Determination of weathering and conservation of sculptured stone by use of the laser method
**ABSTRACT**
Weathering and deterioration of sculptured stone and masonry is a natural process which starts at the same moment the stone is quarried and exposed to exogenous conditions. This process of natural decay has, however, been accelerated due to the emission of different man-made pollutants, domestic and industrial, local and global. The ISOLASER project is based on the laser microprobe technique for determining the depth of natural and induced weathering and the effect of conservation measures of cultural objects of carbonaceous sandstone and marble/limestone. The purpose of the project is to determine the depth of weathering and depth of penetration of conservation agents in unweathered calcite-cemented stone and the weathering profile in linseed oil-treated stone after accelerated weathering cycles in a climatic chamber. The analytical results show that even after such a short period as 5 weeks of exposure the effect of SO₂, NO₂ and elevated humidity on Gotland sandstone can be easily observed in a change of the δ¹³C values in the outermost 2 mm of the stone. Treating the sample with linseed oil has a preserving effect on the rock and hinders the deteriorating effect of SO₂ and NO₂. The oil treatment even preserves the signature of previously incorporated organic carbon. Compilation of a questionnaire representing a broad field within natural sciences in cultural heritage research in Europe, shows an overwhelming positive approach to the project as such. The questioned researchers consider the laser method particularly useful as a complementary method in other investigations and states that the method can without doubt give new dimensions to the analysis of important cultural objects.

**KEY WORDS** Laser; carbon isotopes; sandstone; cultural heritage

**CLASSIFICATION AND/OR SUBJECT GROUP** UDC 551.3.053:535.374
Determination of weathering and conservation of sculptured stone by use of the laser method

EUREKA project EU 1394 EUROCARE ISOLASER

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1 Summary

Weathering and deterioration of sculptured stone and masonry is a natural process which starts at the same moment the stone is quarried and exposed to exogenous conditions. This process of natural decay has, however, been accelerated due to the emission of different man-made pollutants, domestic and industrial, local and global. Up to now there has been no way of putting the decay to a complete stop but only to decrease the rate of it. Preservation of the cultural heritage by regular maintenance using different conservation products has been used since centuries and is one way of prolonging its life. It is therefore of great importance to know the status of an object before any preservation measures have been taken and also what kind of conservation agent should be used in the particular case.

The ISOLASER project is based on the laser microprobe technique for determining the depth of natural and induced weathering and the effect of conservation measures of cultural objects of carbonaceous sandstone and marble/limestone. With the laser-ablation technique, CO₂ is released from the carbonates and analysed on $^{13}$C/$^{12}$C and $^{18}$O/$^{16}$O in a mass spectrometer. The purpose of the project is, to determine and compare the depth of weathering for objects from different ages and from different environments, e.g. northern-, central- and southern Europe, and to determine the depth of penetration of conservation agents in unweathered calcite-cemented stone and the weathering profile in linseed oil-treated stone after accelerated weathering cycles in a climatic chamber.

In order to study the market potential for the laser-technique and also perform more trials, this project was initiated as a 6 month pilot project which will be evaluated before a decision is taken to proceed with the above project on a larger scale. In this pilot project laser analyses have been performed of samples of Gotland sandstone from Valar, Gotland, Sweden. Some of the samples were doped with linseed oil, as conservation agent, by the Central Board of National Antiquities (CBNA), Stockholm, Sweden. Thereafter some of the samples, oil-treated and non-tREATED, were exposed for 5 weeks in climatic chambers at the Norwegian Institute for Air Research (NILU), Kjeller, Norway. The investigation of the European market potential has been undertaken by Restaurator AB, Stockholm, Sweden.

The analytical results show that even after such a short period as 5 weeks of exposure the effect of SO₂, NO₂ and elevated humidity on Gotland sandstone can be easily observed in a change of the δ$^{13}$C-values in the outermost 2 mm of the stone. Treating the sample with linseed oil has a preserving effect on the rock and hinders the deteriorating effect of SO₂ and NO₂. The oil treatment even preserves the signature of previously incorporated organic carbon. The depth of conservation with linseed oil can be easily monitored since the difference in δ$^{13}$C-values between linseed oil (about -30) and the Gotland sandstone (about +2 to +5) is very big. The
laser method is obviously a very potential tool to study the effects of linseed-oil treatment and natural and induced processes, in carbonate-rich rocks.

Compilation of answers to the questionnaire made by Restaurator AB, representing a broad field within natural sciences in cultural heritage research, shows an overwhelmingly positive approach to the project as such. The questioned researchers consider the laser method particularly useful as a complementary method in other investigations and states that the method can without doubt give new dimensions to the analysis of important cultural objects.

They also point out the importance with the technique since calcareous stones are so widely distributed and sometimes difficult to understand in their behaviour, that data concerning depth of weathering and the progress of weathering in the course of time are of considerable importance. There is also suggestions to use the laser method to differentiate between thin scales, detached lime washes or paint layers on calcareous stone since the isotope ratios in the layer and in the stone might be significantly different.

The group also considers that the possibility to use the laser method for determining the provenance of a stone makes the technique very interesting since knowing the site and the stratigraphic position in a quarry is of greatest value. Besides being able to replace a stone with its own special characteristics it also gives a possibility to compare stone with similar nature and to see how deterioration has proceeded after the stone was taken from the quarry and put into a building or sculpture.
2 Analytical part

2.1 Introduction

Our cultural heritage is experiencing an accelerating deterioration partly due to anthropogenic emission of pollutants. It is important to note that deterioration of an object is caused by an interplay between different chemical, physical and biological processes and not only by anthropogenic activity. Man-made processes, however, have in many instances had a catalytic effect on deterioration, last but not least by the synergetic effects from a combination of different processes. The rate of deterioration depends on the environment, kind and amount of pollutants an object is exposed to, but also on the type of material itself. The increase in damage due to air pollution and the resultant visible effects has led to great concern for both the environment, and for the cultural heritage. Therefore there is a need for more qualitative as well as quantitative documentation.

Appropriate actions for the adequate protection and the proper conservation and restoration of the cultural heritage require the accurate evaluation of the origins and status of the materials involved and of their degree and types of deterioration. Our research aims to develop or improve measurement systems to quantify parameters which affect the conservation and maintenance of items, define damage and influence the perception of the user. Also methods to evaluate the efficiency of treatments and products used in the protection and restoration activities. The aim is to find out appropriate sampling protocols and techniques, new field methods, and micro-sample techniques for the measurement of the physical, chemical and microbiological properties of materials used in historic objects. We also want to establish measurement methods for the control of accelerated weathering tests in climatic chambers and methods to establish the origin and composition of cultural items.

Accelerated tests of weathering rates under controlled conditions in the laboratory can be done on fresh samples as well as naturally pre-weathered ones. A common question is the validity of different consolidation agents. How deep do they penetrate the object to be consolidated? What is the resistance to pollution in the climatic chamber after consolidation? And what is the difference between weathered and unweathered consolidated samples after they have been exposed to accelerated weathering tests.

This project is highly innovative in that it utilises the laser-ablation technique to examine natural and induced aspects of stone weathering and conservation in calcareous rocks. In many cases the stone used for masonry or sculptures was treated with different methods to strengthen the surface and prolong the life of the stone. During earlier centuries this was often done using e.g. wax, grease or organic fluids. Linseed oil seems to be the most important one of these. The
masonry is sometimes covered with biologic overgrowth and/or has been treated with different consolidants during an earlier conservation. With the laser technique it is possible to estimate how far into a calcareous rock the weathering has proceeded. It is also possible to measure the effect of biological overgrowth on the substrate and how far organic stone consolidants have reached into the material.

The project also takes into account determination of provenance for the stone material which has been used in a sculpture or building by characterising it by its isotopic signature. This is essential when replacing a weathered stone in order to get one that changes colour, structure etc. in the same way as the original.

