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## The role of marine aerosol in the formation of (double) sulfate/nitrate salts in plasters



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### ABSTRACT

During decades the use of gypsum in different buildings has been very common, especially in the Atlantic lands of Europe. Decay compounds like salt crystallizations are ones of the principal deterioration factors of such historical buildings. In this study, gypsum-based plasters from different inner rooms of the Igueldo Lighthouse (San Sebastian, Spain), a building dated back to 1860 that has been subjected to several repairs within these years, were investigated in order to ascertain the main mineral phases produced during the weathering process. A combination of Raman spectroscopy, X-ray diffraction, infrared spectroscopy in ATR mode, SEM-EDS imaging and Raman imaging was successfully applied to study the distribution of different decay compounds in the gypsum-based matrix and to establish the decay reaction pathway which leads to the formation of the identified decay compounds. Additionally thermodynamic chemical modeling was also performed to explain the formation of specific decaying compounds. According to the location of Igueldo Lighthouse (just above a cliff, close to the sea), this building experiments a wide influence of the marine aerosol ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$  input) and the influence of a high damp environment, giving rise to common efflorescence salts as well as to different mixed-calcium sulfates and mixed sulfate–nitrate salts, such as glauberite, syngenite, polyhalite and humberstonite. Dehydration process of gypsum from the plaster (leading to the presence of anhydrite and bassanite) was also identified.

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### 1. Introduction

Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is one of the oldest materials used in construction. In the Neolithic period, with the development of fire based technologies, calcined gypsum plaster began to be developed, and it was used to assemble the pieces of masonry, seal the joints of the walls and to cover the walls of the houses, being progressively an alternative to the mud mortar. Since that time it began using regularly until nowadays, especially in the Atlantic lands of Europe. During production process, depending on the temperature and duration of the heating, gypsum converts to the hemihydrate (bassanite  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) or to an anhydrous form (anhydrite  $\text{CaSO}_4$ ). Water partial pressure control is difficult and thus  $\text{CaSO}_4\text{--H}_2\text{O}$  system highly variable and phase equilibrium depends on grain size and thermal treatment kinetics. Recent studies have demonstrated that, under atmospheric pressure [1,2], there are up to five compounds produced in this system, such as  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (gypsum, monoclinic),  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  (bassanite monoclinic/rhombohedral),

$\gamma\text{-CaSO}_4$  (anhydrite I, or AI, cubic),  $\beta\text{-CaSO}_4$  (anhydrite II, or AII, orthorhombic) and  $\alpha\text{-CaSO}_4$  (anhydrite III, or AIII, hexagonal). Depending on the pressure (neon gas as pressure-transmitting medium) and gradient, different mineral phases in the dehydration of the  $\text{CaSO}_4\text{--H}_2\text{O}$  system can suffer deformations in their structure [3,4].

In the literature there are several studies that remark also the high influence of organic and inorganic additives which they have been used since the second half of the 20th century in order to control the hydration in gypsum setting/production [5–7]. Sometimes  $\text{NaCl}$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$  solutions can dehydrate gypsum as a result of the lower water vapour pressure of these solutions, modifying its solubility [8]. The later compounds, together with nitrates and sulfates, are present in marine aerosol [9], besides of fatty acids [10]. Some authors point out that in marine aerosol a mixture of ions like  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{Li}^+$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$  are usually present along with structural water and other less common ions from anthropogenic sources (e.g.,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{VO}_2^-$ ) [11–13]. In this way, in the marine aerosol composition, natural and anthropogenic ion inputs are present [14,15]. There are studies that simulated the reactions between cations and anions in the complex  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  –  $\text{H}_2\text{O}$  system [16],

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which can occur in natural environment, promoting the formation of different type of sulfates.

In the literature, several studies describe the formation of decay compounds in building materials as a consequence of the reactions between the original compounds and the ions transported in the marine aerosol. The main pathologies promoted due to these reactions are the formation of efflorescence, sub-efflorescence, loosing and detachment of the building materials, etc. [17–22]. Different decay compounds which have been detected inside the porous and/or over the gypsum surface or in presence of gypsum are listed in Table 1.

Moreover, theoretical models based on density functional theory calculations of the structures and properties of compounds like anhydrite ( $\text{CaSO}_4$ ), polyhalite ( $\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ ) and carnallite ( $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ ) (the last two related with marine influence) have been studied [33]. Other authors, using techniques such as XRD and SEM-EDS have demonstrated the influence and direct relationship that exists in the formation of gypsum and glauberite with the marine aerosol; and their seasons' dependence/periodicity [34].

In this work, a combination of different analytical techniques, including Raman spectroscopy, X-ray diffraction and infrared spectroscopy in ATR mode have been used to identify different decay compounds formed on gypsum plasters from indoor areas of an historical building located in front of the sea, the Igueldo Lighthouse (Donostia-San Sebastian, north of Spain). Moreover, to complete and corroborate the point-by-point spectroscopic results, SEM-EDS imaging and Raman imaging were used to map the distribution of the different decay compounds crystallized on gypsum-based plasters. Finally, thermodynamic calculations to complete the analytical statements taking into account the high influence of marine environment were carried out.

## 2. Materials and methods

### 2.1. Samplings

Plaster samples from the walls of the Lighthouse machine room, where the temperature conditions inside the room range between 27 °C (winter time) and 35 °C (summer time) with a wide range of relative humidity (>90%) were collected using a scalpel. The size of all of them never exceeded  $2 \times 2 \text{ cm}^2$ . Plaster fragments were analyzed directly by means of point-by-point Raman spectroscopy. For the XRD, ATR-FTIR, SEM-EDS imaging and Raman imaging, the same samples were powdered.

### 2.2. Instrumentation

The SEM-EDS analyses were carried out using a EVO®40 Scanning Electron Microscope (Carl Zeiss NTS GmbH, Germany) coupled to an X-Max energy-dispersive X-ray spectrometer (Oxford Instruments,

Abingdon, Oxfordshire, United Kingdom) for electron image acquisitions and elemental analysis (punctual and imaging). Although gypsum alone is not conductive, it was possible to obtain optimal results without carbon or gold coating. The SEM images were obtained at high vacuum employing an acceleration voltage of 30 kV and a 10–400  $\mu\text{m}$  working distance. Different magnifications (reaching up to  $\times 6800$ ) were used for secondary electron images and an integration time of 50 s was employed to improve the signal-to-noise ratio. The EDS spectra were acquired and treated using the INCA software. Furthermore, a mapping of specific microscopic areas in the samples was possible, allowing the evaluation of the distribution of these elements over the sample.

ATR-FTIR spectra were recorded using a Bruker Equinox 55 spectrometer equipped with an extended KBr Beamsplitter and purged with dried air. A liquid nitrogen-cooled MCT detector or a Peltier-cooled DTGS Mid-IR detector was used. Two hundred scans were accumulated between 4000 and 600  $\text{cm}^{-1}$  with a 4  $\text{cm}^{-1}$  resolution with the help of an extended KBr Beamsplitter. A background was collected before each sample's spectra and additional atmospheric compensation was provided by Opus 6.5 Software. Few milligrams of sample powder are required for each measurement using an ATR diamond crystal accessory (Golden Gate®, Specac) which no require any additional sample preparation constraints. The obtained spectra were compared with the spectra of pure standard compounds contained in RRUFF [35] and in the e-VISART infrared databases [36].

