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Roman concrete and Geopolymers

Geopolymers are really here !

Frédéric Davidovits, Ph. D.

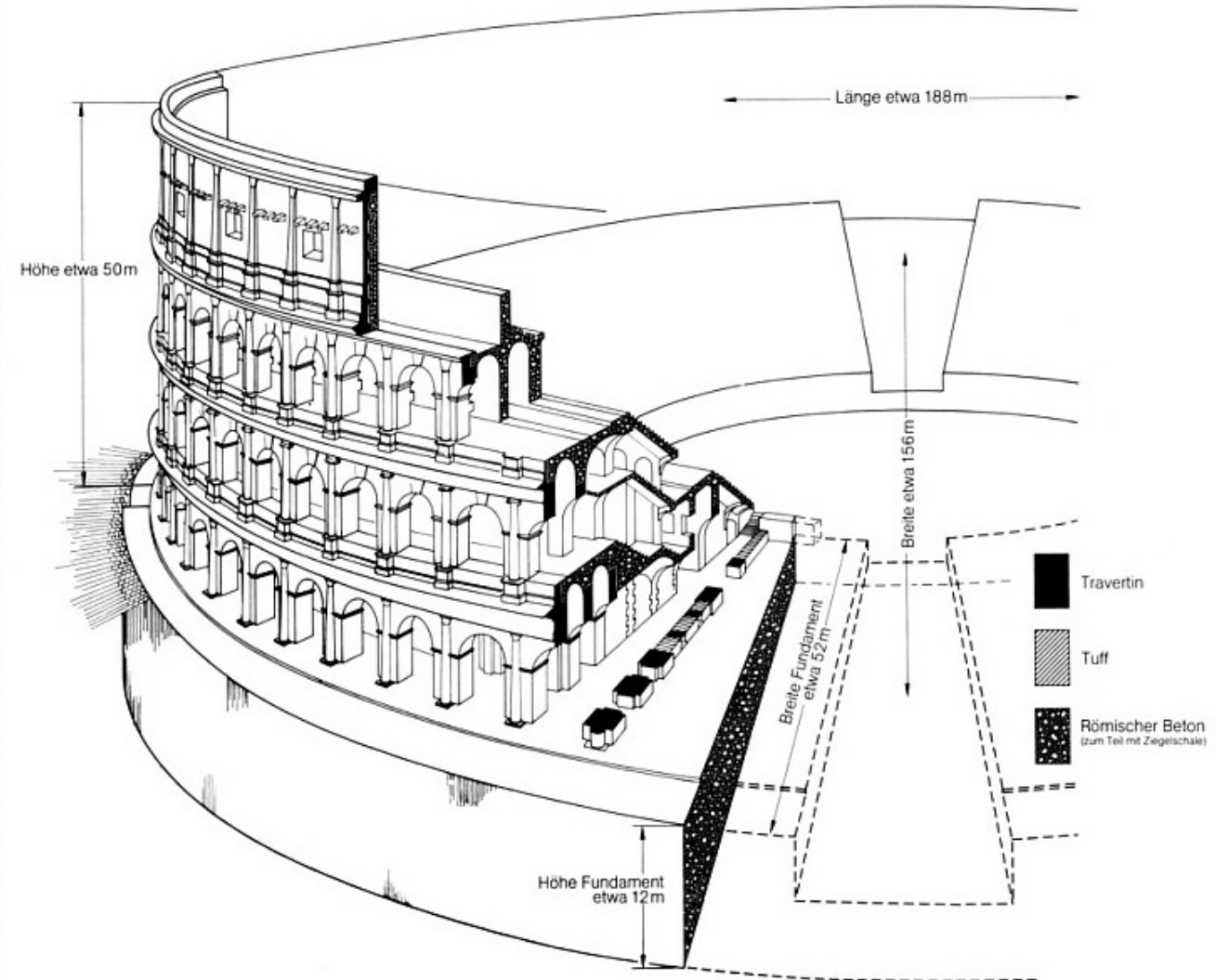
Summary

1. Pier construction, and terrestrial building : Roman Concrete and Vitruvius the Architect.
2. Geopolymer found in ancient Roman concrete !
3. Conclusion and references

Roman Concrete



Roman Pantheon



Colosseo

Roman Concrete : Harbour facilities in Mediterranean sea

- During the Roman period, trade in Mediterranean sea enabled construction of harbour facilities (-70 BC)
- It coincided almost exactly with the wide use of hydraulic concrete
- Example : Caesarea Maritima harbor (23 to 15 BC) for King Herodius, a roman harbor from scratch.
- 53 000 m³ raw materials, 17 500 m³ pozzolana from Napoli (Italy), local limestone from Syria, Egypt, Palestine.
- It took months for the logistics to provide the materials to the field from Italy to Palestine.

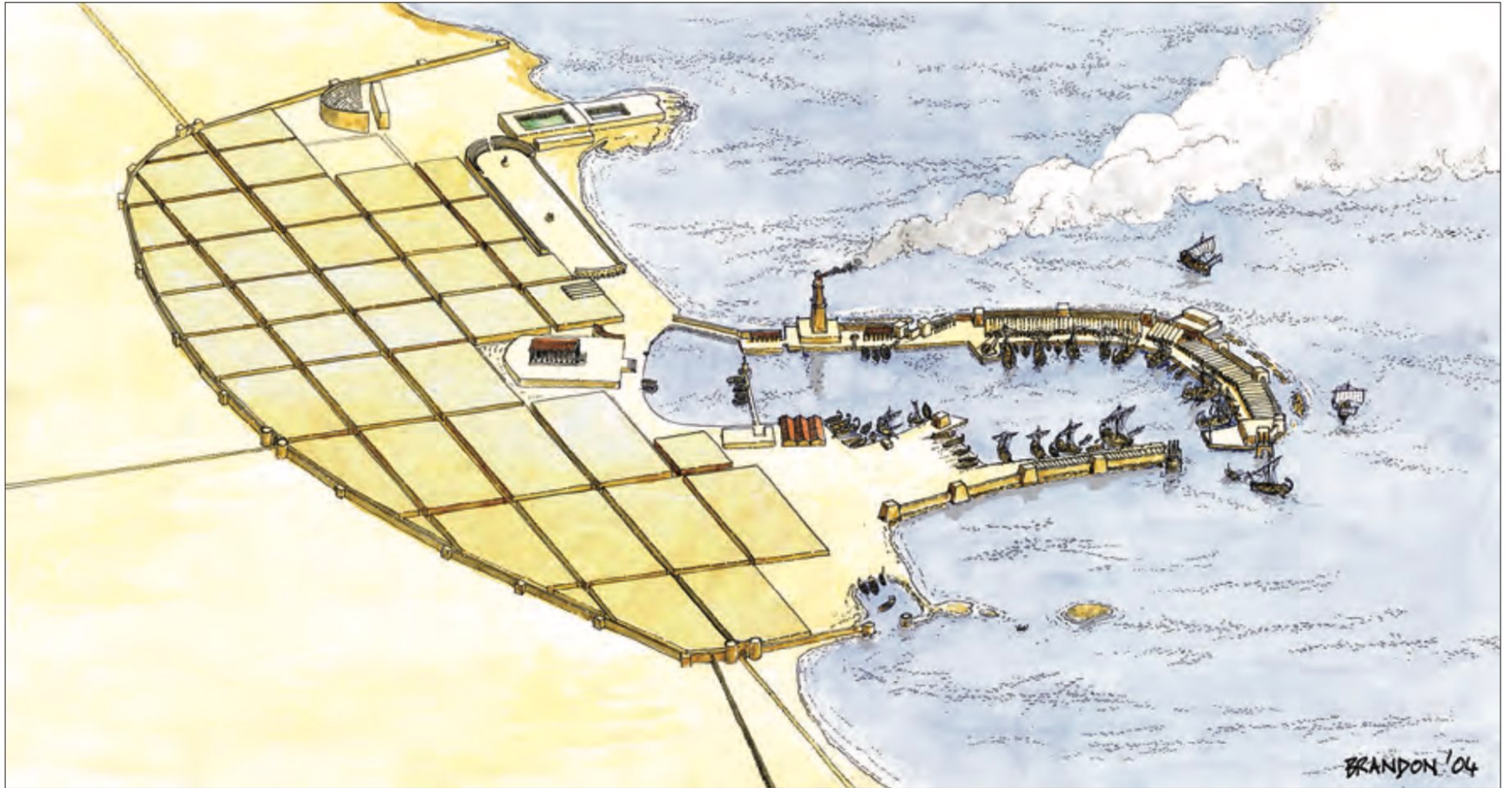
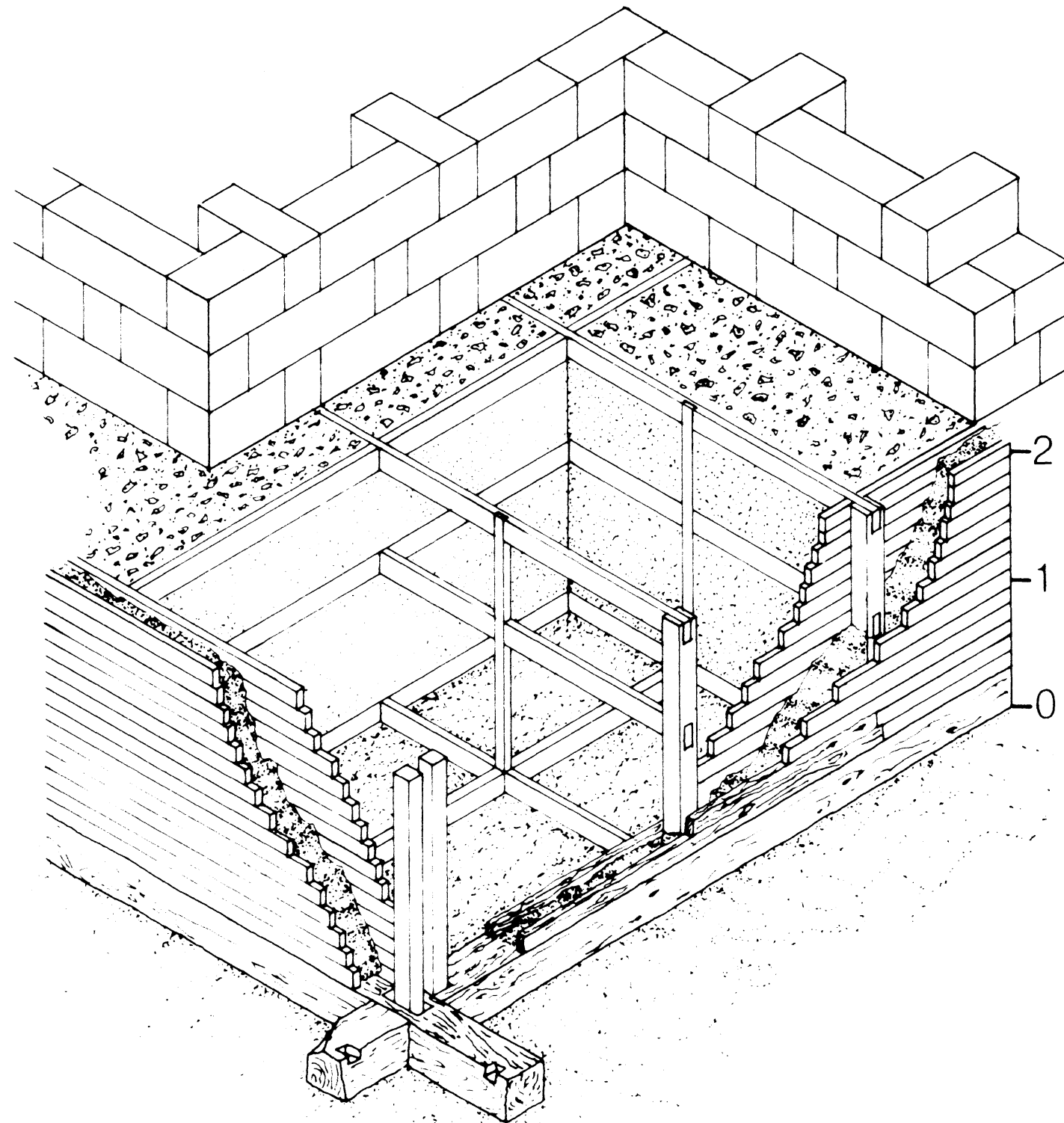


Fig. 4.24. Sebastos, reconstruction of harbour remains (C. J. Brandon).

