Materials Properties, Use and Conservation: Construction Materials and Binders

Pozzolanic binders

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CIBA Centro per i Beni Culturali
Diagnostica . Rilievo . Tecnologie

Binders classification

Table 3.6. Main classes of binding compounds produced by pyrotechnology.

Starting reactive material	***Production process***	***Material-water mixture***	***Final product***	***Mineral phases in the hardened aged material***
Lime-plaster (quicklime)	Calcinations of limestone	Slaked lime (lime putty)	Lime plaster	Calcite
		Slaked lime + fine aggregate	Lime mortar	Calcite + aggregate
		Slaked lime + fine aggregate + pozzolan	Hydraulic mortar (Roman opus caementitium)	Calcite, zeolites, C-S-H + aggregate
	Calcination of dolomite	Slaked magnesia-lime	Dolomitic or magnesian plaster	Calcite, brucite, periclase
Gypsum-plaster (plaster of Paris)	Calcination of gypsum	Bassanite (± anhydrite)	Gypsum plaster	Gypsum
		Bassanite + fine aggregate	Gypsum mortar	Gypsum + aggregate
Portland-clinker	Calcinations of limestones+clay	Portland cement paste	Portland cement	Portlandite, C-S-H, calcite
		Portland cement paste + fine aggregate	Portland cement mortar	Portlandite, C-S-H, calcite + aggregate
		Portland cement paste + fine and coarse aggregate	Concrete	Portlandite, C-S-H, calcite + aggregate
		Cement paste + fine aggregate + pozzolan	Pozzolanic Portland cement mortar	Portlandite, C-S-H, calcite, Ca-aluminosilicates

Pozzolanic binders

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The term "pozzolanic reaction" gathers all the chemical processes occurring among the reactive phases of pozzolana, lime, and water (Massazza, 2002). In more detail, it consists of a recombination of alumino-silicate material and $Ca(OH)_2$ in aqueous solution to form hydrated reaction products (calcium silicate and calcium aluminate hydrates) with binding properties related to their nanostructured crystal habit, according to the following simplified reaction expressed in cement chemistry notation ($A = Al_2O_3$; $C = CaO$; $H = H_2O$; $S = SiO_2$):

$$AS + CH + H \rightarrow C{-}S{-}H + C{-}A{-}H \quad (10.6)$$

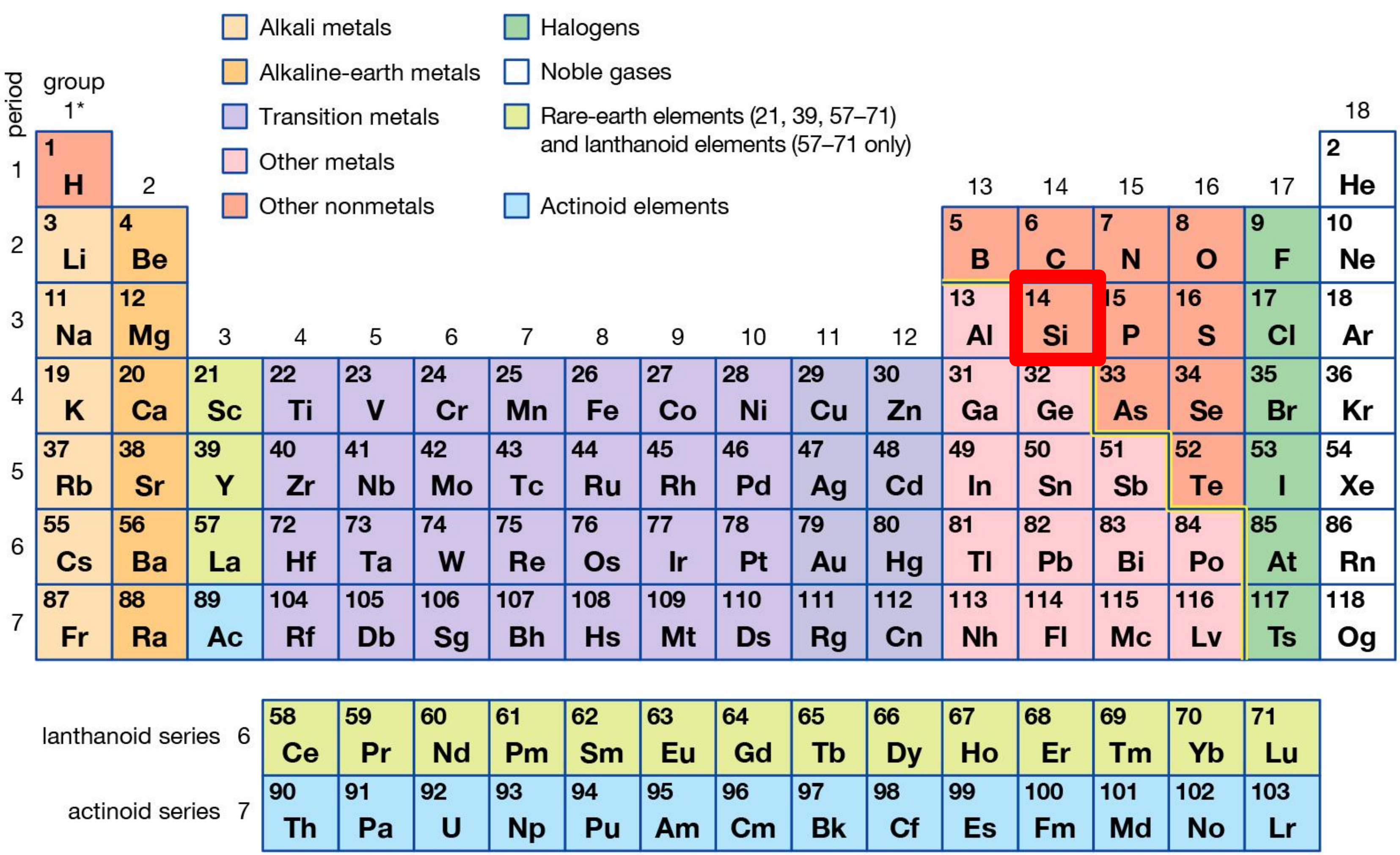
On a general basis, any type of alumino-silicate-based material could produce C−S−H and C−A−H phases when blended with lime and water; however, in practice the reaction could occur only if the system is activated or contains already activated phases. The commonly used pozzolanic materials already contain abundant activated phases, namely:

- Glasses in pyroclastic materials
- Zeolitic phases in tuffs
- Amorphous silica in diatomites
- Amorphous phases in burnt clay minerals (*cocciopesto*)

Secco et al, 2019

Pozzolanic binders

Periodic table of the elements



*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

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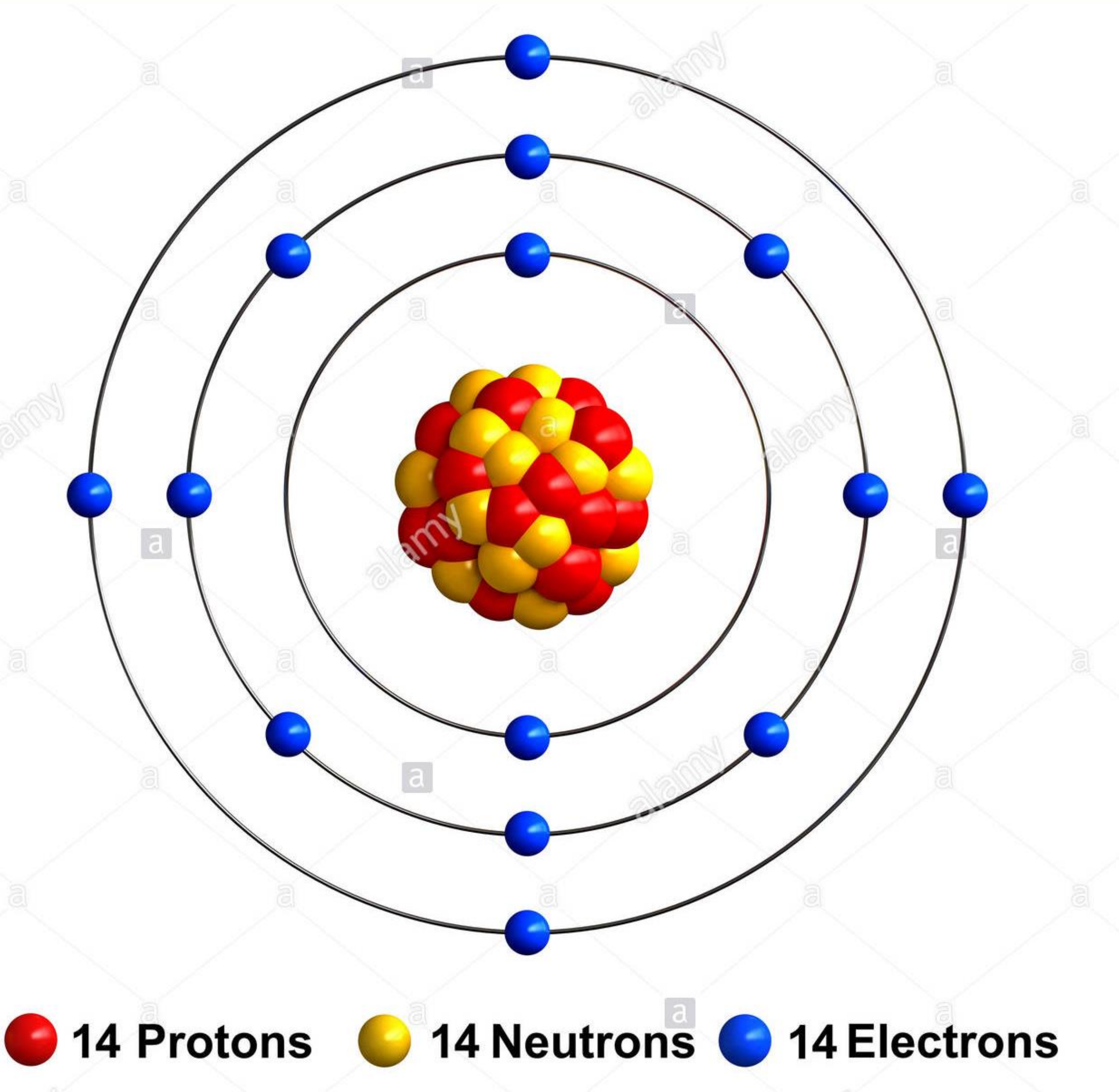
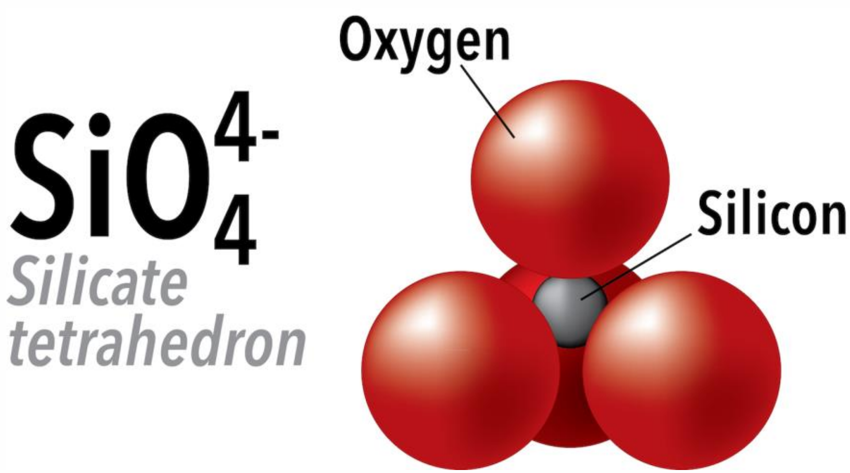
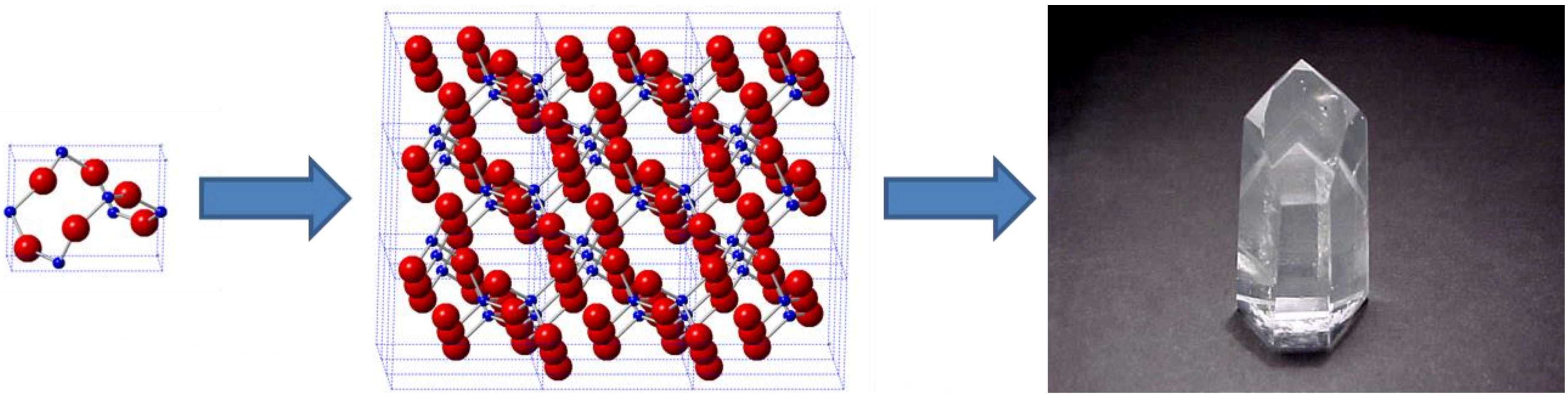
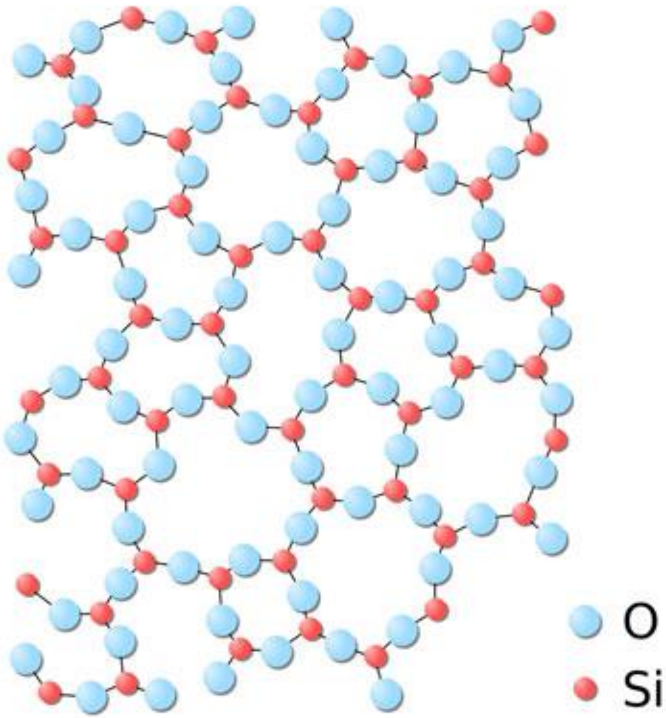


Quartz - SiO_2

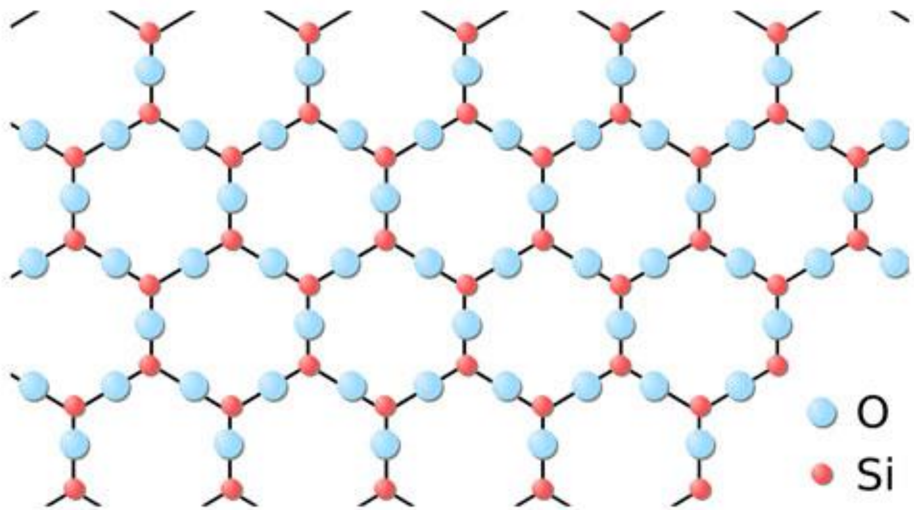




Pozzolanic binders



Glass



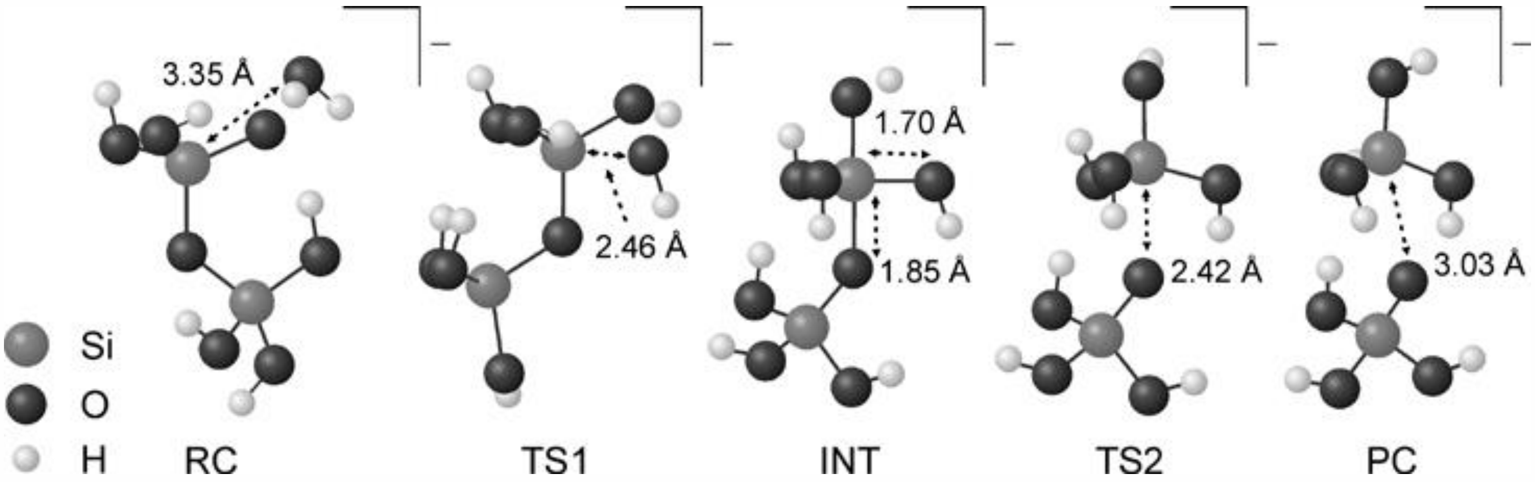
Quartz

Pozzolanic binders

Glass

Quartz

Hydrolysis



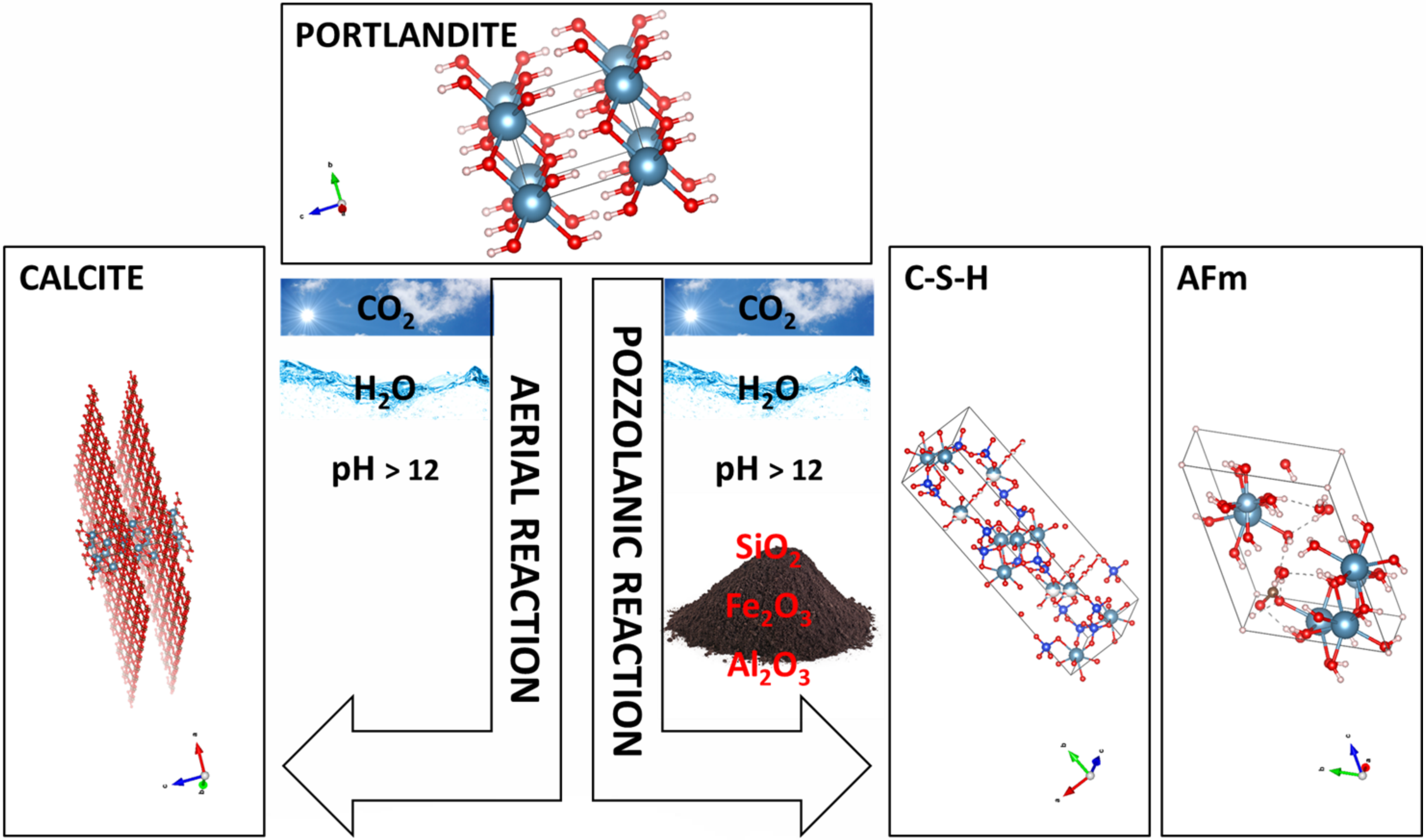
Snellings et al., 2012

$$Ca(OH)_{2(s)} \rightarrow Ca^{2+}_{(aq)} + 2OH^{-}_{(aq)}\ (1);$$

$$SiO_{2(s)} + OH^{-}_{(aq)} \rightarrow HSiO^{-}_{3\,(aq)}\ (2);$$

$$Ca^{2+}_{(aq)} + HSiO^{-}_{3\,(aq)} + OH^{-}_{(aq)} \rightarrow CaSiO_3{\cdot}H_2O_{(s)}\ (3).$$

