WEATHERING AND CONSERVATION DEPTH DETERMINED BY CARBON ISOTOPES RELEASED BY LASER ABLATION

G.Åberg and D.E.Stijfhoorn
Institute for Energy Technology
Box 40, N-2007 Kjeller, Norway

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 exogeneous 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 Eureka 1394 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 a short period of exposure the effect of SO_2, NO_2 and elevated humidity on Gotland sandstone can be easily observed in a change of the $\delta^{13}C$-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 SO_2 and NO_2. A new conservation agent based on the linseed oil characteristics is under development and results from this work will also be presented. The great advantage with this new conservation agent is that it can be tailor-made for every kind of carbonate stone material.

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 fresh samples, and consolidated and non-consolidated samples after the latter 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 characterizing 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.

Analytical procedure

Gotland sandstone

The Gotland sandstone, southeastern Sweden, 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 $\delta^{13}C$-value of about +4.2 (Åberg et al.1995). Six sandstone samples, cubes with a side of 5x5x5 cm, were taken out by Slite AB on Gotland for the analytical work .

Conservation agents

The linseed oil used in this project is a Swedish cold-squeezed linseed oil with a $\delta^{13}C$-value of -30.4 (Åberg et al.1995. Thus, the overall influence of linseed oil treatment would be a lowering of the $\delta^{13}C$-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. The new conservation agent, a mixture of different organic components and polymers in white spirit has a $\delta^{13}C$-value of about -30, thus corresponding to that of linseed oil.

Accelerated weathering

In the first test linseed oil and untreated samples were exposed to SO_2 (about 410 $\mu g/m^3$) and NO_2 (about 235 $\mu g/m^3$) for 5 weeks at a relative humidity of 90%. The gas mixture was pumped through the system with an air-flow of 2 litres per minute. In the second test two different types of Gotland sandstone, two impregnated with the new conservation agent and two not impregnated, were exposed for same amount of time and under similar conditions as above. Unimpregnated samples of all rocks 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 alcohol was used as a cooling agent since water will dissolve the gypsum which will form during the sulphation process at exposure. Slices with a thickness of 3 mm were cut out from the centre of the cube and from each 3 mm slice a 15 mm wide piece was cut. Each piece was marked for orientation.

Plasma asher

A low temperature radio frequency plasma asher was used in order to eliminate organic material in the samples which may disturbe the analyses of the inorganic carbon. There are two types of organics of interest in this investigation, firstly those incorporated in situ at sedimentation, and secondly the conservation agent 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 CO_2 gas released was transferred to a Finnigan MAT 251 mass spectrometer equipped with a microinlet. The optimal precision is approximately ±0.1‰ (one sigma) for both $\delta^{13}C$ and $\delta^{18}O$ in carbonates. All isotope values are given relative to the PDB standard.

The laser-ablation technique can be used for spot-analyses if enough CO_2 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 but when the analytical work is finished the analysed sample can be put back in place by a stone conservator.

Results and discussion

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. With the laser technique it is possible to estimate how far into a calcareous rock the weathering has proceeded and how far organic stone consolidants have reached into the material.

A baluster from the roof of the Royal Palace, Stockholm, Sweden, probably from the 19th century but taken down and replaced at the restoration in 1990 was analysed (Åberg et al. 1995). The baluster has probably been subject to surface treatment with linseed oil. The $\delta^{13}C$-value is strongly negative at the surface, -13.4, but increases continuously to +3.8 (Figure 1). The sample released great amounts of gas when analyzed, the cause being lots of organic material, probably originating from the linseed oil treatment. After analysis, the sample was ground down about 100 µm, in order to remove the previously analyzed part, and then plasma ashed in order to get rid of all organic remains like e.g. previous conservation agents.

The new laser analysis rendered a completely different pattern for the carbon isotopes in comparison with the non-ashed sample. The surface $\delta^{13}C$-value is now -1.7, stabilizes below a depth of one mm and then slowly approaches a value of +3. Obviously, the organic material has been destroyed during the plasma-ashing, while the calcite was left intact.

