Application of total X-ray scattering and pair distribution function analysis to biominerals and environmental materials

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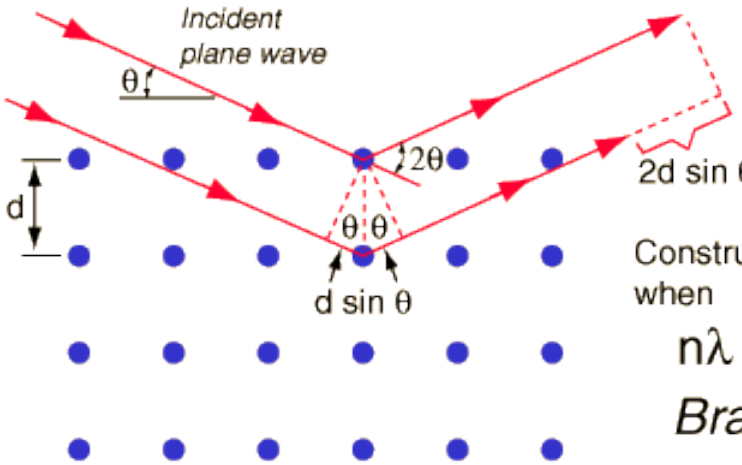
What is total scattering?

Perfect Crystal

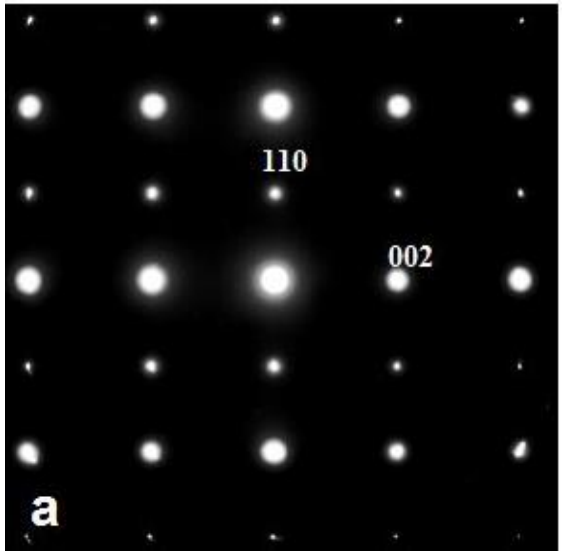


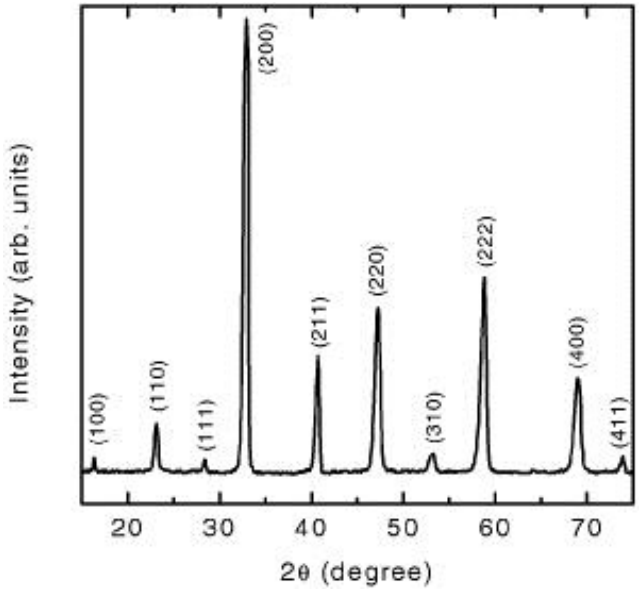
Constructive interference when

$n\lambda = 2d \sin\theta$

Bragg's Law

Periodic array of atoms

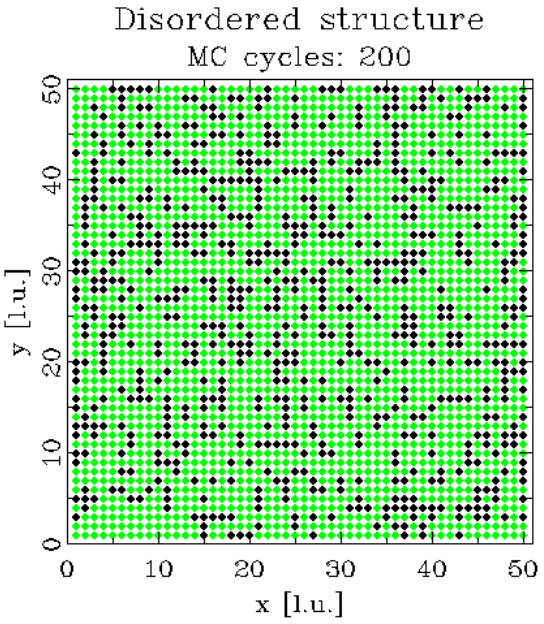


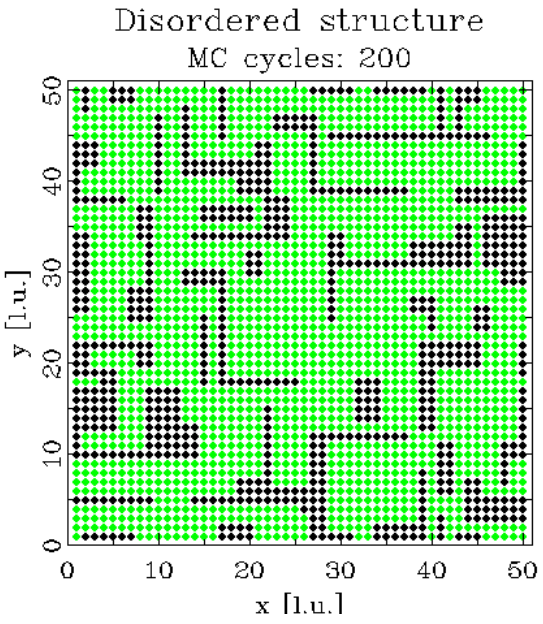


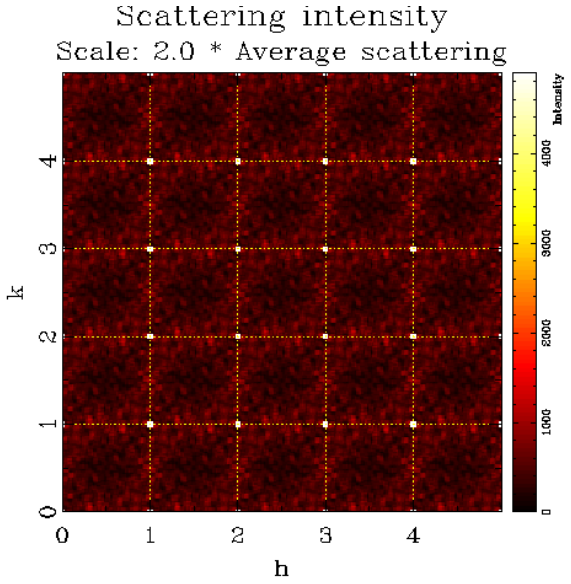
Bragg diffraction gives average long-range order (LRO)

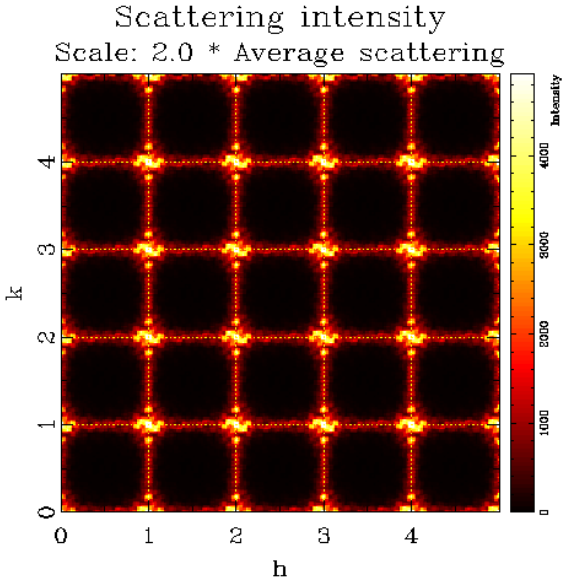
What is total scattering?