Caesarea Maritima harbor : Brandon 2021



Dam of « G zone » in *Caesarea Maritima*
(Haifa, Israel); drawing : R. L.Vann (Oleson
1988)

BUILDING FOR ETERNITY

THE HISTORY AND TECHNOLOGY OF ROMAN CONCRETE ENGINEERING IN THE SEA



by

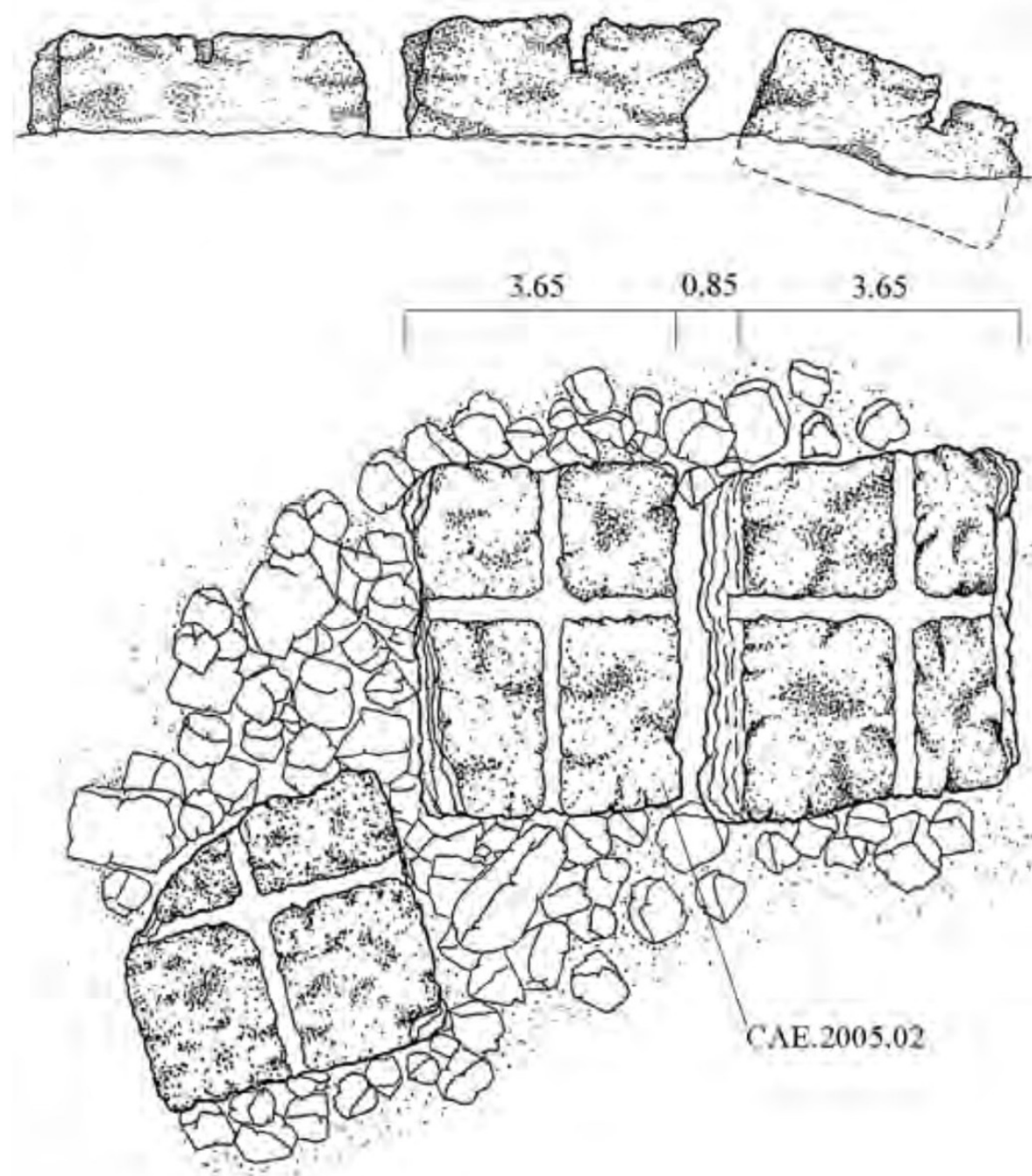
C. J. BRANDON, R. L. HOHLFELDER, M. D. JACKSON AND J. P. OLESON

With contributions by

L. BOTTALICO, S. CRAMER, R. CUCITORE, E. GOTTI, C.R. STERN AND G. VOLA

edited by

J. P. OLESON



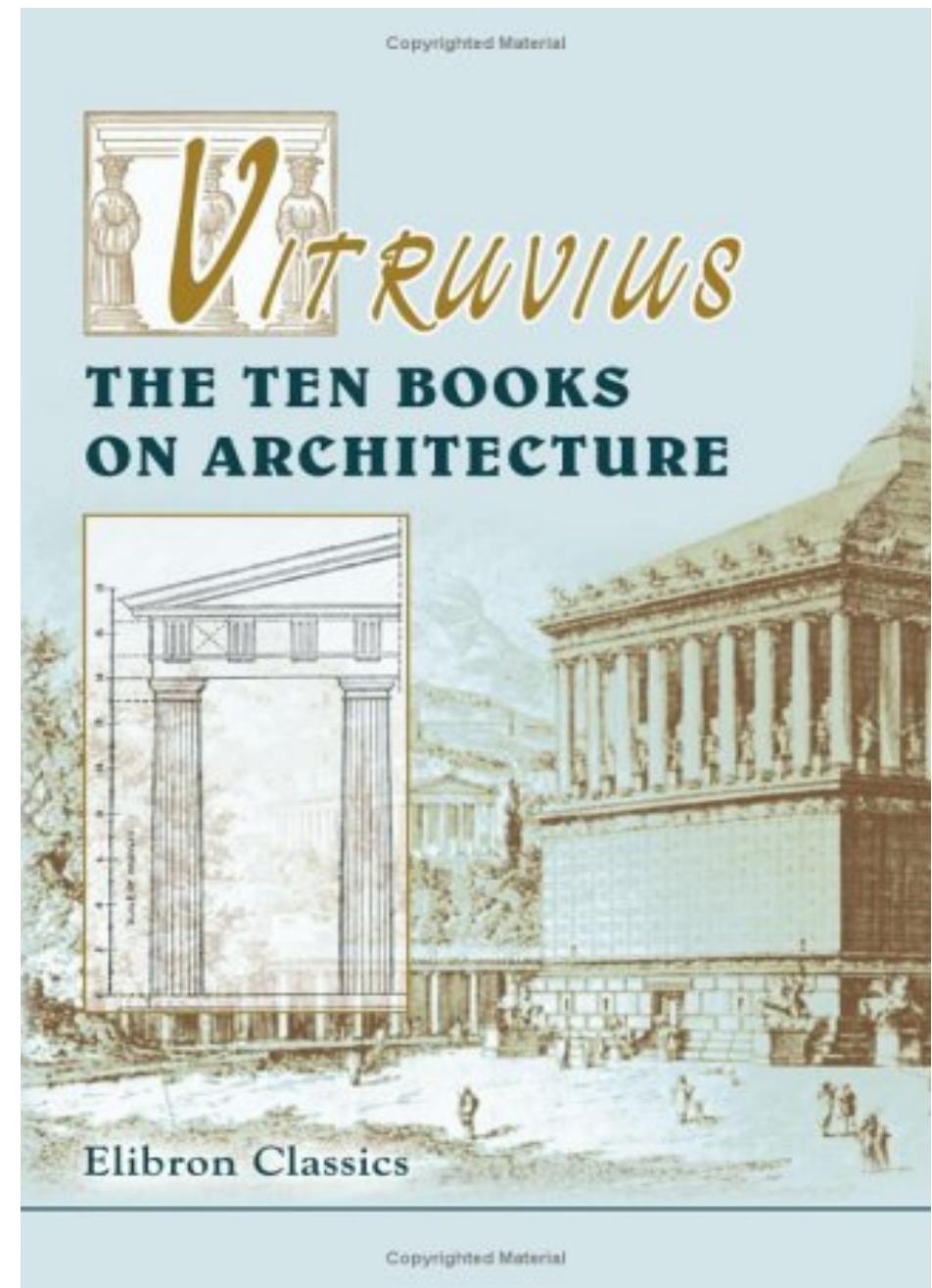
Concrete blocks with wooden planks (Brandon 2021)

Fig. 4.30. Sebastos, drawing of group of blocks from which core CAE.2005.02 was taken (C. J. Brandon after P. Dessauer and L. Reynafarje).

Vitruvius

The one and only !

