# Another source of soluble salts in urban environments due to recent social behaviour pattern in historical centres

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ABSTRACT: In this study, the process of anthropic decay on stone materials and on the lithobiontic microbial colonization associated was investigated by means of both laboratory simulation (granite) and field experiments (dolostone´s historical quarry), all of them stone materials traditionally used in heritage construction. A wide variety of salts including sulphates, phosphates and chlorides resulted from the interaction between urine and stones after a several month urine treatment under controlled conditions. Moreover, the structure of lithobiontic lichen thalli was investigated, after the direct application of human urine in a field experiment carried out in a historical quarry under the most real conditions, revealing cellular damage in the upper cortex and in the photobiont layer.

## 1 INTRODUCTION AND AIMS

The effect of urine on stone building materials has been traditionally considered only as an aesthetical decaying agent. Nevertheless, this anthropic agent exerts a greater incidence in the materials deterioration than it is known up to now. In the last decades, a change in social customs and behaviour has been confirmed, which turns into a high urine interaction, both human and animal, on the buildings façades. It is commonly possible to observe, in the historical centres, how the materials surface of the built heritage is intensely affected as a result of urinations from humans and pets (dogs). This predicament is the consequence of several circumstances: the bottle-phenomenon (open-air drinking session), which gathers a huge quantity of mainly young people ingesting alcohol in the urban open air; the absence of portable urban lavatories; the increase of dogs as pets in the cities; and the growth of homeless living outside. In this new urban scene, besides insalubrious, threats the perdurability of stone materials of the built heritage, accelerating their decay, without any prevention or curative measures, as the significance of this deterioration due to these causes is not known to depth. Urine has a very high water content (95%), and is a potential source of soluble salts and organic molecules with a high nitrogen content (urea, uric acid, ammonium), thus sensitive to generate alteration due to salt crystallization, dissolution and biodeterioration, among others. This study has two main objectives: 1) the investigation of the nature of the salt crystals precipitated as a consequence of the urine-stone interaction during a several month experimental testing phase, and 2) the evaluation of the effects of urine on the lithobiontic community by means of a field experiment in a historic quarry.

## 2 MATERIALS AND METHODS

### *2.1 Laboratory testing: urine-stone specimens interaction*

This laboratory testing was a simulation of what happens in the city centres during the open-air drinking sessions when participants urinate on the stone façades; it also simulates the process of dogs urination on building stone walls.

Granite was the stone selected for the simulation experiment, as it is one of the natural stones traditionally used as building material in the Central area of Spain (Fort et al. 2013). The quarries are located in La Cabrera pluton (Madrid), in the Northeast region of the Guadarrama Mountain Range, which intruded in the Late-Hercynian orogeny; it is a biotitic monzogranite.

Blocks of granite were directly sampled from the quarry, and 12 cubic specimens (50 ± 5 mm side) were cut.

Human composite urine was collected from 21 donors, 10 men and 11 women, and from a wide range of ages. Around 40 l were collected and stored in a freezer at -30ºC.

The cubic specimens of granite were subjected to 100 cycles of urine capillarity test. Each 24 hour cycle consisted of 20 hour drying at 40ºC, 1 hour cooling, and 2 hours of capillary absorption in a urine sheet of 3 mm high. The necessary urine content to perform the test was previously.

At the end of the 100 cycles test (6 months), small regular fragments of the tested cubes were cut, mainly from the corners, to carry out the planned analyses.

An Inspect FEI environmental scanning electron microscope (ESEM), equipped with an Oxford Instrument Analytical 7509 energy dispersive X-ray spectroscopy (EDS), was used to observe and analyzed the precipitated salts in the stone after the laboratory simulation, comparing to a reference granite area with no contamination. Backscattered electrons mode (BSE) was used.

