MICRO-CT IN THE STUDY OF GYPSUM CRUSTS AND PATINA FORMATION ON LEDE STONE

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Summary: µCT is applied for experimental weathering and preservation studies of natural building stone samples. It helps in characterizing weathering depths, weathering zones and fracture orientations in 3D. In addition, time-lapse experiments can prove useful in studying the crust and patina formation, indicating which mineral grains are involved and which processes are dominant.

1. INTRODUCTION

The weathering of building stones is traditionally studied by conventional techniques as optical microscopy, SEM, MIP, and by indirect assessments using water absorption methods, drilling resistance measurements, ultrasound velocity, etc., lacking most of the time true 3D information. Also experimental weathering, or cleaning and preservation methods are assessed by such methods. Here, time lapse micro-CT is used in combination with the traditional techniques for a general characterization and weathering experiments. The material under investigation is Lede stone [1], a sandy limestone which is prominent in northern Belgium's built heritage. The most described weathering phenomena on this stone are the formation of black gypsum crusts [2] and cracks due to frost events [3]. This type of rock also gains a yellow-brownish patina over its initial greyish-green to greyish-yellow colour. Previous studies have used µCT in the assessment laboratory induced weathering of fresh stone samples [4]. The aim of the current study is to characterize weathered samples from within the monuments, and look at the response to further laboratory induced weathering and potential treatments.

2. EXPERIMENTAL METHOD

Weathered samples of Lede stone were retrieved from the restoration of the basilica in Halle and the town church of Wieze in Belgium. These were partly embedded in resin; the embedded parts subsampled for characterization tests and the pristine parts subsampled for ageing and tests. Glauconite grains were hand-picked from Cenozoic sands samples after a first magnetoseperation of the sand grains.
µCT was performed on embedded rock samples to characterize the weathering depth and the occurrence of cracks in 3D. Pristine rock samples were scanned in initial condition and after 28 days of exposure to acid weathering through dry deposition in a sulphurous atmosphere. µCT scanning was performed at the Centre for X-Ray Tomography of the Ghent University (UGCT) using a custom built micro-CT setup. The µCT images were reconstructed with the Octopus reconstruction software, 3D image analysis was performed with Octopus Analysis (formerly Morpho+) [5] and the volumes were rendered using VGStudio MAX software. Complementary analysis of the weathered stone include the use of optical microscopy, SEM-EDX, µXRF mapping using an EDAX EAGLE III µ-probe at the X-ray Microspectroscopy and Imaging Group (XMI, Ghent University), and measurement of the drilling resistance and a scratch test at the University of Mons.
Glauconite grains were exposed to different environments of wetting and heating and to sulphurous and sulphuric acid attack. The iron content of the medium was measured with ICP-MS. Weathered glauconite grains were scanned at UGCT.

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3. RESULTS

The µCT images of weathered stone samples show that different crust layers, typically recognized for black gypsum crusts [5] can be observed. It shows that the weathering depth is up to 25 mm and more. Whilst most gypsum precipitation forms a superficial crust, weathering in depth is typically pronounced by crack formation. Further experimental weathering in laboratory on subsamples with less pronounced cracking indicate substantial growth of the gypsum crust by dry deposition in a sulphurous atmosphere, together the formation of cracks below the precipitation zone. Surface-parallel cracks in buildings are hence not necessarily attributable to frost action, but could also be the result of the sulphation process on itself.
µXRF mapping shows a slight enrichment of Fe in at the surface of the weathered stone samples, causing the yellow-brownish patina. The counts of K are also elevated with respect to the bulk material. The most potential source of K is the weathering of glauconite. Similarly, the superficial Fe could be assigned to glauconite weathering. Laboratory experiments of glauconite weathering show that acid treatment with sulphuric acid releases a hundredfold of Fe compared to weathering under wetting/heating cycles. µCT shows the glauconite grain disintegration after laboratory weathering. Its weathering rate is likely increased by elevated sulphur contents, thereby enhancing patina formation rates. Its potential influence on the formation of gypsum crust themselves is still unclear.
The results indicate that decreasing sulphur dioxide levels in the atmosphere are prosperous for the preservation of Lede stone in monuments. This is especially true for new replacement stones. However, weathered stones which bear the inheritance of the past are superficially more prone to frost action, because of already formed cracks. This also excludes potential new threats such as elevated atmospheric NO_x levels.

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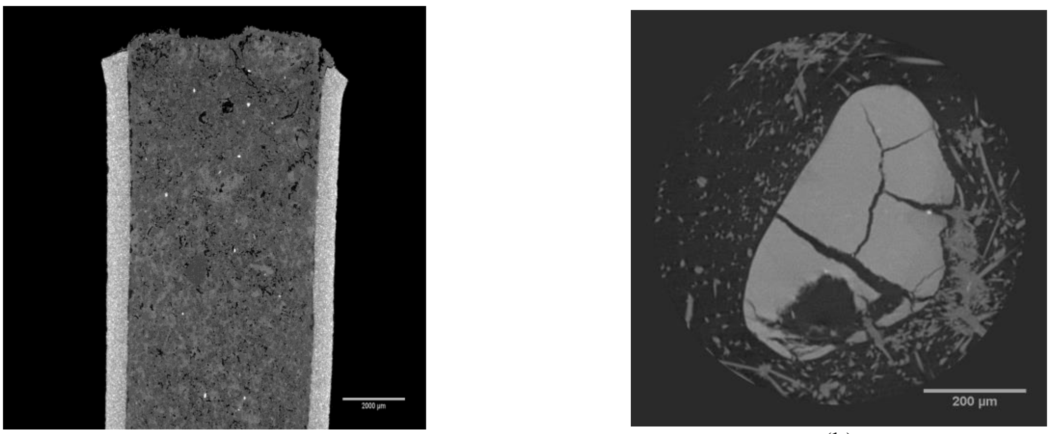

(a) (b)

Figure 1: (a) Gypsum crust growth seen on top of a sagittal section through a Lede stone sample of 6 mm sealed with shrinkage tubing; (b) high resolution image of an individual glauconite grain showing wedge-like splitting and mesopore creation, surrounded by gypsum crystals after acid weathering.