

# PHASE AND MICROSTRUCTURAL CHARACTERIZATION OF HAZARA BARITE, PAKISTAN

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## ABSTRACT

Barite is an industrially precipitated mineral and is used in the drilling oil and gas wells. In the present study, barite samples collected from Hazara division of Khyber Pukhtunkhwa (KPK), Pakistan were investigated using X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). The major phases identified in these samples by XRD are of barium strontium sulfate with sulfur as the second phase. SEM of the examined samples revealed the presence of irregular shaped micro-regions along with minor grains of quartz. The elemental analysis through SEM EDS confirmed that all the samples comprise 74-76 wt% Ba along with small amounts (26-24 wt %) of Sulfur and Strontium.

## 1. INTRODUCTION

The only source of barium is barite. Due to its high specific gravity (4.5) about 76-80wt% of world barite is grounded and used especially in the drilling of oil and gas wells. The density of the mud is increased with barite because it causes faster discharge of cuttings and prevents the blowout<sup>1</sup>. In order to produce high quality barite for drilling mud, the density of barite can be increased by removing the quartz<sup>2</sup>. Barite is used as starting material for the production of barium compounds. It is used as filler in paints and plastics. The estimated amount of barite used in 1995 was about 76-80wt% for oil development, 9-13wt% for industrial use and 5-9wt% for direct use as filler<sup>3</sup>.

Barite deposits are found in all regions of the world. In Europe the most important sources of barite occur in Germany, France, Italy, UK, Belgium and Spain. In Americas significant deposits are found in USA, Canada, Mexico, Brazil and Argentina. In Africa, Morocco is the most important

producer of barite followed by Algeria and Tunisia. In middle and Far East the barite producing countries are India, Iran, Turkey, Indonesia, North Korea, Thailand, Pakistan, Malaysia, Japan and Australia. China is the largest producer of barite and produces  $1.5 \times 10^6$  tons/annum of barite<sup>3</sup>. Pakistan is producing ~ 50,000 metric ton barite. Most commonly barite deposits are associated with quartz, fluorite, carbonates and sulphides that are probably synchronous<sup>4</sup>.

## BARITE DEPOSITS IN PAKISTAN

In Pakistan the most important deposits of barite are hydrothermal replacement deposits in limestone<sup>5</sup>. They are found in Kalat and Quetta divisions but the most important and high grade barite deposits are found in Hazara division of Khyber Pukhtunkhwa (KPK). The barite deposits of Kacchi are about 1.5 miles to east of Kacchi and 13 miles to NW of Haripur. The ore is bluish-white and of high quality with subordinate amounts of quartz. A sample of crude ore contains 76.13wt% of

barium sulfate and 20.39wt% of silica<sup>5-6</sup>. The Faquir Mohammad (33°56'30" N: 73°09'30" E) barite deposits occur at 17 miles to east of Haripur and half mile to SW of village Faquir Mohammad. The barite deposits of Tipra (33°56' N: 73°06'30" E) occur at half mile to north of Haripur-Lora road. Its grade is of high quality with 86.8% of barium sulphate. The largest barite deposit of Hazara is in Kohala (35°06' N: 73°27' E). The deposit is about three miles to SW of Kohala and is quit pure. The estimated reserves are about 25,000 to 30,000 short tonnes with 3-10 tonnes production per day<sup>5</sup>.

## 2. EXPERIMENTAL WORK

Three locally available barite samples named as Barite, Barite-77 and Barite-81 from Kacchi, Beer and Kohala mines of Hazara Division, Khyber Pukhtonkhwa (KPK) were selected for present study. The samples were crushed in a stainless steel mortar & pestle into powder form with 200 mesh particle size. The concerned phases were analyzed by using JEOL 3532, X-ray diffractometer with Cu k<sub>α</sub> (λ=1.54Å) operating at 40kV and 30 mA. For SEM (JEOL JSM 5910 SEM), ~ 4×4×4 mm<sup>3</sup> barite pieces were cut with a TeckCut 4<sup>TM</sup> precision low speed diamond saw (Allied High Tech. Products, USA). The samples were finely polished with a TwinPrep 3<sup>TM</sup> grinding/polishing machine (Allied High Tech Product) polished with diamond paste on imperial adhesive back polishing cloth using water as a lubricant. The smooth polished surfaces were chemically etched with 5% hydrofluoric acid (HF) for one minute. Finally, the samples were mounted onto aluminum stubs with silver paints and gold-coated to avoid charging in the SEM. The surface morphology and approximate size of grains and micro-regions in the sample were examined by using JEOL JSM 5910 SEM. Elemental analyses were carried out

using EDS (Oxford instruments) attached with the SEM.

