Carpathian Journal of Earth and Environmental Sciences, August 2013, Vol. 8, No. 3, p. 15 - 25

CRUSTS ON THE HISTORICAL CITY WALL OF CLUJ-NAPOCA, ROMANIA

Călin P. RĂCĂTĂIANU & Marcel BENEA
"Babeş-Bolyai" University, Faculty of Biology and Geology, Department of Geology, Kogălniceanu 1, 400084, Cluj-Napoca, Romania, email: calincr@gmail.com; marcel.benea@ubbcluj.ro

Abstract: Since the degradation of building stones is a process that cannot be stopped, the three main known types of rock alteration, chemical, physical, and biological affected the Historical Wall of the medieval city Cluj-Napoca, too. The crusts' formation on the wall's surface favours the occurrence of gypsum, whose volumetric expansion leads to the generation of microfissures. The most frequent type of films noticed is represented by the black-stained crust. The crusts are mixture of gypsum, fibrous calcite, isotropic material and silt quartz, small carbonate crystals, and clay indicating the constant present of moisture, pollutants, and black particles from industrial dust, ultra-fine soil components, and also some possible restoration attempts. The dissolutions inside, especially near the surface of the rock formed large amounts of microporosity. Large vugs and cracks were also formed by the breakout of the bioclasts. To understand the mechanism of their formation some microscopic analyses, SEM pictures and XRD analyses have been used.

Keywords: black crusts, weathering, dissolution, Cluj Limestone, building stones

1. INTRODUCTION

As it is the case with all natural products, the natural building stones, such as natural stone monuments (buildings, walls, sculptures or statuaries) are transformed when in direct contact with the atmosphere. Complex physical, chemical and biological processes alter the stone in some general or specific way. Therefore, all types of constructions made of natural building stone are exposed to several factors, such as anthropogenic influences (processing by cutting or shaping generating micro-fissures on the surface of the stone), climatic weathering (as an effect of atmospheric pollution, particularly of "acid rain"), and the geographical (spatial) orientation of the edifice. In polluted urban environments the soiling, patination and crusting are known features (McAlister et al., 2006). The atmospheric pollutants can causes decay of the building stones and of the historic mortars during and after the deposition of gaseous and particulate atmospheric pollutants having as results gypsum coatings (Sanjurjo Sánchez et al., 2011). Black crusts development is mainly associated with surface deposition of complex mixtures of atmospheric particles, gases, environmental dust, salts and microbial fauna, their blackness being commonly explained by the absorption of carbonaceous particles such as soot (Urosevic et al., 2012 and references therein). These crusts types are usually generated by the reaction between atmospheric SO_2 and the deposited carbonaceous aerosols with the product of gypsum, carbon compounds and elemental carbon particles (Hui et al., 2013). Moreover, the salt crystallization, one of the most powerful weathering factors, can damage porous materials through mechanical stress derived from the crystallization of salts in pores from a saturated or supersaturated solution, differential thermal expansion, hydration pressure etc. (Kramar et al., 2011). Also, the crystallization of gypsum and halite inside the stone, but near the surface, can result in the development of new pore sizes, generation of micro fissures, and therefore the increase of the open porosity (Urosevic et al., 2013), generating further weathering processes. The porosity, pore geometry, and specific surface are the main characteristics of the porous media, contributing later to chemical changes of the minerals and to the development of other weathering processes (Mihăilă et al., 2012 and references therein).

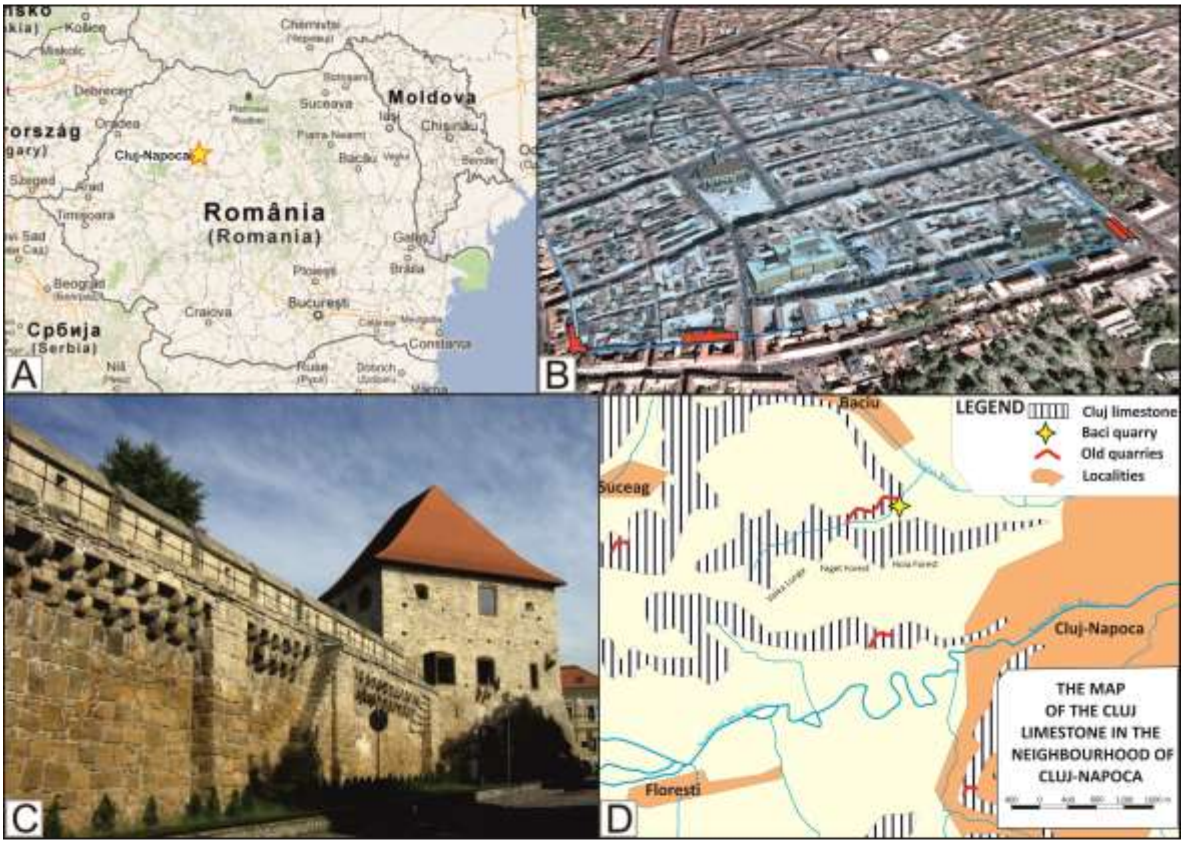

Figure 1: A – The map of Romania with localization of Cluj-Napoca; B – nowadays aerial view of Cluj-Napoca city centre with the former medieval city limits (marked in blue) and the remains of the old city wall (marked in red); C – Nowadays remains of the old city wall of Cluj-Napoca; D – Geological map of the Cluj-Napoca area with indication of the Cluj Limestone quarry (red and yellow).

