Comparative study of two buildings which covered by Zsolnay ceramics, in aspect of deterioration by environmental factors

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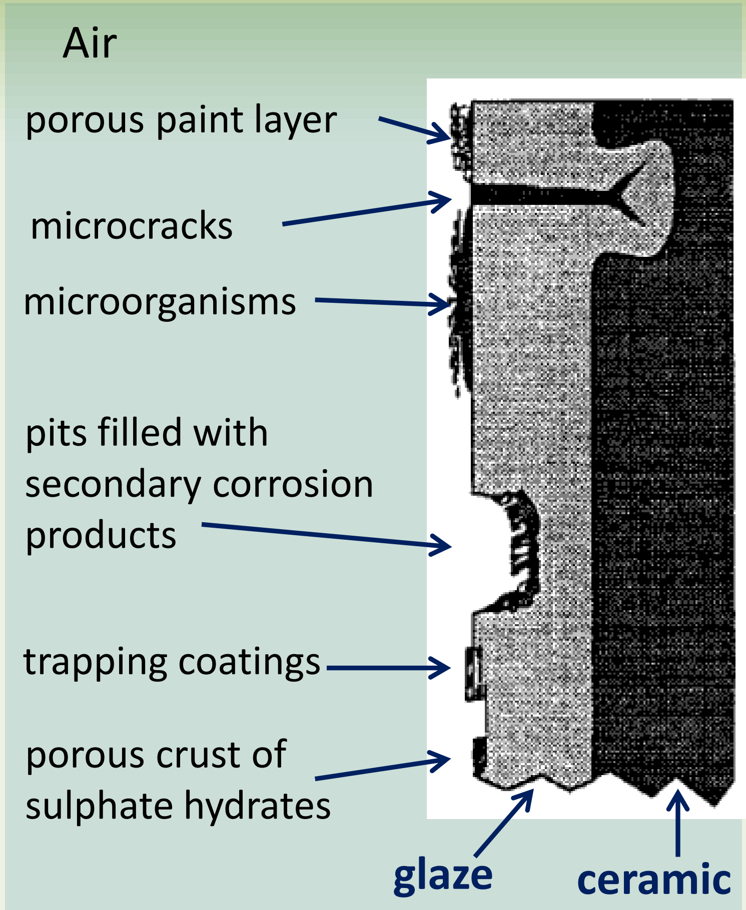
Introduction

Human ↔ Environment
Pollutants deposit on the built environment
from transport, heating and industry
Built environment → Natural and <u>man-made silicate-based materials</u>
Zsolnay building ceramics
- These ceramics have not beenexamined in this aspect before
- Officially, Hungaricum!

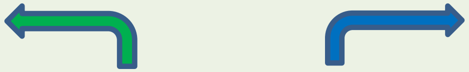


Goals:
- to reveal the effects of air pollutants on building ceramics
- to study the ceramic body and the glaze
- to obtain more information about the Zsolnay ceramics

Buildings and materials

Museum of Applied Arts
(center of the city, high traffic rate)

Geological and Geophysical Institute of Hunagry
(city quarter with moderate traffic)



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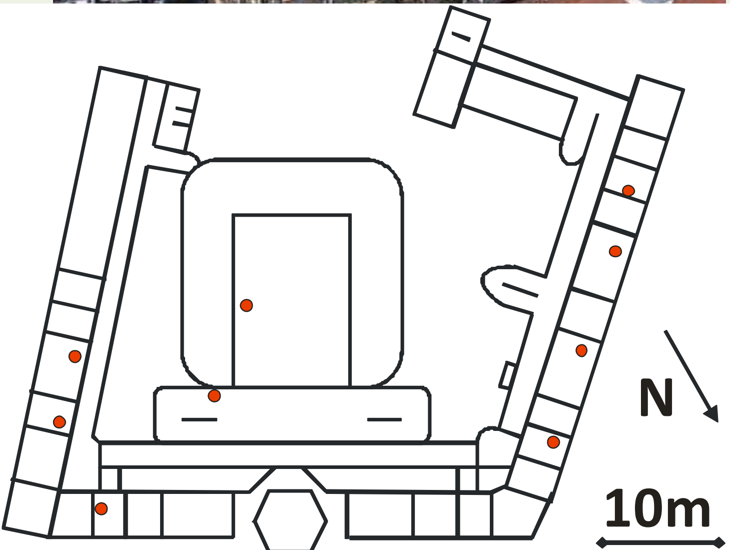
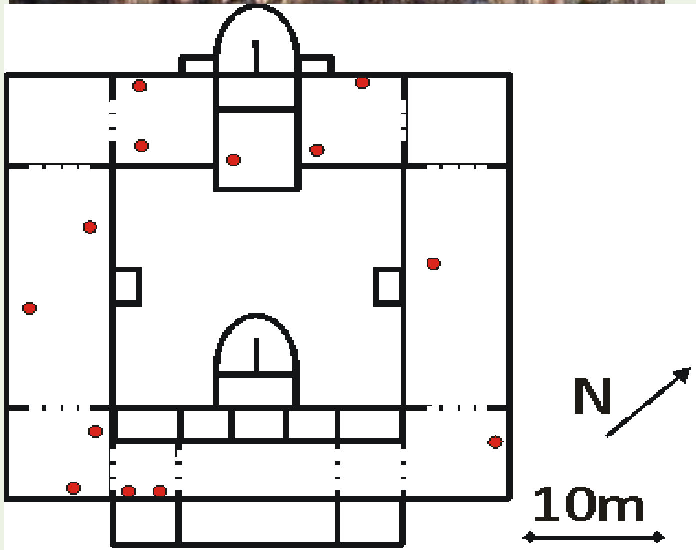


Red dots indicate the sampling sites of the roof



The samples

- Approximately 30-30 glazed ceramic samples
- It was clearly seemed that more types of ceramic material were collected previous suggestion: originate from 3 different time periods

Age of ceramics	Museum of Applied Arts	Geological and Geophysical Institute of Hunagry
1. group) building period	1893-1896	1898-1899
2. group) 1st renovation time	after the 1956 revolution	1945-1946
3. group) 2nd renovation time	1990s	1990s

Results

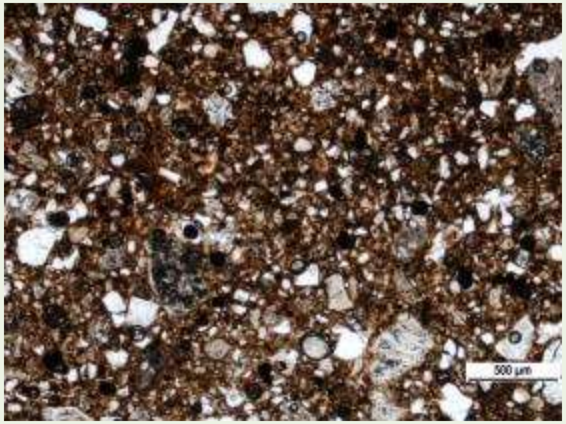
ceramics

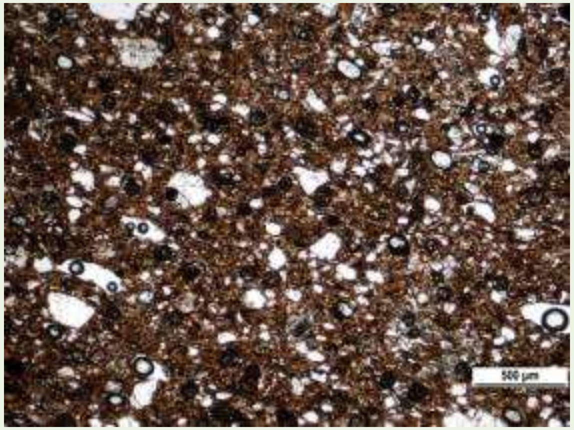
Petrographical analysis

1. group = the oldest ceramics

texture = weakly **hiatal**

- Mostly glassy matrix
- Quartz (in different size) → ~ 25%
- K-feldspar
- Argillaceous fragments
- Some glassy particles
- Ceramic grains
- Granitoid fragments





