

MARBLE NANO EROSION UNDER ACID RAIN EVIDENCED BY ATOMIC FORCE MICROSCOPY

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Abstract: Marble, one of the most precious construction materials, is often used for building decorations and statues. Acid rain falls caused by industrial pollution may harm marble ornaments in a very destructive manner. By X-ray diffraction and optical mineralogical microscopy, calcium sulphate and calcium nitrate are found to be the most important reaction products. Atomic force microscopy approach was used to reveal the erosion structure of the marble samples exposed to a moderate acid rain of pH 4 for about several weeks. Two stages of nano erosion are evidenced. The first stage affects the inside structure of calcite grain, inducing a nano erosion promotion at an exposure from 0 to 6 days. The transition to the second stage is substantially related to the propagation of nano erosion to the grain borders, which is very pronounced on day 6. At this stage the marble ornaments are seriously damaged. The second stage corresponds to the massive erosion of the surface at day 24, with irremediable damage to the marble ornaments. The surface roughness was found to progressively increase during the 24 days of exposure to acid rain.

Keywords: marble, acid rain, nano-erosion, AFM.

1. INTRODUCTION

The marble ornaments and statues are some of the most beautiful art masterpieces. There are ancient, marvelous marble edifices, like the Acropolis in Athens, Greece. The marble of Acropolis was exploited from the Pentelikos Mountain near Athens. Polikreti & Maniatis, 2003, show that pentelic marble featured an orange brown weathering patina due to the particulate matter depositions in time. The long term resistance to weathering proves to be related to the microstructure of each individual marble monolite.

Marble is a metamorphic rock formed by CaCO_3 crystallized in the trigonal crystal system, a mineral called calcite. The calcium carbonate metamorphism ensures the clustering of small calcite crystals under pressure. The growing cluster leads to a compact polycrystalline material (Bestman et al., 2000; Busch et al., 1995). The calcite marble is white; the other colors are given by some inclusions of other minerals such as silicates. The magnesium carbonate MgCO_3 could interfere with calcite forming a complex marble called

dolomite. In our study we refer only to the calcite marble (Melezhik et al., 2005). The presence of inclusions in marble affects the color as well as the mechanical properties (Bagci et al., 2010; Bams & Dewaele, 2007; De Bresser et al., 2005).

Recent studies reveal that the marble surface degradation depends on various factors, such as the calcite purity and the compaction of the microstructure, as well as on the calcite grain shapes (Goudie & Viles, 2000; Schenk et al., 2005). Some of the elongated calcite grains could act as tensor in the marble thermal expansion during extensive heating. Such tensors could promote intergranular cracks (Schenk et al., 2005). The intensity of marble degradation also depends on the environmental conditions. A protective environment could keep a marble statue in a very good shape over time. A harsh environment could damage the marble surface very fast. Diakumaku et al., 1995, as well as Wollenzien et al., 1995, mentioned some black fungi (e.g. *Phoma* and *Alternaria*) which could penetrate the surface grains eroding the cohesion between calcite crystals.

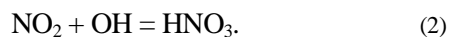
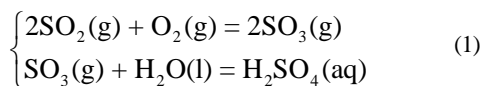
Pigmentation of marble surface was also reported.

By comparison to natural environment, the anthropogenic factors prove to be more invasive at the calcite grains microstructure level. Significant damages are reported, which are caused by deposition of dry particulate matters in urban environmental condition, especially nitrate and sulphate particles (Realini et al., 1995; Sikiotis & Delopoulou, 1992; Sikiotis & Kirkitsos, 1995). The mentioned studies show that in contact with solid deposits of nitrates and sulphates the marble decaying time is about of 6 months.

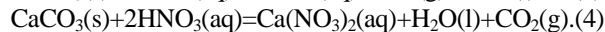
Franzoni & Sassoni, 2011, point out a more invasive effect of acid rain on the natural stones (e. g. sandstones, limestone and marble). The destructive effect is enhanced by the porosity of the stone samples as well as lack of compaction at the microstructure level. For several days of exposure (e.g. 14 days), at a pH range of 4 – 6, significant weight losses were reported (Franzoni & Sassoni, 2011). Based on recent studies, we may conclude that the marble erosion in acid rain conditions starts by an intra-granular deterioration at the nano structural level, which could be extended to an inter-granular level corresponding to the micro structure as observed by Franzoni & Sassoni, 2011. The main scope of the present paper is to characterize this nano structural initiation of marble erosion under acid rain conditions. Atomic force microscopy was employed for the nano erosion investigation.

