

ROLE OF TECTONIC INDUCED METAMORPHISM ON THE PETROGENESES OF BARITE DEPOSITS HOSTED IN TANAWAL FORMATION, PAKISTAN: PETROGRAPHIC AND GEOCHEMICAL PERSPECTIVES

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Abstract

Barite (barium sulfate, BaSO₄) is very important in the oil and gas industry because it is a key ingredient in the oil base mud (OBM) used in the drilling of oil and gas wells. Elemental barium is an additive in optical glass, ceramic glazes, and other products. Based on occurrences, Barite have following four main types: bedded-sedimentary; bedded-volcanic; vein, cavity-fill, and metasomatic and residual. This study considered the formation, occurrence and distribution as well as the utilization and challenges facing in the mining of barite. Extensive fieldwork, selective sampling, petrographic and geochemical analysis were adopted as basic methodology for achieving the objectives of this study. Regional metamorphism in response to local tectonics act as the prominent controlling factors for the formation and paragenesis of barite deposits in the Khanano Dheri Buner area, Pakistan. Genetic relationship of barite deposits hosted in metamorphosed Tanawal Formation located in the lesser Himalayan zone will help in understanding the evolution of other economic mineralization in the region. Field observations, petrographic examination and analytical data interpretation indicate that the formation of barite is closely associated to the tectonic evolution of the region. The deposits are primarily hydrothermal vein deposits, in which barite crystallize from hydrothermal fluids during its migration and circulation in the host formation. This research provides a basic clue for the genesis of barite in high grade metamorphic terrain by hydrothermal mineralization, exhibiting the impact of tectonic evolution, geological history, and stratigraphic framework. Interpretation of geochemical analysis indicate that these barite deposits are epigenetic, formed through the interaction of hydrothermal fluids evolved from solidifying magma in a failed rift system of Permian age. Geochemical analysis reveals significant variations in the concentration of oxides concentrations observed in different samples. We observed inverse relationship between barium oxide (BaO) and sulfur trioxide (SO₃), indication an increase in the concentration of BaO triggers decrease in SO₃ concentration, demonstrating geochemically incompatibility. Furthermore, cross plot of CuO vs FeO represents

an inverse relationship, exhibiting visible geochemical incompatibility between Cu and Fe. Moreover, the concentration of SrO decrease with decreasing CaO, represents direct relationship and probable geochemical compatibility between Ca and Sr. It has been observed that geochemical compatibility of ZnO and CuO varies significantly, indicating direct relationship as well as similar geochemical compatibility. In most of the analyzed samples the concentration of K₂O is higher as compared to FeO, but exhibiting similar increase, represents a possible geochemical compatibility between K and Fe. Similarly, the concentration of ZnO remained relatively constant in the investigated samples and its interpretation reflects that its relationship in cross plot with SrO is inverse. The concentration of CuO decreases with the increasing amount of CaO, reflecting inverse relationship as well as geochemical incompatibility in the investigated samples.

INTRODUCTION

Barite (BaSO₄) is a high density, chemically stable sulphate mineral with significant industrial and economic importance (Bageri et al., 2020; Arabi et al., 2023). Over 80% of barite produced globally is used in the oil industries as a weighting agent in drilling fluids and other industrial application around the world (USGS 2017, 2019; Garside, 2020; Afolayan et al., 2021). Other application of barite is in chemical and industrial process such as mineral fillers in various products e.g., paints, plastics, rubber, concrete, brake pads, and clutch plates and barium chemicals, white pigment and paper industry (Ciullo, 1996; Bonel, 2005; Abraham et al., 2021).

Barite deposit is broadly distributed in space and time and occurring in a range of geological environments, including metamorphic (Hanor, 2000), sedimentary (stratiform/stratabound) (Kontak et al., 2006; Deb and Pal, 2015), marine (Monnin and Cividini, 2006), magmatic e.g. metasomatic and residual concentrations, and volcanogenic or bedded-volcanic (Williams Jones et al., 2000) and hydrothermal vein deposits by hydrothermal solutions and cavity-fill types (Margoum et al., 2015; Nadoll et al., 2019; Walter et al., 2019, 2020; Okubo et al., 2020; Muller and Ehle, 2021). Hydrothermal vein-type deposits generally associated with rift valleys, basement-cover unconformities, and large-scale crustal lineaments or fault systems (Walter et al., 2020). Vein-type barite mineralization also formed under a wide range of pressure, temperature, and different fluid sources in a wide geological time domain (Hanor, 2000; Staude et

al., 2011, Walter et al., 2020, Zou et al., 2021). Hydrothermal barite form through the precipitation of Ba-bearing fluids along faults and fractures, often in association with base-metal sulfides. In rifted or extensional basins, fault controlled hydrothermal discharge and mixing with seawater or meteoric water can result in generation of high-grade barite lenses or veins. On the other hand, stratiform barite is linked to basin processes, biogeochemical cycling, cold-seep or venting environments and diagenetic concentration of barium in restricted basins (Hanor, 2000). Determining which of these genetic pathways operated in the studied area is vital for exploration targeting and assessment of economic potential. Worldwide, the extensional rift basins are characterized by a variety of hydrothermal mineralization (Deb and Goodfellow, 2004). In the Indian shield, barite mineralization is known from Palaeo Archaean to the Neoproterozoic age, both stratiform and vein barites are known notably in the Dharwar Craton (Nee lakantam, 1987; Deb et al., 1991; Radhakrishna and Vaidyanadhan, 1997; Muller et al., 2017).

Pakistan hosts important barite occurrences, most notably in the Khuzdar and Las Bela belt of Balochistan (Klinger and Ahmad, 1973; Ahsan and Khan, 1994), with large reserves e.g., Gunga and Duddar has 12 million tons (Ahsan and Khan, 1994), Bankri has 2000 tons, Kundi has 3000 tons reported by Ahmad and Klinger (1963). Smaller occurrences are reported in Nathiagali, Haripur, Havelian, Hazara and Swabi

and Buner, Khyber Pakhtunkhwa (Calkins et al., 1975; Range, 1977 and Malkani, 2000).

The Tanawal Formation in the Buner District, northern Pakistan, is a quartzose, arenaceous to quartzitic unit with a complex Panjal Thrust Himalayan tectono-stratigraphic history. Its brittle structures and quartzitic lithologies create favorable conduits for hydrothermal fluid flow, making it a plausible host for structurally controlled barite mineralization. Tectonics and metamorphism influence both fluid generation and the pathways that focus mineralizing solutions. Barite veins frequently occur at structural intersections, along reactivated faults and within zones of brittle deformation adjacent to metamorphic or magmatic heat sources (Robinson, 1992; Dora et al., 2022; Samaoui et al., 2023). In the tectonically complex Himalayan foreland, due to the collision numerous thrusts and fractures has produced that served as channels for mineralizing fluids. Differences in pressure, temperature, and fluid chemistry along these structures controlled barite precipitation. Hence, evaluating the structural setting, metamorphic influences, and fluid composition is fundamental to understanding the timing and source of barite mineralization in the Khanano Dheri area.

Previous research on barite deposits in Pakistan has primarily focused on the southern and southwestern regions, particularly the Khuzdar-

Las Bela belt of Balochistan and the Hazara area of Khyber Pakhtunkhwa, where barite occurs mainly as stratabound or vein-type deposits associated with carbonate and shale sequences (Klinger and Richard, 1973; Ahsan and Mallick, 1999; Ali et al., 2021). These studies have discussed the mineralogical characteristics and industrial potential of barite, but few have addressed the detailed genesis, tectonic controls, and geochemical signatures of barite mineralization in the northern Lesser Himalayan domain. In particular, the barite deposits hosted in the Tanawal Formation of Buner District remain poorly characterized in terms of their structural setting, paragenetic sequence, and fluid evolution.

In view of this gap, the present study integrates detailed field mapping, structural measurements, petrography, mineralogy, and geochemistry to: (1) characterize textures and paragenesis of barite veins, (2) determine geochemical fingerprints to constrain fluid sources, (3) assess structural and metamorphic controls on mineralization, and (4) evaluate distribution and economic significance for local barite supply. By linking global deposit models to local petrographic and geochemical evidence, this work aims to develop a genetic model for the Khanano Dheri barite occurrences and provide practical insights for future exploration in similar tectono-metamorphic terrains.

