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X-ray characterisation of bulk stones from the patina to the depth stone

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Abstract. The aim of this study on monumental limestone alteration is to characterise the superficial stone called patina where transformation processes due to air and water occur. We present results on stones from the Chambord castle, so Tuffeau limestone, from the Loire Valley.

Three samples has been studied and compared in relationship with their position on the monument (outside or inside).

In order to describe these samples, different techniques have been used : chemical analysis, optical microscopy. The three main phases are calcite (CaCO₃), quartz and opal (SiO₂), with various granulometry.

X-ray diffraction has been performed on bulk samples. A special sample holder allows to analyse very thin zones, so to describe the mineralogical composition from the epidermis to the depth stone [1]. The stones are constituted of small crystallites which differ in dimension and orientation. This conducts to a semi-quantitative description. Protecting layer of the stone is associated to the rate of dissolution of calcite in patina zone.

1. INTRODUCTION

Tuffeau is an architectural French limestone coming from the Loire Valley and constituted a lot of very important historical monuments, such as the French Renaissance Chambord castle. This monument made with this stone is very sensitive to environment and, with years, the superficial stone zone called patina, which protects the stone [1], show alterations. Both, patina formation and stone alteration are due to water circulation in material (its progress in material, its composition and its ability to dissolve or precipitate minerals). Water comes from rain and rises by capillarity. The patinas are characterised by a mineralogical composition and a texture which evolve from the outside surface to the depth. Surface alterations correspond to matter loss and/or stone cohesion decrease. Alteration origins can be physical (rupture of stone as a result of frost), chemical (mineral dissolutions and/or salt crystallizations with contribution of exterior elements) or biological. Different methods are available to clean or restore the patina. In order to improve the cleaning and restoration methods, it is necessary to accurately determine the physico-chemical properties of the patina. This study concerns the characterisation of the Tuffeau patina by X-ray diffraction. The aims are to identify the crystalline phases and to follow their evolution from the outside surface to the depth stone, in order to understand the physico-chemical processes leading to the patina formation. The studied samples have been architecturally used in rural zone where aggressive environmental effects are lower than for urban zones studied in previous papers [2,3]. Outside and inside samples will be compared.

2. SAMPLES

2.1 Tuffeau stone

Tuffeau stone is a limestone of the Upper Cretaceous and characteristic of the area around Tours, in the Loire Valley. The white tuffeau shows a high porosity (35 to 50 %), so a low density (about 1.5) : it is a material easy to sculpt and useful for vault construction.

Tuffeau contains several mineralogical species : calcite (50 to 70 %), quartz and opal (27 to 42 %), and clay minerals in weak proportion (a few percent)

2.2 Chambord samples

Chambord castle has been built during the XVIth century. Restoration works have been performed at different times and some stones were changed. Three samples from these stones have been selected, been exposed to different alteration conditions.

a) outside column

This sample comes from a XIXth century column, at a 10 m highness and on the east face of the building. This sample will be called OC (outside column).

b) outside shell

This sample comes from a XVIth century stone sculpted with a shell shape. It was used in XIXth century as filling material, and was discovered in 1998, buried under the terrace of the castle. This sample will be called BS(buried shell).

c) inside sample

This sample of XVIth century was removed from a door lintel in roof of the castle. It will be called IL (inside lintel).

The three samples showed patina zones visible to the naked eye as displayed on figure 1 for two of them.

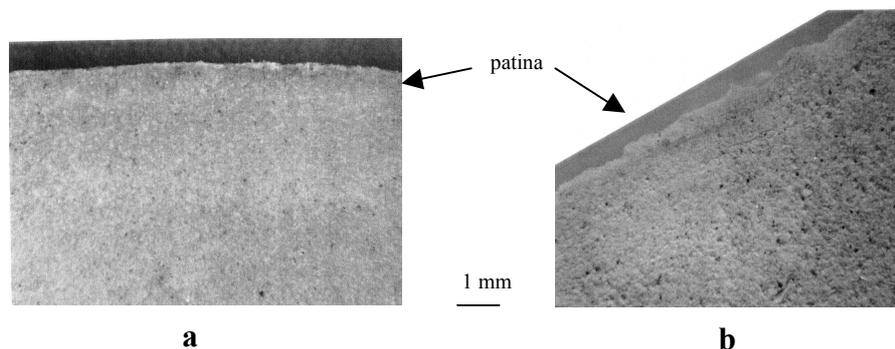


Figure 1. Photography of the outside column (a) and shell (b).

3. CHEMICAL ANALYSIS

Chemical analysis has been performed by ICP (Induced Coupled Plasma) with a JY38 Jobin Yvon device.

