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Clay minerals assemblage in the Neogene fluvial succession of the Pishin Belt, Pakistan: implications for provenance

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Abstract

The Neogene siliciclastic succession of the Pishin Belt comprises the newly proposed Middle to Upper Miocene Dasht Murgha group, Miocene-Pliocene Malthanai formation and Pleistocene Bostan Formation. Sandstones of the succession have been classified as lithic arenites and their detrital modes indicate derivation of material from the Pre-Miocene sedimentary and meta-sedimentary terrains of the Pishin Belt. X-ray diffraction (XRD) analyses indicate that clay minerals in various mudstones and sandstone samples are identical and detrital in nature and include smectite, chlorite, illite, serpentine and kaolinite. Smectite and chlorite are most probably derived from the metavolcanic and mafic volcanic rocks, respectively. Presence of serpentine in samples of the Bostan Formation indicates altered ultramafic rocks as one of the source terrains. Illite is probably recycled from the older sedimentary and metasedimentary successions. The source of kaolinite seems to be pedogenic or lateritic. The clay minerals assemblage in mudstones and sandstones of the Dasht Murgha group, Malthanai formation and Bostan formation appears to have been derived from the nearby-exposed Pre-Miocence mafic/ultramafic rocks of the Cretaceous Muslim Bagh-Zhob Ophiolite and argillites of the Eocene Nisai and Oligocene Khojak formations of the Pishin Belt. The Triassic-Jurassic succession, of the Wulgai and Loralai formations of the adjacent Sulaiman Fold-Thrust Belt, is also believed to have provided some material, however in subordinate amount.

Keywords: Clay mineralogy; X-ray Diffraction; Neogene siliciclastic succession; Pishin Belt.

1. Introduction

The Neogene siliciclastic fluvial succession is exposed at the eastern and south-southeastern margin of the Pishin Belt, which is the northeastern extension of the Makran-Khojak-Pishin Flysch Belt (Bender and Raza, 1995). Its North-South trending Khojak-Pishin segment bends to the northeast around Quetta Syntaxis into the NE-SW trending Pishin Belt (Powell, 1979; Sarwar and DeJong, 1979). It is bounded in the west and northwest by the well-known Chaman Fault, which separates the belt from the Afghan Block of Eurasian Plate (Lawrence et al., 1981; Jadoon and Khurshid, 1996), and in the east and southeast by the southward convex Zhob Valley Thrust (Figs. 1 and 2). The Belt has thrust contact with the Sulaiman Fold-Thrust Belt along the Zhob Valley Thrust (Lawrence and Yeats, 1979; Lawrence et al., 1981; Treloar and Izatt, 1993; Bender and Raza, 1995; Jadoon and Khurshid, 1996; Kazmi and Jan, 1997). The Pishin Belt comprises sedimentary successions of the Eocene through Holocene age, which have been divided into six tectono-stratigraphic zones by Kasi et al. (2012) (Fig. 2; Table 1).

This paper deals with the clay minerals assemblage found in the selected sandstone and mudstone samples obtained from the Neogene fluvial succession of the Pishin Belt and discusses its implications for provenance.

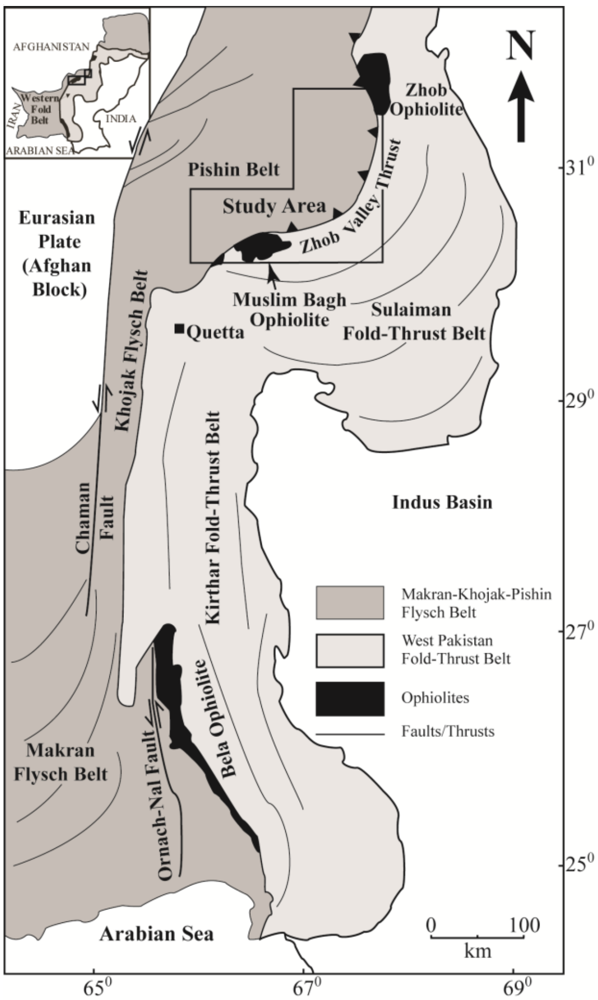


Fig. 1. Generalized geological map of the western part of Pakistan showing the position of Pishin Belt and study area.

