

Clay Mineralogy of Mukdadiya Formation in Shewasoor Area: Northeastern Kirkuk City, Iraq

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Abstract—14 mudstone samples were collected within the sedimentary succession of Mukdadiya Formation (Late Miocene – Early Pliocene) from Shewasoor area at Northeastern Iraq. The samples were subjected to laboratory studies including mineralogical analysis (using X-ray Diffraction technique) in order to identify the clay mineralogy of Mukdadiya Formation of both clay and non-clay minerals. The results of non-clay minerals are: quartz, feldspar and carbonate (calcite and dolomite) minerals. The clay minerals are: montmorillonite, kaolinite, palygorskite, chlorite, and illite by the major basal reflections of each mineral. The origins of these minerals are deduced also.

Keywords—Clay minerals, formation, Mukdadiya mudstone, Shewasoor, XRD.

I. INTRODUCTION

THE study of clay minerals is very important because they reflect the topography and the mineralogy of source rocks and type of weathering which have affected these rocks. Also clay minerals and their relative abundance may record information on climate, eustasy, burial diagenesis, or reworking. The type of clays that is found depends on the interaction of climate, geomorphology, parent rocks, and environment [1].

Distribution of clay minerals in sediments is affected by the detrital input to the sedimentary basin. Mica, chlorite, associated quartz and feldspars constitute typically of terrigenous species [2]. These clay minerals develop generally in areas of steep relief active mechanical erosion limits soil formation, particularly during periods of enhanced tectonic activity [3]. Clay minerals are very common in fine grained sedimentary rocks such as shale, mudstone, and siltstone and in fine grained metamorphic slate and phyllite (normally considered to be less than 2 micrometres in size on standard particle size classifications). It requires special analytical techniques for their identification study such as x-ray diffraction [4], which used in study of Mukdadiya Formation clays.

Weathering products of the silicic granite and gneiss, that form the bulk of crystalline rocks may be potassic clay (illite), kaolinite depending on the intensity of weathering and the length of time during which weathering occurs [5].

Mukdadiya Formation (Late Miocene – Early Pliocene) was

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previously named in Iran as Lower Bakhtiari by [6] and was later changed in Iraq to Mukdadiya Formation [7], [8]. The clastic sequence of Mukdadiya Formation is widely distributed in the foothill and the Mesopotamian plain zones. Due to its thickness (Maximum 2050 m) and its stratigraphic position, it plays an important role in the geology of Middle East [9]. The formation was studied stratigraphically and sedimentologically by many authors, e.g. [10]-[13], [7], [8]. All those authors suggested that the formation is of continental to sub-continental fluvial environment. Moreover, [14] indicated that the formation was deposited in braided and meandering channels in northern Iraq. Otherwise the formation sediments were described as a fluviolacustrine by [15]. The recent geological studies indicate that the clastics which represent the formation are of fluvial environment [23].

The area under study was situated in Shewasoor region, which represent the Northeastern limb of Chamchamal anticline fold. The location of the studied area is: The longitude between (35° 48' 38"-35° 32' 34") and the latitude between (44° 32' 39"- 44° 23' 12"), about 40 km. northeastern of the city center and about 9.5 km. northeast of Redar (Shwan) town (Fig. 1).

Mukdadiya Formation is underlain by Injana formation (Late Miocene), and composed principally of fining upward cycles of clastics, mainly sandstones, pebbly sandstones, grey mudstones and siltstones. Moreover, few gravelly sandstone units were observed [16] (Fig. 2). Its thickness is (supposed) to be (1400-3500) m. It is thought to be deposited in a fluvial environment in a rapidly subsiding foredeep basin. The lower contact of Mukdadiya Formation can be detected on the first appearance of pebbles in the sandstone units [17]. This bed separates between Miocene and Pliocene ages. The upper contact of Mukdadiya Formation with the Bai Hassan formation can be detected on the first appearance of conglomerate unit [18].

The present work aims to shed light on the mineralogy of the Mukdadiya Formation, from data of fourteen mudstone samples were collected within the sedimentary succession of the Formation. As well as deduce the origins of these minerals.