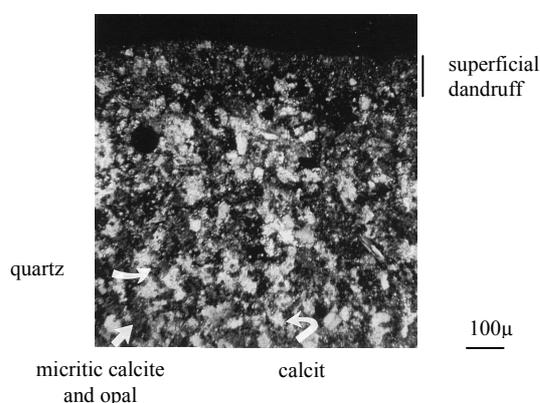
The samples have been scrapped at different depths from the patina surface. The powder has been heated with an acid mixture in order to destroy the structure and obtain a solution containing chemical elements. The quantity determination by ICP is given in massic proportion of equivalent oxides.

With this chemical composition, mineralogical composition can be deduced. Results are displayed in Table 1. Components sum does not reach 100 %, stone containing other minerals in a weak proportion, as phyllosilicates or pyrite.

Tuffeau stone are constituted of calcite, quartz and opal with various proportions which depend of depth and samples. Nevertheless for the three samples there is no evidence of gypsum in opposition with Tuffeau urban samples [2]. Figure 2 shows the polarized light photography of the patina of buried shell sample. The mineralogical species can be observed with various granulometries.

Table 1. Mineralogical composition of the samples under study in different depth zones.

Sample	Depth (μm)	Quartz + Opal (%)	Gypsum (%)	Calcite (%)
Outside column OC	0-100	34.9	0	51.5
	100-400	33.5	0	57.2
	heart	33.7	0	58.2
Inside lintel IL	0-350	42.3	0	49.2
	heart	41.9	0	50.9
Buried shell BS	0-200	25.6	0	60.6
	200-500	21.7	0	70.4
	heart	27.0	0	71.1

**Figure 2.** Polarized light photography of the patina in the outside shell.

4. X-RAY DIFFRACTION

4.1 Method

The registration technique is described in a previous paper [2]. It consists to translate a thin slice of bulk stone in order to control the diffracting zone and measure its position from the patina surface. Diffraction patterns have been recorded by a curved position sensitive detector INEL CPS120, with the Molybdenum wavelength ($\lambda = 0.70926 \text{ \AA}$). The translation step varied between 20 (in the patina zone) and 300 μm (depth stone). The beam width varied between 50 and 150 μm . These conditions permitted to obtain a good description of the mineralogical composition.

4.2 Results

For each samples, several patterns are displayed on figures 3. Quartz, opal and calcite are clearly identified (letters Q, O and C on the figures). The patterns of outside column and inside lintel are very similar.

Mineralogical proportions are determined from integrated intensity (II) in order to minimise the orientation effects. Evolutions versus depth are presented on figures 4.

Outside column (figures 3A and 4A) shows a decreasing of calcite near the surface. Variations of the II permitted to estimate the patina thickness to 700 μm .

For the inside lintel (figures 3B and 4B) calcite decreasing then increasing are observed in the patina zone which is evaluated to 300 μm . A very small amount of gypsum is observed for a 70-80 μm depth. The patterns for buried shell (figures 3C and 4C) shows a lack of calcite at the surface.

