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

MARIE D. JACKSON1,*, SEAN R. MULCAHY2, HENG CHEN3, YAO LI4, QINFEI LI5, PIERGIULIO CAPPELLETTI6, AND HANS-RUDOLF WENK2

1Department of Geology and Geophysics, University of Utah, Salt Lake City, Utah 84112, U.S.A.
2Geology Department, Western Washington University, Bellingham, Washington 98225, U.S.A.
3School of Materials Science and Engineering, Southeast University, Nanjing 211189, People’s Republic of China
4Center for Advancing Materials Performance from the Nanoscale (CAMP-Nano), Xi’an Jiaotong University, Xi’an 710049, People’s Republic of China
5School of Transportation Science and Engineering, Harbin Institute of Technology, Harbin 150090, People’s Republic of China
6Dipartimento di Scienze della Terra, dell’Ambiente e delle Risorse (DiSTAR), Università degli Studi di Napoli Federico II, Naples I-80134, Italy
7Department of Earth and Planetary Sciences, University of California, Berkeley, California 94720, U.S.A.

ABSTRACT

Pozzolanic reaction of volcanic ash with hydrated lime is thought to dominate the cementing fabric and durability of 2000-year-old Roman harbor concrete. Pliny the Elder, however, in first century CE emphasized rock-like cementitious processes involving volcanic ash (pulvis) “that as soon as it comes into contact with the waves of the sea and is submerged becomes a single stone mass (fierem unum lapidem), impregnable to the waves and every day stronger” (Naturalis Historia 35.166). Pozzolanic crystallization of Al-tobermorite, a rare, hydrothermal, calcium-silicate-hydrate mineral with cation exchange capabilities, has been previously recognized in relict lime clasts of the concrete. Synchrotron-based X-ray microdiffraction maps of cementitious microstructures in Baianus Sinus and Portus Neronis submarine breakwaters and a Portus Cosanus subaerial pier now reveal that Al-tobermorite also occurs in the leached perimeters of feldspar fragments, zeolitized pumice vesicles, and in situ phillipsite fabrics in relict pores. Production of alkaline pore fluids through dissolution-precipitation, cation-exchange and/or carbonation reactions with Campi Flegrei ash components, similar to processes in altered trachytic and basaltic tuffs, created multiple pathways to post-pozzolanic phillipsite and Al-tobermorite crystallization at ambient seawater and surface temperatures. Long-term chemical resilience of the concrete evidently relied on water-rock interactions, as Pliny the Elder inferred. Raman spectroscopic analyses of Baianus Sinus Al-tobermorite in diverse microstructural environments indicate a cross-linked structure with Al3+ substitution for Si4+ in Q3 tetrahedral sites, and suggest coupled [Al3+Na+] substitution and potential for cation exchange. The mineral fabrics provide a geoarchaeological prototype for developing cementitious processes through low-temperature rock-fluid interactions, subsequent to an initial phase of reaction with lime that defines the activity of natural pozzolans. These processes have relevance to carbonation reactions in storage reservoirs for CO2 in pyroclastic rocks, production of alkali-activated mineral cements in maritime concretes, and regenerative cementitious resilience in waste encapsulations using natural volcanic pozzolans.

Keywords: Phillsipite, Al-tobermorite, Roman concrete, natural pozzolan, water-rock reaction

INTRODUCTION

Roman marine concrete structures, composed of a volcanic ash-hydrated lime mortar that binds conglomeratic tuff or carbonate rock aggregate (cuementa), have remained intact and coherent for 2000 yr, either fully immersed in seawater or partially immersed in shoreline environments (Brandon et al. 2014). The extraordinary longevity of the concrete seems to result from the long-term durability of poorly crystalline, calcium-aluminosilicate-hydrate (C-A-S-H binder) in the cementing matrix of the mortar (Jackson et al. 2013a), the sequestration of chloride and sulfate ions in discrete microstructural mosaics (Jackson et al. 2012), and, as reported here, pervasive crystallization of zeolite and Al-tobermorite mineral cements in pumice clasts, dissolved feldspar crystal fragments, and relict voids of the cementing matrix (Figs. 1f, 1g, 1h, and 1j).

The mortar of Roman marine concrete is considered the prototype of modern concretes that partially replace Portland cement with natural pozzolan to reduce CO2 emissions and produce resilient C-A-S-H binder (Snellings et al. 2012). Ancient Roman concretes also have C-A-S-H binder, but it was produced through reaction of seawater, lime (CaO) calcined from limestone, and zeolitized volcanic ash, mainly from Campi Flegrei volcano (Fig. 2) (Stanislae et al. 2011; Jackson et al. 2013a, 2014). C-A-S-H is the poorly crystalline analog of Al-tobermorite, a rare, layered, calcium-silicate hydrate mineral composed of aluminosilicate chains bounded by an interlayer region and a calcium oxide sheet (e.g., Komarneni and Roy 1983; Taylor...
Al-tobermorite does not occur in conventional concretes but occurs routinely in the relict lime clasts of Roman marine concrete (Voila et al. 2011; Jackson 2014) and, occasionally, in hydrothermally altered volcanic rocks (Figs. 3 and 4). Al-tobermorite also occurs as an alteration product at the cement–rock interface of toxic and nuclear waste repositories (e.g., Gaucher and Blanc 2006; Lalan et al. 2016). Tobermorite group minerals have a basal interlayer spacing of \(\sim 11\ \text{Å}\) and an orthorhombic sub-cell symmetry with the general formula, \(\text{Ca}_{4+x}(\text{Al}_y \text{Si}_{6-y})\text{O}_{15+2x-2y} \cdot 5\text{H}_2\text{O}\), where \(x = 1\) and \(y = 2\) (Biagioni et al. 2015). Most geological occurrences have

Al\(^{3+}\) substitution for Si\(^{4+}\) in tetrahedral sites, and the generalized mineral formula, \([\text{Ca}_4(\text{Si}_{5.5}\text{Al}_{0.5}\text{O}_{17})\text{H}_2]\text{Ca}_{0.2}\cdot\text{Na}_{0.1}\cdot4\text{H}_2\text{O}\) (Taylor 1992), contains sodium and potassium as interlayer cations (Figs. 3b and 4b). Substitution of Al\(^{3+}\) for Si\(^{4+}\) in Al-tobermorite synthesized at 80–240 \(°\text{C}\) also produces ion-exchange behavior for certain radionuclides and heavy metals as interlayer cations (Komarneni and Roy 1983; Komarneni et al. 1987; Trotignon et al. 2007; Coleman et al. 2014). The crystals could prove useful in cementitious barriers and for nuclear and hazardous waste treatment and disposal if they could be produced in sufficient quantities at low temperature and, potentially, through regenerative, \textit{in situ} cementitious processes over long periods of time.

Natural pozzolans are siliceous and/or aluminous earth materials: volcanic glass, zeolite minerals, opaline chert, and diatomaceous earths. They form part of a broader class of supplemental cementitious materials (SCMs), such as fly ash, a waste product from coal-fired power plants, now incorporated in environmentally friendly cement and concrete technologies (Lothenbach et al. 2011). Pozzolans are defined as materials “which, in themselves, possess little or no cementitious value but which will, in finely divided form and in the presence of water, react chemically with calcium hydroxide [portlandite, \(\text{Ca(OH)}_2\)] to form compounds possessing cementitious properties” (Mehta 1987). Pozzolanic activity is measured through various chemical tests, which determine a material’s reactivity with portlandite and the rate at which it binds \(\text{Ca(OH)}_2\) in the presence of water (Massazza 2004), as well as mechanical tests, which measure compressive strength over 28 days, for example, as a means to predict long-term performance (ASTM-C618 2015). When finely
ground these natural or artificial pozzolanic materials are mixed with Portland cement to produce a blended cement paste that binds largely inert sand- and gravel-sized aggregates. Blended cement pastes generally have a more refined pore structure, increased chemical resistance to the ingress and deleterious action of aggressive solutions, such as seawater, and to expansive alkali-silica reactions associated with reactive aggregates that degrade concretes worldwide (e.g., Massazza 2004; Mehta and Monteiro 2015, p. 169–172), as compared with ordinary Portland cement paste. Although reliable large-scale production of concretes with natural pozzolans has not been fully mastered relative to those with SCMs such as fly ash, recent reductions in fly ash production and availability are now driving new interest in volcanic rock pozzolans (e.g., Celik et al. 2014; Cai et al. 2016).

