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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_2O_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_2O_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 Cyrinica area, Al Jabal Al Akhadar, 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 belonging 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 Majaheer, 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 Akhadar formation, Apollonia formation, and Darnah formation [1,2].

The limestone formations in the Northeastern region given below

Geologic Age	Rock formation
Quaternary	Limestone and marl deposits
	Al Rajma formation
	Al Faidiyah formation
Tertiary	Al Abraq formation
	Darnah formation
	Apollonia formation
Cretaceous	Al Baniyah formation

The Study Area

This study has been conducted on the Daranah 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].

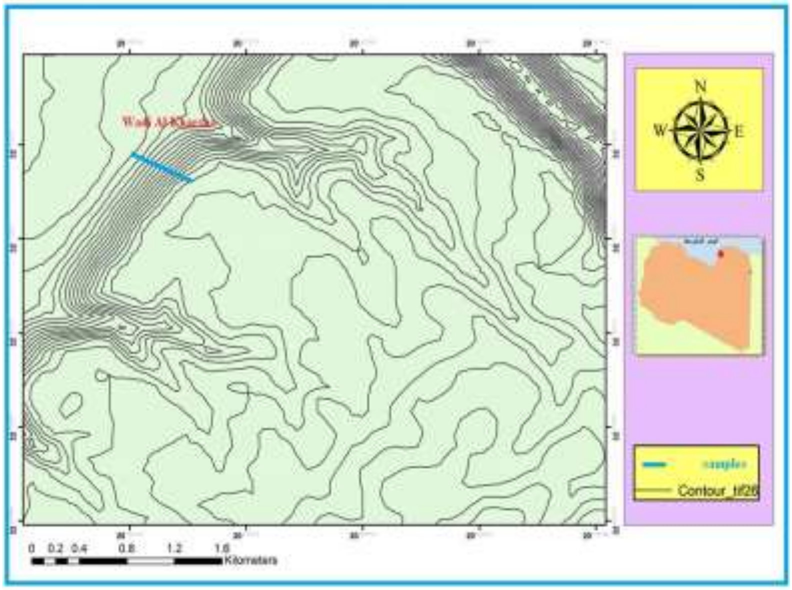

Figure 1: Location map of the study area [4].

Figure 2: Field photos a- limestone outcrops, b- dolomitized limestone, c- weathered limestone.

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, SiO_2, Al_2O_3, and Fe_2O_3, at up to 1500̊ C. The customary used raw materials are limestone as a source for CaO and shale as a source for SiO_2, Al_2O_3 and Fe_2O_3. 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 1500̊ 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 Daranah 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.

Epoch	Age	Fm.	Thickness (m)	Lithological Description
UPER MIDDLE EOCENE	UTETIAN	DARNAH	4	Limestone creamish white, Coarse grained, hard solution and inter skeletal porosity, thickly bedded, wackstone, faunal content, megalospheric Nummulites, , Fossil fragments, and rare gastopoda.
			4	Limestone, light grey, fine- medium grained, hard solution and inter skeletal porosity, thickly bedded, wackstone, faunal content, megalospheric Nummulites, echioids, Fossil fragments, and rare gastopoda.
			12	Limestone, Creamish Yellow, Coarse grained, moderately pelodal bioclastic common syntaxial calcite cement, v. good intergranuler porosity, massive bedded, grainstone, faunal content, microspheric Nummulites, echioids, shell fragments.
			15	Limestone, creamish white , fine- medium grained, moderately hard, good solutional porosity, thickly bedded, wackstone, faunal content, megalospheric Nummulites, operculine, pelecypoda
			46	Limestone, cream , medium coarse grained, hard moderately hard, fair intercrystalline porosity, massive bedded, packstone-grainstone, faunal content, microspheric and smaller sized Nummulitesin lower part,rich in operculine, and echinoids.
			20.5	Limestone, whitish grey, medium grained, hard, thickly bedded, wackstone, faunal content, megalospheric Nummulites, echinoids, rare gastopoda and pelecypoda.
			30	Limestone, light grey, fine- medium grained, fine crystalline matrix, good solutional, porosity, massive bedded, wackstone, faunal content, megalospheric Nummulites, echioids, rich in Fossil fragments, rare gastopoda and echinoids.

