MINERALOGY OF THE MARRAT CLAY DEPOSITS, RIYADH REGION, CENTRAL SAUDI ARABIA

By

AHMED A. ALMOHANDIS
Geology Department, King Saud University, Riyadh, Saudi Arabia

Key words: clay, Marrat Formation, early Jurassic.

ABSTRACT
Clays in the Marrat Formation, which crop out 200 km west of Riyadh, Saudi Arabia, are dominantly composed of brownish red to dark red mudstones and shales. Marrat clays are chiefly composed of kaolinite and lesser amounts of illite. Quartz is the major non-clay mineral. The red colour of the clay is due to hematite present in very small amounts in the samples. The clays were probably formed by partial laterization of acid igneous rocks in the west of the study area. The products were transported to the present area and deposited in a shallow marine environment during early Jurassic in the Toarcian times.

INTRODUCTION
Kaolinitic clay bearing beds have been investigated at the type locality of Marrat Formation (Toarcian). The area under study is situated about 200 km west of Riyadh and is easily accessible (Fig. 1). More than 50 samples have been collected from the Middle Marrat, from two localities namely: Jabal Al Kumait and Khashm Al Qarain which are about 30 km apart. The rocks are dominantly composed of brownish red to dark red mudstone and shales, with less sandy/silty shales and occasional thin beds of calcareous sandstones. A few samples were selected for detailed chemical analysis, X-ray diffraction and differential thermal analysis.

Earlier studies were mostly concerned either with studies of lithologic characteristics and measurement of stratigraphic sections or regional mapping (Steineke and Bramkamp, 1952; Steineke et al., 1958; Powers et al., 1966). Detailed biostratigraphic studies were carried out on the Marrat Formation by Assad (1973). Partial chemical analysis and X-ray work on the Marrat red beds have been done by Abed (1979). Most recent work on part of the area was carried out by Almohandis (1984). The present investigation is concerned with the stratigraphy, mineralogy of the Marrat clays. It is mainly concerned with the
Mineralogy of the Marrat Clay

Qarain member, Middle Marrat as a part of the lower and Middle Jurassic siliciclastic and carbonate rocks. The Marrat Formation unconformably overlies the Minjur Formation (upper Triassic) and is conformably overlain by the Dhruma Formation (Middle Jurassic).

The Marrat Formation consists of lower and upper carbonate units which sandwich a red argillaceous units. The upper and lower carbonate units are both dated as Toarcian on the basis of ammonite fauna (Arkell, 1952).

Assad (1973) divided the Marrat Formation into three members based on Lithology and faunal characteristics. These members are as follows:-

- Hadbah member (Upper Marrat)
- Qarain member (Middle Marrat)
- Shaqra member (Lower Marrat)

Although the Marrat area affords the best exposures of the formation but the complete sequence does not crop out at a single locality. It has been pieced together and a composite has been constructed from several sections, generally along Lat. 25° 02’ N. The total thickness of the formation in the area is over 100 meters.

The Qarain member is composed mainly of brownish red to dark red, in part silty and occasionally sandy mudstones. In its upper part a thin bed of brownish limestone is also found. The total thickness of this member is about 38 meters in the Khashm Al Qarain area and 32 meters in the Kumait area (Figs. 2a & 2b).

MATERIALS AND METHODS

A total number of 57 samples were collected from the Qarain Member at Jabal Al Kumait and Khashm Al Qarain (Fig. 1). Nine samples were selected for XRD, DTA and chemical analysis (Figs. 2a & 2b).

Chemical analyses for major elements were done by wet method. Na and K were determined by flame photometry.

Differential Thermal Analysis (DTA) was carried out in the following way. The whole rock samples were ground in an agate pestle & mortar to ≤ 50 μm size. The ground samples were heated in a static atmosphere of air and the heating rate of 10°C per minute was used throughout the runs. The inert material used was calcined alumina.

X-ray diffraction (XRD) analyses were obtained using Ni-filtered Co Kα radiation from a Philips (PW 1050) diffractometer operated at 800 W (40KV, 20ma) and at a scanning speed of 1°2 θ per minute.
RESULTS

The Marrat clays are composed of kaolinite with illite as a subordinate clay mineral. Quartz is the major non-clay mineral but hematite is also present in very small quantities in most of the samples.

