Novidades Sobre a Nanotecnologia do Concreto e sua Influência na Construção Civil do Futuro

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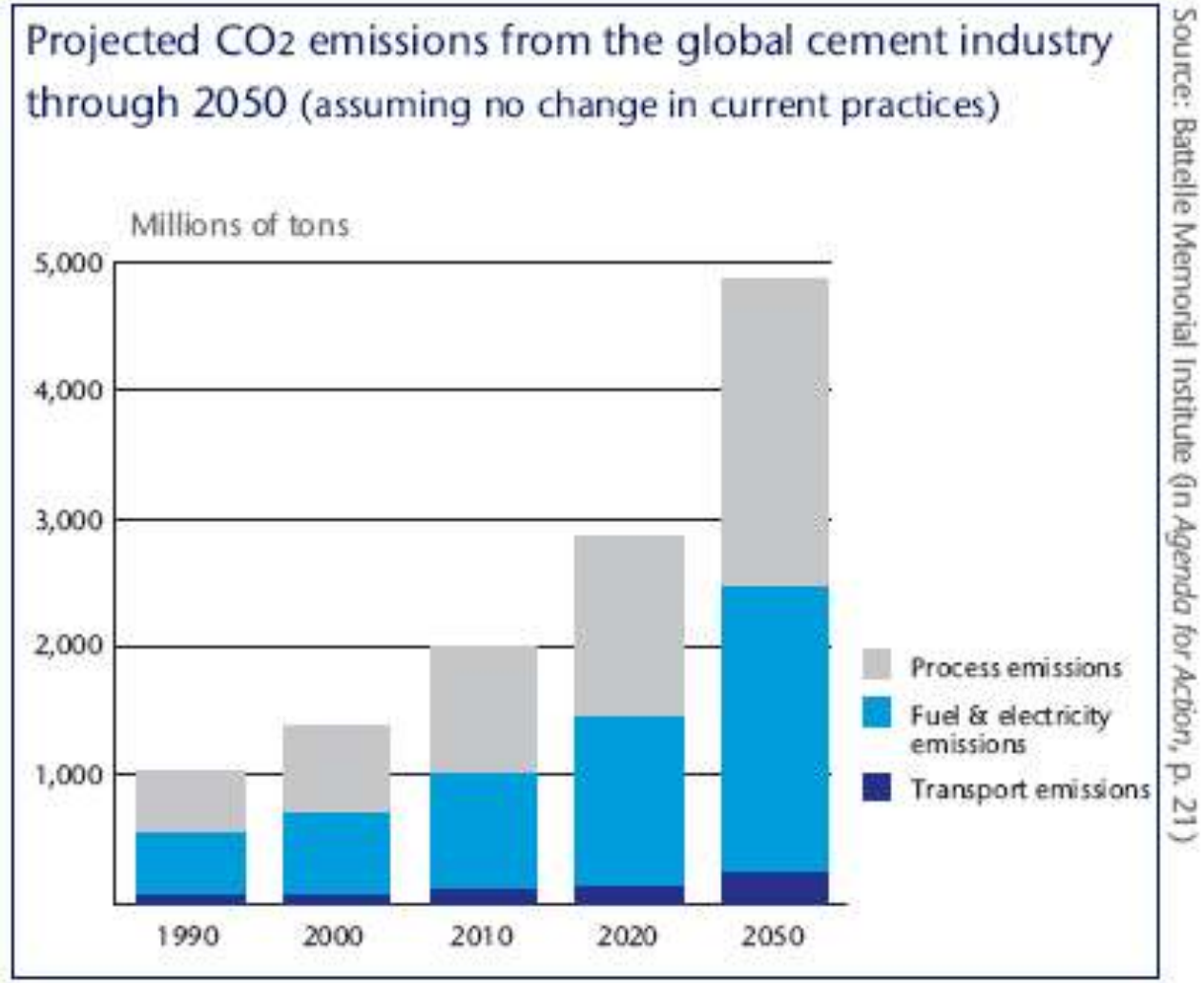
Por que??

- **Somos engenheiros civis, e qual é a importancia da nanotecnologia para o concreto?**

Condição insustentável



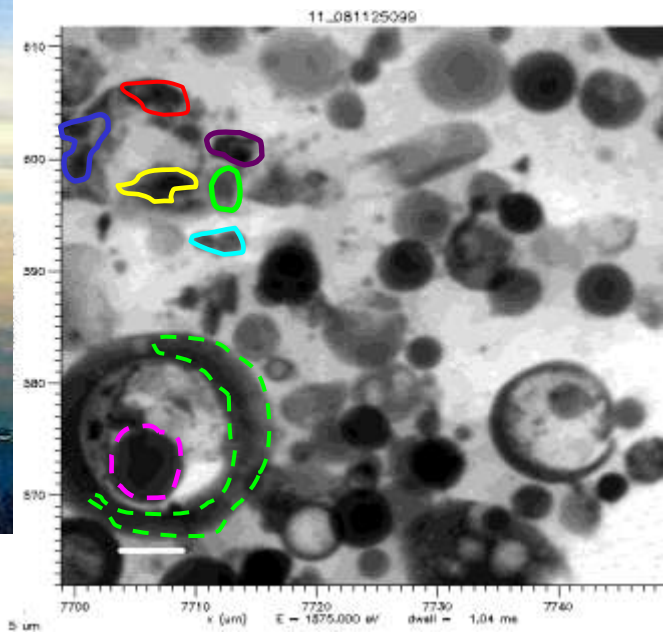
Novas Alternativas

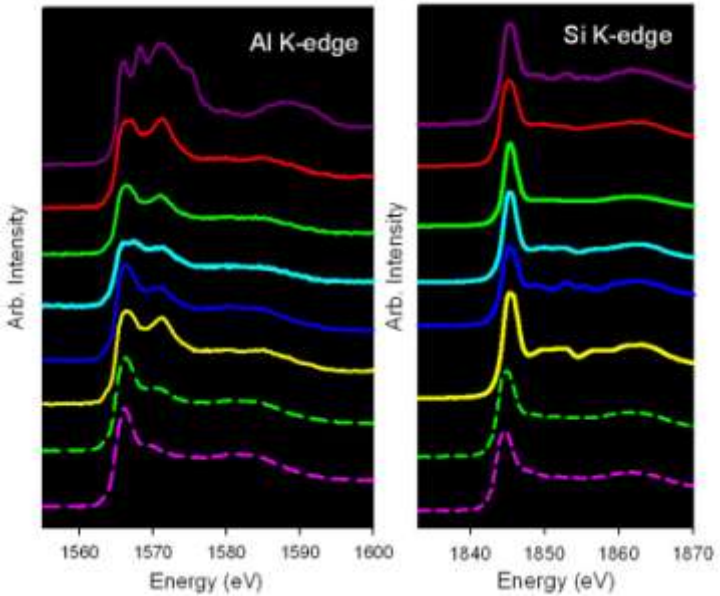
- Italcementi → cimento branco auto-limpável
- Uso de nano-argilas para CSC
- Geopolímeros
- NanoCem
- Calera

Meta:

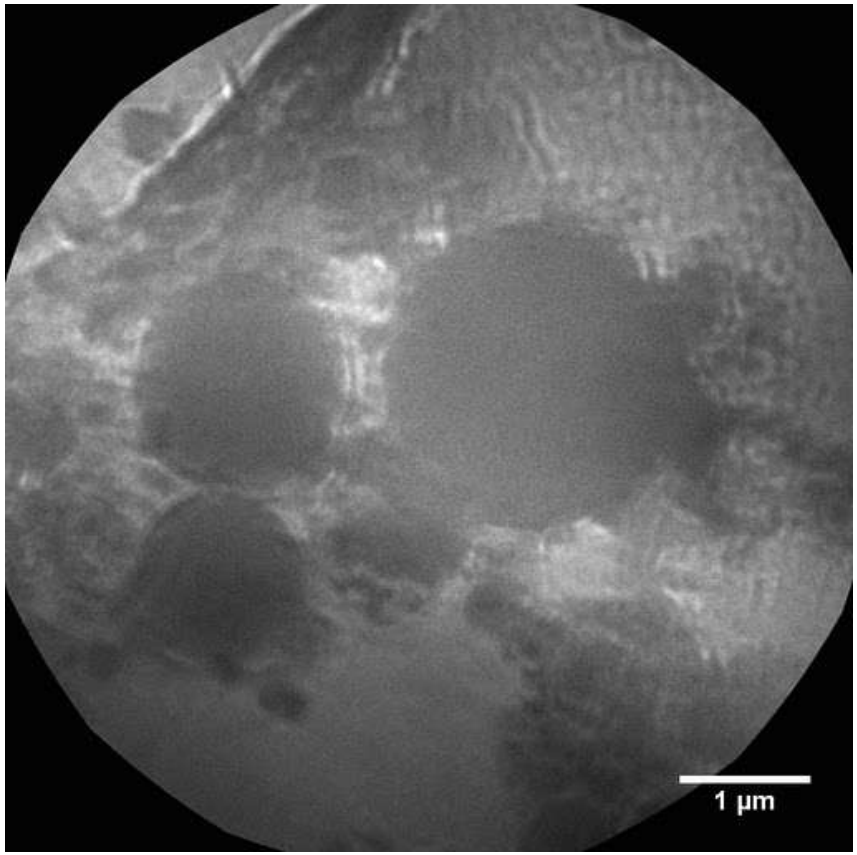
- **Como reduzir 120 anos de experiência com cimento portland em 3-5 anos para um novo cimento?**

Geopolimeros (sem cimento)

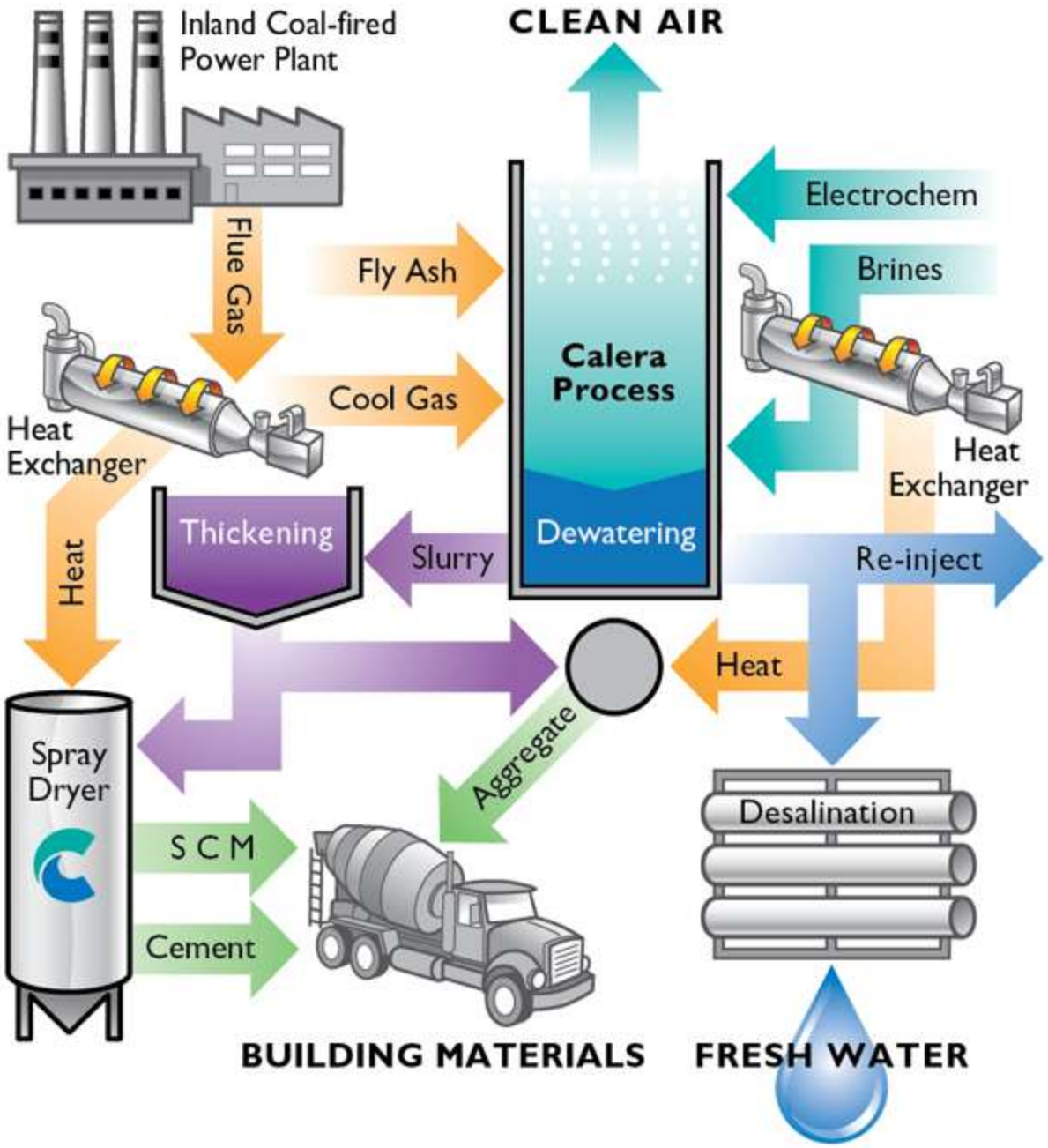




10 M NaOH solution



Processo da Calera



Pesquisa Integrada

Advanced Light Source

Soft x-rays microscopy, Small Angle Scattering, High-Pressure, Microdiffraction, Microtomography, Ambient XPS.

Advanced Photon Source

Total scattering methods (pdf), Nanotomography, Small Angle Scattering.

BESSY

Nanotomography

… more at Los Alamos

Tradição brasileira de excelência no concreto...

- Vários recordes mundiais em pontes e barragens.
- Renome internacional em tecnologia do concreto e projeto estrutural.

O Brasil está em otima fase

- Economia em expansão.
- Construção em alta.
- Previsão de crescimento constante.

Um desafio e um apoio...

- **Por que não fazer do Brasil uma potência na area de nanotecnologia do concreto?**

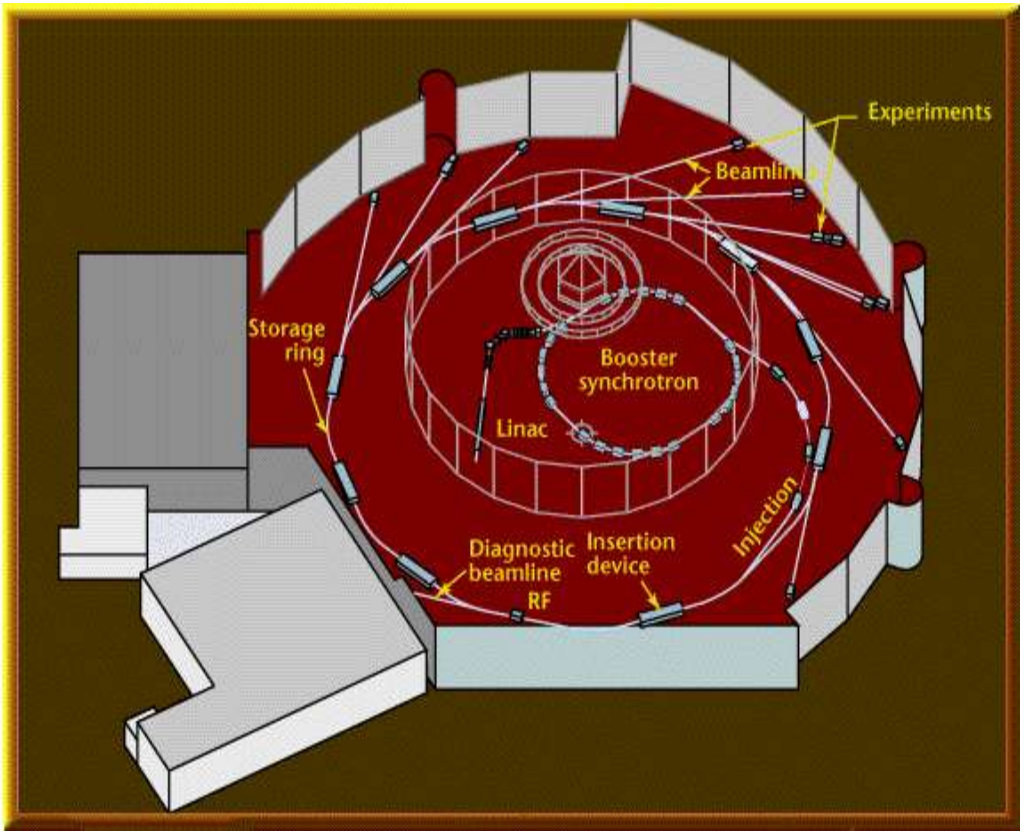
O mais difícil já tem em Campinas…

Advanced Light Source

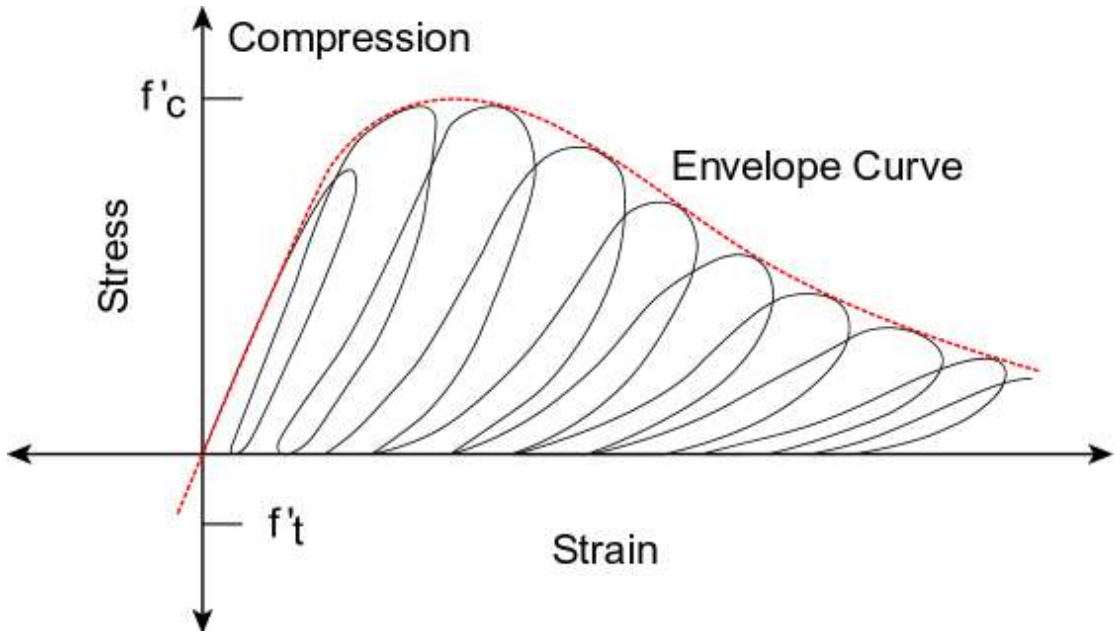
the world's first third-generation synchrotron light source in its energy range

Location

Advanced Light Source at Berkeley



Testes Mecânicos



Pergunta:

