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Lime mortar technology in ancient eastern Roman provinces

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ABSTRACT

Natural pozzolanic aggregates were discovered during the Roman era and have been widely used in hydraulic mortar production. Despite the claims of ancient treatises, the properties of pozzolans and the technology of hydraulic lime mortars were well known and applied in the eastern provinces of the Roman Empire. In this study, the characteristics of lime mortar at the ancient sites of Aigai and Nysa located in Western Anatolia were investigated to elicit the technology applied. The raw material compositions of the mortars, the hydraulic properties of the binders, and the mineralogical and chemical compositions of the natural pozzolans used were determined via X-ray diffraction, X-ray fluorescence spectroscopy, scanning electron microscopy coupled with energy dispersive spectroscopy, and thermogravimetric analysis. The major and trace element compositions of the natural pozzolans were evaluated via multivariate statistical analysis to determine whether the same local raw material resources were used in their manufacture. The analytical results indicated that the Roman mortars were hydraulic, stiff, and durable materials due to the use of natural pozzolanic aggregates mostly comprising dacite. Although the aggregates had similar mineralogical compositions, multivariate statistical analysis revealed that their chemical compositions were clearly distinguishable, indicating the use of different sources of raw materials. Thus, it was inferred that similar pozzolan resources were known and deliberately used to produce hydraulic mortars in the eastern ancient Roman provinces.

1. Introduction

Lime mortars have been among the most frequently used building materials for thousands of years, starting with the discovery of pyrotechnology. Improvements in the properties of lime mortars, which were generally used for decorative purposes until the Roman period, have enabled the production of compact, durable, and stable building materials and have paved the way for important innovations in architecture (MacDonald, 1965; Adam, 2005; Artioli et al., 2019). The most important contribution to this development was the use of natural and artificial pozzolans as aggregates (Ward-Perkins, 1974; Ward-Perkins, 1981; Lancaster, 2019). The invention of curvilinear coverings such as vaults and their variations, the construction of large-span domes, and the discovery of concrete and wall constructions with different facing materials and designs can be directly linked to the development of lime mortar technology (MacDonald, 1965; Adam, 2005). This building material, which enabled these developments, was used on a wide scale in structures from monumental buildings to modest-sized structures over a wide geographical area.

In this study, Roman-period lime mortars produced using natural pozzolans in Western Anatolia were characterised to elicit the lime mortar technology in the eastern provinces of the Roman Empire and to ensure continuity of this ancient tradition and the preservation of archaeological sites in Anatolia. Particularly, the provenance and likelihood of local raw material sources being used were investigated using several statistical analysis methods. To this end, lime mortars produced using natural pozzolans from several buildings in Aigai and Nysa, which were two of the eastern provinces of the Roman Empire in Anatolia, were investigated using characterisation techniques.

1.1. Historical background of Roman mortars produced using natural pozzolans

The first known use of lime mortar was in approximately 4000 BCE in Egypt where it was applied as plastering (Cowan, 1977; Cowper, 1998; Vicat, 2003). In the Greek period, lime was mostly used for decorative purposes such as stuccos, painted renderings, and the linings of cisterns (MacDonald, 1965; Adam, 2005; Cowper, 1998). The use of lime mortar

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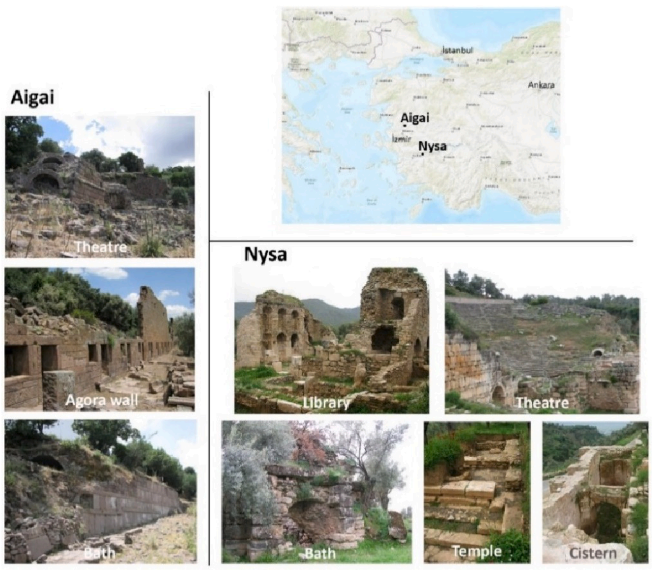


Fig. 1. Locations of Aigai and Nysa and some of their significant buildings.

Table 1
Sources of the studied mortar samples.

Sample Name		Location
Aigai	A1	Stage building of the theatre - Ashlar rear wall
	A2	Agora - Rubble core of terrace wall coated with cut stones
	A3	Vomitorium of the theatre - Rubble core of wall coated with cut stones
	A4	South bath - Stone vault
Nysa	N1	Temple - Rubble stone masonry wall
	N2	Library - Rubble stone masonry east wall
	N3	Library - Rubble stone masonry west wall
	N4	Building (located on the west side of the library) - Stone vault
	N5	Bath - Brick arch
	N6	Bath - Stone arch
	N7	Water basin - Rubble stone masonry wall
	N8	Bridge - Rubble stone masonry footing

for structural purposes was an important achievement of the Romans (MacDonald, 1965; Adam, 2005). The town walls of Cosa founded in southwestern Tuscany, founded in southwestern Tuscany in 275 BCE, is considered an important example of the early use of lime mortars for structural purposes in the Roman period (Ward-Perkins, 1974). The most important contribution of the Romans to lime mortar technology was the systematic utilisation of pozzolan in binders (Ward-Perkins, 1974; Ward-Perkins, 1981). The word pozzolan was derived from the Latin term, *pulvis puteolanus*, which means "Puteoli powder," referring to the volcanic deposits around Puteoli (modern Pozzuoli) (Ward-Perkins, 1974). Vitruvius defined pozzolan as a type of powder formed naturally and found in the Baia–Phlegraean fields near Mount Vesuvius; he recommended its use in lime mortar to obtain specific hydraulic properties (Vitruvius, 1960). However, various local pozzolan sources were used for manufacturing lime mortar in the Roman period due to the organisation and cost of construction sites (Ward-Perkins, 1974). The use of different local pozzolans highlighted the extreme variations in the quality of the materials due to impurities. This eventually led to a reduction in the use of pozzolans in mortar production (Ward-Perkins, 1974). For instance, Vitruvius mentioned that the volcanic earth of Tuscany was not suitable for producing hydraulic lime mortar (Vitruvius, 1960). He noted that the term pozzolan was unknown in countries across the Adriatic, including Anatolia (Vitruvius, 1960). Since the time of Caesar Augustus (27 BC–14 AD), the addition of natural pozzolans, which were derived from local sources around Rome, to lime mortar became common, and this type of mortar was used even in ordinary buildings (Ward-Perkins, 1981). Fifty years after Augustus, Claudius imported natural pozzolans from Puteoli to his harbour at Ostia (Ward-Perkins, 1981). The Pantheon, the Colosseum, the Arch and Markets of Trajan, and the Catacombs of Saint Callistus and Domitilla are some of the significant monumental structures of the Romans wherein hydraulic mortars produced from natural pozzolans were used (Silva et al., 2005; Sánchez-Moral et al., 2005; Jackson, et.al. 2009; Izzo et al, 2018). Also, there are evidences that confirm the use of Phlegraean pozzolans in several sites in the Mediterranean area (Stanislao et al. 2011; Brandon et al. 2014).

The proportions of pozzolans used as aggregates to the lime in Roman mortars were mentioned in historic sources such as *De Architectura* by Vitruvius (90–20 BC) (Vitruvius, 1960), *De Agri Cultura* by Cato (234–149 BCE) (Alberti, 1986), and *Naturalis Historia* by Pliny (23–79 AD) (Goldsworthy and Min, 2009). Vitruvius and Cato recommended the use of lime and pozzolans in proportions of 1:2 and 1:3, whereas Pliny specified a proportion of 1:4. The higher proportion of pozzolans indicated by Pliny may have been due to the high cost of lime after the Great Fire of Rome (64 AD) (Goldsworthy and Min, 2009).

The hydraulic characteristics, mechanical properties, and durability of historic lime mortar directly depended on the properties of the pozzolanic aggregates. Pozzolans are siliceous or siliceous-aluminous materials that also contain amorphous silica or alumina. They react with lime ($Ca(OH)_2$) in the presence of water or moisture to form calcium silicate hydrate (CSH) or calcium aluminate hydrate (CAH) (ASTM C618, 2003). Higher contents of amorphous silica and alumina increase the hydraulic properties of lime mortars. It has been demonstrated that the raw materials selected as pozzolanic aggregates in historic lime mortars met this requirement, and that most historic lime mortars displayed strong hydraulic properties (Jackson et al., 2017; Secco et al., 2020; Miriello et al, 2018; Izzo et al, 2018; Borsoi et al., 2019; Ergenç and Fort 2019). Due to logistical difficulties, local raw material sources were likely preferred for pozzolans, and their application was probably based on trial and error. Choosing the right local raw material sources for pozzolan production from a wide geographical area without any chemical analysis reveals the knowhow behind the lime mortar technology.

