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Contribution to the knowledge of ancient Roman seawater concretes: Phlegrean pozzolan adopted in the construction of the harbour at Soli-Pompeiopolis (Mersin, Turkey)

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Abstract

This study deals with the characterization of ancient seawater concretes from the Roman harbour of Soli-Pompeiopolis, 1st century B.C., at Mersin in Turkey, drilled by the ROMACONS (Roman Maritime Concrete Study) team in 2009. This research activity was performed in collaboration with the Laboratories Department of CTG Italcementi Group and the Earth Sciences Department of the University “Federico II” of Naples. Results confirmed that the Roman engineers extensively used coarse tuff aggregate, lime hydrated in seawater, and pozzolanic volcanic fine sand, the so-called *pulvis puteolanus* of Vitruvius’s treatise *De Architectura* (1st century B.C.). The typical mineralogical association of phillipsite > chabazite > analcime, in particular points out the provenance for the tuff aggregate from the Yellow Neapolitan Tuff (NYT) formation, which is connected to the Campi Flegrei volcanic activity, dated back to 15.000 years ago. As far as the fine pozzolanic sand, of which just some scoria relics have been observed, can be ascribed to the same formation, or, probably, to the *pozzolan* stricto sensu pyroclastic flow from the Campi Flegrei area, as well. EDS microanalyses of different phillipsite crystals showed that the content of major alkaline and alkaline-earth metals was very close to those of phillipsite crystals from NYT, with K higher than Na and Ca, as previously reported in the literature. This fact clearly attests that zeolites were not involved in cation exchange processes within the seawater, despite of their long time curing - approximately two thousand years - in the marine environment.

Key words: Ancient Roman harbours; hydraulic seawater concretes; pozzolanic mortars; *pulvis Puteolanus* of Vitruvius; ROMACONS project; Yellow Neapolitan Tuff (NYT).

Introduction

This paper deals with the characterization of ancient seawater concrete cores from the Roman harbour at Soli-Pompeiopolis (Mersin, Turkey), drilled by the ROMACONS (Roman Maritime Concrete Study, see Oleson et al., 2004; 2006; Hohlfelder et al., 2007) team during last field campaign of August 2009 (Brandon et al., 2010). This activity research was performed in collaboration with the Laboratories Department of CTG Italcementi Group and the Earth Sciences Department of the University "Federico II" of Naples (Vola et al., 2010a).

Since 2002 the ROMACONS team has drilled several Roman concrete maritime constructions along the Mediterranean seacoast. Standard core drilling procedures had been adopted in order to take intact stratigraphic samples (0.09 m in diameter and up to 5.8 m long) which were then analysed in the laboratories of CTG Italcementi with a comprehensive set of physical, mechanical, chemical and mineralogical protocols (Oleson et al., 2006; Brandon et al., 2005; 2008; Jackson et al., 2010a; 2010b, in press; Vola et al., 2010b; 2011). The first group of cores was drilled in 2001-2008 from harbours along the Italian peninsula, from the ports of Claudius and Trajan in Ostia Antica, Nero at Anzio, Cosa and Santa Liberata breakwaters on the Tuscany coast, Baia in the Gulf of Naples, and Egnatia on the Adriatic coast close to Brindisi. The second group, drilled from 2005-2008, comes from more distant harbours, such as at Caesarea Palestinae in Israel, Chersonisos in Crete, and Alexandria in Egypt (Brandon et al., 2005; 2008; Hohlfelder et al., 2007) (Figure 1).

The characteristics of the ancient concretes were compared with a reproduction *pila* constructed in Brindisi harbour by the ROMACONS group in 2004, by mixing the lime-based mortar with a pozzolanic powdered tuff-ash from Bacoli (Pozzuoli, Naples). They used the same tuff-ash uncrushed, as the concrete aggregate, casting them in seawater within an appropriate formwork. The resulting concrete, drilled after 6, 12, 24, 42, and 60 months curing, was very similar to the ancient ones from a chemical and a physical-mechanical perspective (Hohlfelder et al., 2005; Oleson et al., 2006; Gotti et al., 2008), even if the microstructural fabric was apparently very different (Jackson et al., 2010a, in press).

These studies confirmed that the Roman engineers extensively used coarse tuff aggregate, the so-called *caementa*, lime hydrated in seawater, and pozzolanic volcanic fine sand, which is the *pulvis Puteolanus* of Vitruvius, from Campi Flegrei volcanic district (de Gennaro et al., 2000).

Objectives of this work are to improve the knowledge of Roman construction techniques by means of detailed microstructural and compositional examinations of the cementitious binding matrix, and aggregates, to point out the provenance of raw materials, mix-designs proportioning, and, finally, aspects related to the extraordinary durability of ancient concretes in the marine environment.

The history of Roman harbour at Soli-Pompeiopolis

To the west of Mersin, on the south-east Mediterranean coast of Turkey, lie the ruins of the port city of Soloi or Soli-Pompeiopolis, now surrounded by the modern town of Mezitli. The city has a long maritime history. Excavations of the mound beside the Roman-era harbour have revealed Hittite and Late Bronze Age occupation levels (Bing, 1968: 108-13, 117-18; Yağcı, 2001, 159-65; cf Yağcı, 2000; 2001; 2002; 2003a; 2003b). Soloi was later colonized either by Argives or, as seems more likely, by Rhodians from Lindos (Erzen, 1940: 71, n.118; Jacoby, 1950: IIIB, 510; Roebuck, 1959: 64, 112; Blumenthal, 1963: 106; Bing, 1968: 108-13, 117-18). Afterwards the town was ravaged

Figure 1. Ancient Roman concrete harbours, investigated by the ROMACONS Team, along the Mediterranean coast. 1-2: Portus Claudius, ~ 50 B.C., and Portus Traianus, ~ 115 B.C., at Ostia (Rome); 3: Portus Neronis, ~ 60 B.C., at Anzio (Rome); 4: Portus Cosanus, ~ 60 B.C., at Ansedonia, Orbetello (Grosseto); 5: fishpond and pier at Santa Liberata, Orbetello (Grosseto); 6: Portus Iulius and Portus Baianus, mainly 1st century B.C., at Baia (Pozzuoli, Naples); 7: quarry of pozzolanic tuff-ash aggregates at Bacoli, Campi Flegrei (Pozzuoli, Naples); 8: harbour Egnatia, probably 1st century B.C., at Torre Egnazia (Brindisi); 9: modern reproduction of Vitruvius's pier at the harbour of Brindisi; 10: harbour Sebastos breakwaters at Caesarea Palestinae, Israel; 11: harbour Chersonisos, 1st century BC - 1st century A.D., Crete (Greece); 12: harbour Alexandria, 1st century B.C., Egypt, and, 13: harbour Soli-Pompeiopolis, 1st century B.C., near Mersin, Turkey, (photo: Corrado Stanislao and Gabriele Vola).

during the Mithradatic wars (89-81 B.C.), and finally abandoned (Cassius Dio, 36.20; Strabo, 14.5.8; Jones, 1971: 194). In 67 B.C. Pompey the Great restored the city and colonised it with survivors from his successful campaign against the Cilician pirates. He re-named the site Pompeiopolis, and settled his captured pirates here (Magie, 1950: 1180, n.43; Ormerod, 1987: 240-41).

