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Influence of animal glue on mineralogy, strength and weathering resistance of lime plasters



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HIGHLIGHTS

• Animal glue increases weathering resistance of lime-based materials.

• Animal glue reduces crack formation upon drying of plasters and improves adherence.

• Formation of an organic/inorganic hybrid material in the presence of animal glue.

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ABSTRACT

In order to optimize lime plasters for conservation purposes, the influence of animal glue on the mineralogical evolution, mechanical properties, and weathering resistance was studied. The organic additive caused a decrease in carbonation rate and affected mechanical properties negatively, facilitating the formation of large air bubbles in the plaster matrix. However, the weathering resistance (water spraying/SO₂ exposure) improved significantly. The organic additive also reduced crack formation and formed a physical barrier around the calcite crystals, which delayed sulfation. Lime-based composite materials are a valuable alternative to conventional lime plasters, showing improved adherence to the substrate and no significant color changes.

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1. Introduction

Lime has been used as a binder in mortars and plasters since ancient times and earliest examples of its use in architecture by the Natufian date back to ~10,000 BC [1]. Its use declined in the second half of the 19th century with the introduction of Portland cement [2]. However, over the last decades lime experienced a revival as a compatible material for the conservation of architectural heritage [3,4], because of the low chemical and physicalmechanical compatibility of Portland cement with most historic building materials (i.e., low flexibility and permeability, often excessive strength, and source of harmful salts [5]. Lime (calcination $T = \sim 900$ °C) is also a more sustainable, energy efficient building and construction material as compared to Portland cement (i.e., Portland cement requires intensive grinding of the clinker and a very high calcination $T (\sim 1450$ °C)).

Historically, shortcomings regarding the water resistance and strength of lime mortars and plasters prompted the use of inorganic and organic additives [6]. While extensive research has been dedicated to the interactions between lime and inorganic additives such as fly-ash and clays [7–9], only limited data are available on the effect of organic additives on the properties and performance of lime-based materials. Sickels [10] provided a comprehensive list of traditional organic additives of plant and animal origin used in Mediterranean countries and northern Europe since the last century BC, which includes animal glue, egg, blood, casein, fig juice, and gum arabic. In Latin America and India water-soluble plant extracts (e.g., cactus extract) were often added to lime mortars and plasters [11], and in Asia sticky rice, tung oil, as well as blood have been used [12,13]. Only recently, the revived interest in traditional lime technology has prompted research into the effect of traditional organic additives on the lime mortar's properties [14–19]. Generally, a positive effect of organic additives on workability, drying shrinkage, weathering resistance and mechanical properties has been reported [10,19–21].



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However, most of the organic additives likely act as retarder for the carbonation of portlandite, which could negatively affect the mechanical properties and durability of lime mortars, renders, and plaster [16]. To date no systematic study has been performed, which relates the mineralogical and microstructural evolution of lime-based materials in the presence and absence of an organic additive (i.e., animal glue) with mechanical properties and weathering resistance. In an effort to determine whether lime plaster could be prepared with an adequate amount of organic additive, which would allow for a sufficiently rapid carbonation and, at the same time, improve its weathering resistance, plaster samples with varying amounts of organic additive have been exposed to accelerated aging (i.e., water spraying and exposure to a saturated SO₂ atmosphere at high relative humidity, RH). Furthermore, flexural and compressive strength, as well as linear crack development and color changes were measured. Experimental results were related with the samples' mineralogical and microtextural evolution. The findings of this study have important implications for the selection of adequate materials for the conservation and restoration of architectural heritage.

2. Materials and methods

2.1. Materials

Analytical grade Ca(OH)₂ powder (Guinama S.L.U., Spain) and animal glue (rabbit skin glue, ref. 63028, Kremer Pigment GmbH & Co, Germany) were used for plaster preparation. Animal glue is a collagen-based material which is readily available and has been widely used throughout history as an adhesive, binder and additive for plasters and mortars [10]. It is derived from hides and consists of long protein molecules, which are made up of amino acids linked by covalent peptide bonds [22]. Amino acids contain amino and carboxyl functional groups which can form metal-protein complexes with the hydrated lime [23].

