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ORIGINAL ARTICLE

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Superficial alteration and soluble salts in the calcarenite weathering. case study of almohade monuments in Rabat: Morocco

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Abstract This work analyzes the stone superficial deterioration of some monuments in Rabat city. The rock is a calcarenite with porous texture, rich in calcium carbonates and fossils. The techniques used to study the surfaces altered by blackening or black crusts, are the SEM equipped with EDX microprobe, the X-ray diffraction, and the analysis of the soluble salts by ionic chromatography for anions and flame spectrometer for cations. They reveal significant contents of calcium sulphates, mainly gypsum, often associated with sodium chlorides. These salts known to have a destructive effect on the calcareous stones seem to be originated from the contamination by atmospheric pollutants, particularly sulfur dioxide, and by the marine sprays.

Keywords Black crusts · Weathering · Salt deposits · Calcarenite · Almohade monuments · Rabat · Morocco

Introduction

Rabat is the capital city of Morocco; it is located on the Moroccan Atlantic coastline at a slight height. It is built essentially on calcarenitic formations of the plio-quaternary with wavy topography. The climate is Mediterranean subhumid; the average precipitations per year are between 400 mm and 500 mm and the average temperature is 16°C. The predominant winds come from the north-west. The city has more than 1 million inhabitants; it has shown a heavy road traffic in the last decades, which caused a heavy air pollution essentially by sulfur dioxide. The impact of atmospheric pollutants on the Almohade monuments of Rabat, associated to coastal weather, led to apparition of superficial weathering forms on the calcarenite stones, such as black crusts, granular disintegration, and alveolization (Zaouia et al. 2004).

Monuments and material

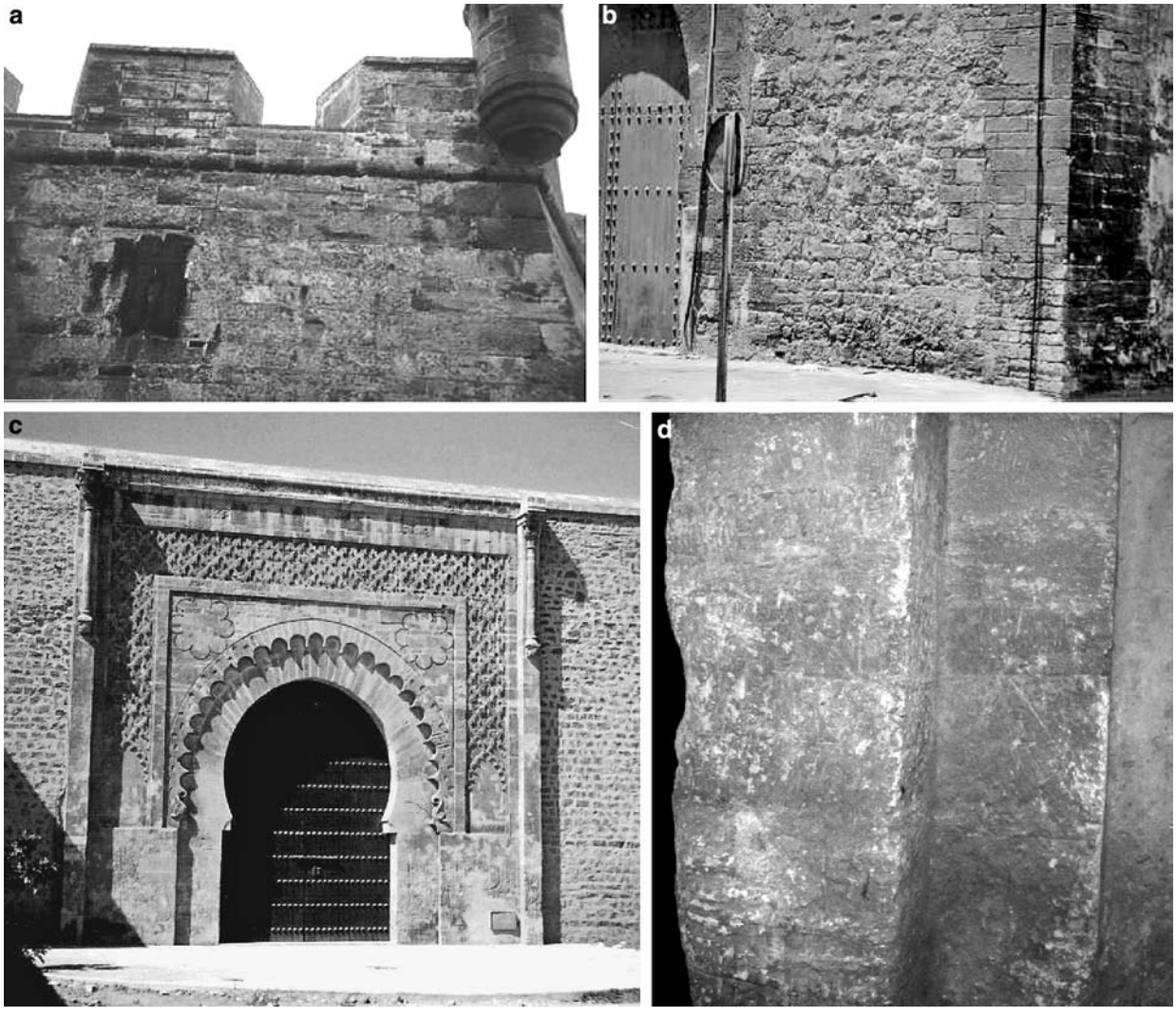
In this paper interest focuses on the stone weathering of some Almohade monuments of the twelth century such as:

