Al-tobermorite and Phillipsite in Roman Seawater Concrete with Zeolitized Pumiceous Pozzolan

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The alkali-rich, zeolitized, trachytic ash of young Campi Flegrei deposits produced a highly complex pozzolanic cementitious system in the hydrated lime-pumiceous ash mortar of a first century BCE Roman concrete breakwater in Pozzuoli Bay. The concrete has remained strong and durable in seawater for 2000 years. X-ray microdiffraction experiments and electron microprobe analyses reveal that Al-tobermorite, a rare, layered calcium-silicate-hydrate with Al^{3+} substitution for Si^{4+}, crystallized in discrete microstructures with variable compositions that reflect diverse geochemical processes. In relict lime clasts, the 1–3 μm crystals have more Ca^{2+}; in pumice vesicles associated with relict phillipsite textures, the crystals are enriched in Al^{3+}, Na^{+}, K^{+}; and in association with dissolving hydrocalumite, a layered calcium-chloroaluminate-hydrate, the crystals have more Cl^{-}. The variable compositions imply metastable equilibria among the pozzolanic reactants, pore fluids, and Al-tobermorite at a very fine scale. In addition, some pores in the cementitious matrix contain potassium-rich phillipsite that crystallized *in situ* to form 50 μm rosettes, similar to relict authigenic textures in the pumiceous Campi Flegrei pozzolan.

In the high pH (>12.4) seawater mortar system buffered by portlandite ($Ca(OH)_2$), dissolution of zeolitized glass produced Al-tobermorite in a range of chemical environments. Elevated temperatures, <75–95 °C, persisted for ~2–3 years, based on an adiabatic thermal model of exothermic C-A-S-H hydration. After all portlandite was consumed, dissolution of relict glass at lower pH and ambient 14–26 °C seawater temperatures apparently produced the potassic phillipsite. Diverse alkali-activated processes in the pozzolanic mortar system open to seawater produced the crystalline silicate phases, which are analogous to rock forming minerals in submarine tephra deposits. These contribute to the exceptional durability of the ancient maritime concrete.