CRITICAL MINERALS IN SEDIMENTARY SYSTEM: A CASE STUDY OF DHOK PATHAN FORMATION, KARAK, KHYBER PAKHTUNKHWA, PAKISTAN

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CRITICAL MINERALS IN SEDIMENTARY SYSTEM: A CASE STUDY OF DHOK PATHAN FORMATION, KARAK, KHYBER PAKHTUNKHWA, PAKISTAN

A thesis is submitted in fulfillment of the requirement for the award of the degree of Master of Science (Geology)

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JULY 2026

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Date: July 17, 2026

Certificate

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ACKNOWLEDGEMENTS

First and foremost, I am profoundly thankful to Almighty Allah, the Most Beneficent and the Most Merciful, whose infinite mercy, blessings, and guidance granted me the strength and ability to successfully accomplish this research work. Without His grace, this achievement would not have been possible.

I would like to convey my sincere appreciation and deepest respect to my supervisor, Dr. Adil Naseer and co-supervisor Dr. Mumtaz Ali Khan, for his constant encouragement, valuable guidance, and scholarly support throughout the entire research process. His constructive suggestions, insightful discussions, and dedicated supervision significantly contributed to the successful completion of this thesis and enriched my academic knowledge and research skills.

I am also deeply grateful to my parents and family members for their endless prayers, unconditional love, patience, and continuous moral support during my academic journey. Their motivation and sacrifices have always inspired me to strive for excellence.

Lastly, I extend my gratitude to all teachers, colleagues, friends, and everyone who directly or indirectly assisted and supported me in completing this research work successfully.

ABSTRACT

The present study evaluates the distribution and preliminary prospectivity of selected critical, economic, and industrial mineral-related elements in the Dhok Pathan Formation of Karak District, Khyber Pakhtunkhwa, Pakistan. The formation, belonging to the Siwalik Group, is mainly composed of fluvial sandstone, mudstone, siltstone, and locally conglomeratic beds. The objective of this research was to determine the elemental concentrations of selected samples and assess the preliminary critical mineral potential of the formation. Twenty soil samples were collected from weathered and oxidized horizons developed on exposed sandstone mudstone/siltstone successions of the Dhok Pathan Formation at Takht-e-Nasrati and Shanawa Gudikhel. The samples were prepared, digested, and analyzed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for selected major, trace, critical, economic, and industrial mineral-related elements. The results show measurable concentrations of critical mineral-related elements including Li, Co, Ni, Cr, Ti, U, V, and Zr. Titanium shows the highest concentration among the critical element group, ranging from 1809.00 to 2904.89 ppm, followed by V, Cr, Ni, Li, Co, Zr, and U. Economic mineral-related elements are mainly represented by Fe and Ti, with Fe ranging from 21852.14 to 31447.00 ppm and Ti ranging from 1809.00 to 2904.89 ppm. Other elements, including Ba, Mn, Sr, Cr, V, Ni, Co, Li, and U, occur in variable concentrations. Industrial mineral-related elements such as Al, K, Na, Ca, and Mg are also present in the analyzed samples. Although the measured concentrations do not indicate ore-grade mineralization, the repeated occurrence of selected critical and trace elements suggests that the Dhok Pathan Formation has preliminary geochemical significance. Further detailed sampling, mineralogical confirmation, and spatial geochemical analysis are recommended before any resource-level interpretation is made.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

The Shanawa Gudi Khel, Takht-e-Nasrati located in the Karak District of Khyber Pakhtunkhwa in Pakistan is a geologically significant region in the sedimentary regime of Dhok Pathan Formation. The Dhok Pathan Formation is the upper Siwalik monastics deposits of the northwestern foreland basin in Himalaya and is predominantly marked with the interventions of fluvial sandstone/mudstones with conglomerates (Johnson et al., 1985; Burbank and Raynolds, 1988). The location holds great opportunities regarding the assessment and the description of dies minerals within a sedimentary system, which helps comprehend mineral formation, deposition limitations, and basin second generation (Hazen et al., 2013; Van Gosen et al., 2014). The Dhok pathan formation in the northwestern Himalayan foreland basin would be shown by stratigraphy of the formation, which has combined fluvial sedimentation and tectonic deformation with diagenetic processes in the Himalayan uplifted development and foreland basin development (Burbank and Raynolds, 1988; Najman, 2006). Physicochemical conditions that predispose to the concentration and dispersion of economically valued minerals occur as channel sand bodies, over bank deposits, intervals rich in clay, and other structurally regulated systems (faults and fractures) (Boggs, 2014). In these types of sedimentary environments, the critical minerals may exist as detrital minerals or authigenic minerals (Hazen et al., 2013). It is also a detrital mineralization, which tends to be caused by the erosion of the source rocks and further sedimentation in the fluvial formations of sandstones and conglomerates (Boggs, 2014). Authigenic enrichment, on the other hand, is formed during post-depositional diagenetic and geochemical events, which include the precipitation of minerals under different redox conditions and the interaction of fluids and rocks (Worden and Burley, 2003). Oxidizing and reducing environments in sedimentary layers are also important to the mobility and sequestration of redox sensitive elements in a redox interface

(Brookins, 1988). To conduct a systematic study of the critical minerals in the Dhok Pathan sedimentary system, the combination of multiple methods is needed, such as detailed stratigraphic logging, study of petrographic analysis, whole-rock geochemistry, and remote sensing techniques (Rollinson, 201). Geochemistry of sediments and groundwater contributes to explaining the distributions of elements, patterns of their concentrations, and their mobility, which allows exhaustively estimating critical mineral potential in foreland basin deposits (Van Gosen et al., 2014).

In Karak District (including Takht-e-Nasrati and Shanawa Gudi Khel), the modern remote sensing weaponry is used to explore the area. The use of satellite images and aerial photography is particularly common to trace sedimentary structures, structural lineaments and areas of hydrothermal or diagenetic change that can contain essential mineral concentrations in the Dhok Pathan Formation (Sabins, 1999; Pour and Hashim, 2015). One method, remote sensing, is particularly useful in locating lithological contacts, fracture systems and alteration halos related to mineralization (Crosta and Moore, 1989). These techniques are usually combined with an extensive geology mapping and stratigraphic analysis to limit lithofacies differentiation, depositional background and strain and structural guidance, that are crucial in the identification of mineralized horizons (Boggs, 2014; Tucker, 2001).

Sedimentary basins are considered the sources of strategic materials as the critical mineral resources are important in the implementation of modern technologies, renewable energy systems, and modern infrastructure (Ali et al., 2017; IEA, 2021). As the world develops an increasing need of rare earth elements and other raw resources employed to manufacture wind turbines, electric cars, and energy storage systems, sedimentary-hosted systems like the Dhok Pathan Formation could help to boost the industrial activity as well as resource security (Ali et al., 2017; IEA, 2021). Establishment of exploration, mining, and processing plants may also increase the economies in the regions, create jobs, and boost the technical capacity besides the robustness of the supply chain (World Bank, 2020).

As per the concept of sustainable resource development, the stakeholders must be engaged at the beginning and in the course of the exploration and evaluation phases (ICMM, 2015). Open and transparent communication of the possible benefits, environmental hazards, and long-term outcome, and community involvement in assessing and monitoring the environment results in responsible and accountable mineral development (ICMM, 2015; UNEP, 2011). A sustainable development model thus aims at striking a balance between economic growth in the form of critical minerals endeavor and environmental safety and community based development (UNEP, 2011; World Bank, 2020).The exploration of critical mineral potential in the sedimentary basin of Takht-e-Nasrati and Shanawa Gudi Khel (Karak District) can offer a proper opportunity to understand the process of sedimentary basin development, minerals enrichment, and critical mineral occurrence in the framework of fluvial depositional environment. This kind of research both bolsters geological understanding of northwestern Himalayan foreland basin as well as long term economic growth and sustainable development of resources. Combined with high environmental governance and participation of people, scientific rigor such as sedimentological study, mineralogical characterization and geochemical modelling in conjunction with remote sensing and application will create a platform of responsible and efficient critical mineral exploration in the area. The Karak region has a convoluted geological design comprising of sedimentary orders impacted by tectonic movement and also attributes brought by the metamorphic and igneous source regions in the neighboring elevations. This geological variability is central in the formation, transport and deposition of important minerals under the conditions of the sedimentary system. The concentration of economically valuable components in sandstone together with other related lithologies can be created due to erosion of source rocks, then the process of fluvial transportation, and diagenetic changes. It is important to know these types of geological and geochemical controls to aid in the design of effective exploration strategies and to evaluate the future economic viability and sustainability of critical minerals development in the Dhok Pathan sedimentary system. Recent research focuses on the importance of the fact that geomicrobiological methods can also be significant in exploring critical minerals in the system of sedimentation. Detecting mineralization beneath the surface has been a relatively non-invasive solution identified as an innovative method using a given microbial assemblage, or as a bio-indicator technique through the use of an indicator-based methodology utilizing specific microbial assemblage (Scotti et al., 2021). Such biological indicators can be useful in marking out the areas of redox-regulated mineral enrichments in fluvial and floodplain deposits; in the case of Dhok Pathan Formation, which has been exposed in Takht-e-Nasrati and Shanawa Gudi Khel. Moreover, health effects, which may arise due to the impact of radon releases and mobilization of trace elements of mineralized sedimentary strata, render complete environmental risk assessments. The spatial differences in groundwater trace elements and soils in the Karak District have been demonstrated to also be correlated with the lithological differences as well as structural characteristics including faults and fractures, implying the significance of long-time environmental surveillance and mitigation of the regions to protect the local population (Khan et al., 2022). Advanced spectrometric and radiometric methods, which allow the distinction of mineralized horizons and barren host strata to be stipulated, are further suitable in exploration of the Dhok Pathan sedimentary system. Elemental mapping is made accurate with the help of high-resolution gamma-ray spectrometry and portable analytical instruments that are essential especially in semi-urbanized locations in which mineralized areas can exist in and around occupied locations. By means of such targeted and technology-driven exploration approaches, surface disturbance and ecological impact have a significant connection to the benevolent direction of environmentally sound resource development (Marchais, 2019). The geological complex of Karak District and especially of Takht-e-Nasrati and Shanawa Gudi Khel is characterized by stratified sedimentary rocks of the Dhok Pathan Formation, which was subjected to local deformations by the tectonic forces and structural parameters. Even though it still consists mainly of sedimentary rocks, the basin has been influenced by the tectonic activity in the region that helped form faults, fractures, and increase the secondary porosity. These structural characteristics contribute greatly in enhancement of permeability, aiding the migration, circulation and subsequent concentration of mineral-bearing fluids in porous sandstone and related lithologies. These are the key geodynamic and diagenetic processes which contribute to the enrichment and localization of critical minerals within the sedimentary systems, and form one of the major interests of the present study (Adamson, 2020).

During the development of a sustainable exploration model of key minerals in the Dhok Pathan sedimentary system, they must incorporate the use of high-quality geophysical methods. Recent measurements of the subsurface like three dimensional seismic studies and electrical resistivity tomography depict the stratigraphic structure and structural faults in a very high resolution and the procedures do not cause larger effects on the surface. The technologies can provide a greater level of precision in targeting mineralized horizons and greatly reduce the use of basic exploratory drilling, consequently decreasing footprint of exploration on the environment and enhancing the efficiency of operations (Rabiei et al., 2021).

Exploiting critical minerals within the Dhok Pathan Formation has great difficulties as well as opportunities in the geological structure of the Karak District and especially in Takht-e-Nasrati and Shanawa Gudi Khel. The variety of assemblages in lithological assemblages based on sediment deposition and determined by the mother-rock terrains uplifted should provide an opportunity to enrich the most important elements in a detrital and diagenetic way. Extensive petrographic, mineralogical and geochemical studies are thus suggested to unravel the origin of the sediments, diagenetic changes and fluid rocks interactions that could regulate local mineral concentrations. Integrated studies of this kind are necessary in defining future areas of critical mineral concentration especially in those related to late-stage diagenetic or hydrothermal events (Saleh and Emad, 2021).

Socio-economic aspects of critical mineral development in the developing region like Karak are also critical. The study weighs the possible economic benefits of resource exploitation such as the creation of new places to work, growth of infrastructure, and increase of revenue on the area as well as the social impacts like land utilization issues, health effects of locally occurring radionuclides on people, and communal well-being (Khan et al., 2022). Economic development, which involves a balanced and inclusive process, and incorporation of environmental protection and social responsibility will play a critical role in the long-run viability and social acceptance of the mining activities. With proper infrastructure planning and health protection, critical minerals exploration and development in Takht-e-Nasrati and Shanawa Gudi Khel may be a step towards regional development to boost the development of transport infrastructure, power supply, communication, and other related areas, including agriculture, education, and medical care, which will benefit the general welfare of the community (Saleh and Emad, 2021).

