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BLACK CRUST VERSUS SUBSTRATE ON HISTORIC STONE: A BRIEF pXRF STUDY AT GOLIA MONASTERY (IAȘI, ROMANIA)

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Abstract

Black crusts are a recurrent alteration feature on historic masonry, particularly in urban environments affected by traffic emissions and atmospheric pollutants. This study investigates the chemical contrast between a dark black-crust band and the underlying stone substrate on the western enclosure wall of Golia Monastery (Iași, Romania), using portable X-ray fluorescence (pXRF) as a non-invasive analytical tool. Fourteen in-situ measurements were performed on a single buttress to quantify key elements (S, Cl, Ca, Ti, Fe, Cu, Zn) and to derive diagnostic ratios (S/Ca, Cl/Ca, Cu/Ti, Zn/Ti, Fe/Ti) together with median-based enrichment factors. The results show that the wall is built of calcareous sandstone, while the black crust represents a composite deposit formed by gypsum crystallization within a matrix of siliciclastic dust and carbonate particles. Among all indicators, S/Ca exhibits the clearest contrast: the median S/Ca ratio in the crust (~0.054) is approximately twice that of the substrate (~0.025), yielding an enrichment factor EF(S/Ca) ≈ 2.1 and confirming sulfate enrichment and gypsum development on the exposed band. By contrast, Cl/Ca remains low in both zones, and Ti-normalized metal ratios (Cu/Ti, Zn/Ti, Fe/Ti) are strongly constrained by detection limits, preventing robust interpretation in terms of traffic-derived particulates. Small but measurable amounts of P suggest a certain degree of bioreceptivity of the crust surface, although this hypothesis requires microanalytical confirmation. From a Conservation Science perspective, the study demonstrates that pXRF-based ratio analysis can rapidly document sulfate-enriched black crusts on heritage stonework while also highlighting the limitations of trace-metal indicators in small in situ datasets and the need for combined chemical, microstructural, and biological approaches.

Keywords: *Portable X-ray fluorescence (pXRF); Black crust; Sulfation; Enrichment factors; Urban air pollution; Heritage stone decay; Bioreceptivity; Golia Monastery*

Introduction

Black crusts on historic masonry commonly develop in traffic-exposed urban settings through atmospheric deposition, episodic wetting–drying, and secondary sulfate formation on

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carbonate-rich matrices [1-3]. The process is typically driven by interactions between airborne pollutants - especially sulfur oxides and particulates - and calcareous substrates, resulting in gypsum formation and progressive darkening of architectural surfaces. Such alteration crusts are a major conservation concern in polluted cities, where they can obscure original stone finishes, promote granular disintegration, and accelerate decay cycles [1, 4-6]. Frequently, calcareous sandstones and limestones are particularly prone to gypsum enrichment and particulate trapping, which darken surfaces and contribute to salt-cycling decay [1, 7]. The microstructure of these stones, combined with repeated moisture fluctuations, fosters the entrapment of pollutants and crust accretion over time. Several recent studies have demonstrated that black crusts can effectively serve as natural archives of urban air pollution history, recording both lithogenic and anthropogenic elemental signatures [1-3, 8]. Within the broader framework of conservation science, such diagnostic investigations are essential for understanding decay mechanisms and for designing compatible conservation materials and strategies [4-6, 9, 10].

In Romania, the scientific characterization of these alteration phenomena remains relatively limited, despite visible deterioration patterns on historic masonry in major cities such as Iași and Bucharest. Previous work on the stone masonry of Galata Monastery in Iași has already highlighted the complexity of local building stones, construction techniques, and decay features in Moldavian monastic ensembles [11], underscoring the need for site-specific diagnostic studies. The case of the Golia Monastery enclosure wall is particularly significant, as it stands in a dense urban setting with notable traffic emissions and cleaning operations that redistribute fine particulates and chemical residues. A recent investigation in Iași has shown that dust binders and coagulant agents used in street-washing (e.g., aluminum sulfate, sodium aluminate, and magnesium chloride) contributed to the contamination and color alteration of the Golia Precinct Wall [12]; these findings illustrate how "urban exotic pollution" can interact with historic surfaces under current environmental pressures.

Portable X-ray fluorescence (pXRF) has become a key tool in conservation science, allowing rapid, non-invasive in-situ characterization of elemental signals and supporting the separation of pollution-derived enrichments from lithogenic background [1, 6, 8, 13]. In crust-affected masonry, ratios such as S/Ca are commonly used as proxies for sulfation and gypsum development [1, 8, 13], while combinations including Cu/Ti, Zn/Ti, or related metal/Ti ratios have been explored as potential indicators of traffic-related inputs [8, 13]. This brief study documents a black-crust band on the historic western enclosure wall (buttress) of Golia Monastery (Iași, Romania), located ~4.83–4.90m from the roadway axis. A visibly dark black-crusted band at ~1.55–1.60m above ground is compared with a cleaner-looking band representing the natural stone substrate at ~2.10–2.15m on the same buttress, with the aim of (*i*) quantifying sulfation via S/Ca ratios, (*ii*) evaluating potential traffic-related signatures, and (*iii*) relating the chemistry to microclimatic controls beneath the eave, within the broader context of conservation-science approaches to historic masonry [4-6].

Experimental part

Site context and geometry

The investigated area corresponds to the western enclosure wall of Golia Monastery (Iași, Romania), a fortified XVIIth-century monastic ensemble reconstructed under Prince (Voivode) Vasile Lupu between 1650 and 1653 [14, 15]. The complex, originally founded by High Chancellor (Logothete) Ioan Golâi in the late XVIth century, is among the most representative monuments of Moldavian ecclesiastical architecture, distinguished by its tall enclosure walls and corner towers [14-16] (Fig. 1a). The examined buttress is situated along the west perimeter of the precinct, oriented approximately northeast to southwest and running parallel to George Enescu Street, a narrow urban road with significant vehicular circulation. The roadway axis lies roughly 4.83–4.90m from the wall base (Fig. 1b).

