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**Physico-chemical stone-mortar compatibility of commercial stone-repair mortars  
of historic buildings from Paris**

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**ABSTRACT**

The physico-chemical compatibility of the most frequently used commercial stone-repair mortars applied to repair surface damage of a common limestone (Euville stone) employed in the basements of historic buildings from Paris was assessed. The characterization of anhydrous raw mortar materials, of stone and mortar samples collected from these buildings and laboratory specimens was carried out.

The presence of chlorides and sulfates (gypsum and mixtures of calcium and sodium sulfates) with minor amounts of nitrates in mortar samples collected from the buildings suggest an origin of salts caused by contamination/pollution coming from past restoration products and environmental pollution. The mortar containing quartz, marble aggregates, portlandite and hydraulic components ( $C_3S$ ,  $C_2S$  and  $C_2AS$ ) with addition of aluminosilicate micro-spherical particles with cementitious properties, and no phyllosilicates, shows a better chemical compatibility with the stone. The mechanical properties of this mortar are also closer to those of the limestone. However, some differences in the hydric properties due to their different pore systems and aesthetic features should be improved in further restoration works.

**Keywords:** *stone-repair mortars; natural stone; historic buildings; compatibility; physico-chemical properties*

## **1. Introduction**

From many architectural purposes, mortars can be used as plasters or renders covering the whole surface of walls or building facades, as bedding, jointing or pointing between stone ashlar or bricks, or even they can be used for rebuilding a decayed structure in restoration works. Some kinds of repair mortars can be applied for surface repairs of architectural surfaces. Various terms are used for these specific mortars, *stone repair mortar*, *reconstitution mortar* or *'plastic' repair mortar*, which have the same or very similar meaning to *surface repairs*, *plastic repairs*, *surface fills*, *loss compensation mortars* or *artificial stone mixtures* [1]. During restoration of heritage buildings, mortars are frequently used for the repointing of joints or for the “plastic” repair of stone, which are designed to fill in missing parts of stone. These mortars are moldable mortars that can be applied in situ, and sets into place by its own adhesion to the substrate [2]. From all the possible terms that can be assigned to this kind of mortars, we have chosen *'stone-repair mortar'*, since it is the clearest name for the purpose of our research, which involve mortars that have been used for repairing or reconstruction of surface damaged stone from restoration works that were carried out in historic buildings. A missing part of an original material is modelled by a new material, which is pliable when applied, and therefore can be adapted into various shapes and finished with required surface textures [1].

Repair mortars used for stone restoration are assumed to be highly compatible with historic materials in terms of physical, chemical and mechanical properties in order to assure the durability of masonry on the long term. A systematic approach for the characterization of historic mortars and materials to be repaired has been defined by

RILEM TC 167 COM which offers a valuable tool to identify mortar components, nature of binder, aggregate, additives, and their relative proportions [3,4]. Ashurst in 1990 [5] described some decision factors on surface repairs, whereas Hughes and Valek in 2003 [6] reviewed the compatibility concept. These mortars must meet a series of requirements from a Cultural Heritage preservation point of view to avoid accelerated deterioration of original material. Material compatibility between repair mortars and the original material suggests that no damage should be caused to the repaired material. For example, the incompatibility among building materials due to the combination of sulfate-bearing mortars and magnesium-rich stone and mortars applied in XVIII restoration works lead to extensive weathering on a historic Monastery (XII century) by magnesium sulfate crystallization processes [7].

Nowadays, most professionals turn to commercial pre-mixed mortars. There are many available commercial mortars ready to use in restoration works, from local and international companies. The advantage is that these are prefabricated, and the manufacturer can guarantee that the content's mix is standardized, creating the same workability and properties for each batch, with consistent composition and working properties. This is much appreciated by restoration architects and contractors [8,9]. However, this advantage can be a disadvantage as well. The specially designed mortar for one specific stone can work just for stones with the same or similar physico-chemical characteristics. Furthermore, in cases where the stone is very heterogeneous, and properties can differ greatly from one stone sample to another, the standardized process will be less successful when aiming to achieve a compatible mortar [10]. Besides, these mixes present an uncertainty about the ingredients they contain. In restoration studies using commercial mortars, aggregates are frequently added to solve the problem of stone heterogeneity [11]. In the case of ready-mixed mortars, powders

can simply be added with the required amount of clean water. However, is important to know the physical properties of the commercial product in order to assure the compatibility with the stone.

The selection of a binder is a starting point of the mix design as it predetermines the physical and mechanical properties of the mortar mix, as well as the capacity of the mix to be adapted to the appropriate form and appearance [1]. Natural Hydraulic Lime mortars (NHL) are produced from a naturally occurring ‘impure’ limestone/chalk. Typically, the impurities are those from clay minerals and other sources of alumina and silica. NHL mortars have been manufactured since the XVIII century by burning these limestones below the clinkering point. These NHL are able to set and harden even under water, as the mechanical strength development is mainly driven by hydration. Carbonation of the slaked lime contributes to the hardening process as well.

Hydraulic Limes mortars (HL) are produced by artificially blending calcium hydroxide, calcium silicates and calcium aluminates. This is commonly achieved by blending mixtures of clays and pure limestone, or calcium hydroxide with suitable pozzolanic materials. Pozzolans or pozzolanic materials (fly ash, burnt clays, etc.) are reactive materials that in the presence of soluble calcium hydroxide form hydrated compounds which act as binders. These are often added to increase strength gain in hydrated, hydraulic and natural hydraulic lime based mortars.

Greeks and Romans first used hydraulic lime mortars with natural pozzolans in ancient times [12] and Phoenicians employed these binders in Jerusalem (10th century BC) [13]. NHL was used mostly during the nineteenth century. They are nowadays used in restoration of historical buildings because their chemical and physical properties are similar to those of materials used by the original builders, and because they ensure the development of superior mechanical properties, without having the general drawbacks

of Portland cement. NHL was the precursor of Portland cement. The main difference in the production of NHL and cement is the burning temperature. Callebaut et al. in 2001 [14] focused on the characterization of nineteenth century hydraulic restoration mortars used in the Saint Michael's Church in Leuven (Belgium), for restoring weathered mortar joints. Based on the presence of a calcium aluminosilicate (gehlenite ( $C_2AS$ )), the dominance of di-calcium silicate (larnite ( $C_2S$ )), the large amounts of portlandite (calcium hydroxide, CH), together with chemical analyses and historical sources, these hydraulic mortars were characterized as NHL mortars.

The ready-mixed mortars are available as powder materials composed of binders, aggregates and additives already packed together in appropriate ratios. The mortars preparation only consists of simple mixing operations with the correct amount of water (which is usually indicated in the technical data sheets). NHLs are frequently employed as binders in the commercial mixes because of their quick setting capability and remarkable mechanical strengths [13,15,16]. The characterization of commercial ready-mixed mortars, allows verifying their real composition and performance characteristics [17]. However, these composition and properties often differ from those declared in the technical specifications supplied by the manufacturers, finding disagreements with the composition declared by the supplier [18]. There is still a lack for testing the physical properties and durability of mortars according to European standard tests, especially in terms of compatibility with stone, and the long-term behaviour of the repaired mortar/stone interface [11].

The aim of this research is to determine the physico-chemical compatibility of the three most frequently used commercial stone-repair mortars applied to repair the surface damage of Euville stone, a common limestone used in the basements of historic buildings in Paris city.

## 2. Materials and methods

### 2.1. Characteristics of selected materials

Three commercial stone-repair mortars (Fig.1a) were selected in this research on the basis of their application on some damaged surface areas of the same type of stone, repaired due to salt crystallization processes, in different historic buildings of Paris. These buildings were repaired in the same period of time corresponding to the restoration campaign 2008-2010. The selected stone is the so-called Euville limestone (Fig.1b) that was used in the outdoor basements of the Grand Palais, Palais de la Découverte and Préfecture de Police historic buildings.

#### 2.1.1. Stone-repair raw anhydrous mortars

Three commercial mortars, ready to mix with water according to recommendations of the manufacturers, are called in this research *Lit*, *Art* and *Alt* mortars. These are mixtures of natural and hydraulic lime mortars (NHL, HL) with or without aerial lime (CL). Lit mortar (*Lithomex Light*) is a material produced by Chaux et Enduits St. Astier (CESA, France), based on a St. Astier natural hydraulic lime binder (NHL) and it was used to repair Euville stone at the Grand Palais building (GP). According to the manufacturer, this is a pure NHL, defined as a natural lime, with hydraulic binders, sand and specific additives. According to Torney et al., 2015 [9], Lithomex mortar contains the following components (expressed as percentage of binder): calcium hydroxide 20%; hydraulic binder (Portland cement) 20%; filler (vermiculite) 5%, fine grained quartz and calcite aggregates and talc filler. The technical data sheet of *Art* mortar (*ArtoPierre TM* by Parexlanko, France) indicates that this is mainly aerial lime (CL, binder, 70% in volume) with hydraulic, mineral and organic additives and mineral pigments. Aggregates are mainly calcareous and siliceous with grains up to 1.5 mm. This mortar was used in the Palais de la Découverte building. Finally, *Alt* mortar (*Altar® Pierre* by

ECP, France) was used to repair Euville stone in the Préfecture de Police building (PP). According to the manufacturer, quartz grains, calcium carbonate, hydraulic binder, additives and mineral pigments, compose this mortar. The mineralogical and chemical composition of the three mortars, before mixing with water (anhydrous raw materials), was initially determined in this research. Then, the mineralogy and hydric and mechanical properties of hardened single mortar specimens (4x4x16 cm) were studied after 28 curing (Fig.1c).

### 2.1.2. Stone

Euville limestone (Oxfordian, Late Jurassic) is a crinoïdal grainstone almost completely composed of calcium carbonate (98%) with a coarse-grained texture and a syntaxial cement of calcite. The fabric was formed by an accumulation of coarse crinoïdal ossicles in submarine dunes. Accessory bivalves and spines of sea urchins are also part of the fossil fauna. The outcrops of this limestone are situated near Commercy (Département de la Meuse, France). The Euville limestone is a famous building stone in France, and also in Belgium, where it is often used in combination with Savonnières limestone and Lede stone, and it has often been used as a replacement stone in many historic buildings in several countries in the world [19,20]. As a restoration measure, some surface areas built with this stone affected by salt crystallization processes have been repaired with several stone-repair commercial mortars. The stone specimens used in this work were supplied by ROCAMAT quarry in Euville, France. The specimens were cut parallel to the bedding with dimensions 4x4x16 cm to perform all the hydric and mechanical tests. For the water vapour permeability test cylindrical specimens 1 cm thick and 4 cm diameter were prepared.



### *2.1.3. Stone and mortar samples collected from the historic buildings*

Three historic buildings from Paris city where the three types of mortars were used to restore Euville stone were selected in order to collect stone and mortar samples. Two small mortar samples were collected, from the Gran Palais building (GP) where Lithomex mortar was used, sample Lit-GP (Fig.2a), and Préfecture de Police building (PP) where Altar Pierre mortar was applied to repair the stone, sample Alt-PP (Fig.2b). At the Préfecture de Police building, a small flake sample of Euville stone (Eu-GP) was also collected from one area with salt crystallization decay that showed efflorescences on the surface of the stone (Fig.2c). It was not possible to collect samples at the Palais de la Découverte building, since the studied area corresponded to a delicate sculpted stone restored with Artopierre stone-repair mortar displaying an apparent good state of conservation.

### *2.1.4. Hardened mortar specimens manufactured in the laboratory*

The water:powder mortar ratios were prepared in the lab, following as much as possible the recommendations of the manufacturers according to their respective technical data sheets. The manufacturer's preparation guidelines of Lithomex mortar state that the materials should be mixed (mechanically or by hand) for between three and five minutes, with water content of 4.5–5.5 L of water per 25 kg of dry material. We used 5 L of water (W) per 25 kg of dry material (M), i.e.  $W:M=0.20$ . In this case, the restorer who used this type of mortar in the Grand Palais historical building recommended us to add a handful of sand to the mixture. Since the amount of aggregate fraction between 1.25 and 0.63 mm in this mortar was much lower compared to the other mortars, according to this information, to grain size distribution analyses and in order to obtain a mortar as similar as possible to the others, 150 g of normalized sand (fraction 1.25-0.63 mm from Ultibat, EN 12620: 2002 + A1: 2008 [21]), was added to 2000g of raw

202 anhydrous mortar. To prepare Artopierre mortar, between 6 and 7 L of water per 30 kg  
203 of dry material is required according to the technical data sheet. We used 6.5 L per 30  
204 kg of raw anhydrous mortar powder (W:M=0.22). To manufacture Altar® Pierre  
205 mortar, from 4 up to 6 volume of dry material per 1 volume of water was recommended.  
206 To prepare the specimens we used 5 volume of dry material per 1 volume of water  
207 (W:M= 0.13).

