SindhUniv. Res. Jour. (Sci. Ser.) Vol. 52 (01) 21-30 (2020)
http://doi.org/10.26692/sujo/2020.03.04
SINDH UNIVERSITY RESEARCH JOURNAL (SCIENCE SERIES)

Mineralogical Studies of Manchar Formation (Pliocene), Laki Range, Pakistan: source and Possible Occurrence of Bauxite

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Received 20th June 2019 and Revised 13th December 2019

Abstract: The petrographic and geochemical studies are carried out in order to understand the mineralogical, geochemical, source and economic potential of the Manchar Formation. The investigation approach involved field studies, followed by laboratory techniques involving thin section study, major element geochemistry and SEM-EDS analysis. Both, the SEM imaging and petrography indicate that the quartz grains are moderate to well sorted with sub angular to sub rounded shape and are mostly monocrystalline. The heavy minerals are seen upto 2% and are mostly ilmenite. Moreover, the shape of grains indicate that the source was not far away and both the primary porosity and permeability have been decreased due to the secondary solutions, that are mostly carbonate in the form of calcite. The whole rock geochemical analysis revealed that at some stratigraphic positions some shales are highly rich in aluminum contents and thus qualify for bauxite deposit but need further evaluation for commercial use. On the basis of present findings, it is concluded that the source area was not far away and it is probable that the sediments came from western highlands instead of Himalayas as is generally thought.

Keywords: Manchar Formation, Bauxite, Mineral Potential, Laki Range, Lower Indus Basin

1. INTRODUCTION

The Neogene sedimentary strata of the Kirthar and Laki Ranges reflect the transition from marine shelf to the continental depositional system, related to the uplift and erosion of the Himalayan orogenic belt. The Late Miocene to Early Pliocene Manchar Formation records the imperative interval of tectonosedimentary history of regional transition from the marginal marine to the fluvial depositional system.

The Manchar Formation; named by William (1969) after Blanford (1876), is largely exposed near famous Manchar Lake of Jamshoro district in Sindh along the eastern flank of Kirthar and Laki Ranges. The rock units are mainly of beach, deltaic, flood plains, estuarine, lacustrine and fluvial origin with well-preserved vertebrate fossils and wood logs. On the basis of mammal bones and silicified wood fossils the Pliocene age was given to the formation by Pilgrim (1908). Preliminary investigation of the Manchar Formation suggested Middle to Late Miocene funnal composition and paleomagnetic data indicated an absolute age of 15.2 Ma (Khan *et al.,* 1984).

Some basic information in the form of depositional environment and lihtology for Manchar Formation is available but detailed mineralogical, geochemical and petrographic studies are lacking. Therefore, present studies were undertaken to know about the economic mineral potential (especially of bauxite) of this formation in particular and source of sediments in general.

General Geology of the Study Area

The study area bears the exposures of six formations which are listed in **(Table 1)** and shown in **(Fig. 2)**. The Laki and Khirthar formations are mainly composed of various types of limestone along with shale and subordinate sandstones. The Nari Formation consists of sandstone, shale and subordinate limestone. The Gaj Formation mainly consists of sandstone with subordinate limestone, conglomerate, and shale. Shale is dark grey, purple, greenish grey and pale brown colour. It is sandy, soft, and partly gypsifereous. Sandstone is dark brown, greenish grey, yellowish brown and ferruginous. The Gaj Formation is conformably overlain by Manchar Formation. The major lithologic units of the Manchar Formation are identified in the light of field features and petrography; shale dominates in the lower part and the upper part of the formation is rich in sandstone. Sandstone is friable, hard and compact with grey, greenish grey and light yellowish in color and is fine, fine-medium and coarse to pebbly grained. Some of the units are cross-bedded. Shale is soft, white, brown, yellow and brick colored. Conglomerate contain pebbles of sandstone and fossilifereous limestone, which resembles with the shales of Nari, Gaj, and Kirthar formations. The Formation transitionally underlie the Dada Conglomerate, unconformably overlie various older formations such as the Gaj, Laki, and

Kirthar. Mammal bones of Pliocene age and silicified wood fossils are reported on the basis of which the Pliocene age is assigned to the formation (Pilgrim, 1908).

Table 1. Stratigraphy of the studied area.

Pleistocene	Dada Conglomerate	Conglomerate, Boulders and Pebbles
Miocene to Pliocene	Manchar Formation	Conglomerate, Sandstone and Shale
Miocene	Gaj Formation	Shale, Sandstone and Limestone
Oligocene	Nari Formation	Sandstone, Limestone and shale
Unconformity		
Eocene	Kirthar Formation	Limestone
	Laki Formation	Limestone, Sandstone and Shale

2. MATERIALS AND METHODS

For the present investigations the fieldworks for sampling and section measurement were conducted along Theri section near Sehwan Sharif, shown in **(Fig. 1).**

During the fieldworks a total of 805 feet thickness for the formation was measured. From the above measured section eighteen samples on the basis of textural and lithologic variations were collected at varying intervals. Along the measured section the Manchar Formation unconformably overlie the Nari Formation. For the petrographic analysis, six (06) consolidated to semi consolidated representative samples were selected for the preparation of standard thin sections. Out of eighteen samples, only four samples were selected for the SEM-EDS analysis based on major lithological variation (lithofacies). The analyses were carried out on JEOL JSM-6490 LV model of the Scanning Electron Microscope at the Centre For Pure and Applied Geology (CPA Geology). For the geochemical investigation, all the collected samples were analyzed on a WD X-Ray Fluorescence (XRF) spectrometer available in CPA Geology, University of Sindh, Jamshoro. The voltage and current were set as 15-60Kv and 20-150mA, minimum and maximum respectively.

