Characterization of marble using Scanning Force Microscopy

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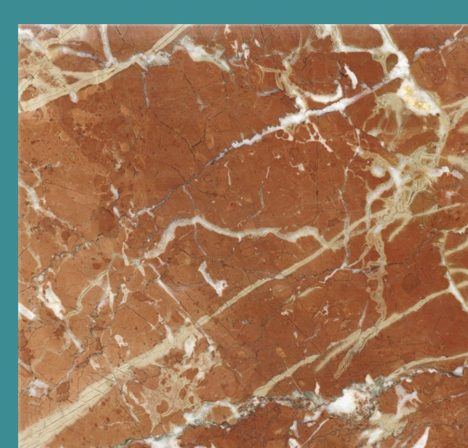
Introduction

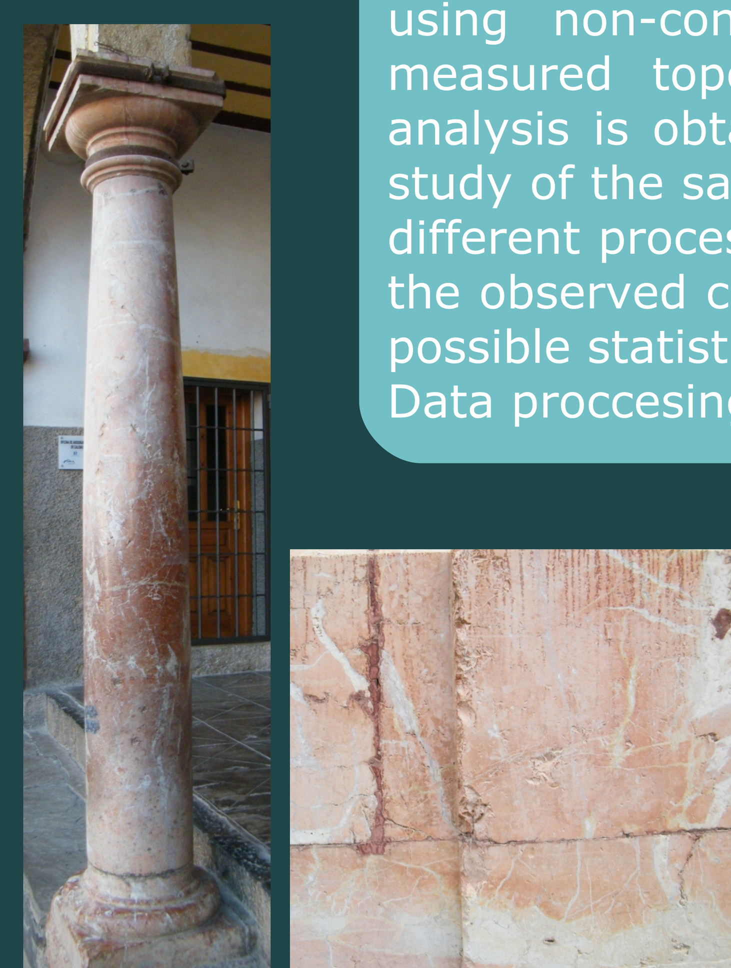
Marble has been used as a building material since ancient times. The facades which use marble as cladding suffer from atmospheric agents and the effects of pollution, and their preservation is important in order to avoid their deterioration and to maintain their aesthetic appearance (colour, brightness,...). Red tone marbles, such as the Rojo Quípar variety, suffer from apparent colour variations and more marked brightness loss than other marbles when exposed to environmental conditions and pollution. Colour variations in marble materials have been attributed to the degree of chromophore oxidation the minerals responsible for colour (stone impurities). In addition to these changes, other physical changes could be the reason for the apparent variations in the colour and brightness of marble [1]. In particular roughness is an important parameter which conditions brightness. In the present work we investigate the nanoscale effect of atmospheric agents (ultraviolet radiation, UV) and pollution (acid rain, H_2SO_4) on the Rojo Quípar marble variety.