Results

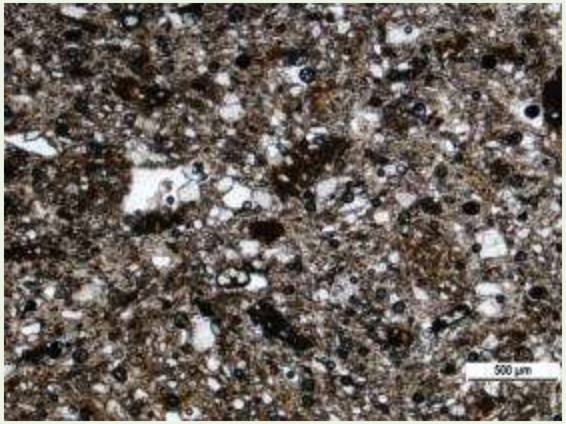
ceramics

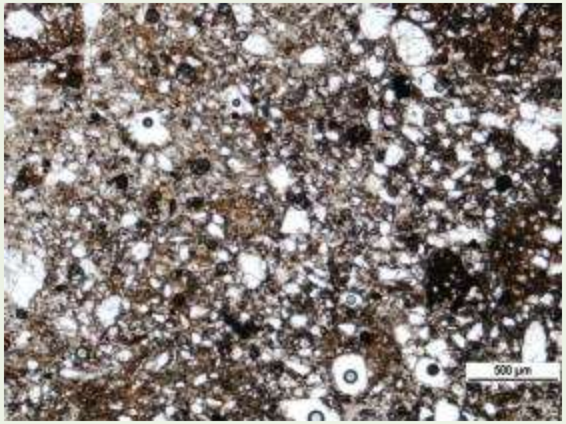
Petrographical analysis

2. group = the middle-aged ceramics

texture = **hiatal**

- Mostly glassy matrix
- Quartz (fine-grained) → ~ 20-25%
- More argillaceous fragments
- Some vesical granitoides
- More ceramic grains
- Few granitoid fragments
- Metagranitoides





Results

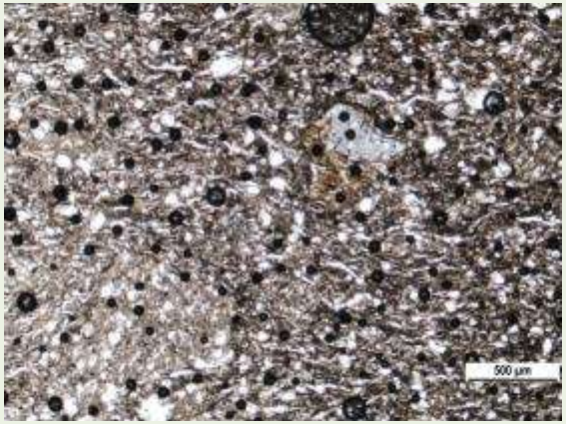
ceramics

Petrographical analysis

3. group = the youngest ceramics

texture = **serial**

- Mostly glassy matrix
- Weakly inhomogeneity
- Quartz(fine grained) → ~ 15%
- Well classified
- More argillaceous particles
- Pores