Disorder and Diffuse Scattering









Example from Reinhard Neder's crystallography webpage

www.lks.physik.uni-erlangen.de/diffraction

Diffuse scatter gives SRO and MRO

Total scattering =

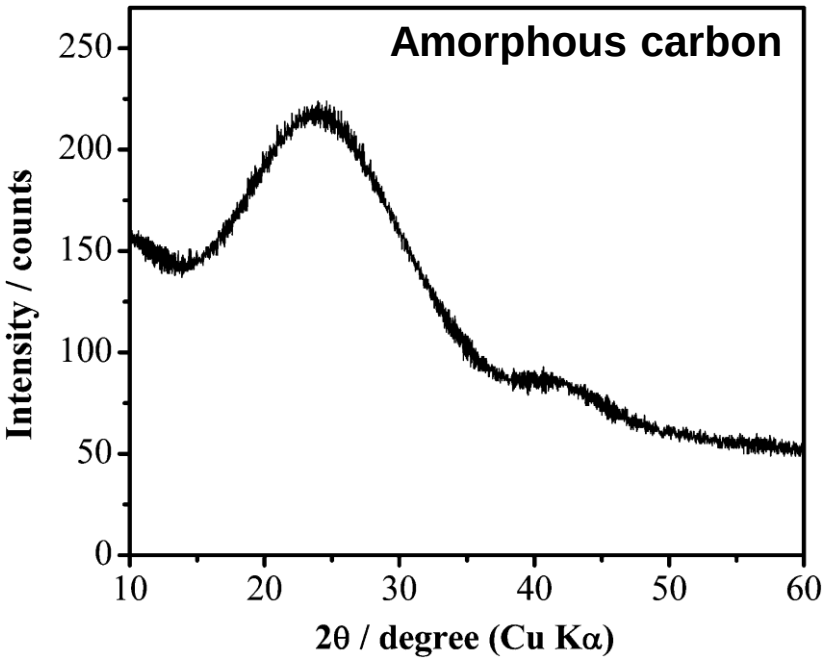
Bragg scattering

+

Diffuse scattering

Provides structure information over a range of length scales

Materials with no long-range order (e.g., glasses, liquids)

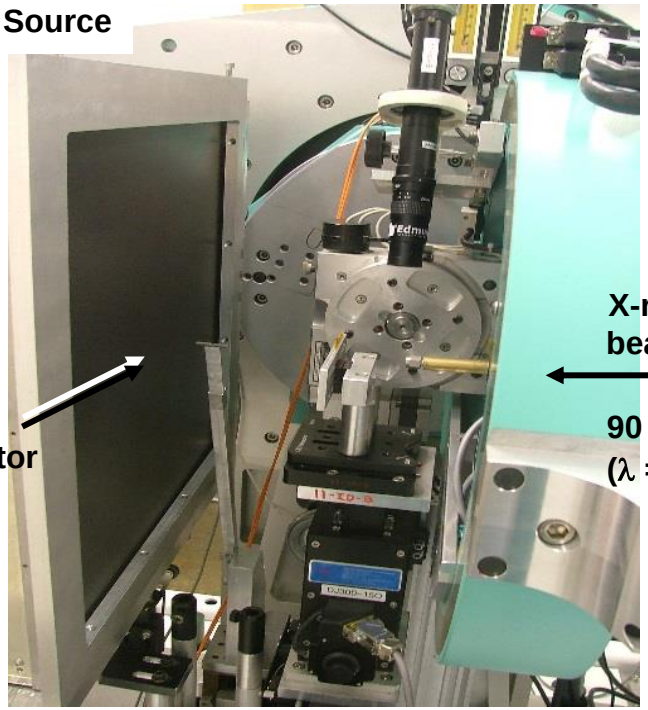


Rajan et al., Energy Environ. Sci. 7, 1110-1116 (2014)

- No Bragg peaks; only broad, diffuse scattering features
- Diffuse intensity is typically orders of magnitude weaker than Bragg intensity
- How do we use total scattering to get SRO and MRO information?

Total X-ray Scattering and the Pair Distribution Function

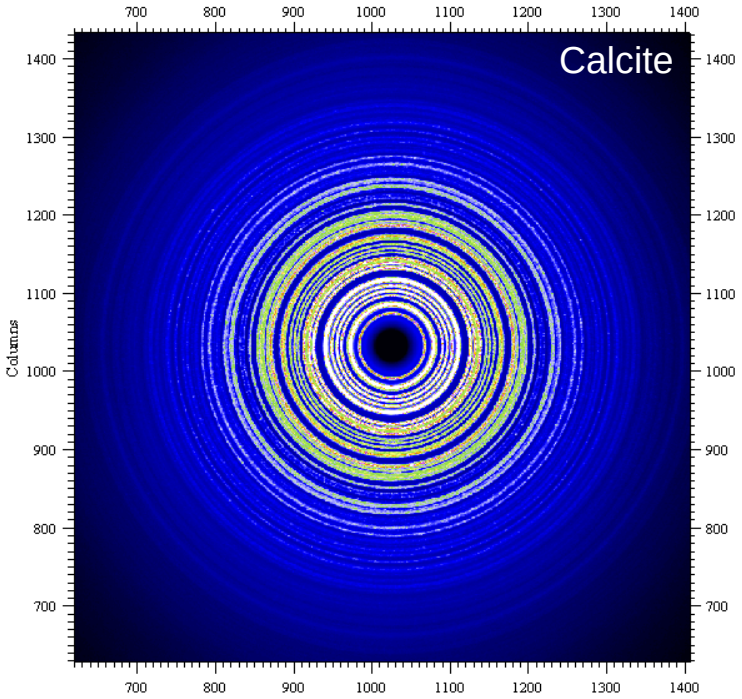
Advanced Photon Source



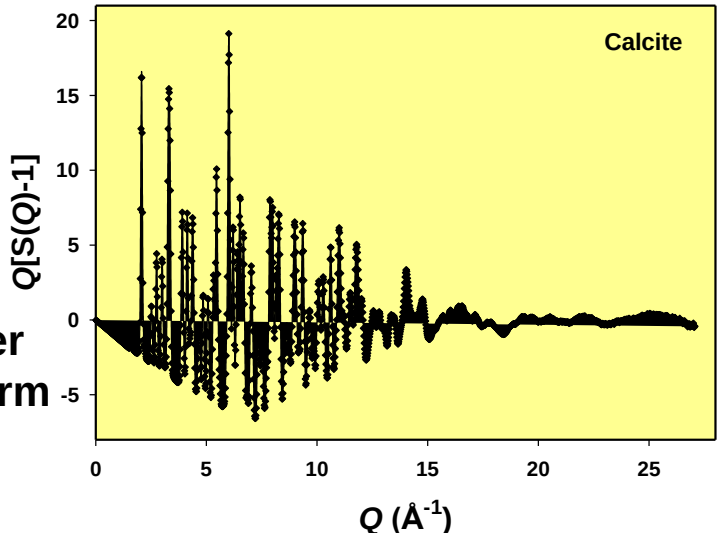
a-silicon area detector

X-ray beam

90 keV
(λ = 0.137 Å)