2. Lithostratigraphy

The studied succession comprises the newly proposed Middle to Upper Miocene Dasht Murgha group, Miocene-Pliocene Malthanai formation and Pleistocene Bostan Formation.

The name Dasht Murgha group was introduced by the author (Kasi, 2012; Kasi et al., 2012) as a distinct lithostratigraphic unit exposed in the Dasht Murgha Syncline, north of the town of Qila Saifullah, which has been designated as its reference section (Fig. 2). The succession is further divisible into the Khuzhobai, Bahlol Nika and Sra Khula formations based on their distinct lithological characters. Detailed lithological characters of these formations are given in Kasi (2012) and Kasi et al. (2012).

Kasi et al. (2012) have also proposed the name Malthanai formation for the Multana Formation of Jones (1961), after the village of Malthanai near the type section. They have thoroughly discussed the lithological characters of the formation.

Jones (1961) named the Bostan Formation after the village of Bostan, 30 km north of the Quetta city. The formation comprises cyclically interbedded packages of conglomerate, mudstone and sandstone. Detailed lithological characters of the formation have been discussed by Kasi (2012) and Kasi et al. (2012).

3. Petrology

In sandstones, framework grains are fine to very coarse, moderately to poorly sorted, angular to subrounded and have grain supported fabric. According to the classification scheme of Pettijohn et al. (1987) majority of the sandstones of the Dasht Murgha group and Malthanai formation are lithic arenites, while some samples are sublitharenites (Kasi, 2012; Kasi et al., 2012). Detrital components include quartz, feldspar (plagioclase, orthoclase, microcline and perthite), muscovite, biotite and chlorite. Biotite flakes show various degrees of alteration to chlorite and in some instances they are completely chloritized.

Lithic fragments are the second most abundant components, which include several varieties of igneous, metamorphic and sedimentary rock fragments. Metamorphic fragments are the most abundant among the lithic fragments. Igneous fragments include granite, gabbro and basic volcanic rocks. Sedimentary fragments comprise shale, mudstone, siltstone, sandstone, radiolarian chert, limestone, chalcedony and fossil fragments. Cementing material includes dominantly carbonate (mostly calcite) and subordinately non-carbonate cement including chlorite, illite, iron oxides and quartz. Further details of the sandstone petrology may be seen in Kasi (2012).

Table 1. Proposed lithostratigraphy and tectono-stratigraphic zones of the Pishin Belt and surrounding areas (modified after the Hunting Survey Corporation (1961) and Shah (1977)).

<table>
<tr><th>Age</th><th>Group</th><th colspan="2">Formation/Member</th><th>Lithology</th><th>Tectono-stratigraphic Zones (after Kasi et al. 2012)</th></tr>
<tr><td>Holocene</td><td>-</td><td colspan="2">Zhob Valley deposits</td><td>Conglomerate, sandstone and shale/siltstone</td><td>Zone VI</td></tr>
<tr><td colspan="5">Thrust/Angular Unconformity</td><td></td></tr>
<tr><td>Pleistocene</td><td>-</td><td colspan="2">Bostan Formation</td><td>Red colored shale/siltstone, conglomerate and sandstone</td><td>Zone V</td></tr>
<tr><td colspan="5">Thurst/Angular Unconformity</td><td></td></tr>
<tr><td>Late Miocene-Pliocene</td><td>-</td><td colspan="2">*Malthanai formation</td><td>Sandstone and conglomerate interbedded with red colored mudstone/siltstone</td><td>Zone IV</td></tr>
<tr><td colspan="5">Thurst/Angular Unconformity</td><td></td></tr>
<tr><td rowspan="3">Early-Middle Miocene</td><td rowspan="3">**Dasht Murgha group</td><td colspan="2">Sra Khula formation</td><td>Dark red mudstone dominated by cyclic alteration of mudstone, siltstone and sandstone</td><td rowspan="3">Zone III</td></tr>
<tr><td colspan="2">Bahlol Nika formation</td><td>Dominantly greyish green sandstone, with subordinate mudstone and occasional conglomerate</td></tr>
<tr><td colspan="2">Khuzhobai formation</td><td>Dominantly maroon mudstone with subordinate reddish brown sandstone</td></tr>
<tr><td colspan="5">Thrust/Angular Unconformity</td><td></td></tr>
<tr><td rowspan="2">Oligocene-Early Miocene</td><td rowspan="2">-</td><td rowspan="2">Khojak Formation</td><td>Shaigalu Member</td><td>Dominantly sandstone with subordinate shale</td><td rowspan="3">Zone II</td></tr>
<tr><td>Murgha Faqirzai Member</td><td>Dominantly shale with subordinate sandstone</td></tr>
<tr><td>Eocene</td><td>-</td><td colspan="2">Nisai Formation</td><td>Highly fossiliferous to reefoid limestone interbedded with marl and thick marine (fossiliferous) shale with occasional thin limestone horizons</td></tr>
<tr><td colspan="5">Nonconformity</td><td></td></tr>
<tr><td>Cretaceous-Palaeocene</td><td>-</td><td colspan="2">Muslim Bagh-Zhob Ophiolite</td><td>Mostly ultrabasic and basic igneous rocks</td><td>Zone I</td></tr>
</table>

