High-performing mortar-based materials from the late imperial baths of Aquileia: An outstanding example of Roman building tradition in Northern Italy

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Abstract
This study provides the first detailed insight into the composition and properties of structural mortars used in a 4th-century AD bath complex in Aquileia, the emblematic center of Roman culture in Northern Italy. Eighteen mortars, taken from different structures of the site, and three stone samples from the vaulting opus caementicum have been analyzed adopting a multianalytical approach integrating optical microscopy, X-ray powder diffraction, X-ray fluorescence, and scanning electron microscopy coupled with energy-dispersive spectroscopy. The properties of the compounds are outstanding, as revealed by the formation of hydraulic phases (i.e., Al-tobermorite and AFm) in most of the samples: the waterproofing capabilities of cocciopesto mortars are remarkable, as revealed by the formation of anthropogenic Al-tobermorite (5.5 wt%) in pool coating samples; the lightweight of the vaults was guaranteed by the use of porous caementa and pozzolanic volcanic aggregates imported from the Gulf of Naples, as demonstrated by petro-mineralogical features and chemical analysis of major and trace elements. This is the first proven case of trade in these building materials to the north of the Italian peninsula. These outcomes shed new light on the robust technical expertise of local artisans in Aquileia and indicate that the Cisalpina province was by no means a peripheral reality in the Roman Empire, as far as mortar-based materials are concerned.

Keywords
Aquileia, cocciopesto, Phlegrean and Vesuvian pumices and lavas, pozzolanic reaction, provenance analysis
1 | INTRODUCTION

In the last decades, the interest in the archaeometric investigation of ancient mortar-based materials has increased thanks to the awareness of its potential for the reconstruction of the technical expertise of ancient societies. Most of the research deals with the characterization of antique “recipes,” focusing on the pozzolanic aggregates and additives, such as fired-clay fragments, pyroclastic rock clasts, and organic ashes, used to strengthen the cohesion and to waterproof the compounds (Lancaster, 2019). Particular attention is paid to correctly identifying the volcanic aggregates referred to by Vitruvius as harenae fossicæ (Vitr., II, 4, 1) and pulvis puteolanus (Vitr., II, 6, 1-2; V, 12, 2). The former are fine ashes related to the magmatic activity of the Alban and Sabatini Hills, and they were usually used in the mortar mixtures of Rome (D’Ambrosio et al., 2015; Jackson et al., 2007; Marra et al., 2013); the latter are tuff-pumiceous rocks outcropping in the Phlegean Fields out of the Gulf of Naples, which were widely traded and primarily used for the construction of seawater piers all along the ancient Mediterranean (Brandon et al., 2014; D’Ambrosio et al., 2015; Marra, Anzidei, et al., 2016).

The crucial role played by the Romans in the diffusion of concrete technology is well known. The invention of the opus caementicum, an economical, versatile, and durable mortar rubble structure (Ginouvès & Martin, 1985, pp. 51-52), was a decisive achievement for complementing the fervid building activity that Rome undertook along with its rapid expansion in the Mediterranean Sea since the 2nd century B.C. (Mogetta, 2015).

Therefore, most of the analytical studies on mortar-based materials have focused on the key contexts of Roman culture in the central-southern part of Italy, where the best examples are represented by Rome (i.e., Belfiore et al., 2014; Boccalon et al., 2019; Jackson, Ciancio Rossetto, et al., 2011; Jackson, Logan, et al., 2011; Jackson et al., 2010; Schmolder-Veit et al., 2019; Silva et al., 2005) and the Vesuvian sites (i.e., Bonazzi et al., 2007; De Luca et al., 2015; Miriello et al., 2010, 2018; Piovesan et al., 2009; Rispoli et al., 2019, 2020; Secco et al., 2019). Further research concerning towns of the provinces of the Empire has been published in the last decades. These include Sicily and Sardinia, Southern France, North Africa, the Iberian Peninsula, Greece, and Asia Minor (i.e., Alonso-Olazabal et al., 2020; Coudelas, 2012; Degryse et al., 2002; De Luca et al., 2013; Gliozzo & Camporeale, 2009; Miritto et al., 2011; Montana et al., 2018; Papavianni et al., 2013; Secco et al., 2020; Stefanidou et al., 2014).

Provincia Gallia Cisalpina (now corresponding to Northern Italy, Slovenia, and Istria) marks a significant gap in this scenario. Over the past few years, the characterization of structural mortars received little consideration (i.e., Baccelle Scudeler & De Vecchi, 2003; Bugini & Folli, 1993, 2007; Costa et al., 2001), and only recently were the first thorough analytical research articles published (Appolonia et al., 2010; Kramar et al., 2011). An important aspect that can be detected is the substantial absence of any evidence of the use of volcanic pozzolans in the mortar-based materials of the region, with few exceptions that, unfortunately, were not confirmed by adequate analysis. The absence of volcanic pozzolans could be due to a supply shortage of these products in the region, but this datum could be simply biased by the lack of in-depth analytical studies.

Regarding the Cisalpina region, Aquileia, located in today’s Friuli Venezia Giulia region (Figure 1a), has been considered a prominent representation of the technical expertise of Roman Northern Italy (Ghedini et al., 2009), and recent analytical research provided new data on the characteristics of mortar-based materials produced in the town in its long history (Dilaria & Secco, 2018; Dilaria et al., 2016, 2019; Secco et al., 2018).

Since its foundation in 181 B.C., Aquileia represented a bridgehead in the spread of the Roman culture to the north of the peninsula. The town developed into a flourishing urban center during the Imperial Age, enriched with monumental buildings and prestigious private houses. In the 4th century AD, Ausonius (Aus. XI, 9, 4) considered Aquileia one of the nine most important and extended cities of the Roman Empire, hosting the Imperial court for some periods. Between the 3rd and 4th century AD, the urban walls were frequently renovated to protect the town from recurring sieges and raids, mirroring a period of great political instability. Indeed, less than one century later, starting from Attila’s invasion (452 AD) until the end of the 5th century AD, Aquileia faced an inevitable decline and transformation of the urban space, due to the loss of its political relevance.

2 | THE CASE STUDY

The Late Imperial bath complex of Aquileia is located in the southwestern portion of the Roman town (Figure 1b). The site was first investigated, between 1922 and 1923, by G. Brusin, then by L. Bertacchi in 1961, and by P. Lopreato during the 1980s (Rubinich, 2013, 2014). Owing to its large size (between 22,500 and 25,000 m²), the building was immediately interpreted as being a bath complex. It was named “Grandi Terme” (literally “Great Baths”), as it was probably one of the largest spas in Roman Italy, comparable with the Baths of Caracalla in Rome (Rubinich, 2018). Since the early 2000s, new excavations to understand its plan have been carried out by the University of Udine and are currently underway under the guidance of Prof. Rubinich (Rubinich, 2014, 2020 and references therein).