At present, the portion of the harbour is well preserved and presents an atypical example of Roman maritime engineering in which well-clamped ashlar masonry encases a hydraulic concrete core. Although founded in part on a natural reef, it was largely an artificial harbour laid out to a symmetrical geometric design (Brandon et al., 2010). The Roman concrete used for underwater construction consisted of a mixture of slaked lime, pozzolanic tuff-ash material and aggregate. The harbour of Pompeiopolis had two opposed, curving moles 320 m long and c. 23 m wide, set 180 m apart, which joined on the landward end in a semicircle (Beaufort, 1817: 240, in Brandon et al., 2010). Most of the eastern mole has now disappeared, and the landward half of the moles is surrounded or covered by silt and sand. During the final field campaign of August 2009, the ROMACONS team drilled two core samples (POM.09.01 and POM.09.02) from the harbour at Soli-

Pompeiopolis. They worked above sea level and were able to drill down through its complete height and well into the bedrock foundation. Core 01 was drilled 5.7 m in from the west face of the structure, while core 02 was taken 3.1 m from the western marginal wall's outer face. Preliminary analyses indicate that the mortar is strongly enriched in pozzolanic materials (Brandon et al., 2010; Vola et al., 2010a). The coarse tuff aggregate looks like the tuff-ash material already seen in the Italian and Caesarea pozzolanic concretes previously investigated by ROMACONS team (Vola et al., 2011), and it is probably arrived as an accidental component of the fine pozzolanic sand shipped from the Pozzuoli area (Hohlfelder et al., 2007).

Analytical Methods

Knowledge of mineralogical composition, and microstructural properties, of cement-based materials is of fundamental significance for the understanding of their chemical and physical properties. In order to reach these results, the following analyses were carried out:

- Concrete cores sampling for thin sections realization;
- Optical and stereoscopic studies on thin sections;
- Modal analyses on thin sections;
- X-ray powder diffraction (XRPD);
- Scanning electron microscopy (SEM);
- Microanalyses (EDS);
- Geological maps investigation.

The main mineralogical features were obtained by optical polarized light microscopy (Leica Laborlux 12 pol) on thin sections. Modal analyses were performed using counting grids of at least 3000 points, using Leica Qwin software for image analyses.

XRPD samples were prepared by dry crushing samples by hand in agate mortar, in order to prevent the loss of information on soluble phases. α-Al_2O_3 was added to each sample in 20 % wt. amount as internal standard. Operative conditions of XRPD analyses were the following: CuKα radiation, 40 kV, 40 mA, 2θ range from 4° to 70°, equivalent step size 0,017° 2θ, 30 s per step counting time on a modular Panalytical X'Pert Pro diffractometer equipped with a RTMS X'Celerator detector. The software for identification of mineral phases was Panalytical Highscore Plus 2.2 with ICSD database. Scanning electron microscopy (SEM) observations were performed on a JEOL JSM5310 instrument at Centro di Servizi Interdipartimentale per le Analisi Geomineralogiche – CISAG – Università "Federico II" of Naples. Chemical analyses were obtained through energy dispersive spectrometry (EDS) on an Oxford INCAx microanalyser. Chemical mapping was performed by INCAEnergy software. The analyzed elements and the respective standards in brackets are: Si and Al (anorthite), Na (albite), K (orthoclase), Ca (wollastonite), Mg (diopside), and Fe (almandine).

Materials

Two set of cores (POM.09.01 and POM.09.02) from Soli-Pompeiopolis harbour were studied: samples were taken from three different portions of the cores (upper, middle and lower). Core POM.09.01 (Figure 2), was taken at 5.7 m from the west wall of the structure, 13.2 m from transversal, and about 5 m north from the hard and compact travertine bedrock outcrop. Core POM.09.02 (Figure 3) core was taken on the west side of the eastern harbour, 0.50 m above sea level, 3 m from transversal wall and 3 m from the western edge.

Results

A macroscopic visual analysis was used as the first approach to investigate the cores, in order to properly identify the concrete type and to direct the successive detailed analyses.

Core POM.09.01 is characterized by the

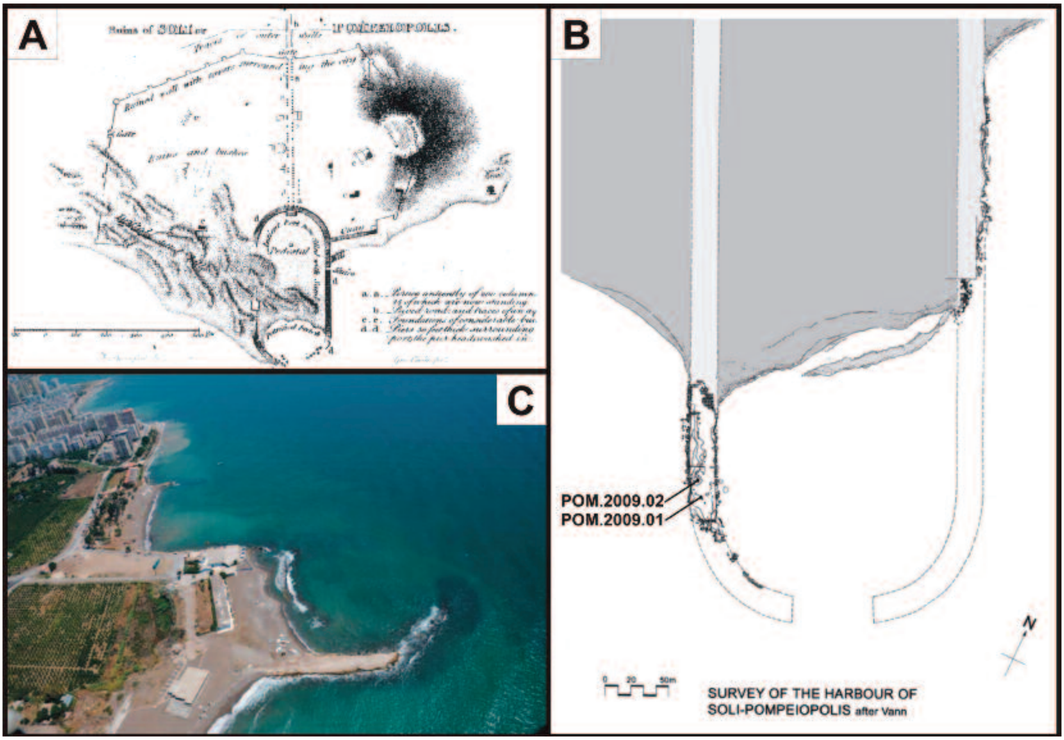

Figure 2. A: Sir Francis Beaufort's plan of the Roman harbour of Soli-Pompeiopolis, Turkey (from Beaufort, 1817; in Brandon et al., 2010); B: plan of the Roman harbour with the location of ROMACONS core drillings (from R.L. Vann, 1995, modified); C: aerial photograph of harbour of Soli-Pompeiopolis, from Prof. Oleson's Internet site, link: http://web.uvic.ca/~jpoleson/Soli%20web%20entry/Soli%202009%20web.htm.

