Mineralogical and Geochemistry Study of Darnah Formation in Wadi Al Kharsha, Northeast Libya

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Abstract

This paper has been carried out to determine the mineralogical and geochemical characteristics of Eocene Darnah limestone which outcrops at Wadi Al Kharsha as an example of the Darnah Formation. The most conspicuous phenomenon is the upward increase of the dolomitization process, whereas, the dolomite content ranges from 4.34 to 15.48% with an average value of 8.99%. The lime (CaO) represents the major predominant with a high content (48.08%), it can be blend with other carbonates to improve its quality to meet the specifications of raw material for cement manufacture. The relationship between calcium (CaO) and magnesium (MgO) exhibits a significantly strong negative linear correlation coefficient ($R^2 = 0.967$), which emphasizes the dolomitization process, while the relationship between SiO$_2$ and Al$_2$O$_3$ is a positive linear significant relationship with a strong correlation coefficient ($R^2 = 0.98$), whereas, the SiO$_2$ increases with increasing of Al$_2$O$_3$. The calculated mineralogical composition revealed that halite, gypsum, and hematite are considered to be minor constituents, almost less than 1.0%.

Keywords: Limestone; Darnah Formation; Mineralogy; Geochemistry; Dolomitization; Characterizations; Cement

Introduction

Limestone occurrences are widespread in Libya. It is found in all the geo-political zones of the country with different degrees of concentration. Weathered limestones are common in many parts of the studied area.

The area has irregular land morphology depending on the lithology and tectonics of the region. The limestone generally forms the highest, sharper peaks with deeply dissected slopes in the hilly terrain. Rock outcrops are common on the upper slopes. Weathering products cover the lower slopes. Peaks around the
region are generally W-E and sometimes NW-SE trending. The climate is an east Mediterranean one. In the region, the summer is mild and humid and the winter is mild and wet. Precipitation occurs mostly in the form of rainfall, intensifying winter [1,2].

Generally, in the point of view of the previous geological studies, Libya has been divided into four main regions as follows:

1. Northwestern region: include Tripoli area, Al Jofra coastal plain, Nafossa mountain, Hamada basin, and northern Gargaf elevations.
2. Northcentral region: include Sirte basin and Al Jofra area.
3. Northeastern region: made up of Cyrenica area, Al Jabal Al Akhdar, Al Sarir, and Al Jaghboub.
4. Southwestern region: represented by Fazan area and Merzq basin.

This study has been performed on the limestone deposits in the Northeastern region which covered by a succession of limestone rocks that belong to the Miocene age of the Cenozoic Era. The chalk rocks of the Cretaceous are outcrop in five areas only are Tokra area, Jardas Al Ahrar, Al Majakeer, Al Uwaliyah, and Ras Al Helal. The deposits of marine sediments of Tertiary age of Eocene, Oligocene, and Miocene are formed in the northeastern part of Libya to include the major part of exposed rocks in this region today that represented by Al Jabal Al Akhdar formation, Apollonia formation, and Darnah formation [1,2].

The limestone formations in the Northeastern region given below

<table>
<thead>
<tr>
<th>Geologic Age</th>
<th>Rock formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quaternary</td>
<td>Limestone and marl deposits</td>
</tr>
<tr>
<td></td>
<td>Al Rajma formation</td>
</tr>
<tr>
<td></td>
<td>Al Faidiyah formation</td>
</tr>
<tr>
<td>Tertiary</td>
<td>Al Abraq formation</td>
</tr>
<tr>
<td></td>
<td>Darnah formation</td>
</tr>
<tr>
<td></td>
<td>Apollonia formation</td>
</tr>
<tr>
<td>Cretaceous</td>
<td>Al Baniyah formation</td>
</tr>
</tbody>
</table>

**The Study Area**

This study has been conducted on the Darnah Formation at Wadi Al Kharsha of Al Jabal Al Akhdar in North–East Libya as shown in Figure 1. Figure 2 shows some outcrops of the study formation that have been exposed to dolomitization and weathering processes. The present study discusses the mineralogical and geochemical characteristics of the Darnah Formation in Wadi Al kharsha as a part of Al Jabal Al Akhdar, which located in northeast Libya. Seven samples have been collected to represent the whole formation [3].
The limestones of the Darnah Formation are traditionally known as the basic raw material of the Portland cement industry in Libya. The present study provides new chemical analysis data which may help in evaluating the specifications of the limestones of the Darnah Formation in the study area as raw material for such industry. The Portland cement industry, depends basically on the interplay reaction between CaO, SiO₂, Al₂O₃, and Fe₂O₃, at up to 1500°C. The customary used raw materials are limestone as a source for CaO and shale as a source for SiO₂, Al₂O₃ and Fe₂O₃. The ratio of limestone to shale is about 3:1. Both limestone and shale are ground, mixed, and ignited thoroughly in a special furnace at 1500°C, to produce what is known as "clinker" [5].

