Research on cements

The Williamson Morphology

- Originally described by Prof. Brady Williamson (U.C. Berkeley).
- He referred to the morphology as “sheaf-of-wheat”.

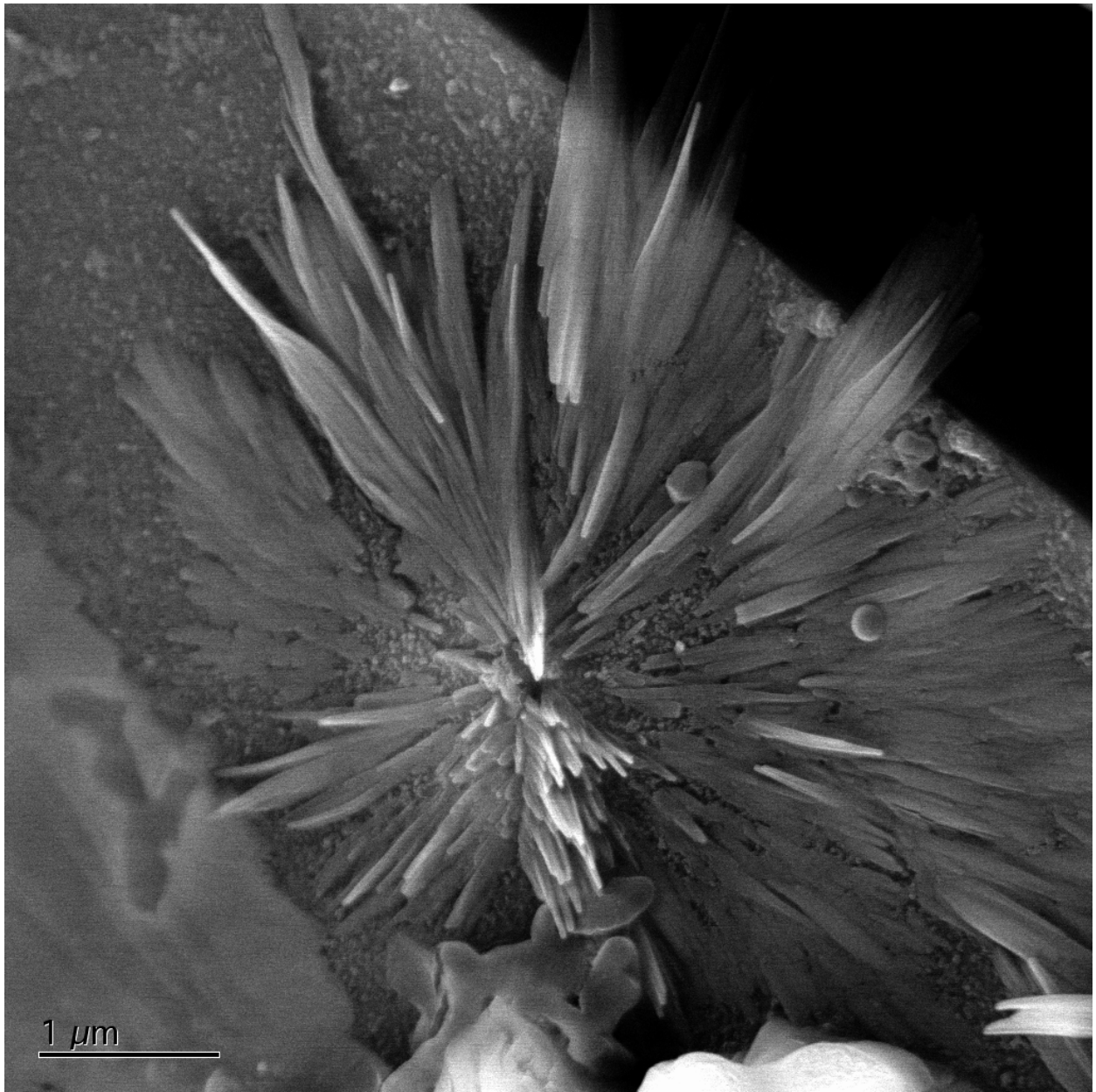
The C-S-H growth mechanism that results in the Williamson morphology:

- An initial product nucleates on the silica surface. This initial product is essentially crystalline.
- Outward growth of this product continues in all directions, but is favored along either the a-axis or the b-axis.
- As growth continues further from the silica source, the products formed have a higher Ca/Si ratio due to the lower silica and higher calcium concentrations.

