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GORDON RESEARCH CONFERENCE
February 25 - March 1, 2024, Ventura, CA
2024 Advanced Materials or Sustainable Infrastructure Development

Abstract:

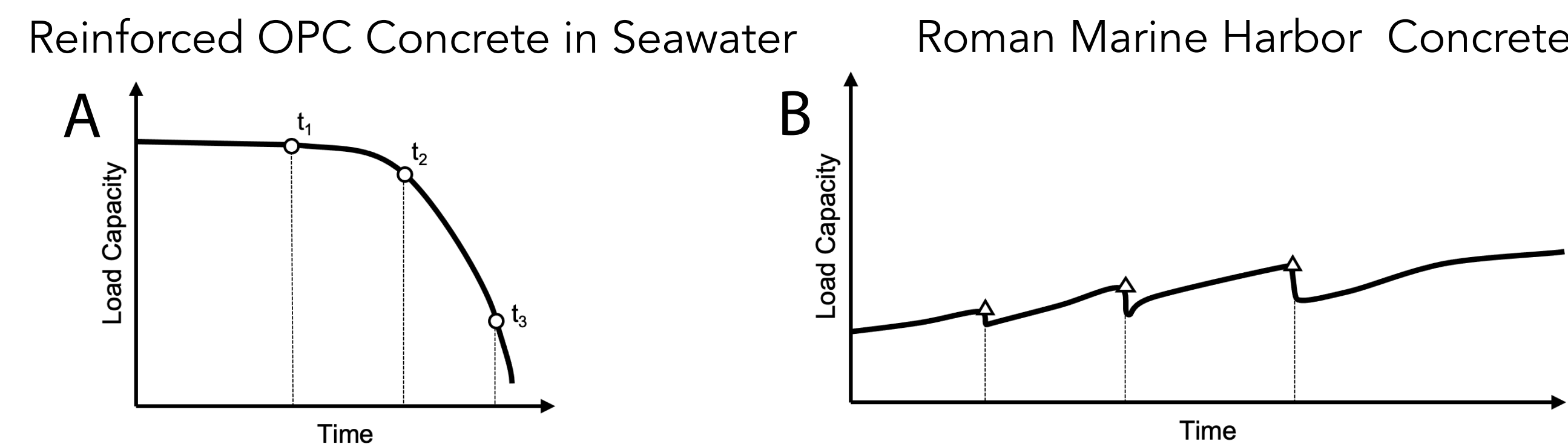
Roman marine concretes are conglomeratic composite materials whose extreme durability derives from the dynamic binding characteristics of mortar prepared from lime and reactive aggregate(s) and long-term, beneficial hydrologic interactions with seawater. Pozzolanic and post-pozzolanic cementitious processes toughen interfacial zones of reactive aggregate with the binding matrix, refine pore space, and produce mineral cements in fractures. The CO₂ footprint associated with production of these materials with reactive volcanic aggregate is less than Portland cement concrete (OPCC) and portends potential service life at the multi-century time scale.

An innovative arc-fracture test measures the structural response of Roman Analog Seawater Concrete fabricated with volcanic aggregate as fractures nucleate and propagate. It then characterizes regenerative repair processes after iterative fracture episodes. Testing results and fine-scale material analyses indicate a ductile initial fracture response followed by self-repair of induced fractures, which result in appreciable recovery of initial structural carrying capacity at 7-13 months post-test hydration. OPCC arcs fabricated with the same volcanic pozzolan show no recovery.

The arc-fracture test is currently implemented at the US Army Corps of Engineers Engineer Research and Development Center Laboratory in Vicksburg, MS, to measure chemical and mechanical resilience in a suite of ecologically sustainable and biocompatible concrete formulations for coastal infrastructure through the Engineering with Nature® program.