The environment of big cities is subjected to various sources of pollution, such as dangerous gaseous emissions from industrial furnaces (e.g. SO₂; NO₂; and NO_x) consists the premises for acid rain formation (Garg et.al., 2001; Lefohn et al., 1999; Thakur et al., 1999). The low pH of acid rain could affect the marble which features a basic tendency; damages of marble surface due to the acid rain were noticed in literature (Navarro & Sebastian, 1996). Recent studies reveal that the acid rain occurrence increases proportionally with the development of industrial facilities and the intensification of auto traffic (Menz & Seip 2004). Moreover acid rain affects archeological sites, for example El Tajin archeological site in Veracruz Mexico (Bravo et al., 2006). Archeological sites are evenly affected. Some recent investigation found that the concrete compressive resistance decreases in acid rain conditions (Fan et al., 2010). The present situation leads us to the current investigation.

Acid rain mainly occurs because of industrial emissions of SO₂; NO₂; and NO_x from the furnace exhausts (Garg et.al., 2001; Thakur et al., 1999). The basic reactions for acid rain formation are described as follows:



Both acids, equation (1) and (2), are formed in upper atmospheric strata being assimilated in rain drops and resulting a low pH solution. Usually, the acid rain has a pH between 3.5 – 5 which depends on the pollution source. There are good premises for calcite erosion due to its reaction with HNO₃ and H₂SO₄. The reactions are:



Considering that acid rain is a mixture of acids, equation (3) and (4), and the final reaction product will be an aqueous solution of calcium sulphate and calcium nitrate. This hypothesis was verified by erosion of a marble slice into an acid rain solution of pH = 4, as shown below.

2. METHODS

The marble used for our current investigation was provided by Ruschita Quarry, Romania. It is situated in the Poiana Rusca Mountains (Meridional Carpathians), nearby Ruschita Village; the geographical coordinates are shown in figure 1.

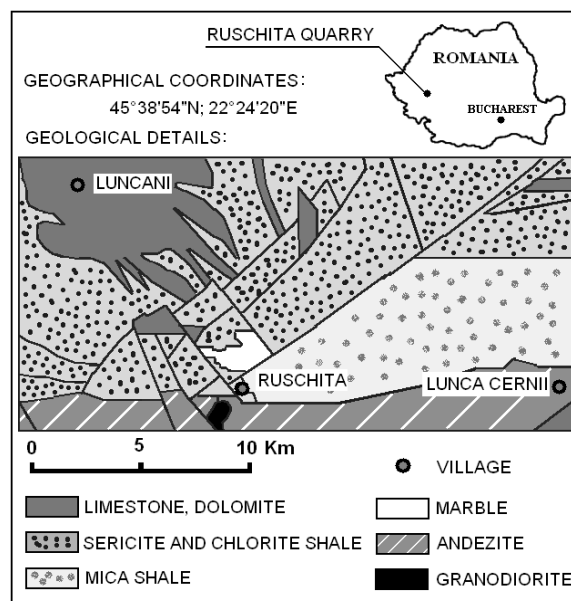


Figure 1. Ruschita area map with geological details according Krautner 1984.

Marble exploitation starts 130 years ago at „Gropan” working place, which is still active. „Dealul lui Ionel” working place is a more recent one assuring the most of marble production. Ruschita geological units belong to the, Poiana Rusca Crystalline dating from Devonian – Carbonaceous (Balintoni, 2000; Muresan, 2004). It presents a strong metamorphism characterized by several formations according (Krautner, 1984): limestone, dolomite, sericite and chlorite shale, mica shale, which

surrounds the marble deposit, (Fig. 1).

Poiana Rusca Crystalline is very abundant in limestone (calcite reach rock) and dolomite (aragonite reach rock). Marble represents a pure calcite rock having a bright white aspect. There were also found some pink and dark grey marble in a less significant amount. These colors are given by other mineral inclusions in the calcite marble. We use for current study only pure calcite marble having a bright white aspect.