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℃ 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_2O_3, Fe_2O_3, MgO, CaO, K_2O, P_2O_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 form of halite. The content of total iron (Fe_2O_3) is considered as hematite. The contents of SiO_2, TiO_2, Al_2O_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 plot 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.

Oxides (%)	Samples numbers							Range (%)	$\bar{x}$ (%)
	Formation bottom Formation top								
	1	2	3	4	5	6	7		
SiO_2	5.85	5.79	5.98	6.48	5.90	5.86	5.91	5.79-6.48	5.96
Al_2O_3	1.60	1.59	1.66	1.79	1.61	1.60	1.63	1.59-1.66	1.64
TiO_3	0.03	0.03	0,03	0.05	0.03	0.03	0.03	0.03-0.05	0.034
Fe_2O_3	0.30	0.30	0.32	0.40	0.50	0.31	0.30	0.30-0.50	0.34
MgO	1.04	1.24	1.75	2.00	2.62	2.46	3.70	1.04-3.70	2.11
CaO	49.51	49.26	48.53	47.78	47.47	47.81	46.23	46.23-49.51	48.08
CL	0.01	0.01	0.01	0.04	0.01	0.02	0.16	0.01-0.04	0.42
SO_3	0.41	0.47	0.40	0.47	0.43	0.59	0.42	0.41-0.59	0.038
L.O.I	41.48	41.31	39.99	41.00	41.43	41.52	41.63	39.99-41.63	41.19
Al_2O_3/SiO_2	0.274	0.275	0.278	0.276	0.273	0.273	0.276	0.278-0.273	0.275
MgO/CaO	0.020	0.025	0.036	0.041	0.055	0.050	0.060	0.020-0.060	0.041
Calculated mineral constituents (%)									
Calcite	84.72	84.14	81.96	79.9	77.67	79.20	73.73	73.73-84.72	80.19

Dolomite	4.34	5.20	7.32	8.36	11.96	10.3	15.48	4.34-15.48	8.99
Gypsum	0.88	1.01	0.80	1.01	0.92	0.84	0.90	0.80-1.01	0.91
Halite	0.05	0.03	0.03	0.10	0.03	0.05	0.41	0.03-0.41	0.10
Hematite	0.30	0.30	0.32	0.40	0.50	0.32	0.30	0.30-0.50	0.35
I.R.	8.75	8.72	8.99	9.64	9.42	8.80	8.87	8.72-9.64	9.03

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

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

Constituents "Oxides"	Sample No.1 Wt.%	Sample No.2 Wt.%
SiO_2	34.01	33.82
$Al2O_3$	19.18	21.91
TiO_3	1.66	2.07
Fe_2O_3	8.91	11.87
MgO	8.36	9.42
CaO	33.29	28.3
SO_3	0.59	0.59
CL	0.008	0.025
K_2O	3.04	3.38

