

PHYSICO-CHEMICAL CHARACTERIZATION OF THE APATITE ORE OF MADAGASCAR BY THE OPTIC EMISSION SPECTROMETRY TO SOURCE PLASMA OF ARGON COUPLES BY INDUCTION (ICP-OES)

Andry Judicaël Ravelona, Andriambinintsoa Ranaivoson Tojonirina, Raharimalala Laurence
Eliane

*Chemistry department - Inorganic chemistry and Industrial Chemistry Laboratory
Faculty of the Sciences-Domain Sciences and Technologies-University of Antananarivo-Madagascar-
P.O. BOX. 906*

ABSTRACT

The ore of apatite is part of ores that constitutes the basement of Madagascar. Numerous research have been done by different methods and one could note that the phosphor is the essential element that constitutes this ore. For our survey a new method has been used in order to really characterize the ore of apatite of Madagascar and this method that is the optic broadcast spectrométrie to source plasma of argon coupled by induction (ICP-OES). According to the literature and our research, this method has never been used for the analysis of the ore of apatite. For our work, one did the methodology that determines the zone of survey of the sampling, the characteristic and the temperature of plasma shown by the different in the first place represent the determination of the diagram of the device and the limits of detection of the optic broadcast spectrométrie then to source plasma of argon coupled by induction (ICP-OES). In second place the results and interpretations as well as the discussions of the analyses done on this ore of apatite. Our survey shows that the analysis of the ore of apatite by this method permits to determine with precision the cations essentials of which aluminum, calcium, chromium, copper, iron, magnesium, manganese, sulfur, sodium, silicon, titanium and the with their respective spectrgrams and the cations in state of trace by their respective concentrations as well as the concentrations of the metallic oxides that compose the ore of apatite of which the calcium carbonate to 56mgL-1 et the dioxide of silicon to 0,96mgL-1 is the main oxides.

Keywords: spectrométrie, precision, ore, apatite, plasma, induction.

I-INTRODUCTION

Madagascar contains a lot of ores and of minerals in his/her/its basement. The apatite is a calcium phosphate [1] It is an ore containing phosphate chlorine, fluorine and the OH ions - [2]. According to the dominance of these three components one speaks of fluorapatite, chlorapatite and hydroxyapatite [3]. The domains of use of the phosphor are developed extensively active of agriculture, of medicine until the technology. The particular chemical composition of the apatite it is the phosphor but there are also other chemical elements that have already been found in done several analyses. It is in this optics that we go to make the survey of the ore of apatite of Madagascar by determination of the chemical compositions by optic broadcast spectrométrie to source plasma of argon coupled by induction (ICP-OES)

Indeed, according to our research, this spectroscopic method is not used again on the survey of the ore of apatite of Madagascar of which one can see with precision all chemical compositions of that will mine those that are in state of trace even [6]. Otherwise, this method uses the plasma that is the fourth state of matters after The strong, the liquid, gas and plasma. Of the loaded gases electrically or "ionized gas."

Plasma requires a contribution of energy to maintain, it is very "hot" in the core, generally between 6 000 to 10 000°C.[6]

2.METHODOLOGY

2.1. Area study

The apatite used for the study is in the south part of Madagascar, in the region of Betroka, in the township of Soanala. The relief to the East of Soanala has a torrential character. In the west he/it is composed of pénéplaines where only the rocks very resistant to the erosion subsist. The main summits of the region are extended enough trays to an altitude adjoining 1500m and of which the lines of the crests between them have the same altitude (Mouflard, 1952).

The main mining resource is essentially constituted by mines of mica. Besides this zone is rich in minerals and stones gems as quartz, the apatite, the ruby, the sapphire and the garnet, and in industrial minerals as graphite, the pyrites and the monazite. [4]