Marble plates were cut by diamond disc into slices having a 2.5 mm thickness, 22 mm length, and 20 mm width. The slices were mirror polished using standard abrasives. The acid rain samples were prepared by mixing equal quantities of HNO₃ and H₂SO₄ diluted with deionized water. Finally, several solutions resulted, in a pH range from 2.2 to 5. pH values were measured by an IAMC pH-100 millivoltmeter.

Erosion product analysis: A marble slice was exposed to the acid rain solution for several days. The solution resulted after reactions was left to dry, and the resulting powder was subjected to X-ray diffraction (XRD) and optical microscopy investigation in order to validate the chemical reactions. XRD was performed on a DRON 3 diffractometer equipped with a data acquisition module and MATMEC VI.0 soft. A monochrome Co K_α radiation was used for all X - ray spectra. Identification of mineral compounds in the samples was done by comparing the resulted values with the XRD standard data base MATCH 1.0 Crystal Impact Co. Optical microscopy was performed on a Karl Zeiss Jena transmitted light mineralogical microscope using transmitted light and cross polarized light method. Microphotographs were digitally captured using a SAMSUNG 8 Mpx digital camera.

The pH influence on the weight loss was determined for a wide range of acid pH 2 – 5. The marble lamellas were exposed for 2 days at acid rain solutions having different pH (e.g. 2.02; 2.25; 2.68; 3.30; 3.60; 4; 4.50; and 5).

The time influence on the marble surface was investigated at pH 4, a value close to the ones observed for usual acid rains. The weight loss was determined by precise mass measuring of each marble slice before and after reaction.

The AFM investigation was performed on a JEOL JSPM 4210 microscope in tapping mode using NSC 11 cantilever (Micromasch) with resonant frequency of 330 kHz. The topography images were acquired at different scanning areas (e.g. 20 μm x 20 μm and 2.5 μm x 2.5 μm). Specific topography values were measured such: image height, image roughness and cross section profile, according to standard procedures of JEOL Win SPM Processing Soft.

3. RESULTS AND DISCUSSION

The XRD pattern resulted for marble sample is presented in figure 2a. It features well developed peaks, which correspond only to the CaCO₃ crystallized as calcite. No impurities were found (e.g. silicates, dolomite, aragonite), which proves the high quality of marble investigated.

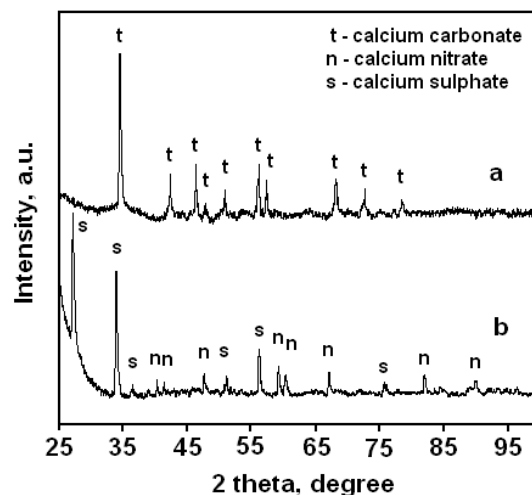


Figure 2. The X-ray patterns for: a) marble sample and b) reaction product sample.

The mineralogical investigation was done on a thin marble section (thickness less than 20 μm) using an optical mineralogical microscope in transmitted cross polarized light, figure 3a. The transmitted light microphotography, figure 3a, features large calcite grains with rounded shapes having over 1 mm diameter. The grain borders are evidenced by the changes in the crystallization direction within them. Their rounded shape, without sharp edges, assures a good cohesion of the marble compact avoiding the mechanical stress related to the microstructure. Darken parallel strips are observed along to the orientation of crystal. These strips are twinned zones inside the grain, which often appear due to mechanical tensions during the metamorphic processes (Lacombe & Laurent, 1996). The twinned areas represent limited zones inside the grain, having a crystallization direction opposite to the grain orientation (as mirror view or more precisely as twin zones).

Optical mineralogical microscopy observations are in agreement to the results from XRD proving that the marble samples are pure calcite without any inclusions or defects (e.g. fissures, mineral inclusions, mechanical tensors). The twinned zones inside the calcite crystals are clearly observed. They are similar to the other published in literature (Dhanapandian et al., 2009). Noteworthy is the high quality of the marble slices.