2. Materials and methods

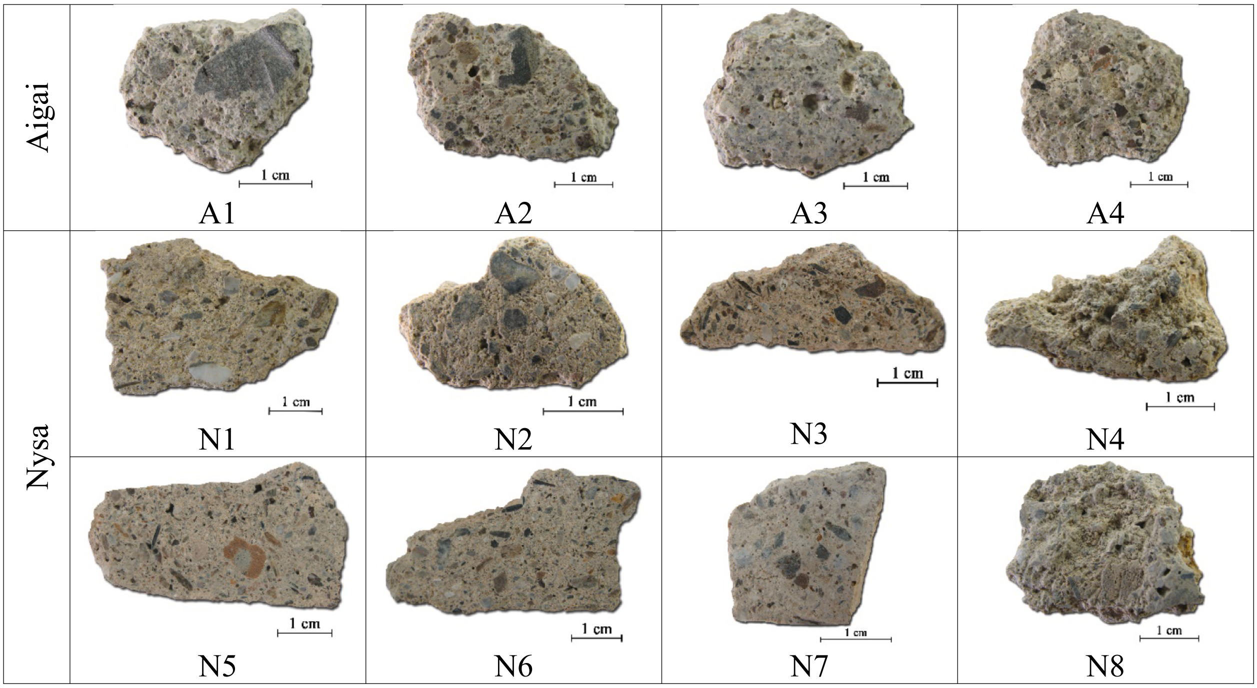
In this study, the characteristics of Roman lime mortars from the ancient cities of Aigai (Manisa) and Nysa (Aydın) produced using natural pozzolans were examined (Fig. 1). Aigai and Nysa are located in Western Anatolia, approximately 130 km from each other.

Western Anatolia was formed by widespread volcanic activity since the Early Miocene period. The volcanic activity formed all types of extrusive igneous rocks, from rhyolites to basalts (Aydar, 1998; Agostini et al., 2005). These igneous rocks were frequently used in the construction of foundations, walls, and the upper structures of buildings. Walls were generally constructed with a rubble inner core coated by different types of materials, such as local stones or bricks. Alternatively, they were built completely from rubble stones, ashlars, or bricks via masonry techniques. The rubble inner core, consisting of rubble stones horizontally laid in a thick lime mortar, can be considered a local interpretation of *opus caementicium* (Roman concrete) in Anatolia (Ward-Perkins 1981). These wall types were used in the construction of different building types in the cities of Aigai and Nysa.

To conduct the experimental part of the study, four mortar samples were collected from the walls and vaults of the theatre, bath and agora buildings of Aigai, while eight mortar samples were collected from the walls, arches, and vaults of the temple, library, water basin, bridge cistern, and bath buildings of Nysa (Table 1).

Experimental studies were conducted to examine the mortars and fine mortar matrices (<63 μm) composed of small grain-sized silica and carbonated lime called "binder," as well as lime and natural pozzolanic aggregates. Several types of analyses were carried out to determine the

Table 2
Macro photos of the investigated samples.



basic physical properties and the raw material compositions of the mortars; the hydraulic properties of the binders; the mineralogical compositions, chemical compositions, and microstructural properties of the aggregates and binders; and the statistical relationships between the chemical compositions and the pozzolanic activities of the aggregates.

Bulk density, porosity, and drying rates, which are the main physical properties of mortars, were determined using standard test methods (RILEM, 1980). The binder/aggregate ratios and particle size distribution of the aggregates were determined after the dissolution of the carbonated lime ($CaCO_3$) in dilute hydrochloric acid (5%), followed by filtering, washing, drying, and sieving of the aggregates using a standard sieve set (Jedrzejewska, 1960).

The hydraulic properties of the mortars were determined from the weight loss percentages of the binders (<63 μm) due to the loss of the bound water of hydraulic products between 200 and 600 °C, as well as due to the loss of carbon dioxide (CO_2) released during the decomposition of carbonated lime between 600 and 900 °C. The weight loss was measured via thermogravimetric analysis (TGA) performed using a Shimadzu TGA-21 (Bakolas et al., 1998; Moropoulou et al., 2000). The analysis was carried out in a static nitrogen atmosphere between 30 and 1000 °C at a heating rate of 10 °C/min.

The mineralogical compositions of the binders, natural pozzolans used as aggregates, and lime lumps were determined by X-ray diffraction (XRD; Philips X'Pert Pro). The analyses were performed on finely ground samples with a grain size<53 μm. The instrument was operated using CuK* radiation and a Ni filter adjusted to 40 kV and 40 mA. Scanning was performed with a °2θ range of 2–60 at a scan speed of 1.60° per minute. A Philips X'Pert Graphics and Identity software program was used to identify the mineral phases in each XRD spectrum.

The microstructural properties of the pozzolans, the characteristics of pozzolan-binder interfaces, and morphologies and microstructures of pozzolans, lime and binders were determined via scanning electron microscopy (SEM (Philips XL 30S FEG)) coupled with X-ray energy dispersive system (EDS). During the analysis, the samples were fixed onto aluminium stubs using carbon adhesive disks and coated with gold to ensure conductivity. Images were collected at different magnitudes (250x, 1000x, 2000x, 10000x, 40000x) using a secondary electron detector at a voltage of 3 kV. Powder samples of pozzolans and the broken and polished surfaces of mortar samples were analysed using secondary electron and backscattered electron modes at different magnifications and at room temperature 20–24 °C. EDS data were collected without using a standard sample.

The pozzolanic activity of the aggregates was determined from the reaction between lime and the aggregates. The differences in electrical conductivity (mS/cm) before and after the addition of fine aggregates (grain size < 53 μm) to a saturated calcium hydroxide solution in a ratio of 1 g:40 ml was measured after 2 min. (Luxán et al., 1989). Electrical conductivity differences of more than 2 mS/cm indicate good pozzolanicity (Luxán et al., 1989).

The chemical compositions of the binders and lime lumps were determined via SEM-EDS. The loss on ignition and major, minor, and trace element compositions of natural pozzolans were assessed via TGA and X-ray fluorescence spectroscopy (XRF). The XRF analyses were performed using a Spectro IQ II instrument. The analyses were conducted on of powdered samples (grain size < 53 μm) of ~ 0.06 g diluted with lithium tetraborate at a dilution factor ~ 0.0744. The Fusion_IQII method was used for the analysis. Results were obtained as percentages (%) for major oxides and as parts per million (ppm) for trace elements.

The XRF results of the pozzolans were evaluated via multivariate analysis to determine the statistical similarities or differences between the major oxide and trace element compositions of aggregates and to determine whether local raw material resources were used in their production. Multivariate analysis is a useful methodology that helps distinguish samples with similar characteristics from those with significantly different values. Initially, a principal component analysis (PCA) was performed (Bro and Smilde, 2014). It was implemented separately to two groups; major oxides and trace elements. Then, it was applied a hierarchical clustering to the first and second most informative factor scores of both groups. Hierarchical clustering was implemented also for each major oxide (CaO, SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MgO, Na_2O, and K_2O) and trace element (P, S, V, Cr, Ga, Sr, Y, Zr, Mo, Cd, Ba, Tl) separately constituting the chemical compositions of pozzolans to determine whether the oxides and trace elements could generate a cluster of samples with similar values. For this purpose, a distance measure using

Table 3
Basic physical properties and raw material compositions of mortars.

