

Cement Microstructures and Durability in Ancient Roman Seawater Concretes

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Abstract Roman hydraulic maritime concretes of the central Italian coast have pumiceous volcanic ash, or *pulvis Puteolanus*, from the Bay of Naples as mortar pozzolan. Petrographic and mineralogical analyses of cement microstructures in relict lime, tuff, and pumice clasts suggest that pozzolanic reaction at high pH produced gel-like calcium-aluminum-silica-hydrate cements. Orthorhombic 11 Å-tobermorite, with unit cell dimensions $a=5.591(1)\text{Å}$, $b=3.695(1)\text{Å}$, $c=22.86(1)\text{Å}$, developed in the residual cores of portlandite clasts and in certain pumiceous clasts, as well.

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Ettringite and calcium-chloroaluminate formed in discrete, perimetral microstructures and in the cementitious matrix. Phillipsite and chabazite cements may reflect later dissolution of alkali-rich volcanic glass at pH 9–10. The cement systems have remained stable for 2,000 years, during partial to full immersion in seawater. Vitruvius’ *De architectura* and other ancient texts describe the raw materials of the concretes, preparation of lime, and construction of submerged wooden forms. Information concerning the materials, formulations, and installations of the concretes was apparently spread by movement of central Italian engineers around the Mediterranean but also, perhaps, by the circulation of sub-literary engineering manuals. Further analytical investigations will determine the diverse chemical processes that produced the cement microstructures, and why the harbour constructions have endured for two millennia.

1 Introduction

Hydraulic, pozzolanic concretes, first developed by the Romans in second century BCE, were widely used in important harbour constructions along the Mediterranean seacoast, over several centuries. Between 2002 and 2009, the ROMACONS group drilled Roman maritime concretes in 11 harbours [1–6]. These structures have remained cohesive and intact in the seawater environment for 2,000 years. ROMACONS drilled a first group of concretes between 2001 and 2006 from harbours along the central Italian coast (Fig. 1): the Cosa (PCO.2003), ~60 BCE, and Santa Liberata breakwaters (SLI.2003, SLI.2004), ~50 BCE, in Tuscany, the ports

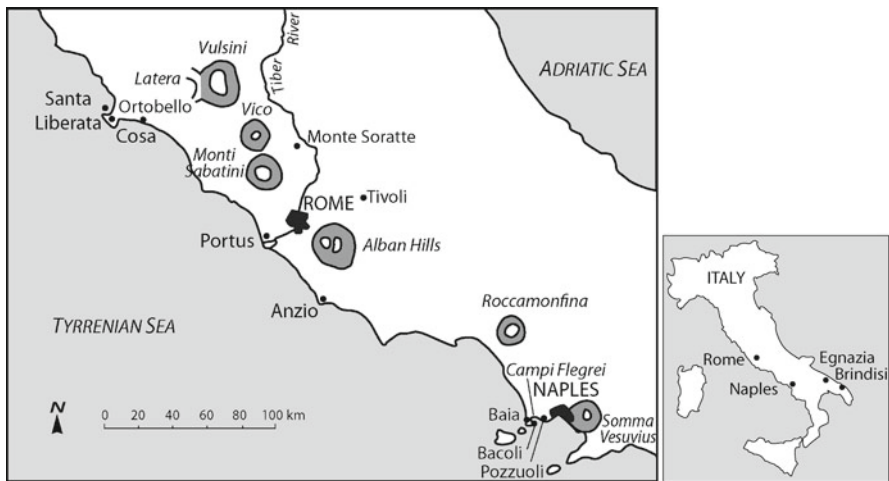


Fig. 1 Ancient Roman harbours and volcanic districts of the central Italian coast

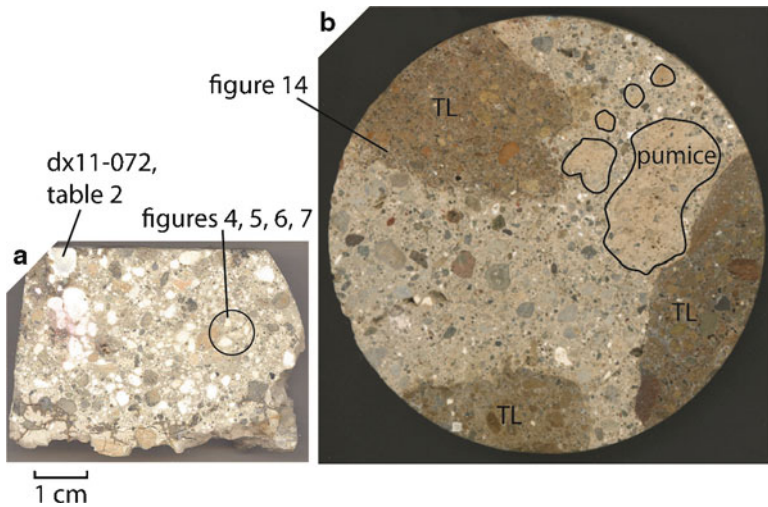


Fig. 2 Photos of mortar fabrics and the locations of analyses of aggregate clasts and cement microstructures (a) Portus Claudius (POR.2002.PO2), (b) Portus Traianus (PTR.2001.01)

of Claudius (POR.2002), ~50 CE, and Trajan (PTR.2002), ~115 CE, at Ostia Antica near Rome, the port of Nero at Anzio (ANZ.2002), ~ 65 CE, and the port structures at Baiae (BAI.2006), mainly first century BCE, in the Gulf of Naples. Between 2005 and 2009, ROMACONS drilled more distant harbours: Egnazia (EGN.2008) on the Adriatic coast near Brindisi, first century BCE, Caesarea Palaestinae (CAE.2005) in Israel and Alexandria (ALE.2007) in Egypt, both first century BCE, Chersonissos (CHR.2007) in Crete, first centuries BCE/CE, and Pompeiopolis (POM.2009) near Mersin in Turkey, of which the visible breakwaters, at least, belong to mid-second century CE [5]. This chapter describes some characteristic cement microstructures in the mortars of concretes from the central Italian coast harbours, to provide a foundation for further investigations into their extraordinary durability and longevity, as well as the expertise of the builders who carried out the underwater constructions. The mortar fabrics are compared to those of a historically accurate *pila* constructed in Brindisi harbour by the ROMACONS group in 2004 and drilled at 6 months (BRI.2005.01), 12 months (BRI.2005.02), and 24 months (BRI.2006) [7, 8], and at 42 months (BRI.2008) and 60 months (BRI.2009) (Table 1). The concretes of the harbours at greater distance from Rome will be described in a future publication.

The ancient concretes are highly complex, composite cementitious materials, with remarkably heterogeneous fabrics (Fig. 2). The fundamental binding substance is a hydraulic pozzolanic mortar, prepared from lime hydrated with seawater and pumiceous volcanic ash, the *pulvis Puteolanus* of Vitruvius [1] (*pulvis*, literally, “powdery earth”), which was sometimes augmented with local sands. *Pulvis Puteolanus*, now popularly called *pozzolana*, is a powdery, incoherent, vitric ash

Table 1 X-ray diffraction analyses of mortar components

Specimen	Predominant cements	Subordinate cements	Pozzolan
PORTUS COSA mid-first century BCE, center of Pier 1 on modern beach ^a			
PCO.03.01A cm	Cal Vat	Etr Str Phi-K	San Qtz Anl
PCO.03.01C wi	Tbm Cal	Str Wo Etr Vat	–
PCO.03.01A p	Phi-K Vat	Tbm Cbz Cal	San Anl
PCO.03.01A p	Phi-K	Vat Tbm	–
PCO.03.01A tuff	Phi-K Cbz-Ca	–	–
SANTA LIBERATA mid-first century BCE; center of <i>pila</i> off northwest <i>piscina</i>			
SLI.04.A mor	Cal	Cbz Clc Vat	Ill San An Anl
SLI.03.01 wi	Etr Tbm	Vat Hyc Cal	–
PORTUS NERONIUS ca. 65 CE; center of <i>pila</i> of southeast breakwater ^a			
ANZ.02.A1 mor	Phi-Na Vat	Tbm Cbz-Ca Cal	San Anl Mus
ANZ.02.A1 wi	Tbm Cal	Wo Etr Vat Brc Hyc Arg–	–
PORTUS CLAUDIUS ca. 50 CE; western mass of north mole ^a			
POR.02.PO2C cm	Cal Vat Arg	Hyc	–
POR.02.PO2A rlc	Tbm Cal	Wo Etr Hyc Gp	–
POR.02.PO2C pum	Cal Vat	Arg Phi Tbm	San
PORTUS TRAIANUS ca. 115 CE; mole and quay at entrance to hexagonal basin ^a			
PTR.02.01 cm	Cal Vat	Etr Hyc Phi	Anl Di San Ill
PTR.02.01 wi	Tbm Cal	Wo Etr Nor Vat Flr Hyc /	–
PTR.02.01 p	Cbz-Ca Cal	Phi-K	Hem Bio Di Mus
BAIAE mid-first century BCE, various structures in Pozzuoli Bay ^a			
BAI.06.01 wi	Cal Tbm	Phi Cbz-Ca Hyt	Sa Anl Ill
BAI.06.02 wi	Cal	Phi Cbz-Ca	Sa Anl Ill
BAI.06.03 wi	Cal Tbm	Phi Cbz-Ca Hyt	Sa Anl Ill
BAI.06.04 wi	Cal	Phi Cbz-Ca Hyt	Sa Anl Ill
BAI.06.05 tuff	/	Phi Cbz-Ca	Sa Anl Ill
BRINDISI HARBOUR , November 2004, 8 m ³ concrete <i>pila</i> ^{b, c, d}			
05-BRI.top mortar, 6 mos	Cal Vat	Hyc Chm	Anl San
05-BRI.bottom mortar	Cal Vat	Hyc Chm Por	Anl San
05-BRI cm	Cal Vat	Hyc	Anl San
05-BRI cm, 12 mos	Cal Vat	Cbz Phi	Anl San
06-BRI cm, 24 mos	Cal Vat	Phi	Anl San
08-BRI cm, 48 mos	Cal Vat Hyc	Cbz Phi	San Anl Ill
08-BRI wi	Cal Por	Vat Hyc Sjg	–
09-BRI cm, 60 mos	Cal Vat	Hyc	Anl Di
09-BRI wi	Cal Por	Ett Hyc	–
08-BRI tuff	Phi-K Cbz-Ca	Cal	Anl Ill San