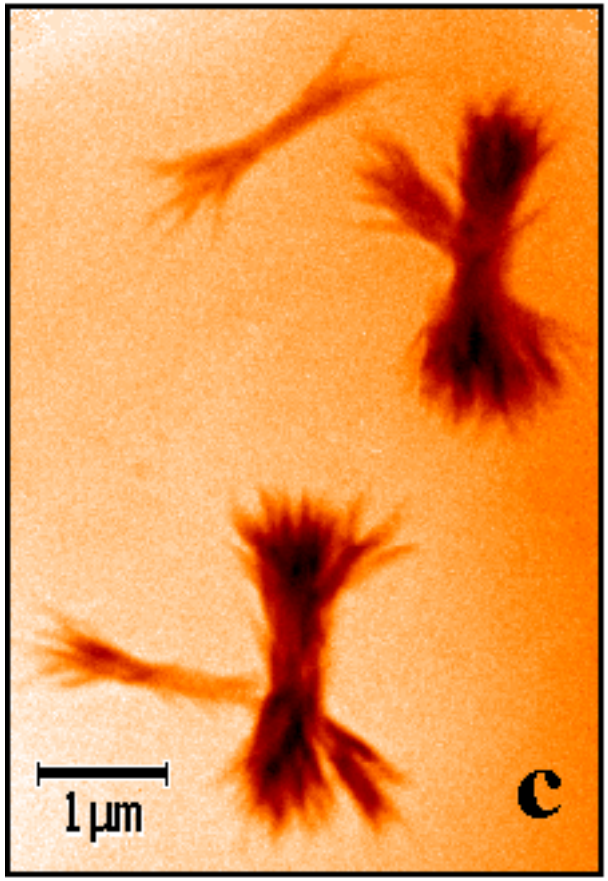
The C-S-H growth mechanism that results in the Williamson morphology:

- The lower silica content at the growing extremities produces silicate defects between the lamellae, resulting in “unfurling” of the sheaf at the ends, leading to the appearance of ribbons “bundled” at the center.
- The growth rates become limited by the rate at which silica can diffuse to the growing extremities.
- Increased silica concentrations around the central plane of the sheaf tend to cause the ribbons to grow towards that area, resulting in a spherulitic morphology

