EUREKA PROJECT E!1394 - EUROCARE ISOLASER (DEF)

1. General description

Project	E! 1394 - EUROCARE ISOLASER (DEF)	**Status**	Finished - 08-FEB-1999
Title	**Determination Of Depth Of Weathering And Conservation In Stone Using The Laser Method On Carbon And Oxygen Isotopes**		
Class	Sub-Umbrella	**Technological area**	Environment
Start date	01-SEP-1995	**End date**	01-JAN-1999
Duration	40 months	**Total cost**	0.06 Meuro
Partner sought	No		
Summary	Co2 Is Released From Carbonates Using The Laser Microprobe Technique & Analysed On C(13) & O(18). Aim: Determination Of Depth Of Weathering; Cf. Penetration Of Conservation Agents In Unweathered/Treated Stone; Ascertain Provenance Of Stone.		

Budget and duration

Phase	Budget(Meuro)	Duration (Months)
Definition phase	0.06	40
Total	**0.06**	**40**

Member contribution

Member	Contribution	Position	Since
Norway	**80.00%**	**Notified Finished**	**08-FEB-1999**
Sweden	20.00%	Notified Finished	08-FEB-1999
Greece	.00%	Notified Withdrawn	08-FEB-1999

Participants

Company	Country	Type	Role
Ife - Institute For Energy Technology	**Norway**	**Large company**	**Main**
Central Board Of National Antiquities	Sweden	Governm./Nat. Admin.	Partner

2. Project outline

Project description

Determination of depth of weathering and conservation by use of the laser method on carbon and oxygen isotopes
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 combination of different processes. The rate of deterioration depends on the environment, and the kind and amount of pollutants to which an object is exposed, but also on the type of material on which it consists. The increase in damage due to air pollution and the visible resultant effects has led to great concern for both our environment and cultural heritage. Therefore, there is a need for more qualitative as well as quantitative documentation.
The project is based on the laser microprobe technique for determining natural and induced weathering and conservation 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:
1. to determine and compare the depth of weathering for different objects from different ages and different environments, e.g. Northern Europe, Central Europe and Southern Europe.
2. to determine the depth of penetration of conservation agents in unweathered, lime-cemented stone and the weathering profile in treated stone after accelerated weathering cycles in a climatic chamber.
In order to get an estimate of weathering rates it is essential to perform accelerated tests under controlled conditions in the laboratory. This 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?
* What is the difference between weathered and unweathered consolidated samples after they have been exposed to accelerated weathering tests?
In this project we hope to initiate appropriate actions for the adequate protection and the proper conservation and restoration of cultural heritage. This requires the accurate evaluation of the origins and status of the materials involved and their degree and types of deterioration.
The research objectives aim to develop and improve the measurement systems to quantify parameters which affect the conservation and maintenance of items, define damage and influence the perception of the user. We also aim to develop methods to evaluate the efficiency of treatments and products used in protection and restoration activities such as appropriate sampling techniques and new

field methods like micro-sample techniques for the measurement of the physical, chemical and microbiological measurement methods for the control of accelerated weathering tests and climatic chamber methods to establish the origin and composition of cultural items.
The project is highly innovative in that with the help of the laser-ablation technique examines many aspects of stone weathering in calcareous rocks, natural and induced, and conservation. In many cases the stone used for masonry or sculptures has been 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 consolidations 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 penetrated the material.
The project also takes into account determination of provenance for the stone material which has been used, 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.

Technological development envisaged

Appropriate actions for the adequate protection and the proper conservation and restoration of our cultural heritage require the accurate evaluation of the origins and status of the materials involved and 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 perception 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 test in climatic chambers and methods to establish the origin and composition of cultural items.
With the laser-ablation technique it is possible to perform different studies of weathering on cultural objects, laboratory investigations of accelerated weathering tests, and monitor the depth of conservation on consolidated samples. The materials to be used in this project are carbonaceous sandstones and limestone/marble from different sites/objects in Scandinavia and Southern Europe. An analysis will be made of (13)C/(12)C and (18)O/(16)O isotopes in the lime.
There is a big difference in weathering depth for the same kind of sculptural rock depending on its geographical location, its environmental site and how it is exposed. Determination of the weathering parameter will thus be of great help in prioritising where to put the conservation measures as the international volume of cultural objects to