2.2. Sample preparation

Plasters with an organic additive content of 1, 2, 5, and 10 wt % were prepared as follows: the appropriate amount of animal glue (i.e., 0.05, 0.1, 0.2, and 0.5 g), was soaked in 8 g deionized water and afterwards heated in a water bath $(47 \pm 2 \circ C)$ under occasional stirring to obtain a homogeneous mixture. Note that the organic additive contents were chosen considering published recommendations [12,14,20]. After cooling to room *T*, the aqueous animal glue solution was mixed with 5 g calcium hydroxide under stirring to obtain a homogeneous mixture, keeping the solid/liquid ratio constant at 1:1.6 by weight. For comparison, calcium hydroxide was mixed with deionized water without the addition of animal glue, maintaining the same solid/liquid ratio as in the case of the animal glue-based plaster samples. Two sets of samples were prepared for the laboratory studies: (I) For accelerated weathering testing (water spraying and SO_2 test), 1 g of plaster was applied on a circular glass slide $(\emptyset$ 3.3 cm), using a pipette to produce plaster thin films. The thickness of the carbonated plaster layer was 0.91 ± 0.14 mm. (II) For mechanical testing small plaster prisms, $5 \times 5 \times 30 \text{ mm}$ in size, were prepared using plasticine molds, maintaining the same additive content and mixing ratio as described above. Samples were cured at ${\sim}20\ensuremath{\,^\circ C}$ and ${\sim}75\%$ RH during the first 28 days. Afterwards the carbonation reaction was accelerated by periodic (every other day) water spraying for another month (see XRD results below).

2.3. Testing

2.3.1. Accelerated weathering test (water spraying)

Plaster thin films (i.e., plaster applied to glass slides) were attached to a vertical plastic grid with double-sided tape and exposed to repeated spraying (1 L/sample/day) with deionized water at a distance of 30 cm. Spraying was repeated 7 times over a 3 week period. Water resistance was determined by measuring the material loss over time. Samples were dried under laboratory conditions for 2 days (i.e., until a constant weight was reached) to determine the weight loss between each spraying. Spraying and drying was performed under laboratory conditions (25 °C and 30% RH).

2.4. SO₂-aging test

A test method used for the determination of the resistance of natural stone to SO₂-induced aging at high humidity was adapted [24] in order to determine the susceptibility to sulfation of completely carbonated plasters. Plaster thin films (i.e., plaster applied to glass slides) were placed on a horizontal plastic grid in a hermetically sealed plastic container (7.5 L) together with a glass dish containing 104 mL diluted sulfurous acid (1.35 wt% SO₂) to generate a saturated SO₂ atmosphere and ~100% RH. Samples were protected from condensation droplets accumulating on the container lid by laboratory paper, which was placed between the lid and the samples. The mineralogical evolution was monitored by XRD after 24, 46, 72, 96, 144, 196, and 338 h. Each time the container was opened, the acid solution was replaced to assure a saturated SO₂ atmosphere.

2.4.1. Mechanical testing

Tensile and compressive strength of prismatic plaster samples were determined using an Instron 3345 (Instron Co., Canton, MA). A load of 500 N at 1 mm/min was applied for tensile strength measurements. Compressive strength was measured with a load of 500 N at 3 mm/min. Reported average values are based on 4 (flexural strength) and 6 (compressive strength) measurements per sample. Note that according to standard test methods [25], mortar strength should be determined after 28 days of curing. Here curing time was extended to 2 months in order to increase the plasters' degree of carbonation.

2.5. Analytical techniques

X-ray diffraction (X'Pert PRO PANalytical B.V., the Netherlands) was used to determine the mineralogical evolution of plasters during carbonation (plaster thin films and prismatic plaster samples) and exposure to the SO₂-aging test. Analyses were performed using Cu-K α radiation, Ni filter, 45 kV voltage, 40 mA intensity and spinner. The exploration range was 3–60 °2 θ and the goniometer speed 0.05 °2 θ s⁻¹. Identification and semi-quantification (±5 wt%) of minerals were carried out using Xpowder software [26].

Morphological features and chemical composition of plaster samples upon carbonation and SO_2 -aging were studied using a Field Emission Scanning Electron Microscope (FESEM, Auriga, Carl Zeiss, Germany), working at 10^{-4} Pa vacuum and 3 kV in secondary electron imaging mode, and 15 kV for elemental analysis (Energydispersive X-ray spectroscopy, EDS). Samples were carbon coated.

Conformational changes in animal glue and mineralogical changes upon carbonation in lime plasters were studied using attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy (Jasco 6200, JASCO Analytical Instruments, Japan). Small powder samples of plasters and pure animal glue were analyzed at 2 cm⁻¹ resolution over 75 scans from 400 to 4000 cm⁻¹.

Linear crack formation (cm^{-1}) was calculated using photographic images of dried plaster thin films applied to glass slides according to the following equation: crack length (cm)/sample area $(cm^2) =$ linear crack density (cm^{-1}) . Average values are based on 3 samples and the standard deviation is included.

Porosity and pore size distribution were determined by means of mercury intrusion porosimetry (MIP), using a Poremaster-60 GT (Quantachrome Instruments, US). Samples were dried at $60 \,^{\circ}$ C during 12 h prior to analysis. The samples' apparent density was determined with a microultrapycnometer (Quantachrome Instruments, US) using He.