The XRD analyses were performed with a PANalytical Xpert PRO powder diffractometer, equipped with a copper tube ( $\lambda_{\text{CuK}\alpha 1} = 1.54060 \text{ \AA}$ ,  $\lambda_{\text{CuK}\alpha 2} = 1.54439 \text{ \AA}$ ), vertical goniometer (Bragg-Brentano geometry), programmable divergence aperture, automatic interchange of samples and secondary monochromator from graphite and PixCel detector. The measurement conditions were 40 kV and 40 mA, with an angular range ( $2\theta$ ) scanned from 5 to 70°. The X'pert HighScore (PANalytical) software in combination with the specific powder diffraction file database (International Centre for Diffraction Data-ICDD, Pennsylvania, USA) was used for the phase identification.

For micro-Raman spectra and Raman Imaging, a Senterra spectrometer (Bruker Optics, Karlsruhe, Germany) equipped with a Peltier-cooled charge-coupled device detector and  $\times 10$  and  $\times 50$  long working distance Olympus objectives was used to collect the Raman spectra excited under a 785 nm light from a diode laser. The Raman image acquisitions of specific areas of the plaster matrix were conducted using the Peak Pick Singular option. The interpretation of all the Raman results was performed by comparing the acquired Raman spectra with the Raman spectra of pure standard compounds collected in the e-VISNICH dispersive Raman database [37]. Additionally, free Raman databases (e.g. RRUFF [35]) were also considered for the assignation of unknown Raman bands. Different spectral analysis tools, OPUS® 7.0 (Bruker Optik GmbH, Ettlingen, Germany (2011)) for Raman Imaging; and Omnic 7.2 (Nicolet) and Wire 2.0 (Renishaw) for spectral treatment and assignation, were used.

Thermodynamic chemical modeling was also performed to explain the formation of specific decaying compounds, considering the composition of the plaster and the input of ions infiltrated in the material. For that purpose the MEDUSA [38] free academic program was used. This program implements its own Hydrochemical Equilibrium-Constant (HYDRA) database. This database was extended manually introducing the logarithm of the formation constant of specific mineralogical phases of interest [39]. Certain constants were obtained also from the Visual MINTEQ [40] database.

## 3. Results and discussion

### 3.1. Point-by-point Raman spectroscopy analyses

In the Raman spectra acquired on the gypsum plaster samples, different kind of sulfates and nitrates bands were distinguished. Most of the bands are centered between 960–1080  $\text{cm}^{-1}$  as in Fig. 1 is illustrated.

**Table 1**  
Mineral phases identified in plaster.

Mineral phase	Chemical formula	Reference
Bassanite	$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	[21]
Anhydrite, types I, II and III	$\text{CaSO}_4$	[1,23]
Glauberite	$\text{CaNa}_2(\text{SO}_4)_2$	[24,25]
Thenardite	$\text{Na}_2\text{SO}_4$	[26,27]
Mirabilite	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	[28]
Metastable mirabilite	$\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$	
Mascagnite	$(\text{NH}_4)_2\text{SO}_4$	[21]
Epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	[29]
(para) Coquimbite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	[27]
Syngenite	$\text{K}_2\text{Ca}(\text{SO}_4) \cdot \text{H}_2\text{O}$	[29]
Starkeyite	$\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$	[21]
Hexahydrate	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	[30]
Eugsterite	$\text{Na}_4\text{Ca}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$	[30]
Darapskite	$\text{Na}_3(\text{SO}_4)(\text{NO}_3) \cdot \text{H}_2\text{O}$	[31]
Polyhalite	$\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$	[32]

This underlines the simultaneous presence of several sulfates such as syngenite ( $\text{K}_2\text{Ca}(\text{SO}_4) \cdot \text{H}_2\text{O}$ , Raman band at  $981 \text{ cm}^{-1}$ ), thenardite ( $\text{Na}_2\text{SO}_4$ , Raman band at  $989 \text{ cm}^{-1}$ ), starkeyite ( $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ , Raman band at  $1001 \text{ cm}^{-1}$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , Raman band  $1008 \text{ cm}^{-1}$ ). In the same micronic spot (under  $\times 100$  objective) nitrates such as niter ( $\text{KNO}_3$ , Raman band at  $1048 \text{ cm}^{-1}$ ) and nitratine ( $\text{NaNO}_3$ , Raman band at  $1067 \text{ cm}^{-1}$ ) were also identified (see Fig. 1). Other compounds identified through Raman analyses include sulfates such as epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), hexahydrate ( $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ), mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), bassanite or gypsum hemihydrate ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) and anhydrite ( $\text{CaSO}_4$ ).

### 3.2. X-ray diffraction and point-by-point Raman spectroscopy revision

To corroborate the Raman spectra assignment, X-ray powder diffraction (XRD) analyses were conducted on the collected samples. The acquired XRD spectra revealed the presence of different compounds, namely, quartz ( $\text{SiO}_2$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), bassanite ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ), polyhalite ( $\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ ), glauberite ( $\text{CaNa}_2(\text{SO}_4)_2$ ), syngenite ( $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ) and humberstonite ( $\text{K}_3\text{Na}_7\text{Mg}_2(\text{SO}_4)_6(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) (see Fig. 2). Considering that XRD hardly detect compounds which are below 5% in the sample and/or are amorphous [41], it is possible to say that the nitrates, sulfates and nitrate-sulfate salts detected are not in trace levels in the analyzed samples and these global analyses by XRD will take a general consideration of all phases.

Taking into account these XRD results, the acquired Raman spectra were re-examined searching the possible presence of overlapped Raman signals. For example, in Fig. 1, the signals at  $981$  and  $1006$  (shoulder in  $1000 \text{ cm}^{-1}$  region)  $\text{cm}^{-1}$  correspond to syngenite stretching mode; the bands at  $989$  and  $1016$  (shoulder in  $1000 \text{ cm}^{-1}$  region)  $\text{cm}^{-1}$  correspond to those of polyhalite; and the  $1008 \text{ cm}^{-1}$  peak to the main band of gypsum. Finally, the bands at  $1013$  (shoulder in  $1000 \text{ cm}^{-1}$  region),  $1048$  and  $1067 \text{ cm}^{-1}$  are clearly related with the stretching modes of humberstonite. Analyzing the whole spectrum shown in Fig. 1, secondary bands of those mineral phases can be ascertained. For example, peaks at  $183$ ,  $632$  and  $723 \text{ cm}^{-1}$  belong to humberstonite; those at  $414$ ,  $492$ ,  $669$  and  $1134 \text{ cm}^{-1}$  belong to gypsum; and two weak bands at  $436$  and  $652 \text{ cm}^{-1}$  belong to polyhalite. Additionally, bands at  $453$ ,  $469$ ,  $485$ ,  $618$ ,  $634$ ,  $1155$ ,  $1169 \text{ cm}^{-1}$  belong to glauberite; and those at  $441$ ,  $492$ ,  $642$ ,  $1139 \text{ cm}^{-1}$  belong to syngenite.

