Mineralogical and microstructural studies of mortars from the bath complex of the Roman villa rustica near Mošnje (Slovenia)

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ABSTRACT

This study deals with the characterization of mortars collected from bath complex of the Roman villa rustica from an archeological site near Mošnje (Slovenia). The mortar layers of the mosaics, wall paintings and mortar floors were investigated. A special aggregate consisting of brick fragments was present in the mortars studied. The mineralogical and petrographic compositions of the mortars were determined by means of optical microscopy, X-ray powder diffraction and FTIR spectroscopy. Analysis of aggregate–binder interfaces using SEM-EDS revealed various types of reactivity rims. In order to assess the hydraulic characteristics of the mortars, the acid-soluble fractions were determined by ICP-OES. Furthermore, the results of Hg-porosimetry and gas sorption isotherms showed that mortars with a higher content of brick fragments particles exhibited a higher porosity and a greater BET surface area but a lower average pore diameter compared to mortars lacking this special aggregate.

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1. Introduction

Roman mortars, recognized for their high durability properties, have been widely investigated in order to determine their mineral, chemical, or microstructural characteristics [1–7]. Despite quite a wide range of studies, information about the detailed mineralogical composition and especially the microstructural characteristics of Roman mortars with special aggregate of brick fragments, that is, brick–lime mortars, is still relatively scarce. These special mortars and plasters were used especially in Roman times in the construction of aqueducts, bridges, and bath buildings, where waterproofing was required [8]. The mortars and plasters were made by mixing crushed bricks with lime, which sets in the presence of water, resulting in increased mechanical strength and reduced water permeability, which is attributed to the hydraulic reaction occurring with lime in the presence of water at the edges of the brick particles [9–14]. The amorphous components of the aggregate are mainly represented by aluminosilicates, which react with lime to produce calcium silicate hydrate and/or calcium aluminate hydrate at the brick–lime interface, giving the mortars a hydraulic characteristic [15].
The use of brick fragments with lime mortar dates from the Minoan period, through the ancient Greek and Roman civilizations [15]. The manufacture of these mortars in the Roman period is well described in the ancient treatise by Vitruvius [17]. According to data in the literature, the use of an aggregate made from crushed bricks became more frequent during the late Roman Empire [6,18]. The Romans spread the use of this material throughout their empire in Europe, northern Africa, and West Asia (Turkey). Fine brick particles were mainly used for rendering and for the upper layers of floors, whereas larger crushed brick particles were recommended not only for masonry walls, arches, and foundations, where high humidity or water were present, but also to improve the performance of mortars under normal conditions [11]. The use of crushed bricks in the joints of load-bearing walls became frequent during the latest part of the Roman Empire, and was continued during the Byzantine period [18], and seems to have been less common during medieval times. The use of crushed or finely ground bricks as an aggregate in ancient mortars were indicated as Horasan in Turkey [19], Surkhi in India, Homra in Arabic countries [20], and Cocciópesto in Roman times [21].

The archaeological site near Mošnje, with the Roman villa rustica, is located in the north-western region of Slovenia. On the basis of small finds, the construction of the villa rustica is believed to date from the first century and it was in use until the fourth century AD [22]. The residence building of the villa rustica had seven rooms, including baths with mosaics and wall paintings. The bath complex consisted of three rooms: the caldarium, the tepidarium, and the frigidarium. The caldarium was the hottest room in the sequence of bathing rooms, heated by a hypocaustum, an underfloor central heating system, with a black and white mosaic floor, followed by warm (tepidarium) and cold (frigidarium) rooms. The distribution of rooms completely conforms to Vitruvius’ recommendations [17]. Mortars with special aggregate, represented by brick fragments, were only used in the bathing area of the main residential building of the villa rustica [22,23].

The present study evaluates the mineralogical, chemical, and microstructural characteristics of mortars from bath complex of the villa rustica at Mošnje. A special attempt was made to characterize the hydraulic mineral phases, present in the mortars with brick fragments.

2. Materials and Methods

2.1. Sampling

Information regarding the mortar samples investigated is provided in Table 1. Sampling was carried out in the bath complex of the residential building of the villa rustica (Fig. 1). The samples of special mortars, such as bedding mortars of the mosaics, floor mortars, and wall paintings, were analyzed. In most of the fragments of the floor mosaic, the stratigraphy of the mortar layers (Fig. 2a) could be recognized, but the wall mosaic was found to consist of only one mortar layer. The red wall paintings (Fig. 2b) were found to consist of two mortar bedding layers. The outer layers were designated as A layers, whereas the inner layers were designated as B layers. The A layer in the floor mosaic is 1.5 cm thick, whereas the preserved B layer is <5 cm thick. Crushed brick particles are present in both layers. Furthermore, the A layer of the wall paintings is up to 8 mm thick, with a reddish binder and brick particles as the prevailing aggregate component. The B layers consist of a white binder with a prevailing sand component, whereas the brick fragments occur only as individual grains. In the single mortar layer of the wall mosaic, the majority of the aggregate consists of crushed brick, while the binder is reddish. The aggregate grains of the floor mortar consist of sand, although individual grains of crushed brick are also present. The binder is pink colored.