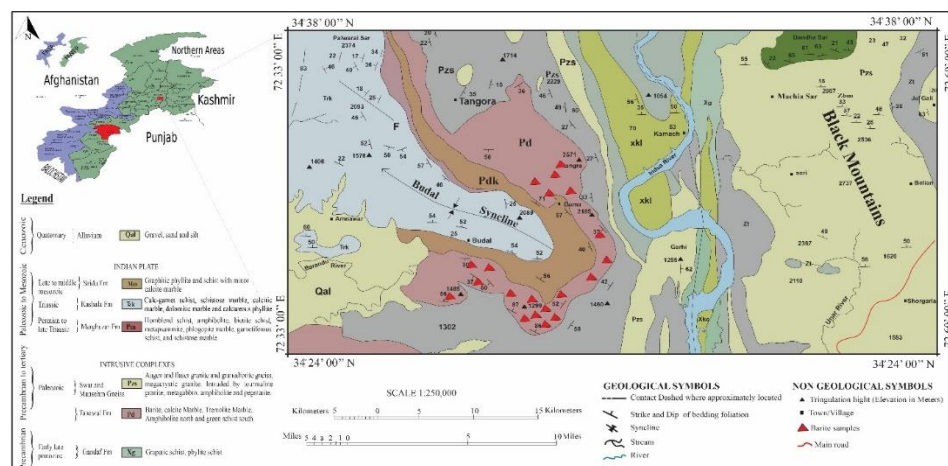


Figure 1. Local geological map of the study area (modified after Hussain et al., 2014). Locations of the collected samples has been marked on the local geological map (red tringles).

2. Study area

The study area is one of the highly tectonic deforms area lies in lesser Himalayas in Northern Pakistan. Barite hydrothermal mineralization is situated in Paleozoic (Precambrian) Tanawal Formation at Longitude 72° 41' 47" E and latitude 34° 25' 46" N, with elevation of 2 m from sea level, which is overlies the Hazara Formation and is unconformably overlain by the Kingriali Formation (Figure. 2). In the northwestern Hazara ranges, Barite deposit of

the Tanawal Formation occurs in the **hanging wall of the Panjal Thrust** (Calkins et al., 1975). Main Geological structural feature observed near the study area is the **Nikanai Ghar Fault**, which exhibits an **east-west (E-W) strike** and **steep southerly dip**. This fault represents a major tectonic discontinuity in the region; however, it describes **fault geometry rather than the bedding orientation within the Tanawal Formation itself** (University of the Punjab, 2002).

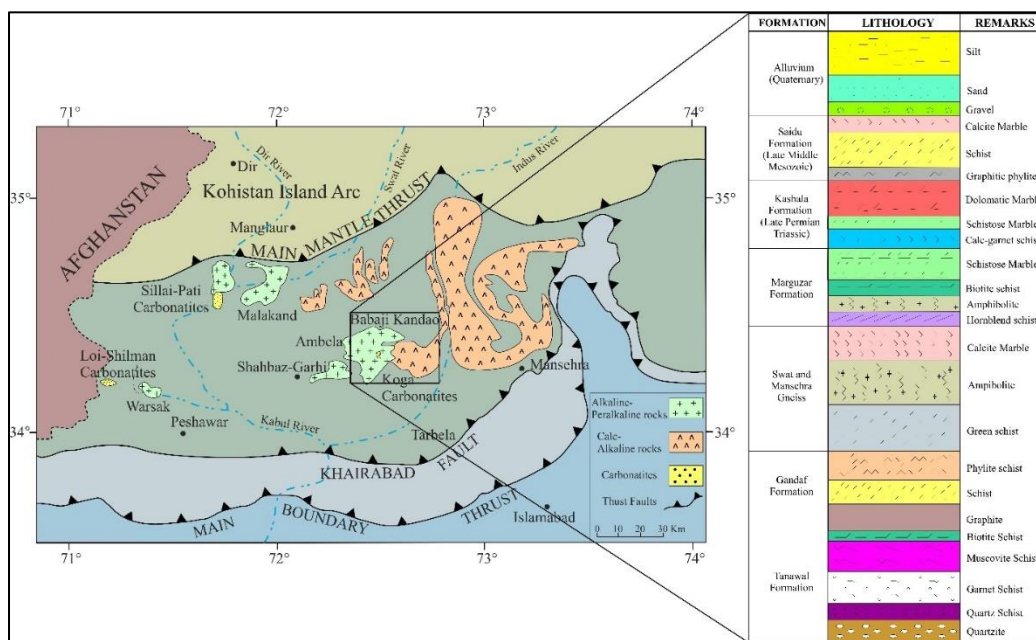


Figure 2. Regional geological map and generalized stratigraphic column of the study area (modified after Ahmad Hussain, Joseph A. DiPietro, Kevin R. Pouge and Irshad Ahmad, 2004).

3. Methodology

The study was initiated with a desk-based review of the regional stratigraphy and tectonic framework. Relevant literature, including Geology of Pakistan (Bender and Raza), Stratigraphy of Pakistan (Shah), Tectonics of Pakistan (Kazmi and Jan), and published research articles, was consulted to establish a geological context and design an effective fieldwork strategy. Field investigations were conducted mainly through foot traverses across the mapped area. Barite-bearing veins were examined, and structural measurements were recorded. Twenty-five representative samples were collected, from

which representative samples were selected for detailed petrographic and geochemical analyses based on their mineralogical and textural characteristics. Hand specimens were first studied in the field, followed by preparation of thin sections at the Department of Geology, Bacha Khan University, Charsadda.

Petrographic examination was carried out under plane polarized and cross polarized light microscope at the National Centre of Excellence in Geology, University of Peshawar and photomicrographs were obtained using an attached digital camera. Observations acquired at magnifications of 5×, 10×, and 20× to identify

barite and related gangue minerals, and to characterize mineralogical connections within hydrothermal veins.

Geochemical analysis of barite was carried out using X-Ray Fluorescence (XRF) spectrometer to evaluate the chemical composition and assess the overall quality. Representative sample for XRF analysis were prepared followed standard procedures: (i) cleaning and washing to eliminate surface contaminants, (ii) pulverizing the samples to approximately 75 μm using a ball mill, and (iii)

drying at temperature of 105 °C until a constant weight was achieved. To enhance the accuracy, the fusion method was applied in which powdered sample were mixed with the lithium tetraborate flux a ratio of 1:10 and heating at temperature of 950-1050 °C to yield homogeneous glass beads. These methods minimize the matrix interferences and particle size effects enabling accurate determination of BaSO_4 concentration.

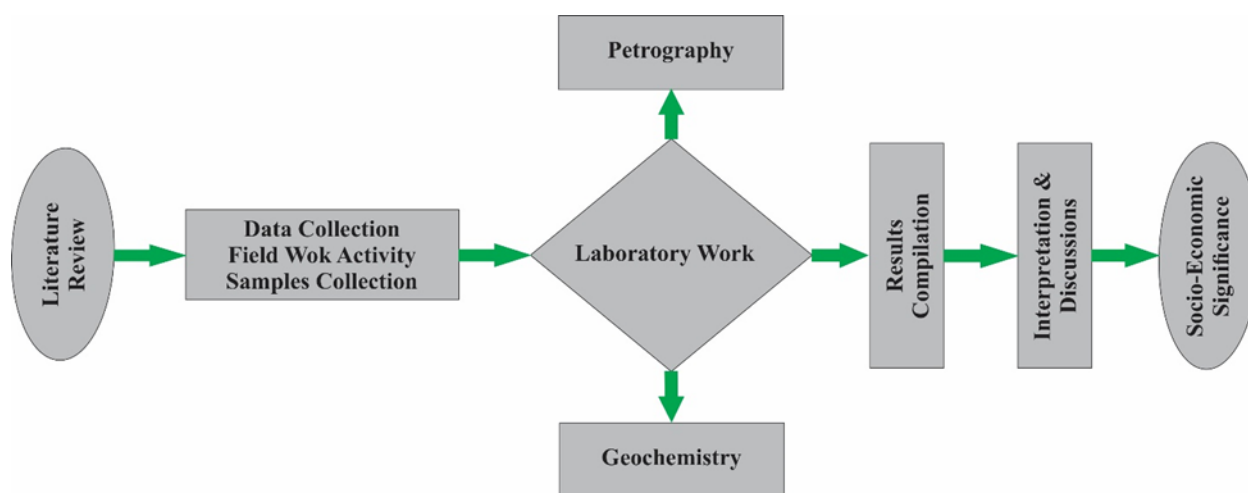


Figure 3. Methodology flow chart of the research work.