Critical mineral extraction in Takht-e-Nasrati and Shanawa Gudi Khel in Karak District requires a thorough and meticulous analysis of its impact in terms of the environment. The ecological footprint of critical mineral exploration within the Dhok Pathan Formation can be enhanced by a large margin through the deployment of modern, minimally invasive exploration methods and by strictly observing the national regulations that govern the ecological factors. In addition, the allocation of part of the project revenues toward local conservation and ecosystem restoration policies would help to safeguard the natural habitat and biodiversity of the area (Scotti et al., 2021).

One of the enablers of sustainable mineral resource governance that is commonly known is investment in structural, educational and institutional development. Creation of a critical mineral sector in other areas like Takht-e-Nasrati and Shanawa Gudi Khel (Karak District) may boost the progress in schools, vocational training facilities and higher education in geology clustering, mining engineering and environmental sciences (World Bank, 2020; ICMM, 2015). Scholarships and technical training also assist in capacity building, increase expertise in the region, enhance the regulatory control, and aids in transparency in resource management (UNDP, 2016). The overall creation of local technical competence will result in informed decisions, the maximization of social economic benefits, and the minimization of environmental and social risk because of mineral extraction (Ali et al., 2017)

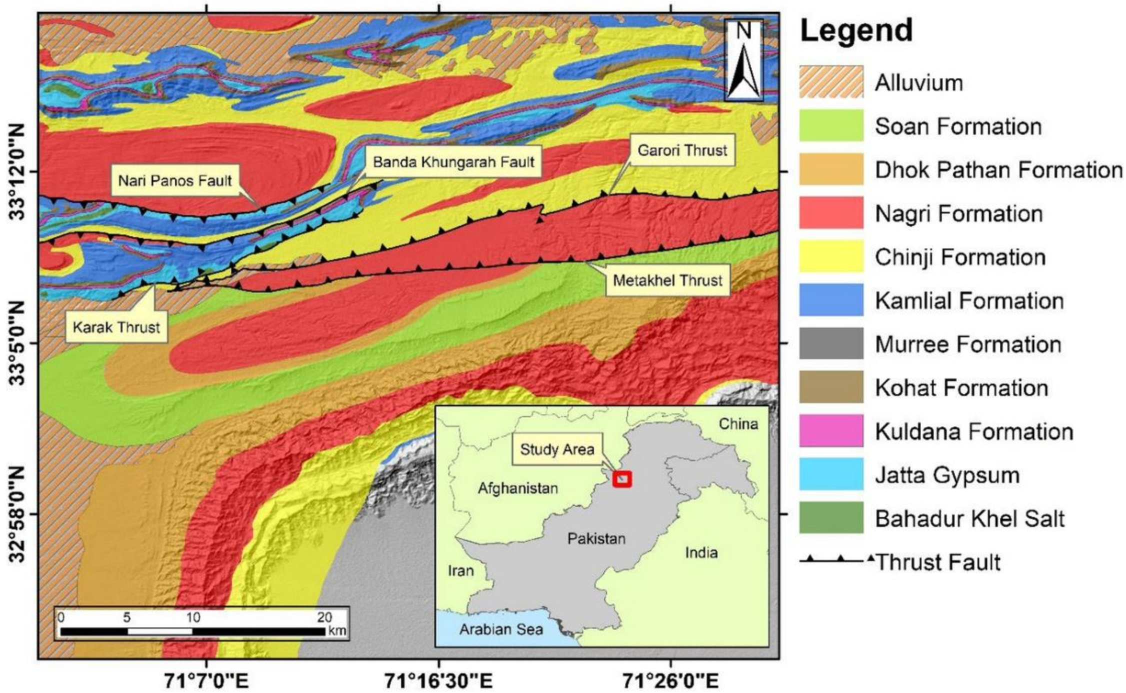

Figure 1.1: Geological Map showing the Karak Thrust on North Garori Thrust on South and the area is bounded by major thrusts (after Khan et al., 2022)

1.2 Study Area

The research site is in the southern side of Karak City; therefore, it provides easy accessibility through the regional highways and main motorways. It is situated in the Khyber Pakhtunkhwa region in northwestern Pakistan with a geographic location of about 33.1277° N latitude and 71.0973° E longitude. To suit the study, samples were also generally gathered in 13 different sites scattered over the entire area to offer representative coverage of the Dhok Pathan Formation lithologies and the cases of sedimentary environments.

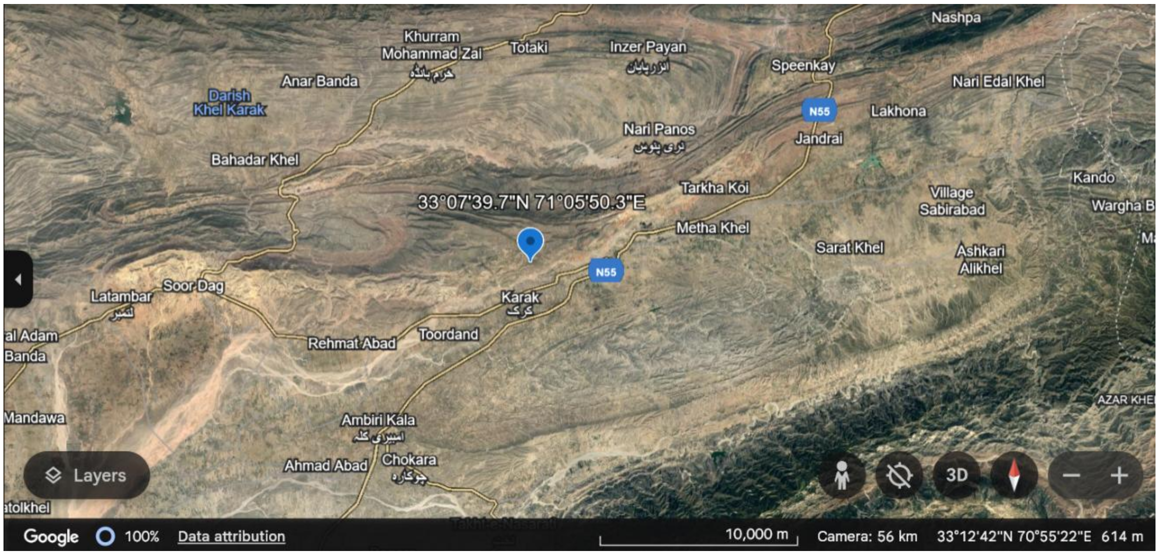

Figure 1.2:Study Area location map (Google Maps)

1.3 Problem Statement

Critical minerals are increasingly important for industrial development, energy technologies, and strategic resource planning. Sedimentary formations can host or retain critical and trace elements through detrital input, weathering, sediment transport, and post-depositional geochemical processes. However, the critical mineral potential of the Dhok Pathan Formation in the Karak area has not been systematically evaluated using sample-based geochemical data.

Previous geological studies in the Karak and Kohat Basin region have mainly focused on regional stratigraphy, tectonics, structural geology, and general mineral occurrences. Limited work has directly examined the elemental distribution of critical, economic, and industrial mineral-related elements in the exposed lithological units of the Dhok Pathan Formation. As a result, the geochemical significance of this formation remains poorly constrained.

This study addresses this gap by analyzing twenty soil samples collected from exposed weathered horizons of the Dhok Pathan Formation at Takht-e-Nasrati and Shanawa Gudikhel. The study uses ICP-OES analysis to determine selected elemental concentrations and to assess whether the formation shows preliminary geochemical indications of critical mineral potential.

1.4 Aim and Objectives

The main objective of the study will be to assess the distribution and potential of critical minerals in the study area with the title being Critical Minerals in Sedimentary Systems: A Case Study of Dhok Pathan Formation, Karak, Khyber Pakhtunkhwa, Pakistan. The objectives of the research are the following specific ones:

1. To analyze the elemental concentration of samples from Dhok Pathan Formation.
2. To assess the resource potential of critical minerals in the study area.

1.5 Literature Review

Due to its complex stratigraphy, tectonic setting and sedimentary successions associated with the Himalayan foreland basin, the Karak and Kohat Basin region have been studied by several authors (Khan et al., 1986; Lillie et al., 1987; Jaumé & Lillie, 1988; Kazmi & Jan, 1997). The previous studies in the area had delineated a fold thrust belt, formed as a result of the continuing convergence of the Indian plate and the Eurasian plate, in the Kohat Plateau and adjoining Trans-Indus ranges (Lillie et al., 1987; Jaumé & Lillie, 1988). In these investigations mapping and stratigraphic correlation, as well as structural interpretation, were used to account for the distribution of the main formations, thrust faults, folds, and basin margins (Meissner et al., 1974; Khan et al., 1986; Shah, 2009). The result of their work indicated that there are repeated and deformed sedimentary sequences in this Karak region where the tectonic events affected the sedimentation, exposure, lithological variation, etc. (Burbank & Raynolds, 1988; Kazmi & Jan, 1997).

Based on stratigraphic studies conducted earlier on the Siwalik Group, it was proposed that the Dhok Pathan Formation constitutes a fluvial group of mainly sandstones, mudstones, siltstones and some local conglomeratic beds (Pilgrim, 1913; Lewis, 1937; Johnson et al., 1985; Behrensmeyer & Tauxe, 1982). The studies found these formations were part of a foreland basin depositional system associated with the uplift and erosion of the Himalayas (Najman, 2006; Zaheer et al., 2022). Sandstone/mudstone alternations signify fluctuations in channel/floodplain environments and conglomeratic environments signify high energy depositional phases (Boggs, 2014). The lithological variation is significant because properties of sediment, including its texture, mineralogical makeup, and weathering characteristics, may affect the distribution of major and trace elements among sedimentary units (Tucker, 2001; Rollinson & Pease, 2021).

The Kohat, Karak and neighboring regions have been mapped by several authors, who have applied geology and structural analysis in order to understand the tectonic framework of this region (Meissner et al., 1974; Khan et al., 1986; Lillie et al., 1987). Structures in the area affected by significant thrusts and/or folds including the structures related to the formation of the Kohat Plateau and Trans-Indus ranges have been documented by them (Jaumé & Lillie, 1988). These structural studies are useful in the present work as they give a background of the region with regard to the exposure and distribution of Dhok Pathan Formation (Shah, 2009). Most were geologic in nature (e.g., regional geology, regional tectonics) or did not specifically address geochemical evaluation of elements related to critical minerals (Ali et al., 2017; IEA, 2021).

Geochemical and mineralogical investigations in sedimentary basins have revealed that critical and trace elements can be found with detrital minerals, clay, iron rich minerals and weathered sedimentary horizons (Rollinson, 1993; Hazen et al., 2013; Borst et al., 2020). Various methods have been used by previous authors, including whole-rock geochemistry, elemental analysis by ICP or element analysis using X-ray diffraction, petrographic analysis, and heavy mineral processing to assess the distributions of elements in sedimentary rocks and soils (Rollinson, 1993; Rollinson & Pease, 2021). These techniques can be used to find out if measurable amounts of chemical elements such as Lithium (Li), Cobalt (Co), Nickel (Ni), Chromium (Cr), Titanium (Ti), Uranium (U), Vanadium (V), Zirconium (Zr), Iron (Fe), Manganese (Mn), Barium (Ba), Strontium (Sr), Aluminum (Al), Potassium (K), Sodium (Na), Calcium (Ca) or Magnesium (Mg) are present within a sedimentary formation (USGS, 2024; Boggs, 2014). Results of these kinds of studies are generally used to do some preliminary assessments but there is a need for additional mineralogical confirmation for the interpretation to be made on a deposit-level (Pell et al., 2021).

In the area of Pakistan, sediment-hosted mineral exploration studies have also shown the significance of sandstone–mudstone successions in the evaluation of trace elements (Hall et al., 2023; Rainoldi et al., 2024). The occurrence of uranium-bearing and trace element-bearing sedimentary units suggests that preferential preservation of certain elements in the fluvial sands and associated fine-grained horizons may occur under favorable geologic and geochemistry conditions (Khan et al., 2022; Ullah et al., 2013). The studies typically include field sampling, lithological description and laboratory elemental analysis to detect anomalous or background concentrations (Rollinson & Pease, 2021). Direct investigations of the critical mineral potential of Dhok Pathan Formation in the Karak area however, are limited.

The literature reviewed reveals that most of the studies conducted on the Karak region are focused on stratigraphic, tectonic and regional geological aspects. The above works are useful geological studies, but do not address elemental distribution of the critical, economic and industrial mineral related elements in the Dhok Pathan Formation adequately. The current research adds to the previous research by analysis of soil samples obtained from the horizons of Dhok Pathan Formation that were exposed. This is a process that offers initial geochemical information which may contribute to determining the potential for continued employment of critical minerals detailed investigation of the formation.

CHAPTER 2

GEOLOGY AND TECTONICS

2.1 Introduction

Khyber Pakhtunkhwa and Baluchistan have been placed centrally along the northwestern edge of the Indian plate as it also touches the Eurasian Plate, being part of the larger Alpine Himalayan orogenic belt, which spans through the Middle East and Central Asia all the way to the Iranian Plateau (Kazmi & Jan, 1997). Tectonic range between the Indian and Asian plates is marked along the Indus suture zone that indicates the remains of the Neo-Tethys ocean (Kazmi & Jan, 1997; Lillie et al., 1987). The Kohistan Island Arc that had been formed due to the intra oceanic subducting composition of the Neo-Tethys contributed a significant part in the structure of the crust in the area before the impact of the Indian Plate into the Eurasian Plate (Kazmi & Jan, 1997). The Karakoram block followed by island arc amalgamation played a key role in basin formation, sediment transport patterns, and provenance as evidenced in the north of Pakistan, thus his intricate tectono-sedimentary history offered conducive environments regarding the creation, transportation and concentration of the important minerals in the foreland basin deposits (Najman, 2006; Burbank & Raynolds, 1988).