Pozzolanic binders



Pozzolanic binders

The birth of hydraulic mortars: pozzolanic reactions

- Greek and Etruscans started to mix some volcanic ash or finely ground pottery (***cocciopesto***) to the mortar, resulting in materials with higher strength and durability. The volcanic tuff of Santorini (the so-called ***Santorini earth***) was a reputed material for the preparation of water resistant mortar

- Silica-lime reactions were also activated, probably by chance, in one of the early instances of pyrotechnology at Aşıklı Höyük, Turkey (8200 to 7400 BC), where lime and volcanic ash particles were mixed in the plaster (Hauptmann and Yalcin 2001). The possibility exists that the silica phytoliths and other alkali minerals derived from plant ashes indeed could have induced pozzolanic-type reactions in other cases of primitive plaster technology.

- The Romans, during the period between 300 BC and 200 AD, crucially improved this technology by using the slaked lime in a mixture with high alkali volcanic ash (***pozzolana***) first from the banks of the river Tevere, and then from the volcanic sands found near Naples, at Pozzuoli; hence the name **pozzolan**.

Pozzolanic binders

LIME PLASTER, CEMENT AND THE FIRST PUZZOLANIC REACTION

A. HAUPTMANN AND Ü. YALCIN

Plastered floor from Aşikli Höyük, Turkey

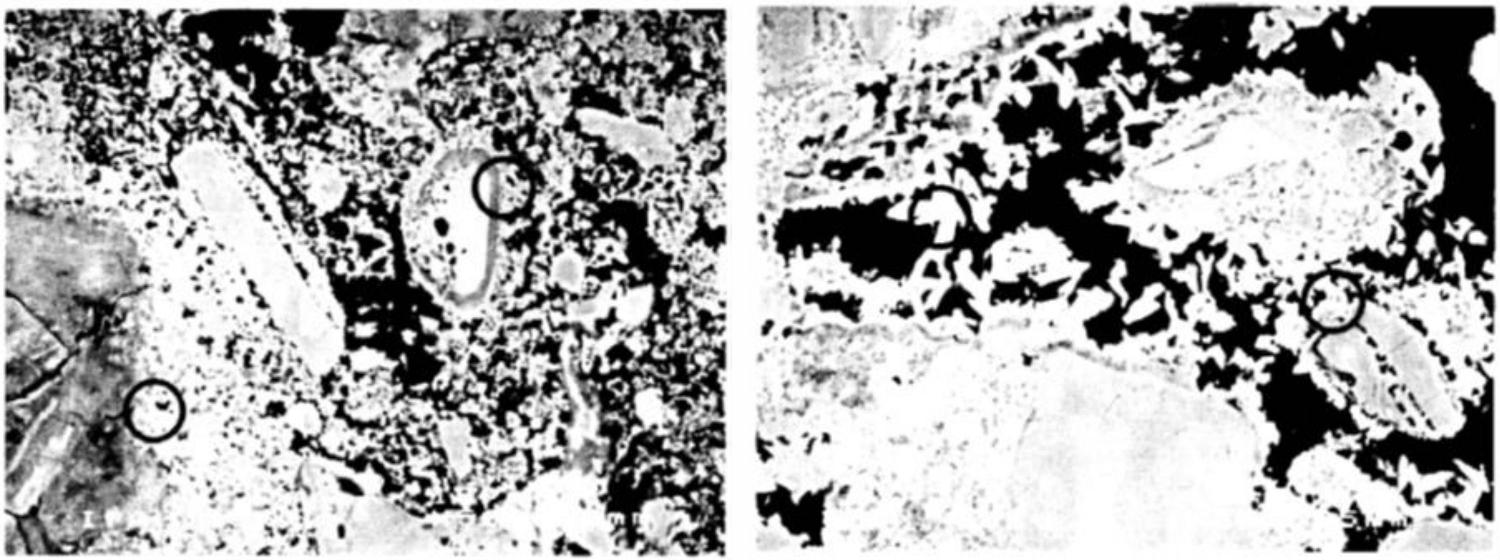
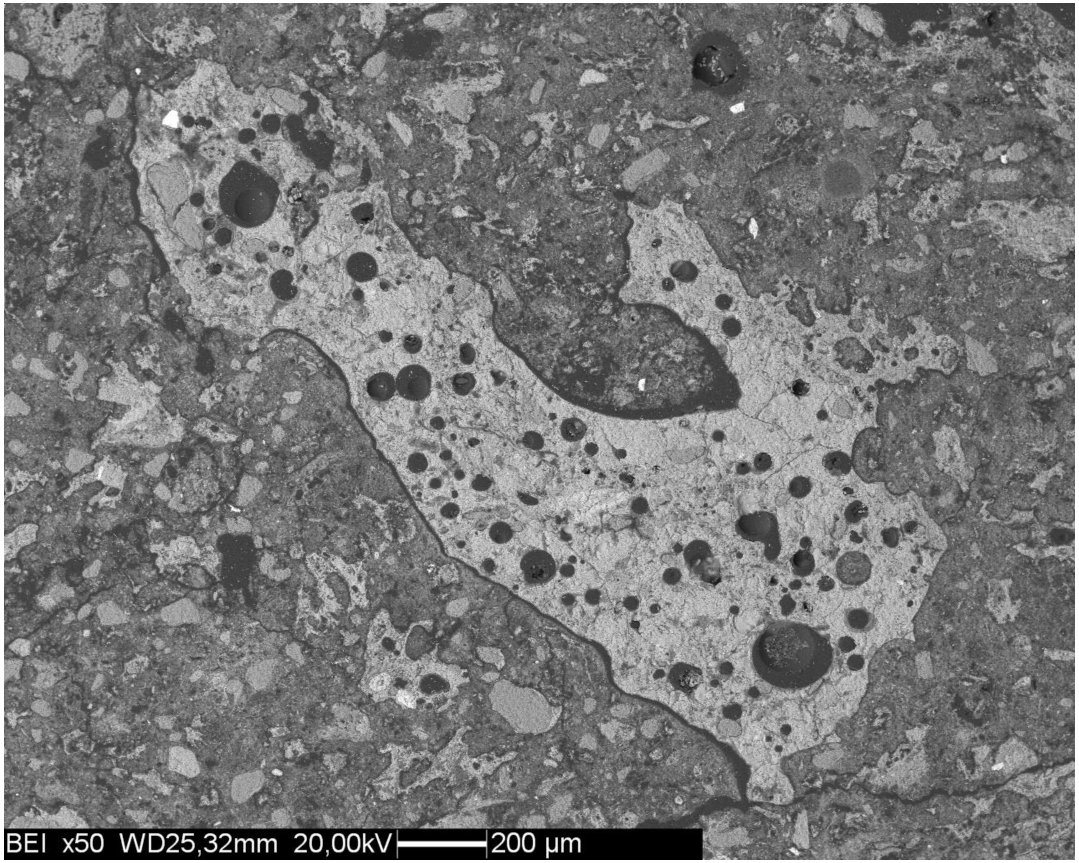


Fig. 2a, b : *Aşıklı Höyük, level II, T-building (Pre-Pottery Neolithic B, ca. 7 500 BC). Microtexture of the sample in figure 1 showing inclusions of volcanic ashes such as glass, feldspar and quartz. At the transition to the fine grained matrix of lime formation of Ca-Si-Al-(H?)-phases (○) such as gehlenitehydrate by pozzolanic reactions. Surface-polished thin section, scanning electron micrograph, back-scattered mode.*

Tell es-Safi (Israel), 1100 b.C.



Regev et al., 2010

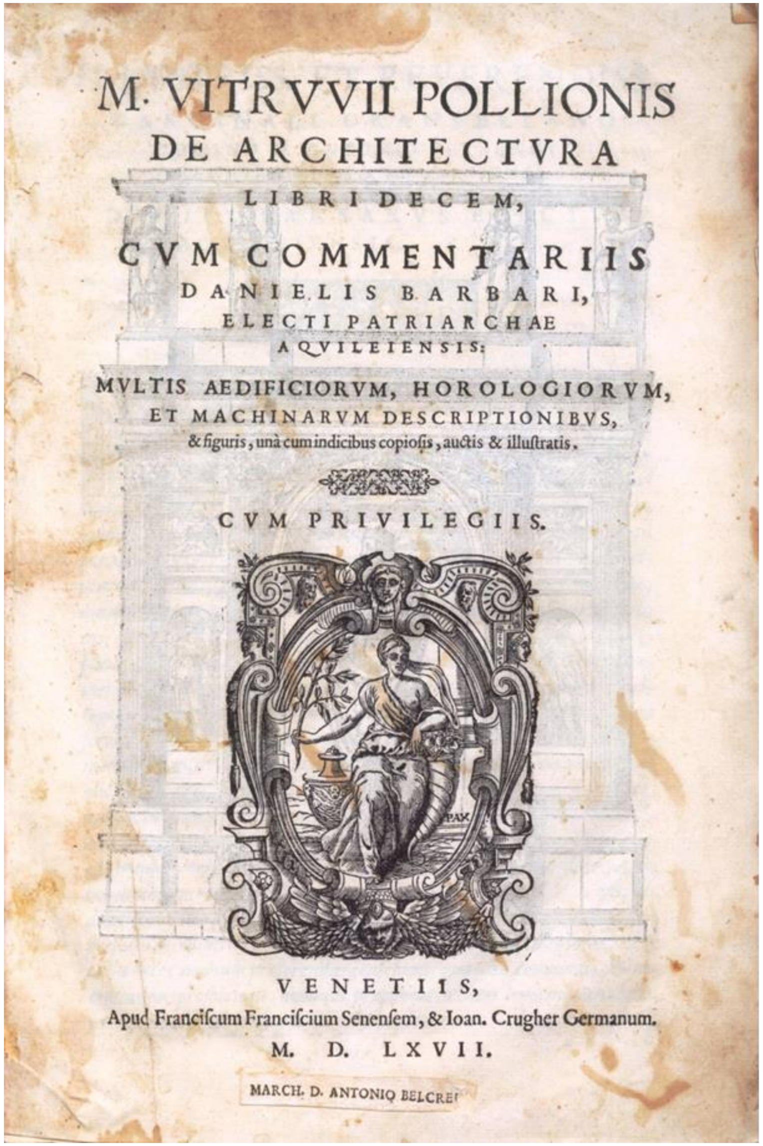
Pozzolanic binders

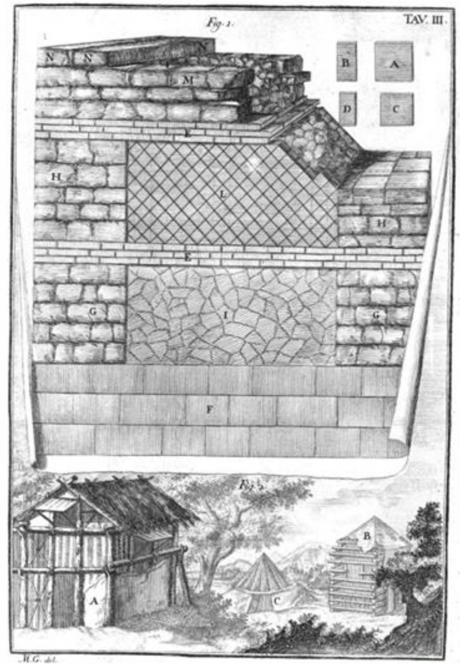
- Recent studies of the evolution of Roman mortars from Republican through Imperial times reveal neat changes in the composition and use of mortar components: detailed investigation of the ash outcrops within and around ancient Rome (especially the Pozzolane Rosse ignimbrite; Jackson et al. 2007) show that specific **zeolite-rich tuffs** with highly reactive properties were carefully selected especially in later Imperial age to produce exceptionally hard and durable mortars.

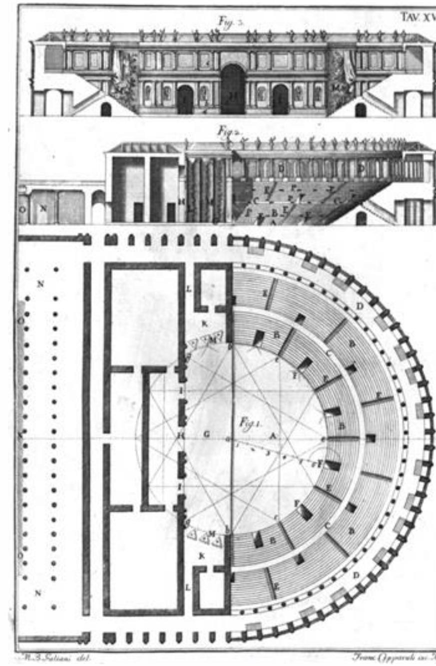
- These important studies not only confirm the early chronology of Roman mortars identified on macroscopic observations (Van Deman 1912a,b), but also confirm the incredibly detailed description of the materials that Vitruvius indicated as ideal for the preparation of quality mortars (black and red sands, or ***harenae fossiciae***: De architectura 2.4.1).

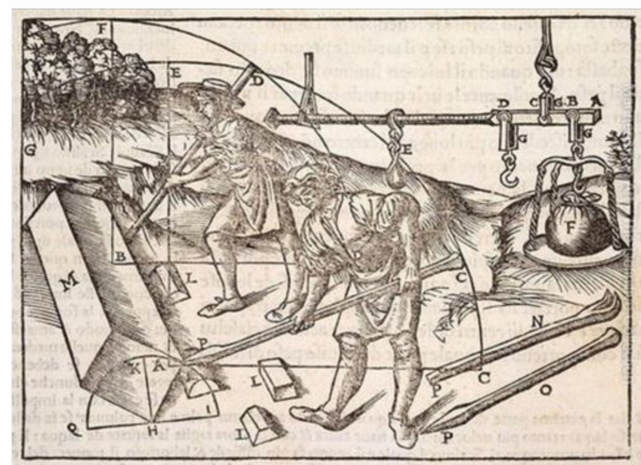
LIBRO SECONDO

Pozzolanic binders

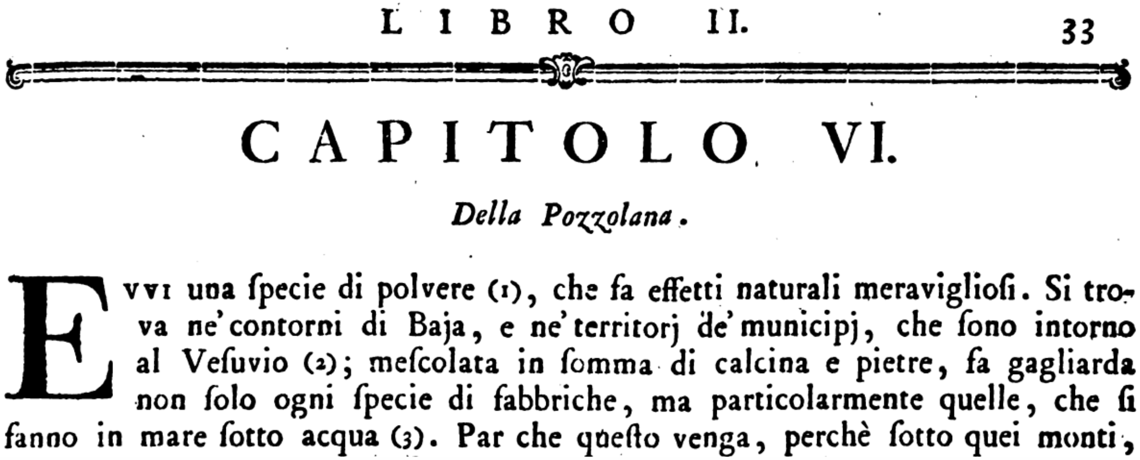








Pozzolanic binders


LIBRO II. 33

CAPITOLO VI.

Della Pozzolana.