Although the exact date of construction is still uncertain, the baths were probably built in the first half of the 4th century AD, as indicated by a dedication to Emperor Constantine by the praepositi operis, which were involved in the construction of the so-called Thermae Felices Constantinianae (Rubinich, 2013, 2014). A later dating to the mid-4th century AD is suggested by the discovery by Lopreato of a coin of Constantius II (348–350 AD) in the foundation of a mosaic pavement. Given the size of the complex, it is likely that the construction lasted for decades and was completed by Constantine’s successors (Rubinich, 2014, 2020).

From a constructive point of view, the entire thermal complex was initially (Phase Ia) built onto an extensive trench above wooden...
pilings fixed into the silty-clayish subsoil of the area. The plan of the complex reflects the typical organization of Roman Imperial thermae (Figure 1c), with symmetrical rooms along an N/S axis whose fulcrum is the 45 × 22 m frigidarium (room A2), paved in opus sectile (Figure 2a). Two equally sized halls (32 × 22 m), respectively A1 (North Hall) and A3 (South Hall), interpreted as palaestrae-apodyteria, were located to the north and south of the frigidarium. Six pools, paired two by two, were located to the north, west, and south sides of the frigidarium, while a 20 m wide natatio was placed eastwards (Figure 2b). The building was also equipped with a sophisticated system of conduits and hydraulic infrastructures for water adduction (Rubinich, 2018). On the west side, the heated rooms were arranged on suspensurae pavements (A12). Bertacchi’s excavations investigated the furnace connected to the heating hypocaust system of the caldarium, which was probably closed by a large exedra as revealed by ground penetrating radar prospections. In the NE sector, recent excavations brought to light a large opus caemencitium (Ginouvé & Martin, 1985, pp. 51–52) platform 13 × 16 (or 20) m, called S20 (Figure 2c), consisting of a base layer of coarse marble fragments and an upper part made of bricks in planar rows bonded with mortar. At least two rectangular basins were installed on the S20 platform, bordering a circular one in the center (Rubinich, 2018, 2020).

Most of the building’s floors were in opus sectile or mosaic, while little is known about the building techniques and materials, as the masonries were robbed down to their foundations by the massive postantique spoliation activities. The preserved parts showed that most of the load-bearing walls were full-body brick structures (Previato, 2015, pp.
Vaults constituted the roofing system in opus caementicium with brick ribs that were low light-weighted with porous volcanic rocks. Over time, the baths were subjected to several renovations that mainly involved the decorations of floors and walls. Ancient restorations are split into two phases: the first phase dates back to between the late 4th century AD and the early 5th century AD (Phase Ib), while the second phase dates back to the first decades of the 5th century AD (Phase Ic).

In Phase Ic, two rooms decorated with mosaics (A17–A18) were built over the pavement of room A16 of Phase Ib (Rubinich, 2020).

During the first centuries of the early Middle Ages, some rooms of the bath complex were occupied by small family units that buried their dead out of the southern perimeter wall (A13). Later, the building collapsed and became a large open-air quarry. Since the 13th century, after the systematic removal of the ruins, the site was used exclusively for agricultural purposes and it was surrounded by a thick wall, called “Braida Murada,” namely, “urban field enclosed by masonry walls” (Rubinich, 2012b).

Eighteen mortar samples were collected from different sectors of the Great Baths (Table 1). They were labeled with the name of the site (GTR) according to the function of the structures they come from:

1. Two samples (WM_1 and WM_2) come from joint mortars of full-body brick masonry walls (Figure 1g);
2. Eight samples are of floor bedding screeds (PREP). In detail, two samples come from the screed of the Phase Ia opus sectile of the frigidarium (PREP_5 and PREP_6) and six from mosaics of Phase Ia (PREP_12), Ib (PREP_2, 7, 10, 11) (Figure 1d,e), and Ic (PREP_1);
3. Three samples are of structural mortars from the S20 opus caementicium platform (PREF_14, 15, 16);
4. Two samples represent pool coatings (CM_1 and CM_2); and
5. Three samples come from the collapsed chunks of the vaults. Two of them (VM_1 and 4) have been collected from the opus caementicium portion (Figure 1f), while the third comes from the joint mortar of the brick ribs (VM_2).
In the samples with a stratified structure (i.e., mosaic screeds), each layer has been individually analyzed and labeled with a progressive number, proceeding from the topmost to the lower portion of the sample (i.e., PREP_7.1, 7.2, 7.3).

Furthermore, three stone samples, representing the three lightweight caementa lithotypes used in the vaults, were collected.

4 | ANALYTICAL METHODS

4.1 | Quantitative optical microscopy (OM) and statistical treatment

All mortar and rock samples were subjected to a preliminary petrographic study performed on 30 μm thin sections analyzed under a Nikon Eclipse ME600 microscope.

Mortar analysis was carried out according to the macroscopic and microstratigraphic analytical procedures described in Standard UNI 11176:2006 “Cultural heritage—Petrographic description of a mortar.” For each sample (or for each layer in the case of the multilayered sample PREP_7), the rates of binder, porosity, and different aggregates (i.e., fired-clay fraction, sand, etc.) were determined by digital image analysis performed using Image-J software (Schneider et al., 2012). The quantification was performed taking OM-TL scans of the thin sections as the reference; these scans were graphically treated with biochromatic thresholding after transforming the RGB images into 8-bit grayscales (Casadio et al., 2005; Marinoni et al., 2005; Miriello & Crisci, 2006). Porosity and aggregates were quantified separately, while estimation of the binder fraction was performed by subtracting from the total area the sum of aggregates and voids percentages. The size distribution of the aggregate was calculated from the mean of two series of ten manual measurements, representing the diameter of a coarse (usually >2.0 mm) and a fine fraction (<2.0 mm) of the aggregate. The sorting was performed based on the standard deviation (SD) between the mean measurements of fine and coarse aggregates. The mass color was defined

