DETERIORATION OF CARBONATE ROCKS AND VULNERABILITY OF CULTURAL HERITAGE IN A CHANGING CLIMATE
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Abstract
Carbonate rocks are the most common buildings materials used in Cultural Heritage thanks to their easy availability even if they are more susceptible to weathering than silicate ones.
For a good maintenance planning of the conservation of Cultural Heritage we need to improve our knowledge of carbonate stone decay by refining the current prediction models of surface erosion rates and forecasts towards the present scenarios of climate change.
In this project, attention is focused on the most common carbonate (Vicenza Stone, Istria Stone, Chiampo Stone, Asiago Stone and Carrara marble) used as building materials in Veneto region: their petrographic and textural features will be studied in relation to the microclimatic factors, recession rates and analysis of superficial topography of stones. Innovative non-destructive and portable techniques will be performed mainly on gravestones from War and historical Jewish cemeteries.

Introduction
About the 90% of stone used in Cultural Heritage (CH) has a carbonatic nature as limestone and marbles. They generally have good aesthetic performances and they also are easily available and workable but, mainly because of their chemical composition, these rock types are more easily subjected to decay with respect to silicate ones particularly towards the environmental impact. It is evident that the problem of their conservation is a big threat in Conservation Science now more oriented, at least in academic debates, to planned maintenance rather than to isolated restoration intervention. There is also an increasing need of educating people about the inestimable cultural and economic loss that the entire humanity is facing as a consequence of a lack of care and vulnerability of Cultural Heritage to environment and climate change.
Stone decay is caused by extreme events and continuous processes which can be natural or anthroponogenic. Extreme events such as floods and storms are hardly predictable and may be described in stochastic terms (e.g. increased probability in response to climate change); decay processes continuously acting on stones are easily identified and quantitatively described. Therefore, they have been studied from different scientific points of view: physical, chemical, mineralogical-petrographical and biological (Winckler, 1982; Brimblecombe, 1987; Camuffo, 1995; Tiano, 2002). In its complexity, degradation phenomena of stone materials can be quantified as a change in the surface topography or material loss, as surface recession, and described by damage or dose-response functions based on factors including air pollution (gas and solid), atmospheric CO₂ concentration, rainfall and temperature. Several of these models have been formulated using linear or multiple regression techniques of surface recession data, obtained by short-term measurements of weight loss on limestone tablets, and specific environmental and climate parameters, such as the Lipfert’s equation, which is one of the most commonly used functions for surface recession:

(1) Loss/m rain = 18.8 + 0.016 H⁺ + 0.18 Vd * SO₂/R
Where Vd = deposition velocity and R = Rainfall

When compared to long-term (over decadal) direct recession measurements (Inkpen et al., 2012a; b) these dose-response models often provided unacceptable underestimation of the surface erosion rate.
Since the Eighties the academic debates has often been facing sustainability and Climate Change (CC) issues at various levels but the first extensive study which related CC with CH was in the frame of the “Noah’s Ark” EU Project “Global climate change impact on the built heritage and cultural landscape” (Lefèvre & Sabbioni, 2010; Bonazza, 2010). It was aimed to determine climatic parameters and changes (temperature, relative humidity, freeze-thaw cycles, solar radiation, wind speeds, rain intensity and pH, precipitation amounts, marine salt concentrations, pollutant agents) most critical to the built CH. Subsequently, to research, predict and describe the effects of climate change on CH, mapping future scenarios at European basis in order to develop mitigation and adaptation strategies for heritage materials
protection in facing climate change and associated impacts. The Noah’s Ark Project used the Global and Regional Climate Models of the Hadley Center with spatial resolution of 295x278 km (World) and 50x50 km (Europe) provided from the IPCC (Intergovernmental Panel on Climate Change) and the Lipfert’s models of limestone recession rates to obtain decay forecasts in the near and far future over the entire European territory (Bonazza et al., 2009).