The life cycle of Roman harbor concretes structures is about two orders of magnitude greater than Portland-type cement seawater concretes. Cement-based concretes are designed to hydrate quickly and maintain durability through a general absence of long-term cementitious evolution or solubility. In maritime environments, however, the concrete commonly begins to decay after a few decades due, in part, to corrosion of steel reinforcement (Mehta 1990). The steel reinforcement counteracts the relative low tensile

![Figure 3](image-url) Compositions of phillipsite and Al-tobermorite in Roman marine mortars and geologic deposits. Electron probe microanalyses (EPMA), as molecular proportions (Tables 1, 2, and S1). (a) Phillipsite, published compositions from [1] Passaglia et al. 1990; [2] de Gennaro et al. 2000; [3] Gatta et al. 2010; [4] Jakobsson and Moore 1986. (b) Al-tobermorite, various geologic deposits (after [5] Jackson et al. 2013a). [6] Aguirre et al. 1998; Clarindbull and Hey 1952; [7] Livingstone 1988; [8] Hemmi and Kusachi 1992; [9,10] Hoffman and Armbruster 1997; Merlino et al. 2001; [11] Mitsuda and Taylor 1978. Roman crystals have Al/(Si+Al) = 0.10–0.16 and Ca/(Si+Al) = 0.45–0.69. Sodium and potassium range from 1–3 wt%. ANZ = Portus Neronis; BAI = Baianus Sinus; PCO = Portus Cosanus; NYT = Neapolitan Yellow Tuff; BT = Bacoli Tuff.

![Figure 4](image-url) Compositions of phillipsite and Al-tobermorite in Roman marine mortars and geologic deposits. Electron probe microanalyses (EPMA), as molecular proportions (Tables 1, 2, and S1). (a) Phillipsite, Ca+Mg-Na-K, see Figure 3 for references to published compositions. Phillipsite compositions in relict voids of Portus Traianus mortar, Ostia, Italy, are similar to phillipsite in Tufo Lionato (TL) tuff coarse aggregate, erupted at 366 ± 5 ka from Alban Hills volcano (Marra et al. 2009). (b) Al-tobermorite, Si-Ca-Na+K, various geologic deposits (after [5] Jackson et al. 2013a). PTR = Portus Traianus. The most silicic compositions are similar to Al-tobermorite in Surtsey basaltic tuff, Iceland (Jakobsson and Moore 1986). Tobermorite is not observed in NYT, BT, and TL, but occurs in deeper Campi Flegrei deposits (Vanorio and Kanitpanyacharoen 2015).
strength and ductility of the concrete and, therefore, is a structural requirement. Although concretes with pozzolanic blended cements generally have reduced calcium hydroxide content relative to conventional concretes with Portland cement alone, the presence of calcium hydroxide as free portlandite may persist for long periods of time depending on the weight percent addition of SCM (Goülic et al. 2005). Highly alkaline pore solutions may thus persist indefinitely and, in the absence of chloride ions in solution, the protective film on steel remains stable as long as solution pH ≥ 11.5 (Mead and Monteiro 2015, p. 179). Interaction of seawater with marine concrete corrodes steel, however, and also may produce expansive reactions with calcium hydroxide (Massaza 1985). By contrast, portlandite is rapidly consumed in Roman pyroclastic rock concrete reproductions, and there is no steel reinforcement in the ancient structures; the volcanic ash mortars show greater ductility and bind a conglomeratic rock framework that reinforces the concrete at the structural scale (Brune et al. 2013; Jackson 2014; Jackson et al. 2014). Roman marine concrete structures throughout the Mediterranean region contain reactive, alkaline, fine sand-to-gravel-sized, pumiceous ash aggregate, commonly with zeolite surface coatings and the massive harbor structures have been left open to seawater ingress for two millennia. Although pozzolanic processes in the ancient concrete have been described (Jackson et al. 2013a), little is known about post-pozzolanic cementitious processes that could benefit chemical resilience long after calcium hydroxide was fully consumed through pozzolanic reaction with the volcanic ash aggregate.

Vitruvius, a Roman architect and engineer writing about 30 B.C.E., described this pozzolanic reaction and the “latent” heat released when tuff, pumiceous ash, and lime (CaO) (tufos, pulvis, and calvus) from the Campi Flegrei and Vesuvius volcanic districts “come into one mixture and suddenly take up water and cohere together” (de Architectura 2.6.1–4) (Appendix Table 1). 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, Italy (Fig. 2, location 4), indicates that elevated temperatures, 65–95 °C, persisted for 2–3 yr (Jackson et al. 2013a). In partially dissolved relic lime clasts, crystallization of Al-tobermorite associated with C-A-S-H likely accompanied this pozzolanic phase of reaction, which apparently terminated early in the history of the marine concrete structures. In a Roman concrete breakwater reproduction, for example, portlandite was fully consumed after 5 yr of hydration in seawater (Oleson et al. 2006; Gotti et al. 2008; Jackson 2014), similar to other experimental seawater concretes with volcanic ash aggregates (Massaza 1985).

Roman natural scientists, Seneca (4 B.C.E–64 CE) and Pliny the Elder (23–79 CE), used geologic analogs to explain the longer term cohesion of the marine concretes, beyond that observed by Vitruvius (Appendix Table 1). Pliny called upon the natural term cohesion of the maritime concretes, beyond that observed by Vitruvius (Appendix Table 1). Pliny called upon the natural rock-fluid interactions inferred by Seneca and Pliny to be recorded by authigenic mineral textures in the pumiceous mortar fabric of submarine and subaerial marine concrete structures. These occur in the dissolved perimeter of feldspar crystals (Fig. 1g), pumice vesicles (Fig. 1h), and pores of the cementing matrix (Fig. 1i).

To investigate these rock-like cementitious processes we compare electron probe microanalysis compositions of phillipite, a potassic, sodic, and/or calcic zeolite, and Al-tobermorite that formed in volcanic deposits with analogous crystals that formed in the marine concrete (Figs. 3 and 4). We map Roman cementitious microstructures with synchrotron-based X-ray microdiffraction (Figs. 5–9) to describe in situ zeolite and Al-tobermorite textures in the Portus Cosanus subaerial pier and the Baianus Sinus and Portus Neronis subaqueous breakwaters (Fig. 2). We then use Roman spectroscopy to identify bonding environments in Baianus Sinus Al-tobermorite from various crystalization environments.

Comparison of these spectra with those previously determined for ideal tobermorite give a qualitative measure of the role of aluminum in a cross-linked crystal structure (Figs. 10–12). The integrated results provide new insights into the low temperature crystallization and stability of phillipite and Al-tobermorite in alkaline aqueous environments and illustrate the beneficial role of authigenic mineral cycling in construction materials with natural volcanic pozzolan over very long service lives.

**Materials and analytical methods**

Roman harbor concrete structures were constructed from about 55 BCE to 115 CE, and cored by the ROMACONS drilling program from 2002 to 2006 (Brandon et al. 2014). The conglomeratic concrete cores contain about 40–45 vol% zeolitized tuff coarse aggregate, and 55–60 vol% pumiceous volcanic ash-hydrated lime mortar. The marine concrete is exposed sub-serially at Portus Cosanus (drill core POC.03.01), Orbetello, (42.4079° N, 11.2933° E), and submerged in seawater at Baianus Sinus (BAI.06.03), Bay of Pozzuoli, (40.8228° N, 14.0883° E), Portus Neronis (ANZ.02.01), Anzio, (41.4432° N, 12.6314° E) and Portus Traianus (PTR.02.02), Ostia (41.7785° N, 12.2520° E). The BT sample comes from an unidentified quarry near Fondi di Baia, at about 40.80° N, 14.07° E; the NYT samples come from outcrops in Naples at 40.89° N, 14.18° E.