| Sample       | Structure                      | Phase | Macroscopic description |
|--------------|--------------------------------|-------|-------------------------|
| GTR_WM_1     | Wall                           | Ia    | Cocciopesto             |
| GTR_WM_2     | Wall (plint)                   | Ia    | Cocciopesto             |
| GTR_PREP_1   | Mosaic floor                   | Ic    | Lime mortar             |
| GTR_PREP_2   | Big tesseræ mosaic             | lb    | Lime mortar             |
| GTR_PREP_5   | Opus sectile floor             | Ia    | Cocciopesto             |
| GTR_PREP_6   | Opus sectile floor             | Ia (uncertain) | Cocciopesto |
| GTR_PREP_7   | Mosaic floor                   | lb    | Cocciopesto (up); concrete (down) |
| GTR_PREP_10  | Mosaic floor                   | lb    | Cocciopesto             |
| GTR_PREP_11  | Mosaic floor                   | lb    | Cocciopesto             |
| GTR_PREP_12  | Mosaic floor                   | Ia    | Cocciopesto             |
| GTR_PREM_14  | S20 opus caementicium platform | Ia    | Cocciopesto             |
| GTR_PREM_15  | S20 opus caementicium platform | Ia    | Cocciopesto             |
| GTR_PREM_16  | S20 opus caementicium platform | Ia    | Cocciopesto             |
| GTR_CM_1     | Pool                           | Ia    | Cocciopesto             |
| GTR_CM_2     | Pool                           | Ia    | Cocciopesto             |
| GTR_VM_1     | Vault (opus caementicium)      | Ia    | Cocciopesto             |
| GTR_VM_2     | Vault (rib)                    | Ia    | Cocciopesto             |
| GTR_VM_4     | Vault (opus caementicium)      | Ia    | Cocciopesto             |
| GTR_VM_1_G   | Vault (opus caementicium)      | Ia    | Volcanic rock           |
| GTR_VM_1_N   | Vault (opus caementicium)      | Ia    | Volcanic rock           |
| GTR_VM_4_R   | Vault (opus caementicium)      | Ia    | Volcanic rock           |
using Munsell soil color charts (Munsell, 1994). To interpret correlation patterns among samples, the petrographic quantitative data were subjected to a multivariate statistical treatment by principal component analysis (PCA). This is a valid procedure for a rough grouping of samples according to their petrographic features (De Luca et al., 2013, 2015; Dilaria, 2020; Mirello et al., 2018). PCA was performed on log-transformed petrographic descriptive variables to obtain a small number of linear combinations that adequately describes the original mortar profiles. A series of principal components representing the data set variability were extracted, according to the following parameters: (i) all the variables were considered for analysis and (ii) no limit was set for the number of principal components to be calculated. Samples were then reported in a scatterplot according to the value of the first two extracted components (PC1, PC2). All statistical analyses were carried out using Statgraphics Centurion PRO 18 software.

### 4.2 X-ray powder diffraction (XRPD)

The mineralogical investigations were performed on the three rock samples and on a selection of representative mortars of the groups identified after the PCA treatment of quantified OM data. Mineralogical profiles were determined by quantitative phase analysis based on X-ray powder diffraction (XRPD-QPA). Measurements were obtained using a Bragg–Brentano θ–2θ diffractometer (PANalytical X’Pert PRO, Cu-Kα radiation, 40 kV and 40 mA), equipped with a real-time multiple strip (RTMS) detector (X’Celerator by Panalytical). QPA profiles were then determined adopting the same methodology as that described in Secco et al. (2019, 2020).

To properly describe the formation of both geogenic and anthropogenic products, XRPD analyses were carried out on bulk samples (XRPD-bulk) and on the separated binder fraction (XRPD-binder) of mortars. The latter analysis was performed using the Cryo2Sonic 2.0 separation procedure (Addis et al., 2019), custom-modified through the addition of a chelating agent to the sedimentation solution (sodium hexametaphosphate 0.5 wt%) to favor the suspension of the finer, noncarbonate phases such as clay minerals and hydrate products, prone to flocculation due to their surface charges, as described in Secco et al. (2020).

### 4.3 Scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS)

SEM-EDS analyses were performed on rock sample VM_1_G and on a selection of representative mortars of the groups identified after the PCA treatment of quantified OM data. Microchemical and microstructural analyses were performed using a Camscan MX2500 microscope, equipped with a lanthanum hexaboride source and an EDAX energy-dispersive microanalysis system. The qualitative interpretation of the fluorescence spectra and the semiquantitative estimation of the percentages, by the weights of oxides, were performed using the dedicated software SEMQuant Phizaf. The SEM-EDS analyses were carried out to (a) analyze the chemical composition of the binders; (b) confirm the distribution of hydraulic phases in the matrices, on the basis of XRPD results (this was done adopting the cementation [CI] and hydraulicity [HI] indices.
in accord with Boynton, 1966; and (c) provide a semiquantitative estimation of major chemical elements of volcanic rock aggregates and caementa, to corroborate X-ray fluorescence (XRF) geochemical analyses.

4.4 | XRF

XRF analysis was performed to determine the provenance of the three vaulting caementa by comparing their major and trace chemical elements with the data in the literature. The analysis was performed using a Bruker S8 Tiger WD X-ray fluorescence spectrometer with an XRF radius of 34 mm, equipped with a rhodium tube operating at an intensity of 40 kW, following the method for correcting matrix effects of Franzini et al. (1972, 1975). The material for XRF analysis was collected from the core of pluri-centimetric fragments of the caementa. We mechanically scraped away the interfacial zones between the rock and the binder in order to avoid intrusion in the analysis, as much as possible (Jackson et al., 2014, p. 186). Samples were analyzed without a preliminary HCl bathing, as this step could affect major and trace elements, in particular Y (D’Ambrosio et al., 2015; Marra, Anzidei, et al., 2016; Marra, D’Ambrosio, et al., 2016). We could affect major and trace elements, in particular Y (D’Ambrosio et al., 2015; Marra, Anzidei, et al., 2016; Marra, D’Ambrosio, et al., 2016).

5 | RESULTS

5.1 | Mortar composition and groups

PCA analysis of quantified OM data was performed to identify groups of mortars having similar features. Because of the high compositional variability, a PCA analysis on the full sample data set was performed to distinguish “concrete” (Ginouvès & Martin, 1985, p. 51) layer PREP_7.3 and a “lime putty” (Ginouvès & Martin, 1985, p. 45) layer PREP_7.1 from the central core, represented by all the other mortars (Figure 3a). A second PCA (PC1 = 34.7% and PC2 = 17.5% of the global variance), performed excluding PREP_7.1 and 7.3, enhanced mortar clustering. Most of the samples are distributed within four groups, while only two are the outliers (Figure 3b,c and Table 2). Gr 1 is the most populated group and it reunites cocciopesto mortars (Ginouvès & Martin, 1985, p. 51) having no peculiar features (WM_1, 2, 7.2, PREP_11, PREF_14, 15, VM_2), as they fall in the middle of the scatterplot at PC1 = 0 ± 2 and PC2 = 0 ± 0.5. Three samples having PC2 < −1 (PREP_10, 12, PREF_16) are reunited in a subordinate group (Gr 1b).

Gr 2 reunites samples CM_1 and 2, falling at PC1 < 0 and PC2 > 0.5. They are characterised by the abundance of fired-clay fragments (FF) and fired-clay powder (FP, ø < 0.10 mm).

Gr 3 clusters lime mortars (Ginouvès & Martin, 1985, p. 50) PREP_1 and 2 falling at PC1 > 3. They are strongly correlated in terms of the abundance of clasts of fluvial sediments (FS), lime lumps, and tesserae chips.

Gr 4 groups samples VM_1 and 4, falling at PC2 > 2.5. The peculiar feature of these mortars consists of the presence of volcanic rocks as aggregates.