*The name "Malthanai formation" has been modified after the Multana Formation of the Jones (1961).
**The name Dasht Murgha group has been proposed by the author.

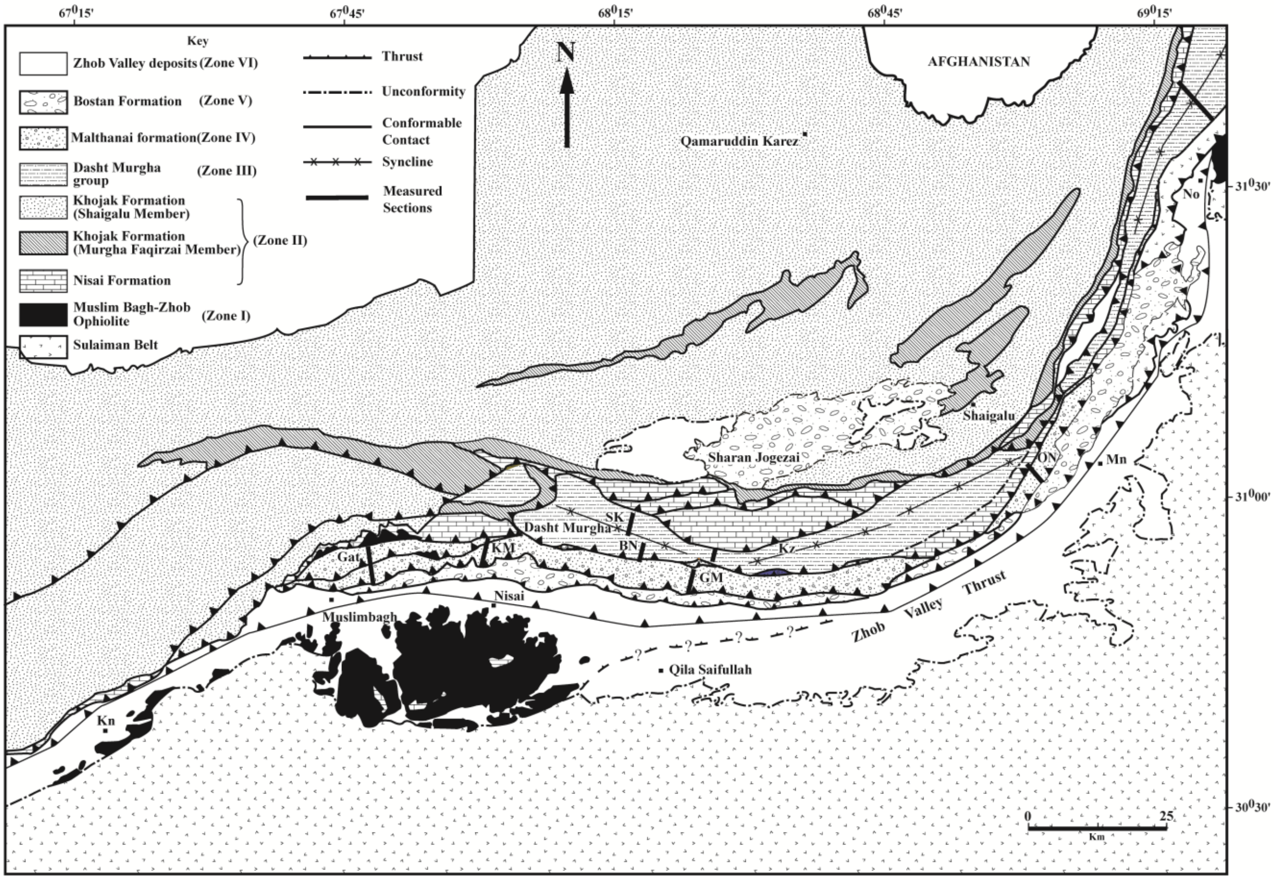


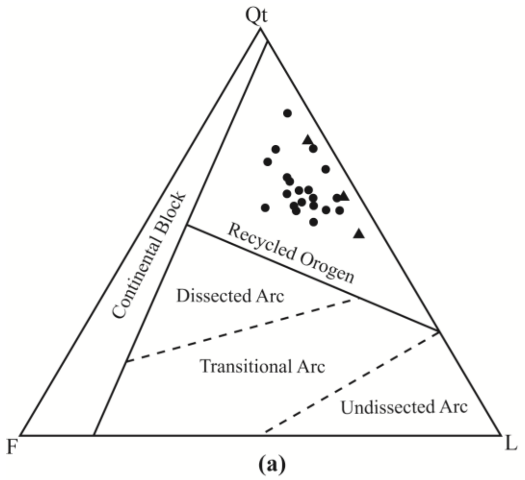
Fig. 2. Geological map showing lithostratigraphy and tectono-stratigraphic zones of the study area (modified after the Jones, 1961). Abbreviations used are: BN (Bahlol Nika), GM (Gardab Manda), KM (Kazha Merzai), Kn (Khanozai), Kz (Khuzhobai), Mn (Malthanai), No (Naweoba), ON (Oblin Nala) SK (Sra Khula).

The QtFL and QmFLt ternary diagrams (after Dickinson and Suczek, 1979; Dickinson et al., 1983) were used to summarize the modal data (Kasi, 2012). On the QtFL sandstones samples of both the Dasht Murgha group (mean: $Qt_{61}F_{11}L_{28}$) and Malthanai formation (mean: $Qt_{60}F_4L_{36}$) fall well within the recycled orogen, while, on QmFLt the samples of the Dasht Murgha group (mean: $Qm_{43}F_{12}Lt_{46}$) and Malthanai formation (mean: $Qm_{49}F_5Lt_{47}$) fall within the transitional recycled provenance (Fig. 3).

4. X-ray diffraction analyses

We studied clay minerals by X-ray diffraction (XRD), which is an effective method for determination of composition of fine-grained crystalline materials and analyzed them by comparing positions of diffraction peaks and their intensity values with the reference patterns of known compounds maintained in the Powder Diffraction File (PDF) (Powder Diffraction File-2, 1993).

In order to identify the clays and other minerals within the argillites, as well as sandstone matrix, of the Dasht Murgha group, Malthanai formation and Bostan Formation we carried out bulk mineralogical analyses on 31 samples. Analyzed samples include 15 mudstone and 4 sandstone samples of the Dasht Murgha group; 6 mudstone and 3 sandstone samples of the Malthanai formation; and 3 mudstone samples of the Bostan Formation. Analyses for clay minerals were carried