- Roman architect, author of *De architectura* (25 B.C.).
- The only complete architectural treaty to survive from classical antiquity
- His treaty has recipes for making cement and concrete



Latin keywords of Roman concrete according to Vitruvius

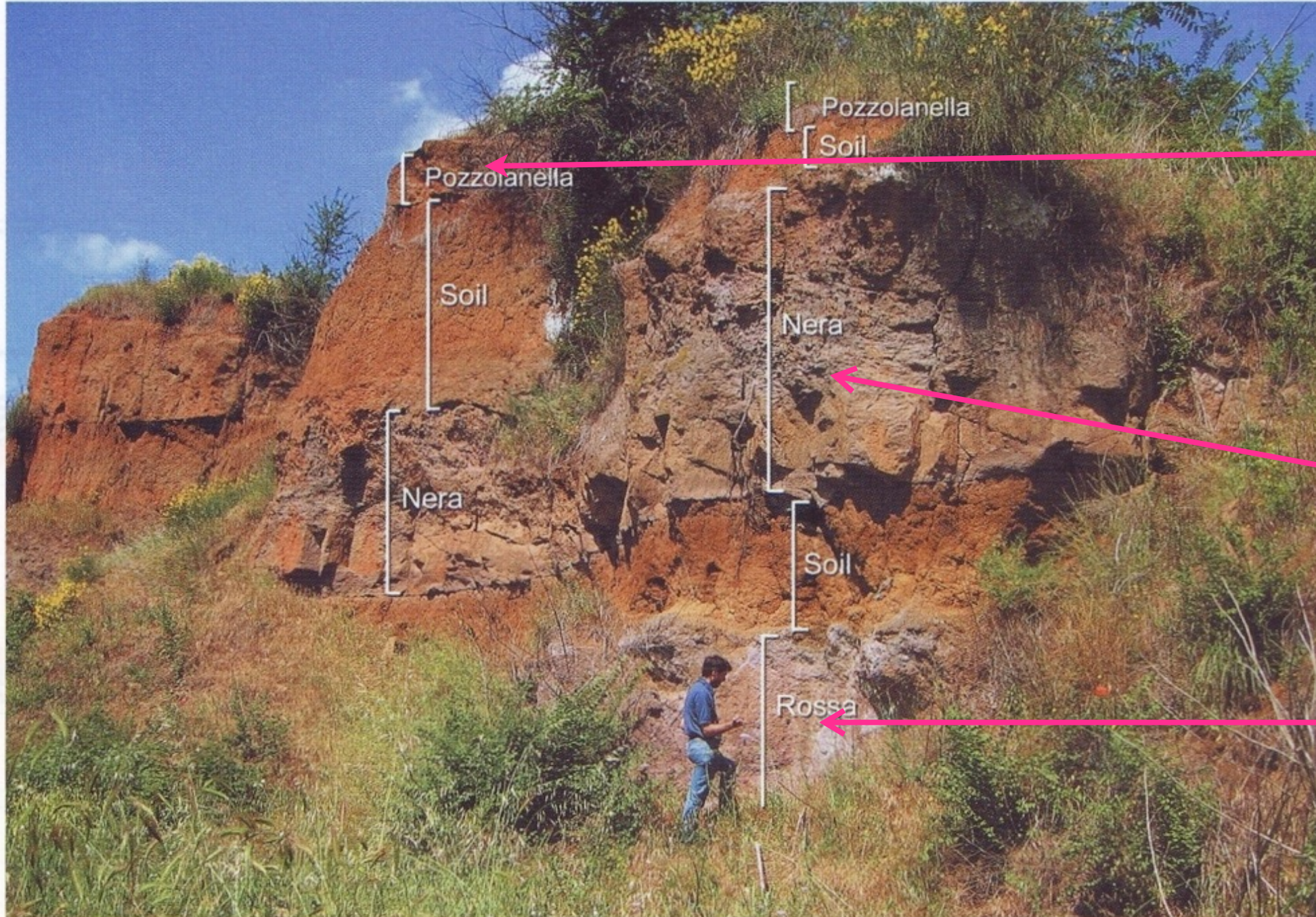
- Lime, hydraulic lime: *calx*
- Sand for concrete : *harena fossicia* « volcanic sand »
- Sand for coatings: *harena fluviatica* « river sand »
- *Caementum* « rubble »,
- *Testa* « crushed metakaolin (kaolinitic clay, calcined at 750 °C) »
- *Pulvis* « pozzolana » for marine concrete

Roman marine concrete

- Concrete which sets underwater without CO_2 = geopolymer
- Lime (*calx*) + « pozzolana »
- Pozzolana:
 1. *pulvis (puteolanus)* = « powder of Puozzoli »
 2. *harena fossicia* = « volcanic sand »
 3. *testa* = crushed metakaolin



Villa Poppea in Oplontis, Napoly :
pozzolana



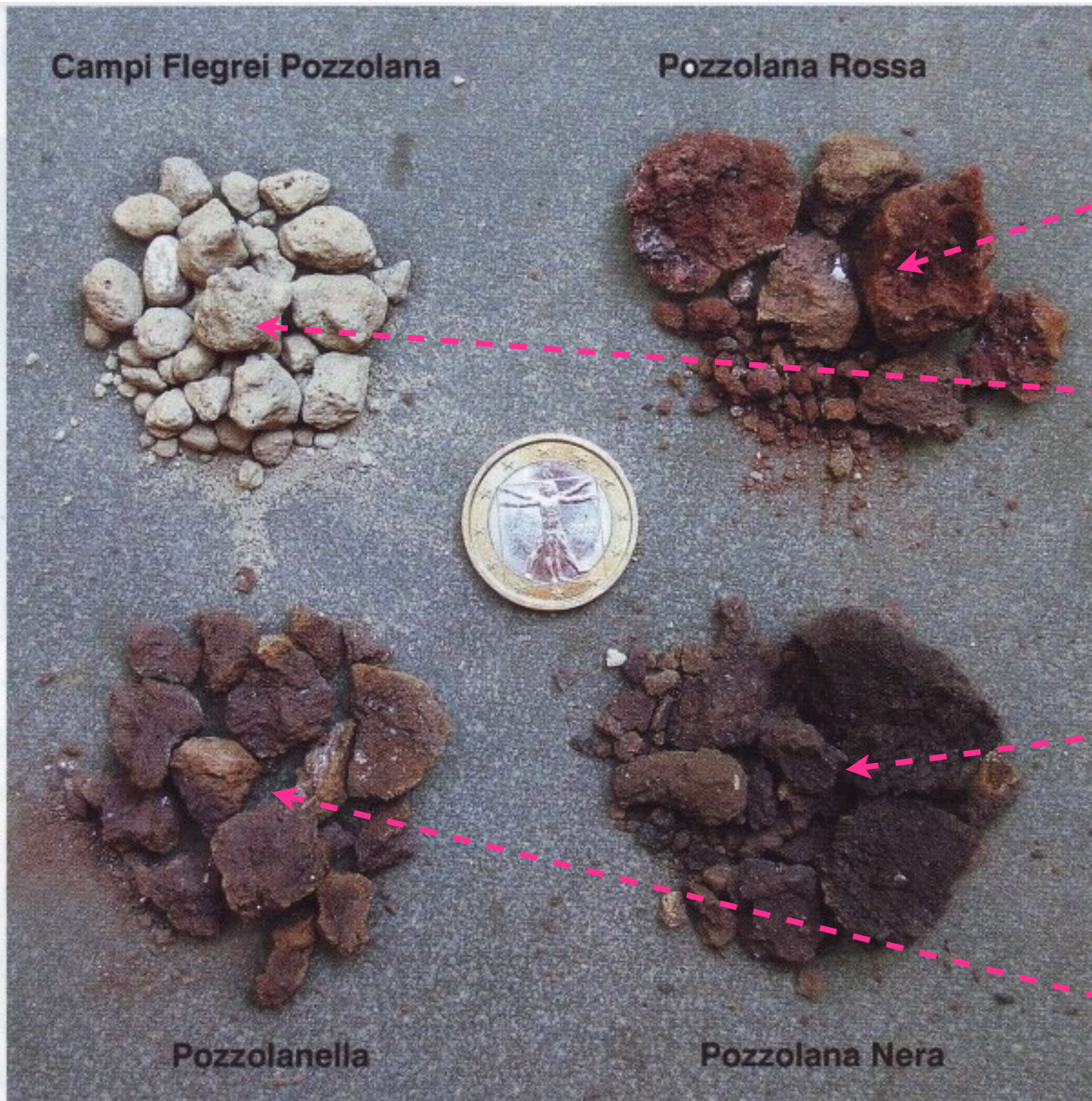
pozzolanella
(grayish,
1360-1670 kg/m³)

pozzolana nera
(black, 1340 kg/m³)

pozzolana rossa
(red, 1600-1900
kg/m³)

PLATE IV. Section through an abandoned pozzolana quarry on Via Nesazio (near Largo Martiri delle Fosse Ardeatine) showing the stratigraphy of the three different types of Colli Albani pozzolana.

Volcanic quarry (Lancaster 2005)



Harena fossicia rubra:
reddish volcanic sand

Pulvis « true pozzolana »

Harena fossicia nigra:
reddish volcanic sand

Harena fossicia cana:
grayish volcanic sand

PLATE III. Four types of pozzolana showing the difference in color between them. The Campi Flegreian pozzolana (*pulvis puteolanus*) at upper left is easily distinguishable from the other pozzolanas quarried near Rome. (Euro = 2.3-cm dia)

After Lancaster 2005

Vitruvian theory of 4 elements explains the “hot mixing”

- “Hot mixing” = use of quicklime to accelerate the setting time of concrete
- Each substance in Nature has four elements: *terra* "earth", *aqua* "water", *aer* "air" and *ignis* "fire »
- Their proportions determine their physical properties (hardness, softness, etc.)

Vitruvian theory of 4 elements

- The volcanic/artificial fire destroys the coherence of any stone,
- Lime is the result of expelled air and water from limestone (Vitr. II, 5) whereas roman lava containing more earth and water than air and fire, withstand better fire and weathering (Vitr. II, 7, 2).

