CHEMICAL AND MINERALOGIC STUDY OF MADAGASCAR CORAL BY SPECTROSCOPY

Andriambinintsoa Ranaivoson Tojonirina

Department of Chemistry, Mineral Chemistry and Industrial Chemistry, Faculty of Sciences-University of Antananarivo, Madagascar-P.O. box 906.

ABSTRACT

Developing countries are faced with the problem of poor nutrition including calcium and magnesium deficiency. However, hard coral is surrounded by an external skeleton, rich in calcium carbonate, which it builds as it grows. They usually live in colonies and form coral reefs. Sometimes pieces of the reef break away from the colony and migrate to the bottom of the sea where they fossilize. Our goal is to study the corals of Madagascar, which are part of the natural marine environments of the east coast of the Grande-ile. Thus, in the first place, the determination of the chemical composition of the coral of Madagascar, on the one hand, by X-ray fluorescence spectroscopy for the chemical elements at Z> 12, and on the other hand, by atomic absorption spectroscopy for the element Mg at Z = 12 not detectable by X-ray fluorescence spectroscopy because of the spectroscope detector. These two methods have shown the absence of toxic chemicals in the corals of Madagascar. In the second place, the determination of the mineralogical composition of the coral of Madagascar by X-ray diffraction spectroscopy of Debye-Scherrer. This method shows that the corals of Madagascar are constituted by the aragonite crystal structure in accordance with the literature. Our study has shown that it is possible to enhance the exoskeleton of corals in Madagascar, which is composed of 91.5% CaO, including 65.36% calcium and 0.21% magnesium.

Keywords: *coral, spectroscopy, aragonite, calcium, magnesium, Madagascar*

1. INTRODUCTION

Developing countries face the problem of calcium and magnesium deficiency because the cost of pharmaceuticals for dietary calcium and magnesium intake is exorbitant. Our study aims to study the chemical and mineralogical composition in order to determine the amount of calcium and magnesium in Madagascar coral, for a possible preparation of a food supplement rich in calcium [1]. Hard coral is surrounded by an outer skeleton (rich in calcium carbonate) that it builds up as it grows. They usually live in colonies and form coral reefs. Sometimes pieces of the reef break away from the colony and migrate to the bottom of the sea where they fossilize [2]. Corals are marine animals, living in symbiosis with algae that make up their own limestone skeleton. These coral structures provide shelters for the thousands of species that make up the coral community. The reefs represent a great geomorphological diversity such as: the fringing reef, the barrier reef, the atoll, the reef bench, the herbaria of phanerograms, the mangroves which are very productive biological systems, reproduction and nursery areas which fix the sediment and coastal protection agents against storms and coastal erosion. These ecosystems would occupy about a third of the shallow tropical coasts of the world: 15% for coral reefs (about 600,000 km2 on the surface), 9% for mangroves, 9% for seagrass [6]. As corals are 97% calcium carbonate [9], which is a mineral that can give two isomorphic series:

- Aragonite structure :

  Crystal system: Orthorhombic

  Crystalline parameters:

  a o = 4,959A°

  b o = 7,968A°

  c o = 5,741A°

  Space group: D162h - Pmcn

- Calcite structure:
  Crystal system: Rhomboedric
  Crystalline parameters:
  a o = 4,989A°
  c o = 17,062A°
  Space group: D62d - R3c

Indeed, in the context of food nutrition, the elements calcium and magnesium are essential constituents: The element calcium is involved in the phenomenon of osteogenesis: bone tissue is made up of $Ca_3 (PO_4)_2$, in the nervous system, in blood coagulation: the blood contains about 75 to 160 mg of calcium per liter, which allows the in stopping the bleeding and in regulating the body for enzyme activation [7]. The element magnesium, of which our daily needs are 350 to 480 mg per day, is involved in nervous balance: the nervous system is dependent on the calcium / magnesium balance; in all the biochemical processes of our organism: the synthesis of nucleic acids and proteins, cell production, in the treatment of thrombosis and cancer [3]. Corals are part of the natural marine environment, animals living in symbiosis with algae and constituting their own limestone skeleton [4]. In addition, Madagascar is a maritime country where we find one of the largest coral reefs in the world, in the eastern and south-eastern part of the island [5]. Thus, it is interesting to make a chemical and mineralogical study on the composition of the corals of Madagascar.

