

PETROGRAPHY AND GEOCHEMISTRY OF LIMESTONE UPPER CRETACEOUS KOMETAN FORMATION (AZMIR ANTICLINE): A PRELIMINARY ASSESSMENT FOR CEMENT PRODUCTION SUITABILITY IN THE KURDISTAN REGION NORTHEAST IRAQ

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ABSTRACT

A succession of slightly siliceous limestone of the Kometan Formation is studied geochemically and stratigraphically. The studied area is located on the SW limb of the Azmir anticline at the northeastern of Sulaimaniyah city. The studied section is situated at longitudes 45°38'310"E and latitudes 35°36'129"N inside the Folded Zone, Kurdistan Region, northeastern Iraq. The exposed section is sampled for lab studies, and inspected by eyes and hand lenses in the field. In this study, petrographic and geochemical analyses of 17 limestone samples were carried out. This study aims to investigate the major oxides of the limestone samples, using the X-Ray Fluorescence (XRF), for preliminary assessment for possible cement production. A petrographic study was also carried out, in order. Depending on the petrographic study, three major microfacies were recognized: lime mudstone microfacies, lime wackestone microfacies, and lime packstone microfacies, which subdivided into four submicrofacies are planktonic foraminifera lime mudstone submicrofacies, planktonic foraminifera lime wackestone submicrofacies, and planktonic foraminifera lime packstone submicrofacies and heterohelix lime packstone submicrofacies. The geochemical analysis shows that a range of variations in constituents: LOI (35.90% to 42.72%), SiO₂ (3.77% to 14.66%), CaO (42.59% to 49.95%), Al₂O₃ (0.44% to 2.22%), Fe₂O₃ (0.02% to 0.78%) and MgO (1.50% to 2.26%); K₂O and Na₂O are present in traces. The high CaO (49.95%) indicates that calcite is the primary carbonate mineral. Due to mineralogical considerations, CaO with LOI shows a positive correlation, whereas CaO with SiO₂ shows a negative correlation. The low MgO contents in calcitic limestone and calcitic limestone with chert nodules recommend a lack of dolomitization process. The silica modulus and lime saturation factor from geochemical data indicated that the siliceous limestone samples from the Kometan Formation and Azmir Anticline can be used in the cement-making process provided they are processed for silica removal treatment to reduce its percentage to less than 8%, as required level, where the CaO can be automatically enriched. Depending on field observation, petrography, and geochemistry analysis, we conclude that the source of the chert or silica minerals is diagenetic processes and depositional environment origin.

1. INTRODUCTION

Limestone is one of the most important sedimentary rocks, which consists mainly of calcite (CaCO_3). They may also contain other carbonate minerals and various noncarbonate impurities. Limestone is the raw material widely used throughout the industry, although limestone is the raw material for the cement industry where chemical properties are important.

Portland cement is produced by calcining finely ground raw materials which consists of a mixture of about 75% limestone and 25% clay. This mixture is burned at about 1450 C in a rotary kiln to form a calcium silicate clinker which is then ground and mixed with a small amount of gypsum which acts as a setting retardant. The chemical composition of the cement largely depends on the geochemistry of the raw materials (Lea, 1970). Limestone for cement production should contain more than (45% CaO); an amount of Fe_2O_3 as well as Al_2O_3 (1% to 2%); free silica (less than 8%); combined $\text{Na}_2\text{O} + \text{K}_2\text{O}$, and P_2O_5 must be less than 0.6% and 0.6% respectively. Magnesia contents of the limestone should ideally be less than 3%, although as high as 5% MgO can be used in the cement industry. Magnesia, sulfur, and phosphorus are regarded as the most undesirable impurities. The presence of phosphorus (P_2O_5) slows down the setting time of Portland cement. To attain these specifications, low-grade siliceous limestone needs to be characterized in terms of its mineralogy and geochemistry. Portland cement is made by the high-temperature reaction of a calcareous material (limestone) with a material containing silica, alumina, and ferrous materials. The product known as clinker consists of four main components: tricalcium silicate Ca_3S , also called alite, dicalcium silicate Ca_2S , also called belite, calcium aluminate Ca_3A , and tetracalcium aluminoferrite Ca_4AF which are then ground into cement with gypsum (Hawkins et al., 1996). Therefore, the constituents, such as calcium oxide CaO , alumina Al_2O_3 , iron oxide Fe_2O_3 , and silica SiO_2 of the limestone must be within permissible limits of the specifications for cement manufacture (Ingram & Daugherty, 1991). It is a fact that high SiO_2 content in the limestone hurts kiln properties and it is one of the most important units for the performance of the cement plant. It is monitored in the form of the silica ratio (SR), which is the ratio between silica and the weighted sum of Al_2O_3 and Fe_2O_3 . As the silica ratio increases, more heat is required to run the kiln. Lime Saturation Factor LSF plays an important role in the manufacture of cement because it contains CaO , the main component of cement. According to Ingram & Daugherty (1991), kiln operation and cement quality are improved when the CaO in the limestone is greater than 44%. Thus, a high LSF and low silica content contribute significantly to the profitability of a cement plant. Mineralogical and geochemical characterization of limestone is essential to continuously supply a cement plant with suitable limestone qualities. However, geochemical assessment of cement production suitability is identified as an important part of the cement manufacturing process that offers enormous potential for effective quarry management.