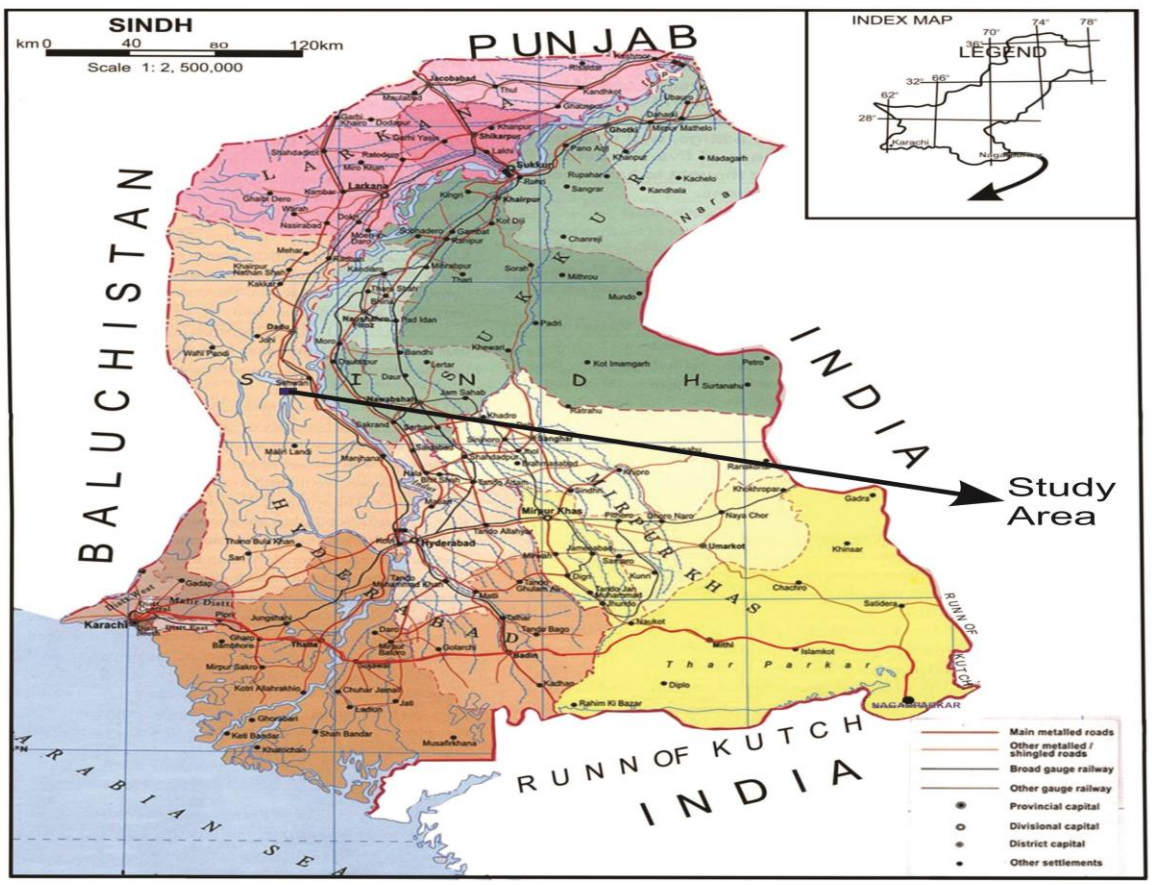

Fig 1. Map of Pakistan showing the location of the studied area.

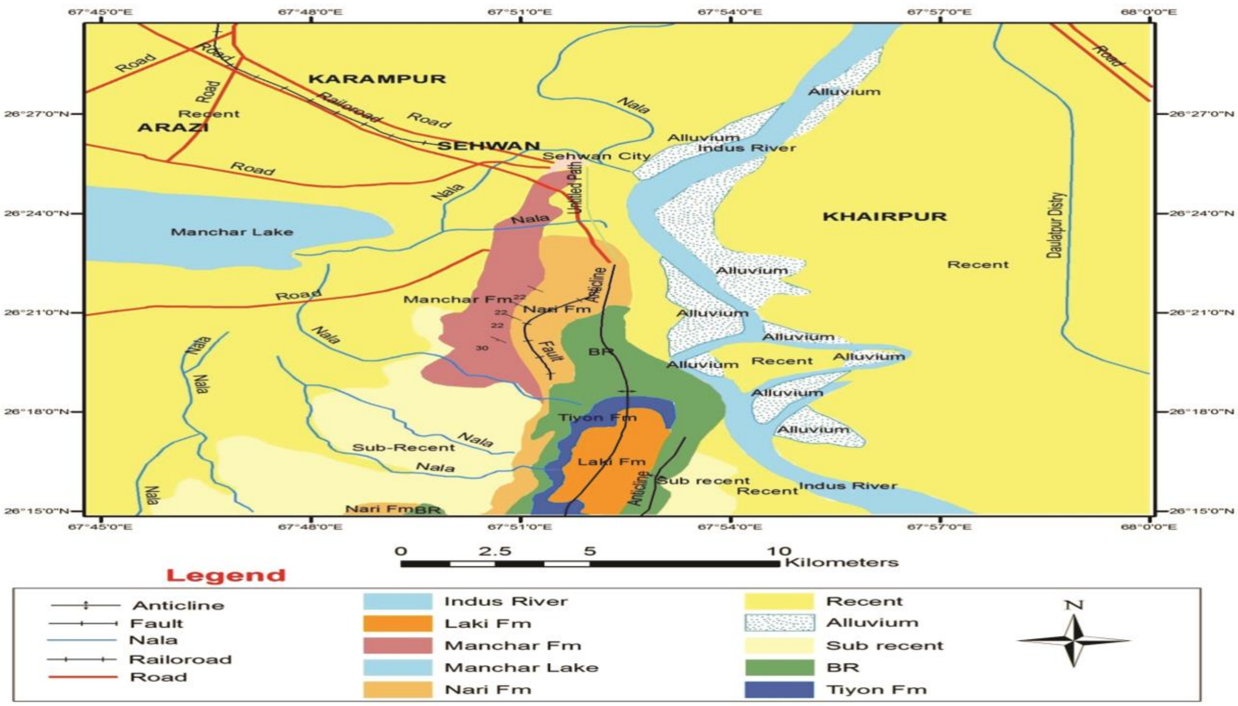

Fig 2. Geological Map of the study area showing different formations and other information.