The results of the chemical analysis are presented in Table I as whole rock analysis. Out of a total of nine selected samples, three are from Jabal Kumait and six from Khashm Al Qarain (Figs 2a, 2b).
Table I

Whole-Rock chemical analysis* of mudstones and shales from Jabal Al Kumait and Khashm Al Qarain

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>MnO</th>
<th>P₂O₅</th>
<th>H₂O⁻</th>
<th>L.O.I</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43.46</td>
<td>1.58</td>
<td>24.60</td>
<td>9.99</td>
<td>3.50</td>
<td>1.65</td>
<td>1.08</td>
<td>1.90</td>
<td>0.03</td>
<td>0.05</td>
<td>1.46</td>
<td>12.34</td>
<td>101.64</td>
</tr>
<tr>
<td>2</td>
<td>46.86</td>
<td>2.00</td>
<td>24.18</td>
<td>9.99</td>
<td>3.50</td>
<td>1.45</td>
<td>0.05</td>
<td>1.90</td>
<td>0.02</td>
<td>0.05</td>
<td>1.44</td>
<td>10.54</td>
<td>101.98</td>
</tr>
<tr>
<td>3</td>
<td>48.92</td>
<td>2.00</td>
<td>20.78</td>
<td>11.98</td>
<td>3.50</td>
<td>1.45</td>
<td>0.47</td>
<td>2.40</td>
<td>0.02</td>
<td>0.07</td>
<td>1.38</td>
<td>8.54</td>
<td>101.51</td>
</tr>
<tr>
<td>4</td>
<td>44.40</td>
<td>1.75</td>
<td>23.01</td>
<td>11.98</td>
<td>3.50</td>
<td>1.25</td>
<td>0.05</td>
<td>2.20</td>
<td>0.02</td>
<td>0.05</td>
<td>1.52</td>
<td>10.84</td>
<td>100.57</td>
</tr>
<tr>
<td>5</td>
<td>43.62</td>
<td>1.80</td>
<td>22.31</td>
<td>12.98</td>
<td>2.50</td>
<td>1.15</td>
<td>0.10</td>
<td>2.10</td>
<td>0.09</td>
<td>0.08</td>
<td>1.38</td>
<td>11.36</td>
<td>99.57</td>
</tr>
<tr>
<td>6</td>
<td>43.78</td>
<td>1.75</td>
<td>22.40</td>
<td>13.98</td>
<td>3.50</td>
<td>1.40</td>
<td>0.47</td>
<td>2.30</td>
<td>0.01</td>
<td>0.05</td>
<td>1.24</td>
<td>10.74</td>
<td>101.62</td>
</tr>
<tr>
<td>7</td>
<td>40.08</td>
<td>1.67</td>
<td>19.85</td>
<td>16.97</td>
<td>4.50</td>
<td>1.95</td>
<td>0.05</td>
<td>1.70</td>
<td>0.02</td>
<td>0.08</td>
<td>2.58</td>
<td>12.16</td>
<td>101.61</td>
</tr>
<tr>
<td>8</td>
<td>71.22</td>
<td>1.90</td>
<td>3.79</td>
<td>6.99</td>
<td>7.50</td>
<td>0.50</td>
<td>0.05</td>
<td>1.40</td>
<td>0.02</td>
<td>0.02</td>
<td>0.30</td>
<td>7.54</td>
<td>101.23</td>
</tr>
<tr>
<td>9</td>
<td>47.04</td>
<td>2.50</td>
<td>12.28</td>
<td>17.97</td>
<td>3.40</td>
<td>1.40</td>
<td>0.03</td>
<td>3.00</td>
<td>0.02</td>
<td>0.06</td>
<td>1.88</td>
<td>8.72</td>
<td>98.30</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>58.10</td>
<td>0.70</td>
<td>15.40</td>
<td>6.70</td>
<td>3.10</td>
<td>2.40</td>
<td>1.30</td>
<td>3.20</td>
<td>—</td>
<td>—</td>
<td>5.00</td>
<td>2.60</td>
<td>—</td>
</tr>
</tbody>
</table>

*Analysed at chemistry Lab., Faculty of Earth Sciences, King Abdul Aziz University, Jeddah

**All values in % Average shale from Mason (1966)
AHMED A. ALMOHANIDS

Lithologic Description

(Jabal Al Kumait)

Creamish Limestone, tough, thickly bedded

(Hadbah Member) (3.5 m)

Dark brownish Red Shale, friable, fissility prominent, thin beds of gray Shale present locally. (8.6 m)

Reddish brown Shale, friable. (2.4 m)

Brownish Red Mudstone, dense, silty at base. (4.0 m)

Brownish Sandstone, fine grained, calcareous, moderately sorted cross-bedded, rippled marks at place. (3.6 m)

Brown Shale, at some places greyish bands, brown mudstone in the middle. (4.4 m)

Brownish Red Sandstone, fine grained with thin laminae of brownish Siltstone (4.2 m)

Brownish Red Mudstone, dense

Brown Shale, fissility at the base. (4.8 m)

Verticle Scale

0 - 2 m.