Results

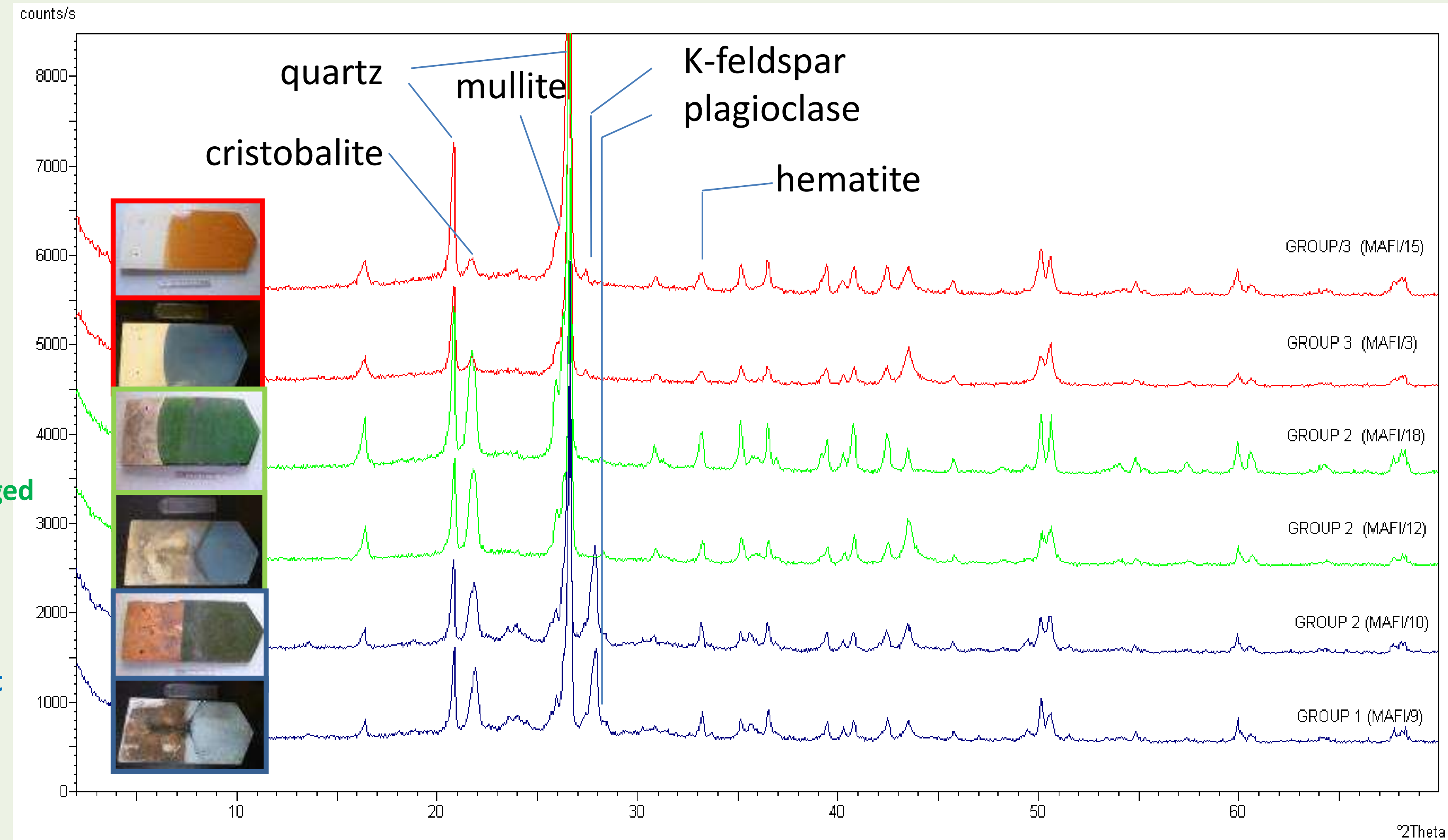
ceramics

XRD analysis

3. group
youngest ceramics

2. group
middle-aged ceramics

1. group
the oldest ceramics

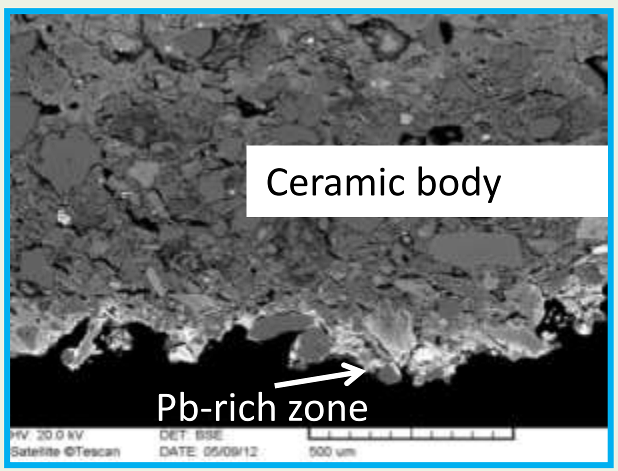


Results

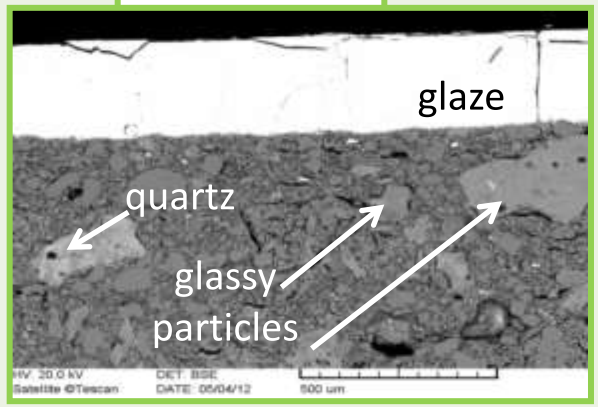
ceramics

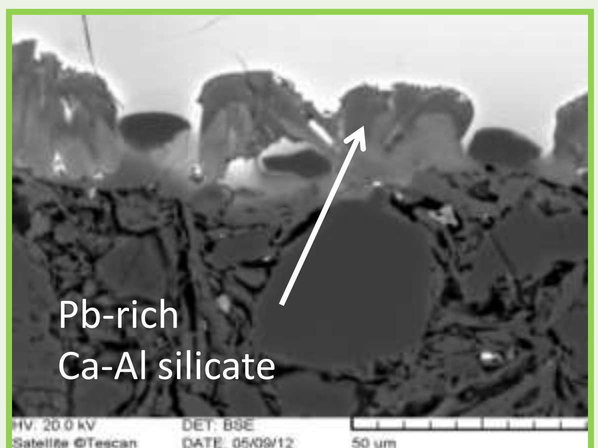
SEM analysis

1. group

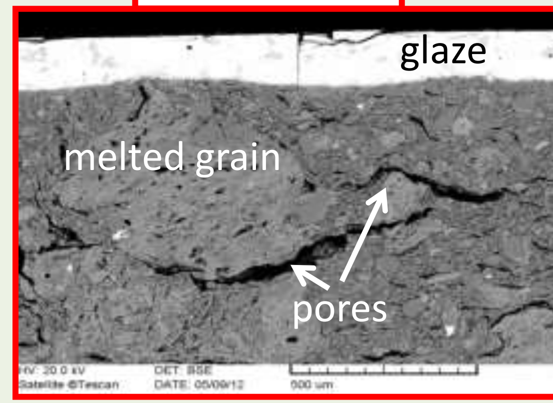


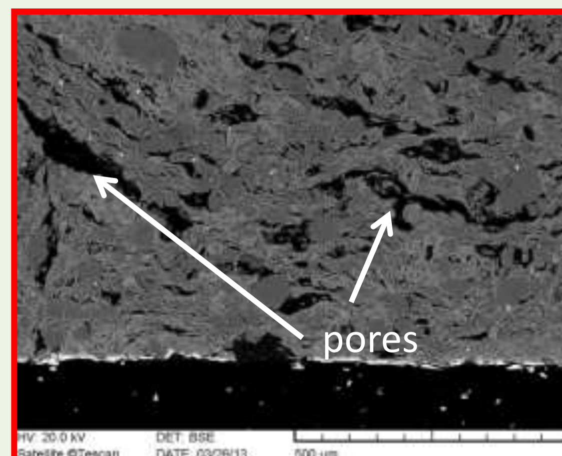
2. group





3. group





Partial Summary
ceramics

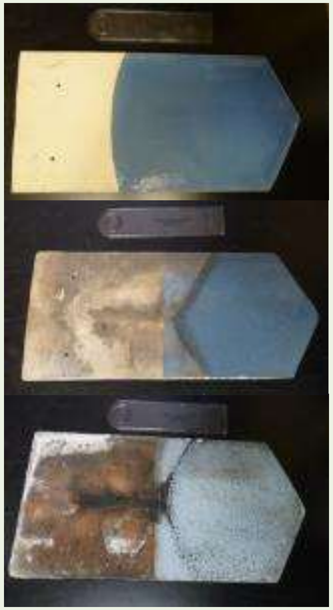
The results of the ceramics confirmed our previous suggestion in connection with ceramic groups

3. group
youngest ceramics
(1990s)

2. group
middle-aged ceramics
(after 1956)

1. group
the oldest ceramics
(1893-1896)

The similarities in building materials (e.g. comparable ceramic materials, age of the ceramics) provide the possibility for us to carry on a comprehensive study about the degradation particularly attention to its different locations (high and low traffic rate) and exposure



3. group
youngest ceramics
(1990s)

2. group
middle-aged ceramics
(1945-1946)

1. group
the oldest ceramics
(1898-1899)

