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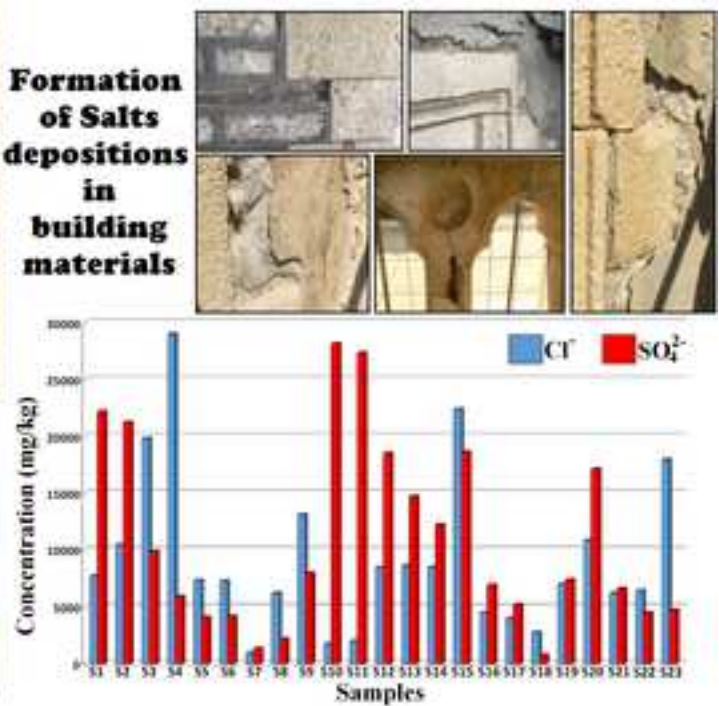
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HIGHLIGHTS

- Nature and distribution of salts crystallizations in building materials of a construction close to the sea has been studied.
- XRD and Raman microscopy allowed to define the wide variety of sulfates presence.
- To define the chlorine presence EDXRF imaging should be implemented in the methodology.
- In some of the building materials both sulfates and chlorides concentration are close to 3% w/w.

Decay processes in buildings close to the sea induced by marine aerosol: Salt depositions inside construction materials

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Abstract

Buildings close to the sea experience different kinds of decay processes related with the influence of marine aerosol. This sea spray is a chemically complex system formed by inorganic salts (sulfates, nitrates and mainly chlorides) and organic matter, together even with airborne particulate matter from the surrounding environment. Buildings close to the sea, erected using different materials such as bricks, plasters, limestones and sandstones, can experience many kinds of chemical reactions promoted by the impact of this sea spray, which favour the formation of salt crystallizations. In this work, a study of salts crystallizing in different kinds of building materials of a construction close to the Bay of Biscay (Villa Belza, Biarritz, France) has been studied in order to evaluate the state of conservation of the materials under study. The construction materials affected by salts were analysed by means of X-ray Diffraction (XRD) and μ -Raman spectroscopy (μ -RS) for molecular analyses, Energy dispersive X-ray Fluorescence spectrometry (μ -ED-XRF) for elemental analyses and soluble salts tests by means of ion chromatography. These analyses revealed different levels of chlorides, nitrates and sulfates. Moreover, using this methodology, some specific chemical reactions that take place in the Villa Belza were understood. This knowledge can help to lay the foundations for possible future restoration works.

Keywords: marine aerosol, limestone, sandstone, XRD, ED-XRF, Ion Chromatography.

43

44 **1. Introduction**

45

46 Buildings erected close to the sea can experience more chemical decay processes than
47 others. These decay processes are usually alterations derived from physical or chemical
48 interaction between building materials and the surrounding environment. This negative
49 influence is closely related with marine aerosol. Marine aerosol is a chemical complex
50 system formed by inorganic salts (**Morillas et al. 2016a; 2018a**) and organic matter
51 (**Bao et al., 2018; Miyazaki et al., 2018**), together with airborne particulate matter
52 (**Calparsoro et al., 2017**). The primary particles transported in the marine aerosol
53 (PMA) can induce different chemical reactions in the atmosphere (**Ceburnis et al.,**
54 **2016; Xiao et al., 2018**), promoting the so-called Secondary Marine Aerosol (SMA)
55 particles (**O'Dowd and de Leeuw, 2007**). These kinds of particles, together with the
56 natural crustal or mineral particles and the metallic airborne particulate matter emitted
57 by anthropogenic sources (road traffic, industry, etc.) can be deposited on building
58 materials from a specific construction following dry deposition processes (**Morillas et**
59 **al., 2016a**). The interactions of these natural and anthropogenic stressors with building
60 materials can promote different kinds of pathologies.

61 One of the most aggressive deterioration pathways promoted by marine aerosol is salt
62 crystallization (**Vallet et al., 2006**) and thus the presence of soluble salts in the building
63 materials used to erect construction. The damages caused by soluble salts in the
64 building materials can be produced as result by several mechanisms based on the kind
65 of crystallization (**Granneman et al., 2019; Derluyn et al., 2014; Celik and Aygun,**
66 **2018**).

67 The formation of these salts is not only an aesthetical problem when they become
68 visible as efflorescences (**Kamh et al., 2017**). The main problem resides when salts
69 precipitate beneath the material as subflorescences (**Morillas et al., 2015**). Indeed, its
70 formation during time can get to crack materials and cause irreparable loss of material
71 in the building. In this way, the level of damage by marine aerosol can vary depending
72 on the characteristics of the material, such as limestone (**Derluyn et al., 2013; 2019**),
73 sandstone (**Raneri et al., 2015**), bricks (**Morillas et al., 2018b**) and plaster (**Morillas et**
74 **al., 2013**).