be taken care of is enormous. The addition of a qualitative natural scientific method, like the laser-ablation technique, to the humanistic-ethic and economic-political ones is therefore of greatest value.
In order to get an estimate of weathering rates it is essential to perform accelerated tests under controlled conditions in the laboratory. This 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?
* What is the difference between weathered and unweathered consolidated samples after they have been exposed to accelerated weathering tests?
In this project we hope to give answers to the above questions.
The laser microprobe analyses will be performed with a high-power Nd-doped YAI garnet (YAG) laser combined with a He-Ne (red) aiming laser for the laser-ablation of a small, well defined area. The laser is operating at 35 A at a vacuum of circa 10(-7) Torr. The diameter of the focused beam is about 10 ?m. The CO2 gas released is transferred to a Finnigan MAT 251 mass spectrometer equipped with a microinlet. The optimal precision is approximately +-0.2% (one sigma) for both Zeta (13)C and Zeta (18)O in carbonates.
The laser-ablation technique can be used for spot-analyses if enough CO2 gas is released, or continously 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. With this technique it is possible to examine gradients perpendicular to the sample surface. A great advantage with the laser technique is that the operator can change the area of analysis while he is working so that no material is lost due to cutting as is the case in conventional analyses.
With the laser-ablation 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 penetrated the material. In the latter cases the stone, after first having been analysed, is put into a low-temperature plasma-asher where all organic material is oxidised, and then re-analysed.

Markets application and exploitation

The INSTITUTE FOR ENERGY TECHNOLOGY has an isotope unit, with highly advanced instrumentation, and is specialized in solving problems which require high precision from minute samples for customers all over the world. The laser set-up together with the mass spectrometer is one few of its kind in the world and is used, apart from the pilot project being the basis for this application, for solving geological (diagenetic) problems for the oil industry and for the study of migration of solutions in crystalline rock for radio-active waste disposal.
The whole concept thus has a wide range of applications for commercial as well as scientific purposes. In marketing the project internationally IFE will serve as a service centre

where the laser set-up will be used to monitor the deterioration of the cultural heritage of stone material. Potential customers may range form different authorities connected to protection of cultural heritage like Central Offices of Historical Monuments and Sites, Central Boards for National Antiquities, Museums, National Trusts, Cultural Heritage Organisations to Environmental Agencies, etc. Apart from operating as a service institute, IFE can also work on a consulting basis to set up similar instrumentation at other institutes.
The cost per sample is in the intermediate price range but the technique is cost-effective in the sense that for a specific investigation not many samples are needed. Moreover, given the clarity in the analysis, the short turn-over analysing time and the information gained, the total cost for an investigation is remarkably low.
The EUREKA and particularly the EUROCARE network will most probably be ideal for disseminating the information internationally and marketing the laser-ablation concept for the study and monitoring of deterioration of cultural heritage composed of stone material.

Project codes

BSI

AUY	conservation
B	measurement, testing and instruments
EIC.OM	weathering (weather action)
KXV	lasers
RXH.D	stone

NACE

9252	Museum activities and preservation of historical sites and buildings

3. Main participant

Company **Ife - Institute For Energy Technology**
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Organisation type Large company
Participant role Main

Contribution to project

Sample preparation in thin section laboratory, plasma-ashing of organic material, laser microprobe sampling, mass spectrometry analyses and accelerated weathering tests in climatic chambers.

Expertise

Being one of the largest technological researh institutes in NORWAY, it has over many years built up the capacity to offer a wide range of analytical services. The institute facilities includes solid source and gas mass spectrometers, XRD, XRF, AAS, ICP, ICP-MS, HPLC, fluid inclusion and fission track analyses, SEM and TEM, etc. A big asset at IFE is the high scientific level of the staff with a competence covering most geo-related problems like dating of rocks and provenance areas, monitoring of transport and exchange reactions and secondary mineralization in the bedrock, seawater stratigraphic problems, environmental issues like weathering and exchange reactions and depletion of the soil pool due to acid rain, and protection and conservation of the cultural heritage. The laser laboratory at IFE was set up in 1989 and has been used scientifically/commercially on a variety of projects since then. The present project was developed on this equipment.

4. Partner

Company **Central Board Of National Antiquities**
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Organisation type Governm./Nat. Admin.
Participant role Partner

Contribution to project

Choice and preparation of samples. Sample characterization and conservation treatment.

Expertise

This organisation is the governmental authority responsible for the protection of Swedish cultural heritage. The major research at the Stone Department at CBNA includes documentation, damage characterization, identification of building stones and their provenance areas for the replacement purposes, and testing out different conservation treatments that suit a particular stone type.