**Problem Statement**

1. These rocks haven't subjected to detailed studies and evaluation.
2. The study spotlight the importance of these rock materials as a natural resource.
3. There is no available concerning data that can be used as a reference. The main objectives of this paper can be summarized as follows:
   1. Study the mineralogical and geochemical characteristics of the Darnah Formation at Wadi Al Kharsha.
   2. Compare the present results with the previously published studies
   3. Evaluate the quality of the studied rocks as raw materials.
4. Potentiality of using these raw materials for the cement industry.
5. The study regards as a preliminary one for a more detailed study later.

### Table 1: Stratigraphic section of part of the exposed Darnah Formation.

<table>
<thead>
<tr>
<th>Epoch</th>
<th>Age</th>
<th>Fm.</th>
<th>Thickness (m)</th>
<th>Lithological Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Mioce</td>
<td>Utetian</td>
<td>Darnah</td>
<td>4</td>
<td>Limestone creamish white, Coarse grained, hard solution and inter skeletal porosity, thickly bedded, wackstone, faunal content, megalospheric Nummulites, Fossil fragments, and rare gastopoda.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>Limestone, light grey, fine- medium grained, hard solution and inter skeletal porosity, thickly bedded, wackstone, faunal content, megalospheric Nummulites, echinoids, Fossil fragments, and rare gastopoda.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12</td>
<td>Limestone, Creamish Yellow, Coarse grained, moderately peloidal bioclastic common syntaxial calcite cement, v. good intergranular porosity, massive bedded, grainstone, faunal content, microospheric Nummulites, echinoids, shell fragments.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>15</td>
<td>Limestone, creamish white , fine- medium grained, moderately hard, good solutional porosity, thickly bedded, wackstone, faunal content, megalospheric Nummulites, operculine, pelecypoda</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>46</td>
<td>Limestone, cream, medium coarse grained, hard moderately hard, fair intercrystalline porosity, massive bedded, packstone-grainstone, faunal content, microspheric and smaller sized Nummulites in lower part, rich in operculine, and echinoids.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20.5</td>
<td>Limestone, whitish grey, medium grained, hard, thickly bedded, wackstone, faunal content, megalospheric Nummulites, echinoids, rare gastopoda and pelecypoda.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td>Limestone, light grey, fine- medium grained, fine crystalline matrix, good solutional, porosity, massive bedded, wackstone, faunal content, megalospheric Nummulites, echinoids, rich in Fossil fragments, rare gastopoda and echinoids.</td>
</tr>
</tbody>
</table>

### Materials and Methods

#### Sample Collection: Seven samples were collected from Daranah Formation at Wadi Al Kharsha from bottom to top.

#### Sample Preparation: Samples were prepared for geochemical analysis by using X-ray fluorescence by crushing about 1kg of each rock sample in a porcelain mortar. Samples are further ground to -80 mesh grain size in an automatic agate mortar. The sample powder is mixed thoroughly and a representative portion of about 10 g is pressed at 90 bar in a pellet-like form. The prepared pellets are kept dry for analysis by X-ray fluorescence spectrometry (XRF) [6]. The analysis using XRF. the spectrometer was conducted at 50kv under methane-argon atmosphere. The analyzed samples are calibrated with a series of natural and synthetic reference materials. The XRF analyses were performed at the laboratories of the Portland cement factory in Hawari, Benghazi. The content of loss on ignition (L.O.I.) was determined gravimetrically by weight loss between 105 and 1000°C upon ignition at the geochemistry laboratory of Benghazi University.
Results and Discussion

To study the mineralogical and geochemistry characteristics of carbonate rocks of the Darnah Formation at Wadi Al Kharsha, the major constituents have been determined, whereas, the weight percentage of major chemical compounds e. g., SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, MgO, CaO, K$_2$O, P$_2$O$_5$, SO$_3$, and Cl and their averages as well as the mineralogical composition, are presented in Table 2 for the investigate limestone samples.

**Petrochemical Calculations**

The theoretical mineral composition of the analyzed carbonate rocks are calculated on the following basis: SO$_3$% is allotted in gypsum, Mg% in dolomite; the remaining CaO% after the requirement of gypsum and dolomite is allotted in the form of calcite. Cl is calculated in the for

m of halite. The content of total iron (Fe$_2$O$_3$) is considered as hematite. The contents of SiO$_2$, TiO$_2$, Al$_2$O$_3$ are collectively considered as a reliable measure of the insoluble residue (I.R.) in the analyzed carbonates. The obtained theoretical mineral composition is given in Table 2. The detailed petrochemical calculations are given by Hutchison [7].