The reaction product was boiled up to solid

phase crystallized from solution. The solid phase was dried and analyzed by XRD. The resulted pattern is presented in figure 2b. Representative diffraction peaks were found for calcium sulphate and calcium nitrate, without any other compound. The purity of reaction product is also observed by mineralogical microscopy, figure 3b. Prismatic crystals of CaSO_4 appear, featuring various lengths from 20 – 200 μm . Also, $\text{Ca}(\text{NO}_3)_2$ crystals having a polyhedral shape appears. Cross polarized light microscopy, figure 3b, feature the CaSO_4 and $\text{Ca}(\text{NO}_3)_2$ crystals in a gray – white chromatic range. This fact means that no other mineral is present in the observed sample. Finally, we conclude that the marble sample erosion occurs in a strict manner, according to equations (3) and (4).

The data in literature mention the formation of a mineral crust over the marble (and limestone, for instance) surface due to weathering (Navarro & Sebastian, 1996; Racataianu & Benea, 2013). The fissures and intergranular cracks allow propagating the weathering compounds to the bulk (Goudie & Viles, 2000).

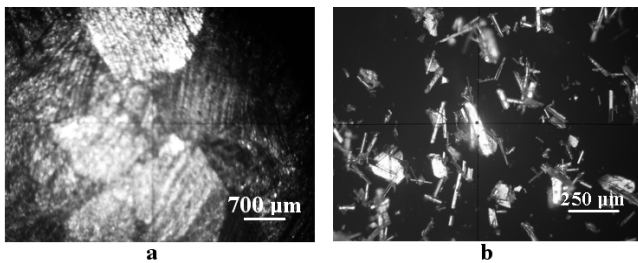


Figure 3. Optical mineralogical microscopy: a) marble thin slice and b) reaction product sample.

In our case, the acid rain solution acts at the grain level as an intensive erosion agent. Due to the water evaporation the reaction product will form a darken crust over the marble surface in conditions of natural weathering. In laboratory conditions, the reaction product is removed from the surface by washing with deionized water. Such procedure will cause a weight loss of the marble slice. The weight loss is a useful indicator of how intense is the surface erosion.

The mass of the initial sample is noted m_i and the mass after exposure is symbolized by m_f . In consequence, the weight loss (W_i) caused by surface erosion during the acid rain exposure can be expressed as follows:

$$W_i = \frac{m_i - m_f}{m_i} \times 100. \quad (5)$$

The pH – influence is very important to establish the erosion dynamics under various acidic ranges. The weight loss variation versus pH is plotted in figure 4a. It results that weight loss decreases strongly with increasing pH. The curve slope (dashed line) indicates

the critical value of pH 4. It corresponds to the average value mentioned in literature (Menz & Seip 2004).