	Density (g/cm^3)	Porosity (%)	L/A	Particle size distribution (%) of aggregates (μm) (by weight) >1180	1180–500	500–250	250–125	125–53	<53
A1	1.58 ± 0.01	36.12 ± 0.15	0.26 ± 0.01	27.9 ± 1.5	22.0 ± 3.8	18.3 ± 1.2	8.1 ± 1.2	2.6 ± 0.8	0.9 ± 0.0
A2	1.72 ± 0.46	31.05 ± 15.05	0.29 ± 0.02	40.8 ± 1.0	26.2 ± 0.6	6.6 ± 1.2	2.6 ± 1.4	0.8 ± 0.8	0.6 ± 0.1
A3	1.51 ± 0.06	36.40 ± 2.78	0.19 ± 0.00	29.5 ± 1.9	37.5 ± 0.2	11.5 ± 0.9	3.4 ± 0.6	1.3 ± 0.2	0.8 ± 0.1
A4	1.56 ± 0.14	35.31 ± 5.68	0.36 ± 0.03	11.2 ± 2.1	28.3 ± 0.3	23.4 ± 2.5	8.0 ± 1.1	2.1 ± 0.2	0.8 ± 0.0
N1	1.76 ± 0.01	32.23 ± 0.08	0.22 ± 0.02	39.9 ± 1.9	19.6 ± 1.8	11.1 ± 2.1	6.7 ± 2.0	3.5 ± 0.8	1.4 ± 0.5
N2	1.64 ± 0.01	35.92 ± 0.51	0.25 ± 0.00	35.2 ± 4.3	23.7 ± 1.6	11.0 ± 1.3	5.5 ± 0.7	3.3 ± 0.4	1.6 ± 0.4
N3	1.84 ± 0.03	24.79 ± 1.18	0.29 ± 0.09	41.0 ± 1.5	16.5 ± 0.5	9.6 ± 3.1	6.5 ± 3.0	2.9 ± 0.1	1.1 ± 0.1
N4	1.62 ± 0.08	35.56 ± 2.83	0.30 ± 0.04	31.3 ± 2.6	22.9 ± 0.3	13.4 ± 0.6	6.3 ± 0.1	2.4 ± 0.3	0.8 ± 0.2
N5	1.75 ± 0.00	29.97 ± 1.50	0.24 ± 0.02	45.5 ± 1.6	18.9 ± 0.9	7.9 ± 0.0	4.7 ± 0.1	2.9 ± 0.1	1.3 ± 0.0
N6	1.91 ± 0.20	24.97 ± 7.13	0.24 ± 0.01	34.9 ± 0.8	15.8 ± 1.4	9.4 ± 0.1	9.3 ± 1.1	8.0 ± 2.2	3.1 ± 0.8
N7	1.72 ± 0.00	32.48 ± 0.35	0.53 ± 0.08	41.0 ± 8.5	11.6 ± 1.3	5.9 ± 2.0	3.5 ± 0.7	2.3 ± 0.6	1.5 ± 0.3
N8	1.64 ± 0.03	35.54 ± 1.51	0.64 ± 0.03	22.0 ± 1.3	14.3 ± 1.8	10.6 ± 0.9	7.9 ± 0.6	3.6 ± 0.0	1.2 ± 0.1

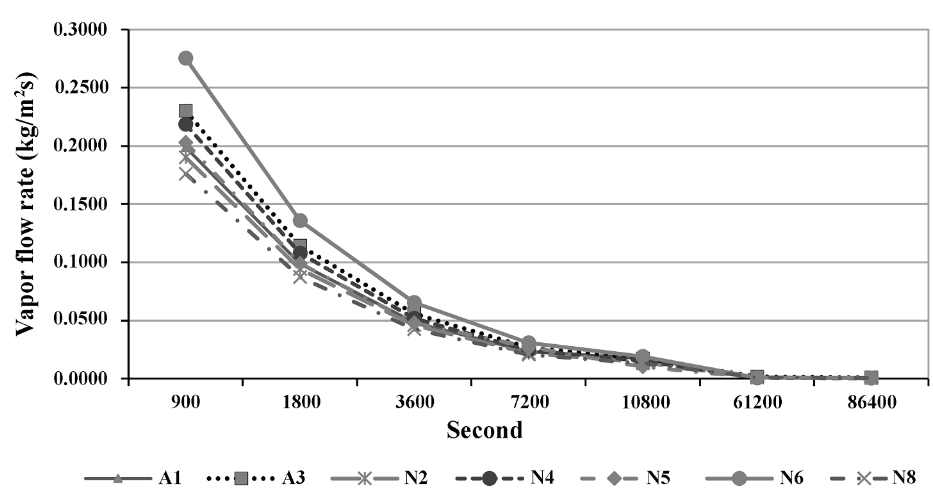


Fig. 2. Drying rates of mortars.

the average linkage method and the Euclidean distance were employed in hierarchical clustering (Rokach and Maimon, 2005; Ward, 1963; Murtagh, 1984). In addition, descriptive statistics were provided for each major oxide and trace element. Also *t*-test, Kolmogorov-Smirnov test, and Kruskal–Wallis test (Kolmogorov, 1933; Smirnov, 1939; Kruskal and Wallis, 1952) were performed for each major oxide and trace element in order to examine the following null (Ho) and alternative hypotheses (Ha):

Ho: Aigai and Nysa have identical chemical composition of materials for a given major oxide or trace element.

Ha: Aigai and Nysa have significantly different chemical composition of materials for a given major oxide or trace element.

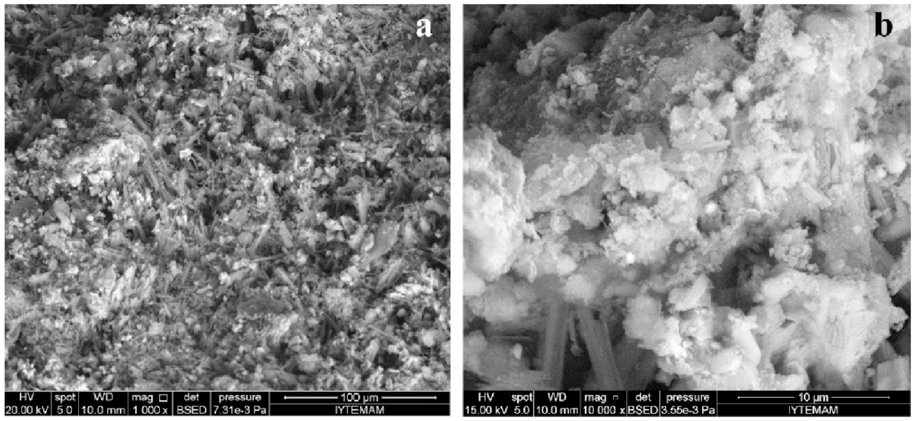


Fig. 3. SEM images showing the homogenous mixture of calcite crystals and pozzolans (a:1000x, b:10000x), where fibrous like particles are pozzolans and more euhedral are calcite crystals.

Table 4
Major oxide compositions (%) of binders determined via SEM-EDS.

	A1	A2	A3	A4	N1	N2	N3	N4	N5	N6	N7	N8
SiO_2	50.14	52.67	44.46	52.71	41.25	49.64	44.99	38.26	47.54	51.30	38.82	40.21
	±2.09	±0.96	±2.95	±1.96	±1.34	±1.46	±2.42	±2.04	±0.47	±0.45	±0.80	±0.47
Al_2O_3	12.12	13.54	11.13	12.62	15.49	15.70	11.70	13.59	12.07	13.14	12.14	9.89
	±0.97	±0.13	±1.23	±0.79	±0.72	±0.74	±0.44	±1.23	±0.13	±0.39	±0.54	±0.61
Fe_2O_3	2.11	2.51	1.54	1.72	6.13	3.81	3.57	3.99	4.99	5.12	4.74	5.64
	±1.16	±0.34	±1.10	±0.42	±0.70	±0.30	±0.42	±0.46	±0.88	±0.38	±1.06	±1.80
MgO	2.15	1.93	2.34	2.35	4.39	2.81	3.92	3.63	3.29	2.80	4.61	5.03
	±0.10	±0.07	±0.54	±0.05	±0.30	±0.72	±0.45	±0.57	±0.13	±0.22	±0.15	±0.31
CaO	29.31	25.30	36.38	26.79	27.75	23.64	31.14	35.84	27.09	22.45	36.06	31.08
	±0.93	±0.69	±3.32	±2.25	±1.76	±1.19	±1.55	±4.42	±1.14	±1.10	±0.77	±1.37
Na_2O	1.54	1.49	2.25	1.82	2.11	1.85	2.55	1.72	1.37	1.93	1.28	1.43
	±0.19	±0.12	±0.42	±0.13	±0.14	±0.46	±0.56	±0.79	±0.41	±0.15	±0.16	±0.11
K_2O	1.99	2.04	1.57	1.67	2.10	2.10	1.83	2.06	3.04	2.33	1.48	5.23
	±0.36	±0.03	±0.35	±0.15	±0.15	±0.20	±0.18	±0.18	±0.18	±0.09	±0.30	±0.05
TiO_2	0.64	0.53	0.34	0.32	0.77	0.45	0.31	0.93	0.63	0.94	0.88	1.08
	±0.18	±0.06	±0.34	±0.32	±0.47	±0.14	±0.29	±0.12	±0.20	±0.20	±0.79	±0.13

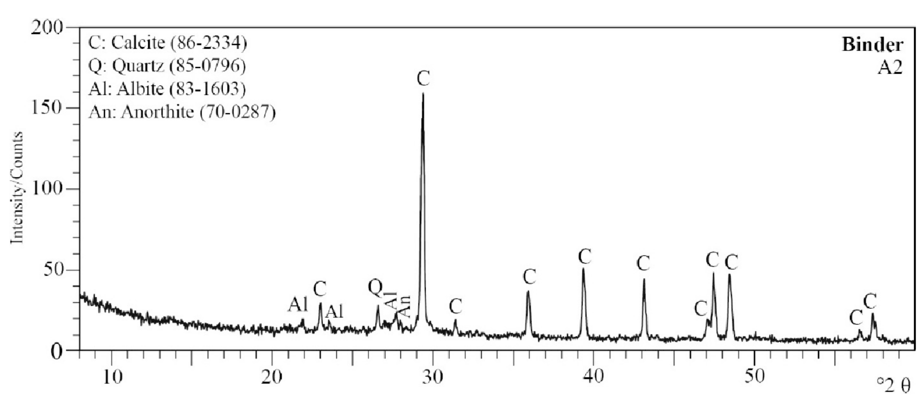


Fig. 4. Typical XRD pattern of binders.