The samples

- Rojo quípar marble (biomicrite-mudstone)
- $CaCO_3$ and iron oxides impurities
- UV sources:
  - Hg lamp 50 W
    - Irradiance ≈ 2.5 kW/m²
    - 50%; 254 nm 5%; 185nm
  - Xe lamp 1800 W
    - $Irradiance_{UV+VIS}$ ≈ 634 W/m²
    - 11%; (290,400) nm — 5.4%; (290,320)nm; 38.2%; (320,360)nm; 56.4%; (360,400)nm
    - $Irradiance_{UV}$ ≈ 64 W/m²
- Acid attack:
  - 0.01% and 0.04% H_2SO_4 solution



Rojo quípar marble



Bleached rojo quípar marbles

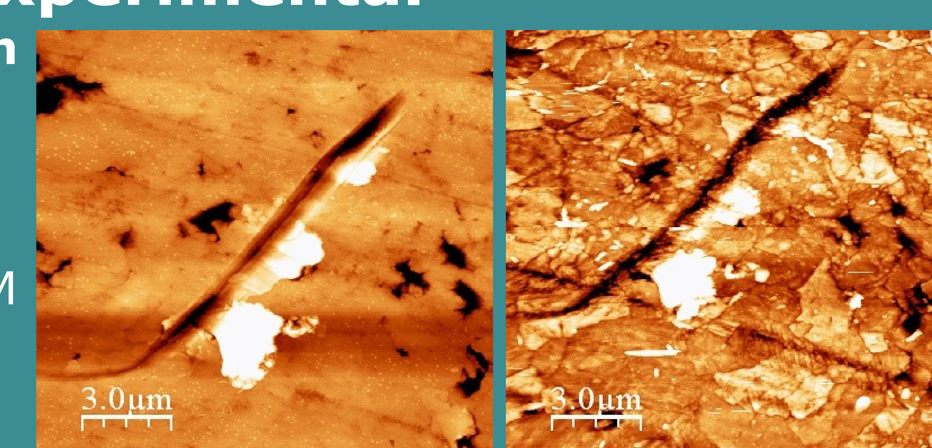
The method

Roughness variations have been monitored on the nano and micrometer scale using non-contact Dynamic Scanning Force Microscopy (DSFM). From the measured topographic images the precise roughness and fractal dimension analysis is obtained. Our experimental setup allowed us to perform a nanoscale study of the same region, even if the sample was taken out of the SFM system for different processes (UV irradiation and acid attack) and therefore we can attribute the observed changes to the real effect of radiation or acid attack as compared to possible statistical variations of surface properties.
Data proccesing with WSxM.

Experimental

Precise re-allocation

We have developed a new micron-precision sample holder integrated in the DSFM system. One example, ex-situ analysis of the same sample region.

