Journal of Materials and Environmental Sciences
ISSN : 2028-2508
CODEN : JMESCN

J. Mater. Environ. Sci., 2017, Volume S, Issue S, Page 4907-4914

http://www.jmaterenvironsci.com

Assessment of Air Pollutant Sources in Deterioration of the Ancient Rampart of Sale City—NW Morocco (SW of the Mediterranean Basin)

M. Azeroual[1*], M. El Wartiti[1], A. Qarbous[2], B. Baghdad[3], M. Bounakhla[4]

[1] *Department of Geology, Faculty of Sciences, Rabat*
[2] *Regional Center for the Professions of Education and Training (RCPET), Rabat*
[3] *Department of Soil Sciences, IAV Hassan II, Rabat*
[4] *National Center for Energy Sciences and Nuclear Techniques (CNESTEN), Rabat*

Received 11 Mar 2017,
Revised 27 Dec 2017,
Accepted 29 Dec 2017

Keywords
- ✓ Calcarenite;
- ✓ Salt weathering;
- ✓ Atmospheric pollution;
- ✓ Stone decay;
- ✓ Salé;
- ✓ NW Morocco.

mouniaz75@yahoo.fr
Phone: +212662885789

Abstract

The ancient rampart of Sale city shows a very advanced degree of deterioration patterns. To determine the relationship between the environment conditions and the stone decay, an elaborate study (X-ray fluorescence, Ion chromatography, X-Ray Diffraction, Scanning electron microscopy and Atomic emission spectrometry) has been carried out on decayed layers at the surface of the rampart. The results show that the deterioration of the stone is mainly related to atmospheric pollutants (SO_2, NO_x) and in the second row the action of marine sprays by Na^+ and Cl^-deposition. The crystallized gypsum ($CaSO_4{\cdot}2H_2O$) characterized the most of surface deposits and it's formed by calcarenite oxidation of ($CaCo_3$) particles reacting to atmospheric sulfur.

1. Introduction

In the NW of Morocco, the rampart of *Sale* city surrounding (Fig. 1) represents the most important cultural heritage in the Mediterranean Basin dating back to the XI century. It's a witness of the various dynasties that ruled in Morocco. During Almoravid times (1060-1147), *Sale* has been a center and a warrior base that opened on North Africa and Andalusian Spain. During the Almohad period (1147-1269), the southern part of the rampart of *Sale* was destructed by the Almohad Sultan *Abdul Mumin*. In 1196, a portion of rampart was rebuilt by *Abu Yusuf Yacub El Mansour*. In 1261, the *Marinids* (1269-1465) have added the huge dungeon "*Borj Eddoumouh*", SW and NE walls respectively located in front of the *Bouregreg* river and the side of the sea. The rampart of *Sale* was restored at the time of the *Alawites* (since 1664) [1].
The original rampart has been constructed essentially by the "*Sale* stone", taken from *Bouknadel* quarries (20 km in the north-east of *Sale*). Petrographic study shows that ornamental dominant type is a gray calcarenite characterized by: (i) a micritic calcite; (ii) an abundance of bioclastes; (iii) the presence of peloids, opaque minerals, potassium feldspar and plagioclase; (iv) a detrital fraction with 10 to 30% of quartz; and (v) a high porosity (20-45%). Actually, the rampart of *Sale* city presents a stone with different forms of damages (black crust, efflorescence, alveolar, peeling, cracks…) (Fig. 2); the black crust is the most observed usually adhering firmly to the stone.
Several studies showed the high levels of atmospheric pollutants (Tab.1) and the harmful of their action in the deterioration of the rampart [2],[3],[4]. Recently, an important study is performed on *Burg al Klab* (Bastion of dogs) tower in extreme East of the rampart; this study identifies the source of causing damage to this part of rampart and its relationship with the atmospheric pollutants [5, 6]. Another work was achieved to determine the physico-chimical characterization of the coatings from *Bab Chaafa* and the used materiel for the restoration [7].