Before nearly 25 years of cement production from the Kometan Formation in the factory that is named Sarchinar cement factory. The Sarchinar cement factory has now stopped production as it is located within the settlement area and cement production in the Kometan Formation which does not have good cement quality as the proportion of silica in the limestone is too high. Therefore, this study aims to examine the major oxides in the limestone exposed in the outcrops, using X-Ray Fluorescence XRF, for a preliminary assessment of these carbonate rocks for possible cement production and treatment of silica. A petrographic study was also carried out, to characterize their mineralogical composition and the nature of the associated biogenic fraction.

2. GEOLOGICAL SETTING

The studied section is located on the SW limb of the Azmir anticline, at the northeastern of Sulaimaniyah city, at the longitudes $45^{\circ}28'310''$ E and latitudes $35^{\circ}36'129''$ N (Figure 1). According to the tectonic subdivision of Jassim & Goff (2006), the studied area is positioned along the boundary between the High Folded and Imbricated Zones almost parallel to the axis of the Azmir Anticline. The investigated area is part of the Balambo-Tanjero Tectonic Zone, which is considered one of the four zones within the unstable shelf in Iraq (Aziz et al., 2001). The area of investigation is located on the northeastern edge of the Arabian platform, within intensive folding and faulting (Amin, 2009). The structural style of this zone is the result of two tectonic periods: Late Cretaceous obduction and Late Tertiary uplift (Jassim & Goff, 2006). During the Late Miocene-Pliocene epoch, this zone was stressed from the northeast and thrust by sheets of the Zagros Suture Zone. The intensity of deformation and imbrications distinguishes it from the Zagros Folded Zone (Al-Qayim et al., 2012).

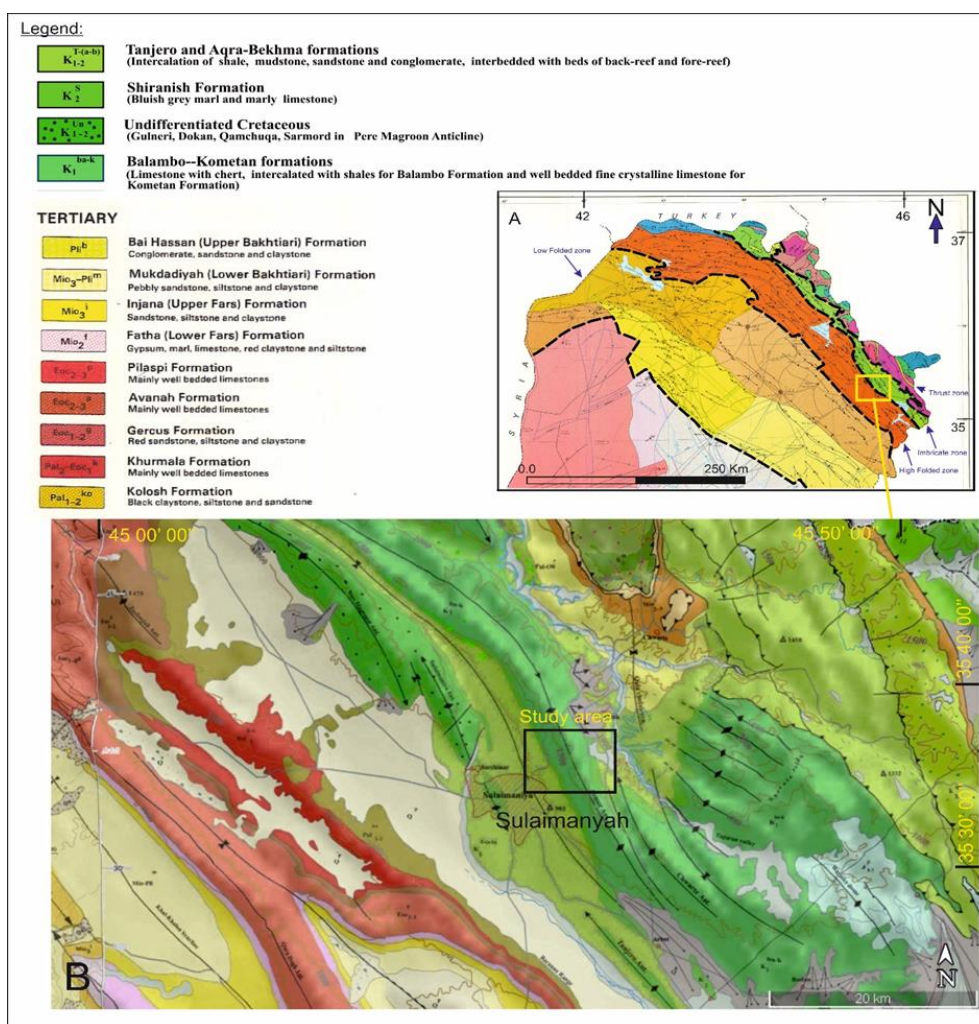


Figure 1: Location map of the studied area, A (The tectonic subdivision map, after (Fouad,2012), B (Geological map modified from Sissakian, 2000).

The Azmir anticline is one of the major anticlines of the High Folded Zone, with a length of around 91 Km and with plunges in its northwest and southeast ends near the Dokan Town and Chanakhchian Villages, respectively. The anticline is 1– 4.5 Km wide and includes many local names can be found along its length, ranging from Sara, Daban, and other cities in the

northwest to the southeast range including anticlines (or mountain) of Qayiwān, Azmir, Sarjor, and Kharajyan.