3. RESULTS (PETROGRAPHY)

Sample # TH-07/14

This sample was taken from the basal part of Manchar Formation near the contact of Nari Formation. It is sandy shale within hard sandstone having weather color as white while the fresh colour is white to greyish. With the help of hydrochloric acid (HCl) it became evident that some of the filled grains of vesicles are carbonatic in composition **(Fig. 3).** During thin section study, it was observed that the main constituent of this sample was quartz ranging from 50-55%. Quartz grains were fine grained, rounded to sub rounded in shape and moderate to well sorted. They were embedded within the groundmass of clays (Fig. 3). Grains were matrix supported and major cementing material is clay but also calcite at places. There are no grain contacts. No feldspar is seen except 1-2% muscovite and less than 1% ore mineral. Few flakes of biotite were observed.

Sample # TH-10/14

This sample is semi consolidated and fine to medium grain sandstone. It contains light yellowish colored nodules which are about 2 cm in size with iron concretes as shown in **(Fig. 3d).** Major constituent was quartz (more than 80%) with few lithic minerals **(Fig. 3e).** Fine to medium grains of quartz were observed which are generally rounded to sub- ounded in shape and moderate to well sorted, majority of grains have suture and point contacts **(Fig. 3e,f).** Light pink/greenish fine matrix supported grains were present which were either clay mineral or calcite. Most of the grains were monocrystalline. The lithic minerals were muscovite and plagioclase feldspar and some grains of ore minerals were also observed.

Sample # TH-11/14

This fine to medium grained, hard and compact light grey sandstone sample **(Fig. 4a)** was taken from hard interbedded band within sandstone unit having 22 feet thickness. Using hydrochloric acid (HCl) it became evident that it was highly calcareous in composition. This sandstone has more than 85% quartz and few lithic minerals of muscovite **(Fig. 4b, c).** Ore minerals were also seen upto 2% but no feldspar was seen. Fine to medium grains of quartz were observed while the shape of grains was sub angular to sub rounded with moderate to well sorting.

Sample # TH-15/14

This sample is fine grained hard shale light green to dark green in color. The HCl test made it evident that it is not calcareous in composition. Under microscope, it is mainly composed of fine grained clay particles.

Sample # TH-18/14

This sample is similar to sample TH-11/14. It was taken from a hard band interbedded with fine to medium grain sandstone bed within sandstone unit. Using HCl it became evident that it was highly calcareous in composition. The major constituent of this section is more than 80% quartz. The quartz grains were observed as fine to medium, angular to sub angular in shape and moderate to well sorted. Majority of quartz grains are corroded from sides as well as from the center. Matrix in the form of clays was seen. 2-3% ore minerals with some flakes of muscovite were observed in this section **(Fig. 4c, d, e).**

Sample # TH-31/14

Like all above mentioned sample sections, this section also presents the major constituent under observation as quartz. The grains of quartz were fine to medium grained, sub angular to sub rounded in shape and moderate to well sorted **(Fig. 5a, b).** The matrix in form of clays was present. Few grains of plagioclase along with some flakes of muscovite were observed. At some places albite twinning was also seen.

Results (General Elemental Analysis using SEM and EDS)

Sample number TH-10/14 shows that the dominant elements of this sample are silicon, calcium and oxygen. It shows that quartz is the major mineral constituent while calcite is on second number. During thin section study, it was difficult to decide about the fine grained matrix that either it is calcite or something else. But the present EDS analysis confirmed that the matrix or cementing material is certainly calcite having higher concentration of calcium (19.99%) as shown in **(Fig. 6a, b).** The lithics are present in a very little amount in the form of muscovite and plagioclase feldspar. Few flacks of biotite were seen within this sample and ilmenite was found as the heavy mineral constituent. No rock fragments observed during the imaging. The textural features of sample TH-10/14 indicates that most of quartz grains are monocrystalline, usually moderate to well sorted. They are embedded within the calcite cement. The signs of point and suture contacts were seen during the examination of whole section. Quartz is generally rounded to sub rounded **(Fig. 6a, b).**

The general elemental analysis of sample # TH-11/14 indicates that silicon, oxygen and carbon along with calcium are the dominant elements. It shows that like TH-10/14, the quartz is the major mineral constituent having higher percentage of silicon; however, the dominant cements are clays and calcite. It was worth noting that the percentage of aluminum is high enough and so far points towards the presence of any type of bauxite. No rock fragments were observed during the entire section imaging. Further, the textural features indicate that quartz grains are usually moderately to well sorted and cemented within the micro-crystalline calcite and clays. At places the point and suture grain contacts were seen during the examination. The quartz is generally sub angular to sub rounded **(Fig. 6c, d).**

The general elemental analysis of sample # TH-18/14 also indicates that like the previous samples; silicon, oxygen along with calcium are the dominant elements of this sample. Therefore it is clear that quartz is the major mineral constituent followed by calcite. The percentage of calcium is 12.73% and the silicon is 17.21 % **(Fig. 7a, b).** Low percentage of aluminum along with iron rejects the presence of any type of clay minerals within this sample. The lithics are in the form of biotite and muscovite. No feldspar was seen while ilmenite was found as the heavy mineral constituent. No rock fragments observed during the imaging. The textural features of sample # TH-18/14 indicate that the quartz grains are usually moderately sorted and embedded within the micro-crystalline calcite cement. No signs of point and suture grain contacts were seen. The quartz grains are generally sub angular to sub rounded.

