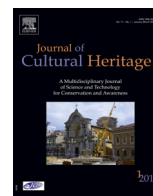




Available online at
ScienceDirect
www.sciencedirect.com

Elsevier Masson France
EM|consulte
www.em-consulte.com/en



Original article

Sourcing limestone masonry for restoration of historic buildings, a spectroscopic pilot study



Laurence Hopkinson^{a,*}, Ken Rutt^{b,2}, Petra Kristova^{b,3}, Joan Blows^{c,4}, Callum Firth^{a,1}

^a School of the Environment and Technology, University of Brighton, Cockcroft Building, Lewes Road, Brighton BN2 4GJ, United Kingdom

^b School of Pharmacy and Biomolecular Sciences, University of Brighton, Huxley Building, Lewes Road, Brighton BN2 4GJ, United Kingdom

^c Havelock Street, Canterbury, Kent CT1 1NP, United Kingdom

ARTICLE INFO

Article history:

Received 23 December 2014

Accepted 18 March 2015

Available online 17 April 2015

Keywords:

Mid-infrared

Raman

CIE $L^*a^*b^*$

Limestone

Masonry

Provenance

Environmental resource management

ABSTRACT

This study presents a combined Fourier transform (FT) mid-infrared, laser Raman and *Commission internationale d'éclairage* (CIE) $L^*a^*b^*$ system analysis of quarry-derived impure limestone and fallen masonry from a medieval listed building situated in the south east of England, to ascertain how spectroscopic information can be collectively employed to identify the most exacting possible replacement stone source. Data shows that subtle differences in [Al] and [Fe³⁺] octahedral and tetrahedral site occupancy in glauconite group clays registered in the mid-infrared [3530 cm⁻¹/3620 cm⁻¹] absorption ratio exerts some influence on $L^*C_{ab}^*h_{ab}^*$ values. Increases in L^* and C_{ab} are associated with decreasing clay content. The overall weakness of correlations between infrared and visible range spectral attributes indicates multiple contributing sources to overall color. Evidence indicates that the degree of laser Raman induced background noise is related to the overall calcite content and that activators of fluorescence at 785 nm excitation wave length may also contribute to rock color. The results are utilized to define closest matching quarry samples to the fallen masonry.

© 2015 Elsevier Masson SAS. All rights reserved.

1. Research aims

Historic buildings are central to cultural heritages. Masonry is always required for maintenance and restoration. Hence, a need exists to develop scientific methods, which ensure exacting matches between historic masonry and replacement stones. The need is acute when dealing with the 800 listed buildings of southern England fabricated whole or in part from Kentish ragstone, which is an impure limestone that ranges in composition and colour. The study aims to demonstrate that by integrating mid-infrared data with laser Raman and visible range color analysis, there is a scientific basis to provide answers to sourcing quality restoration materials that current petrographic based methods

cannot thereby potentially providing a new tool for restoration projects.

2. Introduction

Globally limestone has been worked for construction since antiquity. Consequently the assessment, management and allocation of the most suitable masonry stone for maintenance and repair of historic monuments and buildings has become important with respect to safeguarding cultural heritages [1,2]. The topic represents a scientific challenge partly because the geological source originally exploited will show variability in physical and chemical properties and, in settings where construction spans the millennia buildings may be comprised of a variety of rock types divorced in terms of geographical source location and geological origin. Superimposed on these considerations is the fact that weathering of masonry may take many forms, be distinct from weathering of natural outcrops and, involve a diverse range of highly site specific biogenic and/or abiogenic natural and anthropogenic processes [1,3,4]. Hence, replacement masonry needs not only be a good match in color and texture to the original, but also needs to be durable and weather in a fashion akin to the degraded masonry, therefore ideally sourced from the same geological strata [5]. The

* Corresponding author. Tel.: +44 1273 642 065; fax: +44 1273 642 285.

E-mail addresses: l.hopkinson@brighton.ac.uk (L. Hopkinson),

k.j.rutt@brighton.ac.uk (K. Rutt), p.kristova@brighton.ac.uk (P. Kristova),

jfblovs@btinternet.com (J. Blows), c.firth@brighton.ac.uk (C. Firth).

¹ Tel.: +44 1273 642 289; fax: +44 1273 642 285.

² Tel.: +44 1273 642 065; fax: +44 1273 642 285.

³ Tel.: +44 1273 642 076; fax: +44 1273 642 285.

⁴ Tel.: +44 1227 472 051.

upshot is an internationally recognised need to develop multidisciplinary approaches, which augment important traditional approaches, such as petrographic analysis, X-ray diffraction and subjective color assessment [6].

Comparatively recent approaches to limestone masonry characterisation utilizing color quantification by the *Commission internationale d'éclairage* (CIE) $L^*a^*b^*$ system have been employed to good effect in the fields of limestone characterization, cleaning and architectural stone decay [7–9]. While provenance studies of architectural marble by laser Raman have been undertaken independently to great effect [10], as have identification of clay-based pigments and sourcing carved stone by mid-infrared spectroscopy [11,12]. In addition, remote laser (lidar) induced fluorescence spectra has been applied to characterise the spectral attributes of historic monuments and stones [13]. However, such approaches have been employed sparingly and in isolation. No studies to date have simultaneously employed (CIE) with mid-infrared and Raman data, although collectively these spectroscopic techniques will be sensitive to mineralogy, composition and colour. Hence, such an approach may advance limestone provenance and restoration studies. This paper provides a pilot study examining the spectroscopic attributes of quarry-derived impure limestone (colloquially named Kentish ragstone) of southeast England and fallen masonry from a 15th century grade 1 listed building, donated by English Heritage (United Kingdom), to show how spectroscopic techniques can be harnessed to define the most suitable quarry-based strata for replacement stone selection.