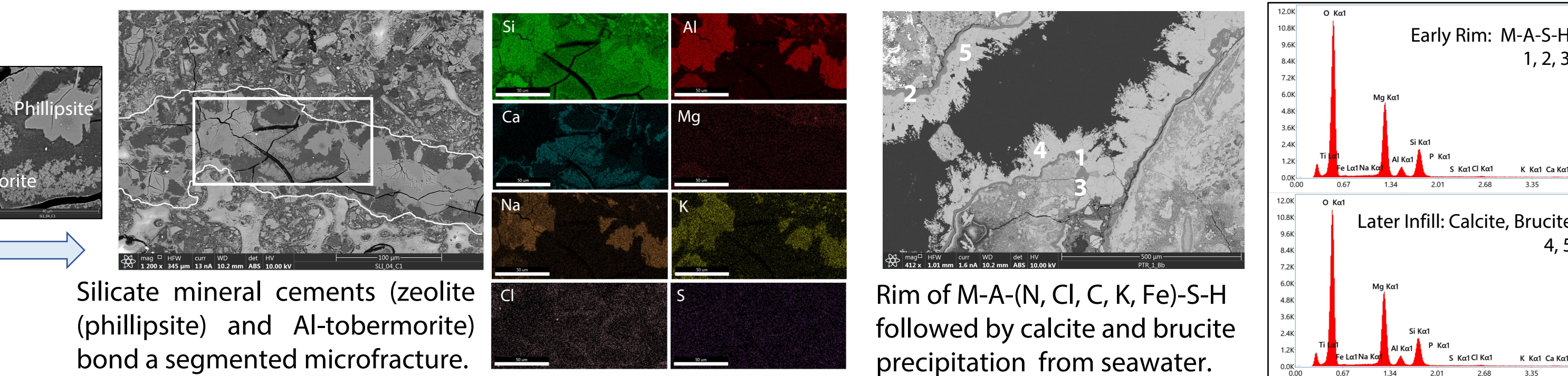
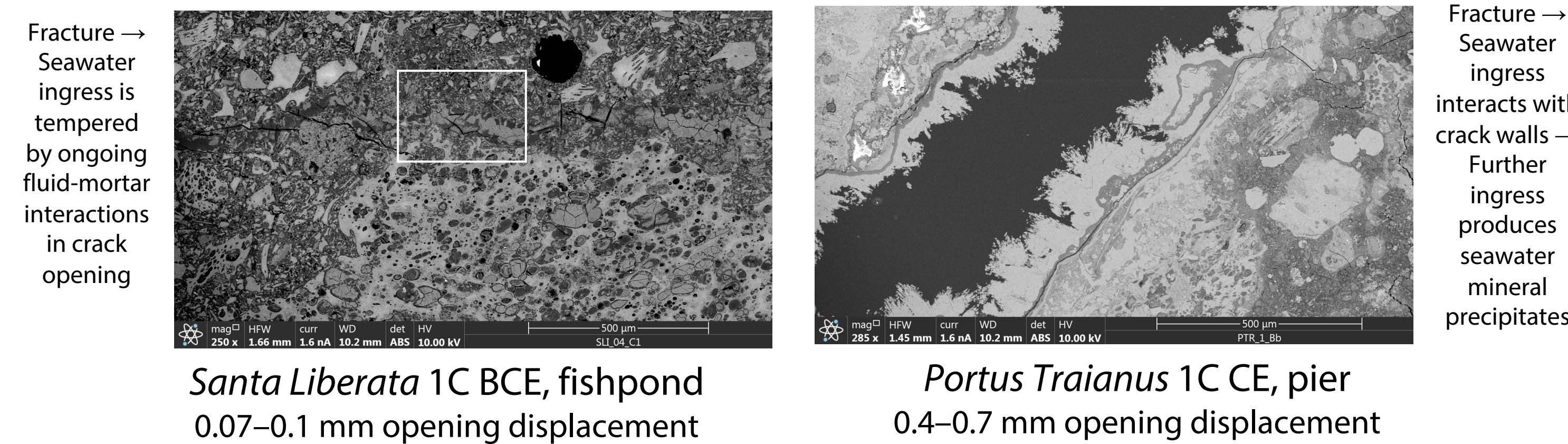
What is Regenerative Repair?



Schematic illustrations of mechanical load carrying capacity with time. A) Durability model for reinforced OPC concrete structure in a corrosive environment proposed by Torres-Acosta et al. (2007). Time t₁, onset of reinforcement corrosion; t₂, load capacity reduced to the service life level; t₃, ultimate strength limit, beyond which collapse occurs. B) Durability model proposed for Roman marine concrete. Lower initial strength and a longer period of strength gain are intermittently interrupted by fracture and “regenerative repair” events.

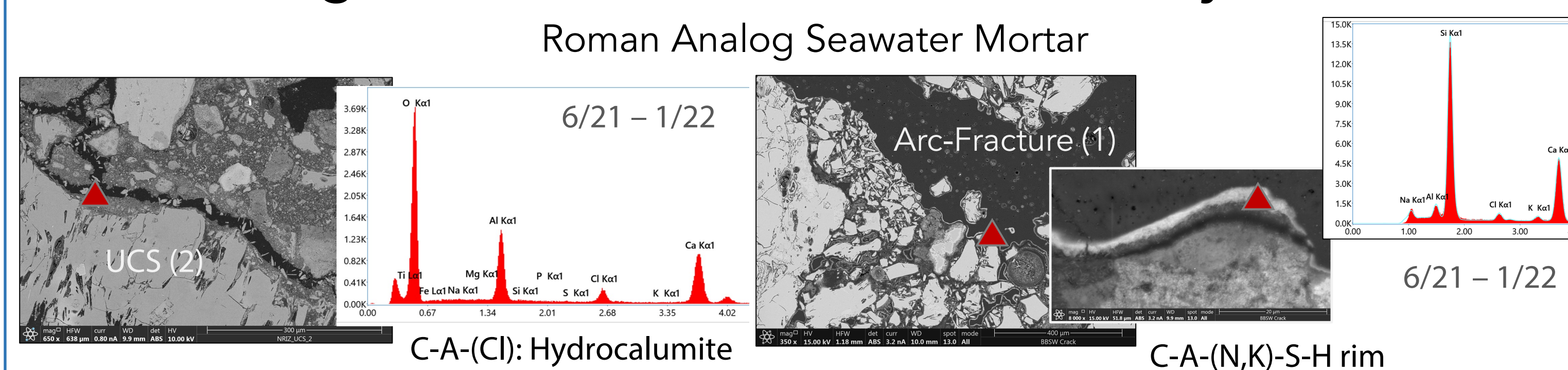
Regenerative Repair Concept: Roman reactive glass concrete recovers structural functionality after fracture through an intrinsic ability to nucleate and grow mineral cements in crack openings whose width and length are generally limited by multiple length scales of reactive aggregate.