presence of a light brown coloured mortar, with coarse aggregates ranging in diameter from 4 mm up to 18 mm, constituted by travertine and volcanic tuff fragments. Frequent white nodules are present (4-8 mm) consisting of reacted lime, apparently produced by the long-time reaction of lime with pozzolanic materials. Small fibrous nodules are also present, constituted by pale yellow to yellowish-brown pumiceous scoriae. Close to sea-level, the mortar color turns from white to pale green, and the porosity, along with the numbers of white nodules and pumiceous scoriae, increase (Brandon et al., 2010).

Core POM.09.02 mortar is homogeneous and compact in the whole core, but locally porosity can increase. In the upper part, its color is brown-yellowish with high content of pumiceous scoriae (11-18 mm) and several angular fragments of white material, probably reacted lime (2-10 mm). The coarse aggregate is constituted by volcanic tuff, calcareous and travertine clasts. This latter type of clast, in the upper part of the core is poorly bonded with the mortar and appears clearly fractured. The pale yellow 2.5Y 7/3 volcanic tuff display many pumiceous scoriae and, whenever wet, presents a light olive brown color 2.5Y 5/4. Micro-portions from investigated cores were sampled

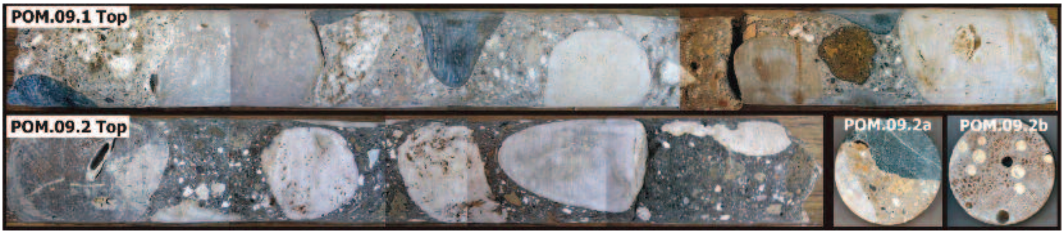

Figure 3. Core boxes and 9 cm sized concrete slices from Soli-Pompeiopolis (POM.09.1 and POM.09.2). Core boxes are stored at CTG Italcementi Lab. Dept. in Bergamo. Coarse size aggregates, rounded in shape, are composed of local travertine, stony corals, amphibolite rock, and some yellow tuff fragments. Strongly enriched pozzolanic mortars are present, as well.

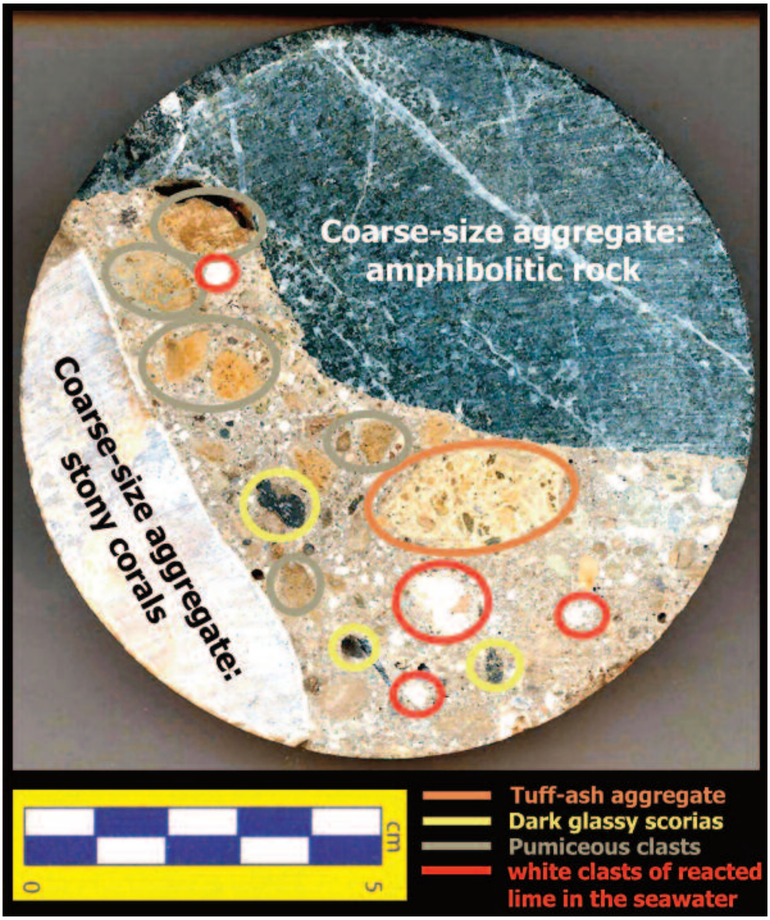

Figure 4. Macrograph from POM.09.2 concrete slice.

