ALS SCIENCE HIGHLIGHT

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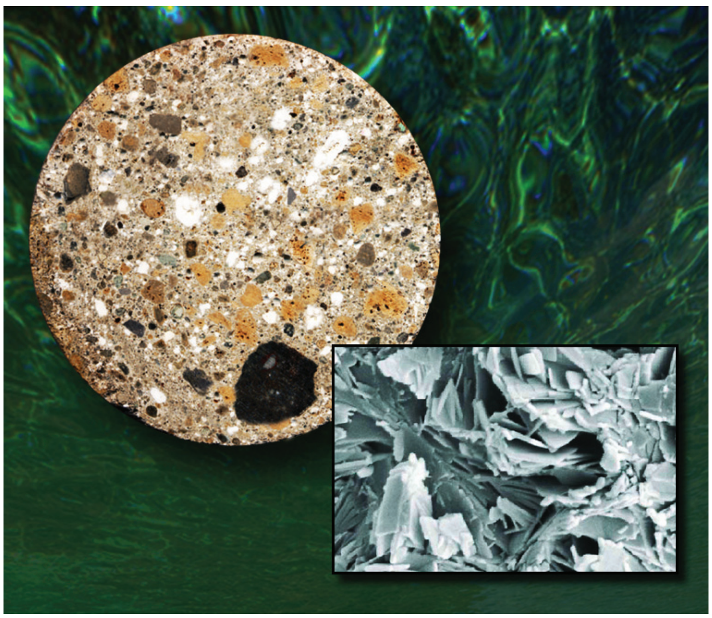
Learning from Roman Seawater Concrete

The material secrets of a concrete Roman breakwater that has spent the last 2000 years submerged in the Mediterranean Sea have been uncovered by an international team of researchers using a variety of techniques, including x-ray microdiffraction, x-ray spectroscopy, and synchrotron-based high-pressure x-ray diffraction. Analyses of the ancient samples pinpointed why the best Roman concrete was superior to most modern concrete in durability, why its manufacture was less environmentally damaging, and how these improvements could be adopted in the modern world.

The most common type of cement used today is called Portland cement, from its similarity to a type of stone that was quarried on the Isle of Portland in Dorset, England. The ancient Romans, however, made concrete by mixing lime and volcanic rock. For underwater structures, lime and volcanic ash were mixed to form mortar, and this mortar and volcanic tuff were packed into wooden forms. The seawater instantly triggered a hot chemical reaction. The lime was hydrated—incorporating water molecules into its structure—and reacted with the ash to cement the whole mixture together.



Drill core of mortar consisting of volcanic ash and hydrated lime, showing yellowish particles of pumice, dark gray fragments of lava, and white particles of relict lime (sample from M. Jackson and the ROMACONS research team). The light gray is the cementitious matrix that binds the concrete. Inset is a scanning electron microscope image of the special Al-tobermorite crystals that are key to the superior quality of Roman seawater concrete.

Using Beamlines 5.3.2, 12.2.2, and 12.3.2 along with other experimental facilities at UC Berkeley, the King Abdullah University of Science and Technology in Saudi Arabia, and the BESSY synchrotron in Germany, the researchers investigated maritime concrete from Pozzuoli Bay in Italy. They found that Roman concrete differs from the modern kind in several essential ways. One is the kind of glue that binds the concrete's components together. In concrete made with Portland cement, this is a compound of calcium, silicates, and hydrates (C-S-H). Roman concrete produces a significantly different compound—one with added aluminum and less silicon. The resulting

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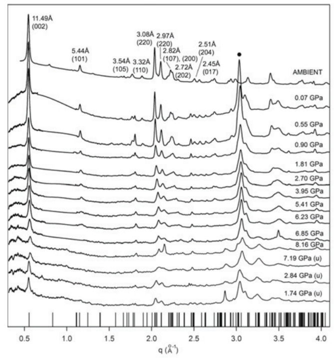
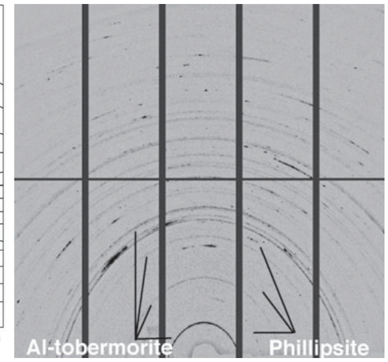
calcium-aluminum-silicate-hydrate (C-A-S-H) is an exceptionally stable binder. At ALS Beamline 5.3.2, x-ray spectroscopy showed that the specific way the aluminum substitutes for silicon in the C-A-S-H may be the key to the cohesion and stability of the seawater concrete.