4. Results

4.1 Field Observation

Field investigations were carried out at the Khanano Dheri, District Buner, Khyber Pakhtunkhwa. The area is comprised of Kashala, Nikhani Ghar, Tanawal, Saidu Schist and Gandaf Formation. The study focused on the Tanawal Formation, consists mainly of quartos schist, quartzite and schistose conglomerate (Figure. 2). The unit is well exposed in the south and southeastern margin of the Mansehra Granite. Barite deposits were observed in the form of vein (hydrothermal fluid) which is hosted by calcitic and dolomitic marble the Tanawal Formation (Figure. 4A). The barite vein has variable thickness and morphology in different areas. The vein has sharp and well develop contact with the host rock marked by alteration halo or ferruginous staining. Barite vein are

typically 1-5 meters thick and 10-50 meters long elongated along strike and dip (Figure. 4A). The color of veins is white to greyish white, and coarse-grained. The studied area barite is hosted by dolomitic marble and by quartzite locally. In many exposures multiple generations of barite veins were observed. The thick massive units are cut or bordered by smaller, irregular barite-filled stringers and fracture infillings (Figure 4B). These secondary veins have pinch-and-swell geometry and are generally discontinuous, indicating reactivation of the same fracture system at various mineralization phases. Most of the veins are parallel to the bedding or foliation planes of the host marble, while some are discordant, crosscutting the host rock (Figure 4C). Barite mineralization is spatially associated with minor metallic occurrences. Specifically, copper and galena traces were observed along the peripheries and fracture zones adjacent to barite-rich veins

(Figures 4D-E). These sulfide minerals occur as small disseminations, streaks, or coatings in the host rock and vein margins, but they are volumetrically minor compare to barite. Overall, the field observation delineates an extensive network of barite veins within the studied area (Tanawal Formation), structurally controlled by faults, joints, and bedding-parallel shear zones.

The outcrops are easily recognizable in the field due to the white color and high density of barite compared to the enclosing rocks. The combination of thick, massive veins and thin fracture-fill barite veins defines the main mode of mineral occurrence in the Khanano Dheri area (Figure 4).

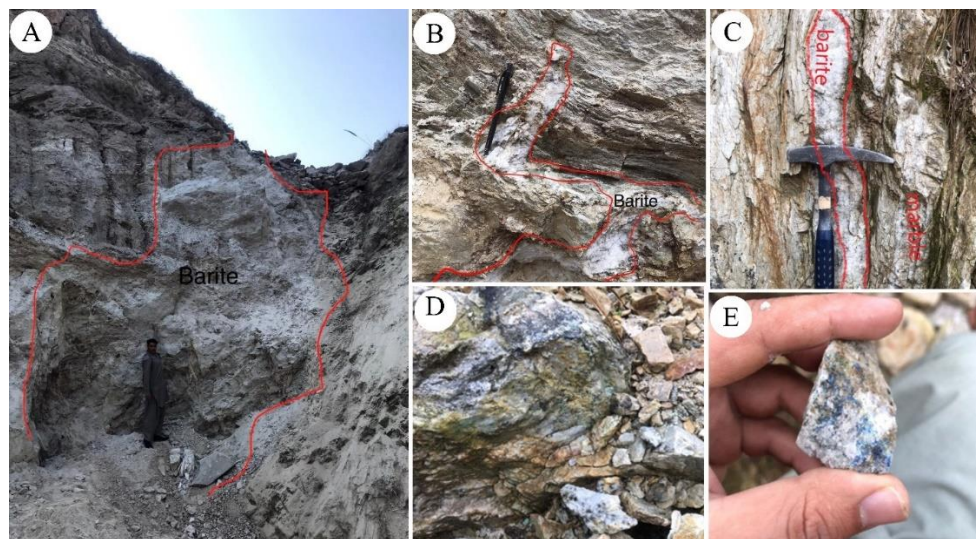


Figure. 4. Field photographs exhibiting prominent features observed during detail outcrop investigations (A) Barite mineralization in a thick vein form in the pre-cambrian Tanawal Formation. Based on cross cutting relationship with the host rock, suggesting its formation in late stages. (B) Numerous amount of small and thin, irregular barite filled veins were also observed in the investigated area. (C) most of the investigated veins are bedding parallel and few are in discordant contact with the inherited sedimentary bedding in the host Tanawal Formation. (D-E) Some traces of copper and galena mineralization were also observed along the periphery of barite mineralization in specific zone.

4.2 Petrography

The petrographic study of barite samples from the Tanawal Formation reveals a dominant association of barite, quartz, and mica minerals, with minor sulfides and accessory carbonates (Figures 5-7). Barite was identified as coarse grained, moderate relief bladed or tubular texture subhedral to anhedral crystals (Figures 5C-D). Under plane and cross polarized light, the cleavages are perfect on (001), nearly perfect on (210), and good on (010) with weak pleochroism, high birefringence and rolling extinction. In thin sectional view, barite is marked by red arrows (Figures 5-7). Quartz is observed and identified in thin section, commonly intergrown with barite

and appears as medium to coarse grained, undulose extension with straight boundary, high visibility and texture rims. Quartz is marked by sky-blue arrows (Figures 5A-D, 6A-D, 7A-D). Biotite is another mineral which is identified by its moderate relief, greenish to brown color, and it is marked by dark blue color arrows in thin sectional view. Other one mineral which is identified is muscovite mica which has distinguished from others minerals by its flaky texture and it is a shade of green red or brown which is marked by yellow color in thin section. Pyrite is another mineral which is identified (Figure 5A-C) it is cubic in form, high relief

opaque in both XPL and PPL and it is marked by white arrow in thin section. Others accessory mineral include calcite, dolomite, galena, azurite, malachite and siderite is also present in barite thin section.

Barite is frequently represented by large plate like or centimeter-scale tabular crystals or automorphic orthorhombic crystals (Figure 6A-C) of varying sizes due to uniform growth rates. It typically appears as white, pink, or gray masses (Figure 7B). The barite veins of the studied area contained 60-70 vol% barite, ~10-20 vol%

quartz, 15-20 vol% biotite and ~1 vol% sulfide minerals in the form of galena, chalcopyrite, and their oxidation minerals (malachite, azurite, iron oxide, and manganese oxide). Due to the remobilization of silicates and sulfides along fractures by hydrothermal fluids, significant network textures have been observed in barite. Microscopically, barite appears as elongated, curved, intertwined, and interlocking long prismatic rods with rolling extinction (Figure 7A-C).

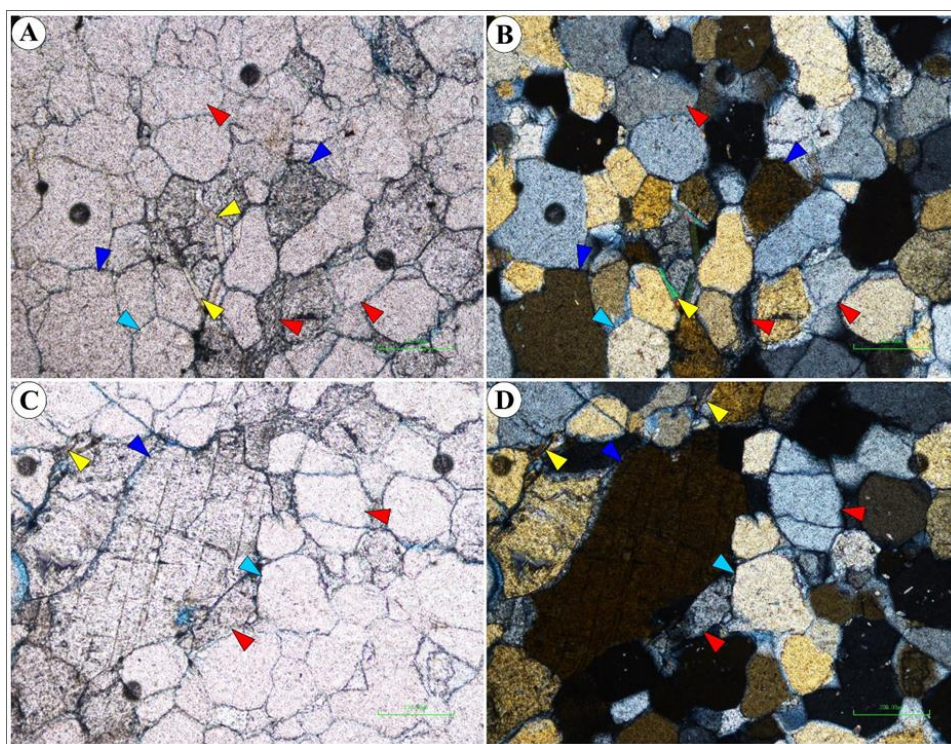


Figure 5. Plain and cross light photomicrographs illustrating textural relationships of barite and associated minerals in the barite vein. (A-B) photomicrographs exhibit anhedral barite grains (red arrows) associated with quartz grains (sky blue arrows). Other associated minerals observed in this association are biotite (dark blue color) and muscovite (yellow color). (C-D) demonstrates anhedral barite grains (red arrows) associated with quartz grains (sky blue arrows). Very large biotite grain (dark blue color) was observed in close association with quartz and barite grains, while muscovite (yellow color) is present in trace amount.