The Williamson morphology observed in the SEM

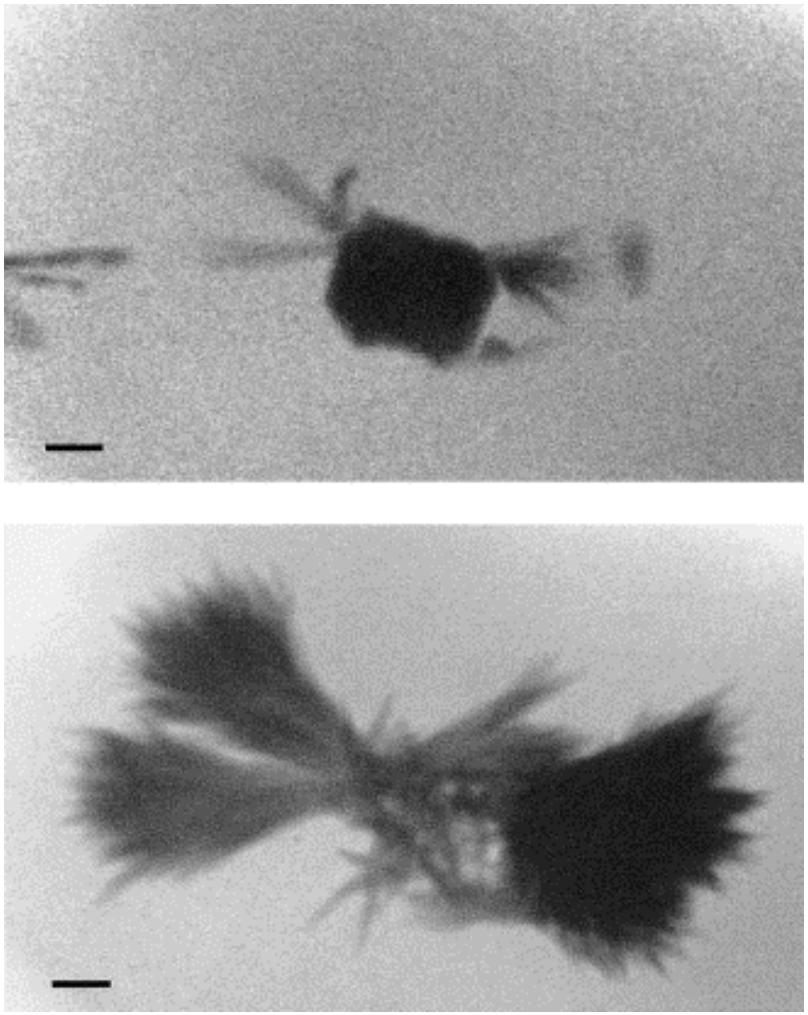


The Williamson morphology observed in the soft x-ray microscope



X-ray image of ASR gel in saturated $Ca(OH)_2$ solution after 30 minutes

The Williamson morphology observed in the soft x-ray microscope

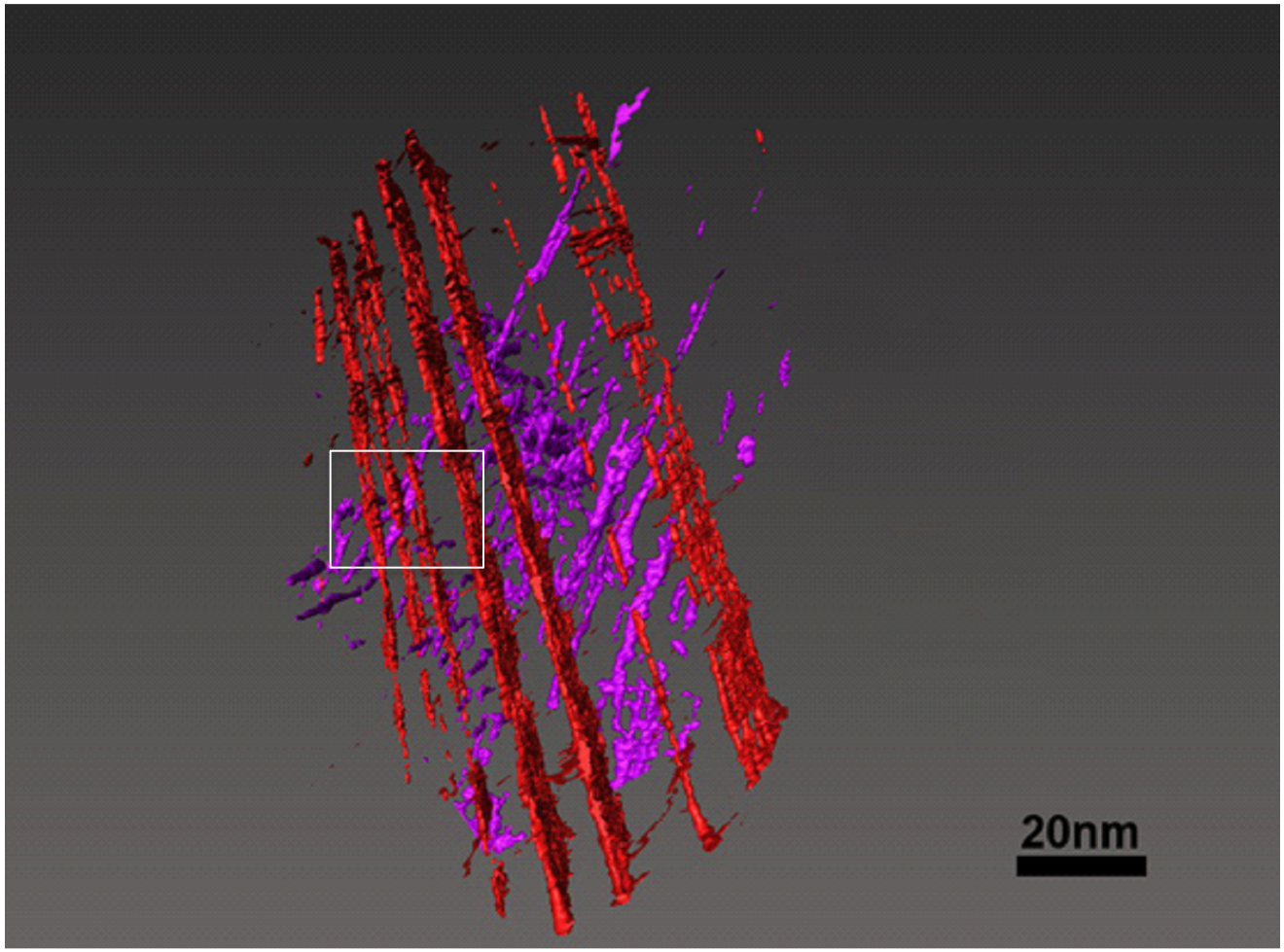


Two X-ray microscopy images of the evolution of the sheaf-of-wheat morphology during the reaction of chemical grade silica gel in a solution of 0.7 M NaOH+0.1 M $CaCl_2$ after 10 min (a) and 19 min (b). Exposure times for the X-ray images measured 3 and 36 s with beam currents of 347.3 and 335.7 mA, respectively. Original magnification was 2400×. Scalebar=0.5 μm.