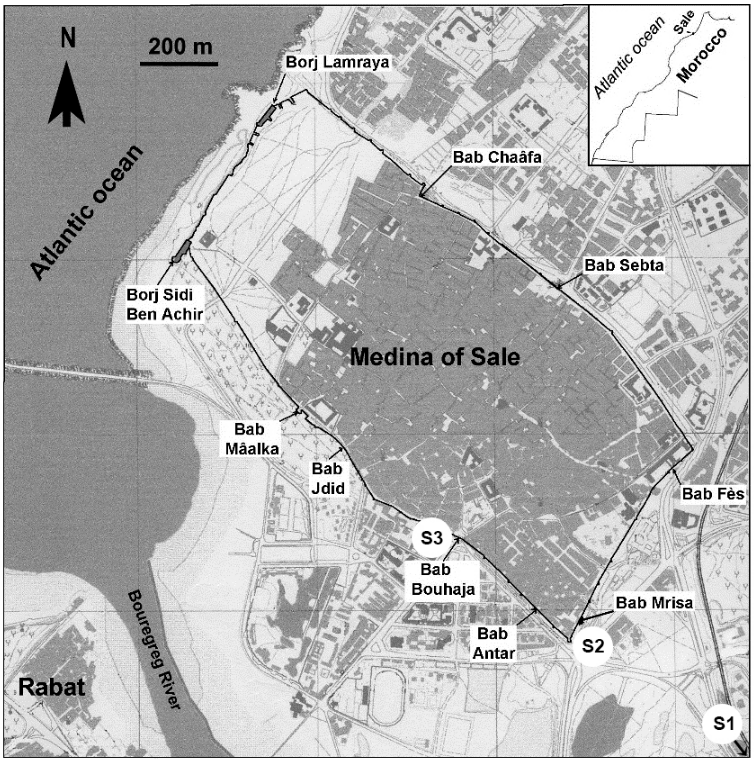

Figure 1: Location of Gates (Babs) in the rampart of Sale city and Sites of Table 1.

In this work, we present analyses (X-ray fluorescence, Ion chromatography, X-Ray Diffraction Scanning, Electron microscopy and Atomic emission spectrometry) performed on samples appropriated on gates (*Bab*) the long of rampart (Fig. 1). We tried to identify factors responsible of stone deterioration in relationship with atmospheric pollutants of *Sale* city and the action of the marine sprays aerosol.

