper part has very well sorted sandstone with translent cross-stratifications, adhesion ripples.	Fluvio-aeolian and marginal marine	HST
		Sirbu Shale	Sirbu shale has two different lithology. Basal part is dominating of Stromatolite and carbonate deposit. Upper part is dominating of grey shale with some sandstone layers.	Shelf-lagoon	MFS TST

		Lower	Sandstone-mudstone inter-bedding, thin conglomerate with dominating wave and storm features. Mudstone is mainly reddish in colour. Abundance of salt pseudomorphs.	Coastal playa	TST
		Bhander Limestone	Dominating in micritic, oolitic and Stromatolitic limestone with tidal-emergence features. Laterally continuous soft-sediment deformation structures.	Shallow marine	
		Ganurgarh Shale	Mudstone-sandstone inter-bedding with abundance wave and emergence features.	Chenier	
	Rewa Formation	Rewa Sandstone	Medium to well sorted sandstone with bimodal cross-stratification, mud draping at basal part and upper part consists of ill-sorted sandstone unimodal trough cross-stratifications, compound cross-stratification.	Tidal-Fluvio-aeoline	HST
		Rewa Shale	Sandstone-shale inter-beds with wave and sole features.	Shelf	MFS TST
	Kaimur Formation	Dhandrual Quartzite	Large scale cross-stratified thick sandstone with inbetween well sorted aeolian sediments.	Shelf to fluvio-aeolian	HST
		Scarp Sandstone	Well sandstone with thin mudstone, quartz rich, large scale cross-stratified.	Shelf to fluvio-aeolian	
		Bijaigarh Shale	Black shale with some intercalation of volcano-clastic sediments	Intertidal to shelf	MFS TST
		Upper Quartzite	Medium grain sandstone with the wave and tide features.	Intertidal to shelf	
		Bhagwar Shale	Reworked volcanoclastic materials.	Intertidal to shelf	
		Lower Quartzite	Sandstone with siltstone, shale in-between. Sandstone contains dominating tidal features.	Intertidal to shelf	

	Rohtas Formation	Rohtas Limestone	Black shale- limestone intercalation transit to pure limestone and dolomite deposit. The limestone contains abundant wave features.	Shelf	HST
		Rampur shale	Black Shales with few volcano-clastic layers in-between and basal part is sandstone-grey shale intercalation with few wave features followed by shale and gutter sandstone.	Shelf	MFS TST
Lower Vindhyan Group	Khenjua Formation	Chorhat Sandstone	Well sorted sandstone and mudstone inter-beds. Sandstone is full of wave features and MISS structures. Mudstone is reddish in colour.	Shallow marine	HST
		Koldaha Shale	Sandstone-shale inter-beds with waves and sole features. Local poorly sorted sandstone intervals with emergence features.	Shelf, deltaic fluvial	MFS TST
	Porcellinite		Volcanic ash, pyroclastic flow/ surge deposits, locally large bombs.	Shallow marine	
	Kajrahat formation	Kajrahat Limestone	Dominating in dolomitic limestone with different sets of Stromatolite and desiccation cracks on top. Few volcano-clastic and siliciclastic beds have also interbedded in-between.	Subtidal to peritidal	HST
		Arangi Shale	Composed of grey shales.	shelf	MFS
	Deoland		Well sorted sandstone, bimodal-bipolar cross-stratification. Local patches of conglomerate. It has a fining upward deposition.	Shallow Shelf	TST

The Upper Vindhyan group have three formations those are Kaimur, Rewa and Bhander. Kaimur Formation have two major divisions like Upper Kaimur and Lower Kaimur. Lower Kaimur have a variation in lithology, like the lower part is dominated by sandstone with some shale deposition also present and identified as tidal bar deposit (Table 1.4) (Chakraborty and Bose, 1990). This sandstone dominated member gradually passes into Bhagwar Shale also

known as Silicified Shale. At the SW part of this Member is dominated by volcanoclastic sediments and NE part is composed of sandstone-shale intercalation. This silicified shale is overlain by sandstone dominated Upper quartzite followed by dark carbonaceous Bijoygarh Shale Which is restricted only NE parts of the basin (Chakraborty, 1993, 1995, 2006; Bose et al., 2001). This dark shale is referred to as a product of deep offshore of the basin (Table 1.4) (Chakraborty, 1993, 1995; Banerjee et al., 2006; Sur et al., 2006; Schieber et al., 2007). Bijoygarh Shale is the uppermost unit of the Lower Kaimur. Upper Kaimur starts with a thick sandstone deposited in a shallow shelf environment named as Scrap Sandstone and then it grades into another sandstone deposit i.e., Dhandraul Quartzite, which is influenced by fluvial to aeolian environment (Table 1.4) (Chakraborty, 1993; Bose et al., 2001). Lithologic characteristics of the Upper Kaimur reflects that, both the Scrap Sandstone and Dhandraul Quartzite are tidally influence fluvial Channel deposit (Quasim et al., 2019). The Rewa Formation starts with a distinctive coarse granular horizon, identified as transgressive lag blanketed just above the Kaimur formation (Bose et al., 2001). As with the initiation of the transgressive cycle the succession is becoming the fining upward greenish grey coloured shale with some storm originated sandstone deposited in between the Shale, known as Rewa Shale which is deposited in storm dominated shelf environment (Table 1.4) (Chakraborty et al., 1996; Bose et al., 2001; Chakraborty and Sarkar, 2005; Sarkar and Banerjee, 2020;). Kimberlite pipes and few volcanogenic horizons are identified within upper part of the Rewa Shale from which coarsening upward cycles were starts to deposit (Chakraborty et al., 1996; Bose et al., 2001). These coarsening upward cycles were grades into Rewa Sandstone indicating a shallow marine-tidal flat environment to fluvio-aeolian transition (Bose and Chakraborty, 1994; Bose et al., 2001). The Bhander Formation is uppermost formation of the Upper Vindhyan Group as well as whole Vindhyan Basin. This Bhander Formation has five distinct units such as Ganurgarh Shale, Bhander Limestone, Lower Bhander sandstone, Sirbu Shale and Upper Bhander Sandstone. Ganurgarh Shale commonly show alternation of sandstone and reddish-grey coloured shale; represents a chenier environment (Chakraborty et al., 1998). This shale is gradually grades to a carbonate depositional environment i.e., shallow marine with open ramp setting and inculcated lagoonal influences. The unit named as Bhander Limestone famous for Stromatolite deposition (Sarkar et al., 1996; Chakraborty et al., 1998; Bose et al., 2001, Sarkar and Banerjee, 2020). Bhander Limestone overlain by Lower Bhander Sandstone consists of red mudstone, glauconite horizons, plethora of salt pseudomorphs are found at the sandstone beds identified as coastal playa depositional setting (Table 1.4; Bose and Chaudhuri, 1990; Chakraborty et al., 1998; Bose et al., 2001; Sarkar and Banerjee, 2020; Mandal et al., 2022)

this Bhandar sandstone again covered by Sirbu shale which is a product of lagoonal environment at the bottom and storm dominated shelf environment at the top (Singh, 1973; Bose et al., 2001, Sarkar et al., 2002). Upper Bhandar sandstone deposited over the Sirbu Shale represents a terrestrial deposit (Bose et al., 2001; Sarkar et al., 2004, 2011; Sarkar and Banerjee, 2020).

1.2.5: Sequence Stratigraphic scenario of the Vindhyan Basin:

Previous workers stated about the twofold classification of Vindhyan Supergroup, where an unconformity divided the whole Vindhyan Supergroup into two groups. Detailed sequence stratigraphic framework of Vindhyan Basin has been represented in Bose et al., 2001, 2015 and Banerjee et al., 2006. Several TST (Transgressive System Tract) and HST (High Strand System Tract) were identified in both the Upper and Lower Vindhyan Groups and each of the group is again flourished by three maximum flooding surfaces (MFS).

The Lower Vindhyan comprises five formations from bottom to top these known as Deoland, Kajrahat, Porcellanite, Khenjua and Rohtas. A glacial conglomerate deposit is present at the base of Deoland formation (Dubey and Chaudhary 1952; Chaudhury 1953; Mathur 1954, 1960, 1981; Ahmad 1955, 1958). Shelf originated Arangi shale is overlies on the Deoland formation which belongs to a transgressive system tract (TST) (Table 1.4; Van Wagoner et al. 1990; Sonnenfeld 1996; Catuneanu 2006) and underlain by Kajrahat limestone which is stromatolitic limestone and it is a coarsening upward HST sequence (High Stand System Tract) (Sarg 1988; Van Wagoner et al. 1990; Catuneanu 2006). Arangi Shale is grey in colour, demarcating the maximum flooding surface (MFS) at its top (Galloway 1990; Sangree et al. 1990). The ~400m thick Porcellanite formation is deposited over this HST sequence Kajrahat formation (i.e., Kajrahat limestone). Porcellanite formation is composed with pyroclastic flow, volcanic ash, surge deposit and tuffaceous sediment (Banerjee 1997; Roy and Banerjee 2002). Porcellanite formation itself indicating a TST sequence (Transgressive system tract) followed by Koldaha Shale which is a thick black shale deposition of lower part of the Khenjua formation representing a rapid transgression. Top of this Koldaha shale Member is again marked as MFS and termination of the underlying TST sequence (Table 1.4; Galloway 1990; Sangree et al. 1990; Bose et al. 1997, 2001; Banerjee and Jeevankumar 2005; Samanta et al., 2016). Koldaha Shale grades into coarsening up Chorhat Sandstone, which is the initiation of another HST sequence composed with few storms generated sandstone bed proliferated by microbial mat related sedimentary structures (Seilacher et al. 1998; Sarkar et al. 2006). This Chorhat sandstone is

gradually grades into off-shore originated Rampur Shale indicates deposition of another TST sequence. Top part of the Rampur shale is black which is indicating the MFS (Table 1.4; Sarkar et al. 2002a; Banerjee et al., 2006a). After the Rampur shale of Rohtas formation another HST is starts to deposit known as Rohtas Limestone, reflects a progradational sequence (Sarkar et al., 2019).

There is a sharp unconformity in between the lower Vindhyan Semri group and Upper Vindhyan group. This younger part of the Vindhyan Basin comprises three formations, named as Kaimur, Rewa and Bhandar. There is a definite trend that the lower part of the formations is shale dominated and gradually the shale grades into coarsening upward sandstone. Due to occurrence of basin subsidence in landward direction, Lower Kaimur sandstone recognized as a fining upward TST sequence and followed by a black shale deposition named as Bijoygarh Shale which indicated the MFS at its top (Table 1.4; Bose et al. 2001; Banerjee et al. 2006a). This Bijoygarh Shale again overlain by a shallow shelf sandstone i.e., Upper Kaimur sandstone demarcating a sharp regression. Marine to terrestrial transition is another important factor identified at this level. A major transgressive lag is present at the base of the Rewa formation and gradually transgression starts with the deposition of Rewa Shale which is greenish-black in colour, organic rich and intervened by thin tuffaceous layers identified as a MFS (Table 1.4). After the condensed zone the Rewa Shale comprises an aggradation sequence followed by rapid progradational sequence i.e., Rewa Sandstone, which is a HST sequence (Table 1.4). This progradational sequence is followed by Ganurgarh Shale, Bhandar Limestone, Lower Bhandar sandstone and Shirbu Shale together build a TST sequence. The lower part of the Shirbu Shale is black in colour recognized as a condensed zone and marked the MFS. After the black shale portion of the Shirbu shale, a coarsening upward sequence started to develop altering shale with Sandstone and finally grades into Upper Bhandar Sandstone (Sarkar and Banerjee, 2020).

1.2.6: *Biotic treasures of Vindhyan:*

The Vindhyan sediments are proliferated with microbiota along with microbial impressions. Biogenic impression are assets of nature specially when the sediment is from Mesoproterozoic time. The biotic impressions delicately preserved within the sandstone, shale and limestone units. The fossils reported from Vindhyan are basically microfossils, organo-sedimentary structures, carbonaceous fossils, Ediacaran fossils, trace and body fossils of metazoans. Palaeobiological remnant of the Vindhyan Supergroup belong to separate categories, viz. stromatolites, megascopic carbonaceous remains, microfossils, small shelly fossil, pseudo-

Ediacaran fossils and microbially induced sedimentary structures (MISS). Stromatolite is a type of microbialite signifies the interaction between benthic microbial mat community and detrital or chemical sediment. These stromatolites are used for bio stratigraphic co-relation by several bio-stratigraphers (Table 1.5; Raaben 1969, 2005; Kumar 1978, 1980; Raha and Sastri 1982). A variety of carbonaceous fossils reported from Vindhyan Supergroup. The fossils are basically identified from the Rohtas Formation and its equivalent in western Vindhyan, the Suket Shale (Jones 1909). This discovery drew the attention of many researchers, and the conflicting ideas about the affinity of these fossils continued for many decades (Table 1.6). Apart from the mega-fossils, few microfossils are also identified from argillaceous and carbonate rocks (Venkatachala et al. 1996). Cyanobacteria were the most prominent microfossils reported therein and eukaryotic acritarch also present there but in a very small quantity. These microfossils are abundantly present both in Upper and Lower Vindhyan groups which covers Meso-Neoproterozoic time period. Eventually these small sized microbiota gives variable age (Srivastava 1971; Sharma and Sergeev 2004). These fossils are sometimes distracted the scientist about their origin whether it is biologic or non-biologic (Table 1.7; Schopf 1975, 2004; Cloud 1976; Schopf and Walter 1983; Brasier et al. 2002). The Vindhyan supergroup is well known for preservation for Ediacaran fossils. A number of Ediacaran fossils were reported from Porcellanite formation, Bhandar Formation (Kathal et al., 2000; Williams and Schmidt, 2003; De, 2003). Various trace and body fossils of metazoans were also reported from Vindhyan Basin. Basically, these features are commonly preserved within the ripple trough (Kumar 1978; Kulkarni and Borkar 1996a). At Chitrakut area, small shelly fossils reported from the phosphoritic stromatolites dolomite in the basal part of the Vindhyan Supergroup. Bengtson et al. (2017, 2009) considered the fossils as the earliest known crown group filamentous and coccoid cyanobacteria and eukaryotic algae. After the invention of metazoans trace fossil from the Kheinjua Formation, a window opened for new researchers of Precambrian palaeobiology. (Sarkar et al., 1996; Seilacher et al., 1998; Rasmussen et al. 2002, 2004). The biogenic discoveries from the Chorhat Sandstone i.e., presence of fossils and early metazoan raised a controversial issue from the beginning (Conway Morris 2000, 2003; Knoll 2003; Fedonkin 2003; Peterson et al. 2005; Seilacher 2007). The Vindhyan Supergroup is famous for excellent preservation of exquisite microbial mat related structures (MRS) on siliciclastic in all over the world (Sarkar et al. 2004, 2005, 2006, 2014b, 2016; Banerjee and Jeevankumar 2005; Banerjee et al. 2006a, 2010, 2014; Sarkar and Banerjee, 2007; Schieber et al. 2007; Eriksson et al. 2010). The best preservation of MRS or MISS (Microbial mat Related structures or Microbial mat induced structure) has been found in the Chorhat Sandstone and the Upper Bhandar Sandstone which is dominantly known as shallow

subtidal to supratidal environment (Sarkar et al. 2006, 2016; Bose et al. 2007; Schieber et al. 2007).

Table 1.5: Stromatolite from the different formations /members of Vindhyan Supergroup (modified after Sarkar and Banerjee, 2020)

Stromatolites	Age	Authors	Name of the Members
Colleniabiactalica, Colleniacolumnari, Colleniaburiatica, Colleniabaicalica	Middle to upper Riphean	Prasad and Ramaswamy (1980); Prasad (1984)	Sirbu Shale
Colleniasymmetrica, Baicaliabaicalica, Maihariamaiharensis, Colleniaundusa, Tungussia, Boxonia	Upper Riphean (900-600 Ma)	Rao et al. (1977); Kumar (1967a); Sarkar (1974); Kumar (1982)	Bhander Limestone
Colleniakusiensis, Colleniacolumnaris, Conophytoncylindricus, Colleniabaicalica	Middle Riphean	Sharma (1996); Singh and Banerjee (1980)	Rohtas Limestone
Collenia cylindrical, Colonellacolumnaris, Collenioclappii	Lower Riphean	Kumar (1976b)	Koldaha Shale
Conophytoncylindricus, Colleniakusiensis, Cryptozonoccidentale, Colonnella sp., Colleniafrequense, Conophytoninclinatum, Kussiellakusiensis, Kussiella, Colonnella	Lower Riphean	Prasad (1980) Prasad (1984) Kumar (1982) Kumar and Gupta (2002)	Kajrahat limestone

Table-1.6. Carbonaceous Mega-fossils reported from the different formation/Member of Vindhyan Supergroup (modified after Sarkar and Banerjee, 2020).

Stratigraphic horizon	Carbonaceous mega-fossils	Authors	Remarks
Sirbu Shale	Fermoria like structures	Misra and Awasthi (1962)	Uncertain
Bhander Limestone and Sirbu shale	Chuariacircularis, Tawuiadalensis	Kumar and Srivastava (1997)	
Rewa Shale	Chuariacircularis, Tawuiadalensis	Rai et al. (1997), Srivastava (2004)	
Suket Shale	Vidhyanellajonesi, Fermoria minima	Sahni (1936)	Revised as Chuariacircularis
Suket Shale	Circular to semi ovoid carbonaceous disc	Misra and Dube (1952)	Chuariacircularis
Suket Shale	Circular form Fermoriaspbrodely ovoid form	Misra (1969)	Chuariacircularis
Suket Shale	Disc-like remain type 1-6	Maithy and Shukla (1977)	Chuariacircularis
Suket Shale	Vavosphaeridiumreticulatum, Vavosphaeridiumvindhyanesi, Kildinellasuketensis, Tasmanitesvindhyanesis	Maithy and Shukla (1977)	Revised as Chuariacircularis
Suket Shale	Chuariacircularis, Tawuiasuketensis, Vindhyaniajonesii	Marthur (1982)	Vindhyaniajonesii is similar to Krishnania acuminate
Suket Shale	Chuariacircularis, Chuariafermorei, Twauiasuketenis, Tawuiarampuranesis	Marthur (1982)	Revised as Chuariacircularis and Tawuiadalensis
Suket Shale	Chauriacircularis	Maithy and Shukla (1984)	

Suket Shale	Tyrasotaenia sp.	Shukla and Sharma (1990)	
Suket shale-Rampur Shale	Carbonaceous disc described as Obolella/ Operculum of Hyolithella	Jones (1909)	Revised as Chuariacircularis
Suket shale-Rampur Shale	Fermoria minima, Fermoria granulosa, Fermoriacapsella, Protobolella jonesi described primitive brachiopod or eurypterids	Chapmann (1935)	Revised as Chuariacircularis
Rohtas Limestone	Spiral impression described as impression of coiled worm	Beer (1919)	Revised as Grypaniaspiralis
Rohtas Limestone	Carbonaceous discs and algal dust	Misra and Bhatnagar (1950)	Revised as Amjhorearohatasae
Rohtas Limestone	Katniasinghi classified under Annelida	Tandon and Kumar (1977)	Similar to Grypania
Rohtas Limestone	Chuaria minima, Tawuadalensis	Maithy and Babu (1988)	
Rohtas Limestone	Krishnania acuminate, Krishnani multistriata	Maithy (1991)	Krishnania possibly represents oldest benthic algal forms
Rohtas Limestone	Chuariacircularis, Grypania sp.	Kumar (1995)	
Rohtas Limestone	Chuariacircularis, chuariagigantia, chuariamelanocentrics, Grypaniaspiralis, Grapania sp., Phylloniabistaria	Rai and Gautam (1998)	Chuariagigantia and Chuariamelanocentric are the synonymy of Chuariacircularis
Rohtas limestone	Chuariacircularis, Tawuadalensis	Srivastava (2004)	

Table-1.7: Carbonaceous Microfossil from Vindhyan Supergroup (Modified after Sarkar and Banerjee, 2020)

Formation	Member	Evidence	Authors	Proposed age
Bhander	Upper Bhander Sandstone			
	Sirbu Shale	<i>Archaeorestis sp.</i> , <i>Spaerophucuspervum</i> , <i>Myxoccoidespsilata</i> , <i>Protosphaeridiumdesum</i> ,	Maithy and Mandal (1983)	Late Proterozoic
			Maithy and Meena (1989)	Late Proterozoic
	Lower Bhander Sandstone			
	Bhander Limestone	<i>Biocatenoidessphaerula</i> , <i>Sphaerophycusparvum</i>	Maithy and Gupta (1983)	Late Proterozoic
	Ganurgarh Shale			
Rewa	Rewa Sandstone			
	Rewa Shale	<i>Myxoccoidespsilata</i> , <i>Nanococcus vulgaris</i>	Maithy and Mandal (1983)	Late proterozoic
Kaimur				
Rohtas	Rohtas Limestone	<i>Myxoccoides globose</i> , <i>Palaeonacystissuketensis</i>	Maithy and Shukla (1977)	Late Riphean
		<i>Misraeapsilata</i>	Maithy and Babu (1988)	1200-940 Ma
		<i>Leisphaeridiadensum</i>	Nautiyal (1986)	1000-900 Ma
Kheinjua	Chorhat sandstone	<i>Eomycetopsis septate</i>		
	Koldaha Shale (Fawn Limestone)	<i>Sphaerophycusparvum</i> , <i>Bontophysalisbelcherensis</i> , <i>Oscillatorioppsisbreviconvera</i>	Kumar and Srivastava (1995)	1200 Ma
		<i>Myxoccoides minor</i> ,	McMena min et al. (1983)	1200 Ma

		<i>Tetraphycus congregates</i>		
		<i>Kildinellaaff.</i>	Nautiyal (1983)	1200-900 Ma
Porcellinite				
Kajrahat		<i>Palaeoanacystissuketensis</i>	Nautiyal (1983)	1200-900 Ma

1.3: Geology of the studied Succession

The present study is based on Rampur Shale Member (maximum thickness ca. 85 m) belongs to the Rohtas Formation of the Lower Vindhyan/Semri Group and is best exposed just at the south and south-east of the Maihar town, Madhya Pradesh, Central India (Sarkar et al., 2006, 2002) (Fig. 1.5) named as Bihara Kola (24° 3' 32.28"N, 80° 36' 36.12"E), Kudri Village (24° 7' 52.7" N, 81° 00' 43.05"E) and Rampur Village (24° 20' 32.48" N, 81° 28' 33.52" E) (Fig. 1.6). Overall, the Rampur Shale is a fining-up TST sequence deposited in shallow marine environments. From the base, the succession contains a retrogradational sandstone overlain by sand /silt and shale alternation and black shale, followed by a grey shale at the top of the sequence (Mandal et al., 2024; Mondal et al., 2022) (Fig. 1.5). It is overlying the siliciclastic Chorhat Sandstone Member of the Khenjua Formation and underlain by the carbonate-dominated Rohtas Limestone Member of the Rohtas Formation (Fig. 1.1). Both bounding members are progradational, forming HST sequences (Bose et al., 2001). A few pyroclastic layers are present at different levels of the sedimentary succession of Rampur Shale Member, dated ca. 1.6 Ga (Rasmussen et al., 2002). Pumice-bearing volcanic clasts, devitrified glass, quenching cracks, and abundant silica cement bear the signature of intermittent underwater volcanic eruption during its deposition (Mondal et al., 2022) (Fig. 1.5). The studied glauconitic horizons are closely associated with these volcanoclastic layers (Fig. 1.5).

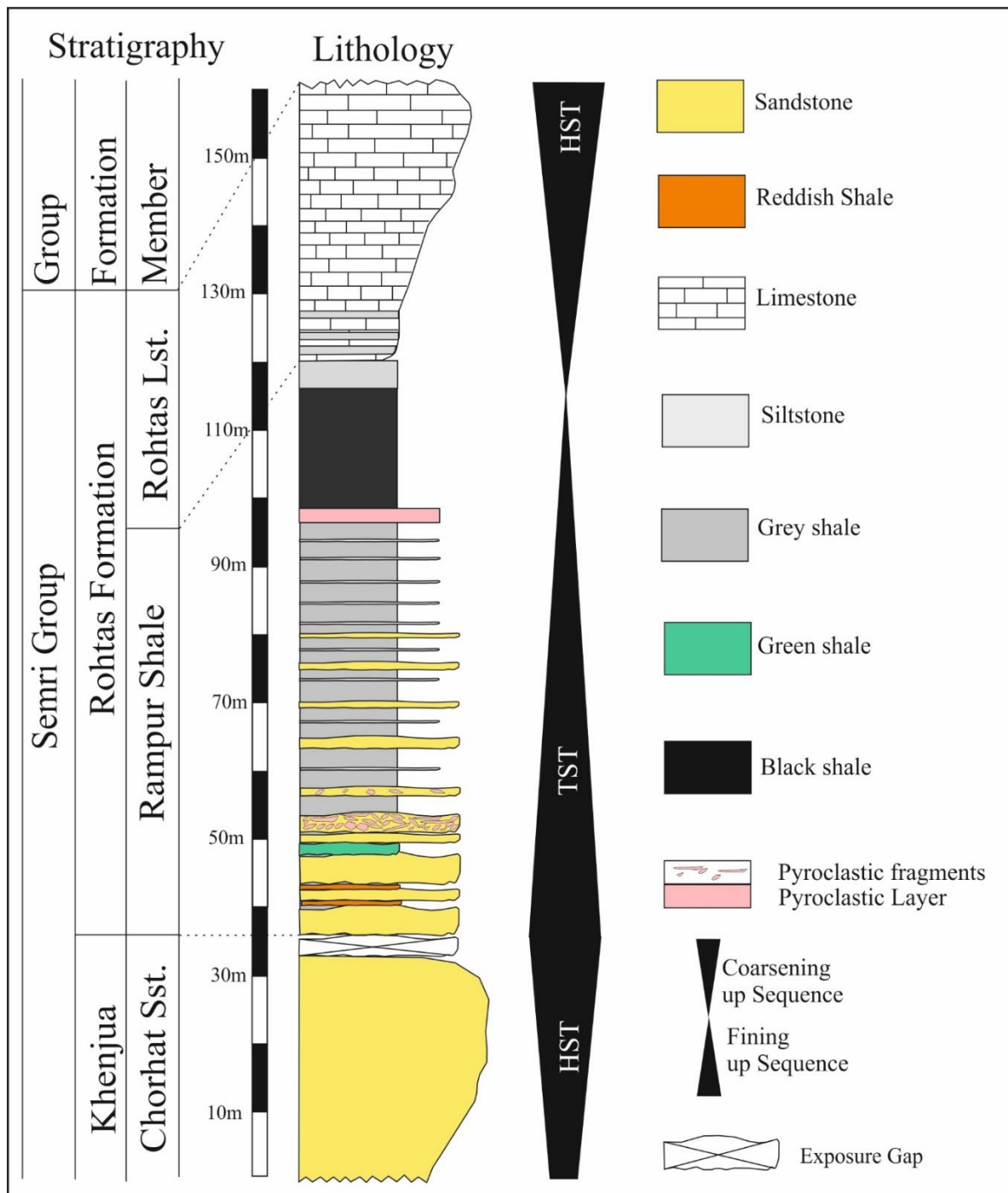


Fig.1.5: Lithostratigraphic position of Rampur shale. Note the underlying Chorhat sandstone and overlying Rohtas Limestone.

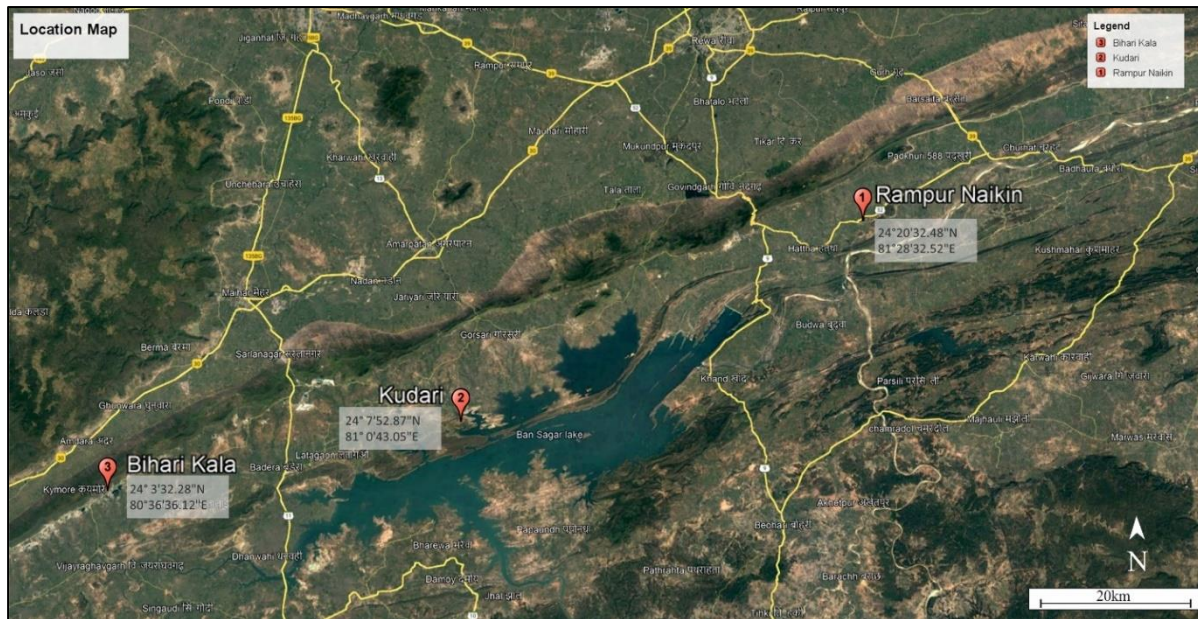


Fig.1.6: Location map for the studied area.

The Black Shale within the Rampur Shale Member in central India is approximately 10m thick and encased by a retrogradational sandstone and sandy/silty shale part below and topped by a 3 m thick grey coloured shale (Fig. 1.5). Glauconite in the enveloping sediment and omnipresent wave imprints in the underlying sandy/silty shale part of the Rampur Shale prompts the marine origin of the Black Shale (Tribovillard et al., 2023). The Rampur shale as a whole is sandwiched between the entirely siliciclastic Kheinjua Formation below and the entirely carbonate Rohtas Limestone (RL) Member above. This entire sedimentary package rests on a ~250m thick Porcellanite Formation largely made of pyroclastic deposits. Pyroclastic deposits have also been recorded within the Rampur Shale itself at two different levels (Fig. 1.5). The entire sedimentary package of Rampur Shale Member addressed here constitutes the upper part of the Semri/Lower Vindhyan Group, overlain by the Rohtas Limestone (RL) which is terminated by an unconformity (Fig.1.5; Mandal et al., 2019). Both the lower and the upper bounding members, namely, the Chorhat Sandstone Member of the Kheinjua Formation and the Rohtas Limestone Member, respectively are progradational sequence (Bose et al., 2001). Between them, the fining-upwards Rampur Shale Member is a retrogradational sequence, represents a Transgressive System Tract (TST) (Bose et al., 2001). In the background of the deposition of the entire Semri Group within an intrinsic rift setting, the emplacement of the Rampur Shale on top of the Chorhat Sandstone is attributed to basin subsidence (Bose et al., 2001). Since the lithologic change in the succession is gradual and short-ranged, the rate of subsidence is envisaged to be generally slow. Small slide planes in plenty, local bipolarity in

their orientation, slicken-lines on them; micro grabens and horsts document the mechanism of slow accommodation space creation (Discussed later). The Black Shale, however, bears fine planar laminae, evincing an overall slow rate of sedimentation.

1.4: Objectives of the Work

The objectives of the thesis is to reveal the sedimentological and geochemical oddities encrypted within the Meso-Proterozoic Rampur Shale and argue with the believe that the Meso-Proterozoic time which is known as “Boring Billion” is actually not so boring. Detailed field work was carried out in different exposers of the Rampur Shale scattered in and around Maihar Town, Madhya Pradesh. Rampur Shale is the lower part/member of the Rohtas Formation recorded as sandwiched between two HST sequences like underlying Chorhat Sandstone of Khenjua Formation and overlain by Rohtas Limestone of Rohtas Formation. Rampur Shale Member representing an overall fining upward TST sequence. Based on the sand: shale ratio the Rampur Shale succession is divided into three segments. The lower Segment of the Rampur Shale Member is made up with sand and occasional interference of shale. This lower segment is a bit sandy and constituted by sandstone with different body geometry, primary sedimentary structures, sole features. The Middle segment is varying in sand: shale ratio; shale proportion is increasing at the upward direction. This segment is consisting of few coarsening upward Para sequences with increase in shale proportion upwardly. The Para sequences are containing sand-silt and shale alteration and ended with a sandstone deposit. Glauconites are unanimously present within the sandstones, silts and shales; preferably within the sandstone. The upper segment is totally sand free section, dominated by black shale followed by grey shale. At this shale dominated part glauconite are not so common, rarely present within the topmost grey shale part. After the grey shale deposition Rampur Shale Member is grades into Overlying Rohtas Limestone. This is the overall scenario of the Rampur Shale succession. Based on this study this thesis aims to,

- Detailed Facies Classification performed to reconstruct the palaeogeography and Sequence Stratigraphic framework of Rampur Shale.
- Primary sedimentary structures and sand: shale ratio successively studied and measured to identify the Para sequences resided within the middle segment.
- Detailed Geochemical analyses were conducted mostly on the shales because they provide better averaging of geochemical properties of the sediments to figure out the Provenance, palaeoredox, Palaeo weathering and palaeoclimatic scenario.

- Glauconites bearing horizon took sole attention as these minerals have applicability to record palaeoceanographic conditions. To execute this study, detailed petrography, XRD analysis, EPMA analysis followed by various geochemical plots for glauconite composition.
- Compare the Rampur Glauconite with other glauconites from different formations of Upper and Lower Vindhyan formations.
- Special attention was to focus on Black shale dominated part and their global distribution to reconstruct the super continental reorganization.
- Detailed microscopic and ultramicroscopic study of the shale dominated Part were performed to highlighting the biota content within the black shale reconcile the past environment like provenance, palaeoweathering, palaeoclimate, palaeoredox scenario of the black shale deposition.
- Few thin turbidite layers were observed within the topmost grey shale. The geochemical analysis helps to reveal the Palaeoenvironmental Dynamics in a Mesoproterozoic Epicontinental Sea.

1.5: Methodology and Instrumentation

This research work is constructed by extensive field work followed by geochemical analysis of the collected samples. The present study was conducted on the best-preserved outcrop sections of Rampur Shale Member in and around the Bihara Kola (location L1 in Fig. 1a), Kudri (Location L2 in Fig. 1a) and Rampur (Location L3 in Fig. 1a) villages spreading over 130 km (Fig. 1a). The essential equipments are used to facilitate this field work are, GPS (MAP76CSX with PC interface cable and accessories), toposheets of the studied area (toposheet no.), geological hammer (East Wing, USA made, length 35 cm), chisel, hand lens and pocket lens, magnet, diagonal scale, knife, permanent rock marker, measuring tape, clinometers, camera, rock cleaning brush, acid (for carbonate testing) etc. Numerous rock samples were collected for petrographic and geochemical analysis. For lower segment the samples were collected by observing the lithofacies following Para sequence packages and at the upper part shale dominated part samples collected at approximately 50 cm intervals. Depending upon the requirements, for thick succession samples were collected in both vertical and lateral variation. During sample collection, exposed surficial part of the outcrops were removed to get the fresh and unaltered samples for geochemical analysis. Friable Shale samples were handled with extra care during collection as well as transportation. Samples were delicately wrapped in aluminum foil to avoid contamination and oxidation for geochemical analysis then covered with bubble

wrap to avoid any type of damage followed by zipped plastic satchel for petrographic study under microscope as well as geochemical analysis.

1.5.1: Petrographic Study:

Near about 110-120 thin sections were prepared from the collected rock samples. Large thin sections for petrographic study and probe slides were prepared from the collected rock samples. Buehler Vacuum Impregnation Unit was utilized for consolidation of soft and friable samples for preparing thin sections. Analysis of field data, petrography was executed in the Sedimentology Laboratory, Department of Geological Sciences, Jadavpur University. Petrographic studies were carried out on thin sections using a Leica DM 2700P polarizing microscope, and photomicrographs were taken using a Leica MC 170 HD camera attached to the microscope, housed at the Sedimentology Lab of Jadavpur University, Kolkata. Computers with higher configurations with dual setup attached with HD camera facilitated the work enormously. Modal proportions and grain-size analysis were performed in computerized transmitted light petrographic microscope (Leica DM LP with 1.6X, 4X, 10X, 20X 50X & 100X magnifications specially attached Leica DC 320 image analyzer and point counting system with CVS PETROG software) placed in the Sedimentology Laboratory and facilitated the work enormously.

1.5.2: Instrument and software used for Geochemical analysis:

To study the fine-grained samples and any specific mineral, geochemical analysis is compulsory. Here for this research work, XRD were performed in the Department of Geological Sciences and of Jadavpur University, Kolkata. XRF was performed in NCESS, South India. Samples were analyzed at IISER Kolkata and Department of Geological Sciences and of Jadavpur University, Kolkata for SEM and EDAX, IIT Bombay for major element oxide concentration (EPMA), IIT Kanpur for REE and trace element concentration of the. Systematically collected and processed samples of rock specimens along with glauconites went through different types of geochemical analysis in different national and international academic institutions and international professional laboratories. Vertical litho-logs, different types of maps, models, rose-diagrams, figures and sketches and geochemical plots were erected by using Computer software like Adobe Photoshop CS4, CorelDraw X7, Geo Rose, Microsoft Office, GCD toolkit and Google Earth were used for these reconstructions and data processing. All the instruments specifications and analytical processes are described below:

A: X-Ray Diffraction analysis (XRD):

Whole rock powder sample (<63 μm grain size) is needed for X-Ray Diffraction (XRD) study. The analysis was performed at the Jadavpur University, Kolkata using Malvern PANalytical X'pert Pro with Cu K α radiation operating at 40 kV 40 mA and utilizing a flat sample stage and theta-theta goniometer setup (goniometer model PW3050/60). The sample was analyzed at room temperature, and the diffraction patterns were first recorded for 5–70° 2 θ with a step size of 0.0150° 2 θ and a scan speed of 1sec/step, and again on the same sample, for 5–28° 2 θ and 55–65° 2 θ ranges, respectively.

B. X-Ray Fluorescence analysis (XRF):

The samples were analyzed with a Bruker model S8 Tiger and S4 Pioneer sequential wavelength dispersive X-ray spectrometers in the sample preparation laboratory of the National Centre for Earth Science Studies (NCESS), India. The analyses were performed on the whole rock samples collected from all of the facies systematically. The powdered whole rock samples were analyzed for major oxides with Bruker model S8 Tiger and S4 Pioneer sequential wavelength-dispersive X-ray spectrometers in the X-ray Fluorescence laboratory of the National Centre for Earth Science Studies (NCESS), India. One gram of the powdered sample was mixed with 5 grams of flux (LiT/LiM/LiBR 49.75/49.75/0.50, Pure) in a platinum crucible with the help of a Katanax X-300 X-Fluxer triple station fusion instrument (each flux was melted at 1050° C) in the sample preparation laboratory of the NCESS, India. The standards used during the XRF analysis are MESS3 and JSD-2. The major oxide weight percentages recalculated by setting aside the LOI values from the dataset. However, whenever a single element is mentioned in thesis, its content is expressed in its atomic weight percentage, calculated by dividing the oxide concentration by the molar mass of the oxide and then multiplying it by the molar mass of the element.

C. Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Spectrometer (EDS) Study:

The micro-textural study of the Shale and Glauconite was performed on the on platinum-coated (sputter coating, ~20 nm thickness) samples using a Carl Zeiss Evo-18 Scanning Electron Microscope (SEM) housed at Department of Geological Sciences Jadavpur University, Kolkata. The carbon concentrations within different geometric forms of microbial mat were determined under an accelerating voltage of 10kV using a tungsten filament as the electron gun in Energy Dispersive X-ray Spectrometry (EDS) attached to the scanning electron

microscope. The magnification range of the SEM spans from 5X to 300X, extending up to 49 KX, with a resolution approaching 2 nanometres. The probe current using here 500mA to 1250mA. The instrument offers operation in two distinct image modes: Secondary Electron Image and Backscattered Electron Image. The EDS is connected with the same SEM. For Energy Dispersive X-Ray platinum coated samples were analyzed.

D: Confocal Microscopy:

Confocal Laser Scanning Microscopy (CLSM) is also used for advanced image analysis. This technology is started to spread rapidly from the 1980's. CLSM can produce 3D image of the specimen studied at high spatial resolution (0.2 μm). For this purpose, thin sections should be prepared in a different way. Sample must be optically more or less translucent. Thickness of the sample should be 150-200 μm . Specimens were analyzed in unpolished petrographic thin sections (finished by a slurry of 600 mesh carborundum powder) and Image acquired by 60X oil immersion objective (numerical aperture 1.4), covered by a 1 μm thick veneer of type FF, fluorescence free, microscopic immersion oil (Schopf et al, 2016). CLSM analysis was done at IICB, Kolkata India, Olympus Fluoview 300 confocal laser scanning microscope system equipped with two "Melles Griot" lasers 1) 488nm 200mW output argon-ion laser 2) 633nm 10mW output helium-neon laser were used in this purpose.

E: Inductively Coupled Plasma Mass Spectrometry (ICP-MS):

Trace and Rare Earth element concentration analyses were performed using Approximately 0.05 g of the sampler powder was first digested in pre-cleaned Teflon beakers (Savillex) at 130 ± 5 °C using a 4 mL mixture of concentrated HF (1 part), concentrated HCl (1 part), and concentrated HNO₃ (2 parts) for 48 h. The acid was then slowly evaporated at 80 ± 5 °C, and again, the samples were redissolved in 3 mL of Aqua Regia acid (2 mL of concentrated HNO₃+1 mL of concentrated HCl). Aqua Regia was fluxed for 24 h. After Aqua Regia digestion step, the samples were dried and re-dissolved in 2% HNO₃. The acid digestion steps were only repeated when digestion was incomplete. For all analytical work, trace-element grade pure acid and 18.2 M Ω cm water from a Millipore water purification system was used. Pure acids were produced by sub-boiling distillation in the Department of Earth Sciences using the Cupola Still system from Pico Trace. Trace-element concentrations were determined at 500 ppm total dissolved solid solutions, whereas for the REEs, it was determined at ~2000 ppm total dissolved solid solutions. Three procedural blanks and reference materials SBC-1 (shale standard, USGS) and AGV-2 (Andesite, USGS) were also digested following the same

procedures. The blanks were analyzed to quantify the total procedural blank, whereas SBC-1 and AGV-2 were analyzed as an unknown to assess the data quality. A 10 µg/g multi-element standard solution from Sigma Aldrich was diluted to 7 appropriate concentrations to construct the calibration curve (0.1 ng/g, 1 ng/g, 10 ng/g, 20 ng/g, 50 ng/g, 75 ng/g, and 100 ng/g), and trace-element concentrations were determined against the calibration curve. Since rock-matrix-matched reference materials were unavailable, all the samples and standards were spiked by ~5 ppb in solution, which was used as an internal standard. The intensities were corrected for matrix effect using as an internal standard. The trace elements concentration (~500 ppm) of total dissolved solid solutions were analyzed using an Agilent Triple Quadrupole Inductively Coupled Plasma Mass Spectrometer (QQQ-ICP-MS) with oxygen and helium as well as without them following the well-established sample preparation protocol and using the established standards (Mukherjee et al., 2019). The analysis was conducted at the Department of Earth Sciences, Indian Institute of Technology (IIT), Kanpur, India. The dataset of Average Shale was used to normalize the major and trace element data (Wedepohl, 1971).

F: Electron Probe Micro-Analysis (EPMA):

Major element concentrations of glauconite were analyzed at department of Earth Sciences, Indian Institute of Technology Bombay. Major element concentration was estimated by using thin sections with a Camera SX 5 Electron Probe Micro Analyzer, maintain following specifications: accelerating voltage 15 kV, specimen current of 40 nA and beam diameter of 1µm (peak: 10–20s and background counting: 5–10s) and analytical error less than 1%. Standards include both synthetic and mineral phases.

G. Continuous Flow Isotope Ratio Mass Spectrometer (CFIRMS):

Same powdered samples from the black shale and grey shale from top part were analyzed for $\delta^{13}\text{C}^{\text{org}}$ values (against Vienna Pee Dee Belemnite, VPDB) at the Stable Isotope Laboratory in the Birbal Sahni Institute of Palaeosciences (BSIP), Lucknow, India. The inorganic carbon was removed by treating the powdered samples with 10% HCl in an Elemental Analyzer (Flash EA 2000HT). The treated samples were filled in a tin capsule and flash combusted at ~1020°C in an oxygenated environment to convert the C of the sample into gaseous oxides (CO_2), and then it was allowed to pass successively through chromium oxide, reduced copper and silver cobaltous to purify the generated gas from the samples. The purified sample CO_2 gas is then introduced into the Continuous Flow Isotope Ratio Mass Spectrometer (CFIRMS; MAT 253) coupled with the ConFlow IV interface. Signals corresponding to masses

of 44, 45 and 46 were measured for both samples, and a reference gas and isotopic composition were calculated. Three pulses of reference CO₂ were allowed to enter the CFIRMS through a reference open split, followed by a single pulse of sample CO₂. Standards were run to check the accuracy of the CO₂ measurements. Analytical precision was monitored by running standards IAEA, CH₃ and CH₆. A routine accuracy of ±0.1 ‰ was obtained for the organic isotope values of the sample.

❖ **Formula used to represent the Geochemical data:**

1. The enrichment factors of the major and trace elements, including REEs, were calculated as $EF_{\text{element X}} = (X/Al)_{\text{sample}} / (X/Al)_{\text{Average Shale}}$ (Tribovillard et al., 2006)
2. Different palaeoweathering indices like an index of chemical alteration (CIA), index of chemical weathering (CIW), Plagioclase Alteration Index (PIA) (Nesbitt and Young., 1982; Harnois, 1988; Fedo et al., 1995, 1996; Qiu et al., 2015; Perri, 2020)
 - $CIA = [Al_2O_3 / (Al_2O_3 + CaO^* + K_2O + Na_2O)] * 100;$
 - $CIW = [Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O)] * 100;$
 - $PIA = [(Al_2O_3 - K_2O) / (Al_2O_3 + CaO^* + Na_2O - K_2O)] * 100$
3. Palaeoclimatic index like C-value (Qiu et al., 2015, Fathy et al., 2021) are calculated using the formula $C\text{-value} = \sum (Fe + Mn + Cr + Ni + V + Co) / \sum (Ca + Mg + Sr + Ba + Na)$ (Fathy et al., 2021).
4. Index for Compositional Variability (Cox et al., 1995) is calculated using the formula, $ICV = (Fe_2O_3 + K_2O + Na_2O + CaO + MgO + MnO + TiO_2) / Al_2O_3$
5. Authigenic enrichment of some trace metals were calculated as

$$TM_{\text{auth}} = TM_{\text{bulk}} - (TM/Al)_{\text{Average Shale}} * Al_{\text{bulk}} \text{ (Scott et al., 2017)}$$

1.6: Thesis Organization

The layout of the present research work follows the objectives that have been already described above section. The entire thesis has been discussed in four parts. Part I contains two chapters. The current chapter-1 demonstrates the geological information about the Vindhyan Basin such as, geology of the basin, tectonic setup, lithostratigraphy and sequence stratigraphy,

geochronology, palaeogeography and palaeoclimate along with the description of rich preservation of Vindhyan biota. Second chapter describes an overall review work on shale along with the special attention on black Shale. In Part-II, Chapter-3, I have discussed the facies classification and depositional environment, sequence development including the detailed petrographic study for better understanding. Chapter 4 displays the overall description of Rampur Shale in aspects of geochemical analysis. The special interests of the studied sedimentary units have detailed in the Part-III i.e., from chapter-5 to chapter-8. The summary and conclusion of this dissertation have been discussed in Part-IV, chapter-9.

CHAPTER: 2

BLACK SHALE RESEARCH: A DETAILED REVIEW

2.1: Introduction

Shale is the most abundant sedimentary rock on the earth surface as well as highly promising for the researchers, though less studied. This rock is characterized by its fine-grained nature dominated by mud sized particles ($<0.06\text{mm}$) with good amount of clay minerals which are mainly derived from terrigenous supply (Schieber, 2011). Shales are differentiated by its fissile texture which split them into thin layers. Shales are also known as mudstone both of them are belongs to same compositional spectrum of sedimentary rocks. Both of them are following the grain size at clay-silt boundary; many of the sedimentary rocks are identified as siltstone but also qualified for shale (Schieber, 2011). Clay is the Primary composition of this type of rocks, but may also contain varying proportions of other minerals such as quartz, calcite, and feldspar, few heavy minerals and iron oxide or sulfide minerals like iron sulfide. Shale generated by the compaction of mud and clay particles over long periods of time, in presence of low-energy environments such as deep ocean basins, lake bottoms and in flood plain. Depending upon the mineral composition, organic content (phytoplankton, zooplankton, foraminifera and primitive microbial mat along with Ediacaran fossils) and palaeogeographic conditions, shale display a coloration pallet typically exhibits various shades of gray, black, brown, red, green, or even purple. This coloration is valuable for lithostratigraphic co-relation which preferably reflects the background story about depositional scenario. Red shale is commonly found in continental environment which is reflecting an oxidized depositional condition (Berner 1971). The marine clays often have a reddish-brown tint (Ziegler and McKerrow 1975). Early studies emphasized that colour is determined by the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio rather than the total iron content (Tomlinson 1916; Pettijohn 1975). McBride (1974) corroborated this notion in a study of continental shales, observing a sequence of colours, red to yellow to green to gray; aligned with decreasing $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios (Fig. 2.1). Notably, the total iron content within shale remained relatively constant throughout. The grey to black shale is originated by slow settling of particles restricted to closed to semi-enclosed basin of shallow to deep marine and lacustrine environment requires a comparatively less oxic or anoxic condition (Tourtelot 1979; Potter et al., 1980; Bohacs et al., 2000). Under this depositional setting the accumulated organic material can outpace organic degradation rate, so that the black shale acted like a beacon to protect the delicate fossils from decomposition (Zhang 2023).

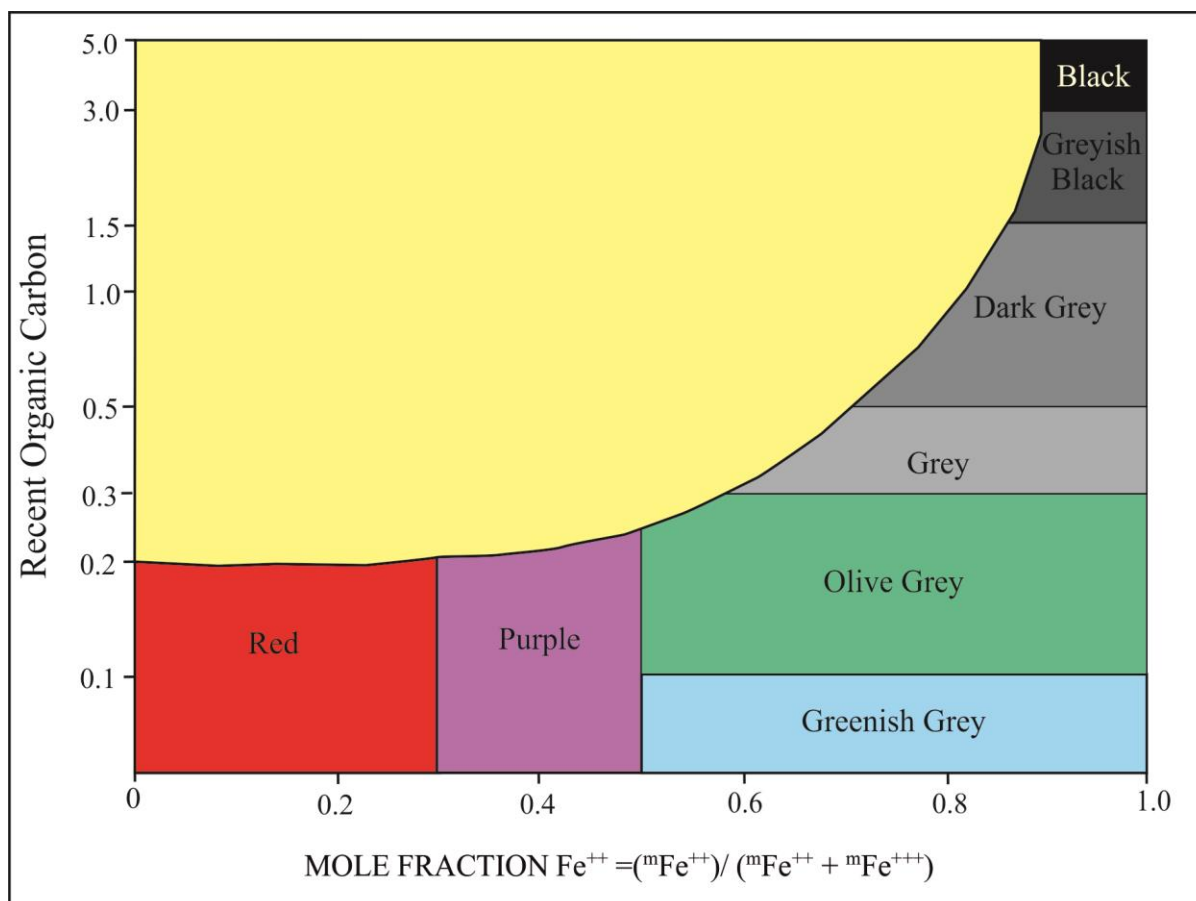


Fig. 2.1: Relationship between shale colour to carbon content and oxidation state of iron (Modified after Potter et al., 1980).

The black and grey coloured shale is again an important resource for the extraction of natural gas and oil due to its high organic carbon content, low porosity, low permeability helps it to act as a permissible source rock. The Black shale is not only confined to a specific geological period, it is found all over the world in different time periods with different composition, specific mineralogy, distinctive depositional conditions offering insights into the diverse environmental contexts of their respective time periods. Additionally, shale serves as an important source of information for geologists and palaeontologists, as it often preserves fossils and records of past environmental conditions, climate changes and evolution of life. Scientists repeatedly target the black shale deposits to reconstruct Earth's history and to understand the processes that shaped its surface. In this review work the author will focus on several factors regarding the deposition of grey to black shale. The colour of the black shale, depositional environment, nutrient supply, sedimentary structure and mineralogy, metal concentration, relationship between shale and organism, geological significance and economic aspects of the black shale deposition through time has been discuss. A comparison

between the Phanerozoic and the Proterozoic black shale has also been made during the present discussion.

2.2: Mystery behind black colour of the shale

The black coloration basically controlled by the presence of organic particles commonly known as kerogen and presence of disseminated pyrite grains (Schieber 2001, 2003; Zhang 2023). Kerogen is a solid, insoluble and complex mixture of organic substances. This includes hydrocarbons, organic molecules, Sulphur/ nitrogen-containing compounds, and heavy metals, commonly found in black shale, demarcate the transitional stage in the formation of hydrocarbon (Crum Brown, 1927; R.C Shelly, 2005). The organic substances within shale are sourced from organic debris i.e., spores, pollens, bacteria, algae, all are accumulated within shale and buried over millions of years then converted to kerogen. The shales which are rich in kerogen are known as oil shale which is release oil-like hydrocarbon from the rock upon heating (Cane, 1976; Cook et al. 1981). Depending upon the sourced material, depositional environment and degree of maturation, the kerogen type and composition varies from Type I, II and III. Type I is sourced from marine algae which is oil prone, Type II originated from a mixed terrestrial and marine source and Type III is gas prone completely terrestrial derived. The study of black shale and its kerogen content is significant in the exploration and understanding of fossil fuel resources (Tissot and Welte, 1984; Spiker et al 1988). Migration of hydrocarbon from the source to reservoir rock can left a dark stain within the source rock shale. Additionally, high maturity of the kerogen resided within shale can influence the black coloration to shale (Buick et al 1998; Rasmussen et al., 2005). Iron sulfide, especially Pyrite (FeS_2) having a distinct black coloration with metallic luster conventionally present within the black shale can add an overall darkness within the shale (Raiswell and Plant, 1980; Gregory et al., 2015). Apart from the pyrite, clay mineral like smectite can add a black hue in shale (Harris et al, 2020). In rare cases, the black coloration may be influenced by few mono-sulfide minerals, such as greigite and/or mackinawite (Berner 1984). These mono-sulfides are not stable over extended geologic periods so, the black coloration typically fades rapidly (within hours) upon exposure to oxygen (Arthur and Segmen 1994).

The interplay of the above-mentioned geological factors like organic content, anoxic conditions, sulfide minerals, clay minerals, bitumen migration, and thermal maturation determines the black coloration of shale. Shale deposits with these characteristics are

commonly found in sedimentary basins and are important for understanding earth's history, past environmental conditions, and the formation of hydrocarbon resources.

2.3: Physical and Geochemical setting for shale deposition

Shale is made up of very fine sediment which is unable to remain in suspended mode in a tranquil water of continental, marine and transitional situation. This fine sediment can be deposited in restricted basins-ones independent of water depth which may range from a few centimeters to hundreds of meters deep (Potter et al., 2012). It can be the product of a deep marine, low energy shelf of shallow marine/ near shore environment if the shore is protected from frequent high energy wave current (Swift, 1969; Sutton et al., 1970; Howard et al., 1972; McCave, 1972; Gibbs, 1973). Mud or shale additionally deposited in semi enclosed lacustrine environment as well as meandering river channel as an overbank deposition during temporary flood events which is extending beneath the natural levees (Fisk, 1947; Hutchinson, 1957; Reeves, 1968; Fisher and Brown, 1972). Extemporaneous flood events are responsible for shale deposition at interdistributary lakes and protected deltas (Fisk et al., 1954; Scruton, 1960; Scott and Fisher, 1969; Koleman and Wright, 1975). For ancient Precambrian black shales most of the shales were deposited in epicontinental shallow seas, influenced by salinity stratification in a brackish water set up (Heckel, 1977; Tyson et al., 1979; Barron et al., 1985; Fleet et al., 1987). Maximum black shales of the earth are deposited in the deepest part of the basin, indicating maximum subsidence and represents the transgressive system tract (TST) followed by Maximum Flooding Zone (MFZ) (Wignall 1991).

2.3.1: Biogeochemical perspective of black shale deposition:

Other than palaeogeographic setting black shale deposition required certain essential geochemical condition. There is a ubiquitous believe that sapropelic sediments accumulation is enhanced by the absence of molecular oxygen. This oxygen deprived zone accelerates the diagenetic alteration and prohibits the organic breakdown at the uppermost sedimentary layer in presence of respiratory micro-organism. Which indicate that black shales are deposited under either decreased or minimum oxygen supply or maximum/ increased oxygen demand (Demaison and Moore, 1980; Wignall 1991). Organic accumulation under anoxic bottom condition certainly allows few specific trace and major element enrichment which are able to

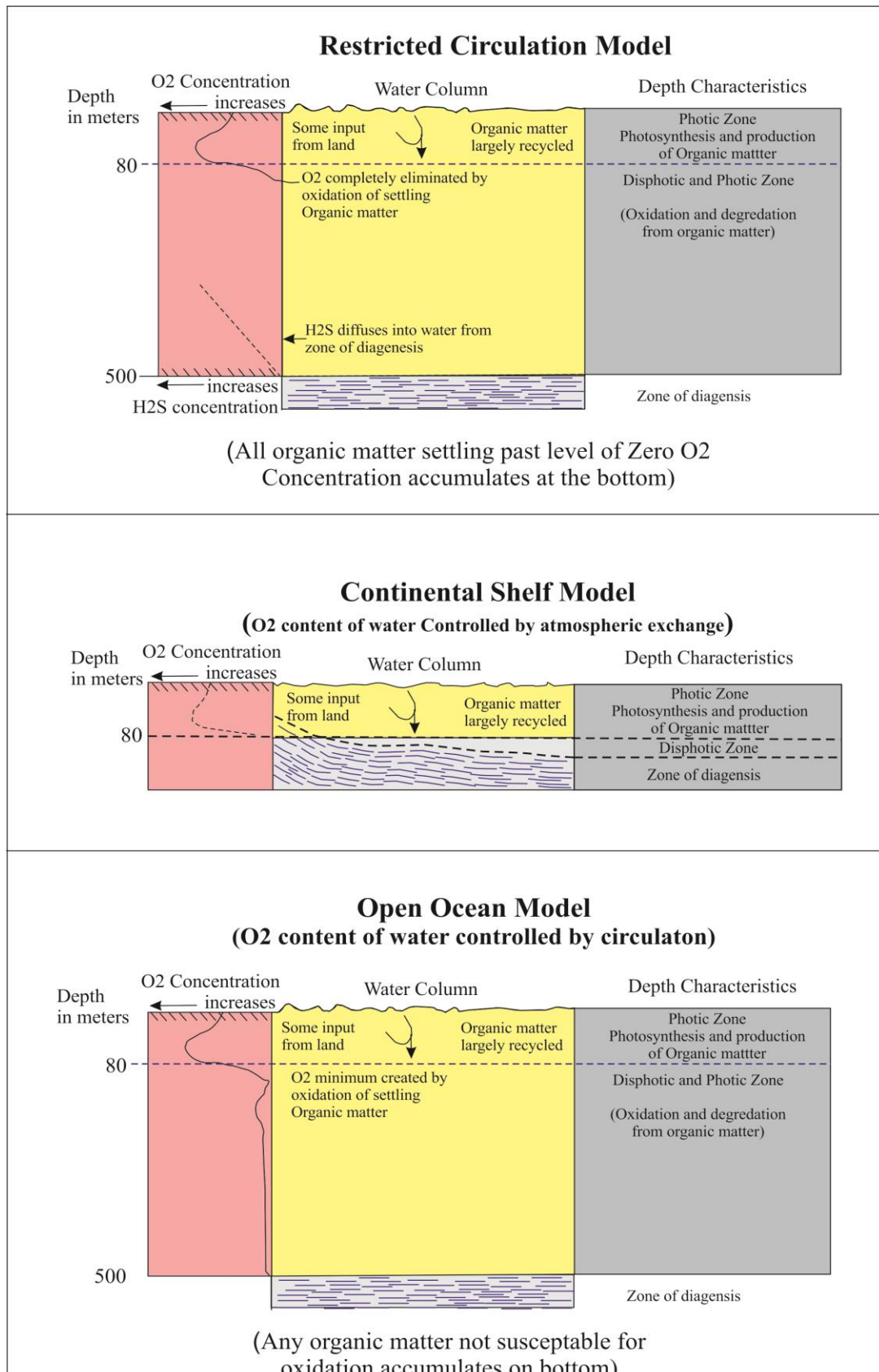


Fig. 2.2: Three different models for deposition of organic rich sediments (Modified after Tourtelot, 1979).

form sulfide phases (Vine and Tourtelot, 1970; Gustafson and Williams, 1981; Jacobs et al., 1985, 1987; Crusius et al., 1996; Piper and Calvert, 2009). This scenario inferred that the stratified water column isolates the photic zone and nutrient reservoir of bottom water (Wignall and Myers, 1988; Hatch and Leventhal, 1992; Turner, 1992; Ettensohn, 1995; Piper and Calvert, 2009). The black shale also displays the palaeoceanographic scenario of the depositional basin. According to Piper and Calvert, 2009, the main source for nutrient supply in a marine condition is riverine sediment, which is restored in the bottom water under oxygen deficient condition, is reflected as primary productivity of the ocean basin. Other than riverine source, benthic biodiversity act as an additional source of organic carbon. The black coloured organic rich shales are confined to the basin center and surrounded by more organic poor mud rock (Sellwood, 1972; Boardman et al., 1984; Wignall 1991). The isolation of anoxic bottom water from photic zone explains diversity of organic enrichment in sedimentary sequence, many sedimentological and palaeontological evidences indicate towards the ventilated condition like oxygenation to denitrifying scenario of the seafloor (Woolnough, 1937; Brockamp, 1944; Demaison and Moore, 1980; Piper and Calvert, 2009). The higher amount of organic debris within black shale reflects the higher degree of preservation compare to primary productivity (Piper and Calvert, 2009). Basins characterized by limited circulation and density stratification often give rise to anoxic bottom waters, exemplified by the renowned case of the Black Sea. There are three proposed models that supports the black shale accumulation such as, restricted basin, open ocean and continental shelf (Fig. 2.2; Didyk et al., 1978; Tourtelot 1979). Temperature and circulation pattern severely affect the oxygen level in seawater and later reflected as dysoxic to anoxic conditions. Stagnant and sluggish water always favors higher rate of organic productivity leading to ocean basin anoxia (Goldhaber, 1978; Tourtelot 1979; White, 1979).

2.4: Sedimentary structures in Shale

Shale is visually homogeneous, do not allow megascopic study during field work due to grain size constrain. Planar lamination and partings are the most common features found in shale. Planar laminations are formed due to suspension fallout of mud sized particles in a presence of calm and quite environment. Depending upon the availability of low energy condition this episodic suspension fall generate stratification in shale which is responsible for the planar lamination. And partings are developed due to abundance of clay minerals within shale. Clay minerals are generally flaky in nature, always have a tendency to orient themselves along the horizontal plane. The presence of clay minerals in higher quantity and

their alignment along a plane gives rise the partings within shale, oftenly known as fissility. Intense weathering rate modify and enhance the fissile nature and turn the shales into splitting in nature. These stratification can be subdivided into several classes (McKee and Weir 1953; Ingram 1954; Lundegard and Samuels, 1980; Potter et al., 1980). Suspension fall out from water column is responsible for continuous horizontal stratification but the presence of any type of bottom current/ traction transport can discontinue these laminae and wavy or lenticular bedding can be developed. Water escape structure like load casts, ball and pillow, flame structures are often found in shales. Clay clasts within and rain prints on the bed surface is also common in shale. In dry areas, desiccation or mud cracks is common. Presence of extreme bioturbation activity or influence of microbial mat can obsolete the fissile nature in shale.

2.5: Mineral chemistry of shale

Shale is the store-house of our nature. Especially the black shale incorporates diverse array of different clay minerals, major, trace, REE elements along with few organic compounds. Petrographic and geochemical study reveals that major component of shale is clay mineral like kaolinite, illite, smectite and sometimes glauconites along with framework silicate like quartz and feldspar. Carbonate component like calcite and dolomite, different sulfides like pyrite (FeS_2) and iron oxide are commonly present within the shale. Along with other inorganic and organic components, clay minerals are well studied for the shale.

2.5.1: Clay mineralogy:

Clay minerals hold a sheet-like structure resided in alternating layer with silica and alumina tetrahedra. Clay minerals are basically detrital but enormously modified during diagenesis and weathering. Depending upon the chemical composition clay minerals reflects different information regarding provenance, diagenetic history, depositional environment like climate, salinity etc. Kaolinite is commonly found in continental and near shore environment and relatively abundant in younger sediment rather than ancient sediment (Grim 1951, Weaver, 1956). Again Millot (1953) stated that marine sediments which are rich in organic matter and sulfide is also enriched with kaolinitic clay. Anaerobic medium and acid reaction is responsible for Kaolinite formation in marine environment whereas marine black shales are again dominated by illite or mixed layer illite-montmorillonite with little amount of kaolinite. Montmorillonite, on the other hand, is the major clay mineral associated with volcanic

material. Illite is basically associated with carbonate rock as it has a relation between a calcareous environment and diagenesis (Weaver 1956). Other than limestone illite is also common for shale as well. Another clay mineral, glauconite, oftenly associated with marine conditions, diagenetically formed from the parent material present in the rock. According to Weaver, (1956) only one clay mineral can show abundance in one particular depositional environment but there is not any definite trend towards the depositional environment for any particular clay mineral. XRD-Powder diffraction method is commonly used for analyzing the chemical composition which helps to discriminate the clay minerals.

2.5.2: Inorganic geochemistry:

Black shale is a warehouse of a variety of major, trace and rare earth elements, which are present in low concentrations but can still play significant roles in its evolution and have potential economic value. The major element composition of black shale is influenced by the composition of the source material from which it was derived. Shale forms from the accumulation and compaction of fine-grained sediment, which can include a diverse range of mineral and organic matter from the erosion of different rock types. That is why SiO_2 , Al_2O_3 , MgO , K_2O , FeO , P_2O_5 , CaO are almost very common in shale (Yamaguchi 2002; El-Anwar et al., 2018; Wang et al., 2023). Apart from the major element black shales are generally enriched in trace metal like, V, Ni, Co, Zn, Mo, U, Th, Zr, Sc, Sr, Sc, Ba, Cu, Ga, Nb, Hf, Ta, Mn, Rb (Kuşcu et al 2016; Wang et al 2023). Black shales also show enrichment in rare earth elements like La, Ce, Y, Ho, Eu which is helpful for interpretation of its evolution (Ibad and Padmanavan 2022).

SiO_2 , Al_2O_3 , TiO_2 , Th, Sc, Gd, Yb, Eu, Zr, La elements are important for source determination (Basu et al., 2017). The distribution patterns of trace elements can help discriminate between different geological sources or environmental reservoirs. SiO_2 , Al_2O_3 , MgO , K_2O , FeO , CaO altogether gives a clarification about weathering scenario vis-a vis, humidity and aridity and also palaeoclimate (Nesbit and Young 1984; Harnois 1988; Fedo et al 1995; Perri 2020). MgO , CaO , Sr, Cu, Ga, Gb, Rb are also useful for temperature determination as well as palaeoclimate determination (Bjørlykke 1974; Fathy et 2021; Eric et al 2023). Ga, Al, Y, Ho, Nb, Ta, Zr, Hf are important indicators for palaeogeographic reconstruction (Nozaki et al 1997; Censi et al 2007; Richardson et al 2022). Trace and major elements provide clues about the origin and formation of black shale deposits. By analyzing their composition, one can infer the depositional environment, and the processes involved in their formation. Sr, Ba, Rb, K are specially used for salinity determination (Sajid et al 2020;

Wei and Algeo 2020). V, Ni, Co, Th, Ce, U are redox sensitive elements and the elemental ratios are important to determine the anoxicity of the depositional environment.

2.5.3: Organic geochemistry:

As black shales are loaded with organic matter, so the organic geochemistry is important for black shale only. We have already discussed the source of organic matter within black shale in section 2.2 and 2.3.1. Black Shale is a competent source rock for hydrocarbon generation, so the organic geochemistry of the shale is analyzed, in search of petroleum. These rock type delicately preserve the organic components which turn into petroleum after diagenesis followed by thermal maturity (Tissot and Welte 1978; Potter et al., 2012). Black shales with 0.5% total organic carbon content are recognized as probable source of hydrocarbon, can produce a significant amount of petroleum oil or gas and with ~2.2% total

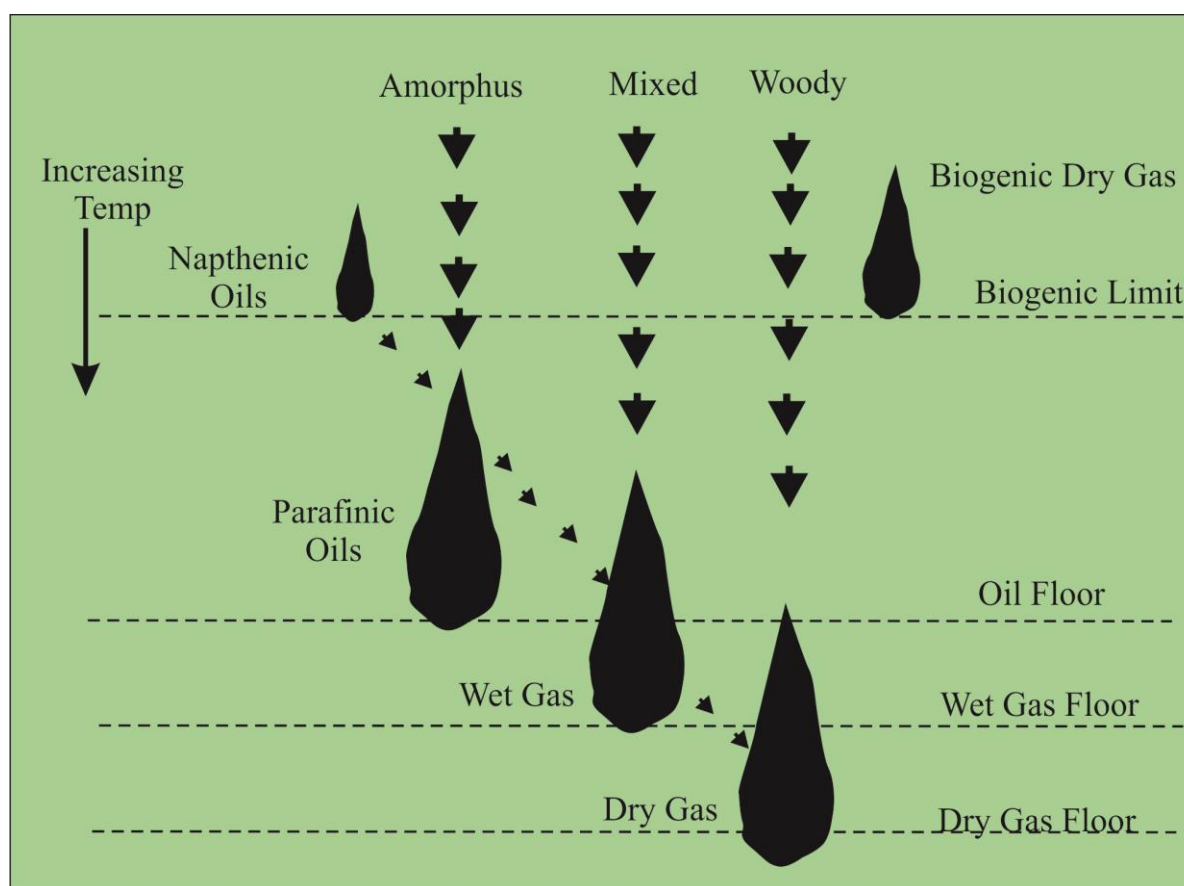


Fig. 2.3: Generation of hydrocarbon from different types of organic matter. Note, with increasing temperature types of hydrocarbons varies from oil to gas (modified after Potter et al., 1980).

organic carbon is the well-known source rock, established as high amount oil or gas production site (Tissot and Welte 1978). Depending upon the type of organic matters like

amorphous (zooplankton/ foraminifera) and woody matter present in the black shale, hydrocarbons are also varied in nature (from gas to oil) (Fig. 2.3). Other than variation of organic matter, thermal maturity is another important factor to control the quality of the hydrocarbon. Optimum temperature can produce high quality hydrocarbon but higher temperature can destroy the hydrocarbon generated within the source rock. This temperature history is highly significant for basin analysis (Connan 1974). The $^{13}\text{C}/^{12}\text{C}$ ratio is used to identify the organic polymers resided within organic matter. This ratio helps to identify the proximity to the shore line in an ancient basin (Gardner and Menzel, 1974; Hedges and Parker 1976).

2.5.4: Metal content in black shale:

The black shales, which contain appreciable amount of organic carbon are exclusively enriched with a variety of metals, especially a good amount of transition metals is resided within it like, Mo, Zn, Ni, Cu, Cr, V, Co, Pb, U, Ag (Vine and Tourtelot 1970). Apart from the transition metals, various types of metal sulfide are commonly found within black shale which are readily identified by petrographic study. These metals sulfides are diagenetically formed within the shale (Mossler 1971; Amstutz and Park 1971; Vulimiri and Cheney 1980; Hoffman 1989; Schieber 1991). Metal rich black shales are usually required a similar depositional environment like carbonaceous (organic) shale. The shales which are rich organic matter basically deposited sedimentation rate is slow and due to this slow accumulation rate metals are also getting a chance to enhance their concentration. These metals are sourced directly from seawater or indirectly from the pre-concentrated planktonic organism. Limited circulation pattern and concomitant volcanic eruption are enriched the metal concentration within the black shale (Maynard, 1983).

2.6: Shales and organism

There are several reasons behind the deposition and preservation of organism within black shales and these organisms are significant research topic for a long time. Probable reasons are (1) the fossils or traces of fossils exclusively used in chrono stratigraphy which provides not only age of the formation but also facilitates the interpretation of how various sub-facies within a shale depositing basin are interrelated over time (Zhu et al 2013). (2) The shales and the existing organisms give insight about the organic composition of the sediment and consequently its hydrocarbon potential (Craig et al., 2013; Zhu et al., 2022). (3) Detailed analysis of sediment characteristics and fossil assemblage conserved within, mutually

indicate about the habitat of that fossils which indirectly infer the depositional environment (Hallam, 1975; Seilacher, 1978; Potter et al., 1980; Archer 1984; Schieber, 1986, 2009; Zhu, 1997). During Proterozoic time black shale only contain variety of microbiota including microbial mat, cyanobacteria, acritarch and few Ediacaran fossils depending on the availability of the organism (Schieber, 1998, 1999, 2007; Knoll, 2008; Sergeev et al., 2012; Schirrmeister, 2016). But during Phanerozoic time annelids and trilobites, bryozoans, some brachiopods and echinoderms, and mollusca are easily fossilized within the black shale (Van et al., 2010). Most pelagic microorganisms, including calcareous microfossils such as Foraminifera, nanoplankton, ostracods, and calcareous algae, as well as siliceous microfossils like radiolaria, diatoms, and silicoflagellates are associated with shales. Besides, organisms producing phosphatic microfossils like conodonts, and organic-walled microfossils such as dinoflagellates and chitinozoa, inhabited the surface waters and hard remains of body parts accumulated in the underlying marine muds (Haig, 2005; Lowery, 2014). In contrast to the body fossils, trace fossils are almost found in the native location where they actually originated (Hallam, 1975; Rimmer et al., 2004). Shales commonly preserve fossils because muddy sediments shield organismal remains from abrasion and the majority of destructive diagenesis and solution processes. Organisms and their preservation significantly influence the hydrocarbon content of a basin (Schopf 1975; Jensen et al., 2005; Gingras et al., 2007). Marine organisms like phytoplankton, zooplankton, and bacteria contribute lipid-rich organic matter helps to generate petroleum and also assist to identify petroleum bearing horizon (Harayama et al., 1999; Neff, 2002; Mossman 2005; Salas et al., 2006; Xue et al., 2015) while terrestrial plant detritus like spores, pollen and lignin-rich organic matter serve as a precursor to natural gas formed in the basin (Staplin, 1969; Hunt, 1991). Biologic productivity, controlled by factors like light, temperature, and nutrient availability, particularly phosphorus and nitrate, dictates the quantity of organic matter. Organic matters are preferentially deposited within black shale due to availability of this nutrient (Murphy, 2000; Piper and Perkins, 2004; Potter et al., 1980). In shale depositing basins with restricted circulation and moderate to low sedimentation rates, low oxygenation rates indicate stable conditions in the shelf and lower shoreface environments favor the accumulation and preservation of organic matter (Calvert, 1987; Calvert and Pederson, 1992; Littke, 1993; Tyson., 1995; Tyson, 2001; Zonneveld, 2010). These muddy sediments exhibit significant diversity of trace fossils and are characterized by a high degree of bioturbation. Trace fossil and bioturbation assemblages are prevalent in shale successions and provide valuable insights into sedimentologic and palaeoecologic characteristics. The abundance of trace fossils or the

intensity of bioturbation can indicate sedimentation rates (Crimes and Harper, 1970, 1977; Reineck and Singh, 1973; Frey, 1975).

2.7: Geological significance of black shale

The black shale is a key rock type that provides important information about Earth's history, environmental conditions, and various geological processes (Ece, 1987; Stein, 1989; Cruse 2004; Jiang, 2011; Zhao et al., 2016; Zhang et al 2018; Li et al., 2023). It has been already mentioned in the earlier section that the composition of black shale including its organic matter content, fossils, and mineralogy, is unanimously used to provide significant information about the ancient climates, oceanic conditions, and source of the sediments. It also acts as a well-known stratigraphic marker, helps to understand tectonic and sedimentary processes along with the evolution of life on earth and the kerogen content of black shale can undergo thermal maturation to produce oil and gas.

2.7.1: Provenance:

Provenance refers to the origin or source area of the sediments which is made with a particular type of primary rock composition. The sediment within the studied rock may be originated from single or multiple sources of varied rock composition. Mineral composition, geochemical characteristics of black shale can offer insights into the source regions (McLennan, 1981). Different source regions have distinctive mineral compositions, and the presence or absence of specific minerals in black shale can help identify the geological source areas (Manikyamba et al., 2008). Mafic dominated source contains higher amount of major element like Mg, Ca, Fe, Al, Ti, trace element like Cr, Ni, Co, V, Sc and overall depleted in REE (except La and Ce) element while Felsic rocks are dominated with major element like Si, K, Na and trace element like Rb, Ba, Sr, Zr, Th, U and REE s are showing enrichment within the felsic rock. These elements are used in ratios and few binary cross-plots as well as ternary diagrams to discriminate the source and tectonic settings. Th/Sc vs La/Sc or Zr/Sc, La/Cr vs Th /Cr, La/Th, Y/Ni vs Cr/V vs Hf and Zr vs TiO₂ are highly used for distinguishing the felsic and mafic dominated source because Sc, Cr, Ti, La are abundant in mafic rock, so the ratio will higher or lower according to the scenario (these binary cross plots are referred in detail in chapter 4) (Bhatia and Crook, 1986; Cullers and Podkovyrov, 2000, Cullers 2002; Basu et al., 2017, Mateen et al., 2022). Si/Al, Fe/Al and Fe/Ti ratios are high in hydrothermal fluid as hydrothermal fluids are silica rich. Fe is mobile in hydrothermal fluid whereas Ti is

least mobile element in hydrothermal field. Again, SiO_2 vs Al_2O_3 and Fe/Ti vs $\text{Al}/(\text{Al}+\text{Fe}+\text{Mn})$ plots are used to identify whether the source is hydrothermally influenced or not (Tchatchueng et al., 2020; discussed in chapter 4). Al_2O_3 vs TiO_2 is used to identify the incorporation of clastic source as Al_2O_3 is the main component of clastic material (Tchatchueng et al., 2020) (more elaborative discussion are in Chapter 4).

2.7.2: Palaeoweathering and palaeoenvironment:

Palaeoweathering refers to the processes of weathering and alteration of rocks and minerals in the Earth's geological past. It involves the physical, chemical and biological breakdown of rocks such as alteration of primary minerals (feldspar) to secondary minerals (clay mineral) through chemical reactions. These weathering scenarios provide information about the prevailing climate and environmental conditions during the time of weathering (Mir et al., 2015; Basu et al., 2017; Ofili et al., 2022). Geochemical and mineralogical investigations are essential tools for researchers studying palaeoenvironments using black shale deposits (Perri and Ohta, 2014). The major oxides like SiO_2 , Al_2O_3 , Na_2O , MgO , CaO , K_2O are extremely useful for interpreting (discuss chapter 1) different palaeoweathering parameters like CIA (Index for chemical alteration), CIW (Chemical Weathering Index), PIA (Index of Plagioclase alteration) and ICV (Index of Chemical Variability). Higher the CIA, CIW and PIA value palaeoweathering rate will be higher and lower the CIA value indicates samples are chemically matured, going through multiple cycles of recycling (Nesbit and Young, 1982; Harnois, 1988; Fedo et al., 1995, 1996; Fathy et al, 2018, 2021).

2.7.3: Ocean Chemistry and Palaeoclimate: Palaeosalinity, Palaeoredox and Palaeoproductivity

Black shale plays a significant role in palaeoclimate reconstruction due to its sensitivity to environmental conditions and its ability to preserve important information about past climates. Here are some key aspects highlighting the importance of black shale in palaeoclimate reconstruction and to understand the ocean chemistry and; determining the salinity, redox condition of the depositional medium (Sajid et al., 2020). Modern ocean often contains microfossils, such as foraminifera, which are sensitive to changes in salinity (Cayre, 1999). Different species of foraminifera have specific salinity preferences, and their presence or absence in black shale layers can be indicative of past salinity conditions. In absence of foraminifera, concentration of certain trace elements in black shale like Strontium (Sr), barium (Ba) can be used as a proxy for salinity (Wei and Algeo, 2020). Apart from Sr and Ba,

Boron (B), Gallium (Ga) and Total Organic Carbon (TOC), and Total Sulphur (TS) ratios in black shale used to infer past salinity variations (Kendall et al 2020; Hu et al 2020). The sedimentary structures within black shale layers, including features such as mud cracks, can provide evidence of changes in salinity (Baria, 1977). For example, the presence of desiccation cracks may suggest periods of increased salinity and can also provide information about past salinity conditions (Schinteie and Brocks, 2017). The types of organisms present and the composition of organic matter can be influenced by salinity levels.

Black shale is a very good Productivity Indicator, often forms in environments with high organic productivity (Brumsack, 2006). The organic carbon content of black shale can be used as an indicator of past biological productivity in the surface waters of ancient oceans (Piper and Calvert, 2009; Sajid et al., 2020; Liu et al., 2021). High productivity is often associated with favorable conditions, such as nutrient availability. It involves studying various indicators preserved in sedimentary archives, such as oceanic sediments, coral reefs, and ice cores, to understand past oceanographic and climatic changes (Kennett, 1983).

Trace and major elements within the black shale helps to infer palaeo-redox conditions (Rimmer, 2004). Redox sensitive trace elements like Cerium (Ce), Uranium (U), Thorium (Th), Vanadium (V), Nickle (Ni), Cobalt (Co), Molybdenum (Mo), Selenium (Se) and Zinc (Zn) are commonly present in the black shale. The ratio among these trace elements is used to reveal the palaeoredox scenario of the depositional environment. Strong enrichment of V, Se, Mo, Zn are indicative of strong anoxic to euxinic condition of the depositional medium (Brumsack, 2006; Tribovillard, 2006). Ce/Ce* (Ce anomaly) is highly sensitive to the anoxicity of the depositional medium; applicable specially for marine condition (Tribovillard, 2006). V/V+Ni, Ni/Co, U/Th all are very useful to determine palaeoredox condition (Jones and Mannings, 1994). Apart from the trace element, total organic carbon content, total sulphur content and enrichment factor of some redox sensitive trace metals is equally important for the same (Algeo and Liu, 2020). Authigenic enrichment of Uranium is an important factor to get idea about the palaeoredox condition (Dang et al., 2022). By examining these records, scientists can gain insights into historical variations on sea surface temperatures, ocean circulation patterns, nutrient availability, and other key aspects of marine environments.

2.7.4: Biomarker in black shale:

The term "biomarker" can refer to specific organic molecular fossil that is preserved in sediments from a living organism which was available at that time (Mackenzie et al., 1984; Welte and Tissot, 1984; Peters et al., 2004). Biomarker can preserve the structure of the organic precursor derived from the remains of ancient living organisms, such as plants, algae, or bacteria (Mackenzie et al., 1984; Huc et al., 1997; Peters et al., 2004). These organic molecules i.e., biomarkers can serve as indicators of palaeoflora, palaeoenvironment and are often used in the field of organic geochemistry and palaeontology to study ancient ecosystems and the history of life on Earth (Peters and Moldowan, 1993). Biomarkers can reveal the thermal history of the kerogen in a petroleum system and interpret the biochemical environment (Ogbesejana et al., 2021). This chemical component has the ability to indicate the actual group of organisms which is contributing in the source rock for crude oil formation (Oliveira et al., 2012). Because of the mobile nature, biomarker is decreased during thermal cracking of particular organic material or breakdown of residual oil in petroleum system. It can differentiate between the organic matter derived from marine or terrestrial organism, prokaryote and eukaryote organism. The biomarker composition varies with palaeogeographic depositional sites and as a result they serve a significant role in palaeoenvironmental reconstruction (Bechtel et al., 2003; Xiao et. al., 2022; Wang et al., 2019; Luo et al., 2019). Biomarker preserved in shale is sensitive to palaeosalinity. In nutshell one can infer a conclusion that biomarkers could give an insight to the depositional environments, ocean-redox conditions, and organic matter enrichments of shales which are critical for exploration and exploitation.

2.8: Economic significance of the black shale

Black shales are enriched with organic matter; act as a significant source rock for hydrocarbon generation after heating for a certain geological time period. After generation of hydrocarbon from black shale, the oil or gas is expelled from the source rock to highly porous and permeable reservoir rock (Zou et al., 2015). Methanogenesis is another important process which can produce bio-gas and gas hydrates from the micro-organism preserved in the black shale during early burial (Dai et al., 2019). Black Shale is economically significant for both conventional and non-conventional (shale gas) hydrocarbon production.

Other than hydrocarbon, black shale is loaded with many precious metals and rare earth elements which are in high demand in our society (Zhang 2023). Redox Sensitive trace

metal like Mo, Ni, Cr, V, Co, U, Th are easily oxidized and removed from the system but these elements are crucially preserved within black shale. Many geological formation containing black shales are rich in metal content; e.g. the black shale of Lower Cambrian Niutitang Formation, in South China is containing high amount of trace metals, Ni, Mo, U and PGE (Shi et al., 2014). There are many records of world's largest metal deposits of copper, lead, zinc which are hosted by black shale (Jung and Knitschike, 1976). Major base metal deposit in shale is also found in Proterozoic province of Australia, North America and Africa. A stratiform Copper-cobalt deposit of Zambia is a world-famous deposit (Fleischer et al., 1976; Garlick 1981). Some noble metals have been also recorded within black shale like Gold and Platinum group of elements which may constitute for future resource (Yermolayev, 1995). Metal enrichment within the black shales is ubiquitously present all through the geologic ages. Tectonic activity especially during subduction the metals preserved within the sediment are activated and enriched such as Porphyry copper and porphyry molybdenum (Campbell and Allen, 2008; Sun et al., 2016). Thus, black shale plays an important role as significant source of economically viable hydrocarbon and metals.

2.9: Black shale deposition through geological time: A comparison between Phanerozoic and Proterozoic black shale

Mud stones and shales are the most abundant sedimentary rocks in the earth surface, made up about 50 percent of all sedimentary rocks. Most of these mudstones and shales reported from different stratigraphic successions of different ages from all the continents in the world are of marine origin, later explored by drilling (Gardner et al., 1977; Dean et al., 1977; Hallam, 1977; Kerr, 1978). Black shales are deposited throughout most of the geologic time and their record is also present as well. The world-wide spatial and temporal distribution of mudstones and shales suggests that most of the geologic settings must be suitable for the deposition of this fine sediment (Fig. 2.4). The oldest organic matter had been recorded from the iron-bearing sedimentary rock of the Nuvvuagittuq supracrustal belt, Canada (4.28–3.77 Ga) and the rocks of the Isua supracrustal belt, west Greenland (~3.78 Ga) (Rosing, 1999). Age of the oldest black shale has been recorded from Western Australia (Pilbara craton, ~3.0 to 2.45 Ga) and South Africa (Kaapvaal craton, ~ 3.5–3.2 Ga) (Kranendonk, 2006; Jin et al., 2023). The black shales reported from Pilbara and Kaapvaal craton are recorded a high proportion of total organic carbon (TOC~29.9%) (Stüeken et al., 2015). A good amount of black shale was deposited in all major cratons during Great Oxygenation Event (GOE; 2.2-1.8 Ga) (Chi Fru et al., 2016; Asel et al., 2018). A huge number of black shales were

deposited in North China, northern Australia, India, Siberia and Baltica during Palaeo-Mesoproterozoic time (~1.8–1.3 Ga) (Zhao et al., 2019). A few of the black shale (aged as ~1.3–0.8 Ga) of West Africa, Siberia, India, Shennongjia, Laurentia, Baltica and São Francisco are highly potential for hydrocarbon generation (Zhao et al., 2019). Neoproterozoic onwards, the black shales

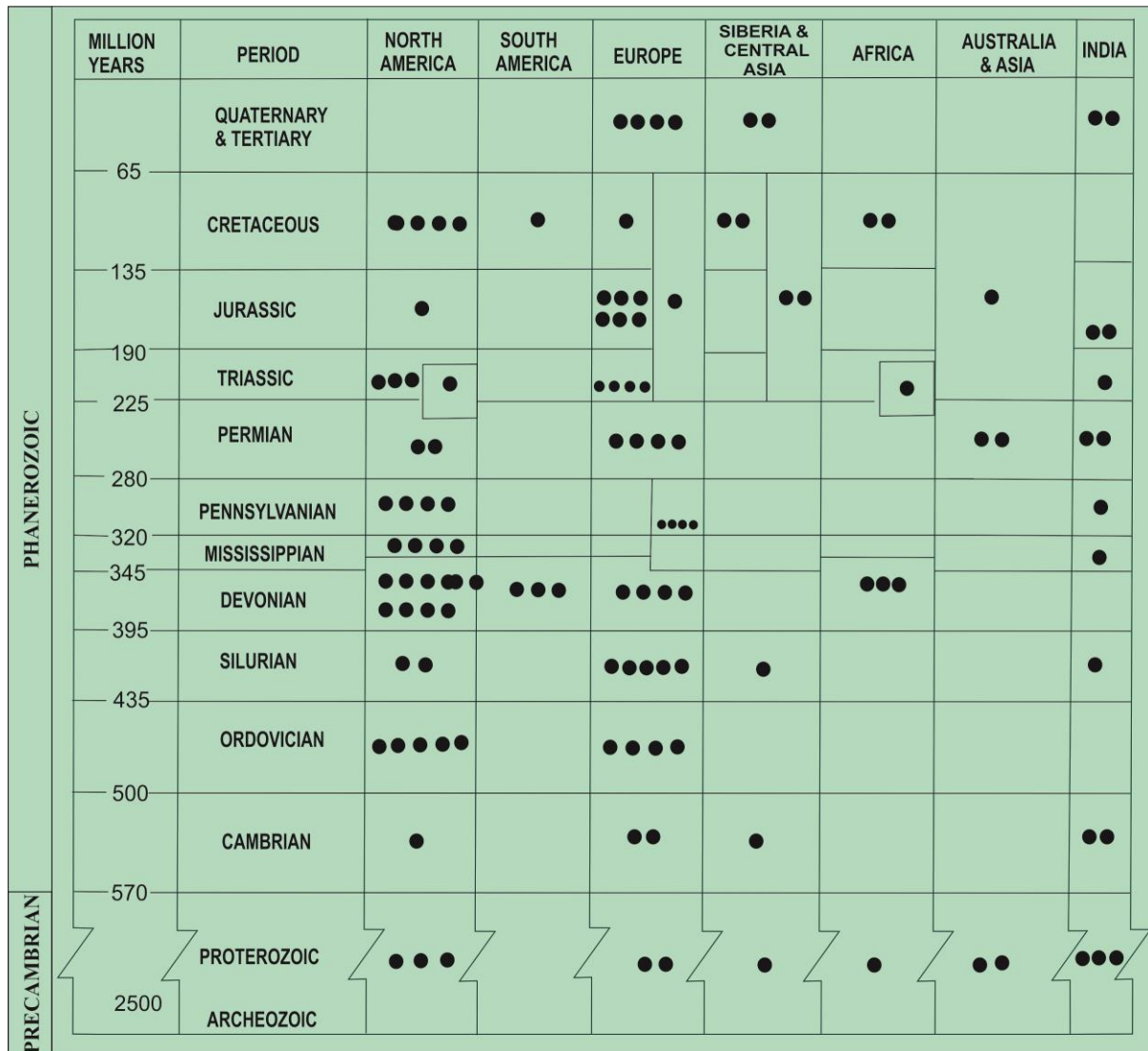


Fig. 2.4: Distribution of Black Shale over space and time (Compiled from Tourtelot, 1970, 1979 and Fulton, 1977)

became widely distributed all over the world with very high organic carbon content and established as well-known hydrocarbon resources. During Jurassic and Cretaceous period again a big pulse of black shale was deposited influenced by frequent global anoxic oceanic events (Jenkyns, 2010).

Phanerozoic black shales are acting as more enriched and promising source for hydrocarbon production than its Precambrian counterparts. Possibly the Proterozoic shales are recycled multiple times compare to their Phanerozoic equivalent (Cawood, 2022).

Secondly, the organic matter which are preserved in black shale are responsible for the uniqueness of that particular shale. This organic matter or kerogen, solely depended upon the living organism prevailed at the time of deposition and thus black shale unwittingly trap the evolutionary history of lifeforms through the geologic time scale. Proterozoic time was flourished by marine life such as cyanobacteria, blue-green algae, Sulphur-reducing bacteria etc. but completely devoid of land derive life. In contrast to Precambrian period, Phanerozoic era is loaded with land derived life, which is reflected in kerogen type (Woodring 1954; Breger and Brown, 1962; Arnold, 1969; Tourtelot, 1979).

2.10: Conclusion

The black shale accumulates a lot of information about the evolution and modification of the primitive to present day earth. Both the spatial and temporal variation of a particular shale formation needs equal special attention in terms of geological, geophysical and geochemical perspective. There are so many high -resolution techniques have been invented, which can magnify the fine grain material and squeeze out the information from the layers of the black shale as the mineralogical and biological study in micron to nanometer scale is important for shale. Additionally, the lithosphere, hydrosphere and biosphere related study in kilometer scale is important to grasp the targeted shale formation and explored it properly.

The Development of a country depends on the natural resources preserved beneath the surface. Nowadays petroleum resources are becoming the most significant property by which the country can rule the world. Besides the conventional hydrocarbon resources, unconventional resources are becoming remarkable and considerable sources of renewable energy. To explores these conventional and unconventional sources of hydrocarbon, research on black shales needs more special attention. Other than hydrocarbon, the trace and REE element which are necessarily accommodated within black shales needs special care and devoted research work to use them properly.

Presently, the climate change because of global warming influenced by rising proportion of greenhouse gases marked as a global crisis. To study the black shale with proper perspective i.e., understanding the organic carbon cycle can decrease this crisis level. The extensive uses of fossil fuel such as conventional hydrocarbon resources can release a huge amount of CO₂ in the atmosphere and added the components to greenhouse gases which catalyze the increase in temperature of the present environment.

PART II

FACIES ANALYSIS, PALEOGEOGRAPHY, PETROGRAPHY, SEQUENCE STRATIGRAPHY AND GEOCHEMISTRY OF RAMPUR SHALE

CHAPTER: 3

FACIES ANALYSIS, PALEOGEOGRAPHY, PETROGRAPHICAL ASPECTS AND SEQUENCE STRATIGRAPHIC SCENARIO

3.1: Introduction

Outcrops of the Rampur shale formation are generally poor in quality because of its weak lithology. Further, because of apparent monotony in its physical character correlation between detached sections, also needs very keen observations and dependence on very subtle characteristics that may often be overlooked. Bedding plane exposures are less. Even then vertical sections are to be synthesized by moving in the dip direction. Thus, sedimentologists generally treat shale formations summarily and thereby leave a major source of geological information unexplored. Process-related facies analysis in terms of physical characteristics of shale is seldom carried out. Consequently, the palaeogeographic interpretations are tenuous and uncertain.

The upward transition from the Chorhat Sandstone to the Rampur shale is abrupt (Fig. 3.1) but the exact contact between these two formations could not be located. Again, at the top part of the Rampur shale Member almost imperceptibly grades into the Rohtas Formation (Fig. 3.1). Owing to this difficulty the thickness of the Rampur shale Formations remains a bit tentative. The total thickness of the formation is about 80-85m. To overcome the aforementioned difficulties in stratigraphy, a high-resolution inventory of minor differences in sedimentary structures, lithology, lateral extent of beds, their thicknesses was taken into account to delineate the Formation into three segments superposed one above another (Fig. 3.1). Basically, the Rampur shale divided into three segments based on the sand: Shale ratio present with in it. Apart from the sand: shale ratio, the purpose is to identify genetic differences between the segment on account of variation in palaeogeography of deposition, in agents that delivered the sediments to the marine basin and sediment sources. Eliciting the depositional modes of ancient sedimentary rock sequence needs an organized classification. There are various ways to achieve the goal but a sedimentologist's choice is always from which glimpses of depositional environment can be perceived. A state of art facies analysis is potential for working out the genetic differences between coexisting sedimentary bodies (Miall, 1980; Walker, 1990; Reading 2009) and adopted by the present author. The different segment of the Rampur Shale further classified accordingly to get a holistic picture of the depositional environment which is always difficult in case of shale rocks. These segments have differences in mineralogy as well as the presence of certain primary sedimentary structures. The basal segment is rich in sand percentage while the upper segment is almost devoid of sand. The middle segment on the other hand dominated by sand/silt alternations along with shales. The

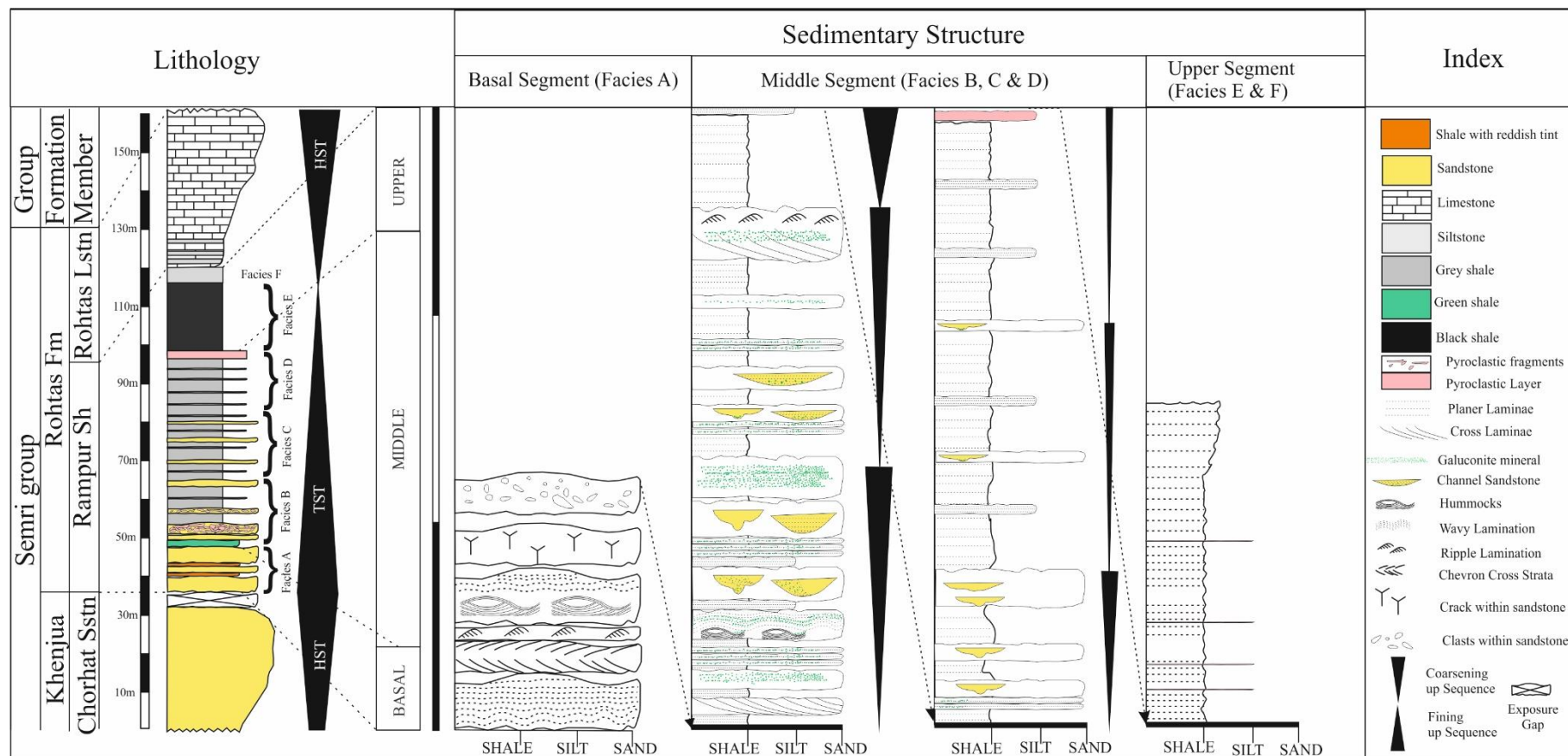


Fig. 3.1: Stratigraphic succession of Rampur Shale, comprising of different segments (basal, middle and upper). Note the underlying Chorhat Sandstone forming a High Strand System Tract (HST) followed by the Transgressive System Tract (TST) present within the Rampur Shale overlain by another HST. Also note the distribution of different facies within the segments and parasequence sets.

upper segment is shale dominated and completely devoid of sand. There are also differences in the presence of primary sedimentary structures between the segments. In order to unveil finer and intrinsic differences between the lithologic constituents of each of the segments were further studied their mineralogy, microscopic and ultramicroscopic features and their geochemical characters from various angles. Sedimentation conditions in terms of palaeoredox changes and biotic influence in tandem with palaeogeographic changes have been explored in next chapters. The segments present with the Rampur Shale and the constituent facies are as follows, from bottom upward:

3.2: Constituting Facies of Basal Segment

As mentioned earlier this segment is dominated by sandstone along with shale and primary sedimentary structures are present within the constituting facies. The thickness of this segment is roughly 10-12m or somewhat more since its base could not be located. Sand: shale ratio for this segment was recorded as 4:1.

3.2.1: Facies A:

Unlike any of the younger ones, this facies is dominated by sandstone that is generally fine-grained and apparently well sorted with thin stringers of shale. They are laterally extensive. Because of extensive weathering, bed identity has generally been lost at places, but where adequately recognizable their max. thickness is recorded to be around 80-85 cm. The majority of beds are characterised by parallel lamination (Fig. 3.2a, b) and wavy lamination (Fig. 3.2c). The wavelength of the laminae is around 8-10cm. These sandstones also incorporate perfect hummocks but in centimetre scale varies between 6-10cm (fig. 3.2d). Some of the beds have typically undulated bases while some of the beds have distinctly sharp bases. In contrast to the sharp bases, the tops of the beds are less sharp. At places, there are chevron cross- strata in beds not exceeding 35cm in thickness (Fig. 3.2e). Despite having apparent good grain sorting, some of the beds bear flat and reddish, iron-stained mud clasts. The mud clasts float within the sandy background sediment, but are dominantly bed-parallel and the sand body holds an eroded or sculpted base (Fig. 3.2f). In these layers the clasts are well rounded at edges and they are of longer dimensions, the clast-size is widely variable within a bed; their maximum length measures about 7cm (fig.3.2f). Locally the concentration of clasts at a horizon, warrant recognition as mud clast conglomerates, though may be as thin as 10cm (Fig. 3.2g). Ripple-forms are present within or on top of beds.



Fig. 3.2: Facies A: Sandstone dominated facies. **a) & b)** Sandstone with planar Lamination. **c)** Wavy Lamination within the sandstone. **d)** Hummocky cross stratification followed by planar lamination. **e)** Chevron cross stratification. **f)** Clast bearing sandstone with sculpted base (marked at base)

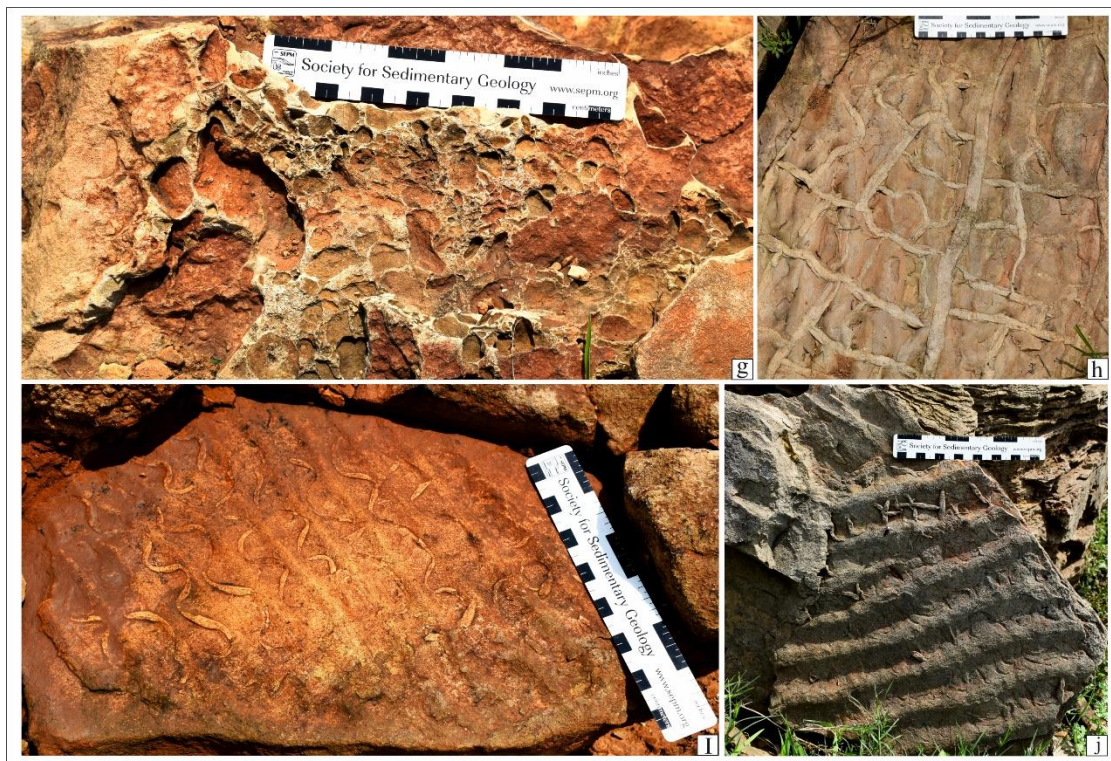


Fig. 3.2: (Facies A continues) **g)** Mud clasts bearing horizon. **h)** Crack within the top surface of the sandstone, cross-cutting each other. **i)** Manchuriophycus crack at the ripple trough. **j)** Spindle shaped crack at the ripple trough. Ripples are bifurcated and flat crested.