- The northeastern rampart of the Kasbah of Oudayas, the first Almohade edifice in Rabat, which is quite close to the ocean, entirely constructed by calcarenitic ashlars that show now much eroded surfaces.
- The gates of the southwestern wall of the old Almohade city, situated at increasing distances of the coastline:
  - The Bab Laalou Gate in the west entry of the old medina shows a very decayed aspect mainly with black crusts in its east faade, now close to a car park;

– The Bab El Hadd Gate is facing the city central marked characterized by heavy traffic and important amounts of sulfur dioxide measured in the air;
– The eastern portal of Bab Rouah Gate is located in a very busy crossroad with important atmospheric pollution caused by vehicles gases.

These monuments are all constructed by the plio-quaternary calcarenite that constitutes the basement of the whole region. A few kilometers to the north of the city, quarries still provide this ornamental rock widely used by stone craftsmen. It is characterized by variable and high porosity (18–47%) and thus an elevated permeability, and generally bad geotechnical quality (Ben Boughaba 2001). Its chemical composition is very rich in calcium carbonates and its rough surface allows a high receptivity to the atmospheric gaseous pollutants and to hydrous marine sprays charged with various salts.

Fig. 1 Sampling sites on the Almohades monuments. (**a**) the north-west wall of the Kasbah of Oudayas. (**b**) the eastern side of Bab Laalou Portal. (**c**) the eastern side of Bab Rouah Portal. (**d**) a sheltered gateway of Bab ElHadd



Experimental methodology

Samples of altered stone surface were taken in each of the studied monuments, according to their alteration degree, and to their height from soil, generally over the rising dump zone. A nonaltered sample of similar calcarenite was taken in the quarry of Bou Knadel in the north of Rabat, for comparison with the altered stones of monuments.

The micromorphology and the chemical and mineralogical composition of the samples were studied by various analytic techniques such as:

– An electronic microscope (SEM) with an X-ray dispersive energy microanalysis apparatus (EDX) model

ZEIZZ DSM-940 was used in the General Service of Electronic Microscopy of the University of Salamanca in Spain.
– An X-ray diffractometer (XRD) PHILIPS PW-1730 (Cu K radiations), an ionic chromatography (METROHM model), and a flame spectrometer were used in the Laboratory of the Institute of the Agro-biological Natural Resources (IRNA-CSIC) of the same University.

Results

Superficial crusts in marine spray-exposed area: case of northwest faade of the Kasbah of Oudayas

The weathering forms on the wall of the Kasbah of Oudayas are mainly represented by superficial crusts (Fig. 1a). A 200 μm thick crust was taken at 5 m from the soil and only a few meters from the ocean. It was analyzed by SEM on its external and internal faces.