The stratigraphic succession that has been uncovered in the Kohat-Karak area with the Dhok Pathan Formation spanning through the Jurassic to the Pliocene age, details the chronological fill up of the Himalayan foreland basin (Shah, 2009; Khan et al., 1986). Precambrian to early Paleozoic metasedimentary rocks which include slate, slaty shale and sandstone are constituents of the structural basement in the northeastern and the northwestern sectors (Meissner et al., 1974). It is also found in isolated instances of Triassic and perhaps also of Permian strata, on the lower margins, which are lithological parallel to the southeastern Salt Range sequence (Meissner et al., 1974; Gee, 1945). The Dhok Pathan Formation, which is dominated mostly by the fluvial sandstone, siltstone and claystone with the same age (Late Miocene–Pliocene), presents a key archive in the study as a depositor of provenance, heavy minerals assemblage, and controls upon the accretion of economically significant and important minerals within the sedimentary system of the Karak area (Pilgrim, 1913; Johnson et al., 1985; Behrensmeyer & Tauxe, 1982; Zaheer et al., 2022).

Karak is geologically a component of the Lesser Himalayan provinces and consists of an uneven mixture of sedimentary, metamorphic and sub-orthogneiss igneous rocks (Kazmi & Jan, 1997; Shah, 2009). The stratigraphic map shows that there are good fold-and-thrust folds and wide fault systems which have a powerful dominance over the sedimentation tendency, the origins of diagenetic change, and the occurrence of minerals (Lillie et al., 1987; Jaumé & Lillie, 1988). It has a succession consisting of Jurassic–Cretaceous carbonate formations, covered by Tertiary clastic formations, and exposures of older Precambrian metamorphic formations (Khan et al., 2022; Meissner et al., 1974). In this tectono-stratigraphic framework, fluvial and continental deposits like Dhok Pathan Formation are of critical interest in terms of heavy mineral and other crucial element provenance, the intensity of weathering and sediment transport processes besides post-depositional processes in the Karak sediment system (Najman, 2006; Rollinson & Pease, 2021; Tucker, 2001).

2.2 Geologic Framework

2.2.1 Geological Formations and Structures

Karak region is located in the western part of the Himalayan Foreland Fold and Thrust Belt, which is located within the large Kohat Basin. The basin is about 70km wide but its geometry changes towards the northern and southern edge as a result of varying compressions between tectonic plates. Geographically, its boundaries to the north are very sharp as the Main Boundary Thrust (MBT) and very sharp to the south, as defined by the Surghar Range but the Kalabagh Fault (KSSF) clearly divides the Surghar and Salt ranges. To the east, the basin turns into the Potwar Plateau, and all the way to the Indus River, but the western boundary is defined by Kurram Fault, separating the relatively less deformed

Eocene Miocene strata in the basin to the Kurram Fault, and the highly folded and faulted Mesozoic sequences in adjacent areas including Samana, Darsamand, Thal, and North Waziristan (Khan et al., 1986; Lillie et al., 1987; Jaume and Lillie, On the south the Bannu Basin marks the southern margin. The MBT in this tectonic model is central to emplacing Mesozoic and younger superimposing on the molasse deposits of the Siwalik Group and thus affects structural traps, sediment dispersal systems and mineral localization (Rehman et al., 2024).

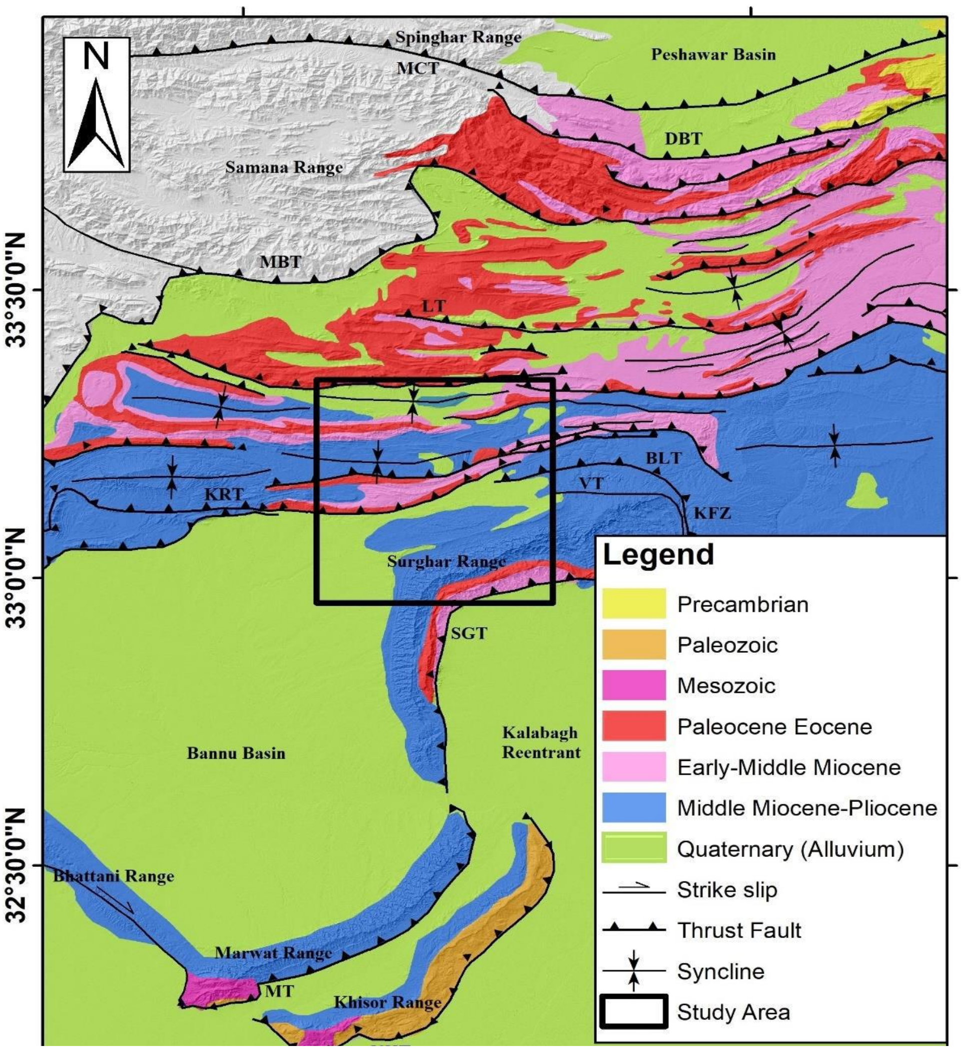

Figure 2.1: Geological map of the Kohat Plateau and Trans Indus Ranges, Showing major Thrusts, and Stratigraphic Successions. BLT: Banda Lakhoni thrust; DBT: Darra back thrust; HT: Hukni thrust; KFZ: Kalabagh Fault Zone; KHT: Khisor thrust; KRT: Karak thrust; LT: Lachi thrust; MBT: Main Boundary thrust (modified after Khan et al., 2022)

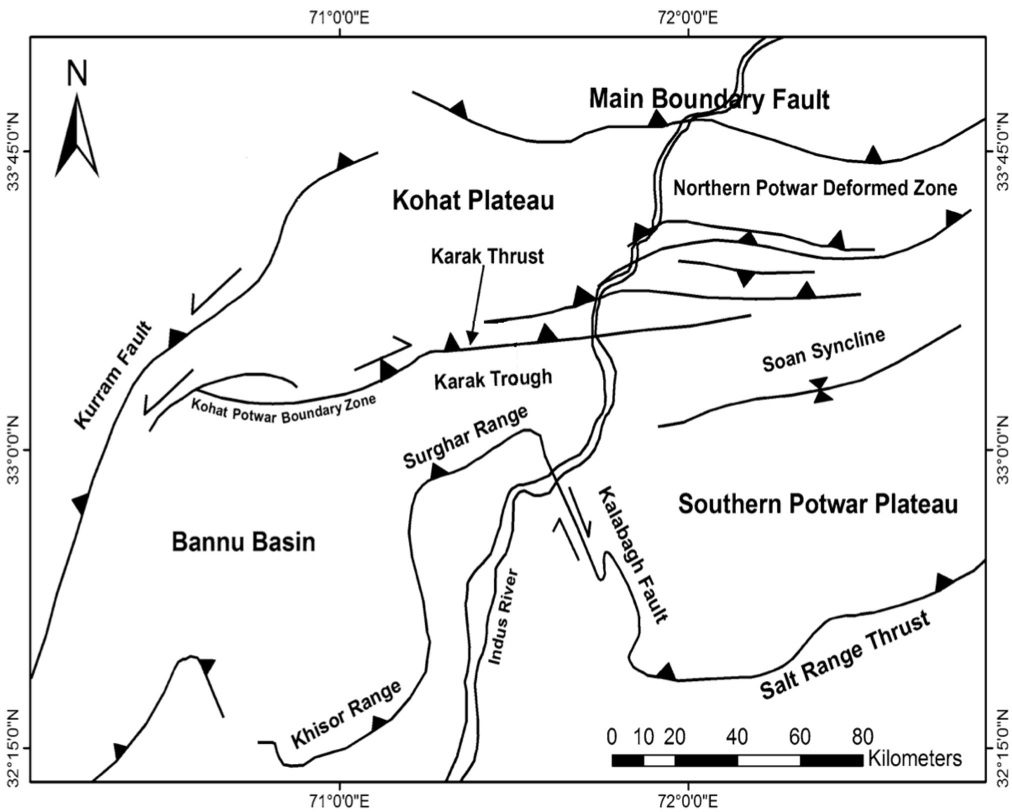

Figure 2.2:Tectonic Map of Karak, Khyber Pakhtunkhwa (Khan et al., 2022)

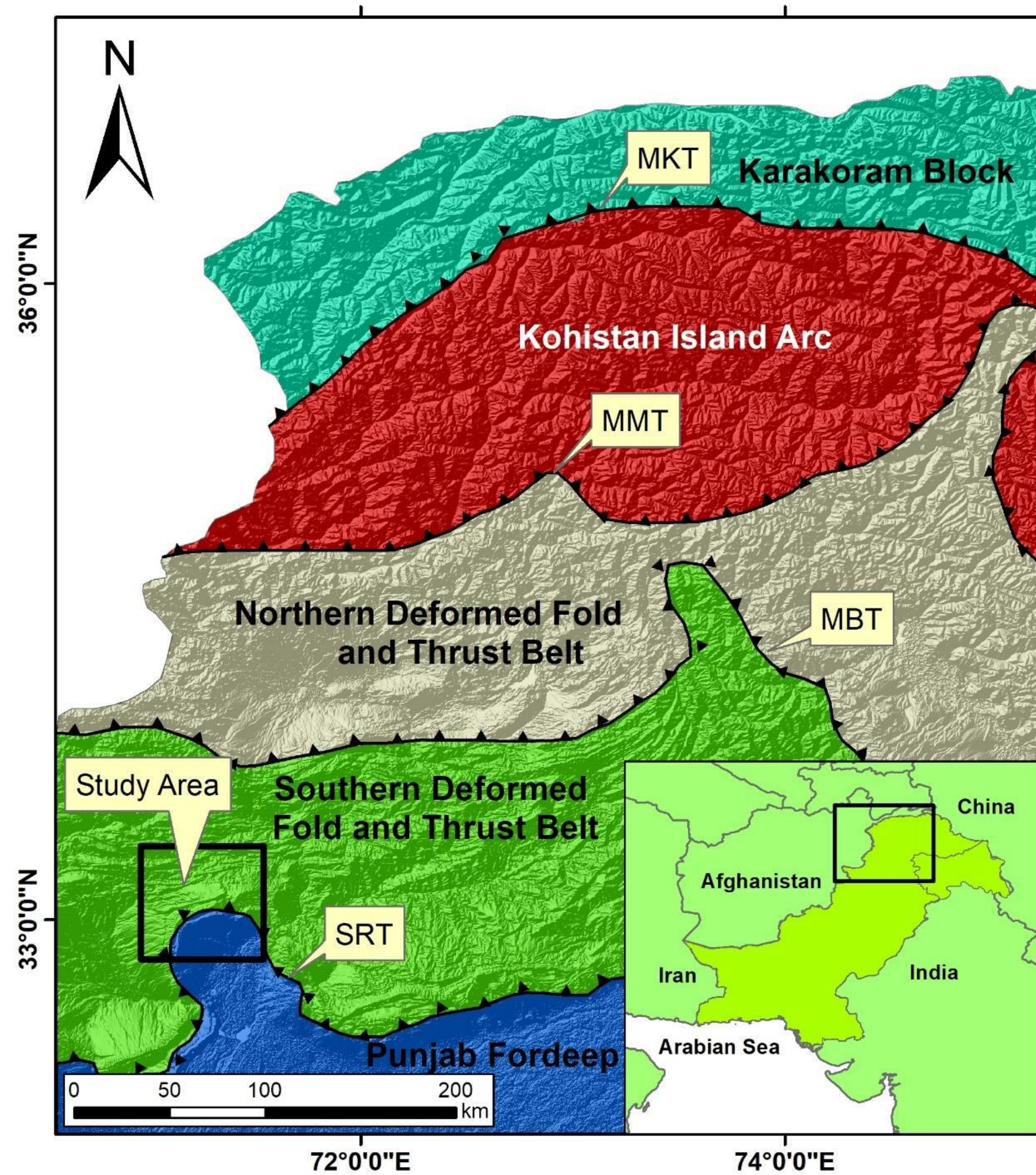

Figure 2.3:Tectonic map of the study area in Pakistan (box shows the study area/sample points, MKT= Main Karakoram Thrust, MMT= Main Mantle Thrust, MBT= Main Boundary Thrust and SRT= Salt Range Thrust (modified after Khan et al., 2022)