Mineral abbreviations follow [9]

cm cementitious matrix, wi white inclusion, p pumice, mor mortar, rlc relict lime clast

^aOleson et al. [1]

^bOleson et al. [7]

^cGotti et al. [8]

^dVola et al. [5]

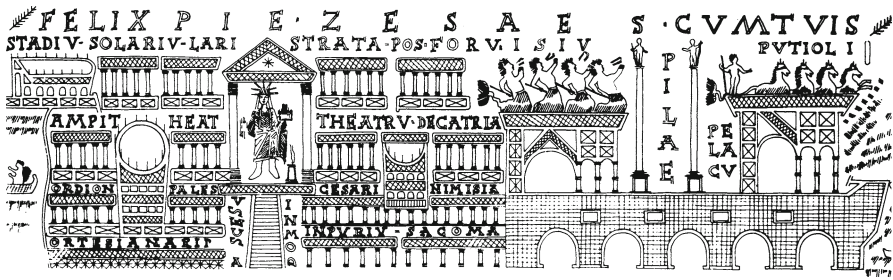


Fig. 3 The arched concrete pier, or *pilae*, at Puteoli harbour, now modern Pozzuoli at Campi Flegrei, about 250 CE. Drawing on glass vessel, Narodny Museum, Prague [20]

pozzolan from the Gulf of Pozzuoli at the northwest sector of the Bay of Naples [1, 7, 8]. A pozzolan is a siliceous, aluminous material that by itself has no cementitious value, but in the presence of moisture chemically reacts with calcium hydroxide ($\text{Ca}(\text{OH})_2$) to form compounds with cementitious properties [10]. Supplemental pozzolanic materials enhance the durability of modern maritime concretes, through various processes [10–14]. The lithologic provenance of *pulvis Puteolanus* seems to be the Neapolitan Yellow Tuff, which erupted from Campi Flegrei caldera about 15 ka, and has both incoherent ash and lithified tuff facies [15]. The decimeter-sized coarse aggregate, or *caementa*, of the Portus Cosa, Santa Liberata, and Baiae concretes is predominantly vitric-crystal tuff, presumably quarried from Campi Flegrei deposits, as well [1, 7]. The Portus structures have vitric-lithic Tufo Lionato tuff from Alban Hills volcano [16]. Builders placed the concrete mixtures in inundated or even completely submerged forms [17, 18], where they set and cured in seawater, out of contact with atmospheric CO_2 . Here, durability corresponds to the capacity of pozzolanic cements to bond the mortar components and coarse aggregate for a very long time.

Harbours were the most important element in the physical infrastructure that supported the Roman imperial economy, and thus made the Roman imperial socio-political system possible. The consistent presence of *pulvis Puteolanus* in the concretes suggests that the experimental formulations may have taken place near the Bay of Naples, but little is known about the spread of this technology, particularly for the immense marine structures built far from central Italy [1, 3, 5]. For example, when was the volcanic ash-hydrated lime formula discovered, and how much did it vary? How was the lime calcined and slaked, the mortar mixed, and the concrete placed in the sea? How did knowledge of the properties of the volcanic ash pozzolan travel to large and small marine construction sites outside of Italy: through the movement of engineers, or by means of technical handbooks on harbour engineering? Analyses of the seawater mortar fabrics and consideration of ancient Roman literary and inscriptional sources [19] provide new insights into Roman builders' expertise and possible applications of their materials and methods to enhancing the durability of modern seawater concretes (Fig. 3).

2 Materials and Methods

The mortar specimens come mainly from discs sliced from 1 to 6 m long, 9 cm diameter drill cores, which are stored in core boxes under ambient, sub-aerial conditions in a warehouse at CTG Italcementi in Bergamo, Italy. Petrographic maps were drawn on digital optical photomicrographs taken with a 2× objective on an Olympus BX51 microscope, to describe the characteristic features of the heterogeneous mortar fabrics. Descriptions of tuff fabrics follow [16]. Polished thin sections, often panoramic in size, 6.5 by 4 cm, were prepared from part of the disc; powders for X-Ray diffraction analyses (XRD) were commonly prepared from the rest. The cementitious binding matrix was lightly crushed or scratched out from the mortar, and sieved to pass the #100 sieve, <0.0159 mm. Relict lime inclusions and volcanic particles, mainly pumice and tuff fragments, were carefully scratched out or hand-picked. XRD analyses used a Bruker D8-Advance X-ray powder diffractometer with Cu K α radiation ($\lambda=1.54184$ Å) and fixed divergence slits at the CTG Italcementi labs (Table 1). A Leo Scanning Electron Microscope (SEM), equipped with a Sirius Energy Dispersive X-ray Spectrometer (EDS) at CTG Italcementi and a JEOL 6,700F Field Emission (6/7/Hosler) instrument at Pennsylvania State University were used in the backscatter electron mode (BSE) with EDS spot or area analyses on polished thin sections, to describe the altered aggregate clasts and cement phases. SEM elemental maps of carbon coated, polished thin sections, acquired with a JSM-6480LV instrument at Northern Arizona University at 20 kV voltage in the high vacuum mode, show Ca, Si, Al, S, Cl, and K concentrations in these fabrics. Major element compositions of bulk mortar specimens appear in [1, 5–8]. Refinements of the lattice parameters of tobermorite from the XRD analyses used the Rietveld method, performed using the fundamental parameters approach with background coefficients, cell parameters, zero-shift error, sample absorption and phase fraction, with the unit cell dimensions of the ICDD #191364 orthorhombic tobermorite model [21] and Topas 3 software (Table 2). The March-Dollase function was used to determine the preferred orientation of the 11 Å tobermorite.

3 Previous Studies of Mortar Fabrics

The seawater mortars have four predominant components: *pulvis* pozzolan composed of coarse gravel to fine silt-sized grayish orange (10YR 7/8–8/5) to yellow gray (5Y 8/3–7/2) vitric tuff, pumice, palagonite, and crystal fragments; occasional sedimentary and/or volcanoclastic sands; a cementitious binding matrix containing clasts <2 mm with diverse cements; and dull white (N9) opaque inclusions, mainly 0.1–1 cm (Fig. 2). The crystalline cements frequently include rock forming mineral cements of the earth's crust, such as tobermorite, a rare crystalline calcium-silica-hydrate, and phillipsite and chabazite, which are zeolitic alkali-rich aluminosilicates (Table 1) [6]. This mineral assemblage occurs in recent volcanic ash deposits immersed in the

Table 2 11 Å Tobermorite lattice parameters from X-ray diffraction analyses of white inclusions, based on the ICDD number 191364 orthorhombic structural model [21]

Tobermorite specimen	Unit cell dimensions (Å)			Volume (Å ³)
	a	b	c	
PORTUS COSA , relict lime dx2010-0947 (PCO.2003.1C)	5.591(1)	3.697(1)	22.85(1)	472.5(1)
PORTUS COSA , relict lime dx09-077 (PCO.2003.1A)	5.5967(1)	3.6929(1)	22.891(1)	473.1(1)
SANTA LIBERATA , relict lime dx2010-0946 (SLI.2003.03)	5.600(1)	3.6929(1)	22.891(1)	474.4(1)
PORTUS CLAUDIUS , relict lime dx11072 (POR.2002.PO2A)	5.581(1)	3.686(1)	22.736(1)	467.8(1)
PORTUS CLAUDIUS , relict pumice dx03-030 (POR.2002.PO2C)	5.530(1)	3.679(1)	22.57(1)	459(1)
PORTUS NERONIS , relict lime dx11-074 (ANZ.2002.A1)	5.5927(1)	3.6942(1)	22.864(1)	472.4(1)
BAIAE , relict lime dx04-055 (BAIA.2001.01)	5.595(1)	3.6980(1)	22.903(1)	473.8(1)

ocean at Surtsey volcano in Iceland [22]. Zeolites commonly cement volcanic ash in seawater and saline lake brines [23–25], and subaerial pyroclastic deposits of central Italy [15, 16, 26]. Paradoxically, the Roman seawater cement assemblages represent temperature fields that are ordinarily considered incompatible in modern cement pastes [10, 27]. In the ancient mortars, tobermorite is often associated with ettringite microstructures (Table 1) [6], but ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}26\text{H}_2\text{O}$) is typically stable up to 70°C at atmospheric pressures, while tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2\cdot 4\text{H}_2\text{O}$) or Al-tobermorite ($\text{Ca}_5\text{Al}_{0.7}\text{Si}_{5.3}\text{O}_{16}(\text{OH})_{1.3}\cdot 4\text{H}_2\text{O}$) is typically synthesized at 120–180°C, although low-temperature forms may develop at 60°C [27, 28]. Phillipsite and chabazite generally precipitate from fluids with 9.1–10 pH [22–24], higher than the 7.9–8.2 pH of Mediterranean seawater, but lower than the 12.7 pH of portlandite ($\text{Ca}(\text{OH})_2$) present at the initiation of curing [7, 11]. Seawater temperatures along the central Italian coast are about 17.5°C in August to 19.0°C in June, and salinity is about 37.5–37.9 between Rome and Naples [29].

A diagenetic microstructural approach provides insights into the ancient cement microstructures. Diagenesis is the study of the physical and chemical changes undergone by a rock after its deposition, including the development of mineral cements during lithification, which result from chemical adjustments to particular environments. Diagenetic perspectives are useful in describing the evolution of cement precipitation in the seawater mortars, and the development of presumably incompatible crystalline cements as chemical responses to changing pH and seawater infiltration over the 2,000 year lifespans of the maritime structures [6, 11]. Microstructural perspectives are useful in describing discrete mortar components at several scales of analysis. For example, integration of petrographic and scanning electron microscope studies and maps, followed by the extraction of specific mortar

components for XRD, illustrates processes of pozzolanic reaction in relict lime and volcanic clasts, the development of diverse cement phases over time, and the subsequent alteration of these components in the seawater concrete system [6, 11–14]. Bulk analyses of the overall mortar composition are generally avoided, because these give averaged results of the heterogeneous fabrics (Fig. 2) and little insight to processes at the millimeter scale.