2.2 Analytical procedure

Gotland sandstone:
The Gotland sandstone belongs to the upper part of the Silurian system, with an age of 410-415 million years. It was deposited in a shallow marine environment. The Silurian Gotland sandstone, a siltstone in fact, has a mean grain size of 0.1 mm. It consists of circa 59% quartz, 1-2% feldspar, 14% clay minerals, 8% calcite, 4% mica, some organic material and with a porosity of about 12%. The sandstone is unsorted with grains of low roundness and it contains dispersed pyrite. Calcite grains are usually corroded, with more or less undefined borders. The colour of the fresh rock is light grey to grey. The Gotland sandstone has been quarried since medieval times for local use as well as for export. Earlier analyses of the Gotland sandstone, from a similar stratigraphic horizon as the rock used in this investigation, gives a δ^13C-value of about +4.2 (Åberg et al. 1995). Six sandstone samples, cubes with a side of 5 x 5 x 5 cm, were taken out by Slite AB on Gotland for the analytical work (Figure 1).

Linseed-oil:
Analyses of linseed oil (Åberg et al. 1995) show that the oil, irrespective of origin has δ^13C-values of about -30 permil. The oil used in this project is a Swedish cold-squeezed linseed oil with a δ^13C-value of -30.4. Thus, the overall influence of linseed oil treatment would be a lowering of the δ^13C-value of the fresh Gotland sandstone. Traditionally, Gotland sandstone in buildings was often coated with linseed oil, as is well known in the case of the Royal Palace in Stockholm. Four out of the six samples in this investigation were impregnated with linseed oil by CBNA in Stockholm. The samples were left standing in oil with a depth of 1 cm for about 5 hours. They were then dried at 50°C for 3 days followed by a week in an exsiccator. Since it is a natural oil it most probably consists of a number of lighter and heavier fractions.
Accelerated weathering:
Three of the samples were exposed to SO2 and NO2 at NILU for 5 weeks (1996-03-08 to 1996-04-11), 2 linseed oil impregnated samples and 1 unimpregnated. The conditions in the three chambers A, B and C at NILU were for SO2; 400, 425 and 410 µg/m³, respectively, and for NO2; 285, 205 and 215 µg/m³, respectively, all at a relative humidity of 90%. The gas mixture was pumped through the system with an air-flow of 2 litres per minute. Three parallels, 2 linseed oil impregnated samples and 1 unimpregnated, were kept for reference.

Sample preparation:
After exposure the samples were cut with a diamond saw at IFE. The blade was 0.4 mm thick and distilled water was used as a cooling agent. Three slices with a thickness of 3 mm were cut out from the centre of the cube in order to have extra backup material for duplicate analyses or in case of a mishap. From each 3 mm slice a 15 mm wide piece was cut. Each piece was marked for orientation (Figure 1).

After cutting the rock samples an inhomogeneity was noticed between them, reflected by the ability to absorb the linseed oil. The depth with which the linseed oil had penetrated the rock samples varied between 11 and 23 mm. A greater weight was therefore put on utilising adjacent samples from each rock cube in order to achieve better comparability between the analyses. It should, however, be pointed out that the primary object with this investigation was not to get absolute values, but distinguish trends in the sandstone after oil treatment and after exposure to SO2 and NO2 in climatic chambers, with the help of laser analyses of carbon and oxygen.

Plasma asher:
A low temperature radio frequency plasma asher was used in order to eliminate organic material in some of the samples. There are two types of organics of interest in this investigation, those incorporated in situ at sedimentation, and the linseed oil the samples were impregnated with. The plasma-ashing took place at circa 60-70°C under vacuum in a chamber surrounded by an induction coil. Oxygen was introduced in the chamber with an over pressure of circa 1-1.5 mB thus oxidising the organic material.

Laser and mass spectrometry:
Laser microprobe analyses were performed with a high-power Nd-doped YAl garnet (YAG) laser combined with a He-Ne (red) aiming laser for the laser-ablation of a small well defined area. The laser was operated at 28 A DC at a vacuum of about 10⁻⁷ Torr. The diameter of the focused beam was about 15 µm. The CO2 gas released was transferred to a Finnigan MAT 251 mass spectrometer equipped with a microinlet. The optimal precision is approximately ±0.2% (one sigma) for both δ¹³C and δ¹⁸O in carbonates. All isotope values are given relative to the PDB standard.
The laser-ablation technique can be used for spot-analyses if enough CO₂ gas is released, or continuously while the sample is moved slowly along an X-Y table. In the latter case the analyses of carbon and oxygen isotopes can be performed along lines parallel to the surface and an integrated value for a specific depth will be obtained. A great advantage with the laser technique is that the operator can change the area of analyses during work and it is possible to examine gradients perpendicular to the sample surface. The technique is destructive in the sense of sampling a drill-core on for example masonry, but when the analytical work is finished the sample can be put back by a stone conservator.

### 2.3 Results

2:II Linseed oil treated, exposed, and not plasma ashed. The δ¹³C-values vary between -1.7 permil and +16.9 permil (Figure 2). The latter extremely high value is unexplained at the moment. The sample contained a lot of unidentified gases. This test emphasise that before analyses a sample has to be cleaned of excess organic material in order to get a reasonable trend. Particularly if the sample recently has been treated with organic compounds. The analyses were performed from the surface and inwards. The heat from the laser beam is probably fractionating and forcing the oil, sucked up by the sample, in front of the laser beam and into the sample. The lighter fractions going furthest.

2:III Linseed oil treated, exposed, and plasma ashed. The sample is analysed from the inside towards the surface. The δ¹³C-values oscillate between +2 permil and +2.4 permil the first 3 mm, then make a dip down to +1 permil at 5 mm (Figure 2). The δ¹³C-value then goes back to the previous value, increases and remains at about +2.8 permil. The results indicate that the sample is still saturated with oil after plasma ashing. There is oil seemingly down to about 20 mm depth or probably even further.

3:I Linseed oil treated, unexposed and not plasma ashed. The sample was analysed from the inside and outwards towards the surface in order not to force oil inwards by the laser. From the surface and to the oil-front at 10 mm the δ¹³C-value decreases, from the common value of non-ashed and unexposed rocks of this test of about +4.5 permil, down to -2 permil (Figure 3). Thereafter the δ¹³C-value increases till a value just above 0 permil.

3:II Linseed oil treated, unexposed but plasma ashed. The sample was analysed from the surface and inwards. After a small increase in δ¹³C-value from +1.8 permil to +2.4 permil in the first 0.5 mm the values slowly decrease down to a δ¹³C-value of +1.4 permil at the oil-front, i.e. how far the linseed oil has penetrated the rock sample (Figure 3). In this sample, adjacent to 3:I, the oil-front is about 10 mm from the surface. After the oil-front the δ¹³C-
values increase towards the common rock value of about +3.5 permil (after plasma ashing). There is probably also a fractionation in the oil with depth in the stone.

4:1 Linseed oil treated, exposed, and plasma ashed. At the surface the $\delta^{13}C$-value is about +2.8 permil but decreases fast to +1.5 permil at 2 mm into the sample (Figure 4). It then oscillates between +2.2 permil and +3.2 permil before it passes the oil front at 23 mm and a value of +2.3 permil at 25 mm. The anomaly at 20 mm coincides with one of the brown layers (Fe-hydroxide?).

4:II Linseed oil treated, exposed, and plasma ashed. This sample was analysed from the inside, over the oil front at 23 mm depth, and towards the surface (Figure 4). The $\delta^{13}C$-value is +4.5 permil at the surface and coincides with the surface values of sample 3:1 and 5:II. Common between 4:II and 3:1 is that they both are oil treated and analysed from the inside towards the surface. However, 3:1 is unexposed and non-ashed while the other, 4:II, is exposed and plasma ashed. The above fact implies that an oil-treated sample is not affected by exposure of SO$_2$ and NO$_2$ at elevated humidity. Such an effect should have been noted at the surface. Moreover, the laser is pushing the linseed oil in front of the beam, or gassing it out, so that the last sample at the surface will give a $\delta^{13}C$-value representative of the rock, in this case about +4.5 permil.

