

Comparative study of thermal and compositional properties of Aïn M'lila dolomite, CaCO_3 , and MgCO_3 using TG and FTIR analyses

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Abstract. *The dolomite of Aïn M'lila (Teioualt quarry, State of Oum El Bouaghi), which is located in the northeast of Algeria, was the subject of our study. Based on the results of TG (vacuum) analysis of this product, our sample was calcined at different temperatures: 300, 650, 820, 920, and 1000°C. In order to compare the FTIR analysis of our calcined products with those of reference products (CaCO_3 and MgCO_3), our products have to be analysed using Infrared Spectroscopy after each calcination. Comparing the FTIR spectra of these carbonates with those of dolomite allows us, despite the difficulty of this method, to deduce the differences between them. In addition, the FTIR spectra of the various carbonates and oxides obtained after each calcination were analysed in detail. In brief, this study aims to create a new spectral database of local carbonate product (dolomite of Aïn M'lila) and comparing its characteristics with those of other carbonates (CaCO_3 and MgCO_3), which leads implicitly to update their databases.*

Keywords: Dolomite ; Aïn M'lila ; Calcination; Thermogravimetric Treatment TG; FTIR Spectroscopy.

1. Introduction

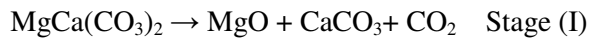
The largest country in Africa, Algeria has proven huge deposits of valuable minerals such as gold, silver, barite, bentonite, diatomite, iron ore, phosphate rock, and dolomite, among others. Additional research will need to be carried out, however, as little is yet known about the characteristics of these deposits especially those of dolomite [1]. Dolomite is a common mineral in both continental and marine sedimentary rocks and metamorphic rocks [2], it's an anhydrous carbonate mineral composed of calcium magnesium carbonate, ideally given by the chemical formula $\text{CaMg}(\text{CO}_3)_2$ [3]. According to the Algerian Ministry of Energy and Mining, the geological reserve of dolomite in Teioualt massive is approximately 18 283 626 tonnes from which 73% are exploitable. Knowing that the quarry of Djebel Teioualt is located in the territory of Ouled Hamla Municipality, Oum El Bouaghi State, on the northeast side of the massive (15km west of Aïn M'lila town).

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It occupies an area of 270 000 m², with the following Lambert coordinates: X = 834.5 – 835.0, Y = 314.5 – 315.0 (see Fig. 1). Since 1980 onwards, its exploitation is done under the aegis of the ALGRAN Company (Algerian Granulats), subsidiary of the ENOF mining company (Company of Nonferrous products). The dolomite-based sorbents are used in low temperatures to reduce the emission of pollutants such as carbon, sulfur and nitrogen oxides, hydrogen chloride, and fluoride [4]. It is used too as additives (Mg supplies), in steels, in glass, in refractories, in ceramics, as fillers for paints and plastics. Dolomite is the best source of magnesium salts in the chemical industry and an important raw material in the refractory industry because it contains a large amount of MgO [5]. Besides, Dolomite is commonly used as a refractory material and as raw material for the production of magnesium, in metallurgy, glass industry [6]. In the other hand, thermal decomposition takes place in two stages (I) and (II), these latter have been generally done as following:



In this paper, we present in detail all products generated from dolomite calcination at different temperatures, after that, comparison between our results and other carbonates adopted as reference products (i.e., CaCO₃ and MgCO₃) is necessary. By the way, analyses were carried out in this study on the basis of thermogravimetric analysis (TG), and Fourier Transform Infrared Spectroscopy FTIR.



Fig. 1. Dolomite quarry location in Teioualt massive

2. Experimental techniques

2.1. Sample preparation

The Fig.2 below illustrates the photographic images of the studied dolomite: as stones before grinding, and as well as powder. More information about data sheets of dolomite targeted in this study, and magnesium carbonate and calcium carbonate powders adopted as references in this work are available in Table 1 and 2 respectively.

3g of powdery samples are weighed accurately into a dry, tared porcelain dish and then placed in a muffle furnace at different temperatures (*i.e.*, 300, 650, 820, 920, and 1000°C) with a rising rate of 15 °C / min for 4 hours. After calcination in air, obtained samples should be cooled immediately in ambient temperature for 10 min. After that, all calcined samples are characterized using FTIR spectroscopy, while the TG analysis has been performed for raw dolomite during calcination at 1200°C.