2. METHODOLOGY

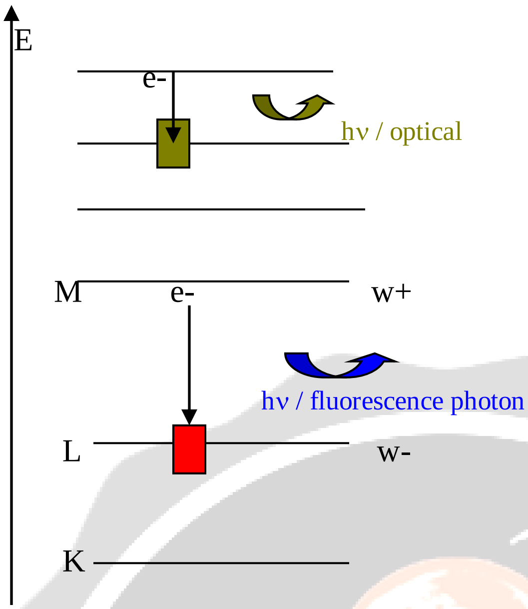
2.1. Study zone

The coral used for the study is found in the south-eastern part of Madagascar.

Fig-1: Localization of coral from Madagascar

2.2. X-ray fluorescence spectroscopy

X-ray fluorescence spectroscopy allows the determination of the chemical composition as well as the concentration of a sample.



We then have:

Atom / sample → gap on K

gap on K ↓ Replenishment of K ↓ Photon emission X_K

Strong excitement (MeV ou KeV) ↑ Atom / sample

photon X

photon γ

-If a gap on K: deexcitation on K, where RX of fluorescence X_K: K_α, K_β
-If a gap on L: de-excitation on L, where RX fluorescence XL: Lα, Lβ, Lγ
-If a gap on M: deexcitation on M, where XM fluorescence RX: Mα, Mβ, Mγ
This fluorescence X photon of energy **E = hν**, is characterized by frequency and intensity.

Frequency ν

$\nu^{1/2} = a\,(Z - b)$ *(Relation de Moseley)*

a et b : constants

Z : atomic number

Intensity I_i

$I_i = S_i \,.\, A_i \,.\, C_i$

$I_i = f\,(Ci),\ (\delta f / \delta Ci) > 0$

I_i: Intensity.

C_i: Concentration.

I_f: sensitivity of the analysis chain. It depends on the geometry of the system and the efficiency of the detector.

Ai: absorption factor. It tends towards unity for a thin sample.

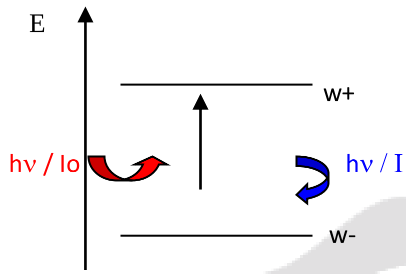
2.3. Atomic absorption spectroscopy Atomic

Atomic absorption spectroscopy is used to highlight the chemical composition of a sample.

Atomic absorption spectroscopy uses as:

- The energy radiation: electro-magnetic radiation in the visible range (λ <µ).
- The energy system: the external electrons of the atom.

The process is absorption process with de-excitation of the atom [14].



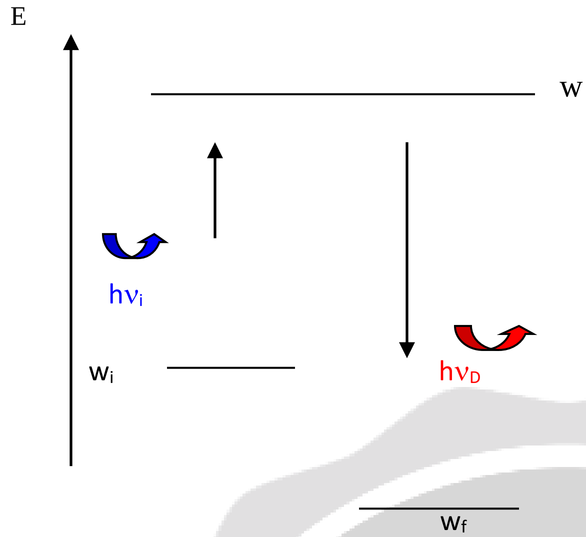
The de-excitation of the atom leads to the absorption of a photon characterized by:
-its frequency, characteristic of the atom.
-its intensity, characteristic of its concentration.
This results in an absorption of radiation linked to the concentration of the element considered by a relation of the form [16]:

