

## ARTICLE

# Salt Weathering in Anisotropic Calcarene: Bedding-plane Controls on Sodium Chloride Precipitation Patterns

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## ABSTRACT

This study investigates the impact of bedding plane orientation on sodium chloride (NaCl) precipitation in a calcarenite stone, subjected to salt weathering cycles. It involves conducting wetting-drying cycles using sodium chloride on two series of specimens sampled parallel and perpendicular to the bedding plane. Capillary imbibition was carried out using saline solutions of two concentrations (15 g/L and 45 g/L). SEM observations show that, across all contaminated samples, halite precipitates mainly on the surface, in the form of efflorescence, while subflorescence remains negligible. The analysis identifies two distinct halite morphologies: (i) cubic crystals of 2 to 10  $\mu\text{m}$  at grain boundaries and (ii) xenomorphic aggregates on pore walls, reflecting that the size and morphology of halite crystals vary according to local nucleation conditions, influenced by the mineralogical composition of the substrates and the degree of supersaturation reached during the cycles. X-ray diffraction analysis revealed significantly higher halite precipitation in samples oriented perpendicular to the sediment bedding (4.53–5.22%) than in those oriented parallel (2.71–4.17%), indicating that bedding plane orientation is a determining factor in weathering processes and the evolution of petrophysical properties. These results demonstrate

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### ARTICLE INFO

Received: 11 August 2025 | Revised: 30 August 2025 | Accepted: 4 September 2025 | Published Online: 9 October 2025

DOI: <https://doi.org/10.30564/jbms.v7i4.11578>

### CITATION

Hraita, M., Rahmouni, A., Zaroual, A., et al., 2025. Salt Weathering in Anisotropic Calcarene: Bedding-plane Controls on Sodium Chloride Precipitation Patterns. *Journal of Building Material Science*. 7(4): 1–15. DOI: <https://doi.org/10.30564/jbms.v7i4.11578>

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that capillary transport is intrinsically anisotropic in calcarenite, with bedding orientation controlling both the amount of precipitated salt and the location of crystallizations. This study thus establishes a solid mechanistic framework for predicting salt weathering patterns in stratified heritage stones, and offers concrete perspectives for optimizing conservation strategies in coastal environments.

**Keywords:** Calcarenite Stone of Rabat; Historical Monuments; Porous Media; Bedding Plane; Sodium Chloride Crystallization; XRD; SEM; Porosity

## 1. Introduction

The built heritage represents a cultural reference of prime importance in any society. It is the part most directly linked to the territory of cultural heritage. In the case of Morocco, historical monuments, both ancient (Phoenician, Carthaginian, Roman) and more recent (Almohad, Merinid, Saadian), constitute a very important national, even universal, cultural treasure such as Lixus, Volubilis, Chellah, Hassan Tower and Koutoubia. In coastal cities, the historical heritage is rich and diverse. It includes a large number of historical sites that were added to UNESCO's World Heritage List in 2012 as cultural structures<sup>[1]</sup>.

In Rabat city, ancient structures, such as the Tour Hassan, Bab El Hadd, Bab Laalou, Kasbah des Oudayas, and Chellah's necropolis, boast rich intricate traditions alongside imposing history<sup>[2-5]</sup>. Equally astounding is that they are tremendous representations of the engineering skills achieved in the region and also serve, quite uniquely, as monuments for astounding architecture in the whole region. Such detailed engineering, and other gorgeous structures like that, were made possible due to the possession of extensive geological resources within the region that add great value to a growing number of traditional structures found<sup>[6]</sup>.

In several countries, the conservation and restoration of heritage sites and historic monuments has always been a priority. However, the problem of the deterioration of these heritage sites remains. Several types of studies are being conducted in this context to develop analytical methods and non-destructive testing techniques suitable for the examination of architectural heritage sites<sup>[7-9]</sup>.

Porous rocks cover large areas of the Earth's surface and are shallow enough to be affected by climate. The depth of penetration of water into rock masses is dependent on many factors, including porosity, composition, texture, grain size, bulk density, fractures, fluid saturation, pore geometry,

connectivity, anisotropy, pressure, temperature, duration of exposure and lithology<sup>[10-12]</sup>.

Due to their location on the oceanfront, these monuments are subject to significant deterioration caused, among other things, by salt precipitation on the surface and subsurface due to capillary action or sea spray. Through ignorance, indifference, or lack of financial resources, they have been left in a state of advanced deterioration. Apart from a few superficial restoration operations (undertaken by the Ministry of Cultural Affairs in recent years), which have been largely ineffective, no major measures have been taken to halt or limit this deterioration. However, only multidisciplinary scientific studies can identify the most appropriate, least costly solutions that will lead to the most sustainable results. It is with this vision of contributing to conservation that our research has been oriented, in order to raise awareness of the need for multidisciplinary interventions and the development of analysis and testing techniques for materials characterization<sup>[3,4,13]</sup>

Calcarenite, a bioclastic sedimentary rock characterized by high porosity (20–40%) and significant permeability, has been widely used since antiquity as a building material in historical architecture in Mediterranean coastal regions<sup>[6,13]</sup>. Although its petrophysical properties facilitate its process and use in construction, they also make it particularly vulnerable to salt weathering, which has been identified as the main degradation factor in marine environments<sup>[14,15]</sup>. This deterioration is mainly induced by the cyclic crystallisation of sodium chloride (NaCl), a salt whose crystallisation pressure can reach up to 39 MPa at ambient temperature, making it one of the most destructive saline agents in coastal areas<sup>[16]</sup>.

The salts penetrate the materials in solution through capillary action, then crystallize during the evaporation process following environmental changes (temperature, relative humidity, etc.). The deterioration, the mechanisms of which

have not yet been fully elucidated, is linked to the repetition of cycles of crystallization and dissolution of salts within the porous network of the material.

The presence of several salts in the same environment influences the properties of each of the salts present. For example, the solubility of gypsum and its compounds is strongly influenced by the presence of other salts<sup>[17]</sup>. Price and Brimblecombe<sup>[18]</sup> observed a change in the equilibrium relative humidity of a salt in the presence of another salt. Sawdy and Heritage<sup>[19]</sup> confirmed that a mixture of several salts causes a change in their respective equilibrium relative humidities. Thus, at a given temperature, a mixture of salts will not have a single equilibrium relative humidity value but several, a whole range of equilibrium relative humidity values that is not necessarily between those of the individual salts. The mixture of salts thus formed may have increased weathering potential<sup>[18]</sup>.