**Electron probe microanalysis (EPMA)**

Samples were analyzed with a Cameca SX-51 electron microprobe equipped with five wavelength-dispersive spectrometers using a 15 keV accelerating voltage, a 10 nA beam current, and a 1–2 μm beam diameter. Counting time was 10 s on peak and background for all elements. Major element compositions of phillipite and clusters of 1–5 μm Al-tobermorite were acquired from polished thin sections of tuffs and mortars prepared according to hydrophobic specifications. New determinations of phillipite compositions in Campi Flegrei Bacoli Tuff (BT) and Neapolitan Yellow Tuff (NYT) deposits and of phillipite and Al-tobermorite compositions in the marine mortars are compared with previously published compositions (Figs. 3 and 4; Tables 1, 2, and Supplemental Table S1). To account for potential Na and K loss and/or Si and Al gain, a time dependent intensity calibration was also applied to these elements using the software Probe for EPMA (e.g., Meier et al. 2011). Oxygen and water content were calculated by stoichiometry. Uncertainties in the weight percent oxides were determined by counting statistics and propagated through the calculation of formula units (Garimand and Day 1990). The fine grain size of Al-tobermorite contributed to lower wt% oxide measurements. Analyses with wt% oxide totals <80 (with H2O calculated by stoichiometry) and low atoms per formula unit were omitted from Table 2. Areas with visible traces of calcium carbonate crystals were not analyzed. Plotting coordinates for ternary diagrams were calculated from the mineral formulations of phillipite and Al-tobermorite. The Si-D0.25Al0.50Si0.50–M0.50Al0.50Si0.50 molecular proportions were calculated as:

1Deposit item AM-17-75993, Supplemental Table S1. Deposit items are free to all readers and found on the MSA web site, via the specific issue’s Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2017/Jul2017_data.html).
Si = Si – Al; D_{0.25}Al_{0.50}Si_{0.50} = 2[2Al(Ca+Mg+Ba+Sr)]/[(Na+K) + 2(Ca+Mg+Ba+Sr)]; M = 2[Al(Na+K)]/[(Na+K) + 2(Ca+Mg+Ba+Sr)], where D and M refer to divalent and monovalent cations, respectively (Deer et al. 2004; Gatta et al. 2010). The plotting coordinates of other ternary diagrams are based on molecular proportions as defined at the apices of a given diagram.

**Synchroton-based X-ray microdiffraction**

Crystalline phases in *Portus Cosanus* and *Baianus Sinus* cementitious microstructures were determined at Advanced Light Source beamline 12.3.2 at Lawrence Berkeley National Laboratory (Tamura et al. 2009) with microdiffraction and microfluorescence analyses (Figs. 5 and 7–9). Polished thin sections were prepared using superglue adhesive, studied with petrographic methods, and then detached from the glass slide by soaking in nitromethane. The 0.3 mm thick mortar slice was then mounted on adhesive tape and loaded in transmission mode into the beam, with the detector tilted at 30–39° to the incident beam. A monochromatic X-ray beam of 8 or 10 keV was focused to a 2 × 5 μm² diameter spot size. A Pilatus 1M area detector placed at 150 mm recorded Debye rings diffracted by crystalline phases. Debye rings at successive d-spacing reflections were integrated radially for 2q, 3° up to 54°, over an arch segment around the cone of diffraction of up to 76° to create intensity vs. d-spacing plots. These are shown as q = 2π/d-spacing, to increase readability of low d-spacing reflections.

**Scanning electron microscopy (SEM)**

Compositional high-resolution energy-dispersive X-ray spectroscopy (EDS) elemental maps of the same *Portus Cosanus* and *Baianus Sinus* microstructures were obtained with a Bruker XFlash 5060F Silicon Drift Detector (SDD) on a Zeiss Merlin Compact Scanning Electron Microscope (SEM) at the Bruker Laboratories in Berlin, Germany (Figs. 7 and 9). Element concentrations are displayed by quantitative mapping (QMap) in normalized mass% using the PB-ZAF quantification method. Element distributions are shown in false color display from black to blue, green, yellow to red, with the highest mass% concentration. Noise was removed by adjusting the maximum intensity threshold for each element. The analyses utilized high voltage, 8 keV, resolution of 379 nm per pixel, and 196 ms residence time (Figs. 7b and 7c), 197 nm per pixel, 88 ms (Figs. 7f and 7g), and 10 keV, 388 nm per pixel, 312 ms (Figs. 7k–7n). Backscattered (BSE) images of tuffs and mortars (Figs. 1b–d, 1f–1j, 6, 7a–7c, 8a–8c, 9a, and 9b) were acquired with the Zeiss EVOMA10 Scanning Electron Microscope at the UC Berkeley Department of Earth and Planetary Science. A secondary electron image (Fig. 1e) of Surtsey tuff from a 1979 drill core was acquired by J.G. Moore in 1979 using an ARL-EMX microprobe at the U.S. Geological Survey, Menlo Park, California.
FIGURE 7. Comparison of microstructures showing Al-tobermorite crystallization in association with zeolite alteration. (a–h) Portus Cosanus, pumice clast. (j–o) Baianus Sinus, relict pores in the cementing matrix. SEM BSE images, energy-dispersive X-ray (SEM-EDS) spectroscopy maps, and X-ray microdiffraction maps (see Figs. 8 and 9 for details). (i) X-ray microdiffraction patterns, Portus Cosanus pumice clast: early Al-tobermorite (A, Fig. 1j, location [1]), later Al-tobermorite (B, Fig. 1j, in vesicle near [1], C, Fig. 8b, location 66) and strätlingite (D, Fig. 8d, location 06). Reference Al-tobermorite diffraction patterns from [1] Jackson et al. (2013a), Baianus Sinus relict lime clast, [2] Yamazaki and Toraya (2001), Al-tobermorite synthesis; SEM-EDS maps b, e, f, and g scaled to red = 20 normalized mass% at each point; SEM-EDS maps l–p scaled to red = maximum mass%: Al, 9.5; Si, 24.7; K, 6.7; Na, 18.6; S, 10.2; Cl, 3.7.

Raman spectroscopy

Raman spectra obtained through a confocal microscope is correlated with crystals in cementitious microstructures previously analyzed with X-ray microdiffraction in Baianus Sinus relict lime clasts, pumice clasts, and relict voids (Figs. 10–12, Table 3). A JYHoriba LabRAM spectrometer at the Department of Chemical Engineering, UC Berkeley, was used in backscattering configuration, with HeNe laser (632.8 nm) excitation line, power at ~5 mW, and through an 100× confocal microscope (aperture = 0.8; laser spot size <1 μm). The spectra evaluate the nearest neighbor bonding environments of the silicate tetrahedron via oxygen corresponding to Q′m [Si (or Al)], where Q′ silicate tetrahedra are connected via O bridging O atoms to m SiO4 (or AlO4). Bands at 1074, 1086, etc., indicate C–O stretching in calcite and vaterite (Black et al. 2007; Snellings 2015). No Raman spectra exist for 11 Å Al-tobermorite and C-A-S-H spectra with spectra of laboratory syntheses of 11 Å tobermorite without sulfate compositions that are similar to phillipsite from NYT and Bacoli Tuff (BT), 8.6 ± 0.6 ka (Fedele et al. 2011); these are shown, for example, by most Portus Neronis phillipsite compositions (Figs. 3a and 4a; Tables 1 and S1).

Although Roman marine mortar has a mesoscale pumiceous structure that is analogous to the clastic fabric of Campi Flegrei tuffs (Figs. 1f–1h), the cementing matrix contains predominantly C-A-S-H binder. In situ dissolution of trachytic glass (Fig. 1f) and alkali feldspar crystal fragments occurred (Fig. 1g), as in the Campi Flegrei tuffs, but the reaction products are not always zeolites. Dissolution of an alkali feldspar crystal fragment in the hardened cementing matrix of the Portus Neronis mortar, for example, produced a 100 μm2 mold (Fig. 5). Al-tobermorite and strätlingite, a hydrated calcium-aluminum phyllosilicate [Ca3Al2(Si2O5)(OH)4]2.5(H2O), with 12.5 Å (0001) basal spacing, crystallized along the perimeter of the remnant feldspar crystal. Dissolution evidently raised solution ionic concentrations in the mold, and crystalline hydrate precipitation occurred in a leached layer behind the dissolution front (Snellings 2015). Alkali feldspar compositions in the mortars range from potassic (9–12 wt% K2O, 1–2 wt% Na2O and CaO) to more sodic (5–7 wt% K2O, 3–5 wt% Na2O, and 1–2 wt% CaO).