Evvi una ſpecie di polvere (1), che fa effetti naturali meraviglioſi. Si trova ne' contorni di Baja, e ne' territorj de' municipj, che ſono intorno al Veſuvio (2); meſcolata in ſomma di calcina e pietre, fa gagliarda non ſolo ogni ſpecie di fabbriche, ma particolarmente quelle, che ſi fanno in mare ſotto acqua (3). Par che queſto venga, perchè ſotto quei monti,

Pozzolanic binders

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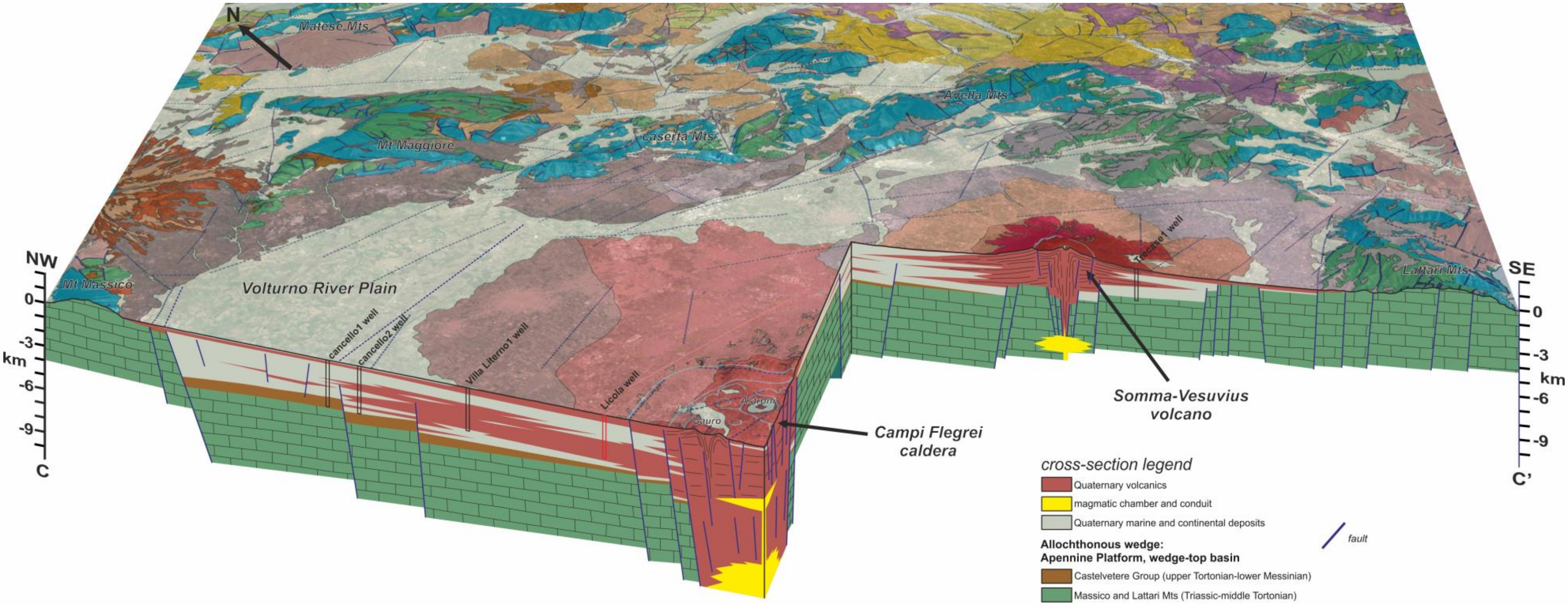

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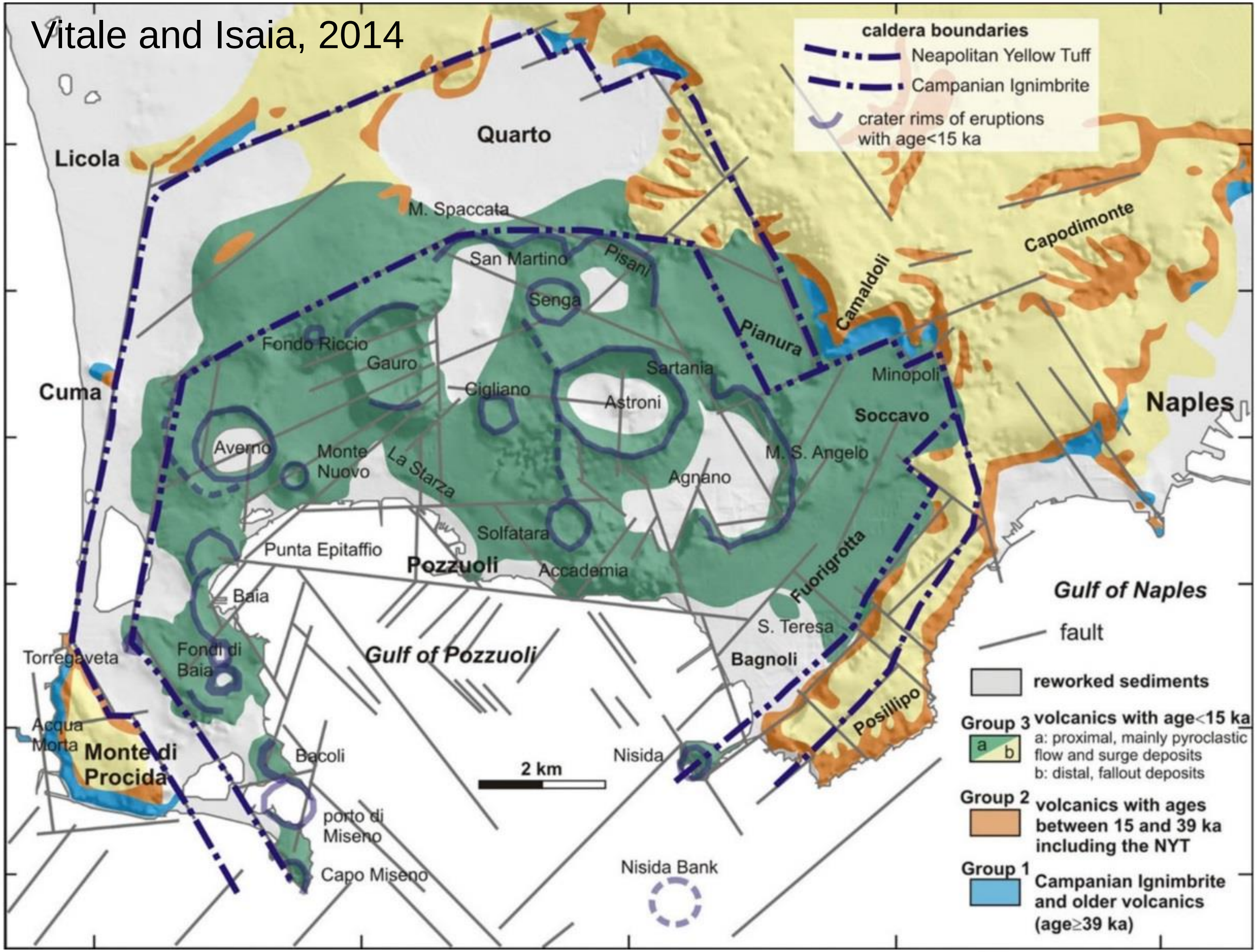
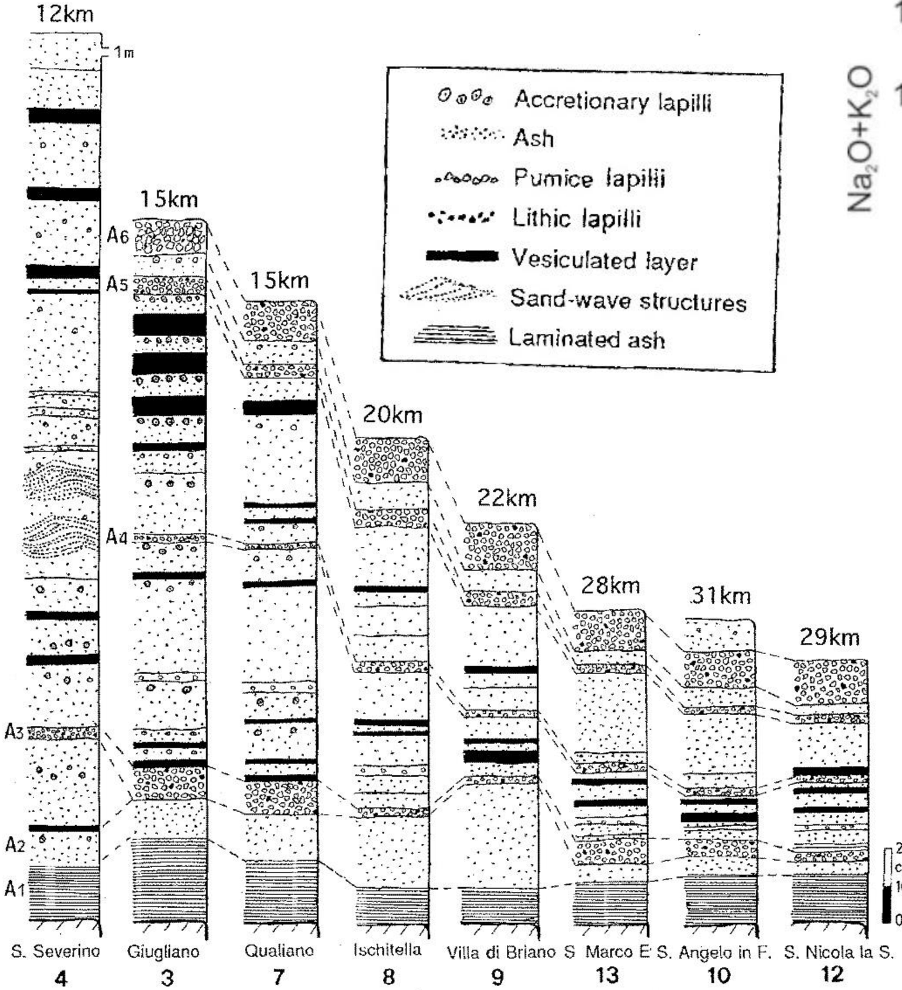
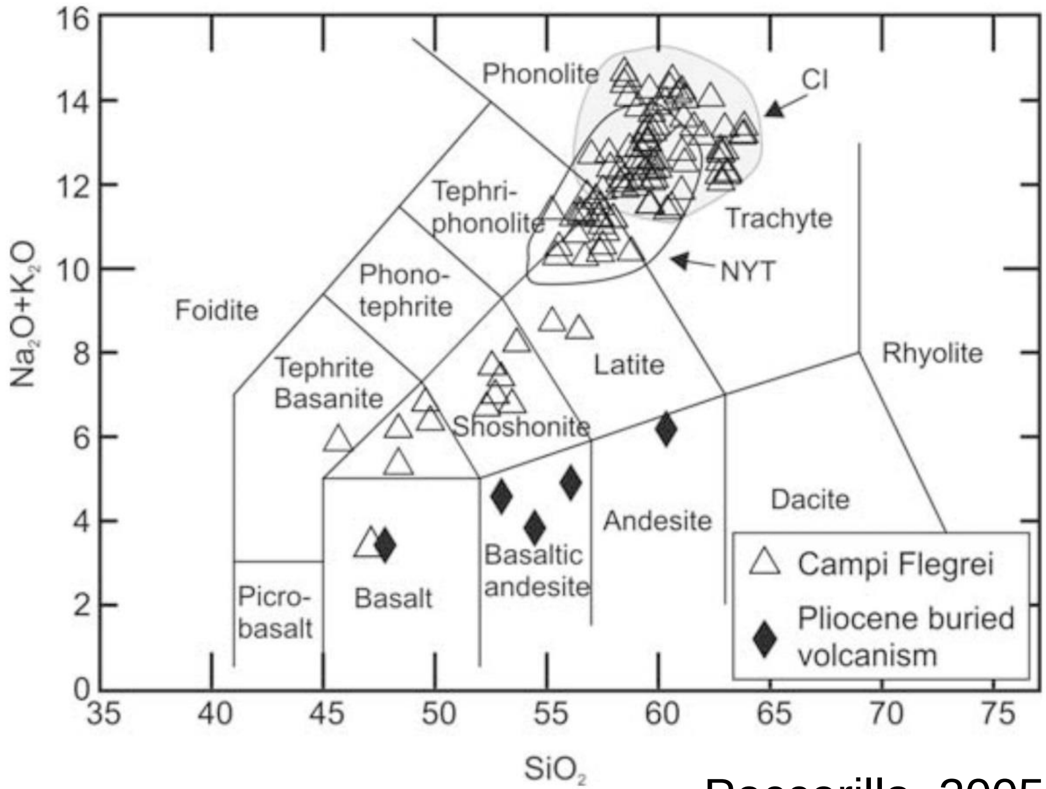


Pozzolanic binders

Scarpati et al., 1993

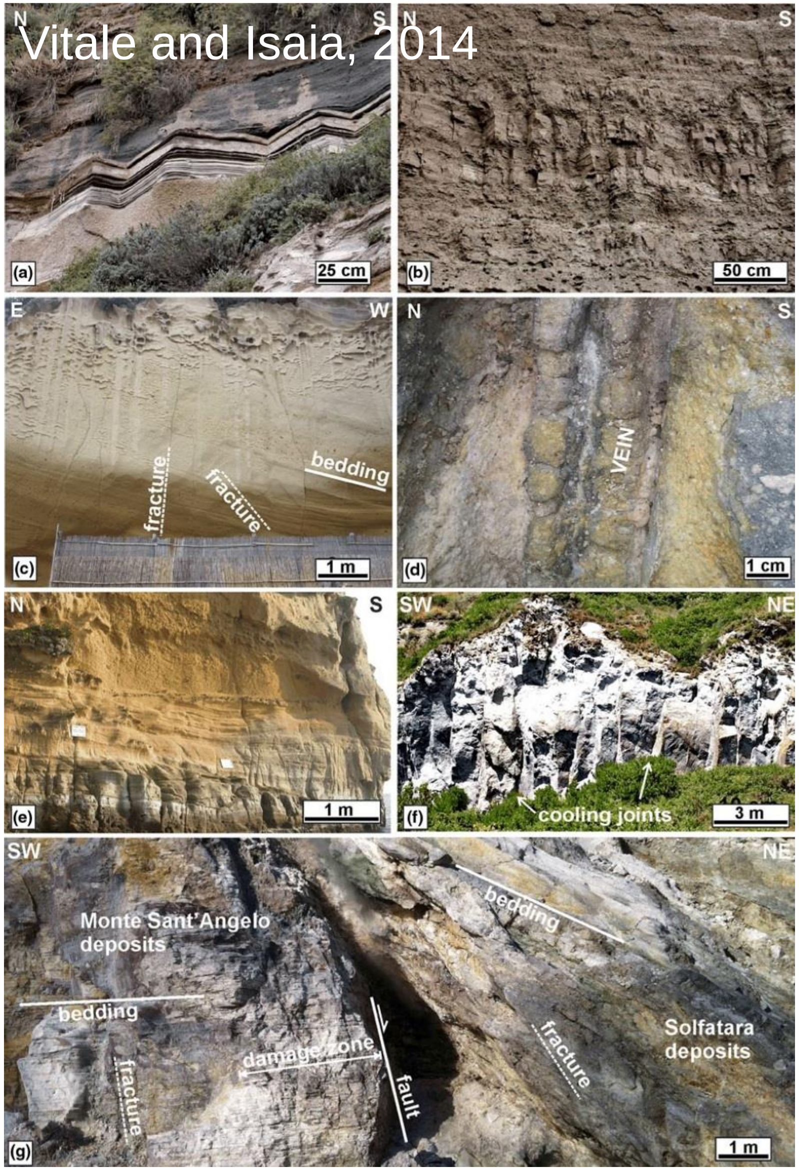


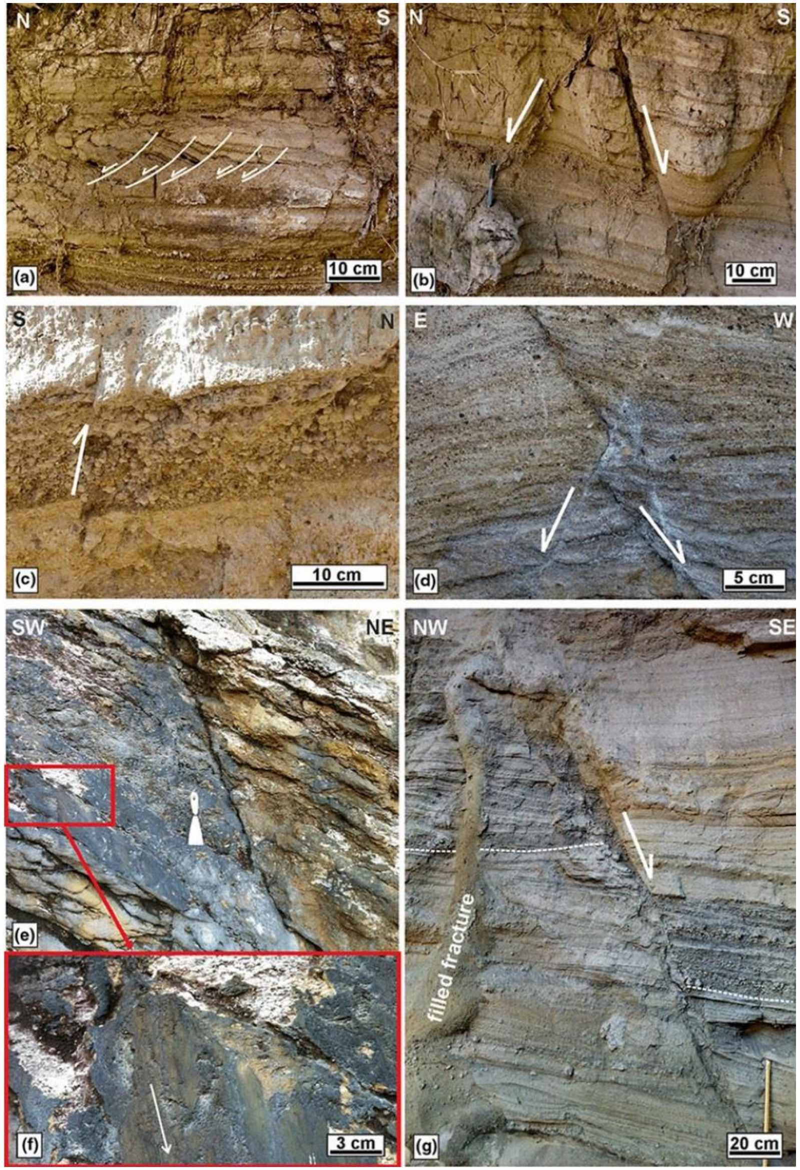


Peccerillo, 2005

Pozzolanic binders

Vitale and Isaia, 2014





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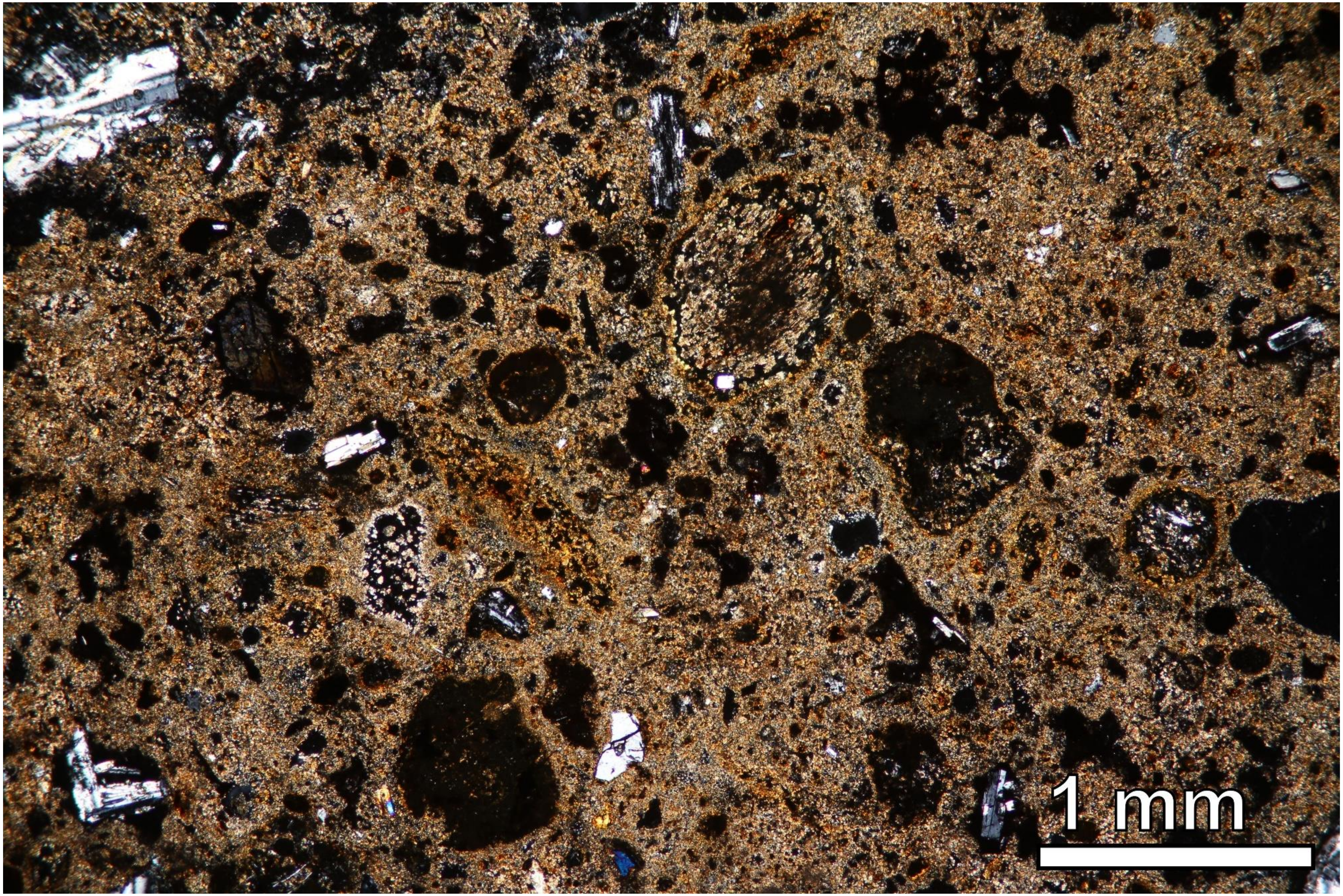
Pompeii special issue

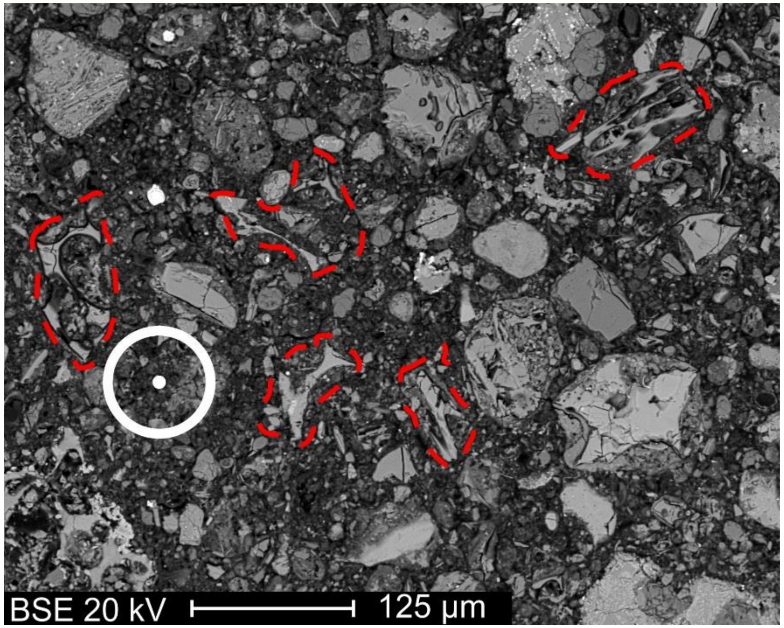
Mineralogical clustering of the structural mortars from the Sarno Baths, Pompeii: A tool to interpret construction techniques and relative chronologies

