CHARACTERIZATION THE LASER CLEANING EFFECTS ON SANDSTONE FROM THE CANADIAN PARLIAMENT BUILDING

by

Yuan Hu

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Abstract

Laser cleaning has been used in the rehabilitation and conservation program of the Canadian Parliament Buildings in order to remove the black crust on sandstone surfaces. This study was carried out to characterize the effect of laser cleaning on sandstone from the Canadian Parliament Buildings. First, characteristics of the sandstone and the black crust itself were studied using microscopy, x-ray fluorescence (XRF) spectroscopy, and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS). Two kinds of sandstone samples, Berea/Ohio sandstone and Nepean sandstone, were taken from the West Block of the Parliament Buildings for testing. The results showed that the black crust was a very thin layer covering the surface of the quartz grains and also filling the gaps between the quartz grains on the surface of the sandstone. The characteristic elements of the black crust were sulfur (S), calcium (Ca), iron (Fe), and lead (Pb). Copper (Cu) and chlorine Cl were detected in some samples. Gypsum in the black crust was confirmed by the back-scattered electron (BSE) images. The Fourier transform infrared (FTIR) spectroscopy results indicated that the organic materials of the black crust contained hydrocarbon oil. Second, surface morphology and elemental composition before and after laser cleaning were studied by microscopy, XRF, and SEM-EDS. The cleaning effect of three laser cleaning systems was discussed in terms of cleaning effectiveness and damage to the sandstone. The results showed that the black crust on the Berea/Ohio sandstone and the Nepean sandstone can be removed by using the LaserArt-100 Cleaning System, the main focus of the study, but that residues of the black crust were still found on the cleaned surface and caused the color of cleaned surface was darker than the fresh sandstone surface. Gypsum crystals were also identified on the cleaned surfaces. XRF and SEM-EDS results indicated that the characteristic elements of the black crust still existed in the residues. No direct damage was found on the cleaned surface. The results of the RILEM tests showed the water absorption rate of the cleaned Berea/Ohio sandstone was increased significantly after laser cleaning. The water absorption rate of the cleaned Nepean sandstone was a little higher than that of the black crust surface, which was near zero. The sandstone would be vulnerable to weathering caused by water when water absorption rate increased. Therefore, keeping
some residues during the laser cleaning would benefit the long-term preservation of the sandstone surface because the residues can prevent water infiltration
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List of Abbreviations

BSE: Backscatter electron
FTIR: Fourier-transform infrared spectroscopy
SEM-EDS: Scanning electron microscopy energy dispersive X-ray spectroscopy
XRD: X-Ray Diffraction
XRF: X-ray fluorescence
Chapter 1

Introduction

The Parliament Buildings, part of the Parliament Hill complex, are a physical symbol of Canada’s commitment to democracy and the principle of freedom. There are four buildings, the Centre Block, the Library of Parliament, the East Block, and the West Block. Figure 1-1 shows Parliament Hill from the air after the reconstruction in the 1920s, after a fire.

![Figure 1-1: View of Parliament Hill from the air (Kindle 1926)](image)

In order to maintain and improve the buildings’ function and preserve the appearance of the façade and valuable architectural heritage elements in the buildings, a major program to rehabilitate the Parliamentary Precinct started in 2002 and the rehabilitation of the West Block began in 2011. Cleaning the façade surfaces using lasers was one component of the rehabilitation of the West Block and the East Block, with the aim of cleaning the black deposit or crust on the surface of the Parliament Buildings especially on West and East Blocks. To clean or remove this black layer, lasers were selected because they are convenient, non-contact and produce no waste. The laser cleaning work of the West Block was finished in 2017.
Figure 1-2 and Figure 1-3 show the condition of cleaned façade surfaces on the West Block and un-cleaned façade surfaces on the East Block. The black crust darkened the stone on the East Block and the uneven distribution of the black crust also had a negative impact on the appearance. The uniform color of the cleaned surface on the West Block was restored after laser cleaning.

![Figure 1-2: Cleaned façade surfaces on the West Block](image1)
(Date of photograph: Feb.9, 2018)

![Figure 1-3: Un-cleaned the façade surfaces on the East Block](image2)
(Date of photograph: Feb.9, 2018)

Nepean sandstone, Berea/Ohio sandstone, and Potsdam stone were the prime building materials for the original structure of the Parliament Buildings in the 1860s and for the reconstructed buildings after a fire disaster in 1916 (Lawrence 2001). These kinds of stone can be seen in the
West Block (Figure 1-2) according to the color and the texture of stone. At the trim of windows and doors, the grey blocks with a smooth, finely finished surface are the Berea/Ohio sandstone and the reddish stone blocks are the Potsdam stone. Most of the facade was constructed with the ashlar, which means individual sandstone was precisely cut. These blocks with an uneven, rough surface are the Nepean sandstone. In this study, the Berea/Ohio sandstone and the Nepean sandstone are the main study materials.

The Berea/Ohio sandstone was quarried in Ohio and it has been widely used in North America since it was quarried in the early 1800s. The Nepean sandstone was taken from a local quarry near Ottawa (Lawrence 2001). Some basic physical properties are shown in Table 1-1.

**Table 1-1: The Physical Properties of Nepean sandstone and Berea/Ohio sandstone**  
(Lawrence 2001)

<table>
<thead>
<tr>
<th></th>
<th>Bulk specific gravity</th>
<th>Pore space (V/V)</th>
<th>Absorption</th>
<th>Permeability</th>
<th>Crushing strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nepean sandstone</td>
<td>2.61</td>
<td>7.22%</td>
<td>2.93%</td>
<td>4.87c.c/in.2/h</td>
<td>22032 lbs./in.2</td>
</tr>
<tr>
<td>Berea/Ohio sandstone</td>
<td>2.15</td>
<td>16.4% (Swanson 2014, 44)</td>
<td>5.8%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The first, more preliminary topic of this thesis was to analyze the materials including the composition of the black crust and its interaction with the sandstone surface. The geological characteristics of the sandstone were also identified by comparing them to the literature and by performing analyses. The second topic was to observe and identify the changes before and after laser cleaning. This included comparing cleaning results from different laser devices. The effects of one laser-cleaning device were studied in depth; this was the system that will be used on the East Block of the Parliament Buildings in 2018. The effects of laser cleaning using two other systems were also investigated. Samples were reexamined from laser cleaning studies Carole Dignard, Senior Conservator at the Canadian Conservation Institute, performed twenty-three years ago, on
sandstone samples taken from the Parliament Buildings. Cleaned recently samples from the West Block were also analyzed. Different laser systems were used in each of the three cases.
Chapter 2

Literature Review

2.1 Development of Lasers in Art Conservation

Laser is an acronym for “light amplification by stimulated emission of radiation.” Since the first laser device was built in 1960 by Theodore H. Maiman at the Hughes Research Laboratories (Maiman 1960), the application of lasers has been increasingly popular in many areas. At first, lasers were used to measure distances accurately and guide bombs or missiles for the military. More laser devices for civilian use were developed with further studying and understanding of laser capabilities. For example, there is a small laser device in every CD-ROM drive and Blu-ray Disc player.

In the 1970s, based on the idea that lasers can selectively vaporize an optically absorbing substance from a reflective material, John Asmus and other researchers finished tests of cleaning black crust on white marble surface and systematically studied the use of laser on cleaning artworks such as stone (Asmus, Murphy, and Walter 1974) and wood-carving (Asmus, Guattari, and Lazzarini 1973). In the 1990s, many European conservation scientists did much research and commercial laser cleaning devices were available. The meeting of LACONA (Lasers in CONservation of Art) has been held 13 times since 1995. This communication promoted the research of lasers for the conservation of art and increased the applications of lasers in conservation. Many studies on laser cleaning on stone and the pertinent information are referred to in this thesis. The handbook Cleaning Safely with a Laser in Artwork Conservation is available on the website of COST (European Cooperation in Science and Technology) and was funded by the European Science Foundation from 2000 to 2006.

In the field of conservation, cleaning is the process that removes foreign substances or substances that result from reactions between foreign materials and substrates because these
substances may cause damage to the surface (for example, encrustation, soiling, corrosion layers, or biological growth). Laser cleaning can be used to remove different crusts or stains on inorganic and organic substrates. The Nd:YAG laser, with radiation at 1064nm, has been the most popular laser, but other kinds of lasers such as lasers with shorter wavelengths have also been used because they are more suitable for paper, stained glass and polychrome surfaces (Cooper 1998, 17).

2.1.1 Interaction Between Laser and Materials and the Mechanism of Laser Cleaning

For materials that do not transmit light, the only two interactions between laser light and a material are absorption and reflection. Reflection of laser light has no effect on the material. When laser light is absorbed by a material, the laser’s energy can transfer to the material. Different effects due to absorption are dependent on the energy level of the laser (which is related to the wavelength) and the chemical characteristics of the material. Cooper assumed that photothermal ablation is the main process at infrared or longer wavelengths (Cooper 1998, 44). The most significant effect of lasers is therefore thermal effects at longer wavelengths, such as the wavelength 1064nm that is used for stone cleaning. This localized, very short heating process can make the temperature on the surface rise to a very high level in a very short time because the energy density of lasers is much higher than normal light. Most explanations of the mechanism of laser cleaning are based on this fact.

This photothermal process can ablate a material’s surface (Cooper 1998, 42). The underlying mechanism of ablation includes several parts. A localized temperature rise may cause thermal stress because of the localized thermal expansion. If this process happens in a very short time and the stress exceeds the yield strength of the material, the result is similar to the effect of the explosion. Dirty particles are then ablated. Also, because the laser results in a very high temperature on the surface and an extremely high rate of temperature rise, the surface material is vaporized very quickly. This vaporization is also explosive and results in the ablation of the surface material.
Lasers at short wavelengths may not transform energy to heat but may break the covalent bond if the photon energy of a laser is above the bond energy of the materials. Cooper assumed that this process called photochemical ablation is the main process at ultraviolet wavelengths (Cooper 1998, 44).

Asmus systematically tested laser cleaning on cultural heritage in his early studies (Lazzarini and Asmus 1973; Asmus, Murphy, and Walter 1974). Two models were used to explain the cleaning behavior of a ruby laser at 680nm. The selective vaporization can explain cleaning behavior in the normal mode (pulse length 0.001 ms-1ms) and at relatively low power intensity ($10^3$-$10^5$W/cm$^2$). The absorption of the darker-colored material is much higher than white or lighter-colored material. As a result, damage to the substrate, such as cracking caused by differently thermal expansion, melting or vaporization, is avoided because vaporization due to the temperature rise happens on the darker crust while the temperature rise on the white substrate is sufficiently small. A different model is needed to explain why the Q-switched Nd:YAG laser is more efficient in crust removal with a shorter pulse. Q-switching is a technique that allows a laser to produce a short pulse with high peak power. Because the heat induced by a Q-switched pulse is deposited so quickly that little heat is conducted away from the surface into the substrate, the maximum temperature rise induced by a Q-switched laser is much higher than that induced by a laser of the same energy, which is operated in normal-mode at 0.1 ms pulse length (Cooper 1998, 43). An ablation mechanism or plasma shock wave mode is responsible for explaining the situation in Q-switched mode (pulse length 5-20ns). The vaporization temperature is easy to reach a much higher power intensity ($10^7$-$10^{10}$W/cm$^2$). The vaporized material from the surface and ambient air is also heated to a high temperature and creates a plasma. When plasma is continually heated through absorbing the energy of laser pulse, a shock wave near the surface is produced due to the high pressure of the heated plasma. The impact or microscopic compression produced by the shock wave
can ablate the material on the surface. Some basic parameters for laser cleaning are explained in Table 2-1.

### Table 2-1: Basic parameters for laser cleaning

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse duration; Pulse length; Pulse width</td>
<td>The time duration that the laser works. The pulse duration of a typical Q-switching Nd:YAG laser is 5-20ns.</td>
</tr>
<tr>
<td>Frequency; Repetition rate</td>
<td>Numbers of pulses per second</td>
</tr>
<tr>
<td>Wavelength</td>
<td>The wavelength of the laser light is quite different due to the laser sources.</td>
</tr>
<tr>
<td>Beam size</td>
<td>The area of laser beam acts on the surface</td>
</tr>
<tr>
<td>Working distance</td>
<td>The distance between the surface and the laser generator</td>
</tr>
</tbody>
</table>

#### 2.1.2 Advantages of Laser Cleaning Compared with Other Cleaning Methods Used before

Cooper (1998, 7) summarized the advantages of laser cleaning over other cleaning methods. Advantages are:

- There is no physical contact with the surface. The material only interacts with the laser light.
- It is possible to clean selectively and remove the dirt from the surface without causing any damage to the surface if the parameters are set carefully. Because of the monochromaticity of the laser radiation, the heating effect of lasers is quite different for diverse wavelengths. Also, the absorption rate or sensitivity to lasers varies for different materials.
- The laser only interacts with the area upon which it impacts. This means cleaning is easy to control because laser cleaning is a localized action.
- Once the laser is turned off or is not in focus, the interaction is also stopped at the same time. This means laser cleaning can be stopped as soon as the laser stops working. This is different from chemical cleaning. Because of residual cleaning agent on the surface, reactions cannot be
terminated completely, even after most cleaning agent is removed from the surface.

- The cleaning effect can be observed as the laser treatment is carried out. For other cleaning methods such as chemical cleaning, it is impossible to assess the cleaning effects before the chemical agent is removed. Furthermore, any risk of irreversible damage can be avoided because laser cleaning can be stopped as soon as any sign of over-cleaning is observed.

- Although there is still some particulate dust created by laser cleaning, laser cleaning is more environmentally friendly than other cleaning methods, especially those methods using hazardous chemicals or creating hazardous waste.

2.2 Laser Cleaning of Stone

2.2.1 Introduction to Cleaning Methods for Stone

Despite the fact that there have been arguments that dirt or any deposition on a stone surface is a part of its history and cleaning may remove the evidence of history, cleaning has usually been the first step of interventions. The primary reason for cleaning is restoration of the appearance. The public is not interested in a dirty monument or a marble sculpture covered with a black crust and researchers cannot identify the fine detail and features of a stone building or limestone sculpture if it is covered with dirt or a crust. Cleaning not only improves the visual appearance but also remove some harmful materials such as soluble salts from the surface, under most circumstances. Conservation treatment such as consolidation is sometimes necessary after cleaning because the cleaned surface is more vulnerable to be attacked by pollution and biological growths.

In the past twenty years, techniques for stone cleaning have become more refined, but the basic techniques still remain the same (Doehne 2010, 30). There are two major methods: physical cleaning and chemical cleaning. Abrading the surface is the main mechanism of physical cleaning and water washing and grit blasting are the common methods (Andrew 1994, 45). Surface roughening and erosion on the underlying stone surface is a potential adverse effect needing to be
considered if physical cleaning methods are used. Chemical cleaning means the surface crust or soiling can be removed by a chemical reaction between the cleaning agent and the crust or dirt. What kind of chemical agent can be used depends on the composition of the dirt and the composition of the underlying stone. Application of a poultice can not only control the duration of the reaction but also reduce migration of chemical agents into the stone (Doehne 2010, 32). The risk of using chemical agents is that chemical materials may stain the stone surface or create a new deposition. Water may be used for physical cleaning and chemical cleaning and may change the distribution and migration of soluble salt in stone. This potential damage due to soluble salt and chemical residues is unobservable in the short-term, but in the long-term, those factors may cause damage such as efflorescence or powdering. Unlike chemical and mechanical cleaning, laser cleaning is a physical process based on localized thermal effects, which can, therefore, avoid the disadvantages of chemical cleaning.

2.2.2 Laser Devices Used for Cleaning Stone

Many tests were done in the 1980s and laser cleaning became a relatively common method in the stone conservation field in the 1990s (Rodriguez-Navarro et al. 2003). With the development of laser techniques, more commercial laser cleaning devices are available and large-scale applications of laser cleaning are possible (Dajnowski, Jenkins, and Lins 2009). Laser cleaning has been successfully used to clean crusts on marble, limestone and sandstone surface. Early application cases showed the ruby laser can successfully clean the black sulphation crust from marble and Q-switched pulse are more efficient but less selective than the normal mode (Lazzarini and Asmus 1973). The test results of Orial and Gaufillet (1989) show that the Nd:YAG laser in Q-switched mode (pulse length 12ns) is more efficient than Nd:YAG laser in normal mode (pulse length 0.4-12ms) to remove encrustation from marble and limestone surfaces. The cleaning tests carried out by Cooper, Emmony, and Larson (1992) concluded that the best laser for removing
pollution encrustation from limestone is the Nd:YAG laser in Q-switched mode. Cooper pointed out that a laser at wavelength 1064nm is able to complete the selective removal of crust from a limestone surface because the black crust is more sensitive to the Nd:YAG’s wavelengths of 1064nm than the underlying limestone (Copper 1998, 14). Klein et al. (2000) cleaned the sandstone samples by four types of lasers with four wavelengths (248, 308, 355, and 1064 nm). The results showed that for the sandstone that was tested, the Nd:YAG laser with wavelengths at 355 and 1064nm are more suitable than the laser with wavelengths at 248 and 308 nm.