75 The crystallization process occurs when the salt solubility is being exceeded, the salt
76 solubility itself being temperature dependent (Onasch et al., 2000; Gomez-Heras and
77 Fort, 2007; Zhang et al., 2014). When occurring in a building material, the pore size
78 (Cultrone and Sebastian, 2008), water absorption capacity (Yang and Wang, 2019),
79 mechanical strength (Chunran and Shicong, 2019) and pore size distribution (Molina
80 et al., 2011) of the material play their role as well in salt-induced decay. The deposition
81 and the crystal solubilization, and subsequently the entry of these soluble salts into the
82 building material promotes the crystal growing in pores, or subsequent crystallizations
83 in existing fissures, which gives rise to tensions promoting the enlargement of these
84 areas (Ruedrich et al., 2007; Thiebaut et al., 2018). Under confined conditions, i.e.
85 within the pores of the building material or within an existing fissure, the crystallization
86 exerts a certain stress on the pore or fissure wall (Espinosa et al., 2008a), proportional
87 to the natural logarithm of the supersaturation degree (Espinosa et al., 2008b). If this
88 physical stress exceeds the tensile strength of the material, deterioration occurs.

89 For all these reasons, analytical monitoring of building materials as well as conservation
90 interventions are strongly recommended in any process of decision-making related to
91 the soluble salts presence (Mendonça Filho et al., 2019; Morillas et al., 2016b), with
92 crystallization-induced decay one of the most aggressive deterioration processes
93 affecting buildings erected in coastal areas.

94 In this work, a multianalytical methodology based on the combination of X-ray
95 Diffraction (XRD) and μ -Raman spectroscopy (μ -RS) for molecular analyses, Energy
96 dispersive X-ray Fluorescence spectrometry (ED-XRF) for elemental analyses and
97 soluble salts tests by means of ion chromatography was applied to the characterization
98 of building materials used for the construction of the Villa Belza (Biarritz, France) and
99 affected by the action of marine aerosol action.

100 **2. Materials and methods**

101 *2.1. Location and Sampling*

102 This study has been carried out on the façades from a building called the Villa Belza,
103 which was built from 1880 until 1895. The construction is located at the coast of
104 Biarritz, France, with direct exposition to sea spray (see Figure S1 from Supplementary
105 Material and Table 1). The study has been performed in the façade opposite to the

106 orientation of the sea, since it was not possible to extract samples from the opposite
107 façade oriented directly to the sea. 23 samples of different kinds of materials
108 (limestones, sandstone, cement and joint and rendering mortars) were collected at
109 different heights (see Figure 1) in order to observe possible differences in the
110 deterioration processes of building materials along the façade.

111 *2.2. Instrumentation*

112 For the molecular characterization of the 23 samples analyzed, XRD analyses were
113 carried out using a powder diffractometer PANalytical Xpert PRO instrument equipped
114 with a copper tube ($\lambda_{\text{CuK}\alpha 1} = 1.54060 \text{ \AA}$, $\lambda_{\text{CuK}\alpha 2} = 1.54439 \text{ \AA}$), a vertical goniometer
115 (Bragg-Brentano geometry), a programmable divergence aperture, an automatic
116 interchange of samples, a secondary monochromator of graphite and a PixCel detector.
117 The measurement conditions were 40 kV and 40 mA, with an angular range (2θ)
118 scanned between 5 and 70°. Moreover, Xpert HighScore (PANalytical) software in
119 combination with the specific powder diffraction file database (International Centre for
120 Diffraction Data - ICDD, Pennsylvania, USA) was used for the data treatment of the
121 diffractograms and the identification of the present mineral phases.

122 In order to obtain complementary molecular information present in the Villa Belza
123 samples, Raman spectroscopy was used. For the micro-Raman analyses, the inVia
124 Renishaw confocal Raman microspectrometer (Renishaw, Gloucestershire, UK)
125 coupled to a DMLM Leica microscope with 5×, 20× and 50× long working distance
126 lens was used. A 514 nm excitation laser (with nominal laser power at 50 mW) was
127 used. The spectrometer was daily calibrated by using the 520.5 cm^{-1} Raman band of a
128 silicon chip. Lasers were set at low power (not more than 1 mW at the sample) to avoid
129 sample decomposition. Data acquisition was carried out using the Wire 4.2 software
130 package (Renishaw). Spectra were acquired in the spectral region between 100 and
131 3000 cm^{-1} . Measurements were acquired between 5-30 s and several scans (between 10-
132 40 scans) were accumulated for each spectrum to improve the signal-to-noise ratio. To
133 interpret all the Raman results, the acquired Raman spectra were compared with Raman
134 spectra of pure standard compounds collected in the e-VISNICH dispersive Raman
135 database (Maguregui et al., 2010) and with free Raman databases (e.g. RRUFF
136 (Downs and Hall-Wallace, 2002)) for the assignation of Raman bands. For the spectral
137 treatment and analysis, Wire 2.0 (Renishaw, Gloucestershire, UK) and OMNIC® 7.2

138 software (Thermo Nicolet, Madison, WI, USA) were used. Once the compounds were
139 identified, they were classified as original or deterioration compounds. A given
140 compound is said to be identified if it appeared at least five times in different spectra
141 from the same sample.

142 For the elemental analysis of the samples, the M4 TORNADO (Bruker Nano GmbH,
143 Berlin, Germany) energy dispersive X-Ray fluorescence spectrometer (EDXRF) was
144 used. Measurements were conducted directly in the rock fragments using poly-capillary
145 lens, which are able to achieve a lateral resolution down to 25 μm (measured at the Mo
146 $\text{K}\alpha$ line). The X-ray Rh anode tube implemented operates at up to 50 kV with a
147 maximum current of 600 μA , which were the conditions considered for the spectral
148 acquisition. The detection of the fluorescence radiation was performed by an XFlash®
149 silicon drift detector with 30 mm^2 sensitive area and energy resolution of 145eV for
150 Mn- $\text{K}\alpha$. In order to improve the detection of the lightest elements ($Z < 19$), filters were
151 not used and measurements were acquired under vacuum (20 mbar). To achieve the
152 vacuum, a diaphragm pump MV 10 N VARIO-B (Vaccubrand, Wertheim, Germany)
153 was used. The live time used for each punctual measurement was 200 seconds. The
154 spectral data acquisition and treatment was performed using the M4 TORNADO
155 software (Bruker Nano GmbH, Berlin, Germany).