The alteration of stones by salts is very active in the presence of water. This water can come from various sources such as dew, fog, rain, and groundwater<sup>[6]</sup>. Salts can penetrate and move through the porous network of rock only when they are dissolved in water. They penetrate and move through porous material by capillary action from the ground and/or by rainwater infiltration. They can also be deposited on the surface of the material during water runoff. Water condensation on the surface can allow salts to penetrate into the porous material<sup>[15]</sup>. Since the behavior of stones with regard to weathering is directly linked to fluid transfer phenomena (water, vapor, air), a detailed study of the water transfer properties of calcarenite rocks is essential. A good understanding of the parameters involved in transfer phenomena (capillary, evaporation, thermal, mechanical, and electrical) allows for a better understanding of the mechanisms of weathering and for the consideration of solutions to limit its progression. Once all these factors have been clearly identified and understood, the protection of the stone can be considered.

Over the years, various hypotheses have been developed, leading to theoretical models, in order to understand the mechanism(s) by which salts cause aesthetic and above all mechanical alterations in the building materials of historic monuments and also in modern structures. The most popular

mechanisms in the scientific literature can be broadly classified into three groups: crystallisation pressure, differential thermal expansion and chemical weathering of carbonate cements<sup>[20–22]</sup>. These mechanisms frequently act in a combined manner to cause progressive and often irreversible material damage.

While these mechanisms are relatively well established, the impact of the intrinsic structural anisotropy of certain materials, such as calcarenite stone, on the amount, morphology and location of salt crystals remains only partially understood. Indeed, calcarenite has an anisotropic pore structure due to its sedimentary stratification, which directly affects capillary flow and therefore the spatial distribution of salts within the material. Previous studies carried out on these same samples, subjected to wetting-drying cycles by sodium chloride solutions<sup>[23]</sup>, have shown that the bedding plane orientation significantly influences capillary kinetics, thermal conductivity and permeability.

This study aims to determine whether the morphology and distribution of NaCl crystals in calcarenite, as well as the amount of precipitated salt, are mainly governed by the direction of capillary flow relative to the bedding plane, or whether they depend more on local nucleation conditions within the pore network. It also seeks to establish whether there is a direct relationship between previous petrophysical results obtained on the same samples (permeability, imbibition kinetics, thermal conductivity) and mineralogical and microstructural data obtained from X-ray diffraction (XRD) and scanning electron microscopy (SEM).

We hypothesize that the precipitated salt amount is greater in samples oriented perpendicular to the bedding plane, due to lower porous connectivity, slowing down the capillary flow and thus promoting local saturation. In contrast, crystal morphology and distribution would be independent of the bedding orientation, essentially reflecting the local physicochemical conditions at nucleation sites.

To address these questions, a combined approach based on X-ray diffraction (XRD) and scanning electron microscopy (SEM) was adopted. These two complementary techniques allow, respectively, to quantify the crystallized phase (halite) and to observe its precise morphology and location in the porous matrix.

## 2. Materials and Methods

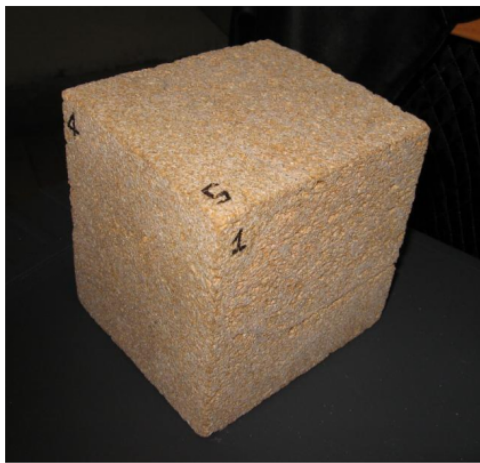
### 2.1. Sampling and Sample Description

The stone most widely used in the construction of these monuments is Plio-Quaternary calcarenite, known locally as ‘Salé stone’. This ochre-yellow sedimentary rock corresponds to coastal sandstone that outcrops more or less continuously between Casablanca and Larache<sup>[6]</sup>.

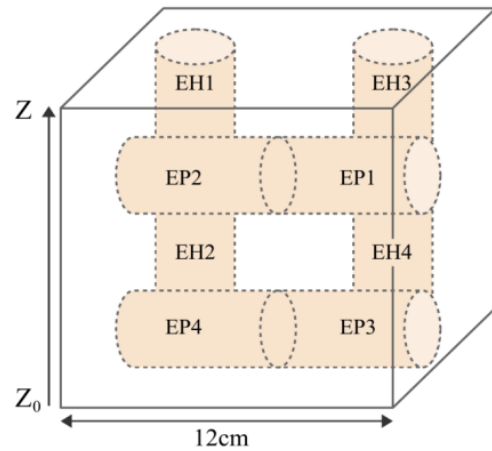
In this study, we chose calcarenite stone, a coarse bioclastic limestone commonly used as a building material in Moroccan architectural heritage, particularly in coastal areas. This sedimentary rock of heterogeneous texture is composed mainly of calcium carbonate (70.79%  $\text{CaCO}_3$ ), with a low

silica content (6%  $\text{SiO}_2$ ) which appears in the form of quartz grains<sup>[9]</sup>. Petrophysical characterizations have detected a high total porosity that varies between 16.52% and 34.9%, a significant permeability between 4.4 and 5.5 Darcy<sup>[24,25]</sup>, as well as a thermal conductivity that ranges between 1.15 and 1.87 W/(m.K). However, the compressive strength is relatively low and varies between 0.01 and 0.84  $\text{kN/cm}^2$ <sup>[13,26]</sup>

Our mineralogical and petrographic analyses were carried out on eight identical cylindrical samples (height : 5 cm; diameter : 3.3 cm), taken from a block of calcarenite from the Rabat quarry (**Figure 1a**). Four specimens were taken parallel to the bedding planes (series 1) and four others perpendicular to it (series 2) (**Figure 1b**).



(a) Calcarenite Block



(b) Core extraction method

**Figure 1.** (a) Block of calcarenite stone extracted from Rabat quarry; (b) Core extraction method, ( $Z_0Z$ ) axis is oriented perpendicular to the sediment bedding plane. Four cylindrical samples (3.3cm in diameter & 5cm height) are cored parallel to the sediment bedding (Series 1), and four others perpendicular to it (Series 2).