The core of this anticline is occupied by the Sarmord Formation, whereas the Balambo and Kometan formations form the rocks of both limbs. According to Ahmed et al. (2015), the core of this fold is composed of Berriasian-Valanginian rocks of the Balambo Formation that crop out along the Sulaimaniyah-Azmar main road. The sedimentary sequence consists of fine-grained limestone, marls, or friable papery shales of Berriasian to Barremian age, this formation is equivalent to the lower part of Balambo Formation. Furthermore, a portion of this series is part of the Sarmord Formation.

3. MATERIALS AND METHODS

At the examined site, the two main methods were carried out: first, the fieldwork involved the description of all field phenomena in the outcrops, such as layer thickness, toughness, color, and other physical properties, and the nature of the contact surfaces between them, as well as the lateral and vertical changes of the layers to record all sedimentary structures in the studied section. A total of seventeen of 17 rock samples are collected from the exposed Kometan Formation. Ten thin sections are prepared from the samples in the lab of Sulaimani University, Department of Geology. The transmit polarized microscope model (Magai) is used for detailed petrographic analysis. The geochemical analysis is performed using an X-ray Fluorescence, and XRF spectrophotometer for chemical analysis of the samples at the Tasluja Cement Plant in Sulaimani Governorate.

4. RESULT AND DISCUSSIONS

4.1 Lithostratigraphy

The Komen Formation consists of a white to yellowish color of well-bedded fine-grained limestone with the spread of chert nodules in different parts of the formation, which are randomly distributed, but often appear in a horizontal pattern near the middle part of the formation (Figure 2). Based on the previous studies, there are several ideas that chert nodules observed in the Kometan Formation are of various sources (some diagenetic and others depositional). McBride & Folk (1979) studied the origin of the chert bed resulting from the diagenetic organization of silica or the complete replacement of limestone beds by silica. Price (1977) concluded that the other sources of chert units are depositional below CCD, the lack of internal sedimentary structure, and steady and slow sedimentation leads to massive chert beds and uniform rain of radiolarians. In the upper part of this sequence, stylolite features appear which are parallel to the bedding plane of limestone. The thickness of the Kometan Formation is about 75 m. It overlies the Gulneri Formation (Al-Khafaf, 2014). The same contact is recorded from the Dukan area (Bellen et al., 1959); (Ameen & Gharib, 2014); (Malak et al., 2021). The upper boundary of this formation is unconformable with Shiranish Formation. The unconformity surface is manifested by the bioturbation surface (Glossifungites ichnofacies) and the existence of Thalassinoides burrows on a hard ground surface at the top of the Kometan Formation (Buday, 1980); (Malak, 2015).

4.2. Petrography Analysis

Three different microfacies types have been determined in the Kometan Formation. Each microfacies was subdivided into several submicrofacies.

4.2.1. Lime mudstone microfacies

This microfacies is less common and reported only in the upper part of the Kometan Formation. Based on (Danham & Ham, 1962), this microfacies is composed of micrite with

few planktonic foraminiferas less than %10 with more than 90% micritic matrix. Planktonic forms such as (*Gansserina gansseri*, *Globotruncanita conica*, *Globotruncana arca*, *Globotruncana sp.* *Archaeoglobigerina sp.* *Muricohedbergella holmdelensis*, *Planoheterohelix planata*, *Planoheterohelix globulosa*, and *Planoheterohelix reussi*, Figures 3a, b and c) within planktonic foraminifera lime mudstone submicrofacies. Irregular reddish-brown iron oxides are distributed within the groundmass of this submicrofacies and also contain several fractured filled with calcite cement. Silicification, cementation, and oxidation are common diagenesis processes observed within this submicrofacies. These sub-microfacies type correlated with SMF3 of FZ1, which represents an open marine, basinal environment (Wilson, 1975); (Fügel, 2010).

