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

3  
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23  
24           **Key words** mid-infrared, Raman, CIE  $L^*a^*b^*$ , limestone, masonry, provenance,  
25   environmental resource management

## 26 **Abstract**

27

28 This study presents a combined Fourier transform (FT) mid-infrared, laser Raman  
29 and Commission Internationale d'Eclairage (CIE)  $L^*a^*b^*$  system analysis of quarry-  
30 derived impure limestone and fallen masonry from a medieval listed building situated  
31 in the south east of England, to ascertain how spectroscopic information can be  
32 collectively employed to identify the most exacting possible replacement stone  
33 source. Data shows that subtle differences in [Al] and [Fe<sup>3+</sup>] octahedral and  
34 tetrahedral site occupancy in glauconite group clays registered in the mid-infrared  
35 [3530cm<sup>-1</sup>/3620cm<sup>-1</sup>] absorption ratio exerts some influence on  $L^*C_{ab}^*h_{ab}^*$  values.  
36 Increases in  $L^*$  and  $C_{ab}$  are associated with decreasing clay content. The overall  
37 weakness of correlations between infrared and visible range spectral attributes  
38 indicates multiple contributing sources to overall color. Evidence indicates that the  
39 degree of laser Raman induced background noise is related to the overall calcite  
40 content and that activators of fluorescence at 785nm excitation wave length may  
41 also contribute to rock color. The results are utilized to define closest matching  
42 quarry samples to the fallen masonry.

43

## 44 **Introduction**

45

46 Globally limestone has been worked for construction since antiquity. Consequently  
47 the assessment, management and allocation of the most suitable masonry stone for  
48 maintenance and repair of historic monuments and buildings has become important  
49 with respect to safeguarding cultural heritages (e.g., Cardell et al., 2007; Park and  
50 Shin 2009). The topic represents a scientific challenge partly because the geological

51 source originally exploited will show variability in physical and chemical properties  
52 and, in settings where construction spans the millennia buildings may be comprised  
53 of a variety of rock types divorced in terms of geographical source location and  
54 geological origin. Superimposed on these considerations is the fact that weathering  
55 of masonry may take many forms, be distinct from weathering of natural outcrops  
56 and, involve a diverse range of highly site specific biogenic and/or abiogenic natural  
57 and anthropogenic processes (e.g., Grossi et al., 2003; Cardell et al., 2007;  
58 Dewanckele et al., 2013). Hence replacement masonry needs not only be a good  
59 match in color and texture to the original, but also needs to be durable and weather  
60 in a fashion akin to the degraded masonry, therefore ideally sourced from the same  
61 geological strata (e.g., Blows et al., 2003). The upshot is an internationally  
62 recognised need to develop multidisciplinary approaches which augment important  
63 traditional approaches such as petrographic analysis, x-ray diffraction and subjective  
64 color assessment (e.g., Török and Přikryl 2010).

65

66 Comparatively recent approaches to limestone masonry characterisation utilizing  
67 color quantification by the Commission Internationale d'Eclairage (CIE)  $L^*a^*b^*$   
68 system have been employed to good effect in the fields of limestone  
69 characterization, cleaning and architectural stone decay (e.g., Laboufe et al., 2000;  
70 Viles et al., 2002; Thornbush and Viles 2004). While provenance studies of  
71 architectural marble by laser Raman have been undertaken independently to great  
72 effect (Jehlička et al., 2009), as have identification of clay-based pigments and  
73 sourcing carved stone by mid-infrared spectroscopy (Wisseman et al., 2012;  
74 Cheilakou 2014). In addition remote laser (lidar) induced fluorescence spectra has  
75 been applied to characterise the spectral attributes of historic monuments and

76 stones (e.g., Pantani et al., 2000). However, such approaches have been employed  
77 sparingly and in isolation. No studies to date have simultaneously employed (CIE)  
78 with mid-infrared and Raman data, although collectively these spectroscopic  
79 techniques will be sensitive to mineralogy, composition, texture, calcite crystallinity,  
80 color and the sources of color. Hence, such an approach may hold a key to  
81 advancing limestone provenance and restoration projects. This paper provides a  
82 pilot study examining spectroscopic attributes of quarry derived impure limestone  
83 (colloquially named Kentish ragstone) of southeast England and fallen masonry from  
84 a 15<sup>th</sup> century grade 1 listed building, donated by English Heritage (United Kingdom),  
85 to show how spectroscopic techniques can be harnessed to elucidate provenance of  
86 fallen historic masonry, contributing factors to visible range color attributes of rocks  
87 and to define the most suitable quarry-based strata for replacement stone selection.

88

### 89 **Kentish Ragstone**

90

91 The building stones of south east England that were worked and used in vernacular  
92 buildings were sourced from a variety of sedimentary formations which range in age  
93 (Lott and Cameron 2005). Of particular significance is the Lower Cretaceous  
94 succession which is divisible into a lower non-marine sequence (Wealden Group),  
95 and an upper interval of marine sediments comprising the Lower Greensand Group  
96 (Fig.1a) the Gault and, Upper Green sand formations (Lott and Cameron 2005). The  
97 Hythe Formation within the lower greensand group is the most important interval in  
98 the succession in terms of building stone resources. The formation shows  
99 considerable lithological variation vertically and laterally between limestones and  
100 sandstones (calcareous and non-calcareous) (Worrasm and Tatton-Brown 1993).

101 Locally the succession comprises alternations of hard, grey to blue grey colored  
102 bioclastic limestone (Ragstone) which are well lithified, widely range in detrital  
103 quartz, glauconite and authigenic microcrystalline quartz content (Fig.1b). The  
104 ragstones occur intercalated with poorly cemented sandstones frequently containing  
105 irregular laminae of argillaceous material (colloquial name Hassock). It is important  
106 to note that the term 'glauconite' encompasses a series of micas that includes di-  
107 octahedral interlayer deficient micas (Rieder et al., 1999), the end members of which  
108 are as yet undefined (Ospitali et al., 2008) and, are commonly important centres of  
109 green color pigmentation in stone masonry (Martinec et al., 2010).

110

111 Quarrying of ragstone has taken place since Roman times and at least 30 disused  
112 quarries have been identified. They are concentrated mainly in the Maidstone area  
113 (Figure 1b) where significant outcrops occur and where stone could be readily  
114 transported to London (Blows 2011). Prior to the Norman invasion (1066 A.D)  
115 ragstone together with glauconitic fine sandstone from the Upper Greensand in  
116 Surrey (Reigate stone), laminated fine sandstone/siltstone from the Thanet beds in  
117 Kent and flint constituted the principal building stones which underpinned the  
118 development of southeast England (Worrasm and Tatton-Brown 1993; Blows 2011).  
119 The intensive nature of the Norman building programme demanded importation of  
120 masonry from France. This bioclastic limestone 'Caen Stone' was widely used in the  
121 construction of cathedrals and castles (Howe 2001; Blows et al., 2003). With the  
122 reformation (16<sup>th</sup> Century) monastic destruction made much masonry stone available  
123 for reuse (Blows et al., 2011). Ragstone use diminished in the 17-19<sup>th</sup> century (Blows  
124 et al., 2003).

125

126 Recent high profile restoration projects have involved the importation of French  
127 limestones (Savonnières and Lepine) (Blows et al., 2003). The net result today is  
128 that many historic buildings are comprised of an eclectic mix of construction  
129 materials with at least ca 800 listed buildings (e.g., the city walls at Canterbury and  
130 the Tower of London) sourced at least in part from Kentish ragstone (Blows 2011).  
131 The richness of the historical legacy of ragstone usage is catalogued in detail by  
132 Worrsam and Tatton-Brown (1993). Presently there is only one operational pit that  
133 extracts masonry grade ragstone (Hermitage quarry, Kent), although the need for  
134 local sourced materials for conservation is explicit and the resurgence in demand for  
135 building stone for conservation projects is recognised at Government and local  
136 levels, notably stimulating the development of the British Geological Survey (BGS)  
137 electronic data base BRITPITS which provides historical records and petrographic  
138 data to locate matching stone for conservationists (Hyslop et al., 2010).