To learn more:

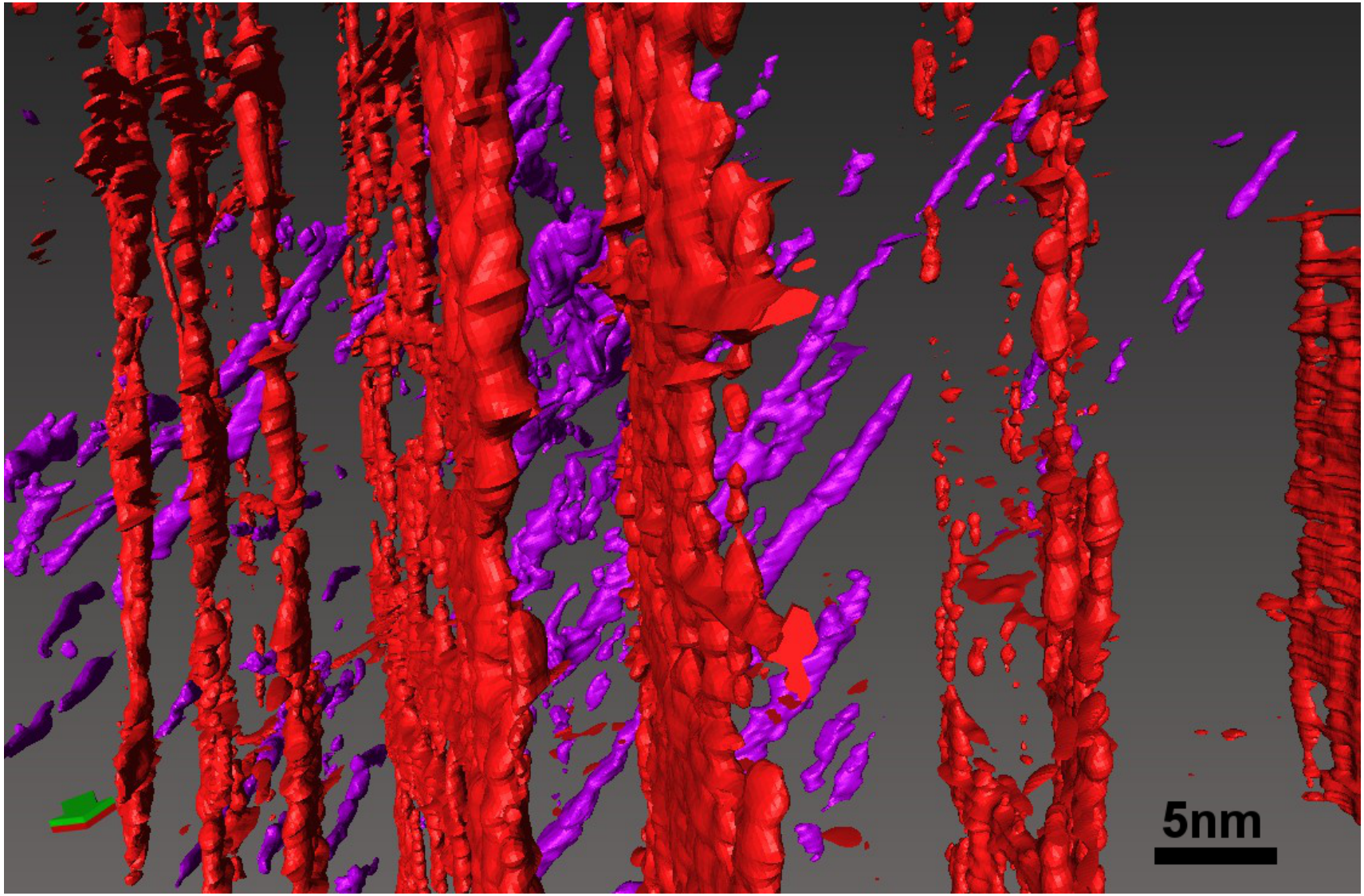
- R.B. Williamson, Constitutional supersaturation in Portland cement
- solidified by hydration, J Cryst Growth 34 (1968) 787 - 794.
- D. Zampini, S.P. Shah, H.M. Jennings, Early age microstructure of the
- paste ± aggregate interface and its evolution, J Mater Res 13 (7) (1998)
- 1888 - 1898
- E. Kurtis, Monteiro, P. J. M., J. Brown, and W. Meyer-Ilse, “Imaging of ASR Gel by Soft X-ray Microscopy,” CCR journal, V28 N3:411-421, (1998).
- Kurtis, K.E., P.J.M. Monteiro, J.T. Brown, and W. Meyer-Ilse, “High resolution transmission soft X-ray microscopy of deterioration products developed in large concrete dams.” Journal of Microscopy-Oxford, V196 (PT3): 288-298, Dec, 1999.
- Gartner, E., K.E. Kurtis and P.J.M. Monteiro, “Proposed mechanism of C-S-H growth tested by X-ray microscopy,” Cement and Concrete Research, V30 (N5): 817-822, 2000.