156 To determine the nature of the main colonizers in the greenish patina visible in some
157 samples (e.g., S8 sample in Figure 1) from Villa Belza, Phase Contrast microscope
158 (PCM) was used. Micro-photographs of the colonized samples were obtained with a
159 Nikon DN100 camera coupled to a Nikon SMZ800 stereoscopic microscope and
160 microphotographs were captured with a Nikon DS Fi1 DS-Fi1 digital microscope
161 camera on a Nikon Eclipse 80i PCM provided with 20 \times , 40 \times , 60 \times and 100 \times objective
162 lenses.

163 The quantification of soluble salts, present in the samples of the limestone, sandstone,
164 cement and joint and rendering mortars from Villa Belza, was conducted by ion
165 chromatography with conductivity detection after post-column ion suppression. Prior to
166 the soluble salt quantification, an extraction of the soluble cations and anions was
167 carried out using an ultrasound-based extraction method. All the samples were
168 homogenized in an agate mortar and dried in an oven at 75 $^{\circ}\text{C}$ until constant weight.
169 After that, powdered and dried samples were subjected to an ultrasound extraction

170 procedure in an ultrasound bath. 100 mg of powdered sample with 100 ml of Milli-Q
171 quality water (Millipore, USA) was placed in an ultrasound bath during 100 min in
172 order to extract soluble salts (anions and cations) from samples. Cations (Ca^{2+} , K^+ , Na^+ ,
173 Mg^{2+} , NH_4^+) and anions (Cl^- , NO_3^- , SO_4^{2-}) were quantified by means of ion
174 chromatography. For cations a Dionex UCS-5000 ion chromatograph and for anions a
175 Dionex ICS-2500 ion chromatograph connected to a conductimetric detector (ED50
176 Dionex conductimetric detector) with post-column suppression (Thermo Scientific™
177 Dionex CERS 500, Dionex Corporation, Sunnyvale, California, USA) was employed.
178 The experimental conditions used for the quantification of these anions are described
179 elsewhere (Prieto-Taboada et al. 2012).

180 **3. Results and discussion**

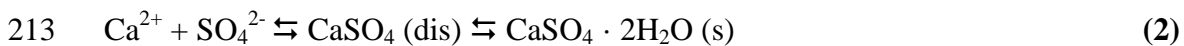
181 *3.1. Molecular analyses of the construction materials*

182 To determine the mineralogical composition of the construction materials of Villa
183 Belza, XRD analyses were carried out. In Table 1, a summary of the semi-quantitative
184 estimation of the minerals present in the analyzed samples in weight percentage (wt %)
185 is presented. This estimation is based on the intensity (height) of the most intense peak
186 or diffraction maximum of each phase, and on the RIR (Reference Intensity Ratio) value
187 contained in the Powder Diffraction Files (PDF) referenced to the database (Zhou et al.,
188 2018). The estimation is based on a single peak for each phase, mainly free of
189 interference with peaks of other phases. In some cases, their relative intensity might be
190 affected in the case of phases with preferential orientation. The RIR values are
191 fundamentally empirical and may vary somewhat between different PDF files of the
192 same mineral. In this calculation, only the identified phases are taken into consideration
193 for the semi-quantitative estimation, reaching the 100 %. In this sense, the unidentified
194 phases and the amorphous (non-crystalline) material that the samples could contain are
195 not considered. These estimations may be useful as a first approach, especially for
196 comparison among samples.

197 As can be seen in the Table 1, the principal mineralogical phases present in almost all
198 the samples were calcite (CaCO_3) and quartz ($\alpha\text{-SiO}_2$) contributing with different
199 percentages according to the type of material. Moreover, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and

200 halite (NaCl) are also present with variation in their percentages (2-7% and 1-2%
201 respectively).

202 The highest content of gypsum was detected in S20 sandstone sample and samples S3,
203 S4 and S23 (rendering mortars). In these last rendering mortars, the highest
204 concentrations (2%) of halite (NaCl) was also detected. Both, sulfates and chlorides, are
205 closely related with the influence of marine aerosol. On the one hand, sulfates present in
206 the sea spray, together with the H₂CO₃ aerosol, can react with the carbonaceous
207 materials giving rise to the subsequent calcium sulfates. In this way, calcium carbonate
208 is a highly soluble carbonate that can be dissolved due to the action of CO₂ dissolved in
209 atmospheric aerosols (see reaction 1) and therefore the solubilized Ca²⁺ can react with
210 the SO₄²⁻ coming from sea spray (see reactions 2) giving rise to gypsum formation after
211 a previous formation of anhydrite (CaSO₄).



214 On the other hand, the halite present in the sample at concentrations between 1-2% can
215 be present in the building materials coming from the dry deposition of marine aerosol.
216 Chlorides can migrate to the inner areas and re-crystallize, promoting NaCl
217 subflorescence, which under natural radiation can produce partial disruption of the
218 porous surface, producing micro-spallings (**Gómez-Heras and Fort, 2007**). This kind
219 of pathology is visible in Villa Belza construction.

220 In samples S4 (rendering mortar) and S15 (joint mortar) apart from the mentioned
221 compounds, additional specific decay compounds were also detected (see Figure 2). In
222 Figure S4, apart from calcite and quartz (matrix composition), halite and portlandite
223 were also detected (see Figure 2A). As explained above, halite presence is related to the
224 marine influence, but portlandite (Ca(OH)₂) presence cannot be connected to this
225 stressor source. Portland cement can suffer different decay processes. The cement
226 typically provides to a building construction an alkaline protection with a pH around 12.
227 Nevertheless, sometimes, due to the surrounding environment, this pH can decrease to
228 10 losing its inherent protection. Consequence of it is the carbonation of the cement
229 (reaction between atmospheric CO₂ and the Ca(OH)₂, which can be catalyzed by
230 chlorides and sulfates from marine aerosol (**Broomfield, 2006**).

