

# The Characterization of Libyan Raw Dolomite Samples Using Chemical Techniques

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## To cite this article:

Alzadma Himed, Mousa May, Balhassn Ali. The Characterization of Libyan Raw Dolomite Samples Using Chemical Techniques. *American Journal of Mechanical and Materials Engineering*. Vol. 4, No. 2, 2020, pp. 18-25. doi: 10.11648/j.ajmme.20200402.11

**Received:** February 15, 2020; **Accepted:** March 9, 2020; **Published:** May 12, 2020

**Abstract:** Dolomite known as dolostone is a double carbonate of calcium and magnesium,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ . After calcite, it is the second most important and abundant of the carbonate minerals. This work aims at processing, investigation and characterization of four different Libyan raw dolomite samples via simple chemical method. Based on a previous geological survey carried out by the industrial research centre (Tripoli), four dolomite samples selected from different locations of Libya namely; El-azizia, Souk El-khamees (sample P1), Nalout, Abu Rashada route, Gherian (sample P2), Sedi El-said, Abu Reshada route, El-gabl El-gharby (sample P3) and Abu Ghilan, north Kaf- Takoot (sample P4), were processed (crushed, ground and sieved), then investigated through their chemical composition using x-ray fluorescence (XRF) technique. Their mineralogical compositions were investigated using x-ray diffraction technique (XRD) and scanning electron microscope (SEM). All the measurement techniques in this work indicated that qualitatively the four investigated samples have a dolomitic nature. It was conformed that the percent of CaO in sample P1 (31.19%) is relatively higher than the standard dolomite (30.8%) which confirms the prediction of the presence of some content of calcite  $\text{CaCO}_3$  accompanied with dolomite sample P1. In spite of the limited variance in the chemical constitutions determined by x-ray fluorescence compared with classical wet method, the results confirm that the four investigated samples are mainly dolomite and that samples P1 and P2 are relatively purer than samples P3 and P4 which contain larger contents of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ .

**Keywords:** Dolomite, X-ray Diffraction XRD, X-ray Fluorescence XRF,  $\text{CaCO}_3$

## 1. Introduction

The mineral dolomite is a combination of the elements calcium, magnesium, carbon and oxygen. Chemically, it is calcium, magnesium carbonate. A large number of other elements may substitute for the calcium, magnesium, varieties containing iron, manganese, cobalt, lead and zinc. When a large amount of iron is present, the mineral ankerite forms and when excess manganese is present the mineral kutnahorite forms instead of dolomite. All these minerals have the same internal structure, but differ chemically from each other [1]. It's well known that dolomite is rarely found in some sedimentary environments, but dolostones are very common in the rock record. Also, most rocks that are rich in

dolomite were originally deposited as calcium carbonate mud's that were postdepositionally altered by magnesium-rich pore water to form dolomite [2]. In addition, in literature the mode of formation, dolomites can be divided into two groups: primary dolomite and secondary dolomite [3]. Dolomites can be harder than calcite,  $\text{CaCO}_3$ , this means it is harder than a piece of copper and softer than mild steel. The hardness of a mineral is also another characteristic used to identify it from other minerals [4]. Dolomite can be found in several different colors ranges from colorless to white with green, brown, or pink tints, it is often has a light pinkish color, but colorless and white are very common. However, it is dolomite's pink color that sets another unique characteristic for dolomite. Crystals of dolomite are well known for their typical beautiful pink color, pearly luster and unusual crystal

habit and it is these clusters that make very attractive specimens [5]. In additions, Dolomite is slightly soluble in water (0.032 gram per liter of water at 17°C). Like calcite (in limestones), dolomite is also dissolve more readily in groundwater that is saturated with carbon dioxide gas, and like calcite, will form caves and sinkholes. Dolomite will also undergo de-dolomitization, or removal of magnesium, when subjected to weathering, or the action of fluids, and will convert to calcite. Dolomite dissolved by groundwater will also give rise to stalactites, stalagmites and travertine when dissolved carbon dioxide gas evaporates, but the formations that precipitate out are almost always the calcium carbonate minerals calcite [6] or aragonite, rather than dolomite. Deposits dolomite are widespread over large areas throughout Libya. The most important areas are Tripoli and Bany-Waleed. Mainly in the north zones, particularly in El-azizia, Souk El-khamees, Gharyan, Nalot, El-gabl El-gharby and surroundings, there are large reserves of the dolomite deposits. The application of dolomite is quarried for building and ornamental stone, road stone, and the production of refractory brick. It is the principal ore of magnesium metal and the source of the magnesium used by the chemical industry [7]. Dolomite is used to make magnesia, which has important medical applications. Dolomite specimens from Iran are very popular among mineral collectors and dealers. Dolomite rock is used as an ornamental and structural stone, and for extracting certain metals from their ores [8]. It is useful in the chemical industry in the preparation of magnesium salts. Dolomite occurs in a different crystal class than the calcite group. This can be noted by the fact that dolomite generally forms more elongated crystals than the calcite group. In addition, dolomite never occurs in scale no hadrons, whereas minerals of the calcite group do. This current work aims processing, investigation and characterization of different Libyan raw dolomite samples.

