

**GEOCHEMICAL ASSESSMENT OF MANSEHRA
GRANITE AND ASSOCIATED PEGMATITE VEINS,
MANSEHRA, KHYBER PAKHTUNKHWA, PAKISTAN**



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09-262242-014

Bahria University Islamabad

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AND ASSOCIATED PEGMATITE VEINS, MANSEHRA,
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DEDICATION

“This thesis is dedicated to my parents”

ACKNOWLEDGEMENT

All praise be to Allah Almighty, who provided me with the courage, determination and motivation to complete this work. These gifts have been a great source of inspiration to me.

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ABSTRACT

The Mansehra Granite of the Lesser Himalaya, northern Pakistan, represents a peraluminous S-type granitoid emplaced during Cambro-Ordovician crustal magmatism and is spatially associated with pegmatite veins formed during late-stage magmatic evolution. Despite its well-established petrogenetic framework, the whole-rock geochemistry and distribution of critical and associated trace elements within the granite-pegmatite system have not been systematically evaluated. This study assesses the geochemical composition and critical mineral potential of the Mansehra Granite and associated pegmatite veins using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Twenty representative samples, comprising fourteen granite (MG-1 to MG-12) and six pegmatite samples (P-1 to P-6), were collected from Mansehra area. The samples were prepared using aqua regia digestion, and analyzed for major, trace, critical, and rare earth elements. The results are interpreted as aqua-regia extractable concentrations rather than total-rock abundances because aqua regia does not completely dissolve refractory silicate minerals and resistant accessory phases. The results indicate that critical-element enrichment is heterogeneous and primarily concentrated within pegmatites (P-4 to P-6). Pegmatite samples exhibit comparatively higher concentrations of Li, Be, Nb, Ge, Sn, W, Sb, U, and rare earth elements than the host granite. Correlation patterns and normalized geochemical signatures further indicate that accessory mineral fractionation and incompatible-element concentration exerted the primary control on trace-element distribution. Although several pegmatite samples display localized enrichment relative to the host granite, the analytical dataset does not demonstrate the presence of an economically viable rare-metal deposit, and the inferred occurrence of accessory minerals is based solely on geochemical signatures rather than direct mineralogical evidence. Future investigations integrating petrography, scanning electron microscopy (SEM), electron probe microanalysis (EPMA), or laser ablation ICP-MS (LA-ICP-MS) are recommended to verify the mineral hosts of critical elements and further constrain the metallogenic potential of the Mansehra Granite and its associated pegmatite veins.

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LIST OF ABBREVIATIONS

ADL	-	Above Detection Limit
BDL	-	Below Detection Limit
EU	-	European Union
GPS	-	Global Positioning System
HREE	-	Heavy Rare Earth Elements
LREE	-	Light Rare Earth Elements
Ma	-	Mega-annum
MBT	-	Main Boundary Thrust
MCT	-	Main Central Thrust
MG-1 to MG-14	-	Mansehra Granite samples 1 to 14
MGC	-	Mansehra Granitic Complex
MKT	-	Main Karakoram Thrust
MMT	-	Main Mantle Thrust
P-1 to P-6	-	Pegmatite samples 1 to 6
PGE/PGEs	-	Platinum Group Elements
Ppm	-	Parts per million
REE/REEs	-	Rare Earth Elements
UCC	-	Upper Continental Crust
USGS	-	United States Geological Survey

CHAPTER 1

INTRODUCTION

1.1 General Statement

The rapid change in the world energy and technological environment has resulted in an unprecedented need in critical minerals and especially lithium (Li), tantalum (Ta), niobium (Nb), rare earth elements (REE), cesium (Cs), tin (Sn), and tungsten (W). These factors are classified as critical since they are essential to contemporary technologies and are prone to breach of the supply chain through geological concentration, geopolitical control, or low substitution ability at the same time (Lehmann, 2021). The use of Lithium-ion batteries in electric vehicle and grid-scale storage systems, rare earth elements in high strength permanent magnets in wind turbines and electric motors, and tantalum and niobium in capacitors, superalloys, and novel aerospace alloys are fundamental components of lithium-ion batteries. Geological mechanisms that concentrate these elements have a close relationship with magmatic differentiation and crustal evolution. Li, Rb, Cs, Nb, Ta, and REE are some of the elements that are incompatible and are likely to become silicate melts instead of becoming initial crystalline forms during partial melting and fractional crystallization (Winter, 2010). The elements accumulate in residual melts with an increasing degree of magmatic systems and especially in highly fractionated granitic magmas. Rare earth element (REE) mineralization is commonly associated with alkaline granites, post-collisional granitic systems, carbonatites, and their related pegmatites, which constitute some of the most important geological settings for REE enrichment worldwide (Cerny and Ercit, 2005; London, 2018).

Granite is a felsic intrusive igneous rock composed predominantly of quartz and feldspar. Granitic magmas may originate through a variety of petrogenetic processes, including partial melting of continental crust, differentiation of mantle-derived magmas, or interaction between crustal and mantle sources under diverse tectonic settings. Granites can be subdivided into several genetic types, including S-type, I-type, A-type, and M-type granites, each bearing distinct source characteristics and magmatic evolution histories (Frost et al., 2001). Convergent tectonic environments enhance crustal thickening, which heightens geothermal gradients and melting of metasedimentary protoliths to form S-type granitic magmas with aluminum being saturated and containing muscovite (Chappell and White, 2001). I-type granites are distinguished from the S-type granites due to their peraluminous chemistry, high initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and high trace element concentrations are suggestive of sedimentary source components (Chappell and White, 2001). Minerals such as plagioclase, K-feldspar, biotite, and hornblende remove the elements that are compatible with magma and leave the incompatible elements in the magma. This systematic geochemical trend, such as Rb and REE enrichment, Sr and Ba depletion, as well as negative Eu anomalies caused by plagioclase fractionation (Winter, 2010; Wu et al., 2017). The extent of magmatic differentiation is hence a major factor that would regulate the ability to be metallogenic in the granitic systems.

The extreme products of this differentiation continuum are the pegmatites. They are very coarse-grained igneous rocks which form out of volatile rich residual melts formed out of granitic magmas. The volatiles (H_2O , F, B, and P) lower the melting viscosity, elevate the mobility of the elements, and assist the quick development of crystals, which results in typical pegmatitic textures (London, 2018). The relationship between peraluminous granites and lithium-cesium-tantalum (LCT) pegmatites have been studied widely to have a genetic connection with collisional orogenic systems all around the world (Cerny and Ercit, 2005). Cerny and Ercit (2005) state that LCT pegmatites are the derivatives of S-type granitic melts that are highly fractionated, and they are enriched with Li, Cs, Ta, Nb, Sn, and the REE. Some of the minerals that may occur in such pegmatites include spodumene, lepidolite, petalite and columbite-tantalite, which are sources of vital metals. The fractional crystallization process is extremely intensive, the magma residence time is intensive, and the volatile is volatile saturation, which enhance and enrich incompatible

elements in the end melt fractions in the pegmatites (London, 2018). Geochemical fertility signals like high Rb/Sr ratios, low K/Rb ratios, fractionation of Nb/Ta, and strongly fractionated REE patterns have thus become fundamental in evaluating the possibility of rare metal in granitoid systems (Wu et al., 2017).

The Himalayan orogen is a very favorable tectonic setting in the context of crustal anatexis and granitoid magmatism on a global geological scale. The mountain belt of the Himalayas was formed as the Indian plate collided the Eurasian plate causing crustal shortening, crustal thickening, and mass thrusting. The Hazara region of north Pakistan is located in the Lesser Himalayan realm and belongs to the Himalayan fold-and-thrust region. Extensive geological studies by Calkins et al (1975) recorded stratigraphy and structural pattern of Hazara Basin showing the existence of major thrust systems and folded sedimentary sequences. The Main Boundary Thrust (MBT) is a major tectonic boundary that marks the differences between the Lesser Himalaya and the Sub-Himalayan zone and indicates much crustal shortening in case of Himalayan convergence (Calkins et al., 1975).

Mansehra city is located in this structurally complicated tectonic regime and within the Mansehra Granitic Complex (MGC), an intrusive body (prominent) that has been emplaced into Precambrian metasedimentary rocks (Calkins et al., 1975; Kazmi and Jan, 1997; Sajid et al., 2018) (Fig. 1.1). The intrusive relationships of the granite found in the Hazara domain were initially described by Calkins et al. (1975) in the form of regional mapping. Later geochronological studies by Sajid et al. (2018) restricted the granite to an Early Paleozoic date using the U-Pb zircon dating technique and explained the granite as a high-K calc-alkaline to peraluminous intrusion formed by the crustal melting processes. The geochemical studies indicated the enrichment of the light rare Earth elements and negative Eu deviations, which suggested the presence of plagioclase fractionation and high magmatic differentiation (Sajid et al., 2018). The S-type affinity of the Mansehra Granite was validated by further petrological studies where Naeem et al. (2021) used the indices of aluminum saturation and mineral assemblages that align with sources of metasedimentary rocks. The presence of pegmatitic veins that are spatially related to the granite indicates about the end-stage of magmatic development and might have concentrated the incompatible elements. In addition, Mehmood et al. (2022) reported enrichment of

rare earth elements in granitic and pegmatitic rocks from the study area, indicating late-stage concentration of incompatible trace elements during magmatic evolution.

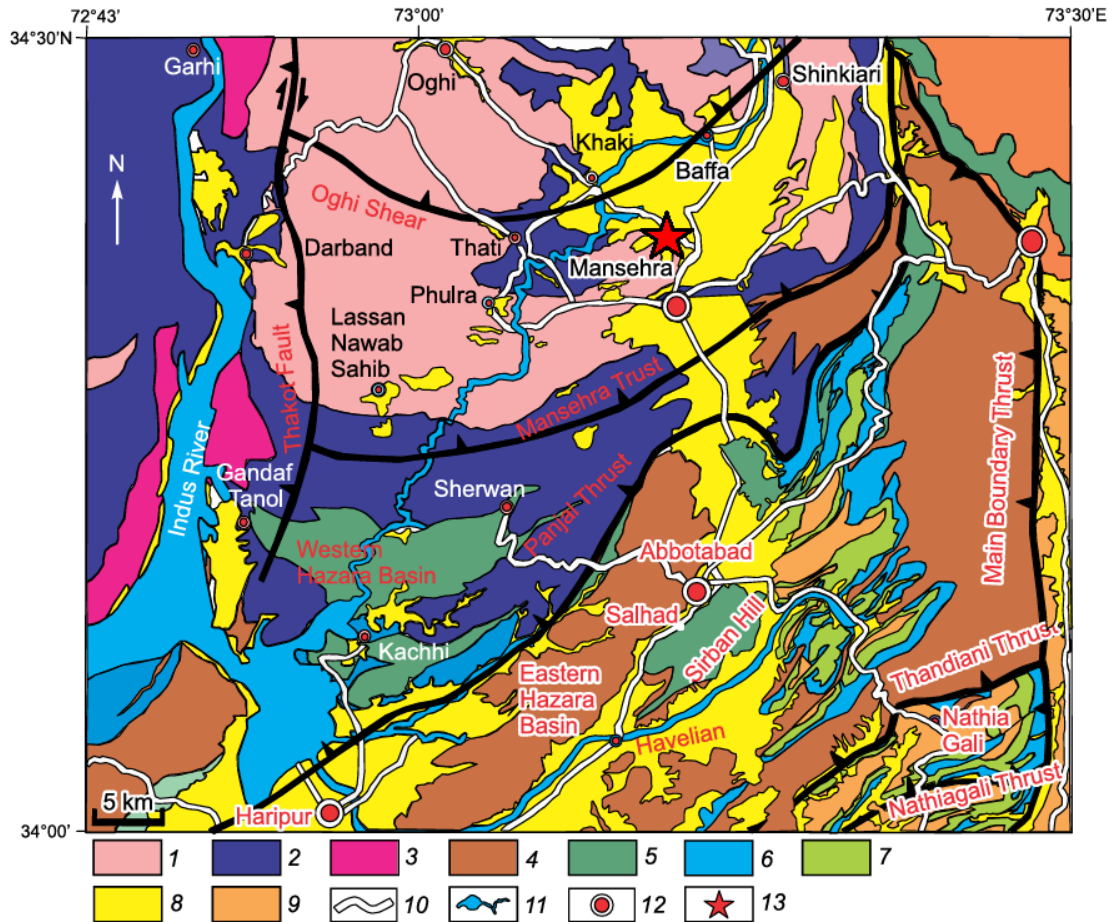


Figure 1.1 Geological Map of the Hazara Basin, 1- Cambrian-Ordovician Mansehra Granite, 2- Meso-Neoproterozoic Tanawal Formation, 3- Paleoproterozoic Metamorphic Rocks, 4- Mesoproterozoic Hazara Formation, 5- Neoproterozoic Cambrian, 6- Jurassic, 7- Cretaceous, 8- Quaternary, 9- Paleogene, 10- Road, 11- River, Reservoir, 12- City, Town, Village, 13- Study Area. (Iqbal et al., 2026)

This is in the face of these defined petrogenetic features, which have seen systematic assessment of the rare-metal fertility parameters of the Mansehra Granite and the related pegmatites being under-estimated. Considering that peraluminous granites that occur in collisional tectonic settings are often the setting of globally significant rare-metal systems (Cerny and Ercit, 2005; Lehmann, 2021), the Mansehra Granite is an area of geological possibility of critical minerals exploration. In order to establish whether this system has geochemical similarity to the fertile LCT-type

granite-pegmatite provinces, the analysis of trace and rare earth elements needs to be made precise.

1.2 Literature Review

Calkins et al. (1975) were the first to systematically determine the geological framework of the Hazara region with their regional mapping of the southern Himalaya defining the stratigraphic succession, structural architecture and emplacement associations of the Mansehra Granite in Precambrian metasedimentary sequences. Even though this initial study offered significant lithostratigraphic and structural constraints, it preceded the modern trace element and rare earth analytical methods and as such, was not used to assess the metallogenic potential of the granitoid system. Further research gradually enhanced the petrogenetic knowledge of the Mansehra Granitic Complex (MGC) but a committed evaluation of its vital mineral potential is deficient.

U-Pb zircon geochronology and whole-rock geochemistry of peraluminous granitoids in the Mansehra area was undertaken by Sajid et al. (2018), implicating magmatism in northern Gondwanan margin tectonics. The Geochemical dataset showed that they had high-K calc-alkaline affinity, light rare earth elements (LREE) enrichment and strong negative Eu anomalies that were attributed to fractionation of plagioclases and crustal melting. These characteristics are typical of developed S-type granites that are created in collisional tectonic circumstances (Chappell and White, 2001). This framework was extended by Mehmood et al. (2021) who reported mineralogical and geochemical indicators that are in line with peraluminous signatures ($A/CNK > 1$) which further support the interpretation of crustal anatexis and fractional crystallization as the key evolutionary mechanisms. Zafar et al. (2019) also supported crustal derivation by xenolith studies that indicated that there was metasedimentary material assimilation, which gave a textural and geochemical evidence of the melt-host interaction during emplacement. According to Mehmood et al. (2022), REE enrichment in granitic and pegmatitic phases of the MGC was observed by ICP-MS, and rare element concentration was also possible. Also, Ahmed

et al. (2014) detected quantifiable levels of thorium in the Mansehra Granite, which gave an indirect confirmation of the existence of REE-bearing accessory minerals, like monazite.

Although the petrogenetic system of the Mansehra Granite can be defined through these studies together, they are lacking in the systematic examination of the rare metal metallogenicity. The literature mainly focuses on setting of the tectonics, magma forming and overall geochemistry but not on the measurements of incompatible elements enrichment in the pegmatitic differentiates quantitatively. This difference is extremely important, as throughout the world, major economically important deposits of lithium, tantalum, niobium, and REE are often found in late-stage pegmatites that are formed out of highly fractionated peraluminous granite (Cerny and Ercit, 2005; London, 2018).

The system of metallogenic frameworks of the world in the rare-metal granites offers a more or less comparative perspective in which the system of Mansehra can be considered. In agreement with other researchers, Cerny and Ercit (2005) defined a general nomenclature of granitic pegmatites into LCT (Li-Cs-Ta) and NYF (Nb-Y-F) groups and interpreted the geochemical trends as indicating geochemical signature of tectonic environment and source. LCT pegmatites are commonly found in S-type, peraluminous granites that are created when two continents collide and NYF pegmatites are usually found in A-type granites that were formed in extensional environments. Since the MGC has been documented as peraluminous and crustally-derived (Mehmood et al., 2021; Sajid et al., 2018), the Mansehra pegmatites would be more congruent to the LCT metallogenic model. Nevertheless, systematic trace element discrimination has not so far been used to test this hypothesis.