The predominant reactive component of the *pulvis* pozzolan seems to be alkali-rich volcanic glass. Neapolitan Yellow Tuff glass contains about 8 wt.% K_2O and 3–4 wt.% Na_2O [15], and the bulk chemistry of the related Bacoli Tuff used in the Brindisi experimental concretes has a similarly alkalic composition [5–8, 15]. Authigenic zeolite cements – phillipsite, chabazite, and analcite – commonly form greater than 50 wt.% of the Neapolitan Yellow Tuff [15]. These minerals have good pozzolanic reactivity with hydrated lime [13]. The Portus Cosanus mortars also contain quartz sands, presumably from beach deposits near the harbour site [1, 7]. The Portus Traianus mortars also contain scoriaceous volcanoclastic sands, from Alban Hills deposits [30].

The lithologic origins and preparation of the lime in the central Italian coast harbour constructions, which span 300 km of the shoreline and about 165 years of construction history, remain unclear. The lime compositions seem to have been rather pure CaO, with little argillaceous or hydraulic component detectable through petrographic studies or XRD analyses. Certain relict lime clasts in the Baiae specimens, however, retain rhombohedral dolomitic pseudomorphs. The material characteristics of lime in European historic mortars typically show large variations, which result from diverse processes of calcination, slaking, and mixing with the mortar aggregate [31–34]. Specifically, temperature variations in the kiln produce underburned particles, with limestone fabrics still partially intact; overburned particles, with dead-burned, refractory fabrics; and viable CaO quicklime particles, which react to form portlandite when slaked [31–34].

Roman archaeologists tend to infer a wet slaking procedure for the mortars of concrete walls and foundations based, in part, on Vitruvius' rather terse recommendations in *De architectura*, completed about 20 BCE [*De arch* 2.5.1]: “We must also be diligent about lime, which is cooked from white stone (*albo saxo*). That [lime] which is from dense and hard [limestone] will be useful in construction. When it will be slaked or quenched (*extincta*), then let it be mixed with sand; if it will be excavated sand (*harenae fossiciae*), three [parts] sand and one [part] lime are mixed together (*infundantur*).” Some archaeologists infer that builders used slaked lime putty ($Ca(OH)_2$) that was matured, or aged [7, 19]. Before construction, it was remoistened and then mixed with the volcanic pozzolan [7]. Installation of the Brindisi experimental pila followed a similar procedure, with wet slaking of aged slaked lime to form stiff putty, immediately followed by the incorporation of *pulvis puteolanus* in a 2.7:1 pozzolan to lime volume ratio [7]. A great deal of effort was required to laboriously mix the lime putty and incorporate the *pulvis* pozzolan into a wet mix that was lowered by baskets into the wooden form submerged in seawater [7]. The experimental mortar had a markedly lower percentage of white nodules than the ancient mortars [7, 8]. In fact, Vitruvius' instructions for mixing mortars for harbour constructions are somewhat obscure

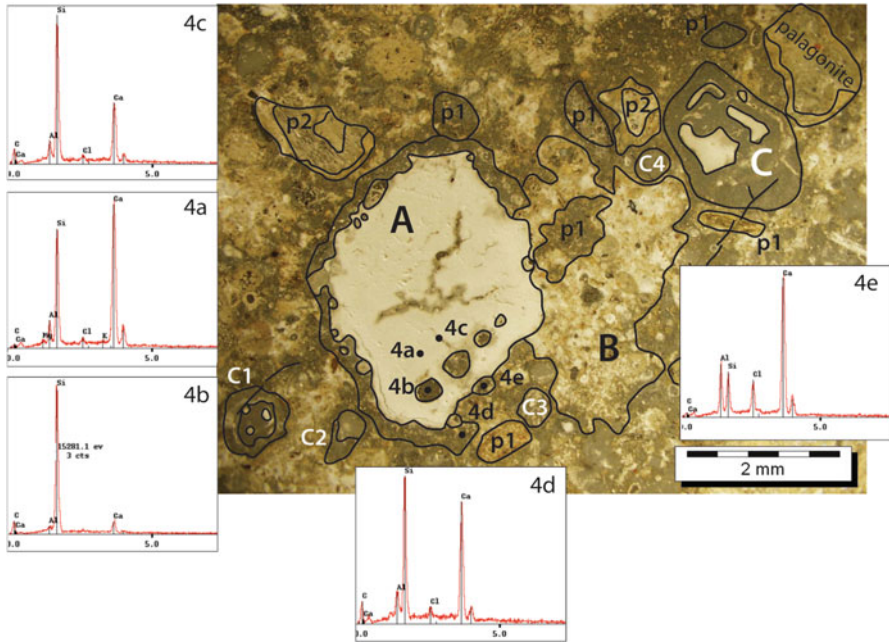


Fig. 4 Optical micrograph (plane polarized light) and SEM-EDS analyses of regions associated with partially dissolved relict lime clasts in a Portus Claudius mortar (POR.2002.PO2)

[*De arch* 5.12.2]: “Earth (*pulvis*) is to be brought from the region extending from Cumae to the promontory of Minerva and mixed (*miscetur*) in the mortar trough (*mortario*) so the [ingredients] correspond two to one.” Here, he implies that *pulvis* was mixed with lime, but he does not clarify the slaking process or mixing method. The presence of white lime nodules in some European historic mortars suggests a “hot mixing” process [31–34]. In some mortars wet aggregate was thoroughly mixed with lime fragments [31]; in others, fine quicklime was dampened with a little water, covered with aggregate to retain the exothermic heat produced by the $\text{CaO} + \text{H}_2\text{O} = \text{Ca}(\text{OH})_2$ reaction, and left for a few days before further mixing and installation [32]; and in still others, lime putty was mixed with aggregate [34]. The ancient concrete fabrics and texts should provide clues to Roman builders’ methods [19].

4 Characteristic Mortar Microstructures

Petrographic and SEM images illustrate microstructures (Figs. 4, 5, 6, 7, 8, 9, 10, 11, and 12) present as white inclusions in the Roman maritime mortars [1, 5–8]. At the time of drilling, the Portus Claudius and Portus Cosa specimens were exposed sub-aerially; the Portus Neronis and Santa Liberata specimens were continuously immersed in seawater for 2,000 years [1].

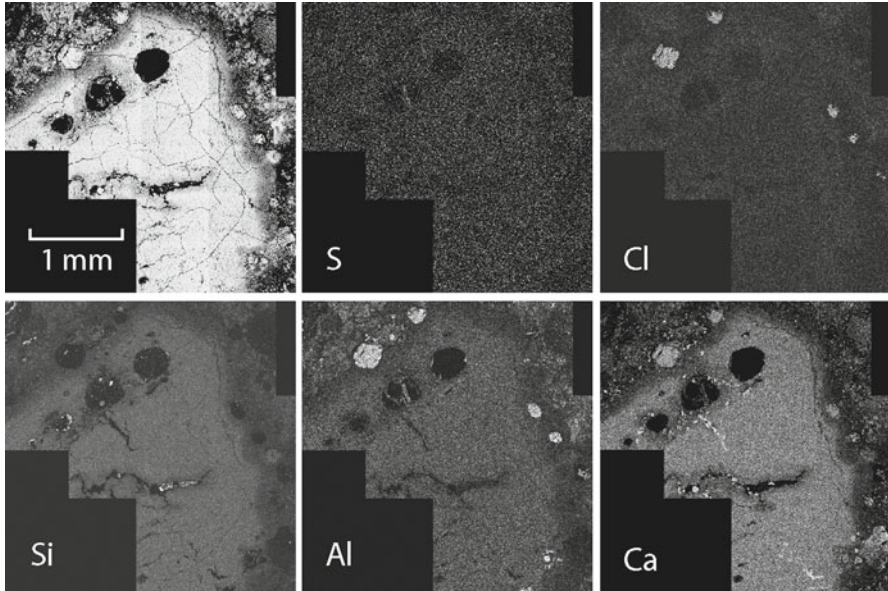


Fig. 5 SEM elemental maps of a subarea of Fig. 4 rotated 180° clockwise, showing a back scattered electron (BSE) image on the *upper left*, and the qualitative distribution of sulfur (S), chlorine (Cl), silica (Si), aluminum (Al), and calcium (Ca) in the partially dissolved relict lime clast. Note the association of Al, Ca and Cl in calcium-chloroaluminate microstructures

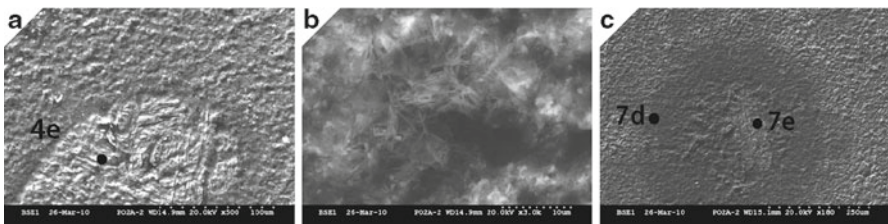


Fig. 6 SEM-BSE images of cement hydrates (a) calcium-chloroaluminate (Fig. 4e), (b) tobermorite (Fig. 7d), (c) silica-calcium-alumina ring and calcium-chloroaluminate core, (Fig. 7d, 3e)

4.1 *Portus Claudius, Relict Lime Clast*

Figures 4 and 5 shows a dull white, altered lime clast (A) in contact with a tuff fragment (B), whose vitric matrix has mottled zones of white opacity associated with poorly crystalline cement hydrates. A neighboring relict lime clast has isolated opaque areas (C), as well. Smaller lime clasts (C1, C2, C3, C4) are partially to wholly dissolved. Smaller pumices (p1) are mainly dissolved; larger pumices (p2) have opaque cores and partially dissolved perimeters. The opaque mass