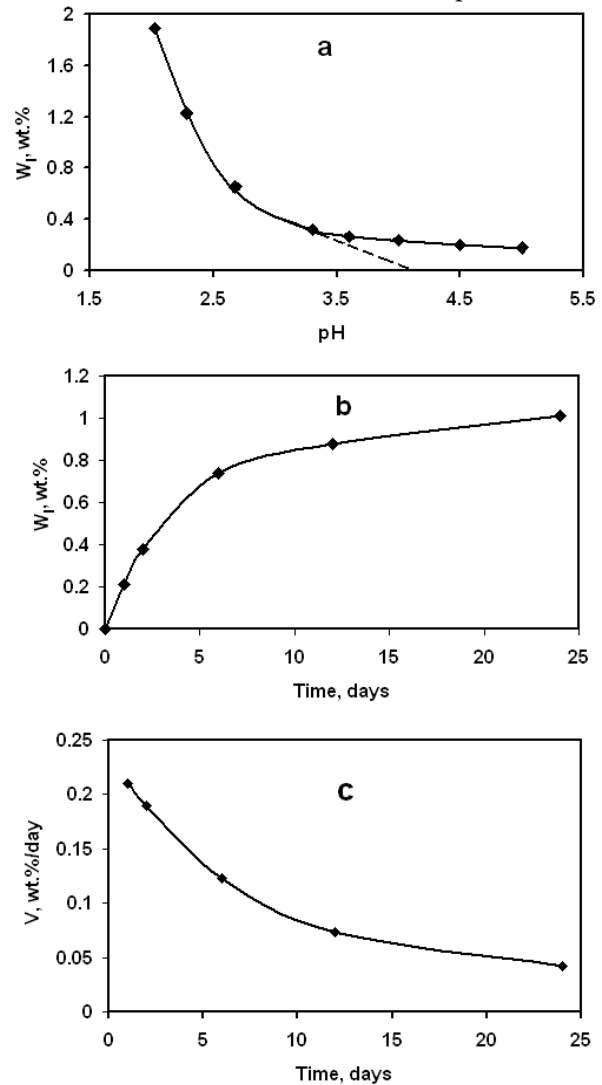


Figure 4. The marble weight loss in presence of acid rain: a) pH influence at 2 days of exposure, b) exposure time influence, and c) erosion speed versus exposure time, (W_i – weight loss, V – erosion speed).

Time influence was investigated at pH 4 for different exposure times: 0, 1, 2, 6, 12, and 24 days. The marble slices weight loss was calculated by equation (5). The weight loss variation with exposure time is presented in figure 4b. A smaller weight loss is observed after 2 days of exposure which is significantly higher after 6 days of exposure. The marble erosion dynamic effect could be better described by using the erosion speed, V , instead of weight loss. The eroded material quantity reported to the total time of erosion process describes the erosion speed (V). To find it, the relation of the weight loss versus exposure time (t) is given by:

$$V = \frac{W_i}{t}. \quad (6)$$

The erosion speed variation is presented in figure 4c. The process of erosion has a high speed for the first 2 days of exposure. It decreases significantly after 6 days of exposure to 24 days. This variation related to the almost constant weight loss observed for longest exposure time could reveal a possible passivation process.

The observed situation plead for the existence of two erosion stages. The first one is the erosion initiating a stage from 0 to 6 exposure days, and the second stage is the propagation of erosion in the surface depth. The erosion stage evidence could be achieved only by a powerful surface micro-analysis method, such as the atomic force microscopy (AFM). Based on our expertise in the AFM field, a tapping mode investigation will be suitable for the current propose (Hosu et al., 2010; Tomoaia – Cotisel et al., 2008).

The resulted topographic AFM images for the mirror polished marble (0 days of exposure) are presented in figure 5. The marble polished surface is better observed at large area in figure 5a, featuring a smoothed surface with some irregularities (the border between two calcite grains).

The cross section, figure 5c, was taken over the most irregular zone on the surface featuring heights around 330 nm, corresponding to a very low roughness of scanned area (40 nm) of figure 5a. This roughness value is very good for a nice glittering of marble blocks used for statues and ornaments.

The cross section through figure 5b reveals the nanostructure inside the calcite grain, figure 5d. The average diameter of calcite nano-formations is around 50 nm. It proves to be a uniform structural level of the marble surface.

Of course, a roughness of 40 nm related to the fine microstructural level is very high by comparison to monomolecular thin films (Mocanu et al., 2012; Tomoaia et al., 2011) but is still very low comparing to other polished surfaces (Urosevic et al., 2010). All features present a very good smoothness of calcite grains surface and a good attenuation of the grain border effect. The question is how the acid rain affects this polished surface. Two ways for chemical etching under acid rain solution appear: enhancement of grain borders and erosion of the inside of calcite grains.

Similar aspects are observed after one day of exposure, figure 6, almost without changes. Still, we must mention that surface roughness increases slightly with 10 nm. The surface texture is good assuring a satisfactory glittering to the observer eyes.

The microstructure of the polished marble slice has changed after 2 days of exposure to the acid (rain) solution. The view of the inside area of a calcite grain is featured in figure 7a. The surface is significantly

affected by acid rain. Some parallel stripes eroded by the acid solution appear; they correspond to the twins inside the calcite crystals. The cross section trough them, figure 7c, evidence a maximum erosion depth of 240 nm. It means that acid rain solution etch the twins inside the calcite grains after two days of exposure. The topography detail in figure 7b reveals surface nano irregularities related to a 71.2 nm roughness, value significantly increased compared to the initial polished marble slice. The macroscopic aspect still shows a nice glittering shine of marble surface.