The calculated mineralogical composition of the Darnah Formation at Wadi Al Kharsha as illustrated in Table 2 suggest the following inferences:

1. The halite, gypsum, and hematite are considered minor constituents (almost below 1.0%).
2. The Darnah limestones are slightly dolomitized, where the content of dolomite ranges between 4.34 and 15.48% with an average value of 8.99%.
3. The concentration of insoluble residue carbonates of the Darnah Formation are ranging between 8.72 and 9.64 % with an average value of 9.03%.
4. Calcite is the main mineral constituent in the analyzed carbonate samples ranging from 73.73% to 84.72%, with an average of 80.19%.

The chemical compositions Tables 2 & 3, as well as the sequential distribution of the mineralogical constituents in the sampled profile, indicates that the dolomitization is increased upward, the dolomite content from about 4.34% to 15.48%. Figures 3& 4 a triangle p

lot between calcite, dolomite, and silica minerals, whereas, it is clear that calcite is the predominant mineral. The phenomena have definitely occurred at the expense of calcite as it decreases from 84.72% to about 73.73%.

**Table 2: Chemical analysis and calculated mineral constituents.**

<table>
<thead>
<tr>
<th>Oxides (%)</th>
<th>Formation bottom</th>
<th>Formation top</th>
<th>Range (%)</th>
<th>$\bar{X}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>5.85</td>
<td>5.79</td>
<td>5.98</td>
<td>6.48</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.60</td>
<td>1.59</td>
<td>1.66</td>
<td>1.79</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.30</td>
<td>0.30</td>
<td>0.32</td>
<td>0.40</td>
</tr>
<tr>
<td>MgO</td>
<td>1.04</td>
<td>1.24</td>
<td>1.75</td>
<td>2.00</td>
</tr>
<tr>
<td>CaO</td>
<td>49.51</td>
<td>49.26</td>
<td>48.53</td>
<td>47.78</td>
</tr>
<tr>
<td>Cl</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.41</td>
<td>0.47</td>
<td>0.40</td>
<td>0.47</td>
</tr>
<tr>
<td>L.0.I.</td>
<td>41.48</td>
<td>41.31</td>
<td>39.99</td>
<td>41.00</td>
</tr>
<tr>
<td>Al$_2$O$_3$/SiO$_2$</td>
<td>0.274</td>
<td>0.275</td>
<td>0.278</td>
<td>0.276</td>
</tr>
<tr>
<td>MgO/CaO</td>
<td>0.020</td>
<td>0.025</td>
<td>0.036</td>
<td>0.041</td>
</tr>
</tbody>
</table>

Calculated mineral constituents (%)

| Calcite     | 84.72 | 84.14 | 81.96 | 79.9 | 77.67 | 79.20 | 73.73 | 73.73-84.72 | 80.19 |


Table 3: Chemical analysis of Terra Rossa from the study area.

<table>
<thead>
<tr>
<th>Constituents &quot;Oxides&quot;</th>
<th>Sample No.1 Wt.%</th>
<th>Sample No.2 Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>34.01</td>
<td>33.82</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>19.18</td>
<td>21.91</td>
</tr>
<tr>
<td>TiO₃</td>
<td>1.66</td>
<td>2.07</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.91</td>
<td>11.87</td>
</tr>
<tr>
<td>MgO</td>
<td>8.36</td>
<td>9.42</td>
</tr>
<tr>
<td>CaO</td>
<td>33.29</td>
<td>28.3</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>Cl</td>
<td>0.008</td>
<td>0.025</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.04</td>
<td>3.38</td>
</tr>
</tbody>
</table>

I.R. = Insoluble residue  \( \bar{x} \) = average value

Figure 3: Vertical distribution of calculated minerals in measured section of Darnah Formation.
Figure 4: Triplot diagram showing the relationship between calcite, dolomite & silica.

Correlation between Major Oxides

Magnesium and Calcium

The mutual correlation between some major constituents is a useful procedure to understand the dependence of such variables. Correlations between lime (CaO) and magnesia (MgO) of limestone rocks were determined. As can be seen in Figure 5 which depicts the reversible correlation coefficient between the two variables, as the MgO increases, the CaO content of rocks decreases. This relationship is very significant (R² = 0.967). An inverse relationship was found, with a strong correlation coefficient between these parameters. However, Figure 6 emphasizes this correlation behavior.

Figure 5: Correlation between CaO and MgO oxides of studied samples.
Figure 6: Correlation between calcium and magnesium oxides.

Alumina and Silica

On the other hand, the relationship between SiO$_2$ and Al$_2$O$_3$ of limestone of different samples is shown in Figure 7. It is obvious that is a linear relationship with a strong correlation coefficient between these parameters. Whereas, the SiO$_2$ increases, the Al$_2$O$_3$ also increases. However, this relationship very significant ($R^2 = 0.98$).