Fig. 2a: Lithologic description of Jabal Al-Kumait rocks.

Lithologic Description

(Khashm Al Qarain)

Creamish Limestone, tough (Hadbah Member)

Yellowish green Sandstone, fine grained, cross-bedded, moderately sorted thin beds of yellowish green, Siltstone and brown Shales (4.5 m)

Dark brown Mudstone, sandy at the base. (10.6 m)

Brownish Sandstone, fine grained, Calcareous (1.65 m)

Brownish Red Shale with thin laminae of brownish Siltstone (13.7 m)

Yellowish green, fine grained Sandstone cross-bedded,

Brownish Red Mudstone, dense friable, poorly sorted (2.95 m)

Dark brown Mudstone, dense (2.2 m)

Brown Shale, fissility is prominent (2.05 m)

Verticle Scale

0 - 2 m.

Fig. 2b: Lithologic description of Khashm Al Qarain rocks.
Mineralogy of the Marrat Clay

In the Kumait samples the silica ranges from 43.46 to 48.92 percent. It seems to decrease downward in order of superposition. Iron oxide varies between 9.99 and 11.98%. There is a general trend of decreasing Fe₂O₃ content downward in the section, alumina has antipathetic relation to Fe₂O₃ and also to SiO₂. The alumina varies from 20.78 to 24.60%. CaO and MgO contents remain nearly uniform throughout the section. The average CaO present in the samples is 3.50%. K₂O generally decreases downward. Alkalies vary from 1.95 to 2.98%. Higher Al₂O₃ and lower alkali values in the argillaceous rocks of Kumait area reflect the dominance of kaolinite in them as compared to the average shale. The smaller amount of Na₂O is probably due to lesser quantity of alkali feldspar. Higher values of CaO and loss on ignition is mainly due to presence of carbonates and gypsum in the Marrat clays.

Compared with the Kumait area the samples of the Qarain area have nearly the same SiO₂ trend. Sample-8 contains the highest percentage (71.22%) mainly because it is highly arenaceous. Fe₂O₃ varies from 6.99 to 17.97% and shows a general attitude of depletion with depth. Alumina ranges between 3.79% and 23.01% being minimum in the arenaceous sample (No. 8) but it has similar trends to the Kumait samples: increasing with depth and having an antipathetic relationship with Fe₂O₃. Titania also decreases with depth. Comparative trends of the same oxides from both of the areas are shown in Fig. 3.

![Fig. 3: Semilogarithmic plots of chemical variation of Marrat clays with respect to their order of superposition.](image-url)
Thermograms of the samples are presented in Fig. 4. Typically a differential thermal analysis curve of kaolinite shows a strong endothermic peak between 530°C and 700°C due to dehydration and dehydroxylation. A moderately strong exothermic peak between 940°C and 1000°C, signifies the recrystallization of kaolinite into a spinel phase (Grim & Rowland, 1942; Smykatz-Kloss, 1974). The endothermic peak between 90°C and 120°C corresponds to the removal of hygroscopic water (moisture) held by the clays.

DTA curves of the samples from Kumait area show endothermic peaks between 950°C and 955°C. The samples also show a moderately strong to strong endothermic peak between 90°C and 120°C due to loss of moisture from the clays.

DTA curves of Qarain samples also show a moderately strong to strong endothermic peak between 90° and 110°C due to removal of hygroscopic water. Other endothermic peaks range between 550°C and 580°C and exothermic peaks between 930°C and 955°C. Sample No. 8 shows an additional endothermic peak at 825°C indicating the presence of illite in considerable amounts besides kaolinite (Gaudette et al., 1964). The presence of quartz could not be confirmed because an endothermic peak around 570°C of kaolinite have masked it. Hematite does not show any thermal transformation up to 1000°C therefore it could not be confirmed by DTA although the brownish red colour of all samples indicates the presence of iron oxide.

X-ray diffractograms of the Marrat samples show general similarities in their pattern which is an indication that the mineral constituents are also the same. The results are presented in Table II.