2.3 Tectonic Evolution

2.3.1 Historical Development of Tectonic Plates in the Region

The impact between the Indian Plate and the Eurasian Plate resulted in the raising of the Himalayas in almost 2,500 km of the northern coast of the Indo-Pakistan plate. The country of Pakistan has a geodynamical hostile location on the northern slope of the Indian Plate and on the southern border of the Afghan-Helmand block. Global convergence along with transform and convergence tectonics especially along the Afghan-Helmand boundary predominate over the deformation pattern in the region. The Indian Plate actively is pushing northward at a guessed pace of 35cm/one year, upholding crustal tightening and thrust piling (DiPietro and Pogue, 2004). Due to this continued convergence, extended southwards-moving thrust sheets which are ancient Himalayan-derived pieces of the hinterland have moved along the Indian Shield northern margin carrying eroded material into the developing foredeep, which continues to edge southwards into position. In this tectonic regime, the geometry of the Kohat Plateau is unique with Cambrian evaporites that accommodate the threshold of the Cambrian acting as a regional decollation horizon that has a far-reaching effect on the structural style and sediment accommodation (Jaume and Lillie, 1988).

In this structurally complex belt, numerous large thrusts such as the Karak, Banda Khungarah, Garori, Methakhel, and Nari Panos faults take in the crustal shortening, as well as stratigraphic repetition. The Karak Thrust has evaporitic units like Jatta Gypsum which are deposited above the Chinji Formation although the Garori thrust and Methakhel thrust does the same thing whereby the younger formation is emplaced above the older Siwalik. Banda Khungarah and Nari Panos are back thrust systems positioned contrasting the older Eocene rocks to Pliocene sequences, which illustrates intense inversion of the tectonic processes. Miami Khel Formation and Jatta Gypsum are displaced south of the Chinji Formation by the east west trending Karak Fault which borders the Kohat Plateau and Bannu Basin (Jaume and Lillie, 1988). The Karak Thrust is situated south of the Karak Thrust, and to its east, west, and south, respectively, there is the Karak Anticline in the

Karak Trough, framed by the Shinghar -Surghar regions to the south, the Shakardara Hills to the east, and the Bannu Basin to the west (Khan et al., 2022). Often stratigraphically, the Karak Trough is prevailed by Miocene sediments of the Siwalik Group which consist of fluvial sandstones, siltstones and mudstones which are especially crucial in judging sediment provenance, basin development and the possible concentration of important minerals in the foreland sedimentary system.

2.3.2 Impact of Tectonic Activities on the Geological Landscape

The elongated motion of the Tectonic involving the meeting of the Indian Plate and the Eurasian Plate has not only shaped the face morphography of the Kohat Karak region, but it has essentially dictated the geological processes under the earth that form minerals, mineral such as uranium and other redox dangerously critical elements. High compressional and crustal thickening and frictional heating of the major structural discontinuities within the Main Boundary Thrust system, along with the related thrust systems, have facilitated the localized metamorphism, fracturing, and the development of related fault networks. They increase secondary porosity and permeability, act as good conduits of mineral carrying hydrothermal and basinal fluids. Structural traps and stratigraphic juxtaposition are created due to thrust stacking, folding as well as fault related fracturing and all these tend to affect the pattern of fluid circulation as well as the localization of mineral deposits in appropriate host lithologies.

The overriding regional exhumation and vertical movement through the continuous convergence of tectonic plates have, to a further extent, The differences in rates of uplift and erosional unroofing influence the provision of sediments, diagenetic changes, and fluid interactions on rocks, which are all essential in comprehending the process of mineral precipitation and preservation (Gallen and Fernández-Blanco, 2021).

2.4 Sedimentological Features

2.4.1 Analysis of Sediment Layers and Their Compositions

Kohat Karak quadrangle described The geological succession of the Kohat Karak quadrangle has a cumulative thickness greater than 20,000 feet of stratum which range in age between the Jurassic basal strata and Nagri Formation of Pliocene age. Superimposing on the Nagri Formation in fine conformity is the Dhok Pathan Formation, which is thought to be more than 5,500 feet thick, but due to varying measurements between the basin. This massive stratigraphic stack has undergone significant tectonic adjustments in terms of extreme folding, thrust re-occurrence as well as fault substitution which are indications of the compressional regime of Himalayan foreland system (Meisner Jr., Charles R., et al., 1974). These structural overprints have important consequences on the evolution of porosity, fluid flow channels and redistribution of mineral phases in the sedimentary host rocks.

The stratigraphy that is exposed shows extreme deformation that is characterized by tight folds, imbricate thrusts, and high angle faults. The Jatta Gypsum, and the Bahadur Khel Salt are among the oldest units of exposure with an age of Eocene origin and which are covered by evaporitic lithologies with interbedded horizons of shale and clay. These are followed by Kohat Formation and Kuldana Formation which is composed of shale and limestone and typical red clay beds. Laying over these are the Siwalik Group succession (Miocene -Pleistocene), which also constitutes the Kamlial Formation, Chinji Formation, Nagri Formation, Dhok Pathan Formation and the Soan Formation. The deposits of molasses, which are mainly sandstone, conglomerate, siltstone and shale, document the progressive basin infillament due to active tectonic loading. One of the east west trending thrusts, which is usually known as Karak Thrust, pushes the Eocene evaporites southwards across the Lower Siwalik formations, which further complicates the structural formation. The Karak Anticline was formed as the southern flank of this thrust surfaces in the Karak Trough and runs northeast southwest and is a major structural trap which affects the subsurface distribution of fluids. Its economic value is also characterized by the necessity of considerable deposits of coal, hydrocarbons, Uranium and even evaporites (Khan et al., 2022).

2.4.2 Correlation Between Sediment Features and Critical Minerals Occurrences

The correlation of the sedimentological parameters and the distribution of the significant minerals can be sufficiently illustrated on the Dhok Pathan Formation of the Karak District. According to recent studies, most such critically important minerals like the rare earth elements (REEs), uranium, vanadium, and other strategic trace metals are often concentrated in certain sedimentary facies, specifically in the fine-grained and organic-enriched horizons or strata with clay matter, where adsorption, ion exchange and the redox-regulating precipitations are not only logical but highly successful. These components can be fixed in authigenic clay minerals, to which the heavy mineral fractions are related or trapped in complexes with the organic matter, in reducing conditions. The granulometry of sediments has an ultimate authority over their concentration; due to a larger surface area, cation exchange capacity, and geochemical activity, finer-grained sediments generally have a higher measure of metal retention (Hazen et al., 2013; Zhang et al., 2023).

These types of sedimentological controls play a vital role in explaining the process of strategic mineral resource enrichment in fluvial sedimentary environments. A thorough lithofacies architecture, depositional environment and post-depositional diagenetic processes evaluation in the Dhok Pathan Formation serves as a predictive tool of defining likely mineralized zones. Moreover, the comprehensive sedimentological studies can be used to interpret the mobility of metals in ground water flows, weathering and basin evolution process, which can be useful in sustainable exploration models and effective resource development plans of important mineral in sedimentary basins.

2.5 Geochemical Characteristics

2.5.1 Major and Trace Element Distribution

The geochemical model of the Dhok Pathan Formation in the Karak District is defined by the distribution of major and trace elements which illustrate its origin, deposition and de-deposition mineralization events that happened to it. The bulk composition is dominated by major oxides (SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO) which are typical of the fluvial sedimentary character of the succession as well as the input of varied source terranes. Conversely, the trace and strategic metals such as uranium (U), thorium (Th), rare earth elements (REEs), vanadium (V), etc. have heterogeneous spatial distributions and are usually linked to specific mineral phases such as clay minerals, heavy mineral assemblage, iron oxides, and phosphatic components of the stratigraphic units.

These are trace and critical elements especially REEs, and they are commonly complex with phosphate minerals, organic matter, and fine-grain siliciclastic fractions and they can be enriched via diagenetic modification, adsorption desorption reactions, as well as fluid rock interaction processes. Redox sensitive situations in the channel-fill deposit and in over bank deposits also affect their mobilization and fixation. Geochemical anomalies described by higher concentrations than the typical upper crust of the continent is significant information about the possibilities of mineralized horizons and a foundation of defining the potential areas of critical minerals exploration in sedimentary basins (Rollinson, 1993; Borst et al., 2020).

2.5.2 Geochemical Anomalies and Their Relevance to Critical Mineral Enrichment

Geochemical abnormalities are primary deposits of zones rich in major mineral elements like but not limited to uranium (U), rare earth elements (REEs), vanadium (V), and other trace elements that are sensitive to redox in the detection of zones that may contain the important mineral elements. Careful geochemical surveys indicate that these abnormalities are typically accompanied by geologic discontinuities (e.g., faulting, fractures), as well as stratigraphic boundaries where hydrological movements cause the movement of elements and their deposition (Brooks, 1998; Hall et al., 2023). The critical metals carried in the oxidized fluids can often be deposited as enrichments at chemical boundaries that are regulated with respect to pH, edges, organic material and clay minerals surfaces and are detectable as events at the basin level. Similar studies in the continental sedimentary systems have stressed the idea that the higher levels of these elements may be bound in organic-rich inclusivity in the reducing horizons due to enhanced methods of adsorption and complexation- just as observed in the case of the stream sediment geochemical mapping of Pakistan, where lithological parameters are identified as potent control on the distribution of these elements.

2.6 Mineralization Processes

2.6.1 Description of Known Critical Mineralization Zones

Karak region is an area that has some localized occurrences of recorded critical minerals in the sandstone and siltstone units of the Dhok Pathan Formation. Although most studies worldwide on key processes in a sedimentary basin examine REE enrichment in non-conventional hosts, uranium ore in sandstone hosts is a valuable analog on which to gain insight into the interactions of fluid pathways, redox front, and depositional architecture to concentrate critical metals (e.g., U, V, Th) (Brooks, 1998). Airborne radiometric surveys and ground geochemistry in the case of the Dhok Pathan Formation show that there are higher elevations of radon in the sandstone coarse layers with a reduced facies and pore-fluid isolation suggesting that reducing facies and pore-fluid isolation affect trace metal fixation (Khan et al., 2022).

The zones of sedimentary mineralization here is usually found within discrete stratigraphic levels that have a relative higher porosity permeability coupled with organic matter or clay-rich barriers that serve to precipitate the metals of migrating solutions. The geometries of paleochannels, interbedding, and differences in the energy of the initial depositional setting are also structural complexities that help in the definition of traps that can concentrate critical metals. All these processes are generally compatible with the familiar sandstone-type mineral systems elsewhere, where mineralized beds are frequently tabular and bound strata and not just concentrated in large veins or within host igneous formations.

2.6.2 The Geological Processes Leading to Critical Minerals Deposition

The process of critical mineral deposition in sedimentary basins is controlled by interplay of the activity of tectonics, sedimentation, diagenesis, and fluid rock interaction. At the Dhok Pathan Formation, anisotropy of permeability has been created through faulting and fracturing processes by tectonic activity which has provided channels of oxidizing, metal-bearing fluids to move through the stack of sediment. When these fluids come into contact with reducing environments that are usually organic-rich facies of floodplains, or paleosol horizons, or layers of clay-rich siltstone they experience redox reactions which result in the precipitation of dissolved metals as discrete mineral phases. This process is analogous to basic processes in other sandstone-hosted critical element systems, in which redox fronts are major agents of immobilization of metals and formation of ores.

Put collectively, these tectono-sedimentary and geochemical processes make a conceptual model of mineral system of critical minerals in the Dhok Pathan Formation.

Exploration targeting can be improved using this model because the redox interface, lithofacies heterogeneity and fluid pathways as the main controls over mineral deposition and enrichment in sedimentary environments.