### 3.3. ATR-FTIR analyses

In order to search some complementary structural specificities of compounds, (i.e. the OH modes, or possibly less crystallized phases) gypsum plaster samples using ATR-FTIR were also analyzed. As an example, in Fig. 3 (top left) a representative ATR-FTIR spectrum obtained from the gypsum plaster, showing very complex and broad IR bands can be observed. In order to resolve (separate) the overlapped IR bands and

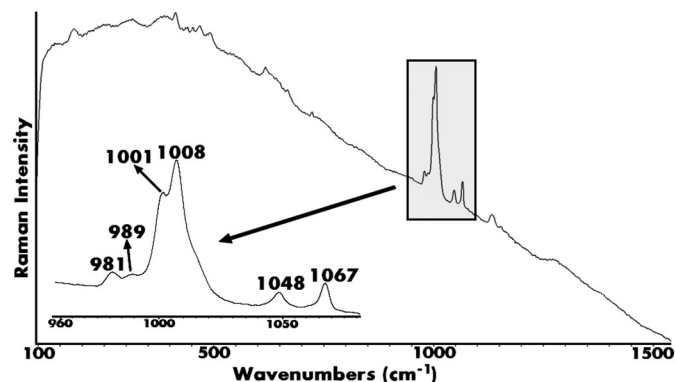


Fig. 1. Raman spectrum showing bands of compounds present in the gypsum-based plaster.

taking into consideration the hypothesis of the similarities between the bandwidths for all compounds, a curve-fitting process based on Gaussian and Laurentian algorithms was applied using Grams 32 software (Galactica, Thermo, US) on three different regions which are common for all the collected IR spectra (Fig. 3). With this spectral-treatment, it was possible to separate gypsum, bassanite, anhydrite, humberstonite, syngenite, polyhalite and glauberite IR bands. Therefore, the IR observations provide us complementary information about the hydration (OH modes) of different compounds because of the specific sensitivity of this technique to some structural features. Concretely, the IR bands between  $3650$  and  $3200 \text{ cm}^{-1}$  belong to OH stretching mode of crystalline water molecules of the hydrated compounds present in the samples. The band at  $3602 \text{ cm}^{-1}$  is related with bassanite. The ones at  $3532$  and  $3403 \text{ cm}^{-1}$  are related with the presence of gypsum, while the peak at  $3474 \text{ cm}^{-1}$  belongs to polyhalite [35]. The peaks at  $3334$  and  $3248 \text{ cm}^{-1}$  can be assigned to the presence of syngenite [35].

In an intermediate range, some bands are observable, like those at  $1620$  and  $1683 \text{ cm}^{-1}$ , related to the sulfate stretching mode of gypsum no water bending contribute to  $1620$ – $1660 \text{ cm}^{-1}$  range, while the band at  $1401 \text{ cm}^{-1}$  could not be assigned to specific compound present in plaster matrix.

In the  $1180$ – $940 \text{ cm}^{-1}$  range, after curve-fitting procedure different bands were identified. All the bands assigned in this area belong to the main bands of anhydrite ( $1095 \text{ cm}^{-1}$ ), gypsum ( $1105 \text{ cm}^{-1}$ ), glauberite ( $1083 \text{ cm}^{-1}$ ), polyhalite ( $1073 \text{ cm}^{-1}$ ) and humberstonite ( $1052 \text{ cm}^{-1}$ ) [35,42]. Apart of those IR signals, the band at  $1005 \text{ cm}^{-1}$  is related with the main band of syngenite, together with their secondary stretching bands at  $1125$  and  $1111 \text{ cm}^{-1}$ . The band at  $1135 \text{ cm}^{-1}$  could be related with both a secondary band of syngenite or polyhalite. The band at  $986 \text{ cm}^{-1}$  could belong to a secondary band of polyhalite or syngenite. Moreover, the bands at  $1033$ ,  $1022$  and  $964$  were also observed but could not be assigned with those compounds.

Finally, in the third region, from  $730$ – $605 \text{ cm}^{-1}$ , IR bands related with syngenite ( $675$  and  $645 \text{ cm}^{-1}$ ), polyhalite ( $656$ ,  $620$  and  $600 \text{ cm}^{-1}$ ), glauberite ( $630$  and  $605 \text{ cm}^{-1}$ ) and gypsum ( $668 \text{ cm}^{-1}$ ) were identified. Apart from this, two additional bands at  $711$  and  $699 \text{ cm}^{-1}$  were also observed, but it could not be assigned and related with the present compounds, which could be related with secondary bands of some nitrates.

This uncertainty was observed in practically all of the ATR-FTIR spectra collected from the samples, making difficult the unequivocal assignment of all the IR features to given compounds, especially in the case of compounds containing the nitrate anion.

### 3.4. Imaging by SEM-EDS and Raman spectroscopy

The molecular results described in the previous sections were confirmed using SEM-EDS (elemental analysis). Concretely, SEM-EDS imaging was applied in order to see the distribution of all the elements representative of each molecular phase identified using Raman, XRD and ATR-FTIR. In this way, in Fig. 4, the distribution of K, O, S, Mg, Ca, Si, Na and Cl in a microscopic area (around  $70 \mu\text{m}$ ) of the plaster can be observed. Analyzing the elemental mappings, halite, quartz, syngenite and polyhalite can be distinguished. Therefore, with the elemental analyses, the presence of NaCl was verified (NaCl doesn't have Raman signature nor observable IR signal in the studied range due to its very ionic character). This example corroborates the good strategy using several techniques in order to obtain the most complete characterization.

As it is going to describe in the following section, NaCl input coming from marine aerosol plays an important role in the formation of most of the new mineral phases. As can be observed in Fig. 5, apart from halite, quartz, syngenite and polyhalite, glauberite distribution was also observed using SEM-EDS imaging. Additionally, in Figs. 4 and 5, SEM-EDS imaging showed the distribution of Ca, S and O related with the gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and also the distribution of Na, S and O was

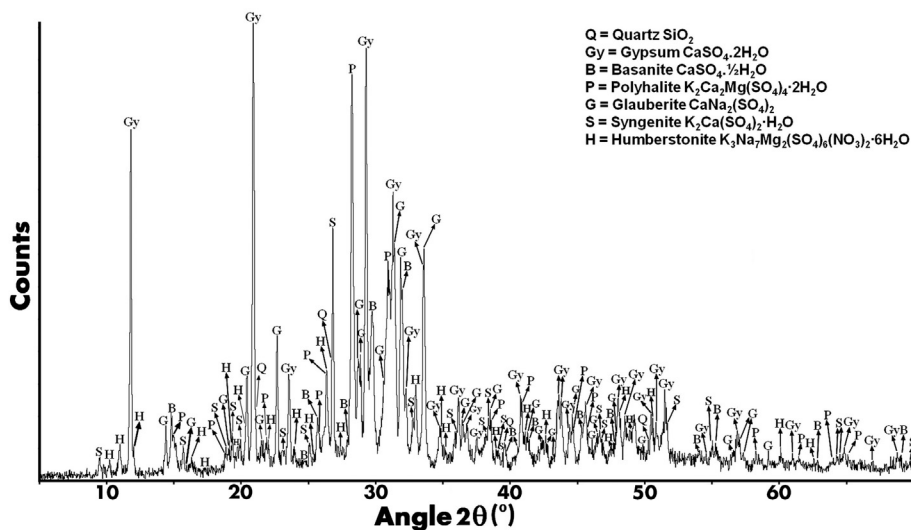


Fig. 2. Representative XRD spectrum of gypsum-based plaster showing the different bands of quartz, gypsum, bassanite, polyhalite, glauberite, syngenite and humberstonite.

clearly observable in certain areas, suggesting the presence of thenardite or mirabilite ( $\text{NaSO}_4\text{--NaSO}_4 \cdot 10\text{H}_2\text{O}$  system). This sodium sulfate system can also have an important influence in the decaying pathways affecting the matrix.

To confirm that the identified molecular phases are not crystallized in a punctual way, Raman imaging analysis were performed. As can be observed in Fig. 6, the presence of glauberite ( $\text{CaNa}_2(\text{SO}_4)_2$ ) with its main Raman band at  $1001\text{ cm}^{-1}$  (see Fig. 6A), polyhalite ( $\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ ) with its main Raman bands at  $1016$  and  $989\text{ cm}^{-1}$  (see Fig. 6B), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) with its main Raman band at  $1008\text{ cm}^{-1}$  (see Fig. 6C), humberstonite ( $\text{K}_3\text{Na}_7\text{Mg}_2(\text{SO}_4)_6(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) with its main Raman bands at  $1013$ ,  $1048$  and  $1067\text{ cm}^{-1}$  (see Fig. 6D) and syngenite ( $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ) with its main Raman bands at  $981$  and  $1006\text{ cm}^{-1}$  (see Fig. 6E) were identified. Although the presence of anhydrite ( $\text{CaSO}_4$ ) is clear, its Raman mapping was not added because it was difficult to mark exactly the peak at  $1016\text{ cm}^{-1}$ . From the images, the heterogeneity and the wide presence of these compounds in the gypsum plaster must be concluded.