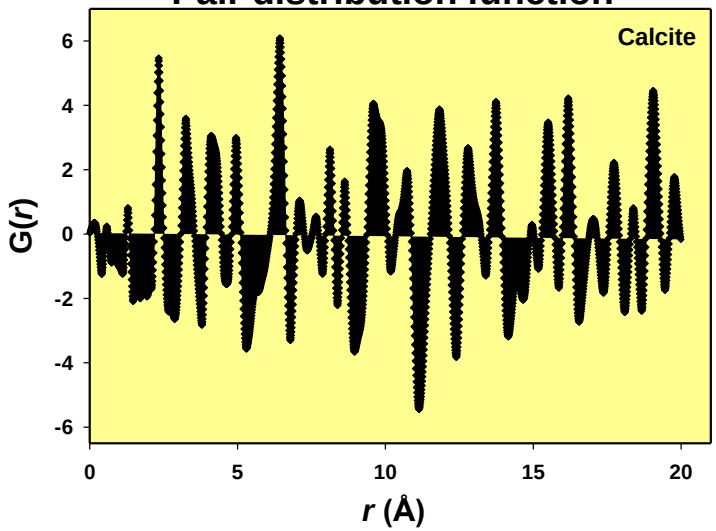


Reduced structure function

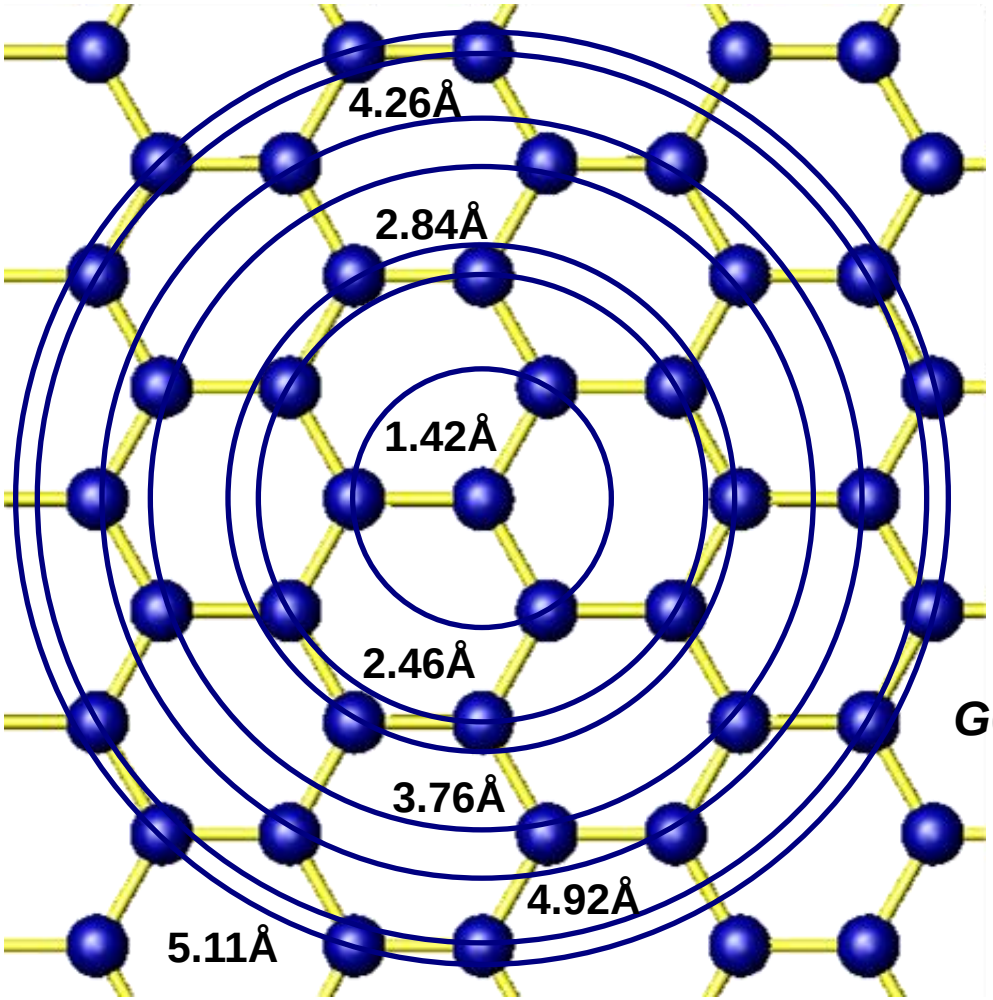


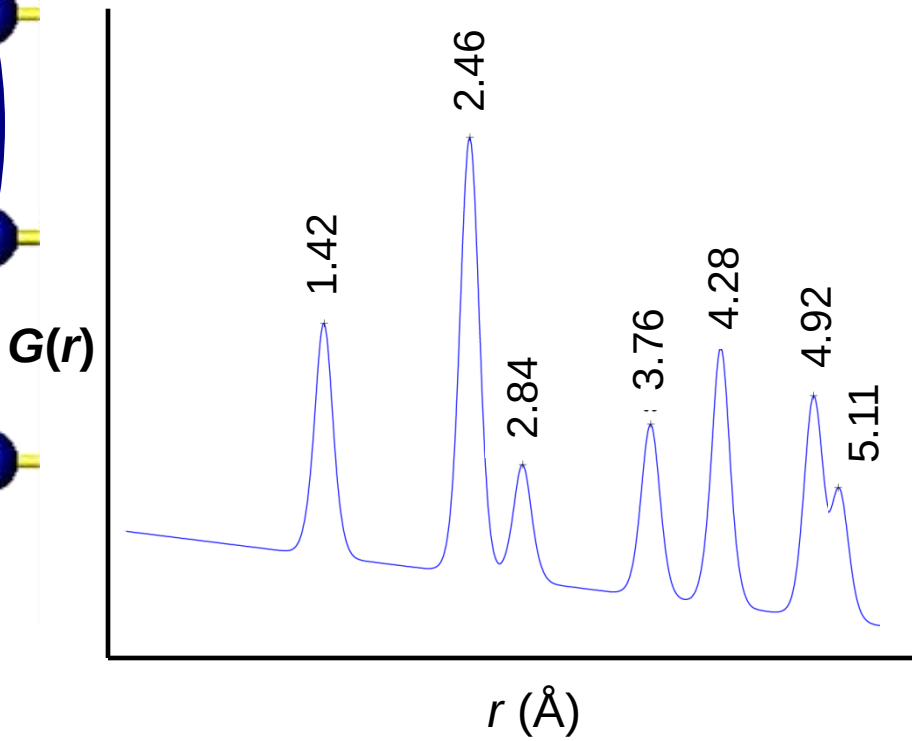
Fourier transform

Pair distribution function



The pair distribution function gives the distribution of interatomic distances, weighted by the scattering power of the atom pair





Adapted from E.S. Bozin

What environmental problems can be studied using total scattering?

Material property:			**Dominant scattering**
			Bragg
Long-range order	➔	Defects in crystals	↕
Limited long-range order	➔	Nanocrystals	↕
No long-range order (SRO, MRO)	➔	Amorphous solids Liquids	↕
			Diffuse

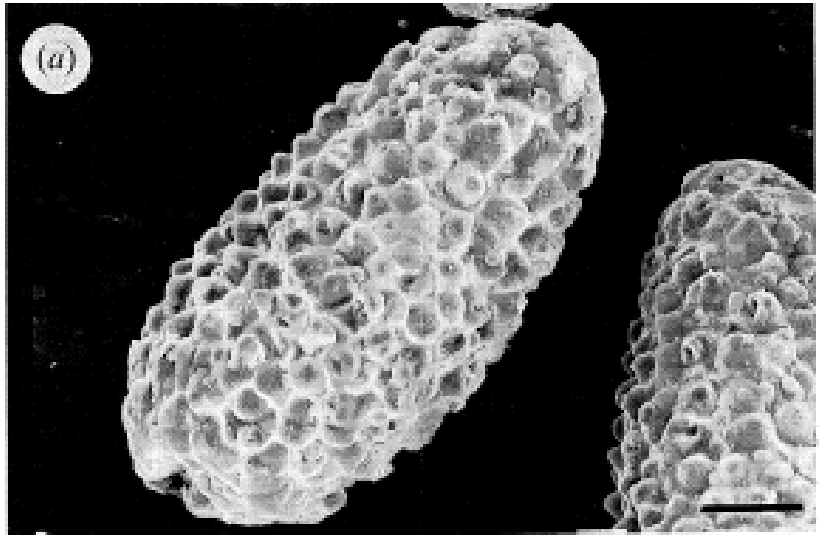
What environmental problems can be studied using total scattering?