Vesicles in the perimeter of a pumice clast in the subaerial Portus Cosanus mortar contain deeply etched, 15–20 μm Campi Flegrei phillipsite crystals surrounded by C-A-S-H and sub-
spherical accumulations of ~5 μm Al-tobermorite (Fig. 1i, locations [1], [2], [3]). These microstructures record deep dissolution of Campi Flegrei phillipsite [1], production of pozzolanic C-A-S-H and Al-tobermorite [2,3], and abrupt termination of pozzolanic reaction before the phillipsite was fully consumed. Experimental mixing of portlandite with phillipsite in Neapolitan Yellow Tuff by Mertens et al. (2009) provides insight into these microstructures. Rapid pozzolanic reaction occurred for a few days until thickening of a reaction rim of hydrates covered the external surfaces of the crystals; the reaction then slowed considerably after 10 days of hydration and proceeded through a diffusion controlled process. The Portus Cosanus pumice vesicles evidently record rapid pozzolanic reaction through pH 12–14 pore solutions derived from seawater, calcium hydroxide, and trachytic ash, as Vitruvius described (Appendix Table 1), but sealing of the surfaces of the phillipsite crystals by C-A-S-H and Al-tobermorite hydration products prevented further pozzolanic reaction. Remarkably, the center of this vesicle and adjacent vesicles (Fig. 6a, location [4]) contain masses of <1–2 μm Al-tobermorite crystals, identified through X-ray microdiffraction. These very fine-grained, irregularly shaped agglomerations of Al-tobermorite in pumice vesicles of the Portus Cosanus, Portus Neronis (Figs. 6b and 6c) and Baianus Sinus mortars are commonly associated with sub-rounded phillipsite aggregations and etched or frayed alkali feldspar crystal fragments. In Portus Neronis and Baianus Sinus pumice vesicles, Al-tobermorite contains 43.2–47.6 wt% SiO₂. These compositions are more siliceous than those of crystals that formed in relict lime clasts in the same mortar specimens.
Figure 9. Authigenic mineral syntheses in relict voids of the cementing matrix, submarine *Baianus Sinus* mortar (Figs. 7j–7o). (a and b) SEM-BSE images showing relict pores with in situ crystalline textures. (c) Diffraction patterns for Roman phillipsite and Al-tobermorite in d and phillipsite in a *Baianus Sinus* pumice vesicle compared with Campi Flegrei (Gatta et al. 2010) and Alban Hills (Gualtieri 2000) phillipsite. (d) X-ray microdiffraction map, showing in situ phillipsite (Phi), Al-tobermorite (Al-tbm), ettringite (Ett), vaterite (Vtr), calcite (Cal), unknown (U). Asterisk (*) represents spotty Debye ring patterns indicative of crystals too coarse (>3 μm) to produce regular diffraction rings with the monochromatic X-ray beam. (e) SEM-EDS maps, silicon (Si), aluminum (Al), sodium (Na), and sulfur (S) concentrations normalized to 20 mass% (red).
and they show a greater range of Al₂O₃ and CaO contents (Figs. 3b and 4b, Table 2). Some compositions are nearly identical to Al-tobermorite that crystallized in 15-year-old basaltic tuff of Surtsey volcano, Iceland (Jakobsson and Moore 1986). Na₂O and K₂O at 1.2–3.0 wt% throughout partially balance Al³⁺ substitution for Si⁴⁺ relative to ideal tobermorite (Mitsuda and Taylor 1978; Komarneni and Roy 1983; Barnes and Scheetz 1991; Taylor 1992). These compositions and the fine-grained habit of the crystals suggest a possible post-pozzolanic origin. They may have precipitated from alkaline fluids in more or less closed chemical systems in vesicles, produced through reaction of feldspar crystals, potassic phillipsite, and trachytic glass, which contains up to 12 wt% Na₂O+K₂O and 2–3 wt% CaO (de Gennaro et al. 2000; Fedele et al. 2011).
Although one might suppose that all zeolite in the mortar has a geological origin, phillipite textures in relite voids of the cementing matrix indicate in situ crystallization (Fig. 1h). X-ray microdiffraction analyses of Baianus Sinus mortar show, for example, phillipite clusters that crystallized on Al-tomboeromite plates in the cementing matrix (Jackson et al. 2013b). Compared with most Campi Flegrei phillipite, the phillipite that formed in relite pores of the marine mortar has lower silica (SiO$_2$, 38–45 wt%), higher alumina (Al$_2$O$_3$, 28–31 wt%), lower Si/Al (1.3–1.6), and greater calcium (CaO, 7–11 wt%) (Figs. 3a and 4a; Tables 1 and 2).

### Table 1. Phillipite compositions measured by EPMA

| Neapolitan Yellow Tuff | Bacoli Tuff (BRI05.01) | Baianus Sinus (06-BAb-03) | Portus Neronis (ANZ.02.01) | Portus Traianus (PTL02.02) | Trajan’s Markets (GRAUL3A9) | Portus Cosanus (PCC03.01) |
|------------------------|------------------------|---------------------------|---------------------------|---------------------------|-----------------------------|---------------------------|
| Ca/(Al+Si)              |                        |                           |                           |                           |                             |                           |
| SiO$_2$                 | 53.1                   | 58.6                      | 58.8                      | 66.7                      | 59.5                        | 58.3                      |
| TiO$_2$                 | 0.02                   | 0.0                       | 0.0                       | 0.0                       | 0.0                          | 0.0                       |
| Al$_2$O$_3$             | 2.2                    | 2.3                       | 2.3                       | 2.0                       | 2.1                          | 2.0                       |
| Fe$_2$O$_3$             | 0.02                   | 0.0                       | 0.0                       | 0.0                       | 0.0                          | 0.0                       |
| MnO                     | 0.02                   | 0.0                       | 0.0                       | 0.0                       | 0.0                          | 0.0                       |
| MgO                     | 0.02                   | 0.0                       | 0.0                       | 0.0                       | 0.0                          | 0.0                       |
| CaO                     | 7.6                    | 8.2                       | 1.1                       | 1.0                       | 1.3                          | 0.9                       |
| Na$_2$O                 | 0.05                   | 0.13                      | 0.8                       | 0.6                       | 0.6                          | 0.5                       |
| K$_2$O                  | 0.03                   | 0.16                      | 7.6                       | 8.2                       | 8.7                          | 8.0                       |
| Sum                    | 91.2                   | 93.5                      | 92.7                      | 80.2                      | 82.0                         | 81.4                      |

* ±2σ lower limit of detection.
* ±2σ lower limit of detection.

### Table 2. Al-tomboeromite compositions from Baianus Sinus and Portus Neronis measured by EPMA

| Baianus Sinus (Bay of Pozzuoli, ROMACONS core BA06.03) | Portus Neronis (Anzio, ROMACONS core ANZ.02.01) |
|-------------------------------------------------------|--------------------------------------------------|
| Large Lime Clast                                      | Pumice Clast                                      |
| LLF1 LLF2 PL2 PAL1                                   | Pumice Clast                                      |
| 39.0 39.9 39.0                                       | 39.0 39.9 39.0                                    |
| 44.2 45.5 45.7                                       | 44.2 45.5 45.7                                    |
| 69.7 71.3 73.4                                       | 69.7 71.3 73.4                                    |
| 29.0 25.8 24.2                                       | 29.0 25.8 24.2                                    |
| 1.1 1.0 1.0                                         | 1.1 1.0 1.0                                       |
| 3.8 3.7 3.7                                         | 3.8 3.7 3.7                                       |
| 1.1 1.1 1.1                                         | 1.1 1.1 1.1                                       |
| 11.2 11.8 11.9                                      | 11.2 11.8 11.9                                    |
| 5.3 5.5 5.5                                         | 5.3 5.5 5.5                                       |
| 1.0 1.0 1.0                                         | 1.0 1.0 1.0                                       |
| 0.0 0.0 0.0                                         | 0.0 0.0 0.0                                       |
| 0.0 0.0 0.0                                         | 0.0 0.0 0.0                                       |
| 0.0 0.0 0.0                                         | 0.0 0.0 0.0                                       |
| 0.0 0.0 0.0                                         | 0.0 0.0 0.0                                       |
| 0.0 0.0 0.0                                         | 0.0 0.0 0.0                                       |
| 0.0 0.0 0.0                                         | 0.0 0.0 0.0                                       |
| 0.0 0.0 0.0                                         | 0.0 0.0 0.0                                       |
| 0.0 0.0 0.0                                         | 0.0 0.0 0.0                                       |
| 0.0 0.0 0.0                                         | 0.0 0.0 0.0                                       |