3. Kentish Ragstone

The historic building stones of south east England were sourced from a variety of sedimentary formations which range in age [14]. Of particular significance is the Lower Cretaceous succession which is divisible into a lower non-marine sequence (Wealden Group), and an upper interval of marine sediments comprising the Lower Greensand Group (Fig. 1A) the Gault and, Upper Greensand formations [14]. The Hythe Formation within the lower greensand group is the most important interval in the succession in terms of building stone resources. The formation shows considerable lithological variation vertically and laterally between limestones and sandstones (calcareous and non-calcareous) [15]. Locally the succession comprises alternations of hard, grey to blue grey colored bioclastic limestone (Ragstone) which are well lithified, widely range in detrital quartz, glauconite and authigenic microcrystalline quartz content (Fig. 1B). The ragstones occur intercalated with poorly cemented sandstones frequently containing irregular laminae of argillaceous material (colloquial name Hassock). It is important to note that the term “glauconite” encompasses a series of micas that includes di-octahedral interlayer deficient micas [16], the end members of which are as yet undefined [17]. The group are important centres of green color pigmentation [18].

Quarrying of ragstone has taken place since Roman times and at least 30 disused quarries have been identified [19] mainly in the Maidstone area (Fig. 1B). Prior to the Norman invasion (1066 AD) ragstone together with glauconitic fine sandstone from the Upper Greensand in Surrey (Reigate stone), laminated fine sandstone/siltstone from the Thanet beds in Kent and flint constituted the principal building stones, which underpinned the development of southeast England [15,19]. The intensive nature of the Norman building programme demanded importation of masonry from France. This bioclastic limestone “Caen Stone” was widely used in the construction of cathedrals and castles [5]. With the reformation (16th Century) monastic destruction made much masonry stone available for reuse [19]. Ragstone use diminished in the 17–19th century [5].

Recent high profile restoration projects have involved the importation of French limestones (Savonnières and Lepine) [5]. The net result today is that many historic buildings are comprised of an eclectic mix of construction materials with at least ca 800 listed buildings (e.g., the city walls at Canterbury and the Tower of London) sourced at least in part from Kentish ragstone [19]. The richness of the historical legacy of ragstone usage is catalogued in detail elsewhere [15]. Presently there is only one operational pit that extracts masonry grade ragstone (Hermitage quarry, Kent), although the need for local sourced materials for conservation is explicit and the resurgence in demand for building stone for conservation projects is recognised at Government and local levels.

4. Analytical methods and techniques

Eight freshly cut slabs of masonry grade Kentish ragstone sourced from separate stratigraphic horizons in Hermitage quarry [samples R1–8], together with three slabs of French limestone: Caen stone [CAE], Lepine [LEP] and Savonnières [SAV], plus specimens of Reigate stone [REI], high purity transparent calcite (Iceland spar) and a freshly cut section through fallen church masonry [CC] were analysed. Ragstone sample [R6] showed distinct 5 cm thick pale colored irregular layering and patches. Consequently the sample was subdivided into two sub samples [R6A] and [R6B] respectively. Thin sections (7 cm × 5 cm) of each were examined by petrographic microscopy.

Raman analyses were conducted on freshly cut rock surfaces employing a Perkin Elmer IdentiCheck Raman spectrometer, fitted with a 785 nm laser and continuous un-gated (dispersive) CCD detector. The measurements were performed using a fiber optic probe with a 100 μm spot size at a working distance of 7.5 mm. The samples were measured in the spectral range 2000–200 cm⁻¹. Each spectrum was collected from 8 scans for 2 s using 70 mW laser power at room temperature and repeated between three and ten times on different areas of the same flat surface of a given rock to ascertain the intensity variation in the same stone versus the variation between different stones.

The same flat surfaces of the rocks were then measured in the visible region with a Perkin Elmer Lambda 35 spectrophotometer. Software enabled color evaluation was performed according to the *Commission internationale d'éclairage* (CIECAT02) $L^*a^*b^*$ system, employing the 2° standard observer, average north sky daylight. Freshly cut internal surfaces of the fallen church masonry (sample [CC]) were analysed as well as paler weathered external surfaces sample [CS]. All freshly cut samples were then lightly manually ground and subject to Fourier Transform mid-infrared analysis (FT-IR). The analyses were performed using a Perkin Elmer Spectrum 65. Data manipulation was performed using PeakFit (Jandel, Scientific Software). All spectral analyses were conducted at least three times on randomly selected samples to ensure representative spectral analyses. All data was collected at the University of Brighton (United Kingdom).

5. Petrography

It is established that ragstones are sufficiently variable in lithological character that it is difficult to select limited numbers of samples “typical” of the many varieties that may be encountered in outcrops [14]. The quarry ragstones are green grey to blue grey in color, with medium (0.25–1 mm) to very coarse grained (1–2 mm) sparite, occasionally cut by < 1–2 mm wide pale siliceous veins and calcite stylolites. The ragstones are largely devoid of macroscopic evidence for a bioclastic component. In thin section, samples consist of 70–95% sparitic calcite, with accessory fine sand-sized rounded pellets of glauconite, detrital quartz,

Download English Version:

<https://daneshyari.com/en/article/1037968>

Download Persian Version:

<https://daneshyari.com/article/1037968>

[Daneshyari.com](https://daneshyari.com)