- **Como medir a propriedades mecânicas dos cristais pequenos?**

High Pressure Powder X-ray Diffraction

- **High pressure generating device**:
  - Diamond Anvil Cell
    - Strongest Material
    - Ko = ~440GPa
    - Transparent to electromagnetic spectrum
  - Theoretically, possible over 500GPa, but usually ~50GPa
  - Extremely small sample size
- **Hydrostatic pressure Medium**
    - 4:1 Methanol/Ethanol solution
    - Up to ~20GPa, nearly hydrostatic pressure
- **Ruby fluorescence technique**
  - Measurement of pressure inside of the cell

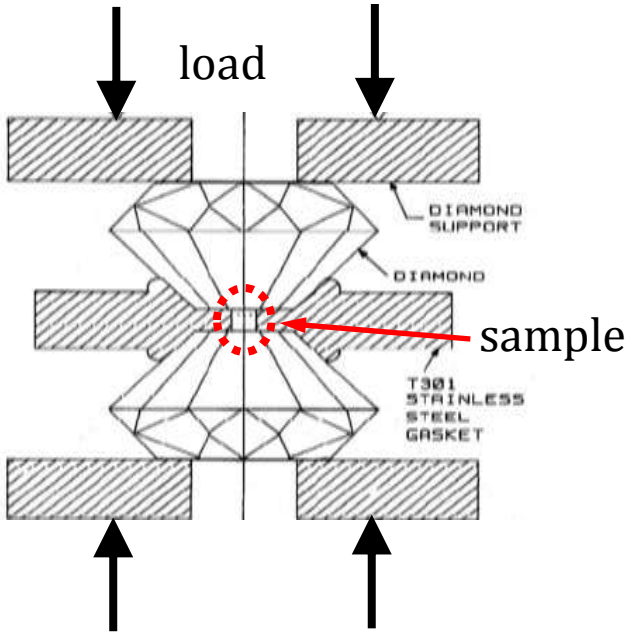


Figure. Schematic of Diamond Anvil Cell

DAC (Diamond Anvil Cell)

X-ray
Detector

X-ray

Sample in the metal gasket

Metal Gasket

Procedimento experimental

- As the pressure increases, the unit cell shrinks.
- Unit cell dimensions (a, b, c, α, β, γ) at a certain pressure can be calculated from X-ray diffraction pattern
- $P(V/V_o)$ can be obtained
- Bulk modulus = $K_T = -V\frac{dP}{dV}$

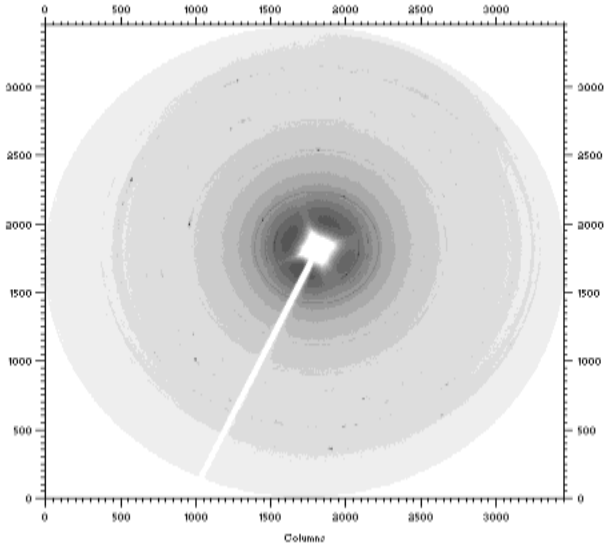
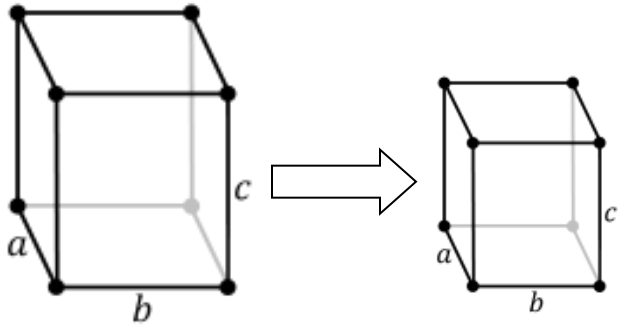
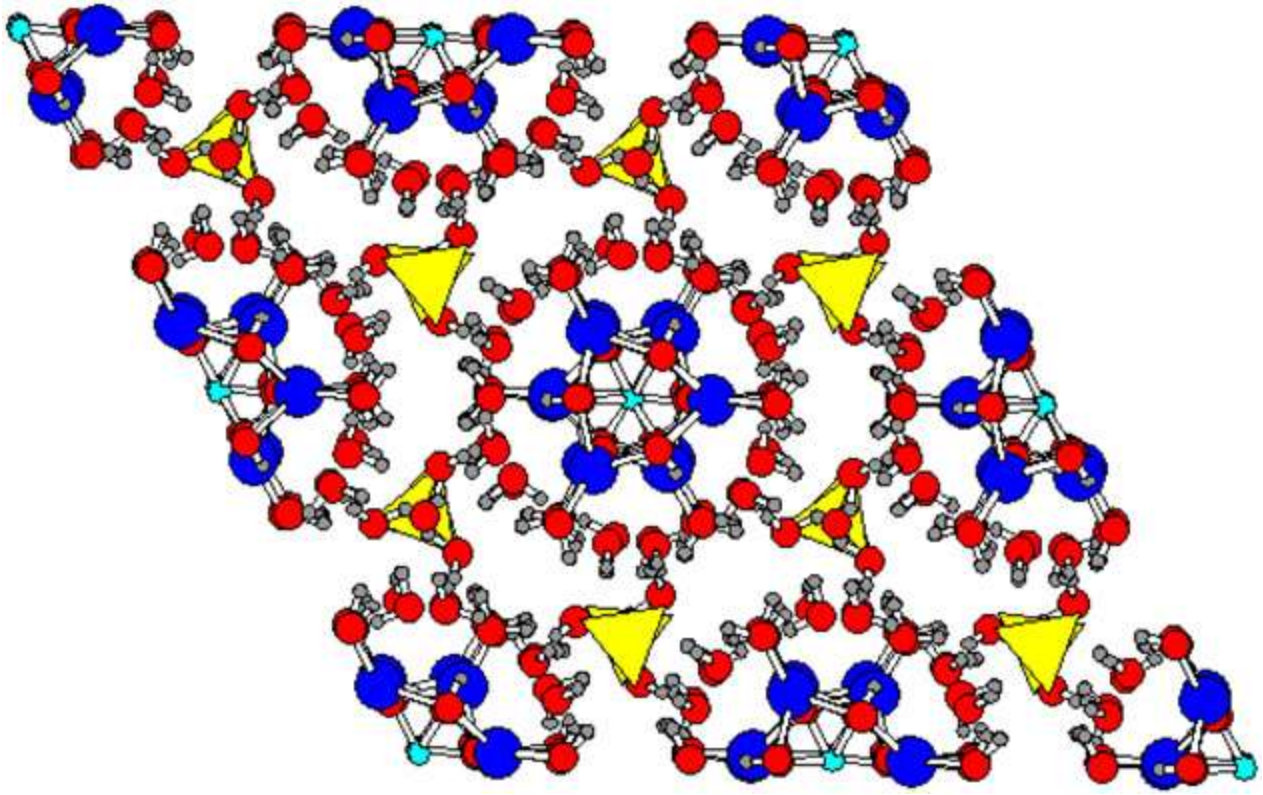


Figure. X-ray diffraction Pattern in beamline 12.2.2 (tobermorite)



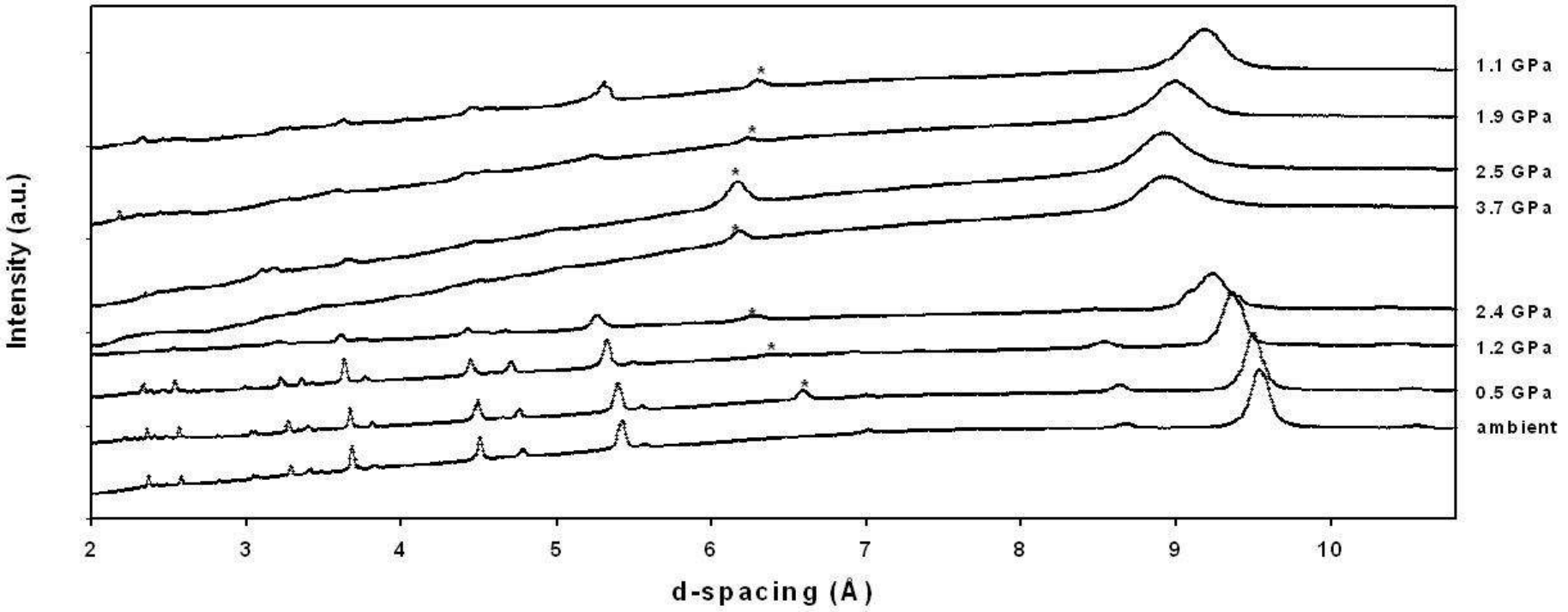
At low pressure **At high pressure**

Estrutura da etringita



Ca atoms are displayed as blue circles, oxygen atoms in red, aluminum atoms in light blue, sulfate tetrahedral in yellow and hydrogen atoms in grey.

Resultado experimental



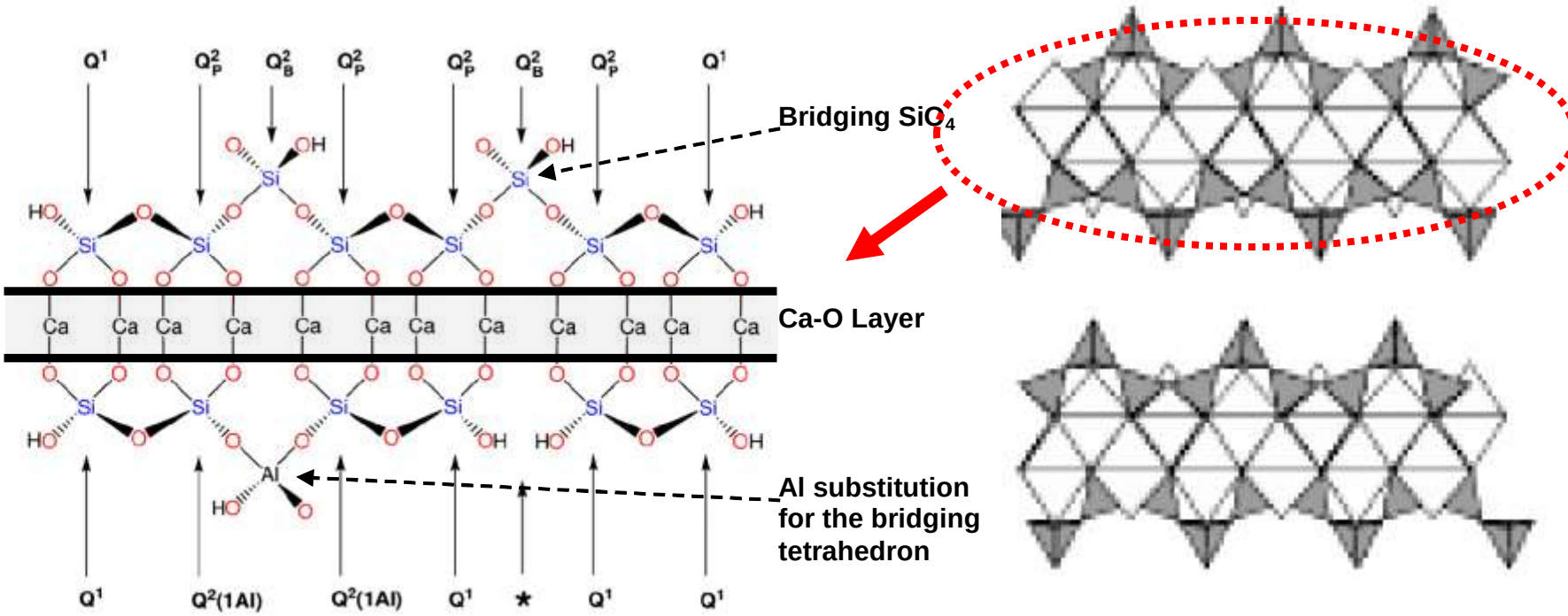
Isothermal bulk modulus of ettringite: 27(7) GPa

Nanopergunta:

O que acontece com as propriedades mecânicas quando o Si e' substituido por Al?

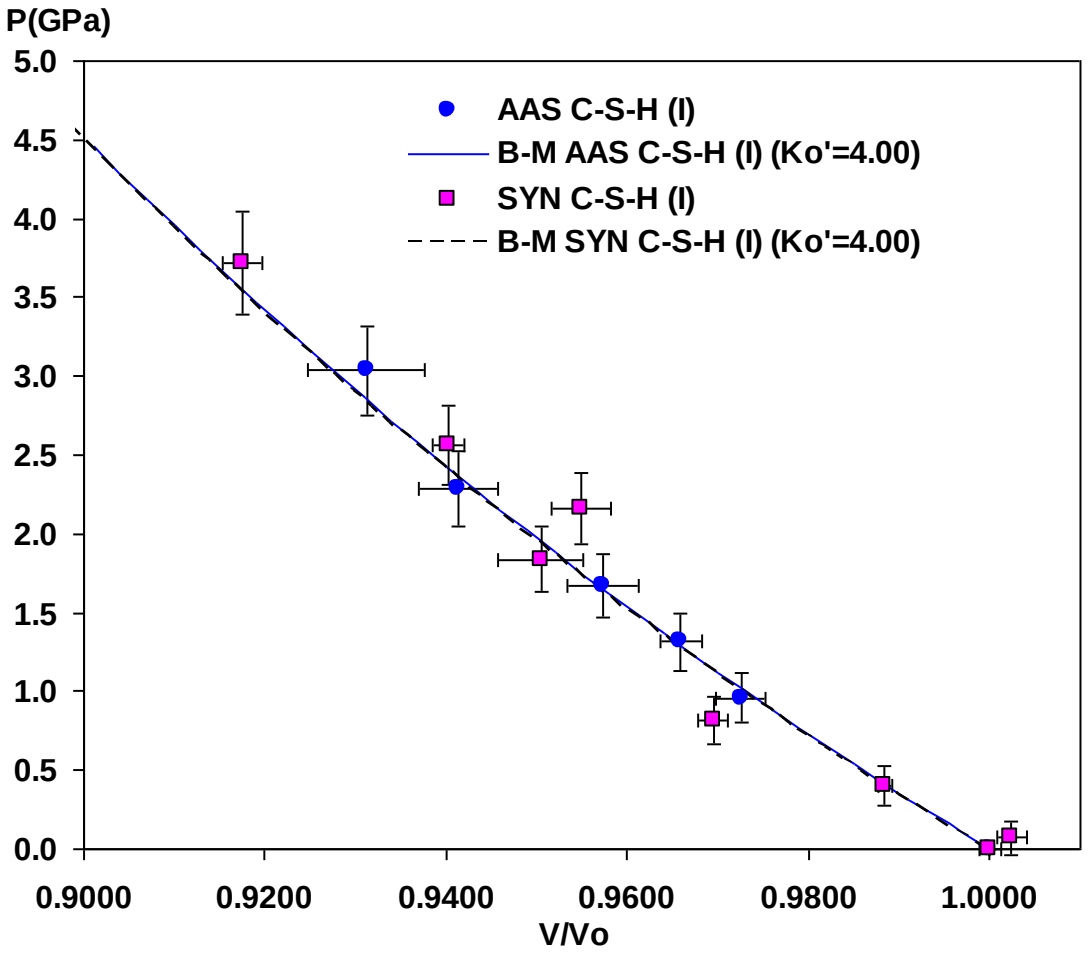
Qual é a diferença estrutural?