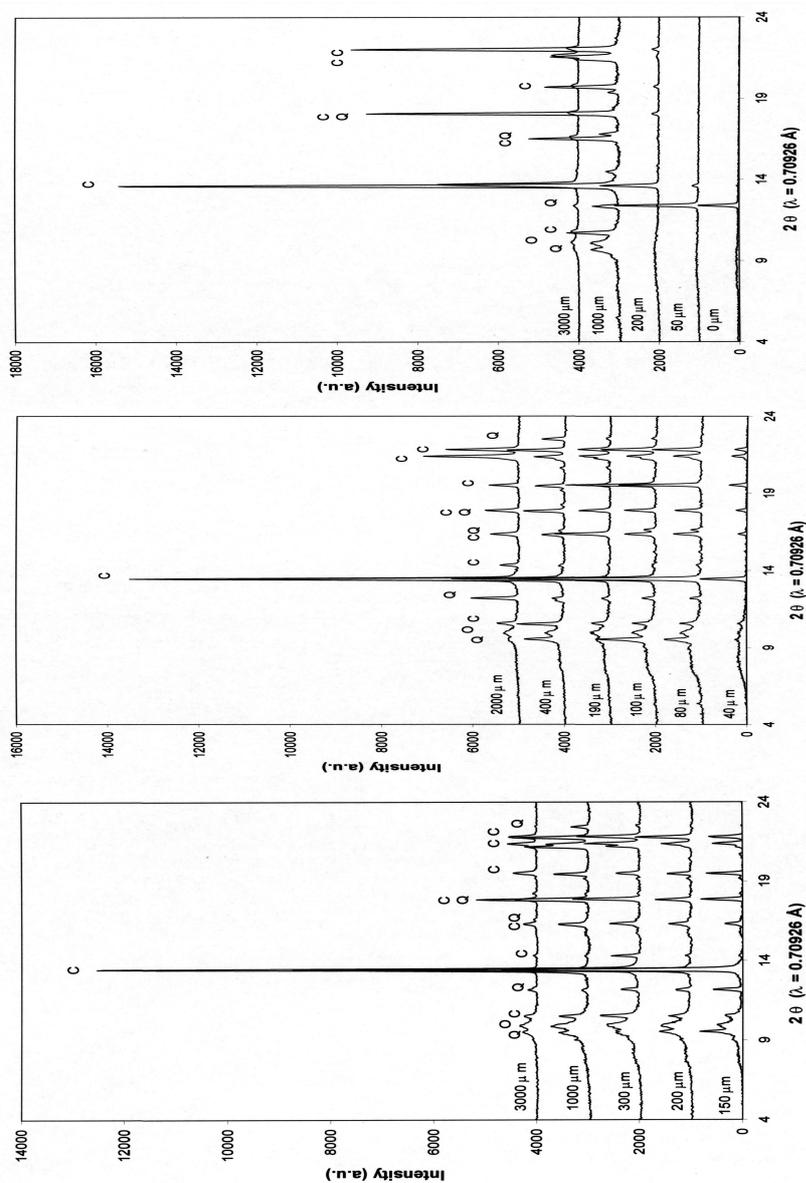


Figure 3-C : BS

Figure 3-B: IL

Figure 3-A : OC

Figure 3. Diffraction patterns for different depths from the patina
 A : outside column sample (OC)
 B: inside lintel sample (IL)
 C: buried shell sample (BS)

5. DISCUSSION

The three samples show the same evolution of calcite/quartz ratio. Calcite dissolution can be observed at the surface of the stone (figures 4) then the curves show a low calcite increasing before reaching the depth stone composition. In addition, the inside lintel shows a surface calcite crystallisation exterior to the stone itself proved by the lack of quartz in this zone (figure 3B).

Different parameters must be taken into account to understand the patina formation.