208 A mechanical mixture was performed in the three mortars using an industrial mixer  
209 (Controlab, France) during 4 minutes, starting at low speed rotation (62 rpm) during 1  
210 min and finishing at high speed (125 rpm). Then, a jolting apparatus was also used  
211 according to the standard test UNE-EN 196-1:2006 [22], applying 25 blows to  
212 homogenize the mixture and avoiding the formation of air bubbles.

213 Eighteen mortar specimens were prepared, six with each type of mortar, two specimens  
214 for the compression-flexural test, two for water absorption under vacuum test and two  
215 for capillary-desorption test. These were prepared by molding the mixtures in rubber  
216 molds (4x4x16 cm). Besides, to carry out water vapor permeability tests, plastic moulds  
217 filled with each mortar mixture were used. These were big enough to prepare by cutting  
218 at least two circular mortar specimens (50 mm diameter x 10 mm thickness) for each  
219 type of mortar. All the specimens were demolded after two days of curing according to  
220 the standard test NF-EN 1015-11 [23].

221 For hardening the mortar specimens (28 days curing) we tried to simulate the average  
222 annual weather conditions of Paris. The specimens were placed in a ventilated climatic  
223 chamber with CO<sub>2</sub> uptake from the environment (400 ppm approx.) at 11°C and 85%  
224 relative humidity (RH)) during 7 days. Then, RH was changed down to 65% during the  
225 next 7 days, followed by laboratory conditions in a climatic room at 20°C and 50% RH  
226 during 14 days, under environmental CO<sub>2</sub> (400 ppm approx.)). The reason why RH was

reduced from 85% down to 65% during the 7-14 curing days was first of all, because the average annual RH in Paris city was in the range 65-85 % RH approx. In a second place because these commercial mortars are mixtures of hydraulic and aerial lime. According to the literature [24,25], a high and a lower RH, respectively, is recommended to set up suitable curing conditions. The European standard AFNOR EN 1015-11 [23] defines the following optimal conditions of temperature and relative humidity for the curing of mortar samples in the laboratory at  $T=20\pm2$  °C and  $RH=95\pm5\%$  for the first 5 days in the mold, the following 2 days removed from the mold, and at  $T=20\pm2$  °C and  $RH=65\pm5\%$  for the following 21 days. So, 85-65% RH and 11°C T conditions were selected the first 14 days in order to simulate as much as possible the environmental curing conditions of Paris and at the same time trying to perform a laboratory test in a gradual way choosing the most suitable as possible curing conditions for these type of mortars. The environmental conditions of the final 14 days to reach 28 curing days had to be performed at  $RH 50\pm5\%$ ,  $T 20^{\circ}\text{C}$  in a climatic room only due to availability and space reasons.

## *2.2. Analytical techniques and experimental test methods*

### *2.2.1. Mineralogical and chemical analyses*

Polarizing optical microscopy was used to study the main mineralogical constituents and textures of the mortar samples collected from the buildings and the hardened single mortar specimens after 28 days curing. The samples were impregnated with epoxy resin mixed with blue dye to fill the porosity in order to be easily recognized under the microscope with parallel nicols. The thin sections were studied with an Olympus BX50 polarized light microscope fitted with an Olympus digital camera.

X-ray diffraction (XRD) was used to determine the mineralogical composition of raw anhydrous mortar samples, hardened single mortar specimens manufactured with them

after 28 days curing and samples collected from the buildings. Furthermore, soluble fractions prepared to carry out ion chromatography analyses were left to evaporate and the product was also analysed by XRD. The analyses were conducted on a Bruker D8 Advance diffractometer with  $\text{CoK}\alpha$  radiation powder. The scanning conditions were  $2\theta$  angles of  $5\text{--}65^\circ$ , scan step size  $0.05^\circ$ , time step  $1^\circ/\text{s}$  in continuous mode, and beam intensity of 40 kV and 35 mA. The diffractometer worked with a  $\text{CoK}\alpha$  radiation, instead of the most common used  $\text{CuK}\alpha$  and so there is a slight variation in the grades of the  $2\theta$  peaks used to identify minerals. The identification of the mineral phases was performed using the Bruker AXS DiffracPlus EVA software also used to carry out semi-quantitative analyses.

Scanning electron microscopy (SEM) coupled with Energy dispersive X-ray spectroscopy (EDS), was used to find weathering products caused by decay processes and to identify the type of salt efflorescences and sub-efflorescences on the top and underneath (some millimetres depth) the surface of stone and mortar fragments collected from the buildings. A SEM microscope Leica S430i was used. The elemental composition of some selected components from these building samples together with the raw anhydrous mortar samples was determined by means of EDS semi-quantitative microanalyses by means of an Bruker micro-analyser spectrometer. Nickel-sputtered fragments from the samples were studied in secondary electrons mode.

In order to perform the chemical composition by EDS analyses of each grain size fraction of the raw anhydrous mortars (aggregates and binder), the grain or particle size distribution was carried out by sieving 200g approx. of each mortar according to the standard test AFNOR NF-EN 1015-1 [26]. The sieve sizes that have been used are the following: 1.60mm, 1.25mm, 0.63mm, 0.315mm, 0.20mm, 0.16mm, 0.080mm and 0.080mm. Then, the largest sizes (1.60-1.25 mm and 1.25-0.63 mm) were impregnated

in epoxy resin and then polished, in order to study their shape and chemical composition by SEM-EDS analyses. Each grain size range of the finest fractions (from 0.63 down to below 0.080 mm) was pressed in small tablets and then analyzed by EDS previously sputtering the samples with nickel (Ni).

Ion chromatography (IC) analysis was performed to quantify the soluble salts present in the raw anhydrous mortars and samples collected from the buildings. Some anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{2-}$  and  $\text{SO}_4^{2-}$ ) and cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$ ) were determined. Approximately 0.1 g of sample was dissolved in 10 ml of Milli-Q ultrapure water and placed it for 5 min in an ultrasonic bath at room temperature. The solution with the solid residue was then left to settle down with a minimum rest period of 24 h. The soluble salts of raw materials and samples collected from the buildings were quantified on a Dionex DX-120 ion chromatograph.

### 2.2.2. *Physical tests*

To determine hydric and mechanical properties, together with physical characteristics such as density, porosity and color parameters, the following tests were carried out in the stone and mortar specimens.

Water absorption by capillarity was carried out to evaluate the liquid water transfer into the materials. The capillary coefficients were calculated for the Euville stone and hardened single mortar specimens. The standard test AFNOR NF EN 1925:1999 [27] was followed; the results are expressed in  $\text{g}/(\text{m}^2 \cdot \text{s}^{1/2})$  instead of  $\text{kg}/(\text{m}^2 \cdot \text{s}^{1/2})$ . Once capillarity saturation was reached, the specimens were spun to ease the water drying under laboratory conditions ( $45 \pm 5$  % RH and  $20 \pm 1^\circ\text{C}$ ) and to calculate desorption coefficient (water loss or evaporation) weighing the specimens at several intervals of time.

301 Water vapour permeability test was carried out in the stone and mortar specimens. The  
302 standard test AFNOR EN 15803:2010 [28], with wet cup was followed to calculate the  
303 water vapor permeability ( $\text{Kg}/(\text{m}^2\text{s})$ ). External relative humidity of 50% and  
304 temperature of 23°C were achieved introducing the specimens in a climatic chamber,  
305 setting these conditions during all the duration of the test.

306 Water absorption under vacuum was performed in the stone and hardened mortar  
307 specimens, to determine differences on apparent density ( $\text{kg}/\text{m}^3$ ), bulk density ( $\text{kg}/\text{m}^3$ ),  
308 and to calculate open porosity (%) as described in standard test AFNOR EN 1936:2007  
309 [29].

310 Flexural strength measurements were carried out in the stone and hardened mortar  
311 specimens, with a maximum load of 8 kN and load rate of 0.05 kN/S. Compression  
312 strength measurements were performed in the four fragments obtained from the  
313 breaking of two specimens after the flexural test. A maximum load of 250 kN and load  
314 rate of 2.4 kN/S was applied until breaking, providing values equal or above 7 MPa,  
315 since this is the minimum value detected by the compression cell. A Quantech 3R press  
316 (Quantum<sup>TM</sup>, Researchers & Realisations, France) that follows the standard test  
317 AFNOR EN196-1:2006 [30] was used.

318 Total Hg-porosity and pore size distribution analysis was carried out by mercury  
319 intrusion porosimetry in the stone and mortar samples collected from the building and  
320 the superficial part of hardened mortar specimens manufactured in the laboratory.  
321 Readings were taken at pore radius of 0.003–200  $\mu\text{m}$  under measuring conditions  
322 ranging from atmospheric pressure to 228 MPa on a Micromeritics Autopore IV 9500.

323 Color parameters were measured on the stone and mortar hardened specimens. L\*  
324 parameter, which accounts for luminosity, hue and saturation (chroma, C), a\* and b\*  
325 coordinates (a\* being the red-green parameter and b\* the blue-yellow) were obtained.

Total color difference  $\Delta E^*$  was provided as a result of the formula  $\Delta E^* = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$ . Measurements were performed with a spectrophotometer Konica MINOLTA CM-2300d using the CieLab color space; standard illuminant was D65 and observer angle, 10°.

### 3. Results

#### 3.1. Characterization of raw anhydrous mortars

The main mineralogical composition of Lit mortar determined by XRD is calcite, quartz, feldspar and phyllosilicates (clinochlore and talc), followed by hydraulic components, larnite (i.e.  $C_2S$  or belite), alite ( $C_3S$ ) and traces of gehlenite ( $C_2AS$ ). Art mortar contains mainly quartz, calcite and portlandite (i.e.  $CH$  or  $Ca(OH)_2$ ) and hydraulic phases, di-calcium silicate (larnite) and tri-calcium silicate (alite), and traces of feldspar and calcium-aluminium silicate (gehlenite). A small hump between 10 and 15° 2 $\theta$  can be observed in the XRD pattern of this mortar, which might be related to the presence of clays. Art mortar XRD pattern shows quartz, feldspar, calcite, portlandite, larnite, alite and traces of gypsum and gehlenite (Fig.3 and Table 1).

The SEM-EDS analyses performed in several areas of mineral grains (aggregates) with sizes between 1.6-1.25 mm and 1.25 mm-0.63 mm of Lit mortar (Fig. 4a) correspond to phyllosilicates compositions (clinochlore and talc), with and without additional K, Ti and Cl only detected in the aggregates in the range between 1.6-1.25 mm (Table 2). Mineral grains of Lit mortar with sizes in the range between 1.25-0.63 mm correspond to calcite composition with some traces of Mg, Al, Si and Na (Fig. 4b). The results of these analyses performed in Art mortar show that the mineral grains in the ranges between 1.6-1.25 mm and 1.25 mm-0.63 mm are mainly, calcite, quartz (that were deposited in the bottom of the prepared epoxy specimen) and similar phyllosilicates than those present in Lit mortar (Fig.4c). By contrast, SEM-EDS analyses carried out in

the grain sizes between 1.60-1.25 mm and 1.25-0.63 mm of Alt mortar show that these are only composed by sub-rounded and sharp calcite composition grains, which partially might correspond to the marble grains added by the manufacturer (Fig.4d). Some of these grains contain some fissures filled with quartz and some impurities such as sodium chloride (NaCl). The composition of these largest grain size aggregates in this latter mortar shows significant differences compared to the other two mortars (Table 2), since Al, Mg and k are not detected and there is no Fe and Ti in the fraction between 1.60-1.25 mm.