- **Al substitution:**
  - The synthetic C-S-H (I) does not contain Al in its structure
  - The alkali-activated slag C-S-H (I) contains Al in its structure

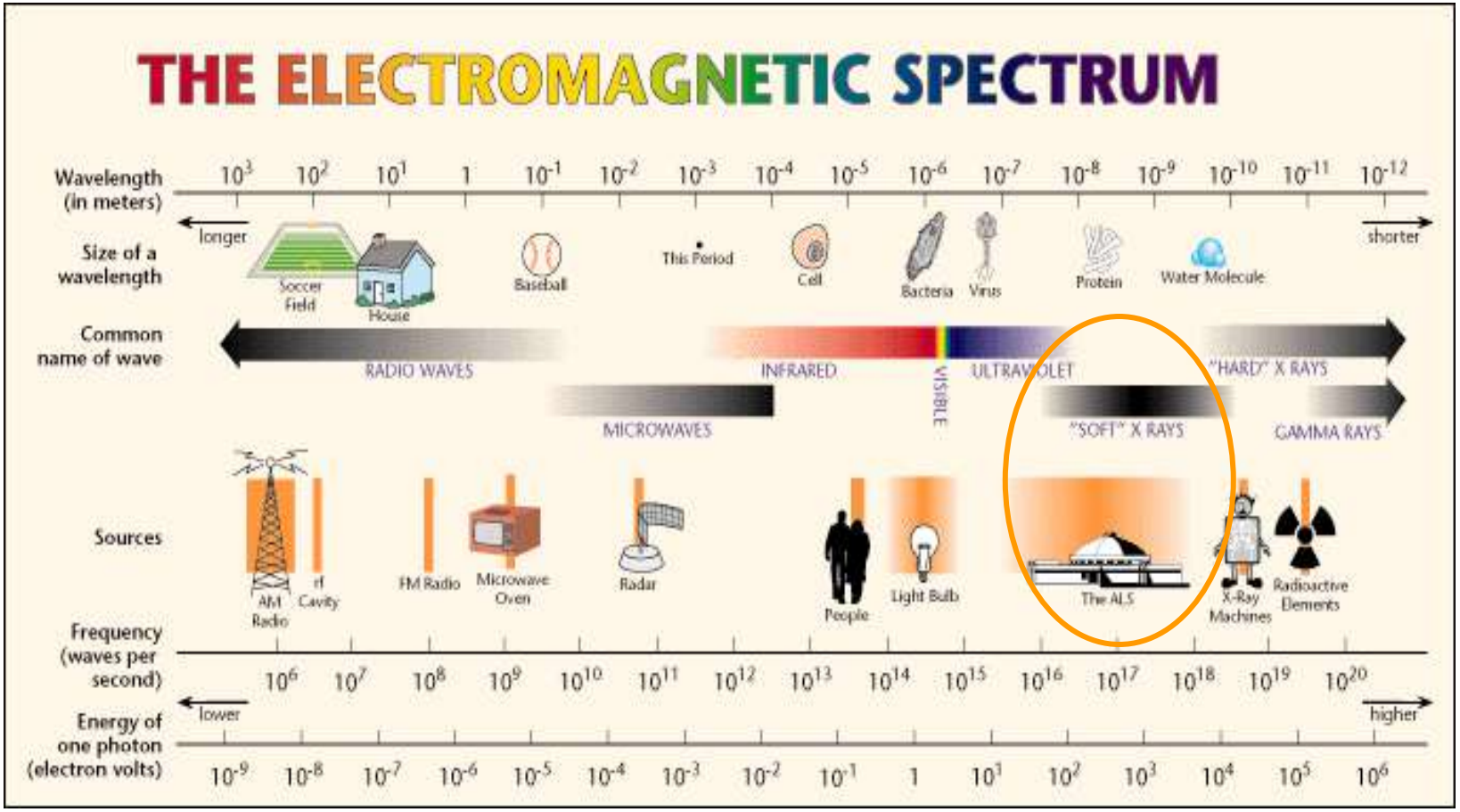


Resultado

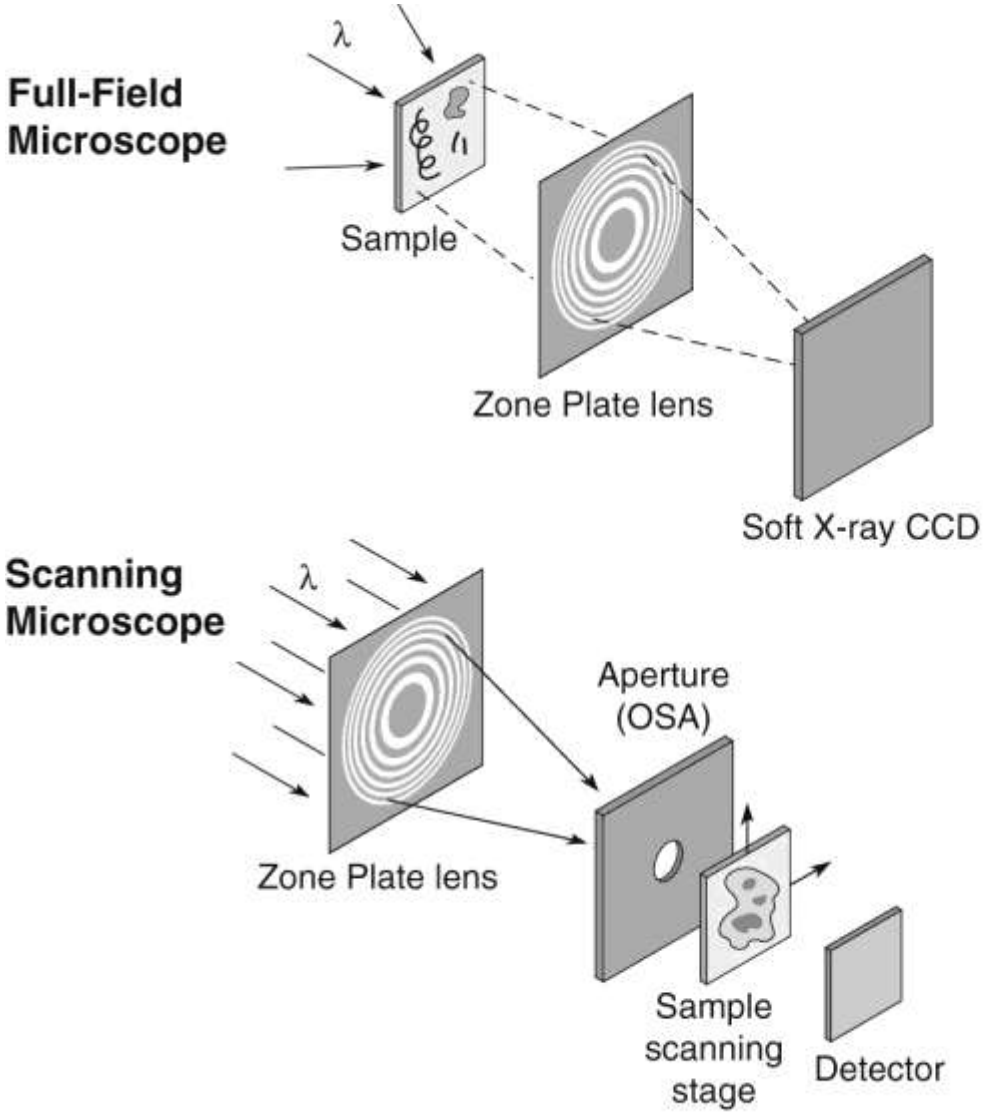
- Não tem diferença nenhuma!



Spectro eletromagnético



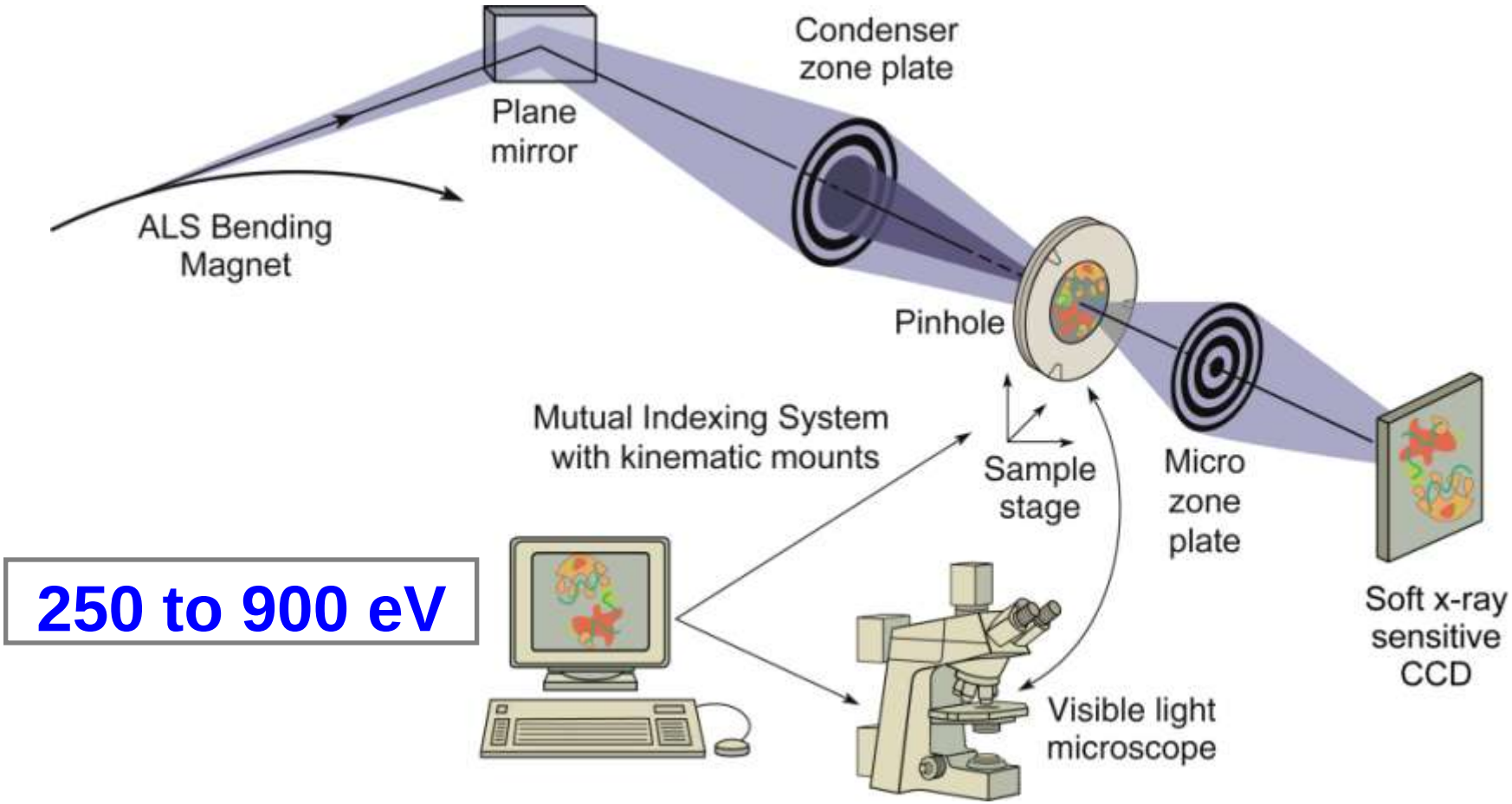
Dois tipos de Microscópios



- 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

Ch09_F21modif_10.04.ai

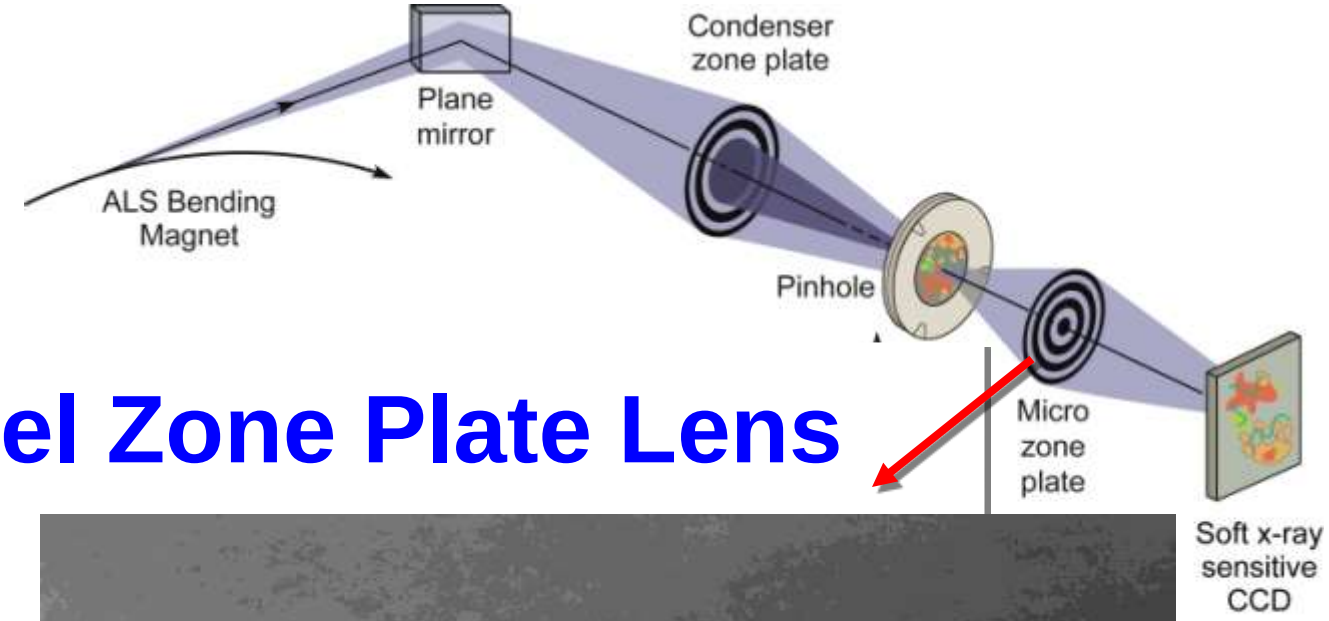


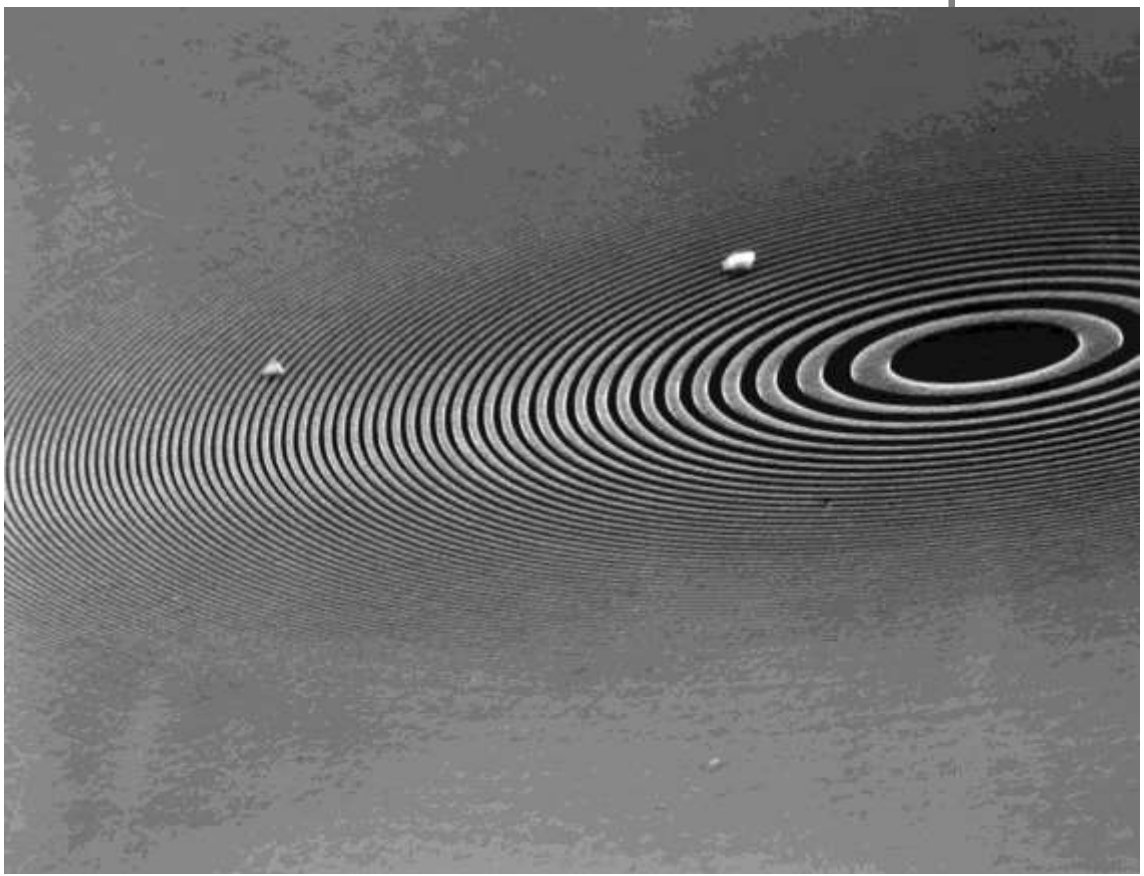
250 to 900 eV

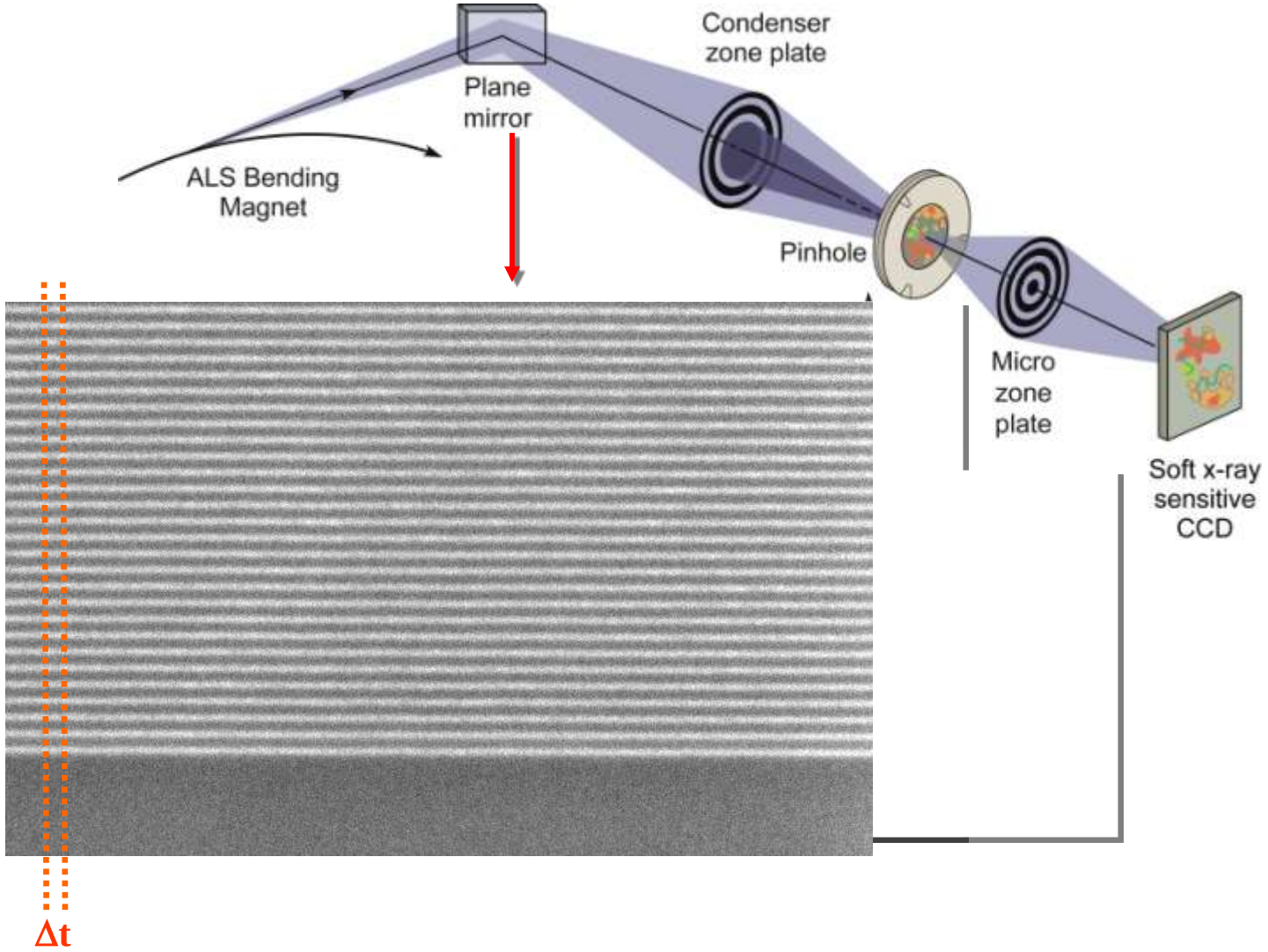
Resolution: 25 nm

Magnification: 1600 to 2400 times

Fresnel Zone Plate Lens



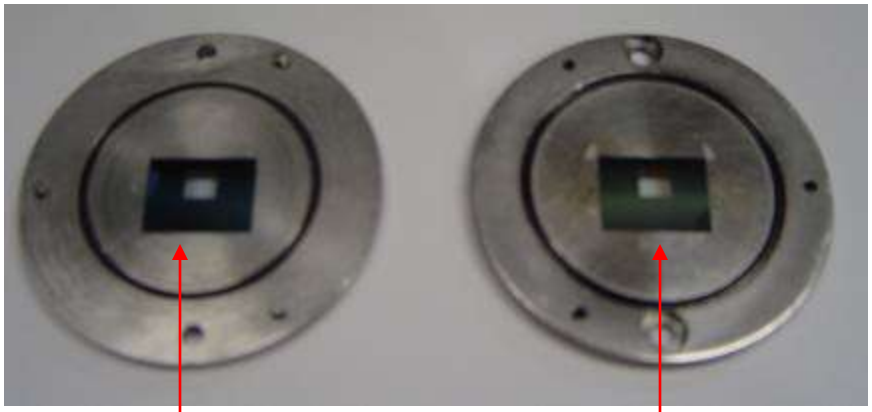


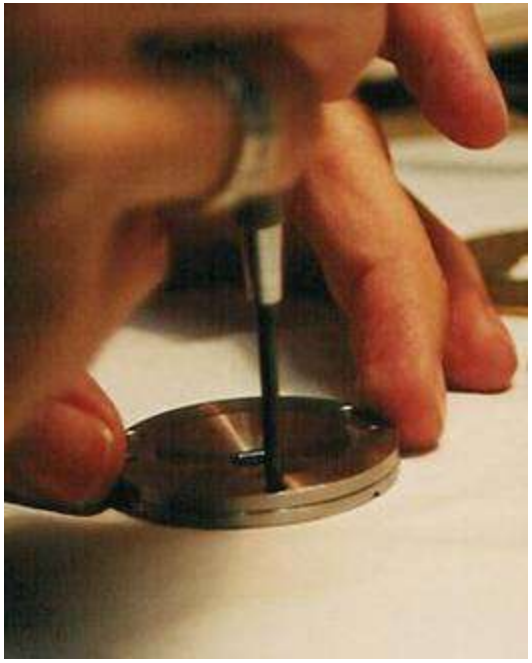


Multilayer Mirror Coatings

Preparação da Amostra

Restriction: sample thickness (less than 10 μm)