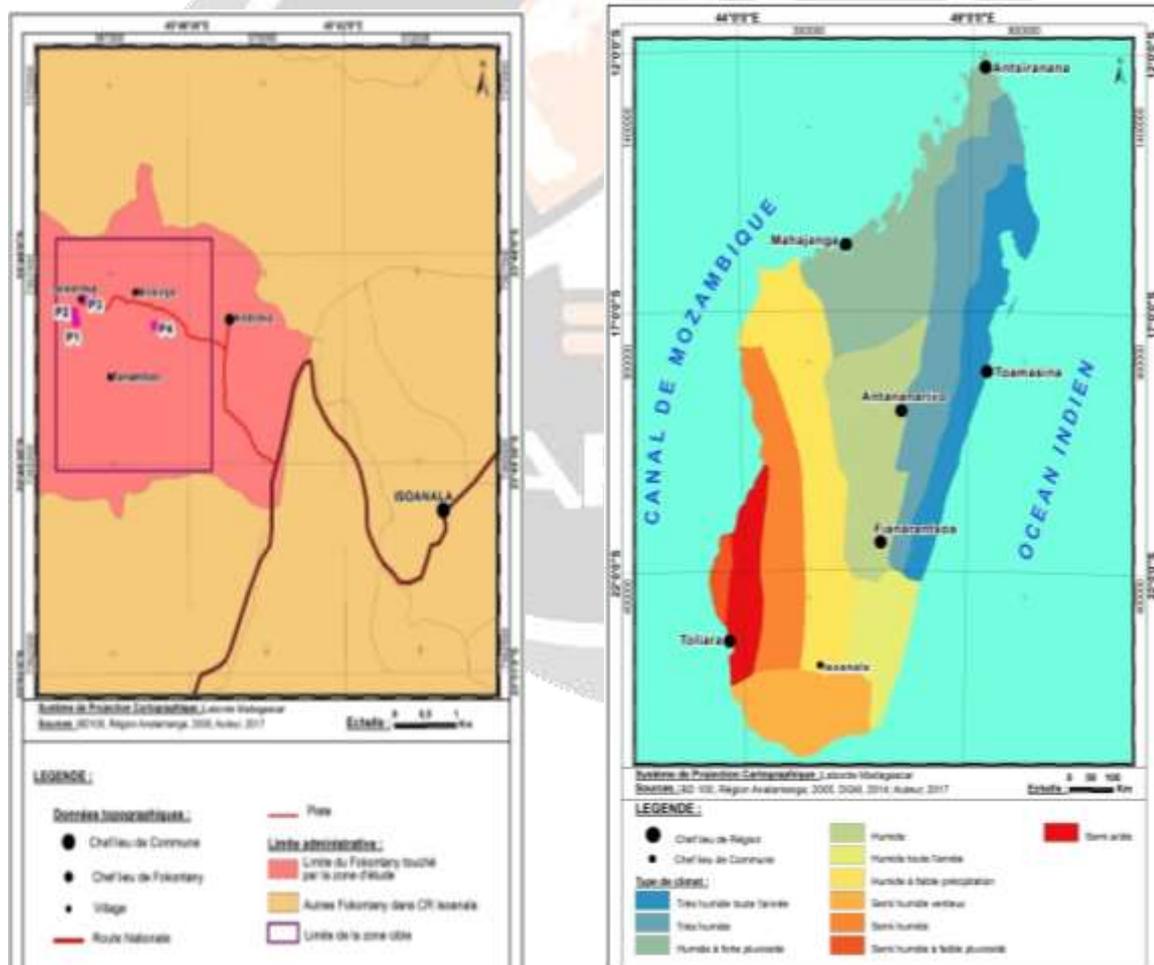


Fig-01 : location of the apatite ore of Madagascar [8]

2.2. Optic broadcast Spectrométrie has source plasma of argon couples by induction (ICP-OES)

2.2.1 Diagram of the device of the plasma of the ICP

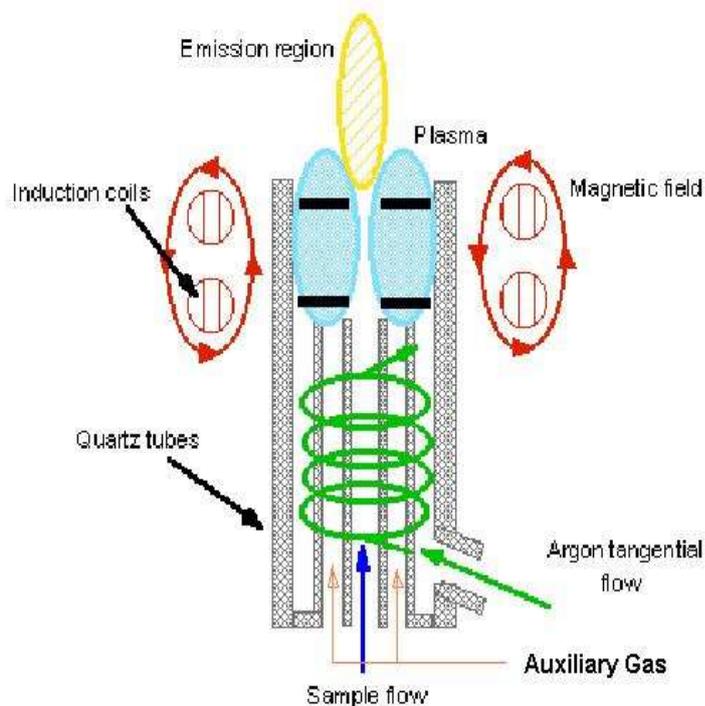


Fig-02 : diagram of the device of the plasma of the ICP [6]

2.2.1. Characteristic of plasma

The characteristic of plasma is shown by the figure 03.

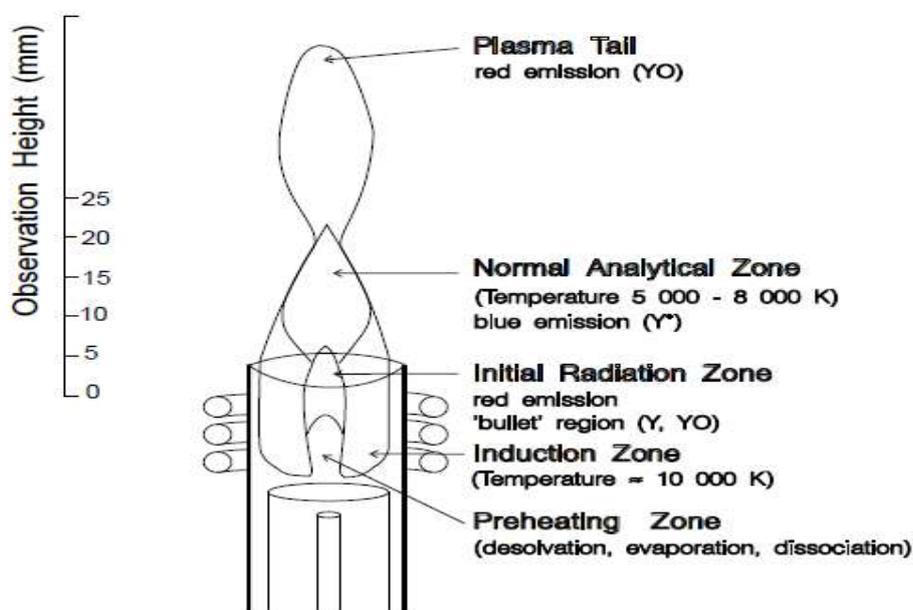


Fig-03 : Characteristic of plasma [6]

2.2.2. Temperature of Plasma

The temperature of plasma is given by figure 04.

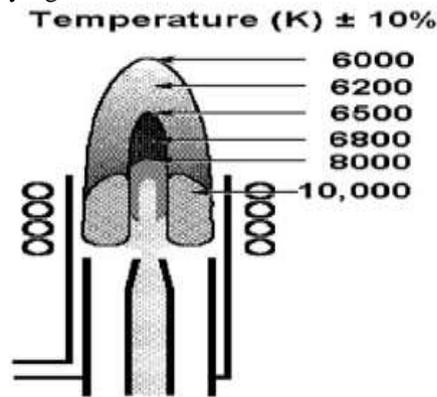


Fig-04 : Temperature of Plasma [6]

The analytic zone is cold in more the gas of the spray diffuser can cool it again more.

The zone of plume is the coldest part of the plasma and the molecules can form themselves.