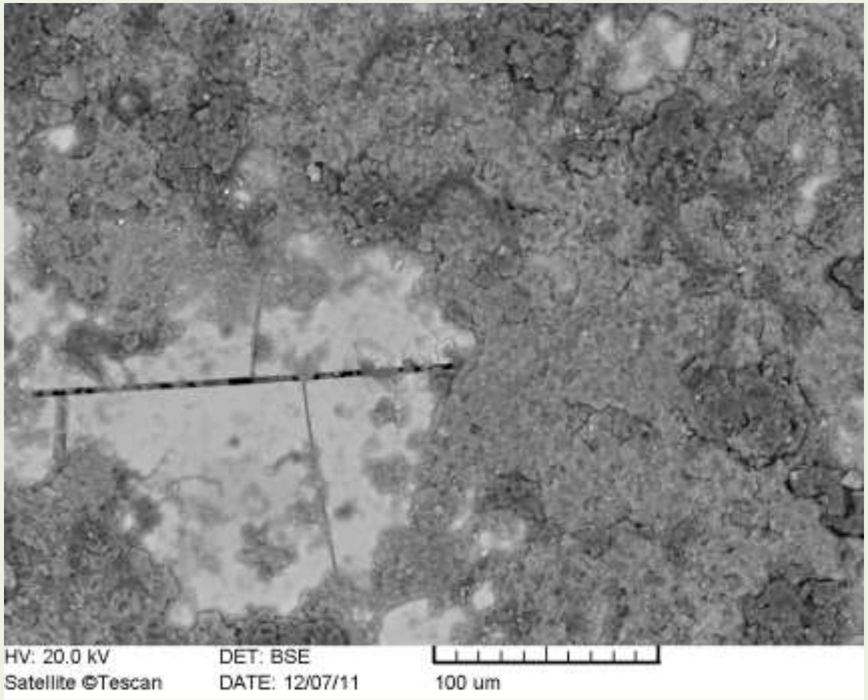
Remark: the third group were not exposured by the environment → We have ignored the further connection with the degradationg phenomenas.

Results - environment

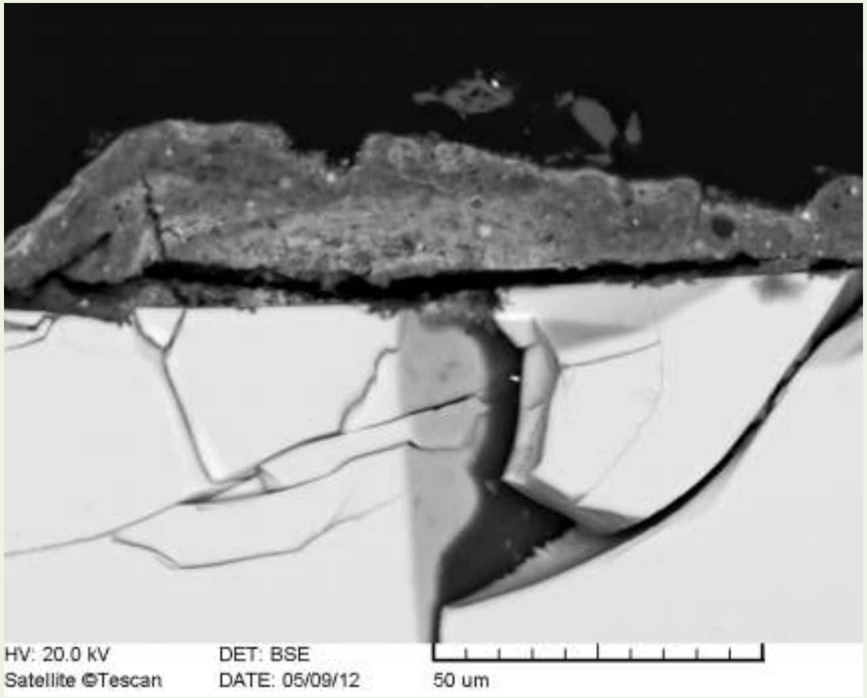
Similarities

SEM analysis

Deposition layer: the thickness of this layer is variable between 10-50 µm. Consist of dust, soot and aerosols in variable quantity.



Paralell to the surface



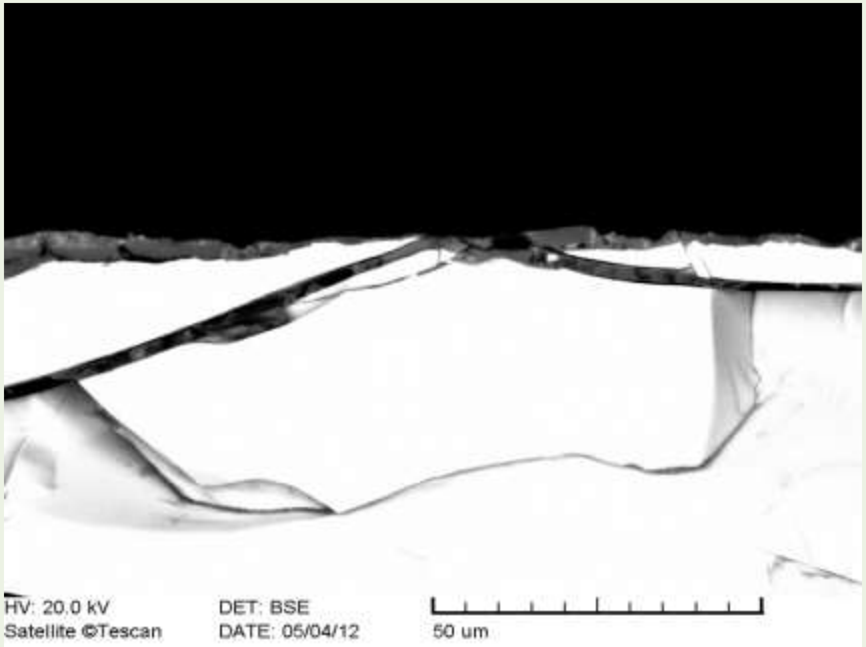
Perpendicular to the surface

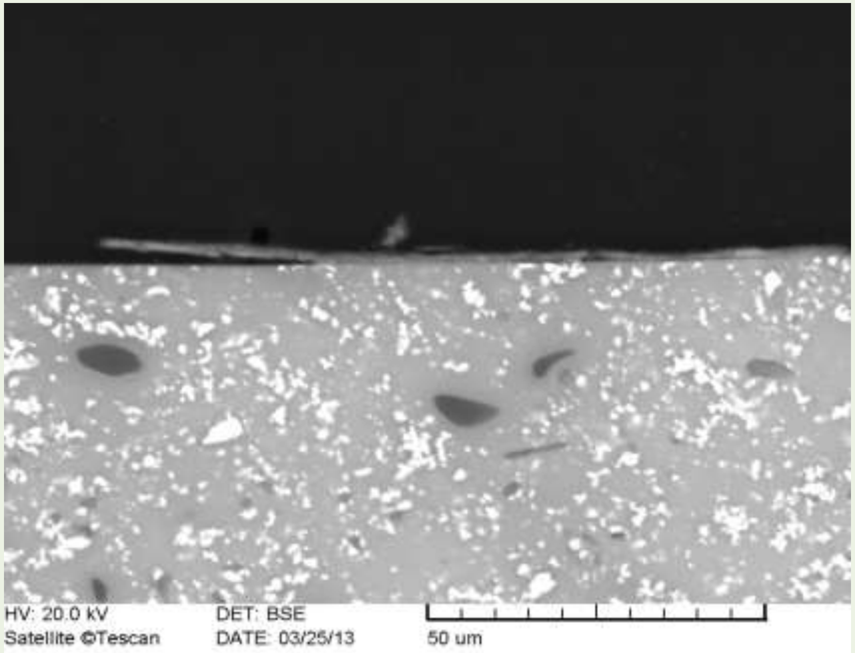
Results - environment

Similarities

SEM analysis

It is also observed that this contamination layer firmly adheres to the surface but some cases cracks and fragments from it and rarely penetrates below the cracked glaze layer.