139

#### 140 **Analytical methods and techniques**

141

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

150

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

160

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

173

## 174 **Petrography**

175



176 It is established that ragstones are sufficiently variable in lithological character that it  
177 is difficult to select limited numbers of samples 'typical' of the many varieties that  
178 may be encountered in outcrops (Lott and Cameron 2005). The quarry ragstones are  
179 green grey to blue grey in color, with medium (0.25-1mm) to very coarse grained (1-  
180 2mm) sparite, occasionally cut by <1-2mm wide pale siliceous veins and calcite  
181 stylolites. The ragstones are largely devoid of macroscopic evidence for a bioclastic  
182 component. In thin section samples consist of 70-95% sparitic calcite, with accessory  
183 fine sand-sized rounded pellets of glauconite, detrital quartz, authigenic  
184 chalcedony, micrite and opaques. The ragstones show similar proportions of calcite  
185 textural types and are classified as sparse (matrix supported) biosparites. Previous  
186 studies indicate that much bioclastic debris is ferroan spar-replaced, with identifiable  
187 fossil fragments restricted to relic non-ferroan grains. Recognisable fragments  
188 consist of bivalve debris, echinoid plates, foraminifera tests, ostracod valves,  
189 bryozoan and algal fragments (Lott and Cameron 2005). All are present in varying  
190 abundances in the ragstones examined in the present study. The fallen masonry  
191 sample, which is also a glauconite-bearing matrix supported biosparite contains a  
192 comparable fossil assemblage to all quarry ragstones and is comparable to four  
193 comparatively quartz and glauconite poor quarry ragstones. The salient petrographic  
194 characteristics of the samples are outlined in Table 1.

195

#### 196 **Mid-infrared [650-2000cm<sup>-1</sup>] region**

197

198 The mid-infrared spectra of calcite is well constrained (e.g., White 1974;  
199 Gunasekaran and Anbalagan 2007). In the 600-2000cm<sup>-1</sup> region the Iceland spar  
200 powder shows the prominent  $\nu_3$  [1407cm<sup>-1</sup>]  $\nu_2$  [873cm<sup>-1</sup>] and  $\nu_4$  [712cm<sup>-1</sup>] vibrations of

201 the  $[\text{CO}_3^{2-}]$  anion in calcite (Fig. 2a). The sample also shows a low intensity band at  
202  $1085\text{cm}^{-1}$  coincident with the Raman active  $\nu_1$  vibration of the  $[\text{CO}_3^{2-}]$  anion in calcite.  
203 Bands at  $[853\text{cm}^{-1}]$  and  $[1795\text{cm}^{-1}]$  have previously been assigned as calcite  
204 combination bands (Böttcher et al., 1997). The [LEP] and [SAV] spectra are  
205 indistinguishable from Iceland spar. Hence they are interpreted as pure (calcite)  
206 limestone. The spectrum of [CAE] shows the prominent bands associated with  
207 calcite and additional silicate-related bands in the  $[700\text{-}1250\text{cm}^{-1}]$  region (Fig. 2a).  
208 The most prominent feature at  $[ca\ 1090\text{cm}^{-1}]$  is attributed to  $\text{SiO}_4$  antisymmetric  
209 stretching vibrations of  $\alpha$ -quartz (e.g., Müller et al., 2012). The low intensity band at  
210  $[1170\text{cm}^{-1}]$  and the couplet at  $[796\text{cm}^{-1}]$  and  $[778\text{cm}^{-1}]$  are also characteristic of  $\alpha$ -  
211 quartz and are assigned to symmetrical stretching of  $[\text{SiO}_4]$  units (e.g., Cheilakou et  
212 al., 2014). In accordance with Beer's law that a linear relationship exists between  
213 absorbance and sample concentration (e.g., Petit 2006) the strength of absorption at  
214  $[778\text{cm}^{-1}]$  plotted against  $[796\text{cm}^{-1}]$  can be used to gauge limestone  $\alpha$ -quartz impurity  
215 content (Fig. 3).

216

217 Ragstone spectra show an additional pronounced peak at  $ca\ [1030\text{cm}^{-1}]$  with a  
218 shoulder at  $[ca\ 910\text{cm}^{-1}]$  consistent with  $[\nu\text{Si-O-Al}]$  and  $[\delta\text{Al-OH}]$  vibrations of sheet  
219 silicates (e.g., Farmer 1974, Cheilakou et al., 2014). Specifically the  $[ca\ 1030\text{cm}^{-1}]$   
220 peak coincides with a strong absorption band reported for glauconite (Fig. 2b). The  
221 Reigate spectrum is distinguished from the Ragstone and Caen stone spectra by  
222 virtue of the absence of evidence for  $\alpha$ -quartz, comparatively low absorption of the  
223  $[\text{CO}_3^{2-}]$  internal modes, and very strong absorption at  $[ca\ 1030\text{cm}^{-1}]$ . The fallen  
224 church masonry shows comparable evidence for glauconite (Fig. 2c). The precise  
225 wavenumber of the strong  $ca\ [1030\text{cm}^{-1}]$  band varies as a function of the percentage

226 of expandable (montmorillonite) layers (Manghnani and Hower 1964). The peak  
227 fitted absorption wavenumber of the ragstones range from [995cm<sup>-1</sup>] sample [R6B] to  
228 [1021cm<sup>-1</sup>] for sample [R7]. Sample [CC] shows peak absorption at [1016cm<sup>-1</sup>]  
229 suggesting that the quarry ragstone and fallen masonry contain expandable  
230 (montmorillonite) layers in the ca 10-30% region. In contrast sample Reigate shows  
231 an absorption peak at [1047cm<sup>-1</sup>] suggesting expandable layers in excess of 40%  
232 (Manghnani and Hower 1964).

233

234 Figure 4 shows triangular-normalized peak absorption of the calcite  $\nu_3$  band  
235 [1407cm<sup>-1</sup>], the ca [1030cm<sup>-1</sup>] sheet silicate band and, the [1090cm<sup>-1</sup>] [Si-O-Si]  $\alpha$ -  
236 quartz band for all samples subsequent to Iceland spar background subtraction at  
237 [1030cm<sup>-1</sup>] and [1090cm<sup>-1</sup>] respectively. The Ragstone samples define a field with  
238 respect to relative strength of normalized absorption at the three frequencies of  
239 interest which distinguishes them from all exotics. The fallen church masonry [CC]  
240 plots in the vicinity of comparatively calcite-rich ragstones.

241

#### 242 **Mid-infrared [2400-4000cm<sup>-1</sup>] region**

243

244 The samples Iceland spar, [SAV] and [LEP] show bands at ca [2506cm<sup>-1</sup>] with  
245 shoulders at [2590cm<sup>-1</sup>] and [2977cm<sup>-1</sup>], together with bands at [2865cm<sup>-1</sup>] and  
246 [2975cm<sup>-1</sup>] which have previously been assigned to calcite overtones (Schenk et al.,  
247 1986). Ragstone samples, [CAE], [CC] and [REI] also show low intensity multi-  
248 component broad absorption band(s) in the ca [3200cm<sup>-1</sup> - 3400cm<sup>-1</sup>] region. For  $\alpha$ -  
249 quartz the ca [3400cm<sup>-1</sup>] band is interpreted to result from superposition of molecular  
250 water from fluid inclusions and hydrogen bonded surface group bands (Flörke et al.,

1982; Frondel 1982; Graetsch et al. 1987). Sheet silicates similarly yield broad band absorption in this region, including glauconite group clays for which maximum absorption is given at  $[3428\text{cm}^{-1}]$  (Moretto 2011). Hence the broad spectral feature in the ca  $[3200\text{cm}^{-1} - 3400\text{cm}^{-1}]$  registers total silicate hosted water.

Ragstones, [REI] and [CC] show numbers of variably resolved low intensity bands in the ca  $[3530-3640\text{cm}^{-1}]$  region (Fig. 5a-e) which coincide with structural [OH] stretching vibrations of minerals of the glauconite-celadonite-leucophyllite group (e.g., Slonimskaya et al., 1986). The samples show a variably resolved low intensity band at ca  $[3623\text{cm}^{-1}]$  assigned to [Al-OH] stretching vibration which is characteristic of muscovite (Farmer 1974; Slonimskaya et al., 1986; Moretto et al., 2011). The ragstones and [CC] also show a variably resolved band(s) at ca  $[3531\text{cm}^{-1}]$  closely coinciding with three closely spaced dioctahedral mica bands reported at  $[3528\text{cm}^{-1}]$ ,  $[3534\text{cm}^{-1}]$  and  $[3545\text{cm}^{-1}]$  respectively. The former is assigned to ferrous and ferric OH groups, the later to ferric iron OH groups (Slonimskaya et al., 1986). Because the  $[3528\text{cm}^{-1}]$  and  $[3534\text{cm}^{-1}]$  bands are at frequencies close to the sum of instrumental error the resultant band at  $[3531\text{cm}^{-1}]$  is frequently reported (Slonimskaya et al., 1986). The main variation in the composition of glauconite relates to iron and aluminium in octahedral position and interlayer potassium (Manghnani and Hower 1964) and, variability in the relative intensity of bands at  $[3620\text{cm}^{-1}]$  and  $[3531\text{cm}^{-1}]$  have been related in measure to variability in [Al] and  $[\text{Fe}^{3+}]$  octahedral and tetrahedral site occupancy (Slonimskaya et al., 1986). When expressed as the ratio  $[3530\text{cm}^{-1}/3620\text{cm}^{-1}]$  ragstone values range from 0.945 [R3] to 1.112 [R5]. Sample [CC] shows a ratio of 1.042. Sample [R2] provides the closest match to [CC] in terms of ferric iron and aluminium crystal-chemical make-up.