Field documentation (photography and observational notes) was obtained during the main investigation campaign in summer 2025 (May–August), under dry weather conditions and natural daylight. A visibly dark black-crusted band at ~1.55–1.60m above ground was compared with a lighter stone substrate band at ~2.10–2.15m on the same buttress, facilitating distinction between crust-affected and less-altered areas (Fig. 1c).

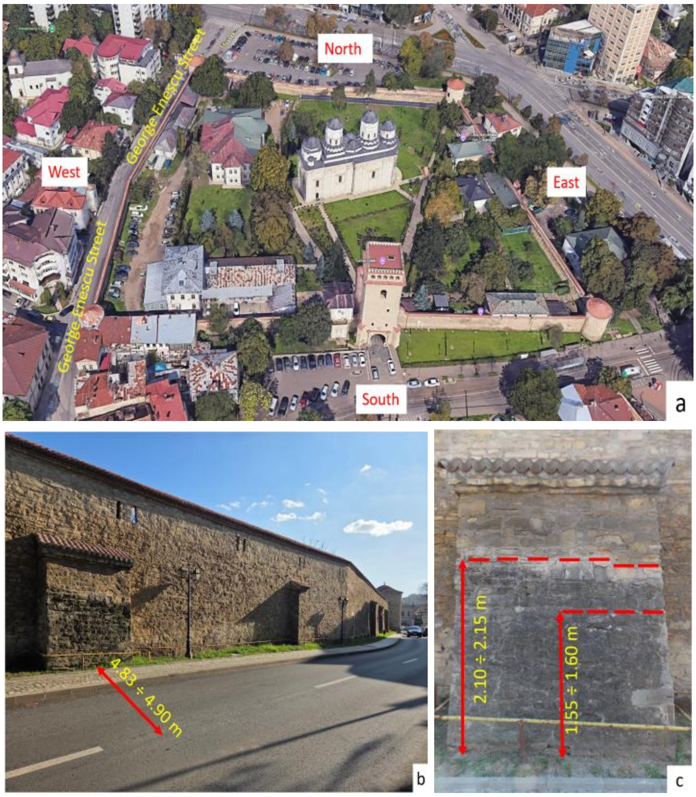

Fig. 1. Site context and geometry of the investigated wall section at Golia Monastery (Iași, Romania): **(a)** aerial view of the Golia Monastery ensemble, showing the orientation of the west wall parallel to George Enescu Street and the relative position of cardinal directions (North–South–East–West) (source: Google Earth); **(b)** street-level view of the western wall and buttresses, with the roadway axis located approximately 4.83–4.90m from the wall base; **(c)** detail of the investigated buttress, showing the black-crust band (~1.55–1.60m) and the substrate reference band (~2.10–2.15m) used for comparative pXRF measurements

Throughout the XXth and early XXIst centuries, the Golia enclosure wall has undergone several major restoration and rehabilitation phases, aimed at consolidating the masonry, renewing mortar joints, and managing moisture ingress along the lower courses. The selected area represents a stable, accessible surface minimally affected by recent interventions, allowing reliable in situ non-invasive pXRF measurements for chemical characterization.

Sampling and measurement design

Two horizontal measurement bands were defined on the same buttress of the western enclosure wall to compare chemically altered and reference stone areas. The black crust band comprised six pXRF measurement spots (IDs 1–6) aligned horizontally at approximately 1.55–1.60m above ground, corresponding to the visibly darkened surface zone described in the previous section (Fig. 2a). The substrate band, representing the cleaner calcareous sandstone beneath the eave, included eight pXRF spots (IDs 7–14) located along a parallel horizontal line at approximately 2.10–2.15m above ground (Fig. 2b). All measurements were performed non-invasively in situ, following gentle surface cleaning with a soft dry brush to remove loose particulates. Each spot was photo-documented both in close-up and within the broader wall context to ensure spatial reference and data traceability.

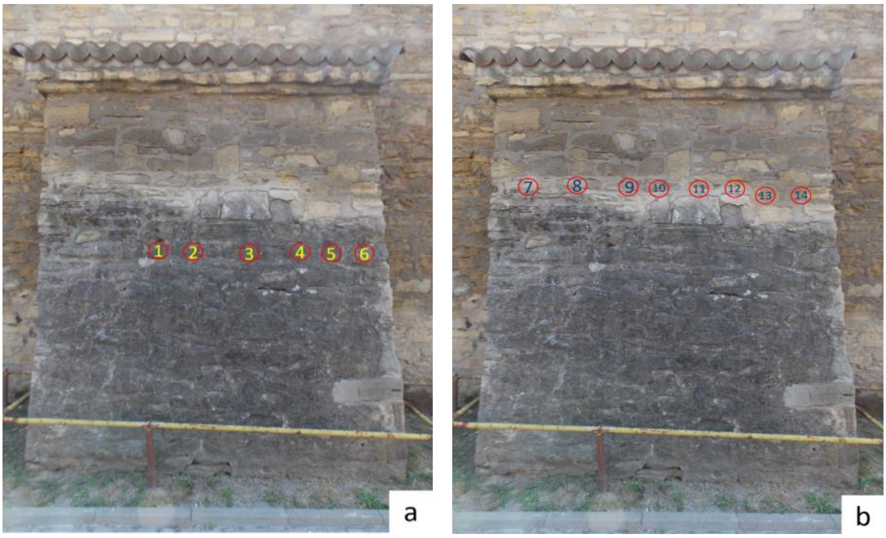

Fig. 2. Sampling design showing the black-crust **(a)** and substrate spots **(b)** measurement bands on the same buttress of the western enclosure wall at Golia Monastery, Iași, Romania

Instrumentation and analytical parameters

Portable X-ray fluorescence (pXRF) measurements were carried out using a Bruker S1 TITAN Model 800 handheld spectrometer, equipped with a 50kV rhodium anode X-ray tube and a silicon drift detector (SDD) with an energy resolution of approximately 145 eV at Mn $K\alpha$. The instrument was operated under the GeoExploration application, with an Oxide 3-phase calibration designed for silicate and carbonate matrices. Each measurement consisted of a three-beam sequence (15, 30, and 50kV), with corresponding tube currents of 8.75, 11.8, and 17µA, and a total live acquisition time of 90s (3×30s per beam). The beam spot was defined by an 8mm collimator, and no external filters were applied ("Blank" mode). All data were automatically normalized and recorded through the *StandardLib.csv* calibration file provided by Bruker.

