# *CONTINUOUS TIME-LAPSE MICRO-CT OF GYPSUM CRUST FORMATION ON NATURAL BUILDING STONE*

Tim De Kock*[1], Jan Dewanckele †[2], Benjamin Blykers[1], Marijn A. Boone[2] and Veerle Cnudde[1]

[1] PProGRess/UGCT, Ghent University, Krijgslaan 281/S8, 9000 Gent, Belgium
[2] TESCAN XRE, Bollebergen 2B box 1, 9052 Zwijnaarde, Belgium

**Keywords:** X-ray tomography, time-lapse imaging, gypsum crust, geomaterials in heritage, weathering

**Summary:** Limestone samples were exposed to an acidic atmosphere inducing gypsum crust formation, a stone deterioration phenomenon in polluted environments. Continuous time-lapse imaging was performed using 360° X-ray µCT scanning for several days to fully depict the process. Challenges in analyzing these dataset were approached using flip point detection in the voxels, creating time-scaled 3D images.

## 1. INTRODUCTION

Despite decreasing atmospheric $SO_2$ contents, limestone samples from heritage structures in areas having a pollution record still contain gypsum and related weathering crusts [1]. Such gypsum crusts are the result of wet and dry deposition of $SO_2$ released as atmospheric gasses or through combustion particles and the subsequent reaction with a carbonate host rock, potentially catalyzed by the presence of other fly ash particles [2]. Laboratory tests have been performed to simulate this process [3], and the relation of gypsum crusts to the microstructure of the stone has been evaluated on different samples [4]. In the recent past, X-ray micro-CT has been used to study gypsum crust formation in a non-destructive way first on sound stone [5], later on an already weathered sample [6] and in combination with exposure to $NO_x$ [7]. Those results have shown a relation between the rock's microstructure and the precipitation of gypsum, and that crust growth is mitigated by self-protection.

## 2. EXPERIMENTAL METHOD

Cylindrical samples (< 5 mm ∅) of Lede stone, a Belgian sandy limestone recognized as global heritage stone resource (IUGS), were cored from a sound stone and a weathered stone having a gypsum crust from a church in Belgium. Both were prewetted and subsequently exposed to an acid atmosphere above a $H_2SO_3$ solution in a closed container [8] for respectively 4 to 6 days (Fig. 1a). The sound stone was left untouched allowing reaction on all sides, while the weathered stone was put in a heat-shrink tube to seal the edges and create a unidirectional reaction front.

A continuous time-lapse X-ray micro-CT acquisition was performed on a TESCAN UniTOM$^{HR}$ (custom configuration) for the duration of the experiments on the sound stone sample and weathered stone sample. In total, respectively 138 and 200 scans were acquired, each individual acquisition taking respectively 30 and 43 minutes and the time between acquisitions being limited to 1 second. All scans were acquired at 100 kV and with a voxel size of 5 µm. The raw data was processed using the batch reconstruction module in the XRE Acquila 4D toolkit. After reconstruction the volumes were registered to compensate for sample movements and tube shifts. Temporal analysis of each voxel in the volume was performed by determining the flip points, points where the grey value of the voxel significantly changed. This results in 3D grey scale volume where the grey value represents the time point at which a significant change occurred in the sample. This 4D volume allows to easily asses changes in space and time and enable to determine the crystal growth and dissolution speeds.

*e-mail: tim.dekock@ugent.be
†e-mail: jan.dewanckele@tescan.com

## 3. RESULTS

During the continuous time-lapse scanning, the formation of a gypsum crust was clearly observed (Fig. 1b). Initial crust formation on sound stone forms as a superficial layer, with outward growing crystals. Underneath, a depleted stone layer develops almost symmetrical in time and space, which can be very well visualized by applying flip point detection (Fig. 1c). The growth kinetics seem to be related to the dynamics of crust formation, with a falling growth rate as a solid crust is forming, and subsequently an increase in speed when local breaches occur due to crystallization pressure. When exposing the naturally weathered sample, it shows high rates of depletion underneath crust, with dissolution occurring deeper in the stone. Preliminary results show the formation of cracks which could mimic the scaling typically observed on monuments. Ongoing spatiotemporal analysis aims to identify the key features responsible for crack formation.

