Clay Mineralogy of Mukdadiya Formation in Zawita, Amadia Areas.

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Abstract
Twenty mudstone samples are chosen, each sample represents the mudstone units of each sedimentary cycle of Mukdadiya Formation in two sections (10 samples from Zawita area and 10 samples from Amadia area) in northern Iraq. X-ray Diffraction technique is used 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. The clay minerals are: kaolinite, chlorite, illite, montmorillonite and palygorskite by the major basal reflections of each clay mineral. The origins of these minerals are deduced also.

Keywords: mudstone, clay mineralogy, XRD analysis, Mukdadiya Formation, Zawita, Amadia.

Introduction:
Mukdadiya Formation (Early Pliocene) is widespread in Iraq, West Iran, East Syria and South Turkey, where this exposure in Iraq covered the oldest Fatha Formation (Middle Miocene) in Low and High Folded Zones such as Zawita, Sarsank, Zakho and Amadia …etc. These exposures spread clearly in syncline folds and on the edges of anticline folds. And others spread less frequently in the areas of Foot Hills Zone as a residue layers in the middle of the syncline folds and on its limbs edge, and generally decrease toward west direction [1].

The areas under study are two regions situated Duhok Governorate in the North of Iraq figure 1. The locations of the studied areas are:
The longitude between (N, 43° 9' 50" – E, 36° 56' 17") and the attitude between (N, 42° 90' 60" – E, 36° 41' 09") in the northern flank of Bekher fold.

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According to Basi and Jassim, (1974) Mukdadiya Formation is composed principally of fining upward cycles of clastics, mainly pebbly sandstone, sandstone and mudstone figure 2. It is believed 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 [2] .This bed separates between Miocene and Pliocene ages, this contact is diachronous and gradational with the underlying Injana Formation. The upper contact of Mukdadiya Formation is an erosional surface, with the Quaternary deposits lying over Mukdadiya Formation as an angular unconformity surface [2].

The study of clay minerals is very important because they reflect the mineralogy of source rocks and the topography and type of weathering which have affected these rocks. The type of clays that is found depends on the interaction of climate, geomorphology, parent rocks, and environment [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 is, 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].
Methodology

Twenty samples are chosen from Mukdadiya Formation (10 from Zawita section and 10 from Amadia section) each sample represents the mudstone units of each sedimentary cycle. X-Ray Diffraction technique is used in identification of both clay and non-clay minerals in order to determine the entire mineralogy of the clay fraction including the clay mineral assemblage. The resulted diffractograms of [normal (N), ethyl glycolated (G), and heated at 550°C (H)], which show the major basal reflections of the clay minerals in the studied samples. The conditions of the XRD instrument are listed below:

<table>
<thead>
<tr>
<th>X-Ray tube</th>
<th>Slits</th>
<th>Measures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target : Cu</td>
<td>Divergence : 1.0 deg</td>
<td>Axis : Theta- 2 Theta</td>
</tr>
<tr>
<td>Wave : 1.54060</td>
<td>Scatter : 1.0 deg</td>
<td>Scan mode : Continuous Scan</td>
</tr>
<tr>
<td>Voltage : 40 KV</td>
<td>Receiving : 0.15 mm</td>
<td>Range : 5.0- 50.0 deg</td>
</tr>
<tr>
<td>Current : 30 mA</td>
<td></td>
<td>Step : 0.05 deg</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Speed : 5.0 deg/min</td>
</tr>
</tbody>
</table>

Clay mineral analysis:

The results of X-Ray analysis show that Mukdadiya mudstones are variable mixtures of non-phyllosilicates [quartz, carbonates (mainly calcite, rarely dolomite), and feldspars] from XRD analysis of powder samples, phyllosilicates, including clay minerals, and inosilicates (palygorskite) from XRD analysis of oriented samples as shown in figures 3 and 4 and discussed below:

1- Quartz:
Quartz is the first in abundance in the studied samples of Mukdadiya mudstones. It is identified in basal reflections of 1.92-4.27 Å in all samples, the major peak at 3.34 Å (s) in sample of (MZ11) in Zawita section that is refer to being Zawita area farther than Amadia area from the source rocks.

2- Carbonates:
Calcite has the second abundance mineral in the Mukdadiya mudstone samples. It is identified in basal reflections of 1.5-3.85 Å in all samples, the major peak at 3.03 Å in sample of (MD20) in Amadia section that’s refer to being Amadia area nearest to the source rocks than Zawita area.
Dolomite is also showed in both sections of Mukdadiya Formation mudstone but in rare amounts; it's identified in basal reflections of 2.2-2.88 A° in all samples.

3- Feldspars:
   Feldspars are found in samples of Mukdadiya mudstone in rare percentage. It was identified in only one peak of (3.19 °A) in clay fraction of all Mukdadiya samples.