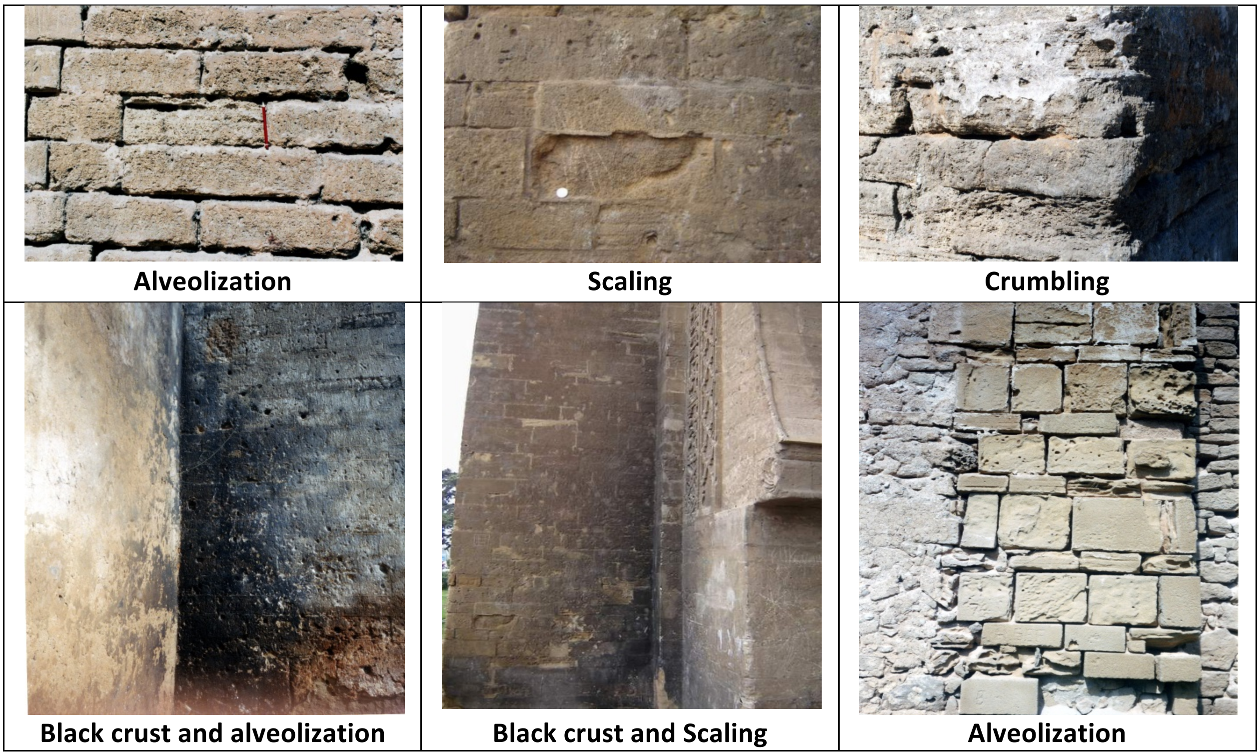

Figure 2: Photos of stone deterioration patterns

Table 1 : Measured annual values of atmospheric pollutants in Sale city [8]

	NO_x $\mu g/m^3$	SO_2 $\mu g/m^3$	MPS $\mu g/m^3$	Pb $\mu g/m^3$	Cd $\mu g/m^3$
El Oulja (I.C) (S_1)	**246**	**450**	**350.9**	**3.1**	**0.03**
Bab Mrisa (S_2)	**166**	**280**	**223.3**	**2.8**	**0.044**
Bab Bouhaja (S_3)	**81**	**123**	**131.7**	**0.9**	**0.031**
WHO standards	**40**	**80**	**75**	**2**	**0.04**
NAAQS	**30**	**20**	**50**	**1**	**0,005**

I.C : industrial complex; WHO: world health organization; NAAQS : National Ambient Air Quality Standards; Sx: Sites, indicated on (Figure.1)

2. Materials and methods

Since 1971, the restoration work was performed along the rampart, including the reconstruction of degraded parts, the filling of the cracks and repairing of the facade and interior coatings. The samples are taken from unrestored parts of gates (*Bab*) (Tab. 2); except sample (BKD) which is a natural stone from *Bouknadel*'s quarry. They were collected at a height of 1.5-2.0 meters from the ground, nearest to high traffic circulation.
The samples mostly correspond to the black crusts, except one sample that corresponds to a mortar. They were grinding to fine powders in an agate mortar: for each sample, 2g powder was mixed with 4g of (H3BO3) boric acid to determine the bulk composition by X-ray fluorescence (Wavelength-dispersive X-ray fluorescence).
To determine the soluble salts and the heavy metals in the study samples, 100 mg of powder sample was dispersed in 100 ml of deionized water and placed in an ultrasonic bath for 25min. The aqueous suspension was filtered through a Millipore filter (pore size 0.2mm). Anions (Cl^-, NO_3^- and SO_4^{2-}) were analyzed with ion chromatography (IC) using a *Dionex 200*.
AnX-ray diffractometer *Philips X'Pert PRO* was used to identify the main crystalline phases in powdered samples. The surface morphological and elemental characterization of the damage layers was obtained by scanning electron microscope SEM-EDX (ESEM 0,1-1,33mbar ; resolution 3,5nm-30KV). The heavy metals are determined by atomic emission spectrometry (AAS) type *Spectra 220 FS Varian*.

3. Results and discussion

3.1. X-ray fluorescence (XRF)

The XRF results (Tab.2) show a high contains of Calcium in the studied samples comparing to the others components. After Calcium, Silicon is found in considerable amounts between 1,86 % and 9,27 %. Sulfur, Sodium, Chlorine and Potassium are presents in most of samples with various concentrations higher than the values of the naturel stone of *Bouknadel* (Bkd: 0,04 %). The Magnesium, Strontium, Phosphorus, Lead and Titanium are detected in the lowest amounts.