Mineral Cements : Ancient Fracture Surfaces



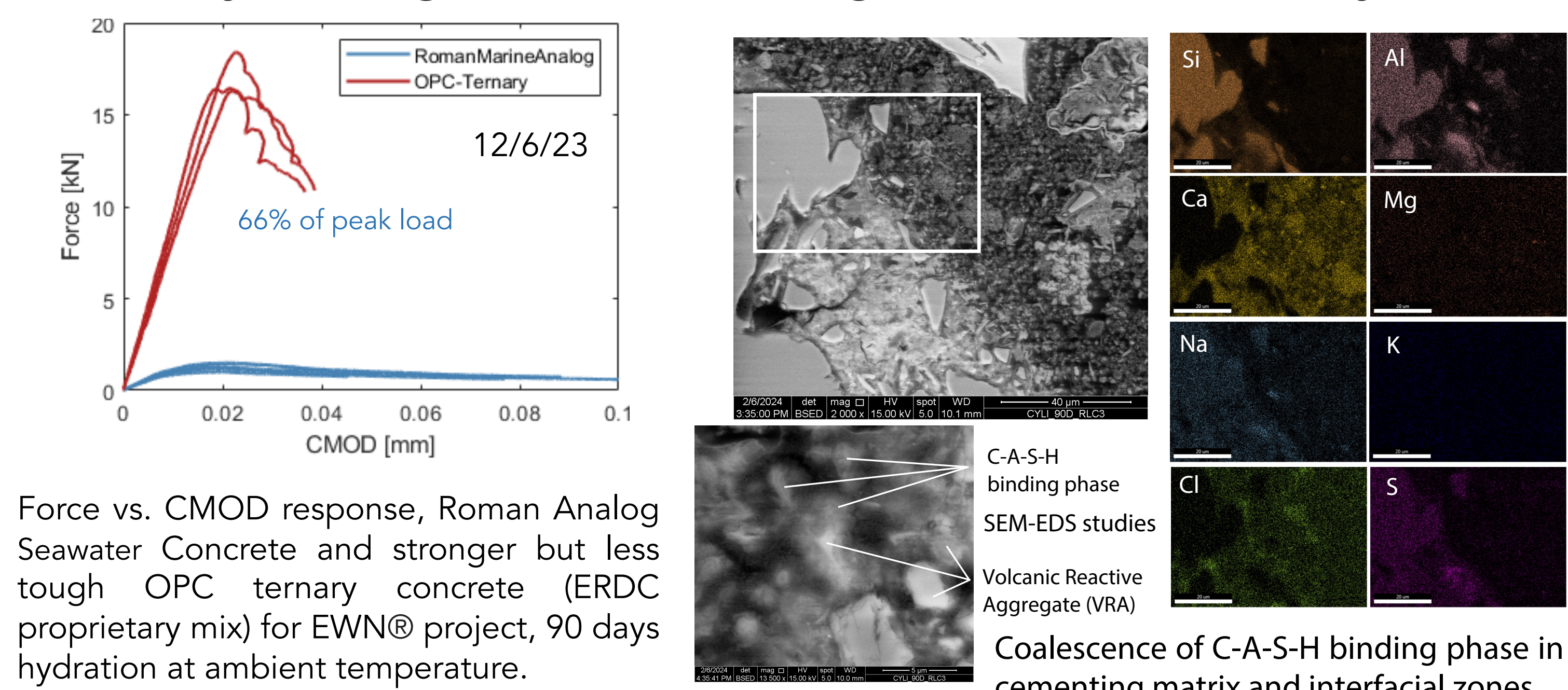
SEM-EDS studies indicate many different mineral assemblages and chronologies.

