Laser cleaning of black weathered Obernkirchen sandstone

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Formation of thin, black, well adhering weathering layers on pure sandstones used as building stone is a well known phenomenon, described in several countries and on several types of sandstones. In the Netherlands, sandstones from the Lower Saxony basin in Germany, notably the Bentheim and Obernkirchen sandstones, have been used for many prominent monuments from the 11th century onwards, and especially in the 14th till 17th century. Both sandstones show the formation of thin black weathering layers. In the present case, after characterization of the black weathering layer on a late 18th century façade cladded with Obernkirchen sandstone, a pilot test was performed to investigate the possibility of cleaning, and, especially, of any harmful effects to the original stone resulting from cleaning. Commercial firms have been invited to clean test panels on the façade. Two firms using a Nd-YAG laser have been invited, a third one using EDTA pastes. The latter proved not successful. In both cases, laser visually succeeded to remove the black layer. Possible deleterious effects of stone cleaning are twofold, viz. direct damage, such as removal of grains or patina from the original stone and damage to working of the stone, or indirect damage, that may arise from a different hygric behaviour of the stone (and façade as a whole) after cleaning. The latter have not been evaluated. Direct damage was evaluated by combination of polarization-and-fluorescence (PFM) and scanning electron microscopy (SEM). Cleaning using a Nd-YAG laser under commercially realistic conditions did not result in any direct damage to the Obernkirchen sandstone.

Key words: Laser cleaning, Obernkirchen sandstone

1 Introduction

Sandstones may develop thin black weathering layers. These layers are formed due to the complex interaction of several processes, including fixation of airborne particles by formation of gypsum (also on Ca-free sandstones), dissolution and precipitation of iron,

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and micro-organisms (Nord & Trönner 1991, 1992, Young 1997, Nijland et al. 2004ab). Generally, these layers are rather thin, - though thickness depends on the type of sandstone substrate-, but well adherent, making damage-free cleaning difficult. Laser cleaning, more widely used on limestones, has been proposed (see overview in Nijland & Wijffels (2003)). In the Netherlands, a notorious example of laser cleaning involved the town hall of Rotterdam, cladded with Rakowicze sandstone (Nijland & Wijffels 2003). Rakowicze sandstone is a very pure sandstone, comparable to the Bentheim sandstone, without a cement between the quartz grains. Obernkirchen sandstone is finer grained sandstone, with different generations of cement. In the present paper, tests of laser cleaning of this sandstone are evaluated.

2 Obernkirchen sandstone

After Romaneque times and prior to the 19th century, sandstone in Dutch monuments is strongly dominated by two types imported from Germany, viz. Bentheim sandstone, obtained just east of the Dutch border, and Obernkirchen sandstone, quarried on the Bückeberg, west of Hannover. The Obernkirchen sandstone is a pure sandstone deposited in the Lower Saxonian basin during the Weald (Cretaceous). It is a light grey to light yellow, fine grained (0.1 – 0.25 mm), reasonably well sorted sandstone (Fig. 1). The rock is

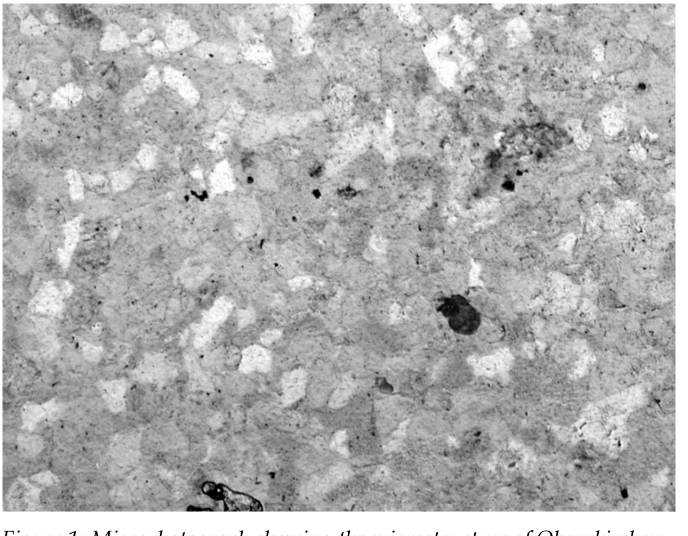

Figure 1: Microphotograph showing the microstructure of Obernkirchen sandstone (sample TNO 00245, plane polarized light, view 2.7 x 1.8 mm)