### 2.2. Justification for Salt Choice

Sodium chloride ( $\text{NaCl}$ ) was chosen as the contaminating salt because of its predominance in degradation processes in coastal environments. Studies carried out on Rabat’s historic buildings, in particular the Chellah citadel and the medieval ramparts—have systematically identified  $\text{NaCl}$  as the main agent of degradation<sup>[27,28]</sup>. In coastal environments,  $\text{NaCl}$  occurs in two stable forms: cubic halite (anhydrous) above  $0.1^\circ\text{C}$ , and a dihydrate form ( $\text{NaCl}\cdot 2\text{H}_2\text{O}$ ), rarely observed, at negative temperatures<sup>[29]</sup>. This hydrated phase is often overlooked in weathering processes. The anhydrous form exhibits temperature-independent solubility between  $0\text{--}100^\circ\text{C}$ ,

and deliquescence at 75% relative humidity, making it particularly active in Mediterranean climates. According to the  $\text{NaCl}\text{--}\text{H}_2\text{O}$  phase diagram, at a temperature of approximately  $0.1^\circ\text{C}$  and a concentration of about 6.15 molal, the three phases - sodium chloride dihydrate ( $\text{NaCl}\cdot 2\text{H}_2\text{O}$ ), halite ( $\text{NaCl}$ ), and saturated aqueous solution-coexist in equilibrium.

The morphology of the crystals depends on phase transition parameters but is only slightly affected by environmental conditions<sup>[21]</sup>. During drying, the lower the relative humidity, the fewer crystals form, and salt crystallizes in a cubic structure (growth at a low degree of supersaturation). In contrast, at high relative humidity, salt crystallization occurs in a dendritic form (growth at a high degree of supersaturation).

## 2.3. Experimental Protocol

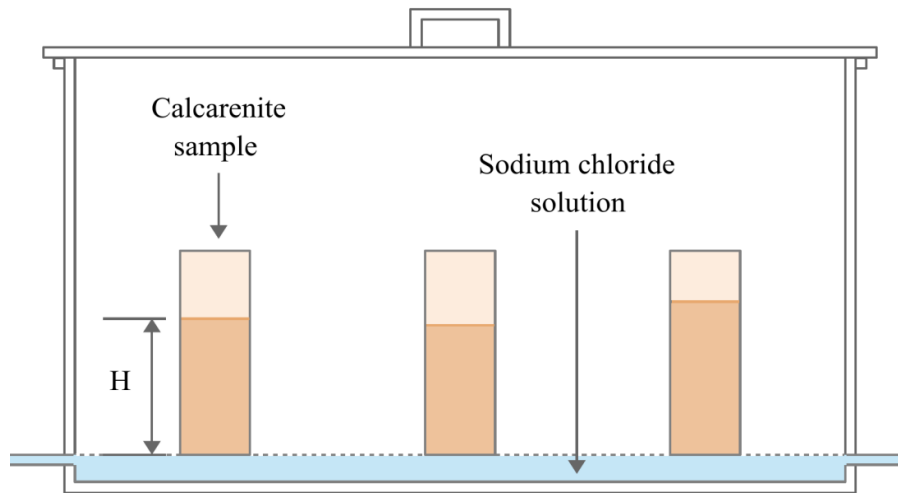
Salt crystallization tests were carried out using an experimental method inspired by protocol No. II.6 of the RILEM standard. Samples from both series 1 and 2 were first dried in an oven at 60°C for 48–72 hours until a constant mass was obtained. Then, the samples were arranged vertically on a grid within a hermetically sealed container to maintain a humidity close to saturation (**Figure 2**). The container contained a sodium chloride (NaCl) solution, at a concentration of 15 g/L or 45 g/L (**Table 1**), the level of which was kept constant at approximately 3 mm from the bottom. This prevented the superposition of evaporation phenomena on those

of capillary imbibition. This experiment was carried out in a climate-controlled room at a controlled temperature (25°C). This process was repeated to complete five imbibition-drying cycles for each sample.

The experimental protocol described in this work is identical to that used in our previous work<sup>[23]</sup>, which focused on the same samples (series 1 and 2) and aimed to characterize the petrophysical properties of calcarenite stone (capillary imbibition kinetics, permeability, thermal conductivity). This continuity makes it possible not only to better understand the alteration mechanisms of this anisotropic material, but also to consider solutions to limit its evolution.

**Table 1.** Sodium chloride (NaCl) saline solutions employed in capillary imbibition tests.

Parameters	Samples Parallel to Stratification Plane (Series 1)				Samples Perpendicular to Stratification Plane (Series 2)			
	EP1	EP2	EP3	EP4	EH1	EH2	EH3	EH4
NaCl concentration / g L <sup>-1</sup>	45	15	45	15	45	15	15	45



**Figure 2.** Experimental setup for capillary imbibition. H represents the height of the capillary fringe.

## 2.4. XRD and SEM Analysis

Mineralogical characterization was performed by X-ray diffraction (XRD) using a Philips AP1700 diffractometer, equipped with a copper anticathode X-ray tube (Cu-K $\alpha$ ,  $\lambda = 1.5406 \text{ \AA}$ ). After the fifth imbibition-drying cycle, representative samples from series 1 and 2 were reduced to fine powder ( $< 2 \mu\text{m}$  particle size) by using the back-loading technique in order to minimize preferential orientation effects. Measurements were performed at 40 kV and 20 mA, with a continuous angular scan from  $3^\circ$  to  $65^\circ$  ( $2\theta$ ) and a step

size of  $0.02^\circ$  and a counting time of 1 s per step (equivalent to a scan rate of  $0.02^\circ/\text{s}$ ). Measurements were conducted at room temperature (25 °C).

Furthermore, fragments of representative samples from the same series, also taken after the fifth imbibition-drying cycle, were observed under a TESCAN VEGA scanning electron microscope (SEM). These fragments were placed in a desiccator (relative humidity, RH = 0%) for 24 hours, then metallized with gold ( $\sim 20 \text{ nm}$ ). Images were acquired in secondary electron (SE) mode, under an accelerating voltage of 15 kV and a working distance (WD) between 22.08 and

24.59 mm.

The SEM system offered a magnification range from  $10\times$  to  $10^6\times$ , allowing detailed observation of the material's microstructure. It was used to examine the shape of grains and pores in three dimensions, measure the properties of the pore network, identify authigenic minerals, and record the crystallisation characteristics of the salt. Combined with XRD analysis, which provided overall mineralogical data, the SEM observations provided additional information on the microstructure. Together, these techniques were crucial in highlighting the anisotropic alteration observed in the

calcarene rock.