231 In sample S15, apart from calcite and quartz, pyroaurite ($\text{Mg}_6\text{Fe}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$)
232 and ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) were also detected (see Figure 2B). As it is
233 known, for the preparation of mortars, sand, water and a binder (hydraulic and non-
234 hydraulic lime or cement) are used. This cement is obtained by calcination of calcite
235 and clay that later is milled producing the clinker (composed by different lime silicates)
236 **(Elsen, 2006)**. Subsequently, the cement included in the constructions can suffer the
237 influence of marine aerosol. The material reacts with the chlorides and sulfates mainly
238 present in the aerosol, leading to chemical reactions inside the cement pores **(García-**
239 **Florentino et al., 2016)**. An example of it is the formation of ettringite
240 **(Apostolopoulou et al., 2018)**, which can lead to expansive reactions leading to
241 material cracking. Regarding pyroaurite ($\text{Mg}_6\text{Fe}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$), there are works
242 that previously described its formation in laboratory controlled conditions. For the
243 formation of this compound, FeCO_3 and Mg-rich environment with oxidation processes
244 at a pH of 8.5 is necessary **(Hansen and Taylor, 1990)**.

245 Additionally, in sample S13 (sandstone) a greenish color was observed. In this sample,
246 the main component was quartz (95% of $\alpha\text{-SiO}_2$), calcite (2% of CaCO_3), gypsum (2%
247 of $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$) and halite (1% of NaCl). The XRD diffractogram of sample S13
248 showed an elevation of the spectral background that suggested the existence of
249 amorphous phases (organic or non-crystalline). Considering that the greenish patina in
250 the sample can be related with a biocolonization (see Figure S2 from Supplementary
251 Material), the sample was investigated by means of Phase Contrast Microscopy (PCM).
252 Thanks to the microscopic observations, many cyanobacteria colonies were identified.
253 As it can be seen in Figure S3A and S3B from Supplementary Material, different
254 characteristics of coccoid cells and cyanobacterial cells in division even showing their
255 pseudo-filaments were observed. Finally, cyanobacterial cells with their endospores or
256 baeocytes were also observed (see Figure S3C and S3D from Supplementary Material).
257 These microscopic observations—suggest that the greenish color is connected to the
258 cyanobacteria colonies; more specifically the *Pleurocapsales* order and the gender
259 *Pleurocapsa*. This kind of cyanobacteria typically colonize high content quartz
260 limestones **(Shalygin et al., 2019)**.

261 In the sample S20, the main mineralogical phases were quartz (80%), calcite (12%),
262 gypsum (7%) and halite (1%). The semi-quantitative content of calcite is relatively low
263 (12%), but taking into account the high content of gypsum (7%), it is clear that a

264 sulfation process is taking place in this area. The calcite present in this sandstone
265 sample can be transformed into gypsum through a sulfation process promoted by the
266 load of sulfates present in the marine aerosol (**Zeza and Macri, 1995**). These reactions
267 have been described previously (see reactions 1-2).

268 Additionally, Raman microscopy was performed to complement the molecular
269 information obtained by XRD. Owing to the fact that using XRD it is not possible to
270 determine amorphous mineral phases or minor compounds (below 1% in weight),
271 Raman microscopy was used to complement the possible detection of additional
272 compounds at minor or trace levels. For this reason, apart from the same mineralogical
273 phases observed by XRD, additional ones were also detected by Raman spectroscopy.
274 In many samples, aluminosilicates such as adularia (KAlSi_3O_8); quartz (SiO_2); rutile
275 (TiO_2); calcite (CaCO_3) and charcoal (C) were also identified

276 In most of the studied samples (S1, S2, S9, S10, S11, S12, S13, S14 and S20) different
277 kind of calcium sulfates were detected (see Figure 3), such as gypsum (main Raman
278 bands at 414, 493, 616, 670, 1008 and 1132 cm^{-1}) (see Figure 3A), bassanite
279 ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, main Raman bands at 430, 488, 627, 668 and 1015 cm^{-1}) (see Figure
280 3B) and anhydrite (CaSO_4 , main Raman bands at 422, 492, 631, 673, 1024 and 1166
281 cm^{-1}) (see Figure 3C). In this last case, the additional band at 1086 cm^{-1} that belongs to
282 calcite (see Figure 3C) was also registered. The identification of calcium sulfate
283 crystallization with different hydration waters is related with the dehydration process of
284 the gypsum previously formed in the different building materials (sandstone, limestone
285 and joint and rendering mortar) from Villa Belza construction. These transformations
286 start when water evaporation processes take place under some specific reactions
287 described elsewhere (**Morillas et al., 2013**). Hydration and dehydration cycles promote
288 an increase and decrease in the size of the crystals formed in the pores of the building
289 materials, which can lead to possible cracks and loss of material.

290 *3.2. Elemental analysis of the construction materials*

291 In addition to the molecular measurements, μ -EDXRF imaging analysis was also
292 performed to extract additional conclusions about the conservation state of the materials
293 used in the Villa Belza construction. First, different single point EDXRF spectra (down
294 to $25\text{ }\mu\text{m}$ of lateral resolution) were acquired to identify the elements of interest. After
295 that, different mappings were performed. In Figure 4, an example of the elemental

296 distribution maps obtained in sample S15 (joint mortar) is displayed. Although some
297 elements such as Pb, As, Fe, Co and Cu are quite homogeneously distributed in the
298 mapped area (see Figure 4A to D), specific hotspots of these elements which show a
299 higher intensity of their respective K_{α} lines (except for Pb, which L_{α} line was used for
300 data interpretation) are also observable. Elements such as Ti-V-Cr (see Fig 4E) are
301 heterogeneously distributed in the sample.

302 Moreover, in the whole section of the joint mortar, aluminosilicates are widely
303 distributed (see K-Al-Si distribution in Figure 4F), probably as adularia or microcline
304 according to XRD and Raman results. In the Figure 4G the clear distribution of the
305 aggregate (Si) and the binder (Ca) is observable. The white central vein in the mapped
306 area is connected not only to Ca, but also to Mg (see Figure 4F and H), which can
307 suggest a mixed presence of calcite and dolomite, the presence of Mg-rich calcite or
308 even dolomite ($\text{CaMg}(\text{CO}_3)_2$). This last carbonate was identified in some of the samples
309 considered in this work (see Table 1). The non-detection of it in sample S15 does not
310 imply that this carbonate is not present, because it can be set under the detection limit of
311 the applied XRD methodology.