The general elemental analysis of sample # TH-31/14 indicates that the dominant elements are silicon, calcium, and oxygen. It shows that quartz is the major mineral constituent and the calcite is on second number. Like the earlier samples the matrix or cementing material is calcite because of higher concentration of calcium (18.19%) as shown in **(Fig. 7c, d).** The presence of any type of clay minerals within this sample is rejected due to low percentage of aluminum along with iron. The lithics are in the form of plagioclase feldspar and muscovite. Few flakes of biotite and albite twinning were seen within this sample. Ilmenite was found as the heavy mineral constituent. No rock fragments observed during the imaging. The textural features indicate that the quartz grains are usually moderately to well sorted and embedded within the calcite cement and generally sub-angular to sub-rounded. No suture grain contact was seen while the point grain contacts were observed throughout the section **(Fig. 7c, d).**

Point Analysis:

Quartz

Like general elemental analysis and petrography, the point analysis also confirms that quartz is the dominant mineral phase of all the analyzed samples. Different point analyses reveal presence of silicon and oxygen bearing minerals in significant amount with only small input of calcium **(Fig. 8a).** It is therefore very much clear that these analyzed grains are quartz while the calcium may have been incorporated from the nearby cementing calcite. Like TH-10/14, the TH-11/14 is also mainly comprised of quartz. The EDS data indicates that a majority of fresh looking and moderately to well sorted grains have higher concentration of silicon and oxygen and are very near to the typical composition of quartz with only a little percentage of calcium **(Table 2).** The SEM images point out that quartz grains are moderately to well sorted and bounded due to the micro-crystalline and sparry calcite cement. These quartz grains are generally sub angular to sub rounded and at some places the signs of point and suture grain contacts are observed **(Fig. 5.4).**

Biotite

Overall examination, imaging and elemental analysis of sample TH-18/14 indicates that the dominant lithic fragment is only the biotite. It is present to about 2-3 %. During thin section study, it was seen that a few flakes of muscovite are there but the elemental analysis indicates that majority of the micas are biotite. The SEM image **(Fig. 8b)** shows that the biotite flakes have bands just like the appearance of albite twinning (as is generally seen under polarizing microscope) but the elemental analysis indicates that these grains/flakes/lithics are neither plagioclase nor muscovite but are iron rich biotite **(Fig. 8b).** The higher percentage of iron and magnesium and lower values of potassium indicate that such biotites may be of quartz latite type. Some of the biotites look as bent grains. In some of the samples, the biotite flakes are of two types: one has albite twinning while the other are a little bent.

Ilmenite

It is usually seen that under Scanning Electron Microscope all the metallic or ore minerals give bright white colours relative to the most common rock-forming minerals which are generally grey in colour. All such grains were analyzed within sample Th-18. The results indicate that the analyzed grains are ilmenites (a titanium ore). This titanium ore also bears a significant proportion of iron, which is also evident from the analysis **(Fig. 8c).**

Cement

After quartz, the dominant mineral of all samples is calcite and is in the form of ultra-fine matrix/cement. The SEM image indicates about many unknown tiny grains that are present as an inclusion within the cementing material. The mineral chemistry of fine-grain matrix shows that the concentration of calcium is higher than silicon, aluminum, oxygen and carbon. Such mineral chemistry of cementing material is pointing towards the calcite and clears the confusion for the presence of clay minerals which was suspected during thin section study **(Fig. 8d).**

Table 2. Major element geochemistry of various rock samples from Manchar Formation, Theri Section, Sehwan Sharif. The concentration of aluminum oxide is highlighted due to the presence of bauxite.

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Total
Th-01A_14	41.60	0.15	7.26	43.00	0.84	0.51	5.49	0.78	0.15	0.24	100.02
Th-01B_14	42.30	0.05	2.44	49.70	0.94	0.49	3.30	0.42	0.18	0.21	100.03
Th-02_14	78.83	0.68	14.56	2.53	0.03	0.49	0.43	0.15	2.22	0.08	99.99
Th-03_14	69.77	0.67	18.26	7.56	0.04	0.60	0.25	0.18	2.55	0.11	100.00
Th-04_14	0.28	0.06	71.80	2.15	0.08	2.67	20.20	1.04	0.55	1.17	100.00
Th-05_14	78.89	0.70	12.05	4.09	0.05	0.73	0.56	0.23	2.60	0.11	100.00
Th-06_14	72.99	0.81	17.26	3.96	0.03	1.35	0.46	0.24	2.78	0.11	100.00
Th-07_14	52.20	0.32	30.60	4.37	0.08	1.62	8.63	1.26	0.33	0.59	100.00
Th-08_14	64.00	0.47	26.40	3.75	0.22	0.53	3.34	0.78	0.10	0.38	99.97
Th-09_14	69.70	0.43	20.70	3.99	0.10	0.60	3.14	0.82	0.13	0.35	99.95
Th-10_14	50.30	0.73	29.30	5.57	0.13	1.12	9.20	2.18	0.83	0.67	100.03
Th-11_14	49.10	0.84	30.80	4.71	0.13	0.99	9.51	2.51	0.77	0.55	99.91
Th-12_14	48.90	0.70	28.70	7.66	0.67	1.23	7.78	3.40	0.50	0.51	100.05
Th-13_14	11.40	0.15	56.80	7.17	0.27	2.50	15.20	4.56	1.08	0.84	99.97
Th-14_14	0.69	0.06	63.80	9.31	0.14	3.34	18.00	3.18	0.57	0.97	100.06
Th-15_14	0.98	0.05	67.60	7.25	0.08	3.01	16.90	2.56	0.60	1.01	100.03
Th-16_14	12.00	0.19	55.00	7.32	0.17	2.57	14.70	6.58	0.59	0.90	100.02
Th-17_14	62.20	0.74	20.60	6.17	0.19	0.97	5.84	2.44	0.48	0.40	100.03
Th-18_14	27.48	0.50	9.64	5.60	1.06	3.15	50.43	0.75	1.15	0.12	99.88