To all these ads the mineralogy of the particular building rocks that influences the overall decay pattern.

In most of these cases, further decay takes place under the influence of new processes triggered by pollutants specific to the region where the building is situated. Moreover, the anthropogenic processes can add to these. In some cases "artificial micro-climates" may be created by specific architecture elements of the building on walls or facades, adding even greater complexity to the weathering processes. In addition to the climatic and pollution influences, the geographical (spatial) orientation of the edifice plays a major role in the future behaviour of the building stone through the direct influence of the sun (resulting in local insolation on the surface of the stone), as well as of rain, wind, air currents, air pollution etc.

We have studied the carbonate rocks used as building materials for the Historical Wall of the medieval city Cluj-Napoca (Fig. 1 A, B, C); they are regionally called the Cluj Limestone (Fig. 1 D). The complex deposition history of these rocks led to the formation of a complex mineral assemblage. The rock exhibits features related to the rock's depositional environment and characteristics that rule different behaviour as construction material and different weathering features. The main characteristics influencing these differences are related to cementation patterns, amounts of non-carbonate, i.e. clay minerals, types and amounts of matrix influencing dissolution, explicit pore-geometry and the amount and spatial distribution of porosity. The dissolution of the limestone components – fragments of fossil remains (mainly consisting of primary aragonite) – generated different types of porosity such as intra-ooid moldic, biomoldic or interparticle porosity. The dissolution accelerated the decay of the building stone; subsequently, severe urban pollution exposure accelerated the decay.

2. THE HISTORICAL CITY WALL OF CLUJ-NAPOCA

The most important and distinctive symbol in over 1900 years of history in Cluj-Napoca, Romania is the wall of the Cluj fortress, which has partially survived up to today. The most prosperous period of time for the Cluj fortress was in the 15^{th} century, when the city - by then a free imperial city - acquired the right to build its own defensive walls, bastions and fortified towers.

Prior to this fortress, the city had undergone two stages of development-Roman colonization from 101-271 AD and a second settlement in the 9th and 10th centuries when the "founding" of the future city began. The construction of the wall, representing the defence of the medieval Cluj Fortress, lasted from the 15^{th} century to the end of the 16th century. The area of the fortress covered 45 ha (Fig. 1 B) provided with impressive fortifications and city wall built exclusively of stones (blocks of rocks) with loopholes (Fig. 1 C). Today only four sections of the original wall still exist (Fig. 1 B). The causes of its decay were primarily demolitions and the use of inappropriate rock types which led to extensive weathering. The mappings indicate that more than 85% of the wall was constructed with Eocene limestone from the vicinity of Cluj, using different facies types of so called Cluj Limestone (Fig. 1 D). Approximately 9% of the wall was constructed of calcareous sandstone from the nearby Feleac Formation. The rest of the volume of the wall represents mortar fillings, bricks and wood. Cluj limestone, deposited on a shallow tropical carbonate platform in the Transylvanian Basin during the late Eocene-Early Oligocene, has a mixed composition generated by its complex mineralogy. The terrestrial input from the surrounding areas during deposition changed the composition of the limestones; quartz, feldspar grains and clay minerals were admixed to the carbonate sediment, resulting in the colour of the rock, its technical characteristics, and different types and degrees of weathering.

Fifteen different facies types of Cluj Limestone were described by thin section analyses, varying from mudstone to wackestone, wackestone - packstone, packstone, packstone - grainstone, grainstone - packstone - wackestone - alternation and grainstone. All the limestones have a high fossiliferous content with foraminifers, peloids, ooids, and gastropods in a micritic matrix. The XRD analyses revealed a relatively homogenous clay content, characteristic of the Tertiary limestones, higher in matrix-rich limestones and almost absent in grainstones. The weak binding of the components inside the carbonate sandstones created perfect conditions for some specific weathering processes.

The different facies types of the limestones used generate different weathering features. The thin section analysis indicated that all the facies types exhibit features which explicitly lead to specific weathering and alterations. Admixtures of silt quartz in the matrix are present locally. The completely dissolved primary aragonitic particles, the dissolutions of the micritized matrix and the breakout of the bioclasts formed vugs and large amounts of microporosity. Completely disintegrated parts, fixed to the fresh rock by a mixture of micritic and silty material with gypsum, formed black-stained crusts.

3. THE MAIN FORMS OF BUILDING STONES DECAY

The main forms of building stone decay are represented by chemical and physical weathering. Beside this, biological decay plays an important role, mainly through its products acting as catalyst in the chemical weathering (Fig. 2).

The chemical weathering is the most frequent process noticed on the surface of the Historical Wall of the medieval city Cluj-Napoca. This process generated different types of crusts as a result of the dissolution of the limestone components calcite and dolomite. The physical weathering influenced the decay of the building stone based on the anisotropy within the rocks and, implicitly, their thermal expansion. As a result, microfissures form in the rocks, eventually leading to loss of material. Because of mechanical stress and the influence of the airborne pollutants, the loss of material can generate additional chemical weathering. Also, the microfissures and the loss of material open the way for further biological decay. Because of intrinsic and extrinsic factors such as mineralogical composition, porosity, permeability, humidity, pH, and climatic exposure, the biological colonisation by bacteria and actinomycetes, cyanobacteria, algae, lichens, fungi, myxomicetes and protozoa takes place. The effect of biochemical metabolism subsequently influences the physical and chemical processes.

4. THE MECHANISMS OF CRUSTS FORMATION

As a rule, the concentration of Ca^{2+}, Mg^{2+} directly determines the type of surface crust to be generated. The crust formation mechanism is directly influenced by pollution, the anions involved in these processes being supplied by pollutants resulted from local industries, and cars' exhaust gases or other pollutants transported by wind (Fig. 2). Carried by rain waters into soils (Fig. 3), these anions are eventually transported inside the building rocks by capillary water (Koch et al., 2008). Thus, the elevation reached by water in a wall depends on capillarity: the smaller the pores, the higher level reached by capillarity.

In the case of the lithic material used for the Historical Wall of the medieval city Cluj-Napoca, the formation of the black crusts is triggered by the long-term influence of regional and local polluting factors and by the heavy traffic in the neighbouring central area of Cluj. The general formation mechanism, as schematically presented in figures 3A and B, can be assumed in this case. Under the conditions of water infiltration in the soil and the ascendant capillary water transport within the walls, humidity levels are constant. Thus, chemical precipitation followed by evaporation and re-precipitation have provided a favourable environment for the formation of crusts. The stability profile for the building rocks points to four distinctive areas of chemical alteration.