312 It is also remarkable that in samples S15, Zn is specifically accumulated in a concrete
313 position in the mapped area (see Figure 4F). In some areas of the analyzed sample, the
314 distribution of Ca and S is coincident (see pink-purple areas in Figure 4H), suggesting
315 the possible presence of calcium sulfates (gypsum, anhydrite or basanite) in the inner
316 part of the joint mortar. Calcium sulfates were not identified in this sample by XRD
317 probably because their concentration was set under the limit of detection of the
318 technique. In this sense, if an elemental study had not been accomplished, the
319 identification of sulfates at low concentrations in the sample would not have been
320 carried out.

321 Apart from sulfates, the high correlation between Na and Cl distribution maps (see
322 Figure 4I) suggests the crystallization of NaCl inside the S15 joint mortar. Once more,
323 this halide was not detected by XRD. Halite crystallizations can promote many physical
324 problems in the building material structures promoting cracks and loss of material.
325 Additionally, Cl-Mg showed coincident distributions (greenish yellow in the Figure 4J)
326 in the corners of the central vein, both elements present in the marine aerosol.

327 Different elemental mappings obtained from S17 and S7 samples respectively are also
328 presented in the Figures S4 and S5 from the Supplementary Material. Regarding the
329 original components in the samples (calcite and aluminosilicates mainly), the
330 conclusions that can be extracted are quite similar to those obtained for sample S15.

331 On the one hand, in sample S17, the areas showing a coincident distribution of Ca and S
332 (see Figure S4 from Supplementary Material) are lower than the ones detected in S15,
333 which suggest a lower presence of calcium sulfates. Once again, the white vein detected
334 in this sample also shows a high correlation between Ca and Mg, being possible to
335 extract the same conclusion previously introduced. In this sample, it is clearly evident
336 that NaCl is widely distributed (see Figure S4 from Supplementary Material),
337 suggesting a high impact of marine aerosol in the mentioned sample. On the other hand,
338 sample S7 belongs to a section of a limestone from the construction. In it, the punctual
339 presence of silicates and some aluminosilicates are also observable (see Figure S5 from
340 Supplementary Material). In some specific areas where aluminosilicates are present, the
341 intensity of the Fe, Ti, V and Cr K_{α} line is also higher, suggesting a possible
342 contribution of these metals in the aluminosilicates. In this sample also, although the
343 intensity of the Ca line is much higher than the one of S, both elements showed a
344 coincident distribution (purple areas in Figure S5 from Supplementary Material), which
345 suggest a possible sulfation of the limestone. In this case, also, the presence of NaCl
346 crystallizations are also visible due to the coincident distribution of Na and Cl (see
347 Figure S5 from Supplementary Material). As in the previous samples, in this case also it
348 was not possible to detect the presence of calcium sulfates and halite in the XRD
349 diffractograms, suggesting that both kind of salts crystallizations could be set at
350 concentrations lower than 1 %. Additionally, many different potassium and iron
351 aluminosilicates, mica ($AC_{2-3}T_4O_{10}X_2$) and possible kaolinite ($Al_2Si_2O_5(OH)_4$) were
352 also observed in S7 as component of the limestones used for Villa Belza construction
353 (see Figure S5 from Supplementary Material). Moreover, others elements such as Co
354 and Mn-Fe are also quite homogeneous distributed and elements such as Ti-Cr-V,
355 heterogeneous distributed in the limestone matrix.

356 *3.3. Quantification of soluble salts*

357 The results obtained from the elemental and molecular spectroscopic analyses suggest
358 that all the building materials used for the Villa Belza construction are affected by the

359 crystallization of mainly sulfate and chloride salts. To confirm the magnitude of this
360 impact, soluble salts were extracted and quantified to determine their specific nature.
361 The concentrations of the anions and cations obtained after the soluble salts test are
362 presented in Figure 5 (see also Table S1 in Supplementary Material). The results are
363 expressed as the average concentration of each ion together with the relative standard
364 deviation (at 95% confidence interval) calculated from three sample portions
365 (subsamples) for each sample.

366 Regarding the quantified ions, the twenty-three building material samples showed the
367 presence of Li^+ and NH_4^+ at low concentrations. Lithium is one of the most common
368 cations present in marine aerosol (**Weller et al., 2008**). Although the presence of
369 ammonium in sea spray as ammonium nitrate (NH_4NO_3) and ammonium sulfate
370 ($(\text{NH}_4)_2\text{SO}_4$) (**Guth et al., 2018; Park et al., 2018**) is widely known, the concentrations
371 determined in all the samples are quite low (average of 28 mg/kg approximately). This
372 could be related with the high solubility of ammonia. The concentration of NH_4^+ in
373 other works related with buildings close to the sea at the Atlantic coast was similarly
374 low (under limit of detection or even non-detected) (**García-Florentino et al., 2016**).

375 Regarding alkali and alkaline earth cations, the concentrations in general terms are
376 higher for Mg^{2+} than for K^+ (506 vs 485 mg/kg respectively). On the one hand, the
377 samples that contain more than 600 mg/kg of K^+ are S3, S4, S20 and S23. Moreover,
378 these three samples have a similar calcite proportion (around 50 %). Calcite is a very
379 soluble compound, in the continuous contact with the H_2CO_3 aerosol, which can react
380 after solubilization with other anions and cations coming from the sea spray giving rise
381 to different K^+ compounds (**Morillas et al., 2013**). On the other hand, as can be seen in
382 the bar chart of Figure 5, the samples that show the highest concentrations of Mg^{2+} are
383 S9, S12, S13, S14, S17 and S19 samples. For the unique only sandstone sample (S9)
384 analyzed in this work, 8% (wt %) of dolomite was detected (see Table 1), thus the high
385 Mg^{2+} concentration could be related with the presence of this carbonate. On the
386 contrary, in the rest of the samples where high concentrations of Mg^{2+} were determined,
387 dolomite was not identified. The high presence of this cation could be related with the
388 presence of salts including this alkaline earth cation such as epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$).
389 Although this compound was not observed, neither by means of XRD nor by means of
390 Raman spectroscopy, its presence cannot be discarded because this decay compound is
391 very common to find in buildings close to the sea (**López-Arce et al., 2009**).