2.2. Methods

In order to characterize the texture of the mortars, to define the type and content of individual components of the aggregate and binder, and to determine the aggregate/binder ratios, the initial approach was to examine polished thin sections of the mortars by polarized optical microscopy. Polished thin sections of the mortar samples were studied using Olympus BX-60 microscope equipment, with a digital camera (Olympus JVC3-CCD). The contents of the measured components were quantified in thin sections by Point Counter equipment in transmitted light using 5× objective; 1000 points/sample were analyzed.

Mineralogical analyses of the mortars were performed on both binder-enriched fraction and aggregate. Both fractions were separated by gently crushing the mortar samples in order to avoid destroying the aggregate particles, and then sieving them through a mesh size less than 63 µm. The fraction between 0 and 63 µm should mainly be comprised of material from the binder in the mortars [24]. Two types of fractions were analyzed and compared: the fraction corresponding to the aggregate and the fraction that had a higher binder concentration. The aggregate was labeled “a”, the binder-enriched fraction “v”, the outer layers of the samples “A”, and the inner layers “B”. After being passed through the sieve, both fractions were analyzed by X-ray powder diffraction (XRD), using a Philips PW3710 X-ray diffractometer equipped with Cu Kα radiation and a secondary graphite monochromator. The data were collected at 40 kV and a current of 30 mA in the range of 2 to 70° 2θ, with a speed of 3.4°/min. The relative amounts of calcite, dolomite, quartz, and muscovite in the samples were determined according to the intensities of the peaks at d100 = 3.04 Å for calcite, d100 = 2.89 Å for dolomite, d35 = 4.26 Å for quartz, and d100 = 10 Å for muscovite.

The Fourier transform infrared spectroscopy (FTIR) spectra of selected samples were recorded using a Bruker IFS 66 FTIR spectrometer. Sixty-four signal-averaged scans of the samples were acquired. Powder pellets were pressed from mixtures of samples with KBr at a ratio of about 1:200. The FTIR spectra were recorded with a spectral resolution of 4 cm⁻¹ in the range of 4000–370 cm⁻¹.

The morphology and chemical composition of the polished thin sections of the samples were examined by the back-scattered electron (BSE) image mode on a scanning electron microscope (SEM) for a low vacuum (between 10 and 15 Pa),
coupled to energy dispersive X-ray (EDS) analyses, using a JEOL 5500 LV equipment.

Chemical analysis of the principal components in the acid-soluble fraction of the mortars was determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES) on an Optima 5300 DV spectrometer in order to evaluate the presence of the hydraulic compounds in the mortars [25]. For this purpose, the aggregate and binder fractions of the mortar samples were subject to attack by 2 M HCl (1:5) at room temperature for 3 h [2]; 50 mg of each mortar fraction (aggregate and binder) was dissolved in 50 ml of this solution. This test is based on the fact that acid-soluble silica can originate from hydraulic binders [2,26,27].

The pore systems of the samples were further investigated by means of mercury intrusion porosimetry (MIP) and gas sorption isotherms. Small representative fragments, approximately 1 cm³ in size, were dried in an oven for 24 h at 105 °C, and then analyzed on Micromeritics® Autopore IV 9500 equipment. The samples contained aggregate as well as binder, and were analyzed within the range of 0 to 318 MPa using penetrometers for solid samples. The N₂ sorption isotherms were obtained at 77 K on a Micromeritics Tristar 3000 Analyzer under continuous adsorption conditions. Prior to these measurements, chip samples were heated at 200 °C for 2 h and outgassed to 10⁻³ Torr using Micromeritics Flowprep equipment. Gas adsorption analysis in the relative pressure range of 0.05 to 0.3 was used to determine the total
specific area — Brunauer–Emmet–Teller (BET) surface area of the samples [28,29]. The total pore volume and micropore volume of the samples were calculated using t-plot analysis. The Barret–Joyner–Halenda (BJH) method was used to obtain pore size distribution curves [30].

3. Results and Discussion

3.1. Optical Microscopy

The aggregate of the investigated samples was found to be medium sorted in the case of the wall mosaic, the A layer of the floor mosaic, and the A layers of the wall paintings. In most of the investigated B layers of the wall paintings and in the floor mortar, the aggregate was found to be well sorted, whereas in the B layer of the floor mosaic the aggregate is poorly sorted. Aggregate grains occur in rounded and semiangular forms. The grain sizes of the aggregate of the investigated samples varied between 0.02 and 14.9 mm. The brick fragments ranged from 0.4 to 7.6 mm in size, with individual grains of up to 14.9 mm.