Material property:			**Dominant scattering**
			Bragg
Long-range order	➔	Defects in crystals	
Limited long-range order	➔	Nanocrystals	
No long-range order (SRO, MRO)	➔	Amorphous solids Liquids	Diffuse

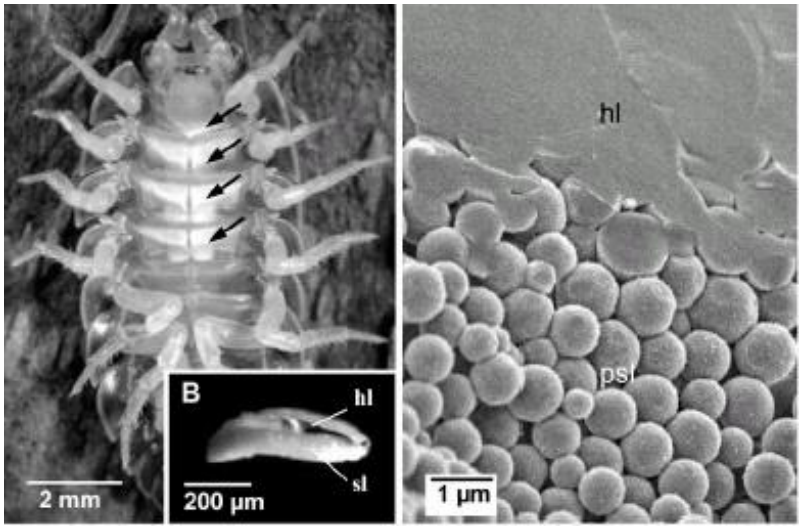
Examples:

1. Amorphous calcium carbonate and biomineralization
2. Cr(III) substitution in ferrihydrite – structural changes
3. Structure of arsenate sorption complexes on alumina and ferrihydrite

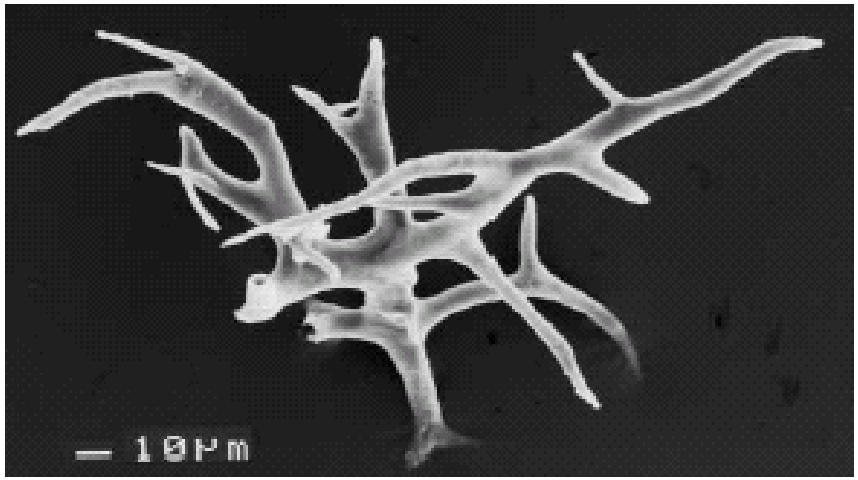
Biomineralization via Amorphous Calcium Carbonate (ACC)



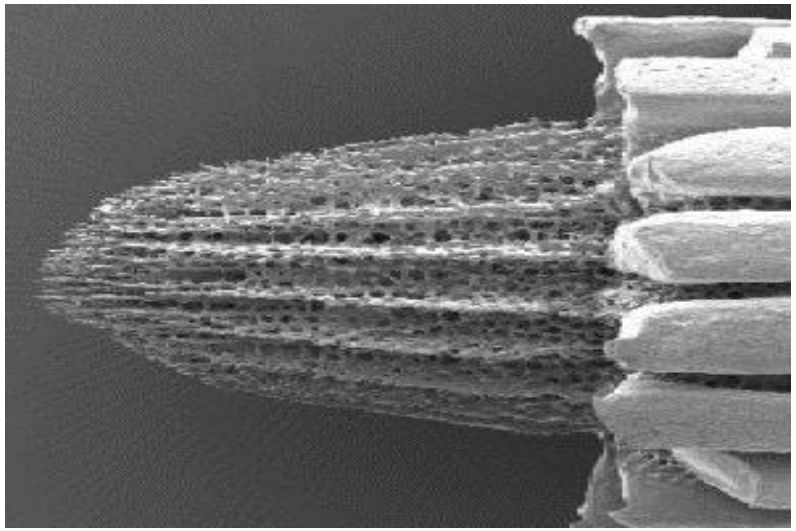
Plant cystoliths (Taylor et al., Proc. Roy Soc Lond B, 252, 75, 1993)



Woodlice (Becker et al., Dalton Trans, 2003, 551)



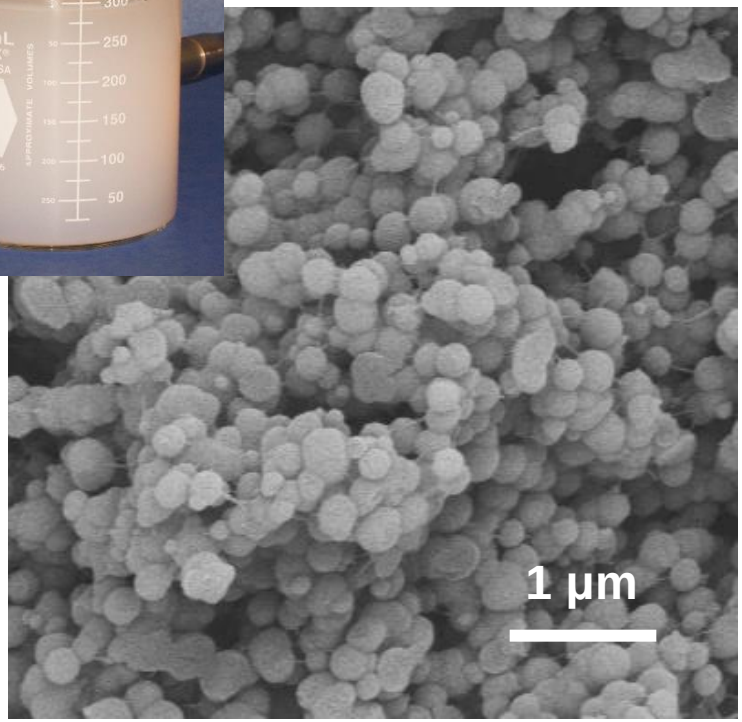
Ascidian (Levi-Kalisman et al., Dalton Trans, 2000, 3977)