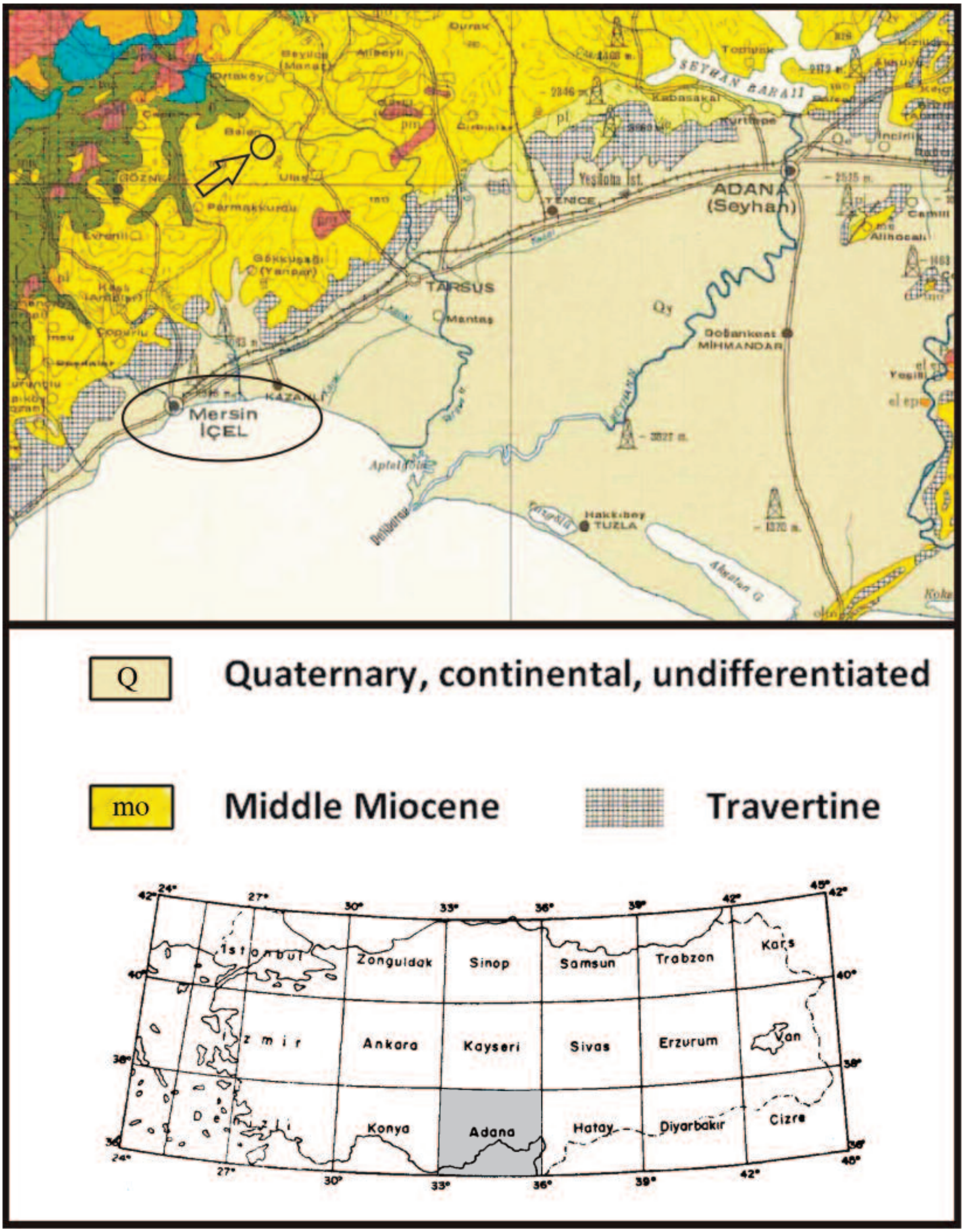

Figure 5. Geological sketch map of Adana at scale 1:000.000 (Bulletin of the Mineral Research and Exploration Institute of Turkey (1962). The black arrow points out the location of modern quarries NW of Mersin.

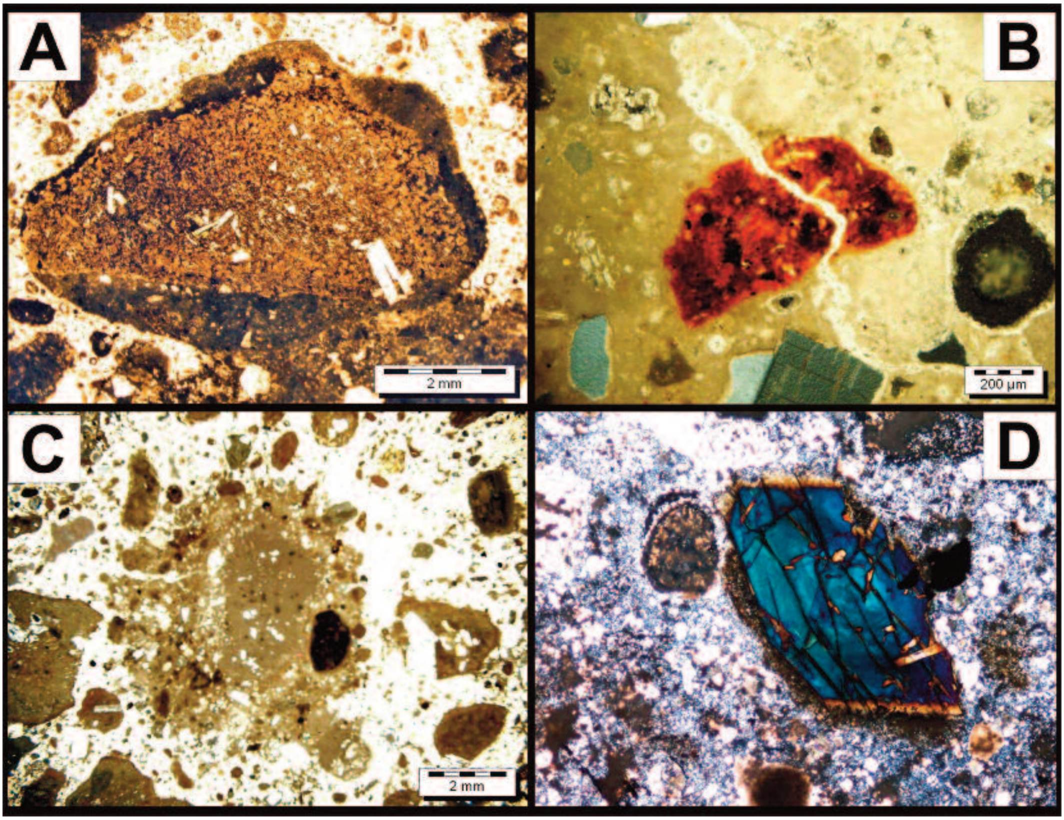

Figure 6. A: volcanic scoria with reaction rim (PPL); B: white granule (CPL); C: ceramic fragment (CPL); D: Pyroxene (CPL); Legend of symbols: P: pyroxene, T: tobermorite, S: scoria, C: ceramic fragment.

in representative zones, and used for the realization of thin section (Figure 4) for optical microscopy and modal analyses.

Coarse grained aggregate (d > 4 mm): Romans generally referred to decimeter-sized rubble aggregates as the *caementa*. They are constituted mainly by tuff and travertine fragments. River cobbles, composed of dark amphibolites and stony corals, both rounded in shape, are present too. The volcanic tuff displays a predominant cineritic matrix, incorporating pumice, lithic fragments and phenocrysts. The matrix shows a fine-grained pyroclastic texture. Travertine aggregates display diameter even larger than 10 mm. This rock may have a local origin, because outcrops few kilometers far from the ancient Pompeiopolis (Figure 5).