Most cleaning on the stone has used the Nd:YAG Q-switched laser. The two concerns are the occurrence of surface damage to the substrate at relatively low fluence (the energy per pulse delivered per unit area) and the yellowish appearance of the surface after cleaning. This has motivated the development of a laser with a longer pulse duration (Siano and Salimbni 2010). Margheri et al. developed a novel fiber-coupled Nd:YAG laser emitting pulses of 20 μs (2000). The authors believed that this laser with an intermediate pulse duration could reduce the risk of both mechanical damage that occurs with short pulse duration and thermal damage that occurs with longer laser pulse duration. Even at high fluence (3–10 J/cm²) this short free running (SFR) laser caused less damage to the underlying substrate than the Q-switched laser at low fluence (1–1.5J/cm²). The reason lies in the much stronger photomechanical process induced by cleaning with QS lasers. In 2012, laser cleaning tests were performed on outdoor sculptures at Chartres cathedral in France and the performance of the two Nd:YAG (1064 nm) laser devices were compared, the long Q-switched (LQS) with pulse length 100ns and the short free running (SFR) with a pulse duration of 0.1ms (Vergès-Belmin et al. 2015). Test results showed that surfaces cleaned with the LQS mode appeared clean and slightly yellow while the SFR mode led to a darker but less yellow appearance.
2.2.3 Parameter Settings and Laser Controls for Stone

The most significant feature of laser cleaning is selectivity because laser absorption is different for different materials. The materials with a higher absorption coefficient can absorb more laser energy than materials with a lower absorption coefficient, so it is more possible to cause damage to materials with higher absorption coefficient if materials with higher absorption coefficient and materials with lower absorption coefficient are under the same laser irradiation. The ablation threshold (Cooper 1998, 55), which means the lowest energy density leading to damage or ablation, is the most critical parameter for laser cleaning. The energy density, known as fluence, is the energy per pulse delivered per unit area and its unit is J/cm$^2$. A successful laser cleaning requires a smaller ablation threshold of the contaminant compared with the ablation threshold of the substrate. If the ablation threshold of the contaminant is higher than the ablation threshold of the substrate, the laser would inevitably damage the substrate as the contaminant was removed. Fortunately, most crust or dirt layers on stone surfaces have lower ablation thresholds. The ablation threshold gap between the threshold of the black crust and the threshold of the substrate is called the self-limiting effect, which means the fluence within the gap could remove the black crust without damaging the substrate. The threshold values need to be measured during laser cleaning tests because threshold values vary for different materials and different parameters (Rodriguez-Navarro et al. 2003).

Cooper considered that three parameters, including pulse energy, the working distance, and the repetition rate, are critical for controlling the cleaning process (Cooper 1998, 59). Siano and Salimbi believed that the best control and cleaning effect, including selectivity and gradualness, can be achieved through parameter optimization and the pulse duration is the crucial parameter (Siano and Salimbi 2010). Ganeev (2014, 91) considered that cleaning should be performed at relatively low fluence ($<1$ J/cm$^2$) to minimize the damage to the underlying substrate when a laser with wavelength 1064nm is used. The reason lies in that the cleaning with low fluence is a very selective process while the removal mechanisms at higher fluence ($>1.5$ J/cm$^2$) become more complex and less selective.
2.2.4 Laser Cleaning of Sandstone

The studies on laser cleaning of sandstone were limited compared with the research on laser cleaning of marble and limestone. Siano et al. have reported a study on optimizing the parameters of laser cleaning on Pliocene sandstone from Siena (Siano et al. 2000). A Nd:YAG laser (1064nm) operating in a short free running (SFR) mode (20μs) was tested. Threshold fluence was estimated at 4 J/cm² for this kind of sandstone. Darkening was due to selective ablation of the yellowish calcareous matrix in the sandstone. Klein et al. (2000) tested and measured the ablation threshold for sandstone. The ablation thresholds for encrustation is 0.85 J/cm² and the ablation thresholds for sandstone is 1.25 J/cm² for a Nd:YAG laser with a wavelength of 1064 nm. Svobodová et al. (2003) carried out experimental laser cleaning on sandstone using a Nd:YAG commercial laser (1064nm, 25ns) at two different fluences. The low fluence was 0.66 J/cm² and the high fluence was 8.39 J/cm², which corresponds to the maximum operating mode of the equipment. Laser cleaning with high fluence caused damage to the sandstone, including “hackle” markings, which are a sign of fracture induced by tensile stress. Iglesias-Campos and Prada-Pérez (2016) explained the role of pulse repetition rate during laser cleaning of black crust from sandstone. A Q-switched Nd:YAG laser with a wide range of repetition rate (5-200Hz) was used in the study. In order to describe the laser cleaning process more accurately, for laser cleaning under high repetition rate, results indicated the average of the total energy applied per spot should be considered.

2.2.5 Advantages and Disadvantages of Laser Cleaning for Stone

Advantages of laser cleaning are obvious because no materials such as chemical agents or water are introduced in the cleaning process and the control of removal is easy to achieve due to the selectivity and sensitivity of the laser with the substrate. Side effects of laser cleaning include potential damage caused by over-cleaning and discoloration of the surface after laser cleaning.
2.2.5.1 Yellowing

Discoloration or yellowing is a critical issue with laser cleaning, especially on stone surfaces. Many laser cleaning examples showed that a cleaned surface may change to a yellow color even when the original surface is not yellow. This phenomenon has been studied and several explanations have been discussed, but no one explanation has been accepted by most researchers as the common mechanism. Vergès-Belmin and Dignard discussed a few hypotheses, which included the uncovering of pre-existing yellow layers, soiling residues, and laser-induced damage on the substrate (2003). Klein et al. studied the laser cleaning effect of cleaned an artificially aged Carrara marble and Fe2O3 pigment powder was added into the artificial dendritic black crust. A high resolution scanning electron microscopy (SEM) image shows iron content in nanometer-sized spheres on the yellowed surface after laser cleaning (1064nm) and the origin of Fe was Fe2O3 pigment powder added within artificial encrustation on mode samples (Klein 2001). A light scattering model was developed to explain the yellowing in situations where there was no underlying yellowish layer or patina (Zafiropulos et al. 2003). Siano and Salimbeni considered that factors causing yellow-orange appearances on marble after laser cleaning are residues of iron oxides, Ca-oxalate films with pigment loads, organic substances, and other pigmented components in the stratification layers (Siano and Salimbeni 2010). A Q-switched laser cannot remove the last pigmented film on white marble when the fluence is 0.1-1J/cm², which is the usual operative value for cleaning. Some efforts were also made to undo this negative consequence by different means. Vergès-Belmin and Labour tried to use poultices to remove yellowing on the Saint Denis cathedral, which had been laser cleaned in 1997 (2007). The yellowing decreased after poultice removal partly because yellow materials were dissolved or detached physically. Other tests were focused on using lasers with different pulse durations or wavelengths. The short, free running (SFR) laser, with a pulse duration of 0.1ms, can reduce the yellowing during a laser cleaning test (Vergès-Belmin et
Oliveira’s simulation tests showed that exposure to UV-B (313nm) is able to bleach the yellowing effect caused by a laser on soiling, based on lamp black and gypsum (2015).

2.2.5.2 Over-cleaning

Theoretically, damage can be avoided by choosing suitable parameters; however, it is possible to damage the stone surface due to over-cleaning, especially with the Nd:YAG Q-switched laser with a short pulse length (1-100ns). Some devices are used to characterize and control the process of laser cleaning, such as the laser-induced breakdown spectroscopy (LIBS) (Scholten et al. 2000). LIBS can examine and monitor the elemental composition of the materials being removed by laser cleaning.

2.2.6 Methods to Characterize the Laser Cleaning Effects

Studies of the characterization, examination of the effectiveness, and damage after laser cleaning are focused on color change, surface morphology, and composition change. Ordaz (2003) summarized the techniques used to characterize the effect of laser cleaning of stone. The common tools to study surface morphology have been optical microscope and scanning electron microscopy (SEM). Many studies demonstrated cleaning effects by showing thin-sections (Siano et al. 2000). Colombo (2007) tested laser profilometry and completed quantitative roughness computations to reveal the effects of laser cleaning on marble samples. Pummer and Erich (2005) compared the cleaning effects of micro-blasting and laser cleaning on polished limestone plates with a black coating. The Universal Surface Tester (UST®) was used to explore the surface mechanically by using a tactile procedure (mistan®). Roughness parameters and topographic representations were calculated. In another study, the roughness of stone surfaces was measured before and after laser cleaning by a TRACEit optical surface (OSR) roughness tester (Vazquez-Calvo et al. 2012). 3D topographic maps showing roughness on a micro-scale (microns) were produced and the roughness was measured. Laser-induced breakdown spectroscopy (LIBS) was used to characterize, control,
and monitor the laser cleaning process by analyzing the materials being removed (Senesi et al. 2016). LIBS results showed the different elemental compositions of the black encrustations at various depths and in the underlying limestone.
Chapter 3
Experimental

3.1 Sample Description

Three sample sets of sandstone obtained in the winter of 2018 included: 1) un-cleaned samples taken from the West Block of the Parliament Buildings, obtained from Phil White who is the Dominion Sculptor at Heritage Conservation Services, 2) previously cleaned samples from the West Block, also obtained from Phil White, and 3) samples obtained from Carole Dignard at the Canadian Conservation Institute (CCI) who performed laser cleaning tests eighteen years ago.

The first set contained the main study samples. There were eight blocks of un-cleaned samples taken from the West Block. Four were Berea/Ohio sandstone and the others were locally quarried Nepean sandstone. The surface of the samples was black because of the black crust. The color of the surface on the Berea/Ohio sandstone samples was much darker than the color of the surface on the Nepean sandstone samples. The size of the samples was 10cm×10cm×3cm. These samples were cleaned by the LaserArt-100 Cleaning System and details will be given in section 3.2.

The second set includes two blocks of the Berea/Ohio sandstone that were taken from the West Block. These two samples were already cleaned with the CL500 Laser System, which was used to clean the West Block. The size of the samples was about 35cm×15cm×6cm and 20cm×12cm×3cm.

CCI’s samples, the third set, included two Berea/Ohio sandstone blocks with test areas that were laser cleaned with a LaserBlast 25 model. Details about the cleaning test will be given in section 3.2. The size of these two blocks was about 10cm×8cm×3cm.

3.2 Sample Preparation: Laser Cleaning and Parameters

3.2.1 Cleaning Test with the LaserArt-100 Cleaning System
For the first set, un-cleaned samples were taken from the West Block of the Parliament Buildings and were cleaned by the LaserArt-100 Cleaning System developed by Allied Scientific Pro. Please see Table 3-1 for the operating specifics. The laser cleaning tests were performed at a recent laser-cleaning workshop held by Heritage Grade in Ottawa on March 1st, 2018 (Figure 3-1). The operator, Kevin Carter, chose all of the parameter combinations. Usually, laser cleaning is carried out not only on dry surfaces but also on wetted surfaces. Two test areas, S4-B and HS2-B, were wetted by spraying deionized water before the test.

![View of laser cleaning test](image)

**Figure 3-1: View of laser cleaning test**

<table>
<thead>
<tr>
<th>Laser type</th>
<th>Nd:YAG laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>1064nm</td>
</tr>
<tr>
<td>Power</td>
<td>100W (10%-100%)</td>
</tr>
<tr>
<td>Peak power</td>
<td>15KW</td>
</tr>
<tr>
<td>Pulse duration (width)</td>
<td>10-350ns</td>
</tr>
<tr>
<td>Frequency</td>
<td>1KHz-1000KHz</td>
</tr>
<tr>
<td>Working distance</td>
<td>30cm</td>
</tr>
<tr>
<td>Scan mode</td>
<td>Line scanning</td>
</tr>
<tr>
<td>Scan width</td>
<td>100mm or 75mm</td>
</tr>
</tbody>
</table>
There were sixteen test areas on two different kinds of sandstones and seven parameter combinations used in the test with the LaserArt-100 Cleaning System (Table 3-2). The sample set S is the Berea/Ohio sandstone and the sample set HS is the Nepean sandstone. The surface condition on S2 (Figure 3-2) is different from S1 (Figure3-3), S3, and S4. The surfaces of the sample S1, S3, and S4 are tougher and pitted. In contrast, there are no pits on the relatively flat surface of S2. The surface condition of S2 is similar to the CCI’s sample. The surface conditions of the samples in the HS set are the same, but more black crusts were attached to samples HS1 and HS2. There are no significant black crusts on HS3 and HS4. In general, the soiling on the Nepean sandstone (the HS samples) does not look as dark as the Berea/Ohio sandstone (the S samples). Images of the samples were captured with the same orientation, with three test areas shown by three stripes: 1) test area A on the left, 2) the control (un-cleaned area) in the middle, and 3) test area B on the right. All images of the samples are in Appendix 1.

**Table 3-2: Different cleaning conditions and parameters**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Test area A</th>
<th>Test area B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pulse duration</td>
<td>frequency</td>
</tr>
<tr>
<td>S1</td>
<td>20ns</td>
<td>850KHz</td>
</tr>
<tr>
<td>S2</td>
<td>10ns</td>
<td>1000KHz</td>
</tr>
<tr>
<td>S3</td>
<td>100ns</td>
<td>160KHz</td>
</tr>
<tr>
<td>S4</td>
<td>60ns</td>
<td>220KHz</td>
</tr>
<tr>
<td>HS1</td>
<td>20ns</td>
<td>850KHz</td>
</tr>
<tr>
<td>HS2</td>
<td>60ns</td>
<td>220KHz</td>
</tr>
<tr>
<td>HS3</td>
<td>100ns</td>
<td>160KHz</td>
</tr>
<tr>
<td>HS4</td>
<td>10ns</td>
<td>1000KHz</td>
</tr>
</tbody>
</table>
3.2.2 Cleaning Test with the CL500 Laser Cleaning System

Two big samples BC (Figure 3-4) and SC (Figure 3-5) from the West Block were cleaned with the CL500 Laser Cleaning System in situ. Basic performance is shown in Table 3-3, but the cleaning conditions and parameters are unknown. Clean Lasersysteme GmbH made the laser cleaning system.

### Table 3-3: Basic performance of the CL500 Laser Cleaning System

<table>
<thead>
<tr>
<th>Laser type</th>
<th>Nd:YAG laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>1064nm</td>
</tr>
<tr>
<td>Power</td>
<td>500W (adjustable from 10-500)</td>
</tr>
<tr>
<td>Peak power</td>
<td>450KW</td>
</tr>
<tr>
<td>Pulse duration (width)</td>
<td>10-350ns</td>
</tr>
<tr>
<td>Frequency</td>
<td>18KHz-40KHz</td>
</tr>
<tr>
<td>Focal distance</td>
<td>120mm</td>
</tr>
<tr>
<td>Scan mode</td>
<td>Line scanning</td>
</tr>
<tr>
<td>Scan width</td>
<td>70mm</td>
</tr>
<tr>
<td>Beam diameter</td>
<td>0.89mm</td>
</tr>
</tbody>
</table>
3.2.3 Cleaning Test with a LaserBlast 25 Model

The CCI sandstone samples were cleaned with a LaserBlast 25 model made by the French company Quantel, a sub-group of Atlas Laser Systems. Paul Heinrichs carried out the tests in 1995. The operating specifics are shown in Table 3-4. Laser cleaning tests were performed on different areas of sample CR (Figure 3-6) and sample CS (Figure 3-7, 3-8, 3-9), which are Berea/Ohio sandstone. Cleaning conditions and parameters are shown in Table 3-5.
Table 3-4: Basic performance of the LaserBlast 25 Cleaning System

<table>
<thead>
<tr>
<th>Laser</th>
<th>Nd:YAG laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>1064nm</td>
</tr>
<tr>
<td>Power</td>
<td>1 W</td>
</tr>
<tr>
<td>Pulse energy</td>
<td>100 to 200 mJ</td>
</tr>
<tr>
<td>Pulse duration (width)</td>
<td>25ns</td>
</tr>
<tr>
<td>Maximum frequency</td>
<td>50Hz</td>
</tr>
<tr>
<td>Laser beam diameter</td>
<td>3mm or 4mm</td>
</tr>
<tr>
<td>Working distance(in focus)</td>
<td>5.5cm or 9cm</td>
</tr>
</tbody>
</table>

Figure 3-6: Test areas on sample CR

Figure 3-7: Test areas on sample CS
Figure 3-8: Test area on sample CS

Figure 3-9: Test areas on sample CS
Table 3-5: Different cleaning conditions and parameters for sample CR and CS

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Power</th>
<th>Repetition rate</th>
<th>Laser beam diameter</th>
<th>Application time</th>
<th>Fluence (J/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR-7</td>
<td>1W</td>
<td>50Hz</td>
<td>3mm</td>
<td>9s</td>
<td>0.282</td>
</tr>
<tr>
<td>CR-8</td>
<td>0.5W</td>
<td>50Hz</td>
<td>3mm</td>
<td>13s</td>
<td>0.141</td>
</tr>
<tr>
<td>CR-9</td>
<td>0.75W</td>
<td>50Hz</td>
<td>3mm</td>
<td>10s</td>
<td>0.21</td>
</tr>
<tr>
<td>CS-1</td>
<td>1W</td>
<td>50Hz</td>
<td>3mm</td>
<td>165s</td>
<td>0.282</td>
</tr>
<tr>
<td>CS-2</td>
<td>1W</td>
<td>50Hz</td>
<td>4mm</td>
<td>160s</td>
<td>0.159</td>
</tr>
<tr>
<td>CS-3</td>
<td>1W</td>
<td>50Hz</td>
<td>4mm</td>
<td>131s</td>
<td>0.159</td>
</tr>
<tr>
<td>CS-8</td>
<td>1W</td>
<td>50Hz</td>
<td>4mm</td>
<td>198s</td>
<td>0.159</td>
</tr>
<tr>
<td>CS-9</td>
<td>1W</td>
<td>50Hz</td>
<td>4mm</td>
<td>56s</td>
<td>0.159</td>
</tr>
<tr>
<td>CS-10</td>
<td>1W</td>
<td>50Hz</td>
<td>3mm</td>
<td></td>
<td>0.282</td>
</tr>
</tbody>
</table>

3.3 Sample Preparation

In order to observe the samples under different types of microscopy, samples were prepared in four different ways: temporary particle slides, thin-section cross-sections, thick-section cross-sections, and scanning electron microscopy (SEM) samples. Temporary particles slides were prepared to observe the black crust on the surface and the surface morphology after laser cleaning. Preliminary observations with thin-section and thick-section samples can display the characteristics of the black crust and how it attaches to the sandstone. Thin-section and thick-section samples also can show the characteristics of the sandstone itself. SEM samples were prepared to detect the surface condition of the samples and the elemental composition.