Statistical analyses were performed using Stata 13, Eviews 4 and 10, the SPSS software package, and Excel. The aim of using several tests to analyse the results was to verify the robustness of the results.

Table 5
Structural H_2O and CO_2 amounts (%), CO_2/H_2O values and mineralogical compositions of binders.

Sample Name	Weight Losses (%)		CO_2/SBW	Mineralogical Composition				
	200–600 °C (SBW)	600–900 °C (CO_2)		Calcite	Quartz	Albite	Anorthite	Muscovite
A1	4.79	13.21	2.76	***	**	*	*	–
A2	5.47	19.90	3.64	***	*	*	*	–
A3	5.41	14.86	2.75	***	*	*	–	–
A4	4.54	17.10	3.77	***	*	*	–	–
N1	4.16	12.96	3.11	***	**	*	–	*
N2	3.54	13.22	3.73	***	**	*	–	*
N3	2.85	18.28	6.41	***	*	*	–	*
N4	4.38	22.05	5.03	***	**	*		*
N5	3.64	12.11	3.33	***	**	*	–	*
N6	3.59	10.73	2.99	***	**	*	–	*
N7	4.01	13.17	3.29	***	**	*	–	–
N8	4.16	20.83	5.00	***	**	*	–	*

The number of stars represent the abundance of mineral peaks.

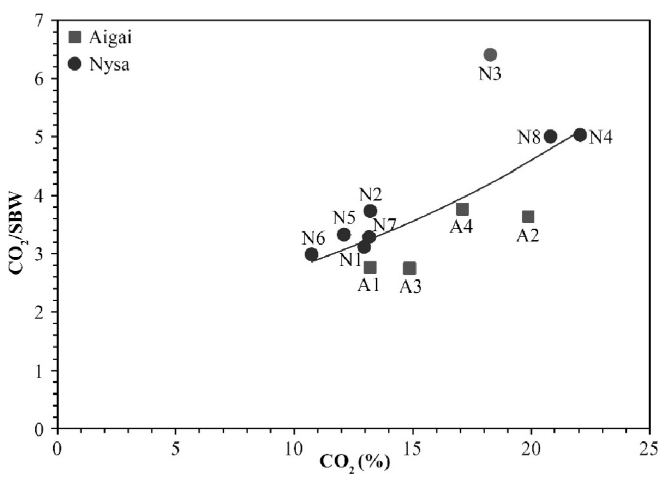


Fig. 5. CO_2/SBW vs. CO_2 (%) diagram.

3. Results and discussion

3.1. General characteristics of mortars

The general characteristics of Roman mortars were examined from two aspects. The first aspect was the basic physical properties and raw material compositions. The second aspect was related to the "binder"

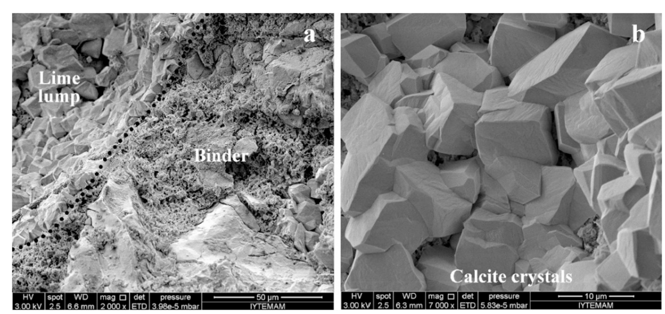


Fig. 7. Lime lump (a:2000x) and small-sized micritic calcite crystals within the lime lump (b:7000x).

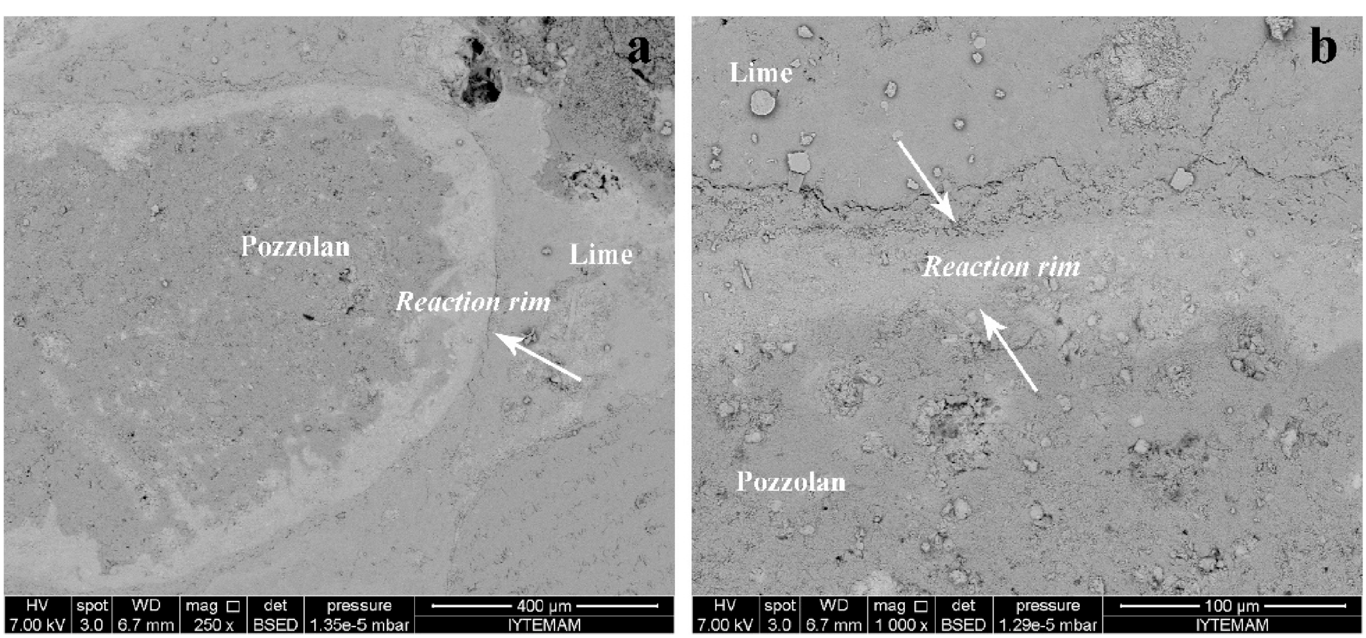


Fig. 6. SEM images (a:250x, b:1000x) of the reaction rims between pozzolans and lime showing the penetration of reaction products through the pozzolan.

Table 6
Pozzolanic activities and mineralogical compositions of aggregates.

Sample Name	Pozzolanic Activity	Mineralogical Composition					
		Quartz	Albite	Anorthite	Muscovite	Phillipsite	Amorphous minerals
A1	6.91	**	***	***	–	–	*
A2	7.64	***	***	**	–	–	**
A3	5.11	**	***	*	*	–	*
A4	6.75	***	**	*	–	–	–
N1	4.10	***	*	*	**	*	–
N2	4.73	***	*	–	**	*	–
N3	3.25	***	*	*	*	–	–
N4	4.49	***	**	–	*	–	–
N5	3.56	***	*	*	*	–	–
N6	4.40	***	**	–	*	–	–
N7	6.02	***	**	–	–	–	–
N8	4.11	**	*	*	*	–	–

The number of stars represent the abundance of mineral peaks.

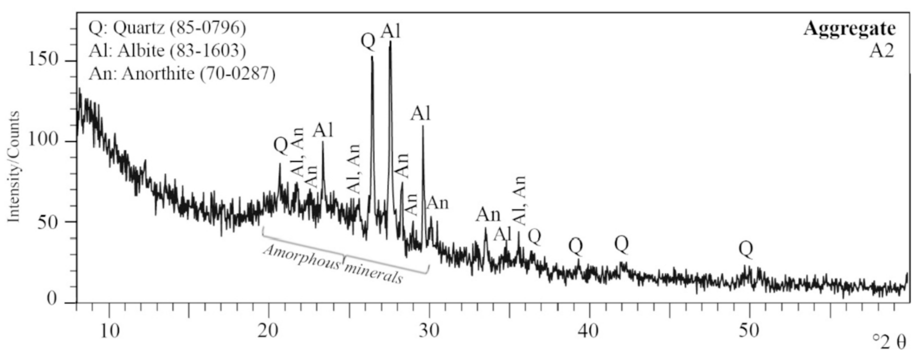


Fig. 8. Typical XRD pattern of aggregates in mortars (A2).