### References


[1] Farkas, O., Siegesmund, S., Licha, T., Török, Á., 2018. Geochemical and mineralogical composition of black weathering crusts on limestones from seven different European countries. ***Environmental Earth Sciences***, 77: 211.

[2] Rodriguez-Navarro, C., Sebastian, E., 1996. Role of particulate matter from vehicle exhaust on porous building stones (limestone) sulfation. ***Science of the Total Environment*****,** 187: 79-91.

[3] Sabbioni, C., Zappia, G., Gobbi, G., 1996. Carbonaeous particles and stone damage in a laboratory exposure system. ***Journal of Geophysical Research: Atmospheres***, 101: 19621-19627.

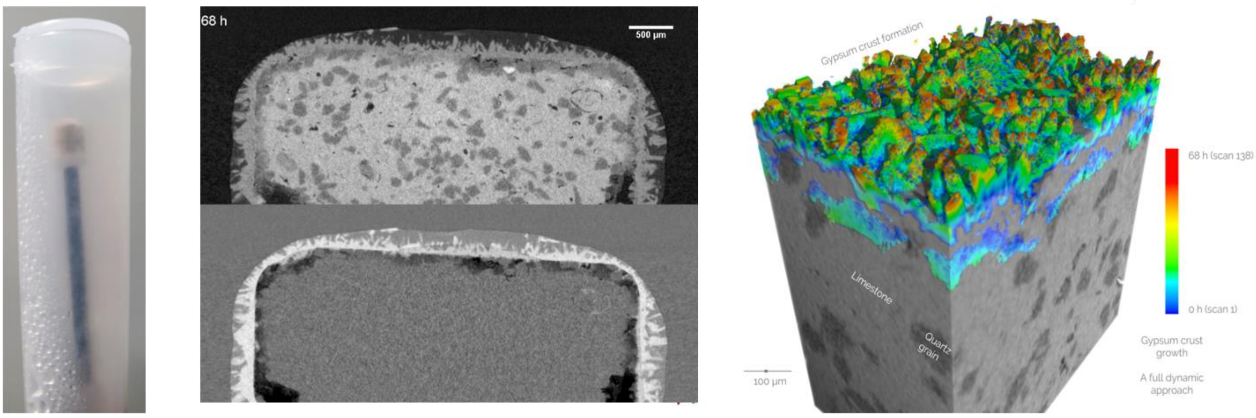
[4] Török, Á., Rozgonyi, N., 2004. Morphology and mineralogy of weathering crusts on highly porous oolitic limestones, a case study from Budapest. **Environmental Geology**, 46: 333-439.

[5] Dewanckele, J., De Kock, T., Boone, M.A., Cnudde, V., Brabant, L., Boone, M.N., Van Hoorebeke, L., Jacobs, P., 2012. 4D imaging and quantification of pore structure modifications inside natural building stones by means of high resolution X-ray CT. ***Science of the Total Environment***, 416: 436-448.

[6] De Kock, T., Van Stappen, J., Fronteau, G., Boone, M.A., De Boever, W., Dagrain, F., Silversmit, G., Vincze, L, Cnudde, V., 2017. Laminar gypsum crust on Lede stone: microspatial characterization and laboratory acid weathering. ***Talanta***, 162: 193-202.

[7] Gibeaux, S., Vázquez, P., De Kock, T., Cnudde, V., Thomachot-Schneider, C., 2018. Weathering assessement under X-ray tomography of building stones exposed to acid atmospheres at current pollution rate. ***Construction and Building Materials***, 168: 187-198.

[8] EN 13919, Natural stone test methods – Determination of resistance to ageing by $SO_2$ action in the presence of humidity, 2003.


(a) (b) (c)

**Figure 1:** (a) sample of Lede stone in a closed container containing $H_2SO_3$ ready for scanning. (b) vertical slice (top) and differential slice (bottom) after 68h of reacting and scanning, where the formation of a superficial gypsum crust can be observed together with calcite cement dissolution immediately under the surface. (c) Time-step scaled render of crystallization and dissolution by flip point detection.