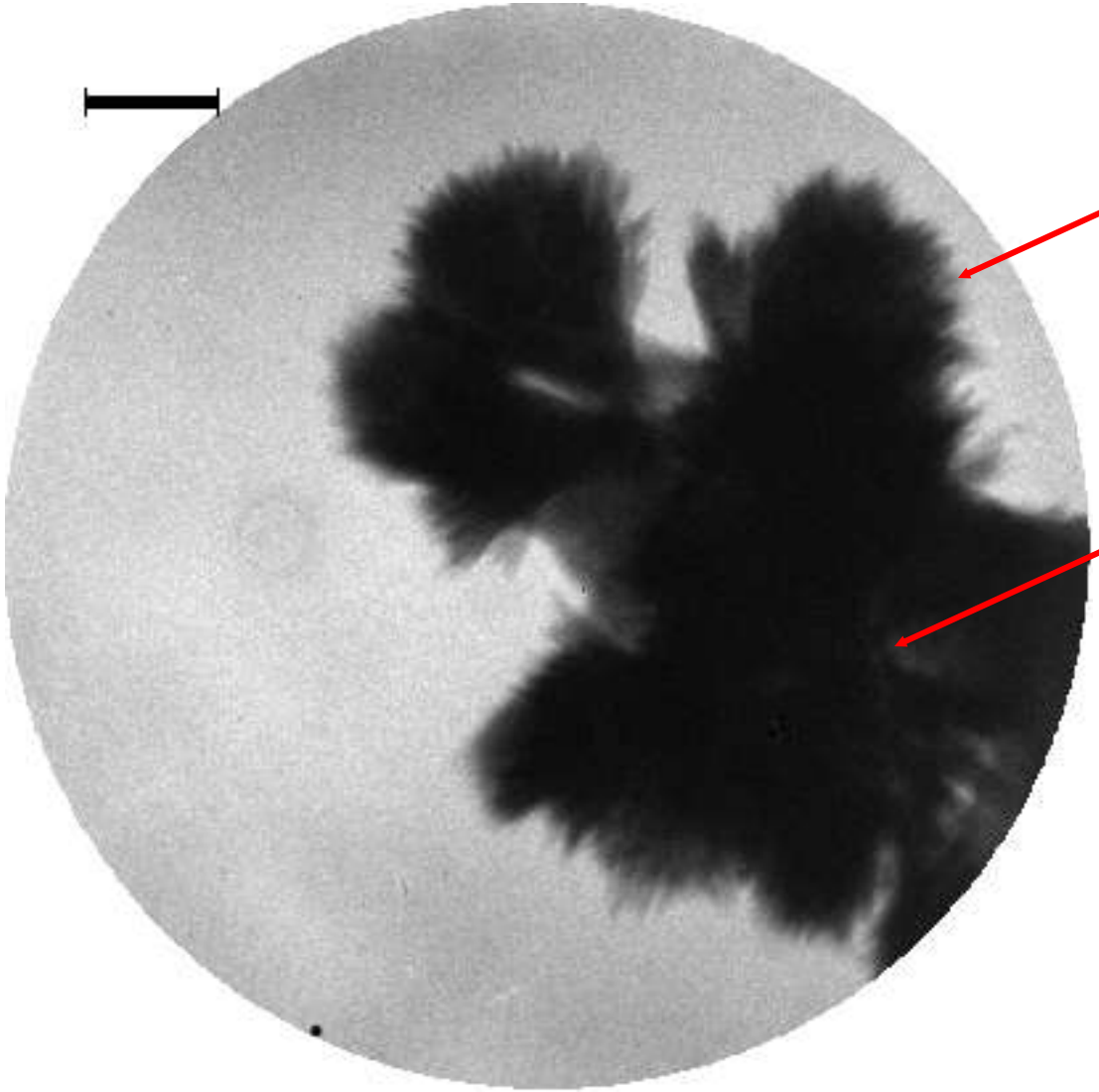


Silicon nitride windows

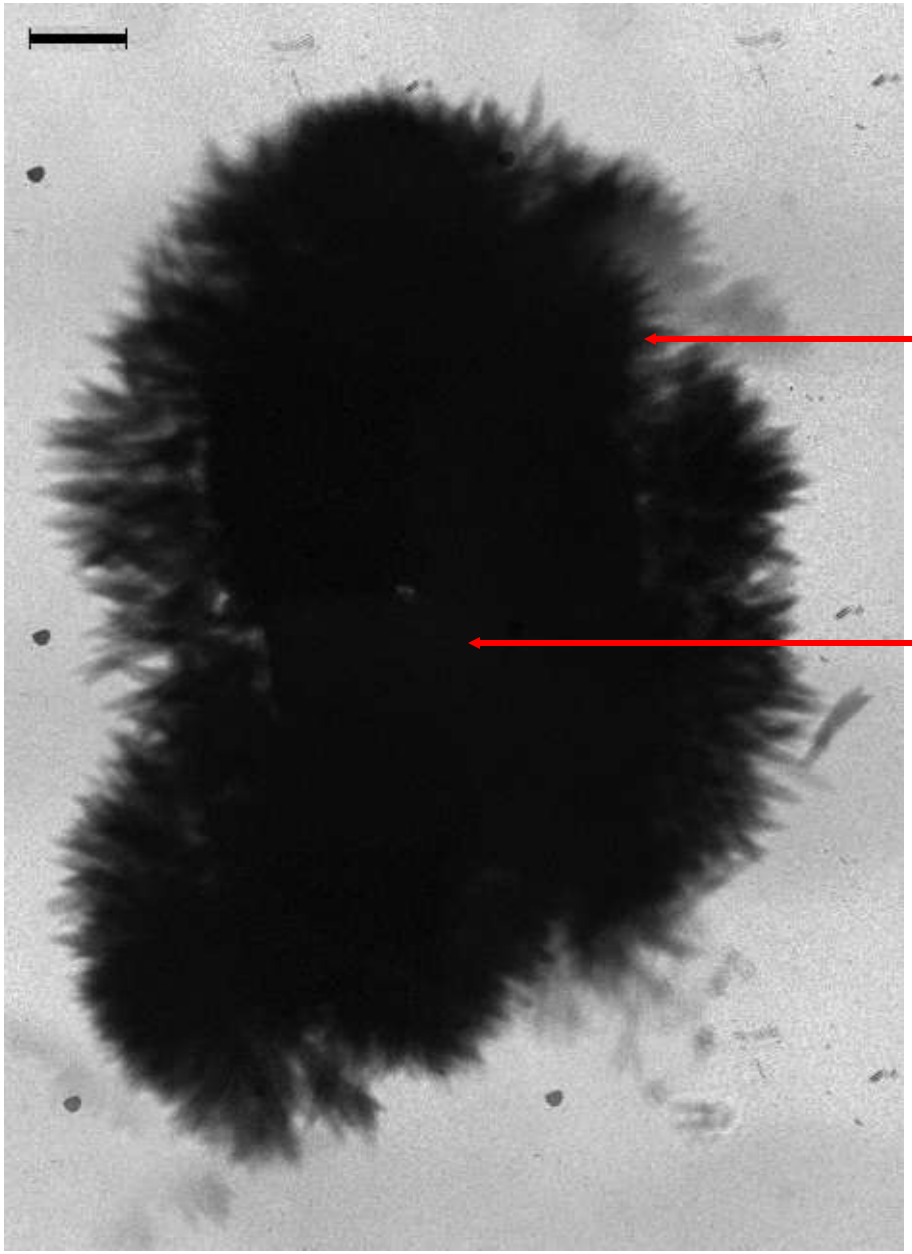
Highly diluted samples (water/cement is 5 before centrifugation)

Imaging as soon as 6 minutes after mixing

Early hydrates forming during the pre-induction period



C3S hydrated for 34 min. in saturated lime and calcium sulfate at w/c=5, 1s exposure time, 516eV, scale bar 1μm.



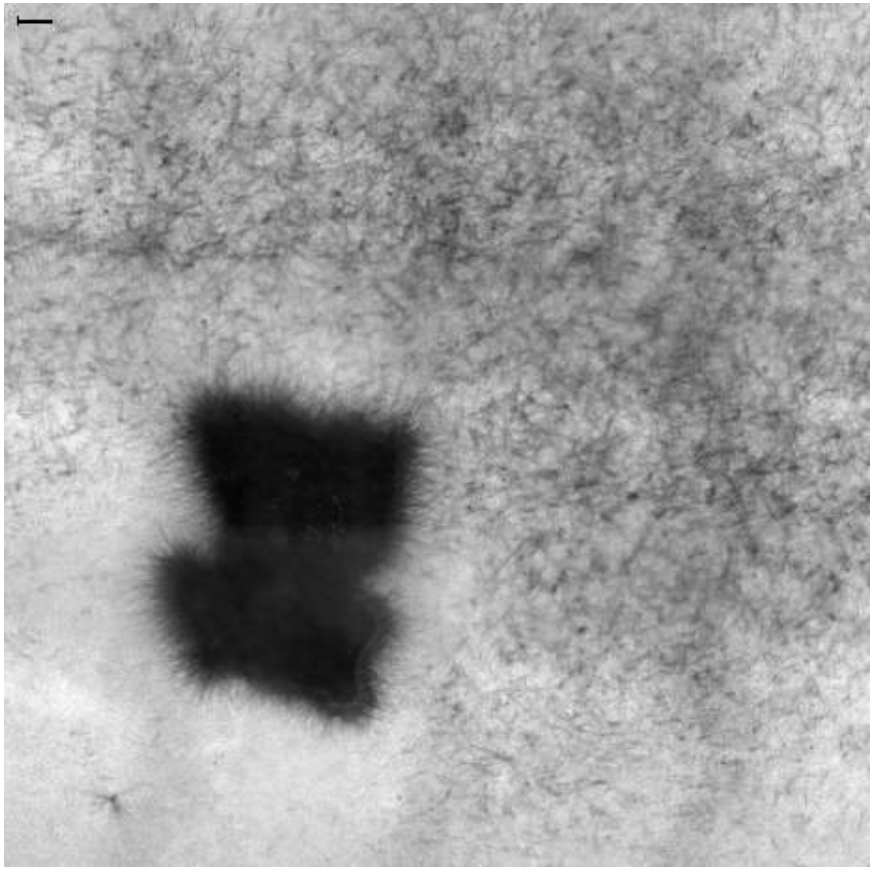
Early hydrates
(Sheaf of wheat)

grain

C3S hydrated for 56 min. in saturated lime and calcium sulfate at w/c=5, 1s exposure time, 516eV, scale bar 1μm.

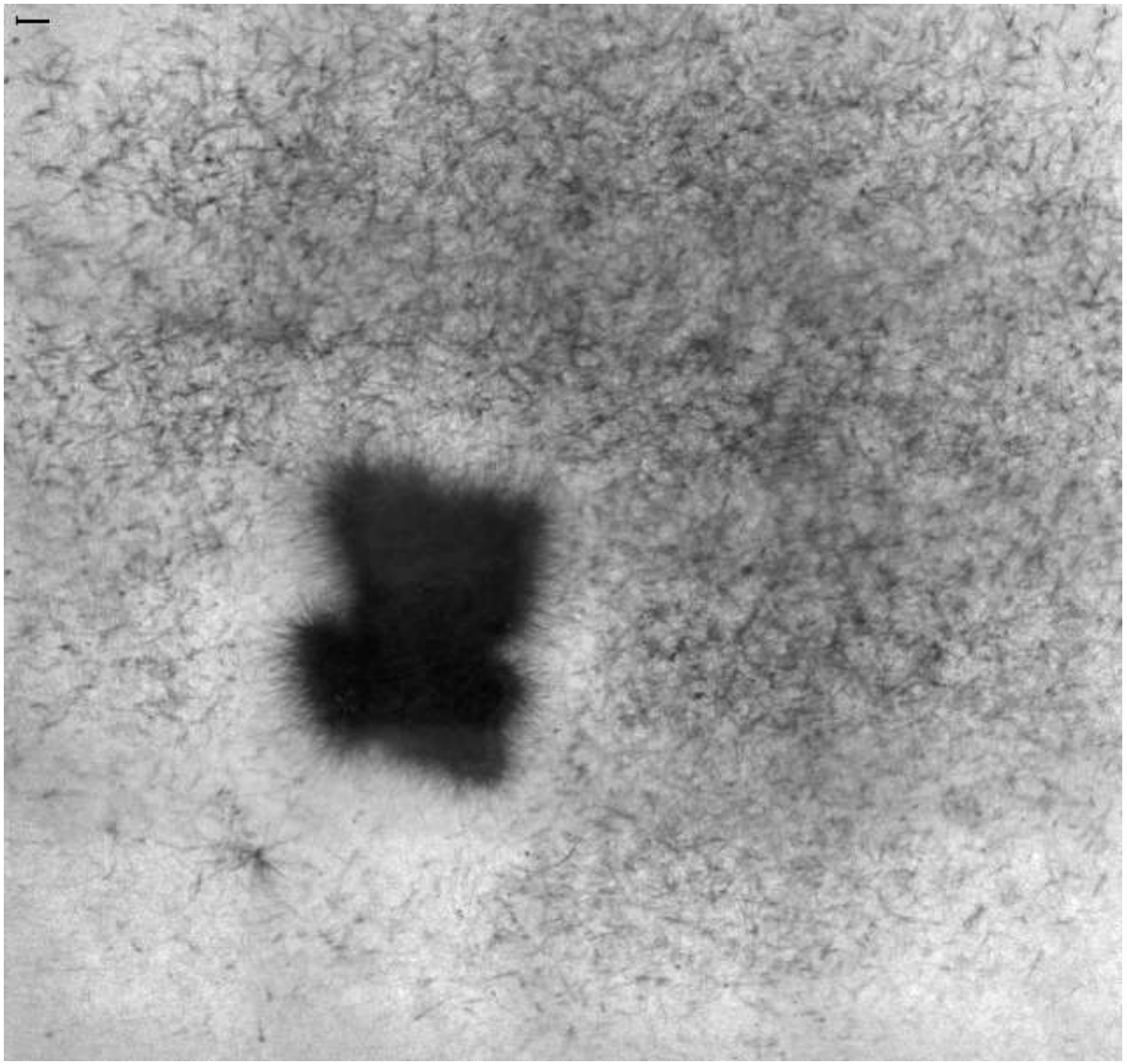
In-situ Massive precipitation

8h 30min.