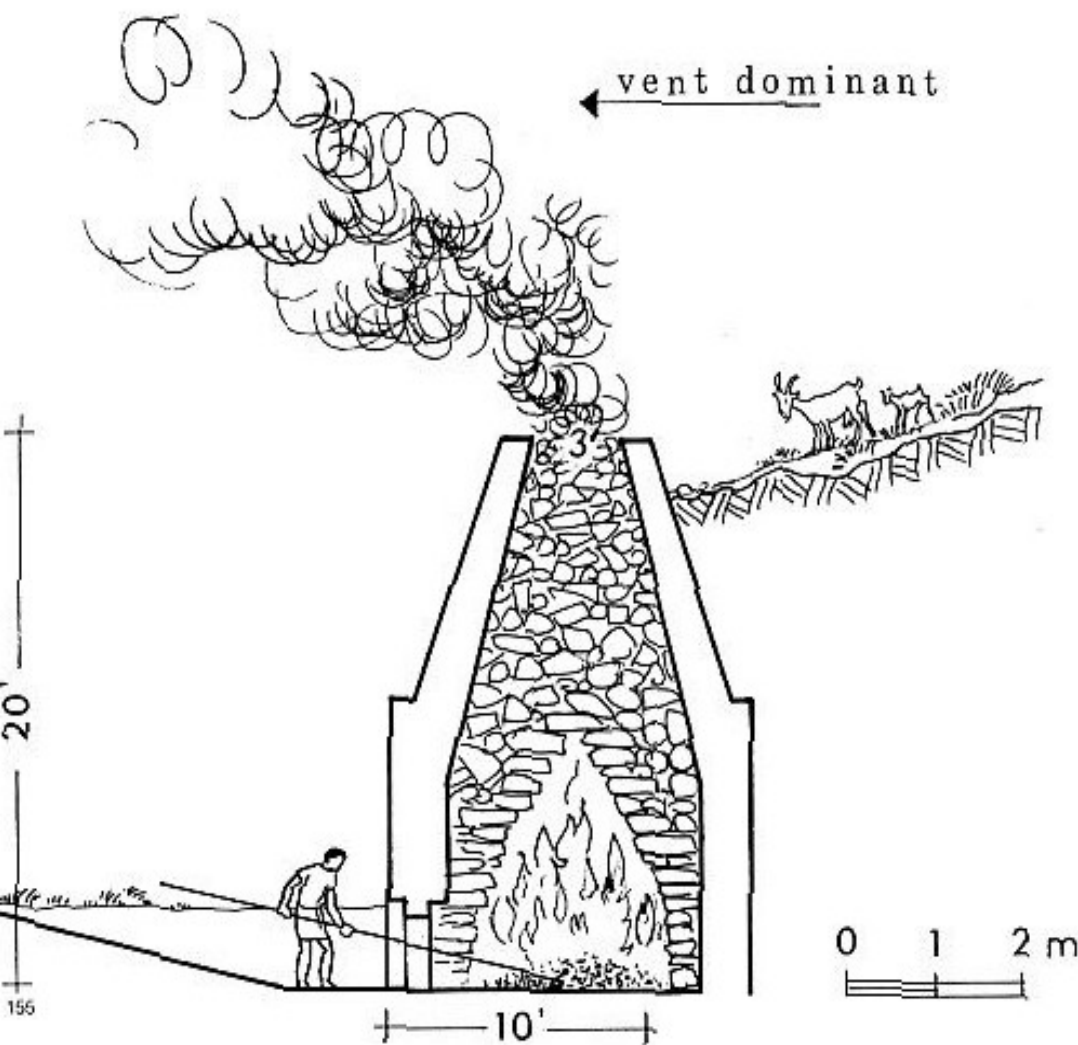
Vitruvian theory of 4 elements

For Vitruvius, any substance (stone, mineral, metal) which has been fired in a kiln such as lime or has undergone the volcanic fire gets new physical or chemical properties for architecture and engineering (Davidovits 2003; Davidovits 2007).

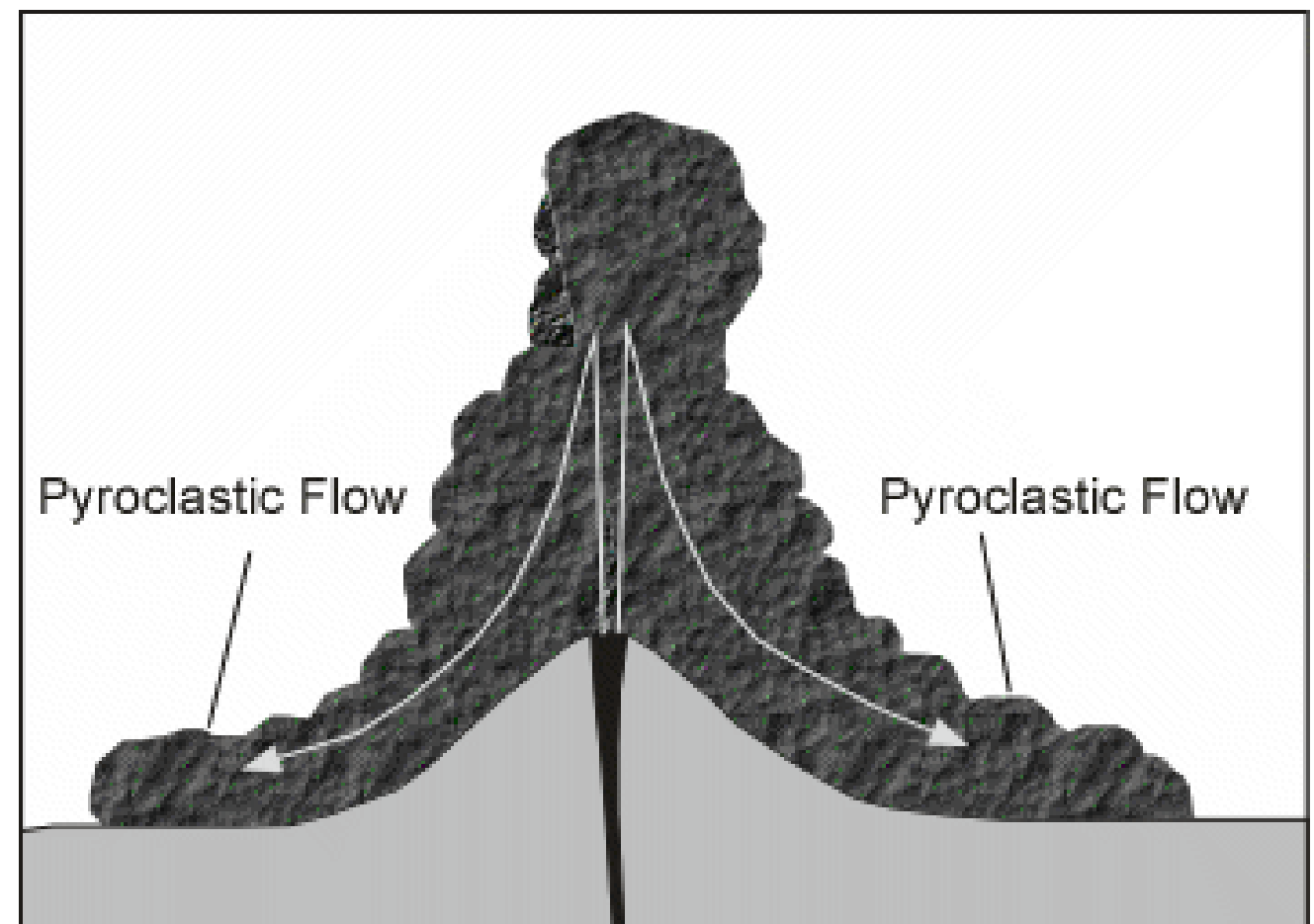
Kiln = volcanism

It enables “hot mixing” for concrete !

How does materials gain their physical properties ?



=



Limekiln = Volcano

List of natural material for mortar/concrete

- Pozzolan: *cinis* “ash”, *terra exusta* “burnt out earth”
- Pumice of Pompeii: *genus lapidis excoctum* “a kind of calcined rock”
- Carboncle: *materia excocta* “calcined rocky material”
- Volcanic sand: *harena fossicia* “extracted volcanic sand”

List of artificial materials for mortar/concrete

- *Calx* « lime »
- *Testa* « calcined kaolinitic clay at 750 °C, metakaolin »
- All those materials have been charred by natural (volcanism) or artificial fire (kiln)

Hot mixing

- In 2023, Seymour et *alii* published an article in « Science advances » in which they showed that hot mixing was used in Roman concrete.
- Lime clasts (calcium silicate) are the source of calcium when the concrete shrinks.
- The calcium migrate through the binder and it allows the concrete to heal itself.

Hot mixing: Mechanistic insights into the durability of ancient Roman concrete

LINDA M. SEYMOUR , JANILLE MARAGH , PAOLO SABATINI, MICHEL DI TOMMASO , [...], AND ADMIR MASIC 

+1 authors

[Authors Info & Affiliations](#)

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Abstract

Ancient Roman concretes have survived millennia, but mechanistic insights into their durability remain an enigma. Here, we use a multiscale correlative elemental and chemical mapping approach to investigating relict lime clasts, a ubiquitous and conspicuous mineral component associated with ancient Roman mortars. Together, these analyses provide new insights into mortar preparation methodologies and provide evidence that the Romans employed hot mixing, using quicklime in conjunction with, or instead of, slaked lime, to create an environment where high surface area aggregate-scale lime clasts are retained within the mortar matrix. Inspired by these findings, we propose that these macroscopic inclusions might serve as critical sources of reactive calcium for long-term pore and crack-filling or post-pozzolanic reactivity within the cementitious constructs. The subsequent development and testing of modern lime clast-containing cementitious mixtures demonstrate their self-healing potential, thus paving the way for the development of more durable, resilient, and sustainable concrete formulations.



Vitruvius' description of « hot mixing »

- Vitruvius (5, 12, 2-3) is describing the « hot mixing » process : adding quicklime to the lime in order to accelerate the setting in the cofferdam while building the pier.
- The workers throw the dry mix consisting of quicklime, pozzolana, aggregates...
- Chemical reactions of slaking lime in the cofferdam: « therefore, when three substances (volcanic tuff, quicklime, pozzolana) formed in like manner by the violence of fire come into one mixture, they suddenly take up water and cohere together, they are quickly hardened by the moisture and made solid, and can be dissolved neither by the waves nor the power of water ».
- Slaking lime by seawater produce the chemical phenomenons described by Vitruvius 2, 6, 1-4.

Quicklime in hydraulic concrete

- This vitruvian concept was discovered in 2005-2007 in Vitruvius text during my Ph. D. redaction.
- The ROMACON team suggested the use of quicklime in their book too (11-15 % of quicklime in weight of the raw materials in dry mix) alongside with traditional slaked lime.
- In 2017, Marie D. Jackson (Univ. of Utah) (Jackson *et alii* 2017): « An adiabatic model of exothermic heat evolved during hydration of lime and production of pozzolanic C-A-S-H binder in a 10 m² by 6 m tall *Baianus Sinus* breakwater in the Bay of Pozzuoli, indicates that elevated temperatures, 65–95 °C, persisted for 2–3 yr. »

Appendix Table 1

Roman texts describing the geologic materials and cementitious processes of marine concrete, translations (Oleson 2014)

	English Translation	Interpretation
Vitruvius 30–22 BCE <i>de Architectura</i> 2.6.1	There is a kind of powdery earth (<i>pulvis</i>) that by its nature produces wonderful results. It occurs in the neighborhood of Baiae and the territory of the municipalities around Mount Vesuvius. This material, when mixed with lime and rubble (<i>calce et caemento</i>) not only furnishes strength to other buildings, but also, when breakwaters (<i>moles</i>) are built in the sea, they set underwater... <u>Thus, when these three substances (pumiceous ash (<i>pulvis</i>), lime (<i>calx</i>), and tuff (<i>tofus</i>)) formed in a similar manner by the strength of fire are brought together in one mixture, and suddenly they are put into contact with [sea-] water, they cohere into a single mass, quickly solidifying, hardened by the moisture, and neither the effect of the waves nor the effect of water can dissolve them.</u>	Hydration of lime and pumiceous volcanic ash from the Campi Flegrei (and Vesuvius) volcanic districts (Fig. 2) with seawater created pozzolanic reactions that produce cementitious hydrates, mainly C-A-S-H, and rapid solidification of massive concrete structures that resisted the erosive action of seawater and the force of impact of storm waves in the marine environment.
Vitruvius 30–22 BCE <i>de Architectura</i> 2.6.4	Therefore, when dissimilar and incompatible materials [lime (<i>calx</i>), pumiceous ash (<i>pulvis</i>), and tuff (<i>tofus</i>)] are taken and mixed in a moist environment the <u>urgent need of moisture suddenly satiated by [sea-] water seethes with the latent heat in these substances and causes them to gather into a unified mass and gain solidity quickly.</u>	Exothermic heat evolved from the production of C-A-S-H binder through pozzolanic reaction of lime, pumiceous ash, and seawater led to rapid solidification of the marine concrete.