The detection range covered major and trace elements relevant to crust formation and lithogenic composition, including Mg, Al, Si, P, S, Cl, K, Ca, Ti, Fe, Cu, Zn, Sr, Ba, and Pb. Elemental concentrations were expressed as oxides (wt%) using Bruker's proprietary algorithm. The typical limits of detection (LOD) ranged from ~0.01–0.02 wt%, depending on the element and acquisition conditions. All analyses were performed non-invasively and in situ, in direct contact with the stone surface, without mechanical preparation or coating. Prior to measurement, each spot was gently cleaned with a soft brush to remove loose particulates, ensuring consistent X-ray interaction. Instrument stability and potential calibration drift were verified daily using a certified Bruker reference.

This analytical configuration provides a suitable balance between signal depth (~50–200µm) and surface sensitivity, enabling the detection of potential pollution-derived enrichments (particularly sulfur and, where concentrations exceed detection limits, selected trace metals) relative to the lithogenic background dominated by calcium and titanium. Similar multi-voltage pXRF protocols have been successfully applied in recent heritage studies on historic stone and black crusts [1, 6, 8, 13].

The results of the in-situ pXRF analysis are summarized in Tables 1 and 2. Spots 1–6 correspond to the black-crust band located at approximately 1.55–1.60m above ground, whereas spots 7–14 correspond to the underlying stone substrate measured at approximately 2.10–2.15m on the same buttress of the western enclosure wall. The listed concentrations (expressed as oxides, wt%) represent the major and trace elements most relevant to crust formation and pollution assessment - specifically sulfur (S), chlorine (Cl), calcium (Ca), titanium (Ti), iron (Fe), copper (Cu), and zinc (Zn). These parameters were subsequently used to compute indicator ratios such as S/Ca, Cl/Ca, Cu/Ti, Zn/Ti, and Fe/Ti, as discussed in the next section.

Table 1. Elemental concentrations (wt%) obtained by portable X-ray fluorescence (pXRF) for black-crust and substrate zones on the western enclosure wall, Golia Monastery (Iași, Romania)

Zone	Spot ID	S (%)	Cl (%)	Ca (%)	Ti (%)	Fe (%)	Cu (%)	Zn (%)
Black crust	1	0.79	0.15	12.69	0.12	0.96	0	0.01
	2	0.42	0	8.99	0.11	0.88	0	0.01
	3	0.32	0.02	5.05	0.09	0.75	0	0.01
	4	0.29	0	9.21	0.13	1.1	0	0.01
	5	0.39	0	6.45	0.18	1.53	0.01	0.02
	6	0.29	0	6.21	0.09	0.8	0	0.02
Substrate	7	0.05	0	10.79	0	0.3	0	0
	8	0.06	0	9.95	0	0.33	0	0
	9	0.25	0.16	18.31	0.05	0.78	0	0
	10	3.59	0.07	15.77	0	0.33	0	0
	11	0.37	0	12.32	0	0.19	0	0
	12	2.41	0.03	7.91	0	0.03	0	0
	13	0.87	0.1	6.9	0	0	0	0
	14	0.18	0.31	8.8	0	0.12	0	0

Table 2. Comparative elemental ratios and enrichment indicators (pXRF) between black crust and substrate zones at Golia Monastery

Zone	Spot ID	S/Ca	Cl/Ca	Cu/Ti	Zn/Ti	Fe/Ti
Black crust	1	0.062	0.012	0	0.083	8
	2	0.047	0	0	0.091	8
	3	0.063	0.004	0	0.111	8.333
	4	0.031	0	0	0.077	8.462
	5	0.06	0	0.056	0.111	8.5
	6	0.047	0	0	0.222	8.889
Substrate	7	0.005	0	0	0	0
	8	0.006	0	0	0	0
	9	0.014	0.009	0	0	15.6
	10	0.228	0.004	0	0	0
	11	0.03	0	0	0	0
	12	0.305	0.004	0	0	0
	13	0.126	0.014	0	0	0
	14	0.02	0.035	0	0	0
Black crust (median ratio values for black-crust spots; n = 6)		0.054	0	0	0.101	8.397
Substrate (median ratio values for substrate spots; n = 8)		0.025	0.004	0	0	15.6
Enrichment Factor (EF) (ratio of median crust/substrate values; EF > 1 implies crustal enrichment)		2.123	0	0	0	0.538

Data processing and indicator ratios

Quantitative interpretation of the pXRF results focused on elemental ratios that serve as diagnostic indicators of crust formation and potential pollution-derived enrichment. Data from the fourteen analyzed spots (Table 1) were grouped into two categories: black crust (spots 1–6) and substrate (spots 7–14). For each group, element concentrations (wt%) were exported from the Bruker S1 TITAN analytical suite and processed to derive comparative geochemical ratios. The selected indicators include S/Ca, reflecting sulfate enrichment and gypsum development [1, 2, 13]; Cl/Ca, which accounts for road-salt and aerosol deposition [7, 8]; and transition-metal ratios such as Cu/Ti, Zn/Ti, and Fe/Ti, explored as potential tracers of traffic-related particulates normalized to a lithogenic reference [1, 3, 7, 13]. Calculations were performed on a weight-percentage basis, as differences in atomic mass between the compared elements are within the typical analytical precision of the instrument. To reduce the influence of local variability, median values and interquartile ranges (IQR) were calculated for each ratio [13]. These non-parametric statistics were chosen due to the limited number of in-situ measurements and the inherently skewed distribution of field XRF data (Fig. 3). Graphical summaries (boxplots) were used to visualize dispersion and to compare the two groups.