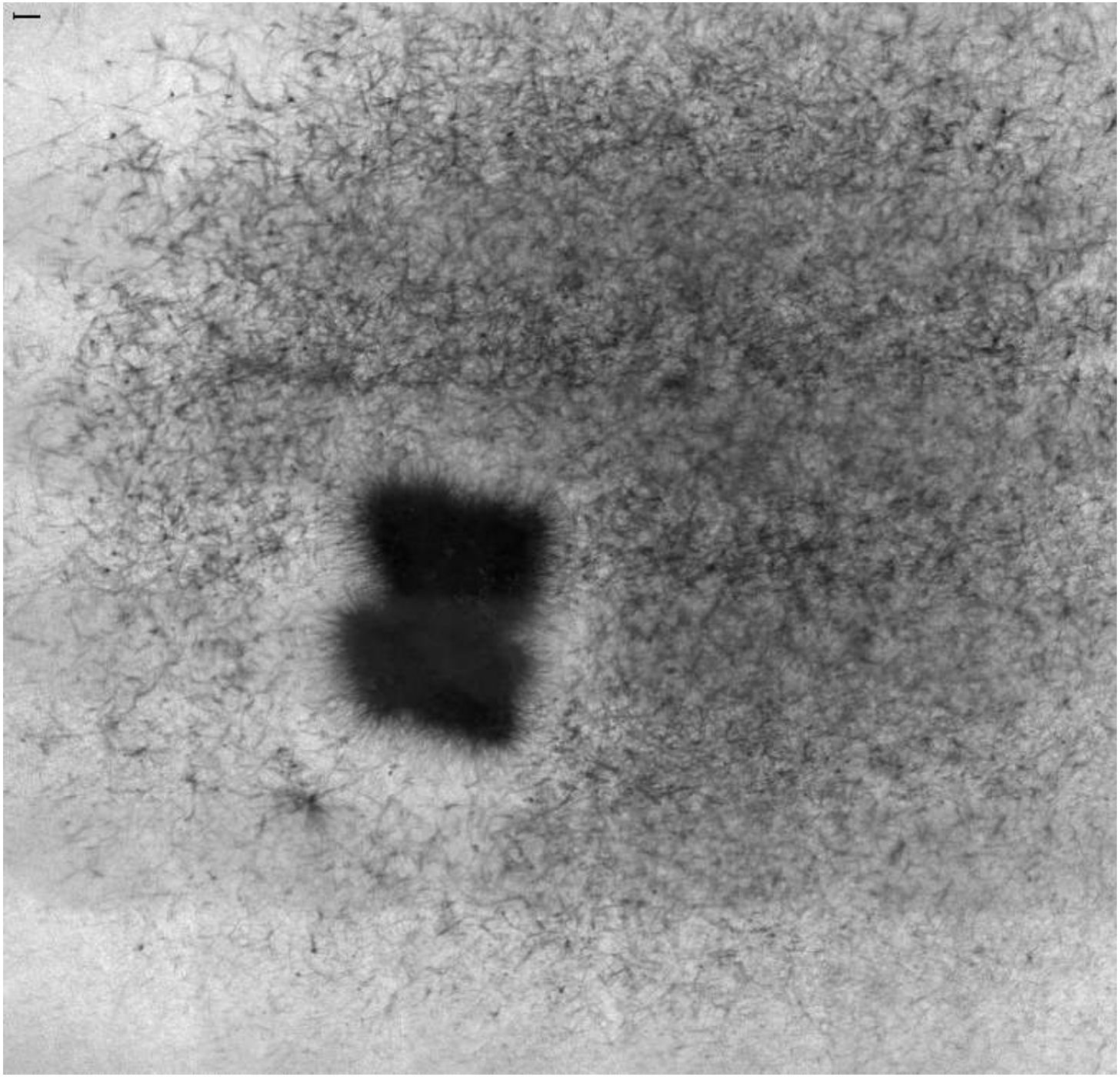


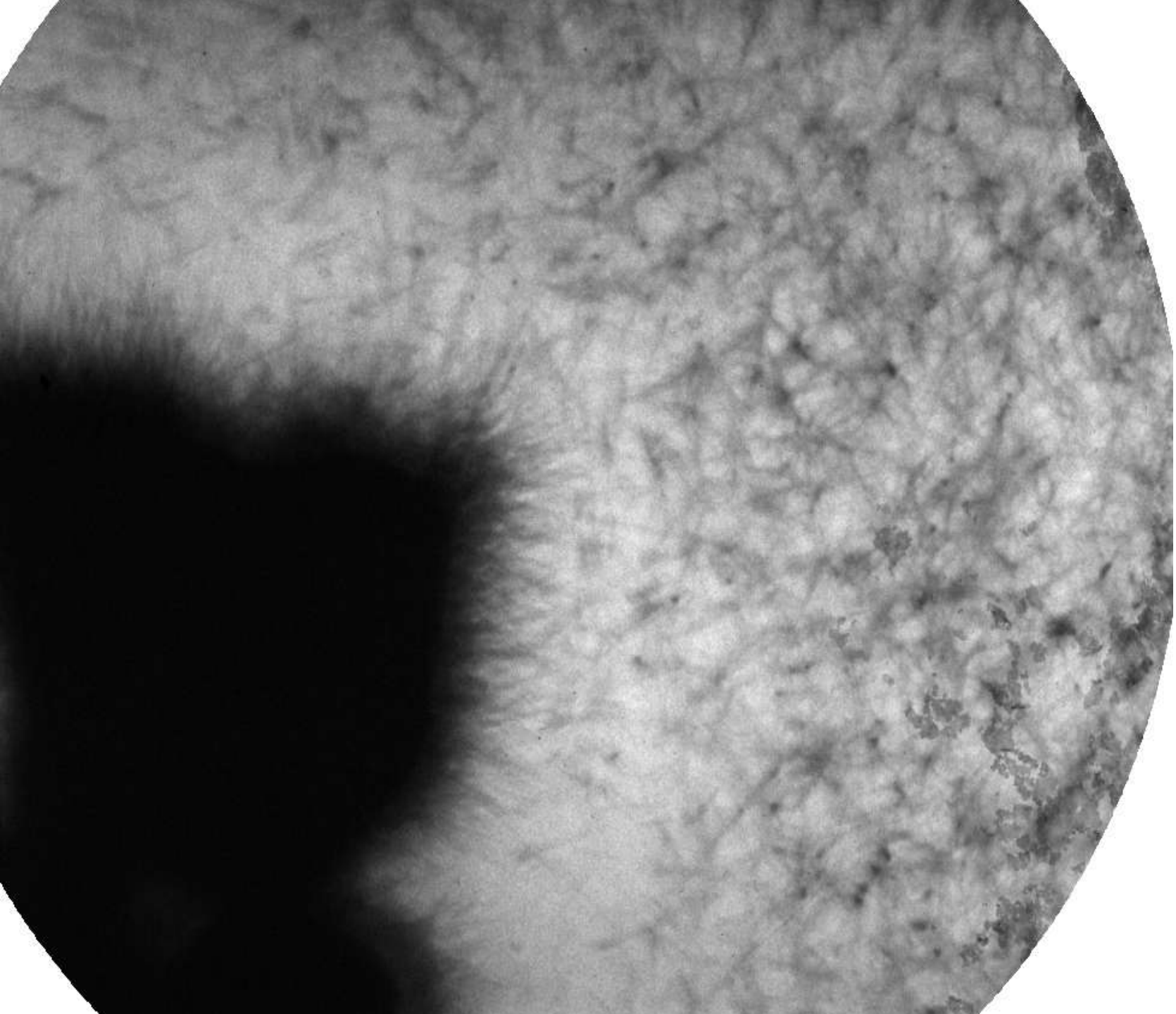
In-situ Massive precipitation

8h 36min.

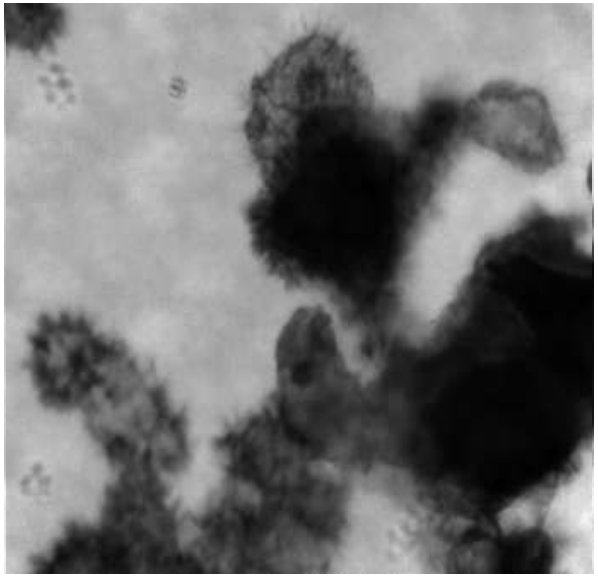


9h 16min.



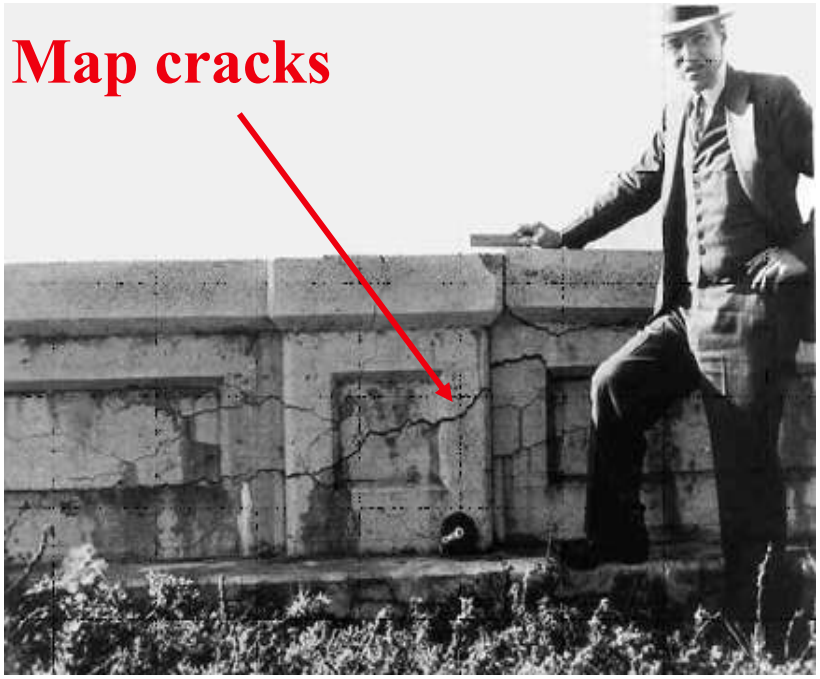


Adições Químicas



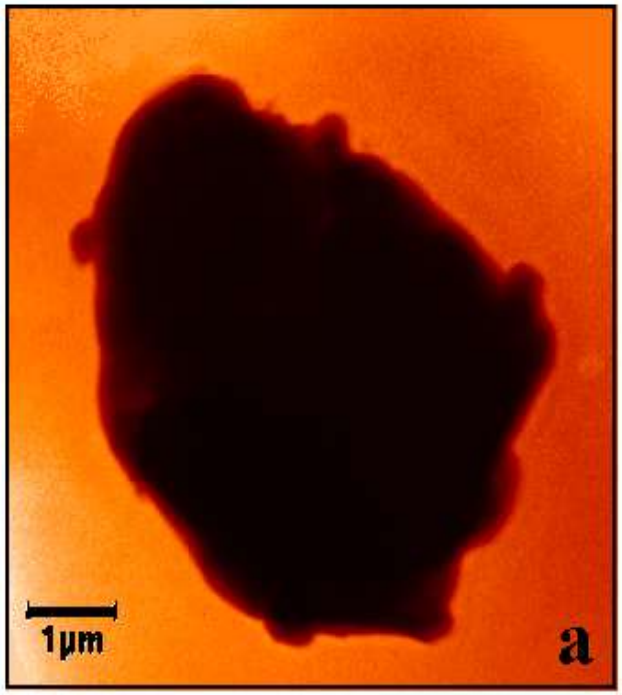
Reação álcali-agregado

Vertical cracks

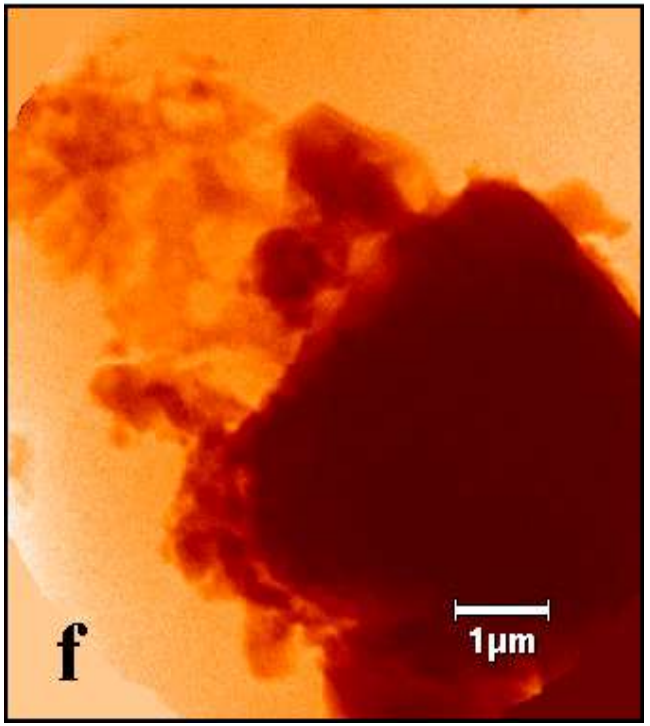


California, 1936

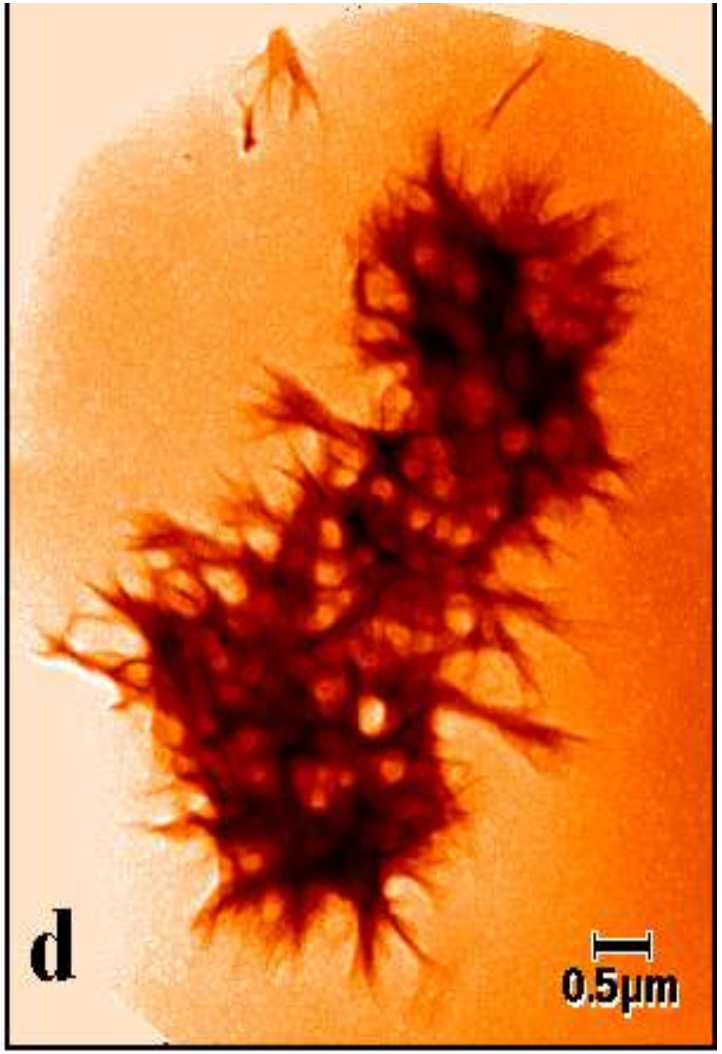
Gel de Furnas



Dissolução em NaOH

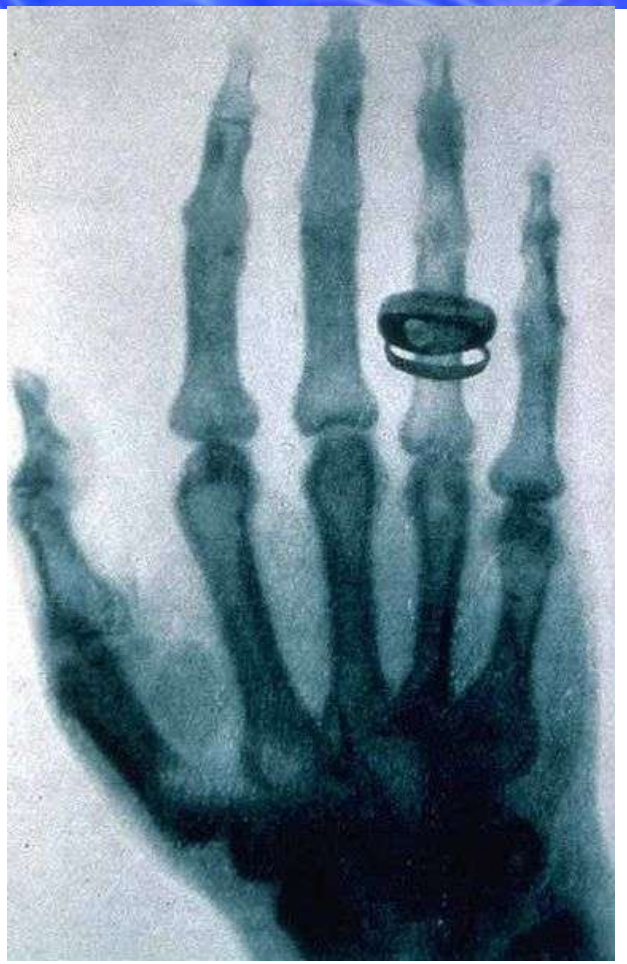


Na presença de $Ca(OH)_2$

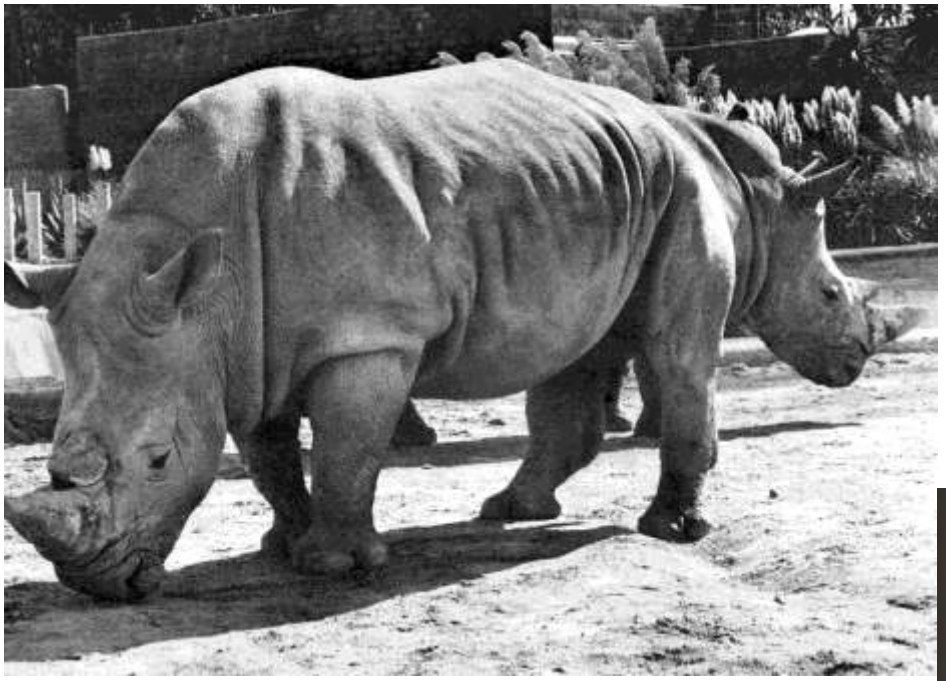


Uso de raios-x para imagens

Wilhelm Conrad Roentgen
first Nobel prize in physics (1901)