Plasma has like source of emission

- The high sensitivity
- The 6 orders of magnitude linearity
- The relatively free matrix effect

2.2.3. Limits of detections of the the ICP-OES

The table 01 shows the elements detected by the ICP-OES

Table 01. . Periodic table of Mendeleïev showing the elements detected by the ICP-OES [7]

ICP-AES Detection Limits (µg/L)																		
Li 0.3	Be 0.1	DL's are based on PE3000 with radial view. Axial view has 5 to 10 times lower DL's.											B 1	C 40	N na			
Na 3	Mg 0.1												Al 3	Si 4	P 30	S 30	Cl na	
K 20	Ca 0.02	Sc 0.3	V 0.5	Ti 0.5	Cr 2	Mn 0.4	Fe 2	Co 1	Ni 5	Cu 0.4	Zn 1	Ga 4	Ge 20	As 20	Se 50	Br na		
Rb 30	Sr 0.05	Y 0.3	Nb 5	Zr 0.9	Mo 3		Ru 6	Th 5	Pd 3	Ag 1	Cd 1	In 9	Sn 30	Sb 10	Te 10	I na		
Cs 10	Ba 0.1	La 1	Hf 4	Ta 15	W 9	Re 5	Os 0.4	Ir 5	Pt 10	Au 4	Hg 1	Tl 30	Pb 10	Bi 20				
		Ce 5	Pr 1	Nd 1		Sm 2	Eu 0.1	Gd 1	Tb 2	Dy 2	Ho 0.4	Er 1	Tm 0.6	Yb 0.3	Lu 0.2			
							Th 70											

2.2.4. Device of an ICP-OES spectrometer

The figure 05 shows the device of an ICP-OES spectrometer

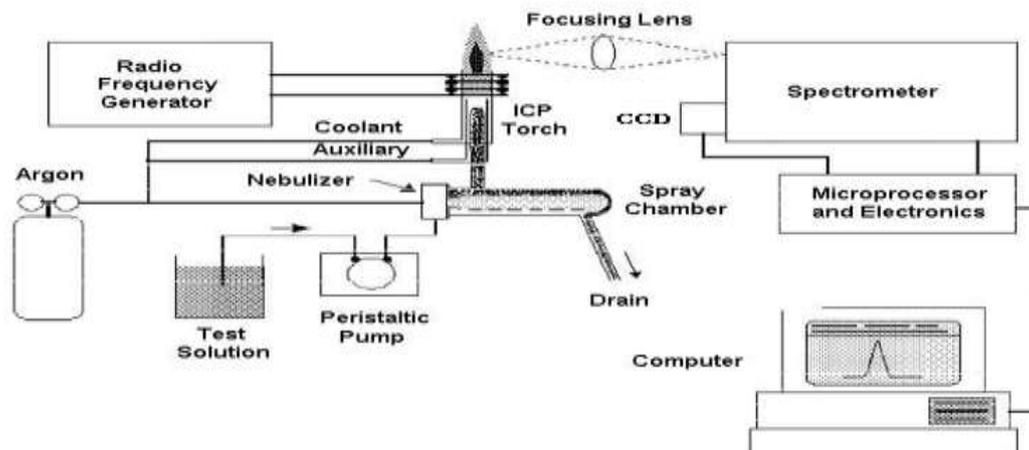


Fig-05 : Device of an ICP-OES spectrometer [6]

The samples are analyzed with the help of an optic broadcast spectrometer to the plasma of argon to coupling inductive Varian 725 are.

3. RESULTS AND DISCUSSION.

75 elements can be detected by ICP-OES [9] of which has some:

Aluminum, Calcium, Copper, Iron, Chromium, Magnesium, Manganese, Sulfur, Silicon, Titanium, Sodium, ..

So we could get the specters of optic emission of these differents elements.

Here is the specter of respectively optic emission of the cations contained in the apatite ore detected by the ICP-OES spectrometer