II. METHOD OF WORK AND MATERIALS

Fourteen samples were collected from selected sites of Mukdadiya formation at Shewasoor region, northeastern Kirkuk City, Iraq. Each sample represents the mudstone units of each sedimentary cycle (Figs. 1 and 2). All samples were sun-dried and then were disaggregated by the use of an agate mortar and pestle. Disaggregation was done gently in order to

retain, as much as possible, the intrinsic grain sizes of the samples.

Mineralogical characteristics of the samples were determined by using X-ray diffraction analysis, type Panalytical Xpert PRO MPD with Ni-filtered and CuK α radiation, for the purpose of diagnosis and assessment of mineral components as well as identifying the type of clay minerals (<2 μ m) in the isolated clayey size. X-ray diffraction analysis was carried out at the scientific center for soil researches in to the Hilwan City, EGYPT. Both randomly oriented powder and oriented slides samples were prepared depending on the procedures described by [19], [20]. They

were scanned over the range from 4° to 40° 2 θ at a scanning speed 2° 20/min (Fig. 3). The oriented slides were analyzed in different stages (non-treated, treated by Glycol ethylene at 60°C/2 hr. in order to distinguish the expandable mineral phases, the slides were heated at 350 °C/2hr and 550°C/2hr. for chlorite detection) (Fig. 4). All basal reflection peaks of minerals were diagnosed according to ASTM cards [21]. The semi quantitative determination of relative amounts of major clay minerals was calculated by using PANalytical X'Pert HighScore software depending up on specific reflections and intensity factors.

