High Pressure X-ray Diffraction
Goal

Measure the response of unhydrous and hydrated phases of cement under high pressure.
Why?

• To obtain elastic properties of the small crystals

• To validate atomistic models
How far have we progressed?

- Not too bad.
- As the list of references indicates we have developed a large data basis.
• References (1)


References (2)


References (3)


Diamond Anvil Cell

- Sample in the metal gasket
- X-ray Detector
- X-ray
- Gasket
- 400μm
- 63μm
- 180μm
Experimental Procedures of XRD

- As the pressure increases, the unit cell shrinks.
- Unit cell dimensions \((a, b, c, \alpha, \beta, \gamma)\) at a certain pressure can be calculated from X-ray diffraction pattern.
- \(P(V/V_0)\) can be obtained.
- Bulk modulus \(K_T = -V \frac{dP}{dV}\).

Figure. X-ray diffraction Pattern in beamline 12.2.2 (tobermorite)
Birch Murnaghan Equation of State

- Equation of State (EOS): $V = f(P, T)$
- EOS of condensed material
  - Volume vs. Hydrostatic Pressure
  - Isothermal Equation

**3rd order Birch Murnaghan EOS**

$$P = \frac{3}{2} K_o \left[ (V / V_o)^{\frac{7}{3}} - (V / V_o)^{\frac{5}{3}} \right] \left[ 1 + \frac{3}{4} (K'_o - 4) \left( (V / V_o)^{\frac{2}{3}} - 1 \right) \right]$$

where,

1. $K_o$=bulk modulus at zero pressure
2. $K'_o$=the derivative of bulk modulus at zero pressure
Experimental results

![Bar graph showing bulk modulus (GPa) for various materials: Monocarboaluminate, tobermorite 14A, C-S-H(I), Portlandite, Ettringite, Strätlingite, and Hemicarboaluminate.](image)
## Tobermorite 14Å

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<td>Al-Ostaz et al. (2010)</td>
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Results

From CELREF:
$K_0 = 47 \pm 3$ GPa
($K_0'=4.0$, assumed), $R^2 = 0.995$

From Rietveld Method:
$K_0 = 47 \pm 4$ GPa
($K_0'=4.0$, assumed), $R^2 = 0.991$

How does it compare to CSH(I)?

AFM Phases

- Strätlingite
- Hemicarboaluminate
- Monocarboaluminate
Calcium Hydroxide  

Monocarboaluminate
Strätlingite

- $\text{Ca}_2\text{Al}_2\text{SiO}_7 \cdot 8\text{H}_2\text{O}$
- slag-containing Portland cements or blended cements and in commercial high alumina cement
- trigonal, $\text{R}_3$ or $\text{R}3$
  - Principal layer: $[\text{Ca}_2\text{Al(OH)}_6]$  
  - Interlayer: $[\text{AlSi(OH)}_8 \cdot \text{H}_2\text{O}]^-$
Results – AFm phases

- Strätlingite, C2ASH8
- Irreversibly transform to an amorphous phase at 3.4 GPa.
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Hemicarboaluminate
\((\text{Ca}_4\text{Al}_2(\text{CO}_3)_{0.5}(\text{OH})_{13} \cdot 5.5\text{H}_2\text{O})\)

- It occurs in ordinary Portland cement with very low carbonate contents.
- trigonal, Rc or R3c system.
Monocarboaluminate

- With rising carbonate activity, hydroxyl-AFm is replaced first by hemicarboaluminate and then by monocarboaluminate.

Projection along [100] of the monocarboaluminate; (a) general view, and (b) detail of interlayer region. Blue and green polyhedral are, respectively, sevenfold Ca polyhedra and sixfold Al polyhedral. White, grey, red, blue, green, and black spheres represent, respectively, O atoms in principal layers, O atoms in interlayers, C, Ca, Al, and H atoms.
Results – AFm phases

- Monocarboaluminate, C₄ACH₁₁
Results – AFm phases

- **Monocarboaluminate (54 GPa)**
  - low compressibility
- **Hemicarboaluminate (15-32 GPa)**
  - pressure-induced dehydration
First-principles elasticity of monocarboaluminate hydrates: density functional theory

LDA: local-density approximation
GGA: Generalized gradient approximation