The average height and spacing of these ripples are 2 cm and 6 cm respectively. Cracks are common on the bed top surface, frequently in form of network, different sets cross-cutting each other (fig. 3.2h). These cracks are preferentially present within the troughs of ripples and warrant identification as *manchuriophycus* (fig. 3.2i). These *manchuriophycus* entities are generally spindle-shaped and at places, parallel to each other at high angle to the ripple crests. The ripple crests are, generally, straight or broadly sinuous and occasionally bifurcated (Fig. 3.2j).

3.3: Constituting Facies of the Middle Segment

The thickness of this segment is roughly 50-55m. The boundary of this segment fixed by a greenish shale layer above the basal segment. The middle segment contains variation in primary sedimentary structures with different dimension and different proportion of lithologies accumulated within them. The sand: shale also varies within this segment from base towards upper part. This segment consists of three facies namely B, C and D with sand: shale ratio shows 3:2, 1:2 then 1:5 respectively.

3.3.1: Facies B:

This facies is characterised by repeated alternation between sandstone and shale. The base of the segment has been fixed with the first appearance of shale which is greenish in colour, thickens up to about 10-12 cm (Fig. 3.3a). The sandstone beds are of two different geometries. Commonly the sandstone beds are tabular or sheet-like (Fig. 3.3b, c). They have bases sharper than their tops. The bed-soles often bear prod marks and groove casts (Fig. 3.3d, e). These sandstones are well sorted and fine-grained and their beds have maximum measured thickness around 10cm, thinning overall upward. The hummocks present in them have wavelength up to 5-8cm (Fig. 3.3f). Besides HCS, the beds also bear planar laminae and low-angle cross-strata (Fig. 3.3g, h).

The dark green glauconitized sediments constitute a major component of this facies, repeatedly appeared within the facies. Many of these beds are enriched in glauconitized pyroclastic fragments (Fig. 3.3i). They are also following the lamina within the sandstone and sometimes appears in massive form, though in small scale (Fig. 3.3j, k). Generally, their dark coloured bodies are wedge-shaped, convex-up bodies, internally massive, locally carrying light coloured fragments apparently derived from the underlying light-coloured fine-grained body (Fig. 3.3l). The convex-up bodies are draped by light coloured parallel laminated sandstone. The other group of major sandstone beds are of lenticular channel geometry; the channels are

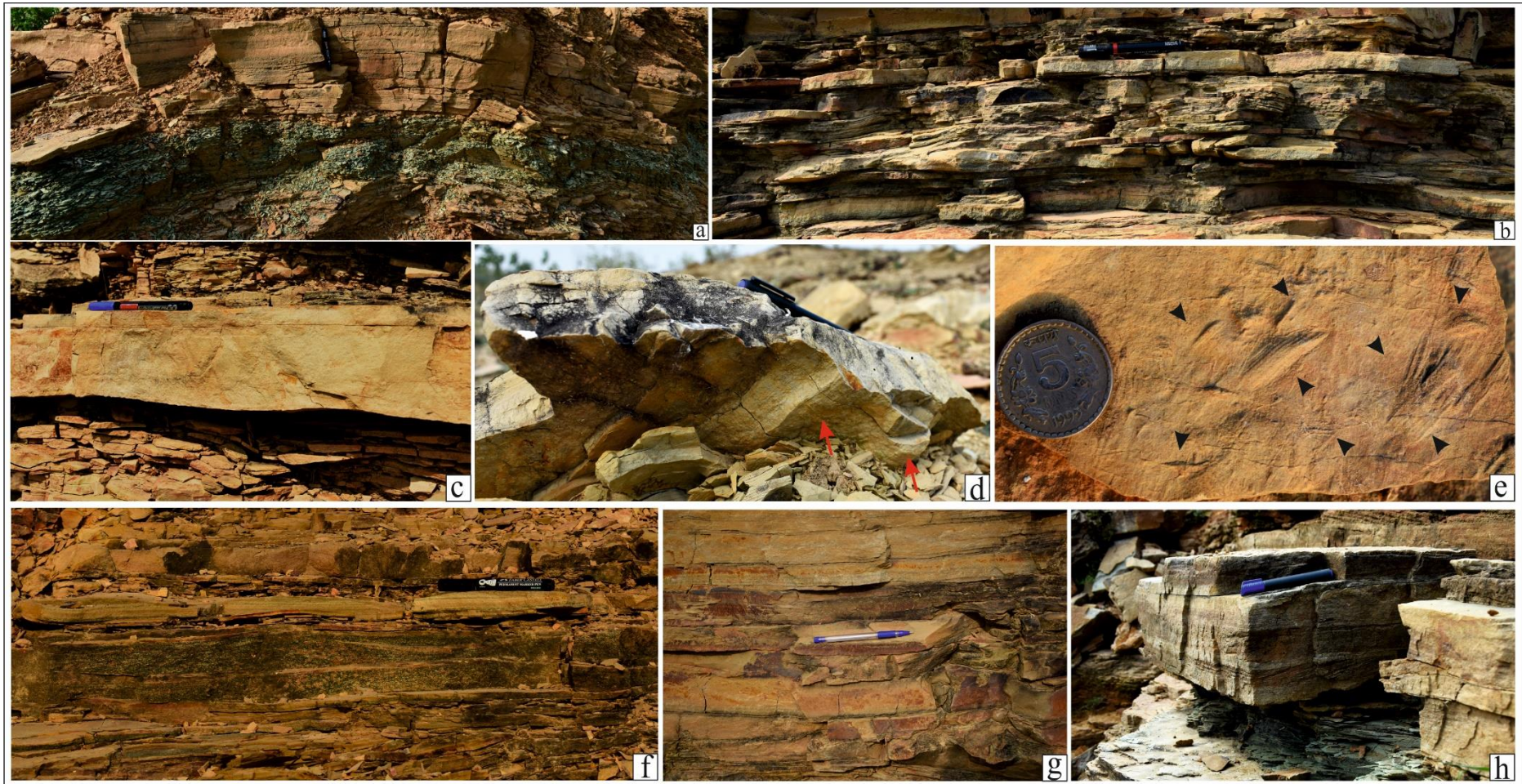


Fig. 3.3: Facies B: **a)** Green Shale layer. **b)** Sheet like sandstone body. **c)** Tabular sandstone body. **d)** Longitudinal groove at bottom of the sandstone (arrowed). **e)** Sole features present at bottom of the sandstone (arrowed). **f)** Hummocky cross-stratified sandstone. **g)** Planar laminated sandstone body. **h)** Low angle cross stratified sandstone body.

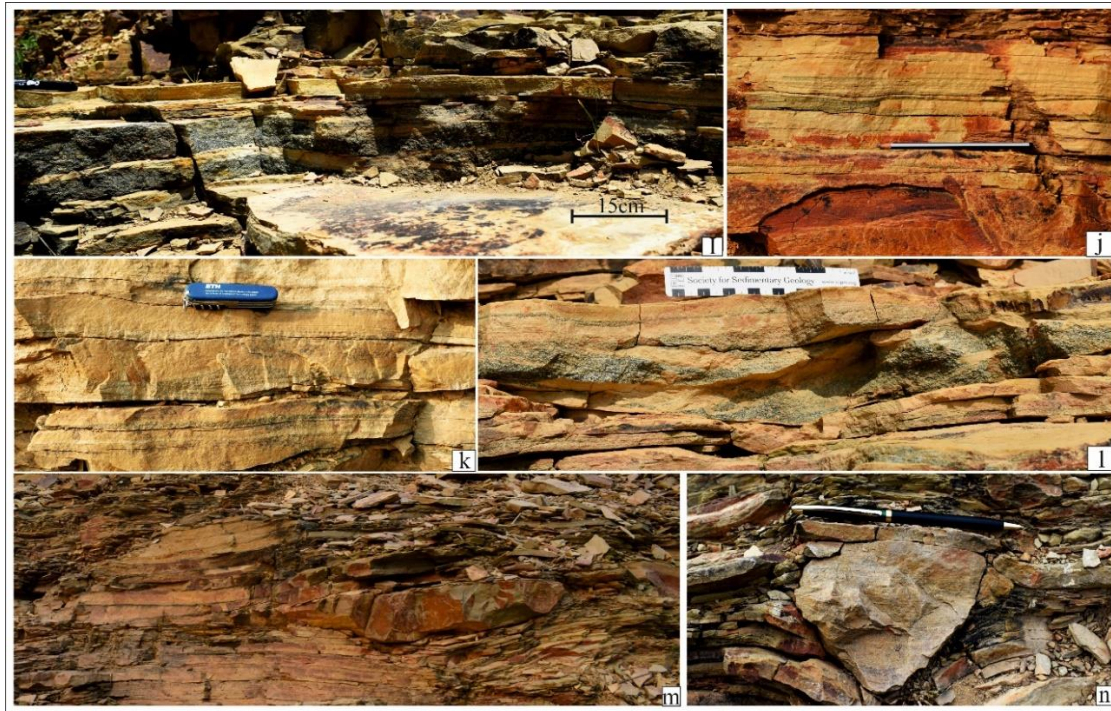


Fig. 3.3: (Facies B continues) **j)** Pyroclast bearing glauconitised sand body. **j) & k)** Glauconite following the depositional lamina. **l)** Wedged shaped sandstone body, internally massive with glauconite grains and light-coloured pyroclastic fragments. Channelised sandstone body **m)** Wide and **n)** Narrow.

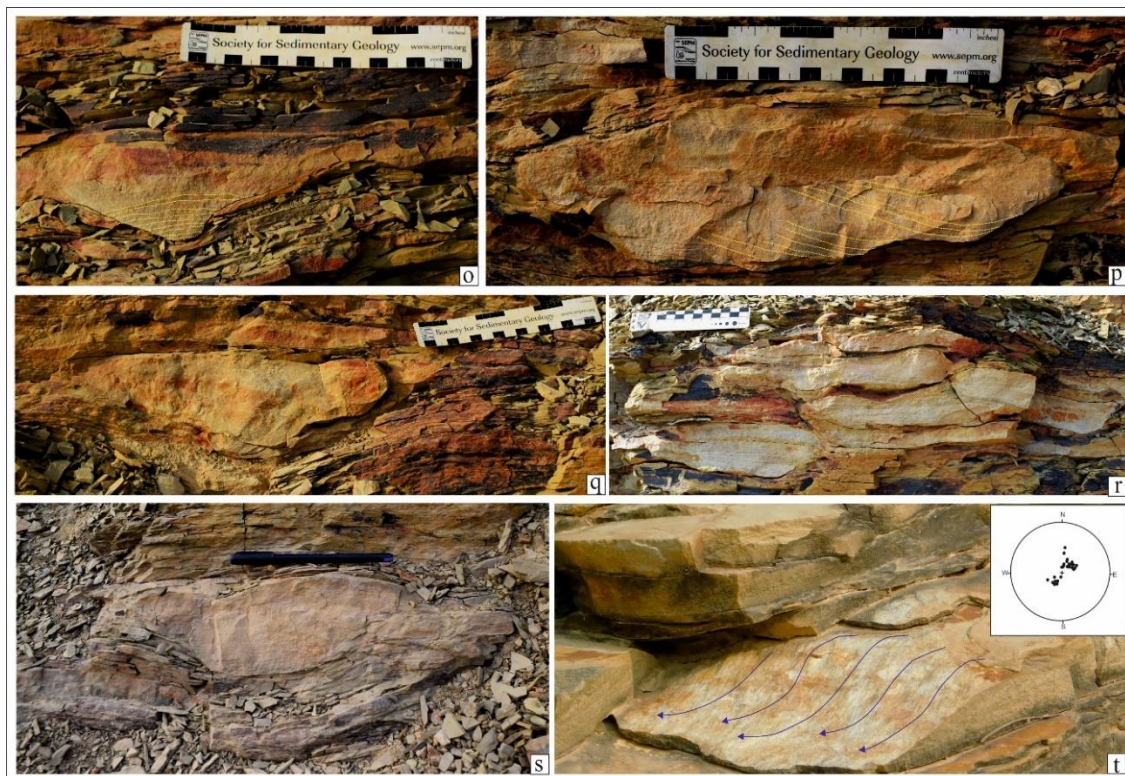


Fig. 3.3: (Facies B continues) **o)** Channel filled sandstone showing planar lamination. **p)** Channel filled sandstone showing cross lamination. **q)** Channel migrated sideways. **r)** Channel sandstones are vertically juxtaposed each other. **s)** Channel sandstone within sheet like sandstones. **t)** Slides planes at the top of the sandstone showing the bipolar orientation.

much wider than deep (Fig. 3.3m), although a few are narrow and steep-walled channels also present (Fig. 3.3n). The channel-fill sandstones are discernibly coarser than the other type of sheet-bedded sandstones. The bases of the channel sandstone are sharp and may have gutter casts underneath showing a consistent NW-SE trend which is shore perpendicular (Fig. Discussed in section 3.5). Coarsest grains tend to concentrate at the base of channels and within the gutters. Gutter contains longitudinal grooves and various sole features at the bottom surface. Sole features are both gutter parallel and gutter normal at the bottom surface (Collinson Thompson, 1982). Brush marks (Ricci Lucchi, 1995) are commonly found within bottom surface with width 5-7mm and relief 1mm (Fig. 3.3d, e). Prod marks are showing bi-polar orientation towards NW-SE (Fig. discussed in section 3.5). Overall grading can discern within the beds. Besides massiveness, the channel-fills also display planar laminae and cross-strata (Fig. 3.3o, p). Strikingly, the channel-fills have internal cuts depicting lateral migration with short jumps. In case of some channels, the migration is oblique, sideways as well as upward (Fig. 3.3q). The channels, as in the facies B, are commonly of multiple generation, juxtaposed together. The channels may be juxtaposed laterally or vertically (with or without intervening shale between them) (Fig. 3.3r). At places, the channel bodies dig through the sheet-like sandstone bodies (Fig. 3.3s). The sheet sandstone beds overall thin upward and the shale beds thicken at their cost. Innumerable slide plains are commonly found on the sandstone bed surface (Fig. 3.3t). The poles of the slide plains are plotted in the stereo plot and reflecting a bi-polar orientation of the slide planes.

3.3.2: Facies C:

The upward transition from the facies B to C is gradational. Despite this, there is some discernible changes between them. Sandstones in Facies C are more fine-grained compare to their facies B counterpart; alternation of shale, silt and fine sandstone is common here. Siltstone layers are 5-10 cm thick, alternating with sand and shale layers. Internally these layers are planar laminated and sometimes showing wedge shaped body geometry which have flat base and concave up top (Fig. 3.4a). The thickness of the sheet sandstones is comparatively smaller within this facies with respect to their counterparts in the facies B. In the latter their thickness varies from 3 to 5 cm, while in the former it varies between 8 to 10 cm. The average grain-size of the sandstones is also becoming finer in the facies C. The sheet sandstones, as within the facies B, have sharp bases with various kinds of primary sedimentary structures on their soles, prod marks, groove casts, brush marks present in the Facies C (Fig. 3.4b). Internally these

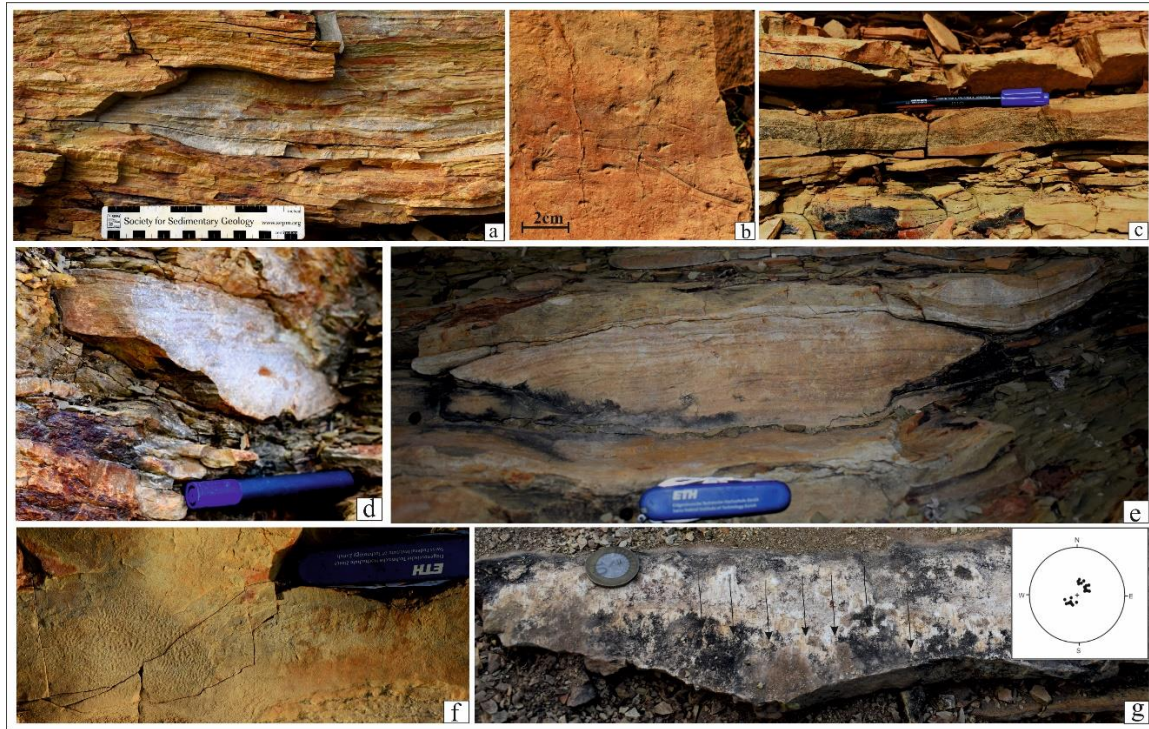


Fig. 3.4: Facies C: **a)** Siltstone body with convex up top and flat bottom **b)** Sole feature preserved at the bottom of the sheet sandstone. **c)** Small hummocks are present in between the sheet like siltstone; presence of glauconites clearly visible along the depositional lamina. **d)** Stepped gutter and longitudinal groove present at the bottom of the sandstone/siltstone. **e)** Planar lamination and wavy lamination are noticed within the channel fill siltstone. **f)** Microbial mat impression is preserved within the siltstone. **g)** Slide plane is clearly visible at the top of the siltstone layers showing a bi-polar orientation.

sandstone beds are overall graded across planar laminae and hummocky cross strata, the latter having maximum wavelength $\sim 5\text{cm}$ (Fig. 3.4c). As in the Facies B, the channel-fills have their bases are distinctly sharper than their tops. Gutters are present at the bottom of the channel form sandstone body along with gutter parallel longitudinal grooves showing an orientation towards NW-SE (Fig. 3.4d, Fig. discussed in section 3.5). The channel fills are overall graded but internally they are planar and wavy laminated (Fig. 3.4e). Glauconites are common in both the silt and sandstone facies following the depositional lamina (Fig. 3.4c). Few microbial mat impressions were noticed on the siltstone/sandstone bed surface (Fig. 3.4f). As in the facies B, slide plains are commonly found on the siltstone/ fine sandstone (Fig. 3.4g), showing bi-polar orientation in the stereo plot.

3.3.3: Facies D:

The common rock type in this facies is shale-siltstone alternations in varying orders. Though here are similarities with the already discussed B and C facies of this segment yet there are some notable differences exist within this facies. The first remarkable difference is that the

channel sandstones are comparatively wider and their maximum width: thickness ratio in this facies is about 11.2 while the same ratio within the facies B is 4.3 (Fig. 3.5a). The second

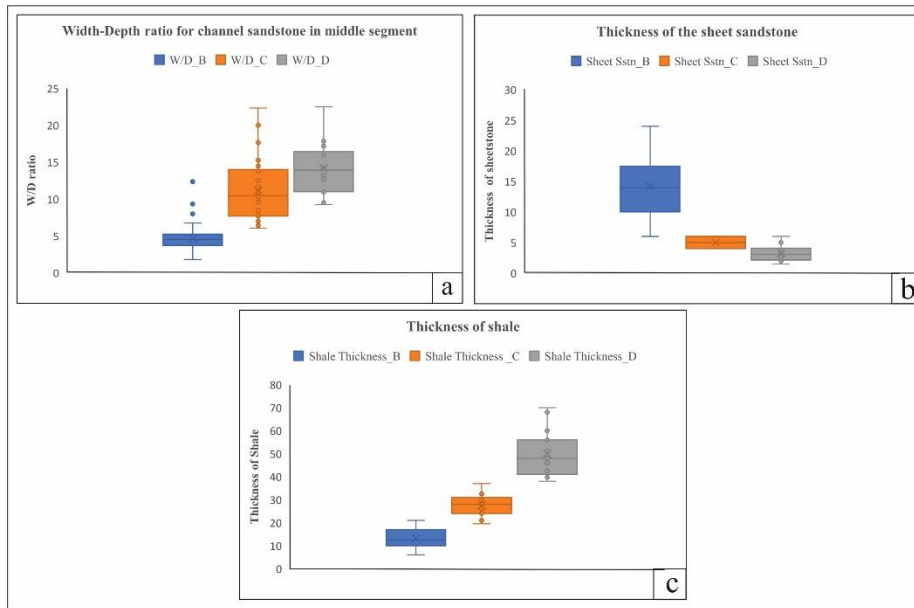


Fig. 3.5: Comparison of the three facies of middle segment (facies B, C, D) based on **a)** Width depth ratio of the channel sandstone **b)** Thickness of the sheet sandstone or siltstone and **c)** Thickness of the shale

difference is that the facies B and C contains more sheet sandstone than the channel sandstone but in Facies D, the channel sandstones outnumber the sheet sandstones compare to previous facies (Fig. 3.5b). Third one is that, sandstone is not very common in

this part; only fine-grained siltstone is alternating with shale. Thickness of the siltstone in sheet like body geometry is also simultaneously decreasing than the previous two parts. The fourth difference is that the intervening shale beds “grey in colour” are generally thicker (maximum 25-30cm in the facies C) (Fig. 3.5c). Both the sheet and channel siltstone contain sole marks at their bases (Fig. 3.5d) and in this association, prod and gutter orientation is differed from the previous two association B and C (Fig. discussed later). Like the facies B and C slide plane is common in the facies D also and poles of the slide plane showing bipolar orientation (Fig. 3.5e). Siltstone layers are internally planar laminated and alternating with shale (Fig. 3.5f). The alternate fine-grained shale and comparative coarser grained siltstone lithologies are broadly folded together. (Fig. 3.5g). Glauconitization is a common feature within siltstone, although rare within shale Shales are generally grey to greenish grey in colour (Fig. 3.5h). The thickness of the shale layers are comparatively increases at this level and reaches up to 50cm (Average), shale layers are juxtaposed one above another (Fig. 3.5i). This facies is ended by a 20 cm thick pyroclastic layer (Fig. 3.5j).

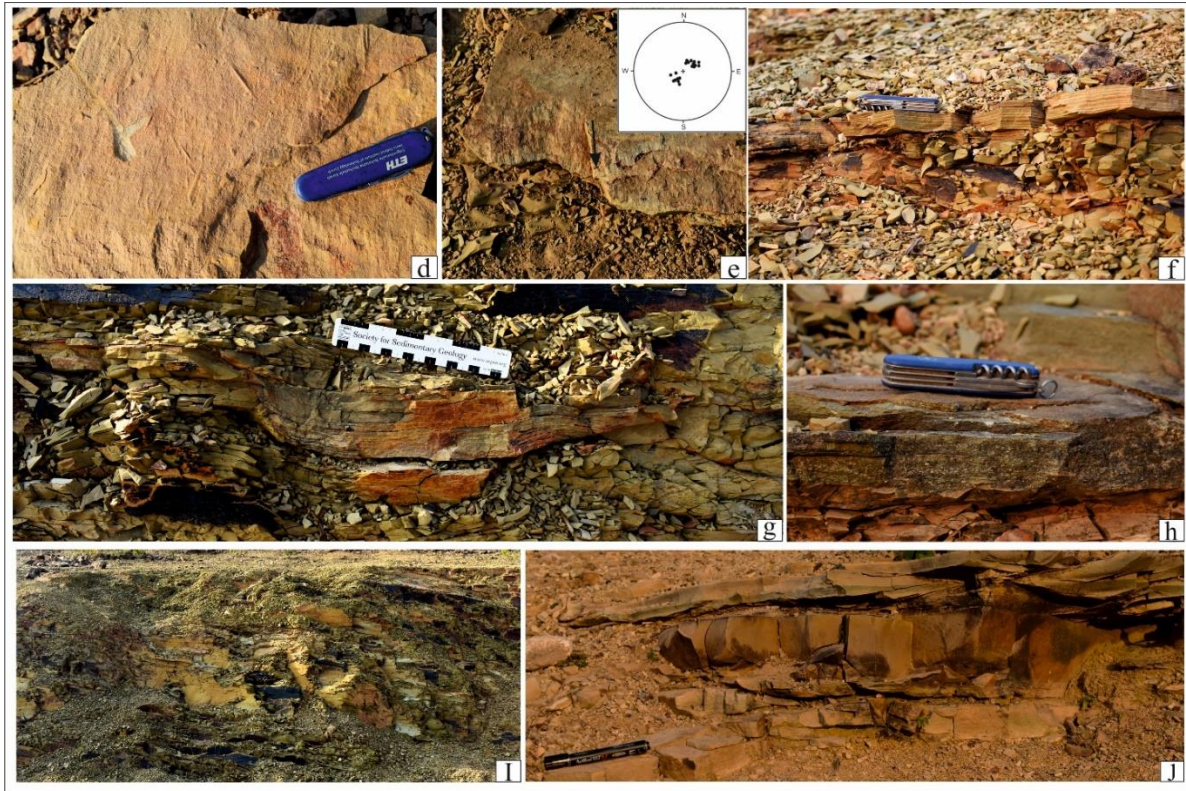


Fig. 3.5: Facies D: **d)** Sole marks at the bottom of siltstone. **e)** Slide plane present at the top of the siltstone layer showing bi-polar orientation **f)** Contact between planar laminated siltstone and shale. **g)** Siltstone layer is broadly folded. **h)** Glauconite present within the siltstone. **i)** Shale layers are juxtaposed above one another. **j)** Thick pyroclastic layer is present at the top of this segment.

3.4: Constituting Facies of the Upper Segment

The thickness of the uppermost segment is ca 15 m (The upper segment represented with black shale (~12m) and light grey coloured shale named as faded shale (~3m). This segment is completely devoid of sand layers.

3.4.1: Facies E:

The presence of sandstone siltstone as channel filling material is eventually decreasing upward at facies D and suddenly disappears at this level. The shales at this level are intensely black in colour (Fig. 3.6a). It is completely fissile in nature, contain very fine planar/parallel lamination and occasionally ripple laminations are present there. The facies is almost homogeneous in nature; only few fine grained tuff layers are alternating with this black shale facies (Fig. 3.6b). Tuff layers are generally lighter in colour along with numerous conchoidal fractures are developed within it (Fig. 3.6c). A thick pyroclastic layer is identified at the base

of this facies E, and somewhere it broadly folded along with the overlying shale layers (Fig. 3.6d).

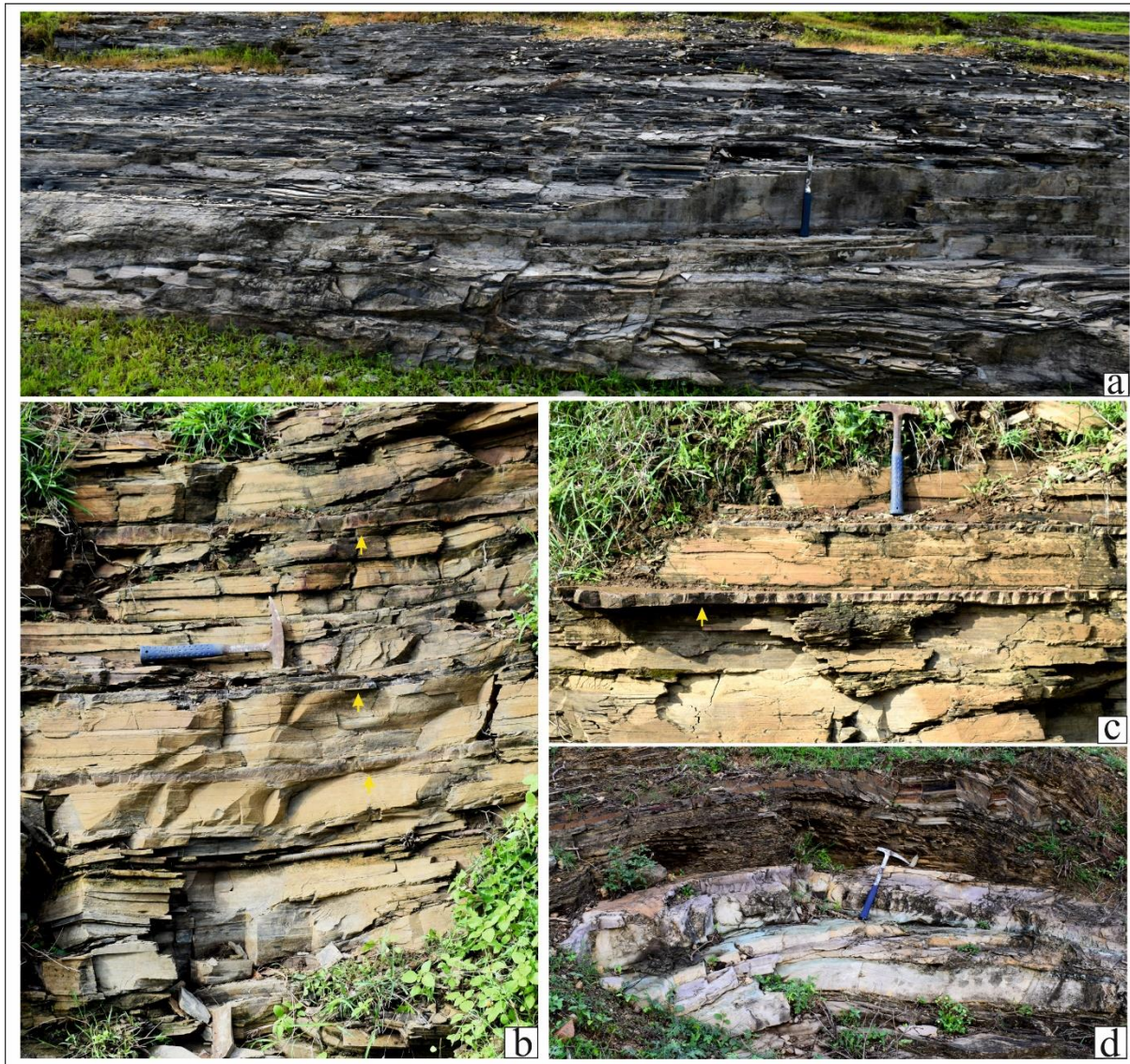


Fig. 3.6: Facies E: **a)** Black coloured shale devoid of sand/siltstone. **b)** Thin (mm-cm scale) tuff layers are intervening with black shale (arrowed). **c)** Conchoidal fractures are occasionally noticed within tuff layers (arrowed). **d)** Thick pyroclastic layer is identified at the bottom of the black shale layer.

3.4.2: Facies F:

This facies is again dominated by grey coloured shale, named as Faded shale and internally typified by fine and even laminae that on weathering give rise to preponderant fissility (Fig. 3.7a). This general motif is disturbed only by intervention of a very minor facies which is a centimetre-scale couplet of a fine-grained tuff and an overlying sub-millimetre-thick mudstone at irregular intervals (Fig. 3.7b). The tuff has sheet-like geometry, pale whitish colour, non-laminated nature and less than or around 1 cm in thickness. The coupled mudstone

is black in colour, and clearly recognizable within this facies by their comparatively darker colour. The tuff layers have their bases sharp, and at places, irregular with little scoops underneath (Fig. 3.7b). The mudstone laminae gradationally overlie them and are commonly composite in nature having interlayers of millimetre-thick grey shale. In these composite layers the darker mudstone micro laminae are laterally detached and broadly lens-shaped.

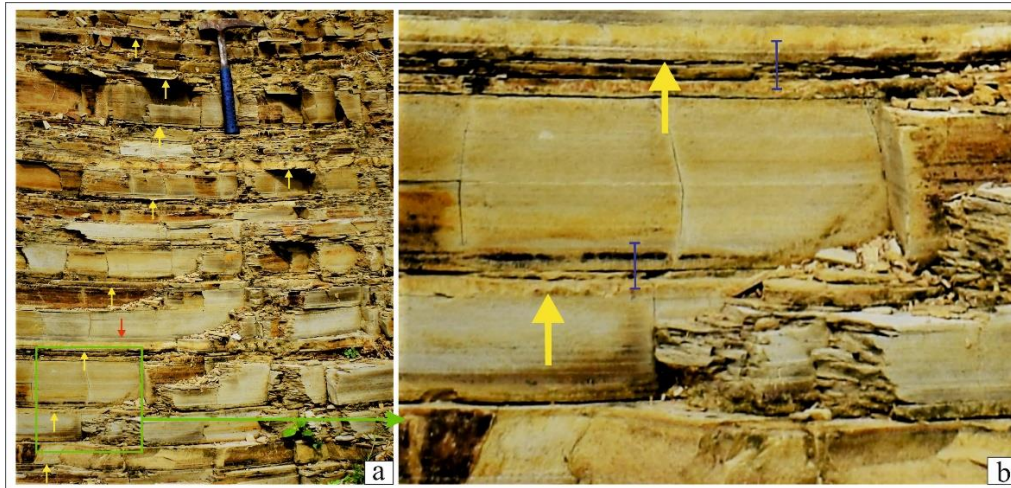


Fig. 3.7: Facies F: **a)** Light coloured grey shale (Faded Shale) showing internal plane lamination with well-developed fissility planes. **b)** Erosional irregularities are noticed at the bottom of the shale layers.

3.5: Depositional Environment and palaeogeography

Despite that fact that at the basal segment, for **Facies A**, mudstones beds are almost absent, frequent present of mud clasts indicate mud deposition took place at intervals between sand deposition. The mud was apparently allowed to settle at low energy levels. In contrast, the sandstone beds were deposited at comparatively higher energy levels. The sandstone beds abundantly displayed wave structures but in very short scales. These sandstone beds are almost certainly deposited by waves that completely erased out their muddy substrata. Because of graded nature of some of the sandstone beds, it seems that sand deposition often, if not always, took place from temporarily waning storms (Arnott, 1993; Sarkar et al., 2002). Very short dimensions of the wave structures, such as hummocky cross-strata, indicate significant depletion in wave energy. Presence of chevron cross-strata explained by superimposition of wave on sand mass dislodged from the beach face and moved downslope.

The sandstone-mudstone alternation might have also been a product of lateral facies transitions, the sand being laid by fair-weather wave only (Sarkar et al., 2002, 2002b). Taking into consideration all its intrinsic features, this segment is interpreted as a lower shoreface deposit (Bose et al., 2001). The networks of cracks and manchuriophycus of varied geometries

and orientations are generally accepted as proxies for pre-existence of microbial mats (Sarkar et al., 2006, 2016; Choudhuri et al., 2023). Presence of cracks on well sorted sandstones is not likely to be retained in such profusion unless one admits that some cohesive material had been present, though they are not preserved anymore. Microbial mat has presumably been imparted the requisite cohesion to the sand bed surfaces (Sarkar and Banerjee, 2020).

At the middle segment, in case of **Facies B**, the increasing shale proportion stands for low depositional energy. The depositional site of this association has likely been relatively distal with respect to the preceding facies association, possibly towards the middle shelf (Sarkar et al., 2002). Sandstones, in contrast, needed increase in the quantum of depositional energy with steep gradient. Sharp bases, presence of gutters and current marks on soles and internal grading document deposition of the beds from temporally waning flows (Myrow, 1992; Sarkar et al., 2002). Wave features, including HCS, further suggests deposition from bottom-hugging light density storm-driven wide-spread underflows. On the contrary, the channel sands were deposited from constricted flows, even though their somewhat coarser grain-size, presence of gutters and current marks at their bed-soles and internal grading point to even stronger, but through-time waning flow events. The channelized deposits might have been laid by rip currents (Sarkar and Koner, 2020), but the snag is that the gutter casts and sole-current features point to bottom-hugging nature of the flows. A more serious snag is the presence of the channels in isolated packages. Juxtaposition of multiple generation channels at same spot would probably mean repetition of localized subsidence.

The convex-up internally massive bodies are likely to be debris flow products. On the other hand, bodies with erosional bases must have been deposited from flows that were turbulent in nature. Presence of innumerable slide planes is indicative of local subsidence that helps to develop local anoxic condition. This local anoxicity favours precipitation of authigenic glauconite in a shallow marine condition (Mandal et al., 2022). Pyroclastic layer often supplies fine sediments which are easily targeted for glauconitization. There may be a possibility that presence of continuous volcanic event to cover the sea water by a thin layer of tuffaceous material which prevent oxygen circulation within the seawater / in a wave agitated zone (Tang et al., 2017) Overall thinning of the sheet sandstones and concomitant increase in shale bed thickness imply a retrogradational trend (Fig.3.7a)

The **Facies C with** higher shale: sandstone ratio suggests that the palaeogeographic position of this facies had been further sea ward. Thinning and decline of the frequency of occurrence of sheet sandstones supports the contention. The decline of the frequency of

occurrence of the sheet sandstone, suggests that the relatively weaker storm could not reach the depositional sight of this facies. Relatively higher frequency of occurrence of channel sandstone indicates that the constricted flows have comparatively higher flow intensity. However, the distal part of the depositional basin, the channels become shallower, as expected. The body geometry of the sandstones and the sole features like prod, brush marks and groove casts preserved at bottom of the sandstones are bears the signature of a storm event (Dzulynski and Walton, 1963; Dzulynski, 1965; Collinson and Thompson, 1982; Ricci-Lucchi, 1995). The internal structures of both the channel and sheet like sandstone i.e., wavy lamination followed by planar lamination are clearly document sand deposition from oscillatory flows like wave and the internally grading indicate temporarily waning nature of the storm (Hequette and Hill, 1993, 1995). The overall sedimentation rate had presumably been low enough to allow prolific growth of microbial consortia.

The depositional environment for **Facies D**, by all indications, had generally been calm and quiet, though fluctuating a bit. As the shale proportion is remarkably high in this facies which imply definitely a comparatively deeper marine condition or at the middle shelf condition. In between the thick shale layers, transport of fine-grained silt certainly needed relatively higher energy input. Deformation of laminae bear indication of tectonic instability already documented in slickensides on sandstone bodies. Glaucontization is more common in muddy sandstones. The shale is sparingly glauconitized because diffusion of potassium from seawater had possibly been inhibited by imperviousness of mud.

The lamination pattern within the channels indicated towards the presence of wave oscillation. The gradual upward thinning of sandstone or siltstone proves that intensity of storm and rate of sedimentation is decreasing. The overall thickness of the sheet sandstone and numbers of channel sandstones decreases upward that depicts deposition under wanning flow. Orientation/ direction of the sole features like groove cast and longitudinal ridges are results of constricted flow; parallel with the gutter cast but other sole marks like prod, skip and brush marks are showing variation in direction. Rose plots of the gutters and prod marks clearly indicate a shift in flow movement from northwest-southeast (NW-SE) to northeast-southwest (NE-SW) (Fig. 3.8). This shift represents a transition from shore-perpendicular to shore-parallel movement.

From previous study it has already been established from the palaeomagnetic data that during the late Proterozoic era, India was situated in the southern hemisphere at a palaeolatitude of approximately 45°S (Williams and Schmidt, 1996; Rao et al., 1997). Gondwanaland

reconstructions based on various geological parameters indicate that India was contiguous with Antarctica, with an open sea to its east (Unrug, 1984; Hoffman, 1991; Condie, 1997). Since breaking away from Gondwanaland, the Indian craton has rotated almost 180° anticlockwise (Unrug, 1984). This rotation suggests an east-northeastern opening of the Vindhyan basin between 750 and 550 Ma. Given this palaeolatitudinal position, the offshore ward downwelling in the nearshore zone veered to the left, making the Coriolis force the most plausible driving factor. So, here the gutter and prod orientation of the present study is shifted from NW -SE to NE-SW (Fig. 3.8)

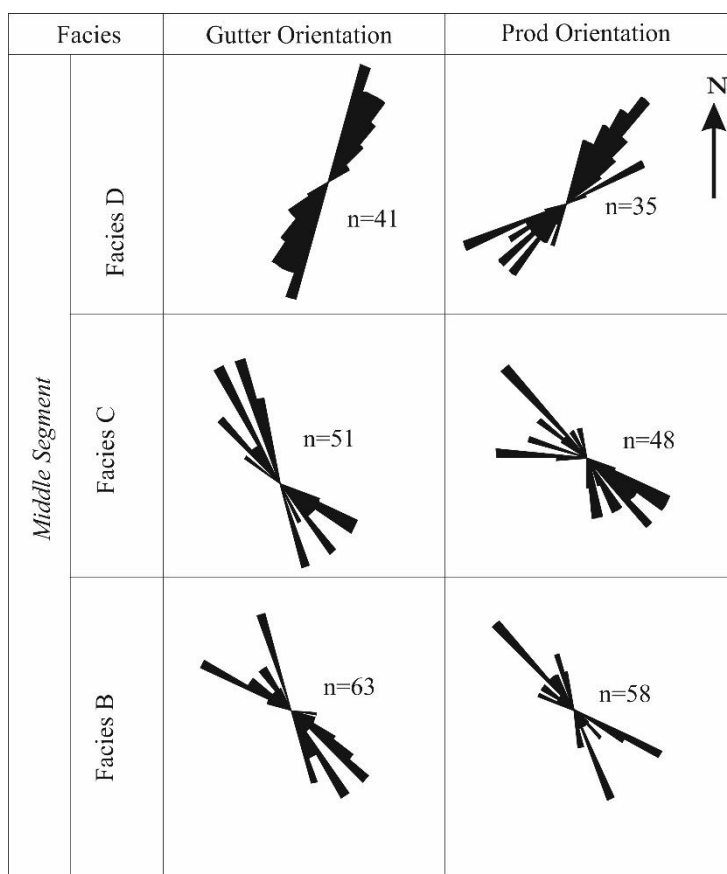


Fig. 3.8: Orientation of both the gutter and Prod marks showing shift from NW-SE to NE-SW. Opening of the Sea at that time was NE-SW.

which is driven by geostrophic currents, which are influenced by the Coriolis force generated by the Earth's rotation (Marsaglia and Klein, 1983; Swift et al., 1983, 1986; Niedoroda et al., 1984; Aigner, 1985; Snedden et al., 1988; Snedden and Nummedal, 1991; Snedden and Swift, 1991; Chakraborty, 1995; Dott, 1996; Myrow and Southard, 1996). The Coriolis force is a deflective force resulting from the Earth's rotation. It acts perpendicular to the direction of motion and to the axis of rotation. In the northern hemisphere; it deflects moving objects to the right, while in the southern hemisphere, it deflects them to the left. When water moves due to the pressure gradient, it is deflected by the Coriolis force. As it continues to move and be deflected, it eventually reaches a point where the Coriolis force balances the pressure gradient force, resulting in a stable, geostrophic flow.

Slicken lines on the slide planes are very common almost all the facies association which is giving a sense of the fault movement. The poles of the slide planes showing a bi-polar orientation which also supports the tectonic scenario of the Vindhyan basin as the basin represents a half graben like structure.

For the uppermost segment, the facies association E are completely devoid of sandstone and facies association E is intensely black in colour which is indicative of a deep marine deposition i.e. product of outer shelf. Light coloured faded shale characterises fine and even laminae with limited textural variability is a likely product of slow deposition in a calm and quiet deep sea but like the black shale, topmost grey shale (faded shale) is not the product of a condensed zone.

3.6: Interesting Aspects of the Rampur Shale under microscope

Usually shales are monotonous, but the Rampur Shale has a variety of primary structures present particularly at the lower part where sandstone/siltstones alternation is present along with shales. Because of the fine grain size, the primary structures are less developed in shale except planar lamination. The resulting monotony of the rocks in field study dictates microscopic study become necessary for those rocks. However, thorough and minutes study of shales provide deep insight into the depositional environment, diagenetic history and palaeo-climatic condition by examining their texture, composition, microscopic level depositional structures if preserved. It also speaks about the alteration scenario of the originally deposited rock. Mineralogical composition also reveals the provenance. Small scale sedimentary structures such as lamination and bioturbation features can signify specific environment and depositional dynamics. By elaboration of small-scale features of sedimentary rock, it is possible to visualize more intricate information related to deposition and diagenesis

During the present study, some particular facies/layers have been targeted from where important revelations made during the microscopic/ultramicroscopic observations. These observations help to enhance and refine the understanding regarding the depositional history of the Rampur Shale so far inferred.

3.6.1: Framework component variations within the facies assemblages from Lower and Middle Segment:

Starting from the sand rich Facies A to siltstone-shale rich Facies D have been studied under microscope. A unique variation has been observed within the quartz assemblages within the sandstone /siltstone alternated facies (Facies A, B, C and D). As observed in field facies classification the sandstone percentage is decreasing with respect to siltstone when moving upward in the stratigraphic succession (from facies A to D). Besides, decreasing of quartz grain size, the percentages of overgrowth bearing quartz grains Polycrystalline quartz grains, rock-fragments also reduced in number up the succession but clay component and zoned feldspar is

common in facies D (Fig. 3.9). Overall, the Sandstones are moderate to well sorted, no marked variations are observed within the facies. Few green coloured sand/silt layers have been observed in association of Facies B, C and D during the field study (discussed in next section). Plenty of pyroclastic fragments along with high amount of silica cement present within the lower part of the Facies B. Facies C and D also contain the pyroclastic fragments but less in number compare to facies B. Pyroclasts, possibly derived from intermittent fine-grained layers. Petrographic view discovered that pyroclasts are concentrated more within the facies B and the sandstone are completely matrix free; framework grains are embedded in a silica cement. This scenario changes at facies D; the pyroclast percentages decreases but that fine muddy matrix as well as patches of fine material is increasing upwards (Fig. 3.10). Several vertical cracks are identified within stratified pyroclastic layer and the layer became fragmented following these cracks (Fig. 3.11a, b) Pyroclastic fragments are known as pyroclasts (Schmid, 1981); which contain crystal fragment, glass fragments and rock fragments (Fig. 3.11c, d). There are different shapes and sizes of pyroclasts are present within the studied thin sections. The pyroclastic fragments are dominantly surrounded by silica cements and silica veins are also common with this association (Fig. 3.11e, f, g). Glass shards contain broken wall fragments of gas bubbles known as bubble wall shards, are present varying in size from 40-70 μ m (Fig. 3.11h, i). They are present as cusate or lunate-shaped fragments as well (Fig. 3.11j). Tripple junction point is a common feature present in this layer (Fig. 3.11k, l). Tripple junction representing remnants of three bubble junctions, or double-concave plates that formed the wall between adjoining bubbles (Pirsson, 1915; Ross et al., 1928; Swineford and Frye, 1946; Ewart, 1963; Heiken, 1972; and others). Tephra, a type of glass shards are also very common in this associations, generally present as various shapes (Fig. 3.11m). Lapilli, also present, are set in a fine-grained ash layer, made up with platy shards tangentially aligned which forming the rim like structure (Fig. 3.11n). Apart from the stratified layer, the rocks of this assemblage contain pumices along with angular to sub-angular quartz grains which contains quenching cracks (Fig. 3.11o).

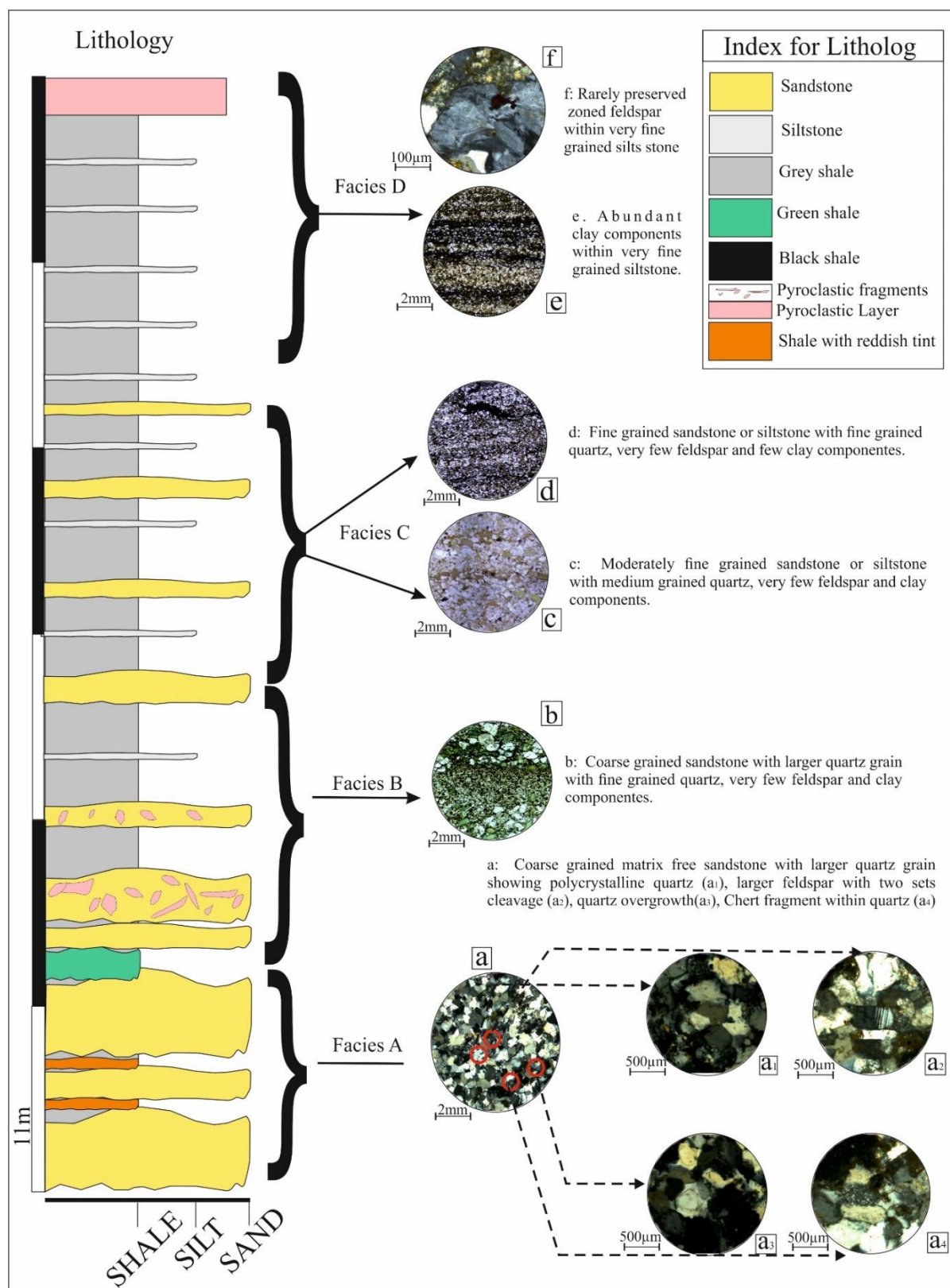


Fig. 3.9: Overall petrographic overview of the sandstone/siltstone bodies present in the Rampur Shale succession; represented with respect to lithologic succession (facies A to D).

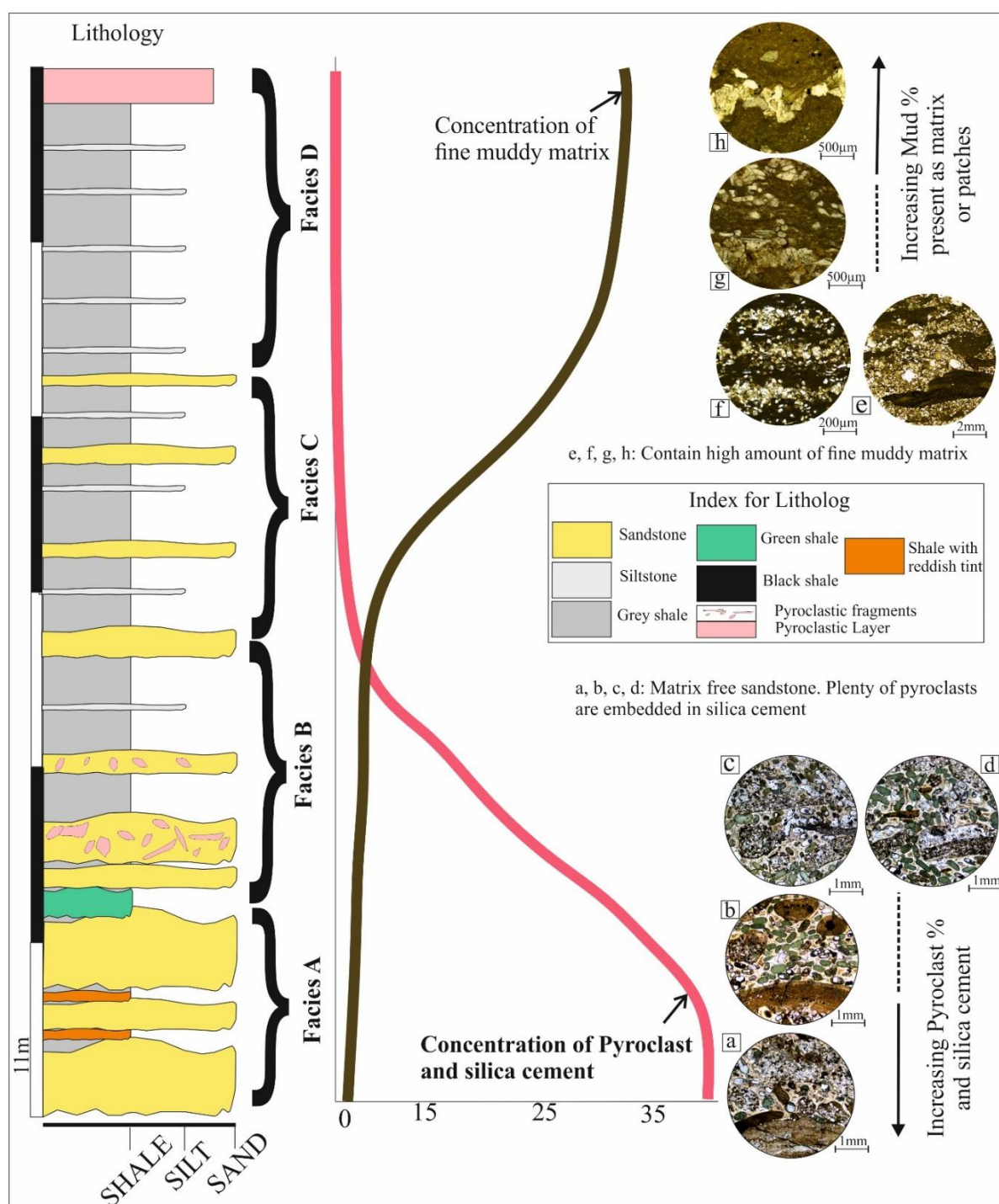


Fig. 3.10: Overall petrographic view of pyroclastic fragments, silica cement and fine muddy matrix present in the succession.

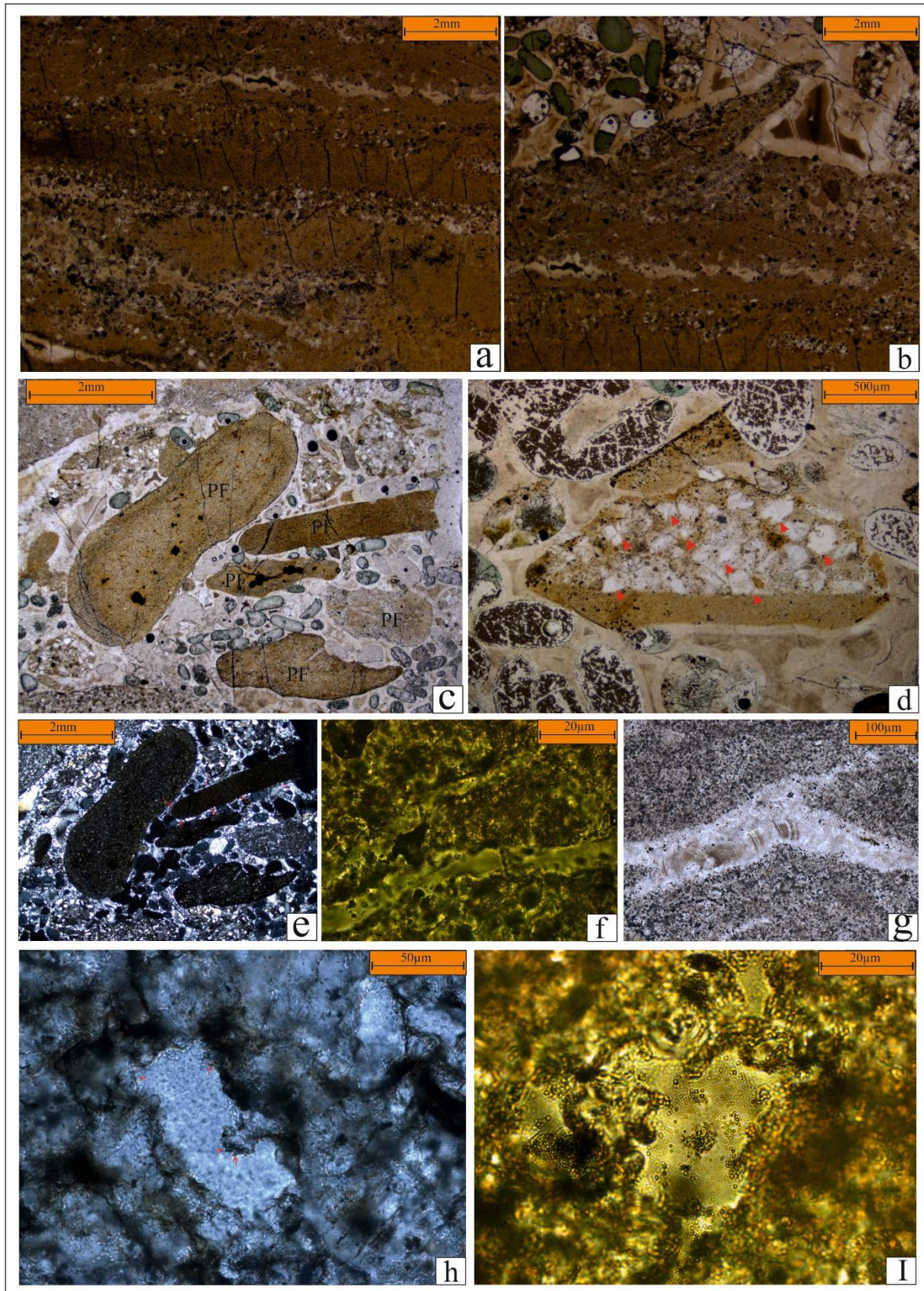


Fig. 3.11: **a)** Stratified Pyroclastic layer along with vertical cracks. **b)** Clasts are generated from the stratified pyroclastic layer. **c)** Pyroclastic fragments present abundantly in the facies B. **d)** Contain, crystals, glass and rock fragments (marked with red arrow). **e)** Silica cement surrounds the pyroclastic fragments. **f) & g)** silica vein has commonly occurred in association with the pyroclast. **h) & i)** Devitrified glass with broken walls of gas bubbles.

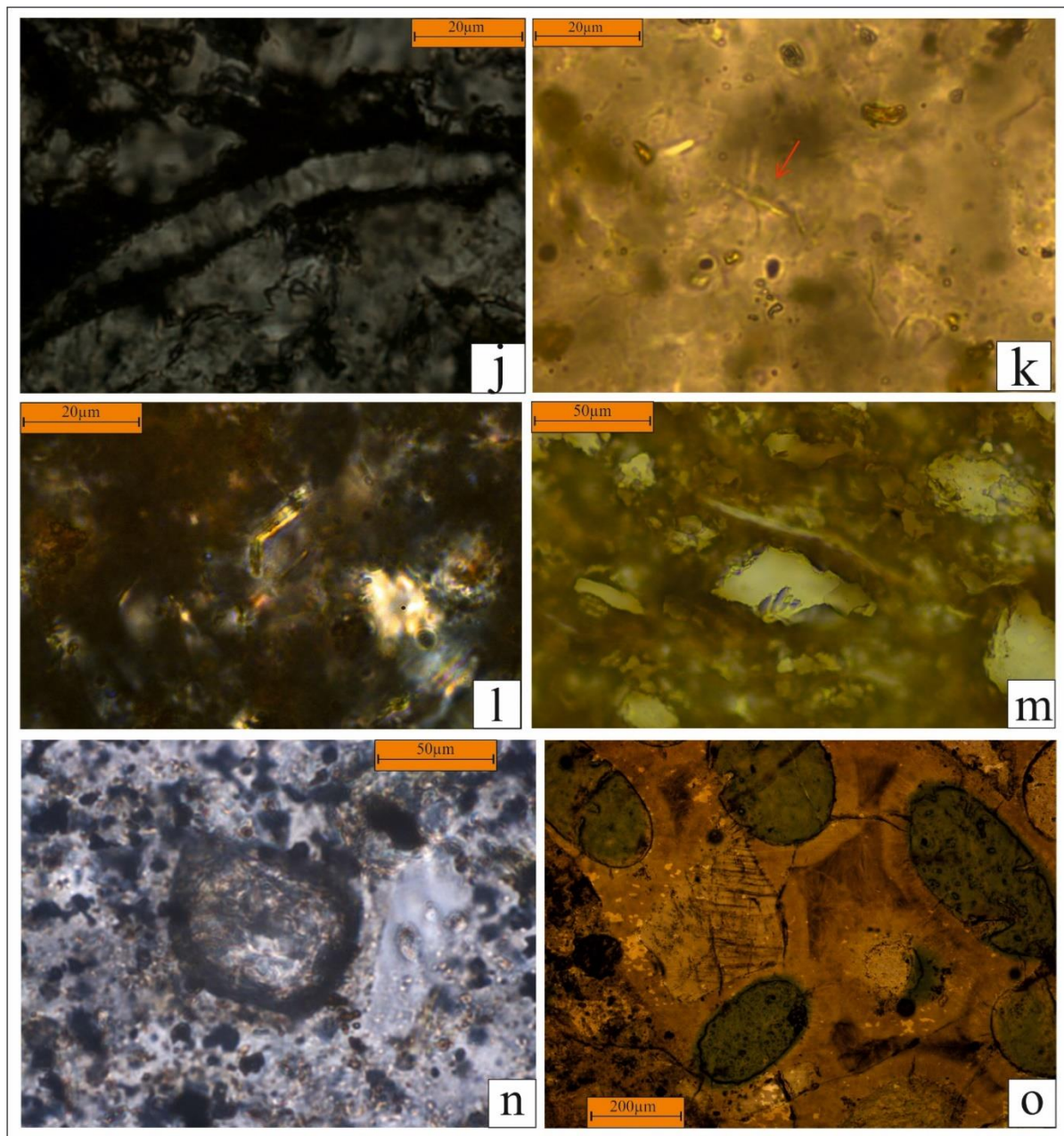


Fig. 3.11 (Continued): **j)** Crescent or cusped shaped glass shards. **k) & l)** Tripple junction point with junction of three bubble wall. **m)** Glass shards with broken bubble wall (tephra). **n) & o)** Lapilli and quenching cracks are recorded under microscope.

3.6.2: Interpretation:

The moderate to well sorted and matrix free nature of the sandstone infers that the sandstones are matured in nature. The presence of more feldspars, polycrystalline quartz grains, overgrowth bearing quartz in the lower part of the facies successions supports the interpretation drawn from the field-based facies analysis. The shoreward part of the facies assemblages likely to be enriched in feldspar, rock-fragments and polycrystalline quartz content. Overgrowth bearing quartz grains also like to be more in the shoreward part, possibly because of their

destruction for more transportation. Presence of pyroclasts along presence of silica cement signifies that there must be some volcanic sources were present. The different shapes and sizes of the pyroclasts are dependent on the disruption process from the volcanic vent or transportation process from the primary source of eruption which is redeposited again within the studied sediments. The rounded to sub rounded pumices also support the contention. They are likely to be generated from the stratified volcanic tuff or ash layer already identified during field study and supports the observation (Fig. 3.11a, b). The gas bubbles with broken bubble walls that are commonly Y -shaped and these are again connected with each other forming junction points also signify volcanic interpretation (Rasmussen et al., 2002). These lapilli are formed in a moist aggregate of ash in eruption clouds, by rain that falls through dry eruption clouds or other processes (Schumacher and Schmincke 1995). The glauconite (will be discussed later) bearing sandstone (within Facies B, C and D) contains few quenching cracks within the quartz grains, indicates that possibly the hot volcanic materials suddenly dipped into the comparatively colder water and due to rapid cooling cracks are developed within the quartz grains and glass as well. The overall scenario indicates that there was a continuous volcanic eruption going on along with the sediment deposition. Decrease in grain sizes from the lower part to successive upper part indicates that the palaeogeography of the depositional system was changed. Coarser grained sandstones were the product of near shore environment but as we move upward, the grain size decreases, it seems like that the palaeogeography of the system moving towards the deeper part of the basin.

3.6.3: Green sandstone/siltstone layer under Microscope:

Sandstone layers with green colour minerals identified within the facies B, C and D. The concentration and mode of occurrence of the green colour minerals could not be identified properly in the field and they are not associated with all the sand layers. The concentration of the green minerals and their size differences are noticed during the field study. Detailed petrographic analysis has been performed to identify the minerals and their variation of mode of occurrences of the minerals present in the different facies. The green minerals identified as glauconites under microscope (the detailed mineralogy and geochemistry of the glauconites discussed in Chapter no. 5) generally associated with coarse to fine grained sheet or channel like sandstone and siltstone body. This green mineral, the glauconites displays a variety of textures, along with two modes of occurrence, such as pellet and cement identified during the petrographic study. The sandstone facies, which hosts abundant glauconite pellets contains subrounded to subangular framework grains of quartz, pyroclastic rock fragments and mica

(biotite), often cemented by silica (chalcedony) cement (Fig. 3.12a). The larger pellets are well rounded with spheroidal to oval shaped but the smaller grains are containing an angular outline basically showing wide variation in their occurrence (Fig 3.12b). Within the facies B, colour of the pellets is varying from green to brownish green (Fig. 3.12c). Glauconite pellets are highly variable in size, shape and colour. Pellets are rounded to sub-rounded and elliptical in shape. Majority of the glauconite pellets show random orientation and appear ‘floating’ within the silica cement (Fig. 3.12a, b). Glauconite pellets exhibit light to dark green pleochroism under plane polarized light and appear bluish green and often exhibit mottled extinction under crossed polarized light (Fig. 3.12d). Some glauconite pellets exclusively bears inclusions of parent material and most of the cases these inclusions are remnant of quartz (Fig. 3.12e). Most of the cases glauconites are completely altered the substrate but in some rare cases it has been found that along the cleavage of the mica or feldspar, glauconite alteration taken place (Fig. 3.12f, g, h). Glauconites present here, in most cases, replacing the previous framework elements like volcanic glass and mimicking the original shape of the glass (Fig. 3.12i, j). Some pellets contain cracks along their boundary (Fig. 3.12k). Pellets amalgamation is frequently noticed (Fig. 3.12l). Often it has been noticed that glauconitization has occurred within the chert cement (Fig. 3.12m). The pellet often bears a dark brown rim around the margin of the pellet (Fig. 3.12n). Authigenic glauconite cement precipitated in the intergranular spaces (Fig. 3.12o). Sometimes it has also been noticed that pellet is developing from the cement precipitation (Fig. 3.12p). Overall, the glauconites of the facies B shows a floating texture within the silica cement; most of the cases glauconite pellets are well rounded embedded in the crystalline silica cement (Fig. 3.12a, b) and the cement form is filling the interstitial spaces between the glauconite pellet and other framework grains (Fig. 3.12q). At facies C, the pellets preferably follow the depositional laminae (Fig. 3.12r). Maintaining similarity with the framework grain, the size of the pellets are getting smaller as we move to the younger facies in the stratigraphic succession. Somewhere pellets are vertically arranged with respect to the bedding plane (Fig. 3.12s). Glauconite concentration is less compared to the facies B. if we concentrate on facies D, we can see sand proportion is less than the shale in these facies. As, glauconite pellets are mainly associated with sandstone, the pellet percentage is again decreases with the sandstone. Apart from the glauconite clay bearing mud, glauconite pellet and few deformed mud clasts are also observed (Fig. 3.12t). Fine muddy matrix is present within which small glauconite and other framework grains are set in (Fig.3.12u). Often glauconites show a close proximity with the pyroclastic fragments. Glauconite pellet recorded even with both coarser and finer fraction of pyroclastic fragments (Fig. 3.13a, b, c, d).

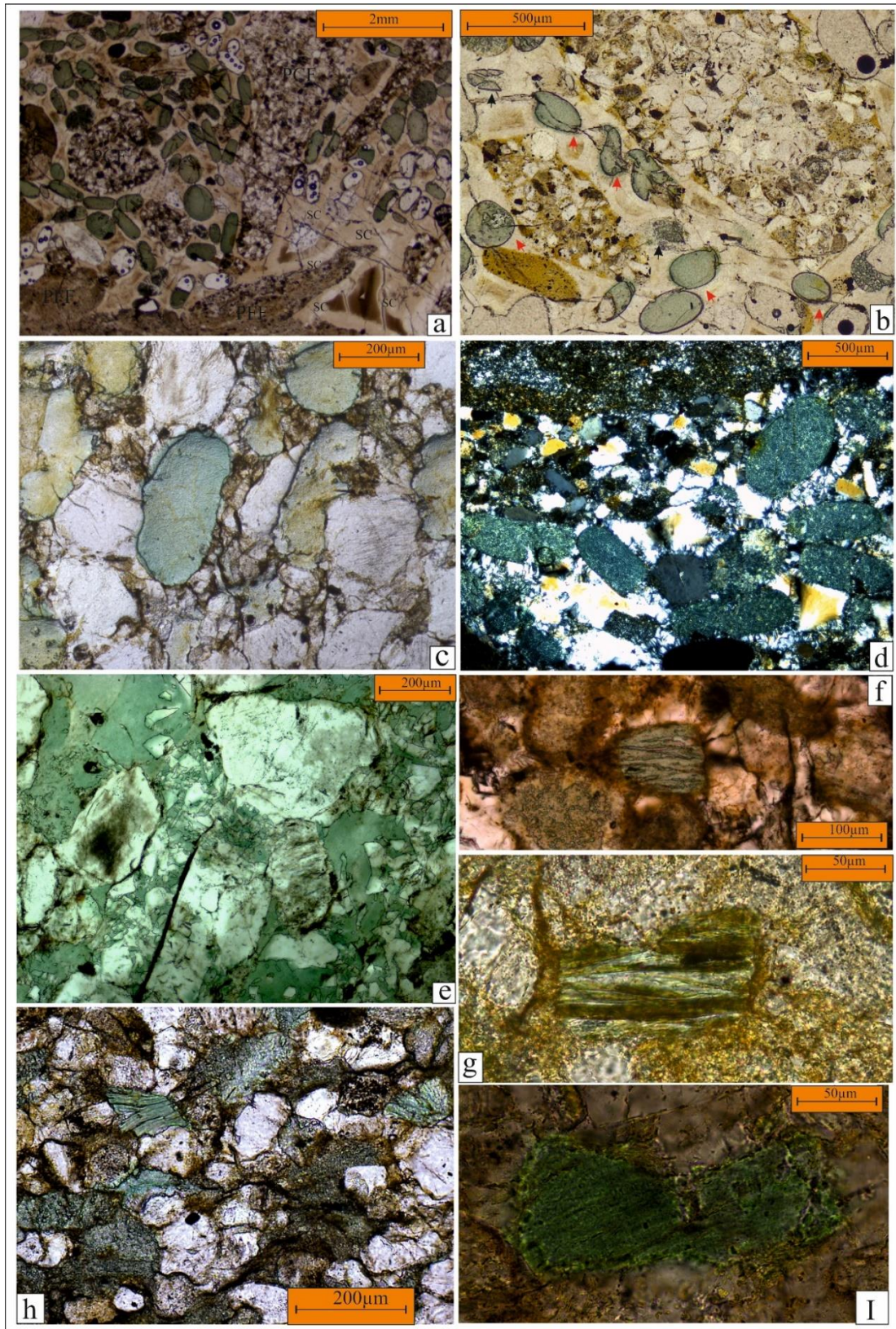


Fig: 3.12: **a)** Glauconite pellets associated with coarser (PCF) and finer (PFF) fractions of pyroclasts, embedded in a silica cement. **b)** Larger pellets are well rounded but smaller fractions of glauconites are subangular. **c)** Glauconite pellets with two different colour variation. **d)** Glauconite under cross polar light. **e)** Quartz inclusions within glauconite pellet. Glauconite replacing **f)** feldspar, **g)** & **h)** mica and **i)** volcanic glass.

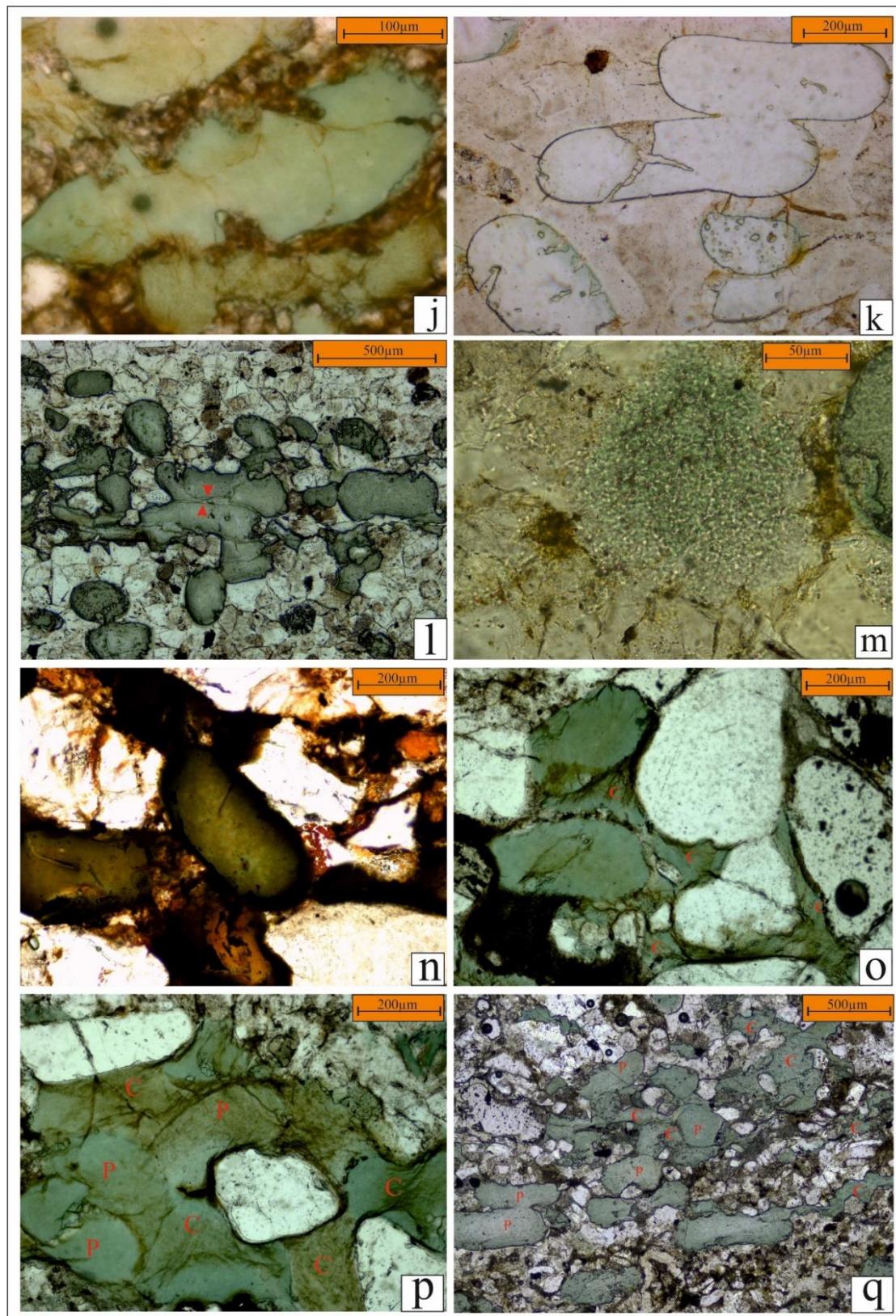


Fig. 3.12 (Continued): **j**) Glauconite mimicking the shape of volcanic glass. **k**) Septarian crack within Glauconite pellet. **l**) Pellet amalgamation is commonly observed. **m**) Glauconite replaces the cherty cement. **n**) Brownish rim around the glauconite pellet. **o**) Glauconite cement precipitated in the intergranular spaces. **p**) & **q**) Glauconite pellet is generated from authigenic glauconite cement (p=pellet & c=cement).

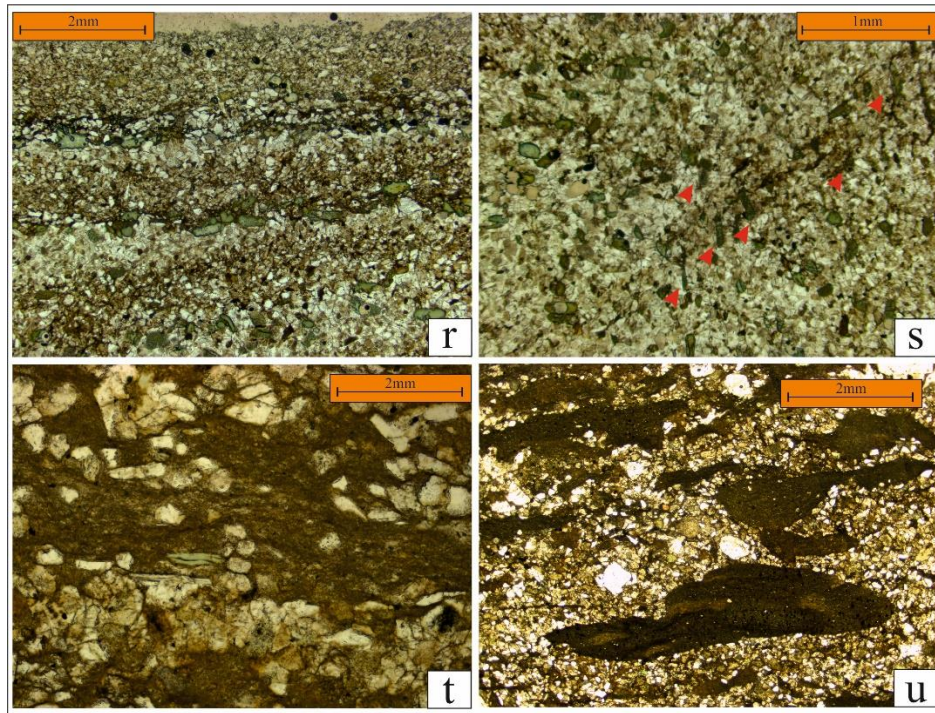


Fig.3.12: r) Galuconite pellets are smaller in size and following the depositional lamina. **s)** Few pellets are showing vertical orientation with respect to bedding plane. **t) & u)** Muddy component is increasing at facies D, deformed patches of clay components are common in this section.

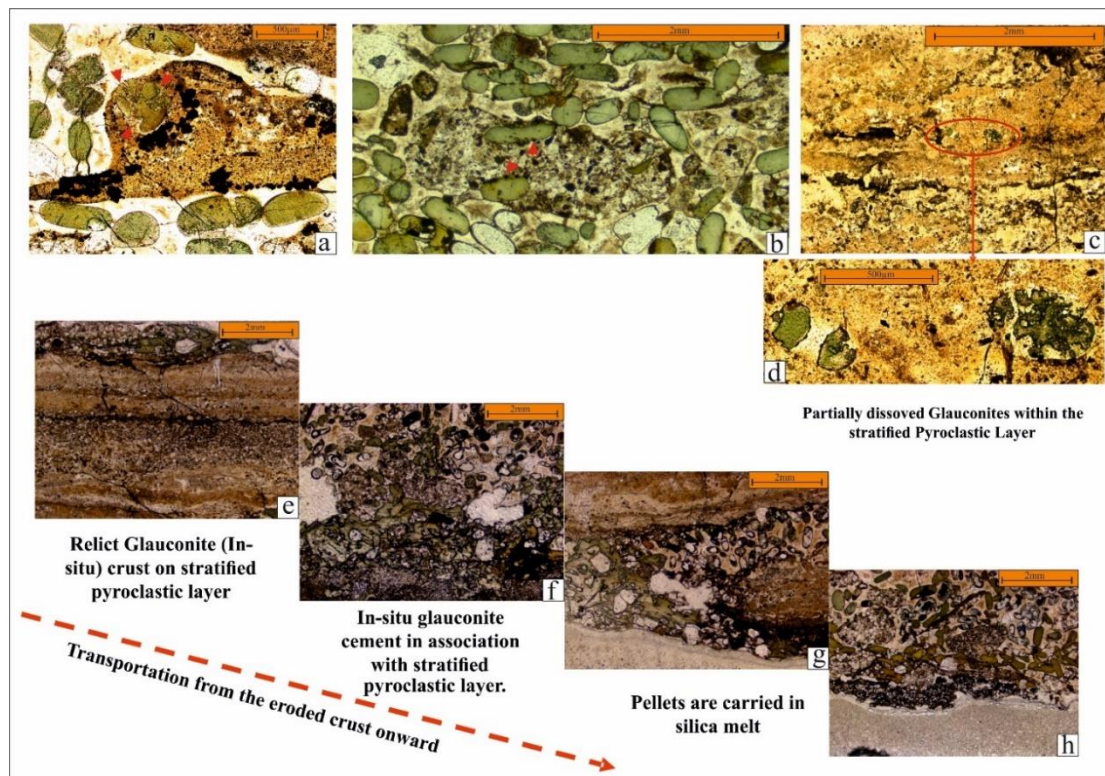


Fig. 3.13: a) Glauconite pellets within finer pyroclastic fragments (arrowed), pyrites are also noticed. **b)** Glauconite pellets within coarser pyroclastic fragments (arrowed). **c) & d)** Glauconite pellet in association with stratified pyroclastic layer. **e)** Thin glauconite crust at the upper part of stratified pyroclastic layer. **f)** Glauconite cement within pyroclastic layer. **g) & h)** both pellets and pyroclasts are embedded in silica cement.

3.6.4: Interpretation:

Glaucinite is a green clay mineral generally associated with sedimentary rocks, deposited in a shallow marine condition under dysoxic/suboxic to anoxic environment, where sedimentation rate is comparably low. This clay mineral is highly sensitive to palaeogeography, palaeoredox and sedimentation rate (Banerjee et al 2015; Mandal et al., 2020, 2022; Nieto et al 2021). As discussed earlier the Rampur shale had been deposited in a shallow marine shelf originated environment. The Rampur Shale Member constitute few Para sequences all through the succession and the glauconites are mostly concentrated at the upper part of the para sequences in two different modes like thin film/matrix mode and pellet like rounded form. Volcaniclastic material dominated two layers are identified at the two different level of the Rampur shale Member and surprisingly glauconite bearing lithology sharply appeared from this first volcano-sedimentary level and gradually the abundance of the glauconite layer varies as move upward (detail discussion in chapter 5). At facies B, Petrographic study reveals that the glauconite pellets are varying from green to brownish green. Green colour is basically the original colour of the glauconite clay but the brownish tint developed possibly due to oxidation of the clay pellet. Sometimes the pellets contain cracks at their edges. The glauconite contains water in their structure, during burial of the mineral, dehydration can occur causing shrinkage and cracks developed. During diagenesis process the chemical and physical conditions of the depositional systems are changed, leading to the growth and coalescence of glauconite grains. The diagenetic environment often promotes the amalgamation of smaller pellets into larger masses. The glauconitization usually preferred feldspar grains for alteration. As glauconite mostly reported form marine environment possibly the availability of elements like iron and potassium within this regime (Burst 1958; Tribovillard et al., 2023). Feldspar, muscovite and biotite are rich in iron and potassium as well as they have well defined cleavage planes; through which sea water can percolate within the mineral structure and there is an ion exchange occur between the pre-existing mineral and marine water (Thompson and Hower, 1975). This exchange of ions can facilitate the replacement of the original mineral structure with glauconite. The quartz does not contain any type of cleavage plane but the grains contain fracture. The angularity of the quartz grains indicating towards their volcanic origin. So, there must be some hydrothermal fluid (rich in iron, magnesium, potassium) was present which percolate through the fractures of the quartz and ion exchange process was performed between quartz and hydrothermal fluid which possibly facilitate the glauconite mineralization. Just like the quartz grain alteration, volcanic glasses are also targeted for glauconitization where mineral rich hydrothermal fluid percolate through the fracture and helps to altered the glass to

glaucinite. Chert cements are made up with cryptocrystalline silica/ quartz which formed through silica precipitation from silica saturated water in marine environment. The alteration process initiates with increased alkalinity or the presence of organic acids (Presence of organic activity within the sandstone is already discussed) under which silica can become more soluble. Iron and potassium must be introduced into the system for glauconite formation, that typically occurs through the circulation of seawater or hydrothermal fluids that are rich in these elements. The silica dissolution releases silicon (Si^{4+}) into the pore waters and make available space for new mineral formation. Glauconite crystallization initiated in presence of iron (Fe^{2+}), potassium (K^+), and dissolved silica. Glauconite forms as a phyllosilicate mineral. The iron (Fe^{2+}), potassium (K^+), and dissolved silica allows growth of glauconite crystals as a phyllosilicate mineral (Meunier, and Albani, 2007; Huggett 2013; Rudmin et al., 2017). Glauconite may initially form on the surfaces of existing chert particles or within the voids created by the partial dissolution of chert (Ivanovskaya et al., 2019). As the glauconite matures, the mineral undergoes further chemical changes, and a dark brown rim is developed outside due to iron enrichment following the pellet margin. Glauconite fills the intergranular spaces by authigenic precipitation. It has been also noticed that small pellets are amalgamated altogether, squeezed by external pressure and form cement in between the other resistant glauconite pellets and framework grains (Mandal et al., 2020). A thin crust of glauconite mineral is observed above the stratified pyroclastic layer which contain few vertical columnar cracks within it. The pyroclasts were generated from the stratified layer along the cracks. Presence of silica cement along with the glauconite and pyroclasts indicate that there must be some outsourcing of silica cement and they carried both the glauconite and pyroclasts within the sandstone (fig. 3.13e, f, g, h). At facies C the glauconites are found to align with the depositional lamina which indicate, that the glauconite pellets are reworked and locally transported, again deposited following the lamination like planar and cross lamination as well (Chafetz 1978). Few pellets are identified as vertically arranged with respect to the bedding plane indicated that there must be some tectonic disturbance present during the deposition. As we move upward the grain size of the sandstone gradually decreases and maintaining the size range, size of the pellets also decreases. Compare to sand proportion mud content is increasing at this facies D, where muds are basically glauconitized. Few large phenocrysts sized zoned feldspar is commonly present which confirms their volcanic origin.

3.7: Sequence Stratigraphic Scenario of the Rampur Shale

The Rampur Shale Member (RS) of the Semri group consists of shale and sandstone deposited in a marine shelf environment, spanning over shallow to deeper part (Sarkar et al., 2002, Sarkar and Banerjee, 2020). The colour of the shale mostly varies from grey to black, with change of palaeogeography of the succession. There is one unique green shale layer present at the initiation of facies B. Considering the sand: shale ratio, presence of primary sedimentary structures and geometry of the sandstones, the entire succession of Rampur Shale is divided into three segment and six distinctive facies (Fig. 3.2-3.7) with variation in palaeogeographic disposition. The lower most facies association dominated by well sorted medium to fine grained sandstone (Sand: Shale=4:1) bearing signatures of storm events. Plenty of mud clasts are present within the sandstone beds also support the contention.

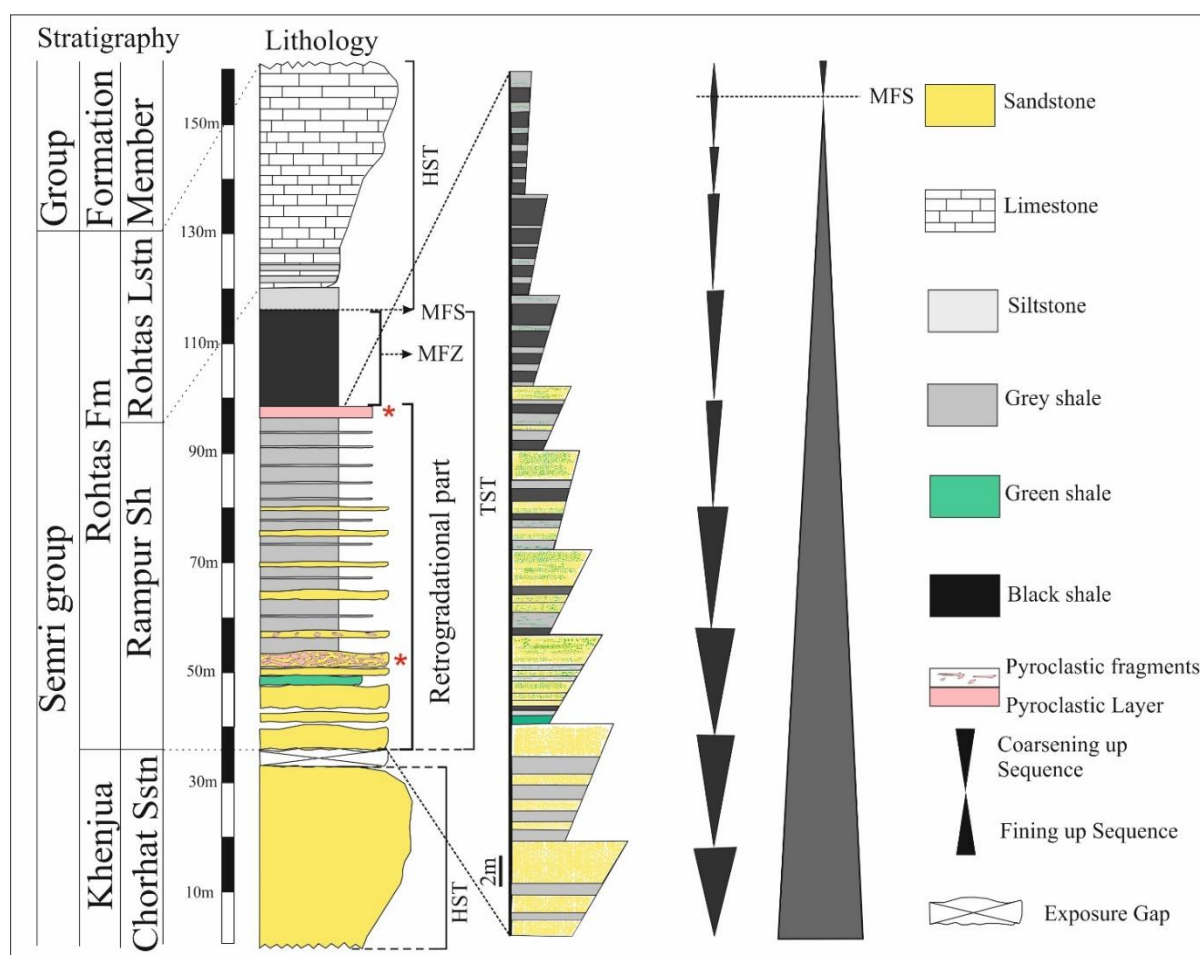


Fig. 3.14: Sequence stratigraphic succession showing sequence stratigraphic elements within the Rampur Shale Member. Overall fining upward TST sequence contain few coarsening up parasequences are marked and glauconites are present at top of the parasequences.

Proliferation of microbial activities is preserved within thick sandstone beds intervening few cm thick shale layers at the basal part. The underlying Chorhat sandstone ranging in

palaeogeography from subtidal to intertidal typically represent a HST (Fig. 3.14). The Rampur Shale represents a typical TST except 3 meters at the top part which is part of overlying HST. The base of the Rampur shale is dominated by sandstones with intermittent presence of shale clasts of ~12m thick, followed by sandstone/siltstone and shale alternations followed by black shale, forming the retrogradational package. This scenario typically indicates towards the end of underlying HST followed by an initiation of a TST sequence (Fig. 3.14). After the sandstone dominating segment, the middle part, approximately 55m thick mostly consists with sand-silt-shale alteration but shale proportion is gradually increasing towards the upper part of the succession which indicate an outer shelf palaeogeography. Field observation suggests individual coarsening-up cycles (parasequence) are present within the lower retrogradational part (Fig. 3.15). The cycles generally initiate with fine-

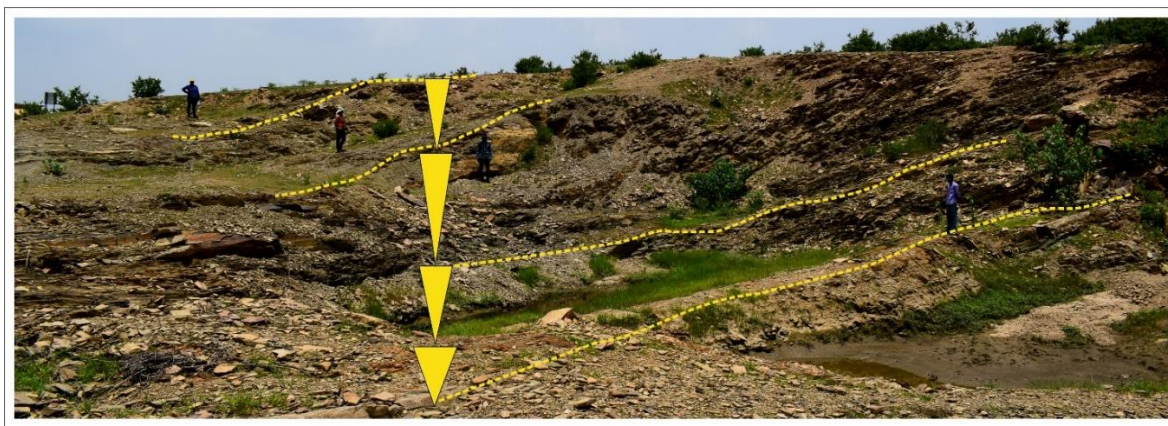


Fig: 3.15. Para sequences identified in the field. Individual package are marked by yellow lines.

grained shale followed by shale/sand alternation and terminates with sandstones (Fig. 3.14, 3.15). Depending upon the facies and sand shale ratio present at the middle part which shows that this part of the Rampur shale is part of a Transgressive system tract (TST). The glauconites are associated within some of these parasequences, generally occupying the top part of the parasequences (Fig. 3.14). The coarsening up parasequences possibly forming because of intermittent subsidence of the Rampur shale basin (the details will be discussed later in chapter 5). The presence of glauconite and slide planes also suggests deepening of the substrate in local scale, possibly help to develop the coarsening up cycles, the parasequences. The presence of glauconite within the enveloping sediments and omnipresent wave imprints within the underlying packages of the RS prompts the marine origin of the Rampur Shale. (Mondal et al., 2022; Tribovillard et al., 2023). Pyroclastic deposits have also been recorded within the RS at two different levels (Fig. 3.14). The upper segment is dominated by black shale within the Rampur Shale Member in the Lower Vindhyan sequence is approximately 15m thick forming

a maximum flooding zone (MFZ). this zone is followed upward by an approximately 3 m thick faded shale upward (Fig. 1a; Mondal et al., 2022). The faded shale forms the base of another major HST which included the overlying Rohtas limestone. The formation under focus here represents a total retrogradational sequence and part of a HST. Overall, the RS is sandwiched between two marine progradational members (Fig. 3.14), the lower part constitutes by the Chorhat Sandstone a HST followed upward by a transgressive system tract (TST) with a condensed zone at the top, characterized by a thick black shale deposit representing the maximum flooding zone (MFZ, Fig. 3.14).

3.8: Conclusion

Overall, this chapter discuss about the facies, palaeogeography, petrography and sequence stratigraphic overview of the whole Rampur Shale Member. Detailed field study followed by petrographic observation reveals that Rampur Shale is represents a fining upward retrogressive sequence with some small coarsening up packages present within it, likely to be the constituting parasequence set. The lower part of the Rampur shale is sand dominated enriched with plenty of microbial mat related structures. Shale proportion is very minimal and sand body contains signatures of primary structures influenced by both wave and storm. Sandstones are matrix free and comparatively coarser in nature. As we move upward, sandstones became finer, mud content increases, storm features are also decreases than the basal part. Microbial mat induced feature is common all through the Rampur Shale. Sandstones, siltstones are rich in glauconite minerals and occasionally, shales are also display glauconite mineralisation within. Different modes of occurrences are noticed within the glauconitic sediments of the middle segments display a close relationship with pyroclastic layer present in the succession. Numerous slide planes with slicken lines are present at the bed surface indicate continuous local subsidence which are passively helps to build up the parasequences. Prod marks are indicating the presence of geostrophic current during sedimentation. Black shale is signifying the maximum flooding zone. So, overall Rampur shale is a deposition of shallow shelf to deeper part of the basin representing a TST sequence. The uppermost grey shale indicates initiation of another HST followed by deposition of Rohtas Limestone.

CHAPTER: 4

GEOCHEMICAL ATTRIBUTES

OF

THE RAMPUR SHALE

4.1: Introduction

Shale is the geochemical treasure hunt of nature because of its extraordinary potential to preserve the geochemical oddities within it. Especially, black shale preserves much information of the earth's history through preserving major, trace and REE elements present within it. The geochemical signatures in black shale, such as trace metal concentrations and stable isotope ratios, provide valuable information about past depositional conditions such as provenance, palaeoclimate, palaeo-weathering pattern, palaeoredox and palaeo-depositional scenarios. Black shales are often enriched in economically valuable metals such as nickel, zinc, copper, and cobalt and rare earth elements (REEs). The weathering of black shales can also release these trace metals and other elements into the environment, impacting soil and water quality.

The Mesoproterozoic Era (1.6 Ga to 1.0 Ga) was an unusual time in the earth's history (Bradley, 2011; Roberts, 2013; Condie, 2021) as it belongs to the “Boring Billion” (1.8 Ga to 0.8 Ga) period (Holland, 2006). Despite being deposited during this Boring Billion period, the Mesoproterozoic Rampur Shale Member reveals a lot of geochemical information regarding the provenance, palaeoclimate, palaeo-weathering, palaeoredox conditions and the depositional scenario of the then Vindhyan Basin (Condie et al., 2001; Manikyamba et al., 2008; Basu et al., 2017; Condie 2021; Xiao et al., 2022; Xie et al., 2023).

This chapter discusses the detailed geochemical attributes of the Rampur Shale Member, following the facies classification. It is already mentioned in previous chapter that, the retrogressive part of the Rampur shale combining lower and middle segment (i.e., facies A, B, C, D) is dominated by sand-silt-shale alternations. Sand-shale ratio varies from facies A to D, whereas the upper segment consists of facies E and F is devoid of sandstone. For geochemical analysis, mostly the shales and associated sandstones/ siltstones from all the facies (A-F) of the Rampur Shale Member have been considered. To maintain the synchronicity with the facies classification, the geochemical analysis of the Rampur Shale is divided into two parts. First part contains the geochemistry of the retrogressive part (lower and middle segment) containing facies A, B, C and D. The other part contains the geochemistry of the shale dominated segment comprising facies E and F. There are some overlapping inferences which support each other, but as they have been analysing separately from different facies, the discussion kept separately according to the delineated segments. The glauconite bearing sandstones of facies B, C and D have been considered for the

geochemistry of glauconite present in Rampur Shale Member. However, the objectives are as follows,

1. To understand the provenance of the Rampur Shale Member
2. To reveal the Palaeoweathering scenario of the studied succession
3. To infer the palaeoclimatic condition
4. To recognise the palaeogeography of the depositional basin
5. To estimate the Palaeoredox scenario
6. Facies wise detailed geochemistry of glauconites present within Rampur Shale.

4.2: Major Element Geochemistry

Overall, the facies A, B, C and D (already discussed in Chapter. 3) are dominantly consists of sand/silt-shale alteration. As mentioned earlier the sand: shale ratio has marked differences within those facies.

Facies A consists of sand: shale ratio with 4:1. The shales within these facies show low Al_2O_3 concentration $\sim 9\%$ while the SiO_2 concentration is very high $\sim 83\%$. Concentration of CaO, MgO, and Na_2O is very less within this facies (Table 1). Average content of CaO percentage is negligible (~ 0.025), MgO percentage is 0.37 and average $\text{Na}_2\text{O}\%$ shows near about 0.2 weight percentage. Average Fe_2O_3 , K_2O and TiO_2 content is 1.5%, $\sim 4.5\%$ and $\sim 0.25\%$ respectively (Table 1).

Facies B, where the sand: shale ratio is 3:2 contain green coloured shale which is unique in its composition. The shale comprising of 17-18% of Al_2O_3 , 62-63% of SiO_2 while the average Fe_2O_3 content is 2-2.5% and K_2O % is $\sim 11\%$. MgO content within the shale varies between 4-4.5% (Table 1). CaO and TiO_2 percentages are also very low (Table 1). On the other hand, the grey shales present within this facies contain 14-15% Al_2O_3 , 71-72% SiO_2 , $\sim 3.5\%$ Fe_2O_3 and $\sim 6.5\%$ K_2O (Table 1). Average MgO content is near about 2 weight %. Both CaO and TiO_2 % is very low $\sim 0.1\%$ and $\sim 0.4\%$ respectively. The sandstones are mostly glauconitised which contain 10-11% of Al_2O_3 , ~ 72 -73% of SiO_2 , near about 4% Fe_2O_3 , 6% of K_2O , $\sim 2\%$ of MgO, $\sim 0.2\%$ CaO and $\sim 0.3\%$ of TiO_2 is present within the sandstones (Table 1).

Facies C shows sand: shale ratio with 1:2. The major element concentration of the shales of this facies shows that Al_2O_3 varies between 15.03-18.2 wt % (Avg. 16.77 %). SiO_2

content within this shale ranges between 67.02-72.3 wt % (Avg. 69.38%), Fe_2O_3 content varies between 3.14-4.5 %, K_2O content ca ~6.6-7.2%, Average MgO content is near about 2 wt%, Both CaO and TiO_2 % is very low ~0.1% and ~0.4% respectively (Table 1). Sandstones contains less amount of Al_2O_3 (~8.5%) but higher amount of SiO_2 (near about 82%) than the previously described shales. Fe_2O_3 , K_2O both are showing low value; ~2.85% and ~3.93% respectively. MgO content is slightly higher, near about 2.64 weight%, Both CaO and TiO_2 % is very low ~0.1% and ~0.15% respectively (Table 1).

Facies D contains sand: shale ratio 1:5. The shales shows variations of Al_2O_3 content within the shales vary from 14.5 to 16.7% and while within the siltstone components, it ranges between 12.4-17.6%. SiO_2 concentration in shales varies in between 69.1-73.7% while for the siltstones this range varies from 66.8 t-76.8% (Table 1). Average Fe_2O_3 concentration in shales is ~3.83% and in siltstone the value is ~3.5%. K_2O concentration in shales is ~7.14% while that in siltstone shows an average value near 6.55%. Average MgO content in shale is 1.61 and the siltstone of this facies contains 1.66% of MgO . CaO , TiO_2 and Na_2O is present both in shale and siltstone in very negligible amount (Table 1).

Facies E is completely devoid of sand / siltstone and dominated by a thick black shale deposition. Al_2O_3 concentration within black shale varies between 6.56 to 17.6 % with an average concentration of 13.02%. SiO_2 % varies from 50.94-86.94% (avg. 67.05). Average Fe_2O_3 concentration in black shales is 1.89% (varies from 0.51-3.61%) (Table 2). CaO % varies between 0.07 to 20.56 with an average value of 5.01%. K_2O value shows a variation between 3.08 to 16.06% with an average value is 9.83%. MgO shows a value raging between 0.19 to 10.87% (Avg. 2.59%). TiO_2 % is very less in the black Shale with an average value 0.04 weight % (Table 2).

Facies F is the topmost sequence of the Rampur Shale Member. Al_2O_3 concentration within this shaley part varies between 7.43 to 16.58 % (avg 11.47%). SiO_2 % varies from 65.31-85.17% (avg. 76.27%). Average Fe_2O_3 concentration in this facies is 2.3% (varies between 0.93-3.38%). CaO % varies between 0.05 to 0.54% with an average value 0.22%. K_2O value shows a variation from 3.35 to 15.26% and average value near 7.66%. MgO shows a value raging between 0.2 to 1.69% (Avg. 1.05%). TiO_2 % is recorded very less amount with an average value of 0.34 weight % (Table 3).

4.3: Trace and Rare Earth Element Geochemistry

Trace and Rare Earth Elements including yttrium (REY) of all the facies were normalised against Average Shale value (Wedepohl 1971). Average shale is a standard, which provides a comparative baseline that represents a mixture of several shale samples collected from different formations. By normalizing against average shale, geologists can identify anomalies or deviations from the expected elemental abundances in different geological samples.

Facies A shales are depleted in trace element concentration compared to average shale value (Fig. 4.1, Table 4). Co, Zr and Hf are slightly enriched rather than the average shale composition. REY pattern is showing a negative trend from LREE to HREE. LREE are slightly enriched than that of the HREE (Fig. 4.2). Average LREE/HREE ratio in this facies is quite high (>14.5) (Table 5).

Facies B again showing depletion in most of the composition of the trace elements. Few shale samples are showing slight enrichment in Li, Ga, Rb, Zr, Cs, Hf, U and Th (Fig. 4.3, Table 4). Especially the green shales are showing a little enrichment in REY concentration (Fig. 4.4). Other samples are either similar or depleted than the standard baseline. LREE/HREE ratio ranges between 7.5-12.4 (Table 5).