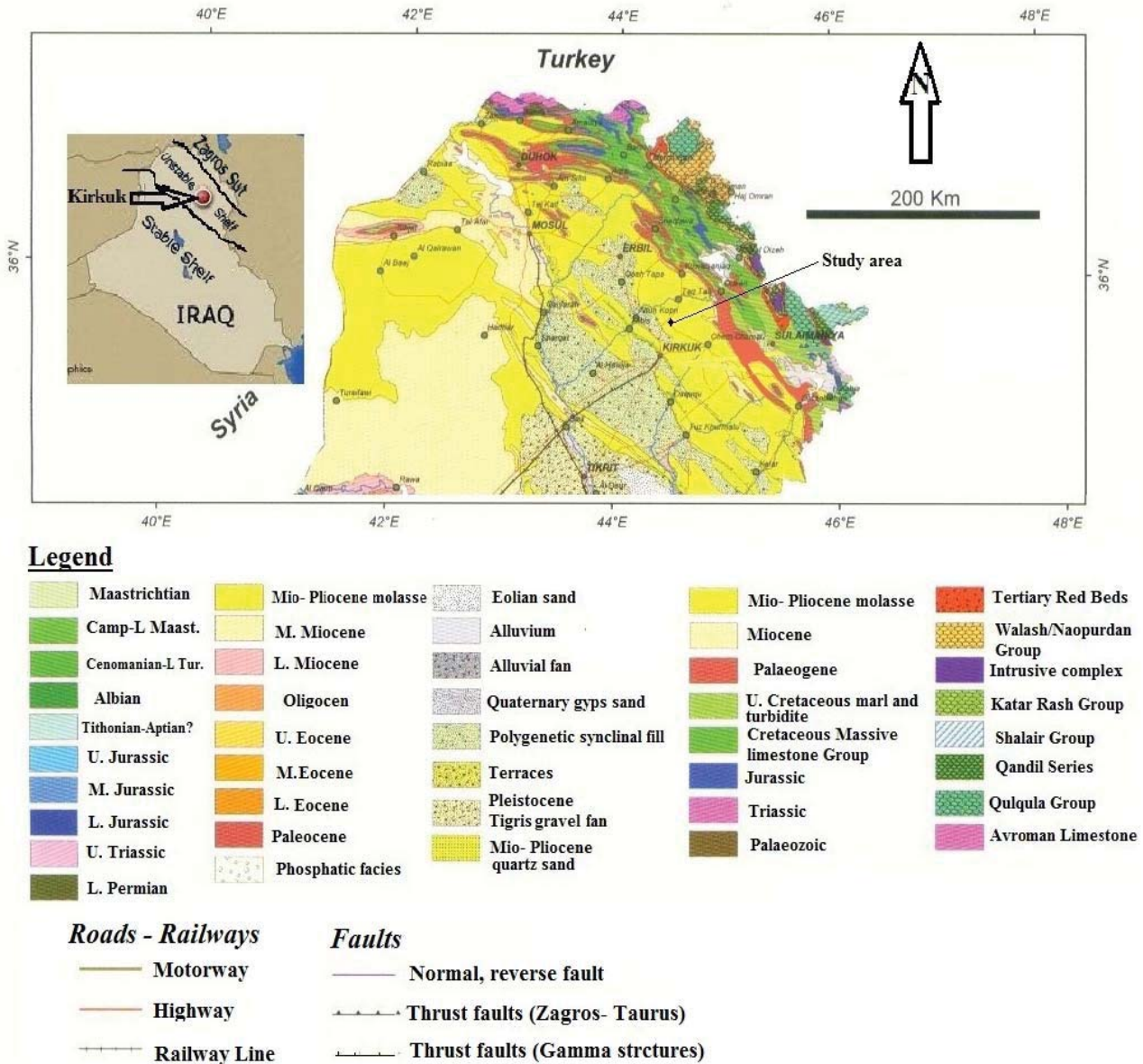


Fig. 1 Geological map of northern Iraq shows the location of the studied are, modified from the [15]

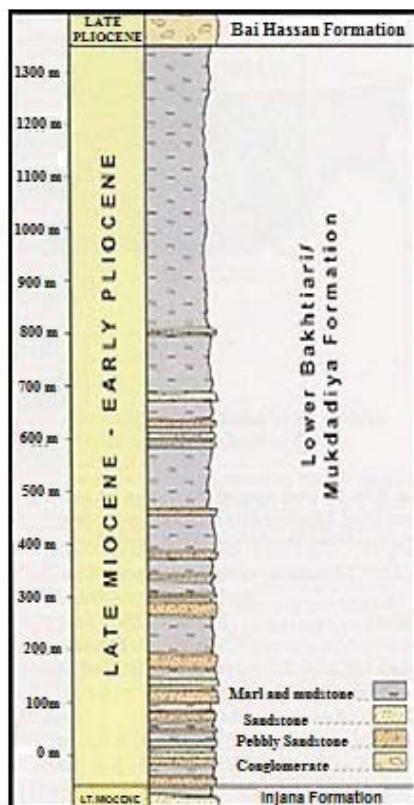


Fig. 2 Stratigraphic column for Mukdadiya Formation, after [8]

III. RESULTS AND DISCUSSION

The mineralogical characterization of the studied sample was based on X-Ray diffraction analyses for mudstone (oriented and non-oriented samples) samples of Mukdadiya formation are shown in (Figs. 3 and 4). The results of X-Ray analysis show that Mukdadiya mudstones are variable mixtures of non-clay (non-phyllsilicates) mineral {quartz, feldspar and carbonate (Calcite and Dolomite)} from XRD analysis of powder samples, clay (phyllsilicates) minerals including montmorillonite, kaolinite, palygorskite, chlorite, and illite from XRD analysis of oriented samples as shown in (Figs. 3 and 4) and discussed below:

A. Non – Clay Minerals

1. Quartz

Quartz is the most abundant non-clay mineral in the studied samples of Mukdadiya mudstones. It is identified in basal reflections of (3.34 and 4.26 °A) for (101 and 100), respectively in all samples (Fig. 3).

2. Carbonates

Calcite is the second abundant non-clay mineral in the Mukdadiya mudstone samples. It was characterized by the peaks (3.04 and Å) for (104) reflections, Dolomite is also showed in the mudstone samples of Mukdadiya Formation in Shewasoor section but in small amounts. The X-ray scanning showed dolomite with characteristic peak of (2.89) Å for (104)

reflection in all samples (Fig. 3).

3. Feldspars

Feldspars are found in samples of Mukdadiya mudstone in a small percentage. It was characterized by the peak (3.2 Å) for (002) reflection of all samples (Fig. 3).