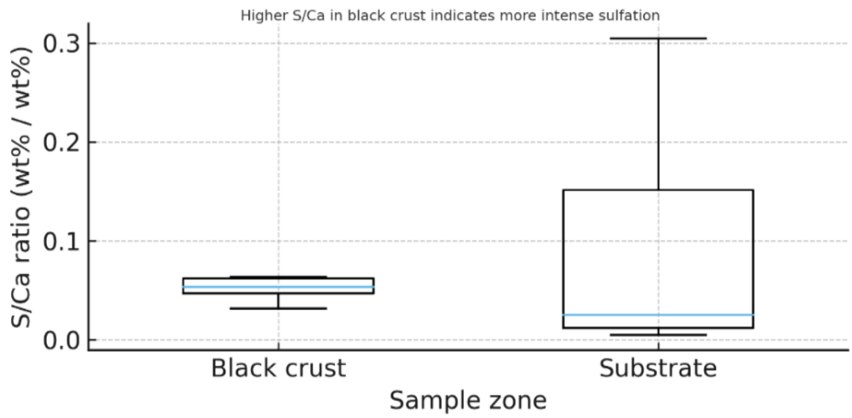

Fig. 3. Boxplot of S/Ca ratios for black-crust (n = 6) and substrate (n = 8) spots on the western enclosure walls buttress of Golia Monastery (Iași, Romania)

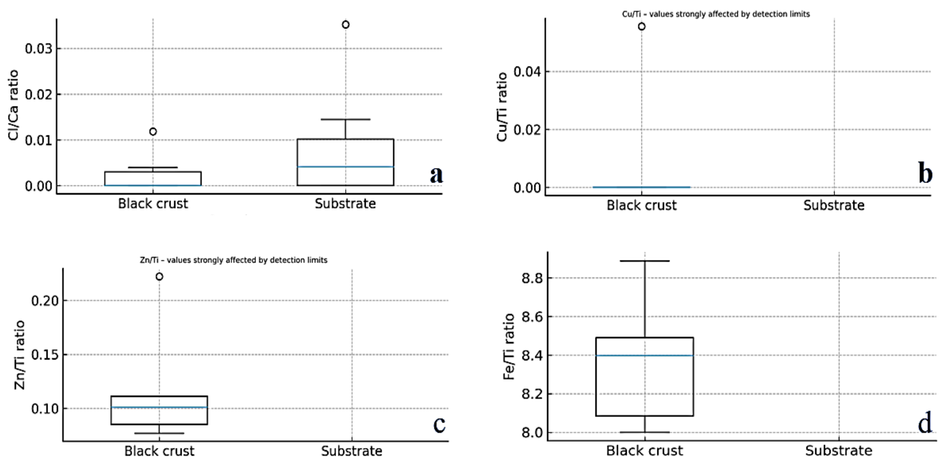

Fig. 4. Boxplots of Cl/Ca (**a**), Cu/Ti (**b**), Zn/Ti (**c**) and Fe/Ti (**d**) ratios for black-crust (n = 6) and substrate (n = 8) spots on the western enclosure wall buttress of Golia Monastery (Iași, Romania)

The black crust shows higher median S/Ca values (EF ≈ 2.1) and a narrow interquartile range, consistent with more intense and relatively uniform sulfation on the crust-affected band, whereas the substrate displays lower median S/Ca but larger variability due to a few sulfate-rich spots.

Cl/Ca values are low in both zones and show slightly higher medians in the substrate, indicating the absence of a persistent chloride enrichment in the black crust. Ti-normalized metal ratios (Cu/Ti, Zn/Ti, Fe/Ti) are strongly constrained by detection limits (Cu, Zn, and Ti at or below LOD in many measurements); their boxplots therefore mainly reflect data scatter and isolated outliers rather than robust traffic-related signatures in this preliminary dataset.

Each individual measurement was cross-referenced with its field photo and coordinate label to ensure traceability between analytical data and visible alteration patterns on the wall surface. Subsequent interpretation of these ratios provided the basis for evaluating sulfation intensity and particulate deposition along the sampled transect, while only allowing a preliminary assessment of possible traffic-related contamination, given the detection-limit constraints on some trace metals.

Titanium (Ti) was selected as a lithogenic reference element, following established environmental-geochemistry and heritage-science approaches [7, 8, 13]. Titanium is expected to originate predominantly from the mineral matrix of the sandstone and to be largely unaffected by anthropogenic inputs or short-term atmospheric deposition. Because of its chemical stability and low mobility under surface weathering, Ti can, in principle, provide a baseline against which enrichment of other elements (such as S, Cl, Cu, Zn, and Fe) may be assessed. In the present dataset, however, Ti concentrations are at or below the detection limit in most substrate spots, so Ti-normalized ratios (especially for Cu and Zn) are only weakly constrained and must be interpreted with caution. Accordingly, ratios such as Cu/Ti, Zn/Ti, and Fe/Ti were computed and reported, but their diagnostic value for traffic-derived particulates is limited in this preliminary study. To quantify the magnitude of crustal enrichment relative to the substrate, enrichment factors (EF) were calculated for the ratio indicators as the quotient between the median value in the black crust and the corresponding median in the substrate:

$$EF_{\text{ratio}} = \frac{\text{median (crust)}}{\text{median (substrate)}} \tag{1}$$

This median-based definition follows the enrichment factor approach commonly used in environmental geochemistry and in previous studies on polluted building surfaces, where EF > 1 indicates relative enrichment in the altered layer, EF ≈ 1 a dominantly lithogenic composition, and EF < 1 a relative depletion in the crust compared with the substrate [7, 8, 13].