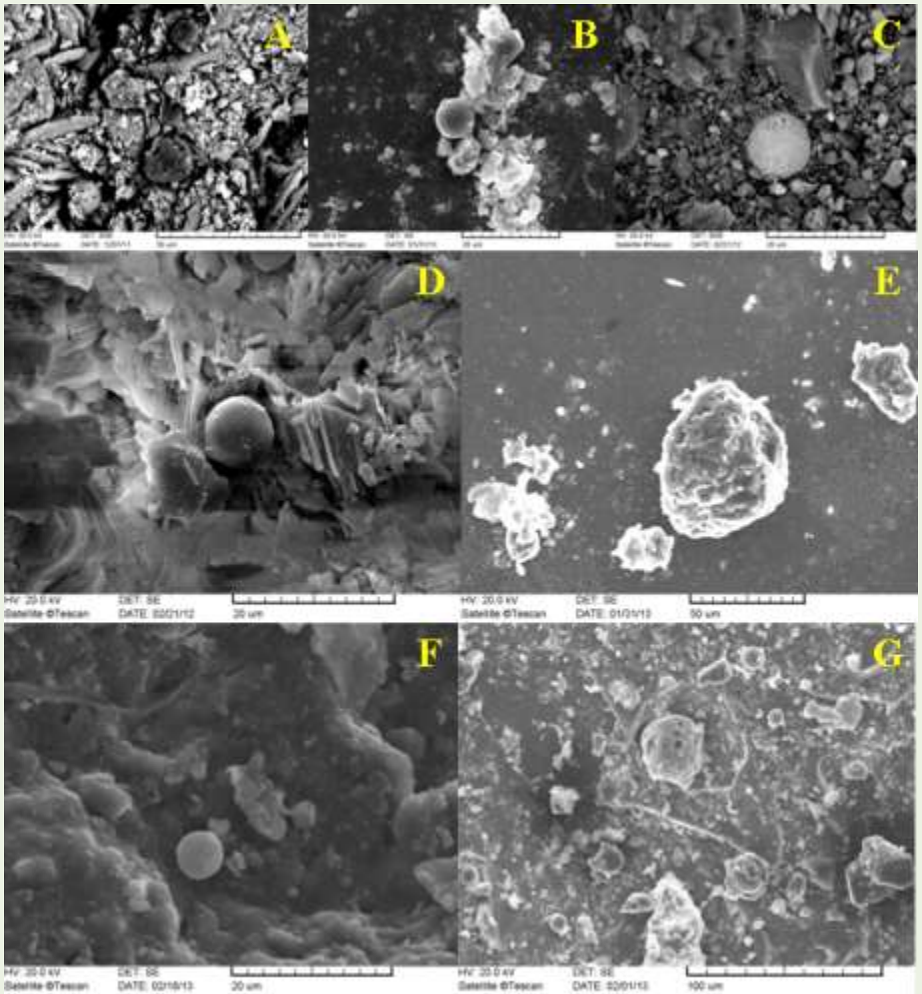
Perpendicular to the surface

Perpendicular to the surface

Results - environment

Similarities

SEM analysis



The observed spherule types on the ceramics:

A) carbonaceous forms

B) rich in Si, Al, K, Ca and smaler amount in Fe and Ti

C) lot of Fe contetn and smaler Si

D) compared to the second type, less in Al, K, Fe (few Pb and Zn) but rich in Ca

smooth alumino-silicate particles

E) lot of Si and Ca content

F) high amount of Si, Al and Fe content

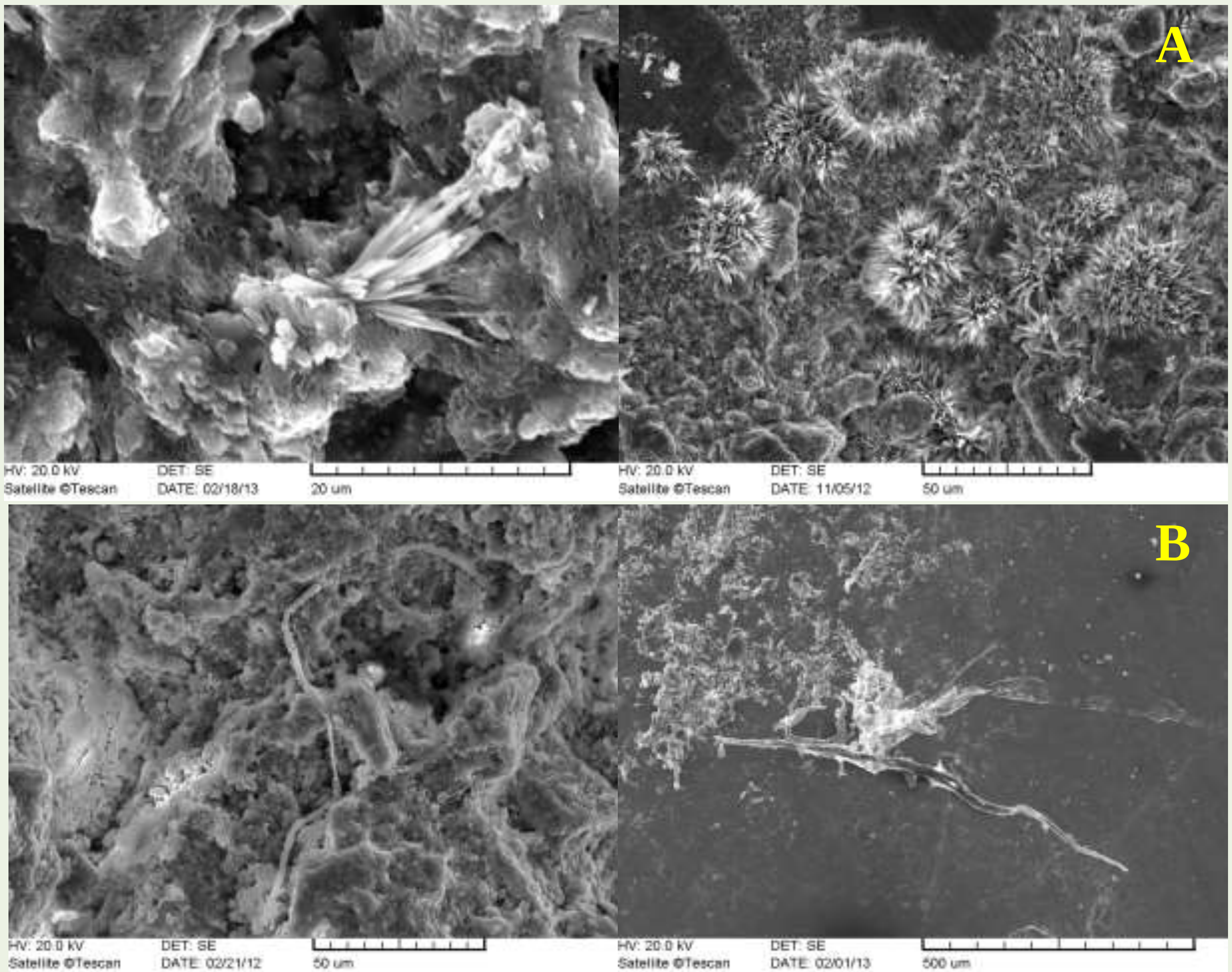
G) S, Si, Ca, Al content

metal particles mainly composed of iron

Results - environment

Similarities

SEM analysis



Salts and living forms appeared on the surface → <u>on both buildings</u>

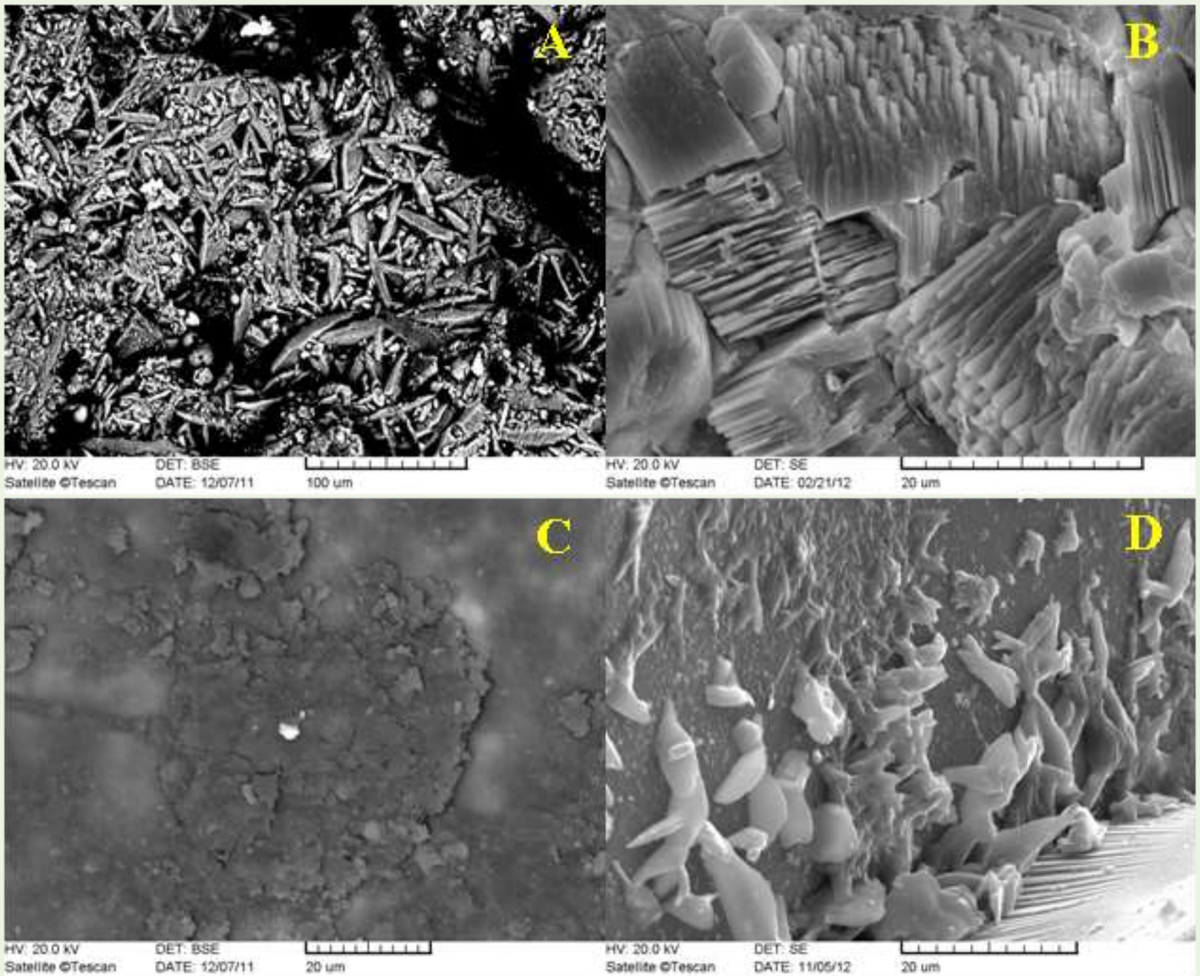
A) Glauberithe ($Na_2Ca(SO_4)_2$)

B) Microbial living forms (mainly hyphaes) often appear on the unglazed, back side of the tiles (on the left) and on the glazed side (on the right)

Results - environment

Differencies

SEM analysis

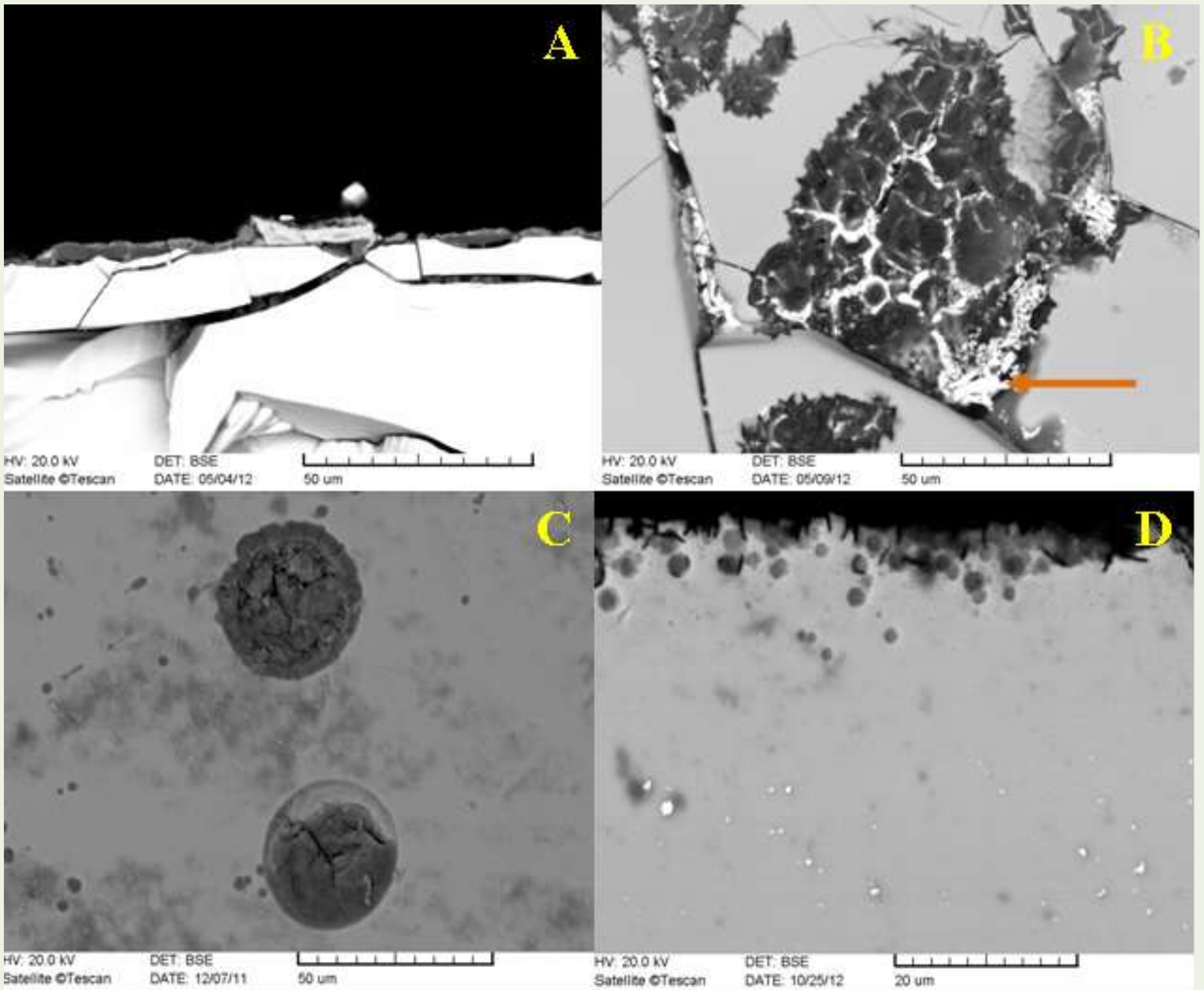


Different gypsum forms → mainly on the Museum of Applied Arts

A) dense, compact gypsum layer on the unglazed, back side of the material
B) laminar morphology on the back side
C) gypsum is covered by the deposition layer
D) gypsum crystals grow in the cracks of the glaze