out on 11 samples, including 7 samples of the Dasht Murgha group, 2 samples of the Malthanai formation and 2 samples of the Bostan Formation. Samples were prepared and analysed in the XRD Laboratory of the Department of Geoscience, Aarhus University, Denmark, by the XRD instrument of PANalytical, Model: X'Pert Pro MPD.



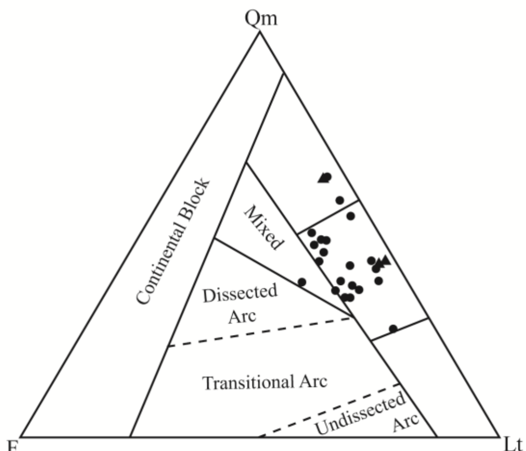


Fig. 3.(a) QtFL compositional diagram (after Dickinson and Suczek, 1979) for sandstones of the Dasht Murgha group and Malthanai formation of the study area; (b)QmFLt compositional diagram (after Dickinson et al., 1983) of sandstones of the Dasht Murgha group and Malthanai formation. Filled circles indicate samples of the Dasht Murgha group and triangles indicate samples of the Malthanai formation.

4.1.Methodology

For the purpose of bulk mineralogical analyses two grams of the samples were dried and grinded in a Wolfram Carbide Mortar. The powder was pressed into a steel sample holder. Analyses for bulk mineralogy were performed on un-oriented and un-fractionated samples under conditions given in Table 2. Minerals were identified using standard index cards of X-Ray-reflections (crystal lattice distances) of the Joint Committee on Powder Diffraction Standards and International Centre of Diffraction Data (JCPDS-ICDD) (1993) of the relevant minerals.

For the purpose of analyses of clay minerals, ≤2 μm fractions were separated from the selected samples by means of sedimentation [i.e. Stoke's Law (Batchelor, 2000)]. A few millilitres of separated clay fraction was smeared onto a glass slide and dried at room temperature, so that the clay minerals orient their 001 faces parallel to the surface of glass slide. Samples were X-rayed 3 times in the following manners, under the instrumental conditions given in the Table 2:

1) Air dried
2) After treatment with ethylene glycol vapours in a desiccator for 24 hours at 60 °C.
3) After heating up to 500 °C for 1 hour.

