THE USE OF RAMAN SPECTROSCOPY TO CHARACTERIZE BIOLOGICAL AND BIOMINERALIC CRUSTS

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Abstract

Raman spectroscopy is a non-destructive technique routinely used to examine organic matter and carbonaceous compounds in a range of geological and biological materials, and so has great potential in heritage science. Sandstones are particularly susceptible to the development of biological and biomineralic crusts wherever water is present. Consequently biological soiling and greening of buildings is a particular problem in the cool, wet climate of Scotland. These crusts are often aesthetically undesirable and may be removed by cleaning, which exposes the underlying face to atmospheric pollutants, such as nitrogen and sulphur-bearing gases, and so *potentially* increases the impact of other weathering agents on the stone. In addition, some crusts may aggressively damage the stone and so are better being removed to prevent further decay.

Here we have been characterizing the crusts that develop on sandstone blocks and identifying chelating compounds created in complex biomineralic crusts. Results of this work will help in the assessment of those crusts that should be removed to prevent biodegradation of the stone and those that should be left intact to protect the stone from other weathering agents. By using portable Raman spectroscopy, conservation scientists will be able to monitor properties in the care of statutory and voluntary bodies so that suitable maintenance plans can be developed for historically important buildings.

Keywords: Raman spectroscopy, biological crusts, sandstone decay

1. Introduction

Biological and biomineralic crusts are difficult to characterize by conventional laboratory techniques and consequently their composition and structure is poorly understood. An ideal method with which to study the crusts would be one that can rapidly analyze both organic and inorganic materials and in their natural state, and here we have explored the applications of Raman spectroscopy in heritage science. Raman spectroscopy is a non-destructive technique that uses a single frequency of laser radiation to illuminate a sample. The photons making up the light may be absorbed or scattered by the sample, or they may simply pass straight through it and without any interaction with the sample. Raman spectroscopy makes use of the scattered light which, in susceptible (or active) molecules, induces nuclear motion, or vibration. This vibration is detected by the subsequent emission of a photon with less energy than that supplied by the laser and which has a characteristic frequency. Analysis of the peaks detected by the spectrometer allows the chemistry of the sample to be determined. Many common rock forming minerals, such as quartz and calcite, are Raman active, as are other minerals, including gypsum and barite, and carbonaceous compounds, making Raman spectroscopy a suitable analytical tool for the analysis of biological crusts on stone. Previous studies have used this technique to demonstrate weathering effects on natural outcrops (Edwards et al. 2002; Russell et al. 2008) and degradation in the built environment (Lepot et al. 2006; Martínez-Arkarazo et al. 2007).

2. Development of crusts on sandstone buildings

The development of crusts on sandstone buildings appears to be controlled by a number of lithological and environmental factors including surface roughness, porosity and permeability, aspect and stone petrology (Young 1997; Warscheid and Braams 2000). This project aims to evaluate whether sandstone composition and cement mineralogy are controlling factors in the development of biomineralic crusts, particularly where water is abundant. Predicted increases in the amount of winter rain and in the intensity of precipitation events (Hulme et al. 2002) mean that environmental conditions may encourage biological activity and that longer periods of stone-wetting will promote movement of soluble salts and metals, leading to the development of complex biomineralic crusts (Smith et al. 2008).

3. Methodology

In order to assess whether Raman microspectroscopy was a suitable analytical tool for the assessment of biomineralic crusts, 3 samples of sandstone from Elgin Cathedral, north-east Scotland, supporting biological growths of algae and lichen were examined using a Renishaw inVia spectrometer at the Centre for Nanometrology at the University of Strathclyde, Glasgow. The samples were studied using both green and red lasers, at wavelengths of 514 and 532 nm, and at 785 nm respectively. The longer wavelength induced fluorescence in the samples, even at low power, making 785 nm unsuitable for further studies. The shorter wavelengths allowed the spatial distribution of both the algae and the lichen to be imaged. On completion of this assessment, additional sandstone samples were obtained and subsequent analysis carried out using the 514 nm laser of a Renishaw inVia spectrometer at the Imaging Spectroscopy and Analysis Centre (ISAAC) at the University of Glasgow.