5:1 Untreated, unexposed and plasma ashed. The sample has its highest $\delta^{13}C$-value of +3.8 permil at 0.5 mm depth, followed by a decrease down to +3.4 permil at 7 mm depth (Figure 5). The $\delta^{13}C$-values undulates about +3.5 permil throughout the sample probably due to natural variations.

5:II Untreated, unexposed and non-ashed. This sample has its highest analysed $\delta^{13}C$-value at the surface (Figure 5). The carbon ratios then oscillate between +4.1 permil and +4.5 permil inwards the sample from the surface. Interesting is the dip in $\delta^{13}C$-value about 1 mm depth. A similar dip occurs at a depth of 12 mm. An explanation could be inhomogeneity in the sandstone as shown for example by the many brown layers.

6:1 Untreated but exposed, and plasma ashed. A 1st track at 0.1 mm was lost due to electronic failure at analyses. The $\delta^{13}C$-values follows a similar trend as sample 5:1 inwards the sample until about 7 mm (Figure 5). Thereafter there is an increase with depth up to a $\delta^{13}C$-value of +4.2 permil, or maybe further, coinciding with the values of 5:II and 6:II.

6:II Untreated but exposed, and non ashed. The low $\delta^{13}C$-value of +3.3 permil at the surface increases over the first 2 mm to +4.6 permil , then oscillates about +4.3 permil, like in sample 5:II (Figure 5). The lowering of the $\delta^{13}C$-value at the surface is apparently an induced
weathering effect from the exposure of the sample to SO$_2$ and NO$_2$ in the climatic chambers at NILU. The CaCO$_3$ in the rock has reacted under the prevailing conditions and an exchange with the carbon in air has taken place. CO$_2$-gas in the atmosphere has a $\delta^{13}$C-value of -7 permil.

2.4 Discussion

2:II and 2:III. These 2 adjacent samples, oil treated and exposed, one plasma ashed and the other not, show the efficiency of the plasma asher (Figure 2). However, even though the plasma ashing has smoothed the $\delta^{13}$C trend there is obviously still some oil left in 2:III as the $\delta^{13}$C-value is about +2 permil through the whole sample in comparison to about +3.5 permil in the untreated but plasma ashed samples (5:1 and 6:1).

3:1 and 3:II. The decrease in $\delta^{13}$C-value with depth in 3:1, the ratio $^{13}$C/$^{12}$C getting more negative inwards (Figure 3), may be due to a fractionation in the oil or that the heavier $^{13}$C might not as easy infiltrate the rock as the lighter $^{12}$C. In sample 3:1 this effect is very obvious as the analyses were performed from the inside and towards the surface. In 3:II, which is adjacent to 3:1, the fractionation trend is there but the effect is not so pronounced since this sample has been in the plasma asher. However, even though the plasma ashing has smoothed the $\delta^{13}$C trend there is obviously still some oil left.

4:1 and 4:II Both samples show a similar trend for the $\delta^{13}$C-values but it is smother in 4:II and also more exaggerated at the surface in this sample (Figure 4). Both samples were treated with linseed oil. After exposure sample 4:II does not seem to be affected by exposure of SO$_2$ and NO$_2$ at elevated humidity. This is noticed if the sample is analysed from the inside and outwards in contrast to 4:1 which was analysed the other way. That is, the laser is pushing out the linseed oil in front of the beam so that the last sample at the surface will give a $\delta^{13}$C-value representative of the rock while the other sample will get an addition of linseed oil with a low $\delta^{13}$C-value. In this case the $\delta^{13}$C-value of sample 4:II at the surface coincides with that of samples 3:1 and 5:II.

5:1 and 5:II. These two samples are adjacent, like all the pairs, and would thus give similar results. The trends are also similar with the ups and downs but the level of the $\delta^{13}$C-values are different, being much higher in 5:II, the non ashed sample (Figure 5). This implies that the rock in itself carries organic material with a higher $\delta^{13}$C-value, incorporated at sedimentation, and which is lost when plasma ashing the sample.

6:1 and 6:II 6:II is the only untreated and exposed sample but not plasma ashed. The low $\delta^{13}$C-value of +3.3 permil at the surface increases over the first 2 mm, then oscillate about +4.3 permil, like in sample 5:II (Figure 5). The lowering of the $\delta^{13}$C-value at the surface is
apparently due to the reaction of the CaCO₃ under the prevailing conditions and leading to an exchange with the carbon in air. The gas mixture was pumped through the system at NILU with an air-flow of 2 litre per minute. CO₂-gas in the atmosphere has a δ^{13}C-value of -7 permil. The general δ^{13}C level of 6:II coincides with that of 5:II (untreated and non ashed), like the similarity between 6:I and 5:I, and thus strengthen the hypothesis that the rock carries organic material emplaced at sedimentation.

When all samples are plotted together (Figure 6) certain main trends can be distinguished. One group consists of those which are not oil treated but exposed/unexposed, plasma ashed/non ashed (5:I, 5:II, 6:I and 6:II). The other group are samples which are oil treated, exposed/unexposed and plasma ashed (2:III, 3:II, 4:I and 4:II), and the third and last group consist of samples which are oil treated, exposed/unexposed but not plasma ashed (2:II and 3:I).

If we not consider the analyses close to the surface in the top group the δ^{13}C-values for the rock is about +4.5 permil (5:II and 6:II). These samples are not oil treated, unexposed or exposed, but not plasma ashed. Parallels of the same samples as above (5:I and 6:I) which were plasma ashed have lower δ^{13}C-values of about +3.5 permil to +4.2 permil as organic material emplaced at sedimentation was removed when plasma ashed. Exposure in the climatic chamber affected the first 2 mm of 6:D by giving an imprint of the δ^{13}C-value of -7 permil in CO₂-atmosphere to the analyses. All these samples have a dip in the δ^{13}C-values at about 1 mm and 7 mm indicating heterogeneity in the samples.

Samples belonging to the middle group; oil treated, exposed or unexposed but plasma ashed (2:III, 3:II, 4:I and 4:II) have δ^{13}C-values in a similar interval of between +1 permil and +3.4 permil, if the surface values not are considered. All these samples probably suffer from linseed oil being left in the sample after plasma-ashing. The problem of too much oil left in the sample can be due to too thick samples and/or too short a time in the plasma-asher. After a thorough plasma-ashing the δ^{13}C-values of the samples should be more in accordance with these of samples 5:I and 6:I.

From this compilation we also find that an untreated sample, non-ashed and unexposed (5:II) may have the same high δ^{13}C-value of about +4.5 permil at the surface as samples which are oil treated, exposed/unexposed, plasma ashed/non ashed have (3:I and 4:II). The latter two samples are analysed from the inside of the sample towards the surface forcing out the oil and thus getting a proper rock δ^{13}C-value of +4.5 permil or same as for 5:II at the surface. In this case the oil treatment has obviously preserved the organic carbon emplaced at sedimentation, and which was not removed selectively by the plasma ashing.
The effect of using linseed oil for conservation can also be seen in sample 4:II when compared to sample 6:II. Sample 4:II was oil treated, exposed to SO₂ and NO₂, plasma ashed and then analysed from the inside towards the surface where it gave a proper rock value of +4.5 permil. In contrast the other samples of the same group, having lower δ¹³C-values, were analysed from the surface and inwards adding linseed oil all the time to the analyses from the oil pushed ahead in front of the laser beam. In comparison to sample 6:II (untreated, exposed but not plasma ashed) where the impact of exposure from SO₂ and NO₂ can be seen in the first 2 mm, no impact can be seen in the linseed oil treated 4:II sample.