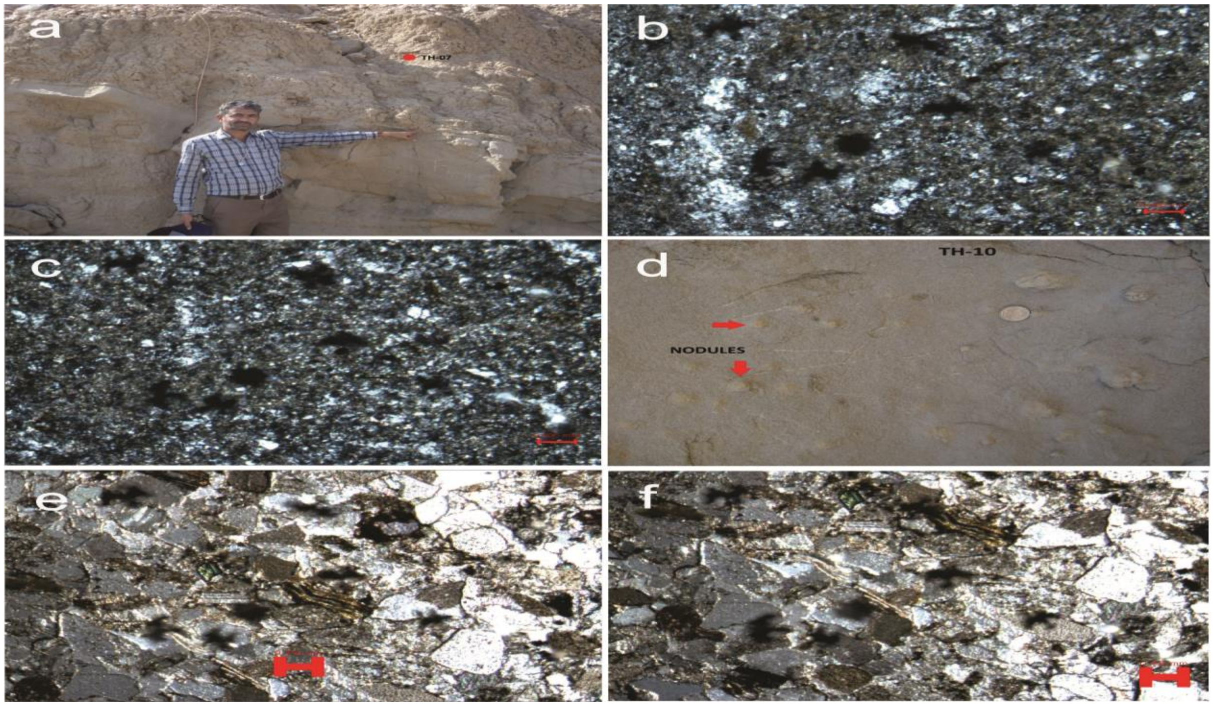

Fig 3. Field and microphotographs of various samples showing different features. a) fine-grained sandstone, b-c) microphotographs of above, where fine-grained quartz are embedded within ultra-fine matrix. D) Fine-grained, hard and compacted grey sandstone, e-f) microphotographs of above, where sub-angular-sub-rounded quartz having different contacts is clearly visible.

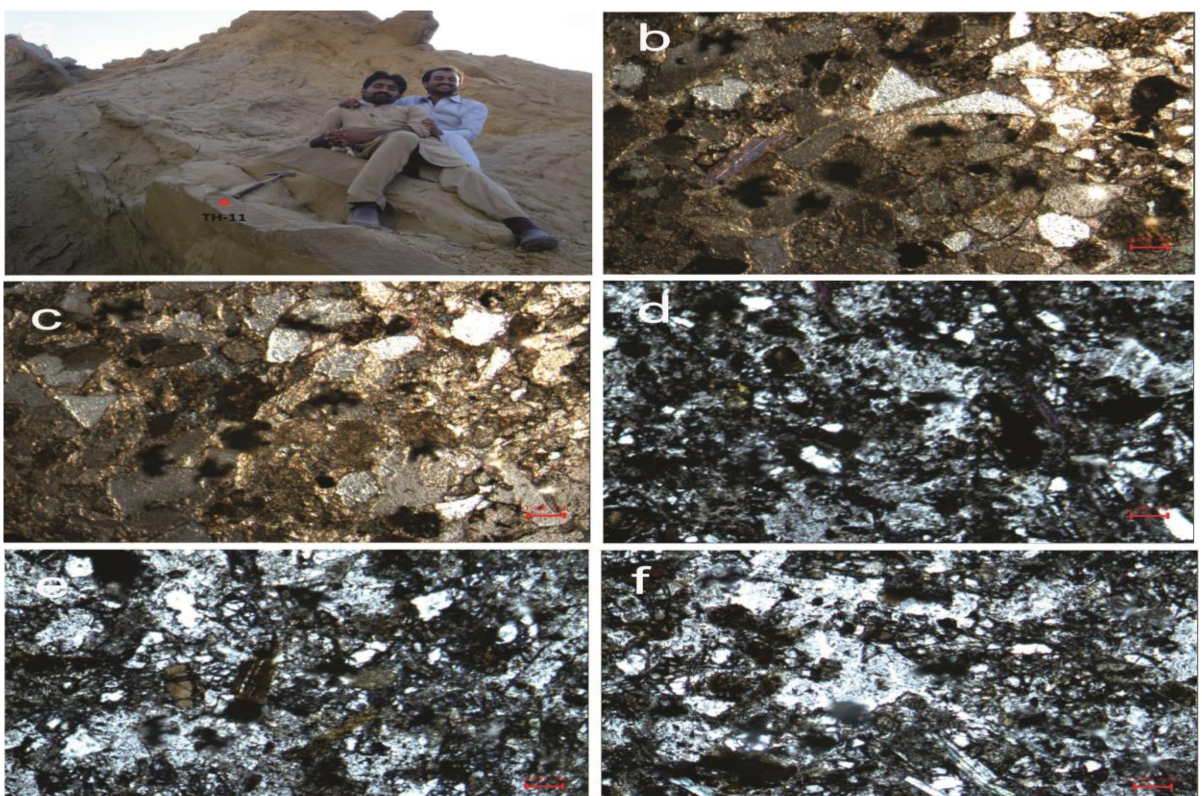

Fig. 4. Field photographs and microphotographs of various samples: a) Field photograph of sample TH-11; b-c) sub-angular to sub-rounded quartz grains embedded within fine matrix of calcite and clays; d-f) fine-grained, sub-rounded quartz grained floating within fine matrix. Some biotite flakes along with ores are also visible.