mainly composed by quartz and rock fragments, with some mica's and heavy minerals (zircon, tourmaline, garnet, rutile); feldspar is rare. Detrital grains are cemented by a primary binder of quartz and clay, and a secondary binder of siderite, quartz, kaolinite, illite and Fe-(hydr)oxides; cement makes up about 15 % of the rock (Chitsazian 1985, Nijland et al. 2004b). Pores are filled by a mixture of these phases (Fig. 2).

The sandstone has been used for many Dutch monuments, such as the town hall of Delft, the Royal Palace in Amsterdam and the Martini tower in Groningen. In the present case, samples have been investigated from the building of the House of Representatives of the Staten-Generaal (the Dutch Parliament), in The Hague. The relevant part of the building was constructed in 1777 – 1793, with the upper part of its façade cladded with Obernkirchen sandstone, the lower part with Belgian blue limestone ('hardsteen'). An example of the black weathering of the Obernkirchen sandstone on the façade is given in figure 3.

3 Test panels

In order to evaluate the possibilities of damage-free cleaning the black weathered Obernkirchen sandstone, three series of test panels have been made. Three commercial contractors have been invited to make the panels. Of these, one used laser cleaning (panels

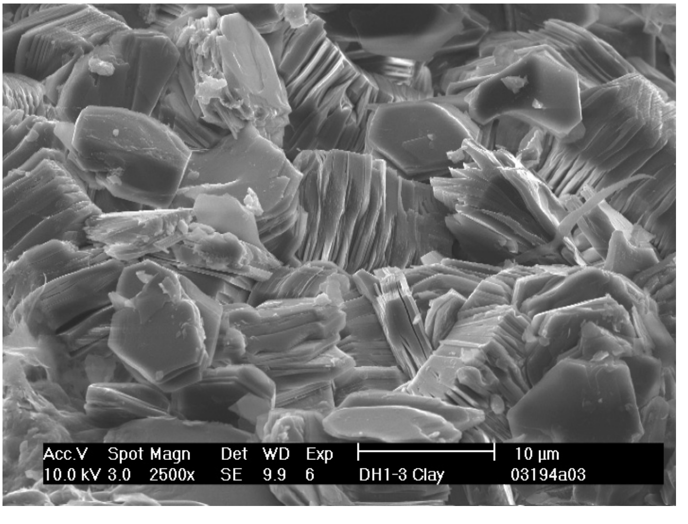

Figure 2: SEM microphotograph showing the pore filling of Obernkirchen sandstone by kaolinite (sample TNO 00420)

C), a second one laser cleaning, partly in combination with dry microblasting (panels A), and a third one an EDTA-based paste. The EDTA-based paste did not show any cleaning effect at all, and is not considered furthermore in this paper.

Contractor A made a series of test panels both with laser alone and laser combined with dry microblasting. For cleaning, an Nd:YAG laser was used. These are shown in figure 4. To determine operating conditions for this laser, a scale bar (the series of snall panels on the right in fig. 4) has been made ranging from almost no cleaning, to cleaning with an intensity that the visual suggestion of damage arises. The scale bar ranges from 700 to 1000, corresponding to an energy density of 0.127 to 0.775 J cm-2 (Grell 2004). Subsequently, other test panels have been made, of which the middle panel on figure 5 is considered a satisfactory result by the cleaning company themselves (Fig. 5). This was cleaned using a scaling of 900 – 950, corresponding to an energy density 0.517 to 0.608 J cm-2. Cores from this panel have been obtained for microscopic investigation (Fig. 6). In addition, a core from the scale bar part with maximum intensity (1000) has been collected as reference (sample TNO 00423).