Adequacy of such systems in economy is illustrated by international case studies. The Tanco pegmatite in Manitoba, Canada, is a classic LCT-type deposit that is rich in lithium, cesium, and tantalum, which was created following a very high degree of fractional crystallization of a peraluminous granitic melt (Cerny and Ercit, 2005). Likewise, the Greenbushes deposit in Western Australia (the world's largest hard-rock lithium deposit) is a genetically related deposit of strikingly evolved granitic pegmatites of crustal anatexis (London, 2018). Neoproterozoic S-type granites that have formed in the collisional orogenic environment are associated with

spodumene-bearing pegmatites in the Aracuai province of Brazil (London, 2018). All these instances would show crustal thickening, incomplete melting of metasedimentary rocks, and extended fractional crystallization are common characteristics across the large rare-metal granite provinces.

Highly fractionated peraluminous granites are widely studied in South China with regard to rare metal mineralization. Wu et al. (2017) established that enrichment of Rb, Cs, Li, Nb, Ta, and REE are associated with an increase in the levels of differentiation, higher Rb/Sr ratios, Sr and Ba depletion, and negative Eu anomalies. These geochemical occurrences are diagnostic evidence of sophisticated magmatic transformation and uncommon-metal prospects. Notably, comparable negative Eu anomalies and LREE enrichment patterns have also been found in the Mansehra Granite (Sajid et al., 2018), which means that the similarity in the evolutionary trends may exist, but detailed incompatible element quantification cannot support this comparison.

According to Lehmann (2021), the rare-metal granites in general are the product of highly evolved peraluminous melts that are created during the collision of continents with each other, especially where volatile saturation allows the exsolution of fluids and the element separation into later melts. The effect of this process is a concentration of Li, Sn, W, Nb, and Ta to residual phases. Such processes are facilitated by the Himalayan orogen that is crustally thickened and anatexitic (Winter, 2010). An enrichment of the rare elements was also tracked in Himalayan leucogranites elsewhere supporting the metallogenic applicability of collisional S-type systems.

An analytical comparison of the Mansehra Granitic Complex reveals that the complex portrays a number of characteristics of rare-metal fertile granites, which include, peraluminous chemistry, crustal anatexis, LREE enhancing, and the negative Eu anomalies. The Mansehra pegmatites, however, are not subject to systematic exploration-scale geochemical characterization as have other systems of exploitation around the world, e.g. Tanco or Greenbushes. There is scanty data on Li, Cs, Ta, Nb, and detailed distribution of REE in the pegmatitic veins per se. Moreover, geochemical indices of fractionation including Rb/Sr ratios, K/Rb ratios as well as

trace element discrimination diagrams have not been fully utilized to assess metallogenic fertility.

Therefore, although regional investigations indicate the petrogenetic adequacy of the Mansehra Granite in enriching rare elements, there still exists a major knowledge gap on the extent, distribution, and economic importance of the critical minerals in the related pegmatitic bodies. There are no systematic sets of incompatible elements, which does not allow us to make a strong correlation with known global rare-metal granite provinces. To bridge this gap, geochemical analysis needs to be specifically addressed such that critical elements abundance and fractionation pattern as well as discrimination parameters are addressed.

International research indicates that peraluminous and crustal, highly fractionated granites that are deposited in collision tectonic environments favor rare-metal pegmatites (Cerny and Ercit, 2005; London, 2018; Lehmann, 2021). Despite the close petrogenetic characteristics in the Mansehra Granitic Complex, the metallogenicity of the complex has not been carefully studied. Extensive geochemical exploration is thus needed on whether it is a fertile rare-metal system or a mere petrogenetic analogue in the absence of any economic mineralization potential.

1.3 Problem Statement

No study to date has systematically quantified the concentrations of critical minerals within the Mansehra Granite and its pegmatitic veins. Without such data, evaluation of mineral resource potential for critical minerals in this sector remains speculative.

1.4 Objectives

1. To analyze the geochemical composition of Mansehra Granite.
2. To determine the abundance of critical minerals in Mansehra Granite and its associated pegmatite veins.

1.5 Research Gaps

Although broad geochemistry, age, isotopic and mineralogy and petrology of the Mansehra Granite and the rocks that surround it have been extensively undertaken, detailed quantitative geochemical studies that give detailed data on critical mineral concentrations within the Mansehra Granite and its pegmatites have not been undertaken in detail.

1.6 Expected Outcomes

1. Geochemical estimation of the critical minerals in Mansehra Granite and its associated pegmatitic veins.
2. Recommendations for future resource evaluation and development strategies in the Mansehra area.

CHAPTER 2

GEOLOGY AND TECTONICS

2.1 Regional Geology and Tectonics of the Investigated Area

The Himalayan orogenic system is the most important orogeny in the history of Earth, which is the leading regional geology of northern Pakistan. The Himalayan belt was formed due to the movement to the north and the subsequent collision of the Indian plate with the Eurasian plate and this process began in the Late Cretaceous to Paleogene and is still going on (Gansser, 1964; Searle et al., 1987). This intercontinental collision caused crustal shortening, crustal thickening, metamorphism, magmatism and formation of a complicated system of thrust faults and fold structures. The Mansehra district of Khyber Pakhtunkhwa occupies a strategically significant area of the northwestern Himalaya and gives a strategically important window on to the tectonic history of the northern edge of the Indian plate (Kazmi and Jan, 1997; Bossart and Ottiger, 1989).

The Himalayan orogeny is further divided into major tectonostratigraphic zones which are divided by major fault systems. These extend southward to northwards, as the Sub-Himalaya (Siwalik zone), the Lesser Himalaya, the Higher Himalaya (Kazmi and Jan, 1997). The Hazara area is mostly within the Lesser Himalayan area with the Main Boundary Thrust (MBT) on the south and the Main Central Thrust (MCT) to the north. The MBT itself is a crustal scale level thrust fault that involves the overriding of older and more metamorphosed Lesser Himalayan rocks above the younger deposits of the foreland basin (Sub-Himalaya) (Calkins et al., 1975; Kazmi and Jan, 1997). The Main Central Thrust (MCT) is one of the principal tectonic structures of the Himalayan orogen and marks the boundary along which the Higher Himalayan Crystalline Sequence has been thrust southward over the metasedimentary and sedimentary rocks of the Lesser Himalaya. The MCT records

significant crustal shortening and tectonic transport associated with the India–Eurasia continental collision (Searle et al., 1987).

The tectonic evolution of the Hazara region represents pre-Himalayan deformations as well as the Himalayan deformations. In the Paleozoic, the crust in the north of the Gondwana resulted in granitoid magmatism and crustal development. According to U-Pb zircon geochronology, the Mansehra Granitic Complex was overruling the Early Paleozoic, and the magmatic activity in the area is thought to have pre-dated the Cenozoic Himalayan collision of the Late Ordovician (Sajid et al., 2018). The granite intruded the Precambrian metasedimentary rocks and presumably had been formed by some melting of crustal sources during tectonic conditions related to the initial convergent and intracontinental movements (Sajid et al., 2018). Naeem et al. (2021) also initiates a petrogenetic interpretation, which derives protoliths that are metasedimentary, such as peraluminous chemistry and mineralogical evidence.

Mansehra city is structurally important in the Lesser Himalayan zone in this regional tectonic system. Mansehra Granitic Complex (MGC) is highly exposed in and around Mansehra and over intruding metasedimentary rocks that comprise the Tanawal Formation (Calkins et al., 1975). The relationships in the field reveal that the granite is intrusive, and the contacts are sharp and there has been contact metamorphism on the adjacent rocks. The granite is generally medium- to coarse-grained and mineralogically constituted of quartz, K-feldspar, plagioclase, biotite, and muscovite, and has accessory minerals like zircon, monazite, and apatite (Sajid et al., 2018; Mehmood et al., 2021). Its S-type affinity is confirmed by the presence of muscovite and aluminum saturation ($A/CNK > 1$) which is similar to crustal anatexis (Chappell and White, 2001).

The wider geodynamic context of Mansehra area is the fact that it is in the northwestern Himalayan syntaxis in which there has been complex interrelation of thrust systems, hereditary basement structures, and magmatic intrusions to provide the current geological architecture. Their presence of Precambrian metasedimentary rocks, Paleozoic granitoids and Cenozoic thrust faults suggests a complex polyphase tectonic history of crustal growth, magmatic emplacement, and compressional reactivation. The structural complexity has some implications on the fluid migration,

metamorphic overprinting, and local mineralization in the granitoid bodies (Bossart and Ottiger, 1989; Kazmi and Jan, 1997).

2.2 Tectonic Framework

The Hazara-Mansehra area is represented by the northwestern extension of the Himalayan orogenic belt which formed due to the convergence and subsequent collision of the Indian and Eurasian plates after the Neo-Tethys Ocean had closed in the Cenozoic (Gansser, 1964; Searle et al., 1987). It was a collision between the continents, which resulted in extensive crustal shortening, lithospheric thickening, regional metamorphism, and the deposition of great thrust sheets in the area of northern Pakistan. The Hazara area takes a structurally sensitive location in the Lesser Himalayan realm, on the interface of key discontinuities at crustal scales, and is marked by imbricate thrusting, syntaxial bending and localized ductile shear deformation (Kazmi and Jan, 1997).

The tectonic architecture of the region is characterized by a series of large structures comprising of the Main Karakoram Thrust (MKT), Main Mantle Thrust (MMT), Main Boundary Thrust (MBT), the Hazara-Kashmir Syntaxis and minor thrusts and shear structures like Hazara Thrust and Oghi Shear Zone (Fig. 2.1). All of these tectonic elements document successive deformational phases that are related to oceanic subduction, arc-continent collisions, and continuous intracontinental shortening.

2.2.1 Main Karakoram Thrust (MKT)

The Main Karakoram Thrust is the northern major tectonic boundary in reference to the northwestern Himalaya. It lies between the Karakoram block and Kohistan-Ladakh island arc complex and can be assumed to be a suture left in the closing of the Paleo-Tethys Ocean before the Himalayan collision (Searle, 1996; Kazmi and Jan, 1997). The MKT is older than the Main Mantle Thrust and captures

previous tectonic accretion events of continental crust and arc terranes of the southern Eurasian margin.

Though MKT lies to the north of the Hazara-Mansehra region, it is also regionally important in that it establishes the architecture of the north of the tectonic architecture of the larger orogenic system in which the MMT and MBT evolved. Grouping of plates into a structural stacking of Karakoram, Kohistan and Indian plates indicates the progressive southward accretion and collision between the Mesozoic and Cenozoic time (Searle, 1996).

2.2.2 Main Mantle Thrust (MMT)

The Kohistan-Ladakh island arc junction with the Indian continental plate is the Main Mantle Thrust which is the western extension of the Indus Suture Zone (Searle et al., 1987). It formed in the Late Cretaceous to Paleogene due to subduction of the Neo-Tethyan oceanic lithosphere and a resultant collision of the continent-arc.

The MMT compares high grade arc and ultramafic rock of the Kohistan terrane with a lower grade metasedimentary rock of the Indian plate (Kazmi and Jan, 1997). High strain mylonitic zones, tectonic melanges, and both ductile and brittle deformations are the characteristics of the structure. The MMT sets the northern edge of the Indian plate crust in Pakistan though it is found to the north of Mansehra and is known to have resulted in crustal thickening and regional metamorphism in the Lesser Himalayan belt. Its tectonic shift was critical in influencing the structural transformation of the Hazara region (Kazmi and Jan, 1997).

2.2.3 Main Boundary Thrust (MBT)

The southern edge of the Lesser Himalaya is the Main Boundary Thrust which divides the old metamorphic and crystalline rocks with the Neogene molasse which are deposited in the Sub-Himalayan foreland basin (Calkins et al., 1975; Kazmi and Jan, 1997). The Hazara area has Precambrian crust that is overlaid by the Siwalik Group sediments and the MBT indicates a considerable amount of shortening of the crust southward in the Himalayan orogeny.

The structural studies have revealed that MBT has undergone series of deformations which form compressional and transgressional parts (Baig and Lawrence, 1987). The thrust is connected with fault-propagation folds, imbricate stacking and the re-occurrence of stratigraphic units.

2.2.4 Hazara-Kashmir Syntaxis

The Hazara-Kashmir Syntaxis is a significant structural curvature at the northwestern end of the Himalayan arc where the overall NW-SE structural direction takes a sharp bend towards the NE-SW one (Gansser, 1964; Kazmi and Jan, 1997). The occurrence of this syntaxial bend indicates that there are shortening and partitioning of complex strains in the orogenic wedge.

The syntaxis is defined by tight to isoclinal folding, lithological unit thrust repetition, and high strain areas. Baig and Lawrence (1987) have viewed the syntaxis to be a culmination that has been created by indenting the Indian plate and the subsequent lateral tectonic flexing of the Himalayan belt. Improved fracture density and structural complexity in this zone determine crustal permeability, strength of deformation and exhumation in Hazara region.

2.2.5 Hazara Thrust

One of the main regional thrusts that can be pointed out in the context of the greater geological mapping of Hazara district is Hazara Thrust (Calkins et al., 1975). It is a component of the complex system of thrusts that had been formed during the process of Himalayan compression and causes the recurrence of the stratigraphic sequences of the Lesser Himalayan domain.

The thrust imposes old metasedimentary rocks on the younger ones and the characteristics of brittle to brittle-ductile deformation, such as fault breccias and shear fabrics, are observed. The Hazara Thrust is a progressive southward shortening and crustal stacking which is related to Cenozoic convergence. It has also affected the geometry of its structure which has had impacts on how crystalline basement rocks are distributed and exposed such as what is found in Mansehra area, which includes granitoid bodies (Calkins et al., 1975; Coward et al., 1988; Kazmi and Jan, 1997).

2.2.6 Oghi Shear Zone

The Oghi Shear Zone, which is found in the northeast of the Mansehra, is a significant ductile deformation zone of the Lesser Himalayan belt having mylonitic fabrics, foliation development and localized high-strain deformation of metasedimentary and granitoid rocks. (Kazmi and Jan, 1997).

This shear zone documents tectonothermal overprinting involving the compression along the Himalayas and shows that preexisting bodies of crystalline material such as the Mansehra Granite had undergone post-emplacement deformation. Oghi Shear Zone is therefore critical evidence of partitioning of strains and structural reactivation in Cenozoic orogenesis in the Hazara area (Le Fort et al., 1980; Kazmi and Jan, 1997).

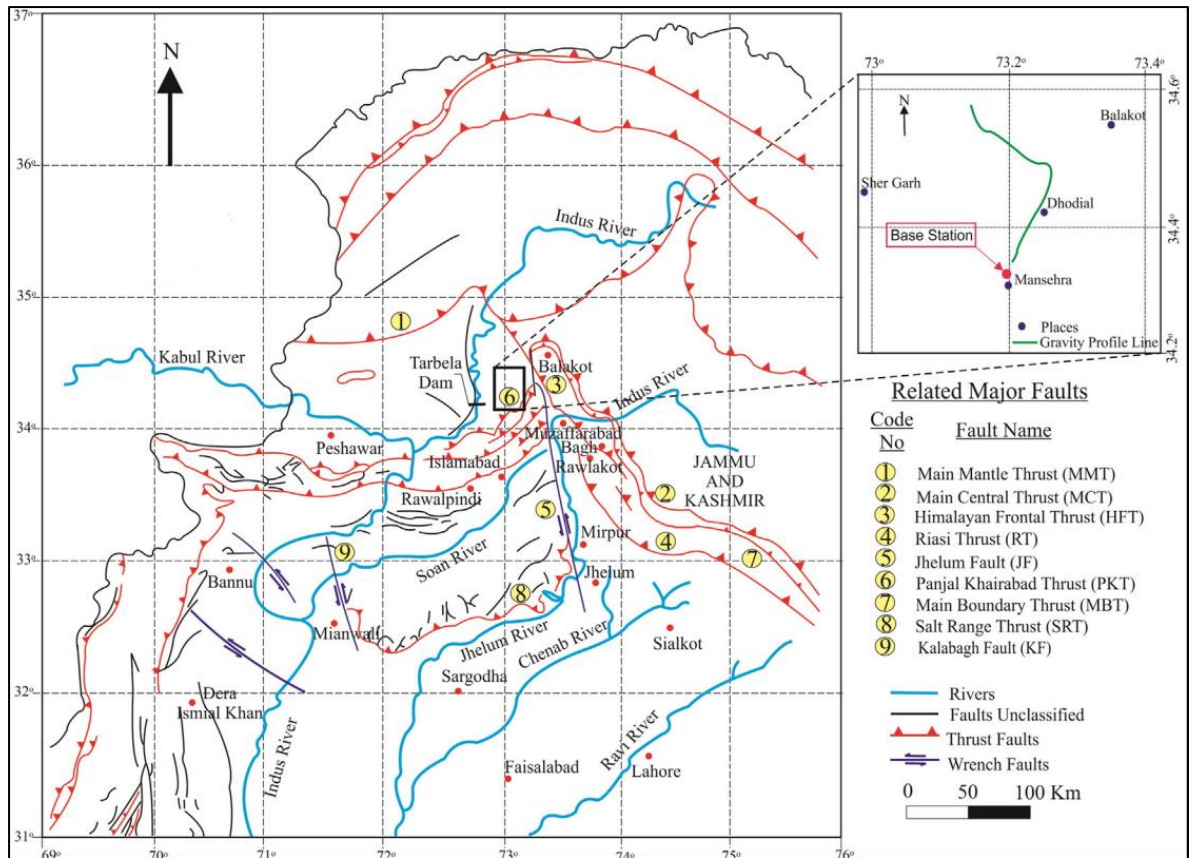


Figure 2.1 Tectonic Map of Northern Pakistan showing the study area after (Awan et al., 2021)

2.3 Geology of the Study Area

Mansehra city is geographically situated in the Hazara basin which is a structural depression of the Indian plate margin intermontane that was formed between the deformed Precambrian-Cenozoic successions (Calkins et al., 1975; Kazmi and Jan, 1997). The basin is a part of the Himalayan orogenic wedge which had been significantly shortened and uplifted in crustal shortening during the Cenozoic convergence between the Indian plate and the Eurasian plate (Coward et al., 1988; Kazmi and Jan, 1997). The geology of Mansehra is dominated by crystalline basement rocks in the immediate area of the city that constitute the major bedrock upon which the city is built. These rocks are widespread because of uplift and erosion related to thrust tectonics and one can observe first-hand the intrusion of granitoid rocks and their metamorphic host rocks. The geological environment is thus described

as having a crystalline core that gets influenced by compressional deformation which is creating a conducive natural laboratory to study the magmatic emplacement, structural change and geochemical evolution of granitoid systems (Calkins et al., 1975; Le Fort et al., 1980; Kazmi and Jan, 1997).