3.2. X-Ray Diffraction (XRD)

The XRD results achieved for the studied samples and confirmed by Scanning Electron Microscopy (SEM) are represented in Tab.3. The samples of decayed stones (crusts) have a similar composition with slight differences. The calcite is the major mineral (50-91%), that explain the high contain of Calcium founded by XRF in the most studied samples. The quartz is also present in all the samples. The maximum is in the sample of *Bab Fes* (BF1: 38%). Gypsum appears in almost all of the crusts of *Bab Mrisa*, *Fes* and *Sebta* (BM1, BF1, BS1) and also in mortar of *Bab Sebta* (BS2). Halite is detected only in *Bab Chaafa* with a low amount (BCh: 3%).

3.3. Ionic chromatography (IC)

The most abundant among anion (Tab.4) is Sulfate (SO_4^{2-}) with very high concentrations achieving in *Bab Fes* BF1 (2040,50 ppm), and Nitrate (NO_3^-) with important values specially in *Bab Sebta* (BS1:112,28 ppm). The Chloride is abundant in all samples with concentrations varying from *Bab Mrisa* (BM2:11,47 ppm) to *Bab Sebta* (BS1: 449,04 ppm). Finally, Sodium (Na^+) and Potassium (K^+) were found mostly in the crust samples of *Bab Mrisa*, *Fes* and *Sebta* (BM1, BF1 and BS1). This soluble cations and anions (Na^+, K^+, SO_4^{2-}, NO_3^-, Cl^-) on the surface are mobilized by rain water in the thin fractures and microporosity (20-45%) inside the "*Sale* stone" consisting of calcarenite and cements. The carbonaceous particles ($CaCO_3$) are very active in forming black crusts when they are wet since they both contain sulphur compounds and catalysts [9] and they can absorb Sulfate from the atmosphere and can serve to nucleate gypsum crystals ($CaSO_4.2H_2O$) [10] [11]. Thus the gypsum in the crust is due to the transformation of the calcite reacting with Sulfate [12]. The gypsum crystallization creates a mechanical stress by increasing volume in the stone, which increases the rate of degradation of the monument stone [13]. So, there is a relationship between the atmospheric pollutants and the chemical composition of the weathered stone. This relationship is confirmed by the absence of any others minerals containing Sulfate as it's shown in XRD results. It's frequently observed the effect of atmospheric pollutants on historic buildings at the Mediterranean coast in Eleusis (Greece) and little less in Bari (Italy), [14].

Table 2: Average concentration (%) of samples measured by XRF (n.d: no detected)

Gates	Bab Mrisa		Bab Fes		Bab Sebta		Bab Chaafa	Quarry of Bouknadel
Sample	**BM1**	**BM2**	**BF1**	**BF2**	**BS1**	**BS2**	**BCh**	**Bkd**
Descrip-tion	Black crust strongly attached to the stone	Fragments of the substrate with damage layer	Black crust strongly attached to the stone	Fragments of the substrate showing alveolization	Black crust	Fragments of mortar	Black crust strongly attached to the stone	Natural stone
Ca	**13.9**	**18.52**	**14.43**	**30.66**	**13.62**	**12.24**	**17.26**	**17.71**
Si	**3.13**	**1.86**	**4.12**	**2.05**	**2.44**	**9.27**	**1.92**	**3.46**
Fe	**1.03**	**0.82**	**1.23**	**0.75**	**0.69**	**2.01**	**0.76**	**0.95**
Al	**1.13**	**0.67**	**1.28**	**0.57**	**0.76**	**4.27**	**0.64**	**1.07**
Mg	**0.48**	**0.5**	**0.46**	**0.43**	**0.3**	**0.99**	**0.53**	**0.26**
Na	**0.97**	**1.3**	**1.68**	**0.13**	**1.01**	**0.16**	**4.5**	**0.12**
Cl	**0.54**	**0.54**	**0.72**	**n.d**	**0.52**	**n.d**	**3.73**	**n.d**
K	**0.12**	**0.35**	**0.38**	**n.d**	**0.23**	**0.4**	**0.23**	**0.1**
Sr	**0.05**	**0.07**	**0.04**	**0.08**	**0.04**	**0.02**	**0.04**	**0.05**
P	**0.06**	**0.23**	**0.1**	**0.09**	**0.05**	**0.06**	**0.04**	**0.11**
S	**0.15**	**0.79**	**1.07**	**0.04**	**0.63**	**0.14**	**0.25**	**0.04**
Pb	**n.d**	**n.d**	**n.d**	**n.d**	**n.d**	**0.3**	**0.25**	**n.d**
Ti	**0.07**	**n.d**	**0.18**	**n.d**	**0.09**	**0.21**	**n.d**	**0.06**
Zr	**n.d**	**n.d**	**n.d**	**n.d**	**n.d**	**0.01**	**n.d**	**n.d**