In my PhD project the attention have been focused on refining the models and equation of surface erosion by considering additional factors with first-order effect on deterioration such as microclimatic factors (air and material surface temperature, relative humidity, wind direction and intensity, pollution), petrographic and textural features of building materials (grain size, porosity, pore-size distribution, mineralogy), and causes for recession drift from linearity (specific surface area, micro-fracturing between grains or along cleavage planes; variation of the pore-size distribution, development of crust, dry deposits, biofilms). To reach the PhD major aim, I am going to apply non-invasive analytical methods, some of them used for the first time on limestones, for determining surface topography and quantify decay processes of stones.

In summary I will try to refine presently available surface recession equations and set up a model of surface recession forecast in a changing climate at a local scale. A set of carbonate rocks commonly used in the Built Heritage of Veneto Region will be considered for this study: Vicenza Stone (Nanto and Costozza varieties), Istria Stone (Orsara variety), Chiampo Stone (Porfiroco and Ondagata varieties), Asiago Stone (Pink, Red, and White varieties), Carrara marble.

**Experimental approach**

In order to obtain useful results to be applied for the planning maintenance of built Heritage of limited area and of specific variety of stones, I need to collect data on the mineralogical composition and on petrographic texture of the stone of interest, on the specific environmental conditions and on the recession rates and decay (both with traditional and innovative techniques).

Traditionally, surface recession is measured using calibers and MEM, often on cemetery gravestones (Meierding, 1981; Dragovich, 1991; Roberts, 2005; Inkpen et al., 2012a & b) because they provide a great number of exposed ‘objects’ with a specific age. I have made set of preliminary measurements of headstones using modern calibers (sensibility: 0,01 mm, which is sensibly better than that of similar data in the literature) in two Commonwealth War Graves Commission cemeteries (Padova and Bordighera). These data will be used as a reference database to test innovative procedures such as Laser Targeting System (LTS) and Structure from Motion microphotogrammetry, in order to obtain volumetric estimations of surface recession and details on the surface topography.

The CWGC cemeteries had been chosen because headstones have the same shape and in Italy they have been carved in Chiampo limestone (Summers, 2007). Hence CWGC cemeteries represent an ideal case study to determine the recession rate in the last century and understand the dominant causes of decay. Cemeteries Survey is in progress also to acquire precise planimetry and insert data on decay in a GIS system, in order to account the investigated characteristics: orientation, exposition to wind, shade by trees or nearby buildings, particular degradation and color alteration of slates, presence of irrigation system and its action, presence of vegetation on the front which can impede no-invasive analysis, presence of the cross or David Star, coat of arms (useful for control points detection).

Jewish cemeteries have also been chosen as case studies; although headstones are not strictly responding to a specific standard type, they tend to be carved using similar rock types. In addition, unlike most of the other cemeteries almost always founded after the Saint Cloud edict of 1806 they are very old and they often date back to the 16th century (es. Padova and Rovigo) or even to the 14th (es. Venice). Therefore they could help us in determining the trends of recession rates in the past decades in order to better

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1 For centuries there were decrees that sanctioned the removal of burial areas (formerly in the churches or their surroundings) from residential areas. But with the age of the Enlightenment these laws have taken root more and more: in 1785 was dismantled the Parisian cemetery of the Innocents and the 1806 the Napoleonic decree of Saint Cloud establishes a significant step in burial legislation. This law also sanctioned anonymous burial as the Jacobin egalitarian conception of death but this point started soon to be no more applied and the Golden Age of Funerarian Art of XIX century flourished.
understand the magnitude of the drift from linearity of surface erosion rates (Bonazza et al, 2009; Lefèvre & Sabbioni, 2010). In the meanwhile quarry slates of 10x10 cm of different rock types will be exposed on a selected building which is will also be used for the environmental monitoring (wind, air and stone surface temperature, relative humidity, etc.). This building should be ideally located in an rather isolated area, not too close to other buildings in order to limit the influence of multiple factors (human interaction, urban canyoning, shadow, etc.) which might be difficult to quantify. The identification of this building is under study in collaboration with the “Sovrintendenza per i Beni Architettonici di Verona, Rovigo and Vicenza” and the “Museo Archeologico di Vicenza”.