Finally, PREP_5 and PREP_6, both having PC1 < −2.5, are separated from the other groups and they can be considered as outliers.

The main petrographic characteristics of the groups reported hereafter are summarized in Table S3:

(1) Gr 1 samples have moderate toughness and a whitish mass color (2.5 YR 8/3). The aerial lime paste has a micritic texture. The binder-to-aggregate ratio (B/A), ranging between 0.7 and 1.6, is typical for very fat mixtures (Ginouvès & Martin, 1985, p. 50). The aggregate fraction (33%–49%) has a moderate sorting (1.3–2.8 SD) and it is made of FS mixed with FF and sporadic FP (Figure 4a). FS clasts fall in the granulometric range of medium to fine sands (Wentworth, 1922). They are represented by carbonate (ø = 2/3 of this fraction, with limestones prevailing on dolostones) and silicate (quartz and chert, ø ≃ 1/3 of this fraction) granules. Scattered minerals of feldspars (albite) and micas (muscovite) have been detected. The FS/FF + FP ratio ranges from 0.2 to 1.4 (with the only exception of WM_1 having FS/FF + FP = 3.4). Sometimes, reaction rims have been found around FF or FP. The binder matrix is zoned, where the areas having low bi-refringence color indicate the occurrence of hydrate phases (Pecchioni et al., 2014). Samples of Gr 1b (PREP_10, 12, PREF_16) can be distinguished from those of Gr 1 for an increased presence of

| Table 2 | Sample distribution in groups after PCA analysis on OM quantitative data |
|---------|-----------------------------------------------------------------|
| Group   | Samples (GTR)                                                  | Main compositional features                                      |
| 1       | WM_1; WM_2; PREP_7.2; PREP_11; PREF_14; PREF_15; VM_2            | Cocciopesto made of FF mixed with FF with the sporadic presence of FP |
| 1b      | PREP_10; PREP_12; PREP_16                                       | Cocciopesto having FS prevailing on FF                           |
| 2       | CM_1; CM_2                                                     | Highly cohesive cocciopesto with abundant FF and diffused FP     |
| 3       | PREP_1; PREP_2                                                 | Binder-rich lime mortars                                         |
| 4       | VM_1; VM_4                                                    | Cocciopesto with volcanic aggregates (lava and pumices)         |
| Outliers| PREP_5; PREP_6; PREP_7.1; PREP_7.3                            |                                                                  |

Abbreviations: FF, fired-clay fragments; FP, fired-clay powder (ø < 0.10 mm); FS, fluvial subrounded sediments; OM, optical microscopy; PCA, principal component analysis.
FS and RM (Figure 4b). For these samples, the B/A ratio is found to be around 0.8 or 0.9.

(2) Gr 2 samples are pinkish (2.5 YR 8/3), highly cohesive cocciópesto mortars, with a consistent occurrence of FF and diffused micrometric FP, closely mixed with the binder. The occurrence of FS is negligible (Figure 4c). The binder matrix has low birefringence colors, likely due to the diffused formation of hydrate products (Pecchioni et al., 2014). Lime lumps are minimal (2%), and the porosity is limited (4%–5%).

(3) Gr 3 samples are binder-rich lime mortars (B/A ratio 1.8 and 1.9). The presence of lime lumps is highly pronounced (16%–24%). The aggregates represent less than 35% of the samples and they are composed of subrounded medium to fine FS with a variable
Gr 4 samples are characterized by the presence of small subrounded clasts of volcanic lava and pumice. They are particularly abundant in VM_4, representing about the 12% of the sample (Figure 4e), while they are less in VM_1. The remaining aggregate’s fraction is composed of FS and FF (with traces of FP). The binder matrix is inhomogeneous. The low birefringence colors detected in certain zones are probably indicative of the strong development of calcium alumino-silicate hydrates (Pecchioni et al., 2014).

Some samples do not cluster within the outlined distribution: the first pair includes layers PREP_7.1 and 7.3, reported in Figure 3a. The former is made of homogeneous lime putty with the sporadic occurrence of FS, while the latter is made of a concrete rich in FS represented by medium to fine gravel (Wentworth, 1922), less frequent coarse FF, and sporadic volcanic rock clasts.

The second pair of outliers is PREP_5 and PREP_6. The former is similar to Gr 2 mortars, as it presents an aggregate entirely composed of coarse FF, but the presence of FP is low (Figure 4f), and the SD of the aggregates is high (3.8). The binder matrix looks extremely zoned: areas characterized by low birefringence alternate with others having high birefringence. On the other hand, PREP_6 is characterized by an aggregate fraction predominantly represented by reused mortar fragments (RM, 37%), while both FF and FS represent minor aliquots.

## 5.2 Hydraulic properties

The hydraulic properties of mortar samples were determined by coupling quantitative XRPD-bulk and binder analyses (Table S4) with punctual semiquantitative SEM-EDS investigations (Table S5).

For some mortars, XRPD-bulk analysis reported high aliquots of calcium (alumino)silicate hydrates C-(A)-S-H and calcium aluminate hydrates C-A-H, whose formation is determined by the pozzolanic interaction between the aerial lime paste with FF and, specifically, FP. Crystalline C-(A)-S-H is structured in the form of anthropogenic tobermorite 11 Å, also known as Al-tobermorite (Jackson et al., 2013, 2017). Crystalline C-A-H consists of AFm phases, in the form of hydrocalumite and hydrotalcite (Matschei et al., 2007). The sum of Al-tobermorite and AFm represents about 4.2 wt% of the bulk sample CM_1 (pool coating) and 2.7 wt% of PREP_5 (opus sectile bedding), respectively (Figure 5a). For both mortars, probably also a relevant fraction of the amorphous component could be related to gel-like C-(A)-S-H or C-A-H. The occurrence of brucite in sample CM_1 can be considered as a newly formed phase connected with the pozzolanic reaction of the material (Jackson et al., 2014; Vola et al., 2011). The absence of this phase in all other analyzed samples makes the calcination of dolomitic limestone (Bläuer-Böhm & Jagers, 1997) unlikely, as suggested also by the EDS investigations of highly calcic lime lumps. The presence of free magnesium ions in the system probably depends on de-dolomitization phenomena of dolomitic aggregates (Katayama, 2010) in a high-pH environment.

Samples from the S20 opus caementicium platform (PREF_14 and 16), as well as sample VM_4, are characterized by the relevant formation of crystalline AFm, but no Al-tobermorite was detected. In VM_4, anomalous high rates of aragonite (5.2 wt%) and vaterite (3.4 wt%) were found. The latter was also documented (2.5 wt%) in PREP_5. These phases represent metastable anthropogenic transitional products formed after decalcification and recarbonation of calcium carbonates along with the pozzolanic reaction of the material (Jackson et al., 2014, 2017; Morandeau et al., 2014; Thiery et al., 2007). Finally, the presence of 1.0 wt% phillipsite in VM_4 can be related to the authigenic zeolitization of volcanic aggregates (De’Gennaro et al., 1990, 2000).