Table 3: Mineralogy amounts (%) of samples measured by XRD and observed by SEM

Gates	Samples	Calcite	Quartz	Dolomite	Gypsum	Halite
Bab Mrisa	**BM1**	**89**	**7**	**0**	**5**	**0**
	BM2	**81**	**19**	**0**	**0**	**0**
Bab Fes	**BF1**	**50**	**38**	**0**	**12**	**0**
	BF2	**63**	**21**	**16**	**0**	**0**
Bab Sebta	**BS1**	**58**	**11**	**0**	**30**	**0**
	BS2	**72**	**22**	**4**	**4**	**0**
Bab Chaafa	**BCh**	**91**	**6**	**0**	**0**	**3**
Quarry of Bouknadel	**Bkd**	**80**	**20**	**0**	**0**	**0**

3.4. Scanning electron microscope (SEM)

The crusts at the surface of the monumental stone of *Sale* city are characterized by a variable hardness, a smooth aspect, and nodular or dendritic shape. At the microscopic scale, under the crust, the stone present a different texture: less porous with little individualized crystals. The observation by scanning electron microscope (SEM) of the crust of *Bab Mrisa* (BM1), shows a low degree of calcite crystallization and amorphous substances (Fig. 3, a). The SEM analyses performed on the substrate with damage layer of *Bab Mrisa* (BM2) (Fig. 3, b) present an etching features in calcite and quartz grains that indicates micro-dissolution processes (chemical alteration), with adjacent subsequent calcite recrystallization [3]. The microscopic damage of calcarenite is mainly related to this succession of crystallization and dissolution of the calcite. The gypsum crust is more water-soluble than the stone itself, and with subsequent rains the soiled area is washed away. The result is a permanently altered stone [15]. Then, it can explain the non-present of gypsum in some samples (*Bab Fes*: BF2). The heavy metals play a catalytic role on the heterogeneous oxidation of Sulfate into sulfuric acid [16] which is responsible for both the 'acid rain' and the natural stone sulfation [17].

Table 4: Composition of samples (PPM) measured by Ionic chromatography (n.d: no detected)

Gates	Samples	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+
Bab Mrisa	**BM1**	1797.3	42.82	161.8	6.6	0.24
	BM2	52.22	30.88	11.47	n.d	n.d
Bab Fes	**BF1**	2040.5	101.56	216.9	96.53	18.98
	BF2	108.33	35.38	14.46	n.d	n.d
Bab Sebta	**BS1**	522.88	123.73	449.04	1.02	0.27
	BS2	623.93	112.28	452.6	n.d	n.d
Bab Chaafa	**BCh**	309.6	114.61	414.28	n.d	n.d
Quarry of Bouknadel	**Bkd**	11.87	2.1	3.34	n.d	n.d