### 3. Results and Discussion

#### 3.1. Salt Precipitation Patterns

At the end of each imbibition-drying cycle, a systematic visual examination revealed distinct halite crystallization patterns across all samples. From the first cycle, the first whitish efflorescences appeared on the surface, forming irregular crystalline crusts, mainly concentrated in the lower part of the samples (**Figure 3**).



(a) series 1



(b) series 2

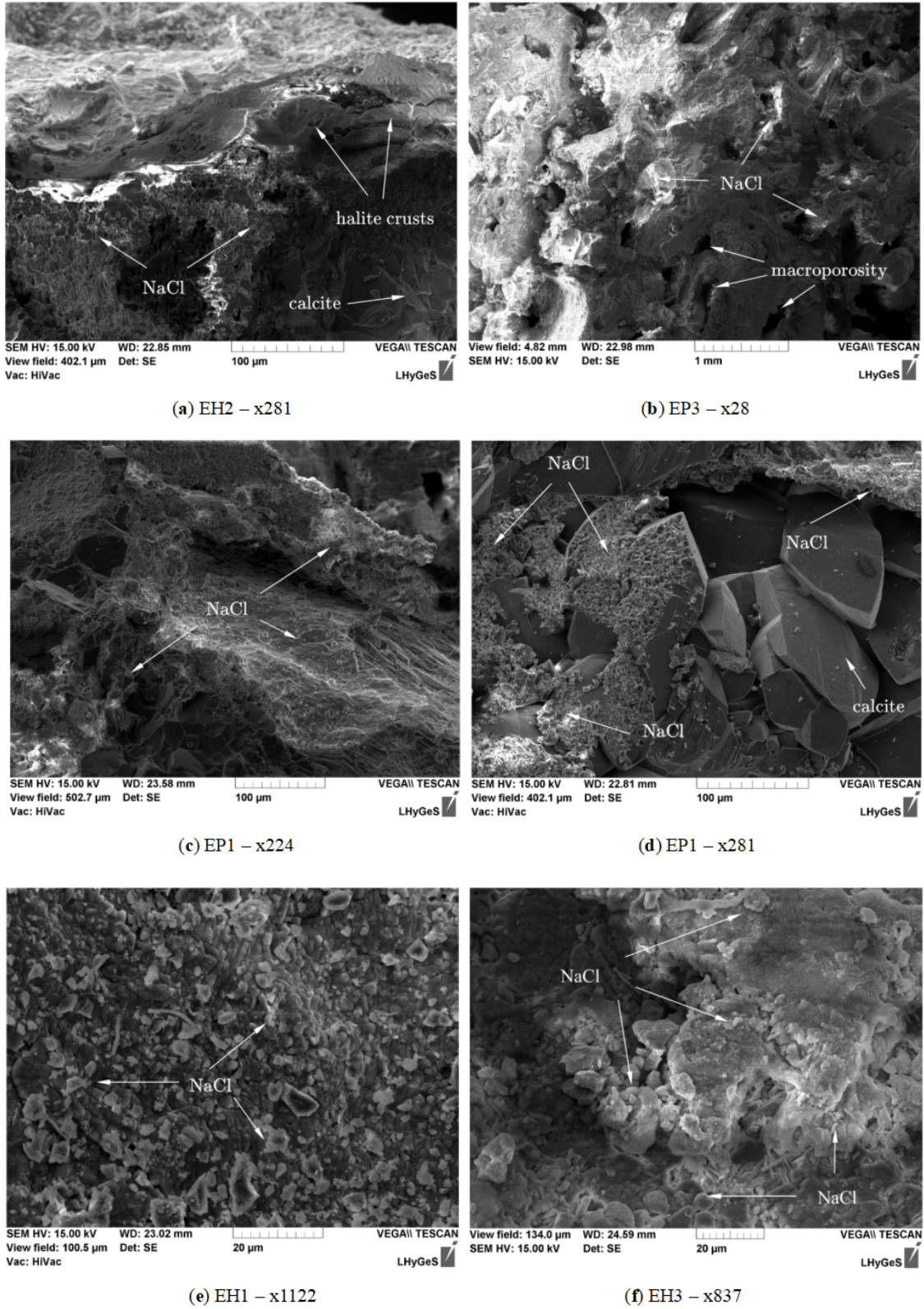
**Figure 3.** The pictures (a) and (b) are taken after the first dissolution-crystallization cycle, and show the NaCl efflorescence formation.

The salt deposits were more visible in the samples exposed to the concentrated solution (45 g/L), and their thickness progressively increased with the number of cycles, evolving from small isolated clusters in the first cycle to interconnected crystalline coatings in the last cycle (**Figures 4a & 5f**). The stone roughness and the natural irregularities of the surface seem to favor the nucleation and distribution of halite deposits.