The external face showed a mammilated and crackled surface (Fig. 2a). Calcitic or quartzitic elements seemed to be loosing their cement by dissolution. The micro-analysis by SEM revealed high contents of sodium chlorides. The sulfates were less important; they generally appeared as particles regaining the crystals of calcite.

The internal face showed a very granular texture; the pores and the cavities were filled by sodium chloride precipitations, which was revealed by the EDX analysis (Fig. 2b, c). The penetration of sodium chloride inside the rock caused structural disorders by disintegration of grains. The XRD of the powdered crust sample and the analysis of soluble salts by IC showed concordant results. The new formation of sodium chloride represented by crystals of halite, more or less developed, is the main mechanism of stone weathering in this part of the Kasbah very near to the ocean. Other minerals of weathering were detected by XRD such as gypsum and mirabilite.

Black crusts in rain-exposed areas at Bab Laalou and Bab Rouah Gates

The Bab Laalou Gate is within walking distance of the coastline. It shows intense damages, such as granular disintegration, alveolar erosion, blackening and black crusts mainly localized in the lower part of the wall (Fig. 1b).

SEM analyses of crust samples over the rising damp zone showed a typical texture of weathered calcareous stones exposed to rain wash. The micro-photography in Fig. 2e shows a grain of quartz whose carbonated cement is partly dissolved and replaced by calcium sulfate as indicated by EDX (Fig. 2f). Gypsum crystals were found in the same crust specimen using XRD technique. Halite and traces of anhydrite were also found in addition to original calcite and quartz.

Furthermore, the results of IC measurements of soluble salts showed the presence of sulfates and chlorides in this crust.

The side of the Bab Rouah Portal facing the east shows irregular black spots distributed on the whole height of the construction and gives it an unpleasant aspect (Fig. 1c).

The SEM observation of a superficial fragment taken 3 m above the soil, showed discontinuous thin crusts characterized by high content of sulfur (upto 37%) separated by eroded surfaces with calcitic composition and granular shape (Fig. 2d).

The XRD technique applied to this sample showed a mineralogical composition dominated by original calcite and quartz, but also rich in gypsum often badly crystallized and some halite and anhydrite.

In addition to sulfates and chlorides, the IC technique revealed the presence of nitrates. This is probably due to the NOx present in the polluted atmosphere in the site.

Black crusts in sheltered gateway of Bab El Hadd

A fragment of encrusted stone surface was sampled on the sheltered area of the Bab El Hadd gate used by cars to get inside the city central market. Black crusts were the most diffused alteration form on these walls (Fig. 1d). Figure 2g represents a SEM microphotography by SEM of a crust fragment showing a crackled aspect of the surface covered by black particles (soot and dust). A stronger magnification revealed the typical structure of gypsum crusts of weathered calcareous stones protected from run wash, but subject to the effects of atmospheric sulfur dioxide. The alteration process is sulfatation of the rock (Del Monte, and Furland, 1995). The microanalysis showed that the main chemical elements were calcium and sulfur. The gypsum recognized by XRD grew as intersected lamellar crystals perpendicular to stone surface. This rough surface caused trapping of more atmospheric particles (Fig. 2h).

The quarry of Bou Knadel

This quarry provides many of the ornamental stones used in the region. The calcarenite sample is the one used by craftsmen. SEM applied on this sample showed variable structures of pores. Grains of calcite and quartz were cemented by microsparite. The microanalyses revealed the absence of sulfur and chlorine. The XRD