Table 2 summarizes all the compounds detected by the five analytical techniques used to characterize the samples. The whole set of analyses conducted by ATR-FTIR, Raman spectroscopy and XRD revealed a complex system of decay compounds. The combined use of XRD data with the Raman spectroscopy information has demonstrated to be an adequate analytical methodology to avoid inaccurate assignments and to detect all the compounds present in different proportions within the samples. The information given by ATR-FTIR itself is not enough to identify the different phases, due to the broad width of IR bands. Finally the use of SEM-EDS and Raman Imaging, complement the analytical information of the decay compounds present in plaster.

### 3.5. Decay pathways and mechanisms

As seen in Table 2, a wide variety of decaying compounds were detected, containing ions like  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{NO}_3^-$ , apart from the  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  coming from the plaster matrix. According to the previous studies performed in the Igueldo Lighthouse [20,21], the deposition

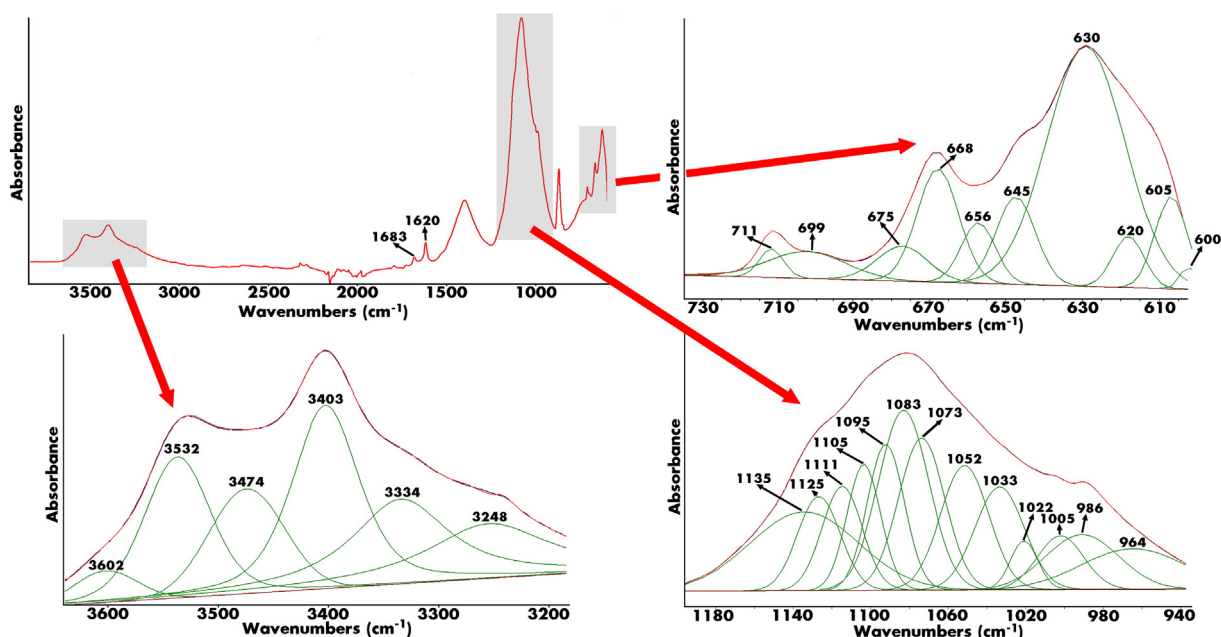


Fig. 3. ATR-FTIR spectrum of a plaster sample with some enlargement and band decomposition of three informative spectral ranges.

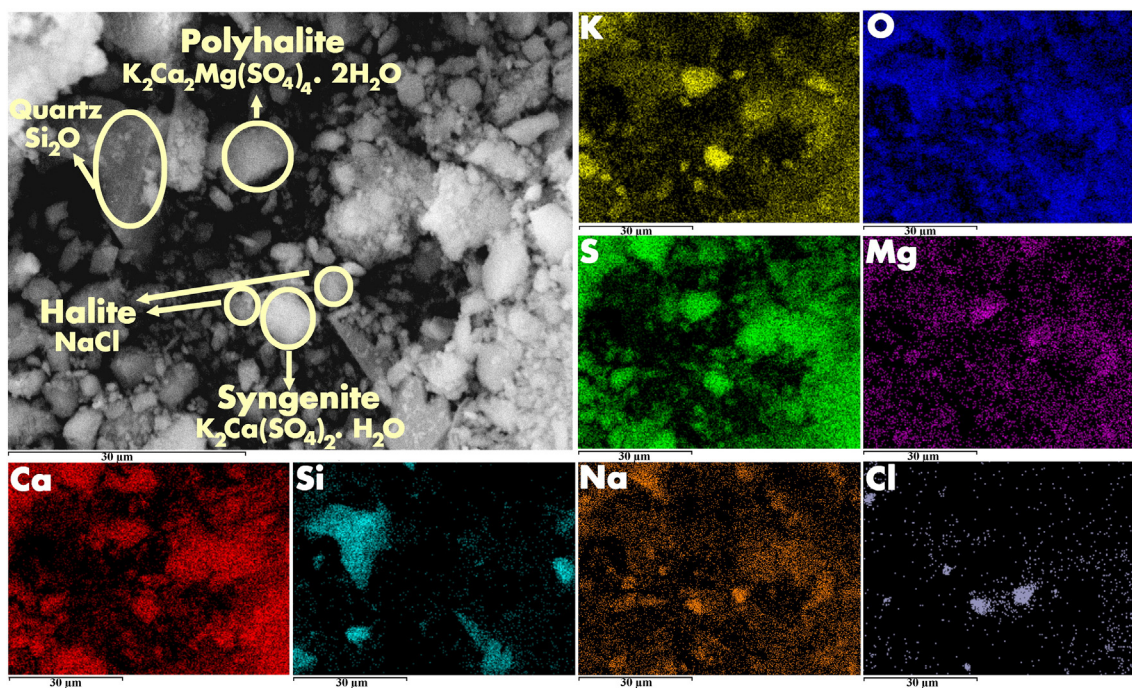


Fig. 4. SEM-EDS imaging showing the presence and distribution of halite, quartz, syngenite and polyhalite.

of high quantities of seagull drops were observed daily in the roof of the building. These drops are the responsible of the nitrate input in the building. Concretely, the ammonium is transformed into nitrates following a processes catalyzed by bacteria [20]. The non-transformed ammonium nitrate migrates downstream (to the walls of the inner rooms of the lighthouse) and it can react with the calcite based plaster, material also used in the Lighthouse construction. The acid ammonium ions react with the basic carbonate leading to the formation of niter ( $\text{KNO}_3$ ) and nitratine ( $\text{NaNO}_3$ ) [21].

The presence of the three  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NO}_3^-$  ions seems to be related to the impact of marine aerosols that enters to the inner parts of the building through capillarity diffusion in the not well sealed walls of the lighthouse. The marine aerosol usually carries different inorganic compounds inside and/or dissolved ions like chlorides such as  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$  [43]; nitrates such as  $\text{NaNO}_3$  [44],  $\text{Ca}(\text{NO}_3)_2$  [45],  $\text{NH}_4\text{NO}_3$  and  $\text{KNO}_3$  [46]; sulfates such as  $\text{Na}_2\text{SO}_4$  [48],  $\text{MgSO}_4$  [49],  $(\text{NH}_4)_2\text{SO}_4$  [50] and even mixed-cation with  $\text{Na}$ ,  $\text{Mg}$ ,  $\text{K}$  and  $\text{Ca}$  sulfates [51].