Another striking find concerns the hydration products in concrete. In theory, C-S-H in concrete made with Portland cement resembles a combination of naturally occurring layered minerals, called tobermorite and jennite. Although these crystals are nowhere to be found in conventional modern concrete, Al-tobermorite (Al for aluminum) occurs in the mortars of all the ancient seawater concretes studied so far. High-pressure x-ray diffraction at Beamline 12.2.2 measured its mechanical properties for the first time and clarified the role of aluminum in its crystal lattice. Al-tobermorite has a greater stiffness than poorly crystalline C-A-S-H and provides a model for concrete strength and durability in future concretes made with environmentally friendly supplemental materials. Finally, microdiffraction studies at Beamline 12.3.2 showed that Al-tobermorite crystallized in the cementitious matrix that binds the Roman concrete, followed by crystallization of the zeolite crystal, phillipsite. Integration of the results from various beamlines revealed the ancient mortar's potential applications for high-performance concretes, including the encapsulation of hazardous wastes.

Environmentally friendly modern concretes already include volcanic ash or fly ash from coal-burning power plants as partial substitutes for Portland cement, with good results. These blended cements also produce C-A-S-H, and with these studies, their long-term performance can be more fully determined. The analyses showed that the Roman recipe needed about 10% lime by weight, made at two-thirds or less the temperature required by Portland cement. Lime reacting with aluminum-rich pozzolanic volcanic ash and seawater formed highly stable C-A-S-H and Al-tobermorite, insuring strength and longevity. Both the materials and the way the Romans used them hold lessons for the future. The ancient concretes provide a sustainable prototype for producing Al-tobermorite in high-performance concretes with natural volcanic ash. The proven endurance of the crystals in seawater for 2000 years indicates exceptionally high durability in a complex pozzolanic concrete composite, on a par with the stable rock forming cementitious minerals of the earth's crust.





Left: Integrated high-pressure powder x-ray diffraction patterns of Al-tobermorite obtained at Beamline 12.2.2. The Al-tobermorite specimen was finely ground and mixed with a silicone oil (as a pressure-transmitting medium) and a few chips of ruby (for measuring pressure using the ruby fluorescence technique). The right side of the y-axis indicates hydrostatic pressure in the diamond-anvil cell. The vertical lines on the x-axis are diffraction peaks from Merlino et al., *Eur. J. Miner.* 13, 577 (2001). Newly emerging peaks (•) in the post-compression sample are from ruby chips. Right: Debye rings diffracted by the crystalline phases in the cementitious matrix of the concrete in monochromatic (10-keV) x-ray microdiffraction experiments at Beamline 12.3.2.

Concrete Solutions?

"It's not that modern concrete isn't good—it's so good we use 19 billion tons of it a year," says Paulo Monteiro of UC Berkeley, who led this study. "The problem is that manufacturing Portland cement accounts for 7% of the carbon dioxide that industry puts into the air." Portland cement is the source of the "glue" that holds most modern concrete together. But making it releases carbon from burning fuel, needed to heat a mix of limestone and clays to 1450 °C (2642 °F)—and from the heated limestone (calcium carbonate) itself. Monteiro's team found that the Romans, by contrast, used much less lime and made it from limestone baked at 900 °C (1652 °F) or lower, requiring far less fuel than Portland cement.

Another powerful incentive for this work is the need for stronger, longer-lasting buildings, bridges, and other structures. "In the middle 20th century, concrete structures were designed to last 50 years, and a lot of them are on borrowed time," Monteiro says. Yet Roman harbor installations have survived for 2000 years. That concrete was made with ash from volcanic regions near what is now the seaside town of Pozzuoli. Ash with similar mineral characteristics, called pozzolan, is found in many parts of the world and could replace some of the world's demand for Portland cement. Stronger, longer-lasting modern concrete, made with less fuel and less release of carbon into the atmosphere, may be the legacy of a deeper understanding of how the Romans made their incomparable concrete.