Structurally, the geology of Mansehra city is described as having strong deformation, which is in the form of folding, thrusting, jointing, and shear fabric development. Close mapping of Hazara district shows that the regional fold axes are mostly of NW-SE direction and NNW-SSE direction and the local variations are as a result of syntaxial bending (Calkins et al., 1975; Kazmi and Jan, 1997). The general orientation of axial planar cleavage in metasedimentary rocks is parallel to this orientation and is a measure of compressional stress fields in relation to south-verging thrusting. The crystalline rocks such as the Mansehra Granite have joint sets that tend to be NW-SE and NE-SW, which means that the rocks have undergone brittle deformation over previously formed ductile fabrics. In outer part of the area, there is weak foliation and shearing in the granite, which indicates tectonic overprinting after emplacement. The region is affected by the larger Hazara-Kashmir syntaxis, in which the structural trend curvature causes rotation of the fold axes and changing strike directions (Gansser, 1964). This structural framework can be specifically applicable to the aims of the current research because the pattern of deformation, fracture networks, and shear zone might govern the localization of pegmatite veins and determine the movement of elements at the late differentiation stage of magma. Geochemical evaluation of the Mansehra Granite and related pegmatites should consequently be considered in this context of structural framework, since tectonic influences may have a profound impact on magma developments, fluid migration patterns and rare and incompatible element distributions. Therefore, lithological, structural, and geochemical data needs to be incorporated to explain the petrogenetic history and metallogenic potential of the granitoid system that is exposed in the Mansehra area.

2.4 Stratigraphy of the Study Area

The stratigraphic sequence of the Mansehra area is a sequence of lithological units that are ranging from the Precambrian age metasedimentary basement rocks to Quaternary alluvial deposits of Recent age. The succession reflects a sedimentation of passive margins on the north of the Indian Plate, for instance, Cambro-Ordovician crustal magmatism, deposition of Paleogene marine carbonates, and Neogene foreland basin molasse sedimentation in Himalayan orogenesis (Calkins et al., 1975; Kazmi and Jan, 1997; Searle et al., 1999). The stratigraphic associations in the area are conformable marine successions and major discontinuities which demonstrate uplift and erosional events of the tectonic plate (Table 2.1).

Table 2.1: Generalized stratigraphic chart of Hazara Basin (Awan et al., 2021)

Formation name	Age
Alluvium	Recent
Siwaliks Group	Miocene to Pliocene
Murree Formation	Early Miocene
Kuldana Formation	Middle to Late Eocene
Chorgali Formation	Early Eocene
Margalla Hill Limestone	Early Eocene
Patala Formation	Late Paleocene
Lockhart Limestone	Early Paleocene
Hangu Formation	Early Paleocene
Mansehra Granite	Cambrian to Ordovician
Abbottabad Formation	Cambrian

Tanawal Formation	Precambrian
Hazara Formation	Precambrian

2.4.1 Mansehra Granite

One major granitoid intrusive body exposed in the Hazara region of the Lesser Himalaya, occupying a key stratigraphic position between the underlying Cambrian Abbottabad Formation and the overlying Paleocene Hangu Formation, is the Mansehra Granite (Offield et al., 1973; Kazmi and Jan, 1997). It is an extensive plutonic body which is distributed in a broad batholithic exposure extending in a horseshoe-shape between Darband, Mansehra, and Garhi Habibullah, with subsidiary outcrops distributed across both limbs of the Hazara-Kashmir syntaxis (Offield et al., 1973). It forms a large lithological unit throughout the central and northern parts of Hazara and is locally termed as gneissose granite where strong ductile deformation has imposed foliation during post-emplacement solid-state deformation (Offield et al., 1973). Importantly, early systematic petrological studies by Le Fort, Debon, and Sonet (1980) classified the Mansehra Granite in the broader context of the “Lesser Himalayan cordierite granite belt”, highlighting its unique aluminous character and therefore its importance in typology evolution of granitoids in Himalayas.

Contacts between Mansehra Granite and the surrounding metasedimentary sequences are mostly gradational, and often parallel to regional foliation, with local shear zones and zones of intense deformation at locations of maximum tectonic strain (Offield et al., 1973). Geologically, the granite is a medium- to coarse-grained, variably porphyritic variety with abundant microcline perthite megacrysts of potassium feldspar that can reach lengths of up to 3-12 cm, embedded in a matrix of quartz, K-feldspar, plagioclase, biotite, and minor muscovite (Offield et al., 1973). Zircon, apatite, and tourmaline are accessory mineral phases, and in some domains, the preferred alignment of feldspar phenocrysts and mica flakes characterizes the development of foliation (Offield et al., 1973). Magma-country rock interaction and

partial assimilation during the formation of the pluton are evidenced by the presence of variably incorporated xenoliths of metasedimentary origin (schist and quartzite). The contact metamorphism is locally well developed, with hornfels and recrystallized aureoles of surrounding country rocks, indicating fairly high thermal gradients during intrusion and cooling (Offield et al., 1973).

Petrographic investigations have demonstrated that the Mansehra Granite is composed predominantly of quartz, microcline, perthitic potassium feldspar, plagioclase, biotite, and muscovite, with accessory phases including zircon, apatite, garnet, epidote, monazite, rutile, and chlorite (Irum, 2014). Quartz generally occurs as anhedral interstitial grains displaying undulated extinction, indicative of post-crystallization deformation, whereas feldspars exhibit characteristic perthitic intergrowths, polysynthetic twinning, and localized sericitization, reflecting subsolidus re-equilibration and hydrothermal alteration. Biotite is the main ferromagnesian mineral and is frequently altered to chlorite, and muscovite is present as primary magmatic crystals as well as alteration products. Deformation features are evident in petrographic sections, such as bent mica flakes, fractured feldspars, recrystallization of quartz and the development of localized foliation, indicating that the pluton experienced significant tectonic deformation after emplacement. Accessory minerals like zircon, monazite and apatite indicate the more evolved felsic magma and magmatic differentiation during crystallization. These petrographic characteristics suggest a post-emplacement alteration of the Mansehra Granite in the deformation phase of its tectonic history, which was derived from the crust. Taken together, these petrographic characteristics indicate that the Mansehra Granite is a peraluminous, crustal origin granitoid, that subsequently experienced deformation and alteration during its post-emplacement tectonic evolution (Irum, 2014).

Geochronological investigations have constrained the emplacement of the Mansehra Granite to the early Paleozoic, with U-Pb zircon ages clustering around ~480 Ma, supporting its correlation with widespread Cambro–Ordovician magmatism across the Lesser Himalayan domain (Sajid et al., 2018). Apart from this, Le Fort et al. (1980) emphasized that the granite is a unique aluminous magmatic suite of the Himalayan belt, and that its genesis is related to melting of crust rather than mantle-derived magmatism. The Mansehra Granite and associated plutonic rocks of the Mansehra Granitic Complex (MGC) fall in the high-K calc-alkaline to peraluminous

field, which is characteristic of rocks with S-type granite affinities formed by partial melting of metasedimentary crust (Mehmood et al., 2021). Discrimination diagrams further indicate depletion in Ba, Sr, Nb, and Ti, alongside enrichment of incompatible elements, which is indicative of high degree of fractional crystallization and progressive evolution of the melt. Emplacement from an evolved felsic magma at mid crustal conditions are further supported by zircon saturation temperatures ranging from 749°C to 852°C (Naeem et al., 2021). All these features suggest that crustal anatexis are the most important petrogenetic process, linked to early Himalayan orogenic thickening along the northern Gondwanan margin (Zafar et al., 2019).

The Mansehra Granite is structurally overlain by regional foliation, shear zones, and localized mylonitic fabrics, especially in areas of severe interaction with adjacent metasedimentary rocks (Offield et al., 1973). These structural anisotropies are important for controlling late-stage magmatic differentiation and provide preferential paths for fluid migration and pegmatite emplacement. Late-stage melt segregation and enrichment of incompatible elements is indicated by the presence of pegmatitic bodies, aplites and micro granitic veins within and surrounding the pluton, which implies a prolonged and complex cooling history (Naeem et al., 2021). In this context, the Mansehra Granite is not only a lithostratigraphic unit in the Hazara region but also an essential magmatic system that controls the genesis and spatial distribution of pegmatites, which are the main target of the present research.

2.4.2 Abbottabad Formation

The Abbottabad Formation is one of the main sedimentary units lying under the Mansehra Granite in the Hazara region and it is dated to the Early to Middle Cambrian using the stratigraphic correlation and paleontological evidence of the region of northern Pakistan (Kazmi and Jan, 1997; Shah, 2009). At Mansehra-Abbottabad the formation is dominated by massive dolomite and limestone that are thick-bedded and subsidiary quartzite and shale horizons. It is usually light grey or bluish grey, fine- to medium-crystalline, and locally stromatolitic meaning that it was deposited in a shallow marine platform to peritidal environment along the northern

margin of the Indian Plate during early Paleozoic time (Shah, 2009). The interbeds of quartzite tend to be fine to medium grained with a well indurated nature, which represents the intermittent deposits of the clastic materials to the carbonate shelf system. The Abbottabad Formation has been reported to be as thick as locally 300 to 600 meters in Hazara basin, but the apparent thickness can increase locally by folding and thrusting (Kazmi and Jan, 1997).

The Abbottabad Formation has a stratigraphic conformity with the Precambrian metasedimentary rocks in some parts of northern Pakistan, but in Mansehra area is intruded by the Cambro- Ordovician Mansehra Granite, creating a definite relationship of intrusive contacts (Offield et al., 1973; Kazmi and Jan, 1997). Local thermally enhanced contact metamorphism in carbonate rock formations was due to the granite emplacement, which is characterized by recrystallization and formation of marble and calc-silicate assemblages around the margins of the intrusive (Offield et al., 1973). Structurally, Abbottabad Formation is involved in the folding and thrusting of the region in accordance with the Himalayan deformation with the northeast-southwest oriented fold axes with the structural grain of Hazara fold-and-thrust belt (Bossart and Ottiger, 1989).

2.4.3 Tanawal Formation

The Tanawal Formation is a thick sequence of the most siliciclastic metasedimentary rocks that are visible in the Hazara area and form a significant constituent of the basement beneath the Abbottabad Formation in the Mansehra area. It is normally placed in the Precambrian due to stratigraphic position and interstate association in the Lesser Himalayan sequence (Kazmi and Jan, 1997; Shah, 2009). Quartzite, quartz-mica schist and phyllite are the predominant lithologies, with the minor metaconglomerate and metasandstone. The quartzites are normally in the near-shore and high-energy shallow marine environments, being medium- to coarse-grained, strongly indurated, and occasionally feldspathic, before high-energy metamorphism of the area. Muscovite, biotite, chlorite, and quartz are found in the schistose and phyllitic units, which is a sign of low- to medium-grade metamorphic

conditions. The Tanawal Formation is very thick in nature and it usually measures several hundred meters in thickness, but at times it can be more than 1,000 meters in the Hazara area, as repetition of tectonic by folding and thrusting complicates the accurate measurement of the thickness (Kazmi and Jan, 1997).

The Tanawal Formation underlies the Abbottabad Formation and it is stratigraphically interpreted that the contact between the two formations is usually unconformable or a representation of a major depositional interval between the Precambrian clastic sedimentation and the Cambrian shallow marine carbonate deposition (Shah, 2009). The Tanawal Formation has some structural participation in the regional Himalayan deformation, with well-developed foliation, tight folds and fault-related fabrics, which trend in the structural direction of the Hazara fold-and-thrust belt (northeast southwest) (Bossart and Ottiger, 1989). The anisotropy of mechanism and the ubiquitous fractures of these metasedimentary rocks favored good structural avenues at the time of emplacement of the Cambro-Ordovician Mansehra Granite. The Tanawal metasediments locally also show contact relationships with the granite, which show thermal metamorphism and recrystallization, which also means that it interacted intrusively (Offield et al., 1973).

2.4.4 Hazara Formation

The Hazara Formation is one of the oldest sedimentary successions that are exposed in the Hazara-Mansehra area and is typically defined as belonging to the Late Proterozoic (Neoproterozoic) by the stratigraphic relationships and lithological correlations in the Lesser Himalayan sequence (Kazmi and Jan, 1997; Shah 2009). The formation in the Mansehra-Abbottabad belt consists largely of slate, phyllite and fine-grained metasiltstone and is mixed with minor horizons of quartzite and thin limestone. The slates are usually dark grey to black, finely laminated, and have well-developed cleavage and phylitic units have muscovite, chlorite, and fine quartz, which are evidence of low-grade regional metamorphism under greenschist facies conditions. The interbeds of quartzite are well compacted and of fine grains, indicating an initial deposition of the sandy material in a rather low-to-middle-energy

marine environment. The Hazara Formation is quite thick and is usually greater than 1,000 meters in the northern part of Pakistan, yet it is very difficult to calculate because of severe folding and tectonic repetition of the Hazara fold-and-thrust belt (Kazmi and Jan, 1997).

The Hazara Formation as the stratigraphy of the Tanawal Formation in most of the Hazara region and can be seen as an initial stage of deposition on the northern margin of the Indian Plate before the Cambrian shallow marine transgression (Shah, 2009). The Hazara and Tanawal rocks are normally said to be conformable but sometimes can be seen to be tectonized (Himalayan deformation). Stratum wise, the Hazara Formation is highly folded and discontinuous with the axes of the folds mostly moving northeast southwest, and perpendicular to the local structural grain of the Lesser Himalaya (Bossart and Ottiger, 1989). These are deformation patterns that are due to compressional tectonics that are related to the collision of the Indo-Eurasian. The cleavage and fracturing that pervades the Hazara Formation are evidence of the mechanical reaction of the Hazara to shortening of the region and is significant in the accommodation of strain at lower structural levels.

CHAPTER 3

METHODOLOGY

3.1 Fieldwork

The Mansehra Granite was sampled in the field within the Mansehra District, Khyber Pakhtunkhwa, Pakistan, and mostly on exposures that were formed next to the N-15 National Highway (Fig. 3.1). The granite has been well exposed in this corridor and more representative material was taken in an active quarry found within the study area. The sampling locations were chosen because of systematic reconnaissance and analysis of lithological continuity, structural integrity, accessibility and surface weathering. Special attention was paid to locating fresh and minimally altered outcrops so that the samples obtained are the true representatives of primary mineralogical and geochemical features of the formation.

