X-ray CT: a powerful technique for the micro-structural analysis of geomaterials.

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ABSTRACT

For the 3D characterisation on a (sub)micron scale of the pore structure of natural stones as well as for the study of their weathering processes, both 3D structural and chemical composition and distribution of pores and minerals are important. These characteristics can be obtained through traditional research techniques (including optical microscopy, SEM, laboratory experiments, etc.) and through highly advanced techniques like high-resolution X-ray CT; after acquisition, the fusion of all this data can provide a better insight in the weathering phenomena occurring in geomaterials.
At the Sedimentary Geology and Engineering Geology group of UGent, X-ray CT technology is applied in the study of geomaterials and is one of the group's main research topics for already more than 15 years. The group acted as co-founder of the 'Centre for X-ray Tomography' (UGCT, UGent), of which the developed flexible high-resolution X-ray CT (HRXCT) scanners and software tools are being used for the 3D characterization of geomaterials, for fluid-flow monitoring inside porous materials and for the study of weathering phenomena of geomaterials. For geologists, who normally work with optical microscopy and scanning electron microscopy to study geomaterials, CT offers an important research tool since it allows to provide information on the 3D structure of the scanned samples as well as limited information on their chemical composition in a non-destructive way. Scanned samples can afterwards always be analyzed by the more traditional research techniques, like optical microscopy and scanning electron microscopy combined with EDX (SEM-EDX), in order to connect the 3D data from the X-ray scanners with the 2D chemical and structural information from microscopy techniques. Additionally, thanks to close collaboration with the research group 'X-ray microspectroscopy and imaging' (headed by Prof. Laszlo Vincze, Ghent University), XRF imaging at a micro- and nanoscale level is integrated in the 3D study of geomaterials and their weathering phenomena. Previous experiments (Cnudde *et al*., 2009; Boone *et al*, in press) convincingly demonstrated the added value of the link between both techniques for the characterization and understanding of the behaviour of geomaterials submitted to changing external conditions. The use of two powerful and complementary "state-of-the-art" techniques combined with information obtained from optical microscopy and SEM-EDX, traditionally used for characterisation, allows to determine and assess structural information and chemical element distributions in 3D in geomaterials and this with a spatial resolution better than 1 micrometer. In this extended abstract some recent case-studies will be discussed.

EXPERIMENTS

High-resolution X-ray CT for 3D petrography of ferruginous sandstone for an investigation of building stone decay

Diestian (Belgian Neogene, Tertiary) ferruginous sandstone has been used as the dominant building stone for civil and religious constructions in the Hageland (region in east-central Belgium). Like all rocks, this stone type is sensitive to weathering. Case hardening was observed in combination with blackening of the exterior parts of the dressed stones. In order to determine the 3D petrography and to identify the structural differences between the exterior and interior parts, X-ray computed tomography (figure 1) was used in combination with more traditional research techniques like optical microscopy and scanning electron microscopy (SEM).