Grazing angle-incidence X-ray diffraction (GIXRD) - PANalytical X'Pert MPD PW-3373 Cu Kα (λ=1.54056 A) radiation powder diffractometer - was employed to identify the nature of the salts. GIXRD analysis was made in the rock specimens after the laboratory testing, and in the area of maximum concentration of salts.

The ion content in granite, before the experiment, was determined by Ion Cromatography (IC). Two composite urine samples were also analyzed, corresponding to two urine collections. A Metrohm 761 Compact IC ion chromatograph was employed, and the analyzed ions: $F^-$, $Cl^-$, $NO_2^-$, $NO_3^-$, $PO_4^{2-}$, $SO_4^{2-}$-, $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$.

### 2.2 *Field experiment: urine- quarry front rock interaction*

This experiment simulated the process of sporadic urinations to evaluate the effects on the existing microorganisms that colonize the quarry front rock.

For this purpose, a historical dolostone quarry, 50 Km North from Madrid city was selected due to the deep knowledge the authors have of both the stone and its biological colonization, being extensively colonized by *Verrucaria nigrescens* Pers. lichen specie (Fort et al. 2008; Cámara et al. 2011; Alvarez de Buergo et al. 2013). The same urine collected for the laboratory testing was used in this experiment.

In order to determine the effect of human urine on the lithobiontic community, a 8 week long field experiment was performed. It consisted of direct urine spraying onto the dolostone of a vertical quarry front, once a week (until saturation) and at a distance ~ 25 cm from the rock surface. The amount of urine in each spraying test was 100 ml, in a rock surface of about 30 cm x 30 cm.

After this treatment, rock fragments were sampled, both treated and untreated, to evaluate the effect of urine on the lichen thalli structure and at cytological level.

Scanning electron microscopy in back-scattered electron mode (SEM-BSE) was used to analyse tested and control-reference rock spots, by means of a Zeiss DMS 960 SEM equipped with a four-diode, semiconductor BSE detector, and an ISIS Link EDS microanalytical system, according to the method developed by Wierzchos & Ascaso (1994).

## 3 RESULTS AND DISCUSSION

### 3.1 *Laboratory testing: urine-granite specimens interaction*

The observation and analysis of the urine-stone interaction area by means of ESEM allowed us to detect a wide variety of salts. In the prism specimen, 3 sections were differentiated in the 1st cm high, from bottom (and in contact with urine) to top (with no interaction at all with urine), based on the distinct distribution of the salts (Fig. 1a), and the resulting colour of the stone surface: 1) Influence section: not in direct contact with urine, but there is some capillary rise that allows urine to reach this area; 2) Interface area: it is the most affected section-fringe by capillary rising, also known as the wick area; 3) Immersion section: it is in direct contact with urine during the capillary test. The non-treated area (higher enough to not be affected by urine) was used as reference for comparison (nº 0 in the plate of Figs. 1a, b-c).

In comparison to the non-treated areas of granite (Figures 1b-c) where no salt crystals were observed, halite (NaCl) and sylvite (KCl) cubic crystals of different size were detected in the influence area (Figs. 1d-e). In the intermediate interface area, round- and amorphous- crystal phases of potassium sulfate and irregular NaCl-crystals embedded in an organic matrix (Figs. 1f-g) were observed. In the bottom immersion area abundant prismatic crystals enriched in Ca and P elements were covering almost completely the entire rock surface (Figs. 1h-i). XRD analyses confirm this calcium phosphate as brushite [$CaHPO_4(H_2O)_2$] (Fig. 2), both in the immersion and interface areas of the stone specimen, being the only detected neoformed mineral, besides the constituting minerals of granite (quartz, anorthite and orthoclase).

The IC analyses (Table 1) of the materials before the testing reveals that, in granite, Ca is the cation with shows the higher content, followed by K. In contrast, urine samples revealed a very high content, especially in chlorides, phosphates and sulphates, and sodium and potassium, as the most abundant anions and cations, respectively.