2.7 Stratigraphy Framework of the Study Area

Stratigraphic sequence exposed in the Karak region is made from Eocene to Neogene sedimentary sequence and includes the Kohat Basin and north-western Himalayan foreland basin system. Bahadur khel Salt, Jatta Gypsum, Kamlial Formation, Kohat Formation, Kuldana Formation, Chinji Formation, Nagri Formation, Dhok Pathan Formation and Soan Formation are the main units reported within the study area. These represent a transition between evaporitic/carbonate dominated deposition and continental clastic sedimentation leading to the development of the Himalayan foreland basin (Meissner et al., 1974; Shah, 2009; Khan et al., 2022).

Below are sequences of evaporite and sediment. Originally mapped as a part of the Kohat Saline Series by Gee (1945) it was renamed the Bahadur Khel Salt by (Meissner et al., 1974). It is composed of halite, minor intercalations of clay and carbonate. The overlying Jatta Gypsum is primarily gypsum with associated shale, dolomitic sandstone and carbonate beds, suggesting evaporitic to marginal-marine depositional conditions (Meissner et al., 1974). The older ones are succeeded by sediments of Eocene age groups called Kohat and Kuldana formations in the stratigraphic framework of the entire area pertaining to Kohat-Karak region (Shah, 2009; Khan et al., 2022).

Overlying Neogene is represented by Rawalpindi and Siwalik Groups. The lower part of the continental clastic succession is represented by the Kamlial Formation which is succeeded upward by the Chinji, Nagri, Dhok Pathan and So'an formations. Pilgrim (1913) introduced the Chinji Stage as it was known then and Lewis (1937) recognized it as the Chinji Formation. Sandstone and shale make up the Chinji Formation, and the vertebrate fossil assemblages of this formation have been utilized to age-correlate the rock formation on a regional scale (Pascoe, 1963; Shah, 2009).

Nagri Formation is lying above the Chinji Formation and is predominantly composed of medium and coarse grade sandstone with occasional shale and conglomeratic deposit. It is a fluvial depositional system, occurring in the Siwalik Group. The Dhok Pathan Formation which overlies the Nagri Formation forms the major focus of the present study. It is an upper Siwalik formation consisting predominantly of sandstone, mudstone, siltstone, clay beds and local conglomerate. Based on previous studies, the Dhok Pathan Formation was interpreted as a fluvial foreland basin succession associated with uplift and erosion of the Himalayas and an influx of sediment from the north (Johnson et al., 1985; Burbank and Raynolds, 1988; Shah, 2009).

The upper part of the rocks exposed in the study area is represented by the Soan Formation. In lithostratigraphic terminology, it first came to be known as the Upper Siwaliks (Medlicott, 1868), but subsequently designated the Soan Formation. The formation is predominantly a conglomerate, containing subordinate sandstone, siltstone and claystone, indicating high energy fluvial sedimentation during the late foreland basin sedimentation (Shah 2009).

The Dhok Pathan Formation was chosen for geochemical campaign in the present study since the formation is well exposed in Takht-e-Nasrati and Shanawa Gudikhel and sandstone–mudstone/siltstone successions which are suitable for the preliminary elemental geochemical analysis are available. It is intermediary of Nagri Formation (below) and Soan Formation (above), this position gives geological background which helps to identify some of the critical, economic and industrial mineral-related elements in the Karak area.

Table 1: Stratigraphic Column of Study Area

Age	**Stratigraphy**	**Formation**	**Thickness in Study Area (m)**
Pliocene	Siwalik Group	Soan Formation	250 – 450
Miocene	Siwalik Group	Dhok Pathan Formation	1000
Miocene	Siwalik Group	Nagri Formation	3000
Miocene	Siwalik Group	Chinji Formation	1000
Miocene	Rawalpindi Group	Kamlial Formation	550 – 600
Oligocene		Unconformity	
Eocene	Cherat	Kohat Formation	1 – 6
Eocene	Cherat	Kuldana Formation	50 – 60
Eocene	Cherat	Jatta Gypsum	50 – 60
Eocene	Cherat	Bahadur khel Salt	100

CHAPTER 3

METHODOLOGY

3.1 Field Observation

Fieldwork was carried out in the exposed sections of the Dhok Pathan Formation at Takht-e-Nasrati and Shanawa Gudikhel, Karak District, Khyber Pakhtunkhwa. The formation was examined in the field through lithological observation, stratigraphic logging, photographic documentation, and systematic sample collection. Particular attention was given to lithological variations within the exposed Dhok Pathan succession, including sandstone, mudstone, siltstone, clay-rich horizons, and locally conglomeratic intervals. These lithological units are characteristic of the fluvial depositional system of the Siwalik Group and represent channel, overbank, and floodplain depositional environments.

A litholog of the exposed Dhok Pathan Formation was prepared to document the vertical arrangement of the observed stratigraphic units. The litholog records changes in lithology, grain size, colour, sedimentary texture, weathering pattern, and the position of sampled horizons. Field photographs were also taken to show the general outcrop condition, sandstone–mudstone/siltstone alternations, weathered reddish-brown horizons, clay-rich intervals, and representative sampling points. These photographs provide visual support for the field-based interpretation and help establish the relationship between the collected samples and the stratigraphic units of the formation.

3.2 Sampling Approach and Justification

The sampling strategy was designed to obtain representative geochemical data from exposed weathered horizons of the Dhok Pathan Formation. Twenty soil/regolith samples were collected from selected horizons developed directly on the exposed formation. The samples were not collected randomly from unrelated surface soil; rather, they were taken from weathered material derived from the Dhok Pathan Formation, especially from fine-grained and oxidized intervals associated with mudstone, siltstone, and clay-rich horizons.

The sampled material was selected because fine-grained units such as mudstone, siltstone, and clay-rich beds commonly have higher surface area, greater adsorption capacity, and stronger ability to retain trace and critical mineral-related elements compared with coarser sandstone units. In addition, reddish-brown to orange oxidized horizons were targeted because such colour changes may indicate iron-oxide enrichment, weathering effects, and possible retention of trace elements within the sedimentary profile.

The collected samples should therefore be described as soil/regolith samples developed over selected fine-grained and weathered horizons of the Dhok Pathan Formation. They are not pure clay mineral separates, nor do they represent only one clay bed throughout the formation. Instead, they represent weathered clay-rich, mudstone–siltstone, and oxidized horizons within the exposed Dhok Pathan succession. This approach was adopted to evaluate the preliminary geochemical distribution of selected critical, economic, and industrial mineral-related elements within the formation.

At each sampling location, the lithology, colour, weathering condition, stratigraphic position, and GPS coordinates were recorded. Approximately 2 kg of material was collected from each site, placed in labelled airtight sample bags, and transported to the laboratory for preparation and ICP-OES analysis. This sampling design allowed the study to relate elemental concentrations to the lithological character of the sampled horizons and to provide a preliminary assessment of the geochemical significance of the Dhok Pathan Formation.

Figure 3.1:Differentiation of lithology in Dhok Pathan Formation

Figure 3.2: Dhok Pathan Formation outcrop exposure, pen for scale

3.3 Critical Minerals Measurement

Extensive field work was undertaken to sample soil to be assessed geochemically to determine the presence of critical minerals in the sedimentary system of Karak District. All in all, soil samples (2 kg each) were systematically sampled at specific sites scattered all over the study area and especially where the Dhok Pathan Formation is exposed. Sampling design was designed in a strategic manner to achieve spatial variability, lithological differences and environmental diversity required to have a representative geochemical assessment. GPS was then used to take the exact geographic coordinates of every sampling location in a field notebook and all the samples were labelled so that they can be easily identified, traceable, and correctly localized during an entire analytical procedure.

A sample of soils was taken out of the stratigraphic horizons that were selected to sample and homogenized in the airtight sample bags as a way of preserving the natural mineralogical and geochemical attributes of the samples. During the sampling and handling processes, a great care was used in order to prevent cross-contamination, loss of moisture or the unintentional alteration of the elemental concentrations. It is all necessary when dealing with such meticulous treatment required to preserve the original geochemical signature of the samples, as well as their reliability in characteristics of trace-Elements analysis.

After the field work, all the samples were taken to the laboratories to carry out in-depth geochemical research. Upon arrival, the standard laboratory protocols were used in order to preserve sample integrity before testing. A controlled condition was enforced on the samples to avoid chemical changes to bring precision and reproducibility when the samples are further determined by the elements.

This is a deliberate and well-regulated methodology that stresses on the adherence to scientific rigor and the significance of comprehensively standardized field and laboratory procedures in the process of critical mineral research. Detailed records and following the relevant methods of analysis are essential to produce quality data, as they aid proper interpretations and increase the knowledge in the important mineral distribution in the sedimentary systems.

3.4 Analytical Technique

The collected soil samples were analyzed in terms of the elemental composition using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). This was an advanced analytical method that was chosen based on high precision, the ability to detect multiple elements and its aptitude to determine major, minor and trace elements in complex analyzing matrices of the environment related to sedimentary mineral systems.

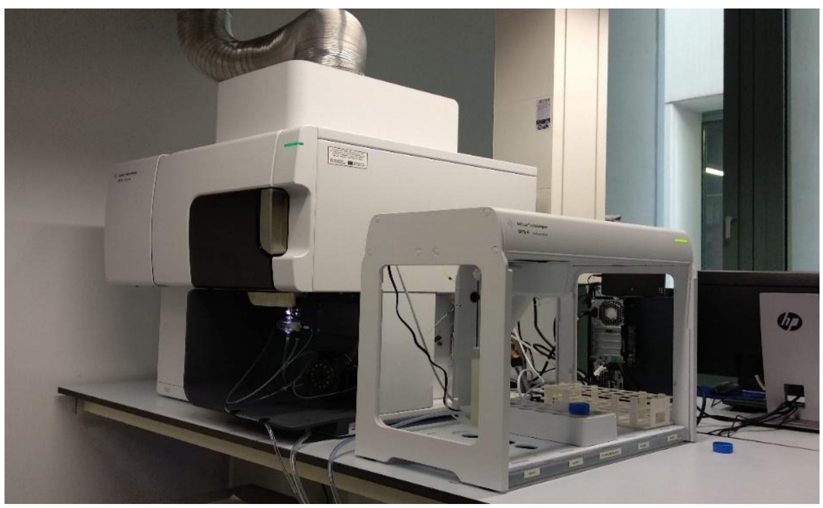

Figure 3.3: 5100 ICP-OES from Agilent Technologies

Table 2:Sample Type and Coordinates

Sample Type	Sample Color	Sample Number	Latitude	Longitude
Soil Sample	Skin	1	N 32°53'43.1"	E 071°04'6.1"
Soil Sample	Orangish Skin	2	N 32°53'42.1"	E 071°04'12.3"
Soil Sample	Beige	3	N 32°52'38.6"	E 071°04'5.7"
Soil Sample	Skin	4	N 32°52'39.0"	E 071°04'7.8"
Soil Sample	Skin	5	N 32°53'38.5"	E 071°04'48.6"
Soil Sample	Skin	6	N 32°53'40.0"	E 071°04'50.2"
Soil Sample	Skin	7	N 32°53'37.5"	E 071°04'45.2"
Soil Sample	Orangish Skin	8	N 32°52'37.2"	E 071°02'34.2"
Soil Sample	Beige	9	N 32°52'39.2"	E 071°02'41.0"
Soil Sample	Beige	10	N 32°52'40.0"	E 071°02'37.9"
Soil Sample	Dark Grey	11	N 32°52'30.9"	E 071°04'30.9"
Soil Sample	Dark Grey	12	N 32°53'33.6"	E 071°04'31.1"
Soil Sample		13	N 32°53'40.0"	E 071°04'50.02"
Soil Sample	Beige	14	N 32°53'41.0"	E 71°04'51.0"
Soil Sample	Dark Grey	15	N 32°53'32.4"	E 071°04'30.8"
Soil Sample	Skin	16	N 32°53'38.9"	E 071°04'47.3"
Soil Sample	Orangish Skin	17	N 32°52'37.6"	E 071°02'34.7"
Soil Sample	Beige	18	N 32°52'39.7"	E 71°04'08.3"
Soil Sample	Dark Grey	19	N 32°53'33.9"	E 071°04'31.5"
Soil Sample	Skin	20	N 32°53'40.4"	E 071°04'49.6"

3.4.1 Sample Preparation

Preparation of samples is the first step in conducting the Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), as shown in the following processes.

3.4.1.1 Soil Samples

First, the sampled soil was uniformly laid on clean and inert trays and allowed to dry by air at room temperature of about 24-32 hours or 48 hours according to the initial moisture level of that soil. The samples were dried thoroughly and then gently disaggregated and filtered using a 2 mm stainless steel mesh to eliminate the coarse fraction, plant residues and other extraneous samples so that only the fine-grained portion could remain and be analyzed. The material that had been sieved was then mixed very well by means of the coning and quartering technique so as to get representative subsamples and allow analytical uniformity.