3.1. Aluminum

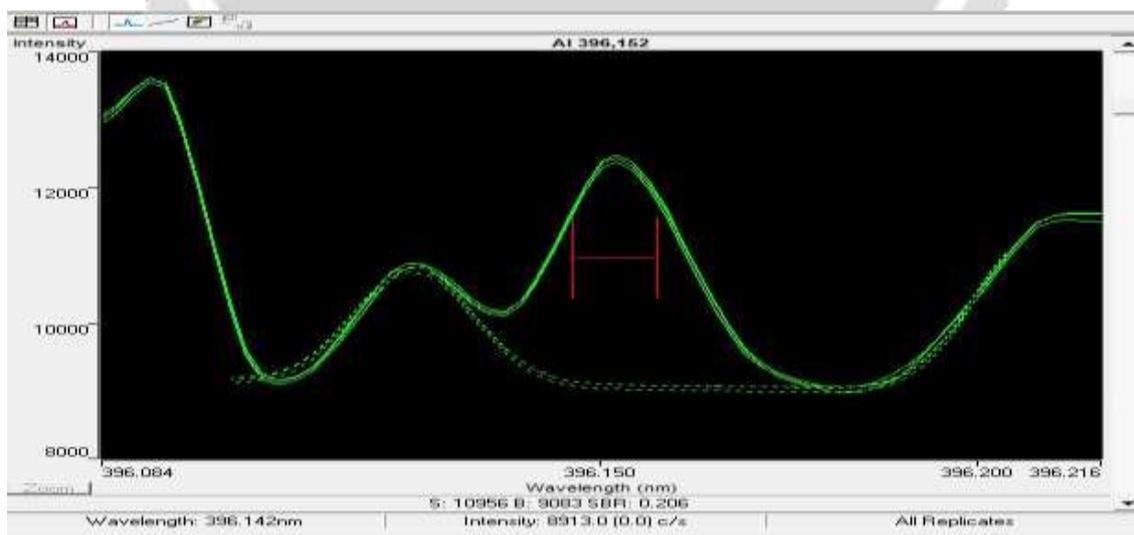


Fig-06 : Optic emission spectrum of aluminum

The wavelength of aluminum is 396,152 nm and its intensity is 8913 c/s

3.2. Calcium

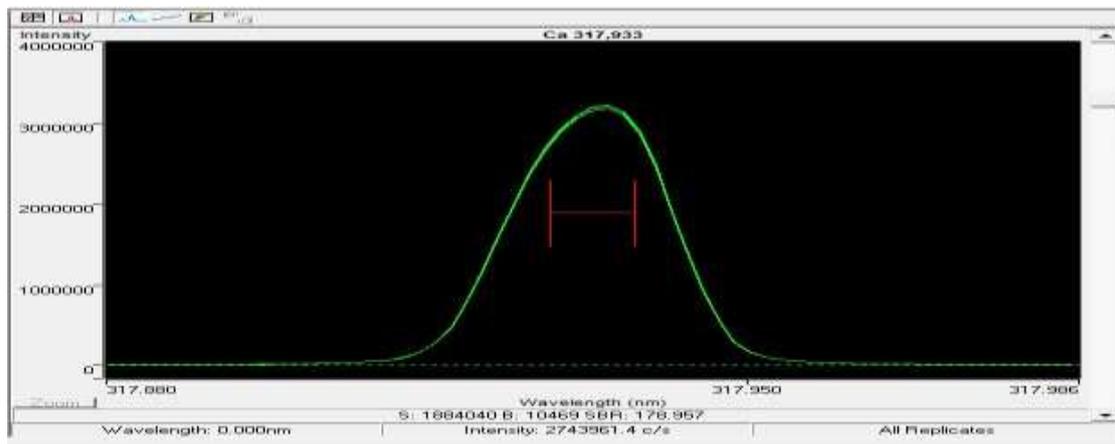


Fig-07 : Optic emission spectrum of calcium

The wavelength of the calcium is 317,933 nm and its intensity is 2743961 c/s

3.3. Chromium

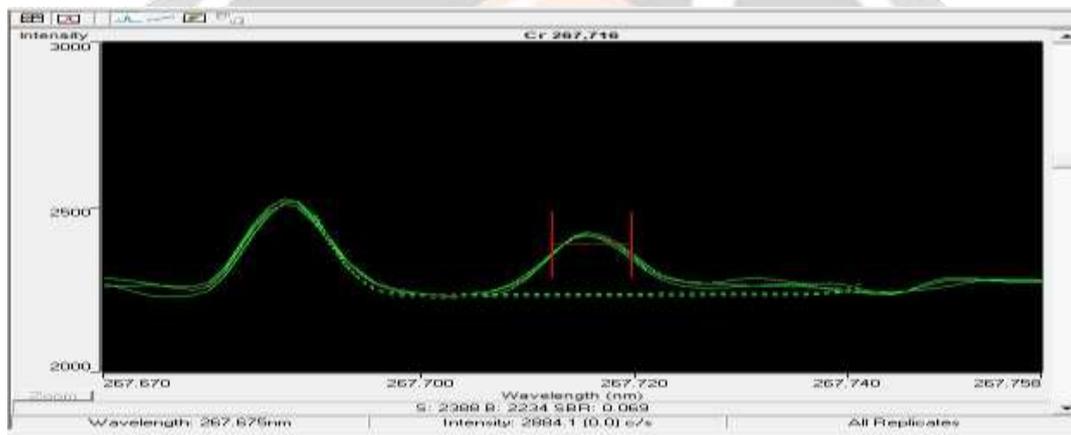


Fig-08 : Optic emission spectrum of chromium

The wavelength of the chromium is 267,716 nm its intensity is 2884,1 c/s

3.4. Copper