In the three mortars, the composition of the aggregates between 0.63 and 0.20 mm is mainly siliceous (Si content between 20 and 40 wt. % approx.), and this is especially marked in Alt mortar (Table 3). Below 0.20 mm the Si content greatly decreases at expenses of Ca content, which especially increase in Art and Alt mortars (between 27 and 40 wt. % approx.). Besides this, the main difference among the three mortars is the Na content in Alt mortar which increases with the decrease of grain size (except in the range between 0.16 and 0.080 mm), from 4 wt. % (between 0.63-0.315 mm) up to 33 wt. % (below 0.080 mm).

Ion chromatography analyses show that none of the anhydrous mortars display nitrates in their composition (Table 4). However, the three have a slight amount of chlorides (circa 5 ppm). The only one displaying soluble sulfates is Lit mortar (23 ppm approx.). The concentration in bulk material (wt.%) of the identified total soluble salts (cations and anions) represents very low percentages in Lit and Alt mortars (2 %) and slightly higher values in Art mortar (circa 5 %). There is a high amount of soluble  $\text{Ca}^{2+}$  in the three mortars and this is especially high in Art mortar. No nitrates or phosphates, neither ammonium have been detected in these samples.



### 3.2. Mortars and stone flake samples collected from the buildings

Petrography of mortars thin sections performed under optical light microscopy shows that Lit mortar from the Grand Palais building has a large quantity of rounded esparitic calcite and quartz grains with submillimetric sizes, together with some micas and many phyllosilicates embedded in a scarce micritic matrix composed by a mixture of calcite and clays. The ratio binder:aggregate is approximately 1:4 (Fig. 5a and 5b). Feldspar grains show up with a high degree of cracking at the surface of the mortar that was in contact with the surrounded environment where the sample was collected. Porosity is mainly fissural and surrounds the mineral grains and goes through the clay minerals and through the matrix. Large pores inside the matrix are associated in some areas to the phyllosilicates showing signs of weathering (Fig.5c and 5d). Thin sections of Alt mortar from Préfecture de Police building also show a high amount of calcite crystals inside sharp fragments of fossiliferous micritic and esparitic limestone rocks, bioclasts and marble fragments of millimetric size. Abundant smaller feldspar and subhedral quartz grains with cement as syntaxial overgrowths are also embedded in a dense dark matrix. The ratio binder:aggregate is approximately 1:3 (Fig.5e and 5f). Small rounded (circa 50  $\mu\text{m}$ ) and larger sub-rounded pores (between 200 and 400  $\mu\text{m}$ ), together with small spherical particles (circa 50  $\mu\text{m}$ ) are present inside this matrix. Some of these particles seem to be stuffed with an amorphous gel, being difficult to distinguish them from the matrix, while many others are empty and filled now with the dyed blue resin used to mark the porosity of the mortar samples (Fig.5g and 5h).

The XRD pattern of Lit mortar collected from the Grand Palais building (Lit-GP), displays the same mineralogy than the obtained in the raw anhydrous mortar, with the exception of the presence of muscovite  $(\text{K}(\text{Li},\text{Al})_2(\text{Si}_3\text{AlO}_{10})(\text{OH})_2)$  and gypsum  $(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$  and the absence of larnite ( $\text{C}_2\text{S}$ ) and alite ( $\text{C}_3\text{S}$ ) (Fig.6). The semi-

quantitative (%) analyses show different concentrations in all the identified phases compared to its corresponding raw material (Table 1). The mineralogy of the salts precipitated from the soluble fraction of Lit mortar prepared to carry out the ion chromatography analyses, that were left to evaporate (Lit-GP-sf), shows an increase of gypsum peaks and the appearance of halite (NaCl). Some residues of non-soluble fraction (quartz, calcite, clinocllore and talc) are also detected.

The XRD pattern of Alt mortar collected from the Préfecture de Police building (Alt-PP) also shows the same mineralogy than the obtained in the anhydrous raw material, with the exception of no detection of gypsum, the absence of alite ( $C_3S$ ) and the presence of a minor amount of larnite ( $C_2S$ ). The semi-quantitative (%) analyses also show different concentrations in all the identified phases compared to its corresponding raw material, especially in the amount of portlandite (Fig.6). No salts are identified in the mortar sample collected from this building and neither in the precipitated soluble fraction. The XRD of Euville stone flake (soluble fraction after evaporation) shows gypsum, halite and traces potassium-sodium sulfate.

The SEM-EDS analyses of the surface of Lit mortar from the Gran Palais, mainly shows Ca, Mg, C, O, Si and Al as the main components present in all the analyzed zones. Underneath the surface it shows aggregates of quartz and mainly Si and Ca (i.e. calcium silicates) as the composition of the binder. There are zones with large amounts of salts composed by S and Ca (i.e. gypsum) and Na and Cl (i.e. sodium chloride) (Fig.7a, zone 1 and zone 2, respectively). A great number of phyllosilicates is also observed.

On the surface of Alt mortar samples from Préfecture de Police building, Si, Ca, Al, C, O, Na and Cl are the main components, with variable amounts in all the analyzed zones. There are zones with large amounts of Na and Cl (sodium chloride). Underneath the surface of Alt mortar, the main composition of the binder is Si and Ca, with Al, C and

426 O. Many micron-size spherical particles can be observed, some of them seem to be  
427 cracked and empty and others seem to be filled with a “viscous” phase. The EDS  
428 analyses show a thin external part mainly composed by aluminosilicates (Fig.7b, zone  
429 1), which might correspond to mullite ( $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ). Some of them display also Ca in  
430 the external part. The analyses of the interior part of these particles show a high increase  
431 in Ca and minor amounts of Na and Mg (Fig. 7b, zone 2). Aggregates of marble  
432 fragments can also be observed. However, they display low amount of C and some Al in  
433 their composition. The EDS analyses of Alt mortar (external and internal parts) indicate  
434 the presence of salts (sodium chloride) together with aluminosilicates, calcium silicates,  
435 calcium aluminosilicates, calcium carbonate and silicon oxides.

436 The surface of Euville stone flake displays salt efflorescences containing S, K, Ca and  
437 Na (Fig.7c, surface zone). Some millimeters depth from the surface, the SEM images  
438 show sub-efflorescences of sodium and calcium sulfate crystals mixed together, which  
439 might corresponds to thenardite and gypsum, respectively (Fig. 7c, interior zone).

440 Table 5 shows the ion chromatography results of soluble salts present in the samples  
441 collected from the buildings. There is a large amount of sulfates in Lit mortar sample  
442 collected from Grand Palais, above 100 ppm. The amount of sulfates in Alt mortar  
443 sample from Préfecture de Police is much lower (21 ppm). The amount of chlorides is  
444 also lower in Alt mortar (11 ppm) compared to Lit mortar (circa 30 ppm). The presence  
445 of nitrates is detected in both mortars, circa 25 ppm in Lit mortar and circa 34 ppm in  
446 Alt mortar. The concentration in bulk material (wt.%) indicates higher percentages of  
447 total soluble salts (cations and anions) in Lit mortar compared to Alt mortar, even  
448 though these values are very small in both cases. The ion chromatography analyses of  
449 the stone flake collected from the Préfecture Police building show a concentration of  
450 sulfates and chlorides of 984 ppm and 17 ppm, respectively. Nitrates were not detected

in this sample. The content of soluble  $K^+$  and  $Ca^{2+}$  in this sample is especially high. The concentration of salts in bulk material in this sample (that contained efflorescences) is much higher compared to the mortars (circa 12 wt.%). No phosphates or ammonium were detected in these samples.

Figure 8 shows the pore size distribution obtained by mercury intrusion porosimetry in the mortars collected from the buildings, which have a very different total porosity accessible to mercury. Lit mortar sample has a higher total Hg-porosity (circa 26%) compared to Alt mortar (circa 16%). The pore size distribution of the former is mainly polymodal with the highest volume of pores with radius in the range between 0.1  $\mu m$  and 3  $\mu m$  (Fig.8a). It displays also larger pores with radius in the range between 3 and 10  $\mu m$ , and smaller pores with radius below 0.02  $\mu m$ . Alt mortar porosimetry curve is mainly bimodal with most of their pores with radius in the range between 0.5 and 1  $\mu m$  and pores below 0.01  $\mu m$  (Fig.8b).

### *3.3. Stone and hardened mortar specimens manufactured in the lab*

#### *3.3.1. Mineralogical characterization*

Thin sections of Lit and Alt hardened mortars under optical light microscopy (Fig.9a-b and Fig.9c-d respectively) show a great similitude with those samples collected from the buildings (Fig. 5). The matrix or binder of the laboratory hardened mortars show lighter colors and rounded pores (500  $\mu m$  approx.) that could be related with a lower degree of maturation and the lack of exposition to weathering agents. The small rounded pores (around 50  $\mu m$ ) that were observed in the thin sections of Alt mortar from the building are not observed in the same mortar manufactured at the lab. In the latter, there are many spherical particles circa 50  $\mu m$  embedded in the matrix that can be clearly distinguished from it by a thin rim filled with the resin (no blue dyed), which indicate

spherical hollow not connected particles. The thin sections of Art mortar show aggregates of calcite, quartz, feldspars and many phyllosilicates with some micas. There are many small rounded pores (filled and not filled with the blue dye, which would represent open and non-connected porosity), together with fissural porosity going through the matrix, and intra particle porosity associated to phyllosilicates (Fig.9e and 9f). Euville stone thin sections show a larger size of the mineral grains compared to the mortars (Fig.9g and 9h). Bioclasts, such as crinoids, sea urchins, brachiopods, coral fragments and pellets can be easily recognized. Syntaxial calcite cement occupies a large part of the stone that gives rise to the cohesion of the grains. Shell fragments are filled with calcite sparitic cement and their edges are surrounded by sparitic and micritic cement in some areas. Heterogeneous macro-pores are left by the syntaxial overgrowth while micro-pores are mainly intra-particle or located between the micrite and sparite crystals around shell fragments. Some quartz and clays can be also observed in minor amounts.

The XRD patterns of the 28 days hardened mortars manufactured in the laboratory reveal the development or increase of portlandite, the decrease of larnite ( $C_2S$ ) and the disappearance of alite ( $C_3S$ ) regarding to the analyses carried out in their corresponding raw anhydrous mortars (Table 1 and Fig.10). In all the mortars the decrease of larnite peaks is evident together with the improvement of crystallinity of portlandite (CH) reflected by the sharpness and intensity increase of the main CH peak .

### *3.3.2. Physical characterization*

A complete characterisation of the physical properties of Euville stone and the 28 days hardened mortar specimens has been done.

Concerning liquid water transfer (Table 6) it can be seen how Lit mortar specimens display a very low capillarity coefficient compare to the rest of mortar specimens. The

total amount of water at the end of the tests (Fig. 11) is also much lower than for the others mortars (Fig. 11a) and Euville stone (Fig.11c). In Lit mortar specimens, evaporation (water loss) is also slower than in the rest of materials but the difference is less important than for capillarity (Fig.11b). Art mortar specimens get more water than the others and in a very quick way. Alt mortar and Euville stone have a similar behaviour during the capillarity test: similar velocity and same water content at the end of the test, but Euville stone losses the water by evaporation much faster than this and the other mortars (Fig.11d). At the end of the evaporation test Euville stone has lost all the water taken during the capillarity test. Water vapour permeability is also quite similar in Alt mortar and Euville stone. Art mortar shows the highest water vapour permeability values while permeability of Lit mortar is in between the values obtained in Art and Alt mortars and Euville stone. We can notice that water vapour permeability and porosity are directly related; roughly we can consider that an  $\times 10^{11}$  factor exists between vapour permeability and open porosity.

Comparing the values of open water porosity and mercury porosity values (Table 7) it can be observed that the former porosity is between 10 and 20% higher than the latter, in all the materials except Lit mortar. For Lit mortar, mercury porosity is slightly higher than water porosity. Bulk density corresponds to the density of “minerals” that form part of these materials. Euville stone specimens have the highest bulk density ( $2.55\text{g/cm}^3$ ), slightly lower than the calcite density ( $2.71\text{ g/cm}^3$ ). Comparing the three mortars, Lit mortar has the highest bulk density, followed by Alt and Art mortars. This can be explained by its mineralogical composition. Apparent density depends on porosity and bulk density, showing that Euville stone is more “compacted” than the mortars. Concerning the mortars, Alt mortar has the highest apparent density, followed by Lit and Art mortars. Apparent density is inversely related to water open porosity, i.e.