Petrographic and textural features of all these samples will be also determined. Grain size, porosity, pore-size distribution, mineralogy (e.g. content in clay minerals, sulphurs, etc.) also affect surface recession rate. A careful evaluation of these features is therefore essential to understand and quantitatively model differences in recession rate of stones exposed to the same environmental conditions, or heterogeneity in the recession rate of a given stone material. Topography can be determined using Spectral domain Optical Coherence Tomography SdOCT (Torun, Poland). Nature of early surface deposits will be determined by X-ray photoelectron spectroscopy (XPS, Dep. Chemical Sciences, UniPD) on the stone plates and on micro-samples collected on the stone surface, and on-site, using a portable laser induced breakdown spectroscopy (LIBS, Dep. Chemical Sciences, UniPD). Atmospheric deposition on building surfaces will be also investigated identifying the carbon species constituting the non carbonate fraction of total carbon in damage layers using a chemical-thermal methodology developed by (ISAC-CNR, Bologna). Soluble fractions (sulfates, nitrates and chlorides) of deposited particles will be also measured by ion chromatography (ISAC-CNR, Bologna). Finally colorimetric parameters will be monitored directly at the building surface using a portable spectrophotometer (ISAC-CNR, Bologna).

All these data will allow refining dose-response functions of carbonate building materials, providing a tool for better designing maintenance plans for Cultural Assets made of carbonate stones by assessing vulnerability of Cultural Heritage in relation to climate change.

Preliminary results and discussion
I have carried out an extensive field survey in Padua World War II CWGC cemetery, located in Chiesanuova neighbourhood, in order to collect data on an extensive group of 517 gravestones, all made up of Chiampo limestone. A strong color alteration has been observed on some slates due to a previous irrigation system which utilized an iron rich water and moreover the more decayed plots are those that not underwent to blasting after the disposal of such an harmful system.

In this cemetery preliminary test using laser scanner and microphotogrammetry have been made on a sample grave which is characterized by a medium state of decay shown by encrustation encrustation and cracks), absence of vegetation on both front and sides, a cross and a common Symbol Army (S.A.A.F) that can be used to increase the number of reference points (other than the general shape contour) to be compared with other gravestones.

First World War CWGC cemeteries of Padua (a group of 25 graves located in the Monumental Cemetery “Maggiore”) and Bordighera, Ligury, Italy (72 graves) have been surveyed and measured with the digital calibers (sensibility: 0.01 mm = 10 μm) in order to identify differences on the decay of stones of the same type and age located in different environments (marine in Bordighera, urban in Padua). In particular, the slate thickness have been measured for three times in four places (two at the base and two on the top) and the average value of the top right thickness has been subtracted from the average of the base right thickness in order to calculate the recession. The same has been done on the left side.

Usually morphology studies mediate measures of thickness at the base and top but this approach leads to a lack of information about the influence of the orientation which can be instead obtained with a simple instrument like a simple instrument like a commercial and cheap caliber. The first rough results are encouraging since the headstone from Bordighera (degree day:1057°C) are generally more recessed than Padua’s ones (degree day: 2383°C). In addition in both places there is a
difference between right and left but this seems not related to the orientation because it changes from row to row or from a terrace to another.

Moreover a great number of stones of the second terrace in Bordighera present encrustations or biological patinas leading to a positive recession value where the top thickness is higher than the base one. This is a proof that measuring of thickness of slate interested by biological patina is not a perfect method to retrieve stone decay. Further studies and surveys are needed to understand better this results with respect to the local climatic factors and wind exposition.