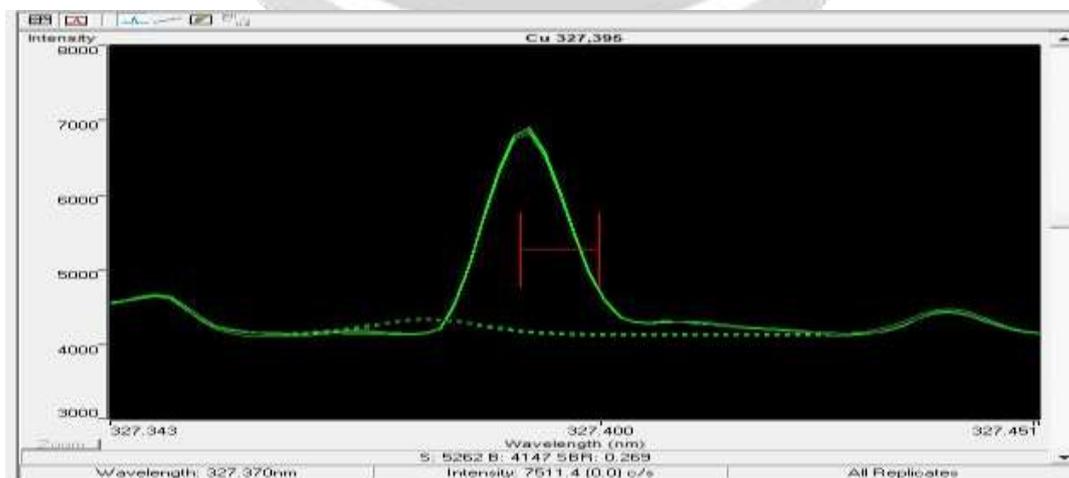


Fig-09 : Optic emission spectrum of copper

The wavelength of the copper is 327,395 nm and its intensity is 7511,4 c/s

3.5. Iron

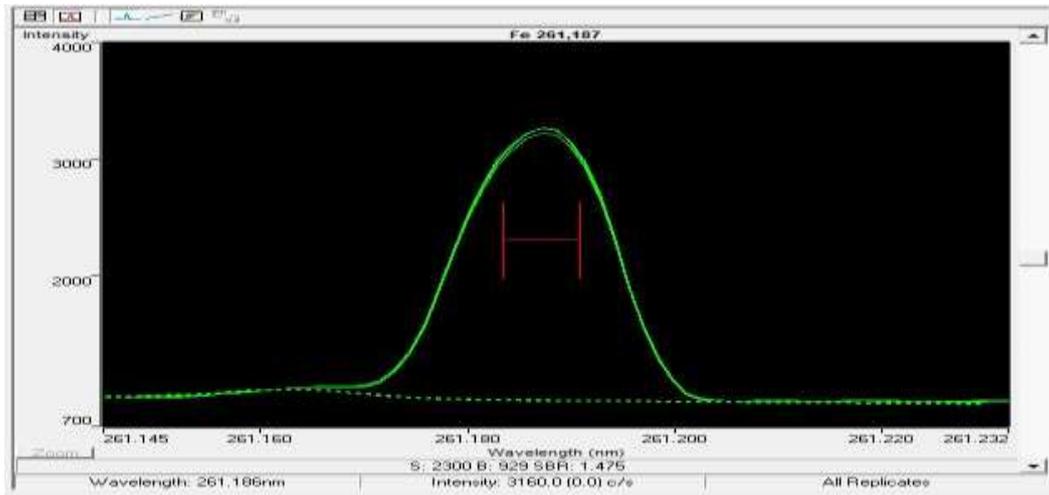


Fig-10 : Optic emission spectrum of iron

la longueur d'onde du cuivre est de 261,187 nm et son intensité est de 3160 c/s

3.6. Magnesium

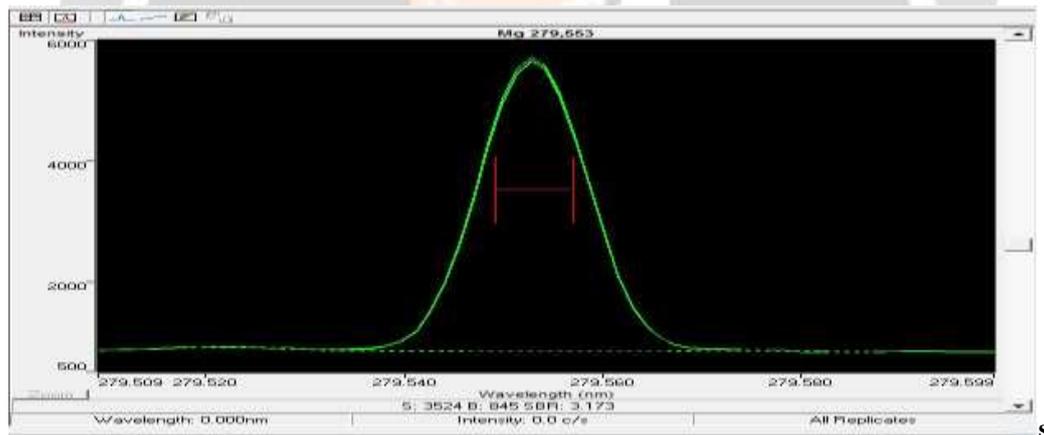


Fig-11 : Optic emission spectrum of magnesium

The wavelength of magnesium is 279,553 nm and its intensity is below the detection limit