Temporary particles slide: Particles or aggregates of particles were taken carefully from the surface of samples by using a scalpel. Particles were lifted onto a glass slide, and then a drop of water (n=1.33) was placed on the particles. The next step was to cover particles with a coverslip. The coverslip was pressed down very gently to make the particles disperse evenly in the water. The slide and coverslip were cleaned with lens paper before they were used.
Cross-sections (thin-section): preparation of samples was completed by Jerzy in the Department of Geology at Queen’s University. The surface was immersed with epoxy resin in order to protect the surface particles from being detached by the polishing process. After the resin was set, the block was attached to a glass slide with epoxy resin. Then the slide was secured in a chuck and the block was cut to approximately 1-2 mm. After it was sanded and polished, the thin-section sample was ready to be observed. The standard thickness of a rock thin-section was about 30 μm.

Cross-section (thick-section): The sample was mounted in epoxy resin (Metlab epoxy and hardener) in a plastic mold. After curing the block was taken from the mold and sanded on a grinder with 240, 320, 400 and 600 grit levels. The samples were then polished with 1000 and 2000 grit sandpaper. The final polishing was finished with a 0.05 μm aluminum oxide solution.

SEM samples: Small blocks of sandstone sample were cut directly from sample blocks to fit the holder in the SEM chamber. The size of the small blocks was about 1cm×2cm×0.8cm and the chamber of SEM was big enough to put 8-10 samples on the holder. These small blocks were also used for observation under the microscope with reflected light.

3.4 Methods of Evaluation and Observation

3.4.1 Physical and Morphology Studies

3.4.1.1 Camera with Micro-lens

The first assessment undertaken in this study was a visual examination. The large-scale observation was carried out by using a Nikon D810 digital camera with a Nikon 105 mm micro-lens. Images of the sample set S and set HS were captured as documents (Appendix 2). In each image, the left side is the control (un-cleaned area) and the right side is the test area.

Preliminary tests showed that reflectance transformation imaging (RTI) using the camera and micro-lens was not a suitable method to observe the sandstone surface. RTI can permit digital enhancement of the subject’s surface shape and color attributes, but the black crust on the sample’s surface was very thin and could not be identified by RTI. Another reason that RTI did not work is
that the resolution and magnification of the micro-lens were not high enough to detect surface topography.

3.4.1.2 Microscopes and Focus Stacking Technique

All samples were examined under the Olympus BX51 microscope with Kohler illumination (transmitted plane-polarized light and cross-polarized light). Zeiss KL500LCD light was used as a normal reflected light and the color temperature was 3000K. All images were obtained through DP 72 camera and the Olympus CellSens imaging software.

According to the features of the samples, different illuminations were utilized to observe samples prepared with various ways. Temporary particles slides and thin-section were observed under transmitted light with Kohler illumination. Thick-section and small blocks that were also SEM samples were observed under reflected light with Zeiss KL500LCD light. The disadvantage of using reflected light is that the over-expose areas (white spots) on the images is unavoidable. Some areas on the quartz particles can lead to specular reflection, a mirror-like reflection of light from the surface. If the images with this specular reflection were processed with focus stacking software, the image would be unreadable. Two white sponges, 1 cm thick, were placed in front of the head of the Zeiss KL500LCD light, so the light direction was changed from a single outgoing direction to a diffuse direction. The diffused light through the white sponge reduced the specular reflection on the surface of the samples.

The difficulty for making observations under the microscope lies in how to get an image with enough depth of field. The depth of field is a range of distance on both sides of the focus plane and all scenes in this range need to be acceptably sharp. Anything that is outside the range appears to lose too much sharpness and the human eye can detect such a change in sharpness. The depth of field of the microscope is shallow. For example, the depth of focus is only 0.022 mm for the objective lens with ten times magnification and the eyepiece with ten times magnification. However, the size of the samples in this experiment is far larger than the depth of field. Only a small area of
the scene is in focus and clear enough if the ordinary method is used. Photos acquired in preliminary tests showed that imaging techniques such as focus stacking could solve this problem. Focus stacking is a technique that can create an image with a greater depth of field by using digital image processing. The software can automatically detect in-focus regions of each image and combine multiple images captured at different focus distances. A created image contains all regions in focus. The software Zerene Stacker was used to perform focus stacking. There are two stacking methods based on different techniques and algorithms in this software. PMax is a *pyramid* approach and DMap is a *depth map* approach (Stacker: Docs. 2018). The pyramid approach allows all Laplacian pyramids created for all images to be fused to create an image with an extended depth of field. In the depth map approach, the regions in which the sharpest pixels exist are detected and all regions with sharpest pixels in a sequence of images are combined to create an image (Kontogianni and Chliverou 2017). PMax mode was used in this study because it is good at preserving detail.

A set of images with typically shallow depth of field was captured with different focusing distances. All images were captured through the Olympus BX51 microscope. By turning the fine focus adjustment knob, the sample moved up or down slightly with the stage and the images with different focusing distance were captured. The minimum movement of the stage height adjustment was one unit (1 micron). Theoretically, if the interval of movement of the stage height between two captures is equal to or lower than the depth of focus, no in-focus regions could be lost. The initial test indicated that a smaller interval could not improve the final image dramatically. In contrast, theoretically, if the interval of stage height movement between two captures was equal to the depth of focus of the objective, some details would be lost in the final image because there would not be enough overlap area. Finally, half of the depth of focus of each objective was adopted as the interval of movement of stage height between two captures. All images for one sample needed to be captured at the same exposure condition. Figure 3-10 and Figure 3-11 are the images of grain and
surface captured without focus stacking and with focus stacking. It is very clear that the focus stacking gave a superior image.

Figure 3-10: A quartz grain of sample S3-A (left: original image without focus stacking, 200×. Right: Focus stacking image containing a combination of thirty eight images, 200×)

Figure 3-11: Un-cleaned area and cleaned area on sample S3-B (left: original image without focus stacking, 40×. Right: Focus stacking image containing a combination of seventy seven images, 40×)

The depth of field is a significant feature of the microscope. Different lenses with different magnifications have different depths of field; the objective lenses used are listed in Table 3-6.
Table 3-6: Optical characteristics of three objective lenses and the stage movement intervals

<table>
<thead>
<tr>
<th>Objective</th>
<th>Magnification</th>
<th>Resolution</th>
<th>Depth of focus (eyepiece WHN10X FN22)</th>
<th>Interval of stage movement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plan N (FN22)</td>
<td>4X</td>
<td>3.4 µm</td>
<td>180 µm</td>
<td>90 µm</td>
</tr>
<tr>
<td>UPlanFLN N (FN26.5)</td>
<td>10X</td>
<td>1.34 µm</td>
<td>22.4 µm</td>
<td>10 µm</td>
</tr>
<tr>
<td>UPlanFLN N (FN26.5)</td>
<td>20X</td>
<td>0.67 µm</td>
<td>7.0 µm</td>
<td>3 µm</td>
</tr>
</tbody>
</table>

3.4.1.3 Water Absorption Test with RILEM Tube

The RILEM tube test, known as “Test No. II.4 Water Absorption Under Low Pressure (Pipe Method)”, was developed by the International Union of Laboratories and Experts in Construction Materials, Systems and Structures (in French, the Réunion Internationale des Laboratoires et Experts des Matériaux, systèmes de construction et ouvrages or RILEM) technical committee. This test method is a simple means for measuring the quantity of water absorbed through the surface over a definite period of time and for studying the water absorption rate of porous materials (RILEM 1980).

To study the absorption of water over time, the RILEM Tube was adopted to test water absorption of the sandstone surface with and without laser cleaning (Figure 3-12). The plastic tubes in the Art Conservation microscopy lab are 12 cm long. The tube is graduated from 0 mL (the top reading mark) to 5 mL (the mark near the bottom of the tube). The tube is connected to a round cylinder. The interior diameter of the cylinder is 2.6 cm.
Holdit® DIXON putty adhesive was used to attach the open end of the cylinder to the sandstone surface during the test. This kind of putty is hydrophobic and the preliminary test showed its water absorption was zero. This means if no water leaks between the putty and the sandstone surface during testing, water is supposed to be absorbed into the sandstone.

Water leaking can dramatically change the results during the test, but this is easily observed because the water would spread along the sandstone surface outside the tube area. Since the putty can leave unsightly oily stains that may affect the substrate’s water repellency, it is better to repeat the test on another area if water leaking happens. The putty between the tube and the sandstone surface form the boundary of the contact area that allows water to permeate into the sandstone. Larger or smaller contact areas can affect the rate of water absorption which further affect the results. For a consistent area, the putty was attached along the interior boundary of the cylinder.

After the tube was sealed on the surface of sandstone with Holdit® DIXON putty adhesive, distilled water was put into the tube. The timer was started after the water was filled to the zero mark in the tube. The water volume absorbed in an hour was recorded.
Because the water absorption rate was quite different according to the various samples, the RILEM recommendations of readings at five-minute, 10-minute, 15-minute, 30-minute, and one-hour intervals were not very suitable in the test. For the samples with high water absorption, the time taken for the water level to get 1mL, 2 mL, 3 mL, 4 mL, 5 mL were recorded. For the samples with low water absorption, the readings at 1-minute, 5-minute, 10-minute, 30-minute, and 60-minute intervals were recorded. For the same reason, a simplified way was used instead of the more complicated test. In the complicated test, the water is added to keep the water lever at the zero mL mark at regular intervals to maintain pressure after water is absorbed and the water added is recorded as the water absorbed by sandstone. No water was added during the simplified test, so less absorption would be expected due to the water pressure diminishing as the water level falls. If the water absorption rate is very slow, the influence of the water pressure can be ignored because the water level would be slightly decreased.

Since there is not enough area for multi-measurements, only one measurement was performed on each sample. The cleaned area on the CCI samples was too small to perform the test and the uncleaned areas on samples HS2, HS3, HS4 were not big enough to perform the test.

3.4.1.4 Color Spectrophotometer

The color change of the surface after laser cleaning is very critical and can quantitatively reflect the change in appearance. Not only was the color difference measured between the cleaned surface and the black, un-cleaned surface studied but the color change was also monitored between the cleaned surface and the fresh surface for each sample. The color measurements were recorded with a spectrophotometer Konica-Minolta CM-700d using Konica Minolta Color Data Software CM-S100w Spectra Magic™ NX (2.40.0004) software. The data was reported using CIE L*a*b* color space defined by the International Commission on Illumination. Three numerical values, L*, a*, and b*, describe the color. L* is the lightness value. A value of zero means black and a value of 100 means white. The value of a* represents green in the negative direction and red in the positive
direction. The value of b* represents blue in the negative direction and yellow in the positive direction. The CIE76 color difference formula was used to calculate ΔE*ab. Each sample was analyzed by taking the average of six measurements at six different locations on the surface. The CM-A 180 target mask (diameter 8mm) was used and accordingly MAV mode was selected during the test.

3.4.2 Chemical Studies

3.4.2.1 X-ray Diffraction (XRD)

XRD is commonly used to identify the minerals in stone, as it can identify crystalline materials. The minimum limit of detection is about 1%-2% w/w, so the minerals cannot be detected if the amount of minerals is below 1%-2% w/w. XRD experiments for the sandstone and black crust samples were performed by Agatha Dobosz in the Department of Geology at Queen’s University with the Panalytical X’pert Pro Powder diffractometer (Philip). Data analysis used X’pert HighScore Plus software (Version 2.2d) and Jade 6.0. Detail parameters of XRD test are shown in Table 3-7.

<table>
<thead>
<tr>
<th>The X-ray tube</th>
<th>PW3376/00 Co LFF DK74886</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution</td>
<td>Normal (0.001)</td>
</tr>
<tr>
<td>Tension</td>
<td>40kv</td>
</tr>
<tr>
<td>Current</td>
<td>45mA</td>
</tr>
<tr>
<td>Start Angle</td>
<td>3.0084</td>
</tr>
<tr>
<td>Final Angle</td>
<td>80.0014</td>
</tr>
<tr>
<td>Step Angle</td>
<td>0.0017</td>
</tr>
<tr>
<td>Dwell Time</td>
<td>1 sec</td>
</tr>
</tbody>
</table>

Table 3-7: Parameters of XRD test

Three samples, which include fresh Berea/Ohio sandstone, fresh Nepean sandstone, and the black crust taken from the surface of Berea/Ohio sandstone, were tested with XRD. All samples were finely powdered in an agate mortar before the test.
3.4.2.2 X-ray fluorescence (XRF) spectroscopy

The Bruker Tracer III Hand-Held X-ray Fluorescence Analyser was used to examine the qualitative distribution of the characteristic elements. For each sample, not only was the surface before and after the laser cleaning tested, but also the surfaces of fresh sandstone were analyzed. The test conditions were X-ray tube at 40KV, 30 microamps and the collection time is about 20 seconds.

3.4.2.3 Fourier Transform Infrared Spectroscopy-attenuated Total Reflectance (FTIR-ATR)

In order to identify whether there was organic material in the black crust, a Nicolet Avatar™ 320 FTIR with a Nicolet SMART Golden Gate™ attenuated total reflectance accessory was employed, operating with 32 scans and at a resolution of 4cm⁻¹. Data were processed using EZ OMNIC® 5.2a software.

The initial test was performed on particles of the black crust taken from Berea/Ohio sandstone sample. The black particles were directly placed between the diamond and sapphire anvils. There was no peak of organic material detected but peaks of quartz were. An alternative pre-treatment was adopted to extract and concentrate the possible organic material in the black crust before testing and acetone was used as extracting agent. A sample of about 2-3 g black crust powder was prepared for XRD test. First, the powder was put into a beaker. Then add 10 mL acetone was placed into the beaker. After mixing with a glass bar for about 2 minutes, the beaker was put on a hot plate and temperature was set to 45-50 ºC. The next step was to centrifuge all the extraction liquid that was put into a centrifuging tube. Concentration was achieved by vaporizing most acetone into the clear extraction liquid on a hot plate. The final concentrate was about 1-2 mL. The FTIR analysis was
carried out on the residues of the concentrate, which had been placed on the diamond window of the FTIR instrument after the acetone evaporated completely from the concentrate.

3.4.2.4 Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS)

The surface elemental information was acquired with the MLA 650 field emission gun environmental scanning electron microscope (FEG ESEM) and multiple high-speed energy dispersive X-ray spectrometers (EDS). All samples were observed directly without surface preparation because all experiments were performed under low vacuum and all images were acquired with its back-scattered electron (BSE) imaging detector.

Despite the fact that secondary electrons (SE) images can show the well-defined, three-dimensional appearance of the surface topography, the BSE detector was used. This was because the contrast between areas with different chemical compositions could be detected in BSE images since heavy elements (high atomic number) appear brighter than light elements (low atomic number).
### 3.4.3 Summary of the Samples’ Description and Research Methodology

Please refer to Table 3-8 for an overview of the samples and experiments.