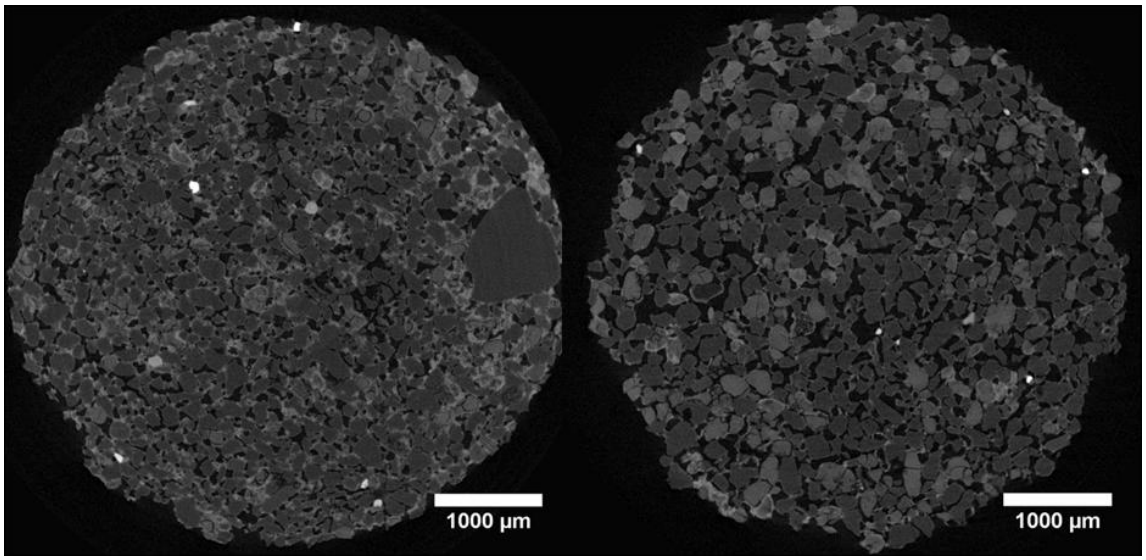

Fig. 1. Reconstructed cross-section after X-ray CT scanning of ferruginous sandstone. Left: detail of the superficial crust; right: section of the non-weathered stone.

The 3D characterization of the ferruginous sandstone was performed with a high-resolution X-ray CT scanner (HRXCT) (Vlassenbroeck *et al*., 2007) in combination with the flexible 3D analysis software Morpho+ (Brabant *et al*., in press), which provides the necessary petrophysical parameters of the scanned samples in 3D. Besides providing the required 3D parameters like porosity, pore-size distribution, grain size, grain orientation and surface analysis, the results of the 3D analysis can also be visualized which enables to understand and interpret the analysis results in a straightforward way. More information on the study of ferruginous sandstone for an investigation of building stone decay can be found in Cnudde *et al*. (in press).

4D characterization and quantification of micro-structural weathering processes inside porous materials

Porous materials, like natural building stones, deteriorate when they are exposed to changing weathering conditions and pollution. In order to evaluate rocks used as building material, several characterisation (petrographic analysis, determination of porosity, pressure resistance, etc.) and durability tests (freeze-thaw resistance, thermal shock resistance, etc.) are mandatory. Their significance lies in the predictability of the

stone's weathering conditions or resistance under known external conditions. After the induced weathering tests, the stone's new physical properties are evaluated with regard to their initial conditions. There thus exists a registration of both the initial 'fresh or pristine' rock's situation before the test and the final 'failed' situation at the end of the test series. However, most of those evaluations are based on visual inspection or indirect registration of the internal micro-structural reorganization. The knowledge of those micro-structural weathering processes are of prime importance to understand the deterioration of the stone in its entirety. Internal quantification of dynamic processes still remains difficult with standard destructive analysis tools. For that purpose, in this study non-destructive high resolution X-ray CT is combined with image analysis to visualize, characterize and quantify different deterioration processes. Here examples of gypsum crystallization, pressure test and freeze-thaw test are given.

Gypsum crystallization in limestones and in calcareous sandstones

Gypsum crystallization on natural building stones due to sulphatation processes is a well-known and widely described phenomenon in deterioration studies (e.g. Török, 2008; Fronteau *et al.*, 2010). The gaseous SO_2 of the polluted environment reacts with the carbonate of the stone, resulting into gypsum ($CaSO_4.2H_2O$) crystallization on the surface and inside the porous structure of the material. Pore analysis by means of X-ray computed tomography in addition to traditional characterisation methods such as optical petrography and water impregnation porosimetry can provide an indication on the controls of this sulphatation processes (De Kock *et al.*, 2009). Furthermore, X-ray computed tomography proves to be a powerful tool to study the sulphatation process itself. In order to obtain quantitative information on porosity and pore structure changes before, during and after sulphatation, the process should be monitored on the same sample. As the pore structure of a rock type can be very heterogeneous, control of the pore structure on sulphatation can be very complex. As most conventional research techniques like optical microscopy or scanning electron microscopy are destructive, porosity changes before, during and after crystallization processes are difficult to monitor because samples have to be destroyed to allow observation.