Fig. 2. Images of the dolomite mineral studied (as stones) -left, and the dolomite powder – right

2.2. Fourier Transformation Infrared Spectroscopy (FTIR)

IR spectra are obtained using a Perkin–Elmer spectrometer at the resolution of 8 cm⁻¹. Fourier Transforms Infrared (FTIR) technique is used in the transmission mode in range of 4000 - 400 cm⁻¹, while, for each sample, 120 scans are used. After the oxidation, about 100 µg of the oxides are scraped. The oxide is then compressed with 23 ± 2mg of KBr in a cold at 150 MPa isostatic press (CIP) in order to obtain a 200 - 250 µm thick pellet. All infrared spectra are reporting absorbance ($A = -\log(I/I_0)$) as a function of the incident wave numbers.

Table 1 Technical data sheet of dolomite powder analysed in this study

-a- Physical characteristics

Color	Hardness (Mohs)	Density	Melting temperature (°C)
Light grey	3.5-4	2.89	1400

-b- Chemical composition

CaO	MgO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	Loss on ignition (at 500°C)
31.45	20.38	0.20	0.036	0.034	0.02	47.00

The grain size is lower than 75µm (97% of the totality)

Table 2 Technical data sheets of magnesium carbonate and calcium carbonate powders adopted as references in this work.

Compound	society	Cas n°	Assay
MgCO ₃	Riedel-de-Haen	39409-82-0	MgO-40%, Camax-1%, Heavy metals as Pb-max0.005%, ChlorideCl-max0.05, Fe-max0.05.
CaCO ₃	Sigma-Aldrich	471-34-1	CaCO ₃ MW100.09 g/mol, d=2.93g, 98.5-100.5% based on anhydrous substance, ≤ 2% loss on drying 200°C. Chloride (C-) ≤200mg/kg, Fluoride(F-) ≤50mg/kg Sulfate (SO-24) ≤2000mg/Kg, As ≤ 2mg/kg Ba : in accordance, Cu ≤ 10mg/Kg, Fe ≤ 200mg/kg, Hg ≤ 0.5mg/kg, Pb≤ 1mg/kg, Zn ≤ 10mg/kg.

2.3. TGA analysis

Dolomite powders were subjected to thermogravimetric analysis (TGA) using NETZSCH STA 409 PC/PG instrument, with α -alumina as the reference material at a heating rate of 10°C/min in azote (flow rate 10 ml/min), where, sample mass was estimated to be about 33 mg.

3. Results and discussion

3.1. TG Analysis

The thermal decomposition characteristics of dolomite with reference to the TG curve are displayed in Fig. 2(a), the first derivative and the second derivative are also depicted in Fig. 2(b), 2(c) respectively, while Fig. 2(d) represents the enlarged second derivative. The derivatives allow us to detect precisely the characteristic temperature values related to each transformation occurred during the heating, after that, different calcinations are performed based on these values. By the way, characteristic temperatures recorded in this study are: 300, 650, 820, 920, and 1000°C.

Moreover, the calcination for 4 hours at about 300 °C leads to dehydration and dehydroxylation of dolomite (elimination of H₂O and OH hydroxides). At around 650 °C, formation of MgO and eventually CaO oxides is begun accompanied with CO₂ departure. Predominant formation of MgO and CaO are detected at 820°C and 920 °C respectively, finally, mixture of MgO and CaO oxides are formed about 1000 °C. More information about temperature ranges, mass loss, and physicochemical phenomena corresponding to these transformations are listed in Table 3.