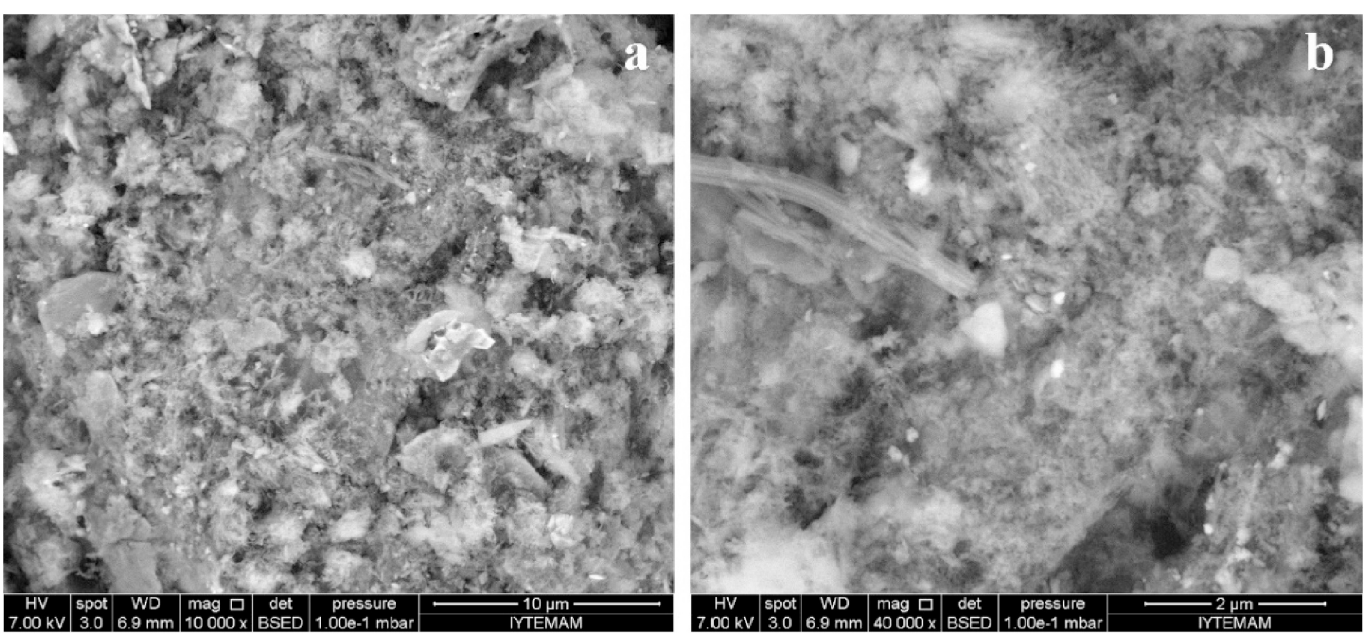


Fig. 9. SEM-EDS images of natural pozzolanic aggregates showing the amorphous particles (a:10000x, b:40000x).

section of the mortars, which was defined as a fine matrix comprising aggregates and carbonated lime ($CaCO_3$) (Bakolas et al., 1995; Middendorf et al., 2005; Uğurlu Sağın et al., 2012). Binders are considered to be the main component determining the hydraulic character and high strength of the mortar (Bakolas et al., 1995; Middendorf et al., 2005; Velosa et al., 2007; Mirieollo et al., 2010; Kramar et al., 2011; Mirieollo et al., 2011). Thus, the hydraulic properties, mineralogical and chemical compositions, and microstructural properties of the binders were determined.

The mortar samples had a greyish colour, a stiff and compact structure, good cohesion, and a smooth texture (Table 2). Their basic physical properties were described by their densities, porosities, and drying rates. Densities between 1.5 and 1.7 g/cm^3 in Aigai mortars and between 1.6 and 1.9 g/cm^3 in Nysa mortars were measured. Porosities

Table 7
Loss on ignition (LOI) and major oxide compositions (%) of natural pozzolanic aggregates determined via XRF.

	A1	A2	A3	A4	N1	N2	N3	N4	N5	N6	N7	N8
SiO_2	70.74	71.34	67.91	74.69	68.31	68.82	70.95	71.09	74.51	75.58	79.62	71.41
Al_2O_3	9.51	5.81	9.96	10.37	11.30	11.92	11.08	12.26	9.84	11.69	5.01	13.23
Fe_2O_3	4.74	2.67	2.44	4.42	5.95	4.05	3.45	4.21	4.05	1.20	1.36	2.22
MgO	1.56	1.93	2.17	1.45	2.53	2.30	2.15	2.37	2.11	1.00	1.68	2.26
CaO	2.33	1.15	2.53	2.23	0.72	0.41	0.86	0.59	0.53	0.64	0.34	0.55
Na_2O	0.53	1.19	1.76	0.55	1.94	1.38	1.85	1.66	1.35	0.59	1.04	1.78
K_2O	0.93	0.44	0.85	1.15	1.46	1.68	1.82	1.70	1.31	1.48	0.58	1.82
TiO_2	0.84	0.52	0.44	0.84	1.28	0.94	0.82	0.82	0.83	1.06	0.41	1.05
P_2O_5	0.05	0.07	0.05	0.01	0.13	0.04	0.04	0.07	0.06	0.001	0.02	0.06
LOI	8.77	14.88	11.89	4.29	6.38	8.46	6.98	5.23	5.41	6.76	9.94	5.62

Table 8
Trace elements compositions (ppm) of natural pozzolanic aggregates determined via XRF.

	A1	A2	A3	A4	N1	N2	N3	N4	N5	N6	N7	N8
P	198.1	311.7	228.3	41.4	547.8	236.1	284.3	308.9	281.7	5.1	98	239.8
S	332.4	504.5	231.3	214.3	315	255.5	323.1	342.8	364.7	376.1	279.7	356.6
V	–	85	69	–	117	116	86	102	99	–	8.5	117
Cr	382	520	282	469	531	352	356	419	300	460	521	400
Ga	66	72	43	68	44	112	47	96	49	53	2	48
Sr	272.6	175	257.3	287.5	97.1	121.1	298.3	141.8	92.3	142.6	66.5	114.4
Y	–	–	22.7	–	37.5	82	47	86.7	45.7	–	50.6	56.4
Zr	415.4	248.2	121.5	427.7	267.6	431.9	310	451.7	255.8	427.9	276.1	545.6
Mo	47	13	72	180	54	65	33	5	5	72	74	80
Cd	67,1	178	65	97.4	53.2	159.4	72.3	270.4	58,8	57,7	202	77.5
Ba	527	167	288	700	401	331	292	300	172	615	25	374
Tl	291	220	277	337	436	115	440	242	388	248	378	438

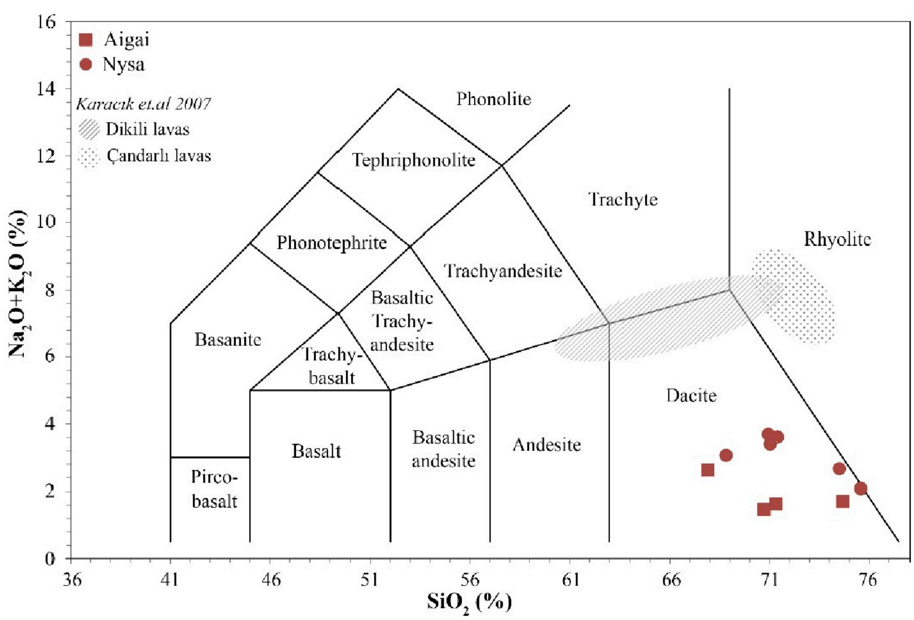


Fig. 10. Total alkali vs silica (TAS) diagram (Le Bas et al., 1986) for rock classification of aggregates.

(by volume) ranged between 31 and 36 % in Aigai mortars and between 25 and 36 % in Nysa mortars (Table 3). These values displayed almost the same range as those of lime mortars used in several Roman-period buildings located in Italy (Sánchez-Moral et al., 2005; Jackson et al., 2009; Jackson et al., 2011; Rispoli et al., 2020), Slovenia (Kramar et al., 2011), Tunisia (Farci et al., 2005), and Turkey (Aslan-Özkaya and Böke, 2009). This similarity can be an indicator of continuity of the traditions of lime mortar manufacturing techniques in different parts of the Central Roman Empire and its provinces.

Drying rates were described by the vapour flow rate (g) of water evaporated from the surface of the sample in a set period. The results revealed that ∼ 50 % of the water adsorbed inside the pores evaporated within 30 min, with vapour flow rates of 0.0985–0.1140 kg/(m^2 s) for the Aigai mortars and 0.0871–0.1356 kg/(m^2 s) for the Nysa mortars (Fig. 2). These values indicate that macropores, which enable rapid evaporation, formed a high percentage of the total porosity of the mortars (Elert et al., 2003). The high percentage of macropores ($r > 2.5$ μm) also made the Roman lime mortar durable to freeze–thaw cycles (Carretero et al., 2002; Cultrone et al., 2004).