**Table 3-8: Summary of samples’ description**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Description</th>
<th>Sample preparation</th>
<th>Examination methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Berea sandstone from West block (cleaned by the LaserArt-100 Cleaning System)</td>
<td>Laser cleaning Temporary particles slides SEM samples Thick-section Thin-section</td>
<td>Water absorption Color change Surface observation with optical microscopy SEM-EDS XRF</td>
</tr>
<tr>
<td>S2</td>
<td>Nepean sandstone from West block (cleaned by the LaserArt-100 Cleaning System)</td>
<td>Laser cleaning Temporary particles slides SEM samples Thick-section Thin-section</td>
<td>Water absorption Color change Surface observation with optical microscope SEM-EDS XRF</td>
</tr>
<tr>
<td>S3</td>
<td>Cleaned Berea sandstone from West Block (cleaned by the CL500 Laser Cleaning System)</td>
<td>SEM samples</td>
<td>Water absorption Color change Surface observations with optical microscopy SEM-EDS XRF</td>
</tr>
<tr>
<td>S4</td>
<td>Cleaned and un-cleaned Berea sandstone from CCI(cleaned by the LaserBlast 25 Cleaning System)</td>
<td>SEM samples</td>
<td>Color change Surface observation with optical microscope SEM-EDS XRF</td>
</tr>
<tr>
<td>HS1</td>
<td>Nepean sandstone from West block (cleaned by the LaserArt-100 Cleaning System)</td>
<td>Laser cleaning Temporary particles slides SEM samples Thick-section Thin-section</td>
<td>Water absorption Color change Surface observation with optical microscope SEM-EDS XRF</td>
</tr>
<tr>
<td>HS2</td>
<td>Nepean sandstone from West block (cleaned by the LaserArt-100 Cleaning System)</td>
<td>Laser cleaning Temporary particles slides SEM samples Thick-section Thin-section</td>
<td>Water absorption Color change Surface observation with optical microscope SEM-EDS XRF</td>
</tr>
<tr>
<td>HS3</td>
<td>Nepean sandstone from West block (cleaned by the LaserArt-100 Cleaning System)</td>
<td>Laser cleaning Temporary particles slides SEM samples Thick-section Thin-section</td>
<td>Water absorption Color change Surface observation with optical microscope SEM-EDS XRF</td>
</tr>
<tr>
<td>HS4</td>
<td>Nepean sandstone from West block (cleaned by the LaserArt-100 Cleaning System)</td>
<td>Laser cleaning Temporary particles slides SEM samples Thick-section Thin-section</td>
<td>Water absorption Color change Surface observation with optical microscope SEM-EDS XRF</td>
</tr>
<tr>
<td>SC</td>
<td>Cleaned Berea sandstone from West Block (cleaned by the CL500 Laser Cleaning System)</td>
<td>SEM samples</td>
<td>Water absorption Color change Surface observations with optical microscopy SEM-EDS XRF</td>
</tr>
<tr>
<td>BC</td>
<td>Cleaned Berea sandstone from West Block (cleaned by the CL500 Laser Cleaning System)</td>
<td>SEM samples</td>
<td>Water absorption Color change Surface observation with optical microscope SEM-EDS XRF</td>
</tr>
<tr>
<td>CS-1</td>
<td>Cleaned and un-cleaned Berea sandstone from CCI(cleaned by the LaserBlast 25 Cleaning System)</td>
<td>SEM samples</td>
<td>Color change Surface observation with optical microscope SEM-EDS XRF</td>
</tr>
<tr>
<td>CS-2</td>
<td>Cleaned and un-cleaned Berea sandstone from CCI(cleaned by the LaserBlast 25 Cleaning System)</td>
<td>SEM samples</td>
<td>Color change Surface observation with optical microscope SEM-EDS XRF</td>
</tr>
<tr>
<td>CS-3</td>
<td>Cleaned and un-cleaned Berea sandstone from CCI(cleaned by the LaserBlast 25 Cleaning System)</td>
<td>SEM samples</td>
<td>Color change Surface observation with optical microscope SEM-EDS XRF</td>
</tr>
<tr>
<td>CS-8</td>
<td>Cleaned and un-cleaned Berea sandstone from CCI(cleaned by the LaserBlast 25 Cleaning System)</td>
<td>SEM samples</td>
<td>Color change Surface observation with optical microscope SEM-EDS XRF</td>
</tr>
<tr>
<td>CS-9</td>
<td>Cleaned and un-cleaned Berea sandstone from CCI(cleaned by the LaserBlast 25 Cleaning System)</td>
<td>SEM samples</td>
<td>Color change Surface observation with optical microscope SEM-EDS XRF</td>
</tr>
<tr>
<td>CS-10</td>
<td>Cleaned and un-cleaned Berea sandstone from CCI(cleaned by the LaserBlast 25 Cleaning System)</td>
<td>SEM samples</td>
<td>Color change Surface observation with optical microscope SEM-EDS XRF</td>
</tr>
<tr>
<td>CR-7</td>
<td>Cleaned and un-cleaned Berea sandstone from CCI(cleaned by the LaserBlast 25 Cleaning System)</td>
<td>SEM samples</td>
<td>Color change Surface observation with optical microscope SEM-EDS XRF</td>
</tr>
<tr>
<td>CR-8</td>
<td>Cleaned and un-cleaned Berea sandstone from CCI(cleaned by the LaserBlast 25 Cleaning System)</td>
<td>SEM samples</td>
<td>Color change Surface observation with optical microscope SEM-EDS XRF</td>
</tr>
</tbody>
</table>
Chapter 4

Results

4.1 Characterization of Sandstone and Black Crust

4.1.1 Characterization of Sandstone

The physical characteristics found in the literature of the two kinds of sandstone are shown in Table 1-1. The color of the Berea/Ohio sandstone is normally grey, but some near-surface areas may have been yellow or buff. The Nepean sandstone is white to cream in color, but there are also yellow or buff areas in the sandstone. From the results of this research, the Nepean sandstone seemed harder than Berea/Ohio sandstone because it took more time to cut Nepean sandstone than to cut Berea/Ohio sandstone. There are no apparent bedding planes in the samples of either type of sandstone.

4.1.1.1 Mineral Composition of Sandstone

Samples of the two kinds of sandstone were tested with XRD. The results (Figure 4-1) shows the minerals in the Berea/Ohio sandstone sample were mainly quartz and a little amount of clay mineral (kaolinite). Only quartz was identified in the Nepean sandstone sample (Figure 4-2).

Figure 4-1: XRD result of the Berea/Ohio sandstone (sample S1)
4.1.1.2 Thin-section Results

Thin-sections showed that most grains in the Berea/Ohio sandstone were quartz that were sub-angular in shape (Figure 4-3). A small number of sandstone fragments and feldspar were identified in the thin-section under cross-polarized light (Figure 4-4.), but it was hard to identify clay minerals or other minerals filling in between quartz grains. There was some yellow material between grains (Figure 4-3) in the thin-section sample under the plane-polarized light, which had no obvious extinction under the cross-polarized light when rotating the stage. The yellow color may be due to the iron in the material, but this would need to be tested with elemental examination such as SEM-EDS or XRF. The range of size of the quartz grains is 50µm-200µm. In the thin-section of Nepean sandstone (Figure 4-5, Figure 4-6), the bulk of grains are quartz, and the range of size of quartz grains is 50µm-500µm.
Figure 4-3: The thin-section of the Berea/Ohio sandstone (sample S2) under plane-polarized light (100×)

Figure 4-4: The thin-section of the Berea/Ohio sandstone (sample S2) under cross-polarized light (100×)
Despite the fact that both kinds of sandstone have similar mineralogical compositions, they were quite different in terms of mineralogical structure. Grains were more compact in the Nepean sandstone than in the Berea/Ohio sandstone, and there was less cement between grains in the Nepean sandstone than in the Berea/Ohio sandstone. Cement consists of mineral materials that bind the grains in the sandstone. The variations in micro-structure of the quartz grains matched the
differences in pore space (V/V). According to the physical properties in Table 1-1, the pore space of the Nepean sandstone (7.22%) was less than half of that of the Berea/Ohio sandstone (16.4%).

In the back-scattered electron (BSE) image of the Berea/Ohio sandstone (Figure 4-7a), the cement was distinguishable by the lighter gray coloring. The elemental maps (Figure 4-7b, c, d) show that most iron was distributed in the cement that is filled between quartz grains and that minerals containing sulfur and iron were found in the cement.

Figure 4-7: The cement between quartz grains is shown with an (a) back-scattered electron image and the EDS elements maps for (b) iron, (c) sulfur, and (d) silicon.

4.1.2 Characterization of Black Crust

The appearance of the black crust was quite different for the various sandstone samples (Figure 4-8a, b, c). The black crusts on the Berea/Ohio sandstone samples (Figure 4-8a and b) looked darker than that on the Nepean sandstone sample (Figure 4-8c). Even the surface topography of the Berea/Ohio sandstone samples was different. The black crusts on the CCI’s samples (sample set CS and CR) and sample S2 were flat and the black layers cover the surfaces evenly. On the
other hand, the surfaces of S1, S3 (Figure 4-8 b), and S4 were rough and uneven. Furthermore, there were also green stains on these three samples.

![Images of sample surfaces](image)

(a) The surface of the black crust on S2  
(b) The surface of the black crust on S3  
(c) The surface of the black crust on HS1

Figure 4-8: The appearance of the black crust on the Berea/Ohio sandstone (a, b) and the Nepean sandstone (c)

The attachment of the black crust on the sandstone surface was so strong that it was very hard to remove it with water and a plastic brush. Further cleaning tests with other chemical materials and physical treatments were not performed due to a shortage of samples and because this was not the focus of the thesis.

XRD results of the crust (Figure 4-9) showed that there were no peaks of other minerals except peaks of quartz, which means the powder taken from the black crust surface were mainly quartz grains of sandstone. However, this did not mean there were no other minerals in the black crust. It is possible that the content of other minerals is quite low and therefore cannot be detected because of the XRD minimum detection limit being about 1-2% w/w.
4.1.2.1 Medium-scale and Small-scale Observation under Microscope

The surface conditions of black crust on the Berea/Ohio sandstone were shown in Figure 4-10 to Figure 4-16. In Figure 4-10 and Figure 4-11, it was clear that the black crust was a very thin layer covering the quartz grain’s surface that was exposed to the atmosphere. The thickness of the black layer was hard to estimate from the images. The texture of the black crust was clearly shown in Figure 4-12 and Figure 4-13. The surface of the black crust was rough. The waxy green stains (Figure 4-14) on the Berea/Ohio sandstone appeared like patina. For a definite identification, the composition would need to be identified by XRF or SEM-EDS. In the images of the thin-section (Figure 4-15) and thick-section (Figure 4-16), the black crust not only covered the surface of quartz grains but also filled the gaps between quartz grains and open pores on the surface. The thickness of the black crust was no more than 50 µm.
Figure 4-10: Quartz grains with the black crust on the Berea/Ohio sandstone (sample S1) under plane polarized light (200×, focus stacking)

Figure 4-11: A quartz grain with the black crust on the Berea/Ohio sandstone (sample S2) under plane polarized light (200×, focus stacking)
Figure 4-12: A fragment of the Berea/Ohio sandstone with the black crust (sample S2) under plane-polarized light (100×, focus stacking)

Figure 4-13: A fragment of the Berea/Ohio sandstone with black crust (sample S2) under reflected light (100×, focus stacking)
Figure 4-14: Green stains on the Berea/Ohio sandstone with black crust (sample S3) under reflected light (40×, focus stacking)

Figure 4-15: The black crust on the Berea/Ohio sandstone surface in thin-section (sample S2) under plane-polarized light (100×)
The black crust on the Nepean sandstone was quite different in terms of color and structure. The images from Figure 4-17 to Figure 4-21 illustrated the appearance of black crust on the Nepean sandstone. The black crust on the Nepean sandstone was not a continuous film (Figure 4-18, Figure 4-19), so the surface was not completely covered by the black crust. As a result, the color of the surface was not as black as the color of the black crust on the Berea/Ohio sandstone and the sandstone surface could be recognized. The thin-section (Figure 4-20) and thick-section (Figure 4-21) samples further demonstrated that there was less black crust deposited on the Nepean sandstone surface.
Figure 4-17: An aggregate of quartz grains of the Nepean sandstone with black crust (sample HS1) under plane-polarized light (200×, focus stacking)

Figure 4-18: A fragment of the Nepean sandstone with the black crust (sample HS1) under plane-polarized light (100×, focus stacking)
Figure 4-19: The surface of Nepean sandstone with black crust (sample HS1) under reflected light (100×, focus stacking)

Figure 4-20: The black crust on the Nepean sandstone surface in thin-section (sample HS1) under plane-polarized light (100×)
4.1.2.2 Results from SEM with BSE Imaging of Black Crust

In the BSE image of Figure 4-22, the black crust on Berea/Ohio sandstone looked like a very even film covering the surface and this matched observations under the microscope. The film was continuous and smooth, so the angular quartz grains were covered with this film. The small particles in the black crust were clearly shown in Figure 4-23. Such an appearance indicated that the black crust was made up of particles bound with material that could create the texture of a film. The black crust on the Nepean sandstone was shown in Figure 4-24. The black crust only covered some grains on the surface and some angular grains were not covered by the black crust. It seemed that there were less binding materials between particles in the black crust and that more particles could be identified in the black crust in the BSE image of Figure 4-25.
Figure 4-22: BSE image of the black crust on the Berea/Ohio sandstone (sample S1)

Figure 4-23: BSE image of small particles in the black crust on the Berea/Ohio sandstone (sample S1)

Figure 4-24: BSE image of the black crust on the Nepean sandstone (sample HS2)

Figure 4-25: BSE image of black crust on the Nepean sandstone (sample HS1)

4.1.2.3 XRF and SEM-EDS Results of Black Crust

Generally, the XRF results indicated that the elements detected in the black crust surface were silicon (Si), sulfur (S), potassium (K), calcium (Ca), iron (Fe), copper (Cu), lead (Pb) and zirconium (Zr), but the relative peak intensity of these elements are different from the various sandstone samples.

Unmarked peaks in the spectra originate in the instrument and were seen in the background spectrum. The peaks at 2.70 KeV, 2.83, and 2.86 KeV and 2.94 KeV are detector Rh lines. The
peak at 4.66 KeV is the escape peak of detector material (Si) stimulated by Fe Kα X-rays. The peaks at 19.0 KeV, 20.2 KeV, and 21.2 KeV are three broad “instrument peaks”.

Figure 4-26: XRF results of the fresh Berea/Ohio sandstone (sample S1) and the Nepean sandstone (sample SH1)

Figure 4-27: XRF results of the black crust on the Berea/Ohio sandstone (samples S1, S2, S3, and S4)
Figure 4-28: XRF results of the black crust on the Nepean sandstone (samples HS1, HS2, HS3, and HS4)

The peaks of Si and K appeared in all XRF spectra of the black crust (Figure 4-27 and Figure 4-28), but this did not indicate that Si and K were the characteristic elements of the black crust since Si and K peaks were also the significant peaks in the spectra of fresh sandstone (Figure 4-26). One possibility is that XRF can detect the elemental composition of the sandstone under the black crust and the other one is that there are Si and K in the black crust itself. The peaks of S and Ca were very significant in all XRF spectra of the black crust, but there were no significant peaks of S and Ca in the XRF spectra of fresh Nepean sandstone and fresh Berea/Ohio sandstone. Because the characteristic elements of gypsum (CaSO₄·2H₂O) are S and Ca, the existence of S and Ca means gypsum may be one of the materials in the black crust.

The peak of Fe was relatively the highest peak in all XRF spectra of the black crust and fresh sandstone (the Berea/Ohio sandstone and the Nepean sandstone). Whether or not there were materials containing Fe element in the black crust was not clear because the minerals with Fe were the cementing materials in sandstone.
Interestingly, Cu was identified in some Berea/Ohio sandstone samples (sample S1, S3, and S4) and some Nepean sandstone samples (sample HS2 and HS3). The peak of Cu in XRF spectra of sample HS2 and HS3 was low, but it was very high in XRF spectra of sample S1, S3, and S4. It was clear that Cu was one characteristic element of black crust.

Another unexpected peak that appeared in all XRF spectra of the black crust was Pb. The Pb peaks in the XRF spectra of the black crust on the Nepean sandstone samples (sample HS1 to HS4) were relatively lower than those in the XRF spectra of the black crust on the Berea/Ohio sandstone samples (sample S1 to S4, CCI’s sample set CR and CS).

The peaks of Zr appeared in both spectra of fresh sandstone and black crust surface, and it may be a characteristic element of the sandstone.

The characteristic elements identified with XRF were further characterized with SEM-EDS. For the sample S1, the characteristic elements S, Ca, Fe, Cu, and Pb detected at spot A and spot B in Figure 4-29 and spot C was a particle with high Fe. On the other test area (Figure 4-30), S, Ca, Fe, Cu, and Pb were detected at spot A, but the peaks of Pb were quite low. S1, S, Ca, Cl and Cu were found at spot B. There was no Cu or Pb on the test spot of sample S2 (Figure 4-31). The presence of Cl and Cu on test area of S4 (Figure 4-32) indicated that this may be a patina stain and there were also other characteristic elements such as S, Ca, Fe, and Pb. The results of sample HS1 (Figure 4-33) showed that Ca and Fe were found, but other characteristic elements of the black crust on the Berea/Ohio sandstone were not detected on this test area. For the sample HS2 (Figure 4-34), S, Ca, and Fe were detected at three test spots.
Spot A
High: Al, Si, P, S, Ca, Fe, Cu, Pb;
Low: Mg, Cl, K

Spot B
High: Al, Si, P, S, Ca, Fe, Cu, Pb;
Low: Mg, Cl, K,

Spot C
High: Al, Si, P, Fe, Cu;
Low: S, Mg, K, Ca, Cl, Pb

Figure 4-29: Elemental distribution of un-cleaned area on sample S1

Spot A
High Al, Si, S, Ca, Fe, Cu;
Low: P, Mg, K, Pb, Cl

Spot B
High: Al, Si, Cu, Cl, S, Ca;
Low: Fe, Mg, K

Figure 4-30: Elemental distribution of un-cleaned area on sample S1
Spot A
High: Al, Si, K, Ca, Fe

Spot B
High: Al, Si, K, S, Ca;
Low: Na, Mg, P, Fe

Spot C
High: Al, Si, K, S, Ca, Fe;
Low: Mg, P, Cu

Spot D
High: Al, Si, S, K, Ca, Fe;
Low: Mg, P

Figure 4-31: Elemental distribution of un-cleaned area on sample S2

Area A
High Al, Si, S, Ca, Fe, Cl, Cu, Pb;
Low: Mg, P, K

Figure 4-32: Elemental distribution of un-cleaned area on sample S4
Figure 4-33: Element distribution of un-cleaned area on sample HS1

Area A
High: Al, Si, K, Ca, Fe;
Low: Mg, S
Area B
High: Al, Si, K, Ca, Fe;
Low: Mg, S
Area C
High: Al, Si, K, Ca, Fe;
Low: Mg, S, Cu

Figure 4-34: Element distribution of un-cleaned area on sample HS2

Area A
High: Al, Si, K, S, Ca, Fe;
Low: Mg
Area B
High: Al, Si, K, S, Ca, Fe;
Low: Mg
Area C
High: Al, Si, K, S, Ca, Fe;
Low: Mg

Figure 4-35 shows round particle in the black crust, which is believed to be a man-made iron particle, deposited with other soilings on the surface. Crystals of gypsum could be identified in the black crust on the Berea/Ohio sandstone surface (Figure 4-36 and Figure 4-37).
The elemental distribution map of the black crust in the thin-section (Figure 4-38) showed that the S and Ca concentration areas overlapped, which means that there was gypsum in the black crust. There were also high amount of Al and Fe detected in the black crust, but no lead.
(a) Image under plane-polarized light
(b) BSE image
(c) Aluminum EDS map
(d) Iron EDS map
<table>
<thead>
<tr>
<th>(e) Calcium EDS map</th>
<th>(f) Sulfur EDS map</th>
</tr>
</thead>
<tbody>
<tr>
<td>(g) Lead EDS map</td>
<td>(h) Silicon EDS map</td>
</tr>
</tbody>
</table>

Figure 4-38: BSE images and elemental maps of Al, Fe, Ca, S, Pb, and Si for the black crust on the Berea/Ohio sandstone in thin-section sample.
4.1.2.4 FTIR Result of Black Crust

The FTIR results (Figure 4-39) showed the reference spectrum of a hydrocarbon oil and the spectrum of the extract from the black crust (red). The strong peaks at 2853 cm\(^{-1}\) and 2893 cm\(^{-1}\) can be attributed to the stretching of the -CH\(_2\) and -CH\(_3\). These strong peaks and other medium peaks at 1464 cm\(^{-1}\) and 1375 cm\(^{-1}\), which are the bending of -CH\(_2\) and -CH\(_3\), indicated that the black crust may contain hydrocarbon oil. The C=O stretching at 1715 cm\(^{-1}\) and 1732 cm\(^{-1}\) and other weak absorptions indicated that there are other organic compounds present. The broad absorption centred at 1080 cm\(^{-1}\) and the weak doublet at 800/778 cm\(^{-1}\), are due to silica.

