



XRD and Infrared study of limestone from Chadawanka (Tahoua, Niger)

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Abstract

This work is a contribution to improving knowledge on the natural limestone of Chadawanka (Tahoua, Niger). The collected limestone samples were analyzed by infrared spectroscopy. The results obtained, supplemented by those of the thermal analysis ATG-DTG and the X-ray diffraction (XRD), show that the Chadawanka limestone is calcite of high quality. X-ray diffraction shows that the structure of sample is hexagonal with space group $R\bar{3}C$. Unit cell parameters are: $a = 4,988 \text{ \AA}$, $c = 17,06 \text{ \AA}$ and $\gamma = 120^\circ$. Thermal analysis indicates two domains centered at 150°C and at 800°C correspond respectively to desorption of the adsorbed and structural water molecules and to the decomposition of CaCO_3 into calcium oxide (CaO) and carbon dioxide (CO_2). The ATG results show constancy in weight at 56.06 %. Using the mass loss associated with the decomposition of CaCO_3 , it is estimated that the sample consists exclusively of CaCO_3 . The fundamental vibrations of the CO_3^{2-} ion are observed around 1427 cm^{-1} , 874 cm^{-1} and 712 cm^{-1} . The band at 1427 cm^{-1} corresponding to the degenerate frequency ν_3 is attributed to the asymmetric stretching of the C-O bond. The band at 874 cm^{-1} corresponding to the single frequency ν_2 is attributed to an out-of plane bending of the C-O bond and the frequency ν_4 at 712 cm^{-1} is attributed to the planar bending vibration. A frequency value for the infrared-inactive normal vibration ν_1 has been obtained at 1085 cm^{-1} from the observed frequencies of the two combination bands.

1. Introduction

Carbonate rocks are composed by complex mixtures of minerals and are rarely formed by a pure mineral. They mostly contain calcium magnesium carbonate ($\text{MgCa}(\text{CO}_3)_2$) and calcium carbonate (CaCO_3). Thus, they can be classified into two dominant minerals: dolomite ($\text{MgCa}(\text{CO}_3)_2$) and limestone (CaCO_3) in the form of calcite, vaterite or aragonite [1-2]. The major elements of these minerals are calcium (Ca^{2+}), magnesium (Mg^{2+}) and carbonate (CO_3^{2-}) [3-5]. These major elements can be accompanied by other minor elements depending on the physical phenomena, spatial distribution of mineral mixtures or chemical compositions [2, 4, 6]. The most encountered minor elements are Si, Al, Fe, K and Na. These indicate the presence in small quantity of silicates (quartz, feldspar or clay). Various other elements can be incorporated in particular: Ag, B, Be, Ba, Bi, Br, Cl, Cd, Cr, Cu, Ga, Li, Mn, Mo, Pb, Rb, Sn, Sr, Ti, V, Y, Zn and Zr [7- 8].

Carbonate rocks are particularly used in the construction sectors as cement raw materials or in the agricultural industry. Rocks of high purity in calcite or dolomite are used in the production of fertilizers, in the neutralization of acid soils, in pharmaceutical products as additives, in stationery, in plastics or in paint [9-11]. In addition, calcium oxide (CaO) derived from calcite is used for water treatment or for desulfurization in gas pipes [9-11]. Calcium oxide also used to control pH or to precipitate metals and sulfates [10].

Carbonate minerals have relatively similar physical properties and are therefore difficult to distinguish. For example, calcite and dolomite crystallize respectively in the hexagonal and rhombohedral systems while aragonite which is of the same composition as calcite crystallizes in the orthorhombic system. However, in cold dilute hydrochloric acid calcite dissolves faster compared to dolomite. In addition, calcite is easier to grind compared to dolomite [12].

The use of these rocks in development projects requires a better knowledge and a thorough study of their physico-chemical characteristics. In this study, the results of the complementary use of vibrational spectroscopy (infrared), thermogravimetric analysis, and powder X-ray diffraction in the process of identification of the limestone from Chadawanka (Tahoua, Niger) is presented. The identification is based on the comparison of the results of our study with the corresponding literature data.

2. Material and Methods

2.1. Material

The elaboration samples in this study: white limestone has been collected at village of Chadawanka (Tahoua, Niger). The geographic coordinates of the area are Latitude N 14° 59' 56.8250''; Longitude E 6° 07' 18.0380''. The samples of the rock are crushed, and sieved to a particle size $\leq 125 \mu\text{m}$. This powder will be used for various analyzes.