The raw material compositions of the mortars were defined by the lime/aggregate ratios and the particle size distributions of the aggregates. Lime/aggregate ratios were 0.19–0.36 in the Aigai mortars and

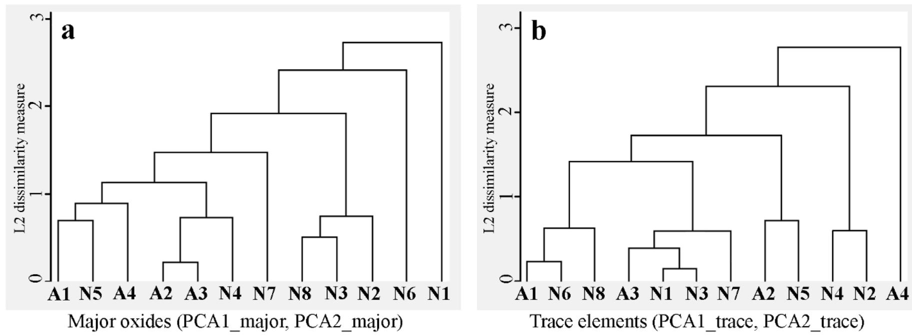


Fig. 11. Multivariate hierarchical cluster analysis on principle factors (Note: V and Y trace elements are discarded from PCA analysis as they include missing values.)

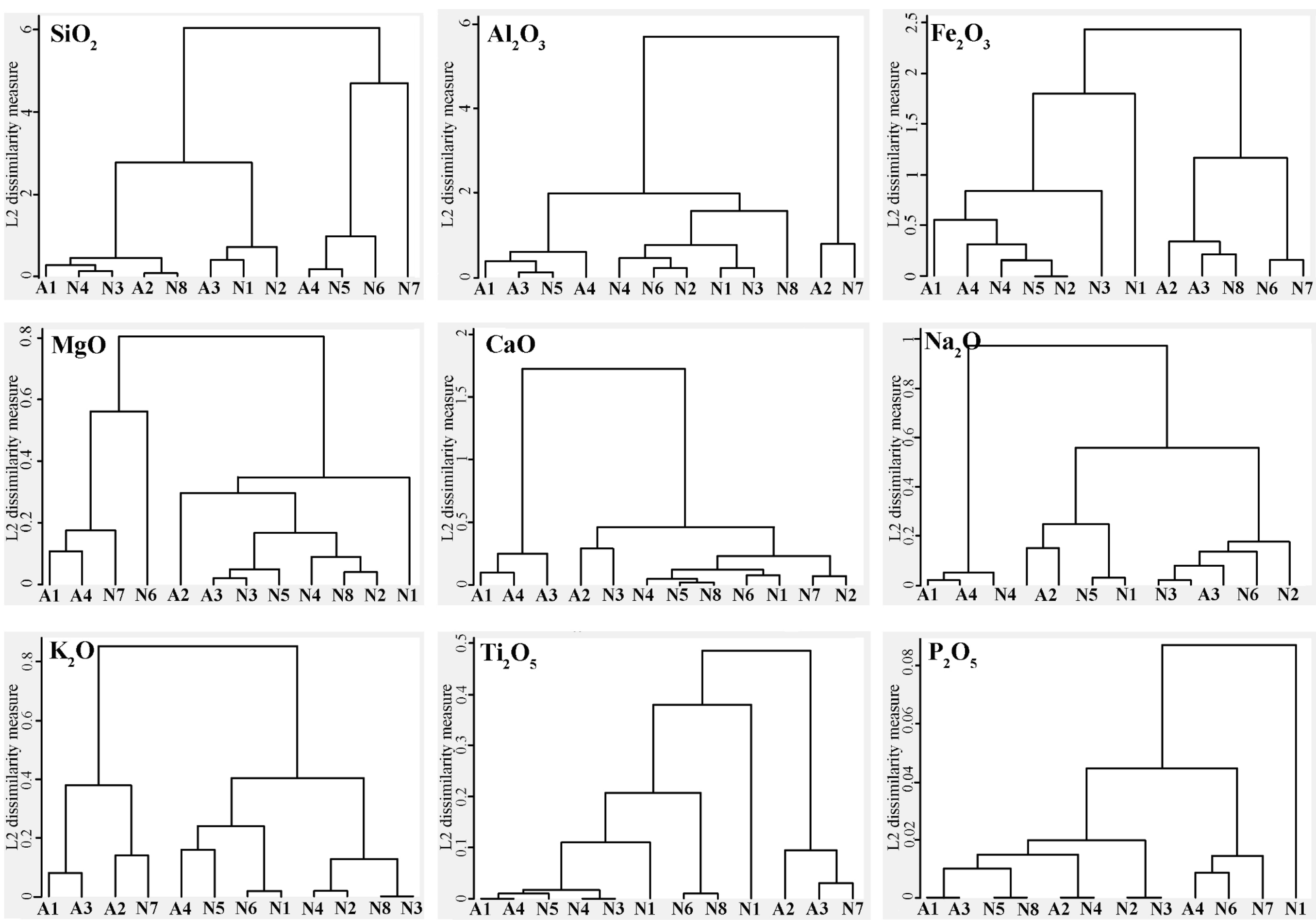


Fig. 12. Hierarchical clustering results, the dendrogram graphs of major oxides, Source: Own Calculation/estimation.

0.22–0.64 in the Nysa mortars (Table 3). Aggregates with particle sizes greater than 1180 μm constituted the major fraction and formed 11.2–45.5 % of the total aggregate in all samples. These values are similar to the lime/aggregate ratios of lime mortars from different Roman-period buildings (Degryse et al., 2002; Benedetti et al., 2004; Sánchez-Moral et al., 2005; Franquelo et al., 2008; Robador et al., 2010).

Binders comprising small-grain pozzolans (<63 μm) and lime revealed a uniform structure in which calcite crystals and pozzolans were homogenously mixed and strongly adhered to each other (Fig. 3). This adhesion made the mortars being stiff, hard, and compact.

The binders chemically comprised large amounts of SiO_2 and CaO; moderate amounts of Al_2O_3; and smaller amounts of Fe_2O_3, Na_2O, K_2O, and TiO_2 (Table 4). The chemical compositions of the Aigai and Nysa samples were very similar, except for Fe_2O_3, which was higher in the Nysa samples. This difference may be attributed to the chemical composition of the pozzolans. However, it is not possible to make a definite inference with sufficient precision for statistical evaluation.

The binders were mainly composed of calcite ($CaCO_3$) originating from carbonated lime, as well as quartz (SiO_2), albite ($NaAlSi_3O_8$), and anorthite ($CaAl_2Si_2O_8$) originating from aggregates (Fig. 4, Table 5). Paracrystalline hydrated calcic aluminosilicates, namely CSH, formed from reactive pozzolanic aggregates and lime binder were not detected. This was likely due to the amorphous character of CSH, or because its principal peaks overlap with those of calcite (Secco et al., 2018; Luxán and Dorrego, 1996). Muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$) was the other mineral phase identified in the Nysa mortars.

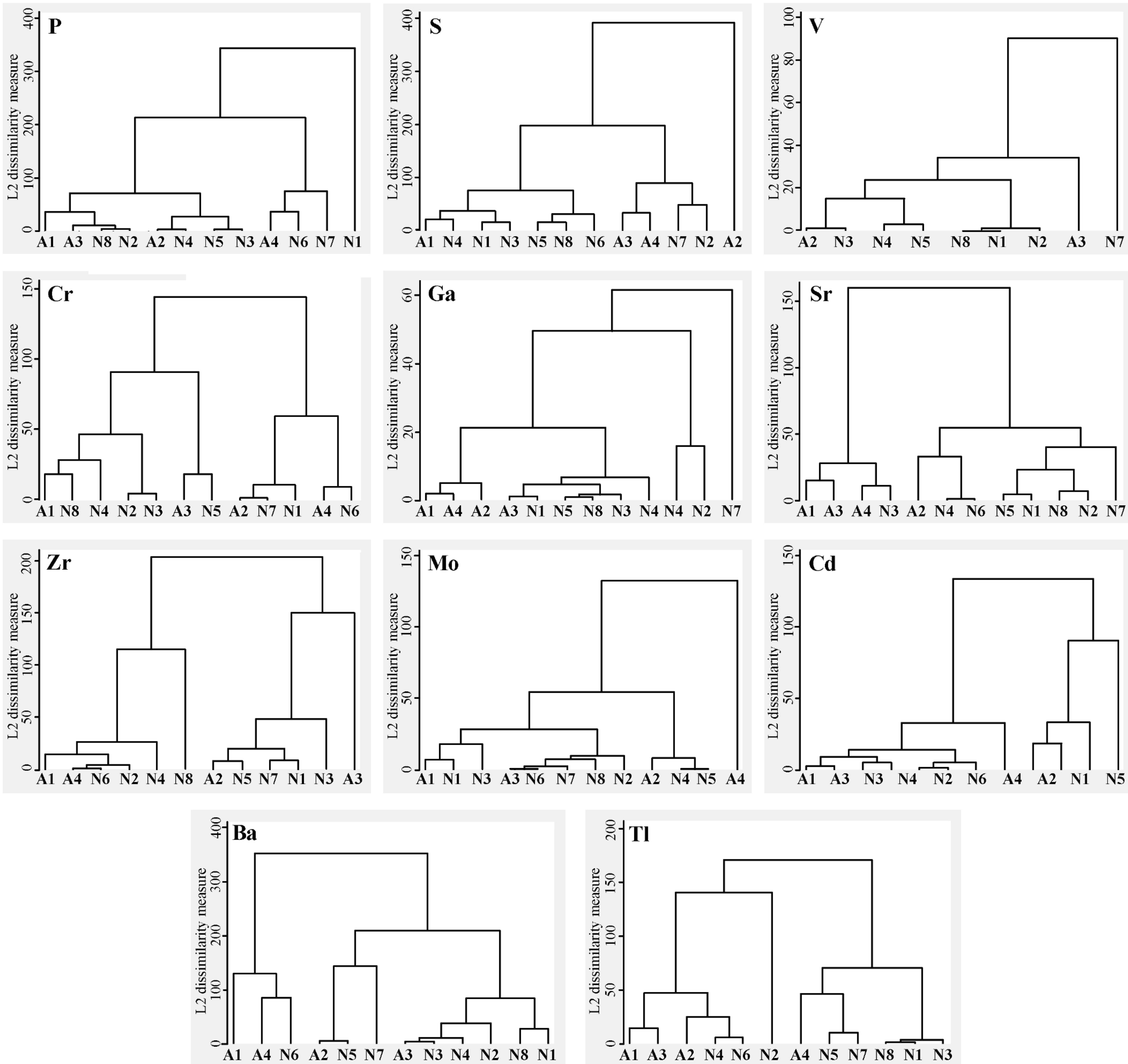


Fig. 13. Hierarchical clustering results, The dendrogram graphs of trace elements, Source: Own Calculation/estimation.