Kaolinite was identified by a 7Å basal spacing in the powder diffraction patterns and illite by a 10Å spacing. The reflections at 7.15Å (001), 3.57Å (002) and 2.37Å (003) are diagnostic for kaolinite and these reflections disappear/collapse upon heating to 550°C. Another advantage of heating is the differentiation between kaolinite and chlorite particularly if 14Å reflection of chlorite is not pronounced (Grim, 1968). The shape and the relative intensities of the reflection at 4.43, 4.34 and 4.13Å reveal that the kaolinite shows a moderate weak degree of crystallinity (Murray and Lyons, 1956).

Illite is recognized by a reflection of 10A (Bradley & Grim, 1961) which does not change by thermal treatment (Molloy & Kerr, 1961). Reflections between 20-30° 2θ and close examination of the intensity ratio I (001)/I (002) shows that the illite present in most of the clay fraction is a 2M polytype and dioctahedral (Bradley & Grim, 1961; Carrol, 1970). The 10A (001) basal reflection is sharp, hence it is most likely a secondary fine grained mica which has possibly been formed by the weathering and transformation of micas and feldspars (Stoch & Sikora, 1976).
Quartz is present even in the clay fraction and is easily recognized by the reflection at about 3.34Å and 4.26Å. The presence of hematite is indicated by the presence of small reflection peaks at about 2.69Å and 2.55Å. The characteristic basal reflections of hematite are at 2.70, 2.52 and 1.70Å.
Table II

D-Spacings (Å) and intensities of disoriented, air dried samples from Kumait and Qarain clays

<table>
<thead>
<tr>
<th>SAMPLES</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>DA</th>
<th>I/I₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>dA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.07</td>
<td>19</td>
<td>9.97</td>
<td>15</td>
<td>9.97</td>
<td>32</td>
<td>10.01</td>
<td>12</td>
<td>9.97</td>
<td>18</td>
<td>10.01</td>
<td>14</td>
</tr>
<tr>
<td>7.14</td>
<td>100</td>
<td>7.14</td>
<td>100</td>
<td>7.14</td>
<td>100</td>
<td>7.14</td>
<td>100</td>
<td>7.14</td>
<td>100</td>
<td>7.14</td>
<td>100</td>
</tr>
<tr>
<td>4.43</td>
<td>24</td>
<td>4.40</td>
<td>22</td>
<td>4.41</td>
<td>60</td>
<td>4.36</td>
<td>16</td>
<td>4.34</td>
<td>19</td>
<td>4.34</td>
<td>10</td>
</tr>
<tr>
<td>——</td>
<td>——</td>
<td>——</td>
<td>——</td>
<td>3.90</td>
<td>7</td>
<td>3.82</td>
<td>3</td>
<td>——</td>
<td>——</td>
<td>——</td>
<td>——</td>
</tr>
<tr>
<td>3.57</td>
<td>60</td>
<td>3.57</td>
<td>60</td>
<td>3.57</td>
<td>62</td>
<td>3.57</td>
<td>50</td>
<td>3.57</td>
<td>59</td>
<td>3.57</td>
<td>60</td>
</tr>
<tr>
<td>3.32</td>
<td>42</td>
<td>3.35</td>
<td>49</td>
<td>3.34</td>
<td>70</td>
<td>3.34</td>
<td>27</td>
<td>3.34</td>
<td>35</td>
<td>3.34</td>
<td>100</td>
</tr>
<tr>
<td>3.24</td>
<td>8</td>
<td>—</td>
<td>—</td>
<td>2.97</td>
<td>6</td>
<td>3.23</td>
<td>6</td>
<td>3.23</td>
<td>5</td>
<td>3.23</td>
<td>9</td>
</tr>
<tr>
<td>2.69</td>
<td>4</td>
<td>—</td>
<td>—</td>
<td>2.69</td>
<td>18</td>
<td>2.69</td>
<td>10</td>
<td>2.69</td>
<td>14</td>
<td>2.69</td>
<td>15</td>
</tr>
<tr>
<td>2.55</td>
<td>20</td>
<td>2.55</td>
<td>28</td>
<td>2.59</td>
<td>27</td>
<td>2.56</td>
<td>7</td>
<td>2.55</td>
<td>13</td>
<td>2.55</td>
<td>16</td>
</tr>
<tr>
<td>2.49</td>
<td>25</td>
<td>2.49</td>
<td>13</td>
<td>2.48</td>
<td>12</td>
<td>2.49</td>
<td>12</td>
<td>2.49</td>
<td>18</td>
<td>2.49</td>
<td>18</td>
</tr>
<tr>
<td>——</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>——</td>
<td>——</td>
<td>——</td>
<td>2.37</td>
<td>8</td>
<td>2.43</td>
<td>13</td>
<td>2.43</td>
</tr>
<tr>
<td>2.34</td>
<td>27</td>
<td>2.34</td>
<td>15</td>
<td>2.33</td>
<td>26</td>
<td>2.33</td>
<td>12</td>
<td>2.37</td>
<td>21</td>
<td>2.33</td>
<td>10</td>
</tr>
<tr>
<td>2.24</td>
<td>12</td>
<td>2.27</td>
<td>12</td>
<td>2.24</td>
<td>24</td>
<td>2.28</td>
<td>8</td>
<td>2.28</td>
<td>9</td>
<td>2.27</td>
<td>10</td>
</tr>
<tr>
<td>1.98</td>
<td>12</td>
<td>1.99</td>
<td>12</td>
<td>2.10</td>
<td>4</td>
<td>1.98</td>
<td>5</td>
<td>1.98</td>
<td>10</td>
<td>1.97</td>
<td>6</td>
</tr>
<tr>
<td>——</td>
<td>1.81</td>
<td>12</td>
<td>1.81</td>
<td>12</td>
<td>1.78</td>
<td>5</td>
<td>1.84</td>
<td>7</td>
<td>1.81</td>
<td>7</td>
<td>1.83</td>
</tr>
</tbody>
</table>
DISCUSSION AND CONCLUSION