4.2. Results of the analyses

4.2.1. Bulk minerals analyses

Through the bulk mineral analyses, we identified illite, chlorite, quartz, plagioclase, K-feldspar, calcite, dolomite and serpentine (Table 3). The mineral assemblage of the Dasht Murgha group, Malthanai formation and Bostan Formation are almost identical (Fig. 4).

Table 2. Instrumental conditions for bulk mineralogical and clay mineralogical analyses with XRD.

Parameters	**Bulk mineralogy**	**Clay mineralogy**		
		Untreated	Glycol treated	Heated at 500°C
Interval 2Θ	2° - 65°	2° - 65°	2° - 35°	2° - 35°
Voltage	45kV	45kV	45kV	45kV
Current	40mA	40mA	40mA	40mA

Program	Long	Long	Short	Short

Table 3. List of minerals identified by bulk mineralogical analyses with XRD in Dasht Murgha group, and Malthanai and Bostan formations.

S.No	**Minerals**	**Chemical Formula**
1	Chlorite	$(Mg, Al)_6 (Si, Al)_4 O_{10} (OH)_8$
2	Illite	$(K,H_3O)Al_2Si_4O_{10}OH)_2$
3	Quartz	SiO_2
4	Plagioclase	$Na(AlSi_3O_8)$-$Ca(Al_2Si_2O_8)$
5	Alkali-feldspar	$(K, Na) [AlSi_3O_8]$
6	Calcite	$CaCO_3$
7	Dolomite	$CaMg(CO_3)_2$
8	Serpentine	$Mg_6Si_4O_{10}(OH)_8$

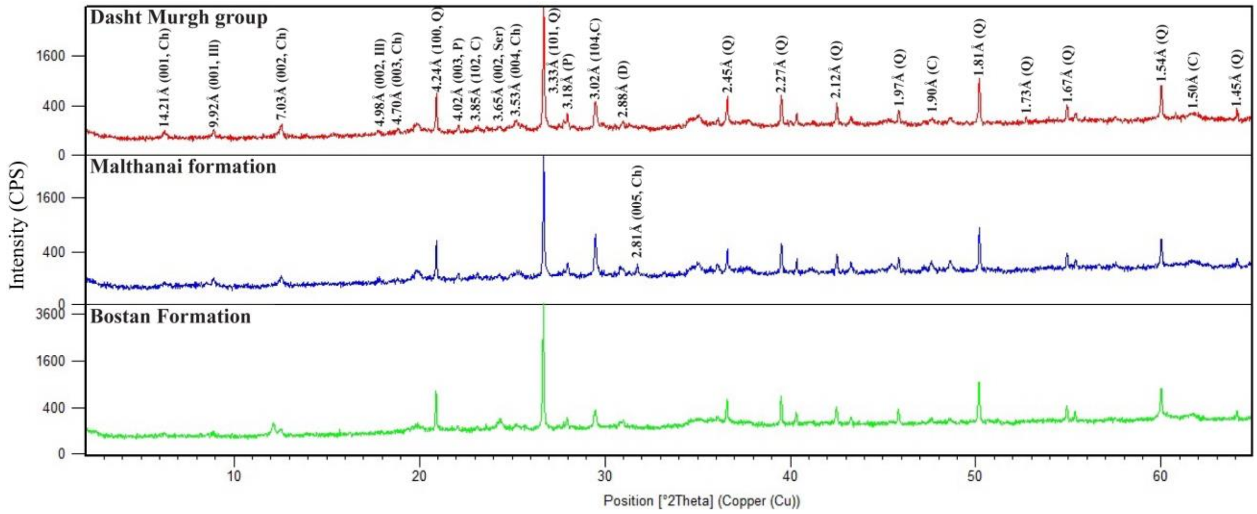


Fig. 4. X-Ray diffractograms showing 2θ and Å values of the relevant faces of various minerals dentified in samples of the Dasht Murgh group, Malthanai formation and Bostan Formation in bulk mineralogical analyses. Abbreviations used: Ch = chlorite, Ill = illite, Q = quartz, P = plagioclase, C = calcite, Ser = serpentine, D = dolomite.

4.2.2. Clay mineral analyses

The following minerals were identified in the ≤ 2 µm fraction: smectite, kaolinite, illite, chlorite, quartz, plagioclase, K-feldspar, calcite, dolomite, pyrite and serpentine (Table 4; Figs. 5, 6 and 7). The mineral assemblage of the Dasht Murgha group (Fig. 5), Malthanai formation (Fig. 6) and Bostan Formation (Fig. 7) are almost identical, except that serpentine is also present in some samples of the Bostan Formation.