## 2. Experimental Procedures

### 2.1. Materials Used

Four raw dolomite samples were selected from different locations in Libya based on a previous geological survey, carried out by Industrial researches centre (Tripoli) [8]. The first sample was taken from El-azizia, Souk El-khamees, the second from Nalout, Abu Rashada route, Gherian, the third from Sedi El-said, Abu Reshada route, El-gabl El-gharby and the fourth from Abu Ghilan, north Kaf-Katkoot. About 5 Kg of each dolomite sample was taken two meters deeply far from the surface, then processed and investigated through their mineralogical compositions. The selected dolomite batches were crushed individually, then grinded until completely passed through (125 micron) standard sieve. To obtain well representative samples, the individual batches were well hand mixed then quartered into four equal portions, two of them, from the opposite sides, were removed while the two other portions were taken, well hand mixed and quartering is repeated several times until the finally

obtained 200g from each dolomite batch. Figure 1 shows the quartering technique of the dolomite batches [9].

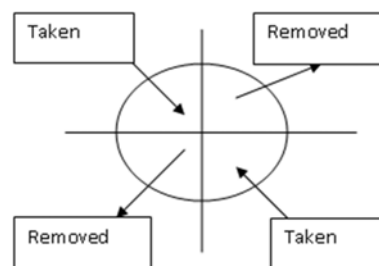


Figure 1. Quartering technique, for obtaining representative samples.

Visual observations shown in Figure 2 indicate that the four investigated dolomite samples are translucent to transparent, have a pearly luster and are characterized with different colors commonly white, (sample P1 selected from El-azizia, Souk El-khamees), yellowish white (sample P2 selected from Nalout, Abu Rashada route, Gherian), light, brown, (sample P3 selected from Sedi El-said, Abu Reshada route, El-gabl El-gharby) and, dark brown (sample P4 selected from Abu Ghilan, north Kaf- Katkoot). The samples are characterized with perfect cleavage. These observations give a first impression that the selected samples under investigation are dolomite rocks as reported by J. George et al [10].

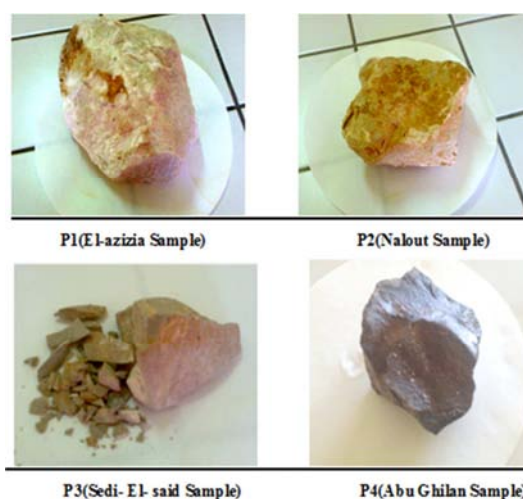


Figure 2. Photos of the studied samples.

### 2.2. Sample Characterization

#### 2.2.1. X-ray Fluorescence (XRF)

About 10 g of each finely ground dolomite sample (passed completely through 75  $\mu\text{m}$  standard sieve) was used to investigate their chemical constitution using x-ray fluorescence technique (XRF) through comparing tested samples with a standard dolomite sample as a reference material. An instrument XRF (BRUKER-XRF-3400, Egypt) was used for this purpose.

#### 2.2.2. Infrared (IR) Spectra

About 10 mg of the substance as a fine powder was mixed well with spectroscopic pure KBr powder in agate mortar.

The mixture was then pressed about 8 ton/cm<sup>2</sup> in a special disc under vacuum, using a hydraulic press.

### 2.2.3. X-ray Diffraction (XRD)

About 0.5 g of each dolomite sample was investigated through its solid phase mineralogical compositions using x-ray diffraction technique (XRD). A Philips 1730 diffractometer with Ni filtered Cu K $\alpha$  radiation at a scan speed of 120 min<sup>-1</sup> was used.

### 2.2.4. Scanning Electron Microscope (SEM)

The microstructure and solid phase analysis of some selected samples was investigated using scanning electron microscope (A Philips XL30 scanning electron microscope attached with an EDX unit with accelerating voltage 30 kv and magnification up to 20.000 x). The polished surfaces were then cleaned under water by ultrasonic before coating under vacuum with thin layer of gold for SEM investigation.