Contractor C operated rather differently, not recording specific conditions, but cleaning 'intuitively'. In this case, a Nd-YAG laser was used too. An overview of the test panels C is

Figure 3: Example of black weathered Obernkirchen sandstone on the façade of the Staten-Generaal, The Hague (january 2003)

given in figure 7. These test panels are distinctly more yellow than those made by contractor A. An overview of cores for microscopic investigation is given in figure 9.

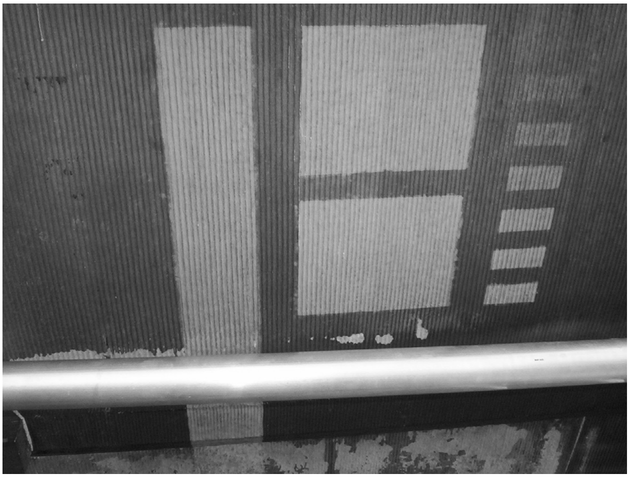

Figure 4: Overview of test panels A. On the right, scale bar made to determine operating conditions of the laser. In the middle, test panels considered to be the right 'end product' by the cleaning company themselves. A detail of these is given in figure 5. For explanation, see text.

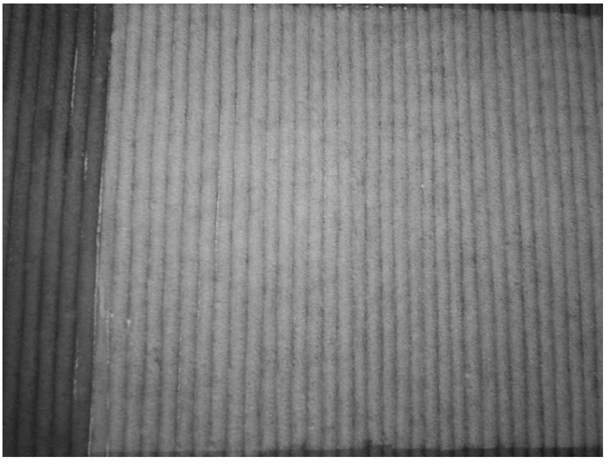

Figure 5: Test panel A considered to be the right 'end product' by the cleaning company themselves. The slightly lighter coloured part in the middle was pre-cleaned by dry microblasting prior to laser, the right part was cleaned by laser only. At the leftmost part of the picture the non-cleaned black weathered sandstone.

4 Evaluation of cleaning

The effect of cleaning in terms of direct damage has been evaluated by a combination of polarization-and-fluorescence microscopy (PFM) and scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS).
On the Obernkirchen sandstone, the black weathering layer is present on and behind the first sand grains (up to about 5 grains deep), as well as in pores open to the surface (Fig. 9).