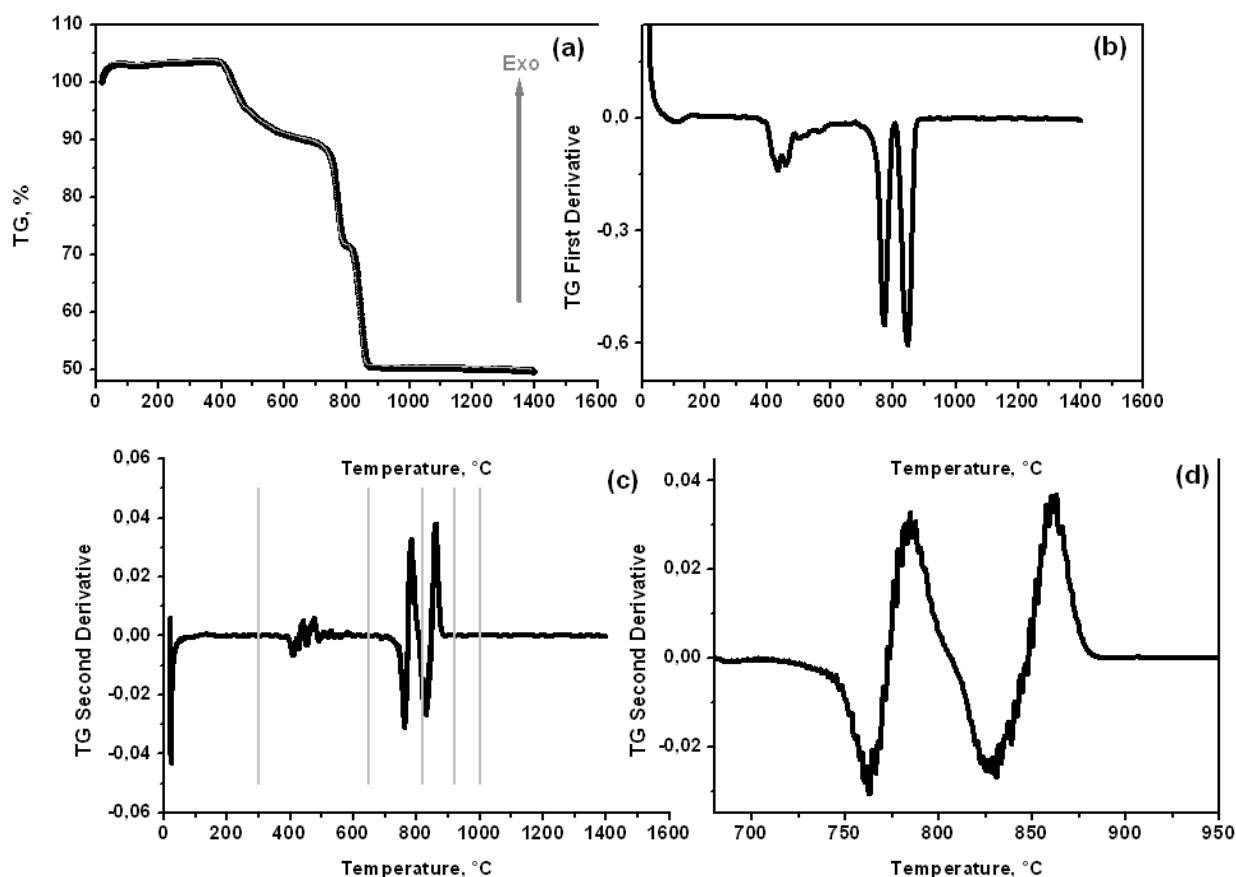


Fig.3. (a) TG curve of raw dolomite under study, (b) the first derivative, (c) the second derivative, and (d) enlarged second derivative from 675 to 950 °C

Table 3 The TG results of dolomite analyzed: Temperature ranges, Mass loss, and Physico-chemical phenomena

	Corresponding temperature interval	Loss of mass %	Corresponding phenomenon
Stage 1	20-780°C	13.60	Dehydration and dehydroxylation
Stage 2	780-830°C	18.68	Formation of MgO, and departure of CO ₂
Stage 3	Supérieur à 830°C	21.59	Formation of CaO, and departure of CO ₂

On the other hand, Fig. 4 shows the mass losses of dolomite compared to that of CaCO₃ and MgCO₃ during calcination in air at the various temperatures already chosen. As it can be clearly seen from Fig. 4, the temperature increase below 300 °C does not cause any noticeable further mass loss in dolomite. However, the weight loss of dolomite was observed to be constantly changing from 300 until 800 °C due to the dehydroxylation and departure of CO₂. At 500°C, dolomite lost a significant amount of its mass, which deals well with information provided by its data sheet, *i.e.*, its loss of mass after calcination at 500°C was estimated to 47%.