#### Cation ratios

#### Al/3(Al+Si)

| Ca/Al+Si | 0.77 0.77 0.68 0.67 | 0.76 0.77 0.76 | 0.59 0.51 0.48 0.45 | 0.65 0.69 0.68 |
|----------|---------------------|----------------|---------------------|------------------|
| 0.01 0.0 | 0.01 0.0 0.1 0.1 | 0.01 0.1 0.1 | 0.01 0.1 0.1 | 0.01 0.1 0.1 |
| 0.01 0.0 | 0.01 0.0 0.1 0.1 | 0.01 0.1 0.1 | 0.01 0.1 0.1 | 0.01 0.1 0.1 |
| 0.01 0.0 | 0.01 0.0 0.1 0.1 | 0.01 0.1 0.1 | 0.01 0.1 0.1 | 0.01 0.1 0.1 |
| 0.01 0.0 | 0.01 0.0 0.1 0.1 | 0.01 0.1 0.1 | 0.01 0.1 0.1 | 0.01 0.1 0.1 |
| 0.01 0.0 | 0.01 0.0 0.1 0.1 | 0.01 0.1 0.1 | 0.01 0.1 0.1 | 0.01 0.1 0.1 |
| 0.01 0.0 | 0.01 0.0 0.1 0.1 | 0.01 0.1 0.1 | 0.01 0.1 0.1 | 0.01 0.1 0.1 |
TABLE 3. Assignments of Raman frequency shifts to silicate and aluminate linkages in Baianus Sinus C-A-S-H and Al-tobermorite compared with previous studies of C-S-H and tobermorite

| Previous studies | Baianus Sinus mortar | Inferred Linkage<sup>abc</sup> |
|------------------|----------------------|-----------------------------|
|                  | Frequency (cm<sup>-1</sup>) | Assignment | Frequency (cm<sup>-1</sup>) |                   |
| C-S-H<sup>a</sup> | 11Å tobermorite<sup>b</sup> | \(\nu_3(\text{SiO}_4\text{)}\) | Al-tobermorite |                   |
| Ca/Si=0.83       | 441–540              | Internal deformations       | Ca/(Si+Al) = 0.8<sup>c</sup> | 11Å Al-tobermorite |
|                  | 600–630              | \(\nu_3(\text{SiO}_4\text{)}\) | Symmetric bending 600–700 | 442–451          |
|                  | 660–680<sup>b,c,d</sup> |                      | 668–671          | 428–443          |
|                  | 850                   | \(\nu_3(\text{SiO}_4\text{)}\) | Symmetric stretching 800–1200 | – |
|                  | 998–1010<sup>e</sup> |                      | 996              | 806–809          |
|                  | 1040–1114            | (1068 vaterite)<sup>f</sup> | (913–1012)<sup>g</sup> | SS Q<sup>3</sup> (0AA) |
|                  |                      | to be determined          | 1110–1113       | SS Q<sup>3</sup> (1AI) |

<sup>a</sup> Kirkpatrick et al. (1997).
<sup>b</sup> Richardson et al. (2010).
<sup>c</sup> http://rruff.info/Tobermorite R060147, Crestmore Quarries, Riverside, California.
<sup>d</sup> Black et al. (2007).
<sup>e</sup> Black (2009), 950–1000 cm<sup>-1</sup> band is also attributed to anti-symmetric stretching of Q<sup>2</sup> silicate linkages.
<sup>f</sup> Jackson et al. (2013).
<sup>g</sup> Frost et al. (1998), FT-Raman analysis of kaolinite, 645 band records SS of (SiO<sub>4</sub>) tetrahedral units when the incident laser beam is directed parallel to the c-axis of layered crystals.
<sup>h</sup> Weak bands at 913–918, 934–93, 990–1000, 1000–1012.
<sup>i</sup> Strong bands at 998–1010.
<sup>j</sup> Kirkpatrick et al. (1995).
<sup>k</sup> Kirkpatrick et al. (1997).
concentrations coincide with X-ray microdiffraction analyses indicating newly formed cementitious hydrates, mainly ettringite and Al-tobermorite (Figs. 9d and 9e). Ettringite, a hydrous calcium-aluminum-sulfate [Ca6Al2(SO4)3(OH)12], crystallized in zones with higher sulfur concentrations. Al-tobermorite crystallized in narrow zones with higher calcium and lower silica contents. The acicular crystals protrude from the etched surfaces of the phillipsite fabrics into relic pore space (Fig. 1j). This interfacial relationship is illustrated by X-ray microdiffraction patterns showing both phillipsite and Al-tobermorite at the submicrometer scale (Figs. 9c, 9d, locations 54 and 57). Similar phillipsite and Al-tobermorite mineral assemblages have been described in basaltic tuff at Surtsey volcano, Iceland, at 100 °C 15 years after eruption (Jakobsson and Moore 1986) (Fig. 1e). The Baianus Sinus microstructures demonstrate that Al-tobermorite crystallization can occur at ambient seawater temperatures, 14–26 °C (Damiani et al. 1987), in a highly potassic and sodic system produced through alteration of phillipsite, which itself precipitated in the mortar fabric. The complex mineral textures indicate cycling of low-temperature, post-pozzolanic reactions in pores of the cementing matrix as a response to evolving fluid interactions over time.

Raman spectroscopy

Raman spectroscopic analyses referenced to previous 29Si and 27Al nuclear magnetic resonance (NMR) studies provide insights into the roles of Al3+, Na+, and K+ in Baianus Sinus Al-tobermorite from diverse microstructural environments, as compared with ideal tobermorite [Ca5Si6O17(OH)2] (Biagioni et al. 2015), Baianus Sinus C-A-S-H, and calcium-silicate-hydrate C-S-H binder (Figs. 10–12). X-ray microdiffraction analyses of Al-tobermorite in relic lime clasts, pumice clasts, and relic voids show relatively uniform patterns, with 11.20–11.24 Å of Al-tobermorite in relict lime clasts, pumice clasts, and relict voids precipitated in the mortar fabric. This interfacial relationship is illustrated by X-ray microdiffraction analyses of Q3(1Al) in 29Si NMR study of Roman Al-tobermorite (Fig. 11) may indicate both Al–O stretching and SiO2–CaAl2O4 glass crystallization can occur at ambient seawater temperatures, 14–26 °C (Damiani et al. 1987), in a highly potassic and sodic system produced through alteration of phillipsite, which itself precipitated in the mortar fabric. The complex mineral textures indicate cycling of low-temperature, post-pozzolanic reactions in pores of the cementing matrix as a response to evolving fluid interactions over time.

Raman spectroscopy

Raman spectroscopic analyses referenced to previous 29Si and 27Al nuclear magnetic resonance (NMR) studies provide insights into the roles of Al3+, Na+, and K+ in Baianus Sinus Al-tobermorite from diverse microstructural environments, as compared with ideal tobermorite [Ca5Si6O17(OH)2] (Biagioni et al. 2015), Baianus Sinus C-A-S-H, and calcium-silicate-hydrate C-S-H binder (Figs. 10–12). X-ray microdiffraction analyses of Al-tobermorite in relic lime clasts, pumice clasts, and relic voids show relatively uniform patterns, with 11.20–11.24 Å of Al-tobermorite in relict lime clasts, pumice clasts, and relict voids precipitated in the mortar fabric. This interfacial relationship is illustrated by X-ray microdiffraction analyses of Q3(1Al) in 29Si NMR study of Roman Al-tobermorite (Fig. 11) may indicate both Al–O stretching and SiO2–CaAl2O4 glass crystallization can occur at ambient seawater temperatures, 14–26 °C (Damiani et al. 1987), in a highly potassic and sodic system produced through alteration of phillipsite, which itself precipitated in the mortar fabric. The complex mineral textures indicate cycling of low-temperature, post-pozzolanic reactions in pores of the cementing matrix as a response to evolving fluid interactions over time.

Raman spectroscopy

Raman spectroscopic analyses referenced to previous 29Si and 27Al nuclear magnetic resonance (NMR) studies provide insights into the roles of Al3+, Na+, and K+ in Baianus Sinus Al-tobermorite from diverse microstructural environments, as compared with ideal tobermorite [Ca5Si6O17(OH)2] (Biagioni et al. 2015), Baianus Sinus C-A-S-H, and calcium-silicate-hydrate C-S-H binder (Figs. 10–12). X-ray microdiffraction analyses of Al-tobermorite in relic lime clasts, pumice clasts, and relic voids show relatively uniform patterns, with 11.20–11.24 Å of Al-tobermorite in relict lime clasts, pumice clasts, and relict voids precipitated in the mortar fabric. This interfacial relationship is illustrated by X-ray microdiffraction analyses of Q3(1Al) in 29Si NMR study of Roman Al-tobermorite (Fig. 11) may indicate both Al–O stretching and SiO2–CaAl2O4 glass crystallization can occur at ambient seawater temperatures, 14–26 °C (Damiani et al. 1987), in a highly potassic and sodic system produced through alteration of phillipsite, which itself precipitated in the mortar fabric. The complex mineral textures indicate cycling of low-temperature, post-pozzolanic reactions in pores of the cementing matrix as a response to evolving fluid interactions over time.