Some preliminary test were carried out in Padua with a LTS on a CWGC grave of WWII made up of Chiampo limestone and on a Nanto limestone sculpture located in an claustrum of Sant’Antonio’s Basilica. This technique has a sensibility of 1-2 mm and its application for a precise measure of decay is not advised but it is useful for the 3D take-over and study of complex object like sculptures that couldn’t otherwise be measured. On the same CWGC grave has been also performed microphotogrammetry full frame Reflex Camera (Castelli, Dip. Geoscienze, UniPd). This technique has a high precision (sensibility ~ 50 μm and probably it could be ameliorated) and even if it is less precise and it has longer time acquisition (and elaboration of images in 3D models) than caliber it gives a lot of information about the surface topography, so it is really powerful instrument.

**Future research plan**

After an initial stage dedicated to the identification of the most suitable limestone materials to consider in the frame of this research, I was able to obtain all the stone slates and I am starting with the textural and petrographic characterisation.

Within the next months I will go to Torun (Poland) as a visiting student, and develop the ideal instrumental set-up for Sd-OCT, a technique based on low-coherence interferometry successfully applied to the analysis of water penetration in sandstones, to profilometry of non-transparent objects and to recognition of multilayer pigments in paintings, but never applied to limestones (Targowski & Iwanicka, 2012). This technique will be performed on a set of test slates before being transported and applied directly on the surface of the Cultural assets.

Moreover, I will continue the collection of recession data both using calibers and photogrammetric techniques, in order to improve our database about surface recession at different environmental conditions and orientation, and I will perform the petrographic and textural characterisation on the quarry samples of the stone materials (the same used for the stone slates to be exposed) by Optical Microscopy (OM), Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), Multiple Internal Reflection FTIR, X-Ray Microtomography (m-CT).

I will test the applicability of other innovative techniques for the study of stone decay and stone characterization through in situ analysis of surface deposits by LIBS and ER-FTIR and on micro-samples by XPS.

Atmospheric deposition on building surfaces will be also investigated identifying the carbon species constituting the non-carbonate fraction of total carbon in damage layers using a chemical-thermal methodology developed by ISAC-CNR, Bologna where I will measure the soluble fractions (sulfates, nitrates and chlorides) of deposited particles by Ion Chromatography (IC).

The exposition of the slates on adequate stages in the monitoring site, as well as the setting up of the monitoring system, is also a task that is planned to be concluded in the next few months. The analysis of the local time series of climatic parameters will be also conducted during the next year.

At last, some work will be made for the preparation of scientific papers and presentation as communication to congresses on the preliminary results.

**References**


TIANO P. 2002. *Biodegradation of Cultural Heritage*, Seminar article, NU of Lisbon, DCR, 7-12


**SUMMARY OF ACTIVITY IN THIS YEAR**

**Courses:**
- PERUZZO L.: “Introduzione al SEM”, Dip. Geoscienze, Università degli Studi di Padova (2 h)
- DAVIES G.: “Academic English”, CLA, Università degli Studi di Padova (starting now)

**Schools and Workshops:**
- International Summer School ENVIMAT – Environment - material interaction, 30th June – 2nd July 2015, University of Ferrara (Italy), with A.i.Ar grant
- Doctoral Course Sciences and Materials of the Cultural Heritage from Pollution to Climate Change, 5th – 7th October 2015, UNIVEUR – Villa Rufolo, Ravello (SA, Italy), with Univeur financial support

**Communications:**


**Posters:**


**Publications:**

**SALVINI, S.** in press. Sustainable proposals for an accessible culture. In: *Proceedings of 5th International Herity Conference 4-6 December 2014 “Service for Cultures: A visit of Quality”*, Florence, Italy. (from an oral communication)


**SALVINI, S.** 2015. The ‘Foce’ monumental cemetery in Sanremo: mirror of the city as outstanding tourist destination during the Belle Epoque (1880-1915). In *ASCE Annual General Meeting Proceedings*, pg. 32-46 (from an oral communication)

**SALVINI, S.** in preparation. Atmospheric corrosion of iron and bronze artifacts: influence of climate change and environment. How to use this information for planned maintenance?

**Other:**
- Collaboration arranged with Prof. P. Targowski, University of Torun (Poland) and D.ssa A.Bonazza (ISAC-CNR, Bologna).