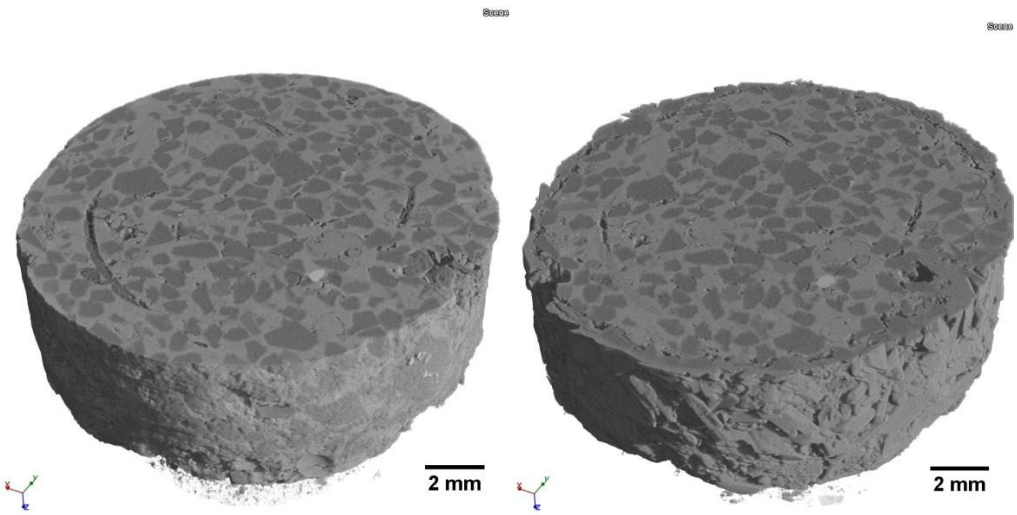

Fig. 2. Reconstructed volume after HRXCT scanning of Ledian (Belgian Eocene, Tertiary) calcareous sandstone before weathering (left) and after exposure to an acid environment (right).

With the aid of non-destructive high-resolution X-ray computed tomography various types of porous limestones and calcareous sandstones could be investigated before, during and after in vitro-induced gypsum crystallization processes. Besides the visualization of the gypsum crystallization itself (figure 2), also quantitative information on porosity and pore structure changes could be obtained. For each stone type, radial porosity, open and closed pore structure, partial porosity and distribution of equivalent and maximum opening of the pores has been calculated with the software program Morpho+.

Pressure test

After applying uniaxial pressure on a natural building stone, reorganisation of the internal structure might be possible. High resolution X-ray computed high tomography enables to measure and quantify those internal changes. The green structure on the left in figure 3 corresponds with the micro-cracks induced by the pressure test in a Noyant Fine limestone (French Eocene, Tertiary). The pore structure not affected by the micro-cracks (i.e. the 'isolated porosity') is coloured red (right figure). If a micro-crack affects an interconnected pore network, the whole network is considered as being influenced by the micro-crack and thus rendered green. Therefore, the term 'micro-crack porosity' would be more appropriate. Visualization of both types of pore structures thus provides an excellent overview of the stones' internal behaviour under increasing external pressure.

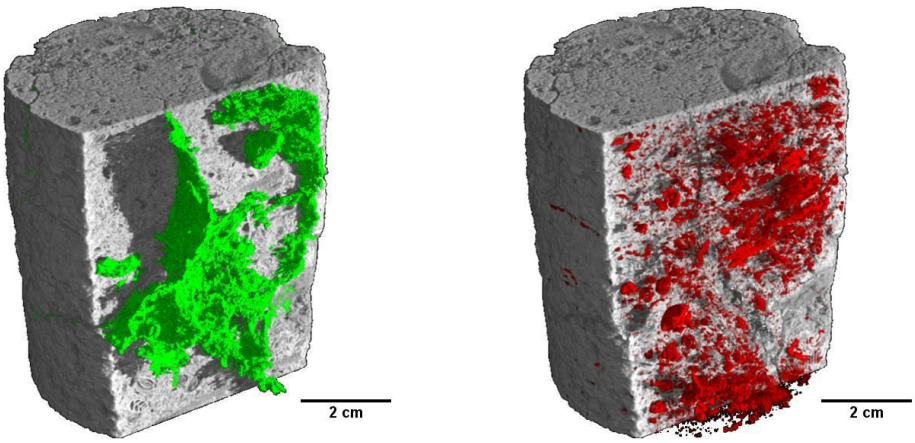

Fig. 3. Reconstructed volumes of the Noyant Fine limestone after a pressure test. On the left figure, the induced micro-crack and interconnected micro-crack porosity is visualised. On the right figure, the isolated, not affected pore structure is given.