Raman spectroscopy

Raman spectroscopic analyses referenced to previous 29Si and 27Al nuclear magnetic resonance (NMR) studies provide insights into the roles of Al3+, Na+, and K+ in Baianus Sinus Al-tobermorite from diverse microstructural environments, as compared with ideal tobermorite [Ca5Si6O17(OH)2] (Biagioni et al. 2015), Baianus Sinus C-A-S-H, and calcium-silicate-hydrate C-S-H binder (Figs. 10–12). X-ray microdiffraction analyses of Al-tobermorite in relic lime clasts, pumice clasts, and relic voids show relatively uniform patterns, with 11.20–11.24 Å of Al-tobermorite in relict lime clasts, pumice clasts, and relict voids precipitated in the mortar fabric. This interfacial relationship is illustrated by X-ray microdiffraction analyses of Q3(1Al) in 29Si NMR study of Roman Al-tobermorite (Fig. 11) may indicate both Al–O stretching and SiO2–CaAl2O4 glass crystallization can occur at ambient seawater temperatures, 14–26 °C (Damiani et al. 1987), in a highly potassic and sodic system produced through alteration of phillipsite, which itself precipitated in the mortar fabric. The complex mineral textures indicate cycling of low-temperature, post-pozzolanic reactions in pores of the cementing matrix as a response to evolving fluid interactions over time.

Raman spectroscopy

Raman spectroscopic analyses referenced to previous 29Si and 27Al nuclear magnetic resonance (NMR) studies provide insights into the roles of Al3+, Na+, and K+ in Baianus Sinus Al-tobermorite from diverse microstructural environments, as compared with ideal tobermorite [Ca5Si6O17(OH)2] (Biagioni et al. 2015), Baianus Sinus C-A-S-H, and calcium-silicate-hydrate C-S-H binder (Figs. 10–12). X-ray microdiffraction analyses of Al-tobermorite in relic lime clasts, pumice clasts, and relic voids show relatively uniform patterns, with 11.20–11.24 Å of Al-tobermorite in relict lime clasts, pumice clasts, and relict voids precipitated in the mortar fabric. This interfacial relationship is illustrated by X-ray microdiffraction analyses of Q3(1Al) in 29Si NMR study of Roman Al-tobermorite (Fig. 11) may indicate both Al–O stretching and SiO2–CaAl2O4 glass crystallization can occur at ambient seawater temperatures, 14–26 °C (Damiani et al. 1987), in a highly potassic and sodic system produced through alteration of phillipsite, which itself precipitated in the mortar fabric. The complex mineral textures indicate cycling of low-temperature, post-pozzolanic reactions in pores of the cementing matrix as a response to evolving fluid interactions over time.

Raman spectroscopy

Raman spectroscopic analyses referenced to previous 29Si and 27Al nuclear magnetic resonance (NMR) studies provide insights into the roles of Al3+, Na+, and K+ in Baianus Sinus Al-tobermorite from diverse microstructural environments, as compared with ideal tobermorite [Ca5Si6O17(OH)2] (Biagioni et al. 2015), Baianus Sinus C-A-S-H, and calcium-silicate-hydrate C-S-H binder (Figs. 10–12). X-ray microdiffraction analyses of Al-tobermorite in relic lime clasts, pumice clasts, and relic voids show relatively uniform patterns, with 11.20–11.24 Å of Al-tobermorite in relict lime clasts, pumice clasts, and relict voids precipitated in the mortar fabric. This interfacial relationship is illustrated by X-ray microdiffraction analyses of Q3(1Al) in 29Si NMR study of Roman Al-tobermorite (Fig. 11) may indicate both Al–O stretching and SiO2–CaAl2O4 glass crystallization can occur at ambient seawater temperatures, 14–26 °C (Damiani et al. 1987), in a highly potassic and sodic system produced through alteration of phillipsite, which itself precipitated in the mortar fabric. The complex mineral textures indicate cycling of low-temperature, post-pozzolanic reactions in pores of the cementing matrix as a response to evolving fluid interactions over time.

Raman spectroscopy

Raman spectroscopic analyses referenced to previous 29Si and 27Al nuclear magnetic resonance (NMR) studies provide insights into the roles of Al3+, Na+, and K+ in Baianus Sinus Al-tobermorite from diverse microstructural environments, as compared with ideal tobermorite [Ca5Si6O17(OH)2] (Biagioni et al. 2015), Baianus Sinus C-A-S-H, and calcium-silicate-hydrate C-S-H binder (Figs. 10–12). X-ray microdiffraction analyses of Al-tobermorite in relic lime clasts, pumice clasts, and relic voids show relatively uniform patterns, with 11.20–11.24 Å of Al-tobermorite in relict lime clasts, pumice clasts, and relict voids precipitated in the mortar fabric. This interfacial relationship is illustrated by X-ray microdiffraction analyses of Q3(1Al) in 29Si NMR study of Roman Al-tobermorite (Fig. 11) may indicate both Al–O stretching and SiO2–CaAl2O4 glass crystallization can occur at ambient seawater temperatures, 14–26 °C (Damiani et al. 1987), in a highly potassic and sodic system produced through alteration of phillipsite, which itself precipitated in the mortar fabric. The complex mineral textures indicate cycling of low-temperature, post-pozzolanic reactions in pores of the cementing matrix as a response to evolving fluid interactions over time.
spectra, where a tetrahedral 1566.7 eV absorption edge broadens to an octahedral 1571.0 eV absorption edge. These complexities may also be recorded by $^{27}$Al NMR, which has a weak octahedrally coordinated Al-O component at 10.88 ppm (Jackson et al. 2013a, 2013b). Components of both Al-O stretching and complex motions of silica and aluminum against tetrahedral oxygen may therefore occur at the Raman 443 and the 800–840 maxima (McMillan and Piriou 1982; McMillan et al. 1982). It is not clear how these spectra might record possible octahedrally coordinated Al$^{3+}$ substitution for Ca$^{2+}$ within the interlayer of the crystals (Abdolhosseini Qomi et al. 2012).

**Baianus Sinus C-A-S-H** shows uniform Raman spectra over a diverse range of cementitious microstructures (Fig. 11). A broad band centered at 668 cm$^{-1}$ corresponds to symmetrical bending (SB) of Q$_2$(0Al), and could also include SB of Q$_2$(1Al), given oxygen may therefore occur at the Raman 443 and the 800–840 complex motions of silica and aluminum against tetrahedral al. 2013a, 2013b). Components of both Al-O stretching and Si along its flow path. Zeolites crystallize when the cation to hydrogen ion ratio and other ionic activities are relatively high (Sheppard and Hay 2001). Early-formed zeolites commonly alter to other zeolites; phillipsite, for example, commonly alters to analcime, and analcime can be replaced by laumontite, K-feldspar, or albite (Hay and Sheppard 2001). Authigenic textures thus record dynamic physico-chemical environments and phase-stability relationships over time in open-to-closed hydrologic systems.