Figure 7: Correlation between SiO$_2$ and Al$_2$O$_3$ oxides.

Petrographic Characteristics

The petrographic features of dolomite can be summarized as follows:

a. Dolomite crystals are generally equidimensional with fine crystal size. It occurs as disseminated or clustered rhombs in the groundmass rather than in bioclastic. The latter are more affected by recrystallization and cementation by microsparite or sparite.
Dolomitization is a replacement mechanism, taking place between solid CaCO$_3$ and aqueous yielded the Mg$^{2+}$, as the following equation:

$$2\text{CaCO}_3 + \text{Mg}^{2+} \rightarrow \text{CaMg(CO}_3)_2 + \text{Ca}^{2+}$$

Solid aqueous Solid aqueous [8].

b. The dolomite rhombs are hypidiomorphic to xepnomorphic with or without a ferruginous opaque nucleus. They are laching any clear zoning.

c. Dolomite appears of relatively higher relief due to encrustation by ferruginous materials, which in parts displayed highly dolomitized zones reddish hues. Sometimes the oxidation is too extensive to obscure entirely the optical properties of dolomite.

d. Dolomitization occurs as irregular patches.

e. The secondary porosity due to dolomitization is mostly filled with sparite.

These petrographic characteristics of dolomite suggest that the solutions that caused dolomitization were markedly enriched in ferruginous material, i.e., oxidizing solutions containing Fe$^{3+}$ besides Mg$^{2+}$.

The mechanism, being a replacement reaction, should take place under non-precipitative pH (i.e., under acidic conditions). The dolomitization process in the study area increases near the ground surface, via oxidizing solution enriched in Mg$^{2+}$ and Fe$^{3+}$, and under acidic conditions.

**The non-carbonate Fraction**

The most important non-carbonate chemical constituents are SiO$_2$ and Al$_2$O$_3$ which may form clays and free silica (quartz). The SiO$_2$, Al$_2$O$_3$ ratio in the studied carbonate average 0.28, which may suggest more quartz, rather than clays. In the analyzed Terra Rossa, the SiO$_2$, Al$_2$O$_3$ ratio increases to about 0.7, suggesting more contribution of clay minerals. The presence of TiO$_2$(0.034%) is due to atomic substitution in the octahedral sites of Al in the illite lattice [8].

The chemical analysis of two Terra Rossa samples from the study area (Table, 2) indicates that they are rich in both MgO and Fe$_2$O$_3$, (8.89%, and 10.36% in average MgO and Fe$_2$O$_3$ respectively). The Terra Rossa can, therefore, be considered as an adequate source of both dolomitization ingredients, namely Mg$^{2+}$ and Fe$^{3+}$. The prevailing semi-arid conditions may facilitate easy leaching of Mg$^{2+}$ and Fe$^{3+}$ from Terra Rossa to the meteoric water [7].

The comparison between the data of the present study and the average data of limestones used for the Portland cement industry in Libya published by Rao and Doughri [9], as readily illustrated in (Figure 8) suggests the following:

1. The contents of MgO, CaO, and Al$_2$O$_3$ in the present study are closely similar to the published average.
2. The limestones of the present study are relatively enriched in SiO$_2$, but depleted in Cl, compared to the published average.

However, both the increase of SiO$_2$ and decrease of Cl act in favor of the limestone quality [10,11].
Figure 8: Comparison between the present data and published average of Darnah.

**Conclusion**

The conclusion which can be drawn, based on the experimental results are:

- The upward increase of the dolomitization process of Darnah Formation due to the intensive weathering process of surface solutions rich in Mg$^{++}$ that replace Ca$^{++}$.
- The relationship between calcium oxide (CaO) and magnesium oxide (MgO) exhibits a significantly strong negative linear correlation coefficient ($R^2 = 0.967$), which emphasizes the dolomitization process.
- The lime (CaO) represents the major predominant constituent (48.08%) which can be used as raw material for cement manufacture.
- The calculated mineralogical composition revealed that halite, gypsum, and hematite are considered to be minor constituents of almost less than 1.0%.
- Much better results can be obtained if the upper few meters, which showed to have a higher degree of dolomitization, which is highly recommended to be excluded from quarrying.
Recommendations

In the light of the previous study and the obtained results it could be recommended by:
- These geologic formations required extensive study to evaluate.
- Perform a general survey for raw materials that can be exploited in the different industries.
- Libya possesses huge reserves of carbonate rocks of high quality for a cement industry.
- The studied limestone rocks can be used for cement manufacture after mixing with other carbonates to upgrading and improve their specifications.
- The total alkalies must be determined to recognize their content because they regard as impurities for cement and causing burning problems in the kiln.
- These natural resources can support the national income if it is taken into consideration.
- The authorities should be taken into account the sustainable development of these resources for the next generations.

References


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