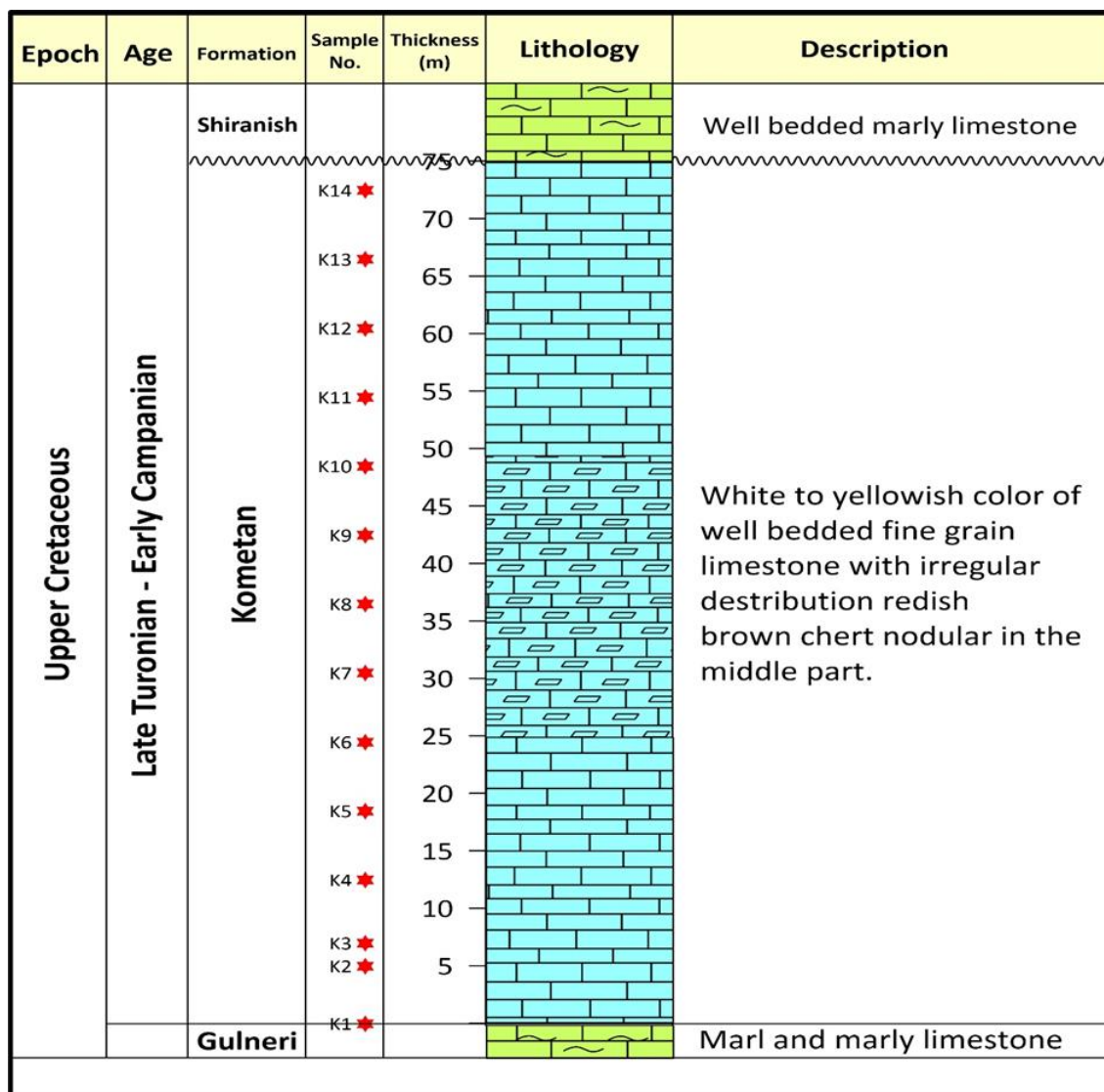


Figure 2: Lithostratigraphy column of Kometan Formation at studied area.

4.2.2. Lime wackestone microfacies

This microfacies is also less commonly recognized in the upper part of the Kometan Formation. It is composed mainly of micrite and skeletal grains with a percentage of more than > 10 (Danham & Ham, 1962). Skeletal grains similar to most other facies like planktonic foraminifera (*Globotruncana arca*, *Globigerinelloides ultramicrus*, *Globotruncana sp.*,

Marginotruncan coronata, Planoheterohelix planata, Planoheterohelix globulosa and Planoheterohelix reussi (Figures 3d, e, f and g) within planktonic foraminifera wackestone sub-microfacies. Silicification, cementation, and oxidation are well-defined within these sub-microfacies. This submicrofacies type correlated with SMF3 of FZ1, which described deep-sea environment (Wilson, 1975); (Fügel, 2010).