![FTIR spectrum](image)

**Figure 4-39: The infrared spectrum of an acetone extract from the black crust and a hydrocarbon oil**

4.2 Characterization of Effects before and after Laser Cleaning

4.2.1 Surface Morphology Changes

Images of surface morphology under normal illumination, optical microscope, and SEM were shown in the appendices.
4.2.1.1 Description of the Color of the Sandstone and the Surface Crust

Images of large-scale observations with a micro-lens are shown in appendix 2. In each image, the left side was the control (un-cleaned area) and the right side was the test area. Figure 4-40 is a representative image of a large-scale observation.

Figure 4-40: Large-scale observation of the sample S1-A under the 105mm micro-lens

The differences between the cleaned area and the un-cleaned area were quite significant in terms of color and surface texture in sample set S and HS, except for the sample HS-4. There was no obvious black crust on HS-4, so the appearance was the same even after laser cleaning. The color of the cleaned areas was different. In sample set S, area B on sample S1 and area B on S3 had the lightest color. The color of area A on sample S1 was the darkest. The same pattern of color variability appeared in sample set HS. Area B on sample HS1 and area B on HS3 have the lightest color. The color of area A on sample HS1 is the darkest. The color change was partly caused by cleaning settings and the reason will be explained in the discussion section.

The boundary between the un-cleaned area and the cleaned area was very clear in most samples, but a zone of transition existed in sample S1, S3, and S4. In Figure 4-40, the bright lines were
identified as the marks of the laser scanning and the dark lines were un-cleaned areas. The scanning lines on other samples were also clearly shown in Figure A2-1, Figure A2-2, Figure A2-5, and Figure A2-7 of appendix 2. The formation of the lines was discussed in the discussion section.

4.2.1.2 Medium-scale and Small-scale Observation Results under Microscope

Medium-scale and small-scale images with a microscope using reflected light are shown in Appendix 3.

For the sample set S (Figure A3-1 to Figure A3-16) and HS (Figure A3-17 to Figure A3-31), two magnifications were used for each sample and the boundary between the un-cleaned area and the cleaned area was captured in each image.

In all test areas of sample set S, most of the black crust covering the quartz grains was removed by laser cleaning with all the different parameters. However, there were some residues of black crust in the gaps between the quartz grains. For all the test areas, the quartz grains were not removed after laser cleaning.

The test area A on sample S3 (Figure A3-9, A3-10) and the test area B on sample S4 (Figure A3-15, A3-16) were cleaned with the same parameters (Table 3-2), except that water was used on test area B before laser cleaning. It seems that the color of quartz grains on test area B of sample S4 is lighter than that on test area A of sample S3, and there are more residues on test area A of sample S3 than that on test area B of sample S4. The cleaning effect on both test areas will be explained in the discussion section.

The situation of the sample set HS was a little different. There was not as much black crust on the Nepean sandstone as on the Berea/Ohio sandstone. The black crust on most test areas of sample set HS was removed by laser cleaning and no quartz grains were removed. The cleaning on test area B of sample HS2 (Figure A3-23, A3-24) looked darker than other test areas and there were more residues on the cleaned surface. This is a test area where water was used and the effect of water will be discussed in the discussion section.
For the sample BC, there are some black particles on the cleaned surface (Figure A3-32, A3-33), but there are no black particles on the fresh surface (Figure A3-34). The cleaned surface of sample SC is shown in Figure A3-35.

For the sample set CS (Figure A3-36 to Figure A3-41) and CR (Figure A3-42 to Figure A3-44), the boundary between the un-cleaned area and the cleaned area was captured in each image. The black crust was removed and the quartz grains were not removed on CS-1, CS-2, CS-3, and CS-10. The residues of black crust remained on the cleaned area of CS-9. For the test areas CR-7 (Figure A3-42), CR-8 (Figure A3-43), and CR-9 (Figure A3-44), the black crusts were removed on CR-7 and CR-9. The residues of black crust were very clear and remain on CR-8.

Images of the particles of the cleaned surfaces with the microscope under transmitted plane-polarized light were shown in appendix 4. The particles were taken from sample set S and HS and sample preparation was not performed on sample set CS, CR, and sample BC and SC.

The residues of the black crust were clearly shown in the images of the particles. For the sample set S (Figure A4-1 to Figure A4-9), the residues are mainly distributed in the gap of quartz grains. For sample set HS (Figure A4-1 to Figure A4-9), the residues were found on test area A of sample HS1 (Figure A4-10, Figure A4-11), test area B of HS1 (Figure A4-12), test area A of sample HS2 (Figure A4-14), test area B of sample HS2 (Figure A4-15), and test area B of sample HS3 (Figure A4-17). There are few black residues on test area A of sample HS3 (Figure A4-16), test area A of sample HS4 (Figure A4-18), and test area B of sample HS4 (Figure A4-19).

4.2.1.3 Observation Results of Thin-section Samples under Microscope

The cleaned surface was hard to identify in the images captured from the thin-section samples for a few reasons. The first reason is that the black crust layer was not a continuous film on the surface as seen in the surface image. Secondly, the black crust could easily be polished away during the preparation of thin-section slides because the black crust was a very thin layer. Therefore, some residues of the black crust after laser cleaning may have been removed by polishing and it is
impossible to know whether there were residues on a cleaned surface. Another problem was that after polishing, in some areas the particles of sandstone were detached from the surface and there was no original surface. The images of thin-section are shown in appendix 5.

4.2.1.4 Observation Results of Thick-section Samples under Microscope

The images captured of thick-sections showed that thick-sections were more useful than thin-sections in this study. The sandstone samples in the thick-sections were preserved very well during polishing since they were mounted in epoxy resin. Therefore, the structure and distribution of black crust in the gaps between quartz grains and in the pores were clearly shown in the images. The focus stacking technique was also used for some images of thick-section samples so that the surface inside the epoxy resin could be captured. The images showing the thick-sections are shown in Appendix 6.

For the sample set S (Figure A6-1 to A6-12), the quartz grains on the surface were preserved well in every test area and the black crust that the laser could reach was removed completely. The black crust that could not be exposed to the laser still remained in the gap of the quartz grains or on the side of the quartz grains.

For the sample set HS (Figure A6-13 to A6-24), the black residues remained on test area A of sample HS1 (Figure A6-13), test area B of HS1 (Figure A6-15), test area A of sample HS2 (Figure A6-16), and test area B of sample HS2 (Figure A6-17). Few black residues remained on test area A of sample HS3 (Figure A6-19), test area B of sample HS3 (Figure A6-21), test area A of sample HS4 (Figure A6-22), and test area B of sample HS4 (Figure A6-23).

4.2.1.5 Observation Results of SEM (BSE images)

Back-scattered electron (BSE) images of the samples are shown in appendix 7. Most images were captured of the cleaned area and some images were the original black crust surface. The
boundary of the cleaned area and the un-cleaned area was captured in Sample S2 (test area A and B), S3 (test area B), S4 (test area B), HS1 (test area B), HS2 (test area A), and HS3 (test area A).

For the sample set S (Figure A7-1 to A7-15), the surface morphology was totally different between the cleaned area and the un-cleaned area. The black crust was a thin, layer that covered most quartz grains on the surface and fills the gaps and the pores between quartz grains. The bright color indicated there were elements with high atomic numbers in this layer. On the surface after laser cleaning, the quartz grains on the surface could be clearly seen. Not only the crusts on quartz grains but also some crusts in pores between the grains were removed. The residues that could be identified on the cleaned surface are gypsum. Gypsum was found on test area B on sample S1 (Figure A7-4) and test area A on sample S4 (Figure A7-13). The investigation results from the black crust indicated gypsum was the main component of the black crust and there was no evidence to show it is a component of sandstone.

For the sample set HS (Figure A7-16 to Figure A7-27), the black crust layer was removed after laser cleaning from each test area. The angular quartz grains were unearthed from the black crust and the gaps and pores between quartz grains were recovered. Figure A7-19 and Figure A7-24 show the boundary of the cleaned area and un-cleaned area on test area B of sample HS1 and test area A of sample HS3. The crust layer covering the quartz grain was removed during laser cleaning and there was no damage to the quartz grains scanned by the laser beam.

On the cleaned surface sample SC (Figure A7-28) and BC (Figure A7-29), the angular quartz grains indicated there was no black crust layer remaining. The bright grains on the surface may have been the cement of the sandstone or the residues of black crust.

For the sample set CS, the condition of the cleaned areas was different. On the cleaned surface of CS-1 (Figure A7-30), most of the crust and soiling on the surface were removed after laser cleaning, but there were gypsum crystals on the surface of quartz grains (Figure A7-31). More residues remained on the cleaned surface of CS-2 (Figure A7-32). Some of the films of black crust
were still covered the quartz grains on the sample CS-9 (Figure A7-33, Figure A7-34) and the cleaning effect on CS-10 (Figure A7-35) was similar to that on CS-1. Most of the black crust was removed after laser cleaning, but gypsum was found on quartz grains (Figure A7-36).

It seems that the surface morphologies of CR-7 (Figure A7-37), CR-8 (Figure A7-39), CR-9 (Figure A7-41) were similar. The angular quartz grains could be clearly seen and the film of black crust that covered the gaps and pores between quartz grains were also removed. However, the distribution of gypsum on the cleaned surface was different. Gypsum was the residue after laser cleaning and it had been identified in previous samples. On the surface of CR-7 (Figure A7-38), a few gypsum crystals attached to the quartz grains and the edges and angles of the quartz grains could be recognized. There were more gypsum and soiling that covered the quartz grains on the surface of CR-8 (Figure A7-40). On the surface of CR-9 (Figure A7-42), the quartz grains could not be identified because gypsum covered them.

4.2.2 Chemical Composition Changes

4.2.2.1 XRF Results

The qualitative elemental analysis using XRF was performed on fresh surfaces, un-cleaned surfaces with the black crust, and cleaned surfaces of each sample (appendix 8). In order to compare the elemental composition for each sample, the spectrograms of each sample were stacked in one graph. For sample sets S1 to S4, HS1 to HS4, sample CS, and sample CR (Figure A8-1 to A8-8 and A8-10 to A8-11), the XRF examinations were performed not only on the surface after laser cleaning but also on the original surface with the black crust and on the fresh sandstone surface. For samples BC and SC (Figure A8-9), only cleaned surfaces and fresh surfaces were tested.

In the XRF spectra of sample set S (Figure A8-1 to Figure A8-4), there were no differences in elemental composition between the cleaned surface and un-cleaned surface. Elemental compositions of two cleaned areas, A and B, were same. The characteristic elements of the black
crust from sample S1, S3, and S4 were sulfur (S), calcium (Ca), copper (Cu), and lead (Pb). These elements were also detected on the cleaned surface no matter which laser cleaning condition was used. Other elements such as silicon (Si), potassium (K), iron (Fe), and Zirconium (Zr) also appeared on fresh sandstone surface. The characteristic elements of black crust on sample S2 were S, Ca, and Pb and the peaks of S, Ca, and Pb were obvious on XRF spectra of cleaned surface.

In the XRF spectra of sample set HS (Figure A8-5 to Figure A8-8), the spectra of the black crust were similar to the spectra of the cleaned area of the samples HS1, HS2, HS3, and HS4. The elements S, Ca, and Pb were characteristic elements in the black crust of samples HS1, HS2, HS3, and HS4, but the peak of Pb was weak compared with the peak in the samples S1, S2, S3, and S4. The peaks of Si, K, Fe, and Zr were significant in the spectra of the cleaned surface, the black crust, and the fresh surface of the samples HS1, HS2, HS3, and HS4.

In the XRF spectra of sample BC (Figure A8-9), the spectra of the cleaned surfaces were similar to the spectra of the fresh surfaces. There were no peaks of S, Ca, Pb, or Cu in the spectra. The situation of sample CS is different. The peak of S, Ca, and Pb appeared only in the spectra of the cleaned surface but not in the spectra of the fresh surface.

In the Figure A8-10, the spectra of CS1, CS2, CS3, CS9, and CS10 were similar to the spectrum of the black crust but the peaks of S, Ca, Pb were relatively a little lower. The peaks of Si, K, Fe, and Zr appeared in the fresh surface, cleaned surface, and black crust. In Figure A8-11, the spectra of CR7, CR8, and CR9 were similar to the spectrum of black crust surface. The characteristic elements of black crust S, Ca, and Pb appeared on the cleaned surface, but the peaks of S and Ca were weaker than those from the black crust.

4.2.2.2 SEM-EDS Results (Characteristic Elements)

The XRF results showed that the characteristic elements of black crust still existed on cleaned surfaces on the Berea/Ohio sandstone and the Nepean sandstone. This meant the residues of black crust remained on the surface in terms of elemental composition. Examination on the residues with
SEM-EDS was helpful to understand the change in the elemental composition after laser cleaning. The minerals or materials contained characteristic elements, including S, Ca, Cl, Fe, Cu, and Pb, and these were also further characterized with SEM-EDS.

In BSE images, materials with heavy elements (high atomic number) have brighter grey scale than those with light elements (low atomic number), so it was easy to recognize the residues of black crust that contains heavy elements such as Cu and Pb. As iron is a component of minerals in both kinds of sandstone and also a component of the black crust, it was hard to understand the source of iron that was detected on the cleaned surface. Another possible residue that may remain after laser cleaning was gypsum, which was a component of black crust and not a component of sandstone. Gypsum was identified in the cleaned samples by its characteristic element S and Ca and by its specific crystal form. The results under the microscope showed that the residues were in the gaps between the quartz grains after laser cleaning, so the investigation was focused on these areas. The results of SEM-EDS are shown in Appendix 10.

For the sample set S (Figure A9-1 to A9-12), the soiling that contains Cu and Pb was found in test areas of samples S1, S3, and S4. These residues remain in the gaps between quartz grains. Iron also appeared with Cu or Pb in the residues. However, iron was also detected in some particles and no Cu or Pb was found. In Figure A9-4 and Figure A9-6, Fe was detected in spot A and no other characteristic elements were found. These areas may be the cement of the sandstone. The molten state of the high-iron particles in Figure A9-6 indicated that the laser did not remove this particle completely but changed its appearance. Although Pb was detected on the cleaned surface of sample S2 by XRF, Pb was not found on the cleaned surface by SEM-EDS. Gypsum was found on all test area of sample set S. Crystals of gypsum were found on the surface of quartz grains (Figure A9-1, Figure A9-3, Figure A9-5, Figure A9-7, and Figure A9-12). Other gypsum was found because elements S and Ca were detected in the residues that also contained Cu or Pb. In Figure A9-10 and
Figure A9-11, Cl and Cu were detected in some spot because the residues of patina remained on the surface.

For the sample set HS (Figure A9-13 to Figure A9-19), Pb was not detected in the soiling or cement of the sandstone between the gaps of quartz grains. S and Ca were detected on the test area A of sample HS1 (Figure A9-13), the test area B of sample HS1 (Figure A9-14), the test area A of sample HS3 (Figure A9-17), and the test area B of sample HS3 (Figure A9-18). Fe was detected in those residues where S and Ca were detected. Fe was also identified on test area A of sample HS1 (Figure A9-13); as no S and Ca were detected, it was determined that the Fe was in cement.

On the cleaned surface of sample BC and SC, no residues were detected containing S, Ca, and Pb and no crystals of gypsum were found. According to observations under the microscope, there were black particles on the cleaned surface of the sample BC (Figure A3-32). SEM-EDS results (Figure A9-20) show that there was a high content of iron in these particles. The high content of iron was also identified on the surface of the sample SC (Figure A9-21).

For the sample set CS (Figure A9-22 to A9-25), Pb was not detected on the cleaned surface of test area CS-1, CS-2, or CS-9. Gypsum was found on the on the cleaned surface of test area CS-1 and CS-9. The SEM-EDS results of the sample set CR showed that the gypsum still exists on the cleaned surface of CR-7 (Figure A9-27), CR-8 (Figure A9-28), and CR-9 (Figure A9-29).

4.2.3 Physical Properties Changes

4.2.3.1 Water Absorption Rate

Despite the fact that the RILEM tube test is not an accurate quantification of water absorption on a porous surface, the data can reflect a characteristic of water absorption. All data are summarized in Appendix 10.

For the sample set S (the Berea/Ohio sandstone), the results of the water absorption rate (Figure A10-1 to Figure A10-4) showed that there was a distinct difference between cleaned samples and un-cleaned samples with the black crust. The water absorption of samples with the black crust was
near zero in one hour; in contrast, the water absorption rate of cleaned samples was very close to the water absorption rate of the fresh surface, which is 5mL in about ten minutes. For the sample S2 (Figure A10-2), the water absorption rate of the fresh surface was 5 mL in about five minutes and the water absorption rate of test area A and B were 5 mL in fifteen minutes and twenty-one minutes respectively. For the sample S3 (Figure A10-3), the water absorption rate of test area A (5 mL in about seven minutes) was higher than that of the fresh surface (5 mL in about nineteen) while the water absorption rate of test area B is much lower. For the sample S4 (Figure A10-4), the water absorption rate of test area A (5 mL in about seven minutes) and B (5 mL in about ten minutes) were close to that of the fresh surface (5 mL in about nine minutes).