Young Fracture Surfaces (7 months hydration)

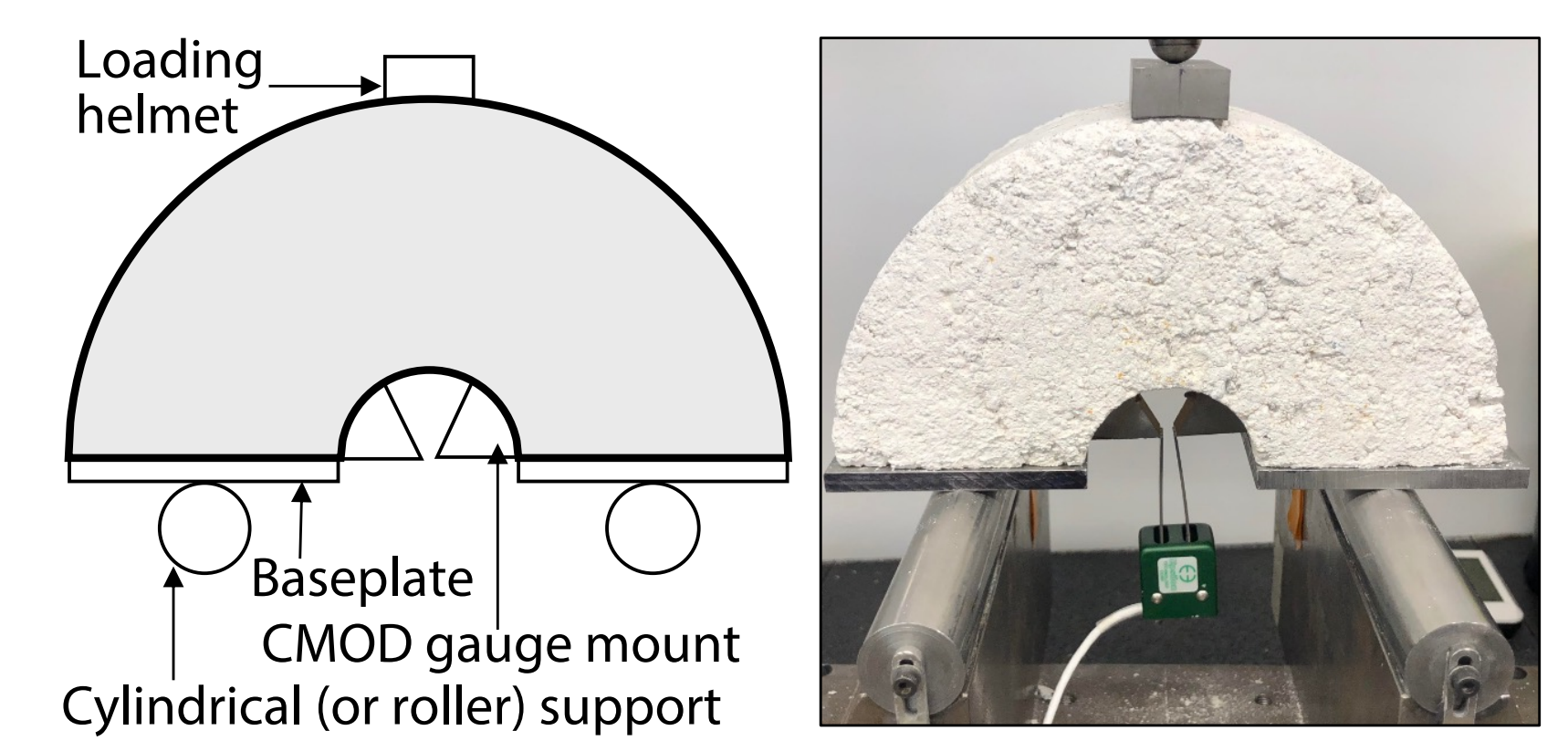


Early prototype. After testing at 3 months hydration and at 7 months subsequent hydration in seawater fluid, portlandite remains present and pozzolanic processes are ongoing. [Note that our Markets of Trajan wall mortar replica had consumed all portlandite by 90 days, with strätlingite crystallization in interfacial zones substantially increasing fracture energy and toughness (Jackson et al. 2014, PNAS).]

Very Young Roman Analog Concrete (90 Days)