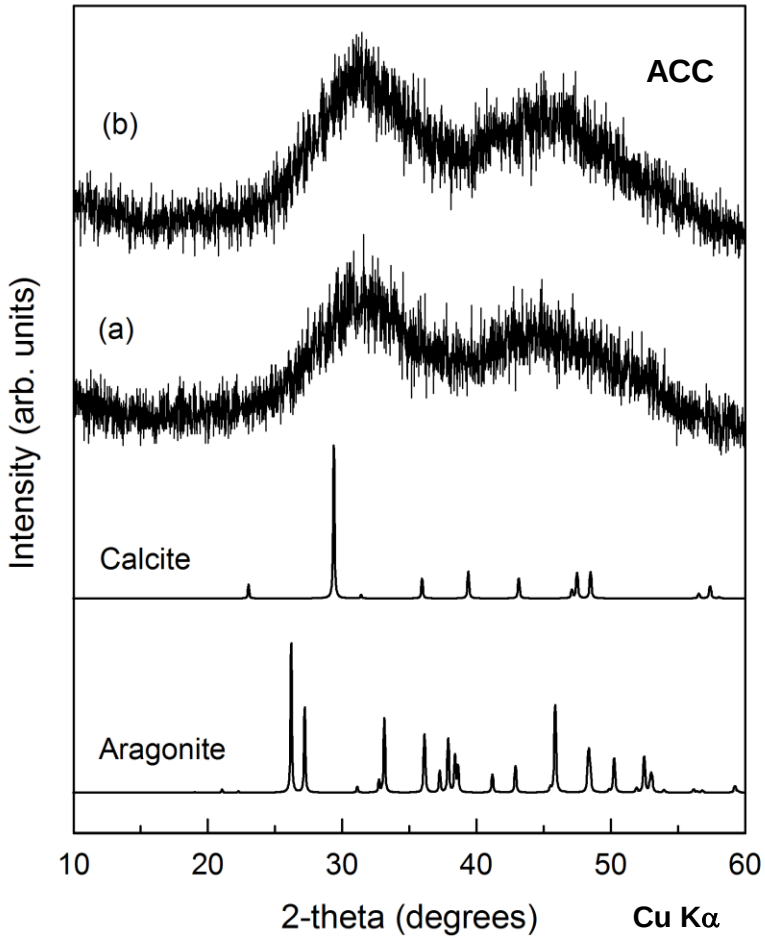


Echinoderm spine (Politi, Weiner; http://wis-wander.weizmann.ac.il/site/en/weizman)

Calcium carbonate is an unlikely noncrystalline solid

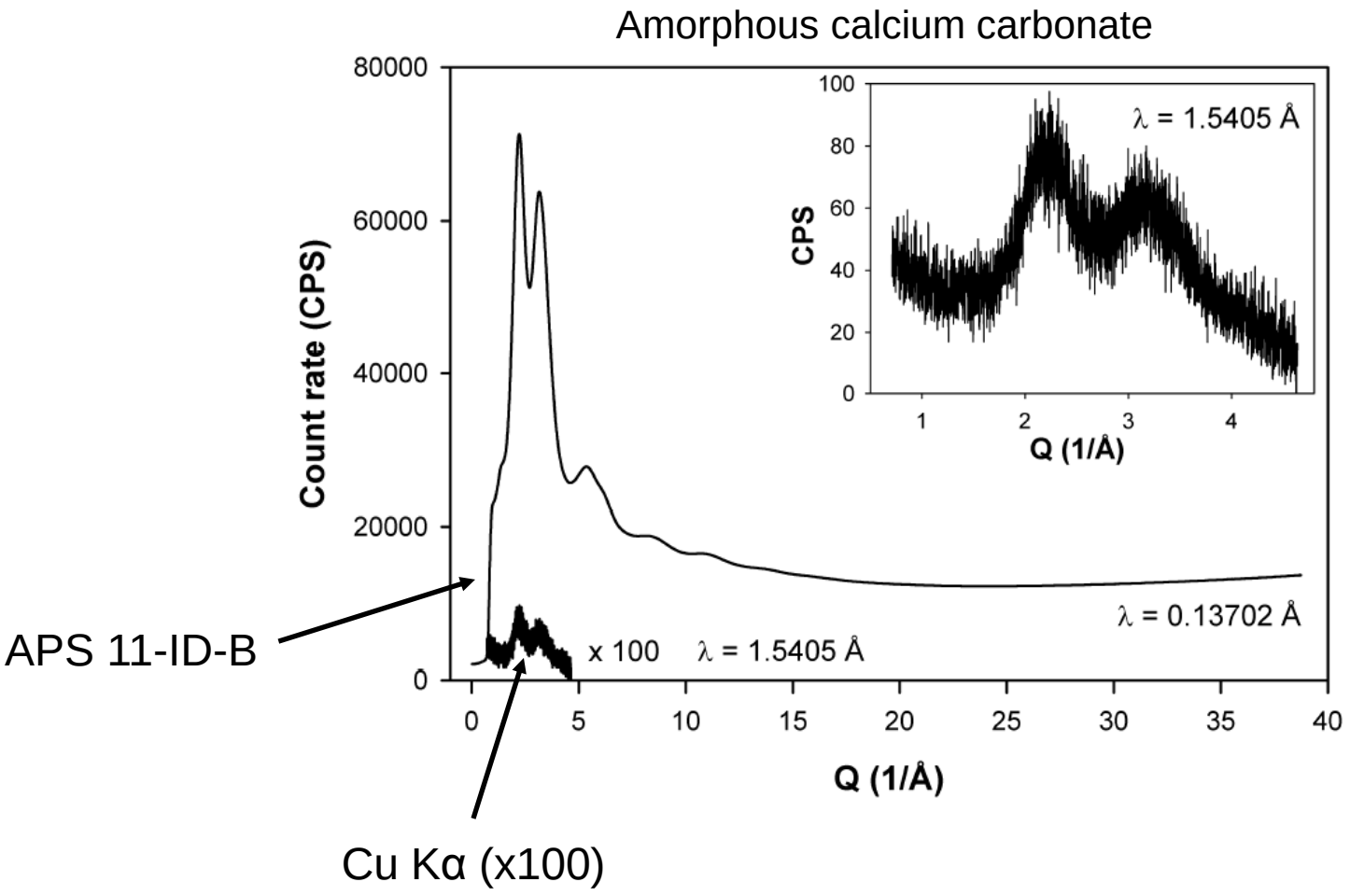
- CO_3 not an effective glass former
- ACC is kinetically stabilized
  - High supersaturation
  - Rapid precipitation





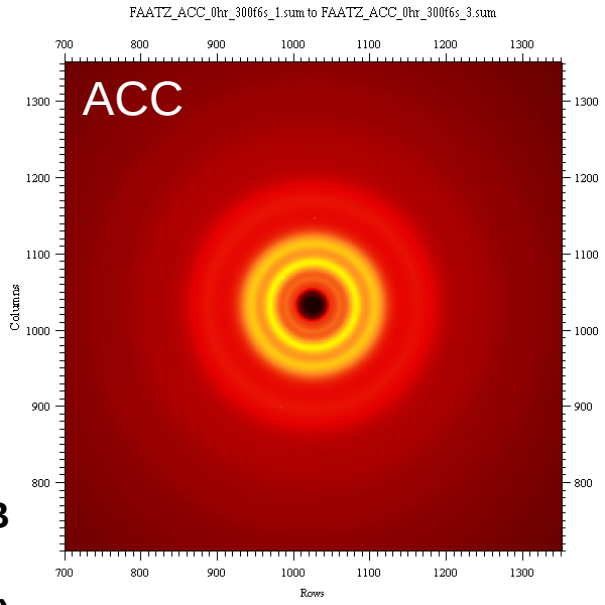
Synthetic ACC is hydrated: $CaCO_3 \cdot H_2O$