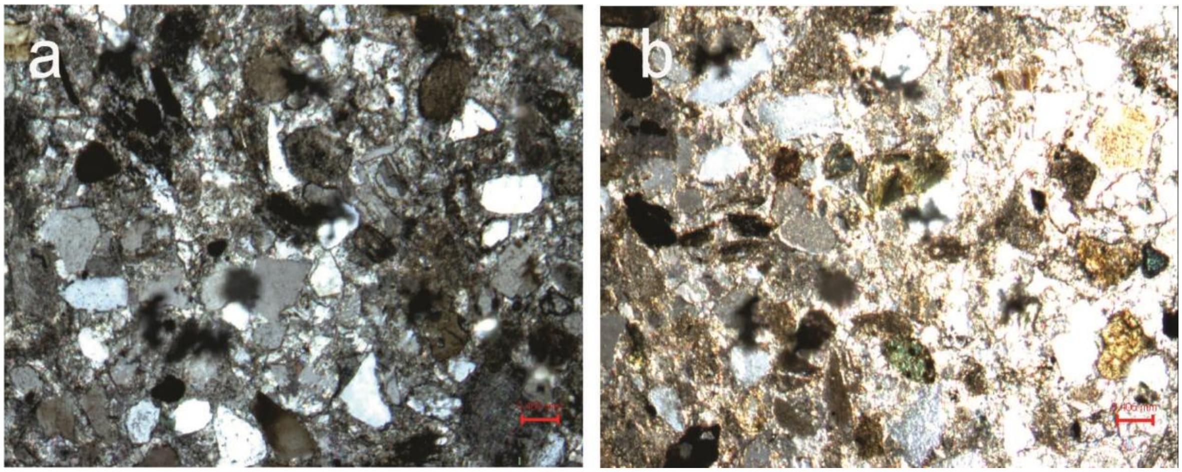

Fig 5. Moderately-sorted and sub-rounded quartz having point and suture contacts. A few ore minerals are also visible.

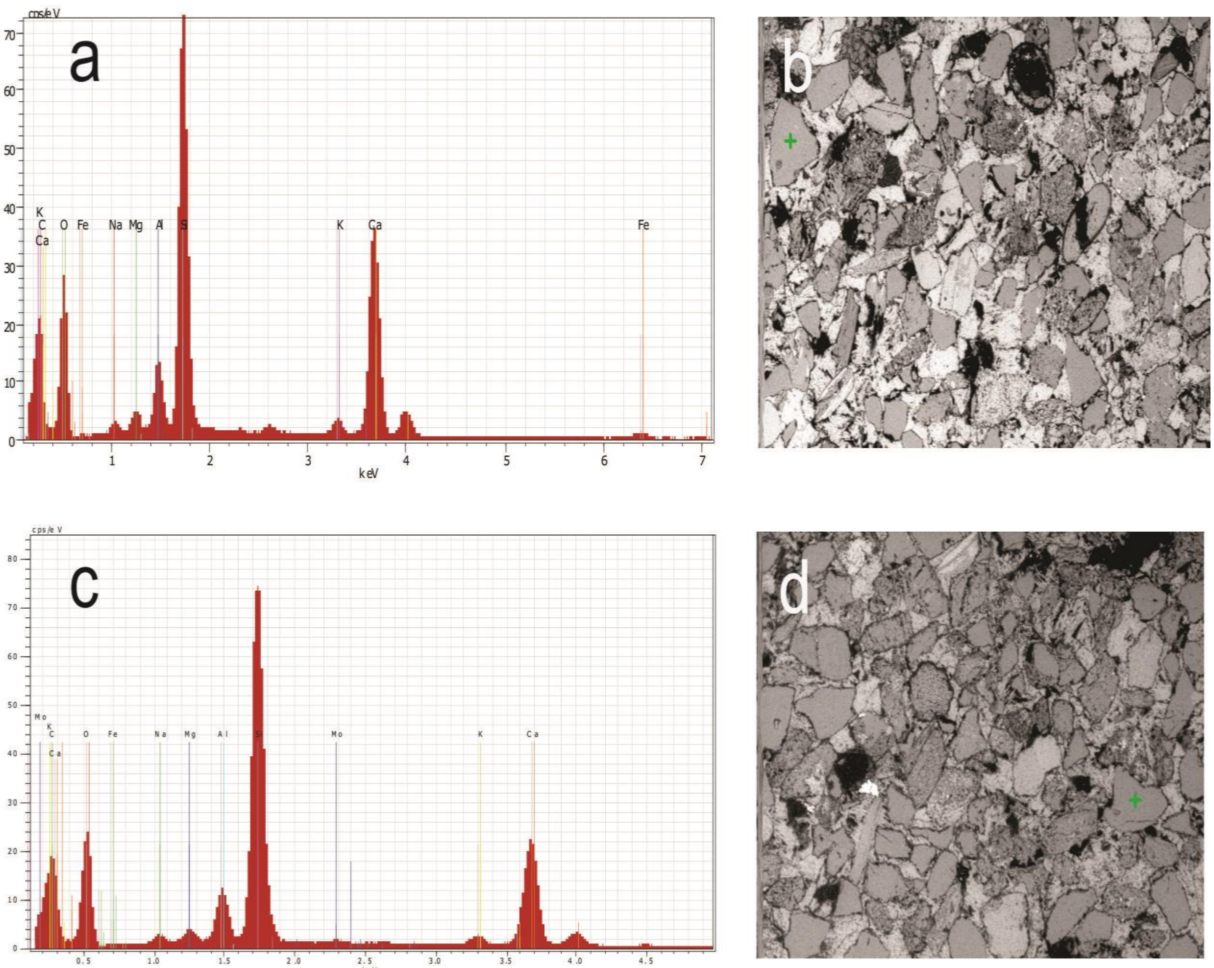

Fig. 6. a-b) Elemental spectrum and SEM image of TH-10. The peaks of silicon, calcium and oxygen are high enough and pointing the presence of quartz and calcite. The sub-angular to sub-rounded quartz grains with grey color are very common throughout the image; c-d) Elemental spectrum and SEM image of TH-11 with almost similar features.

