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Weathering of limestone after several decades in an urban environment

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ABSTRACT

The alteration of "Saint-Maximin Roche fine" limestones exposed to the Parisian urban environment during more than 60 years has been studied. It leads to changes of the texture and morphology, to the neo-formation of gypsum on the subsurface and to the deposition of carbon containing phases on the surface. Depending on the location of the blocks on the monuments, the alteration states are different related to different water activities that could influence the further alteration processes. The multiscale characterization has enabled to correlate the macrometric properties to the mesoscopic behavior, what is essential to understand the alteration mechanisms.

1. Introduction

In many countries, the preservation of the building heritage is a cultural and scientific challenge. Therefore, the weathering processes of stone building materials have been widely studied on different materials types evolving in various environments [1–3]. Indeed, the alteration of the materials depends on both parameters intrinsic and extrinsic, so that its study requires interdisciplinary knowledge on material and environmental sciences [4–7].

As far as the extrinsic parameters to the materials are concerned, first, the climate plays a role on the natural ageing of the buildings. Secondly in a polluted area, atmospheric pollution directly affects the evolution of materials due to the chemical reactions induced by dry [8] and wet [9] deposition and their alteration kinetics (i.e. [10]). For over 200 years, the increase in energy production has caused high atmospheric emissions in the form of gaseous pollutants (SO_2, CO_2, NO_x) and particulate matter (PM). Gases cause an acidic deposit that could increase the materials dissolution and/or the crusts formation [11–13]. The most common phases observed on limestone samples exposed to an urban area are sulphate containing phases [10,14–17]. Among them, gypsum ($CaSO_4$, $2H_2O$) formation is due to the interaction between the atmospheric SO_2 and the calcite from the stone. SO_2 is oxidized in SO_3 which is dissolved by condensation water and leads to H_2SO_4 formation [18]. This product reacts with the Ca^{2+} (from the dissolution of the calcite) and leads to the gypsum formation. In Paris and Paris suburb, according to the air quality survey network Airparif, since the 1950s, the concentration of SO_2 has decreased from 360 $\mu g\,m^{-3}$ to a low value of around 1 $\mu g\,m^{-3}$ in the last years [19]. However, the maximum values have reached up to 750 $\mu g\,m^{-3}$ in the 1990s. Such extreme events could also play a role on the ageing of the monuments. In the Parisian basin since the 1990s the PM10 maxima (particles less than 10 μm in diameter) values could be over 400 $\mu g\,m^{-3}$ [20]. For instance, in March 2014, Paris and its suburbs have been affected by an especially high rate of particulate peaks. In the Paris urban environment, soot represents almost 90% of suspended particles and of deposed particles in number [21]. Chemically inert, graphite is organized in carbonaceous nanospheres (about 10 nm in diameter) called Black Carbon or Elemental Carbon. Coated on this graphitic nucleus, adsorbed hydrocarbons, volatile organic compounds (VOCs), sulphates and in lesser extent nitrates can be fixed [22]. This mixture of organic and inorganic prod-

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ucts can cause the increase in soot hydrophilic property [23] and promote water fixation or catalytic sulfation reactions (e.g. [24]). Furthermore the environment at city scale plays a role on the ageing of the materials, but also the local environment directly affects the alteration. The alteration on a single building can be very different from one location to another. It depends on the exposition (sides sheltered or not from rain, exposed to sun radiations), the height (subject to capillary rise or not, different water composition in the upper part and in the lower part of the building), the architecture (sculptures, frontage, windows...)... (e.g. [25]). All these parameters need to be taken into consideration and classified to propose a study of the alteration as exhaustive as possible.

Concerning the intrinsic properties of the material, its chemical and physical composition plays a role on the water transfer (aqueous or vapour) and on the exchanges with the environment. In the case of porous materials, the properties of the pore network will influence the water transfer [26]. Water is the main alteration factor as it can react directly with the material (e.g. dissolution process) or convey the aggressive agents (e.g. gypsum formation induced by the dissolution of gaseous SO_2). Consequently, to determine its transfer mode inside the material is of primary importance for the study of the alteration. Moreover, the pore network can be modified by dissolution or crystallization processes [11] that will influence the subsequent alteration. The chemical composition of the material will also influence the chemical reactions and their associated kinetics. Therefore, the alteration is expected to be different on pristine and weathered materials with modified altered zones. The nature and the location of these altered zones could play a significant role in the subsequent alteration (changes in kinetics) and evolve as a function of time.