To determine elements of importance and trace elements geochemically, the homogenized soil of about 10 grams was acid digested with aqua regia a blend of concentrated nitric acid (HNO_3) and hydrochloric acid (HCl), in the ratio of 1:3. Digestion was performed at controlled heating conditions in order to increase the dissolution of minerals and prevent vigorous boiling avoiding a significant loss of volatile components. Using the solution after full digestion, it was left to cool down, diluted with deionized water and filtered in order to get rid of any remaining residual insoluble impurities. The last filtrate underwent instrumental analysis by reducing and transferring it to appropriately labeled polyethylene bottles and placing it in 4º C (four degrees celsius) following prior storage.

This is a well-thought-out preparation process, which guarantees the highest extraction rate of environmentally accessible and structurally bound elements contained within the sediment matrix. The ready-to-use solutions were then measured through Inductively Coupled Plasma-Optical Emission Spectroscopy, ICP-OES, to detect high-precise content of the important elements whether the rare earth elements (REEs), the elements in transition, and other strategic minerals. This kind of rigorous laboratory preparation is necessary to provide valid, reproducible, and reliable geochemical data, which is fundamental to the assessment of the vital mineral distribution of the sedimentary system of the Dhok Pathan Formation.

3.5 Principal of ICP-OES

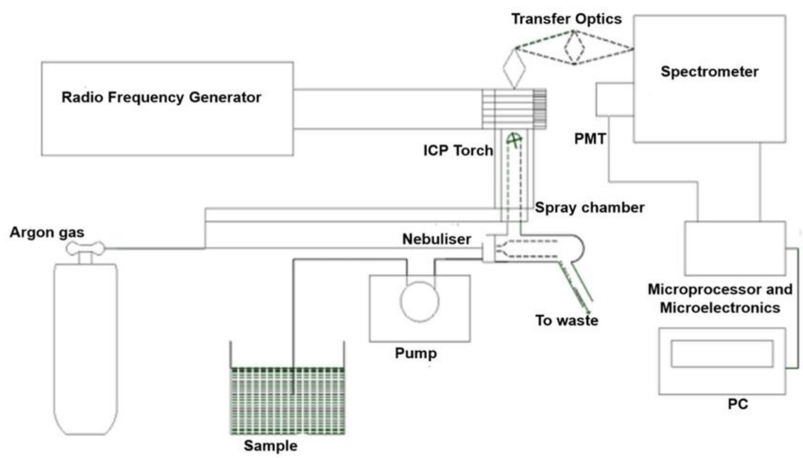

Figure 3.4: Schematic Diagram for ICP-OES system (ETL, 1997−2004)

Inductively Coupled Plasma November, Optical Emission Spectroscopy (ICP-OES) is a sophisticated multi- element analysis method that is commonly applied to determine the presence and quantities of major, minor and trace elements simultaneously with high precision and sensitivity. Under such an arrangement, the ready liquid sample is fed to the system first via a nebulizer that transforms into a fine aerosol. This aerosol is carried into the plasma torch in which atomization and excitation take place. The radio frequency (RF) generator is used to ionize the plasma through the use of the argon gas, owing to its chemical inert nature, and the ionized plasma is produced through the use of the radio frequency (RF) generator which generally falls within the region of 27 to 40 MHz The argon plasma that results has very high temperatures that are usually between 6 000 to 10 000 K and this is enough to energize atoms and ions in the sample.

These high temperatures cause the electrons in the outer shell of atoms to take in energy and get into higher energy levels which can be symbolized as: $X + \text{energy} \rightarrow X^*$

where X is the ground atomic state and X stars (stars) indicated the excited atomic state. When such excited electrons revert to their low energy state, they release electromagnetic radiation in wavelengths of specific elements. This emitted radiation is what underlies qualitative identification as well as quantitative determination.

The emitted light is then passed through a spectrometer in which a diffraction grating separates the radiation into the various wavelengths. Photomultiplier tubes or solid-state detectors, which are elemental line calibrated, are then used to detect these wavelengths. The intensity of the measured emission at any given characteristic wavelength is directly proportional to the concentration of corresponding element in the sample.

It is also necessary to maintain the constant temperature of the plasma to proceed with a high degree of reliability in the ways of the excitation and the achievement of consistent results in the analysis. The determination of the quantification is done by the use of calibration curve constructed with known concentrations of standards. Even though spectral interferences can be caused by overlapping emission lines, these are reduced by proper wavelength selection, background correction strategies and sophisticated instrumental programs.

3.6 Sample Analysis

The Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) consists of multiple steps in the sample analysis stage, which are tightly controlled in order to ascertain elemental concentrations in geological and environmental samples with proper accuracy and reliability. It starts by having the samples digested, especially when using solid like soil and sediments and then it is converted into a liquid state that is nebulized. This digestion normally entails the disintegration of the sample shaft in strong acids. In the case of sediment samples, the most used type of digestion is the aqua regia which uses the proportions of nitric acid (HNO_3) and hydrochloric acid (HCl) (1:3) (HNO3 + 3 HCl). The sample which has been homogenized is treated (about 10 grams) with almost 10 mL of nitric acid and 30 mL of HCl and then a steady and consistent heating on a heating plate using approximately 95º C (ninety-five degrees celsius) is carried out to facilitate proper dissolution and at the same time minimal evaporation.

Contrariwise, in water analysis, the samples are normally filtered and treated with acid before being analyzed. Nitric acid is then added to stabilize the dissolved metals at a pH lower than 2 and allow stabilization so that they are not adsorbed on the sides of the containers. Even in the instances where the particulars of bound metals need to be determined, mild digestion can also be used. After being ready, the liquid sample is added to the ICP-OES instrument using a nebulizer to transform it into a fine aerosol and easy transportation into the plasma torch.

Inside the plasma chamber, a radio frequency source ionizes the argon gas producing temperatures of between 6,000 and 10,000 Kelvins. Such extreme temperatures guarantee full solvent evaporation, atomization as well as excitation of the elements present in the sample. When excited atoms pass back to lower energy states, they emitted light of characteristic wavelengths. A diffraction grating separates the emitted radiation based on wavelength and then the radiation is measured by photomultiplier tubes or solid-state detectors adjusted to measure specific elemental lines. The concentration of a particular element in the sample is directly proportional to the intensity of the emitted light. The calibration curves constructed with known standard solutions at known concentrations which have been formed and used to realize the quantitative determination allows a precise interpretation of the emission signals.

3.7 Quality Control and Assurance

Quality Control (QC) and Quality Assurance (QA) are both important parts of the analytical process in the Inductively Coupled Plasma- Optical Emission Spectroscopy (ICP-OES), and they are used to obtain accurate, precise, and reproducible elemental data. Quality Control: This is the methods and process measures used within the operational procedures used in the analysis to check on performance of instruments and their data integrity. This involves the making and use of multi-element calibration standards to make credible calibration curves which are used to determine the concentrations of unknown samples. Analytical blanks are also served with the samples to identify possible contamination caused by reagents, glass, or laboratory settings. Duplicate samples are run to determine precision and repeatability, and spiked samples (matrix spikes) are run which determine the recovery rates and the methods accuracy during the processes of digestion and instrumental detection.

Quality Assurance, on the other hand, is a wider management structure, which justifies and confirms QC operations. It entails establishment and vigorous enactment of Standard Operating Procedures (SOPs) so that there is methodological uniformity, reproducibility, and transparency in the workings of the lab. Laboratory staff is also under regular training and technical competency assessment to ensure that they stick to the best analytical practice. The maintenance of the optimal performance and the reduction of the downtime is maintained by the introduction of scheduled instrument calibration and preventive maintenance programs.

Inter-laboratory comparisons, proficiency testing programs, and regular analysis of certified reference materials (CRMs) accomplish external quality validation demonstrating the level of analytical accuracy and the comparative ability of the laboratory to the recognized standards. Documentation containing calibration records, maintenance logs, quality control charts and analyst reports are well documented to improve traceability and accountability. Internal audits and management review also ensure the analytical outputs are more reliable because this is done periodically.

Combined with QC and QA standards, these combined QC and QA systems facilitate the scientific authority, credibility, and regulatory obedience of ICP-OES tests. The related stringent quality control is especially important in the intricate geochemical studies of the sediments, when reliable trace-elements information supports interpretations on vital mineral distribution, environmental analysis and resource appraisals.

3.8 Data Interpretation

ICP-OES Data Interpretation Unsaturated spectral emissions are the inputs processed into analytical data one step at a time to a multi-step analytical process the product of which becomes dependable quantitative elemental concentrations. This procedure is essential in the assessment of the geochemical segregation of essential minerals in the sedimentary matrices like those in the Dhok Pathan Formation. It starts with the interpretation of calibration curves constructed out of certified reference standards of known concentrations. The emission intensities at wavelengths of the individual elements are plotted against the element concentration, and regression analysis is put across to determine linearity. Statistical parameters such as correlation coefficients (R^2) are determined as evidence of calibration accuracy and the consistency of quantification of unknown samples.

In the instrumental analysis, a number of remedial approaches are implemented in order to reduce the bias in the analysis. Background correction and wavelength selection are used to deal with spectral interferences caused by overlapping emission lines and matrix effects due to differences in sample composition, viscosity, or dissolved solids are overridden using matrix matching, internal standards or dilution protocols. The determination of Limits of Detection (LOD) and Limits of Quantification (LOQ) is an additional aspect used to define the analytical performance of ICP-OES because it determines the lowest concentration of rare earth elements (REEs), vanadium, and other trace elements that can be detected and measured reliably within the sample matrix.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction to the Geochemical Dataset

This chapter presents the elemental results obtained from twenty soil/regolith samples collected from weathered horizons of the Dhok Pathan Formation exposed in the Karak area. The analytical dataset includes selected critical mineral-related elements, economic mineral-related elements, and industrial mineral-related elements determined through ICP-OES analysis. The results are first presented in raw tabulated form, followed by descriptive statistical treatment and comparison with established geochemical background values. This structure allows the measured concentrations to be interpreted objectively before broader geological implications are discussed.

In the present thesis, the term "critical mineral-related elements" is used in a preliminary geochemical sense. It does not imply the discovery of an ore deposit or a resource-grade accumulation. Instead, the term refers to elements that are internationally recognized as strategically important for modern industry, clean-energy technologies, advanced manufacturing, and supply-chain security, including Li, Co, Ni, Cr, Ti, U, V, and Zr (International Energy Agency [IEA], 2023; U.S. Geological Survey [USGS], 2024).

4.2 Raw Geochemical Data

The elemental concentrations obtained from ICP-OES analysis of the twenty soil/regolith samples collected from the Dhok Pathan Formation are presented in Tables 3-5. The analytical results include major, trace, critical, economic, and industrial mineral-related elements. These data represent the laboratory measurements and form the basis for the interpretation presented in the following sections. Because of the large number of analyzed elements and samples, the raw analytical data have been divided into three tables to improve readability and presentation. Table 3 presents the results for Soil Samples 1–8,

Table 4 presents the results for Soil Samples 9–16, and Table 5 contains the results for Soil Samples 17–20. All elemental concentrations are reported in parts per million (ppm).

Table 3:ICP-OES elemental concentrations (ppm) of Soil Samples 1–8 collected from the Dhok Pathan Formation.

Element	Soil#1	Soil#2	Soil#3	Soil#4	Soil#5	Soil#6	Soil#7	Soil#8
Al	98606.00	71774.00	94646.00	94597.00	92515.00	94421.00	60895.00	99205.19
As	3.00	2.14	1.87	2.43	1.62	23.46	2.95	3.38
Ba	633.00	434.00	615.00	661.00	666.00	728.00	322.00	621.95
Ca	57118.00	27329.00	49255.00	52555.00	41973.00	32898.00	22523.00	57114.79
Co	7.83	7.56	7.45	6.78	6.04	5.50	6.57	7.56
Cr	49.41	48.43	49.76	45.12	43.57	38.49	42.83	46.00
Cu	8.41	10.82	9.49	7.76	6.66	6.84	9.76	9.21
Fe	30237.00	24637.00	28041.00	27566.00	22975.00	22322.00	22567.00	31447.00
K	17344.00	11141.00	17563.00	16869.00	17991.00	10806.00	11939.00	17086.40
Li	16.10	12.10	17.26	15.93	16.24	17.23	11.78	14.07
Mg	11842.00	5450.00	11432.00	11626.00	10003.00	9535.00	5396.00	11354.65
Mn	718.00	485.00	606.00	622.00	483.00	384.00	450.00	675.97
Na	15857.00	12104.00	15973.00	16362.00	18145.00	18103.00	9662.00	15421.37
Ni	21.30	25.93	24.56	22.28	22.19	21.25	24.48	21.34
P	335.00	413.00	399.00	369.00	333.00	347.00	334.00	349.49
Pb	7.68	183.00	8.25	12.42	15.39	18.89	202.00	8.22
Sr	338.00	244.00	307.00	344.00	344.00	341.00	197.00	341.93
Ti	2841.00	2631.00	2697.00	2496.00	2114.00	1809.00	2240.00	2904.89
U	2.84	1.23	2.67	2.51	2.19	2.38	1.15	2.91
V	83.62	77.20	75.98	72.12	62.17	58.41	70.68	77.88
Zn	39.90	40.25	47.23	36.42	35.28	35.41	34.37	39.39
Zr	7.88	4.75	6.48	7.28	4.84	4.60	4.30	7.13

Table 4:ICP-OES elemental concentrations (ppm) of Soil Samples 9–16 collected from the Dhok Pathan Formation.