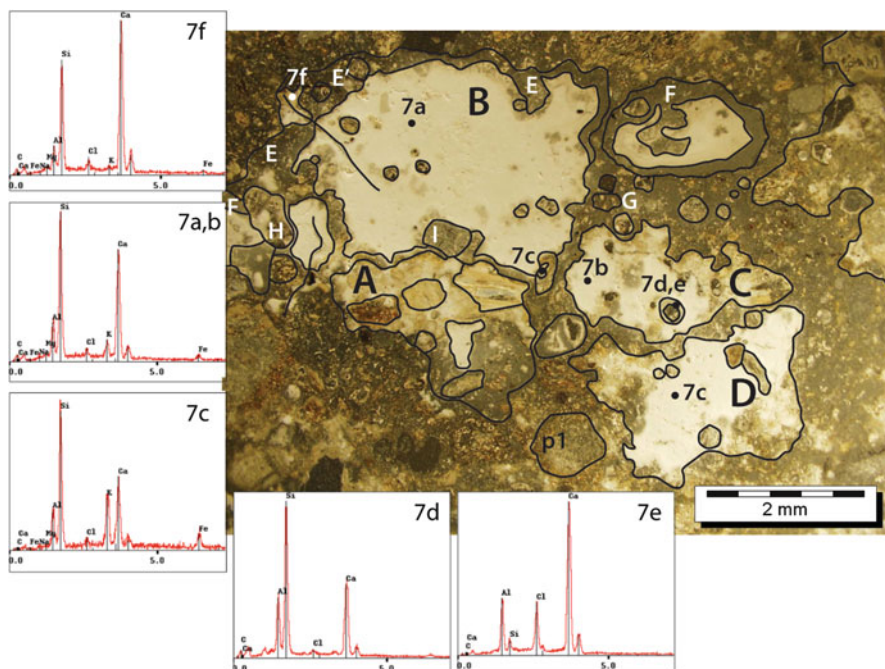


Fig. 7 Optical micrograph (plane polarized light) and SEM-EDS analyses of regions associated with pumiceous tuff clasts of *pulvis Puteolanus* in a Portus Claudius mortar (POR.2002.PO2)

(A) has a cryptocrystalline fabric, dark gray and light brown (5Y 4/2) in plane polarized light (PPL), with a composition compatible with aluminum-bearing tobermorite (Fig. 4a). Four sub-spherical openings have silica-rich points (Fig. 4b), perhaps dissolved *tintinnides* macrofossils. A dissolution fissure and the perimetral rind have calcium-silica-aluminium-hydrate (CASH) compositions (Fig. 4c, d). The rind makes a distinct boundary with the cementitious matrix. It contains quartz crystals shattered during calcining of the host limestone, and bead-like microstructures with calcium-silica-chloroaluminate cores and drying shrinkage (Figs. 4e, 6a). The cementitious matrix has microcrystalline calcite, vaterite, aragonite and hydrocalumnite (Table 1). The SEM elemental maps (Fig. 5) show concentrations of silica (Si), aluminum (Al) and calcium (Ca) associated with CASH at the center of the partially dissolved relict lime clast (Fig. 4a) and concentrations of calcium, aluminum and chlorine (Cl) in the interfacial zones. There are no sulfur (S) concentrations or ettringite. The maps suggest a “shrinking core” process [35]: the dissolution at (A) terminated before the entire portlandite clast was consumed, and the residual opaque nucleus records the development of cryptocrystalline CASH, but tobermorite crystals are not well-developed. Gel-like CASH formed in the dissolved rims of lime clasts.

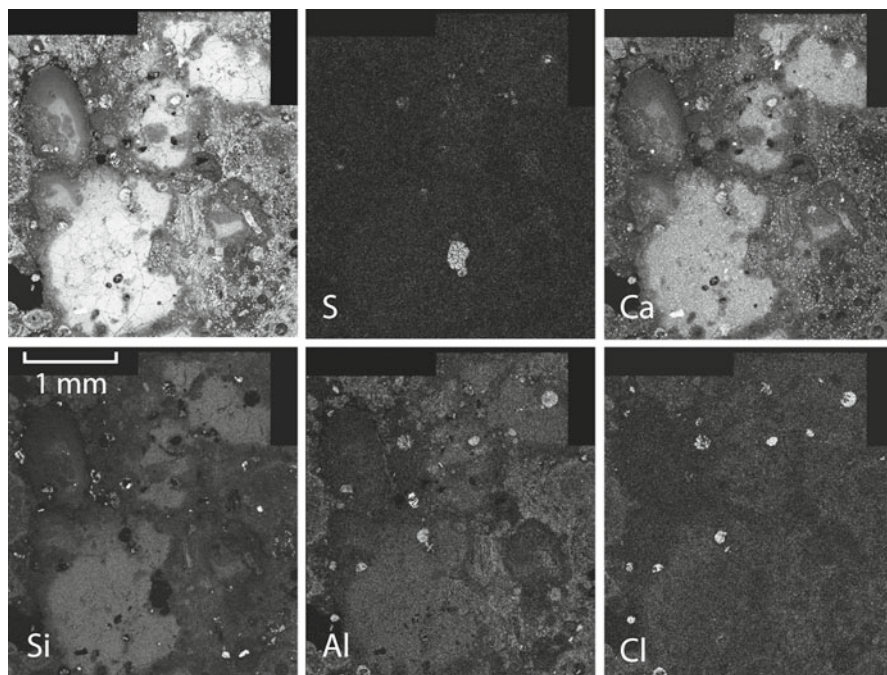


Fig. 8 SEM elemental maps and BSE image (*upper left*), rotated 90° clockwise from Fig. 7, showing the qualitative chemical compositions of the relict vitric tuff regions

4.2 *Portus Claudius, Relict Tuff Clast*

Figures 7 and 8 show a cluster of dull white, vitric tuff clasts. Pumice and glass fragments are preserved in a patchy yellowish orange (10YR 7/6, PPL) volcanoclastic texture (A) that grades to lightly opaque gray (N4, PPL), similar to Fig. 4b. Traces of volcanoclasts also occur in the deeply opaque, dark gray (5Y 4/2, PPL) masses at B, C, and D. Potassic-magnesium-iron-calcium-aluminum-silica-hydrate cements (KMFCASH) (Fig. 7a, b) reflect altered volcanic ash, as does the opaque core of a pumice with a dissolved perimeter (Fig. 7c). Tobermorite fibers containing aluminum occur in the most densely opaque mass (D) (Figs. 6b, 7b). The rind around the largest tuff clast (B) varies from lightly opaque (E') to colorless (E), similar to the rim of the partially dissolved lime clast nearby (F); lightly opaque CASH patches also occur in this rind (Fig. 7f). An annular microstructure has an opaque calcium-chloroaluminate inner zone and CASH outer zone (Figs. 6c, 7d, e). Sub-spherical microstructures 0.1–1 mm in diameter may contain a similar muddy opacity (G) or ettringite crystals with second order birefringence and low (-) relief (H), or even a complex combination of both materials (I). Overall, the maps record the perimetral dissolution of vitric tuff clasts, and precipitation of a gel-like CASH rind (E, E'); a gradational alteration to white cryptocrystalline opacity in residual tuff cores (A, B, C, D) with locally crystalline tobermorite (D) (Fig. 6b); and peripheral

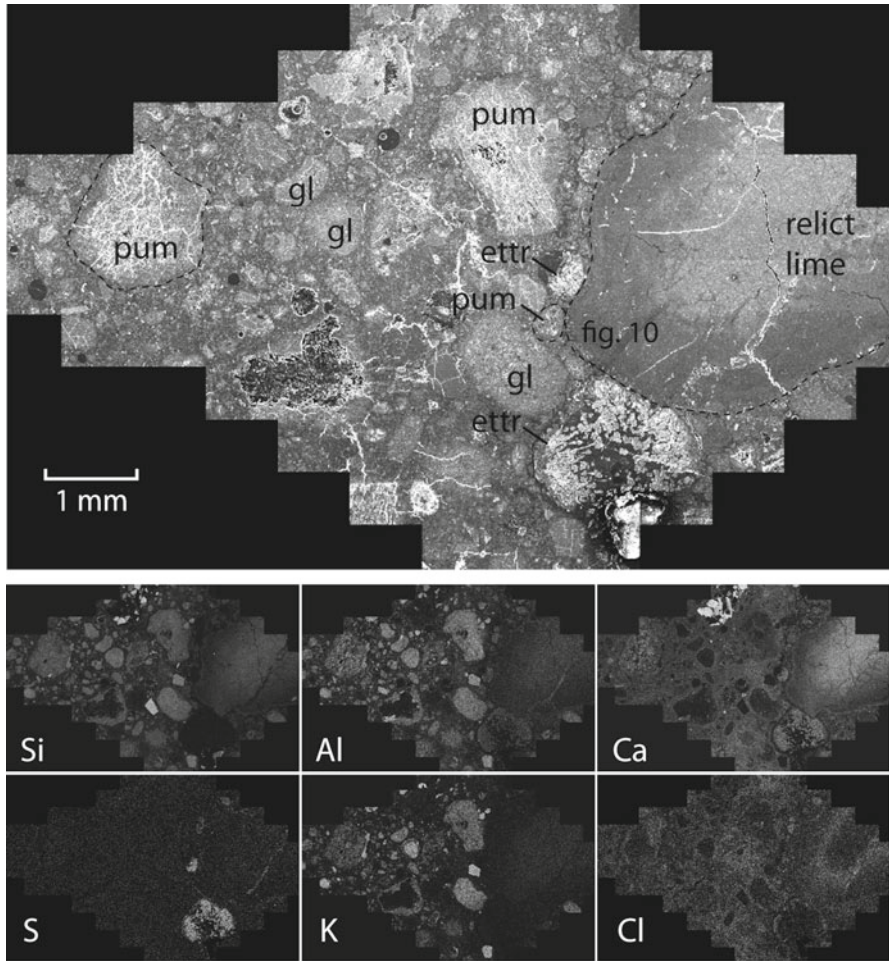


Fig. 9 SEM elemental maps and a BSE image (*top*) of a Portus Neronis (ANZ.2002) relict lime clast tobermorite specimen dx11-074), its interfacial zone, and the surrounding pumiceous cementitious matrix. The chlorine image is enhanced to emphasize its weak but diffuse distribution. *pum* pumice, *gl* glass fragments, *ettr* ettringite

sulphate and chlorine microstructures (G, H, I). The complex but highly discrete chemical concentrations are shown by SEM elemental maps (Fig. 8).

4.3 Portus Neronis, Relict Lime and Pumice Clasts

The SEM elemental map of Fig. 9 shows the pumiceous cementitious matrix of the Anzio harbor mortar, to the left, and a relict lime clast, to the right, with fracture traces as fine white lineations that traverse its partially dissolved perimeter.