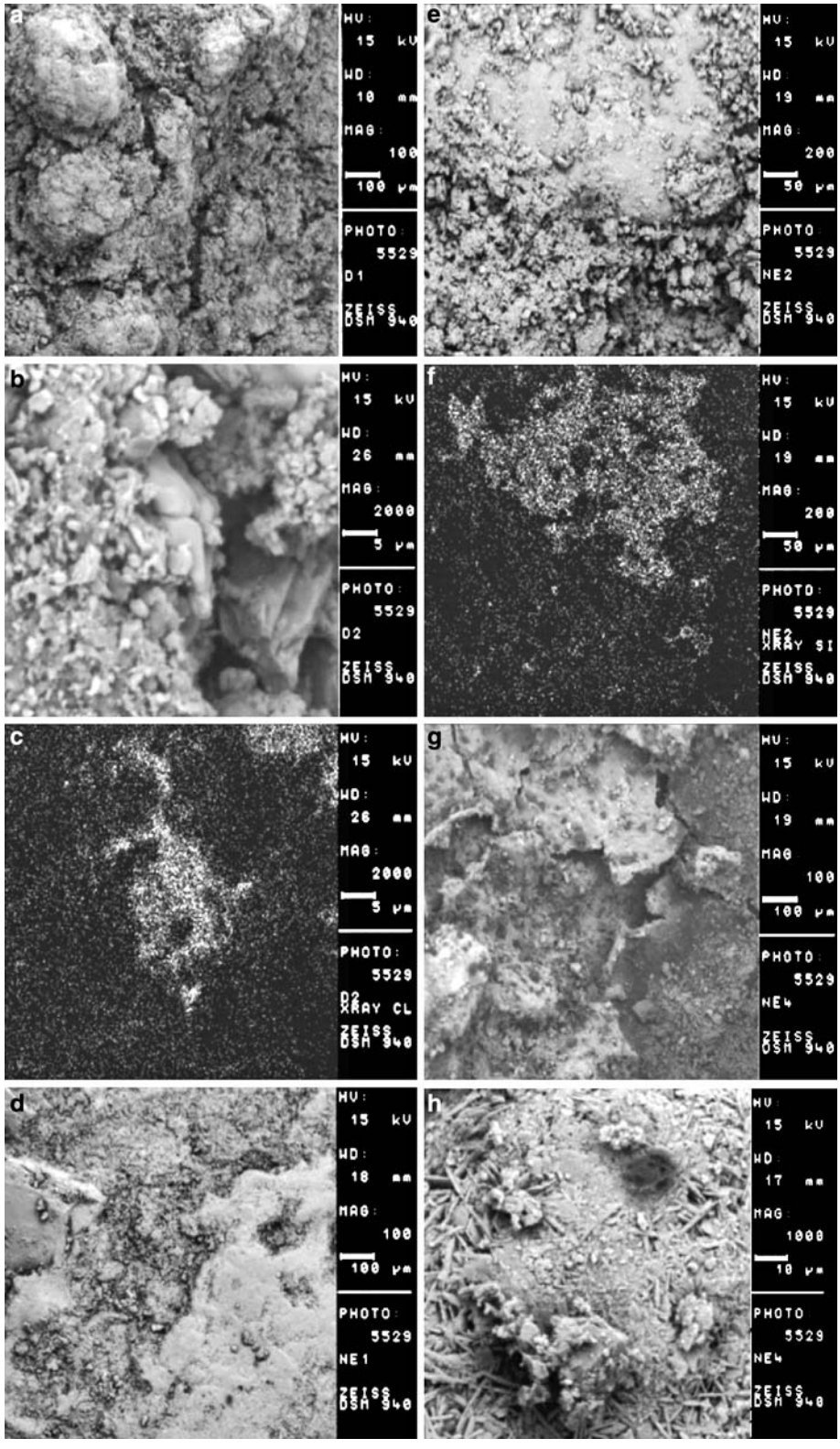


Fig. 2 SEM images of superficial crusts. (**a**–**c**) superficial crust fragment of the northwestern wall of Kasbah of Oudayas. (**a**) crackled and mammilated external surface. (**b**) the internal face with accumulation of halite in pores, and (**c**) the image of EDX microanalyses of Cl. (**d**) gypsum crusts and eroded surfaces of a superficial stone sample of the east faade of the Bab Rouah exposed to run wash. (**e** and **f**) grain of quartz in dissolved cement and disseminated particles of gypsum (image **e**) and an image of EDX analyses of Si (image **f**) in a black crust at the Bab Laalou Portal. (**g**) gypsum crust in sheltered area of the Bab El Hadd Gate, and (**h**) its typical lamellar structure with intersected crystals of gypsum covered by atmospheric particles

used on powdered sample of this calcarenite showed a paragenese formed by calcite, quartz, potassic plagioclase, and other trace minerals. The contents of sulfates, chlorides, and nitrates analyzed by IC were very low.