3.7. Manganese

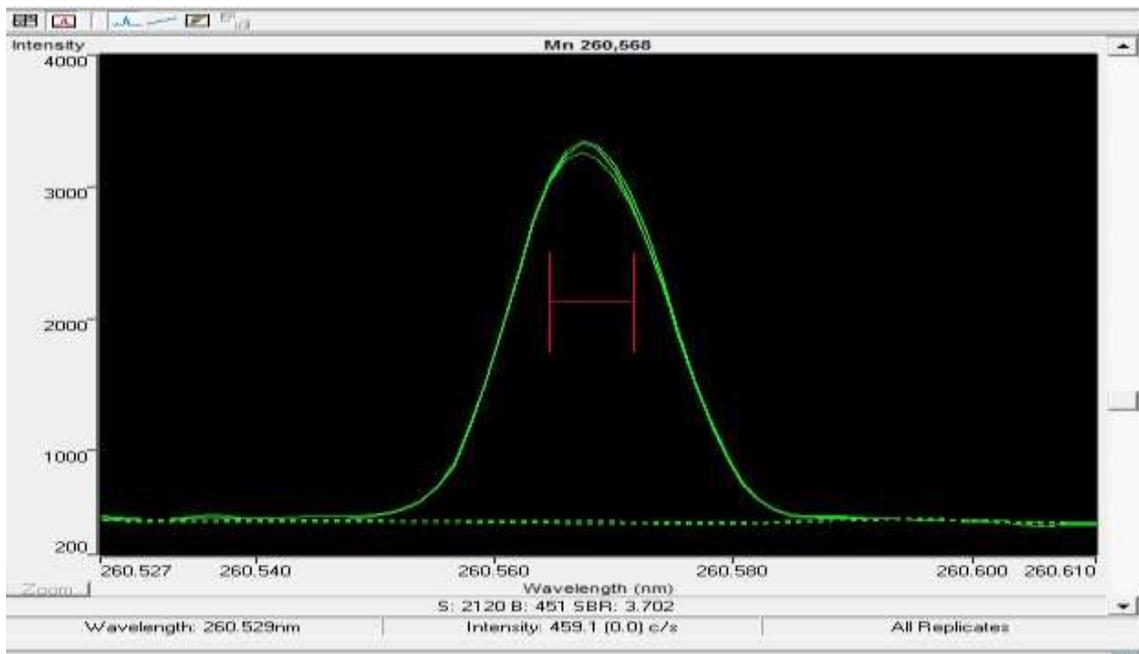


Fig-12 : Optic emission spectrum of managanese

The wavelength of the manganese is 260,568 nm and its intensity is 459,1 c/s

3.8. Sulfur

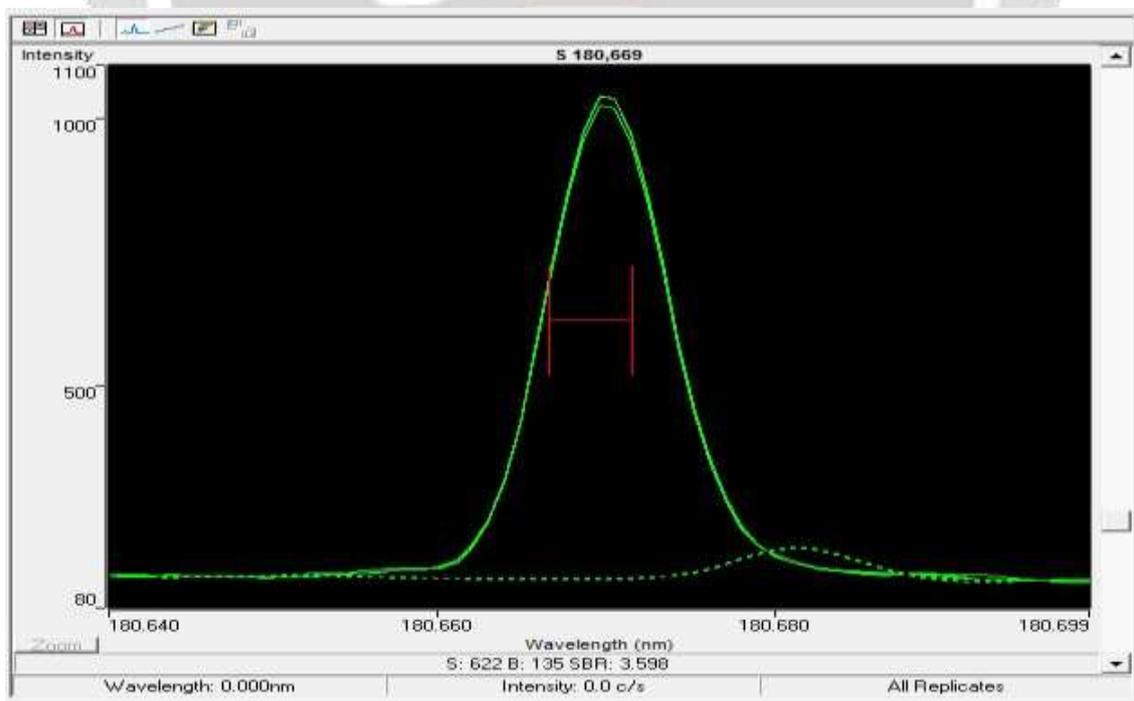


Fig-13 : Optic emission spectrum of sulfur

The wavelength of sulfur is 180,669 nm and its intensity is below the detection limit