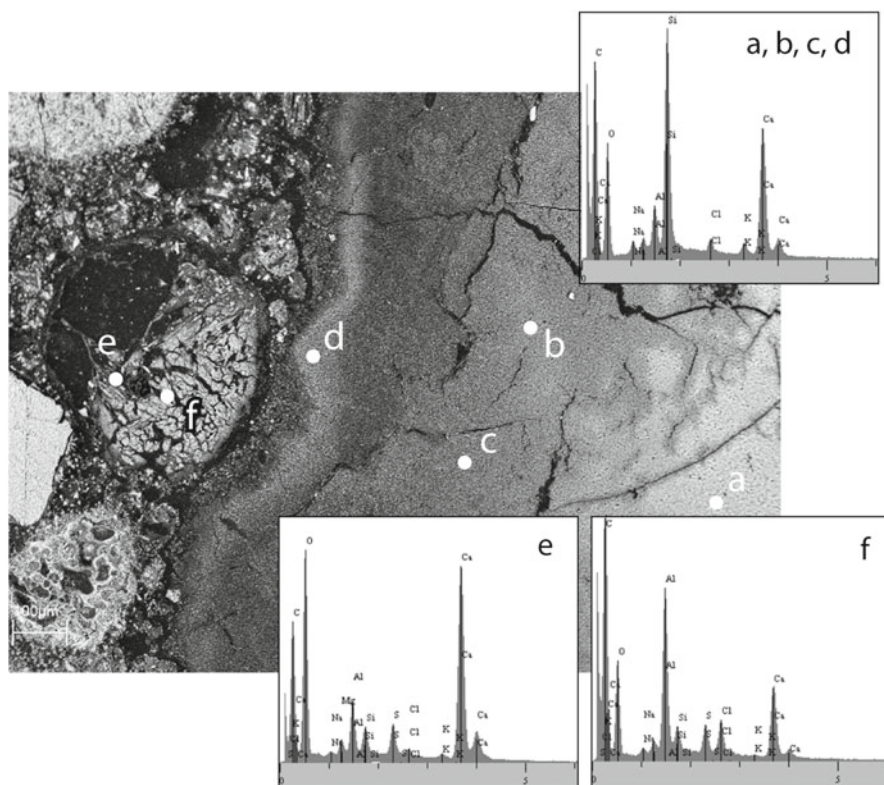


Fig. 10 SEM-BSE images and EDS analyses of CASH (a, b, c, d), ettringite (e), and altered ettringite (f) of the interfacial zone of the relict lime clast of Fig. 9, Portus Neronis

The complex CASH rind (Figs. 9, 10) has a rather uniform composition, going from the petrographically opaque center (Fig. 10a) to the colorless perimeter (Fig. 10b, c, d). The nucleus is tobermorite (Table 2, analysis dx11-074). Ettringite occurs in two sub-spherical microstructures along the interfacial zone, shown by concentrations of calcium, sulfur, and aluminum (Fig. 9). Most of the ettringite is altered (Fig. 10e), and contains a small amount of silica, and it further decomposes to poorly crystalline material enriched in aluminum, calcium, and chlorine (Fig. 10f). In contrast, in a Portus Cosa mortar, relatively fresh ettringite crystals (Fig. 11a) traverse a relict void surrounded by a complex CASH rim (Fig. 11c). The more altered ettringite crystals show decreased aluminum, calcium and sulfur, and enrichment in silica (Fig. 11b). Further examination of these textures will give insights into the processes that sequestered sulfate and chlorine ions in the mortar fabric.

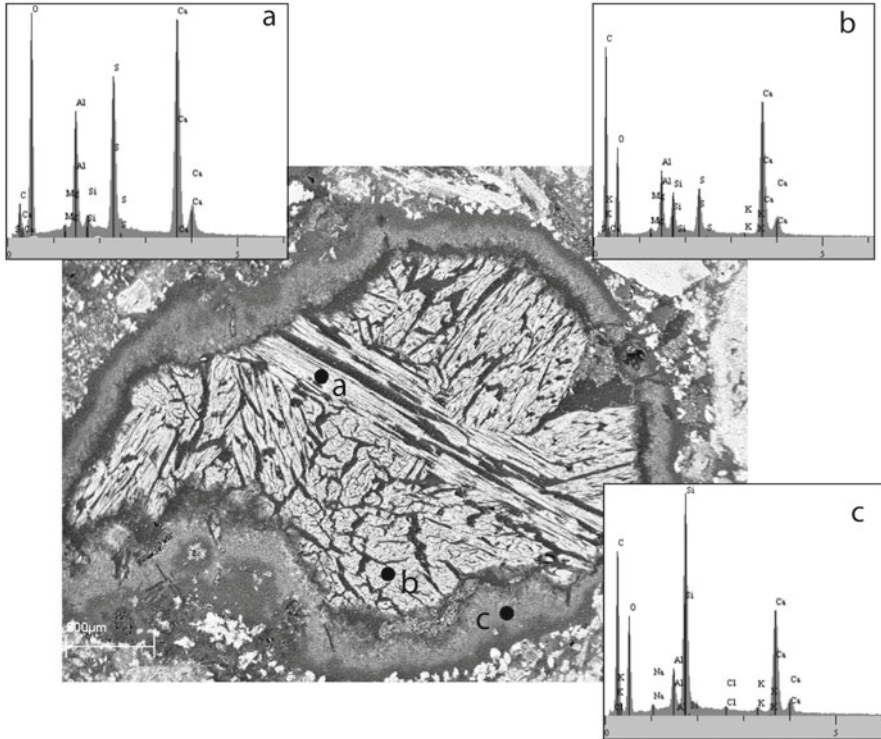


Fig. 11 SEM-BSE images and EDS analyses of ettringite (a), altered ettringite (b), and CASH rind (c) surrounded by the cementitious matrix of a Portus Cosa mortar (PCO.2003.01)

4.4 Variations in the Microstructures of White Inclusions

Petrographic studies of white inclusions in the seawater mortars reveal important textural relationships (Fig. 12). The partially dissolved relict lime clasts of the Portus Cosa mortar retain traces of cracks with opening displacements that protrude about 50–150 μm into the cementitious matrix (Fig. 12a, b). These textures suggest quicklime particles that hydrated to portlandite *in situ* and expanded [31–34]. They then partially dissolved, developing petrographically colorless CASH gel in their perimetral zones and opaque CASH or Al-tobermorite in their relict portlandite cores. In the Santa Liberata mortar (Fig. 12c), the gel-like CASH in the fractured lime clast altered to sparry calcite, but the opaque cryptocrystalline CASH appears relatively unaltered. Relict lime clasts in the Baiae mortar commonly have intact and homogeneous opaque cores (Fig. 12d), surrounded by a less opaque zone, and a dissolution rind with colorless CASH and alteration to calcite. The absence of fracturing suggests that the clast may have entered the seawater system as portlandite, either as a previously matured slaked lime particle, or as a recently hydrated particle,

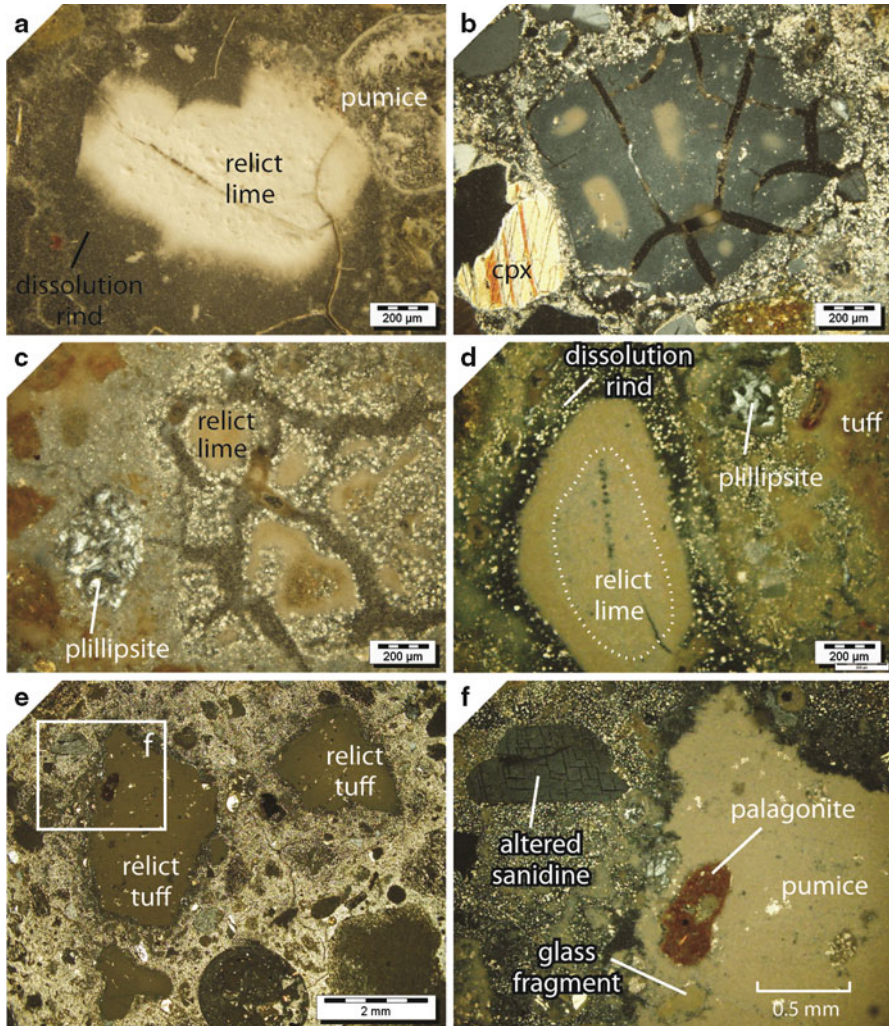


Fig. 12 Optical micrographs of white inclusions, (a) and (b) lime clasts with fractures, Portus Cosa (PCO.2003.01), (c) lime clast with fractures, Santa Liberata (SLI.2003), (d) lime clast with homogeneous texture, Baiae (BAIA.2006.03), (e) and (f) tuff clasts partially altered to opaque cements, Baiae (BAIA.2006.03), (a) and (e) are plane polarized light (PPL), (b, c, d, f) are crossed polarized light (XPL). Note the phillipsite microstructures in the cementitious matrix of (c) and (d)

perhaps damp-slaked with the *pulvis* pozzolan before immersion in seawater. The vitric matrix of a relict tuff particle, which contains palagonite, pumice, and sanidine crystal fragments (Fig. 12e, f), developed a white opacity, similar to the tobermorite in the Portus Claudius mortar (Figs. 6b, 7b, c, d, 8). Another pumice, adjacent to a relict lime clast (Fig. 12a) has similarly opaque cement, presumably CASH. The Santa Liberata and Baiae mortars have localized phillipsite cement microstructures in their cementitious matrix (Fig. 12c, d).