Appendix table 1 (Jackson *et alii* 2017)

An unfinished Pompeian construction reveals ancient Roman building techniques

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 Check for updates

Ellie Vaserman¹✉, James C. Weaver¹, Claire Hayhoe²,
Celestino Grifa^{3,4}, Roberto Scalesse⁵, Valeria Amore⁶,
Gennaro Iovino⁶, Gabriel Zuchtriegel⁶ & Admir Masi¹

Recent excavations at Pompeii's Regio IX have uncovered an unfinished construction site, offering insights into Roman building practices before the eruption of Mount Vesuvius in 79 CE. Microstructural analysis of materials collected from previously completed construction, and adjacent dry, raw material piles reveals that quicklime was pre-mixed with dry pozzolan before the formation of Roman concrete. This construction method results in an exothermic reaction within the mortar clasts, key contributors to the self-healing and pozzolanic hydraulic mortars. The analysis of reaction rims and aggregates demonstrate aggregate/matrix interfacial remodeling originating from the dissolution of lime clasts diffusing amorphous phases and various polymorphs (including calcite and aragonite). Furthermore, the analysis of masonry materials and tools permits elucidation of the construction workflow, including the steps required to process aggregates (caementa). These findings advance our understanding of Roman construction and long-term material evolution, providing a basis for developing more durable and sustainable building materials inspired by ancient practices.

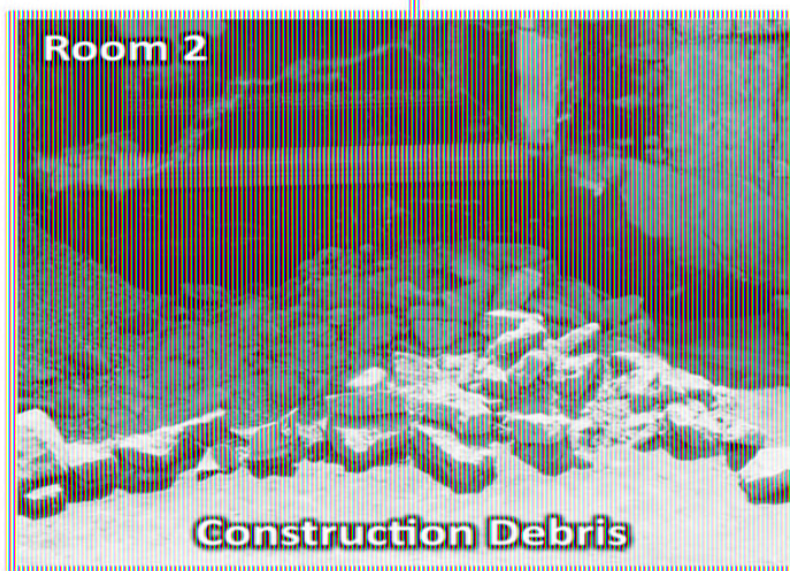
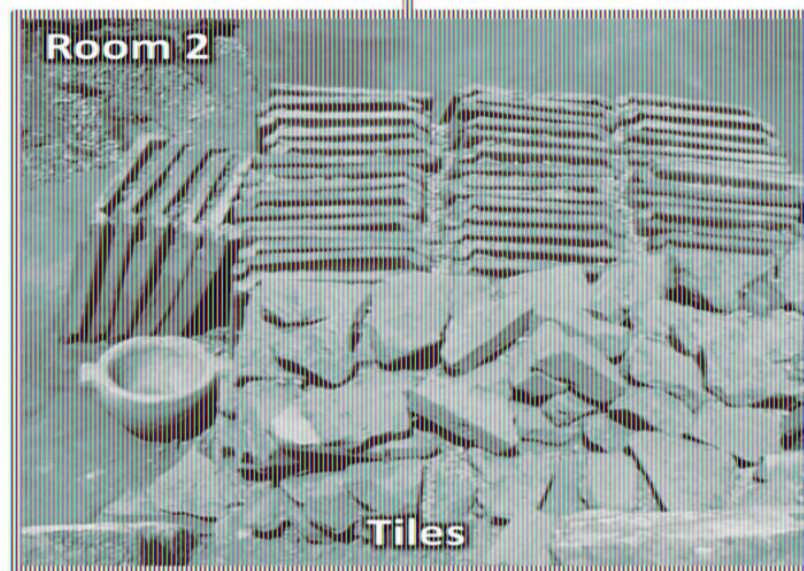
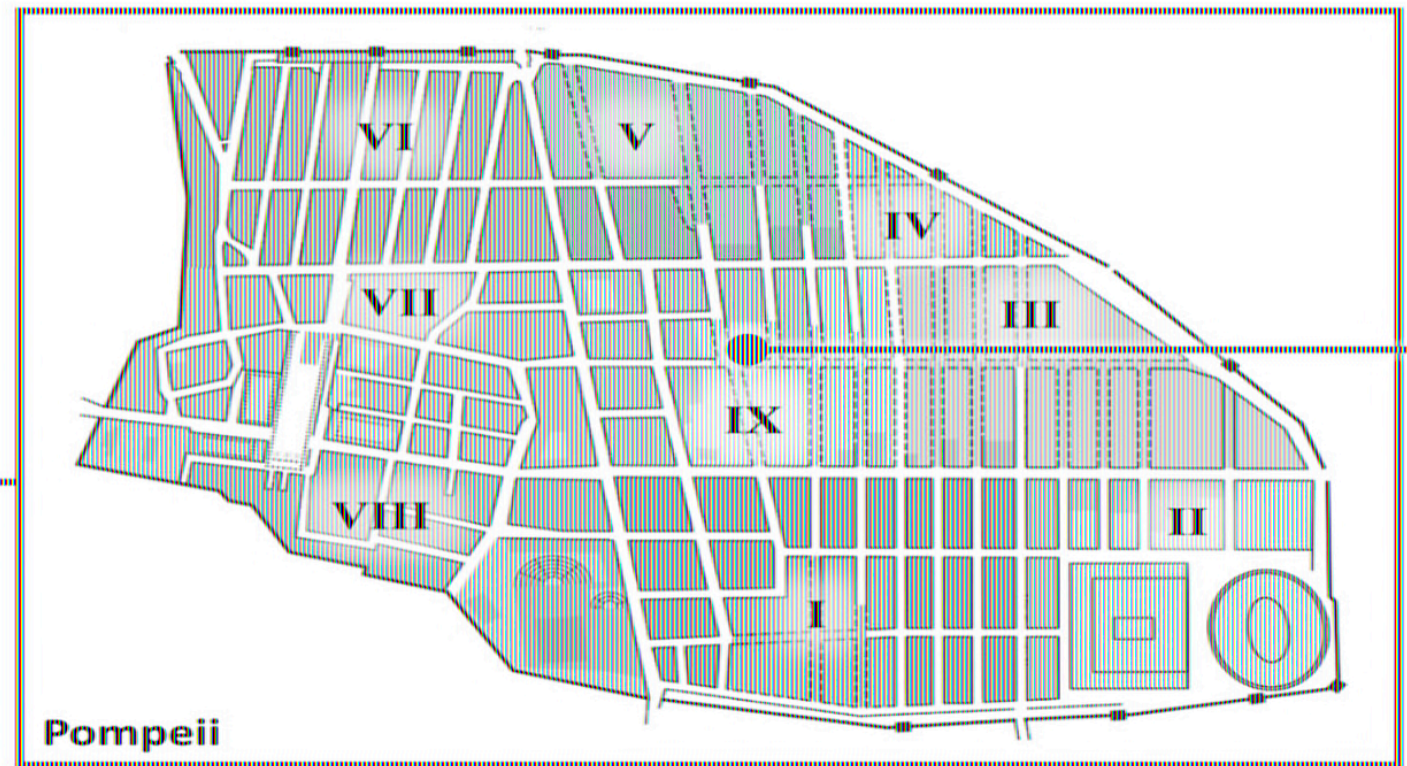


Fig. 1 | Pompeii Archeological Park site map, with *Regio IX* denoted in light blue (upper, middle) and *Domus IX 10, 1* shown in additional detail, with color-coded piles of raw construction materials (right): purple: debris; green: piles of dry pre-mixed materials; blue: piles of tuff blocks. The excavations have revealed numerous accumulations of demolished and stacked building materials

consisting of lava and limestone rubble, ceramics and amphorae, set aside for restoration work on the walls. The two materials were collected for analysis (R numbers, while the numbers of adjacent

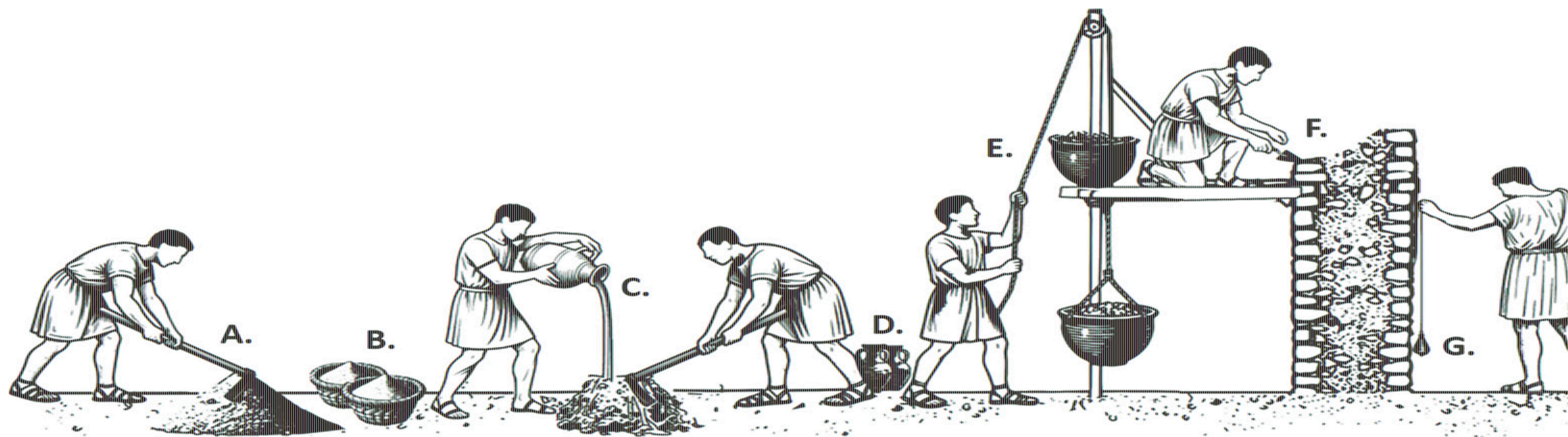
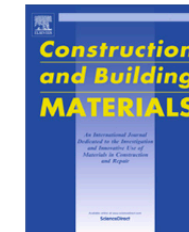