The distinction between the micro-crack porosity and the surrounding but not affected pore structure is obtained on the basis of the ratio of the equivalent diameter to the maximum opening, calculated in Morpho+. The micro-crack porosity will have a large equivalent diameter but a small maximum opening (sphericity << 1), while the original pores will be more spherical (sphericity ≤ 1). Besides visualization, the micro-crack porosity and the amount of isolated porosity have also been determined with Morpho+. HRXCT not only makes it possible to visualize the internal reorganization but also offers the possibility to calculate the ratio of the crack density and the isolated but not affected pore structure.

Freeze-thaw cycle

Another durability test is the freeze-thaw cycle test. Before and after the experiment the stone's situation is evaluated by visual inspection, mass weighting and/or sound speed propagation. With the aid of HRXCT, intermediate stages during the process can be investigated and quantified, by which the aperture and the evolution of the micro-cracks could be visualized in three dimensions and calculated. The material loss after the last cycle could be evaluated by taking into account constant scan, reconstruction and threshold parameters and also the same volumes of interest. Clearly, HRXCT combined with image analysis contributes to better insights into the characterization and durability assessment of natural building stones. The complex processes of deterioration are recorded in a non-destructive way and finally 4D quantitative data has been obtained. Figure 4 presents the disintegration of a foraminifer (unicellular organism with a calcareous skeleton) inside the Noyant Fine limestone due to systematic freezing and thawing.

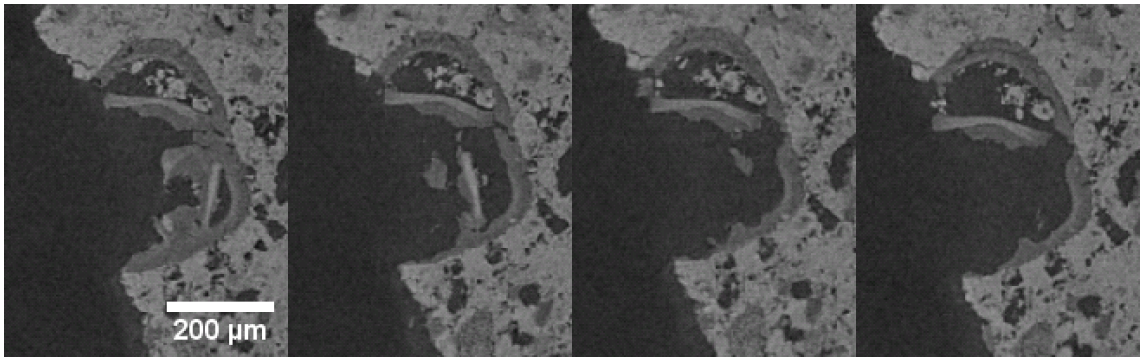

Fig. 4. Disintegration of a foraminifer in the Noyant Fine limestone. Left: before weathering, after 1 freeze-thaw cycle, after 2 cycles, after 3 cycles and after 4 freeze-thaw cycles (right).

Building stone provenance studies

Even though sedimentary building stones from a given region or a specific geological setting are often classified under the same name, petrophysical properties may differ due to facies differences between several depositional locations. This has implications for cultural heritage conservation and archaeological studies. Both bear a need for the knowledge of a stone's provenance (i.e. excavation site). For the conservation of our cultural heritage, a stone selected for renovation and restoration works must resemble the original stone type as much as possible from both an aesthetical and a technical point of view. The stone properties which define this aesthetical and technical aspect may vary between various excavation sites; so insights in a stone's provenance are helpful. For archaeological research, it is even more crucial to know the exact origin of stone artefacts or building stones in ancient monuments. They provide information on the activities during certain historical periods, trade and/or migration routes, equipment,... Provenance studies of natural building stones and artefacts might be done with the aid of optical petrography and chemical analysis. In addition, 3D quantitative image analysis by means of X-ray CT gathered data is a freshly-explored, useful tool. The possibility of quantifying dense minerals in sedimentary rocks, mineral-specific grain-sizes and grain parameters, porosity, etc. (figure 5) allows to build up quantitative datasets for different outcrop locations. This can be used to compare possible

provenance areas for a given stone type, as being done for the Flemish '*fieldstone',* e.g. Behiels (2010).