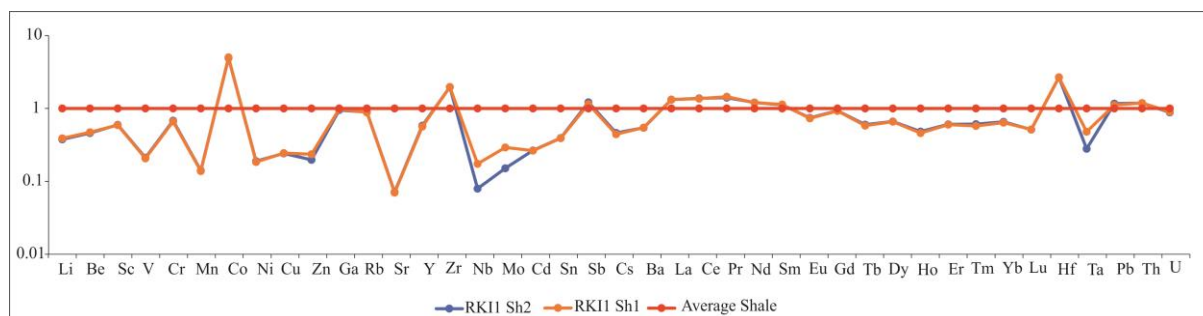


Fig. 4.1: Trace element concentration in the facies A (respect to Average Shale).

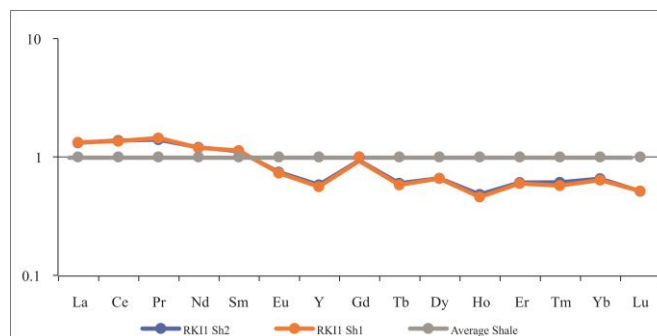


Fig. 4.2: REY concentration in the facies A (respect to Average Shale).

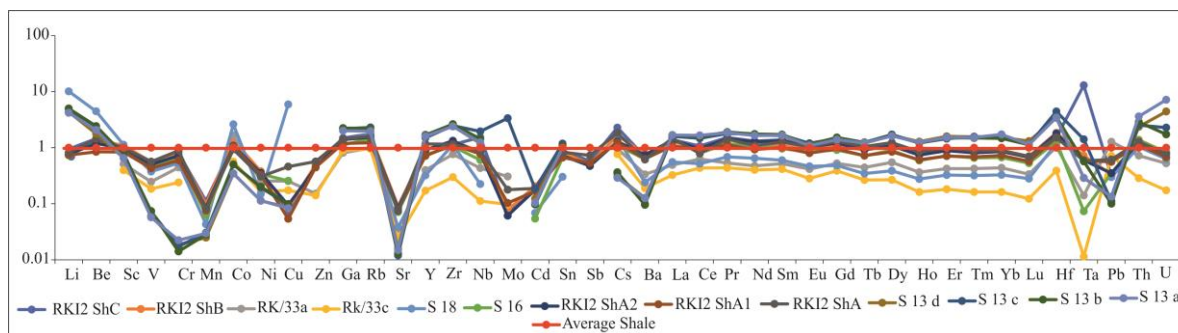


Fig. 4.3: Trace element concentration in facies B (respect to Average Shale).

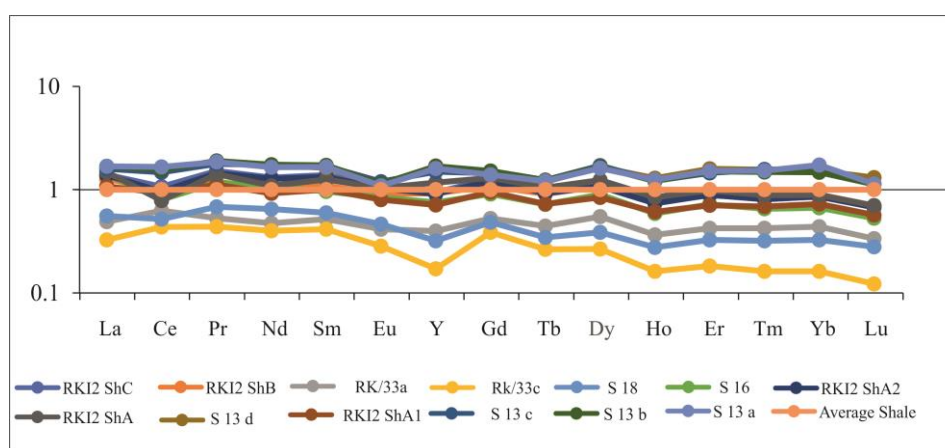


Fig. 4.4: REY concentration in the facies B, (respect to Average Shale).

Facies C reflects depletion from the standard baseline. Except Li, Be, Co, and Cs, all the trace elements are depleted in the studied sample in comparison to the average shale (Fig. 4.5, Table 4). The shale samples of this facies do not follow a definite pattern but the glauconitic sandstones are showing depletion in REY content than the other shale samples (Fig. 4.6). LREE/HREE ratio are slightly lower than that of the glauconitic sandstone component present in this facies C. Average LREE/HREE ratio for glauconitic sandstones hold greater value (>11) than the shales of this facies (avg. value ~ 8.87) (Table 5).

Facies D reflects slightly enriched Co, Ga, Rb, Zr, Cs, Hf, Th content in the samples but rest of the elements are depleted compares to the average shale value (Fig. 4.7, Table 4). Few shale samples of this facies are enriched in LREE than HREE but most of them are are depleted from the standard baseline (Fig. 4.8). LREE/HREE ratio for both the siltstone and shale are varies between 5.98-11.71 (Table 5).

Facies E, the black shale contains a higher value of selenium which is overshadowing all the other trace elements (Fig. 4.9, Table 6). Other than Selenium (Se) this facies is

enriched in Zn, Hf, Yb and Th concentration (Fig. 4.9). REEs are not showing any specific trend (Fig. 4.10), LREE/HREE holds an average value of 7.39 (Table 7).

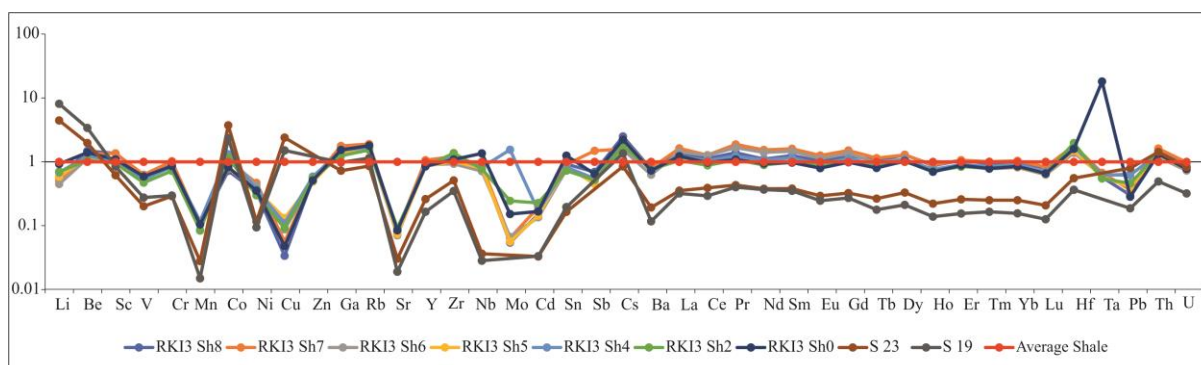


Fig. 4.5: Trace element concentration in facies C (respect to Average Shale).

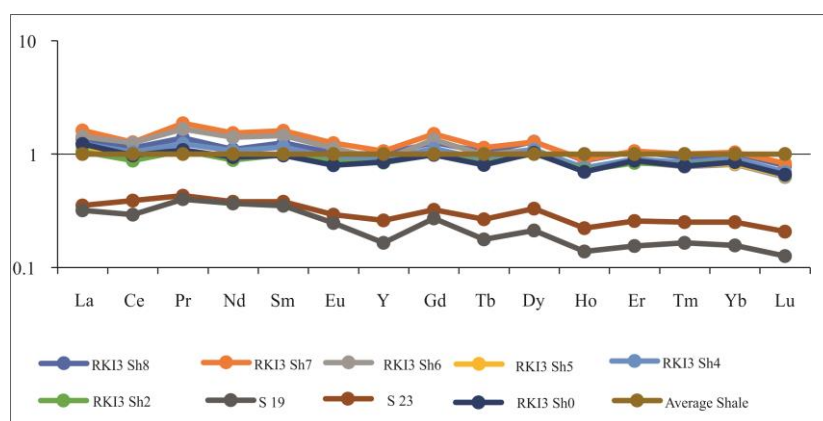


Fig. 4.6: REY concentration in the facies C, (respect to Average Shale).

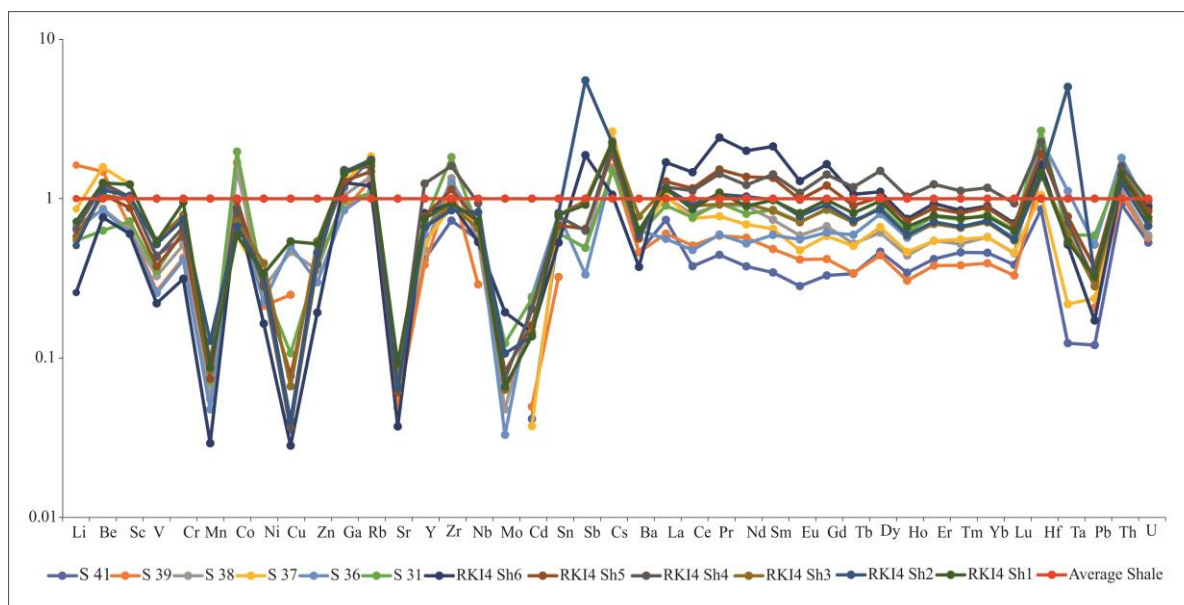


Fig. 4.7: Trace element concentration in facies D (respect to Average Shale).

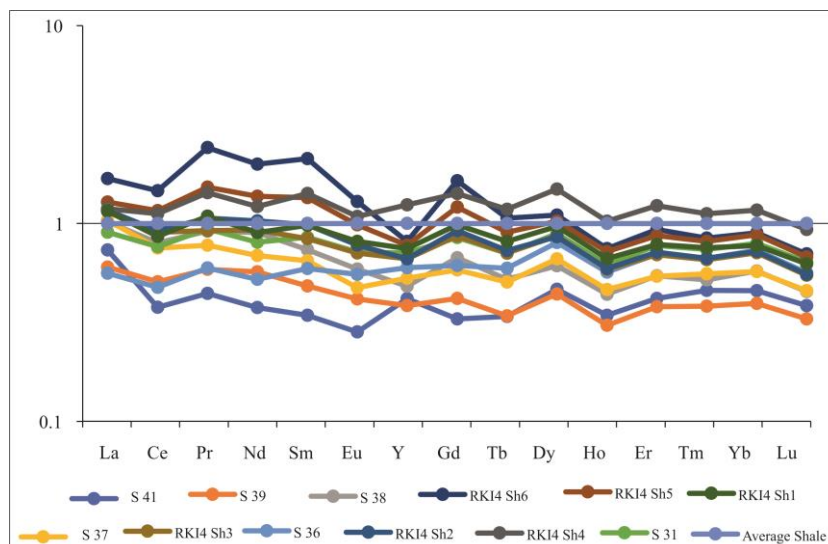


Fig. 4.8: REY concentration in the facies D (respect to Average Shale).

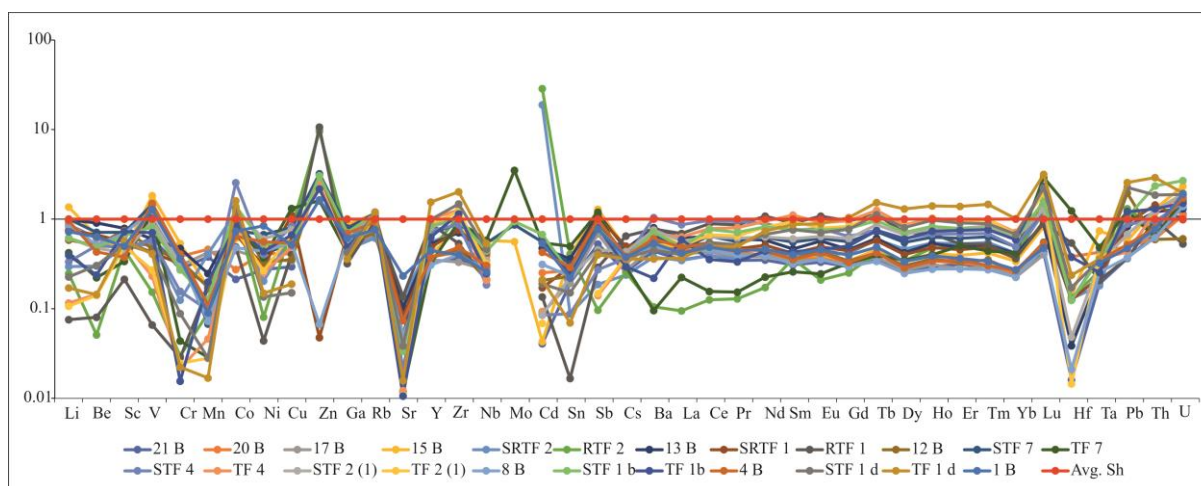


Fig. 4.9: Trace element concentration in facies E (respect to Average Shale).

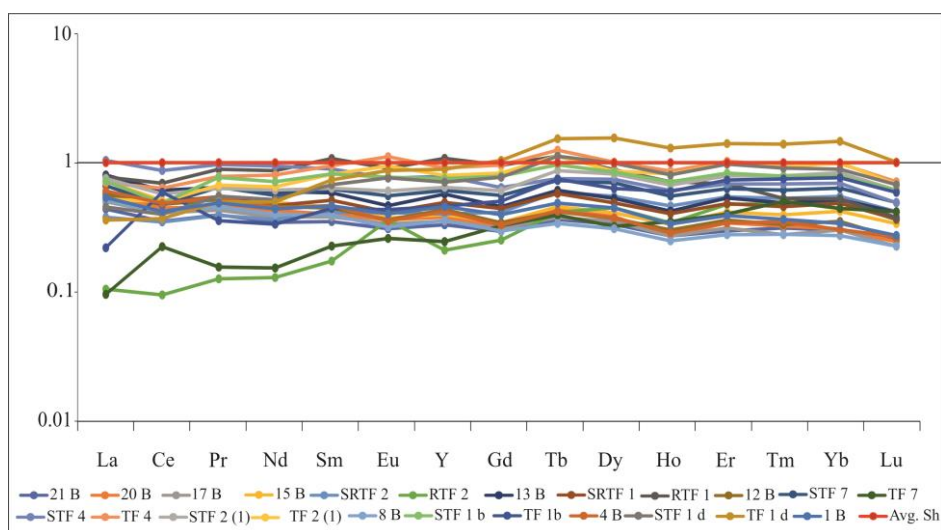


Fig. 4.10: REY concentration in the facies E (respect to Average Shale).

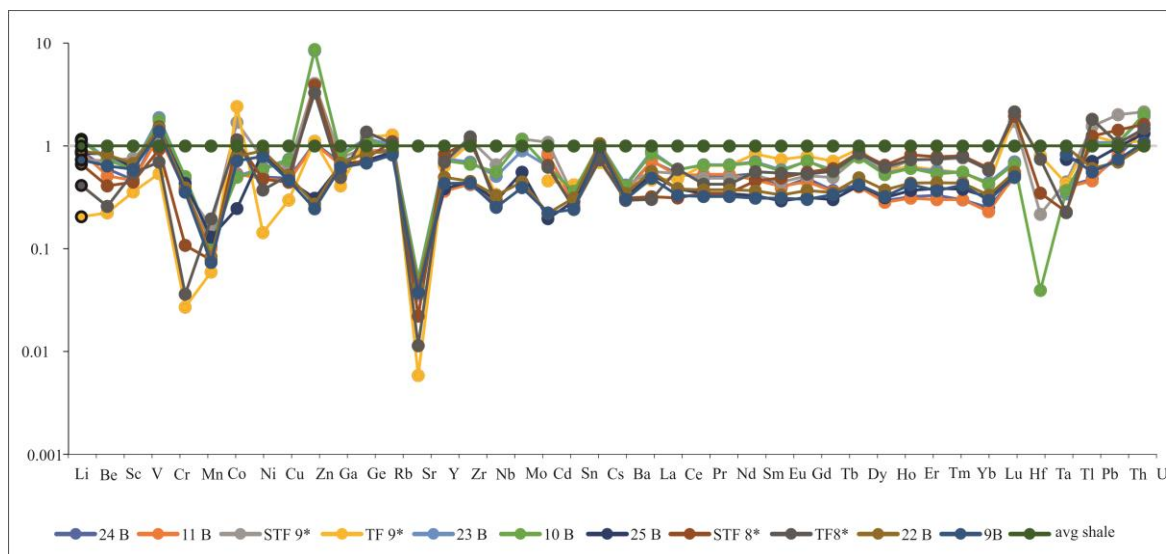


Fig. 4.11: Trace element concentration in facies F (respect to Average Shale).

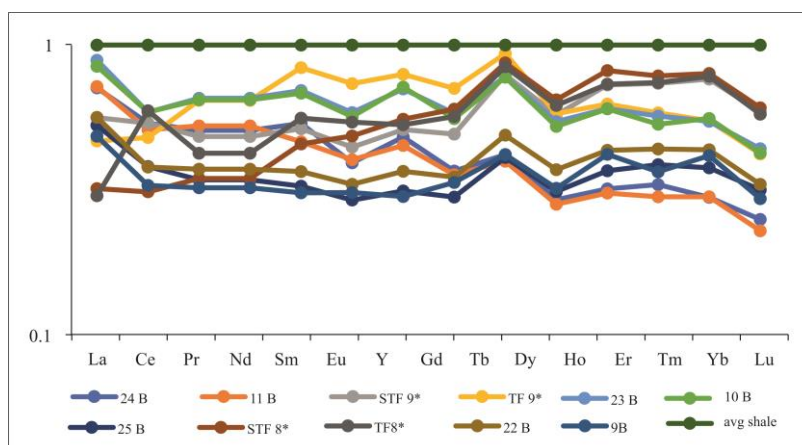


Fig. 4.12: REY concentration in the facies F (respect to Average Shale).

Facies F contains light grey colour shale as mentioned earlier. Average shale normalised trace element data plot shows noticeable enrichment in Se and slight enrichment in Zn within this facies F (Fig. 4.11, Table 8). Rest of the trace elements are showing similar composition with the average shale. REY plot overall reflects a flattened pattern (Fig. 4.12). LREE/HREE ratio for this facies is ca. 7.87 (Table 9).

4.4: Results: Geochemical Proxies used to identify the evolution of Rampur Shale

4.4.1: Geochemical Proxies used for lower (sand-rich) and middle (sand-silt-shale alternation) segment (Facies A, B, C & D):

Major elements Al, Fe, Ti, Si and trace element Zr, Mn, Eu, Gd, Yb, V, Ni, Th, Co, La, Sc, Cr, Hf are highly useful to detect the provenance (Fig. 4.13) (Taylor and McLennan,

1985; Bhatia and Crook, 1986; Floyd and Leveridge, 1987; McLennan et al., 1993; Condie, 1993; Cullers, 1994, 2000; Cullers and Podkovyrov, 2000; Cullers, 2002; Bankole et al., 2020; Tchatchueng et al., 2020). Various oxides like Al_2O_3 , K_2O , Na_2O , CaO and their elemental fractions such as Al, Fe, Ca, Mn, Ti, Na, Mg are very important to calculate the Palaeoweathering and palaeoclimatic parameters (Fig. 4.14) (Nesbit and Young, 1982; Harnois, 1987; Cox et al., 1995; Fedo et al., 1995; Sheldon and Tabor 2009; Xu et al., 2017; Guoliang et al., 2018; Šajnovic et al., 2019; Perri, 2020; Ding et al., 2021; Ding et al., 2021; Harshitha et al., 2023; Eric et al., 2023). Redox sensitive trace metal like V, Ni, Th, U are highly used to determine the palaeoredox scenario (Fig. 4.15) (Jones and Manning 1994; Tribovillard et al., 2006; Kato et al., 2015; Steadman et al., 2020; Malik and Alvi, 2021; Wu et al., 2022). Al_2O_3 , TiO_2 and SiO_2 are very stable and commonly present in sedimentary rock. Al_2O_3 and TiO_2 are indicative of clastic input. Fe/Al ratio at lower and middle segment of the Rampur Shale Member is 0.1-0.49 and average Si/Al ratio is 4.55. Fe/Ti ratio is very low for the facies A-D and shows a variation from 6.44-34.5. Al/(Al+Fe+Mn) ratio in the facies A- D of the lower and middle segment of the Rampur Shale Member is low ranging between 0.67-0.85 (Table 5). Eu/Eu* varies from 0.6-0.92 (Avg. 0.7926) within the same associations whereas (Gd/Yb)_{SN} varies from 0.7-2.39 (Table 5); La/Sc ranges up to 7.9 and Ti/Zr value ranges up to 38. Cr/V ratio varies from 0.1-2.2 and Y/Ni varies from 0.6-8.9 in retrogressive (lower and middle segment) part (Table 5). Hf varies from 1.09 to 12.39 and La/Th varies from 0.8-4.4 (Table 4, 5). La/Yb value lies between 8.2-22.9 and REE_{Total} ranges from 66.63-357.48 (Table 5). Average value of Zr/Sc, Th/Sc and Nb/Sc is 19.22, 1.57 and 1.15 respectively (Table 5). TiO_2 % is exceptionally lower (~0.4) and Zr concentration in the sediment is near about 202.6 (Table 1, 4). Facies A- D in the lower and middle segments of the Rampur Shale Member show positive relationship in the Al_2O_3 vs TiO_2 binary plot where r^2 value is 0.4 (Fig. 4.13). In case of Al_2O_3 vs SiO_2 binary plot, the samples from all the facies are lies mostly out of the hydrothermal field (Fig. 4.13). Chemical Index for Alteration (CIA) value for this lower- and middle-segment ranges between 60.1-71.9 (Avg. 67.77), Chemical Index for Weathering (CIW) value varies from 97.9-99.9 (Avg. 98.9) and Plagioclase Alteration Index (PIA) varies from 95.9-99.9 (avg. 98.2) (Table 5). C-Value ranges from 0.5 to 2.4 (avg. 1.79) and average Index for Chemical Variability (ICV) value is 0.89 (Table 5). Average Zr/Hf is 41.7, Y/Ho is near about 30.3, Nb/Ta is 15.71 (Table 5), average Ce anomaly is 0.83, while V/V+Ni ratio shows an average value ~0.7 and Th/U varies from 1.6 to 6.7 (average value s 5.13) (Table 5).

4.4.2: Interpretation:

4.4.2.1: Provenance:

Clastic sedimentary rock composition is dependent on source of sediments, their weathering, transportation and diagenesis that modify them. REEs are believed to remain little altered during deposition and hence REE composition of a sedimentary rock helpful to

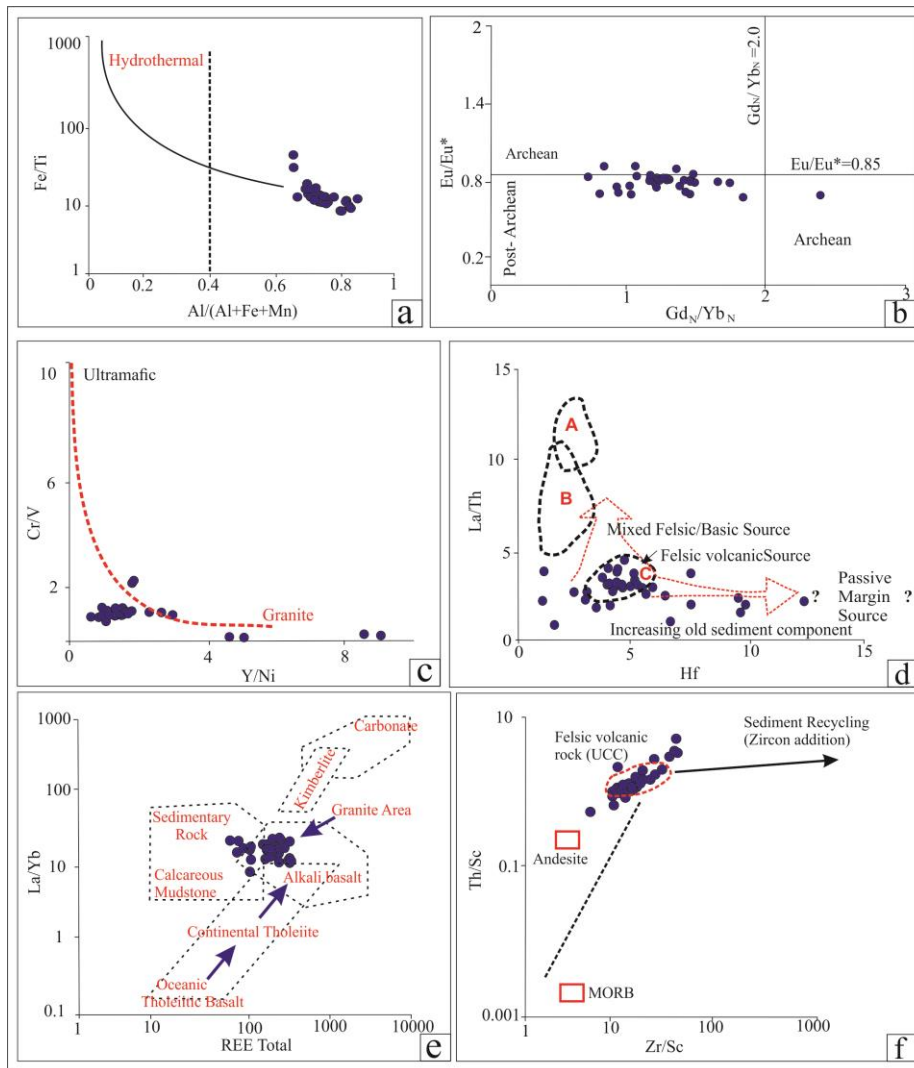


Fig. 4.13: Cross plot of **a)** Fe/Ti vs Al/(Al+Fe+Mn), **b)** Eu/Eu* vs Gd_N/Yb_N , **c)** Cr/V vs Y/Ni **d)** La/Th vs Hf **e)** La/Yb vs REE (total), **f)** Th/Sc vs Zr/Sc. All are represented here to reveal the provenance of the studied samples.

plots like La-Th-Sc and La-Co-Zr/10 are used following the previous work regarding tectonic set up of the provenance (Bostrom 1970, 1973; Bhatia and crook 1986; Floyd and Leveridge, 1987; ; McLennan et al., 1993; Hayashi et al 1997; Cullers and Podkovyrov, 2000; Cullers 2002; Obasi 2015; Meng et al., 2017; González et al., 2017; Somsekhar et al., 2018;

determine the source rock composition and palaeo-weathering conditions (Taylor and McLennan 1981). For Provenance determination of the studied section, Fe/Al, Si/Al, and Fe/Ti, ratios have been used. Different binary plots like Fe/Ti vs Al/(Al+Fe+Mn), SiO_2 vs Al_2O_3 , TiO_2 vs Al_2O_3 , Eu/Eu* vs $(Gd/Yb)_N$, Y/Ni vs Cr/V, Hf vs La/Th, $REE_{(Total)}$ vs La/Yb, Zr(ppm) vs TiO_2 (%), Zr/Sc vs Th/Sc and La/Sc vs Ti/Zr are used and ternary

Tchatchueng et al., 2020; Mateen et al 2022;). Elements like Sc, Co, Zr, Th, Ti and La are relatively stable and hence are often used to adjudge tectonic setting and source rocks provenances (Yan et al., 2021).

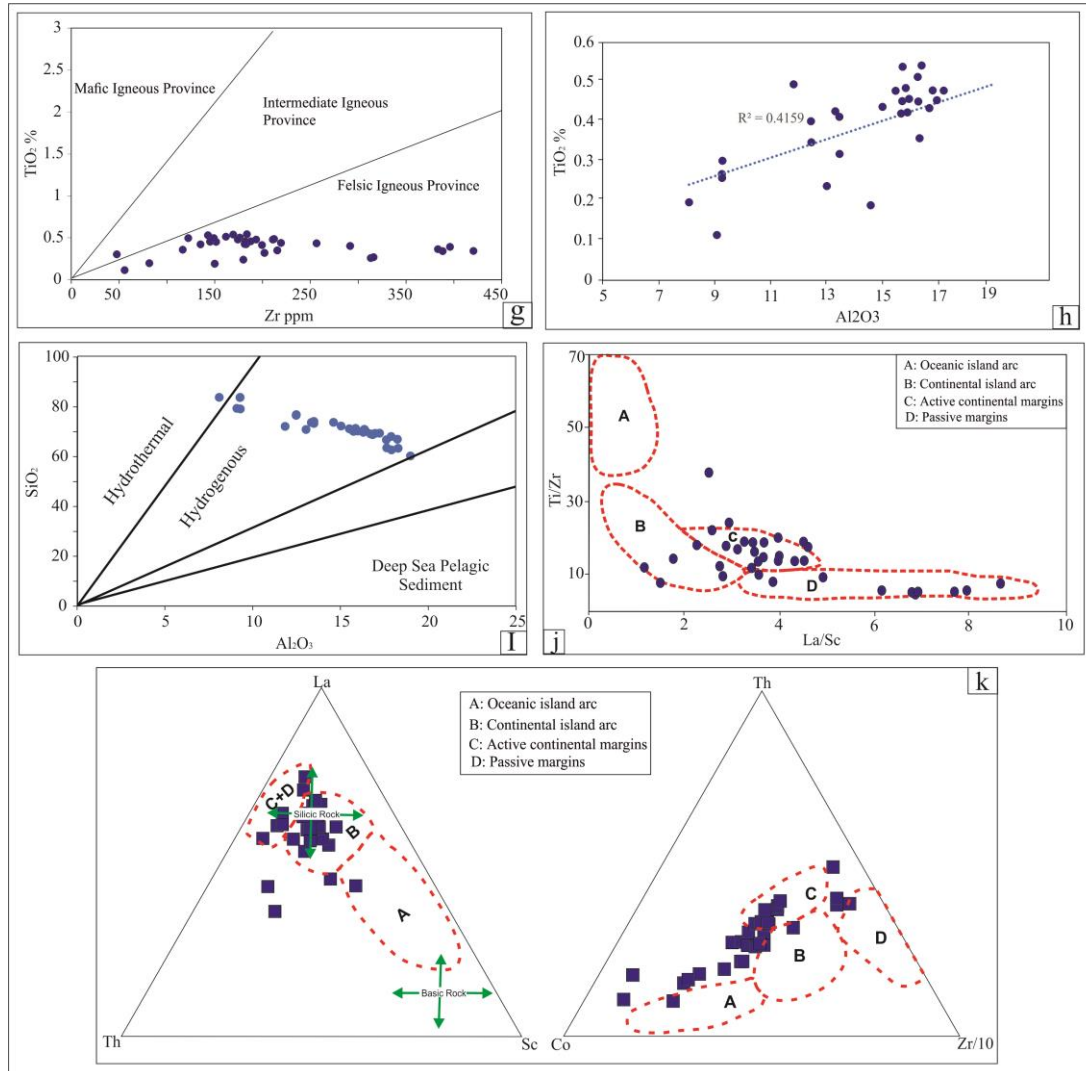


Fig. 4.13 (Continued): Binary plots of **g)** $\text{TiO}_2\%$ vs Zr ppm, **h)** TiO_2 vs Al_2O_3 , **i)** SiO_2 vs Al_2O_3 , **j)** Ti/Zr vs La/Sc . **k)** Ternary plots of La-Th-Sc and Th-Co-Zr/10 reveals the provenance and tectonic settings.

Normally Fe, Ti present as major element and Sc, Mn as trace element, show relatively higher concentration in the mafic rocks whereas Si, La, Th, Zr shows higher in concentration in the felsic rock. But Al concentration is almost same both in the mafic and felsic source. Al is a very common element present in clay mineral which can give a sense to terrigenous supply and also the grain size sorting (Young and Nesbitt, 1998). For sedimentary rock Fe/Al ratio is slightly higher in coarse grained rock rather than the fine-grained sediment (Table 5; Jung et al., 2016; Wang et al., 2012). As mentioned earlier the lower part of Rampur

Shale is dominated by sand dominated, and the Fe/Al ratio is higher in this lower part compared to the upper shale dominated part (Table 5). Higher Si/Al ratio indicates high input of Si-rich terrigenous supply (Table 5; Kohler et al., 2010). Generally, the higher Fe/Ti ratio indicates towards Hydrothermal input (Tamehe et al., 2018; Tchatchueng et al., 2020). Here the ratio is showing very low value compare to hydrothermal source and also the Fe/Ti vs Al/(Al+Fe+Mn) binary plot does not show any type of hydrothermal input all over the succession (Fig. 4.13a; Bostrom 1973; Barrett, 1981). The studied succession shows negative Europium anomaly which is indicative of a felsic source rock. Plagioclase is rich in Eu and more commonly occur in Archaean rocks than in post-Archaean rocks. $Eu/Eu^* < 1$ indicates that removal of plagioclase from the melt which is common in felsic magmatic process. When Eu/Eu^* is plotted against $(Gd/Yb)_{SN}$ then the binary plot shows that most of the samples are belongs to post Archean time which means that the sediment load was derived mostly from basement Mahakoshal Group which is Palaeoproterozoic in age (Fig. 4.13b; McLennan and Taylor, 1991; Bakkiraj et al., 2010). Ni content in ultramafic rock is generally higher compare to granitic rock. So, the ratio Y/Ni value will be higher in granitic source rock compare to ultramafic equivalent. Again, for V, which is showing a higher value in granitic rock and Cr/V ratio is quite lower for granitic source and the value is higher for ultramafic rock (Mongelli et al., 2006; Mateen et al., 2022). Here for the studied sample, the Cr/V vs Y/Ni plot shows that samples have an affinity towards felsic/granitic source (Fig. 4.13c; Mongelli et al., 2006; Mateen et al., 2022). To support this contention, several other proxies have been used. Th concentration is higher in felsic rock so the ratio La/Th is lower towards acidic arc source and Hf concentration is also lower for Felsic dominated source rock. So that, Hf vs La/Th plots indicate the samples are plotted in an area which indicate felsic volcanic source (Fig. 4.13d; Floyd and Leveridge, 1987). REE vs La/Yb plot for the studied samples indicates affinity towards felsic source (Fig. 4.13e; Allegre and Minster, 1978; Bhatia and Crook, 1986; Floyd and Leveridge, 1987; Okon, 2015; Somsekhar et al., 2018). The plot of Zr/Sc vs Th/Sc shows felsic volcanic provenance of the samples as Th/Sc ratio is commonly higher in felsic rock (Fig. 4.13f; Meng et al., 2017). Lower TiO_2 and higher Zr content is the characteristics of felsic rock and the plot TiO_2 (%) vs Zr (ppm) also shows felsic provenance for the studied succession, supports the previous contention (Fig. 4.13g; Hayashi et al., 1997). TiO_2 vs Al_2O_3 shows positive co-relation indicating towards higher clastic input (Fig. 4.13h; Tchatchueng et al., 2020). The binary plot SiO_2 vs Al_2O_3 reflects that the samples do not belong to hydrothermal field (Fig. 4.13i; Tchatchueng et al., 2020). The binary plot Ti/Zr vs

La/Sc, ternary plot La-Th-Sc and Th-Sc-Zr/10 plots does not reflect any definite tectonic setting of the source area (Fig. 4.13j, k; Bhatia and Crook 1986; Floyd and Leveridge, 1987; Cullers 2002).

4.4.2.2: *Palaeoweathering scenario:*

To reveal the palaeoweathering scenario, Chemical Index of Alteration (CIA), Chemical Index of Weathering (CIW) and Plagioclase Alteration Index (PIA) have been considered. CIW can be calculated with the formula, $[\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{CaO}^*)] \times 100$ (Harnois, 1988; Condie 1993), while the ratio $[\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{CaO}^* + \text{K}_2\text{O})] \times 100$ is used to calculate CIA (Nesbitt and Young 1982). Another proxy PIA is calculated by $[(\text{Al}_2\text{O}_3 - \text{K}_2\text{O}) / (\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{CaO}^* - \text{K}_2\text{O})] \times 100$ (Fedo et al., 1995). Fresh or less weathered rocks attain a value of CIA, CIW and PIA near about 50 but the value near 100 indicates that the rocks are highly weathered which contain a high amount of clay component such as kaolinite, Smectite, Illite etc. (Fedo et al 2013; Condie 1993; Perri 2020). Higher intensity of weathering rate indicates that removal of labile elements like K^+ , Ca^{++} , Na^+ from the system in compare to relatively stable residual constituent, suggests slow sedimentation rate, prolonged transportation history, warm and humid climate whereas low weathering rate disclose rapid sedimentation, less transportation along with cold and arid climate (Fedo et al., 1995; Oni and Olatunji, 2017). Higher CIA, CIW and PIA indicates rocks with abundant clay component and feldspar (primary phase) readily converted to clay mineral (secondary phases). In the studied samples the CIA value is slightly moderate value (~68) but CIW and PIA values show average value near about 100 (avg. value 98.2 & 98.9 respectively) (Fig. 4.14a; Table 5). CIW and PIA value generally ignored $\text{K}_2\text{O}\%$ because of leaching or remobilization of the K^+ during diagenesis and metamorphism. K^+ ions are incorporated during diagenesis and helps to form clay minerals through ion exchange procedure. Clay components strongly adsorb the K^+ ions and make it immobile (Harnois 1988). The moderate value of CIA and high value of CIW and PIA in the facies A, B, C and D, indicates high rate of weathering intensity, slow sedimentation rate, prolonged transportation under Warm and humid condition. There is another parameter known as Index of Chemical variability (ICV) which is a ratio of almost all the major element with respect to Al_2O_3 ; $(\text{Fe}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{MnO} + \text{TiO}_2) / \text{Al}_2\text{O}_3$ (Cox et al 1995; Perri 2014). Immature rocks show higher values of ICV (>1) which means labile cations are resided within the system and enriched with respect to Al_2O_3 . Rocks with higher ICV (>1) contain less amount

of clay component and lower value (<1) indicate higher clay mineral within it. The samples of lower and middle segment is showing lower values of ICV (~ 0.89) which indicate the samples were recycled multiple times (Table 5).

4.4.2.3: *Palaeoclimatic scenario:*

Few traces and major elements are useful to decipher the palaeoclimatic conditions such as Mg/Ca, Sr/Cu, Fe/Mn and C -value are used as palaeoclimatic proxies (Lerman, 1989; Roy and Roser, 2013; Sarki Yandoka et al., 2015). Mg/Ca is useful for carbonate samples which indicate incorporation of Mg within Carbonate structure (Song et al., 2019), as Rampur Shale have a gradational contact with the overlying Rhotas Limestone Formation, CaO concentration is increases at the upperpart and the ratio shows comparatively lower value. In the lower and middle segment of the Rampur Shale the Mg/Ca (avg. 6.66) and Fe/Mn (avg. ~ 450) ratio are generally higher (Fig. 4.14b; Table 5). Additionally, the Mg/Ca ratio is greater than 2 and Fe/Mn ratio greater than 180, indicate that the sediment was deposited under warm and humid condition (Song et al., 2019; Fathy et al., 2021). Sr/Cu is another ratio highly used for fine grained sediments to determine palaeoclimatic condition (Roy and Roser, 2013; Sarki Yandoka et al., 2015). Strontium is relatively immobile, commonly associated with plagioclase in Sedimentary rock. Plagioclase along with Sr is released from sediment during the weathering. So higher Sr concentration tends to be more abundant in areas with less intense chemical weathering. Cu is another trace element that is more mobile than Sr and can be influenced by biological activity like vegetation. Cu tends to be taken up by plants and can be depleted in soils with high biological productivity. During the Precambrian time there was no such vegetation to affect the Cu content in sediment but chemical weathering was intensely present during the time period. At this retrogressive part of Rampur Shale, the average Sr/Cu ratio is 4.9 whereas at the upper part facies E, the value is ~ 0.94 and the value is ~ 0.44 within facies F (Table 5, 7, 9). All through the succession the Sr/Cu <5 indicates low concentration of Sr and high weathering rate reflects a warm and humid condition and the value greater than 5 suggests arid climate (Sarki Yandoka et al., 2015; Xu et al., 2017). C-value is used to evaluate ancient palaeoclimatic condition and calculated by $[C\text{-value} = \Sigma (Fe + Mn + Cr + Ni + V + Co) / \Sigma (Ca + Mg + Sr + Ba + Na)]$ (Qiu et al., 2015; Fathy et al., 2021). C-value measured at the lower and middle segment of the Rampur shale is ~ 1.8 (Table 5); Elevated C value which is > 0.6 indicates humid climate and low value < 0.4 promotes arid climatic condition (Qiu et al., 2015; Fathy et al., 2021). The binary plot between CIW and C-value indicates that most of

the samples are concentrate within the humid part (Fig. 4.14c; Qiu et al., 2015; Fathy et al., 2021). Another bivariate discrimination diagram between SiO_2 and $\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{K}_2\text{O}$, commonly discriminate the palaeoenvironmental scenario with the help of chemical maturity. The present samples indicate towards increase in chemical weathering intensity from Semi-Humid to humid condition (Fig. 4.14d; Suttner and Dutta, 1986; Fathy et al 2021).

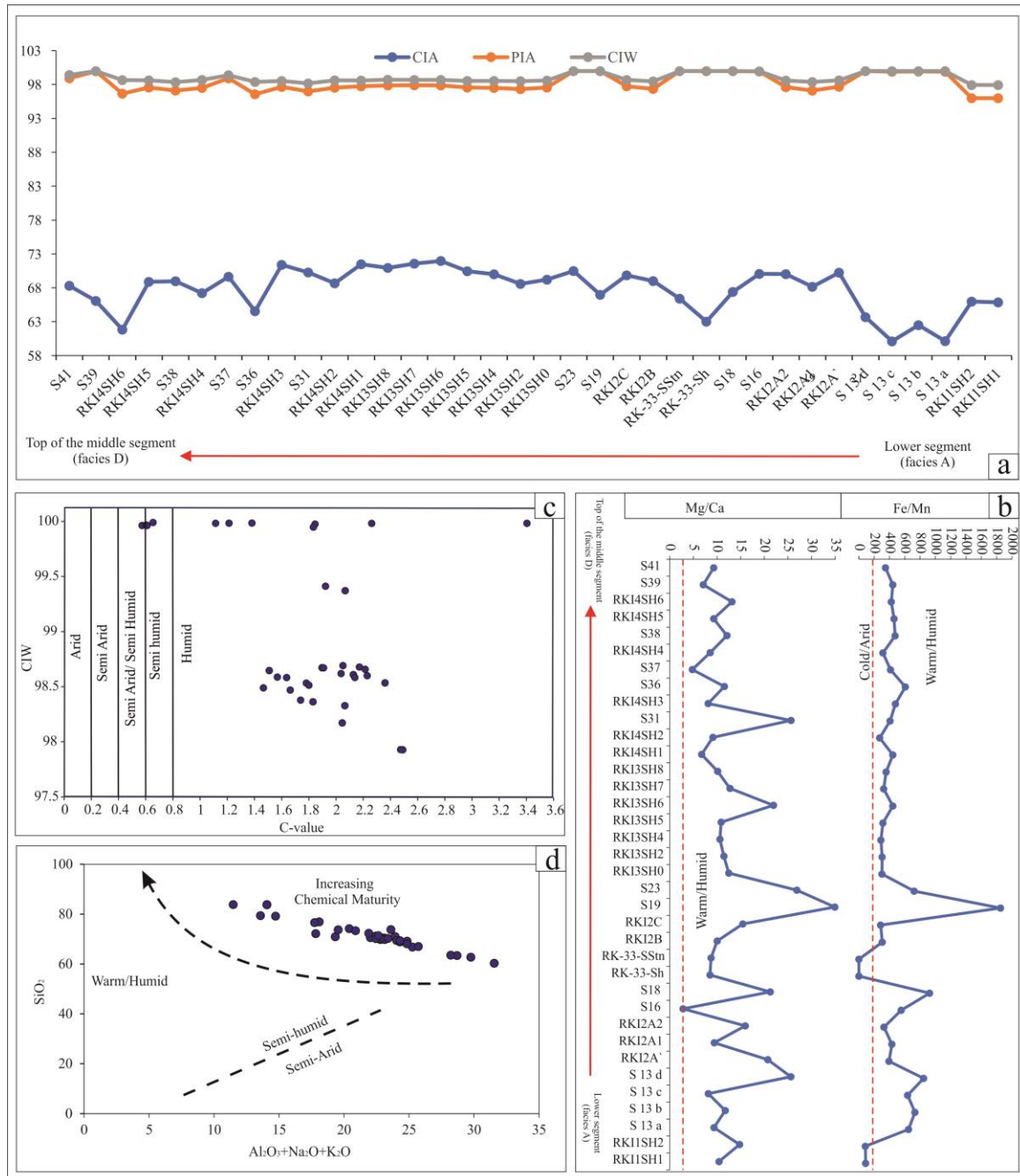


Fig. 4.14. Vertical distribution of **a)** CIA, CIW and PIA, **b)** Mg/Ca and Fe/Mn. Bivariate discrimination plot between **c)** CIW and C-value and **d)** SiO_2 and $(\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{K}_2\text{O})$.

4.4.2.4: Palaeodepositional scenario:

Decoupling of the known elemental pairs, such as Zr-Hf and Nb/Ta, that are released during weathering as geochemical twins further corroborate the palaeogeographic condition of the Rampur Shale. Close similarity in atomic radius dictates these pairings. Between Zr and Hf, the latter is preferentially scavenged. Zr is more compatible in marine sediment than Hf; so, Zr/Hf ratio is quite higher for marine sediment ranges between 45-350. For the Rampur shale samples, the Zr/Hf ratio varies from 31.9-45 partially supporting the marine origin (Table 5; Firdaus et al., 2011,2018; Rudnick and Gao, 2003). Nb and Ta both are common in fine grained, chemically matured sediment. In marine condition Nb is compatible over Ta. The ratio ranges between 14-85 for modern marine water whereas for Rampur Shale the average ratio is 15.9, supports this contention (Table 5; Firdaus et al., 2011,2018). The Y/Ho ratio increases as Ho is preferentially scavenged because of its higher complexation capacity (Planavsky et al., 2010). This ratio is almost always greater than 30 and ranges up to 35.5 in lower part and at the upper part this ratio ranges up to 36 (Table 5). It thus closely depicts marine signature but is perhaps slightly retarded in the epicontinental sea which were much shallower than the present sea, in which the deposition took place (Liu and Byrne, 1997; Hill et al., 2000; Mandal et al., 2022). The occurrence of glauconite in the RS, suggests deposition of the latter in a marine environment (Mandal et al., 2022). This view is in perfect sync with the consensus about the marine origin of the whole Rampur Shale member (Schieber et al., 2007). Why do not put some of your observations, may be already discuss

4.4.2.5: Palaeosalinity:

Sr/Ba ratio is often used as a palaeosalinity proxy. In seawater, Sr is present in relatively high concentrations, and Ba is present in as traces; their ratios are higher in marine sediments than in brackish and freshwater sediments. In marine fine-grained siliciclastic sediments, Sr is mostly adsorbed by clay minerals or fixed in the organic fraction, whereas Ba can be related to biogenic productivity. In a recent study it has been observed that the Sr/Ba ratio is 0.14-0.28 in modern freshwater sediments, 0.27-0.66 in brackish sediments and 0.24-0.82 in marine sediments (Sajid et al. 2020; Wei and Algeo, 2020). The procedure yields Sr/Ba ratios in the majority of data are, however, too low even with reference to the freshwater values (Table 5). Sajid et al., 2020, depicted that $Rb/K < 0.004$ for freshwater 0.004-0.006 infers fresh to brackish environment of deposition, >0.006 suggests saline water. Here the studied samples of Rampur Shale member show a value which is far less than the

fresh water range (Table 5). So palaeosalinity is not reflected properly for the marine water within which the sediment deposited.

The unbelievably low values of Sr/Ba and Rb/K ratios in these facies (A, B, C, D) of Rampur shale might have been caused by the differential remobilization of the individual components. As the palaeoclimate during the deposition was mostly warm and humid, the evaporation rate was comparatively less, so the salt deposition may be quite difficult at that time. Nevertheless, due to the epicontinental nature of the RS depositional basin, as envisaged by Mandal et al. (2022), palaeosalinity is expected to have been far less than that of the open sea. Freshwater supply from almost all sides could have caused considerable dilution, as expected when the basin was almost land-locked in the middle of a supercontinent.

4.4.2.6: Palaeoredox:

To determine the palaeoredox scenario Ce/Ce*, V/V+Ni, Th/U, concentration of Mn, Cd and Zn all through the succession has been used as proxy. Ce anomaly (Ce/Ce*) is calculated by the formula $\{(2 \times \text{Ce}_{\text{SN}}) / (\text{La}_{\text{SN}} + \text{Pr}_{\text{SN}})\}$ (Tostevin et al, 2016). Most of the REEs contain +3 oxidation state whether Ce has a uniqueness that it can exist both in +3 and +4 state. Due to presence of oxygen, Ce+3 can be oxidised into Ce+4 and no longer participated in solid solution ion exchange reaction and left from the system. Marine water became depleted in Ce with respect to other trivalent REEs (German and Elderfield, 1990; German et al., 1991; Tostevin et al., 2016). Here the studies sample also shows slightly negative Ce anomaly indicating that the sea water not devoid of oxygen (Fig. 4.15a). Zinc and Cadmium, for instance, function as a micronutrient, released through Organic decay. Under a slightly dysoxic-anoxic condition, these elements become insoluble and eventually precipitate in the sediment. (Rosenthal et al., 1995; Morford and Emerson, 1999; Chen et al., 2021; Bryan et al., 2021). Organic matter and sulfides are the most important carriers of Cd to sediment. This explains that Cd spike coinciding with that of Zn at the same stratigraphic level (Fig. 4.15b; Chen et al., 2021; Ye et al., 2022). Mn^{+2} is highly soluble under reducing condition and show depletion in the sediment deposited under reducing condition (Fig. 4.15b; Tribouillard et al. 2006). General enrichment in Mn accompanying these spikes also corroborates the same contention. The V and Ni both are redox sensitive element and easily deposited under reducing condition. V is reduced from V(V) to V(IV); produce vanadyl ion (VO^{2+}) under reducing condition and easily deposited in sediment. Ni released from organometallic

compound during Organic Matter decay (Tribovillard et al. 2006). V/V+Ni ratio is invariably >0.6 (Fig. 4.15c), indicating strongly reducing conditions and probably stratified water (Hatch and Leventhal, 1992; Jones and Manning, 1994; Riquier et al., 2005; Cai, et al., 2009; Zuo et al., 2020).

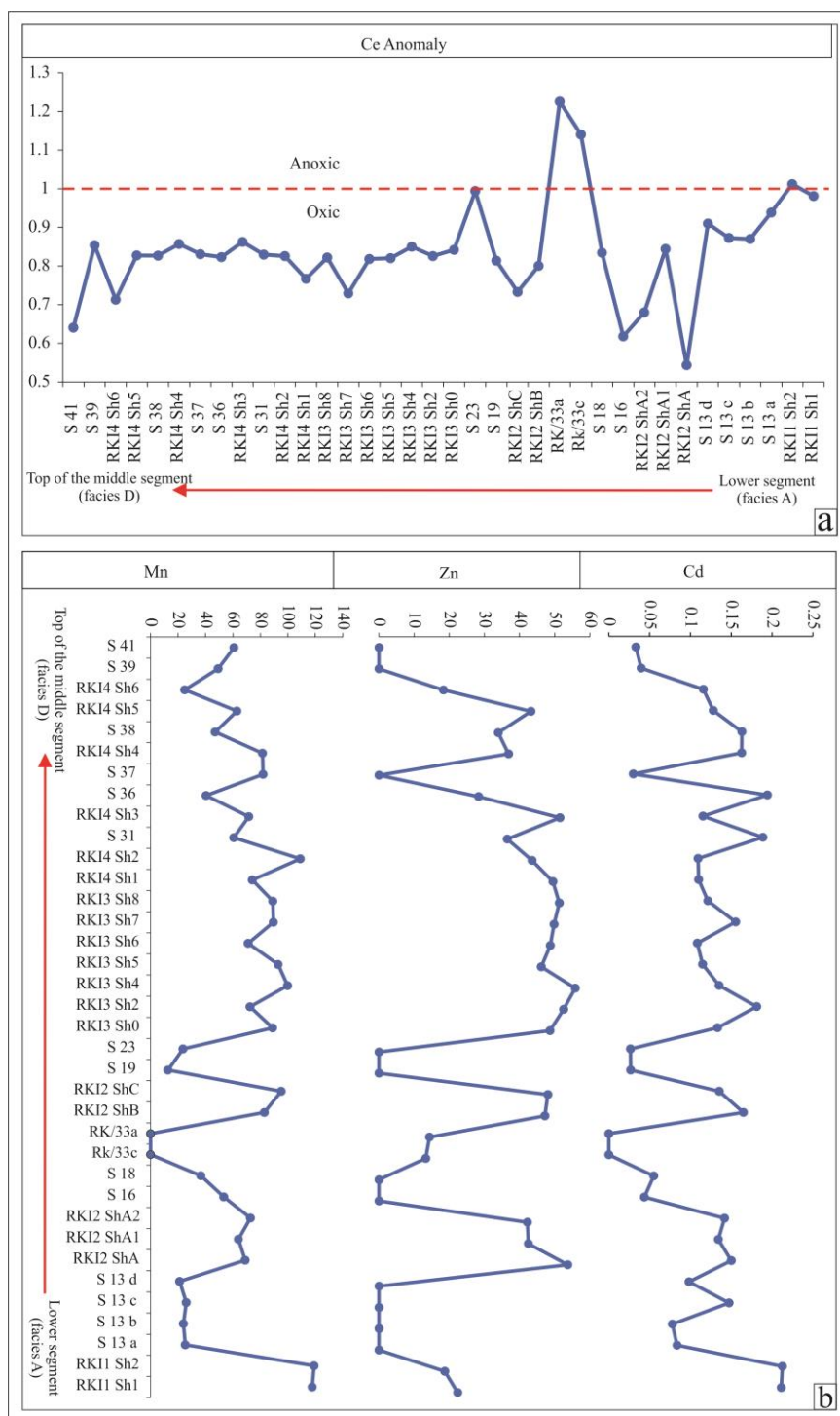


Fig. 4.15. Variation of **a)** Ce anomaly and **b)** Mn, Zn and Cd all through the lower and middle segment of the Rampur Shale.

Both elements remain in solution under oxidizing conditions but are enriched in sediment upon reduction. Ni is strongly associated with the pyrite fraction and V with the organic fraction, especially chlorophyll (Lewan and Maynard, 1982; Tabatabaei et al., 2012). The existence of chlorophyll or its precursor in 1.5 Ga-old Rampur Shale is no more a travesty, as most workers now believe that oxygenic photosynthesis and chloroplasts were invented early, possibly before 2.8 Ga (Suzuki and Bauer, 1995; Des Marais, 2000; Blankenship, 2010). The cross plot between Th/U and V/V+Ni also supports this context that the samples were deposited under dysoxic to anoxic condition (Fig. 4.15d; Luo et al., 2015a; Wu et al., 2022).

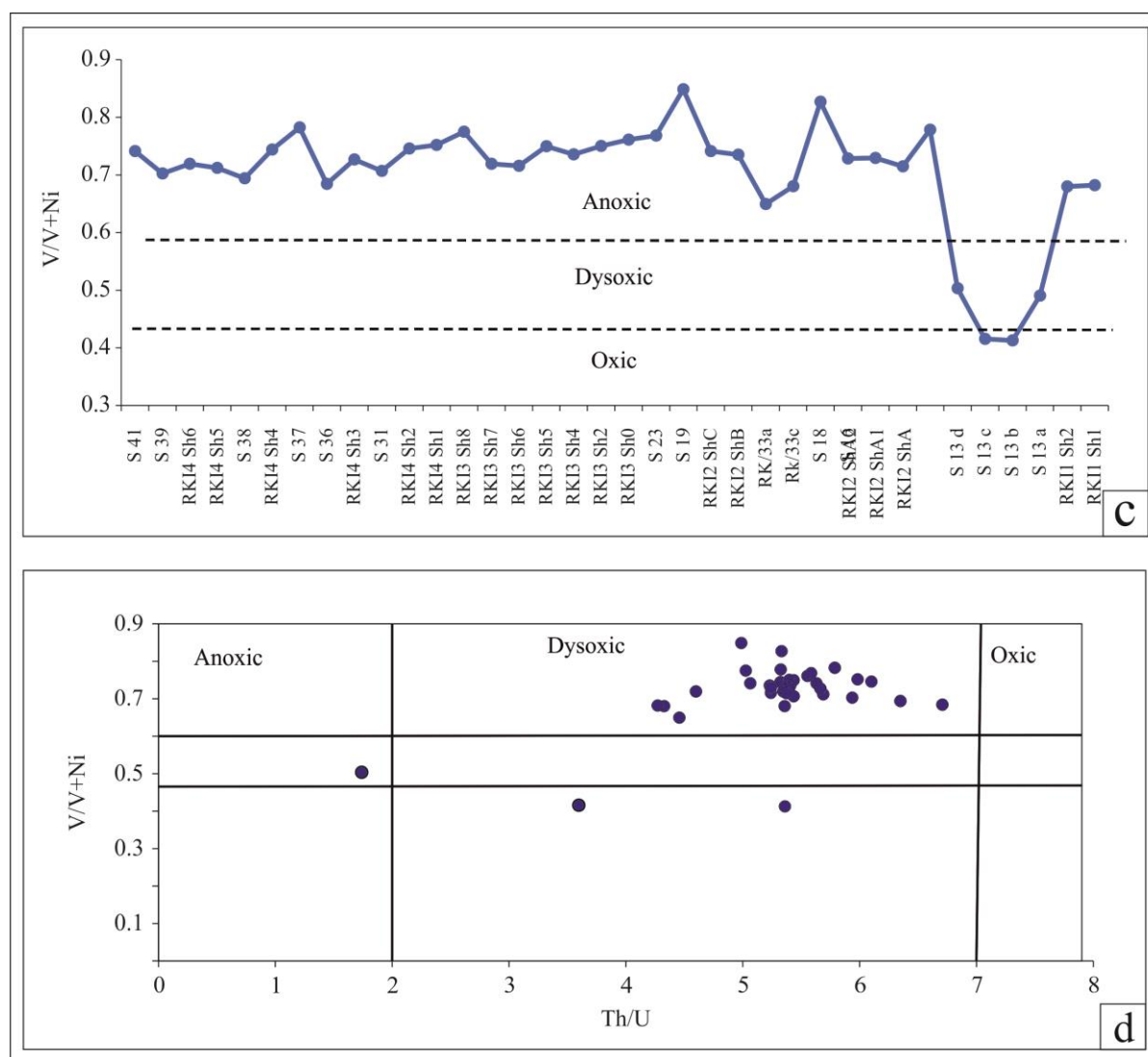


Fig: 4.15 (Continued): Vertical variation of **c)** V/V+Ni (stratigraphy wise). **d)** Bivariant discrimination plot between V/V+Ni and Th/U.

4.4.3: Geochemical Proxies used for the upper Shale dominated Segment (Facies E and F):

The Upper shale dominated portion contain two facies namely Facies E and F. Both the facies E and F are showing positive relationship which infer higher rate of clastic input. The Al_2O_3 vs TiO_2 binary plot where r^2 value is 0.43 and 0.18 respectively. Bivariant discrimination diagram between Al_2O_3 and SiO_2 , most of the samples lies within the hydrogenous field and very few of them are in marginal hydrothermal field (Fig. 4.16a). Fe/Ti ratio is very low for both the facies E and F this range is 1.3-11.5 and for facies F, Fe/Ti ratio is 4.1-11.2 (Table 7 and 9). Fe/Al ratio for Black shale part it is 0.04-0.5 and for the uppermost grey shale part this ratio is ranging from 0.07-0.47. $\text{Al}/(\text{Al}+\text{Fe}+\text{Mn})$ ratio in facies E varies between 0.65-0.95 and for F the range is from 0.67-0.93. Average Si/Al ratio is 4.98 in facies E and 6.61 in facies F. Eu/Eu^* For facies E this value is varies in between 0.85-1.8 (Avg. 0.99) and for facies F the value is 0.77 to 1.0 (avg. 0.89). $(\text{Gd}/\text{Yb})_{\text{SN}}$ varies from 0.6-2.06 for black shale part and 0.6-1.6 for the facies F which is top most part of this succession. Cr/V in the black shale part is 0.01-0.5 and in the top part this ratio is 0.03-0.2. the, Y/Ni ratio varies from 0.3-12.09 in the black shale part and 0.3-2.6 in the upper part. Zr concentration in black ranges from 52.8 to 322.18 and from 67.39 to 195.63 for the top most facies F. TiO_2 varies from 0.24 to 0.60 and from 0.26 to 0.49 for Facies E and F respectively. Average value for CIA, CIW and PIA for black shale part is 58.14, 98.75, 93.87 and for facies F these values are 50.6, 96.7 and 90.75 respectively. Average ICV values for black shale is 1.16 and 0.97 for the facies F (Table 7, 9). For facies E, Mg/Ca ratio shows an average value of 1.84 (ranges between 0.01-4.47) (Table 7), Sr/Cu is varying from 0.06-3.01 (Average value 0.94) and average value recorded for Fe/Mn is 144.51 (Table 7). The same ratios calculated for facies F and the average values are 4.92, 0.44 and 181.6 respectively (Table 9). C -value was calculated for both the facies and value shows a range from 0.02-2.36 (Avg. 0.93) and 1.1-3.7 (avg. 2.29) (Table 7, 9). Average Ga/Al ratio for facies E is 0.00016, Zr/Hf value is varying from 18.29-52.91 (Avg. 40.9), Y/Ho ranges from 26.9-36.0 (avg. 31.2), Th/U ranges from 1.6-5.58 and average Nb/Ta value is 38.6. Facies F records these ratios as 0.0002 (for Ga/Al), 44.48 (for Zr/Hf), 32.37 (for Y/Ho), 2.29 (for Th/U) and 15.44 (for Nb/Ta) (Table 7, 9). Sr/Ba and Rb/K for facies E is 0.095 and 0.00195 respectively whereas these ratios recorded in facies F are 0.05 and 0.0027 respectively represented in Table 7 and 9. V/V+Ni, V/Cr, and Th/U ratios calculated for both the facies and the values lies between 0.63-0.87 (average 0.78), 1.8-65.6 (Average 10.62) and 1.2-5.9

(avg. 2.26) respectively for black shale (Table 7) and 0.76-0.87 (average 0.8), 5.03-27.7 (average 10.09), 1.6-2.1 (avg. 2.29) respectively for facies F (Table 9).

4.4.4: Interpretation:

❖ Facies E (Black Shale dominated Part):

The Detailed Geochemistry of the Black shale dominated part is discussed in Chapter 6

❖ Facies F (Grey shale dominated Part):

4.4.4.1: Provenance:

In the grey shales of Facies F, SiO_2 vs Al_2O_3 plot does not reflect any hydrothermal input (Fig. 4.16a; Wonder et al., 1988) but TiO_2 vs Al_2O_3 shows positive co-relation indicating towards higher clastic input (Fig. 4.16b; Tchatchueng et al., 2020). Generally, Fe/Ti shows high value for hydrothermal but here the Fe/Ti vs $\text{Al}/(\text{Al}+\text{Fe}+\text{Mn})$ shows that the studied samples does not show any type of hydrothermal signature (Fig. 4.16c; Tchatchueng et al., 2020; Bostrom 1973; Barrett, 1981). Eu/Eu^* vs $\text{Gd}_\text{N}/\text{Yb}_\text{N}$ plots are used to determine source of the samples. The representing scatter plot shows that the few samples are belongs to Archean time zone and few are from Post Archean time zone (Fig. 4.16d; McLennan and Taylor, 1991; Bakkiraj et al., 2010). Binary plot of Cr/V vs Y/Ni showing an affinity towards Granitic source (Fig. 4.16e; Mateen et al., 2022). Th/Cr vs La/Cr cross plot how that all the samples are from felsic dominated source (Fig. 4.16f; Cullers 2002). Zr (ppm) vs TiO_2 (%) shows samples are originated from dominant Felsic source (Fig. 4.16g; Hayashi et al., 1997).

4.4.4.2: Palaeoweathering Scenario:

Al_2O_3 , CaO, Na_2O and K_2O are used to calculate CIA, PIA and CIW (Formula is already discussed in 4.4.1.2.2) (Harnois 1988; Condie 1993; Fedo et al., 1995; Oni and Olatunji, 2017). CIA value is little bit lower (~50.6) indicate moderate rate of weathering but CIW (~96.7) and PIA (~90.7) shows higher which signifies that higher rate of weathering (Table 9; Fig. 4.17a). ICV is calculated by the combining almost all the major element ratio with respect to Al_2O_3 . Higher values of ICV (>1) indicate less amount of clay component and lower value of ICV (<1) indicate abundancy of clay component. This grey shale samples shows that most of the sample shows values are >1 and overall average ICV value is 0.97 which is <1 (Table 9; Cox et al 1995; Perri 2014;). ICV<1 means the samples are recycled multiple times.

4.4.4.3: Palaeoclimate:

Mg/Ca, Fe/Mn, Sr/Cu and C-value used as a proxy for determination of the palaeoclimate. Mg/Ca > 2 and Fe/Mn > 180 signifies warm and humid climate (Fathy et al., 2021; Song et al., 2019) the grey shale shows average Mg/Ca value for this succession is around 4.9 where Fe/Mn shows an average value of 181.64; both the values signifies that the grey shale was deposited under a warm and humid condition (Fig. 4.17b; Table 9). Sr/Cu ratio is used here again a palaeoclimate indicator; Sr/Cu value < 5 signifies warm and humid condition and > 5 signifies about cold and arid climate (Roy and Roser, 2013; Sarki Yandoka et al., 2015). The studied grey shale is indicated towards a warm and humid climate as the average value is ~0.44 (Table 9). C-value is calculated by using few selected major and trace element and used as palaeoclimate proxy. C-value > 0.6 is indicate humid climate (Table 9; Fathy et al., 2021). When C value is plotted against CIW, all the points are plotted in humid region (Fig. 4.17c; Qiu et al., 2015; Fathy et al., 2021).

4.4.4.4: Palaeoceanography:

Zr-Hf, Y-Ho and Ga-Al all are known as geochemical twins. Between Zr and Hf, the latter is preferentially scavenged, and the ratio between these two elements in this grey shale facies ranges between 32.5-57 (Table 9) but the ratio in modern marine range is ranges in between 45 to 350 (Rudnick and Gao, 2003; Firdaus et al., 2011). The Y/Ho ratio is almost always greater than 30 and ranges up to 35.3 in the grey shale (Table 9) which is indicating towards marine deposit (Planavsky et al., 2010). Ga/Al ratio ranges from 8.8×10^{-5} to 0.3×10^{-3} . For marine sediment this Ga/Al ratio is ranges between $0.2-0.4 \times 10^{-3}$, which indicate few of the value have belonged to this range (Table 9; Shiller and Frilot, 1996). Bouska, (1981) concluded that the Th/U ratio is lower than 7.0 in marine deposits, but in this grey shale the value is far less (~2.29) (Table 9).

4.4.4.5: Palaeoredox condition:

For detecting the palaeoredox scenario, V/V+Ni, V/Cr and Th/U have been used (Jones and Manning, 1994; Tribovillard et al., 2006). V, Ni, Cr, U, Th all are highly redox sensitive trace elements. V/V+Ni is a proxy to determine redox condition of the depositional system. V/V+Ni > 0.6 is indicating towards anoxic condition and the value of this ratio in gray shale varies between 0.76-0.85 (Table 9; Fig. 4.18a). V/Cr ratio > 4.25 indicate anoxic depositional condition and for grey shale facies this ratio is 10.09 (avg.) which is strongly

indicating towards anoxic-dysoxic condition (Table 9; Fig. 4.18a). Bivariant discrimination diagram between V/V+Ni and Th/U indicate that the samples were deposited under anoxic to dysoxic condition (Fig. 4.18b; Luo et al., 2015a; Wu et al., 2022).

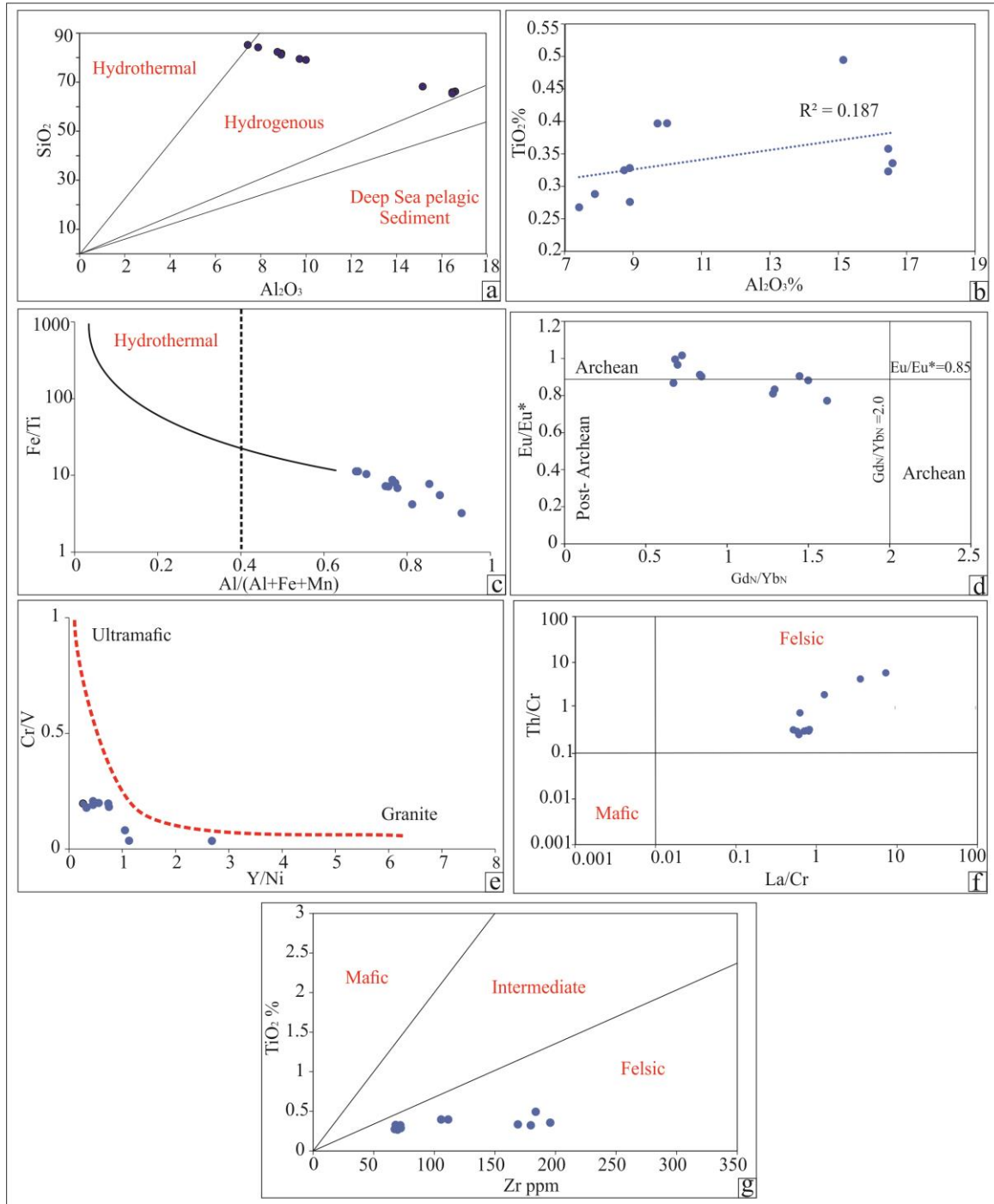


Fig. 4.16: Bivariant discrimination plot between **a)** SiO₂ and Al₂O₃, **b)** TiO₂ and Al₂O₃, **c)** Fe/Ti and Al/(Al+Fe+Mn), **d)** Eu/Eu* and Gd_N/Yb_N, **e)** Cr/V and Y/Ni, **f)** La/Cr and Th/Cr, **g)** TiO₂% and Zr ppm are represented to reveal the provenance.

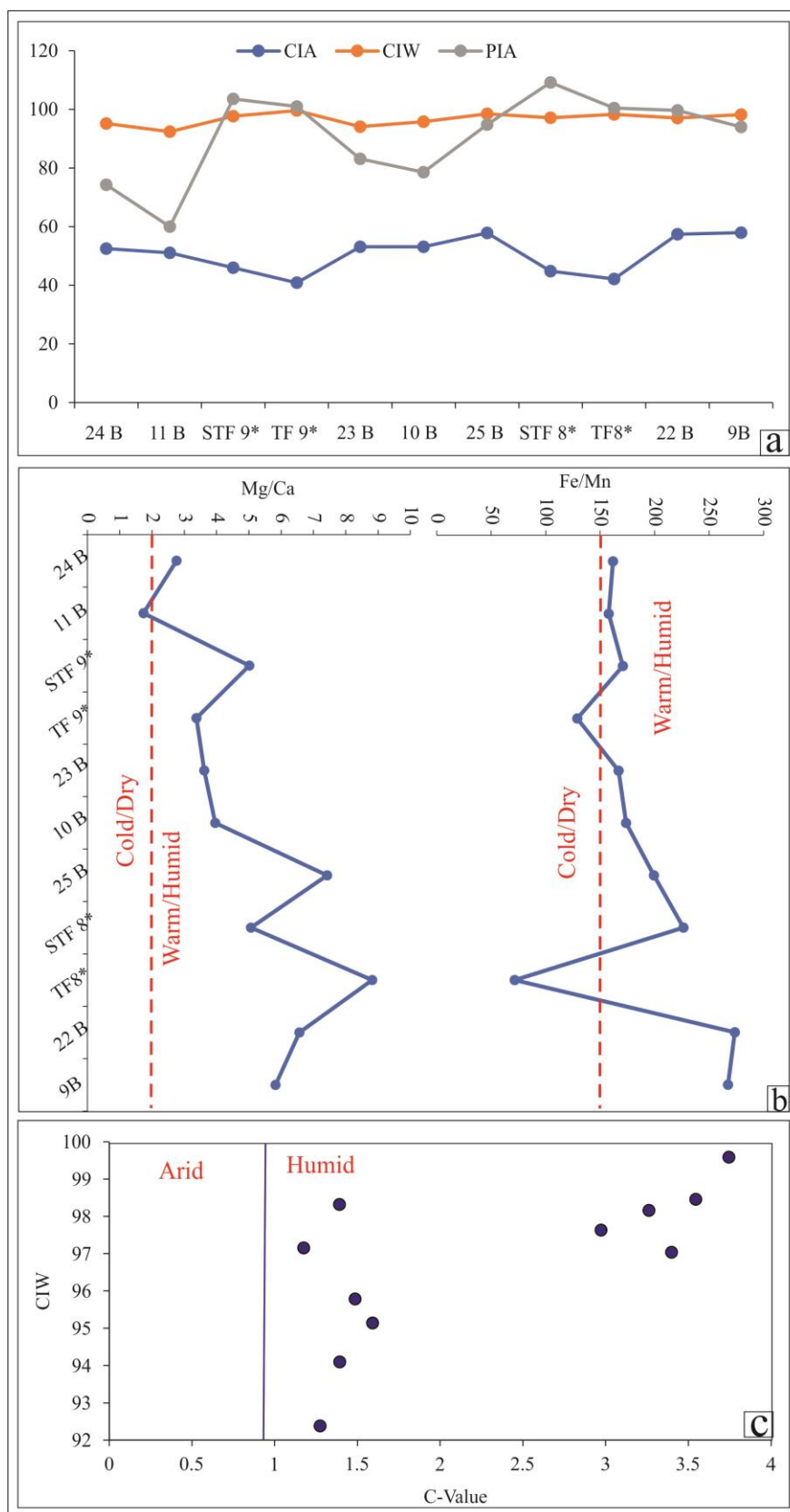


Fig. 4.17: Vertical variation (stratigraphy wise) of **a)** CIA, CIW and PIA, **b)** Mg/Ca and Fe/Mn. **c)** Bivariant discrimination plot between CIW and C-Value.

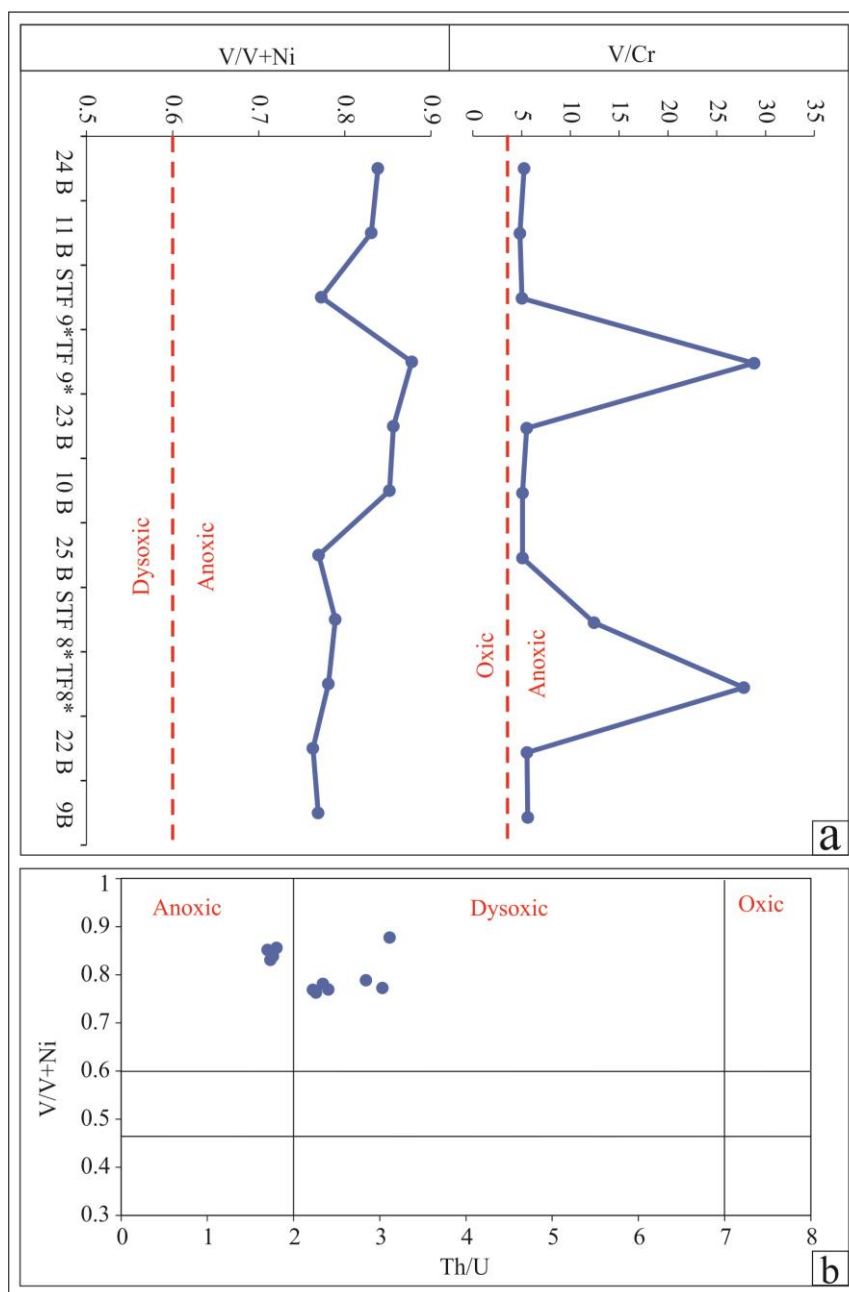


Fig. 4.18: Distribution of Redox Proxy **a)** $V/V+Ni$ and V/Cr from base to top within facies F. **b)** Bivariant discrimination plot between $V/V+Ni$ and Th/U for palaeoredox reconstruction.

4.4.5: Geochemistry of the Glauconites from Middle Segment:

As mentioned in the previous chapter that middle segment of the Rampur shale (facies B, C, D) is infested with glauconite minerals. Detailed Petrography has been described in previous chapter 3. Petrographic study reveals that, glauconites are commonly associated with sandstone or siltstone but some rare occurrence with shale is also found. Starting from facies

B to facies D, different modes of glauconites were present there. The modes of occurrences are as follows:

1. Glauconites pellets within silica cement or silica vein
2. Glauconite as cement in intergranular parts
3. Partially dissolved glauconite grains
4. Transported bed parallel glauconite pellet,
5. Tectonically modified vertical glauconite pellet.
6. Glauconite within shale.

As the glauconites show some interesting and unique geochemical signature the author prefers to discuss some of the important aspects of glauconites within this chapter.

4.4.5.1: Mineral chemistry of glauconite:

The glauconites of Rampur shale contains significant amount of SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , K_2O and negligible amount of CaO , Na_2O , TiO_2 in weight %. Generally, in glauconite K_2O content varies from 3-9% based on maturity (nascent-mature) of the glauconite, SiO_2 varies from 47-50%, Al_2O_3 contains 5-8% and MgO contains 3-4% (Odin and Matter 1981). Here for the studied Rampur Shale Glauconite, the SiO_2 contents more or less same (55-60%; Avg. 59%) in all the studied glauconite. Al_2O_3 content is (~16%; ranges from 13.2-22.1%). Concentration of Fe_2O_3 is lower (7-8%). The studied samples of Rampur Shale are slightly enriched in K_2O (~9%). And the main distinguishing property is MgO content. MgO content in Rampur Shale reaches up to 11.5wt% (Avg. 8%). The geochemical oddities are represented as follows (Fig. 4.19-4.25; Table 10).

The appearance of Glauconite initiated from facies B, as we move upward to the Rampur Shale succession i.e., facies C then facies D, the mode of occurrences of the glauconites are changed accordingly. Glauconites present within the Rampur shale are concentrated mainly in the middle segment i.e within Facies B, C and D. Petrographic study shows that there are differences within the glauconites present in facies B, C and D. At facies B, the glauconites are floating within the silica vein (Fig. 4.19a). Binary plots between Fe_2O_3 vs Al_2O_3 , MgO vs K_2O , SiO_2 vs Al_2O_3 and MgO vs Al_2O_3 shows a prominent negative relationship (where $R^2=0.739$, $R^2=0.37$, $R^2=0.678$, $R^2=0.94$ respectively) (Fig. 4.19b, c, e and f). Apart from these binary plots only Fe_2O_3 vs MgO plot showing a prominent positive relationship ($R^2=0.6$) (Fig. 4.19d). The chemical relationship for authigenic glauconite which

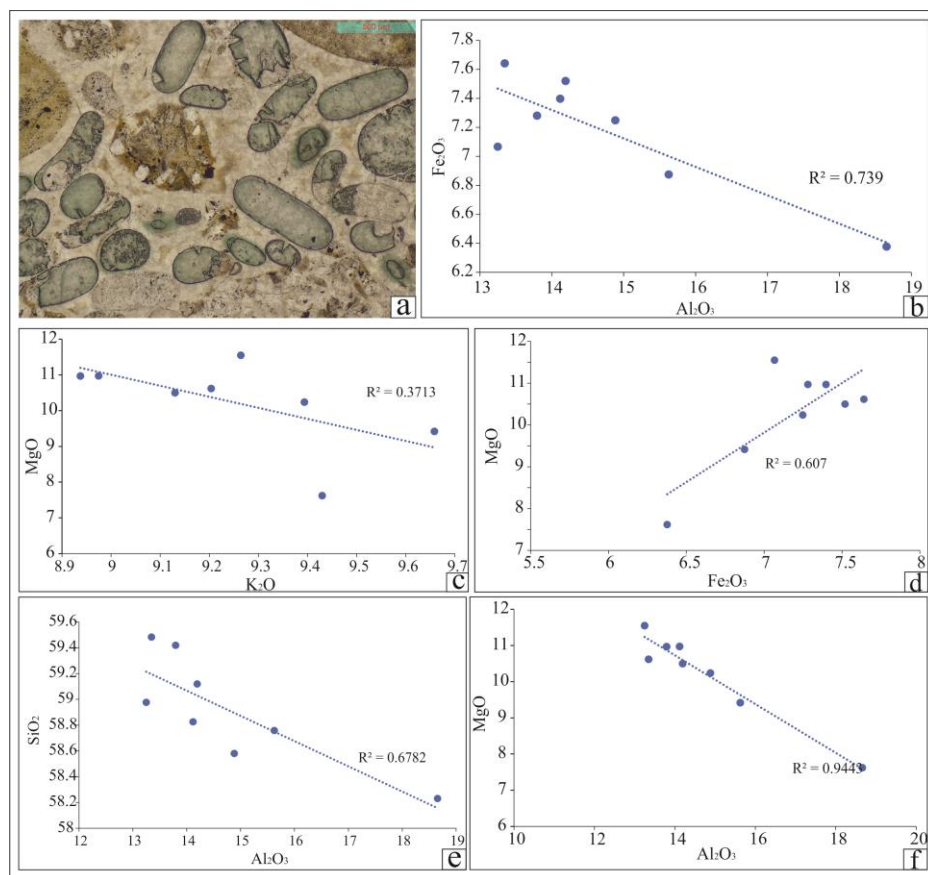


Fig. 4.19: a) Petrographic image of glauconite pellet embedded in a silica cement. Cross plot of b) Fe_2O_3 vs Al_2O_3 , c) MgO vs K_2O , d) MgO vs Fe_2O_3 , e) SiO_2 vs Al_2O_3 , f) MgO vs Al_2O_3 ; all the relationships represented here to characterise the different modes of glauconites.

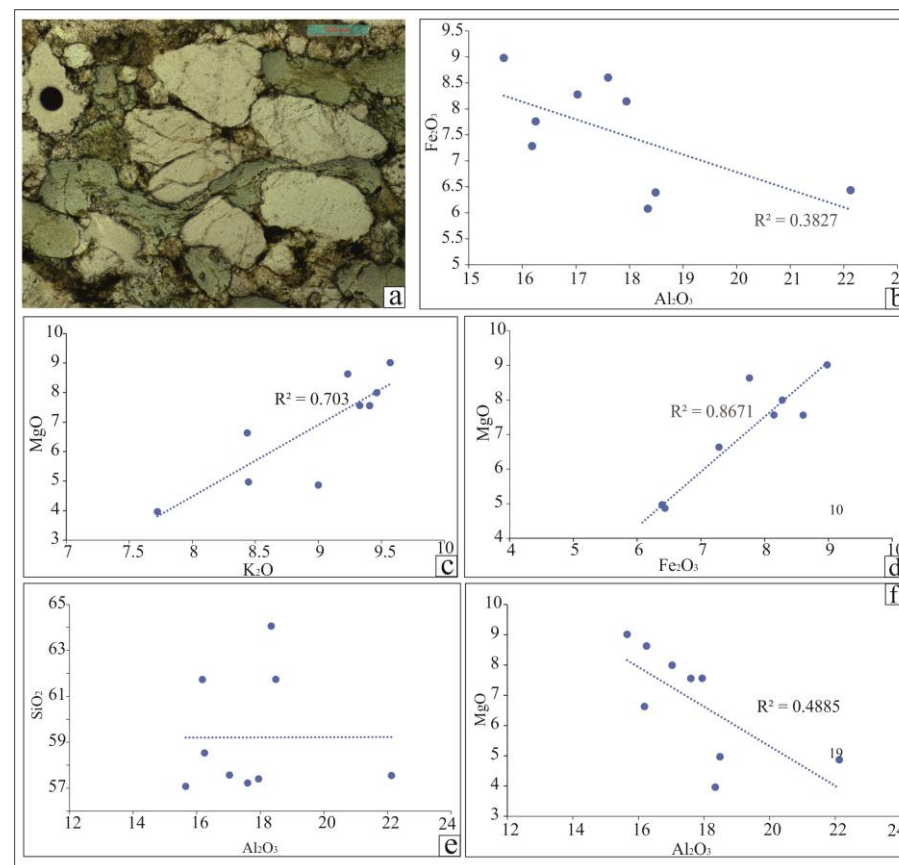


Fig. 4.20: a) Petrographic image of glauconite cement in the intergranular spaces. Cross plot of b) Fe_2O_3 vs Al_2O_3 , c) MgO vs K_2O , d) MgO vs Fe_2O_3 , e) SiO_2 vs Al_2O_3 , f) MgO vs Al_2O_3 ; all the relationships represented here to characterise the different modes of glauconites.

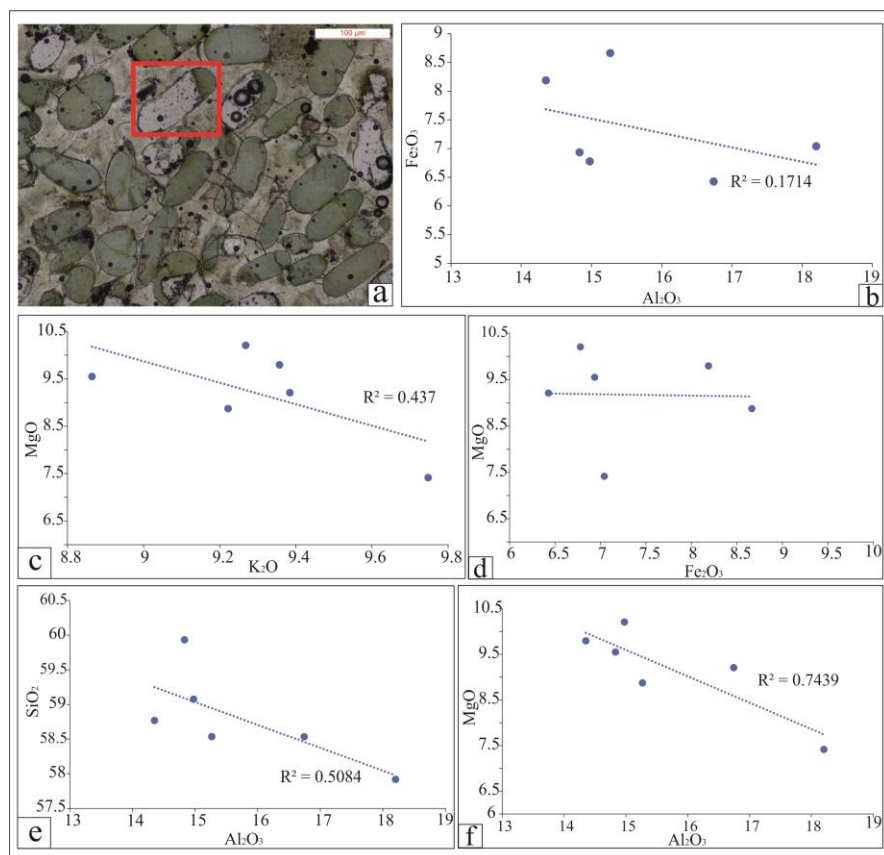


Fig. 4.21: a) Petrographic image of partially dissolved glauconite pellet. Cross plot of **b)** Fe_2O_3 vs Al_2O_3 , **c)** MgO vs K_2O , **d)** MgO vs Fe_2O_3 , **e)** SiO_2 vs Al_2O_3 , **f)** MgO vs Al_2O_3 ; all the relationships represented here to characterise the different modes of glauconites.

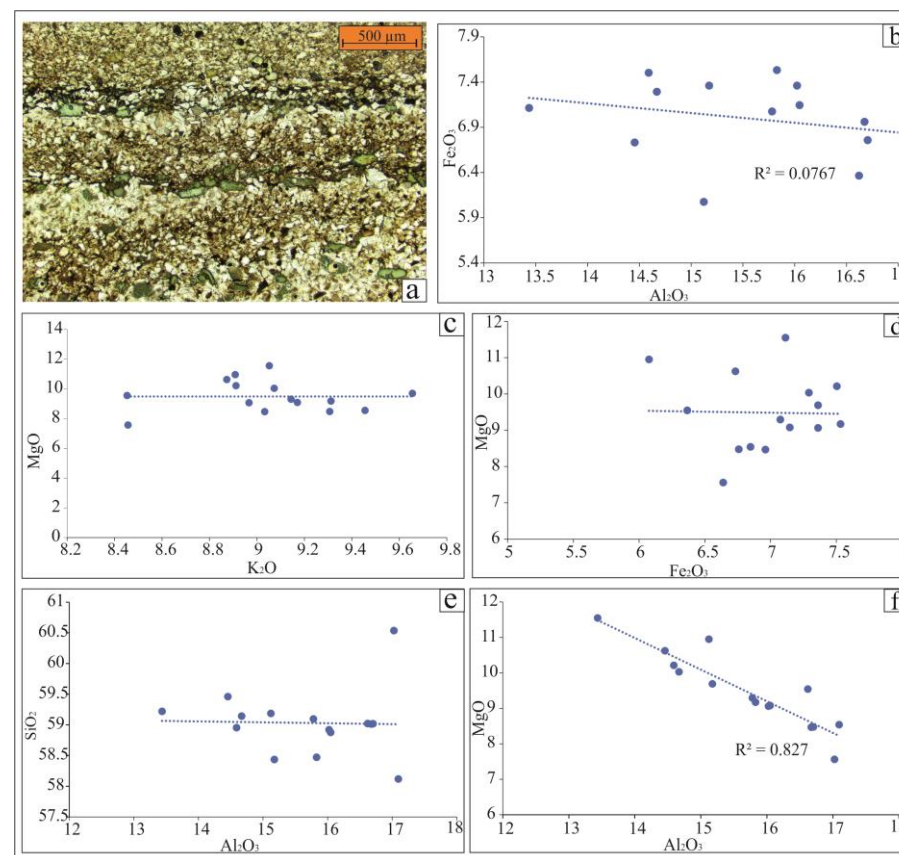


Fig. 4.22: a) Petrographic image of bed parallel glauconite pellet. Cross plot of **b)** Fe_2O_3 vs Al_2O_3 , **c)** MgO vs K_2O , **d)** MgO vs Fe_2O_3 , **e)** SiO_2 vs Al_2O_3 , **f)** MgO vs Al_2O_3 ; all the relationships represented here to characterise the different modes of glauconites.

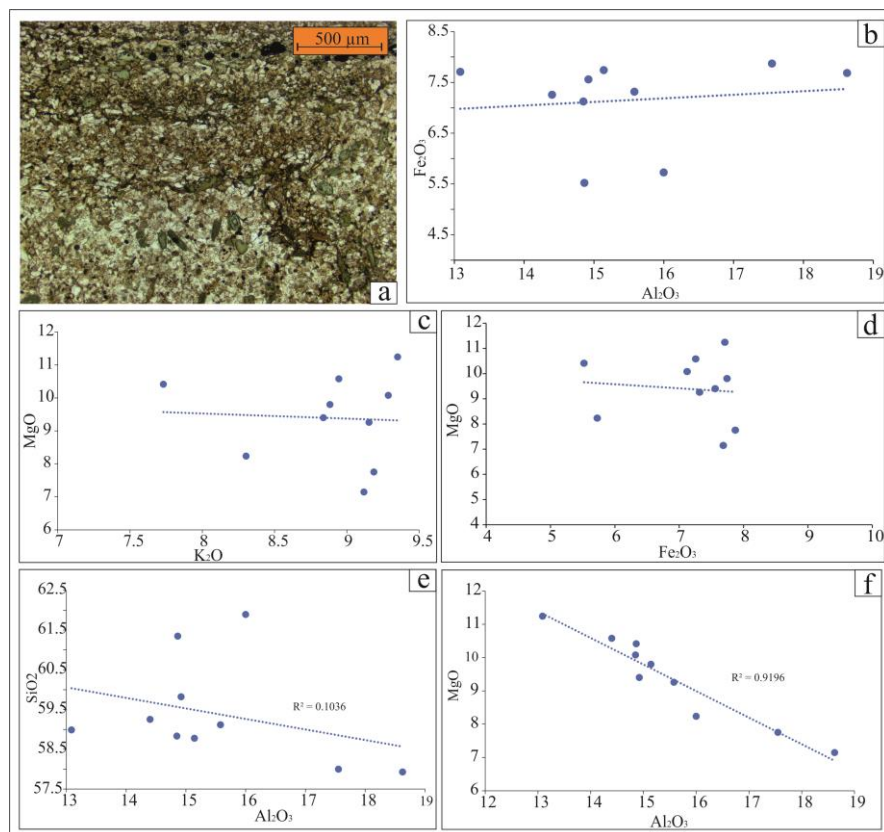


Fig. 4.23: a) Petrographic image of tectonically affected glauconite pellet (vertically arranged). Cross plot of b) Fe_2O_3 vs Al_2O_3 , c) MgO vs K_2O , d) MgO vs Fe_2O_3 , e) SiO_2 vs Al_2O_3 , f) MgO vs Al_2O_3 ; all the relationships represented here to characterise the different modes of glauconites.

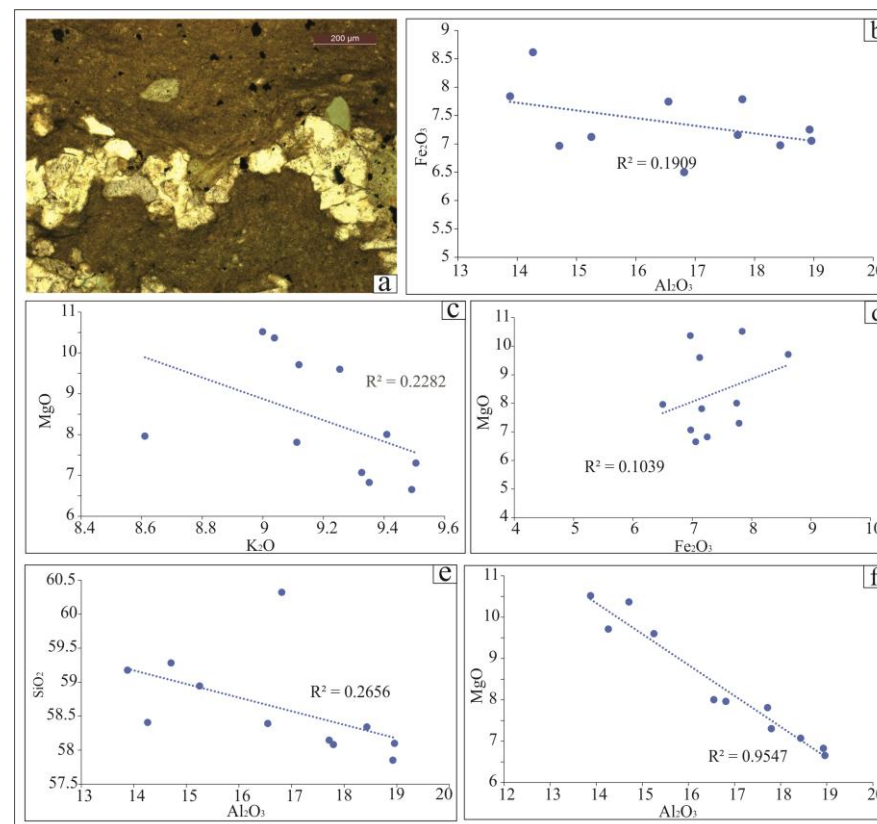


Fig. 4.24: a) Petrographic image of glauconite pellet within Shale. Cross plot of b) Fe_2O_3 vs Al_2O_3 , c) MgO vs K_2O , d) MgO vs Fe_2O_3 , e) SiO_2 vs Al_2O_3 , f) MgO vs Al_2O_3 ; all the relationships represented here to characterise the different modes of glauconites.

fills the intergranular spaces of the sandstone (Fig. 4.20a) are follows. Binary plots between Fe_2O_3 vs Al_2O_3 and MgO vs Al_2O_3 shows a prominent negative relationship ($R^2 = 0.38$, $R^2 = 0.48$ respectively) (Fig. 4.20b, f); for SiO_2 vs Al_2O_3 plot does not reflect any relationship between them. MgO vs K_2O (Fig. 4.20e) and MgO vs K_2O and Fe_2O_3 vs MgO binary cross plot for these glauconites are showing positive relationship ($R^2 = 0.7$, $R^2 = 0.86$ respectively) (Fig. 4.20c, d). Few glauconite grains are partially dissolved in nature where few grains are intact within the silica cement (Fig. 4.21a) are also chemically analysed. Cross plots between Fe_2O_3 vs Al_2O_3 , MgO vs K_2O , SiO_2 vs Al_2O_3 and MgO vs Al_2O_3 shows a prominent negative relationship ($R^2 = 0.17$, $R^2 = 0.43$, $R^2 = 0.5$, $R^2 = 0.74$ respectively) (Fig. 4.21b, c, e, f); whereas Fe_2O_3 vs MgO shows no relationship among them (Fig. 4.21d). The glauconite grains present within the overlying C facies are mostly parallel to bedding plane, pellets are following the depositional lamina (Fig. 4.22a). The plots between Fe_2O_3 vs Al_2O_3 shows a slightly negative relationship ($R^2 = 0.07$) (Fig. 4.22b); for SiO_2 vs Al_2O_3 and Fe_2O_3 vs MgO and MgO vs K_2O plot does not reflect any relationship (Fig. 4.22c, d, e). MgO vs Al_2O_3 binary cross plot for glauconite are showing a negative relationship ($R^2 = 0.82$) (Fig. 4.22f). Few pellets are vertically arranged with respect to depositional lamina (Fig. 4.23a). Binary plots between Fe_2O_3 vs Al_2O_3 , MgO vs K_2O and Fe_2O_3 vs MgO shows almost no relationship (Fig. 4.23b, c, d); for SiO_2 vs Al_2O_3 and MgO vs Al_2O_3 plot is reflecting a negative trend ($R^2 = 0.1$, $R^2 = 0.9$ respectively) (Fig. 4.23e, f). Finally at the upper part (equivalent to facies D) the glauconites are associated with the shale and silty part (Fig. 4.24a). In this part Binary plots between Fe_2O_3 vs Al_2O_3 , MgO vs K_2O , SiO_2 vs Al_2O_3 and MgO vs Al_2O_3 shows a negative relationship ($R^2 = 0.19$, $R^2 = 0.2$, $R^2 = 0.2$, $R^2 = 0.9$ respectively) (Fig. 4.24b, c, e, f). Fe_2O_3 vs MgO binary cross plot for these glauconite are showing feebly positive relationship ($R^2 = 0.1$) (Fig. 4.24d).

4.4.5.2: Interpretation:

In general, glauconite contain Si and Al in tetrahedral site, Al, Fe (Fe^{+2} , Fe^{+3}) and Mg in octahedral site and K remains in the structure as interlayer cation (Thompson and Hower 1975). From facies B to facies D, the glauconite bearing layers of the Rampur shale are showing some distinctiveness among them. The cross plot between Fe_2O_3 vs Al_2O_3 is always showing a negative relationship for all the varieties of glauconites which means continuous substitution activity is going on in between iron and aluminium. Both Fe and Al are

occupying the octahedral sites of glauconite mineral. SiO_2 vs Al_2O_3 again showing negative relationship for most of the studied glauconites because of substitutional relationship. Both Al and Si are belonging to tetrahedral site. Fe_2O_3 Vs MgO shows positive relationship for two varieties of glauconites in the facies B; this is because both Fe and Mg are incorporating in the octahedral sites. Fe_2O_3 vs K_2O representing a compositional variation towards Illite to glauconite. In glauconite structure K^+ is entered as interlayered cation and Fe^{+2} is incorporated at the octahedral site. During Precambrian time all the glauconites are poorer in iron showing a composition of Fe-illite rather than true glauconite (Dasgupta et al., 1990; Deb and Fukuoka 1998, Banerjee et al., 2008,2015; Tang et al., 2017; Bansal et al 2020; Mandal et al 2020; Mandal et al., 2022). K_2O content of all the glauconite from three members are indicating towards matured or highly evolved glaucony variety (Odin and Matter,1981; Amorosi 1995, Amorosi 1997; Mandal et al., 2020, Mandal et al., 2022). K_2O vs MgO plot again showing a variable relationship for different types of the glauconites because K^+ is entered as interlayered cation and Fe^{+2} is incorporated at the octahedral site. So, these two oxides are not maintaining a definite trend (Fig. 4.25). MgO vs Al_2O_3 always shows a negative trend for their relationship which reflecting that both the cations are incorporating in octahedral sites by replacing another element. Here the substitutional relationship is so prominent.

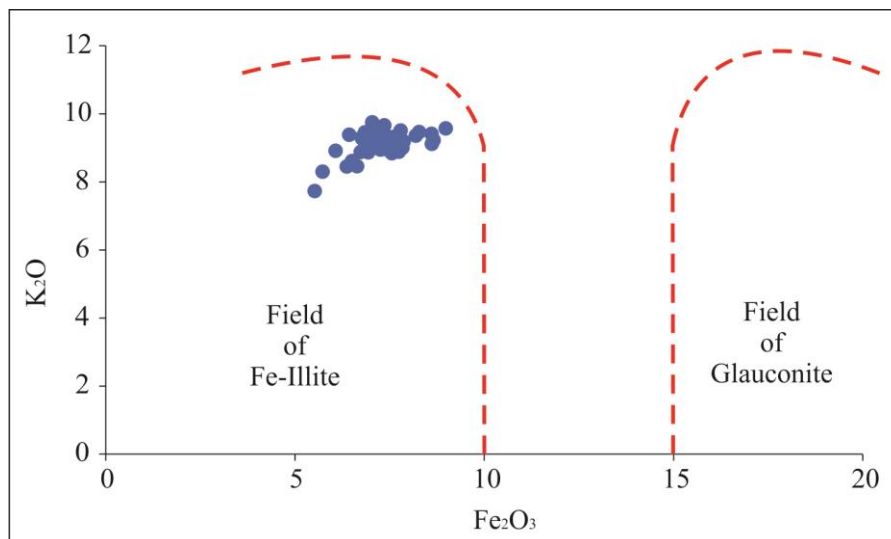


Fig. 4.25: Bivariate discrimination diagram between K_2O and Fe_2O_3 shows that all the modes of glauconites from Rampur shale are plotted in the Fe-Illite field.

4.5: Conclusion:

Analysing all the major and trace element concentrations of the whole succession of Rampur Shale Member, several proxies have been calculated by using these trace and major element to determine the source of the sediments, palaeoweathering condition, Palaeoclimate, palaeogeography and palaeoredox scenario of the depositional medium.

1. Using several proxies for all the sediments from retrogressive part (comprising facies A, B, C and D) and upper part (comprising facies E and F) shows that the sediments are sourced from mostly felsic dominated region.
2. The weathering indices like CIA, CIW and PIA are showing very high value which is indicative of very high weathering intensity.
3. Several palaeoclimatic proxies and binary cross plots are strongly indicate that during the deposition of Rampur Shale the climate was warm and humid.
4. Using the geochemical twins, the palaeogeography of the depositional system reveals that the Rampur Shale member was deposited in a marine setting.
5. The geochemical proxies for palaeoredox condition show that the depositional condition was mostly anoxic to dysoxic in nature but somewhere fluctuations of the palaeoredox condition also demarcated and show that depositional medium not fully devoid of oxygen.
6. Facies wise point analysis was performed to find out the geochemical oddities of the glauconites present in the Rampur Shale. Binary cross plots between several major oxides showing a prominent strong relationship for the glauconites within the facies B and D whether it is positive or negative. Another important finding within Rampur that the glauconites are exceptionally enriched in magnesium (Mg). Normally, the glauconites contain 3-4% of magnesium whereas the Rampur Glauconites contain 8-9% of Mg (average), sometimes even it exceeds 11% (detailed discussion and origin of this high Mg glauconites are discussed in Chapter 5).