Why we want a synchrotron X-ray source for PDF

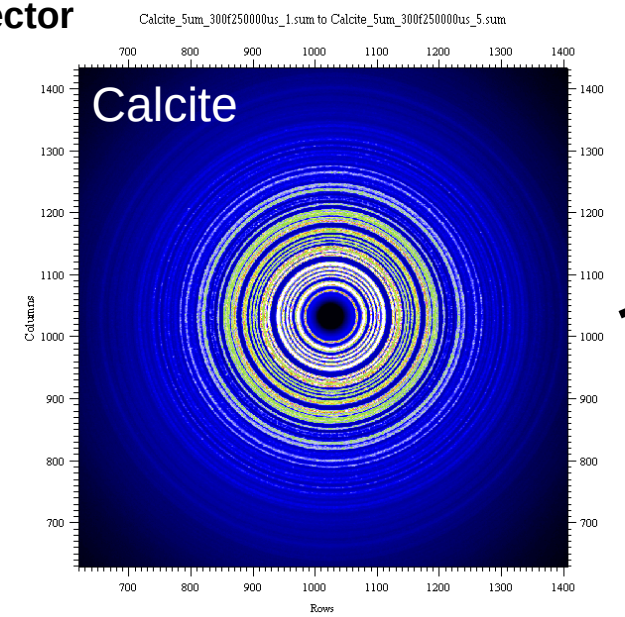


Complete scattering spectrum collected in a few seconds to a few minutes

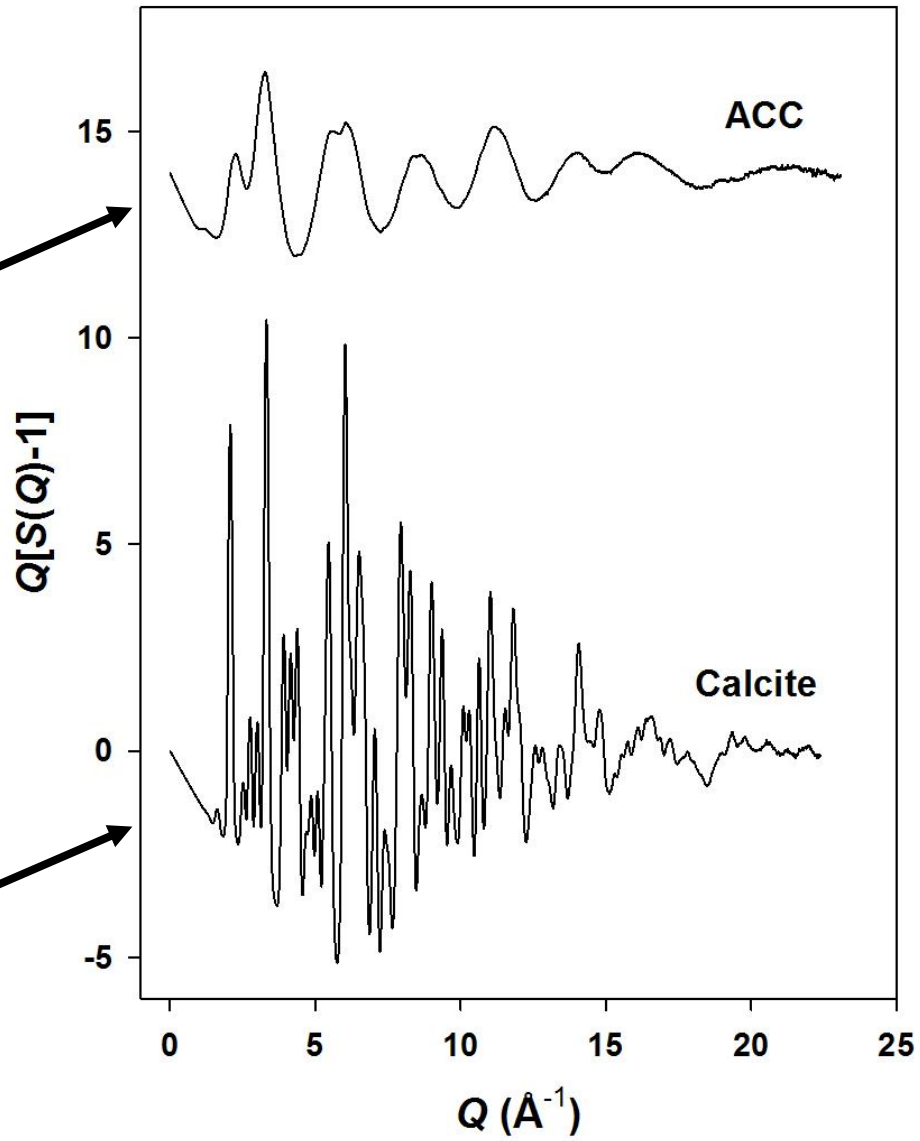
Total X-ray scattering and PDF analysis of ACC



APS 11-ID-B
~90 keV
(λ = 0.137 Å)
a-Si area detector



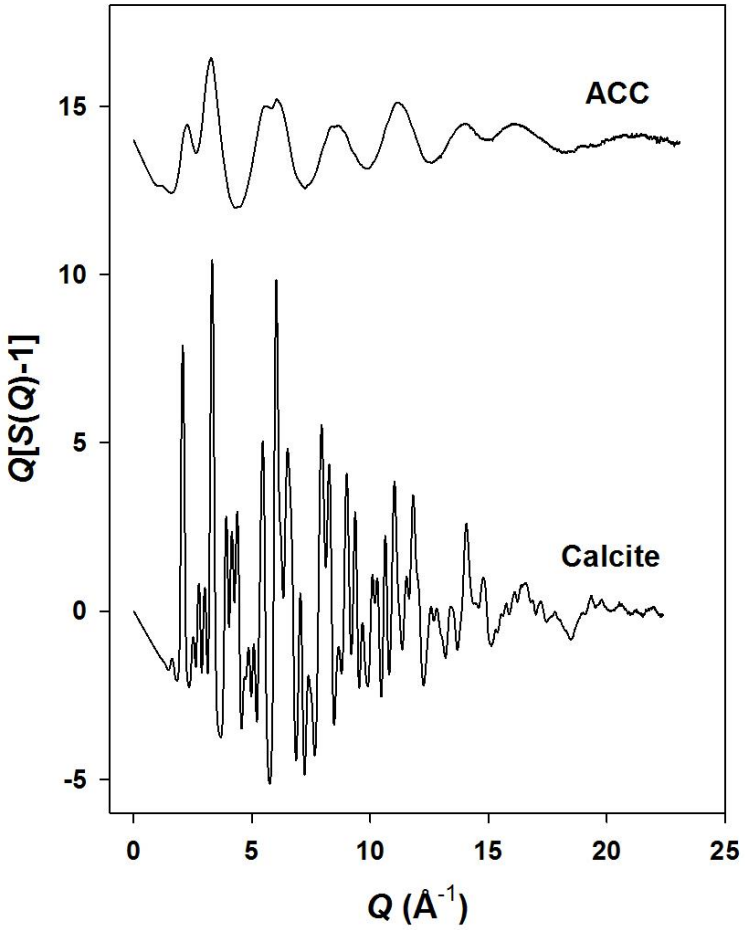
Reduced structure function



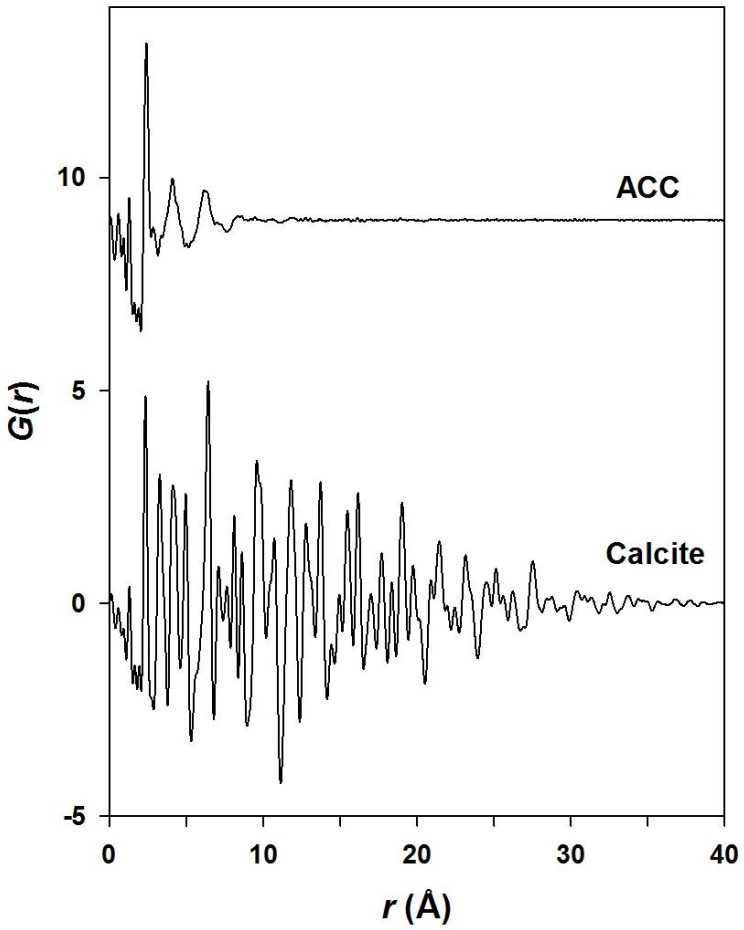
Michel et al., *Chem. Mater.*, 20, 4720 (2008)