In Campi Flegrei deposits, post-eruptive hydrolysis and dissolution of trachytic ash components. These reactions release hydroxyl ions, and the solution becomes more alkaline and enriched in Na, K, Ca, and Si along its flow path. Zeolites crystallize when the cation to hydrogen ion ratio and other ionic activities are relatively high (Sheppard and Hay 2001). Early-formed zeolites commonly alter to other zeolites; phillipsite, for example, commonly alters to analcime, and analcime can be replaced by laumontite. Al-tobermorite is considered to have a hydrothermal origin in geologic occurrences (Claringbull and Hey 1952; Mitsuda and Taylor 1978; Livingstone 1988; Henmi and Kusachi 1992; Hoffman and Armbruster 1997; Aguirre et al. 1998) and has been previously produced in laboratory syntheses always at ≥80 °C (e.g., Komarneni and Roy 1983). Alkali-activated Pozzolanic production of zeolite and Al-tobermorite has been produced in autoclaved aerated concrete, heated at 110–200 °C in 12 h to 7 days (Grutzek et al. 2004), and through NaOH-activated trachytic rock aggregate mixed with calcium hydroxide and heated at 150–175 °C for 24 h (Youssef et al. 2010). Relatively low-temperature crystallization of phillipsite and Al-tobermorite has occurred, however, in the pores of Portland cement paste in contact with a claystone interface at 70 °C one year after installation (Laan et al. 2016). Furthermore, Al-tobermorite has been identified throughout a 181 m core drilled through Surtsey in 1979, at temperatures from 25 °C in surficial deposits to 140 °C in hydrothermally altered tuff (Jakobsson and Moore 1986) (see Fig. 1e). The distinguishing feature of the Roman marine mortar system is to record low-temperature processes of authigenic mineral cycling, which involve the reaction of volcanic ash components; production of alkaline fluids in microenvironments; precipitation of new minerals, principally phillipsite in these microstructures; and evolving pore solution chemistries that produce Al-tobermorite crystallization in subaerial and submarine structures.
Systems that begin as relatively simple states and evolve to states of increasing complexity are a recurrent characteristic of mineral evolution and Earth processes, as well as emerging technologies (Hazen et al. 2008). Vitruvius described the relatively simple mixture of volcanic ash (putvis), lime (calx), and tuff aggregate (tofus) that cohered pozzolanaically in seawater. Pliny the Elder and Seneca called upon geologic analogs to explain concrete resilience after 100–150 yr of service life. Advanced analytical techniques now show the complexity of Roman marine concrete technologies, whose initial protocols for developing an effective pozzolan cementsitious system evolved through authigenic mineral cycling to produce cementsitious systems with the chemical range and longevity of water-rock interactions in pyroclastic rocks of Earth’s upper crust. Roman builders evidently had these objectives in mind when designing the maritime concrete structures (Brandon et al. 2014).

The cementing fabrics of Roman concrete breakwaters and piers constructed with volcanic ash mortars provide a well-constrained template for developing cementsitious technologies through low-temperature rock-fluid interactions, cation-exchange, and carbonation reactions that occur long after an initial phase of reaction with lime that defines the activity of natural pozzolans (Massazza 2004). Some aspects of the Roman post-pozzolanic system have been reproduced by geopolymertype cementitious systems, where alkali mediated dissolution and precipitation reactions involving little or no calcium occur in aqueous reaction substrates (Provis and Bernal 2014). These systems do not, however, produce on-going, beneficial precipitation of cementsitious hydrates through evolving alteration of reactive aggregate(s). Coupled dissolution and precipitation processes produced through the reactivity of synthetic calcium (alumino)silicate glasses, basaltic glasses, and borosilicate glasses with aqueous solutions at varying pH (Snellings 2015; Jantzen et al. 2017) have a great deal of relevance for gaining further understanding of multiple pathways to low-temperature Al-tobermorite crystallization. This especially concerns variable solution chemistries produced in microenvironments associated with authigenic dissolution of the alkaline components of pozzolanic volcanic ash—alkali feldspar, trachytic glass, and relic zeolite textures. Carbonation of zeolite in the pumice clasts of the subaerial mortar also apparently released alkaline earth elements associated with low-temperature crystallization of Al-tobermorite. The platy and acicular Al-tobermorite crystals may increase ductility and resistance to fracture (Jackson et al. 2014), possibly leading to the increasing mechanical resilience of the concrete that Pliny observed [...] and stronger every day (fortiorem cotidie) (Appendix Table 1).

**IMPLICATIONS**

That in situ production of alkaline pore fluids derived from low-temperature intersections of seawater-derived fluids with components of trachytic Campan Flegrei pumiceous ash drives zeolite and Al-tobermorite crystallization in Roman marine concrete is a surprising discovery, since (1) laboratory Al-tobermorite syntheses have not been produced at ambient temperatures, and (2) release of alkali cations from rock aggregate in Portland cement concrete generally produces expansive alkali-silica gels that degrade structural concretes worldwide. By contrast, the alkaline fluids in Roman subaerial and submarine concrete piers and breakwaters produce precipitation of phillipsite and Al-tobermorite mineral cements that refine pore space, enhance bonding in pumice clasts and sequester alkali cations, principally sodium and potassium.

Roman marine concretes can provide guidelines for the optimal selection of natural volcanic pozzolans that have the potential to produce of regenerative cementsitious resilience through long-term crystallization of zeolite, Al-tobermorite, and strätlingite mineral cements. The cross-linked structure and Al³⁺ bonding environments of the Roman Al-tobermorite crystals, recorded by Raman spectra through a range of cementsitious microstructures and crystallization pathways, provide clues to creating new pathways for cation-change in high-performance concretes. Furthermore, the chemical and mechanical resilience of the marine concrete provides keys to understanding dynamic mineral cements in young, oceanic pyroclastic deposits, as at Surtsey (Jakobsson and Moore 1986), the seismic response of a volcanic edifice, as in deep Campi Flegrei deposits (Vanorio and Kanitpanyacharoen 2015), and carbon mineralization reactions, as occur in porous basaltic storage reservoirs for anthropogenic CO₂ (Matter et al. 2016). Roman prototypes for brine-based concretes could conserve freshwater resources, generate multiple low temperature pathways to pozzolanic and post-pozzolanic Al-tobermorite sorbents with coupled Al³⁺ and exchangeable alkali cation sites, and extend applications of natural volcanic pozzolans to environmentally friendly, alkali-activated structural concretes and cementsitious barriers for waste encapsulations.

**ACKNOWLEDGMENTS**

We extend special thanks to M. Patzschke, Bruker Laboratories, Berlin, and to N. Tarrara and M. Kuma, Advanced Light Source (ALS) beamline 12.3.2, for assistance with the coupled compositional and X-ray microdiffraction maps of Portus Cosanus and Baiae Sinus microstructures. T. Teague and C. Carraro, U.C. Berkeley, provided analytical support. J.G. Moore, U.S. Geological Survey, shared valuable perspectives on Surtsey deposits. J.P. Oleson, C. Brandon, and R.L. Hofhöfler of the Romancon program drilled the cores of the harbor concrete structures with support from CTG Gul cement, Bergamo, Italy. Data acquired at ALS beamline 12.3.2 at Lawrence Berkeley Laboratories were supported by the Director of the Office of Science, Department of Energy, under Contract No. DE-AC02-05CH11231. Acquisition of Raman spectra in the UC Berkeley Department of Chemical Engineering was funded by National Science Foundation (NSF) grant 1410557. H.-R. Wenk acknowledges support from National Science Foundation grant EAR-1343908.

**REFERENCES CITED**

Abdolhosseiní Qomi, M.J., Ulm, F.-J., and Pellenq, R.J.-M. (2012) Evidence on the dual nature of aluminium in the calcium-silicate-hydrates based on atomistic simulations. Journal of the American Ceramic Society, 95, 1128–1137.

Aguirre, L., Dominguez-Bell, S., Monata, D., and Winke, O. (1998) An occurrence of tobermorite in Tertiary basalts from Patagonia, Chile. Canadian Mineralogist, 36, 1149–1155.

ASTM (2015) Standard specification for coal fly ash and raw or natural pozzolan for use in concrete (C618-15). ASTM International, West Conshohocken, Pennsylvania, www.astm.org.

Barnes, M.W., and Schiebeck, B.E. (1991) The chemistry of Al-tobermorite and its coexisting phases at 175 °C. In B.E. Schiebeck, A.G. Landers, I. Oder, and H. Jennings, Eds., Specialty Cements with Advanced Properties, 179, 243–271. Material Research Society Symposium Proceedings, Warrendale, Pennsylvania.

Behrens, G., Kuhn, L.T., Ubc, R., and Heuer, A.H. (1995) Raman spectra of vateritic calcium carbonate. Spectroscopy Letters, 28, 983–995.

Biagioni, C., Merlino, S., and Bonaccorsi, E. (2015) The tobermorite supergroup: A new nomenclature. Mineralogical Magazine, 79, 485–495.

Black, L. (2009) Raman spectroscopy of cementsitious materials. Spectroscopic Properties Inorganic Organometallic Compounds, 40, 72–127.

Black, L., Breen, C., Yarwood, J., Garbev, K., Stemmerman, P., and Gasharova, B. (2007) Structural features of C–S–H(1) and its carbonation in air—A Raman spectroscopic study. Part II: Carbonated phases. Journal of the American Ceramic Society, 90, 908–917.