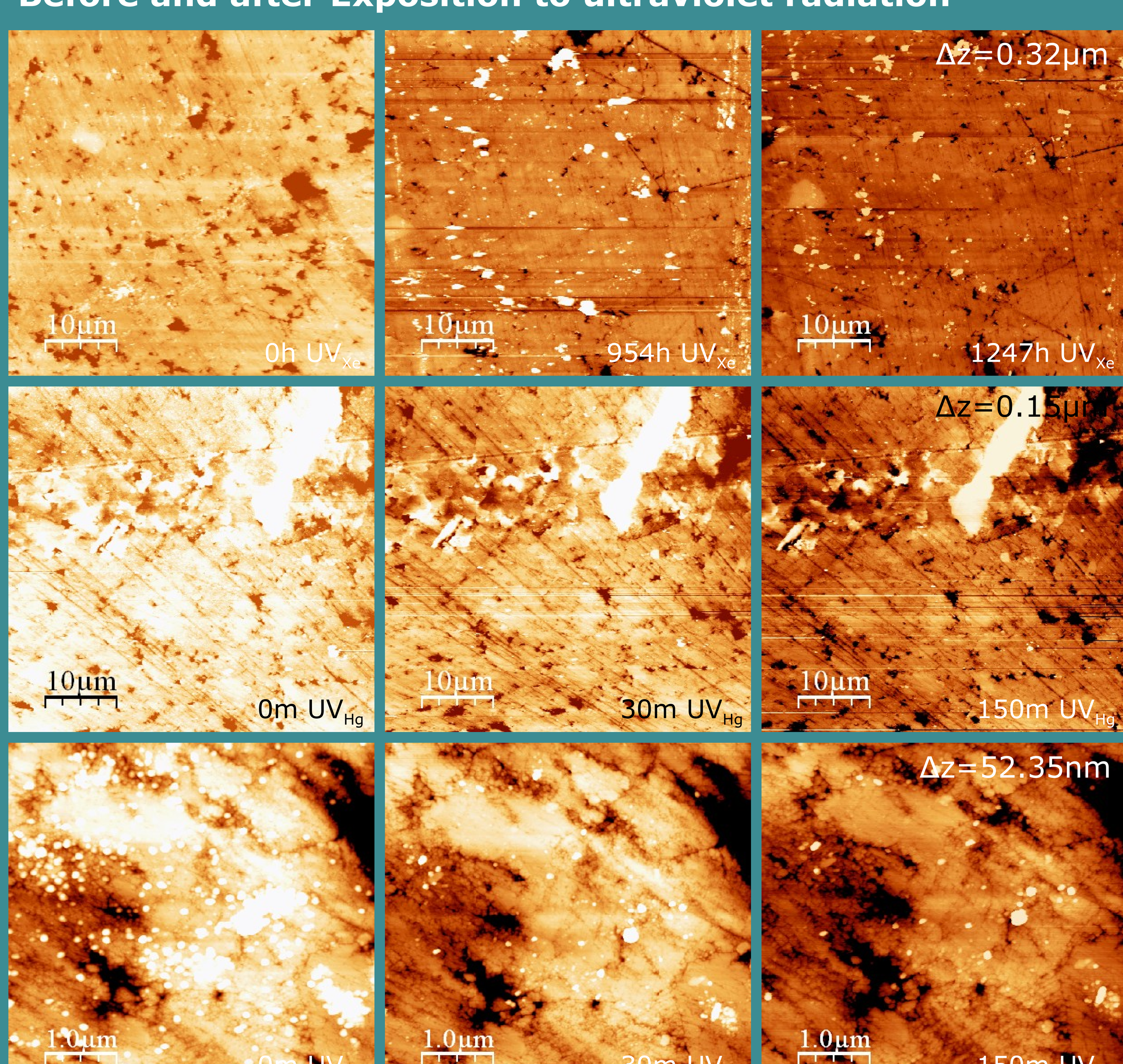


Before acid attack — After 5s of acid attack

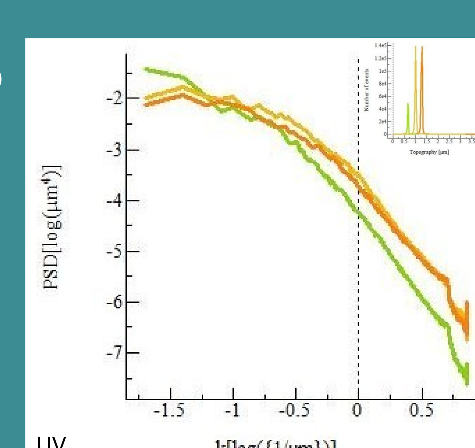
Results

