

Research Article

Observation of the Laser Cleaning Effect on the Gotland Sandstone Elemental Composition

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Changes of the elemental composition due to laser surface cleaning of a naturally crusted historical sandstone were investigated by means of the SEM/EDX technique. Data obtained for stone samples prior to and after laser irradiation were compared with those for noncrusted, reference ones. It has been observed that the crust removal resulting from ablative cleaning was accompanied by a decrease of the partial content of elements Al, S, K, Ca, and Mg in the range of 60–80% of their initial value recorded for the noncleaned, crust-covered stone surface. In the stone layer just under the crust coverage, a structure characterized by intergranular spaces between the SiO₂ grains being the main sandstone component filled with degraded binder was observed. From the coincidence of the binder destruction and chemical composition of the crust, the stone surface destruction due to the long-term interaction of environmental pollution was deduced. The spatial distributions of individual elements obtained by mapping after laser irradiation indicated that besides SiO₂ the content of elemental components in the sandstone surface layer decreased by 50%, whereas for Fe with the initial content of 4% and other surface remnants: P, Ti, Zn, and Cl—all below 1%, insignificant changes were only revealed. It was concluded in agreement with the literature that surface cleaning by means of the 1064 nm laser does not cause removal of iron from the sandstone surface.

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1. INTRODUCTION

The laser cleaning is presently a well-established technique in conservation of artworks. It assures a localized, well-controlled removal of undesirable layers from the surfaces of historical objects made of various materials such as stone, glass, paper, wood, metal, and so forth by means of laser ablation [1, 2]. This rapid, noncontact process results from conversion of an initial photoexcitation into kinetic energy of particle motion, leading to ejection of atoms, ions, molecules, clusters, and aggregates from the irradiated surface [1–3]. Since 1972 successful applications of laser cleaning to various historical objects such as wall, oil and tempera paintings [4, 5], documents made on paper or parchment [6], photographs, sculptures and architectural details [7, 8], and stained-glass windows [9] have been reported. Most of the experimental data collected so far indicate that laser cleaning represent a useful and efficient technique allowing one to execute difficult, often unique restoration tasks.

One of the main advantages of laser cleaning consists in its usefulness in cases of objects which are fragile or sensitive to chemical solvents used in conventional cleaning methods. Here, the Gotland sandstone represents a good example. It is a soft, quite porous material frequently used in the past for construction and monuments in numerous locations of the Pomeranian Region [10]. Despite the stone composition, structure, and reaction with most common atmospheric pollution which were extensively investigated, the restoration of objects made of this material still represents a difficult task [10–13]. Most of the problems are related to the stone softness, porosity, and composition and occur mainly during cleaning and consolidation of historical objects. In particular, for the case of laser cleaning the problem of changes in the chemical composition has been extensively discussed in relation to the post processing surface discoloration [14–16].

In this work the SEM technique together with elemental analysis and mapping of the distribution of individual elements by means of the Energy Dispersive X-ray Spectroscopy is applied for investigation of the laser cleaning effect on

the historical sandstone material. The experimental data obtained for the laser cleaned samples and reference ones at various stages of the cleaning process are analysed and discussed.

2. EXPERIMENTAL

Samples of sandstone used for measurements were extracted from historical monuments in Gdansk. For ablative removal of the naturally developed black crust, the pulsed Nd:YAG laser (6 nanoseconds FWHM) operating at wavelength of 1064 nm, and constant fluence of 1 J cm^{-2} was applied. Parameters of interaction were selected in accordance with results of earlier studies [17]. For each sample the irradiated spot was completely cleaned after application of up to 30 laser pulses and the cleaned area had a nearly circular shape of 1 cm in diameter. The SEM + EDX analysis was performed at locations selected so in the central parts as well as in the border regions of the laser processed areas.

The laser-cleaned and reference samples were analysed under conditions of the low vacuum mode provided by a JEOL scanning electron microscope 5310 LV equipped with a LINK Pentafet 6587 energy dispersive X-ray spectrometer (EDS) operated by an Oxford LINK ISIS system. For optical inspection magnifications of $50\times$, $150\times$, and $750\times$ were applied. The data on elemental composition of selected sample's fragments were collected by means of EDS and mapped in the form of coloured images using the CAMEO numerical procedure.