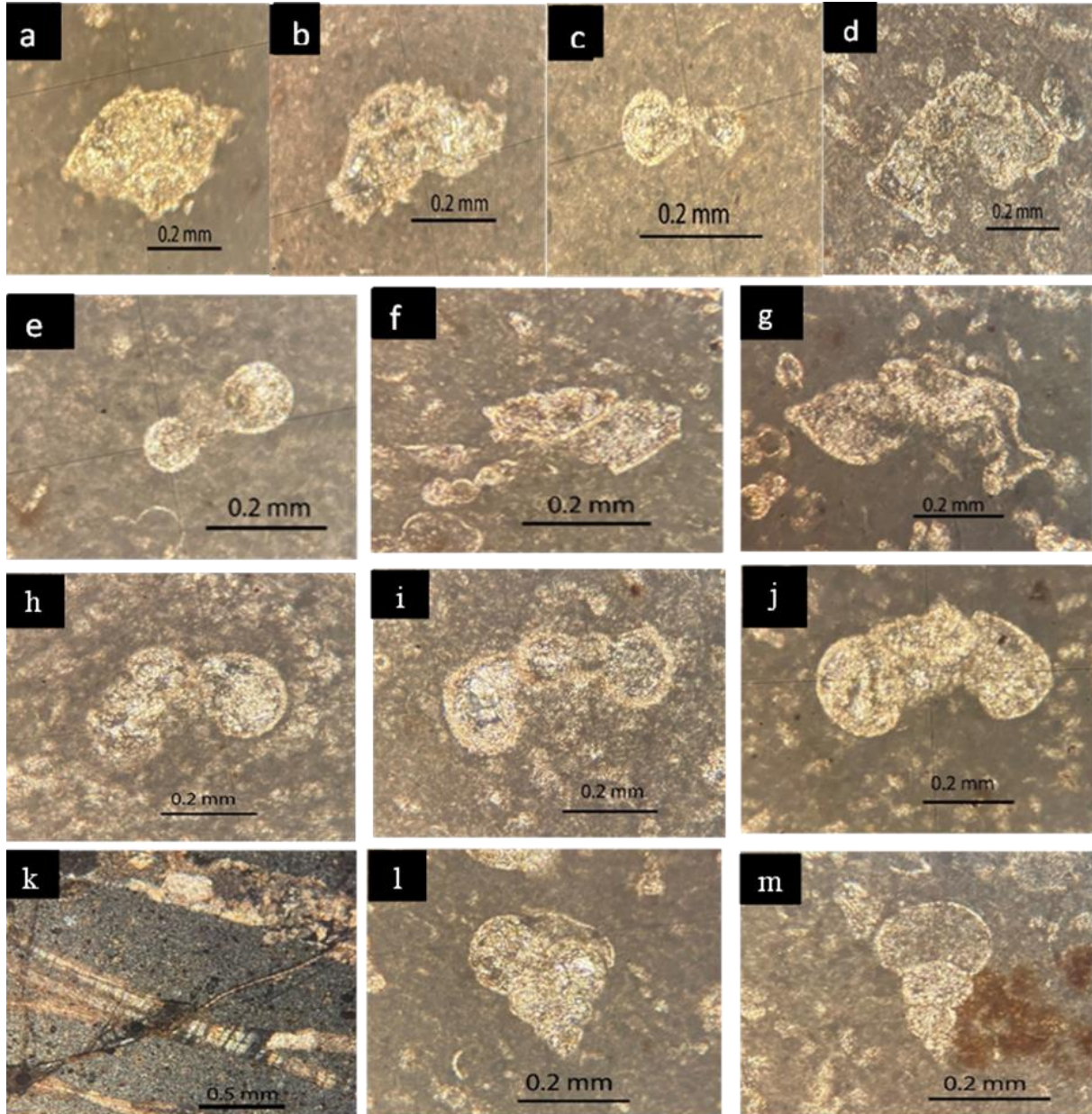


Figure 3: **a)** *Globotruncana* sp. s.no.13, **b)** *Globotruncanita arca* (Cushman) s.no.14, **c)** *Archaeoglobigerina* sp. s.no.14, **d)** *Globotruncana arca* (Cushman) s.no. 11, **e)** *Globigerinelloides ultramicrus* (Subbotina) s.no.12, **f)** *Globotruncana* sp s.no.11, **g)** *Marginotruncana coronata* (Bolli) s.no.12, **h)** *Whiteinella brittonensis* (Loeblich & Tappan) s.no.1, **i)** *Helvetoglobotruncana helvetica* (Bolli) s.no.2, **j)** *Whiteinella aprica* (Loeblich & Tappan) m- s.no.4 *Marginotruncana* sp. s.no.5, **k)** Silicification and cementation s.no.6, **l)** *Planoheterohelix planata* (Ehrenberg) s.no.7, and **m)** *Planoheterohelix globulosa* (Ehrenberg) s.no.9.

4.2.3. Lime packstone microfacies

This microfacies are the most commonly recorded in the lower and middle parts of the Kometan Formation. Microscopically study of this microfacies enables to recognize the planktonic foraminifera lime packstone submicrofacies (Figures 3h, i, and j) and heterohelix lime packstone submicrofacies (Figures 3l, and m). These submicrofacies are composed of micritic ground mass and skeletal grain with a percentage of more than > 50 (Danham & Ham, 1962). The present planktonic foraminifera is *Whiteinella brittonensis*, *Helvetoglobotruncana helvetica*, *Whiteinella aprica*, *Whiteinella brittonensis*, *Marginotruncana* sp., *Planoheterohelix planata*, *Planoheterohelix globulosa*, *Planoheterohelix reussi*, *Dicarinella primitive*, *Hedbergella delrioensis*, and *Globotruncana* sp., with rare calcispher. Various types of diagenesis processes highly affect skeletal grains and groundmass such as silicification, cementation, and oxidation at different rates. Several fractures contained within these sub-microfacies are filled with fibrous calcite, and some other fractures are filled with coarse crystal calcite cement and quartz crystal. The present silica cement within the groundmass can occur as microcrystal quartz indicated late diagenesis but coarse crystalline quartz in fracture indicated very late diagenesis (Figure 3k). These submicrofacies types are formed in open marine, bathyal basins similar to SMF3 of FZ1 (Wilson, 1975); (Fügel, 2010).

The overall petrographic study shows that they contain a high percentage of silica minerals in the Kometan Formation, which is more likely to be derived from either the radiolarian or from clay minerals diagenesis (Price, 1977; McBride & Folk, 1979). It can be interpreted that the Kometan Formation deposit in open marine, basinal environments caused increasing silica minerals. (Balaky, 2006) mentioned that the deposition environment leads to an increased amount of silica minerals because silica precipitates below CCD.

4.3. Geochemistry

The chemistry of the cement in general and Portland cement in particular largely depends upon the geochemistry of its raw materials, i.e., limestone. Approximately 75% of the Portland cement raw material consists of lime (CaO) bearing material (Lea, 1976). The major and minor elemental chemistry of the randomly hand-picked limestone samples from the Kometan Formation is presented in (Tables 1 and 3). Chemical analyses revealed that the limestone samples contain lime (CaO) as the major constituent, followed by Loss on Ignition (LOI) and silica SiO₂ (Table 1). Alumina Al₂O₃ and iron oxide Fe₂O₃ form the minor constituents while magnesia, alkalis (soda and potash), TiO₂, and MnO₂ are present in traces. SiO₂, Al₂O₃, and Fe₂O₃ along with CaO of the limestone form the main ingredients that make up the cement, but should be within permissible limits.

4.3.1. Calcitic Limestone

From the Calcitic limestone collected 14 samples; the spacing between each sample is approximately 5 meters collected for detailed study. From (Table 1) the SiO₂ content in this limestone varies widely, ranging from (3.77% to 14.66%), contributed by quartz. This siliceous limestone sample cannot be directly used for the cement industry as the sample contains silica over 8%. The lime (CaO) content varies between (42.59% and 49.95%) and is due to the presence of calcite in the limestone. The CaCO₃ content is between 76.01% and 89.15% (Table 4). Depending on the percentage of SiO₂, CaO, and CaCO₃ in the limestone, this means impure to low-purity limestone according to the classification of limestone (Table 2) (Harrison, 1993).