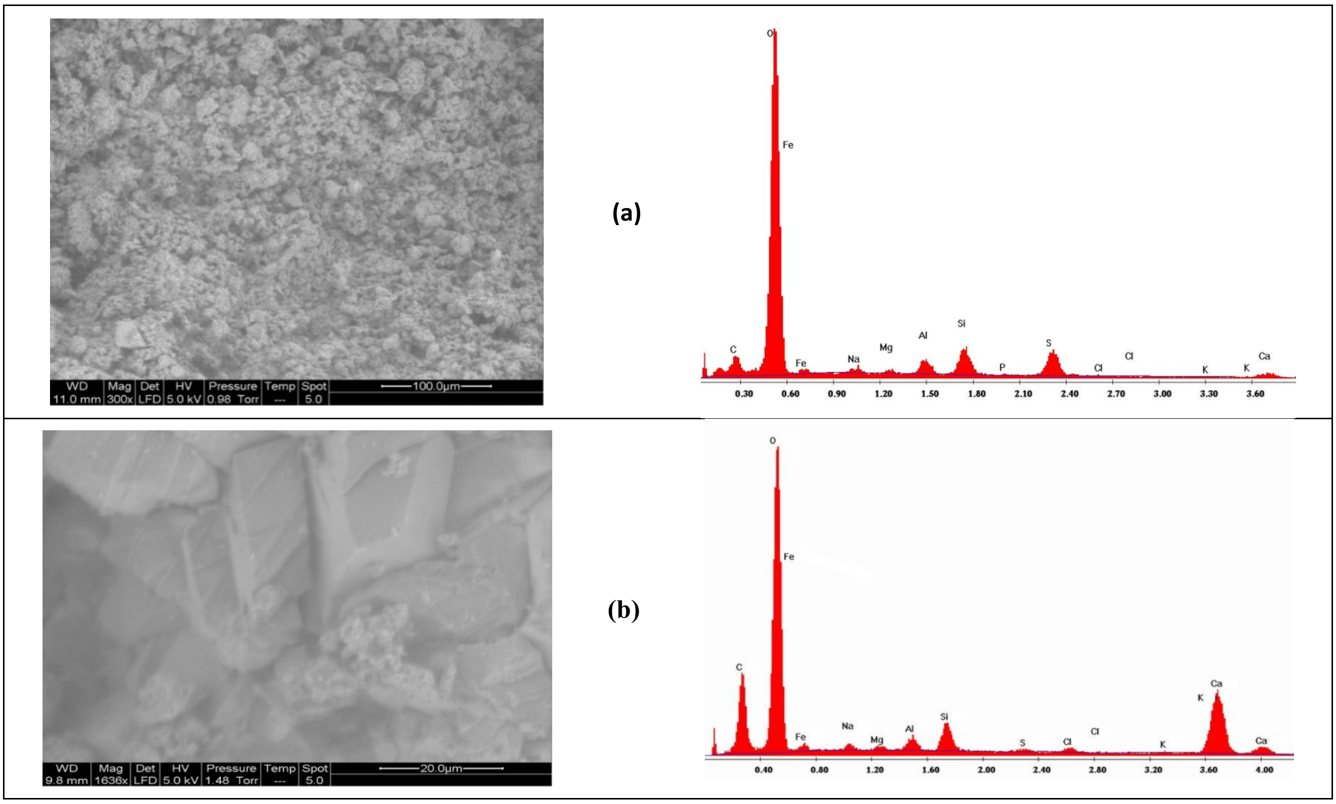

Figure 3: Scanning electron microscopy (SEM – EDX) (a) sample BM1 (b) sample BM2

3.5. Enrichment factors (EF)

To identify the main factor of deterioration of monumental stone surface, we calculated the Enrichment factors of the various elements of *Sale* stone. The Titanium has been used as the indicator element [18], and the element composition of *Bouknadel* stone (Tab.2) as a values of non-deteriorated stone. The obtained results are presented in Tab.5 by:

$$FE (X) = (X/Ti)_{Black\ crust} / (X/Ti)_{Bouknadel\ stone}$$

With X: the concentration of the investigated element.