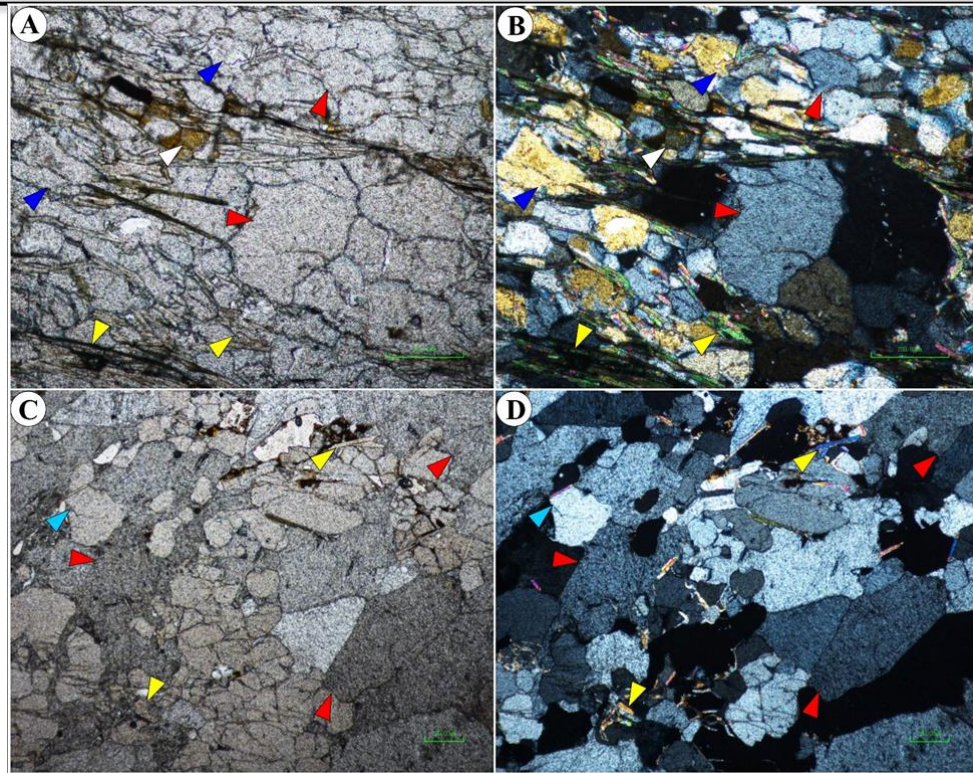


Figure 6. Conventional plain and cross light petrographic observations observed are (A-B) very coarsely crystalline, well developed anhedral barite grains (red arrows) was observed in direct association with medium to coarsely crystalline quartz crystal (sky blue arrows). Trace minerals associated with this setting are biotite (dark blue color) and muscovite (yellow color). (C-D) demonstrates anhedral barite grains (red arrows) associated with quartz grains (sky blue arrows). Medium grained biotite grain (dark blue color) was observed in close association with quartz and barite grains, while muscovite (yellow color) is present in trace amount.

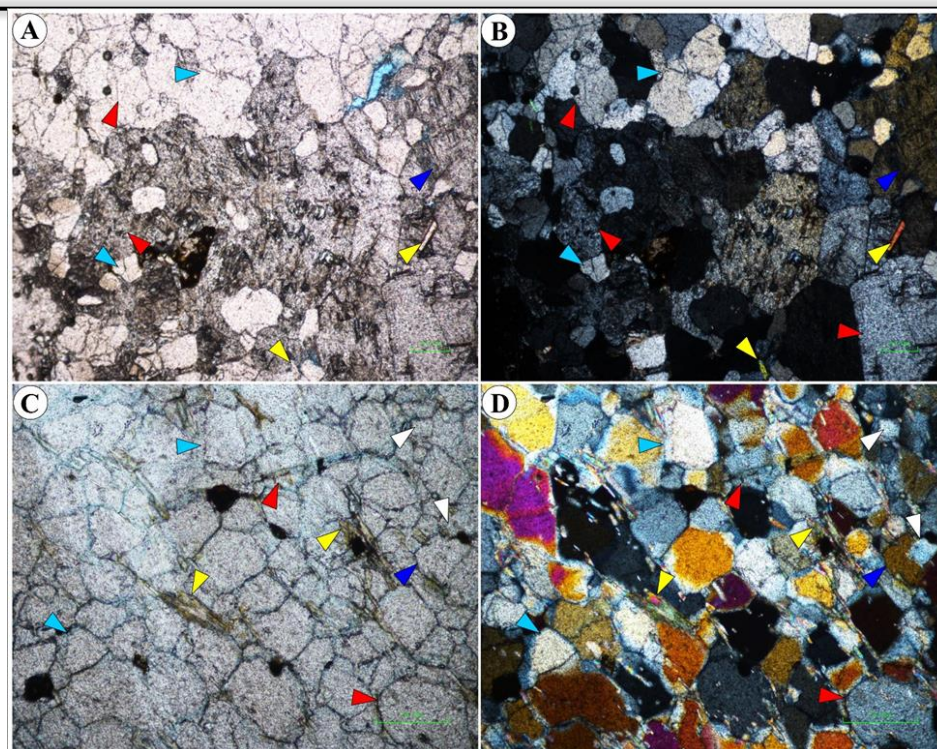


Figure 7. Plain and cross light photomicrographs indicate (A-B) photomicrographs exhibits well developed coarsely crystalline anhedral barite grains (red arrows) associated with coarse quartz crystal (sky blue arrows). Trace minerals associated with this setting are biotite (dark blue color) and muscovite (yellow color). (C-D) demonstrates anhedral barite grains (red arrows) associated with quartz grains (sky blue arrows). Medium grained biotite grain (dark blue color) was observed in close association with quartz and barite grains, while muscovite (yellow color) is present in trace amount.

4.3 Geochemistry

Geochemical studies using XRF on representative rock samples from the Tanawal Formation were employed to determine their elemental composition. XRF is an analytical technique that quantifies various elements within a rock sample. The geochemistry of different oxides was examined using X-ray fluorescence spectroscopic analysis. The different major element and oxides composition present in rock samples are presented in Table 1 and 2. The major element composition of the analysed samples are given; the specific gravity of the analysed samples ranges from 3.73 (BS-1) to 4.27 (BS-18). The BaSO_4 content of the analyzed samples varies from 75.4 (BS-1) to 94.3 (BS-11). The highest BaSO_4 concentration occurs in sample BS-11 (94.3), followed by BS-18 (93.1), BS-14 (92.8), and BS-13

(90.3), whereas the lowest is recorded in BS-1 (75.4). There is an inverse trend between Silica (SiO_2) and BaSO_4 , ranging from 1.56 (BS-11) to 14.55 (BS-1). Whereas calcium carbonate (CaCO_3) content varies from 0.71 (BS-11) to 6.78 (BS-1), indicating local calcite or dolomite contamination. While the Fe_2O_3 content is generally very low, between 0.00-0.21, with slightly elevated values in BS-20 (0.21) and BS-19 (0.19), showing negligible iron substitution in the investigated sample. The oxide composition in the analysed sample is given; the BaO values range from 52.91 (BS-6) to 67.04 (BS-3). The highest BaO concentration in BS-3 (67.04) corresponds to one of the highest BaSO_4 contents, confirming consistent enrichment of barium across the samples. Whereas the lowest BaO is observed in rock sample BS-6 (52.91),

which also exhibits relatively elevated SiO_2 and SO_3 contents. CaO values are very low, typically 0.03-0.37, with the maximum in BS-4 (0.37) and the minimum in BS-17 (0.03). The FeO content is negligible (< 0.10), while the maximum value is 0.08 in sample BS-18. The K_2O concentrations are generally low (0.01-1.17), the highest value is 1.17 in BS-20, which may reflect traces of K-

bearing silicate impurities. SO_3 contents range from 31.47 (BS-3) to 46.5 (BS-16). SrO varies from 0.06 (BS-19) to 1.09 (BS-5), with most samples showing 0.3-1.0, indicating limited strontium substitution for barium in the barite lattice.

Table 1. Major oxides detected during qualitative analysis of the representative barite samples collected from Precambrian Tanawal Formation, using X-Ray Florescence Spectrometry.