PART III

ASPECTS OF SPECIAL INTERESTS

CHAPTER: 5

**Sedimentology, geochemistry, origin and
implication of high-Mg glauconites from
Rampur Shale Member**

5.1: Introduction

Glauconite, one of the most abundant authigenic clay minerals being rich in cations such as potassium, iron, and magnesium, is abundant in marine sedimentary rocks ranging from the Paleoproterozoic to Recent (Thompson and Hower, 1975; Odin and Matter, 1981; Amorosi et al., 2007; Banerjee et al., 2008, 2016a, 2020; Huggett and Cuadros, 2010; Baldermann et al., 2013, 2017; López-Quirós et al., 2020; Giresse, 2022; Roy Choudhury et al., 2022b, 2022a; Starzec et al., 2023a; Rubio and López-Pérez, 2024). The mineral glauconite, representing a 2:1 dioctahedral clay mineral structure, is characterized by a wide compositional spectrum with a wide range of variation in SiO₂ (47–50 wt%), K₂O (2–10 wt%), Al₂O₃ (5–8 wt%), Fe₂O₃(total) (5–25 wt%) and MgO (3–4 wt%) content (Odin and Fullagar, 1988; El Albani et al., 2005; Meunier and El Albani, 2007; Amorosi et al., 2007; Baldermann et al., 2017; Roy Choudhury et al., 2021). Several factors, including low sedimentation rate, nutrient-charged seawater, and suboxic to dysoxic redox conditions, promote abundant authigenic glauconitization (see Roy Choudhury et al., 2021 for more references). The Phanerozoic glauconites, including those forming in modern ocean basins, tend to form in outer shelf and slope environments and represent a compositional continuum between Fe-rich but K-poor glauconitic-smectite and Fe- and K-rich glauconitic end-member composition. The Precambrian glauconites, on the other hand, are mostly restricted to shallow marine depositional environments and represent restricted chemical composition of Fe-poor and K-rich glauconite similar to that of Fe-illites (Odin and Matter, 1981; Odin and Fullagar, 1988; Dasgupta et al., 1990; Deb and Fukuoka, 1998; Banerjee et al., 2008, 2015; Bansal et al., 2020; Mandal et al., 2020; Starzec et al., 2023a; Rubio and López-Pérez, 2024). High abundance of glauconite pellets (exceeding 50% of the total rock volume) within fine-grained sedimentary rocks is often correlated with the ‘condensed’ and ‘mega-condensed’ sections for sequence stratigraphic implications (Amorosi, 1995; Amorosi et al., 2007; Mandal et al., 2020), which is difficult to interpolate for Precambrian glauconites, especially when their abundance is noted within sandy, coarse-grained sediments. As glauconite preferentially forms at the sediment-seawater interface by the active cation exchange between seawater and the substrate during episodes of low sedimentation, it is often used as a proxy to the paleogeographic conditions, including the paleoredox and sedimentation rate (Odin and Matter, 1981; Amorosi et al., 2007; Meunier and El Albani, 2007; Baldermann et al., 2013, 2017; Banerjee et al., 2020; López-Quirós et al., 2020; Tribouvillard et al., 2021; Giresse, 2022). The unique chemical composition frequently reflects the complex evolutionary pathway of glauconite maturation, resulting in a

conspicuously anomalous composition of glauconite, rich in potassium, iron, magnesium, and/or aluminum and silicon (Amorosi et al., 2007; Baldermann et al., 2013; Banerjee et al., 2008, 2015; Mandal et al., 2020; Roy Choudhury et al., 2022b, 2021). In rare instances, the octahedral Mg content of glauconite, representing two- to three-fold higher MgO concentration than the average (~3 wt% of MgO), has been attributed to glauconite formation under unique depositional micro-millieu (Drits et al., 2010a; Banerjee et al., 2008, 2019). However, the implications of the geochemistry of glauconites within the Proterozoic epicontinental oceans are still poorly constrained, prompting further investigations. The enigmatic geochemical signatures of glauconites formed abundantly within the Proterozoic shallow marine sediments; thus, they deserve special attention to test their applicability to record paleoceanographic conditions.

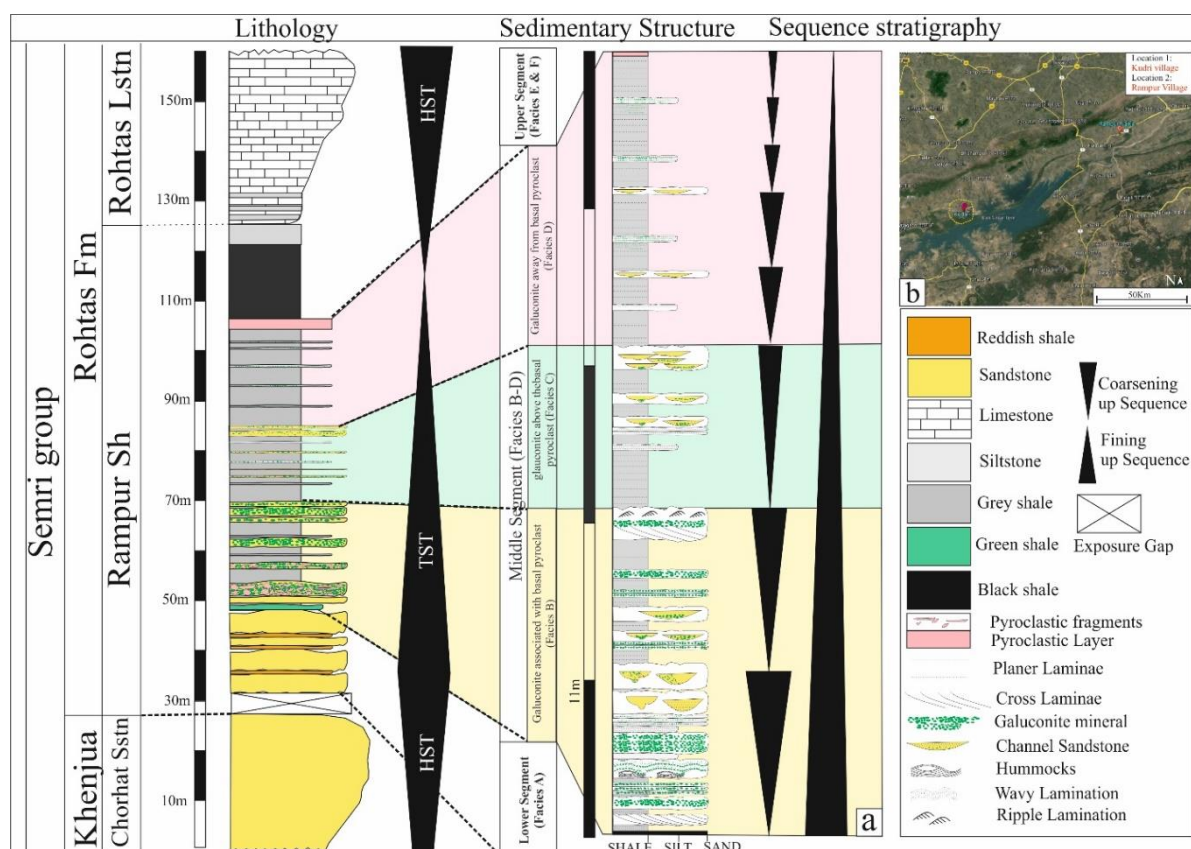


Fig. 5.1: a) Stratigraphic Succession along with different segments, lithology, primary sedimentary structures and occurrences of glauconite, reflecting the sequence stratigraphic scenario of Rampur Shale in Lower Vindhyan Semri Group. b) Location map for the Rampur Shale exposure

The current study aims to integrate the sedimentology and sequence stratigraphy of the glauconite-rich horizons of the Mesoproterozoic Rampur Shale Member of the Semri Group, Vindhyan Basin, India. Moreover, with the help of detailed mineralogical and mineral chemical studies, the factors promoting abundant green marine clay minerals within shallow marine

sediments are also investigated. The Rampur Shale Member of the Lower Vindhyan/Semri Group is sandwiched between the older Chorhat Sandstone and the younger Rohtas Limestone members and exposed around Maihar, Madhya Pradesh (Fig. 5.1; Bose et al., 2001; Sarkar et al., 2002). This paper aims to A) study the occurrence of the glauconites within the system tracts forming the Rampur Shale Member, B) investigate the origin of the Mg-rich glauconites, and finally, C) understand the paleoceanographic condition during the Mesoproterozoic time. In addition, a comparative study of glauconites is presented within two Upper Vindhyan and one Lower Vindhyan Member.

5.2: Results

5.2.1: *Sedimentology of the succession:*

The ~85 m thick Rampur Shale Member of the Semri Group consists predominantly of sandstones, siltstones, and shales with the occasional juxtaposition of thin volcanoclastic layers. Considering the sand : shale ratio, the presence of primary sedimentary structures, and the geometry of the sandstone and shale units, the Rampur Shale Member is divided into six distinctive facies (facies A–F; Fig. 5.1a). The lowermost 20 m of the succession is primarily characterized by laterally persistent, sheet-like sandstone bodies with occasional hummocky cross-stratification and sand: shale ratio of 4:1. The overlying ~55 m of the succession, comprising facies B, C, and D, is characterized by mm- to cm-scale thick sandstone, siltstone and shale alternations with variable content of green glauconite grains. The uppermost facies E is completely devoid of sandstone and represents a ~10 m thick, laterally persistent black shale deposit, at places, capped by a ~3 m faded shale unit.

The 30 m thick glauconite-bearing Facies B initiates with the first appearance of a green shale intercalating with approximately 10 cm thick light grey shales and sandstones (Fig. 5.2a) depicting sand: shale ratio of 3:2. In addition, several fine-grained, light-coloured, pyroclast-rich layers are observed within this facies. The sandstone beds are well-sorted and fine-grained, thinning and fining upwards, and exhibit tabular and sheet-like geometries with individual bed thicknesses ranging from 30 cm (Fig. 5.2b,c). These sandstones display small-scale hummocky to cross-stratifications (HCS) with 5–6 cm wavelengths, planar lamination, and low-angle cross-stratification (Fig. 5.2d). Besides the tabular and sheet-like geometries, some sandstone beds manifest lenticular channel geometry with wider and more profound channels and sharp bases with bed-soles often marked with gutters, prod marks, and groove casts (Fig. 5.2e,f,g). Green, rounded to sub-rounded, fine sand-sized pellets are abundant throughout this facies;

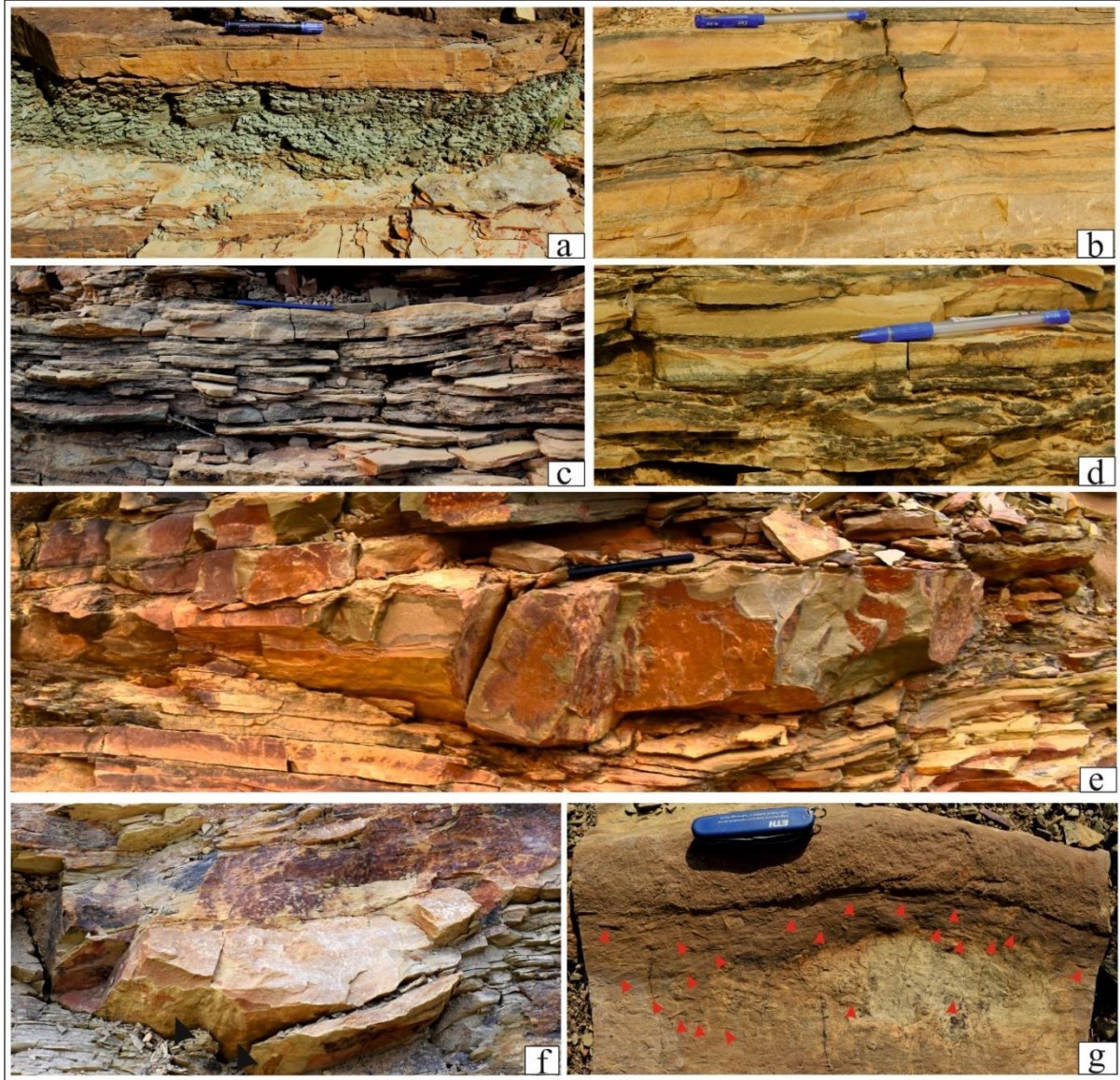


Fig. 5.2: a) Green shale overlain by sandstone. b) Tabular Sandstone. c) Sheet sandstone. d) Small scale hummocks within the sandstone. e) Channel-like sandstone. f & g) Sole-features at the bottom of the sandstone (arrowed).

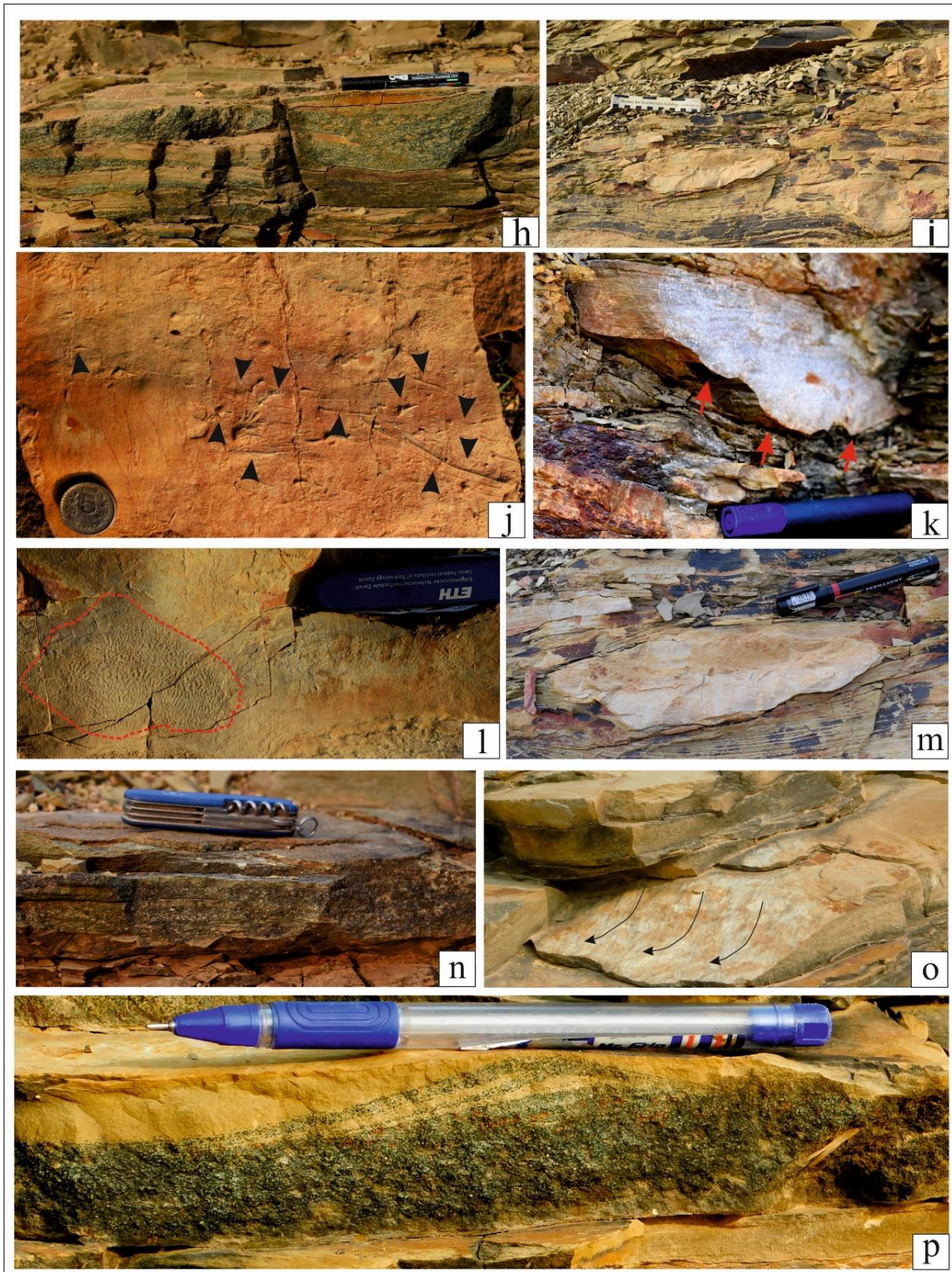


Fig. 5.2 (Continued): **h)** Pyroclast bearing glauconitic sandstone. **i)** Sand percentage decreases (confined within gutter only) and shale increases (Sand: Shale =2:3). **j)** Sole features at the bottom of the sandstone. **k)** Biogenic impression on top surface of the siltstone. **l)** Gutters at the bottom of the channel sandstone. **m)** Glauconites accumulates at the bottom of the channel fill. **n)** Glauconite within siltstone at the top part. **o)** Slide planes within sandstone. **p)** Glauconites following the depositional lamina.

however, the lower parts of the Facies B are more enriched in glauconite pellets randomly orientated within the sandstone beds and the associated pyroclastic deposits (Fig. 5.2h). The facies B grades into the ~15 m thick facies C, demarcated by laterally persistent, very fine-grained sandstones and shales with a sand: shale ratio of 2:3 (Fig. 5.2i). The sheet sandstones compared to those below, with finer average grain size. The channel sandstones often exhibit step gutters, prod marks, groove casts, and occasional biogenic mat impressions; however, minor occurrences of thin (individual bed thickness ranging from 10 to 15cm), very fine-grained sheet sandstones are also observed (Fig. 5.2j, k, l). The intercalating shale units are comparatively thicker (20–25cm). The concentration of glauconite pellets within the sandstone and shales decreases upward, and the glauconite pellets exhibit a preferred orientation within channel fills, occasionally confined to the base of gutters (Fig. 5.2m). The overlying ~10 m thick Facies D marks a fine-grained succession and lacks comparatively thick sandstone units, resulting in a sand : shale ratio of 1:5. The shale exhibits grey to greenish-grey hues. In contrast, the sandstone or siltstone occurs predominantly in channel forms, wider and shallower compared to underlying intervals. The sandstones and siltstones present all over the succession are unanimously glauconitised (Fig. 5.2n). Numerous slide planes occur at various levels within these parts (Fig. 5.2o). In many places, glauconites are following the depositional lamina (Fig. 5.2p).

5.2.2: Interpretation:

The glauconite is present within facies B, C, and D, with varying concentrations, with facies B having the highest concentration of glauconite (~50% of the total rock by volume) occurring in association with abundant pyroclastic fragments. The other sedimentary features, i.e., the sheet-like body geometry and primary sedimentary structures preserved within the sandstone, indicate that the sandstones are the products of high-energy events within an overall low-energy environment. Ripple lamination at the top of the sandstone is possibly the product of a waning current. Hummocky cross-stratification/low angle cross strata and sole features on the sandstone undersurfaces, e.g., prod and brush marks and step gutters, also indicate the presence of the high energy environment during the deposition of sandstone beds. This well-sorted, fine-grained, sand-dominated section, intervened by thin mud laminae, is likely to be deposited in a lower shoreface environment, i.e., the inner shelf of the depositional basin. The sandstone beds, prominently exhibiting wave structures, indicate deposition by waves that thoroughly erased their muddy substrate. It appears that sand deposition predominantly

occurred during the subsidence of storm activity. The increasing abundance of shales suggests a low-energy depositional environment. Channel sands likely formed from constricted flows, with gutters and prod marks indicating stronger current velocities at their bed soles. Turbulent flows likely deposited bodies with erosional bases. The progressive thinning of sheet sandstones and simultaneous thickening of shale beds suggest a progradational trend in the deposition.

5.2.3: Morphology of the glauconites and mode of occurrence:

The green pellets bearing Rampur Shale Member are confined to the coarse to fine-

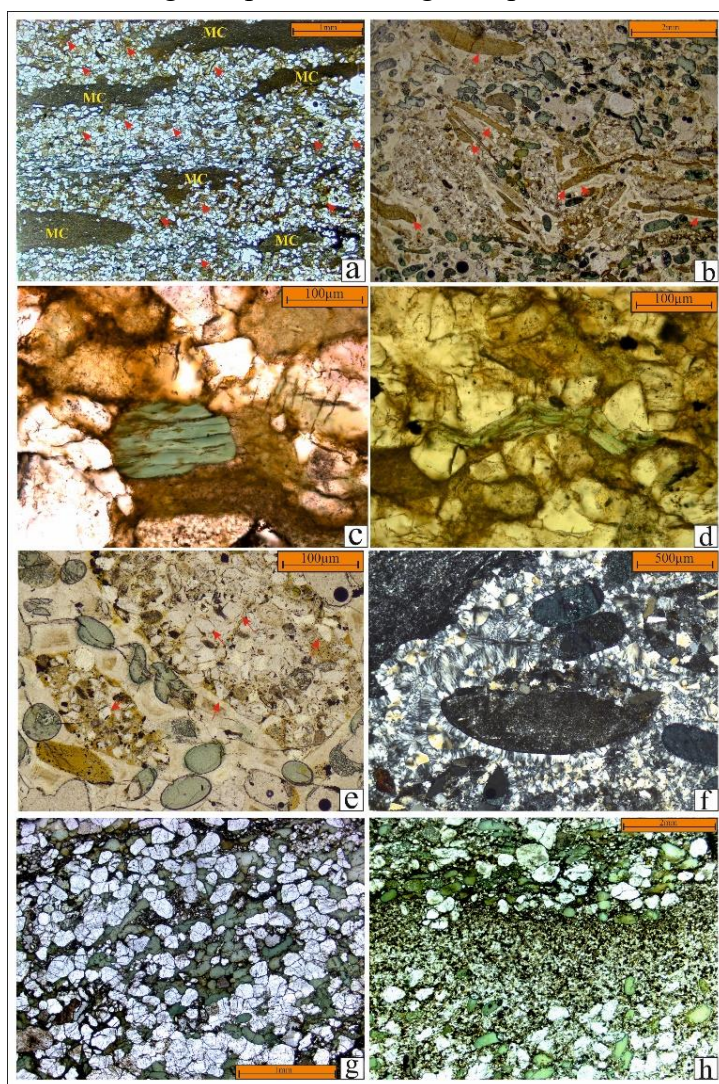


Fig. 5.3: a) Fine sandstone and siltstone with abundant mud clasts (MC) with tiny glauconite pellets (marked with red arrow). b) Glauconite associate with framework pyroclasts (red arrow), quartz, c) feldspar, d) mica and e & f) chalcedony cements. g & h) Glauconite associated with sandstone showing bi-modal size distribution of angular grains (Fig. 5.3g,h). The pellets manifest a fining-upward nature similar to that of the

grained sheet or channel-like sandstone and siltstone bodies of facies B–D (Fig. 5.2). The fining-upward sandstone facies grades into very fine sandstone and siltstone with abundant mud clasts composed of clay-sized tuffaceous particles with tiny glauconite pellets (Fig. 5.3a). The sandstone units of facies B, contain sub-rounded to sub-angular framework grains of quartz, K-feldspar, and mica (majority biotite) with pyroclastic rock fragments and lithic fragments, cemented by silica (chalcedony) (Fig. 5.3b,c,d,e,f). The framework quartz grains exhibit bimodal size distribution, with the larger grain population (size ranging from 0.4 mm to 0.35 mm) having dominantly sub-rounded grains with cracks, while the finer grain population (size ranging from 0.08 mm to 0.06 mm) representing mostly sub-

sedimentary packages of the Rampur Shale Member, where coarse sand-sized pellets dominate the lower part while fine sand-sized pellets define the upper part. The feldspar grains, notably represented by K-feldspar, increase abundance from facies B to facies D (Fig. 5.3i). Some opaque iron-rich minerals occur as accessory minerals.



Fig. 5.3 (Continued): **i)** K-feldspar at facies D. **j)** Colour variation in glauconite pellet under PPL and **k)** Glauconite under CPL. **l)** Glauconite in cement form. **m)** Glauconite along the depositional lamina. **n)** Dehydration cracks within glauconite. Partially altered **o)** feldspar to glauconite, **p)** biotite to glauconite. **q)** Angular quartz inclusion within glauconite.

The rounded to sub-rounded pellets within the sandstone and siltstones appear light to dark green under plane-polarized light and bluish-green interference colour with mottled extinction under cross-polarized light (Fig. 5.3j,k). The green glauconite pellets occur in two distinct modes, where glauconite pellets are the dominant mode with a minor concentration of green glauconitic cement. While the glauconite pellets have an average dimension of $\sim 50\mu\text{m}$ (Fig. 5.3e,g), the glauconitic cement forms within the inter-granular spaces have an average length of $200\text{--}300\mu\text{m}$ (Fig. 5.3l). The pellets are randomly distributed within the lower part of the section, and individual grains appear to be ‘floating’ within the silica (chalcedony) cement without prominent grain contacts (Fig. 5.3b, e, f). However, at the upper part, glauconite pellets are often concentrated along small-scale cross-stratifications (Fig. 5.3m). The pellets frequently

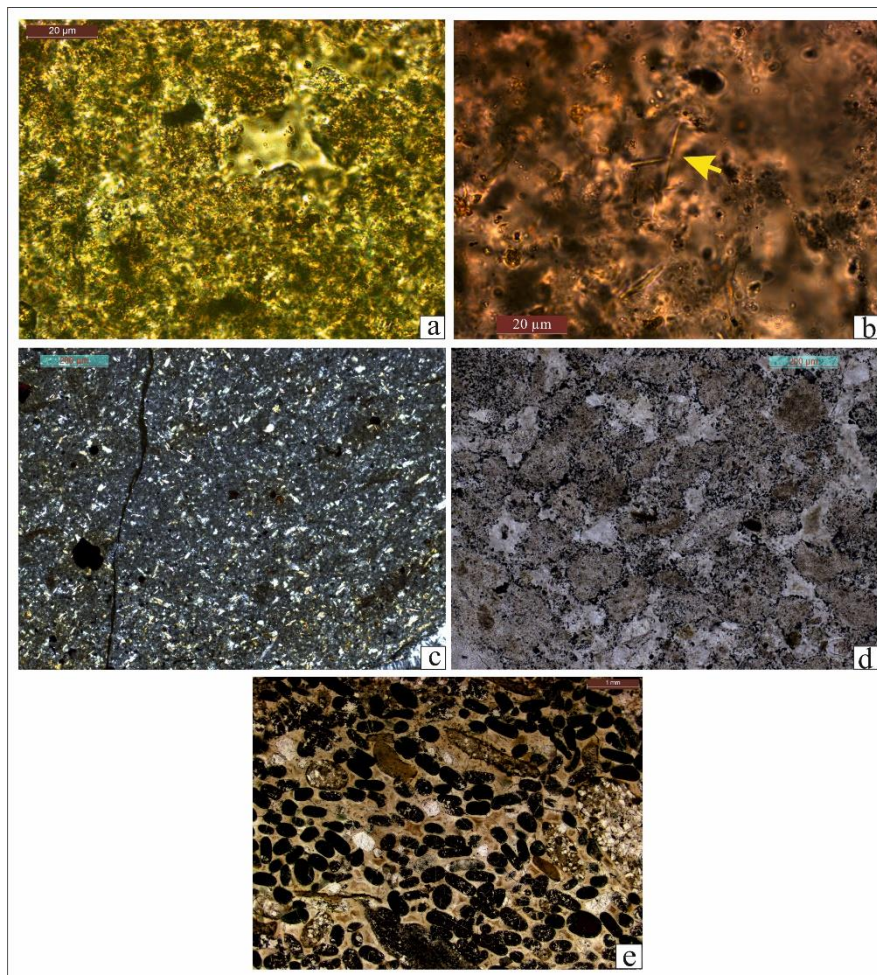


Fig. 5.4: a) Glass shards with raptured bubble walls. b) Tripple junction point. c) Welded tuff structure within pyroclast. d) Networks of vacuoles scattered all around the pyroclastic infested layer. e) Hyaloclastite texture within glauconite bearing pyroclastic layer.

display shrinkage cracks (Fig. 5.3n). In most cases, the pellets are completely glauconitized without any trace of the substrate; however, in some rare cases, incipient glauconite formation can be observed along the cleavage of the mica and feldspar (Fig. 5.3o,p). Some glauconite pellets have tiny quartz inclusions (Fig. 5.3q). The frequent presence of glass shards, numerous recrystallized bubble-wall shards with triple

junction (Figs. 5.4a,b), pumice, devitrified glass with quenching cracks, and the remnants of raptured gas bubble (Fig. discussed in chapter 3), welded tuff within shale layers associated

with pyroclastic (Fig. 5.4c), networks of vacuoles filled by chalcedony cement are abundantly present within the sandstone (Fig. 5.4d). The pyroclastic rock fragments and glauconites typically show a hyaloclastite texture (Fig. 5.4e). The concentration of glauconite pellets within the succession is variable, with abundant (>50% of the rock by volume at places) pellets at the lower part of the succession (facies B), which drastically reduces to 10–15% of the rock by volume within the middle part (facies C) before reaching ~ 40% of the rock volume within the upper part of the succession (facies D) (Fig. 5.5a). Along with the glauconite, the pyroclastic fragments and mud content is also varying from facies B to D. Facies B contain higher amount of pyroclastic fragments and lower amount of mud content while the scenario is totally reverse for facies D (Fig. 5.5b). The glauconite pellet-bearing sandstone within the lower part of the succession often exhibits large pyroclastic fragments with vertical cracks as framework particles (Fig. 5.3b).

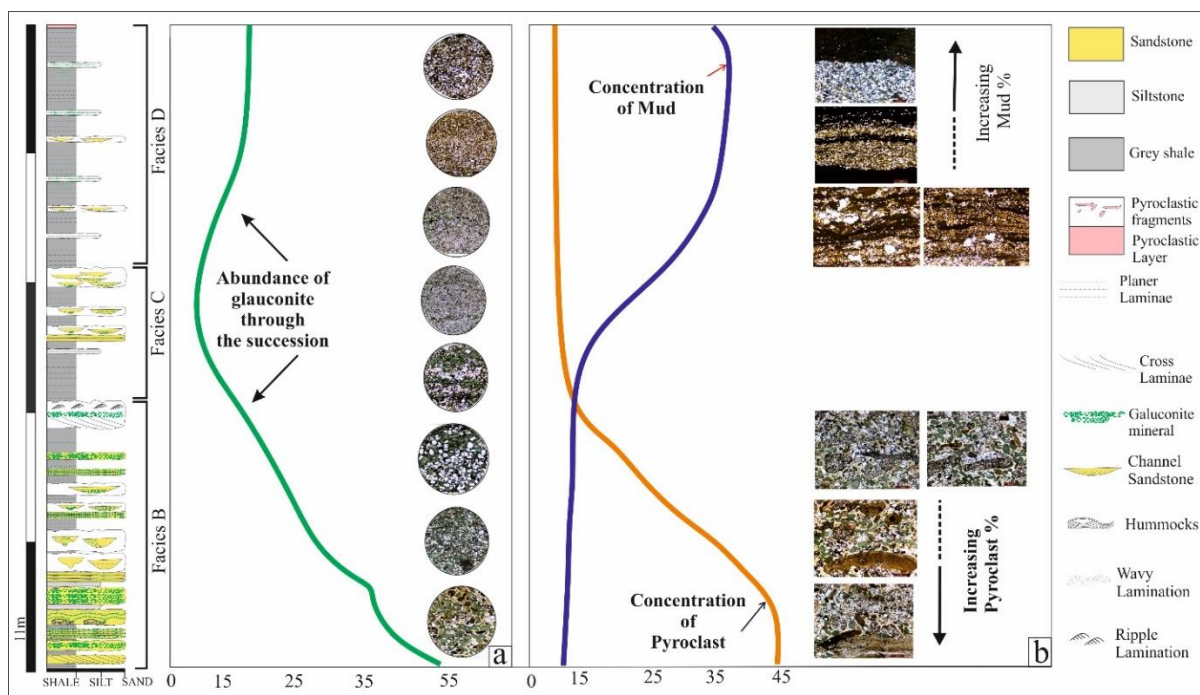


Fig. 5.5: a) Distribution of glauconite concentration across facies. **b)** Note the variation of pyroclastic fragments and mud concentration along the facies.

5.2.4: Micro-texture and mineralogy of the glauconite:

The micro-textural studies of the glauconite pellets, as revealed in the Secondary Electron Imaging (SEI mode), manifest the characteristic ‘rosette’ texture comprised of tiny (1–3 μm along the long axis), curved blebs of glauconite arranged in a ‘rose-petal’ like structure (Fig. 5.6a). At places, glauconite alteration from feldspar can be observed (Fig. 5.6b). The

abundance of fine-grained clay minerals can be confirmed from the broad-based reflections at the lower diffraction angles ($5\text{--}28^\circ 2\theta$). The sharp but asymmetric reflection at $\sim 9^\circ 2\theta$ corresponds to the basal spacing of $9.98 \text{ \AA}$. Quartz and minor feldspar are also recorded in the whole-rock X-ray diffraction analysis.

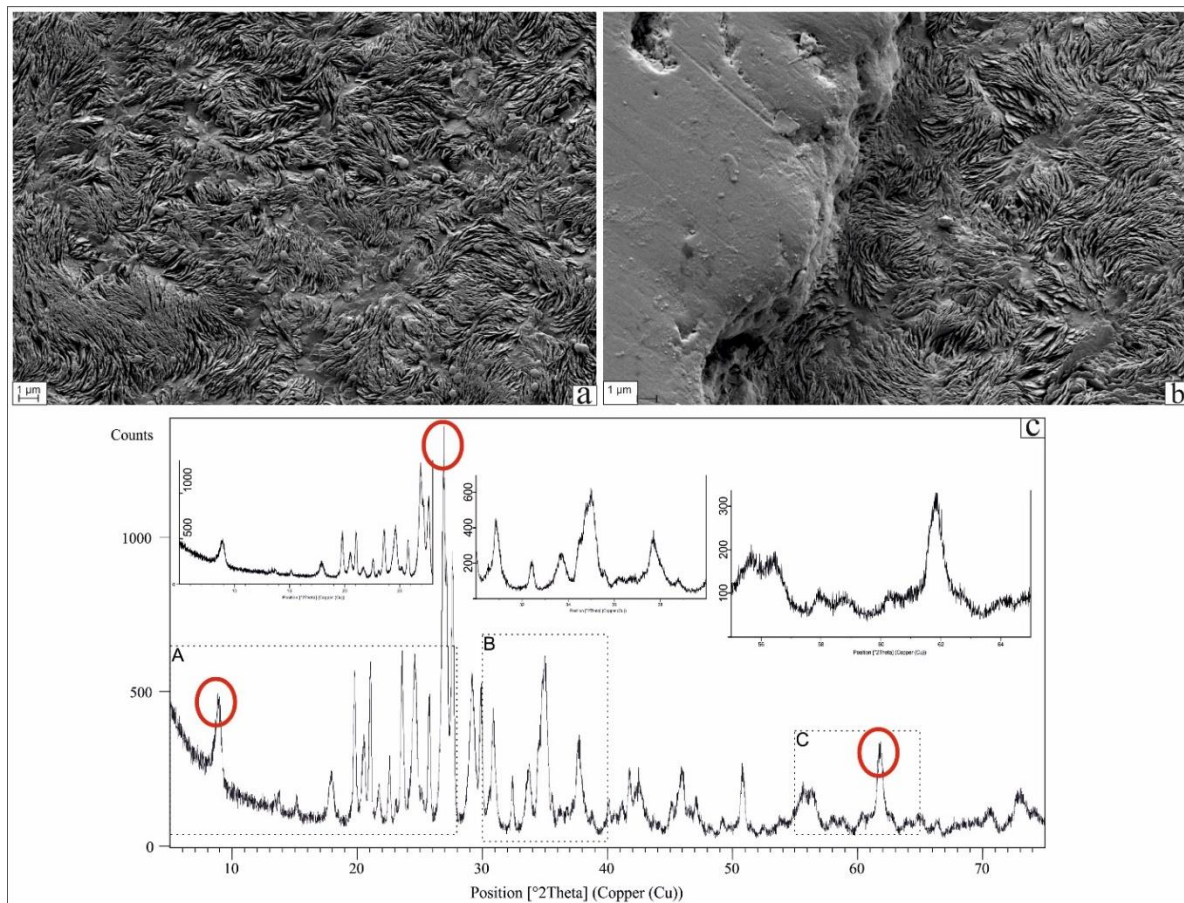


Fig. 5.6: **a)** Glauconite is showing rosette texture comprised of tiny curved blebs of glauconite arranged in a 'rose-petal' like structure. **b)** At places glauconites are altered from feldspar. **c)** XRD spectroscopy of Glauconite bearing horizon (red circles marks the characteristics peaks for glauconite).

The equidistant, broad-based, and asymmetric reflections of (001), (002), (003), (004) and (005) can be observed at $9.98 \text{ \AA}$, $4.95 \text{ \AA}$, $3.31 \text{ \AA}$, $2.52 \text{ \AA}$ and $2.01 \text{ \AA}$ are typical of glauconite (Thompson and Hower, 1975; Odin and Matter, 1981; Banerjee et al., 2015; Starzec et al., 2023a). The strong basal reflections of even-numbered peaks (i.e., (002) and (004)) might indicate the presence of illite; however, the green clay minerals can be exclusively characterized as glauconite from the reflections at $3.07 \text{ \AA}$ and $3.62 \text{ \AA}$, respectively, which are characteristics of (112) and $(11\bar{2})$ reflections of glauconite and are absent in illites. The relatively higher intensity of (002) and (004) peaks might have resulted from low iron substitution in the octahedral site of the glauconite (Thompson and Hower, 1975), which is confirmed by the mineral geochemical analysis of the glauconite pellets (discussed later). The

(060) reflection at 1.50 Å corroborates the di-octahedral nature of the clay mineral (Moore and Reynolds, 1997). The possibility of the green clay minerals being celadonite can be ruled out from the obscured (11 $\bar{1}$) and (021) reflections and overlapping reflections of (13 $\bar{1}$) and (130) (Singh et al., 2023). The mineralogical analysis suggests a highly ordered glauconite structure with negligible smectite interstratification (Thompson and Hower, 1975; Odin and Matter, 1981; Amorosi et al., 2007; Roy Choudhury et al., 2021; Singh et al., 2023).

5.2.5: Mineral chemistry of glauconite:

The major elemental composition of glauconite was determined from the point analysis of individual glauconite pellets, and the results are provided in Table 11. All the analytical data plots were normalized to 100% on an anhydrous basis for different cross-plots.

The glauconites within facies B to D of the Rampur Shale Member represents overlapping chemical composition (Table 11). The K₂O concentration of glauconite is very high, with most of the glauconites having >8 wt% K₂O (Table 11). The glauconites within the lower facies (facies B) are slightly enriched in K₂O with an average of 8.7 wt% compared to the overlying facies with average K₂O concentration of 8.6 wt% respectively for facies C and D. The Fe₂O₃(total) concentration of these glauconites are low (<15 wt%) and varies from 5.3–15.2 wt% (avg. 7.7 wt%) , with facies C having the highest average Fe₂O₃(total) concentration of 8.3 wt%. The Al₂O₃ content remains high, varying from 11.1–23.5 wt.% (avg. 14.9 wt.%). The MgO content is exceptionally high, varying from 2.0 to 11.1 wt.% (avg. 7.6 wt.%). The SiO₂ content varies between 55.6 to 60.4 wt.% (avg. 55.4 wt.%).

Apart from few datapoints, the glauconites of the Rampur Shale do not reflect any compositional difference among facies. The glauconites from the Rampur Shale Member have consistently high K₂O content (avg. 8.6 wt% with most of the glauconites having >8 wt% of K₂O) irrespective of their stratigraphic position (Table 11). The high K₂O content corroborates the ‘highly-evolved’ maturation stage of glauconite (Odin and Matter, 1981; Dasgupta et al., 1990; Deb and Fukuoka, 1998; Amorosi et al., 2007; Banerjee et al., 2008, 2015; Huggett and Cuadros, 2010; Baldermann et al., 2013). This interpretation can be substantiated by the lack of smectite interstratification in the X-ray diffractogram (Fig. 5.6c) and the profusion of the ‘rosette’ micro-texture of the glauconites (Fig. 5.6a). The Fe₂O₃(total) content of the glauconites remains low (<15 wt%), occupying the ‘field of ferric illite’ and ‘compositional gap’ of Odin and Matter (1981) in the K₂O vs. Fe₂O₃(total) cross-plot (Fig. 5.7a; Table 11).

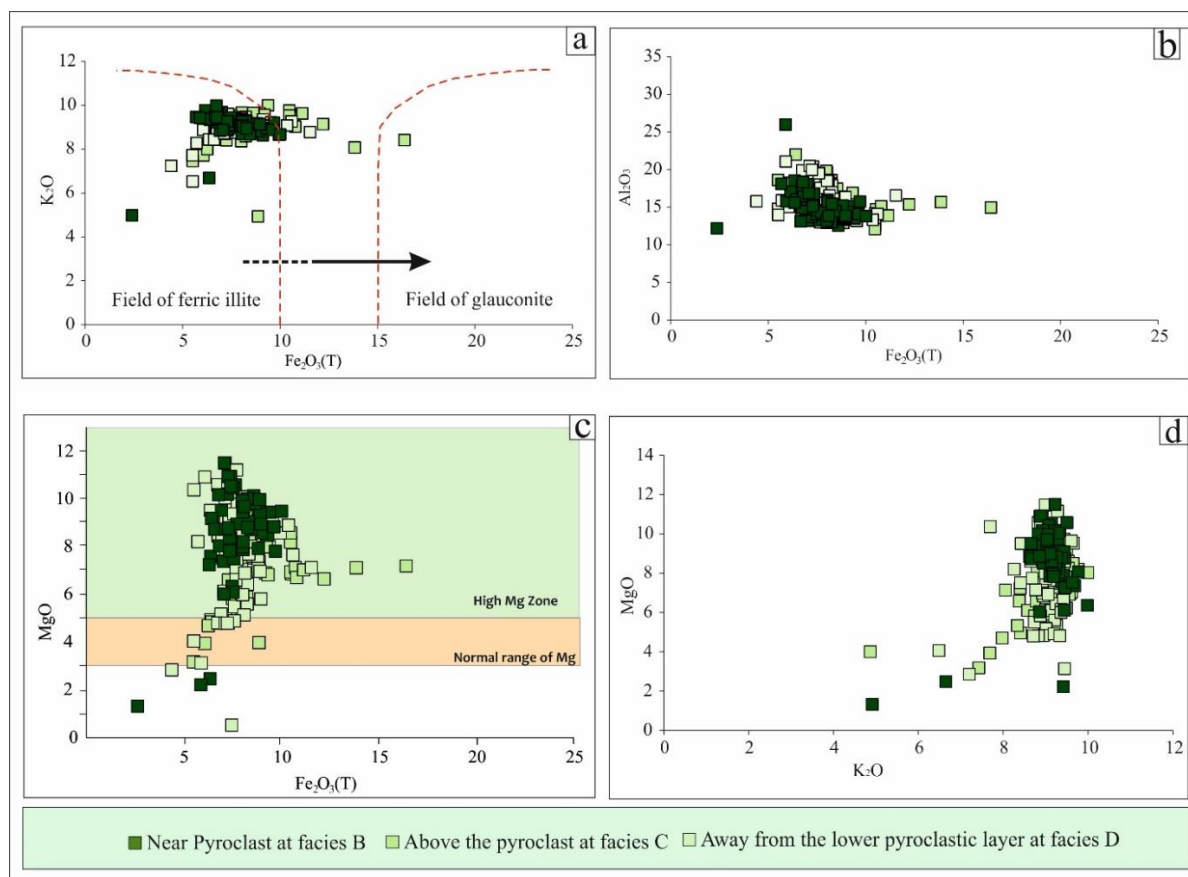


Fig 5.7: Binary Cross plot Between **a)** K₂O and Fe₂O₃, **b)** Al₂O₃ and Fe₂O₃, **c)** MgO and Fe₂O₃ **d)** MgO and K₂O.

The poor negative correlation between Al₂O₃ and Fe₂O₃(total) is an artifact of Al-for-Fe substitution in the octahedral layers of the clay mineral, in this case, glauconite (Fig. 5.7b). The high Al₂O₃ content evinces an alumina-rich substrate for glauconitization, which, in this case, can be feldspar. Berg-Madsen (1983) categorized glauconites with similar high Al₂O₃ (>12 wt%) and low Fe₂O₃(total) (<15 wt%) composition as ‘high-alumina’ glauconite, irrespective of its maturation stage (Table 11). The glauconites of the Rampur Shale Member and the majority of the Precambrian glauconites can be designated as ‘high-alumina’ glauconites. In addition, the MgO content of the glauconites of the Rampur Shale Member is remarkably high (~8%; sometimes exceed 11%) and only comparable to limited glauconite deposits (Table 11; Banerjee et al., 2008, 2015; Drits et al., 2010b). The clusters of data points among different bivariate plots involving the MgO, Fe₂O₃(total), and K₂O contents (~9%) suggest equable maturation culminating into ‘highly-evolved’ glauconites of the Rampur Shale Member (Fig. 5.7c,d; Table 11). The formation of ‘highly-evolved’ glauconites, representing a long residence time at the sediment-seawater interface, can provide sufficient time for Mg to be incorporated into the octahedral site.

5.2.6: Whole-rock geochemistry of the glauconite-bearing sediments:

The major and trace elemental geochemistry of the whole-rock samples of the glauconitic sandstone and associated shale are provided in Table 12 and 13. The average whole-rock SiO_2 and Al_2O_3 contents are approximately 70 wt% and 14 wt%, respectively (Table 12). The average $\text{Fe}_2\text{O}_3(\text{total})$ concentration of the sandstones is 3.5 wt%. K_2O content is significantly high, with an average of ~7 wt% (Table 12). The MgO content often exceeds 2 wt% (Table 12). The calculated CIA, CIW, and PIA values for the glauconite-rich sandstones vary from 60–70, 97–99, and 95–99, respectively (Table 14). ICV values are <1 throughout the succession. Although the CIA values shows lower values for glauconitic sandstones, the PIA, CIW and ICV values of the glauconitic sandstone of facies B–D are consistently higher (Fig. 5.8 Table 14).

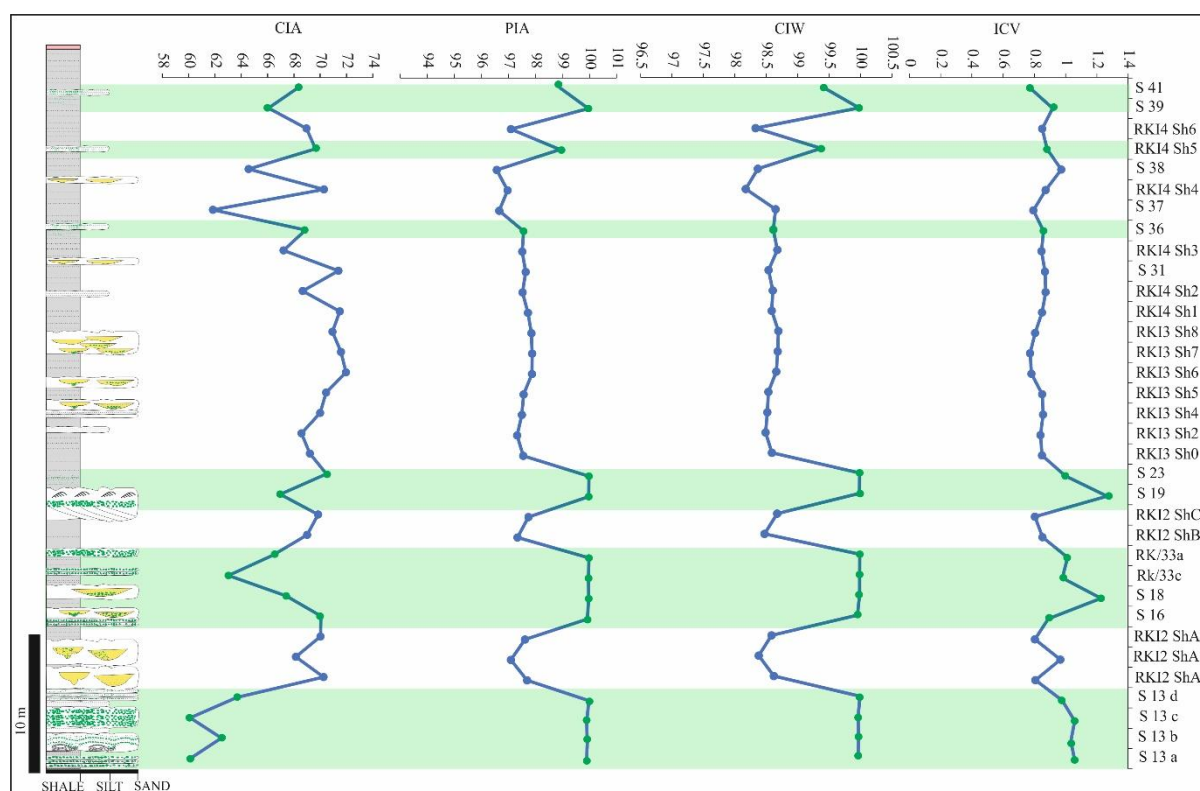


Fig. 5.8: Stratigraphic distribution of CIA, CIW, PIA and ICV for the Facies B, C and D (glauconite bearing horizons are marked with green dots)

The studied whole-rock geochemistry of the Rampur Shale sediments exhibits high CIA (>65), CIW (>95), PIA (~100), and lower (<1) ICV in the sediment and strongly signifies high intense weathering (Table 14). The climatic index (c-value) is also higher (>0.6) in the sediment, which signifies warm and humid conditions that intensify the rate of chemical weathering (Table 14). CIW vs C-value cross-plot also supports this context (Fig. 5.9a). The low CIA value for the glauconitic sandstone might have resulted from the K-enrichment

related to glauconite, however, other weathering indices, which do not incorporate the K_2O content, reflect a high intensity weathering prevailing during the deposition of the glauconitic sandstone. The $V/(V+Ni)$ ratio, ranging from 0.41–0.8, strongly suggests dysoxic to anoxic depositional conditions (Table 14) (Jones and Manning, 1994; Hatch and Leventhal, 1992; Wu et al., 2022), which can be further substantiated by the $V/(V+Ni)$ vs. Th/U cross-plot (Fig. 5.9b; Wu et al., 2022; Luo et al., 2015). Y/Ho ratio shows a mean value greater than 30, suggesting a marine depositional environment (Table 14).

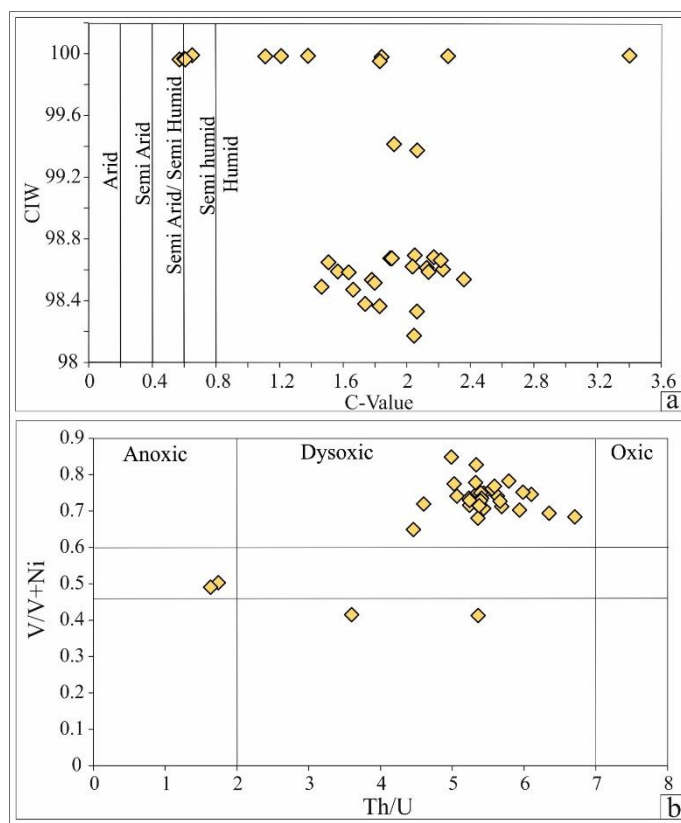


Fig. 5.9: a) Cross plot between CIW and C-value. **b)** Cross plot between $V/(V+Ni)$ vs Th/U

5.3. Discussion

5.3.1 Origin of glauconites in Rampur Shale Member:

The K_2O content of glauconite is considered to be a proxy of its maturation, where glauconite minerals with >8 wt% of K_2O indicate highly-evolved glauconite (Odin and Matter, 1981; Amorosi et al., 2007; Baldermann et al., 2017). The nascent and slightly evolved glauconites (with K_2O ranges from 2–4 and 4–6 wt%, respectively), formed relatively rapidly (within a few thousand years), often exhibit the relicts of the substrate from which it has formed. On the other hand, the evolved and highly-evolved varieties (with K_2O content ranging from 6–8 wt% and 8–10 wt%, respectively) represent long residence time at the sediment-water

interface (10^5 – 10^6 years) and are usually homogenous in composition. In most cases, the Rampur Shale glauconites, with K_2O content exceeding 8 wt%, represent a highly evolved maturation stage, indicative of the long residence time (Table 11).

Glaucinite authigenesis is achieved via three (3) different mechanisms with distinctly separate chemical evolution pathways (see Banerjee et al., 2016a for more references). It can either form via the simultaneous incorporation of potassium and iron into a degraded layer lattice structure ('Layer Lattice Theory,' Burst, 1958), by authigenic precipitation of glauconitic-smectite gel (Fe-rich) and its subsequent evolution via incorporation of potassium into the crystal structure ('Verdissement theory,' Odin and Matter, 1981) or by pseudomorphic replacement of crystalline structures in high a_K^+ micro-environment (Dasgupta et al., 1990). The Proterozoic glauconites, often found along the cleavages of the feldspar grains and are K-rich but iron-poor (often <15 wt% of Fe_2O_3 (total)) in composition, are considered to be exclusively formed from feldspar alterations (Dasgupta et al., 1990; Deb and Fukuoka, 1998; Banerjee et al., 2015; Bansal et al., 2020; Mandal et al., 2020,2022; Starzec et al., 2023b). The glauconite pellets in the Rampur Shale Member are mostly sub-rounded to elliptical without compositional zonation and mineral inclusions (Fig. 5.3), making identifying the substrate for glauconitization challenging. The basal part of the glauconitic sandstones within the Rampur Shale Member is inundated with pyroclastic deposits (Fig. 5.3b). Petrographic observations reveal that these pyroclastic deposits comprise very fine sand-sized particles of quartz and feldspar set in a fine-grained clayey matrix. At the basal part of the section, the glauconitic sandstones exhibit frequent intercalation of a few mm- to cm-thick pyroclastic deposits (Fig. 5.3b). At places, these glauconitic sandstones show cross-bedding structures, indicative of current reworking (Fig. 5.2p). Sporadic episodes of reworking might have resulted in the formation of clay pellets, which can serve as a substrate for glauconitization within the Rampur Shale Member. The cohesive nature of clayey pyroclastic deposits might have facilitated the roundness of the clay pellets (Fig. 5.3).

5.3.2. Stratigraphic significance of Precambrian glauconite in Vindhyan basin and genesis of high-Mg glauconite:

A comparative study has been performed here to compare the Mg content of Precambrian and phanerozoic glauconite; data collected from different research articles of previous researchers like Guimaraes et al., 2000; Bandopadhyay, 2007; Banerjee et al., 2008; Mingxiang 2008; Drits et al., 2010; Banerjee et al., 2015; Tang et al 2017; Bansal et al 2019; Mandal et al 2020, 2022; Algabri et al., 2020. The survey reveals that Precambrian glauconite generally

contain higher amount of Mg than it's Phanerozoic counter parts (Fig. 5.10). Comparing the Precambrian glauconites, it has been noticed that, Rampur Shale records highest amount of MgO in its structure (Fig. 5.10).

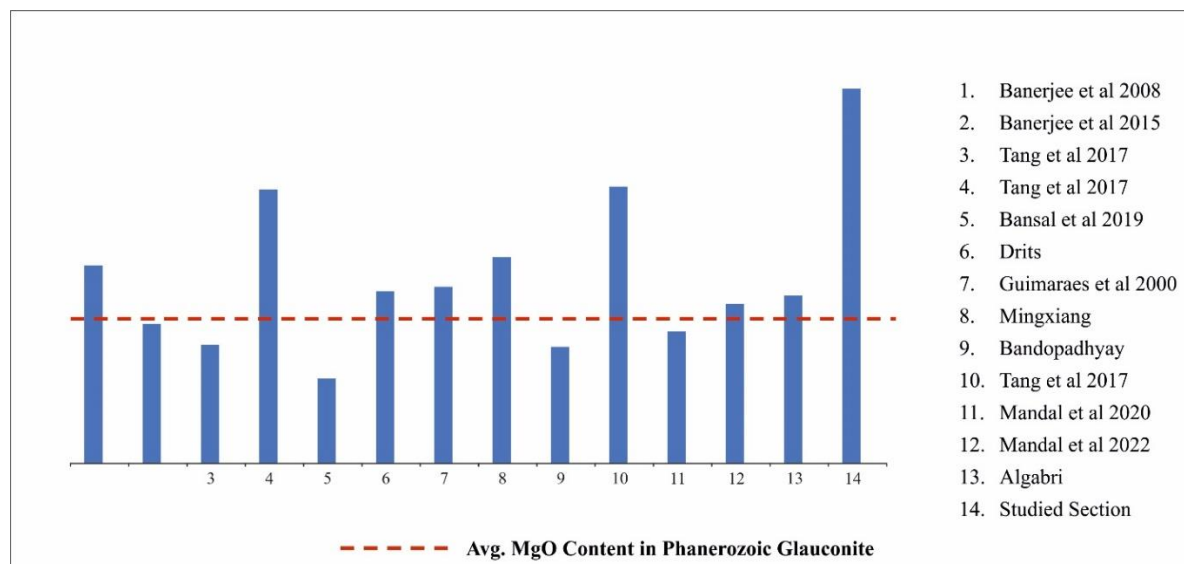


Fig. 5.10: Comparison of MgO content in Precambrian and Phanerozoic Content (red line indicates the average MgO content in Phanerozoic glauconite)

The Rampur Shale Member of the Semri Group comprises sandstone-siltstone-shale alternations along with glauconite-bearing sandstone and siltstone alternations deposited in a marine shelf environment (Sarkar et al., 2002; Mondal et al., 2022). Although recent investigations of Precambrian sedimentary succession reveal significant concentrations of authigenic clay mineral formation, especially in the form of glauconite, many of these glauconite deposits are subjected to late diagenetic alteration (chiefly chloritization) processes, altering the chemistry and structure of the glauconite (Tang et al., 2017; Bansal et al., 2020; Ma et al., 2022; Starzec et al., 2023b; Zhang et al., 2023). In contrast, the slightly deformed and mildly metamorphosed Vindhyan sedimentary successions in central India host abundant authigenic glauconite deposits, restricted to sediments ranging in age 1.7 Ga to 0.9 Ga, where the authigenic glauconites are well preserved without alteration including the Chorhat Sandstone (CS; Banerjee et al., 2008) and Rampur Shale (RS; present study) of Lower Vindhyan Group and the Lower Quartzite (LQ; Mandal et al., 2020) and Lower Bhandar Sandstone (LBS; Mandal et al., 2022) of the Upper Vindhyan Group. Mineral geochemical investigations indicate a more-or-less comparable K_2O (~7-8 wt%) and SiO_2 (55-60 wt%) concentrations among these glauconites. These glauconites are invariably rich in Al_2O_3 content, with the Rampur Shale having the least concentration (Fig. 5.11a). The TFe_2O_3 concentrations

are typical of Precambrian glauconites, ranging from ~5–12 wt% (Fig. 5.11b). However, these

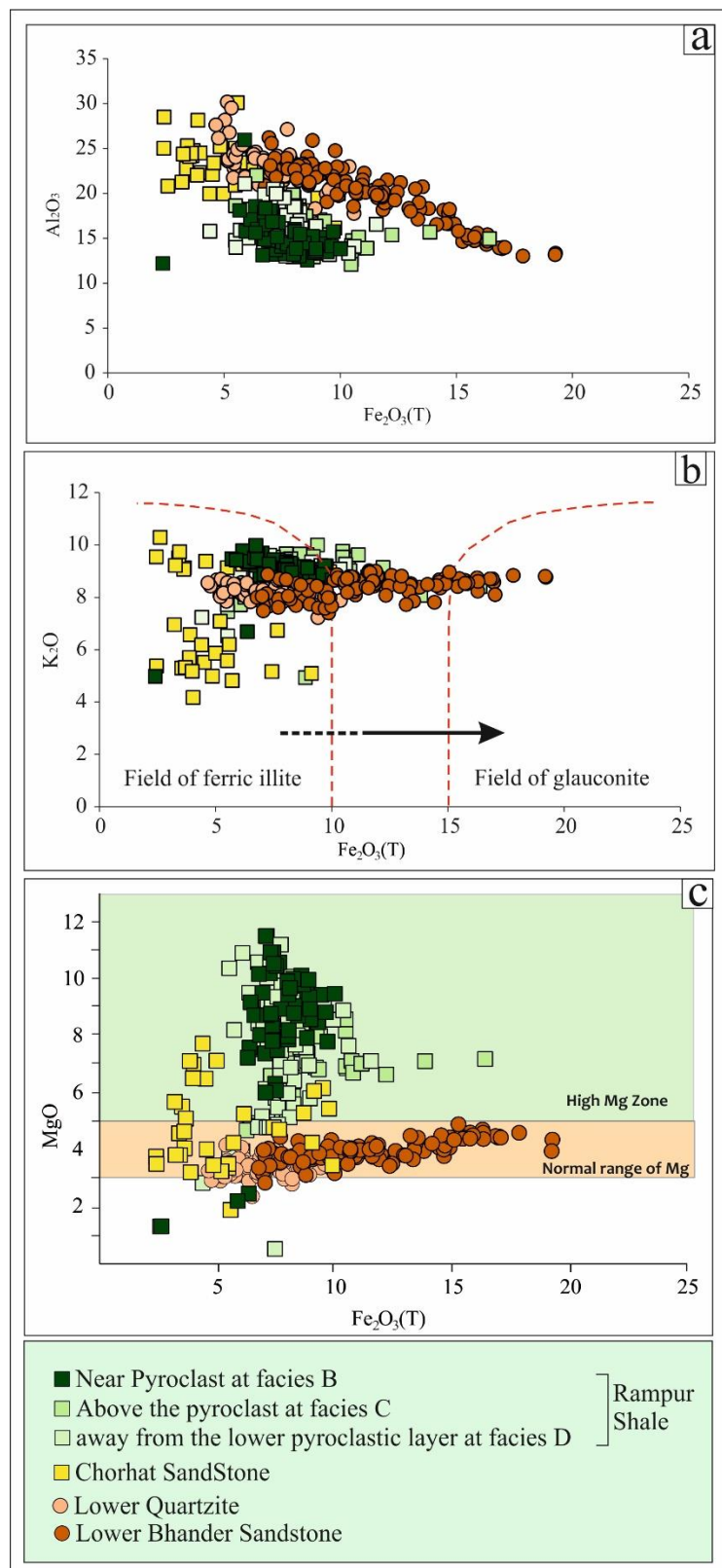


Fig: 5.11: Binary Cross plot Between **a)** Al₂O₃ and Fe₂O₃, **b)** K₂O and Fe₂O₃ and **c)** MgO and Fe₂O₃.

glauconites exhibit a distinct variation in MgO concentration. While the Upper Vindhyan glauconites have a low MgO concentration (3–5 wt%), typical of glauconites, the Lower Vindhyan glauconites have a conspicuously high MgO concentration (Fig. 5.11c). The elevated MgO concentration in glauconites within the Lower Vindhyan sedimentary successions are strikingly different from stratigraphically similar glauconite deposits across the globe (Dasgupta et al., 1990; Deb and Fukuoka, 1998; Banerjee et al., 2015; Tang et al., 2017; Ma et al., 2022; Starzec et al., 2023b; Zhang et al., 2023).

Compositionally, the glauconites from the Rampur Shale Member are distinct due to their high MgO content (av. 7.88), which frequently exceeds 11 wt% (Table 11). The high Mg content of these glauconites can result either from the interstratification of chlorite or smectite within the glauconite structure or from the supply of Mg into the octahedral

layers from the ambient sediments and seawater, supplied by the dissolution of ferromagnesian

minerals (Banerjee et al., 2019, 2015, 2008; Drits et al., 2010a). The high K₂O content of the glauconites and lack of compositional variability aided with mineral chemical analysis demarcates ‘highly-evolved’ glauconite, refuting the smectite (and/or chlorite) interstratification as the origin of high-Mg glauconites within the Rampur Shale Member. On the other hand, the unaltered pyroclastic intercalations lack a significant proportion of ferromagnesian minerals. The whole-rock geochemical analysis of these pyroclastic intercalations also suggests a dominantly felsic nature with low MgO content (avg. 2.20) (Table 12). The thin pyroclastic intercalations with low MgO content and lack of ferromagnesian minerals suggest that the alteration of fine-grained pyroclastic materials is inadequate for the supply of Mg within the glauconites. Glauconite authigenesis preferentially occurs at the sediment-seawater interface, where seawater and the ambient sediments provide the nutrient elements (including Fe, Mg, and K) necessary for glauconitization. The ambient seawater during the formation of the glauconites of the Rampur Shale Member can also supply the elevated Mg content of these glauconites. Similar Mg-rich glauconite compositions were reported from the underlying Chorhat Sandstone (CS), where the excess Mg in the glauconite structure has been attributed to the magnesium-rich Paleoproterozoic ocean (Banerjee et al., 2008). Magnesium within clay minerals can occupy the octahedral site (‘structural’ Mg) and interlayer site (‘exchangeable’ Mg) (Wimpenny et al., 2014). Glauconite, belonging to the 2:1 ‘illite’ clay family, primarily has ‘structural’ magnesium. The interaction between the clay mineral and the microbial community can also facilitate this incorporation of magnesium into the octahedral structure of the clay mineral (Burne, 2016). The Rampur Shale Member, rich in organic matter (Singh and Chakraborty., 2022,2023), possibly attained a Mg-rich composition by the combination of factors, including i) a pyroclastic source-rock supplying fine-grained sediments, ii) magnesium incorporated from the Mg-rich oceans during the Mesoproterozoic time and iii) clay mineral and microbial interaction.

5.3.3. Factors influencing glauconite formations within the Rampur Shale Member:

Glauconites are primarily associated with shales deposited in deeper shelf and slope conditions in modern oceans; however, during the Precambrian, abundant glauconitization is mostly observed within fine to very fine sandstones deposited within shallow, continental margins (Dasgupta et al., 1990; Tang et al., 2017; Ma et al., 2022; Starzec et al., 2023b; Rubio and López-Pérez, 2024 and references therein). The formation of authigenic glauconite in marine depositional conditions is governed by several factors, including the availability of iron in the seawater, depositional redox condition, and iron reduction reactions (El Albani et al.,

2005; Meunier and El Albani, 2007; Taylor and Macquaker, 2011a; Baldermann et al., 2013, 2017; Banerjee et al., 2020; López-Quirós et al., 2020; Tounekti et al., 2021). Iron is delivered to the shallow marine environments in the form of Fe-(oxy)hydroxide (ferrihydrite, hematite, and goethite) that are the products of continental weathering (Taylor and Macquaker, 2011b; Tang et al., 2017; Roy Choudhury et al., 2021; Tounekti et al., 2021). The high CIA, CIW, and PIA values of the Rampur Shale sediments suggest intense weathering, supplying the major source of iron for abundant glauconite formations. The climatic index (c-value) is also higher (>0.6) in the sediment, which signifies warm and humid conditions resulting in intense chemical weathering. In addition to the supply of iron, an oxygen-depleted, suboxic to dysoxic depositional environment allows iron to mobilize in the Fe^{2+} state, occupying octahedral sites of the clay minerals (Meunier and El Albani, 2007; Baldermann et al., 2017). The $\text{V}/(\text{V}+\text{Ni})$ ratio and the $\text{V}/(\text{V}+\text{Ni})$ vs. Th/U cross-plot of the Rampur Shale sediments evince dysoxic to anoxic depositional conditions, resulting from the combination of factors, including organic matter degradation and basin subsidence as evidenced from the abundant slide planes (Fig. 5.3o). The high rate of weathering and variable elemental input may have facilitated unique Mg-rich composition of seawater.

The abundant slide planes within the Rampur Shale Member suggest local subsidence and the development of localized anoxia, creating favorable conditions for glauconite formation. The proportion of shale increases upward, alternating with very fine sandstone or siltstone, recording small-scale sea-level fluctuations. Step gutters are more intensely present in this segment, which indicates episodic current flow during storms. The Plethora of microbial mat impressions conveys the presence of biogenic activity. The organized occurrence of glauconite at the transitional part manifests that it was both syndepositional and reworked, likely transported from lower sediment layers. The low concentration of glauconite indicates that some of it may have been lost during transportation. Numerous slide planes within the sandstone and siltstone bodies throughout the segment express occasional subsidence, responsible for the local anoxicity development required for glauconite mineralization. The amount of glauconites successively decreases as we move away from the pyroclastic association.

5.4: Conclusion

The sedimentology and geochemistry of the authigenic glauconites of the Rampur Shale Member reveal the following conclusions:

- (a) Glauconitic succession of Rampur Shale is a depositional record of the inner to middle shelf, i.e., within the storm wave base and below the storm wave base. The fining-up succession of Rampur Shale from thick sandstone to black shale with some volcanic deposits within is the sedimentation of the transgressive system tract. However, the glauconitic horizon is not directly linked to MFS; the instant of the MFS glauconitic unit is the marine flooding surfaces.
- (b) Glauconite originated by pseudomorphic replacement of pyroclastic sediment with increasing Fe^{2+} , Fe^{3+} and Mg at suboxic conditions via the intake of Fe^{2+} , Fe^{3+} , and Mg substitute Al in the octahedral site.
- (c) Including the high rate of weathering of continental rock in warm and humid climates, volcanic input was the major source of seawater chemistry. Intake of variable elements by the glauconitization process stabilizes the marine chemistry.
- (d) Suboxic to dysoxic depositional condition was influenced by intrabasinal tectonics during the Proterozoic. The synchronous volcanism and ash floor also enhance the low-oxygenated condition and influence the glauconitization processes.

CHAPTER: 6

Sedimentology, Sequence Building and Geochemical Reappraisal of the Mesoproterozoic Black Shale

6.1: Introduction

Black shales, which are characteristically fine-grained and rich in organic carbon (Total Organic Carbon, TOC > 1%), exclusively preserve a wealth of information about the Earth's ancient processes and conditions owing to its unique geochemical signatures (Piper & Calvert, 2009). They provide insights into past environments, climate changes, ancient biosphere, and the composition of Earth's oceans and atmosphere (Nesbit and Young, 1982; Jones and Manning, 1994; Cullers, 2002; Tribovillard et al., 2006; Sheldon and Tabor, 2009; Fathy et al., 2021). The Meso- to Neoproterozoic times are equally cryptic for witnessing several global scale events, including supercontinent reorganization as well as atmospheric oxygenation (Condie et al., 2001; Holland 2006). These all-momentous episodes are crucially documented within the black shale. The black shales are generally deposited in basins with anoxic bottom water conditions and rich in certain trace metals, as they get readily absorbed by organic matter or precipitated as insoluble sulfide phases (Pasava et al., 1996). Despite the plethora of literature on black shales, the Mesoproterozoic black shales remain enigmatic regarding the applicability of different palaeodepositional and palaeoceanographic parameters. The present study on the ~1.5 Ga-old Black Shale (BS) within the shallow marine Rampur Shale Member (RS) of the Vindhyan Supergroup in Central India (Fig. 6.1a) has been used as a testing ground, and effort has been made to reconstruct the above-mentioned perspectives. A detailed state-of-the-art facies analysis has been done to understand the depositional regime and palaeogeographic disposition, which guided the identification of different system tracts. The major part of the Rampur Shale Member is a transgressive system commencing with sandstone, followed by sand-shale alternation and a thick black shale deposition, which in turn passes through a Faded Shale (Mondal et al., 2022). The RS gradually passes into a shallow water limestone (Sarkar et al., 2019). During the present endeavour, a TST (transgressive system tract) has been identified within the lower part of the RS, while the upper part, which gradually passes from a Faded Shale to Rohtas Limestone, can be correlated with an HST (highstand system tract) through a maximum flooding zone (MFZ, Fig. 6.1b., Mandal et al., 2019). The paper also emphasizes the condensed black shale zone (MFZ) of Mesoproterozoic time to scrutinize the apparent geochemical oddities under consideration. The microbial structures present within this zone have also been characterized. A detailed major, trace, and rare earth elemental geochemistry of the BS has been carried out to explore its implications to understand the sediment provenance, palaeoweathering, palaeoclimate, palaeoredox, and palaeosalinity.

The global distribution of black shale during Mesoproterozoic has been traced and their implications in global tectonics and supercontinent reconstruction have also been discussed.

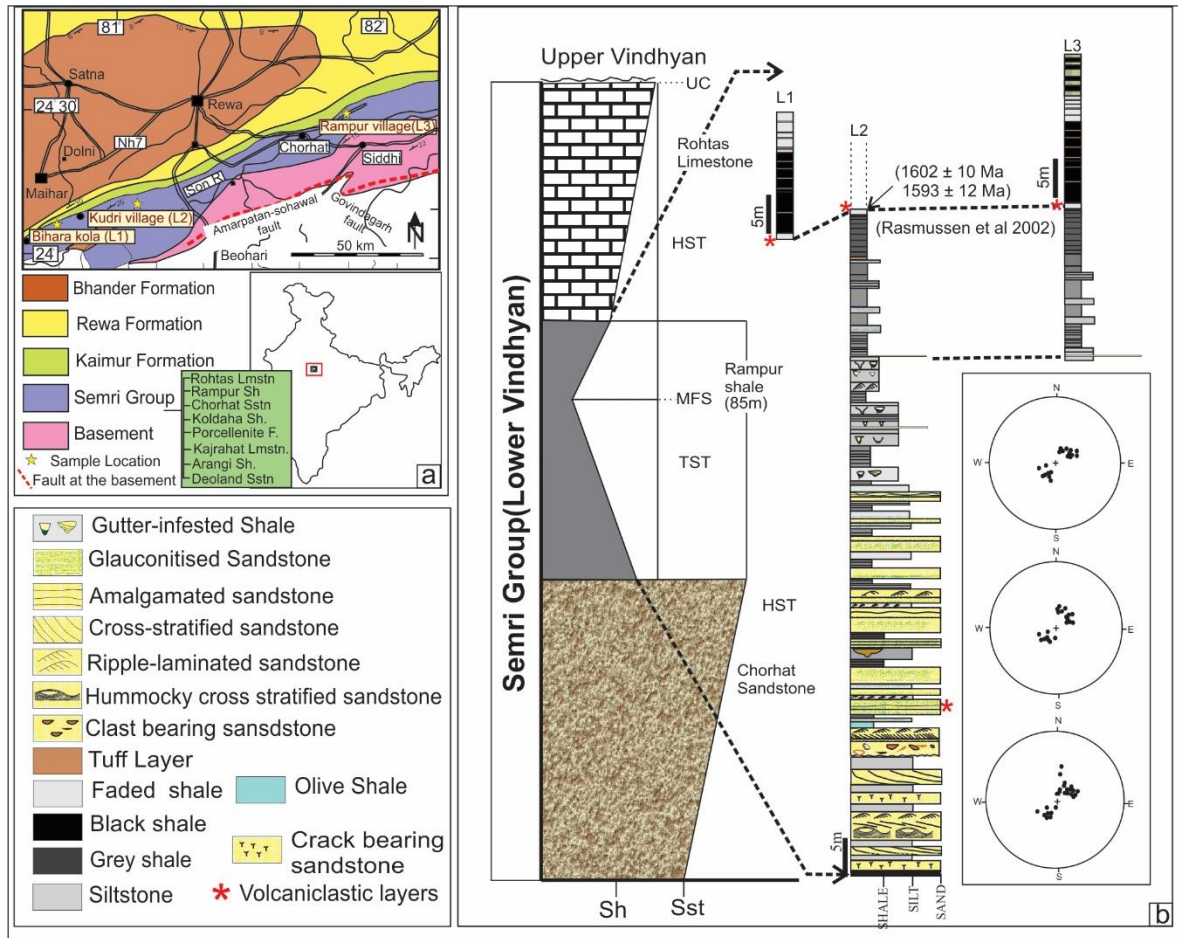


Fig. 6.1: a) Location map showing the geographic extent of the Vindhyan rocks and the studied area (marked by asterisk) with outcrop locations and the sampling locations marked **b)** Stratigraphic succession of the studied Rampur Shale Member from different locations (L1, L2 and L3) along with the orientation of the poles of the slide planes plotted in stereo-net.

6.2: Facies and Depositional Environment:

The Rampur Shale Member of the Semri group consists of sandstone and shale deposited in a marine shelf environment (Sarkar et al., 2002). The colour of the shale varies from grey and green to black, with a change of palaeogeography of the succession. Considering the varying sand: shale ratio, presence of primary sedimentary structures and geometry of the sandstones, the entire succession of Rampur Shale is divided into six distinctive facies showing variation in palaeogeographic disposition (Fig. 6.2a; Table 6.1). The Black Shale segment within the Rampur Shale Member in the Lower Vindhyan sequence is approximately 10 m thick and encased by retrogradational sandstone and sandy/silty shale packages below and an approximately 3 m thick Faded Shale (FS) above (Fig. 6.1b; Mondal et al., 2022).

Table 6.1: Descriptions of Facies (based on field visit)

Facies	Facies Description	Interpretation
Facies A	This segment representing the lowermost part of the succession, is dominantly composed of sandstone beds with rare preservation of shale beds and have a sand: shale ratio of 9:1. Sandstone beds are of sheet like geometry consisting of small scale hummocky cross-stratification, ripple lamination and planar lamination (Fig. 2b,c). Bifurcated ripple crests are common. Within the lowermost succession of this segment, the sandstone body have accommodated a network of syneresis cracks and they are preferentially present within the troughs of ripples (Fig. 2d,e). The syneresis cracks are generally polygonal or spindle shape and filled by fine sand grains and exhibit cross-cutting relationship at the top of the sand bed. Despite having apparent good grain sorting, some of the beds bear flat and reddish, iron-stained rounded mud clasts. The mudclasts (7-8 cm to mm scale) float within the sandy sediment, but are dominantly bed-parallel (Fig. 2f).	The sandstone beds abundantly displayed wave structures certainly deposited by waves that completely erased out their muddy substrate. it seems that sand deposition often, if not always, took place from temporarily waning storms. Taking into consideration all its intrinsic features, this interval is interpreted as a lower shoreface deposit. The networks of cracks (manchuriophycus) of varied geometries and orientations are generally accepted as proxies for pre-existence of microbial mats. Microbial mat has presumably been imparted the requisite cohesion to the sand bed surfaces.
Facies B	The base of the facies has been fixed with the first appearance of shale which is greenish in colour (Fig. 2g). Apart from the green color, thin intercalations of light grey colored shale is also present between the sandstones. Maximum thickness of individual shale intercalation is ~10 cm. The sandstone beds are of two different geometries. Commonly the sandstone beds are tabular or sheet-like in geometry (Fig. 2h, i). These sandstones are well sorted and fine-grained and their beds have maximum measured thickness around 20-30cm, thinning and finning overall upward. The small scale hummocky cross-stratifications (HCS) associated with this sandstone have wavelength up to 5-6cm (Fig. 2h). Besides HCS, the beds also bear planar laminae and low-angle cross-strata (Fig. 2i). In many of these beds, the lower part is enriched in glauconitized pyroclastic fragments (Fig. 2j). These Glauconitised bodies are wedge-shaped, convex-up bodies, internally massive, locally carrying light colored sandstone fragments apparently derived from the light-colored sheet sandstone (Fig. 2j). The other group of sandstone beds is of lenticular channel geometry; the channels are wider as well as deeper (Fig. 2k), They have bases	The shales present within these facies stand for low depositional energy. The depositional site of this interval is likely been relatively distal with respect to the preceding interval, possibly on the inner shelf. Sharp bases, presence of gutters and prod marks on soles and internal finning upward beds document deposition of the beds from temporally waning flows. Wave features, including HCS, further suggests deposition from bottom-hugging light density storm-driven wide-spread underflows. On the contrary, the channel sands were likely to be deposited from constricted flows. Presence of gutters and prod marks at their bed-soles signify even stronger current strength. Bodies with erosional bases must have been deposited from flows that were turbulent in nature. Overall thinning of the sheet sandstones and concomitant increase in shale bed thickness imply a retrogradational trend.

	sharper than their tops. The bed-soles often bear gutters, prod marks, groove casts and somewhere biogenic mat impression structures are present (Fig. 2l,m). Slide planes are common in more or less all the segment (Fig.2n).	
Facies C	The upward transition from the second to the third interval is gradational. Despite this, there is some discernible changes between them. The thickness of the sheet sandstones is comparatively smaller (10-15cm) within the third interval with respect to their counterparts in the second interval (Fig. 2o). The average grain-size of the sandstones present in these facies also becomes comparatively finer. The second remarkable difference with the preceding facies is that the channel-sandstones outnumber the sheet sandstones in this interval. The channel sandstones of this facies are comparatively smaller in both dimensions. The intervening shale beds are mostly gray in color and generally thicker (20-25cm).	The higher shale: sandstone ratio compared to preceding facies suggests the paleogeographic position of the third interval had been further sea ward. Thinning and decline of the frequency of occurrence of sheet sandstones supports the contention. The decline of the frequency of occurrence of the sheet sandstone, the possible products of sheet sandstone suggests that the relatively weaker storm could not reach the depositional sight of this segment. Relatively higher frequency of occurrence of channel sandstone indicates that the constricted flows are comparatively higher flow intensity. However, the distal part of the depositional basin, the channels become shallower, as expected.
Facies D	This facies is consisting of shale beds with occasional input of plane laminated sandstone-siltstone beds. Shale is grey to greenish grey in colour. Sandstone/siltstone is restricted as channel forms (Fig. 2p). The channel is wider and shallower compared to underlying intervals. Innumerable slide planes are present at different level of this segment of facies and showing bipolarity amongst the slide planes (Fig. 2n). A pyroclastic layer is present at the top part of this segment.	The sand-shale ratio of this segment also reveals the basin ward deep-water deposition. Slide planes are indication of subsequent sagging or basin subsidence. Possibly the relatively deeper paleogeography helped to preserve the pyroclastic layer.
Facies E & F	Topmost segment is represented by these facies, a sand/silt free, shaly lithology. These shales are characteristically black in colour (Fig. 2q). This black shale interval is often punctuated by few sheet-like volcanoclastic layers ranging in thickness from 1 to 5 cm (Fig. 2q; marked with red arrow)) with sharp contact. Black shale with fine, mm-scale thick laminae and very crude ripple lamination observed at places. Apart from the black shale ca. 3m faded shale is present at the top part in some part of the studied sequence.	Black shale deposition possibly indicates the peak of the transgression. Black shale is deposited at the deeper-most part of the basin representing a condensed zone. Faded shale, possibly indicate towards the initiation of regression. In spite of limited preservation of primary sedimentary structures, these black shale interval holds immense potential for revealing the depositional history by using its petrological and geochemical signatures.

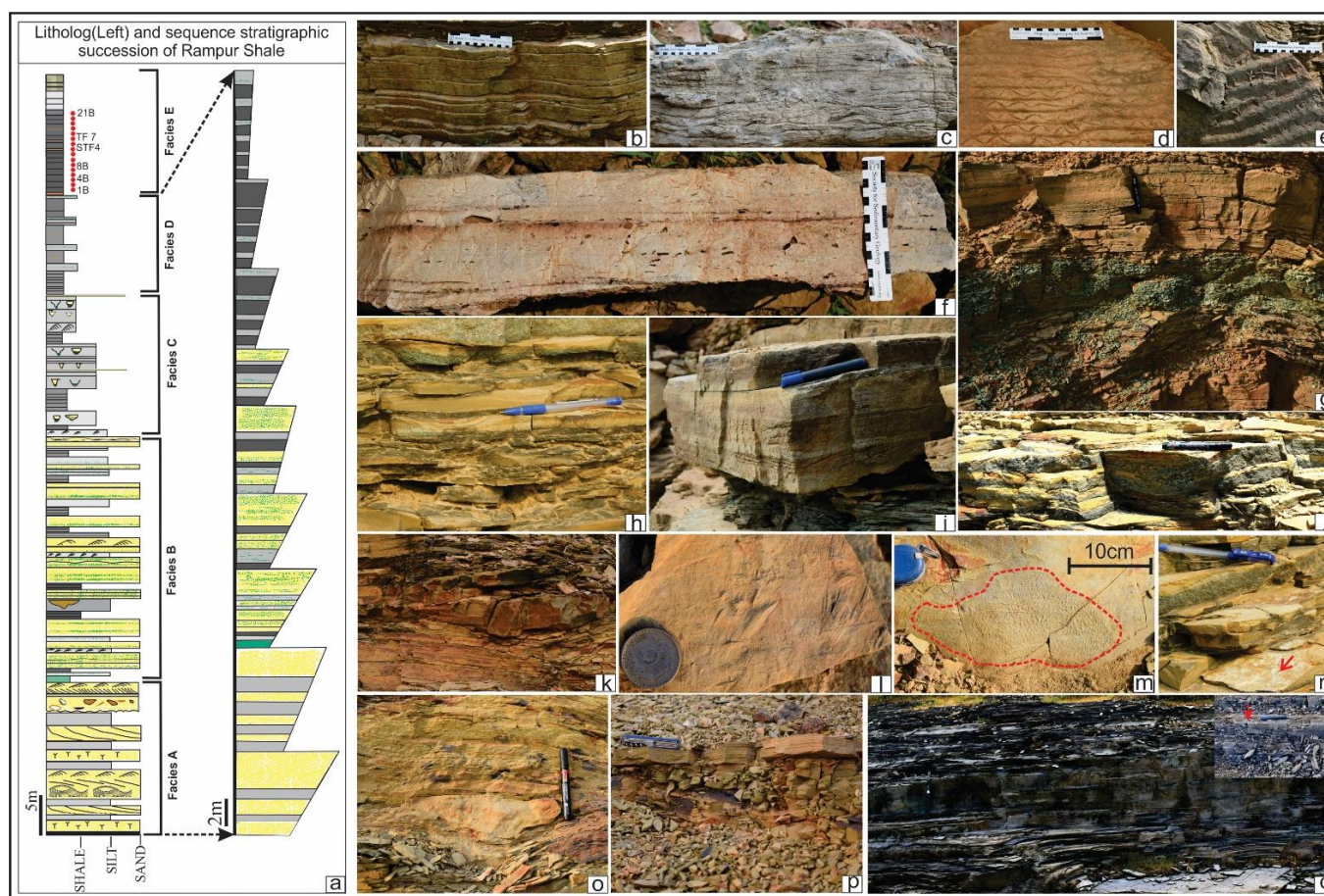


Fig. 6.2: **a)** Composite lithology (left) and the sequence stratigraphic succession (right) of the Rampur Shale Member delineating several **b)** Field photographs of the sandstone body with sheet-like geometry. **c)** Hummocky cross-stratified sandstone. **d)-e)** Presence of cracks at the ripple trough of the sandstone. **f)** Several mud clasts present within the sandstone body (figs. b-f represents the Facies A). **g)** Appearance of green Shale Layer in between sandstone body. **h)-i)** Sandstone with sheetlike and tabular geometry. **j)** Glauconitised sandstone body. **k)** Sandstone with lenticular body geometry (channel-like sandstone). **l)** Tool marks are dominant at the bed sole. **m)** Biogenic mat-like impression is somewhere documented within the bed top (Figs. g-k represents the Facies B). (Figs. l-m both are present in facies B and C). **n)** Slide planes at a level of Rampur Shale Member. **o)** Sandstone body in between shale layers in facies C. **p)** Sheet-like siltstone body within shale layer in facies D. **q)** Black shale dominated layer of Facies E; the red arrow indicates the tuff layer within black shale.

Individual coarsening-up cycles (parasequence) are present within the lower retrogradational part. The individual parasequences generally initiate with fine-grained shale followed by shale/sand alternation and terminate with sandstones (Fig. 6.2a). The glauconites are associated with some of the parasequences. The presence of glauconite minerals and the omnipresent wave imprints within the underlying packages of the RS prompts the marine origin of the BS (Mondal et al., 2022; Tribovillard et al., 2023). Pyroclastic deposits also present within the RS at two different levels (Fig. 6.1b). Pumice-studded uneven pyroclastic layers, volcanic glass, devitrified quartz, and stockwork of silica veins along with quenching cracks bear attestation to intermittent volcanic eruptions on the seafloor on which the RS was built up. The formation under focus here represents the top of a retrogradational sequence sandwiched between two marine progradational sequences (Fig. 6.1b). The underlying Chorhat Sandstone Member constitutes a HST followed upward by TST of the Rampur Shale Member with a condensed zone at the top, characterized by a thick black shale deposit representing the maximum flooding zone (MFZ) (Fig. 6.1b). The overlying Faded Shale member of the RS Member and overlying Rohtas Limestone Member together constitute another HST (Fig. 6.1b; Bose et al., 2001; Mondal et al., 2022).

6.3: Results

6.3.1: *Microbial mat structures recorded within the Black shale:*

The BS unit shows an abundance of microbial mat growth under the microscope (Fig. 6.3). Depending on their geometry, the microbial mat micro-structures are divided into three major groups, viz. crinkly laminated (CL), lensoid-dumble (LD), and spheroidal (S) (Fig. 6.3). Apart from these mat structures, some irregular mat chips are also dispersed within the BS. The microbial mat bodies display a strong colour difference from darker lensoid and spheroidal mat bodies to lighter crinkly laminated mats.

The CL microbial mat shows false cross-stratification, jagged ends, bifurcation, micro-loading, lateral accretion, and up-warping of crinkly lamination under polarized light (Figs 6.3a, b). It has a variable thickness ranging from 0.1-1.5 mm. Microbial mat laminae and associated dolomite crystals are syn-depositional with the shale (Fig. 6.3b). Compared to CL, both S and LD microbial mat groups are generally smaller in dimension and less frequent in abundance. Lensoidal bodies are generally 0.1-1mm long with a maximum width of about 0.1-0.25 mm. Often, the middle parts of lensoidal mat bodies are slightly depressed and form a dumble-shaped mat body. The S microbial mat group is 0.1-1mm in diameter and contains a

thin tail-like feature at both ends. The carbon concentration ranges from 6-8 wt%, 8-15 wt% and 9.5-12 wt% for crinkly lamination, lensoid bodies and spheroidal mats respectively (Figs. 6.3c-e).

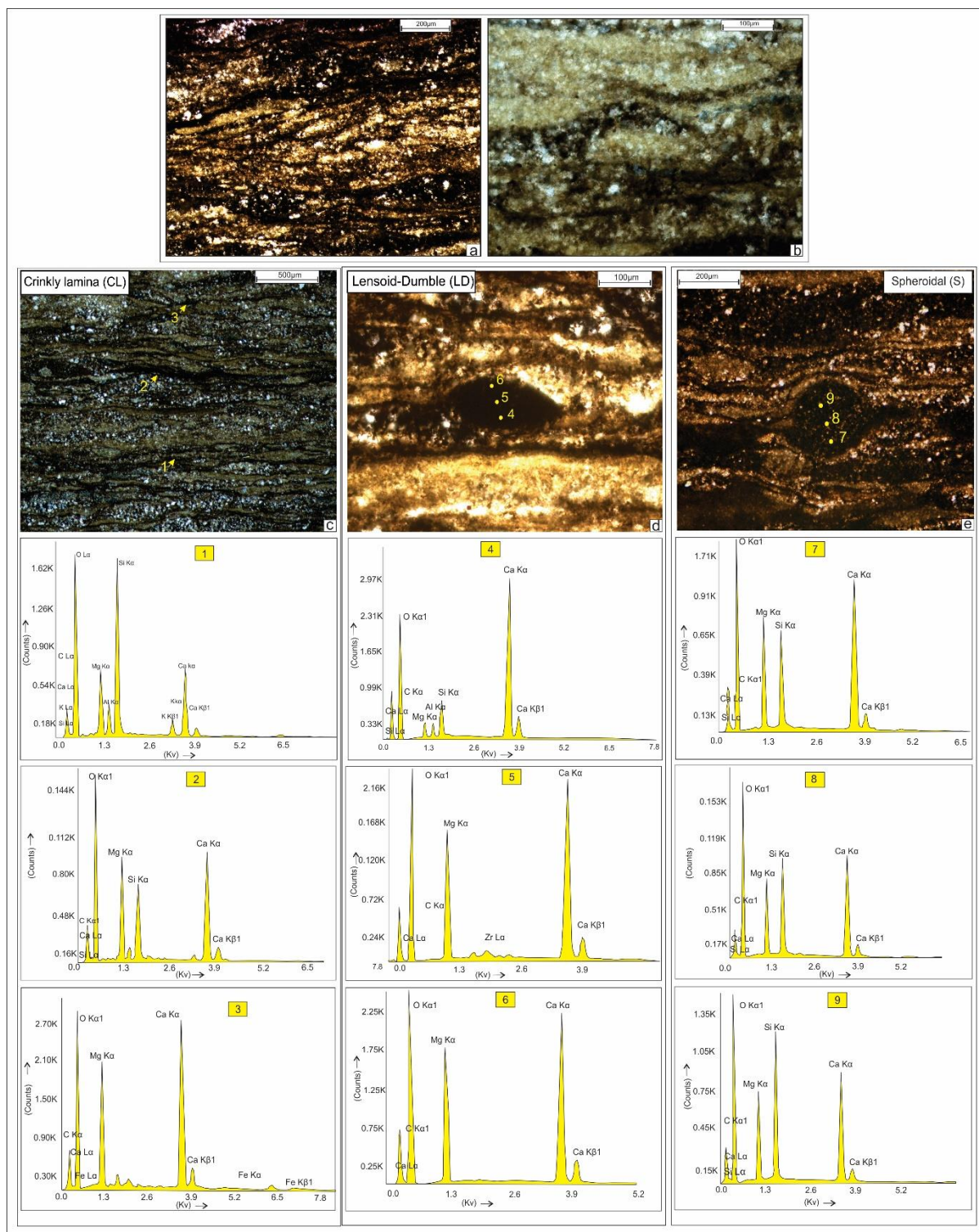


Fig. 6.3: Petrographic images of the microbial mat structures documented from the Black Shale. **a)-b)** False cross-stratification and jagged ends within crinkly laminated (CL) microbial mat. **c)** Crinkly lamination (CL), **d)** Lensoidal body (LD) **e)** Spheroidal (S) mat body along with the carbon wt% measured under SEM-EDAX.

6.3.2: Geochemistry of the Black Shale:

With respect to the Average Shale (Wedepohl, 1971), some major elements (such as Ca, Mg, K and Si) concentrations within the BS exhibit significant enrichment, while Al, Fe, Na, and Ti are mostly depleted (Fig. 6.4a; Table 2). Apart from the Cd, Hf, Se and Zn, all the trace elements are depleted, and Mn content is abysmally poor compared to the Average Shale (Fig. 6.4a; Table 6). In most samples, the TOC content is above 0.5%, with a maximum value of 1.83% (Table 7) and $\delta^{13}\text{C}$ values range between -25.2 and -33.6‰ (Table 7). The Average Shale normalized REE geochemistry of the BS does not follow any typical pattern regarding LREE, MREE and HREE but shows considerable variation (Fig. 6.4b). The LREE (La–Eu)/HREE (Gd–Lu) stratigraphic trend represents a yo-yo pattern with alternating LREE enrichment compared to HREE. However, for the uppermost part of the BS, the value peaks with an average of 7.41 (Fig. 6.4c). The concentrations of different major, trace and REE were plotted in different bivariate schemes and the results are discussed here (Figs. 6.5–6.10).

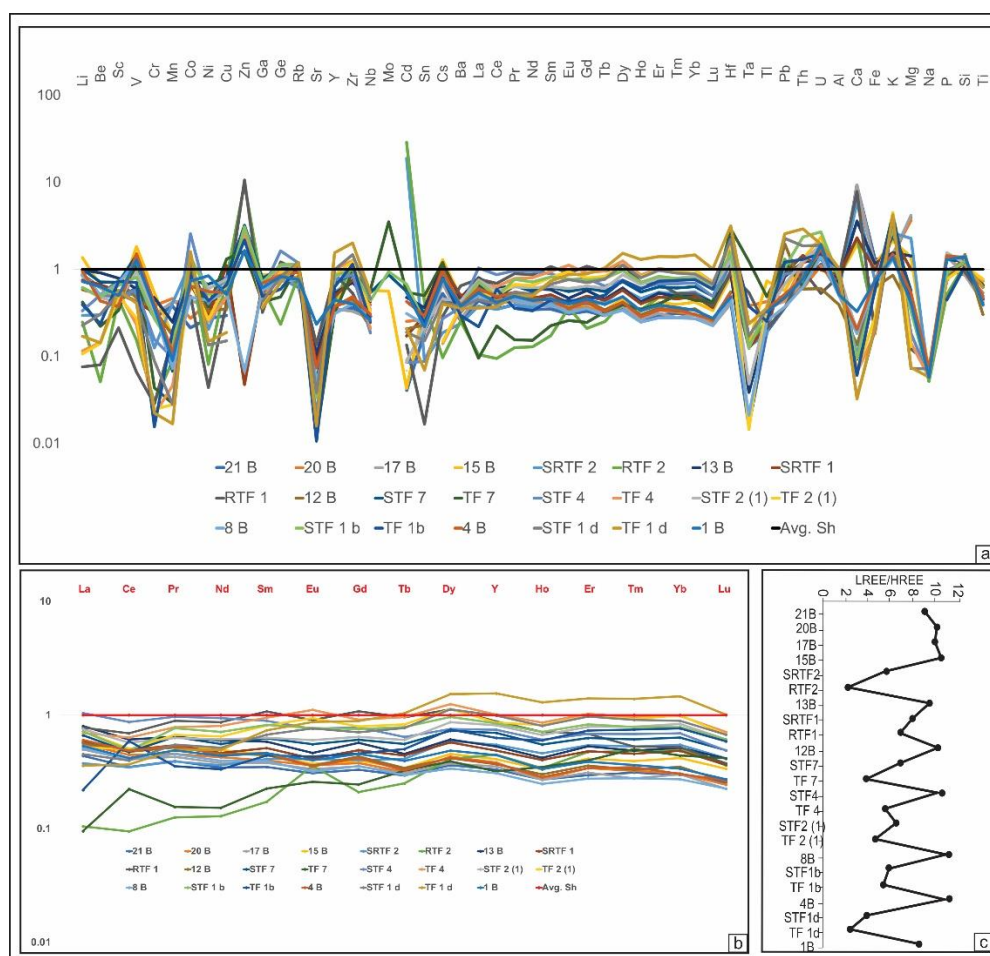


Fig. 6.4: a)-b) Distribution pattern of Major, trace and rare earth element concentration measured from the black Shale. c) The variation of LREE/HREE of the Black shale of the Rampur Shale Member plotted along the lithology.

The major, minor and trace elemental analysis of the black shale of the Rampur Shale Member reveals a depletion in metal content with respect to the Average Shale (Wedepohl, 1971) (Fig. 6.4a). The REE content also exhibits a flattened pattern (Fig. 6.4b) and the LREE/HREE distribution depicts a zigzag pattern throughout the succession (Fig. 6.4c). Different chemical plots were used to ascertain the provenance of the sediments. The Fe/Ti ratio shows a wide range, varying from 1.06 to 11.56 while the Al/(Al+Fe+Mn) ratio remains high (avg. 0.83) (Fig. 6.5a; Table 7). The La/Cr ratio ranges between 0.64 to 14.31 (avg. 2.97) and Th/Cr ratio ranges between 0.21 to 17.8 (avg. 2.40) (Fig. 6.5b; Table 7). The TiO₂ values ranges from 0.24 to 0.60 wt% (avg. 0.40 wt%) and the Zr content of the studied shale ranges from 52.83 to 322.18 ppm (avg. 133.96 ppm) (Fig. 6.5c; Table 2,6). The Eu/Eu* value ranges from 0.84 to 1.17 (avg. 0.95) (Fig. 6.5d; Table 7). The Gd_N/Yb_N values, except for one sample, remains <2.0 with an average of 1.03 (Fig. 6.5d; Table 7). The Nb/Sc, Th/Sc and Zr/Sc ratios are highly variable at the lower part and decrease towards the upper part of the black shale (Fig. 6.5e). The CIA value is anomalously low at the lower part but increases slightly at the upper part of the succession. Other indices of chemical weathering, such as CIW and PIA, record very high values (Fig. 6.6a; Table 7). The Mg/Ca, Sr/Cu, Ga/Rb and Ba/Sr ratios record a wide range at the lower part but attain comparatively high values with a narrow range at the upper part (Figs. 6.6b–e). The Zr/Hf, Y/Ho and Nb/Ta do not follow any restricted pattern and display highly variable values along the succession (Figs. 6.7a–c). The Se/Co ratio gradually increases towards the upper part of the succession (Fig. 6.8a). Except from two intervals at the lower and the middle parts of the BS, the Ce anomaly remains constant (Fig. 6.8b). The redox-sensitive elements, such as Cd and Zn remain undetected in most of the studied sample; however, the Mn concentration records a gradual increase towards the upper part of the succession (Fig. 6.8c). The V/V+Ni and V/Cr values are highly variable at the lower part and records persistent high values at the upper part of the succession (Figs. 6.8d, e; Table 7). The Ni/Al, La/Yb and U/Th ratios are highly variable (Figs. 6.10c, d). The Zr/Rb ratio shows consistently low values; however, the Si/Al and Zr/Al ratios exhibit some spikes in their values throughout the succession (Fig. 6.10e).

6.4 Discussion

6.4.1 Provenance of the Black Shale:

The abysmally poor Mn concentration and the low Fe/Ti value, as well as the bivariate plot of Al/(Al+Fe+Mn) vs. Fe/Ti, seem to rule out any major contribution from hydrothermal

sources (Fig. 6.5a; Boström, 1970; Barrett 1981; Tchatchueng et al., 2020). The Cr/Zr ratios are also too low, refuting any hydrothermal source of the sediments (Table 7). La/Cr vs Th/Cr cross plot indicate the sediments of BS comes from a felsic dominated source area (Fig. 6.5b). The TiO_2 (in wt%) vs Zr (in ppm) plot shows also corroborates the felsic igneous province (Fig. 6.5c; Hayasi et al., 1997). The Gd_N/Yb_N vs. Eu/Eu^* cross-plot indicates that some of the terrigenous components were contributed by plagioclase-rich Archaean sources (Fig. 6.5d; McLennan and Taylor, 1991; Cullers, 2000; Moyen, 2020). Nonetheless, the documented trends of decreasing Nb/Sc, Zr/Sc and Th/Sc ratios up the BS succession strongly suggest that the supply from mafic sources increased in proportion through time (Fig. 6.5e; Cullers et al., 1988; Cullers, 1994, 2000; Cullers and Podkovyrov, 2000; Armstrong-Altrin et al., 2004). The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio varies between 23.5-47.7 (average 33.01), and the TiO_2/Zr ratio varies between 17.8-63.4 (average 35.3), indicating felsic source rocks for provenance (Table 7; Hayashi et al., 1997). Presumably, all the geochemical signatures of the BS suggest that the lower crustal rocks were gradually exhumed as the upper crustal rocks were eroded out.

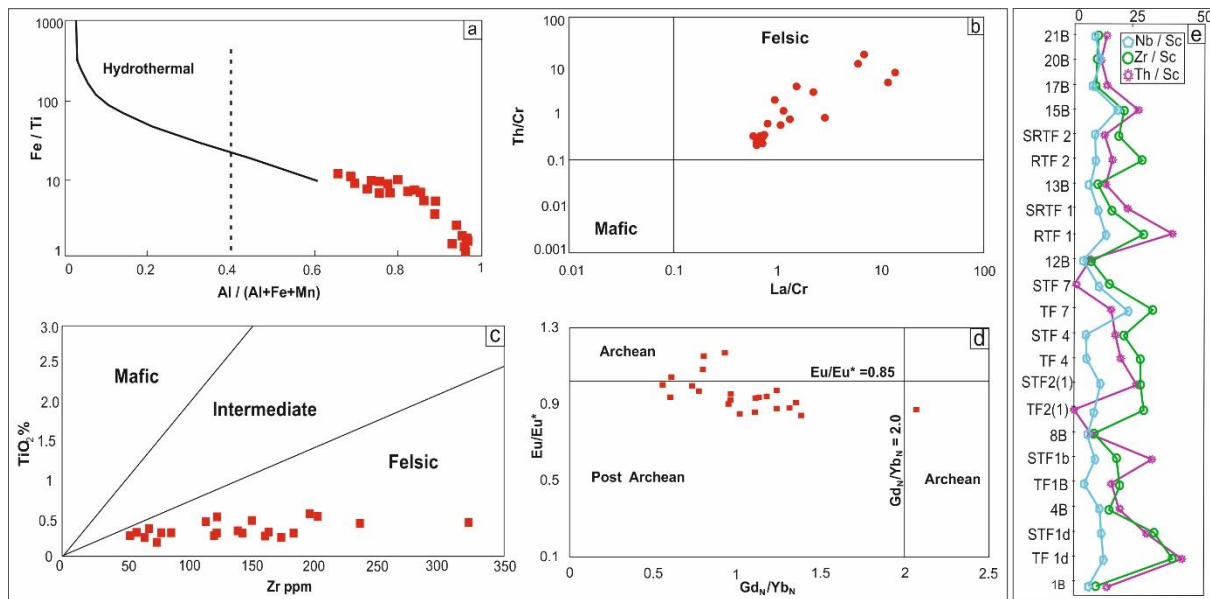


Fig. 6.5: Cross plots of a) Fe/Ti vs $\text{Al}/(\text{Al}+\text{Fe}+\text{Mn})$ b) Th/Cr vs La/Cr; c) TiO_2 vs. Zr and d) Eu/Eu^* vs. $(\text{Gd}/\text{Yb})_N$. e) Variation of Nb/Sc, Zr/Sc, Th/Sc; used to ascertain the provenance and distinguishing for source determination of the black shale.