The results revealed that all of the samples had similar petrographical and mineralogical compositions. According to the results of the microscopic analysis, most of the mortars were made of a sand aggregate with a prevailing carbonate component and added crushed brick. The carbonate component consisted of grains of sparitic and micritic limestones and grains of dolomite, whereas the silicate component consisted of grains of sandstone, quartz, chert, muscovite, tuff, and plagioclase. The rounded shape, the size (large grains), and the small quantity of tuff indicate that the tuff was not intentionally added but occurred as part of the sand aggregate. In mortars from the bath complex of the villa, where waterproofing was required, crushed brick was added to the aggregate as either individual particles or as a prevailing aggregate component of the mortar. These brick fragments consisted of quartz, muscovite, carbonate (sparitic and micritic limestone), and limonite nodules. Some of the brick fragments also contained chert, sandstone, and plagioclase. The rounded shape of the sand aggregate indicates that local raw material was used in the preparation of these mortars, i.e. the fluvioglacial sand deposits of the Pleistocene terraces of the River Sava [31].

The ratios of the sand/crushed brick components varied considerately between the samples as well as among the
layers (Fig. 4a). The crushed brick component is enhanced in the A layer of the mortar layers of the floor mosaic (ANM 134a) and the A layer of the wall paintings (ANM 138A; Fig. 3a). The sand component (silicate and carbonate grains) in these samples is in the minority. Moreover, the mortar layer of the wall mosaic (ANM 136) is almost entirely composed of brick particles. It is important to note that, besides having bigger brick fragments, brick powder is also present in the A layer of the floor mosaic (ANM 134A), while the amount of brick component in the B layer of the mosaics is smaller. A similar mortar stratigraphy and a similar composition of the floor mosaic were reported by Starinieri [32]. Furthermore, the brick fraction in the B layers of the wall paintings (ANM 138B) and the floor mortar (ANM 140) only occurs as individual grains, and the aggregate in these mortar layers is mainly composed of the sand component (Fig. 3b). In addition to the ground brick fraction, a fine fraction (powder) is also present in all of the samples except the B layers of the wall paintings.

As can be seen from Fig. 4b, the aggregate prevails over the binder in both layers of the wall paintings (ANM 138A, ANM 138B, ANM 139A, and ANM 139B), in the B layer of the floor mosaic (ANM 134B), and in the single layer of the wall mosaic (ANM 136), whereas in the A layer of the floor mosaic the amount of aggregate (ANM 134A) is almost equal to the amount of binder. The binder prevails over the aggregate only in the sample of floor mortar (ANM 140), where the binder:aggregate ratio is 2:1.

The majority of the samples examined have binders that are based on lime and pozzolanic materials. The latent hydraulic material with pozzolanic characteristics was found to consist of a brick component, especially in its fine fraction. The fine fraction of the brick particles is present in all samples, with the exception of the B layers of the wall paintings (ANM 139B, ANM 138B, and ANM 141B), suggesting the lime-hydraulic binder in these samples. On the other hand, pozzolanic material was not added to the B layers of the wall paintings, so that the binder consists of lime. Lime lumps, which are generally fissured, were found to be present in all samples from all mortar layers, and they varied in size from 0.2 to 1.8 mm. The samples with abundant brick fragments (ANM 134A, ANM134B, ANM 136, ANM 138A, ANM 139A, and ANM 141A) showed a characteristic compact matrix, so that the absence of fissures was obvious. It has been reported that brick powder with dimensions of less than 63 μm should be considered as a binder owing to the pozzolanic reaction of these particles with lime [6,12,16,33]. Reaction rims were observed around individual brick particles in almost all of the samples. Reaction rims were also observed around some carbonate grains.

### 3.2. X-ray Powder Diffraction

The results of the XRD analysis (Table 2) indicate that dolomite, calcite, quartz, and feldspar were the main mineralogical components of all of the samples investigated. The presence of illite/muscovite, clinochlore, and hematite was also confirmed. The presence of clinochlore could indicate tuff particles in the mortars, whereas the illite/muscovite and hematite in the samples can be attributed to the brick components. The brick fragments consisted of calcite, dolomite, quartz, feldspars, muscovite, and hematite.

With regard to the aggregate fraction (labeled “a”), calcite, dolomite, and quartz were present in all samples. Feldspars were present in the majority of samples, whereas illite/muscovite was present in the minority of samples.
absent in the samples of the B layers of the wall paintings. Regarding the binder-enriched fraction (labeled "v"), calcite, quartz, feldspars, and dolomite were present in all of the samples. Illite/muscovite was present in the samples of the A layers of the red wall paintings, the A layers of the floor mosaic, and the wall mosaic. It was clear that illite/muscovite is related to the brick particles, as its presence fits in with the presence of brick particles. Hematite normally occurred in these samples, too. Both minerals indicate the presence of latent hydraulic materials in the mortar (brick fragments). The presence of these two minerals is a clear indication of the firing temperature. Unaltered illite/muscovite indicates that the firing temperature was lower than 900 °C [34], whereas the presence of hematite indicates a firing temperature of about 850 °C [35]. On the other hand, the presence of carbonate particles in the brick particles shows that the firing temperature was sometimes lower than 800 °C. The presence of feldspars could be attributed to the brick particles, as anorthite forms in the process of burning clay [35]. It could also be related to the tuff grains. Heating destroys the crystal structure of clay, resulting in pozzolanic amorphous substances such as metakaolin. The heating temperature should not be too high, since at temperatures over 800 °C the pozzolanic activities of the brick additive are lost due to the reduction of the surface area and the formation of high temperature mineral phases such as mullite and cristobalite [36].