Arc-Fracture Test

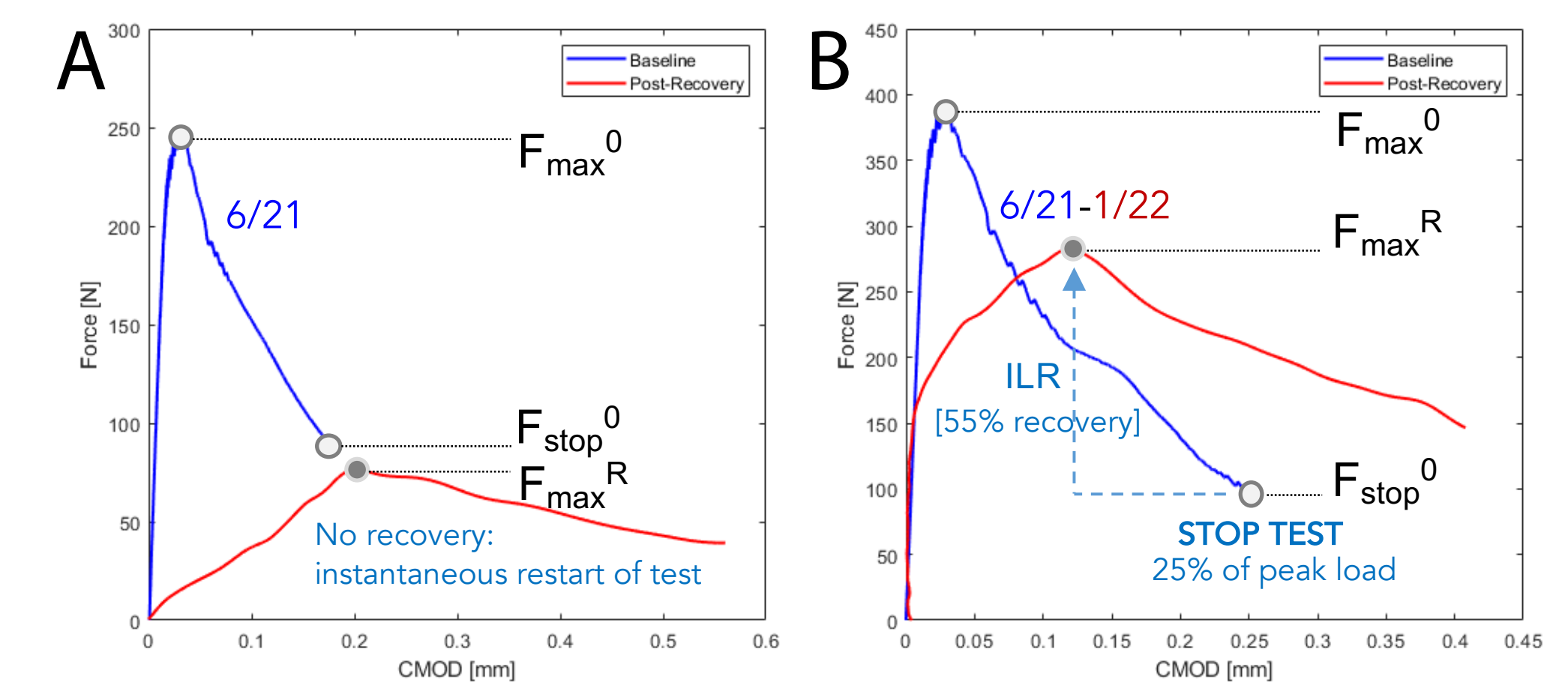


Schematic illustration of Arc-Fracture test and photo of Roman Analog Seawater Mortar specimen. A non-moving cylindrical support is pictured, but roller supports were used in previous test programs (Brune et al. 2013, EFM). CMOD: Crack Mouth Opening Displacement.

The Arc-Fracture test measures the chemical and mechanical resilience of cementitious materials and their potential longevity, as opposed to initial strength. Through interspersing periods of recovery time between load cycles, material self-repair capabilities are assessed.

Regenerative Repair Factor

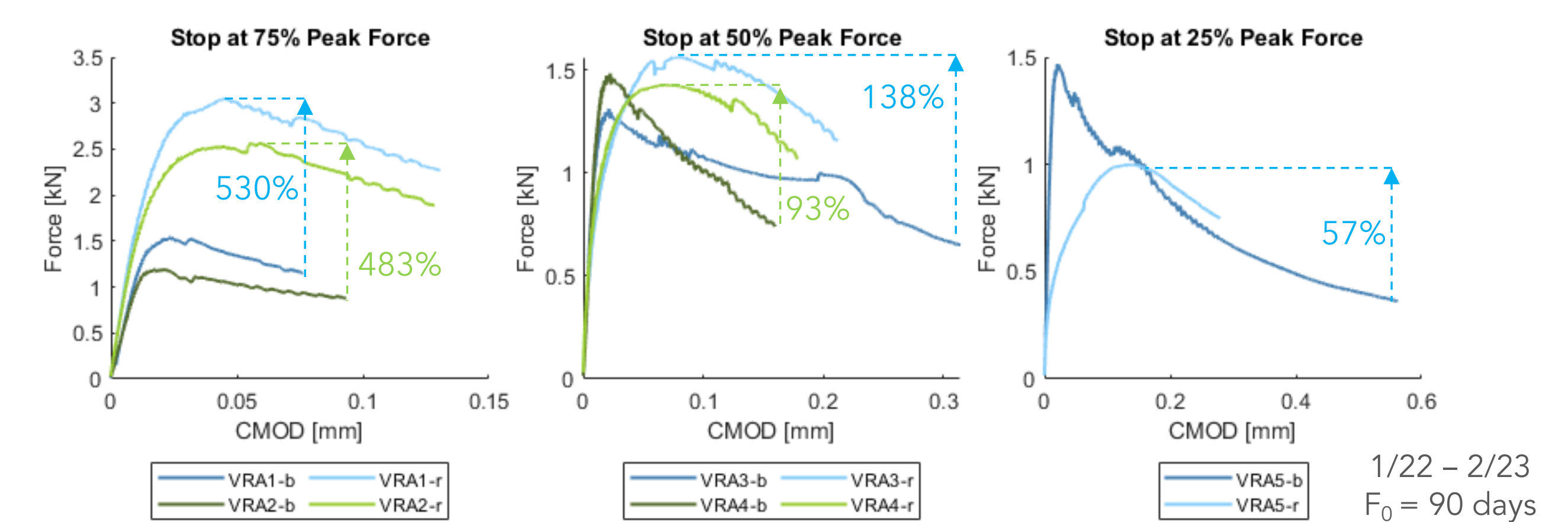
$$ILR = (F_{max}^R - F_{stop}^0) / (F_{max}^0 - F_{stop}^0)$$