2.2. X-rays diffraction

The XRD analysis was performed by a diffractometer model Siemens D5000 type, equipped with a copper anticathode (Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$), operating at 40 kV and 30 mA, on uncompressed powders in order to collect the maximum of the diffraction lines and a better identification of the phases. The diffractogram was recorded at room temperature in 2 θ mode by scanning from 5° to 120° in steps of 0.02°/s.

2.3. Thermal analysis

Thermogravimetric (ATG) analyzes were carried out using an A 5c 1000c apparatus in an inert atmosphere.

2.4. Fourier Transform Infra-Red

Samples were prepared for infrared analysis by the potassium bromide pressed-pellet technique at a concentration of 1%. The spectrum was performed in the range 400 to 4000 cm^{-1} on a Nicolet 20 SX Fourier transform spectrometer.

3. Results and discussion

3.1. X-rays diffraction analysis

The analysis of the X-ray diffraction spectra was done according to the AMCSD (American Mineralogist Crystal Structure Database). In the literature, it was shown that the X-ray diffraction makes it possible

to discriminate between minerals from the calcite group and aragonite. Namely, the rather intense diffraction maximum in calcite appear at around $2\theta = 30^\circ$ as well as the existence of a very strong maximum in the aragonite around $2\theta = 27^\circ$ [13].

The analysis of the X-ray diffraction shows that the structure is hexagonal with space group $R\bar{3}C$. Unit cell parameters are: $a = 4.988 \text{ \AA}$, $c = 17.06 \text{ \AA}$ and $\gamma = 120^\circ$. The X-ray diffraction spectrum is given in Figure 1. In table 1, the values of the inter-reticular distance of the sample spectrum are reported and are compared with those of the literature [14, 15]. These results indicate that the sample consists exclusively of calcite because no trace of another phase was highlighted.

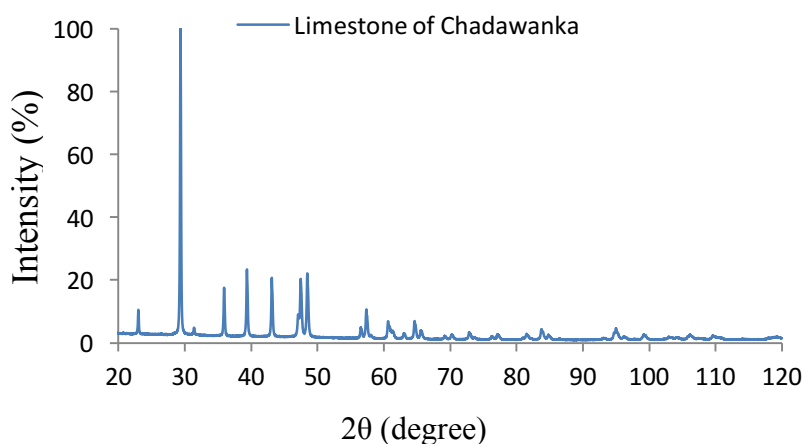


Figure 1: XRD spectra of limestone of Chadawanka.

Table 1: Comparison of the inter-reticular distances (d) with the values of the literature.

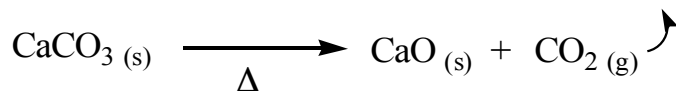
This work		Markgraf [14]		Antao [15]		This work		Markgraf [14]		Antao et al [15]	
d (Å)	Intensity	d (Å)	Int	d (Å)	Int	d (Å)	Int	d (Å)	Int	d (Å)	Int
3.86	w	3.85	m	3.85	w	1.60	w	1.60	w	1.60	vw
3.04	vs	3.03	vs	3.04	vs	1.53	w	1.52	w	1.53	w
2.85	vw	2.84	vw	-	-	1.47	vw	1.47	vw	1.52	vw
2.50	s	2.49	m	2.49	m	1.44	w	1.44	w	1.44	w
2.29	m	2.28	m	2.28	m	1.42	vw	1.42	vw	1.43	vw
2.10	m	2.10	m	2.09	m	1.36	vw	1.35	vw	1.34	vw
1.93	w	1.93	w	1.93	w	1.34	vw	1.34	vw	1.34	vw
1.91	m	1.91	m	1.92	m	1.30	vw	1.30	vw	1.30	vw
1.88	m	1.87	m	1.88	m	1.23	vw	1,23	vw	1.24	vw
1.63	vw	1.62	vw	1.63	vw	1.18	vw	1.18	vw	1.18	vw

vs : very strong; s : Strong ; m : medium ; w: weak; vw : very weak.