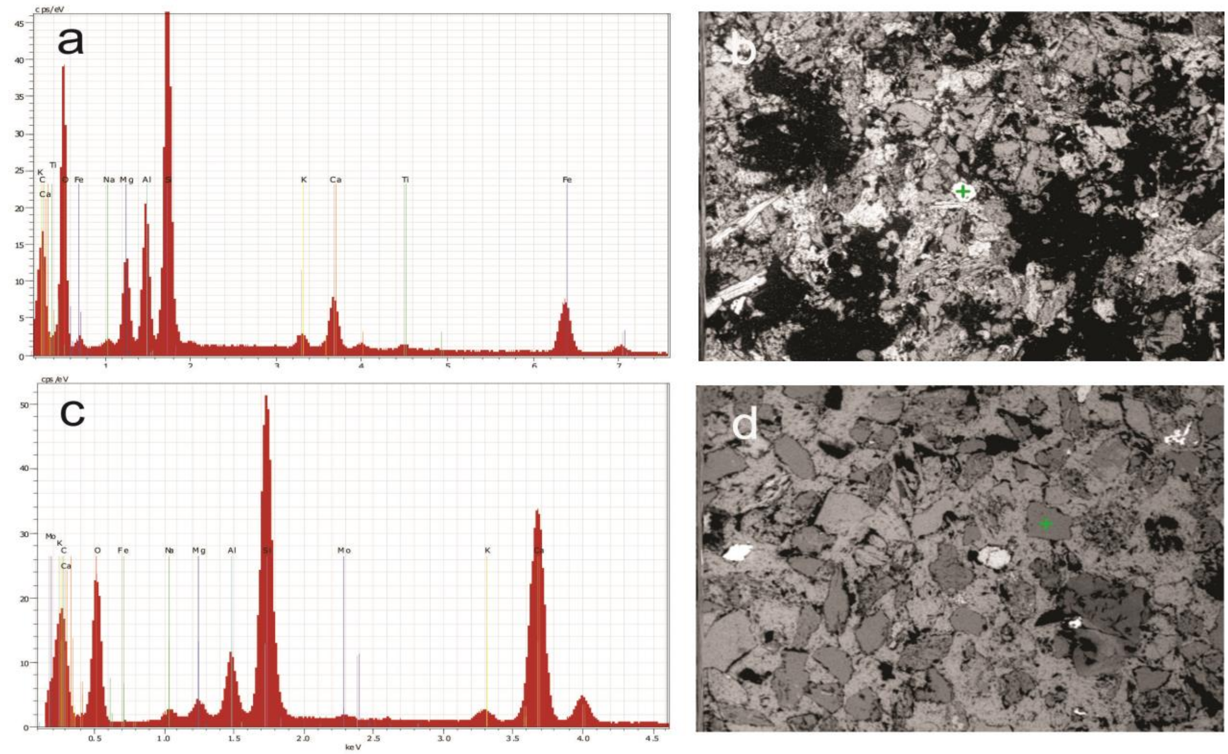

Fig. 7: a-b) Elemental spectrum and SEM image of TH-18. It is a non-homogeneous sandstone with significant proportion of quartz as well as of calcite cement. The flakes of muscovite and biotite are there along with certain ores such as the ilmenite etc.; c-d) Elemental spectrum and SEM image of TH-31. It is mostly composed of sub-rounded and moderately-sorted quartz grains that are embedded within calcite. The point and suture contacts within grains are also visible.

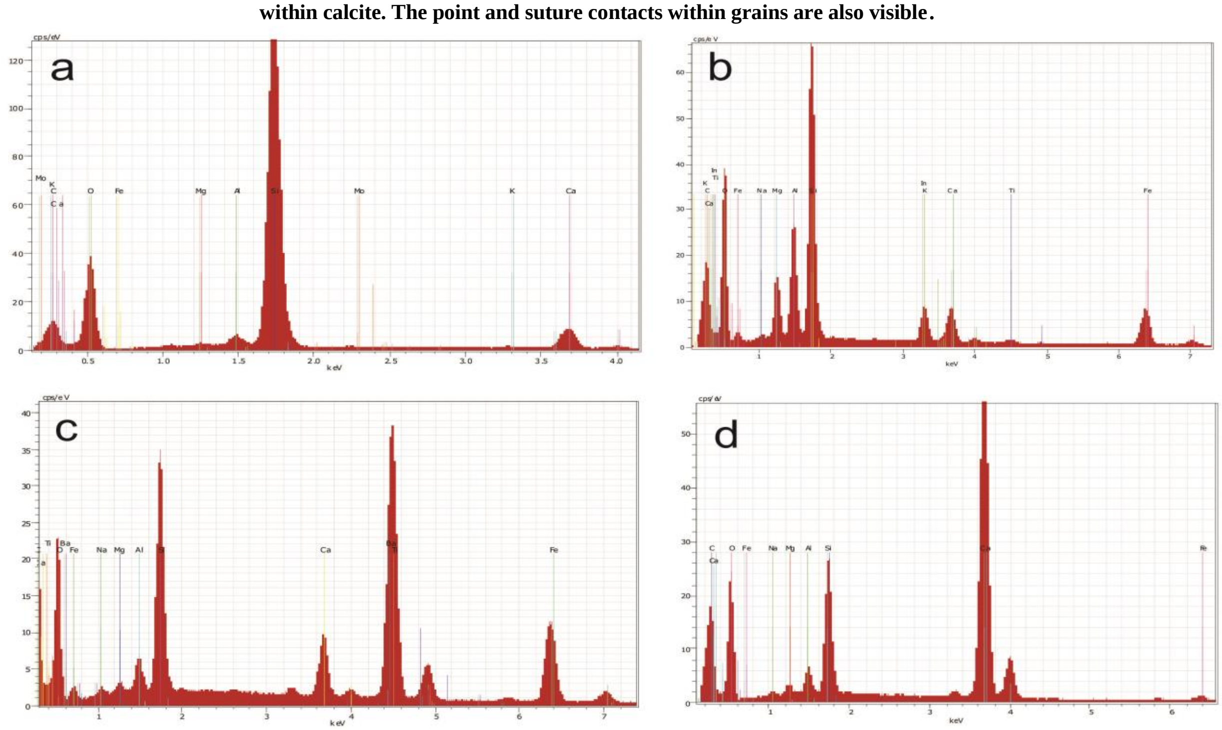

Fig. 8. Elemental spectra showing the point analyses for quartz (a), biotite (b), ilmenite (c) and calcite cement (d).