2.5 Conclusions

The different analyses can be compiled into 3 groups (Figure 6);

* not treated with linseed oil but exposed/non-exposed, and plasma-ashed/non-ashed,
* treated with linseed oil, exposed/non-exposed, and plasma-ashed,
* treated with linseed oil, exposed/non-exposed, and not plasma-ashed

Analysing oil treated samples from the surface and inwards or from the inside towards the surface have different implications;

* Analysing from the surface the laser beam during analyses will force the oil front inwards the sample and give rise to varying results from the mixture of organic CO₂ and carbonate CO₂,
* The linseed oil most probably consists of different oil fractions, lighter and heavier, but the heat from the laser beam may also fractionate the linseed oil. Lighter fractions will penetrate the rock to a greater depth than the heavier fractions,
* Samples which are oil treated but not plasma ashed will give enigmatic results, especially if analysed from the surface and inwards,
* The same problem appears if an oil treated sample has not been plasma ashed long enough - or being too thick - leaving some organic remains in the sample.
* However, when analysing from inside the sample and outwards, the laser beam during analyses will force the oil front towards the surface, gassing out the oil, and the last surface sample will be free of added oil and give the rock the proper δ¹³C-value,
* Even after a short period of 5 weeks exposure the effect of SO₂ and NO₂ on Gotland sandstone can be easily observed in a lowering of the δ¹³C-values in the outermost mm of the sample,
* Treating the sample with linseed oil has a preserving effect on the rock and hinders the deteriorating effect of polluting gases like SO₂ and NO₂. The oil treatment even preserves the signature of organic carbon incorporated at sedimentation,
* The depth of conservation with linseed oil can be easily monitored, especially since the difference in δ^{13}C-values between linseed oil (about -30 permil) and a carbonate rock (about +2 permil to +5 permil) is very big.

* The laser method is obviously a very potential tool for discriminating between different treatments and processes, natural and induced, in carbonate rocks. The penetration of a conservation agent, like linseed oil, can be followed inside the rock and also its protective effect when compared to a not treated rock.

2.6 References


3 Market survey

An investigation of the market potential was made by Mr. Tord Andersson at Restaurator AB, Stockholm, Sweden. The correspondence is compiled in Appendix 1 with comments in Swedish by Mr. Andersson. Due to each person's own personal interpretation of the handed out material there is a natural heterogeneity in the answers concerning this investigation of the market potential for the laser method as a help in safeguarding the cultural heritage. Comments and clarifications (in Italics) are therefore needed to each answer.

A common question concerns if the method is destructive or non-destructive. The method is destructive since the equipment is stationary and not of field type and samples have to be taken at site and brought to the laboratory. The samples (drill-cores) can however be put back into the object after analyses. Another comment related to the above is whether sample is lost due to cutting. Traditionally a sample is cut out from a stone and the carbonates digested in phosphoric acid in order to release CO₂. This means that taking a suite of samples from the surface and inwards means losing material at each cutting which is particularly severe if there are great isotopic changes within a short distance. With the laser, sampling of CO₂ can be made continuously since it is just a question of moving the laser beam (with a diameter of about 15μm) to the spot where the sample will be taken.

The letter of Mr. Andersson to selected persons working with the cultural heritage reads as follows:

Dear Colleague,

With this letter and the project description enclosed I would like to ask you if you could help me with an evaluation of the methods described.

The Norwegian Institutt for Energiteknikk has a very serious approach to research and through Dr. Åberg a special interest in stone decay and restauration. On me it looks like the laser techniques could be of great interest as a complementary method of analysis to more traditional techniques.

When you have studied the papers for some days I hope you don't mind if I get in touch with you by phone or fax.

I look forward to getting your opinion how short it ever is.

Yours sincerely

Tord Andersson
Dr. F. Buzek, geologist  
Czech Geological Survey  
Prague

* From the answer of Dr. B. it is not clear if he had got all background material accompanying the letter from Mr. Andersson, especially since Dr. B. got the letter passed to him from colleagues.

* Weathering. To Dr. B. it is difficult to imagine that there is some type of fractionation process which is active in \(^{13}\)C and \(^{18}\)O. This is correct since there is probably no fractionation process but an exchange between carbon and oxygen in \(\text{CO}_2\) in air, and carbon and oxygen in the stone. This is also verified in the accelerated tests in this project.

* Dr. B. would expect some type of carbon background from plants, bacteria or micro-organism. This is correct and has been shown in the previous paper (Åberg et al. 1995) where a surface covered with lichens was analysed. Lichens preferably enriches the lighter carbon isotope leaving the heavier \(^{13}\)C behind in its thallus.

* Dr. B. states that to differentiate former conservatory materials based on organic matrix, they may be different from chemicals produced from oil, but now all of them will have nearly the same \(^{13}\)C in alkyl or alkoxylic groups. This is not a problem as long as the \(\delta^{13}\)C signature of an conservatory material like linseed oil has a value of about -30 when the stone to be preserved (like the Gotland sandstone) has a value of about +2 to +5.

* Dr. B. does not complain against the application of the method and is positive to a cooperation.

Dr. E. Charola, chemist  
University of New York  
President of World Monument Fund

* Dr. C. says that the technique appears to be extremely interesting and could prove very useful.

* Dr. C. has the remark about the sampling being destructive. This comment is correct since the equipment is stationary in the laboratory and not of field type and samples have to be taken at the site and brought to the laboratory. The samples (drill-cores) can however be put back into the object after analyses.
* Dr.C. comments on determination with the laser of previous treatments, and of biological material growing on the stone, and remarks that this does not necessarily determine all weathering etc. Any kind of weathering will be found, that is, if the weathering has caused any kind of alteration which can be seen in a change in isotope ratio from the ratio of the investigated stone. The main task is, with the help of stable isotopes, to see alterations or changes of the stone due to biological - chemical activity from the surface and inwards, and to see how deep into the stone the alteration proceeds. After conservation the following step is to monitor the conservation measures with the laser.

Dr. M. Monte, biologist
CNR - Centro Conservazione Opere d’Arte
Rome

* Dr.M. has discussed the laser project with the director of his institute, Prof. P. Testa, who is a physicist. They find the method interesting because it is non destructive. Which is not perfectly true as mentioned earlier.

* Dr.M. is very interested in applications connected to measuring biological growth which is a strong problem when safeguarding the cultural heritage. In the few tests made on lichens (see paper) it seems to be possible to discriminate between different biological overgrowth.

Dr. J. Riderer, chemist
Rathgen-Forschungslabor
Berlin

* Dr.R. finds the information about the laser method very convincing and that further research and connection with other techniques like the georadar seems very promising.

* Dr.R. thinks that there should be a wide interest in the laser technique since calcareous stones are so widely distributed and sometimes difficult to understand in their behaviour, that data concerning depth of weathering and the progress of weathering in the course of time are of considerable importance.

* Dr.R. also thinks that the study of weathering behaviour of different parts of one monument could reveal important information about the causes of decay.

* Dr.R. finally hopes that the laser technique will be subject of a discussion during the next international congress on stone decay in Berlin, September 1996.
Prof. R. Snethlage, geologist
Bayerisches Landesamt für Denkmalpflege
München

* Prof. S. finds the method interesting and agrees that it is innovative and that it allows to answer some important questions in conservation. However, it is a disadvantage that the sampling is destructive. A remark which goes back to the unclarity in the project description.

* Prof. S. means that weathering depth and detection of former treatments can be done more easily with other methods. Strength measurements would give a correlation of the effectiveness of a conservation treatment and IR directly show the material which was used. Suggesting strength measurements imply that a conservation agent type silica ester has been in mind. This kind of treatment changes the properties of the treated stone which may introduce other problems for the preservation. Using, for example, a natural oil will not change the properties of the stone but preserve it, therefore a strength measurement is of no use and will not give different results before and after an oil treatment, but, using a laser, the stable isotopes will tell how far the oil treatment has penetrated the stone. It is doubtful that IR will directly show what material was used. Stable isotopes, on the other hand, will not show exactly what conservation agent which has been used but organic derivatives have δ13C values from about -20 to -30 and downwards and analyses of the stone itself will give a reference value to be compared to (see analytical results).