In practice, this approach could be robustly applied only to S/Ca and, with reservations, to Fe/Ti, because Cu/Ti and Zn/Ti medians collapse to ~0 due to values at or below the detection limit in both zones. For S/Ca, EF ≈ 2.1 clearly indicates sulfate enrichment in the black crust, whereas Cl/Ca yields EF ≈ 0, suggesting no net chloride enrichment. For Fe/Ti, EF < 1 reflects a higher median ratio in the substrate, but this result is strongly influenced by a single substrate spot with Ti above the detection limit. Overall, the EF framework - initially developed in environmental geochemistry and subsequently adapted to heritage materials [7, 8, 13] - is here used primarily to highlight the robust crustal enrichment in sulfur, while underscoring the limited diagnostic power of Ti-normalized metal ratios in this small pXRF dataset.

Results and discussion

Elemental patterns

The pXRF results highlight clear but nuanced differences in the surface chemistry between the black-crust band and the underlying stone substrate of the western enclosure wall at Golia Monastery. As shown in Table 1, calcium (Ca) is the dominant element across all analyzed spots, confirming the calcareous nature of the sandstone blocks. Titanium (Ti) and iron (Fe) occur at low levels, reflecting the lithogenic background of the stone; however, Ti frequently lies at or near the detection limit in the substrate, which constrains the robustness of Ti-normalized ratios [8, 13].

Sulfur (S) displays higher concentrations in the black-crust spots (1–6) than in most substrate spots (7–14), although a few substrate measurements also show elevated S contents. This pattern is characteristic of sulfation processes, whereby sulfur from atmospheric pollutants (SO_2 and sulfates) reacts with calcium carbonate in the stone to form gypsum ($CaSO_4 \cdot 2H_2O$) [1, 2, 13]. The consistently higher S/Ca ratios in the black crust (Table 2; Fig. 3) support the interpretation of secondary sulfate formation on the exposed band, in line with prolonged atmospheric exposure and wetting–drying cycles beneath the eave [1, 3].

Chlorine (Cl) is present only in minor amounts and does not show a systematic enrichment in the black crust. Slightly higher Cl values in some substrate spots may reflect episodic deposition of road salts or aerosol particles transported from nearby traffic and urban activities [7], but the overall Cl signal remains weak. Trace metals such as copper (Cu) and zinc (Zn) are generally at or below the detection limit in both zones, with only isolated measurable values in the crust. This suggests that metallic particulate inputs are limited in the investigated micro-context or lie near the sensitivity threshold of the chosen pXRF configuration.

Iron (Fe) shows moderate concentrations in both crust and substrate, consistent with a mixed origin: partly lithogenic, linked to the original stone matrix, and partly associated with settled dust and minor metallic particulates [1, 13]. Overall, the black crust exhibits a chemical signature dominated by Ca and S, with only minor and poorly resolved contributions from Cl, Cu, and Zn. The underlying substrate retains a composition typical of minimally altered calcareous sandstone, with lower median S/Ca and trace-metal ratios. These differences provide the basis for the ratio indicators (S/Ca, Cl/Ca, Cu/Ti, Zn/Ti, and Fe/Ti) and enrichment factors discussed below.

In a complementary way, major-element data (Si, Al, Mg, K, and Ca) indicate that the black crust is not a pure gypsum veneer but a composite deposit formed by gypsum crystallization within a matrix of siliciclastic dust and carbonate particles. The underlying stone shows a similar Ca-Si-Al-Mg-K framework, consistent with a calcareous sandstone, whereas the crust exhibits proportionally higher S/Ca superimposed on this lithogenic background. This composite character, combining sulfate salts with trapped mineral dust and minor organic or biogenic inputs, is typical of urban black crusts on calcareous stones and helps explain their dark color and mechanical coherence [1, 3, 7, 13].

In addition to these elements, small but measurable amounts of phosphorus (P) were detected in both the black crust and the substrate. P concentrations tend to be slightly higher in several crust spots than in the underlying stone, although the absolute values remain low. Such a pattern may reflect the contribution of phosphate-rich materials—such as bird droppings, organic biofilms, or other lithobiontic communities—superposed on the gypsum-dust assemblage. While the present pXRF dataset does not allow a detailed biological attribution, the occurrence of P in the black crust suggests a certain degree of bioreceptivity of the buttress surface, which could favor the colonization and persistence of microorganisms that, in turn, influence the formation and stability of the alteration layer [17].

Rare earth elements (e.g., Ce, La) were detected only at trace levels near the detection limit, precluding any robust interpretation in terms of fuel-borne catalysts or specific industrial inputs. Although Ce-bearing additives are known to occur in some diesel fuels and can be traced in particulate emissions [18], the very low and scattered signals observed at Golia do not allow a meaningful source attribution in this preliminary dataset.

Ratio indicators and enrichment

The elemental ratios derived from the pXRF dataset (Table 2) provide a clearer view of the processes governing surface alteration at the Golia Monastery wall. Among all parameters, the S/Ca ratio shows the most robust contrast between the black crust and the underlying substrate. The median S/Ca value in the crust (~0.054) is approximately twice that of the substrate (~0.025), indicating enhanced sulfation and gypsum development along the crust-affected band [1, 2]. This trend is clearly illustrated by the S/Ca boxplot (Fig. 3), where the black-crust distribution is shifted towards higher values, while the substrate shows lower medians but a broader spread due to a few sulfate-rich spots. These observations are consistent with field evidence of darkened, compact deposits on the lower buttress courses and support the interpretation of sulfate enrichment driven by atmospheric exposure [3, 8].