B. Clay Mineral

1. Montmorillonite

Montmorillonite has the chemical composition $(Mg, Ca)O \cdot Al_2O_3 \cdot 5SiO_2 \cdot 4H_2O$ [19]. It is a dioctahedral member of the smectite group [22]. The basic structural unit is a layer consisting of two inward-pointing tetrahedral sheets with a central alumina octahedral sheet. These layers are continuous in the a and b directions, but the bonds between layers are weak and have excellent cleavage, allowing water and other molecules to enter between the layers causing expansion in the (c) direction [22]. Montmorillonite mineral is recognized based on the basal reflection (001) at ($d=14.2 - 15A^\circ$) and other basal reflection (002) at ($5.5 A^\circ$), when treated it by ethylene glycol become ($d=17.18A$) and become at ($10 A^\circ$) by heating with $550 C^\circ$ (Fig. 4).

Montmorillonite is abundant in soil of arid to semi-arid climate [22]. It is also of detrital origin in alkaline environment because of the weathering of basic igneous rocks which is rich in ferromagnesian minerals. These mineral needs a dry or semi-dry environment, alkaline, limited movement of water, and low washing that allows concentration of Al, Ca, Mg and Fe in the depositional system [1]. Montmorillonite mineral was founded in all samples of Mukdadiya formation; this is consistent with the study of [23]. The Presence of montmorillonite mineral in clays of Mukdadiya Formation refers to sediments formed as a result of alteration of volcanic ash from volcanic activity in source regions, which is deposited in river environment and altered to montmorillonite [23]-[26]. This process required: High percentage of silica and magnesium in volcanic ash, aqueous alkaline environment must be available [22], [27]. Volcanic ash cannot alter to montmorillonite without presence of enough amounts of silica and magnesium and presence of high percentage of salinity and that is available in alkaline environment [3], [28].

2. Kaolinite

The structural formula of kaolinite mineral is $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ [19]. It is a mineral of dioctahedral kaolinite group [22]. The primary structural unit of this group is composed of one octahedral sheet connected with one tetrahedral sheet [22]. Kaolinite group are recognized depending on its basal reflection (001), ($d=7.1 A^\circ$) and at (002), ($d=3.6 A^\circ$). By heating ($550C^\circ$), the peak of mineral disappears due to the collapse of crystallography structure [29], [4], and remains unchanged by glycolation Fig. 4. Kaolinite is formed chiefly during weathering and soil formation and it is very stable in the hydrosphere. According to [30], [22], kaolinite Kaolinite mineral form from weathering of K-feldspar and also from laterite soils.

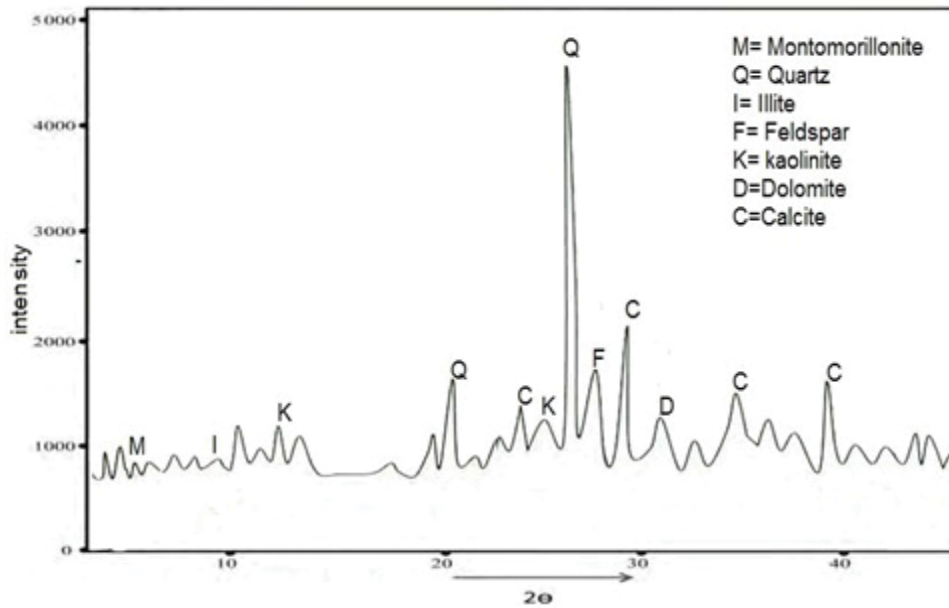


Fig. 3 Diffractograms of XRD analysis of Mukdadiya formation from Shewasoor section