TEM Nanotomography of C-S-H



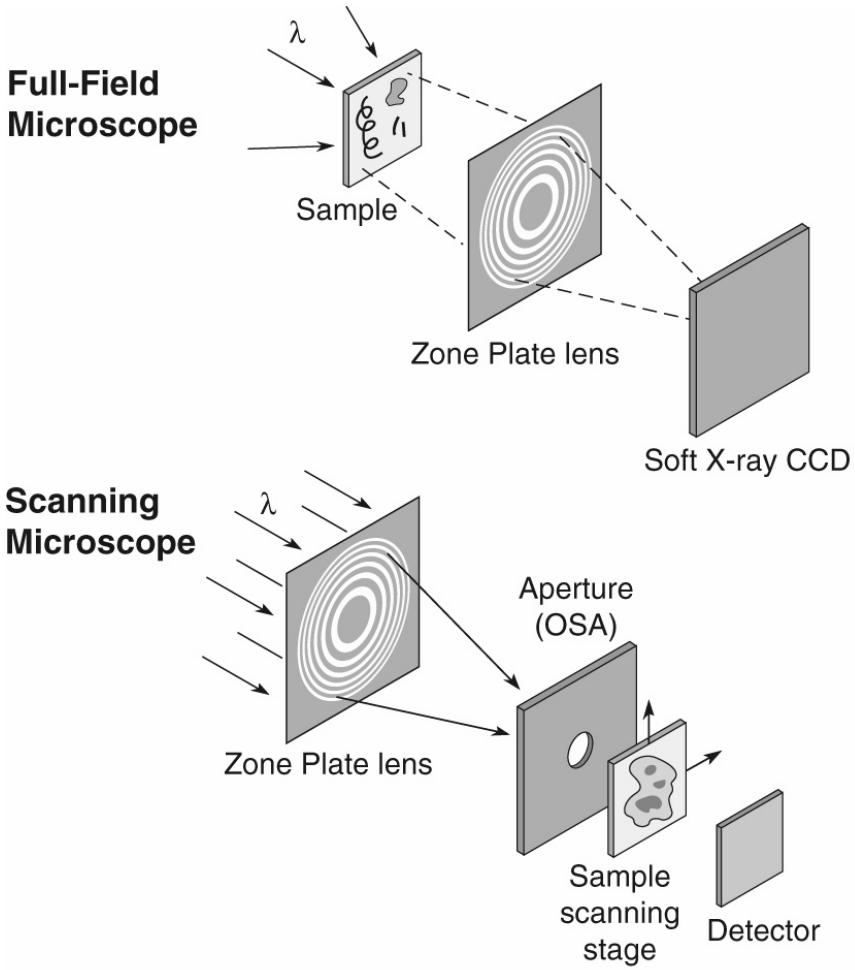
Taylor et al, JACers, 2015

TEM Nanotomography – Closer look



Taylor et al, JACers, 2015

Soft X-Ray Microscopes



- Best spatial resolution
- Modest spectral resolution
- Shortest exposure time
- Bending magnet radiation
- Higher radiation dose
- Flexible sample environment (wet, cryo, labeled magnetic fields, electric fields, cement, ...)

- Least radiation dose
- Good spatial resolution
- Best spectral resolution
- Requires spatially coherent radiation
- Long exposure time
- Flexible sample environment
- Photoemission (restricted magnetic fields), fluorescence imaging