For the Nepean sandstone, the water absorption of sample HS-1 with the black crust was near zero in one hour. The water absorbed in one hour ranged from 0.3 mL to 1.2 mL on the cleaned surface. For the sample HS1 (Figure A10-5), the water absorption rate of test area A (0.5 mL in one hour) and B (0.4 mL in one hour) was lower than that of the fresh surface (1.1 mL in one hour). For the sample HS2 (Figure A10-6), the water absorption rate of test area A (1.2 mL in one hour) was little higher than that of test area B (0.8 mL in one hour) and the fresh surface (0.8 mL in one hour). For the sample HS3 (Figure A10-7), the water absorption rate of the fresh surface (0.3 mL in one hour) was lower than that of test area A (0.5 mL in one hour) and test area B (1 mL in one hour). For the sample HS4 (Figure A10-8), the water absorption rate of the fresh surface (0.7 mL in one hour) was lower than that of test area A (1 mL in one hour) and test area B (0.9 mL in one hour). The results of the sample set HS showed that the difference of the water absorption between cleaned samples and a fresh surface was not significant.

For the samples BC (Figure A10-9) and SC (Figure A10-10), the water absorption of the fresh surface was about 5 mL in 4 minutes, but the water absorption rate of the cleaned surface was very different. The water absorption of the cleaned surface on sample BC was near zero in one hour and the water absorption of the cleaned surface on sample SC was 5 mL in 8 minutes. The result on
sample SC was reasonable because the water absorption would increase when the black crust was removed. The abnormal result of sample BC indicated there might have been something that prevented the water from permeating the stone. Another possibility is that the surface was treated with water repellent materials.

4.2.3.2 Color Change

The residue of the black crust on the cleaned surface was an important factor that influenced the color of the cleaned surface. The color of the cleaned surface can reflect how much residue was left on the cleaned surface. Therefore, the color change is a method for evaluating the effectiveness of laser cleaning. Data from color measurements are shown in Appendix 11. For each sample, two differences were calculated for ΔE*ab by using the CIE76 color difference formula. One was the color difference between the black crust surface and the cleaned surface and the other one was the color difference between the fresh surface and the cleaned surface. The results are shown in Table 4-1.
Table 4-1: The results of color difference.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>The color difference between the black crust surface and the cleaned surface</th>
<th>The color difference between the fresh surface and the cleaned surface</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$\Delta L_{1}^*$</td>
<td>$\Delta a_{1}^*$</td>
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<tr>
<td>S1-A</td>
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</table>

Note: $\Delta E_{1}^* = [L_{*}^{black crust} - L_{*}^{cleaned surface}]^2 + (a_{*}^{black crust} - a_{*}^{cleaned surface})^2 + (b_{*}^{black crust} - b_{*}^{cleaned surface})^2]^{1/2}$

$\Delta E_{2}^* = [L_{*}^{cleaned surface} - L_{*}^{fresh surface}]^2 + (a_{*}^{cleaned surface} - a_{*}^{fresh surface})^2 + (b_{*}^{cleaned surface} - b_{*}^{fresh surface})^2]^{1/2}$

S1-A means test area A on sample S1.
Chapter 5

Discussion

The discussion covers mainly six aspects. First, the black crust is further discussed and the origin of the black crust is explained. Second, the laser devices involved in the study were compared and an estimation of the fluences is given for the LaserArt-100 Cleaning System. In the third discussion section on the surface morphology changes, topics are focused on the effectiveness of the laser cleaning and any direct damage caused by laser cleaning. The effectiveness of the laser cleaning was determined by whether the black crust was removed effectively by laser cleaning. The residues were identified by visual inspection under the microscope. Another concern is whether there is any damage to the surface after laser cleaning. The images captured by light microscopy and SEM were analyzed to investigate the direct damage when laser cleaning was performed. The fourth section concentrated on the chemical composition that allowed the identification of the remaining residues from the black crust, after laser cleaning. Characteristic elements of the black crust, detected by XRF and SEM-EDS, were considered to be signs of the residues of the black crust. Physical properties, including water absorption rate and color, are discussed in the fifth part. The results of water absorption rate are discussed to explain the risk of potential future damage over time due to changes in the sandstone surface after laser cleaning. The appearance of the stone samples is also evaluated by visual inspection and by spectrophotometer that measures color change. The color differences are also discussed as an indicator of the cleaning effectiveness because the color change after laser cleaning was associated with the residues that remained on the surface. The effect of water during laser cleaning is discussed in the final part.

5.1 The Characteristics of the Black Crust

The black crust is thicker on the Berea/Ohio sandstone samples than on the Nepean sandstone samples, so the discussion is focused on the black crust on the Berea/Ohio sandstone samples. The
main methods of investigating the black crust were visual observation using microscope and SEM, analysis of elemental composition by XRF and SEM-EDS, and FTIR. The results of these qualitative methods are sufficient for characterizing the black crust. From the visual observation by microscopy, the black crust is a thin layer that not only covers the quartz grains but also fills the gap between the quartz grains. In the images of the thin-section and thick-section, the thickness of the black crust was confirmed. According to the measurements, the thickness of the black crust is no more than 50 µm and only about one tenth to one fifth of the quartz grain’s size. The elemental composition results from XRF indicate the characteristic elements of the black crack vary according to the surface conditions. On the relatively flat surfaces of sample S2 and sample sets CR and CS, the characteristic elements of the black crust are S, Ca, Fe, and Pb. On the rough surfaces of samples S1, S3, and S4, the characteristic elements of the black crust also include Cu in addition to S, Ca, Fe, and Pb. Furthermore, the green stains of the rough surface also contain Cl and Cu. Gypsum was identified and confirmed by SEM-EDS results and the images of gypsum crystals. FTIR results show that the black crust may contain organic materials such as hydrocarbon oil.

There is no doubt that the black crust was the result of industrial and atmospheric pollutants. There was once a pulp and paper mill directly across the Ottawa River (Petrescu-Comnene 2005) and the pollution a few decades ago was much worse. Wet and dry acid deposition reacted with the calcium carbonate that was leached from the lime mortar on the sandstone surface. Gypsum crystals were formed as the result of the reaction. Only a thin layer of crust containing a limited amount of gypsum developed over time due to an insufficient supply of Ca²⁺. On the surface of marble or limestone, such a layer could be quite thick. The copper compounds were derived from the corrosion of the copper roof and rainwater brought them to the sandstone surface. Other airborne particulates and particles created by the combustion of fossil fuels were also important sources for the black crust. Lead is associated with lead tetraethyl added to gasoline. The black color may be due to soot and iron compounds in the black crust. Combustion of coal and gasoline can create
airborne soot, which contains elemental carbon and organic carbon. GC-MS results from other research showed that there were 60 different organic compounds, including n-alkanes, alkylated aliphates, and other hydrocarbons, in the black crust on the outdoor monuments in Europe (Nord 1993).

Black crust on limestone or marble is not stable because exogenous sulphur can react with the limestone and marble and generate more gypsum. In this study, the sandstone under the black crust is well preserved and no sign of further deterioration was found on all samples. It seems the crust is a relatively harmless layer.

5.2 Comparison of Laser Cleaning Systems and the Parameters

Before any evaluation of the cleaning effects with various laser devices, it is necessary to compare the features of the laser devices and the parameters. Detailed information about the basic performances of laser devices is shown in Table 3-1, Table 3-3 and Table 3-4. Two modern industrial laser devices, the LaserArt-100 Cleaning System and the CL500 cleaning system, and one small laser cleaning device (a LaserBlast 25 model from Atlas Laser Systems) from 1995 were involved. Unfortunately, less information exists for the CL500 cleaning system. It is a laser cleaning system similar to the LaserArt-100 Cleaning System. According to the data sheet describing the basic performance of the LaserArt-100 Cleaning System and the LaserBlast 25 model from Atlas Laser Systems, they are both Nd:YAG lasers with a 1064 nm wavelength. Other critical performances such as power, pulse duration, frequency, and beam size are different for two laser devices. The maximum power of the LaserBlast 25 model is 1W and the maximum power of the LaserArt-100 Cleaning System is 100W. The pulse duration of the LaserBlast 25 model is 25ns, but the pulse duration of the LaserArt-100 Cleaning System is from 10ns to 350ns. The maximum frequency of the LaserBlast 25 model is only 50Hz, but the frequency of LaserArt-100 Cleaning System can be adjusted from 1 KHz to 1000KHz.

The beam diameter of the LaserBlast 25 model is 3 or 4mm. The beam size of the LaserArt-
100 Cleaning System was unavailable from the product presentation. However, on a number of samples, there are some scanning lines on the boundary between the cleaned area and the un-cleaned area and the lines provided a reasonable estimate of the beam diameter. The working distance may change slightly for the different settings, so the scanning line width is a little different for each sample. The beam diameter was estimated by measuring the width of the bright line, assuming that the section of the beam is a circle. Blue lines in Figure 5-1 to 5-4 mark the width of some beam scanning traces. The fluences used for the cleaning tests were calculated according to the estimated beam diameter and the results are shown in table 5-1. The formula is the fluence =Pulse energy (J)/area of the beam on the surface (cm²). Obviously, the fluences of the LaserBlast 25 model (0.141J/cm² to 0.282J/cm²) are lower the fluences of the LaserArt-100 Cleaning System.

Figure 5-1: Scanning lines on test area A of sample S1. (100×, focus stacking)

Figure 5-2: Scanning lines on test area A of sample S3 (40×, focus stacking)
Table 5-1: Parameters, estimated beam size, and the fluences of the LaserArt-100 Cleaning System

<table>
<thead>
<tr>
<th>Test area</th>
<th>Power (W)</th>
<th>Repetition rate (KHz)</th>
<th>Pulse duration (ns)</th>
<th>Pulse energy (J)</th>
<th>Beam diameter (mm)</th>
<th>Fluence (J/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2-A HS4-A</td>
<td>75%</td>
<td>1000</td>
<td>10</td>
<td>7.50×10⁻³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1-A HS1-A</td>
<td>90%</td>
<td>850</td>
<td>20</td>
<td>1.06×10⁻⁴</td>
<td>0.18</td>
<td>0.42</td>
</tr>
<tr>
<td>S2-B HS4-B</td>
<td>90%</td>
<td>550</td>
<td>30</td>
<td>1.63×10⁻⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S4-A HS2-A</td>
<td>90%</td>
<td>220</td>
<td>60</td>
<td>4.09×10⁻⁴</td>
<td>0.24</td>
<td>0.90</td>
</tr>
<tr>
<td>S3-A S4-B (water)</td>
<td>90%</td>
<td>160</td>
<td>100</td>
<td>5.63×10⁻⁴</td>
<td>0.25</td>
<td>1.15</td>
</tr>
<tr>
<td>S2-B (water) HS3-A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1-B HS1-B</td>
<td>90%</td>
<td>90</td>
<td>200</td>
<td>1.00×10⁻³</td>
<td>0.29</td>
<td>1.51</td>
</tr>
<tr>
<td>S3B HS3B</td>
<td>90%</td>
<td>80</td>
<td>350</td>
<td>1.125×10⁻³</td>
<td>0.33</td>
<td>1.31</td>
</tr>
</tbody>
</table>

It is clear that the LaserArt-100 Cleaning System uses a relatively low energy pulse at very high repetition rates and creates a small laser beam that can scan the surface very fast. Such a scanning mode allows the laser to achieve a faster cleaning rate. However, it is harder to control the cleaning level because of the high repetition rate. On the other hand, the LaserBlast 25 model is the typical type of laser that is used in conservation. Very low repetition rates make it possible to control the cleaning level, but the cleaning speed is slow. Obviously, a laser device like the LaserArt-100
Cleaning System is more suitable for cleaning buildings or monuments because the cleaning level does not need to be finely controlled, while efficiency and cleaning speed are required. A laser device like the LaserBlast 25 model is more suitable for small objects or places where precise control is the primary consideration during the laser cleaning process.

Laser cleaning is a complicated process and the cleaning effect may vary due to the laser device and parameters used, as well as the surface conditions. Strictly speaking, it would be impossible to compare the cleaning effect between the new laser device and the laser device used twenty-three years ago if the samples were not cleaned with the same fluence and pulse duration, which are the most critical parameters. However, it seems that the removal of the black crust was achieved by using the LaserBlast 25 model with lower fluences and the LaserArt-100 Cleaning System with higher fluences.

Only some parameters were used with the LaserArt-100 Cleaning System because the laser operator chose the parameter combinations from his experience, rather than being systematic. This meant that a comparison of the effectiveness of the laser cleaning was limited to these parameter combinations. The discussion of the effectiveness of laser cleaning could not, therefore, aim to find the best parameters for cleaning the sandstone on the Parliament Buildings.

5.2 Surface Morphology Changes

5.2.1 Examination of the Residues

The most significant change for the surface morphology was that the black crust on the surface had been removed on all samples, but residues of black crust were still found on most samples. Detection of the residual black crust is an indication of the effectiveness of the cleaning.

There are two kinds of residues. One type is the residues that were not removed completely during the interaction with a laser. The other kind of residue is the black crust that remains in the
pores or in the gaps between quartz grains after laser cleaning because no interaction happened between these residues and the laser during laser cleaning.

5.2.1.1 Residues Due to Interaction with a Laser

On the cleaned surface, two kinds of residues were found on the surface of quartz grains. The most significant one is gypsum that was still attached on the surface of quartz grains. The other one is the filmy residues causing the darkish surface of the quartz grains. Both kinds of residues were the results of the interaction between the black crust and a laser.

Gypsum crystals survived the laser cleaning and maintained their crystal shape. Figure 5-5 shows a BSE image of gypsum crystals on test area A of sample S3. In fact, the fluences that were used in the cleaning tests were lower than the fluence that can cause damage to gypsum. The damage threshold of selenite, a crystal formed from the mineral gypsum, is quite high. A study showed that no damage was found on the selenite surface after a significant number of laser pulses in the selected fluence range from 0.5 ± 0.2 J/cm² to 6.5 ± 0.2 J/cm². The tests were performed with a Q-switched Nd:YAG laser system (pulse duration 6 ns) at a wavelength of 1064 nm. XRD and Raman spectroscopy results proved that there were no changes in the crystalline phase of calcium sulphate dihydrate (CaSO₄·2H₂O), the crystal structure of natural gypsum (Grammatikakis et al. 2015).
Most gypsum in the black crust that was not attached to the quartz grains was removed during the process of laser ablation. The gypsum in the black crust could be removed because the surrounding crust had a lower damage threshold during vaporization and ablation. When all materials surrounding the gypsum particles were removed, the gypsum could not stay on the surface.

Some gypsum crystals attached to the quartz grains could survive the laser cleaning because a laser with low fluence cannot damage the gypsum or the quartz grain substrate. In BSE images (Figures A7-2, 4, 13, 31, 36, 38, 40, and 42), crystalline gypsum was identified by its specific crystal and confirmed by elemental composition. For the LaserArt-100 Cleaning System, the highest fluence was about 1.5 J/cm². Crystalline gypsum was found on most test areas of sample set S (the Berea/Ohio sandstone) but was not found on test areas of sample set HS (the Nepean sandstone). The reason why there was no crystalline gypsum on the quartz surface of the Nepean sandstone needs to be studied further. For sample sets CS and CR which were cleaned by the LaserBlast 25 Cleaning System, crystalline gypsum was found on most test areas. The highest fluence used for the LaserBlast 25 Cleaning System was 0.282 J/cm². For cleaned samples SC and
BC, no crystalline gypsum was found. The explanation could be determined if more information about laser cleaning using the CL500 Laser Cleaning System was available.

Gypsum crystals were attached to the quartz grain and there were no other materials between the gypsum and the quartz grain. The attachment was so strong that a laser with low fluence could not break it. Theoretical, a high-fluence laser that could damage the gypsum would also cause damage to the quartz. Laser cleaning or other mechanical cleaning methods may not suitable under such circumstances. Conventional cleaning methods based on a chemical agent that could dissolve the gypsum may be suitable if it was necessary to remove all the residual gypsum.

The cleaned surface that was supposed to be similar to fresh sandstone was still dark in color in some samples. Residues that remained in the gaps between the quartz grains partly contributed to the darkish surface. Further investigations using microscopy and SEM indicated the quartz grains were also covered by something that caused the darker color. The color of the cleaned quartz grains was therefore not as light as the original color of the fresh quartz grains. This color change was observed in most samples and the level was different according to fluences of laser cleaning. The color of quartz grains in test area A of sample S1 is obviously darker than the color of fresh quartz grains in Figure 5-6. Figure 5-7 shows the appearance of the filmy residues that contain S, Ca, Fe, Cu, and Pb. This thin residue may be related to the dark color of quartz grains in test area A of sample S1.
The cleaned surface of test area B on sample S3 (Figure 5-8) was the lightest test area in sample set S. Some quartz grains were as light as the fresh grains and others were still darker (Figure 5-9). This may indicate that the black crust covering the quartz grains was not removed completely by laser cleaning and the residues remaining on the surface of quartz grains led to the darkish color. Another possibility is that this is the so-called “patina” below the black crust. However, unlike the limestone and marble, there is no sign of such a layer exists on the surface of quartz grains when examining the thin-section and thick-section samples.

The darkish quartz grains were not significant in the test areas for sample set HS. Because the
condition of the black crusts varied on different samples, a slightly dark color can be noticed on the cleaned areas A and B of Sample HS1 (Figure 5-10, Figure 5-11). In Figure 5-11, the darkish quartz grains are easier to recognize when compared with the fresh sandstone grains.