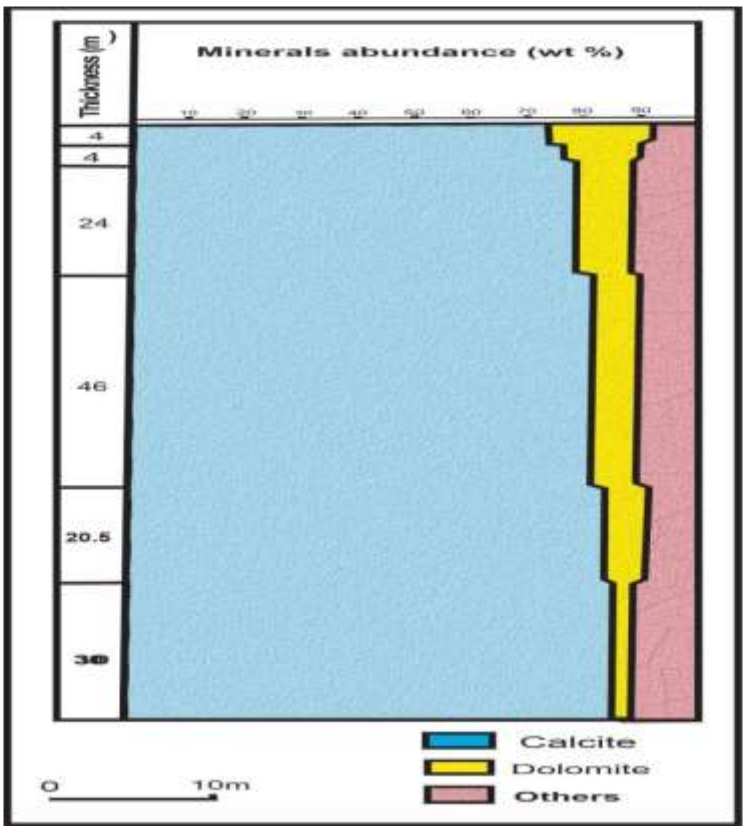

Figure 3: Vertical distribution of calculated minerals in measured section of Darnah Formation.

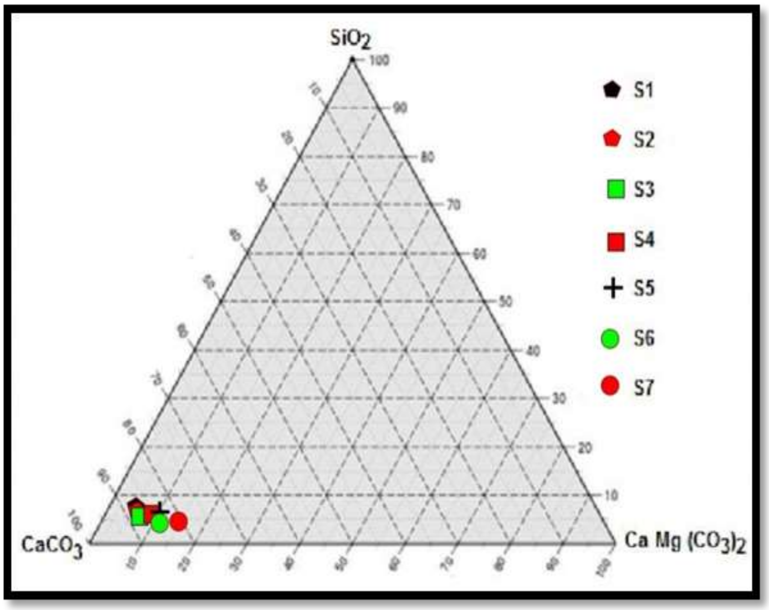

Figure 4: Triplot diagram showing the relationship between calcite, dolomite & silica.

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 (R^2 = 0.967). An inverse relationship was found, with a strong correlation coefficient between these parameters. However, Figure 6 emphasizes this correlation behavior.