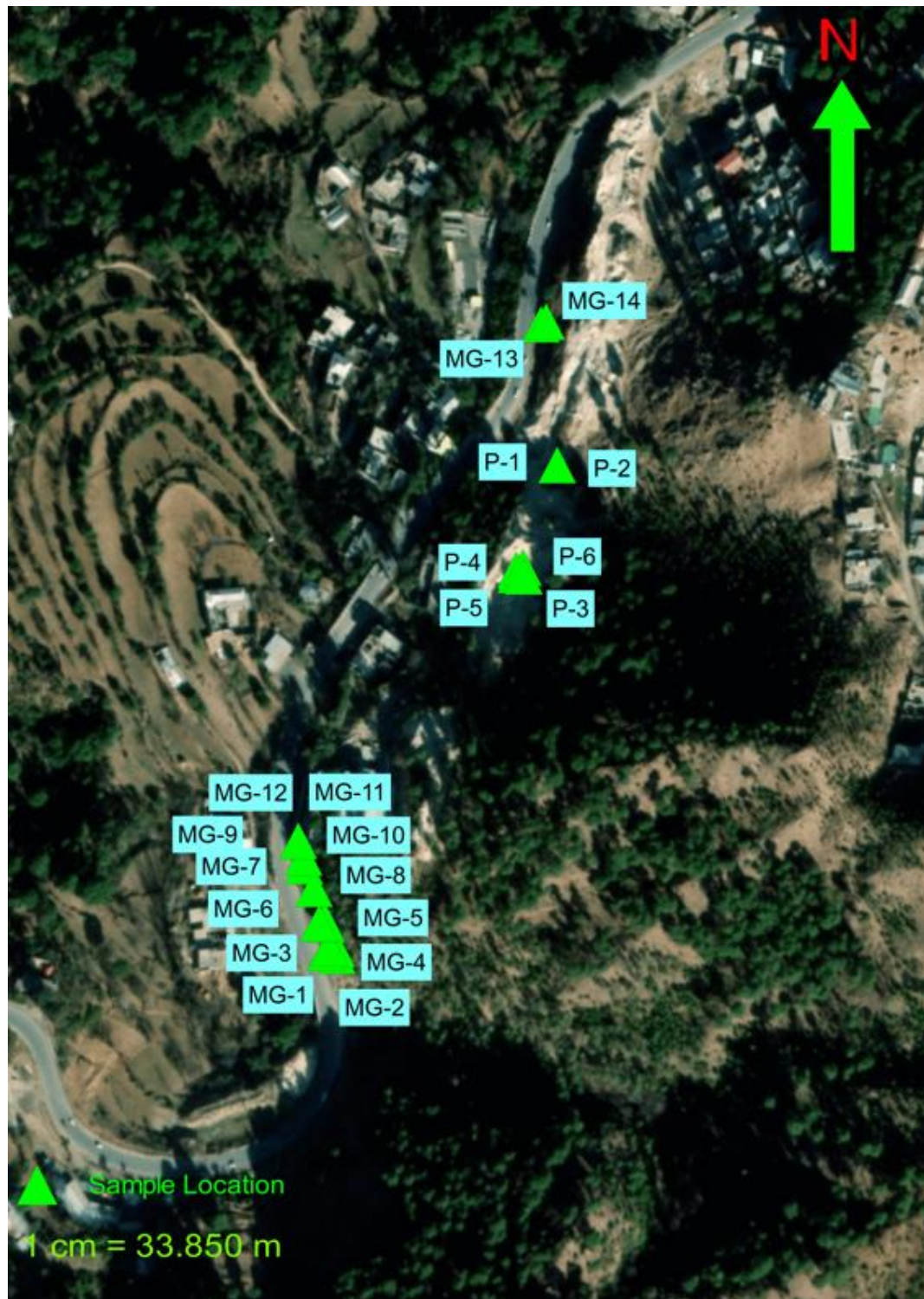


Figure 3.1 Sample location map. (Source: ESRI, 2026)



Figure 3.2 Granite outcrop showing a pegmatite vein, emplaced along a structural discontinuity within the host rock. The pegmatite displays a distinct contact with the surrounding granite, indicative of late-stage magmatic intrusion

Twenty (20) samples of granite and the related pegmatitic veins were also taken out of representative exposures along lateral continuity of approximately 200 feet where rock samples from MG-1 to MG-14 are granite samples and P-1 to P-6 are pegmatite samples (Fig. 3.2; Fig. 3.4). The weathered rinds and altered surface material were also removed carefully during the sampling before the extraction to ensure that new rock surfaces are obtained.

All rock samples were then marked by attaching a distinctive identification code and kept in clean sample bags of high-density polyethylene. Non-metallic and chemically inert containers were used to reduce the possibility of cross-

contamination. Each sampling site had its geographic position noted with a GPS device and elaborate field notes were drafted with descriptions of the lithological aspects, mineralogical observations, and any structural aspects and the conditions of the site (Fig. 3.3). Field photographs were also collected in a systematic manner to archive the outcrop relationships and the context of the sample, hence making the data traceable and reproducible.



Figure 3.3 A xenolith (metasedimentary origin) outcrop where surface alteration is evident, resulting in localized disaggregation of the rock mass

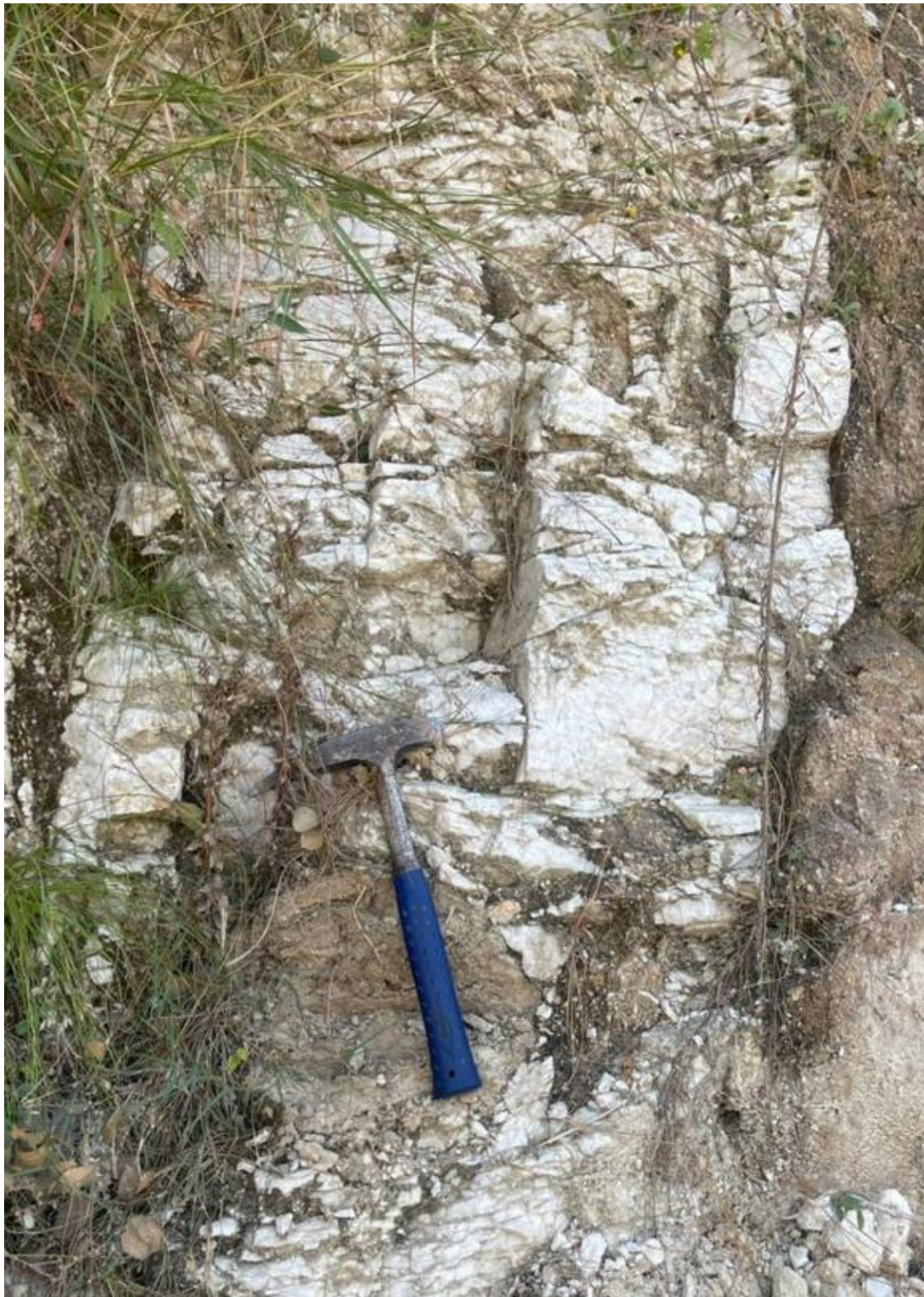


Figure 3.4 Outcrop exposure of a coarse-grained pegmatite discordantly crosscutting granitic host rock

3.2 Sample Preparation

The collected rock samples were first air-dried at ambient laboratory temperature in order to eliminate any moisture left. In order to avoid possible changes or volatilization of temperature-sensitive mineral phases and trace elements, thermal oven drying was avoided. Samples were dried and then mechanically disaggregated and sieved through 30-mesh and 100-mesh stainless steel sieves to obtain fine fraction to be used to analyze geochemistry. The fine material that was retained was homogenized and weighed on an analytical balance before chemical digestion.

In determining elements (especially trace and critical metals), sample digestion was undertaken using conventional methods appropriate to use in Inductively Coupled Plasma Mass Spectrometry (ICP-MS) which is the most commonly used technique in geochemical analysis of many elements because it is very sensitive and has low limits of detection (Hall et al., 1996). Digestion of the powdered samples was done in freshly prepared aqua regia, which was a solution of one-third concentration of nitric acid (HNO₃) and two-thirds concentration of hydrochloric acid (HCl) (Fig. 3.5). The acid mixture is used to oxidize metallic phases and form soluble chloro-complexes, hence allowing efficient dissolution of most sulfides, oxides and trace metal-bearing phases. The main reaction that controls the formation of aqua regia is the following:



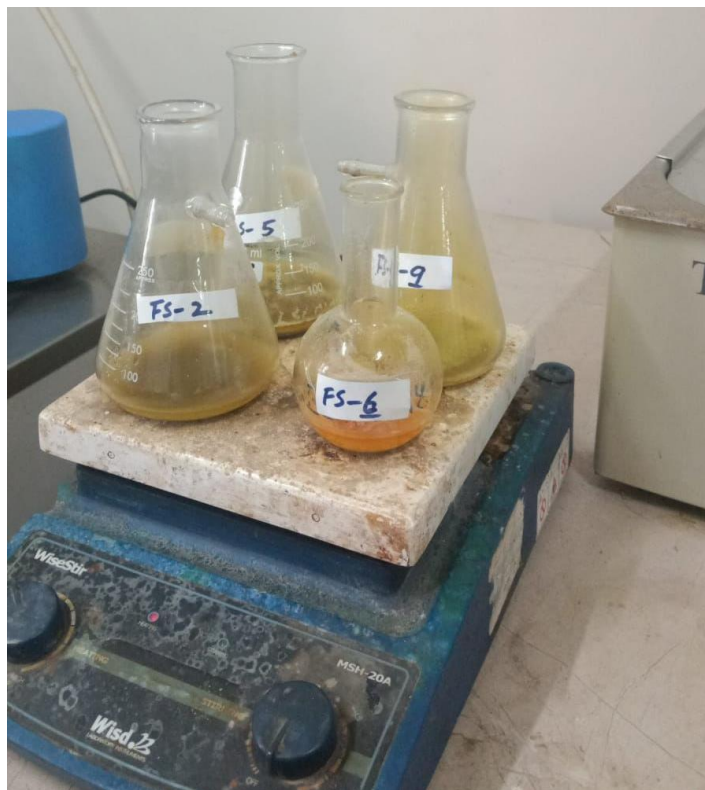


Figure 3.5 Heating sample solution for digestion of sample fines in acid

Although aqua regia digestion is widely employed for routine geochemical investigations because of its efficiency in dissolving most sulfides, carbonates, oxides, and other acid-soluble phases, it is considered a partial digestion technique and does not completely dissolve highly refractory silicate minerals such as zircon, monazite, xenotime, or resistant oxide minerals containing Sn and Ta (Hall et al., 1996; Potts, 1992). Consequently, the concentrations of elements hosted within these resistant mineral phases may be underestimated or reported below the instrumental detection limit. This limitation was considered during the interpretation of the ICP-MS results, particularly for elements commonly associated with refractory accessory minerals.

Work done in the laboratory was in line with the standard operating procedures (SOPs) including personal protective equipment (lab coats, nitrile gloves, protective goggles, and KN95 masks) and supervision of laboratory staff during the preparation process. Glassware was also properly cleaned with distilled water before use to reduce contamination i.e. flasks, beakers and spatulas. All containers were well marked using permanent markers to trace samples after heating in a hot plate. Bottles that were to be used in ICP-MS analysis were also pre-cleaned using distilled water.

After digestion and controlled heating, the solutions were transferred out of the hot plate and diluted with about 30 mL of distilled water to remove some of the acid strength and bring the samples to the level of analytical concentration. The solutions were left to cool down to reach the room temperature before being filtered (Fig. 3.6).

Preliminary filtration was done using standardize filter paper in the laboratory to get rid of coarse undissolved residues. A second step in a syringe filtration process was then carried out to remove any residual total dissolved solids (TDS) and fine particulates so that the final solutions were clear and could be analyzed using ICP-MS. During the preparation, the contamination-control measures were observed strictly to retain the accuracy of the analysis and reliability of the data.

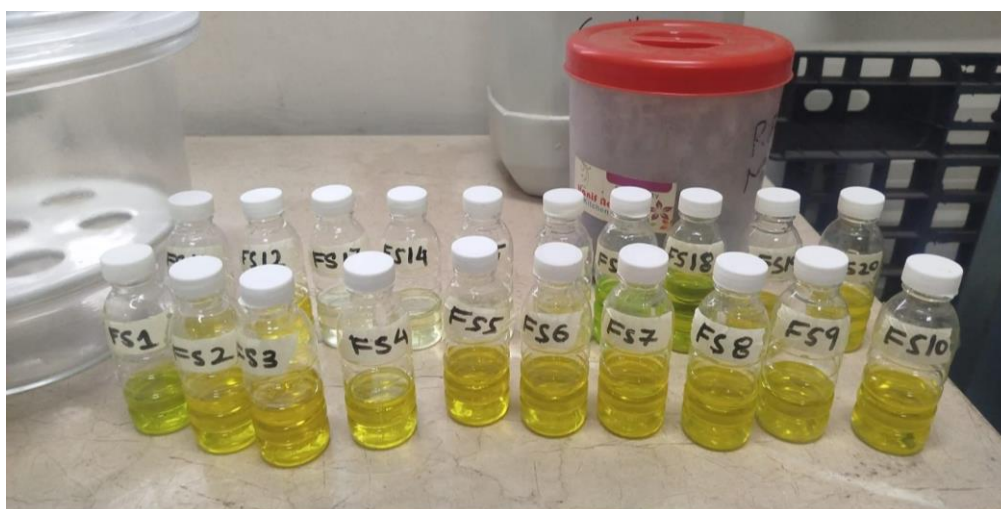


Figure 3.6 Final digested samples in bottles

3.3 Inductively Coupled Plasma Mass-Spectrometry (ICP-MS)

The elemental composition of the collected granite and pegmatite samples was determined using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Fig. 3.7). Prior to analysis, the powdered samples were digested using aqua regia to bring the target elements into solution. ICP-MS was selected for this study because of capability to simultaneously determine multiple major, minor, and trace elements in geological materials (Hou and Jones, 2000). The prepared solutions were introduced

into the instrument through a nebulizer, where they were converted into a fine aerosol and transported into an argon plasma for atomization and ionization.

The generated ions were extracted through the interface system and separated according to their mass-to-charge ratios using a quadrupole mass analyzer before being detected by an electron multiplier detector (Thomas, 2013). Quantification of elemental concentrations was performed using external calibration standards, while quality control measures including blanks, standards, and instrument calibration procedures were employed to ensure analytical accuracy and precision. The resulting geochemical data were subsequently used to evaluate the distribution and enrichment of elements within the Mansehra Granite and associated pegmatite veins.

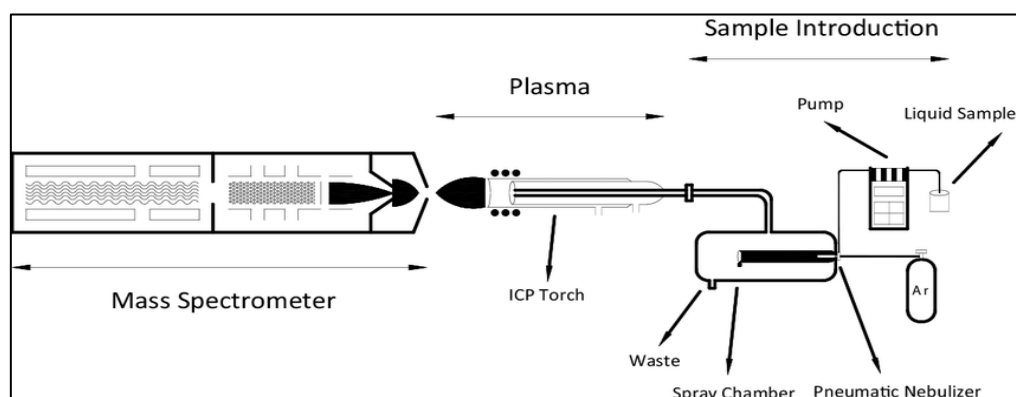


Figure 3.7 Schematic figure of ICP-MS (Kashani and Mostaghimi, 2010)

3.3.1 Quality Assurance and Quality Control (QA/QC)

Quality assurance and quality control (QA/QC) are fundamental components of geochemical investigations to ensure the reliability and consistency of analytical data generated by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Potts, 1992). All sample preparation and elemental analyses were conducted following standardized laboratory procedures. The analytical dataset comprised elemental concentrations together with values reported as Below Detection Limit (BDL) and Above Detection Limit (ADL), representing the analytical range and detection capabilities of the instrument. During data processing, BDL values (left-censored

observations) were substituted using one-half of the instrument detection limit ($0.5 \times \text{DL}$) (Reimann et al., 2008). For the purpose of data interpretation, ADL values were conservatively assigned the highest measured concentration of the corresponding element within the dataset and were subsequently interpreted with caution owing to the uncertainty associated with concentrations exceeding the calibrated analytical range.