Most of the remaining samples have feeble hydraulic properties, and only WM_2 and PREP_1 can be considered aerial compounds (no AFm phases are detected).

To properly describe and quantify the formation of the hydraulic phases, targeted XRPD-binder analyses were carried out on a limited selection of samples (Figure 6), which reported the same trend as that obtained from the XRPD-bulk analysis.

The formation of Al-tobermorite and AFm is still extremely evident in CM_1 (Al-tobermorite + AFm = 7.5 wt%) and in PREP_5 (Al-tobermorite + AFm = 4.3 wt%) (Figure 5b). Furthermore, the abundant amorphous fraction is likely related to the occurrence of gel-like C-(A)-S-H/C-A-H products. The high SiO₂ rates in the presence of Al₂O₃, reported in Figure 7a,b,b1,b2.
demonstrate the formation of C–(A)–S–H in the outer perimeter of a lime lump in CM_1.

The remaining samples PREF_16, VM_2, and VM_4 are moderately hydraulic, as the formation of AFm is limited. XRPD-binder analysis detected the presence of hydroxyapophyllite (0.2 wt%) in VM_4: this is a silicate hydrate commonly associated with zeolites, whose formation is due to the pozzolanic interaction between calcium and potassic components of volcanic rocks (Rochelle et al., 2016).

SEM-EDS punctual analyses on the binder matrix confirmed XRPD investigations (Figure 5c,d).

The highest HI and CI (0.72 and 1.68), indicative of eminently hydraulic mixtures, were detected in sample CM_1. This confirms how the strong pozzolanic interaction between the micrometric fired-clay powder and the aerial lime contributes to the formation of calcium silicoaluminate hydrates (Coutelas et al., 2004; Lancaster, 2019; Teutonico et al., 2000). The high HI and CI are also found in sample PREF_14 (0.45 and 1.08, respectively). On the other hand, the chemical investigation of sample PREP_5 confirmed the zoning hypothesized after OM investigations: low birefringence areas are characterized by HI and CI of 1.11 and 2.57, respectively, while high birefringence areas have HI and CI of 0.15 and 0.41 (mean HI and CI: 0.48 and 1.15), respectively.

VM_1, VM_4, and WM_1 showed HI and CI between 0.16 and 0.31 and 0.40-0.74, indicative of moderately hydraulic mixtures. However, also in these cases, the matrix appears zoned, with eminently calcic carbonated areas surrounded by C–(A)–S–H/C–A–H-enriched zones with low birefringence (Figure 7c,d,d1,d2). For sample VM_4, the high HI and CI (0.31 and 0.74) could also depend on the strong interaction between lime and the reactive glassy fraction of the volcanic aggregates, acting as natural pozzolans. Most of these clasts altered and showed strong development of CaO-enriched fluids even in the inner cores (Figure 7e,f,f1,f2).

Finally, HI ≤ 0.06 and CI ≤ 0.15 of samples PREP_1 and PREP_7.2 indicate mixtures presenting low to null hydraulic properties.
5.3 | Provenance of raw materials

The majority of the raw materials used in the production of the mortar-based materials of the Great Baths were locally sourced. From a petro-mineralogical point of view, carbonate and silicate aggregates are fully compatible with the sediments of the Isonzo–Natisone–Torre fluvial network. These are characterized by a dominant component of calcareous/dolomitic sands and gravels, with a secondary presence of chert and quartz sands (Gazzi et al., 1973; Marocco, 2009).

Less is known about the carbonate rocks used for the production of lime. SEM-EDS analyses were performed on lime lumps of some samples (WM_1; PREP_1, 7.2, 14; CM_1). In most cases, for samples with pronounced hydraulic properties, we observed an intense development of gel-like C–A–S–H in the micropores of lime lumps. This indicated a clear alteration of the original geochemical profile of the binder. Only in PREP_1 and WM_1 did the analyzed lime lumps yield high CaO and low MgO contents, suggesting the calcination of almost pure calcic limestones (Zacharopoulou, 2009). This profile is compatible with the geochemistry of the limestones locally outcropping in the Isontine and Triestine Karst (G. B. Carulli & Onofri, 1960; Cucchi et al., 2015; Cucchi & Gerdol, 1985; Tentor et al., 1994) as well as in Istria (Lazzarini, 2006).

The provenance of the three volcanic vaulting lightweight caementa and aggregates detected in VM_1 and VM_4 samples was also determined. These rocks were surely imported in Aquileia, as no volcanic districts are present nearby, as the region is dominated by limestone and dolostone outcrops (G. Carulli, 2006). OM and XRPD investigations on caementa samples were performed for a preliminary determination of their provenance. XRPD data have been recalculated at 100% after the removal of binder-related phases, that is, calcite (Table S6). VM_1_G is a yellowish (2.5 Y 8/4), highly vesicular pyroclastic pumice (Figure 8a1). Its texture is glassy (Figure 8a2). The rare phenocrysts are represented by biotite, Ca-plagioclases (bytownite/anorthite), K-feldspars (sanidine), and sporadic augite. The quartz content is extremely low (0.9 wt%). The zeolitization products are extremely pronounced: 48.3 wt % phillipsite and 1.9 chabazite. Percentages have been normalized at 100% after the removal of calcite (31.7 wt%) and vaterite (0.6 wt%). These latter phases are related to the neoformation of CaO-based metastable products into the voids of the rock, along with the pervasive
pozzolanic reaction of the material, as revealed through SEM-EDS investigations of the sample (Figure 8a3–a6).

VM_1_N is a vesicular grayish-brown (2.5 Y 5/2) pumiceous scoria (Figure 8b1,b2), rich in K-feldspar (sanidine–anorthoclase) microlites (56.4 wt%), associated with Ca-plagioclases of the anorthite–bytownite type (11.0 wt%). Augitic phenocrysts are more frequent than biotite ones. The glassy fraction is low in comparison with sample VM_1_G (13.0 wt%), as well as phillipsite (11.9 wt%). On the other hand, the percentage of quartz is higher (3.2 wt%).

VM_4_R is a highly vesicular tephritic lava (Figure 8c1) with a porphyritic–hyalopilitic texture (Figure 8c2). The groundmass is predominantly made of K-feldspars of sanidine (46.4 wt%) and subordinated Ca-plagioclases (17.3 wt%). Phenocrysts of augite are frequent (8.2 wt%). The presence of zeolites is feeble (phillipsite 1.0 wt %, chabazite 0.2 wt%). The dark-red color of the sample (2.5 YR 6/4) depends on the concentration of hematite (6.0 wt%).