Topographic images of Rojo quípar marble

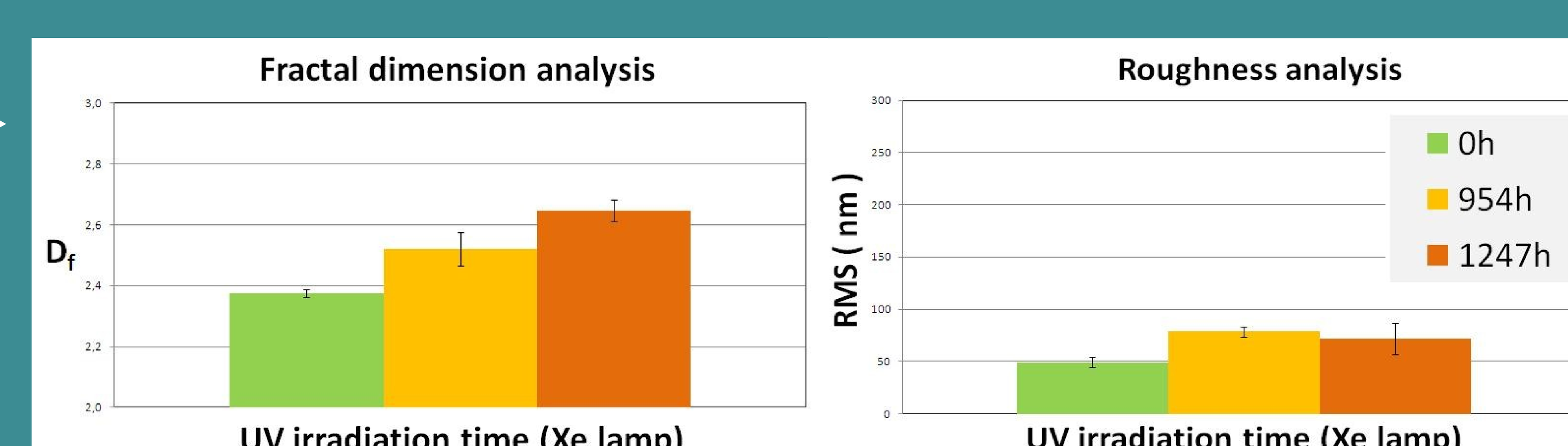
Before and after Exposition to ultraviolet radiation