The weathering process by salts efflorescence on calcarenitic stones

The calcarenite of Almohade monuments in Rabat is characterized by high porosity and a chemical composition dominated by calcium carbonates, which gives the rock a high susceptibility to acid attack by gaseous atmospheric pollutants. Sulfur dioxide fixed by the aqueous phase washing the stone surface as fog, dew, marine spray, and rising dump in the particularly humid climate of Rabat (70% of r.h.), produces acid species corroding the stone surface.

The result of the interaction between calcarenite and the previous atmospheric pollutants is the formation of new mineral species in the rock, often accompanied by structural degradation. The most frequent weathering minerals in our investigation are gypsum and halite. Their crystallization is responsible for most of the damages in the Almohade monuments as in the calcareous monumental stones of the Mediterranean region exposed to marine and/or polluted atmosphere (Zezza 1993).

Gypsum

The circulation of acid solutions followed by the dissolution of carbonated cement causes a sulfatation process which transforms calcium carbonates into calcium sulfates, probably according to the most mentioned reaction (Del Monte and Furlan 1995), simplified as follows:

$$\mathrm{CaCO_{3(s)}} + \mathrm{SO_{2(g)}} + \frac{1}{2}\mathrm{O_2} + \mathrm{H_2O} \rightarrow \mathrm{CaSO_4.2H_2O(s)} + \mathrm{CO_{2(g)}}$$

When the water drift stops, the evaporation leads to migration and condensation of charged solution to the surface and then the deposition and crystallization of gypsum occurs.

Another possibility is the absorption of sulfur dioxide gas directly into the pores and cavities of the rough and humid stone surface; the sulfatation that results is then catalyzed by water present on the surface.

It thus suggests that the mechanism of superficial deposit of sulfates is more or less intense according to the exposition degree of the studied area to the run wash. In the more exposed parts, gypsum crystallization was discontinuous, and the formed crusts are irregular and thin. On the other hand, in sheltered areas, the process leads to the growth of thicker gypsum crusts with typical structure (Del Monte and Furlan 1995) with lamellar and intersected morphology of salt crystals, which is linked to the substratum humidity (Zehnder 1993). Gypsum can also appear as aggregates, xenomorphic, concealing the structure and filling the pores. Generally, the blackening of gypsum crusts is caused by the incorporation of solid particles as soot and dusts (Del Monte and Furlan, 1995).

Halite

In Rabat, halite was detected in various amounts in all samples of monuments in altered surfaces. On the northwestern side of Kasbah of Oudayas, this soluble salt constitutes the more important indicator of stone weathering. The direct exposition to marine sprays led to fixing of marine sodium chlorides on the rough surface of calcarenite and their transportation through the pores to various depths according to the rate of rock humidity. The deposition of halite beyond the surface and the pressure due to its crystallization force generated some disorders in the stone structure, and so its decay (Auger 1988). This resulted in the loss of stone material and the receding of original surface.

Conclusion

The weathering process of calcarenite in Almohade monuments, are linked to the textural characteristics: the bad geotechnical properties, the chemical carbonated composition of the calcarenite, and the presence of soluble salts in the porous system. The sulfates and chlorides affect the stone material by solution, migration, and crystallization mechanisms. Their origin is linked to the natural chemical weathering process of the rock in contact with atmospheric agents enriched by pollutants and marine products. The black crust obtained by stone sulfatation is the most frequent altered form in the observed samples with various intensities according to their exposition to run. The state of the surface below the crust is altered, and the weathering process seems to be active in this interface inducing more damage. The role played by the atmospheric pollutant sulfur dioxide is evident. It has led to intense weathering of Almohade monuments in only some decades, in agreement with the fast growing of the traffic in Rabat.

The marine climate, with characteristic humidity and marine sprays, is the important local factor contributing to the calcarenite weathering. Other decay forms such as biogenic crusts, red patinas, and alveolization are reported. The factors and process of alteration must be studied in order to provide specific techniques of pre-

vention, restoration, and optimal use of calcarenite, which is still widely used in the region as ornamental stone for the buildings.

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