Considering both the composition of the urine and of the granite, the neoformed salts were those expectable: halite, sylvite, potassium sulphate (arcanite or similar) and brushite. In the granite, $Ca^{2+}$ accounts for anorthite (calcium plagioclase, $CaAl_2Si_2O_8$) and $K^+$ for orthoclase (potassium feldspar, $KAlSi_3O_8$) and biotite (potassium, iron and magnesium silicate, black mica, $K(Mg,Fe^{2+})(Al,Fe^{3+})Si_3O_{10}(OH,F)_2$ ). A vertical zoning and distribution was also observed, with phosphates in the bottom, sulphates in the intermediate area and chlorides in the top, according to their solubility, and similarly as it happens in the building stone walls. The bottom section is the area with more concentration of neoformed salts (Fig. 1h). Of special remark is the absence of nitrates ($NO_3^-$), and moderate to low concentration on $NO_2^-$, compared to what should be expected, result that was previously obtained by some of the co-authors analyzing the effect of pigeon droppings (Gomez-Heras et al 2004).

Table 1. Ion cromatography analysis of samples of granite and urine (mg/L)

| Materials | $F^-$ | $Cl^-$ | $NO_2^-$ | $NO_3^-$ | $PO_4^{2-}$ | $SO_4^{2-}$ | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Granite | 0.24 | 0.19 | 0.06 | 0.42 | - | 0.42 | 0.73 | 1.62 | 6.41 | - |
| Urine1 | 51.5 | 2944 | 90.5 | - | 1926 | 1379 | 2392 | 1626 | 121.4 | 72.2 |
| Urine2 | 40.2 | 3034 | 79.7 | - | 1792 | 1141 | 1998 | 1755 | 94.2 | 47.0 |

### *3.2 Field experiment urine- quarry front rock interaction*

The observation by SEM-BSE of control (untreated) and treated rock with urine spraying samples revealed cellular damage in the upper cortex and in the photobiont layer of *Verrucaria nigrescens* lichen thallus (Fig. 3). Control lichen thalli showed an intact/complete lichen thallus and viable algal and fungal cells in the photobiont layer (Fig. 3d, asterisks and arrows). In contrast, in the treated lichen thalli is possible to observe some breakages in the upper cortex with some dead fungal hyphae exposing the photobiont layer to the environment (Fig. 3e, arrowheads). Moreover, additional effects were detected in the photobiont layer, such as an increase in the proportion of algal cells and fungal hyphae showing only their cell wall due to the disappearance of the cytoplasmic content (Fig. 3e, asterisks and arrows).

Similar effects on lithobiontic lichen thalli were obtained, but in a lower degree, to those reported in previous studies with biocide treatments for the removal of the microbial colonization, in the same dolostone quarry, that contributes to the biodeterioration of stone monuments (Alvarez de Buergo et al. 2013; Cámara et al. 2011; Speranza et al. 2013). Disappearance of the upper cortex in some points of the thallus predominance of empty fungal and algal cells in the upper cortex and photobiont layer of the thalli were some of the most common effects detected after the urine-dolostone interaction. This means that in contrast to what it could be expected, that urine could contribute and favor microbial colonization, it affects it.