The hydraulic properties of the binders were determined via TGA (Bakolas et al., 1995; Middendorf et al., 2005). Weight losses between 200 and 600 °C were due to the structurally bound water (SBW) of hydraulic products, such as CSHs and CAHs. Weight losses between 600 and 900 °C were due to the loss of CO_2 released during the decomposition of carbonated lime. The ratio of the weight losses due to CO_2 and SBW between 1 and 10, indicate the hydraulic characteristics of the mortar (Bakolas et al., 1998; Moropoulou et al., 2000). The CO_2/SBW ratios were found to be in the range of 2.75–3.77 for Aigai mortars and 2.99–6.41 for Nysa mortars, revealing that all the mortars were hydraulic (Fig. 5, Table 5).

Hydraulicity is the most important factor determining the durability and mechanical strength of the Roman period mortars and is a common feature of mortars taken from different regions (Kramar et al. 2011; Secco et al. 2018; Secco et al. 2020; Silva et al., 2005; Genestar et al., 2006; Mirieollo et al., 2011; Miriello et al, 2018; Rispoli et al., 2020).

The hydraulic properties of the mortars were also investigated based on their microstructural features. Products of the hydraulic reactions (CSH and CAH) between pozzolans and lime were observed in the rims penetrating through the pozzolans, which had widths of 35–50 μm (Fig. 6). EDS analysis revealed that these formations were composed mainly of CaO (24.1–54.0 %), SiO_2 (32.3–56.06 %) and Al_2O_3 (10.1–16.6 %). The durability, stiffness, and mechanical strength of the mortars were attributed to the formation of CSH and CAH because these hydraulic reactions generate strong adhesion bonds between pozzolans and lime (Moropoulou et al., 2002).

3.2. Characteristics of lime used in the production of mortars

It was assumed that small, white, soft fragments referred to as "lime lumps" were representative of the lime used in the mortars and had the same chemical composition as the raw material (Bakolas et al., 1995; Bruni et al., 1997; Barba et al., 2009). In the XRD patterns of lime lumps from both the Aigai and Nysa mortars, only sharp calcite peaks were

Table 9
Descriptive Statistics and inferential test results of equality between Aigai and Nysa depending on major oxide compositions (%), Source: Own Calculation/estimation.

	Indicator	Major Oxides (%)								
		SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5
Aigai	Mean	71.17	8.9125	3.5675	1.7775	2.06	1.0075	0.8425	0.66	0.045
	Median	71.04	9.735	3.545	1.745	2.28	0.87	0.89	0.68	0.05
	Max	74.69	10.37	4.74	2.17	2.53	1.76	1.15	0.84	0.07
	Min	67.91	5.81	2.44	1.45	1.15	0.53	0.44	0.44	0.01
	SD	2.782792	2.097941	1.180152	0.332603	0.619355	0.587899	0.296802	0.210396	0.025166
Nysa	Mean	72.53625	10.79125	3.31125	2.05	0.58	1.44875	1.48125	0.90125	0.052625
	Median	71.25	11.495	3.75	2.205	0.57	1.52	1.58	0.885	0.05
	Max	79.62	13.23	5.95	2.53	0.86	1.94	1.82	1.28	0.13
	Min	68.31	5.01	1.2	1	0.34	0.59	0.58	0.41	0.001
	SD	3.796382	2.531417	1.618513	0.491703	0.165443	0.459143	0.406885	0.254077	0.03863
	T-Test (P-Value)	0.249722	0.106792	0.381509	0.143812	0.007803***	0.123418	0.007232***	0.061447*	0.345526
	Kruskall-Wallis(Chisquare Stat)	0.462	2.885*	0.463	1.846	7.385***	2.337	4.892**	1.046	0.007
	Kolmogorov-Smirnov Test(D-Stat)	0.25	0.75*	0.375	0.5	1***	0.5	0.875**	0.5	0.25

Note: * represents statistical significance at 10 % (0.05 < p-value < 0.1), ** at 5 % (0.01 < p-value < 0.05), *** at 1 % (p-value < 0.01), Al_2O_5's p-value for Kolmogorov-Smirnov test is just 0.1, therefore, accepted as significant at 10 %.

detected. SEM-EDS observations revealed that the calcite crystals were micritic with sizes smaller than 5 μm (Fig. 7). It was found that lime lumps were composed mainly of CaO (89–93 %) and included other major oxides (SiO_2 (0–6 %), MgO (0–2 %), Al_2O_3 (0–3 %), and Na_2O (0–3 %)). The hydraulic properties of the lime lumps were determined by calculating the hydraulic indices (HIs) considering the chemical compositions of the white lumps according to the Boynton formula (Eq. (1)) (Boynton, 1980).

$$HI = \frac{\%Al_2O_3 + \%Fe_2O_3 + \%SiO_2}{\%CaO + \%MgO} \tag{1}$$

A lower index indicates a weaker hydraulic character of the lime. The indices were found to be 0.0–0.09 for the Aigai mortars and 0.06–0.1 for the Nysa mortars (Boynton, 1980). The mineralogical and chemical compositions and the HIs demonstrated that the lime used in the production of the investigated mortars could be categorised as non-hydraulic and as “fat lime.” Despite the use of non-hydraulic limes, the strong hydraulic properties of the mortars could be confidently associated with the pozzolanic character of the aggregates.

3.3. Mineralogical, chemical and microstructural characteristics of aggregates

The aggregates used in the studied mortars were greyish natural stones. Their pozzolanic properties were investigated by measuring the electrical conductivity differences before and after the addition of fine aggregates (<53 μm) to a saturated calcium hydroxide solution. Electrical conductivity differences higher than 2 mS/cm revealed good pozzolanicity using this technique (Luxán et al., 1989). The electrical conductivity differences of the natural pozzolans were between 5.11 and 7.64 mS/cm for the lime mortars from Aigai and between 3.25 and 6.02 mS/cm for the lime mortars from Nysa (Table 6). These results revealed that all aggregates were volcanic and could be regarded as highly reactive pozzolans.

XRD analysis revealed that the mineralogical compositions of the natural pozzolans from both sites were similar. The main mineral phases identified in the XRD patterns were quartz (SiO_2), albite ($Na(AlSi_3O_8)$), anorthite ($CaAl_2Si_2O_8$), muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$), and amorphous substances represented by a diffuse band in the 2θ range of 20–30° (Fig. 8). In addition, traces of the mineral phillipsite were detected in the XRD patterns of some samples from Nysa (N1, N2, and N5).

The pozzolans had an irregular morphology and were composed of small, amorphous particles (Fig. 9). Higher magnifications of the amorphous particles revealed rod-shaped nanoparticles that increased the surface area of the pozzolans. A high specific surface area can effectively enhance the reactivity of the pozzolan to lime.

The major oxide (%) and trace element (ppm) compositions of the pozzolans were determined via XRF analysis. The results revealed that pozzolans mainly comprised large amounts of SiO_2, moderate amounts of Al_2O_3 and Fe_2O_3, and smaller amounts of MgO, CaO, Na_2O, K_2O, TiO_2, and P_2O_5 (Table 7). The trace elements detected in the pozzolans were P, S, V, Cr, Ga, Sr, Y, Zr, Mo, Cd, Ba, and Tl (Table 8).

The major oxide compositions were evaluated to determine the geochemical character of the pozzolans using a total alkali versus silica (TAS) diagram. According to the TAS diagram, the aggregates were classified as dacite (Fig. 10). Dacite is a volcanic rock composed mainly of silicon and aluminium with pozzolonic vitreous compounds (Yu et al., 2015).

Western Anatolia, in which Aigai and Nysa are located, is a region rich in active fault lines and volcanic sequences in dacite and andesite. The Dikili-Çandarlı volcanic suite in the northern part of the Aegean region, which is close to Aigai, is a particularly important and well-known example of these sequences (Karacık et al., 2007). In the TAS diagram, Çandarlı lavas fall in the rhyolite region while Dikili lavas mostly fall the dacite region (Fig. 10). However, the pozzolonic aggregates used in the mortars shows lower concentrations of Al, Fe, Mg, Ca and, above all K and Na, with respect to Dikili dacite in the TAS diagram. This is probably due to the heterogeneity of the pozzolanic aggregates or compositional changes occurred during the separation treatment of the aggregates. The micro chemical compositions of juvenile volcanic fragments in the aggregate that reflect the composition of the magma source via SEM-EDS analysis in thin section should be conducted to investigate the possibility of the use of Dikili lava in the future studies.