The Cl/Ca ratio remains low in both zones and shows slightly higher median values in the substrate than in the crust (Table 2; Fig. 4a). This behavior suggests the absence of a persistent chloride enrichment in the black crust and points instead to weak and possibly episodic inputs of road-salt or marine-type aerosols on the wall surface [7, 8]. In other words, Cl does not emerge as a dominant driver of black-crust development in this micro-context.

Ti-normalized metal ratios (Cu/Ti, Zn/Ti, Fe/Ti) were also explored as potential indicators of traffic-related particulates (Figs. 4b–d). However, their diagnostic value is strongly constrained by detection-limit issues: Cu and Zn are at or below the LOD in most spots, and Ti is frequently below the LOD in the substrate. As a result, median Cu/Ti and Zn/Ti values collapse to ~0 for both crust and substrate, and the corresponding boxplots mainly illustrate data scatter and isolated outliers rather than systematic crustal enrichment. The Fe/Ti ratio yields a higher median in the substrate than in the crust, but this outcome is controlled by a single substrate measurement in which Ti is quantifiable; thus, EF(Fe/Ti) must be interpreted with caution and cannot be taken as strong evidence for Fe depletion in the crust.

To summarize these contrasts quantitatively, enrichment factors (EF) were calculated as the ratio between median values in the black crust and in the substrate for each indicator (Table 3). A detailed interpretation of each ratio and its environmental meaning is provided in Appendix A.

For S/Ca, EF $\approx$ 2.1 clearly indicates significant sulfate enrichment in the black crust relative to the stone beneath, in agreement with the gypsum-forming mechanism inferred from the literature [1–3, 7, 8]. In contrast, EF for Cl/Ca is close to zero, underscoring the absence of a chloride-dominated signal. EF values for Cu/Ti and Zn/Ti are not reported, because the corresponding medians are effectively zero owing to the predominance of <LOD values in both zones. For Fe/Ti, EF < 1 reflects the higher median ratio in the substrate, but, given the scarcity of reliable Ti data, this result is considered non-diagnostic.

Table 3. Summary of diagnostic ratio indicators and enrichment trends (buttress of western enclosure wall from Golia Monastery, Iași, Romania)

Indicator	Diagnostic meaning	Trend (Crust vs. Substrate)
S/Ca	Sulfation and gypsum formation	Strongly ↑ (crust enriched; EF(S/Ca) ≈ 2.1)
Cl/Ca	Road salt/aerosol input	No enrichment in crust (EF(Cl/Ca) ≈ 0; slightly higher Cl/Ca in substrate)
Cu/Ti	Brake wear particles	Not diagnostic in this dataset (Cu near/below LOD in both zones; Cu/Ti medians ≈ 0)
Zn/Ti	Tire abrasion / non-exhaust traffic	Inconclusive (Zn near LOD and Ti < LOD in substrate; Zn/Ti only weakly defined for crust)
Fe/Ti	Dust and mixed sources	Lower Fe/Ti in crust (EF(Fe/Ti) ≈ 0.54; substrate ratio controlled by a single Ti-detected spot)
EF (S, Cu, Zn, Fe)	Anthropogenic enrichment	Only sulfur shows EF > 1; Cu and Zn below LOD, Fe not enriched in crust

Legend/notes:
↑ = higher median value in the black crust relative to the substrate (crustal enrichment);
↓ = lower median value in the black crust relative to the substrate (relative depletion);
≈ = similar median values in both zones (no clear contrast).
EF = enrichment factor calculated as the ratio between the median value in the black crust and the corresponding median in the substrate for a given indicator (e.g., EF(S/Ca) ≈ 2.1). In this dataset, EF is robustly defined only for S/Ca (and, with reservations, for Fe/Ti); it is not reported for Cu/Ti and Zn/Ti because median ratios collapse to ~0 due to detection-limit constraints.

Overall, the ratio indicators and EF values highlight sulfur - as expressed through S/Ca - as the primary and most robust chemical proxy for atmospheric alteration of the Golia buttress, whereas Cl/Ca and the Ti-normalized metal ratios (Cu/Ti, Zn/Ti, Fe/Ti) remain of limited diagnostic value in this preliminary pXRF dataset.

For a concise explanation of the environmental and mineralogical significance of each ratio indicator and its qualitative trend (↑, ↓, ≈), see Appendix A.

Conclusion

This brief pXRF study on the western enclosure wall buttress of Golia Monastery (Iași, Romania) provides a first quantitative glimpse into the chemical contrast between a dark black-crust band and the underlying calcareous sandstone substrate. The elemental patterns confirm that the wall stone is dominated by Ca, with a siliciclastic contribution (Si, Al, Mg, K), while the black crust represents a composite alteration layer formed by sulfate salts, trapped mineral dust, and minor biogenic inputs, rather than a pure gypsum veneer.

Among all investigated indicators, the S/Ca ratio emerges as the most robust proxy for surface alteration at Golia. Median S/Ca in the black crust (~0.054) is approximately twice that of the substrate (~0.025), yielding an enrichment factor EF(S/Ca) ≈ 2.1 and clearly indicating enhanced sulfation along the crust-affected band. This result is consistent with gypsum formation driven by atmospheric sulfur, in agreement with previous work on urban black crusts on calcareous stones [1–3, 7, 13]. In contrast, Cl/Ca remains low in both zones and shows slightly higher median values in the substrate, suggesting that chloride does not play a dominant role in crust formation at this site and likely reflects only weak, episodic road-salt or aerosol inputs [7, 8].