Textural features of prismatic plaster samples were studied using X-ray computerized axial microtomography (u-CT, Zeiss Xradia 510 Versa, Germany). This equipment allows the visualization of distribution patterns of materials with different attenuation values (depending on density and chemical composition) through a reconstruction of sets of parallel cross-sections, perpendicular to the axis of rotation within the scanner. Equipment settings: 1.56 µm pixel size, 1996 images, 80 kV accelerating voltage and 88 µA beam current, 50-70 s exposure time, LE4, 5 or 6 source filter, 60 mm source-sample distance and 70 mm detector-sample distance, and 4x magnification. Image reconstruction was done with Reconstructor Scout and Scan (Zeiss, Germany) using a 0.5 Recon filter and 3201 projections. Dragonfly Pro (Object Research System, Canada) was used for advanced post-processing and quantification of image data for material characterization. Porosity calculations were performed by defining manually the gray value range used for segmentation.

Color parameters of carbonated plaster thin films before and after SO₂-aging were measured with a Minolta CM-700d portable spectrophotometer using a 10° observer, 8 mm measuring aperture, and standard daylight illuminant D65 (color temperature: 6504 K). Data were expressed in CIEL*a*b* color space, where L* is luminosity or lightness (black = 0 and white = 100); a* from +a* (red) to $-a^*$ (green), and b* from +b* (yellow) to $-b^*$ (blue). Color changes were expressed as ΔL^* , Δa^* , Δb^* , and ΔE^* ($\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$. Average values based on 10 measurements are reported.

3. Results and discussion

3.1. Mineralogical evolution upon carbonation in the presence of organic additive

XRD analyses of plaster thin films revealed that the rate of carbonation was significantly reduced in the presence of the



organic additive (Fig. 1). Larger amounts of additive were more effective in slowing down carbonation (Table 1). It was also observed that the rate of carbonation slowed down significantly over the course of the curing process (i.e., after 3 days), especially in the case of samples containing ≥ 5 wt% animal glue. Remarkably, between 3 and 28 days, the carbonation rate was slightly higher in samples containing 1 and wt% organic additive than in the one without additive. Most likely, the hygroscopic animal glue acted as a moisture retainer in the former samples and slowed drying. The carbonation process was thus facilitated because it requires water in order to proceed according to the following reaction: $Ca(OH)_2$ (s) + CO_2 (g) + H_2O (aq) \rightarrow $CaCO_3$ (s) + $2H_2O$ (aq) + heat \uparrow (74 kJ/mol) [27]. Findings by Walker and Pavia [28] support this hypothesis regarding the positive effect of water retainers on the carbonation reactions. In the case of samples containing 5 and 10 wt% additive this effect was not observed, likely because the large amounts of animal glue formed a superficial film around portlandite particles (see FESEM below), obstructing the access of water and CO₂ to the carbonation front and, thus, delaying portlandite dissolution and carbonation (Table 1). After 28 days, carbonation was still incomplete and samples were moistened by periodic (every other day) water spraying to speed up the process. According to XRD analysis, carbonation was complete in all plaster thin film samples after an additional 11 days (Fig. 1). These results again underline the importance of water in the carbonation process. Note that fully carbonated samples only contained calcite and no other calcium carbonate polymorph was detected.

3.2. Effect of the organic additive on morphological features of carbonated plasters

FESEM images (Fig. 2) document the effect of the organic additive on the morphological features of carbonated plaster thin films containing calcite as the only crystalline phase according to XRD. In the case of samples prepared with 0 and 1 wt% organic additive, typical scalenohedral calcite crystals were observed (Fig. 2a and b). However, in the former sample aggregated nano-sized crystals could be clearly distinguished in these calcite crystals, while in the latter the scalenohedral crystals were more compact and showed a smoother surface (Fig. 2b). In the remaining samples a granular structure covered with the organic additive predominated and scalenohedral calcite crystals were not detected (Fig. 2c-e). In samples with 5 and 10 wt% additive (Fig. 2d and e) calcite was covered with a continuous film of animal glue, which likely acted as a physical barrier for CO₂ and slowed down the carbonation of portlandite (see XRD results above). Furthermore, part of the portlandite transformed into rhombohedral calcite crystals with rounded edges in the sample with 10 wt% organic additive (Fig. 2f, dashed arrows). Note that the rhombohedral form is the equilibrium shape of calcite. However, in the presence of excess Ca²⁺ and at high pH, scalenohedral calcite crystals preferentially form, because {2 1 3 4} scalenohedral faces interact more strongly with excess Ca^{2+} than non-polar {1 0 1 4} rhombohedral faces [29].

It can be assumed that the scalenohedral calcite crystals form an interlocked structure with superior mechanical properties [29] as compared to the rhombohedral or granular structure in samples with higher organic additive content.