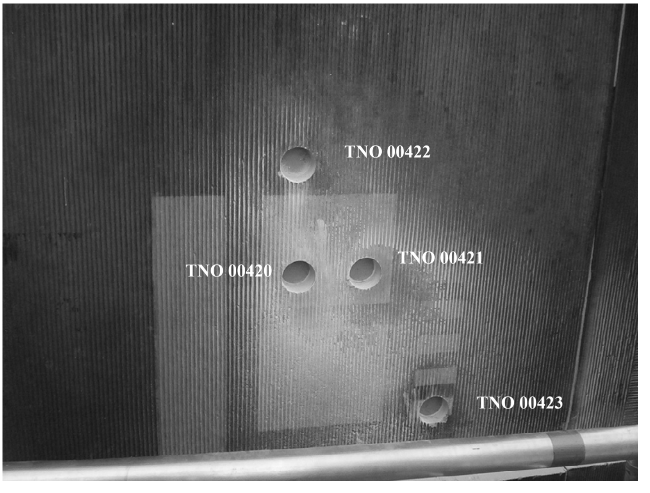

Figure 6: Overview of samples for microscopic evaluation obtained from test panel A

Figure 7: Test panel C cleaned by laser

Though not documented, it appeared from thin sections that during a past intervention a stone consolidant was applied that is present locally just below the surface of the sandstone.

Both in the samples cleaned with laser only (sample TNO 00422) and pre-cleaned by dry microblasting (sample TNO 00421) from test panel A, the black weathering layer has been

Figure 8: Overview of samples for microscopic evaluation obtained from test panel C

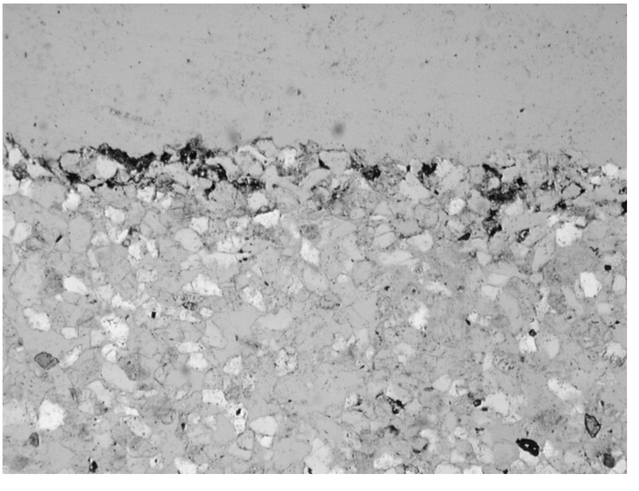

Figure 9: Microphotograph showing the nature of the thin black weathering layer on non-cleaned Obernkirchen sandstone (sample TNO 00422, plane polarized light, view 2.7 x 1.8 mm)

removed from top of the sand grains, but is still locally present behind the grains and in deeper pores open to the surface (Fig. 10). Quartz grains themselves stay untouched, and no deterioration of clay minerals or stone consolidants occurred. Even in the sample from the part cleaned with maximum intensity (sample TNO 00423), some soiling material remains in the deeper pores and behind quartz grains.

On electron microscopic scale, quartz grains in the non-cleaned sample are covered by the thin black weathering layer, that is enriched in both sulfur and lead. Abundant small foreign particles are present on top of the quartz grains (Fig. 11). Both in the samples cleaned by dry microblasting followed by laser (Fig. 12) and by laser alone (Fig. 13), these particles are to a great extent removed, without damage or removal of the grains of the sandstone themselves. No damage features, such as removal or pitting of quartz grains, or tiny (radial) microcracks around the grains due to thermal shock are observed, nor are there any signs of (partial) melting or sintering.

In the sample cleaned with maximum intensity (sample TNO 00423), the black weathering layer on top is almost completely removed, and the surface became rather porous (Fig. 14). The surface of some quartz grains shows pitting.