## 3. Result and Discussions

### 3.1. Sample Chemical Analysis

Table 1 indicates the chemical compositions of the four investigated samples. The results show that the samples composed mainly of 25.67% - 30.80% CaO, 16.90% - 19.94% MgO and 34.87% - 47.98% loss on ignition (L. O. I.) which corresponds to the release of CO<sub>2</sub>, these results are close, with different proportions, to the standard composition of dolomite

sample that composed of 30.41% CaO, 21.86% MgO and 47.72% loss on ignition [11]. The table also indicates that samples (P1) and (P2), have the closest chemical composition to the standard dolomite sample. In addition to the main constituents of dolomite (CaO, MgO and CO<sub>2</sub>), some other impurities are present namely; SiO<sub>2</sub> which is very limited in samples (P1) and (P2) 0.85% and 1.22% respectively, but increases to 7.29% and 15.89% in samples (P3) and (P4) respectively. This indicates that samples (P3) and (P4), are not pure dolomite, they contain some quartz mineral (SiO<sub>2</sub>). The samples contain also some impurities of R<sub>2</sub>O<sub>3</sub> (Fe<sub>2</sub>O<sub>3</sub>+Al<sub>2</sub>O<sub>3</sub>) which are also limited in samples (P1) and (P2) 0.41% and 0.5% respectively, but increase to 1.12% and 5.89% in samples (P3) and (P4) respectively. The results indicate that samples (P1) and (P2) are relatively purer dolomite compare to samples (P3) and (P4). The relatively higher purity of samples (P1) and (P2) explain their white or yellowish white color, while the presence of considerable contents of iron oxide and silica in samples (P3) and (P4) explains their relatively darker color, especially sample (P4) which has the darkest color since it contains the largest content of Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. Also, these results indicate the closest specific gravity of the pure dolomite samples (P1) and (P2) to that of the standard value of dolomite and the relatively farer specific gravity values of impure samples (P3) and (P4) to the standard one. In addition, to these compositions, a little content of insoluble residue (insol. res.), not soluble in dilute HCl, 0.58% - 0.9% are also present.

**Table 1.** Chemical composition of the investigated samples as determined by wt%.

Oxide, %	P1 (El-azizia)	P2 (Nalout)	P3 (Sedi- El- Said)	P4 (Abu Ghilan)
CaO	30.80	30.21	28.85	25.67
MgO	19.38	19.94	18.26	16.60
SiO <sub>2</sub>	0.85	1.22	7.29	15.89
Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub>	0.41	0.5	1.12	5.89
Insol. Res.	0.58	0.63	0.9	0.69
L. O. I.	47.98	47.5	43.58	34.87

### 3.2. X-ray Fluorescence (XRF)

Table 2 indicates a detailed chemical composition for the major and minor components as determined by x-ray fluorescence method (XRF). Based on the above chemical analysis results determined with two different techniques (classical wet method and XRF), it was confirmed that the

four selected samples are mainly dolomite minerals with different compositions and impurities. Sample (P1) is expected to be dolomite with some content of calcite, sample (P2) is pure dolomite while samples (P3) and (P4) are impure dolomite. The various compositions of the investigated dolomite samples make them suitable for various chemical, metallurgical and agricultural applications.

**Table 2.** Chemical composition of the investigated samples by x-ray fluorescence (XRF).

Oxide, %	Sample no.				Standard Oxide, %
	(P1) El-azizia	(P2) Nalout	(P3) Sedi- El- Said	(P4) Abu Ghilan	
CaO	31.19	30.73	28.31	22.89	30.4
MgO	18.27	18.04	16.08	12.83	21.7
SiO <sub>2</sub>	0.89	1.27	7.31	18.93	0
Al <sub>2</sub> O <sub>3</sub>	0.11	0.13	0.56	3.53	0
Fe <sub>2</sub> O <sub>3</sub>	0.33	0.41	0.73	2.63	0
Na <sub>2</sub> O	0.019	0.15	0.89	1.17	0
K <sub>2</sub> O	0.15	0.12	0.63	1.09	0
SO <sub>3</sub> <sup>2-</sup>	0.004	0.11	0.43	0.55	0
Cl <sup>-</sup>	0.108	0.113	0.25	0.41	0
L. O. I	48.09	47.5	44.02	35.19	47.9
Insol. res.	0.8	1.4	0.79	0.78	0

### 3.3. IR Spectral Analysis

Figure 3 shows the IR spectra of the four investigated samples. Comparing with the standard behavior of dolomite [12]. The results indicate that qualitatively the four investigated samples have a dolomitic nature. The characteristic dolomite bands observed at  $726\text{ cm}^{-1}$ ,  $878\text{ cm}^{-1}$  and the broad band at  $1438\text{ cm}^{-1}$  representing out of plane bending ( $\nu_2$ ), the asymmetric stretching ( $\nu_3$ ), and the in plane bending ( $\nu_4$ ), modes of the carbonate group are found to be

active [13]. Additionally, bands due to silicates ( $1033\text{ cm}^{-1}$ ) are visible especially in samples (P3) and (P4) which indicates the presence of same impurities in such samples. Peaks due to H-bonded water (at  $\approx 3400\text{ cm}^{-1}$ ) are also visible. The broad bands at  $3100\text{--}3700\text{ cm}^{-1}$  can be interpreted as two  $\text{H}_2\text{O}$  stretching modes. Free water molecules have stretching mode at  $3700\text{ cm}^{-1}$ . The modes at  $3428\text{--}3444\text{ cm}^{-1}$  would correspond to  $\text{O}\cdots\text{H-O-H}$  bond [14].