6.4.2: Palaeoweathering and Palaeoclimatic conditions during deposition of the Black Shale:

The intensity of weathering can be estimated by comparing labile components and their common weathering product, clay or its dominant cation, the refractory element Al^{3+} . The

Chemical Index of Alteration (CIA) (Fig. 6.6a; Nesbitt and Young, 1982; Perri, 2020) yields wide-ranging values, ranging from as low as 50.6 to 67.3 at the top part of the succession with an average of 58.14. On the other hand, the Chemical Index of Weathering (CIW, Harnois, 1988) of most of the samples is high (> 96) (Fig. 6.6a). The discrepancies between CIA and CIW values might result from possible episodes of K-enrichment (K-metasomatism) for the BS (Wedepohl, 1971; Fedo et al., 1995). The high CIW values suggest a very high weathering intensity (Harnois, 1988). The wide variability of PIA values (average 93.88) of the succession further endorses the high weathering intensity (Fig. 6.6a; Fedo et al., 1995, 1996; Perri, 2020).

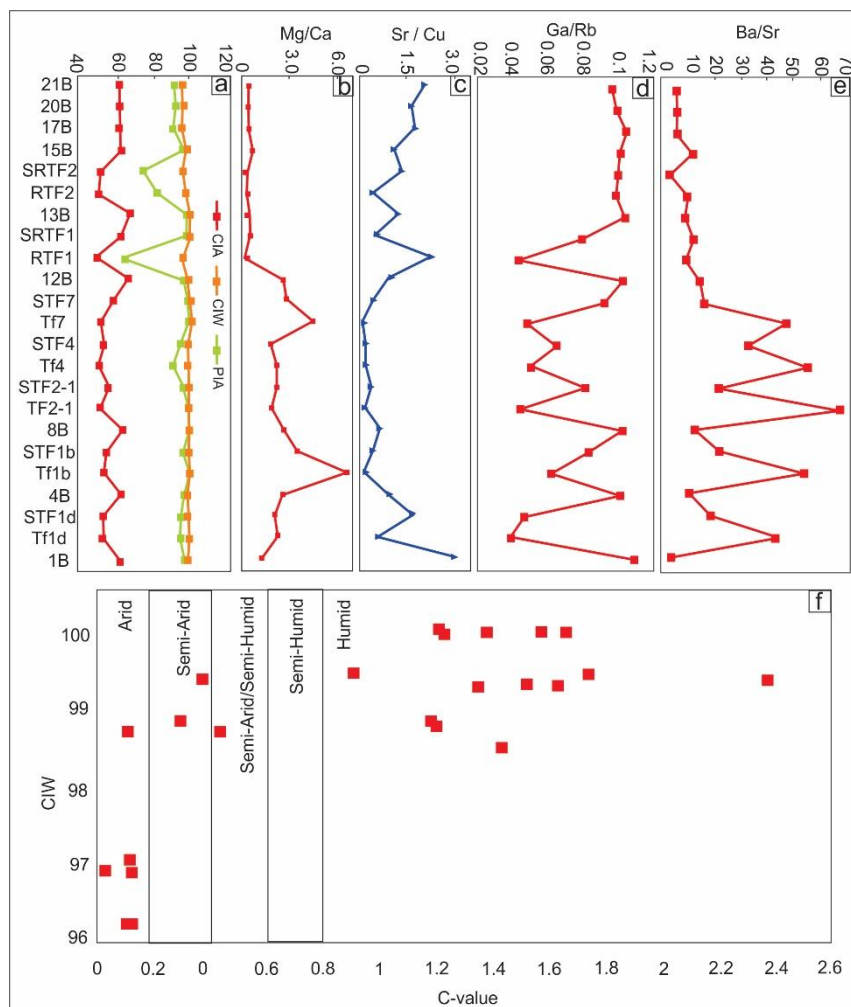


Fig. 6.6. The variation of **a)** CIA, CIW, PIA **b)** Mg/Ca **c)** Sr/Cu **d)** Ga/Rb and **e)** Ba/Sr plotted against the lithology. **f)** Cross plot of C-value vs. CIW of the Black shale part of Rampur Shale Member.

Sr is more readily soluble in water than Ba (Sheldon and Tabor 2009), and the high Ba/Sr ratio is indicative of highly leached sediments. The Ba/Sr index of the BS marks a drastic change in leaching (~ 29 at the lower part and ~ 8 at the upper part), which is well anticipated considering the combination of wide variability in the composition of source rocks and their weathering rates (Fig. 6.6e). Along with these above-mentioned proxies, REEs are also very closely related with the palaeo weathering intensity. Under strong weathering conditions, HREE become more mobile than LREE, and the studied Black Shale shows a higher $\Sigma \text{LREE} / \Sigma \text{HREE}$ ratio (avg. 7.39), indicating a high weathering intensity (Fig. 6.4c; Kimoto et al., 2006; Stevens and Quinton, 2008; Xu et al., 2017).

High weathering intensity ($CIW > 96$ & $PIA \sim 99$) points to a humid climate during BS deposition. The C value is an excellent proxy for palaeoclimate, which involves enrichments of several major and trace elements in arid to humid climatic conditions (Cao et al., 2012; Ma et al., 2015; Fu et al., 2016; Fathy et al., 2018a, 2021). A high C-value (> 0.6) indicates a humid

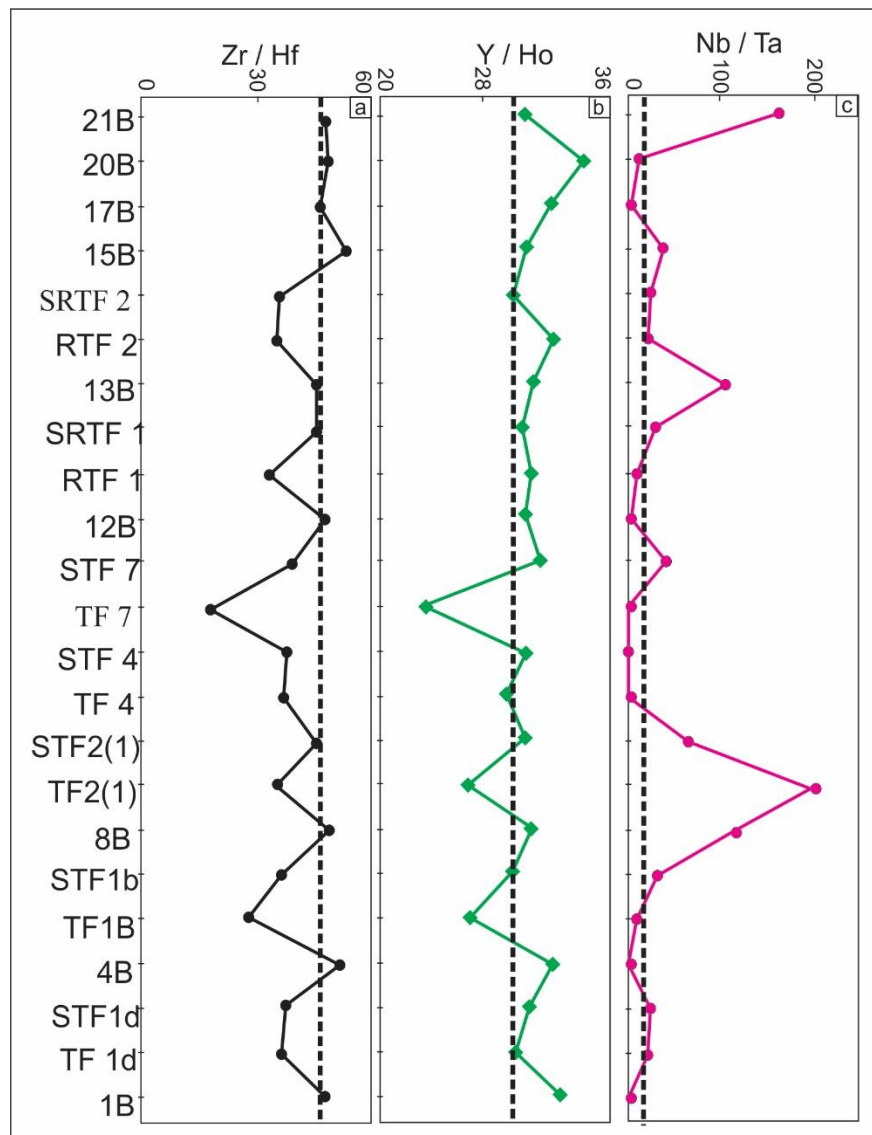


Fig. 6.7. a)-c) Vertical variation of the Zr/Hf, Y/Ho, Nb/Ta ratio within the black shale.

climatic condition (Qiu et al., 2015; Fathy et al., 2021) which perfectly suits the BS, which has an average C-value of 0.937 (Table 7). The CIW vs. C-value plot of most samples suggests a humid climate (Fig. 6.6f; Fathy et al., 2021). The average Mg/Ca ratio of the BS (1.84) is characteristic of a warm and humid climate; however, the decreasing Mg/Ca ratio upward within the succession (Fig. 6.6b) is in tune with the contention of decreasing humidity through time (Fathy et al., 2021). Shales that form in warm and

humid climates are generally kaolinitic and enriched in Ga, while those in cold and arid climates are commonly illitic and rich in Rb (Han et al., 2020). The studied BS are rich in illite, and the Ga/Rb ratio is quite low, ranging from 0.040 to 0.11, indicating a generally cold and arid climate (Fig. 6.6d). The stratigraphic variation of Ga/Rb ratio suggests that the palaeoclimate comparatively stabilized after initial precariousness. The Sr/Cu ratio, on the other hand, varies from 0.10 to 3.02 within the BS (Fig. 6.6c), which suggests a fluctuating palaeoclimate during the depositional history of Black Shale (Xie et al., 2018). Apart from the

above, trace and major elements and the REE data are also important indicators of palaeoclimatic conditions (Xu et al., 2017). A high Σ REE indicates warm and humid conditions but a low Σ REE indicates cold and dry conditions. For the studied BS, this value is relatively high (avg. 115.31), suggesting warmer palaeoclimatic conditions during deposition (Table 7).

Documentation of a treasure of microbial mat features in the petrographic study points to deposition within the photic zone, approximately 200 meters of water depth. The geochemical proxies such as Zr-Hf, Y-Ho, and Nb-Ta further corroborate this contention (Figs. 6.7a–c). Between Zr and Hf, the latter is preferentially scavenged, and the ratio between these two elements in the BS ranges between 18.3 and 52.9 compared to the modern marine range of 45 to 350 (Fig. 6.7a; Rudnick and Gao, 2003; Firdaus et al., 2011). The Y/Ho ratio increases as Ho is preferentially scavenged because of its higher complexation capacity (Planavsky et al., 2010). This ratio is almost always greater than 30 and ranges up to 36 in the BS (Fig. 6.7b). It thus closely depicts a marine signature but is perhaps slightly retarded in the epicontinental sea in which the deposition of BS took place (Mondal et al., 2022). In their global coverage, Qin et al. (2005) noted that the V/Zn ratio is lower than 1.33 in continental deposits and greater than 3.59 in marine deposits. In this BS, Zn is not often detectable, but where recorded, the ratio invariably exceeds 3.59, suggesting a marine deposition (Table 7). The Nb/Ta ratio within the BS ranges from 4.2 to 197 (avg. 38.64) (Table 7). Nb and Ta also have similarities in their ionic radii, although Nb is comparatively more mobile and higher in oceans than in freshwater (Firdaus et al., 2011). Since hydrothermal input was never formidable, the wide range of Nb/Ta values might be related to widely variable travel distances over the wide hinterland (Fig. 6.7c).

6.4.3: Palaeoredox, palaeosalinity, and palaeoproductivity of the Black Shale:

Steadman et al. (2020) unveiled that both Selenium (Se) and Cobalt (Co) are susceptible to oxidation-reduction (redox) processes, reacting uniquely to atmospheric oxygenation. The peak for Se overshadows all other trace elements in their distribution curve (Fig. 6.8a). Se occurs in acidic, reducing, and organic-rich environments (McNeal and Balistrieri., 1989) and becomes less mobile in oxygen-depleted conditions because of the insoluble nature of selenides, Se(0), and organo-selenium complexes (Mukherjee and Large, 2020). This trend is well corroborated by the substantial amount of authigenic Se content varying from ~ 40-141ppm (Table 15). Interestingly, Se concentrations are depleted in nutrient-like distribution on the sea surface while its compounds sink and replace sulfur in pyrite found on the seafloor mud. Selenium generally shows enrichment in marine sediments. Selenium is highly available

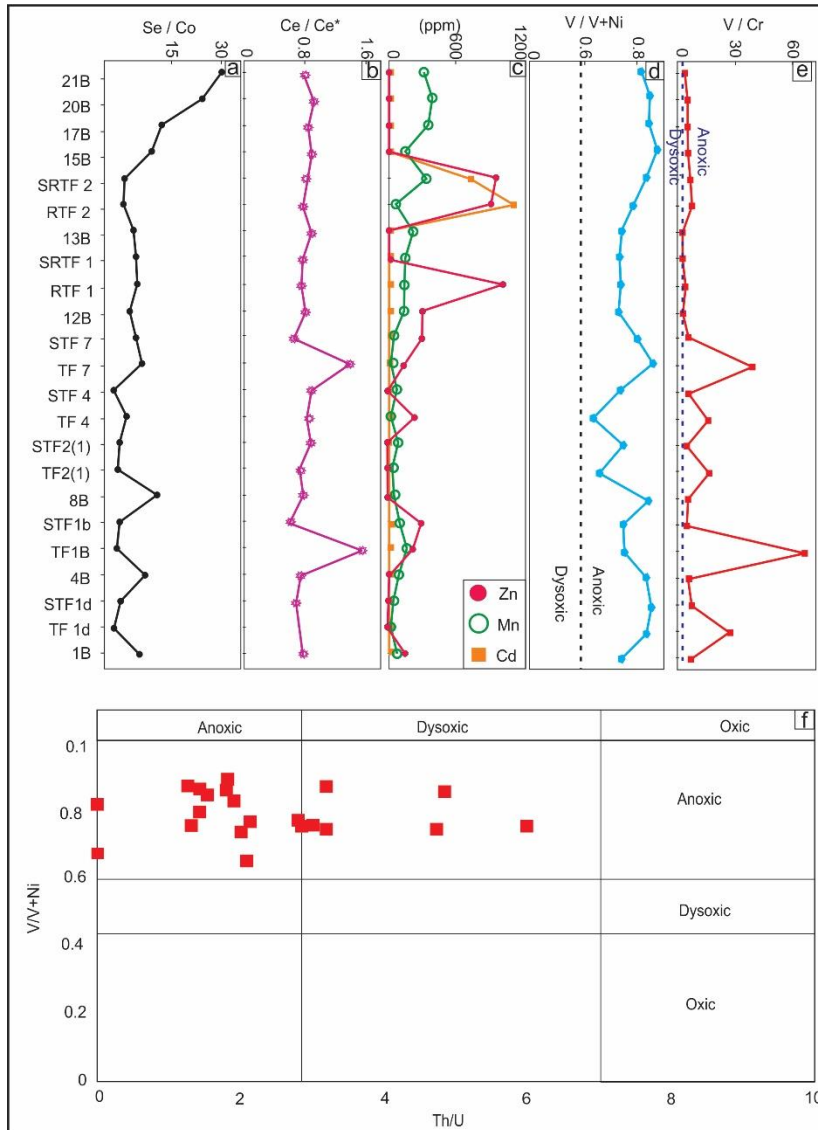


Fig. 6.8. a)-e) Vertical distribution of Se/Co, Ce/Ce*, Zn, Mn, Cd, V/V+Ni and V/Cr and **f)** cross plot of Th/U vs. V/V+Ni within the black shale succession.

for precipitation in an anoxic environment compared to an oxic environment (Kipp et al., 2019). Co also precipitates at a reducing redox condition (Tribovillard et al., 2006). The Se/Co ratio increases drastically within the BS succession, suggesting greater O₂ depletion during the penultimate stage of the BS depositional history (Fig. 6.8a; Large et al., 2014). The slightly negative Ce anomaly (avg. 0.93) in most samples also indicates that the bottom water was not devoid of oxygen (Fig. 6.8b, Wright et al., 1984; de Baar et al., 1985; Murray et al., 1990). Zinc and Cadmium, for instance, function as micronutrients released through organic decay. Under a slightly dysoxic to anoxic condition, these elements become insoluble and eventually precipitate along with the sediments. Cadmium, especially in the BS, is absent for some of the samples (Fig. 6.8c; Rosenthal et al., 1995; Morford and Emerson, 1999; Chen et al., 2021; Bryan et al., 2021). Organic matter and sulfides are the most important carriers of Cd to sediment. This explains the tallest Cd spike coincides with that of Zn at the same stratigraphic level (Fig. 6.8c; Chen et al., 2021; Ye et al., 2022). The coupled Cd-Zn spikes within the upper stratigraphic level of the BS may demarcate the oxic-anoxic interface (Little et al., 2015). An enrichment in the Mn concentration accompanying these spikes further attests to our interpretation (Fig. 6.8c). Mn⁺² is highly soluble under reducing conditions and shows depletion in the sediment deposited under reducing conditions (Tribovillard et al., 2006). Authigenic U in the BS ranges up to 5.64

ppm and may suggest anoxic conditions (Table 15; Jones and Manning, 1994). However, since U is incorporated in marine sediment as it interacts with the porewater, the inferred anoxic condition could have developed beneath the sediment-water interface, possibly within the first few centimetres of depth. Mo, which requires more intense anoxic conditions for precipitation and the presence of free H₂S (Tribovillard et al., 2006; Algeo and Tribovillard, 2009; Piper and Calvert, 2009; Reinhard et al., 2013; Wang et al., 2021) has contents below the detection level in all but one sample from the BS. This may be partly because of the muted Mesoproterozoic molybdenum inventory (Wang et al., 2021). Since a hydrothermal sink or source of Mo is unlikely (Bjornsson et al., 1972; Emerson and Husted, 1991), MoEF ranging up to 3.4 in the BS can perhaps be best explained by particulate shuttles from the sea surface (Table 15; Algeo and Tribovillard, 2009). The V and Ni are both redox-sensitive trace elements. While V is reduced from V(V) to V(IV) to produce vanadyl ion (VO²⁺) under reducing conditions and easily deposited in sediment, Ni gets released from organometallic compounds during organic matter decay (Tribovillard et al., 2006). The high V/(V+Ni) ratio (Fig. 6.8d) indicates strongly reducing conditions and probably stratified water (Hatch and Leventhal, 1992; Jones and Manning, 1994; Riquier et al., 2005; Cai et al., 2009; Zuo et al., 2020). While the reduction of Ni occurs in moderate to low redox conditions, that of V takes place at the lower end, making their ratio a valuable index to distinguish between anoxic and euxinic conditions. Ni is strongly associated with the pyrite fraction and V with the organic fraction, especially chlorophyll (Lewan and Maynard, 1982; Tabatabaei et al., 2012). The existence of chlorophyll or its precursor in 1.5 Ga-old BS is no longer a travesty, as most workers now believe that oxygenic photosynthesis and chloroplasts originated much earlier, possibly before 2.8 Ga (Suzuki and Bauer, 1995; Des Marais, 2000; Blankenship, 2010). Under oxygenated conditions, Cr is present in seawater as chromate anion (CrO₄⁻), and if the condition becomes anoxic, the Cr(IV) is reduced to Cr(III) (Tribovillard et al. 2006). Vanadium covaries with chromium, having closely similar ionic radii, but their ratios (V/Cr) show a very wide scatter within the BS and exceed 4.25 in most cases, suggesting a strong anoxic condition development within the sediment (Fig. 6.8e). However, the strong depletion of CrEF indicates that possibly the entire Cr budget in the BS is detrital (Table 15; Dill, 1986), and the high values of V support strong reductive conditions but without the presence of H₂S in the water column. However, NiEF is less than 1.0 in all but one sample, while CoEF is greater than 1.0 in at least 50% of the samples studied (Table 15). Liu and Algeo (2020) considered the enrichment factors of individual redox-sensitive elements as better guides than their ratios in revealing palaeoredox conditions. Except for Cr, the range of enrichment factors of all other redox-sensitive elements, including

Cu, Zn, Pb, U, and Mo, exceeds 1.0 (Table 15). The Th/U ratio is also widely variable, ranging from 1.5 to 3, and indicates the dysoxic (to suboxic) condition of deposition (Table 7; Jones and Manning, 1994). The cross-plot of Th/U and V/V+Ni represents that the studied black shale sediments are deposited under anoxic conditions (Fig. 6.8f; Luo et al., 2015a; Wu et al., 2022). Collectively, most trace element ratios used as palaeoredox proxies indicate that the Black Shale of Rampur Formation is deposited in a suboxic to anoxic palaeoredox condition. The lack of redox-sensitive trace metal enrichment within the Black Shale, the lack of covariation among trace metals, and the low Mo concentration within the Black Shale may indicate the possibility of open ocean circulation preventing ocean-floor anoxia (Scott et al., 2017). This interpretation can be further supplemented by the negative values of the authigenic enrichment of certain trace metals (including Mo, Ni, Cu, and Cr) (Table 15). The Black Shale of the Rampur Shale Member, hosting abundant organic matter, with high TOC content (avg. >0.5%) and possibly S content (approx. 0.91; Singh and Chakraborty, 2023), indicates the development of sub-oxic to anoxic pore-water condition possibly resulting from organic matter degradation (Algeo and Rowe, 2012; Scott et al., 2017). The lack of mafic source rock coupled with a high abundance of illitic clay minerals (Fig. 6.9) possibly resulted in metal-depleted Black Shale facies within the Rampur Shale Member, even in sub-oxic to anoxic bottom water conditions.

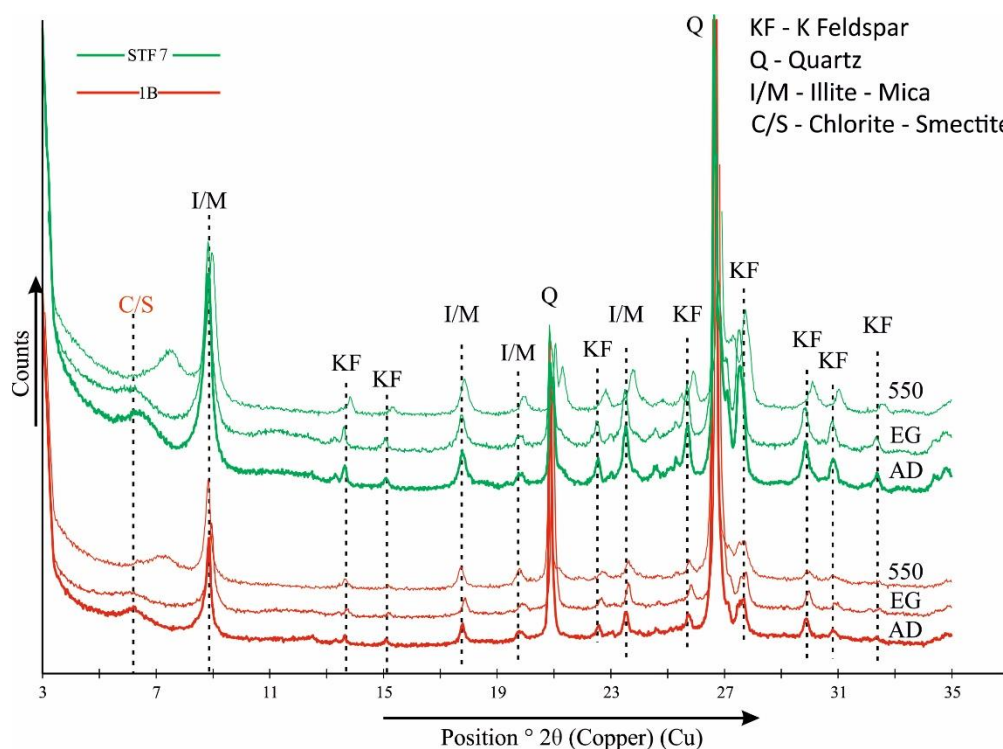


Fig. 6.9: X-Ray Diffraction analysis of the clay fraction (<2 micron) of sample no STF7 and 1B performed under air-dried (AD), Glycolated (Gly) and heated (550° C for 1 hour) conditions.

The Sr/Ba ratio is often used as a palaeosalinity proxy, considering that Sr is relatively abundant compared to Ba in seawater, resulting in a higher Sr/Ba ratio in marine sediments with respect to brackish and freshwater sediments (Table 7). In marine fine-grained siliciclastic sediments, Sr is adsorbed mainly by clay minerals or fixed in the organic fraction, whereas Ba can be related to biogenic productivity. A strong caveat against the application of the Sr/Ba ratio as a palaeosalinity proxy is that carbonate-hosted Sr may mask the signal emitted from clay minerals. The trace elemental analysis of the BS yields Sr/Ba ratios ranging from 0.014 to 0.32 (Table 7). Most of the data, however, are too low to be compared with the freshwater values and hence unacceptable (Wei and Algeo, 2020). Apart from Sr/Ba, Rb/K is another proxy for palaeo-salinity determination, but this ratio is also very low for this studied shale (avg. 0.195) compared to freshwater (Liu and Cao, 1984; Sajid et al., 2020; Table 7).

The unbelievably low values of Sr/Ba and Rb/K ratios in the BS might have been caused by the differential remobilization of the individual components. As the palaeoclimate during the BS deposition was mostly warm and humid, the evaporation rate was comparatively less, so the salt deposition may be quite difficult at that time. Nevertheless, due to the epicontinental nature of the RS depositional basin, as envisaged by Mondal et al. (2022), palaeosalinity is expected to have been far less than that of the open sea. Freshwater supply from almost all sides could have caused considerable dilution, as expected when the basin was almost land-locked in the middle of a supercontinent.

Several working groups have tried to find proxies for restriction in water and sediment trace element chemistries within a few modern marine basins experiencing different degrees of restriction or openness. The major characteristics noted in restricted basins with respect to the open upwelling settings are as follows: (i) the (bio)-productivity rate is lower, (ii) bottom water is likely to be sub-oxic rather than euxinic, while surface water remains oxic, (iii) the importance of the ‘particulate shuttle’ is generally lesser and increases when the sill that restricts the basin is down and (iv) elements that undergo reductive dissolution remain largely trapped within the basin and eventually precipitate. Different element concentrations and ratios have thus been noted between restricted basins and open upwelling zones. Cd, Mo, and Mn are extremely sensitive and vary broadly from restricted to upwelling basins. Cd and Mo are mostly undetectable within the studied BS samples. Co and Mn are also important proxies for deciphering the basin conditions, and the $\text{CoEF} \times \text{MnEF} > 2$ vs. Al% of the Black Shale suggests upwelling conditions prevailed during the deposition of the Black Shale (Fig. 6.10a; Little et al., 2015; Sweere et al., 2016; McArthur, 2019). Mn within the BS is highly depleted,

whereas the Co concentration in the studied section is nearly the same as the average Shale, which produces fluctuating basin conditions from upwelling to restricted as observed from the Co ppm X Mn% vs Al% cross-plot (Fig. 6.10b). Low palaeosalinity suggests freshwater input from almost all sides of the basin, as it occurs in a lake or an epicontinental sea (Mondal et al., 2022). A comparative increase in the Sr/Ba ratio points to a sharp increase in palaeosalinity in the late phase of basin filling, presumably because of the enhanced rate of supply of water from the open ocean. This could have resulted from subsidence leading to an increase in depth with respect to the basin surface area, consequently restricting the extent of vertical mixing of water and replenishment of oxygen into the bottom water. Evidence of basin subsidence, such as the presence of numerous slide planes at different levels of the succession, agrees well with this contention of a late increase in basin depth.

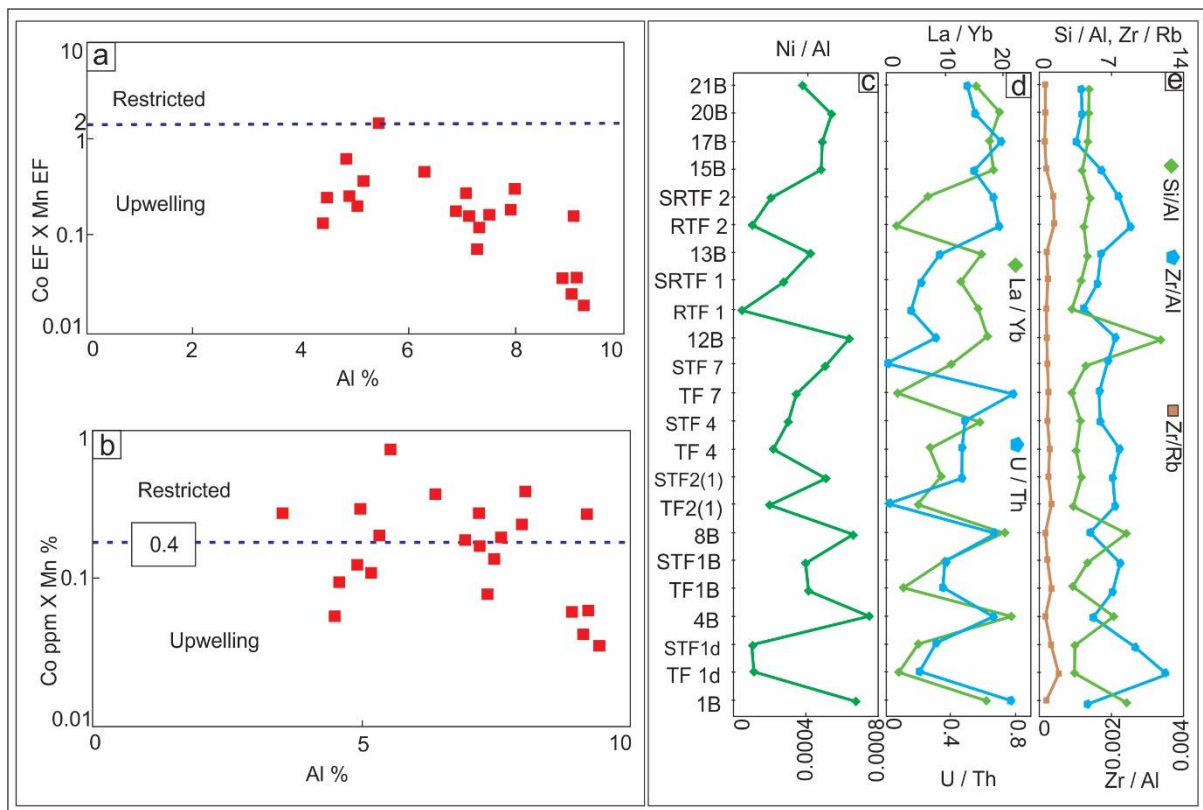


Fig. 6.10: a) Cross plot of Al% vs. CoEF X MnEF, b) Al% vs. Co(ppm) X Mn (wt%) and vertical variation of c) Ni/Al, d) La/Yb, U/Th, e) Si/Al, Zr/Al and Zr/Rb within the black shale succession.

As a result, the consumption of available oxygen by organisms could have led to the establishment of an anoxic regime on the basin floor while the overlying water column remains oxic. Predictably, that process helped the Y/Ho ratio acquire the marine-diagnostic threshold value of 35 (Fig. 6.7b; Planavsky et al., 2010). The upward-increasing trend of Ni/Al, La/Yb, and U/Th ratios of the BS succession following a declining trend indicates rapid enhancement

of the sedimentation rate, which might have resulted from high weathering intensity as well as gradual peneplanation (Figs. 6.10c, d; Ding et al., 2021). The increase in the sedimentation rate can also be associated with the increasing tilt of the basin flank and slope, which is evident from the presence of turbidites within the overlying FS unit of the RS Member (Figs. 1, 10 of Mondal et al., 2022).

6.4.4: Records of Mesoproterozoic black shales worldwide in relation to global tectonics:

The studied BS of the Vindhyan basin evolved on a stable cratonic basement, i.e., Aravalli or Bhandara craton, during the Meso-Neoproterozoic time (Rogers, 1993; Erikson et al., 1999; Bose et al., 2001). Overall, the Vindhyan sedimentary succession is mildly metamorphosed and almost undeformed. Apart from the palaeo-seismic deformational features (Sarkar et al., 1995; Bose et al., 1997), the Lower Vindhyan/ Semri Group contains a thick succession of volcanic tuff known as the Porcellanite Formation, which signifies an extensive felsic volcanic activity during Meso-Neoproterozoic time (Ross and Smith, 1961, Banerjee et al., 2006). Throughout the Vindhyan succession, several sea-level fluctuations are recorded, and the black shales present within the Vindhyan Supergroup invokes a clear indication of the marine transgression event demarcating the maximum flooding Zone (MFZ). The black shale of the Rampur Shale Member is also supporting this contention (Bose et al., 2001).

The sedimentation of the Rampur Shale Member initiated with a marine transgression possibly resulted from the basin deepening/sagging process, as evidenced by numerous faults and associated slide planes (Figs. 6.1b, 6.11). Marine transgression initiated with the deposition of facies A at the basin margin, which is gradually overlain by facies B, C and D as the transgression progressed (Fig. 6.11). Deposition of the black shale followed by Faded Shale (basin margin equivalent) suggests termination of the marine transgression within the basin which is succeeded by highstand deposition of the overlying Rohtas Limestone.

The widespread formation of black shale in geologically significant time intervals is often associated with supercontinent amalgamation and break-up (see Basu et al., 2017 for more references). Supercontinent break-up promoted restricted ocean circulation along with deep ocean anoxia, global to regional-scale volcanic episodes, deposition of BIFs, marine transgression events and high burial rate of organic carbon at the shelves promoting black shale deposition worldwide (Fig. 6.12; Table 16) (Condie et al., 2001; Condie, 2004). On the other hand, amalgamation of supercontinents results in restricted palaeogeographic distribution of black shales confined within offshore marine basins or in freshwater depocenters within the

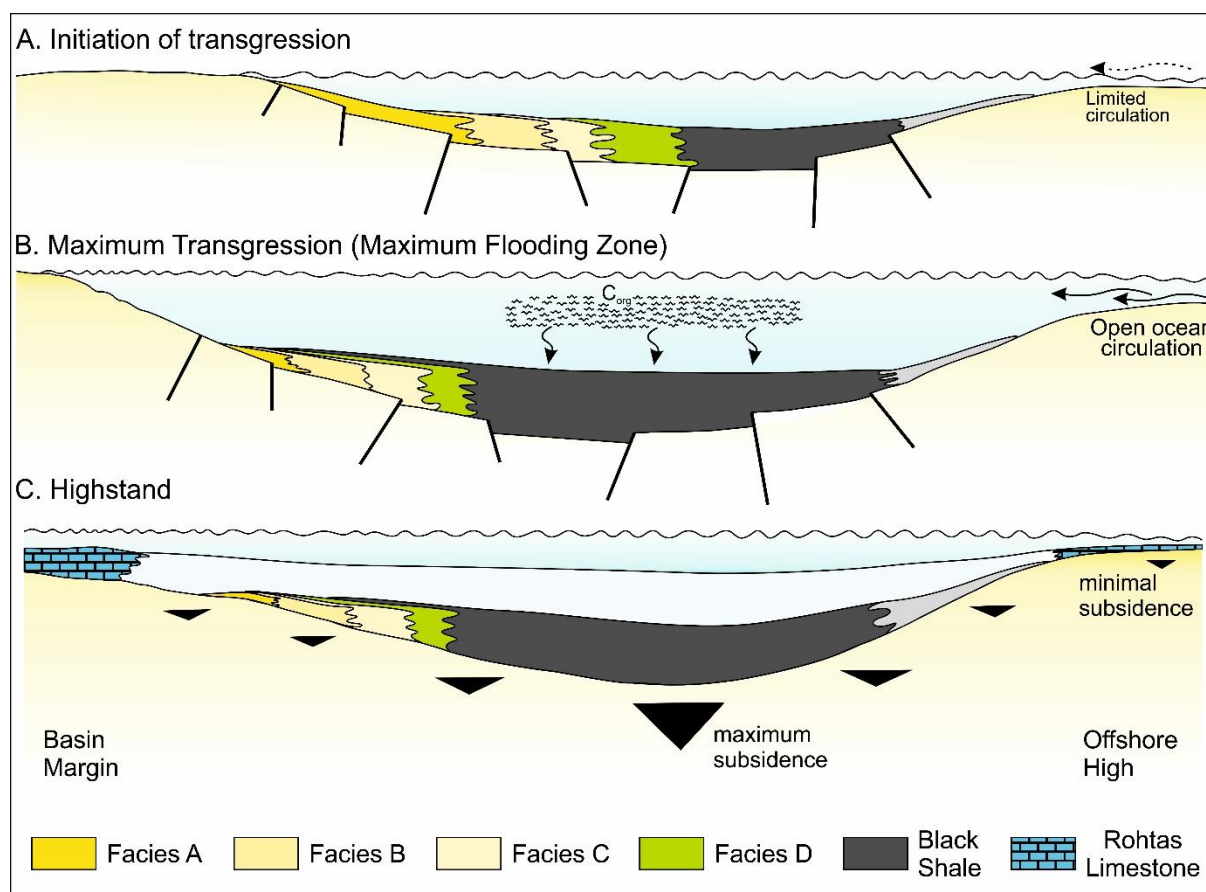


Fig. 6.11: Depositional Scenario of Rampur Shale Member along with the sequence stratigraphy and facies development within the depositional basin.

interior of the basin (Basu et al., 2017). Many sedimentary basins during the Mesoproterozoic time (1.6-1.0 Ga) exhibit thick black shale deposits (Table 16). As new ocean ridges are formed, atmospheric CO₂ concentration increases, which ushers in warmer climatic conditions, facilitating high chemical and physical weathering (higher CIW, PIA) of the source rocks (Berner and Berner, 1997; Condie, 2004; Basu et al., 2017). In the case of the black shale in the Rampur Shale Member, the coincidence of this secular increment in basin depth and increasing peneplanation at the source of sediments likely resulted in marine transgression. The black shale of the Rampur Shale Member was built up in consequence with higher weathering intensity and comparatively warm and humid conditions (Fig. 6.6f). However, the occurrence of numerous slide planes at successive stratigraphic levels and volcanic tuff layers (Fig. 6.1b) indicates that global tectonics could have been the prime mover of subsidence in the Rampur basin. Not only in the Vindhyan Basin, a phase of black shale deposition occurred throughout the Proterozoic time with maximum deposition during Palaeo-Mesoproterozoic time (Condie 2001; Fig. 6.12). A global-scale event of supercontinent break-up was initiated during the late Palaeo-Mesoproterozoic time (Pandey and Rao, 2020; Basu et al., 2017). Almost all the

continents were assembled and formed the Columbia Supercontinent during ca. 1.8-1.5 Ga (Rogers and Santosh, 2002) which again rifted and reassembled again to form the Rodinia Supercontinent during the 1100-700 Ma (Rogers and Santosh 2002; Evans et al., 2011). Yakubchuk (2010) suggested that Columbia was amalgamated by ca. 1.85 Ga and remained largely intact until 1.1–1.0 Ga. Pesonen et al. (2012) claimed that the amalgamation of Columbia occurred ca. 1.53 Ga, and it broke up at ca. 1.18 Ga during several rifting episodes. It is observed that globally more black shales deposition preferred during supercontinent breakup (Condie, 2004). Compiling all the pieces of evidence, it is quite logical to assume that the supercontinent Nuna or Columbia started to break up before 1.5 Ga when the underlying Porcellanite Formation of an estimated thickness of ~250 m was deposited (Zhao et al., 2011).

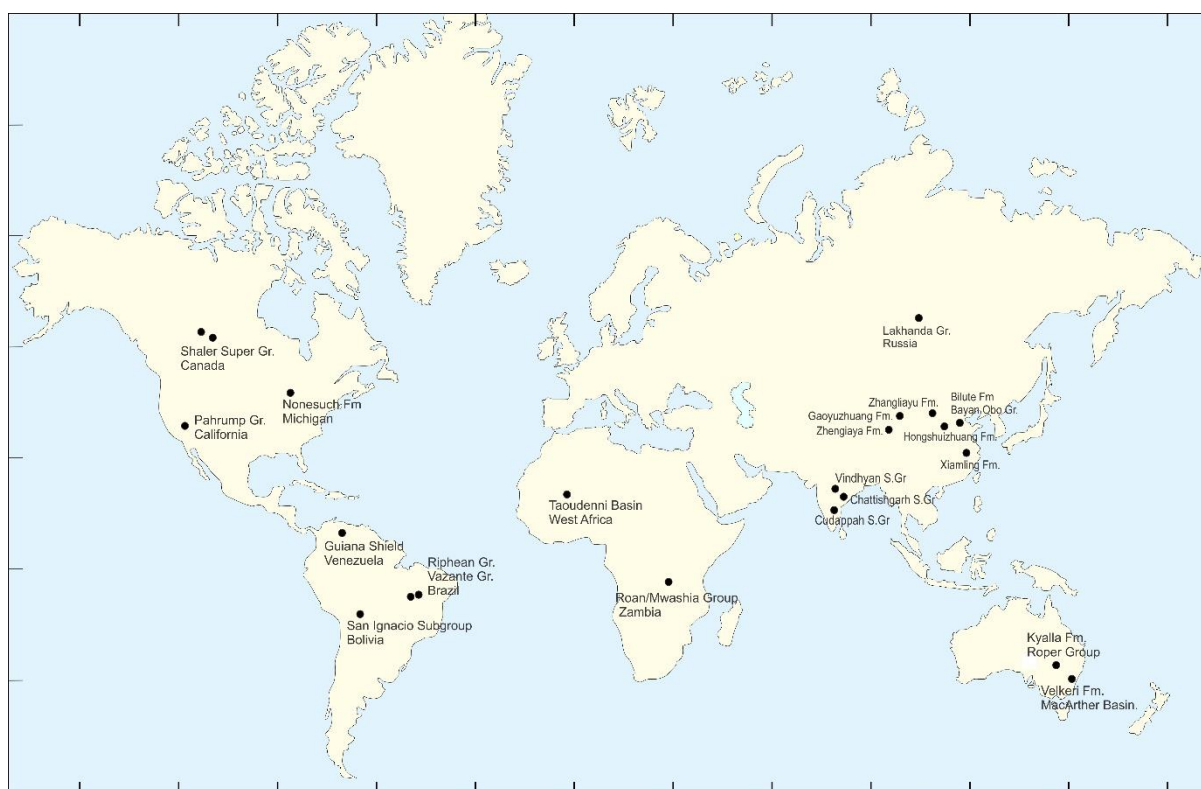


Fig. 6.12: World-wide deposition of Black shale during Mesoproterozoic time.

6.5: Conclusions

The conclusions of the present deliberation are as follows:

1. The sedimentological and geochemical investigation of the BS unit within the 1.5 Ga-old RS Member, Semri Group, India, reveals that the BS formed during the peak stage of transgression at the top part of a TST followed by a HST present within the RS. The

- occurrences of slide planes within the lower retrogradational part indicate occasional subsidence. This subsidence helps to develop a sub-oxic to dysoxic environment, occasionally facilitating glauconite mineralization within an overall shallow-marine condition.
2. The major, minor, and trace elemental composition of the BS suggests a predominance of felsic source rocks with increased input from mafic sources at the later stage of deposition. The source sediments derived from high-intensity weathering under warm-humid conditions facilitating chemical weathering and element leaching for which shales became metal depleted; even though the hinterland was wide and the sediment source was compositionally variable.
 3. The deposition of the BS is characterized by low atmospheric oxygenated conditions, typical of the early Mesoproterozoic time, with a low bio-productivity rate and absence of active hydrothermal sources. The absence of a hydrothermal signature may reduce the nutrient supply. The bottom water condition was probably sub-oxic to anoxic.
 4. The Palaeo-Mesoproterozoic time is riddled with black shale deposition globally representing high-intensity weathering, warm and humid palaeoclimatic conditions, high atmospheric CO₂, restricted basin conditions reasonably in sync with the breakup of the Mesoproterozoic supercontinent, named Nuna or Columbia. The concurrence of tectonic subsidence and volcanic eruptions in close quarters suggests that the supercontinent had already started to break up before 1.5 Ga.

CHAPTER: 7

Paleoenvironmental Dynamics in a Mesoproterozoic Epicontinental Sea: A Case Study from Rampur Shale

7.1: Introduction

Shales keep their intrinsic variability hidden under the veil of their mundane homogeneity. Genetic implication thereof, thus, seldom remains accessible. The variability may be physical, only subtly, may be petrographically at the minutest level, or perhaps geochemical at elementary level. The Mesoproterozoic marine Faded Shale, only about 3m in thickness, at the top of the retrogradational Rampur Shale Formation (RSM) and beneath the progradational Rohtas Limestone Formation (RLM) shows variability on all three counts (Fig. 7.1a, b). It immediately overlies the Black Shale (BS; Paikaray et al., 2008) from which it clearly distinguishes itself by a lighter grey color. This paper focuses upon this formation of limited thickness for eight reasons: One, between the BS and the RLM, it was never distinguished. Second, its comparatively lighter color with respect to the BS makes apparent presence of a second minor facies interspersed with the dominant grey shale facies at multiple stratigraphic levels (Fig. 7.1a). Third, the centimeter-scale minor facies bears physical evidence of resedimentation and hence provides opportunity to study products of two different paleogeographies in one (Fig. 7.1b). Fourth, the two facies bear contrasting geochemistry. Fifth, they, now vertically juxtaposed, provide a rare window to look at lateral variation in paleoenvironment within a Mesoproterozoic basin in a scale much broader than usual. Sixth, being placed between a siliciclastic Transgressive Systems Tract (TST) and a carbonate Highstand Systems Tract (HST), this formation unveils a fortuitous revelation of paleoenvironmental evolution in course of such a transition that lacks Phanerozoic-type Maximum Flooding Surface (MFS). The seventh, considering the Mesoproterozoic age of the rocks, is the query whether there had been an environmental stasis in their depositional basin or not. The final question was, had the paleoenvironment been dynamic, how did it vary through space and time and what drove the mechanism. Overprinting of diagenesis and prolonged weathering, nonetheless, makes tracking of this evolution a challenging task.

The work been carried out around the Bihara Kola village, Madhya Pradesh, Central India (Fig. 7.1c). The paper is geochemistry-centric, but its foundation is in field and petrographic observations.

7.2: Physical Attributes

7.2.1: Field attributes:

The dominant facies, SI, constituting the FS is grey in color and internally typified by fine and even laminae that on weathering give rise to preponderant fissility. This general motif is disturbed only by intervention of a very minor facies, ST which is a centimeter-scale

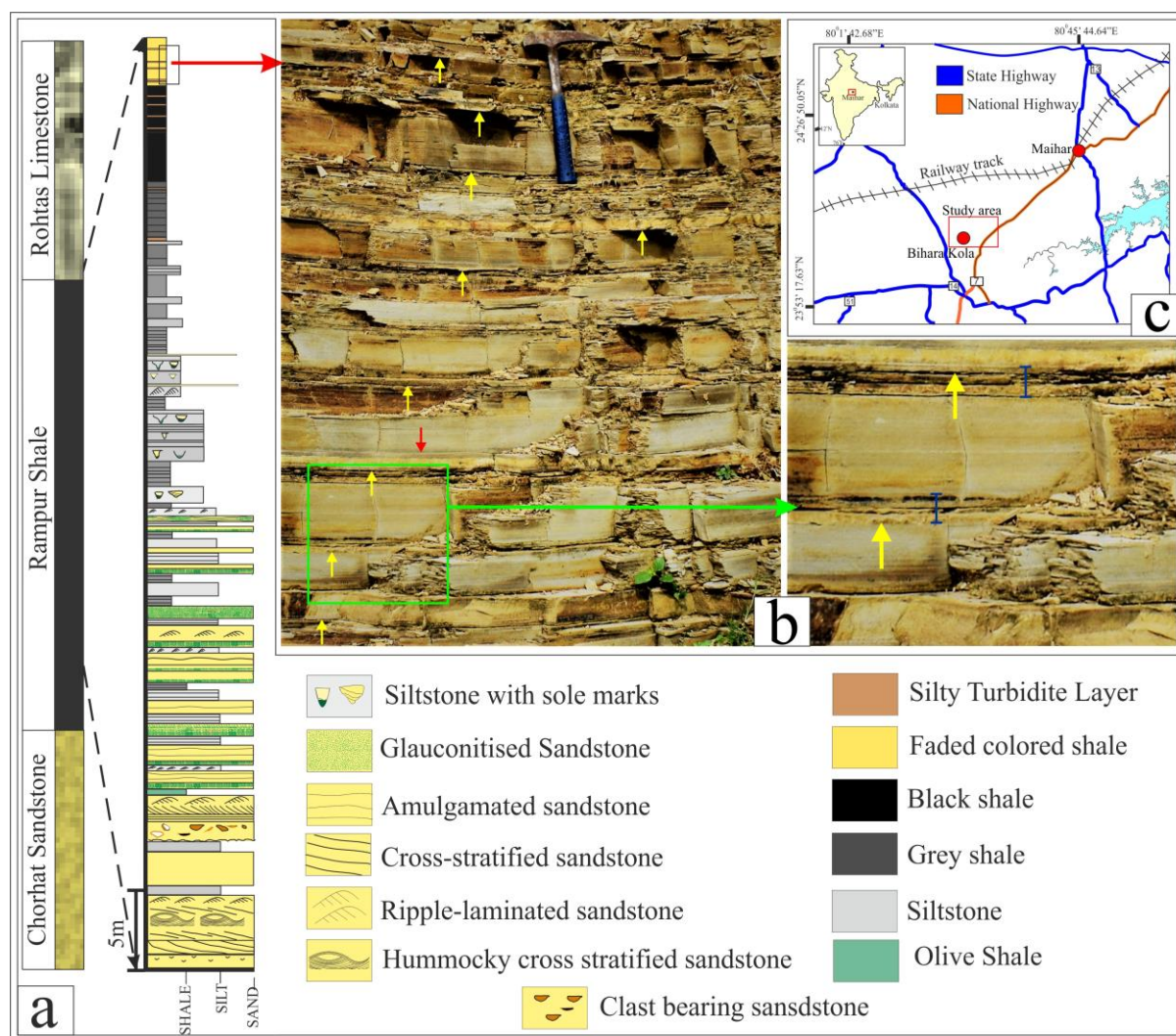


Fig. 7.1: a) Variation of lithology and sedimentary structures within the Rampur Shale succession encased between Chorhat Sandstone below and Rohtas Limestone above. **b)** Photograph of a portion of the Faded Shale depicting the alternations between its facies SI and ST (yellow arrows and the red arrow pointing an example of the dark muddy component of the same facies), a portion of the photo is further enlarged on right highlighting amalgamation of multiple ST beds. **c)** The location of the study area with a map of India (within inset) on right top.

couplet of a fine-grained siltstone and an overlying dark colored sub-millimeter-thick mudstone at irregular intervals (Fig. 7.1b). The siltstone has sheet-like geometry, pale whitish color, non-laminated nature and less than or around 1 cm in thickness. The coupled mudstone is black in color, and clearly recognizable within the FS by their comparatively

darker color. The siltstone layers have their bases sharp, and at places, irregular with little scoops underneath. They are internally graded (Fig. 7.2a). The dark mudstone laminae gradationally overlie them and are commonly composite in nature having interlayers of submillimeter-thick grey shale. In these composite layers the darker mudstone microlaminae are laterally detached and broadly lens-shaped. Composite or not, the dark colored mudstone grades upward into the overdominant facies SI (Fig. 7.1b).

7.2.2: Petrographic attributes:

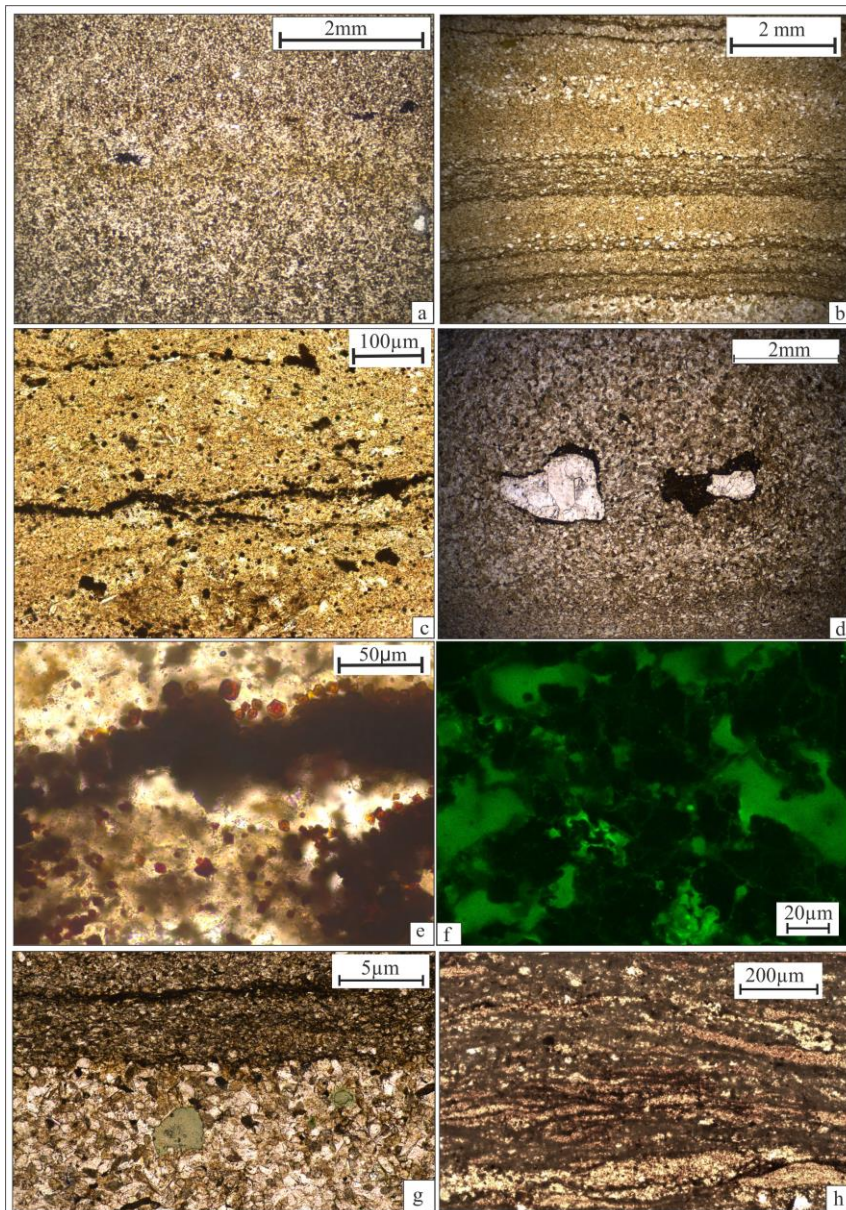


Fig. 7.2: **a)** Feebly developed grading within the silty component of the ST facies, **b)** the microfacies comprising the subfacies SI within the FS, **c)** pyrite preferably concentrated along crinkled carbonaceous dark laminae, but also remaining disseminated throughout the background sediment in the facies SI. **d)** fine-grained siltstone component in the ST facies with uncommon deterioration of grain-size sorting in presence of rock fragments, **e)** Organic lumps surrounded by siderite crystal in the ST facies, **f)** facies SI containing numerous patches of organic matter appearing green under Confocal Microscope, **g)** sharp contact between silty subfacies with the overlying crinkly laminated subfacies of the facies SI, **h)** false cross-strata within the crinkly laminated microfacies within the facies SI (plain polarized light).

Three distinctive microfacies constitute the SI facies and they are (i) massive mudstone, almost uniform in texture, (ii) mudstone containing subordinate population of silt-sized grains and (iii) mudstone characterized by bunch of crinkled laminae. Microfacies (i) and (iii) commonly alternate between themselves and have their contacts usually sharp. The microfacies (ii) also contains silt-sized grains like the microfacies (i), but they are generally smaller in size (Fig. 7.2b). The mutual contacts between the microfacies are generally planar. The microfacies (iii) has the crinkled laminae in various arrangements (see below). Pyrite crystals are often present along these crinkled laminae, but are also found disseminated within the other two microfacies (Fig. 7.2c).

The texture of the siltstone microfacies of the ST facies is variable between beds, especially regarding the mud content. It turns extremely poor in grain-size sorting where inordinately large rock fragments are incorporated (Fig. 7.2d). Some beds are significantly more enriched in lumps of organic matter (OM) and these beds distinctly more enriched in siderite (Fig. 7.2e). The lumps of OM bear identifying hues under confocal microscope (Fig. 7.2f). Some siltstone beds are also variably enriched in glauconite. The glauconite is usually present in form of peloids whose length matches well with that of the associated quartz grains. At places, the glauconite grains have irregular forms with delicate edges (Fig. 7.2g).

7.2.3: Interpretation:

The FS is interpreted to have formed at the penultimate stage of a marine transgression (Banerjee, 1997; Schieber et al., 2007). Its characteristic fine and even laminae with limited textural variability is a likely product of slow deposition in a calm and quiet deep sea. The crinkled laminae with frequent bifurcations and jagged torn ends as well as local arrangement in form of false cross-stratification suggests prolific growth of microbial mat within the SI facies (Fig. 7.2h). Preferred pyrite concentration along the crinkled laminae and fly-paper effect in trapping platy minerals further corroborate microbial origin of the latter (Schieber et al., 2007). The occasionally intervening siltstone-mudstone couplets thus appear to be products of minor silty/shaly turbidites (ST), each of which was episodic and waned through time allowing carbonaceous mud to settle at the end of the resedimentation process. It is likely that collapse of shelf-margin generated these mass flows time to time. Siderite formation in OM-rich siltstones suggests influence of microbiota in shallow water sediment (Lin et al., 2020). The laterally detached nature of the dark colored of mudstone microlaminae alternating with the indigenous faded shale (SI) was presumably deposited

from oscillation of the turbidites that rebounded repeatedly within the semi-enclosed epeiric sea in which the Rampur Shale was deposited (Eriş et al., 2012). Seismoturbidites of similar character have been reported from the modern intracontinental marine Kumburgaz Basin, Sea of Marmara (Yakupoglu et al., 2019).

7.3: Geochemical Attributes

Geochemical analysis was conducted upon samples of SI from 7 successive stratigraphic levels and on 4 samples of two couplets of ST at two discrete stratigraphic levels. Sample collection from the ST was particularly restricted because of difficulty in recognition and thinness. The results of the analyses are as follows:

7.3.1: Results:

As far as the major oxide compositions of the rocks, are concerned, SiO_2 is moderate to high, Al_2O_3 is moderate, Fe_2O_3 and MgO are rather low, Na_2O is also low, although K_2O is moderate to high, low is TiO_2 , but what is most remarkable is that Mn is very low and measured only with help of ICP-MS (Table 17, 18). The Enrichment factor with respect to Average Shale in case of K is around 2.5 to about 4.5, may reach up to 2.9 in case of P, up to 2.1 in case of Fe, but Si EF is comparatively lower in case of the ST facies (Table 19). The most remarkable aspect of trace element composition of these rocks, nevertheless, is perhaps the enormous enrichment factor of Se with respect to Average Shale; it is distinctly higher within the SI population, and within the ST couplets comparatively higher within the darker muddy component (Table 19; Fig. 7.3a). Without Se, the trace element distribution curve when normalized against Average Shale turns rather flat. However, some degree of enrichment in Zn is still mentionable (Table 19; Fig. 7.3a). As for the REYs (REE+Y) the entire population is depleted in comparison to Average Shale (Fig. 7.3b). The REY distribution curves are widely variable in geometry between the samples. The majority of the curves depict MREY enrichment, some are LREY enriched, some are HREY enriched and the rest are, more or less, flattened (Fig. 7.4 a, b, c, d).

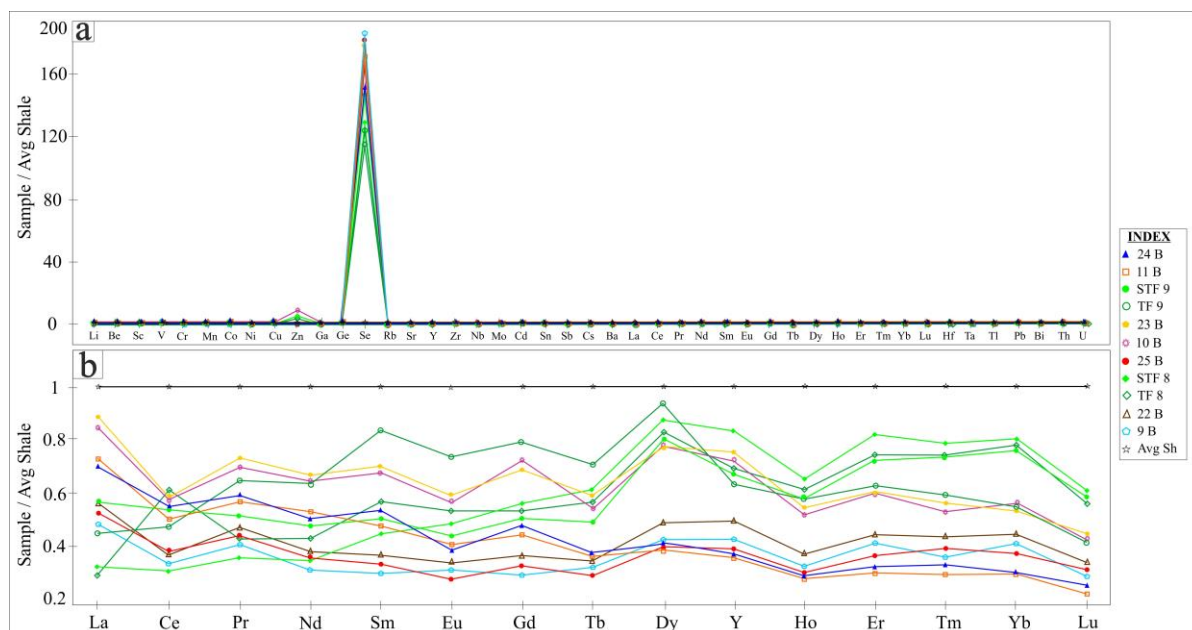


Fig. 7.3: **a.** Trace elements and **b.** REY distribution pattern in the FS, normalised against Average Shale.

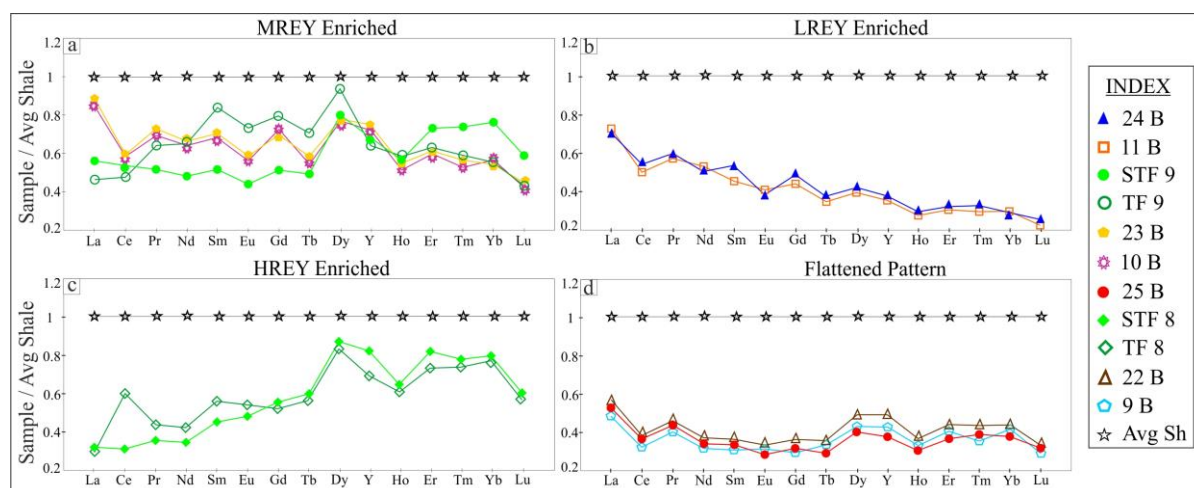


Fig. 7.4: Diverse patterns in REY distribution in the FS with reference to Average Shale.

7.3.2: Discussion:

7.3.2.1: Sediment translocation:

The main bulk of sediment, in these siliciclastic rocks is land-derived and constituted by quartz, feldspar, mica and heavy minerals that were delivered to the seafloor as either bedload or suspension load. The rest assumed solid form within the sea itself or within the already settled sediment. The Si vs Al plot the SI and ST facies components form two distinct clusters and their correlation is negative in the SI and almost non-existent in the ST (Fig.

7.5a). It thus appears that Si was delivered mainly in form of quartz bed load, while the ST facies has significant amount of clay in excess and importantly, the fine siltstone component

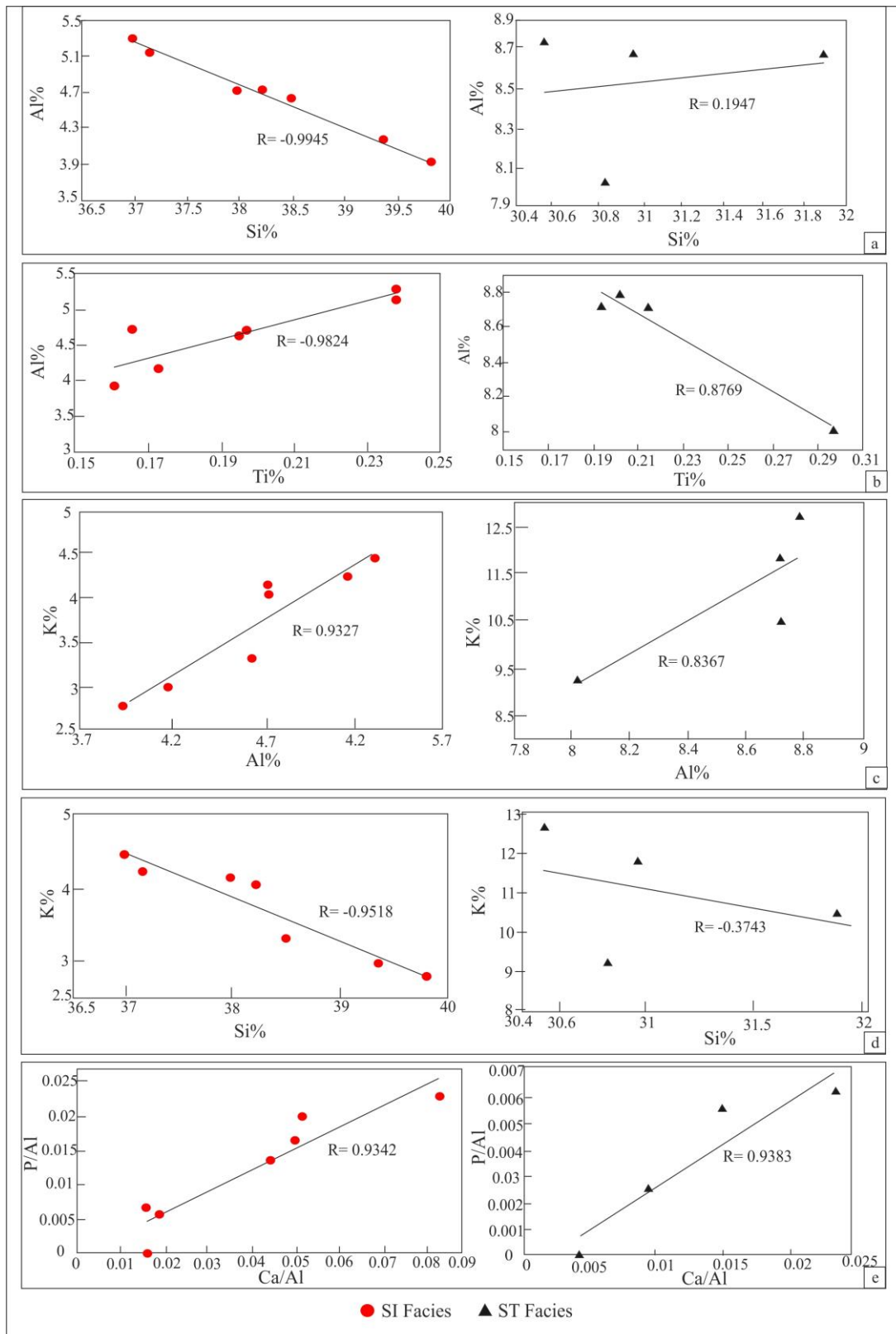


Fig. 7.5: Comparison between elementary relations in the two facies, viz., SI and ST, within the FS: a) Al vs Si, b) Al and Ti, c) Al vs K, d) Si vs K, e) Ca/Al vs P/Al.

of this facies is also enriched in clay. The difference in clay content between the two facies is readily explained by the assumed difference in the process of sediment translocation between the two facies. Comparatively higher Si EF in the SI facies is possibly due to the fact that slowly settling SI facies had greater opportunity to incorporate volcanic ash. It is relevant to mention that existence of tuff layers within the RSM has already been reported (Rasmussen et al., 2002). On the contrary, the Ti vs Al correlation within the SI facies is positive, but within the ST facies it is negative (Fig. 7.5b). The Ti/Al ratio ranges from 0.022 and 0.037 in the ST facies, and from 0.04 and 0.046 in the SI facies (Table 20). The comparatively low values of the ratio in the ST facies possibly owe to rapid en masse and hindered grain settling, greater proportion of Al being entrapped in consequence. In contrast, Hf/Al and Nb/Al ratios and the Zr contents are considerably higher in the ST facies than in the SI facies (Table 18, 20). This higher proportion of these high field strength elements within the ST facies is apparently related to higher depositional energy of shallow shelf-margin setting where this ST facies was derived from (Table 18; März et al., 2010). Anyway, the enrichment in high field strength elements strongly favors initial proximity of the site of initial deposition of the ST facies to their source. Relation of K with Al is strongly positive in both the SI and ST facies, but negative with Si (Fig. 7.5c, d). The former is attributable to abundant presence of illite (Meunier and El Albani, 2007) and the latter implies that Si was delivered mostly in form of quartz in both the cases. Enrichment factor of Ca, Na, and P is in the negative, but that for K is significantly greater within the ST facies, especially within its silty layers; the reason for this higher proportion in relatively coarser component may be because of greater content of very fine grains of K-feldspar. Although the enrichment factor of Ca is negative in all the samples, but for P it is distinctly more enriched in most of the samples and its maximums belong to the ST facies (Table 19). Ca/Al vs P/Al plot depicts very strong covariance (Fig. 7.5e). This relation suggests that the ST facies is significantly more enriched in apatite (März et al., 2010) and this interpretation goes well higher concentration of Zr in the same facies with respect to the other. This selective enrichment of the event deposits in apatite clearly favors the contention that these deposits were derived from shallow oxic zone and their geochemistry is largely inherited from the site of their primary emplacement. We are tempted to suggest upwelling at the shelf margin, but the snag is the Mesoproterozoic age of the deposit. Despite the fact that instances of upwelling in 1.4 Ga-old Xiamaling Formation and 1.6-1.55 Ga-old Yanlio Basin of the North China Craton have been suggested by Canfield et al. (2018) and Zhang et al. (2018), we are in favor of further study with respect to the Rampur

Shale specifically. Comparatively lower La/Yb ratio in the ST facies with respect to the SI

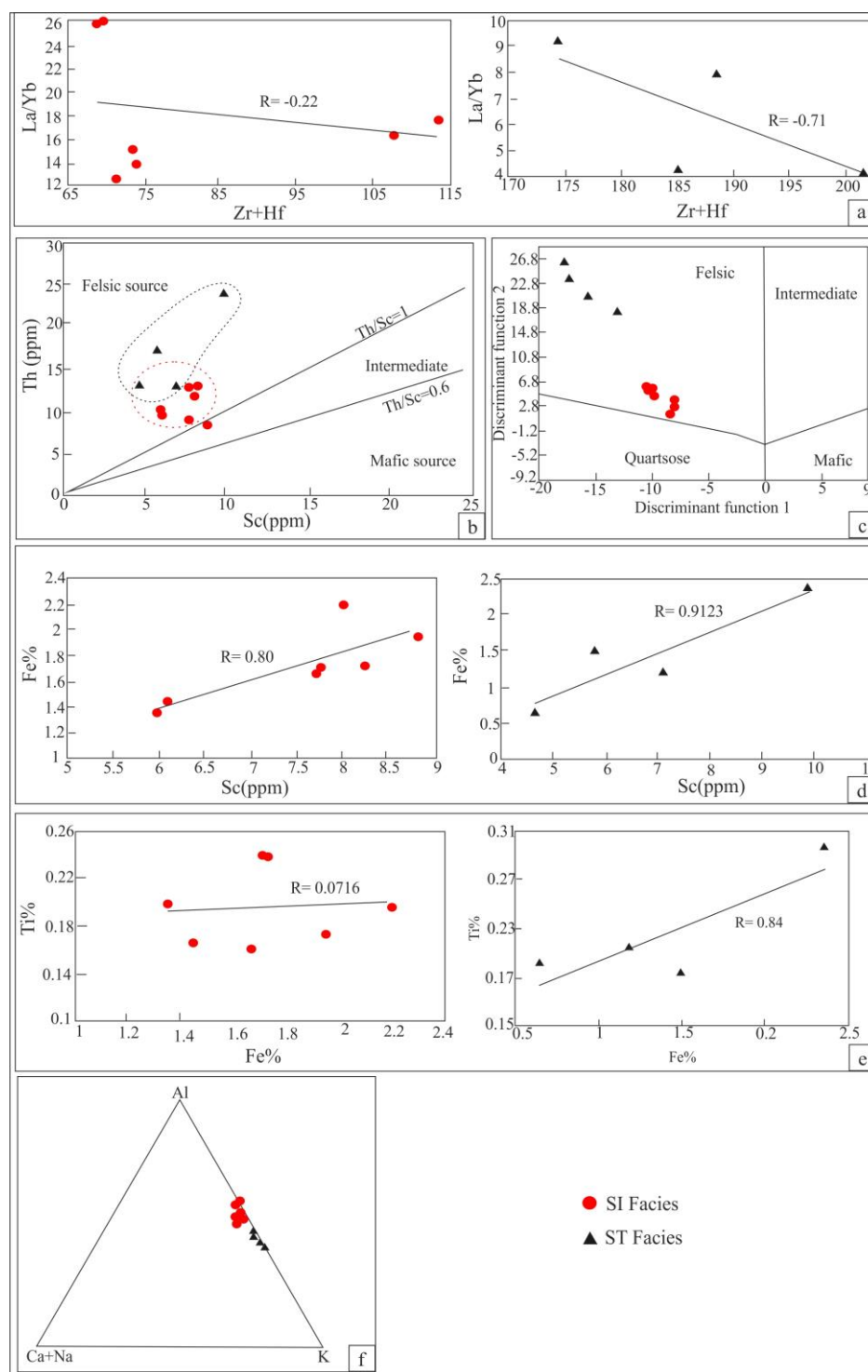


Fig. 7.6: a) Plots suggesting source shifts of sediments between facies SI and ST: La/Yb vs. Zr+Hf, b) Th vs Sc. c) Discrimination function 1 vs 2, d) Sc vs Fe and e) Fe vs Ti. f) triangular plot Al - Ca+Na - K.

facies can be correlated to relatively shorter distance of travel, considering its presumed initial deposition on the shelf (Table 20; Nyobe et al, 2018). The reason for this contention is that Zr imbibing Hf tends to settle close to its source and incorporates HREE in preference to LREE, just as Zr+Hf maintains very strong correlation with La/Yb in the ST facies, though this same relation is a bit diluted in case of the SI facies (Fig. 7.6a). One of

the most remarkable facts is

that Mn content in the FS varies from only 62 to 166 ppm, while in Average Shale it is 850 ppm (Table 18). Considering paucity of oxygen in the Mesoproterozoic atmosphere, Mn possibly had only restricted opportunity to precipitate in the seas and that can possibly explain why the maximal of Mn content is achieved within the ST facies that was presumably

deposited primarily on the shallow shelf. The same explanation of depletion of atmospheric oxygen could be the cause for the meager content of Mo. However, as in the case of Mn, the Mo content is mostly non-detectable within the ST; however, one clayey component is enriched in Mo presumably scavenged by organic matter (Table 18; Lyons et al., 2003). Apparently that is the reason for Mo EF rising up to 1.9 within the SI facies, and up to 1.2 in a carbonaceous mud within the ST facies, despite general scarcity of the element (Table 19).

7.3.2.2: Sediment source variability:

Enrichment factors of Si and K in the FS well exceed 1.0 and suggest a felsic source of the sediment, in general (Table 19). Common enrichment of the formation in Rb, Zr and Th also corroborates this contention (Table 18). However, high Sc EF and Fe EF and presence of Mg and Ti, albeit moderate in proportion, do not rule out minor contribution from a mafic source too. The nature of sediment source can be assessed by comparing contents of incompatible elements vs. compatible elements. The plot Sc vs Th places the ST facies well within the felsic zone, but puts the SI facies at the boundary with the intermediate zone, occasionally even overlapping (Fig. 7.6b). Distinctly larger Th/Sc values in the ST in comparison to that in the SI asserts the same contention further (Table 20). Discriminant 1 vs discriminant 2 plot (Roser and Korsch, 1988) puts both the populations within the felsic zone, but makes their difference better pronounced (Fig. 7.6c). Fe vs Sc covariance is positive in both the clusters implying that the Fe had been derived for both the clusters largely from ferro-magnesium minerals on weathering (Fig. 7.6d). Fe vs Ti covariance is distinctly stronger in case of the ST than in the SI facies (Fig. 7.6e). It is imperative that in the ST facies the Fe component is largely allogenic and within the SI facies it is largely authigenic. It is probably safe to say that felsic source always dominated, but a significant difference in source composition existed between the two facies. Among many such differences, the La/Ti, Yb/Ti and Ta/Ti ratios were distinctly lower and the Y/Ti ratio was slightly lower in the ST facies with respect to SI facies (Table 20). This difference can possibly be best explained by the assumption that the SI facies received sediment from all around the basin-margin, while the ST facies might have been derived from only certain tectonically weaker zone/s on the shelf-margin.

7.3.2.3: *Weathering variability at source:*

Weathering indices determined from sedimentary rocks aim to quantify the deficiency of elements of high mobility with respect to elements of low mobility (Kim et al., 2019). The FS succession is distinctly poorer in CaO with respect to the immediately underlying BS (cf. Paikaray et al., 2008), and also in feldspar and has its major bulk of K in clay. Hence the most suitable procedure is to assess the extent of their weathering is, possibly, CIA (Nesbitt and Young, 1982). The triangular plot of CIA clearly separates out the two facies, although, agreeably, increase in number of samples may obscure the separation (Fig. 7.6f). The CIA values, nonetheless suggest that the source of ST facies was subjected to comparatively lesser weathering than the source of SI facies. However, Mao et al., (2011) noted that hydraulic sorting affects the CIA values and coarser grains yield lower values, as happened here too. Further Simon et al. (2019) found in their experiment that terrigenous mud, when delivered to a sea, absorb 75% of the sodium, approximately 25% of the calcium and 10% of the magnesium that abound in sea water. Hence the CIA data may be misleading in paleoclimate reconstruction from marine sediments. We thus adopted the alternative methodology dependent on ionic bond strength of elements. K/Rb ratio reflects significantly higher degree of weathering in the ST facies than in the SI facies (Table 20). Similar contradiction between CIA and K/Rb has been reported in several other cases (Chen et al., 2012). The pattern of distribution of Ba/Sr ratio, another weathering index, is also similar (Table 20). Nesbitt et al. (1980) found Rb and Cs especially sensitive to climate, and Rb/Ti as well as Cs/Ti ratios do not differ much between the two facies to claim discrete climatic setting for the two facies (Table 20; Yan et al., 2007). However, source shifting under similar paleoclimate still remains a distinct possibility.

7.3.2.4: *Paleoenvironment:*

Encased between the marine shelf-originated CSM and the RLM, the RSM with the FS on its top is also most plausibly marine in origin. Numerous wave structures in the lower part of the RSM (Banerjee, 1997) and presence of glauconite in the RSM and more specifically within the FS, further strengthens the marine interpretation of the FS. Environment of ocean of the past that controlled its biology, hydrology and sedimentology, cannot be configured directly. Chemistry and biology of its sedimentary record, nonetheless, provide proxies that can reasonably help estimate its environmental parameters. The two major aspects of such proxy reconstruction lead to tracking the ocean-atmosphere circulation

system and the chemistry of carbon cycle. Elementary geochemistry of sediment with its limited reach can, at least, points to qualitative primary distinctions between environmental conditions of deposition between the facies SI and the facies ST, even though the distinction may not always be precise in parametric characterization.

7.3.2.5: *Paleoalkalinity:*

Dissolved inorganic carbon (DIC) in sea water occurs in four species, viz., dissolved CO_2 , carbonic acid, bicarbonate ion and carbonate ion. The relative concentration of these species is controlled by alkalinity of the sea water, i.e. its acid treating capacity. Foraminiferal Ba/Ca has been commonly utilized to determine the seawater alkalinity and because the residence time of Ba is around 9,000 years, the measurements may help to gain insight about the whole ocean changes (Henderson, 2002). Increased continental weathering causes greater concentration of Ba in the oceans. That, in turn, boosts up not only ocean alkalinity, but also ocean's biotic productivity. The Mesoproterozoic sea under consideration, however, did not house any foraminifera, but microbiota thrived within it. Martinez-Ruiz et al., (2018) experimentally demonstrated that Extracellular Polymeric Substances (EPS) of marine microbiota bio-accumulate Ba. An amorphous P-rich phase is formed at the initial stage of this bio-accumulation and that evolves into barite crystals. Since this barite is biochemically generated, this microbial EPS-bound barite can also be correlated with productivity and the Ba/Ca ratio can give us inkling about alkalinity variation in the Mesoproterozoic sea as well. This ratio, in the FS, varies from 0.05 to 0.5 and the silty component of the ST population has a tendency to acquire higher values than the SI population (Table 20). The Ba/Ca variation curve in the SI facies succession is almost a mirror image of the variation curve of V/V+Ni (Fig. 7.7a) implying decrease in alkalinity with increasing reductive condition, i.e., increasing depth (see below). More reducing condition implies greater preservation of organic matter and more acidic condition. Hence the mirror imaging of the depth-wise variation curve of Ba/Ca with V/V+Ni curve serves as a cross-check for the alkalinity determination from the former (Fig. 7.7a). Similar authentication can be had from the rough mirror imaging of the Ba/Ca curve with the curve of authigenic uranium enrichment (Fig. 7.7a; see below). Where organic matter accumulates in quiet water under a restricted sea or a lake, oxygenation process ceases and P_{CO_2} increases reducing alkalinity.

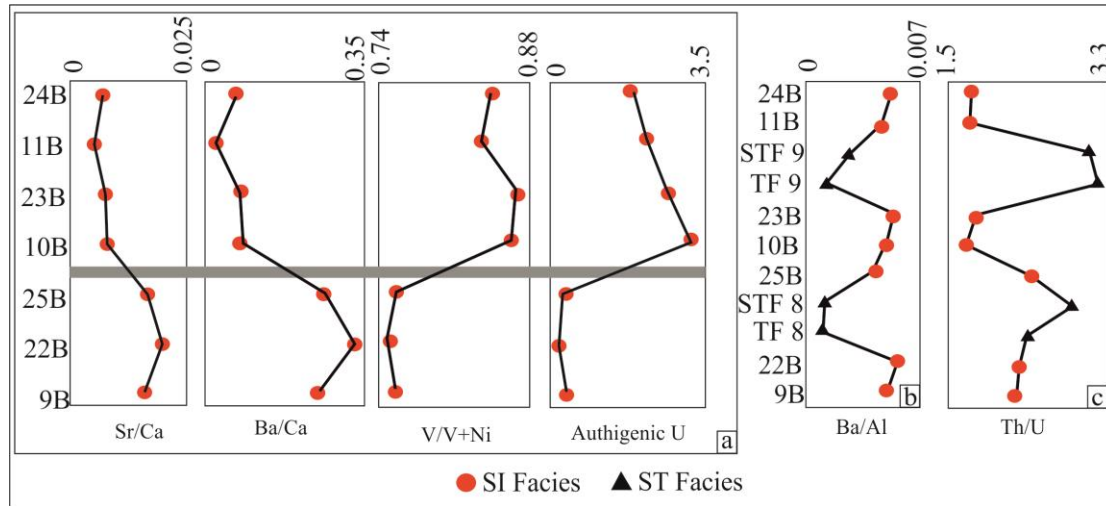


Fig. 7.7: a) Vertical distributions of alkalinity and/or temperature-sensitive ratios against of a redox-sensitive element ratio or a singular element (the grey band marks a sharp deviation), **b)** stratigraphic distribution of Ba/Al and **c)** Th/U.

7.3.2.6: Organic Productivity:

Since Ba bioaccumulates owe their origin largely to microbiota in the modern seas, it can be inferred that the same population was even more responsible for accumulation of marine Ba in the sea of entirely microbiotic world of the Mesoproterozoic age, in which the FS had been deposited. Microbiota proliferation in the FS is well documented in its $\delta^{13}\text{C}_{\text{org}}$ range from -26.0 to -31.8 PDB (Table 18). Ba EF provides a good insight about the amount of authigenic Ba precipitated and hence our tool-box has something to depict the difference in organic productivity between the SI and ST facies (Table 19; Marcantonio et al., 2020). The Ba EF ranges from 0.59 to 0.76 in the SI facies and 0.299 to 0.46 in the ST facies. Apparently the pelagic shale witnessed a significantly higher productivity rate than the shallow shelf where the ST facies had been primarily emplaced. However, the Ba content in the FS we encountered is ~242ppm, while that in Average Shale is as high as 580ppm (Table 18). This drastic reduction in Ba in FS can possibly be attributed to very low gradient of epeiric coastal setting of the Proterozoic time. Besides, organic productivity depends on terrigenous dilution (Canfield, 1994). Ba/Al is thus a preferred proxy for organic productivity (McManus et al., 1998). The Al content in the SI facies reaches up to 52910 ppm, but is raised up to 87775 ppm in the ST facies (Table 18). This is well expected as stated earlier, but the highest record is still slightly shorter than that of Average Shale. Against this background the Ba/Al ratio ranges from 0.0039 to 0.0066 within the SI facies, but drops sharply at the levels of the ST facies, especially in its silty components (Fig. 7.7b).

Another useful proxy for organic productivity could be P/Ti (Canfield, 1994; Ding et al., 2021). Like Al, Ti content too is less than half of that of Average Shale (Table 17). As in the previous case, the ST facies tends to have lower P/Ti ratio values with respect to the SI facies, but there is considerable overlapping (Table 20). Since the mere content of elements may be variably misleading, their Enrichment Factors are preferred (Brumsack, 2006). The P EF/Ti EF ratios reconfirm the clear tendency of lowering of organic productivity in the ST facies in the midst of an overall trend of increasing productivity stratigraphically upward (Table 20).

7.3.2.7: Sedimentation rate:

Th/U is a dependable proxy for sedimentation rate (Ding et al., 2021). Th is land-derived and has a short residence time in sea water, whereas U is precipitated only from seawater, although not directly. Hence the ratio between these two elements is likely to serve as a proxy for sedimentation rate. The ratio is higher, despite slight overlapping, in case of the ST facies than in the SI facies implying comparatively higher sedimentation rate for the ST facies than the SI facies (Fig. 7.7c). This contention is perfectly agreeable to one of our previous contentions: probably the ST facies was derived from shelf-margin where upwelling might have taken place, perhaps during inrush of fresh ocean water into the stagnant basin. The SI succession also shows gradual increase in sedimentation rate upward. Contextually, the same trend is hinted at the immediately preceding application too, but here it is steadier and more pronounced. Hence the FS on top of the Black Shale may constitute the base of the highstand system tract that followed the maximum basin deepening phase.

7.3.2.8: Nutrient distribution:

Marine cyanobacteria have an absolute requirement for Co that cannot be met by other metals (Swanner et al., 2014). Early bacteria and archaea had greater number of genes that encode for Co-binding proteins (Zhang and Gladyshev, 2010). These Co-binding proteins first appeared after 3.3 Ga (David and Alm, 2011). Cobalt is a non-conservative element and has a short residence time within ocean water and hence responds quickly to perturbations in sources or in sinks (Noble et al., 2012). Oxic conditions suitable for Co scavenging were likely confined to Middle Proterozoic surface waters (Poulton et al., 2004). In the FS, Co content is comparatively lower in the SI facies varying 4.66 ppm to 15.00 ppm, while in the ST facies it varies from 21.11 ppm to 45.89 ppm (Table 18). This Co enrichment

in the ST facies strongly corroborates upwelling or, more plausibly in the Mesoproterozoic background of the formation, inrush of comparatively oxygen-rich water from the open sea surface on the shelf-margin where the ST facies had supposedly come from.

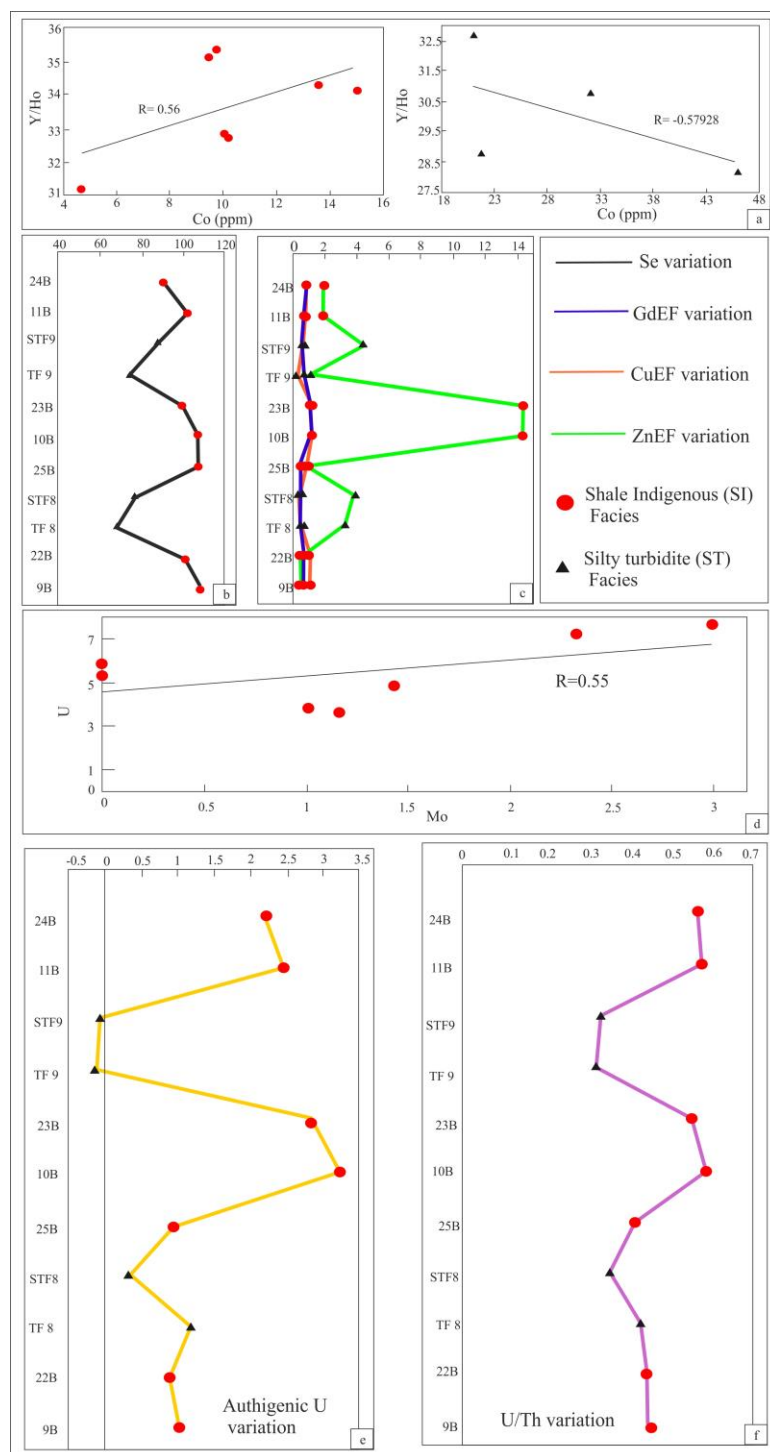


Fig. 7.8: a) Difference in Y/Ho vs Co correlation between the SI and ST facies, stratigraphic variation of b) Se content, c) Gd EF, Cu EF and Zn EF variation. d) U vs Mo correlation in the SI facies e) stratigraphic variation of authigenic U and U/Th.

Y and Ho having almost similar ionic radius and charge occur as “geochemical twins” (Bau, 1999). Nevertheless, because of difference in electron configuration, Ho is more prone to ionic bonding and hence is preferentially scavenged by $\text{Fe}(\text{OH})_3$ and MnO_2 in marine water. Y/Ho ratio is higher in the SI facies than in the ST facies with slight overlapping in their ranges. The values ranging from 28 to 33 in the ST facies are too low for marine values, >35 . Nevertheless, Y is also preferentially scavenged when covalent bonds are established (Bau, 1999; Censi et al., 2007; Lagarde et al., 2020). Censi et al. (2007) reported a preferential scavenging by biogenic matters during their formation. Comparative lowering of Y/Ho ratio in the paleogeography swept by fresh ocean water delivering greater amount of nutrient is not, therefore, unlikely. Further,

within the ST facies the dark mud component has slightly higher ratio than the silty component. In corroboration to this contention Y/Ho vs Co correlation is negative within the ST facies, but positive within the SI facies (Fig. 7.8a).

7.3.2.9: *Paleoredox condition*

Abundance of microbial mats and preserved patches of organic matter (OM) recorded under confocal microscope (Fig. 7.2c, f, h) makes paucity of oxygen in the depositional site of the SI facies apparent, notwithstanding very slow rate of deposition. OM enrichment often causes enrichment in several metals, like V, Mo, U, Fe and Cu. Their marine fractions can be estimated by comparing their contents with those in the Average Shale; the ST facies, presumably derived from the shelf-margin, is invariably poorer than the SI facies (Table 17, 18). Mn oxide dissolves in reducing environment and Pi et al. (2014) suggested Mn content >260 ppm as oxic, but in the FS it remains considerably depleted with respect to Average Shale at all levels implying anoxic condition of deposition (Brumsack, 2006). Pyrite is abundantly present within the SI facies, but in the ST mudstone its presence is negligible. This observation further corroborates deposition of the SI facies mostly in anoxic/euxinic condition. Besides, enrichment of some elements that need reducing condition for precipitation also reflects the marked difference in redox condition between the depositional environments of the SI facies and that of the ST facies, prior to its resedimentation. Abundance of Se, presumably associated with pyrite, also highlights euxinic condition in the SI facies depositional site. In the stratigraphic depth-profile Se concentration in the SI facies is distinctly higher than in the ST samples (Fig. 7.8b). Similar stratigraphic distribution of Vanadium leads to the similar conclusion. V is delivered to the sea in solution and precipitates there only in reducing condition, and hence considerably higher VEF in the SI facies with respect to the ST facies further strengthens the above contention (Table 19; Tribovillard et al., 2006). Abundantly occurring microbial mats in the facies SI possibly consumed much of vanadium (Gustafsson, 2019). Some cyanobacteria species are known to use vanadium nitrogenase for nitrogen fixation (Darnajoux et al., 2017). V is commonly released from rocks under weathering and delivered to the sea in solution, and precipitates there only in reducing condition. However, those vanadate ions adsorbed in Mn-particles that escape dissolution on the surface and enter into the anoxic subsurface sediment, are also released when their carrier Mn-oxide goes into solution, but take the form of highly surface-reactive vanadyl form, $[V(IV)O_2^+]$. It gets readily incorporated within the sediment.

Tribovillard et al. (2006) thus reasoned that $V/V+Ni$ is one of the proxy for paleoredox condition. In the SI facies at majority of sampled stratigraphic levels this ratio exceeds or remains just below 0.86 (Table 20) and implies that the basinal water was stratified and strongly reduced. At all other levels, the SI facies yields the ratio values exceeding 0.76 (Table 20), still indicating stratified water and anaerobic environment. In the ST facies too, the ratio ranges between 0.77 to 0.88 (Table 20) and implies that the shelf-margin had also been beneath the chemocline, at least, at times. Apparently, the chemocline in the basin had been shallow indeed. The comparatively lower EF values of Zn, Cu and Gd, the elements commonly preferring sulfidic environment for precipitation, in the ST facies suggests that shelf was possibly comparatively less reducing than the deeper basin-floor. Probably the chemocline dropped at times (Fig. 7.8c). Mo precipitates in anoxic condition, but under the severely oxygen-depleted atmosphere of the Mesoproterozoic age, not much of Mo is expected to have precipitated beneath the marine shallow shelf. Indeed, in one muddy ST component Mo EF attains 1.3. Yet, larger Mo EF is attained in the SI facies, although in several samples of the SI and the ST facies Mo is not detectable (Table 18, 19). On the relatively deep Mesoproterozoic seafloor Mo was possibly deposited with Fe oxyhydroxide and Mn-oxide particulate shuttle. In reducing deep seawater, however, these shuttles can be assumed to have dissolved releasing Mo that most probably co-precipitated subsequently with organic matter or with Fe, Zn and Cu sulphides (Kabata-Pendias, 2001). These observations also corroborate the contention that the deeper seafloor had been more anoxic than the shelf, but parts of the shelf had also been under a shallow chemocline. As a complimentary, the high EF values for uranium attaining 4.5 (Table 19) suggest absorption of the element within organic matter; slow sedimentation rate should have certainly facilitated the process. As the sea water seeped through the sea-bottom, the progressively reductive front presumably also helped U to precipitate (Tribovillard et al., 2006). Mo, on the other hand, maintains a positive covariance with U ($R = 0.68$) (Fig. 7.8d) in the SI facies. In one dark muddy ST sample of shallow shelf origin, however, the Mo EF is substantially high and this Mo is apparently adsorbed within organic matter that apparently enriches the sample of dark colour. That would also imply that the chemocline had been really shallow and Mo had precipitated possibly within 0-3cm from the sediment-water interface on the shelf as reported from some modern-day shelves by German and Elderfield (1990). Both Mo and U precipitate from seawater under reducing condition, but they have little covariance between themselves. This observation further corroborates the contention that the two elements were delivered to the sediment mass through different pathways; Mo was delivered through particulate shuttle.

Marine U precipitates only from seawater, but only when the solution interacts with sediment in reducing ambience beneath the sediment-water interface. Its enrichment factor in the SI is generally higher than that in the ST facies, but one sample of the latter is richer even with respect to all the samples of the SI facies, once again emphasizing shallow chemocline on the shelf. Authigenic U content can be calculated from

$$(\text{authigenic U}) = (\text{total U}) - \text{Th}/3 \text{ (Wignall and Myers, 1988).}$$

Higher range of authigenic U (avg= 1.97) in the SI facies with respect to that in the ST counterpart (avg= 0.32) once again confirms comparatively more stringent reducing environment of deposition for the SI facies (Fig. 7.8e; Table 20). The same paleoenvironmental difference between the two populations, despite occurring now in the same palaeogeography, is implied also in their respective U/Th values (SI avg= 0.51 and ST avg=0.34; Table 20; Arsairai et al., 2016). The U/Th ratio exceeds 0.50 in the majority of the SI facies samples and varies between 0.33 to 0.43 in the rest implying that the basin water redox condition varied between anoxic and dysoxic (Fig. 7.8f; Wang et al, 2017). All the above mentioned paleoredox-sensitive curves for the SI display fluctuations in concert and suggest a wobbling nature of the chemocline (Figs. 7.8b-f). U/Th values between 0.41 and 0.5 do suggest such fluctuations in the redox condition. Introduction of the turbidites at certain stratigraphic levels adds stronger deflections to the same paleoredox-simulating curves. Considerable change in oxygen fugacity is even better reflected in the wide vertical variation in the SI facies from Cu enrichment to Zn enrichment (Table. 19; Wang et al., 2017). Mn content in the FS, as a whole, is, nevertheless, far depleted than Average Shale (Table 18) implying that the chemocline never intercepted the deeper seafloor; otherwise, sediment-water interface could have been Mn-enriched at some stratigraphic levels.

It is, however, important to remind that the abundance of pyrite and Se, presumably incorporated within the pyrite, though points to anoxic-euxinic condition, but that condition could have, partly or wholly, developed subsurface also, thanks to the enhanced activity of sulfur reducing bacteria. No doubt, some microbial mat laminae are selectively pyritized; but, in general, pyrite remains disseminated throughout the sediment indicating their dominant subsurface early diagenetic origin (Fig. 7.2c). Retention of organic matter, nonetheless, points to productivity rate higher than what available oxygen could decompose. Hallberg (1982) used (Cu+Mo)/Zn ratio to determine redox condition at the bottom of the Baltic Sea. The notion in favor of his methodology was that in an anoxic environment precipitation of Cu is favored over Zn because of difference in solubility product of CuS and ZnS. Plotting of the

same ratio, without Mo (which is often not detectable), against $U_{\text{authigenic}}$ a strong negative covariance arises in the SI (Fig. 7.9a(i)). The imperative is that with rapid decline in near-surface U enrichment was accompanied by enrichment in CuS at the expense of ZnS. Implicitly sulfate reduction process operated close to the sediment surface creating a geochemical ambience favorable for preservation of undecomposed organic matter. Such an ambience can be further tested from Ba/Ca ratio because Ba precipitates utilizing SO_4 released from decomposing organic matter (Table 20; Jones and Manning, 1994; Liguori et al., 2016). The ratio is distinctly lower in the SI facies (avg. 0.16) than in the ST facies (avg. 0.25) suggesting higher rate of organic matter decomposition in the latter, presumably for greater availability of oxygen. Both the averages are, nonetheless, considerably higher than the ratio in Average Shale (0.037) indicating unusual rate of organic matter accumulation in both the SI and the ST facies. The SI decidedly had an ambience of lower pH, possibly lower than 5, in presence of relatively high content of dissolved Carbon dioxide. Considerable lowering of Ca content in the FS with respect to the immediately subjacent Black Shale bears attestation to this fact (Paikaray et al., 2008).

Iron decouples from siliciclastic particulates and reprecipitates in form of sulfides only in anoxic condition (Lyons and Severmann, 2006) and thus the Fe/Al ratio can be a potential index to distinguish between oxic and anoxic sea-bottoms of the past (Lyons et al., 2003; Lyons and Severmann, 2006). Iron in sediments forming under modern anoxic basins, like the Black Sea, Effingham Inlet, Orca Basin, and Cariaco Basin bears attestation to this fact (Lyons et al., 2003, Lyons and Severmann, 2006). In contrast to the Fe/Al ratio base line of 0.38 in shales deposited in oxic condition (Raiswell et al., 2008), this ratio is considerably elevated in shales deposited under anoxic condition (Gill et al., 2011). In the FS the Fe/Al ratio turns out to be 0.474 to 0.074 (the ST facies occupying the lower rungs having the highest value at 0.295) (Table 20). This estimate does not exactly support development of anoxic condition anywhere within the water depth achieved during deposition of the FS, but it surely reconfirms deposition of SI under considerable depletion of oxygen and that of ST facies was subjected to comparatively lesser paucity of oxygen, prior to its re-sedimentation. REY concentration in the FS, as a whole, is depleted with respect to that of the Average Shale. Low trace metal concentration has been reported from many Proterozoic euxinic shales and that is interpreted as a consequence of enhanced trace metal drawdown within expanded deeper water euxinic environments (Och and Shields-Zhou, 2012). In contradiction to this hypothesis REE concentration is comparatively higher in the ST turbidites that were arguably deposited primarily in shallower and overall less reductive water. We thus prefer the

interpretation of Gilleaudeau and Kah (2013), with a caveat: the observed general scarcity of REY in the FS was caused by metal drawdown in the enormously expanded coastal area of the epeiric sea. The caveat is that the common MREY and HREY enrichment in the SI facies implies that some REYs with comparatively smaller ionic radii could still be preferably trapped in the deep sea by the organic matter (OM). Therefore, we propose that LREE/REE ratio can be inversely related to OM content and in that way to oxygen availability in the depositional environment. Plot of this proxy also shows fluctuations within the succession of SI facies and thereby implies secular changes in redox condition (Fig. 7.9b). It thus seems that the epicontinental Mesoproterozoic sea under present consideration had its chemocline wobbling through time. Among the most used paleoredox indices, the V/V+Ni, Ni/Co, U/Th ratios (Galarraga et al., 2008) V/Cr ratio (Jones and Manning, 1994; Arsairai et al., 2016) and authigenic U content (Wignall and Myers, 1988) unanimously testify increasingly reducing condition in the deeper part of the sea than in the shelf and also subscribes to the contention of secular changes in the redox front (Fig. 7.7a, 7.9b).

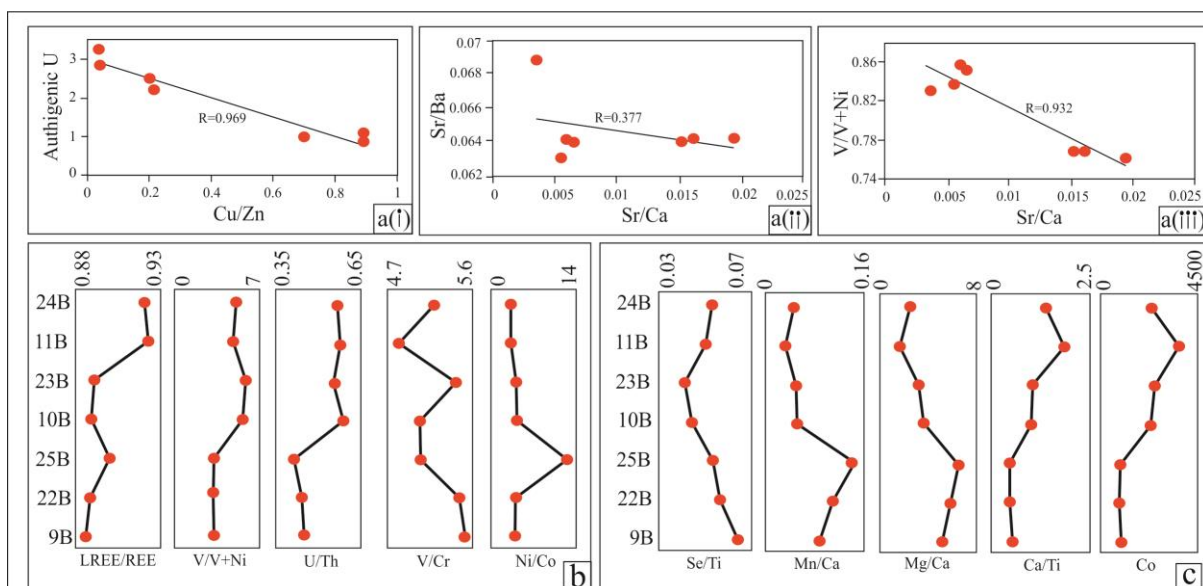


Fig. 7.9: **ai)** Plots of Authigenic U vs. Cu/Zn, **aii)** Sr/Ba vs. Sr/Ca and **aiii)** V/V+Ni vs. Sr/Ca, Vertical variations in **b)** LREE/Total REE, V/V+Ni, U/Th, V/Cr and Ni/Co for SI, and variation in **c)** Se/Ti, Mn/Ca, Mg/Ca, Ca/Ti and Co for SI.