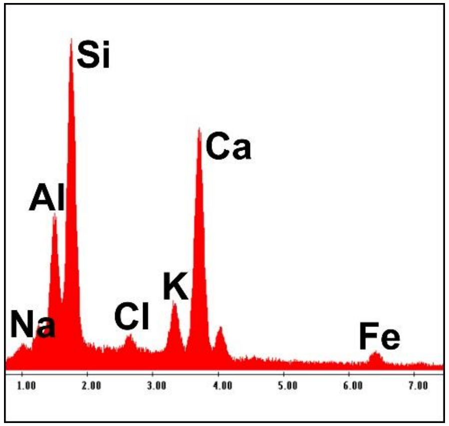
Michele Secco[a,b,*], Caterina Previato[c], Anna Addis[d], Giulia Zago[b], Angelique Kamsteeg[a], Simone Dilaria[c], Caterina Canovaro[d], Gilberto Artioli[b,d], Jacopo Bonetto[c]

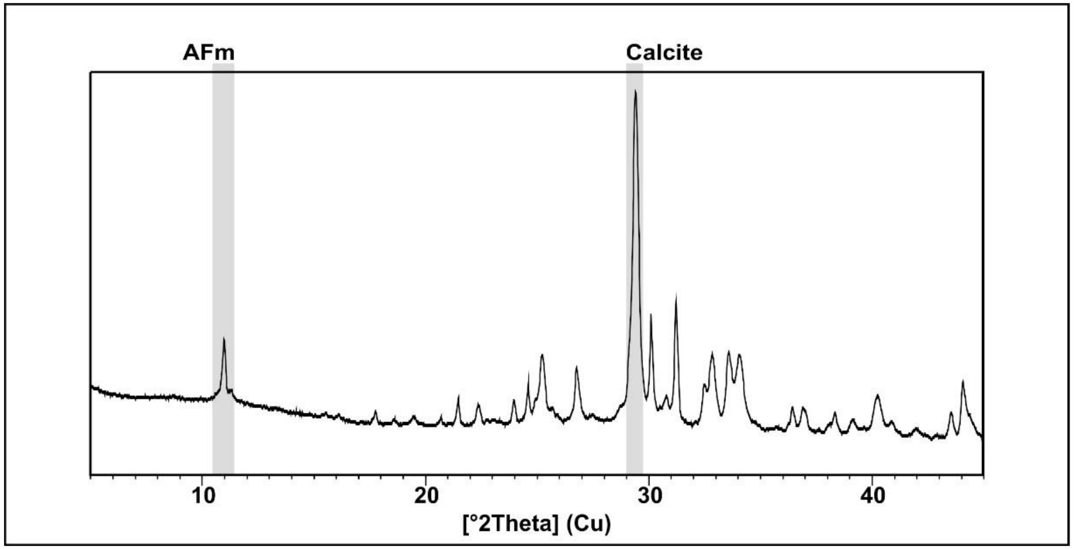
Pozzolanic binders

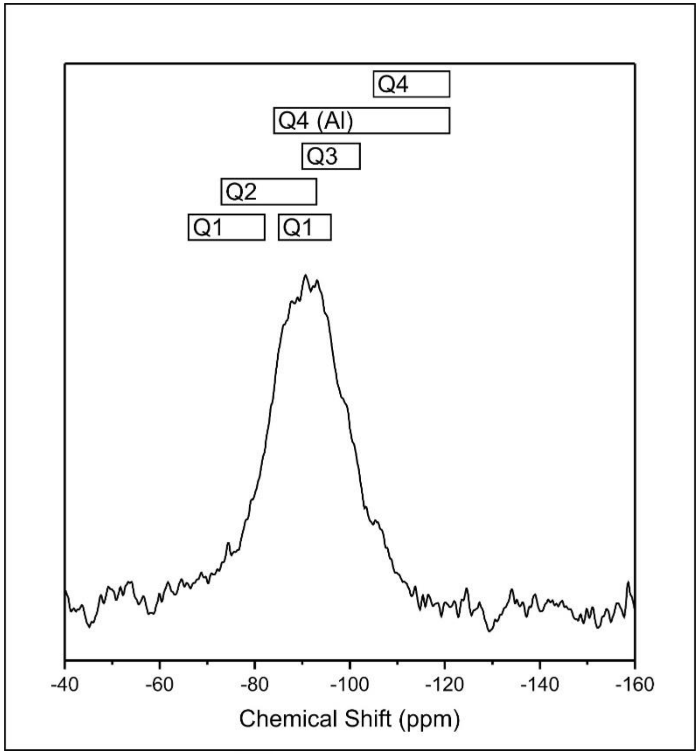


Pozzolanic binders



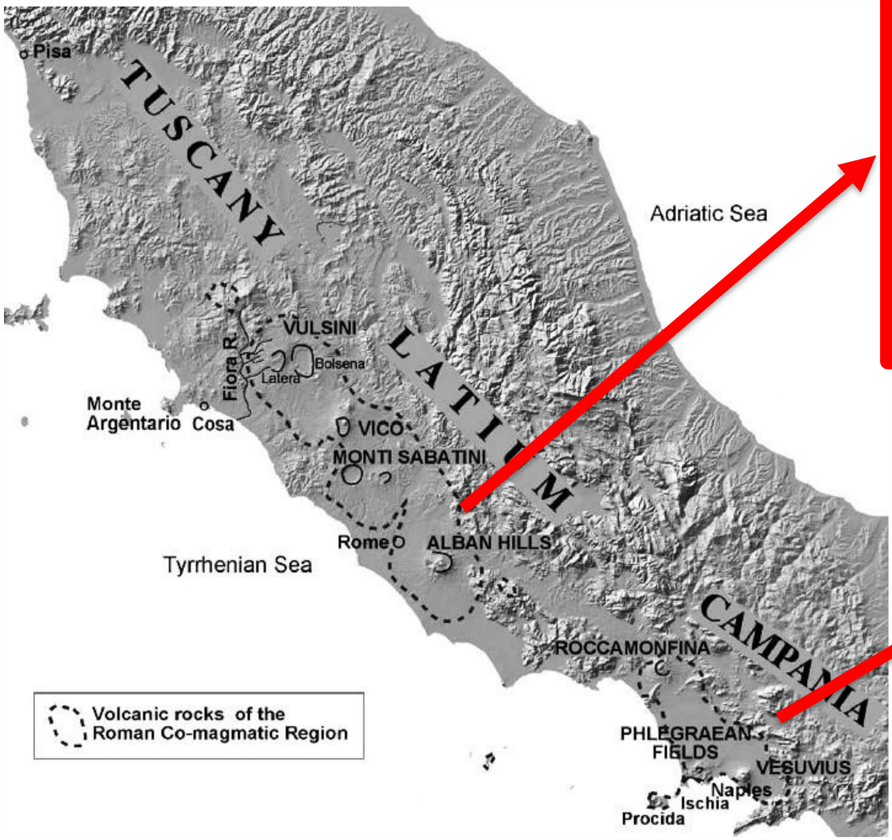




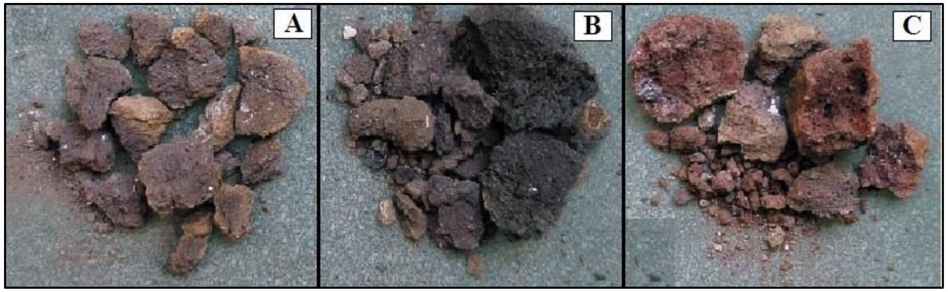


Pozzolanic binders

Jackson et al. 2007
Marra et al. 2013
D'Ambrosio et al. 2015



Harenae fossiciae (Vitr. II, 4, 1)



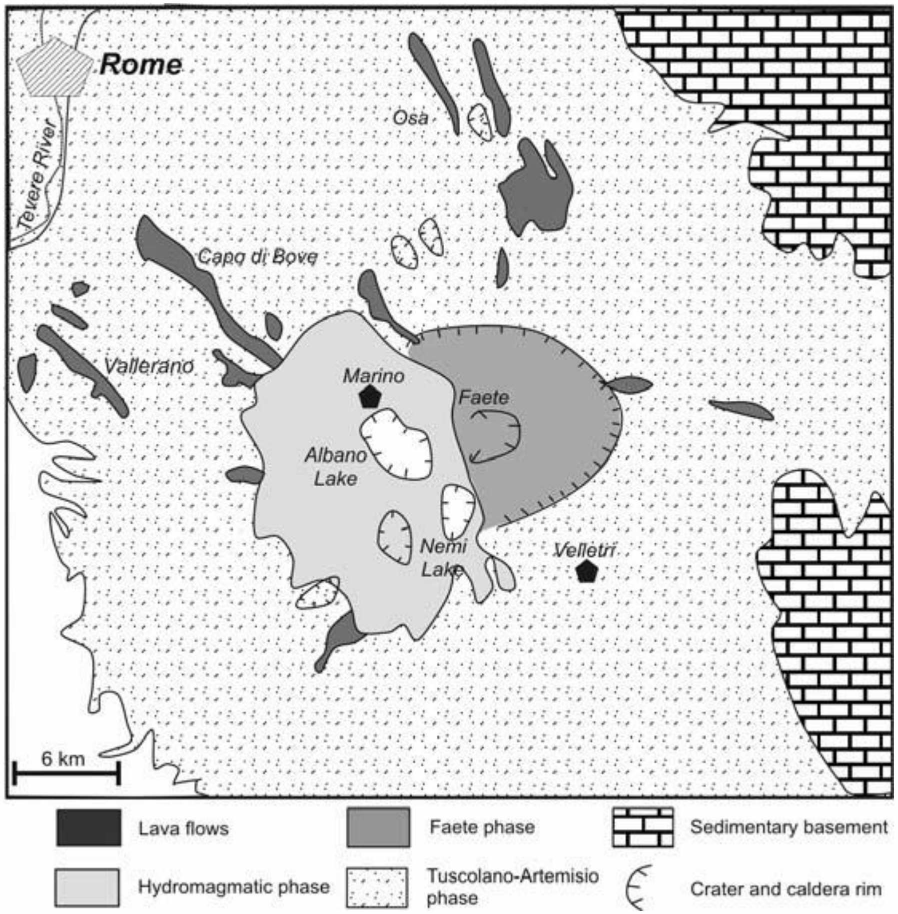
POZZOLANELLA
POZZOLANA NERA
POZZOLANA ROSSA

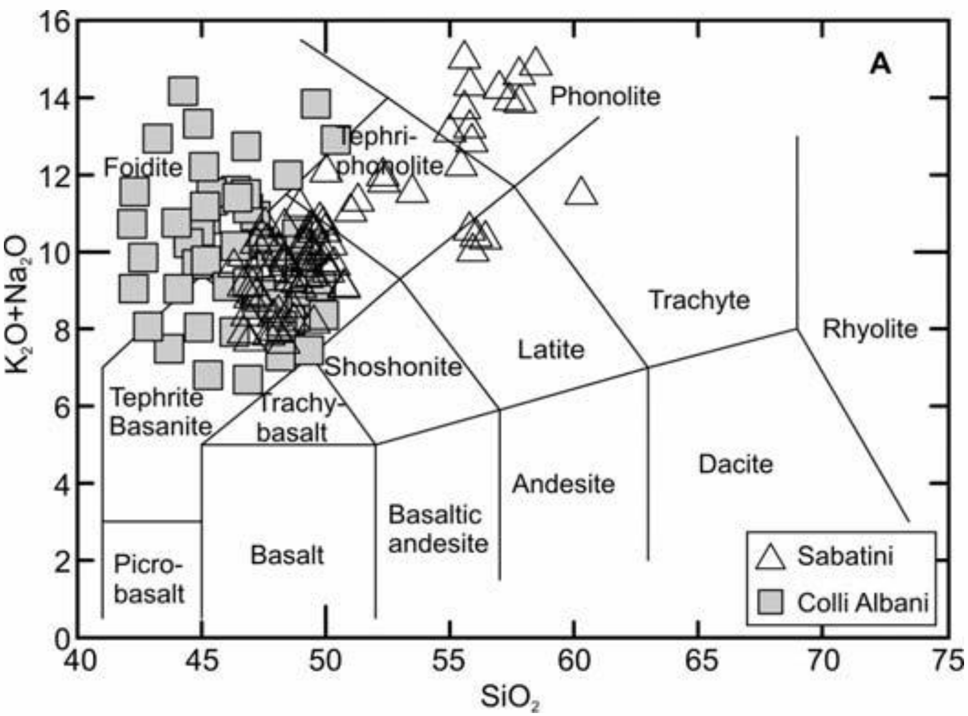
Pulvis puteolanus (Vitr. II, 6, 1-2)

Neapolitan yellow tuff volcanic ash

Neapolitan yellow tuff pumice

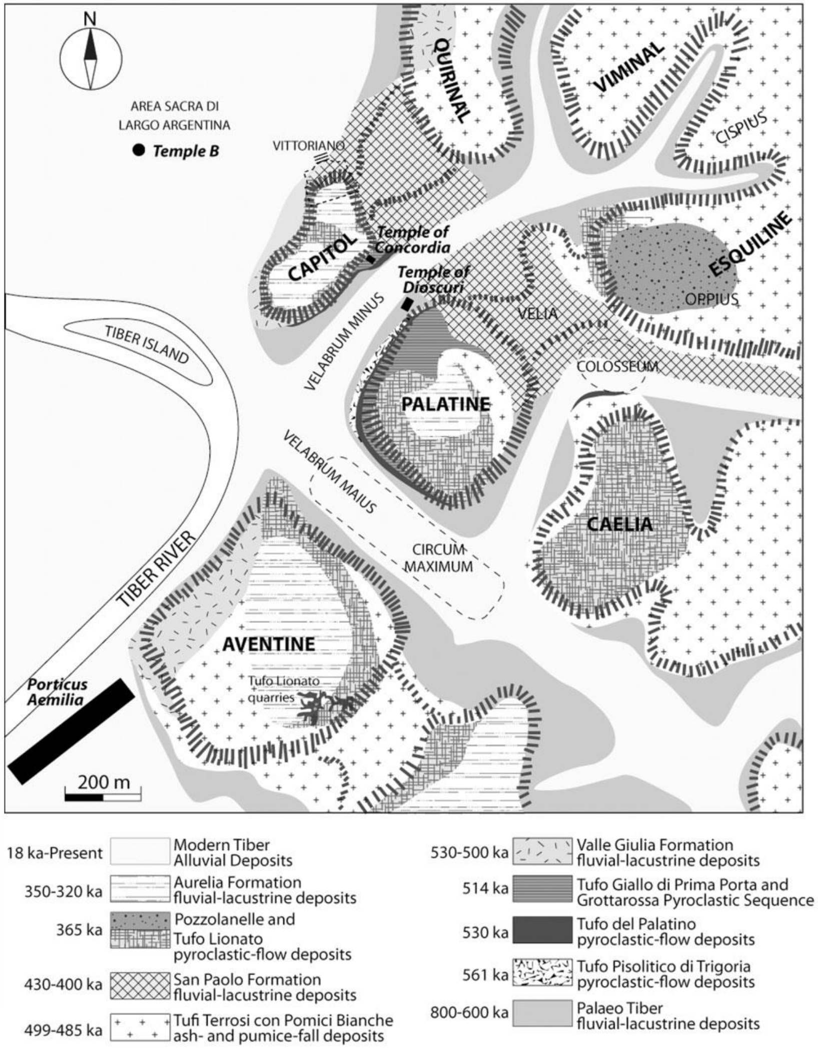
Pozzolanic binders

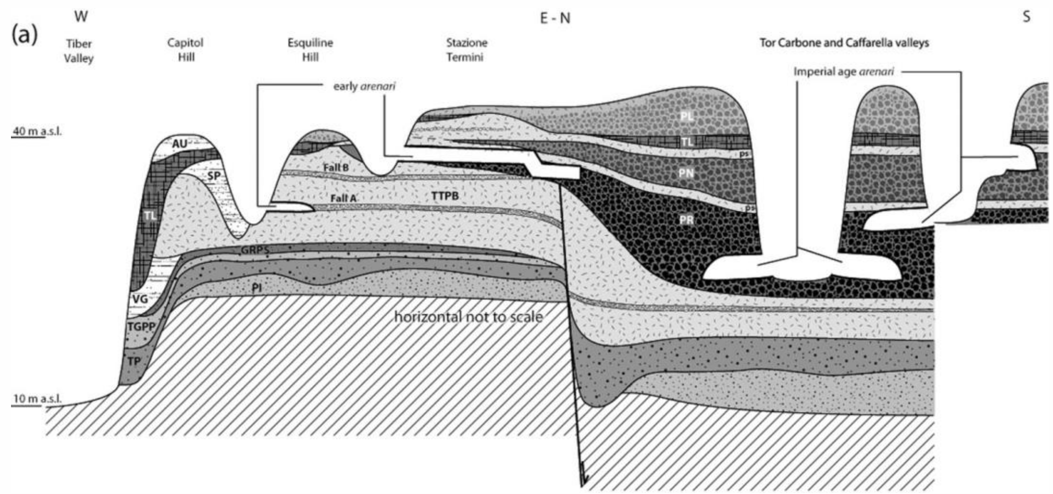




Peccerillo, 2005

Pozzolanic binders





Marra et al., 2016

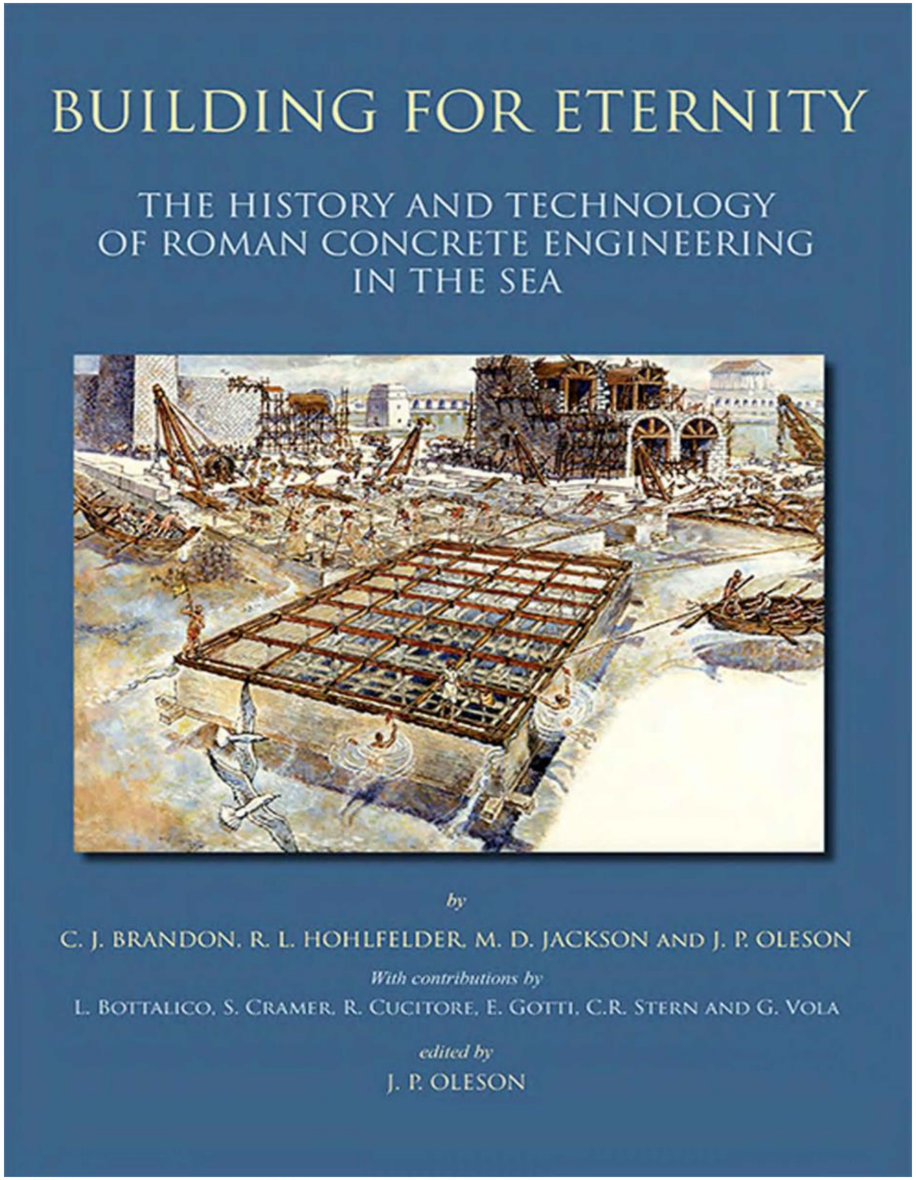
Pozzolanic binders

Marra et al., 2016

Pozzolanic binders

The physico-chemical and engineering characteristics of mortars used for the construction of Roman harbours are presently investigated in the frame of the ROMACONS project (Brandon et al. 2005, Oleson et al. 2006). Not only the outstanding properties and durability are confirmed, but surprisingly the tuffs used in the mortars of the harbor of King Herod in Caesarea Maritima (Israel) seem to have been transported all the way from the Bay of Naples.