The origin of suites of clay minerals in many rock types is a problem which is commonly discussed in the literature. Researchers have different points of view but it is generally accepted that weathering and diagenetic processes are the two main factors which produce clay minerals. Other factors also play an important role in their formation such as pressure, temperature, time, tectonics, source rocks, general depositional environment and climatic conditions at source as well as the site of deposition (Keller, 1970; Millot, 1970).

Conditions responsible for the formation of kaolinite at the earth surface have been listed by Keller (1964). Basically, kaolinite is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. As a weathering product, the production of kaolinite needs certain conditions such as:

i) a high Al: Si ratio

ii) An acid environment and

iii) the absence of Na, Ca, K, Mg and Fe

Therefore, it is logical to assume that kaolinite forms in a terrain and climate where leaching dominates and the pH is low. Thus for the genesis of kaolinite the parent material must first be rich in alumina, the efficient removal of most metal cations and excess of $\text{H}^+$ ions combined with efficient removal of silica in solution by associated $\text{Na}^+$ and $\text{K}^+$ ions is very necessary (Keller, 1956); under such conditions kaolinite may develop by intense weathering of rocks rich in ferromagnesian minerals or from more sialic rocks such as granites, and granodiorites.

The mineralogical and chemical studies of the Marrat clays indicate the dominance of kaolinite as the major clay mineral. Quartz occurs as an inert diluent with a very small amount of feldspar. The red colour is due to the hematite identified from the X-ray analysis.

It is suggested that partial laterization of acid igneous rocks of the Arabian shield in a humid tropical environment, is the probable process by which the Marrat clay deposits were formed. The weathered products were transported from the west to the present area and deposited in a shallow environment during the Toarcian times of the lowermost Jurassic.

REFERENCES


Mineralogy of the Marrat Clay


تتميز رواسب مرات الطينية التي تبعد عن الرياض بالملكة العربية السعودية حوالي 200 كيلومترًا بأنها تتكون أساسًا من صخور الوحل بني اللون إلى الحمراء القائمة، والطفل. وتتكون معادنها الطينية من معدن الكولينيايت مع نسبة أقل من معدن الاته، أما معدن الكوارتز فهو المعدن الرئيسي غير الطيني. إن اللون الأحمر لهذه الرواسب الطينية يعود إلى معدن الهيماتايت الموجود بكميات قليلة جدًا فيها. ويعتمد أن تكون هذه الرواسب الطينية قد تكونت بوساطة اللترية الجزيئية لصخور النارية الحمضية إلى الغرب من منطقة الدراسة. وقد نقلت منتجات التجوية إلى منطقة الدراسة وترسبت في بيئة بحرية ضحلة خلال العصر الجوراسي المبكر في أزمة فترة التوارسيان.