## 3. RESULTS AND DISCUSSION

Although various radiometric anomalies have been recorded in different barite veins and faults<sup>7-8</sup>; however, radioactivity is not associated with the studied barite mineralization. The lack of radioactive elements in the discovered barite mineralization is greatly advantageous in increasing its economic significance<sup>9</sup>. The Hazara barite samples were tested on a digital radiation detector Gama scout and the activity found was ~ 0.20 μ seconds/h which is not hazardous and dangerous for human health.

The mean specific gravity of the samples was determined by High Precision Densitometer Md-300s at Materials Research Laboratory, University of Peshawar. The specific gravity of sample Barite is 4.144 g/cm<sup>3</sup>, Barite-77 is 3.752 g/cm<sup>3</sup> and Barite-81 is 4.367 g/cm<sup>3</sup>.

The XRD patterns of the samples are shown in Figure 1. From the position of the diffraction peaks and the relative peak intensities, the determined phase and chemical composition of the samples corresponding to the observed XRD peaks matched PDF# 39-1469 for barium strontium sulfate and PDF# 13-141 for Sulfur. As apparent from the XRD peak width and relative intensities, the examined samples were fully crystalline. Table 1 shows the d-values and the intensities of the three representative barite samples. It is found that the peak positions of the samples matched with barium strontium sulfate and sulfur phases as given in the Table 1. The X-ray diffraction pattern of the raw barite ore shows the less broad peaks indicating the rough and coarse nature and larger crystallite size of the particles.

Mineral samples of barite were polished with diamond paste on imperial adhesive back polishing cloth using water as a lubricant. The

samples were coated with a thin layer of evaporated gold for conduction and examined in a JSM 5910 (JEOL Japan) analytical SEM operating at 20kV. Oxygen was not measured directly but was calculated on the basis of XRD result using assumed stoichiometries to the other elements analyzed.

Figure 2 is a secondary electron image (SEI) of Hazara barite samples showing different

grains containing varying composition of sulfur, strontium and barium as detected by EDS. The presence of peaks for Fluorine in the EDS spectra may come from the remnant decomposition products of hydrofluoric acid (HF) used as etchant in this study. In Figure 2 (a) the elemental and oxide compositions of the grains labeled by A, B and C as

Table 1. A comparison of the d-spacings and relative intensities with relevant PDFs.

| Sample#1<br>Barite |      | Sample#2<br>Barite-77 |      | Sample#3<br>Barite-81 |      | Ba <sub>0.75</sub> Sr <sub>0.25</sub> SO <sub>4</sub><br>PDF 39-1469 |      | Sulfur (S) Rosickyite, Syn.<br>(PDF 13-141 ) |      |
|--------------------|------|-----------------------|------|-----------------------|------|--|------|--|------|
| d-value            | I/Io | d-value               | I/Io | d-value               | I/Io | d-value  | I/Io | d-value                                      | I/Io |
| 4.2956             | 41   | 4.3080                | 38   | 4.2874                | 36   | 4.314  | 24   |  |      |
| 3.8570             | 44   | 3.8836                | 38   | 3.8736                | 37   | 3.869  | 39   |  |      |
| 3.7921             | 42   | 3.7794                | 38   | 3.7857                | 37   |  |      | 3.79   | 14   |
| 3.5477             | 59   | 3.5421                | 70   | 3.5477                | 63   | 3.539  | 28   |  |      |
| 3.4139             | 100  | 3.4088                | 100  | 3.4139                | 100  | 3.406  | 100  |  |      |
| 3.2924             | 47   | 3.2901                | 47   | 3.2996                | 41   | 3.281  | 60   | 3.29   | 100  |
| 3.0806             | 52   | 3.0785                | 51   | 3.0764                | 50   | 3.070  | 97   | 3.10   | 10   |
| 2.8168             | 43   | 2.8168                | 40   | 2.8151                | 40   | 2.8081   | 48   |  |      |
| 2.7137             | 45   | 2.7121                | 44   | 2.7121                | 40   | 2.7197   | 34   |  |      |
| 2.3121             | 40   | 2.3019                | 36   | 2.3167                | 36   | 2.3090   | 15   |  |      |
| 2.1974             | 40   | 2.1964                | 37   | 2.2026                | 35   | 2.1949   | 22   | 2.18   | 4    |
| 2.0961             | 47   | 2.1083                | 44   | 2.1092                | 44   | 2.0947   | 69   | 2.10   | 2    |
| 1.6704             | 41   | 1.66                  | 38   | 1.66                  | 35   | 1.6754   | 6    | 1.679  | 2    |