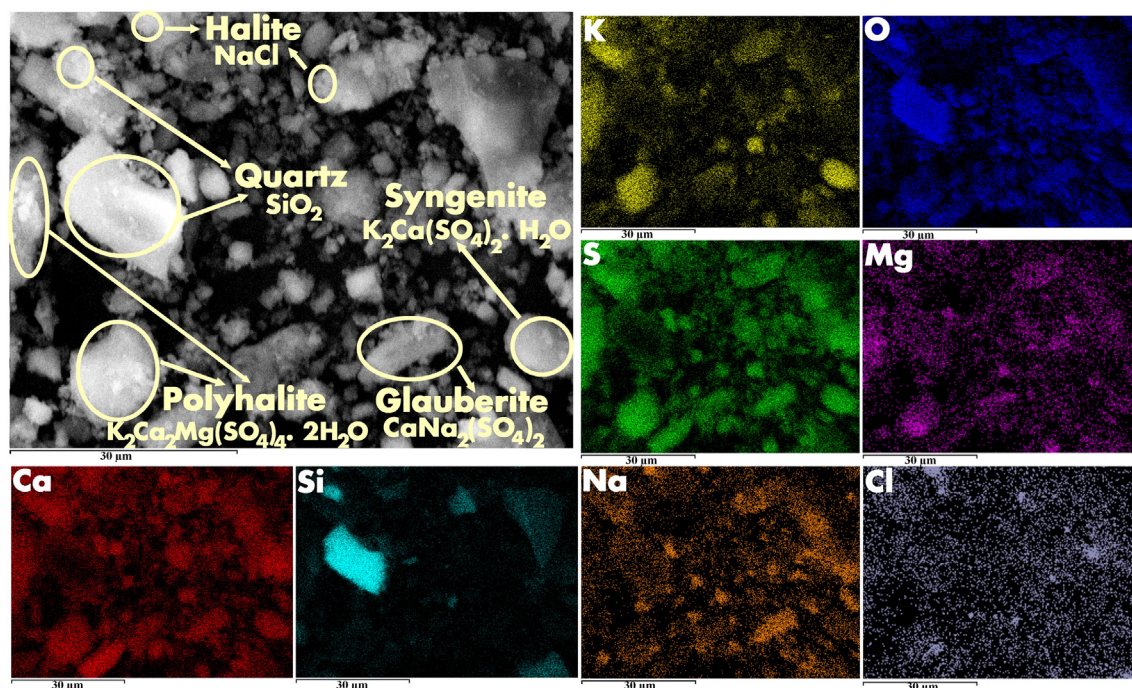
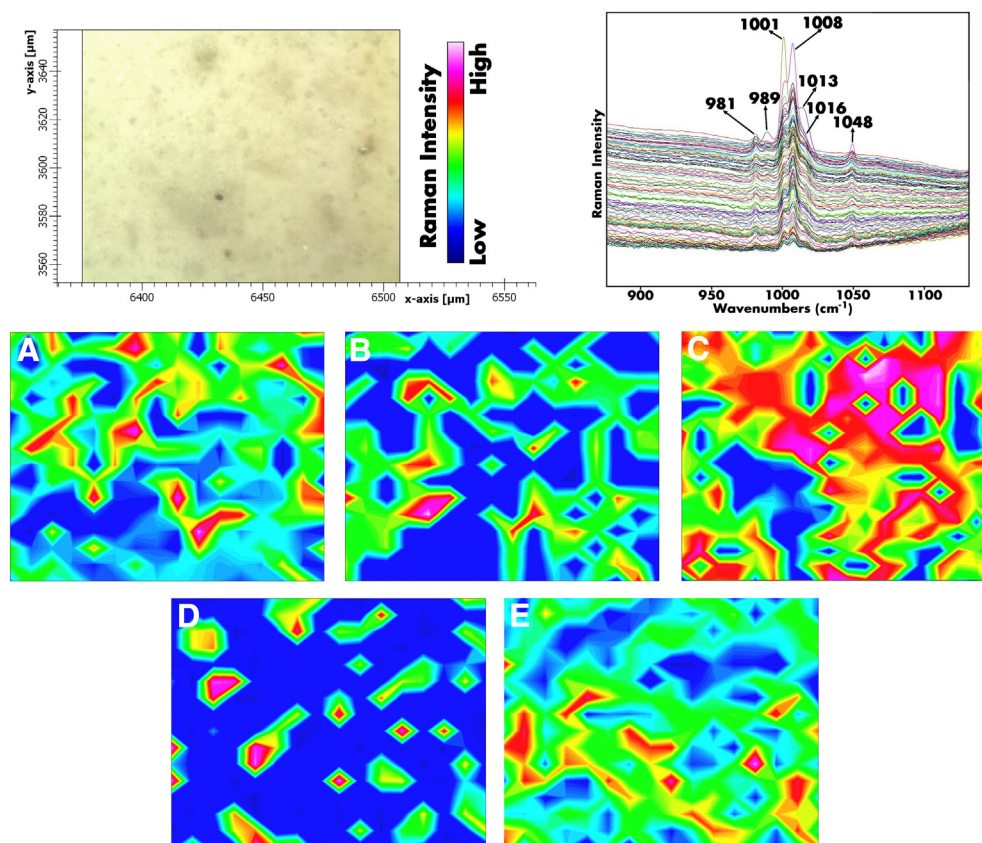


Fig. 5. SEM-EDS imaging showing the presence and distribution of halite, quartz, syngenite, polyhalite and glauberite.

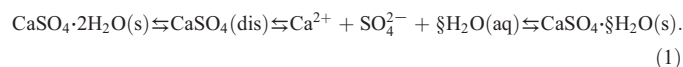


**Fig. 6.** Raman imaging of a plaster sample showing the distribution of (A) glauberite (represented according to the 1001  $\text{cm}^{-1}$  band), (B) polyhalite (represented according to the 989  $\text{cm}^{-1}$  band), (C) gypsum (represented according to the 1008  $\text{cm}^{-1}$  band), (D) humberstonite (represented according to the 1048  $\text{cm}^{-1}$  band) and (E) syngenite (represented according to the 981  $\text{cm}^{-1}$  band). The top left image shows the mapped area.

Moreover, as it has been described in the sampling section, plaster samples have been taken in a room where the average temperature depending on the season ranges between 27 and 35 °C. In this room all the machine system required for the proper functioning of the lighthouse is present. The complex systems of reactions that explain the decaying pathways occurring in the gypsum plaster of the inner areas of the Igueldo Lighthouse is summarized in Fig. 7 and are explained below.

The first decaying step starts with the partial dissolution of gypsum when the water from outside enter the inside walls reaching to the gypsum based plasters. Gypsum is not an insoluble compounds,

having an intrinsic solubility due to the presence of the dissolved  $\text{CaSO}_4(\text{dis})$  complex of the same stoichiometry than the solid phase. Then, this soluble complex  $[\text{CaSO}_4(\text{dis})]$  dissociates in free calcium ( $\text{Ca}^{2+}$ ) and sulfate ( $\text{SO}_4^{2-}$ ) ions if the water content in the porous material is enough. When this water starts evaporating, the saturation condition of bassanite ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) is reached and this compound is precipitated. The whole set of interactions is summarized in Reaction 1:



**Table 2**

Mineral phases identified in this work on/into the plaster matrix.