Table 1: Geochemical characteristics of limestone samples from Kometan Formation.

Sample Number	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	LOI	Total	Type of Limestone
1	3.77	0.44	0.02	49.95	2.00	0.19	0.04	0.04	42.72	99.17	Massive
2	7.57	0.72	0.10	47.85	2.00	0.21	0.10	0.04	40.48	99.07	Massive
3	9.35	0.77	0.09	47.09	1.85	0.11	0.10	0.04	39.69	99.09	Siliceous
4	8.98	0.91	0.38	46.57	1.81	1.14	0.13	0.04	39.16	99.12	Siliceous
5	6.45	0.86	0.07	48.25	1.90	0.09	0.14	0.04	41.63	99.43	Massive
6	6.45	0.86	0.07	48.25	1.90	0.09	0.14	0.04	41.63	99.43	Massive
7	10.64	1.14	0.13	46.24	1.68	0.14	0.19	0.04	39.27	99.47	Siliceous
8	14.66	0.76	0.13	44.55	1.56	0.10	0.10	0.04	37.93	99.83	Siliceous
9	15.48	1.01	0.33	43.50	1.81	0.12	0.14	0.03	37.32	99.74	Siliceous
10	11.51	2.22	0.78	44.20	1.63	0.19	0.24	0.07	35.90	96.74	Siliceous
11	14.30	1.37	0.45	42.59	1.50	0.13	0.20	0.03	38.27	98.84	Siliceous
12	13.36	1.06	0.53	44.59	1.67	0.34	0.10	0.04	38.29	99.98	Siliceous
13	12.03	1.06	0.34	44.66	2.26	0.12	0.09	0.04	38.63	99.23	Siliceous
14	12.84	1.28	0.45	43.70	1.61	0.69	0.16	0.04	38.13	98.90	Siliceous

Table 2: Classification of Limestone Ore by Purity.

Oxides					
Purity classification	CaCO ₃ % wt.	CaO % wt.	MgO % wt.	SiO ₂ % wt.	Fe ₂ O ₃ % wt.
Very high purity	> 98.5	> 55.2	< 0.8	< 0.2	< 0.05
High purity	97 – 98.5	54.3 – 55.2	0.8 – 1.0	0.2 – 0.6	0.05 – 0.1
Medium purity	93 – 97	52.4 – 54.3	1.0 – 3.0	0.6 – 1.0	0.1 – 1.0
Low purity	85 – 93	47.6 – 52.4	> 3.0	< 2.0	> 1.0
Impure	< 85.0	< 46.6		> 2.0	

Table 3: Geochemical analysis of chert beds from the Kometan Formation.

Sample Number	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	LOI	Total	LSF %
1	59.31	0.71	0.67	22.23	0.82	0.44	0.05	0.00	15.57	99.80	13.28
2	48.01	0.67	0.87	28.78	1.07	0.28	0.04	0.01	20.20	99.93	21.19
3	57.43	0.52	1.22	23.38	0.83	0.39	0.02	0.01	15.65	99.45	14.41

Table 4: Lime saturation factor, alumina ratio, and silica ratio data.

Sample Number	LSF	SR	AR	Types of Limestone	CaCO ₃ %
1	456.25	8.20	22.00	Massive	89.15
2	219.44	9.23	7.20	Massive	85.40
3	175.55	10.87	8.56	Siliceous	84.04
4	178.08	6.96	2.39	Siliceous	83.11
5	255.49	6.94	12.29	Massive	86.11
6	255.49	6.94	12.29	Massive	86.11
7	149.59	8.38	8.77	Siliceous	82.53
8	106.92	16.47	5.85	Siliceous	79.51
9	98.54	11.55	3.06	Siliceous	77.64
10	126.42	3.84	2.85	Siliceous	78.88
11	102.46	7.86	3.04	Siliceous	76.01
12	115.56	8.40	2.00	Siliceous	79.58
13	129.64	8.59	3.12	Siliceous	79.71
14	116.96	7.42	2.84	limestone	77.99

LOI of this limestone sample varies from (35.90% to 42.72%). Which is mostly contributed by the carbonate minerals. The CaO content in this limestone shows a strong positive correlation with that of the LOI (Figure 4). This may be due to the reason that LOI is contributed mainly by the carbonate content of calcite. CaO shows a very strong negative correlation with that of the silica (Figure 5). This is attributed to CaO and SiO₂ being two different mineral phases and they are not related to CaO (from calcite) and SiO₂ (from quartz). Alumina (Al₂O₃) in these samples ranges from (0.44% to 2.22%) and shows a negative correlation with CaO and a positive correlation with iron, magnesium, soda, potash, and manganese oxide which could be due to clay material present in the limestone samples. Among other constituents that are commonly important is MgO (1.50% to 2.26%) which might have been derived either from the magnesium-containing skeletal debris or due to post-depositional additions or during diagenesis. The chemical composition of the limestone reflects its mineralogical composition.

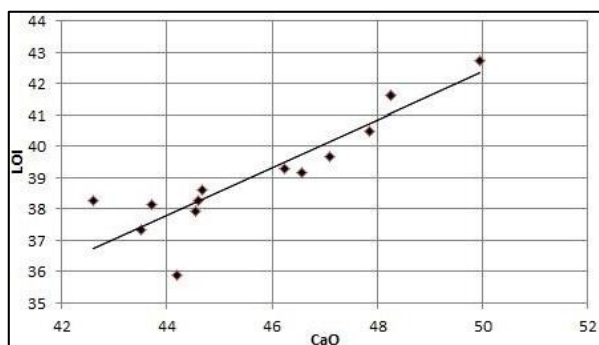


Figure 4: Representation CaO vs. LOI with positive correlations.