Early prototype of Roman Analog Seawater Mortar fabricated with lime, volcanic reactive aggregate (VRA, pozzolan), artificial seawater and hydrated in artificial seawater.

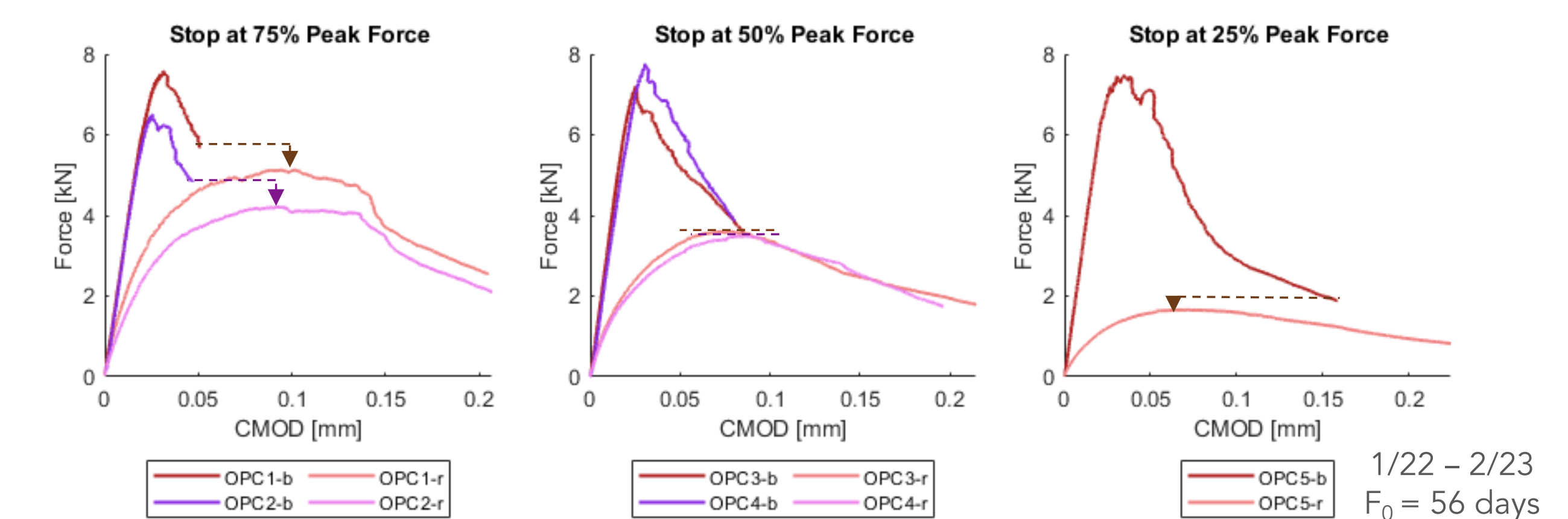
Measured quantities from a baseline test on pristine arc specimens (blue) and a post-recovery tests (red) are used to compute ILR, Index of Load Recovery (Ferrara et al. 2014), as a measure of a regenerative repair factor. A) Instantaneous restart of test produces no recovery. B) After 7 months hydration in seawater fluid, the Roman Analog Seawater Mortar has recovered 55% of its original load carrying capacity.