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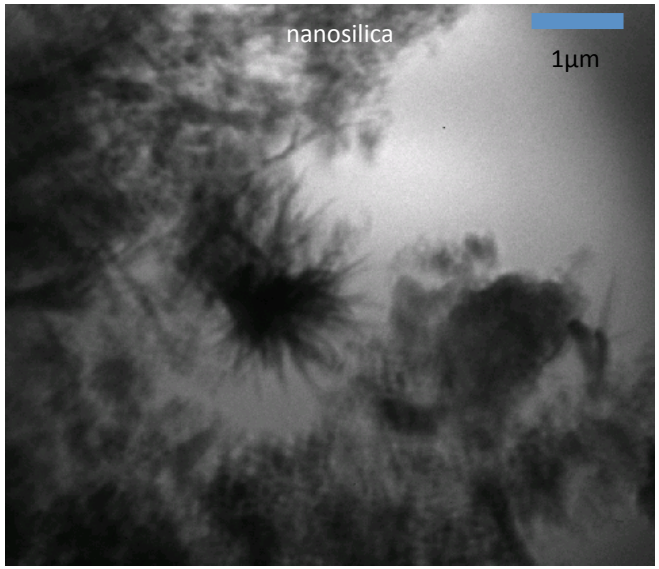
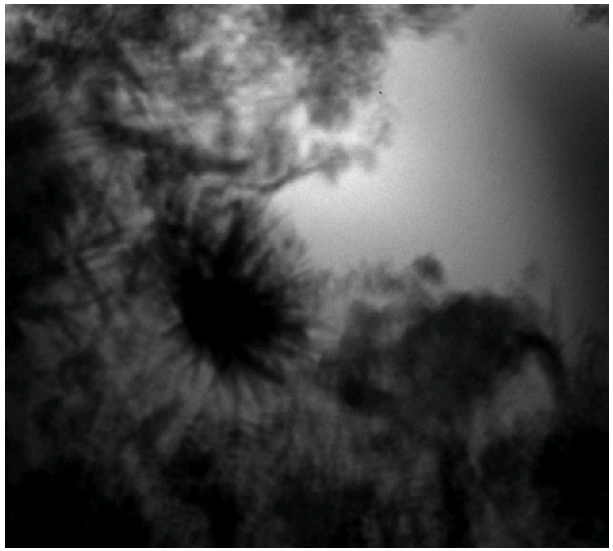
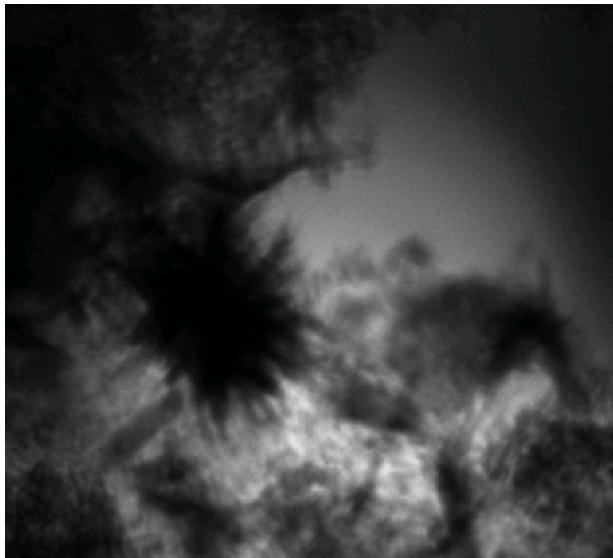
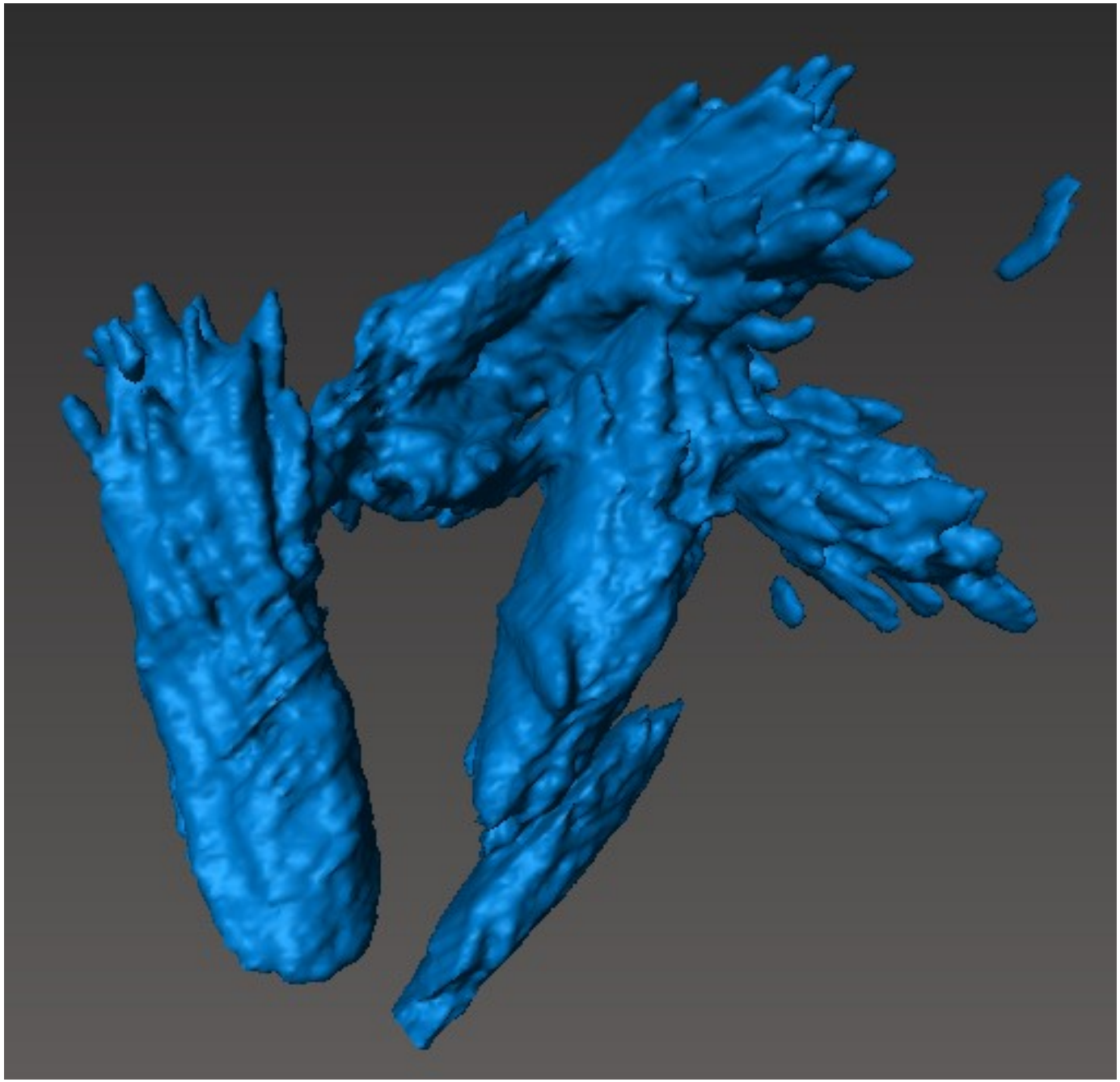
Nucleation