Sample	Specific gravity	BaSO_4	SiO_2	CaCO_3	Fe_2O_3
BS-1	3.73	75.4	14.55	6.78	0
BS-2	3.95	83.6	9.02	3.23	0
BS-3	4.13	88.2	5.65	2.02	0.03
BS-4	4.07	85.8	7.41	2.72	0.02
BS-5	4.11	86.11	5.19	4.00	0
BS-6	3.91	82.3	4.00	3.91	0
BS-7	3.76	81.2	4.32	5.72	0.01
BS-8	4.04	85.1	2.67	2.98	0
BS-9	4.16	88.50	5.12	1.94	0.03
BS-10	4.09	86.23	5.33	4.45	0.04
BS-11	4.22	93.45	1.56	0.77	0.02
BS-12	3.98	84.47	9.53	2.01	0.05
BS-13	4.14	90.30	4.25	2.31	0.03
BS-14	4.18	92.78	3.09	0.23	0.04
BS-15	3.78	81.4	12.44	2.30	0.01
BS-16	3.97	85.14	4.67	3.00	0.03
BS-17	4.24	92.78	1.38	1.4	0.05
BS-18	4.27	93.10	1.11	1.52	0.08
BS-19	4.17	89.1	4.08	2.65	0.19
BS-20	3.99	87.19	7.60	1.22	0.21

Table 2. Minor oxides detected during qualitative analysis of the representative samples using X-Ray Florescence Spectrometry.

Sample	BaO	CaO	FeO	K_2O	SO_3	SrO
BS-1	64.59	0.33	0	0	34.5	1
BS-2	57.89	0.25	0	0.03	39.63	1.07
BS-3	67.04	0.29	0.03	0	31.47	1.02
BS-4	62.33	0.37	0.02	0.04	35.07	1.09
BS-5	61.51	0.31	0	0.01	36.13	1.09
BS-6	59.43	0.23	0	0.441	38.1	0.41
BS-7	52.91	0.27	0.01	0.561	43.75	0.39
BS-8	58.12	0.25	0	0.531	40.01	0.40
BS-9	53.75	0.33	0.03	0.339	45.03	0.45
BS-10	56.19	0.28	0.04	0.435	37.61	0.37

BS-11	63.46	0.26	0.02	0.48	36.3	0.31
BS-12	59.50	0.29	0.05	0.45	38.5	0.41
BS-13	55.11	0.27	0.03	0.46	43.7	0.39
BS-14	62.79	0.28	0.04	0.49	35.9	0.4
BS-15	55.24	0.05	0.01	0.018	44.7	0.6
BS-16	53.11	0.07	0.03	0.014	46.5	0.9
BS-17	54.66	0.09	0.05	0.019	44.1	0.8
BS-18	57.74	0.30	0.08	0.39	42.3	0.2
BS-19	56.74	0	0.19	1.13	41.5	0.06
BS-20	60.11	0.03	0.21	1.17	37.7	0.09

4. Interpretation of Geochemistry

To better understand the compositional relationships among the analyzed oxides and their genetic implications, a detailed geochemical compatibility analysis was conducted. These compatibility trends have been outlined in the following subsections, focusing on the major elemental associations between mineral stages and oxides and trace element correlations.

4.1 Major Elemental Compatibility among Mineral Phases

4.1.1 Geochemical Compatibility of BaSO₄ and SiO₂

Variable concentrations of BaSO₄ determined in the examined rock samples are from 93.45% to 75.4%, whereas the concentration of SiO₂ contents were also observed, i.e., from 14.55% to 1.11% (Table 1). The detected BaSO₄ and SiO₂ were then used to determine their geochemical compatibility in the inspected rock samples. For relative trend a cross plot between BaSO₄ and SiO₂ has been established (Figure 8A). The geochemical relationship of BaSO₄ and SiO₂ shows a that barite is dominance over silica content, with BaSO₄ ranges from 75.4% (BS-1) to 93.45% (BS-11), whereas SiO₂ content is low (below 10%). Samples having higher SiO₂ content, i.e., BS-1 (14.55%) and BS-15 (12.44%), shows reduced BaSO₄ contents, demonstrating localized siliciclastic or hydrothermal input. In contrast, the most barite-enriched samples, including BS-11 (93.45% BaSO₄, 1.56% SiO₂) and BS-18 (93.1% BaSO₄, 1.11% SiO₂), demonstrate near-complete exclusion of silica. The cross plot of these oxides indicates an inverse

relationship between the concentrations of BaSO₄ and SiO₂ (Figure 8A). This inverse trend shows that BaSO₄ and SiO₂, are geochemical incompatible due to barite rich environments which suppressing silica accumulation. Overall, the distribution shows robust lithological control, where samples rich with BaSO₄ content represent primary ore zones, while the high content of SiO₂ shows minor external contributions.

4.1.2 Geochemical Compatibility of BaSO₄ and CaCO₃

Oxides with variable concentrations were detected in the investigated rock samples, which include BaSO₄ from 75.4% (BS-1) to 93.45% (BS-11) and CaCO₃ (0.23% to 6.78%), respectively. The relative distribution of BaSO₄ and CaCO₃ content shows that barite is dominant in the studied samples. Samples such as BS-1 (BaSO₄ = 75.4%, CaCO₃ = 6.78%) and BS-7 (BaSO₄ = 81.2%, CaCO₃ = 5.72%) record slightly elevated CaCO₃, but this is always associated with reduced BaSO₄ (Figure 8B). Conversely, the most barite-enriched samples, including BS-11 (93.45% BaSO₄, 0.77% CaCO₃) and BS-14 (92.78% BaSO₄, 0.23% CaCO₃), demonstrate near-complete exclusion of carbonate phases. From the above oxide values a reverse trend has been established between BaSO₄ and CaCO₃ indicates these two oxides is not geochemically compatible, because barite mineralization taking place in unfavorable environments for substantial carbonate enrichment. This distribution highlights lithological control, where zones rich with BaSO₄ represent primary barite ore, while

minor CaCO_3 enrichments reflect restricted carbonate contribution.

4.1.3 Geochemical Compatibility of CaCO_3 and SiO_2

Variable concentrations of calcium carbonate and silica were observed in the investigated rock samples, a cross plot of CaCO_3 vs SiO_2 has been established (Figure 5D) which demonstrates their geochemical compatibility. The results show that SiO_2 content is relatively higher in several samples, i.e., 15.2% in BS-1, 10.1% in BS-12, and nearly 13.5% in BS-15, whereas CaCO_3 content is much lower in these samples, fluctuating around 2.3-3.1%. Conversely, samples such as BS-5, BS-6, and BS-7 show more balanced and overall lower concentrations of both oxides, with SiO_2 values averaging about 5.4-6.2% and CaCO_3 between 3.2-4.5% (Figure 8C). The given cross plot exhibits an inverse relationship between CaCO_3 and SiO_2 , where samples having more content of SiO_2 show lower concentration of CaCO_3 and vice versa (Figure 8C). The behavior of geochemical concentration of these oxides can be explained by their different lithological affinities. The samples enriched with SiO_2 are most likely in association with siliceous material or hydrothermal silica input, which tends to dilute or replace carbonate stages throughout deposition or later diagenesis. This is evident in the investigated sample i.e., BS-1 and BS-15, where high silica contents correspond to very low content of carbonate, suggesting that the process of siliciclastic or hydrothermal was dominant. In contrast, relatively higher concentration of CaCO_3 , such as in BS-6 (4.7%) and BS-7 (4.3%), occur where SiO_2 is reduced, indicating that the environment was dominated by carbonate, probably connected to primary carbonate deposition or local carbonate replacement zones.

4.1.4 Geochemical Compatibility of CaCO_3 and Fe_2O_3

CaCO_3 values determined in representative rock samples are ranging from 0.23% to 6.78% whereas Fe_2O_3 values are from 0% to 0.21%. In order to understand the geochemical relationship

between CaCO_3 and Fe_2O_3 distribution in the investigated rock samples, a cross plot between CaCO_3 and Fe_2O_3 has been established (Figure 8D). The CaCO_3 and Fe_2O_3 relationship indicates that concentration of calcium carbonate is relatively higher as compared to Fe_2O_3 concentration. Samples enriched in CaCO_3 , such as BS-1 (6.78%) and BS-7 (5.72%), contain negligible Fe_2O_3 (0-0.01%), while Fe_2O_3 -rich samples, for instance BS-19 (0.19%) and BS-20 (0.21%), are associated with very low CaCO_3 contents ($\leq 2.65\%$). The cross plot CaCO_3 and Fe_2O_3 illustrates an inverse relationship between the concentrations of calcium carbonate and iron oxide, indicating that these are not geochemically compatible (Figure 8D). The high concentration of CaCO_3 reflects carbonate rich lithologies with slight iron input, whereas higher Fe_2O_3 in CaCO_3 poor samples points to localized iron enrichment from silicate or oxide phases.