The data processing by means of CAMEO allowed to perform an elemental analysis based on SEM photographs of the studied area. In this way not only elements present in the sample surface layer were detected but also their spatial distribution was obtained. The data have been presented in the form of coloured areas characterized by the hue and saturation. The hue was assigned to a defined excitation range of the recorded spectrum and expressed quantitatively in keV. The colour saturation gave information on the quantity of a given element and the various picture colours related to detected elements allowed to conclude on their elemental distribution.

3. CHANGES IN ELEMENTAL DISTRIBUTION DUE TO LASER CLEANING

Among various chemical, physical, mechanical, and biological causes of stone degradation the most typical damages of historical substance can be observed in urban areas, especially in industrial regions. Particularly active in attacking stone are the atmospheric pollutions. Oxygen, carbon dioxide, sulphur and nitrogen oxides, sulphuretted hydrogen, solid particles originating from fuels and floating dust—all are continuously present in air and cause changes in the rock minerals. The water usually intensifies action of these species by penetrating the rock and introducing the pollutant solutions or dispersions deep into the material. As a result, the binder components react with water solutions of air pollutants, producing salts which migrate through grain interspaces and are deposited on the stone surface [12, 13]. In this way the black encrustation is formed: a tight, rough layer

accumulating dirt and dust particles, consisting of binder elements and air pollutants.

Black encrustation is the only layer of historical stony objects that should be treated during laser cleaning. Despite the fact that laser cleaning is a self-limiting process because of different absorbance of the black layer and the underlying substrate, it has to be performed with proper caution. The object should be thoroughly examined before cleaning, and a continuous process monitoring during the ablative crust removal is highly advisable. The sample examination before and after laser cleaning delivers useful data, too. In the case considered here, the combined SEM + EDS technique was applied for a detailed surface inspection and also in order to observe changes of the elemental composition at selected locations of the sample studied. Results of the EDS study performed for the crusted and noncrusted samples of the Gotland sandstone before and after laser application are presented in Table 1.

The data indicate a large oxygen content detected for excitation in the range of 0.1–1 keV. The CAMEO mapping in this excitation range reveals nearly exclusively this element represented by numerous, garish-green coloured pixels. This is caused by the fact that oxygen is present in all the minerals in sandstone and in the encrustation, too. Apart from oxygen the remnants of other elements: carbon and zinc are revealed. The value of carbon concentration was excluded from validation due to the data processing applied. The presence of Zn in the top layer of crusted stone results from capturing of this element from the polluted atmosphere. The EDS data indicate that Zn is not removed during the laser cleaning process.

In the excitation range of 1–2 keV the differences in CAMEO prints obtained for the laser cleaned and non-cleaned samples become quite distinct—see Figure 1. The largest changes due to the laser surface cleaning are observed in concentrations of aluminum and silicon. The pictures of noncrusted grains show that most of them are composed of silicon grains exclusively which is represented by the blue colour on the CAMEO print. In case of the non-cleaned reference sample—the left-hand side of Figure 1, the prevailing part of the surface picture corresponds to silicon. For the intergranular spaces filled with crust the presence of aluminum, being component of glauconite, micas, feldspars and maybe clays formed by weathering, is also detected and shown by a green coloured areas. It can be clearly observed in the mapping, that due to laser cleaning most of the aluminum present on the sample surface is removed. This is confirmed by the numerical data of Table 1, which indicate that the Al concentration decreases four times due to the cleaning but it is still twice as large as that measured for the noncrusted substrate.

Also in the range of 2–4 keV the differences between the reference and laser-cleaned samples are clearly visible. On the CAMEO images, see Figure 2, show the interface between the cleaned and noncleaned parts of the stone surface and thus the two different areas can be distinguished. The first one corresponding to locations covered with crust is blue and navy-blue, and the green area with numerous red, yellow, and navy-blue spots corresponds to the laser cleaned areas.

TABLE 1: Elements detected before and after laser cleaning by means of the EDX technique: concentrations are given in (%) and the corresponding excitation energy values in keV; data obtained for sandstone samples covered and not covered with encrustation.