525 the highest the open porosity the lower the apparent density. Apparent density values  
526 obtained by mercury porosimetry correspond very well to values obtained by water  
527 immersion test. For bulk density it can be observed the same pattern than for porosity,  
528 mercury porosimetry values are slightly lower than water porosity values, except for Lit  
529 mortar specimens.

530 Pore size distribution (PSD) is different for all the samples, where it can be considered  
531 two different cases. First, Lit and Art mortars display a clear bimodal PSD which is  
532 quite similar, with an average pore radius circa  $0.10\mu\text{m}$  for Lit and  $0.13\mu\text{m}$  for Art  
533 mortar; median pore radius are about  $0.5\mu\text{m}$  for Lit and  $0.4\mu\text{m}$  for Art, in both cases  
534 the median radius is higher than average radius. Alt mortar and Euville stone show  
535 average pore radius higher than median radius,  $0.04\mu\text{m}$  and  $0.01\mu\text{m}$  for Alt mortar  
536 respectively, and  $1.4\mu\text{m}$  and  $0.8\mu\text{m}$  for Euville stone, respectively. Euville limestone  
537 has larger pores than the mortars, above  $10\mu\text{m}$  (Fig.12). In all the mortars median  
538 radius is smaller than the modal pick, indicating a bias to the smaller pores; Euville  
539 limestone has a median bigger than the mode, reflecting the bias to the biggest pores.  
540 Difference between mode and median is smaller in Euville stone than in mortars,  
541 because it has a more symmetrical PSD. This difference is more important in Alt mortar  
542 and we can observe a big “tail” in the distribution that takes place in the range of  
543 smallest pores.

544 The comparison between capillarity coefficients and pore size distributions for Art and  
545 Alt mortars and Euville limestone, indicates a direct relation between capillarity  
546 coefficients and pore sizes. In order to avoid the effect of water volume absorbed during  
547 the capillarity test, the capillarity coefficient (C) has been divided by the porosity values  
548 (P), in this way, the obtained values correspond to the median pore radius values of  
549  $0.82\mu\text{m}$  (Euville),  $0.41\mu\text{m}$  (Art) and  $0.01\mu\text{m}$  (Alt) (Table 7). A linear regression among

these values gives an equation  $C/P = 1.2461 \times (\text{median pore radius}) + 1.9591$ , with a regression coefficient of  $R^2 = 0.9438$ .

Results of mechanical tests obtained in these stone and hardened mortar specimens are presented in Table 8. Art mortar has a mechanical behaviour different from the others, since the flexural and compression strengths are much lower than the obtained in the other mortars. The experimental resolution of the mechanical tests machine used is not adapted to Art mortar specimens. So if this mortar is not considered, a very good linear regression between flexural strength and apparent density ( $R^2 = 0.999$ ) can be obtained.

The spectrophotometry results are compiled in Table 9. The highest total color difference ( $\Delta E^*$ ) between each mortar and Euville stone is obtained in Art mortar (circa 8), followed by Alt (circa 5) and Lit mortar that shows the lowest differences (circa 3).

## 4. Discussion

### 4.1. Chemical and mineralogical characterization

The original chemical and mineralogical composition of the raw anhydrous mortars exert a great influence on their final physico-chemical properties in a short and in a longer term, and hence on the compatibility with the stone to be repaired and their durability [31]. Quartz, calcite, feldspar and larnite/belite, alite and traces of gehlenite (hydraulic components,  $C_2S$ ,  $C_3S$  and  $C_2As$ , respectively) are present in the three raw anhydrous mortars (Fig.3 and Table 1). The main difference in their mineralogy determined is the absence of phyllosilicates in Alt mortar and the absence of aerial lime (portlandite) in Lit mortar. The former contains high quantity of portlandite and calcium and aluminosilicates (larnite, alite and gehlenite) while the latter has abundant phyllosilicates (clinochlore and talc) and no portlandite. Art mortar composition is in between the two other mortars, with portlandite, larnite and alite, and some phyllosilicates (vermiculite, which was only possible to identify in the XRD and



petrography of the 28 days hardened mortars and not in the XRD of the raw anhydrous materials (although the presence of phyllosilicates was inferred by a small hump between 10 and 15 °2θ in the XRD pattern). The identified soluble salts determined by ion chromatography represent insignificant values in the concentration in bulk material (wt.%), around 2 % in Lit and Alt mortar, which should not represent a salt crystallization problem or development of salt efflorescences, and a slightly higher content in Art mortar (5%). However, is important to take into account that these percentages include a high concentration of soluble calcium ( $\text{Ca}^{2+}$ ), which could be combined with other anions that were not possible to identify with the chromatographic column used in these analyses. Soluble calcium combined with other anions such as carbonates ( $\text{CO}_3^{2-}$ ), silicates ( $\text{SiO}_4^{4-}$ ) or hydroxides ( $\text{OH}^-$ ) could form part of these mortars, especially in Art mortar with a higher concentration of soluble  $\text{Ca}^{2+}$  (Table 4).

The characterization of stone and mortar samples collected from the historic buildings has been useful to know the current composition and texture of the mortars set under real conditions and five years of hardening and to study the weathering products causing decay in these materials. The identification of salt minerals by XRD, SEM-EDX and the quantification of soluble salts by ion chromatography have served to plan the accelerated ageing test to assess the durability of stone-mortar specimens in the lab [31].

The presence of chlorides and sulfates (gypsum and mixtures of calcium and sodium sulfates) with minor amounts of nitrates suggest an origin of salts caused by contamination/pollution coming from past restoration products and environmental pollution (Fig.6, Fig.7 and Table 5).

Lit mortar, classified as a NHL according to the manufacturer, displays a high amount of phyllosilicates that could have favour cracking of the mortar at the interface stone-mortar observed at the Grand Palais building when mortar samples were collected

(Fig.2). In the frame of Dimppa Project [32] on site measurements with non-destructive techniques were carried out in this building in the same type of mortar and stone. High salt index values were found at the interface between Lit mortar and Euville stone, together with large differences on the thermal behaviour between both materials. Restorers frequently use clay rich sands because they can increase workability and matching the right colour for the restoration mortar. However, the main effect of clay fines ( $<63\ \mu\text{m}$ ) in aggregates is an increase of the water demand, due to their high surface area, for a constant mortar consistency that gives rise to a poor quality mortar [33]. However, it does not mean that NHL produce bad results in this type of restoration works, it just depends on the type, proportion and grain size of the minerals in the original composition and the compatibility with the stone substrate. The characterization of original mortars and plasters from Crete was carried out with the evaluation of the repairs prepared with NHL as binding material, siliceous sand and crushed brick as aggregates [34]. After three years of intervention with these NHL-based mortars and plasters, macroscopic survey and analyses on the applied materials revealed that no cracks or release of soluble salts occurred.

In this case, this NHL mortar collected from the Grand Palais building (Lit mortar) has a higher total porosity and a polymodal pore size distribution, compared to the HL mortar collected at the Préfecture de Police building (Alt mortar). The hardened mortar specimens manufactured and cured during 28 days in the lab, show the presence of fissural porosity mainly through the matrix of Lit mortar (Fig.9). The XRD patterns of all the hardened mortars manufactured in the laboratory (Fig.10) reveal the development of portlandite (CH) in Lit mortar or its increase in Art and Alt mortars, the decrease of larnite ( $\text{C}_2\text{S}$ ) and the disappearance of alite ( $\text{C}_3\text{S}$ ) regarding to the analyses carried out in their corresponding anhydrous raw materials (Fig.3). In Art mortar the decrease of

625 C<sub>2</sub>S peaks can be observed together with the improvement of crystallinity of CH peaks  
626 and the appearance of vermiculite or clinocllore peaks. In Alt and Lit mortars there is  
627 also a decrease in C<sub>2</sub>S and disappearance of C<sub>3</sub>S peaks and the improvement of  
628 crystallinity of portlandite reflected by the sharpness and intensity increase of the main  
629 portlandite (CH) peak. This is explained because the hydration of C<sub>3</sub>S and C<sub>2</sub>S produce  
630 CH and some of new CH amount can also crystallize, inside of the CSH (calcium  
631 silicate hydrates) structure being well sheltered [13]. This fact has been related to the  
632 improvement of mortar strength [35-37], while C<sub>3</sub>S contributes to the strength at early  
633 ages, C<sub>2</sub>S and the carbonation process give their strengths at long term [13].

634 The addition of micro spherical aluminosilicate particles (diameter of 50 µm) similar to  
635 fly ash (FA), into Alt mortar was confirmed through the SEM-EDS analyses, where  
636 these appear empty, cracked or filled with a viscous gel rich in calcium (Fig.7b). Using  
637 fly ash with small and spherical shape in mortar or concrete can reduce water demand of  
638 the mixtures [38]. Chemically, fly ash has pozzolanic activity, which is attributed to the  
639 presence of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. It reacts with calcium hydroxide (CH) during cement  
640 hydration, to form additional calcium silicate hydrate (CSH), calcium aluminate hydrate  
641 (CAH) [39] and calcium aluminosilicate (CAS) gels. This can also be explained by the  
642 denser and darker color matrix of Alt mortar under light optical microscopy and higher  
643 physico-chemical compatibility with Euville stone compared the other mortars. The  
644 addition of these spherical micro-capsules, seem to have been added to Alt mortar  
645 mixture in order to improve the mechanical properties acting as a self-healing  
646 cementitious material. Besides these spherical particles, the abundant circular air voids  
647 uniformly distributed in the binder's matrix of both Alt and Art mortars, that creates an  
648 apparently high visible porosity is most probably due to the addition of an air  
649 entrainment agent in the mortar mix [17].

The binder:aggregate ratio between 1:3 and 1:4 of the mortars from the buildings (Fig.5) is in agreement with ratios of similar mortars used in restoration works of historic buildings in other countries. Pecchioni et al. in 2005 [40] study some Florentine Palaces (Italy) and the analytical results show that the aggregates were composed by silicate sand and the binder/aggregate ratio ranged between 1:1 and 1:3, with presence of larnite.

Even though petrography and physical properties of Euville stone have been deeply studied [19,20], due to its high heterogeneity, the petrography and physical properties of the specific specimens used in this research was carried to study the compatibility with the stone-commercial mortars. The heterogeneity of this limestone has been also observed through on-site measurements on historic buildings and in-lab measurements with non-destructive techniques [32].

#### *4.2. Physical characterization*

In this research we have characterized water (liquid and vapour) transfer through mortars by means of imbibition properties (capillarity rise), evaporation (desorption test) and water vapour permeability. The results show that capillarity imbibition, evaporation and vapour permeability values of 28 hardened Art mortar specimens are higher than in the others mortars. The reason is the high porosity of this mortar with pore sizes slightly larger than the others. Art mortar specimens have physical properties close to those of Euville limestone but with a capillarity coefficient lower than the stone and a very low evaporation degree.

The mechanical behaviour of Lit and Art mortar specimens is very different from the obtained in Euville stone, being less resistant, especially in compression strength; Art mortar is the only one with higher flexural and compression strength values close to those of Euville stone.

675 The low open water porosity values of Lit mortar and the slightly higher values  
676 obtained through mercury porosity compared to water porosity can be explained by the  
677 hydrophobic characteristics of this mortar. Among other reasons, such as the content of  
678 clays in its composition, the possible presence of a water-repellent product in the mortar  
679 composition could explain crack formation, observed both at the interface of stone-  
680 mortar repaired areas at the Grand Palais building. Besides, in the case of these Lit  
681 mortar specimens, also a smooth coating is observed on the surface. This surface  
682 coating, ‘skin’ or ‘scum’ is known as laitance and is formed when fine lime particles  
683 held in suspension migrate to the outer surface of the wet material. This laitance is  
684 believed to hinder the vapour permeability of lime-based materials, and negatively  
685 impact upon the substrate beneath by causing accelerated masonry decay associated  
686 with entrapment of moisture. Therefore, it is recommended to remove this laitance from  
687 this type of restoration mortar, especially when applied to permeable substrates [9].