The sanidine, documented in all samples and especially in VM_1_N, is a recurrent mineral in the vulcanism of the Roman Comagmatic region (Marra et al., 2013; Peccerillo, 2005). The presence of authigenic phillipsite, which is particularly abundant in samples VM_1_G and VM_1_N, is common in the Phlegranean products of the NYT formations (De’Gennaro et al., 1990, 2000). This zeolite is frequently documented in Roman mortars and concretes containing Phlegranean pyroclasts (Jackson et al., 2014; Rispoli et al., 2019, 2020; Stanislao et al., 2011; Vola et al., 2011).

On the other hand, textural and petro-mineralogical features of sample VM_4_R are fully compatible with the Vesuvian “foam lava” (Cinque & Irollo, 2004; Di Girolamo, 1968; Marra et al., 2013), a porous lava pillow formation of the Somma-Vesuvius eruptive unit (Langella et al., 2009; Santacroce, 1987).

Geochemical analyses performed through XRF provided a better definition of the provenance of the three samples (Table S7).

FIGURE 9  TAS scatterplots of the clast of lightweight caementa and volcanic aggregates of the vaults. (a) Sample distribution in relation to volcanic rocks’ chemistry (after Le Bas et al., 1986); (b) sample distribution in relation to the Phlegranean fields areas of the Campanian Ignimbrite (CI), Neapolitan Yellow Tuff (NYT), and post-NYT events (data from Marra, Anzidei, et al., 2016; Morra et al., 2010; Peccerillo, 2005); (c) sample distribution in relation to the three main eruptive facies of the Vesuvian products’ fields (data from Morra et al., 2010; Peccerillo, 2005); and (d) sample distribution in relation to the fields occupied by the products of the Roman magmatic province, Tuscan Magmatic province, and Ischia-Procida-Vivara’s volcanoes (data from Avanzinelli et al., 2009; Boari et al., 2009; Marra et al., 2009; Peccerillo, 2005). TAS, total alkali silica.
All the caementa samples plot in the total alkali silica (TAS) fields (Le Bas et al., 1986) occupied by the slightly - middle SiO$_2$ undersaturated volcanic rocks (Figure 9a).

VM$_1$N falls in a trachyandesite field compatible with the area of the Phlegraean vulcanism (Morra et al., 2010; Peccerillo, 2005) (Figure 9b). It shows good overlap with some products of the NYT or later volcanic activities (12–8.4 and <8.4 k.a. B.P.) (Marra, Anzidei, et al., 2016).

VM$_4$R, on the other hand, plots in between the Somma-Vesuvius products older than 8.9 k.a. B.P. and those younger than 79 AD (Peccerillo, 2005; Santacroce et al., 2008) (Figure 9c).

Finally, VM$_1$G returns anomalous low values of alkali and silica. The surprisingly high content of CaO demonstrates the deep development of C-(A)-S-H and CaO-enriched fluids in the sample, as suggested by the results of the XRPD analysis too. The high loss of ignition (LOI) of the sample (19.2) confirms this assumption. Both VM$_1$N and VM$_4$G samples have a > 3.0 (4.1 and 3.5, respectively), which is indicative of a slight alteration too (Lancaster et al., 2011; Marra et al., 2013). This aspect does not make XRF major elements suitable for an in-depth provenance analysis.

To acquire a better major chemical element profile for VM$_1$G, we performed six punctual SEM-EDS investigations on three areas of the volcanic glass that appeared unaltered. The mean values for each zone of the sample under investigation are reported in Table S8. In the TAS, they cover a wide area ranging from the trachyte’s to the phonolite’s fields (Figure 9a). Also, in

![Figure 10](image-url)
this case, therefore, SEM data cannot be considered as conclusive. Also, the geochemical profile of the \textit{caementa} reported in the TAS cannot be considered as indicative of a specific volcanic district. In fact, as shown in Figure 9d, good matches can also be traced with certain products of Ischia-Procida’s and Roccamonfina’s volcanoes of the Campanian district (Peccerillo, 2005), as well as with some products of the Latial and Tuscan Magmatic Province (Avanzinelli et al., 2009; Boari et al., 2009). Nevertheless, all the samples do not match with the ultrapotassic products of the Alban Hills (Boari et al., 2009; Marra et al., 2009; Peccerillo, 2005).

Considering the high variability of the TAS, the analyses of Zr/Y versus Nb/Y and Nb/TiO$_2$ versus Zr/TiO$_2$ were crucial to confirm the provenance revealed by the Zr/TiO$_2$ vs Nb/TiO$_2$ plot (D’Ambrosio et al., 2015). The Zr/TiO$_2$ versus Nb/TiO$_2$ plot can be considered reliable, as TiO$_2$ appears to be more stable than Y, even after HCl attack (D’Ambrosio et al., 2015). Therefore, the provenance of sample VM$_1$-G is surely Campania, while a stronger correlation with the post-NYT products may be tracked only on the basis of the Zr/TiO$_2$ versus Nb/TiO$_2$ plot.

Finally, as outlined before, sample VM$_4$-R presents the peculiar petro-mineralogical and textural features of the Vesuvian lava pillows. In the TAS diagram, it overlaps the Vesuvian products. In the Nb/Y versus Zr/Y plot (Figure 10b), it falls within the Sorrento field, overlapping the area of the Sarno eruption (22 k.a. B.P.) (Marra et al., 2013) as well as that of the lava flows dated 36–18 k.a. B.P. and documented with a deep borehole in the southern flank of Somma-Vesuvius (Di Renzo et al., 2007). It also slightly overlapped the NYT field, but considering the TAS diagram as well as its petro-mineralogical features, it is not compatible with the low SiO$_2$-undersaturated products of NYT activity. In detail (Figure 10c), the Nb/Y versus Zr/Y profile of VM$_4$-R matches with that of some lava samples taken from the vaults of a series of Imperial buildings in Rome (Basilica Ulpia 022, Forum of Caesar 021, Basilica Julia 023), analyzed in Lancaster et al. (2011). These were attributed by Marra et al. (2013) to the Somma-Vesuvius lavas cropping on the southern flanks of the volcano (36–18 k.a. B.P.).

Combining OM, XRPD, SEM-EDS, and XRF analyses, the provenance of the three lightweight caementa was defined. VM$_1$-G and VM$_1$-N came from the Phlegraean volcanic units of the post-NYT activity (i.e., Astroni, Agnano, Archiaverno, and Miseno units), cropping around Puteoli. Nevertheless, the Vesuvian provenance of sample VM$_1$-G cannot be completely excluded. VM$_4$-R, on the other hand, can be safely assigned to Vesuvian lava formations older than 8.9 k.a. B.P.

The origin of volcanic clasts used as aggregate is barely determinable, as they are usually altered due to the pozzolanic reaction. The unaltered glassy portions of two volcanic aggregates in sample VM$_4$, labeled VM$_4$-a and VM$_4$-b, was detected and analyzed by SEM-EDS (Table S8). In the TAS (Figure 9a), they fall roughly in the same fields occupied by the lightweight caementa, but the exact sourcing area can differ.