4.1.5 Geochemical Compatibility of BaSO_4 and Fe_2O_3

Detected BaSO_4 values i.e., ranging from 75.4% (BS-1) to 93.45% (BS-11), and Fe_2O_3 values (i.e., 0% to 0.21%) in the representative rock samples exhibit measurable variability. In order to better understand their latitudinal trend of elemental composition in different rock samples, a cross plot of BaSO_4 versus Fe_2O_3 has been established (Figure 8E). The cross plot demonstrates a strong dominance of barite, while Fe_2O_3 remains extremely low across all samples. In the examined rock samples having higher values, such as BS-19 (0.19%) and BS-20 (0.21%), occur together with constantly high BaSO_4 contents (89.1% and 87.19%, respectively). This distribution shows that BaSO_4 and Fe_2O_3 are geochemically incompatible, where mineralization of barite develops in environments that exclude significant iron enrichment. The very less concentration of Fe_2O_3 suggests minimal contribution from ferromagnesian or iron-bearing silicates, supporting that the mineralization is overwhelmingly barite dominated with very less iron oxide influence.

4.1.6 Geochemical Compatibility of SiO₂ and Fe₂O₃

The SiO₂ vs Fe₂O₃ relationship indicates that both oxides occur normally in low concentrations, though silica shows extensive variation i.e., ranging from 1.11% to 14.55% and Fe₂O₃ ranging from 0% to 0.21% respectively. Most samples with high SiO₂ concentration, such as BS-1 (14.55%) and BS-15 (12.44%), contain very less concentration of Fe₂O₃ ($\leq 0.01\%$), while the highest Fe₂O₃ enrichments such as BS-19 (0.19%) and BS-20 (0.21%), correspond to

moderate silica values (4-7%) as shown in Figure 8F. The cross plot of SiO₂ vs Fe₂O₃ illustrates an inverse relationship between the concentrations of silicon oxide and iron oxide suggesting limited geochemical compatibility, with silica mostly representing detrital or siliceous input, while Fe₂O₃ reflects minor iron oxides from accessory phases. Their distribution highlights distinct sources and minimal overlap within the barite mineralization system.

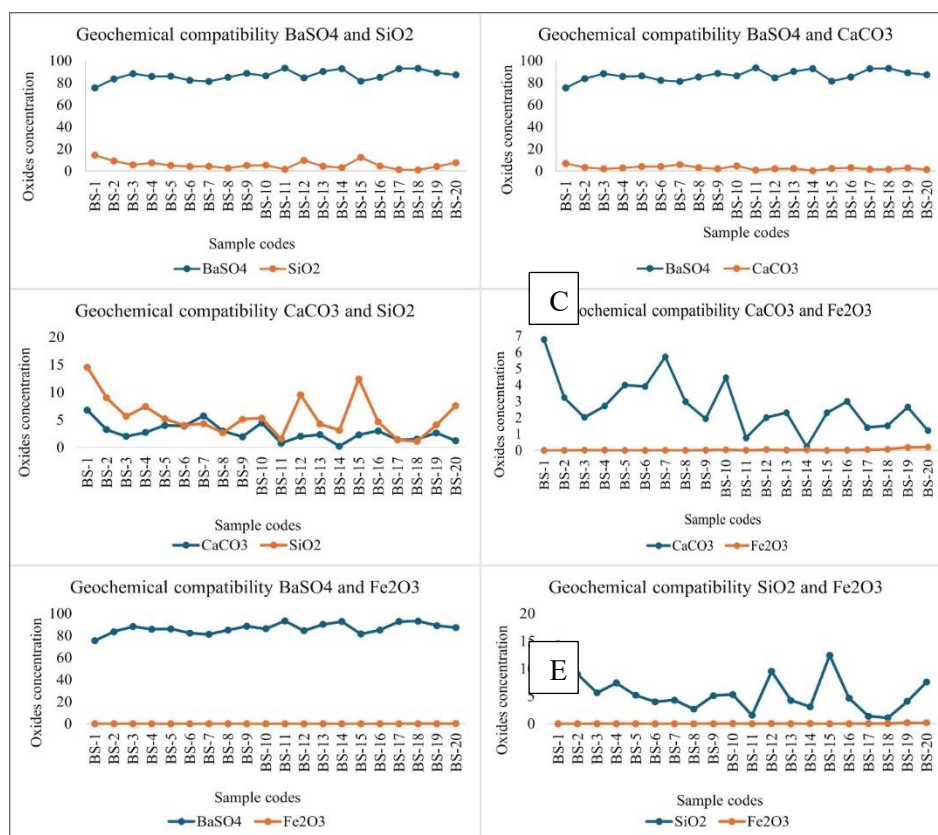


Figure 8. Cross plots of the major composition observed in the analyzed samples exhibiting i.e., BaSO₄ vs SiO₂ (wt.%), BaSO₄ vs CaCO₃ (wt.%), CaCO₃ vs SiO₂ (wt.%), CaCO₃ vs Fe₂O₃ (wt.%), BaSO₄ vs Fe₂O₃ (wt.%), and SiO₂ vs Fe₂O₃ of the barite samples and their corresponding host rock samples. (A) cross plot of BaSO₄ vs SiO₂ (wt.%) reflects that the concentration of BaSO₄ decreases with increasing SiO₂ contents in barite samples, representing inverse relationship and geochemically incompatibility of barite and quartz. (B) cross plot of BaSO₄ vs CaCO₃ (wt.%) reflects that the concentration of BaSO₄ decreases with increasing SiO₂ contents and vice versa in the barite samples, reflecting inverse relationship and geochemically incompatibility of barite and quartz. (C) cross plot of SiO₂ vs CaCO₃ (wt.%) reflects that the concentration of SiO₂ increases with increasing CaCO₃ contents and vice versa, reflecting direct relationship and geochemically compatibility of calcite and

quartz. (D-F) cross plots of CaCO_3 vs Fe_2O_3 (wt.%), BaSO_4 vs Fe_2O_3 (wt.%), and SiO_2 vs Fe_2O_3 of the barite samples and their corresponding host rock samples reflects that the concentration of CaCO_3 , and SiO_2 increases but due to very low values of Fe_2O_3 no increase or decrease was observed in the cross plots.

4.2 Oxide-Level Relationships and Trace Compatibility

4.2.1 Geochemical Compatibility of BaO and FeO

The compatibility study between BaO and FeO reveals a strong dominance of BaO, with concentrations ranging from ~53% to 67%, while FeO remains negligible across all the representative samples. In some samples e.g., BS-19 and BS-20, FeO shows slight enrichment, BaO values remain relatively high, indicating no positive correlation. Representative samples like BS-3 (BaO = ~67%, FeO ≈ 0) and BS-11 (BaO = ~63%, FeO ≈ 0) confirm that FeO is effectively absent in barite-rich compositions (Figure 9A). This pattern demonstrates that BaO and FeO are not geochemically compatible, reflecting selective mineralization conditions in which barite crystallized independently of iron-bearing phases.

4.2.2 Geochemical Compatibility of BaO and K_2O

Variable barium oxide values, i.e., ranging from 52.91% (BS-7) to 67.04% (BS-3) and potassium oxide in trace amount (0-1.17%) were detected in the investigated samples. In order to understand the geochemical compatibility of the elemental composition in the analyzed rock samples, across plot between BaO and K_2O has been established (Figure 9B). Samples such as BS-3 (BaO = 67.04%, K_2O = 0) and BS-11 (BaO = 63.46%, K_2O = 0.48) highlight the dominance of BaO with negligible potassium contribution (Figure 9B). The highest K_2O values, observed in BS-19 (1.13%) and BS-20 (1.17%), are accompanied by moderate BaO levels (~56-60%), suggesting that potassium enrichment is unrelated to barite mineralization. Furthermore, it indicates that BaO and K_2O are not geochemically compatible, with BaO reflecting barite formation and K_2O likely introduced from minor silicate or clay impurities rather than being part of the mineralizing system.

4.2.3 Geochemical Compatibility of BaO and SO_3

The geochemical relationship between BaO and SO_3 shows a strong positive compatibility, reflecting the stoichiometric control of barite (BaSO_4). BaO concentrations vary between 52.91% (BS-7) and 67.04% (BS-3), while SO_3 ranges from 31.47% (BS-3) to 46.50% (BS-16). Samples enriched in BaO, such as BS-3 (BaO = 67.04%, SO_3 = 31.47%) and BS-11 (BaO = 63.46%, SO_3 = 36.30%), consistently display corresponding SO_3 values that balance the barite composition (Figure 9C). Conversely, higher SO_3 contents, such as in BS-16 (46.50%) and BS-15 (44.70%), are associated with relatively lower BaO values (53.11% and 55.24%). This relationship shows that BaO and SO_3 are geochemically compatible, and their coupled variations directly reflect barite mineralization processes. The above-mentioned data confirm that the investigated rock samples demonstrate well crystallized barite with minor variations because of compositional heterogeneity or impurities.