Fig. 7 | Schematic summary of the ancient production of Roman concrete. Each step in the schematic captures a specific part of the preparation and building process, highlighting both the materials and the tools used. **A** Preparing the dry mortar mix: This process begins with a dry, pre-mixed pile of pozzolan and quicklime. **B** Adding *cocciopesto*: To enhance the mortar's water resistance and durability, Romans often added *cocciopesto*, a mix containing ground terracotta or pottery fragments. **C** Hydrating the mortar: The dry mortar mixture is then hydrated, where workers would carefully add water to initiate a chemical reaction with the quicklime. **D** Slaking lime: slaking, or hydration of quicklime to produce slaked lime before being added to the mortar mix, often took place in smaller vessels. This step was not included in the preparation of Roman concrete and was generally used in the preparation of finishing and repairing mortars and fresco

decorations. **E** Transporting mortar in br pottery vessels, served as practical conta were readily available on Roman constru repurposing broken pottery that would c mortar with a trowel: The mortar was the trowel, carefully layering it between *caer* geometric and structural integrity with a workers used a plumb line to verify vertica helped maintain precision during the con stability, especially in tall or expansive str To create aggregate, an essential compon to break larger stones into smaller pieces

Geopolymer in Roman Concrete



Multi-scale imaging, strength and permeability measurements: Understanding the durability of Roman marine concrete

Jackson MacFarlane^{a,*}, Tiziana Vanorio^a, Paulo J.M. Monteiro^b

^aStanford Rock Physics Laboratory, Stanford, CA, USA

^bDepartment of Civil and Environmental Engineering, University of California, Berkeley, United States



HIGHLIGHTS

- Roman marine concrete undergoes ductile creep when tri-axially stressed.
- Creep is identified by coupling triaxial loading and time-lapse tomographic imaging.
- Pervasive fibrous minerals contribute to the low permeability and high ductility.
- The matrix is comprised of both calcium-aluminum-silicate-hydrate and geopolymer.
- Reduced aggregate debonding enhances ductility and preserves matrix permeability.

GRAPHICAL ABSTRACT



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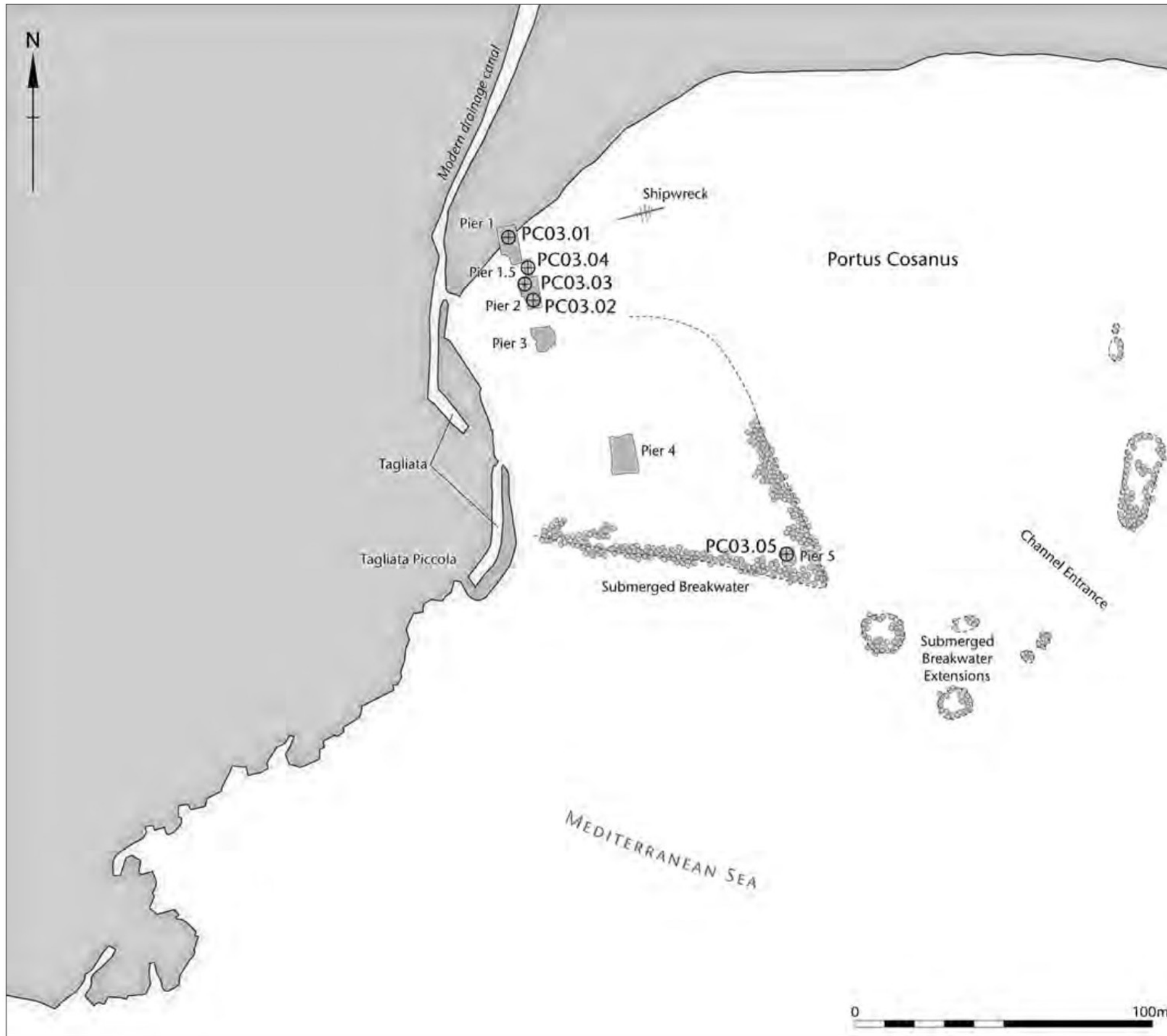
Durability

Permeability

Ductility

ABSTRACT

Roman-era concrete is the iconic embodiment of long-term physicochemical resilience. We investigated the basis of this behavior across scales of observations by coupling time-lapse (4-D) tomographic imaging of macroscopic mechanical stressing with structural microscopy and chemical spectroscopy on Roman marine concrete (RMC) from ancient harbors in Italy and Israel. Stress-strain measurements revealed that RMC creeps and exhibits a ductile deformation mode. The low permeability of concrete samples was linked to mortar-dominated microstructures showing no debonding with the aggregates. Structural and chemical imaging shows the presence of well-developed sulfur-rich, fibrous minerals that are intertwined and embedded in a crossbred matrix having the chemical traits of both a calcium-aluminum-silicate-hydrate and a polymerized alkali-alumino-silicate. This latter likely reflects the ultra-alkaline volcanic nature of the primary source materials. We hypothesize that the fine interweave of sulfur-rich fibers within this crossbred matrix enhances aggregate bonding, which altogether contributes to the durability of RMC.



ROMACON
samples showing
geopolymers in
roman marine
concrete in Cosa
(60 BC): Brandon
2021

Fig. 4.10. Plan of Portus Cosanus (Will Foster Illustration).

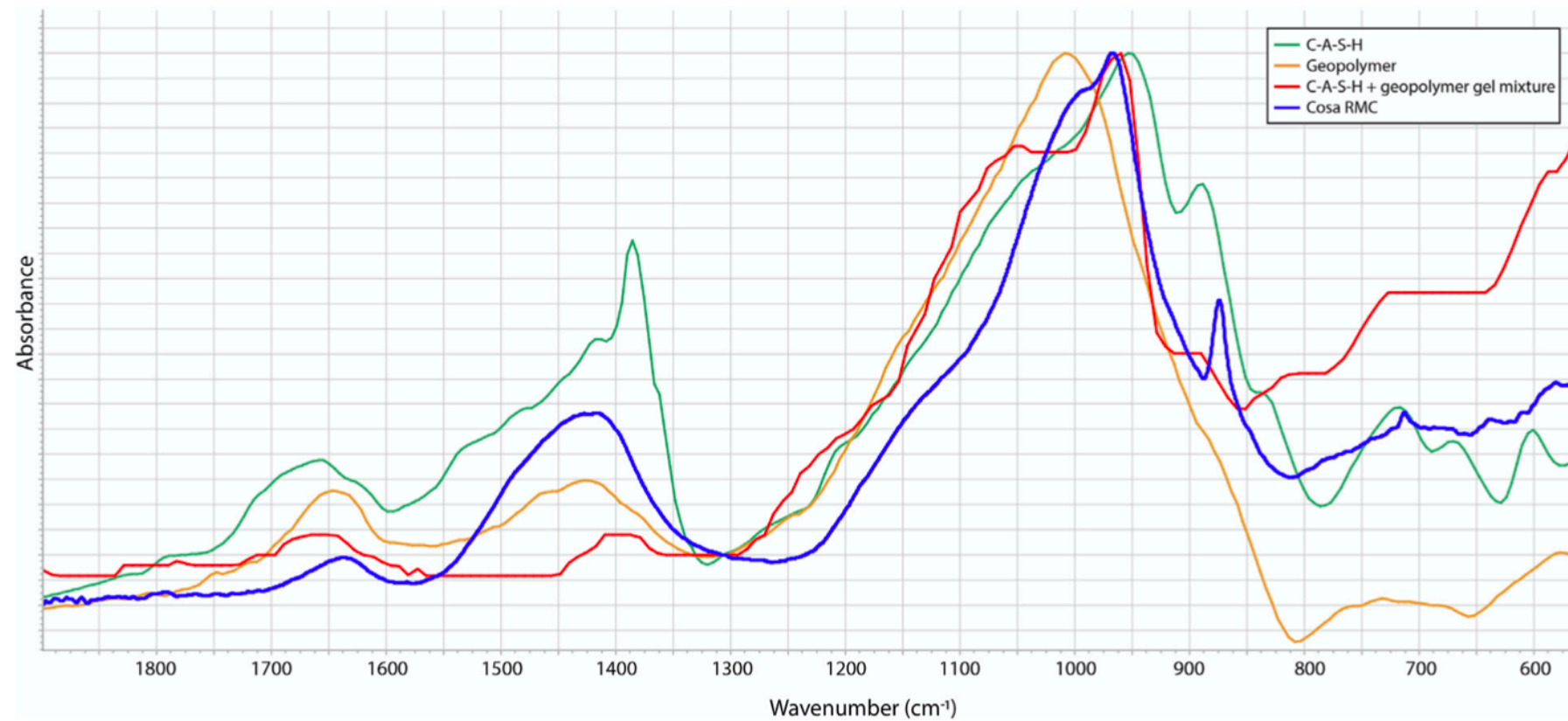


Fig. 6. FTIR spectra for a sample from Cosa (blue), a C-A-S-H and geopolymer (N-A-S-H) gel mixture (red) [39], C-A-S-H (Ca/Si 1.0 and Al/Si 0.2) (green) [38], geopolymer (alkali-activated pozzolan) (orange) [40]. The Roman concrete spectrum falls between the three waveforms and shares similar peaks. The absorbance has been normalized for comparison.