3.10. Sodium

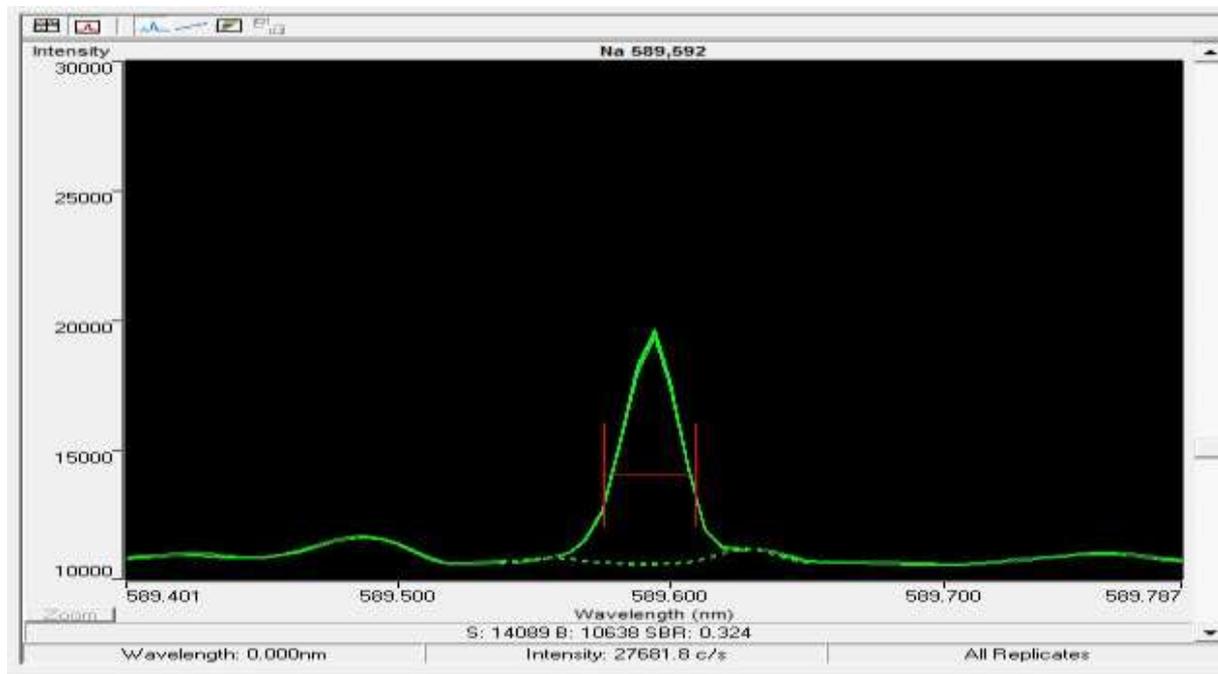


Fig-14 : Optic emission spectrum of sodium

The wavelength of sodium is 589,592 nm and /its intensity is 27681,8 c/s

3.11. Silicon

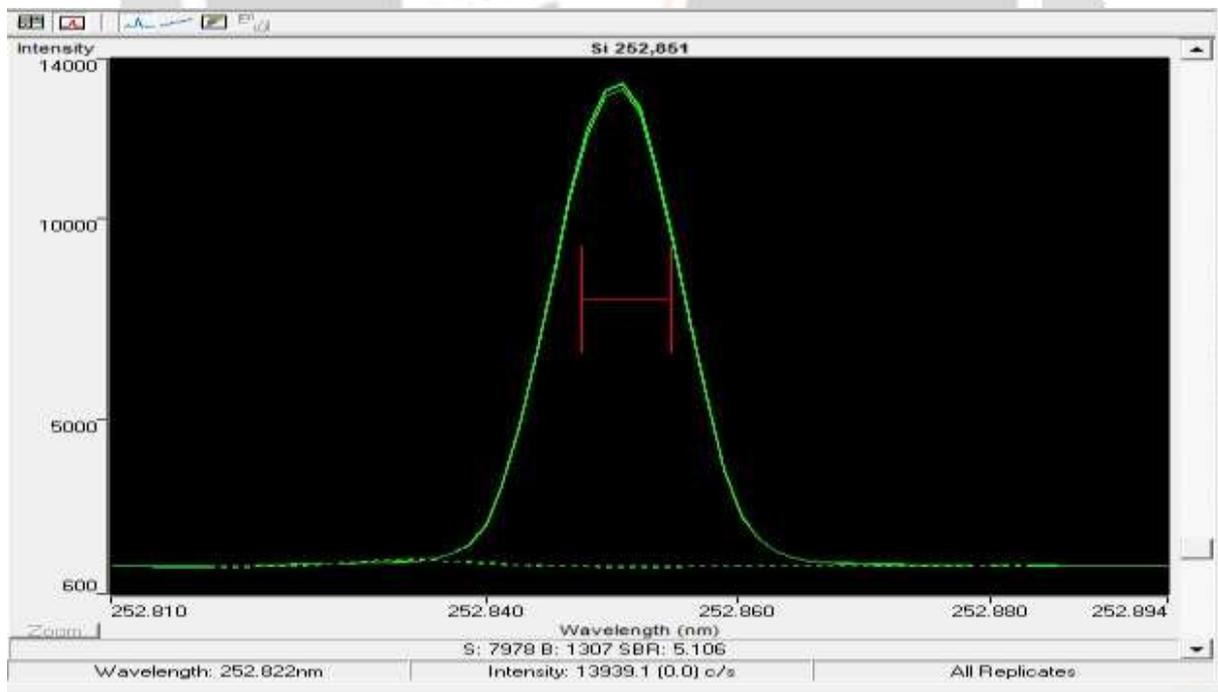


Fig-15 : Optic emission spectrum of silicon

The wavelength of silicon is 252,851 nm and its intensity is 13939,1 c/s

3.12. Titanium

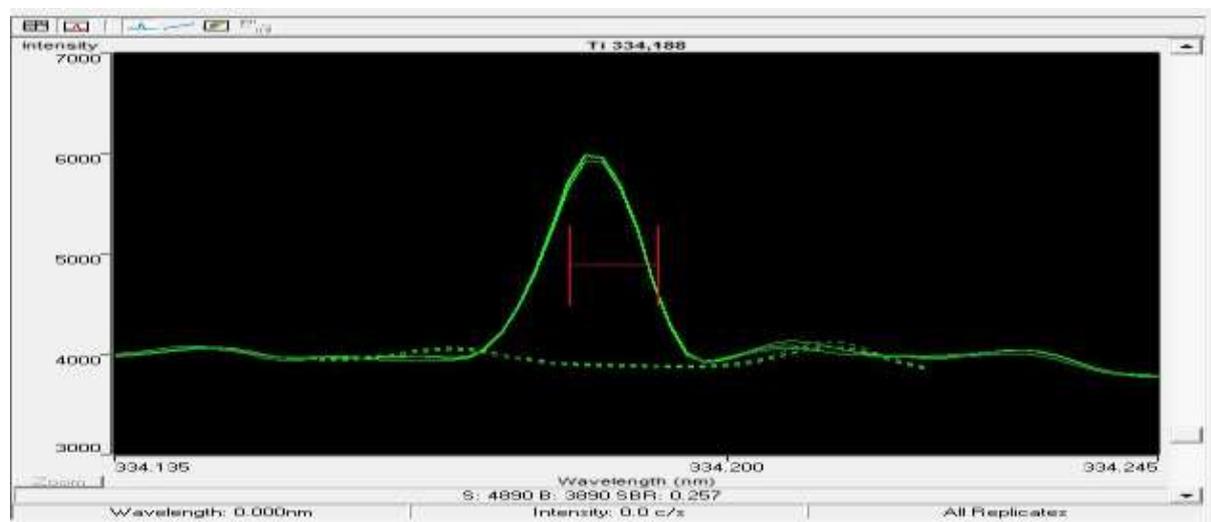


Fig-15 : optic emission spectrum of titanium

the wavelength of titanium is 334,188 nm and its intensity is below detection limit

3.13. Interprétation

According to the results of spectra (intensity according to the wavelength) and the concentrations of the cations present in the apatite ore, one notes that the intensity of the peak of the spectrum is proportional to the concentration of the cation that wants to say that more the peak of the observed element is raised the concentration more in the apatite ore is raised it is observed for the following elements:

- Aluminum (Al) the intensity of the peak in the spectrum is 8913 c/s and a wavelength is 396,142 nm with a concentration of 0,17 mgL⁻¹
- Calcium (Ca) the intensity of the peak in the spectrum is 2743961,4 c/s and a wavelength is 317,93 nm with a concentration of 78,3 mL⁻¹
- Iron (Fe) the intensity of the peak in the spectrum is 3160 c/s and a wavelength is 261,187 nm with a concentration of 0,885 mgL⁻¹
- Manganese (Mn) the intensity of the peak in the spectrum is 459,1 c/s and a wavelength is 260,529 nm with a concentration of 0,257 mgL⁻¹
- Sodium (Na) the intensity of the peak in the spectrum is 27681,8 c/s and a wavelength is 589,592 nm with a concentration of 0,54 mgL⁻¹
- Silicon (Si) the intensity of the peak in the spectrgram is 13939,1 c/s and a wavelength 252,822 nm with a concentration of 6,435 mgL⁻¹

3.14. Other constituent chemical elements the apatite ore of Madagascar

Other chemical elements have been found by this method of analysis of which the concentrations of the first minor elements and more precisely the cations constitute the ore of apatite are given by the table 02

Table 02. First minor elements in the ore of apatite

MINOR ELEMENTS	Al	As	Bi	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Mg	Mn	Mo
CONCENTRATION FOR THE FIRST TEST (mgL ⁻¹)	0,16	<0.1	<0.1	78,3	<0.02	<0.05	<0.01	<0.05	0,873	<0.04	<0.02	<0.03	0,257	0,095
CONCENTRATION FOR THE SECOND TEST (mgL ⁻¹)	0,18	<0.1	<0.1	78,3	<0.02	<0.05	<0.01	<0.05	0,888	<0.04	0,24	<0.03	0,256	0,13

The table 03 determines the concentrations of the second minor elements and more precisely the cations constitute the ore of apatite.

Table 03. Second minor elements in the ore of apatite

MINOR ELEMENTS	Na	Nb	Ni	Pb	S	Sb	Se	Si	Sn	Sr	Te	Ti	U	V	Zn	Zr
CONCENTRATION FOR THE FIRST TEST (mgL ⁻¹)	0,32	<0.2	<0.05	<0.2	3,79	<0.1	<0.2	6,34	<0.3	0,580	<0.5	<0.01	<0.3	0,016	<0.05	<0.02
CONCENTRATION FOR THE SECOND TEST (mgL ⁻¹)	0,76	0,23	<0.05	<0.2	3,79	<0.1	<0.2	6,53	<0.3	0,595	<0.5	<0.01	<0.3	0,018	<0.05	<0.02

The table 04 determines the concentrations of the cations that compose the ore of apatite.