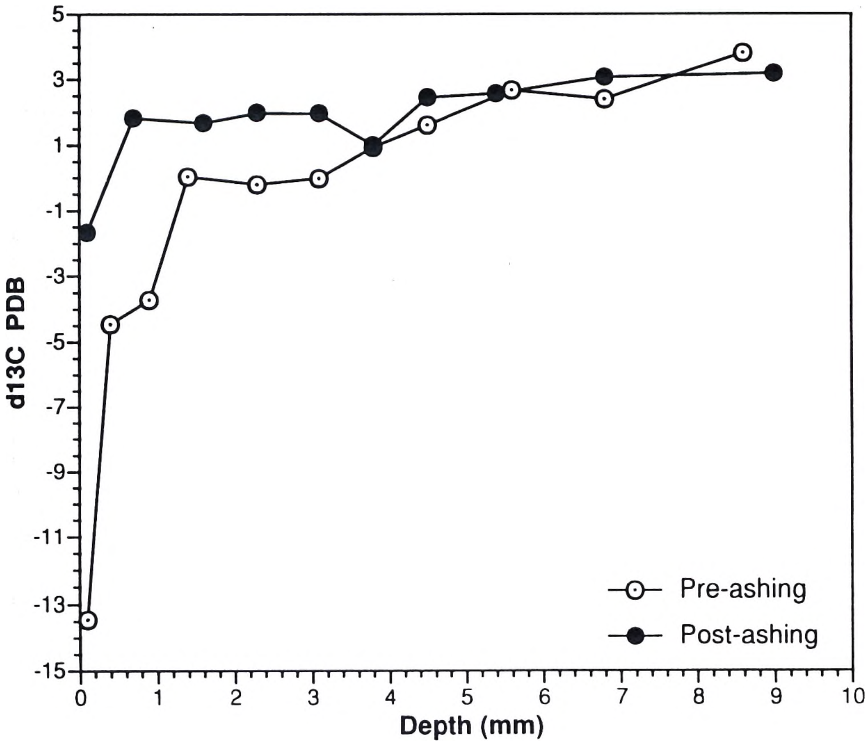

Figure 1. Baluster from the Royal Castle in Stockholm which was replaced at the 1990 renovation but probably originates from the 19th century. The baluster has been treated previously with linseed-oil (probably tens of years ago). The sample was analysed before and after plasma-ashing.

It is also possible to measure the effect of biological overgrowth on the substrate. In the countryside, buildings with Gotland sandstone will, with time, be colonised by organisms of different types. In this case, lichen growth is common on rain-exposed surfaces. Algae are also prolific in sheltered environments with no direct sunshine but high humidity. Lichens do not extract carbon from the air, but utilize the substrate. The thallus of calcophile lichens on Gotland sandstone have $\delta^{13}C$-values of about -20 per mil (PDB-scale) or lower (Åberg et al.1995). Lichens enrich the lighter isotopes of C (and O) and expel the heavier, and thus give rise to strongly negative $\delta^{13}C$-values 1 to 2 mm below the surface (Figure 2).

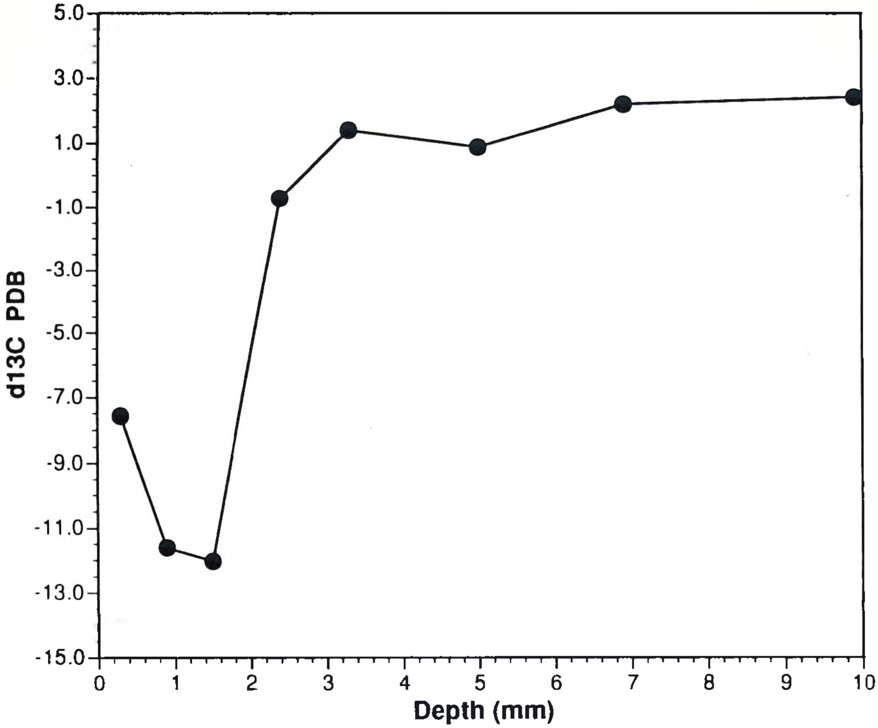

Figure 2.. Weathered surface of Gotland sandstone, from the medieval Sundre Church Gotland, covered by lichens which have a d13C about -20 to -24. Lichens fractionate carbon isotopes, enriching the lighter 12C isotope in its thallus and expelling the heavier 13C isotope at the surface of the stone.