## 276 **Laser Raman Analysis**

277

278 The application of Raman spectroscopy to finger-print carbonates is well  
279 documented (e.g., White 1974; Edwards et al., 2005; Gunasekaran and Anbalagan  
280 2007; Sun et al., 2014), as is the issue of excessive background noise associated  
281 commonly with laser induced fluorescence, which is frequently encountered when  
282 dealing with natural calcite crystals and which at its extreme makes it impossible to  
283 obtain valid Raman spectra (e.g., Aminzadeh 1997; Gaft et al., 1998). In addition  
284 sample morphology, defect structure, crystallinity and grain size/porosity variability  
285 can also generate excessive background scattering. Therefore an array of sample  
286 specific physical and chemical attributes may serve to degrade or obscure the  
287 Raman signal.

288

289 Due to the extreme background noise induced by the operating conditions employed  
290 in this study valid Raman spectra were not obtained from samples [LEP] and [SAV].  
291 All remaining Raman spectra show low intensity peaks superimposed on a broad  
292 generally high sloping background (Fig. 6a), suggestive of noise originating primarily  
293 from fluorescence (e.g., Vitek et al., 2012). Photo-bleaching had no effect on  
294 improving Raman signal to background noise. Of the samples from which a Raman  
295 signal was attained the symmetrical stretching mode of the  $[\text{CO}_3^{2-}]$  anion at *ca*  
296  $[1088\text{cm}^{-1}]$  and calcite-assigned lattice modes at  $[282$  and  $156\text{cm}^{-1}]$  were resolved.  
297 The low intensity  $\nu_3$  and  $\nu_4$  vibrations of calcite reported at  $[1436\text{cm}^{-1}]$  and  $[713\text{cm}^{-1}]$   
298 respectively (Edwards et al., 2005) were either unresolved or barely resolved. Also  
299 resolved to variable extents in some samples were extremely low intensity bands in  
300 the *ca*  $[545, 445, \text{ and } 380\text{cm}^{-1}]$  regions, broadly coincident with previously described

301 Raman active bands for glauconite group minerals (Ospitali et al., 2008) together  
302 with evidence for extremely low intensity bands in the vicinity of  $[465\text{cm}^{-1}]$  and  
303  $[207\text{cm}^{-1}]$  consistent with  $\alpha$ -quartz. The degree of background noise expressed as  
304 intensity units ( $I$ ) per  $\text{cm}^{-1}$   $[(I \text{ at } 200\text{cm}^{-1} - I \text{ at } 2000\text{cm}^{-1}) / 1800\text{cm}^{-1}]$  ranges from  
305  $108.15 I \text{ per cm}^{-1}$  (sample [CAEN]) to  $11.75 I \text{ per cm}^{-1}$  (sample [R8]). The standard  
306 deviation derived from ten analyses of a single sample is  $\pm 14.90$ . Fig. 6b shows  
307 sample  $I \text{ per cm}^{-1}$  values minus the corresponding value for [CC]. It is evident that  
308 [CC] shows similar fluorescence background noise to the quarry ragstones.

309

### 310 **Visible range Analysis**

311

312 The CIE  $L^*a^*b^*$  color model is defined by ( $a^*$ ) which represents how red or green a  
313 color is (where negative values indicate green and positive indicates red);  $b^*$   
314 indicates how blue or yellow a color is (where negative equals blue and positive  
315 indicates yellow) and the lightness of the color ( $L^*$ ) (where 0 = black, 100 = white).  
316 The precision of these units is typically  $ca \pm 0.1$  unit (e.g., Laboufe et al., 2000). Any  
317 color is described by the lightness ( $L^*$ ) chroma ( $C_{ab}^*$ ) and hue ( $h_{ab}^*$ ) where  $C_{ab}^* =$   
318  $\sqrt{(a^{*2} + b^{*2})}$  is the radial component and  $h_{ab}^* = \text{arc tan } b^*/a^*$ . Fig. 7a shows the  
319 samples examined in this study plotted in cylindrical  $L^*, C_{ab}^*, h_{ab}^*$  space. It is evident  
320 that [CC] plots within the general field of color space defined by ragstones. It is also  
321 evident from the  $L^*, C_{ab}^*, h_{ab}^*$  data from cut internal surface of the fallen masonry  
322 [CC] relative to exterior surfaces of the masonry [CS] that chromatic weathering  
323 involved an increase in chroma and slight lightening while the hue remained  
324 relatively constant (Fig. 7a). It has previously been reported that ragstone color can

325 change as a function of glauconite oxidation during weathering (Lott and Cameron  
326 2005).

327

328 Color is frequently expressed as a single metric  $E^* = \sqrt{((L^* \times L^*) + (a^* \times a^*) +$   
329  $(b^* \times b^*))}$  and can be employed to ascertain total color difference ( $\Delta E^*$ ) based on  
330  $L^*, a^*, b^*$  color difference of samples relative to [CC], where  $\Delta E^* =$   
331  $\sqrt{((L^* - L^* [CC])^2 + (a^* - a^* [CC])^2 + (b^* - b^* [CC])^2)}$  indicates that [R7] shows  
332 closest approach to [CC] (Fig. 7b). Guidelines for tolerance of acceptable color  
333 difference in the context of replacement stone suitability in relation to the research  
334 documented here do not exist. However it is interesting to note that  $\Delta E^* \approx 2.3$  is cited  
335 as constituting a just noticeable difference in digital image processes (Sharma 2003).

336

### 337 **Interpretation**

338

339 It is evident that the four closest visible range color matches to [CC] in  $L^*, C_{ab}^*, h_{ab}^*$   
340 and  $\Delta E^*$  space show the closest matching spectral attributes in the  $[600\text{cm}^{-1}$  to  
341  $2000\text{cm}^{-1}]$  mid-infrared region (Fig. 3), i.e. relatively calcite-rich ragstones, which also  
342 show a comparatively discreet range of values in  $L^* C_{ab}^* h_{ab}^*$  space (Figure 6a). Of  
343 these in terms of the visible color in  $\Delta E^*$  space and mineralogical make-up sample  
344 [R7] provides the closest match to the fallen masonry [CC]. In terms of petrography  
345 sample [R7] is slightly coarser grained, more authigenic silica-rich and bioclast-poor  
346 than [CC]. However all ragstones and sample [CC] show seemingly random surges  
347 in calcite crystal sizes and contain at least some authigenic silica. Hence  
348 petrographic disparities between [CC] and [R7] may well be encompassed in the  
349 natural variability inherent in any individual ragstone in relation to the dimensions of

350 an individual thin section employed. Furthermore the 'closeness' of the nearest  
351 match quarry rock type to [CC] must be seen in the context of the quarry  
352 representing the single present day source of masonry grade ragstone.

353

354 Specific causes for the colors exhibited by ragstone are not known in detail beyond  
355 the fact that common to all are varying but limited abundances of glauconite. For any  
356 given mineral the visual effect of color stems from some combination of intrinsic  
357 constituents, impurities, defects and specific structures. Physical formalisms of these  
358 parameters for specific minerals reside in crystal field theory, molecular orbital  
359 theory, band theory and physical optics (Nassau 1978). Complications arise from the  
360 fact that more than one type of color-causing agent can be present in a mineral  
361 (Nassau 1978). This complexity is greatly compounded when considering lithified  
362 aggregates of minerals, particularly given that glauconite constitutes a mineral group  
363 (Rieder et al., 1999). Hence the colors of ragstones are certain to be the sum  
364 product of multiple contributing factors.

365

366 Samples [LEP] [SAV] and [CAE] show the greatest lightness and chroma of all  
367 samples examined. The former two limestones contain only traces of impurities. The  
368 latter contains significant detrital quartz. All three are devoid of clays. Hence one  
369 visible range attribute of clay based impurity in limestones appears to be an overall  
370 lowering of lightness and saturation. In this respect it is interesting to note that [R1]  
371 shows the lowest chroma and lightness of any sample is glauconite-rich (Table 1).  
372 However, the silicate-rich ragstone sample [R3] shows a very similar infrared  
373 spectral profile to [R1] in the  $[600\text{cm}^{-1}\text{-}2000\text{cm}^{-1}]$  region and, by inference extensively  
374 similar proportions of clays, quartz and calcite (Figure 3). Yet [R3] shows the



375 greatest  $L^*$  of all ragstones, and is widely separated in  $L^*$ ,  $C_{ab}^*$ ,  $h_{ab}^*$  space from [R1]  
376 (Fig. 7a), Further, a very weak negative correlation exists ( $r = -0.57$  at the 95%  
377 confidence level) between the  $[3530\text{cm}^{-1}/3620\text{cm}^{-1}]$  ratio and  $E^*$  (Table 2). Hence  
378 within the limits of resolution afforded by FT-IR to detect traces of clay-based  
379 absorption in the [OH] region, data suggests that the greater the site occupancy by  
380 iron relative to aluminium in glauconite the lower the  $L^*$  value and corresponding  
381  $C_{ab}^*$ . Therefore FT-IR evidence suggests that chemistry of the glauconite group  
382 contributes to color as well as overall modal abundance of the mineral group.  
383 However the weakness of the correlation between  $E^*$  and  $[3530\text{cm}^{-1}/3620\text{cm}^{-1}]$  must  
384 also reflect the multiple nature of the parameters contributing to visible color. In this  
385 respect it is of note that sample [R2] shows the closest match to [CC] in terms of  
386 ferric iron and aluminium crystal-chemical make-up, yet [R7] provides the overall  
387 closest match to [CC] in terms of  $\Delta E^*$ .