The external area (Fig. 3) represents the external crust consisting of the black crust, salts and

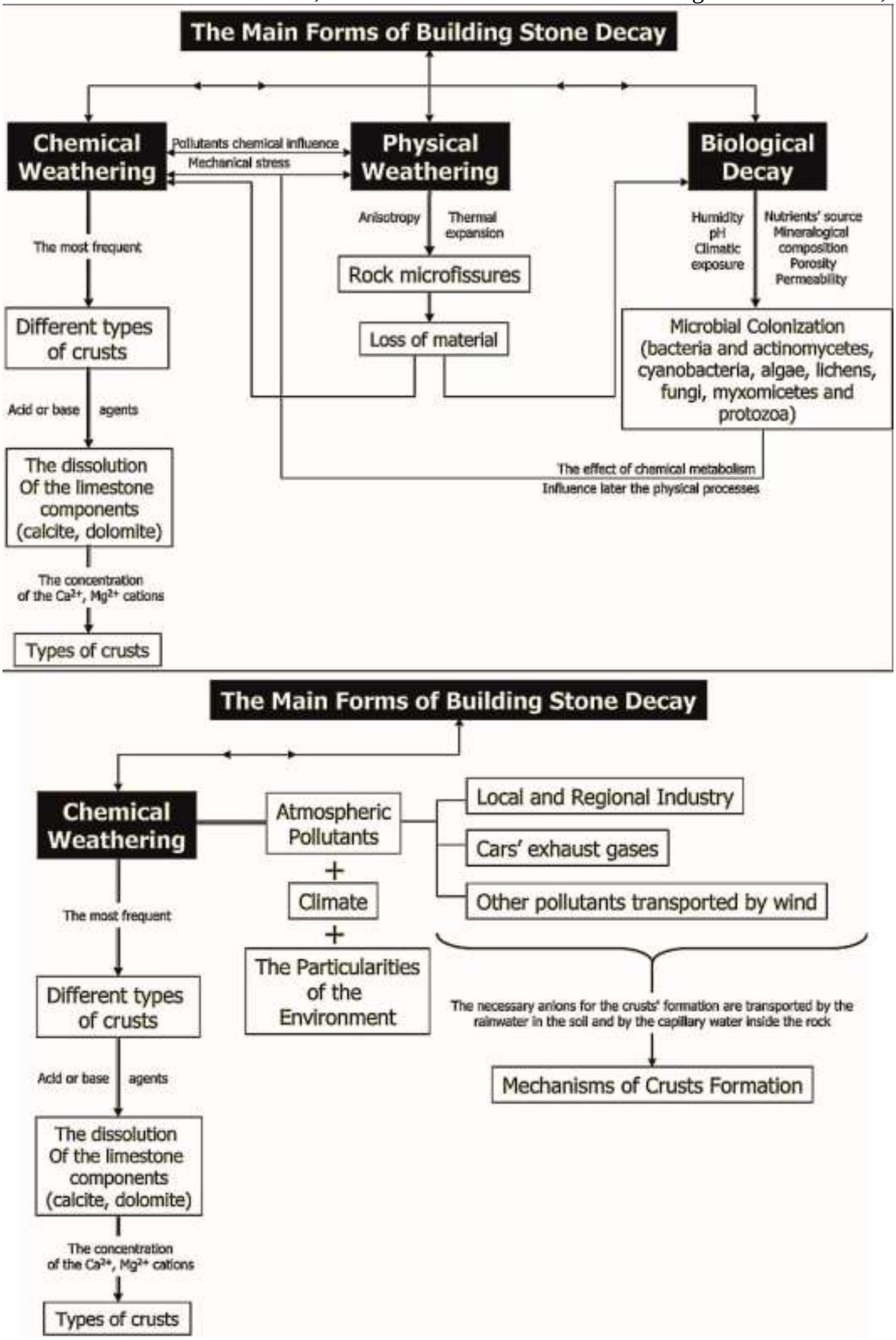

Figure 2. The main forms of the building stone decay.

dust); then there is the original surface of the lithic material with deposits of gypsum and salts precipitation, followed by the internal crust. The latter, together with the most intensely weathered area represent the environment characterized by continuous transformations under the influence of water supply, compounds transported by capillarity and dissolution of the carbonate cement. The transition area is located in the buffer level between the fresh rock and the area of continuous and intense alteration, which progressively advances towards the rock's interior.

The following formation mechanisms could be inferred (Fig. 4): atmospheric CO_2 triggers the formation of carbonate crusts (carbonation) according to the chemical reaction $CO_2 + H_2O + CaCO_3 \rightarrow Ca(HCO_3)_2$. At the same time, SO_4^{2-} leads to the formation of gypsum crusts ($CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2$) where $CaCO_3$ reacts with H_2SO_4 at the surface and inside the pores of the limestone (Davis, 1981). H_2SO_4 results from the reaction of SO_3 with atmospheric water ($SO_3 + H_2O \rightarrow H_2SO_4$), SO_3 being the atmospheric oxidation product of SO_2 ($SO_2 + O \rightarrow SO_3$). Thus, gypsum ($CaSO_4 \cdot 2H_2O$) forms as a fine film at the surface of the rock that theoretically would provide protection to the surface. Practically, the chemical reaction involves an increase of volume, accompanied by mechanical stress that leads to the occurrence of microfissures. The microfissures represent, in fact, the pathway for subsequent alteration processes represented by dissolution, recrystallization, formation of secondary porosity etc.

Additionally, the capillary water carries along some soluble cations from the inner areas of the rock to the surface, where the crusts form (Koch et al., 2008). Climatic variations significantly contribute to salt formation and accumulation in the rock pores. For example, NaCl increases gypsum solubility. The SO_2^{-4}/Cl ratio in rain water varies according to the amount of SO_2 in the air, thus representing a regional pollution index.

Previous published articles mention the black crusts formation as products of acid rains closely related to the formation of gypsum at the rock surface. The black crusts generally represent a mixture of crystals of $CaCO_3$, $CaSO_4$, clay minerals, heavy metals (such as Fe, Ti, Pb, Mn, Cu, Cr, Zn, Ni) compounds, and products of the chemical reactions of NO_x[1] in the atmosphere. In a first stage, such salts are washed away by precipitations; subsequently, due to evaporation salts re-precipitate, this time including black carbon particles resulted from hydrocarbons products. In essence, the black crusts result from the interaction between chemical alterations, microbial colonisation and the incorporation of airborne particles such as dust, metal salts, oxides, nitrogen, sulphurous compounds, metals, radionuclides, carbon particles (Davis, 1981, Sabbioni et al., 1998, Bai et al., 2003, McAlister et. al, 2006, Török et al., 2011) (Fig.4).