The possibility of performing accelerated tests of weathering rates under controlled conditions in the laboratory is valuable since a common question is the validity of different consolidation agents. This test can be done on fresh samples as well as naturally pre-weathered ones. How deep do the conservation agent penetrate the object to be consolidated? What is the resistance to pollution in the climatic chamber after consolidation? And what is the difference between consolidated and unconsolidated samples after they have been exposed to accelerated weathering tests. The analytical results (Åberg et al. 1996) show that even after such a short period as 5 weeks of exposure the effect of SO_2, NO_2 and 90% relative humidity on Gotland sandstone can be easily observed in a change of the $\delta^{13}C$-values in the outermost 2 mm of the stone (Figure 3).

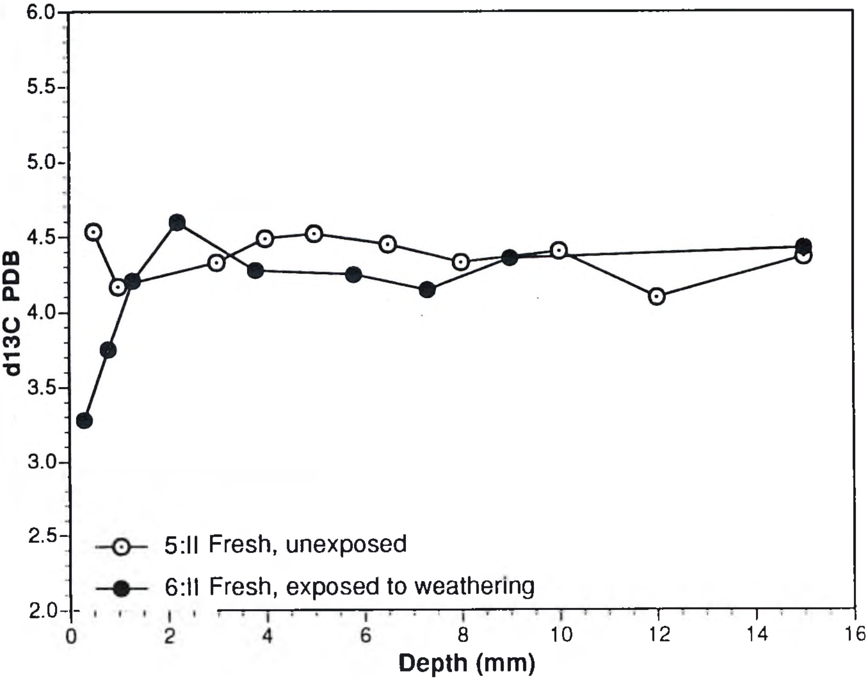

Figure 3. Sample of Gotland sandstone (6:II) exposed to SO2, NO2 and 90% RH. The CaCO3 in the sandstone, with a higher d13C-value of about +4.3, has reacted under the prevailing conditions and during the formation of gypsum an exchange with the CO2 carbon in air, with a low d13C-value of about -7, has taken place. The result of the process being a lowering of the total d13C-value in the outermost parts of the sample.

However, treating the sample with linseed oil has a preserving effect on the rock and hinders the deteriorating effect of SO_2 and NO_2. The oil treatment even preserves the signature of previously incorporated organic carbon (Åberg et al. 1996). The depth of conservation with linseed oil can also be easily monitored since the difference in $\delta^{13}C$-values between linseed oil (about -30) and the Gotland sandstone (about +2 to +5) is very big. The laser method is thus a very potential tool to study the effects of previous treatments and natural and induced processes, in carbonate-rich rocks of the Gotland type.