Range of excitation energy	Element	Spectral line	Energy value (keV)	Mapping colour ascribed	Average concentration (%)		
					Before cleaning	After cleaning	Stone without crust
0.1–1 keV	Carbon	$K\alpha$	0.28	Yellow	—	—	—
	Oxygen	$K\alpha$	0.52	Green	52.99	52.99	61.25
	Zinc	$L\alpha$	1.01	Navy-blue	0.99	0.99	0
	Sodium	$K\alpha$	1.04	Navy-blue	0	0	0
1–2 keV	Zinc	$L\alpha$	1.01	Red	0.99	0.99	0
	Sodium	$K\alpha$	1.04	Red	0	0	0
	Magnesium	$K\alpha$	1.25	Yellow	0.40	0.12	0.10
	Aluminum	$K\alpha$	1.49	Green	2.90	0.75	0.36
	Silicon	$K\alpha$	1.74	Blue	31.22	39.01	36.55
	Silicon	$K\beta$	1.84	Blue			
2–4 keV	Phosphorus	$K\alpha$	2.01	Navy-blue	0.59	0.66	0
	Phosphorus	$K\alpha$	2.01	Red			
	Sulphur	$K\alpha$	2.31	Red	1.05	0.26	0
	Sulphur	$K\beta$	2.46	Yellow			
	Chlorine	$K\alpha$	2.62	Green	0.14	0	0.12
	Chlorine	$K\beta$	2.82	Green			
	Potassium	$K\alpha$	3.31	Green	1.1	0.22	0.11
	Potassium	$K\beta$	3.59	Blue			
	Calcium	$K\alpha$	3.69	Blue	4.36	0.88	0.09
	Calcium	$K\beta$	4.01	Navy-blue			
4–10 keV	Calcium	$K\beta$	4.01	Red			
	Titanium	$K\alpha$	4.51	Red	0.26	0.34	0.39
	Titanium	$K\beta$	4.93	Red			
	Iron	$K\alpha$	6.40	Green	3.96	3.47	1.57
	Iron	$K\beta$	7.06	Green			
	Zinc	$K\alpha$	8.64	Blue	0.99	0.99	0
	Zinc	$K\beta$	9.57	Navy-blue			
	Zinc	$K\beta$	9.57	Navy-blue			

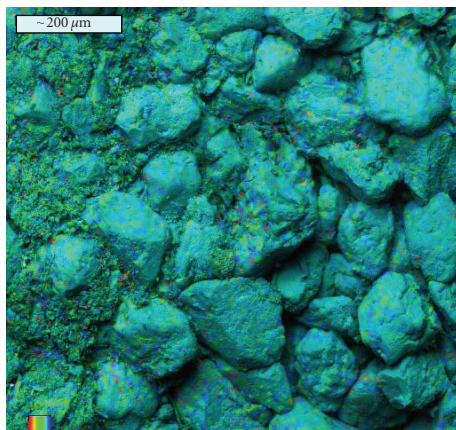


FIGURE 1: CAMEO print of the interface between the laser cleaned (right) and noncleaned (left) areas of the stone surface; excitation range 1–2 keV.

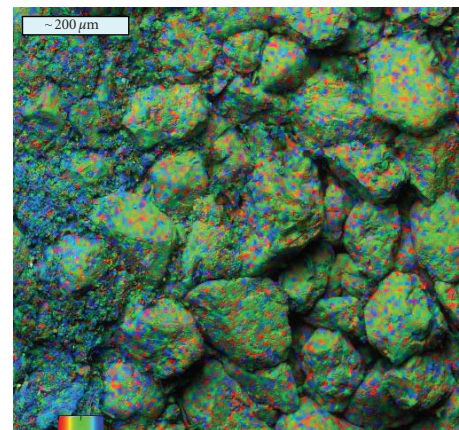


FIGURE 2: CAMEO print of the interface between the laser cleaned (right) and noncleaned (left) areas of the stone surface; excitation range 2–4 keV.

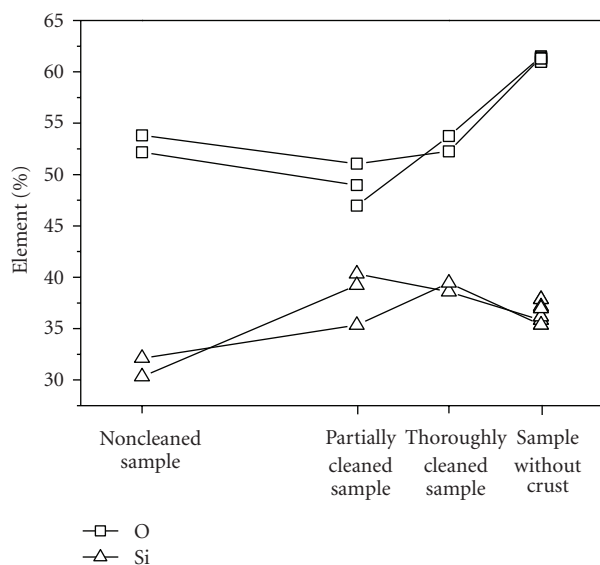


FIGURE 3: Change in concentration of Si and O measured for successive stages of laser cleaning; data for the noncrusted, reference sample are given for comparison.