Sporadic clasts of volcanic rocks have also been documented in layers PREP 7.2 and 7.3. Their presence is probably accidental. No provenance analyses have been performed for the volcanic rocks in these samples.

6 | DISCUSSION

The analysis of the samples collected from the site of the Great Baths proved to be extremely important within the framework of the archaeological research carried out in Aquileia.

The distribution of the samples in the groups is in agreement with the structural use of the mortars: those collected from the vaults...
in opus caementicium (Gr 4) can be distinguished from those referring to hydraulic infrastructures (Gr 2). Both these groups differ from the most populated one, represented by the samples coming from floor bedding layers and wall joints (Gr 1). The chronology of production does not particularly bias the composition of the samples, but it must be highlighted that Gr 3 comprises only mortars related to phases later than la.

The outstanding quality of the mortar-based materials of the complex is highlighted by the hydraulic properties of most of the samples. An experienced chain of production can be perceived in the slight differences in composition and hydraulic characteristics of the samples, which depend on the structural use: joint mortars and bedding mixtures for some types of floors (i.e., mosaics) are quite ordinary; on the other hand, the manufacture of mortars applied in critical structural units, such as hydraulic infrastructures and roofing systems, required the proper choice of raw materials and correct preparation of the mixture. This degree of “mixing care” has been parametrized by comparing samples according to their hydraulic properties, and quantifying the formation of calcium silicoaluminate hydrates through XRPD and SEM-EDS investigations.

The best mortars are the pool coatings that guarantee excellent waterproofing. XRPD data of sample CM_1 report a hydraulic rate three to five times higher than that of the cocciopesto mortars used in all the other water tanks of Aquileia (Dilaria, 2020). This trend does not change if we compare the H/Cl of CM_1 with that of cisterns’ coating mortars from other Roman sites (De Luca et al., 2015; Miriello et al., 2018; Rispoli et al., 2019, 2020; Secco et al., 2020).

Further distinctions exist in “recipes” for pavements’ bedding mortars according to the floor type. Good hydraulic properties have been reported for the sole sample PREP_5, coming from the sub-strate of the opus sectile pavement of the frigidarium. This is a common feature of the opus sectile pavements of Aquileia (Dilaria et al., 2016; Secco et al., 2018). Hydraulic compounds produced along with the pozzolanic reaction ensure waterproofing and strengthening of the material (Navrátilová & Rovnaníková, 2016, with references therein) to adequately support the heavy stone slabs of the revetment.

Mosaics’ bedding mortars differ from the opus sectile ones. In most cases, mosaics were set on a single layer of cocciopesto with low hydraulic properties, while in only one case (PREP_7) was the pavement placed over a bedding distributed in up to three different layers, in agreement with the Vitruvian standard (Vitr. VII, 1, 1–7): a 3.5–5.0 cm thick cocciopesto layer (nucleus) (layer PREP_7.2) and an inner concrete stratum with gravel and FFs, about 7.0–8.5 cm thick (rudus) (layer PREP_7.3), are placed over a layer of loose stones, FFs, and marble chips (statumen). Above the screed, tesserae were set on a thin lime putty film (Dunbabin, 1999; Moore, 1968, pp. 281–288), represented by the layer PREP_7.1. This is the typical Roman mosaic-making technique, which was usually adopted in the Republican and High Imperial Age. On the other hand, during the Late Imperial Age, the mosaics in Aquileia were set on shoddy beddings made of a single layer of friable sandy lime mortar laid over earthen dumps (Dilaria, 2020; Dilaria et al., 2016; Secco et al., 2018). The adoption of this weak making method can be recognized in the making of Phase Ib and Ic mosaics of the northern sector of the Great Baths, which were placed over mortars of the Gr 3. This demonstrates that the restorations of the complex were carried out by artisans with a lower level of experience than those who were working in the original building phase.

Samples PREP_14 and 16, collected from the S20 platform, are characterized by moderate hydraulic properties. Good impermeabilization was necessary for this structure, equipped with an sophisticated system of tanks and pools (Rubinich, 2020). The slight compositional differences among S20 samples (PREP_14, 15, and 16), observed via OM, are probably due to the width and depth of the platform, whose construction required a long time for completion. These nuances in the composition could reflect the daily preparation of mixtures (Coutelas, 2012). Similar considerations can be outlined for samples PREP_10 and 11 too, coming from different areas of a Phase Ib mosaic. On the other hand, the different composition and the abundant presence of RM in the sample PREP_6, which were not detected in PREP_5, could testify to important (undated) restoration of the SW portion of the pavement of the frigidarium.

The vaulting system of the baths is also sophisticated as demonstrated by the use of lightweight opus caementicium. The abundant presence of pluri-centimetric porous caementa testifies to a huge supply of material from the Gulf of Naples. Although no mention is reported in Latin treaties, the use of lightweight pumices, lava, or tuffs in the opus caementicium vaults of Roman monumental buildings has been archaeologically proven since the mid-1st century B.C., becoming established by the early 2nd century AD (Lancaster, 2005, pp. 59–64; Lancaster, 2011; Lancaster, 2015, pp. 29–38; Lancaster et al., 2011). A finer fraction of these volcanic rocks constitutes the aggregates of some mortars, but connecting this use to the Vitruvian concept of pozzolana (see section 1) may be incorrect. Their use was primarily intended for providing further light-weight properties to the vaults, as supposed by Bianchi et al. (2011), Jackson et al. (2010), Jackson, Logan, et al. (2011), who interpreted, in this way, analogous evidence from vaults of monuments in Rome. Furthermore, the hydraulic properties surely increase the strength of the opus caementicium structure exposed to major mechanical stress. The higher amount of porous volcanic aggregates in sample VM_4 in comparison with VM_1 may indicate the progressive lightening of the opus caementicium castings at higher elevations. This was a well-known practice in Roman times, with a famous example represented by the Pantheon (Lancaster, 2005, p. 62). Therefore, VM_4 might come from the uppermost portion of a vault, which was supposed to have higher light-weighting capabilities.

Considering the dating of the Great Baths, the use of imported rocks as vaulting caementa is one of the latest attestations of this tradition in the Roman Empire. The presence of Phlegrean pumices in the vaults of the Thermæ of Diocletian in Rome (see paragraph 5.3),
whose construction, dated between 296 and 308 AD, was concluded a few decades before that of the baths of Aquileia, demonstrates that the exportation of these raw materials from Campania lasted during the Late Imperial Age, even though this trading network in the Mediterranean reached its climax a couple of centuries before (Hohlfeder & Oleson, 2014).

Another recurring aspect in Roman public buildings is the combined use of vaulting lightweight caementa quarried from different zones (Bianchi et al., 2011; Marra et al., 2013). This could be related to the different supplies of raw materials as the construction progresses, but it could also depend on the specific plan for gradually reducing the weight of the vaults at different heights using different materials (Marra et al., 2013).