Elements	Soil#9	Soil#10	Soil#11	Soil#12	Soil#13	Soil#14	Soil#15	Soil#16
Al	70805.69	98307.71	92495.20	91391.30	97227.41	62907.60	72464.82	91163.80
As	1.51	2.28	1.94	2.71	23.11	3.08	1.44	20.34
Ba	451.13	628.48	644.60	699.58	743.05	319.97	458.34	670.29
Ca	26178.67	51672.70	52258.22	40309.40	34474.93	23595.74	26164.28	33484.82
Co	6.82	8.35	6.88	6.24	5.95	7.17	7.08	6.10
Cr	51.94	53.06	48.01	40.35	40.23	40.20	43.97	42.21
Cu	12.08	8.68	7.09	6.28	7.60	9.04	11.84	6.07
Fe	25226.44	28769.05	27342.78	22752.14	21852.14	22406.34	25549.21	22966.10
K	10891.69	17771.51	16849.54	18726.64	10766.83	12123.72	11611.66	10607.01
Li	13.13	16.63	13.77	18.18	15.66	10.74	13.28	17.94
Mg	5525.30	10874.48	11242.50	10364.94	9562.95	5703.66	5382.32	9280.60
Mn	458.55	600.43	585.25	497.32	355.49	442.59	486.17	408.93
Na	11506.21	15369.13	17176.86	17791.67	17264.80	9831.98	11831.27	18825.77
Ni	26.89	24.01	20.53	23.44	20.84	22.85	25.67	22.24
P	387.32	391.47	342.02	358.60	326.84	345.05	404.25	324.03
Pb	180.64	7.49	14.13	16.00	16.49	203.50	183.33	19.23
Sr	237.43	321.00	334.17	364.60	319.38	190.69	252.70	326.58
Ti	2608.75	2741.97	2643.62	2109.00	1846.25	2228.23	2533.62	1837.01
U	1.31	2.73	2.47	2.22	2.35	1.28	1.42	2.16
V	83.32	79.68	73.44	65.09	61.96	69.47	81.17	56.67
Zn	43.88	50.38	34.88	34.08	34.16	36.32	42.09	35.23
Zr	5.27	6.99	7.03	5.03	4.37	4.01	4.64	4.02

Table 5: ICP-OES elemental concentrations (ppm) of Soil Samples 17–20 collected from the Dhok Pathan Formation.

Elements	Soil#17	Soil#18	Soil#19	Soil#20
Al	92182.98	92176.29	93083.99	59217.62
As	2.05	1.73	2.36	1.58
Ba	654.53	642.81	653.47	319.04
Ca	54272.34	48914.55	41495.37	21586.56
Co	7.63	8.08	5.81	5.72
Cr	45.31	52.47	43.51	43.51
Cu	7.39	10.57	5.77	9.49
Fe	26953.67	26820.47	23591.16	22735.55
K	16243.07	17754.12	18498.79	11403.16
Li	17.20	18.79	16.00	10.17
Mg	11517.12	11515.56	10224.53	5163.53
Mn	629.85	644.25	454.99	433.62
Na	16804.27	15453.71	18287.63	9906.78
Ni	21.36	22.70	23.97	24.05
P	355.97	420.59	310.02	346.76
Pb	11.97	9.01	12.73	207.27
Sr	329.40	287.66	350.03	197.62
Ti	2481.29	2539.18	2032.52	2269.82
U	2.58	2.64	2.09	1.07
V	74.68	83.30	57.98	75.91
Zn	39.07	51.84	34.39	33.64
Zr	6.57	7.06	4.96	3.75

The raw geochemical data presented in Tables 3–5 show variations in elemental concentrations among the analyzed samples. These variations are interpreted in the following sections by examining the distribution of individual elements, comparing the measured concentrations with published background values and previous studies, and evaluating their significance for the preliminary critical mineral potential of the Dhok Pathan Formation.

4.3 Critical minerals

The concentrations of selected critical mineral related elements by ICP-OES are shown in Figure 4.1. They are lithium (Li), cobalt (Co), chromium (Cr), nickel (Ni), titanium (Ti), uranium (U), vanadium (V) and zirconium (Zr). Geochemistry and critical mineral potential of Dhok Pathan Formation is preliminary assessed from the distribution of these elements.

The abundance of different elements in the analyzed samples in the context of the presence of critical minerals is presented in Figure 4.1. Titanium (Ti) is the most abundant element with concentration of 1809.00 to 2904.89 ppm. The second most abundant element is vanadium (V) at 56.67-83.62 ppm followed by chromium (Cr) with a range of 38.49-53.06 ppm. The concentration of the element Ni is in the range of 20.53 to 26.89 ppm, and the concentration of the element Li is in the range of 10.17 to 18.79 ppm. The concentrations of cobalt (Co) are comparatively low ranging from 5.50 ppm to 8.35 ppm, while the concentration of zirconium (Zr) and uranium (U) are the lowest, ranging from 3.75 ppm to 7.88 ppm and 1.07 ppm to 2.91 ppm, respectively.

The higher Ti concentration than the other analyzed critical elements could be a result of resistant detrital minerals weathering out of the source rocks and being concentrated in the fluvial sedimentary environment of the Dhok Pathan Formation (Boggs, 2014; Rollinson and Pease, 2021). Similarly, the presence of vanadium, chromium, nickel, lithium, cobalt, uranium and zirconium is indicative of them being dispersed in the weathered soil/regolith above the formation and not as discrete economic mineral deposits. The observed elemental distribution supports the concept of the fluvial sedimentary successions being heterogeneous, as lithologic, grain size and weathering intensity changes can affect elemental concentrations (Johnson et al., 1985; Burbank & Raynolds, 1988).

Several mineralization related elements were detected in the samples analyzed, but their values are not indicative of ore grade mineralization. Rather, these are initial geochemical enrichments and require additional study using detailed mineralogical characterization, petrographic analysis, increased sampling, and subsurface exploration. These types of investigations are needed to understanding the mode of occurrence and economic importance of these elements in the Dhok Pathan Formation (Hazen et al., 2013; Van Gosen et al., 2014).

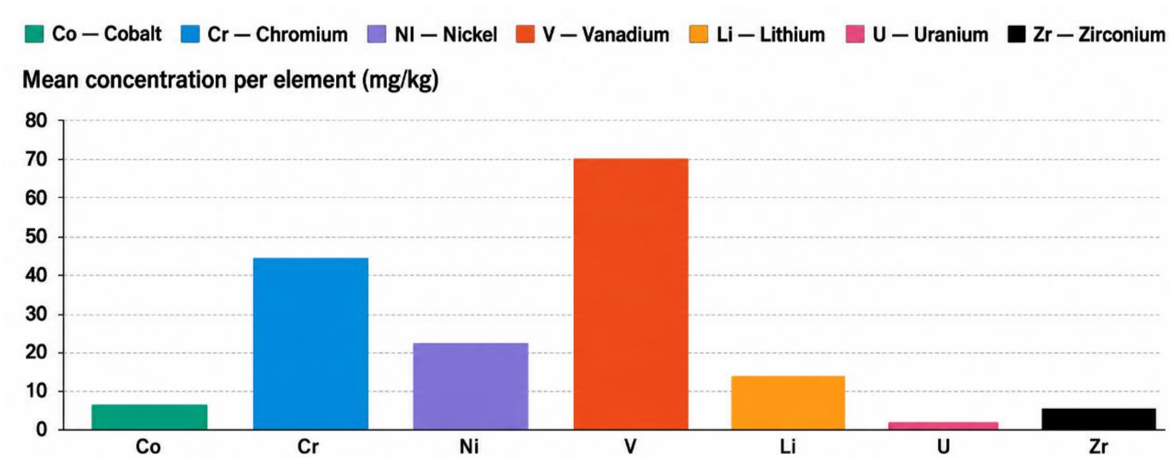

Figure 4.1: Critical Minerals

4.4 Economic Minerals

The geochemical analysis of the studied soil samples shows that Dhok Pathan Formation comprises a significant set of economically useful mineral-related elements, and Fe and Ti are the most salient constituents in the dataset. Iron shows concentrations ranging from 21852.14 to 31447.00 ppm with an average of 25337.85 ppm, whereas titanium ranges from 1809.00 to 2904.89 ppm with an average of 2380.21 ppm. These relatively higher concentrations indicate that iron-bearing and titaniferous detrital fractions continue to contribute to the fluvial sediments. This finding is aligned with the lithological nature of the Dhok Pathan Formation that is composed of fluvial sandstones, mudstones, siltstones, and conglomeratic horizons (minor) that have the potential to increase the retention of economically valuable elements (Shah, 2009; Ali et al., 2017; Pell et al., 2021).

Besides Fe and Ti, the findings indicate some significant abundances of other elements like Ba, Mn, Sr, which can also find some industrial value as per their host phases and occurrence mode. Barium ranges from 319.04 to 743.05 ppm with a mean value of 578.31 ppm, manganese from 355.49 to 718.00 ppm with a mean of 521.07 ppm, and strontium from 190.69 to 364.60 ppm with a mean of 298.41 ppm. The relative enrichment of these elements implies that the sediments could have been enriched by clay-rich, carbonate-linking, or other chemically reactive mineral fractions. It is already suggested in the first draft, that clay-rich and iron oxide-bearing horizons in the Dhok Pathan Formation have the potential to elevate the adsorption and retention of key elements, which validates the perception that these units of sediment serve as good geochemical traps to a variety of elements of economic interest (Ali et al., 2017; Pell et al., 2021).

There are also consistent concentrations of Cr, V, Ni, Co, Li and U in the dataset, which, though not as high as that of Fe and Ti, are of significance in a resource-evaluation sense. Chromium ranges from 38.49 to 53.06 ppm, vanadium from 56.67 to 83.62 ppm, nickel from 20.53 to 26.89 ppm, cobalt from 5.50 to 8.35 ppm, lithium from 10.17 to 18.79 ppm, and uranium from 1.07 to 2.91 ppm. These elements can be thought to be widely scattered through the sedimentary sequence as indicated by their relatively uniform distribution over the samples and not confined to an isolated horizon. The composition of such elemental suites in fluvial sedimentary systems is often affected by the varying grain-size, redox interfaces, clay adsorption, iron oxide association, and detrital heavy-mineral input, which are already mentioned in the geological and geochemical context of the thesis (Hazen et al., 2013; Borst et al., 2020; Zhang et al., 2023; Ali et al., 2017).

However, there is another trend followed by Pb and As, which are characterized by a significant local variation instead of complete uniform enrichment. The lead concentrations vary between 7.49 and 207.27 ppm with arsenic being between 1.44 and 23.46, meaning that the elements are not well distributed but just a few samples have the elements in high concentration. This is an indication of local geochemical anomalies, which may be associated with lithological horizons, adsorptive clay beds or secondary geochemical concentrations during diagenesis. Thus, despite the fact that the general geochemical data indicate that the Dhok Pathan Formation includes a number of elements that could be of economic value, the current results can be viewed as indicators of geochemical potential but not as the proven mineralization of an economic value. A more thorough analysis of the host minerals (mineralogical, petrographic, and phase-specific), the enrichment process, and the economic feasibility of these elements in the study region would need further investigation (Shah, 2009; Ali et al., 2017; Pell et al., 2021).

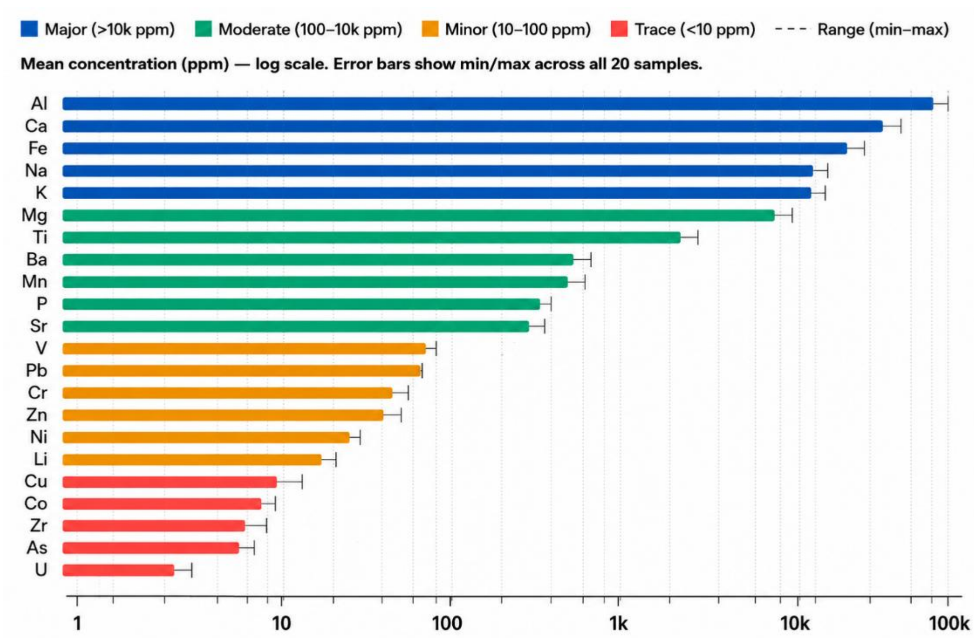

Figure 4.2: Economic Mineral Abundance

4.5 Industrial Minerals

The lab results show that the Dhok Pathan Formation has a powerful industrial-mineral-related constituent with the major component being aluminosilicate. High concentrations of Al (59,217.62-99,205.19 ppm, mean 86,004.18 ppm), together with substantial K (10,607.01-18,726.64 ppm, mean 14,699.36 ppm) and Na (9,662.00-18,825.77 ppm, mean 15,083.87 ppm), suggest the abundance of clay-rich and feldspathic sediment fractions in the analyzed samples. This observation aligns with the geological description of the Dhok Pathan Formation in the first draft where the unit is defined by fluvial sandstones, mudstones, siltstones, and subordinate conglomeratic horizons, and the intervals of clay-rich environment that may serve as key geochemical hosts and sedimentary traps (Shah, 2009; Khan et al., 2022; Pell et al., 2021). It is based on this that the study area may possess sediments that have potential to be used in clay-based industrial uses, especially in construction materials and analysis of raw-materials in ceramics.