During calcination at the temperature range studied, CaCO₃ involves behavior rather similar to that of dolomite while MgCO₃ tends to seriously lose mass from the first calcination (at 0 °C). It is noted also that the losses of masses in air of dolomite and CaCO₃ are less important than that related to MgCO₃ due to its high-water content.

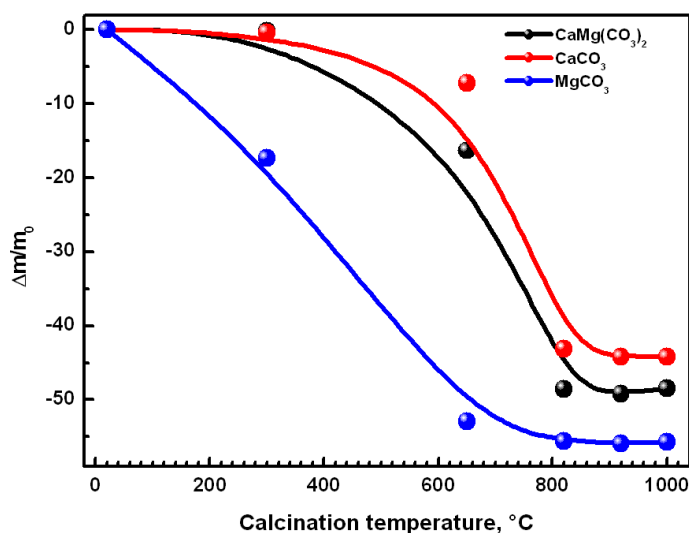


Fig. 4. Mass loss of various carbonates as a function of calcination temperature

3.2. FTIR Spectroscopy

The FTIR spectra of as-received compounds are also performed, where Fig. 5 shows the spectra of initial compounds and indicates the main absorption bands at 3648, 3448, 2880, 2525, 1880, 1446, 881 and 726 cm^{-1} . For carbonate ions, the band ν_1 estimated towards $\sim 1080 \text{ cm}^{-1}$ is inactive in infrared spectroscopy. The intense IR peak near $\sim 1400 \text{ cm}^{-1}$ is due to the antisymmetric stretch (ν_3), Infrared modes near 800-876 cm^{-1} are attributed to the out-of-plane band (ν_2), and infrared modes around 700 -713 cm^{-1} region are due to the in-plane bending mode (ν_4). Peaks at ~ 1800 , 2500-2600, and 2880-2980 cm^{-1} are resulted from combinations of ($\nu_1 + \nu_4$), ($\nu_1 + \nu_3$), and ($2\nu_3$) modes respectively. The band located at 3454 cm^{-1} has been attributed to H-bonded water of dolomite humidity [8-22]. Table 4 summarizes the values of absorption bands and their assignment.

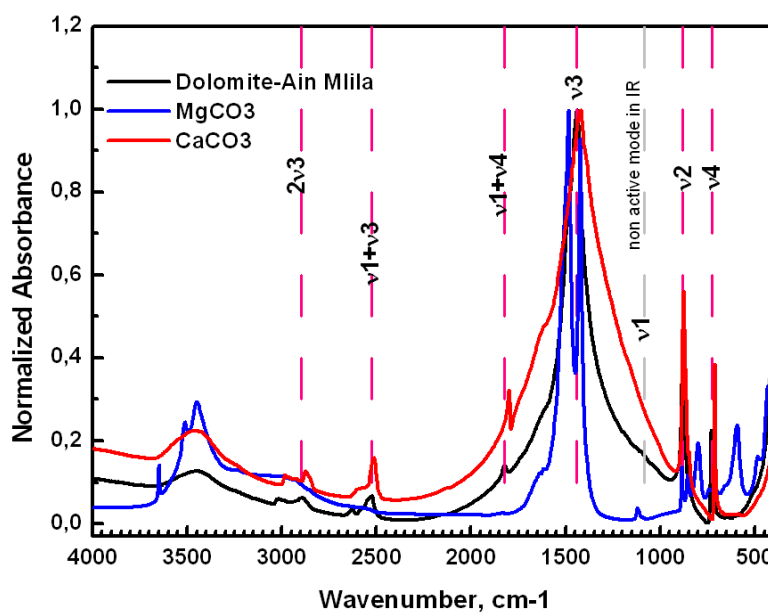


Fig. 5. FTIR spectra of as received dolomite, MgCO_3 , and CaCO_3

Table 4 FTIR results of dolomite, CaCO_3 , and MgCO_3 ; their corresponding assignments; and some references