Compressão da terceira dimensão



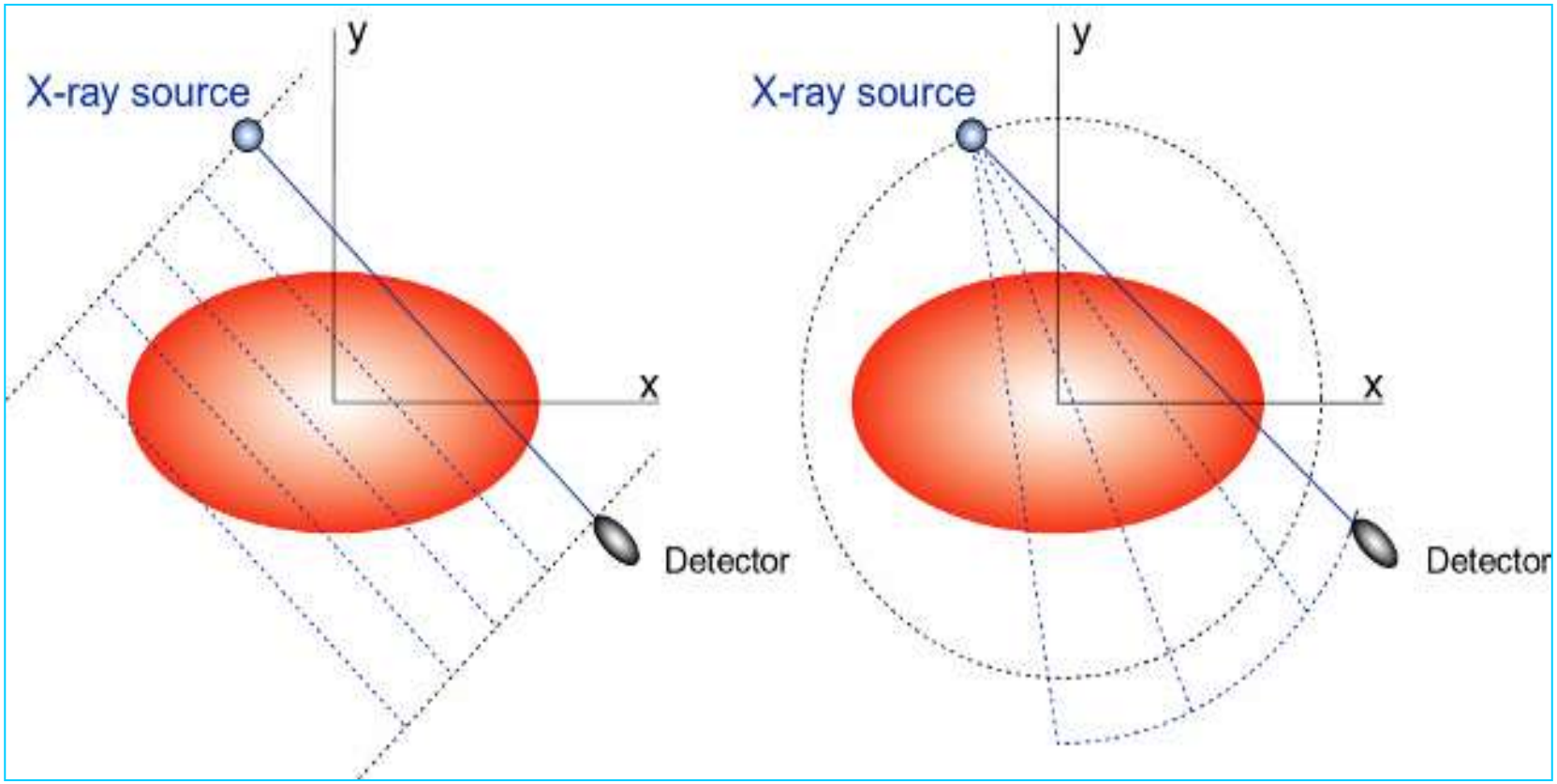
Desenvolvimento da tomografia

Sir Godfrey N. Hounsfield

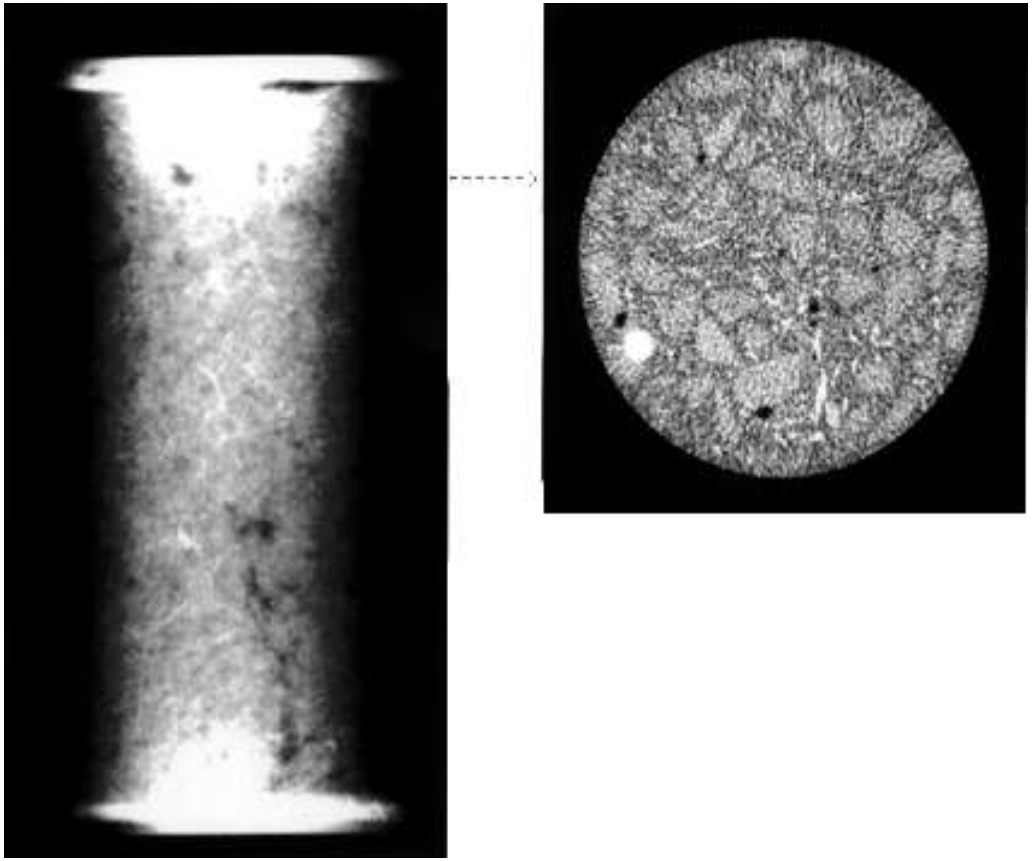
Allan M. Cormack

Nobel Prize in Physiology or Medicine 1979

Tomografia: Configuração

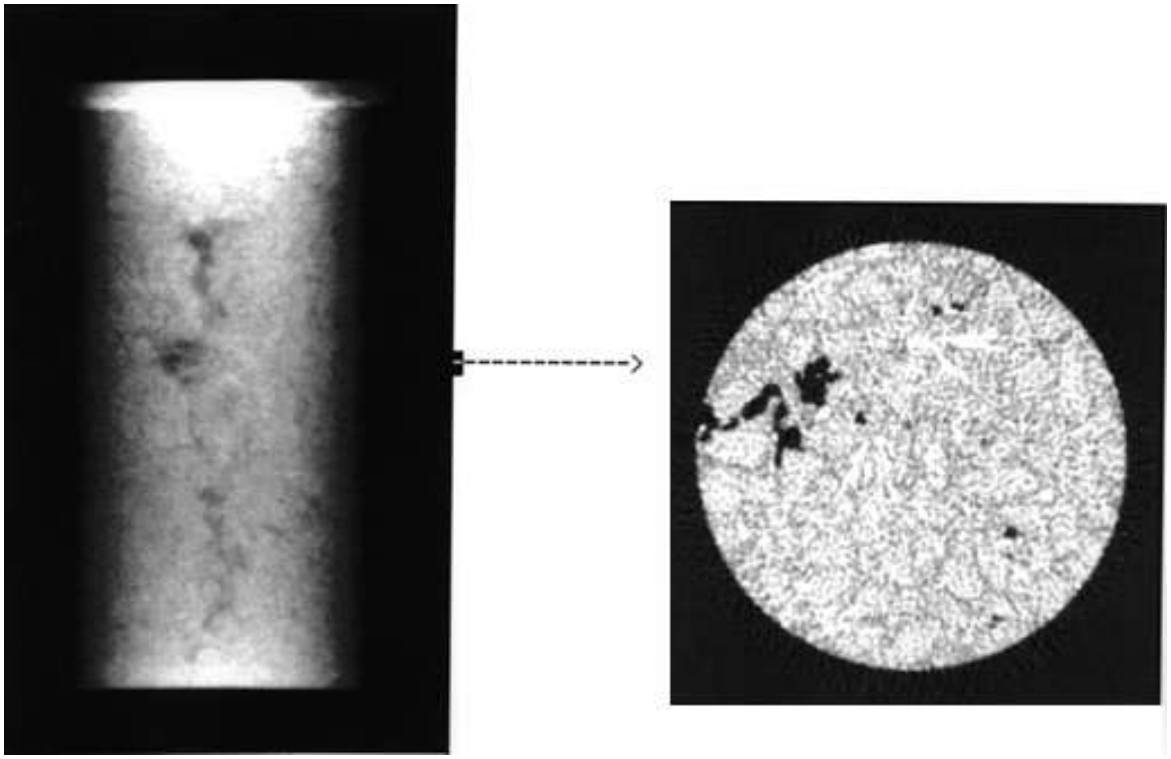


Exemplos



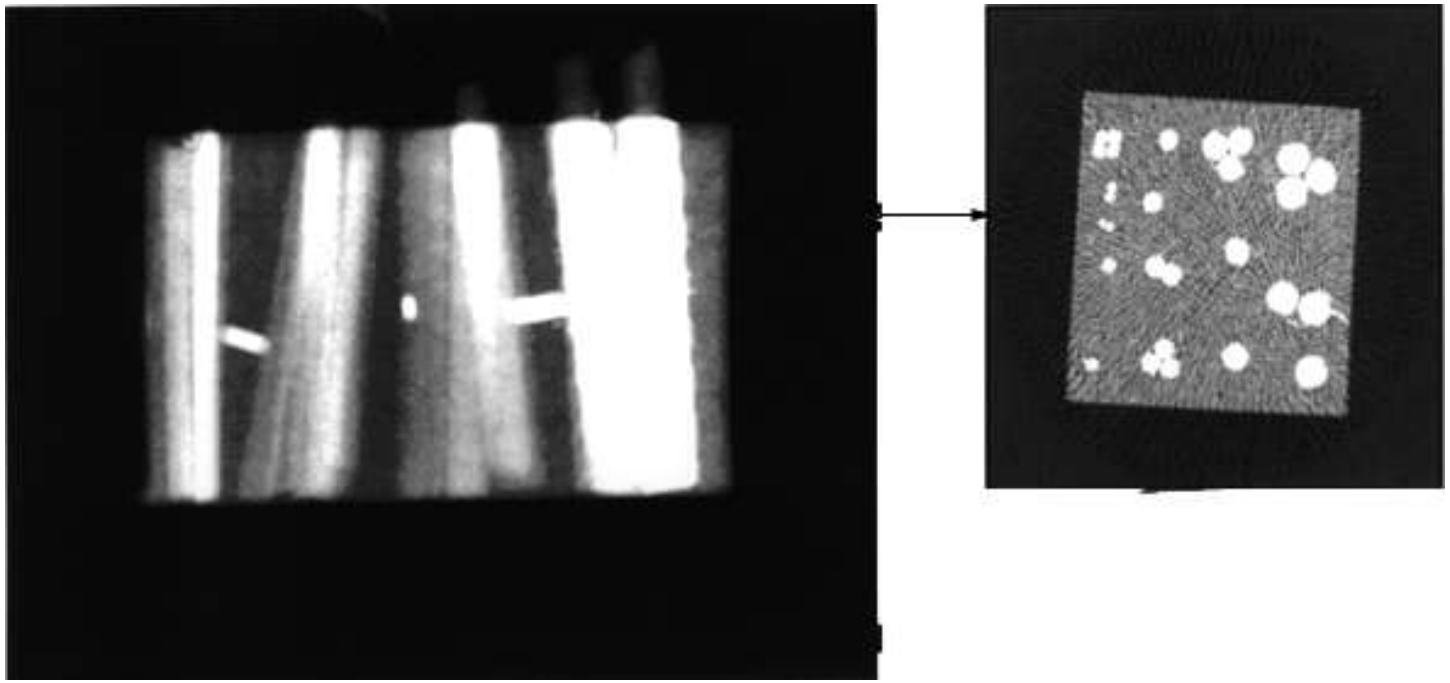
Radiografia (esquerda) and tomografia (direita) de cp de concreto com fibras

Exemplos



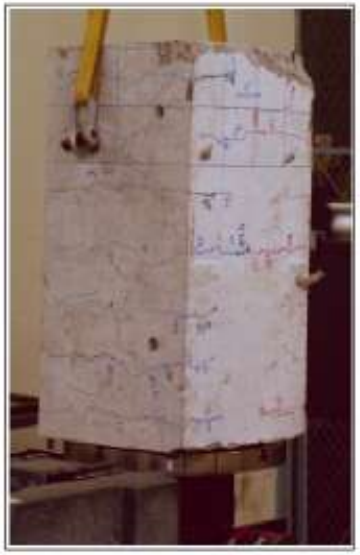
Radiografia (esquerda) e tomografia (direita) de cilindros de concreto com fibras

Localização das barras

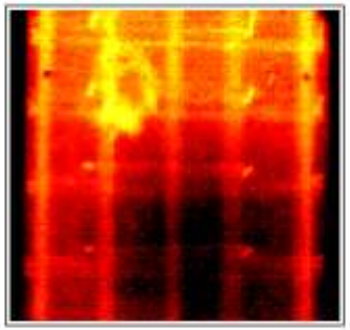


Radiografia (esquerda) and e tomografia (direita).

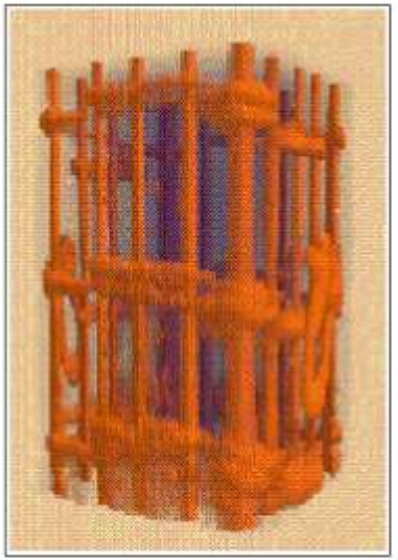
Concreto armado



reinforced concrete column



radiography

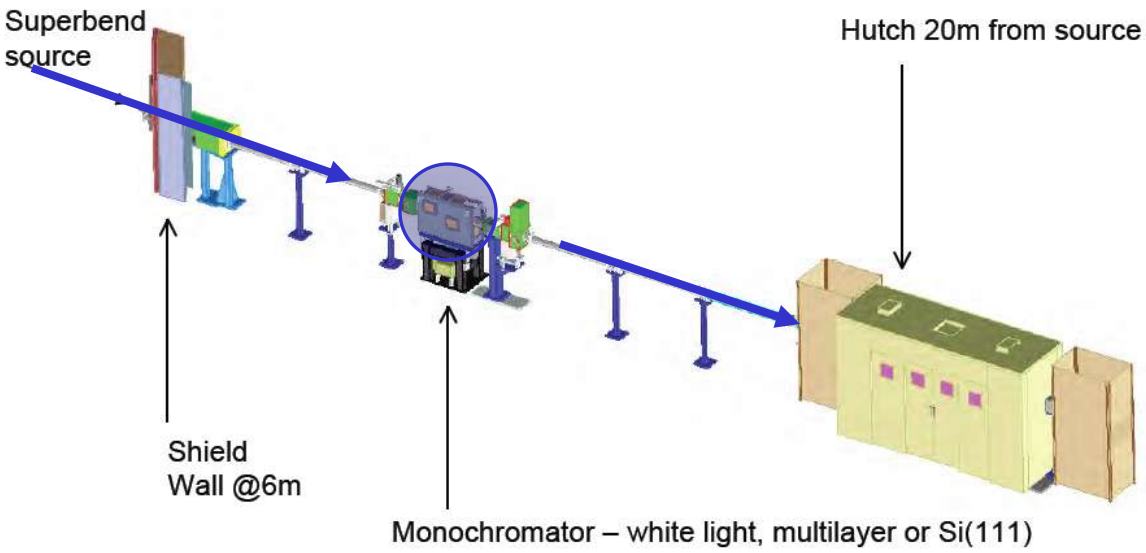


3-D tomography

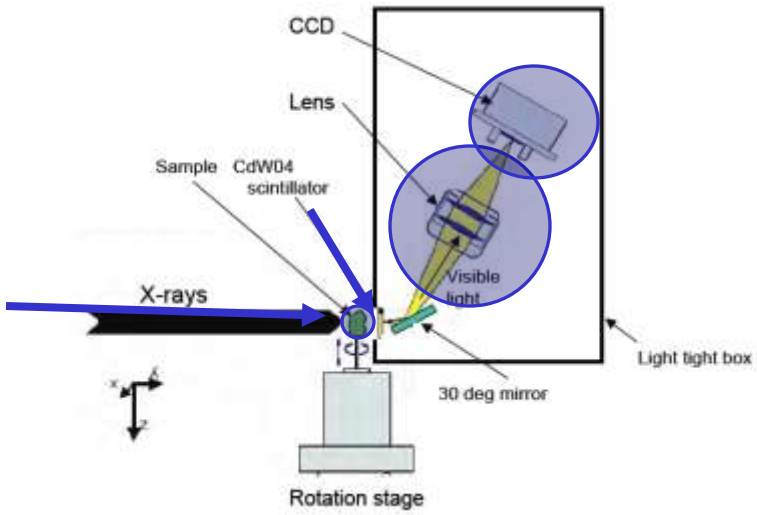
images courtesy of Dr. Harry Martz from LLNL

Engenheiros preferem maiores resoluções

Synchrotron XMT



XCMT

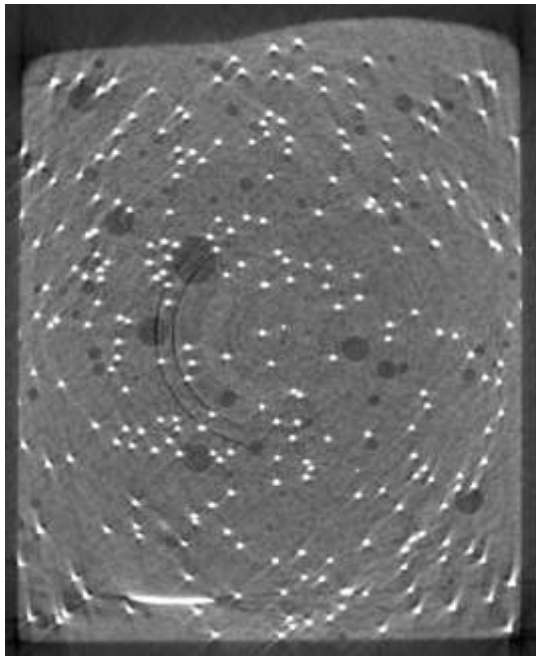


XCMT 2D Detector

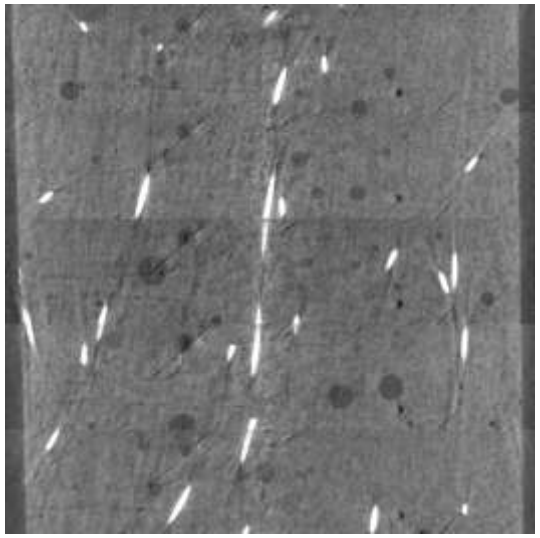
Image courtesy of A.Macdowell

1. Superbend Polychromatic beam from the storage ring
2. Monochromator: isolates, then sends off monochromatic beam
3. Monochromatic Beam
4. Sample on rotating stage, partial beam absorbance
5. Scintillator – converts X-rays to visible light
6. Visible light
7. A CCD captures the raw image, to be processed, reconstructed, and rendered on a PC