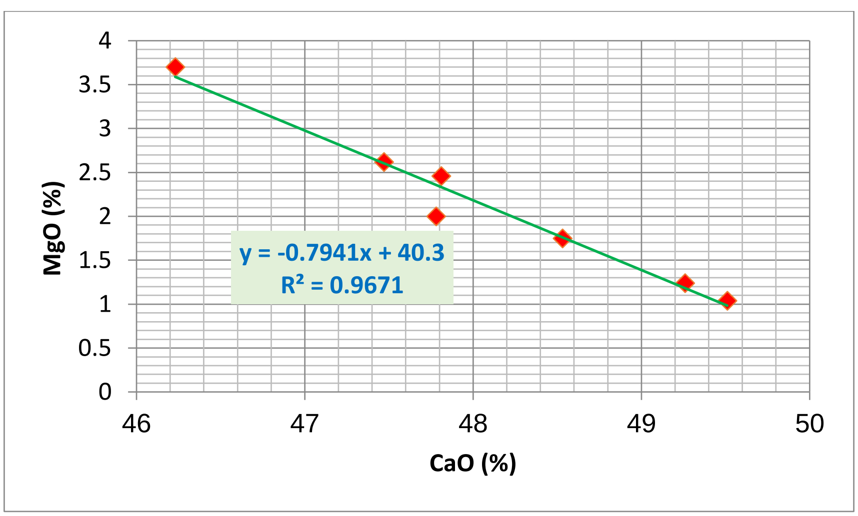

Figure 5: Correlation between CaO and MgO oxides of studied samples.

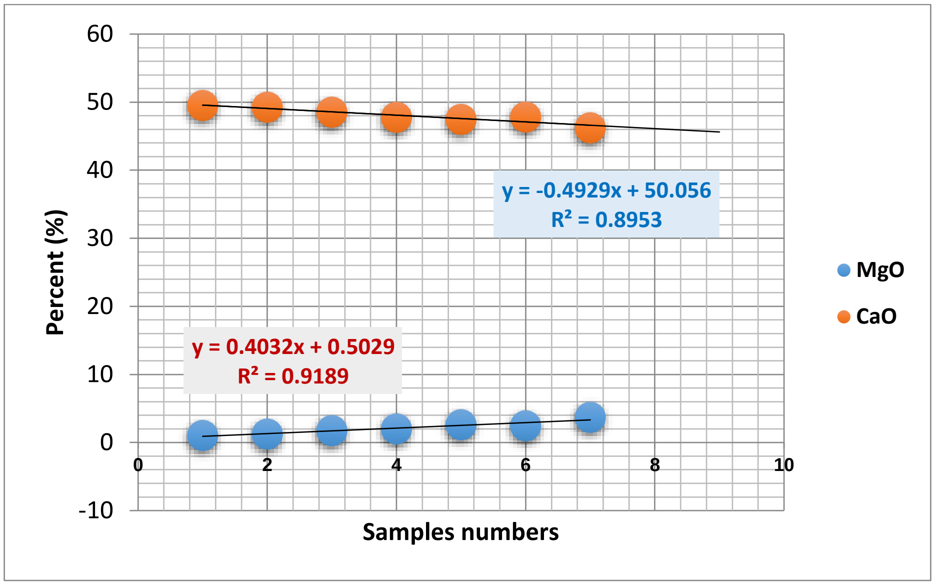

Figure 6: Correlation between calcium and magnesium oxides.

Alumina and Silica

On the other hand, the relationship between SiO_2 and Al_2O_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_2O_3 also increases. However, this relationship very significant (R^2 = 0.98).

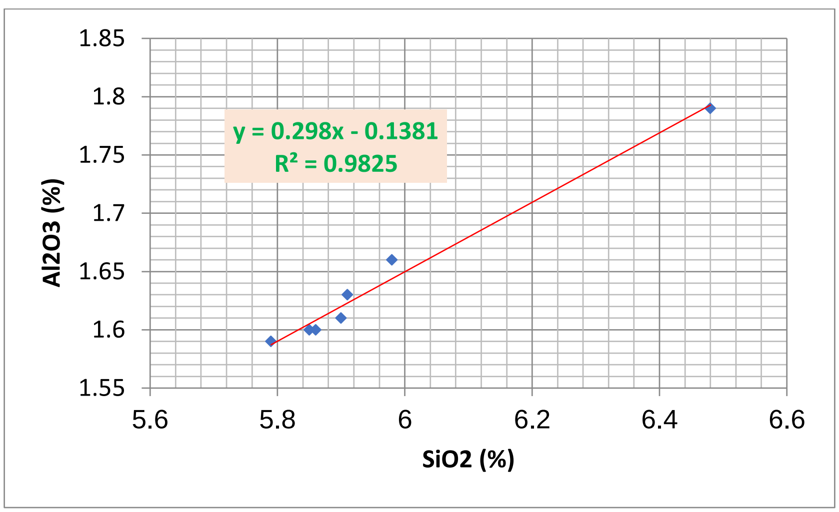

Figure 7: Correlation between SiO_2 and Al_2O_3 oxides.