Results - environment

Differencies



A, D perpendicular and B, C paralell to the surface

Glaze started to weather:

A) cracks and microcracks fragment the glaze and depositions penetrate and fill it

B) the lead - the main component of the glaze - leached out (arrow shows) and accumulate in the cracks and the edge of the glaze and ceramic material

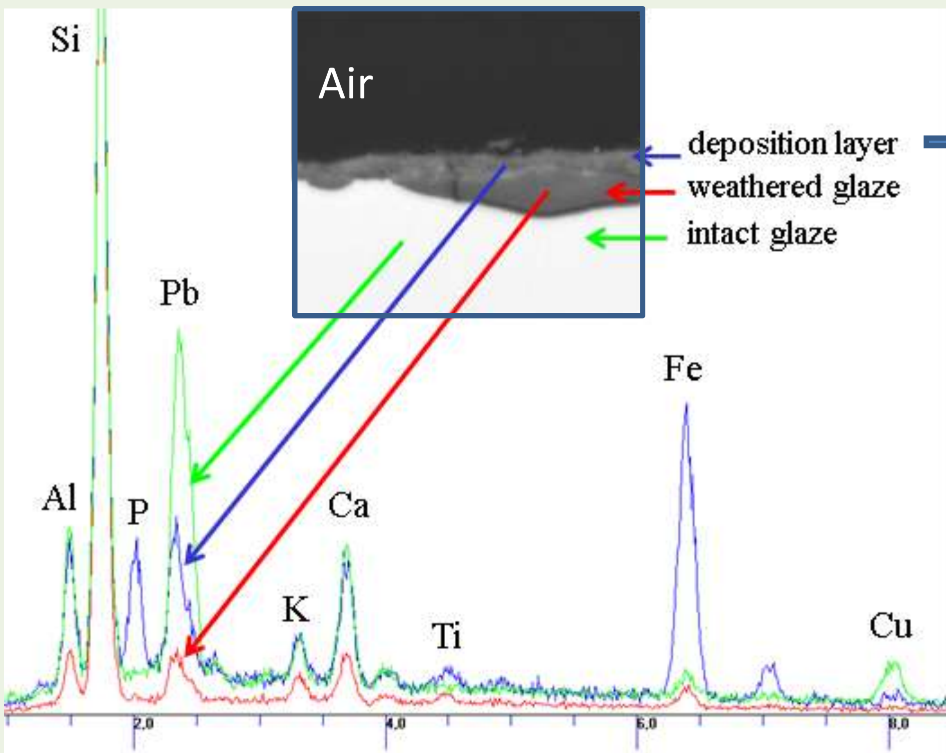
C-D) pitting corrosion (in size about 5-60 μm) appeared in the glaze and tended from the surface to the inner parts

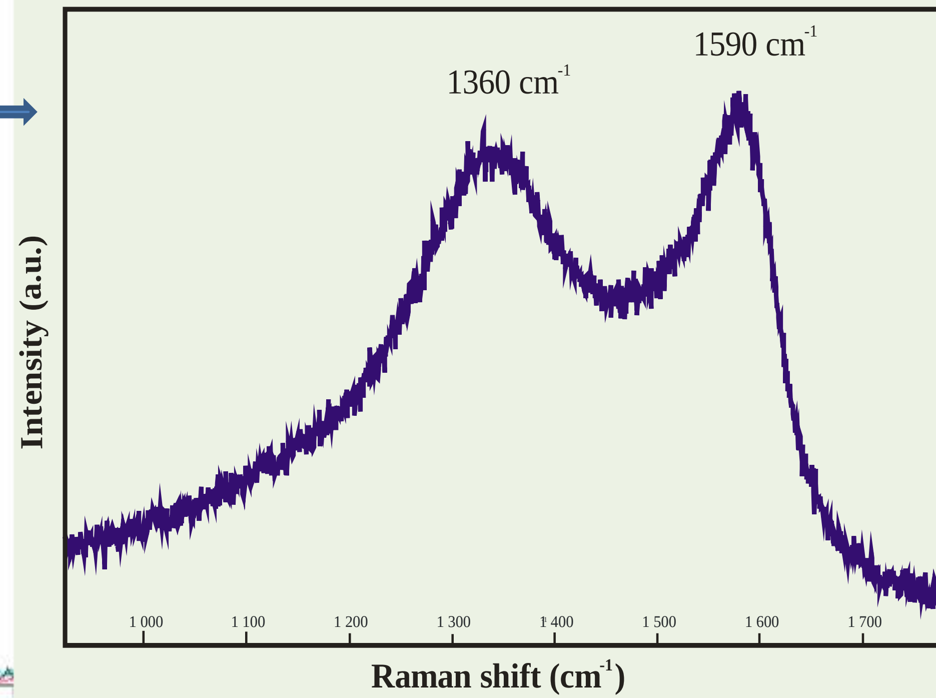
Results - environment

Differencies

The most conspicuous result of the deterioration is the appearance of a very thin (~5µm) **weathered surface** layer of glaze on some <u>tiles from the Museum</u>

Raman spectra with this characteristics can be particularly similar to the **product of gasoline combustion**