The main differences in the enriched binder between the two layers studied were expressed by the presence of illite/muscovite in the layers, occurring as the aggregate and as the binder-enriched fraction in the A layer. On the other hand, illite/muscovite was absent in the B layer, where the lack of this mineral phase was evident in the aggregate as well as the binder-enriched fraction.

According to the results of the semi-quantitative X-ray powder diffraction analysis (Fig. 5a), dolomite prevailed in the aggregate fraction followed by calcite, quartz, and illite/muscovite. The absence of muscovite was evident in the samples that contained brick fragments only as individual grains (B layers). Regarding the binder-enriched fraction, the quantity of calcite and dolomite was, in general, enhanced in the samples that did not contain brick powder (Fig. 5b). When comparing the aggregate and binder-enriched fractions, the results of the analysis revealed the prevalence of calcite in the aggregate fraction over the binder-enriched fraction in all of the samples with added brick particles. Calcite prevailed in the binder-enriched fraction in samples that did not contain brick aggregate as the major component. Dolomite and quartz also prevailed in the aggregate fraction compared to the binder fraction, whereas muscovite was enhanced in the binder fraction.

In order to identify hydraulic compounds such as calcium silicate hydrate and calcium aluminate hydrate, the X-ray diffractograms were studied between 2 and 70° 2θ [2,37]. In order to verify the presence of calcium silicate hydrate–afwillite (9–454), peaks at d100 =3.19 Å, d100 =2.84 Å, and d100 =2.74 Å were examined according to Maravelaki-Kalaitzaki et al. [3]. In addition, two peaks at d80 =6.46 Å and d80 =5.74 Å were also checked. In order to verify the presence of tobermorite (10–0373) in the samples, the occurrence of peaks at d100 =11.3 Å and d120 =2.83 Å [2], and also peaks at d90 =5.55 Å and d90 =1.85 Å, was investigated. For calcium aluminate hydrate–katoite (98-006-0999), a peak at d100 =2.04 Å was investigated.

The results revealed that in all of the samples investigated, peaks at d =3.19 Å and d =2.84 Å were present, but they overlapped with the d-values of plagioclase and/or muscovite. Peaks at d =2.74 Å, d =6.46 Å, and d =5.74 Å were not present. A peak at d =2.83 Å overlapped with plagioclase. Other peaks indicating tobermorite were not observed in the samples investigated. Moreover, a peak at d =2.04 Å was absent in all of the samples investigated. Thus, the absence of d-values at d90 =6.46 Å, d90 =5.74 Å, d90 =5.55 Å, and d90 =1.85 Å indicates that the observed d-values at d =3.19 Å and d =2.84 Å could not be ascribed to hydraulic components. The presence of possible hydraulic components in the samples with crushed bricks was not confirmed since the expected XRD peaks of calcium silicate hydrate and calcium aluminate hydrate were not observed. This was probably due to the amorphous character of these hydraulic products [36].

3.3. FTIR Spectroscopy

The FTIR analysis provides additional information to XRD analysis. The FTIR spectra of the selected samples, first separated by layers and separated into aggregate and binder-enriched fractions of the mortars, were compared (Fig. 6). These data are in accordance with the XRD results.
The FTIR spectra indicated that all of the samples contained carbonate phases, such as calcite and dolomite. In the samples where semi-quantitative XRD analysis revealed a higher quantity of dolomite, the FTIR spectra exhibited enhanced characteristic peaks of dolomite, for instance the $v_4$ symmetrical $\text{CO}_3$ deformation at around 729 cm$^{-1}$. In addition, in these spectra an absorption band was observed at 1822 cm$^{-1}$ (the $v_1 + v_4$ combination mode). In the 1100–400 cm$^{-1}$ region, vibrational bands corresponding to $\text{Si-O}$ and $\text{Si-O-Si}$, and $\text{Al-O}$ and $\text{Al-O-Al}$ were detected in all of the samples. These vibrational bands could be attributed to the muscovite, feldspars, and quartz. This region was even clearer, with enhanced bands in the samples that contained brick particles (the A layers of the mortars), especially in the binder-enriched fraction.

The FTIR spectra indicated that the same absorption bands were found in the samples of the binder-enriched fraction and samples of the aggregate, although in differing amounts. The spectra did not reveal a significant difference in composition when comparing the aggregate and binder-enriched fractions of the same mortar layers that contained brick powder. Quartz, with a characteristic band at 1030 cm$^{-1}$, prevailed in all spectra of the aggregate compared to the binder-enriched fraction. It was confirmed that the aggregate samples of the A layer contained a higher quantity of the silicate component, whereas carbonate grains prevailed in the aggregate samples of the B layer. When comparing binder-enriched fractions between layers of the same samples, it was clear that the silicate component was more abundant in the A layer than in the B layer. This could be attributed to the presence of finely grained brick particles that act as pozzolans. On the other hand, the spectra of the binder fraction of the B layers only yielded traces of pozzolans. When comparing the spectra of the aggregate to that of the binder-enriched fraction, in both layers, it was observed that the binder-enriched fraction contained a higher quantity of silicate components than the aggregate fraction. This is in accordance with the results of the semi-quantitative XRD analysis, which showed a higher quantity of muscovite in the binder-enriched fraction.