Dolomite $\text{MgCa}(\text{CO}_3)_2$ (cm^{-1})	CaCO_3 (cm^{-1})	MgCO_3 (cm^{-1})	Assignment	references
		432	Bending, and stretching vibration bands of M-O.	[14-17]
		486		
		594		
	712	714	$\nu_4(\text{CO}_3^{2-})$	[7-8-9-18]
728		744		
882	876	800-854-886	$\nu_2(\text{CO}_3^{2-})$	[7-8-9-18]
		1120	$\nu_1(\text{CO}_3^{2-})$	[7-8-9-18]
1438	1422	1422-1484	$\nu_3(\text{CO}_3^{2-})$	[7-8-9-18]
	1628		Bending vibration of water	[7-8-9-18]
1822	1800		$\nu_1 + \nu_4(\text{CO}_3^{2-})$	[7-8-9-18]
2524-2628	2512-2600		$\nu_1 + \nu_3(\text{CO}_3^{2-})$	[7-8-9-18]
2886-3016	2874-2982	2974	$2 \nu_3(\text{CO}_3^{2-})$	[7-8-9-18]
3448	3454	3240-3446-3514	Stretching vibration of water	[7-8-9-18]
		3648	Stretching vibration in the case of $\text{Mg}(\text{OH})_2$	[7-8-9]

For easy comparison, superpositions of FTIR spectra corresponding to (a) dolomite, (b) MgCO_3 , and (c) CaCO_3 calcined at various temperatures (ambient temperature, 300, 650, 820, 920, and 1000 °C) are displayed in Fig. 5. As shown in Fig. 6(a), the spectra indicate at ambient temperature, 300, and 650 °C the predominant presence of carbonates characterized by the ~ 720 , 800 and 1480 cm^{-1} bands corresponding to the bending and stretching vibrations.

At 650 °C, the vibration band detected at about 1480 cm^{-1} corresponds to the formation of oxide MO (M = Mg, Ca), while at 820, 920, and 1000 °C we note the vanishing of the above-mentioned band. Besides, we also observe at 1630 and 3430 cm^{-1} two bands related to the bending and stretching vibrations of H_2O respectively. Furthermore, the characteristic peak situated around 3650 cm^{-1} indicates the presence of the OH present in the $\text{Ca}(\text{OH})_2$, and also $\text{Mg}(\text{OH})_2$ compounds.

Fig. 6(b) represents the FTIR spectra of calcined carbonate which taken Mg (CO_3) as a reference compound. It should be noted that this compound initially has a large amount of MgO. At room temperature and at 300 °C, the spectra are similar to those of the data corresponding reference (MgCO_3) [23-24]. At 650 °C and above this temperature the part corresponding to the formation of the Mg-O bond is well apparent in the portion of spectra between 400 and 900 cm^{-1} .

Then the figure (6d) groups the results of FTIR analyse relating to the calcination of the CaCO_3 used as a reference. For spectra below 820 °C, we note the predominance of carbonates represented by the bands situated at 720, 800 and 1450 cm^{-1} with the onset of formation of the CaO at 650 °C. After 820°C, we observe

the predominance lines corresponding to the Ca-O bonds. Above 820 °C, the carbonates are negligible [25-26-27].