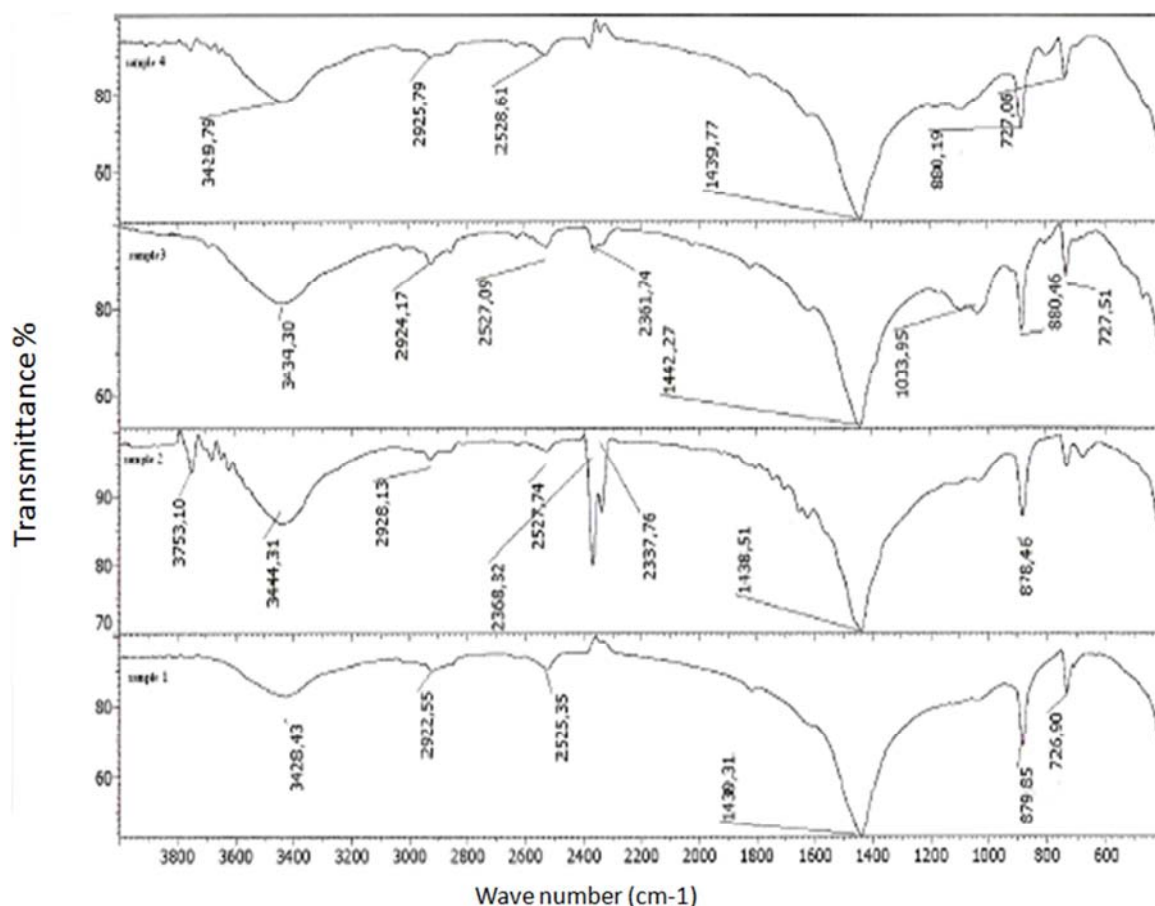


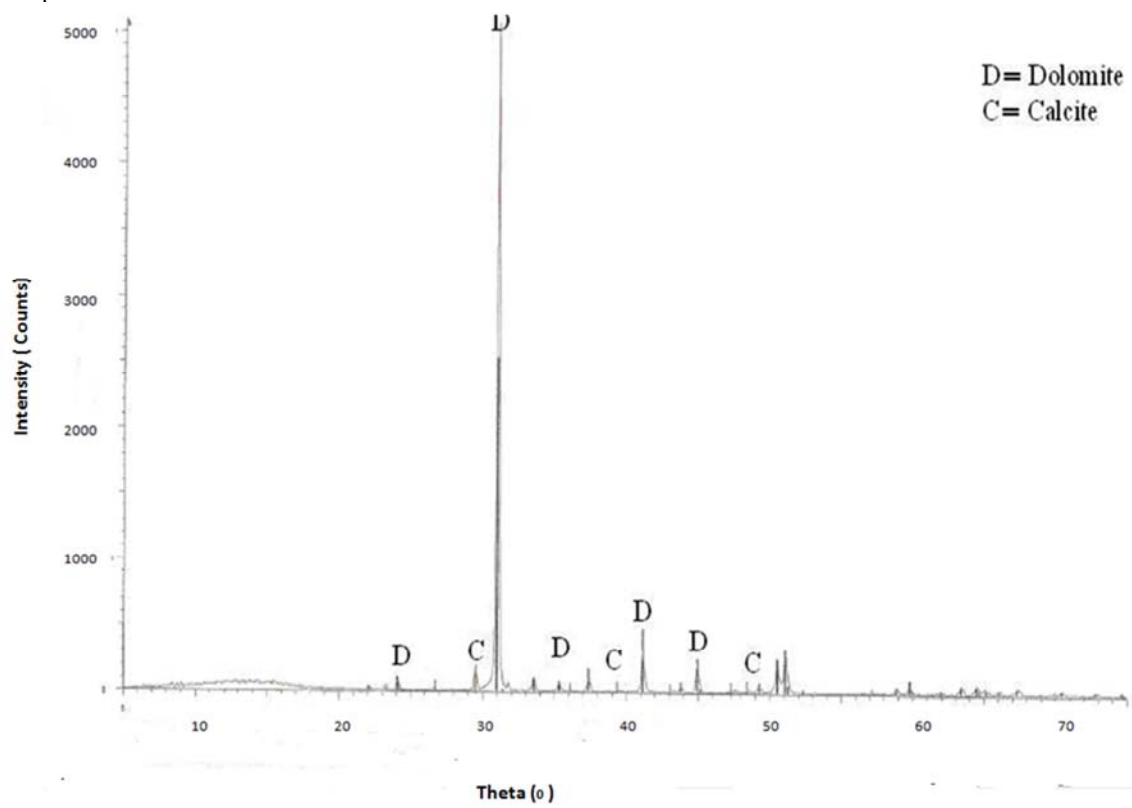
Figure 3. IR spectra of the investigated samples.

### 3.4. X-ray Diffraction Analysis (XRD)

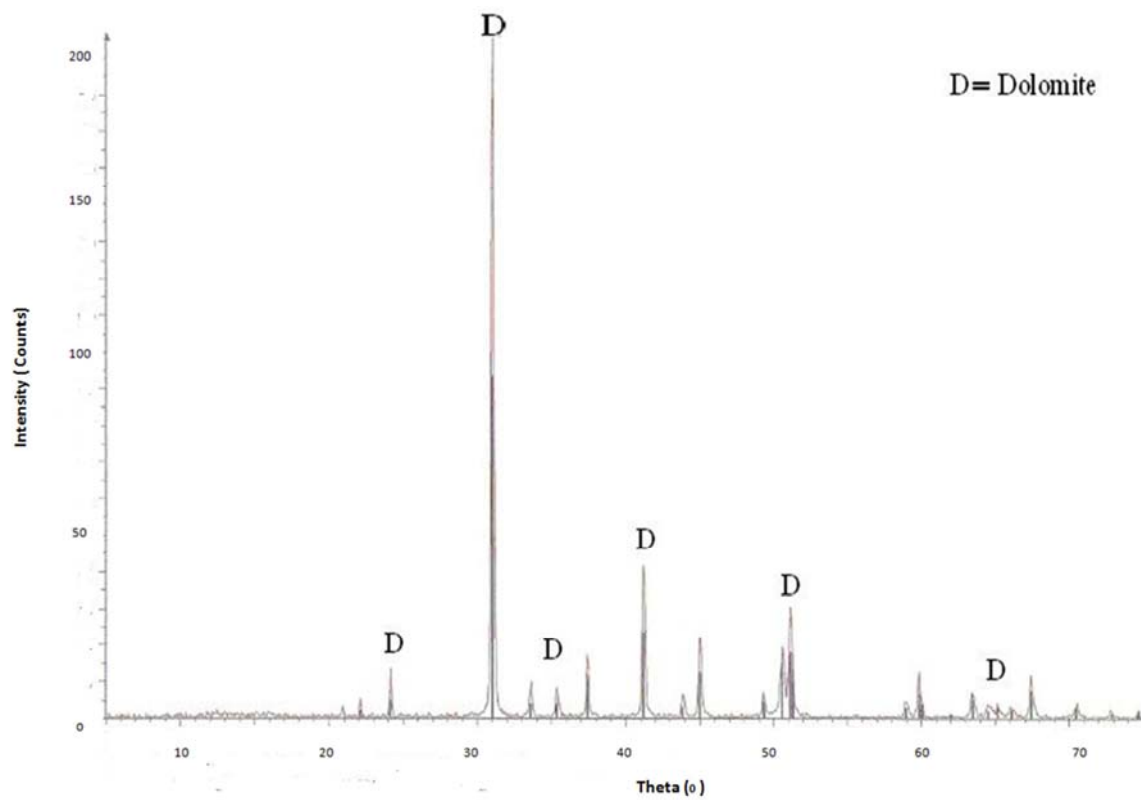
Figures (4-7) show x-ray diffraction patterns of the powders of the investigated samples. Figure 4 shows the sample P1. It is composed mainly of dolomite mineral  $\text{CaMg}(\text{CO}_3)_2$  in addition to a little content of calcite mineral  $\text{CaCO}_3$ . All of the main peaks characterizing dolomite mineral could be detected including the main peak (100% intensity) at  $2\theta = 31^\circ$ , in addition to the other peaks with relatively lower intensities at  $2\theta = 24^\circ, 33.5^\circ, 37.5^\circ, 41^\circ, 45^\circ, 50.5^\circ$  and  $51^\circ$  (JCPDS card no. 84-1208) [15]. Also, few peaks with very low intensity characterizing calcite mineral  $\text{CaCO}_3$  could be observed at  $2\theta = 29.5^\circ, 39.2^\circ, 47.2^\circ$ , and  $48.5^\circ$  (JCPDS card no. 86-0174). (Joint Committee on Powder Diffraction and Standards) Figure 5 shows the sample P2, it is pure dolomite, no peaks characterizing any