5. MACROSCOPIC OBSERVATIONS

The production of crusts and the stability profile is confirmed by macroscopic and microscopic evidence. The four areas illustrated in figure 3 were clearly noticed macroscopically in the material sampled from the Historical Wall of the medieval city Cluj-Napoca (Fig. 5 B). Microscopically one can notice gypsum neoformation at the surface of the rock, overlaid (sealed) by a black crust (Fig. 5 A). The weathering processes, due to the inside dissolutions, chemical reactions and gypsum formation, leads to back weathering processes. The "yellow layer" (Fig. 5 C) is the result of the dissolutions and chemical reactions in the "red layer" (Fig. 5 C). On the "border" between these two layers microfissures occurs, being later filled in by gypsum crystals. This leads to mechanical stress and in the end to detaching of parts of the rock.
When the "yellow layer" is detached, and the material is lost, the "red layer" moves further into the fresh rock (green area in Fig. 5 C) and the weathering process continues in cycles.

6. THIN SECTION ANALYSIS

Eocene limestones were used in the construction of the old town wall. Fifteen different facies types of limestones were discovered in all four studied locations. Because of the uncontrolled excavations during the construction as well as the lack of a scientific approach over the long period of time needed to complete the town wall, the building stones were used randomly within the wall.

[1] NOx is a generic term for mono-nitrogen oxides NO (nitric oxide) and NO_2 (nitrogen dioxide). They are produced from the reaction of nitrogen and oxygen gases in the air during combustion, especially at high temperatures. In areas of high motor vehicle traffic, such as in large cities, the amount of nitrogen oxides emitted into the atmosphere as air pollution can be significant. NOx gases are formed where there is combustion. NOx react to form smog and acid rain.

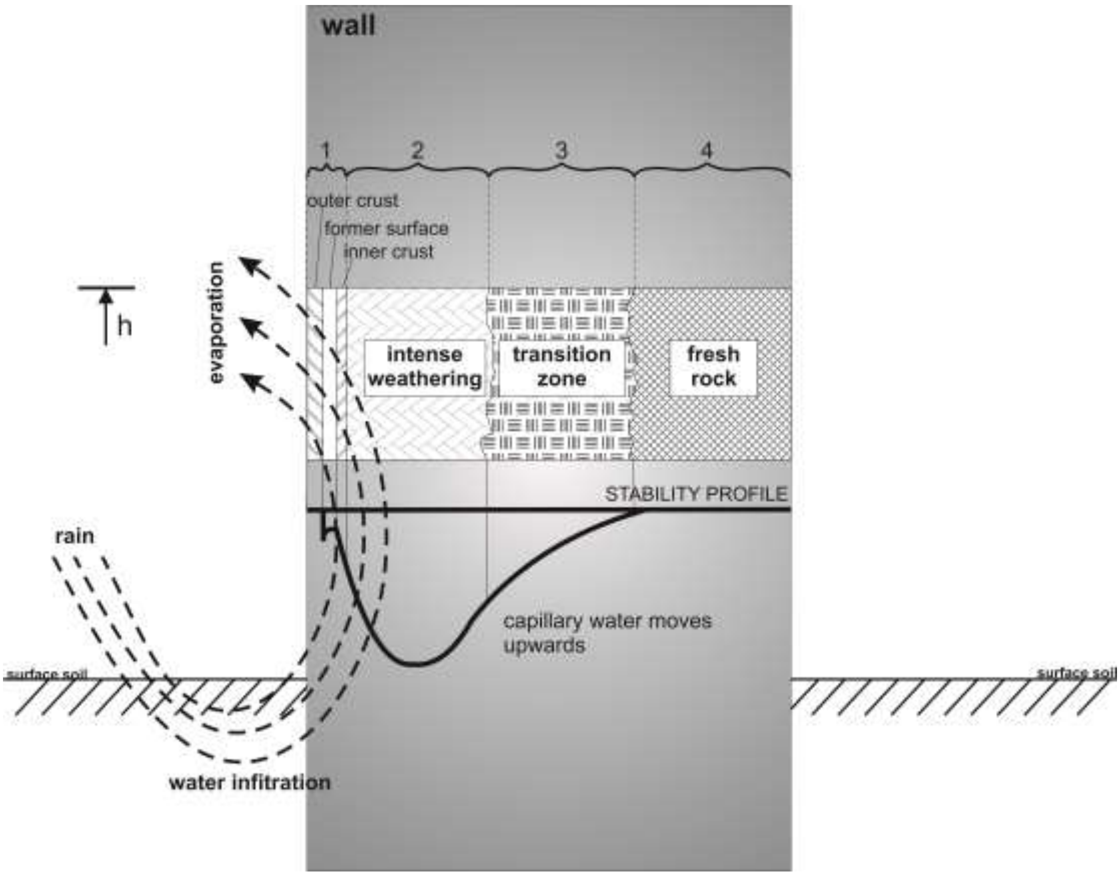

Figure 3. Schematic representation of the alteration process due to water transportation and crusts formation and the stability profile for the building rocks (modified after Hohl, 1981; Koch et al., 2008) – wall transversal section. 1 = external crust (salts and dust composed of outer crust, former surface and inner crust), 2 = zone of intense decay due to the dissolution of the carbonate cement, 3 = transition zone (salts), 4 = fresh rock, h = height reached by capillary water.