5 Characteristic Zeolite Cement Microstructures

Zeolite cements occur in the vesicles of relict pumice clasts, shown by the phillipsite rosettes in a Santa Liberata partially dissolved pumice fragment (Fig. 13a) as well as in discrete voids in the cementitious binding matrix, shown in a Portus Cosa mortar (Fig. 13b). Discrete chabazite microstructures also occur in pumice clasts and the cementitious matrix (Table 1) [6]. In the Portus Traianus concrete (Fig. 2), the zeolitized palagonitic fabric of the Tufo Lionato coarse aggregate apparently altered *in situ*, so that the fine vitric fraction was almost entirely consumed to produce dense new phillipsite cements that are intergrown with the natural, authigenic phillipsite of the tuff [16]. The *pulvis Puteolanus* that was presumably derived from an incoherent facies of the Neapolitan Yellow Tuff likely contained natural zeolites,

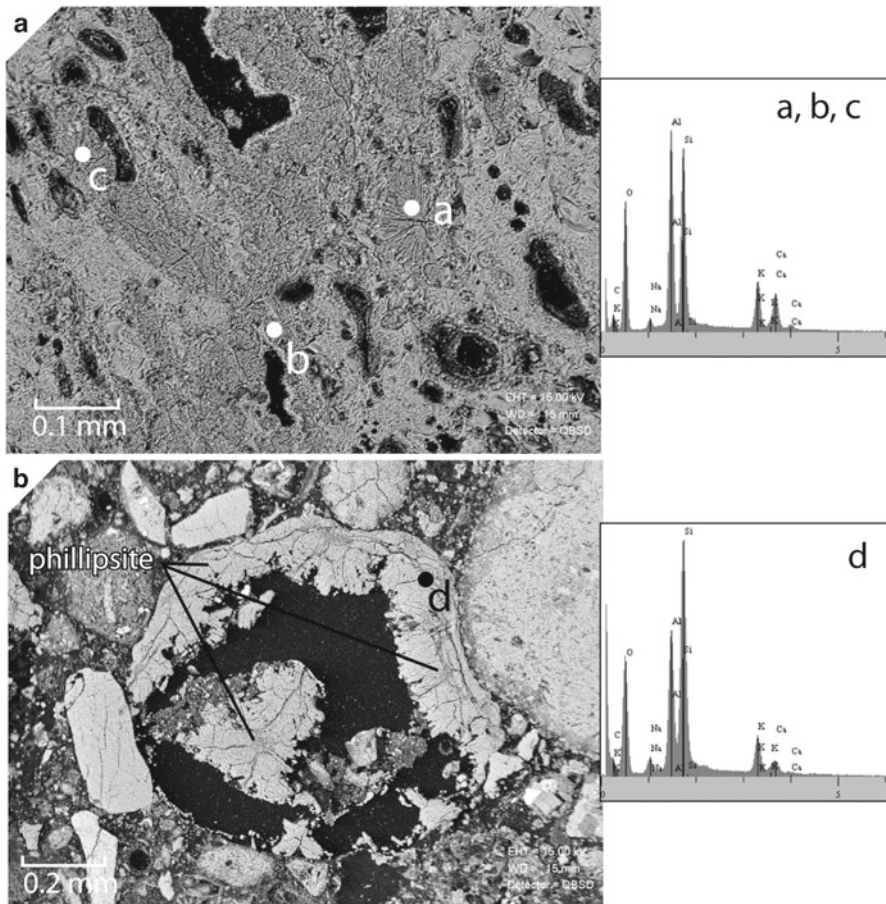


Fig. 13 SEM-BSE images and EDS analyses of phillipsite in (a) pumice vesicles, Santa Liberata (SLI.2003) and (b) a void in the cementitious matrix, Portus Cosa (PCO.2003 01)

but it is not known if all the zeolite was consumed during pozzolanic reaction. The phillipsite of the Neapolitan Yellow Tuff has Si:Al at about 2.54–2.82 and Na:K at 0.42–0.68 [15]. In comparison, Si:Al in phillipsites of marine and saline lake ash deposits ranges from 2.44–2.79 [24] to 3.12–4.06 [23], while phillipsites in the recent Surtsey basalt tephra deposits have Si:Al at 2.04–2.46 [22]. Further analyses will distinguish more precisely the compositions of phillipsite and chabazite that formed in the mortars, but qualitative, preliminary EDS analyses suggest variable ratios (Fig. 13) with both potassic and sodic phillipsite and calcic chabazite (Table 1). The presence of fresh, euhedral zeolite cements within the binding matrix suggests that (1) the pH of interstitial fluids in the mortar fabric fell significantly from that of the elevated levels of the portlandite-buffered system, and (2) once formed, the zeolite crystals remained stable and did not participate in further pozzolanic reactions. These *in situ* zeolite cements, and those of the harbour concretes at greater distances from Rome [6], may reduce the porosity of the mortar fabrics and tuff coarse aggregates and contribute to the overall durability of the maritime structures through reductions in permeability and seawater ingress at long curing times [10, 11].

6 Brindisi Experimental Mortars

The cementitious binding matrix of the young Brindisi mortar, formulated with matured lime putty hydrated with seawater and then incorporated with *pulvis pozzolan*, has a rather consistent assemblage of microcrystalline calcite, vaterite, and hydrocalumnite, and little or no portlandite [5–8]. Portlandite does, however, persist in occasional coarse white inclusions (Table 1). Similarly, the cementitious matrix of the ancient mortars has a predominantly calcite, vaterite, and/or aragonite, and hydrocalumnite assemblage, with subordinate cement phases having close associations with lime and volcanic clasts (Table 1, Figs. 4, 5, 6, 7, 8, 9, 10, 11, 12, and 13). Although tobermorite is associated with relict lime clasts and certain altered vitric tuff clasts in the ancient mortars (Table 1, Figs. 4, 5, 6, 7, 8, and 9), it is not detected in the experimental mortar. However, ettringite is associated with a portlandite inclusion in the 2009 Brindisi mortar specimen (Table 1). At the petrographic scale, the Brindisi mortar fabric appears quite different from the ancient mortars (Fig. 14). The cementitious matrix of the 2005 mortar, drilled at 12 months curing, is composed of irregular sub-centimetric zones with rather evenly dispersed pumice shards and volcanic crystals, and tiny relict plates of portlandite (Fig. 14a). The narrow opaque selvages that surround these zones incorporate very fine vitric ash shards, and they become progressively more opaque, as in the 2008 mortar, drilled at 48 months curing (Fig. 14b). The cementitious matrix of the 2009 mortar shows low birefringence, and amorphous CASH predominates. Puzzlingly, the 2008 mortar shows a stronger evolution of cements, with two distinctive constituents: a densely opaque brownish matrix (Fig. 14b), probably composed of poorly crystalline cements in altered vitric ash, and a fine grained, first order birefringent microcrystalline cementitious phase. Phillipsite and chabazite in the 2008 mortar are associated with vitric tuff clasts, but it is not clear when these formed (Table 1).

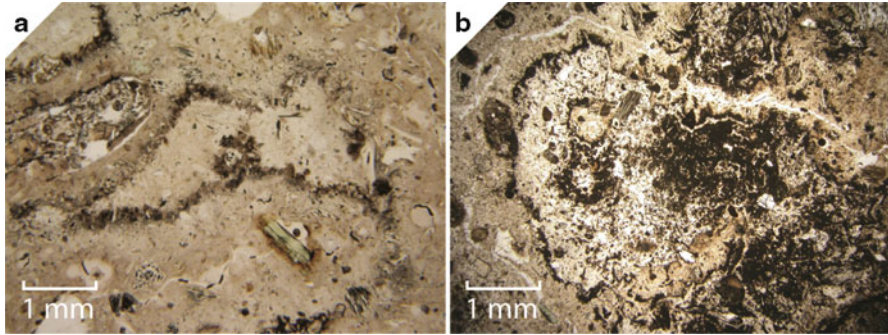


Fig. 14 Optical micrographs, plane polarized light, showing the cementitious matrix of the Brindisi concrete experiment (a) BRI.05, 12 months curing, (b) BRI.08, 48 months curing

7 Tobermorite Compositions and Lattice Parameters

Refinements of the lattice parameters of tobermorite identified through XRD analyses of relict lime clasts and one pumice clast (Table 2) provide a reference for gaining insights into the crystallization processes of calcium-silica-hydrate in the ancient seawater mortars. Although tobermorite is generally considered to form at elevated temperatures, usually through geothermal or autoclave processes at $>120^{\circ}\text{C}$ [21, 27, 28, 36], recent studies have detected tobermorite in historic mortars through XRD analyses [37–39]. However, little is known about the crystalline structure of these cements, which presumably formed in a low temperature environment. Diffractograms of relict lime clasts from Portus Claudius (Fig. 2, dx09-077), Portus Neronis (Figs. 9, 10, dx11-074), and Portus Iulius at Baiae (Fig. 15, dx04-055) show a uniform coincidence of tobermorite peaks.

The ICDD 191364 orthorhombic structural model ($\text{Ca}_{2.25}[\text{Si}_3\text{O}_{7.5}(\text{OH})_{1.5}] \cdot 1\text{H}_2\text{O}$) [21] fits the unit cell dimensions of the ancient tobermorites quite well (Table 2), as shown by the good correspondence with the Portus Neronis specimen (Fig. 16), rather than a monoclinic structure [36]. Calculations of the unit cell dimensions with Al^{3+} in the Roman seawater tobermorite suggest that aluminum substitution may not have a strong effect on the lattice parameters.