other minerals could be detected. Figure 6 shows the sample P3 it was mainly dolomite mineral with a little content of quartz mineral ( $\text{SiO}_2$ ). In addition to the peaks characterizing dolomite some peaks with relatively lower intensity characterizing quartz could also be observed at  $2\theta = 21^\circ, 26.5^\circ$  and  $36.5^\circ$  (JCPDS card no. 89-1813). Figure 7 shows the sample P4, it is composed mainly of dolomite in addition to quartz, but the content of quartz in sample (P4) is relatively higher than in sample (P3), this was observed from the relatively higher intensity of quartz peaks in sample (P4) than in sample (P3). The X-ray diffraction results confirm the results of chemical analysis which predict that (i) sample (P1) is mainly dolomite with very low content of calcite, (ii) sample (P2) is pure dolomite, (iii) samples (P3) and (P4) are mainly dolomite with some contents of quartz. Similar results [16] indicated that more carbonate phase was present in

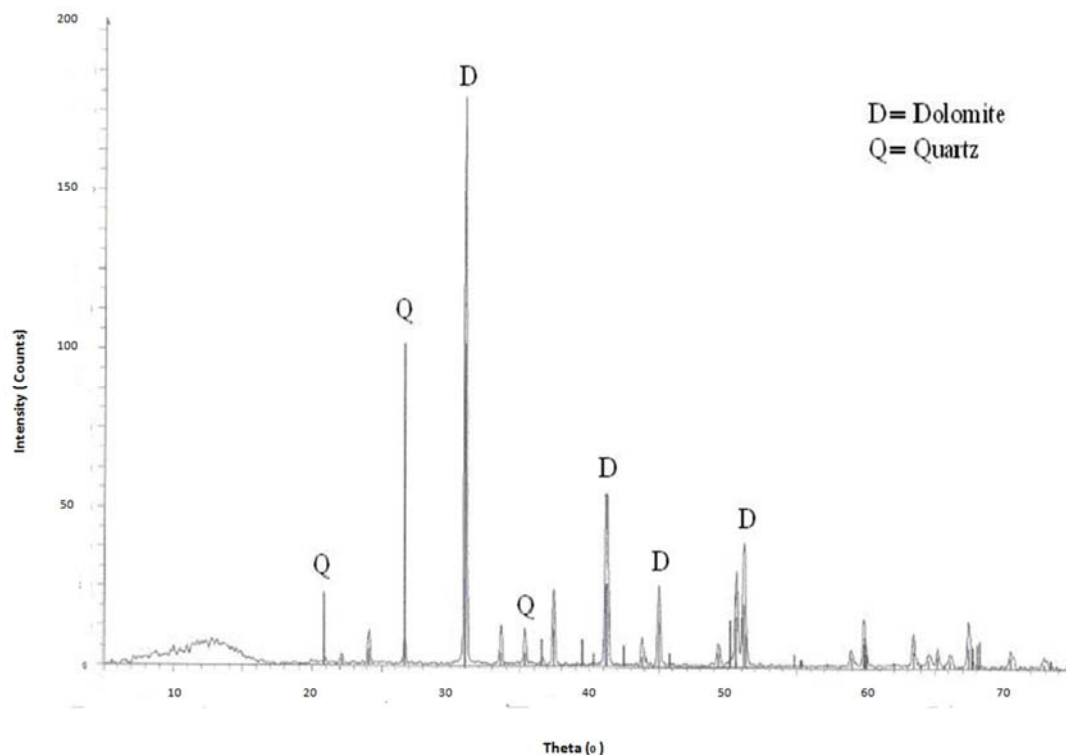
dolomite sample.