Remarkably, some of the rhombohedral calcite crystals had rounded edges. This morphological feature has been related with the formation of an organic-inorganic hybrid material [30]. According to Orme et al. [31] rounding of grow steps, macroscopically manifested as crystal edge rounding, is caused by the adsorption of amino acids to specific, non-structurally equivalent steps of calcite, leading to step pinning. Theoretically, these new hybrid



Table 1

Influence of the o	organic additive co	ontent on the a	legree of carbo	onation (calculated	d values based	on XRD results)

Organic Content (wt%)	CaCO ₃ content (wt%) after 28 days	Decrease in carbonation degree (%)°	Increase in CaCO ₃ (wt%/day)		
			1–3 d	3–28 d	>28 d
0	77.5	0	20.4	0.66	3.75
1	70.7	9	17.3	0.76	4.88
2	65.8	15	15.9	0.73	5.70
5	47.6	39	12.7	0.38	4.76
10	35.4	54	9.7	0.25	5.87

* After 28 days, with respect to the sample without organic additive.

* During water spraying.



Fig. 2. FESEM images of carbonated plaster: a) with 0 wt% organic content; b) with 1 wt% organic additive; c) with 2 wt% organic additive (solid arrow shows presence of animal glue); d) with 5 wt% organic additive (solid arrows show calcite covered by animal glue); e) with 10 wt% organic additive (solid arrows show calcite covered by animal glue); e) with 10 wt% organic additive (solid arrows show calcite covered by animal glue); e) with 10 wt% organic additive (solid arrows show calcite covered by animal glue); e) with 10 wt% organic additive (dashed arrows indicate rhombohedral calcite crystals with rounded edges).

materials, mimicking biominerals, could confer improved weathering resistance to the carbonated plasters [32].

3.3. ATR-FTIR analysis of plasters

ATR-FTIR data of partially carbonated plaster samples confirmed XDR results, showing a decrease in the degree of carbonation as the organic additive content in plasters increased (Fig. 3). This was indicated by an increase in the v(OH) band (O—H stretching, indicative of portlandite) at 3640 cm⁻¹, a decrease of the v₃- and v₂-asymmetric (CO_3^{2-}) band (indicative of carbonates) at 1400 and 871 cm⁻¹, respectively, and a decrease in the v₄-symmetric (CO_3^{2-}) band (indicative of calcite) at 711 cm⁻¹.

ATR-FTIR analysis also revealed a blue shift of the amide I band of animal glue from 1628 to 1649 cm⁻¹ upon mixing with Ca(OH)₂ (Fig. 3, only visible in plaster containing 10 wt% organic additive). This shift indicates an important change in the conformational structure, from β -sheet to random coil, causing a reduction in the number of hydrogen bonds-between N—H and C=O groups of protein chains, which thus offer sites (i.e., carboxyl groups) for the formation of Ca-protein complexes [16,33,34]. Note that possible changes in the position of the amide II band at 1526 cm⁻¹ could not be determined because this band was masked by the highintensity v₃-asymmetric (CO₃²⁻) band. These results together with FESEM observations, showing calcium crystals with morphological features typical of hybrid materials, suggest some organic-



Fig. 3. ATR-FTIR spectra of pure animal glue and partially carbonated plaster containing 0, 2, and 10 wt% organic content after 14 days of curing.

inorganic interactions between the animal glue and the portlandite/calcite, which could possibly influence the plasters properties and durability.

3.4. Crack formation upon drying

Crack formation in lime plasters is commonly related to shrinkage during drying [34]. Early-age cracking during drying was significantly reduced in the presence of the organic additive (Table 2 and Fig. 4). The linear crack density decreased by 70% when only 1 wt% of animal glue was added and an addition of >5 wt% completely prevented crack formation. Crack formation is controlled by the evaporation rate and the surface tension of the liquid phase [35]. The surface tension of water (72.8 mN m^{-1}) decreases significantly upon addition of animal glue. According to Sauer and Aldinger [36] the surface tension of a 10 wt% aqueous animal glue solution falls between 37 and 50 mN m⁻¹, depending on the glue's content in fatty acids and neutral fats. Actually, rabbit skin glues generally have a relative high fat level and result in glue solutions with comparatively low surface tension, which reduces the capillary pressure during drying [22,37]. Crack formation will also be reduced because the drying rate is lower in the presence of animal glue, which is a hygroscopic material with a relatively high moisture holding capacity (i.e., 1 g of animal glue contains 0.3-0.5 g H₂O at 30-90% RH [38]). It has long been established that slower drying reduces crack formation [39]. A reduction of drying cracks is of great importance because it will lead to improved durability upon weathering. Cracks can be considered as weak spots where deterioration will occur preferentially as evidenced by the accelerated weathering test results (see below).