The finely grained component, which was present in the binder fraction as a pozzolan, represents an additional source of reactive $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$. In the case of the B layers of the samples investigated, the presence of pozzolans was reduced. Additional vibrations due to the possible formation of new hydraulic phases were not detected in the binder-enriched fractions. The enhanced vibrations in the 900–1200 cm$^{-1}$ region of the samples investigated coincided with the addition of brick particles, and thus indicated the presence of pozzolans. Their higher quantity
in the binder-enriched fraction compared to the aggregate fraction was also proven by the results of the XRD analysis.

3.4. **SEM-EDS Analysis**

The SEM-EDS examination of the binders revealed a homogeneous calcitic matrix in all of the B layers of the mortars. Minor amounts of Mg were also detected. The lime lumps in the binder, without the addition of brick particles (ANM 138b, ANM 139b, and ANM 141b), were exclusively composed of calcite.

On the contrary, the chemical composition of the binders in the layers with brick aggregates (the A layers) revealed a heterogeneous binder consisting of two components: (i) a lime binder that was strongly carbonized in some places, resulting in the binder-enriched fraction compared to the aggregate fraction was also proven by the results of the XRD analysis.

**Fig. 7** – SEM-BSE images of thin sections of the mortars investigated. a) Calcitic rims around the brick fragments. Sample ANM 139A. b) Reactivity rim around a brick fragment, indicating a pozzolanic reaction. Sample ANM 140. c) Dissolution of a dolomitic grain. Sample ANM 136. d) A dolomitic grain with rim. Sample ANM 134A. e) Dolomitic grain with rim in a hydraulic matrix. Sample ANM 134A. f) Dolomitic grains with rims in a calcitic matrix. Sample ANM 134A.
in a very compact matrix, and (ii) a hydraulic binder, with Ca, Mg, Si, and Al as its major elements. Analysis of the lime lumps in the mortar layers with brick fragments also revealed the presence of Si, Al, Mg, and Ca, suggesting the hydraulic nature of the binder. According to some authors [38,39], this confirms the presence of hydraulic compounds in the lumps.

In the mortar composites with added brick particles, two types of reactivity rims were observed around the brick grains. The formation of calcium carbonate rims around individual grains of brick (Fig. 7a) probably occurred due to the fact that Ca is more mobile than Si and tends to migrate to the aggregate grains. A similar process occurs in the case of cement composites. During the hydration process calcium hydroxide frequently accumulates at the interface between the grain and the cement matrix [40]. The observed reactivity rims (with a thickness of about 20 μm) could represent weakened areas of the mortars. A reactivity rim indicating a pozzolanic reaction [2,36] was only observed in sample ANM 140 (Fig. 7b). Chemical analysis of this rim, which had a width of about 100 μm, revealed the presence of Al, Ca, and Mg in the analyzed area.

Furthermore, two other phenomena were observed in the case of the dolomitic grains, whereas the limestone grains remained unaltered. In sample ANM 136, corrosion of the dolomitic grains was observed due to the reaction between the components in the hydraulic binder and the dolomitic grains (Fig. 7c). In the case of the floor mosaic (ANM 134 A and B), both corrosion and a reaction rim with a width of about 100 μm were observed in the dolomitic grains (Fig. 7d). These rims were observed in the hydraulic binder (Fig. 7e) as well as in the calcitic binder (Fig. 7f). Chemical analysis of the rims indicated the presence of Al, Si, Mg, and O as enrichments, and Ca as an impoverishment (Table 3). The results of a mapping study of the dolomite grain investigated and its rim are shown in Fig. 8.

In the unusual reaction rim of the dolomitic grain, for which a mechanism could not be explained at this stage of the research, it was evident that the concentration of Ca decreased while the concentration of Mg, O, and C increased. The enrichment of Al and Si was also observed.

In order to determine the distribution of elements over the reaction rim, linear scans were performed on polished surfaces of the samples. A similar distribution of the elements was found in all of the aggregate grains analyzed, with Ca ions diffusing into the silica grains, and Si ions diffusing in the opposite direction, i.e. into the cement matrix. The results of a linear scan performed on the dolomite rim are shown in Fig. 9. These results showed that the highest concentration of Ca ions occurred in the middle of the reaction rim, with a decreasing trend towards the silica aggregate. On the other hand, the concentration of Si

| Table 3 - Results of the EDS analysis of the corroded dolomitic grains in the mortar samples. |
|---|---|
| **Element** | **Average chemical composition of the center of the dolomitic grain (wt.%)** | **Average chemical composition of the reaction rim (wt.%)** |
| C     | 15.32 | 7.88 |
| O     | 56.94 | 68.18 |
| Mg    | 9.89  | 14.98 |
| Al    | 0.55  | 6.17  |
| Si    | 0.88  | 2.78  |
| Ca    | 16.41 | 0.01  |

Fig. 8 – SEM-EDS elemental mapping of a dolomitic grain with a reaction rim. Sample ANM 134.
ions decreased from the SiO₂ matrix toward the cement paste. The highest concentration of Al and Mg was observed in the aggregate, with a decreasing trend in the direction of the binder. A gap in the concentration of Ca was also observed at the rim. The distribution of Si at the rim was generally insignificant, although in some cases there was also evidence of the enrichment of Si at the rim (Table 3). On average, the concentration of K and Na ions was less than 1 at.% with a slight enrichment being evident at the point of contact of the rim with the aggregate. The standard deviation of the atomic concentrations measured at each point did not exceed 2%.