Surface degradation progresses after 6 days of exposure into the grain structure, forming erosion clusters as observed in figure 8a. The cross section profile in figure 8c evidences the nano-clusters with an average diameter of 1.5 μm , corresponding to the entire scanned area roughness of 166 nm. The nano-clusters topography is better observed in figure 8b. It has a rounded irregular shape due to the solid-liquid chemical reaction. The erosion depth increases at 480 nm (double than at 2 days of exposure) as observed in cross section. The fact corresponds to the first point of increased weight loss in the variation presented in figure 4. The nanostructure after 6 day of exposure proves enhanced calcite grain erosion. This corresponds to the beginning of the second erosion stage marked at macroscopic level by the disappearance of marble luster.

The AFM topography after 12 days of exposure is presented in figure 9. The general aspect features a highly damaged surface. The entire scanned area roughness in figure 9a is situated at 206 nm. The cross section in figure 9c reveals the enhanced erosion of nano-clusters having an average diameter of 1.5 μm (similar to those observed at 6 days of exposure). The nano-cluster morphology is better observed in figure 9b. These nano-clusters feature a more altered surface than those observed after 6 days, due to the prolonged contact with acid rain solution. The macroscopic aspect is similar to an unpolished marble surface. The erosion tendency also affects the calcite grain borders.

Finally, at 24 days of exposure we observe a totally ruined marble surface, figure 10. The entire scanned area roughness increases at 292 nm, as observed in figure 10a. The local height in the scanned area has over 3000 nm turning on the surface nanostructure into an eroded fine microstructure. This situation is similar to a mechanical abrasion. The cross section reveals larger erosion clusters having around 2 μm diameter, with a damaged aspect. The nano-structural detail in figure 10b shows the deep erosion of calcite grains and the enhanced erosion of grain borders.

The situation observed for 12 and 24 days of exposure corresponds to a consistent damage of the surface quality, which affects permanently the details of the statues and ornaments.

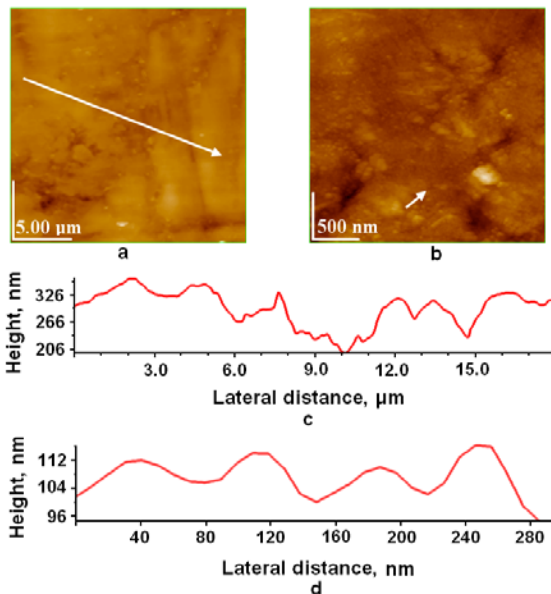


Figure 5. AFM images for mirror polished marble: a) topography 20 μm x 20 μm , b) topography 2.5 μm x 2.5 μm , and c) cross section on image a, d) cross section on image b. Area RMS 42 \pm 2 nm.

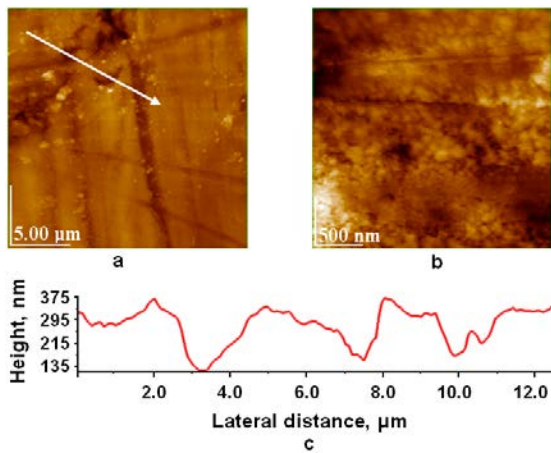


Figure 6. AFM images for sample exposed 1 day: a) topography 20 μm x 20 μm , b) topography 2.5 μm x 2.5 μm , and c) cross section on image a. Area RMS 48.5 \pm 3 nm.