* Prof. S. suggests using the laser method to differentiate between thin scales, detached lime washes or paint layers on calcareous stone since the isotope ratios in the layer and in the stone must be significantly different. This is an interesting and enlarging approach to what is already described above about analyses of conservation agents.

Dr. J. Weber,
Hochschule für Angewandte Kunst
Wien

* Dr. Weber has a good impression of the proposal for the project because he feels that there is lack of suitable methods for the assessment of both depth of weathering and depth of penetration of impregnation treatments. From this point of view, any appropriate new method, like the proposed, is welcome.

* Dr. Weber also asks if the mass spectrometer in principle can detect sulphur isotopes. If so, this could yield additional information on the source of gypsum (e.g. by reaction of SO2 or
sulphate aerosol, or by gypsum deposited from dust. The mass spectrometer is made to run sulphur isotopes as well as carbon and oxygen ones. In this case the $^{34}$S/$^{32}$S ratio is determined. Preliminary investigations to differentiate between atmospherically transported sulphur and sulphur carried by the rock itself (e.g. in the form of pyrite) has been performed on so called black crusts with good results.

Dr. G. Wheeler, chemist
University of New York
New York

* Dr. W. is very interested in the results from the project and states that if the technique can separate weathering, biological growth, and still determine the source of the stone it is truly a useful technique.

Dr. E. de Witte, chemist
Royal Institute for Cultural Heritage
Brussel

* Dr. deW. finds the documents concerning the laser method interesting and has the impression that it is a proposal for a project but is confused about what really will be done since there are similarities between the proposal and the previous publication. The last is true since this is not a proper research project but development of a research project into a market oriented project and where this study is part of an investigation of the market potential for the laser method.

* Dr. deW. also states that the method has to be described as "destructive" since samples have to be taken. This is quite true and unfortunately this has not been brought forward clearly enough, neither in the paper nor the proposal.

* Dr. deW. wants comparisons with other methods and also adds that detecting origin of samples, provenance areas, with isotope measurements is not new. Referring to the above, this is not a research project but a market oriented project and there is no funding for comparative studies. Moreover, we are quite aware of other provenance studies with the help of different isotope systems but this matter is taken up here as part of the potential in the laser technique.

* Dr. deW. concludes that the method can without doubt give new dimensions to the analysis of important cultural objects.
Summarizing the questionnaire
by Tord Andersson,

A compilation of the answers from the research group, representing a broad field within natural sciences in cultural heritage research, shows an overwhelmingly positive approach to the project as such. As a complementary method the research group consider the laser method particularly useful and also looks upon it as relatively non-destructive (with some reservation for misinterpretation). Moreover, in a drill-core, split lengthwise in two parts, analyses can be repeated on identical material.

Personally I consider the method extremely valuable since it covers broad and important fields within stone research and the conservation of stone. To a main part because of the possibility to measure weathering and depth of weathering and the possibility to study the effect of different conservation agents.

The possibility to use the laser method for determining the provenance of a stone makes the technique very interesting since knowing the site and the stratigraphic position in a quarry is of greatest value. It gives a possibility to compare stone with similar characteristics and to see what has happened since it was taken from the quarry and put into a building or sculpture.

Moreover, provenance determinations makes it possible to map distribution of stone and the development of the stone industry during the last 1000 year. This information would give invaluable knowledge to a research area which is an important complement to both that of building history and art history.

Since use of the laser methodology is in an initial stage in cultural heritage work I strongly urge further funding for the development of this technique and recommend that this knowledge shall be diffused to all researchers and staff handling the preservation and conservation of the cultural heritage of stone.
4 Appendix

4.1 Answers from the market investigation
Dear Colleague,

With this letter and the project description enclosed I would like to ask you if you could help me with an evaluation of the methods described.

The Norwegian Institutt for Ennergiteknikk has a very serious approach to research and through Dr. Aberg a special interest in stone decay and restauration. On me it looks like the laser techniques could be of great interest as a complementary method of analysis to more traditional techniques.

When you have studied the papers for some days I hope you don't mind if I get in touch with you by phone or fax.

I look forward to getting your opinion how short it ever is.

Yours sincerely,

Tord Anderson
Marknadsundersökning för projektet; 
Determination of Depth of Weathering and Conservation by use of the laser method on carbon and oxygen isotopes.

Undersökningen har utförts genom brevkontakt med ett antal utvalda personer, representanterande olika forskningsfält inom den i huvudsak naturvetenskapliga delen av den internationella kulturmiljövården.

Förfrågningen har koncentrerats till Europa och USA. Utvalet har gjorts självständigt av undertecknad baserat på personliga kontakter men också utifrån den vetenskapliga litteraturen inom området.

Utskicket gjordes i januari 1996 (se bilaga 1). Svar har företrädesvis lämnats på fax. En påstötning har gjorts i juni-96 till de personer som kan ha betydande synpunkter på projektets innehåll och värde. Övriga som inte svarat bedöms i detta skede kanske inte riktigt så insatta i metodiken så att de kan ha några vetenskapliga synpunkter av värde.

Tillfrågade personer/institutioner och deras specialiteter.

Dr. Giovanni Allesandrini geolog
Centro Studio Gino Bozza
Politechnico di Milano
Milano, Italien
Allesandrini är en av Italiens ledande personer inom den italienska stenkonserveringen med specialisering kring forskning på konserveringsprodukter och metoder.

Dr. Andreas Arnold fysiker, geolog
ETH i Zürich
Institut för Denkmalpflege är en av världens ledande experter på fukt- och saltproblem i oorganiska byggnadsmaterial.

Dr. Elena Charola kemist
University of New York
Ledare för World Monument Fund.
Anlitas ofta som internationell expert vid utvärdering av konservering och konserveringsbehov.
Dr. Vasco Fassinen kemist
Laboratorio Scientifico i Venedig.
Arbetar för närvarande med en utvärdering av i stort sett alla stora konserveringar som gjorts i Venedig sedan 1967.

Dr. Wolfgang Krumbein biogeolog
University of Oldenburg.
Specialist på biogeologisk nedbrytning av sten och puts.

Dr. Michaela Monte biolog
CNR Centro Conservazione Opera d’Arts.
Arbetar med biologisk nedbrytning och skydd mot detta.

Prof. P. Mirwald mineralog
Universität Innsbruck.
Tidigare ansvarig för forskningen vid Zolieninstitut in Bochum, Tyskland.

Prof. Lorenzo Lazzarini petrolog
Avd. för arkitektur vid Universitetet i Venedig.
En av de ledande forskarna inom stenkonserveringsområdet.
Specialist på proveniensbestämning

Dr. Owen Lewis arkitekt
School of Architecture Dublin University.
Arbetar inom EU med bl a proj. Eurocare.

Dr. I Delgado-Rodrigues petrolog
En av de ledande personerna inom ICOMOS stengrupp

Dr. D. Jeannatte geolog
Inst. de Geologi Universitetet i Strassburg.
Arbetar med sandstensforskning på katedralen i Strassburg.

Mr. J. Philippon kemist
Ministere de la Culture, Paris.
Ansvarig för forskning inom konservering i Frankrike.

Dr. F. Buzek geolog
Stable Isotope Laboratory Tscekien.
Isotopgeolog som arbetar med konserverings- och vittringsfrågor.

Dr. E. deWitte kemist
Royal Institute for Cultural Heritage.
En av de ledande forskarna på konsolidering av sten.
**Prof. Jimenez** är skeptisk till mätningens noggrannhet (the great steps between subsequent analysed spots). Han tror i övrigt på metodens användbarhet då den inte förstör den provtagna ytan.

**Dr. Buzek**, som är den person som framstår som den mest kunniga inom området isotopgeologi är tveksam till huruvida de resultat som framkommer motsvarar vittring. Han är även tveksam till om behandling av sten kan avläsas. Han är dock intresserad att delta i ett framtida samarbete.