$\log I_0/I = k \cdot l \cdot C$

Such that: I <Io (Beer's law - Lambert)
I_o: Intensity of incident monochromatic light beams
I: Intensity of the emerging monochromatic light beams.
l: Thickness of the solution (cm)
C: Concentration of the absorbent body in the solution (g / l)
k: Molecular excitation coefficient. Its value depends on the temperature, the nature of the dye, the wavelength of the incident light.

2.4. X-ray diffraction spectroscopy

X-ray diffraction makes it possible to determine the mineralogical composition of a compound. In X-ray diffraction spectroscopy, we have as:
-Energy radiation: RX (electro-magnetic λ ~ A °)
-The energy system: atom (electron or electrons)
-The Process: coherent X-photon scattering [14].



Statement: $w_i + h\nu_i = w_f + h\nu_D$
for, $w_i = w_f$,
we have, $h\nu_i = h\nu_D$

The method used to obtain X-ray difraction figures is the Debye-Scherrer powder method [17].
A parallel beam of monochromatic X-rays falls on a sample as a powder contained in a thin-walled capillary glass tube, arranged on a fiber.
The powder consists of finely divided crystals, oriented at random.
A certain number of these crystals whose reticular planes of Miller index h, k, l, of distance dhkl, making the angle θ with the incident ray verify the Bragg relation:

$$n\lambda = 2\, d_{hkl} \sin\theta$$

n : *Diffraction order*
λ : *X-ray wavelength.*
d_{hkl} : *Distance between the reticular planes of Miller indices h,k,l.*
θ : *Bragg angle.*

The crystals whose reticular planes verify this relationship give rise to rays diffracted in the 2θ direction. The method then consists in recording the angle θ of diffraction for each group of rays diffracted by a family of reticular planes of Miller index h, k, l and inter-distance d_{hkl}. We obtain a diffractogram giving the angular position and the intensity of the X diffraction lines using an X photon detector.

3. RESULTS AND DISCUSSIONS

3.1. X-ray fluorescence spectroscopy results

The results of the X-ray fluorescence spectrometry analyzes of the coral sample.

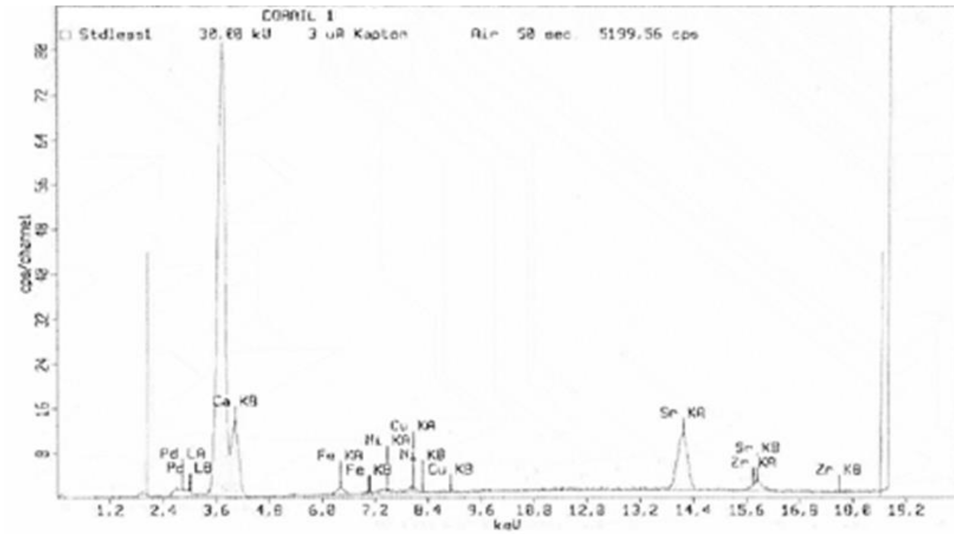


Fig-2: X-ray fluorescence spectrum of coral from Madagascar

The elements given by the spectrometer are in oxide form, table 1 shows the concentrations expressed as % in oxide and % in element.