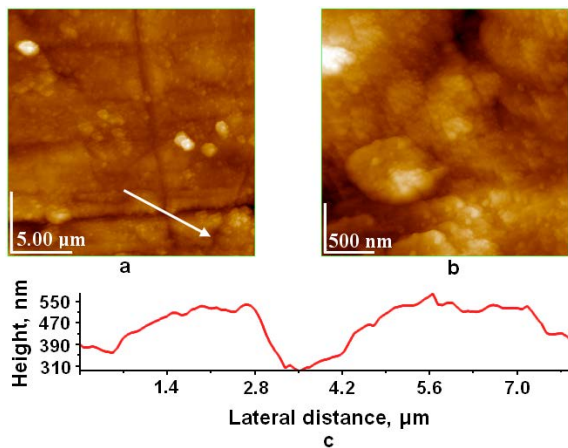


Figure 7. AFM images for sample exposed 2 days: a) topography 20 μm x 20 μm , b) topography 2.5 μm x 2.5 μm , and c) cross section on image a. Area RMS 63.9 \pm 3 nm.

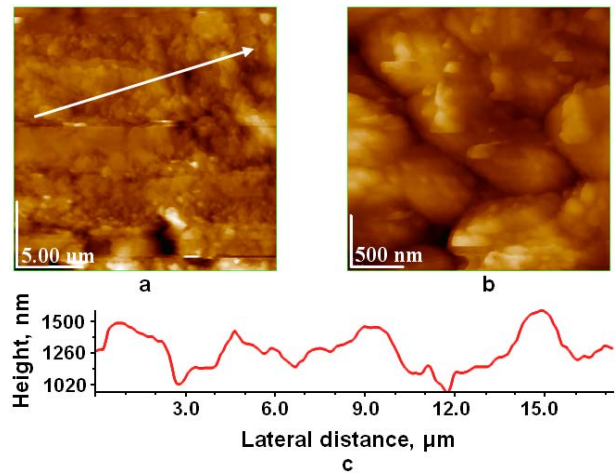


Figure 8. AFM images for sample exposed 6 days: a) topography 20 μm x 20 μm , b) topography 2.5 μm x 2.5 μm , and c) cross section on image a. Area RMS 166 \pm 5 nm.

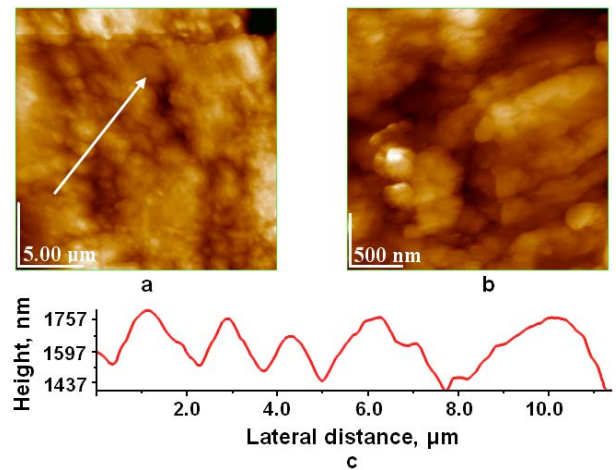


Figure 9. AFM images for sample exposed 12 days: a) topography 20 μm x 20 μm , b) topography 2.5 μm x 2.5 μm , and c) cross section on image a. Area RMS 206 \pm 5 nm.

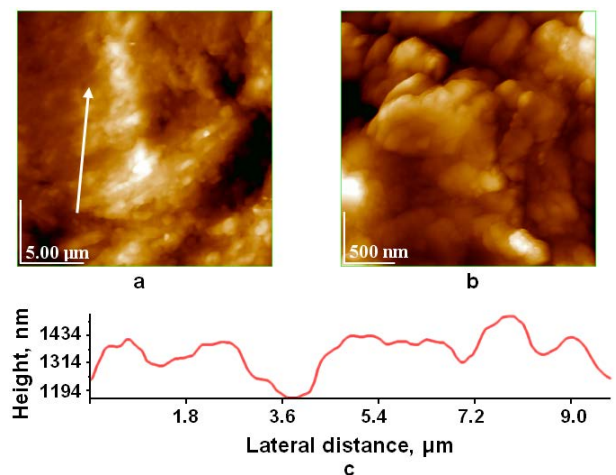


Figure 10. AFM images for sample exposed 24 days: a) topography 20 μm x 20 μm , b) topography 2.5 μm x 2.5 μm , and c) cross section on image a. Area RMS 292 \pm 5 nm.