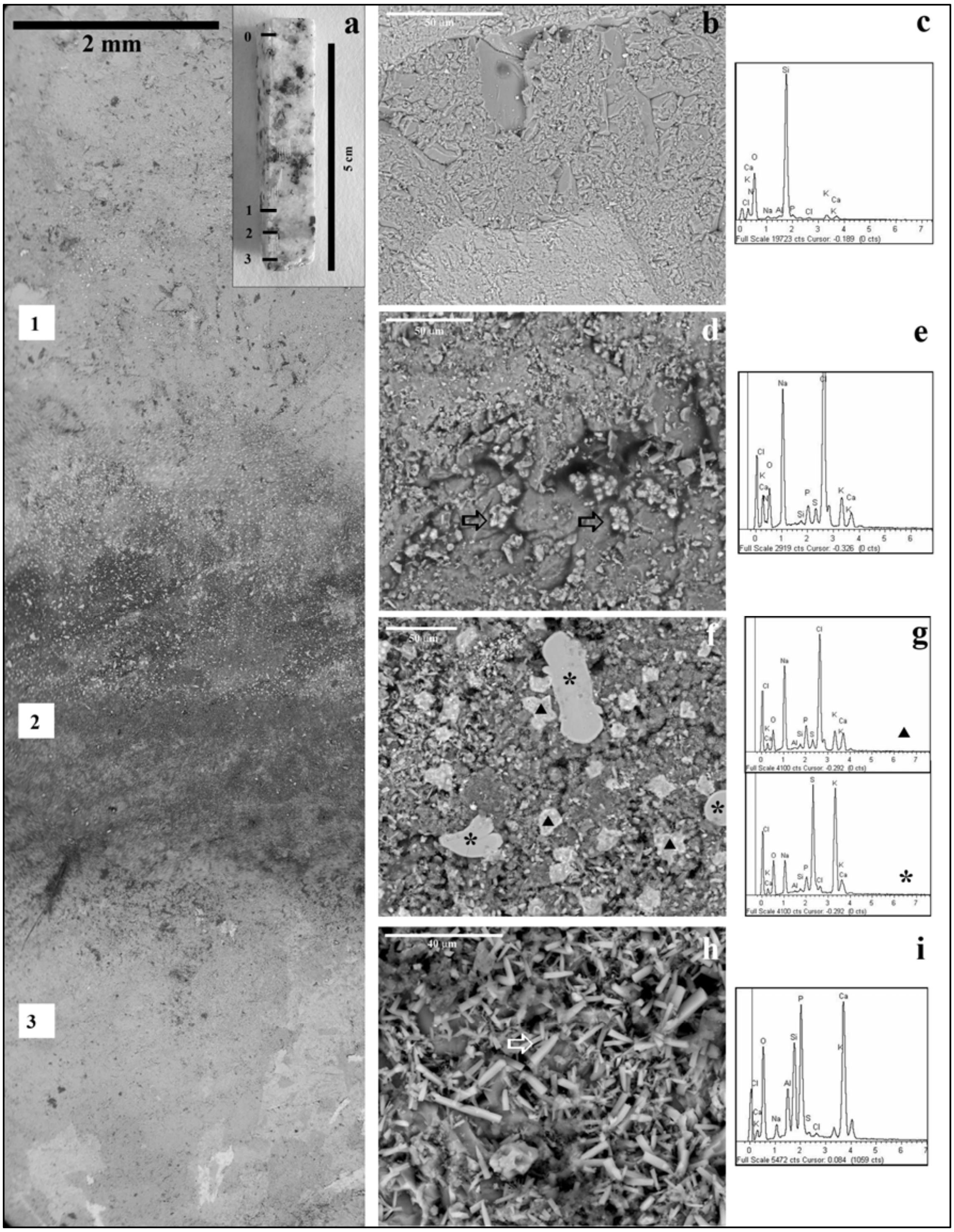


Figure 1. a) Macroscopic image and ESEM images (BSE mode) of the granite specimen after 100 cycles of urine capillarity; b) Non-treated area of granite showing a quartz crystal with no signs of neo-formed salts and c) corresponding EDS spectrum; d) ESEM image of the influence top area (1) showing aggregates of cubic crystals (arrows) of micrometer-size randomly dispersed around a rock fissure e) EDS spectra revealing the presence of Na and Cl; f) ESEM image of the interface-intermediate area (2) with amorphous round-shaped crystals (asterisks) and irregular cubic crystals (triangles) embedded in a organic matrix g) their corresponding EDS spectra reveling potassium sulfate SK (asterisk)- and sodium chloride (triangle) nature; h) ESEM image and EDS spectrum of the immersed-bottom area (3) showing abundant prismatic crystals enriched in P and Ca elements (arrow).