Table-1: Concentration of elements of Coral from Madagascar

Coral elements	Oxides	Oxides (%)	Elements (%)
Ca (Z = 20)	CaO	91.5%	65.36%
Fe (Z = 26)	Fe_2O_3	0.68%	0.47%
Ni (Z = 28)	NiO	0.09%	0.07%
Cu (Z = 29)	CuO	0.27%	0.21%
Sr (Z = 38)	SrO	2.9%	2.39%
Zr (Z = 40)	ZrO	0.08%	0.07%
Pd (Z = 46)	PdO	4.4%	3.76%
		Σ Ci = 99,92%	**Σ Xi = 72,33%**

3.2. Atomic absorption spectroscopy results

After a measurement on the absorption spectrometer, we were able to obtain the amounts of magnesium and calcium present in coral. The results are collated in Table 2.

Table-2: Results of absorption spectroscopy

Magnesium	**Dilution**	**Reading**	**X(ppm)**	**X(%)**	**X(%o)**
1st Test	1/10 1/100 1/1000	-- 0,41 --	-- 2052 --	-- 0,207 --	-- 2,06 --
2nd Test	1/10 1/100 1/1000	-- 0,41 --	-- 2049 --	-- 0,205 --	-- 2,05 --
3rd Test	1/10 1/100 1/1000	-- 0,41 --	-- 2049 --	-- 0,203 --	-- 2,04 --

3.3. X-ray diffraction spectroscopy results

The X-ray diffraction spectrum of coral is given in figure 3.

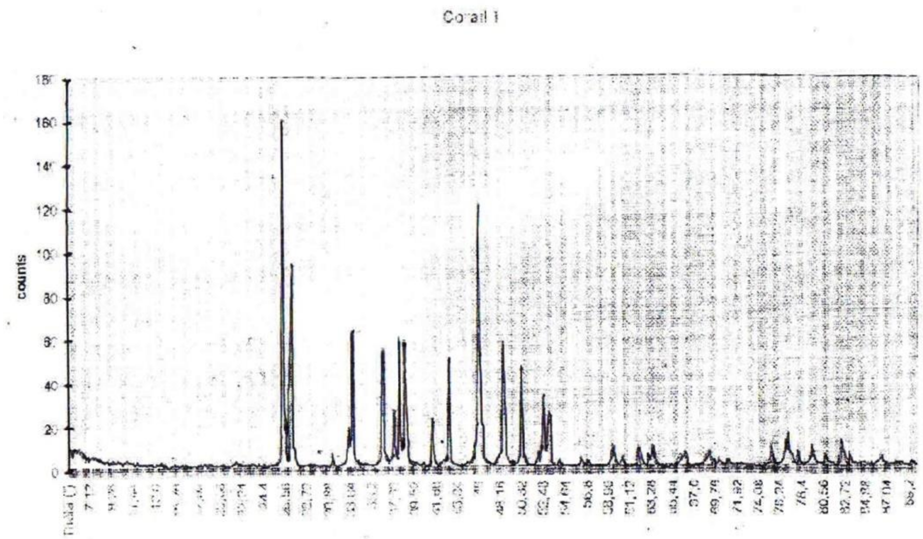


Fig-3: X-ray diffraction spectrum of coral from Madagascar

We have the results of the analysis of the X-ray diffraction spectroscopy.