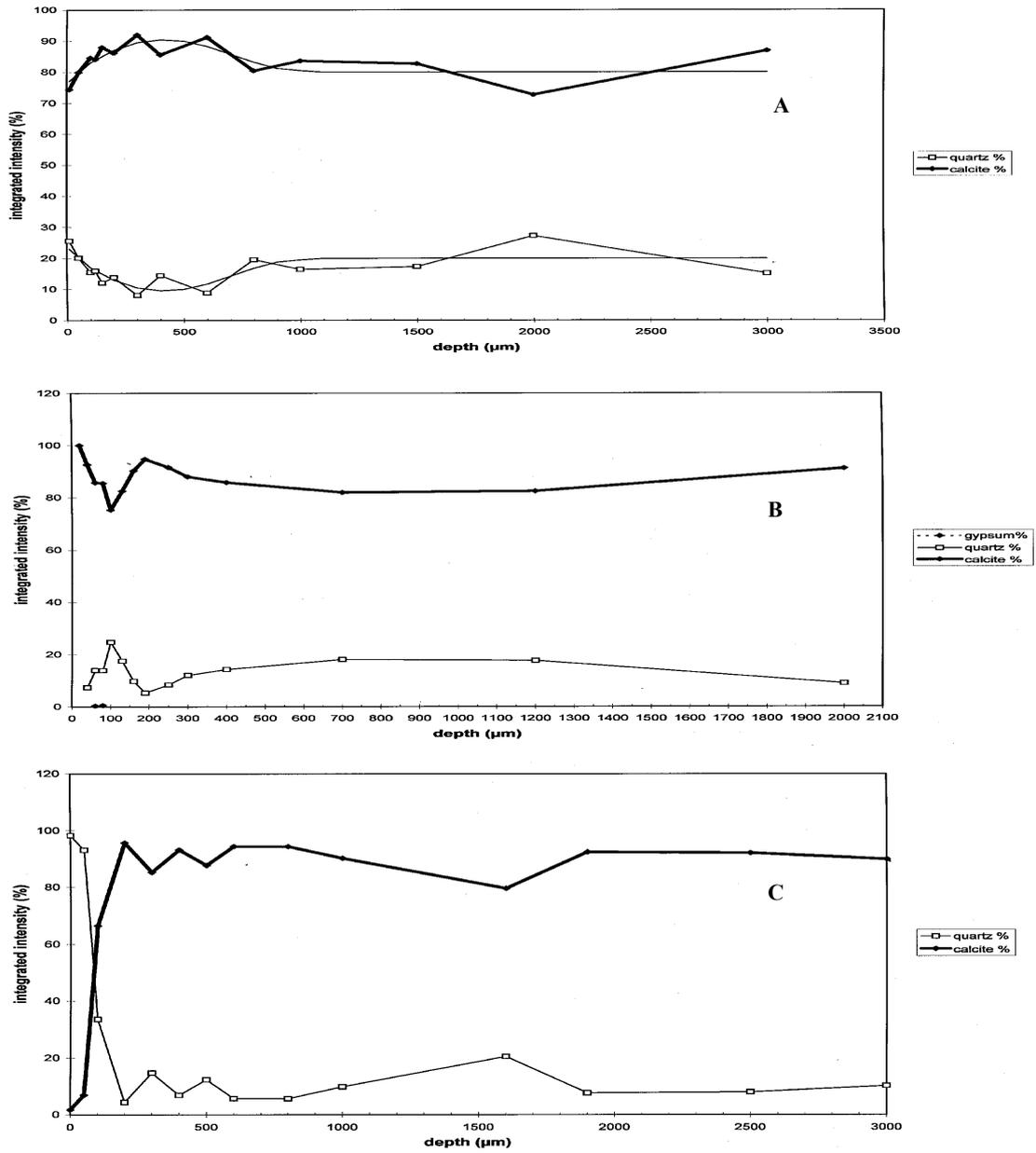


Figure 4. Mineralogical evolution for different depths from the patina
 A: outside column sample (OC)
 B: inside lintel sample (IL)
 C: buried shell sample (BS)

Exposition to the rain water : hydration – deshydration cycles conduct to dissolution-crystallisation of salts (especially the calcite) of the stone which induce mineralogical and structural modifications [1]. Most exposed samples show a deeper patina : The patina depth for the outside column (700 µm) is greater than the inside lintel one (300µm).

Exposition to a sulfured atmosphere : The presence of sulfur in the ambient air can lead to gypsum formation at the surface of the stone [2, 3]. The low polluted environment explain the lack of gypsum in outside column sample. For the inside lintel, gypsum presence suggests exposition to sulfur during the use of the room (lighting, heating or biological activity).

Exposition time : The mineralogical modifications is directly associated to the time exposure. By comparing the curves on figures 4 a most important modification can be seen for the buried shell (used in XVIth century) than for the outside column (XIXth).

6. CONCLUSION

This X-ray diffraction method permitted to follow the mineralogical phases from the patina to the depth stone because samples are analysed without destruction as scrapping the stone layer to obtain powders. Porosity analysis by different techniques (image analysis, mercury porosimetry,...) has been performed [4]. The porosity is lower near the stone surface which could correspond to the calcite excess observed with X-ray diffraction.

The crystallographical hypothesis is to consider the bulk sample as a powder. Size distribution of crystallites is a very important parameter. Systematical measurements have been performed with different beam sizes [4] : for each analysed position patterns were very similar (figure 5). Even very accurate results in relation of orientation effect can not be obtained, phases composition evolution can be followed with the method.

Works are in progress to improve the results quantification: phase mixtures with different granulometries are studied in order to reproduce the stone patterns for a given composition.

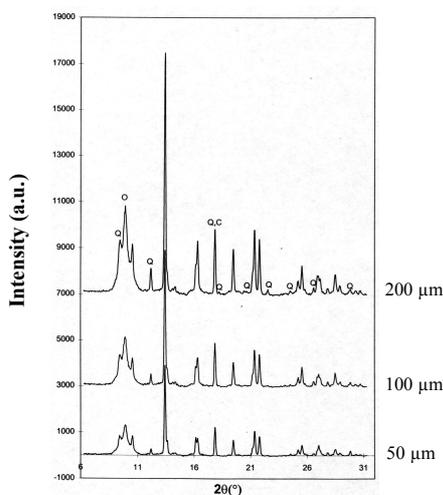


Figure 5. Comparison of patterns registered for a given position and different beam sizes (tuffeau from the quarry of S^t Cyr en Bourg, France).

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