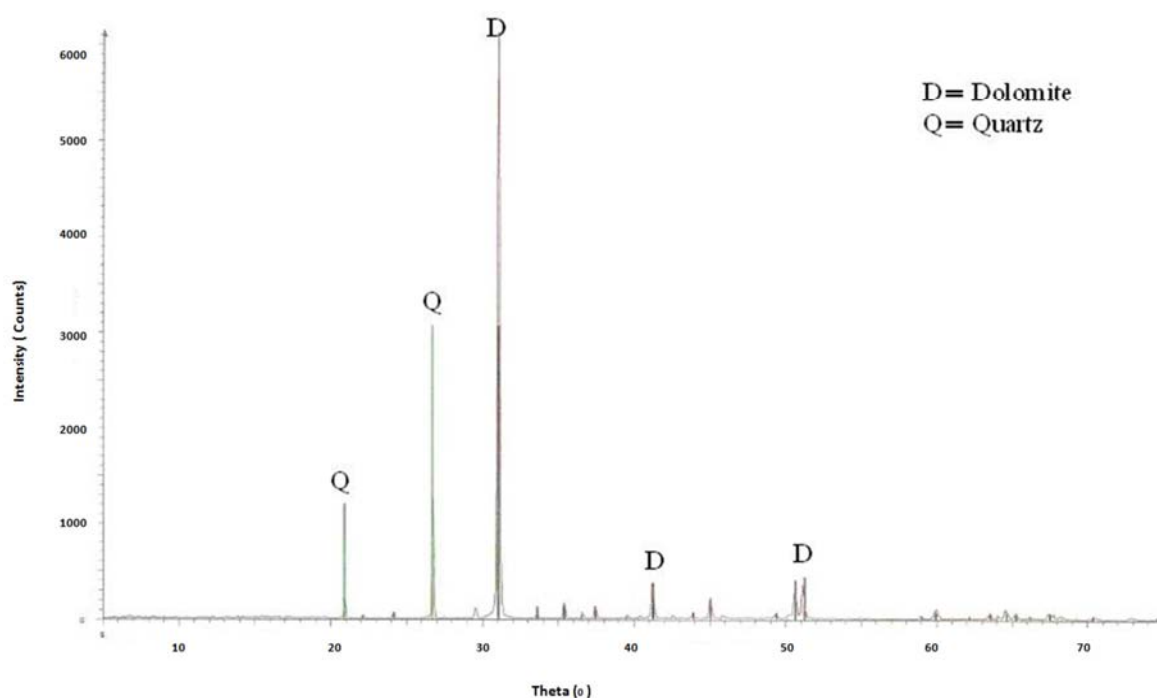
*Figure 4. XRD patterns of sample P1.*



*Figure 5. XRD patterns of sample P2.*



**Figure 6.** XRD patterns of sample P3.



**Figure 7.** XRD patterns of sample P.

### 3.5. Scanning Using the Electron Microscope (SEM)

Figure 8 shows the photomicrographs of representative samples taken from the four investigated raw dolomite batches. The figure shows that the dolomitic nature predominates all over the matrices of the four samples, planar subhedral to euhedral crystalline characterizing dolomite [17,

18] constitute the majority of the matrices in the photos of the four samples. It could also recognize the homogeneity of the matrix in sample (P2) (Figure 8b) which reflect the purity of this sample. On the other hand, some white crystals characterizing calcite could be observed deposited on the dolomite crystals (Figure 8a) while the glassy crystals with



sharp edges [19] and walls characterizing quarts could be observed in sample (P3) (Figure 8c), which are larger more obvious in sample (P4) (Figure 8d), these crystals could not

be recognized in samples (P1) or (P2). These results confirm those results which obtained from XRD and XRF.