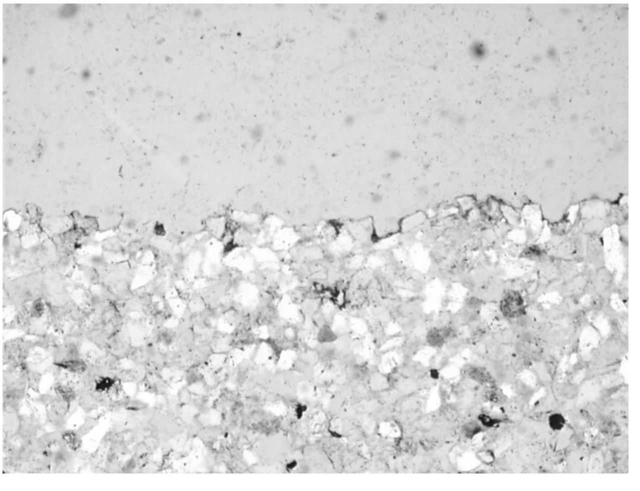

Figure 10: Microphotograph illustrating the removal of the thin black weathering layer from the surface of the quartz grains after cleanin by laser, with some material remaining in the deeper pores (sample TNO 00421, plane polarized light, view 2.7 x 1.8 mm)

Sandstone in laser cleaned test panel C has a more dense surface layer and the thin black weathering layer is more continuous on top (Fig. 15). As with the other test panel, laser cleaning resulted in the removal of the thin black weathering layer on top of the quartz

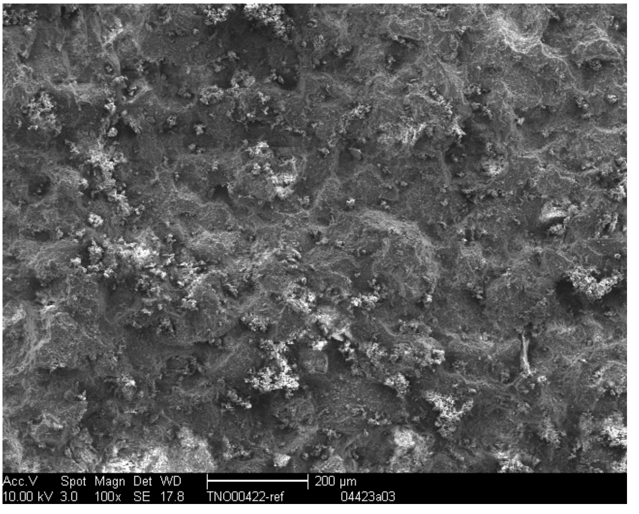

Figure 11: SEM microphotograph of the surface of non-cleaned Obernkirchen sandstone from test panel A (sample TNO 00422)

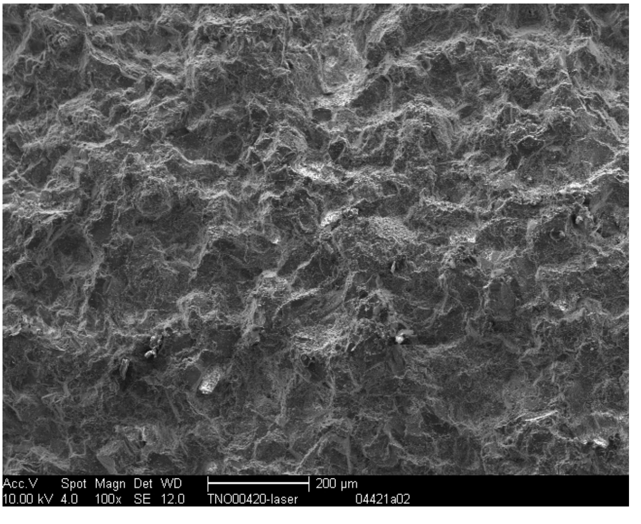

Figure 12: SEM microphotograph of the surface of Obernkirchen sandstone from test panel A cleaned by dry microblasting followed by laser (sample TNO 00420)

grains, leaving some material behind grains and in deeper pores (Fig. 16). No damage to quartz grains or interstitial clay minerals was observed. From electron microscopy, it shows that the surface is comparable to that of samples cleaned by laser ± dry microblasting from test panel A (Fig. 17). No indications of damage have been observed.