3.5. Chemical Analysis

The results of the chemical analysis of the acid-soluble fractions (after acid attack on the aggregate and binder-enriched fraction of the mortars) are given in Table 4. An increased quantity of SiO₂, Al₂O₃, and Fe₂O₃ was observed in the mortars with added brick particles, indicating pozzolanic materials and thus the hydraulic characteristics of these mortars.

The soluble silica content was higher in the A layers than in the B layers of the mortar samples investigated. Furthermore, the SiO₂ content was also higher in the binder-enriched fraction than in the aggregate fraction of the same layer, except for sample ANM 134. The situation was the same for the A and the B layers of the samples investigated. The values of Al₂O₃ and Fe₂O₃ positively correlated with the content of SiO₂. The values of MgO were higher in the B layers than in the A layers of the samples. When comparing the two fractions of the same layer, the content of MgO attributed to the dolomite grains, was always higher in the aggregate fraction. From the results of the petrographic analysis it was evident that the
prevailing component of the aggregate in the B layers was the carbonate fraction. On the other hand, in the A layers, the content of Al₂O₃ was almost always higher than the content of SiO₂, with the exception of sample ANM 141, where quantitative analysis by optical microscopy showed a prevailing carbonate fraction. On the contrary, the B layers were enriched with SiO₂. Moreover, the Al₂O₃ content was always higher in the binder-enriched fraction than in the aggregate fraction. The Fe₂O₃ content was also almost always higher in the binder fraction. Additionally, it was always higher in the A layers, suggesting their origin in the brick fragments. The CaO content was always higher in the binder-enriched fraction than in the aggregate fraction, and higher in the B layers than in the A layers.

The correlation matrix (Table 5) exhibits a high correlation between SiO₂-Al₂O₃-Fe₂O₃-K₂O-TiO₂-P₂O₅, indicating the presence of brick particles. Calcium oxide exhibits a negative correlation with SiO₂, MgO, and K₂O. Furthermore, a negative correlation was found between MgO and SiO₂, Al₂O₃, Fe₂O₃, MnO, TiO₂, and P₂O₅.

Acid-soluble silica could originate from hydraulic binders, although crushed brick should also be considered due to its

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<td>0.013</td>
<td>0.009</td>
<td>0.290</td>
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<tr>
<td>Bv</td>
<td>1.51</td>
<td>1.47</td>
<td>0.36</td>
<td>47.78</td>
<td>1.92</td>
<td>0.038</td>
<td>0.083</td>
<td>0.026</td>
<td>0.011</td>
<td>0.580</td>
</tr>
<tr>
<td>ANM 136</td>
<td>1.95</td>
<td>2.69</td>
<td>0.30</td>
<td>10.36</td>
<td>2.23</td>
<td>0.033</td>
<td>0.235</td>
<td>0.014</td>
<td>0.013</td>
<td>0.280</td>
</tr>
<tr>
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<td>1.29</td>
<td>1.72</td>
<td>0.27</td>
<td>28.97</td>
<td>5.62</td>
<td>0.035</td>
<td>0.205</td>
<td>0.018</td>
<td>0.010</td>
<td>0.442</td>
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<td>Av</td>
<td>1.35</td>
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<td>0.26</td>
<td>31.08</td>
<td>2.08</td>
<td>0.032</td>
<td>0.169</td>
<td>0.027</td>
<td>0.010</td>
<td>0.698</td>
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<tr>
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<td>0.13</td>
<td>35.66</td>
<td>11.98</td>
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<td>0.049</td>
<td>0.012</td>
<td>0.001</td>
<td>0.055</td>
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<td>0.20</td>
<td>0.23</td>
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<td>8.03</td>
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<td>0.075</td>
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<td>1.39</td>
<td>0.30</td>
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<td>8.14</td>
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<td>0.117</td>
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<td>29.49</td>
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<tr>
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<td>0.16</td>
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<td>11.57</td>
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<td>0.039</td>
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<td>0.37</td>
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<td>2.98</td>
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<td>0.36</td>
<td>43.00</td>
<td>4.33</td>
<td>0.042</td>
<td>0.095</td>
<td>0.033</td>
<td>0.008</td>
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<tr>
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<td>1.04</td>
<td>0.49</td>
<td>38.76</td>
<td>2.03</td>
<td>0.039</td>
<td>0.092</td>
<td>0.045</td>
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<td>ANM 141 Aa</td>
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<td>0.85</td>
<td>0.24</td>
<td>33.58</td>
<td>9.72</td>
<td>0.035</td>
<td>0.148</td>
<td>0.016</td>
<td>0.004</td>
<td>0.083</td>
</tr>
<tr>
<td>Av</td>
<td>1.36</td>
<td>1.51</td>
<td>0.26</td>
<td>34.14</td>
<td>1.96</td>
<td>0.041</td>
<td>0.137</td>
<td>0.017</td>
<td>0.008</td>
<td>0.292</td>
</tr>
<tr>
<td>Ba</td>
<td>0.25</td>
<td>0.11</td>
<td>0.14</td>
<td>39.25</td>
<td>12.87</td>
<td>0.033</td>
<td>0.065</td>
<td>0.013</td>
<td>0.001</td>
<td>0.041</td>
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<td>Bv</td>
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<td>0.22</td>
<td>0.17</td>
<td>45.70</td>
<td>5.59</td>
<td>0.038</td>
<td>0.055</td>
<td>0.012</td>
<td>0.003</td>
<td>0.127</td>
</tr>
</tbody>
</table>