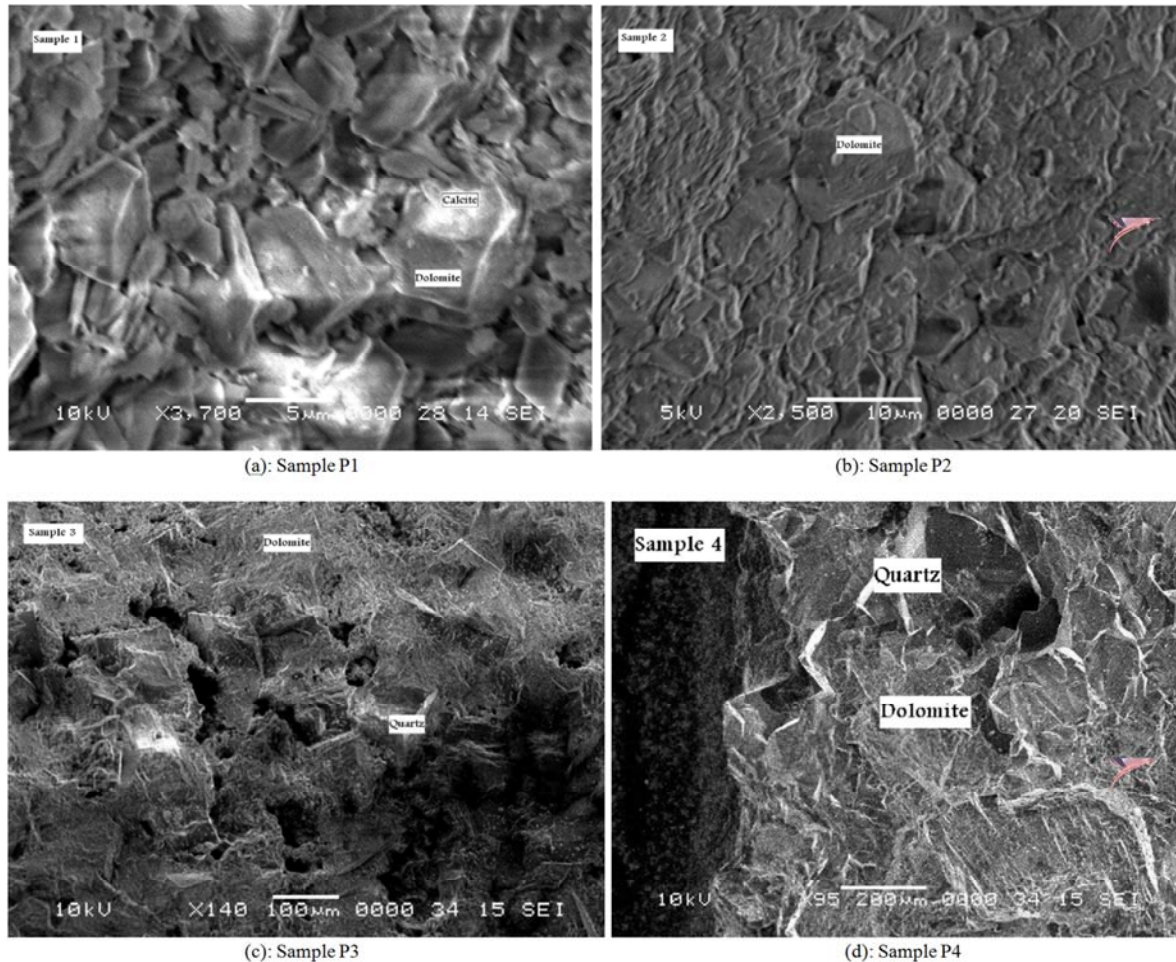


Figure 8. SEM photomicrograph of the raw dolomite samples.

## 4. Conclusions

Four different dolomite samples were selected from different locations of the north of Libya. The main findings can be summarized in the following points:

1. The appearance and the shape through visual observations indicate, that the four investigated dolomite samples are translucent to transparent.
2. Classical wet method of chemical analysis indicates that the four samples composed mainly of 21.77% - 29.25% CaO, 14.38% - 16.40% MgO and 34.87% - 47.98% loss on ignition (L. O. I.) which corresponds to the release of  $\text{CO}_2$ , these results are close, with different proportions, to the standard composition of dolomite sample that composed of 30.8% CaO, 21.5% MgO and 47.7% loss on ignition.
3. The x-ray fluorescence (XRF) analysis indicates that the four investigated samples, contain 22.89 - 31.19% CaO, 12.83 - 18.27% MgO in addition to 0.78 - 1.4% loss on ignition ( $\text{CO}_2$ ). However, the percent of CaO in sample P1 (31.19%) is relatively higher than the standard

dolomite (30.8%) which confirms the prediction of the presence of some content of calcite  $\text{CaCO}_3$  accompanied with dolomite sample P1. In spite of the limited variance in the chemical constitutions determined by x-ray fluorescence compared with classical wet method, the results confirm that the four investigated samples are mainly dolomite and that samples P1 and P2 are relatively purer than samples P3 and P4 which contain larger percentage of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ .

4. IR spectra of the four investigated samples indicated that qualitatively the four investigated samples have a dolomitic nature. The characteristic dolomite bands observed at  $726\text{ cm}^{-1}$ ,  $878\text{ cm}^{-1}$  and the broad band at  $1438\text{ cm}^{-1}$  representing out of plane bending ( $\nu_2$ ), the asymmetric stretching ( $\nu_3$ ), and the in plane bending ( $\nu_4$ ), modes of the carbonate group are found to be active.
5. The scanning using the electron microscope indicates that the dolomitic nature predominates all over the four samples, the euhedral rhombohedral crystals characterizing dolomite constitute the majority of the

matrices in the photos of the four samples.

## Acknowledgements

The authors acknowledge the help provided by the technicians for their guidance to perform the experiments.

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