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Analogize Studies on the Geochemistry of Bentonite Clays of Shaheed Ghat Formation (Early Eocene) from Eastern Sulaiman Range, Pakistan

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Abstract. The purpose of this research work was to designate the mineralogical and chemical characterization of the bentonite clay of Shaheed Ghat formation (Ghazij group). Two analytical techniques such as X-ray fluorescence (XRF) and X-ray diffraction (XRD), were applied to describe bentonite clay material from Eastern Sulaiman range (ESR) which comprises of three districts (DG Khan, Musakhel and Barkhan) of Pakistan. No comprehensive geochemical description of the area has been carried out to date. The results obtained from six different localities (ESR of Pakistan) were compared with each other, with indigenous areas of Punjab (Attock and Jhelum), KPK (Cherat, Garhi Chandan, Azakhel and Jhandola), Azad Jammu and Kashmir (Bimber) and three international countries Turkey (Tireboule), Brazil (Bao Vista) and Nigeria (Gombe state). From the XRF analysis, the major oxides in the selected clay samples are as $SiO_2 > Al_2O_3 > Fe_2O_3 > CaO > MgO > K_2O > TiO_2 > SO_3 > Mn_2O_3 > SrO$. The average value of silica (SiO_2), alumina, (Al_2O_3), iron (Fe_2O_3) and magnesium (MgO) contents of bentonite clays are 50, 12.57, 10.90 and 2.84 wt.%, respectively. The XRD result shows that Montmorillonite, Albite, quartz, Smectite and Illite are the major clay minerals. All the outcomes from the six sections (Zinda Pir, Khajuri, Rakhi Nala, Kingri, Kot Muhammad Khan and Rarkan) were close to the reported indigenous and international values.

Keywords: analogize studies, geochemistry, bentonite clay, eastern Sulaiman range

Introduction

Bentonite is a type of clay produced commonly from the weathering, transportation and alteration of volcanic ash. This type of clay is rich in smectite group clay minerals usually montmorillonite. Bentonite have a strong colloidal effects and its volume upsurges several times by adding water.

Due to the special swelling properties of bentonite clay, it is widely used in industry *i.e*. foundry, pelletizing, construction material, environmental protection, drilling, oil/food industries, agriculture, pharmaceuticals, detergents, paints, paper and catalyst processing. Bentonite encompasses a variation of supplementary minerals *i.e*. quartz, feldspar, calcite, Kaolinite, Illite, Albite and gypsum etc.

Structurally, each layer of bentonite clay organized of two structural sheets (octahedral and tetrahedral). The layers of montmorillonite are composed of a 2:1 structure *i.e*. two tetrahedral silica layers incorporating a central octahedral alumina layer. (Banik *et al*., 2015; Xi *et al*., 2007). According to British geological survey (BGS) Turkey, Brazil and Pakistan falls in the list of top 10 countries by bentonite production (Brown *et al*., 2018).

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Location. Administratively the research area involving three districts of Pakistan two from Balochistan Province (Musakhel and Barkhan) and one from Punjab province (Dera Ghazi Khan) and covering 4500 sq. km area. Shaheed Ghat formation is well exposed in these six sections from which three sections placed at Musakhel (Khajuri, Kingri and Kot Muhammad Khan), one from Barkhan (Rarkan) and two from Dera Ghazi Khan (Zinda Pir and Rakhi Nala) as shown below in Fig.1.

Geological setting. The study area lies in the eastern part of sulaiman range, where stratigraphy starts from Paleocene to recent and a complete stratigraphy set of early Eocene (Ghazij group) age exposed extensively. Ghazij group comprises four formations that are from older to younger as Shaheed Ghat formation → Drug formation → Toi formation → Baska formation.

Shaheed Ghat formation. It is mainly clay/shale with uncommon limestone bands. Clay/shale is grey, khaki

and calcareous with few gypsum sheets. The thickness of Shahed Ghat formation varies from 200 to 500 m at different localities. Lower and upper contacts of Shaheed Ghat formation with Dunghan (paleocene) and drug (eocene) are conformable correspondingly. Its age is also early eocene (Shah, 2009) and also shown in Fig. 2.

Material and Methods

Geochemical analysis done by Geoscience advance research laboratories (GARL) of Geological survey of Pakistan (GSP) Islamabad. PVA (Polyvinyl alcohol) added to the sample and powder pill produced by pressing the sample powder by HTP 40 (HERZOG Machine fabric GmbH Co., Osnabruck). For the preparation of powder pill, following steps were applied in the flow chart of Fig. 3.