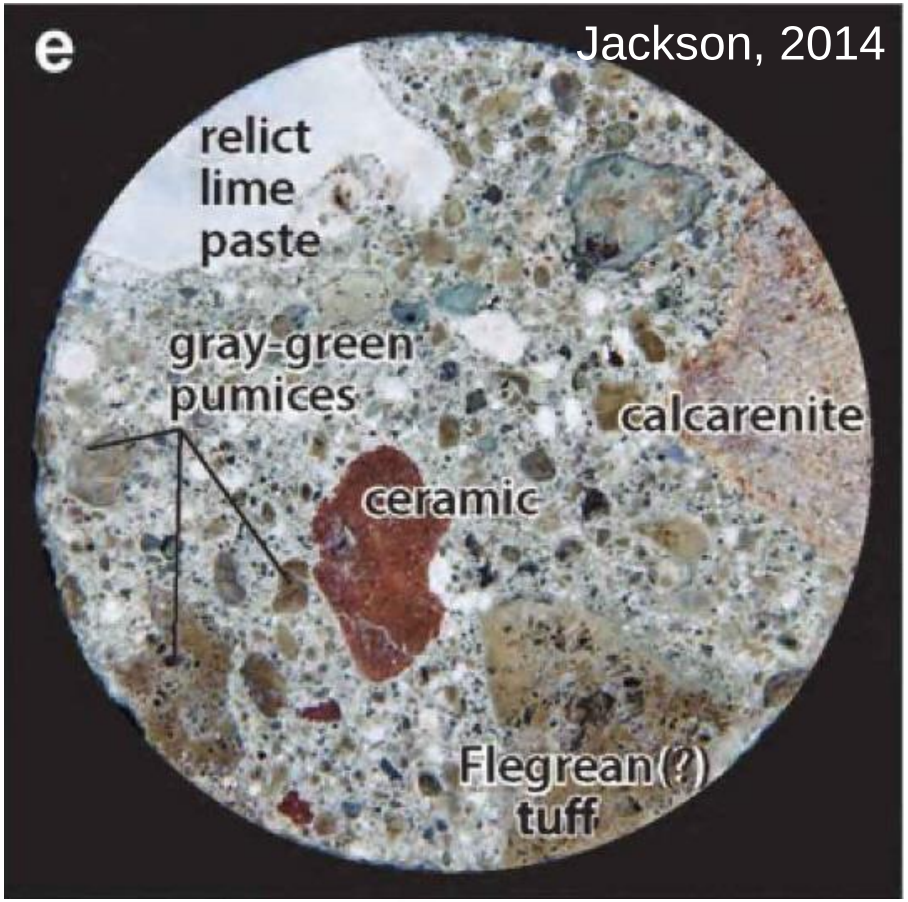
Pozzolanic binders



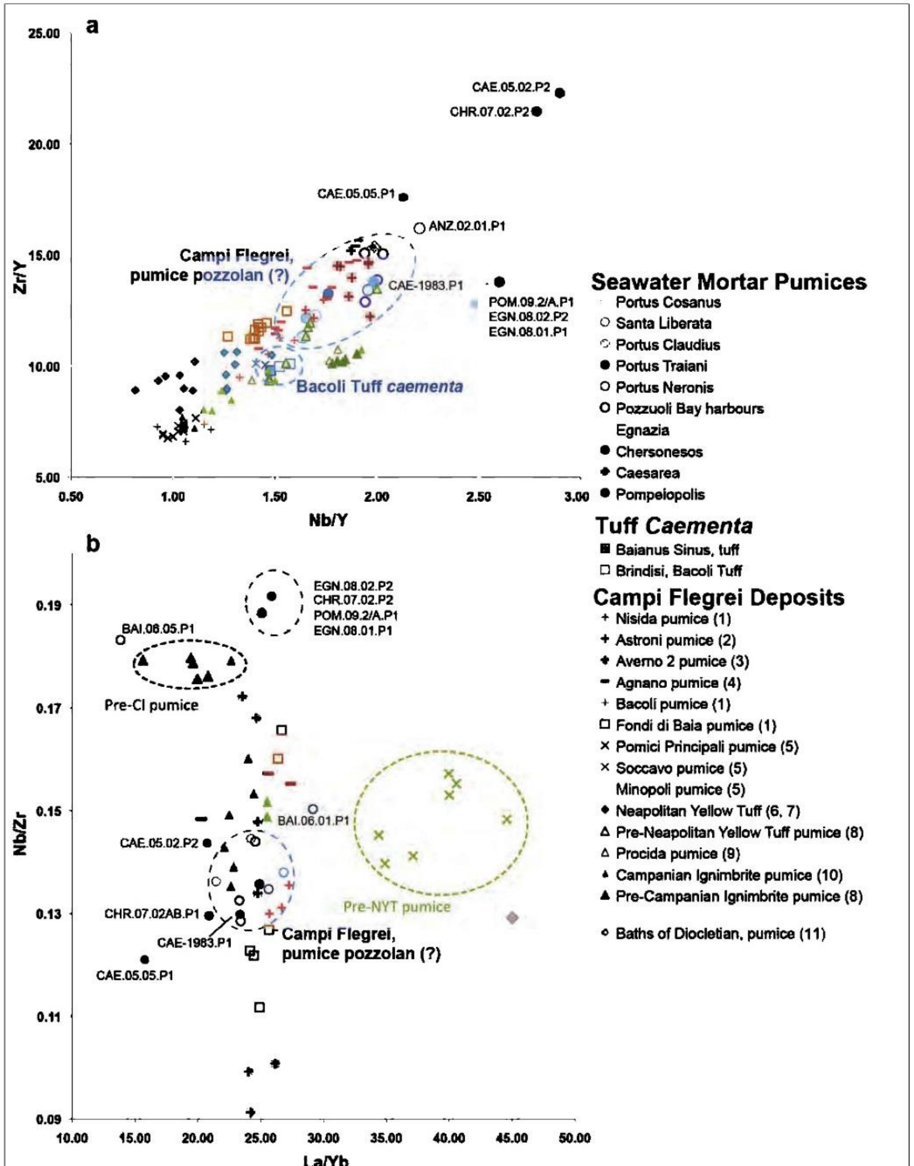
Pozzolanic binders

Caesarea Maritima, Israel

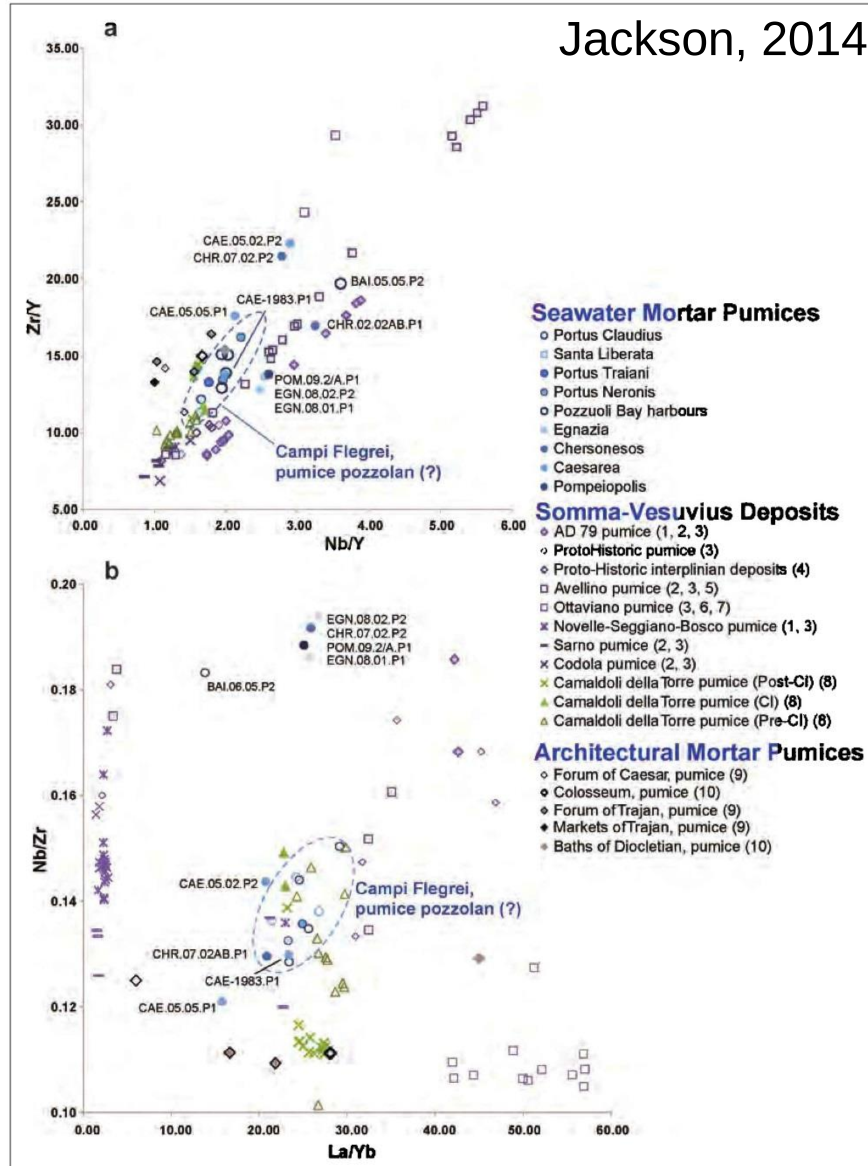
Pozzolanic binders



Pozzolanic binders



Jackson, 2014



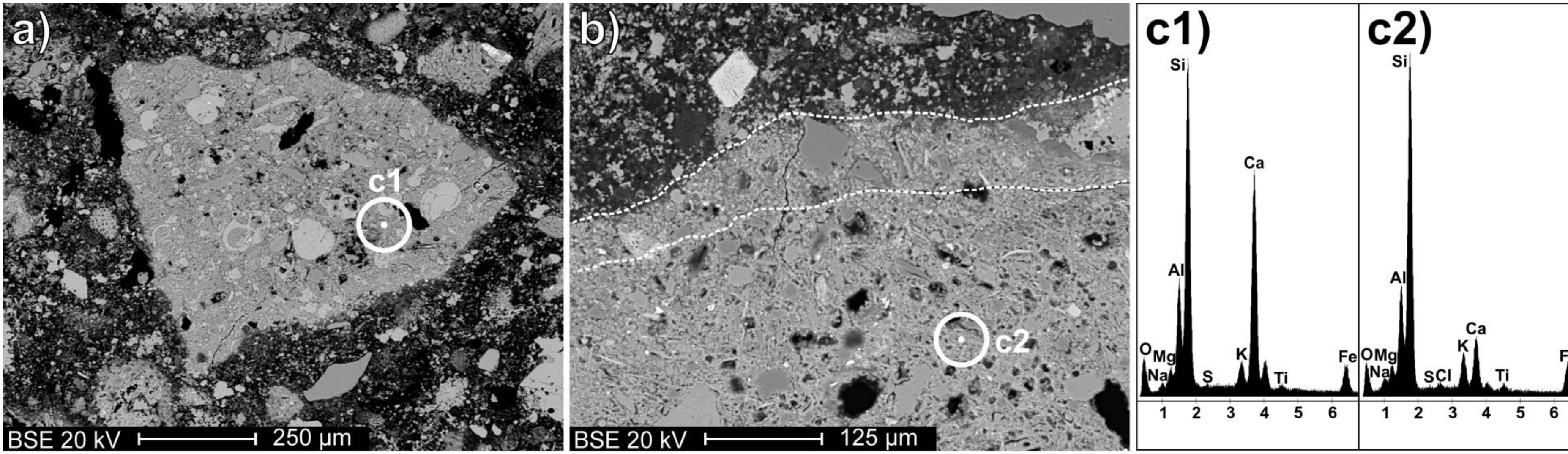
Pozzolanic binders

The Romans are known to have used all the known occurrences of zeolitic tuffs, including Santorini (Greece) and the volcanic tuffs present in the German Eifel area known as Trass. When volcanic sand was not available, finely ground pottery and ceramics was used to induce hydraulicity to the material, a technique that originated in Minoan Crete (Moropoulou et al. 2000).