3.5. Accelerated weathering (water spraying)

The presence of animal glue improved the weathering resistance of carbonated plasters significantly. Generally, water spraying and subsequent drying led to increased crack formation, causing the samples' disintegration and detachment from the glass slide (Fig. 5). The sample without animal glue was completely lost after only 2 weathering cycles, while the samples containing 1 and 2 wt% organic additive withstood 5 and 10 cycles, respectively. Samples with \geq 5 wt% animal glue, in contrast, did not show any signs of alteration after 11 cycles and still adhered well to the glass slide at the end of the test. This suggests that plaster containing

Table 2					
Linear crack density	(cm^{-1})) in dried	plaster	sam	oles

_			
	Organic content (wt%)	Linear crack density (cm ⁻¹) and standard deviation	Reduction in linear crack density (%)
	0	0.10 ± 0.013	0
	1	0.03 ± 0.003	70
	2	0.02 ± 0.011	80
	5	0	100
	10	0	100



Fig. 4. Crack formation in dried plaster samples with different organic content.



Fig. 5. Plaster samples after 2 weathering cycles. The plaster sample without organic additive showed increased crack formation and severe material loss.



Fig. 6. Weight loss in plaster samples with different organic additive content exposed to water spraying.

 \geq 5 wt% animal glue would likely have an improved bond with the substrate when used for finishing purposes.

Remarkably, samples with ≥ 5 wt% animal glue did not suffer any material loss and gained 1.52 ± 0.21 wt% during the first few weathering cycles (Fig. 6). This weight gain might be related with the carbonation of a small amount of portlandite, which still remained in these carbonated samples but was not detected by XRD (i.e., a weight gain of 1.52 wt% corresponds to the carbonation of 5.8 wt% of portlandite).

The calculated weight loss per weathering cycle was very small in all samples and, generally, increased slightly with the plasters' additive content (i.e., the weight loss was calculated to be 0.17, 0.24, 0.28, 0.24, and 0.30 wt% per cycle in samples containing 0, 1, 2, 5, and 10 wt% of animal glue, respectively). Overall the results show that the weathering resistance increased with increasing additive content, and that the main benefit of the presence of organics seemed to have been the reduced crack formation, which ultimately improved the resistance to the impact of water spraying. Considering weight loss data (Fig. 6), a decrease in dissolution rate of plasters was not observed in the presence of organics. Thus, the proteinaceous additive did not seem to improve the plasters' hydrophobic nature as suggested by Ravi et al. [19]. Note that according to FESEM and ATR-FTIR analysis, some organicinorganic hybrid material (i.e., rhombohedral calcite crystals with rounded edges) might have formed in samples containing organic additive. It has been suggested that this type of hybrid material would not only have improved physical-mechanical properties, but would also be more resistant to chemical weathering [32,34]. In samples containing animal glue, however, preferential leaching of the water-soluble additive could have been responsible for the larger weight loss detected as compared to the sample without organic additive and, thus, masked any improvement in weathering resistance (i.e., reduced dissolution rate). This aspect will have to be investigated in a future study.

3.6. SO₂-aging test

Even though, all samples suffered sulfation, transformation of calcite into calcium sulfite (CaSO₃/CaSO₃·0.5H₂O) was generally delayed in the presence of the organic additive (Fig. 7). Note that in all samples calcium sulfite was identified as the only alteration product during the first 196 h of the SO₂-aging test. Amoroso and Fassina [40] have commented on the fact that this phase commonly precedes gypsum during sulfation. Gypsum was actually only detected at the end of the test after 336 h of exposure, when 5 ± 2.1 wt% of gypsum had formed in all samples. Higher concentrations of organic additive were more effective in delaying the formation of calcium sulfite. Indeed, in the absence of organics, trace amounts of calcium sulfite were already detected after 24 h of exposure. In the presence of 10 wt% animal glue, in contrast, trace amounts of this phase were first detected after 144 h. XRD analyses showed that all samples contained CaSO₃ as well as CaSO₃·0.5H₂O.



Fig. 7. Calcite content (wt%) based on semiquantitave XRD results of lime plaster samples with different amounts of organic additive during the SO₂-aging test.

Remarkably, in samples with 0 and 1 wt% organic additive, the former phase was only detected in trace amounts, whereas in samples with higher organic content, CaSO₃ made up \sim 50% of the alteration products. Apparently, the formation of the hemihydrate was inhibited significantly in the presence of large amounts of the hygroscopic organic additive. At the end of the test all samples with an additive content \leq 5 wt% showed the same degree of sulfation, now containing only 15–20 wt% of calcite. The sample with 10 wt% organic additive, in contrast, still contained ~45 wt% calcite. The reason for the improved chemical weathering resistance shown by this sample might be twofold. On the one hand, the large amount of animal glue seemed to have simply acted as an effective barrier by forming a superficial film around the calcite crystals and hindering the access of water and SO₂ to the calcite surface, thus delaying sulfation [18]. On the other hand, the formation of an organic-inorganic hybrid material could have also contributed to the improved weathering resistance in the case of samples containing 10 wt% organic additive (Fig. 2f).