According to data in Table 1, the blue colour corresponds to calcium ascribed to the binder compounds: calcite, glauconite, and feldspars. Other elements in this part of spectrum are chlorine, potassium, and also phosphorus and sulphate represented by the green, red, and yellow colours, respectively. From this element collection only the presence of potassium and calcium can be clarified by their migration from the inner layers of sandstone. The elements Cl, P, and S can originate from the exterior and, as it will be discussed further in the text, they are residual components of minor contribution to the layer composition.

The highest spectral range does not show up any marked changes in the superficial stone layer due to laser cleaning. The presence of the $K\beta$ line of calcium and also $K\alpha$ and $K\beta$ lines of more massive elements: titanium, iron, and zinc is revealed. In the corresponding CAMEO prints it can be observed, that in the entire map the green colour corresponding to Cl, and K prevails but there are numerous spots of other colours, from amongst which the yellow one corresponding to iron, a component of glauconite, occurs most frequently. In this case and from data in Table 1 it can be concluded that the Fe concentration does not practically change due to the laser cleaning, though, it is twice as large as for the noncrusted substrate.

4. RESULTS OF THE EDS ANALYSIS

From EDS measurements the semiquantitative data characterizing the chemical composition of the crusted and laser-cleaned Gotland sandstone were obtained and the results are shown on Figures 3–5. The data were collected for four different samples: (1) crusted one before cleaning, (2) crusted partially cleaned, (3) crusted thoroughly cleaned and (4) a clean sandstone without crust. Three series of measurements

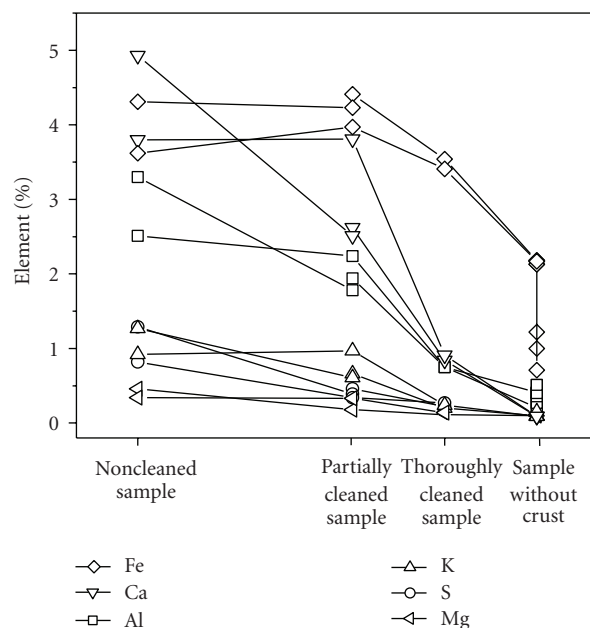


FIGURE 4: Concentration of aluminum, sulfur, potassium, calcium, magnesium, and iron in samples measured at successive stages of laser cleaning; data for the noncrusted, reference sample are given for comparison.

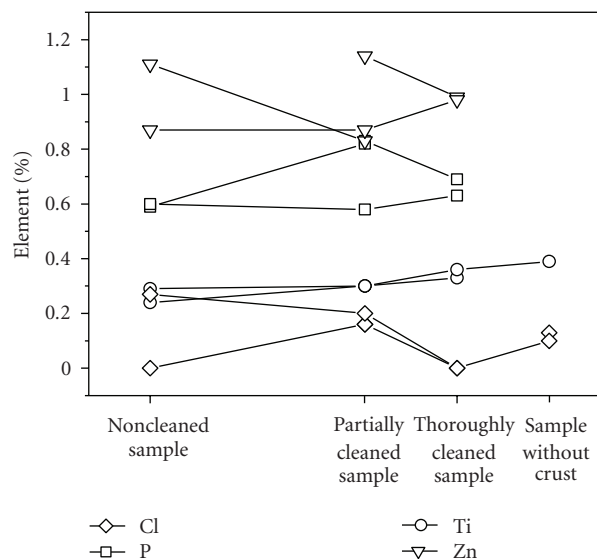


FIGURE 5: Concentration of phosphorus, titanium, zinc, and chlorine in samples measured at successive stages of laser cleaning; data for the noncrusted, reference sample are given for comparison.

were performed for each element and the results are averaged percentage values related to the summary content of 100% of the all elements detected in a given sample. The list of elements does not contain carbon in agreement with discussion of the EDS study summarized in [18].