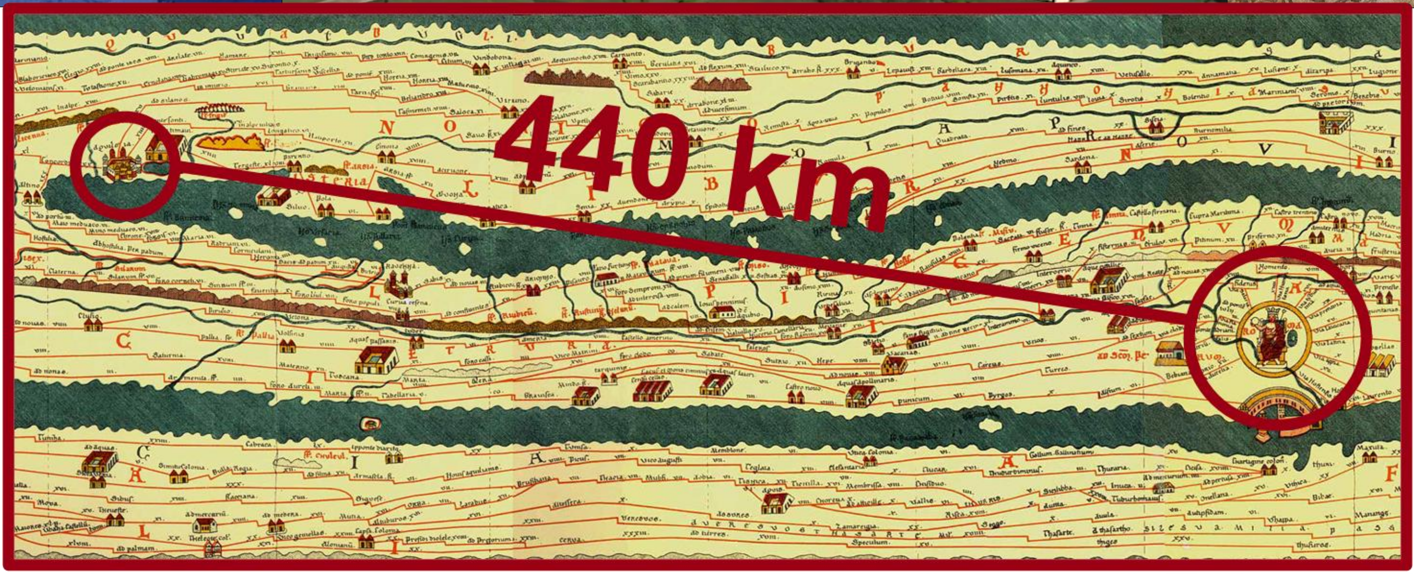
Cocciopesto

Pozzolanic binders

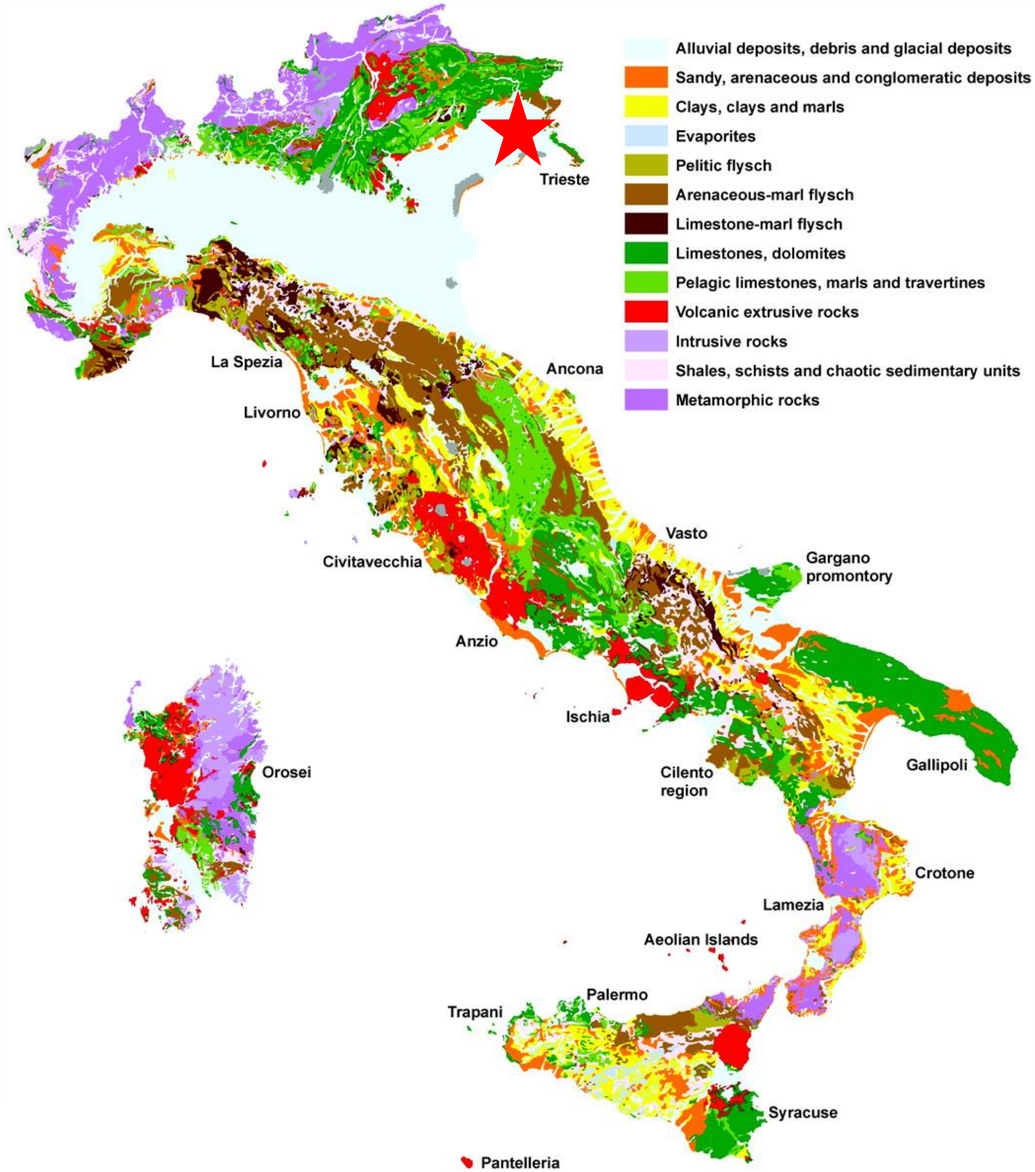
Cocciopesto



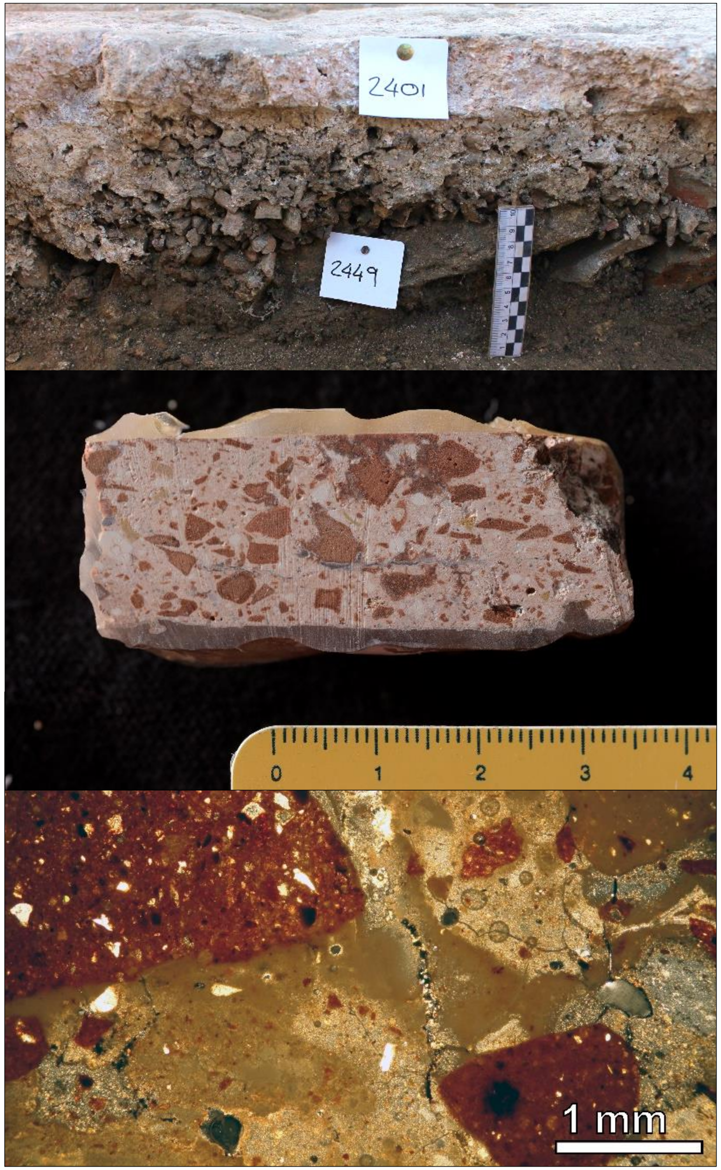
Pozzolanic binders



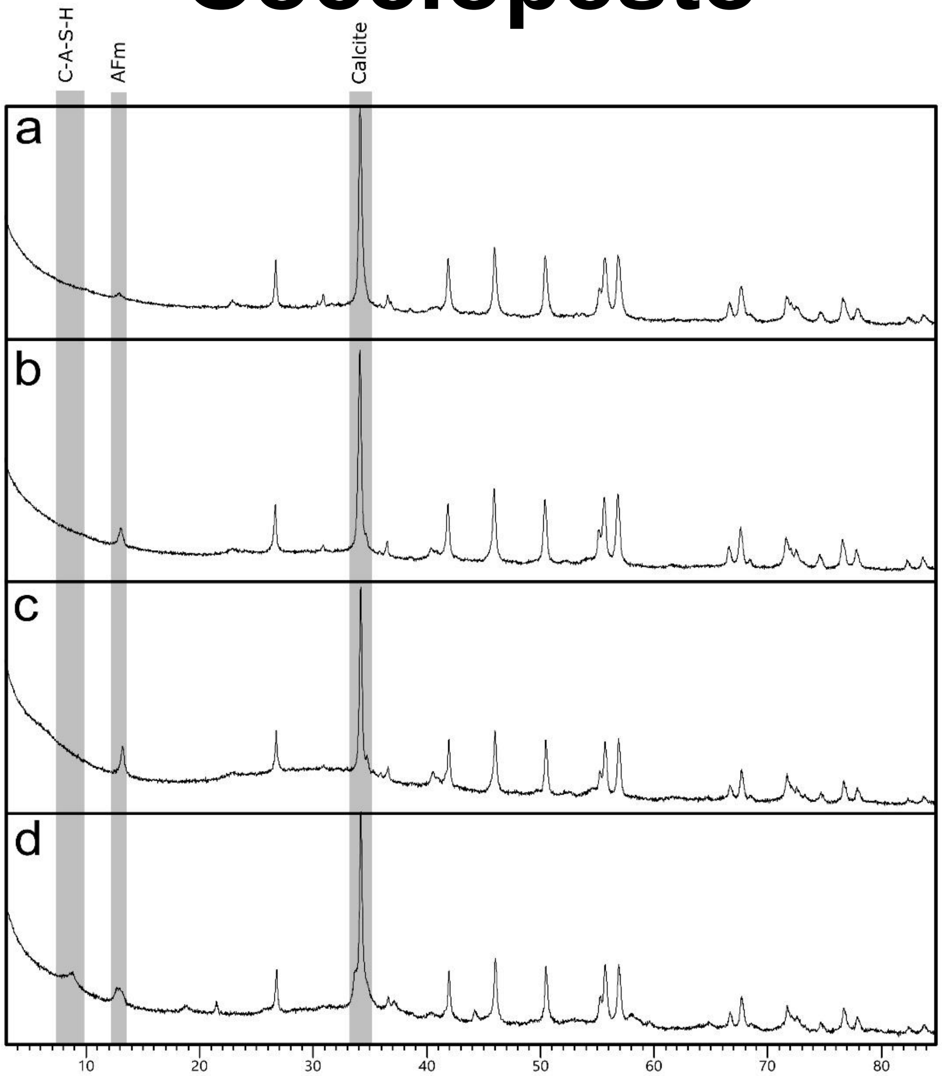
Pozzolanic binders



Pozzolanic binders

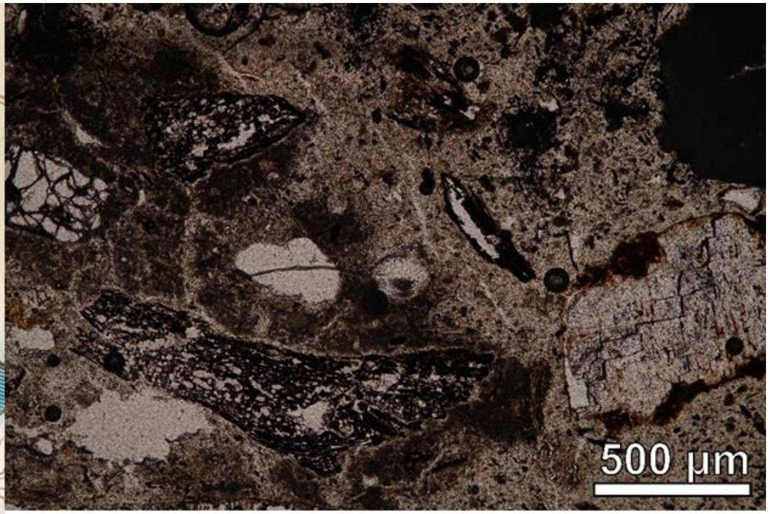


Cocciopesto

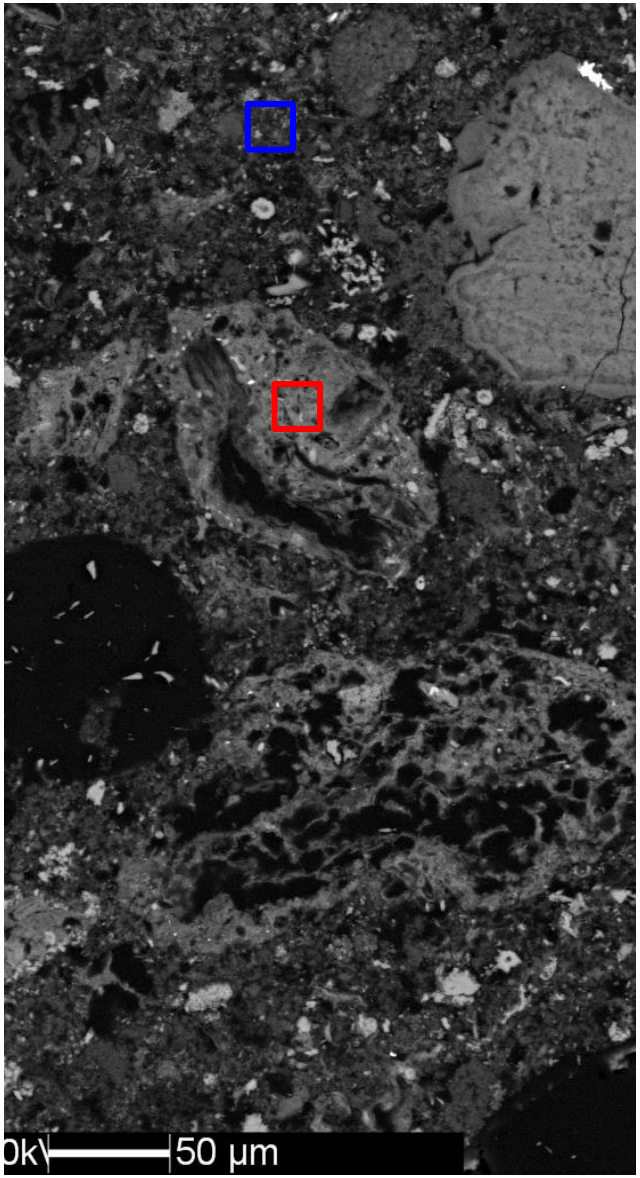


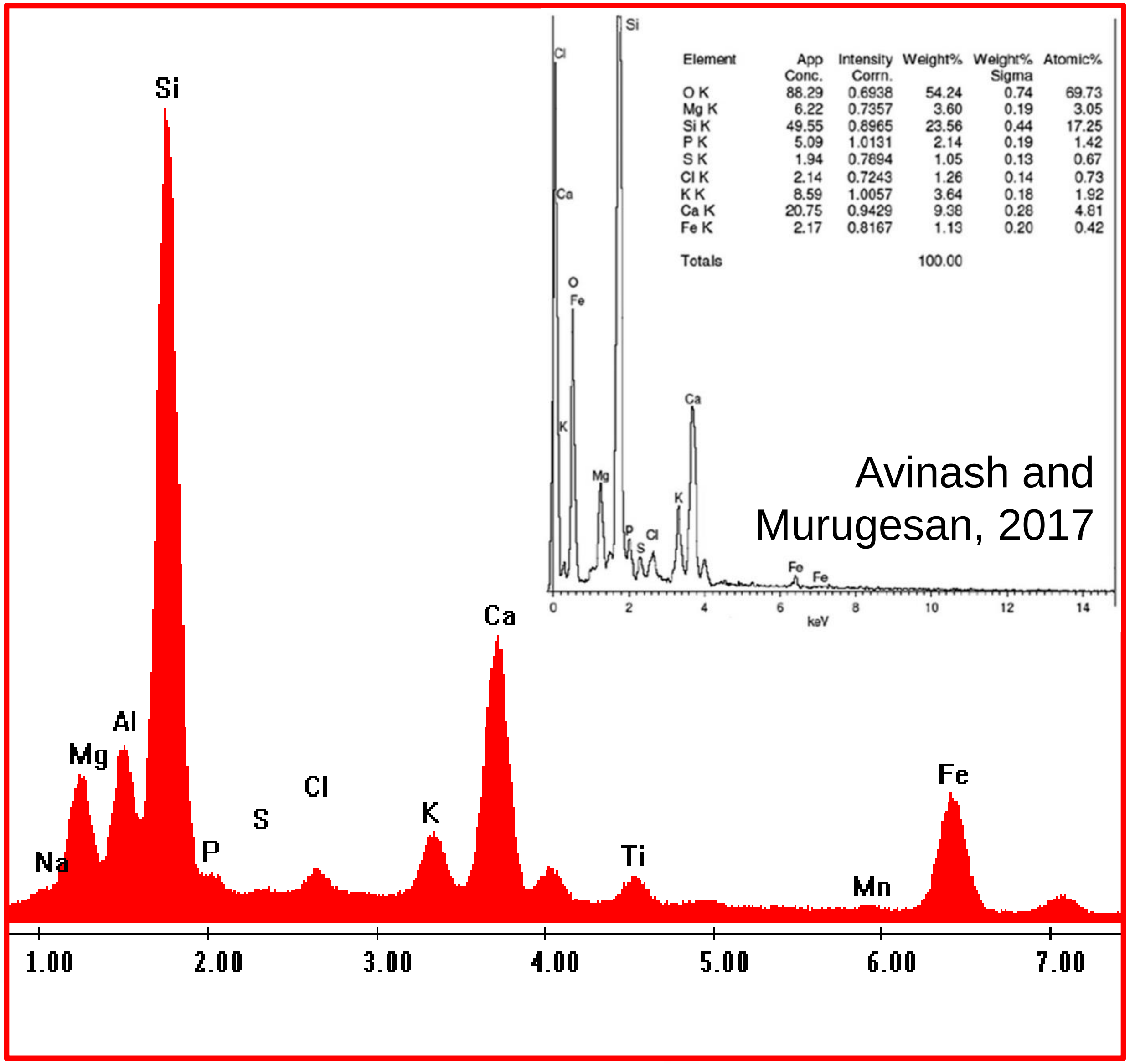
Ashes from organics combustion

Ashes from organics combustion



Pozzolanic binders



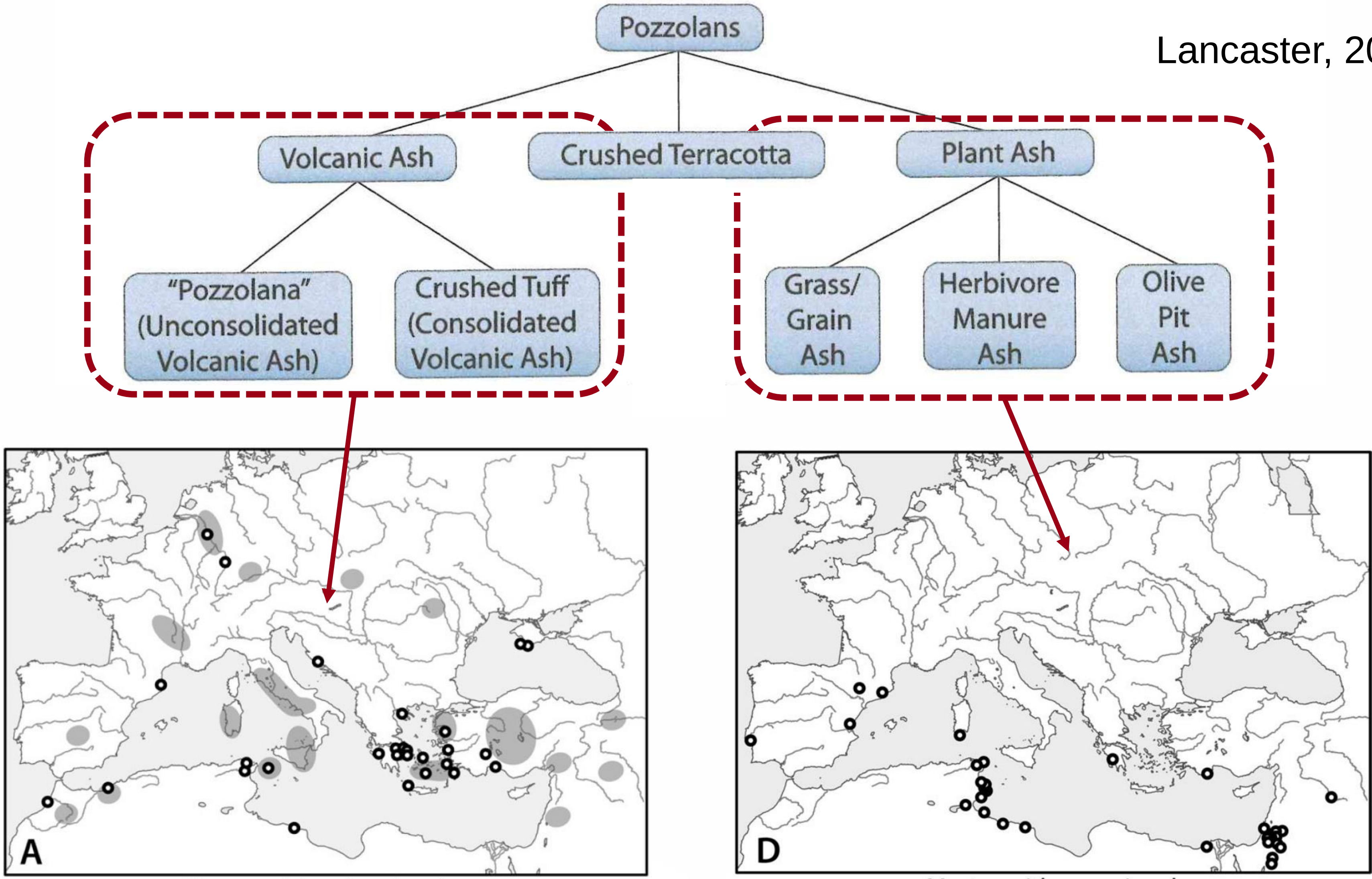


Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
O K	88.29	0.6938	54.24	0.74	69.73
Mg K	6.22	0.7357	3.60	0.19	3.05
Si K	49.55	0.8965	23.56	0.44	17.25
P K	5.09	1.0131	2.14	0.19	1.42
S K	1.94	0.7894	1.05	0.13	0.67
Cl K	2.14	0.7243	1.26	0.14	0.73
K K	8.59	1.0057	3.64	0.18	1.92
Ca K	20.75	0.9429	9.38	0.28	4.81
Fe K	2.17	0.8167	1.13	0.20	0.42
Totals			100.00		