Line Scan Analysis

When a line passing through all of the mineral constituents drawn through sample Th-10 it became evident that all of the minerals identified in above mentioned sections are present. It is very much clear that throughout the line scan, the dominant color is of silicon and it only depletes where a grain of calcite is touched as is shown on the right and left side of the scan. The horizontal line drawn through sample Th-11 passing through all the mineral constituents indicates that like above observations, the quartz and calcite are the dominant minerals of this sandstone. On the basis of visual estimate it is concluded that the quartz crystals are more than 85% of the grain population in the sample.

Source of Sediments

It is very much clear from the obtained results of petrography and SEM images that the sandstones of Manchar Formation are dominantly composed of quartz with lithics of biotite, muscovite and ilmenite. A few grains of plagioclase were also seen. The dominant cementing material is calcite; however, the clays in some samples also there to play the part of cement. In terms of textural features; it is evident that the shape of majority of grains is sub angular to sub rounded. The grains are mainly floating within the calcite cement; however, at places, the point and suture contacts are also there. On such textural and mineral character; it may be said that the source of sediments was not far away.

Possible Occurrence of Bauxite

A few deposits of Bauxite in Pakistan are reported from Salt Range and lesser Himalayas (Ahmad 1969, Kazmi and Jan 1997, Kazmi and Abbas 2001) but at present no showings and commercial deposits are reported from Laki and Kirthar ranges. In present study; a few geochemical analyses show high values of Al_2O_3 (Table 2) in some of the rock samples collected from the Manchar Formation near Sehwan Sharif. The obtained results of whole rock geochemistry show that the Al_2O_3 ranges from 29.3 to 71.8 wt % (Table 2). Along with whole rock geochemical analysis through XRF; the obtained results of EDS clearly show the presence of various types of aluminum ore. Such higher values clearly indicate the presence of some type of bauxite and demand further exploration of bauxite deposits within Manchar Formation, exposed in different sections of Laki and Kirthar ranges.

4. DISCUSSION

Bauxite is formed from the laterite soil, rigorously leached of silica and other soluble materials in wet tropical or subtropical climate. Bauxite has not a definite chemical composition but rather is a mixture of clay minerals, hydrous aluminum oxides, aluminum hydroxides, and insoluble materials like siderite, quartz, hematite, magnetite, and goethite. Bauxite is characteristically a soft "Hardness from1-3", white, gray to reddish brown material having low specific gravity and pisolitic structure.

In Pakistan, the bauxite deposits are reported mainly from Salt Range and lesser Himalayas and these deposits largely occur along major unconformities (Ahmad 1969, Kazmi and Jan, 1997, Kazmi and Abbas, 2001). In Salt Range, the major deposits are reported from the Katha-Pail area (>100 m.t) and they are in the form of a clay-bauxite-laterite bed and are 1 to 7 meters thick (Fahad *et al.,* 2009). The ore contain 35.5% to 72.5% alumina, 8.68% to 50% silica and 10% to 20% iron (Ashraf *et al.,* 1972). The chemical composition declare it as low grade bauxite having high silica, moderate to low iron and alumina. The major minerals of this ore body are: boehmite and kaolinite with minor quantities of diaspore and gibbsite (Khan and Hussain 1970; Cheema 1974; Cruijs, 1975; Kazmi and Abbas 2001). Next locality is Chhoi-Akhori (46.5 m.t), where bauxite deposits occur in a highly tectonised sedimentary sequence of the Kalachitta hills (Fahad *et al.,* 2009). Hussain and Naqvi (1973) analyzed some samples from the Chhoi area; where Al_2O_3 is 74.24-86.84%, Fe_2O_3 is 0.64-0.74%, SiO_2 is 6.0-7.0% and TiO_2 is 3.65-4.28%. In addition, small and scattered bauxite deposits are also reported around the two outcrops of Abbottabad Group near Muzaffarabad and Kotli (Malik 1970, Ahmad and Siddiqui 1992, Kazmi and Jan 1997, Kazmi and Abbas 2001).

On the basis of a few earlier studies some non-metallic industrial minerals such as the celestite, fuller's earth, gypsum etc are known but no occurrence of bauxite are reported yet either from Laki or Kirthar Range (Ahmed and Siddiqui 1992; Ahmed 1969). The present study on Manchar Formation shows that it bears potential of various minerals especially bauxite and uranium-bearing minerals. The present geochemical analyses clearly indicate that some of the samples, especially the shales have higher percentage of aluminum (e.g., 71.8 wt. %) and low values of silica and iron oxide (Table 2) and thus qualify for bauxite. These rock units are thick enough to be exploited for the metal aluminum. Moreover, the percentage of other cations such as Fe_2O_3, SiO_2 and others are also within permissible limits (Table 2), so far, this formation may be a potential source of aluminum, if further studies such as XRD may be carried out to know about the type of aluminum minerals.

5. CONCLUSION

According to present field and mineralogical studies, it is concluded that Manchar Formation is mostly composed of sandstone, siltstone and shale.

Moreover, the textural features of grains indicate that the source was not far away. It is found that some of the rock units especially the shales have great potential for various bauxite minerals; where Al_2O_3 contents range from 30-71 % and needs more attention for further exploration and characterization in other sections of this formation.

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