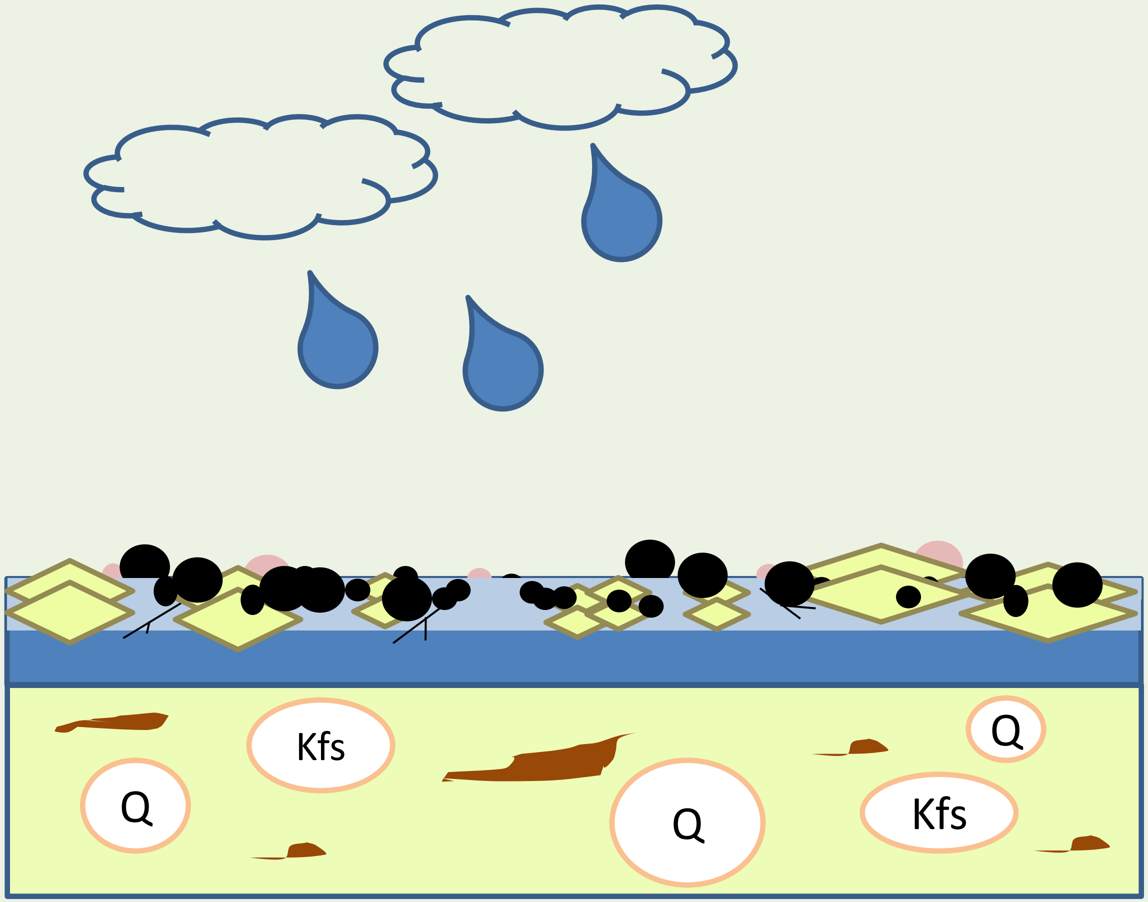




Conclusion of the weathering

sulphatidation process

The principal gaseous pollutants (e.g. SO_2, NO_x, CO_2) and the contacting water easily form different acids



Steps:

1) natural, artificial dust accumulated on the surface

2) precipitation: rain + gaseous pollutants = acidic rain

3) minerals and salts (mainly sulphates) appeared → gypsum, glauberite, thenardite

4) cracking the surface…

5) and leaching from the surface → Na, Ca, Al, Pb

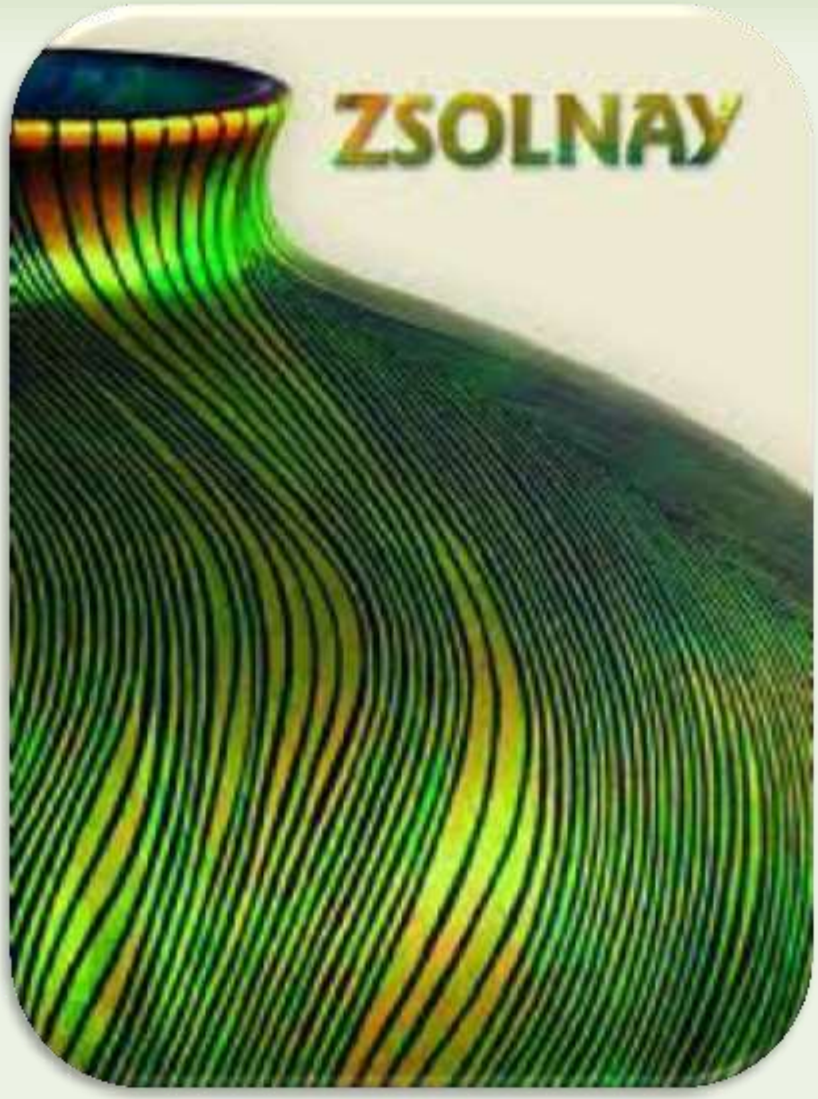
6) continue the process

Summary

- **The purpose**: study the Zsolnay building ceramics and its deterioration mechanisms by environmental factors
- Two buildings were examined; the Museum of Applied Arts and The Hungarian Geological and Geophysical Institute
- Similarities: black deposition layer, spherules (mainly artificial), salts, living forms
- Differencies: **weathering phenomena** in the case of the **Museum of Applied Arts**
  - leached **elements** (Ca, K, Al, Pb, Cu) **migrated** to the upper **deposition/alteration mix layer** which consist of additional particles from the atmosphere which bonded to the surface
  - the weathered layer equal to the **depleted "gel-layer"**
  - **Sulphatidion process**: gypsum appeared (dust or leached Ca-content + acidic rain)
  - **Pb content** from the weathered layer not migrated to the upper deposition layer fully. It was also **appeared in the cracks and microcrackes** →clearly seen at the Pb line of the X-ray spectra
  - **Fe and P** attribute to the **environmental ilnfuences**

Summary: The ceramics of the Museum of Applied Arts are in worse condition, perhaps due to the situation of the building (in the middle of the city).

Thank you for your attention



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Results

glaze

- Yellow and green lead-glaze
- Thickness ~180-300 µm
- Colored by iron (yellow) and copper (green)

- Inclusions:
  - 1. group) many small K-feldspar
  - 2. group) few courser feldspar
  - 3. group) some feldspar and metal-rich (Cr, Fe, Co, Zn) inclusions

- Bright and dark blue lead-glaze
- Thickness ~180-280 µm
- Colored by cobalt

- Inclusions:
  - Contain a lot of small tin-oxide (cassiterite) crystallites