Scoriae/pumice: both these clasts are present in the tuff and form discrete particles within the fine pozzolanic sand, the *pozzolan* strictu senso. Pumice in the tuff display often rounded shapes, with typical pumiceous texture, and are deeply altered, with colour ranging from red 10R 5/6 to light greenish gray 10G 7/1; their walls are covered with zeolite clusters. As regards those present in the fine *pozzolan* s.s., polarized microscope observations do not reveal any reaction in their inner part, as testified by the "fresh" aspect of vugs and shards surfaces; they do not display any zeolite minerals, neither in vugs nor on the vitreous surface, thus leading to hypothesize that they represent relicts of the coarse fraction of the *pozzolan* s.s. The only hint of reaction with lime is testified by scoriae with a reaction rim, gradually fading into the groundmass of the concrete (Figure 6a).

Ceramic fragments: they are rare and can be considered non-relevant for the characterization of this concrete (Figure 6b).

White grains: they are hardened lumps of lime reacted with the seawater, characterized by the following features a) brown colour in the inner part whenever observed in plane polarized light, and b) no birefringence in crossed polarized light (Figure 6c).

Phenocrysts: magmatic crystals are present both in the groundmass and in the volcanic aggregate. They come probably from the fine pozzolanic sand, the *pozzolan* s.s., used in the mixture and/or from tuff aggregate crushed during the preparation of mixture for casting the concrete. They are mainly sanidine, plagioclase and clinopyroxene (Figure 6d). This latter displays a yellowish or olive green color, weak pleochroism, prismatic stubby habitus, and typical extinction at 93°, with second order brilliant interference colors.

Zeolites: These mineral phases are present only in pumice vugs of the Yellow Neapolitan Tuff fragments. They display colorless diverging radial habitus, low relief and birefringence, typical of phillipsite.

Cementiceous matrix: the binding matrix was generally defined by Romans as the *opus caementitium*. This is an hydraulic material composed by the reaction products of seawater, lime (or hydraulic lime) and pozzolanic materials. Hydration products that may be found nowadays could not totally correspond to the original ones, considering that further reactions with the marine environment could have developed during almost two thousand years. Diffuse micro-cracks within the cement paste could be ascribed to: a) shrinking or expansion phenomena due to temperature variation related to hydration reactions or b) the arising of internal tensions as a consequence of salt crystallization from seawater. Results of modal analysis of four selected samples are reported in Table 1.

The volcanic tuff used as aggregate for the mortar (11-35 vol. %) is mainly constituted by pumiceous scoriae, volcanic fragments, sanidine, pyroxene and a cineritic matrix. Few aggregates of carbonate rocks and ceramic fragments are present too. Cement paste is mainly constituted by "sparry" microcrystalline calcite (24-58 vol. %), gel-like C-S-A-H (10-31 vol. %), and reacted lime (3-9 vol. %). Total porosity ranges from 3 to 6 % and the binder/aggregate ratio reaches, in sample POM.09.02 (middle part) and POM.09.01 (upper part), values close or higher than 4, which is higher if compared to those values from other Roman mortars drilled by the ROMACONS team (Vola et al., 2010a, 2010b; Stanislao and Rispoli, unpublished data).

XRPD patterns of analyzed samples (POM 4, POM 6, POM 11, POM 12) allowed us to identify the mineral phases reported in Table 2.

The presence of mineral phases derived from concrete curing and hardening is clear, in association with other phases not found in other Roman concretes, such as ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12}\bullet 26(H_2O)$] and tobermorite [$Ca_5Si_6O_{16}(OH)_2\bullet 4H_2O$]. The first one is related to the reaction of Ca-alluminates with the seawater. More complex to justify, and worth to be studied deeply, is the formation of tobermorite, being this phase associated with high temperatures and pressures (Collepardi et al., 2009), not compatible with temperature produced during hydration reactions (Jackson et al., in press; Vola et al., 2011).

Electron micoscopy observations on mortar fragments (SEM: secondary electron image) and polished thin sections (BSE: back-scattering electron image) allowed us to recognize that

Table 1. Modal analyses of selected portion of cores.

Core	POM.09.1	POM.09.2	POM.09.2	POM.09.2
Part	Upper	Upper	Middle	Lower
Constituents (Vol.%)				
Pumiceous scoriae	10.5	17.3	7.6	29.7
Biotite	-	0,2	-	0.1
Quartz	0.7	1.5	0.9	0.4
Plagioclase	0.2	0.5	0.3	0.3
Calcite	0.1	1.2	0.3	0.2
Alkaline feldspar (sanidine)	0.3	1.2	0.2	0.3
Pyroxene	0.9	1.0	1.0	0.8
Ash-Tuff	4.2	4.0	1.3	5.2
Volcanic lithic fragments	2.4	1.0	1.9	-
Red Bricks	-	1,0	0.4	-
Carbonate rock fragments	-	-	2.0	-
Gel-like C-S-A-H *	10.2	23.9	30.8	15.9
Microcrystalline matrix	58.4	38.0	40.7	24.2
Dull grains of reacted lime	9.0	3.0	7.5	4.0
Grains of sparite (>200µm)	-	-	-	13.0
Porosity	3.1	6.2	5,1	5.9
Total points	3000	3000	3000	3000
Total Binder	77.6	64.9	79,0	57.1
Total Aggregate	19.3	28.9	15,9	37.0
Total tuff aggregate	17.1	22.3	10,8	34.9
Binder/Aggregate ratio	4.0	2.2	4,9	1.5

* C-S-A-H: Calcium-Silica-Aluminates Hydrated

Table 2. XRPD analyses from selected samples.

Core	Part	Sample	Main cement phases	Pozzolanic aggregates:primary crystals and secondary alterations
POM.09.1	Middle	POM 4	Cal, Tbm	Phi, Ms
POM.09.1	Top	POM 6	Cal, Tbm, Etr	Phi, San, Ms
POM.09.2	Top	POM 11	Cal, Tbm, Etr	Phi, San, M, Hal, Qtz
POM.09.2	Middle	POM 12	Cal, Tbm	Phi, Cha, San, Sm, Hal, Ms

Cal: calcite Tbm: tobermorite, Etr: ettringite, Phi: phillipsite, Ms: mica, San: sanidino, Cha: chabazite, Hal: halite, Qtz: quartz, Sm: smectite.

vugs fillings are constituted mainly by ettringite, (Figure 7a). SEM observation allowed to find phillipsite in the tuff fragments, mainly in the pumice vugs, (Figure 7b). This was confirmed also by thin section observations and their relative EDS analyses (Figure 8, Table 3). Even if this particular zeolite was exposed for almost two thousand years to seawater, it is remarkable that his cationic content does not display any Na-enrichment as a consequence of cation exchange processes; its chemical composition is definitely very close to Neapolitan Yellow Tuff (NYT) phillpsite, K being the predominant extra framework cation (de Gennaro et al., 2000) of phillipsite from this deposit.