3.4. Statistical analysis of chemical compositions of aggregates via multivariate analysis

In addition to the detailed geochemical comparison, the major oxide and trace element compositions of the natural pozzolans were subjected to multivariate statistical analysis in order to identify samples with similar compositions, to classify the samples into homogenous groups, and to distinguish similar samples from those with significantly different compositions. Four statistical methods were employed. First, a principal component analysis (PCA) was applied to both sets of major oxide and trace elements separately (Bro and Smilde, 2014). The first and second most informative factor scores of both groups were saved, i.e., the PCA1_major and PCA2_major variables represented the two most informative factors of the major oxides, whereas the PCA1_trace and PCA2_trace variables represented the two most informative factors of the trace elements.

Second, multivariate hierarchical clustering was implemented using the factor scores obtained from the PCA analysis. In detail, the variables PCA1_major and PCA2_major were used to cluster the major oxides,

Table 10
Descriptive Statistics and inferential test results of equality between Aigai and Nysa depending on trace elements compositions (ppm), Source: Own Calculation/estimation.

	Indicator	Trace Elements (ppm)											
		P	S	V	Cr	Ga	Sr	Y	Zr	Mo	Cd	Ba	Tl
Aigai	Mean	194.875	320.625	77	413.25	62.25	248.1	22.7	303.2	78	113.4667	420.5	281.25
	Median	213.2	281.85	77	425.5	67	264.95	22.7	331.8	59.5	97.4	407.5	284
	Max	311.7	504.5	85	520	72	287.5	22.7	427.7	180	178	700	337
	Min	41.4	214.3	69	282	43	175	22.7	121.5	13	65	167	220
	SD	113.0343	133.2074	11.31371	104.4138	13.07351	50.26881	NA	146.2065	72.17109	58.18809	238.9428	48.21048
Nysa	Mean	250.2125	326.6875	92.21429	417.375	56.375	134.2625	57.98571	370.825	48.5	139.1333	313.75	335.625
	Median	260.75	332.95	102	409.5	48.5	117.75	50.6	368.95	59.5	118.45	315.5	383
	Max	547.8	376.1	117	531	112	298.3	86.7	545.6	80	270.4	615	440
	Min	5.1	255.5	8.5	300	2	66.5	37.5	255.8	5	53.2	25	115
	SD	159.3345	42.19998	38.69308	82.45161	33.80168	71.04934	18.92771	107.3269	30.524	86.30619	171.7238	120,1831
	T-Test (P-Value)	0.25339	0.467168	0.196788	0.473849	0.337804	0.005889***	NA	0.225666	0.241223	0.308567	0.232334	0.146057
	Kruskall-Wallis(Chisquare Stat)	0.462	0.462	2.161	0.029	0.26	4.154**	2.333	1.846	0.182	0.029	0.115	1.038
	Kolmogorov-Smirnov Test(D-Stat)	0.5	0.5	0.8571	0.25	0.5	0.875**	1	0.5	0.25	0.375	0.375	0.625

whereas the trace variables PCA1_trace and PCA2_trace were used to cluster the trace elements. A distance measure was adopted using the average linkage method and the Euclidean distance (Rokach and Maimon, 2005; Ward, 1963; Murtagh, 1984).

Third, the same hierarchical clustering procedure was applied to each individual major oxide and trace element in a univariate fashion. This procedure enables the detection of individual major oxides or trace elements that can be used to effectively distinguish between samples from the two sites.

Fourth, to support the results from an inferential point of view, various statistical tests including the *t*-test, the Kolmogorov-Smirnov test, and the Kruskal-Wallis test were implemented for each major oxide and trace element to formally test the statistical differences between the two groups (Aigai and Nysa). We examined whether the means (or medians) of the groups and the general distributional characteristics of the groups were significantly different (Kruskal and Wallis 1952, Kolmogorov 1933, Smirnov 1939). The reason for using several tests rather than focusing only on only one was to verify the robustness of the results with respect to the different methodologies.

Statistical analyses were performed using Stata 13, Eviews 4 and 10, the SPSS software package, and Excel.

The multivariate cluster dendrograms in Fig. 11 indicate that the principal components failed to distinguish between the samples from Aigai and Nysa. As shown in Fig. 11(a) and 11(b), the chemical compositions of the samples did not create distinct clusters for either the major oxides or the trace elements.

However, various individual major oxide and trace elements were detected, which could be used to distinguish between the two groups. Related hierarchical clustering analysis revealed that CaO, K_2O, Al_2O_3 (although weakly) (Fig. 12), Sr, Ga, and Y generated clusters that distinctly separated the pozzolans used in the Aigai and Nysa mortars (Fig. 13). Among these elements, the clusters formed by CaO were the most prominent. Pozzolans in the Aigai mortars had higher levels of CaO, with an average of 2.06 %, whereas pozzolans in Nysa mortars were characterised by lower levels of CaO, with an average of 0.58 % (Table 9). The pozzolans used in Aigai mortars had lower K_2O (0.84 %), higher Sr (248 ppm), lower Al_2O_3 (8.91 %), higher Ga (62.25 ppm), and lower Y (22.7 ppm) contents than those of the pozzolans used in the Nysa mortars (K_2O: 1.48 %, Sr: 134 ppm, Al_2O_3: 10.79 %, Ga: 56.3 ppm, and Y: 57.9 ppm) (Table 10).

The differences in mean values and general distributional characteristics of the two groups were statistically significant for CaO (p-value < 0.01), K_2O (p-value < 0.05), Al_2O_3 (p-value < 0.1), and Sr (p-value $<$ 0.05) according to the *t*-test, the Kolmogorov-Smirnov test, and the Kruskal–Wallis test. No statistically significant difference was observed between the two groups when Ga was analysed, although it enabled visual distinction between the Aigai and Nysa groups in the cluster analysis. In a similar manner, the element Y enabled the separation of the two groups; however, the statistical tests did not yield useful results due to missing observations.

In addition to differences in the mean values, all other characteristics of the distributions, including the first (mean) and second moments (standard deviation), verified that the pozzolans used in the Aigai and Nysa mortars had significantly distinguishable chemical compositions with respect to CaO, Sr, Al_2O_3, and K_2O. In other words, the statistical properties clearly revealed that the pozzolans used in the Aigai and Nysa mortars exhibited different intensities for CaO, K_2O, Al_2O_3, and Sr.

The results of the clustering analysis and different inferential tests were evident and robust. Therefore, one can deduce that, in the production of the pozzolanic aggregates in Aigai and Nysa, different sources of raw materials were used.

These statistically significant differences in the chemical compositions of the aggregates revealed that mortar was produced using different dacite sources in Aigai and Nysa, two ancient cities located relatively close to each other. Although different raw material sources were used, all the aggregates had a high pozzolanic quality, ensuring that the mortars were hydraulic. This observation revealed that, in both provincial cities which were far from the Imperial centre, the specific application was consciously considered in lime mortar production.

4. Conclusions

The lime mortars from the ancient sites of Aigai and Nysa produced using natural pozzolanic aggregates were stiff and durable materials. They have survived until today because of their hydraulic properties. The hydraulic properties of the investigated mortars were associated with the strong pozzolanic characteristics of their dacite aggregates which comprised quartz, albite, anorthite, muscovite and amorphous minerals. The existence of amorphous minerals and the rod-shape nano particles which increase the surface area enhanced the reactivity of pozzolanic aggregates with lime.

The aggregates used in the Aigai and Nysa mortars had similar mineralogical but different chemical compositions. All pozzolans mainly comprised large amounts of SiO_2, and moderate amounts of Al_2O_3 and Fe_2O_3. The statistical discrimination between their CaO, Sr, Al_2O_3, and K_2O contents revealed that different raw material sources, which were probably local and from different volcanic areas of Western Anatolia, were selected for production. The selection of local raw material resources that could produce mortars with similar characteristics reveals an awareness of mortar production techniques and the spread of mortar technology throughout the eastern provinces of the Roman Empire. The use of different analytical techniques and evaluation methods was crucial in revealing this information.

Roman lime mortars are important materials in the history due to the invention and widespread use of pozzolans in their production, their hydraulic and mechanical properties and durability, their use for structural purposes, and the innovations they bring to architecture. Although lime mortar is no longer a widely used material in the construction industry, it is important to elicit thousands of years of tradition and ancient knowledge regarding their production and pass this knowledge to future generations, both in terms of protecting cultural heritage and preserving historical value. In conservation studies to be carried out in archaeological sites, the characteristics of original lime mortars, and the possible sources of lime and pozzolans should be determined. It is important to investigate local resources and volcanic deposits around the study area in order to identify the raw material resources. New mortars should be compatible with the original mortars and should be produced by using lime and pozzolans obtained from their original sources.

CRediT authorship contribution statement

Elif Uğurlu Sağın: Conceptualization, Methodology, Investigation, Writing – original draft, Writing - review & editing, Visualization. **Hasan Engin Duran:** Methodology, Formal analysis, Writing – original draft, Writing - review & editing, Visualization. **Hasan Böke:** Methodology, Investigation, Writing – original draft, Writing - review & editing.

Declaration of Competing Interest

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