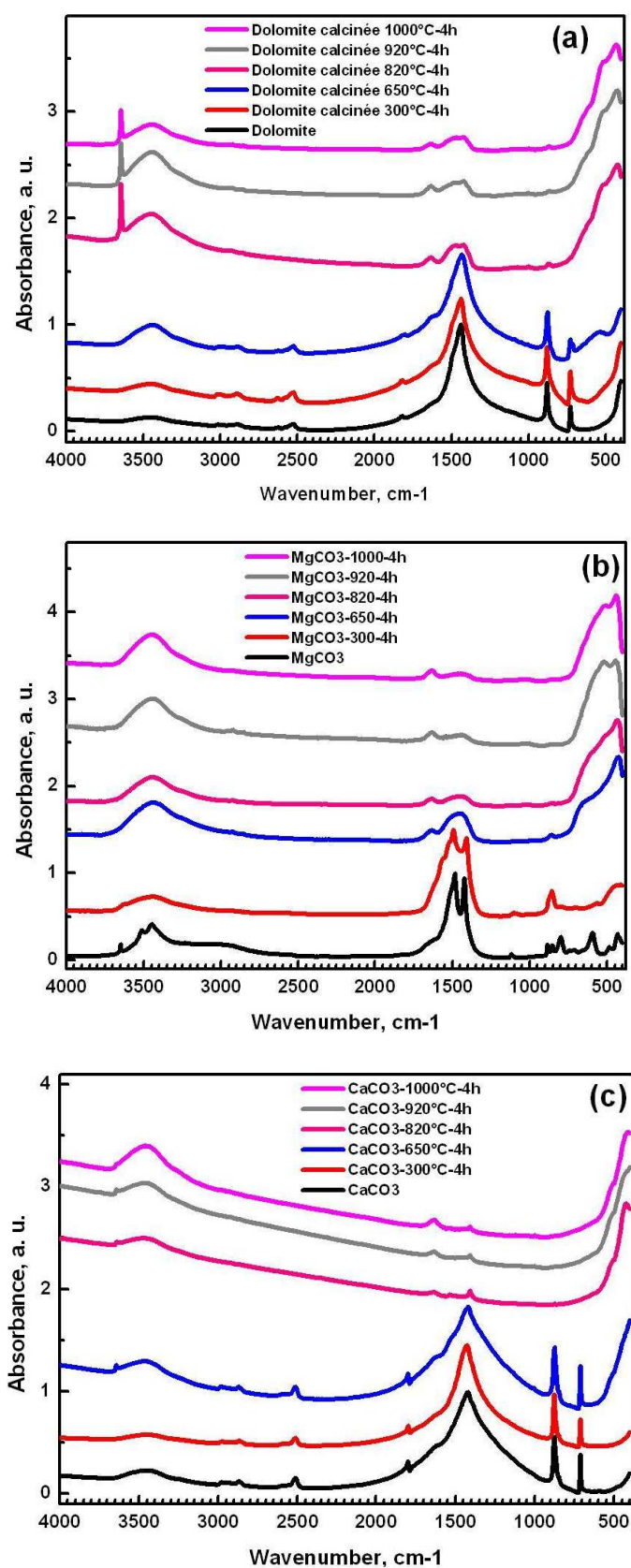
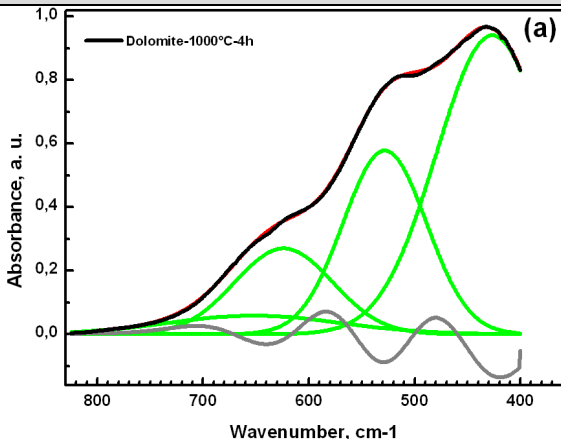
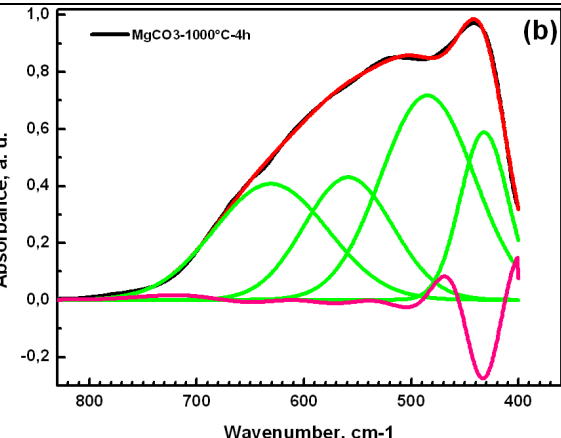


Fig.6. FTIR spectra of calcined (a) dolomite, (b) MgCO_3 , and (c) CaCO_3 for 4 hours at 300, 650, 820, 920, and

1000°C.