Table 5: Enrichment factors of samples Vs natural stone of Bouknadel (Ti as indicator element)

Gates	Samples	Ca	Si	Fe	Al	Mg	Na	K	Sr	P	S
Bab Mrisa	BM1	0.67	0.78	0.93	0.91	1.58	6.93	1.03	0.86	0.47	3.21
	BM2	-	-	-	-	-	-	-	-	-	-
Bab Fes	BF1	0.27	0.40	0.43	0.40	0.59	4.67	1.27	0.27	0.30	8.92
	BF2	-	-	-	-	-	-	-	-	-	-
Bab Sebta	BS1	0.51	0.47	0.48	0.47	0.77	5.61	1.53	0.53	0.30	10.50
	BS2	0.20	0.77	0.60	1.14	1.09	0.38	1.14	0.11	0.16	1.00
Bab Chaafa	BCh	-	-	-	-	-	-	-	-	-	-
Quarry of Bouknadel	Bkd	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Sulfur is the element which represents the higher Enrichment factor values in all the crusts (BS1: 10,50). Firstly, that explains the high levels of SO_4^{2-} founded in the samples of the fact that it's a non-carbonate element; and secondly, it's considered due to atmospheric deposition [14] [19] [5].

The contribution of sea-water and mineral dust to each element is represented by the concentration of indicator elements, which are Na and Al, respectively [20]. The average composition of sea-water was taken from [21], while the composition of mineral dust from [22]. The EF of SO_4^{2-}, NO_3^-, S, Cl and Ca is more than 10 for the most of the samples (Tab. 6, 7); this indicates that they are not coming from the sea and also a presence of a significant contribution of secondary anthropogenic aerosol [23]. The Na, Mg and Fe seem to originate mainly from the sea or the mineral dust in the fact that EF is less than 10 for the most of samples (Tab. 7) [23]. This should be accompanied by similar enrichment of Cl as it's showed in the results, except at *Bab Fes* (BF2) and *Bab Sebta* (BS2), where the EF of Cl and Na presents small values, which can be explained by the meteoric leaching [15]. The high value of chloride in *Bab Chaafa* (BCh) is due to mineralization of Halite detected by XRD. The EF of Si and K is less than 1 for the most samples. So, they behave as non-enriched elements in the investigated samples.

Therefore, the origin of components found in the investigated samples is from: 1. the anthropogenic pollution which is the main source of SO_4^{2-} and NO_3^-; 2. The aerosol is mainly influenced by the marine spry enriching the concentration of Na^+, Cl^-, Mg and Fe.

Table 6: Enrichment factors of samples vs. Sea Water (Na+ as indicator element)

Gates	Samples	SO_4^{2-}	NO_3^-	Cl^-	K^+
Bab Mrisa	BM1	1085.37	1341.85	13.63	1.01
	BM2	-		-	-
Bab Fes	BF1	84.25	217.60	1.25	0.78
	BF2	-		-	-
Bab Sebta	BS1	2043.17	25088.60	244.83	1.06
	BS2	-	-	-	-
Bab Chaafa	BCh	-	-	-	-
Quarry of Bouknadel	Bkd	-	-	-	-

Table 7: Enrichment factors of samples vs. soil dust (Al as indicator element)

Gates	Samples	Ca	Si	Fe	Mg	Na	Cl	K	S
Bab Mrisa	**BM1**	**27.34**	**0.81**	**1.47**	**1.63**	**2.45**	**298.67**	**0.33**	**13.83**
	BM2	**61.43**	**0.81**	**1.97**	**2.87**	**5.54**	**503.73**	**1.63**	**32.65**
Bab Fes	**BF1**	**25.05**	**0.94**	**1.55**	**1.38**	**3.75**	**351.56**	**0.93**	**9.77**
	BF2	**119.53**	**1.05**	**2.12**	**2.90**	**0.65**	**-**	**-**	**43.86**
Bab Sebta	**BS1**	**39.82**	**0.94**	**1.46**	**1.52**	**3.80**	**427.63**	**0.95**	**16.45**
	BS2	**6.37**	**0.64**	**0.76**	**0.89**	**0.11**	**-**	**0.29**	**1.46**
Bab Chaafa	**BCh**	**59.93**	**0.88**	**1.92**	**3.19**	**20.09**	**3642.58**	**1.12**	**19.53**
Quarry of Bouknadel	**Bkd**	**36.78**	**0.95**	**1.43**	**0.93**	**0.32**	**-**	**0.29**	**14.60**

Conclusion

The deterioration of the ancient rampart of *Sale* City seems to be mostly related to the action of anthropic pollution in the first priority and marine spray in the second row. It must be emphasized that this research strongly confirms the great interdependence that exists between the degradation of *Sale* stone and urban po llution. It's concluded that the decay patterns observed is mainly caused by the traffic activities emissions and influenced by the
marine spray. This will be mainly considered for decision on the preventive conservation strategy of cultural heritage near to traffic roads and the restoration of studied rampart.