| Table 5 – Correlation matrix for the results of the acid-soluble fractions investigated (marked correlations are significant at p < 0.05). |
|------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| SiO₂ | 1.00 | | | | | | | | |
| Al₂O₃ | 0.98 | 1.00 | | | | | | | |
| Fe₂O₃ | 0.80 | 0.79 | 1.00 | | | | | | |
| CaO | −0.53 | −0.60 | −0.17 | 1.00 | | | | | |
| MgO | −0.60 | −0.60 | −0.58 | 0.11 | 1.00 | | | | |
| Na₂O | 0.22 | 0.12 | 0.32 | 0.26 | −0.40 | 1.00 | | | |
| K₂O | 0.80 | 0.79 | 0.49 | −0.72 | −0.38 | 0.28 | 1.00 | | |
| MnO | 0.16 | 0.21 | 0.56 | 0.06 | −0.52 | 0.15 | −0.03 | 1.00 | |
| TiO₂ | 0.95 | 0.94 | 0.92 | −0.38 | −0.63 | 0.29 | 0.71 | 0.33 | 1.00 |
| P₂O₅ | 0.62 | 0.66 | 0.63 | −0.11 | −0.80 | 0.24 | 0.40 | 0.63 | 0.68 | 1.00 |
high concentration in the aggregate of A layers. Thermally decomposed clay minerals that form brick fragments are thought to be soluble in HCl [41,42], and hence it is not possible to prove that Si and Al originated from the calcium silicate hydrate and calcium aluminate hydrate.

### 3.6. Porosity and Pore Size Distribution

Porosity was determined on pieces of mortar, where the binder and aggregate were not separated. Table 6 shows the parameters that were determined by mercury intrusion porosimetry (total porosity, average pore diameter, bulk density, and apparent density), whereas Figs. 10 and 11 show the representative pore size distribution for layers A and B, and for samples ANM 136 and ANM 140.

The porosity values ranged from 23.9 to 49.7%. In general, the total porosity of mortar A layers of the floor mosaic and wall paintings (the layers containing brick aggregate) was higher in comparison with the B layers of the floor and wall paintings (the layers containing stone aggregate), except in the case of samples ANM141A and ANM141B. Furthermore, the average pore size diameter of the brick-containing layers (the A layers) was lower than the average pore size diameter of the mortar layers with stone aggregate. The bulk densities of the samples were within the range of 1.24 g/mL to 2.04 g/mL, whereas the apparent densities were within the range of 2.47 g/mL to 2.78 g/mL.

The mortars with brick fragments were more unimodally distributed, with the largest intrusion being around 0.3 μm. A bimodal distribution of pores was characteristic for the wall painting mortar layer (sample ANM 139A), with a minor intrusion peak at around 12 μm and a larger intrusion peak at around 0.3 μm. Among the A layer samples studied, sample ANM 134A differed from the others by exhibiting a broad pore size distribution within the range of 7 to 0.2 μm, without a well-defined peak.

Among the samples with stone aggregate, samples ANM 138B, ANM 139B, and ANM 141B indicated a distinctive bimodal distribution of pores, which was reflected by a higher median pore diameter (of around 1 to 2 μm). In these samples, finely ground brick particles were absent, which indicate that their presence contributed to the shift toward smaller pores. Nevertheless, the main peak, with a higher intrusion, was at around 0.7 to 0.4 μm, except in the case of ANM 141B, where the distribution curve was slightly shifted to the left. The highest porosity of all of the stone mortar samples was found in sample ANM 134B.