From a compilation (Åberg et al. 1996) we find that samples which are oil treated, exposed/unexposed, plasma ashed/non ashed may have the same high $\delta^{13}C$-value of about +4.5 permil at the surface (Figure 4, samples 3:I and 4:II), for this kind of rock, as a fresh untreated sample, non plasma-ashed and unexposed (Figure 3, sample 5:II). Sample 3:I is treated with linseed oil, unexposed and not plasma ashed. From the surface and to the oil-front at 10 mm the $\delta^{13}C$-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 4). Thereafter the $\delta^{13}C$-value increases till a value just above 0 permil. In this case the oil treatment has obviously , at the surface, preserved the original carbon signature emplaced at sedimentation.

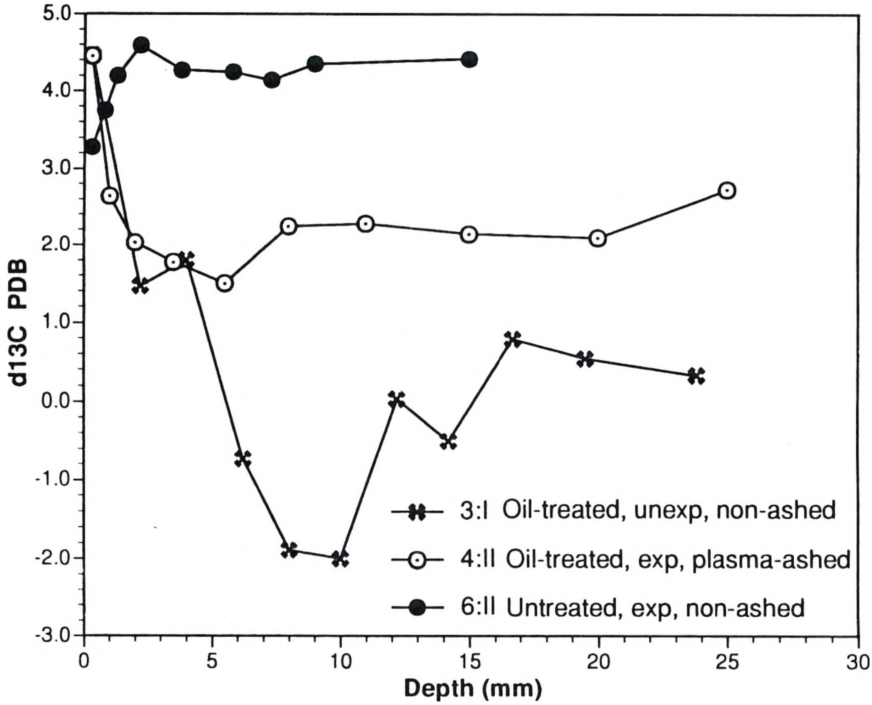

Figure 4. Samples 3:I and 4:II, which were treated with linseed-oil with a d13C-value of about -30 permil, were analysed from the inside and towards the surface where they got the sandstone d13C-value of about +4.5. In contrast to 4:II sample 6:II, which was exposed to SO2 and NO2 but not treated with linseed-oil in advance, show a weathering effect with low d13C-values at the surface due to an exchange between CO2 carbon in air (d13C about -7) and calcite carbon in the stone (+4.5). Linseed-oil is obviously preserving the sandstone against aggressive pollutants transforming the calcite cement (CaCO3) to gypsum (CaSO4•2H2O).

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 SO_2 and NO_2 and plasma-ashed. In comparison to sample 6:II (not treated with linseed oil, exposed but not plasma ashed) where the impact of exposure from SO_2 and NO_2 can be seen in the first 2 mm, no impact can be seen in the linseed oil treated 4:II sample. 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, NO_2 and 90% RH. 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. 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.

Conclusions

* Even after a short period of exposure, the effect of SO_2, NO_2 and a relative humidity of 90%, on fresh Gotland sandstone can be easily observed in a lowering of the $\delta^{13}C$-values in the outermost mm of the sample,
* Treating the sample with the above type of conservation agent has a preserving effect on the rock and hinders the deteriorating effect of polluting gases like SO_2 and NO_2.
* The depth of conservation with linseed oil or a similar conservation agent can be easily monitored, especially since the difference in $\delta^{13}C$-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.

References

Åberg, G., Löfvendahl, R., Stijfhoorn, D & Råheim, A., 1995: Provenance and weathering depth of carbonaceous Gotland sandstone by use of carbon and oxygen isotopes. Atmospheric Environment 29, 781-789.

Åberg, G., & Stijfhoorn, D., 1996: Determination of weathering and conservation of sculptured stone by use of the laser method. Internal report, IFE/KR/E-96/004, Institute for energy technology, Kjeller, Norway.