The change of percentage contents of silicon and oxygen observed for consecutive stages of the laser cleaning process

TABLE 2: The average concentration change of selected elements in samples due to the laser cleaning.

Element	Al	S	K	Ca	Mg	Fe
Concentration before cleaning (%)	3	1	1	4.5	0.4	4
Concentration after cleaning (%)	0.75	0.2	0.2	0.9	0.12	3.5
Relative decrease (%)	75	80	80	80	60	12.5

is presented in Figure 3. These two elements make together 80–90% of the total mass of the sample material and their concentration increases with the surface cleaning progress and removal of the crust. The initial quantity characterizing the silicon and oxygen content of 84% before cleaning grows up to 87% for the partially cleaned sample and reaches the value of 92% after completion of the process. This in agreement with the elemental mapping already discussed reveals the presence of Si and O due to quartz grains, and agrees also with the result of contaminants removal due to laser ablation. It is worth noting that as the relative concentration of silicon grows, the oxygen level remains stable around 53% during the laser cleaning process. It is caused by the fact that Si as a component of quartz is gradually exposed by the cleaning process while the oxygen level remains unaffected as it is present in almost every chemical compound in the sandstone as well as in the crust.

A strong decrease in concentration due to laser cleaning is observed for the elements: aluminum, sulfur, potassium, calcium, magnesium, and iron—Figure 4. The corresponding average concentration of selected elements before and after cleaning and also the relative concentration changes are summarized in Table 2. Almost all the elements listed decrease several times their share in the top material layer. Iron is the only exception—its concentration after cleaning is almost the same as before laser application. This coincides with conclusions from the CAMEO elemental mapping, and is also in agreement with results of EDS studies on marble performed by other authors [14], which demonstrated that after the laser cleaning of stone under similar conditions, for example, by means of the 1064 nm, Q-switched Nd:YAG laser, iron remains on the sample surface. Moreover, it is worth noticing that concentrations of other elements shown in Figure 4 lie below 1% for the case of thoroughly cleaned substrate.

Almost all the elements listed in Table 2 originate from sandstone. The only exception is sulphur which comes from atmospheric pollutants. In the presence of water the sulphur oxides migrate in the form of water solution into the sandstone bulk, where they react with minerals, creating new compounds. Most likely these compounds move to the top layers of the stone and are deposited on its surface in the encrustation after evaporation of water [13].

The range and changes of concentration of the other elements: Cl, P, Ti, and Zn are relatively small—from 0 up to 1.2%, see Figure 5. The low content and weak concentration dependence on the cleaning stage both indicate that these elements belong to residual components of the studied sample layers.

The results show that the surface layer of the noncrusted, historical Gotland sandstone contains mainly the following elements: silicon, oxygen, calcium, potassium, aluminum, iron, magnesium, chlorine, and titanium. For the case of crust-covered sandstone two groups of elements are revealed. The one refers to the elements originally present in the non-destructed stone substrate: magnesium, aluminum, chlorine, potassium, calcium, and iron. The zinc, sulphur, and phosphorus belong to the second group of chemical components originating from the polluted environment and captured by the sandstone surface.

5. CONCLUSIONS

Samples of the naturally crusted historical sandstone were investigated by means of the SEM and EDX techniques in order to observe changes in the chemical composition due to the surface cleaning with laser. Based on the EDX data, also the elemental mapping at consecutive stages of the cleaning process was performed by means of the CAMEO image processing package. It was observed that besides SiO₂ the content of elements Al, S, K, Ca, and Mg in the sandstone surface layer decreased 3–5 times after the laser irradiation, whereas for Fe of an initial content of 4% and other surface remnants P, Ti, Zn, and Cl—all below 1%, only insignificant changes were revealed. In the cleaned region, silicon was predominantly observed while in the noncleaned region also aluminum and calcium were detected. The presence of these elements being natural components of Gotland sandstone was clarified by their migration in form of solutions and under the influence of polluted atmosphere into the top surface layer.

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