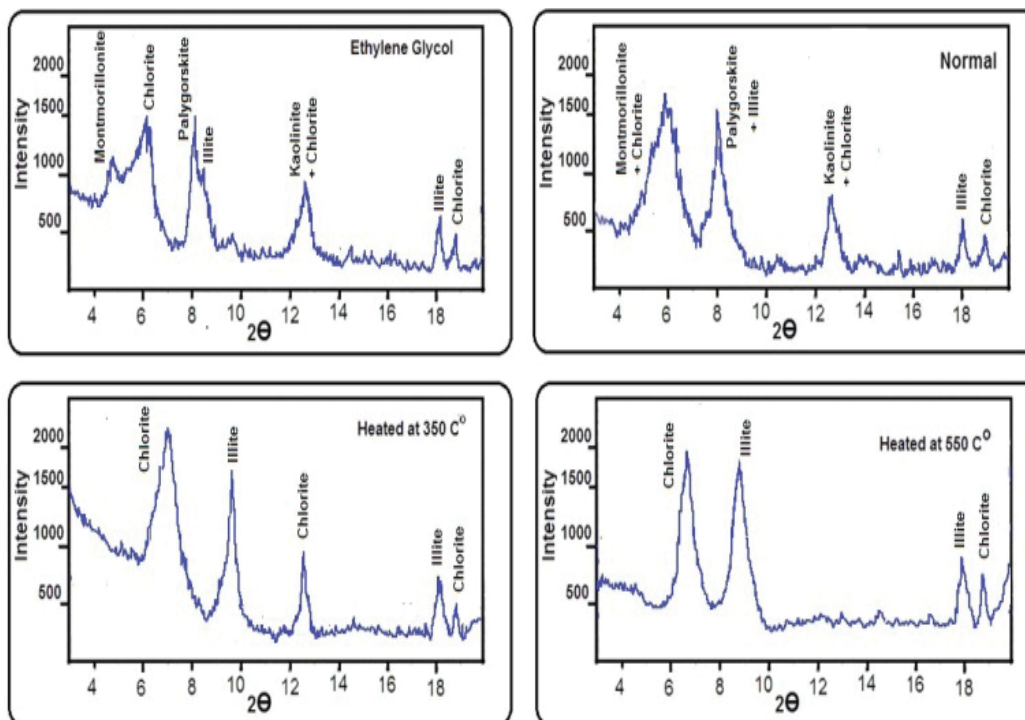


Fig. 4 X-ray Diffraction pattern of the oriented clay minerals in the Shewasoor area

Kaolinite is most probably of detrital origin derived mainly from the older reworked sedimentary rocks and partly from weathering of acidic igneous source rocks [22]. This mineral forms where solutions have low silica and alkali cation activities [1]. Kaolinite occurred in all studied samples (Fig. 4).

3. Illite

Illite has a three-sheet layer structure, composed of two

silica tetrahedral sheets with a central octahedral sheet [22]. Because it is difficult to estimate semi-quantitatively the percentages of palygorskite, therefore, illite is combined with palygorskite in most of the studied samples. Illite identification is based on basal peak (10Å) which does not expand when glycolated and not collapse when heated to 550C° [31] (Fig. 4).

Illite group which are the dominant clay minerals in argillaceous rocks, form by the weathering of silicates

(primarily feldspar), through the alteration of other clay minerals, and during the degradation of muscovite [32]. It is moderate occurrence in the studied samples of Mukdadiya formation. In general, illite forms as a result of weathering of acidic igneous rocks which contain high amounts of (K^+ , Mg^{2+}), [22]. According to [3], [33], illite mineral derived from igneous and metamorphic rocks which formed by direct weathering and erosion or alteration of aluminosilicate minerals, primarily Alkali-Feldspar minerals and muscovite which existed in acidic igneous and metamorphic rocks in continental environment. Reference [34] showed that kaolinite could be transformed into illite after moving to marine environment and being transformed after sedimentation and burial. Illite also results from weathering of potash-feldspar in igneous or sedimentary rocks. Reference [35] suggests a detrital origin for the illite. Illite in the studied samples derived from shale and metamorphic sources because of its detrital origin where it is derived from the weathering of metamorphic rocks and shales [1].