688 From the results of the mechanical properties, especially flexural strength, in the case of  
689 Alt and Lit mortars and Euville stone it depend, on the apparent density of the material,  
690 which is a function of porosity and bulk (mineral) density.  $C_2S$  phases, such as larnite,  
691 and the carbonation process provide strength in a longer term, while limestone  
692 aggregates also increase strength, due to the calcite syntaxial growth, which develops  
693 strength thereby enhancing the binder–aggregate interface [13]. This can explain the  
694 highest strength values in Alt mortar specimens with higher content in these mineral  
695 phases.

696 Regarding to spectrophotometry results, the highest total colour difference ( $\Delta E^*$ )  
697 between each mortar and Euville stone is obtained in Art mortar (circa 8), followed by  
698 Alt (circa 5) and Lit mortar that shows the lowest differences (circa 3). According to  
699 suitability criteria used to assess conservation treatments,  $\Delta E^*$  values lower than 5

according to the standard NORMAL 20/85 [41], and close to 3 according to other authors [42,43], would not be visually detectable by the human eye and it would not significantly affect the colorimetric parameters of the substrate, which only Lit and Alt mortars would fulfil this criteria after 28 days of hardening.

Repair mortars used for stone restoration are assumed to be highly compatible with historic materials in terms of physical, chemical and mechanical properties in order to assure the durability of masonry on the long term [3]. In this sense, these characteristics in Alt mortar are closer to those of Euville stone, compared to the other mortars, with the exception of some differences in the hydric properties due to their different pore systems and aesthetic features that should be improved in further restoration works. The obtained results cannot allow us to conclude which is the best mortar to restore Euville stone, and further studies about mortar-stone interactions will be necessary. This work is an essential step on the research concerning the compatibility and the potential durability of mortars and stone in masonry building restoration.

## **5. Conclusions**

The chemical and mineralogical composition of Euville limestone,(mainly composed of calcium carbonate) and all the studied anhydrous hydraulic mortars (NHL, HL) composed by di-calcium silicate ( $C_2S$ , larnite/belite), tri-calcium silicate ( $C_3S$ , alite), traces of di-calcium alumina silicate ( $C_3AS$ , gehlenite) with presence or absence of phyllosilicates (vermiculite, clinocllore and talc) and aerial lime (portlandite) seems to be critical in the chemistry of the 28 days hardened mortars. The mortar containing calcite, portlandite and no phyllosilicates (Altar Pierre) shows better chemical and mineralogical compatibility with the stone.

The soluble salts content of the raw anhydrous mortars is negligible. The presence of chlorides and sulfates (gypsum and mixtures of calcium and sodium sulfates) with

minor amounts of nitrates present in mortar samples collected from historic buildings of Paris suggest an origin of salts caused by contamination/pollution coming from past restoration products and environmental pollution.

Regarding to physical compatibility, the mortars containing higher amounts of phyllosilicates (clinochlore and talc) develop cracks on their surfaces or fissures close to the stone-mortar interface, as observed in Lithomex mortar samples collected from Grand Palais building. However, the aesthetical compatibility obtained from the total color difference values between this mortar and the stone indicates that this is not visually detectable by the human eye.

The addition of marble aggregates and 50-micron spherical aluminosilicate particles to Altar Pierre mortar, favoured hydrolyses reactions and produced a lower porosity matrix with closer hydric and mechanical properties to those of the Euville stone compared to the other two mortars. So, the physico-chemical properties of this mortar are closer to those of the stone, with the exception of some differences in the hydric behaviour due to their different pore systems and aesthetic features that should be improved in further restoration works.

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## 870    FIGURE CAPTIONS

871    **Figure 1.** Mortar and stone materials. a) Raw anhydrous ready to mix mortars (left: *Lit* mortar;  
872    center: *Alt* mortar; right: *Art* mortar); b) Euville stone specimen used for water vapour  
873    permeability test; c) 28 days hardened mortars specimens (Left: *Lit* mortar; center: *Alt* mortar;  
874    right: *Art* mortar) after capillarity water absorption test.

875    **Figure 2.** Mortar and stone samples collected from historic buildings of Paris. a) Lit mortar  
876    from Grand Palais building; b) Alt mortar from Préfecture Police building; c) Euville stone  
877    flake from Préfecture Police.

878    **Figure 3.** X-ray diffraction patterns (XRD) of the raw anhydrous mortars (Lit: Lithomex; Art:  
879    ArtoPierre;. Alt: Altar Pierre)

880    **Figure 4.** SEM-EDS analyses performed in several areas of mineral grains with sizes between  
881    1.6-1.25 mm and 1.25 mm-0.63 mm of Lithomex (Litho, Lit), ArtoPierre (Arto, Art) and Altar  
882    Pierre (Altar, Alt) mortars. a) phyllosilicates (clinochlore and talc), with and without additional  
883    K, Ti and Cl with sizes between 1.6-1.25 mm in Lit mortar; b) calcite grains (1.25 mm-0.63  
884    mm) in Lit mortar; c) phyllosilicates (1.25-063 mm) in Art mortar; d) calcite grains (1.25 mm-  
885    0.63 mm) in Alt mortar.

886    **Figure 5.** Thin sections obtained by light optical microscopy in mortar samples collected from  
887    historic buildings of Paris. a) Lit mortar from Grand Palais building (Lit-GP); b) same former  
888    image with crossed nicols; c) Lit mortar, detail of fissural porosity (in blue); d) same former  
889    image with crossed nicols; e) Alt mortar from Préfecture Police building (Alt-PP); f) same  
890    former image with crossed nicols; g) Alt mortar, detail of same sample showing porosity (in  
891    blue).

892    **Figure 6.** X-ray diffraction pattern of mortar samples collected from historic buildings of Paris.  
893    Lit-GP (Lithomex mortar from Grand Palais); Alt -PP (Altar Pierre from Préfecture Police); Lit-  
894    GP-sf (evaporated soluble fraction together with non-soluble residues).

**Figure 7.** Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) analyses performed on the surface of mortar and stone samples collected from historic buildings of Paris. a) Lit mortar from the Grand Palais; b) Alt mortar from Préfecture de Police; c) efflorescences in Euville stone flake from Préfecture de Police.

**Figure 8.** Connected porosity and pore size distribution obtained by mercury intrusion porosimetry in mortar samples collected from historic buildings of Paris. a) Lit mortar from Grand Palais; b) Alt mortar from Préfecture de Police.

**Figure 9.** Thin sections observed by light optical microscopy of the 28 days hardened mortars manufactured in the lab and of Euville stone. a) Lit mortar with parellel nicols; b) same former image with crossed nicols; c) Alt mortar with parellel nicols; d) same former image with crossed nicols; e) Art mortar with parellel nicols; f) same former image with crossed nicols; g) Euville stone with parellel nicols; h) same former image with crossed nicols.

**Figure 10.** X-ray diffraction pattern of 28 days (28d) hardened mortars manufactured in the laboratory (Lit: Lithomex mortar; Art: Artopierre mortar; Alt: Altar Pierre mortar).

**Figure 11.** Representation of hydric properties of 28 days hardened mortars and stone specimens. a) capillarity water absorption of mortars; b) water desorption (water loss) of mortars; c) capillarity water absorption of Euville stone; d) water desorption (water loss) of Euville; e) water vapor permeability of mortars; f) water vapor permeability of Euville stone.

**Figure 12.** Connected porosity and pore size distribution obtained by mercury intrusion porosimetry in 28 days hardened mortars and Euville stone.

917 Table 1. Semi-quantitative (%) X-ray diffraction (XRD) analyses of the raw anhydrous and 28 days hardened mortars together with mortar samples  
 918 from historic buildings from Paris

Mortar	Calcite	Quartz	Feldspar	Gypsum	Clinochlore	Talc	Dolomite	Muscovite	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>2</sub> AS	CH	halite
Lit-raw	20	10	5	Nd*	10	45	traces	Nd*	5	5	traces	Nd*	Nd*
Art-raw	15	50	traces	Nd*	Nd*	Nd*	Nd*	Nd*	5	10	traces	20	Nd*
Alt-raw	20	35	15	traces	Nd*	Nd*	Nd*	Nd*	5	10	traces	15	Nd*
Lit-GP*	14	14	10	5	21	20	Nd*	16	Nd*	Nd*	traces	Nd*	Nd*
Lit-GP <sub>-sf</sub> *	15	5	Nd*	8	49	18	Nd*	Nd*	Nd*	Nd*	Nd*	Nd*	5
Alt-PP	15	60	14	Nd*	Nd*	Nd*	Nd*	Nd*	Nd*	6	traces	5	Nd*
Lit-28D	20	21	5	Nd*	26	28	Nd*	Nd*	Nd*	traces	Nd*	Nd*	Nd*
Art-28D	20	61	9	Nd*	traces	Nd*	Nd*	Nd*	Nd*	5	traces	5	Nd*
Alt-28D	18	50	20	Nd*	Nd*	Nd*	Nd*	Nd*	traces	6	traces	6	Nd*

919 \*Nd: No detected; Lit: Lithomex mortar; Alt: Altar Pierre mortar; Art: ArtoPierre mortar; raw: anhydrous raw mortar; GP: Grand Palais building; PP:  
 920 Préfecture Police building; sf: evaporated soluble fraction; 28D: 28 days hardened mortar; C<sub>2</sub>S: Di-calcium silicate, Ca<sub>2</sub>SiO<sub>4</sub> (larnite/belite); C<sub>3</sub>S: Tri-  
 921 calcium silicate, Ca<sub>3</sub>SiO<sub>5</sub> (alite); CH: Calcium hydroxide (portlandite); C<sub>2</sub>AS: gehlenite

922

923 Table 2. Qualitative elemental analyses performed by punctual energy dispersive spectroscopy (SEM-EDS) on several  
 924 grains of the largest grain size fractions (aggregates) of the raw anhydrous mortars embedded in epoxy resin.

Mortar	Lit mortar		Art mortar		Alt mortar	
Grain size interval	1.60-1.25mm	1.25-0.63mm	1.60-1.25mm	1.25-0.63mm	1.60-1.25mm	1.25-0.63mm
Normalized wt. %						
Ca	Present	Present	Present	Present	Present	Present
Si	Present	Present	Present	Present	Present	Present
Al	Present	Present	Present	Present	No detected	No detected
Mg	Present	Present	Present	Present	No detected	No detected
O	Present	Present	Present	Present	Present	Present
C	Present	Present	Present	Present	Present	Present
K	Present	No detected	Present	Present	No detected	No detected
Na	Present	Present	Present	No detected	Present	No detected
Fe	Present	Present	Present	Present	No detected	Present
Ti	Present	No detected	Present	Present	No detected	Present
Cl	Present	No detected	Present	Present	Present	Present

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Table 3. Semi-quantitative (%) energy dispersive spectroscopy (EDS) analyses performed on the finest grain size fractions (aggregates and binder) of the raw anhydrous mortars pressed on tablets.