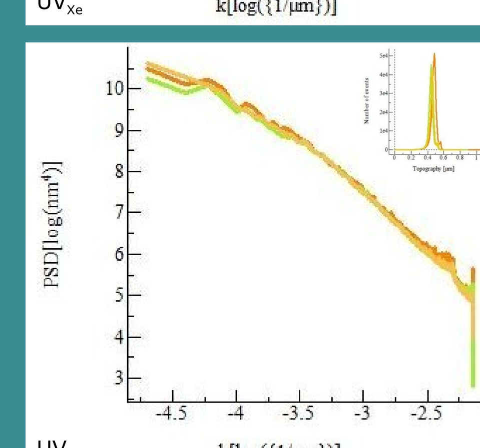


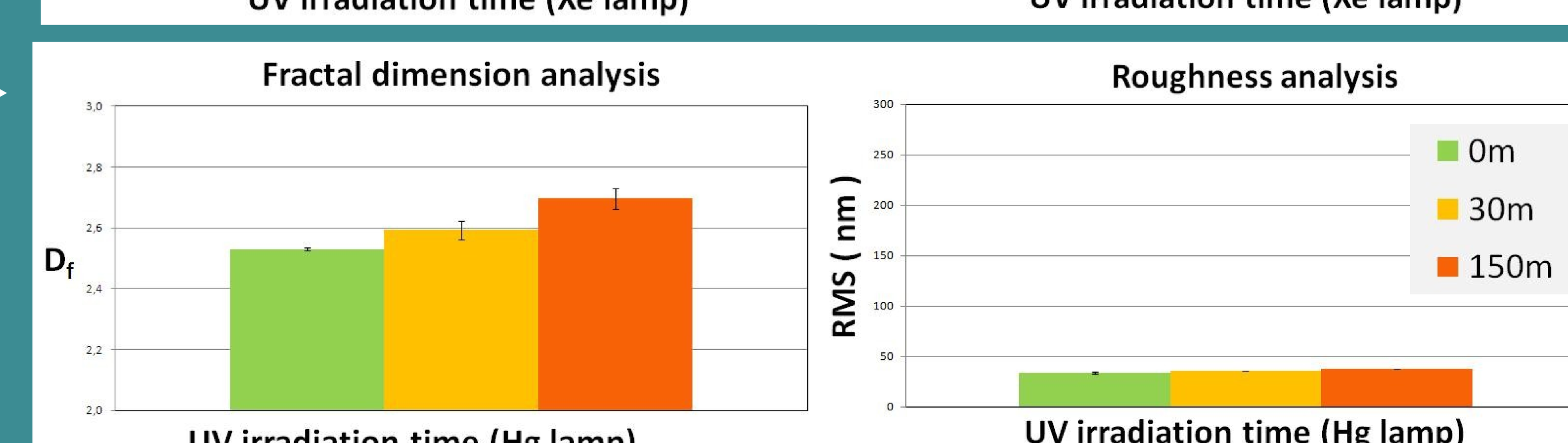
PSD →



D_f →



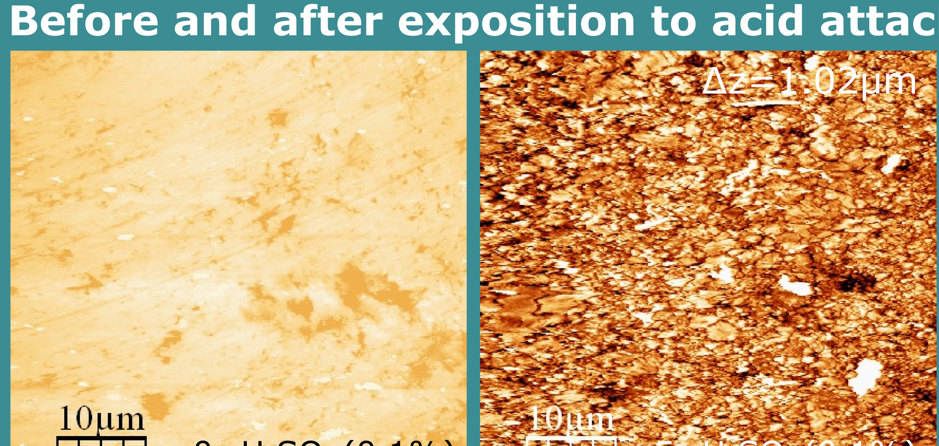


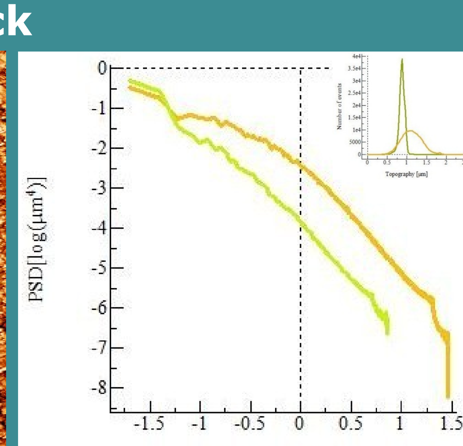


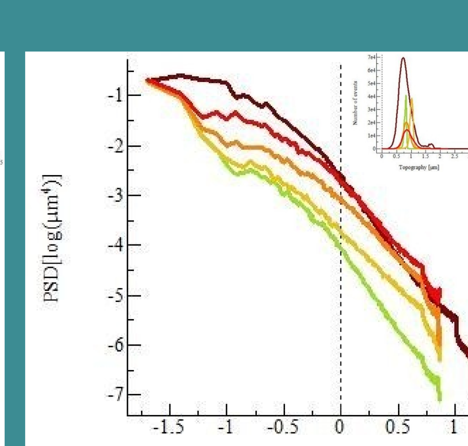
The heights of the surface in each point are computed to get the root mean square roughness (RMS) of the images. RMS depends on the scale but Roughness takes place on many different length scales.
The topographic values let us obtain the fractal dimension of the images. By means of Fourier analysis, power spetrum density (PSD) is generated. PSD is a log-log graph which contains very much information about surface roughness on different scales. The PSD slope is related to Hurst exponent (H) and fractal dimension (D_f):