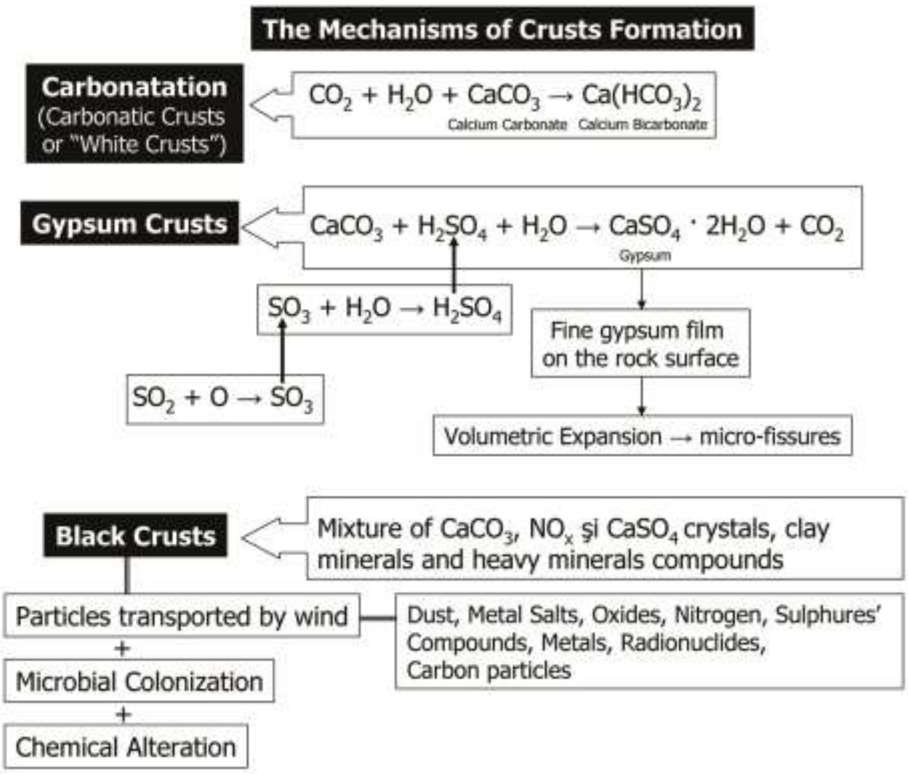

Figure 4: The mechanisms of crust formation

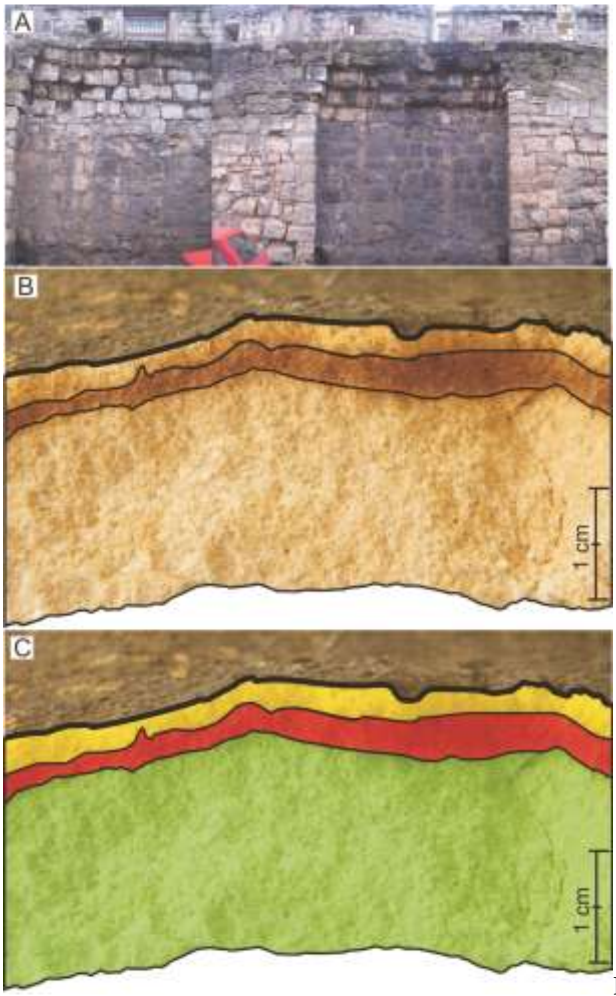

Figure 5: A – Section of Historical Wall of the medieval city Cluj-Napoca covered by black crust; B and C – cross-section of a sample collected from the studied medieval wall.

The facies features and the constant presence of moisture in the lower part and the insolation in the upper part generated conditions for the formation of crusts composed of gypsum, black particles from industrial dust and ultra-fine soil components. Along with these fine crusts, gypsum crystals grew in the fractures oriented parallel to the surface, as a result of insolation and thermal expansion of the limestone surface. Huge fires affected several parts of the wall. The thermal expansions generated by this thermal treatment generated abundant fractures which predominantly run parallel to the surface. Very minor admixtures of silt quartz in the matrix are present locally. The dissolution of the matrix enlarged the fractures, which took a longitudinal orientation. Moldic and vuggy porosity are predominantly present, due to the dissolution of primary micritic matrix. The facies exhibited can be included in the bioaccumulation facies types. The microfacies information was important for highlighting the depositional environment, which was a shallow tropical carbonate platform.

On Plate 1, figures A and, B the limestones composed of well-sorted ooids (0.2 – 0.4 mm size) are penetrated by fractures, which later have been healed by granular calcite. Nearly all ooids are well-preserved, sometimes revealing a radial internal texture of the cortices which might indicate a specific environment of deposition with higher salinity. Isopachous rims of marine phreatic cements can be recognized. The relic interparticle pore space was commonly not closed completely by subsequent granular calcite. Therefore the limestone has a relatively large amount of fine relic interparticle porosity. Commonly cores of ooids (about 15 %) are missing, probably due to dissolution of former aragonitic components which served as cores for the ooids. The surface of the block is covered locally by relics of a former crust composed of fine gypsum needles and a mixture of black particles from industrial dust and ultra-fine soil components.

Gypsum and black crusts are present at the surface of the wall. In other parts of the surface of the limestone the growth of gypsum crystals resulted in an uplift of fragments of the rock by crystallisation pressure. The crystals grow with c-axes perpendicular to the surface, with the highest crystallisation pressure perpendicular to the surface of the block. These crystals grow primarily in fine fractures oriented parallel to the surface, probably caused by insolation and thermal expansion of the limestone surface.

On Plate 1, (Figs. C and D) some benthic foraminifera are floating in a tight micritic matrix together with very minor amounts of fragments of thin mollusc shells. Some amounts of angular quartz fragments of silt size (20 – 50 μm) can also be observed. Locally samples occur which are covered by a thin skin (300 – 600 μm thickness) of a mixture of isotropic material and silt quartz, tiny carbonate crystals, and some clay. This outer layer is interpreted as a former restoration attempt, in the course of which the limestone was covered with a silicate ester (?) mixture.

On Plate 1, (Fig. E) the well-cemented limestone with ooids shows marked dissolution and re-crystallisation features as well as no interparticle porosity. Relics of isopachous rim cements (yellow arrows) occur around ooids. The relic interparticle pore space is filled by granular calcite. The surface of the dimension stone is partly covered by a thin sinter crust (red arrow). On Plate 1, (Fig. F) abundant medium-sized, ooids and thin-walled miliolids (0.1 – 0.3 mm) and other mollusc fragments are the main allochems of the limestone. Mollusc fragments are predominantly preserved as micrite envelopes, revealing large biomoldic porosity due to dissolution of former aragonitic shells.