4- Kaolinite:
   Kaolinite group are recognized depending on its basal reflection (001), (d=7.1 A°) and at (002), (d=3.6 A°). By heating (550°C), the peak of mineral disappears due to the collapse of crystallography structure [4], and remains unchanged by glycolation. Kaolinite occurred in all studied samples. Kaolinite forms in weathering profiles and soils. The origin of kaolinite is detrital because of the weathering of feldspar in igneous rocks or from old sediment [6]. This mineral forms where solutions have low silica and alkali cation activities [3].

5- Illite:
   Illite identification is based on basal peak (10A°) which does not expand when glycolated and not collapse when heated to 550°C [7]. Illite mineral is found in all samples of Mukdadiya Formation. 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 [8]. generally Illite forms as a result of weathering of acidic igneous rocks which contain high amounts of K⁺, Mg²⁺ or as a result of entering smectite the K⁺, Mg²⁺ [6]. The occurrence of illite in the studied samples indicates shale and metamorphic sources because of its detrital origin where it is derived from the weathering of metamorphic rocks and shales [3].

6- Montmorillonite:
   Montmorillonite mineral is recognized based on the basal reflection (001) at (d=14.2 - 15A°) and other basal reflection (002) at (5.5 A°), when treated it by ethylene glycol become (d=17.18A) and become at (10 A°) by heating with 550 °C. Montmorillonite is abundant in soil of arid to semi-arid climate [6]. It is also of detrital origin in alkaline environment because of the weathering of basic igneous rocks which is rich in ferromagnesian minerals. Mafic silicates in many climates will decompose to montmorillonite [3]. Montmorillonite mineral was founded in all samples of Mukdadiya Formation.

7- Chlorite:
   Chlorite is determined based on basal reflection (001) peaks at (d=14-14.6 A°) and (003) at (d=4.7-4.9 A°). Upon heating above 550°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. Chlorite mineral is found in all samples of Mukdadiya Formation. Chlorite is of 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 authigenic forms [8]. The formation of chlorite prefers arid conditions [9].

8- Palygorskite:
   Palygorskite mineral is identified on basal reflection (110) at 10.5A° peak which broadens upon heating at 550 °C and remain unchanged during glycolation saturation. Palygorskites requisite alkaline conditions and high silicon and magnesium activities for stability [10]. They are also loosely associated with low latitudes and semi-arid climates. Most major deposits of this mineral were originally formed in shallow seas and lakes as chemical sediments, or by the reconstitution of smectites, in open oceans by the hydrothermal alteration of volcanic materials [11].
Figure 3: Diffractograms of XRD analysis of Mukdadiya Formation from Zawita section.

Figure 4: Diffractograms of XRD analysis of Mukdadiya Formation from Amadia section.
Origin and geologic importance of clay minerals

The clay minerals are usually transported by waters (rivers, streams, Drainage basins) and deposited in deposition at basins are formed and derived from source rocks (original) and from soils of drainage basins to deposition basins from weathering with different factors, which lead for varies mixture from clay minerals clastic origin [9]. From most studies, water transport different clay minerals (clastic origin) to river source, delta basins, deposition basins like: illite, chlorite, kaolinite, vermiculite and Montmorillonite [9]. After deposition the minerals in this basins and burial in continuous deposition are affected by diagenesis because flowing residue solution and vertical columnar pressure which some minerals altered to another clay minerals [9;12].

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 [6; 9], (Fig 5). Chlorite mineral formed in nature by weathering and erosion for Ferro-magnesium 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 [6; 9], chlorite is stable in basic environment and altered to other clay minerals in acidic environment where be unstable [13; 14].

Illite mineral derived from igneous and metamorphic rocks [6; 9] 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 [13], and later this clay minerals transport to deposition basins in shape of tiny clastic clay [6; 9; and 15].

Kaolinite mineral form from weathering of K-feldspar too [6; 15] and also from laterite soils [9].

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 [16;17;18]. This process required:  Aqueous alkaline environment must be available [6;19], high percentage of silica and magnesium in volcanic ash. Volcanic ash cannot alter to montmorillonite without presence of enough amounts of silica and magnesium [20] and presence of high percentage of salinity and that is available in alkaline environment [9]. Montmorillonite has also been described as having been derived from the decomposition of pegmatite and from spodumene [6; 9].

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. Palygorskite results from the weathering and erosion of basaltic volcanism igneous rocks. It occurred in the semi-arid and arid regions [6].

Figure 5: Major requirements and condition for clay minerals Formation. Adapted from [15].
Conclusions:
From the result of the clay fraction mineralogy the following conclusion may be suggested:
1- The clay minerals found in the studied samples (Kaolinite, Illite, Montmorillonite, Chlorite and Palygorskite) was derived from different types of source rocks.
2- Most of these minerals are detrital in origin they formed by weathering of different source rocks such as basic and few acidic igneous, metamorphic, and old sedimentary rocks. The occurrence of kaolinite refers to increase of igneous and metamorphic source rocks. Illite indicates shales and metamorphic sources.
3- The identified clay minerals suggest that the conditions in source rocks are likely suffered from arid to semi-arid climate conditions.
4- The clay mineral assemblages in the studied samples are most probably of detrital origin with low effect of diagenesis and transformation during transportation.

References