Brisard et al. American Mineralogist, 2012

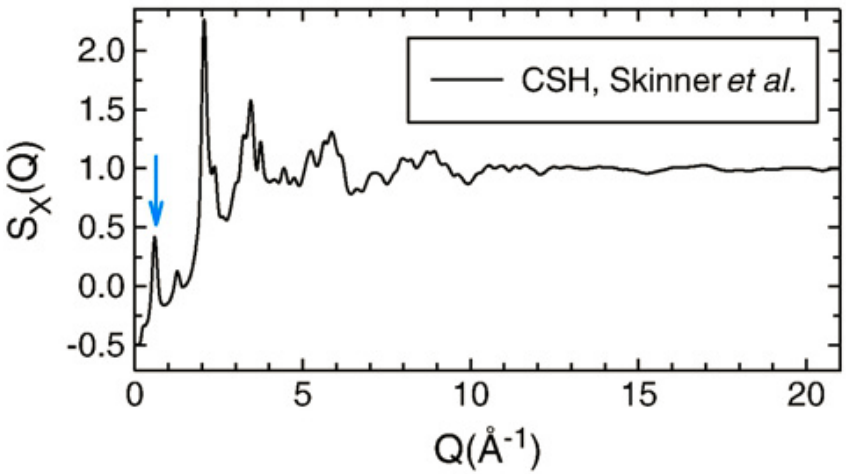
Pair Distribution Function

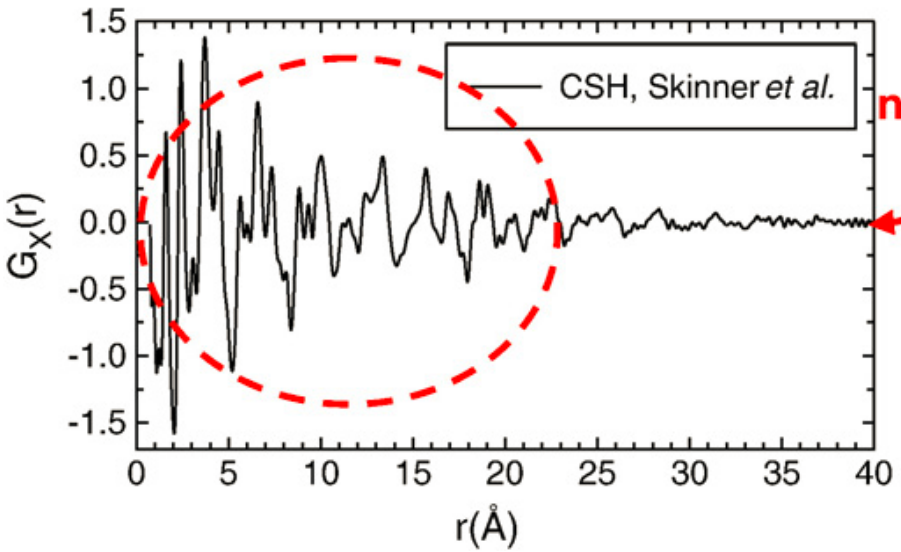
L. Skinner, S. R. Chae, C. J. Benmore H. R. Wenk & P. J. M. Monteiro Nanostructure of Calcium-Silicate-Hydrates in Cements, Physics Review Letters, **104**, 195502 (2010).