388

389 A positive correlation ( $r = 0.61$  at the 95% confidence level) exists between the  
390 strength of absorption at  $[1404\text{cm}^{-1}]$  and the magnitude of Raman background noise  
391 and a corresponding weak negative correlation ( $r = -0.57$ ) between Raman  
392 background noise and the intensity of absorption at *ca*  $[1030\text{cm}^{-1}]$ , suggesting an  
393 association between the abundance of calcite and Raman background noise (Table  
394 1). Known fluorescence centres in calcite include  $\text{Mn}^{2+}$  and various trace elements  
395 (Aminzadeh 1997; Gaft et al., 1998), structural defects and, organic centres such as  
396 bitumen, kerogens and caratones (e.g., Wang et al., 1997; Urmos et al., 1991;  
397 Bozlee et al., 2005). Raman background noise can also vary with energy transfer  
398 within crystals, sensitization, reabsorption and quenching (Marfunin 1979). The  
399 calcite component of ragstones is biogenic in origin and has been subject to patchy

400 ferroan spar replacement (Lott and Cameron 2005). Hence the rocks are transition  
401 metal bearing and, at least a fraction of the accessory opaque material identified in  
402 thin section is likely organic in origin and unresolvable by FT-IR due to either low  
403 concentrations and or partial overlap of organic bands with calcite overtones.

404

405 Although the causative activators of fluorescence cannot be categorically resolved  
406 by petrography positive correlations (95% confidence level) between Raman  
407 background noise with  $E^*$  ( $r = 0.58$ ) and  $C_{ab}^*$  ( $r=0.66$ ) suggests that at least some of  
408 the fluorescence activator(s) may also possess visible range spectral attributes.  
409 However because the intensity of background is specific to the wavelength  
410 employed, the objective, the power, the focusing et cetera it seems unlikely that  
411 fluorescence background alone could not be used as a diagnostic tool, but instead a  
412 secondary additional element to reinforce an hypothesis.

413

## 414 **Conclusions**

415

416 Petrographic analysis suggests any one of four possible relatively silicate impurity-  
417 poor quarry-derived limestone horizons as most suitable close matches to the fallen  
418 historic masonry. From these  $L^*$ ,  $C_{ab}^*$ ,  $h_{ab}^*$  values in conjunction with absorption  
419 characteristics in the  $[600\text{cm}^{-1}$  to  $2000\text{cm}^{-1}]$  mid-infrared region independently  
420 identify a single stratigraphic horizon [R7] within the quarry as the closest matching  
421 limestone to the fallen historic masonry. Hence integrating CIE  $L^*a^*b^*$ , mid-infrared  
422 and Raman analysis shows potential as tool for quarry resource management. It is  
423 conceivable that the advent of expanded spectroscopic data sets could facilitate  
424 development of quantified spectroscopic replacement stone criteria to augment

425 existing approaches to provenance studies and resource management. The  
426 questions then become what constitute acceptable differences between the various  
427 spectroscopic attributes that define each limestone and the historic masonry they are  
428 designed to replace.

429

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431

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436

### 437 **References**

438

439 Aminzadeh A (1997) Fluorescence bands in the FT-Raman spectra of some calcium  
440 minerals. *Spectrochim. Acta.* A53: 693-697

441

442 Blows J.F., Carey P.J., Poole A.B (2003) Preliminary investigations into Caen Stone  
443 in the U.K; its use, weathering and comparison with repair stone. *Build. Environ.* 38:  
444 1143-1149.

445

446 Blows J.F (2011) *Strategic Stone Study, a building stone atlas of Kent.* English  
447 Heritage.

448

449 Böttcher M.E., Gehlken P., Steele D.F (1997) Characterization of inorganic and  
450 biogenic magnesian calcites by Fourier Transform infrared spectroscopy. *Solid State*  
451 *Ionics*. 101-103: 1379-1385.

452

453 Bozlee B.J., Misra A.K., Sharma S.K., Ingram M (2005) Remote Raman and  
454 fluorescence studies of mineral samples. *Spectrochim. Acta A61*: 2342-2348.

455

456 Cardell C., Benavente D., Rodríguez-Gordillo J (2007) Weathering of limestone  
457 building material by mixed sulphate solutions. Characterization of stone  
458 microstructure, reaction products and decay forms. *Materials Characterization*. 59:  
459 1371-1385.

460

461 Cheilakou E., Troullinos M., Koui M (2014) Identification of pigments on Byzantine  
462 wall paintings from Crete (14<sup>th</sup> century AD) using non-invasive fiber optics diffuse  
463 reflectance spectroscopy. *Journal Archaeological Sci.* 41, 541-555.

464

465 Dewanckele J., Boone M.A., De Kock T., Boever W., Brabant L., Bonne M.N.,  
466 Fronteau G., Dils J., Van Hoorebeke L., Jacobs P., Cnudde V (2013) Holistic  
467 approach to pre-existing flaws on the decay of two limestones. *Sci. Total*  
468 *Environment*. 447, 403-414.

469

470 Edwards, H.G.M., Jorge Villar S.E., Jehlicka J., Munshi, T. (2005). FT-Raman  
471 spectroscopic study of calcium-rich and magnesium-rich carbonate minerals.  
472 *Spectrochim. Acta. A61*:2273–2280.

473

474 Farmer V.C. (1974) The layer silicates. In: V.C. Farmer, (ed). The infrared spectra of  
475 minerals. Mineral. Soc. Monogr. 4:227–284.  
476

477 Flörke O.W., Köhler-Herbertz P., Langer K., Tönges I (1982) Water in microcrystalline  
478 quartz of volcanic origin. Contrib. Mineral. Petrol. 80: 324-333.  
479

480 Frondel C (1982) Structural hydroxyl in chalcedony (type B quartz). American  
481 Mineral. 67: 1248-1257.  
482

483 Gaft M., Reisfeld R., Panczer G., Blank P.H., Boulon G (1998) Laser-induced time-  
484 resolved luminescence of minerals. Spectrochim. Acta. A54: 2163–2175.  
485

486 Graetsch H., Flörke O.W., Mieke G (1987) Structural defects in microcrystalline  
487 silica. Phys. Chem. Miner. 14: 249-257.  
488

489 Grossi C.M., Esbert R.M., Díaz-Pache F., Alonso F.J (2003) Soiling of building  
490 stones in urban environments. Build. Environ. 38, 147-159.  
491

492 Gunasekaran S., Anbalagan G (2007) Spectroscopic characterisation of natural  
493 calcite minerals. Spectrochim. Acta. A68: 656-664.  
494

495 Howe J.A (2001) The geology of building stones. Edward Arnold 1910-reprinted  
496 edition. London: Donhead Publishing.  
497

498 Hyslop E., McMillan A., Cameron D., Leslie A., Lott G (2010) Building stone  
499 databases in the UK: practical resource for conservation. *Engineering Geol.* 115:  
500 143-148.

501

502 Jehlička J., Št'astná A., Příklad R (2009) Raman spectral characterization of  
503 dispersed carbonaceous matter in decorative crystalline limestones. *Spectrochim.*  
504 *Acta.* A73: 404-409.

505

506 Labouffe M., Bromlet P., Oriol G., Wiedemann G., Simon-Boisson C (2000)  
507 Assessments of laser cleaning rate on limestone and sandstones. *J. Cult. Heritage.*  
508 S21-27.

509

510 Lott G., Cameron D (2005) The building stones of South East England : mineralogy  
511 and provenance. In: 10th Euroseminar on Microscopy Applied to Building Materials,  
512 Paisley, Scotland, 21<sup>st</sup> - 25<sup>th</sup> June 2005.

513

514 Manghnani M.H., Hower J (1964) Glauconites: cation exchange capacities and  
515 infrared spectra. Part II. Infrared absorption characteristics of glauconites. *Amer.*  
516 *Miner.* 49:1631-1642.

517

518 Marfunin A.S (1979) *Spectroscopy, luminescence, and radiation centers in minerals.*  
519 Springer-Verlag, Berlin, Heidelberg, New York.