Avinash and Murugesan, 2017

Pozzolanic binders

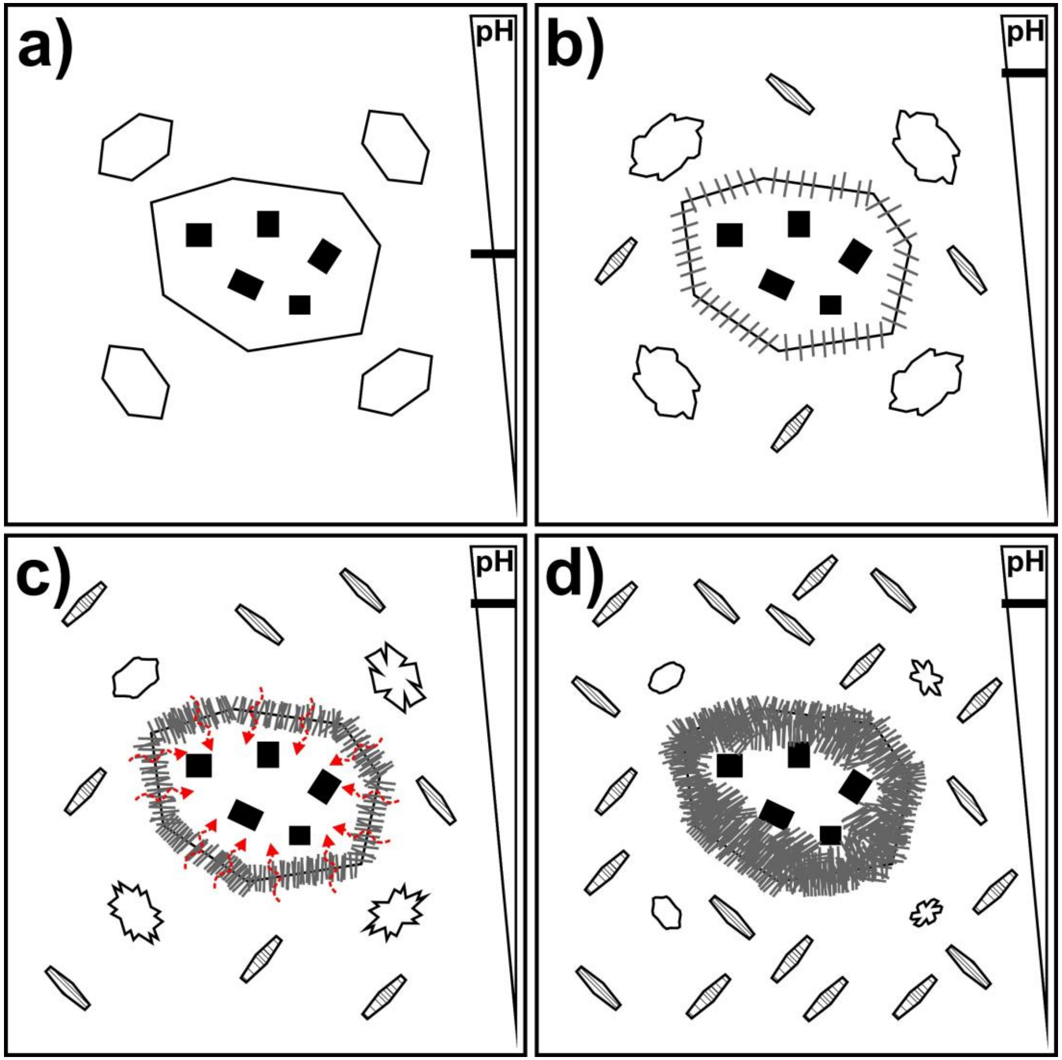
Lancaster, 2019



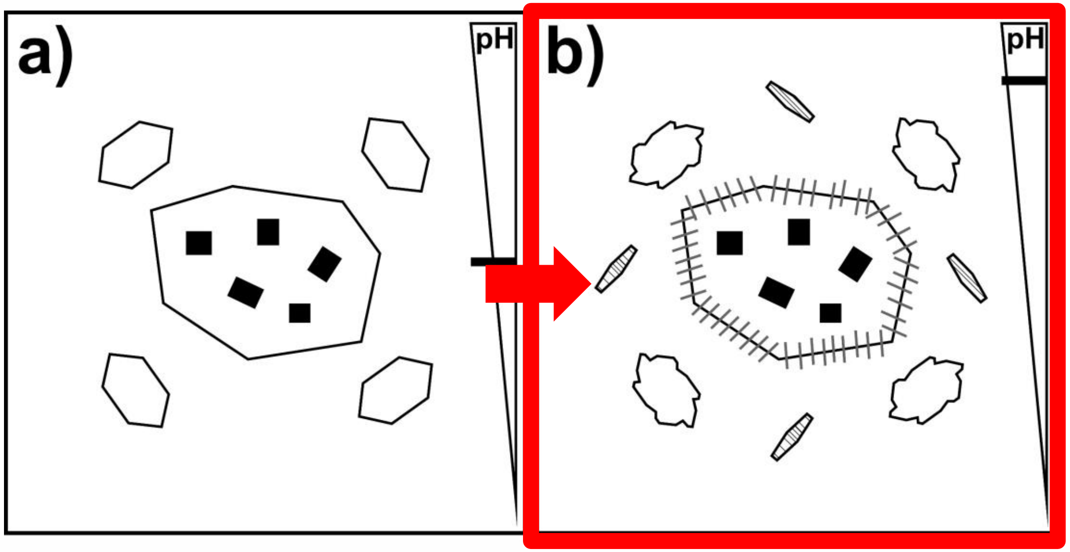
Mortar with volcanic ash

Mortar with organic ash

Reaction paths

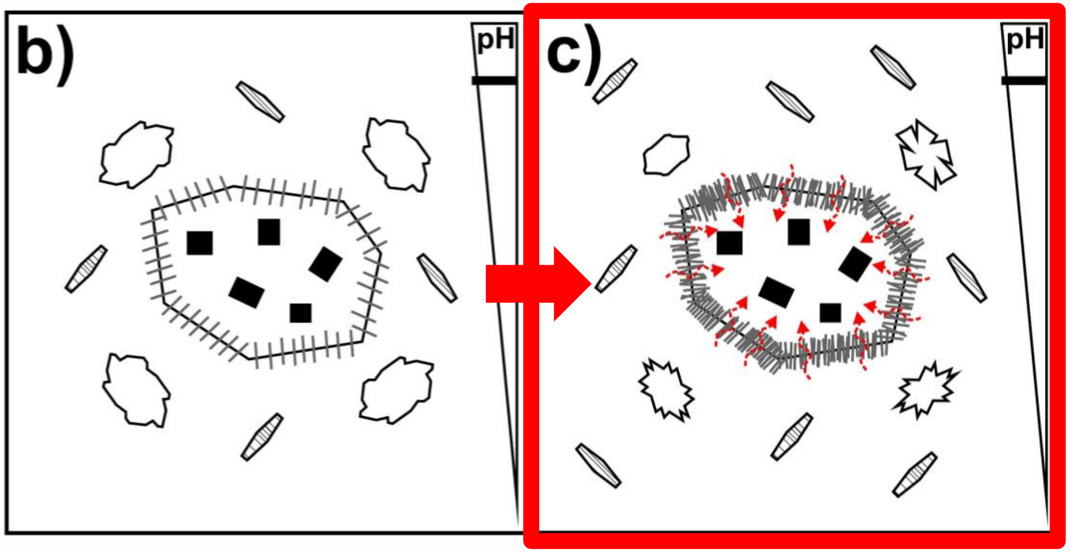


Reaction paths



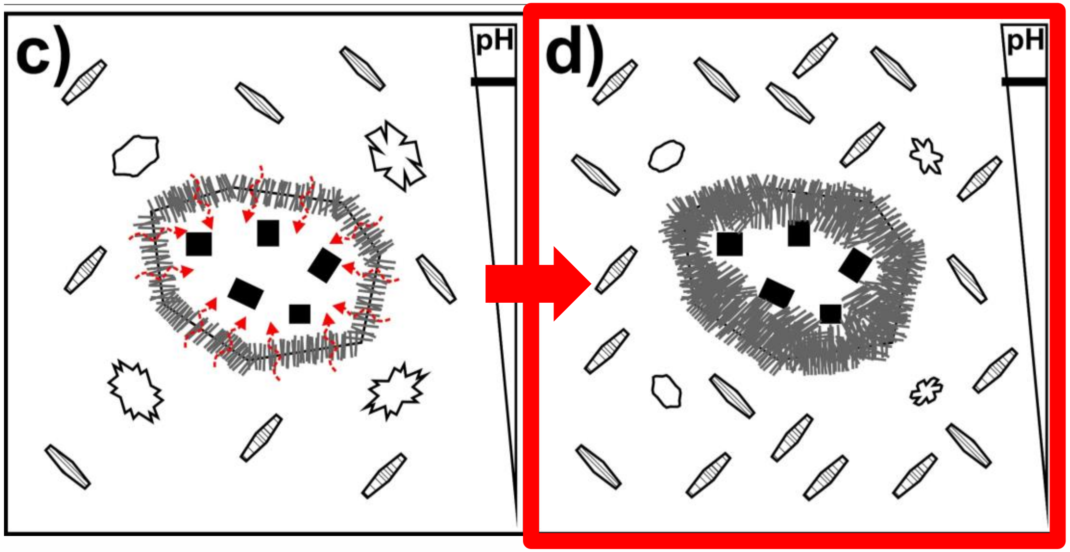
Initial dissolution period. $Ca(OH)_2$ dissolution produces an alkaline solution saturated in Ca and hydroxyl ions, with a pH over 12. At high pH values silica solubility increases, causing the pozzolana products to dissolve according to hydrolysis processes at the mineral-water interface. Dissolution occurs at first in far-from-equilibrium, highly undersaturated condition, with a progressive slow-down of the reaction until reaching of $Ca(OH)_2$ saturated conditions. During this phase, a layer of C-S-H phases replaces the external dissolved layers of the pozzolan grains, covering the unaltered grain core, while it is believed the C–A–H phases precipitate far from the pozzolana grains due to the greater diffusivity of alumina due to the smaller electric charge and lesser oxygen content.

Reaction paths



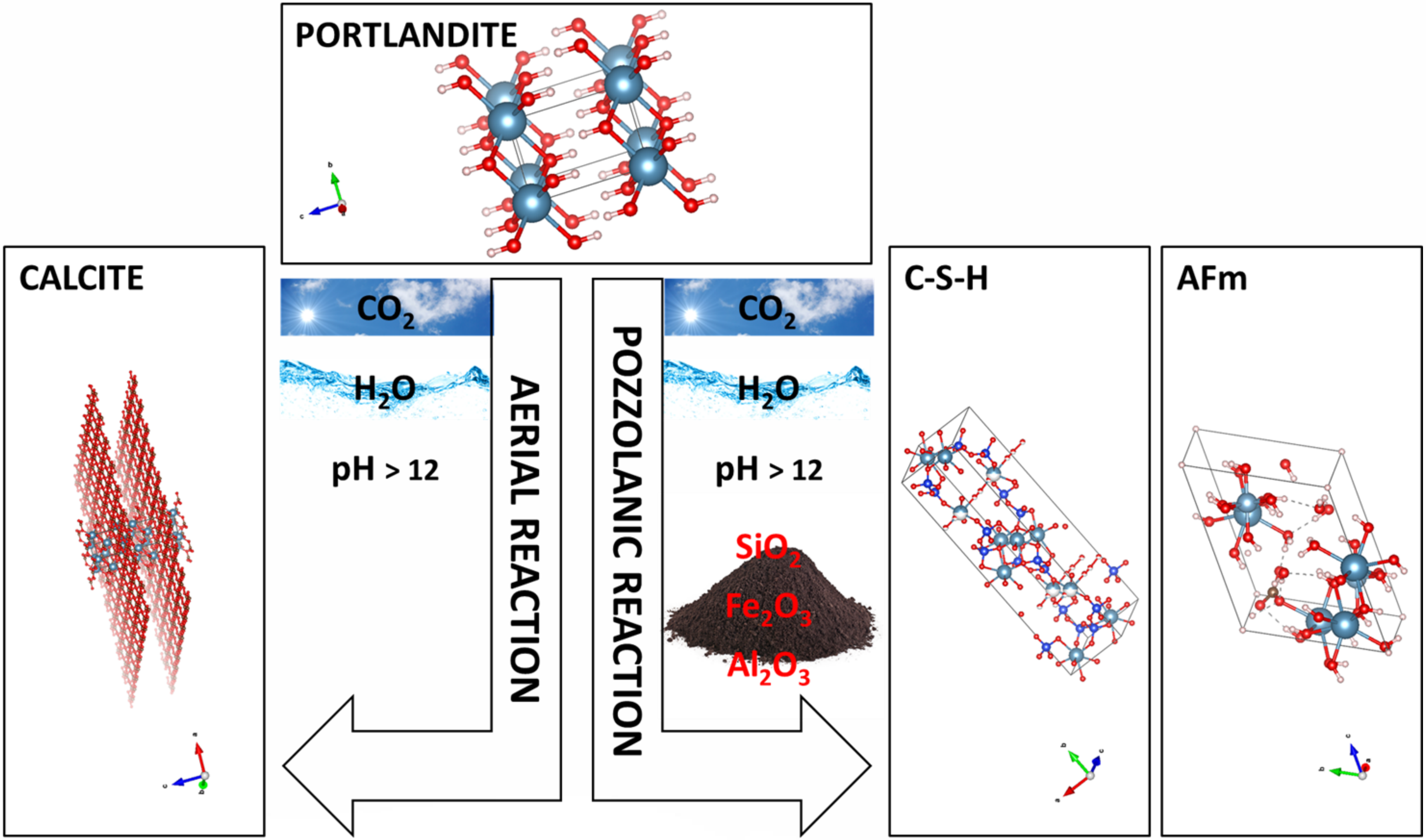
Induction period. After the initial dissolution period, a dormant phase occurs, linked to the previously described formation of a protective layer enclosing the reacting pozzolana particles. Such periods terminates after the rupture of the passivating layer, related to its semi-permeable characteristics, which allows osmosis of water from the outer to the inner, more concentrated solution, and rupture due to the osmotic pressure.

Reaction paths



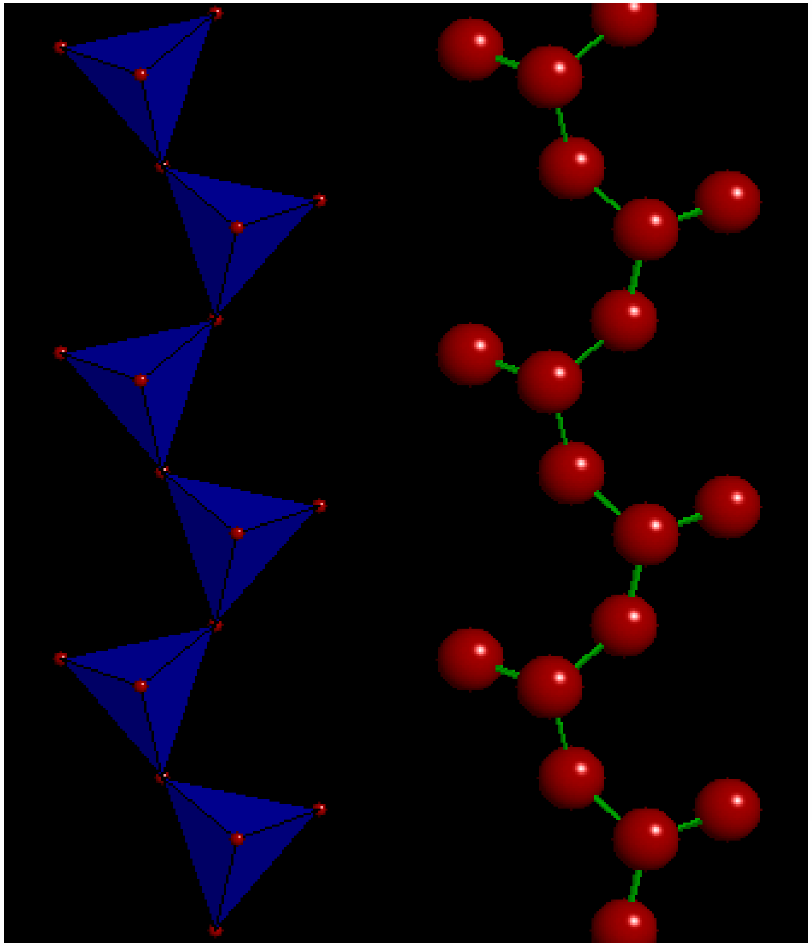
Main reaction period. The rupture of the passivating layer causes a massive triggering of nucleation and growth of reaction products. Such exponential reaction rate increase is short-lived due to the rapid transition toward a diffusion-controlled regime. Other factors contributing to the slow-down of the reaction are the consumption of the smaller, more reactive, particles and a lack of space or densification of the C–S–H rim that hinders the free growth of the hydrate particles. From this moment on, the reaction process proceeds indefinitely until total drying of the system or total consumption of the reactants.

Pozzolanic binders

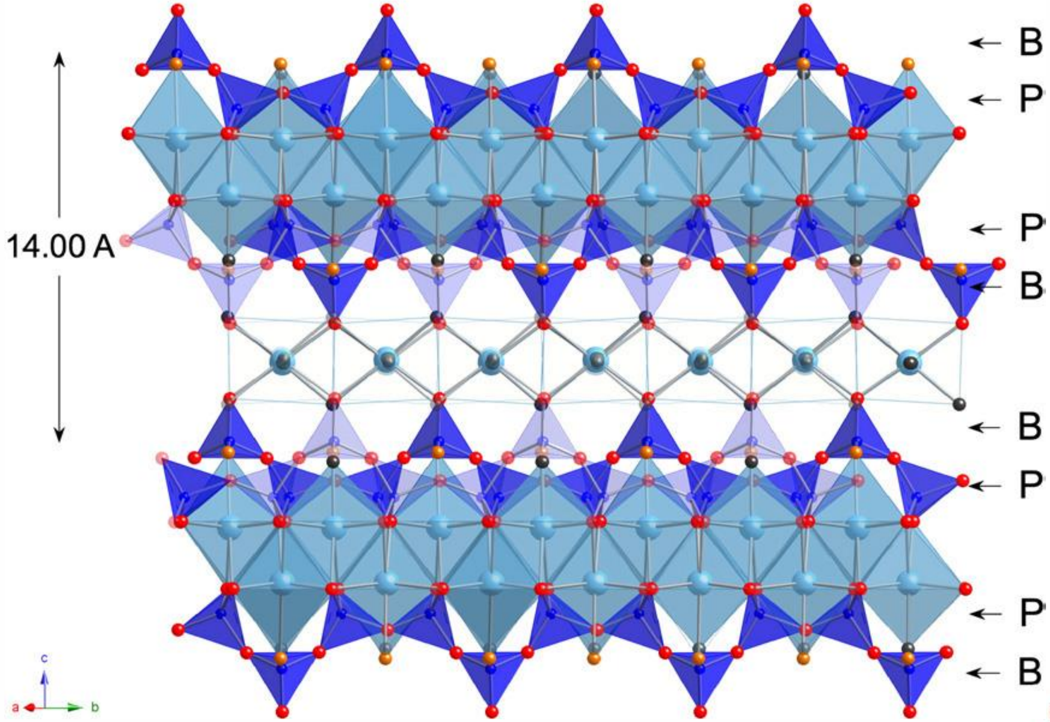


C-S-H crystal structure

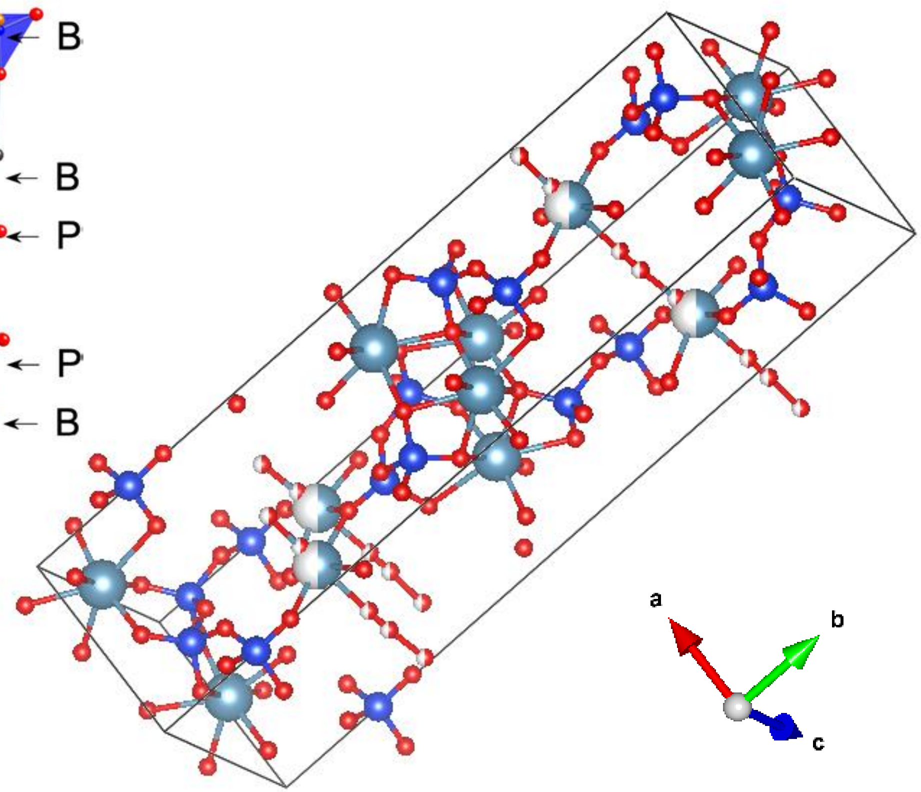
- **Inosilicates** (chain silicates).
- (**SiO_3**) radical.
- Orthorhombic-monoclinic-triclinic symmetry.
- Ca/Si ratio: between 0.8 and 2.3.
- Complete solid solution between tobermorite (Ca/Si: 0.8) and jennite (Ca/Si: 2.3).
- Variable amount of structural water (variable basal d-spacing).