Roman Marine Analog : Force vs. CMOD



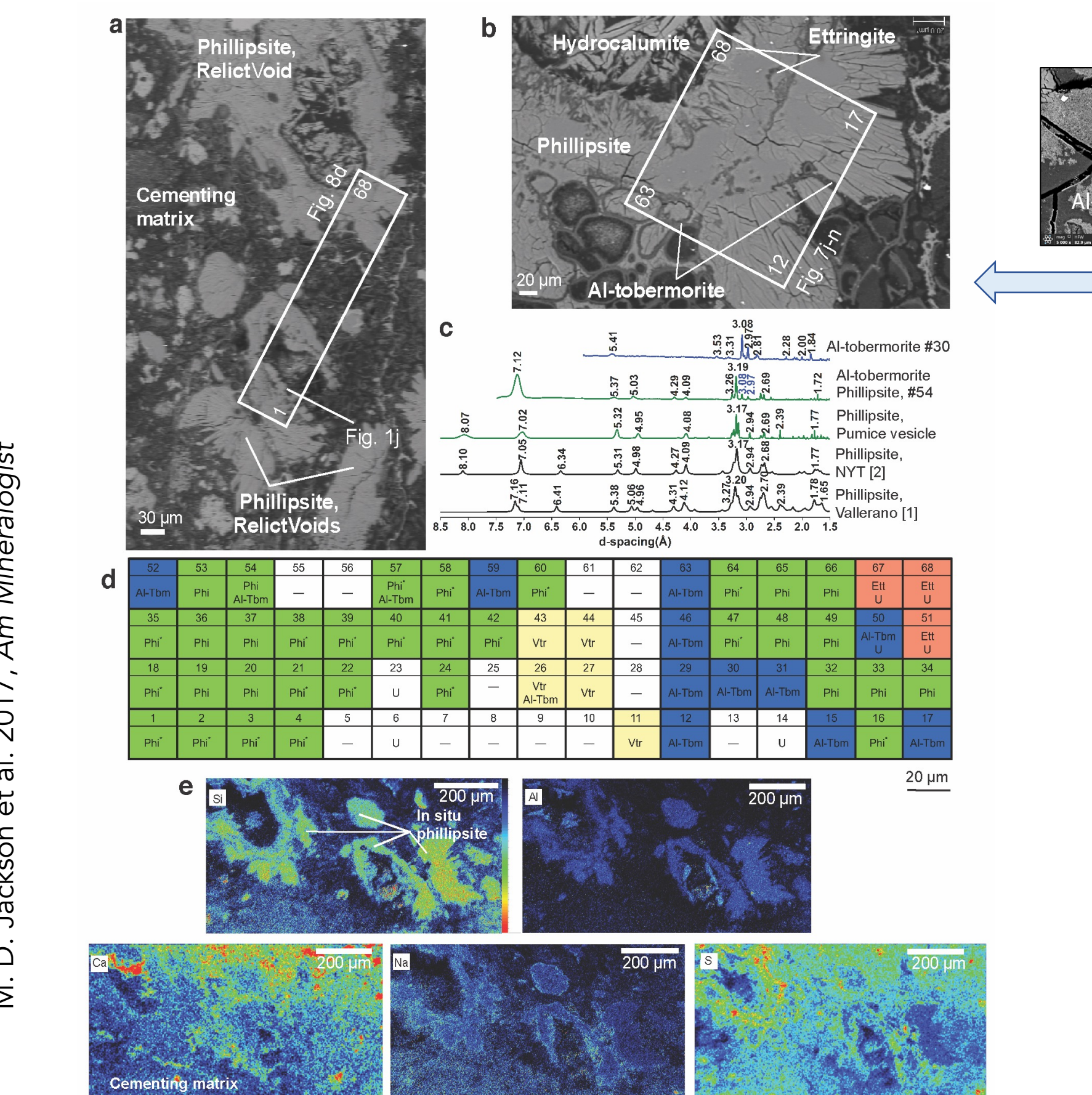
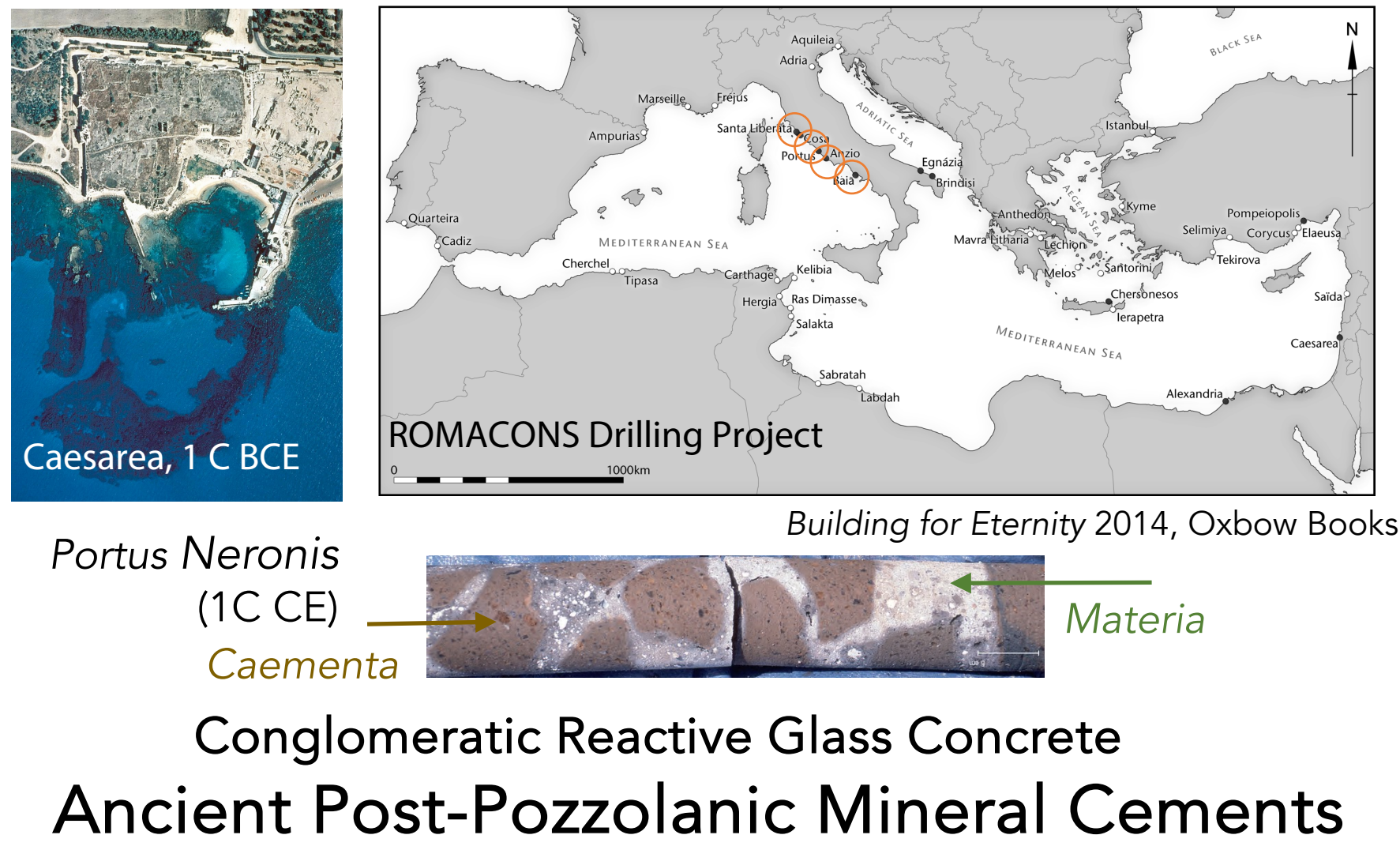
Force vs. CMOD responses showing ILR values for Roman Analog Seawater Mortar with volcanic reactive aggregate (VRA). The test at 90 days hydration is stopped at 75%, 50% and 25% of peak load and the arcs are returned to hydration in seawater fluid at 40 °C and 60 °C for 13 months. ILR ranges from 57% to 530%, largely due to ongoing pozzolanic production of C-A-(N,K)-S-H binding phase.