PLATE 1

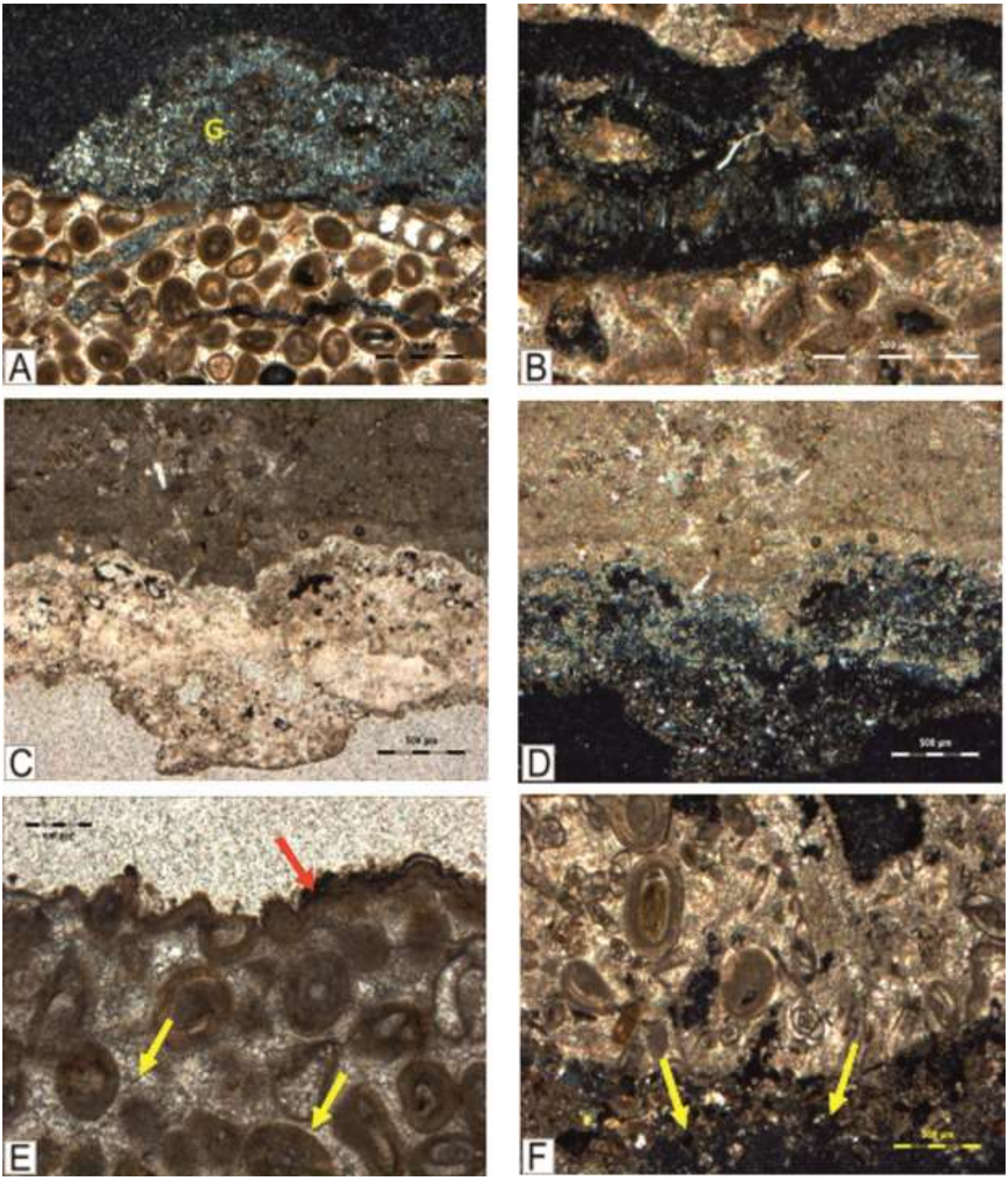

Plate 1. Microscopic analyses of crusts formation:
Figure A. (Oolitic grainstone): Locally the surface is covered by a crust composed of mixture of fine-crystalline gypsum needles (G) black particles from industrial dust and ultra-fine soil components (Crossed Nicol); Figure B. (Oolitic grainstone): In other parts of the surface of the limestone the growth of gypsum crystals (G) resulted in an uplift of fragments of the rock by crystallisation pressure. The crystals grow with c-axes perpendicular to the surface, (Crossed Nicol); Figures C, D. (Miliolid wackestone): Only some miliolids occur in the micritic matrix. The sample is covered by a nearly isotropic crust with some siltquartz (lower part); this is interpreted as relics of a former restoration attempt. (C (Parallel Nicol); D (Crossed Nicol); Figure E. (oolitic, foraminiferal, bioclastic packstone-grainstone): Relics of isopachous rim cements (yellow arrows) occur around ooids. The relic interparticle pore space is filled by granular calcite. The surface of the dimension stone is partly covered by a thin sinter crust (red arrow), (Parallel Nicol); Figure F. (Ooidbearing, foraminiferal bioclastic packstone-grainstone): The limestone is covered locally by a thin crust (yellow arrows) which is composed of silt-sized quartz and brownish organic rich (?) matter, (Crossed Nicol).

In addition, large well-preserved ooids occur, which are not dissolved, indicating their primary Mg-calcite mineralogy. Micritic matrix is commonly recrystallized. The limestone is covered locally by a thin crust (yellow arrows) composed of silt-sized quartz and brownish organic-rich (?) matter.

7. X-RAY ANALYSIS

In order to complete the information, X-ray analysis were performed on samples collected from the external parts of three limestone blocks from the Historical Wall of the medieval city Cluj-Napoca. The X-ray diffraction (XRD) patterns were obtained by using a Shimadzu XRD6000 diffractometer equipped with Bragg-Brentano geometry, Cu-anticathode (Cu-K_a , λ_{Cu} = 1.541874 Å, 40kV, 30 mA), 2 theta = 2 – 65°, $\Delta 2\theta$= 0.02°, and graphite monochromator. The diffractograms are presented in figure 6. As it was expected, common minerals like gypsum, calcite, and quartz are identified, and only in one sample, lepidocrocite and alumohydrocalcite.

The presence of lepidocrocite can be a consequence of the weathering of other iron-bearing minerals from the mineralogical composition of the limestone (e.g. pyrite). In the case of alumohydrocalcite, it is well known that is formed at low temperature by the action of carbonated waters on allophane or clay minerals (e.g. dickite, caolinite) in dolomites and limestones.

Clay minerals can be transported as particles by wind and deposited on the surface of the wall as thin layers of dust, being later involved with the other compounds in the crusts´ formation.

8. SEM ANALYSES

The same sample investigated by scanning electron microscopy (SEM) reveals the formation of idiomorphous elongated gypsum crystals at the rock surface, having their *c*-axes perpendicular to the surface. On figure 7A and 7B, the prismatic gypsum crystals are visible surrounding fossil remnants (foraminifera). Later, during the weathering caused by gypsum, the bioclasts are expelled from the rock (Fig. 7C). Crusts with a layered structure formed by elongated gypsum crystals are presented in figure 7D.

Degradation of building rocks is a process that cannot be stopped; nevertheless their intensity is the result of extrinsic, environmental factors generating, controlling and accelerating this degradation. The main forms of degradation of building rocks are represented by chemical alteration, physical disintegration and biological degradation; these forms act simultaneously and their effects concur.