Mineral phase	Chemical formula	Raman	XRD	ATR-FTIR	SEM-EDS	Raman imaging
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	X	X	X		X
Bassanite	$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	X	X	X		X
Anhydrite, types I,II, III	$\text{CaSO}_4$	X		X		
Nitratine	$\text{NaNO}_3$	X				
Niter	$\text{KNO}_3$	X				
Thenardite	$\text{Na}_2\text{SO}_4$	X			X	
Mirabilite	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	X			X	
Mascagnite	$(\text{NH}_4)_2\text{SO}_4$	X				
Starkeyite	$\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$	X				
Hexahydrate	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	X				
Epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	X				
Halite	$\text{NaCl}$		X		X	
Quartz	$\text{SiO}_2$	X	X		X	
Glauberite	$\text{CaNa}_2(\text{SO}_4)_2$	X	X	X	X	X
Polyhalite	$\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$	X	X	X	X	X
Syngenite	$\text{K}_2\text{Ca}(\text{SO}_4) \cdot \text{H}_2\text{O}$	X	X	X	X	X
Humberstonite	$\text{K}_3\text{Na}_7\text{Mg}_2(\text{SO}_4)_6(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	X	X	X		X
Total identified		16	8	7	7	6

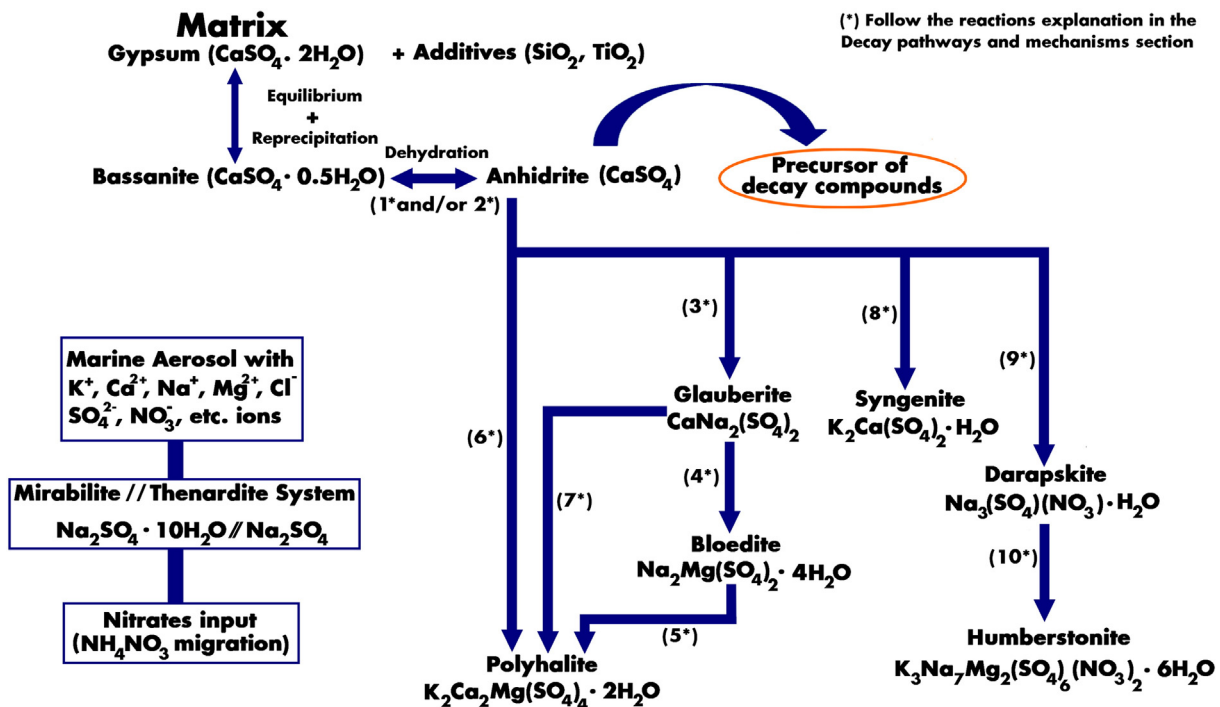
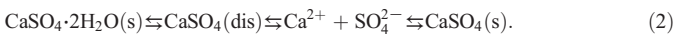


Fig. 7. Decay pathway reactions diagram, showing the reactions which lead to the formation of glauberite, bloedite, polyhalite, syngenite, darapskite and humberstonite.

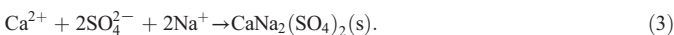
When the temperature rises to the maximum (or simply with time), that water is completely evaporated and thus, anhydrite ( $\text{CaSO}_4$ ) could be formed instead of bassanite, following Reaction 2:



As it was shown in a previous work, compounds such as thenardite ( $\text{Na}_2\text{SO}_4$ ) and mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) can be present in high quantities around this gypsum-based matrix if it suffers the impact of the marine aerosol [21]. Also the formation of other simple sulfates, like mascagnite ( $(\text{NH}_4)_2\text{SO}_4$ ), epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) and starkeyite ( $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ ), was explained [21]. However, in the present work we have identified a greater amount of mixed sulfates and their formation requires ascertaining the chemical reactions involved.

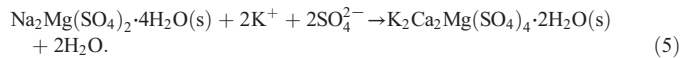
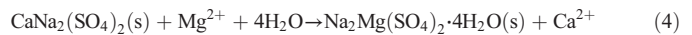
Some works in the literature mentioned that the precursor of many decay compounds, with large quantity of dissolved sulfates, is the anhydrite ( $\text{CaSO}_4$ ) [52]. From anhydrite it is possible to find other compounds like glauberite ( $\text{CaNa}_2(\text{SO}_4)_2$ ) [53]. There are studies about the influence of saline environment in the formation of glauberite [54] or the possibility to obtain glauberite in a system with anhydrite, thenardite and water at 25 °C [55]. However, the formation of a solid phase directly from another solid phase is not always a thermodynamic favored process.

In our case, the three forms of solid calcium sulfate (gypsum, bassanite and anhydrite), when enter in contact with water, dissolve partially due to the presence of the soluble  $\text{CaSO}_4(\text{dis})$  complex species, that dissociates to free calcium ( $\text{Ca}^{2+}$ ) and sulfate ( $\text{SO}_4^{2-}$ ) ions. If that water contains  $\text{Na}^+$  from the marine aerosol, Reaction 3 is thermodynamically favored, leading to the formation of glauberite:

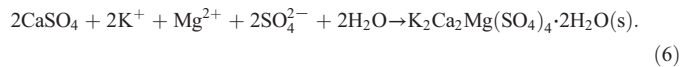


Glauberite has been proposed [56] as the precursor of the formation of other mixed sulfate compounds like polyhalite ( $\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ ),

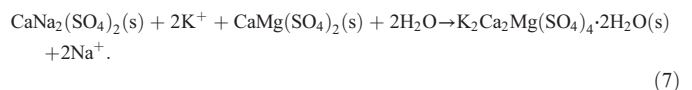
that can also be formed through another intermediate compound such as bloedite ( $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ) (Reactions 4 and 5):



In this point, it is necessary to highlight that in the measurements performed in the gypsum plaster, it was not possible to find bloedite, but its presence should not be discarded. However, Reactions 4 and 5 starts from a solid phase, ending in another solid phase, a process that could not be completed due to passivation side-reactions. To overcome this problem, there are authors that suggest the direct formation of polyhalite from anhydrite impacted by a constant source of  $\text{K}^+$  and  $\text{Mg}^{2+}$  coming from marine aerosol, in form of  $\text{MgSO}_4$  and  $\text{K}_2\text{SO}_4$ , under less than 30 °C temperature conditions [57] (Reaction 6):



Apart from this, there is another work that mentions the possibility to obtain polyhalite from glauberite [58] but the reaction starts from two solid phases (Reaction 7):



However, polyhalite can be formed from the dissolved calcium ( $\text{Ca}^{2+}$ ) and sulfate ( $\text{SO}_4^{2-}$ ) ions (dissociated from the soluble  $\text{CaSO}_4(\text{dis})$  complex) that enter in contact with dissolved  $\text{K}^+$  and  $\text{Mg}^{2+}$  from the marine aerosol, following a similar reaction like 6. Even the formation of bloedite can be explained by the interaction (direct reaction) of  $\text{SO}_4^{2-}$  with  $\text{Na}^+$  (from  $\text{NaCl}$ ) and  $\text{Mg}^{2+}$  (from  $\text{MgCl}_2$  or  $\text{MgSO}_4$  or both) also from the marine aerosol.