OPCC w/ Volcanic Pozzolan : Force vs. CMOD



Force vs. CMOD responses for OPCC (with 25 wt% cement replacement with volcanic pozzolan and VRA coarse aggregate). Stop load conditions at 75%, 50% and 25% of peak load at 56 days hydration are followed by 13 months hydration at RH 98%. A negative (or negligible) index of load recovery (ILR) is measured by the subsequent Arc-Fracture test.

Roman Marine Harbor Concrete



M. D. Jackson et al. 2017, Am Mineralogist

Baianus Sinus, 1 C BCE, Zeolite and Al-tobermorite mineral cements in relict voids, cementing matrix. (a, b) SEM-BSE images (c) XRPD, phillipsite and Al-tobermorite in *Baianus Sinus* pumice compared with Campi Flegrei (2, Gatta et al. 2010) and Alban Hills (1, Gualtieri 2000) phillipsite. (d) μ XRD map, phillipsite (Phi), Al-tobermorite (Al-tbm), ettringite (Ett), vaterite (Vtr), calcite (Cal), unknown (U). (e) SEM-EDS maps, silicon (Si), aluminum (Al), sodium (Na), and sulfur (S) concentrations normalized to 20 mass% (red).

X-ray microdiffraction and microfluorescence, Advanced Light Source Beamline 12.3.2
Experiments at Advanced Light Source Beamline 12.3.2 investigated submicron-sized crystals with powder microdiffraction using a monochromatic beam (Stan & Tamura, 2019; Tamura et al., 2009). The rock slice mounted on tape was loaded in transmission mode, with the detector placed at 39° to the incident beam. A monochromatic X-ray beam of 8 or 10 keV was focused to a 2-5- μ m spot size. A DECTRIS Pilatus 1M area detector placed at about 150-mm recorded Debye rings from crystalline phases. The experimental geometry was calibrated using α -Al₂O₃ powder. X-ray diffractograms were produced with d-spacing reflections integrated radially for 2θ 3-54° mainly over a 76° arc segment (a) around the cone of diffraction. These are shown as intensity versus d-spacing plots to illustrate variations in phyllosilicate mineral reflections or as intensity versus $Q = 2\pi/d$ spacing to increase the readability of lower d-spacing reflections from other phases.

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Funding
Department of Energy ARPA-E award DE-AR0001139; US Army Corps of Engineers, Engineering with Nature® award W912HZ23P0098. Data acquired at the Advanced Light Source acquired through the Department of Energy Office of Science User Facility under contract DE-AC02-05CH11231. Special thanks to the ROMACONS drilling project, the University of Utah Department of Mechanical Engineering Composites Laboratory, the University of Utah Nanofab Laboratory, Jeff Kessler, Alik Nielson, Mike Czabaj, Bradley Cottle, and Paulo Perez.