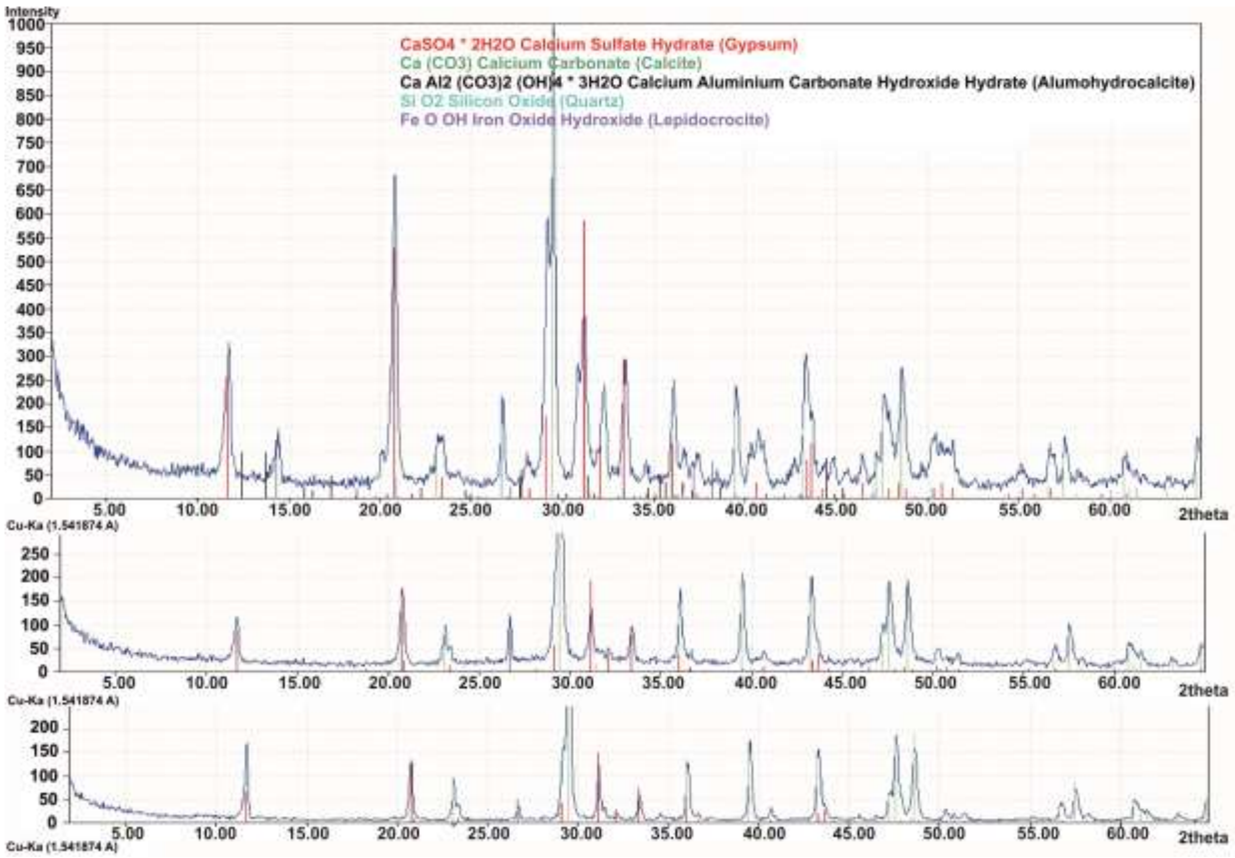

Figure 6. X-ray diffractions of the analysed samples collected from the Historical Wall of the medieval city Cluj-Napoca.