Most of the white grains are constituted by

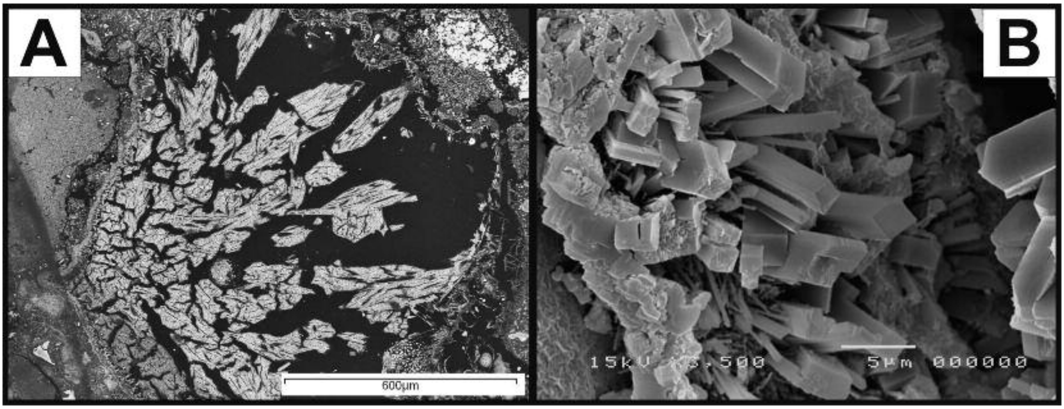

Figure 7. A: ettringite crystals in vugs, BSE image (POM 4); B: Phillipsite. SEM images of crystals (POM 6).

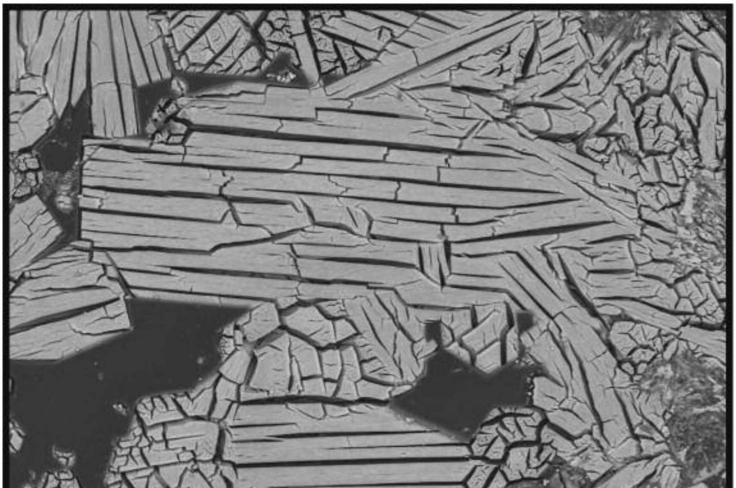

Figure 8. Phillipsite prismatic crystals, BSE image (POM 12).

Table 3. EDS microanalyses from selected samples.

Core	POM.09.2	POM.09.2	POM.09.2	POM.09.1	POM.09.1	POM.09.2
Part	Bottom	Top	Top	Top	Top	Top
Sample	POM12	POM11	POM11	POM4	POM4	POM 11
Phase	Calcite	Calcite	Analcime	Tobermorite	Phillipsite	Ettringite
Wt. %						
SiO_2	-	-	57.57	42.56	55.14	0.54
Al_2O_3	0.33	0.15	22.30	6.94	17.31	10.21
Fe_2O_3	0.64	0.12	0.28	0.09	0.09	0.03
TiO_2	0.28	-		0.15	0.30	0.13
CaO	52.56	53.22	0,51	36.44	1.23	32.86
MgO	0.86	0,78	0.26	0.01	0.12	0.68
SO_3	-	-	-	0.24	-	19.58
Na_2O	-	0.08	12.27	0.20	4.04	1.45
K_2O	-	-	0.23	0.72	8.77	0.89
Mn_2O_3	-	0.16	0.23	-	-	0.10
P_2O_5	-	-	0.07	-	-	
Total	54.67	54.71	93.83	87.32	87.00	66.48

tobermorite, Ca-silicate hydrate displaying various crystalline habitus (Figure 9, Table 3).

Volcanic tuff fragments are constituted by glass scoriae, sanidine, pyroxene and zeolites (phillipsite, analcime and subordinated chabazite. This latter association allowed us to hypothesize that these fragments come from NYT (de Gennaro et al., 2000), and the chemical composition of phillipsite (Table 3), as mentioned before, confirm this assertion.

From SEM analyses, clasts of calcareous rocks (Figure 10) are evident, and their presence can be related to residual limestone not completely calcinated. These clasts could not be interpreted as lime carbonated lumps, since it is well known, in fact, that Romans used to produce slaked lime (*calce spenta*) directly on the building sites, or in production sites within tanks (*bagnoli*). From these tanks, the milk of lime was decanted in large pits (*calcinaie*), then covered with soil in order to prevent the reaction with atmospheric CO_2, allowing preservation of the binder for a longer time.

In order to achieve further information on the provenance of pozzolanic materials used to cast concrete, microanalyses of pyroxene and sanidine from the cement paste were performed. As regards pyroxenes, their chemical analyses allow classification as diopside, following the wollastonite-enstatite-ferrosilite diagram (Figure 11); hence restricting their provenance from alkaline magmatic districts.