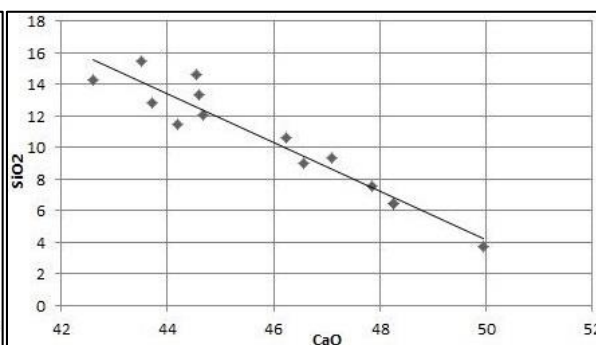


Figure 5: Representation of CaO vs. SiO₂ with Negative correlation.

4.3.2. Calcitic Limestone with Chert Nodule

Chert is a hard, dense, or compact sedimentary rock composed of micro- or cryptocrystalline quartz crystals containing amorphous silica (opal) and impurities such as calcite or iron oxide (Bates & Jackson, 1980). In the present study, a late diagenetic displacement process was likely involved in the formation of chert nodules, with groundwater transferring the dissolved silica, demonstrating the porosity of mostly slightly calcareous dolomite rocks, which 3 samples of chert nodules from the traverses of the Kometan Formation show that the percentage of silica is more than 48% (Table 3). In such a case, the existing low-grade siliceous limestone samples, considered as chert nodules in different parts of the formation, randomly distributed, but often appearing in a horizontal pattern near the central part of the formation, can be effectively used not only for conserving the mineral resources. Limestone can be graded in many ways. One alternative is to crush limestone to a size of -3 mm and process it in a washer and classifier, while the other involves grinding the raw feed to less than 200 mesh and subjecting it to froth flotation treatment (Ananth et al., 1997); (Rao et al., 1997); (Rao et al., 2009); and (Rao et al., 2010).

4.4. Industrial Quality and Cement Production

Limestone is an invaluable raw material in the chemical industry. Cement has long been manufactured based on practical experience acquired during the manufacturing process (Rao et al., 2009). When comparing chemical analyses of Portland cement (Feed raw materials and/or clinker), (Bensted et al., 1995), and (Moore, 1982) recognize the existence of a link between the lime content and the combination of silica, alumina, and iron oxide. These

modulus, considering the three major chemical ratios are: Limestone Saturation Factor $\{(\text{LSF} = \text{CaO} / (2.8 \text{ SiO}_2 + 1.2 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3))\}$, Silica Ratio $\{\text{SR} = \text{SiO}_2 / (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)\}$, Alumina Ratio $\{\text{AR} = (\text{Al}_2\text{O}_3) / (\text{Fe}_2\text{O}_3)\}$. LSF is the most important factor because it controls how much CaO may be added to the mixture. Clinker which gives cement its strength is created by mixing limestone and shale in a ratio of 4:1 and then firing the mixture in a rotary kiln (Scott, 1983); and (Agbazue, 1992).

4.4.1. Lime Saturation Factor (LSF)

The LSF is a ratio of CaO to the other three main oxides. Applied to clinker, according to (D. S. Rao et al., 2011). It is calculated as:

$$\text{LSF (MgO} \leq 2\%) = 100 (\text{CaO} + 0.75 \text{ MgO}) / 2.8 \text{ SiO}_2 + 1.2 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3$$

$$\text{LSF (MgO} \geq 2\%) = 100 (\text{CaO} + 1.5 \text{ MgO}) / 2.8 \text{ SiO}_2 + 1.2 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3$$

The lime saturation factor is used for kiln feed control. A higher LSF makes it difficult to burn raw mix. The reactivity of the raw mixture for cement making is influenced greatly by pyrolysis. The pyrolysis characteristics of limestone are greatly influenced by the particle size of calcite crystal, the crystal shape that is characteristic of limestone itself, and outside impurities such as SiO_2 , Al_2O_3 , and Fe_2O_3 as well as the existence of the state of accompanying minerals (Park et al., 2004). The LSF controls the ratio of alite (Tricalcium silicate) to belite (Dicalcium silicate) in the clinker. A clinker with a higher LSF will have a higher proportion of alite to belite than a clinker with a low LSF (Johansen et al., 2002). Typical LSF values in modern clinkers are 90 – 98%. But if it is 80% it does not create any problems in the cement manufacturing process and cement strength, but should not go below this range (Ali, 2010). Values above 100 indicate that free lime is likely to be present in the clinker (Ingram & Daugherty, 1991). This is because, in principle, at $\text{LSF} = 100$ all the free lime should have combined with belite to form alite. If the LSF is higher than 100, the surplus free lime has nothing with which to combine and will remain as free lime. In practice, the mixing of raw materials is never perfect and there are always regions within the clinker where the LSF is locally a little above, or a little below, the target for the clinker as a whole (Rao et al., 2010). This means that there is almost always some residual free lime, even where the LSF is considerably below 100. It also means that to convert virtually all the belite to alite, an LSF slightly above 100 is needed. For the present samples, only the siliceous limestone LSF value falls in the normal range of chemical ratio, used in the industry for the production of Portland cement. Although it ranges from (98.54 to 178.08) (Table 4), LSF ranges from 219.44 to 456.25 in Calcitic limestone samples (Massive limestone) which indicates that the CaO value is highly erratic and needs to be in a uniform range for cement making.