520

521 Moretto L.M., Orsega E.F, Mazzocchin G.A, (2011) Spectroscopic methods for the  
522 analysis of celadonite and glauconite in Roman green wall paintings J. Cult. Heritage  
523 12: 384–391.

524

525 Martinec P.M., Vavro M., Scucka J., Maslan M (2010) Properties and durability  
526 assessment of glauconitic sandstone: a case study on Zamel sandstone from  
527 Bohemian Cretaceous basin (Czech republic. Engineering Geol. 115:175-181.

528

529 Müller C.M., Molinelli A., Karlowatz M., Aleksandrov A., Orlando T., Mizaikoff B  
530 (2012) Infrared attenuated total reflectance spectroscopy of quartz and silica micro-  
531 and nanoparticulate films. J. Phys. Chem. C116: 37-43.

532

533 Nassau K (1978) The origins of color in minerals. Amer. Miner. 63: 219-229.

534

535 Ospitali F., Bersani D., Di Lonardo G., Lottici P.P (2008) ‘Green earths’: vibrational  
536 and elemental characterization of glauconites, celadonites and historical pigments. J.  
537 Raman Spec. 39:1066-1073.

538

539 Pantani L., Ballerini G., Cecchi G., Edner H., Lognoli D., Johansson T., Raimondi V.,  
540 Svanberg S., Tiano P., Tomaselli L., Weibring P (2000) Experiments on stony  
541 monument monitoring by laser-induced fluorescence. J. Cult. Heritage 1:345-348.

542

543 Park H.D., Shin G.H (2009) Geotechnical and geological properties of Mokattam  
544 limestones: Implications for conservation strategies for ancient Egyptian stone  
545 monuments. Engineering Geol. 104:190-199.

546

547 Petit S (2006) Fourier transform infrared spectroscopy. In Bergaya F, Theng B.K.G,  
548 Lagalay G (eds) Handbook of clay science, vol. 1. Chapt.12: 909-918. Elsevier Ltd.

549

550 Radley J.D., Allen P (2012) The non-marine Lower Cretaceous Wealden strata of  
551 southern England. Proc. Geol. Assoc. 123: 245-318.

552

553 Rieder M., Cavazzini G., D'yakonov Yu.S., Frank-Kamenetskii V.A., Gottardi G.,  
554 Guggenheim S., Koval P.V., Müller G., Neiva A.M.R., Radoslovich E.W., Robert J.L.,  
555 Sassi F.P., Takeda H., Weiss Z., Wones D.R (1999) Nomenclature of the micas.  
556 Miner. Mag. 63:267-279.

557

558 Schenk H.J., Witte E.G., Müller P.J., Schwocha K (1986) Infrared estimates of  
559 aliphatic kerogen carbon in sedimentary rocks. Organic Geochem. 10:1099-1104.

560

561 Sharma, G (2003). Digital Color Imaging Handbook (1.7.2 ed.). CRC Press.

562

563 Slonimskaya M.V., Besson G., Dainyak L.G., Tchoubar C., Drits V.A (1986)  
564 Interpretation of the IR spectra of celadonites and glauconites in the region of OH-  
565 stretching frequencies. Clay Miner. 21:377-388.

566

567 Sun J., Wu Z., Cheng H., Zhang Z., Frost R.L (2014) A Raman spectroscopic  
568 comparison of calcite and dolomite. Spectrochim. Acta. A117:158-62.

569



570 Thornbush M., Viles H (2004) Integrated digital photography and image processing  
571 for quantification of coloration on soiled limestone surfaces in Oxford, England. *J.*  
572 *Cult. Heritage.* 5:285-290.

573

574 Török Á., Příklad R (2010) Current methods and future trends in testing, durability  
575 analyses and provenance studies of natural stones used in historic monuments.  
576 *Engineering Geol.* 115:139-142.

577

578 Urmos J., Sharma S.K., Mackenzie F.T (1991) Characterisation of some biogenic  
579 carbonates with Raman spectroscopy. *Amer. Miner.* 76: 641-646.

580

581 Vitek P., Ali E.M.A., Edwards H.G.M., Jehlička J., Cox R., Page K (2012) Evaluation  
582 of portable Raman spectrometer with 1064nm excitation for geological and forensic  
583 applications. *Spectrochim. Acta.* A86:320-327.

584

585 Viles H.A Taylor M.P, Yates T.J.S Massey S.W (2002) Soiling and decay of N.M.E.P  
586 limestone tablets. *Sci. Total Environ.* 38, 147-159.

587

588 White, W. B. (1974). The carbonate minerals. In V. C., Farmer, ed. The infrared  
589 spectra of minerals. *Mineral. Soc. Monogr.* 4:227–284.

590

591 Wisseman S.U., Hughes R.R., Emerson T.E., Farnsworth K.B (2012) Refining the  
592 identification of native American pipestone quarries in the mid-continental United  
593 States. *J. Archaeological Sci.* 39:2496-2505.

594

595 Worssam B.C., Tatton-Brown T (1993) Kentish Rag and other Kent building stones.  
596 Archaeologia Cantiana. vol. CXII. 93-125.

597

## 598 Captions

599

600 **Table 1** Petrographic summary of samples. Modal abundances are based on semi-  
601 quantitative visual assessment.

602

603 **Table 2** The correlation coefficient and significance (bracketed) for the various  
604 measured spectral attributes. Correlation coefficients range from -1 through to +1. 0.  
605 In general 0.05 or less is considered to be significant in environmental research (e.g.  
606 5% of cases are wrong and 95% are right). The values marked in bold are significant  
607 at the 95% confidence level.

608

609 **Figure 1 (a)** Simplified geological map of Kent adapted from Radley and Allen  
610 (2012). **(b)** Diagrammatic vertical section through showing the west to east variation  
611 in the lithological character of the Hythe beds between Sevenoaks and Ashford  
612 (adapted from Worssam and Tatton-Brown 1993). The location of Hermitage quarry  
613 is marked with a star.

614

615 **Figure 2 (a)** Mid-infrared spectra in the [600-2000cm<sup>-1</sup>] region of interest, showing  
616 **(a)** Pure calcite (solid line) and Caen stone (dashed line). **(b)** Reigate stone and  
617 quarry ragstones. **(c)** Fallen church masonry.

618

619 **Figure 3** Strength of absorption at [796cm<sup>-1</sup>] versus [778cm<sup>-1</sup>] see text for details.

620

621 **Figure 4** Triangular-normalized peak absorption of the calcite  $\nu_3$  band [ $1407\text{cm}^{-1}$ ],  
622 the *ca* [ $1030\text{cm}^{-1}$ ] sheet silicate band and, the [ $1090\text{cm}^{-1}$ ] (Si-O-Si)  $\alpha$ -quartz band.

623

624 **Figure 5 (a-e)** FT-IR spectra of samples in the  $2400\text{cm}^{-1}$  to  $4000\text{cm}^{-1}$  region of  
625 interest. Sample identification is presented in a box next to each spectrum. See text  
626 for details. **(f)** Bar chart showing the [ $3530\text{cm}^{-1}/3620\text{cm}^{-1}$ ] absorption intensity ratio of  
627 quarry samples minus the corresponding ratio for sample [CC].

628

629 **Figure 6 (a)** Examples of Raman spectra of limestones and Iceland spar. All spectra  
630 were acquired employing identical operating conditions **(b)** Bar chart showing the  
631 subtracted difference in intensity units per  $\text{cm}^{-1}$  relative to sample [CC].

632

633 **Figure 7 (a)** Ragstones and samples [CC], [CAE], [SAV],[LEP] and [REI] plotted in  
634 cylindrical  $L^*C_{ab}^*h_{ab}^*$  space. The dashed circular line denotes the four closest  
635 ragstone matches to the fallen church masonry [CC]. The arrow denotes the path of  
636 chromatic weathering of the fallen church masonry from freshly cut internal surfaces  
637 sample [CC] to weathered exterior surfaces [CS]. **(b)** Bar chart showing the  $\Delta E^*$   
638 values of limestone samples relative to sample [CC].