Results and Discussion

Geochemistry is apprehensive with the chemical practices due to which all the elements are distributed in the earth, atmosphere and how they have transformed with time (John, 2009). For this purpose, many techniques are available but here we applied only two (XRD and XRF). Six characteristic sections (Zinda Pir, Khajuri, Rakhi Nala, Kingri, Kot Muhammad Khan and Rarkan) were selected for the mineralogical and chemical categorization of the bentonite clay of Shaheed Ghat formation. Five samples from each sections were collected for the laboratory work, therefore following values are the average results of 5 samples each.

The XRD outcomes (Table1) displays that most of the clay samples from 6 different sections are rich in

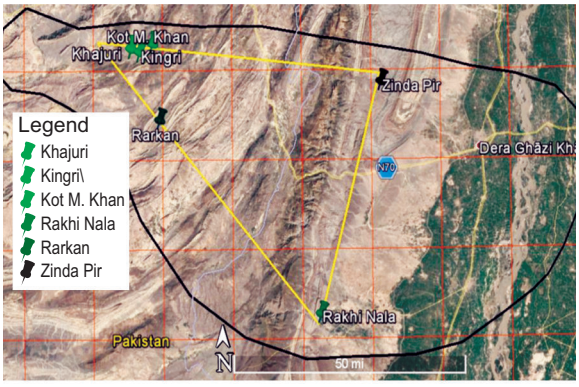

Fig. 1. Location map of the research area (source: google earth pro).

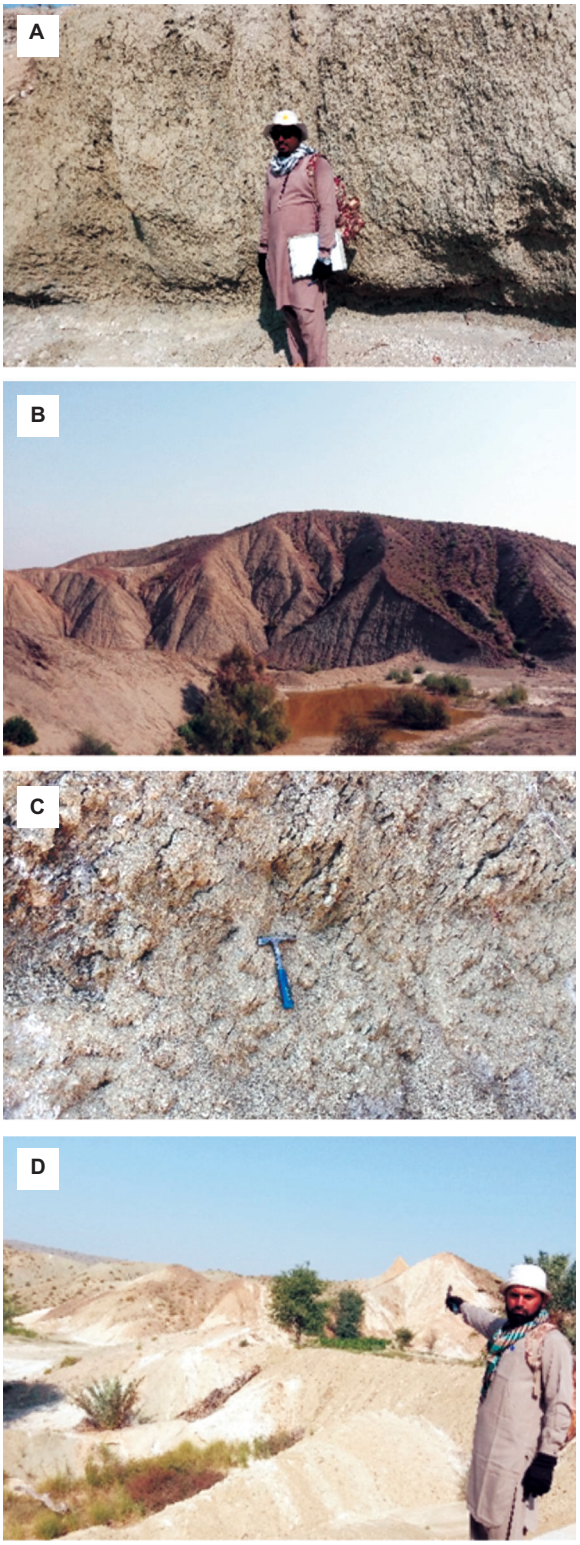

Fig. 2A-D. Field snaps of Shaheed Ghat formation (olive grey colour with gypsiferious shale and few limestone bands).