4. Palygorskite

The structural formula of palygorskite mineral is $Si_8Mg_5O_{20}(OH)_2(OH)_4 \cdot 4H_2O$ [19]. Palygorskite is a kind of crystalloid hydrous magnesium-aluminum silicate mineral and have chemically absorbed water within its structure, similar to that of smectite. Palygorskite mineral is identified on basal reflection (110) at $10.5A^\circ$ peak which broadens upon heating at $550^\circ C$ and remain unchanged during glycolation saturation (Fig. 4).

Palygorskites requisite alkaline conditions and high silicon and magnesium activities for stability [36]. They are also loosely associated with low latitudes and semi-arid climates. Palygorskite may be found in variety of sedimentary environments as well as in hydrothermal deposits. It was mainly reported in brackish and lacustrine environments, but marine and fluvial environments may also contain palygorskite, as well as weathering products of Mg-rich rocks and soil of arid and semi-arid regions [37]. Reference [22] illustrated that palygorskite results from the weathering and erosion of basaltic volcanism igneous rocks. It occurred in the semi-arid and arid regions. Palygorskite appears to be stably associated with montmorillonite. palygorskite refer to increase of magnesium element and pH (hydrogenic number) which reflects the change of marine environment to alkaline arid environment, which is a suitable environment for the formation of this mineral so that the increased salinity and silica with increasing temperature and evaporation with the lack of rainfall, which caused an increase of pH of the deposition environment [38]. References [39], [40] illustrated that palygorskite deposited in different geological environments, including marine, lagoonal, lacustrine and fluvial. And palygorskite was formed by authigenesis in evaporitic environments, whereas the other clay minerals are detrital in origin. Reference [41] explained the new formation of palygorskite from layer transformation of smectite.

5. Chlorite

The general structural formula of chlorite mineral is $(Mg,Fe,Al)_6(Si,Al)_4O_{10}(OH)_8$. The basic structure of the chlorite consists of negatively charged mica-like (2:1) layers regularly alternating with positively charged brucite-like octahedral sheets [22].

Chlorite is determined based on basal reflection (001) peaks at ($d=14-14.6 A^\circ$) and (003) at ($d=4.7-4.9 A^\circ$). Upon heating above $550^\circ C$, (001) chlorites peak may increase dramatically whereas Fe-chlorite and the higher-order peaks may be weakened [4]. Peak positions are unchanged by ethylene glycol (Fig. 4).

Chlorite mineral is found in all samples of Mukdadiya Formation. Chlorite is detrital in sedimentary environments, and especially in sedimentary materials derived from the glaciation of metamorphosed rocks.

Clay minerals formed as a result of different geological process (weathering and erosion) on the source rocks so that some minerals altered to clay minerals [22], [3]. Chlorite mineral formed in nature by weathering and erosion for Ferromagnesium minerals especially biotite (which exist in acidic and basic igneous, and metamorphic rocks) after remove Ti and Fe elements from these minerals under basic alkali conditions, where chlorite mineral transports to the depositional basins in shape of tiny clastic mud [22], [3], chlorite is stable in basic environment and altered to other clay minerals in acidic environment where be unstable [34]. Also [32] illustrated that chlorite is detrital origin where it forms because of alteration of ferromagnesian minerals in metamorphic and basic igneous rocks therefore chlorite's occurrence correlated with increase of igneous and metamorphic rock fragments, and common constituents of argillaceous sedimentary rocks in both detrital and outogenic forms. The formation of chlorite prefers arid conditions [3].

IV. CONCLUSIONS

The present study of the clay mineralogy of Mukdadiya Formation Shewasoor area, suggested the following conclusion:

1. The identified clay minerals are: Montmorillonite, kaolinite, illite, palygorskite and chlorite. These minerals were derived from different types of source rocks and the conditions in source rocks are likely suffered from arid to semi-arid climate conditions.
2. The genesis of montmorillonite, illite, chlorite and kaolinite is detrital, they formed by weathering of different source rocks such as basic and few acidic igneous, metamorphic, and old sedimentary rocks. Illite indicates shales and metamorphic sources. The low amount of kaolinite indicates the minority of acidic igneous rocks in the source area and dominated arid climate in the source area also.
3. Major phase transformations were not observed in the clay mineral deposits of Mukdadiya formation with exception of low effect of diagenesis and transformation

during transportation and the new formation of palygorskite from layer transformation of smectite.

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