SO₂-aging not only altered the plasters' mineralogical composition, it had also a significant effect on their morphological features. Scalenohedral calcite crystals were replaced by nano-sized sulfite crystals (Fig. 8a), which contained Ca and S according to FESEM-EDS. In a few cases the new phase grossly resembled the original shape of the scalenohedral calcite crystals (Fig. 8b, arrow). The SO₂-aged plaster sample with 10 wt% organic additive showed triangular particles, made up of aggregated nano-sized crystals (Fig. 8c). Remarkably, FESEM-EDS revealed that these crystals had a lower S/Ca ratio than the nanosized-sulfite crystals in the remaining samples. Likely, the core of these crystals still contained larger amounts of calcite, which is in agreement with XRD data, showing a significantly higher calcite concentration in the sample containing 10 wt% organic additive at the end of the aging test. After 336 h of SO₂-aging, all samples contained relatively large gypsum crystal clusters, 5-15 μm in size (Fig. 8d and e). Some morphological variations were observed in the case of the plaster samples containing organic additive, which revealed more compact, blocky gypsum crystals as compared to the rod or blade-like crystals in the sample without organics (Fig. 8d and e). Similar (blocky)



Fig. 8. FESEM images of plaster after 336 h of SO₂-aging: a) with 0 wt% organic additive; b) with 1 wt% organic additive (arrow indicates particle resembling the scaleonohedral shape of the former calcite crystal); c) with 10 wt% organic additive; d) gypsum crystals in sample containing 0 wt% organic additive, and e) blocky gypsum crystal in sample containing 10 wt% organic additive.

Table 3
Flexural and compressive strength and mineralogical composition of prismatic lime plaster samples.

Organic Content (wt%)	Flexural strength (MPa)	Compressive strength (MPa)	Mineralogical composition (wt%) [*]	
0	0.95 ± 0.27	3.45 ± 0.51	Calcite Portlandite	93 7
1	0.53 ± 0.24	2.02 ± 0.10	Calcite Portlandite	81 19
2	0.66 ± 0.30	2.14 ± 1.04	Calcite Portlandite	83 17
5	0.55 ± .13	2.25 ± 1.04	Calcite Portlandite	56 44
10	0.40 ± 0.12	1.93 ± 0.39	Calcite Portlandite Vaterite	52 43 5

* Based on semiquantitative (±5 wt%) XRD analysis of samples cured for 2 months.

morphological features have been described previously in the case of gypsum precipitated in the presence of citric acid [41]. Note that in spite of the important mineralogical transformations suffered by the plaster samples upon SO₂-aging, they all remained intact after completion of the test.

3.7. Mechanical testing and mircotextural features of prismatic plaster samples

After 2 months of curing, the samples without animal glue had a compressive and flexural strength of 3.45 ± 0.51 and 0.95 ± 0.27 MPa, respectively (Table 3). These values are considerably higher than those commonly reported for aerial lime mortars cured for 2 months [42,43]. However, it has to be kept in mind that the samples were almost completely carbonated and that they contained no aggregate, which could interrupt the binder matrix and create an interfacial transition zone with inferior mechanical properties [44,45].

Samples containing animal glue revealed a reduction in flexural and compressive strength of up to 30-60% and 35-45%, respectively, as compared to samples without organic additive (Table 3). The lowest strength was measured for samples with 10 wt% organic additive. Note that in the case of the prismatic samples. carbonation was generally significantly delayed in the presence of the organic additive, especially in the case of samples with 5 and 10 wt% animal glue, which still contained ~45 wt% portlandite after 2 months of curing (Table 3). The lower degree of carbonation certainly had a negative effect on the mechanical properties. Furthermore, vaterite was detected in the prismatic sample containing 10 wt% organic additive. FESEM images (Fig. 1, Supplementary Materials) revealed the presence of large ($\sim 5 \,\mu m$) spheres, consistent with the morphology commonly described for metastable vaterite, which is typically stabilized in the presence of organics such as amino acids [46]. These large spheres might have disrupted the structure formed by the calcite crystals, further reducing mechanical strength.

Another even more important factor, which negatively influenced mechanical properties, seemed to have been the presence of large air bubbles, formed in all plaster samples containing the organic additive as revealed by microtomography (see below). According to Schellmann [22] animal glue acts as a foaming agent, facilitating the formation of air bubbles during plaster preparation, which are entrapped in the plaster matrix during an early curing stage. These results are in agreement with previous findings, demonstrating an important decrease in mechanical strength of air entrained concrete as the size and total volume of air voids (air bubbles) increased [47,48].