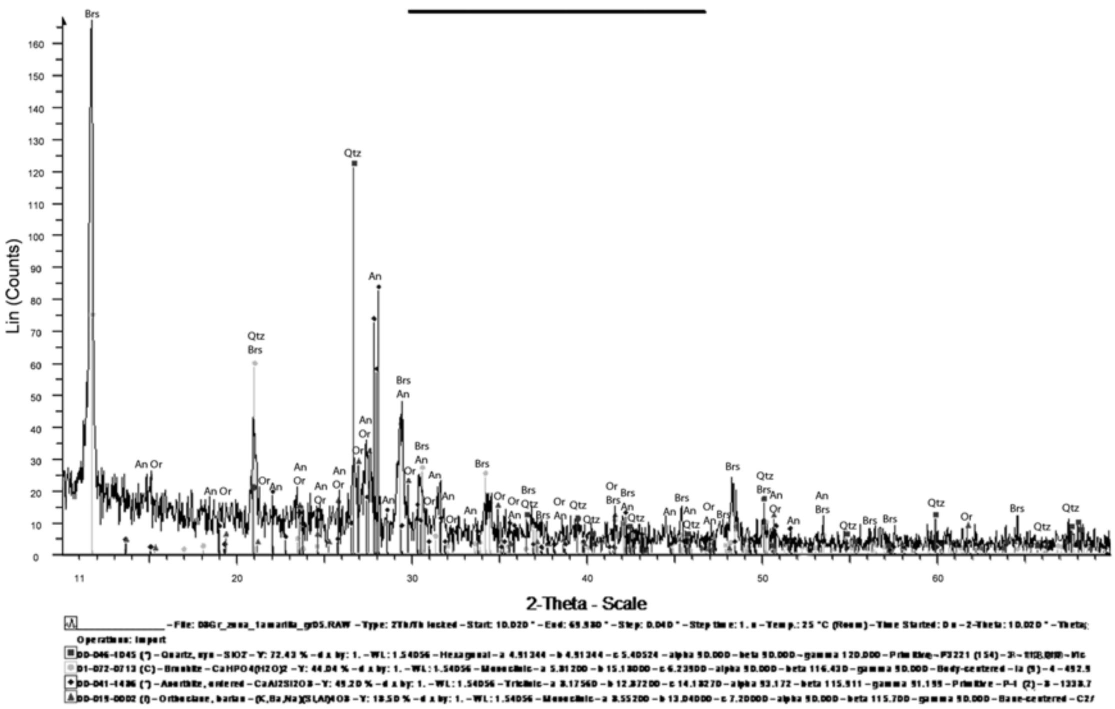


Figure 2. X-ray diffraction pattern obtained from the urine immersion area-bottom section granite specimen after 100 capillary test cycles; quartz, anorthite, orthoclase, brushite.