8 Inferences from Cement Microstructures

The predominance of alkali-rich vitric tuff in the ancient concretes suggests that geological perspectives can be useful in understanding their puzzling but pervasive cement assemblages. Hydrothermal alteration of basaltic glass tephra at $24\text{--}169^{\circ}\text{C}$ during the 12 years following the 1963–1967 eruption of Surtsey volcano, Iceland, for example, released elements that migrated and combined to form analcite, phillipsite, and tobermorite [22]. The 11 \AA tobermorite formed mainly below sea level at $70\text{--}169^{\circ}\text{C}$ [22]. Locally elevated pH, above the typical $7.5\text{--}8.4$ of seawater, developed

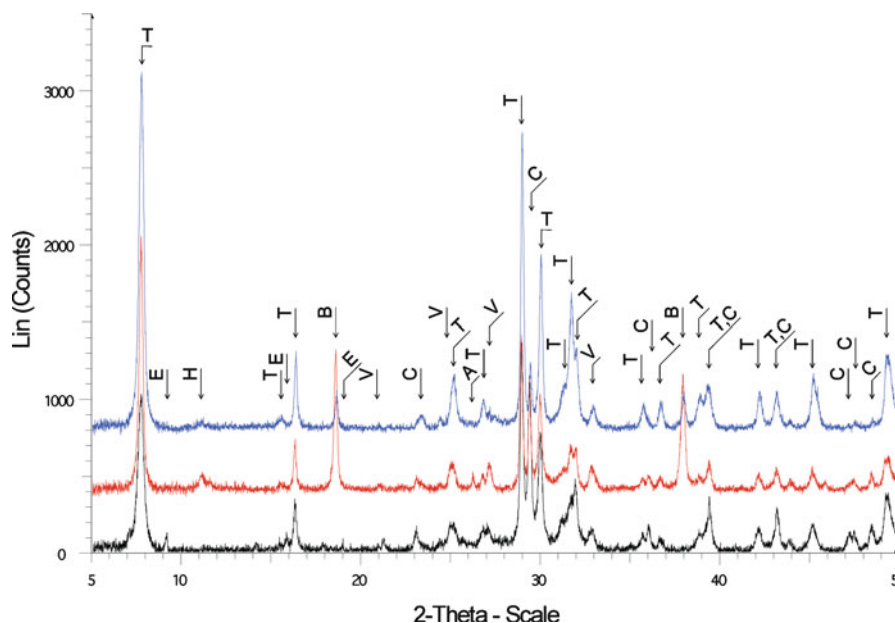


Fig. 15 X-ray diffractograms of tobermorite in relict lime clasts (Table 2) (Top) Portus Claudius dx09-077, (Middle) Portus Neronis dx11-074, (Bottom) Baiae, Portus Iulius dx04-05. *T*-11 Å tobermorite, *E* ettringite, *H* hydrocalumite, *B* brucite, *V* vaterite, *A* aragonite, *C* calcite

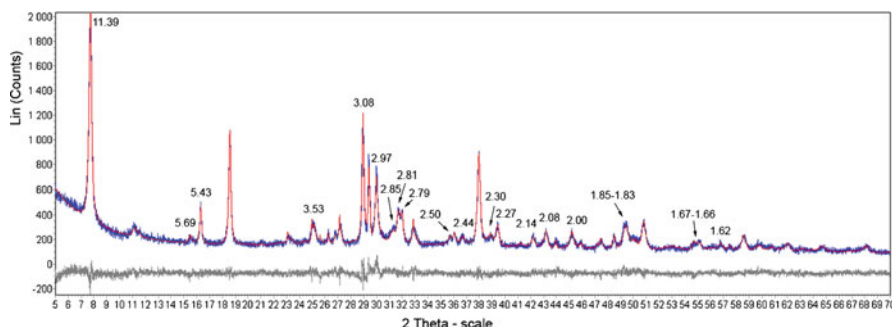


Fig. 16 Rietveld whole profile fitting of Portus Neronis specimen dx11-074, tobermorite *d* values in Å, Upper curves: measured polyphase diffractogram and results of fitting to orthorhombic 11 Å tobermorite [21], Lower curve: difference between the diffractogram and calculated curve

when hydrolysis of basalt glass formed smectite [22–25]. Phillipsite crystallized in basaltic glass vesicles in variable amounts. In saline lakes, silica-rich rhyolite and silica-poor trachytic volcanic ash sediments alter over a few hundred to a few thousand years, to form phillipsite at pH ~9.1–10 [23, 25]. Their Si:Al and Na:K vary, reflecting the composition of dissolving glass and saline lake brines, and their silica and aluminum activities [23–25].

Pozzolanic reaction is the sum of dissolution and topochemical reactions at particle surfaces at high pH, ≥ 12.7 , and the subsequent precipitation of cements [13]. The perimetral dissolution of the lime and vitric tuff clasts (Figs. 4, 7, 9), and their gel-like, silica-rich CASH rinds, now partially altered to microcrystalline calcium carbonate (Fig. 12b, c), record this process. The maximal amount of $\text{Ca}(\text{OH})_2$ that the volcanic pozzolan could combine was evidently not as great as the total lime in the ancient system. Many hydrated lime clasts were only partially dissolved; yet, after 5 years curing of the Brindisi experimental mortar, portlandite persists only in the coarsest lime particles (Table 1). In the ancient mortars, the release of SiO_2 and $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ into solution by pozzolanic processes [9, 11] may have reacted with the portlandite at elevated pH to form CASH and, eventually, 11 Å tobermorite (Figs. 4, 5, 6, 7, 8, and 9) [6, 35]. The tobermorites have some aluminum substitution, common in most cement hydration systems [28], but this does not seem to affect the lattice parameters. Pozzolanic reactions in tuff clasts produced amorphous KMFCASH (Fig. 7a, b, d), and some tobermorite, as well.

The strong bonding of lime and the lack of free $\text{Ca}(\text{OH})_2$, would have had a favorable effect on concrete durability [10–14]. The lime leaching rate would have been very low, so there was little apparent increase in porosity, which facilitates penetration of aggressive ions and erosion in modern portland cement concretes [6–10]. Because there was little $\text{Ca}(\text{OH})_2$ to react with seawater salts – NaCl , CO_3^{2-} , SO_4^{2-} , Mg^{2+} – gypsum and ettringite did not apparently form quantities large enough to produce dangerous expansions [9–14]. Instead, ettringite seems to occur in microstructures along the interfacial zones of relict lime clasts (Figs. 9, 10), in isolated voids (Fig. 11), or adjacent to vitric tuff clasts (Figs. 6, 7, 8) [6]. If, at $\text{pH} > 12$, the high solubility of aluminum caused it to preferentially migrate to voids farther from pozzolan grains [11, 35], precipitation of chloroaluminate (Figs. 4, 5, 6), perhaps as Friedel's salt [40], and sulphoaluminate would have been favored in these discrete microstructures. Phillipsite may be associated with dissolution of alkali-rich volcanic glass [15, 16, 22–24] at lower pH, 9.1–10, and eventual precipitation in relict pumice glass and voids (Figs. 12c, d, 13) [6].

Wollastonite (CaSiO_3) (Table 1) may reflect lime that was over-calcined at $> 848^\circ\text{C}$. Indeed, pseudo-calcite indicative of dead-burned lime occurs in both the Portus Claudius and Portus Cosa mortars. If the lime was calcined from the limestone bedrock of the Appennines at Monte Soratte near Rome, then it is ~95 wt.% CaO [30]. However, the lithologic origins of the limestones are, as yet, unknown and Roman builders' methods for slaking the lime and hydrating the wet mortar mix remain unclear. The textures of some relict lime clasts suggest that they were emplaced as quicklime particles that hydrated *in situ* (Fig. 12a, b, c), but others may derive from previously slaked and matured lime (Fig. 12d). The elevated temperatures often associated with tobermorite crystallization remain enigmatic. Significantly, Bacoli tuff-lime pastes hydrated in distilled water at ambient temperatures formed crinkly foil tobermorite after 5 years curing [41].

Modern, low permeability concretes generally show good durability in the marine environment, if steel reinforcements remain free of corrosion and expansion from chlorine attack [10–12]. Deterioration occurs when permeability is high, due to inadequate

initial consolidation or subsequent microcracking, for example. Chemical attack then increases the porosity of the cement paste, reduces mechanical strength, and encourages erosion and loss of constituents [10–14]. In submerged structures, surficial CO_2 and magnesium ion attack can produce insoluble reaction products – aragonite, brucite, and ettringite – that reduce permeability and seawater ingress [10]. Although chlorine can penetrate more deeply into the concrete, its chemical interaction with aluminate and ferric phases to form stable Friedel’s salt ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$) can beneficially influence durability by slowing the movement of chlorine ions towards steel reinforcements [10–13, 40]. Concrete mixtures with pozzolanic supplements, such as metakaolin, silica fume, and fly ash, reduce calcium hydroxide and produce dense, stable C-S-H. They limit the formation of abundant gypsum and ettringite and, thus, related expansions and cracking in the interior of structures [10–14]. *Pulvis Puteolanus* pozzolan has similar aluminate and ferric components. Its vitric and zeolitic pozzolanic constituents may be associated with the sequestration of chlorine and sulphate ions in crystalline microstructures (Figs. 7, 8, 9, 10, and 11), and the preservation of the cohesiveness of the ancient unreinforced concretes even in intertidal and splash zones [1], which are most vulnerable to attack [10–12]. Roman technologies for maritime concrete constructions may have applications for enhancing modern concrete durability in the marine environment.

9 Ancient Technologies: Raw Materials and Installation of Roman Maritime Concretes

In *De architectura*, Vitruvius emphasizes that the pozzolanic aggregate of mortars in marine concretes should come from the Bay of Naples and, more specifically, from the area around Baiae with *pulvis Puteolanus* deposits.

There is also a variety of powder (*pulvis*) which naturally effects an admirable result. It originates (*nascitur*) in the Baiae region and in the territory of the municipalities around Mount Vesuvius. When mixed with lime (*calx*) and rubble (*caementa*), it not only furnishes stability in building, but also, when a pier is erected in the sea the [*pulvis*, *calx*, and *caementa*] become solid underwater. (*De arch.* 2.6.1)

In his *Questions about Nature (Quaestiones Naturales)*, the first century CE philosopher Seneca mentions *pulvis* from Puteoli in the context of calcareous waters that naturally cement sedimentary deposits.