4. Initial Findings

The samples investigated to date include a suite of 6 sandstone types used in a previous study to determine the effects of abrasive cleaning and the use of biocides on biological growth (Young 1997). Since 1993, 144 blocks of stone approximately 5 x 5 x 2 cm in size have been left to weather on a test-rig in Aberdeen (north-east Scotland) with the samples equally divided between north- and south-facing aspects. Four of the sandstone types are dominated by algal growth and 2 are covered by a mixed lichen flora. There is now no apparent difference between untreated blocks and those that were cleaned prior to the start of the trial and the north and south facing subsets support similar biological communities.

Initial analysis using Raman spectroscopy shows that the surfaces of all 6 sandstone types are dominated by the biomarker carotene, a substance used to protect cell chloroplasts from photo-oxidation (Figure 1a).

Raman analysis of sandstone recovered from the façade of Glasgow University (south-west Scotland) shows that carotene is also prevalent in black crusts; peaks characteristic of amorphous carbon are also observed in Raman spectra from these samples (Figure 1b), consistent with inorganic soot particulates.

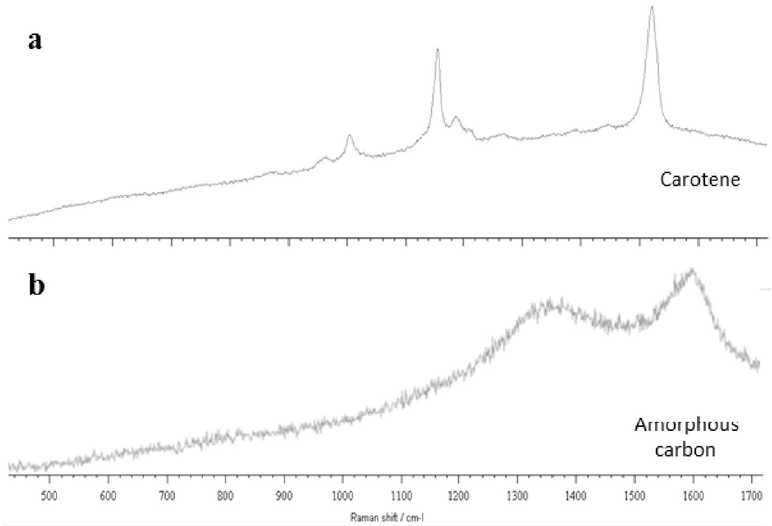
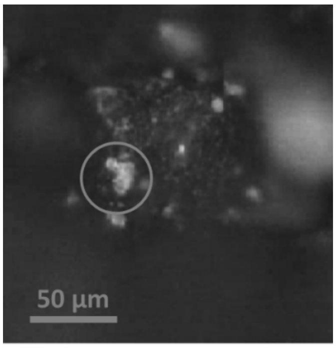


Figure 1. Raman spectra showing characteristic peaks of the biomarker carotene (a), which protects algal cells from photo-oxidation, and of amorphous carbon (b) derived from inorganic atmospheric particulates.

Some lichens are known to produce organic acids which interact with the underlying stone, forming chelates as metallic ions are removed from the rock, or which dissolve carbonate that is then precipitated as calcium oxalate (Chen 2000; references therein). To date, no secondary compounds have been identified in the samples examined, indicating that more work needs to be done to determine if these are present. A number of grains fluoresce or are not Raman active so that it is not possible to identify every mineral present using this technique.

The crusts examined do contain mineral grains within the biological material (Figure 2) but these are quartz grains, or accessory minerals (rutile or zircon), plucked from the substrate (Viles 1995).



5. The Use of Raman spectroscopy in heritage studies

Because it is non-destructive, Raman spectroscopy is potentially a useful tool for determining the composition of crusts on sandstone buildings. It is hoped that results from this study will help determine which biological growths have negligible impact on their substrate, or which offer a degree of bioprotection, and which crusts may potentially damage the underlying stone. Some attempts have been made to assess the use of hand-held Raman spectrometers in the field (Martínez-Arkarazo et al. 2008), but the spectral resolution of the portable devices does not yet match that achievable in the laboratory (Sorak et al. 2012). Even with this constraint, it is possible to differentiate between many mineral phases (quartz versus calcite, for example) but the resolution may not yet be sufficient to detect key biological compounds. It is hoped that use of Raman spectroscopy to study biological and biomineralic crusts will improve understanding of these complex structures and contribute to the wider use of spectroscopy in heritage science.

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