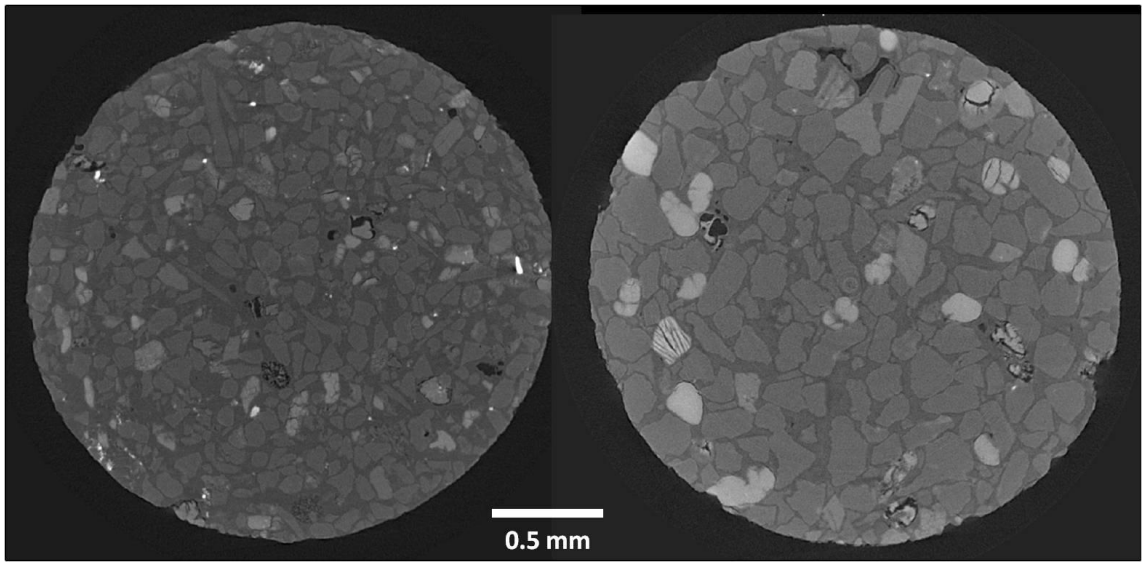

Fig. 5. Examples of 2D cross-sections gained by X-ray CT (slices) of two fieldstone samples with similar macroscopic appearances. Left: fieldstone from outcrop in Beernem; right: fieldstone from outcrop in Flobecq.

3D petrography using combined micro-CT and micro-XRF measurements on ore mineralization

The detailed description of the mineral content and textures within rocks is usually done by optical microscopy on thin or polished sections and with other more modern techniques such as scanning electron microscopy (SEM) and X-ray fluorescence (XRF). These techniques provide detailed information about the mineral phases in a 2D plane of the rock, but a full distribution of the mineral phases in 3D is often hard to attain or deduct. High-resolution X-ray CT (HRXCT) makes it possible to visualize the different structures in the rock in 3D in a non-destructive manner. Although the HRXCT visualization technique is based upon the atomic number and the density of the components in the rock, no direct chemical information about these components is provided. This makes it often hard to clearly identify and analyze the different mineral phases in the rock. However by combining conventional 2D analysis techniques with 3D visualization techniques, it is possible to acquire a complete 3D identification and description of the different mineral phases and textures in the rock sample.