3.8. Density and porosity of prismatic plaster samples

The true density (Table 4) of prismatic plaster samples was $4.4\%\pm0.7$ lower than the theoretical density calculated based on mineral composition and animal glue content (i.e., density of calcite, vaterite, portlandite, and animal glue being 2.71, 2.54, 2.23, and 1.27 g/cm^3 , respectively). The very low bulk density values are not surprising, considering the high porosity (>50%) of all lime plaster samples, independent of organic content. Generally, a porosity of 25–40% is reported for cured lime mortars [42,49]. However, in the absence of an aggregate, the reported porosity of cured lime pastes is significantly higher and might reach values between 53.7 and 66%, depending on the pastes' water/lime ratio [50].

The addition of animal glue resulted in a significant modification of the pore size distribution. MIP results revealed that samples without organic additive had a unimodal pore size distribution with a peak centered at 1.3 μ m pore diameter (Fig. 9). In the presence of animal glue, pore size distribution curves changed to a bimodal type with the second peak centered at 2 μ m pore diameter. The height of the second peak increased with increasing organic additive content. Actually, the sample containing 10 wt% animal glue no longer showed a bimodal pore size distribution and had only one peak centered at 2 μ m pore diameter. MIP data also showed that all samples containing organic additive had an important portion (>5%) of pores with a diameter between 2 and 400 μ m, whereas in the sample without organic additive the volume of pores with a diameter >2 μ m only amounted to ~0.6%

Table 4		
Density and porosity of prismatic li	me plaster samples	cured for 2 months.

Organic Content (wt%)	True density (g/cm ³)	Bulk density (g/cm ³)	MIP Total porosity (%)	MIP [°] porosity (%)	μ-CT porosity (%)
0	2.54	1.21	52.4	0.6	10.1
1	2.50	1.18	53.0	7.0	13.1
2	2.51	1.18	52.8	5.7	14.6
5	2.37	1.08	54.5	8.3	19.9
10	2.34	1.09	53.3	8.5	21.5

Pore volume corresponding to pores with a diameter between 2 and 400 μ m.



Fig. 9. Pore size distribution of plasters with different organic additive content: a) logarithmic differential pore volume and b) cumulative pore volume.

(Table 4). For comparison, the porosity calculated from μ -CT image data is included in Table 4. The discrepancies between MIP and µ-CT-based porosity data can be explained by the different pore size detection limits of each technique [51]. With MIP, pores with a diameter >400 µm can not be measured. Nevertheless, they are of importance for the evaluation of the plasters mechanical properties, leading to a significant reduction in strength (Table 3). μ -CT analysis, in contrast, allows the detection of pores with a diameter >400 µm. However, under the current equipment settings the spatial resolution is limited to ${\sim}3.5\,\mu m$ according to the manufacturer, and pores with a smaller size can not be detected. The μ -CT data (Table 4) revealed a considerable porosity increase in samples containing animal glue due to the presence of large voids (Fig. 10). The sample without organic additive showed only a small number of pores with a diameter $<100 \,\mu m$ (Fig. 10a), while large air bubbles of up to 700 µm were visible in the sample containing 2 wt% animal glue (Fig. 10b). Visagie [47] demonstrated that concrete strength decreased drastically as air void size increased beyond 100 µm diameter. Additionally, the sample with 10 wt% organic additive revealed several large air voids of irregular shape (Fig. 10c). Likely these voids were caused by the highly viscose aqueous animal glue solution, which complicated homogeneous mixing with the calcium hydroxide powder as well as uniform distribution of the lime paste during molding. Note that the µ-CT porosity of the sample without organic additive seems to be overestimated considering that all pores are within the detection limits of MIP and that most of the pore volume corresponds to pores with a diameter <2 µm, which is below the theoretical detection limit of μ-CT.

The reconstructed μ -CT images of plaster samples did not allow a clear differentiation between the animal glue and the lime matrix (Fig. 10). Based on its molecular weight, calcite should be brighter than portlandite and the organic additive. However, only larger calcite crystal accumulations will be detectable as bright, whitish grains (Fig. 11a), while individual small calcite crystals will result in darker grey levels, depending on the presence of portlandite, organic additive, and pores in their surroundings (Fig. 11b). This effect has to be considered in order to avoid errors in the interpretation of reconstructed μ -CT images based on different grey levels.