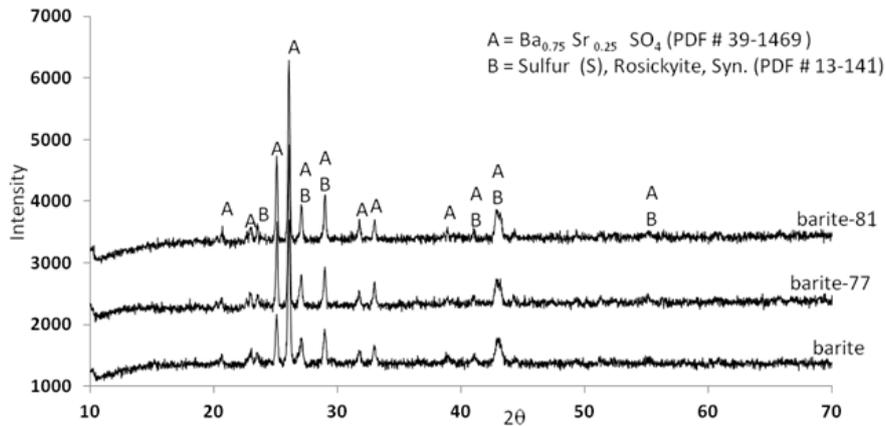


Figure 1. XRD pattern of Barite sample showing the presence of barium strontium sulfates (A) and Sulfur (B) phases.

determined from EDS and oxides formula are summarized in Table 2. In Figure 2 (b) the dark black grains labeled by ‘A’ indicating pure quartz (99wt% silica). The light dark region (B) around the region (A) indicating

the presence of 20.48 wt% Sulfur, 2.87 wt% Strontium and 76.65 wt% Barium. Figure 3b shows the microstructure of the sample comprises of well connected dark regions with sharp edges. The elemental and oxide

compositions of different marked regions summarized in Table 3. labeled by A, B, C and D of Figure 3a are

Table 2. EDS analysis of marked micro-regions A, B and C in Figure 2a.

| Region          | S (wt %) | SO <sub>2</sub> (wt %) | Sr (wt %) | SrO (wt %) | Ba (wt %) | BaO (wt %) |
|-----------------|----------|------------------------|-----------|------------|-----------|------------|
| A               | 21.4     | 32.7                   | 3.37      | 3.0        | 75.23     | 64.2       |
| B(Bright Lines) | 21.2     | 32.5                   | 3.46      | 3.1        | 75.30     | 64.3       |
| C               | 20.7     | 31.7                   | 2.70      | 2.4        | 76.63     | 65.8       |

Table 3. Composition of micro regions of barit-77 sample of Figure 3a.

| Region         | S (wt %) | SO <sub>2</sub> (wt%) | Sr (wt %) | SrO (wt%) | Ba (wt %) | BaO (wt%) |
|----------------|----------|-----------------------|-----------|-----------|-----------|-----------|
| A              | 20.76    | 31.9                  | 3.2       | 2.9       | 76.0      | 65.2      |
| B              | 20.10    | 30.9                  | 3.9       | 3.7       | 75.9      | 65.4      |
| C              | 99% Si   | 99% Si                | 99% Si    | 99% Si    | 99% Si    | 99% Si    |
| D (Mix grains) | 20.15    | 31.0                  | 3.9       | 3.4       | 76.0      | 65.5      |

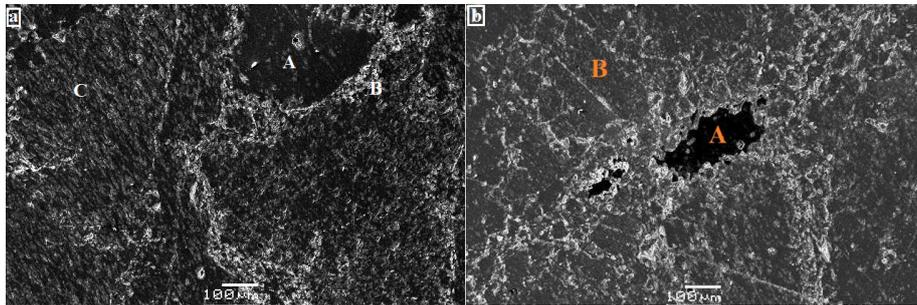


Figure 2 (a-b). SEI of Hazara barite sample showing different grains of different composition.