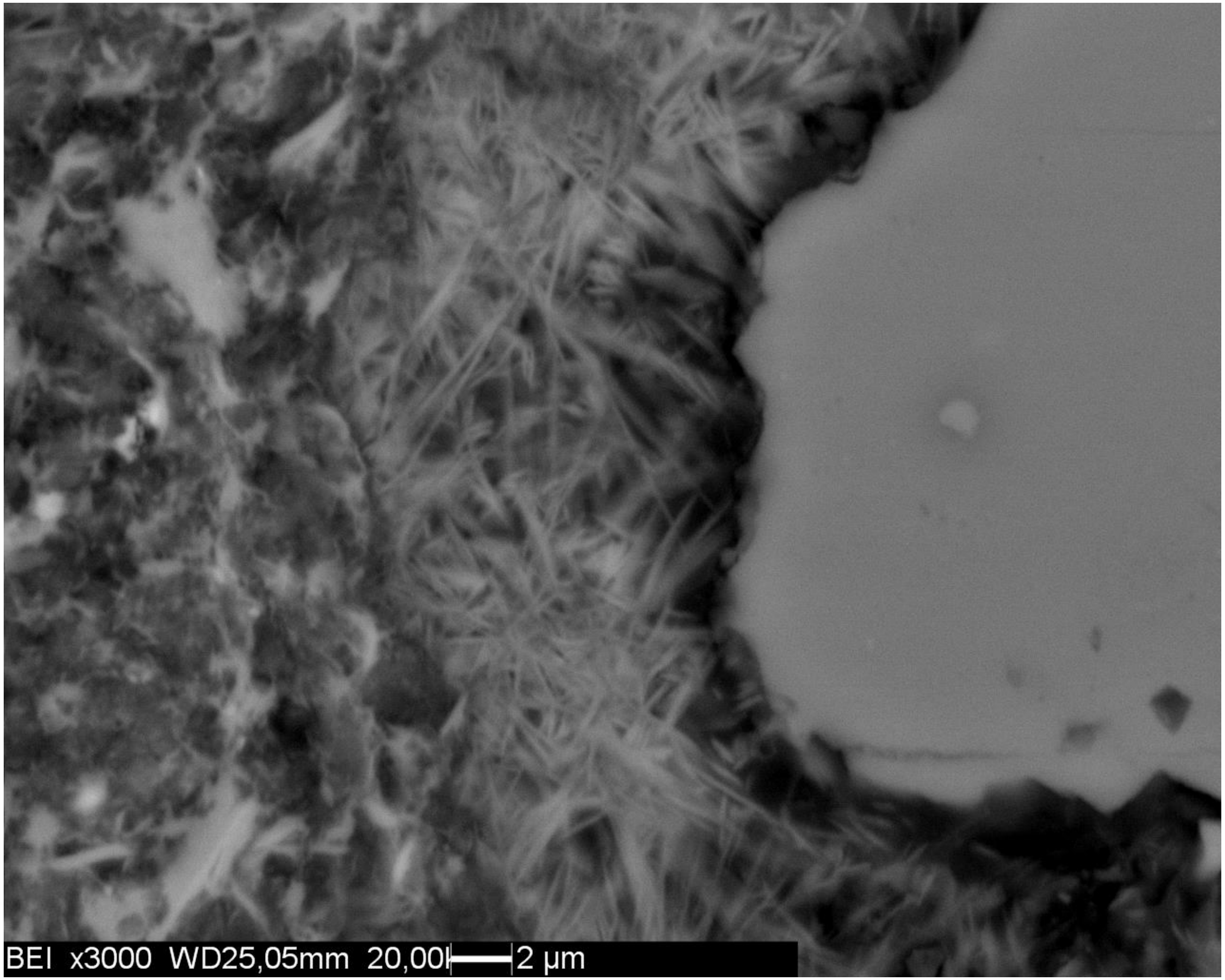
C-S-H crystal structure



Richardson, 2008



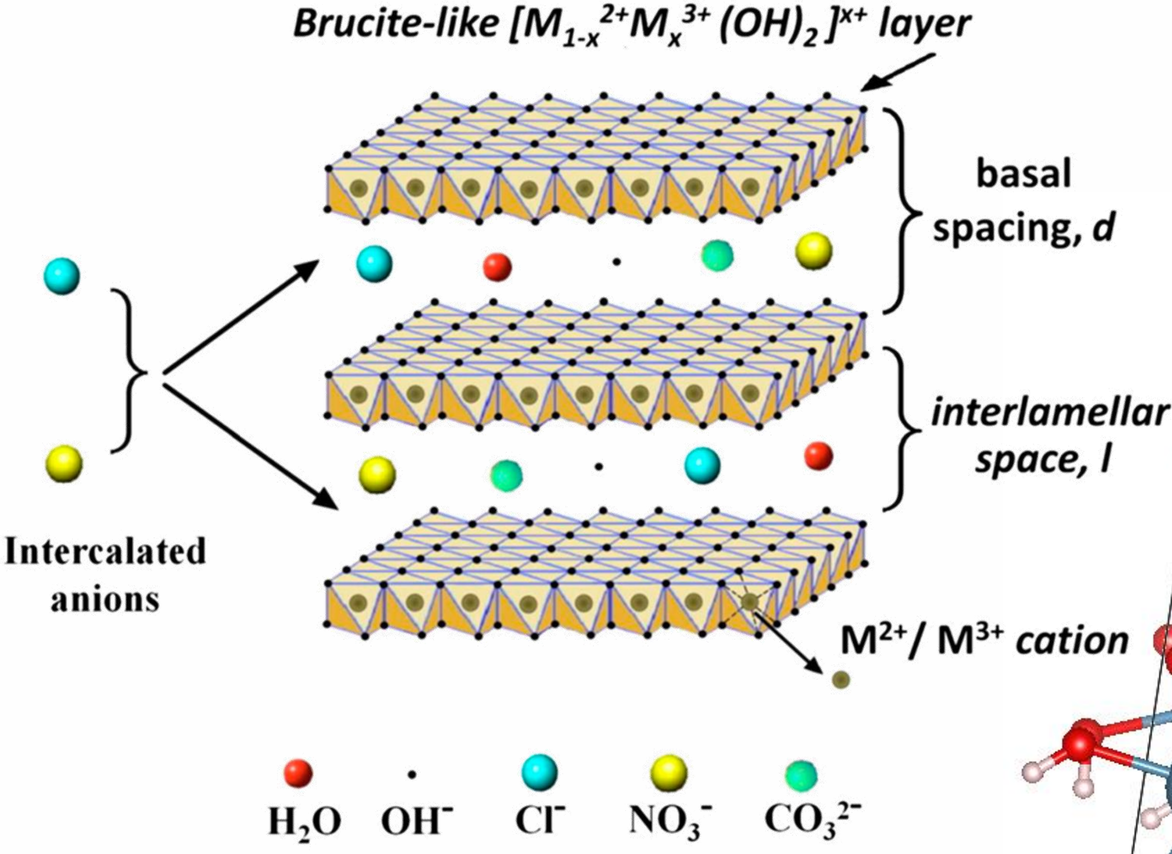
C-S-H morphology

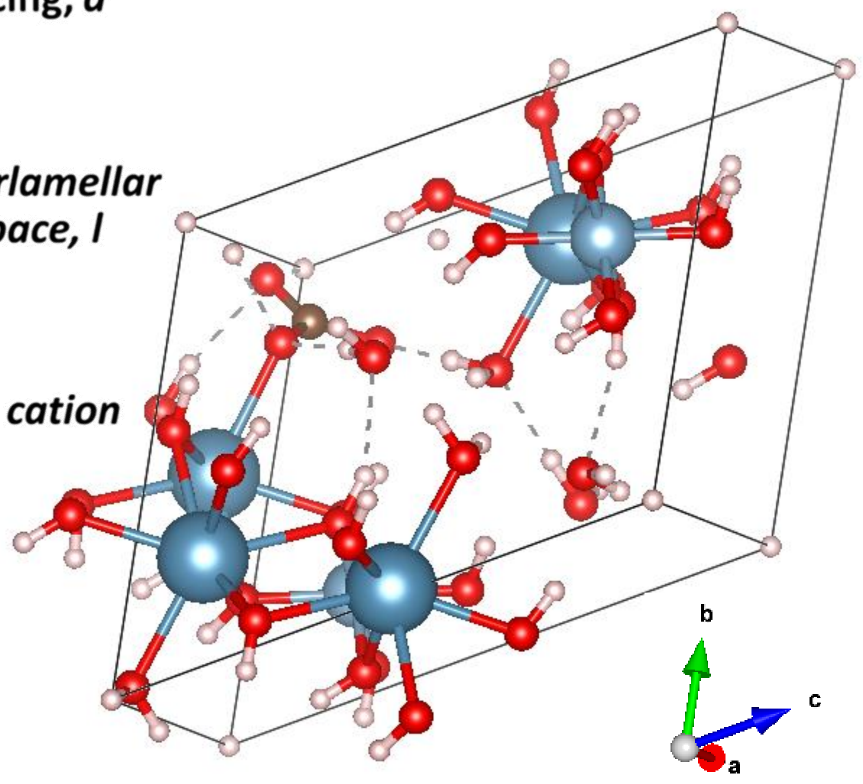


AFm crystal structure

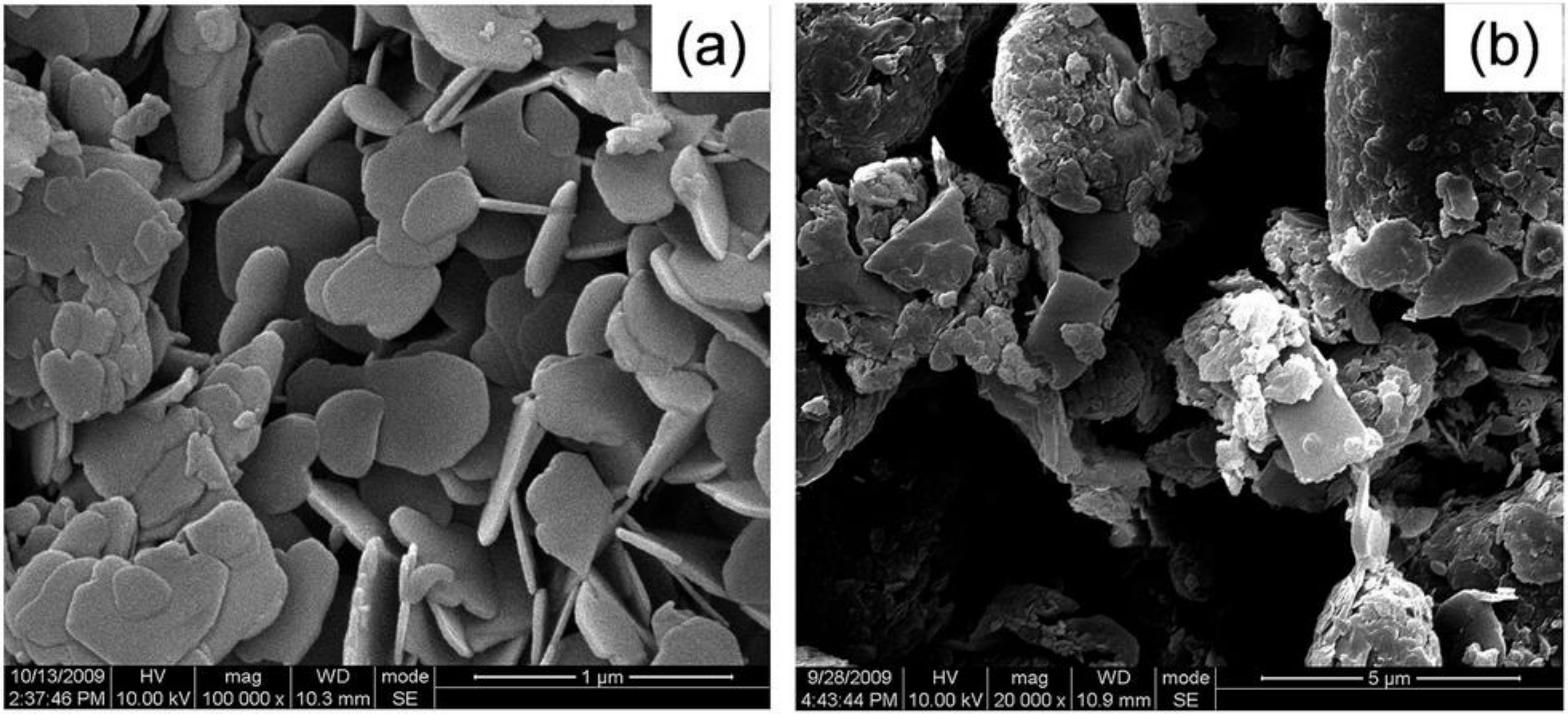
- **Layered double hydroxides (LDH)**.
- Hexagonal symmetry.
- Brucite-like structures.
- Layers of cations with octahedral coordination.
- Substitution of divalent ions (Ca^{2+}, Mg^{2+}) with trivalent ions (Al^{3+}, Fe^{3+}).
- Anions in the interlayer (OH^-, CO_3^{2-}, SO_4^{2-}) to compensate charge.
- Most common LDH's: hydrotalcite (Mg, Al), hydrocalumite (Ca, Al), calcium monocarboaluminate.
- Ample solid solutions.

AFm crystal structure





AFm morphology



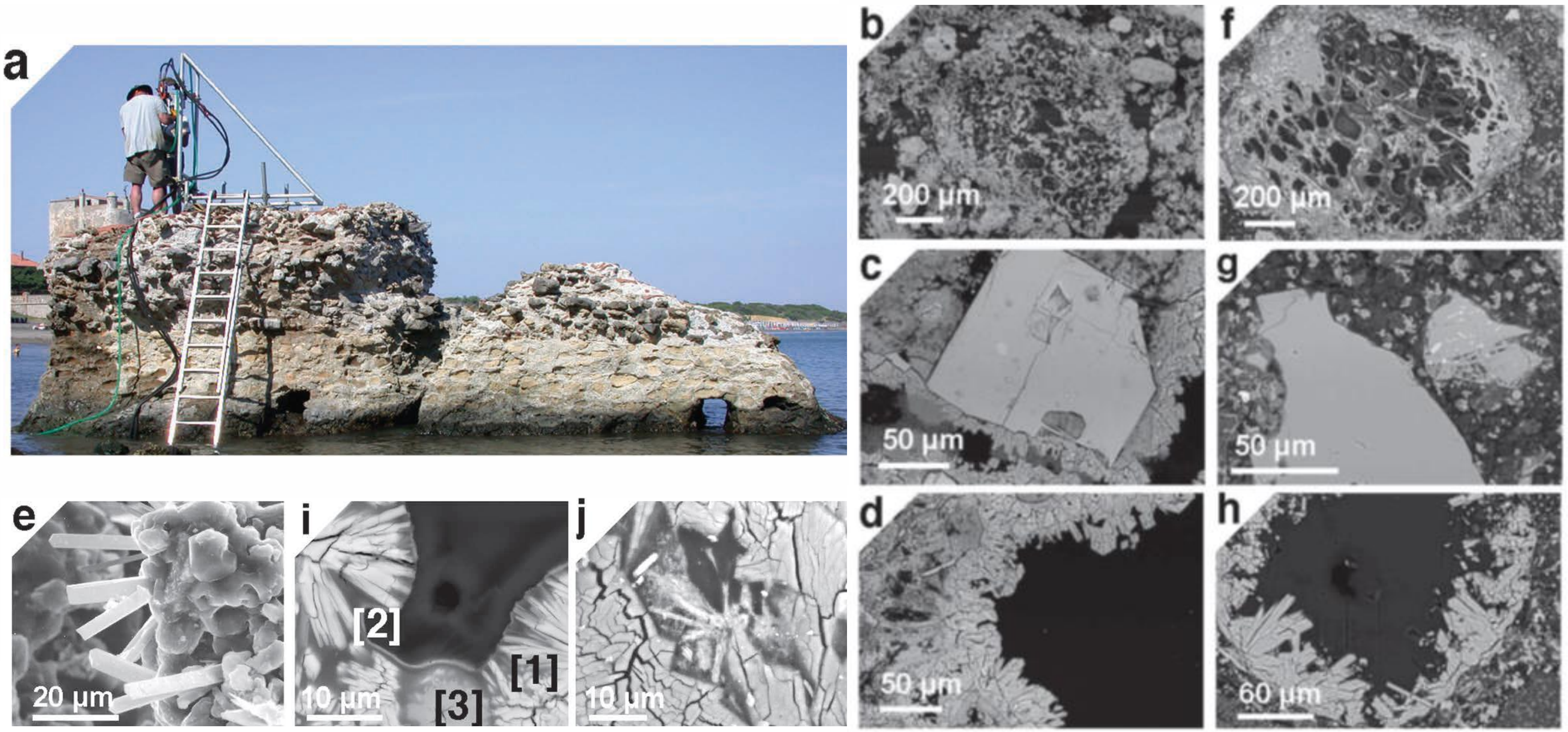
Portus Cosanus pier, Orbetello, Italy

American Mineralogist, Volume 102, pages 1435–1450, 2017

Phillipsite and Al-tobermorite mineral cements produced through low-temperature water-rock reactions in Roman marine concrete

Marie D. Jackson[1,*], Sean R. Mulcahy[2], Heng Chen[3], Yao Li[4], Qinfei Li[5], Piergiulio Cappelletti[6], and Hans-Rudolf Wenk[7]

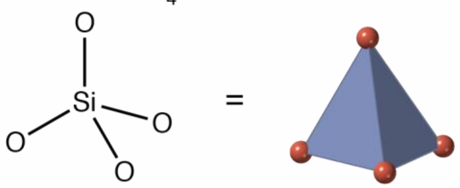
Jackson et al., 2017



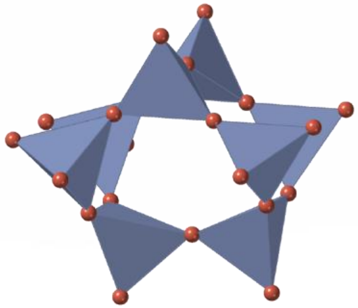
ZEOLITES

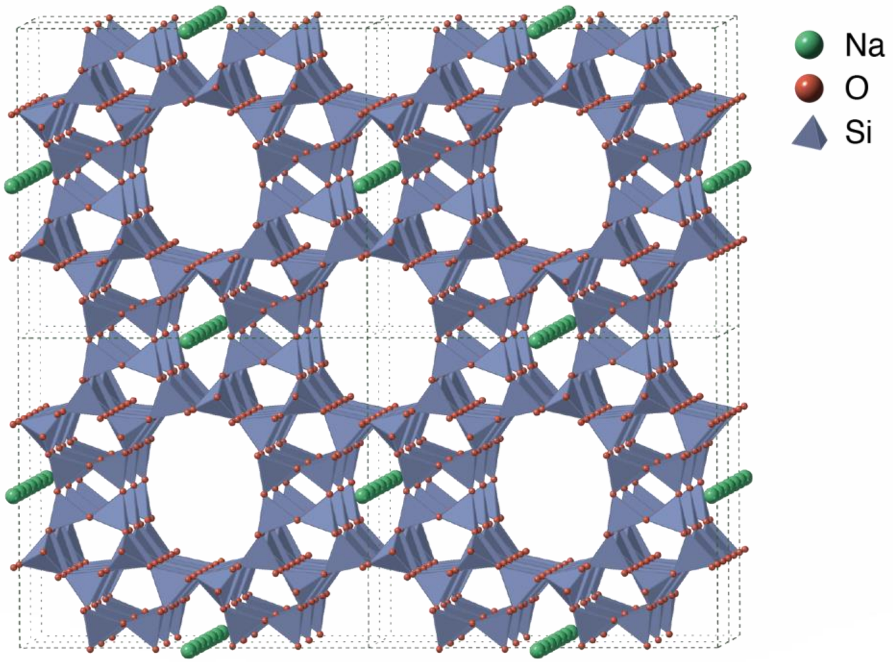
- Tectosilicate scaffold (Si, Al) and Na^+, K^+ and H_2O ions in varying amounts.
- The tetrahedra form a continuous network of channels and cavities with variable dimensions.
- H_2O is weakly bound through hydrogen bonds to the anions of the lattice. It can leave the structure by heating through the channels, leaving the structure without causing its collapse.

SiO_4 tetrahedron



secondary building unit (cage)





Mordenite (MOR framework)

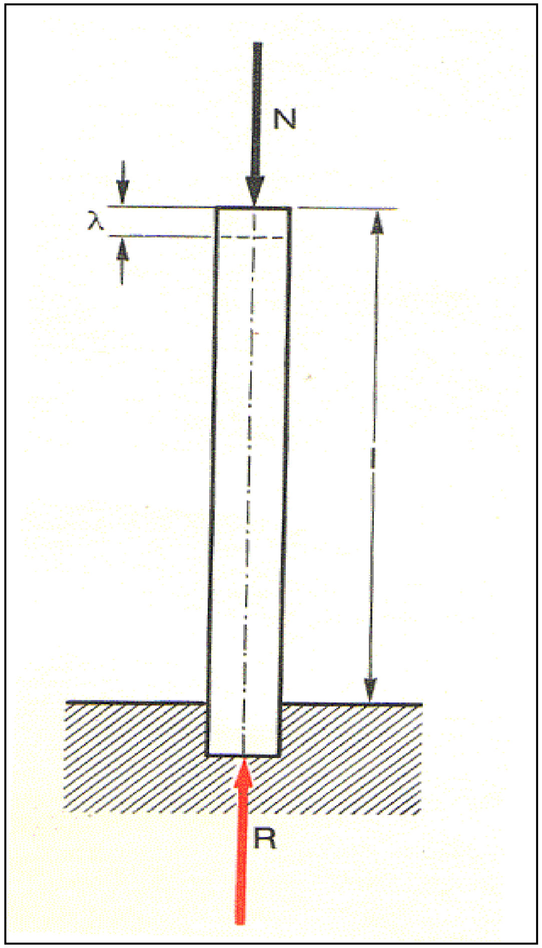
ZEOLITES

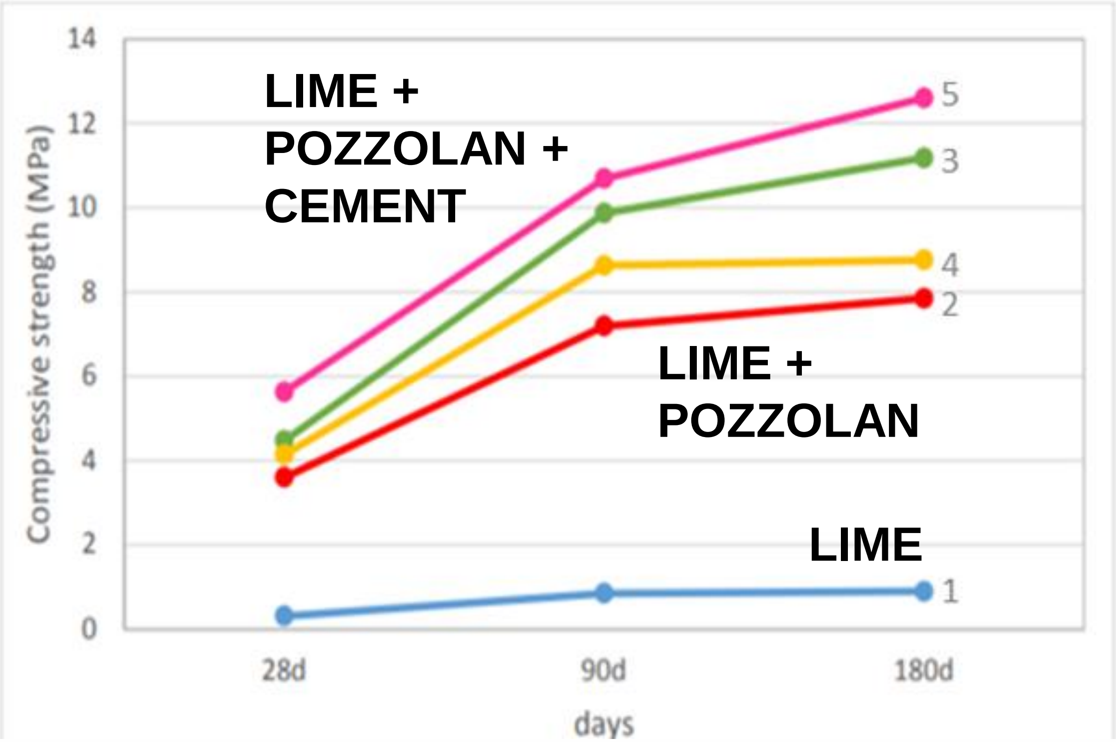
Analcime
$NaAlSi_2O_6 \cdot (H_2O)$
Equidimensional

Clinoptilolite
$(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36} \cdot 12H_2O$
Tabular

Mordenite
$(Ca,Na_2,K_2)Al_2Si_{10}O_{24} \cdot 7(H_2O)$
Fibrous

Compressive strength





THANK YOU FOR YOUR ATTENTION!