**Dr. Riderer** tror på grundval av de resultat som redovisas att metoden har en framtid speciellt i kombination med andra tekniker t ex georadar. Han menar vidare att speciellt kalkbunda stenars vittring är så svårtolkade. Han ser fram mot en givande diskussion i Berlin (7:e internationella stenkongressen) i september. Om nya resultat framkommit finns det möjligheter att presentera dessa.

**Dr. Monte**, som är biolog, har studerat "projetet" tillsammans med Prof. P. Testa, som är fysiker. Denne ser metodens fördelar i att den är icke förstörande. Som biolog är Monte främst intresserad av hur man kan mäta de olika biologiska arternas nedbrytande "kraft".

**Dr. Charola** säger sig inte vara insatt i denna teknik, men hon ser den ändå som extremt intressant och kan komma att bli mycket användbar. Hon menar vidare att titeln skall modifieras, då det ändå finns begränsningar i vilken typ av vittring som kan detekteras. Hon menar också att metoden inte är helt oförstörande, då man ändå måste ta en bit sten ur monumentet.

**Prof. Krumbein** anser sig inte kunna utvärdera projektet utan hänvisar till en specialist i England.

**Dr. deWitte** säger sig ha läst med stort intresse men tycker att målet med projektet är något oklart. Han kan inte se vad som är riktigt nytt i utvecklingen. Han tycker vidare inte att metoden är mindre förstörande än många andra, "då man måste ta prov är den förstörande".

Han saknar jämförelser med andra tekniker. Han tror dock att metoden utan tvivel kan ge nya dimensioner i analysen av viktiga monument.

**Dr. Wheeler** säger att om metoden kan skilja på vittring, biologisk påväxt och ändå bestämma stenens ursprung så är det en användbar teknik. Han lämnar adress och referens till en specialist inom området som studerat tekniken på antik marmor.
Dr. G. Wheeler kemist
University of New York, cons.dep.
Forskare inom konservering av sten med specialisering på konsolidering.

Dr. J. Riderer kemist
Rathgen-Forschungslabor Berlin.
Har varit verksam inom den internationella stenkonserveringsdebatten i ca 30 år. Stor erfarenhet.

Prof. Saiz Jimenez kemist/geolog?
Instituto de Recursos Naturales y Agrobiologia de Sevilla.
ledande spansk forskare inom stenkonservering, spec. granit.

Prof. A. Vendel kemist
Hochschule für Angenante Kunst i Wien.
Ansvarig för Eurocare 1995 1996

Prof. Rolf Snettlager geolog
Bayer. Landesamt für Denkmalpflege.
Ledande tysk forskare med samordningsansvar för forskning inom den tyska kulturmiljövården.

Inkomna svar och kommentarer

Svar har i dagstället inkommit från:

Rolf Snettlager
Elena Charola
Josef Riderer
George Wheeler
Wolfgang Krumbein
Michaele Monte
Eddie deWitte

Av dessa svar framgår att de tillskrivna tagit sig god tid att studera projektet och dessutom har man fört frågorna vidare till specialister för att få hjälp.

Dr Rolf Snettlager menar att studier av vittringsdjup och utvärdering av konserveringsprodukter kan låta sig göras lättare med andra metoder, som är mer lämpade. Han exemplifierar t ex IR och hållfasthetstest. "Lasermetoden" borde främst lämna sig för att undersöka gamla ytbehandlingar t ex färg.
Dear Dr. Anderson,

as I worked with Dr. Sramek on some stable isotope application in the past, his former colleagues pass me your letter to reply. I am not sure if my answer will be what you expect. I do not complain against the application, but I am not sure if the results reflect weathering. For me it is difficult to imagine that there is some type of fractionation process which is active in 13C and in 18O. More probably I would expect some type of carbon background not only soot but generally any residua from plants, bacteria or microorganism. They may reflect some climatic or environmental effects in metabolism of carbon, that are latter analysed. How it is linked to weathering process I cannot realize. Also proposed application on following treatment procedure seems to me rather unclear. If you want to differentiate former conservatory materials based on organic matrix, they may be different from chemicals produced from oil, but now all of them will have nearly the same 13C in alkyl or alkoxyl groups (if you do not use any special prepared).

If you want to put together some people to get samples or other type of cooperation, let me know. Me I did only sulphur isotopes to identify the possible sources of atmospheric pollution (crusts).

With best regards

Yours sincerely,

F. Buzek
Dear Goran,
sorry to reply so late but I was out. Tell the truth I am not sure about
my remarks I send in letter. But seems to me that identification of oil
traces is OK, only change of carbonate with CO2 is quite unusual. I do
not know how you can clean the surface, maybe it is impossible in such
small quantity. What I know that people studying stone weathering should
be happy with your explanation. Carbonate balance of any microcatchment
study is always difficult. We are doing small quantity of C and N and
background effect can be troublesome.
In 1993 I did some sulphur isotopes in sulphate crust and I got some
quite useful results from Belgium. I hope I will start writing paper now
in summer - so if you want I will sent you a copy of manuscript, just to
know how we did it.
I would like to ask you for some other favour - I am planning to run some
study on coal bed methane and isotopic effect with adsorption, desorption
and migration phenomena - do you think that some of your colleagues will be
interesting to share results?

Best regards
frantisek
TO: Tord Anderson  
Restaurator  
FAX: 46 (8) 651-9803  
FROM: A. Elena Charola  
fax 1 (516) 482-1126  
DATE: February 27th, 1996

Dear Tord,

I received your letter of February 13th and the enclosed project description as well as a copy of the relevant paper from the 1993 UNESCO/RILEM Conference.

In the first place I have to admit that I am not familiar with the technique described, so I cannot judge the actual work. However, it appears to be extremely interesting and could prove very useful. Possibly that is what this proposal is about.

If this is the case, in the first place I would suggest a slight modification of the title: **Possibility of determining the depth of ...** since from what I understood of the Paris paper, what can be determined are previous treatments and biological material growing on the stone. But this does not necessarily determine all weathering, unless one starts from the premise that biological colonization occurs only on weathered surfaces. I am not sure this is the case.

One last minor consideration: the claim that “no material is lost due to cutting” is not quite accurate if I understood correctly that all the analyses are carried out in a laboratory which implies that samples have been cut from the monument. Maybe indicating that “the amount of material due to cutting is reduced” would be more appropriate.

Some minor English changes: the word “exogenic” is used and I assume that “exogenous” is meant. “lime-cemented stone” should be “calcite-cemented stone” or “stone with a calcareous binder”

I hope that if this project continues you will let me know when results are published (even in Swedish, I’ll try to muddle through it).

I hope that these comments may be useful to you. I am faxing them rather than awaiting your call because I will be away as of this Thursday.

Regards,

A.

PS: Tell Pedro I got his letter yesterday.
The project describes the possibility of using laser ablation technique to evaluate stone weathering. By applying the laser ablation technique, CO₂ is released from the carbonaceous stone and subsequently the isotopic ratio of O and C is analyzed. The variations in the isotopic ratio of C and O between the affected outer layer and the unaffected inner part are large enough to be determined by mass spectrometry; especially for C, large variations are observed. One advantage of applying the laser ablation technique is that no losses of the stone occur during the cutting process. The beam penetrates the stone and subsequent layers may be analyzed. The distance between the subsequent analyzed spots varies between 300 and 1000 mm, which seems quite large. These large steps may be do not permit to analyze the most interesting outer weathered layer of the stone. When proceeding deeper inside the stone, it is possible that problems will arise in focusing the laser beam.

The technique offers the possibility to determine very precisely the isotopic variations in the deteriorated layer. However, since the depth resolution of the technique is not very high, it is possible that the layer, containing the different isotopic composition from the bulk, is so thin that it can not be determined, when proceeding in steps of around 500 micrometers. The most weathered part of the stone, where the isotopic ratio is most different from the bulk composition, may be very thin due to removal of the layer by subsequent rain events. The large steps will make it quite difficult to determine accurately to which depth consolidants enter the stone.
Your letter

Dear Tord,

in case you want to have a serious evaluation of the technique you must contact Dr. R. Evershed, School of Chemistry, University of Bristol. Contracts close Bristol BS8 1TS, U.K.