Table-3: Analysis of the X-ray diffraction spectroscopy of coral

CORAIL

Theta (°)	Sin(Theta)	d_{hkl}(A°)	I(mm)	I/Io(%)	I/Io
13,08	0,2263113	3,403	49,2	30,9	f
13,12	0,2269913	3,393	159,1	100	TF
13,16	0,2276711	3,383	136,6	85,9	F
13,6	0,2351421	3,276	52,5	33	f
13,64	0,2358206	3,266	93,8	59	m
13,68	0,236499	3,257	48	30,2	f
16,56	0,2850193	2,702	52,8	33,2	f
16,6	0,2856884	2,696	62,9	39,5	f
18,08	0,3103446	2,482	53,8	33,8	f
18,12	0,3110082	2,477	56,2	35,3	f
18,96	0,324908	2,371	61,4	38,6	f
19	0,3255682	2,366	41	25,8	tf
19,24	0,3295259	2,337	59,8	37,6	f
19,28	0,3301849	2,333	40,5	25,5	tf
21,48	0,3661764	2,103	51,5	32,4	f
22,92	0,3894455	1,978	91,1	57,3	m
22,96	0,3900884	1,975	122,8	77,2	F

23	0,3907311	1,971	81,7	51,4	m
24,16	0,4092862	1,882	46,6	29,3	tf
24,2	0,409923	1,879	58,8	37	f
24,24	0,4105597	1,876	54,9	34,5	f
25,12	0,4245155	1,814	47,2	29,7	tf

f: low
tf: very low
m: average
F: high
TF: very high

3.4. Discussions

We compare the diffractogram of coral1 from Madagascar with the X-ray diffractograms of aragonite and calcite. The X-ray diffractogram of each mineral is given on the ASTM sheet.

Table-4: Comparison of diffractograms of coral with that of aragonite and calcite.

CORAL (Taolagnaro)		**$CaCO_3$ ARAGONITE structure / ORTHORHOMBIC** a $_o$ = 4,959A° b $_o$ = 7,968A° c $_o$ = 5,741A° ASTM (5-0453)		**$CaCO_3$ CALCITE structure / RHOMBOEDRIC** a $_o$ = 4,989A° c o = 17,062A° *ASTM (5-0586)*	
d$_{hkl}$ (A°)	**I/Io (%)**	**d**$_{hkl}$ (A°)	**I/Io (%)**	**d**$_{hkl}$ (A°)	**I/Io (%)**
		4,212	2		
3,404	30,92			3,86	12
3,393	100	3,396	100		
3,383	85,86	3,273	52		
3,276	33				
3,266	58,96				
3,257	30,17				
				3,035	100
2,702	33,19	2,700	46	2,845	3
2,696	39,53				
2,482	33,82	2,481	33	2,495	14
2,477	35,32				
		2,409	14		
2,371	38,59	2,372	38		
2,366	25,77				
2,337	37,59	2,341	31		
2,333	25,46				
2,104	32,37			2,285	18
1,978	57,26	2,106	23		
				2,095	18

1,975	77,18	1,977	65		
1,971	51,35				
1,882	29,29			1,927	5
1,879	36,96			1,913	17
1,876	34,51	1,877	25		
1,814	29,67				
				1,875	17
		1,814	23		
		1,742	25		
		1,728	15		
				1,626	4
				1,604	8
				1,587	5
		1,557	4		
				1,518	4
				1,510	3
				1,473	2
		1,466	5		
				1,422	1

It can be seen that the main X-rays of the aragonite structure are observed on the two samples of corals from Madagascar.
It is deduced from this that the samples of the corals consist of $CaCO_3$ in the Aragonite form.

4. CONCLUSIONS

Developing countries face the problem of calcium and magnesium deficiency. However, in this work, the hard coral is surrounded by an external skeleton rich in calcium carbonate that it builds as it grows. During this study, we were able to determine the composition of Madagascar's coral, whether chemical or mineralogical. In determining the chemical composition, we used two methods including:

- X-ray fluorescence spectroscopy, which shows that Madagascar's coral is mainly composed of 91.5% CaO, its means 65.36% of Calcium and other compounds in very small quantities. And after this analysis, in comparison with the toxic elements of the literature, the coral of Madagascar does not contain poison elements such as: Pb, As, Sc, Cr VI, Cyanides, Cd, Ba, and NO_3.
- As X-ray fluorescence spectroscopy does not detect the element magnesium, we used atomic absorption spectroscopy which diffraction gives: 0.205% magnesium in the coral of Madagascar. In the determination of the mineralogical composition, we used X-ray diffraction spectroscopy which allows to demonstrate that the coral of Madagascar crystallizes in the aragonite form of calcium carbonate CaCO3.

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