![Figure 5-10: Cleaned surface of test area A on sample HS1 (right side) (40 ×, focus stacking).
Estimated fluence=0.42J/cm²
Pulse duration=20ns](image1)

![Figure 5-11: Cleaned surface of test area B on sample HS1 (right side) and the fresh sandstone (right top corner) (40×, focus stacking).
Estimated fluence=1.51J/cm²
Pulse duration=200ns](image2)

On the sample BC (Figures A3-32 and Figures A3-33) and SC (Figures A3-34 and Figures A3-35), this darkish color was not significant and there were no residual black crusts on either sample. It is assumed that high fluence was used and all black crusts were removed.

For the sample set CS, the appearance of quartz grains in samples CS-1 and CS-2 are shown in Figures 5-12 and Figure 5-13. The color of the quartz grains in sample CS-2 (Figure 5-13) was a little darker than that in CS-1 (Figure 5-12) because less residue was left on the surface of quartz grains when higher fluence was used for sample CS-1. For sample set CR (Figure 5-14 to Figure 5-16), the relationship between the level of darkish color of quartz grains and the fluence was more clear. With an increase of fluence, there was less residue on the quartz grains and the color of the quartz grains was closer to the color of the fresh ones.
Figure 5-12: Cleaned area (right side) on sample CS-1 (100×, focus stacking).
Fluence =0.282 J/cm²
Pulse duration=25ns

Figure 5-13: Cleaned area (right side) on sample CS-2 (100×, focus stacking).
Fluence =0.159 J/cm²
Pulse duration=25ns

Figure 5-14: Cleaned area (right side) on sample CR-7 (100×, focus stacking).
Fluence =0.282 J/cm²
Pulse duration=25ns

Figure 5-15: Cleaned area (right side) on sample CR-8 (100×, focus stacking).
Fluence =0.141 J/cm²
Pulse duration=25ns

Figure 5-16: Cleaned area (right side) on sample CR-9 (100×, focus stacking).
Fluence =0.21 J/cm²
5.2.1.2 Residues Remaining due to No Direct Exposure to the Laser

Some residues remained in the pores or in the gaps between quartz grains after laser cleaning. The distribution of the residual black crusts is clearly shown in the images of the following thin-section (Figure 5-17) and thick-section (Figure 5-18). Most of the black crusts on top of the quartz grains were removed by laser cleaning. The residual black crusts remained in positions that were not exposed to the laser directly, so there was no interaction between those black crusts and the laser.

![Figure 5-17](image1)
**Figure 5-17: Residual black crust on test area A of sample S3 (100×, plane polarized light)**

![Figure 5-18](image2)
**Figure 5-18: Residual black crust on test area B of sample S2 (100×, reflected light)**

Using a laser with higher fluence may remove these residues, but the risk of damaging the sandstone would be correspondingly higher. If the black crust between the gaps of the quartz grains was removed during laser ablation with a higher fluence, the quartz grains could be detached when the black crust was being ablated.

The residues that remain in the pores or in the gaps between the quartz grains may prevent water from penetrating the sandstone, so any physical or chemical erosion caused by water could be reduced. From this point of view, keeping some residues benefit the long-term preservation of the sandstone surface.
5.2.2 Examination of Direct Damage

Beside the presence of residues, another consideration is whether there is damage caused by laser cleaning. Any changes to the sandstone itself were investigated in terms of morphology. In the images captured using microscopy and SEM, the original quartz grains were seldom removed during the laser ablation process. Figure 5-19 and Figure 5-20 show that the quartz grains were stable after laser ablation even when relatively higher fluence was used in the tests. When the laser scanned the surface, there were no changes to the quartz grains on the surface.

![Figure 5-19: Boundary of the un-cleaned area (left side) and cleaned area B (right side) on sample S3 (100×, focus stacking)](image1)

![Figure 5-20: BSE image of the boundary of the un-cleaned area (left bottom) and cleaned area B (right top) on sample S3](image2)

5.3 Chemical Composition Changes

Theoretically, the effectiveness of removing the crust can be determined by comparing the characteristic elements of the black crust before cleaning and after cleaning. Qualitative results of from XRF and SEM-EDS were used to determine the characteristic elements from the black crust on the cleaned surface and identify any residues. The characteristic elements of the black crust, including S, Ca Cl, Cu, Fe, and Pb, are discussed below.
5.3.1 S and Ca (Gypsum)

Gypsum is one of the main components of the black crust. Gypsum can be identified by its specific shape and elemental composition. Unlike the situation with Cu and Pb, S and Ca can be detected everywhere on the black crust because the gypsum exists throughout the black crust. After laser cleaning, the crystalline gypsum that was attached to the quartz grains is easy to identify by its specific crystal shape and elemental composition. For the gypsum that remains in the residues after laser cleaning, detection of S and Ca is the only way to confirm its existence because the gypsum crystal surrounded by other materials in the residues is hard to identify by its crystal.

XRF results show that S and Ca were detected in all cleaned samples except for sample BC. The surface condition of sample BC before laser cleaning was not documented, so it is hard to explain why there was no gypsum on sample BC.

5.3.2 Element Cl

Cl is a characteristic element of the black crust on Sample S1, S3, and S4 and it appears only when green stains were detected. The SEM-EDS results show that the green stains are the corrosion products of copper and may contain atacamite (Cu$_2$Cl(OH)$_3$). After cleaning, Cl was detected in the residues on test area B of sample S4 (Figure A9-11). This means some patina stains were not completely removed.

5.3.3 Element Cu

Cu was identified on three samples: S1, S3, and S4. According to the results, Cu was found not only in the green patina stains but also in the black crust of those samples. After laser cleaning, Cu can still be detected on the sandstone surface and appears with S, Ca, Fe, and Pb. The existence of Cu confirms the residual black crust remains on sandstone surface.
5.3.4 Element Fe

XRF results showed that Fe was found on fresh Nepean sandstone and Berea/Ohio sandstone and in the black crust. SEM-EDS results also indicated that Fe was detected with the characteristic elements S, Ca, Pb, or Cu in the black crust. After laser cleaning, XRF results proved the existence of iron on the cleaned surface. Further examination with SEM-EDS results showed that, if Fe still appeared with the characteristic elements of the black crust (S, Ca, Pb, or Cu), it belonged to the residues of black crust and if no other characteristic elements of the black crust (S, Ca, Pb, or Cu) were detected with Fe, it was part of the elemental composition of sandstone.

5.3.5 Element Pb

Pb was a characteristic element of the black crust and it appeared in the black crust of both Nepean sandstone and Berea/Ohio sandstone. After laser cleaning, Pb was detected in the residues of all samples except for sample BC.

5.4 Physical Properties Changes

5.4.1 Water Absorption Rate

After laser cleaning, the water absorption rate of sample set S (the Berea/Ohio sandstone) increased significantly. The water absorption rate of cleaned samples is close to the water absorption rate of fresh surfaces and the water absorption rate of samples with the black crust is near zero. For the Nepean sandstone, the water absorption rates of the black crust surfaces are zero and the water absorption rates of the cleaned surfaces and fresh surfaces are a little higher. The water absorption rate of the fresh Nepean sandstone is much lower than that of the fresh Berea/Ohio sandstone because of the lower porosity of the Nepean sandstone (Table 1-1). The black crust on sandstone surface can prevent water from soaking into sandstone.

The water absorption rate obtained using the RILEM tube can provide useful information about the potential vulnerability of stone to water-related deterioration. Water plays an important role in
the deterioration processes affecting porous material such as stone and brick. The water within the pore structure of stone is involved in the physical destruction of the pore structure if the stone undergoes wet/dry or freeze/thaw cycling. These two processes can particularly cause deterioration of sandstone because of its high porosity and high clay mineral content. Normally, the water absorption rate should increase when weathering happens on the stone because the weathering process can increase the porosity of stone. The water absorption rate can predict the degree of deterioration that has occurred. In contrast, water permeability is also an indicator of the vulnerability of stone to water-related deterioration. A stone surface with a high water absorption rate is more vulnerable to weathering than a stone surface with a relatively low water absorption rate.

Conservation intervention measures aim to reduce the water absorption of the stone surface and therefore effectively prevent the stone from water-related deterioration. In fact, a weathering crust or atmospheric soiling on sandstone surface can play such rule and is beneficial to preserving the stone surface. The sandstone surface becomes vulnerable when the black crust is removed completely and the risk of damage from water infiltration is much higher. The residues of black crust remaining in the gaps between the quartz grains may be beneficial to resisting the weathering from the water.

5.4.2 Color Change

\( \Delta E_1^* \), the color difference between the black crust surface and the cleaned surface, can be considered an indicator of the cleaning effect since the color of the cleaned surface is related to the residual material on the surface. \( \Delta E_2^* \), the color difference between the fresh surface and the cleaned surface, can reflect the level of darkness. The results again (Table 4-1) show that the color difference can mainly be attributed to the difference in lightness (\( \Delta L^* \)).

Visual inspection determined the following for sample set S. Test area B on sample S3 (S3-B) is the brightest. Test areas A on sample S3 (S3-A) and test areas B on sample S1 (S1-B) are slightly
less light. Test areas A and B on S2 and S4 (S2-A, S2-B, S4-A, S4-B) are much darker and the
darkest is test areas A on sample S1 (S1-A). The trend in $\Delta L_1^*$ values for sample set S (Figure 5-21) matched visual inspection. Also, $\Delta L_1^*$ values matched $\Delta E_1$ values, realising that the overall color difference is mainly caused by $\Delta L_1^*$.

![Figure 5-21: Comparsion of $\Delta L_1^*$ of sample set S](image)

The fluences used for S3-B, S3-A, and S1-B, the lighter areas, are higher than 1J/cm$^2$ and the fluences used for other test areas are lower than 1J/cm$^2$. Despite the fact that the pulse duration also influences the cleaning effect, the tendency in sample set S is that the higher the fluence, the lighter in color the cleaned surface will be.

The color of the cleaned surfaces for the sample set S is still darker than the color of fresh surfaces. The value of $\Delta L_2^*$ (the lightness difference between the fresh surface and the cleaned surface) is more than -20 only for S3-B, S3-A, and S1-B. These three test areas are lighter than the other test areas because of the relatively higher fluence. Another phenomenon is that the values for $\Delta b_2^*$ range from -7.15 to -4.91 for all test areas in sample set S. This means the fresh surface is more yellowish than the cleaned surface. The yellow color of the Berea/Ohio sandstone is due to the iron in the cement of sandstone. This phenomenon was discussed by Martin Cooper (1998, 63). Some cement may have been removed or laser cleaning may have modified the oxidation state of iron. As a result, the level of yellow decreased.
For the sample set HS, the conditions of the black crust were different. There was less black crusts on sample HS4, so the comparison was focused on sample HS1, HS2, and HS3. Test area B on sample HS1 and test area B on sample HS3 were the lightest test areas. The other test areas were slightly darker. The \( \Delta L_1^* \) values of sample set HS (Figure 5-22) matched the visual inspection. The estimated fluences for test area B on sample HS1 and test area B on sample HS3 were higher than the fluences for other test areas. The \( \Delta E_2^* \) values for test area B on sample HS3 was only 2.77 and the \( \Delta L_2^* \) was -2.1, which means the color of HS3-B was close to the fresh sandstone. The \( \Delta E_2^* \) values of other test areas ranged from 11.32 to 27.47.

![Figure 5-22: Comparsion of \( \Delta L_1^* \) of sample set HS](image)

For the sample set CS and CR, the test areas were divided into three group according to the value of \( \Delta L_1^* \) (Figure 5-23). The values of \( \Delta L_1^* \) for the sample CS-1 and CR-7 were more than 30 and the values of \( \Delta L_1^* \) of the sample CS-2, CS-3, CS-8, CS-10, and CR-9 ranged from 23.33 to 27. Samples CS-9 and CR-8 had the smallest values for \( \Delta L_1^* \). The tendency for sample set CR was clear. A higher value of \( \Delta L_1^* \) meant a more intense cleaning effect was achieved by using higher fluence. The fluence for the sample CR-7, CR-8, CR-9 were 0.282 J/cm\(^2\), 0.141 J/cm\(^2\), and 0.21 J/cm\(^2\) respectively. The situation for sample set CS was a little different. Although the same fluence was used for CS-2, CS-3, CS-8, CS-9 (fluence = 0.159 J/cm\(^2\)), the value of \( \Delta L_1^* \) of CS-9 was lower than that of others. The reason may have been the time spent on cleaning was not long enough.
The cleaned surfaces of all the samples looked slightly darker than the fresh surfaces except for samples BC and SC which had smaller color changes (\(\Delta E_2^*\)). The color difference between the fresh surface and the cleaned surface was 1.59 for sample SC and 5.17 for sample BC, which means the color of the cleaned surface was close to the fresh sandstone for these two samples.

**5.5 Effect of Water during Laser Test**

During the laser cleaning test, two test areas were wetted to investigate the effect of water. The same parameters, 100ns for pulse duration and 160KHz for repetition rate, were used for the wetted surface and un-wetted surface.

For the Berea/Ohio sandstone, test area A on sample S3 was not wetted and test area B on sample S4 was wetted. In Figure 5-24 and Figure 5-25, the color change of both test areas by eye and under the microscope was at the same general level; however, the spectrophotometer results of the color differences indicated the values of \(\Delta E_1^*\) of test area A on the sample S3 and test area B on sample S4 were 21.58 and 16.70 respectively. This result did not match the visual inspection perfectly. Higher \(\Delta E_1^*\) means fewer residues on the surface. It seems that the water was not helpful for improving the cleaning effectiveness for the Berea/Ohio sandstone.
Figure 5-24: Test area A on sample S3 (not wetted) (40×, focus stacking)

Figure 5-25: Test area B on sample S4 (wetted) (40×, focus stacking)
Chapter 6

Conclusion

The goal of this study was to characterize the laser cleaning effects on sandstone from the Parliament Buildings. Two kinds of sandstone, the Berea/Ohio sandstone and the Nepean sandstone, were examined. Both kinds of sandstone were widely used as building materials in the Parliament Buildings. XRD results showed that quartz is the main mineral in both kinds of sandstone and there is also a small amount of clay mineral (kaolinite) in the Berea/Ohio sandstone. SEM-EDS and XRF results showed that minerals containing iron are the cement in both sandstones.

There were more black crusts on the Berea/Ohio sandstone samples than on the Nepean sandstone samples. In order to characterize the black crust, several methods were used. The results of visual inspection using microscopy showed that the black crust was a very thin layer covering the quartz grain’s surface and also filled the gaps between the quartz grains on the surface of the Berea/Ohio sandstone. The thickness of the black crust was no more than 50 µm. On the Nepean sandstone surface, the amount of black crust was too little to form a continuous film. The elemental composition of the black crust was identified using XRF and SEM-EDS. The characteristic elements of the black crust were S, Ca, Fe, and Pb. Cu and Cl were detected in some samples and were related to copper corrosion. The gypsum in the black crust was confirmed by the BSE images. The FTIR results indicated that the organic materials of the black crust contained hydrocarbon oil.

Tests on the Berea/Ohio sandstone and the Nepean sandstone were performed using the LaserArt-100 Cleaning System with different parameters. The black crust on both kinds of sandstone can be removed by laser cleaning, but results showed that residues of black crust were still found on the cleaned surface. Gypsum crystals were identified on the cleaned the surfaces of both kinds of sandstone by BSE images. XRF and SEM-EDS results indicated that the characteristic elements of the black crust, including S, Ca, Pb, Fe, Cu, still existed in the residues. The results of
the RILEM tests showed the water absorption rate of the Berea/Ohio sandstone with the black crust was near zero and the water absorption rate of the cleaned Berea/Ohio sandstone was increased significantly after laser cleaning. The water absorption rate of the cleaned Nepean sandstone and the fresh surface were a little higher than the water absorption rate of the black crust surface, which was near zero. The color differences between the fresh surfaces and the cleaned surfaces of the sandstone samples were significant. The darker color of the cleaned surfaces was due to the residual black crust remaining on the surface, including the residues remains in the gap between quartz grains and the filmy residues covering the quartz grains. Water seems not to improve the effectiveness of cleaning on the Berea/Ohio sandstone.

For the sample BC and SC, there were no obvious residues on the cleaned surface and the color change was not obvious. Black particles containing iron were detected on the surface on BC and Pb was found on the surface of SC.

The sample sets CR and CS were cleaned by the LaserBlast 25 model twenty-three years ago, but the tests still are valuable to reference. The LaserBlast 25 model achieved the same cleaning effect on the Berea/Ohio sandstone by using relatively lower fluence compared with the LaserArt-100 Cleaning System. Residues were found on the cleaned surface and gypsum was identified. The lightness of the quartz grains increased with an increase of fluence.