3.9. Color change in plasters due to organic additive content and upon SO_2 -aging

Color is an important parameter in the case of plasters and renders used in conservation interventions and is also often used to quantify the degree of alteration [52]. Color measurements of carbonated plaster thin films showed an only minor increase in Δb^* and subsequently in ΔE^* , while L* and a* remained basically unchanged (Δa^* and $\Delta L^* < \pm 0.3$ units) as the amount of animal glue increased (Fig. 12a). The change towards a slightly more yellowish tint was always below the detection limit for the human eye (i.e., ΔE^* higher than three units is considered the threshold of the perceptible detection limit for the human eye [53]). After 336 h of SO₂-aging severe color changes had occurred in all plasters due to yellowing (increase in b* and a slight decrease in L*), especially in samples prepared with 5 and 10 wt% organic additive (Fig. 12b). The change in a* was always below one unit. ΔL^* was between 1.5 and 2.2 units, being slightly higher in the samples



Fig. 10. Reconstructed µ-CT images of plaster samples (1.5 × 1.5 × 1.5 mm) containing a) 0 wt% organic additive; b) 2 wt% organic additive, showing large air bubbles, and c) 10 wt% organic additive after curing for 2 months (arrows showing air voids due to non-uniform distribution of the highly viscous lime paste during molding).



Fig. 11. Schematic showing the influence of calcite grain accumulation and pores on the final grey level in reconstructed μ -CT images. White circles = calcite, black circles = pores, grey = portlandite/organic additive.

containing 5 and 10 wt% additive. Overall, the experimental results revealed that an additive content >5 wt% significantly increased the susceptibility to yellowing during SO₂-aging, possibly induced by acid hydrolysis of proteins during the SO₂-attack [54].

4. Conclusions

Our results show that the presence of animal glue had an important effect on the lime plasters' mineralogical evolution, weathering resistance, and mechanical properties. The degree of carbonation decreased with increasing organic additive content. Low carbonation rates in the presence of organic additive also resulted in the stabilization of metastable vaterite, which likely had a negative effect on the mechanical properties and might also influence durability negatively since eventual transformation into calcite will be accompanied by a volume decrease and changes in crystal morphology. FESEM and ATR-FTIR results suggest the formation of organic-inorganic hybrid material in the presence of animal glue. However, the amount of this biomimetic material must have been small and no clear evidence for its positive effect on the plasters' weathering resistance and mechanical strength was obtained. In future studies it should be evaluated whether organic-inorganic interactions could be promoted by changing the preparation protocol of lime plasters (i.e., adding the organic additive during the hydration of quicklime).

Nevertheless, the chemical weathering resistance with respect to water spraying and SO₂-exposure generally improved in the presence of animal glue. The improved water resistance was due to a decrease in crack formation (i.e., drying-induced cracks being weak spots, facilitating deterioration processes), especially in the case of samples containing $\geq 5 \text{ wt\%}$ animal glue, which survived prolonged weathering without any visible signs of alteration. The presence of organic additive also improved the adherence of the plaster to the smooth surface of the glass slides, suggesting a better bond of the plaster laver with the substrate. All lime plaster samples suffered sulfation upon SO₂-exposure. However, the transformation of calcite into calcium sulfite was significantly delayed as the samples' organic additive content increased. SEM images revealed that animal glue surrounded calcite crystals and acted as a physical barrier for SO₂ and water, which was especially effective in the case of samples containing >5 wt% organic additive. Future research should evaluate whether the organic additive also improves the long-term sulfation resistance of lime plasters exposed to contaminated urban air.

Flexural and compressive strength decreased in the presence of the organic additive. Mechanical properties were not only influenced by the plasters' degree of carbonation (the degree of carbonation being lower in the presence of animal glue), but also by the presence of large air bubbles in the plaster matrix, which, as revealed by microtomography, increased in volume with increasing organic additive content. Apparently, animal glue acted as a foaming agent and facilitated the formation of air bubbles during plaster preparation. However, it has to be kept in mind that plasters are used for finishing purposes and not for load bearing applications. Thus, strength might be a subordinate parameter.

Color parameters were not significantly influenced by the addition of animal glue. However, exposure to UV radiation and contaminants might cause a degradation of the organic additive over time and induce more important color changes. In fact, SO₂-exposure during accelerated aging caused a ~25% larger color change in samples containing \geq 5 wt% animal glue as compared to the sample without organic additive.

Considering reduced crack formation, improved adherence and superior weathering resistance, it can be concluded that the use of lime-based composite materials present a valuable alternative to



Fig. 12. Color change induced by the presence of animal glue (a) in unaged carbonated plasters and (b) in carbonated plasters exposed to accelerated SO₂-aging for 336 h.

conventional lime plasters without organic additives. However, an animal glue content of \geq 5 wt%, might be inadvisable, slowing carbonation significantly and possibly inducing color changes during long-term outdoor exposure. In any case, carbonation can be accelerated by water spraying.

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Compliance with ethical standards

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Declaration of Competing Interest

No conflict of interest exists.

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