392 The highest concentration of cations were registered for Ca^{2+} and Na^+ . Calcium was one
393 of the most concentrated elements (average concentration around 14236 ± 4790 mg/kg).
394 This matches with the XRD and Raman analyses where calcite and gypsum were
395 detected and this element is thus related with the presence of these compounds. In the
396 samples S4 (rendering mortar) and S15 (joint mortar), where the highest concentration
397 of Ca^{2+} was observed, decay compounds such as portlandite and ettringite were
398 detected. The presence of Na^+ (average concentration of 5068 ± 3102 mg/kg) in all the
399 samples is closely related with the halite (NaCl) salts crystallizations detected in the
400 samples (**Cardell et al., 2003**). The concentration of Na^+ is the highest in samples S3,
401 S4 and S23 (11960, 10890 and 11330 mg/kg for S3, S4 and S23 respectively). This
402 observation matches with the XRD results (see Table 1), where besides that these three
403 samples have a similar calcite proportion (around 50 %), they have the highest
404 proportion of halite (2%). In marine environments, for approximately every 5000 mg/kg
405 of Na^+ concentration, the construction material can be lost 1% (wt %) (due to spalling)
406 and form halite in marine environments induced by marine aerosol.

407 Finally, the highest concentrations of anions are those of Cl^- and SO_4^{2-} , with average
408 concentrations of 9254 ± 7002 and 10926 ± 8328 mg/kg respectively. Samples S3, S4
409 and S23 show the highest Cl^- and Na^+ concentration. This observation corroborates the
410 findings presented above in which the halite was detected clearly in the three cases.
411 Moreover, samples S1, S2, S10, S11, S12, S13, S15 and S20 hold the higher SO_4^{2-}
412 concentrations. According to Table 1, all of these sulfate concentrations are related with
413 the presence of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in these samples except for the case of S15 for
414 which the sulfate is linked to the presence of ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$).

415 **4. Conclusions**

416 The multianalytical methodology based on the use of XRD and Raman spectroscopy for
417 molecular analyses and μ -ED-XRF for elemental analyses, together with soluble salts
418 quantification by means of ion chromatography allowed to define the nature and
419 concentration of the salts which affect the conservation state of the building materials
420 (limestone, sandstone, rendering and joint mortars) used in a construction next to the
421 sea, the Villa Belza building.

422 Thanks to XRD and Raman spectroscopy, it was possible to identify different kind of
423 sulfate crystallizations in building materials, whose concentration was set around 0.08-3

424 % depending the considered building material. The identification of gypsum,
425 dehydrated and hemihydrated calcium sulfates (anhydrite and basanite) suggests that
426 dehydration/hydration cycles are taking place in the materials, which promote a
427 volume/size change in the salt crystallized in their pores, which can be responsible for
428 crack formations and fissures in the building material.

429 Apart from sulfates, chlorines were also detected by XRD. Considering the limit of
430 detection of the technique (around 1% (wt %)), it becomes mandatory to use additional
431 techniques to detect its presence. To perform a non-invasive study, μ -EDXRF imaging
432 will be a good alternative, which allows to perform a screening of the samples to detect
433 the presence of chlorine salts crystallizations. In the Villa Belza building materials, Na
434 and Cl maps showed a coincident distribution, confirming the presence of halite in the
435 samples. Thanks to the soluble salts test, it was possible to asses that the concentration
436 of chlorides was between 0.1 and 3 %.

437 According to the extracted results, it can be affirm that this methodology can be
438 integrated as a routine tool to extract conclusions related to the conservation state of
439 building materials. In this case, that the building materials of Villa Belza are notoriously
440 affected by the influence of marine aerosol, being the main cause of salts
441 crystallizations. Building materials affected by salts can be desalinated following
442 different procedures and methodologies (e.g., chemical and mechanical methods, use of
443 slaughter mortars, immersion baths, electrochemical methods, etc.). However, the
444 constant input of salts coming from marine aerosol will promote subsequent
445 crystallization in the materials. In this sense, for future restorations of the construction,
446 if the materials will be replaced, appropriate materials resistant to this influence should
447 be selected. Therefore, this methodology capable of determining the original
448 composition of the affected building material and the nature and content of the newly
449 formed salts can be useful for civil engineers, architects, restorers and other scientist
450 that aim to preserve building materials of constructions erected not only in a marine
451 environment, but also in other locations affected by different environmental stressors.

452

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616

617 **FIGURE CAPTIONS**

618 **Figure 1.** Location, type of material and sampling of the 23 samples from Villa Belza
619 building (Biarritz, France).

620 **Figure 2.** XRD of building materials in Villa Belza of **A)** S4 (rendering mortar) with
621 the presence of calcite (CaCO_3), quartz (SiO_2), halite (NaCl) and portlandite ($\text{Ca}(\text{OH})_2$)
622 and **B)** S15 (joint mortar) with the presence of quartz (SiO_2), calcite (CaCO_3), ettringite
623 ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) and pyroaurite ($\text{Mg}_6\text{Fe}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$).

624 **Figure 3.** Raman spectra of S1, S2, S9, S10, S11, S12, S13, S14 and S20, indicating the
625 presence of **A)** gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$); **B)** basanite ($\text{CaSO}_4\cdot \frac{1}{2}\text{H}_2\text{O}$) and **C)** anhydrite
626 (CaSO_4).