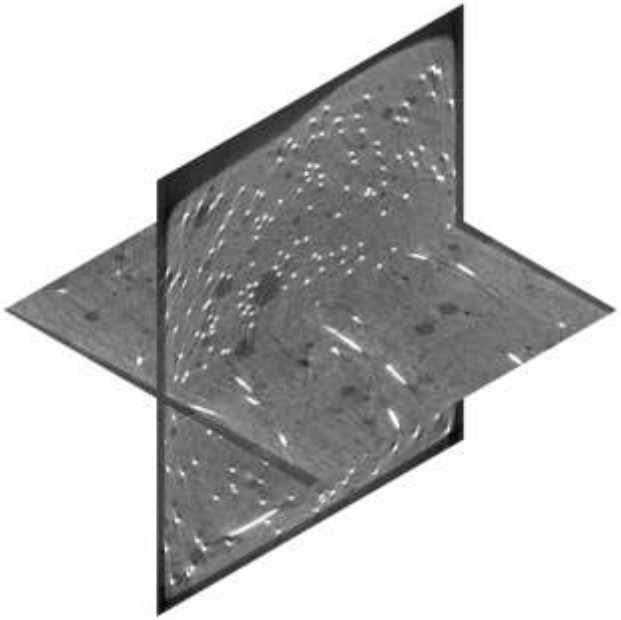
Fibras



xy plane tomogram



yz plane



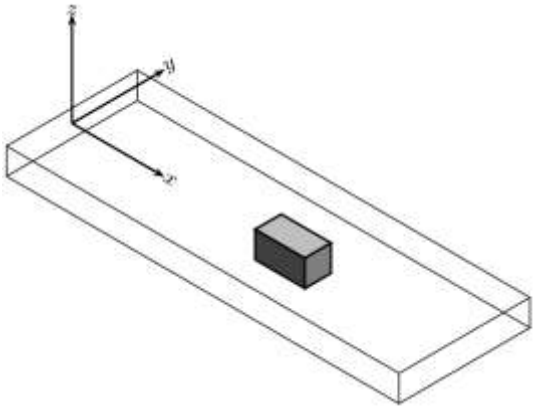
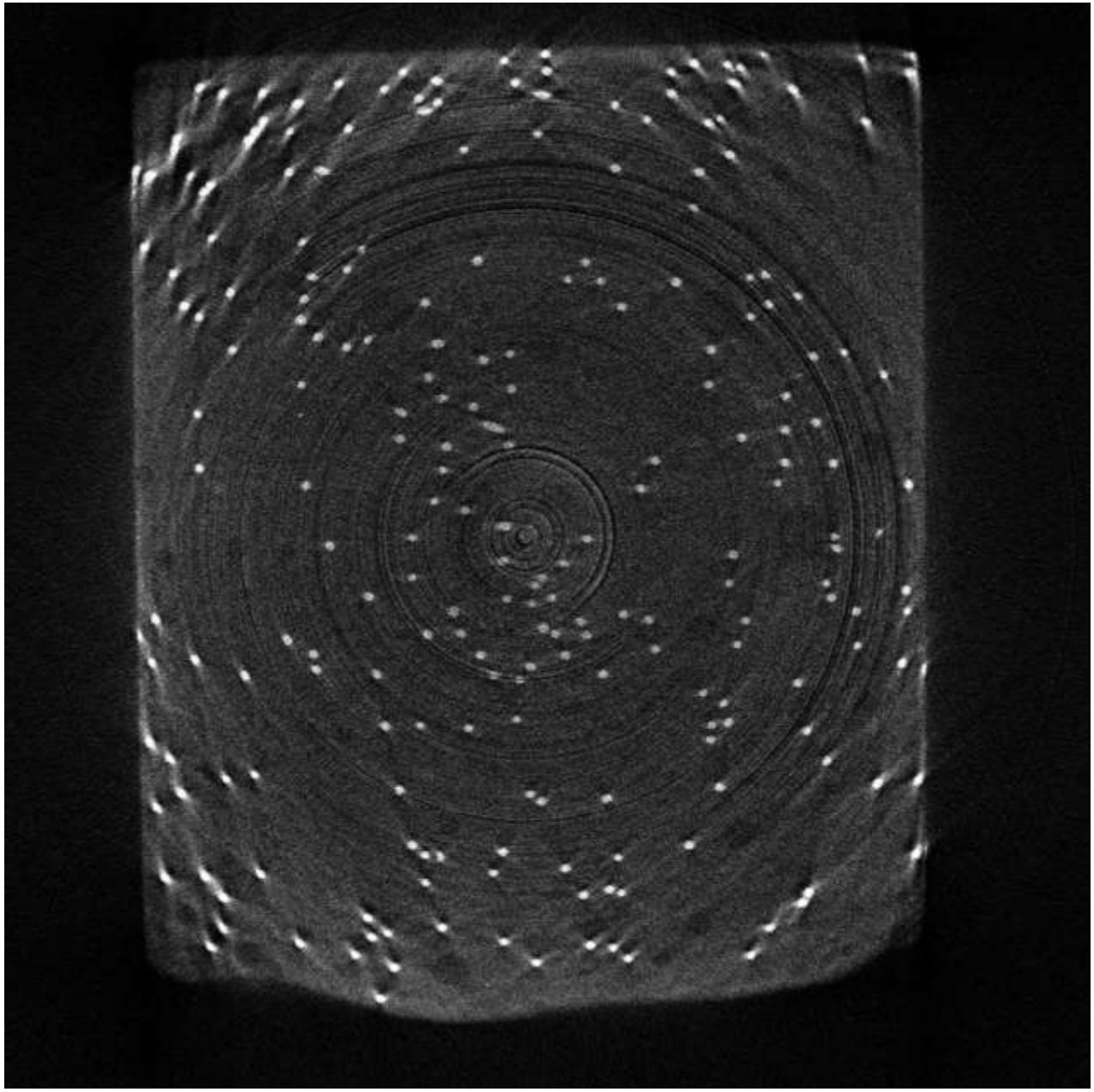


Image courtesy of S. Brisard

- **Smaller sample size used (20 mm x 20 mm)**
- **Scanned volume (approximately 20mm x 20mm x 25 mm)**
- **White light absorption mode with filtered x-rays (E>30keV) using metal filters**
- **11.55 x 2 = 23 µm/pixel resolution**



Fiber isolation

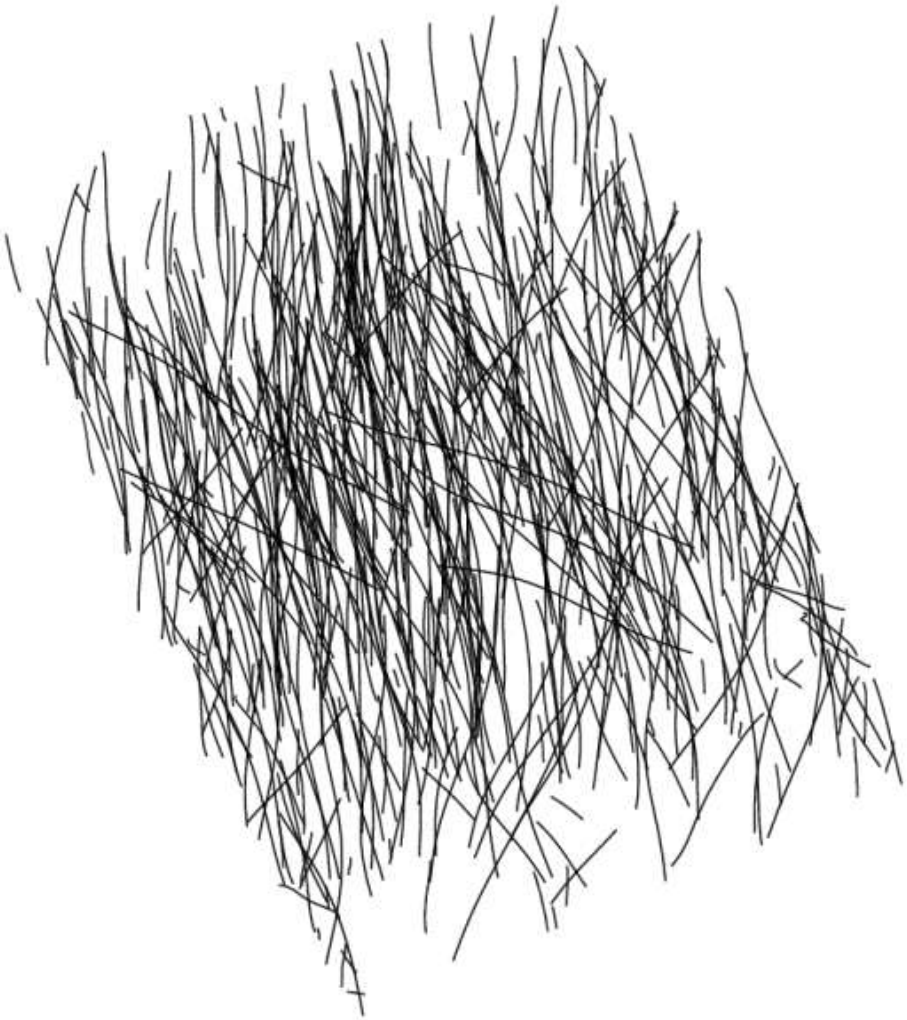


Image courtesy of S. Brisard

Nanotomografia

- **Objetivo: Obter imagens em 3-d com resoluçao superior a 20 nm**

Centros de excelência

- BESSY (soft x-rays)
- APS (hard x-rays)
- Stanford (hard x-rays)
- Berkeley (soft x-rays, under development with the KAUST project)

Desafios

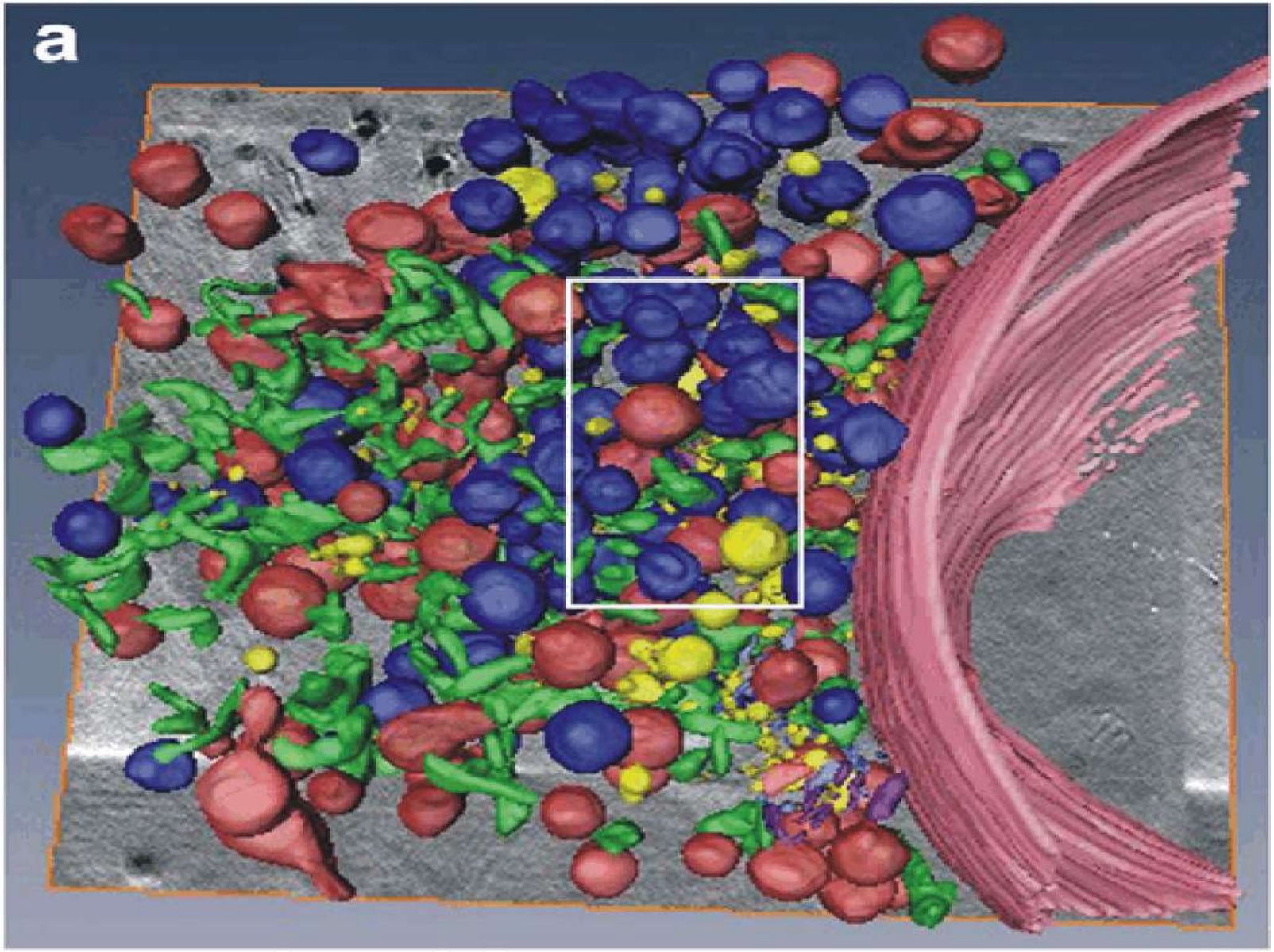
- Alinhamento das imagens
- Estabilidade do sistema
- Tomografia com ângulo limitado

BESSY x-ray

Courtesy from G. Schneider

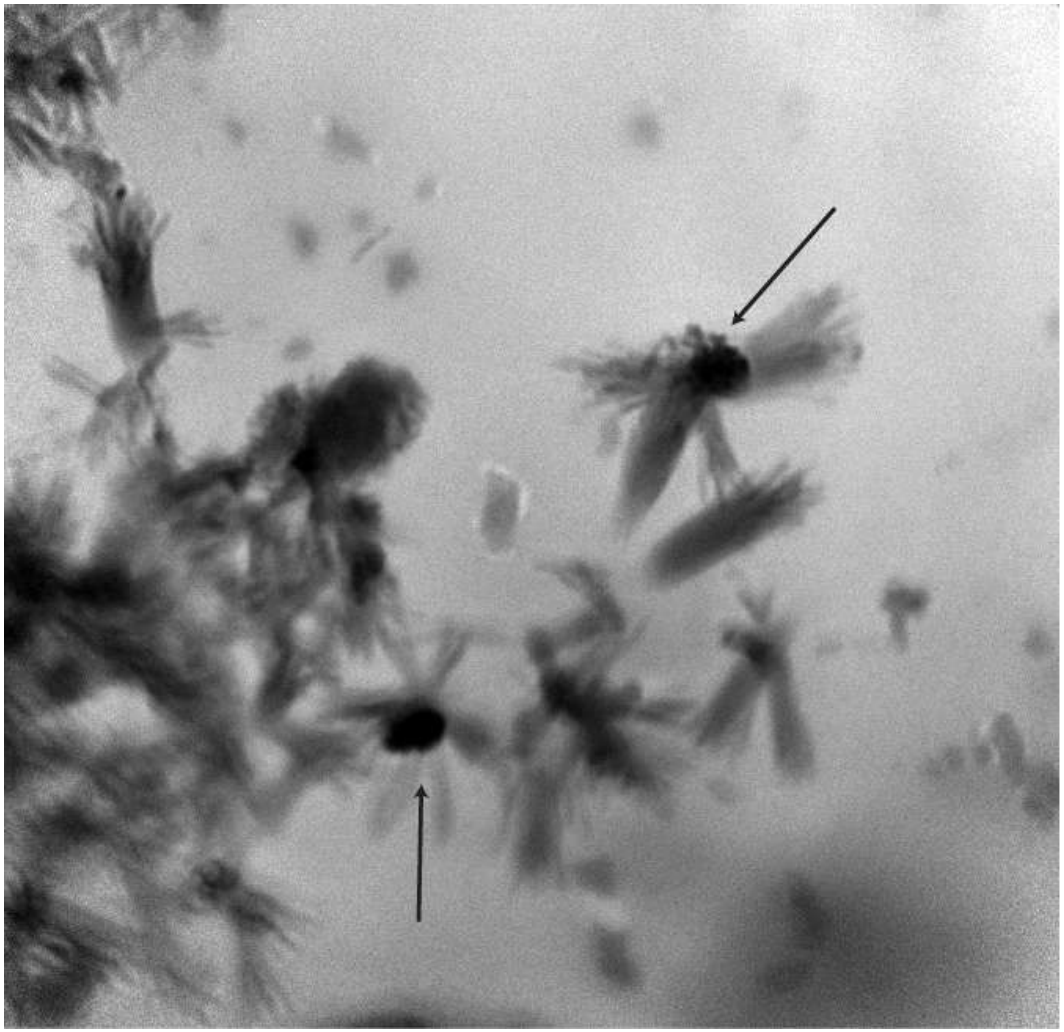
3D structure of mammalian cells

HELMHOLTZ ZENTRUM BERLIN
für Materialien und Energie



Courtesy from G. Schneider

Por que nanotomografia?



Em BESSY, Berlin

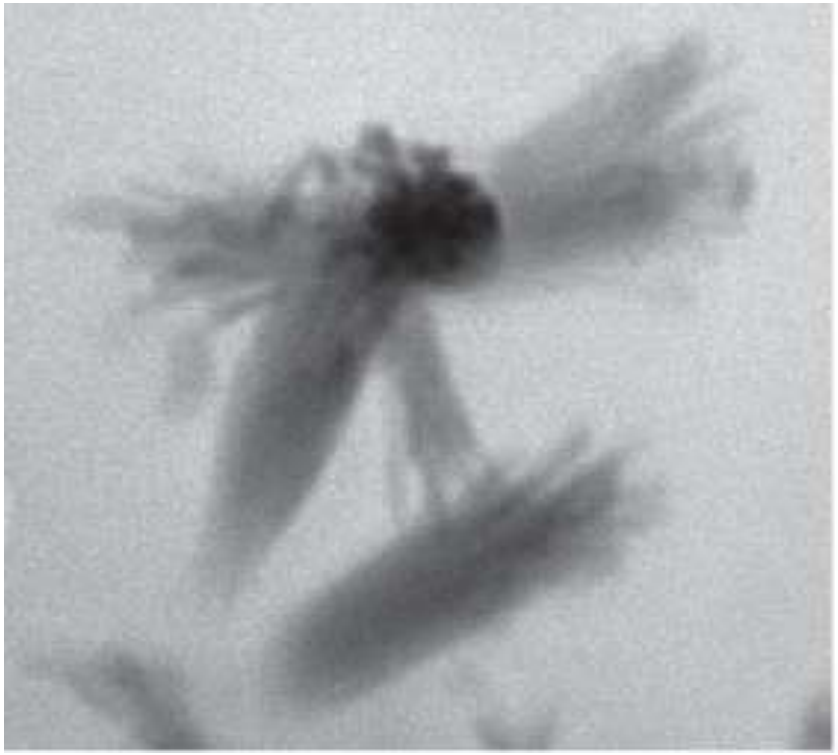
- **This transmission image seems to show that the “sheet of wheat” (or “stars”) have a core which acts as a nucleation point (see arrows)**

Work with Brisard, Levitz and Chae

Teoria incorreta!