Grain size	0.63-0.315 mm			0.315-0.20 mm			0.20-0.16 mm			0.16-0.080 mm			<0.080 mm		
Mortar	Lit	Art	Alt	Lit	Art	Alt	Lit	Art	Alt	Lit	Art	Alt	Lit	Art	Alt
Normalized wt. %															
Ca	13.1	19.7	3.8	11.0	11.3	5.4	9.3	38.3	27.0	7.5	32.6	28.3	3.9	39.7	33.0
Si	19.2	23.0	39.0	20.7	33.1	41.2	11.0	8.0	6.3	5.2	5.5	5.6	8.0	2.4	6.3
Al	0.5	0.4	1.1	0.6	0.6	1.5	0.8	0.4	1.4	1.2	0.5	1.7	1.9	0.5	1.8
Mg	0.5	0.5	0.2	0.4	0.4	0.2	1.2	0.4	1.8	4.8	0.5	2.2	7.7	0.5	1.8
O	52.3	45.6	50.8	50.7	48.0	48.0	59.8	46.7	54.8	61.8	52.5	54.0	61.9	49.1	50.2
C	12.6	10.8	4.6	14.7	6.2	2.5	17.6	5.8	7.1	19.3	7.4	7.3	16.1	7.3	6.0
S	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	1.0	0.3	0.4	0.7	0.4	0.4	0.8
K	0.2	0.0	0.8	0.2	0.4	1.2	0.0	0.2	0.1	0.0	0.2	0.0	0.0	0.1	0.0
Na	0.0	0.0	3.8	0.0	0.0	5.4	0.0	0.0	27.0	0.0	0.4	0.4	0.0	0.0	33.0

\*Lit: Lithomex mortar; Art: Artopierre mortar; Alt: Altar Pierre mortar

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931 **Table 4.** Soluble salt content determined by ion chromatography analyses of the raw anhydrous mortars

Soluble salts		Anions (ppm)				Cations (ppm)					Wt. (%)
Samples		Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	
anhydrous mortar	Lit	5	23	0	0	22	0.00	3	1	129	2
	Art	5	0	0	0	16	0.00	3	1	534	5
	Alt	6	0	0	0	22	0.00	3	3	165	2

932



933 **Table 5.** Soluble salt content determined by ion chromatography analyses of mortar and stone samples collected from Grand

934 Palais (GP) and Préfecture Police (PP) buildings.

Soluble salts		Anions (ppm)				Cations (ppm)					wt.
Samples		Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	(%)
Mortar	Lit-GP	30	105	25	0	22	0	9	5	97	3
From buildings	Alt-PP	12	21	34	0	17	0	2	2	15	1
Stone flake	EU-PP	17	984	0	0	58	0	152	7	261	13

935

936 **Table 6.** Results from hydric characterization of 28 days hardened mortars and stone specimens

Properties / samples	Lit mortar	Art mortar	Alt mortar	Euville stone
Capillary Coefficient (g/m <sup>2</sup> .s <sup>0.5</sup> )	11.63	73.85	43.20	45.60
Desorption Coefficient (g/m <sup>2</sup> .s <sup>0.5</sup> )	-5.16	-29.41	-7.79	-49.80

Water vapour permeability Kg/ (m.s.Pa)	3.08E-11	4E-11	1.79E-11	1.57E-11
Open porosity (%)	31.1 ± 1.1	39.1 ± 1.0	25.0 ± 0.2	16.5 ± 1.0
Apparent density (g/cm <sup>3</sup> )	1.67 ± 0.00	1.58 ± 0.01	1.88 ± 0.03	2.25 ± 0.02
Bulk density (g/cm <sup>3</sup> )	2.45 ± 0.04	2.59 ± 0.00	2.51 ± 0.01	2.69 ± 0.01

937

938 **Table 7.** Mercury intrusion porosimetry results obtained in 28 days hardened mortars and stone

Properties / samples	Lit mortar	Art mortar	Alt mortar	Euville stone
Porosity (%)	32.24	31.77	21.13	14.92
Apparent density (g/cm <sup>3</sup> )	1.69	1.57	1.88	2.17
Bulk density (g/cm <sup>3</sup> )	2.49	2.30	2.38	2.55
Average pore radius (μm)	0.10	0.13	0.04	1.47
Median pore radius (μm)	0.48	0.41	0.01	0.82
Mode pore radius (μm)	0.76	0.95 (0.28)	0.34 (0.25)	0.60

939

940 **Table 8.** Flexural and compression strength of 28 days hardened mortars and Euville stone.

Strength (MPa)	Lit mortar	Art mortar	Alt mortar	Euville stone
Flexural	$3.91 \pm 0.05$	$2.22 \pm 0.08$	$4.22 \pm 0.16$	$4.84 \pm 0.35$
Compression	9.01*	<7	$15.65 \pm 2.88$	$27.07 \pm 5.25$

941 \* In the other specimens compression was <7

942 **Table 9.** Colour parameters ( $L^*$ , lightness;  $a^*$  and  $b^*$  colour coordinates;  $C^*$ , Chroma;  $\Delta E^*$ , total colour difference) obtained in

943 28 days hardened mortar specimens and Euville stone.

Material	$L^*$	$a^*$	$b^*$	$C^*$ (D65)	Hue (D65)	$\Delta E^*$
Lit	$78.44 \pm 0.10$	$2.35 \pm 0.02$	$11.32 \pm 0.04$	$11.56 \pm 0.04$	$78.30 \pm 0.06$	3.22
Art	$88.05 \pm 0.11$	$0.93 \pm 0.03$	$6.34 \pm 0.08$	$6.47 \pm 0.08$	$81.72 \pm 0.13$	7.80
Alt	$76.36 \pm 0.06$	$1.60 \pm 0.01$	$9.56 \pm 0.03$	$9.70 \pm 0.04$	$80.50 \pm 0.06$	5.16
Stone	$81.38 \pm 1.09$	$2.68 \pm 0.28$	$10.06 \pm 1.44$	$10.41 \pm 1.45$	$74.98 \pm 1.46$	Reference