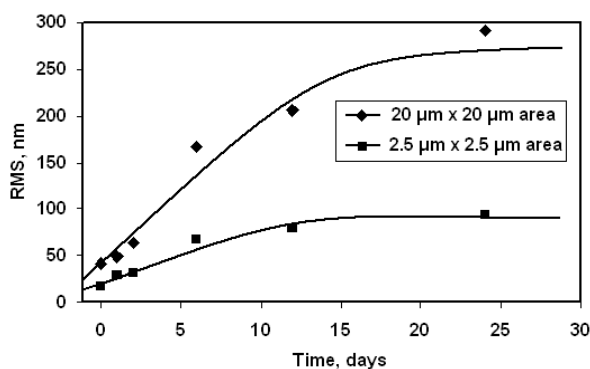


Figure 11. Surface RMS dependence on time for two distinct scanned areas of 20 μm x 20 μm and 2.5 μm x 2.5 μm .

The most representative surface parameter is the surface roughness. We collected all roughness features resulted from the scanned area (20 μm x 20 μm and 2.5 μm x 2.5 μm) and plotted them versus exposure time, (Fig. 11). Both variations present the same allure, revealing the chemical erosion tendency. The roughness values resulted for 2.5 μm x 2.5 μm are situated beneath 100 nm because of the close relation with the observed nanostructure. The roughness values for 20 μm x 20 μm scanned area overtake 100 nm after 6 days of exposure. It reveals two ranges of values: low roughness from 0 to 6 days of exposure and high roughness after 6 days. This situation is in a good concordance with the variation of the weight loss and erosion speed observed in figure 4.

The transition point between low erosion and high erosion grade is situated around 6 days of exposure. The micro- and nano-structural data are correlated to describe the nano-erosion of polished marble samples.

The first stage represents the initiation of erosion at the calcite grain level being promoted on the crystal twins. The glittering property of the marble surface is progressively reduced due to the erosion nano-cluster formation. This stage has low weight loss and does not destroy irreversibly the surfaces of the art object. It took roughly until 6 day of exposure.

The second stage starts after 6 days of exposure at acid rain solution. It is characterized by a significant weight loss related to a progressive increasing of the nano-cluster size even up to the fine micro-scale. The damages caused to the marble surface are permanent in this stage and ruin almost irretrievably the statues and ornaments.

The environmental situation typical for a big city is attributed to the acid rain falls as mentioned in literature (Lefohn et al., 1999; Thakur et al., 1999). The pH value could also vary due to the regional industry profile and its disposing in territory. The acid rain usually has a pH between 4 and 5 and fall for a small time period, maximum 2 days. The marble art objects

exposed to certain conditions will be affected in a nondestructive manner. The question is what happens after the acid rain fall ends. The art objects must be washed with well water and mopped with cotton scraps. If not, there will form a thin crust of nano-erosion product containing calcium sulphate mixed with calcium nitrate. This thin crust preserves the corrosion feature and keeps it for the following exposure at the next acid rain fall. The situation will continue to degrade the marble surface faster. Considering this action for many years, the second stage of erosion could be activated without a continuous exposure at acid rain for 12 or 24 days. This fact will conduct to a considerable depreciation of the marble art object. For instance, a preserving nano-strategy could be developed in order to protect the precious marble surface by a thin nano-structured protector film. This will be a future challenge in the marble preservation field.

4. CONCLUSIONS

The performed investigations prove that the calcite marble is strongly affected by acid rain. Exposing the marble samples to a moderate value of pH of acid rain (e.g., pH 4) we observe two stages of erosion. The first stage affects the inside structure of calcite grain inducing a promotion of nano erosion during this stage that took place from 0 to 2 days of exposure. The transition to the second stage is a propagation of nano erosion to the grain borders having a very pronounced character after 6 day of exposure. In this stage the surface of marble artifacts is seriously damaged. The second stage corresponds to the massive erosion of the surface, with irremediable damage to the quality of marble art objects and ornaments. The roughness of marble nanostructure increases with 250 nm after 24 days of exposure. The damages caused by long term exposure to acid rain solution are better observed by comparing this value with the initial one (of 42 nm).

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