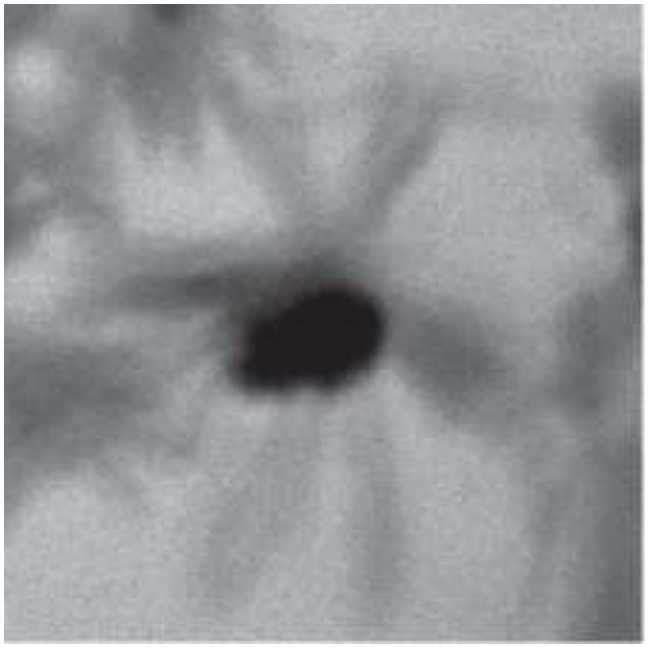
Work with Brisard, Levitz and Chae

Comparação

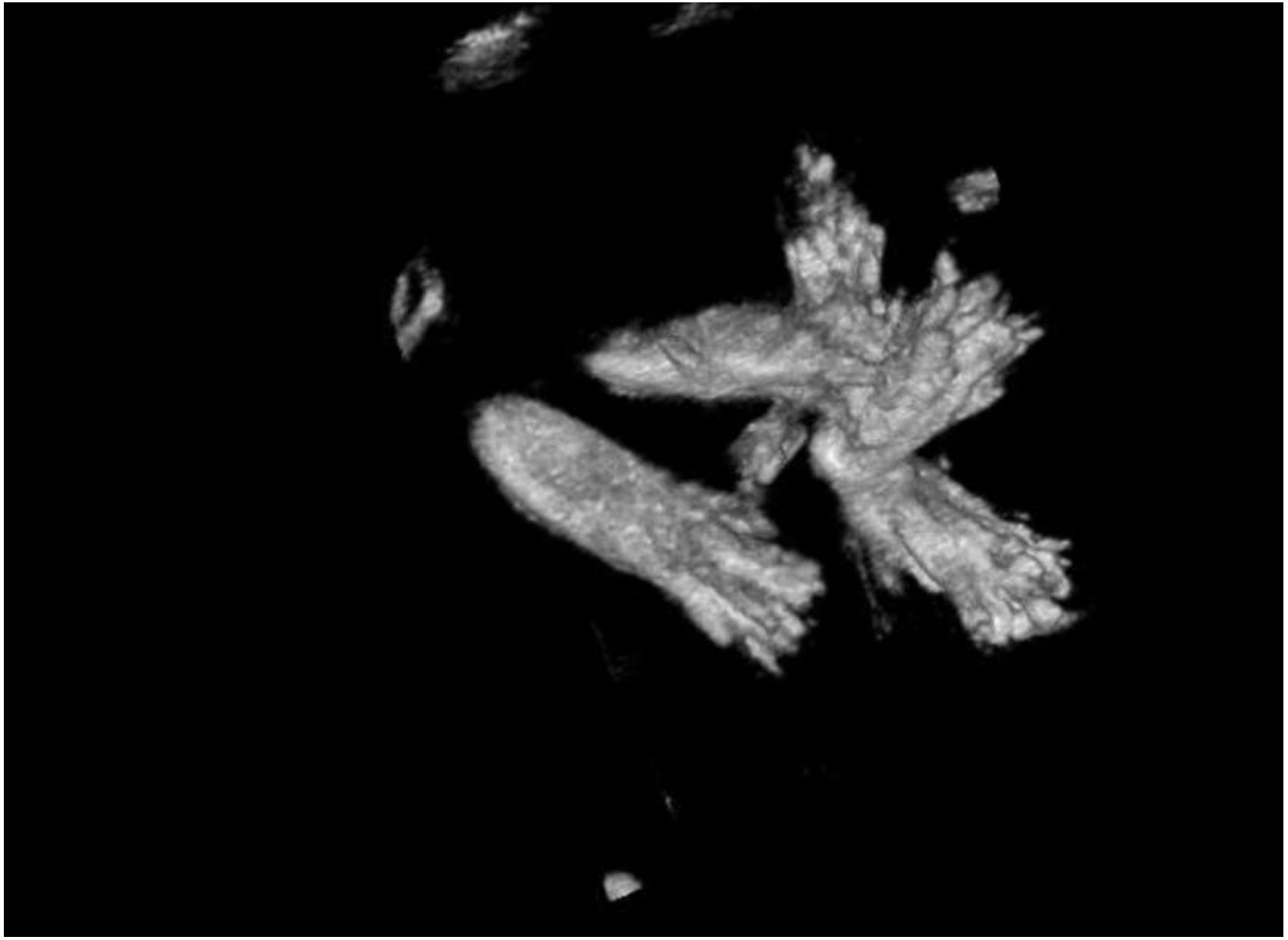


Work with Brisard, Levitz and Chae

Comparação

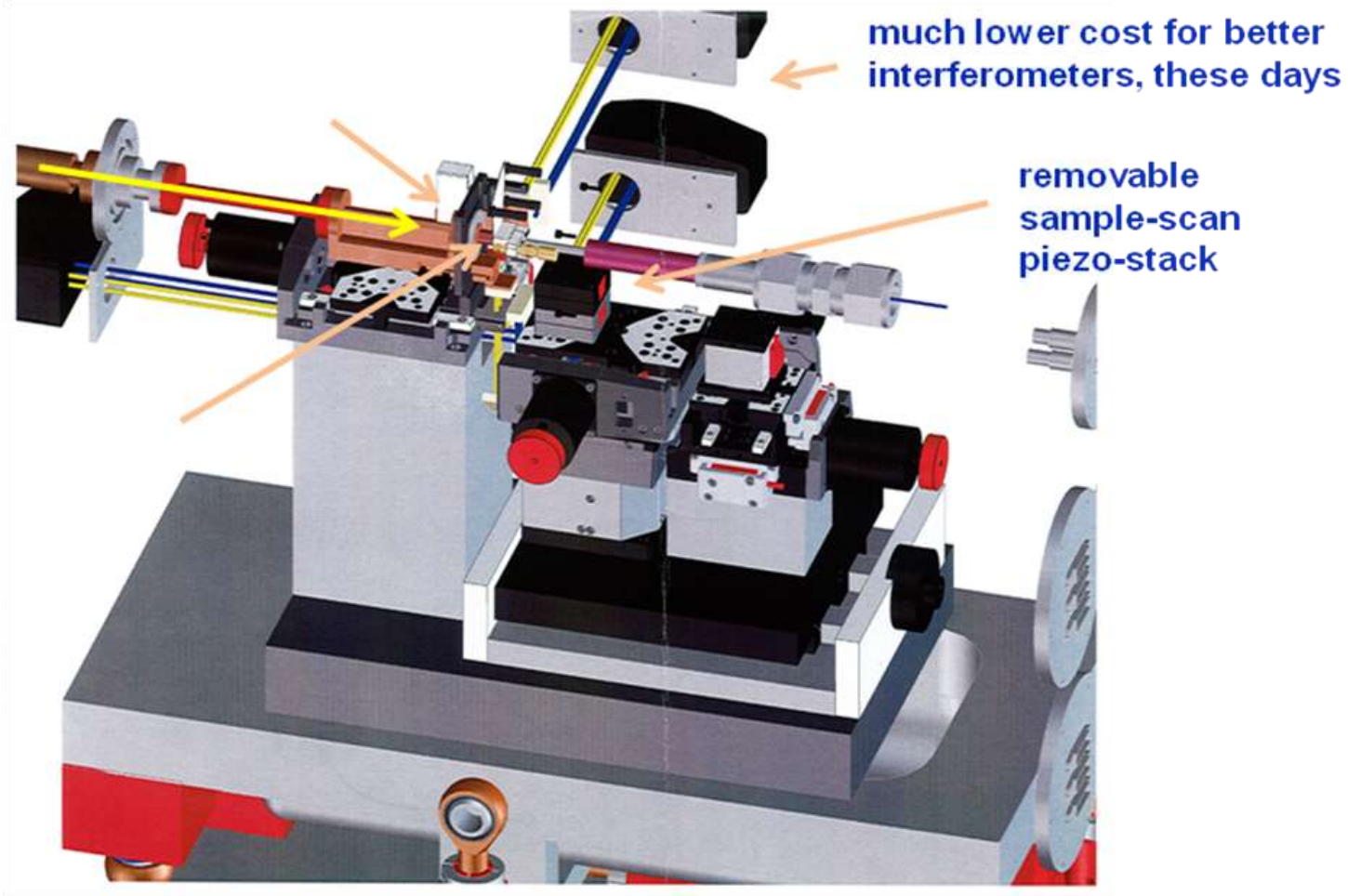


Work with Brisard, Levitz and Chae

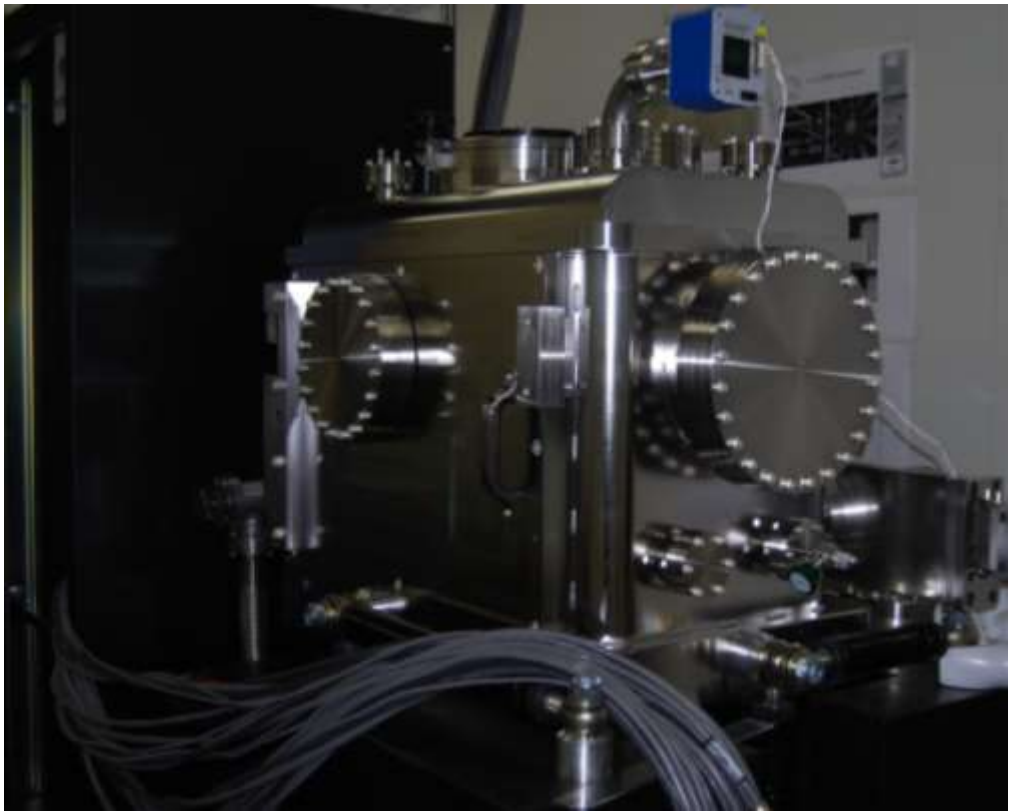


Work with Brisard, Levitz and Chae

Novo Projeto



Quase pronto…

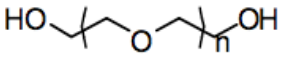
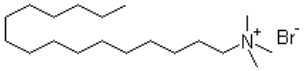


Pesquisas possíveis

- **1) Efeito de adições químicas nos produtos de hidratação:**
  - Plastificantes e superpastificantes
  - Modificadores de viscosidade
- **2) Carbonatação do C-S-H**
- **3) Interação do cloretos com etringita, C-S-H etc.**
- **4) Incorporadores de ar**
- **5) Localização dos sulfatos na DEF**
  -

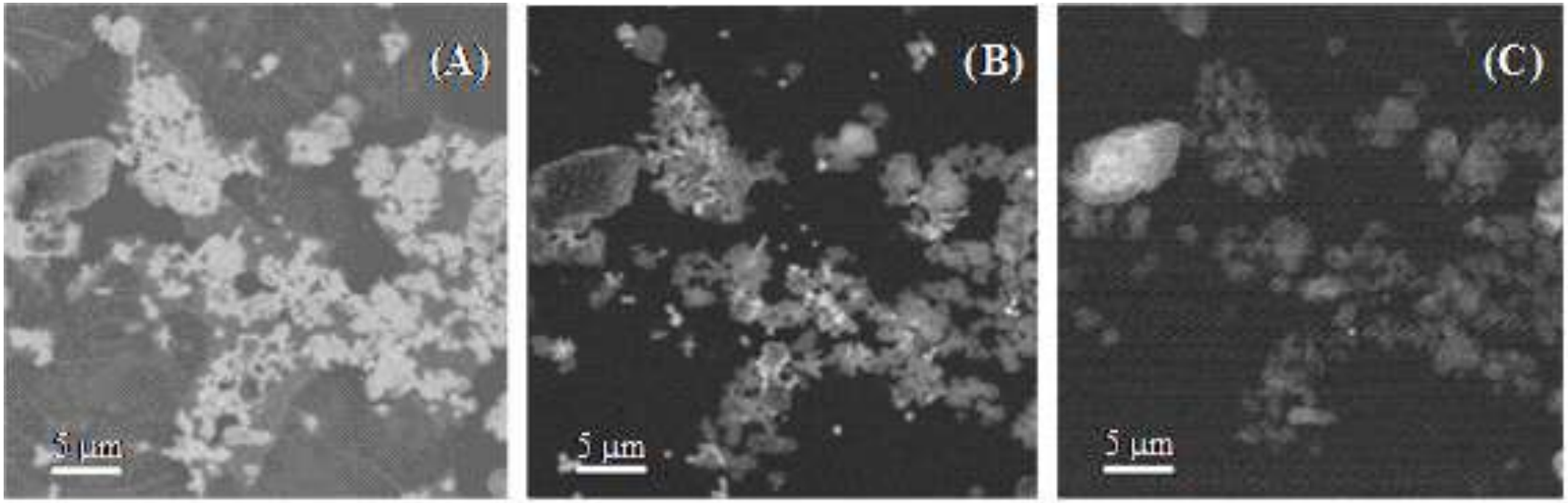
Examplo: Efeitos de Polímeros no CSH

- Hexadecyltrimethylammonium (HDTMA) and polyethylene glycol (PEG200).

Chemical Name	Chemical Formula	Molecular Weight (g/mol)	Structure
Polyethylene glycol (PEG)	$H(OCH_2CH_2)_nOH$	200	
Hexadecyltrimethylammonium, bromide (HDTMA)	$C_{19}H_{42}BrN$	354.46	

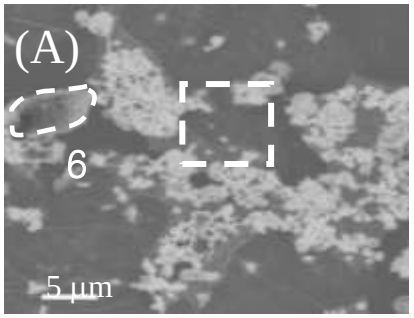
Efeitos de Polimeros no CSH

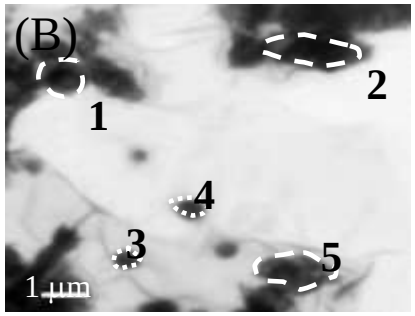
- Resultados: HDTMA-CSH

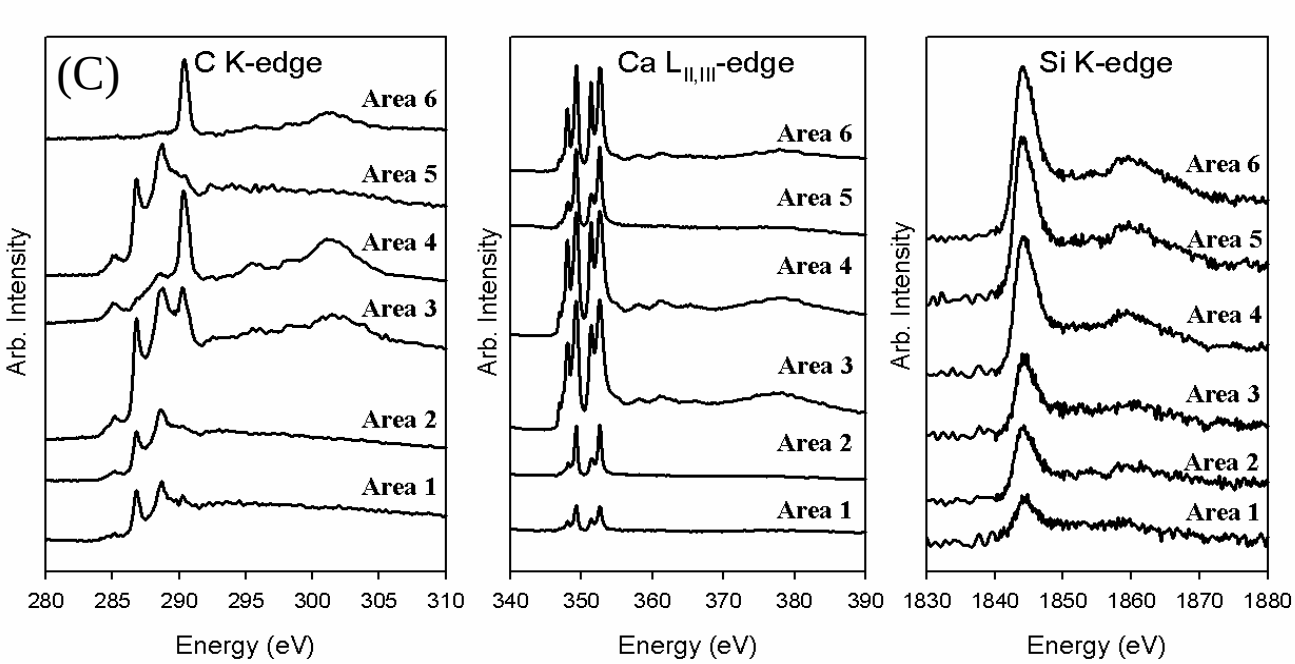


  - STXM images contrast (i.e., image map) of HDTMA-CSH sample taken at (A) C K-edge; (B) Ca LII,III-edge, and (C) Si K-edge.
  - Strong spatial correlation observed for carbon and calcium, confirming HDTMA interaction with CSH
  - HDTMA is likely to be adsorbed to the Ca but less likely to Si, suggesting that HDTMA is likely to be adsorbed to the edges or defect sites of the layer structure of CSH

Results: HDTMA-CSH Samples







- (A) image taken at C K-edge; (B) image of smaller area outlined in (A) magnifying fine structures of HDTMA-CSH sample; and (C) NEXAFS spectra at C K-edge, Ca LII,III-edge, and Si K-edge. Numbers indicate the locations from where the spectra are taken as shown in (A) and (B).
- Difference in carbon and calcium NEXAFS spectra observed
- Spatial heterogeneity observed

Conclusões

As novas técnicas de Microscopia de raios-X, Microscopia a baixas temperaturas, Microtomografia e Nanotomografia permitem um novo entendimento da estrutura do concreto.