Table 1. XRD results of clay from Shaheed Ghat formation of ESR of Pakistan

Locality	Location	Identified minerals
Zinda Pir	N: 30 22 07 E:70 29 06	montmorillonite, kaolinite, Illite and quartz
Khajuri	N: 30 27 53 E:69 44 18	montmorillonite, albite, illite, smectite
Rakhi Nala	N: 29 58 19 E: 70 06 50	montmorillonite, kaolinite, illite
Kingri	N: 30 27 45 E: 69 46 04	montmorillonite, albite and quartz, smectite
Kot Muhammad Khan	N: 30 30 38 E: 69 49 49	montmorillonite, albite, Illite and quartz
Rarkan	N: 30 11 10 E: 69 50 27	montmorillonite, kaolinite, illite

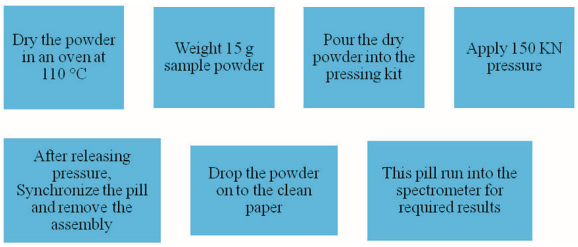

Fig. 3. Preparation of powder pill.

Montmorillonite, Illite and Smectite which are the foremost and energetic part of bentonite clay.

It is being deciphered from Table 2 and bar graph shown in Fig. 4, that the quality of bentonite clays of Shaheed Ghat formation deviating as Khajuri > Kingri > Kot Muhammad Khan > ZindaPir > RakhiNala > Rarkan.

When we equate the average values of bentonite clay (Table 3) of ESR with other indigenous (Punjab, KPK and Kashmir) values of bentonite clay of Pakistan. It demonstrations that the values of SiO_2, SO_3 and P_2O_5 are approximately equal, the values of Fe_2O_3, CaO, MgO and K_2O are greater, however the values of Al_2O_3 and TiO_2 are lower than other indigenous values. Where˜ (approximately equal), (high value) and (low value).

When we compare the middling standards of bentonite clay (Table 4) of ESR (Pakistan) with international countries (Turkey, Brazil and Nigeria). It indicates that the values of Al_2O_3, LOI, MgO and SO_3 are almost equal, the values of Fe_2O_3, CaO, Mn_2O_3, SrO, TiO_2 and K_2O are higher, however the values of SiO_2 is lower

Table 2. XRF results of clay from Shaheed Ghat formation of ESR of Pakistan

Major oxides	Zinda Pir	Khajuri	Rakhi Nala	Kingri	Kot Muhammad Khan	Rarkan	Average
SiO_2	47.12	63.22	42.53	54.86	51.65	40.62	50
Al_2O_3	12.71	15.87	9.4	14.12	13.56	9.77	12.57
Fe_2O_3	12.49	10.21	9.93	10.66	12.45	9.7	10.9
CaO	5.07	0.7	15.43	4.22	5.1	16.19	7.78
MgO	3.83	3.32	3.25	1.99	2.16	2.52	2.84
K_2O	2.39	1.41	1.76	2.2	2.48	1.99	2.03
TiO_2	1.07	1.26	0.86	1.43	1.42	0.85	1.14
SO_3	0.59	0	0.88	0.41	0.49	0.65	0.5
MnO	0.17	0.03	0.15	0.45	0.28	0.1	0.19
SrO	0.19	0.02	0.17	0.06	0.06	0.48	0.16
LOI	14.13	3.96	15.49	9.3	10.18	17.13	11.69
SUM	99.96	100	99.85	99.7	99.83	100	99.8

than other international countries. These parameters characterize that the clay/shale of Shaheed Ghat formation is more basic and heavier which established under CaO and iron contents.

where:

(approximately equal), ↑ (high value) and ↓ (low value).

It is being interpreted from Fig. 5 which is Bar graph 2, that the quality of ESR bentonite is almost same with international countries (Turkey, Brazil and Nigeria) which are the top listed for the mining of bentonite in the worldby British geological survey (BGS).

Therefore, the ESR also have a bright potential of bentonite which can be used for the prosperity of the

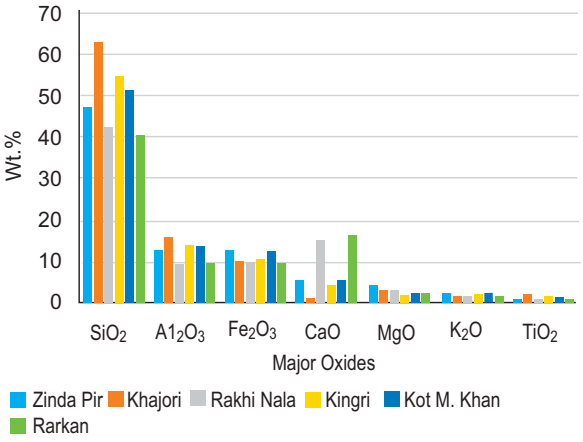

Fig. 4. Bar graph of major oxides into wt%.