The formation of syngenite ( $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ) can be explained by the interaction of  $\text{K}^+$  from the marine aerosol with the dissolved



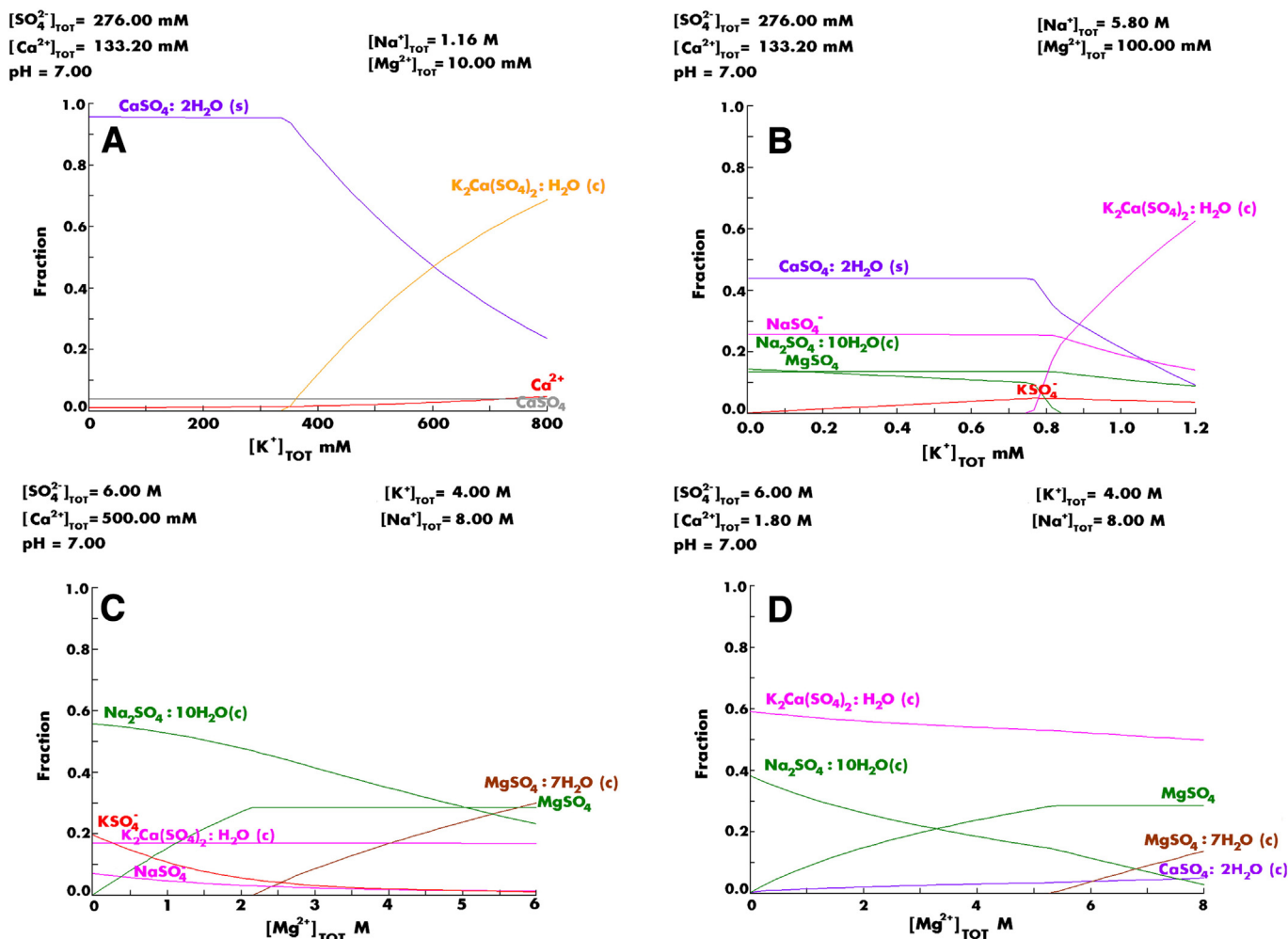
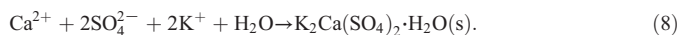


Fig. 8. Mole fraction diagrams showing the formation of syngenite and additional mineral phases in the gypsum-based plaster at high concentrations of sulfates and lower (A) or higher concentrations (B) of  $\text{Na}^+$  and  $\text{Mg}^{2+}$  respectively. The (C) and (D) diagrams cover low concentrations of sulfates at higher or lower concentrations of  $\text{Ca}^{2+}$  respectively.

calcium ( $\text{Ca}^{2+}$ ) and sulfate ( $\text{SO}_4^{2-}$ ) ions (dissociated from the soluble  $\text{CaSO}_{4(\text{dis})}$  complex) from anhydrite, bassanite or gypsum (Reaction 8):



In this case the role of dissolved  $\text{K}^+$  coming from marine aerosol has high importance as it has been highlighted in other works [53,59,60]. Although the formation of polyhalite from syngenite is also possible at temperatures between 230 and 280 °C [61], this must be discarded because that temperature range cannot be reached in the inner rooms of the lighthouse.

In order to understand better the chemical reactions leading to the formation of syngenite in the gypsum-based plaster, thermodynamic chemical modeling was used (see Fig. 8). The possibility of formation of new sulfate in the plaster was searched through theoretical calculations using the MEDUSA software. To perform the chemical modelling several concentrations of the different components (ions) must be tested to see if the new solid phases are formed, or not. In a previous work [21], the soluble anions and cations were quantified in this gypsum plaster. According to those results, the  $\text{Mg}^{2+}$  and  $\text{Na}^+$  concentrations were higher in this gypsum plaster than in the rest of the building materials analyzed. Considering this variability in the concentration range of the ions, two thermodynamic simulations were performed. One of them included the lower concentrations of both  $\text{Na}^+$  and  $\text{Mg}^{2+}$  (1.16 M for  $\text{Na}^+$  and 10 mM for  $\text{Mg}^{2+}$ ) and the other simulation increased the

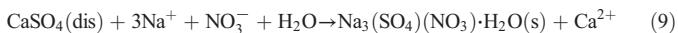
concentration of both cations (5.80 M for  $\text{Na}^+$  and 100 mM for  $\text{Mg}^{2+}$ ) till a situation reached when evaporation is important.