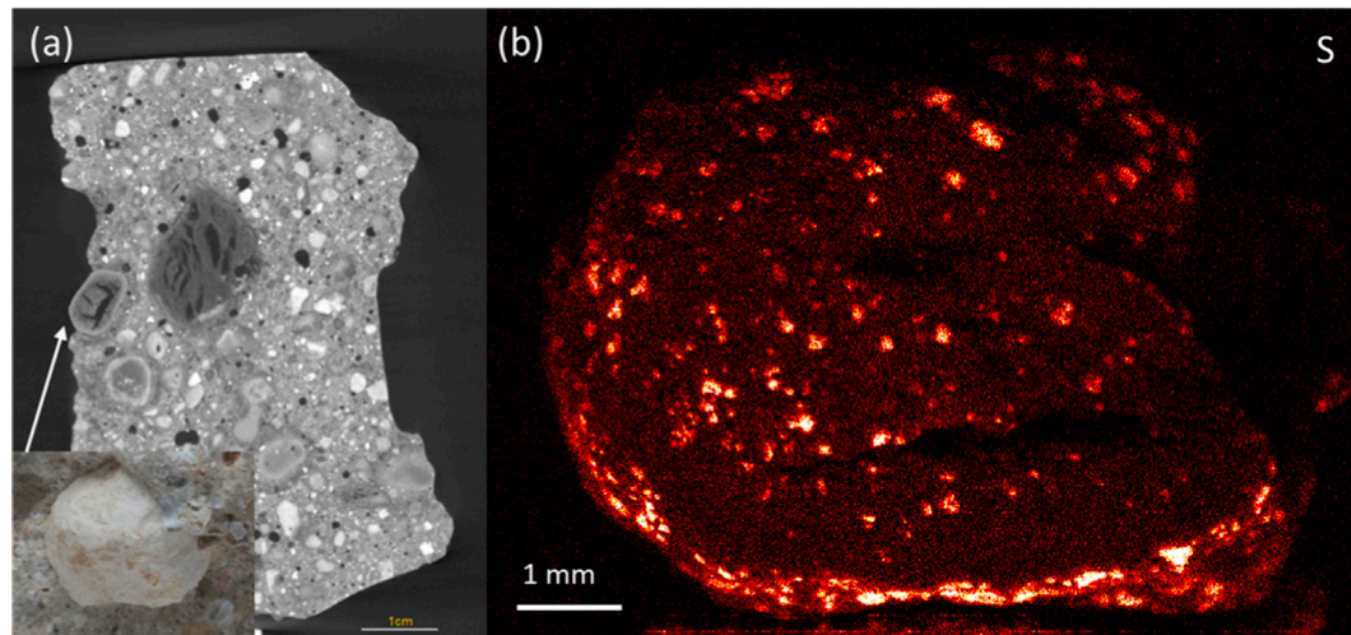


Fig. 7. CT reconstruction showing the relict lime clast of interest (optical image inset). (b) Surface micro-XRF of the relict lime clast showing the intensity of sulfur concentration. The energy spectra for two regions of interest are shown in Figure A.6.

A3.2. Portus Cosanus, modern Ansedonia, 7 km southeast of Ortebello (Tuscany, Italy)

The Cosa harbour complex consists of a marine harbour and associated intra-coastal lagoon regularized around 50 BC with concrete fish tanks, flow regulators, and a breakwater of concrete *pilae* founded on a rubble foundation (pp. 63–69; Fig. 4.10). The lagoon and harbour basin are bordered on the north and east by limestone ridges. Five *pilae* associated with the harbour breakwater survive in various degrees of preservation. For those closest to shore (nos 1 to 3; Fig. 4.11) the concrete in the upper part of the structure contains an abundance of sedimentary sand, while the lower part of the structure in contact with sea-water has tuffaceous coarse aggregate, and a greater proportion of pumiceous pozzolan relative to sedimentary sand. The contact between these different concrete compositions occurs close to modern sea level. The mole at Sapri also contains different concrete mixes above and below sea level (Scognamiglio 2008). Fluctuations in sea level seem to have been small during the last 2000 years (Lambeck *et al.* 2004), so the builders possibly intended the top of the *pilae* to protrude several metres above sea level. It seems likely that the lime was quarried and calcined locally, since the hill on which the city was built, and the hills adjacent to the harbour are underlain by limestone, and there was probably abundant forest cover (Brown 1951: 17, 1980: 6). The mortars of all the cores contain various proportions of the local beach sand, composed of quartz, feldspar, and iron-oxide crystals (Table A4.1). The addition of beach sand to the mortar of harbour concrete is not mentioned in ancient texts, and it does not occur in measurable amounts in any of the other sea-water concretes sampled.

PCO.2003.01. Taken 7 June 2003 from the centre of the top surface of Pier 1 on the modern beach (2.11 m asl; UTM 4697618). The coring hole depth was 2.23 m, yielding a core of L 1.65 m (74% recovery). The pier appears to be the result of one sequence of construction. Although limestone coarse aggregate was used in the top 0.50 m of the *pila* and volcanic tuff in the lower section, the mortar appears rather uniform throughout. A fragment of charcoal (D 0.01 m) at 0.35 m below the top of the pier yielded a ¹⁴C date of 2020 ±40 BP, giving a range of 57 BC to AD 33 (TO-11233; Oleson *et al.* 2004: 225). The base of the recovered core is composed mainly of tuff crumbled during the coring process, and perhaps suggests that the concrete in the lower portion of the pier had a lower proportion of mortar. The top of this structure did not protrude above sea level.

Description: A uniform, compact concrete in a core that was recovered in several large sections (Table A3.4; Figs. A3.7–9). The light greenish grey to dark greenish grey (Gley 1 7/N to 7/10Y) mortar contains common particles of light yellowish-grey pumice, white inclusions, and relict lime clasts. These are generally small (D up to about 0.01 m, but mainly D < 0.005

Table A3.4: PCO.2003.01 drill core summary.

Depth	Description
0.0 to -0.50 m	Irregular, light grey (Gley 1 8/N to 7/N) limestone <i>caementa</i> (D ≤ 0.10 m) and mortar. This upper mortar may be slightly more granular than that below -0.50 m, but the difference is subtle. Where the two types of concrete meet, there is no obvious seam, but the lower mortar is slightly more yellow brown than the light greenish grey to dark greenish grey (Gley 1 7/N to 7/10Y) elsewhere in the core.
-0.50 to -1.65 m	Yellow brown (10YR 5/6 to 4/4) pumiceous tuff similar to the SLI.2003.01 and the other Cosa concretes, containing black glass fragments (Vola <i>et al.</i> 2011) and yellow brown pumice fragments.
-0.50 to -1.30 m	The proportion of tuff <i>caementa</i> seems quite low, perhaps about 10 volume %.
-1.30 to -1.65 m	The mortar contains large white inclusions, up to D 0.03 m, and there are irregular voids up to D 0.03 m. The core sample terminates with tuff crumbled during the sampling procedure.

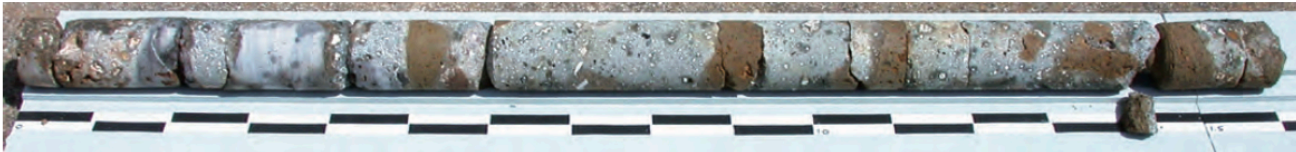


Fig. A3.7: PCO.2003.01. Overview of core, pumiceous tuff *caementa* and one limestone fragment, and pumiceous mortar with abundant lime clasts. Scale bar is 10 cm.



Fig. A3.8: PCO.2003.01, detail, 0 to -0.58 m. Pumiceous tuff and gray limestone *caementa*, and mortar with relict lime clasts and possible clots of relict lime putty.

m), and uniform in size and distribution. Pumice clasts removed from the mortar have a trace element signature that falls in the compositional field of pumice deposits in the Campi Flegrei volcanic district (Fig. 7.13, Table A4.2, specimen PCO.03.01.AC.P1). There are also common small tuff fragments in the mortar, occasional small fragments of ceramic, and small voids (D 0.003 to 0.02 m) indicating flaws in compaction at the macroscopic scale. The *caementa* are roughly trimmed limestone for the top 0.5 m, and then moderate yellowish-brown tuff below.

PCO.2003.02. Taken 9 June 2003 from the south end of the top surface of Pier 2 just off the modern beach (2.51 m asl; UTM 4697597). The coring hole depth was 2.10 m to top of a beam hole, 2.38 m to bottom of beam hole, *ca.* 3.50 m to the bottom



Fig. A3.9: PCO.2003.01, detail, -0.50 to -1.10 m. Pumiceous tuff *caementa* and pumiceous mortar with abundant lime clasts.

of the pier, yielding a core of L 1.60 m (48% recovery). The core tube passed through an empty beam hole from the wooden formwork, explaining the low recovery rate. The portion from -0.05 m to -0.50 m was intact, -0.50 m to -0.70 m was lost, and section -0.70 m to -1.60 m was broken but complete. It is likely that the lower portion of the core came from below the sea level water table.

Description: A rather compact concrete with a mortar that is light grey (1 Gley 7/N) overall, with abundant beach sand, as in PCO.2003.03, small tuff clasts, common white inclusions and relict lime clasts (D ≤ 0.01 m), and occasional small voids (Table A3.5; Figs. A3.10–12). A mortar with a greater proportion of pumiceous ash appears at *ca.* -0.95 m depth, but without any visible seam. The mortar contains occasional fragments of crushed ceramic throughout.

Latin geopolymer C-(N,K)-A-S-H

- The Aqua Traiana aqueduct to Rome (109 CE) was sampled by a team who published extraordinary results.
- Medeghini et alii (2024) analysed samples of the aqueduct taken around the Bracciano Lake north of Rome
- Roman builders used the best local volcanic sand (*carbunculus* described by Vitruvius).
- Binding matrix : C-(N,K)-A-SH “gel” with no calcite (CaCO_3)
- The calcium was completely consumed by the hydraulic reaction, sealing it in a highly stable, insoluble amorphous gel that prevents leaching by flowing water.