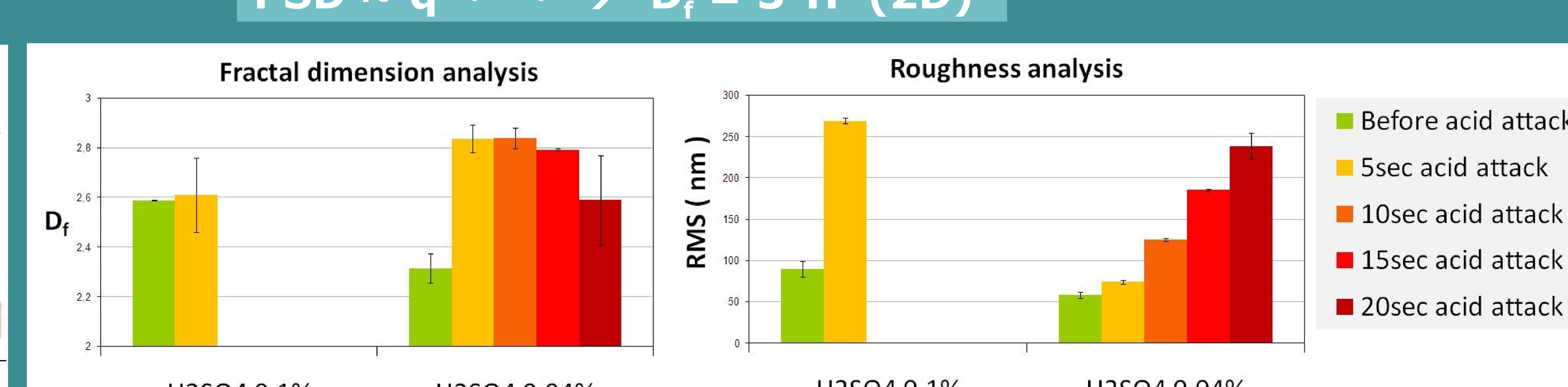
$$PSD \sim q^{-2(H+1)} \rightarrow D_f = 3-H \quad (2D)$$

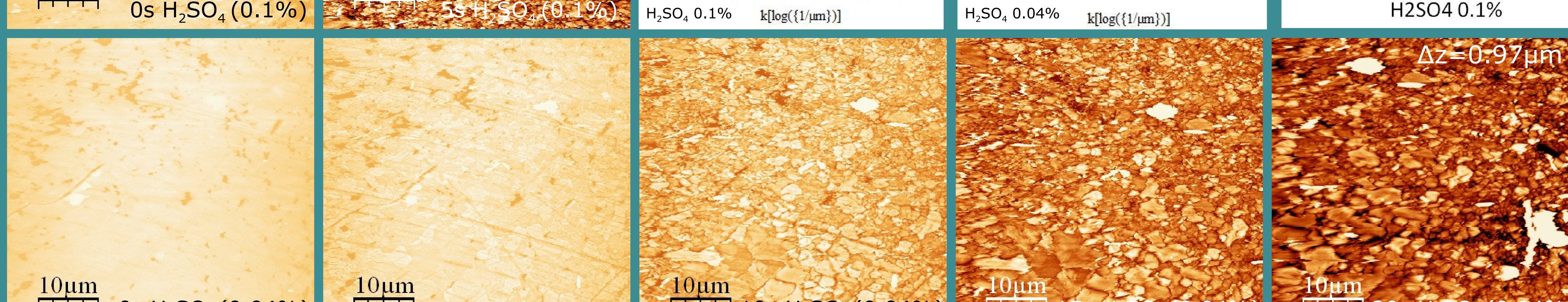
Before and after exposition to acid attack











Conclusions

UV as well as H_2SO_4 produces an increase in the roughness of the samples, which could explain brightness loss and apparent colour variation observed in the facades that have been exposed to solar radiation or occasional episodes of acid rain over a period of years. Others have related surface roughness variations of the stones to changes in colour [1]. However, they didn't use fractal dimension to characterize roughness variations, only Ra parameter. In the future, we would like to expand data by measuring relations between roughness variations and colour changes through fractal dimension and colourimetric coordinates.

[1] Benavente, D., Martínez-Verdú, F., Bernabeu, A., Viqueira, V., Fort, R., García del Cura, M.A., Illueca, C., Ordoñez, S., "Influence of Surface Roughness on Color Changes in Building Stones", Color Research and application, **28**, 5, 343-350 (2003).