In France, 52% of the stone buildings are made out of limestone, so that the preservation of this type of stone is of primary importance [27]. Thus, the present work belongs to an ongoing study aiming to understand the alteration processes on limestone exposed to an urban polluted area, such as the Parisian basin. We have selected a specific limestone type from different monuments that have evolved in the same urban environment (Paris and Paris suburb). This limestone is widely used for the restoration of historical monuments in France, especially in the Parisian basin, the so-called "Saint-Maximin roche fine" limestone. This limestone from the Lutetian period (43 Million years) is relatively homogeneous from a chemical and physical point of view. Though the pristine stone has already been studied by several authors [28–31], to our knowledge, few have been done on real samples exposed during a long period to an urban atmosphere. In this context we have identified the alteration patterns formed on different "Saint-Maximin roche fine" limestone samples that have evolved in the Parisian urban environment following a multiscale methodology. These alteration patterns have been compared in order to identify the role of the local conditions and propose a reaction scenario of the alteration.

2. Material and methods

2.1. Materials

Limestone at two different alteration stages has been studied: pristine material from quarries (Q) of Saint-Maximin (Oise, France) dealing as reference and samples from various monuments in Paris and Paris suburbs. Two stones from the "Basilique of Saint-Denis" (SD limestone, 12th c.), and the pre-Haussmannian monument of the "Comédie Française" (C limestone, 17th c.) have been selected. These stones are part of restoration stone blocks of the 2nd part of the 20th century (ca 1950) and no surface treatment has been applied since the replacement. The SD limestone has been collected on a west oriented wall at a 19 m height, so that it was exposed to rainfall but not to capillary rises. The C limestone was located at the first floor of the building and was also only subject to rainfall events. Thus the materials from the buildings have been exposed during a comparable period to a similar environment and at different heights.

The morphology and the mineralogy of the samples have been observed directly on the surface, and on cross sections from mesoscopic to nanometre scales. Moreover, thin section performed for the double staining of pore network enabled petrographic observations.

2.2. Surface analyses

The limestone surface state has been characterized using complementary analytical tools, from macro- to micrometric scale. Rugosimetric measurements have been performed to determine the surface roughness of the stone that could have been influenced by the alteration processes (dissolution and/or phases precipitation). Moreover, the mineralogical composition of the stone and of the altered zones have been determined using macro- and microbeam surface analyses such as X-Ray Diffraction (XRD), Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS) and Raman microspectrometry (micro-Raman).

2.2.1. Roughness measurement

The surface roughness of the samples has been measured using an interferometric microscope VEECO NT1100. The data have been acquired at $\times 5$ magnitude on 100 randomly selected zones, corresponding to a 1 cm^2 surface that was large enough to be representative of the whole sample. An 800 μm vertical scanning has been selected in VSI mode (Vertical Scanning Interferometry) with a 1% modulation threshold. According to the Standard ISO25178 [32], the roughness is now defined by the 3D surface texture parameters. The amplitude parameters such as Sa (arithmetic surface roughness), Sq (quadratic surface roughness) replace the traditional Ra (arithmetic roughness) and Rq (quadratic roughness) previously used for the 2D quantification. However, a mean value such as those given by Sa or Sq does not reveal a clear difference between altered stone samples. Thus another amplitude parameter must be used. Defined in the Standard ISO25178 as the maximum height from the highest point to the deepest valley, the Sz gives a best estimation of the magnitude of the surface roughness and is a good indicator of the surface complexity. For each studied samples, 100 values of Sz were measured. In order to obtain a statistical distribution of the Sz, these data were fitted to a combination of normal modes using the least square iterative routine. This treatment allows to identify the amplitude, the median value and the standard deviation of the different modes representing the number distribution of the roughness (dN/dSz expressed in% number per range of 50 μm of roughness).

2.2.2. Elemental and mineralogical characterization

The morphology and the elemental composition of the samples have been investigated with a tabletop low-vacuum SEM.

To identify the mineralogical composition of the alteration phases, PXRD (Powder X-Ray Diffraction) has been performed on the bulk samples using an Empyrean diffractometer from Panalytical equipped with a multichannel PIXcel 3D detector and a filtered-copper X-ray source (1.5418 Å). Typically, each pattern was recorded in the 10°–60° 2θ range (0.013° for 150 s). It should be noted that the sample is mounted on a five-axis cradle with motorized movements to obtain a perfectly plane position. The phases have been identified using the Inorganic Crystal Structure Database (ICSD) with a selection of the best correlation. The Highscore soft-