3.2. Thermal analyzes

The static method of thermal analysis involves the determination of the weight of the sample and the measurement of the temperature. It consists in heating the sample placed in the crucible suspended from the balance in the oven until the sample reaches a constant mass. It can, therefore, reveal only phenomena

associated with a loss or gain in weight. Changes in weight are involved in such reactions as the loss of carbon dioxide or water, and in the oxidation. Theoretical value indicates pure calcite and aragonite contain 56.08% CaO and 43.92% CO₂. The process of dissociation of calcite or aragonite is not reversible because carbon dioxide is lost in the atmosphere [16].



The thermal analysis is not able to distinguish between calcite and aragonite because it does not reveal the thermal effect that accompanies the transition. The ATG and DTG curves of the sample are shown in Figure 2.

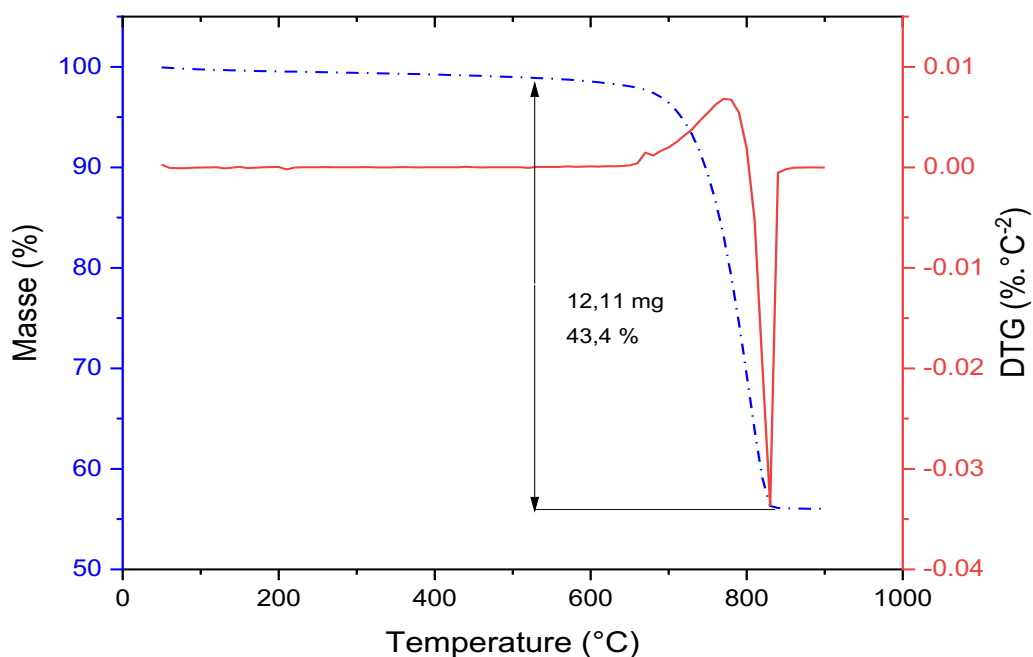


Figure 2: ATG and DTG curves of limestone from Chadawanka.

Figure 2 shows a domain centered at 150°C corresponding to desorption of the adsorbed and structural water molecules. Another area centered at 800°C corresponding to the decomposition of CaCO₃ into calcium oxide (CaO) and carbon dioxide (CO₂). The data in Figure 2 show constancy in weight at 56.06%. They are in accord with the theoretical value [16] and hence the sample was completely dissociated. Using the mass loss associated with the decomposition of CaCO₃ [17-18], it is estimated that the sample consists exclusively of CaCO₃. The ATG results are in agreement with those of the XRD.

3.3. Infrared spectroscopy

The main absorption bands of carbonate spectra in the 400-4000 cm⁻¹ wavenumber have been attributed to the carbonate ion (CO₃²⁻) due to the vibrations of the carbon and oxygen atoms along the crystallographic axes. The discrimination between the calcite and aragonite type of the carbonate minerals by infrared spectroscopy is a rather easy. Namely, due to the lower local symmetry of the CO₃²⁻ ions in the aragonite type minerals (C_s) compared to the calcite type (D₃). The free carbonate ion has the D_{3h} symmetry and six (3N-6, number of atoms) authorized normal modes of vibrations [19].