627 **Figure 4.** μ -ED-XRF imaging of the S15 sample from Villa Belza (Biarritz, France)
628 showing the elemental distribution maps of some of the detected elements. (For
629 interpretation of the references to color in this figure, the reader is referred to the web
630 version of this article.)

631 **Figure 5.** Bar charts showing cations and anions concentrations (mg/kg units) on each
632 Villa Belza sample.

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Table 1[Click here to download Table: Table 1.docx](#)**Table 1.** Semi-quantitative information of mineralogical phases detected by XRD in the analyzed samples from Villa Belza (Biarritz, France).

Samples	Type of Material	Calcite (CaCO ₃)	Gypsum (CaSO ₄ ·2H ₂ O)	Halite (NaCl)	Quartz (SiO ₂)	Mica (AC ₂₋₃ T ₄ O ₁₀ X ₂)	Dolomite (CaMg(CO ₃) ₂)	Microcline (KAISi ₃ O ₈)	Kaolinite (Al ₂ Si ₂ O ₅ (OH) ₄)	Portlandite (Ca(OH) ₂)	Ettringite Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O	Pyroaurite Mg ₆ Fe ₂ (CO ₃)(OH) ₁₆ ·4H ₂ O
S1	Limestone	96 %	4 %	< 1 %	-	-	-	-	-	-	-	-
S2	Limestone	93 %	3 %	1 %	3 %	-	-	-	-	-	-	-
S3	Rendering mortar	50 %	-	2 %	48 %	-	-	-	-	-	-	-
S4	Rendering mortar	41 %	-	2 %	54 %	-	-	-	-	2 %	-	-
S5	Rendering mortar	39 %	-	< 1 %	61 %	-	-	-	-	-	-	-
S6	Rendering mortar	51 %	-	< 1 %	49 %	-	-	-	-	-	-	-
S7	Limestone	92 %	-	-	8 %	< 1 %	-	-	< 1 %	-	-	-
S8	Rendering mortar	12%	-	-	88 %	-	-	-	-	-	-	-
S9	Sandstone	55 %	2 %	1 %	34 %	-	8 %	-	-	-	-	-
S10	Limestone	96 %	4 %	-	-	-	-	-	-	-	-	-
S11	Limestone	95 %	5 %	-	-	-	-	-	-	-	-	-
S12	Rendering mortar	15 %	3 %	-	82 %	-	-	-	-	-	-	-
S13	Sandstone	2 %	2 %	1 %	95 %	-	-	-	-	-	-	-
S14	Sandstone	14 %	4 %	-	82 %	-	-	-	-	-	-	-
S15	Joint mortar	28 %	-	-	67 %	-	-	-	-	-	4 %	1 %
S16	Sandstone	15 %	-	-	75 %	-	-	10 %	-	-	-	-
S17	Joint mortar	28 %	-	-	70 %	-	2 %	-	-	-	-	-
S18	Cement	17 %	-	1 %	82 %	-	-	-	-	-	-	-
S19	Rendering mortar	16 %	-	< 1 %	84 %	-	-	-	-	-	-	-
S20	Sandstone	12 %	7 %	1 %	80 %	-	-	-	-	-	-	-
S21	Rendering mortar	14 %	-	< 1 %	86 %	-	-	-	-	-	-	-
S22	Limestone	75 %	-	< 1 %	24 %	-	-	-	-	-	-	-
S23	Rendering mortar	49 %	-	2 %	49 %	-	-	-	-	-	-	-

Figure 1
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Villa Belza (Biarritz, France)



Figure 2
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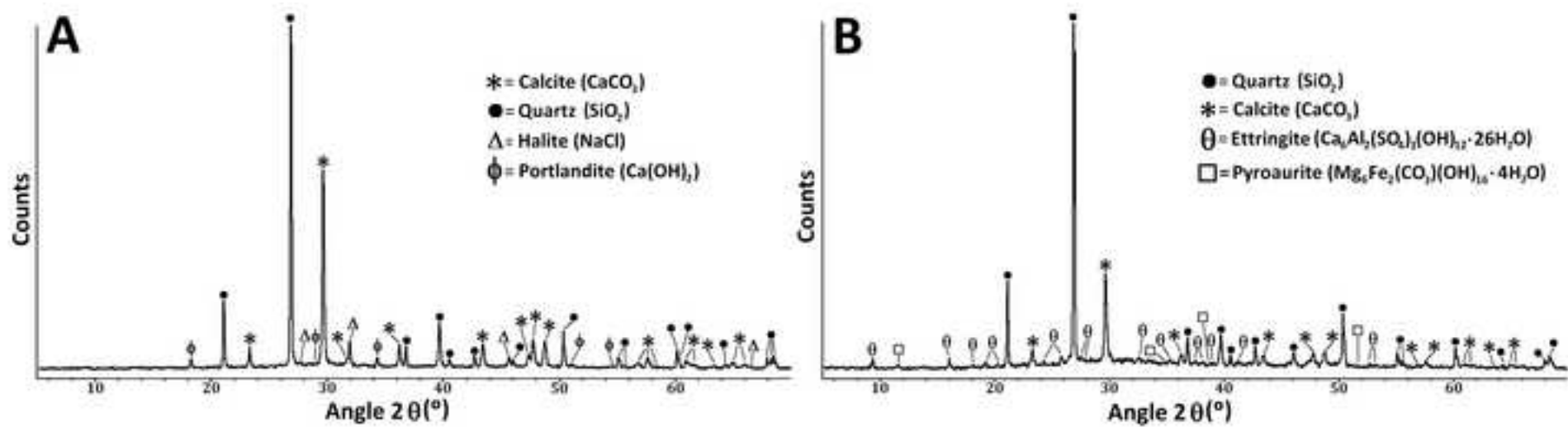