Although detailed laboratory QA/QC parameters, including certified reference material recoveries, duplicate analyses, and instrumental precision, were not provided with the analytical dataset, the reported elemental concentrations were evaluated with due consideration of analytical detection limits and data censoring. Consequently, only quantifiable analytical values were used for geochemical interpretation, while the limitations associated with censored data were acknowledged throughout the study to ensure scientifically sound interpretation of the results.

CHAPTER 4

RESULTS

4.1 Critical Minerals

The geochemical composition of the Mansehra Granite and pegmatite veins have shown that it includes a package of key minerals that have concentrations, spatial distributions and intrasample variations which provide important information on the magmatic history of the complex (Table 4.1). In the context of this study, the critical minerals are defined according to the nomenclature of the United States Geological Survey (USGS) and the Critical Raw Materials scheme of the European Commission, which distinguishes between critical elements, based on their economic significance and vulnerability of the supply-chain. Examples of elements that are computed and measured here are lithium (Li), beryllium (Be), gallium (Ga), germanium (Ge), niobium (Nb), tantalum (Ta), vanadium (V), uranium (U), tin (Sn), tungsten (W), chromium (Cr), hafnium (Hf), zirconium (Zr), antimony (Sb), manganese (Mn), nickel (Ni), and cobalt (Co). Indium (In), selenium (Se), and bismuth (Bi) are referred to as geochemically insignificant in this rock suite for being below detection limits in all samples. Each of the identified critical minerals is systematically discussed in paragraphs that follow, in terms of its concentration range, inter-sample variability, industrial importance, and a comparison of the geochemical behavior of each mineral between the granite and the pegmatite samples.

Lithium levels in Mansehra Granite samples exhibit a moderate range of detectable values that is consistent, with the granite suite (MG-1 to MG-14) results in 0.059 ppm in MG-9 to 0.469 ppm in MG-5, with mid values of 0.162 ppm (MG-1), 0.280 ppm (MG-2), 0.313 (MG-3), 0.155 ppm (MG-4), 0.372 ppm (MG-6), 0.060 ppm (MG-7), 0.082 ppm (MG-8), 0.253 ppm (MG-10), 0.082 ppm (MG-11), and 0.078 ppm (MG-12). The lithium levels among the pegmatite samples (P-1 to P-6) are significantly suppressed in the earlier pegmatite samples with P-1, P-2, P-3, and P-4 registering 0.002 ppm, 0.003 ppm, 0.006 ppm, and 0.009 ppm respectively. A strong enrichment however is seen in P-5 (0.389 ppm) and P-6 (0.782 ppm) and indicates that the later-stage crystallizing pegmatite veins had a great deal of Li enrichment. MG-13 (2.286 ppm) and MG-14 (1.655 ppm) are the most anomalous lithium values. The correlation analysis of the granite and pegmatite suites shows a subtle correlation, with most of the granite samples having moderate Li levels that could be indicative of the protolith melt composition, and the initial pegmatite samples (P-1 to P-4) having a relative depletion of Li, which may be due to their emplacement as early crystallizing and volatile-poor phases. The extreme hike in Li in P-5, P-6, MG-13 and MG-14 agrees with the step-wise enrichment of lithophile elements during the late magmatic phases, which has been widely reported in leucogranite as well as S-type granite related pegmatites, similar to the Himalayan leucogranite province (Le Fort et al., 1980).

Beryllium is also found in most of the granites and pegmatites and this indicates that it is attracted by the fractionated silica-rich magmatic environment. Within the granite suite, Be concentrations range from 0.005 ppm in MG-9 to 0.024 ppm in MG-3, with values of 0.006 ppm in both MG-1 and MG-2, 0.015 ppm in MG-4, 0.014 ppm in MG-5, 0.015 ppm in MG-6, 0.007 ppm in MG-7, 0.011 ppm in MG-8, 0.019 ppm in MG-10, 0.011 ppm in MG-11, and 0.008 ppm in MG-12. The concentrations of Be are generally lower in P-1 (0.001 ppm), P-2 (0.001 ppm) and P-3 (0.001 ppm) compared to P-4, which is below detection limit. A marked enrichment occurs in P-5 (0.048 ppm), P-6 (0.028 ppm), MG-13 (0.147 ppm) and MG-14 (0.143 ppm) (Fig. 4.2).

Germanium has a highly discontinuous distribution in the sample suite, most of the samples, both granite and early pegmatite, being below the detection limits. MG-3 (0.031 ppm) and MG-6 (0.077 ppm) are the only granite samples, which have

detectable Ge concentrations. In the pegmatite suite, Ge is not present in P-1, P-3 and P-4, but increases to 0.143 ppm in P-2, to 0.111 ppm in P-5 and has a dataset maximum of 0.373 ppm in P-6.

Niobium is one of the most strongly detected critical minerals of the granite samples, with values ranging between 0.026 ppm in MG- 9 to 0.209 ppm in MG-5, with intermediate values of 0.057 Niobium is below the detection limits in P-1, P-2 and P-3, and P-4 has 0.039 ppm, P-5 has 0.218 ppm and P-6 has 0.112 ppm. The most striking Nb value in the dataset is the one of MG-14 (5.837 ppm). Geochemically, Nb is a high field strength element (HFSE) that typically is enriched in peraluminous granites and related pegmatites. The high Nb content in MG-14 and the ADL outcome in MG-13 indicate the maximum values in the suite and probably indicate the existence of Nb-bearing oxide mineral phases including columbite-tantalite or pyrochlore which often crystalize out of highly evolved granitic melts. The fact that the granite (MG-1 to MG-12) background concentrations are lower than the extreme enrichment of MG-13 and MG-14 implies that there was a late-stage Nb-rich mineralizing event in the Mansehra Granite.

In the granite samples, Ta is detected in MG-4 (0.014 ppm), MG-6 (0.008 ppm), MG-9 (0.013 ppm), MG-10 (0.017 ppm), MG-11 (0.009 ppm), and MG-12 (0.015 ppm), while MG-1, MG-2, MG-3, MG-5, MG-7, and MG-8 fall below detection. P-3 of the pegmatites has a detectable concentration of 0.011 ppm, and P-1, P-2, P-4, P-5 and P-6 are below detection. The maximum Ta reading in the dataset is found in MG-13 (0.047 ppm). The highly coherent geochemical nature of Nb and Ta in pegmatitic and granitic systems is not new and the fact that Nb does not systematically correlate with Ta in this data set is interesting.

One of the most frequently found critical minerals in this research is vanadium. The V concentration in MG-1 to MG-12 ranges from 0.045 ppm in MG-9 to 0.222 ppm in MG-3, with values of 0.076 ppm (MG-1), 0.124 ppm (MG-2), 0.086 ppm (MG-4), 0.198 ppm (MG-5), 0.161 ppm (MG-6), 0.054 ppm (MG-7), 0.086 ppm (MG-8), 0.145 ppm (MG-10), 0.097 ppm (MG-11), and 0.111 ppm (MG-12). The initial samples of pegmatite exhibit a drastic lowering of V, P-1 and P-2 cannot be detected, P-3 has 0.009 ppm V and P-4 has 0.012 ppm V. The later sampled pegmatites, however, exhibit a turnaround in concentrations with P-5: 0.840 ppm and

P-6: 2.208 ppm being even higher. The highest values of the whole data are seen in MG-13 (6.103 ppm) and MG-14 (4.998 ppm), which are rather abnormal in a granitic setting and are an order of magnitude higher than others in the bulk of the granite. MG-13 and MG-14 report strongly anomalous V values, linked to the high levels in the late-stage pegmatites P-5 and P-6 (Fig. 4.1).

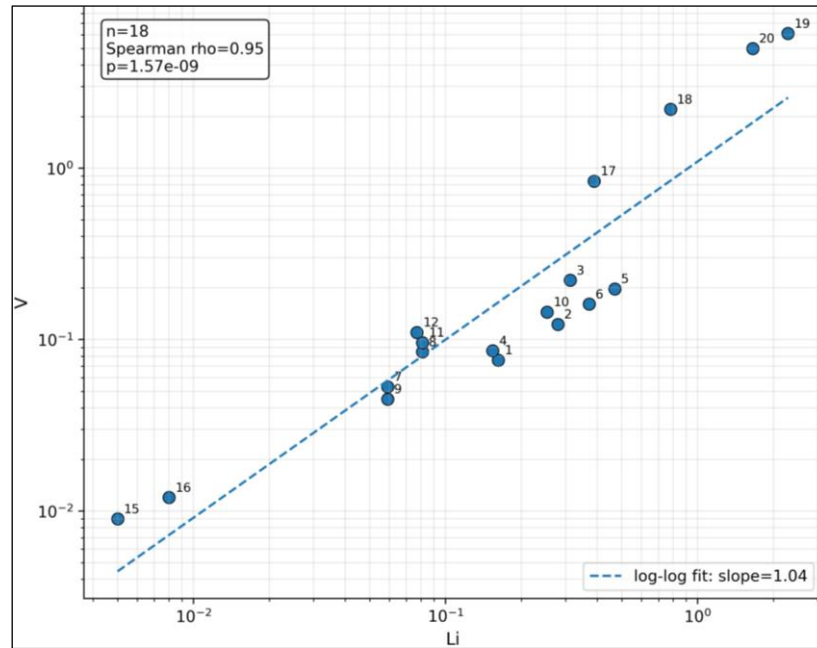


Figure 4.1 Log-log cross plot of lithium (Li) versus vanadium (V) concentrations across all samples with valid paired measurements ($n=18$). The dashed line represents the best-fit power-law regression (slope=1.04). Spearman rank correlation coefficient and associated p-value are shown in the inset, indicating a highly significant positive association consistent with co-enrichment during progressive magmatic fractionation

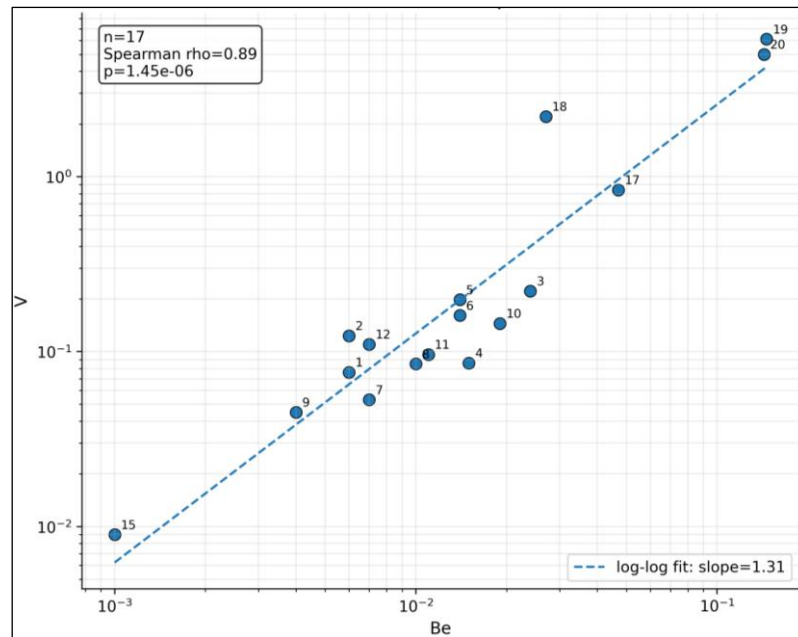


Figure 4.2 Log-log cross plot of beryllium (Be) versus vanadium (V) concentrations for samples with valid paired measurements ($n=17$). The dashed regression line (slope=1.31) indicates a super-linear enrichment relationship. The strong Spearman correlation ($\rho=0.89$, $p=1.45 \times 10^{-6}$) supports co-mobilization of Be and V during late-stage magmatic differentiation

Within the granite samples, Uranium concentrations range from below detection in MG-1 and MG-9 to a maximum of 0.363 ppm in MG-5, with values of 0.133 ppm (MG-2), 0.327 ppm (MG-3), 0.156 ppm (MG-4), 0.324 ppm (MG-6), 0.045 ppm (MG-7), 0.050 ppm (MG-8), 0.165 ppm (MG-10), 0.221 ppm (MG-11), and 0.116 ppm (MG-12). P-1, P-2 and P-3 of the pegmatites are below detection, with P-4, P-5 and P-6 of Uranium at 0.074, 0.103 and 0.249 ppm respectively. MG-13 (0.970 ppm) and MG-14 (0.785 ppm) contain the highest concentrations of uranium and are significantly higher than the values of the early granites and are the richest samples of uranium in the dataset. The geochemical distribution of Uranium in this research is very closer to the pattern of magmatic fractionation meaning that U concentrations are generally on the rise towards the early-crystallizing, mafic-enriched parts of the granite to the more evolved, leucocratic parts and finally to the late-stage pegmatite veins and adjoining areas. The relatively low U in the early pegmatites (P-1 to P-3) relative to the host granite may indicate the sequestration of

the U in the accessory phases zircon, monazite or uraninite in the granite body, at an earlier stage before the expulsion of late-stage melts that formed the more U-enriched generations of pegmatites and the mineralized regions represented by MG-13 and MG-14.

The distribution of Tin across the sample suite is of a rather unique and geologically informative pattern. MG-1 only gives a significant reading of 0.705 ppm within the granite, and the other eleven granite samples (MG-2 up to MG-12) are below detection limits, meaning that Sn did not completely dissolve in the granitic melt and must have been scavenged into the early-forming sulphide or oxide phases. P-1, P-2, P-3 and P-4 are all below the limit of detection, whilst P-5 and P-6 both are above detection limit (ADL), an indicator of the highest concentration of Sn in the entire set of data. MG-13 and MG-14 granite give 0.018 ppm of Sn each, a rather small number, but again substantiating the general but patchy occurrence of Sn in minute amounts.

Tungsten levels are smaller than detectable in most samples of granite and early pegmatites, where it only tends to accumulate on the most mature products of magmatic systems. MG-9 has the highest W value of 0.037 ppm, and this is the only one among all the granite samples that produce a detectable value. P-1 to P-4 within the pegmatite samples are consistently below the detection level. But P-5 gives a significantly higher value of 0.454 ppm and P-6 gives 0.078 ppm, the two richest W samples in the sample set. Tungsten is essential in the production of cemented carbide cutting tools, drilling machines, armor-penetrating ammunition, electrical contacts, X-ray tubes, and high-performance alloys in aerospace and defense applications. Its preferential distribution in P-5 and, to a smaller degree, P-6, reiterates this distribution pattern of Sn and Ge in these two samples, which collectively points to these two pegmatite samples being a relatively advanced and mineralogically enhanced phase of crystallization that concentrated on a series of high-value, refractory critical elements.

Chromium in this research shows very heterogeneous distribution of the data between very low levels, almost all below the detection limit, in the early samples of granite, and very high levels, in distinct samples. MG-2 (0.050 ppm), MG-3 (0.004 ppm), and MG-5 (0.007 ppm) are the only granite samples that show detectable Cr with the rest of the nine granite samples being below detection. P-1, P-2, and P-3 have

values below detection in the pegmatite suite, P-4 has a value of 0.018 ppm, and P-6 has 0.014 ppm. The highest value of the Cr recorded in the pegmatite suite is found in the P-5 (2.630 ppm), which is disproportionately high in comparison with all other samples. Granite MG-13 (1.186 ppm) and MG-14 (1.047 ppm) also exhibit very high Cr, outside of the pegmatites. Anomalous Cr concentration in P-5, a pegmatite sample, is unexpected that such a system of granitic and leucocratic rocks has a significant amount of Cr, which is generally a mafic and ultramafic mineral.

Hafnium and zirconium are geochemically consistent elements that are normally discussed together because of their almost identical ionic radii, and because of their widespread occurrence in the mineral zircon, where Hf commonly replaces Zr. Early granite samples result in values of 0.004 ppm (MG-1), 0.006 ppm (MG-3), 0.006 ppm (MG-6), 0.006 ppm (MG-7), 0.006 ppm (MG-8), and 0.004 ppm (MG-9), while MG-2, MG-4, MG-5, MG-10, MG-11, and MG-12 are below detection. P-1 gives 0.003 ppm, P-2 gives 0.006 ppm, P-4 gives 0.036 ppm, and P-6 gives 0.006, and P-3 and P-5 are below the detection level among the pegmatites. The highest Hf values are found in MG-13 (0.042 ppm) and MG-14 (0.033 ppm). The concentrations of zirconium are very low in general and nearly undetectable in both types of rocks, with only detectable values found in MG-4 (0.001 ppm), MG-5 (0.004 ppm), and MG-10 (0.002 ppm) of the early granite, P-4 (0.019 ppm), P-5 (0.008 ppm), and P-6 (0.013 ppm) among pegmatites and MG-13 (0.081 ppm) and MG-14 (0.051 ppm) among the remaining two granite samples. These low yet continually measurable levels of Hf and Zr in this data indicate the presence of accessory zircon grains dispersed during the granitic and pegmatitic stages of the Mansehra Granite. The mildly high Hf and Zr in P-4 and the concentration peaks in MG-13 and MG-14 are in line with the concentration of relict grains of zircon in more evolved magmatic areas (Fig. 4.3).