7.4: Paleoenvironmental Dynamics

The FS, like the 9m-thick BS below, is completely devoid of current and wave structures and bears only evenly planar laminae, besides having intermittent centimeter-scale thin graded turbidite sheets. Glauconite occurrence strongly suggests its deposition under a sea. Hence it is not unwise to consider FS deposition on a sea-floor beneath the storm wave

base. In-situ growth of microbial laminae delimits its depth to the photic zone, perhaps within 150 metres. The FS thus provides a narrow window to look at a sea-bottom of the Mesoproterozoic period, the interpretation of whose general redox condition is marred by two diagonally opposite theories. Considering the large-scale disappearance of iron formations by around 1.8 Ga, Holland (2006) suggested oxygenation of the sea-bottom thereafter. On the contrary, taking into account the abundant occurrence of OM-rich sulfidic shales, Canfield (1998) suggested permanently stratified sea with anoxic bottom between 1.8 and 0.8 Ga. Subsequently, however, several examples of the Mesoproterozoic sea-bottoms with fluctuating redox conditions have been brought to the fore by several workers, including Canfield himself (Zhang et al., 2016). The geometry of the REY distribution curves denies uniform redox front through time at the sea-bottom on which the FS had been deposited. The majority of the REY distribution curves depict MREY enrichment; even those described as, more or less, flat also have a slight middle bulge. Some curves also show HREY enrichment. OM enrichment of the sediment is evident in this observation as well as in petrography (Freslon et al., 2014). This OM enrichment may suggest anaerobic degradation because that is far inefficient than the aerobic pathway for degradation (Brumsack, 2006). It is especially so when the very slow rate of sedimentation, as reflected in the fine, even and planar laminae, could have facilitated the oxygenation process enormously, had oxygen been present in adequate quantity. Pertains to this is the “constant O₂ model” for the post-3.8 Ga earth of Yamaguchi (2002). The V/V+Ni ratio in the SI facies is, however, strongly in favour of stratified nature of the epicontinental sea in which the FS was deposited and simultaneously indicates not an environmental stasis, but wobbling of the chemocline that at times became very shallow. Occasional accumulation of Mo on the shelf, in larger quantity than in Average Shale, further asserts that the chemocline, indeed, turned very shallow at times.

The FS is at the transition between a transgressive systems tract, the Rampur Shale and a highstand system tract, the Rohtas Limestone. At the turnover from the Black Shale to the FS, the Ca²⁺ content drops (compare Paikaray et al. 2008), but then increases overall upward before passing up into the limestone. This trend is well reflected also in the stratigraphic variation of various element ratios, such as Ca/Ti, Sr/Ca, Mg/Ca, Ba/Ca, Mn/Ca ratios (Fig. 7.7a, 7.9c). The trends are not, however, steady, even if we consider only the SI facies; but remarkably all the deflections are similar in nature and located at the same stratigraphic levels. The deflections were, therefore, likely to be caused by some systemic control. The upward increase in Ca/Ti ratio indicates progressive dwindling of terrigenous material supply. The upward decrease in the Sr/Ca is generally considered as increase in

seawater temperature, increasingly favoring carbonate precipitation. The upward depletion in this ratio further suggests shallowing (Wei et al., 2004) and moderate negative correlation of this ratio with Sr/Ba is further corroborative of the proclaimed shallowing through time (Fig. 7.9a(ii)). Mn/Ca and Mg/Ca ratios, more or less, replicate the same trend as Sr/Ca and further corroborate paleoenvironment transformation conducive for carbonate precipitation. These Mn/Ca and Mg/Ca ratios too are generally applied on foraminifera to determine seawater temperature (Petersen et al., 2019). Their trends in the FS thus strengthen the contention of secular increase in seawater temperature further (Fig 7.9c; Tostevin et al., 2016). The overall upward increase in Ca is in complete accord with the perceived transformation of a stagnant epicontinental sea to an open seaway. Carbonate deposition presumably also needed oxidizing condition. Relative increase in the Mn budget on top of the SI succession also corroborates this fact (Table 18; Grandjean and Albarede, 1989), although Ca content still remained depleted with respect to Average Shale. In other words, availability of dissolved oxygen increased despite the trend of mild increase in temperature. Synchronised fluctuations in the aforementioned ratios along the SI facies succession clearly demonstrate temporal variations in temperature and availability of dissolved oxygen. However, the environmental fluctuations inferred must have been of much longer cycle than seasons because 1cm-thick mud that was deposited slowly and then compacted, would certainly cover hundreds of thousand years. The staggered variation in authigenic U content in the SI facies from 0.91 to 3.3 ppm also corroborates such an environmental cycle controlling the redox front within the basin (Table 20; Marcantonio et al., 2020). Upward decrease in Se content and its ratio with Ti imply overall decrease in pyritization of the sediment and in turn, attests to progressive improvement in supply of dissolved oxygen to the basin (Fig. 7.9c). Upward decrease in V/V+Ni ratio strongly corroborates this contention and almost perfect mirror-imaging of its trend in vertical variation in the Sr/Ca ratio suggests a strong correlation to change in water depth (Fig. 7.7a). Very strong negative correlation (Fig. 7.9a(iii); $R=0.932$) between these two ratios clearly indicates that when the water depth increased, possibly due to basin subsidence, the basin water turned comparatively less reducing. Taking all the temporal changes in sediment geochemistry together it seems that the studied epicontinental basin had its connection to the open ocean comparatively improved through time, presumably for drowning of the sill that kept it isolated (cf. Healy & Harada 1991). The most significant change in the redox front in the depositional basin is recorded at the mid-level of the SI facies succession and that change was clearly not synchronized with any of the incidents of turbidite incursion or presumable seismic event (Fig. 7.10). This fact, however, does not necessarily

mean that basin subsidence and basin opening had been independent of each other because there could be a time lag for changing the redox condition of the basin after the start of a fresh ocean water inrush. We still believe that the two processes were interrelated, but offset in timing. It is an exemplary geochemical revelation of paleo-environmental dynamism that has little physical expression. It is thus reasonable to assume that with greater opening the basin water turned less reducing as it received more dissolved oxygen. This course of basin-opening, as evident earlier, had not been a steady process and the basin opening alternated with longer periods of tectonic still stands. The latter episodes likely to have caused enhancement of the rate of sedimentation on the shelf zone, as has been noted earlier. (Co X Mn) increased significantly in the ST facies possibly because of increase in terrestrial input

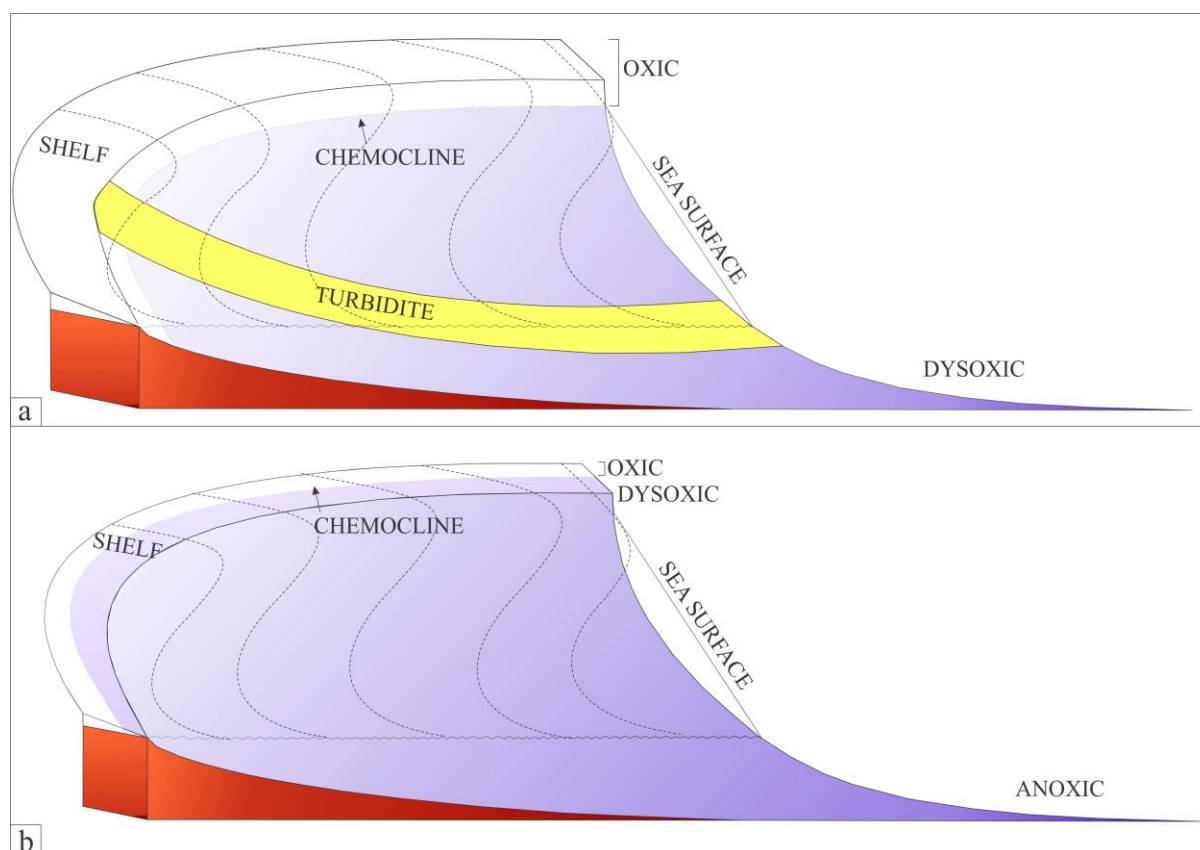


Fig. 7.10: a) A schematic model of change in redox level in the semi-enclosed basin in response to tectonic subsidence. Basin subsided and turbidites were triggered as the water from the open ocean rushed in causing transgression of the sea. Gradually the chemocline in the enclosed basin dropped. **b)** In the quieter interval the shoreline shifted seaward increasing the rate of sedimentation and the chemocline rose as the sill at the entry point of the basin (not shown) grew again to restrict access to the open ocean.

(Table 20) as depicted also in increased contents of Al_2O_3 , TiO_2 , Zr and Hf (Table 17, 18). It would mean that progradation had already been initiated, at least on the shelf where rate of sedimentation was considerably higher. In this scenario the enhanced rate of sedimentation

during the longer periods of still stands presumably facilitated turbidite generation from the shelf-margin time to time (Fig. 7.10). In the FS succession built up beyond the shelf-margin and in the deeper sea, featured by generally slow rate of deposition, the net result had apparently been progressive shallowing of the basin. Notwithstanding this shallowing, however, the relatively longer periods of progradation on the shelf had little physical effect on the apparently aggradational trend in the deeper sea, except adding centimeter-scale turbidites time and again (Fig. 7.10).

7.5: Conclusions

The Mesoproterozoic Faded Shale in central India was deposited in a semi-enclosed marine basin at the interlude between growth of a Transgressive System Tract and a Highstand System Tract. Its deposition took place at very slow rate and was conducive for proliferation of microbial mat and associated microbiotic consortia. This quietude was broken only when minor turbidites were triggered by seismic jerks at certain structurally weak zones at the shelf-margin where sedimentation rate had been higher during the intervals between successive events of basin subsidence. The basin-water had been stratified and the seafloor largely remained dipped in anoxic-dysoxic condition under a chemocline that extended also to the shelf. Nevertheless, the chemocline had not been static, but responded with a time lag to the inrush of fresh marine water from the open ocean on occasions of basin subsidence. Amount of dissolved oxygen and alkalinity of water increased as the PCO_2 dropped in consequence. Through time the bottom water overall warmed up as the basin gradually filled up and turned increasingly conducive for carbonate precipitation. This progradational tone in sediment geochemistry is, nonetheless, hardly reflected in the physical aspects of this Faded Shale, still maintaining an aggradational trend.

CHAPTER: 8

Finger Prints of Microbial Life Encrypted within Meso-Proterozoic Rampur Shale

8.1: Introduction

Progresses of scientific knowledge and advanced scientific instrumentation always go hand in hand. It's always exciting to find the traces of life in adverse and extreme conditions in early earth. The minute earliest life forms are difficult to identify without the help of these high-end instruments. Low oxygenated atmosphere, high surface temperature, toxic climatic-environment, continuous volcanic eruption, incompatible chemical composition of the oceanic and atmospheric condition was the major hindrance of life to begin with. Study of ancient organic rich sediments, particularly black shale, of deep times (Precambrian; Archean-Proterozoic) provides at times tell-tale evidences of initial life form of early Earth. Although, there is still debate on how earliest life was surviving in the then high temperature ($\sim 200^{\circ}\text{C}$; Hardardottir, 2011; Zarkhov and Bidemann, 2019; Zakharov et al., 2021), high pCO_2 ($\sim 1\%$; Riding 2006; Brasier et al., 2011) and likely to be toxic ocean. However, life there is no doubt that life was originated in Archean earth; but study of variability in life form in a slightly comfortable earth during the Proterozoic time is always interesting as it provides crucial information, how life evolved in ocean from single to multi cell to Ediacaran (Morris 1985; Bowyer et al., 2017).

The Vindhyan succession has always been the center of focus to global scientific community because of excellent preservation record of the Proterozoic time. It's a happy hunting ground for the scientific community particularly who are working with microbiota (Seilacher et al., 1998; Sarkar et al. 2004, 2005, 2006, 2014b, 2016; Banerjee and Jeevankumar 2005; Banerjee et al. 2006a, 2010, 2014; Sarkar and Banerjee, 2007; Schieber et al. 2007; Eriksson et al. 2010, Kumar et al., 2011; Chaudhuri et al., 2023). Rampur Shale is one of the most important shale horizons of Semri Group, where so far little work has been done related to microbiota (Banerjee et al. 2006a; Sur et al. 2006). Hence, during the present deliberation an in-depth study has been conducted on Rampur Shale Member of the Rohtas Limestone Formation for the early life form and their effect, if any, on the then sedimentation process (Nofkee, 2003, 2010, 2013; Schieber et al., 2007). Rampur Shale overlies on Chorhat Sandstone which is highly focused in the world literature for its spectacular preservation of microbial life and their role on sedimentation; generally known as MISS/MRS (Microbial Mat Induced Sedimentary Structures or Microbial mat related Structures; Giesela et al., 2002, Sarkar et al., 2004). The Rampur Shale succession overall is a transgressive system track (TST) package except its uppermost 3m (Bose et al., 2001, Mandal et al., 2022; Fig. 8.1). A

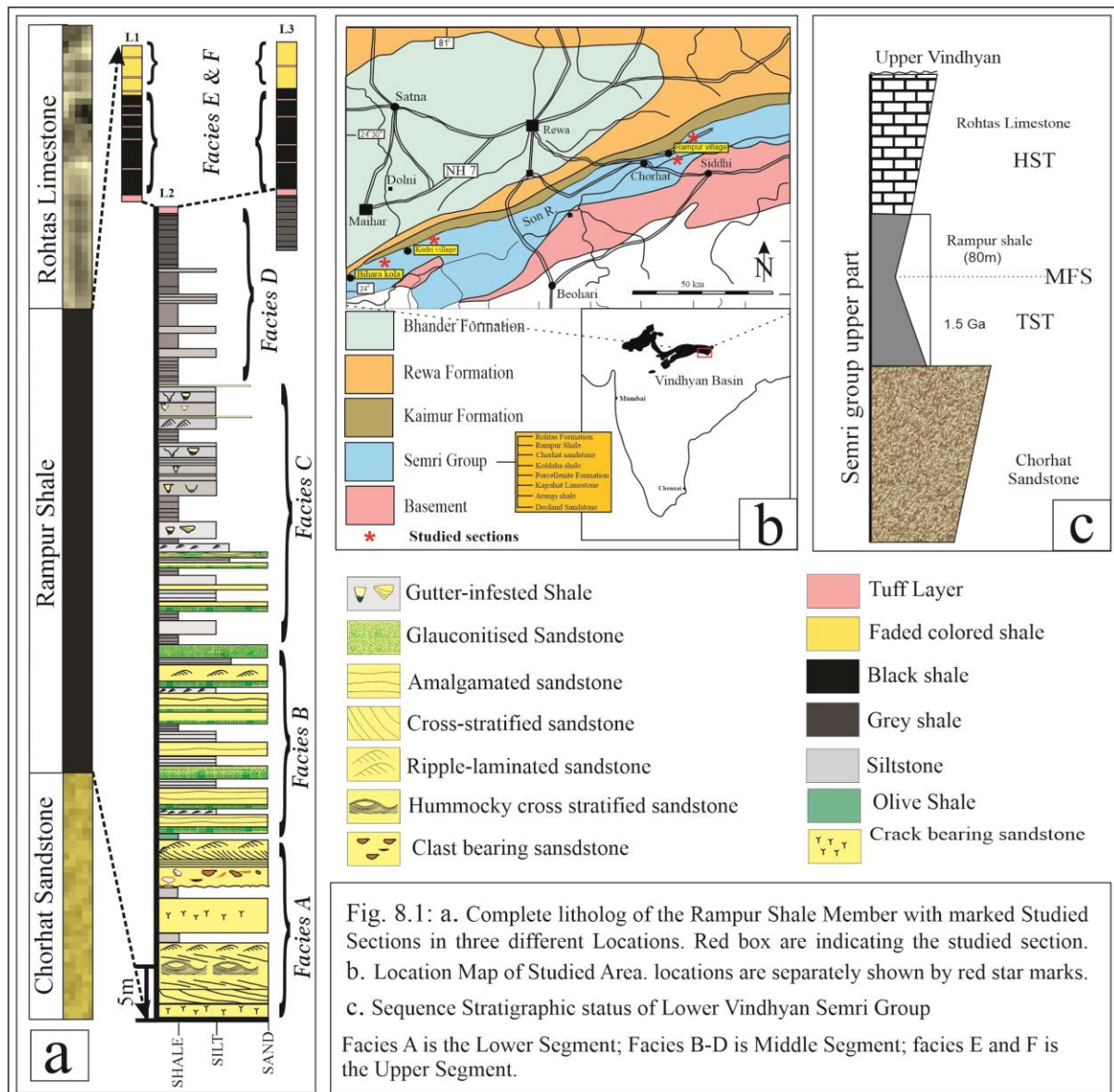
major part of the Rampur Shale is black in color likely to be the most promising area for ancient marine bio-diversity study, like the other already studied black shales in the world (Blumenberg et al., 2012; Barghoorn et al., 1965). The Vindhyan black shale attains a good amount of organic carbon i.e., >1% (Singh et al., 2020) and the δC^{13} value is highly negative (-25 to -30). Apart from the organic carbon content the shale is also known for its extraordinary preservation of microbial structures and texture. In the following sections the details of microbiotic life form their biodiversity preserved within the Rampur black shale has been discussed. Along with these variations of different forms, their compositions also been studied to portray the microbial evolution and their effect on sedimentation.

8.2: Observational aspects

8.2.1: Macroscopic structures-texture within Rampur Shale:

Rampur Shale of Semri group is consisting of both sandstone and shale. Sand is dominated at the lower part, followed by sand-shale-silt alteration in packages and grades to a thick shale deposition (Fig.8.1a). Color of shale varies from grey to black up the succession before grading into faded shale. Based on sand-shale ratio succession of Rampur Shale is divided into three segments and six (6) facies (already discussed in chapter 3). The Lower most segment is identified as facies A, dominantly composed of sandstone beds with rare preservation of shale beds. Sandstone beds are of sheet like geometry consisting of hummocky cross-stratification, cross stratification, ripple lamination and planar lamination (Fig.8.2 a-e). The bedding surface of the sandstone bodies have preserved several types of cracks (Discussed in next section).

Middle segment, Facies B is also dominating in sandstone with intercalation of light grey colored shale in-between. Maximum thickness of shale is ~10cm. Besides sheet like geometry of sandstone beds, amalgamated nature is also found. Hummocky cross stratification is also common here. Facies B contain a good proportion of shale compare to previous facies A. Apart from the grey shale a green shale layer was identified within this facies (Fig. 8.1a). Except few thin laminae, the shale does not preserve any others structures. Syneresis cracks at the bed surface and tool marks at the bottom surface of the sandstone are also common (Fig. 8.2f).



The next facies, within this middle segment is facies C. This facies gradually changed its lithology with increasing shale proportion associated with few cm-scale thick siltstones and sandstone beds within. Few gutter casts are present the bottom of the sandstone bed (Fig. 8.2g). The sandstone and shale bed surfaces are commonly loaded with microbial mat impressions (discussed in next section).

Facies D is more shaley than the previous facies but occasional input of sandstone-siltstone beds are present there which is reflected in litholog (Fig. 8.1a). The grey to greenish grey colored shale proportion is very high compare to sandstone. Again, plethora of mat impressions are present on the bed surfaces (discussed in next section).

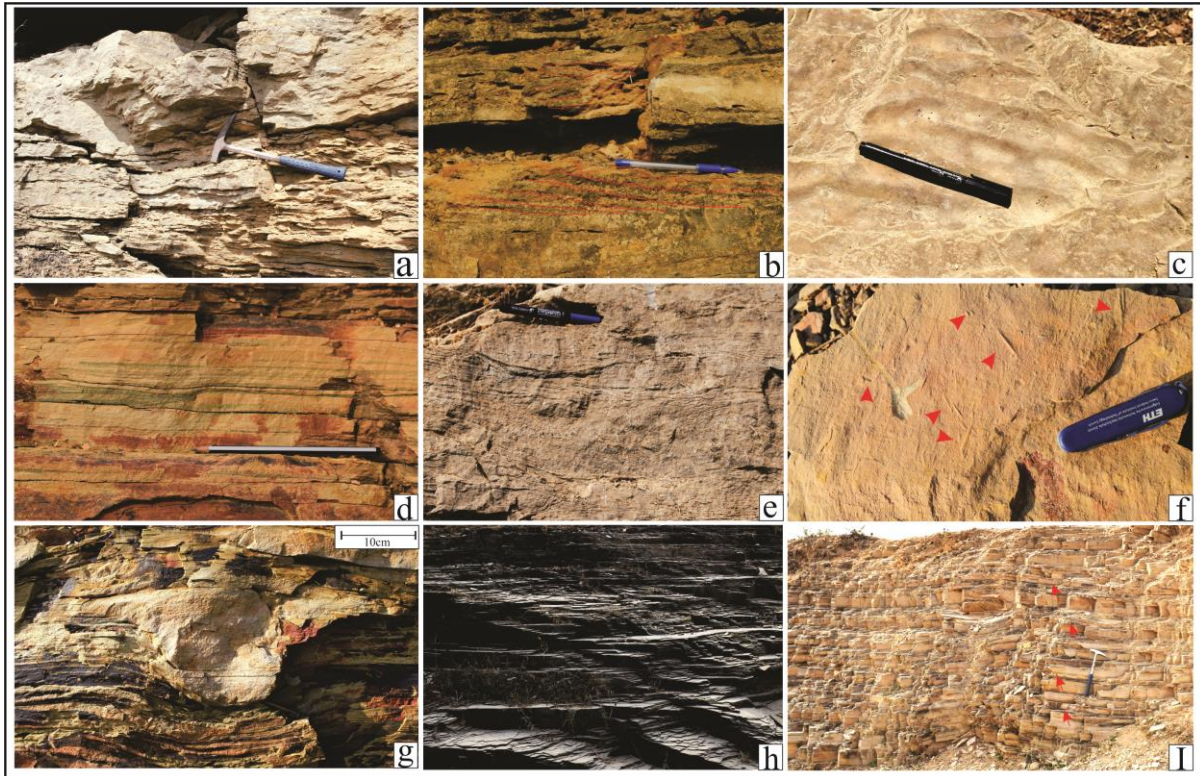


Fig. 8.2: Field feature of Rampur Shale: **a)** Sheet like sandstone body. **b)** Cross-stratification within the sandstone (marked). **c)** Ripple marks present on the bed surface of the sandstone. **d)** Planar lamination presents within in the sheet like sandstone body. **e)** Hummocky cross stratification. **f)** Tool marks present at the bottom surface (arrowed). **g)** Gutter cast within shale layers. **h)** Black shale dominated facies **i)** grey shale at the top part (Tuff layers are marked with red arrow).

At the Upper segment Facies E is devoid of sandstones and completely dominated by shale and these shales are black in color. Within the dominantly black shale this facies preserved few thin (~1-2cm) sheet like volcanoclastic tuff layer (Fig. 8.1a). These tuff beds have appeared on black shale with sharp contact and corrugated marks present at the contact. Black shale is mostly homogeneous in nature with fine laminations present within it (Fig. 8.2h).

Facies F is also shale dominated with grey colour and only planar laminations are present. This grey shale is also alternating with few tuff layers (~1-2cm) (Fig. 8.2i).

8.2.2: Focus on MISS/MRS within Rampur Shale: recorded in sand-dominated part:

Microbial mats are very delicate in nature and easily get decomposed under influence of oxic environment. Microbial mat was very common in the Precambrian seas in absence of metazoan. Their presence can be felt but preservation is very difficult. So various proxy structures are noticed within the bed-surfaces, preserved by the influences of microbiota.

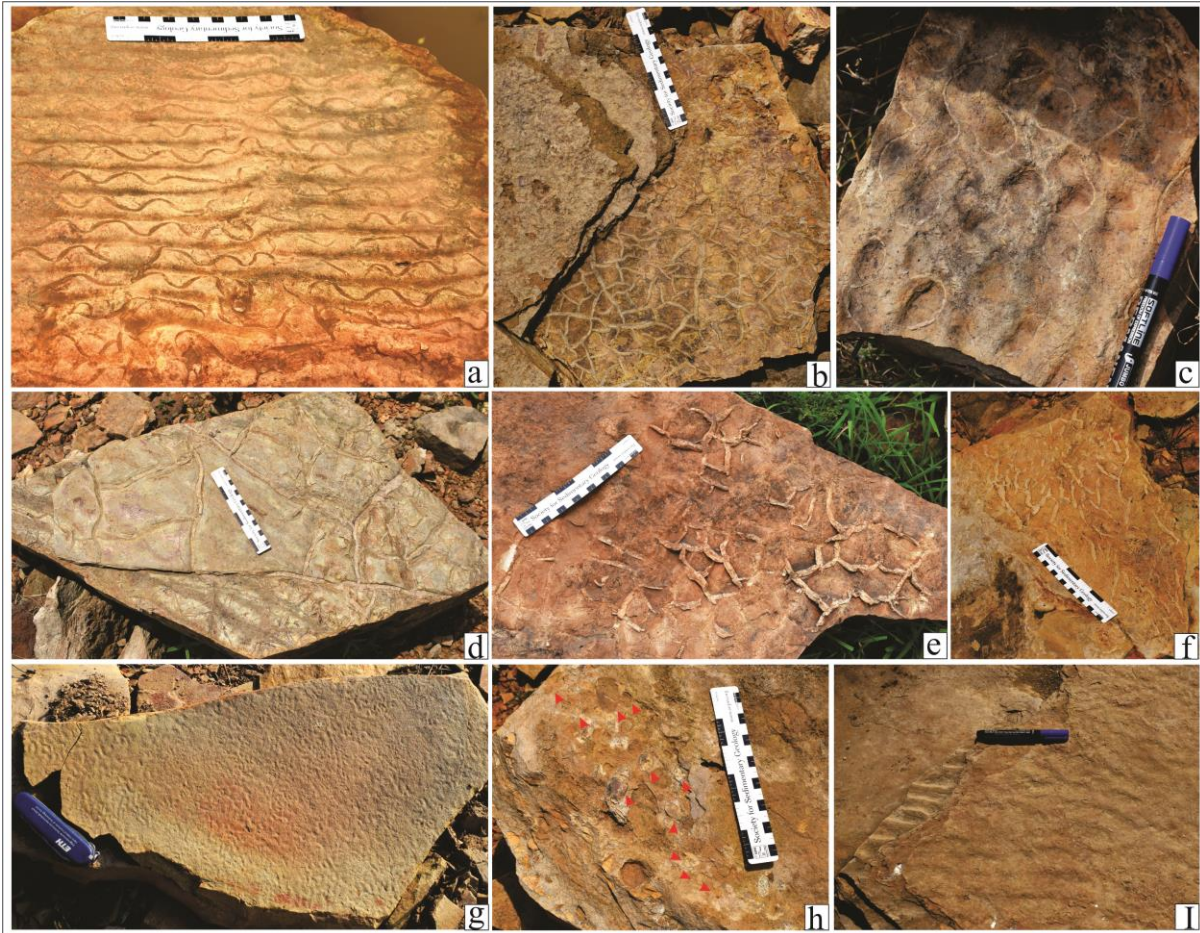


Fig. 8.3: MISS preserved within Rampur Shale: **a)** Sinusoidal **b)** Polygonal **c)** Circular **d)** Rectangular **e)** Spindle shaped geometry of cracks. **f)** Ridge-like structures preserved within sandstone. **g)** Wrinkle structure recorded within shale. **h)** Sand-chips present on bed surface **i)** Palimpsest ripple recorded on sandstone surface.

These microbial induced sedimentary structures (MISS) or microbial mat related structures (MRS) observed throughout the Rampur shale. Within the non-cohesive sandstone and siltstone bed surfaces different types of cracks (syneresis, desiccation and manchuriophycus), palimpsest ripples, ridge, wrinkle structures and sand chips are commonly preserved (Fig. 8.3). Cracks are millimeter to centimeter scale primary structures formed at the bedding surface during the lithification of the sediment. The geometry of the cracks varies from sinusoidal, polygonal, circular, rectangular to spindle-shaped (Fig. 8.3a-e). The cracks are generated preferably on crest or trough of the rippled sandstone. Other than the cracks, few ridge-like structures are present at the bed surface of the sandstones. Ridges are reflecting similar geometry with the cracks with 0.5-1 cm in height (Fig. 8.3f). Wrinkle structure is also frequently observed which have fine ridges and crinkled appearance (Fig. 8.3g). In the lower sand-dominated part, few surfaces are observed which loaded with sand-chips, having

different shapes e.g. circular, elliptical and sometimes the chips are not maintaining any definite geometries. Sand chips with different color were disseminated on the top of the sandstone beds looks like an intraformational conglomerate (Fig. 8.3h). In some cases, overlying sediment is replicate the sedimentary structure of underlying bed where a thin layer of sediment is deposited above the underlying sedimentary structures and bears the impression of underlying structure, known as palimpsest ripple (Fig. 8.3i). All these structures were documented in different segments of the Rampur Shale.

8.3: Microstructures and chemistry recorded within Rampur Shale: special emphasis on Black shale

The black shale is homogeneous in field and can't be described in detailed in naked eye; so, for further description of the black shale we are highly dependent on the microscopic and ultramicroscopic study followed by geochemical analysis. Black shales generally records proliferation of rich microbial community, so expected that this Black shale of Rampur Shale Member is also preserves a lot of information regarding biogenic diversity. The microscopic and ultramicroscopic study was performed preferably for shale dominated Facies E and F. In addition to this some sand/silt alternations from the lower facies assemblage has also been scanned under microscope which contain biogenic impressions.

8.3.1: Variability in microbial mat structures under petrographic microscope:

Biogenic impressions that are preserved in the sandstones recognized in field study. The petrographic study reveals that the intervening shale from lower and middle segment, contains thin stringers of microbial mat lamina along with few pyrite grains present preferentially following the microbial mat lamina (Fig. 8.4a-c). Commonly the flaky minerals within the shale layers are strictly maintaining an orientation and aligned along a plane, later, which helped to develop the fissility planes. Here, the petrography of the shale shows random orientations of the mica flakes resided within the thin layers (Fig. 8.4d).

Microscopic observation of black shale records abundance microbial mat growth within the shale layers. Depending on their geometry, the present author has divided them into three major groups e.g., Crinkly laminated (CL), lensoid-dumbbell (LD) and Spheroidal (S) shaped (Fig.8.5, 8.6). Microbial mat bodies are not only different in aspects of shape and size, they also have different shades i.e., lensoid and spheroidal mat bodies are darker than

the crinkly laminated mat. Under polarizing microscope, it has been found that innumerable numbers of euhedral (rhomb shaped) dolomite crystals are scattered on the black shale which are basically grows in association with all the varieties of microbial community irrespective of their geometries (Fig.8.5,8.6).

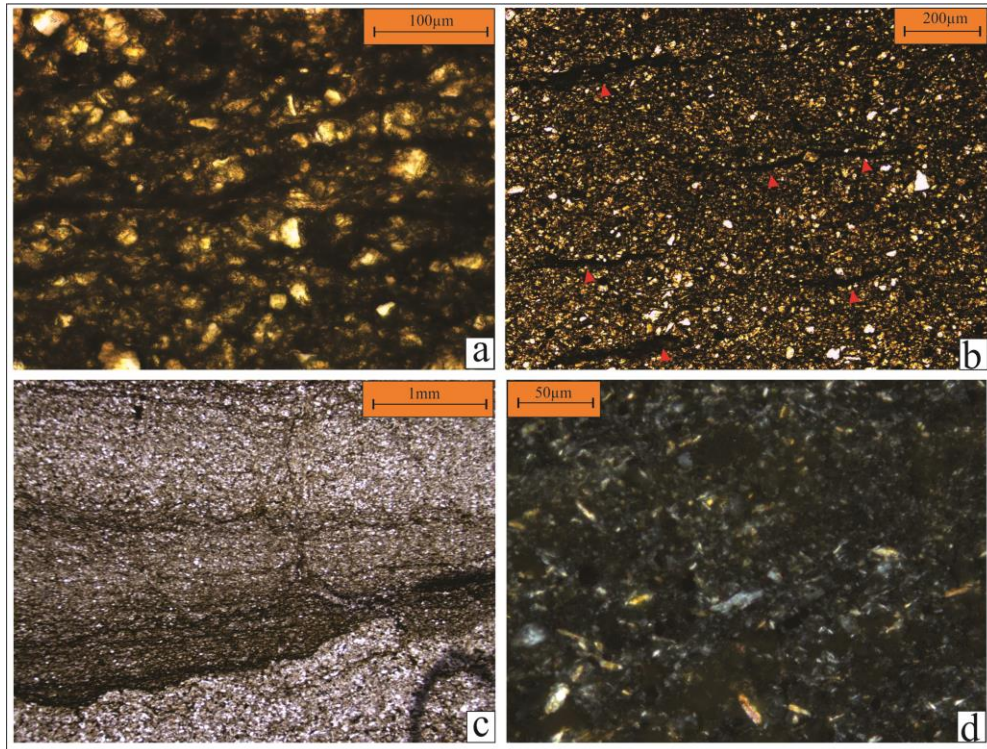


Fig. 8.4: Petrography of the shale: **a)** microbial mat laminae within sandstone-shale alternative facies. **b)** Flakes of carbonaceous shale are associated with siltstone (arrowed). **c)** Microbial mat within silty shale at the shale dominated part. **d)** Fly-paper effect with in shale.

Crinkly laminated microbial mat reflects a wavy texture all over the petrographic study. These are continuous to discontinuous lamina, varying in thickness from 0.01mm to 0.1mm (Fig. 8.5a). These laminae are continuously joining, branching and laterally accreted within the shale which means crinkly laminated mat shows convergence, divergence as well as bifurcation therein, they can easily torn apart (Fig. 8.5a, b). A false cross lamination-like structure is noticed within the mat infested layers (Fig. 8.5c). Plenty of rhombic shaped authigenic dolomite crystals are associated with crinkly lamina. Dolomite crystals are draped by crinkly laminated mat (Fig. 8.5d). Few trough-like structures are developed within the crinkly lamination (Fig. 8.5e). Micro-loading is recorded prominently within this black shale facies (Fig. 8.5f). The next geometric form explicit about a lensoidal or dumbbell shaped mat body repeatedly appeared along with the crinkly laminated mat variation within this black shale facies (Fig. 8.6a). Occasionally few lensoidal bodies

contain a tail like structure in one end which make it an elongated body (Fig. 8.6b). The microscopic observation shows that well-developed lensed shaped mat variety is commonly associated with growing lumps (Fig. 8.6c). Just like the crinkly laminated mat, the lensoidal or dumbbell shaped bodies are also contained rhombic shaped dolomite crystals (Fig. 8.6d). The lensoidal mat body accumulated few strings of filament like texture within it (Fig. 8.6e). A series of lensoidal lumps is noticed to grow within shale facies (Fig. 8.6f).

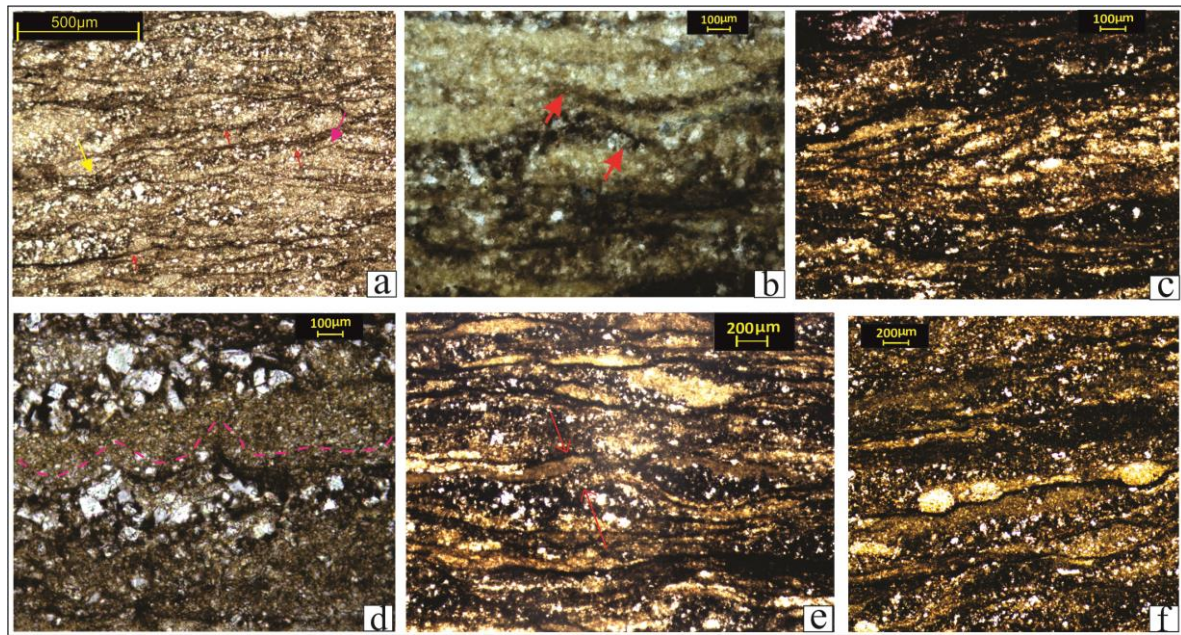


Fig. 8.5: Representing the Petrography of black shale under polarizing microscope; **a)** Joining (yellow arrow), branching (pink arrow) and lateral accretion (red arrow) within microbial mat **b)** Jagged ends **c)** False cross lamination **d)** draped dolomite-crystals **e)** overlying mat layers **f)** Micro-loading within mat.

The next variation of microbial mat looks like a circular pin-cushion type structure (Fig. 8.6g). In few cases, the circular mat body contains two thin tail-like structures at two ends (Fig. 8.6g). This variety made up with coccoidal shaped micro-biotic bodies (Fig. 8.6h). The circular mat body contains few cements balls type circular structure in between the mat (Fig. 8.6i). This variety of mat body again contain rhombic shaped dolomite crystals within it (Fig.8.6g-i). The thin cm scale tuff layers were not readable in field study, so that these layers were chosen to study under microscope. Petrographic study under microscope shows that these layers contain very fine grain material. High resolution study reveals that, devitrified glasses were commonly present within these fine-grained tuff layer with broken gas bubbles (Fig. 8.7a, b). Elongated glass shards (tephra) commonly present within the tuff layers recorded in petrographic view (Fig. 8.7c). Gas bubbles also trapped within devitrified glass (Fig. 8.7d), segmented filamentous body is also present within the tuff layer (Fig. 8.7e, f). A

few circular like structure, with darker core and lighter rim is preserved within the tuff layers, commonly named as acritarch (Fig. 8.7g).

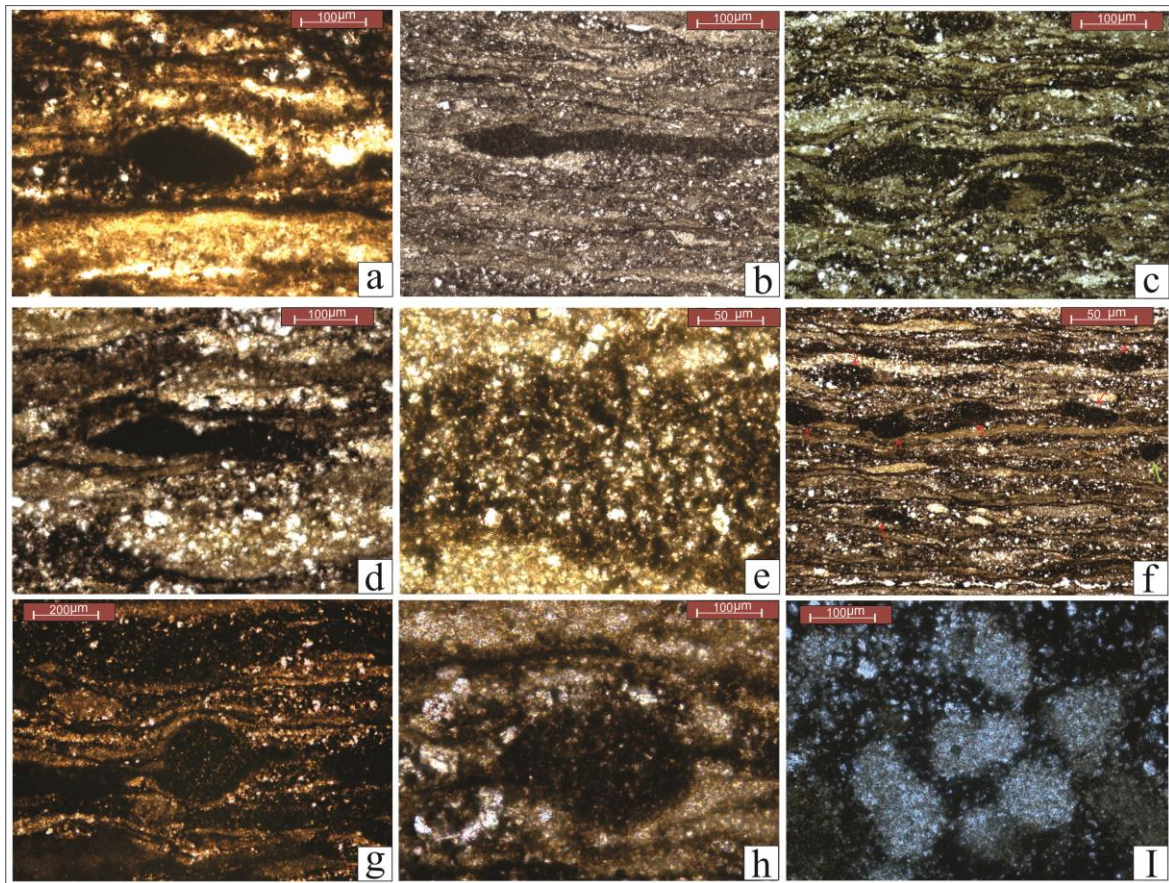


Fig. 8.6: Petrographic observation of Microbial mat. **a)** Lensoidal mat body. **b)** A tail like structure associated at one end of the lensoidal body. **c)** Two lumps are growing within shale. **d)** Lensoidal body is depressed at mid-part and looking like a dumbbell shaped mat. **e)** Filamentous structures are developed within lensoidal body. **f)** A series of lensoidal body growing simultaneously. **g)** Circular mat body with tail like structure at both the end. **h)** Coccoidal lumps are within the spheroidal body. **i)** few balls like structures are developed in associated with spheroidal mat body.

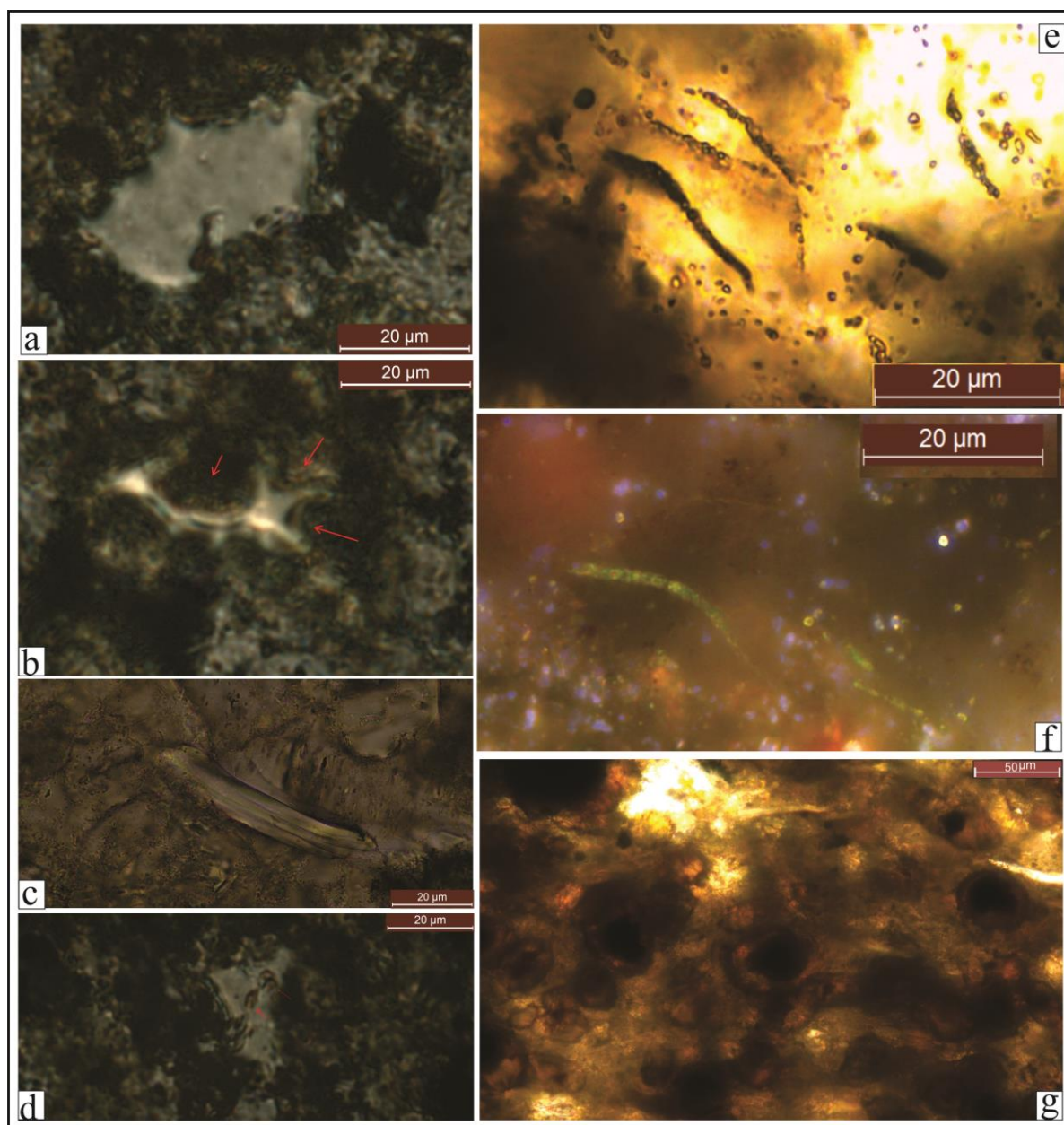


Fig. 8.7: Petrographic study of volcanic tuff alternating with the black and grey shale; **a)** In situ devitrified glass. **b)** Remnant Boundary of broken gas bubbles within devitrified glass (arrowed). **c)** Elongated glass shards (tephra) present within the tuff layer. **d)** Gas bubbles entrapped within devitrified glass. **e)** Segmented filamentous body under light microscope. **f)** Segmented filamentous body under refracted microscope. **g)** Acritarch like structure is preserved in tuff.

8.3.2: Compositional variation with change of geometry: Ultra-Microscopic Study:

To picturize the variable form of microbial mat geometries, few thin sections were scanned under SEM as well as EDS analysis was done for chemical composition of the desired part. Concentration of carbon were determined in each geometric form of microbial mat using EDAX.

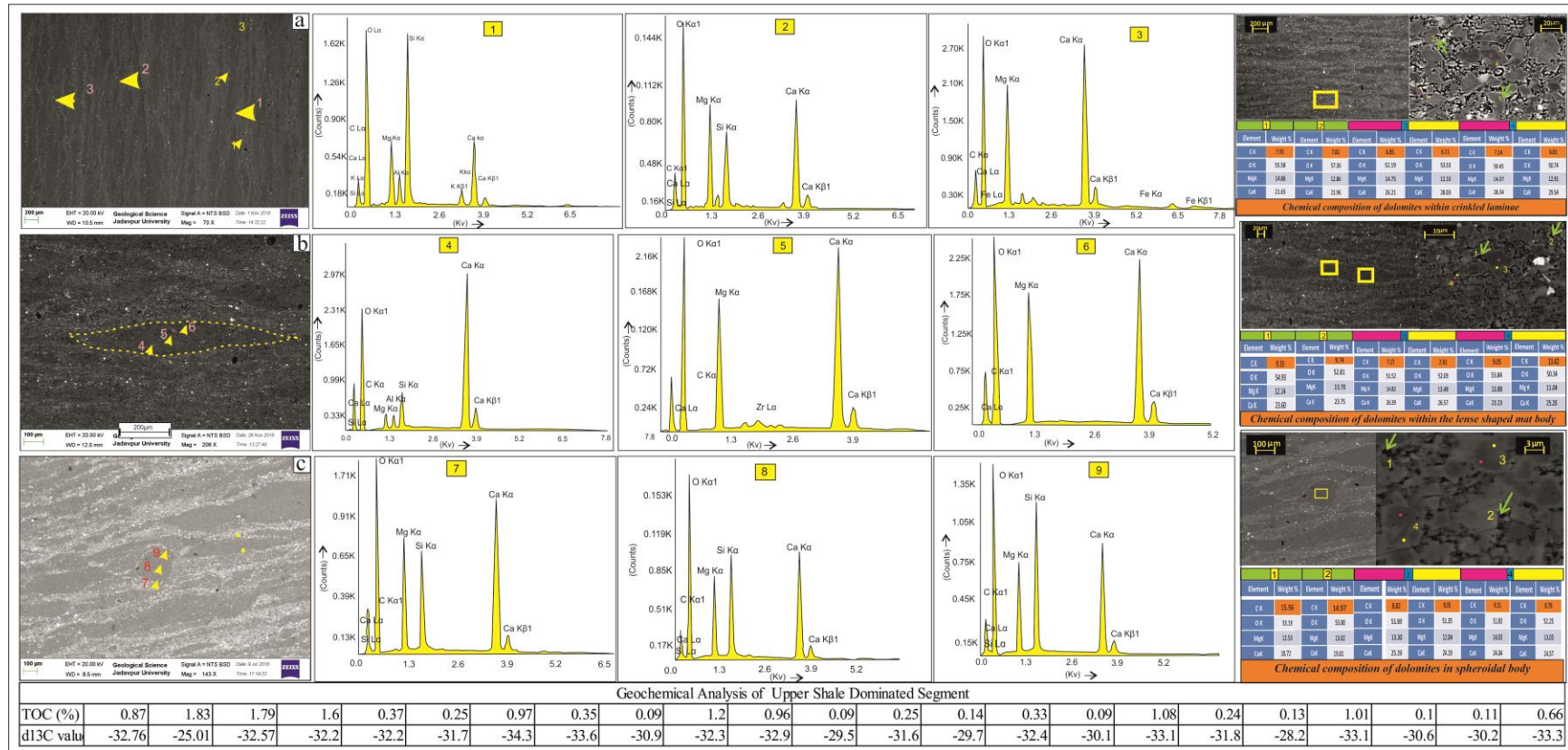


Fig: 8.8: Geometrical variation in mat bodies and associated dolomite crystals (green arrow) within the different mat bodies: **a)** crinkly laminated mat body **b)** lensoidal shaped mat bodies **c)** spheroidal or pin cushion shaped mat bodies under scanning electron microscope along with corresponding EDX analysis.

The geometric variations of the microbial mat present within black shale studied under SEM. Back scattered image is also exteriorizing these geometrical mat body (Fig.8.8). EDAX analysis reflects that the crinkly laminated mat records near about 10-12% carbon content (Fig. 8.8a), and lense shaped body of mat contain 9-14% of carbon (Fig. 8.8b) whereas, 6-8% carbon is measured for spheroidal mat body (Fig. 8.8c). All the geometric variation of the mat body contains rhombic shaped dolomites. These dolomites are basically zoned dolomite, which have a darker core and lighter rim. The cores are slightly rich in magnesium than the rim part whereas, the rim contain more calcium than the core. The core content near about 13-14% magnesium and ~25% calcium but the rim content 10-12% magnesium and ~29% calcium (Fig. 8a, b, c). Along with the dolomite crystal series of pyrite grains are preferentially deposited following the microbial mat lamina (Fig.8.8d, e).

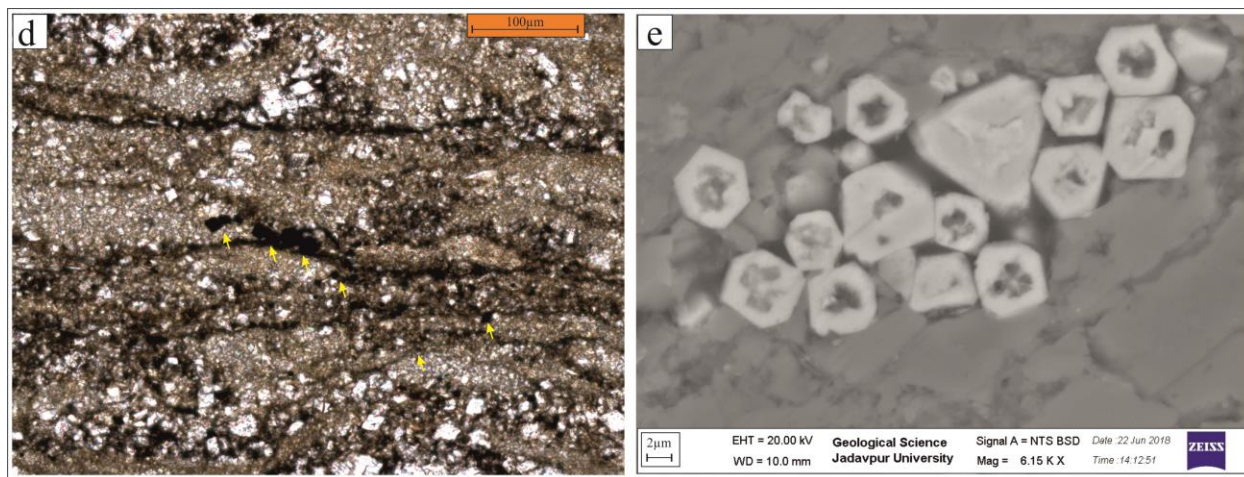


Fig. 8.8 (Continued): Series of euhedral pyrite crystals are arranged in a row, **d)** under petrographic microscope, **e)** under SEM.

The black shale also holds few extraordinary unique biotic structures, which possess a biasness with these microbial mat body. SEM study imply that mat body records wonderful preservation of filamentous type structure along with few globular structures, observed under SEM, in association with the microbial mat. EDAX analysis shows that near about 65% carbon is present within filamentous structure (Fig. 8.9a). A variety of bulbous form of microbiota is preserved within shale facies. These bulbous forms (Fig. 8.9b) of microbial mat fragments also contains highly variable Carbon content which is greater than 50%. A few degenerated and fragmented hair brush-like form shows a high carbon content (~35%) (Fig. 8.9c). Besides, the filamentous

and hair-brush like morphology, another variety of microbiota is present which represent a half cylindrical form (Cylindrical form in half with intermittently placed cross-walls) (Figs. 8.9d). Carbon content is indeed high in the cylinder walls and on the cross-walls (~45-46%).

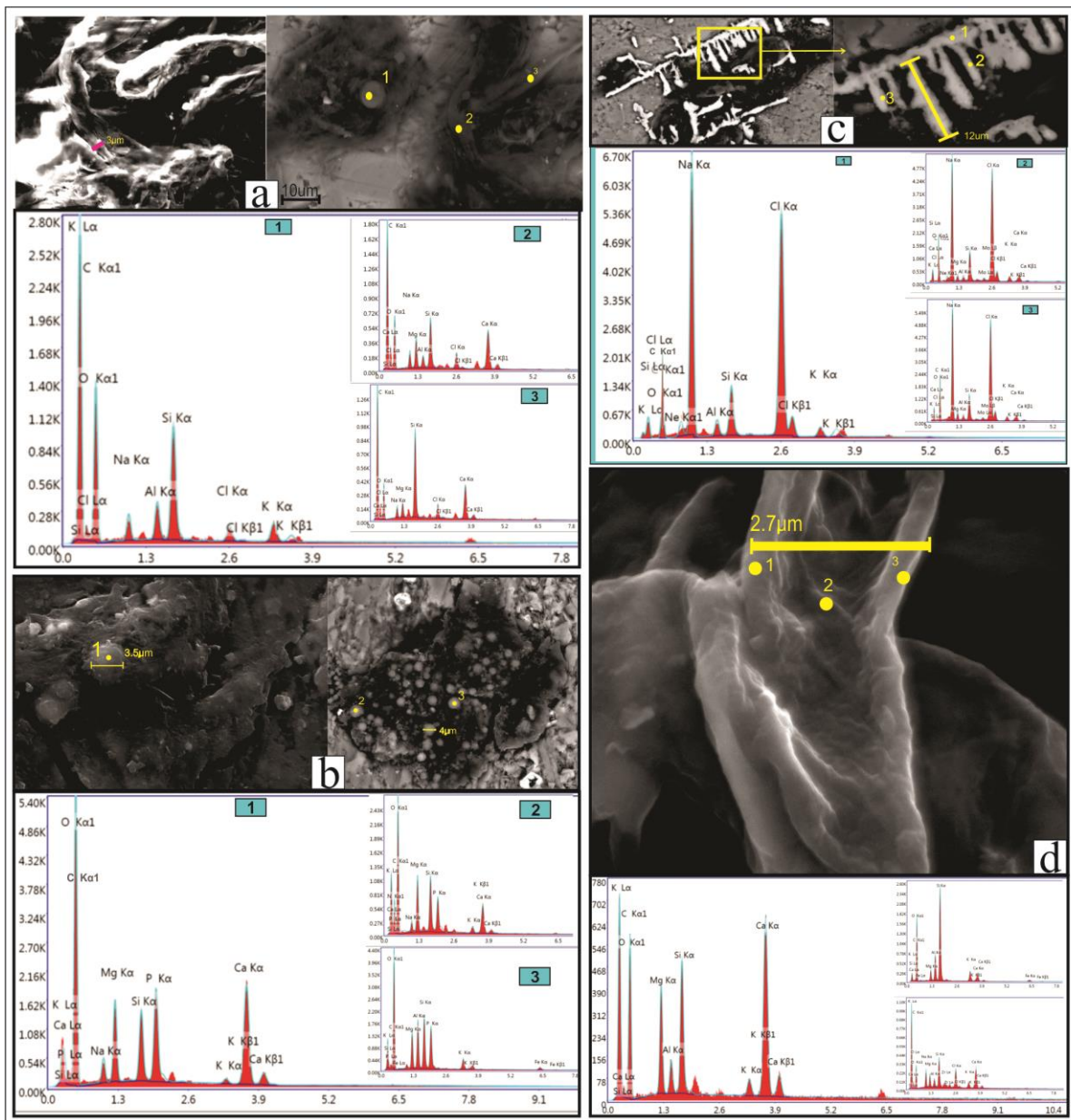


Fig. 8.9: Black Shale under Scanning Electron Microscope. **a)** filamentous form within microbial mat laminae **b)** bulbous form within the mat chips **c)** comb like structure in microbiota **d)** half cylindrical shape shown in microbial mat.

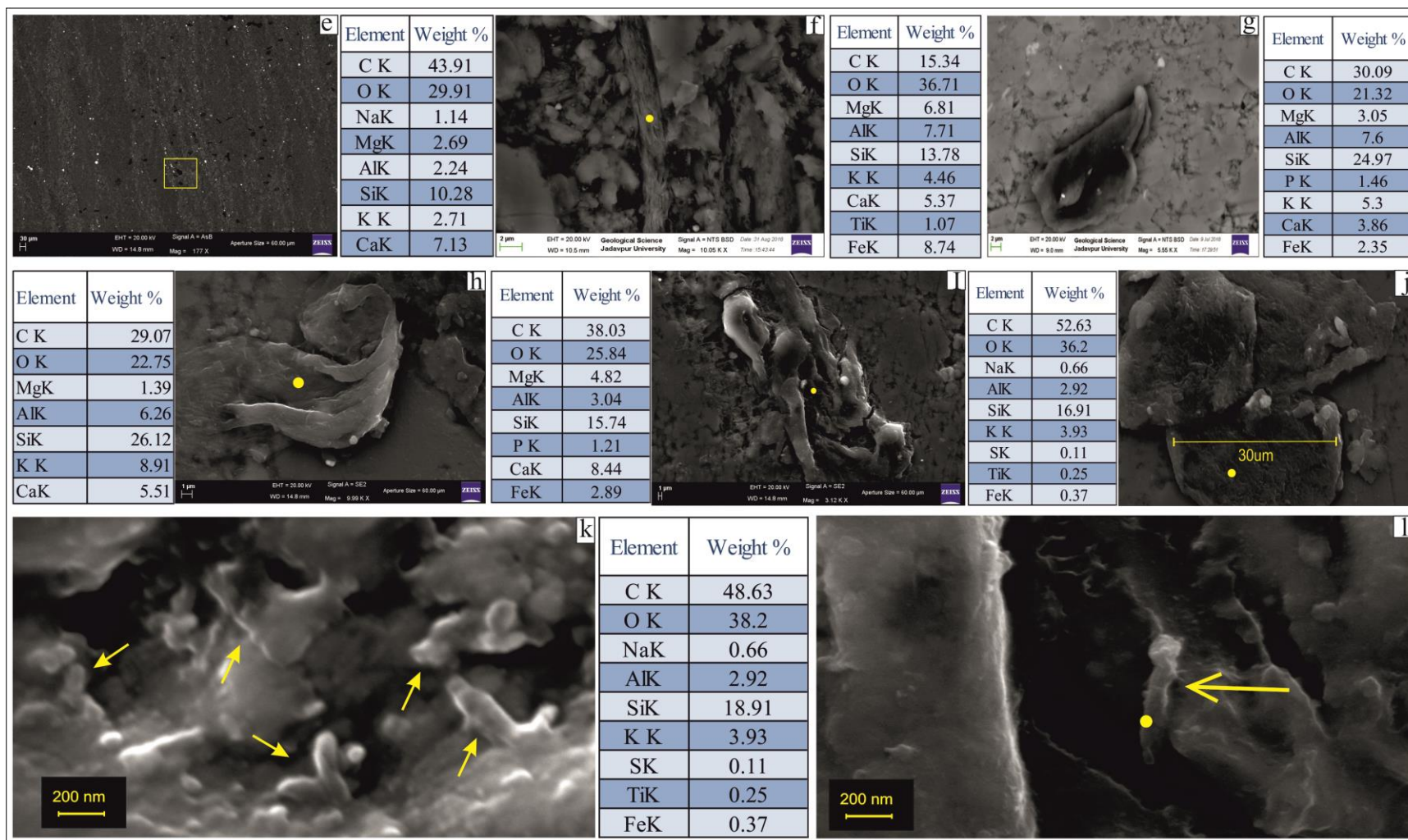


Fig. 8.9 (Continued): Black Shale under Scanning Electron Microscope **e)** Microbial Mat-chips are present within the shale layers. **f)** Pipe like structures are preserved within the black shale. **g-h)** Folded form. **i)** Elongated rope like variety. **j)** Disc or Saucer shaped structure. **k-l)** Capsule Shaped or rod-shaped variety observed within black shale; similar with the cyanobacterial form present in modern environment. EDAX analysis data is also represented here.

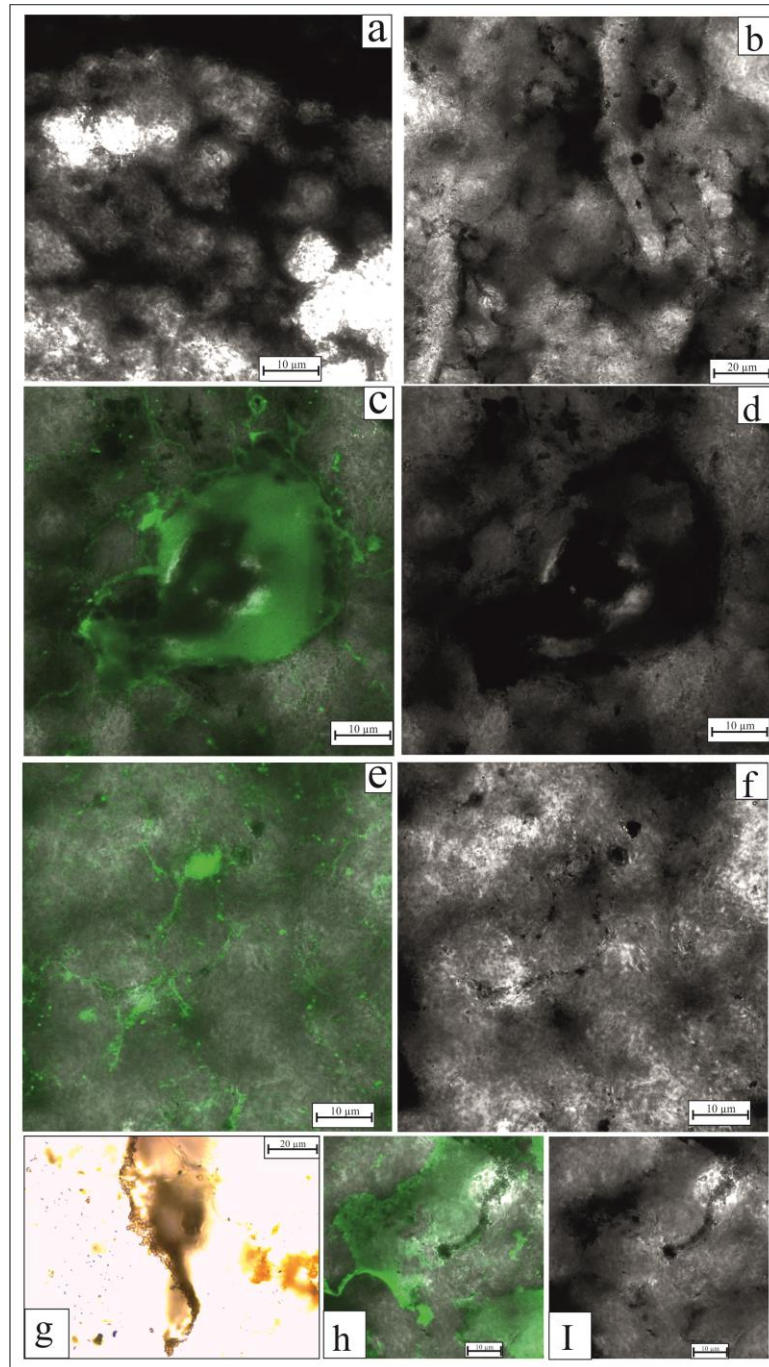


Fig. 8.10: CLSM Study of Shale and Tuff layers. **a)** Three-dimensional coccoidal ball. **b)** Pipe like structures are observed under confocal microscope **c-d)** Folded microbial form within black shale under CLSM covered by permineralized matrix, after deep focusing on the next inner level of the rock, the structure is identified. **e-i)** Segmented microbiota under CLSM covered by permineralized matrix, after deep focusing on the next inner level of the rock, the structure is identified. **g)** Petrographic variety is also presented here.

This degenerated mat fragments is not visible under petrographic study because these are extremely tiny in size, present only within the black shale facies. (Fig. 8.9e) These are studied under the scanning electron microscope. These mat bodies do not hold any dolomite

crystal within it. Only few special shaped mat structures are recorded e.g., rod or capsule shaped mat body, pipelike structure, folded mat fragments, recurved mat body, braided mat structures and dish and saucer type structure (Figs.8.9f-l). EDAX analysis shows that this spectacular form of microbial consortia was also found with very high enrichment in Carbon i.e., ~48%, ~15%, ~30%, ~29%, 38%, and 52% respectively.

Confocal laser scanning microscopy (CLSM), non-intrusive and non-destructive process which produce 3D images, provide necessary insight regarding the morphology of ancient organic-walled fossils. During the present study, some samples of black shales and alternating volcanic tuffs have analyzed under CLSM. The micro scale-size filamentous shape (~100µm), globular shaped body (~10µm diameter) are recognized within the black shale under the microscope (Fig. 8.10a-b). Internal structures are not well preserved but the shape is prominent. Few segmented filament-like structures and curled microbial body revealed during deep penetration of the laser beam which were embedded within the matrix at a certain depth (Fig. 8.10c-i).

8.4. Discussion and Interpretation: Rampur shale as an Organic Store House:

8.4.1: Depositional scenario:

In connection with the overall field observation, the lower part of the Rampur shale contains sheet like and amalgamated sandstone which are emphasizing the storm signature. The sharp, erosional base and hummocky cross-stratification also support the context. This scenario reflects that it is a shallow marine deposition in an inner shelf setting. The middle part is completely made up with sand-shale-silt alteration with increasing shale proportion at the upper part. In between the sand-shale-silt alteration the sandstone contains several tool marks and gutter cast at the bottom part which clearly indicate the presence of high energy environment like storm. As shale is dominating at the upper part of the succession and comparatively less amount of sandstone is present there, indicating a progression towards calm and quite environment deposited at middle part of the shelf. The upper segment is dominated by shale; black shale followed by grey shale reflects an outer shelf deposit. The overall scenario reveals the Rampur shale is deposited in shallow marine condition starting from inner to outer shelf setting (Bose et al., 2001, 2015).

8.4.2 Significance of MISS:

Presence of cracks on bed surface of the sandstone is a proxy which suggests the influence of microbial mat that significantly affected cohesive and non-cohesive sediment. Desiccation might be responsible for generating cracks at the mat bearing sediment- air interface i.e., after the sediment got exposed (Schieber 2004; Schieber et al. 2007). Cross-cutting relationships is common for syneresis cracks which is likely to be deposited below the sea surface (Sarkar and Banerjee, 2020). The trough confined sinuous geometry of the cracks are generally short and acutely oriented with the trough axis. This variety of crack is quite similar with desiccation of mats, widely known as ‘*Manchuriophycus*’ (Pflüger 1999; Schieber 2004; Parizot et al. 2005; Choudhuri et al., 2022, 2023). The cracks may be generated at the sediment-air or sediment-water interface. Another type of crack is generated irrespective of the ripple crest and trough. This is also a type of shrinkage crack but difficult to say whether it is deposited in exposed surface or underwater (Parizot et al. 2005).

Preservation of cracks at the top of the beds indicates artificial cohesiveness within the sand particles developed due to interferences of microbial mat (Stolz, 2000, Sarkar et al., 2014, 2020; Choudhuri et al., 2022, 2023). Microbial mat is also known as bio-film, show similarity and differential structures and composition point intimating interaction with microbial community, surrounding environment and surficial substrate. Cyanobacteria plays a major role as the primary producer of microbial mat or biofilms. An exorbitance of cyanobacterial community caused the generation of laminated biogenic structure within a solid substrate like sandstone, limestone or shale. Microbial mat releases a sticky liquid called EPS (Extra Polymeric Substances; John F. Stolz, 2000; Krumbein 1994) which help to develop cohesiveness in nature so that cracks can easily be developed on the non-cohesive sand particle.

There are few anti-form ridges like structures were present at the sandstone originated by deformation of syneresis cracks like doming, rupturing and buckling of microbial mat, commonly known as petee structures (Reineck et al. 1990; Gerdes et al. 1993, 1994; Schieber 1999, 2004; Gehling 1999). Wrinkle structure is another proxy which represent the presence of microbiota, especially in a sand-dominated environment. Continuous loading followed by dewatering, gas buildup, wave or current shear can describe the origin of this structure (Noffke et al. 2003a; Pflüger 1999; Gerdes et al. 2000; Hagadorn and Bottjer 1999; Bouougri and Porada 2002; Banerjee and Jeevankumar 2005; Banerjee et al. 2010, 2014). Palimpsest

ripples can carry the impression of hydrodynamic condition of the underlying bed which trap the sand particles by the microbial filaments (Pflüger and Sarkar 1996). The sand-clast bearing surface implies presence of elastic binding material i.e., EPS secreted by microbial mat (Pflüger and Greese 1996) or sometimes these chips can be influenced by storm event.

8.4.3: Insight from Microscopic view:

Apart from the MISS structures in field study, the lower and middle segment shows few stringers of mat lamina which is basically carbonaceous flakes embedded in silty shale (Schieber 1986) (Fig. 8.11). The upper segment facies E shows the microscopic biogenic imprints in the rock record. Black shale contains the signature of the microbial life which are exemplified by the different microscopic and ultramicroscopic features. Micro-loading, jagged ends, upwarping, lateral accretion, false cross laminations are possibly formed during sedimentation (Sur et al., 2006; Schieber 1998, Schieber 1986). Micro-loading is a structure related to microbial mat, generally these loading form within same lithology where load formation is impossible, only they can form if the microbiota present can change the density. Jagged ends are nothing but bears the signature of cohesiveness of the mat body. The microbial mats are cohesive in nature, they can't be break but they can be torn apart due to extension or overstretching (Schieber 1998, Schieber 1986). Dolomite crystals are draped by crinkly microbial laminae infers that syn-genetically precipitated along with the development of the microbial lamina which is following the dolomite crystals (Schieber 1998). Upwarping is nothing but confirm the pre-existing substances and continues the depositional flow without disturbing former substance. Lateral accretion is the indication of prolific growth of microbiota within the mentioned facies. It is known that flaky minerals (e.g. muscovite, biotite) are oriented in a particular direction within the shale which develop the fissility plane within shale. In the studied section the petrography shows that the random orientation of mica flakes interprets that extreme biotic proliferation trap the flaky minerals and prohibit them from alignment in a certain orientation, known as "fly paper effect" (Schieber 1998, Sarkar et al., 2006.).

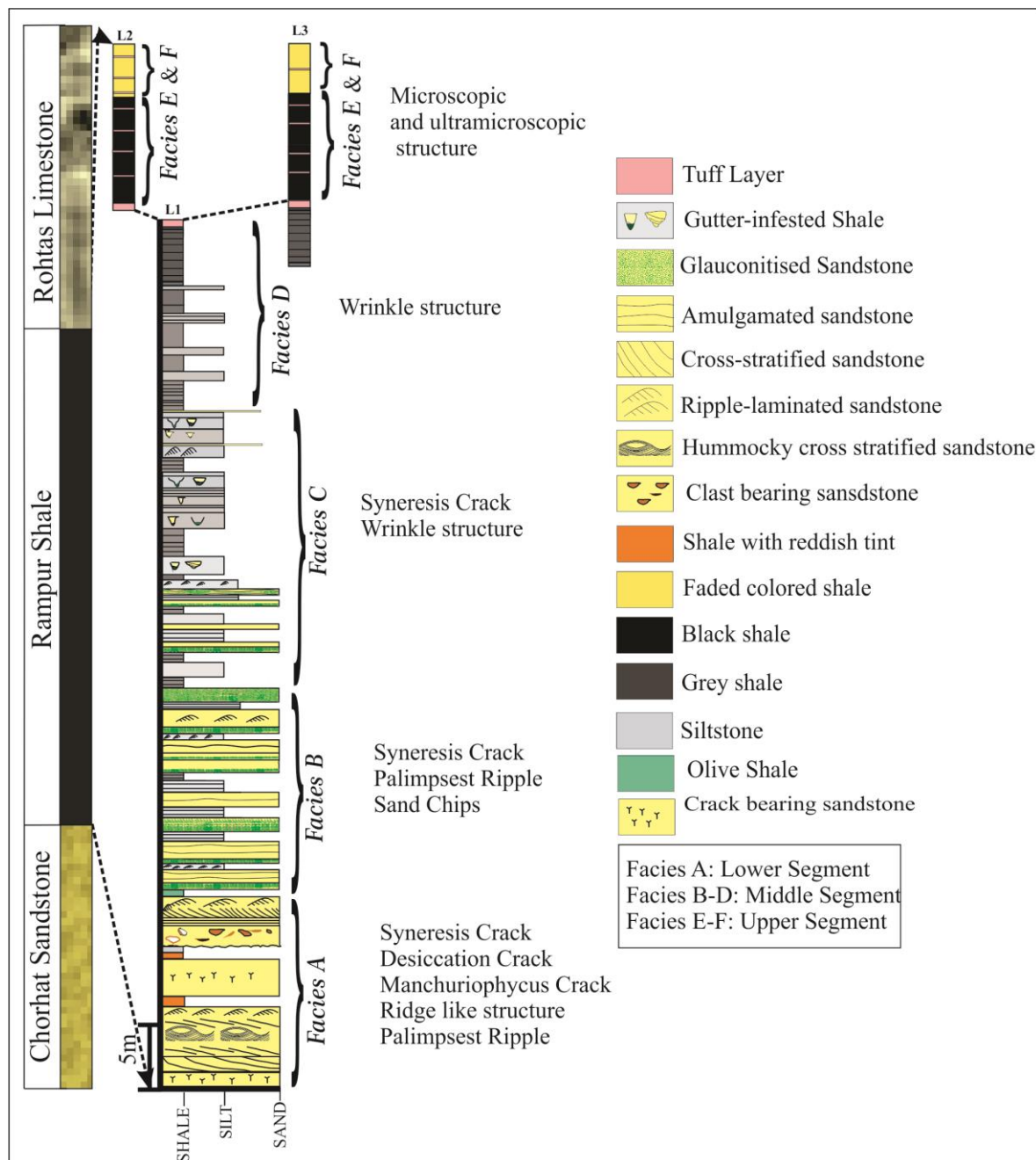


Fig. 8.11: Distribution of biogenic impressions within the Rampur Shale.

8.4.4: Insight from Ultra-Microscopic study:

Some ultramicroscopic such as filamentous, saucer shaped, bulbous, comb-like, half cylindrical, capsule shaped, Rod-like structure which are observed under SEM, are exactly looks similar with cyanobacterial form found in modern days. (Chafetz 1990; Chafetz and Buczynski ,1992). After EDX analysis all the individual forms are showing rich in carbon

(already mention in previous section) may be these are organic carbon. Chafetz and Buczynski (1992) states that dead cyanobacteria are highly susceptible for precipitation of calcium carbonate. This process is enhanced after burial, as the depth increased i.e., beneath the photic zone (Simkiss and Wilbur 1989), the precipitation of calcium carbonate is also deposited at a higher rate and the mat get lithified. The increase and abundance of calcium carbonate precipitation influenced by prominent presence of cyanobacteria (Dalrymple, 1965; Monty, 1965; Horodyski, 1977; Krumbein et al., 1977). So, it can be inferred that the innumerable dolomite crystals are precipitated within the black shale are nothing but influenced by these cyanobacterial community. As that time the Ocean was Mg rich (Banerjee et al., 2008), the Mg^{+2} easily incorporated within the calcium carbonate structure and dolomite crystal formed. Besides, within the sheaths of microbial mat Mg^{+2} content will be more, this additional Mg^{+2} ion can enhance the dolomitization process. The black shale of Rampur Shale Member is showing highly negative $\delta^{13}C$ (-25 to -33‰ in avg.). TOC content is also very high 0.75 to 1.89. which supports this biogenic scenario.

Biogenic fingerprints are also impregnated within the volcanic tuff, alternating with the black shale in the upper segment. Here, some remnant boundaries of gas bubbles, quenching cracks (Fig. 8.7) confirms its volcanic origin. Quenching cracks within the gas bubbles are generally formed due to rapid cooling of a hot material. Petrographic study clearly shows these quenching cracks and gas bubbles within the tuff layer present within the black shale as well as uppermost grey shale (faded shale). Some segmented filamentous structures were found within the tuff layer and the shape was confirmed after the CSLM study. CSLM allows complementary information at different focal level. It also produces a high-resolution image and reflects the relationship among the variable microbial communities. This detailed study also helpful to detect the microbial ecology of the then time. Images obtain out of this technique are slightly out of focus. The most useful outcome of this technique is that cyanobacterial community can be easily distinguished as they emit natural fluorescence without any staining. Some filamentous along with some networking-like textures are emitting autofluorescence, became brighter and spontaneously recognizable under the confocal laser scanning microscope. A series of image has been presented here which represent that microbiota is impregnated within a permineralized matrix body. As the laser beam is penetrating within the surface the filamentous structure is becoming clearer and more prominent (Fig. 8.10) (Schopf, 1992, Schopf, 1993; Schopf et al., 2006, 2009). In case of modern microbiota, biomass calculation is very difficult in the classical method whether it

is too easy to calculate the accurate biomass under the CSLM (Sole et al., 2001) but in our case biomass calculation is not possible but verification of the origin i.e., whether it is biogenic or non-biogenic, can be determine accurately due to instinctive fluorescence.

8.5: Conclusion

In conclusion it can be summarized that Rampur shale member is highly potential for Mesoproterozoic biogenic study in various aspect. Here organic enrichment has been proven only in petrographic aspects with minor geochemical analysis like EDAX analysis and TOC with organic isotope in a selected manner. Depending upon the depositional environment, i.e., in deeper part of shelf, the availability of the oxygen is less at that part. Under this low oxygenic condition, a diversity of microbial assemblage have been identified. Microbial community also develop in a shallow marine inner shelf part but their microscopic evidences are not preserved due to dominating oxic condition. At the deeper part there is a less oxygenic condition is prevailed which helps to preserve the bio-assemblage and prohibit decomposition. Extreme biogenic production has exhausted the oxygen budget so that many of the microbiota are able to avoid destruction. The biota also preserved within the volcanogenic tuff layer. This layer also contains a variety of metals which supplies the required nutrient to the microbiota preserved there. Impervious volcanic glass has provided a fortuitous window to get acquainted with Meso-Proterozoic cyanobacterial forms.

PART IV

COMPENDIUM

CHAPTER: 9

Summary & Conclusion

The Rampur Shale (RS) of the Son Valley in India was built up within the Vindhyan basin at a time that is known to geologists as a "barren" period (Bradley, 2011; Roberts, 2013; Holland, 2006; Condie, 2021) and whose age is well constrained at 1.5 Ga (Rasmussen et al., 2002). Despite being predominantly shaly, it reveals under close scrutiny a plethora of geological information about the "barren" period that otherwise could have remained in oblivion for long. In fact, some of the insights, so generated, are not obtainable from coarser lithologies.

The RS is sandwiched between the marine shelf-originated Chorhat Sandstone below and Rohtas Limestone at the upper part, the latter links up gradationally with the RS to constitute the Rohtas Formation (RF). The RS is thus designated as a Transgressive Systems Tract (TST). Despite having limited lithologic variability, the 85m-thick RS is divisible in three segments, and six facies viz., the ~12m-thick basal part with its plinth in sandstone with a very little amount of shale alternation within, identified as facies A (sand: shale ratio is 4:1). The middle segment is considered as sand-silt-shale alternation associated with pyroclastic fragments and glauconitic mineralization. Primarily divided as facies B, C and D based on sand: shale ratio varies from 3:2, 1:2 and 1:5 respectively. Other than sand: shale ratio, concentration of glauconite and pyroclastic fragments also differ from facies B to D. Upper segment is devoid of shale, based on coloration this segment again divided into two facies, such as facies E and F.

Notwithstanding overall monotony, the Basal Part of the RS has an overall, though not steady, fining upward trend. The sandstone beds in the lowermost rung (**facies A**) are tabular and sheet-like geometry, eroded base with several mud-clasts within. The sand beds are internally stratified by chevron or hummocky cross-strata and top surface ornamented by wave ripples. All these features combinedly suggest deposition of sand from temporally waning storm waves. Various other penecontemporaneous structures, like manchuriophycus, sand ridges, sand chips, sinuous and spindle shaped cracks, palimpsest ripples indicate prolific microbial mat growth during sedimentation. At the middle segment, starting from facies B, upward increasing intervention of shale depicts progressive deepening of the basin. The in-situ sandstone bodies are found both in sheet-like or tabular form. At places sheet sandstones are amalgamated in nature. Both the sand bodies are sculpted at base with gutters and bipolar prod marks. Again, indicating towards a depositional environment interfering with storm events. A green colored shale layer along with pyroclastic bearing sandstone layer are introduced at base of facies B. The pyroclastic-rich sandstone beds and some younger sandstones become glauconite-enriched. The mode of

occurrence of glauconite varies widely. At places it is in form of in-situ void-filling cement and elsewhere clastic. At other places it is, in-situ diagenetic affecting other clastic mineral grains like quartz, feldspar, mica and pyroclastic fragments. Somewhere else it may be tectonically affected. They are mostly of "evolved" variety, compositionally closer to ferric Illite, like all other Precambrian counterparts. Mg-enrichment of the Rampur glauconite is another interesting aspect discussed here. Compared with other glauconites reported from different formations of upper and lower Vindhyan groups, it has been mentioned that volcanic exhalation might have stimulated the chemical composition of glauconite.

The laterally discontinuous sand/siltstone beds above bear slicken-lines at their edges that are sharply beveled. Micro-grabens created thereby suggest progressive basin deepening owing to intracratonic rifting extending ENE-WNW. The sand/silt supply was restricted during storms plausibly because of ongoing inundation of the coastal zone. On the muddy substratum the grabens guided the flows of coarser clastics and those flow paths are now sculpted as isolated channels. Deposition of coarser clastics started only after the erosional prowess of the storm-flows came to naught.

Geochemical properties of sediments indicate their derivation mostly from felsic source on post-Archaeon continental margin under warm and humid climatic regime. Rate of sedimentation decreased through time as the basin deepened. Because of paucity of atmospheric oxygen, the seafloor generally remained dysoxic, notwithstanding frequent fluctuations in the content of dissolved oxygen. Through time the paucity of dissolved oxygen had turned more acute because of enhanced microbial growth. Palaeosalinity in this epicontinental sea under humid climatic regime had been low, even comparable to fresh water at times.

The middle segment gradationally passes into the Black Shale (facies E) in which TOC is moderately high. Characteristically, however, the BS is metal-poor, as a consequence of atmospheric oxygen depletion. Deposition took place mostly suboxic/dysoxic condition. Slow rate of sedimentation far away from terrigenous sources favored organic matter accumulation. Topmost part of the RS belongs to a light grey shale (Faded Shale). Its planar laminae attest to low rate of sedimentation beneath the wave base. The environmental condition favored microbial mat growth and growth of microbial consortia. However, geochemically distinctive, paper-thin and normally graded siltstone/mudstone reflected turbidites disrupted the placidness intermittently. The sediment source had still been dominantly felsic, although mafic contribution from Archaeon mafic

sources increased more than ever. Palaeoclimate had still been warm and humid. Palaeosalinity of the basinal water remained low. The sea-floor had, in general, been dysoxic/anoxic under a chemocline that occasionally extended up to the shallow shelf. The chemocline was not, however, static and moved up and down depending on amount of influx of fresh seawater. The sedimentation rate increased upward through the FS. This progradational trend is not recognizable in the lithologic succession, but there is clear indication for increase in palaeotemperature. That possibly turned the depositional environment conducive for carbonate deposition and ensured eventual transition to the RL.

The upper segment (facies E and F) both are enriched with biogenic matters, especially the black shale (facies E) contains microbial mats of three discrete forms varying in chemical composition. Multiple forms of microbiota are detected. Biogenic respiration created the oxygen paucity on the sea-floor. Marine transgression attained its maxima. Nevertheless, the bio productivity rate was relatively higher shoreward presumably of greater supply of nutrients from the land. Being an organic rich black shale, the Rampur shale is not a well-known source for explorable hydrocarbons like petroleum oil or gas. The satisfactory reason towards moderate TOC % and low organic isotopic ratio which supports the Rampur shale to be unsuited as hydrothermal source rock. The microbiotas which were present enormously within the BS succession may be less effective to produce hydrocarbon generation. Absence of hydrothermal signature may reduce the nutrient supply which causes decrease the bio-productivity rate. Bottom water condition was suboxic to dysoxic which condition is not suitable for that much organic carbon preservation and the Rampur shale with high thermal maturity became non-productive for hydrocarbon generation.

ANNEXURE

Facies		Sample	Al ₂ O ₃ (%)	CaO (%)	Fe ₂ O ₃ (%)	K ₂ O (%)	MgO (%)	Na ₂ O (%)	P ₂ O ₅ (%)	SiO ₂ (%)	TiO ₂ (%)
D	Galuconitic sandstone	S41	16.35	0.14	3.02	7.49	1.51	0.09	0.04	71.00	0.36
		S39	13.48	0.20	3.12	6.92	1.69	0.00	0.03	74.14	0.41
	Shale	RKI4SH6	14.60	0.05	1.51	8.81	0.82	0.20	0.04	73.78	0.19
		RKI4SH5	15.92	0.16	4.13	6.96	1.75	0.22	0.06	70.37	0.42
	Galuconitic siltstone	S38	12.47	0.09	3.18	5.40	1.36	0.21	0.04	76.89	0.35
	Shale	RKI4SH4	16.71	0.17	3.65	7.92	1.72	0.22	0.05	69.12	0.43
	Galuconitic siltstone	S37	17.60	0.37	4.84	7.56	2.10	0.11	0.07	66.81	0.53
		S36	13.49	0.13	3.51	7.18	1.74	0.22	0.06	73.35	0.32
	Shale	RKI4SH3	15.73	0.19	4.87	6.07	1.82	0.23	0.06	70.57	0.45
	Galuconitic siltstone	S31	12.46	0.05	3.53	5.04	1.61	0.23	0.06	76.62	0.40
	Shale	RKI4SH2	15.69	0.16	4.24	6.93	1.70	0.22	0.06	70.57	0.42
		RKI4SH1	16.30	0.24	4.70	6.27	1.93	0.23	0.06	69.81	0.45
C	Shale	RKI3SH8	18.24	0.17	4.52	7.23	2.00	0.24	0.07	67.02	0.50
		RKI3SH7	17.22	0.11	4.13	6.61	1.73	0.23	0.04	69.45	0.48
		RKI3SH6	17.87	0.07	4.50	6.72	1.92	0.24	0.06	68.11	0.50
		RKI3SH5	16.29	0.17	4.16	6.59	2.16	0.24	0.07	69.81	0.51
		RKI3SH4	15.98	0.17	4.09	6.61	2.09	0.24	0.07	70.30	0.46
		RKI3SH2	15.03	0.15	3.15	6.65	1.98	0.23	0.07	72.30	0.44
		RKI3SH0	16.82	0.16	3.84	7.24	2.31	0.24	0.07	68.84	0.48
	Galuconitic sandstone	S23	8.09	0.06	2.45	3.39	1.98	0.00	0.00	83.83	0.20
		S19	9.09	0.08	3.38	4.48	3.44	0.00	0.00	79.41	0.11
B	Shale	RKI2C	16.97	0.10	3.86	7.10	1.89	0.23	0.05	69.34	0.45
		RKI2B	15.50	0.17	3.62	6.72	1.98	0.24	0.07	71.23	0.48
		RK-33-SStn	11.84	0.12	4.14	5.99	1.24	0.00	0.03	72.19	0.49
		RK-33-Sh	9.29	0.10	2.23	5.45	1.01	0.00	0.02	79.16	0.30
	glauconitic Sandstone	S18	13.03	0.18	4.84	6.30	4.43	0.00	0.05	70.94	0.24
		S16	15.74	0.58	4.22	6.72	1.93	0.00	0.12	70.15	0.54
	Shale	RKI2A2	15.86	0.10	3.40	6.56	1.95	0.23	0.06	71.35	0.49
		RKI2A1	13.33	0.19	3.94	6.01	2.09	0.22	0.09	73.70	0.43
		RKI2A`	16.43	0.07	3.88	6.73	1.79	0.23	0.05	70.28	0.54
	Green Shale	S 13 d	18.27	0.14	2.56	10.43	4.39	0.00	0.04	63.39	0.34
		S 13 c	18.97	0.44	2.36	12.58	4.28	0.00	0.04	60.32	0.39
		S 13 b	17.63	0.32	2.51	10.58	4.47	0.00	0.00	63.57	0.34
		S 13 a	17.90	0.36	2.34	11.86	4.04	0.00	0.00	62.74	0.36
A	Shale	RKI1SH2	9.28	0.02	1.43	4.59	0.36	0.20	0.03	83.84	0.26
		RKI1SH1	9.27	0.03	1.48	4.61	0.38	0.20	0.03	83.73	0.27
		Avg. Sh	16.70	2.20	2.80	3.60	2.60	1.60	0.16	58.90	0.78

Table-1: Major element concentration (oxide form in weight % and element form in both weight % and ppm) in Lower and Middle segment comprising Facies A, B, C and D

	Facies	Sample	Al (%)	Ca (%)	Fe (%)	K (%)	Mg (%)	Na (%)	P (%)	Si (%)	Ti (%)
D	Galuconitic sandstone	S41	8.66	0.10	2.11	6.22	0.91	0.07	0.02	33.18	0.21
		S39	7.13	0.14	2.18	5.74	1.02	0.00	0.01	34.65	0.25
	Shale	RKI4SH6	7.73	0.04	1.05	7.31	0.50	0.15	0.02	34.49	0.11
		RKI4SH5	8.43	0.11	2.89	5.78	1.05	0.17	0.03	32.89	0.25
	Galuconitic siltstone	S38	6.60	0.07	2.22	4.49	0.82	0.16	0.02	35.94	0.21
	Shale	RKI4SH4	8.84	0.12	2.56	6.58	1.03	0.17	0.02	32.31	0.26
	Galuconitic siltstone	S37	9.32	0.27	3.38	6.28	1.27	0.08	0.03	31.23	0.32
		S36	7.14	0.09	2.45	5.96	1.05	0.17	0.03	34.28	0.19
	Shale	RKI4SH3	8.33	0.14	3.41	5.04	1.10	0.17	0.03	32.98	0.27
	Galuconitic siltstone	S31	6.60	0.04	2.47	4.18	0.97	0.17	0.03	35.81	0.24
	Shale	RKI4SH2	8.30	0.11	2.97	5.76	1.03	0.16	0.03	32.98	0.25
		RKI4SH1	8.63	0.17	3.29	5.20	1.16	0.17	0.03	32.63	0.27
C	Shale	RKI3SH8	9.65	0.12	3.16	6.01	1.21	0.18	0.03	31.33	0.30
		RKI3SH7	9.11	0.08	2.89	5.48	1.04	0.17	0.02	32.46	0.29
		RKI3SH6	9.46	0.05	3.14	5.58	1.16	0.18	0.03	31.84	0.30
		RKI3SH5	8.62	0.12	2.91	5.47	1.30	0.18	0.03	32.63	0.31
		RKI3SH4	8.46	0.12	2.86	5.49	1.26	0.18	0.03	32.86	0.27
		RKI3SH2	7.95	0.10	2.20	5.52	1.19	0.17	0.03	33.79	0.26
		RKI3SH0	8.90	0.11	2.69	6.01	1.39	0.18	0.03	32.18	0.29
	Galuconitic sandstone	S23	4.28	0.04	1.71	2.81	1.19	0.00	0.00	39.18	0.12
		S19	4.81	0.06	2.37	3.72	2.07	0.00	0.00	37.11	0.07
B	Shale	RKI2C	8.98	0.07	2.70	5.89	1.14	0.17	0.02	32.41	0.27
		RKI2B	8.20	0.12	2.53	5.58	1.19	0.18	0.03	33.29	0.29
		RK-33-SStn	6.27	0.09	2.90	4.97	0.75	0.00	0.01	33.74	0.30
		RK-33-Sh	4.92	0.07	1.56	4.52	0.61	0.00	0.01	37.00	0.18
	glauconitic Sandstone	S18	6.90	0.13	3.38	5.23	2.67	0.00	0.02	33.16	0.14
		S16	8.33	0.42	2.95	5.58	1.17	0.00	0.05	32.79	0.32
	Shale	RKI2A2	8.39	0.07	2.38	5.45	1.18	0.17	0.03	33.35	0.29
		RKI2A1	7.06	0.13	2.76	4.99	1.26	0.16	0.04	34.45	0.26
		RKI2A`	8.69	0.05	2.71	5.58	1.08	0.17	0.02	32.85	0.33
	Green Shale	S 13 d	9.67	0.10	1.79	8.66	2.65	0.00	0.02	29.63	0.20
		S 13 c	10.04	0.32	1.65	10.44	2.58	0.00	0.02	28.19	0.23
		S 13 b	9.33	0.23	1.76	8.78	2.70	0.00	0.00	29.71	0.21
		S 13 a	9.47	0.26	1.64	9.85	2.43	0.00	0.00	29.33	0.22
A	Shale	RKI1SH2	4.91	0.01	1.00	3.81	0.22	0.15	0.01	39.19	0.15
		RKI1SH1	4.91	0.02	1.04	3.82	0.23	0.15	0.01	39.14	0.16
		Avg. Sh	8.84	1.57	1.96	2.99	1.57	1.19	0.07	27.53	0.47

Table-1: Major element concentration (oxide form in weight % and element form in both weight % and ppm) in Lower and Middle segment comprising Facies A, B, C and D

Facies		Sample	Al (ppm)	Ca	Fe (ppm)	K (ppm)	Mg (ppm)	Na	P (ppm)	Si	Ti
D	Galuconitic sandstone	S41	86550.80	980.18	21102.27	62176.50	9096.85	704.41	184.15	331849.56	2149.97
		S39	71347.15	1437.88	21810.08	57449.83	10190.52	0.00	131.70	346518.26	2472.13
	Shale	RKI4SH6	77269.67	376.12	10526.70	73128.48	4950.43	1483.64	183.73	344855.70	1135.59
		RKI4SH5	84252.71	1136.13	28906.95	57797.34	10544.19	1651.11	277.49	328903.77	2540.91
	Galuconitic siltstone	S38	66022.86	678.80	22216.06	44851.33	8208.84	1565.85	184.21	359379.11	2087.40
	Shale	RKI4SH4	88422.26	1211.36	25560.70	65774.87	10348.09	1650.41	231.14	323070.44	2603.33
	Galuconitic siltstone	S37	93174.76	2652.65	33820.40	62763.66	12661.08	786.74	323.94	312260.87	3178.15
		S36	71376.41	912.09	24545.57	59589.23	10517.07	1656.91	278.46	342832.90	1912.37
	Shale	RKI4SH3	83260.05	1353.60	34072.20	50396.43	10976.33	1717.36	275.51	329845.52	2711.93
	Galuconitic siltstone	S31	65966.84	377.43	24672.54	41820.63	9680.61	1723.89	276.55	358103.04	2405.70
Shale	RKI4SH2	83046.02	1128.12	29659.92	57564.55	10279.49	1639.47	275.53	329831.04	2522.99	
		RKI4SH1	86299.52	1725.78	32895.66	52028.31	11648.50	1713.57	274.90	326272.19	2705.95
C	Shale	RKI3SH8	96532.74	1193.78	31615.01	60054.21	12086.44	1781.37	318.91	313259.00	3003.57
		RKI3SH7	91135.20	817.90	28887.00	54839.11	10413.86	1698.06	181.61	324631.96	2868.54
		RKI3SH6	94611.61	527.90	31438.68	55795.47	11580.25	1800.54	276.29	318356.76	2972.65
		RKI3SH5	86220.56	1197.90	29086.72	54696.51	13012.57	1787.52	320.01	326288.87	3076.74
		RKI3SH4	84562.40	1190.17	28607.85	54861.94	12614.80	1775.99	317.94	328561.57	2744.96
		RKI3SH2	79541.28	1043.47	22027.20	55230.35	11948.07	1702.14	318.57	337937.66	2625.38
		RKI3SH0	89025.15	1116.49	26877.59	60083.26	13941.47	1777.10	318.14	321757.34	2871.53
	Galuconitic sandstone	S23	42837.65	444.37	17104.50	28128.78	11935.03	0.00	0.00	391841.04	1180.17
		S19	48128.17	593.48	23666.64	37222.67	20717.56	0.00	0.00	371144.90	684.39
B	Shale	RKI2C	89830.55	738.71	26963.95	58943.53	11405.58	1687.01	225.53	324112.31	2725.95
		RKI2B	82023.61	1189.31	25313.70	55771.67	11915.76	1774.70	317.71	332940.47	2867.64
		RK-33-SStn	62669.12	857.64	28955.16	49722.99	7477.20	0.00	137.47	337416.06	2965.23
		RK-33-Sh	49171.97	714.70	15596.62	45240.45	6090.30	0.00	80.30	369993.84	1807.19
	glauconitic Sandstone	S18	68967.74	1256.45	33848.93	52278.27	26689.14	0.00	225.65	331578.49	1425.67
		S16	83323.51	4153.04	29483.42	55778.51	11658.64	0.00	507.17	327896.04	3229.73
	Shale	RKI2A2	83933.42	738.33	23770.93	54453.87	11773.45	1686.14	270.50	333505.35	2910.31
		RKI2A1	70565.99	1337.83	27565.79	49895.78	12604.31	1620.21	408.44	344474.19	2555.68
		RKI2A`	86946.96	521.79	27135.67	55842.15	10817.27	1702.32	227.58	328466.96	3250.81
	Green Shale	S 13 d	96716.69	1032.95	17906.21	86552.19	26456.51	0.00	180.21	296267.05	2042.01
		S 13 c	100422.68	3168.87	16514.79	104424.48	25803.43	0.00	179.99	281939.97	2348.62
		S 13 b	93312.59	2297.60	17552.15	87805.15	26951.57	0.00	0.00	297124.59	2051.26
		S 13 a	94729.49	2602.84	16374.31	98466.87	24344.67	0.00	0.00	293265.45	2182.93
A	Shale	RKI1SH2	49112.56	147.70	9972.85	38082.70	2180.72	1456.51	135.28	391866.46	1548.36
		RKI1SH1	49050.69	221.02	10381.78	38249.12	2299.87	1453.06	134.96	391371.01	1606.47
		Avg. Sh	88393.10	15723.40	19583.20	29883.60	15678.00	11870.40	698.24	275298.60	4675.32

Table-1: Major element concentration (oxide form in weight % and element form in both weight % and ppm) in Lower and Middle segment comprising Facies A, B, C and D

Facies	Sample	Al ₂ O ₃ (%)	CaO (%)	Fe ₂ O ₃ (%)	K ₂ O (%)	MgO (%)	Na ₂ O (%)	P ₂ O ₅ (%)	SiO ₂ (%)	TiO ₂ (%)
Facies E	21B	9.2028	20.3317	3.6062	5.0187	10.3264	0.0000	0.1605	50.9363	0.3638
	20B	9.8785	17.9512	3.2140	5.4606	9.4701	0.0000	0.2257	53.3161	0.4192
	17B	9.2676	20.5572	3.1117	5.2348	10.8740	0.0000	0.2247	50.3258	0.3258
	15B	13.5366	4.1995	3.2189	7.6636	3.6133	0.1066	0.2452	66.8301	0.5649
	SRTF2	10.3723	13.0047	2.0870	9.4179	5.8941	0.0839	0.1363	58.6261	0.3251
	RTF2	13.1188	5.0733	0.6457	12.2989	0.9532	0.0820	0.0820	67.4388	0.3075
	13B	11.9578	7.8704	3.2612	5.5876	3.6852	0.0000	0.1522	66.9638	0.5001
	SRTF-1	14.2617	5.0440	2.7265	8.5885	2.5797	0.0000	0.1573	66.2752	0.3461
	RTF1	13.9199	17.2729	0.5080	13.1071	0.3150	0.1321	0.0000	54.3589	0.3658
	12B	6.5579	0.3005	1.7280	3.0804	0.9230	0.0966	0.1181	86.9379	0.2361
	STF7	13.8067	0.4360	2.0866	9.2598	1.4741	0.0000	0.2076	72.3554	0.3633
	TF7	17.1800	0.2033	1.5655	15.4519	1.0776	0.0000	0.0712	63.9423	0.5185
	STF4	15.1483	0.2298	1.8074	12.8500	0.4806	0.0940	0.1567	68.8466	0.3865
	TF4	17.2008	0.1433	0.5222	16.0745	0.3686	0.0921	0.1229	64.9125	0.5734
	STF 2-1	15.0057	0.4243	2.0180	11.4871	1.1073	0.1035	0.2484	69.2332	0.3622
	TF2-1	17.5977	0.1535	0.7776	16.0630	0.3376	0.0000	0.1228	64.3544	0.6036
	8B	8.4307	0.4034	1.8413	4.6860	1.2724	0.0000	0.2172	82.8592	0.3000
	STF 1b	13.4810	0.2090	1.7139	10.4504	0.8569	0.0941	0.1463	72.7349	0.3240
	TF1b	17.1864	0.1338	1.6260	14.4077	1.0497	0.0000	0.0720	65.1436	0.3602
	4B	9.5348	0.4496	2.1119	5.3947	1.3905	0.1150	0.2300	80.3973	0.3659
	STF 1d	16.9865	0.0734	0.5767	14.2602	0.1887	0.1153	0.0000	67.3168	0.4823
	TF1d	17.1709	0.0715	0.6235	15.2289	0.1942	0.0920	0.0000	66.1284	0.4906
	1B	8.5791	0.7192	2.0651	4.9522	1.0685	0.0925	0.2055	81.9891	0.3082
	avg Sh	16.70	2.20	2.80	3.60	2.60	1.60	0.16	58.90	0.78

Table-2: Major element Concentration (oxide forms are represented in weight % and element forms are represented in both weight % and ppm) of facies E (Upper Segement)

Facies	Sample	Al (%)	Ca (%)	Fe (%)	K (%)	Mg (%)	Na (%)	P (%)	Si (%)	Ti (%)
Facies E	21B	4.8706	14.5311	2.5223	4.1663	6.2272	0.0000	0.0701	23.8097	0.2181
	20B	5.2282	12.8297	2.2480	4.5331	5.7108	0.0000	0.0985	24.9221	0.2513
	17B	4.9049	14.6922	2.1764	4.3457	6.5574	0.0000	0.0981	23.5243	0.1953
	15B	7.1642	3.0014	2.2514	6.3619	2.1790	0.0791	0.1070	31.2391	0.3387
	SRTF2	5.4895	9.2945	1.4597	7.8183	3.5544	0.0622	0.0595	27.4042	0.1949
	RTF2	6.9431	3.6259	0.4516	10.2099	0.5748	0.0608	0.0358	31.5236	0.1843
	13B	6.3287	5.6250	2.2810	4.6385	2.2223	0.0000	0.0664	31.3016	0.2998
	SRTF-1	7.5480	3.6050	1.9070	7.1297	1.5557	0.0000	0.0686	30.9797	0.2075
	RTF1	7.3671	12.3450	0.3553	10.8809	0.1899	0.0980	0.0000	25.4095	0.2193
	12B	3.4708	0.2148	1.2086	2.5572	0.5566	0.0717	0.0515	40.6382	0.1416
	STF7	7.3072	0.3116	1.4594	7.6871	0.8889	0.0000	0.0906	33.8218	0.2178
	TF7	9.0925	0.1453	1.0950	12.8274	0.6498	0.0000	0.0311	29.8892	0.3108
	STF4	8.0173	0.1643	1.2641	10.6674	0.2898	0.0698	0.0684	32.1817	0.2317
	TF4	9.1035	0.1024	0.3652	13.3443	0.2223	0.0684	0.0536	30.3427	0.3437
	STF 2-1	7.9418	0.3032	1.4115	9.5360	0.6678	0.0768	0.1084	32.3624	0.2171
	TF2-1	9.3136	0.1097	0.5439	13.3347	0.2036	0.0000	0.0536	30.0818	0.3619
	8B	4.4620	0.2883	1.2879	3.8901	0.7673	0.0000	0.0948	38.7317	0.1798
	STF 1b	7.1348	0.1494	1.1987	8.6754	0.5168	0.0698	0.0639	33.9992	0.1942
	TF1b	9.0959	0.0956	1.1373	11.9606	0.6330	0.0000	0.0314	30.4507	0.2159
	4B	5.0463	0.3213	1.4771	4.4784	0.8385	0.0853	0.1004	37.5809	0.2194
	STF 1d	8.9901	0.0525	0.4034	11.8382	0.1138	0.0856	0.0000	31.4666	0.2892
	TF1d	9.0877	0.0511	0.4361	12.6423	0.1171	0.0682	0.0000	30.9111	0.2941
	1B	4.5405	0.5140	1.4444	4.1111	0.6444	0.0686	0.0897	38.3250	0.1848
	avg Sh	8.8385	1.5723	1.9584	2.9885	1.5679	1.1870	0.0698	27.5322	0.4676

Table-2: Major element Concentration (oxide forms are represented in weight % and element forms are represented in both weight % and ppm) of facies E (Upper Segement)

Facies	Sample	Al ppm	Ca ppm	Fe ppm	K ppm	Mg ppm	Na ppm	P ppm	Si ppm	Ti ppm
Facies E	21B	48705.72	145310.86	25222.89	41662.96	62272.188	0	700.5136	238096.8	2181.203
	20B	52282.14	128297.22	22479.799	45331.2	57108.27	0	985.1467	249220.9	2513.263
	17B	49048.67	146922.15	21763.886	43456.52	65574.334	0	980.4988	235242.8	1953.021
	15B	71642.24	30014.048	22514.161	63619.47	21789.657	790.72692	1069.885	312390.6	3386.701
	SRTF2	54895.46	92944.73	14597.438	78182.98	35543.627	622.43104	595.0142	274041.9	1949.115
	RTF2	69431.18	36258.737	4516.1515	102099	5747.9471	608.26894	357.8313	315235.7	1843.323
	13B	63286.77	56249.897	22809.979	46385.16	22223.129	0	664.1896	313015.6	2997.876
	SRTF-1	75480.29	36049.78	19070.029	71297.49	15556.611	0	686.4828	309796.6	2074.647
	RTF1	73671.26	123449.5	3553.292	108808.5	1899.4351	979.90043	0	254095.1	2192.884
	12B	34707.71	2147.8588	12086.319	25571.86	5566.3239	716.61908	515.2538	406382.3	1415.608
	STF7	73071.99	3116.1009	14594.148	76870.53	8889.4093	0	906.0936	338218.3	2178.226
	TF7	90925.33	1453.0853	10949.702	128273.7	6498.1437	0	310.5561	298891.7	3108.164
	STF4	80172.64	1642.6452	12641.182	106674.1	2898.0192	697.52821	683.901	321816.7	2317.37
	TF4	91035.12	1024.4497	3652.189	133442.8	2222.7337	683.60192	536.1974	303426.8	3437.346
	STF 2-1	79417.62	3032.464	14114.545	95360.29	6677.5618	767.73259	1083.937	323623.5	2171.463
	TF2-1	93135.87	1096.8386	5438.5799	133347.2	2036.0467	0	535.8134	300818.3	3618.896
	8B	44619.71	2883.3454	12878.715	38901.21	7672.8996	0	948.0521	387317.1	1798.468
	STF 1b	71348.36	1493.782	11987.305	86754.1	5167.6539	697.74689	638.5077	339991.9	1942.189
	TF1b	90958.89	956.1696	11372.846	119605.8	6330.1513	0	314.3913	304507.1	2159.396
	4B	50462.73	3212.9744	14771.026	44783.84	8385.1877	853.15839	1003.789	375809.1	2193.711
	STF 1d	89900.91	524.57796	4033.6217	118381.5	1138.1692	855.66321	0	314665.5	2891.628
	TF1d	90876.94	511.33483	4360.7144	126423.1	1171.0711	682.41415	0	309110.5	2941.177
	1B	45404.68	5140.1418	14444.203	41110.89	6443.6618	685.98993	896.7841	383249.9	1847.868
	avg Sh	88384.75	15723.4	19584.04	29885.4	15679.04	11869.76	698.272	275322.2	4676.178

Table-2: Major element Concentration (oxide forms are represented in weight % and element forms are represented in both weight % and ppm) of facies E (Upper Segement)

Facies	SAMPLE NAME	Al ₂ O ₃ (%)	CaO (%)	Fe ₂ O ₃ (%)	K ₂ O (%)	MgO (%)	Na ₂ O (%)	P ₂ O ₅ (%)	SiO ₂ (%)	TiO ₂ (%)
F	24 B	8.9116	0.3373	2.0644	4.8442	1.1037	0.0000	0.2146	81.7579	0.2759
	11 B	8.9033	0.5436	1.9284	4.9748	1.1180	0.0000	0.2462	81.2373	0.3282
	STF 9*	15.1480	0.1649	3.3800	11.1291	0.9790	0.1030	0.1030	68.2175	0.4946
	TF 9*	16.5847	0.0509	0.9259	15.2620	0.2035	0.0000	0.0000	66.2371	0.3358
	23 B	9.7173	0.3561	2.4624	5.0876	1.5263	0.0916	0.1933	79.4685	0.3968
	10 B	9.9972	0.3258	2.4433	5.3447	1.5271	0.0000	0.1629	79.1019	0.3970
	25 B	8.7408	0.1015	3.1369	3.9795	0.8934	0.0000	0.0711	82.3318	0.3249
	STF 8*	16.4608	0.2813	2.1357	12.6061	1.6878	0.0729	0.1250	65.9474	0.3230
	TF8*	16.4573	0.1124	1.6968	14.2085	1.1755	0.0920	0.0511	65.3181	0.3578
	22 B	7.8856	0.0927	2.7795	3.5825	0.7206	0.0824	0.0000	84.2086	0.2882
	9B	7.4257	0.1030	2.3791	3.3473	0.7106	0.0000	0.0515	85.1747	0.2678
	Avg Sh	16.7000	2.2000	2.8000	3.6000	2.6000	1.6000	0.1600	58.9000	0.7800

Facies	SAMPLE NAME	Al (%)	Ca (%)	Fe (%)	K (%)	Mg (%)	Na (%)	P (%)	Si (%)	Ti (%)
F	24 B	4.7165	0.2410	1.4439	4.0214	0.6656	0.0000	0.0937	38.2168	0.1654
	11 B	4.7121	0.3885	1.3488	4.1298	0.6742	0.0000	0.1074	37.9735	0.1968
	STF 9*	8.0171	0.1178	2.3641	9.2388	0.5903	0.0764	0.0450	31.8875	0.2965
	TF 9*	8.7775	0.0364	0.6476	12.6697	0.1227	0.0000	0.0000	30.9618	0.2013
	23 B	5.1429	0.2545	1.7223	4.2235	0.9204	0.0679	0.0844	37.1467	0.2379
	10 B	5.2910	0.2328	1.7089	4.4369	0.9209	0.0000	0.0711	36.9753	0.2380
	25 B	4.6261	0.0726	2.1941	3.3036	0.5387	0.0000	0.0310	38.4851	0.1948
	STF 8*	8.7119	0.2010	1.4938	10.4649	1.0178	0.0541	0.0546	30.8264	0.1936
	TF8*	8.7100	0.0804	1.1868	11.7951	0.7089	0.0682	0.0223	30.5322	0.2145
	22 B	4.1734	0.0662	1.9441	2.9740	0.4346	0.0611	0.0000	39.3624	0.1728
	9B	3.9301	0.0736	1.6640	2.7787	0.4285	0.0000	0.0225	39.8140	0.1605
	Avg Sh	8.8385	1.5723	1.9584	2.9885	1.5679	1.1870	0.0698	27.5322	0.4676

Table-3: Major element concentration (Oxide forms are represented in weight % and element forms are both in weight % and ppm) in facies F (Upper Segment).