In order to better clarify the differences between FTIR spectra of the three calcined carbonates, we have focused on their spectra region ranging from 400 to 830 cm^{-1} obtained at 1000 °C. This differentiation, which was made on the basis of Gaussian decomposition and the second derivative, aims to extract exactly the values of the vibration bands. As shown in Fig.7, the decomposition of the spectra in this region permits to obtain four lines in the three types of calcined compounds. The parts of these FTIR spectra represent the vibration states of the M-O, or O-M-O type links whether of the stretching or bending type respectively. The peak intensities of MgO are more intense compared to that of CaO, in the portion between 550 and 750 cm^{-1} .

FTIR Spectra	The peak position (cm^{-1}) Xc	The peak width (cm^{-1}) W	The peak area (arbitrary units) A
	(a)		
	426.51	105.69	124.58
	528.20	78.99	57.23
	623.71	92.97	31.46
	651.68	163.06	11.94
	(b)		
	432.02	44.59	32.91
	484.75	87.29	78.48
	558.56	82.53	44.50
	630.72	106.18	54.19

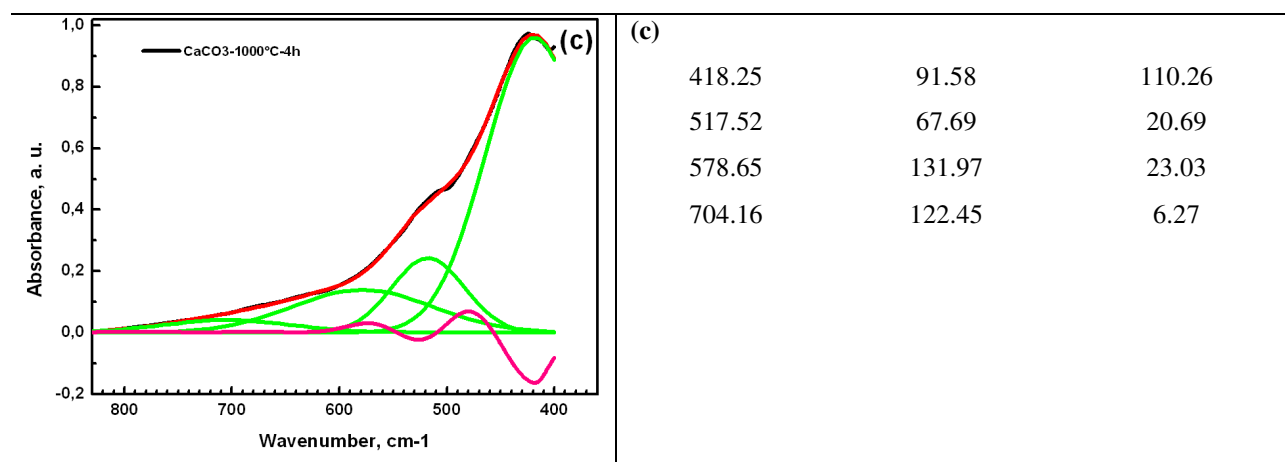


Fig.7. The FTIR spectra of (a) dolomite, (b) MgCO₃, and (c) CaCO₃ calcinated at 1000°C

4. Conclusions and outlook

In summary, we have studied the thermal and compositional properties of Aïn M'lila's dolomite using TG analysis and FTIR spectroscopy. Our results show that calcination of dolomite for 4 hours at transformation temperatures leads to various phenomena *i.e.*, dehydration and dehydroxylation at about 300 °C, formation of MgO with CO₂ departure at around 650 °C, formation of MgO and CaO at 820°C and 920 °C respectively, and mixture of MgO and CaO about 1000 °C. Besides, weight loss of dolomite, CaCO₃, and MgCO₃ as a function of calcination temperature demonstrates that MgCO₃ is the highest water content carbonate. Moreover, FTIR spectra of as-received carbonates reveal that their main absorption bands situated at 3648, 3448, 2880, 2525, 1880, 1446, 881, and 726 cm⁻¹, which corresponds well with the literature. Comparison between FTIR spectra of these carbonates gives us a detailed view of their compositional properties in spite of the difficulty to discern between them and between their calcination products. Furthermore, signatures of these compounds in their initial states, as well as their oxides which obtained after calcinations, serve to update and enrich their spectral databases. Finally, chemical and physical characterization of raw natural dolomite will be the subject of a forthcoming work.

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