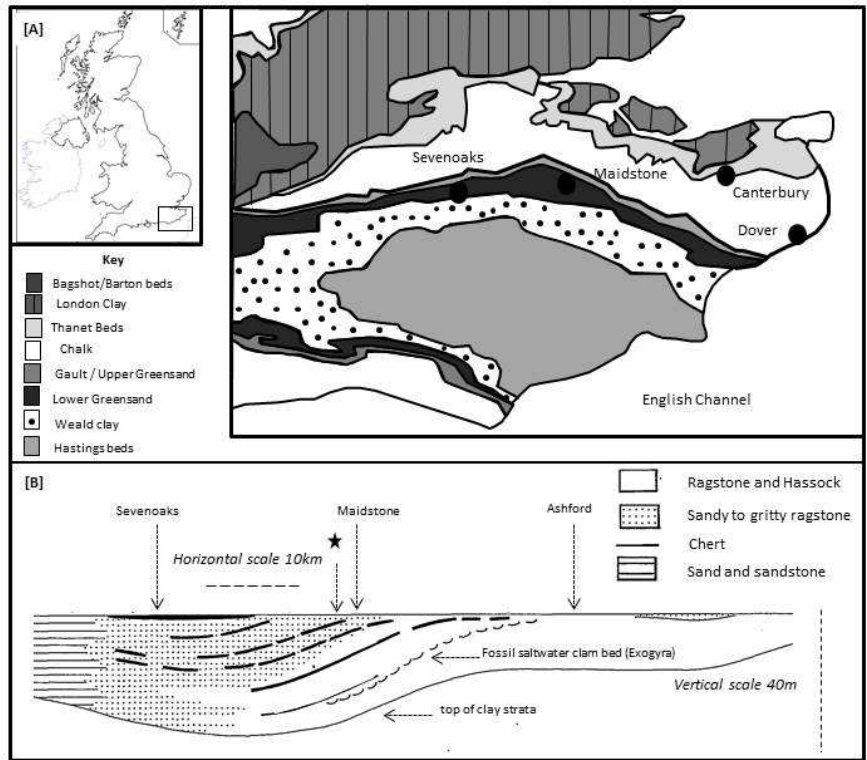
Sample	Classification	Sparite	Bioclastic debris	Micrite	Detrital quartz	glauconite	Authigenic SiO <sub>2</sub>	Opaque material	Others (e.g., illite, lithic fragments)	Summary description
R1	Biosparite	52	17	2	16	7	2	3	≤1	Coarse (0.5-1mm) sparite matrix, locally anastomosing <1mm wide very fine grained (ca 100µm) sparite veins and stylolites. Sparse very fine sand-sized sub-rounded quartz and glauconite locally defining laminations. Foliated bivalve shell fragments and disaggregated echinoderms common. Sparse traces of ostracods, micritic walled foraminifera, bryozoans and nodular micritic algae present.
R2	Biosparite	58	27	3	5	3	1	2	≤1	Coarse (0.5-1mm) sparite matrix, randomly orientated elongate to sub rounded coarse sand-sized lithic fragments of glauconite-cemented silt-sized quartz grains, plus finer grained sub-rounded crystals of quartz and glauconite. Trace chalcedony infill. Bivalve shell fragments with foliated structures and disaggregated echinoderms common, Fragmented bryozoans, micritic walled foraminifera, articulated and disarticulated ostracods and sparse nodular micritic algae present.
R3	Biosparite	53	23	4	3	3	9	2	3	Medium grained (0.25-0.5mm) sparite matrix. Light pale blue grey 2cm-wide domains defined by chalcedony matrix with subordinate sparite. Cross-cut by stylolites and glauconite-lined fractures flanked symmetrically by ca 2mm wide domains of very fine grained sparite. Foliated bivalve shell fragments and disaggregated echinoderms common, rich in micritic-walled foraminifera, ostracods plus fine sand sized micritic algae nodules. Transverse sections of bryozoans identified.
R4	Biosparite	56	17	9	6	7	2	2	1	Coarse (1-3mm) sparite matrix, medium to fine sand sized rounded particles of glauconite and detrital quartz, locally defining laminations. Trace illite present. nodular micritic algae. Foliated bivalve shell fragments, disaggregated echinoderms and micritic wall-lined foraminifera and bryozoans present with rare ostracods.
R5	Biosparite	63	16	3	10	1	3	3	≤1	Medium grained (0.25-0.5mm) sparite cement, with dispersed medium to fine grained detrital crystals of quartz and glauconite. Foliated bivalve shell fragments and disaggregated echinoderms common, micritic wall-lined foraminifera, bryozoans, ostracods and algal micritic nodules identified.
R6A/B	Biosparite	72	15	2	3	4	1	2	≤1	Domains of very coarse grained sparite (1-3mm) hosting 3-5 cm wide discontinuous pale buff-grey coloured irregular-shaped enclaves devoid of bioclasts, composed of fine grained (0.25-0.5mm) sparite (R6A). The remainder of the sample (R6B) shows foliated bivalve shell fragments, disaggregated echinoderms, micritic wall-lined foraminifera rare ostracods, algal nodules and evidence of bryozoans (R6B). Enclaves and host rock contain fine sand-sized detrital quartz and limited glauconite.
R7	Biosparite	52	18	7	6	5	8	3	≤1	Coarse grained (1-3mm) sparite, pale centimetre wide band rich in chalcedony. Sub-rounded detrital quartz and glauconite (medium to fine sand sized) arranged in sparite matrix supported laminations. Disaggregated echinoderms, nodular micritic algae (<1.5mm). Foliated bivalve shell fragments disaggregated echinoderms and micritic wall-lined foraminiferal tests common. Disarticulated ostracods, rare. Transverse sections of bryozoans identified. Sparse traces of brown coloured algal nodules range in size up to 1.5mm.
R8	Biosparite	64	17	3	6	3	4	2	≤1	Uniform very coarse (1-3mm) sparite, medium to fine grained sub-rounded detrital quartz and glauconite. Foliated bivalve shell fragments and disaggregated echinoderms common, micritic wall-lined foraminifera, ostracods, nodular micritic algae and fragmented bryozoan identified.
[CC]	Biosparite	60	22	8	3	2	1	3	≤1	Medium (0.25-0.5mm) to coarse grained (0.5-1mm) sparite matrix. Sparse fine sand sized clasts of detrital quartz and glauconite. Irregular ca 0.3mm wide ca 10mm long irregular calcite stylolites and chalcedony seams. Foliated bivalve and echinoderm shell fragments common, micritic-lined foraminifera tests present together with scarce disarticulated and articulated ostracods. Fragmented bryozoans identified.
[REI]	Sandstone	12	5	5	2	58	5	2	11	Poorly lithified, friable and porous. Glauconite commonly occurring as rounded grains or as moulds of spicule chambers and foraminifera tests (Davies 1916). Note that the proportion of glauconite to Siliceous sponge spicules in Reigate stone can vary considerably and a detrital quartz component is commonly sparse or absent (Lott and Cameron 2005).
[CAE]	oobiosparite	37	15	30	12	0	0	5	≤1	Grain size <250µm. Matrix supported. Micritic wall-lined foraminifera tests and undifferentiated bioclastic debris.
[SAV]	oosparite	65	5	18	7	0	0	3	≤1	Grain supported. Ooids <2.5mm, matrix <125µm grain sizes.
[LEP]	oomicrite	22	4	66	3	0	0	5	≤1	Ooids <250µm, matrix supported (grain size <60µm).

	1034cm <sup>-1</sup>	1090cm <sup>-1</sup>	1404cm <sup>-1</sup>	3530cm <sup>-1</sup> /3620cm <sup>-1</sup>	Raman int. per cm <sup>-1</sup>	C <sub>ab</sub> *	H <sub>ab</sub> *
1090cm <sup>-1</sup>	0.582(0.029)						
1404cm <sup>-1</sup>	-0.876 (0.000)	-0.902 (0.000)					
3620cm <sup>-1</sup> /3530cm <sup>-1</sup>	0.217 (0.457)	-0.135 (0.645)	-0.035 (.906)				
Raman int. per cm <sup>-1</sup>	-0.568 (0.034)	-0.524 (0.055)	0.612 (0.020)	-0.203 (0.486)			
C <sub>ab</sub> *	-0.506 (0.065)	-0.168 (0.566)	0.368 (0.196)	-0.380 (0.180)	0.662 (0.010)		
H <sub>ab</sub> *	0.421 (0.134)	0.122 (0.677)	-0.296 (0.305)	0.033 (0.910)	-0.378 (0.183)	-0.573 (0.032)	
E*	-0.451 (0.105)	0.022 (0.942)	0.226 (0.436)	-0.574 (0.032)	0.576 (0.031)	0.766 (0.001)	-0.435 (0.120)