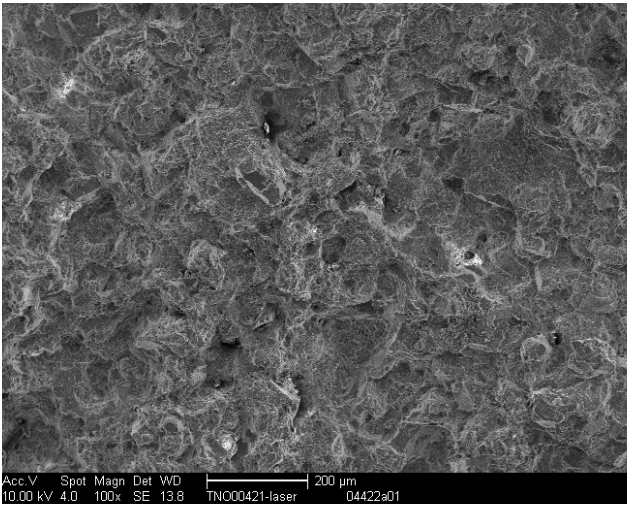

Figure 13: SEM microphotograph of the surface of Obernkirche sandstone from test panel A cleaned by laser (sample TNO 00421)

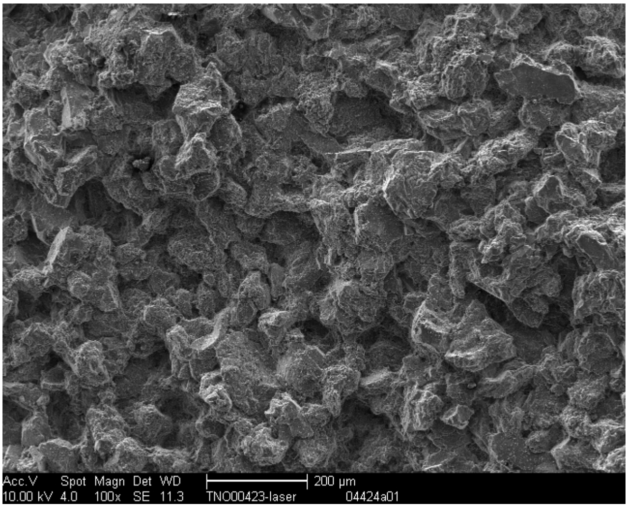

Figure 14: SEM microphotograph of the surface of Obernkirchen sandstone from test panel A cleaned by laser at maximum intensity (sample TNO 00423)

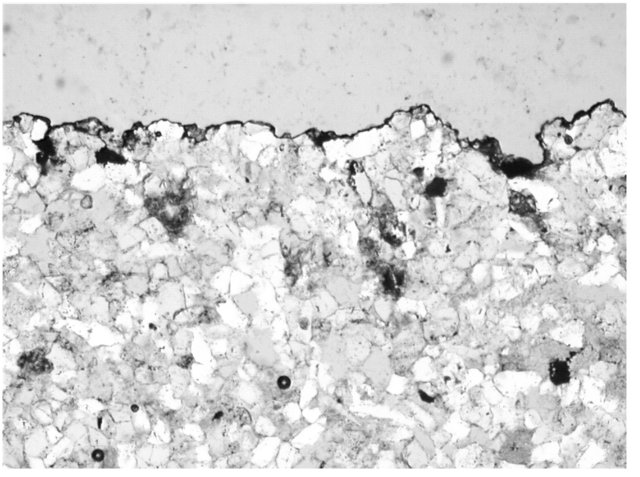

Figure 15: Microphotograph showing the more continuous thin black weathering layer on non-cleaned Obernkirchen sandstone from test panel C (sample TNO 00427, plane polarized light, view 2.7 x 1.8 mm)