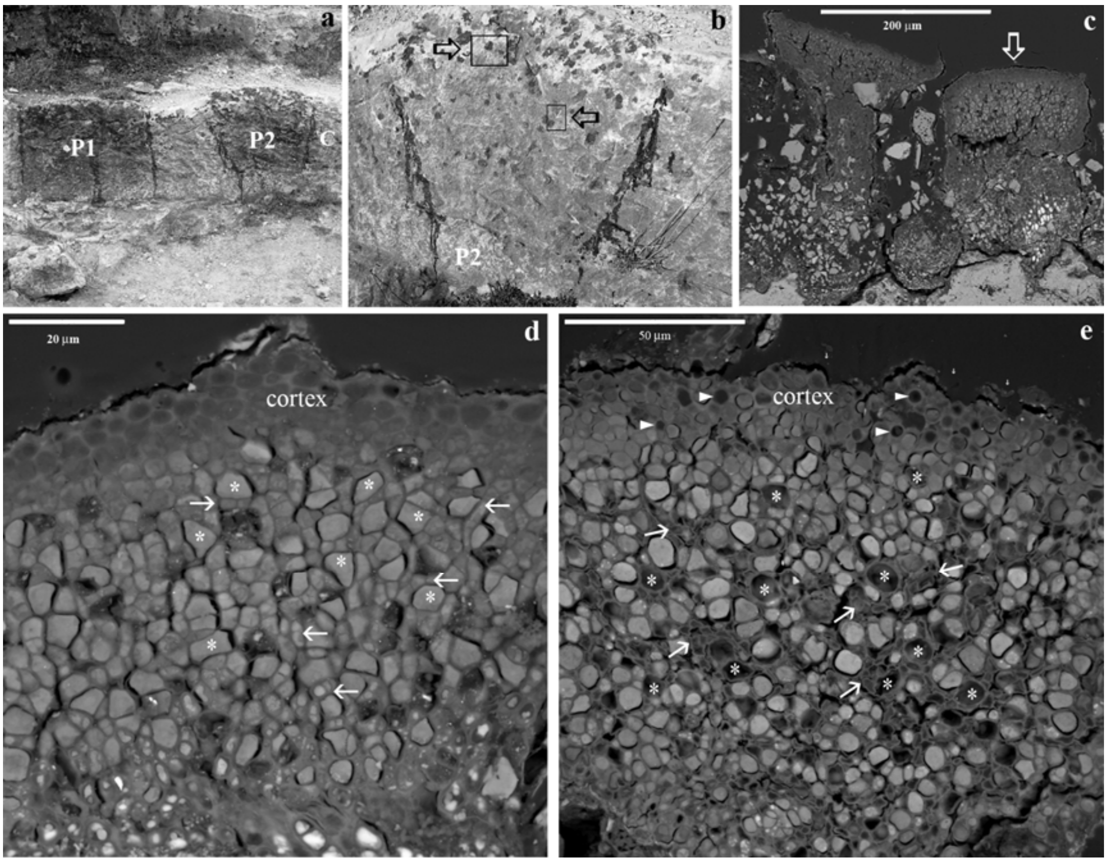


Figure 3. a) General view of the dolostone quarry front (control, C and experimental plots, P1 and P2); b) Detailed view of P2 plot indicating the lichen thalli selected for analysis (arrows); c-d) SEM-BSE images of the areolar structure and d) upper cortex (arrow in Fig. 4c) of a healthy epilithic lichen thalli of *V. nigrescens* (algal cells: asterisks and fungal hyphae: arrows, in the photobiont layer); e) SEM-BSE image showing the upper cortex of a lichen thalli after the experiment. Note the increase of empty spaces in the upper cortex (arrowheads) and in the photobiont layer (dead algal cells: asterisks; dead fungal hyphae: arrows).

## 5 CONCLUSIONS

The results derived from this study shows that urine should be considered not only as an aesthethical agent of built heritage decay, but also as a highly aggressive deterioration chemical agent, for being a detonation of crystallization processes. Salt crystallization is one of the most harmful causes of stone decay and it has been extensively studied (Benavente et al. 2004; Price 1996), but in no case urine has been considered as a potential source of soluble salts. Sulfate, chloride and phosphate crystals (potassium sulphate, halite, sylvite and brushite), were detected in the rock surfaces of granite used in the laboratory testing.

On the contrary, the expected scenario of urine as a contributor to increase microorganisms growth, did not take place, at least, for the effects caused in the specific lithobiontic lichen thalli present in the selected case study.

Consequently, the results of this novel study indicates that more investigation should be devoted to the effects of urine in building materials, in order to not only a scientific knowledge advance, but to research in measures to minimize the negative consequences on stone materials, especially those constituting cultural heritage.

## 6 ACKNOWLEDGMENTS

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