The water [of the Hebrus River] is adulterated and throws a sediment (*limus*) of such a nature that it cements and hardens objects. In just the same manner that the powdery earth of Puteoli (*Puteolanus pulvis*) becomes rock if it touches water, so by contrast, if this water touches something solid it clings to it and forms concretions. (*QN* 3.20.3)

There is a similar comment in Pliny’s *Natural History*:

But other creations belong to the Earth itself. For who could marvel enough that on the hills of Puteoli there exists a dust (*pulvis*)—so named because it is the most insignificant part of the Earth—that, as soon as it comes into contact with the

waves of the sea and is submerged, becomes a single stone mass, impregnable to the waves and every day stronger, especially if mixed with stones quarried at Cumae. (*HN* 35.166)

Seneca and Pliny undoubtedly knew that *pulvis* had to be mixed with lime to make a coherent mortar, so they may be glossing over the full pozzolanic formula to make a rhetorical point. On the other hand, these observant natural scientists may be referring to natural concretes, or volcanic tuffs, that form through lithification of ash during alteration by ground and surface waters [16, 24] or, perhaps, even to the indurated ash deposits that occur in seawater and seacliffs along the Bay of Naples, as at Procida and the Parco Virgiliano at Posillipo, for example. Late third century BCE builders or engineers may have noticed this phenomenon and experimented with substitution of *pulvis* for beach or river sands in mortars.

Early experimentation with mortars for maritime construction could have very well taken place at Puteoli, which in the third and second centuries BCE was the only important port in the vicinity of the *pulvis* deposits. Until the completion of the Claudian and Trajanic harbours at Portus (Fig. 1), Puteoli served as the major harbour for the city of Rome, 200 km away, particularly for grain imports [42]. In the early second century BCE, a long breakwater composed of large, closely spaced concrete piers (*pilae*) connected by low concrete vaults (Fig. 3) was constructed to accommodate the growing sea trade serving Rome. In early first century CE Strabo praised the natural suitability of the local “sand-ash” at Puteoli for the construction of concrete breakwaters.

Puteoli has become a very great emporium, since it has an artificially constructed harbour, something made possible by the natural qualities of the local sand (*ámmos*), which is well suited to the lime and takes a firm set and solidity. Therefore, by mixing the sand-ash (*ammokonía*) with the lime, they can run moles out into the sea and in this way make the exposed shore into a protected bay, so that the biggest cargo ships can anchor there safely. (*Geography* 5.4.6)

In second century CE, Dio Cassius also described the properties of the dust (*kónis*) used at Baiae harbour (*History* 48.51.3–4), built by Agrippa in 37 BCE [19].

Lime was the most expensive ingredient in a concrete mix [20]. Pliny (*HN* 36.176) states that skimping on lime in a mortar mix was the main reason for the collapse of buildings in Rome. Vitruvius emphasizes the need for selectivity (*De arch.* 2.5.1; cf. Pliny *HN* 36.174): “...one must be careful that, in regard to lime (*calx*), it is burned from white rock, whether [hard] or [softer] limestone (*silex*). The lime from close-grained, harder stone will be the most useful in structural forms, while that made from porous stone will be best in plaster.” He discusses the calcining of limestone (*De arch.* 2.5.2–3); explicitly states that lime should be slaked before it is added to the mortar mix (*De arch.* 2.5.1); and describes the exothermic reaction produced by hydration of quicklime (*De arch.* 2.5.3). Pliny (*HN* 36.176), however, refers to “old building laws” requiring the ageing of *intrita*, which in context should be slaked lime putty, for 3 years prior to use.

Vitruvius provides the only extant description of how Roman builders constructed concrete structures in the sea, including the method of placement of pozzolanic mortars and coarse aggregate in wooden formwork [1, 4, 6, 17, 18].

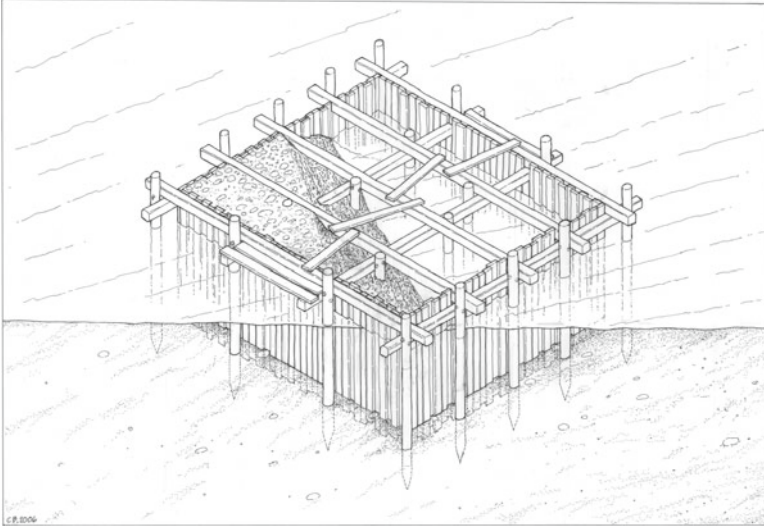


Fig. 17 A inundated timber form, constructed *in situ* on the sea floor, based on Vitruvius' description [*De arch.* 5.12.3], and underwater investigations of Roman maritime structures [17]

If, however, we have no natural harbour situation suitable for protecting ships from storms, we must proceed as follows. If there is an anchorage on one side and no river mouth interferes, then a mole composed of concrete structures (*structurae*) or rubble mounds (*aggeres*) is to be built on the other side and the harbour enclosure constructed in this manner. Those concrete structures that are to be in the water must be made in the following fashion. In the designated spot, formwork (*arcae*) enclosed by stout posts and tie beams (*stipitibus robusteis et catenis inclusae*) must be let down into the water and fixed firmly in position. Then the area within it at the bottom, below the water, must be levelled and cleared out, [working] from a platform of small crossbeams (*ex transtris?*). There, the coarse aggregate (*caementa*) and the mortar (*materia*) from the trough mixed as described above (p. 7) must be heaped up (*caementis ex mortario materia mixta...ibi congerendum*), until the space left for the concrete within the form has been filled (*De arch.* 5.12.3).

The impressions of timber formwork on concrete structures indicate that builders drove wood piles into the seabed and framed these with horizontal beams (Fig. 17) [18]. Vertical boards, mainly about 25–30 cm wide and 3–8 cm thick, were placed closely together against the beams, with gaps generally less than 2 cm, and pounded into the seafloor. The impressions of horizontal cross beams on Portus Neronis concrete indicate that these were placed about 1 m above the ancient sea level. Continuous runs of concrete in long moles, as at Baiae (Fig. 3), were laid in sections with the end bulkhead of the formwork removed after each casting. The surviving timber planking at several sites suggests that builders left the formwork in place after the concrete had set, perhaps to protect the structure from erosion in its early stages of curing [18]. Ongoing analyses will further clarify Roman methods for

preparing lime, mixing mortars, and hydrating concretes in seawater; engineers' understanding of the mechanisms of pozzolanic reaction and curing; and the effects of these processes on the durability of the seawater structures.

10 How Did Expertise with These Technologies Spread?

Roman engineers had a nuanced understanding and sophisticated knowledge of the geologic materials and preparation of both terrestrial and submarine lime-volcanic ash mortars, based on empirical experience [1–8, 30] as well as stationary and floating forms for placing concretes in marine environments [1–8, 17, 18] How did the technical information for these technologies travel around the Mediterranean? The two enormous breakwaters sheltering the outer basin at Caesarea in Israel, for example, were constructed of about 35,000 m³ of hydraulic concrete in first century BCE. The mortars have *pulvis Puteolanus* shipped 2,000 km from Puteoli, about 24,000 m³ weighing 52,000 ton [3]. It seems likely that Herod requested technical assistance from Rome for this colossal project, probably from his friend Agrippa, who built the Portus Iulius harbour near Puteoli. Agrippa would have sent harbour engineers from Italy, military engineers who reflected the same practical expertise as their contemporary, Vitruvius—himself a retired military engineer—who evidently recommended the use of *pulvis Puteo-lanus*, augmented with local sand, coarse aggregate, and lime [1, 5]. Elaborate single-use barge forms identical to those documented at Caesarea were used in the concrete structures in the Alexandria harbour in first century CE [17, 18]. While the movement of military engineers around the Mediterranean is the most likely explanation for the spread of harbour construction technology, it is also possible that sub-literary manuals incorporating technical information in written and graphic form moved with these engineers, or even independently. Traces of manuals of this type (*commentarii*) have been discerned in the archaeological evidence for military and agricultural equipment, and wooden pumps [19, 43]. They could have also existed for concrete construction in the sea. This could help explain the use of *pulvis Puteolanus* in the concrete of small, out of the way harbours such as Chersonisos on Crete, where imperial involvement was unlikely.

11 Conclusions

Mortars of Roman maritime concretes from the central Italian coast have remarkably consistent cement compositions and microstructures, associated with the dissolution of lime and vitric tuff clasts at high pH, precipitation of gel-like CASH in perimetral rinds, and crystallization of orthorhombic 11 Å tobermorite in clast nuclei. Ettringite and calcium-chloroaluminate precipitated in discrete microstructures and voids. Phillipsite and chabazite crystallized at lower pH, possibly from dissolution of volcanic glass. The diverse microstructures in relict lime clasts,

including *in situ* expansive fracturing in some clasts and homogeneous textures in the residual cores of others, indicate that further analyses are needed to clarify methods for slaking lime, mixing mortars, and hydrating the concretes in seawater. Even so, it is clear that engineers developed extraordinarily effective technologies for the selection and transport of lime and *pulvis Puteolanus* to harbour sites, the preparation of hydraulic mortars, the installation of concrete mixes in forms submerged in seawater, and the distribution of this expertise through the Mediterranean. The mortar cements have analogies to durable natural rock cements that develop in volcanic ash submerged in seawater and saline lakes. They display a striking resistance to chemical dissolution and attack.

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