Facies	SAMPLE NAME	Al ppm	Ca ppm	Fe ppm	K ppm	Mg ppm	Na ppm	P ppm	Si ppm	Ti ppm
F	24 B	47164.7797	2410.3381	14439.0003	40213.6027	6655.8976	0.0000	936.6225	382168.2200	1654.2395
	11 B	47120.6818	3885.3524	13487.5827	41297.7979	6742.1730	0.0000	1074.3531	379734.6950	1967.7735
	STF 9*	80170.8649	1178.3707	23640.5464	92388.1573	5903.4296	764.4652	449.7210	318875.0070	2965.3350
	TF 9*	87774.7376	363.5923	6476.0137	126697.0520	1227.1382	0.0000	0.0000	309617.9860	2012.9323
	23 B	51429.1077	2545.2847	17222.8657	42234.6537	9204.0386	679.3704	843.7294	371466.7180	2379.0497
	10 B	52910.1367	2328.3061	17089.2526	44369.0382	9208.7399	0.0000	710.8719	369752.9700	2380.2649
	25 B	46260.6322	725.5563	21940.7426	33036.0257	5387.3183	0.0000	310.1347	384850.9150	1947.5638
	STF 8*	87119.0088	2010.3992	14938.0577	104648.8660	10177.7647	541.0188	545.6084	308263.9970	1936.2027
	TF8*	87100.4243	803.6182	11868.2562	117951.2400	7088.8174	682.4886	223.0531	305322.2890	2144.8441
	22 B	41734.3531	662.1710	19440.7543	29739.7611	4345.5476	610.9609	0.0000	393623.9150	1728.0498
	9B	39300.8433	736.0873	16640.3714	27787.1036	4285.4580	0.0000	224.7401	398139.5950	1605.3630
	Avg Sh	88384.9170	15723.4220	19584.1240	29885.2920	15678.9360	11869.7120	698.2736	275321.5710	4676.1624

Table-3: Major element concentration (Oxide forms are represented in weight % and element forms are both in weight % and ppm) in facies F (Upper Segment).

	Facies	Sample	Li	Be	Sc	V	Cr	Mn	Co
D	Galuconitic sandstone	S 41	43.2855	3.5550	13.0288	57.2151	51.4950	60.6891	14.0067
		S 39	107.2001	4.4372	8.7157	34.1390	38.3212	49.2821	32.0518
	Shale	RKI4 Sh6	17.0069	2.2889	7.8101	28.6324	28.2848	24.8392	16.4980
		RKI4 Sh5	38.3273	3.1876	11.3782	48.9139	54.2428	62.8760	18.5914
	Galuconitic siltstone	S 38	41.4711	2.5932	8.2836	42.4003	46.1412	47.0174	28.5501
	Shale	RKI4 Sh4	42.4242	3.7467	13.3452	55.8376	59.8121	81.5505	16.0155
	Galuconitic siltstone	S 37	56.7835	4.7310	15.9924	70.3588	69.5652	81.9322	11.1349
		S 36	45.2544	2.5394	7.9386	33.1979	37.0812	40.4933	15.5377
	Shale	RKI4 Sh3	36.8843	3.1606	12.8069	71.1826	71.3026	71.5516	13.6672
	Galuconitic siltstone	S 31	36.0236	1.8899	9.3669	45.7986	56.3775	60.6316	37.4386
	Shale	RKI4 Sh2	33.5383	3.3983	13.5561	67.2953	66.7967	109.0014	12.6979
C		RKI4 Sh1	47.4843	3.7627	15.9767	69.7681	85.2606	74.1111	11.1744
	Shale	RKI3 Sh8	38.0574	4.4214	17.5486	78.8864	88.1402	89.0814	13.7049
		RKI3 Sh7	33.2457	3.9640	17.6098	81.5247	91.9816	89.5184	19.7268
		RKI3 Sh6	29.5272	3.3867	14.3571	72.5702	80.1058	71.0671	22.6011
		RKI3 Sh5	38.3763	3.5320	13.9436	72.8500	75.5778	92.8437	15.0991
		RKI3 Sh4	44.8863	3.6708	13.6860	69.2103	74.8501	99.8287	24.9730
		RKI3 Sh2	46.2894	3.1384	12.2851	61.1363	65.0191	72.5449	22.1760
		RKI3 Sh0	61.2249	4.1972	14.1304	76.7294	77.3787	88.9178	15.6473
	Galuconitic sandstone	S 23	292.9291	5.9075	8.0363	26.2585	26.0663	23.7093	70.5729
		S 19	534.3365	10.1940	10.9228	35.8357	26.7348	12.7796	44.5089
B	Shale	RKI2 ShC	62.4735	4.3495	13.8865	72.8617	72.2247	95.1941	21.9461
		RKI2 ShB	50.4817	3.9900	14.3667	71.6984	73.0624	82.9441	25.5727
		RK/33a	0.0000	0.0000	6.6682	31.9946	39.8789	0.0000	31.8259
		Rk/33c	0.0000	0.0000	5.1367	23.9493	21.5949	0.0000	10.6894
	glauconitic Sandstone	S 18	667.4661	13.3207	14.6277	48.6637	47.7473	36.6352	49.6453
		S 16	48.2521	3.8940	12.5676	61.8351	60.3125	53.3668	20.7498
	Shale	RKI2 ShA2	50.4409	3.5838	12.7458	65.1388	64.8045	72.8086	20.5776
		RKI2 ShA1	48.7642	2.5389	10.8666	55.8248	53.5861	64.0214	20.0232
		RKI2 ShA	53.8654	4.2894	12.9951	72.9138	79.3953	68.9376	17.7042
	Green Shale	S 13 d	285.0930	5.3274	8.5373	7.8229	1.6816	21.1567	6.5590
		S 13 c	327.2033	6.4258	10.4096	9.4329	1.5512	25.9341	9.5361
		S 13 b	330.0205	7.2766	9.8533	9.6296	1.2699	23.9766	9.5344
		S 13 a	275.9262	6.2417	8.4889	7.4205	2.0126	25.2446	6.6165
A	Shale	RKI1 Sh2	24.8951	1.3781	7.7511	27.3783	61.2602	119.1080	93.6939
		RKI1 Sh1	25.6561	1.4181	7.6934	26.9184	59.4887	117.7847	95.3426
		Average Shale	66.0000	3.0000	13.0000	130.0000	90.0000	850.0000	19.0000

Table 4: Trace and REE concentration (ppm) in Lower and Middle segment comprising facies A, B, C and D.

	Facies	Sample	Ni	Cu	Zn	Ga	Rb	Sr	Y
D	Galuconitic sandstone	S 41	19.9695	1.5881	0.0000	22.3902	250.7864	14.6596	17.0942
		S 39	14.4478	11.2239	0.0000	16.1566	184.2417	14.9173	15.7542
	Shale	RKI4 Sh6	11.1690	1.2705	18.3333	23.9147	168.5933	11.1756	33.2784
		RKI4 Sh5	19.7672	3.4721	43.2119	24.4435	207.5525	18.2618	31.7839
	Galuconitic siltstone	S 38	18.6985	20.8525	33.9564	19.9118	192.9867	23.1737	19.7267
	Shale	RKI4 Sh4	19.2080	1.6526	36.9024	28.7783	223.6959	20.1876	50.9875
	Galuconitic siltstone	S 37	19.5456	3.5862	0.0000	24.0104	258.0191	21.1968	21.6972
		S 36	15.3193	22.7752	28.3483	16.0658	154.6781	22.7683	24.4794
	Shale	RKI4 Sh3	26.7586	2.9952	51.4332	27.2491	237.1199	23.5477	27.1996
	Galuconitic siltstone	S 31	18.9942	4.8222	36.4962	18.3125	151.8832	19.9136	29.0374
C	Shale	RKI4 Sh2	22.9435	1.8223	43.5569	27.9853	245.8112	19.3692	27.2184
		RKI4 Sh1	23.0198	24.2481	49.5027	27.4431	239.3895	27.7712	30.6635
		RKI3 Sh8	22.9229	1.5202	51.2941	31.4343	260.2522	25.2213	40.7615
		RKI3 Sh7	31.8412	2.5389	49.7816	33.7267	266.0268	24.4382	43.5257
		RKI3 Sh6	28.8102	3.9382	48.7339	29.4936	233.3825	21.1954	36.8050
		RKI3 Sh5	24.3415	5.9167	46.1739	26.5299	237.2679	22.2568	34.9251
		RKI3 Sh4	24.8930	4.9144	55.8554	28.4888	239.3194	25.7361	36.5080
		RKI3 Sh2	20.3422	4.1448	52.5289	23.5379	214.7234	27.6241	34.4706
		RKI3 Sh0	24.0883	2.1570	48.6427	29.1228	250.7000	25.4072	34.9351
	Galuconitic sandstone	S 23	7.9218	107.5438	0.0000	13.8184	120.4024	9.0966	10.6659
		S 19	6.3883	67.8812	0.0000	18.5931	160.5936	5.6930	6.7700
B	Shale	RKI2 ShC	25.4045	3.2359	48.0431	28.3181	246.5221	23.3250	38.5072
		RKI2 ShB	25.8350	3.7410	47.2071	26.7657	234.5343	27.0427	37.7477
		RK/33a	17.2820	11.4285	14.4131	15.4192	138.2394	10.6050	16.3122
		Rk/33c	11.2453	7.7890	13.3118	16.8255	133.3293	7.4773	7.0000
	glauconitic Sandstone	S 18	10.1783	266.5088	0.0000	25.9494	240.1255	11.3705	13.1300
		S 16	23.0644	11.5418	0.0000	21.2545	203.0107	21.2854	30.9204
	Shale	RKI2 ShA2	24.1811	4.2492	42.2385	26.3912	215.9898	25.0756	37.3645
		RKI2 ShA1	22.2668	2.4170	42.4720	22.6043	171.3332	23.2044	29.1604
		RKI2 ShA	20.7710	20.6329	53.6766	27.2313	225.5831	22.2354	47.9184
	Green Shale	S 13 d	7.7219	3.8612	BDL	40.7625	279.4162	4.7746	69.4396
		S 13 c	13.2801	4.2732	BDL	41.3868	321.9490	3.6102	61.4225
		S 13 b	13.6986	4.4442	BDL	42.5078	308.9473	3.9057	69.0691
		S 13 a	7.7030	3.7618	BDL	38.0824	277.0127	4.4656	65.5567
A	Shale	RKI1 Sh2	12.8764	10.8560	18.7012	18.0170	124.8570	21.3783	23.8659
		RKI1 Sh1	12.5514	10.9838	22.4174	18.5995	123.3881	21.0553	23.0594
		Average Shale	68.0000	45.0000	95.0000	19.0000	140.0000	300.0000	41.0000

Table 4: Trace and REE concentration (ppm) in Lower and Middle segment comprising facies A, B, C and D.

Facies		Sample	Zr	Nb	Mo	Cd	Sn	Sb	Cs
D	Galuconitic sandstone	S 41	116.5567	9.9870	0.0000	0.0332	3.8123	0.0000	10.5429
		S 39	199.3134	5.2029	0.0000	0.0396	1.9358	0.0000	8.6152
	Shale	RKI4 Sh6	150.0511	9.6157	0.5031	0.1158	3.1808	2.8099	5.8181
		RKI4 Sh5	182.7919	12.9334	0.2145	0.1279	4.0869	0.9694	10.6867
	Galuconitic siltstone	S 38	215.3271	9.7922	0.1239	0.1629	3.6440	0.7415	12.3643
	Shale	RKI4 Sh4	256.3326	16.8642	0.1922	0.1628	4.6578	0.9430	11.7339
	Galuconitic siltstone	S 37	142.8803	12.3827	0.0000	0.0299	4.2300	0.0000	14.4789
		S 36	202.0754	12.8533	0.0857	0.1944	4.8215	0.5010	8.4101
	Shale	RKI4 Sh3	145.1443	11.7001	0.1644	0.1153	4.7575	1.4509	12.5792
	Galuconitic siltstone	S 31	291.6052	11.7703	0.3221	0.1886	3.6425	0.7373	8.2467
C	Shale	RKI4 Sh2	135.1660	14.8090	0.2780	0.1094	4.8884	8.2879	12.3356
		RKI4 Sh1	151.4211	12.9904	0.1719	0.1099	4.7210	1.3752	12.3674
		RKI3 Sh8	176.2225	14.6551	0.1412	0.1213	5.5067	1.0417	13.7393
		RKI3 Sh7	193.1951	15.7728	0.1668	0.1553	5.4917	2.2260	8.7667
		RKI3 Sh6	149.1387	12.8293	0.1740	0.1085	4.5668	0.7582	8.5603
		RKI3 Sh5	161.7432	14.3424	0.1465	0.1150	5.0792	0.6762	12.3848
		RKI3 Sh4	187.7710	14.7615	4.0185	0.1352	4.9201	0.8196	12.2449
		RKI3 Sh2	219.3449	13.9331	0.6358	0.1813	4.3555	0.7812	9.7825
		RKI3 Sh0	174.2055	24.4243	0.3962	0.1333	7.5044	0.9664	12.2723
	Galuconitic sandstone	S 23	81.6278	0.6537	0.0000	0.0264	0.9887	0.0000	4.6705
		S 19	55.8465	0.5118	0.0000	0.0267	1.1753	0.0000	7.4495
B	Shale	RKI2 ShC	182.0458	27.4445	0.1955	0.1354	5.2903	0.8673	12.5445
		RKI2 ShB	210.6949	15.2420	0.2013	0.1648	4.9211	0.7698	9.0510
		RK/33a	122.3328	7.7890	0.7969	0.0000	0.0000	0.0000	5.3233
		Rk/33c	47.5456	2.0121	0.2531	0.0000	0.0000	0.0000	4.2221
	glauconitic Sandstone	S 18	179.9479	4.0455	0.0000	0.0551	1.8094	0.0000	8.2450
		S 16	169.2649	10.8420	0.0000	0.0434	3.9788	0.0000	6.0627
	Shale	RKI2 ShA2	212.0601	14.3120	0.1592	0.1419	4.3397	0.7063	7.0946
		RKI2 ShA1	181.0981	13.8885	0.2686	0.1342	4.0346	0.7996	6.7909
		RKI2 ShA	183.6636	15.8451	0.4629	0.1502	4.9825	1.0884	10.0772
	Green Shale	S 13 d	388.2692	21.5103	BDL	0.0983	6.1728	BDL	1.6939
		S 13 c	395.9777	35.0997	8.6917	0.1473	7.0937	BDL	1.9409
		S 13 b	420.3556	25.7931	BDL	0.0777	6.4994	BDL	2.0018
		S 13 a	383.2105	22.3396	BDL	0.0834	6.0007	BDL	1.5959
A	Shale	RKI1 Sh2	313.0953	1.4337	0.3924	0.2127	2.3602	1.8236	2.5444
		RKI1 Sh1	316.0276	3.1315	0.7591	0.2114	2.3429	1.7221	2.4369
		average Shale	160.0000	18.0000	2.6000	0.8000	6.0000	1.5000	5.5000

Table 4: Trace and REE concentration (ppm) in Lower and Middle segment comprising facies A, B, C and D.

	Facies	Sample	Ba	La	Ce	Pr	Nd	Sm	Eu
D	Galuconitic sandstone	S 41	266.8204	29.3899	35.8581	4.3052	14.6519	2.5104	0.4529
		S 39	267.1777	24.0937	48.2143	5.6888	22.1937	3.5281	0.6646
	Shale	RKI4 Sh6	216.4715	67.5545	139.0129	23.4495	77.8917	15.5467	2.0650
		RKI4 Sh5	325.3823	51.2957	110.3324	14.8013	53.5307	9.8630	1.5780
	Galuconitic siltstone	S 38	353.5723	40.8276	76.0343	8.8776	35.0841	5.3779	0.9406
	Shale	RKI4 Sh4	344.3422	47.4486	106.5058	13.8725	47.5622	10.3593	1.7390
	Galuconitic siltstone	S 37	344.4787	41.4377	71.4478	7.5203	26.8983	4.7263	0.7591
		S 36	367.1930	22.3966	45.1937	5.7802	20.3946	4.3236	0.8865
	Shale	RKI4 Sh3	449.4572	46.8990	85.7139	8.9256	36.1756	6.1190	1.1357
	Galuconitic siltstone	S 31	345.7054	36.1575	72.6145	9.1086	31.3675	6.2195	1.1503
	Shale	RKI4 Sh2	345.2710	46.5354	87.4119	10.3382	40.2271	7.1961	1.2447
C		RKI4 Sh1	367.0389	46.1473	81.7208	10.5764	35.0931	7.1399	1.2989
	Shale	RKI3 Sh8	442.0602	54.5825	107.5908	13.4944	43.0664	9.1666	1.6317
		RKI3 Sh7	463.0365	64.7506	120.9644	18.1877	59.8137	11.7305	2.0084
		RKI3 Sh6	364.2990	56.8198	119.8195	16.1394	54.8894	10.6596	1.8035
		RKI3 Sh5	433.9965	45.6421	86.0128	10.3432	35.8835	7.3328	1.3519
		RKI3 Sh4	419.3510	49.0986	99.3552	11.9691	41.5943	8.4042	1.4800
		RKI3 Sh2	442.8763	42.0194	83.4342	10.4423	34.6909	7.2402	1.3596
		RKI3 Sh0	424.4506	49.0809	92.4907	10.5283	36.7314	7.1159	1.2756
	Galuconitic sandstone	S 23	111.9166	14.1344	37.0353	4.1820	14.8069	2.7843	0.4686
		S 19	67.8964	12.7895	27.8228	3.8788	14.3108	2.5585	0.3945
B	Shale	RKI2 ShC	400.7225	55.5945	101.2601	14.7274	50.9609	10.1154	1.6920
		RKI2 ShB	445.6192	50.9060	93.6773	11.5595	39.8040	7.9839	1.4527
		RK/33a	193.1588	19.5893	59.4589	5.1554	18.4586	3.7954	0.6619
		Rk/33c	109.5718	13.0293	41.3977	4.2540	15.5957	3.0289	0.4528
	glauconitic Sandstone	S 18	139.2757	22.2350	49.1510	6.6351	25.3288	4.3571	0.7434
		S 16	359.8641	56.8204	76.0442	11.3484	41.9741	7.0158	1.3456
	Shale	RKI2 ShA2	428.1355	55.0212	91.1012	14.0148	49.7189	9.6590	1.6502
		RKI2 ShA1	365.6591	42.9992	87.9547	10.8514	36.0683	7.3280	1.2789
		RKI2 ShA	355.5810	59.2147	74.7723	13.7397	42.6641	9.1531	1.6589
	Green Shale	S 13 d	73.7137	65.6159	152.1389	18.2414	67.2767	11.8445	1.7715
		S 13 c	57.5141	63.6167	139.8201	17.2943	67.7017	12.2982	1.9129
		S 13 b	55.3521	67.4742	148.2406	18.4419	68.0701	12.5202	1.8265
		S 13 a	73.3472	67.4634	157.7598	17.9677	64.2685	12.1363	1.7436
A	Shale	RKI1 Sh2	314.4221	52.7820	130.7959	13.6001	47.1036	8.1617	1.1897
		RKI1 Sh1	316.3696	53.0885	129.3610	14.0539	46.7132	8.2763	1.1710
		average Shale	580.0000	40.0000	95.0000	9.7000	39.0000	7.3000	1.6000

Table 4: Trace and REE concentration (ppm) in Lower and Middle segment comprising facies A, B, C and D.

	Facies	Sample	Gd	Tb	Dy	Ho	Er	Tm	Yb
D	Galuconitic sandstone	S 41	2.3064	0.4064	2.5593	0.5494	1.6302	0.2758	1.6921
		S 39	2.9235	0.4092	2.4257	0.4895	1.4805	0.2292	1.4579
	Shale	RKI4 Sh6	11.5181	1.2789	6.0718	1.1941	3.6355	0.5066	3.3235
		RKI4 Sh5	8.4677	1.0846	5.6458	1.1537	3.3938	0.4874	3.2489
	Galuconitic siltstone	S 38	4.7008	0.6259	3.3664	0.7033	2.1226	0.3116	2.1262
	Shale	RKI4 Sh4	9.9115	1.4177	8.2123	1.6444	4.8034	0.6731	4.3247
	Galuconitic siltstone	S 37	4.0782	0.6063	3.6443	0.7419	2.1131	0.3338	2.1129
		S 36	4.2902	0.7124	4.4097	0.9090	2.7303	0.3999	2.7079
	Shale	RKI4 Sh3	6.0590	0.8513	4.7665	0.9394	2.7099	0.3937	2.6304
	Galuconitic siltstone	S 31	5.9417	0.8494	4.8934	0.9918	3.0173	0.4438	2.9377
	Shale	RKI4 Sh2	6.4489	0.8750	4.7134	0.9465	2.7892	0.4008	2.6732
		RKI4 Sh1	6.8885	0.9735	5.3195	1.0639	3.0527	0.4525	2.8665
C	Shale	RKI3 Sh8	8.8491	1.2519	7.0746	1.4007	4.1242	0.5617	3.7779
		RKI3 Sh7	10.5550	1.3701	7.0561	1.4318	4.1486	0.6032	3.8415
		RKI3 Sh6	9.4245	1.1835	6.0441	1.1826	3.3423	0.4655	3.0152
		RKI3 Sh5	7.4459	1.0279	5.8491	1.1375	3.3722	0.4781	3.0591
		RKI3 Sh4	7.8407	1.0763	5.9945	1.2159	3.5208	0.5057	3.3825
		RKI3 Sh2	6.9392	0.9968	5.5565	1.1492	3.2658	0.4807	3.1442
		RKI3 Sh0	6.9075	0.9630	5.6437	1.1184	3.4269	0.4708	3.1419
	Galuconitic sandstone	S 23	2.2627	0.3192	1.8173	0.3552	1.0061	0.1505	0.9299
		S 19	1.8985	0.2131	1.1668	0.2214	0.6051	0.0989	0.5784
B	Shale	RKI2 ShC	8.8643	1.1519	6.0754	1.2015	3.4379	0.4935	3.1567
		RKI2 ShB	7.6053	1.0901	5.9232	1.2203	3.4946	0.5198	3.3225
		RK/33a	3.6871	0.5344	3.0093	0.5830	1.6540	0.2545	1.6209
		Rk/33c	2.7102	0.3183	1.4682	0.2590	0.7101	0.0972	0.5993
	glauconitic Sandstone	S 18	3.3745	0.4140	2.1267	0.4422	1.2714	0.1917	1.2090
		S 16	6.3464	0.8625	4.9260	0.9421	2.8120	0.3932	2.4732
	Shale	RKI2	8.4597	1.1045	5.9097	1.1798	3.4619	0.4851	3.1729
		RKI2 ShA	6.6377	0.8694	4.6401	0.9753	2.7511	0.4116	2.6880
		RKI2 ShA	9.0680	1.2572	6.7920	1.3605	3.8415	0.5293	3.3023
	Green Shale	S 13 d	10.0488	1.4348	9.0811	2.0591	6.1973	0.9387	5.6507
		S 13 c	10.1351	1.4865	9.4135	1.9482	5.6705	0.9448	5.7774
		S 13 b	10.6310	1.4845	9.1340	1.9411	5.8654	0.8929	5.4529
		S 13 a	9.7556	1.4578	8.9108	1.9953	5.9136	0.9141	6.4013
A	Shale	RKI1 Sh2	6.5241	0.7182	3.6366	0.7722	2.3674	0.3655	2.4254
		RKI1 Sh1	6.4892	0.6965	3.6210	0.7344	2.3324	0.3442	2.3599
		average Shale	7.0000	1.2000	5.5000	1.6000	3.9000	0.6000	3.7000

Table 4: Trace and REE concentration (ppm) in Lower and Middle segment comprising facies A, B, C and D.

	Facies	Sample	Lu	Hf	Ta	Pb	Bi	Th	U
D	Galuconitic sandstone	S 41	0.2694	2.4001	0.2480	2.4101	0.0000	11.0436	1.9614
		S 39	0.2310	3.9685	0.0000	4.1343	0.3251	12.5121	2.1071
	Shale	RKI4 Sh6	0.4910	4.6031	1.0277	3.4386	1048.6095	15.2077	3.3056
		RKI4 Sh5	0.4746	5.3503	1.5447	7.3338	1961.1638	17.5530	3.0858
	Galuconitic siltstone	S 38	0.3172	5.8190	1.3579	7.7965	1829.1068	13.8647	2.1838
	Shale	RKI4 Sh4	0.6539	6.3502	1.3998	6.0764	2536.0281	19.1586	3.5998
	Galuconitic siltstone	S 37	0.3209	2.9517	0.4366	4.7278	0.0000	15.5042	2.6790
		S 36	0.3951	6.5938	2.2355	10.2774	4750.9297	21.6229	3.2229
	Shale	RKI4 Sh3	0.3833	3.9902	1.2081	5.6413	2173.2299	15.1028	2.6654
	Galuconitic siltstone	S 31	0.4480	7.4808	1.1870	11.7889	1937.4550	18.3505	3.3750
	Shale	RKI4 Sh2	0.3875	3.8410	10.0494	6.5798	2122.5482	15.1975	2.4905
		RKI4 Sh1	0.4380	4.0766	1.0722	6.4678	2094.7651	16.8674	2.8189
C	Shale	RKI3 Sh8	0.5541	4.4971	1.1515	6.0073	660.7736	18.3259	3.6466
		RKI3 Sh7	0.5807	5.0312	1.3461	7.3108	1186.5057	19.3207	3.6140
		RKI3 Sh6	0.4390	3.8652	1.2145	12.9916	2192.4502	14.1734	2.7046
		RKI3 Sh5	0.4530	4.1901	1.1564	8.0773	2025.9704	15.3810	2.8289
		RKI3 Sh4	0.4867	4.8548	1.2530	12.3441	2193.0125	16.3641	3.1284
		RKI3 Sh2	0.4589	5.5192	1.0950	9.1819	1413.6895	16.3677	3.0324
		RKI3 Sh0	0.4605	4.4555	36.1326	5.6820	1796.1858	15.8617	2.8557
	Galuconitic sandstone	S 23	0.1453	1.5537	0.0000	15.9068	1.1970	17.1255	3.0654
		S 19	0.0884	1.0231	0.0000	3.7365	0.0648	5.8890	1.1807
B	Shale	RKI2 ShC	0.4731	4.2644	25.9496	6.2370	2647.8008	14.6067	2.8845
		RKI2 ShB	0.4905	5.1459	1.4486	6.6869	2106.4627	16.5568	3.0622
		RK/33a	0.2349	2.8998	0.2808	25.4258	0.0000	8.6478	1.9397
		Rk/33c	0.0858	1.0903	0.0229	14.3182	0.0000	3.4270	0.6396
	glauconitic Sandstone	S 18	0.1955	3.3622	0.0000	5.9503	1.5367	12.4295	2.3310
		S 16	0.3704	3.6222	0.1465	6.9959	0.0000	16.3821	3.0369
	Shale	RKI2 ShA2	0.4728	4.9987	1.1982	6.9881	2017.8135	14.9129	2.8457
		RKI2 ShA1	0.3990	4.2365	1.1769	11.1838	1952.0758	13.4633	2.5054
		RKI2 ShA	0.4903	4.2703	1.1655	12.2735	2259.1264	15.2840	2.8705
	Green Shale	S 13 d	0.9185	9.5303	0.5760	2.6271	BDL	28.3670	16.3209
		S 13 c	0.7972	12.3871	2.8304	2.2158	1.8629	30.3670	8.4405
		S 13 b	0.7892	9.8381	1.1393	2.0099	BDL	34.3670	6.4105
		S 13 a	0.7948	9.6131	0.5803	2.6894	BDL	43.1854	26.4723
A	Shale	RKI1 Sh2	0.3589	7.4701	0.5600	23.2240	1061.9550	14.1612	3.2723
		RKI1 Sh1	0.3611	7.4589	0.9563	22.1695	1079.6597	14.2569	3.3372
		average Shale	0.7000	2.8000	2.0000	20.0000	0.1000	12.0000	3.7000

Table 4: Trace and REE concentration (ppm) in Lower and Middle segment comprising facies A, B, C and D.

				Provenance												
Facies		Sample	LREE/HREE	Fe/Al	Si/Al	Fe/Ti	Al/(Al+Fe+Mn)	GdN/YbN	Eu/Eu*	Y/Ni	Cr/V	La/Th	REE Total	La/Yb	Zr/Sc	Th/Sc
D	Galuconitic sandstone	S 41	8.9967	0.2438	3.8342	9.8151	0.8035	0.7205	0.8408	0.856	0.9	2.6613	96.8575	17.3693	8.9461	0.8476
		S 39	10.8209	0.3057	4.8568	8.8224	0.7655	1.0599	0.9221	1.0904	1.1225	1.9256	114.0296	16.5262	22.8682	1.4356
	Shale	RK14 Sh6	11.6176	0.1362	4.463	9.2698	0.8799	1.8319	0.6838	2.9795	0.9879	4.4421	353.54	20.3264	19.2125	1.9472
		RK14 Sh5	10.0766	0.3431	3.9038	11.3766	0.7441	1.3776	0.7703	1.6079	1.1089	2.9223	265.3575	15.7884	16.0651	1.5427
	Galuconitic siltstone	S 38	11.7095	0.3365	5.4433	10.6429	0.7478	1.1686	0.8349	1.055	1.0882	2.9447	181.4161	19.2018	25.9943	1.6737
	Shale	RK14 Sh4	7.1897	0.2891	3.6537	9.8185	0.7752	1.2114	0.7668	2.6545	1.0712	2.4766	259.1284	10.9717	19.2078	1.4356
	Galuconitic siltstone	S 37	10.9515	0.363	3.3513	10.6415	0.7332	1.0202	0.7714	1.1101	0.9887	2.6727	166.7409	19.6114	8.9343	0.9695
		S 36	5.9787	0.3439	4.8032	12.8352	0.7438	0.8374	0.9195	1.5979	1.117	1.0358	115.5295	8.2708	25.4549	2.7238
	Shale	RK14 Sh3	9.8737	0.4092	3.9616	12.5638	0.7092	1.2176	0.8332	1.0165	1.0017	3.1053	203.7022	17.8298	11.3333	1.1793
	Galuconitic siltstone	S 31	8.0222	0.374	5.4285	10.2559	0.7273	1.0691	0.8454	1.5288	1.231	1.9704	176.141	12.3079	31.1314	1.9591
C	Shale	RK14 Sh2	10.0316	0.3572	3.9717	11.7558	0.7361	1.2751	0.8159	1.1863	0.9926	3.062	212.188	17.408	9.9709	1.1211
		RK14 Sh1	8.6429	0.3812	3.7807	12.1568	0.7236	1.2702	0.8275	1.3321	1.2221	2.7359	203.0315	16.0987	9.4776	1.0558
		RK13 Sh8	8.3181	0.3275	3.2451	10.5258	0.7528	1.2381	0.8094	1.7782	1.1173	2.9784	257.1265	14.4479	10.042	1.0443
		RK13 Sh7	9.3776	0.317	3.5621	10.0703	0.7588	1.4523	0.806	1.367	1.1283	3.3514	307.0424	16.8555	10.9709	1.0972
		RK13 Sh6	10.3652	0.3323	3.3649	10.576	0.7502	1.6521	0.8033	1.2775	1.1038	4.0089	285.2279	18.8443	10.3878	0.9872
		RK13 Sh5	8.1746	0.3374	3.7844	9.4537	0.7471	1.2866	0.8171	1.4348	1.0374	2.9674	209.389	14.9203	11.5998	1.1031
		RK13 Sh4	8.8207	0.3383	3.8854	10.4219	0.7466	1.2253	0.8145	1.4666	1.0815	3.0004	235.9245	14.5157	13.7199	1.1957
	RK13 Sh2	8.1481	0.2769	4.2486	8.3901	0.7826	1.1665	0.857	1.6945	1.0635	2.5672	201.1778	13.3641	17.8546	1.3323	
	RK13 Sh0	8.9109	0.3019	3.6142	9.36	0.7675	1.1621	0.8129	1.4503	1.0085	3.0943	219.3556	15.6213	12.3284	1.1225	
	Galuconitic sandstone	S 23	10.508	0.3993	9.1471	14.4933	0.7144	1.2862	0.8313	1.3464	0.9927	0.8253	80.3978	15.2003	10.1574	2.131
S 19		12.6792	0.4917	7.7116	34.5807	0.6702	1.735	0.7932	1.0597	0.746	2.1717	66.6255	22.1124	5.1128	0.5391	
B	Shale	RK12 ShC	9.429	0.3002	3.608	9.8916	0.7685	1.4843	0.7975	1.5158	0.9913	3.8061	259.2044	17.6117	13.1095	1.0519
		RK12 ShB	8.6783	0.3086	4.0591	8.8273	0.7636	1.2099	0.8329	1.4611	1.019	3.0746	229.0496	15.3216	14.6655	1.1524
		RK/33a	9.252	0.462	5.3841	9.7649	0.684	1.2023	0.7905	0.9439	1.2464	2.2652	118.6975	12.0854	18.3458	1.2969
		Rk/33c	12.4448	0.3172	7.5245	8.6303	0.7592	2.3902	0.7056	0.6225	0.9017	3.8019	84.0066	21.7392	9.256	0.6672
	glauconitic Sandstone	S 18	11.7561	0.4908	4.8077	23.7425	0.6705	1.4753	0.8613	1.29	0.9812	1.7889	117.6756	18.3909	12.3019	0.8497
		S 16	10.172	0.3538	3.9352	9.1288	0.7383	1.3563	0.9006	1.3406	0.9754	3.4684	213.6744	22.974	13.4683	1.3035
	Shale	RK12 ShA2	9.1216	0.2832	3.9735	8.1678	0.7788	1.4093	0.8148	1.5452	0.9949	3.6895	245.4116	17.3408	16.6377	1.17
		RK12 ShA1	9.6262	0.3906	4.8816	10.7861	0.7186	1.3053	0.8189	1.3096	0.9599	3.1938	205.8526	15.997	16.6656	1.239
		RK12 ShA	7.5523	0.3121	3.7778	8.3473	0.7617	1.4514	0.8134	2.307	1.0889	3.8743	227.8439	17.9311	14.1333	1.1761
	Green Shale	S 13 d	8.7228	0.1851	3.0632	8.7689	0.8436	0.94	0.7241	8.9926	0.215	2.3131	353.2178	11.6121	45.4794	3.3227
		S 13 c	8.3665	0.1645	2.8075	7.0317	0.8586	0.9273	0.7633	4.6251	0.1644	2.0949	338.8171	11.0113	38.0396	2.9172
		S 13 b	8.7473	0.1881	3.1842	8.5568	0.8415	1.0305	0.706	5.042	0.1319	1.9633	352.7644	12.374	42.6615	3.4879
		S 13 a	8.8907	0.1729	3.0958	7.5011	0.8524	0.8055	0.7131	8.5106	0.2712	1.5622	357.4825	10.5391	45.1423	5.0873
	A	Shale	RK11 Sh2	14.7733	0.2031	7.9789	6.4409	0.8295	1.4218	0.7254	1.8535	2.2375	3.7272	270.8014	21.7622	40.3936
RK11 Sh1			14.9163	0.2117	7.9789	6.4625	0.8237	1.4534	0.7103	1.8372	2.21	3.7237	269.6027	22.4957	41.0775	1.8531

Table 5: Elemental ratio used to interpret the geochemical evolution of facies A, B, C and D (Lower and Middle Segment).

			Provenance		Weathering Intensity				Palaeoclimate				
	Facies	Sample	La/Sc	Ti/Zr	CIA	PIA	CIW	ICV	Mg/Ca	Sr/Cu	Fe/Mn	Al ₂ O ₃ +Na ₂ O+K ₂ O	C value
D	Galuconitic sandstone	S 41	2.2558	18.4457	68.3079	98.9239	99.4139	0.7714	9.2808	9.2309	347.7111	23.9371	1.9207
		S 39	2.7644	12.4032	66.0656	99.9561	99.9786	0.9161	7.0872	1.3291	442.5556	20.4004	1.8424
	Shale	RK14 Sh6	8.6496	7.568	61.837	96.6616	98.649	0.7933	13.1619	8.7959	423.7937	23.608	1.5072
		RK14 Sh5	4.5083	13.9005	68.8951	97.5608	98.6129	0.858	9.2808	5.2595	459.7451	23.103	2.1252
	Galuconitic siltstone	S 38	4.9287	9.6941	68.9588	97.0921	98.3307	0.8499	12.0932	1.1113	472.5076	18.0878	2.0643
	Shale	RK14 Sh4	3.5555	10.156	67.216	97.5102	98.6755	0.8459	8.5426	12.2158	313.4339	24.8517	1.896
	Galuconitic siltstone	S 37	2.5911	22.2435	69.6467	98.9076	99.3738	0.8813	4.773	5.9106	412.7851	25.2704	2.065
		S 36	2.8212	9.4636	64.5597	96.5683	98.3653	0.972	11.5307	0.9997	606.1642	20.887	1.8295
	Shale	RK14 Sh3	3.662	18.6844	71.3883	97.6409	98.5381	0.8675	8.109	7.8619	476.1903	22.0328	2.3591
	Galuconitic siltstone	S 31	3.8601	8.2499	70.2821	96.9724	98.1739	0.8718	25.6488	4.1295	406.9252	17.7334	2.0453
C	Shale	RK14 Sh2	3.4328	18.6659	68.674	97.5236	98.6029	0.8728	9.1121	10.6288	272.106	22.8454	2.2273
		RK14 Sh1	2.8884	17.8704	71.4921	97.7236	98.5863	0.8486	6.7497	1.1453	443.8698	22.8031	2.1372
		RK13 Sh8	3.1104	17.0442	70.9263	97.8535	98.6938	0.8049	10.1245	16.5903	354.9003	25.7125	2.0497
		RK13 Sh7	3.677	14.8479	71.5799	97.8791	98.6821	0.7723	``	9.6254	322.6935	24.0533	2.1703
		RK13 Sh6	3.9576	19.9321	71.9631	97.8718	98.6614	0.7809	21.9365	5.382	442.3804	24.8391	2.2136
		RK13 Sh5	3.2733	19.0224	70.4538	97.564	98.5349	0.8496	10.8628	3.7617	313.2869	23.1196	1.7804
		RK13 Sh4	3.5875	14.6187	69.9916	97.4954	98.5161	0.8555	10.5991	5.2368	286.5694	22.8247	1.7991
		RK13 Sh2	3.4204	11.9692	68.5836	97.3233	98.4905	0.8389	11.4504	6.6648	303.6352	21.9105	1.4645
		RK13 Sh0	3.4734	16.4836	69.2211	97.5503	98.5896	0.849	12.4869	11.779	302.2744	24.297	1.5669
	Galuconitic sandstone	S 23	1.7588	14.4579	70.4806	99.9764	99.9863	0.9978	26.8581	0.0846	721.4258	11.4819	1.3786
B	Shale	S 19	1.1709	12.2548	66.9652	99.9679	99.9837	1.265	34.9085	0.0839	1851.905	13.5769	1.1109
		RK12	4.0035	14.974	69.8408	97.7421	98.6743	0.804	15.4399	7.2083	283.2523	24.2997	1.9066
		RK12	3.5433	13.6104	69.0096	97.3336	98.472	0.8524	10.0191	7.2287	305.1897	22.4545	1.6624
		RK/33a	2.9377	24.2391	66.3997	99.9761	99.9882	1.0122	8.7183	0.9279	0	17.83	3.4015
	glauconitic Sandstone	Rk/33c	2.5365	38.0097	63.02	99.9648	99.9855	0.9786	8.5215	0.96	0	14.74	2.2595
		S 18	1.5201	7.9227	67.409	99.9715	99.9853	1.2266	21.2417	0.0427	923.9461	19.3278	1.2099
		S 16	4.5212	19.0809	70.0609	99.9155	99.9515	0.889	2.8073	1.8442	552.4671	22.4617	1.8305
	Shale	RK12	4.3168	13.724	70.0262	97.6099	98.5847	0.8032	15.9461	5.9012	326.485	22.6446	1.6349
		RK12	3.957	14.1121	68.1513	97.0888	98.3801	0.9663	9.4214	9.6006	430.5717	19.5611	1.7382
		RK12	4.5567	17.6998	70.2495	97.6883	98.622	0.8069	20.7312	1.0777	393.6267	23.3834	2.0361
	Green Shale	S 13 d	7.6858	5.2593	63.6655	99.9795	99.9912	0.9776	25.6126	1.2366	846.3618	28.6993	0.6509
		S 13 c	6.1113	5.9312	60.1175	99.8916	99.9634	1.0572	8.1428	0.8449	636.7982	31.5525	0.5706
		S 13 b	6.8479	4.8798	62.4873	99.9188	99.9675	1.0337	11.7303	0.8788	732.0541	28.2071	0.6005
		S 13 a	7.9472	5.6964	60.1267	99.8925	99.9637	1.0601	9.3531	1.1871	648.6263	29.7592	0.6074
A	Shale	RK11 Sh2	6.8096	4.9453	65.9826	95.9901	97.9317	0.74	14.7649	1.9693	83.7294	14.0628	2.4898
		RK11 Sh1	6.9005	5.0833	65.8616	95.9695	97.9321	0.7536	10.4058	1.9169	88.142	14.0707	2.4741

Table 5: Elemental ratio used to interpret the geochemical evolution of facies A, B, C and D (Lower and Middle Segment).

			Palaeogeography			Palaeosalinity		Palaeoredox		
	Facies	Sample	Zr/Hf	Nb/Ta	Y/Ho	Sr/Ba	Rb/K	Ce/Ce*	V/V+Ni	Th/U
D	Galuconitic sandstone	S 41	48.5625	40.2665	31.1125	0.0549	0.0040	0.6405	0.7413	5.6305
		S 39	50.2241	0.0000	32.1824	0.0558	0.0032	0.8538	0.7026	5.9381
	Shale	RKI4 Sh6	32.5975	9.3568	27.8684	0.0516	0.0023	0.7127	0.7194	4.6006
		RKI4 Sh5	34.1646	8.3729	27.5494	0.0561	0.0036	0.8271	0.7122	5.6883
	Galuconitic siltstone	S 38	37.0044	7.2111	28.0483	0.0655	0.0043	0.8269	0.6940	6.3488
	Shale	RKI4 Sh4	40.3662	12.0476	31.0073	0.0586	0.0034	0.8570	0.7440	5.3221
	Galuconitic siltstone	S 37	48.4060	28.3595	29.2474	0.0615	0.0041	0.8305	0.7826	5.7874
		S 36	30.6461	5.7495	26.9298	0.0620	0.0026	0.8232	0.6842	6.7091
	Shale	RKI4 Sh3	36.3751	9.6843	28.9532	0.0524	0.0047	0.8623	0.7268	5.6662
	Galuconitic siltstone	S 31	38.9804	9.9160	29.2777	0.0576	0.0036	0.8295	0.7068	5.4371
C	Shale	RKI4 Sh2	35.1908	1.4736	28.7560	0.0561	0.0043	0.8255	0.7457	6.1022
		RKI4 Sh1	37.1436	12.1159	28.8224	0.0757	0.0046	0.7667	0.7519	5.9838
		RKI3 Sh8	39.1861	12.7275	29.1018	0.0571	0.0043	0.8219	0.7748	5.0254
		RKI3 Sh7	38.3997	11.7173	30.3990	0.0528	0.0049	0.7289	0.7191	5.3461
		RKI3 Sh6	38.5850	10.5636	31.1227	0.0582	0.0042	0.8178	0.7158	5.2405
		RKI3 Sh5	38.6009	12.4024	30.7047	0.0513	0.0043	0.8203	0.7496	5.4372
		RKI3 Sh4	38.6776	11.7808	30.0253	0.0614	0.0044	0.8498	0.7355	5.2308
		RKI3 Sh2	39.7423	12.7239	29.9959	0.0624	0.0039	0.8258	0.7503	5.3976
		RKI3 Sh0	39.0994	0.6760	31.2369	0.0599	0.0042	0.8421	0.7611	5.5543
	Galuconitic sandstone	S 23	52.5361	0.0000	30.0291	0.0813	0.0043	0.9939	0.7682	5.5868
		S 19	54.5860	0.0000	30.5832	0.0838	0.0043	0.8140	0.8487	4.9878
B	Shale	RKI2 ShC	42.6898	1.0576	32.0489	0.0582	0.0042	0.7330	0.7415	5.0639
		RKI2 ShB	40.9440	10.5222	30.9340	0.0607	0.0042	0.8003	0.7351	5.4068
		RK/33a	42.1870	27.7364	27.9789	0.0549	0.0028	1.2258	0.6493	4.4584
		Rk/33c	43.6066	88.0122	27.0249	0.0682	0.0029	1.1403	0.6805	5.3582
	glauconitic Sandstone	S 18	53.5214	0.0000	29.6894	0.0816	0.0046	0.8345	0.8270	5.3323
		S 16	46.7302	74.0132	32.8200	0.0591	0.0036	0.6180	0.7283	5.3944
	Shale	RKI2 ShA2	42.4230	11.9447	31.6705	0.0586	0.0040	0.6800	0.7293	5.2405
		RKI2 ShA1	42.7467	11.8012	29.8999	0.0635	0.0034	0.8441	0.7149	5.3738
		RKI2 ShA	43.0095	13.5953	35.2212	0.0625	0.0040	0.5434	0.7783	5.3244
	Green Shale	S 13 d	40.7406	37.3412	33.7234	0.0648	0.0032	0.9097	0.5032	1.7381
		S 13 c	31.9670	12.4008	31.5283	0.0628	0.0031	0.8726	0.4153	3.5978
		S 13 b	42.7273	22.6397	35.5818	0.0706	0.0035	0.8698	0.4128	5.3611
		S 13 a	39.8633	38.4980	32.8563	0.0609	0.0028	0.9385	0.4907	1.6313
A	Shale	RKI1 Sh2	41.9130	2.5601	30.9054	0.0680	0.0033	1.0117	0.6801	4.3276
		RKI1 Sh1	42.3690	3.2746	31.4003	0.0666	0.0032	0.9810	0.6820	4.2721

Table 5: Elemental ratio used to interpret the geochemical evolution of facies A, B, C and D (Lower and Middle Segment).

Facies	Sample	Li	Be	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Ga	Ge	Se	Rb	Sr
E	21 B	56.9042	1.8474	5.6854	80.9208	24.8300	321.6013	4.0411	18.5545	13.2481	0.0000	8.7794	1.3260	105.9101	90.3624	27.4315
	20 B	60.4054	1.5116	6.3145	156.7750	34.5121	391.0357	5.2062	28.1961	18.2794	0.0000	11.3614	1.2763	113.3407	114.0043	30.4723
	17 B	55.2106	1.8272	5.8746	133.8762	27.1963	358.1199	8.4670	24.1876	15.4035	0.0000	9.5554	1.2107	107.2032	91.1719	26.9077
	15 B	90.1959	1.9562	5.6854	237.6982	48.1123	147.0420	11.5135	34.4786	20.5379	0.0000	16.4817	1.3538	117.8883	162.2950	22.9702
	SRTF 2	19.4833	0.8994	6.3145	69.0861	11.2244	346.9762	22.9270	13.8163	29.6449	940.5126	8.6783	1.2675	98.0573	86.3206	38.9642
	RTF 2	16.3310	0.1532	5.8746	19.9540	2.6750	76.0692	23.4460	5.4821	35.9114	904.9868	11.8400	0.3724	94.5866	119.2906	14.9665
	13 B	64.7623	2.7280	10.2718	77.7863	42.5201	209.7784	18.3142	27.0413	25.2326	0.0000	14.9286	1.6714	115.9505	143.5080	30.9008
	SRTF 1	49.6079	1.9999	7.3007	55.1879	28.4951	151.8174	12.8751	20.1265	49.6456	4.5256	12.7439	1.6968	89.4450	158.7165	24.2265
	RTF 1	4.9831	0.2412	2.7736	8.5637	2.5534	143.7910	9.3486	2.9834	18.3224	1009.9987	6.0687	1.9505	67.0715	134.8351	41.1761
	12 B	38.6141	1.5278	9.7057	60.9287	31.3072	146.8173	19.5141	22.1799	15.9535	297.9865	10.1207	1.3746	107.5188	98.4484	14.9006
	STF 7	66.0655	2.1375	9.2351	189.1666	34.6633	57.4281	14.1713	45.7096	36.3002	304.5979	15.1276	1.6065	97.9267	162.4091	15.1955
	TF 7	27.7922	0.6663	4.3868	151.2437	3.9206	24.3887	17.3594	25.1683	59.2046	153.0621	8.0420	0.7721	142.0762	160.8320	3.5842
	STF 4	22.0515	1.5182	6.2722	75.2306	14.0488	81.9106	48.5498	27.4266	37.3069	BDL	10.8628	2.6116	105.7965	165.2174	6.4006
	TF 4	7.6481	0.4338	7.0668	30.0296	1.9479	39.1145	15.5278	17.1650	21.8821	237.1284	8.0614	1.7745	73.7681	154.6926	3.6569
	STF 2 (1)	40.5071	1.4137	5.5056	123.1564	27.2269	98.1946	24.3781	40.9468	34.4196	BDL	12.7943	1.7496	82.8434	156.4949	11.6854
	TF 2 (1)	7.0249	0.4226	6.4357	35.1960	2.2150	23.7231	14.2267	18.1184	30.4616	0.0000	6.9588	1.5151	40.1844	151.4412	3.2367
	8 B	57.2716	1.5343	9.0643	161.4482	31.6732	61.4705	9.1126	29.7365	24.3021	6.3876	10.9796	1.1715	102.8703	107.0140	15.4139
	STF 1 b	40.8351	1.4526	8.4686	106.0483	24.4514	108.4048	26.4245	35.8253	23.7098	290.2328	13.4406	1.8142	89.6166	160.9790	10.0609
	TF 1b	26.0358	0.7128	9.3913	91.7823	1.3989	168.4608	16.1194	29.5953	29.9887	206.4899	9.2557	0.9505	43.6173	147.5798	3.1755
	4 B	63.1804	1.2927	4.8859	195.1292	36.6756	93.8464	12.2072	37.8922	24.3111	0.0000	13.2018	1.3634	109.8807	129.4456	22.1144
	STF 1 d	14.9331	0.9118	6.8827	54.6964	7.9505	23.9630	25.2593	9.2075	6.7719	BDL	8.1277	1.3251	92.9730	167.9489	11.5254
	TF 1 d	11.2449	0.4309	7.4138	53.0938	2.0103	14.3163	30.3971	10.1321	8.4636	0.0000	6.8015	1.1248	67.6311	166.9106	4.7427
	1 B	47.7750	1.9012	6.4757	165.9694	32.5316	76.2142	13.9414	57.2071	23.1234	155.8633	11.6721	1.3167	106.9446	106.7715	69.7782
	avg shale	66.00	3.00	13.00	130.00	90.00	850.00	19.00	68.00	45.00	95.00	19.00	1.60	0.60	140.00	300.00

Table 6: Trace and REE concentration (ppm) in facies E of Upper Segment

Facies	Sample	Y	Zr	Nb	Mo	Cd	Sn	Sb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu
E	21 B	13.6031	57.4556	5.1766	0	0.0325	1.1558	0	2.896	150.3632	17.4949	33.2551	3.8211	13.4545	2.5482	0.4931
	20 B	15.6805	67.5646	7.0259	0	0.202	1.5959	0	4.5739	183.7421	22.2883	42.3312	4.4149	16.6046	2.9123	0.5777
	17 B	14.4172	52.834	4.8856	0	0.0713	1.1518	0	3.7794	155.2741	19.92	38.7804	4.1603	14.773	2.7759	0.5366
	15 B	16.7736	121.9521	10.4058	1.4582	0.0343	2.3509	0	7.0883	274.4697	28.7874	48.1619	5.1565	19.1879	3.2783	0.5963
	SRTF 2	22.5031	119.6053	5.6358	0	15.0715	0.5262	0	1.0251	138.2721	15.0682	32.9489	3.7853	14.1501	3.0023	0.6562
	RTF 2	18.348	172.9168	5.4743	0	22.8952	2.4542	0	0.5294	147.3078	4.1917	8.9815	1.219	5.0331	1.2615	0.5724
	13 B	21.6991	112.8754	8.002	0	0.3791	2.1651	0	6.2905	270.4262	32.0646	57.9677	6.2447	23.3312	4.2607	0.7433
	SRTF 1	19.9683	120.8827	7.6052	0	0.137	1.7649	0	5.7975	289.7501	23.3742	46.8821	5.281	18.1408	3.7347	0.663
	RTF 1	36.0758	85.1876	3.7538	0	0.1084	0.0997	0	1.5926	376.0382	30.9632	65.711	8.6371	33.7235	7.8598	1.4457
	12 B	15.1557	73.6693	3.8184	0	0.1658	1.383	0	5.1996	218.1405	22.7231	45.1534	5.0234	17.8643	3.2433	0.5757
	STF 7	28.6019	141.1659	9.7023	2.2471	0.4439	1.8732	0	4.4252	249.8328	26.5463	44.9544	6.2561	21.7529	4.5486	0.8867
	TF 7	13.1127	149.5896	10.4841	9.1053	0.4356	2.9885	0	6.578	170.122	3.8166	21.217	1.5087	5.9621	1.6493	0.414
	STF 4	30.4752	138.6603	3.3346	0	0.068	0.5244	0	1.4968	212.076	41.6304	82.4968	9.3695	36.7413	6.5099	1.2111
	TF 4	41.4133	201.8565	3.75	0	0.0745	BDL	0	0.7689	203.8216	27.8774	60.2442	7.585	31.2796	6.9122	1.7774
	STF 2 (1)	33.3917	162.4816	6.2491	0	0.0689	1.3563	0	2.4985	251.5567	30.103	54.3433	6.11	23.8971	4.6126	0.9652
	TF 2 (1)	35.2435	195.7639	5.7257	0	0.055	BDL	0	0.8111	218.1565	20.8994	47.2832	6.4978	25.351	5.923	1.5063
	8 B	12.6156	64.2405	4.7905	0	0.2495	1.3867	0	4.4618	194.5149	20.3833	38.7826	4.4076	15.4651	2.8711	0.5082
	STF 1 b	34.6637	160.2839	7.9001	2.4465	0.5391	1.4986	0	4.4026	217.7566	28.7594	46.2411	7.4399	27.7753	5.9766	1.2308
	TF 1b	25.8326	182.7379	4.448	0	0.4453	1.4666	0	4.4019	171.0011	8.7734	56.0681	3.444	13.0144	3.2261	0.6918
	4 B	15.3037	77.6364	5.4574	0	0.3413	1.7419	0	5.39	222.6592	24.1484	46.0906	5.228	17.3485	3.4012	0.565
	STF 1 d	40.6311	235.6076	8.3233	0	0.1512	0.9025	0	2.3277	214.7431	18.1086	37.8063	5.3274	20.1332	4.9194	1.22
	TF 1 d	63.6721	322.1753	9.6194	0	0.1681	0.4163	0	2.195	207.1682	14.3541	34.9734	4.8157	19.313	5.362	1.392
	1 B	18.2587	63.9045	4.641	0	0.4312	1.3172	0	4.2467	218.2829	21.4379	39.764	4.7326	17.097	3.3765	0.6402
	avg shale	41	160	18	2.6	0.8	6	1.5	5.5	580	40	95	9.7	39	7.3	1.6

Table 6: Trace and REE concentration (ppm) in facies E of Upper Segment

Facies	Sample	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Tl	Pb	Bi	Th	U
E	21 B	2.3142	0.3529	1.9907	0.4321	1.1546	0.1873	1.1044	0.179	1.1963	0.0321	0.2656	7.3014	0	8.0572	4.2295
	20 B	2.6473	0.3794	2.3714	0.4354	1.3325	0.1938	1.1344	0.1707	1.3876	0.7608	0.597	9.8799	0	7.2818	4.0624
	17 B	2.4737	0.3704	2.0677	0.4309	1.2176	0.1662	1.1134	0.1576	1.1247	0	0.6028	9.2681	0	8.4746	5.955
	15 B	2.7769	0.4109	2.5081	0.5314	1.6132	0.2361	1.5515	0.236	2.3046	0.2841	1.0321	11.3764	0	15.6443	8.6361
	SRTF 2	2.8042	0.4955	3.2629	0.7386	2.1168	0.3176	2.0301	0.2918	3.3086	0.2585	0.2532	26.1831	BDL	8.329	5.5212
	RTF 2	1.4684	0.3009	2.273	0.5465	1.8507	0.2889	1.8666	0.2524	4.8483	0.2655	0.3691	25.9285	0	9.7972	6.8604
	13 B	3.9913	0.5466	3.3547	0.6742	2.0748	0.2925	1.9124	0.2895	2.4904	0.077	0.3392	16.4917	0	14.4784	4.8491
	SRTF 1	3.4411	0.5291	3.1649	0.6434	1.8757	0.2739	1.794	0.2557	2.6495	0.2503	0.3153	18.112	BDL	17.2846	3.654
	RTF 1	7.5636	1.1463	6.1761	1.1374	2.6704	0.3171	1.936	0.2633	2.5203	1.0834	0.2903	7.2989	0	11.7157	1.9562
	12 B	3.0293	0.4106	2.2949	0.4816	1.3992	0.1986	1.2979	0.1814	1.5421	0	0.3794	39.2103	0	7.1198	2.2289
	STF 7	4.254	0.6692	3.9976	0.8789	2.4521	0.3669	2.3456	0.3433	3.5714	0.2489	0.5171	18.9907	BDL	--	--
	TF 7	1.7137	0.3897	2.1588	0.5589	1.5589	0.3009	1.6313	0.2918	8.1758	2.4688	0.6775	24.3793	2.1414	7.6223	6.0092
	STF 4	5.4752	0.7704	4.1425	0.9721	2.6626	0.4092	2.5634	0.342	3.6913	0	0.495	17.6449	BDL	11.3857	5.6232
	TF 4	6.3742	1.1496	6.8684	1.3772	3.9954	0.5749	3.6407	0.4977	5.4729	0	0.5077	8.5852	0	14.2559	6.8494
	STF 2 (1)	4.5034	0.7267	4.7731	1.0698	3.0747	0.4741	3.0928	0.428	3.5686	0.0964	0.4513	13.4759	BDL	15.0203	7.1333
	TF 2 (1)	5.5698	0.9942	6.2139	1.3076	3.8392	0.555	3.682	0.4752	5.5868	0.029	0.5315	10.1418	0	--	--
	8 B	2.4948	0.3547	1.8604	0.3962	1.0776	0.1669	1.0068	0.1577	1.3212	0.0421	0.3574	7.4121	0	7.4677	5.1415
	STF 1 b	5.2711	0.9425	5.2939	1.1386	3.2384	0.4716	2.8991	0.4281	4.3857	0.2492	0.5032	20.9301	BDL	28.2454	9.9772
	TF 1b	3.2127	0.6022	4.1011	0.9579	2.8533	0.4478	2.8269	0.4119	6.4752	0.7516	0.3542	24.0511	0	15.6673	5.5711
	4 B	2.9282	0.393	2.317	0.4555	1.3296	0.2089	1.1213	0.1863	1.5075	0	0.4878	10.3587	0	9.5684	6.3724
	STF 1 d	4.9412	0.924	6.1727	1.286	3.794	0.545	3.2882	0.4715	6.2167	0.3434	0.4925	45.2042	1.2224	22.3091	6.9957
	TF 1 d	6.214	1.2469	8.4208	2.0743	5.4767	0.8331	5.4132	0.7065	8.8362	0.4746	0.5031	51.284	0.593	34.9491	7.2356
	1 B	3.1921	0.4743	2.6748	0.5354	1.5161	0.2181	1.2499	0.1908	1.338	0	0.4531	9.4038	0	9.2911	7.1174
	avg shale	7.00	1.20	5.50	1.60	3.90	0.60	3.70	0.70	2.80	2.00	1.40	20.00	0.00	12.00	3.70

Table 6: Trace and REE concentration (ppm) in facies E of Upper Segment

Facies E		Provenance																		
Facies E (Black Shale)	SAMPLE	REE	LREE	Al/	Fe/Ti	Fe/Al	Si/Al	GdN/	Eu/	Y/Ni	Cr/V	Cr/Zr	TiO ₂ /	Al ₂ O ₃ /	La/Yb	La/Cr	Th/Cr	Nb/Sc	Zr/Sc	Th/Sc
	21 B	78.78	9.21	0.66	11.56	0.52	4.89	1.11	0.93	0.73	0.31	0.43	63.32	25.29	15.84	0.70	0.32	0.91	10.11	1.42
	20 B	97.79	10.29	0.70	8.94	0.43	4.77	1.23	0.97	0.56	0.22	0.51	62.05	23.56	19.65	0.65	0.21	1.11	10.70	1.15
	17 B	88.94	10.12	0.69	11.14	0.44	4.80	1.17	0.94	0.60	0.20	0.51	61.66	28.45	17.89	0.73	0.31	0.83	8.99	1.44
	15 B	115.03	10.66	0.76	6.65	0.31	4.36	0.95	0.90	0.49	0.20	0.39	46.32	23.96	18.55	0.60	0.33	1.83	21.45	2.75
	SRTF 2	81.67	5.77	0.79	7.49	0.27	4.99	0.73	1.00	1.63	0.16	0.09	27.18	31.90	7.42	1.34	0.74	0.89	18.94	1.32
	RTF 2	30.11	2.40	0.94	2.45	0.07	4.54	0.42	1.80	3.35	0.13	0.02	17.78	42.67	2.25	1.57	3.66	0.93	29.46	1.67
	13 B	137.75	9.49	0.73	7.61	0.36	4.95	1.10	0.86	0.80	0.55	0.38	44.30	23.91	16.77	0.75	0.34	0.78	10.99	1.41
	SRTF 1	110.05	8.19	0.80	9.19	0.25	4.10	1.01	0.85	0.99	0.52	0.24	28.63	41.21	13.03	0.82	0.61	1.04	16.56	2.37
	RTF 1	169.55	6.99	0.95	1.62	0.05	3.45	2.07	0.87	12.09	0.30	0.03	42.94	38.06	15.99	12.13	4.59	1.35	30.71	4.22
	12 B	103.88	10.18	0.74	8.54	0.35	11.71	1.23	0.88	0.68	0.51	0.42	32.05	27.77	17.51	0.73	0.23	0.39	7.59	0.73
	STF 7	120.25	6.86	0.83	6.70	0.20	4.63	0.96	0.92	0.63	0.18	0.25	25.74	38.00	11.32	0.77	0.00	1.05	15.29	0.00
	TF 7	43.17	4.02	0.89	3.52	0.12	3.29	0.56	1.00	0.52	0.03	0.03	34.66	33.14	2.34	0.97	1.94	2.39	34.10	1.74
	STF 4	195.30	10.26	0.86	5.45	0.16	4.01	1.13	0.94	1.11	0.19	0.10	27.88	39.19	16.24	2.96	0.81	0.53	22.11	1.82
	TF 4	160.15	5.54	0.96	1.06	0.04	3.33	0.93	1.17	2.41	0.06	0.01	28.40	30.00	7.66	14.31	7.32	0.53	28.56	2.02
	STF 2 (1)	138.17	6.62	0.85	6.50	0.18	4.07	0.77	0.97	0.82	0.22	0.17	22.29	41.43	9.73	1.11	0.55	1.14	29.51	2.73
	TF 2 (1)	130.10	4.75	0.94	1.50	0.06	3.23	0.80	1.15	1.95	0.06	0.01	30.84	29.15	5.68	9.44	0.00	0.89	30.42	0.00
	8 B	89.93	10.97	0.78	7.16	0.29	8.68	1.31	0.88	0.42	0.20	0.49	46.70	28.10	20.25	0.64	0.24	0.53	7.09	0.82
	STF 1 b	137.11	5.97	0.86	6.17	0.17	4.77	0.96	0.95	0.97	0.23	0.15	20.21	41.61	9.92	1.18	1.16	0.93	18.93	3.34
	TF 1b	100.63	5.53	0.89	5.27	0.13	3.35	0.60	0.94	0.87	0.02	0.01	19.71	47.71	3.10	6.27	11.20	0.47	19.46	1.67
	4 B	105.72	10.83	0.77	6.73	0.29	7.45	1.38	0.84	0.40	0.19	0.47	47.13	26.06	21.54	0.66	0.26	1.12	15.89	1.96
	STF 1 d	108.94	4.09	0.96	1.39	0.04	3.50	0.79	1.08	4.41	0.15	0.03	20.47	35.22	5.51	2.28	2.81	1.21	34.23	3.24
	TF 1 d	110.60	2.64	0.95	1.48	0.05	3.40	0.61	1.04	6.28	0.04	0.01	15.23	35.00	2.65	7.14	17.39	1.30	43.46	4.71
	1 B	97.10	8.66	0.76	7.82	0.32	8.44	1.35	0.91	0.32	0.20	0.51	48.23	27.83	17.15	0.66	0.29	0.72	9.87	1.43

Table 7: Elemental ratio used to interpret the geochemical evolution of Black Shale dominated Facies E, Upper Segment

Facies E		Palaeoweathering				Palaeoclimate				Palaeoceanography					
Facies E (Black Shale)	SAMPLE	CIA	CIW	PIA	ICV	Mg/Ca	Sr/Cu	C Value	Fe/Mn	Ga/Al	Zr/Hf	Y/Ho	Th/U	Nb/Ta	V/Zn
	21 B	63.12	96.25	92.10	4.31	0.43	2.07	0.12	78.43	0.00	48.03	31.48	1.91	161.13	0.00
	20 B	63.11	96.91	93.35	3.70	0.45	1.67	0.12	57.49	0.00	48.69	36.01	1.79	9.23	0.00
	17 B	62.35	96.25	91.78	4.33	0.45	1.75	0.10	60.77	0.00	46.98	33.46	1.42	0.00	0.00
	15 B	63.33	98.72	97.09	1.43	0.73	1.12	0.43	153.11	0.00	52.92	31.56	1.81	36.62	0.00
	SRTF 2	51.60	97.07	75.33	2.97	0.38	1.31	0.12	42.07	0.00	36.15	30.47	1.51	21.80	0.07
	RTF 2	51.27	98.72	82.78	1.48	0.16	0.42	0.11	59.37	0.00	35.67	33.57	1.43	20.62	0.02
	13 B	67.63	98.87	97.90	1.75	0.40	1.22	0.29	108.73	0.00	45.32	32.18	2.99	103.89	0.00
	SRTF 1	62.18	99.40	98.50	1.35	0.43	0.49	0.37	125.61	0.00	45.63	31.04	4.73	30.39	12.19
	RTF 1	50.68	96.94	64.88	2.28	0.02	2.25	0.03	24.71	0.00	33.80	31.72	5.99	3.46	0.01
	12 B	67.35	98.51	97.23	0.97	2.59	0.93	1.43	82.32	0.00	47.77	31.47	3.19	0.00	0.20
	STF 7	59.85	99.98	99.94	0.99	2.85	0.42	1.22	254.13	0.00	39.53	32.54	0.00	38.99	0.62
	TF 7	52.64	99.99	99.89	1.10	4.47	0.06	1.37	448.97	0.00	18.30	23.46	1.27	4.25	0.99
	STF 4	53.92	99.38	96.05	1.05	1.76	0.17	2.36	154.33	0.00	37.56	31.35	2.02	0.00	0.00
	TF 4	51.55	99.47	92.46	1.03	2.17	0.17	0.91	93.37	0.00	36.88	30.07	2.08	0.00	0.13
	STF 2 (1)	56.42	99.30	97.10	1.03	2.20	0.34	1.34	143.74	0.00	45.53	31.21	2.11	64.83	0.00
	TF 2 (1)	52.28	100.00	100.01	1.02	1.86	0.11	1.65	229.25	0.00	35.04	26.95	0.00	197.63	0.00
	8 B	64.26	99.98	99.94	1.01	2.66	0.63	1.22	209.51	0.00	48.62	31.84	1.45	113.83	25.28
	STF 1 b	56.11	99.31	96.98	1.01	3.46	0.42	1.62	110.58	0.00	36.55	30.45	2.83	31.70	0.37
	TF 1b	54.40	100.00	99.98	1.02	6.62	0.11	1.57	67.51	0.00	28.22	26.97	2.81	5.92	0.44
	4 B	63.37	98.78	97.24	1.03	2.61	0.91	1.19	157.40	0.00	51.50	33.60	1.50	0.00	0.00
	STF 1 d	54.16	99.32	95.90	0.92	2.17	1.70	1.51	168.33	0.00	37.90	31.59	3.19	24.24	0.00
	TF 1 d	52.84	99.46	95.42	0.97	2.29	0.56	1.74	304.60	0.00	36.46	30.70	4.83	20.27	0.00
	1 B	62.93	98.84	97.30	1.07	1.25	3.02	1.18	189.52	0.00	47.76	34.10	1.31	0.00	1.06

Table 7: Elemental ratio used to interpret the geochemical evolution of Black Shale dominated Facies E, Upper Segment

Facies E		Palaeoredox			Palaeosalinity		Basin restriction		Organic content	
Facies E (Black Shale)	SAMPLE NAME	V/V+Ni	V/Cr	Th/U	Sr/Ba	Rb/K	Co EF X Mn EF	Co(ppm)*Mn%	TOC (%)	d13C values (‰; VPDB)
	21 B	0.81	3.26	1.91	0.18	0.00	0.26	0.13	0.87	-32.76
	20 B	0.85	4.54	1.79	0.17	0.00	0.36	0.20	1.83	-25.01
	17 B	0.85	4.92	1.42	0.17	0.00	0.61	0.30	1.79	-32.57
	15 B	0.87	4.94	1.81	0.08	0.00	0.16	0.17	1.60	-32.20
	SRTF 2	0.83	6.15	1.51	0.28	0.00	1.28	0.80	0.37	-32.20
	RTF 2	0.78	7.46	1.43	0.10	0.00	0.18	0.18	0.25	-31.70
	13 B	0.74	1.83	2.99	0.11	0.00	0.46	0.38	0.97	-34.30
	SRTF 1	0.73	1.94	4.73	0.08	0.00	0.17	0.20	0.35	-33.60
	RTF 1	0.74	3.35	5.99	0.11	0.00	0.12	0.13	0.09	-30.90
	12 B	0.73	1.95	3.19	0.07	0.00	1.15	0.29	1.20	-32.30
	STF 7	0.81	5.46	0.00	0.06	0.00	0.07	0.08	0.96	-32.90
	TF 7	0.86	38.58	1.27	0.02	0.00	0.02	0.04	0.09	-29.50
	STF 4	0.73	5.35	2.02	0.03	0.00	0.30	0.40	0.25	-31.60
	TF 4	0.64	15.42	2.08	0.02	0.00	0.04	0.06	0.14	-29.70
	STF 2 (1)	0.75	4.52	2.11	0.05	0.00	0.18	0.24	0.33	-32.40
	TF 2 (1)	0.66	15.89	0.00	0.01	0.00	0.02	0.03	0.09	-30.10
	8 B	0.84	5.10	1.45	0.08	0.00	0.14	0.06	1.08	-33.10
	STF 1 b	0.75	4.34	2.83	0.05	0.00	0.27	0.29	0.24	-31.80
	TF 1b	0.76	65.61	2.81	0.02	0.00	0.16	0.27	0.13	-28.20
	4 B	0.84	5.32	1.50	0.10	0.00	0.22	0.11	1.01	-33.10
	STF 1 d	0.86	6.88	3.19	0.05	0.00	0.04	0.06	0.10	-30.60
	TF 1 d	0.84	26.41	4.83	0.02	0.00	0.03	0.04	0.11	-30.20
	1 B	0.74	5.10	1.31	0.32	0.00	0.25	0.11	0.66	-33.30

Table 7: Elemental ratio used to interpret the geochemical evolution of Black Shale dominated Facies E, Upper Segment

SAMPLE NAME	Li	Be	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Ga	Ge	Se	Rb	Sr
24 B	58.1156	1.7946	6.0803	175.6986	33.4684	89.2608	10.1682	33.8185	21.8237	101.0748	13.0734	1.4340	90.9990	125.9783	13.3817
11 B	57.9357	1.5325	5.9713	160.7889	33.2808	85.4550	10.0537	32.7333	20.4718	99.7075	12.3519	1.4561	102.6278	119.0643	13.7092
STF 9*	48.3776	2.1421	9.8600	171.7029	34.0757	138.3370	32.0819	50.4515	28.0580	384.2507	14.5358	1.5366	87.7768	167.9782	10.5952
TF 9*	13.4928	0.6671	4.6305	69.9220	2.4267	50.1932	45.8933	9.7385	13.3834	105.7812	7.7356	1.9385	74.4754	179.1212	1.7470
23 B	76.6987	2.2365	8.2185	245.1015	44.4903	103.2209	9.7385	41.0947	33.4445	801.9990	15.8111	1.8836	100.0092	143.3469	15.5021
10 B	73.8068	2.1824	7.7421	230.1945	45.3114	98.3513	9.4248	39.9885	32.7277	821.3504	15.2886	1.8153	107.3920	135.2528	15.0107
25 B	55.6764	2.5224	7.9986	198.0385	38.8564	110.0582	4.6630	59.2851	20.6181	29.4418	12.3107	1.1550	107.7736	121.0486	11.6159
STF 8*	43.6974	1.2201	5.7802	120.2418	9.6711	65.9500	21.1072	32.1682	19.8895	369.7160	11.0742	1.2096	76.8290	153.6281	6.6183
TF8*	27.1459	0.7738	7.0842	90.3255	3.2507	165.8482	21.8166	25.3083	23.2030	311.0959	9.3637	2.1857	68.4138	147.5309	3.4223
22 B	58.6843	2.4511	8.7949	195.9320	35.2658	71.0732	15.0001	60.8287	23.0252	25.8757	12.9046	1.3579	101.3459	123.9258	12.8396
9B	48.0382	1.9109	7.7051	179.2335	31.8780	62.2684	13.5627	53.7713	20.7147	23.1720	11.7300	1.0893	108.8957	114.5998	11.1823
avg shale	66.00	3.00	13.00	130.00	90.00	850.00	19.00	68.00	45.00	95.00	19.00	1.60	0.60	140.00	300.00

SAMPLE NAME	Y	Zr	Nb	Mo	Cd	Sn	Sb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu
24 B	15.3546	67.3938	4.7672	0.0000	0.6519	1.7421	0.0000	4.8841	212.6351	28.4486	51.0486	5.7300	19.8149	3.9146	0.6284
11 B	14.8540	68.0707	5.3030	BDL	0.6737	1.5924	0.0000	4.9443	199.1754	28.7785	48.4374	5.6126	20.5460	3.3889	0.6450
STF 9*	28.2378	183.6909	11.8200	3.0336	0.8659	1.9067	0.0000	4.0614	240.0020	22.4899	51.0900	5.0108	18.8911	3.7562	0.7116
TF 9*	26.1288	168.9515	6.0383	0.0000	0.3660	2.5064	0.0000	3.7904	184.9499	18.6692	45.6244	6.2409	25.1400	6.0978	1.1789
23 B	30.8105	111.4209	9.1021	2.3289	0.5039	2.1510	0.0000	5.7774	241.8568	35.4506	55.6736	7.0443	25.5414	5.0920	0.9352
10 B	29.4880	105.6677	10.0522	3.0026	0.4958	2.1739	0.0000	5.6867	234.6329	33.7996	55.7960	6.7889	25.2423	4.9827	0.9061
25 B	15.6302	71.9483	5.2527	1.4428	0.1570	1.7349	0.0000	5.1386	181.3317	21.1461	36.2386	4.3312	13.3727	2.3828	0.4674
STF 8*	33.8474	179.6386	5.3401	0.0000	0.5185	1.4857	0.0000	4.8170	180.0561	12.7992	29.6318	3.4905	13.5418	3.3274	0.7779
TF8*	28.5237	195.6338	4.8033	0.0000	0.4962	1.4973	0.0000	4.0225	171.3628	12.0888	56.4542	4.3157	16.5353	4.0880	0.8680
22 B	20.3163	72.2706	5.9187	1.1613	0.1768	1.8687	0.0000	5.7786	200.3620	22.5481	36.0958	4.4676	14.5791	2.6745	0.5304
9B	17.6226	69.7371	4.5397	1.0181	0.1786	1.4406	0.0000	5.4231	175.1511	19.3929	31.1883	3.9338	12.5650	2.2609	0.4965
avg shale	41.00	160.00	18.00	2.60	0.80	6.00	1.50	5.50	580.00	40.00	95.00	9.70	39.00	7.30	1.60

Table 8: Trace and REE concentration (ppm) in Facies F, Upper Segment

SAMPLE NAME	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Tl	Pb	Bi	Th	U
24 B	3.3745	0.4411	2.3068	0.4688	1.2448	0.1983	1.1046	0.1753	1.3815	0.0000	0.5607	9.5213	0.0000	9.4996	5.3984
11 B	3.1503	0.4288	2.1889	0.4525	1.2058	0.1800	1.1106	0.1604	1.4395	0.0000	0.5524	9.1526	0.0000	10.1998	5.8934
STF 9*	3.5758	0.5919	4.3445	0.9178	2.8428	0.4426	2.8204	0.4121	4.8396	0.4313	0.6268	31.0977	BDL	24.0592	7.9370
TF 9*	5.5503	0.8503	5.1395	0.9274	2.4412	0.3503	2.0293	0.2950	5.4676	1.6110	0.5998	25.1700	0.0000	12.8548	4.1268
23 B	4.9356	0.6980	4.2736	0.8717	2.3526	0.3412	2.0188	0.3073	1.9540	0.0000	0.4771	21.5749	0.0000	12.9272	7.1746
10 B	5.0116	0.6688	4.2589	0.8397	2.3511	0.3200	2.0658	0.2970	1.8726	0.0787	0.5154	20.3187	0.0000	12.8311	7.5574
25 B	2.2011	0.3589	2.2540	0.5007	1.4380	0.2321	1.3972	0.2217	1.4666	0.0000	1.0337	14.1507	0.0000	11.7268	4.8778
STF 8*	3.8870	0.7219	4.7690	1.0365	3.1861	0.4695	2.9532	0.4257	5.4468	0.6929	0.3194	24.8194	BDL	17.0422	6.0016
TF8*	3.7137	0.6807	4.6299	0.9915	2.8578	0.4451	2.8845	0.4040	6.0120	1.4798	0.3141	36.3035	0.0000	12.7114	5.4316
22 B	2.5713	0.4205	2.6910	0.5951	1.6918	0.2630	1.6132	0.2317	1.5537	0.0000	1.3763	12.0918	0.0000	8.3251	3.6836
9B	2.1049	0.4032	2.3055	0.5135	1.6400	0.2194	1.5396	0.2068	1.3991	0.0000	1.1557	11.1437	0.0000	8.8508	3.9819
avg shale	7.00	1.20	5.50	1.60	3.90	0.60	3.70	0.70	2.80	2.00	1.40	20.00	0.10	12.00	3.70

Table 8: Trace and REE concentration (ppm) in Facies F, Upper Segment

Facies F		Provenance								Palaeoweathering				
	SAMPLE NAME	LREE/HREE	Al/(Al+Fe+Mn)	Fe/Ti	Gd _N /Yb _N	Eu/Eu*	Y/Ni	Cr/V	La/Cr	Th/Cr	CIA	CIW	PIA	ICV
	24 B	11.7654	0.7645	8.7285	1.6148	0.7724	0.454	0.1905	0.85	0.2838	52.5286	95.138	74.2527	0.9382
	11 B	12.0994	0.7764	6.8542	1.4994	0.882	0.4538	0.207	0.8647	0.3065	51.0495	92.3826	59.9788	0.9632
	STF 9*	6.3927	0.7712	7.9723	0.6701	0.8675	0.5597	0.1985	0.66	0.7061	45.9427	97.634	103.5067	1.0413
	TF 9*	5.8551	0.9308	3.2172	1.4457	0.9054	2.683	0.0347	7.6931	5.2971	40.8567	99.5875	100.943	0.9918
	23 B	8.2119	0.748	7.2394	1.2923	0.8334	0.7497	0.1815	0.7968	0.2906	53.0808	94.0998	83.1297	0.9815
	10 B	8.064	0.7548	7.1796	1.2823	0.8101	0.7374	0.1968	0.7459	0.2832	53.1186	95.785	78.5793	0.9656
	25 B	9.0587	0.6772	11.2657	0.8327	0.9119	0.2636	0.1962	0.5442	0.3018	57.8097	98.4558	94.7989	0.9296
	STF 8*	3.6431	0.8531	7.7151	0.6957	0.9664	1.0522	0.0804	1.3235	1.7622	44.8329	97.1547	109.149	1.0201
	TF8*	5.6812	0.8786	5.5334	0.6805	0.9952	1.127	0.036	3.7188	3.9104	42.1717	98.3224	100.3942	1.0516
	22 B	8.0273	0.6814	11.2501	0.8425	0.9036	0.334	0.18	0.6394	0.2361	57.369	97.0397	99.5749	0.9215
	9B	7.818	0.7018	10.3655	0.7226	1.0168	0.3277	0.1779	0.6083	0.2776	57.9453	98.1615	93.991	0.8818

Facies F		Paleoclimate				Paleogeography				Paleoredox	
	SAMPLE NAME	Mg/Ca	Sr/Cu	Fe/Mn	C-Value	Ga/Al	Zr/Hf	Y/Ho	Th/U	V/V+Ni	V/Cr
	24 B	2.7614	0.6132	161.7620	1.5907	0.0003	48.7839	32.7521	1.7597	0.8386	5.2497
	11 B	1.7353	0.6697	157.8326	1.2739	0.0003	47.2882	32.8292	1.7307	0.8309	4.8313
	STF 9*	5.0098	0.3776	170.8910	2.9724	0.0002	37.9557	30.7662	3.0313	0.7729	5.0389
	TF 9*	3.3750	0.1305	129.0217	3.7437	0.0001	30.9007	28.1736	3.1149	0.8777	28.8131
	23 B	3.6161	0.4635	166.8545	1.3926	0.0003	57.0216	35.3453	1.8018	0.8564	5.5091
	10 B	3.9551	0.4587	173.7572	1.4858	0.0003	56.4298	35.1153	1.6978	0.8520	5.0803
	25 B	7.4251	0.5634	199.3558	3.5446	0.0003	49.0585	31.2152	2.4041	0.7696	5.0967
	STF 8*	5.0626	0.3328	226.5057	1.1759	0.0001	32.9806	32.6561	2.8396	0.7889	12.4332
	TF8*	8.8211	0.1475	71.5610	1.3915	0.0001	32.5403	28.7671	2.3403	0.7811	27.7866
	22 B	6.5626	0.5576	273.5313	3.3984	0.0003	46.5141	34.1400	2.2600	0.7631	5.5559
	9B	5.8219	0.5398	267.2363	3.2607	0.0003	49.8455	34.3217	2.2227	0.7692	5.6225

Table 9: Elemental ratio used to interpret the geochemical evolution of Facies F, Upper Segment

Raw Data						
Variety of glauconites based on petrography	DataSet/Point	Al ₂ O ₃	SiO ₂	K ₂ O	FeO	MgO
Glauconites pellets floating within silica cement	32 / 1	14.515	54.582	8.972	5.748	8.747
	37 / 1	12.59	56.116	8.683	6.488	10.015
	42 / 1	12.61	56.141	8.819	6.055	10.994
	43 / 1	14.293	56.262	9.022	6.266	9.833
	44 / 1	13.582	56.598	8.635	6.406	10.555
	45 / 1	13.233	57.002	8.574	6.287	10.522
	54 / 1	13.503	56.248	8.687	6.44	9.988
	55 / 1	18.05	56.342	9.124	5.554	7.373
Glauconite in between grains	73 / 1	17.6	58.78	8.04	5.477	4.729
	74 / 1	21.75	56.572	8.847	5.695	4.785
	75 / 1	17.301	60.431	7.285	5.162	3.738
	80 / 1	15.445	58.92	8.052	6.258	6.329
	81 / 1	16.428	52.555	8.54	6.712	6.924
	82 / 1	14.964	53.909	8.503	6.433	7.949
	18 / 1	15.618	52.795	8.679	6.833	7.333
	19 / 1	14.153	51.603	8.652	7.309	8.148
Partially dissolved glauconite grains	20 / 1	16.221	52.739	8.669	7.136	6.966
	35 / 1	14.082	56.909	8.417	5.927	9.069
	38 / 1	14.167	54.317	8.557	7.236	8.233
	40 / 1	16.891	53.751	9.046	5.881	6.881
	47 / 1	16.108	56.317	9.029	5.566	8.86
	50 / 1	13.631	55.816	8.887	6.999	9.303
	52 / 1	14.114	55.676	8.735	5.75	9.62

Recalculated Value						
Variety of glauconites based on petrography	Al ₂ O ₃	SiO ₂	K ₂ O	FeO	MgO	Fe ₂ O ₃
Glauconites pellets floating within silica cement	15.6255	58.7579	9.6584	6.1878	9.4162	6.8752
	13.3455	59.4834	9.2040	6.8773	10.6160	7.6414
	13.2469	58.9766	9.2644	6.3608	11.5493	7.0675
	14.8817	58.5794	9.3936	6.5241	10.2380	7.2489
	14.1164	58.8251	8.9748	6.6581	10.9703	7.3978
	13.7941	59.4192	8.9376	6.5536	10.9682	7.2817
	14.1922	59.1188	9.1304	6.7687	10.4978	7.5207
	18.6550	58.2304	9.4298	5.7402	7.6201	6.3779
Glauconite in between grains	18.4862	61.7398	8.4448	5.7528	4.9671	6.3919
	22.1248	57.5468	8.9995	5.7931	4.8675	6.4368
	18.3411	64.0641	7.7230	5.4723	3.9627	6.0803
	16.1819	61.7312	8.4362	6.5566	6.6310	7.2850
	17.9441	57.4052	9.3281	7.3314	7.5630	8.1460
	16.2474	58.5325	9.2323	6.9847	8.6307	7.7607
	17.0294	57.5661	9.4633	7.4505	7.9957	8.2782
	15.6542	57.0767	9.5697	8.0843	9.0123	8.9824
Partially dissolved glauconite grains	17.6005	57.2242	9.4063	7.7429	7.5584	8.6031
	14.8305	59.9339	8.8644	6.2420	9.5510	6.9355
	15.2678	58.5376	9.2219	7.7983	8.8727	8.6646
	18.2011	57.9201	9.7476	6.3371	7.4147	7.0412
	16.7420	58.5337	9.3844	5.7851	9.2087	6.4278
	14.3519	58.7679	9.3570	7.3692	9.7950	8.1879
	14.9759	59.0758	9.2684	6.1011	10.2074	6.7790

Table 10: Geochemical analysis of the glauconites classified under microscope

Raw Data						
Variety of glauconites based on petrography	DataSet/ Point	Al ₂ O ₃	SiO ₂	K ₂ O	FeO	MgO
Bed parallel glauconite	5 / 1	15.098	56.539	8.748	6.092	8.891
	7 / 1	16.159	54.939	8.938	5.826	8.074
	8 / 1	14.054	56.662	8.692	6.288	9.611
	16 / 1	15.297	56.122	8.741	6.131	8.653
	17 / 1	12.93	56.991	8.711	6.162	11.111
	18 / 1	14.17	54.57	9.016	6.187	9.048
	25 / 1	15.004	55.428	8.827	6.427	8.694
	26 / 1	15.951	56.358	8.887	5.809	8.093
	27 / 1	13.977	56.477	8.537	6.47	9.782
	10 / 1	13.541	55.699	8.312	5.676	9.951
	11 / 1	15.07	55.415	8.433	6.232	8.524
	13 / 1	14.317	56.035	8.434	5.177	10.367
	14 / 1	15.663	55.438	8.485	5.886	7.953
	15 / 1	16.182	57.466	8.23	5.579	9.294
	16 / 1	15.959	56.744	7.927	5.602	7.086
Vertical glauconite pellets	19 / 1	14.858	56.381	8.73	6.282	8.831
	20 / 1	17.012	56.22	8.905	6.868	7.517
	21 / 1	12.247	55.204	8.751	6.495	10.521
	29 / 1	10.991	45.366	5.717	3.675	7.7
	30 / 1	13.836	54.825	8.654	5.975	9.391
	1 / 1	14.397	55.889	8.446	6.627	9.319
	2 / 1	14.067	56.401	8.332	6.414	8.865
	3 / 1	13.531	55.679	8.405	6.138	9.941
	6 / 1	17.793	55.345	8.711	6.609	6.828
	7 / 1	15.506	59.992	8.048	4.996	7.983

Recalculated Value						
Variety of glauconites based on petrography	Al ₂ O ₃	SiO ₂	K ₂ O	FeO	MgO	Fe ₂ O ₃
Bed parallel glauconite	15.7810	59.0967	9.1437	6.3676	9.2932	7.0750
	17.0937	58.1168	9.4550	6.1630	8.5410	6.8477
	14.6694	59.1431	9.0726	6.5633	10.0318	7.2925
	16.0477	58.8762	9.1700	6.4319	9.0777	7.1465
	13.4359	59.2207	9.0518	6.4031	11.5457	7.1145
	15.1741	58.4368	9.6549	6.6254	9.6891	7.3615
	15.8280	58.4721	9.3118	6.7800	9.1715	7.5332
	16.7040	59.0186	9.3065	6.0832	8.4751	6.7591
	14.5902	58.9549	8.9116	6.7539	10.2112	7.5042
	14.4553	59.4598	8.8732	6.0592	10.6229	6.7324
	16.0232	58.9202	8.9664	6.6262	9.0632	7.3624
	15.1224	59.1873	8.9085	5.4682	10.9502	6.0758
	16.6736	59.0149	9.0325	6.2658	8.4661	6.9619
	16.6201	59.0218	8.4528	5.7300	9.5456	6.3667
	17.0255	60.5360	8.4567	5.9764	7.5595	6.6403
Vertical glauconite pellets	15.5785	59.1151	9.1533	6.5866	9.2592	7.3184
	17.5499	57.9976	9.1866	7.0852	7.7547	7.8723
	13.0861	58.9862	9.3506	6.9400	11.2418	7.7110
	14.8633	61.3493	7.7312	4.9698	10.4129	5.5219
	14.8477	58.8339	9.2868	6.4119	10.0777	7.1243
	15.1410	58.7773	8.8825	6.9695	9.8006	7.7438
	14.9201	59.8216	8.8373	6.8030	9.4026	7.5588
	14.3996	59.2532	8.9445	6.5320	10.5791	7.2577
	18.6238	57.9292	9.1177	6.9176	7.1468	7.6861
	15.9978	61.8946	8.3032	5.1544	8.2362	5.7271

Table 10: Geochemical analysis of the glauconites classified under microscope

Raw Data						
Variety of glauconites based on petrography	Data Set/ Point	Al ₂ O ₃	SiO ₂	K ₂ O	FeO	MgO
Glauconite within shale	1 / 1	18.337	56.046	9.059	6.323	6.614
	2 / 1	18.27	55.989	9.146	6.12	6.414
	3 / 1	16.438	58.977	8.419	5.721	7.786
	4 / 1	17.054	55.971	8.771	6.202	7.52
	9 / 1	13.224	56.387	8.575	6.724	10.023
	10 / 1	17.713	56.065	8.962	6.032	6.795
	11 / 1	16.849	54.991	8.999	6.636	6.913
	12 / 1	14.128	56.945	8.682	6.023	9.958
	13 / 1	13.494	55.256	8.627	7.336	9.187
	14 / 1	15.641	55.189	8.893	6.589	7.566
	24 / 1	14.63	56.549	8.878	6.151	9.21

Recalculated Value						
Variety of glauconites based on petrography	Al ₂ O ₃	SiO ₂	K ₂ O	FeO	MgO	Fe ₂ O ₃
Glauconite within shale	18.9279	57.8521	9.3509	6.5268	6.8271	7.2519
	18.9592	58.1010	9.4910	6.3509	6.6559	7.0564
	16.8126	60.3210	8.6108	5.8514	7.9634	6.5015
	17.7168	58.1463	9.1119	6.4430	7.8123	7.1589
	13.8782	59.1766	8.9992	7.0567	10.5189	7.8406
	18.4324	58.3421	9.3260	6.2770	7.0710	6.9744
	17.7963	58.0827	9.5049	7.0091	7.3017	7.7878
	14.7078	59.2819	9.0383	6.2702	10.3667	6.9668
	14.2635	58.4071	9.1190	7.7543	9.7109	8.6159
	16.5487	58.3918	9.4091	6.9714	8.0051	7.7459
	15.2494	58.9433	9.2539	6.4114	9.5999	7.1237

Table 10: Geochemical analysis of the glauconites classified under microscope

RAW DATA										
Facies B	DataSet/ Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Cr ₂ O ₃	MnO	Fe ₂ O ₃
	37 / 1	0.0030	10.0150	12.5900	56.1160	8.6830	0.2200	0.1440	0.0000	7.2088
	42 / 1	0.0160	10.9940	12.6100	56.1410	8.8190	0.1680	0.0490	0.0770	6.7277
	43 / 1	0.0270	9.8330	14.2930	56.2620	9.0220	0.1660	0.0610	0.0300	6.9622
	44 / 1	0.0560	10.5550	13.5820	56.5980	8.6350	0.2010	0.0000	0.0490	7.1177
	45 / 1	0.0500	10.5220	13.2330	57.0020	8.5740	0.1740	0.0000	0.0000	6.9855
	54 / 1	0.0660	9.9880	13.5030	56.2480	8.6870	0.1750	0.0040	0.0000	7.1555
	55 / 1	0.0510	7.3730	18.0500	56.3420	9.1240	0.1880	0.0240	0.0000	6.1710
	35 / 1	0.0470	9.0690	14.0820	56.9090	8.4170	0.2190	0.0370	0.0640	6.5855
	38 / 1	0.0150	8.2330	14.1670	54.3170	8.5570	0.2210	0.0000	0.0000	8.0399
	40 / 1	0.0550	6.8810	16.8910	53.7510	9.0460	0.2090	0.0000	0.0650	6.5344
	47 / 1	0.0370	8.8600	16.1080	56.3170	9.0290	0.1920	0.0730	0.0000	6.1844
	50 / 1	0.0210	9.3030	13.6310	55.8160	8.8870	0.1880	0.0530	0.0000	7.7766
	52 / 1	0.0550	9.6200	14.1140	55.6760	8.7350	0.1420	0.0000	0.0820	6.3888
	1 / 1	0.0560	8.1720	14.7310	55.7270	8.8140	0.2060	0.0190	0.0000	5.5340
	2 / 1	0.0240	7.5170	15.9170	54.7430	9.1140	0.1740	0.0000	0.0190	5.7300
	3 / 1	0.0690	7.9650	15.1690	56.5210	8.8670	0.1830	0.0000	0.0160	6.2930
	5 / 1	0.0750	7.5210	15.7530	56.3950	8.9780	0.1440	0.0000	0.0230	6.4110
	6 / 1	0.0610	6.8030	16.9570	55.4690	8.8630	0.2160	0.0000	0.0000	5.3170
	22 / 1	0.0570	8.4670	13.5850	55.0460	8.7910	0.2110	0.0210	0.0000	6.9940
	23 / 1	0.0430	8.2920	15.1560	56.0270	8.8680	0.1480	0.0000	0.0000	6.0740
	24 / 1	0.1140	9.8940	12.2850	55.9640	8.8930	0.1600	0.0430	0.0080	6.2380
	26 / 1	0.0500	1.3070	11.9800	77.6300	4.8300	0.1480	0.0350	0.0180	2.3290
	28 / 1	0.0770	6.9660	15.2530	54.5490	8.9050	0.3690	0.0140	0.0380	6.2930
	30 / 1	0.0730	5.7840	16.3270	53.1000	9.0860	0.4400	0.0720	0.0200	6.1230
	31 / 1	0.0880	5.6100	16.8220	53.8700	8.6630	0.4930	0.0100	0.0000	6.2110
	1 / 1	0.0510	8.3770	13.3790	55.4490	8.5040	0.3280	0.0000	0.0000	7.2010
	2 / 1	0.0730	9.5500	11.8110	55.6180	8.3930	0.4610	0.0160	0.0000	8.0670
	3 / 1	0.1010	7.5500	15.2690	55.8920	8.8660	0.1350	0.0000	0.0000	7.6750
	4 / 1	0.1000	7.6100	14.9910	55.6210	8.8430	0.1100	0.0070	0.0000	7.6220
	5 / 1	0.1390	8.9820	12.7830	55.2200	8.4810	0.1940	0.0000	0.0500	8.9480
	6 / 1	0.1200	9.1750	12.9760	55.7370	8.6240	0.2040	0.0140	0.0000	8.4120
	7 / 1	0.0920	8.9050	13.4710	55.4480	8.3010	0.1300	0.0280	0.0000	8.4650
	8 / 1	0.1440	8.4060	14.3610	55.2000	8.1930	0.0670	0.0050	0.0010	8.6680
	10 / 1	0.1350	9.2950	12.6230	55.5200	8.5210	0.1170	0.0000	0.0120	8.1760
	11 / 1	0.1370	9.4490	12.7320	55.1290	8.3280	0.2140	0.0400	0.0390	8.3930
	12 / 1	0.1240	7.9890	13.4860	54.1290	8.3890	0.9170	0.0350	0.0000	8.7320
	14 / 1	0.1290	9.3830	12.1840	55.3450	8.6860	0.0430	0.0000	0.0090	7.7020
	15 / 1	0.0460	7.7710	14.8350	55.0360	8.7070	0.2760	0.0320	0.0220	7.5930
	16 / 1	0.1160	7.4440	15.9280	55.4620	8.6230	0.2580	0.0000	0.0000	6.9720
	17 / 1	0.1110	8.3410	14.3250	56.0600	8.7620	0.1010	0.0000	0.0140	6.9000
	18 / 1	0.1360	8.2090	13.0040	56.3920	8.7120	0.3880	0.0000	0.0000	8.5590
	22 / 1	0.2110	5.7020	15.9030	57.3680	8.3630	0.1390	0.0070	0.0560	6.6770

Table 11: Geochemical analysis for glauconites of the Rampur Shale (Facies B, C, and D)

RAW DATA										
Facies B	DataSet/ Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Cr ₂ O ₃	MnO	Fe ₂ O ₃
	23 / 1	0.1590	7.3380	14.0220	53.5790	8.4510	0.5210	0.0000	0.0020	8.1320
	25 / 1	0.1120	2.1850	13.7660	60.2550	5.8580	0.3260	0.0840	0.0000	5.6010
	26 / 1	0.2020	2.0090	23.5080	47.9810	8.5230	2.9040	0.0450	0.0000	5.3220
	30 / 1	0.2310	8.8850	12.5480	53.3730	8.1140	2.9640	0.0000	0.0000	7.5140
	31 / 1	0.2370	8.2440	13.6480	53.6710	8.1660	2.2750	0.0560	0.0260	7.9710
	32 / 1	0.1780	9.3060	12.3360	55.5430	8.4730	0.0910	0.0490	0.0660	7.4720
	33 / 1	0.1180	7.3310	14.7420	53.5760	8.5970	0.1220	0.0020	0.0170	9.0800
	34 / 1	0.1760	9.1960	13.0960	55.8090	8.5490	0.1300	0.0310	0.0000	7.6630
	35 / 1	0.1100	8.4350	14.7590	55.5910	8.5350	0.1370	0.0690	0.0000	7.9020
	36 / 1	0.1060	8.5640	13.1940	56.1040	8.6800	0.1010	0.0330	0.0050	8.5340
	40 / 1	0.2090	8.3770	13.3320	55.0250	8.3700	0.0480	0.0500	0.0130	9.0930
	42 / 1	0.3120	8.9530	13.0020	54.1050	8.1470	0.1970	0.0110	0.0000	9.4260
Facies C	73 / 1	0.0830	4.7290	17.6000	58.7800	8.0400	0.2590	0.0000	0.0040	6.0855
	74 / 1	0.1090	4.7850	21.7500	56.5720	8.8470	0.2760	0.0690	0.0760	6.3277
	75 / 1	0.0760	3.7380	17.3010	60.4310	7.2850	0.2470	0.0270	0.0000	5.7355
	80 / 1	0.0700	6.3290	15.4450	58.9200	8.0520	0.2230	0.0000	0.1040	6.9533
	81 / 1	0.0760	6.9240	16.4280	52.5550	8.5400	0.2420	0.0000	0.0380	7.4577
	82 / 1	0.0450	7.9490	14.9640	53.9090	8.5030	0.2450	0.0030	0.0000	7.1477
	18 / 1	0.0900	7.3330	15.6180	52.7950	8.6790	0.2030	0.0200	0.0000	7.5921
	19 / 1	0.0970	8.1480	14.1530	51.6030	8.6520	0.3200	0.0000	0.0070	8.1210
	20 / 1	0.0600	6.9660	16.2210	52.7390	8.6690	0.2590	0.0180	0.0680	7.9288
	1 / 1	0.0660	5.7220	18.9160	56.7260	8.8570	0.1610	0.0000	0.0510	7.3340
	2 / 1	0.0330	5.8430	16.9800	54.5590	8.9090	0.2180	0.0270	0.0130	7.3170
	3 / 1	0.0910	6.5720	15.8250	54.2440	8.6180	0.2770	0.0100	0.0000	7.4220
	5 / 1	0.0500	7.0390	12.0090	51.3790	8.7660	0.2200	0.0000	0.0200	8.2360
	7 / 1	0.0220	7.5760	12.9170	53.4420	8.7660	0.2050	0.0510	0.0000	8.1460
	10 / 1	0.0370	7.7440	14.8150	55.9150	8.5270	0.2190	0.0340	0.0000	7.7160
	11 / 1	0.1390	5.0500	18.5540	55.1620	7.8940	0.3130	0.0220	0.0000	7.5820
	12 / 1	0.0850	5.9150	18.0260	56.0360	8.3040	0.4420	0.0650	0.0100	7.9760
	13 / 1	0.0340	7.4540	15.1840	53.0080	8.5830	0.1370	0.0000	0.0000	8.5930
	14 / 1	0.0350	7.0520	14.6610	55.8830	8.8860	0.2190	0.0390	0.0000	8.4320
	15 / 1	0.0900	6.3310	17.0960	56.1840	8.4610	0.2670	0.0250	0.0000	7.9080
	16 / 1	0.0380	7.4970	16.5550	56.7840	8.6710	0.1510	0.0000	0.0000	7.2700
	23 / 1	0.1130	3.1210	18.2600	63.7540	7.2850	0.1370	0.0210	0.0000	5.3950
	28 / 1	0.0450	6.1690	17.4690	55.7000	8.6620	0.2640	0.0000	0.0000	7.9320
	29 / 1	0.1780	6.5640	14.0340	55.4900	8.8050	0.1550	0.0000	0.0000	10.0310
	30 / 1	0.1960	6.3480	14.5840	53.4110	8.6610	0.1070	0.0000	0.0000	11.6040
	31 / 1	0.0670	6.5190	13.2610	54.6680	8.9610	0.1990	0.0080	0.0240	9.8170
	33 / 1	0.0200	6.7770	13.1750	55.5600	8.9430	0.1700	0.0000	0.0000	10.1760
	34 / 1	0.0130	6.5170	14.6160	56.2600	8.7210	0.1950	0.0000	0.0000	10.4430
	35 / 1	0.0470	6.5960	13.0020	54.2560	8.9910	0.1730	0.0040	0.0000	10.4240
	36 / 1	0.0110	6.8210	15.6540	55.6540	8.5870	0.2320	0.0080	0.0000	8.4130