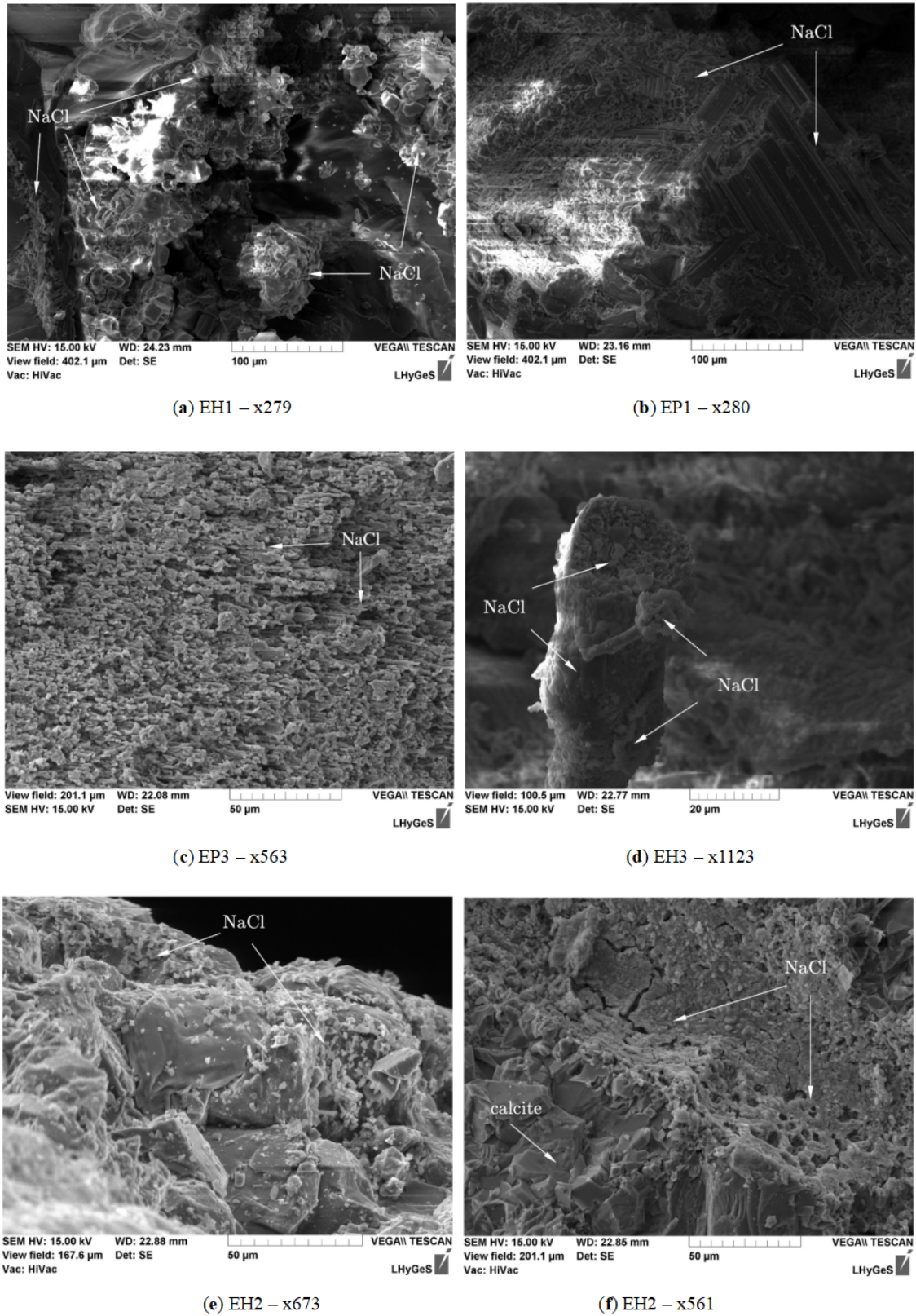
**Figures 4 & 5** show scanning electron microscopy (SEM) images of several fragments of salt-contaminated calcarenite. The images selected for analysis were chosen to focus on areas at or very close to the surface (Series 1 and 2), primarily to visualise the precipitated halite. The observations show that, for all the contaminated samples, whatever the applied concentration, sodium chloride precipitates mainly on the surface, in the form of efflorescences (e.g., **Figures 4a-c; Figure 5f**). The amount of salt precipitated at depth (subflorescence) is very low, even negligible,

and the subflorescence sites could rarely be identified during the analysis.

The progressive accumulation of halite crystals during wetting–drying cycles leads to the formation of crystalline deposits that exert significant crystallization pressure. This stress disrupts the cohesion of the stone's solid matrix, causing scaling and microcracking. This progressive weakening is consistent with studies on cementitious materials, where exposure to chloride and sulfate ions leads to significant reductions in compressive strength due to internal expansion, cracking, and matrix disruption<sup>[30]</sup>. Furthermore, Hosseini et al.<sup>[31]</sup> emphasized that increased porosity accelerates degradation in aggressive environments, as it enhances fluid penetration and reaction kinetics. Although NaCl does not chemically react with calcite in the same way as sulfuric acid, its crystallization within pores generates mechanical stresses analogous to expansive chemical reactions, particularly in materials with high interconnected porosity like the Rabat calcarenite.



**Figure 4.** Multi-scale SEM characterization of halite crystallization patterns in (a, e, f) bedding-perpendicular calcarenite cores (EH1-EH3) and (b, c, d) bedding-parallel cores (EP1, EP3) following five capillary cycles.



**Figure 5.** Multi-scale SEM characterization of halite crystallization patterns in (a, d, e, f) bedding-perpendicular calcarenite cores (EH1-EH3) and (b, c) bedding-parallel cores (EP1, EP3) following five capillary cycles.

Numerous studies, both microscopic (capillary tubes) and macroscopic (stones)<sup>[32]</sup>, have shown that, for similar materials, sodium chloride almost systematically precipitates in efflorescence, independently of the physicochemical conditions. Conversely, sodium sulfate generally forms subflorescences. This difference in behavior has been attributed to a difference in liquid/vapor surface tension between the two solutions<sup>[33]</sup>, which may cause a variation in capillary pressure. The surface tension of the NaCl solution ( $\gamma_{\text{NaCl}} = 84 \text{ mN/m}$ ) is in fact higher than that of  $\text{Na}_2\text{SO}_4$  ( $\gamma_{\text{Na}_2\text{SO}_4} = 81 \text{ mN/m}$ ). Higher tension accentuates the capillary pressure gradient, responsible for a more active transport of the solution towards the surface, thus promoting the formation of efflorescence. Conversely, in the case of sodium sulfate, the transport is slower, which favors evaporation inside the material, and therefore the formation of subflorescence.

The results also show that NaCl crystals preferentially form on pore walls (**Figure 4b**), on grain faces of quartz, secondary calcite, micrite, as well as at grain boundaries (e.g., **Figures 4c-d**). However, they are rarely observed on smooth surfaces of primary calcite (**Figure 4d**) or in macropores (**Figure 4b**). Halite generally precipitates as xenomorphic clusters, although some formations exhibit sub-automorphic cubic crystals measuring 2 to 10  $\mu\text{m}$  in size (**Figures 4e-f**).

Crystal morphology varies considerably depending on local precipitation conditions. Size and shape differences (**Figures 4e-f; 5a-f**) appear to be related to the local chemical composition (O, Ca, C, Fe, Si) and mineralogical context (primary vs. secondary grains, sparite vs. micritic textures), as well as to the degree of solution supersaturation. Indeed, a high degree of supersaturation favors rapid nucleation at the expense of growth, resulting in the formation of smaller crystals ( $< 5 \mu\text{m}$ ; e.g., **Figures 4e & 5c**), while a lower degree of supersaturation allows equilibrium crystal growth, leading to larger crystals ( $< 10 \mu\text{m}$ ; e.g., **Figures 5a-b**).