4.3. Mineral assemblage

4.3.1. Illite

Strong peaks at 10 Å and 5 Å are attributed to the basal reflections [001] and [002] of illite, respectively, whereas, the 3.32 Å peak is attributed to the [003] reflections (Figs. 4, 5, 6 and 7). Most of the 10 Å peaks are asymmetrical towards low angles. Heat treatment enhances the 10 Å and 5 Å peaks, accompanied by a slight increase in basal spacing, which confirms the mineral as illite. In samples of the Dasht Murgha group the d-spacing [001] range from 9.88 to 10.18 Å, with a mean of 10.03 Å. In samples of the Malthanai formation d-spacing [001] range from 9.89 to 9.98 Å, about a mean of 9.93 Å, and in samples of the Bostan Formation d-spacing [001] range from 9.83 to 10.05 Å, about a mean of 9.94 Å. The illite is muscovitic in composition because the [001] values are less than 9.98 Å (biotitic illite has >10.1 Å values), when observed in glycolated samples (Petschick et al., 1996). Also according to Esquevin (1969) high 5 Å /10 Å ratio (>0.40) correspond to AI-rich (muscovitic) octahedral illites, which is also the character of illite in our samples.

Table 4. List of minerals identified with XRD analysis of the Dasht Murgha group, Malthanai formation and Bostan Formation.

S.No	**Minerals**	**Chemical Formula**
1	Smectite	$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$
2	Kaolinite	$Al_4Si_4O_{10}(OH)_8$
3	Chlorite	$(Mg, Al)_6 (Si, Al)_4 O_{10} (OH)_8$
4	Illite	(K,H_3O)Al2Si4O10 (OH)2
5	Quartz	SiO_2
6	Plagioclase	$Na(AlSi_3O_8)$-$Ca(Al_2Si_2O_8)$
7	K-feldspar	$KAl_3Si_3O_8$
8	Calcite	$CaCO_3$
9	Dolomite	$CaMg(CO_3)_2$
10	Serpentine	$Mg_6Si_4O_{10}(OH)_8$
11	Pyrite	FeS_2

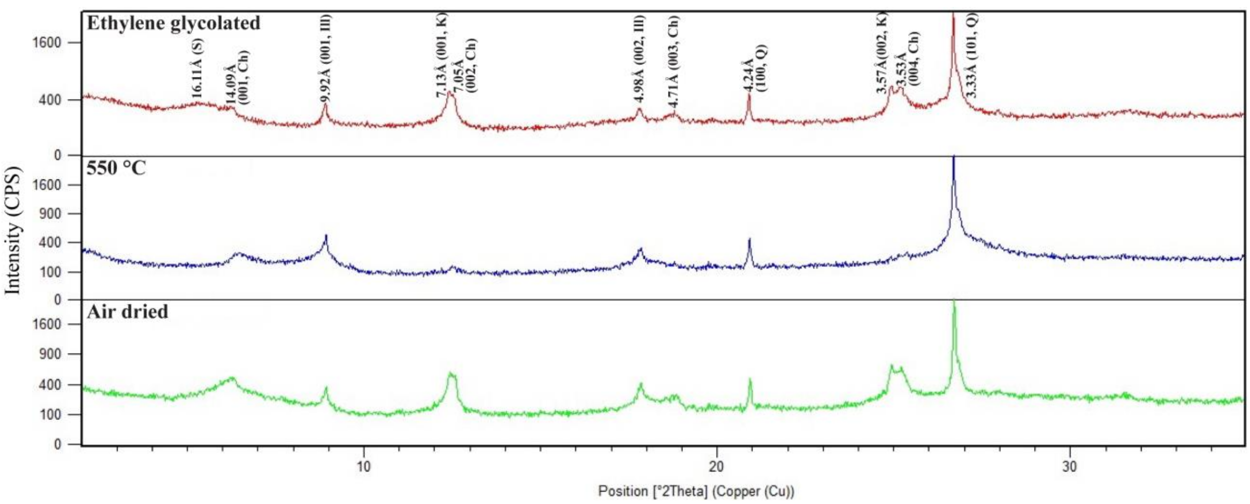


Fig. 5. X-Ray diffractogram of clay fraction of mudstone of the Dasht Murgha group, showing effects of different treatments on clay minerals.