Table 04. Concentration of the cations composing the ore of apatite (mgL⁻¹)

Cation	Al	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	S	Si	Ti	Zn
Reference	0,0061	<0.004	<0.001	<0.002	<0.002	<0.002	<0.04	<0.04	<0.02	<0.002	0,0563	<0.004	0,0027	<0.01	<0.004	<0.005
Test n°01	0,0672	22,4	<0.001	<0.002	0,0024	0,0028	<0.04	<0.04	<0.01	0,0205	0,023	<0.004	0,373	0,447	0,0055	<0.005
Test n°02	0,0674	22,0	<0.001	<0.002	0,0023	0,0027	<0.04	<0.04	<0.01	0,0202	0,026	<0.004	0,362	0,440	0,0055	<0.005
Test n°03	0,0765	22,1	<0.001	<0.002	0,0015	0,0032	0,061	<0.04	<0.01	0,0197	0,023	<0.004	0,381	0,452	0,0039	<0.005

One can also determine the complex oxides [10] metallic composing this ore of apatite with this method of analysis and the principle of analysis is the same.

The Table 05 determines the concentrations of the oxides that compose the ore of apatite of our study.

Table 05. Concentration of the metallic oxides composing the ore of apatite (mgL⁻¹)

Oxydes métalliques	Symboles chimiques	Concentrations (mgL ⁻¹)
Oxyde d'aluminium	Al ₂ O ₃	0,13
Carbonate de calcium	CaCO ₃	56
Oxyde de fer	Fe ₂ O ₃	0,06
Carbonate de magnésium	MgCO ₃	0,03
Oxyde de manganèse	Mn ₂ O ₃	0,03
Silice ou Dioxyde de Silicium	SiO ₂	0,96

The concentration in Calcium carbonate is raised very 56 mgL⁻¹ because the ore of apatite is essentially composed of calcium and it is shown by the general formula of the apatite.

The concentration of the silica is as enough elevated in this picture 0.96 mgL⁻¹, this elevated enough concentration can be explained by the presence of element Silicon in this apatite.

One can also note the concentration of the aluminium oxide in the apatite that is not negligible whose concentration is of 0.13 mgL⁻¹ and it is due to the presence of element Iron in this ore.

3.15. DISCUSSIONS

- The determination of the chemical composition by the specter of optic broadcast of the ore of apatite permits to see with precision the cations that compose the ore of apatite
- According to the specters one can determine the different above, pressed constitutes ore.
- It is the intensity of their specter that describes the majority or the minority of the cations, so one can see that the calcium that is the cation adult of the ore of apatite has a very elevated intensity with I = 2743961 c/s
- The cations miners whose intensities have been detected are: silicon with an I intensity = 13939,1 c/s, aluminum with an I intensity = 8913 c/s, iron with an I intensity = 3160 c/s and finally the manganese with I = 459,1 c/s.
- By the optic emission spectra we could determine other cations of which the intensities of their specters are raised enough as the chromium also (I = 2884,1 c/s), the copper (I=7511,4 c/s), sodium (I = 27681 c/s)
- One could also see other cations whose specter is observed but the value of the intensity of the specter has not been determined it concerns magnesium, sulfur and titanium.

4. CONCLUSION

The analyses of the ore of apatite by the ICP-OES spectrométrie permit to determine with precision the cations essentials that compose it by their respective spectrgrams and the cations that don't have a spectrgram, their concentrations in the ore of apatite can be determined in the pictures 02, 03 and 04.

The concentrations in metallic oxides composing this ore of apatite are determined in the picture 05, one can note that the concentration of the calcium carbonate is raised very to 56 mgL⁻¹ because the ore of apatite is composed mainly of calcium and it is shown by the general formula of the apatite. The concentration of the silica is as enough elevated in this picture 0.96 mgL⁻¹, this elevated enough concentration can be explained by the presence of element Silicon in this ore of apatite.

One can also note the concentration of the aluminium oxide in the apatite that is not negligible and it is due to the presence of element iron in this ore.

The optic broadcast spectrométrie to source plasma of argon coupled by induction (ICP-OES) permits to determine the cations presents in the ore of apatite that it is the cations essentials that compose it or of the cations in elements traces and also the metallic oxides.

5. REFERENCES

1. Lacroix A. 1922. Minéralogie de Madagascar. Challamel. Paris.
2. Besairie H., 1966. Gîtes minéraux de Madagascar. Ann. Géol. Madagasikara. Fasc. Xxxiv.
3. <http://www.patrickvoillot.com/fr/apatite-25.html> consulté le 21 décembre 2019
4. Kapoma J. 2009, Comparaison des caractéristiques gemmologiques des apatites du nord et du sud de Madagascar (Cas d'Ambilobe et d'Isoanala.), mémoire d'ingénieur 90 p. ESPA, Université d'Antananarivo.
5. Soares C.J., Mertz-Kraus, Guedes S., Stockli, D.F., Zack T. 2015, Characterisation of Apatites as Potential Uranium Reference Materials for Fission-track Dating by LA-ICP-MS, Journal of Geostandards and Geoanalytical Research, 39 (3), 305-313

6. <http://www.spiralconnect.univ-lyon1.fr/spiral-files> consulté le 21 décembre 2019
7. <https://www.eag.com/fr/resources/appnotes/icp-oes-and-icp-ms-detection-limit-guidance/> consulté le 21 décembre 2019
8. 21. Behier, J. 1963, Carte minéralogique de Madagascar. Archive Service Géologique Madagascar.
9. <https://www.inspection.gc.ca/sante-des-animaux/aliments-du-betail/inspection-des-aliments-du-betail/methodes-analytiques-pour-la-determination-des-ele/fra> consulté le 21 décembre 2019
10. <https://www.eag.com/fr/resources/whitepapers/high-performance-inductively-coupled-plasma-optical-emission-spectroscopy-hp-icp-oes-for-composition-analysis-of-complex-oxides/> consulté le 21 décembre 2019