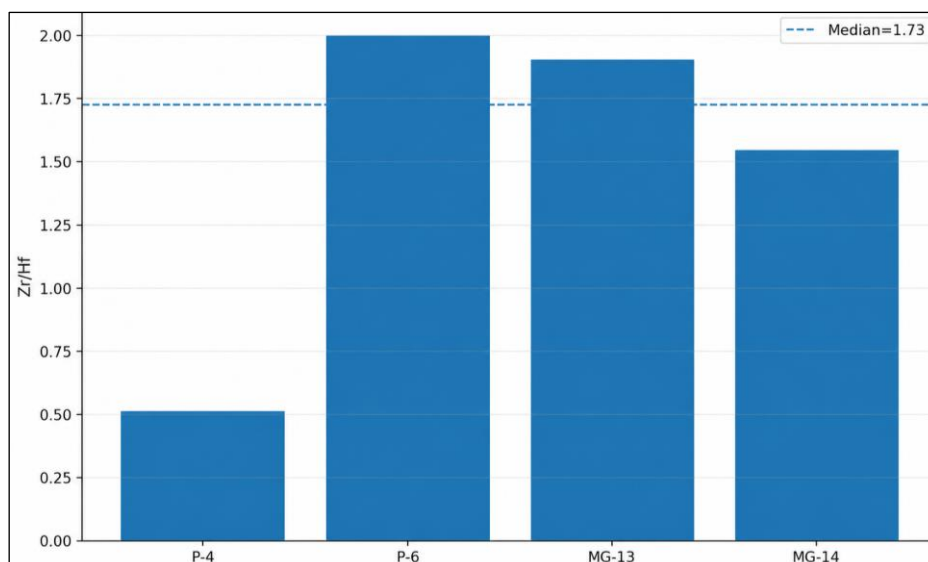


Figure 4.3 Bar chart of Zr/Hf ratios for the four samples yielding simultaneous detections of both zirconium and hafnium (P-4, P-6, MG-13, MG-14). The dashed line denotes the dataset median (1.73). The low and variable Zr/Hf ratios are consistent with preferential incorporation of both elements into zircon accessory grains during advanced stages of magmatic differentiation

One of the most regularly observed critical minerals throughout the entire sample suite is antimony which is commonly spread throughout both the granite and pegmatite phases. The early granite samples reflect Sb concentrations ranging from 0.024 ppm in MG-5 to 0.100 ppm in MG-6, with values of 0.084 ppm (MG-1), MG-2 is below detection, 0.063 ppm (MG-3), 0.048 ppm (MG-4), 0.062 ppm (MG-7), 0.084 ppm (MG-8), 0.075 ppm (MG-9), 0.067 ppm (MG-10), 0.052 ppm (MG-11), and MG-12 below detection. P-1 has a value of 0.069 ppm, P-2 shows a value of 0.130 ppm, P-3 is 0.057 ppm, P-4 is below detection, P-5 has a very high value of 0.992 ppm and P-6 has a value of 0.459 ppm. MG-13 and MG-14 respectively give 0.069 and 0.077 ppm. The relative homogeneity of the low-level Sb in the granite body, versus the high levels in the late-stage pegmatites, is a strong indication that the antimony was indeed mobilized and enriched by evolving magmatic fluids in the late stages of activity of the Mansehra Granite, and the zones of high levels in the pegmatites are therefore of special economic interest.

The Nickel values are significantly lower, with MG-1 (2.597 ppm) and MG-9 (0.029 ppm) the only ones that record any detectable level of Ni, and MG-2 through MG-12 all below detection. P-4 (0.106 ppm) is the only pegmatite that can give a detectable value of Ni whereas P-5 and P-6 have ADL designations; P-1, P-2, and P-3 are non-detectable. MG-13 (0.384 ppm) and MG-14 (0.240 ppm) are granite samples as well where you can find the detectable Ni values. The co-enrichment of Mn and Ni in the late-stage pegmatite samples P-5 and P-6, along with the values of the ADL of both elements in MG-13 and MG-14, imply that some sort of Mn-Ni mineralizing phase, possibly rhodonite, columbite-manganite, or a secondary assemblage of oxides and hydroxides occurred. The high Ni in MG-1 (2.597 ppm) in the granite is an anomaly compared to the other granite members and can be called a pyroxene accessory phase with high crystallization temperatures (pentlandite) or a Ni-bearing pyroxene that was trapped in this granite sample.

The cobalt levels have been found to be below limit in almost all samples examined, except one sample of pegmatite, P-4 provides 0.107 ppm. All other samples are below detection limits. Although effectively none of this quantitative data shows cobalt, it is one of the most globally important of all strategic minerals, a vital part of a lithium-cobalt-oxide (LCO), NMC, and NCA battery cathode chemistries in electric vehicles, of superalloys in gas turbine blades in aircraft and power generation, of cutting tools hard metals, and of medical implant alloys. The fact that it is only found, in a single sample, in P-4 is of geochemical interest; P-4 is one of the pegmatite samples and presents a unique chemical picture, with high Co, Cr and Mn compared to other pegmatite samples.

Rb concentrations are the highest recorded for this element in the entire dataset, MG-3 (4.238 ppm), MG-5 (4.200 ppm), MG-6 (3.106 ppm), MG-2 (2.989 ppm), MG-10 (3.075 ppm), MG-4 (2.325 ppm), MG-1 (2.252 ppm), MG-11 (1.339 ppm), MG-9 (1.241 ppm), MG-7 (1.240 ppm), MG-12 (0.769 ppm), and MG-8 (0.650 ppm). The concentrations of Rb are usually lower in the pegmatites: P-1 (0.402 ppm), P-3 (0.290 ppm), P-2 (0.190 ppm), and P-4, P-5 and P-6 are all below detection limits. MG-13 and MG-14 both give ADL results, which means that they are one of the most Rb-enriched in the dataset. Rubidium is a lithophile alkali metal, which typically replaces potassium in feldspars and micas and the pattern of its concentration in this study bears a strong resemblance to the potassium of each rock type and the extent of

fractionation. The significant loss of Rb in the early pegmatite (P-1 to P-4) relative to the granite, and then by the ADL enhancement in MG-13 and MG-14, is in keeping with the redistribution of the alkali elements during late-magmatic exsolution of feldspar, with Rb potentially being preferentially washed away by earlier crystallized grains. The difference in the consistent Rb-enriched granite suite and the intermittent Rb distributions of the pegmatites offers a convenient geochemical discriminator to evaluate the stage of evolution and crystallization of the separate pegmatite veins in the Mansehra Granite.

The critical mineral geochemistry of the Mansehra Granite and pegmatites show various critical elements having different enrichment patterns. Elements like Li, Be, Ga, Nb, V, U, Sb, and Rb can be found in low amounts throughout the main granite body. The pegmatite samples (P-1 to P-3) tend to show depletion of most of these elements compared with the granite, probably due to their crystallization being addressed by a relatively early, volatile-poor fraction of the melt in which many incompatible elements were still locked up. The late-stage pegmatites P-5 and P-6 show a stunning and selective enrichment of a group of high-value critical minerals, especially Sn (ADL), Ge (0.373 ppm), W (0.454 ppm), V (2.208 ppm), Cr (2.630 ppm), Sb (0.992 ppm), and Ni (ADL). MG-13 and MG-14 of the granite demonstrate ADL or maximum values of Nb (5.837 ppm), V (6.103 ppm) and Rb (ADL) and high levels of Li, Be, Ga, U and Hf, are the most geochemically anomalous rock bodies identified in this research (Fig. 4.4).

Table 4.1: Concentration of Critical Minerals in samples compared with Crustal Abundance (Rudnick and Gao, 2014) where Above Detection Limit (ADL) and Below Detection Limit (BDL)

Sample No.	Li	Be	Ge	Nb	Ta	V	U	Rb
MG-1	0.162	0.006	BDL	0.057	BDL	0.076	BDL	2.252
MG-2	0.280	0.006	BDL	0.079	BDL	0.124	0.133	2.989
MG-3	0.313	0.024	0.031	0.126	BDL	0.222	0.327	4.238
MG-4	0.155	0.015	BDL	0.051	0.014	0.086	0.156	2.325
MG-5	0.469	0.014	BDL	0.209	BDL	0.198	0.363	4.200
MG-6	0.372	0.015	0.077	0.190	0.008	0.161	0.324	3.106
MG-7	0.060	0.007	BDL	BDL	BDL	0.054	0.045	1.240
MG-8	0.082	0.011	BDL	0.037	BDL	0.086	0.050	0.650

MG-9	0.059	0.005	BDL	0.026	0.013	0.045	BDL	1.241
MG-10	0.253	0.019	BDL	0.117	0.017	0.145	0.165	3.075
MG-11	0.082	0.011	BDL	0.043	0.009	0.097	0.221	1.339
MG-12	0.078	0.008	BDL	0.035	0.015	0.111	0.116	0.769
MG-13	2.286	0.147	BDL	ADL	0.047	6.103	0.970	ADL
MG-14	1.655	0.143	BDL	5.837	BDL	4.998	0.785	ADL
P-1	0.002	0.001	BDL	BDL	BDL	BDL	BDL	0.402
P-2	0.003	0.001	0.143	BDL	BDL	BDL	BDL	0.190
P-3	0.006	0.001	BDL	BDL	0.011	0.009	BDL	0.290
P-4	0.009	BDL	BDL	0.039	BDL	0.012	0.074	BDL
P-5	0.389	0.048	0.111	0.218	BDL	0.840	0.103	BDL
P-6	0.782	0.028	0.373	0.112	BDL	2.208	0.249	BDL
Crustal Abundance	~24	~2.1	~1.4	~12	~0.91	~97	~2.7	~84

Sample No.	Sn	W	Cr	Hf	Zr	Sb	Ni	Co
MG-1	0.705	BDL	BDL	0.004	BDL	0.084	2.597	BDL
MG-2	BDL	BDL	0.050	BDL	BDL	BDL	BDL	BDL
MG-3	BDL	BDL	0.004	0.006	BDL	0.063	BDL	BDL
MG-4	BDL	BDL	BDL	BDL	0.001	0.048	BDL	BDL
MG-5	BDL	BDL	0.007	BDL	0.004	0.025	BDL	BDL
MG-6	BDL	BDL	BDL	0.006	BDL	0.100	BDL	BDL
MG-7	BDL	BDL	BDL	0.006	BDL	0.062	BDL	BDL
MG-8	BDL	BDL	BDL	0.006	BDL	0.084	BDL	BDL
MG-9	BDL	BDL	BDL	0.004	BDL	0.075	0.029	BDL
MG-10	BDL	BDL	BDL	BDL	0.002	0.067	BDL	BDL
MG-11	BDL	BDL	BDL	BDL	BDL	0.052	BDL	BDL
MG-12	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
MG-13	0.018	0.037	1.186	0.042	0.081	0.069	0.384	BDL
MG-14	0.018	BDL	1.047	0.033	0.051	0.077	0.240	BDL
P-1	BDL	BDL	BDL	0.003	BDL	0.069	BDL	BDL
P-2	BDL	BDL	BDL	0.006	BDL	0.130	BDL	BDL
P-3	BDL	BDL	BDL	BDL	BDL	0.057	BDL	BDL
P-4	BDL	BDL	0.018	0.036	0.019	BDL	0.106	0.107
P-5	ADL	0.454	2.630	BDL	0.008	0.992	ADL	BDL
P-6	ADL	0.078	0.014	0.006	0.013	0.459	ADL	BDL
Crustal Abundance	~2.3	~1.9	~83	~3.7	~165	~0.4	~47	~17.3

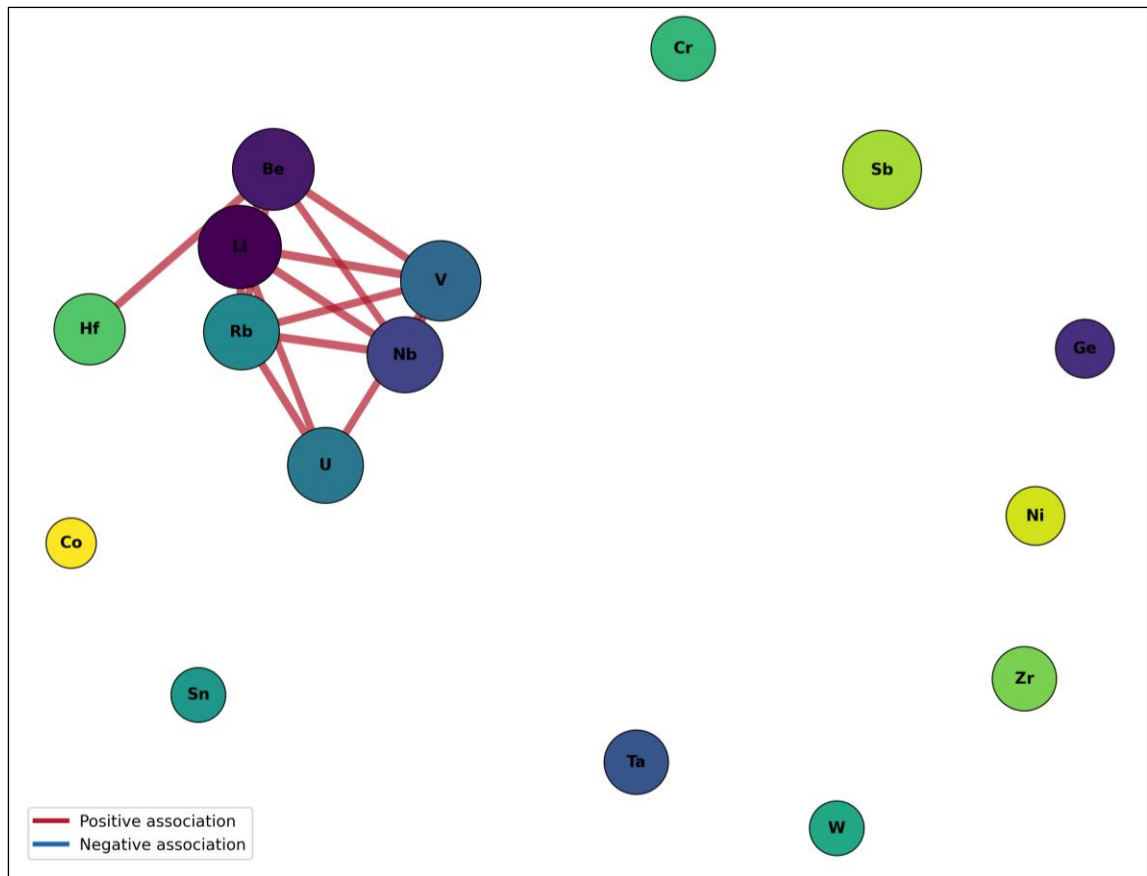


Figure 4.4 Network diagram of statistically significant strong correlations (Spearman $\rho \geq 0.80$) among critical minerals. Node size reflects the number of significant correlations for each element, highlighting the Li-Be-V-U-Nb-Rb co-enrichment cluster and the independently behaving Cr-Hf-Zr-Sb group

4.1.1 Comparative Analysis of Critical Mineral Results with Crustal Abundance

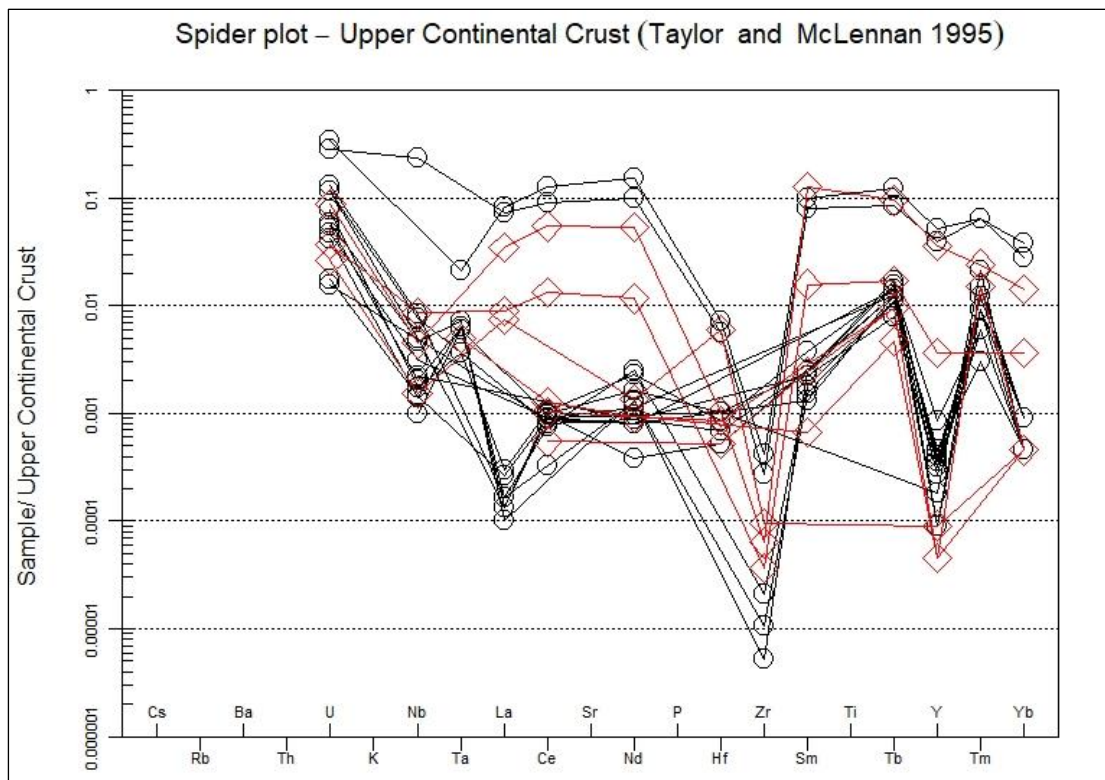


Figure 4.5 Upper continental crust (UCC)-normalized multi-element spider diagram for all granite (open circles) and pegmatite (red diamonds) samples, normalized to the UCC reference values of Taylor and McLennan (1995)

The abundance of Lithium (Li) in the samples studied ranges from 0.002 to 2.286 ppm, while the average abundance in the upper continental crust is 24 ppm (Rudnick and Gao, 2014). All of the measured values are below crustal abundance, however the gradual increase of Li in P-5, MG-13 and MG-14 indicates enrichment at advanced stages of magmatic evolution. The same behavior is noticed with Beryllium (Be), which has a maximum concentration of 0.147 ppm, but an average crustal abundance of 2.1 ppm (Rudnick and Gao, 2014). The enrichment of Li and Be in the evolved samples reflect what is known of the incompatibility of these lithophile elements, with tendency to be concentrated in residual melts during fractional crystallization (Fig. 4.5).