The thermodynamic simulation shown, at low concentration of both ions, the formation of syngenite ( $\text{KCa}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ) as the first mineralogical phase (see Fig. 8A). Note that the concentration of  $\text{K}^+$  in this simulation ranges between 0 and 1.2 mM, because the experimental concentration of  $\text{K}^+$  in the gypsum plaster was shown to be always lower than the  $\text{Na}^+$  and  $\text{Mg}^{2+}$  ones [21]. As can be observed in Fig. 8B, at higher concentrations of  $\text{Na}^+$  (5.80 M), mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) is the next phase to be formed. Taking into consideration the concentration of soluble  $\text{Na}^+$  identified in the gypsum plasters [21], the  $\text{Na}^+$  concentration in this last simulation can be considered reasonable. According to the spectroscopic results, sodium sulfate was identified in many measurements performed on the gypsum plaster, but also in additional measurements performed in other building materials from the inner rooms of the Lighthouse [21]. It is necessary to remark that the anhydrous phase (thenardite,  $\text{Na}_2\text{SO}_4$ ) was detected instead of mirabilite, as seen from laboratory Raman spectroscopy analyses. Considering the short range of temperature to transform one sodium sulfate form in the other, the dehydration process of the original mirabilite should be considered during the transport and storage of the samples. In the simulations presented in Fig. 8A and B, it can be observed that gypsum disappears, while both new sulfate phases are formed. Maybe for this reason, in some Raman spectra any gypsum traces were detected together with syngenite and thenardite.

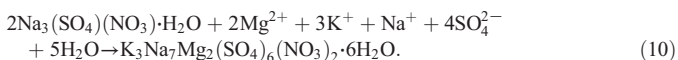
Considering that sulfate ions are consumed when the new sulfate phases are formed, an additional situation in which the concentration of sulfate ions is not so high was necessary to be taken into account. The competition among phases can be seen in Fig. 8C when the relative magnesium ( $\text{Mg}^{2+}$  input can come from marine aerosol) concentration increases. When the concentration of  $\text{Mg}^{2+}$  reaches to a certain level, the presence of mirabilite starts decreasing while epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) is formed, being syngenite nearly constant.

When we considered the same situation (lower concentrations of sulfate ions), but at lower concentrations of  $\text{Ca}^{2+}$ , a similar tendency was observed, but in this case epsomite together with gypsum are formed (see Fig. 8D). In our previous analysis performed on the plaster from the Igueldo lighthouse [21], the simultaneous presence of epsomite and gypsum was always detected in the Raman spectra. This thermodynamic simulation means that it is possible to observe the formation of epsomite in the gypsum plaster of Igueldo Lighthouse at relative high concentrations of  $\text{Mg}^{2+}$  and lower concentrations of dissolved  $\text{SO}_4^{2-}$  in the plaster. In this way, the magnesium coming from marine aerosol in form of sulfates or chlorides seems to have also an important role in the chemical decaying of the system.

Finally for the formation of the most complex mixed compound identified in this work, humberstonite ( $\text{K}_3\text{Na}_7\text{Mg}_2(\text{SO}_4)_6(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), it seems to require firstly the formation of darapskite ( $\text{Na}_3(\text{SO}_4)(\text{NO}_3) \cdot \text{H}_2\text{O}$ ) [52,62], by the input of dissolved  $\text{Na}^+$  coming from marine aerosol and the input of nitrates from other sources, (seagull dropping and/or marine aerosol), as suggested elsewhere [20] on the dissolved  $\text{CaSO}_4(\text{dis})$  complex species (Reaction 9):



After the formation of darapskite, this compound can be transformed, by the input of dissolved  $\text{K}^+$  and  $\text{Mg}^{2+}$  from the marine environment, to humberstonite following Reaction 10:



Other authors suggest the formation of humberstonite by repeated natural leaching of nitrates over sulfate bearing materials [42,52,63], as well as the consequence of the reaction between dissolved sulfates coming from the plaster and sodium nitrate coming from the marine aerosol [9].

#### 4. Conclusions

The principal source of deterioration affecting gypsum-based plasters of the interior areas of Igueldo Lighthouse is the marine aerosol (and rain charged with seawaters) which enters to the inner parts of the walls through cracks and pores from the outside walls of the building. The reaction of the different ions of the marine aerosol with the dissolved calcium and sulfate ions present in the matrix leads to the formation of a wide variety of compounds, most of them well crystallized as revealed the XRD analyses.

The analytical methodology, combining XRD, SEM-EDS, ATR-FTIR and micro Raman spectroscopy (point-by-point and imaging), was required to identify the presence of the whole set of compounds summarized in Table 2. The combined use of Raman and XRD measurements identified most of the new complex compounds. Chloride salts were also identified by using XRD and SEM-EDX measurements on the samples from gypsum plasters, suggesting that the input of sodium and magnesium, also present in the new crystals, can come from the chlorides transported by the marine aerosol (e.g.  $\text{NaCl}$ ,  $\text{MgCl}_2$ ,  $\text{KCl}$ ) [8].

Regarding the new salts crystallized in the plaster, it has been possible to assign the main Raman bands of the double sulfate–nitrate salt humberstonite ( $\text{K}_3\text{Na}_7\text{Mg}_2(\text{SO}_4)_6(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ). X-ray diffraction (XRD) and attenuated total reflectance infrared (ATR-FTIR) analyses confirmed the presence of humberstonite. Apart from this salt,

glauberite ( $\text{CaNa}_2(\text{SO}_4)_2$ ), syngenite ( $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ) and polyhalite ( $\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ ) were also identified by means of Raman spectroscopy. The presence of these salts was corroborated by means of XRD and ATR-FTIR. For instance, the efficiency of Raman scattering arises from the big intensity of the symmetric stretching mode of well defined molecular ions such as  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , etc., whatever the orientation of the analyzed crystal. Efflorescence salts usually form well defined crystals with anisotropic shape and thus bending mode intensity occurring in the  $300\text{--}700\text{ cm}^{-1}$  range is very dependent of the analyzed spot. Furthermore bending modes have E or F character that implies many modes at very close wavenumbers. This implies overlapping of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  bending modes and their identification/use requires chemometric techniques. For all these reason the symmetric stretching bands are the most useful for phase identification if the instrument resolution is sufficient to separate the different peaks. The vibrational infrared spectra counterpart arises from the asymmetric stretching modes with generally F character, i.e. three bands. Thus the overlapping is important and phase identification is difficult.

Therefore, the combined use in these X-ray based and vibrational spectroscopic techniques was proven to be an adequate analytical methodology to avoid inaccurate assignments that can be done only using only one spectroscopic technique. Moreover, the use of the images from SEM-EDS and Raman allowed us to confirm the complex distribution of the new salts in the whole matrix.

Considering all the new mineral phases identified, a complete decaying pathway diagram, containing several reactions, was proposed. In this diagram, gypsum, bassanite and anhydrite are the precursors of the new crystalline phases, through its partial dissolution as the  $\text{CaSO}_4(\text{dis})$  complex species. The different calcium sulfates, in continuous contact with the marine environment and other surrounding sources of chemicals, like  $\text{NH}_4\text{NO}_3$ , experiment different reactions giving rise to new sulfates and double sulfate/nitrate salts. These compounds are primarily sub- and/or crypto-efflorescences which during time will affect the integrity and durability of the material (in this case gypsum) as well as the aesthetic appearance of the interior facades. In some areas of the rooms, the tiles covering some walls were being detached due to the formation of these new salts in the gypsum plaster placed under the tiles, which weaken its role as a joint mortar.

This more in-depth work on gypsum based materials, complements the previous works [20,21] developed on other kind of building materials (carbonate and sandstone based materials) also from inside of the Igueldo Lighthouse (San Sebastian, Basque Country, north of Spain) where different kind of pathologies can be explained by the chemical reactivity between original materials and ions transported by the marine aerosol, with the contribution in this particular case of seagull dropping, as an extra source of ammonium and nitrate.

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