The heterogeneous growth of halite on pore walls indicates a strong crystal-substrate interaction, suggesting a

surface-controlled nucleation mechanism<sup>[32]</sup>. However, the exact mode of sodium chloride nucleation remains debated. Bouzid<sup>[34]</sup>, for example, considers that nucleation probably occurs in several rapid steps. In capillary tube observations, he noted that precipitation begins with the formation of small cubic crystals at the air/solution interface, which subsequently coalesce to form a massive precipitate, a phenomenon sometimes visible under an optical microscope.

It should be noted that the microstructural observations obtained by SEM do not, at this stage, allow us to explain the petrophysical differences observed after the salt weathering cycles between series 1 and 2, particularly with regard to capillary kinetics, thermal conductivity and permeability. These results have been discussed in detail in our previous work<sup>[23,35]</sup>.

### 3.2. X-ray Diffraction Analysis

The results of the mineralogical analysis by X-ray diffraction (XRD), presented in **Table 2 & Figures 6 & 7**, show that calcite ( $\text{CaCO}_3$ ) and quartz ( $\text{SiO}_2$ ) constitute the two main crystalline phases of the studied calcarenite. These minerals are identified by their characteristic peaks, located respectively at  $29.46^\circ 2\theta$  ( $d_{104} = 3.03 \text{ \AA}$ ) for calcite and  $26.67^\circ 2\theta$  ( $d_{011} = 3.34 \text{ \AA}$ ) for quartz. These positions confirm the results obtained on sound samples<sup>[13,24]</sup>. In addition, the diffractograms highlight the presence of sodium chloride (NaCl), precipitated after salt weathering cycles. This secondary phase is identifiable by an intense peak at  $31.7^\circ 2\theta$  ( $d_{200} = 2.82 \text{ \AA}$ ), characteristic of its cubic crystal structure.

A mineralogical XRD analysis by Samaouali et al.<sup>[6]</sup> on a sound calcarenite sample from the Rabat quarry revealed the presence of dolomite,  $\text{CaMg}(\text{CO}_3)_2$ , as a trace phase (0.002%). Dolomite crystallizes in the trigonal system (space group  $R\bar{3}$ ) with a rhombohedral lattice. Its presence, even in such low concentrations, could influence the mechanical and chemical properties of the calcarenite.

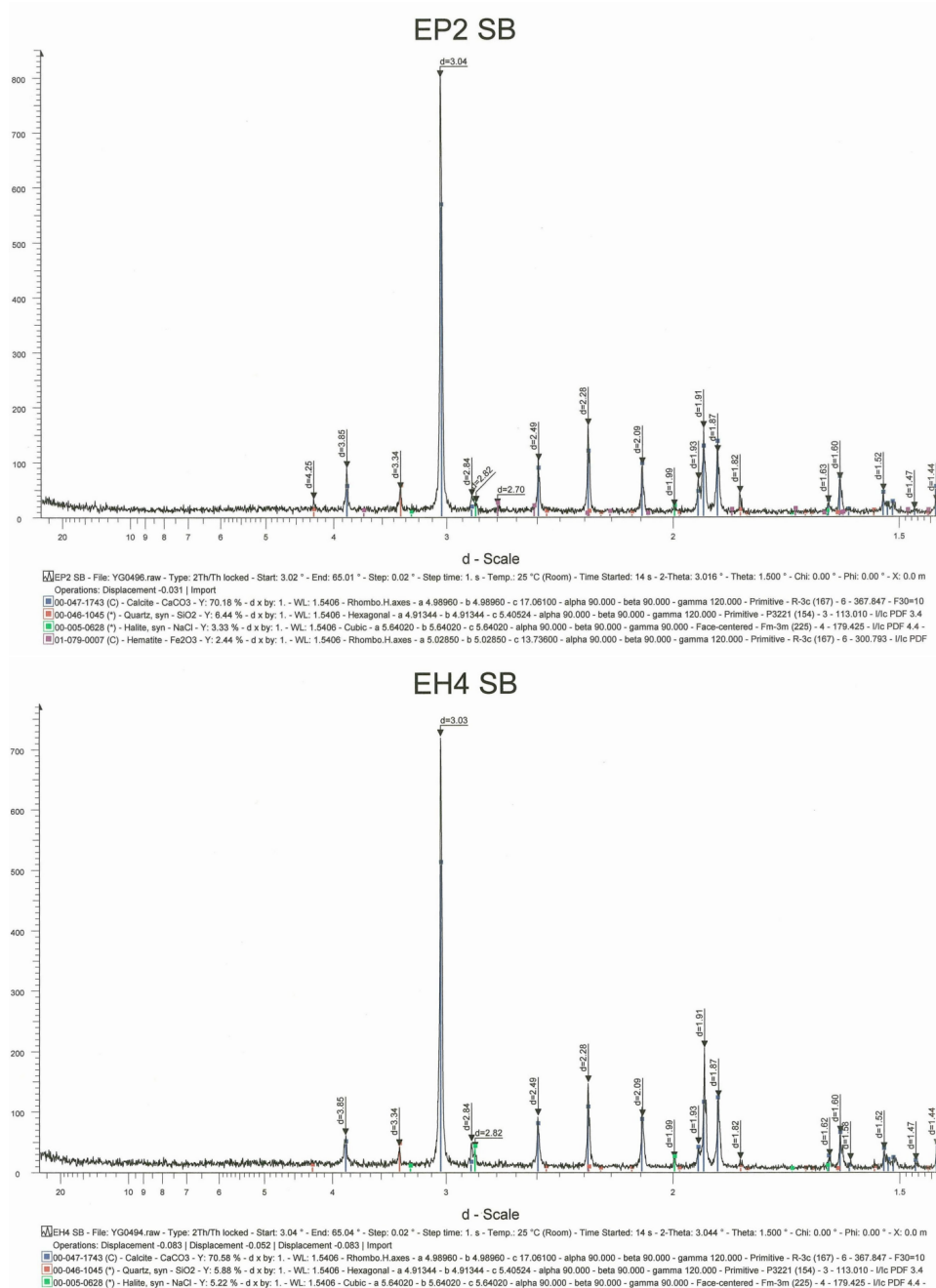
**Table 2.** Mineralogical composition of NaCl-contaminated calcarenite after five wetting-drying cycles.