Acknowledgements
- The authors are very thankful to CNESTEN for getting (X-ray fluorescence, Ion chromatography, X-Ray Diffraction, Scanning electron microscopy and Atomic emission spectrometry) analyses recorded.

References

1. I. Alaoui, D. Mrini, *Éclat* (1997) 199.
2. B. Baghdad, M. Azeroual, M. Naimi, A. Taleb, M. El Wartiti, *Act. II. J. Géosci. Env.* (2003) 319-326
3. M. Azeroual, B. Baghdad, M. Bounakhla, A. Doukkali, M. El Wartiti, *Phys. Chem. News* 33 (2007) 59-64.
4. M. Bounakhla, F. Zahry, M. Tahri, B. Baghdad, I. Garcia Orellana, M. Garci Leon, *Conf. Nuc. Conv. Anal.Tech. App.* (2010) 22-24.
5. I. Ozga, A. Bonazza, S. Ait Lyazidi, M. Haddad, A. Ben-Ncer, N. Ghedini, C. Sabbioni, *J. Cult. Herit.* 14 (2013) S25-S33.
6. I. Ozga, N. Ghedini, C. Giosuè, C. Sabbioni, F. Tittarelli, A. Bonazza, *Sci. Total Environ.* 490 (2014) 776-784.
7. F. Allali, M. Monsif, N.I. Kandri, A. Zerouale, *J. Mater. Environ. Sci.* 5 (2014) 2205- 2211.
8. M. Bounakhla, A. Fatah, K. Embarch, M.I. Majah, R. Azami, A. Sabir, A. Nejjar, R. Cherkaoui, A. Gaudry, *J. Phys. IV* 107 (2003) 211-213.
9. E. Charola, *US/ICOMOS Sci. J.* 3 (2001) 18-58.
10. D. Camuffo, *Acidic precipitation, Springer*, (1990), 229-265.
11. M. Del Monte, *Com. Univ. Med., Scu. Univ. Conserv.Monum.* (1991) 101-110.
12. H. Böke, E.H. Göktürk, E.N. Caner-Saltık, Ş. Demirci, *App. Surf. Sci.* 140 (1999) 70-82.

13. C. Rodriguez-Navarro, E. Doehne, *Earth Surf. Process. Landforms* 24 (3) (1999) 191-209.
14. K. Torfs, R. Van Grieken, *Atmos. Environ.* 31 (1997) 2179-2192.
15. M.F. Striegel, E.B. Guin, K. Hallett, D. Sandoval, R. Swingle, K. Knox, F. Best, S. Fornea, *Prog. Org. Coat.* 48 (2003) 281-288.
16. C. Sabbioni, G. Zappia, G. Gobbi, *J. Geophys. Res.: Atmos.* 101 (1996) 19621-19627.
17. P. Urone, H. Lutsep, C.M. Noyes, J.F. Parcher, *Environ. Sci. Technol.* 2 (1968) 611-618.
18. C. Sabbioni, *Sci. Total Environ.* 167 (1995) 49-55.
19. P. Maravelaki-Kalaitzaki, G. Biscontin, *Atmos. Environ.* 33 (1999) 1699-1709.
20. B. Schneider, *Atmos. Environ. (1967)* 21 (1967) 1275-1283.
21. J.P. Riley, R. Chester, *Introduction to marine chemistry* (1971).
22. B. Mason, H. Moore, *Inc., New York* (1966).
23. R. Chester, M. Nimmo, M. Alarcon, C. Saydam, K. Murphy, G. Sanders, P. Corcoran, *Oceanol. Acta* 16 (1993) 231-246.

(2017) ; http://www.jmaterenvironsci.com