4.4.2. Silica Ratio (SR)

The silica ratio is sometimes called the silica modulus, which has a particularly large influence on the firing process and some cement properties. The silica ratio is defined as: $\text{SR} = \text{SiO}_2 / (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ and its large variation in the clinker can be an indication of poor uniformity in the kiln feed. Changes in coating formation in the burning zone, burnability of the clinker, and ring formations within the kiln can often be traced to changes in silica modulus in the clinker. As a rule, clinker with high silica modulus at an AR of about 1.4, of more clinker liquid at a lower temperature (Minor constituents such as MgO can alter this optimum AR). The AR for the present samples ranges from 2.00 to 22.00 (Table 4) more difficult to burn and exhibits poor coating properties. When SR is increased, the amount of liquid phase is decreased and vice versa. So SR has a great influence on the formation of the liquid phase (Mirza & Fatah, 2018). The SR also affects the grindability of the clinker, when there is a more liquid phase which means that SR is low and this causes the lower grindability

of the clinker (Tokyay, 1999). Liquid phase = $71 / 0.53 + SR$ (Fundal, 1980 in (Fatah & Mirza, 2021)). When SR is too low, there may be much melt phase and the sulfur coating can become thick (Rao et al., 2010). Low silica modulus often leads to ring formations in cement. A high silica ratio means that more calcium silicates are present in the clinker and less aluminate and ferrite which leads to the harder it is to burn (Johansen et al., 2002). SR is typically between 2.0 and 3.0 for Portland cement clinker (Moore, 1982) and according to (Aldieb & Ibrahim, 2010), SR ranges between (1.9 – 3.2). The SR governs the proportion of silicate phases in the clinker. The SR for the present samples ranges from 6.94 to 9.23 in massive limestone samples and ranges from 3.840 to 16.47 in siliceous limestone samples (Table 4), which indicates that the samples are higher in SiO_2 content and needs to be brought down to below the specified limits for cement making. The silica modulus and lime saturation factor from geochemical data indicated that the siliceous limestone samples from the Kometan Formation of the Azmir Anticline, can be used in the cement making process provided they are processed for silica removal treatment (to less than 8%) as required level where the CaO can be automatically enriched.

4.4.3. Alumina Ratio (AR)

The alumina ratio is defined as $AR = (Al_2O_3) / (Fe_2O_3)$. It determines the possible relative proportions of aluminate and ferrite phases in the clinker. In addition, an increase in clinker AR means that the clinker contains proportionately more aluminate and less ferrite (Fatah et al., 2020). Clinker with higher AR results in cement with high early strength (Mirza et al., 2016). For ordinary Portland cement clinker, the AR is typically between 1 and 4 (Rao et al., 2011). An AR roughly equal to 1.4 is easier to burn when the AR is higher or lower. This is because an AR of around 1.4 has more clinker liquid at a lower temperature (minor components such as MgO can alter this optimal AR). The melting temperature depends on the alumina modulus whereas the lowest temperature is reached when the AR is around 1.6, which is the optimum in terms of clinker mineral formation and nodule formation (Johansen et al., 2002). The AR also influences the color of clinker and cement. The AR for the present samples ranges from 2.00 to 12.29, except that sample number one is 22.00 (Table 4), reflecting the high purity of the limestone samples. The higher the AR, the lighter the cement (Frigione et al., 1983).

5. CONCLUSIONS

However, from the petrographic as well as geochemical data, the following conclusion is drawn.

- Depending on petrographic study, three major microfacies were recognized: lime mudstone microfacies, lime wackestone microfacies and lime packstone microfacies, which subdivided into four submicrofacies, are: planktonic foraminifera lime mudstone submicrofacies, planktonic foraminifera lime wackestone submicrofacies, and planktonic foraminifera lime packstone submicrofacies and heterohelix lime packstone submicrofacies.
- Different diagenesis processes influenced the carbonates of the Kometan Formation, which are silicification, cementation, and oxidation.
- Depending on the submicrofacies types of the Kometan Formation indicate the deposition in the open deep marine environment.
- From the geochemical study, we concluded that calcium oxide (CaO) is the dominant constituent of the limestone from the Kometan Formation, which is because the limestone

is primarily calcite and this supports the suitability of limestone of this deposit for cement production.

- The relatively high level of CaO and low values of other oxides (SiO₂, MgO, Fe₂O₃, and Al₂O₃), according to the classification of limestone ore by purity indicated an impure to low purity of the limestone hence its suitability as raw materials for manufacturing Portland cement, and it is classified as impure to low purity depending on the percentage of CaO, CaCO₃, and SiO₂.
- They have a simple mineralogy, and yet they have variable silica and lime contents. CaO with LOI shows strong a positive correlation whereas CaO with SiO₂ shows a strong negative correlation because of mineralogical factors.
- Geochemical studies of the Kometan limestone have been carried out and the results of major oxide concentrations, supported by petrographic analysis, have given some insights into the deposit and discriminate between shelf and deep sea carbonate. The silica modulus and lime saturation factor from geochemical data indicated that the siliceous limestone samples from the Kometan Formation in the Azmir Anticline can be used for cement production provided they are processed for silica removal treatment (to less than 8%) at a required level where the CaO can be automatically enriched.
- By field observation, petrography studies, and geochemistry analysis, it is concluded that the source of silica minerals (chert) came from the diagenesis process and depositional environment.

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