Niobium (Nb) and Tantalum (Ta) have lower concentrations than the average crustal levels. The peak concentration of Germanium (Ge) is 0.373 ppm, significantly lower than the crustal abundance of 1.4 ppm (Rudnick and Gao, 2014). Similarly, the highest Nb concentration of 5.837 ppm is lower than the average crustal abundance of 12 ppm, and Ta is 0.047 ppm, less than the crustal abundance of 0.9 ppm (Rudnick and Gao, 2014). However, the enrichment of Nb in MG-14 suggests that it may contain Nb-bearing accessory minerals such as columbite-tantalite or pyrochlore, which are frequent in highly fractionated granitic systems (Barth et al., 2000).

Vanadium (V) and chromium (Cr) are highly depleted in relation to their crustal abundances. The highest concentration of V is 6.103 ppm, which is significantly lower than its average crustal abundance of 97 ppm, the highest concentration of Cr is 2.630 ppm, significantly lower than the average crustal abundance of 92 ppm (Rudnick and Gao, 2014). This depletion is predicted due to their common association with mafic and ultramafic rocks as opposed to felsic granitoid systems. The concentration of Cr, however, is elevated in P-5, which could be due to a localized concentration caused by accessories minerals.

The maximum Uranium (U) concentration was 0.970 ppm. This is lower than the average crustal abundance of 2.7 ppm reported by Rudnick and Gao (2014). The progressive enrichment of uranium toward more evolved pegmatite samples indicates that uranium was an incompatible element in magmatic differentiation and became increasingly enriched in last magmatic stages.

Germanium (Ge), tungsten (W), and tin (Sn) are selectively concentrated in the late-stage pegmatites, especially in P-5 and P-6. Although they have lower concentrations than the average crustal abundances of 2.1 ppm for Sn, 1.9 ppm for W, and 1.4 ppm for Ge (Rudnick and Gao, 2014), their presence in evolved pegmatitic zones is significant. The presence of above-detection-limit Sn values, along with elevated W and Ge concentrations indicates that these pegmatites were highly fractionated parts of the magmatic system that were capable of concentrating these elements.

The enrichment of antimony (Sb) is most significant of all elements studied relative to the average crustal abundance. The abundance of Sb in P-5 is 0.992 ppm, more than twice the average abundance of crustal material (0.40 ppm) (Rudnick and

Gao, 2014). This enrichment is a sign of efficient mobilization and concentration of antimony in the late magmatic processes, and it suggests that evolved pegmatite veins are likely to be sites for Sb mineralization (Fig. 4.6).

The concentrations of hafnium (Hf), zirconium (Zr), nickel (Ni), cobalt (Co), and rubidium (Rb) compared to their average crustal abundance are lower. The maximum concentration for Hf is 0.042 ppm, which is significantly lower than the average crustal abundance of 5.3 ppm, and the highest concentration for Zr is 0.081 ppm, which is low compared to the average crustal abundance of 193 ppm (Rudnick and Gao, 2014). The maximum concentrations for Ni and Co are 2.597 ppm and 0.107 ppm, respectively. Ni and Co are highly depleted compared with average crustal abundances of 47 ppm and 17.3 ppm (Rudnick and Gao, 2014). The highest measured concentration of rubidium is 4.238 ppm, much less than the average crustal abundance of 84 ppm (Rudnick and Gao, 2014). Such depleted concentrations are typical of the felsic and peraluminous nature of the Mansehra Granite, which has low proportions of ferromagnesian and heavy-mineral phases.

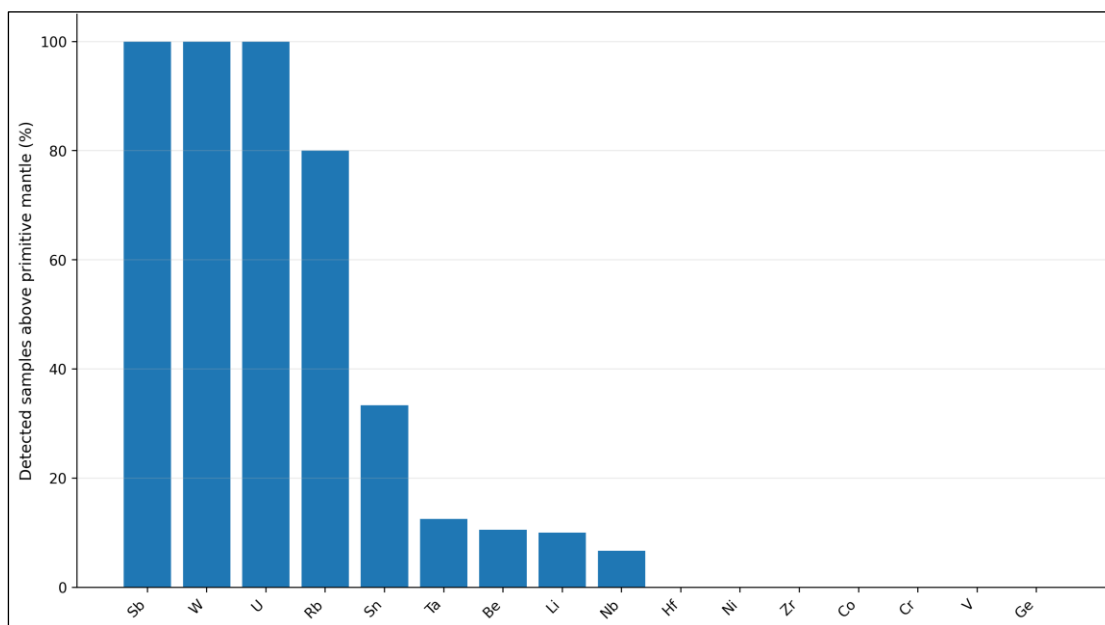


Figure 4.6 Bar chart showing the frequency at which detected samples exceed primitive mantle values for each critical element, expressed as a percentage of detected samples. Elements are arranged in descending order of enrichment frequency, with Sb, W, and U consistently exceeding the primitive mantle reference

Comparison with upper continental crust abundances shows that the Mansehra Granite and associated pegmatites are generally depleted in most critical elements as compared to average upper continental crustal abundances (Rudnick and Gao, 2014). Localized enrichments of the elements are seen in the evolved pegmatites and mineralized samples, but at lower concentrations they remain below levels typically associated with economically extractable deposits. On the basis of the geochemical data recorded in this study, the study area does not seem to have significant economic potential in terms of critical mineral extraction.

Though the potential for critical minerals is limited, the Mansehra Granite still has industrial importance as a raw material. Granite is used as a dimension stone in construction, such as building facades, flooring, wall cladding, countertops, monuments, aggregates, and decorative architecture because of its mineralogical composition, durability, high compressive strength, low porosity and appearance. The granite studied therefore is not a suitable source of critical minerals, but it has significance in construction and building stone industry.

4.2 Other Elements

The geochemical data for the Mansehra Granite and pegmatites includes a wide range of non-critical elements. These include the precious metals, gold (Au) and silver (Ag); the base metals, copper (Cu), lead (Pb), zinc (Zn), cadmium (Cd) and thallium (Tl); the platinum group elements, palladium (Pd), platinum (Pt), iridium (Ir), and ruthenium (Ru); the major rock-forming elements, aluminum (Al), silicon (Si), iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), phosphorus (P) and sulfur (S); the minor and accessory elements, barium (Ba), strontium (Sr), titanium (Ti), boron (B), manganese (Mn); the rare earth elements (REEs), yttrium (Y), scandium (Sc), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), erbium (Er), thulium (Tm), ytterbium (Yb), and Mercury (Hg), molybdenum (Mo), rhenium (Re), rhodium (Rh), indium (In), selenium (Se), and bismuth (Bi) were not detected in any samples and hence are considered

geochemically unimportant for the rocks in the studied rock suite. All these elements demonstrate a certain concentration range as well as inter-sample variability, and their geochemistry in granite and pegmatite veins will be discussed in the following sections.

Gold is sporadically distributed in the dataset; in only four samples, measurable amounts of gold were detected. In the granite suite trace values of 0.006 ppm and 0.008 ppm are recorded in MG-8 and MG-11, respectively. The highest Au concentrations are recorded in MG-13 (0.366 ppm) and MG-14 (0.114 ppm); the spatial association with high arsenic concentrations in both these samples (MG-13: 0.261 ppm; MG-14: 0.037 ppm) is consistent with the gold-arsenopyrite paragenesis typical of intrusion-related gold mineralization systems (Lehmann, 2021). Arsenic is otherwise limited to granite phase (0.007-0.108 ppm in selective samples) and is universally below detection in all pegmatite veins. The granite suite shows a much wider range of distribution for silver (range 0.002 to 0.023 ppm) and the pegmatites (P-1 to P-4: range 0.007 to 0.012 ppm). The most significant Ag enrichment takes place in P-5 (0.151 ppm), which is the highest Ag value in the data set, and is indicative of the chalcophile behavior of silver.

The distribution of copper, lead, and zinc is one of the most coherent in the data set, with all of these elements being depleted in the early pegmatites and highly enriched in the late pegmatites and late granites. Copper is found in all samples from the granite suite (0.012-0.317 ppm). MG-1 has an ADL designation, and MG-13 and MG-14 have the highest precisely quantified concentrations of copper at 1.125 ppm and 0.599 ppm, respectively. While the early pegmatites are relatively copper depleted (P-1 to P-4: 0.007-0.038 ppm), Both late pegmatites (P-5 and P-6) have ADL copper values. Lead is sporadic within the granites and only present in MG-1, MG-3, MG-9, MG-13 and MG-14, at 0.271, 0.115, 0.685, 0.871, and 0.597 ppm respectively. Lead is absent in the early pegmatites and returns to ADL designations in P-5 and P-6. Zinc is the most evenly distributed of the base metals, from 0.042 ppm to 1.593 ppm throughout the granite suite and maximum quantified concentrations of 1.953 ppm and 1.709 ppm for MG-13 and 14, respectively, and ADL in the late pegmatites. Cadmium follows a similar pattern, increasing from a fairly low granite base of 0.001-0.002 ppm to higher pegmatite values (P-4: 0.007 ppm; P-5: 0.033 ppm; P-6: 0.018 ppm). Thallium, however, is anomalous with the highest concentrations found in the

early pegmatites, P-1 (0.070 ppm) and P-2 (0.055 ppm), with no concentrations detected in P-3 to P-6.

The occurrence of significant amounts of platinum-group elements in this silicic system is unexpected and geochemically important. With concentrations ranging from 0.056 ppm to 0.132 ppm, palladium is detected in eight of the granite samples, with concentrations as high as 0.513 ppm in P-5 and 0.299 ppm in P-6. In the granites, ruthenium is present in very low concentrations (0.003 to 0.045 ppm), but its concentration in P-5 is comparatively higher (1.038 ppm) and together with the ADL iridium designation for the same sample, it defines P-5 as the most PGE-enriched sample in the data set. The concentration of Ir in MG-1 is also anomalous (0.381 ppm) compared with the next highest granite concentration. Platinum is low and localized in the granite and early pegmatites (0.010-0.029 ppm), whereas it is absent from the late pegmatites, which are highly enriched in Pd, Ir and Ru. The presence of PGEs in this felsic system is most likely a secondary process involving remobilization of PGE-bearing phases from a mafic enclave component as described by Zafar et al. (2019).

The major rock-forming elements (aluminum, silicon, iron, calcium, magnesium, sodium, potassium, and phosphorus) show a systematic bimodal distribution which directly reflects the crystallization history of the Mansehra Granite. The consistently high to ADL concentrations of all major elements define the main granite body (MG-1 to MG-12) as having a mature mineralogical assemblage of K-feldspar, plagioclase, biotite, muscovite, quartz and apatite. The ADL designation for both potassium and phosphorus of the whole granite suite is in perfect agreement with the S-type classification of Naeem et al. (2021) and Sajid et al. (2018) as the parent melt of the granite was strongly peraluminous, K-feldspar saturated and apatite bearing. The pegmatites (P-1 to P-3) are virtually depleted in all major elements, with aluminum below detection or at trace levels, the concentration of 0.002-0.111 ppm for iron, 0.076-8.008 ppm for calcium, the absence of magnesium, and the complete absence of sodium, indicating crystallization from an early melt fraction that contains few volatiles and is rich in quartz or mineralogy rich in tourmaline. The late pegmatites and late granites show a sharp reversal toward enhancement in terms of ADL values, which are an enrichment of aluminum, iron, calcium, magnesium, sodium, and potassium, substituting the mineralogically less complex late-stage

assemblages. The enrichment of silicon from below detection levels in the early pegmatites, to 5.753 ppm in P-5, 6.049 ppm in P-6 and 6.218 ppm in MG-14, is consistent with quartz veining and silicic alteration occurring in the peripheral zones of evolving granitic intrusions which are normally observed as a result of residual silica mobilization (London, 2018). The distribution of sulphur is fairly homogenous in both rock types (0.448-3.456 ppm in granite; 0.448-1.867 ppm in pegmatites), reflecting a relatively widespread background sulphide mineralization event.

Minor elements, such as barium, strontium, titanium, boron and manganese, are geochemically informative elements and support the two-stage pegmatite crystallization model. Barium, in general, closely follows potassium, with a low background level in the granite (0.009-0.046 ppm), depleted through the early pegmatites, then sharply enriched in the late pegmatites (P-5-P-6: 0.305-0.679 ppm) and a data maximum of 5.547 ppm at MG-14, indicating secondary barite or barium-enriched orthoclase precipitation in the most evolved pegmatites. The granite suite and pegmatites are virtually devoid of strontium except for its high concentration in P-6 (1.892 ppm) and MG-13 (2.344 ppm). The late pegmatites (P-5: 2.374 ppm) show a progressive increase in titanium with granite (0.160-1.236 ppm) and the ADL values are encountered in MG-13 and MG-14. The manganese enrichment arc is similar to that of the other elements, being severely depleted in the early pegmatites (0.016-0.028 ppm), and re-enriched in P-5 (5.431 ppm) and P-6 (2.251 ppm) with ADL values in MG-13 and MG-14. Boron is the most geochemical diagnostic of this group, with uniform detection throughout the granite (0.005-0.132 ppm), and with dataset max of 1.218 ppm and 0.917 ppm in MG-13 and MG-14.