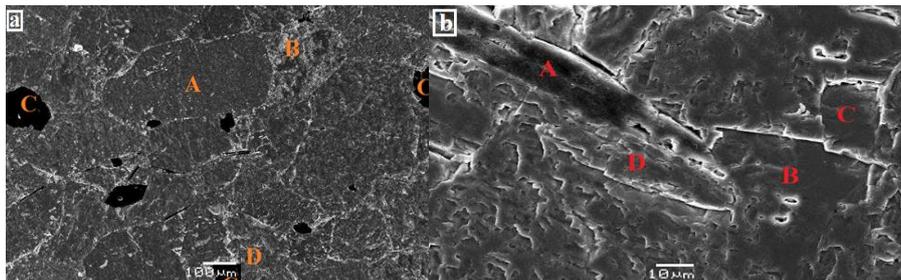


Figure 3 (a-b). SEI of Hazara barite-77 sample showing different grains of different composition.

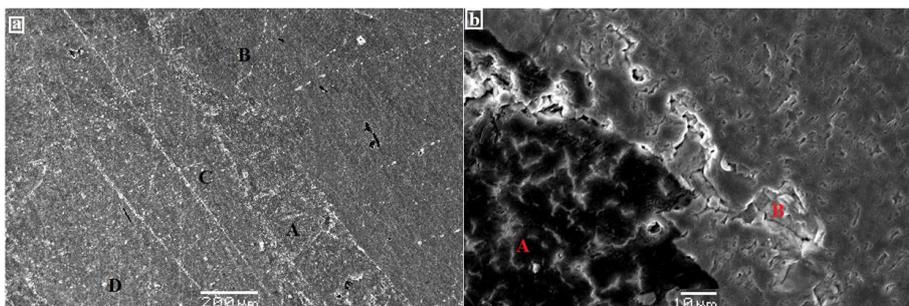


Figure 4 (a-b). SEI of Hazara barite-81 showing different grains of different composition.

The composition of grain A in Figure 3b consists of elements Mg, Al, Si, K, Fe and Nb. Similarly the compositions of grains B, C and D contains S (21.37wt %), Sr (3.72wt %) and Ba (74.91wt %); similarly, the oxides of same regions are BaO (63.98 wt%), SrO (3.36 wt%) and SO<sub>2</sub> (32.65wt%).

The elemental and oxide composition of Figure 4a consist of barium, sulfur and strontium as detected in the grains labeled as A, B, C and D a very slight variation of <3wt% in BaO, <2wt% in SrO and ~ 1wt% in SO<sub>2</sub>. Similarly, the composition of Figure 4b marked as grain 'A' with dark morphology comprise of different elements 28.41 wt% MgO, 61.44 wt% CaO and 10.13 wt% Fe<sub>2</sub>O<sub>3</sub>; however the labeled grain B consist of 25.53 wt% SO<sub>2</sub>, 2.0 wt% SrO and very high content 72.46 wt% of BaO.

## CONCLUSION

This study presents preliminary findings from a three different sites of barite reserves in Hazara region. Also sufficient number of samples have not been analyzed and studied from the concerned sites of barite reserves. Therefore neither these findings are conclusive regarding the barite samples studied nor could the findings be generalized in the larger context. Notwithstanding these limitations of the study, we conclude that the examined samples comprised barite as the major phase along with sulfur as a minor phase. Most of the micro-regions examined were irregular shaped. EDS results were consistent with our XRD findings.

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## REFERENCES

1. Oil Companies Material Association (OCMA): Specification No. DFCP 3, Cecil Chambers, London 1973. American Petroleum Institute (API): API RP 13B, 6th ed., Washington, D.C., 1976.
2. Sachtleben, DE-OS 1955881, 1969.
3. Ulmanns encyclopaedia of industrial chemistry barium and barium sulfide, 6<sup>th</sup> ed., 2002 by Wiley-VCH.
4. Ahsan SN and Mallick KA. Geology and Genesis of Barite Deposits of Lasbela and Khuzdar Districts, Baluchistan, Pakistan, Resource Geology, 1999; 49(2): 105–111.
5. Ahmad Z. Directory of mineral deposits of Pakistan. Records of Geological Survey of Pakistan. 1969; 15 (3): 55-59.
6. Shah SMI, Stratigraphy of Pakistan Memoirs of the Geological survey of Pakistan. 2009; 22: 348-50.
7. El-agami, Wahab A, Haroun YS. Apatite alteration and its relation to REE fractionation and U-mineralization: A Case study of Western Desert and Sinai, Egypt. The 4<sup>th</sup> international Conf. on the geology of Africa. 2005.
8. Morsy, MA. Geology and radioactivity of late Cretaceous – Tertiary sediments in the Northern Western Desert, Egypt. Ph.D. Thesis, Fac. Sci, Mansoura Uni., Egypt, 1987.
9. Haroun YS, Raslan MF. Occurrence of barite mineralization in bahariya depression, western desert, Egypt Physicochem. Probl. Miner. Process. 2010; 44:41-52.