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FIGURE 1

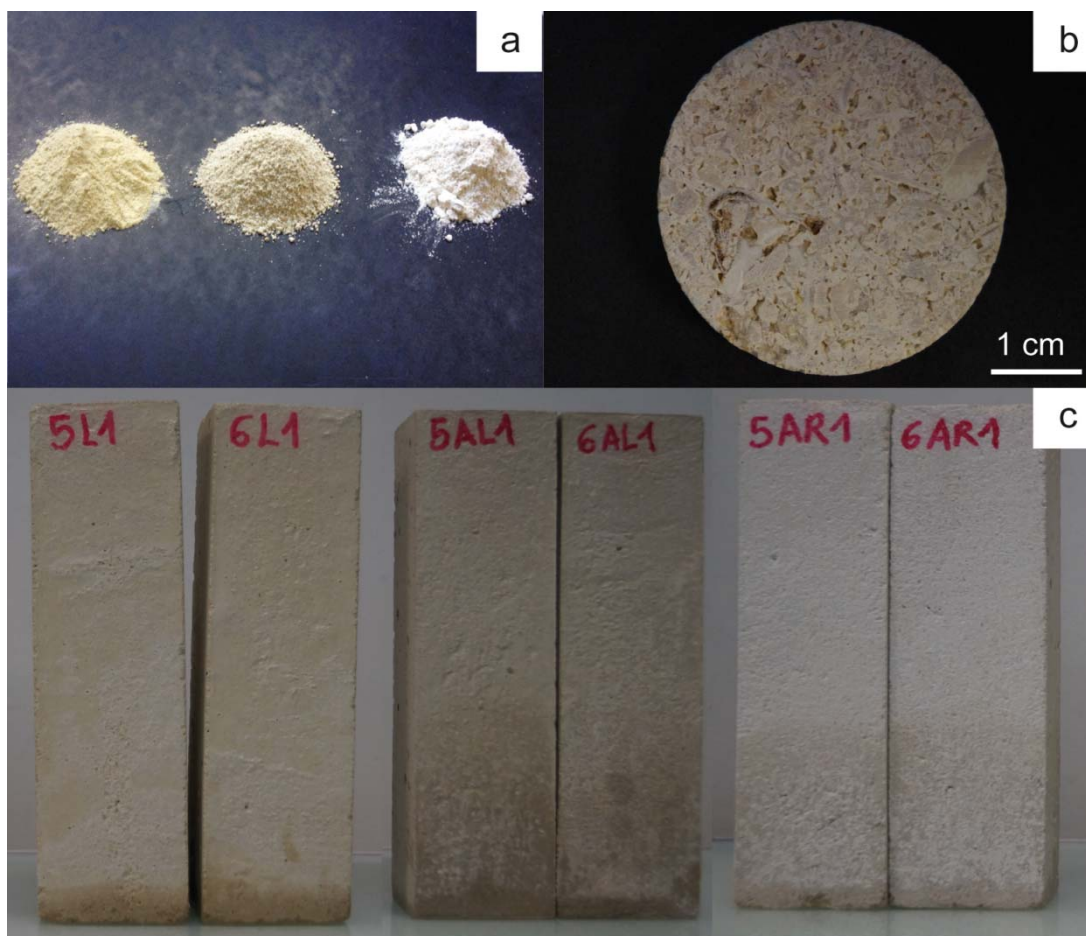


FIGURE 2

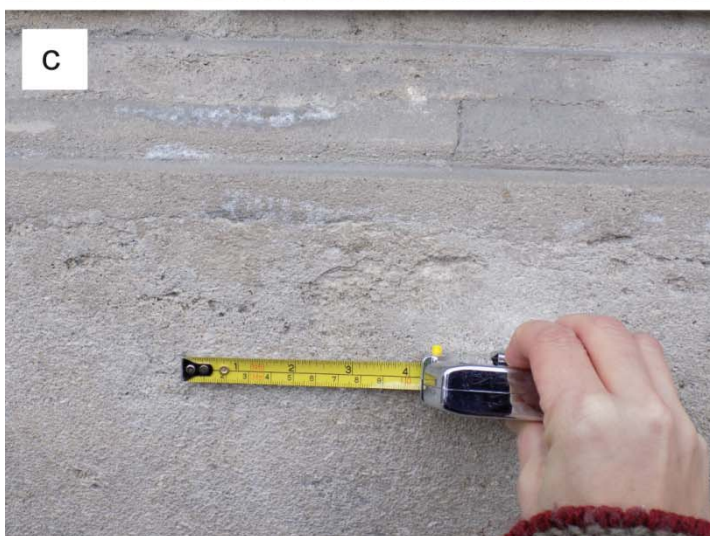




FIGURE 4

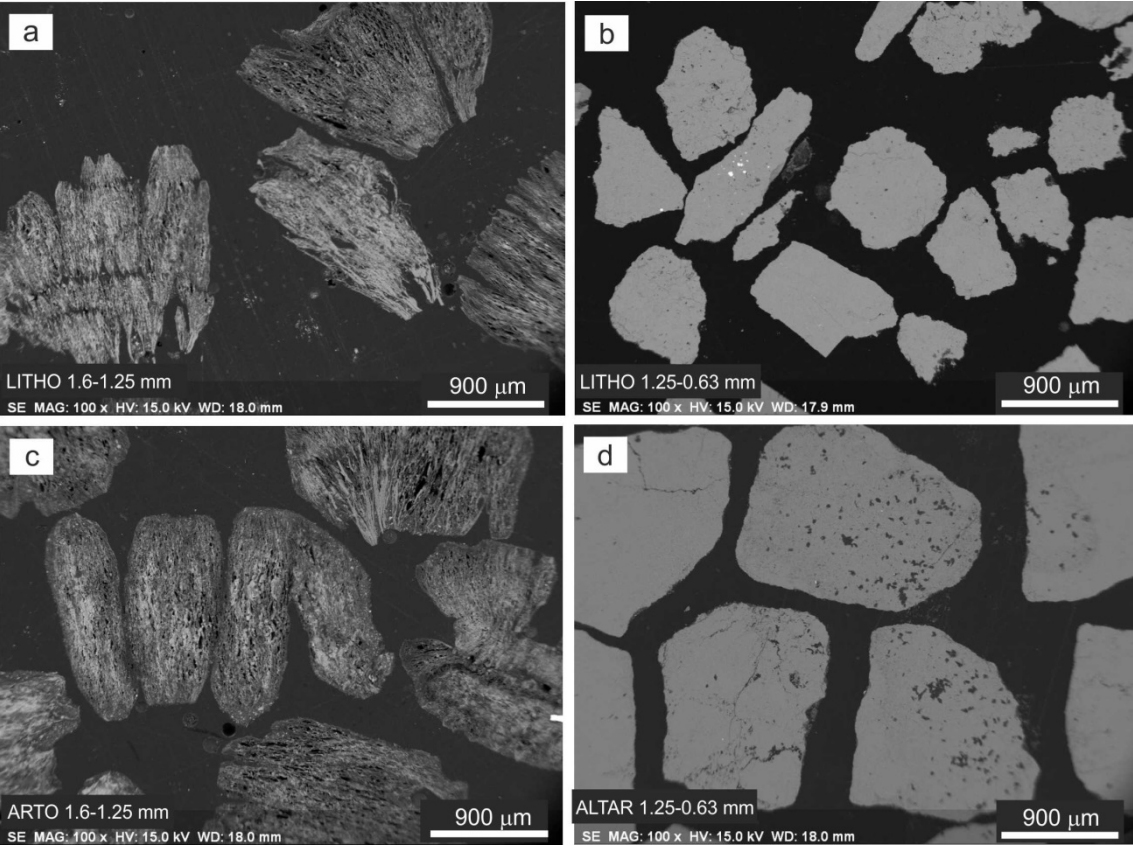
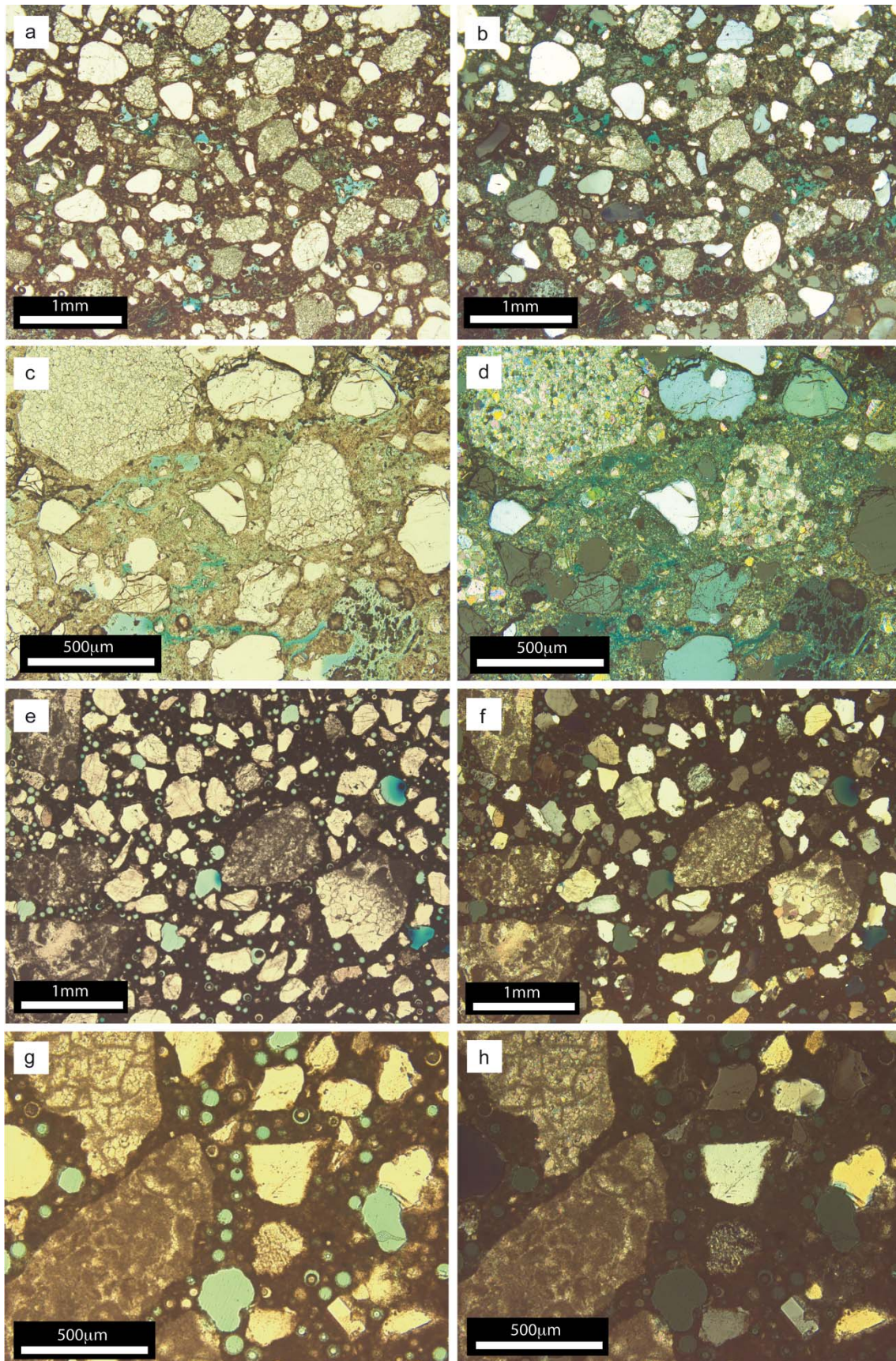