640

641 Table 2

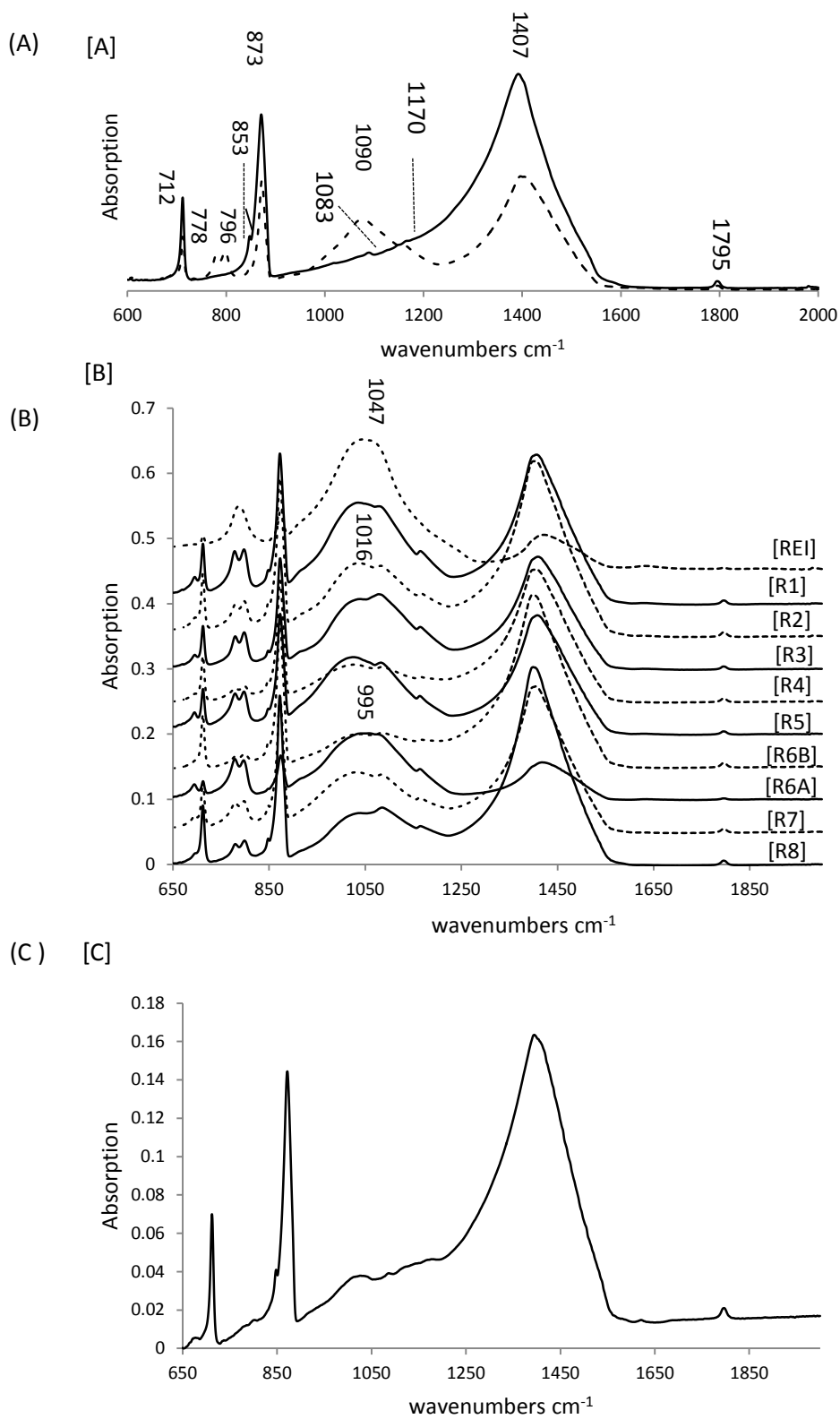
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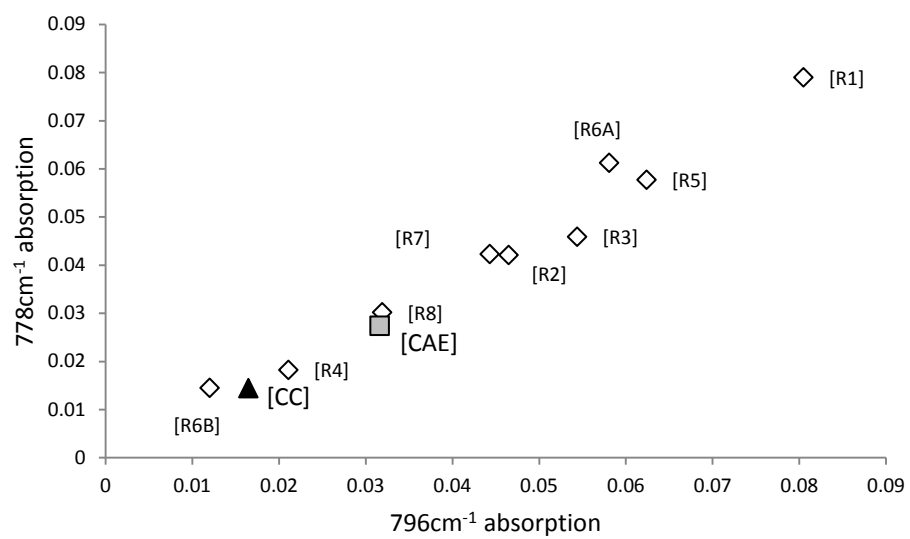
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644 Figure 1

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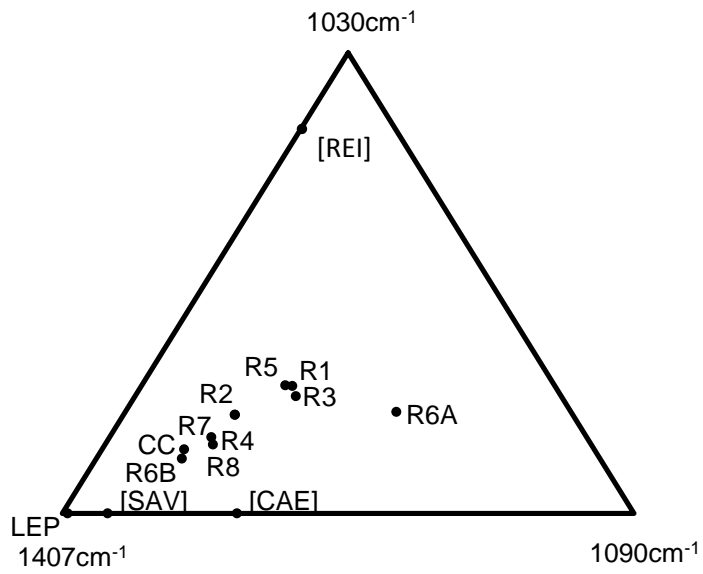
646 Figure 2



647

648 Figure 3

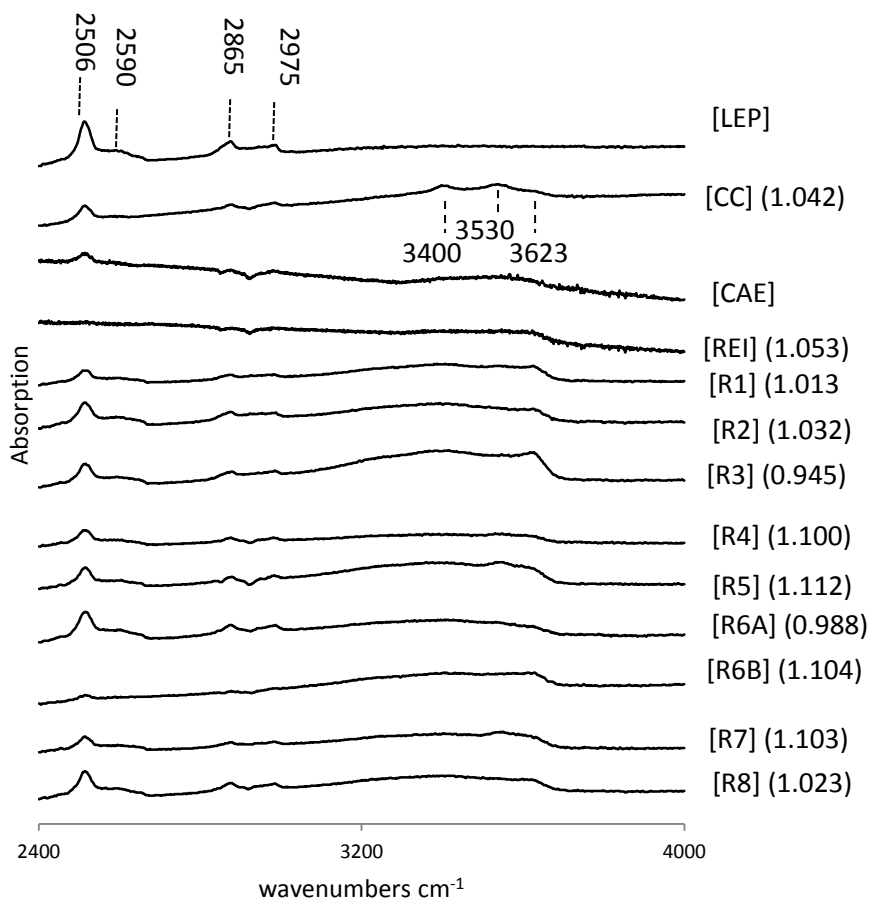




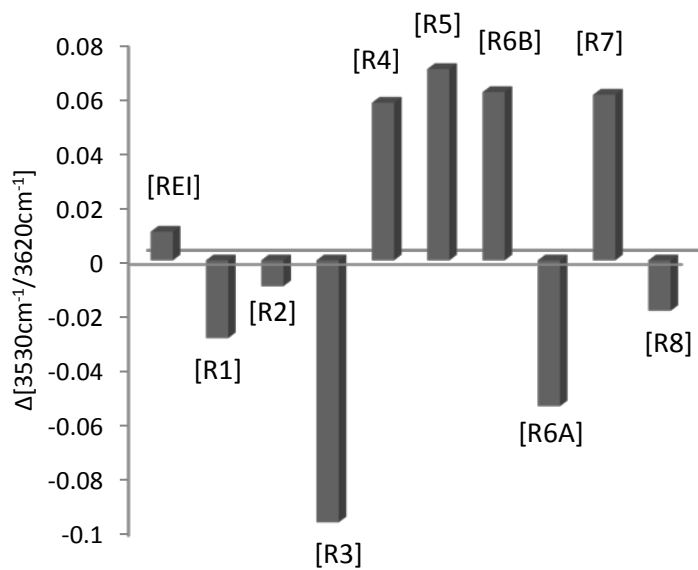
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650 Figure 4