The geochemistry of the rare earth elements in the Mansehra Granite shows a well-ordered history of multiple stages of concentration, with the sequential crystallization of accessory mineral phases controlling the rare earth element (REE) geochemistry (Bea, 1996; London and Cerny, 2008). The REE content of the main granite body is characterized by a fairly uniform background REE content with moderate enrichment in the light REEs and fairly uniform detection of the heavy REEs throughout the 12 granite samples, indicating the disseminated occurrence of zircon and apatite as the primary host phases throughout the granitic mass (Bea, 1996). The pegmatites (P-1-P-4) are generally REE depleted with most of the individual elements being below or at the minimum detection limits, reflecting the

crystallization of a leucocratic, early melt fraction that lacked much monazite, xenotime and allanite. A sharp REE enrichment trend begins in the late pegmatites and is the most pronounced in the evolved granite domain, where the whole REE spectrum is enriched at the same time. The LREE enrichment in MG-13 and MG-14 is particularly pronounced: Ce attains 8.254 ppm and 5.731 ppm, Nd reaches 3.936 ppm and 2.603 ppm, La reaches 2.472 ppm and 2.207 ppm, Pr reaches 1.122 ppm and 0.908 ppm, Sm reaches 0.442 ppm and 0.358 ppm, and Gd reaches 1.204 ppm and 0.900 ppm. The high thorium (MG-13: 1.820 ppm; MG-14: 1.394 ppm) concentrations in the same samples, together with the elevated uranium concentrations (MG-13: 0.970 ppm), all confirm the presence of monazite as the most important accessory phase within these evolved zones, where thorium is well known to be charge coupled into the monazite crystal structure (Ahmed et al., 2014). Similarly, in these samples, HREE enrichment appears coherent for yttrium (1.159 ppm, 0.857 ppm), erbium (0.210 ppm, 0.144 ppm), lutetium (0.169 ppm, 0.123 ppm), and dysprosium (0.161 ppm, 0.106 ppm) in MG-13 and MG-14, respectively. The concentrations of europium are fairly constant throughout the granite (max. 0.007 ppm) and pegmatites (0.002-0.003 ppm). Scandium is uniquely enriched in MG-13 and MG-14 (0.099 ppm and 0.086 ppm respectively) (Fig. 4.7).

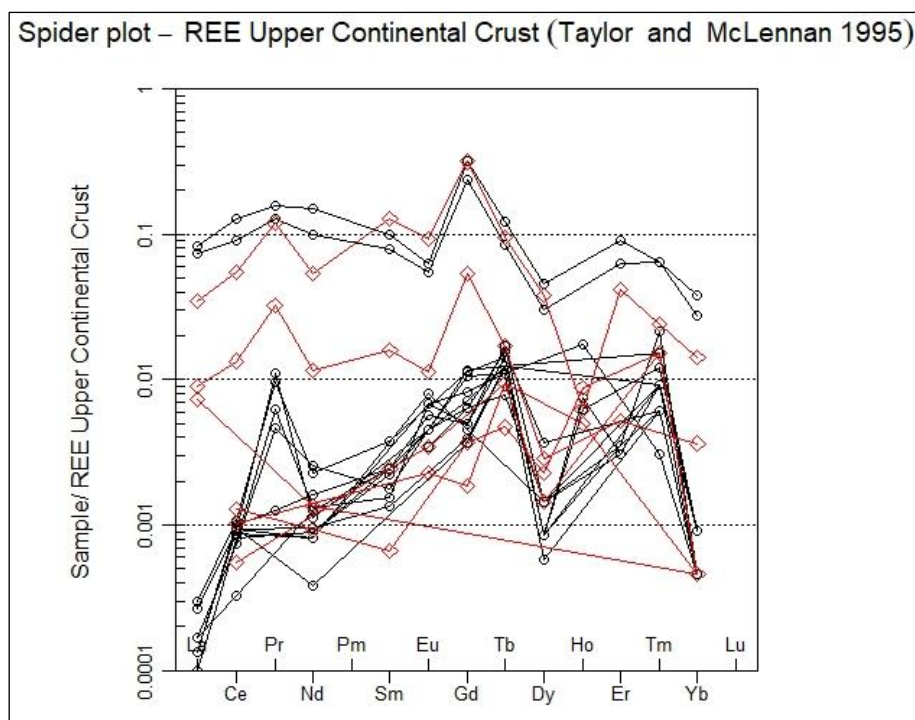


Figure 4.7 Rare earth element (REE) spider diagram for all granite (open circles) and pegmatite (red diamonds) samples, normalized to the upper continental crust reference of Taylor and McLennan (1995)

Tellurium is found at levels below detection in 6 granite samples and at 0.013-0.049 ppm in the remaining samples, it is not detected in the early pegmatites and becomes increasingly enriched in the late pegmatites (P-5: 0.103 ppm; P-6: 0.060 ppm) and granites (MG-13: 0.156 ppm; MG-14: 0.100 ppm). Geochemical association of Te with anomalous gold concentrations in MG-13 is coherent with gold-telluride association typical of intrusion related mineralizing system for gold, indicating a Te-Au mineralizing event in the most evolved parts of the Mansehra complex. Thorium is one of the most ubiquitous elements in the entire analytical suite, with concentrations ranging from 0.013 ppm to 1.820 ppm in all granite samples. This distribution is similar to the LREE enrichment trend and supports the hypothesis of monazite enrichment as the dominant process in the more mineralogically advanced parts of the Mansehra Granite.

As a whole, the geochemical data presented in this section describe a magmatic system in which the early pegmatite generation represents a

compositionally barren, volatile-deficient crystallization stage, whilst the late pegmatites and late granite samples define a terminal mineralized zone in which base metals, precious metals, platinum-group elements, rare earth elements, and critical accessory indicator elements are simultaneously concentrated in low to trace amounts. This multi-element enrichment convergence in P-5 through MG-14 constitutes a coherent and geologically robust geochemical anomaly consistent with the metallogenic character of LCT-type, highly fractionated peraluminous granite-pegmatite systems documented globally, including the Cuonadong and Lalong dome systems of the Tethyan Himalaya (Xie et al., 2020; Li et al., 2023), and provides the strongest available geochemical basis for identifying these evolved rock volumes as the primary target for follow-up mineralogical characterization and resource evaluation within the Mansehra Granitic Complex.

4.2.1 Comparative Analysis of Other Elements Results with Crustal Abundance

The abundance of the elements analyzed in the Mansehra Granite and the associated pegmatite veins in the analyzed samples has been compared with the average abundance for the Upper Continental Crust (UCC) according to Rudnick and Gao (2014). Most of the elements analyzed in the Mansehra Granite and the associated pegmatite veins are found at concentrations that are well below the average abundance of the Upper Continental Crust (UCC). Precious metals (Au, Ag), and the platinum-group elements (Pd, Pt, Ir, and Ru) as well as base metals (Cu, Pb, Zn, and Cd) are typically found in low concentrations and are not economically significant. Likewise, most of the rare earth elements (REEs) are enriched in MG-13 and MG-14 but are still not particularly high in concentration to be considered an economically viable REE deposit.

Some elements (Cu, Pb, Zn, Mn, Ba, Sr, Th, Te, and the REEs) are found to be locally enriched in the pegmatites (P-5 and P-6) and granite samples (MG-13 and MG-14) as a result of progressive magmatic differentiation and concentration of incompatible elements at the later crystallization stages. The high concentration of

REEs in association with elevated Th and U concentrations indicate the presence of accessory minerals like monazite, zircon and apatite, which were important host minerals during magmatic evolution (Bea, 1996; Ahmed et al., 2014).

The concentration of these elements is generally low, though there are some enrichments at localized scales, which are not high enough for commercial extraction. Thus, the geochemical data indicate that industrial potential for Precious Metals, base metals, Platinum Group Elements and Rare Earth Element in the Mansehra Granite and related pegmatite veins is limited. While the rocks studied in this work are not economically important for metal extraction, the Mansehra Granite is still very economically significant as a dimension stone and construction stone. Due to its high percentage of quartz-feldspar, resistance to weathering and attractive qualities, it is used in building stone, flooring, wall paneling, decorative stonework, monuments, aggregates and other civil engineering projects.

CHAPTER 5

DISCUSSION

Twenty samples of the Mansehra Granite and related pegmatites yield a geochemical dataset of ICP-MS data, which show a highly evolved, peraluminous magmatic system, where trace element patterns are controlled by both fractional crystallization and accessory mineral phase control and by the progressive enrichment of incompatible elements into the late-stage magmatic residues. The near-universal sub-crustal abundances found for all elements analyzed are not unusual for such a petrogenetic system, as the Mansehra Granite crystallized from a metasedimentary protolith that was geochemically not unusual in any specific suite of metals (Rudnick and Gao, 2014). This interpretation is in accordance with the geochronological and geochemical framework proposed by Sajid et al. (2018) which constrained the age of emplacement of the Mansehra Granitic Complex to ~480 Ma using U-Pb zircon geochronology and determined a high-K calc-alkaline to peraluminous signature with strong LREE enrichment and pronounced negative Eu anomalies, which are interpreted as the result of plagioclase fractionation during crustal melting. According to the present ICP-MS results, the granite suite shows above detection limit (ADL) concentrations of Rb, depleted concentrations of Ba and Sr, and a systematically low concentration of Ti, a combination noted by Chappell and White (2001) as diagnostic of highly evolved S-type granite evolution and recently identified by Wu et al. (2017) as diagnostic critical fertility indicators in highly fractionated granites of South China.

The negative Eu anomaly, with Eu consistently between 0.003 and 0.007 ppm throughout the main granite body, is a direct result of the fractionation of plagioclase, which is able to accommodate divalent Eu^{2+} in its crystal lattice at the expense of the trivalent REE neighbors (Bea, 1996). Such signatures are reported many times in peraluminous, collisional granites from the Himalayan belt, such as in the highly fractionated leucogranites of the Tethyan Himalaya, as documented by Wu et al.

(2020), where similarly subdued Eu anomalies are accompanied by progressive LREE enrichment from two-mica granites to muscovite granites to pegmatite-aplite phases. The Mansehra Granite is an example of this type of evolution. In the main granite body (MG-1 to MG-12), Ce ranges from below detection to 0.068 ppm and Nd from 0.010 to 0.066 ppm, whereas MG-13 and MG-14 record dramatically elevated Ce at 8.254 and 5.731 ppm, La at 2.472 and 2.207 ppm, and Nd at 3.936 and 2.603 ppm respectively. The enrichment of Th (1.820 ppm in MG-13) and U (0.970 ppm) together with LREE indicates monazite as the most important accessory mineral controlling the REE budget in the evolved zones, in agreement with the well-established charge coupled substitution of Th^{4+} for Ce^{3+} in the monazite lattice (Ahmed et al., 2014; Bea, 1996). The above inference is supported worldwide: Xie et al. (2020) documented LREE, Th and U co-enrichment in the highly fractionated leucogranites and pegmatite-aplite phases of the Cuonadong dome in the eastern Himalaya and attributed the pattern to crystallization of monazite during terminal evolution of melt. The enrichment of Y (1.159 ppm) and Er (0.210 ppm) and Lu (0.169 ppm) in MG-13 further shows a mixed assemblage of accessory minerals (monazite, zircon and xenotime) typical of granites of peraluminous affinity, as commonly found in granites globally (Bea, 1996). The progressive enrichment of both Hf (0.042 ppm) and Zr (0.081 ppm) in the MG-13 and MG-14, is further evidence for disseminated crystallization of zircons in the most Late-Stage magmatic domain, as shown in the leucogranites of the Lalong Dome in the Tethyan Himalaya, which contain both zircon, columbite-group mineral and beryl that co-crystallized in the most evolved granite domains of the leucogranites (Li et al., 2023).

The pegmatite samples (P-1 to P-4) are systematically lower in virtually all element categories than the host granite with Li content dropping to 0.002-0.009 ppm, Be dropping to 0.001 ppm or below detection limit, and Nb, Ta, V, U, and Rb returning below detection limit in most samples. This whole depletion is consistent with crystallization from an early melt fraction depleted in volatiles that has been extracted prior to the concentration of incompatible element inventory in the residual melt, as observed by London (2018) in initial pegmatite veins that are leucocratic and represent quenched melt rather than true residual differentiates. The geochemical reversal in the pegmatites (P-5 and P-6) and granite samples (MG-13 and MG-14) is, therefore, consistent with the onset of true residual-melt crystallization, in which

incompatible elements that have concentrated as the result of prolonged fractional crystallization are freed into a relatively small volume of volatile-rich late-stage melt. The co-enrichment of W (0.454 ppm, P-5), Sn (ADL, P-5-P-6), Ge (0.373 ppm, P-6), Sb (0.992 ppm, P-5), V (2.208 ppm, P-6), and Mn (5.431 ppm, P-5) collectively defines an anomalous late-stage assemblage geochemically similar at much lower absolute concentrations to the Sn-W-Be mineralization documented in the Cuonadong dome pegmatites by Xie et al. (2020). The co-enrichment of W and Sn is in line with the fluid partitioning models of Linnen and Cuney (2005), who showed that these elements are highly incompatible in silicate melts close to volatile saturation, and they tend to partition into the exsolving aqueous fluids, a process identified by Lehmann (2021) as characteristic of highly evolved leucogranite-related systems in the Himalayan metallogenic context. The higher Nb contents observed in MG-14 (5.837 ppm) and ADL (2.535 ppm) than the granite background (0.026-0.209 ppm) also indicate that the columbite-tantalite or pyrochlore was formed during the most evolved stages of the system, as seen by Barth et al. (2000), Wang et al. (2017), who reported Nb enrichment in columbite-group oxides in the most differentiated phases of the Himalayan leucogranite plutons.

In Pakistan, the Mansehra Granite has instructive comparisons within the Regional context in the northern Orogenic domain of the country. The Be-Li-Nb-Ta pegmatites of the Shigar Valley, Gilgit-Baltistan, recently characterized as crustal anatexis in a syn-collisional tectonic setting (Karim et al., 2026) with peraluminous geochemistry, negative Eu anomalies and depletion in Ba-Sr-Ti, are the closest geochemical analogue to the Mansehra Granite, and their higher content of rare metals may result from more advanced fractional crystallization or from more fertile metasedimentary protoliths. The pegmatite bodies that host a documented REE mineralization in chevkinite and monazite in syenite associated bodies in Tangir-Darel, Kohistan Island Arc, are genetically different from the other pegmatites of the orogeny, which belong to the NYF-type metallogenic system and are linked to alkaline crustal melts instead of peraluminous crustal melts (Hussain et al., 2020). The Swat-Dir belt of Khyber Pakhtunkhwa has also been found to be a region of REE and critical mineral potential, in the granitic and pegmatite terranes, from preliminary assessments undertaken by Geological Survey of Pakistan (Malkani, 2020), which

further underscores the regional importance of systematically characterizing peraluminous granitoid systems in this sector.

The Au-As-Te association concentrated in MG-13 (Au 0.366 ppm, As 0.261 ppm, Te 0.156 ppm) constitutes a geochemically coherent intrusion-related gold signature consistent with transport of gold as bisulfide and chloride complexes in reduced fluids exsolved from crystallizing granites (Lehmann, 2021). Whereas, the irregular PGE concentrations, Pd 0.513 ppm and Ru 1.038 ppm in P-5, together with Ir ADL in the same sample are most likely remobilized signatures from incorporated mafic xenolith material, consistent with the melt-host interaction observed by Zafar et al. (2019). The overall geochemical data suggest that the magmatic system has progressed toward rare-metal enrichment but not reached the extreme fractional crystallization conditions necessary to form ore grade concentrations similar to the globally important LCT-type deposits of Greenbushes, Tanco or the Cuonadong dome (Cerny and Ercit, 2005; London, 2018; Xie et al., 2020).

It must be emphasized that the presence of accessory minerals like monazite, xenotime, zircon and columbite group minerals, observed here and discussed, was inferred only from the bulk geochemical signatures and elemental associations as determined by ICP-MS analysis. The distribution patterns of REEs, Nb, Ta, Th, U, Zr, Hf and related trace elements are consistent with the established geochemical behavior of these accessory mineral phases in highly evolved peraluminous granitic and pegmatite systems (Bea, 1996; London, 2018; Cerny and Ercit, 2005) but have not been confirmed by direct mineralogical or petrographic evidence. Thus, the proposed mineralogical interpretations should be considered geochemically derived, and not mineralogically proven. It is recommended that future studies be conducted to confirm the occurrence, composition and paragenesis of these accessory minerals and further narrow down the metallogenic interpretation of the Mansehra Granite and related pegmatite veins, using petrographic examination, scanning electron microscopy (SEM), electron probe microanalysis (EPMA) or laser ablation ICP-MS (LA-ICP-MS).

CONCLUSIONS

The geochemical assessment of the Mansehra Granite and its associated pegmatite veins using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) established the elemental composition of the investigated rocks and provided a geochemical dataset for the study area. The analytical results demonstrate that the majority of trace elements, critical minerals, and rare earth elements occur at low concentrations, with many values reported below the detection limit. Although relatively higher concentrations of selected elements, including Li, Be, Nb, Rb, Th, U, Zr, Hf, Sb, and W, were recorded in Samples MG-13, MG-14, P-5, and P-6 compared with the remaining samples, their abundances remain substantially below levels generally associated with economically significant rare-metal mineralization. Consequently, the investigated Mansehra Granite and associated pegmatite veins are interpreted to be geochemically barren with respect to economically viable concentrations of critical minerals and rare earth elements. Furthermore, the inferred occurrence of accessory minerals such as monazite, xenotime, and zircon minerals is based solely on bulk-rock geochemical signatures and elemental associations and therefore remains geochemically inferred rather than mineralogically verified. Overall, this study represents a geochemical characterization of the Mansehra Granite and its associated pegmatites and contributes to the regional geological knowledge of the Mansehra Granitic Complex rather than indicating the presence of economically exploitable critical mineral resources.

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