Figure 3
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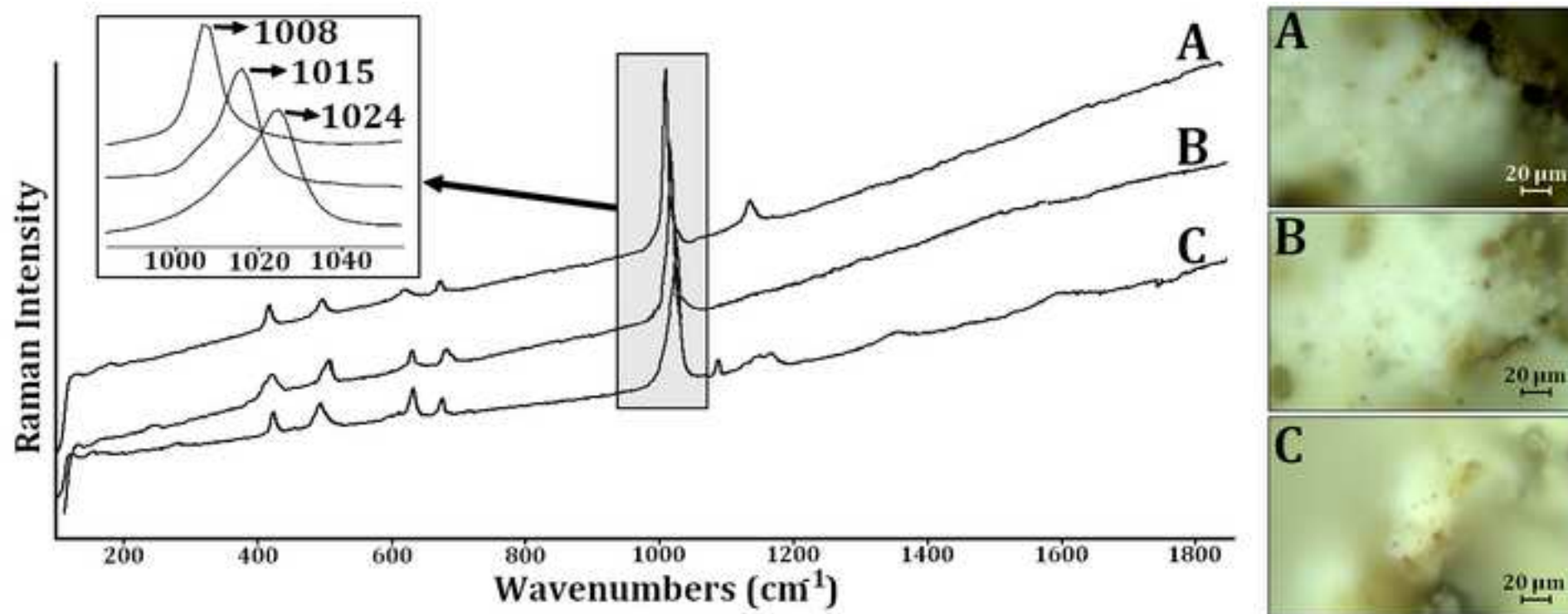


Figure 4
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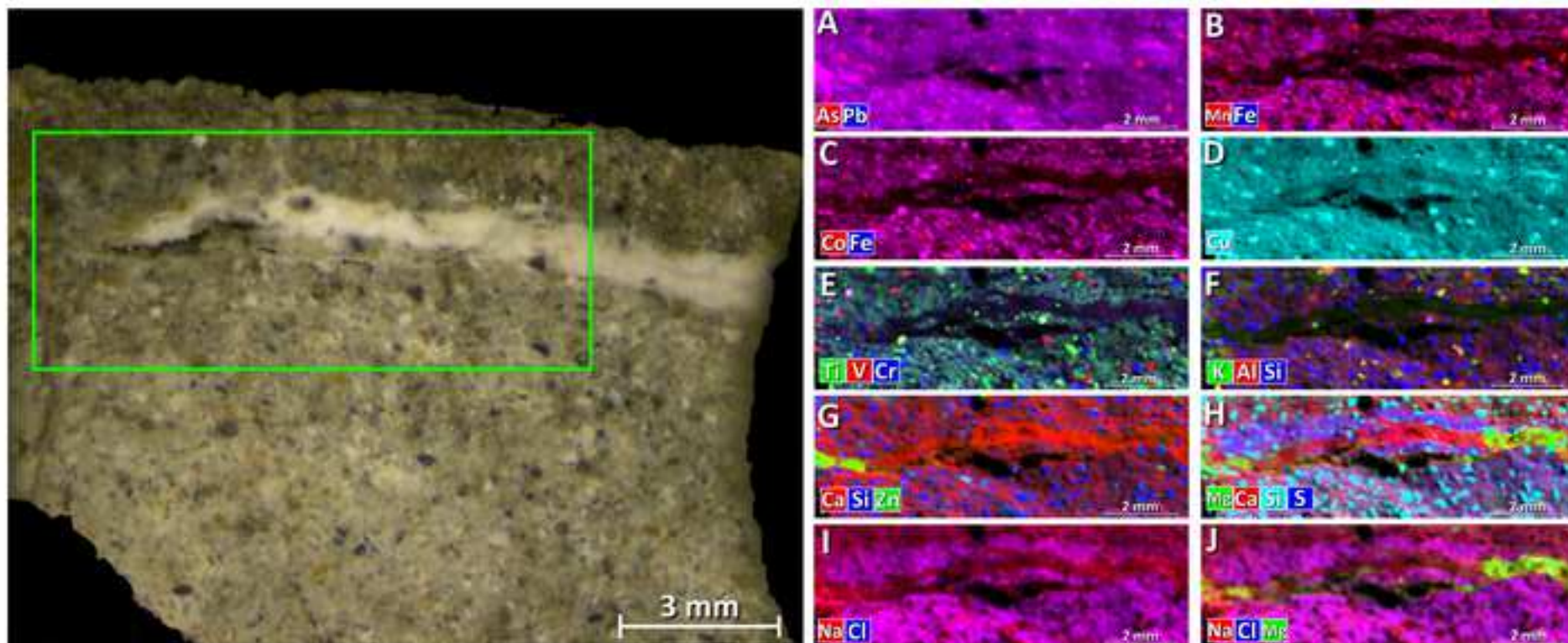


Figure 5
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