The most important factor for laser cleaning is the optimization of the parameters through testing. An ideal cleaning is a balance between cleaning effectiveness and not causing damage. In this study, the residues would be removed more completely if a higher fluence was used, but the risk of damage would be higher. The sandstone could be more vulnerable to weathering caused by water. Conversely, some of the black crust would remain on the surface if lower fluence was applied. The color of the surface would be not ideal, but residues on the cleaned surface could be beneficial to resisting the weathering.
For a laser cleaning system like the LaserArt-100 Cleaning System, a high repetition rate allowed for a faster cleaning rate, but further testing and study is still needed to control the cleaning level. The optimization of critical parameters such as fluence and pulse duration is required to get the appropriate balance between cleaning effectiveness and minimization of damage.
Bibliography


Appendices

Appendix 1: Photo documentation of sample set S and HS after laser cleaning

Figure A1-1: The appearance of sample S1

Figure A1-2: The appearance of sample S2

Figure A1-3: The appearance of sample S3

Figure A1-4: The appearance of sample S4
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Figure A1-6: The appearance of sample HS2

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Figure A2-5: The boundary of the un-cleaned area (left side) and cleaned area A (right side) on sample S3

Figure A2-6: The boundary of the un-cleaned area (left side) and cleaned area B (right side) on sample S3
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Figure A2-8: The boundary of the un-cleaned area (left side) and cleaned area B (right side) on sample S4

Figure A2-9: The boundary of the un-cleaned area (left side) and cleaned area A (right side) on sample HS1

Figure A2-10: The boundary of the un-cleaned area (left side) and cleaned area B (right side) on sample HS1

Figure A2-11: The boundary of the un-cleaned area (left side) and cleaned area A (right side) on sample HS2

Figure A2-12: The boundary of the un-cleaned area (left side) and cleaned area B (right side) on sample HS2
Figure A2-13: The boundary of the un-cleaned area (left side) and cleaned area A (right side) on sample HS3

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Figure A3-3: un-cleaned area (left side) and cleaned area B (right side) on sample S1 (40×, focus stacking)

Figure A3-4: un-cleaned area (left side) and cleaned area B (right side) on sample S1 (100×, focus stacking)

Figure A3-5: un-cleaned area (left side) and cleaned area A (right side) on sample S2 (40×, focus stacking)

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Figure A3-11: un-cleaned area (left side) and cleaned area B (right side) on sample S3 (40×, focus stacking)

Figure A3-12: un-cleaned area (left side) and cleaned area B (right side) on sample S3 (100×, focus stacking)
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Figure A3-15: un-cleaned area (left side) and cleaned area B (right side) on sample S4 (40×, focus stacking)

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Figure A3-17: un-cleaned area (left side) and cleaned area A (right side) on sample HS1 (40×, focus stacking)

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Figure A3-19: un-cleaned area (left side) and cleaned area B (right side) on sample HS1 (40 ×, focus stacking)

Figure A3-20: un-cleaned area (left side) and cleaned area B (right side) on sample HS1 (100 ×, focus stacking)

Figure A3-21: un-cleaned area (left side) and cleaned area A (right side) on sample HS2 (40 ×, focus stacking)

Figure A3-22: un-cleaned area (left side) and cleaned area A (right side) on sample HS2 (100 ×, focus stacking)

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Figure A3-27: un-cleaned area (left side) and cleaned area B (right side) on sample HS3 (40 X, focus stacking)

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Figure A3-44: un-cleaned area (left side) and cleaned area (right side) on sample CR-9 (100 ×, focus stacking)
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Figure A4-2: Aggregates of quartz grains taken from cleaned area B on sample S1 (200×, focus stacking)

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Figure A4-6: Aggregates of quartz grains taken from cleaned area A on sample S3 (200×, focus stacking)
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Figure A4-8: A quartz grain taken from cleaned area A on sample S4 (200 ×, focus stacking)

Figure A4-9: A quartz grain taken from cleaned area B on sample S4 (200 ×, focus stacking)

Figure A4-10: A aggregate of quartz grains taken from cleaned area A on sample HS1 (100 ×, focus stacking)

Figure A4-11: A quartz grain taken from cleaned area A on sample HS1 (200 ×, focus stacking)
Figure A4-12: A aggregate of quartz grains taken from cleaned area B on sample HS1 (100 ×, focus stacking)

Figure A4-13: A aggregate of quartz grains taken from cleaned area A on sample HS2 (100 ×, focus stacking)

Figure A4-14: A aggregate of quartz grains taken from cleaned area A on sample HS2 (200 ×, focus stacking)

Figure A4-15: A aggregate of quartz grains taken from cleaned area B on sample HS2 (200 ×, focus stacking)

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Figure A4-17: A aggregate of quartz grains taken from cleaned area B on sample HS3 (200 ×, focus stacking)

Figure A4-18: A fragment taken from cleaned area A on sample HS4 (100 ×, focus stacking)

Figure A4-19: A fragment taken from cleaned area B on sample HS4 (100 ×, focus stacking)
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Figure A5-2: Cleaned area B on sample S1 under plane-polarized light (100×)

Figure A5-3: Cleaned area A on sample S2 under plane-polarized light (40×)

Figure A5-4: Cleaned area B on sample S2 under plane-polarized light (100×)

Figure A5-5: Cleaned area A on sample S3 under plane-polarized light (40×)

Figure A5-6: Cleaned area B on sample S3 under plane-polarized light (40×)
Figure A5-7: Cleaned area A on sample S1 under plane-polarized light (40×)

Figure A5-8: Cleaned area B on sample S4 under plane-polarized light (40×)

Figure A5-9: Cleaned area A on sample HS2 under plane-polarized light (100×)

Figure A5-10: Cleaned area B on sample HS2 under plane-polarized light (100×)

Figure A5-11: Cleaned area A on sample HS3 under plane-polarized light (100×)

Figure A5-12: Cleaned area B on sample HS3 under plane-polarized light (100×)
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Figure A5-14: Cleaned area B on sample HS4 under plane-polarized light (100×)
Appendix 6: Images of thick-section

Figure A6-1: Cleaned area A on sample S1 under reflected light (100×)

Figure A6-2: Cleaned area B on sample S1 under reflected light (200×)

Figure A6-3: Cleaned area A on sample S2 under reflected light (100×)

Figure A6-4: Cleaned area B on sample S2 under reflected light (100×)

Figure A6-5: Un-cleaned area on sample S2 under reflected light (100×)

Figure A6-6: Cleaned area A on sample S3 under reflected light (100×)
Figure A6-7: Cleaned area A (left side) and uncleared area (right side) on sample S3 under reflected light (100×)

Figure A6-8: Cleaned area B on sample S3 under reflected light (100×)

Figure A6-9: Cleaned area A on sample S4 under reflected light (100×)

Figure A6-10: Cleaned area A on sample S4 under reflected light (100×)

Figure A6-11: Cleaned area B on sample S4 under reflected light (100×)

Figure A6-12: Cleaned area B on sample S4 under reflected light (100×)
Figure A6-13: Cleaned area A on sample HS1 under reflected light (100×)

Figure A6-14: Un-cleaned area on sample HS1 under reflected light (100×, focus stacking)

Figure A6-15: Cleaned area B on sample HS1 under reflected light (100×)

Figure A6-16: Cleaned area A on sample HS2 under reflected light (100×)

Figure A6-17: Cleaned area B on sample HS2 under reflected light (100×, focus stacking)

Figure A6-18: Cleaned area B (right side) and un-cleaned area (left side) on sample HS2 under reflected light (100×, focus stacking)
Figure A6-19: Cleaned area A on sample HS3 under reflected light (100×)

Figure A6-20: Cleaned area A (right side) and un-cleaned area (left side) on sample HS3 under reflected light (100×)

Figure A6-21: Cleaned area B on sample HS3 under reflected light (100×)

Figure A6-22: Cleaned area A on sample HS4 under reflected light (100×)

Figure A6-23: Cleaned area B on sample HS4 under reflected light F (100×)
Appendix 7: Images of SEM (BSE mode)

Figure A7-1: Un-cleaned area on sample S1

Figure A7-2: Cleaned area A on sample S1

Figure A7-3: Cleaned area B on sample S1

Figure A7-4: Gypsum on cleaned area B of sample S1
Figure A7-5: Cleaned area A on sample S2

Figure A7-6: Cleaned area A (up) and un-cleaned area (low) on sample S2

Figure A7-7: Cleaned area B on sample S2

Figure A7-8: Cleaned area B (up) and un-cleaned area (low) on sample S2
Figure A7-9: Cleaned area A on sample S3

Figure A7-10: Cleaned area B on sample S3

Figure A7-11: Cleaned area B (up) and un-cleaned area (low) on sample S3
Figure A7-12: Cleaned area A on sample S4

Figure A7-13: The gypsum on the cleaned area A of sample S4

Figure A7-14: Cleaned area B on sample S4

Figure A7-15: Cleaned area B (right side) and uncleaned area (left side) on sample S4
Figure A7-16: Cleaned area A on sample HS1

Figure A7-17: Un-cleaned area on sample HS1

Figure A7-18: Cleaned area B on sample HS1

Figure A7-19: Cleaned area B (up) and un-cleaned area on sample HS1
Figure A7-20: Cleaned area A on sample HS2

Figure A7-21: Cleaned area A (left side) and uncleaned area (right side) on sample HS2

Figure A7-22: Cleaned area B on sample HS2

Figure A7-23: Cleaned area A on sample HS3
Figure A7-24: Cleaned area A (low) and un-cleaned area (up) on sample HS3

Figure A7-25: Cleaned area B on sample HS3

Figure A7-26: Cleaned area A on sample HS4

Figure A7-27: Un-cleaned area on sample HS4
Figure A7-28: Cleaned area on sample SC

Figure A7-29: Cleaned area on sample BC

Figure A7-30: Cleaned area (low) and uncleaned area (up) on sample CS-1

Figure A7-31: Gypsum on cleaned surface of CS-1
Figure A7-32: Cleaned area on sample CS-2

Figure A7-33: Cleaned area on sample CS-9

Figure A7-34: Cleaned area on sample CS-9 (left side) and CS-10 (right)

Figure A7-35: Cleaned area on sample CS-10
Figure A7-36: Gypsum on cleaned surface of sample CS10

Figure A7-37: Cleaned area on sample CR-7

Figure A7-38: Gypsum on cleaned area on sample CR-7

Figure A7-39: Cleaned area on sample CR-8
Figure A7-40: Gypsum on cleaned area on sample CR-8

Figure A7-41: Cleaned area on sample CR-9

Figure A7-42: Gypsum on cleaned area on sample CR-9
Appendix 8: XRF results

Figure A8-1: XRF results of sample S1

Figure A8-2: XRF results of sample S2
Figure A8-3: XRF results of sample S3

Figure A8-4: XRF results of sample S4
Figure A8-5: XRF results of sample HS1

Figure A8-6: XRF results of sample HS2
Figure A8-7: XRF results of sample HS3

Figure A8-8: XRF results of sample HS4
Figure A8-9: XRF results of sample BC and SC

Figure A8-10: XRF results of sample set CS
Figure A8-11: XRF results of sample set CR
Appendix 9: SEM-EDS results

<table>
<thead>
<tr>
<th>Spot A</th>
<th>High: Si, S, Ca; Low: Mg, Al, K, Fe, Cu</th>
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</thead>
<tbody>
<tr>
<td>Spot B</td>
<td>High: Al, K, Si; Low: S, Fe, Cu</td>
</tr>
<tr>
<td>spot C</td>
<td>High: Al, K, S, Ca Ti, Fe, Cu; Low: Mg</td>
</tr>
<tr>
<td>Spot D</td>
<td>High: Al, K, S, Ca, Fe, Cu, Pb; Low: Mg</td>
</tr>
</tbody>
</table>

Figure A9-1: Element distribution of cleaned area on test area A of sample S1

Figure A9-2: Residues on cleaned area on test area A of sample S1
| Spot A | High: Al, Si, S, Ca, Fe, Cu; Low: Mg, K, Cl |
| Spot B | High: Si, S, Ca; Low: Al, K, Fe, Cu |

Figure A9-3: Residues on cleaned area on test area B of sample S1

| Spot A | High: Al, Si, K, Ca, Fe |
| Spot B | High: Al, Si, K, S, Ca; Low: Na, Mg, P, Fe |

Figure A9-4: Residues on cleaned area on test area A of sample S2

| gypsum | High: Al, Si, S, Ca; Low: Mg, K, Fe |

Figure A9-5: Gypsum residues on cleaned area on test area B of sample S2
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<th>Spot A</th>
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<tbody>
<tr>
<td>High: Al, Si, Fe;</td>
</tr>
<tr>
<td>Low: K, S, Ca</td>
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<table>
<thead>
<tr>
<th>Gypsum</th>
</tr>
</thead>
<tbody>
<tr>
<td>High: Si, S, Ca;</td>
</tr>
<tr>
<td>Low: Al, K</td>
</tr>
</tbody>
</table>

| Figure A9-6: Cements on cleaned area on test area B of sample S2 |

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<td>High: Al, Si, K, S, Ca, Cu, Fe;</td>
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<tr>
<td>Low: Mg, P, Cl</td>
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<tr>
<td><strong>Area B (un-cleaned surface)</strong></td>
</tr>
<tr>
<td>High: Al, Si, S, Ca, P, Fe;</td>
</tr>
<tr>
<td>Low: Mg, K, Cu, Cl</td>
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<table>
<thead>
<tr>
<th>Spot C</th>
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<tbody>
<tr>
<td>High: Al, Si, S, Ca, Cu, Fe;</td>
</tr>
<tr>
<td>Low: Mg, K, P, Cl</td>
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</tbody>
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| Figure A9-7: Gypsum residues on cleaned area on test area A of sample S3 |

| Figure A9-8: Residues on cleaned area on test area B of sample S3 |
Spot A
High: Al, Si, Ca, Fe;
Low: Mg, S, P, Cu, Cl, Ti

Spot B
High: Al, Si, Ca, P, Cu, Fe;
Low: Mg, S, K, Cl

Figure A9-9: Residues on cleaned area on test area A of sample S4

Area A
High: Al, Si, Cl, Fe, Cu, Pb;
Low: Mg, S, P, Ca

Area B
High: Al, Si, K, Cl, Fe, Cu;
Low: S, P, Ca

Area C
High: Al, Si, Fe, Cu, Pb;
Low: Mg, Cl, S, P, Ca

Figure A9-10: Residues on cleaned area on test area A of sample S4

Area A
High: Al, Si, K, Cl, Fe, Cu, Pb;
Low: Mg, S, P, Ca

Spot B
High: Al, Si, K, S, Ca, Cl, Fe, Cu, Pb;
Low: Mg, P

Figure A9-11: Residues on cleaned area on test area B of sample S4
Spot A
High: Al, Si, S, Ca;
Low: Fe, Cu

Area B (un-cleaned area)
High: Al, Si, Ca, Cl, Fe, Cu;
Low: Mg, K

Figure A9-12: Gypsum residues on cleaned area on test area B of sample S4

Spot A
High: Al, Si, P, Fe;
Low: S, Ca, K
Spot B
High: Al, Si, K, Ca, Fe;
Low: Mg
Spot C
High: Al, Si, S, K, Ca, Fe;
Low: Mg

Figure A9-13: Elemental distribution of cleaned area on test area A of sample HS1

Area A
High: Al, Si, K, S, Ca, Fe;
Low: Mg

Figure A9-14: Elemental distribution of cleaned area on test area B of sample HS1
Area A
High: Al, Si, K, S, Ca, Fe;
Low: Ti
Spot B
High: Al, Si, K, S, Ca, Fe;
Low: Ti

Figure A9-15: Un-removed residues on test area A of sample HS2

Area A
High: Al, Si, K, Ca, Fe, Ti;
Low: S, P
Spot B
High: Al, Si;
Low: K, S, Ca, Fe

Figure A9-16: Elemental distribution of cleaned area on test area B of sample HS2

Area A
High: Al, Si;
Low: K, S, Ca, Fe
Area B
High: Al, Si, K, S, Ca, Fe

Figure A9-17: Un-removed residues on test area A of sample HS3
<table>
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<tr>
<th>Figure A9-18: Un-removed residues on test area B of sample HS3</th>
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| **Area A**  
high: Al, Si, S, K, Ca, Fe |

<table>
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<tr>
<th>Figure A9-19: Elemental distribution of cleaned area on test area A of sample HS4</th>
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</table>
| **Area A**  
High: Al, Si, K, Ca;  
Low: S, Fe |

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<thead>
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<th>Figure A9-20: Particles with high iron on cleaned surface of sample BC</th>
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| **Spot A**  
High: Mg, Al, Si, Cl, Ca, Fe  
High Fe particle  
Spot B  
High: Mg, Al, Si, Cl, Ca, Cr, Fe  
High Fe particle |
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<tr>
<th>Spot A</th>
<th>High: Al, Si, K, Ca, Fe</th>
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<tbody>
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<td>High Fe particle</td>
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Figure A9-21: Particles with high iron on cleaned surface of sample SC

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Figure A9-22: Gypsum residues on cleaned surface of sample CS-1

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<tbody>
<tr>
<td>Low: Mg, P</td>
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<tr>
<td>Cement or feldspar</td>
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<table>
<thead>
<tr>
<th>Area B</th>
<th>High: Al, Si, K, Ca, Fe;</th>
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<tbody>
<tr>
<td>Low: P</td>
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<td>Cement of the sandstone</td>
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Figure A9-23: element distribution of cleaned surface of sample CS-2
Area A
High: Al, Si, S, Ca, Fe;
Low: Mg, K
Residues with gypsum

Figure A9-24: Residues on cleaned surface of sample CS-9

Figure A9-25: Gypsum on cleaned surface of sample CS-10

Spot A
High: Al, Si, S, Ca, Fe;
Low: Mg, K

Spot B
High: Al, Si, S, Ca, Fe;
Low: Mg, K

Figure A9-26: Residues on cleaned surface of sample CR-7
<table>
<thead>
<tr>
<th>Figure A9-27: Gypsum on cleaned surface of sample CR-7</th>
<th>Gypsum crystal on quartz grains</th>
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<td>Figure A9-28: Gypsum on cleaned surface of sample CR-8</td>
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<td>Figure A9-29: Gypsum residues on cleaned surface of sample CR-9</td>
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Appendix 10: Water absorption graphs

Figure A10-1: Water absorption rate of sample S1

Figure A10-2: Water absorption rate of sample S2

Figure A10-3: Water absorption rate of sample S3

Figure A10-4: Water absorption rate of sample S4

Figure A10-5: Water absorption rate of sample HS1

Figure A10-6: Water absorption rate of sample HS2
Figure A10-7: Water absorption rate of sample HS3

Figure A10-8: Water absorption rate of sample HS4

Figure A10-9: Water absorption rate of sample BC

Figure A10-10: Water absorption rate of sample SC
## Appendix 11: Data of color measurements

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<th>SD</th>
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