4.2.4 Geochemical Compatibility of BaO and SrO

Variable concentrations of BaO (ranging from 52.9% to 67.04%) and SrO (0.06% to 1.09%) were detected during the geochemical investigation of the representative rock samples (Table 2). In order to understand the probable geochemical relationship between BaO and SrO in various rock samples, a cross plot between BaO and SrO has been established. The BaO concentration is high while the SrO shows very low concentration which reveals a distinct geochemical relationship between these two oxides (Figure 9D). This indicates that Barium is dominant in the investigated sample, confirming Barite (BaSO_4) as the major mineral phase. The less amount of SrO suggests that Strontium shows a limited but significant substitution for Barium into the Barite crystal matrix. This

substitution is likely due to the same ionic radii and comparable geochemical behavior of Ba^{2+} and Sr^{2+} ions. The BaO and SrO are geochemical incompatibility but shows a positive pattern, suggesting that Sr can replace Ba in the crystal structure, the extent of such replacement remains restricted. These results in the studied rock sample describe that Sr as a trace element incorporated into Barite through isomorphic substitution mechanisms.

4.2.5 Geochemical Compatibility of CaO and SrO

Major and minor oxides detected in the investigated rock samples collected from the study area include variable concentrations of CaO (0-0.37%) and SrO (0.06-1.09%), respectively (Figure 9E). The CaO vs SrO geochemical compatibility shows a positive trend. The higher CaO concentration of CaO i.e., 0.25-0.37% in samples BS-1 to BS-5 correspond with higher SrO values i.e., 1.0-1.09%, reflecting the geochemical affinity between calcium oxide and strontium oxide due to their same ionic radii and substitution behavior in mineral crystal. On the other hand, very low content of CaO i.e., BS-19 (0.0%) and BS-20 (0.03%) coincide with the lowest SrO values i.e., 0.06% and 0.09%, demonstrate the coupled behavior of these two oxides (Figure 9E). The geochemical compatibility between CaO and SrO in the investigated rock samples of barite is controlled by calcium bearing phases or lattice substitution processes,

4.2.6 Geochemical Compatibility of SrO and FeO

Variable concentration of strontium oxide, and iron oxide were detected in the investigated rock samples (Table 2). The geochemical compatibility between SrO and FeO is weak to moderate negative. The values of SrO range from 0.06% to 1.09%, with relatively higher concentration in BS-2 (1.07%) and BS-4 (1.09%) (Figure 9F). The FeO occurs in trace amounts i.e., 0-0.21%, showing enrichment in rock sample BS-19 (0.19%) and BS-20 (0.21%) where SrO concentration is very low i.e., 0.06% and 0.09%,

respectively. The cross plot of these oxides indicates an inverse relationship between the concentrations of strontium oxide and iron oxide. The negative relationship suggests that SrO is in association with barite mineralization due to its geochemical affinity with barium, while iron oxide originates from oxide impurities or minor silicate. This inverse relationship between SrO and FeO suggests that iron oxide does not play a substantial role in the Strontium bearing mineral phases of the investigated samples.

4.2.7 Geochemical Compatibility of CaO and FeO

Variable calcium oxide values, and iron oxide values were detected in the investigated rock samples (Table 2). The comparison between CaO and FeO shows weak geochemical compatibility (Figure 9G). CaO concentrations are generally low (0-0.37%), with slightly higher values in BS-1 (0.33%) and BS-4 (0.37%), while FeO occurs in minor to trace amounts (0-0.21%). Samples BS-19 (CaO=0.00%, FeO = 0.19%) and BS-20 (CaO = 0.03%, FeO = 0.21%) reveal an inverse relationship, where FeO is relatively enriched despite negligible CaO. This suggests that both oxides are present only as minor impurities, likely sourced from carbonate or silicate phases, and do not exhibit significant geochemical association with barite mineralization.

4.2.8 Geochemical Compatibility of K₂O and SrO

Major and minor oxides detected in the investigated rock samples collected from the study area include variable concentrations of K₂O and SrO respectively. The K₂O and SrO geochemical relationship reveals an inverse correlation. Samples having low K₂O concentration i.e., 0-0.04%, (BS-1 to BS-5) show high concentration of SrO i.e., 1.0-1.09%, demonstrating Strontium enrichment under potassium poor environments. While samples having high content of K₂O values (0.39-1.17%) in sample BS-18 to BS-20 shows reduced SrO concentration (0.20-0.09%), highlighting a competitive geochemical behavior (Figure 9H). This suggests that Strontium incorporation in

barite bearing assemblages is inhibited by increasing potassium activity, because of

mineralogical controls or substitution competition in the crystal lattice.

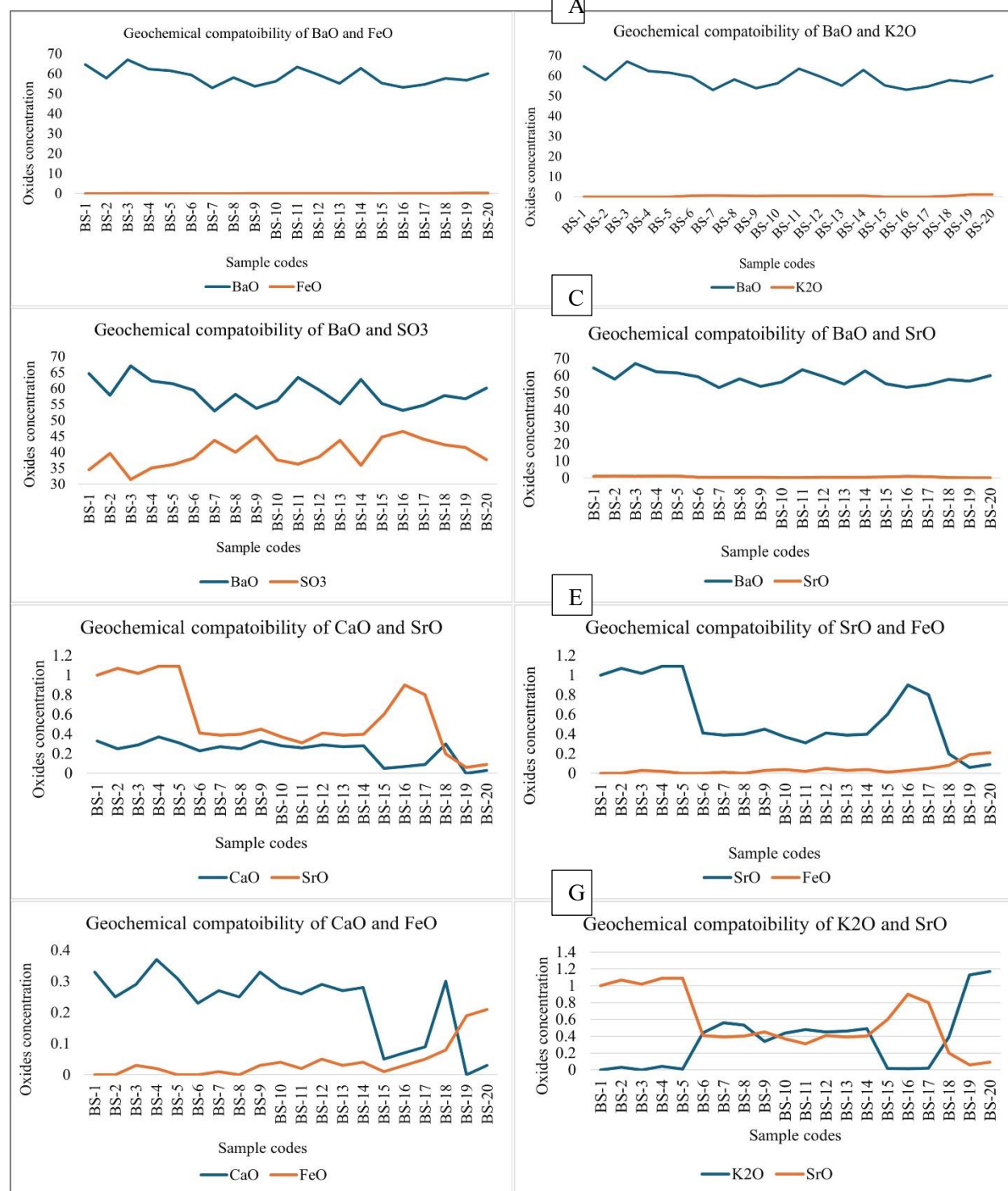


Figure 9. Cross plots of the minor oxides observed in the analyzed samples exhibiting i.e., BaO vs FeO, BaO vs K2O, BaO vs SO3, BaO vs SrO, CaO vs SrO, SrO vs FeO, CaO vs FeO and K2O vs FeO and BaO

vs K₂O of the barite samples and their corresponding host rock samples. (A-B) cross plots of BaO vs FeO and BaO vs K₂O of the barite samples and their corresponding host rock samples reflects that the concentration of BaO increases but due to very low values of FeO no increase or decrease was observed in the cross plots. (C) cross plot of BaO vs SO₃ reflects that the concentration of BaO decreases with increasing SO₃ contents and vice versa in the barite samples, reflecting inverse relationship and geochemically incompatibility of BaO and SO₃. (D) cross plots of BaO vs SrO of the barite samples and their corresponding host rock samples reflects that the concentration of BaO increases but due to very low values of SrO no increase or decrease was observed in the cross plots. (E) cross plot of CaO vs SrO reflects that the concentration of CaO decreases with increasing SrO contents and vice versa in the barite samples, reflecting inverse relationship and geochemically incompatibility of CaO and SrO. (F-G) cross plot of SrO vs FeO and CaO vs FeO, a gradual increase of FeO were observed with increasing concentration of CaO and SrO reflecting direct relationship and geochemically compatibility of CaO, FeO and SrO. (H) cross plot of K₂O vs SrO reflects that the concentration of K₂O decreases with increasing SrO contents and vice versa in the barite samples, reflecting inverse relationship and geochemically incompatibility of K₂O and SrO.