Table 3. Analogize studies of bentonite clays from ESR with indigenous area's, Pakistan (Khan *et al*., 2017)

Major oxides	Punjab		KPK				Kashmir	Eastern
	Attock	Jhelum	Cherat	GarhiChandan	Azakhel	Jhandola	Bimber	Sulaiman range
SiO_2	49.8	48.3	51.3	52.3	50.1	53	50.3	50≈
Al_2O_3	18.3	18.6	21.5	16.1	18.8	18.7	17.9	12.57↓
Fe_2O_3	3.3	3.2	5.9	4.5	4.9	7.6	3.4	10.9↑
CaO	0.4	0.3	0.4	0.4	0.7	0.7	0.5	7.78↑
MgO	0.3	0.1	0.3	0.2	0.2	0.2	0.2	2.84↑
TiO_2	2.6	2.6	1.1	3.2	2.2	2.5	1.9	1.14↓
K_2O	0.4	1.5	0.4	1.1	4.2	0.6	1.5	2.03↑
SO_3	0.3	0.6	1.4	1.3	1.2	1.9	0.6	0.5≈
P_2O_5	0.2	0.1	0.2	0.1	0.1	0.2	0.2	0.16≈
LOI	20.5	19.7	14	16.5	14.4	14.1	18.9	11.69≈

Table 4. Analogize studies of bentonite clays from ESR with Turkey, Brazil and Nigeria (Abdullahi *et al*., 2017; Arslan *et al*., 2010; Gopinath *et al*., 1988)

Major oxides	Eastern Sulaiman range of Pakistan	Tireboule of northeast Turkey	Bao vista of northeast Brazil	Gombe state Nigeria
SiO_2	50↓	68.76	59.55	48.16
Al_2O_3	12.57≈	12.54	16.04	14.86
Fe_2O_3	10.9↑	1.08	8.37	4.8
CaO	7.78↑	1.06	0.77	1.81
MgO	2.84≈	2.9	2.4	2.08
K_2O	2.03↑	0.48	0.74	1.6
TiO_2	1.14↑	0.15	0.88	0.94
SO_3	0.5≈	0	0	0
Mn_2O_2	0.19↑	0.04	0.05	0
SrO	0.16↑	0	0	0
LOI	11.69≈	12.36	10.91	11.2

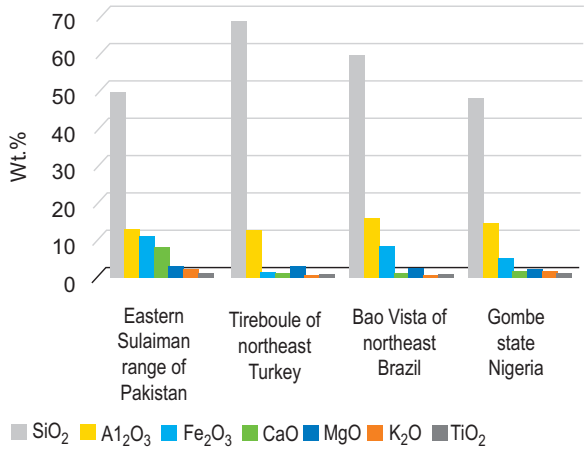

Fig. 5. Analogize studies of bentonite clays from ESR with Turkey, Brazil and Nigeria.

country Pakistan. As there are three main types of bentonite clay (i) Na bentonite (ii) Ca bentonite (a mineralogical different clay but displaying analogous effects) and (iii) K bentonite. Hence, this area is enriched in Ca bentonite which is the chief dynamic component of fuller's earth. Ca bentonite may be altered to Na bentonite by an ion exchange procedure.

Conclusion

- XRD represents that the shale/clay of Shaheed Ghat formation is abundant in montmorillonite, albite, illite and quartz, while XRF shows SiO_2, Al_2O_3, Fe_2O_3 and CaO with maximum values that are the major elements of bentonite. In general, the SiO_2, Al_2O_3, Fe_2O_3 and CaO values vary from 63.2 to 40.6 (wt. %), 15.8 to 9.4 (wt. %), 12.4 to 9.4 and 16 to 0.7 (wt. %) correspondingly. These dissimilarities could be due to the physical and chemical properties of bentonite clays and its impurities.
- All the laboratories result of ESR is analogous with each other, local areas and top listed international countries (Turkey and Brazil) by bentonite but the iron content Fe_2O_3 of this research area is higher than other areas. So, there is a dire need to emphasis on ESR with respect to the iron content.
- The research area lies in the poor belt of Pakistan and the best place to build bentonite industries. The industry will collect raw material very easily and the local habitants may get proper earning facilities. This step will generate the revenue for the Government of Pakistan and prosperity of the area.

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Conflict of Interest. The authors declare no conflict of interest.

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