Table 11: Geochemical analysis for glauconites of the Rampur Shale (Facies B, C, and D)

RAW DATA										
Facies C	DataSet/ Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Cr ₂ O ₃	MnO	Fe ₂ O ₃
	37 / 1	0.0100	8.0180	15.9540	56.7950	8.6120	0.1370	0.0230	0.0000	7.5800
	38 / 1	0.0000	5.1470	18.8700	56.4790	8.7200	0.1460	0.0000	0.0550	7.5270
	39 / 1	0.0870	7.5280	11.5600	53.7500	8.9510	0.2020	0.0260	0.0000	9.6120
	40 / 1	0.1590	7.8910	11.0800	54.0590	8.7440	0.1640	0.0000	0.0000	9.6080
	41 / 1	0.0750	5.5330	17.8510	55.1480	8.2920	0.2920	0.0800	0.0140	7.5980
	42 / 1	0.0700	5.0050	18.6380	53.6890	8.7030	0.2840	0.0540	0.0000	7.4970
	44 / 1	0.0690	8.4890	13.8680	57.5300	8.7030	0.2420	0.0020	0.0640	8.8010
	1 / 1	0.0750	8.7670	12.4430	56.2840	8.6000	0.2370	0.0000	0.0000	7.6390
	2 / 1	0.0400	8.3590	13.0090	56.2210	8.6670	0.2660	0.0000	0.0830	8.0160
	3 / 1	0.0570	9.6370	13.0610	57.2590	8.5960	0.1640	0.0480	0.0000	7.6380
	4 / 1	0.0260	9.1960	12.3460	56.8470	8.5520	0.1930	0.0000	0.0000	8.4640
	5 / 1	0.0410	9.0150	12.7000	56.6330	8.6280	0.2210	0.0130	0.0000	7.9030
	6 / 1	0.1290	6.8890	15.1320	52.7780	7.7660	0.3210	0.0680	0.0000	13.3710
	7 / 1	0.0640	6.6920	13.8420	48.6090	7.7690	0.3420	0.0000	0.0230	15.2060
	8 / 1	0.0330	6.3940	14.7790	53.5640	8.8220	0.2610	0.0000	0.0250	8.5030
	11 / 1	0.0880	9.8200	12.5490	57.8170	8.6050	0.2090	0.0000	0.0000	7.9270
	12 / 1	0.1020	6.6390	16.3900	55.8110	8.6780	0.2630	0.0010	0.0690	9.0460
	13 / 1	0.0980	9.0240	12.7420	55.5810	8.8480	0.2230	0.0000	0.0030	7.9360
	14 / 1	0.0720	8.7600	11.9440	54.7700	8.8900	0.1890	0.0370	0.0000	7.4010
	18 / 1	0.1120	4.0490	14.3470	68.4130	4.9250	0.2630	0.1310	0.0000	8.9740
	23 / 1	0.0500	7.2600	14.5010	55.9910	8.9420	0.2240	0.0070	0.0000	8.1340
	25 / 1	0.0240	8.0230	13.1610	55.7300	9.1140	0.2830	0.0000	0.0000	8.1460
	26 / 1	0.0540	9.0340	12.8840	55.0600	8.7430	0.2010	0.0000	0.0000	6.7880
	27 / 1	0.0590	7.8220	15.4750	56.7120	8.8540	0.2310	0.0540	0.0000	7.4810
	28 / 1	0.0660	7.8930	15.0920	56.0820	9.1160	0.2130	0.0140	0.0000	7.1540
	29 / 1	0.0860	8.3680	14.5740	56.6890	8.6990	0.2290	0.0300	0.0150	7.6630
	30 / 1	0.0120	4.6110	15.7600	63.3920	7.8180	0.2610	0.0360	0.0340	6.1290
	32 / 1	0.0000	6.2340	15.0320	52.4400	7.9680	0.1060	0.0210	0.0370	6.8120
	37 / 1	0.0460	9.4130	12.2560	56.5810	8.6140	0.1950	0.0000	0.0090	7.5430
	38 / 1	0.0200	7.3930	14.7540	55.7280	8.9760	0.1230	0.0000	0.0000	7.8040
	39 / 1	0.0300	7.8170	14.6190	57.6380	8.5410	0.1890	0.0610	0.0020	8.1820
	40 / 1	0.0820	9.0020	12.2820	56.7100	8.6440	0.1710	0.0250	0.0000	8.7340
Facies D	5 / 1	0.0480	8.8910	15.0980	56.5390	8.7480	0.1760	0.0100	0.0000	6.7688
	7 / 1	0.0520	8.0740	16.1590	54.9390	8.9380	0.2190	0.0040	0.0680	6.4733
	8 / 1	0.0470	9.6110	14.0540	56.6620	8.6920	0.1850	0.0290	0.0000	6.9866
	16 / 1	0.0440	8.6530	15.2970	56.1220	8.7410	0.2320	0.0490	0.0000	6.8122
	17 / 1	0.0420	11.1110	12.9300	56.9910	8.7110	0.2150	0.0330	0.0000	6.8466
	18 / 1	0.0430	9.0480	14.1700	54.5700	9.0160	0.1830	0.0000	0.0000	6.8744
	25 / 1	0.0180	8.6940	15.0040	55.4280	8.8270	0.1740	0.1400	0.0000	7.1410
	26 / 1	0.0410	8.0930	15.9510	56.3580	8.8870	0.2050	0.0640	0.0140	6.4544
	27 / 1	0.0500	9.7820	13.9770	56.4770	8.5370	0.2650	0.1950	0.0000	7.1888
	10 / 1	0.0880	9.9510	13.5410	55.6990	8.3120	0.1540	0.1470	0.0000	6.3066

Table 11: Geochemical analysis for glauconites of the Rampur Shale (Facies B, C, and D)

RAW DATA										
Facies D	Data Set/ Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Cr ₂ O ₃	MnO	Fe ₂ O ₃
	11 / 1	0.0520	8.5240	15.0700	55.4150	8.4330	0.0930	0.0210	0.0270	6.9244
	13 / 1	0.0690	10.3670	14.3170	56.0350	8.4340	0.1050	0.0740	0.0000	5.7522
	14 / 1	0.0550	7.9530	15.6630	55.4380	8.4850	0.1230	0.1010	0.0000	6.5399
	15 / 1	0.0740	9.2940	16.1820	57.4660	8.2300	0.1490	0.1480	0.0000	6.1988
	16 / 1	0.0270	7.0860	15.9590	56.7440	7.9270	0.1910	0.0720	0.0720	6.2244
	19 / 1	0.0180	8.8310	14.8580	56.3810	8.7300	0.1950	0.0000	0.0000	6.9799
	20 / 1	0.0290	7.5170	17.0120	56.2200	8.9050	0.2210	0.0750	0.0000	7.6310
	21 / 1	0.0360	10.5210	12.2470	55.2040	8.7510	0.1870	0.0970	0.0000	7.2166
	29 / 1	0.0660	7.7000	10.9910	45.3660	5.7170	0.3450	0.0200	0.0420	4.0833
	30 / 1	0.0490	9.3910	13.8360	54.8250	8.6540	0.3290	0.0680	0.0000	6.6388
	1 / 1	0.0400	9.3190	14.3970	55.8890	8.4460	0.0980	0.0390	0.0790	7.3633
	2 / 1	0.0490	8.8650	14.0670	56.4010	8.3320	0.0810	0.0000	0.0000	7.1266
	3 / 1	0.0300	9.9410	13.5310	55.6790	8.4050	0.0960	0.0770	0.0260	6.8199
	6 / 1	0.0110	6.8280	17.7930	55.3450	8.7110	0.1020	0.0000	0.0880	7.3433
	7 / 1	0.0400	7.9830	15.5060	59.9920	8.0480	0.1240	0.1960	0.0000	5.5511
	1 / 1	0.0500	8.3440	13.7910	55.9270	8.7140	0.2110	0.0460	0.0000	8.1200
	2 / 1	0.0240	7.3550	13.5110	55.6620	8.8630	0.1460	0.0180	0.0220	10.1550
	3 / 1	0.0170	8.1240	14.4310	55.1810	8.9240	0.2250	0.0040	0.0280	7.5880
	4 / 1	0.0600	7.4320	15.2540	56.8490	8.9080	0.2710	0.0530	0.0000	8.5670
	5 / 1	0.0290	8.2890	12.4090	54.9100	8.7070	0.2530	0.0000	0.0490	8.5030
	14 / 1	0.0870	5.8020	17.7550	55.0180	8.6990	0.2920	0.0000	0.0000	7.5610
	17 / 1	0.0830	7.3540	16.5370	57.1840	8.7130	0.2600	0.0000	0.0320	7.5660
	18 / 1	0.0640	6.7350	15.6330	56.4410	8.6060	0.2640	0.0000	0.0600	8.5950
	19 / 1	0.0470	6.1850	17.1820	55.4550	8.8620	0.1830	0.0060	0.0000	7.9300
	20 / 1	0.0340	5.1510	15.5790	54.6850	8.4490	0.2700	0.0000	0.0000	7.5730
	21 / 1	0.0550	7.3930	15.4170	55.9840	8.6300	0.2610	0.0800	0.0350	7.9880
	22 / 1	0.0650	6.7940	15.7340	52.9210	8.3280	0.2000	0.0000	0.0000	10.9780
	24 / 1	0.0420	8.6510	12.4930	55.7030	8.7340	0.2120	0.0000	0.0000	9.0470
	25 / 1	0.0700	8.2070	13.1860	55.3310	8.5630	0.1870	0.0320	0.0230	8.9110
	26 / 1	0.0370	8.3890	13.5180	57.2050	8.4320	0.2500	0.0000	0.0000	9.7010
	27 / 1	0.0780	8.4720	12.6490	55.0840	8.6060	0.2010	0.0000	0.0000	9.8420
	5 / 1	0.1110	7.1940	14.6100	55.8290	8.0550	0.2630	0.0580	0.0540	6.6420
	9 / 1	0.1260	6.1690	16.3350	54.1370	8.7620	0.2450	0.0790	0.0000	7.1430
	10 / 1	0.1820	4.9360	18.6410	55.8410	8.5450	0.2190	0.0720	0.0000	6.5670
	11 / 1	0.1970	5.2570	18.6560	55.2850	8.3270	0.2210	0.1490	0.0260	7.2470
	12 / 1	0.1330	5.6870	17.4130	53.7050	8.6510	0.2500	0.0140	0.0380	6.5240
	13 / 1	0.1550	4.9050	17.6370	55.6900	8.5580	0.2930	0.0370	0.0370	7.6850
	14 / 1	0.1570	6.4690	15.4940	54.9960	8.4700	0.2820	0.0330	0.0000	7.6090
	17 / 1	0.0760	4.4860	18.4970	54.8380	8.3110	0.5100	0.0040	0.0000	6.2700
	18 / 1	0.1220	5.3280	14.9320	54.1380	8.1100	0.4010	0.1440	0.0260	8.1820
	21 / 1	0.0950	4.5700	19.3860	55.3260	8.3840	0.2500	0.0000	0.0450	6.9220

Table 11: Geochemical analysis for glauconites of the Rampur Shale (Facies B, C, and D)

RAW DATA										
Facies D	Data Set/Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Cr ₂ O ₃	MnO	Fe ₂ O ₃
	24 / 1	0.0820	4.4860	19.1220	54.3860	8.1260	0.4760	0.0210	0.0000	6.6440
	28 / 1	0.1340	2.7080	14.9920	65.7950	6.8330	0.1970	0.0810	0.0110	4.1650
	32 / 1	0.1170	7.5720	14.7350	55.8580	8.4990	0.2380	0.0180	0.0000	7.4920
	38 / 1	0.1100	8.5170	13.1170	56.4900	8.4490	0.2140	0.0000	0.0530	7.9980
	39 / 1	0.1060	5.5100	16.9490	52.9420	8.5840	0.2510	0.0000	0.0000	7.3540
	40 / 1	0.1050	4.5600	18.1060	54.2760	8.5480	0.2460	0.0000	0.0000	7.0530
	41 / 1	0.1100	4.4740	18.5520	54.0810	8.6680	0.2800	0.0000	0.0000	6.7230
	42 / 1	0.1310	4.0120	13.8120	68.6280	6.4060	0.2590	0.0830	0.0380	5.4360
	43 / 1	0.1840	2.9230	19.5920	55.7420	8.7840	0.2530	0.0120	0.0280	5.4790

RECALCULATED DATA										
Facies B	DataSet /Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Cr ₂ O ₃	MnO	Fe ₂ O ₃
	37 / 1	0.0032	10.5443	13.2554	59.0820	9.1419	0.2316	0.1516	0.0000	7.5898
	42 / 1	0.0167	11.4998	13.1901	58.7238	9.2247	0.1757	0.0513	0.0805	7.0372
	43 / 1	0.0279	10.1732	14.7875	58.2084	9.3341	0.1717	0.0631	0.0310	7.2030
	44 / 1	0.0579	10.9046	14.0319	58.4728	8.9210	0.2077	0.0000	0.0506	7.3535
	45 / 1	0.0518	10.8991	13.7072	59.0447	8.8812	0.1802	0.0000	0.0000	7.2358
	54 / 1	0.0689	10.4230	14.0911	58.6978	9.0653	0.1826	0.0042	0.0000	7.4671
	55 / 1	0.0524	7.5758	18.5465	57.8917	9.3750	0.1932	0.0247	0.0000	6.3408
	35 / 1	0.0493	9.5034	14.7564	59.6346	8.8201	0.2295	0.0388	0.0671	6.9009
	38 / 1	0.0160	8.8006	15.1438	58.0620	9.1470	0.2362	0.0000	0.0000	8.5943
	40 / 1	0.0589	7.3647	18.0783	57.5293	9.6819	0.2237	0.0000	0.0696	6.9937
	47 / 1	0.0382	9.1529	16.6404	58.1785	9.3274	0.1983	0.0754	0.0000	6.3888
	50 / 1	0.0219	9.7235	14.2471	58.3388	9.2887	0.1965	0.0554	0.0000	8.1281
	52 / 1	0.0580	10.1463	14.8862	58.7220	9.2129	0.1498	0.0000	0.0865	6.7384
	1 / 1	0.0600	8.7627	15.7958	59.7551	9.4511	0.2209	0.0204	0.0000	5.9340
	2 / 1	0.0257	8.0622	17.0714	58.7132	9.7750	0.1866	0.0000	0.0204	6.1456
	3 / 1	0.0726	8.3769	15.9534	59.4439	9.3255	0.1925	0.0000	0.0168	6.6184
	5 / 1	0.0787	7.8919	16.5299	59.1763	9.4208	0.1511	0.0000	0.0241	6.7272
	6 / 1	0.0651	7.2615	18.0998	59.2074	9.4603	0.2306	0.0000	0.0000	5.6753
	22 / 1	0.0612	9.0875	14.5806	59.0800	9.4352	0.2265	0.0225	0.0000	7.5065
	23 / 1	0.0455	8.7646	16.0198	59.2202	9.3734	0.1564	0.0000	0.0000	6.4202
	24 / 1	0.1218	10.5706	13.1251	59.7912	9.5012	0.1709	0.0459	0.0085	6.6646
	26 / 1	0.0509	1.3292	12.1838	78.9508	4.9122	0.1505	0.0356	0.0183	2.3686
	28 / 1	0.0833	7.5337	16.4961	58.9949	9.6308	0.3991	0.0151	0.0411	6.8059
	30 / 1	0.0802	6.3543	17.9368	58.3356	9.9819	0.4834	0.0791	0.0220	6.7267
	31 / 1	0.0959	6.1133	18.3312	58.7030	9.4402	0.5372	0.0109	0.0000	6.7682
	1 / 1	0.0547	8.9796	14.3415	59.4379	9.1158	0.3516	0.0000	0.0000	7.7190
	2 / 1	0.0777	10.1608	12.5664	59.1750	8.9298	0.4905	0.0170	0.0000	8.5829

Table 11: Geochemical analysis for glauconites of the Rampur Shale (Facies B, C, and D)

RECALCULATED DATA										
Facies B	DataSet /Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Cr ₂ O ₃	MnO	Fe ₂ O ₃
	3 / 1	0.1058	7.9068	15.9905	58.5330	9.2849	0.1414	0.0000	0.0000	8.0377
	4 / 1	0.1054	8.0186	15.7960	58.6076	9.3178	0.1159	0.0074	0.0000	8.0313
	5 / 1	0.1466	9.4750	13.4846	58.2508	8.9465	0.2046	0.0000	0.0527	9.4391
	6 / 1	0.1260	9.6313	13.6214	58.5092	9.0529	0.2141	0.0147	0.0000	8.8304
	7 / 1	0.0970	9.3895	14.2039	58.4648	8.7526	0.1371	0.0295	0.0000	8.9256
	8 / 1	0.1515	8.8442	15.1097	58.0778	8.6201	0.0705	0.0053	0.0011	9.1199
	10 / 1	0.1430	9.8465	13.3720	58.8142	9.0266	0.1239	0.0000	0.0127	8.6611
	11 / 1	0.1450	10.0031	13.4786	58.3617	8.8163	0.2265	0.0423	0.0413	8.8851
	12 / 1	0.1322	8.5170	14.3772	57.7062	8.9434	0.9776	0.0373	0.0000	9.3091
	14 / 1	0.1380	10.0373	13.0337	59.2045	9.2917	0.0460	0.0000	0.0096	8.2391
	15 / 1	0.0488	8.2391	15.7287	58.3515	9.2315	0.2926	0.0339	0.0233	8.0504
	16 / 1	0.1224	7.8521	16.8012	58.5024	9.0957	0.2721	0.0000	0.0000	7.3542
	17 / 1	0.1173	8.8158	15.1405	59.2513	9.2608	0.1067	0.0000	0.0148	7.2928
	18 / 1	0.1426	8.6048	13.6310	59.1111	9.1321	0.4067	0.0000	0.0000	8.9717
	22 / 1	0.2235	6.0386	16.8418	60.7545	8.8567	0.1472	0.0074	0.0593	7.0711
	23 / 1	0.1724	7.9584	15.2076	58.1092	9.1655	0.5651	0.0000	0.0022	8.8196
	25 / 1	0.1270	2.4777	15.6100	68.3264	6.6427	0.3697	0.0953	0.0000	6.3513
	26 / 1	0.2232	2.2200	25.9774	53.0212	9.4183	3.2091	0.0497	0.0000	5.8811
	30 / 1	0.2467	9.4896	13.4018	57.0048	8.6661	3.1657	0.0000	0.0000	8.0253
	31 / 1	0.2513	8.7429	14.4739	56.9188	8.6601	2.4127	0.0594	0.0276	8.4533
	32 / 1	0.1903	9.9515	13.1916	59.3954	9.0607	0.0973	0.0524	0.0706	7.9902
	33 / 1	0.1261	7.8335	15.7525	57.2485	9.1863	0.1304	0.0021	0.0182	9.7024
	34 / 1	0.1859	9.7158	13.8362	58.9635	9.0322	0.1373	0.0328	0.0000	8.0961
	35 / 1	0.1151	8.8289	15.4483	58.1873	8.9336	0.1434	0.0722	0.0000	8.2711
	36 / 1	0.1112	8.9844	13.8417	58.8580	9.1061	0.1060	0.0346	0.0052	8.9529
	40 / 1	0.2211	8.8630	14.1054	58.2170	8.8555	0.0508	0.0529	0.0138	9.6205
	42 / 1	0.3314	9.5090	13.8094	57.4650	8.6529	0.2092	0.0117	0.0000	10.0114
Facies C	73 / 1	0.0868	4.9477	18.4138	61.4979	8.4118	0.2710	0.0000	0.0042	6.3669
	74 / 1	0.1103	4.8425	22.0116	57.2523	8.9534	0.2793	0.0698	0.0769	6.4038
	75 / 1	0.0801	3.9414	18.2422	63.7186	7.6813	0.2604	0.0285	0.0000	6.0475
	80 / 1	0.0728	6.5861	16.0724	61.3135	8.3791	0.2321	0.0000	0.1082	7.2357
	81 / 1	0.0824	7.5048	17.8061	56.9636	9.2564	0.2623	0.0000	0.0412	8.0833
	82 / 1	0.0485	8.5689	16.1310	58.1131	9.1661	0.2641	0.0032	0.0000	7.7051
	18 / 1	0.0975	7.9422	16.9154	57.1807	9.4000	0.2199	0.0217	0.0000	8.2228
	19 / 1	0.1065	8.9439	15.5355	56.6437	9.4971	0.3513	0.0000	0.0077	8.9143
	20 / 1	0.0646	7.4961	17.4553	56.7520	9.3286	0.2787	0.0194	0.0732	8.5321
	1 / 1	0.0675	5.8487	19.3350	57.9825	9.0532	0.1646	0.0000	0.0521	7.4964
	2 / 1	0.0351	6.2226	18.0833	58.1039	9.4879	0.2322	0.0288	0.0138	7.7924
	3 / 1	0.0978	7.0622	17.0053	58.2899	9.2608	0.2977	0.0107	0.0000	7.9756
	5 / 1	0.0570	8.0245	13.6903	58.5723	9.9933	0.2508	0.0000	0.0228	9.3891
	7 / 1	0.0241	8.3139	14.1750	58.6469	9.6198	0.2250	0.0560	0.0000	8.9394
	10 / 1	0.0389	8.1510	15.5936	58.8536	8.9751	0.2305	0.0358	0.0000	8.1215

Table 11: Geochemical analysis for glauconites of the Rampur Shale (Facies B, C, and D)

RECALCULATED DATA										
Facies C	DataSet /Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Cr ₂ O ₃	MnO	Fe ₂ O ₃
	11 / 1	0.1468	5.3317	19.5891	58.2394	8.3344	0.3305	0.0232	0.0000	8.0050
	12 / 1	0.0878	6.1068	18.6106	57.8532	8.5733	0.4563	0.0671	0.0103	8.2347
	13 / 1	0.0366	8.0157	16.3281	57.0021	9.2297	0.1473	0.0000	0.0000	9.2405
	14 / 1	0.0368	7.4070	15.3991	58.6963	9.3333	0.2300	0.0410	0.0000	8.8565
	15 / 1	0.0934	6.5700	17.7414	58.3051	8.7804	0.2771	0.0259	0.0000	8.2066
	16 / 1	0.0392	7.7316	17.0730	58.5607	8.9423	0.1557	0.0000	0.0000	7.4975
	23 / 1	0.1152	3.1819	18.6163	64.9981	7.4272	0.1397	0.0214	0.0000	5.5003
	28 / 1	0.0468	6.4100	18.1513	57.8755	9.0003	0.2743	0.0000	0.0000	8.2418
	29 / 1	0.1869	6.8908	14.7328	58.2529	9.2434	0.1627	0.0000	0.0000	10.5305
	30 / 1	0.2065	6.6884	15.3660	56.2748	9.1254	0.1127	0.0000	0.0000	12.2262
	31 / 1	0.0716	6.9704	14.1792	58.4534	9.5815	0.2128	0.0086	0.0257	10.4968
	33 / 1	0.0211	7.1472	13.8946	58.5946	9.4315	0.1793	0.0000	0.0000	10.7318
	34 / 1	0.0134	6.7349	15.1046	58.1409	9.0126	0.2015	0.0000	0.0000	10.7921
	35 / 1	0.0503	7.0551	13.9069	58.0322	9.6168	0.1850	0.0043	0.0000	11.1495
	36 / 1	0.0115	7.1514	16.4122	58.3498	9.0029	0.2432	0.0084	0.0000	8.8205
	37 / 1	0.0103	8.2550	16.4256	58.4738	8.8666	0.1410	0.0237	0.0000	7.8041
	38 / 1	0.0000	5.3093	19.4648	58.2594	8.9949	0.1506	0.0000	0.0567	7.7643
	39 / 1	0.0949	8.2079	12.6041	58.6048	9.7595	0.2202	0.0283	0.0000	10.4802
	40 / 1	0.1734	8.6048	12.0822	58.9488	9.5349	0.1788	0.0000	0.0000	10.4771
	41 / 1	0.0790	5.8314	18.8137	58.1221	8.7392	0.3077	0.0843	0.0148	8.0078
	42 / 1	0.0745	5.3279	19.8403	57.1524	9.2644	0.3023	0.0575	0.0000	7.9806
	44 / 1	0.0706	8.6828	14.1846	58.8434	8.9017	0.2475	0.0020	0.0655	9.0019
	1 / 1	0.0797	9.3221	13.2309	59.8479	9.1446	0.2520	0.0000	0.0000	8.1227
	2 / 1	0.0423	8.8305	13.7427	59.3919	9.1558	0.2810	0.0000	0.0877	8.4681
	3 / 1	0.0591	9.9907	13.5403	59.3604	8.9115	0.1700	0.0498	0.0000	7.9183
	4 / 1	0.0272	9.6168	12.9110	59.4485	8.9434	0.2018	0.0000	0.0000	8.8513
	5 / 1	0.0431	9.4741	13.3468	59.5172	9.0674	0.2323	0.0137	0.0000	8.3055
	6 / 1	0.1337	7.1423	15.6883	54.7183	8.0515	0.3328	0.0705	0.0000	13.8626
	7 / 1	0.0692	7.2309	14.9567	52.5236	8.3947	0.3695	0.0000	0.0249	16.4306
	8 / 1	0.0357	6.9213	15.9979	57.9816	9.5496	0.2825	0.0000	0.0271	9.2043
	11 / 1	0.0907	10.1221	12.9351	59.5959	8.8698	0.2154	0.0000	0.0000	8.1709
	12 / 1	0.1052	6.8444	16.8971	57.5377	8.9465	0.2711	0.0010	0.0711	9.3259
	13 / 1	0.1038	9.5538	13.4900	58.8439	9.3674	0.2361	0.0000	0.0032	8.4019
	14 / 1	0.0782	9.5152	12.9737	59.4919	9.6564	0.2053	0.0402	0.0000	8.0391
	18 / 1	0.1107	4.0004	14.1749	67.5924	4.8659	0.2598	0.1294	0.0000	8.8664
	23 / 1	0.0526	7.6333	15.2467	58.8703	9.4018	0.2355	0.0074	0.0000	8.5523
	25 / 1	0.0254	8.4917	13.9298	58.9854	9.6464	0.2995	0.0000	0.0000	8.6218
	26 / 1	0.0582	9.7387	13.8890	59.3549	9.4250	0.2167	0.0000	0.0000	7.3175
	27 / 1	0.0610	8.0899	16.0051	58.6546	9.1573	0.2389	0.0558	0.0000	7.7373
	28 / 1	0.0690	8.2537	15.7817	58.6448	9.5326	0.2227	0.0146	0.0000	7.4809
	29 / 1	0.0893	8.6847	15.1256	58.8347	9.0283	0.2377	0.0311	0.0156	7.9530
	30 / 1	0.0122	4.7026	16.0729	64.6508	7.9732	0.2662	0.0367	0.0347	6.2507

Table 11: Geochemical analysis for glauconites of the Rampur Shale (Facies B, C, and D)

RECALCULATED DATA										
Facies C	DataSet /Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Cr ₂ O ₃	MnO	Fe ₂ O ₃
	32 / 1	0.0000	7.0321	16.9566	59.1540	8.9882	0.1196	0.0237	0.0417	7.6842
	37 / 1	0.0486	9.9443	12.9478	59.7748	9.1002	0.2060	0.0000	0.0095	7.9688
	38 / 1	0.0211	7.7987	15.5636	58.7861	9.4686	0.1297	0.0000	0.0000	8.2322
	39 / 1	0.0309	8.0522	15.0589	59.3723	8.7980	0.1947	0.0628	0.0021	8.4282
	40 / 1	0.0857	9.4114	12.8406	59.2891	9.0371	0.1788	0.0261	0.0000	9.1312
Facies D	5 / 1	0.0499	9.2346	15.6815	58.7242	9.0861	0.1828	0.0104	0.0000	7.0304
	7 / 1	0.0548	8.5055	17.0227	57.8754	9.4157	0.2307	0.0042	0.0716	6.8193
	8 / 1	0.0488	9.9837	14.5990	58.8595	9.0291	0.1922	0.0301	0.0000	7.2576
	16 / 1	0.0459	9.0182	15.9427	58.4908	9.1099	0.2418	0.0511	0.0000	7.0997
	17 / 1	0.0434	11.4689	13.3465	58.8266	8.9916	0.2219	0.0341	0.0000	7.0671
	18 / 1	0.0458	9.6353	15.0898	58.1123	9.6013	0.1949	0.0000	0.0000	7.3206
	25 / 1	0.0189	9.1107	15.7232	58.0848	9.2501	0.1823	0.1467	0.0000	7.4833
	26 / 1	0.0427	8.4243	16.6040	58.6651	9.2508	0.2134	0.0666	0.0146	6.7186
	27 / 1	0.0518	10.1397	14.4882	58.5425	8.8492	0.2747	0.2021	0.0000	7.4517
	10 / 1	0.0934	10.5639	14.3749	59.1293	8.8239	0.1635	0.1561	0.0000	6.6950
	11 / 1	0.0550	9.0144	15.9371	58.6034	8.9182	0.0984	0.0222	0.0286	7.3228
	13 / 1	0.0725	10.8951	15.0463	58.8893	8.8636	0.1103	0.0778	0.0000	6.0452
	14 / 1	0.0583	8.4285	16.5996	58.7529	8.9924	0.1304	0.1070	0.0000	6.9310
	15 / 1	0.0757	9.5087	16.5559	58.7937	8.4201	0.1524	0.1514	0.0000	6.3420
	16 / 1	0.0286	7.5141	16.9232	60.1724	8.4059	0.2025	0.0764	0.0764	6.6005
	19 / 1	0.0188	9.1996	15.4782	58.7345	9.0944	0.2031	0.0000	0.0000	7.2713
	20 / 1	0.0297	7.7011	17.4285	57.5965	9.1230	0.2264	0.0768	0.0000	7.8179
	21 / 1	0.0382	11.1617	12.9928	58.5659	9.2839	0.1984	0.1029	0.0000	7.6561
	29 / 1	0.0888	10.3592	14.7867	61.0330	7.6913	0.4641	0.0269	0.0565	5.4934
	30 / 1	0.0522	10.0127	14.7520	58.4545	9.2269	0.3508	0.0725	0.0000	7.0783
	1 / 1	0.0418	9.7407	15.0486	58.4184	8.8282	0.1024	0.0408	0.0826	7.6965
	2 / 1	0.0516	9.3393	14.8196	59.4185	8.7778	0.0853	0.0000	0.0000	7.5079
	3 / 1	0.0317	10.5079	14.3026	58.8542	8.8843	0.1015	0.0814	0.0275	7.2089
	6 / 1	0.0114	7.0961	18.4918	57.5185	9.0531	0.1060	0.0000	0.0915	7.6316
	7 / 1	0.0411	8.1927	15.9134	61.5681	8.2594	0.1273	0.2011	0.0000	5.6969
	1 / 1	0.0525	8.7644	14.4859	58.7450	9.1531	0.2216	0.0483	0.0000	8.5291
	2 / 1	0.0251	7.6810	14.1098	58.1290	9.2558	0.1525	0.0188	0.0230	10.6051
	3 / 1	0.0180	8.5948	15.2673	58.3790	9.4412	0.2380	0.0042	0.0296	8.0278
	4 / 1	0.0616	7.6309	15.6622	58.3701	9.1464	0.2783	0.0544	0.0000	8.7962
	5 / 1	0.0311	8.8986	13.3217	58.9486	9.3474	0.2716	0.0000	0.0526	9.1284
	14 / 1	0.0914	6.0936	18.6475	57.7835	9.1363	0.3067	0.0000	0.0000	7.9411
	17 / 1	0.0849	7.5249	16.9213	58.5128	8.9155	0.2660	0.0000	0.0327	7.7418
	18 / 1	0.0664	6.9867	16.2171	58.5500	8.9276	0.2739	0.0000	0.0622	8.9162
	19 / 1	0.0490	6.4528	17.9259	57.8560	9.2457	0.1909	0.0063	0.0000	8.2733
	20 / 1	0.0371	5.6147	16.9815	59.6080	9.2096	0.2943	0.0000	0.0000	8.2548
	21 / 1	0.0574	7.7137	16.0857	58.4122	9.0043	0.2723	0.0835	0.0365	8.3345
	22 / 1	0.0684	7.1501	16.5586	55.6946	8.7645	0.2105	0.0000	0.0000	11.5534

Table 11: Geochemical analysis for glauconites of the Rampur Shale (Facies B, C, and D)

RECALCULATED DATA										
Facies D	DataSet /Point	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Cr ₂ O ₃	MnO	Fe ₂ O ₃
	24 / 1	0.0443	9.1176	13.1669	58.7077	9.2051	0.2234	0.0000	0.0000	9.5350
	25 / 1	0.0741	8.6837	13.9520	58.5451	9.0604	0.1979	0.0339	0.0243	9.4286
	26 / 1	0.0379	8.6013	13.8601	58.6525	8.6454	0.2563	0.0000	0.0000	9.9465
	27 / 1	0.0822	8.9243	13.3243	58.0247	9.0654	0.2117	0.0000	0.0000	10.3674
	5 / 1	0.1196	7.7508	15.7408	60.1502	8.6785	0.2834	0.0625	0.0582	7.1561
	9 / 1	0.1355	6.6336	17.5653	58.2143	9.4219	0.2635	0.0849	0.0000	7.6810
	10 / 1	0.1916	5.1956	19.6215	58.7781	8.9945	0.2305	0.0758	0.0000	6.9124
	11 / 1	0.2066	5.5125	19.5627	57.9720	8.7317	0.2317	0.1562	0.0273	7.5992
	12 / 1	0.1439	6.1538	18.8422	58.1129	9.3610	0.2705	0.0151	0.0411	7.0595
	13 / 1	0.1632	5.1633	18.5658	58.6229	9.0087	0.3084	0.0389	0.0389	8.0897
	14 / 1	0.1679	6.9180	16.5694	58.8130	9.0579	0.3016	0.0353	0.0000	8.1371
	17 / 1	0.0817	4.8241	19.8910	58.9707	8.9373	0.5484	0.0043	0.0000	6.7425
	18 / 1	0.1335	5.8304	16.3400	59.2430	8.8747	0.4388	0.1576	0.0285	8.9535
	21 / 1	0.1000	4.8116	20.4110	58.2514	8.8273	0.2632	0.0000	0.0474	7.2880
	24 / 1	0.0878	4.8059	20.4857	58.2647	8.7055	0.5099	0.0225	0.0000	7.1178
	28 / 1	0.1412	2.8530	15.7950	69.3192	7.1990	0.2076	0.0853	0.0116	4.3881
	32 / 1	0.1238	8.0102	15.5878	59.0909	8.9909	0.2518	0.0190	0.0000	7.9256
	38 / 1	0.1159	8.9702	13.8149	59.4957	8.8986	0.2254	0.0000	0.0558	8.4236
	39 / 1	0.1156	6.0090	18.4839	57.7364	9.3614	0.2737	0.0000	0.0000	8.0200
	40 / 1	0.1130	4.9088	19.4910	58.4279	9.2019	0.2648	0.0000	0.0000	7.5925
	41 / 1	0.1184	4.8166	19.9724	58.2217	9.3317	0.3014	0.0000	0.0000	7.2377
	42 / 1	0.1326	4.0605	13.9790	69.4580	6.4835	0.2621	0.0840	0.0385	5.5017
	43 / 1	0.1979	3.1431	21.0673	59.9396	9.4455	0.2721	0.0129	0.0301	5.8916

Table 11: Geochemical analysis for glauconites of the Rampur Shale (Facies B, C, and D)

Facies		Sample	Al ₂ O ₃ (%)	CaO (%)	Fe ₂ O ₃ (%)	K ₂ O (%)	MgO (%)	Na ₂ O (%)	P ₂ O ₅ (%)	SiO ₂ (%)	TiO ₂ (%)
D	Glaucinitic siltstone	S41	16.3519	0.1371	3.0172	7.4902	1.5086	0.0949	0.0422	70.9991	0.3587
		S39	13.4795	0.2012	3.1184	6.9208	1.6900	0.0000	0.0302	74.1374	0.4124
	Shale	RKI4SH6	14.5985	0.0526	1.5051	8.8096	0.8210	0.2000	0.0421	73.7817	0.1895
		RKI4SH5	15.9178	0.1590	4.1331	6.9627	1.7486	0.2226	0.0636	70.3688	0.4239
	Glaucinitic siltstone	S38	12.4736	0.0950	3.1764	5.4031	1.3613	0.2111	0.0422	76.8890	0.3482
	Shale	RKI4SH4	16.7055	0.1695	3.6547	7.9237	1.7161	0.2225	0.0530	69.1208	0.4343
	Glaucinitic siltstone	S37	17.6034	0.3712	4.8356	7.5610	2.0997	0.1060	0.0742	66.8081	0.5302
		S36	13.4851	0.1276	3.5095	7.1786	1.7441	0.2233	0.0638	73.3489	0.3190
	Shale	RKI4SH3	15.7302	0.1894	4.8716	6.0711	1.8203	0.2315	0.0631	70.5703	0.4524
	Glaucinitic siltstone	S31	12.4630	0.0528	3.5277	5.0380	1.6054	0.2324	0.0634	76.6160	0.4014
	Shale	RKI4SH2	15.6898	0.1578	4.2408	6.9347	1.7047	0.2210	0.0631	70.5672	0.4209
		RKI4SH1	16.3045	0.2415	4.7034	6.2677	1.9318	0.2310	0.0630	69.8058	0.4514
C	Shale	RKI3SH8	18.2378	0.1670	4.5203	7.2346	2.0044	0.2401	0.0731	67.0216	0.5011
		RKI3SH7	17.2181	0.1144	4.1303	6.6063	1.7270	0.2289	0.0416	69.4548	0.4786
		RKI3SH6	17.8749	0.0739	4.4951	6.7215	1.9204	0.2427	0.0633	68.1123	0.4959
		RKI3SH5	16.2895	0.1676	4.1588	6.5891	2.1580	0.2409	0.0733	69.8093	0.5133
		RKI3SH4	15.9763	0.1665	4.0903	6.6091	2.0920	0.2394	0.0729	70.2956	0.4580
		RKI3SH2	15.0276	0.1460	3.1494	6.6535	1.9814	0.2294	0.0730	72.3016	0.4380
		RKI3SH0	16.8194	0.1562	3.8429	7.2381	2.3120	0.2395	0.0729	68.8398	0.4791
	Glaucinitic sandstone	S23	8.0933	0.0622	2.4456	3.3886	1.9793	0.0000	0.0000	83.8342	0.1969
		S19	9.0928	0.0830	3.3838	4.4841	3.4357	0.0000	0.0000	79.4063	0.1142
B	Shale	RKI2C	16.9716	0.1034	3.8553	7.1008	1.8915	0.2274	0.0517	69.3437	0.4548
		RKI2B	15.4966	0.1664	3.6193	6.7187	1.9761	0.2392	0.0728	71.2324	0.4784
		RK-33- SStn	11.8400	0.1200	4.1400	5.9900	1.2400	0.0000	0.0315	72.1900	0.4947
		RK-33-Sh	9.2900	0.1000	2.2300	5.4500	1.0100	0.0000	0.0184	79.1600	0.3015
	Glaucinitic Sandstone	S18	13.0300	0.1758	4.8397	6.2978	4.4261	0.0000	0.0517	70.9411	0.2378
		S16	15.7422	0.5811	4.2155	6.7195	1.9334	0.0000	0.1162	70.1532	0.5388
	Shale	RKI2A2	15.8574	0.1033	3.3988	6.5599	1.9525	0.2273	0.0620	71.3533	0.4855
		RKI2A1	13.3319	0.1872	3.9413	6.0108	2.0903	0.2184	0.0936	73.7001	0.4264
		RKI2A`	16.4268	0.0730	3.8798	6.7272	1.7939	0.2295	0.0521	70.2753	0.5423
	Green Shale	S 13 d	18.2726	0.1445	2.5602	10.4267	4.3875	0.0000	0.0413	63.3862	0.3407
		S 13 c	18.9727	0.4434	2.3613	12.5797	4.2792	0.0000	0.0412	60.3209	0.3918
		S 13 b	17.6294	0.3215	2.5096	10.5777	4.4696	0.0000	0.0000	63.5697	0.3422
		S 13 a	17.8971	0.3642	2.3412	11.8620	4.0373	0.0000	0.0000	62.7440	0.3642
		Avg. Sh	16.7000	2.2000	2.8000	3.6000	2.6000	1.6000	0.1600	58.9000	0.7800

Table 12: Major element concentration in glauconite associated sediments (oxide form in weight % and elemental form both in weight % and ppm concentration)

Facies		Sample	Al	Ca	Fe	K	Mg	Na	P	Si	Ti
D	Glaucinitic siltstone	S41	8.6551	0.0980	2.1102	6.2176	0.9097	0.0704	0.0184	33.1850	0.2150
		S39	7.1347	0.1438	2.1810	5.7450	1.0191	0.0000	0.0132	34.6518	0.2472
	Shale	RKI4SH6	7.7270	0.0376	1.0527	7.3128	0.4950	0.1484	0.0184	34.4856	0.1136
		RKI4SH5	8.4253	0.1136	2.8907	5.7797	1.0544	0.1651	0.0277	32.8904	0.2541
	Glaucinitic siltstone	S38	6.6023	0.0679	2.2216	4.4851	0.8209	0.1566	0.0184	35.9379	0.2087
	Shale	RKI4SH4	8.8422	0.1211	2.5561	6.5775	1.0348	0.1650	0.0231	32.3070	0.2603
	Glaucinitic siltstone	S37	9.3175	0.2653	3.3820	6.2764	1.2661	0.0787	0.0324	31.2261	0.3178
		S36	7.1376	0.0912	2.4546	5.9589	1.0517	0.1657	0.0278	34.2833	0.1912
	Shale	RKI4SH3	8.3260	0.1354	3.4072	5.0396	1.0976	0.1717	0.0276	32.9846	0.2712
	Glaucinitic siltstone	S31	6.5967	0.0377	2.4673	4.1821	0.9681	0.1724	0.0277	35.8103	0.2406
C	Shale	RKI4SH2	8.3046	0.1128	2.9660	5.7565	1.0279	0.1639	0.0276	32.9831	0.2523
		RKI4SH1	8.6300	0.1726	3.2896	5.2028	1.1649	0.1714	0.0275	32.6272	0.2706
		RKI3SH8	9.6533	0.1194	3.1615	6.0054	1.2086	0.1781	0.0319	31.3259	0.3004
		RKI3SH7	9.1135	0.0818	2.8887	5.4839	1.0414	0.1698	0.0182	32.4632	0.2869
		RKI3SH6	9.4612	0.0528	3.1439	5.5795	1.1580	0.1801	0.0276	31.8357	0.2973
		RKI3SH5	8.6221	0.1198	2.9087	5.4697	1.3013	0.1788	0.0320	32.6289	0.3077
		RKI3SH4	8.4562	0.1190	2.8608	5.4862	1.2615	0.1776	0.0318	32.8562	0.2745
		RKI3SH2	7.9541	0.1043	2.2027	5.5230	1.1948	0.1702	0.0319	33.7938	0.2625
		RKI3SH0	8.9025	0.1116	2.6878	6.0083	1.3941	0.1777	0.0318	32.1757	0.2872
	Glaucinitic sandstone	S23	4.2838	0.0444	1.7104	2.8129	1.1935	0.0000	0.0000	39.1841	0.1180
		S19	4.8128	0.0593	2.3667	3.7223	2.0718	0.0000	0.0000	37.1145	0.0684
B	Shale	RKI2C	8.9831	0.0739	2.6964	5.8944	1.1406	0.1687	0.0226	32.4112	0.2726
		RKI2B	8.2024	0.1189	2.5314	5.5772	1.1916	0.1775	0.0318	33.2940	0.2868
		RK-33-SStn	6.2669	0.0858	2.8955	4.9723	0.7477	0.0000	0.0137	33.7416	0.2965
		RK-33-Sh	4.9172	0.0715	1.5597	4.5240	0.6090	0.0000	0.0080	36.9994	0.1807
	Glaucinitic Sandstone	S18	6.8968	0.1256	3.3849	5.2278	2.6689	0.0000	0.0226	33.1578	0.1426
		S16	8.3324	0.4153	2.9483	5.5779	1.1659	0.0000	0.0507	32.7896	0.3230
	Shale	RKI2A2	8.3933	0.0738	2.3771	5.4454	1.1773	0.1686	0.0270	33.3505	0.2910
		RKI2A1	7.0566	0.1338	2.7566	4.9896	1.2604	0.1620	0.0408	34.4474	0.2556
		RKI2A`	8.6947	0.0522	2.7136	5.5842	1.0817	0.1702	0.0228	32.8467	0.3251
	Green Shale	S 13 d	9.6717	0.1033	1.7906	8.6552	2.6457	0.0000	0.0180	29.6267	0.2042
		S 13 c	10.0423	0.3169	1.6515	10.4424	2.5803	0.0000	0.0180	28.1940	0.2349
		S 13 b	9.3313	0.2298	1.7552	8.7805	2.6952	0.0000	0.0000	29.7125	0.2051
		S 13 a	9.4729	0.2603	1.6374	9.8467	2.4345	0.0000	0.0000	29.3265	0.2183
		Avg. Sh	8.8393	1.5723	1.9583	2.9884	1.5678	1.1870	0.0698	27.5299	0.4675

Table 12: Major element concentration in glauconite associated sediments (oxide form in weight % and elemental form both in weight % and ppm concentration)

Facies		Sample	Al	Ca	Fe	K	Mg	Na	P	Si	Ti
D	Glaucinitic siltstone	S41	86550.80	980.18	21102.27	62176.50	9096.85	704.41	184.15	331849.56	2149.97
		S39	71347.15	1437.88	21810.08	57449.83	10190.52	0.00	131.70	346518.26	2472.13
	Shale	RKI4SH6	77269.67	376.12	10526.70	73128.48	4950.43	1483.64	183.73	344855.70	1135.59
		RKI4SH5	84252.71	1136.13	28906.95	57797.34	10544.19	1651.11	277.49	328903.77	2540.91
	Glaucinitic siltstone	S38	66022.86	678.80	22216.06	44851.33	8208.84	1565.85	184.21	359379.11	2087.40
	Shale	RKI4SH4	88422.26	1211.36	25560.70	65774.87	10348.09	1650.41	231.14	323070.44	2603.33
	Glaucinitic siltstone	S37	93174.76	2652.65	33820.40	62763.66	12661.08	786.74	323.94	312260.87	3178.15
		S36	71376.41	912.09	24545.57	59589.23	10517.07	1656.91	278.46	342832.90	1912.37
	Shale	RKI4SH3	83260.05	1353.60	34072.20	50396.43	10976.33	1717.36	275.51	329845.52	2711.93
	Glaucinitic siltstone	S31	65966.84	377.43	24672.54	41820.63	9680.61	1723.89	276.55	358103.04	2405.70
	Shale	RKI4SH2	83046.02	1128.12	29659.92	57564.55	10279.49	1639.47	275.53	329831.04	2522.99
		RKI4SH1	86299.52	1725.78	32895.66	52028.31	11648.50	1713.57	274.90	326272.19	2705.95
C	Shale	RKI3SH8	96532.74	1193.78	31615.01	60054.21	12086.44	1781.37	318.91	313259.00	3003.57
		RKI3SH7	91135.20	817.90	28887.00	54839.11	10413.86	1698.06	181.61	324631.96	2868.54
		RKI3SH6	94611.61	527.90	31438.68	55795.47	11580.25	1800.54	276.29	318356.76	2972.65
		RKI3SH5	86220.56	1197.90	29086.72	54696.51	13012.57	1787.52	320.01	326288.87	3076.74
		RKI3SH4	84562.40	1190.17	28607.85	54861.94	12614.80	1775.99	317.94	328561.57	2744.96
		RKI3SH2	79541.28	1043.47	22027.20	55230.35	11948.07	1702.14	318.57	337937.66	2625.38
		RKI3SH0	89025.15	1116.49	26877.59	60083.26	13941.47	1777.10	318.14	321757.34	2871.53
	Glaucinitic sandstone	S23	42837.65	444.37	17104.50	28128.78	11935.03	0.00	0.00	391841.04	1180.17
		S19	48128.17	593.48	23666.64	37222.67	20717.56	0.00	0.00	371144.90	684.39
B	Shale	RKI2C	89830.55	738.71	26963.95	58943.53	11405.58	1687.01	225.53	324112.31	2725.95
		RKI2B	82023.61	1189.31	25313.70	55771.67	11915.76	1774.70	317.71	332940.47	2867.64
		RK-33-SStn	62669.12	857.64	28955.16	49722.99	7477.20	0.00	137.47	337416.06	2965.23
		RK-33-Sh	49171.97	714.70	15596.62	45240.45	6090.30	0.00	80.30	369993.84	1807.19
	Glaucinitic Sandstone	S18	68967.74	1256.45	33848.93	52278.27	26689.14	0.00	225.65	331578.49	1425.67
		S16	83323.51	4153.04	29483.42	55778.51	11658.64	0.00	507.17	327896.04	3229.73
	Shale	RKI2A2	83933.42	738.33	23770.93	54453.87	11773.45	1686.14	270.50	333505.35	2910.31
		RKI2A1	70565.99	1337.83	27565.79	49895.78	12604.31	1620.21	408.44	344474.19	2555.68
		RKI2A`	86946.96	521.79	27135.67	55842.15	10817.27	1702.32	227.58	328466.96	3250.81
	Green Shale	S 13 d	96716.69	1032.95	17906.21	86552.19	26456.51	0.00	180.21	296267.05	2042.01
		S 13 c	100422.68	3168.87	16514.79	104424.48	25803.43	0.00	179.99	281939.97	2348.62
		S 13 b	93312.59	2297.60	17552.15	87805.15	26951.57	0.00	0.00	297124.59	2051.26
S 13 a		94729.49	2602.84	16374.31	98466.87	24344.67	0.00	0.00	293265.45	2182.93	
	Average Shale	Avg. Sh	88393.10	15723.40	19583.20	29883.60	15678.00	11870.40	698.24	275298.60	4675.32

Table 12: Major element concentration in glauconite associated sediments (oxide form in weight % and elemental form both in weight % and ppm concentration)

Facies		Sample	Li	Be	Sc	V	Cr	Mn	Co	Ni
D	Glaucinitic siltstone	S 41	43.2855	3.5550	13.0288	57.2151	51.4950	60.6891	14.0067	19.9695
		S 39	107.2001	4.4372	8.7157	34.1390	38.3212	49.2821	32.0518	14.4478
	Shale	RKI4 Sh6	17.0069	2.2889	7.8101	28.6324	28.2848	24.8392	16.4980	11.1690
		RKI4 Sh5	38.3273	3.1876	11.3782	48.9139	54.2428	62.8760	18.5914	19.7672
	Glaucinitic siltstone	S 38	41.4711	2.5932	8.2836	42.4003	46.1412	47.0174	28.5501	18.6985
	Shale	RKI4 Sh4	42.4242	3.7467	13.3452	55.8376	59.8121	81.5505	16.0155	19.2080
	Glaucinitic siltstone	S 37	56.7835	4.7310	15.9924	70.3588	69.5652	81.9322	11.1349	19.5456
		S 36	45.2544	2.5394	7.9386	33.1979	37.0812	40.4933	15.5377	15.3193
	Shale	RKI4 Sh3	36.8843	3.1606	12.8069	71.1826	71.3026	71.5516	13.6672	26.7586
	Glaucinitic siltstone	S 31	36.0236	1.8899	9.3669	45.7986	56.3775	60.6316	37.4386	18.9942
C	Shale	RKI4 Sh2	33.5383	3.3983	13.5561	67.2953	66.7967	109.0014	12.6979	22.9435
		RKI4 Sh1	47.4843	3.7627	15.9767	69.7681	85.2606	74.1111	11.1744	23.0198
		RKI3 Sh8	38.0574	4.4214	17.5486	78.8864	88.1402	89.0814	13.7049	22.9229
		RKI3 Sh7	33.2457	3.9640	17.6098	81.5247	91.9816	89.5184	19.7268	31.8412
		RKI3 Sh6	29.5272	3.3867	14.3571	72.5702	80.1058	71.0671	22.6011	28.8102
		RKI3 Sh5	38.3763	3.5320	13.9436	72.8500	75.5778	92.8437	15.0991	24.3415
		RKI3 Sh4	44.8863	3.6708	13.6860	69.2103	74.8501	99.8287	24.9730	24.8930
		RKI3 Sh2	46.2894	3.1384	12.2851	61.1363	65.0191	72.5449	22.1760	20.3422
		RKI3 Sh0	61.2249	4.1972	14.1304	76.7294	77.3787	88.9178	15.6473	24.0883
	Glaucinitic sandstone	S 23	292.9291	5.9075	8.0363	26.2585	26.0663	23.7093	70.5729	7.9218
		S 19	534.3365	10.1940	10.9228	35.8357	26.7348	12.7796	44.5089	6.3883
B	Shale	RKI2 ShC	62.4735	4.3495	13.8865	72.8617	72.2247	95.1941	21.9461	25.4045
		RKI2 ShB	50.4817	3.9900	14.3667	71.6984	73.0624	82.9441	25.5727	25.8350
		RK/33a	0.0000	0.0000	6.6682	31.9946	39.8789	0.0000	31.8259	17.2820
		Rk/33c	0.0000	0.0000	5.1367	23.9493	21.5949	0.0000	10.6894	11.2453
	Glaucinitic Sandstone	S 18	667.4661	13.3207	14.6277	48.6637	47.7473	36.6352	49.6453	10.1783
		S 16	48.2521	3.8940	12.5676	61.8351	60.3125	53.3668	20.7498	23.0644
	Shale	RKI2 ShA2	50.4409	3.5838	12.7458	65.1388	64.8045	72.8086	20.5776	24.1811
		RKI2 ShA1	48.7642	2.5389	10.8666	55.8248	53.5861	64.0214	20.0232	22.2668
		RKI2 ShA	53.8654	4.2894	12.9951	72.9138	79.3953	68.9376	17.7042	20.7710
	Green Shale	S 13 d	285.0930	5.3274	8.5373	7.8229	1.6816	21.1567	6.5590	7.7219
		S 13 c	327.2033	6.4258	10.4096	9.4329	1.5512	25.9341	9.5361	13.2801
		S 13 b	330.0205	7.2766	9.8533	9.6296	1.2699	23.9766	9.5344	13.6986
		S 13 a	275.9262	6.2417	8.4889	7.4205	2.0126	25.2446	6.6165	7.7030
		average Shale	66.0000	3.0000	13.0000	130.0000	90.0000	850.0000	19.0000	68.0000

Table 13: Trace and REE concentration in glauconite associated sediments from Middle segment (Facies B, C, D)

Facies		Sample	Cu	Zn	Ga	Rb	Sr	Y	Zr
D	Glaucinitic siltstone	S 41	1.5881	0.0000	22.3902	250.7864	14.6596	17.0942	116.5567
		S 39	11.2239	0.0000	16.1566	184.2417	14.9173	15.7542	199.3134
	Shale	RKI4 Sh6	1.2705	18.3333	23.9147	168.5933	11.1756	33.2784	150.0511
		RKI4 Sh5	3.4721	43.2119	24.4435	207.5525	18.2618	31.7839	182.7919
	Glaucinitic siltstone	S 38	20.8525	33.9564	19.9118	192.9867	23.1737	19.7267	215.3271
	Shale	RKI4 Sh4	1.6526	36.9024	28.7783	223.6959	20.1876	50.9875	256.3326
	Glaucinitic siltstone	S 37	3.5862	0.0000	24.0104	258.0191	21.1968	21.6972	142.8803
		S 36	22.7752	28.3483	16.0658	154.6781	22.7683	24.4794	202.0754
	Shale	RKI4 Sh3	2.9952	51.4332	27.2491	237.1199	23.5477	27.1996	145.1443
	Glaucinitic siltstone	S 31	4.8222	36.4962	18.3125	151.8832	19.9136	29.0374	291.6052
	Shale	RKI4 Sh2	1.8223	43.5569	27.9853	245.8112	19.3692	27.2184	135.1660
		RKI4 Sh1	24.2481	49.5027	27.4431	239.3895	27.7712	30.6635	151.4211
C	Shale	RKI3 Sh8	1.5202	51.2941	31.4343	260.2522	25.2213	40.7615	176.2225
		RKI3 Sh7	2.5389	49.7816	33.7267	266.0268	24.4382	43.5257	193.1951
		RKI3 Sh6	3.9382	48.7339	29.4936	233.3825	21.1954	36.8050	149.1387
		RKI3 Sh5	5.9167	46.1739	26.5299	237.2679	22.2568	34.9251	161.7432
		RKI3 Sh4	4.9144	55.8554	28.4888	239.3194	25.7361	36.5080	187.7710
		RKI3 Sh2	4.1448	52.5289	23.5379	214.7234	27.6241	34.4706	219.3449
		RKI3 Sh0	2.1570	48.6427	29.1228	250.7000	25.4072	34.9351	174.2055
	Glaucinitic sandstone	S 23	107.5438	0.0000	13.8184	120.4024	9.0966	10.6659	81.6278
		S 19	67.8812	0.0000	18.5931	160.5936	5.6930	6.7700	55.8465
B	Shale	RKI2 ShC	3.2359	48.0431	28.3181	246.5221	23.3250	38.5072	182.0458
		RKI2 ShB	3.7410	47.2071	26.7657	234.5343	27.0427	37.7477	210.6949
		RK/33a	11.4285	14.4131	15.4192	138.2394	10.6050	16.3122	122.3328
		Rk/33c	7.7890	13.3118	16.8255	133.3293	7.4773	7.0000	47.5456
	Glaucinitic Sandstone	S 18	266.5088	0.0000	25.9494	240.1255	11.3705	13.1300	179.9479
		S 16	11.5418	0.0000	21.2545	203.0107	21.2854	30.9204	169.2649
	Shale	RKI2 ShA2	4.2492	42.2385	26.3912	215.9898	25.0756	37.3645	212.0601
		RKI2 ShA1	2.4170	42.4720	22.6043	171.3332	23.2044	29.1604	181.0981
		RKI2 ShA	20.6329	53.6766	27.2313	225.5831	22.2354	47.9184	183.6636
	Green Shale	S 13 d	3.8612	BDL	40.7625	279.4162	4.7746	69.4396	388.2692
		S 13 c	4.2732	BDL	41.3868	321.9490	3.6102	61.4225	395.9777
		S 13 b	4.4442	BDL	42.5078	308.9473	3.9057	69.0691	420.3556
		S 13 a	3.7618	BDL	38.0824	277.0127	4.4656	65.5567	383.2105
		average Shale	45.0000	95.0000	19.0000	140.0000	300.0000	41.0000	160.0000

Table 13: Trace and REE concentration in glauconite associated sediments from Middle segment (Facies B, C, D)

Facies		Sample	Nb	Mo	Cd	Sn	Sb	Cs	Ba	La
D	Glaucconitic siltstone	S 41	9.9870	0.0000	0.0332	3.8123	0.0000	10.5429	266.8204	29.3899
		S 39	5.2029	0.0000	0.0396	1.9358	0.0000	8.6152	267.1777	24.0937
	Shale	RKI4 Sh6	9.6157	0.5031	0.1158	3.1808	2.8099	5.8181	216.4715	67.5545
		RKI4 Sh5	12.9334	0.2145	0.1279	4.0869	0.9694	10.6867	325.3823	51.2957
	Glaucconitic siltstone	S 38	9.7922	0.1239	0.1629	3.6440	0.7415	12.3643	353.5723	40.8276
	Shale	RKI4 Sh4	16.8642	0.1922	0.1628	4.6578	0.9430	11.7339	344.3422	47.4486
	Glaucconitic siltstone	S 37	12.3827	0.0000	0.0299	4.2300	0.0000	14.4789	344.4787	41.4377
		S 36	12.8533	0.0857	0.1944	4.8215	0.5010	8.4101	367.1930	22.3966
	Shale	RKI4 Sh3	11.7001	0.1644	0.1153	4.7575	1.4509	12.5792	449.4572	46.8990
	Glaucconitic siltstone	S 31	11.7703	0.3221	0.1886	3.6425	0.7373	8.2467	345.7054	36.1575
	Shale	RKI4 Sh2	14.8090	0.2780	0.1094	4.8884	8.2879	12.3356	345.2710	46.5354
		RKI4 Sh1	12.9904	0.1719	0.1099	4.7210	1.3752	12.3674	367.0389	46.1473
C	Shale	RKI3 Sh8	14.6551	0.1412	0.1213	5.5067	1.0417	13.7393	442.0602	54.5825
		RKI3 Sh7	15.7728	0.1668	0.1553	5.4917	2.2260	8.7667	463.0365	64.7506
		RKI3 Sh6	12.8293	0.1740	0.1085	4.5668	0.7582	8.5603	364.2990	56.8198
		RKI3 Sh5	14.3424	0.1465	0.1150	5.0792	0.6762	12.3848	433.9965	45.6421
		RKI3 Sh4	14.7615	4.0185	0.1352	4.9201	0.8196	12.2449	419.3510	49.0986
		RKI3 Sh2	13.9331	0.6358	0.1813	4.3555	0.7812	9.7825	442.8763	42.0194
		RKI3 Sh0	24.4243	0.3962	0.1333	7.5044	0.9664	12.2723	424.4506	49.0809
	Glaucconitic sandstone	S 23	0.6537	0.0000	0.0264	0.9887	0.0000	4.6705	111.9166	14.1344
		S 19	0.5118	0.0000	0.0267	1.1753	0.0000	7.4495	67.8964	12.7895
B	Shale	RKI2 ShC	27.4445	0.1955	0.1354	5.2903	0.8673	12.5445	400.7225	55.5945
		RKI2 ShB	15.2420	0.2013	0.1648	4.9211	0.7698	9.0510	445.6192	50.9060
		RK/33a	7.7890	0.7969	0.0000	0.0000	0.0000	5.3233	193.1588	19.5893
		Rk/33c	2.0121	0.2531	0.0000	0.0000	0.0000	4.2221	109.5718	13.0293
	Glaucconitic Sandstone	S 18	4.0455	0.0000	0.0551	1.8094	0.0000	8.2450	139.2757	22.2350
		S 16	10.8420	0.0000	0.0434	3.9788	0.0000	6.0627	359.8641	56.8204
	Shale	RKI2 ShA2	14.3120	0.1592	0.1419	4.3397	0.7063	7.0946	428.1355	55.0212
		RKI2 ShA1	13.8885	0.2686	0.1342	4.0346	0.7996	6.7909	365.6591	42.9992
		RKI2 ShA	15.8451	0.4629	0.1502	4.9825	1.0884	10.0772	355.5810	59.2147
	Green Shale	S 13 d	21.5103	BDL	0.0983	6.1728	BDL	1.6939	73.7137	65.6159
		S 13 c	35.0997	8.6917	0.1473	7.0937	BDL	1.9409	57.5141	63.6167
		S 13 b	25.7931	BDL	0.0777	6.4994	BDL	2.0018	55.3521	67.4742
		S 13 a	22.3396	BDL	0.0834	6.0007	BDL	1.5959	73.3472	67.4634
		average Shale	18.0000	2.6000	0.8000	6.0000	1.5000	5.5000	580.0000	40.0000

Table 13: Trace and REE concentration in glauconite associated sediments from Middle segment (Facies B, C, D)

	Facies	Sample	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
D	Glaucconitic siltstone	S 41	35.8581	4.3052	14.6519	2.5104	0.4529	2.3064	0.4064	2.5593
		S 39	48.2143	5.6888	22.1937	3.5281	0.6646	2.9235	0.4092	2.4257
	Shale	RKI4 Sh6	139.0129	23.4495	77.8917	15.5467	2.0650	11.5181	1.2789	6.0718
		RKI4 Sh5	110.3324	14.8013	53.5307	9.8630	1.5780	8.4677	1.0846	5.6458
	Glaucconitic siltstone	S 38	76.0343	8.8776	35.0841	5.3779	0.9406	4.7008	0.6259	3.3664
	Shale	RKI4 Sh4	106.5058	13.8725	47.5622	10.3593	1.7390	9.9115	1.4177	8.2123
	Glaucconitic siltstone	S 37	71.4478	7.5203	26.8983	4.7263	0.7591	4.0782	0.6063	3.6443
		S 36	45.1937	5.7802	20.3946	4.3236	0.8865	4.2902	0.7124	4.4097
	Shale	RKI4 Sh3	85.7139	8.9256	36.1756	6.1190	1.1357	6.0590	0.8513	4.7665
	Glaucconitic siltstone	S 31	72.6145	9.1086	31.3675	6.2195	1.1503	5.9417	0.8494	4.8934
C	Shale	RKI4 Sh2	87.4119	10.3382	40.2271	7.1961	1.2447	6.4489	0.8750	4.7134
		RKI4 Sh1	81.7208	10.5764	35.0931	7.1399	1.2989	6.8885	0.9735	5.3195
		RKI3 Sh8	107.5908	13.4944	43.0664	9.1666	1.6317	8.8491	1.2519	7.0746
		RKI3 Sh7	120.9644	18.1877	59.8137	11.7305	2.0084	10.5550	1.3701	7.0561
		RKI3 Sh6	119.8195	16.1394	54.8894	10.6596	1.8035	9.4245	1.1835	6.0441
		RKI3 Sh5	86.0128	10.3432	35.8835	7.3328	1.3519	7.4459	1.0279	5.8491
		RKI3 Sh4	99.3552	11.9691	41.5943	8.4042	1.4800	7.8407	1.0763	5.9945
		RKI3 Sh2	83.4342	10.4423	34.6909	7.2402	1.3596	6.9392	0.9968	5.5565
		RKI3 Sh0	92.4907	10.5283	36.7314	7.1159	1.2756	6.9075	0.9630	5.6437
	Glaucconitic sandstone	S 23	37.0353	4.1820	14.8069	2.7843	0.4686	2.2627	0.3192	1.8173
		S 19	27.8228	3.8788	14.3108	2.5585	0.3945	1.8985	0.2131	1.1668
B	Shale	RKI2 ShC	101.2601	14.7274	50.9609	10.1154	1.6920	8.8643	1.1519	6.0754
		RKI2 ShB	93.6773	11.5595	39.8040	7.9839	1.4527	7.6053	1.0901	5.9232
		RK/33a	59.4589	5.1554	18.4586	3.7954	0.6619	3.6871	0.5344	3.0093
		Rk/33c	41.3977	4.2540	15.5957	3.0289	0.4528	2.7102	0.3183	1.4682
	Glaucconitic Sandstone	S 18	49.1510	6.6351	25.3288	4.3571	0.7434	3.3745	0.4140	2.1267
		S 16	76.0442	11.3484	41.9741	7.0158	1.3456	6.3464	0.8625	4.9260
	Shale	RKI2 ShA2	91.1012	14.0148	49.7189	9.6590	1.6502	8.4597	1.1045	5.9097
		RKI2 ShA1	87.9547	10.8514	36.0683	7.3280	1.2789	6.6377	0.8694	4.6401
		RKI2 ShA	74.7723	13.7397	42.6641	9.1531	1.6589	9.0680	1.2572	6.7920
	Green Shale	S 13 d	152.1389	18.2414	67.2767	11.8445	1.7715	10.0488	1.4348	9.0811
		S 13 c	139.8201	17.2943	67.7017	12.2982	1.9129	10.1351	1.4865	9.4135
		S 13 b	148.2406	18.4419	68.0701	12.5202	1.8265	10.6310	1.4845	9.1340
		S 13 a	157.7598	17.9677	64.2685	12.1363	1.7436	9.7556	1.4578	8.9108
		average Shale	95.0000	9.7000	39.0000	7.3000	1.6000	7.0000	1.2000	5.5000

Table 13: Trace and REE concentration in glauconite associated sediments from Middle segment (Facies B, C, D)

	Facies	Sample	Ho	Er	Tm	Yb	Lu	Hf	Ta	Pb
D	Glaucanitic siltstone	S 41	0.5494	1.6302	0.2758	1.6921	0.2694	2.4001	0.2480	2.4101
		S 39	0.4895	1.4805	0.2292	1.4579	0.2310	3.9685	0.0000	4.1343
	Shale	RKI4 Sh6	1.1941	3.6355	0.5066	3.3235	0.4910	4.6031	1.0277	3.4386
		RKI4 Sh5	1.1537	3.3938	0.4874	3.2489	0.4746	5.3503	1.5447	7.3338
	Glaucanitic siltstone	S 38	0.7033	2.1226	0.3116	2.1262	0.3172	5.8190	1.3579	7.7965
	Shale	RKI4 Sh4	1.6444	4.8034	0.6731	4.3247	0.6539	6.3502	1.3998	6.0764
	Glaucanitic siltstone	S 37	0.7419	2.1131	0.3338	2.1129	0.3209	2.9517	0.4366	4.7278
		S 36	0.9090	2.7303	0.3999	2.7079	0.3951	6.5938	2.2355	10.2774
	Shale	RKI4 Sh3	0.9394	2.7099	0.3937	2.6304	0.3833	3.9902	1.2081	5.6413
	Glaucanitic siltstone	S 31	0.9918	3.0173	0.4438	2.9377	0.4480	7.4808	1.1870	11.7889
C	Shale	RKI4 Sh2	0.9465	2.7892	0.4008	2.6732	0.3875	3.8410	10.0494	6.5798
		RKI4 Sh1	1.0639	3.0527	0.4525	2.8665	0.4380	4.0766	1.0722	6.4678
		RKI3 Sh8	1.4007	4.1242	0.5617	3.7779	0.5541	4.4971	1.1515	6.0073
		RKI3 Sh7	1.4318	4.1486	0.6032	3.8415	0.5807	5.0312	1.3461	7.3108
		RKI3 Sh6	1.1826	3.3423	0.4655	3.0152	0.4390	3.8652	1.2145	12.9916
		RKI3 Sh5	1.1375	3.3722	0.4781	3.0591	0.4530	4.1901	1.1564	8.0773
		RKI3 Sh4	1.2159	3.5208	0.5057	3.3825	0.4867	4.8548	1.2530	12.3441
		RKI3 Sh2	1.1492	3.2658	0.4807	3.1442	0.4589	5.5192	1.0950	9.1819
		RKI3 Sh0	1.1184	3.4269	0.4708	3.1419	0.4605	4.4555	36.1326	5.6820
	Glaucanitic sandstone	S 23	0.3552	1.0061	0.1505	0.9299	0.1453	1.5537	0.0000	15.9068
		S 19	0.2214	0.6051	0.0989	0.5784	0.0884	1.0231	0.0000	3.7365
B	Shale	RKI2 ShC	1.2015	3.4379	0.4935	3.1567	0.4731	4.2644	25.9496	6.2370
		RKI2 ShB	1.2203	3.4946	0.5198	3.3225	0.4905	5.1459	1.4486	6.6869
		RK/33a	0.5830	1.6540	0.2545	1.6209	0.2349	2.8998	0.2808	25.4258
		Rk/33c	0.2590	0.7101	0.0972	0.5993	0.0858	1.0903	0.0229	14.3182
	Glaucanitic Sandstone	S 18	0.4422	1.2714	0.1917	1.2090	0.1955	3.3622	0.0000	5.9503
		S 16	0.9421	2.8120	0.3932	2.4732	0.3704	3.6222	0.1465	6.9959
	Shale	RKI2 ShA2	1.1798	3.4619	0.4851	3.1729	0.4728	4.9987	1.1982	6.9881
		RKI2 ShA1	0.9753	2.7511	0.4116	2.6880	0.3990	4.2365	1.1769	11.1838
		RKI2 ShA	1.3605	3.8415	0.5293	3.3023	0.4903	4.2703	1.1655	12.2735
	Green Shale	S 13 d	2.0591	6.1973	0.9387	5.6507	0.9185	9.5303	0.5760	2.6271
		S 13 c	1.9482	5.6705	0.9448	5.7774	0.7972	12.3871	2.8304	2.2158
		S 13 b	1.9411	5.8654	0.8929	5.4529	0.7892	9.8381	1.1393	2.0099
		S 13 a	1.9953	5.9136	0.9141	6.4013	0.7948	9.6131	0.5803	2.6894
		average Shale	1.6000	3.9000	0.6000	3.7000	0.7000	2.8000	2.0000	20.0000

Table 13: Trace and REE concentration in glauconite associated sediments from Middle segment (Facies B, C, D)

Facies		Sample	Bi	Th	U
D	Glaucconitic siltstone	S 41	0.0000	11.0436	1.9614
		S 39	0.3251	12.5121	2.1071
	Shale	RKI4 Sh6	1048.6095	15.2077	3.3056
		RKI4 Sh5	1961.1638	17.5530	3.0858
	Glaucconitic siltstone	S 38	1829.1068	13.8647	2.1838
	Shale	RKI4 Sh4	2536.0281	19.1586	3.5998
	Glaucconitic siltstone	S 37	0.0000	15.5042	2.6790
		S 36	4750.9297	21.6229	3.2229
	Shale	RKI4 Sh3	2173.2299	15.1028	2.6654
	Glaucconitic siltstone	S 31	1937.4550	18.3505	3.3750
C	Shale	RKI4 Sh2	2122.5482	15.1975	2.4905
		RKI4 Sh1	2094.7651	16.8674	2.8189
		RKI3 Sh8	660.7736	18.3259	3.6466
		RKI3 Sh7	1186.5057	19.3207	3.6140
		RKI3 Sh6	2192.4502	14.1734	2.7046
		RKI3 Sh5	2025.9704	15.3810	2.8289
		RKI3 Sh4	2193.0125	16.3641	3.1284
		RKI3 Sh2	1413.6895	16.3677	3.0324
		RKI3 Sh0	1796.1858	15.8617	2.8557
	Glaucconitic sandstone	S 23	1.1970	17.1255	3.0654
		S 19	0.0648	5.8890	1.1807
B	Shale	RKI2 ShC	2647.8008	14.6067	2.8845
		RKI2 ShB	2106.4627	16.5568	3.0622
		RK/33a	0.0000	8.6478	1.9397
		Rk/33c	0.0000	3.4270	0.6396
	Glaucconitic Sandstone	S 18	1.5367	12.4295	2.3310
		S 16	0.0000	16.3821	3.0369
	Shale	RKI2 ShA2	2017.8135	14.9129	2.8457
		RKI2 ShA1	1952.0758	13.4633	2.5054
		RKI2 ShA	2259.1264	15.2840	2.8705
	Green Shale	S 13 d	BDL	28.3670	16.3209
		S 13 c	1.8629	30.3670	8.4405
		S 13 b	BDL	34.3670	6.4105
		S 13 a	BDL	43.1854	26.4723
		average Shale	0.1000	12.0000	3.7000

Table 13: Trace and REE concentration in glauconite associated sediments from Middle segment (Facies B, C, D)

	Facies	Sample	CIA	PIA	CIW	ICV	C value	Y/Ho	V/V+Ni	Th/U
D	Glauconitic siltstone	S 41	68.3079	98.9239	99.4139	0.7714	1.9207	31.1125	0.7413	5.6305
		S 39	66.0656	99.9561	99.9786	0.9161	1.8424	32.1824	0.7026	5.9381
	Shale	RKI4 Sh6	61.8370	96.6616	98.6490	0.7933	1.5072	27.8684	0.7194	4.6006
		RKI4 Sh5	68.8951	97.5608	98.6129	0.8580	2.1252	27.5494	0.7122	5.6883
	Glauconitic siltstone	S 38	68.9588	97.0921	98.3307	0.8499	2.0643	28.0483	0.6940	6.3488
	Shale	RKI4 Sh4	67.2160	97.5102	98.6755	0.8459	1.8960	31.0073	0.7440	5.3221
	Glauconitic siltstone	S 37	69.6467	98.9076	99.3738	0.8813	2.0650	29.2474	0.7826	5.7874
		S 36	64.5597	96.5683	98.3653	0.9720	1.8295	26.9298	0.6842	6.7091
	Shale	RKI4 Sh3	71.3883	97.6409	98.5381	0.8675	2.3591	28.9532	0.7268	5.6662
	Glauconitic siltstone	S 31	70.2821	96.9724	98.1739	0.8718	2.0453	29.2777	0.7068	5.4371
	Shale	RKI4 Sh2	68.6740	97.5236	98.6029	0.8728	2.2273	28.7560	0.7457	6.1022
		RKI4 Sh1	71.4921	97.7236	98.5863	0.8486	2.1372	28.8224	0.7519	5.9838
C	Shale	RKI3 Sh8	70.9263	97.8535	98.6938	0.8049	2.0497	29.1018	0.7748	5.0254
		RKI3 Sh7	71.5799	97.8791	98.6821	0.7723	2.1703	30.3990	0.7191	5.3461
		RKI3 Sh6	71.9631	97.8718	98.6614	0.7809	2.2136	31.1227	0.7158	5.2405
		RKI3 Sh5	70.4538	97.5640	98.5349	0.8496	1.7804	30.7047	0.7496	5.4372
		RKI3 Sh4	69.9916	97.4954	98.5161	0.8555	1.7991	30.0253	0.7355	5.2308
		RKI3 Sh2	68.5836	97.3233	98.4905	0.8389	1.4645	29.9959	0.7503	5.3976
		RKI3 Sh0	69.2211	97.5503	98.5896	0.8490	1.5669	31.2369	0.7611	5.5543
	Glauconitic sandstone	S 23	70.4806	99.9764	99.9863	0.9978	1.3786	30.0291	0.7682	5.5868
		S 19	66.9652	99.9679	99.9837	1.2650	1.1109	30.5832	0.8487	4.9878
B	Shale	RKI2 ShC	69.8408	97.7421	98.6743	0.8040	1.9066	32.0489	0.7415	5.0639
		RKI2 ShB	69.0096	97.3336	98.4720	0.8524	1.6624	30.9340	0.7351	5.4068
		RK/33a	66.3997	99.9761	99.9882	1.0122	3.4015	27.9789	0.6493	4.4584
		Rk/33c	63.0200	99.9648	99.9855	0.9786	2.2595	27.0249	0.6805	5.3582
	Glauconitic Sandstone	S 18	67.4090	99.9715	99.9853	1.2266	1.2099	29.6894	0.8270	5.3323
		S 16	70.0609	99.9155	99.9515	0.8890	1.8305	32.8200	0.7283	5.3944
	Shale	RKI2 ShA2	70.0262	97.6099	98.5847	0.8032	1.6349	31.6705	0.7293	5.2405
		RKI2 ShA1	68.1513	97.0888	98.3801	0.9663	1.7382	29.8999	0.7149	5.3738
		RKI2 ShA	70.2495	97.6883	98.6220	0.8069	2.0361	35.2212	0.7783	5.3244
	Green Shale	S 13 d	63.6655	99.9795	99.9912	0.9776	0.6509	33.7234	0.5032	1.7381
		S 13 c	60.1175	99.8916	99.9634	1.0572	0.5706	31.5283	0.4153	3.5978
		S 13 b	62.4873	99.9188	99.9675	1.0337	0.6005	35.5818	0.4128	5.3611
		S 13 a	60.1267	99.8925	99.9637	1.0601	0.6074	32.8563	0.4907	1.6313

Table 14: Elemental ration used for glauconite associated sediments of middle segment of Rampur Shale comprising Facies B, C and D.

Sample	Cr EF	V EF	Cu EF	Zr EF	Mo EF	Pb EF	U EF	Se (Authigenic) ppm	U (Authigenic) ppm	Mo (Authigenic) ppm	Ni (Authigenic) ppm	Cu (Authigenic) ppm	Cr (Authigenic) ppm
21B	0.50	1.13	0.53	0.65	0.00	0.66	2.07	105.58	2.19	-1.43	-18.92	-11.55	-24.77
20B	0.65	2.04	0.69	0.71	0.00	0.84	1.86	112.99	1.87	-1.54	-12.03	-8.34	-18.73
17B	0.54	1.86	0.62	0.60	0.00	0.84	2.90	106.87	3.90	-1.44	-13.55	-9.57	-22.75
15B	0.66	2.26	0.56	0.94	0.69	0.70	2.88	117.40	5.64	-0.65	-20.64	-15.94	-24.84
SRTF2	0.20	0.86	1.06	1.20	0.00	2.11	2.40	97.68	3.22	-1.61	-28.42	1.70	-44.67
RTF2	0.04	0.20	1.02	1.38	0.00	1.65	2.36	94.12	3.95	-2.04	-47.94	0.56	-68.03
13B	0.66	0.84	0.78	0.99	0.00	1.15	1.83	115.52	2.20	-1.86	-21.65	-6.99	-21.92
SRTF-1	0.37	0.50	1.29	0.88	0.00	1.06	1.16	88.93	0.49	-2.22	-37.95	11.22	-48.36
RTF1	0.03	0.08	0.49	0.64	0.00	0.44	0.63	66.57	-1.13	-2.17	-53.7	-19.19	-72.46
12B	0.89	1.19	0.90	1.17	0.00	4.99	1.53	107.28	0.78	-1.02	-4.52	-1.72	-4.03
STF7	0.47	1.76	0.98	1.07	1.05	1.15	0.00	97.43	-3.06	0.10	-10.51	-0.90	-39.74
TF7	0.04	1.13	1.28	0.91	3.40	1.18	1.58	141.46	2.20	6.43	-44.79	12.91	-88.67
STF4	0.17	0.64	0.91	0.96	0.00	0.97	1.68	105.25	2.27	-2.36	-34.26	-3.51	-67.59
TF4	0.02	0.22	0.47	1.22	0.00	0.42	1.80	73.15	3.04	-2.68	-52.87	-24.47	-90.75
STF 2-1	0.34	1.05	0.85	1.13	0.00	0.75	2.15	82.30	3.81	-2.34	-20.15	-6.01	-53.64
TF2-1	0.02	0.26	0.64	1.16	0.00	0.48	0.00	39.55	-3.90	-2.74	-53.54	-16.96	-92.62
8B	0.70	2.46	1.07	0.80	0.00	0.73	2.75	102.57	3.27	-1.31	-4.59	1.58	-13.76
STF 1b	0.34	1.01	0.65	1.24	1.17	1.30	3.34	89.13	6.99	0.35	-19.07	-12.62	-48.20
TF1b	0.02	0.69	0.65	1.11	0.00	1.17	1.46	43.00	1.76	-2.68	-40.39	-16.32	-91.22
4B	0.71	2.63	0.95	0.85	0.00	0.91	3.02	109.54	4.26	-1.48	-0.93	-1.38	-14.71
STF 1d	0.09	0.41	0.15	1.45	0.00	2.22	1.86	92.36	3.23	-2.64	-59.96	-39.00	-83.59
TF1d	0.02	0.40	0.18	1.96	0.00	2.49	1.90	67.01	3.43	-2.67	-59.79	-37.81	-90.53
1B	0.70	2.49	1.00	0.78	0.00	0.92	3.74	106.64	5.22	-1.34	22.27	0.01	-13.70

Table 15: Enrichment factor and Authigenic Fractions for some chosen Trace elements from black shale of Rampur Shale (Facies E, Upper Segment).

Reference	Basin Name	Formation Name	Age of Black Shale	Tectonic setting of deposition	Paleogeographic Scenario
Basu et al; 2017	Cuddapah Basin, South India	Srisailam formation	1575 Ma		Shallow marine/tidal flat shoreline to intertidal sand flat environments with fluvial influence
Sarkar et al 2010		Cumbum Shale	1418±8 Ma		Coastal to shallow marine depositional environment
Sur et al 2006; Banerjee et al 2006;	Vindhyan Basin, Central India	Rampur Shale, Bijoygarh shale	1500 Ma	Passive margin	Shallow marine shelf environment
Paikaray et al 2008		black shales of Vindhyan super group	1500 Ma	Passive margin	Shallow marine shelf environment
Sarkar et al 2002		Rampur Shale	1500 Ma	Passive margin	Shallow marine shelf environment
Ansari et al 2021	Chhattisgarh Basin	Chanderpur Group	1400-1000 Ma		Shallow marine environment
Rivie et al 2017; Kunzmann et al 2019; Zhang et al 2018; Zhang et al 2022; Page et al 2000	North Australian Craton, MacArthur Basin, Australia	Mainoru Formation of Roper Group.	1490 Ma		
Abott et al 2001; Rivie 2017; Munson 2014, 2016;		Kyalla Formation	1320 Ma		
Zhang et al 2022; Munson and Rivie 2018; Warren et al 1998		Velkerri Formation	1361± 37 Ma		
Zhu et al 2016; Wang, C., 2009; Knoll, K.H. 2011; Zhang et al 2013; Xu et al 1991; Qin et al 2010; Li et al 2014, Li et al 2010; Gao et al 2007; Tosti and Riding 2016; Tang et al 2018	North China Craton	Gaoyuzhuang Formation	1560±5 Ma		Distal turbidites or tempestites deposited near storm wave base
		Yangzhuang Formation	1.5-1.4 Ga		
		Wumishan Formation	1483±13 Ma		
		Hongshuizhuang Formation	1437 ± 21 Ma		
		Tieling Formation	1420 Ma		
		Xiamaling	1400-1350 Ma		
Young (1981) Rainbird et al. (1996)	NW Territories, Canada	Shaler Supergroup	1000±70 Ma		
Cox et al. (1995)	Arizona, USA	Grand Canyon Supergroup,	1100±60 Ma		
Litherland et al, 1986	Bolivia, South America	San Ignacio Subgroup	1250±50 Ma		
Richard Hanson 1998	Zambia, Africa	Roan/Mwashia group	1000 Ma		
Schieber, J., 1998	Montana, USA	Belt Supergroup	1450-850 my		Lacustrine
Roberts (1974)	California	Belt Supergroup Pahrump Group	1000±100 Ma		Marine or Lacustrine??

Table 16: References related to Worldwide Black Shale Deposition

Facies	SAMPLE	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂
SI	24 B	8.91	0.34	2.06	4.84	1.10	0	0.21	81.76	0.28
	11 B	8.90	0.54	1.93	4.97	1.12	0	0.25	81.24	0.33
ST	STF 9*	15.15	0.16	3.38	11.13	0.98	0.10	0.10	68.22	0.49
	TF 9*	16.58	0.05	0.93	15.26	0.20	0	0	66.24	0.34
SI	23 B	9.72	0.36	2.46	5.09	1.53	0.09	0.19	79.47	0.40
	10 B	10.00	0.33	2.44	5.34	1.53	0	0.16	79.10	0.40
	25 B	8.74	0.10	3.14	3.98	0.89	0	0.07	82.33	0.32
ST	STF 8*	16.46	0.28	2.14	12.61	1.69	0.07	0.13	65.95	0.32
	TF8*	16.46	0.11	1.70	14.21	1.18	0.09	0.05	65.32	0.36
SI	22 B	7.89	0.09	2.78	3.58	0.72	0.08	0	84.21	0.29
	9B	7.43	0.10	2.38	3.35	0.71	0	0.05	85.17	0.27
	Avg Sh	16.7	2.2	2.8	3.6	2.6	1.6	0.16	58.9	0.78

Facies	SAMPLE	Al ppm	Ca ppm	Fe ppm	K ppm	Mg ppm	Na ppm	P ppm	Si ppm	Ti ppm
SI	24 B	47164.78	2410.338	14439	40213.6	6655.898	0	936.6225	382168.2	1654.239
	11 B	47120.68	3885.352	13487.58	41297.8	6742.173	0	1074.353	379734.7	1967.774
ST	STF 9*	80170.86	1178.371	23640.55	92388.16	5903.43	764.4652	449.721	318875	2965.335
	TF 9*	87774.74	363.5923	6476.014	126697.1	1227.138	0	0	309618	2012.932
SI	23 B	51429.11	2545.285	17222.87	42234.65	9204.039	679.3704	843.7294	371466.7	2379.05
	10 B	52910.14	2328.306	17089.25	44369.04	9208.74	0	710.8719	369753	2380.265
	25 B	46260.63	725.5563	21940.74	33036.03	5387.318	0	310.1347	384850.9	1947.564
ST	STF 8*	87119.01	2010.399	14938.06	104648.9	10177.76	541.0188	545.6084	308264	1936.203
	TF8*	87100.42	803.6182	11868.26	117951.2	7088.817	682.4886	223.0531	305322.3	2144.844
SI	22 B	41734.35	662.171	19440.75	29739.76	4345.548	610.9609	0	393623.9	1728.05
	9B	39300.84	736.0873	16640.37	27787.1	4285.458	0	224.7401	398139.6	1605.363
	Avg Sh	88384.92	15723.42	19584.12	29885.29	15678.94	11869.71	698.2736	275321.6	4676.162

Table 17: Major oxide concentration of topmost grey shale (Faded Shale, facies F) samples in weight percentage (deducting LOI).

Facies	SAMPLE	Li	Be	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Ga	Ge	Se	Rb	Sr	Y	Zr	Nb	Mo	Cd	Sn	Sb
SI	24 B	58.12	1.79	6.08	175.70	33.47	89.26	10.17	33.82	21.82	101.07	13.07	1.43	91.00	125.98	13.38	15.35	67.39	4.77	0.00	0.65	1.74	0.00
	11 B	57.94	1.53	5.97	160.79	33.28	85.46	10.05	32.73	20.47	99.71	12.35	1.46	102.63	119.06	13.71	14.85	68.07	5.30	BDL	0.67	1.59	0.00
ST	STF 9*	48.38	2.14	9.86	171.70	34.08	138.34	32.08	50.45	28.06	384.25	14.54	1.54	87.78	167.98	10.60	28.24	183.69	11.82	3.03	0.87	1.91	0.00
	TF 9*	13.49	0.67	4.63	69.92	2.43	50.19	45.89	9.74	13.38	105.78	7.74	1.94	74.48	179.12	1.75	26.13	168.95	6.04	0.00	0.37	2.51	0.00
SI	23 B	76.70	2.24	8.22	245.10	44.49	103.22	9.74	41.09	33.44	802.00	15.81	1.88	100.01	143.35	15.50	30.81	111.42	9.10	2.33	0.50	2.15	0.00
	10 B	73.81	2.18	7.74	230.19	45.31	98.35	9.42	39.99	32.73	821.35	15.29	1.82	107.39	135.25	15.01	29.49	105.67	10.05	3.00	0.50	2.17	0.00
	25 B	55.68	2.52	8.00	198.04	38.86	110.06	4.66	59.29	20.62	29.44	12.31	1.15	107.77	121.05	11.62	15.63	71.95	5.25	1.44	0.16	1.73	0.00
ST	STF 8*	43.70	1.22	5.78	120.24	9.67	65.95	21.11	32.17	19.89	369.72	11.07	1.21	76.83	153.63	6.62	33.85	179.64	5.34	0.00	0.52	1.49	0.00
	TF8*	27.15	0.77	7.08	90.33	3.25	165.85	21.82	25.31	23.20	311.10	9.36	2.19	68.41	147.53	3.42	28.52	195.63	4.80	0.00	0.50	1.50	0.00
SI	22 B	58.68	2.45	8.79	195.93	35.27	71.07	15.00	60.83	23.03	25.88	12.90	1.36	101.35	123.93	12.84	20.32	72.27	5.92	1.16	0.18	1.87	0.00
	9B	48.04	1.91	7.71	179.23	31.88	62.27	13.56	53.77	20.71	23.17	11.73	1.09	108.90	114.60	11.18	17.62	69.74	4.54	1.02	0.18	1.44	0.00
	Avg Sh	66	3	13	130	90	850	19	68	45	95	19	1.6	0.6	140	300	41	160	18	2.6	0.8	6.0	1.5

Facies	SAMPLE	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Tl	Pb	Bi	Th	U	$\delta^{13}\text{C}$ (‰; VPDB)
SI	24 B	4.88	212.64	28.45	51.05	5.73	19.81	3.91	0.63	3.37	0.44	2.31	0.47	1.24	0.20	1.10	0.18	1.38	0.00	0.56	9.52	0.00	9.50	5.40	-31.5
	11 B	4.94	199.18	28.78	48.44	5.61	20.55	3.39	0.65	3.15	0.43	2.19	0.45	1.21	0.18	1.11	0.16	1.44	0.00	0.55	9.15	0.00	10.20	5.89	-31.8
ST	STF 9*	4.06	240.00	22.49	51.09	5.01	18.89	3.76	0.71	3.58	0.59	4.34	0.92	2.84	0.44	2.82	0.41	4.84	0.43	0.63	31.10	BDL	24.06	7.94	-29.5
	TF 9*	3.79	184.95	18.67	45.62	6.24	25.14	6.10	1.18	5.55	0.85	5.14	0.93	2.44	0.35	2.03	0.29	5.47	1.61	0.60	25.17	0.00	12.85	4.13	-29.6
SI	23 B	5.78	241.86	35.45	55.67	7.04	25.54	5.09	0.94	4.94	0.70	4.27	0.87	2.35	0.34	2.02	0.31	1.95	0.00	0.48	21.57	0.00	12.93	7.17	-31.4
	10 B	5.69	234.63	33.80	55.80	6.79	25.24	4.98	0.91	5.01	0.67	4.26	0.84	2.35	0.32	2.07	0.30	1.87	0.08	0.52	20.32	0.00	12.83	7.56	-28.6
	25 B	5.14	181.33	21.15	36.24	4.33	13.37	2.38	0.47	2.20	0.36	2.25	0.50	1.44	0.23	1.40	0.22	1.47	0.00	1.03	14.15	0.00	11.73	4.88	-26.8
ST	STF 8*	4.82	180.06	12.80	29.63	3.49	13.54	3.33	0.78	3.89	0.72	4.77	1.04	3.19	0.47	2.95	0.43	5.45	0.69	0.32	24.82	BDL	17.04	6.00	-32.2
	TF8*	4.02	171.36	12.09	56.45	4.32	16.54	4.09	0.87	3.71	0.68	4.63	0.99	2.86	0.45	2.88	0.40	6.01	1.48	0.31	36.30	0.00	12.71	5.43	-28.2
SI	22 B	5.78	200.36	22.55	36.10	4.47	14.58	2.67	0.53	2.57	0.42	2.69	0.60	1.69	0.26	1.61	0.23	1.55	0.00	1.38	12.09	0.00	8.33	3.68	-26
	9B	5.42	175.15	19.39	31.19	3.93	12.57	2.26	0.50	2.10	0.40	2.31	0.51	1.64	0.22	1.54	0.21	1.40	0.00	1.16	11.14	0.00	8.85	3.98	29.2
	Avg Sh	5.5	580	40	95	9.7	39	7.3	1.6	7	1.2	5.5	1.6	3.9	0.6	3.7	0.7	2.8	2	1.4	20	0.1	12	3.7	----

Table 18: Trace elements including REY concentration in ppm along with the values of average shale and also $\delta^{13}\text{C}_{\text{Org}}$ values.

Facies	SAMPLE	Li EF	Be EF	Sc EF	V EF	Cr EF	Mn EF	Co EF	Ni EF	Cu EF	Zn EF	Ga EF	Ge EF	Se EF	Rb EF	Sr EF	Y EF	Zr EF	Nb EF	Mo EF	Cd EF	Sn EF	Sb EF	Cs EF	Ba EF	La EF	Ce EF	Pr EF
SI	24 B	1.65	1.12	0.88	2.53	0.70	0.20	1.00	0.93	0.91	1.99	1.29	1.68	284.21	1.69	0.08	0.70	0.79	0.50	0	1.53	0.54	0	1.66	0.69	1.33	1.01	1.11
	11 B	1.65	0.96	0.86	2.32	0.69	0.19	0.99	0.90	0.85	1.97	1.22	1.71	320.83	1.60	0.09	0.68	0.80	0.55	0	1.58	0.50	0	1.69	0.64	1.35	0.96	1.09
ST	STF 9*	0.81	0.79	0.84	1.46	0.42	0.18	1.86	0.82	0.69	4.46	0.84	1.06	161.28	1.32	0.04	0.76	1.27	0.72	1.29	1.19	0.35	0	0.81	0.46	0.62	0.59	0.57
	TF 9*	0.21	0.22	0.36	0.54	0.03	0.06	2.43	0.14	0.30	1.12	0.41	1.22	124.99	1.29	0.01	0.64	1.06	0.34	0	0.46	0.42	0	0.69	0.32	0.47	0.48	0.65
SI	23 B	2.00	1.28	1.09	3.24	0.85	0.21	0.88	1.04	1.28	14.51	1.43	2.02	286.44	1.76	0.09	1.29	1.20	0.87	1.54	1.08	0.62	0	1.81	0.72	1.52	1.01	1.25
	10 B	1.87	1.22	0.99	2.96	0.84	0.19	0.83	0.98	1.21	14.44	1.34	1.90	298.99	1.61	0.08	1.20	1.10	0.93	1.93	1.04	0.61	0	1.73	0.68	1.41	0.98	1.17
	25 B	1.61	1.61	1.18	2.91	0.82	0.25	0.47	1.67	0.88	0.59	1.24	1.38	343.18	1.65	0.07	0.73	0.86	0.56	1.06	0.37	0.55	0	1.79	0.60	1.01	0.73	0.85
ST	STF 8*	0.67	0.41	0.45	0.94	0.11	0.08	1.13	0.48	0.45	3.95	0.59	0.77	129.91	1.11	0.02	0.84	1.14	0.30	0	0.66	0.25	0	0.89	0.31	0.32	0.32	0.37
	TF8*	0.42	0.26	0.55	0.71	0.04	0.20	1.17	0.38	0.52	3.32	0.50	1.39	115.70	1.07	0.01	0.71	1.24	0.27	0	0.63	0.25	0	0.74	0.30	0.31	0.60	0.45
SI	22 B	1.88	1.73	1.43	3.19	0.83	0.18	1.67	1.89	1.08	0.58	1.44	1.80	357.71	1.87	0.09	1.05	0.96	0.70	0.95	0.47	0.66	0	2.23	0.73	1.19	0.80	0.98
	9 B	1.64	1.43	1.33	3.10	0.80	0.16	1.61	1.78	1.04	0.55	1.39	1.53	408.16	1.84	0.08	0.97	0.98	0.57	0.88	0.50	0.54	0	2.22	0.68	1.09	0.74	0.91

Facies	SAMPLE	Nd EF	Sm EF	Eu EF	Gd EF	Tb EF	Dy EF	Ho EF	Er EF	Tm EF	Yb EF	Lu EF	Hf EF	Ta EF	Tl EF	Pb EF	Bi EF	Th EF	U EF	Ca EF	Fe EF	K EF	Mg EF	Na EF	P EF	Si EF	Ti EF
SI	24 B	0.95	1.00	0.74	0.90	0.69	0.79	0.55	0.60	0.62	0.56	0.47	0.50	0	0.75	0.89	0	1.59	2.98	0.29	1.38	2.52	0.80	0	2.51	2.60	0.66
	11 B	0.99	0.87	0.76	0.84	0.67	0.75	0.53	0.58	0.56	0.56	0.43	0.50	0	0.74	0.86	0	1.83	2.47	0.46	1.29	2.59	0.81	0	2.89	2.59	0.79
ST	STF 9*	0.53	0.57	0.49	0.56	0.54	0.87	0.63	0.80	0.81	0.84	0.65	0.80	0.24	0.49	1.71	0	1.18	2.25	0.08	1.33	3.41	0.42	0.07	0.71	1.28	0.70
	TF 9*	0.65	0.84	0.74	0.80	0.71	0.94	0.58	0.63	0.59	0.55	0.42	0.86	0.81	0.43	1.27	0	1.08	1.95	0.02	0.33	4.27	0.08	0	0	1.13	0.43
SI	23 B	1.13	1.20	1.00	1.21	1.00	1.34	0.94	1.04	0.98	0.94	0.75	0.54	0	0.59	1.85	0	3.45	1.92	0.28	1.51	2.43	1.01	0.10	2.08	2.32	0.87
	10 B	1.08	1.14	0.95	1.20	0.93	1.29	0.88	1.01	0.89	0.93	0.71	0.56	0.07	0.61	1.70	0	2.37	2.45	0.25	1.46	2.48	0.98	0	1.70	2.24	0.85
	25 B	0.66	0.62	0.56	0.60	0.57	0.78	0.60	0.70	0.74	0.72	0.61	0.49	0	1.41	1.35	0	1.51	2.79	0.09	2.14	2.11	0.66	0	0.85	2.67	0.80
ST	STF 8*	0.35	0.46	0.49	0.56	0.61	0.88	0.66	0.83	0.79	0.81	0.62	0.86	0.35	0.23	1.26	0	0.70	1.01	0.13	0.77	3.55	0.66	0.05	0.79	1.14	0.42
	TF8*	0.43	0.57	0.55	0.54	0.58	0.85	0.63	0.74	0.75	0.79	0.59	0.86	0.75	0.23	1.84	0	1.07	1.65	0.05	0.61	4.00	0.46	0.06	0.32	1.13	0.47
SI	22 B	0.79	0.78	0.70	0.78	0.74	1.04	0.79	0.92	0.93	0.92	0.70	0.45	0	2.08	1.28	0	2.27	4.54	0.09	2.10	2.11	0.59	0.11	0	3.03	0.78
	9 B	0.72	0.70	0.70	0.68	0.76	0.94	0.72	0.95	0.82	0.94	0.66	0.42	0	1.86	1.25	0	1.66	2.42	0.11	1.91	2.09	0.61	0	0.72	3.25	0.77

Table 19: Enrichment factors for chosen trace, REY and major elements of topmost grey shale (Faded shale).

	SAMPLE	Ti/Al	Hf/Al	Nb/Al	La/Yb	Th/Sc	La/Ti	Yb/Ti	Ta/Ti	Y/Ti	K/Rb	Ba/Sr	Rb/Ti	Cs/Ti	Ba/Ca	V/ V+Ni
Facies SI	24 B	0.035	2.9E-05	0.00010	25.76	1.56	0.017	0.0007	0	0.0093	319.21	15.89	0.0762	0.0030	0.088	0.839
	11 B	0.042	3.1E-05	0.00011	25.91	1.71	0.015	0.0006	0	0.0075	346.85	14.53	0.0605	0.0025	0.051	0.831
	23 B	0.046	3.8E-05	0.00018	17.56	1.57	0.015	0.0008	0	0.0130	294.63	15.60	0.0603	0.0024	0.095	0.856
	10 B	0.045	3.5E-05	0.00019	16.36	1.66	0.014	0.0009	3E-05	0.0124	328.05	15.63	0.0568	0.0024	0.101	0.852
	25 B	0.042	3.2E-05	0.00011	15.13	1.47	0.011	0.0007	0	0.0080	272.92	15.61	0.0622	0.0026	0.250	0.770
	22 B	0.041	3.7E-05	0.00014	13.98	0.95	0.013	0.0009	0	0.0118	239.98	15.60	0.0717	0.0033	0.303	0.763
	9B	0.041	3.6E-05	0.00012	12.60	1.15	0.012	0.0010	0	0.0110	242.47	15.66	0.0714	0.0034	0.238	0.769
Facies ST	STF 9*	0.037	6E-05	0.00015	7.97	2.44	0.008	0.0010	0.0001	0.0095	550.00	22.65	0.0566	0.0014	0.204	0.773
	TF 9*	0.023	6.2E-05	0.00007	9.20	2.78	0.009	0.0010	0.0008	0.0130	707.33	105.87	0.0890	0.0019	0.509	0.878
	STF 8*	0.022	6.3E-05	0.00006	4.33	2.95	0.007	0.0015	0.0004	0.0175	681.18	27.21	0.0793	0.0025	0.090	0.789
	TF8*	0.025	6.9E-05	0.00006	4.19	1.79	0.006	0.0013	0.0007	0.0133	799.50	50.07	0.0688	0.0019	0.213	0.781

	SAMPLE	P EF/ Ti EF	Th/ U	Y/Ho	Authigeni c U	U/Th	Fe/Al	V/Ni	Ni/Co	V/Cr	Ca/Ti	Sr/Ca	Mg/Ca	Ca/Mn	Co*Mn (ppm)	Ba/Al	P/Ti
Facies SI	24 B	3.79	1.76	32.75	2.23	0.57	0.306	5.20	3.33	5.25	1.46	0.0056	2.76	0.037	908	0.0045	0.57
	11 B	3.66	1.73	32.83	2.49	0.58	0.286	4.91	3.26	4.83	1.97	0.0035	1.74	0.022	859	0.0042	0.55
	23 B	1.02	1.80	35.35	2.87	0.56	0.335	5.96	4.22	5.51	1.07	0.0061	3.62	0.041	1005	0.0047	0.35
	10 B	0.00	1.70	35.12	3.28	0.59	0.323	5.76	4.24	5.08	0.98	0.0064	3.96	0.042	927	0.0044	0.30
	25 B	2.38	2.40	31.22	0.97	0.42	0.474	3.34	12.71	5.10	0.37	0.0160	7.43	0.152	513	0.0039	0.16
	22 B	2.00	2.26	34.14	0.91	0.44	0.466	3.22	4.06	5.56	0.38	0.0194	6.56	0.107	1066	0.0048	0.00
	9B	1.07	2.22	34.32	1.03	0.45	0.423	3.33	3.96	5.62	0.46	0.0152	5.82	0.085	845	0.0045	0.14
Facies ST	STF 9*	1.89	3.03	30.77	-0.08	0.33	0.295	3.40	1.57	5.04	0.40	0.0090	5.01	0.117	4438	0.0030	0.15
	TF 9*	0.70	3.11	28.17	-0.16	0.32	0.074	7.18	0.21	28.81	0.18	0.0048	3.38	0.138	2304	0.0021	0.00
	STF 8*	0.00	2.84	32.66	0.32	0.35	0.171	3.74	1.52	12.43	1.04	0.0033	5.06	0.033	1392	0.0021	0.28
	TF8*	0.94	2.34	28.77	1.19	0.43	0.136	3.57	1.16	27.79	0.37	0.0043	8.82	0.206	3618	0.0020	0.10

Table 20: Elemental ratio used and authigenic U and Co*Mn values in the topmost grey Shale (Faded Shale)

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