Lancaster (2006, 2011) and Lancaster et al. (2011) suggested a shift in time in the sorting of the lightweight caementa in the vaulted buildings of Rome: while Vesuvian lavas were imported until the late 3rd century AD, the use of volcanic rocks other than the Vesuvian ones was prevalent in later ages. This hypothesis, which has been dubiously linked to a decline in land transport from Vesuvian quarries after the economic crisis of the 3rd century, is in contrast with the data from Aquileia here discussed.

However, the import of lightweight materials for vaulting structures was uncommon in Northern Italy in Roman times, even if the terms of comparison are very few. In fact, since the Middle Ages, most of the buildings in this region underwent marked spoliation of the construction materials and the roofing systems have been preserved only in a few cases. In the Villa of Sirmione (Garda Lake), dated to the Augustan era, the use of volcanic rocks other than Vesuvian ones is prevalent in later ages. This hypothesis, which has been dubiously linked to a decline in land transport from Vesuvian quarries after the economic crisis of the 3rd century, is in contrast with the data from Aquileia here discussed.

The proximity to seaside or fluvial networks and to adequately equipped ports is an important factor affecting the trade of building stones other than marbles and decorative lithotypes (Russell, 2013, pp. 95–140). As far as Aquileia is concerned, the imported rocks could have been shipped from the harbors of Puteoli, Baia, and Miseno (Gianfrotta, 1998) to the river docks of Aquileia or, considering the late dating of the Baths, to the seaport of the neighboring Grado (Rebecchi, 1980). However, the maritime route from Campania to the northern Adriatic Sea is not straightforward, and the Gulf of Naples does not represent the closest area to Aquileia for the procurement of lightweight caementa. In the vaults of the Palace of Diocletian in Split (Croatia), Lancaster (2015, p. 33), reports the use of locally mined porous calcareous tufa, known as sedra. This reference demonstrates that near quarries for the provisioning of lightweight stones were still active in the 4th century AD and easily reachable by sea.

The choice for the supply of the materials from the Gulf of Naples has some alternative explanations: (a) the centuries-old knowledge of the prominent light-weighting capabilities of the Campanian porous rocks, which were largely used in the concrete vaulted buildings of Rome (Lancaster, 2011, 2015; Lancaster et al., 2011; Marra et al., 2013); (b) the provenance of the committee or craftsmanship from central-southern Italy; (c) and the little diffusion of regional building materials, as the sedra calcareous tufa, out of the territories in which they were used.

Besides the use of porous caementa for opus caementicium, a finer fraction of the volcanic rocks from Campania was used as pozzolanic aggregate of vaulting mortars too. The trade of pozzolans from southern Italy to the north has been proven in other circumstances so far. The mention of the presence of Phlegrean pumices in the mortars of the harbor piers and vaults of the baths of Forum Iulii (Frejus) (Excoffon & Dubar, 2011), as well as in the joint mortars of the 3rd-century B.C. urban walls of Ravenna (Costa et al., 2001), was not validated by conclusive analysis. As recently discussed by Dilaria et al. (2019) and Dilaria (2020), pumices from Campi Flegrei are not even present in a concrete block in the foundations of the Republican urban walls of Aquileia (Bonetto et al., 2016) as, in this case, hydraulic properties were provided by a sort of natural hydraulic binder derived from the calcination of cherty limestones (Dilaria, 2020; Dilaria et al., 2019). The unique term of comparison on the use of pyroclastic rocks in Cisalpina, as pozzolan in stricto sensu, comes from the opus caementicium foundation of the orchestra (Dilaria, personal observation) of the theater of Aquileia (Ghiotto et al., 2021). Ongoing analysis will be focused on determining their exact provenance.

7 | CONCLUSIONS

In this study, we outline how decisive the analysis of ancient mortars is to solve traditional archaeological questions, such as the trading of raw materials and the technical expertise of crafts in antiquity. The data reported in this paper are rooted in the interrelationship between archaeology and geosciences and are focused on the understanding of archaeological sites and ancient socioeconomic relations through the investigation of geomaterials such as mortar-based ones.

Adopting this multidisciplinary approach, we are now able to fill the gap, re-evaluating the towns of ancient Cisalpina no longer as peripheral entities of the Empire, but rather as deeply rooted in the technical awareness of the Roman tradition. In fact, the full outcomes of the research demonstrate how remarkable the financial effort for the construction of the Great Baths was: only a high-ranked committee, such as the Constantinian imperial family, could have guaranteed the best workmanship and building materials available on the market at the time. No other public or private building in Aquileia achieved the same high-quality standard as far as mortar-based materials are concerned (Dilaria, 2020). Besides, the superb manufacture of mosaic decorations, which are considered a driving model for the Late Imperial iconography of Aquileia and, in a broader sense, Cisalpina (Novello, 2017), confirms the outstanding features of the building.

Finally, the late dating of the Great Baths provides new scenarios about the transfer of artisans and materials from the center to the north.
of the peninsula during the Late Imperial Age, which requires further analysis. It is well known that the beginning of the 4th century represented for the main towns of Northern Italy (Aquilíea, Ravenna, and Mediolanum in particular) a period of remarkable development and socio-political centrality. As stated by Ausonius, Aquileia became one of the largest cities of the Roman Empire, and the Great Baths can be considered one of the best examples of the constructive impulse of the time.

Unfortunately, the constructive flour of the early 4th century ended quickly. The limited care devoted to the making of bedding mortars of the mosaics of the northern sectors in phases Ib and, in particular, Ic, indicates that the great achievement represented by the construction of the Great Baths was almost completely depleted by the end of the century.

ACKNOWLEDGMENT
Francesca Andolfo is gratefully acknowledged for revising the English text. Open Access Funding provided by Universita degli Studi di Padova within the CRUI-CARE Agreement.

AUTHOR CONTRIBUTIONS
Simone Dilaria, Jacopo Bonetto, and Michele Secco designed the research; Gilberto Artioli and Jacopo Bonetto supervised the research project; Simone Dilaria and Marina Rubinich performed the samplings; Simone Dilari and Michele Secco performed the sample preparation; Simone Dilaria, Michele Secco, Domenico Miriello, and Donatella Barca analyzed the samples; Simone Dilaria, Jacopo Bonetto, Marina Rubinich, and Michele Secco interpreted the archaeometric results; Simone Dilaria drafted Sections 1, 3, 4.1, 5, 6, and 7; Marina Rubinich drafted Section 2; Michele Secco drafted Sections 4.2 and 4.3; and Domenico Miriello drafted Section 4.4. All authors collaborated in the revision of the manuscript.

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**How to cite this article:** Dilaria, S., Secco, M., Rubinich, M., Bonetto, J., Miriello, D., Barca, D., & Artioli, G. (2022). High-performing mortar-based materials from the late imperial baths of Aquileia: An outstanding example of Roman building tradition in Northern Italy. *Geoarchaeology, 37*, 637–657. https://doi.org/10.1002/gea.21908