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, tacking place between solid $CaCO_3$ and aqueous yielded the Mg^{2+}, as the following equation:

$2CaCO_3 + Mg^{2+} \rightarrow CaMg(CO_3)_2 + Ca^{2+}$

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_2O_3 which may form clays and free silica (quartz). The SiO_2, Al_2O_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_2O_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_2O_3, (8.89%, and 10.36% in average MgO and Fe_2O_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_2O_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].

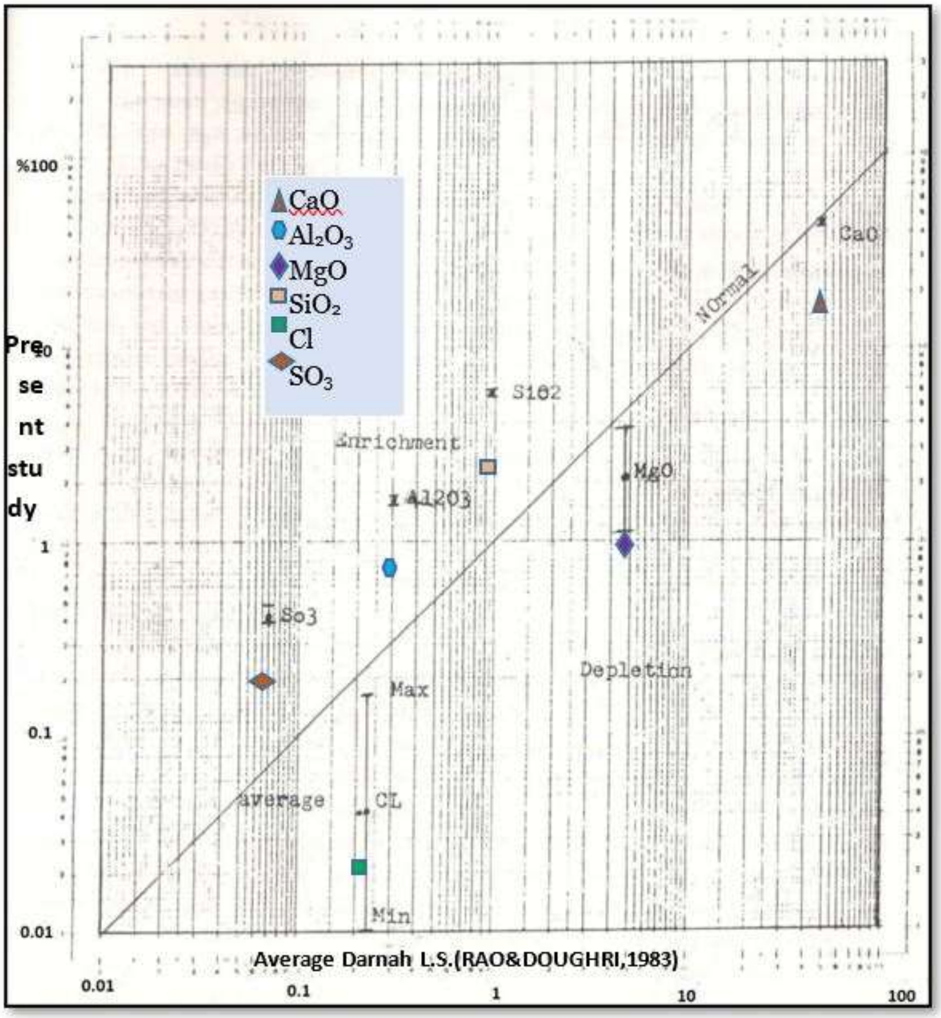

Figure 8: Comparison between the present data and published average of Darnah.

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.

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