A second important industrial-mineral signal is represented by the relatively high concentrations of Ca (21,586.56-57,118.00 ppm, mean 39,758.67 ppm) and Mg (5,163.53-11,842.00 ppm, mean 9,149.81 ppm), supported by notable Sr (190.69-364.60 ppm) and Ba (319.04-743.05 ppm) values. These geochemical features indicate that there might be carbonate-rich and potentially small evaporitic or chemically reacting mineral fractions in the sedimentary sequence. This interpretation is compatible with the larger stratigraphic context that has already been addressed in the thesis, in which the basin documents a shift in the environment to carbonate-evaporite conditions and in which the heterogeneity of lithologies is deemed significant in the distribution of minerals and the mineral composition of sediments (Kazmi and Jan, 1997; Najman, 2006; Shah, 2009). Thus, industrially speaking, the sediments studied might not only be of interest due to their aluminosilicate content, but also as a provider of carbonate bearing material that can be used in the production of lime, cement, filler and other related industrial applications.

The dataset reveals the measurable P (310.02-420.59 ppm), Fe (21,852.14-31,447.00 ppm) and Ti (1,809.00-2,904.89 ppm), which means that the industrial-mineral assemblage is not necessarily a clay-carbonate in its nature, but These components can exist as accessory phases in heavy minerals or iron oxides, or phosphate bearing horizons, which were emphasized in the first draft as critical factors with regard to geochemical retention and mineral concentration (Ali et al., 2017; Pell et al., 2021). But to be accurate when discussing the thesis, it is preferable to say that the current ICP-OES findings indicate industrial mineral potential and not established industrial mineral deposits since the elemental data cannot define the actual mineral species. Specific industrial minerals would have to be confirmed by mineralogical and petrographic analyses, specifically XRD, thin-section petrography, and fine-scale phase identification.

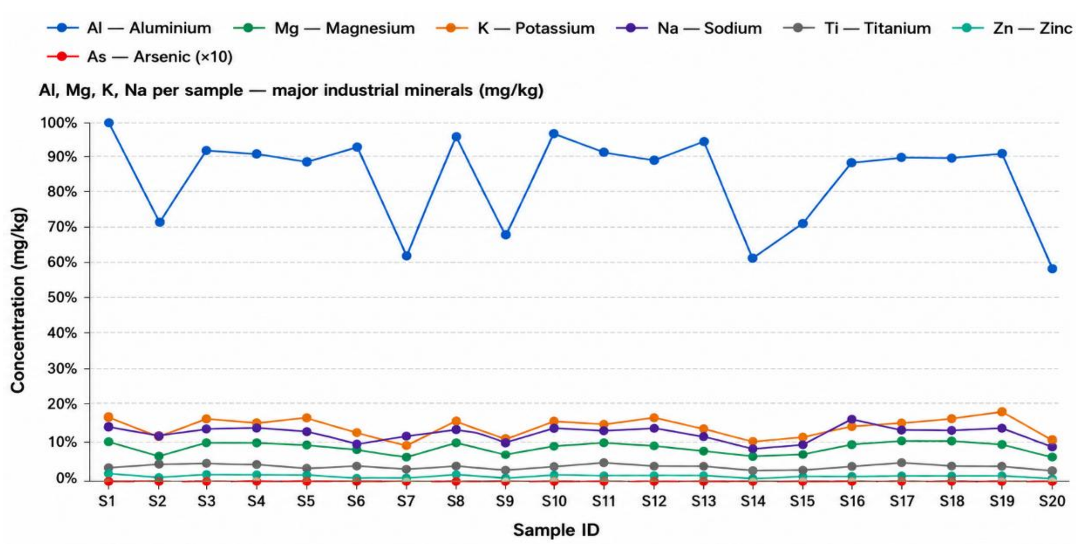

Figure 4.3: Industrial Mineral Abundance

4.6 Discussion

The geochemical data indicate that weathered soil/regolith samples from the Dhok Pathan Formation contain measurable concentrations of critical, economic, and industrial mineral-related elements. The elemental assemblage is dominated by Fe and Ti, with moderate V and Cr and lower Ni, Li, Co, U, and Zr, reflecting a mixed geochemical signature shaped by detrital input, lithological variation, weathering, clay-rich horizons, iron-oxide development, and possible post-depositional redistribution. These elements fall within the critical mineral categories recognized by the (USGS, 2024; IEA, 2021), and the geochemical interpretation of such multi-element datasets follows established analytical frameworks as outlined by (Rollinson, 1993; Rollinson and Pease, 2021).

The Dhok Pathan Formation is a fluvial unit of the Siwalik Group comprising sandstone, mudstone, siltstone, clay-rich intervals, and local conglomeratic beds. The stratigraphic position and fluvial character of the Siwalik formations have been well documented by (Pilgrim, 1913; Johnson et al., 1985; Zaheer et al., 2022). This lithological heterogeneity controls the distribution of trace and critical elements within the succession, as sedimentary facies exert a primary influence on elemental hosting, a principle discussed by (Tucker, 2001; Rollinson, 1993). Hazen et al., (2013) noted that clay minerals play a significant role in trace element retention through adsorption and ion exchange, while Borst et al., (2020) demonstrated that regolith-hosted clay deposits can absorb rare earth and associated elements. The observed geochemical patterns in this study are therefore best interpreted in terms of sedimentary facies, weathering state, and mineral-host controls rather than as direct evidence of economic mineralization.

Measured concentrations are generally within background to moderately elevated ranges. Ti and Fe are the most abundant elements but do not confirm economic mineralization. (Rollinson, 1993) provided reference frameworks for comparing elemental concentrations against crustal and shale averages, and the values obtained in this study remain within such background ranges. Rainoldi et al., (2024) discussed the association of vanadium with sediment-hosted deposits and Fe-oxide phases, which is consistent with the moderate V concentrations observed here. (Brookins, 1988) described the Eh–pH behavior of redox-sensitive elements such as V and Cr, which may help explain their moderate retention in the weathered horizons of the Dhok Pathan Formation. Ni, Co, Li, U, and Zr occur at low concentrations without significant enrichment.

Uranium values range from 1.07 to 2.91 ppm, which are low to near background. Hall et al., (2023) described the characteristics of sandstone-hosted uranium deposits, and the concentrations recorded in this study fall well below the thresholds associated with such mineralization. (Ullah et al., 2013; Khan et al., 2022) reported on uranium occurrence in the Karak region, and the values obtained here are consistent with their observations of low-level, background uranium presence in the area. Low Zr values indicate limited zircon-rich heavy mineral concentration, while measurable but modest Li values are best attributed to clay-rich or aluminosilicate-bearing weathered material until confirmed by mineralogical analysis, as Hazen et al., (2013) demonstrated that clay minerals serve as important hosts for such elements.

The study carries several significant implications at a preliminary geological level. First, it provides baseline geochemical data for the Dhok Pathan Formation in the Karak area, where direct critical mineral-related geochemical investigations have not been previously reported. (Ali et al., 2017; IEA, 2023) have emphasized the global need for expanded geochemical baseline studies in under-explored geological terrains, and the present work contributes to that objective. Second, the consistent occurrence of Ti, V, Cr, Ni, Li, Co, U, and Zr confirms that the formation is not geochemically sterile. Third, higher Fe and Ti concentrations warrant future investigation of Fe–Ti-bearing phases and heavy mineral contributions. Fourth, the association of trace elements with weathered fine-grained horizons should be tested through facies-specific sampling and mineralogical confirmation. Pell et al., (2021) highlighted the importance of integrated analytical approaches in evaluating the mineral potential of under-characterized geological units, which supports the need for such follow-up work.

The dataset comprises twenty soil/regolith samples collected from weathered surface horizons, providing a preliminary but not exhaustive representation that may reflect both primary composition and secondary weathering effects. (Tucker, 2001) noted that weathering can significantly modify the original geochemical signature of sedimentary rocks. ICP-OES yields bulk elemental concentrations without identifying mineral phases, as discussed by (Rollinson, 1993); hence the host minerals of Ti, V, Cr, Ni, Li, Co, U, Zr, and Fe remain uncertain. No sequential extraction, XRD, SEM-EDS, thin-section petrography, or heavy mineral separation was conducted, and resource-level or ore-grade claims are therefore not warranted.

Future research should priorities detailed sampling. (Najman, 2006) discussed provenance-based sampling strategies in the Himalayan sedimentary basins, which provide a useful methodological template for such work. This should be supplemented by XRD, SEM-EDS, petrographic analysis, heavy mineral separation, and sequential extraction to resolve mineral hosts and elemental partitioning, following the analytical protocols described by (Rollinson and Pease, 2021). GIS-based spatial geochemical mapping should also be undertaken to assess whether elemental anomalies are laterally continuous or confined to isolated weathered horizons. (Sabins, 1999; Pour and Hashim, 2015) demonstrated the utility of remote sensing and spatial mapping techniques in mineral exploration contexts, and similar approaches would benefit future investigations of the Dhok Pathan Formation.

In summary, the Dhok Pathan Formation contains measurable critical mineral-related elements, particularly Ti, V, Cr, Ni, Li, Co, U, and Zr, but concentrations are generally insufficient to define ore-grade mineralization. The principal contribution of this thesis is the establishment of a baseline geochemical framework for future critical mineral assessment of the formation in the Karak area, contributing to the broader global effort for critical mineral evaluation.

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

Twenty soil samples from the Dhok Pathan Formation in the Karak area yielded measurable concentrations of critical minerals Through ICP-OES analysis. The following critical minerals were obtained in the data set Ti, V, Cr, Ni, Li, Co, Zr, U.

Critical minerals present in sample suite having high ppm values; Ti, from 1809.00 to 2904.89 ppm. Vanadium ranges from 56.67 to 83.62 ppm, Cr from 38.49 to 53.06 ppm, Ni from 20.53 to 26.89 ppm, Li from 10.17 to 18.79 ppm, Co from 5.50 to 8.35 ppm, Zr from 3.75 to 7.88 ppm, and U from 1.07 to 2.91 ppm. The results indicate that the sample material contains measurable levels of some important elements associated with critical minerals, of which the concentration of Ti, V, and Cr are comparatively higher than the other elements in the group of critical mineral-related elements analyzed.

Major elements related to the economy are Fe and Ti, which are mostly found in economic minerals. Iron ranges from 21852.14 to 31447.00 ppm, while Ti ranges from 1809.00 to 2904.89 ppm. It is seen that both Fe and Ti are the most abundantly economic mineral related elements in the analyzed data set with the values listed above. The elemental data cannot identify the mineral phases that contain these elements.

The contents of Al, K, Na, Ca, Mg, Fe and Ti which are related to the industry of minerals are also analyzed within the samples. The presence suggests the sampled weathered material contains significant amounts of major element constituents that are generally associated with aluminosilicate, feldspathic, carbonate related and Fe-Ti bearing materials.

5.2 Recommendations

Further sampling needs to be made from well-defined lithological units of the Dhok Pathan Formation, such as sandstone, mudstone, siltstone, clay-rich horizons, and weathered soil horizons, to examine the elemental variations between different lithologies. More samples are needed in the different measured sections at Takht-e-Nasrati and Shanawa Gudikhel to investigate the variation in elements concentrations laterally and vertically. Scripted mineralogical analysis should be performed by X-ray diffraction analysis, SEM – EDS, thin-section petrography and heavy mineral analysis to determine the mineral phases of Ti, Fe, V, Cr, Ni, Li, Co, Zr and U concentrations. In future work, selected elements should be tested to determine if they associate with either fine-grained material or clay-rich material by conducting grain-size analysis and clay mineral studies. Spatial geochemical mapping should be done to determine if any specific area of the Dhok Pathan Formation is relatively enriched in critical elements, economic elements or industrial mineral elements related to production.

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