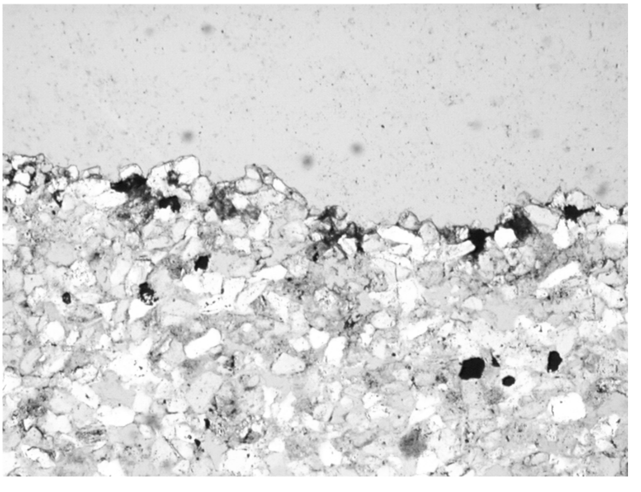

Figure 16: Microphotograph showing the partial cleaning obtained by laser on test panel C, with some material of the black weathering layer remaining in deeper pores and behind quartz grains (sample TNO 00426, plane polarized light, view 2.7 x 1.8 mm)

5 Conclusion

Two test panels of laser cleaning using different Nd:YAG lasers and one test panel with additional pre-cleaning by dry microblasting on black weathered Obernkirchen sandstone (made by two commercial contractors on site) have been evaluated by microscopic techniques. Cleaning is shown to cause no damage of material, provided that conditions are appropriately chosen. There is, however, a clear difference in colour (more and less yellowish) between both on site cleaned sandstone panels. Yellowing is a well-known phenomenon after laser cleaning of marbles, especially in case of Nd:YAG lasers operating at 1064 nm (Klein et al. 2000b, 2001, Vergès-Belmin & Dignard 2003, Pouli et al. 2006). It has not widely been reported in case of sandstone. In principle, analogous explanations may apply. The colour effect may be due to (organic) remnants of soiling, whether or not transformed by the energy of the laser, or, alternatively, represent former surface treatments (based on organic oils) that came into view again after cleaning. It seems unlikely that oxidation of iron causes the yellowish colour, as energy of the laser generally results in discouloration of iron-rich sandstones, giving them a more pale colour (Siano et al. 2000, McStay et al. 2005). Remarkably, colour differences are distinct between both laser cleaned test panels of the same Obernkirchener, of same age and type of soiling, but within each panel, the colour is more or less homogeneous. The colour effect on sandstone is apparently not yet understood.

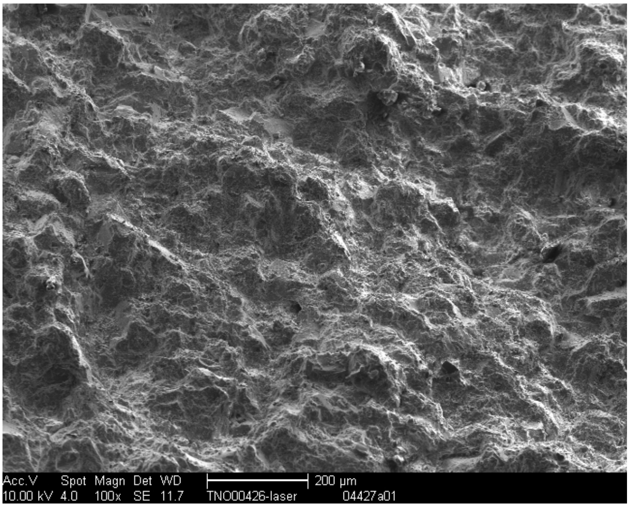

Figure 17: SEM microphotograph of the surface of Obernkirchen sandstone from test panel C cleaned by laser (sample TNO 00427)

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