In this case study a sample of an ore mineralization from the Harz Mountains (northern Germany) was analyzed. A cylindrical sample with a diameter of 10 mm was scanned using HRXCT. Based upon the attenuation coefficient, 4 different types of components could clearly be separated in the resulting 3D image. Chemical information was added by analyzing the top and bottom surface of the sample using µXRF surface mapping. In this surface analysis 5 different mineral phases could be identified: i) a highly Cu-rich phase occurring in veins that is identified as malachite ($Cu_2CO_3(OH)_2$), ii) a rounded mineral phase rich in Cu, Fe and S (chalcopyrite $CuFeS_2$), iii) a Si-rich phase (quartz SiO_2), iv) a sparse Ba-rich phase (barite $BaSO_4$) and v) a Fe-rich ground mass. The µXRF mappings were then matched with the top and bottom slices of the 3D HRXCT image. This demonstrated that the 2 types of components with the lowest attenuation coefficient corresponded to the quartz and the Fe-rich ground mass. The 4th and highly

attenuating component matched with the barite and the 3rd type of component corresponded to both the malachite and the chalcopyrite mineral phases. Due to the same attenuation coefficient of malachite and chalcopyrite, these mineral phases could not be separated based purely upon their attenuation coefficient or their gray value. However based upon the texture of the mineral phases (i.e. rounded for the chalcopyrite and vein-like for the malachite), the different minerals could be separated in the 3D HRXCT image using the Morpho+ analysis software. Different parameters like distribution, size and form could be analyzed for each mineral. Figure 5 shows the 3D visualization of the ore sample with the different mineral phases. This case study clearly illustrates the potential of combining different analysis techniques with HRXCT for 3D petrographic analysis.

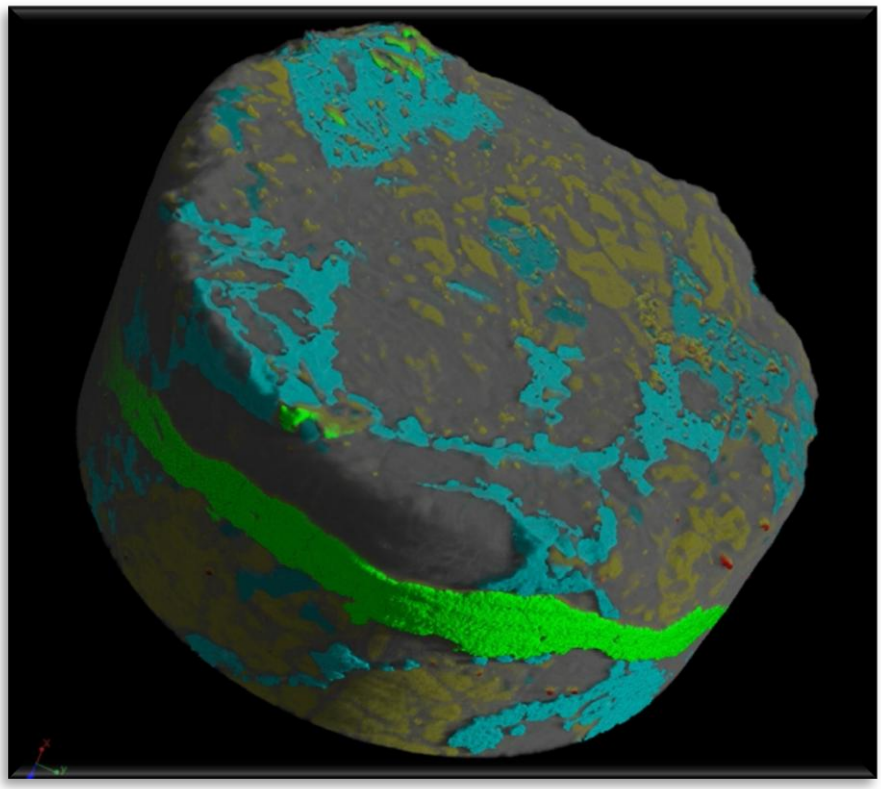

Fig. 6. Distribution of various mineral phases in an ore mineralisation. With ascending attenuation coefficient: quartz (blue), Fe-rich ground mass (grey), malachite (green), chalcopyrite (yellow) and barite (red).

CONCLUSION

By combining traditional research techniques with high-resolution X-ray CT, a fourth dimension to the study of geomaterials can be obtained. Besides structural analysis of these materials, also monitoring of changes of their internal behavior can be performed. With the access to this powerful technique a new specialization field in geology becomes emerging, adding important information and insights to the study of geomaterials.

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