5. Discussion and Genetic Implications

The integration of field observation, petrographic studies, and geochemical data provides reliable evidence of hydrothermal barite system and structurally controlled in the Tanawal Formation, shedding light on the hydrothermal processes and tectonic framework responsible for its formation. This study therefore focuses on (1) constraining the timing and source of mineralizing fluids, (2) documenting the paragenetic sequence recorded in the veins, and (3) assessing the economic significance of these high-grade barite occurrences for local supply. Petrographic studies reveal that barite is associated with quartz, biotite, muscovite, and minor sulfides e.g., pyrite, galena, while geochemical data having dominant composition of Ba and SO₄ with minor Sr substitution. Together, these findings suggest late, fault hosted hydrothermal veins modified by regional deformation. Field observations (Figure 4) demonstrate that barite mineralization in the studied area (Tanawal Formation) occurs predominantly as vein-type bodies filling fractures, joints, and shear planes within quartzose and dolomitic host rocks. The veins, typically 1-5 m thick and extending 10-50 m along strike, exhibit sharp and well-defined contacts with the enclosing lithologies. These structural characteristics, along with massive, white to grey barite infill, suggests a hydrothermal vein origin, while mineralizing fluids during late tectonic activity migrated through fault and

fracture systems. The presence of cross-cutting relationships with the host rock (Figure 4A) suggests that barite emplacement postdates the main deformation phase of the Tanawal Formation, implying a late-stage hydrothermal event.

Petrographic studies reinforce the field evidence (Figures 5-7). Barite appears as coarse-grained, anhedral to subhedral crystals showing high birefringence and perfect cleavage on (001). It is in close association with quartz, biotite, muscovite, and pyrite, forming an interlocking mosaic texture that reflects simultaneous crystallization from a hydrothermal fluid. The frequent occurrence of quartz-barite intergrowths (Figures 5A-D, 6AB) indicates silica saturation in the fluid, while its association with pyrite (Figures 5CD) suggests reducing conditions during deposition. Trace muscovite and biotite (Figures 6CD, 7A-C) show partial alignment with the schistose host fabric, indicating minor metamorphic overprint related to Himalayan deformation. Geochemical data (Tables 1 and 2) further confirm the hydrothermal origin. The barite samples from the studied area shows high BaSO₄ contents (75.4-94.3 wt.%, avg. ~86-88 wt.%), which indicates remarkably pure mineralization. BaO values (55.24-65.08 wt.%) and SO₃ (36.1-54.5 wt.%) confirm barite as the dominant phase. The inverse relationship between BaSO₄ and SiO₂ (1.56-14.55 wt.%) point out that the investigated samples richest in

barite contain the least quartz impurity, consistent with hydrothermal precipitation rather than sedimentary accumulation. Minor CaO and Fe_2O_3 suggest limited inclusion of carbonates and sulfides from host rocks. Trace element patterns also support a hydrothermal setting. SrO contents (0-0.51 wt.%) indicate limited Sr substitution within the barite lattice a typical feature of hydrothermal barite (Hanor, 2000). CuO (up to 0.29 wt.% in BS-5) and ZnO (≤ 0.19 wt.%) point to minor sulfide mineralization, consistent with field evidence of copper and galena traces along vein margins (Figure 4DE). While the specific gravity values (3.7-4.27) correlate positively with BaSO_4 content, reaffirming high-grade barite purity.

Collectively, the petrographic and geochemical studies show precipitation from hydrothermal fluids rich in Ba and SO_4 , migrating along fault-controlled pathways in a reducing environment. The association of these oxides in association with quartz and muscovite suggests that the fluids is in interaction with sedimentary rock i.e., siliciclastic and metamorphic rocks, acquiring silica and alkalis during circulation of these fluids. With minor metamorphic reactivation likely remobilized or re-sealed existing veins during the later deformation, creating the observed textural variations. Therefore, the complete mineral assemblage, texture, and chemistry support a late-stage tectonic hydrothermal genesis of barite in the Tanawal Formation.

The integrated evidence reveals that barite mineralization in the studied area (Tanawal Formation) is not only structurally controlled but also economically significant. The high concentration of BaSO_4 (up to 94 wt.% as shown in Table 2) and low concentration of FeO , CaO , and K_2O indicate a high chemical grade, suitable for use in the oil and gas industry as a weighting agent and in other industries application such as chemical and pigment industries. Although some veins are moderate in size i.e., 1-5 m thick and 10-50 m long, their cumulative tonnage in the studied area (Khanano Dheri) area may represent an important local resource for small to medium scale extraction. In geological point of view,

localization of barite along faults and fractures parallel to the Lesser Himalayan structural grain indicates strong tectonic control on fluid migration. The Tanawal Formation, nearby the Mansehra Granite and influenced by Panjal Thrust related deformation, providing an ideal brittle host for hydrothermal circulation. The upward migration of Ba and SO_4 bearing fluids during late orogenic uplift mirrors barite systems in Hazara, Swabi, and the Indian Dharwar Craton, where mineralization follows reactivated faults under compressional transpressional regimes (Deb et al., 1991; Malkani, 2000; Müller et al., 2017).

Hence, the genetic model proposed in this study supports a late tectonic, fault hosted hydrothermal origin, where basinal fluids carrying dissolved barium interacted with sulfate-rich or carbonate horizons, precipitating barite upon cooling and fluid mixing. To understanding the relationship of this tectonic and hydrothermal is critical for targeting new mineralized zones within the Tanawal Formation and adjacent terranes. Overall, the integrated data suggest that the barite veins of the Tanawal Formation at Khanano Dheri formed through hydrothermal activity linked to post metamorphic deformation. The veins were precipitated from Ba and SO_4 bearing fluids circulating along fractures within the quartz-rich metasedimentary rocks. The mineral assemblage such as barite, quartz, biotite, muscovite, and minor pyrite/galena are coupled with high BaSO_4 purity, characterizes epigenetic hydrothermal systems rather than stratiform or SEDEX origins. From an applied standpoint, the high-grade purity and predictable structural setting make these veins a valuable local resource. However, given their limited lateral continuity, exploration should target structural corridors, particularly fault intersections, dilational zones, and lithological contrasts within the Tanawal Formation. Geophysical and geochemical prospecting could further delineate subsurface extensions and guide resource evaluation. The findings from this study therefore clarify the genetic evolution of barite in the Tanawal Formation and provide a framework for future

exploration in similar tectono-metamorphic settings of northern Pakistan.

6. Conclusion

This study reveals that barite mineralization in the Khanano Dheri area of Buner District, Pakistan, formed predominantly through hydrothermal processes associated with faulting and regional tectonism during the Himalayan Orogeny. Field observations show that barite occurs mainly as veins within quartz-rich rocks such as quartzose sandstone and quartzite, indicating structural control and a genetic link with silica-bearing lithologies. Petrographic investigations confirm the presence of barite intergrown with quartz, biotite, muscovite, and minor pyrite, reflecting crystallization from hydrothermal fluids. Geochemical analyses further support this origin, showing high BaSO_4 purity with limited trace element variation and elevated Sr contents, characteristic of deep-sourced hydrothermal fluids. The regional metamorphism and deformation of the Tanawal Formation likely facilitated fluid migration and mineral precipitation along fault and fracture systems. Altogether, these findings demonstrate that the Khanano Dheri deposits represent structurally controlled, late-tectonic hydrothermal mineralization with significant economic potential. Beyond advancing geological understanding, this study provides a foundation for targeted exploration and sustainable utilization of barite resources within northern Pakistan tectono-metamorphic terrains.

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