Since no calcic pyroxenes (augite) were found, subalkaline or calcalalkaline volcanic products such as those form Eolian or Cicladi islands can be excluded. A further comparison, using analyses from a database at the Dipartimento di Scienze della Terra dell'Università Federico II di Napoli, with crystal-chemical information from minerals of Somma Vesuvio and Campi Flegrei districts, and the use of the diagram of Figure 12, allowed us to hypothesize that pyroxenes present in Pompeiopolis concretes are comparable with those from Campi Flegrei, being the representative

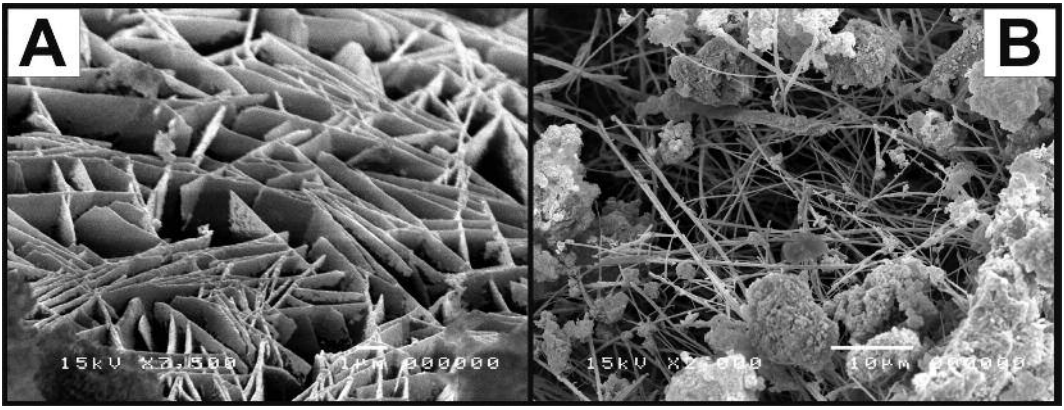

Figure 9. Tobermorite. A: SEM image of platy crystals (POM 4); B: SEM image of acicular crystals.

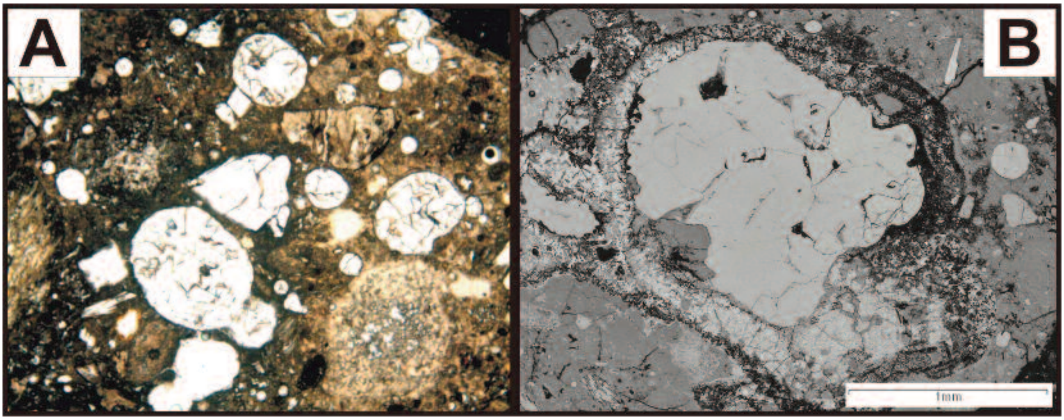

Figure 10. A: Calcite grains (POM 12); B: Calcite grain, BSE image (POM 12).

points characteristic of lower Ca content. Anyway, the already confirmed presence of NYT as aggregate, reinforce our hypotesis that also pozzolana could have a provenance fom Campi Flegrei.

If feldspars are concerned, the representative composition of the investigated samples classify them as alkaline feldspars (sanidine) with a composition ranging from Or_{45} to Or_{60} (Figure 13), once again close to those from NYT (de Gennaro et al., 2000).

Discussions and conclusions

Mineralogical and petrographic examinations performed on geomaterials from concrete cores drilled at the harbour of Soli-Pompeiopolis point out that an hydraulic raw material was mixed with the lime for casting the seawater concrete. Curiously, the lime's provenance is still unknown, even if it is reasonable to think that it was produced on site using locally available raw materials. The Geological Map of Turkey at the scale of 1:100.000, Adana sheet, shows that

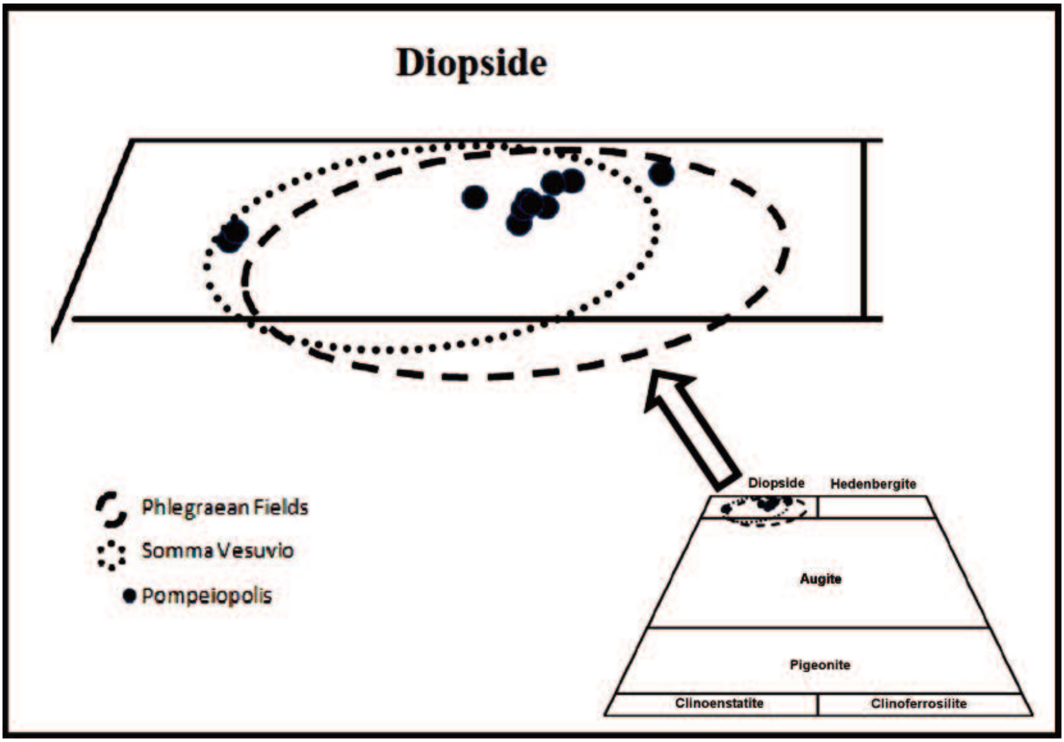

Figure 11. Wo-En-Fe classification diagram.