Brandon, C., Hofhöfler, R.L., Jackson, M.D., and Oleson, J.P. (2014) Building for Eternity: The History and Technology of Roman Concrete Engineering in the Sea.
Jackson, M.D., and Chae, S.R. (2017) Connectivity and chemical properties of Al-tobermorite in Roman seawater concrete. American Mineralogist, 98, 1669–1687.

Jackson, M.D., Moon, J., Gotti, E., Taylor, R., Chae, S.R., Kunz, M., Emwas, A.H., Murali, C., Guttman, P., Lee, S., and others. (2013a) Unlocking the secrets of Al-tobermorite in Roman seawater concrete. American Mineralogist, 98, 1669–1687.

Jackson, M.D., Moon, J., Gotti, E., Taylor, R., Chae, S.R., Kunz, M., Emwas, A.H., Murali, C., Guttman, P., Levitt, A., and others. (2013b) Material and elastic properties of Al-tobermorite in ancient Roman seawater concrete. Journal of the American Ceramic Society, 96, 2598–2606.

Jackson, M.D., Landis, E.N., Brune, P.B., Vitti, M., Chen, H., Li, Q., Kunz, M., Wenk, H.-R., Monteiro, P.J.M., and Ingraffea, A.R. (2014) Mechanical resilience and cementitious processes in Imperial Roman architectural mortar. Proceedings of the National Academy of Sciences, 111, 18485–18489.

Jackson, S., and Moore, J.G. (1986) Hydrothermal minerals and alteration rates at Surtsey volcano, Iceland. Geological Society of America Bulletin, 97, 648–659.

Jantzen, C.M., Crawford, C.L., Trivelpiece, C., Pareisz, J.M., and Picket, J.B. (2017) Accelerated Leach Testing of GLASS (ALTGLASS): II. Mineralization of Hydrogels by Leachate Strong Bases. International Journal of Applied Glass Science, 8, 84–96 (SRNL-STI-2014-00381).

Koizumi, S., and Roy, D. (1983) Tobermorites: A New family of cation exchangers. Science, 221, 647–648.

Koizumi, S., Breval, E., Miyake, M., and Roy, R. (1987) Cation exchange properties of (Al+Na)-substituted synthetic tobermorites. Clays and Clay Minerals, 35, 385–390.

Kirkpatrick, R.J., Yarger, J.L., McMillan, P.F., Yu, Y., and Cong, X. (1997) Raman spectroscopy of C-S-H, tobermorite, and jennite. Advances in Cement Based Materials, 5, 93–99.

Lalani, P., Dauzéras, A., DeWindt, L., Bartier, D., Sammaljärvi, J., Barnichon, J.-D., Techer, I., and Delétilieux, V. (2016) Impact of a 70 °C temperature on an ordinary Portland cement paste/claystone interface: An in situ experiment. Cement and Concrete Research, 83, 164–178.

L’Hôpital, E.L., Lothenbach, B., Scriven, K., and Kulik, D.A. (2016) Alkaline uptake in calcium alumina silicate hydrate (C-A-S-H). Cement and Concrete Research, 85, 122–136.

Livingstone, A. (1986) Rieyrite, tobermorite, calcian analcime and bytownite from amygdulites in Skye basalt. Mineralogical Magazine, 52, 711–713.

Lothenbach, B., Scriven, K., and Hooton, R.D. (2011) Supplementary cementitious materials. Cement and Concrete Research, 41, 217–229.

Métraux, F., Jackson, M.D., Decamp, D., and Ventura, G. (2009) Large mafic eruptions at Alban Hills Volcanic Zone (Central Italy). Journal of Volcanic and Geothermal Research, 179, 217–232.

Massazza, F. (1985) Concrete resistance to seawater and marine environment. II Cemento, 82, 26–85.

——— (2004) Pozzolana and pozzolanic cements. In P.C. Hewlett, Ed., Lea’s Chemistry of Cement and Concrete, 4th ed., pp. 471–602, Elsevier, Oxford.

Métraux, F., Stute, M., Snabbjörnsson, S.O., Oelkers, E.H., Gislason, S.R., Aradottir, E.S., Sigfusson, B., Gunnarsson, I., Sigurdardottir, H., Gunnlaugsson, E., and others. (2016) Rapid carbon mineralization for permanent disposal of calcium carbonate. Science, 352, 1312–1314.

McMillan, P., and Piriou, B. (1982) The structures and vibrational spectra of dickite, kaolinite, and their intercalates. Analyst, 123, 611–616.

Gatta, G.D., Cappelletti, P., and Langella, A. (2010) Crystal chemistry of phosphates from the Neapolitan Yellow Tuff. European Journal of Mineralogy, 22, 779–786.

Gaucher, E.C., and Blanc, P. (2006) Cement/clay interactions—a review: Experiments, natural analogues, and modeling. Waste Management, 26, 776–788.

Giaramita, M.J., and Day, H.W. (1990) Error propagation in calculations of structural formulas. American Mineralogist, 75, 170–182.

Gotli, S., Lorenzo, M.P., Guerrero, A., and Hernández, M.S. (2005) Calcium hydroxide saturation factors in the pore solution of hydrated Portland cement fly ash paste. Journal of the American Ceramic Society, 79, 1041–1046.

Gotti, E., Oleson, J.P., Battolico, L., Brandon, C., Cucitore, R., and Hohlfelder, R.F. (2008) A comparison of the chemical and engineering characteristics of alkali-cementitious systems and Portland cement: a modern reproduction of Vitruvian hydraulic concrete. American Mineralogist, 93, 1693–1702.

Grutzeck, M., Kwan, S., and DiCola, M. (2004) Zeolite formation in alkali-activated materials in concretes: a comprehensive review. Environmental Science and Technology, 38, 65–76.

Monteiro, P.J.M. (2014) High-volume natural volcanic pozzolan and limestone materials in concretes: a comprehensive review. Environmental Science and Technology, 48, 4051–4064.

Hoffman, C., and Armbuster, T. (1997) Quitoform of jennite. Neues Jahrbuch für Mineralogie, 164, 399–412.

Jackson, M.D., and Kosso, K. (2013) Scintia in republican era stone and concrete masonry. In J.R. Evans, Ed., A Companion to the Archaeology of the Roman Empire, 1st ed., pp. 268–284, Blackwell, New York.

Jackson, M.D., Vola, G., Višniャský, D., Olesen, J.P., Scheetz, B., Brandon, C., and Hohlfelder, R.L. (2012) Cement microstructures and durability in ancient Roman seawater concretes. In J. Válek, C. Groot, and J. Hughes, Eds., Historic Mortars, Characterisation, Assessment and Repair, p. 49–76, Springer, Berlin.
Notes: Increasing complexity in Roman construction durability and architectural design through invention, technology transfer, and competitive selection is de-

APPENDIX TABLE 1. Roman texts describing the geologic materials and cementitious processes of marine concrete, translations (Oleson 2014)

| Roman Text | English Translation | Interpretation |
|------------|---------------------|----------------|
| Vitruvius | There is a kind of powdery earth (pulvis) 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 (calce et caemento) not only furnishes strength to other buildings, but also, when breakwaters (moles) are built in the sea, they set underwater. Thus, when these three substances (pumiceous ash (pulvis), lime (calce), and tuff (tofus)) 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. | 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 | Therefore, when dissimilar and incompatible materials (lime (calce), pumiceous ash (pulvis), and tuff (tofus)) are taken and mixed in a moist environment the urgent need of moisture suddenly satiated by (sea-)water seethes in these substances and causes them to gather into a unified mass and gain solidity quickly. | 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. |
| Strabo | Puteoli has become a very great emporium because it has an artificial constructed harbor, 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-as (ammonkonia) 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 largest cargo ships can anchor there safely. | In the decades following Vitruvius’ descriptions of pozzolanic reaction in the marine concrete, pumiceous volcanic ash shipped from the harbor at Puteoli became a requisite component of maritime harbor construction. |
| Seneca | The water is adulterated and throws a sediment (limus) of such a nature that it cements (adglaünet) and hardens objects. Just as the (volcanic ash) Puteolanus pulvis becomes rock (saxum est) if it touches water so, by contrast, if this water touches something solid it clings to it and forms concretions. | Geologic processes for calcium carbonate cements in the Hebruis River Thrace, and in travertine deposits near Rome, are compared with hydration of pulvis ash to form tuff. |
| Pliny the Elder | 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. | A geologic analogy to explain rock-like cohesion in marine concrete that improves over time calls upon the hydration processes through which pulvis ash cements itself to form tuff. |