Certainly I am not an expert in this field.

I would like to meet you sooner or later.

Best regards

Prof. Dr. W.E. Krumbein
To: Dr. Tord Anderson  
Hantverkargatan 7, Box 221 14, 
104 22 Stockholm  
fax: 08 - 651 98 03

From: Dr. Michela Monte  
C.N.R. - Centro "Conservazione Opere d'Arte"  
via Monte d'Oro, 28  
00186 Roma  
fax: 06 - 6871462

Dear Colleague,

I am sorry for the late answer to you about the paper: "Determination of depth of weathering and conservation by use of the laser method on carbon and oxygen isotopes." I have been out of Rome.

I have not experience in the use of the laser because I am biologist. For this reason, I have given the paper to Prof. P. Testa, director of this Institute, he is a physicist. He said me that the method is very interesting above all because it is a non-destructive testing. It has a wide range of applications: in biological field, it can allow to measure the effect of biological growth and I am very interested because it is a strong problem. For biologists, is very important to ascertain damage power of the species (bacteria, actinomycetes, fungi, algae and lichens).

Awaiting to know the results of further experiences, I thank you very much.

Sincerely yours

(dr. Michela Monte)

Michela Monte
Dear Colleague,

Exluse me for the delay, but actually I have absolutely no time (we have an important meeting on June 98) - I transmitted your letter to Miss Veronica Bélanger (20, rue de Paris, 75016 Paris, Tel: 33 60 0005 01 45, Fax: 33 164 68 84 87). I think she is able to give you answers. I am not a specialist in this matter and she knows a lot of people.

Yours sincerely,

[Signature]
Telefax
0046 8 6519803

Mr. Tord Andersson
Restaurator Tord Andersson Conservation AB
Hamverkargatan 7
Box 22114
S 10422 Stockholm

Dear Mr. Andersson,

thank you very much for your informations concerning laser techniques for the analysis of carbon and oxygen isotopes. The informations published by Aberg and his colleagues are convincing enough that a further research and a connection with other techniques like the geonuclear seems very promising. I think there should be a wide interest in this technique since calcareous stones are so widely distributed and sometimes so difficult to understand in their behaviour that data concerning the depth of weathering and the progress of weathering in the course of time are of considerable importance. This becomes obvious in Berlin, where there are no close deposits of natural stone and building stones from different locations have been brought to build the town. So we have here this broad variety of different marbles, of limestones from different provenonces and of calcareous sandstones, where the progress of weathering usually is not considered thoroughly. Especially the study of the weathering behaviour of different parts of one monument could reveal important informations about the causes of decay. I hope that this technique will be subject of a discussion during the next international congress in september in Berlin, since R. Lofvendahl will be here. If there are new results or new applications there would be still enough time to prepare a paper for this congress.

Thank you again for this information
and best wishes

Ilm Riederer
Project on laser and isotopes

Dear Tord Andersson

With interest I have read the proposal about the use of carbon and oxygen isotope chemistry in the field of conservation. I would agree that the method is innovative and allows to answer some important questions in conservation. However, it is a disadvantage that it is destructive because samples have to be taken.

I have not the same opinion about the application areas of the isotope measurements. Although it can be used for the determination of the weathering depth and the detection of former treatments these measurements can be done more easily with other methods which have a better relation to the problem. Strength measurements give a correlation to the effectiveness of a treatment. IR measurements directly show the material which was used - if any traces are found at all. Basically this is also possible with isotope measurement, but for an interpretation the standard spectra are still missing and the work to establish all these data would be immense.

In my opinion the method is more and particularly useful in the detection of old washes or paint layers. From my experience I know that especially in sheltered areas - on natural stones very often thin layers are found whose origin is not clear. Are these thin scales or detached lime washes or paint layers which were transformed into gypsum. Such questions which can not be solved with other methods in the case of carbonate stone can be answered by isotopic chemistry because the isotope ratios in the layer and in the stone must be significantly different.

If you have further questions please contact me.

Sincerely yours

Rolf Suhrthage
Dear Tord,

Prof. Vendl handed me your letter and background papers concerning the laser-analytical project. He asked me to give some comment on it instead of himself, and to ask you to apologize the delay.

As analytical methods of this kind are neither my field of expertise and in order to avoid any further delay, my comments will be rather short, as follows:

- In principle, I feel that there is lack of suitable methods for the assessment of both depth of weathering and depth of penetration of impregnation treatments. Just from this point of view, any appropriate new method is welcome.
- Personally I think that the future belongs to non-destructive or low-destructive in situ-measurements. I wonder if, in a second stage of development, such application could be possible in case of the proposed method? Could the mass spectrometer in some way be connected to a laser-cleaning unit? As you know well, such cleaning methods are about to conquer the market, and it would be a wonderful thing to have simultaneous analysis of what you clean away. Maybe this is not possible for technical reasons, but if it was, it would be worth to follow-up.
- Finally: can the mass spectrometer unit in principle also detect sulphur isotopes? In the case of gypsum crusts, this could yield additional information on the source of gypsum (e.g. by reaction of SO₂ or sulphate aerosol, or by gypsum deposited from dust).

The above is not criticism, because I have a good impression of the proposal, but only some additional remarks.

Very best regards

Johannes Weber
Dear Todd,

I was very interested in the results of the project. If the technique can separate weathering, biological growth, and still determine the source of the stone, it is truly a useful technique.

I have given you the name of a specialist in isotope analysis who should be interested in your work.

Best regards,

George

P.S. I hope to see you in Berlin in September.
KONINKLIJK INSTITUUT VOOR HET KUNSTPATRIMONIUM
INSTITUT ROYAL DU PATRIMOINE ARTISTIQUE
ROYAL INSTITUTE FOR CULTURAL HERITAGE
Jubelpark 1 B-1040 Brussel, Belgium

FAX MESSAGE

To: RESTAURATOR
  c/o: Mr. Torst ANDERSON
  Fax: 02.46.8.651 98 03
  Date: 11 March 1996

From: Eddy DE WITTE
  Tel. : +32(0)2.739.68.41
  Fax : +32(0)2.732.01.05
  e-mail : eddy@kikirpa.be
  Ref. : Project LASER Method

Dear Mr. Anderson,

I have read with great interest the documents you send me. I have the impression that it is a proposal for a project, but I am somewhat confused about what really will be done.

The publication which was added gives a description of preliminary work that has been carried out. Parts of the project are identical to parts of the proposal. I do not see what is really new in this project.

I also have some remarks on the technique and the description of the technique:

- The authors give the impression that this technique is less destructive than others. I would however attract the attention to the fact that whenever samples have to be taken, the method has to be described as "destructive".
- There is a lack of comparison with other techniques. It is nice to invent a new technique, but in order to prove its advantages, one should do tests on identical samples with as well existing as with the new technique.
- The method of detecting the origin of rock samples by isotope measurements is not new. I really miss references to the work of Moens on the identification of the provenance of marble.

To conclude I would like to state that the method can, without any doubt, give new dimensions to the analysis of important cultural objects, but that a well-defined description of what really will be done and with which existing methods it will/can be compared should be described.

Yours sincerely,

Dr. Eddy DE WITTE
head of department
Sammanfattning


Viss tveksamhet har framföpts angående metodens kapacitet, främst från forskare som är initierade i isotopundersökningar, men de prover som gjorts och redovisas tycktes ändå lovansvärda.

Personligen anser jag att metoden är oerhört värdefull då den greppar över ett stort, brett och viktigt fält inom området sten och stenkonservering. Dels att kunna mäta vittring och vittringsdjup inklusive den biologiska aktiviteten, dels att undersöka effekten av både organiska och oorganiska konserveringsprodukters penetration.