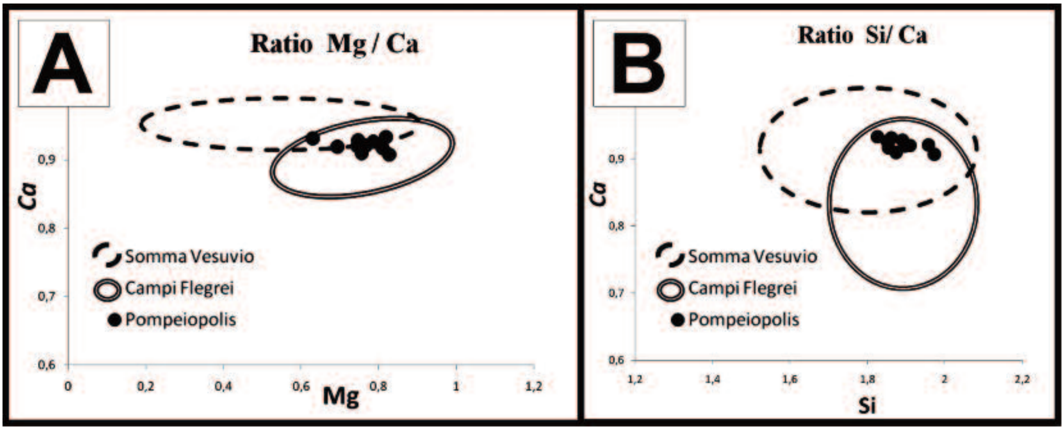

Figure 12. A: Mg/Ca ratio; B: Si/Ca ratio.

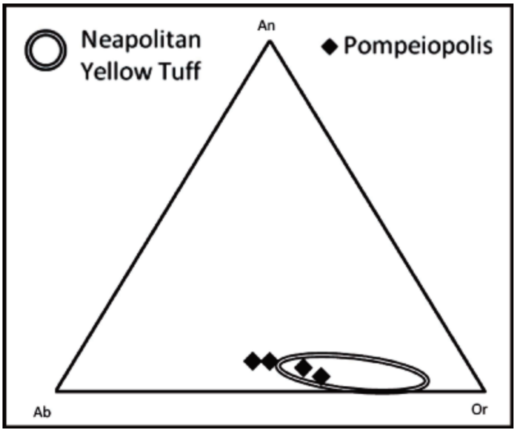

Figure 13. Ab-An-Or classificative diagram for feldspars.

important carbonate rocks outcrop some kilometers North of the ancient town of Soli-Pompeiopolis (Bulletin of the Mineral Research and Exploration Institute of Turkey, 1962) (see Mersin in Figure 5). This fact generally supports our hypothesis. Most likely, the firing of the lime and its extinction were not perfectly done, because the presence of residual intact limestone grains (Figure 10, left) and not-well reacted lime clusters were also observed (Figure10, right). Similarly, travertine aggregates, which amount to ~ 15 % of the total lithic fragments of the mortar, seem to have a local origin, because travertine outcrops and quarries are reported in the geological map of Turkey, Adana sheet, as well (Bulletin of the Mineral Research and Exploration Institute of Turkey, 1962). The absence of fossils in the calcareous aggregate do not confirm at all their provenance, thus leading to the hypothesis that lime has been obtained by travertine firing.

As for the yellow tuff aggregate fragments, their mineralogical-petrographic composition and especially the typical mineralogical association of phillipsite > chabazite > analcime, allow us to say that they surely come from the Neapolitan Yellow Tuff (NYT) formation, which is connected to the Campi Flegrei volcanic activity, dated back to 15,000 years ago. Contrary to the initial working hypothesis, EDS microanalyses of phillipsite crystals showed that the content of major alkaline and alkaline-earth metals was very close to those of phillipsites from NYT, with K higher than Na and Ca, as previously reported in the literature (de' Gennaro et al., 2000). It clearly seems that these minerals were not involved in cation exchange processes within the seawater, despite of their long curing time - approximately two thousand years - in the marine environment.

As regards the pozzolanic fine-grained sand adopted in the mixture with the lime, this study did not clarify if it was the Phlegrean *pozzolan* s.s. or a powder from the NYT. It is common knowledge that Romans widely used the first to cast hydraulic limes, especially the one from Baia (Sersale, 1991; Rosi and Sbrana, 1987 and references therein), that is a volcaniclastic sediment connected to the eruptive event at Fondi di Baia, dated back to 9,600 years ago; however it is not possible to exclude that the latter, coming from the NYT, had been used too.

The presence of isolated pyroxene phenocrysts within the cementiceous binding paste, which composition is ascribed to an alkaline volcanism, lead to a pozzolanic material from the Campania Region, and specially from the Campi Flegrei area. Obviously it is not possible to be more precise about its nature, because this composition is typical either of the Phlegrean *pozzolan* s.s., or the NYT. Most likely available data lead to seem that they could be the *pozzolan* s.s., because the fine scoriae/pumices observed within the cementiceous paste never presented alteration to zeolites, hence they should not related to the NYT.

Extremely interesting is the composition of the cementiceous binding matrix, with the contemporary presence of gel-like C-S-A-H, derived from the reaction between the lime and the pozzolanic material in the seawater, calcite, ettringite, and, finally, tobermorite. The presence of calcite is likely connected to the not-well reacted clast of underburned lime, although it is not possible to exclude that some carbonation subsequently happened, from the residual portlandite, since concretes were drilled and stored in a subaerial environment. Ettringite is to be ascribed to the interaction between calcium aluminates and ion sulphates from the seawater, which precipitated within the mortar porosities. As far as the tobermorite, there is not a reliable interpretation to explain its formation, at the current state of knowledge. This phase is concentrated within relict of lime clasts, but also inside mortar porosities. Tobermorite is also reported in all the other ancient seawater concretes drilled by the ROMACONS team (Vola et. al., 2010a; 2010b; 2011) and its formation was previously related to those of natural rock-forming cement systems in pyroclastic deposits immersed in the ocean and in saline lake brines (Jackson et al., 2010b, in press). Literature attests that tobermorite forms at higher temperatures, 150-200 °C, than those of lime-based materials; moreover it is well-known that the heat of hydration in pozzolanic cements is lower than normal cements (Massazza and Costa, 1979; Collepardi et al., 2009). The long curing time in the marine environment is probably the key-factor in understanding the formation of tobermorite from gel-like C-S-A-H at ordinary temperatures. This topic will be the object of forthcoming researches.

Preliminary results from petrographic examinations carried out last year at CTG Laboratory Department on spherical crystals with the “rosette” textures (Vola et al., 2010b), have been, partially, contradicted. Actually, this study allows us almost to exclude the formation of new zeolites for mortars from Pompeiopolis. However, the presence of smectite in the mortar of specimen POM 12, could be related to the previously presumed reaction process, because this argillaceous mineral generally forms at the early stage of the hydration of zeolithic glassies in the seawater. Subsequently, the precipitation of zeolite mineral is generally achieved (de Gennaro et al., 1993). Moreover smectite is not related to the NYT, because analyses of the tuff aggregate never showed its presence. In conclusion, the crystallization process of authigenic zeolites should have taken a longer curing time to form, considering either the low temperature of the system, or the reaction between lime and pozzolan, which is generally very fast in the seawater, and should inhibit the latter.

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