Ti-normalized metal ratios (Cu/Ti, Zn/Ti, Fe/Ti) were explored as potential tracers of traffic-related particulates, but their diagnostic value is strongly limited by detection thresholds:

Cu and Zn are at or below the LOD in most spots, and Ti is frequently below the LOD in the substrate. As a consequence, Cu/Ti and Zn/Ti medians collapse to ~0 for both crust and substrate, and no meaningful enrichment factors can be derived. Fe/Ti displays a somewhat higher median in the substrate, but this pattern is controlled by a single Ti-quantifiable spot and is therefore not considered diagnostic. Overall, the present dataset points to sulfur - rather than heavy metals or chloride - as the clearest anthropogenic signal preserved in the black crust, superposed on a largely lithogenic Ca–Si–Al–Mg–K framework.

Small but measurable amounts of phosphorus (P) were detected in both crust and substrate, with slightly higher values in several crust spots. Although the absolute P contents remain low, this pattern may reflect the contribution of phosphate-rich materials, such as bird droppings or organic biofilms, superposed on the gypsum-dust assemblage. While the pXRF data alone cannot resolve the specific biological agents involved, the occurrence of P in the crust suggests a certain degree of bioreceptivity of the buttress surface, favoring the colonization and persistence of lithobiontic communities that may influence the formation and long-term stability of the alteration layer. Confirming this hypothesis will require complementary microanalytical and microbiological investigations (e.g., SEM–EDS, FTIR, biofilm characterization).

Methodologically, this case study illustrates both the strengths and the limitations of portable XRF in heritage contexts. On the one hand, pXRF provides rapid, non-invasive access to key chemical contrasts (e.g., S/Ca) and allows a minimal-impact comparison between crust and substrate on a single architectural element. On the other hand, the restricted number of spots and the frequent occurrence of values near the detection limit underline the need for cautious interpretation of trace-metal ratios and enrichment factors, especially when using Ti as a lithogenic reference. Future work should therefore extend the number of pXRF transects, combine in-situ measurements with laboratory micro-analyses, and integrate additional indicators (e.g., colorimetry, moisture dynamics) within a broader conservation-science framework [4-6, 10].

Beyond its strictly local scope, the Golia buttress study also contributes to the growing body of diagnostic investigations that support evidence-based conservation strategies for historic masonry [4, 6, 10]. Such targeted case studies can be further evaluated through artefactometrical and altmetric approaches, which quantify the scientific and societal impact of research on cultural heritage objects [19]. In this sense, the present work not only documents a specific example of sulfate-enriched black crust in an urban Romanian context but also provides a methodological template that can be replicated, compared, and assessed across different monuments and research networks, helping to connect local conservation practice with the wider international discourse in heritage science.

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References

[1] J.S. Pozo-Antonio, C. Cardell, V. Comite, P. Fermo, *Characterization of black crusts developed on historic stones with diverse mineralogy under different air quality*

environments, **Environmental Science and Pollution Research**, **29**(20), 2022, pp. 29438-29454. https://link.springer.com/article/10.1007/s11356-021-15514-w.

[2] F. Wang, Y. Fu, D. Li, Y. Huang, S. Wei, *Study on the mechanism of the black crust formation on the ancient marble sculptures and the effect of pollution in Beijing area*, **Heliyon**, **8**(9), 2022, Article Number: e10442. https://www.cell.com/heliyon/fulltext/S2405-8440(22)01730-3.

[3] M. Marszalek, K. Dudek, A. Gawel, *Black crust from historic buildings as a natural indicator of air pollution: a case study of the Lipowiec Castle, Babice, Southern Poland*, **Sustainability**, **16**(9), 2024, Article Number: 3816. https://www.mdpi.com/2071-1050/16/9/3816.

[4] I. Sandu, *Modern Aspects Regarding the Conservation of Cultural Heritage Artifacts*, **International Journal of Conservation Science**, **13**(4), 2022, pp. 1187-1208.

[5] I. Sandu, I.C.A. Sandu, *New Interdisciplinary Aspects on Science for Conservation of Cultural Heritage (II)*, **Egyptian Journal of Archaeological and Restoration Studies**, **3**(2), 2013, pp. 73-83. DOI: 10.21608/EJARS.2013.7277.

[6] I.C.A. Sandu, P. Spiridon, I. Sandu, *Current Studies and Approaches in the Field of Cultural Heritage Conservation Science. Harmonizing the Terminology in an Interdisciplinary Context*, **International Journal of Conservation Science**, **7**(3), 2016, pp. 591-606.

[7] L. Bityukova, *Air pollution effect on the decay of carbonate building stones in old town of Tallinn*, **Water, Air, and Soil Pollution**, **172**, 2006**,** pp. 239-271. https://link.springer.com/article/10.1007/s11270-006-9078-1.

[8] N. Prieto-Taboada, I. Ibarrondo, O. Gomez-Laserna, I. Martinez-Arkarazo, M.A. Olazabal, J.M. Madariaga, *Buildings as repositories of hazardous pollutants of anthropogenic origin*, **Journal of Hazardous Materials**, **248-249**, 2013, pp. 451-460. https://www.sciencedirect.com/science/article/pii/S0304389413000137.

[9] I. Sandu, *New Materials and Advanced Procedures of Conservation Ancient Artifacts*, **Applied Sciences-Basel**, **13**(14), 2023, Article Number: 8387. https://doi.org/10.3390/app13148387.

[10] I. Sandu, G. Deak, Y. Ding, Y. Ivashko, A.V. Sandu, A. Moncea, I.G. Sandu, *Materials for Finishing of Ancient Monuments and Process of Obtaining and Applying*, **International Journal of Conservation Science**, **12**(4), 2021, pp. 1249-1258.

[11] B. Ratoi, V. Pelin, I. Sandu, M. Branzila, I. G. Sandu, *Hidden Message in Stone Masonry of Galata Monastery - Iasi City, Romania*, **International Journal of Conservation Science**, **9**(1), 2018, pp. 151-164,

[12] C. Postolachi, A. Cocean, S. Garofalide, B.S. Munteanu, G. Cocean, N. Cimpoesu, V. Pelin, I. Cocean, S. Gurlui, *Urban Exotic Pollution: The Harmful Environmental Footprint for Health and Historical Architecture*, **International Journal of Environmental Research and Public Health**, **20**(6), 2023, Article Number: 4715. https://www.mdpi.com/1660-4601/20/6/4715.