FIGURE 5





# FIGURE 6

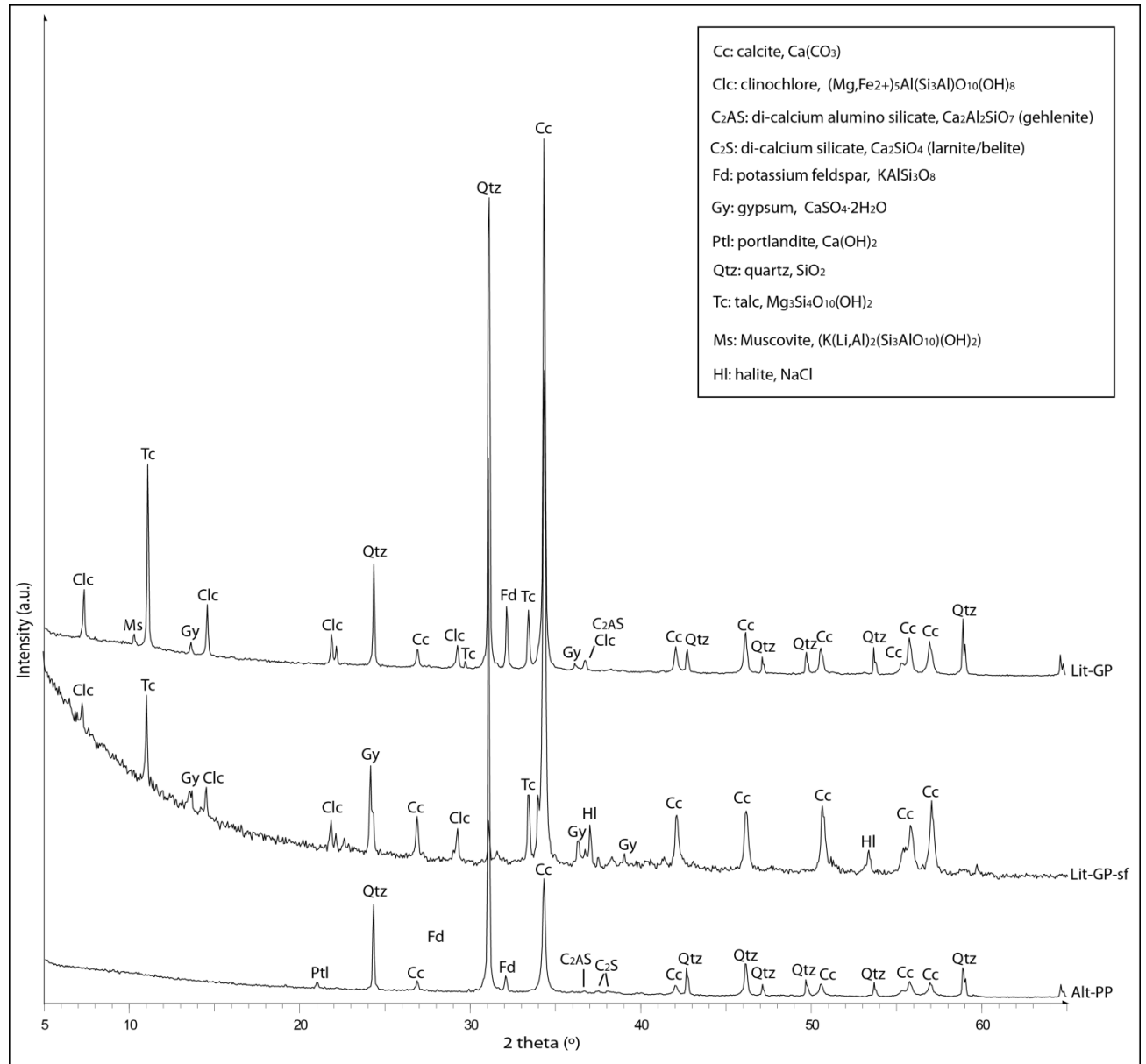


FIGURE 7

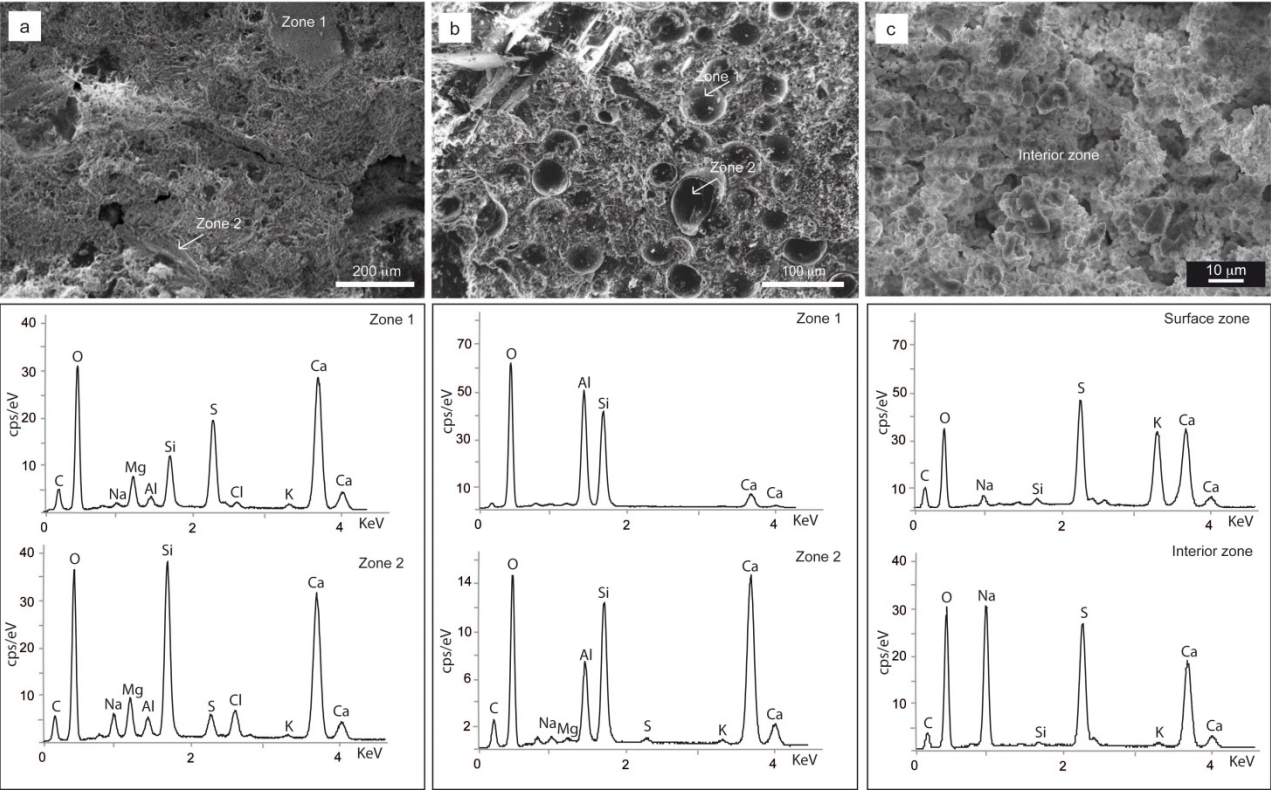


FIGURE 8

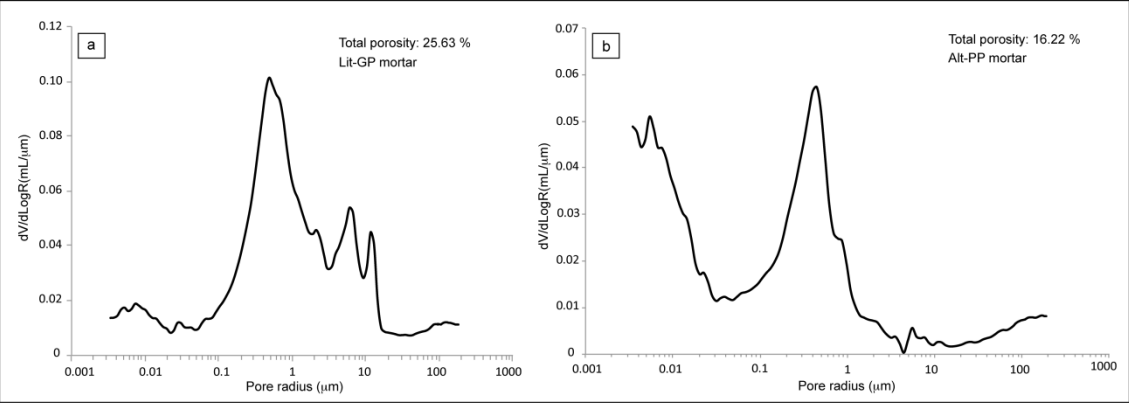
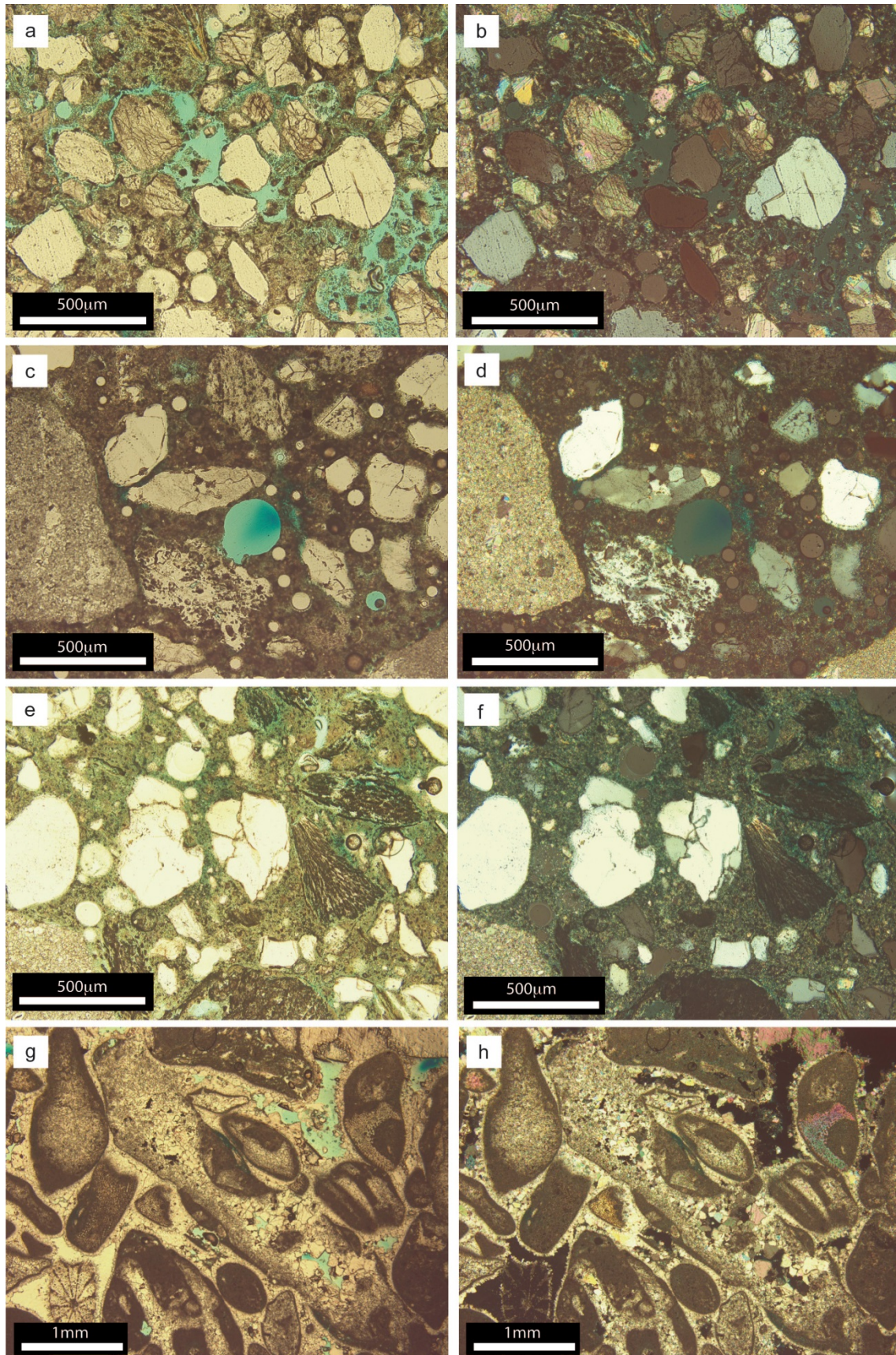




FIGURE 9



# FIGURE 10

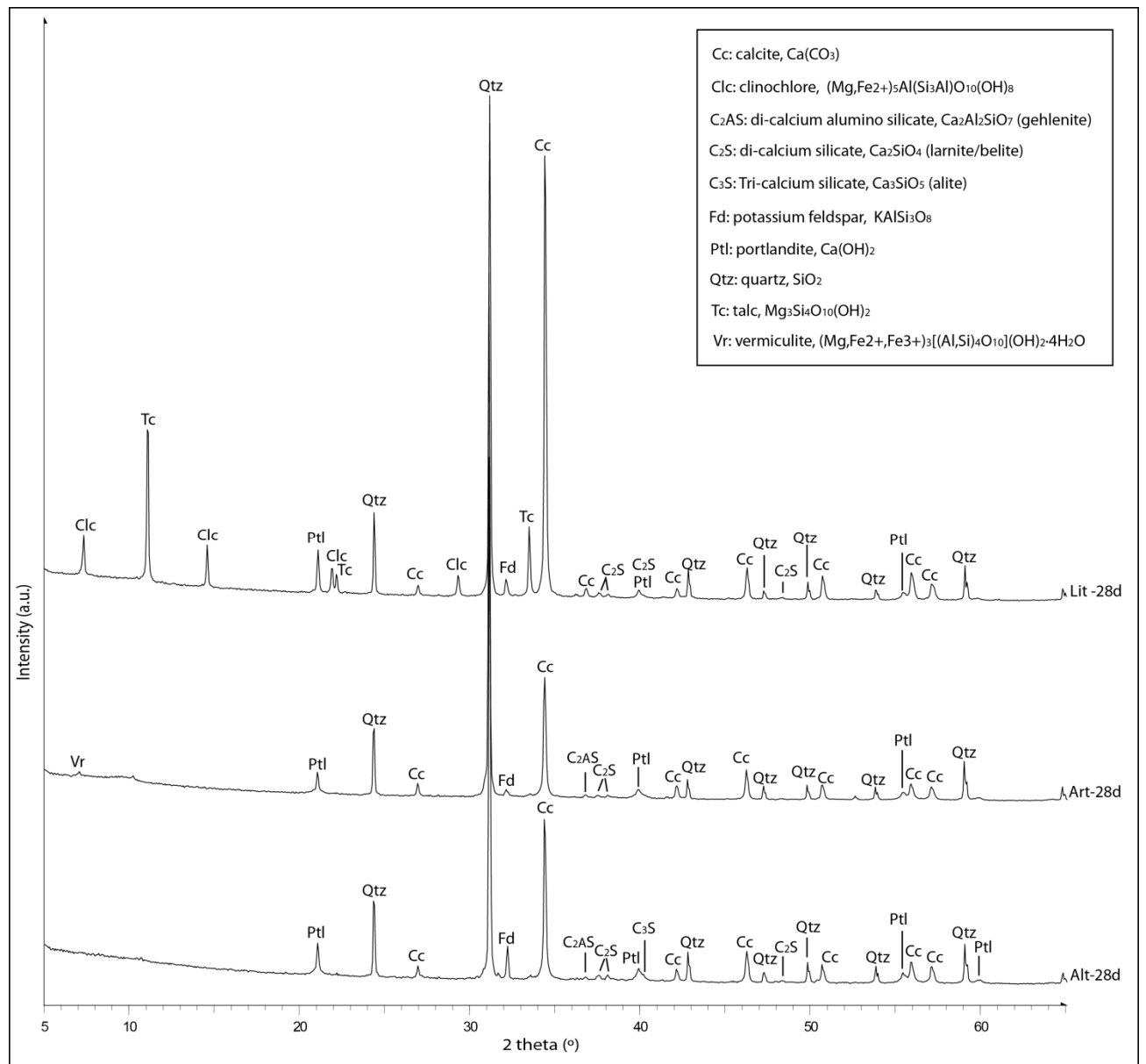


FIGURE 11

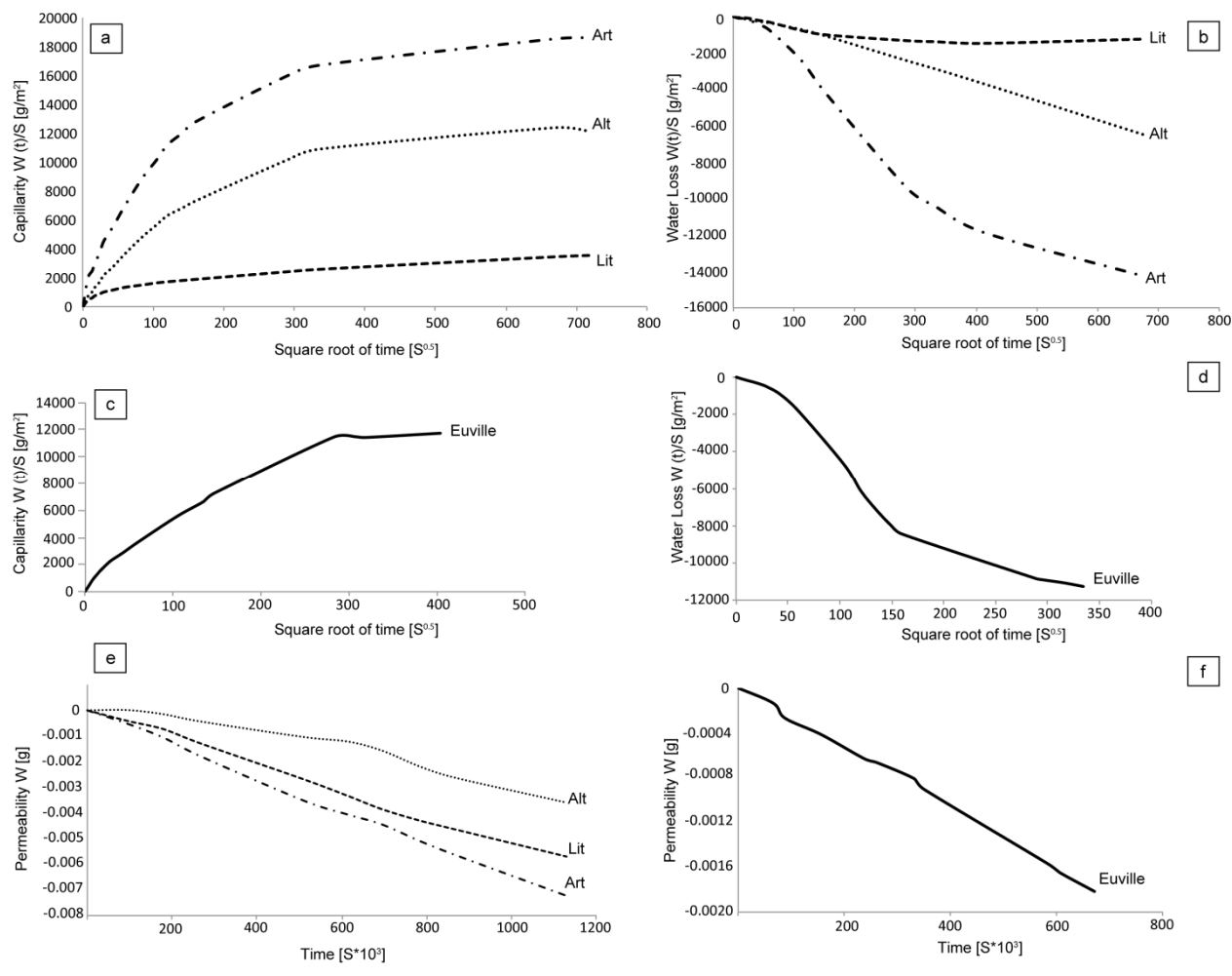


FIGURE 12