C. Meral, C.J. Benmore and Paulo J.M. Monteiro, The study of disorder and nanocrystallinity in C-S-H, supplementary cementitious materials and geopolymers using pair distribution function analysis, Cement and Concrete Research, 41, 696-710, 2011.

Sezen Soyer-Uzun, Sejung Rosie Chae, Chris J. Benmore, Hans-Rudolf Wenk, Paulo J. M. Monteiro, Compositional Evolution of Calcium Silicate Hydrate (C-S-H) Structures by Total X-Ray Scattering, Journal of the American Ceramic Society, Volume: 95 Issue: 2 Pages: 793-798, FEB 2012

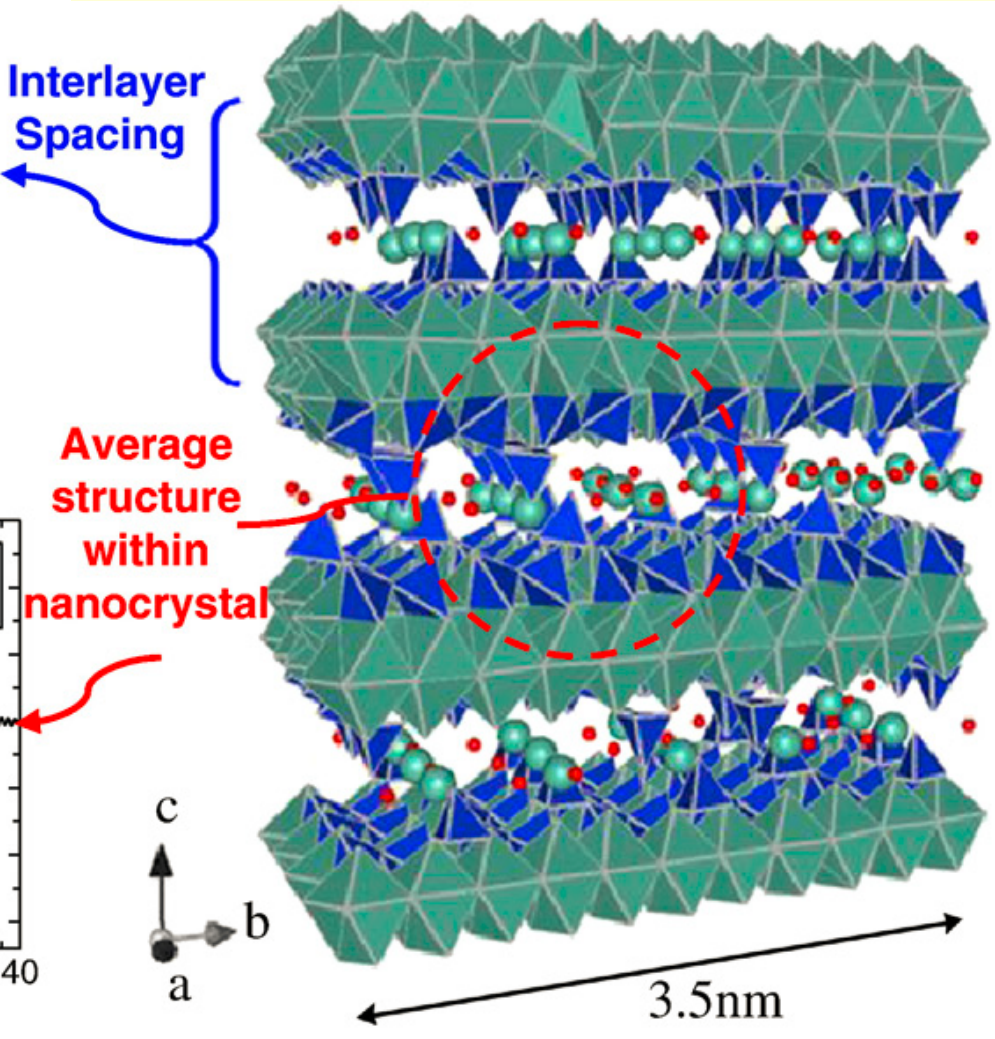
X-ray structure factor Sx(Q) of synthetic C–S–H (I)





X-ray pair distribution function of synthetic C–S–H (I) has no correlated structure beyond 3.5 nm

The molecular model of C–S–H (I) obtained by reverse Monte Carlo refinement. The initial structure is based on Hamid 1.1 nm tobermorite crystal structure.



The final structure is refined to be consistent with the measured data. Green polyhedral: CaO, blue tetrahedral: SiO, red spheres: inter layer O from water, green spheres: interlayer Ca.