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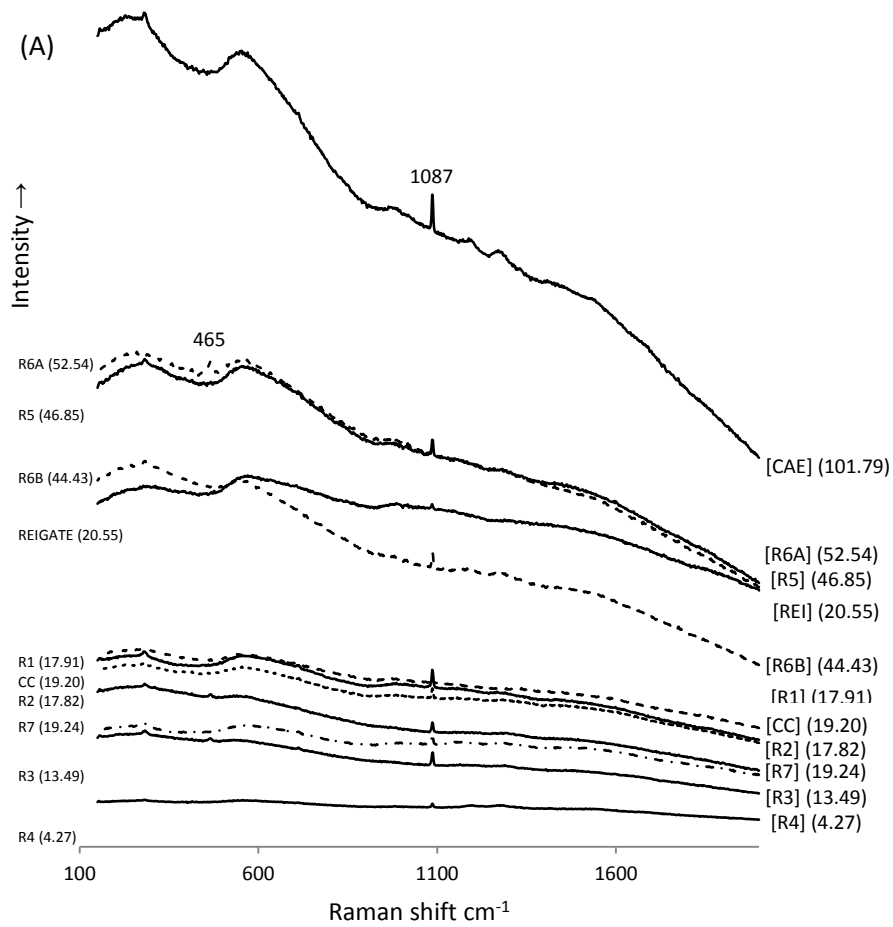
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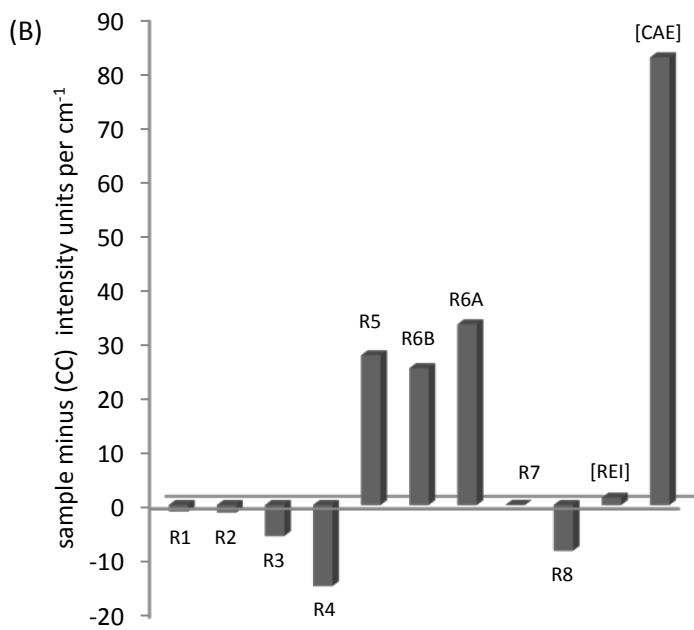
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654 Figure 5

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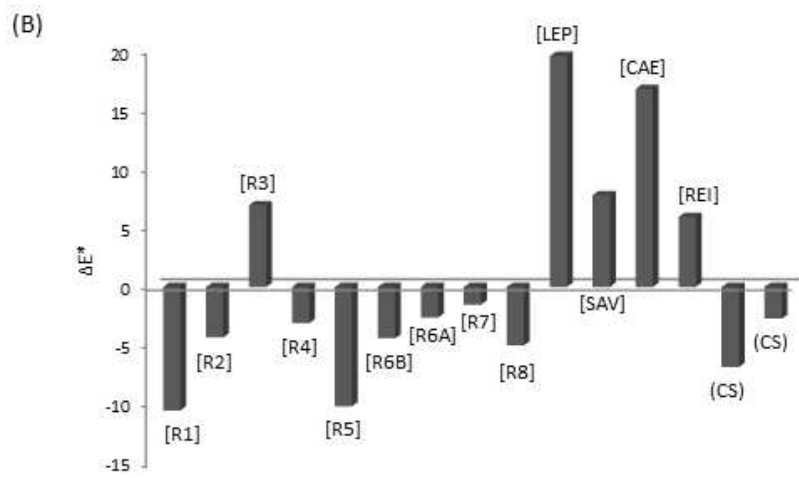
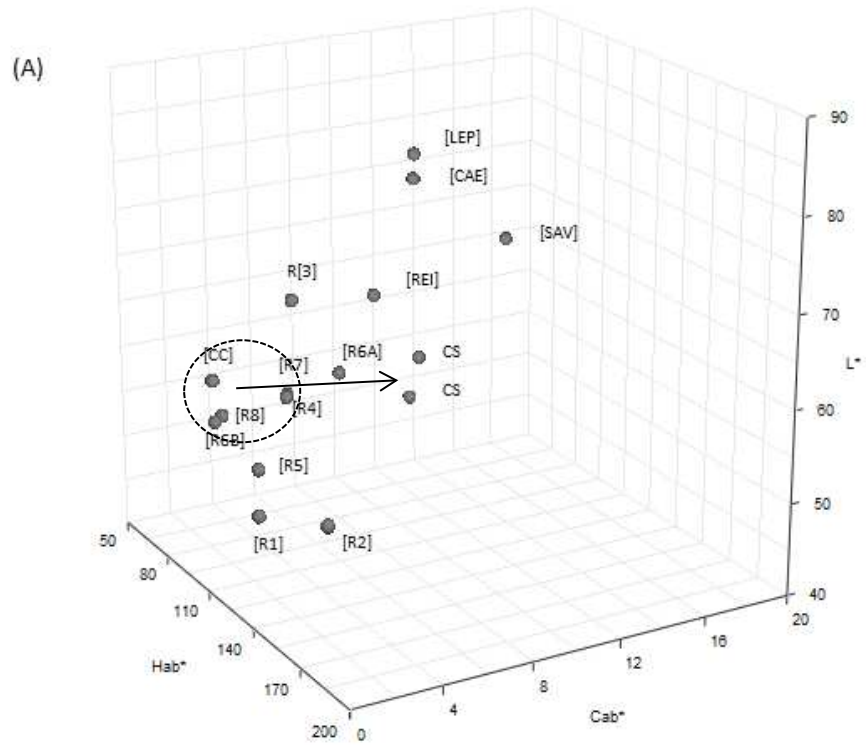


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658 Figure 6



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660 Figure 7