The secret of ancient Roman hydraulic mortar: the lesson learnt from the past for future cements

Laura Medeghini^{a,b,*}, Laura Calzolari^a, Michela Botticelli^c, Melania Di Fazio^a, Caterina De Vito^a, Ida Pettiti^d, Fabrizio Bardelli^e, Silvano Mignardi^a

^a Department of Earth Sciences, Sapienza University of Rome, Piazzale A. Moro, 5, 00185, Rome, Italy

^b CNIS, Sapienza University of Rome, Piazzale A. Moro, 5, 00185, Rome, Italy

^c Kelvin Centre for Conservation and Cultural Heritage Research, University of Glasgow, Kelvin Hall, 1445 Argyle Street, Glasgow, G3 8AW, UK

^d Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro, 5, 00185, Rome, Italy

^e CNR-Nanotec, Institute of Nanotechnology, Piazzale Aldo Moro, 5, 00185, Rome, Italy

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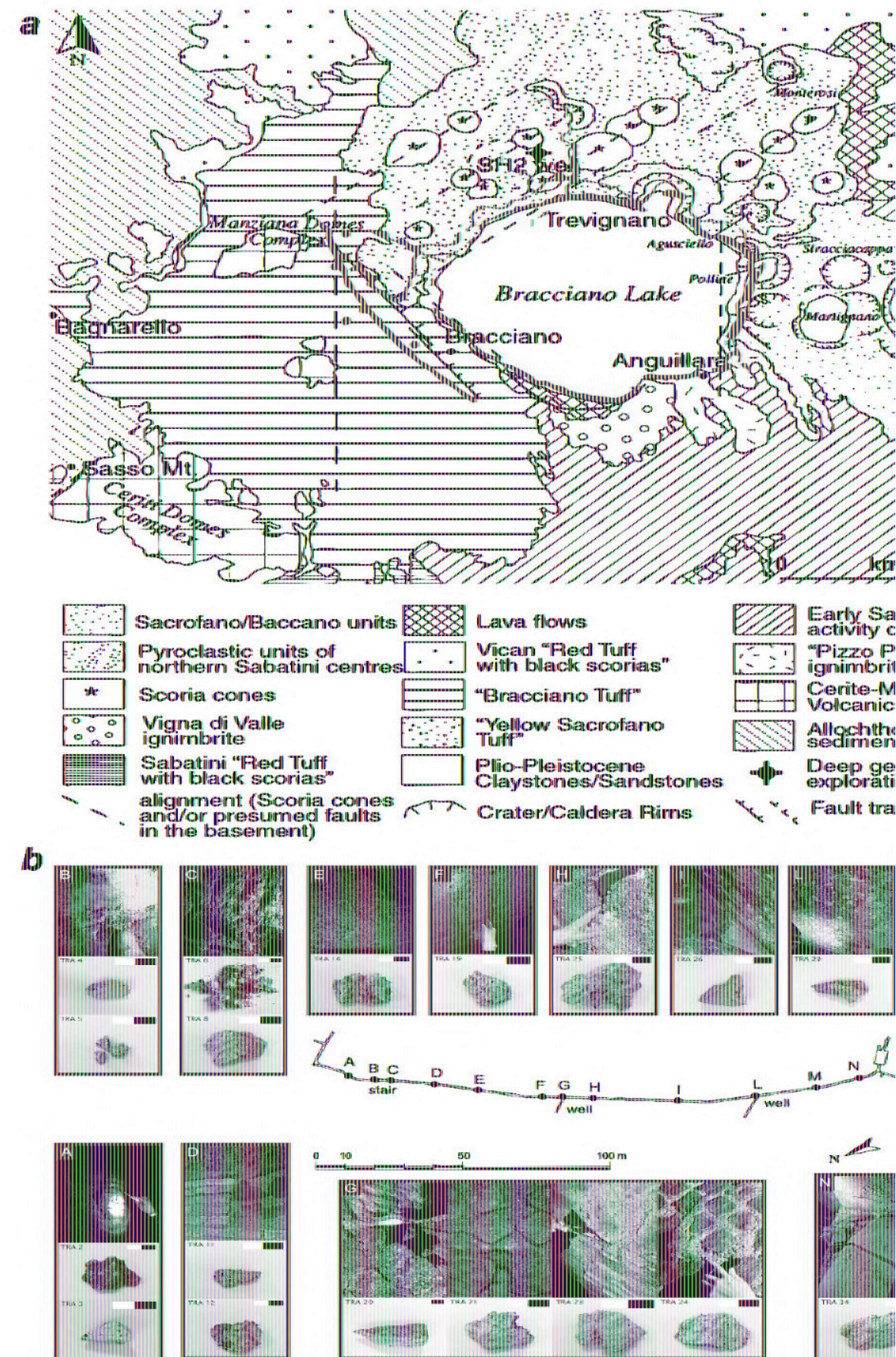
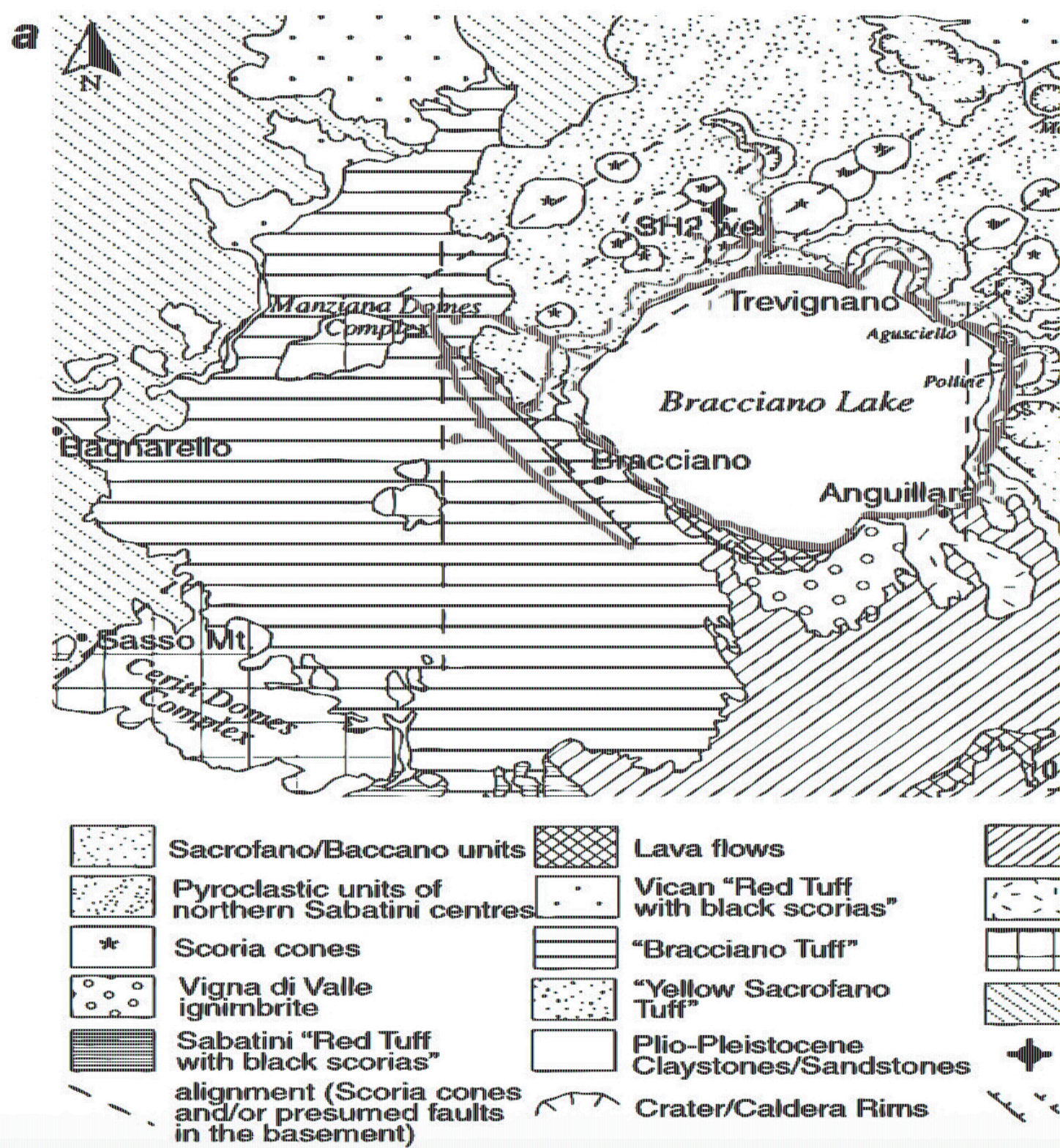
Keywords:

Amorphous material
C-A-S-H
C-(N,K)-A-S-H
Pozzolan
Mortar
Microstructure

ABSTRACT

Aqua Traiana is an ancient Roman aqueduct, built to supply water to the ancient city of Rome and still working nowadays. This work is focused on the characterization of its mortars, and in particular the binders, to identify the reasons of such a durable resistance. Samples collected inside the aqueduct were analysed by Optical Microscopy (OM) in thin sections, X-ray Powder Diffraction (XRPD), Scanning Electron Microscopy with Energy-Dispersive X-ray Spectroscopy (SEM-EDS), High Resolution Field Emission Scanning Electron Microscopy (HR-FESEM-EDS), Electron Microprobe (EMPA), Differential Scanning Calorimetry coupled with Thermogravimetric Analysis (DSC-TGA), Fourier-Transform Infrared spectroscopy (FTIR), X-ray Absorption Near Edge Structure (XANES) spectroscopy and N₂ adsorption/desorption measurements. The presence of an amorphous gel-like C-(N,K)-A-S-H binder and the complete absence of calcite in Trajan Age samples constitute a unique case, and may be the reason of the high hydraulicity of the mortar. Establishing how these features were produced could allow them to be replicated in high-durability and high-compatibility restoration mortars.

- “Recent studies on geopolymers focused the attention on the materials and the alkaline activation, which could represent an alternative to cement production. In these studies, the product obtained by the main reaction, *id est* an amorphous aluminosilicate gel with small amount of zeolites, is similar to what identified in the ancient mortars studied in this work, suggesting that past recipes could be used as a guide to develop better and more sustainable cements.”
- Geopolymers are in Roman concrete.



L. Calzolari, "Unlocking the secrets of hydraulic Roman mortars for new applications", Ph. D. Thesis, Uni. Roma La Sapienza, 2024.

Figure 1. (a) Geological map of the Sabatini Volcanic District, modified after [28]: the light of the Trajan aqueduct around Lake Bracciano; (b) segment of the aqueduct with the location N) and corresponding sample (Table 1).

Conclusion

- Geopolymers are now found in archaeological binders, like roman concrete, used by Roman builders.
- The question is now open in human history :
 1. when was geopolymers used ?
 2. who used them ?

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