Parameters	Samples Parallel to Stratification Plane (Series 1)				Samples Perpendicular to Stratification Plane (Series 2)			
	EP1	EP2	EP3	EP4	EH1	EH2	EH3	EH4
Calcite ( $\text{CaCO}_3$ ) (%)	64.82	70.18	78.42	78.40	96.45	33.28	49.28	70.58
Quartz ( $\text{SiO}_2$ ) (%)	13.03	6.44	6.62	12.23	8.15	4.55	3.54	5.88
Halite (NaCl) (%)	2.71	3.33	4.17	2.73	4.53	-	-	5.22
Hematite ( $\text{Fe}_2\text{O}_3$ ) (%)	-	2.44	-	-	-	-	-	-

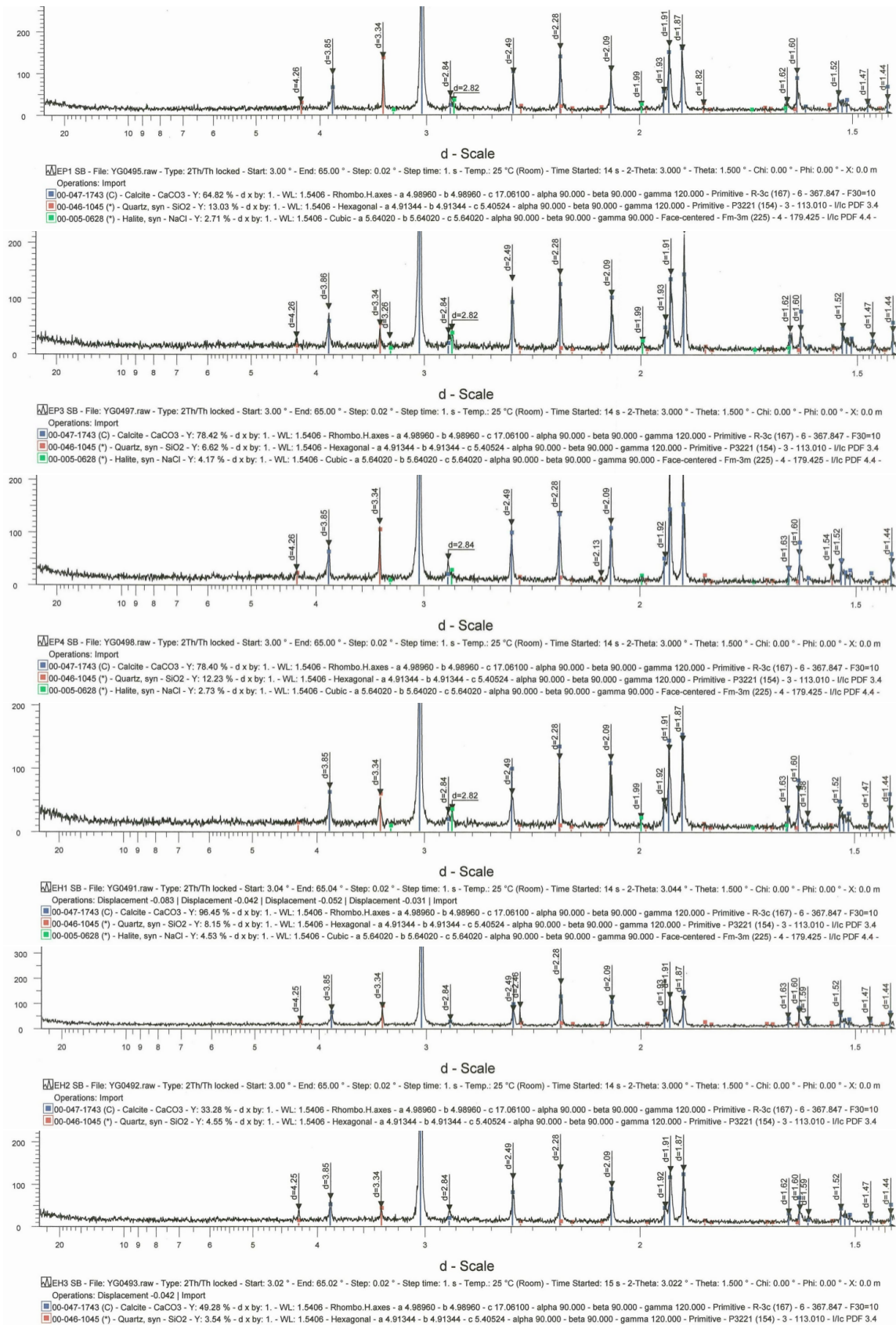
Comparative analysis of the two sample series - oriented parallel (series 1) or perpendicular (series 2) to the stratification planes - reveals significant differences in the relative proportions of the mineral phases. Calcite, the dominant phase, presents more homogeneous contents in series 1 (64.82–78.42%) than in series 2 (33.28–96.45%), suggesting a distribution influenced by sedimentary anisotropy. Quartz, although in lower proportion, shows a systematically higher abundance in samples from series 1 (6.44–13.03%) compared

to those of series 2 (3.54–8.15%). This difference could reflect a preferential granulometric segregation according to the bedding planes.

In addition, XRD analysis reveals the presence of another crystalline phase, hematite ( $\text{Fe}_2\text{O}_3$ ) in sample EP2, with a significant content of 2.44%. Weakly incorporated into the mineral matrix, this phase is characterized by a rhombohedral crystalline structure, identifiable by a main peak at  $33.15^\circ 2\theta$  ( $d_{104} = 2.70 \text{ \AA}$ ).



**Figure 6.** XRD patterns (Intensity vs. d-spacing) of NaCl-weathered calcarenite samples EP2 (parallel-to-bedding) and EH4 (perpendicular-to-bedding) after five wetting-drying cycles.



**Figure 7.** XRD patterns (Intensity vs. d-spacing) of NaCl-weathered calcarenite samples EP1, EP3, EP4 (parallel-to-bedding) and EH1, EH2, EH3 (perpendicular-to-bedding) after five wetting-drying cycles.

The most significant observation concerns the amount of halite precipitated after the five wetting-drying cycles. The NaCl contents vary between 2.71 and 4.17% for series 1 and between 4.53 and 5.22% for series 2. On average, the amount of precipitated salt is 1.42 times higher in samples oriented perpendicular to the bedding-plane. This result corroborates previous petrophysical observations<sup>[23]</sup>, according to which the permeability decreases more and the thermal conductivity increases more strongly in samples oriented perpendicular to the bedding planes. These variations can be explained by a more pronounced salt saturation and an alteration of the porous network localized in certain areas, linked to the material's anisotropy.