Total X-ray scattering and PDF analysis of ACC

Reduced structure function

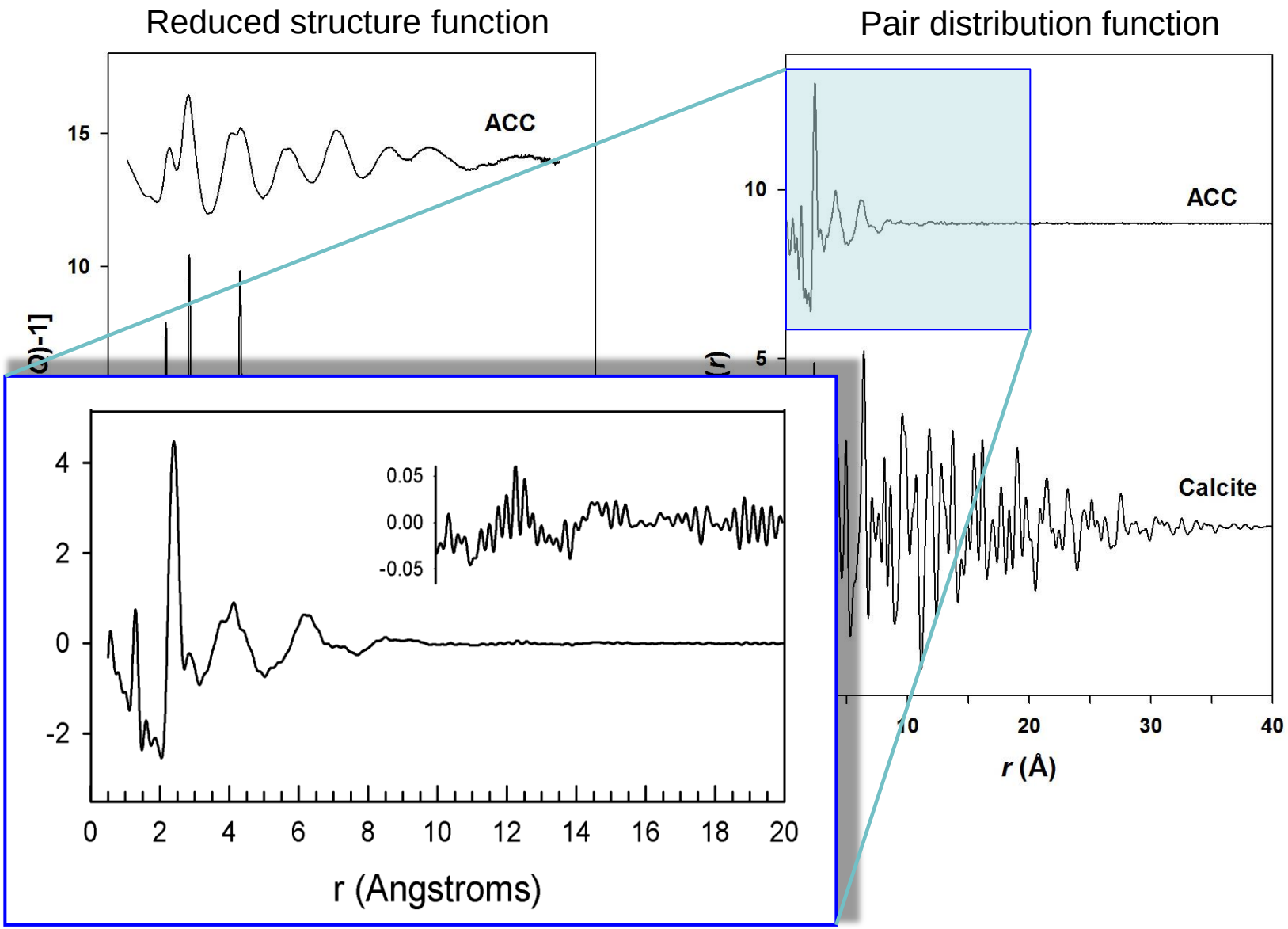


Pair distribution function



Michel et al., *Chem. Mater.*, 20, 4720 (2008)

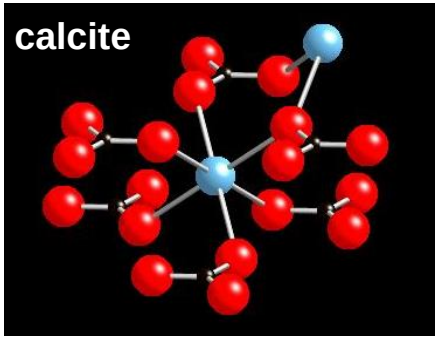
Total X-ray scattering and PDF analysis of ACC

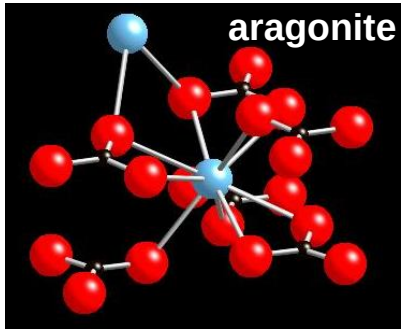


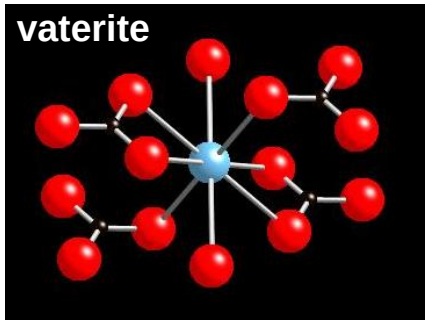
Michel et al., *Chem. Mater.*, 20, 4720 (2008)

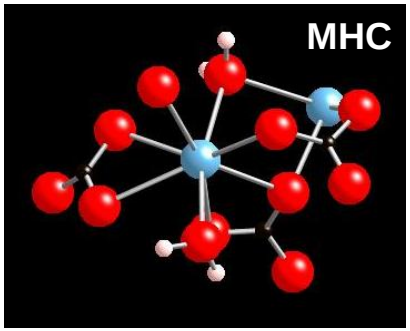
What about the structure of the ACC phase?