Att man dessutom kan utnyttja metoden för att proveniensbestämma sten gör tekniken mycket intressant. Stenens ursprung och läge i ett brott är ovärderlig kunskap av flera skäl.

För det första så får man möjlighet att med stor sannolikhet jämföra sten med lika ursprungsegenskaper. Man kan alltså ”se” vad som skett med stenen i byggnadens skulpturer under de år som gått sedan den ”togs” ur stenbrottet.

För det andra ger denna metod en möjlighet att kartlägga stendistribution och stenindustriers utveckling under ca 1000 år. Denna vitskap skulle ge ovärderlig kunskap till ett forskningsområde som är ett viktigt komplement till både den byggnadshistoriska och konsthistoriska forskningen.

Då metodiken befinner sig i ett initialstadium finns det all anledning att satsa på vidare utveckling samtidigt som man sprider denna kunskap till forskare och byggnadsvårdare i världen.

Tord Andersson
4.2 Compilation of analytical results
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4.3 Figures
Figure 1. Showing size, preparation and analysis of the Gotland sandstone. Linseed-oil treatment, exposure in climatic chambers to SO2, NO2, and 90% RH, cutting, plasma ashing and laser analysis. Due to sample heterogeneity duplicatyes of the same samples were used. Therefore the labels “to plasma” do not apply in all cases but is corrected in text and sample description.
Figure 2. Difference between non-ashed (2:II) and ashed (2:III) samples after linseed oil treatment and exposure to SO2 and NO2. The ashing in 2:III has not been complete since the d13C-value undulates about +2 (linseed oil has a d13C-value of about -30 permil).
Figure 3. The treatment with linseed-oil can be seen down to a depth of about 10 mm. Sample 3:i was analysed from the inside of the sample and towards the surface, pushing out the oil and reaching a proper rock value of +4.5 permil at the surface. Sample 3:ii (not completely plasma-ashed) was analysed from the surface and inwards pushing the remains of oil (with a d13C-value of about -30 permil) in front of the laser beam.
Figure 4. The treatment with linseed-oil has protected the sandstone against the exposure of SO2 and NO2. Both samples are plasma-ashed but 4:1 is analysed from the surface and inwards thereby getting a lower d13C-value at the surface. The sample (4:11) was analysed from the inside and outwards and got a surface d13C-value of about +4.5 permil like in the unexposed but linseed-oil treated sample in Figure 3. These values are in contrast to that of about +3.3 permil in the exposed but not linseed-oil treated and protected sample (6:11) in Figure 5.
Figure 5. Samples 5:1 and 6:1 are parallels to 5:II and 6:II, but plasma ashed. The decrease, after ashing, from about +4.5 permil to +3.5 permil shows that the sandstone carries organic material incorporated at sedimentation. Sample 6:II was exposed to SO2, NO2 and 90% RH. The CaCO3 in the sandstone, with a higher d13C-value of about +4.3 permil, has reacted under the prevailing conditions and during the formation of gypsum an exchange with the CO2 carbon in air, with a low d13C-value of about -7 permil, has taken place. The result of the process being a lowering of the total d13C-value in the outermost 2 mm of the sample.
Figure 6. Compilation of all results. Three groups can easily be distinguished.
1. Samples in the top group have not been treated with linseed oil and have thus no memory of the oil in contrast to the middle group. The difference between non-plasma ashed and plasma-ashed samples is due to organic material incorporated at sedimentation.
2. All samples in the middle group have been plasma ashed to a different degree depending on the original oil content, sample thickness and time in the plasma asher.
3. In the bottom group there is only one sample, oil treated but not plasma ashed. The laser analyses from inside and towards the surface however reveals the oil front at about 10 mm depth in this sample and the original $d^{13}C$-value of about +4.5 permil at the surface.
4.4 Analytical protocol from the exposure at NILU
Testing av gotlandsk sandstein i klimaskap type Chalmers

Før forsøket startet ble eksponeringskamrene vasket med sprit og gjennomluftet med tørr "ren" luft. Deretter ble permeasjonsrørene (SO₂ og NO₂) tilkoblet og kjørt for å stabilisere kamrene. Til slutt ble fuktigheten innstilt på 90 % rel.hum., og kamrene kjørt videre uten prøver for endelig stabilisering.

Alle permeasjonsrørene ble veid før og etter forsøket. Vektdifferansen viser forbrukt SO₂, henholdsvis NO₂, under forsøket, dvs. den gassmengde prøvene har vært utsatt for.


Ett for ett ble kamrene kontrollert ved hjelp av en SO₂-monitor og en NOₓ-monitor. Dessverre har NOₓ-monitoren vist seg å være noe upålitelig, så målingene fra den er ikke tatt hensyn til. Under og etter eksponeringen ble det tatt stikkprøver av NO₂ og SO₂ for analyse på laboratoriet. Resultatene av vektetpmålingene foreligger i tabell 1, og resultatene fra monitor og gassanalysene i tabell 2.

<table>
<thead>
<tr>
<th>Kammer A</th>
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<th>Kammer C</th>
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<tr>
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<td>Gassrør</td>
<td>Konsentrasjon</td>
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<tr>
<td>NO₂</td>
<td>285</td>
<td>284</td>
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<tr>
<td>SO₂</td>
<td>173</td>
<td>401</td>
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Tabell 1: Vekttap på permeasjonsrørene (μg/m³).
Tabell 2: Verdier før, under og etter eksponering (µg/m³).

<table>
<thead>
<tr>
<th></th>
<th>Kammer A</th>
<th>Kammer B</th>
<th>Kammer C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂ før eksponering</td>
<td>363</td>
<td>413</td>
<td>387</td>
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<tr>
<td>SO₂ under eksponering</td>
<td>150-220</td>
<td>220-280</td>
<td>170-250</td>
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<tr>
<td>SO₂ etter eksponering</td>
<td>300-350</td>
<td>370-420</td>
<td>320-360</td>
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**Analyseresultater**

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<tr>
<td>SO₂ under eksponering</td>
<td>x</td>
<td>392</td>
<td>275</td>
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<tr>
<td>SO₂ etter eksponering</td>
<td>283</td>
<td>356 (408)</td>
<td>367</td>
</tr>
<tr>
<td>NO₂ under eksponering</td>
<td>192</td>
<td>185</td>
<td>160</td>
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<tr>
<td>NO₂ etter eksponering (foreligger ennå ikke)</td>
<td>252</td>
<td>190</td>
<td>174</td>
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</table>

x: Feil analyse.

Plott fra monitor SO₂ (µg/m³) er vedlagt. Figur 1, 2 og 3 viser de midlere verdier av monitorresultatene for SO₂ gjennom forsøket. Som en ser av figurene er det en tendens til reduserte konsentrasjoner under forsøket. Størst reduksjon er det i kammer A. I kammer A fikk en også den største reduksjonen av gasskonsentrasjoner når prøvene ble lagt inn.

Selv om resultatene er noe idealisert, så mener vi at den adsorberte mengden av SO₂ har vært tilnærmet konstant under forsøket.

Tabell 3 viser den reduserte konsentrasjonen som skyldes adsorpsjon i kamrene.

Tabell 3: Gjennomsnittlig adsorbert mengde SO₂ under eksponering av stein beregnet ut fra figur 1-3.

<table>
<thead>
<tr>
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<td>Kammer B</td>
<td>~125</td>
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<td>Kammer C</td>
<td>~125</td>
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Med hilsen

Thor Ofstad
Lab.tekniker

Vedlegg
Kammer A
SO₂

Før eksponering

Etter eksponering

Kammer B
SO₂

Før eksponering

Etter eksponering

Kammer C
SO₂

Før eksponering

Etter eksponering
Instituttet har en årsomsetning på rundt 380 mill.kr.


The Institute’s annual turnover is approx. NOK 380 million.

The total number of employees is approx. 600 (1995). In addition 12-15 foreign scientists attached to the Halden Project.