It should be noted that XRD analysis did not detect halite crystals in samples EH2 and EH3, contrary to visual observations made with the naked eye and confirmed by scanning electron microscopy (SEM). This apparent disparity is due, among other things, to the superposition of two peaks belonging to two different mineral phases that cannot be distinguished on the diffractogram. X-ray diffraction (XRD) analysis, often, cannot give accurate results if used alone (**Figure 7**). This is why it is considered necessary to combine several complementary analysis techniques, physical or chemical (SEM, XRD, ICP-AES, SFX), to obtain the most reliable results.

All these results demonstrate a high degree of mineralogical heterogeneity intrinsic to calcarenite stone, which is reflected in the variability of its petrophysical properties (porosity, imbibition kinetics, permeability, thermal conductivity). This structural heterogeneity plays a central role in the material's response to salt weathering. It notably explains why variations induced by salt precipitation during cycles, such as reduced permeability or increased thermal conductivity, are more pronounced in samples perpendicular to the bedding plane (series 2), as demonstrated in our previous work<sup>[35]</sup>.

In fact, salt precipitation locally modifies the texture and connectivity of the porous network, by obstructing certain capillary channels and disrupting the preferential capillary transport pathways. This in turn leads to a heterogeneous redistribution of salt over the wetting-drying cycles, favouring supersaturation in specific zones of the material matrix. This reciprocal relationship between fluid capillary transport, salt precipitation and evolution of hydric properties is a

key mechanism in the progressive weathering of anisotropic porous materials such as calcarenite stone.

This study highlights the complex interactions between structural anisotropy and salt precipitation in calcarenite. It reveals that, while the capillary flow direction controls the amount of deposited salt, the morphology and distribution of crystals are mainly determined by local nucleation conditions. These results make an original contribution to the understanding of salt weathering mechanisms in anisotropic materials and offer relevant perspectives for the optimization of heritage conservation strategies, particularly by taking into account the stratigraphic orientation of stones during desalination and protection interventions.

## 4. Conclusions

In this work, we present the results of an analytical study of sodium chloride-induced salt weathering of calcarenite stone, combining two complementary techniques: X-ray diffraction (XRD) and scanning electron microscopy (SEM). Five imbibition-drying cycles were performed on calcarenite samples taken parallel (series 1) and perpendicular (series 2) to the bedding planes, using sodium chloride solutions at two concentrations (15 g/L and 45 g/L). Analyses revealed a dominant formation of halite efflorescence on the sample surfaces, while a minor fraction of salt remains trapped in the porous network. These salt deposits caused significant changes in the structure and texture of the tested samples, resulting in a progressive decrease in permeability and a slight increase in thermal conductivity over the course of the salt weathering cycles.

SEM observations reveal that salt crystals develop as xenomorphic clusters on pore walls, on the faces of quartz and calcite grains (primary, secondary, and micritic), as well as at intergranular boundaries. The size and morphology of salt crystals vary significantly depending on local nucleation and growth conditions, influenced both by the chemical and mineralogical composition of the substrates and by the degree of supersaturation reached during the weathering cycles. A key finding of this study is the influence of the direction of capillary rise relative to the bedding on salt precipitation and thus calcarenite damage. Indeed, samples oriented perpendicular to the strata exhibit significantly greater halite accumulation (4.53–5.22%) than those oriented parallel (2.71–4.17%).

Thus, the orientation of the bedding planes appears to be a determining factor in salt crystallization processes and the evolution of petrophysical properties. It influences not only the total amount of precipitated salt, but also its spatial location and its impact on the pore structure.

These results provide a robust interpretative framework, coherently linking microstructural phenomena (XRD, SEM) to macroscopic behaviors measured in the laboratory and observed in situ. The systematic correlation between these different scales of analysis confirms the fundamental importance of structural anisotropy in predicting the weathering patterns of stone materials exposed to marine environments.

The broader impact and practical significance of this study are substantial. By establishing quantitative relationships between calcarenite's structural anisotropy and salt weathering progression, this work provides both a predictive framework for damage assessment and a scientific foundation for developing targeted conservation strategies. The demonstrated orientation effects underscore the need for material-specific preservation methodologies, particularly for vulnerable coastal heritage structures, especially in light of predicted increases in coastal salt spray concentrations and more extreme wetting-drying cycles associated with climate change.

Finally, these findings open up relevant perspectives for optimizing built heritage conservation strategies, particularly by taking into account the orientation of bedding planes in the design of desalination treatments, the application of hydrophobic barriers, and the management of capillary drainage. In direct continuation of this work, our future research aims to better understand the salt crystallization processes in many heritage building materials, and to determine the location and conditions under which damage occurs. To achieve this, it is essential to use other techniques, such as helium pycnometry, inductively coupled plasma atomic emission spectrometry (ICP-AES), and X-ray fluorescence spectrometry (XRF), among others.

Another promising research avenue concerns sodium sulfates ( $\text{Na}_2\text{SO}_4$ ), widely recognized as one of the most destructive salts for porous materials. Despite their frequent use in laboratory durability tests and their widespread presence in soils and groundwater, their role in stone degradation remains partially misunderstood due to the complexity of

the  $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$  phase system. Studying their impact on the weathering of calcarenite would undoubtedly contribute significantly to the field of petrophysics. Such research should aim to clarify the role of sodium sulfates in stone damage, particularly the relationship between the two hydrates: heptahydrate and mirabilite.

## Author Contributions

M.H.: Conceptualization, methodology, investigation, formal analysis, writing—original draft preparation, project design, and supervision. A.R.: Validation, review, and editing. A.Z.: Review and validation. Y.G.: Project administration and funding acquisition. All authors have read and agreed to the published version of the manuscript.

## Funding

This work received no external funding.

## Institutional Review Board Statement

Not applicable.

## Informed Consent Statement

Not applicable.

## Data Availability Statement

All data generated during this study are included in this published article.

## Acknowledgments

This research was carried out with the support of the French-Moroccan cooperation program (PAI-Volubilis, Grant No. MA/07/168), a collaborative initiative between the University of Strasbourg (France) and Mohammed V University in Rabat (Morocco). The authors extend their gratitude to Mrs. Fabienne from the Institute of Earth Physics of Strasbourg (IPGS) for her valuable technical support in conducting X-ray diffraction analyses.

## Conflicts of Interest

The authors declare no conflicts of interest.

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