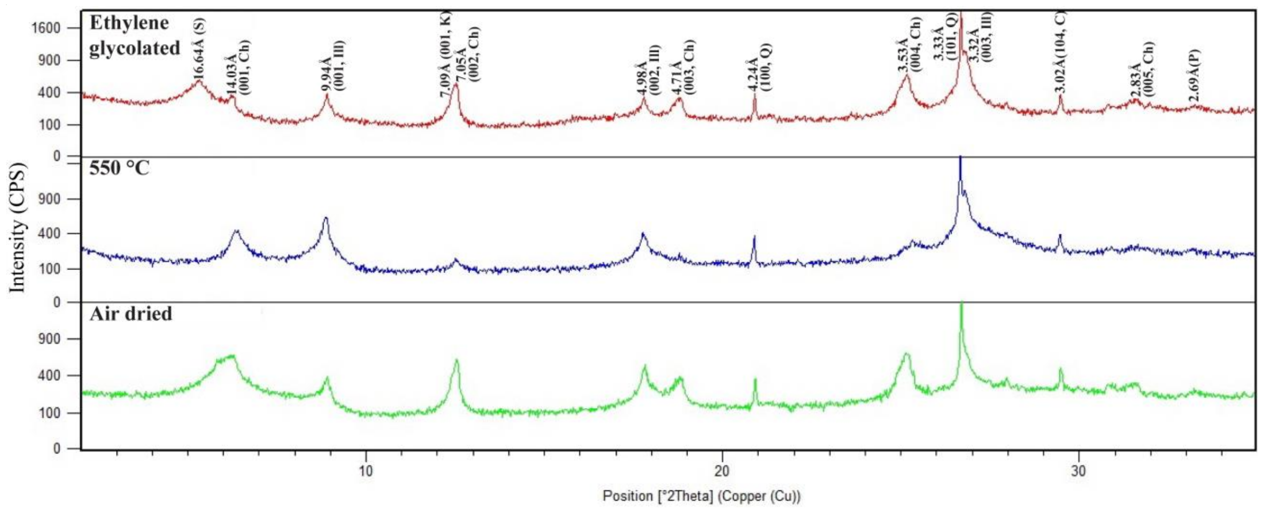


Fig. 6. XRD diffractogram of clay fraction of mudstone of the Malthanai formation, showing effects of different treatments on clay minerals.

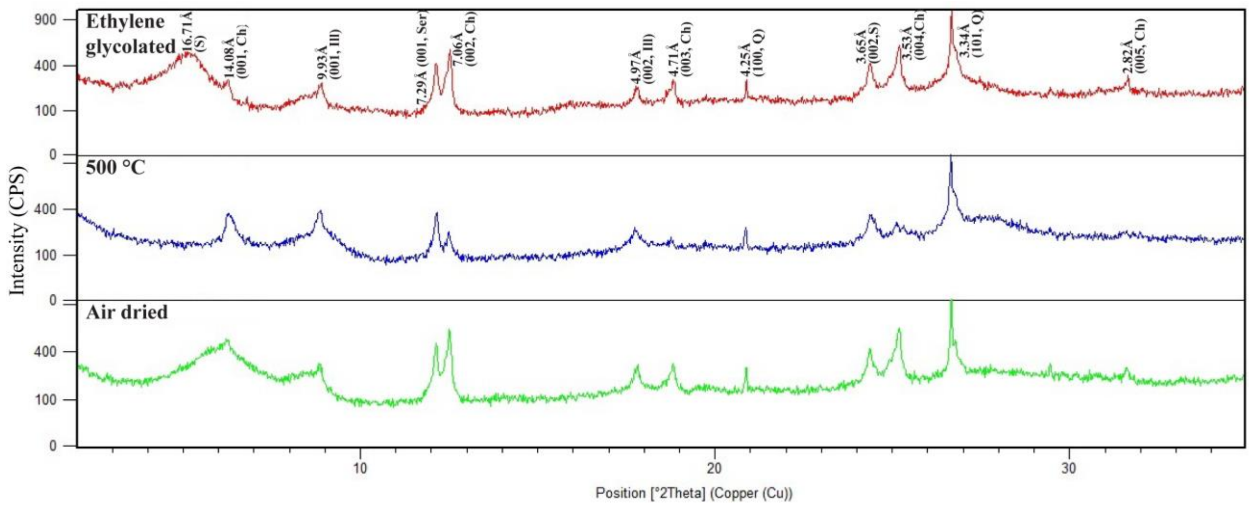


Fig. 7. XRD diffractogram of clay fraction of mudstone of the Bostan Formation, showing effects of different treatments on clay minerals.

4.3.2. Chlorite

The presence of chlorite is confirmed by strong reflections at 14 Å [001], 7Å [002], 4.7 Å [003], 3.5 Å [004] and 2.82 Å [005] (Figs. 4, 5, 6 and 7). Heat treatment enhances the 14 Å [001] reflection, whilst causing collapse of the 4.7 Å peak and depression of the 7 Å and 3.5 Å peaks. Treatment with ethylene glycol helps to distinguish the 14 Å peak of chlorite from the smectite peak (Eslinger and Piever, 1988). The even-order basal reflections [002] and [004] are always very strong; this character may be attributed to richness in iron (Carroll, 1970; Hepworth, 1981). The dioctahedral chlorite typically have more intense [003] reflections and retain their [002] peaks after heat treatment. Lack of these characters in the studied samples implies that trioctahedral chlorite is dominant.

4.3.3. Smectite

In the Dasht Murgha group smectite reflections vary from 16.11 Å to 16.67 Å, while in the Malthanai formation they range from 16.37 Å to 16.64 Å. In the Bostan Formation reflections range from 16.65 Å to 16.71 Å. Treatment with ethylene glycol splits the smectite peak from 14 Å chlorite peak, whereas, in the heat treatment the smectite peak collapses totally (Figs. 5, 6 and 7).