In the carbonate of the calcite type, fewer than the expected number of frequencies are generally observed because of the double degeneracy of two of the six frequencies, thus limiting to four the number of fundamental absorption bands characteristic of calcite minerals type. In the carbonate of the aragonite group, six fundamental frequencies are authorized because of removal of the degeneracies prevalent in ν_3 and ν_4 [19].

The frequencies correspond are:

- ✓ ν_1 : non-degenerate totally symmetrical stretching vibration;
- ✓ ν_2 : an out-of plane bending;
- ✓ ν_3 : doubly degenerate asymmetric stretching vibration;
- ✓ ν_4 : doubly degenerate planar bending vibration.

The vibrations allowed according to the selection rule for the different symmetry groups are reported in table 2 and the diagrams of the active vibration modes in IR and Raman are reported in figure 3.

Table 2: vibrations allowed according to the selection rule for groups D_{3h} , D_3 and C_s [20].

D_{3h} (ion libre)	D_3 (calcite)	C_s (aragonite)
A_1' (ν_1) Raman	A_1 (ν_1) active en Raman	
A_2'' (ν_2) IR	A_2 (ν_2) active en IR	A' ($\nu_1, 2\nu_3, 2\nu_4$) IR and Raman
E' (ν_3, ν_4) IR and Raman	E (ν_3, ν_4) IR and Raman	A'' (ν_2) IR and Raman

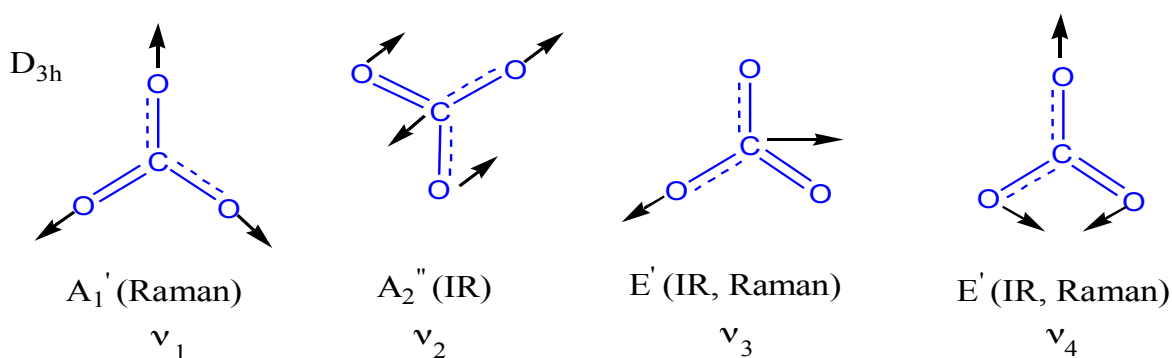


Figure 3: Diagrams of the active vibration modes in IR and Raman of the CO_3^{2-} ion.

Calcite and aragonite have the main vibration bands in common. However, the bands around 1083 cm^{-1} and 699 cm^{-1} are observed in the spectrum of aragonite but absent in that of calcite [21]. Figure 4 shows the IR spectrum of the sample. Table 3 gives the remarkable bands in this study compared to those of the literature.

The difference between the calcite and aragonite leads to appearance of the band due to the ν_1 mode in the spectrum of aragonite (at 1083 cm^{-1}) which is absent in the spectrum of calcite. Another difference between the two types of spectra is the appearance of two bands in the spectrum of aragonite (at 712 and 699 cm^{-1}) instead of one (at 712 cm^{-1}) in the spectrum of calcite in the region of the ν_4 [13].

The infrared spectrum of sample is show in Figure 4. The most intense bands around 1427 cm^{-1} , 874 cm^{-1} and 712 cm^{-1} correspond to the fundamental vibrations of the CO_3^{2-} ion. The wide and intense band at 1427 cm^{-1} corresponding to the degenerate frequency ν_3 is attributed to the asymmetric stretching of the

C-O bond. The Broadening of the band around 1427 cm^{-1} will indicate the presence of one or more crystalline forms in the sample. When one mineral predominates, broadening diminishes and a "shoulder" appears on either the shorter or longer wavelength side adjacent to the peak of the dominant form [21]. The shape of this band shows that the sample consists of a unique crystalline form.

Table 3: Remarkable infrared vibration bands of the sample compared to those of the literature.