Mortar sample ANM 136 could be distinguished from all of the other samples by two clear peaks with similar intrusions: one at

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity (%)</th>
<th>Average pore diameter (nm)</th>
<th>Median pore diameter by volume (nm)</th>
<th>Bulk density (g/mL)</th>
<th>Apparent density (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANM 134 A</td>
<td>49.72</td>
<td>66.4</td>
<td>698.0</td>
<td>1.243</td>
<td>2.471</td>
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<tr>
<td>ANM 134 B</td>
<td>41.76</td>
<td>71.0</td>
<td>422.4</td>
<td>1.450</td>
<td>2.574</td>
</tr>
<tr>
<td>ANM 136</td>
<td>46.57</td>
<td>59.8</td>
<td>388.9</td>
<td>1.335</td>
<td>2.500</td>
</tr>
<tr>
<td>ANM 138 A</td>
<td>34.48</td>
<td>127.4</td>
<td>380.4</td>
<td>1.621</td>
<td>2.474</td>
</tr>
<tr>
<td>ANM 138 B</td>
<td>30.29</td>
<td>322.3</td>
<td>997.5</td>
<td>1.888</td>
<td>2.709</td>
</tr>
<tr>
<td>ANM 139 A</td>
<td>34.25</td>
<td>71.6</td>
<td>380.8</td>
<td>1.825</td>
<td>2.776</td>
</tr>
<tr>
<td>ANM 139 B</td>
<td>30.89</td>
<td>203.8</td>
<td>1105.7</td>
<td>1.879</td>
<td>2.719</td>
</tr>
<tr>
<td>ANM 140</td>
<td>36.43</td>
<td>81.5</td>
<td>420.3</td>
<td>1.658</td>
<td>2.607</td>
</tr>
<tr>
<td>ANM 141 A</td>
<td>23.94</td>
<td>61.6</td>
<td>558.5</td>
<td>2.036</td>
<td>2.677</td>
</tr>
<tr>
<td>ANM 141 B</td>
<td>32.96</td>
<td>503.9</td>
<td>2326.4</td>
<td>1.809</td>
<td>2.699</td>
</tr>
</tbody>
</table>

Fig. 10 – Log differential intrusion versus pore size of the samples of the A layers.
around 3 μm and the other at around 0.3 μm. The sample of the floor mortar (ANM 140) was slightly bimodal, with a main intrusion peak at around 0.5 μm.

The values of the BET-specific surface area varied from 2.3909 ± 0.0218 to 51.1361 ± 0.2025 m²/g. Table 7 shows that the A layers had a higher BET surface area, a higher pore volume, and a higher average pore size with respect to the B layers of the samples investigated. Sample ANM 136 had a similar BET surface area to samples of the A layers, whereas sample ANM 140 had a similar BET surface area to the B layers. The differences in pore size distribution between the two layers can be seen in Fig. 12. The two samples with a higher total pore volume (ANM 134A and ANM136) showed a pore size distribution with a clear maximum of ca. 50–60 Å, whereas the other samples did not show a clear maximum or were smaller than the detection limit (<20 Å). The volume of pores accessible to gas was larger in the case of the A layers. Similar to the previous results, the higher BET surface area in the A layers was the result of the presence of a brick aggregate. Moreover, higher BET surface area values in the A layers indicate a higher proportion of clay minerals [36] in these samples, in agreement with the XRD data (Fig. 5). All of the samples studied had a type II physisorption isotherm, which is characteristic of non-porous and macroporous materials [43].

### 4. Conclusions

The results revealed that all of the mortar samples investigated had similar petrographic and mineralogical compositions. Most of the mortars consisted of a fluvio-glacial deposit fraction (sand) with a prevailing carbonate component, and the addition of crushed brick. The ratios of the sand/brick fragments varied between the samples, as well as among the layers. The addition of crushed brick resulted in a hydraulically latent material, which was needed to provide the hydraulic characteristic of mortars in the bath complex, where waterproofing was required. On the other hand, a lime binder was recognized in mortar layers that lacked brick particles.

The results of the XRD analysis indicated that dolomite, calcite, quartz, and feldspar were the main mineralogical constituents of all the samples investigated. In addition, the presence of illite/muscovite and hematite in the samples can be attributed to the brick component. Enhanced vibrations of the FTIR spectra in the 900–1200 cm⁻¹ region of the samples investigated coincided with the addition of brick particles, and thus indicate the presence of pozzolans. In the samples containing brick fragments, increased quantities of SiO₂, Al₂O₃, and Fe₂O₃ were also observed, suggesting pozzolanic materials and thus the hydraulic characteristic of these materials.
mortars. Furthermore, several reaction rims were observed in the case of brick fragments or dolomitic grains of the aggregate. Two types of reaction rims were identified around the brick fragments: one indicated a pozzolanic reaction and the other consisted of a densified layer of secondary calcite. Furthermore, in the case of some dolomitic grains corrosion had occurred, and some dolomitic grains revealed an unusual type of reaction rim, for which the mechanism could not be explained at this stage of the research.

The results of the Hg-porosimetry revealed that porosity was higher in the case of the mortar layers with the addition of brick fragments. On the other hand, the average pore diameter was higher in the case of the mortar layers without brick fragments. The absence of brick particles in the mortar layers of the wall painting resulted in a distinctive bimodal distribution of the pores and a shift toward larger pores, which indicates the filling of pores when brick particles were present. Furthermore, layers with a higher content of brick particles yielded a higher BET surface area, a higher pore volume, and a higher average pore size in comparison with the layers of the samples with no brick fragments.

Fig. 12 – Results of the N₂ adsorption measurements. (a) The volume of pores accessible to BET was significantly higher in samples with enriched brick fragments than in mortars without these fragments. (b) The N₂ physisorption isotherms for the samples investigated.
Acknowledgments

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