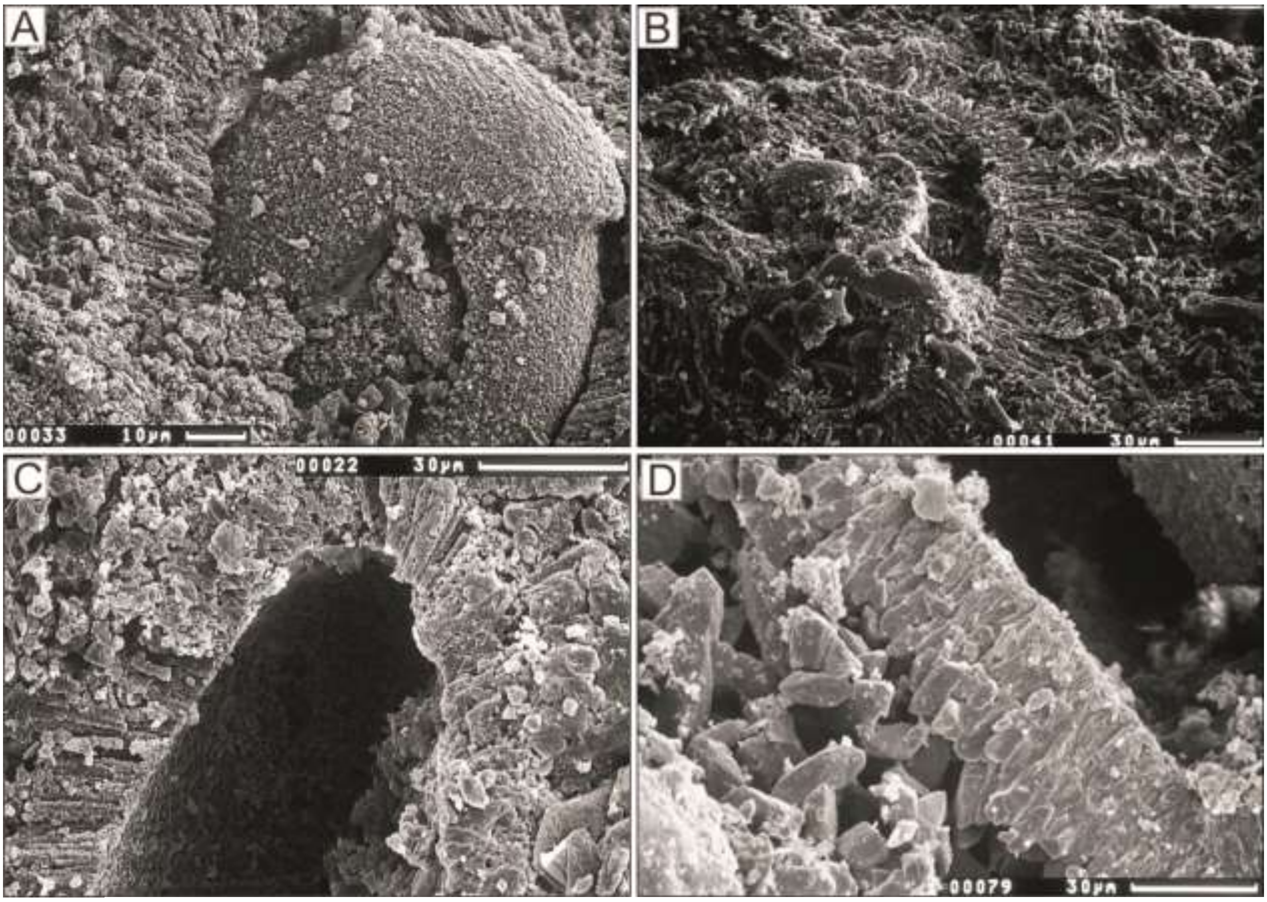

Figure 7. Scanning Electron Microscope (SEM) micrographs of limestones crusts samples from the Cluj medieval city wall. White scale bars = 10 µm A; 30 µm B, C, D. Legend: A and B – idiomorphous gypsum crystals surrounding a bioclast (foraminifera); C – pore resulting after removal of bioclasts; D – crust with a layered structure formed by prismatic gypsum crystals.

9. CONCLUSIONS

The crusts' formation mechanisms are the combined result of relatively simple chemical reactions between carbonation-related chemical compounds and those originating in the environment. These crusts favour the occurrence of gypsum films at the rock surface whose volumetric expansion leads to the generation of microfissures.

The most frequent types of films noticed at the surface of the Historical City Wall of Cluj-Napoca are represented by the black-stained crust. The variables influencing their intensity are the presence of gypsum underneath the black crust, the characteristics of the lithic material, and the environmental factors.

The crusts analysed are mixture of gypsum, fibrous calcite, isotropic material and silt quartz, small carbonate crystals, and clay indicating the constant present of moisture, pollutants, and black particles from industrial dust, ultra fine soil components, and also some possible restoration attempts.

In some cases the black crusts protect the stone, but in most of the cases led to more severe and complex weathering due to the reaction of gypsum, carbonate content, acid rain, clay minerals, dust particles and salts.

The dissolutions inside, especially near the surface of the rock formed large amounts of microporosity. Large vugs and cracks were also formed by the breakout of the bioclasts. Gypsum crystals also grew in the fractures oriented parallel to the surface, as a result of insolation and thermal expansion of the limestone surface.

Further studies have to be accomplished to understand the decay ratio of the Historical city wall's building stones covered by black crust during a certain period of time in Cluj's environment.

ACKNOWLEDGMENTS

The financial support was provided via the Sectoral Operational Programme for Human Resources Development 2007-2013, co-financed by the European Social Fund, under the project number POSDRU 89/1.5/S/60189 with the title „Postdoctoral Programs for Sustainable Development in a Knowledge Based Society".

The study was also partially supported by PN-II-ID-PCE-2011-3-0881 project funds (UEFISCDI-CNCS/Romanian Ministry of Education). The authors wish to thank Dr. Dana Pop for the English corrections.

REFERENCES

Bai, Y., Thompson, G.E., Martinez-Ramirez, S. & Brueggerhoff, S., 2003: *Mineralogical study of salt crusts formed on historic building stones*, The Science of the Total Environment, Elsevier, 302, 247–251

Davis B.L., 1981: *Quantitative Analyses of Crystalline and Amorphous Airborne Particulates In The provo-Orem Vicinity, Utah,* Atmospheric Environment, 15, 613-618.

Hohl R., 1981: *Die Entwicklungsgeschichte der Erde,* VEB F.A. Brockhaus Verlag, Leipzig, 703 p.

Hui Z., Meifeng S., Wei S., Zhiguo L., Bingjian Z., Renzhi L. & Runping Z., 2013: *Damage or protection? The role of smoked crust on sandstones from Yungang Grottoes*, Journal of Archaeological Science, 40, 935-942

Koch R., **Răcătăianu P.C. and Bucur I.I.**, 2008: *Examples Of Weathering And Deterioration Of Tertiary Building Stones At St. Michaels Cathedral In* Cluj-Napoca (Romania), *Studia UBB Geologia* 53, (2), 25-39

Kramar, S., Mirtic B., Knöller K. & Rogan-Šmuc N., 2011: *Weathering of the black limestone of historical monuments (Ljubljana, Slovenia): Oxygen and sulfur isotope composition of sulfate salts,* Applied Geochemistry, 26, 1632–1638.

Maxim, I., Al, Lucca, V., Marincaş, V., Clichici, O., Şuraru, N., Dusa, A., Florei, N., Şuraru, M., Moţiu, A., Ghiurca, V., Nicorici, E., Baluţă, C. & Ghergariu, L., 1959: *The Coarse-grained Limestone on the territory of Cluj-Napoca City (Building materials),* Communication at the scientific session of Victor Babeş and Bolyai Universities on 20th of May 1959, 7-59 pp.

McAlister J.J., Smith B.J. & Torok A., 2006: *Element partitioning and potential mobility within surface dusts on buildings in a polluted urban environment, Budapest,* Atmospheric Environment, 40, 6780–6790

Mihăilă A., Răcătăianu C.P., & Benea M., 2012: *The Decay of tertiary Sandstone In a Non-polluted Environment: Carta Cistercian Monastery in Sibiu County, Romania,* Carpathian Journal of Earth and Environmental Sciences, 7, (2), 67 – 82.

Mutihac, V., Stratulat M.I. & Fechet R.M., 2007: Geology of Romania, Editura Didactică şi Pedagogică, Bucureşti, 249 pp. (in Romanian)

Sabbioni, C., Zappia, G., Ghedini, N., Gobbi, G. & Favoni, O., 1998: *Black Crusts on ancioent mortars*, Armospherrc Environment, Elsevier, 32, (2), 215-223

Sanjurjo Sánchez J., Vidal Romaní J.R & Alves C., 2011: *Deposition of particles on gypsum-rich coatings of historic buildings in urban and rural environments,* Materials, 23, (2), 813–822

Török, A., Licha, T., Simon, K., & Siegesmund., S., 2011: *Urban and rural limestone weathering; the contribution of dust to black crust formation,* Environmental Earth Sciences, 63, (4), 675-693

Urosevic M., Yebra-Rodríguez A., Sebastián-Pardo E. & Cardell C., 2012: *Black soiling of an architectural limestone during two-year term exposure to urban air in the city of Granada (S Spain)*, Science of the Total Environment, 414, 564–575

Urosevic, M., Sebastian-Pardo E. & Cardell C., 2013: *An experimental study on the influence of surface finishing on the weathering of a building low-porous limestone in coastal environments*, Engineering Geology, doi:10.1016/j.enggeo.2012.12.013

Received at: 18. 01. 2013
Revised at: 25. 07. 2013
Accepted for publication at: 07. 06. 2013
Published online at: 12. 06. 2013