Wavenumber of remarkable vibration bands			Assignments
This work	Hunt [22]	Huang [23]	
712 cm^{-1}	713 cm^{-1}	714 cm^{-1}	an in-of plane bending
874 cm^{-1}	877 cm^{-1}	877 cm^{-1}	an out-of plane bending
1427 cm^{-1}	1439 cm^{-1}	1434 cm^{-1}	asymmetric stretching
1797 cm^{-1}	1792 cm^{-1}	1818 cm^{-1}	$\nu_1 + \nu_4$
2512 cm^{-1}	2487 cm^{-1}	2551 cm^{-1}	$\nu_1 + \nu_3$

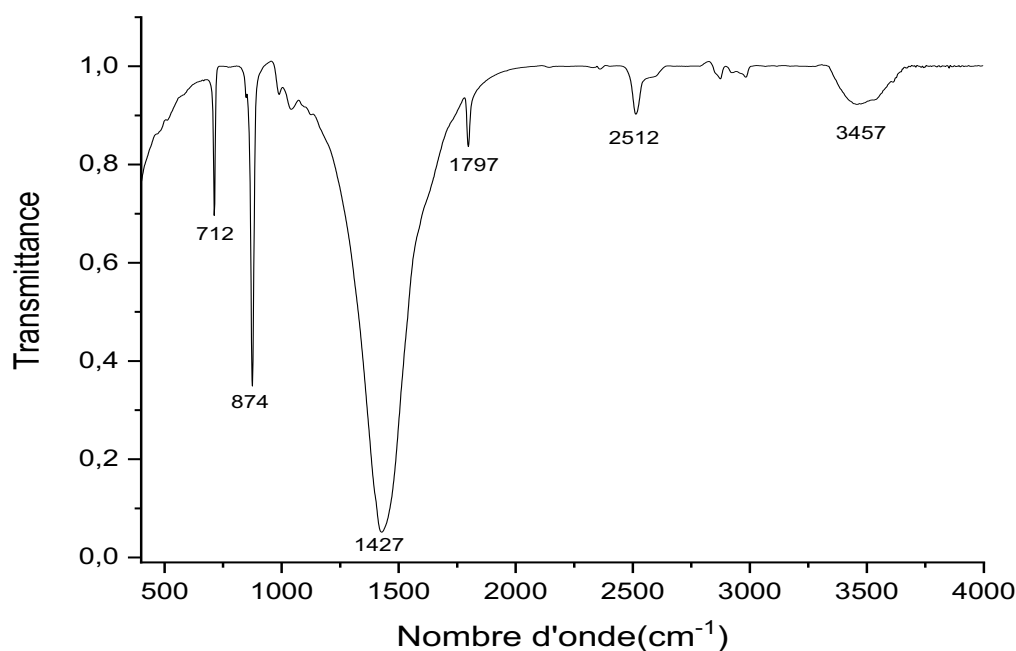


Figure 4: Infrared spectrum of limestone of Chadawanka.

The band at 874 cm^{-1} corresponding to the single frequency ν_2 is attributed to an out-of plane bending of the C-O bond [24]. In the pure calcium carbonate compound, this band was observed at 873 cm^{-1} [25]. The fundamental frequency ν_4 at 712 cm^{-1} in the spectrum is attributed to the planar bending vibration. This band makes possible to distinguish the different crystalline phases of limestone. Indeed, the investigations showed that it appears at 713 cm^{-1} in calcite, at 744 cm^{-1} in vaterite and as a doublet at 700 cm^{-1} and 713 cm^{-1} in aragonite [26, 27]. This result shows that the limestone used in this study is a calcite crystalline phase.

The two low intensity bands around 1797 cm^{-1} and 2512 cm^{-1} are respectively assigned to the combinations of the frequencies $\nu_1 + \nu_4$ and $\nu_1 + \nu_3$. These bands allow us to find the frequency of the fundamental vibration ν_1 inactive in IR at 1085 cm^{-1} . This value is agree to that (1088 cm^{-1}) obtained by Porto et al. from the polarized Raman spectrum of calcite [28]. This result further confirms that the sample consists only of calcite. The bands at around 3100 cm^{-1} and 3457 cm^{-1} are respectively assigned to the symmetric and anti-symmetric stretching of the O-H bond of water according to the literature [25].

4. Conclusion

This objective of this work is a contribution to improving knowledge on the limestone accumulations of Chadawanka (Tahoua, Niger). This objective is justified by the fact that these accumulations are little known because very little work has been done. The study of the sample by XRD and FTIR spectroscopy allow us to conclude that the sample is in calcite form. The frequency of the fundamental vibration ν_1 inactive in IR is observed at 1085 cm^{-1} .

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