4.3.4. Kaolinite

Kaolinite is not a common clay mineral found in the analyzed samples. However, in the Dasht Murgha group kaolinite reflections are indicated by 3.57 Å [002] and 7.15 Å [001] peaks. In the Malthanai formation reflections are indicated by peaks at 3.54 Å [002] and 7.00 [001] Å, whereas, in the Bostan Formation reflections are indicated by peaks at 3.55 Å [002] and 7.13 [001] Å. Heat treatment causes enhancement of the 14 Å peak of chlorite and collapses or depress the other peaks (7.15 and 3.55 Å). This situation suggests the presence of kaolinite, in coexistence with chlorite at 7.0 and 3.5 Å peaks.

4.3.5. Calcite

Calcite is detected by the presence of its 3.02 Å [104], 3.84 Å [102], 2.09 Å, 1.9 Å and 1.5 Å reflections (Fig. 3). These characters are present in all the analyzed samples, however, the 3.02 Å [104] reflection is the strongest.

4.3.6. Feldspar

The presence of the 3.18-3.19 Å and 4.02 Å reflections in diffractograms of all the samples (Fig. 3) correspond to the plagioclase, whereas presence of the 3.22-3.24 Å reflections corresponds to the K-feldspar.

4.3.7. Dolomite

Reflections at 2.88-2.90 Å are attributable to the dolomite (Fig. 3).

4.3.8. Quartz

Reflections at 4.24 Å [100], 3.33 Å, 2.45 Å, 2.27 Å, 2.12 Å, 1.97 Å, 1.81 Å, 1.73 Å, 1.67 Å, 1.54 Å and 1.45 Å (Fig. 3) belong to quartz. Strong peaks are at 3.33-3.34 Å [101] and 4.24 Å [100], whereas, 3.33-3.34 Å reflection being the strongest.

4.3.9. Pyrite

The presence of 2.69 Å and 2.7 Å peaks in the Dasht Murgha group and Bostan Formation corresponds to pyrite (Fig. 5).

4.3.10. Serpentine

The presence of 7.28-7.29 Å [001] and 3.64-3.65 Å [002] reflections correspond to serpentine, which is present only in one sample of the Bostan Formation (Fig. 6).

5. Discussion

Clay mineral assemblages in the fluvial successions, like those of the Dasht Murgha group, Malthanai formation and Bostan Formation, are mostly detrital and are useful to understand the provenance of sediments, composition and climate of the source terrains (Chamley, 1989). Since river channels are just transit environments, they generally deposit abundant clay minerals in the downstream alluvial plains and floodplain areas (Suresh et al., 2004). Due to the paucity of research on clay mineralogy of Neogene fluvial succession in Pishin Belt, we compared our results with a similar succession of the Himalayan foreland basin, India, (Suresh et al., 2004). Similar assemblage of clay minerals have been reported from the Late Neogen fluvial succession (Siwalik Group) of the Subathu sub-basin, which is a part of central Himalayan foreland basin (Suresh et al., 2004).

Smectite is generally believed to have been provided by mafic volcanic rocks, which are poor in silica, whereas, chlorite is provided by metavolcanic rocks (Biscaye, 1964, 1965; Petschick et al., 1996; Raiverman and Suresh, 1997). Presence of serpentine in samples of the Bostan Formation also indicates altered ultramafic rocks as one of the source terrain. Aluminum-rich illite (muscovitic illite) found in our samples is chemically stable and resistant to alteration in the source area. Low-grade metamorphic and sedimentary rocks are generally believed to be the main sources of illite (Craddock, 1982). Kaolinite might have come from pedogenic or lateritic sources.

The QtFL and QmFLt plots of the study area suggest derivation of detritus from recycled and transitional recycled orogenic sources (Kasi, 2012). Detrital modes of the sandstones and petrology of the conglomerates show that the detritus for the Miocene-Pleistocene succession has mainly been derived from the Pre-Miocene sedimentary and meta-sedimentary terrains of the Pishin Belt from the west, which include Eocene Nisai and Oligocene Khojak formations. The Sulaiman Fold-Thrust Belt from the east, which includes Triassic Wulgai Formation and Jurassic Loralai Formation, also subordinately provided material and the Muslim Bagh-Zhob Ophiolite exposed along the western margin of the Indian Plate has provided mafic and ultramafic detritus.

6. Conclusions

Dasht Murgha group, Malthanai formation and Bostan Formation are characterized by smectite, chlorite, illite, serpentine and kaolinite clay-mineral assemblages suggesting piedmont drainage with distinct clay-mineral population. We believe that these clay-mineral assemblages have been derived from nearby-exposed Muslim Bagh-Zhob Ophiolite, shales/mudstones of the Eocene Nisai Formation, Oligocene Khojak Formation within the Pishin Belt and Triassic-Jurassic Wulgai and Loralai formations from the adjacent Sulaiman Fold-Thrust Belt.

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