[13] S.A. Ruffolo, V. Comite, M.F. La Russa, C.M. Belfiore, D. Barca, A. Bonazza, G.M. Crisci, A. Pezzino, C. Sabbioni, *An analysis of the black crusts from the Seville Cathedral: A challenge to deepen the understanding of the relationships among microstructure, microchemical features and pollution sources*, **Science of the Total Environment**, **502**, 2015, pp. 157-166. https://www.sciencedirect.com/science/article/abs/pii/S0048969714013333.

[14] * * *, **Golia Monastery – European Heritage Awards** / Europa Nostra Winners.

European Heritage Awards, 2012, https://www.europeanheritageawards.eu/winners/golia-monastery/

[15] * * *, **Golia Monastery – Iași**, Travel Cultural Heritage Guide, Iași Travel, 2023, https://iasi.travel/en/stories/golia-monastery/.

[16] * * *, **Directorate for Culture**, Iași County, Historical Monuments: Golia Monastery Ensemble, 2023, https://djc.monumenteiasi.ro/monument_de_arhitectura.php?id=360.

[17] T.C. Dakal, S.S. Cameotra, *Microbially induced deterioration of architectural heritages: routes and mechanisms involved*, **Environmental Sciences Europe**, **24**, 2012, Article Number: 36. https://doi.org/10.1186/2190-4715-24-36.

[18] F.R. Cassee, E.C. van Balen, C. Singh, D. Green, H. Muijser, J. Weinstein, K. Dreher, *Exposure, Health and Ecological Effects Review of Engineered Nanoscale Cerium and Cerium Oxide Associated with its Use as a Fuel Additive*, **Critical Reviews in Toxicology**, **41**(3), 2011, pp. 213-229. https://doi.org/10.3109/10408444.2010.529105.

[19] I. Sandu, E. Lupascu, I.C.A. Sandu, Y. Ivashko, *Artefactometrical Assessment of Works of Art by Summing the Impact Grids of Altmetric Quantification*, **Egyptian Journal of Archaeological and Restoration Studies**, **13**(2), 2023, pp. 185-195. DOI: 10.21608/ejars.2023.330901.

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Appendix A – Interpretation of column "Trend (Crust vs. Substrate)" in Table 3

- **S/Ca – strongly ↑ (major enrichment)**
  Higher S/Ca ratios in the black crust reflect active sulfation processes. Atmospheric sulfur (SO_2, sulfates) reacts with calcium carbonate in the stone, forming gypsum ($CaSO_4 \cdot 2H_2O$). In this dataset, the median S/Ca ratio in the crust (~0.054) is about twice that of the substrate (~0.025), and EF(S/Ca) ≈ 2.1, confirming secondary sulfate accumulation on the exposed surface [1,2,8,13].
- **Cl/Ca – ≈ / slightly ↓**
  Cl/Ca values are low in both crust and substrate. Slightly higher median Cl/Ca in the substrate indicates that chloride is not preferentially concentrated in the black crust; instead, it likely reflects weak, episodic deposition of road salts or aerosols on the wall [7,8]. Chlorine does not appear to be a primary driver of black-crust formation at this site.
- **Cu/Ti – not diagnostic**
  Cu/Ti ratios are strongly affected by detection limits: Cu is at or below the LOD in most spots, and Ti is frequently below the LOD in the substrate. Median Cu/Ti values therefore collapse to ~0 for both zones, and no meaningful enrichment factor can be defined. As a result, Cu/Ti cannot be used here as a reliable tracer of traffic-derived particulates.
- **Zn/Ti – inconclusive**
  Zn behaves similarly to Cu in this dataset, with most measurements near or below the detection limit and Ti < LOD in the substrate. Although a few crust spots show measurable Zn/Ti, the overall trend is too poorly constrained to support a robust interpretation of Zn as a non-exhaust traffic marker at Golia. The indicator is thus labelled as "inconclusive".
- **Fe/Ti – ↓ (cautious interpretation)**
  Fe/Ti ratios show a somewhat higher median in the substrate than in the crust (EF(Fe/Ti) < 1), but this result is largely controlled by a single substrate measurement in which Ti is quantifiable. Given the mixed lithogenic and atmospheric origin of iron and the scarcity of reliable Ti data, Fe/Ti is not considered a strong indicator of crustal enrichment or depletion, and its trend must be interpreted with caution [1,8].
- **EF (S, Cu, Zn, Fe)**
  In this study, EF values based on median ratios emphasise the robust enrichment of sulfur (EF(S/Ca) ≈ 2.1) in the black crust, while Cu/Ti and Zn/Ti do not yield meaningful EF values and Fe/Ti suggests no clear enrichment. Overall, sulfur emerges as the only element for which a consistent anthropogenic enrichment pattern can be demonstrated within the black-crust layer, whereas other tested indicators remain limited by detection-limit constraints [7,8,13].

Legend / notes:
↑ = higher median value in the black crust relative to the substrate (crustal enrichment); ↓ = lower median value in the black crust relative to the substrate (relative depletion); ≈ = similar median values in both zones (no clear contrast).
EF = enrichment factor calculated as the ratio between the median value in the black crust and the corresponding median in the substrate for a given indicator (e.g., EF(S/Ca) ≈ 2.1). In this dataset, EF is robustly defined only for S/Ca (and, with reservations, for Fe/Ti); it is not reported for Cu/Ti and Zn/Ti because median ratios collapse to ~0 due to detection-limit constraints.

Interpretations correspond to elemental ratios and enrichment trends presented in Table 3.