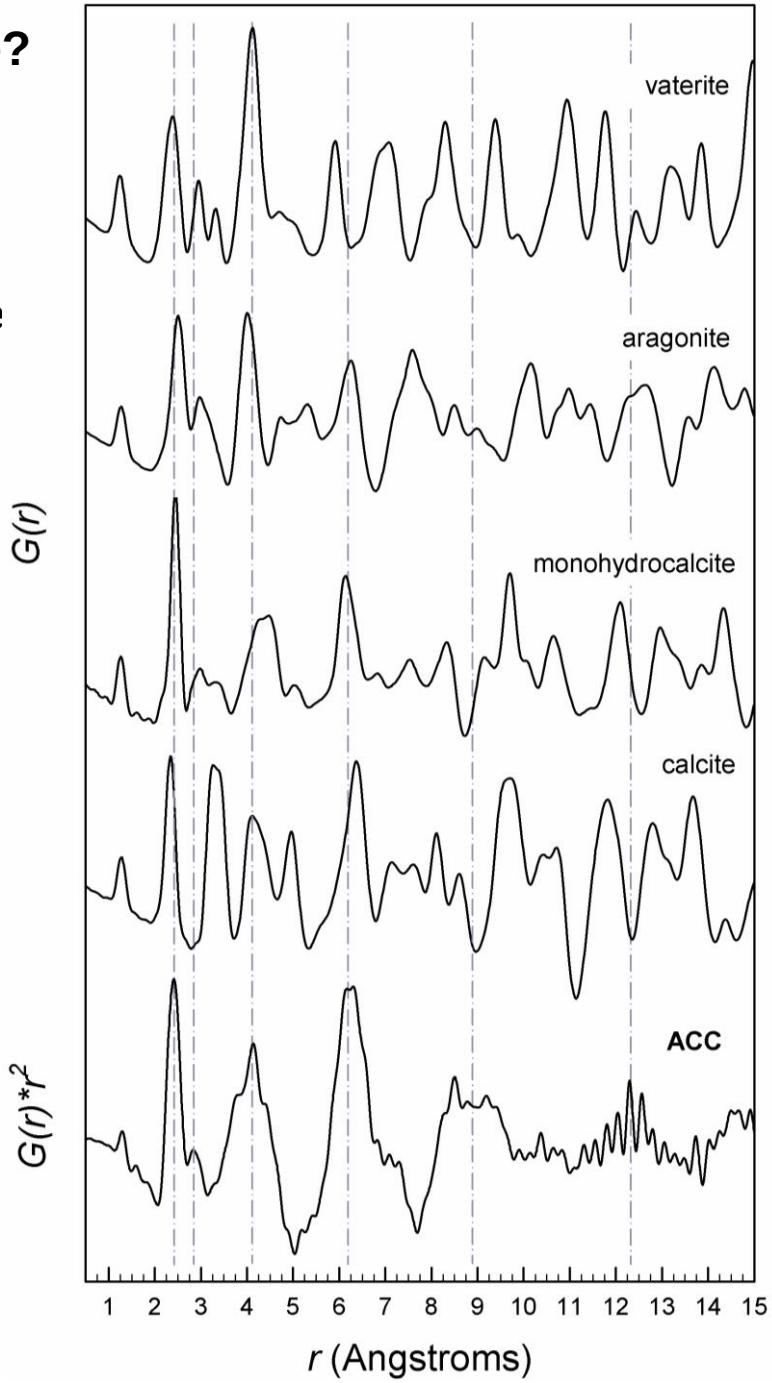
- PDF for ACC distinct from crystalline polymorphs
- Low-r peaks can be assigned from basic knowledge
- Challenge is to derive 3-D structure model from 1-D representation





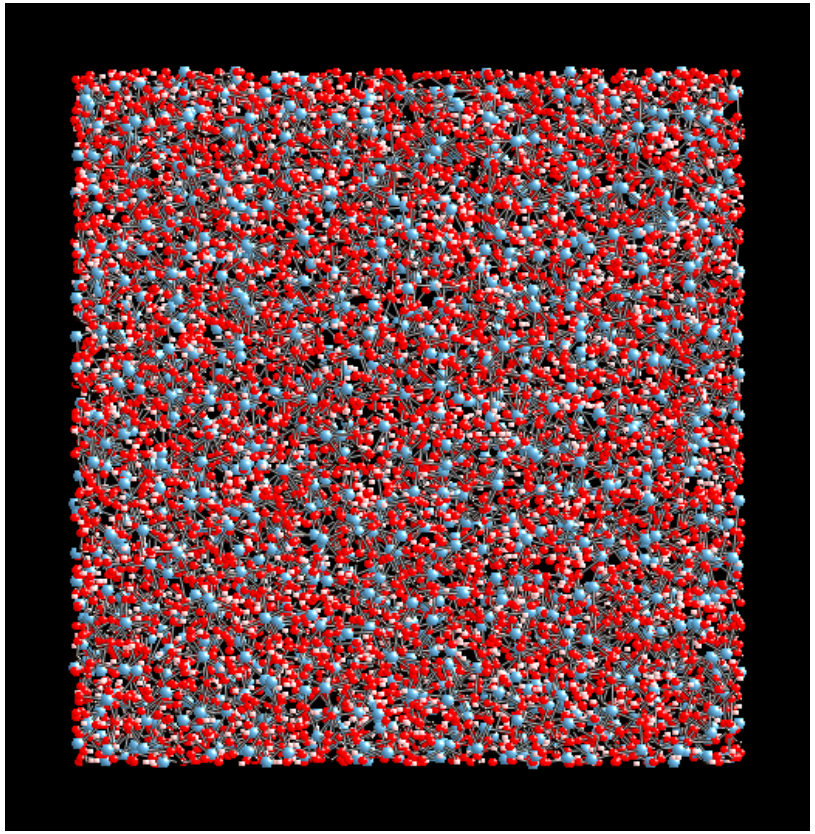


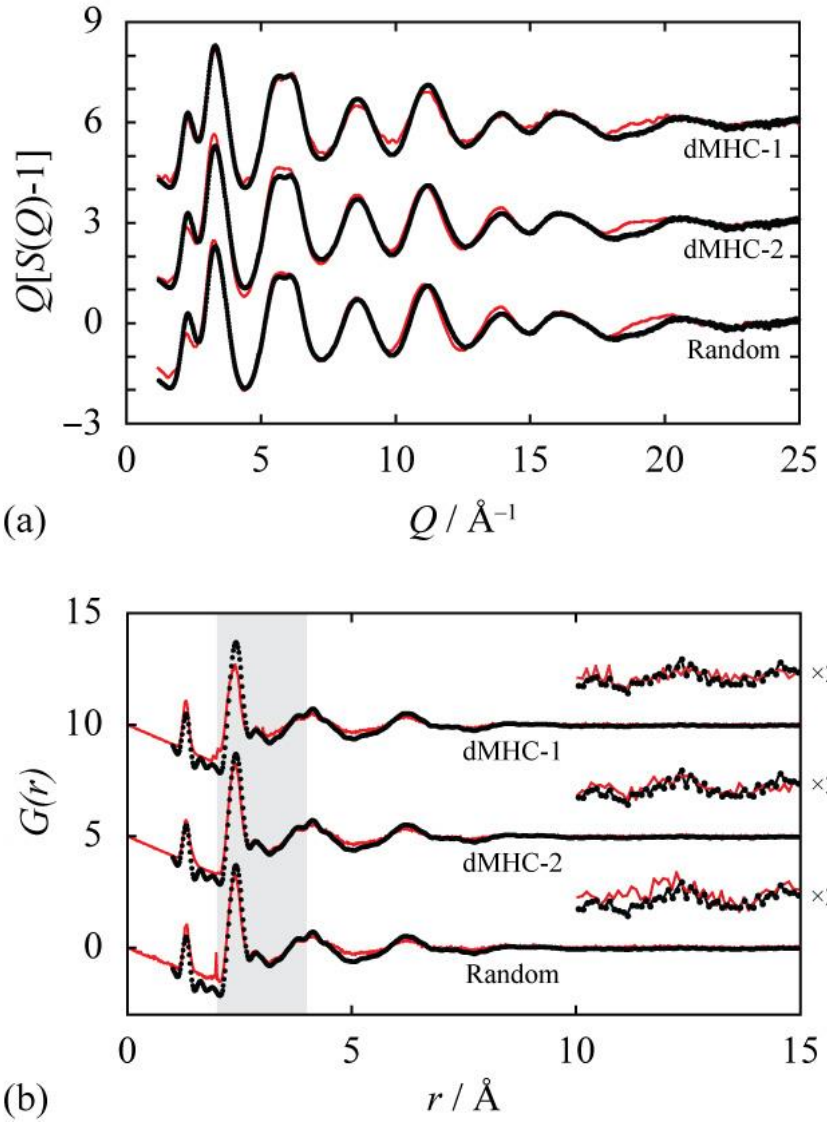




Reverse Monte Carlo Refinement

- RMCProfile (Tucker et al.)
- Random initial models (~10,000 atoms)
- Random movements that improve fit to *Q*[S(Q)-1] are statistically favored
- Restraints based on known coordination

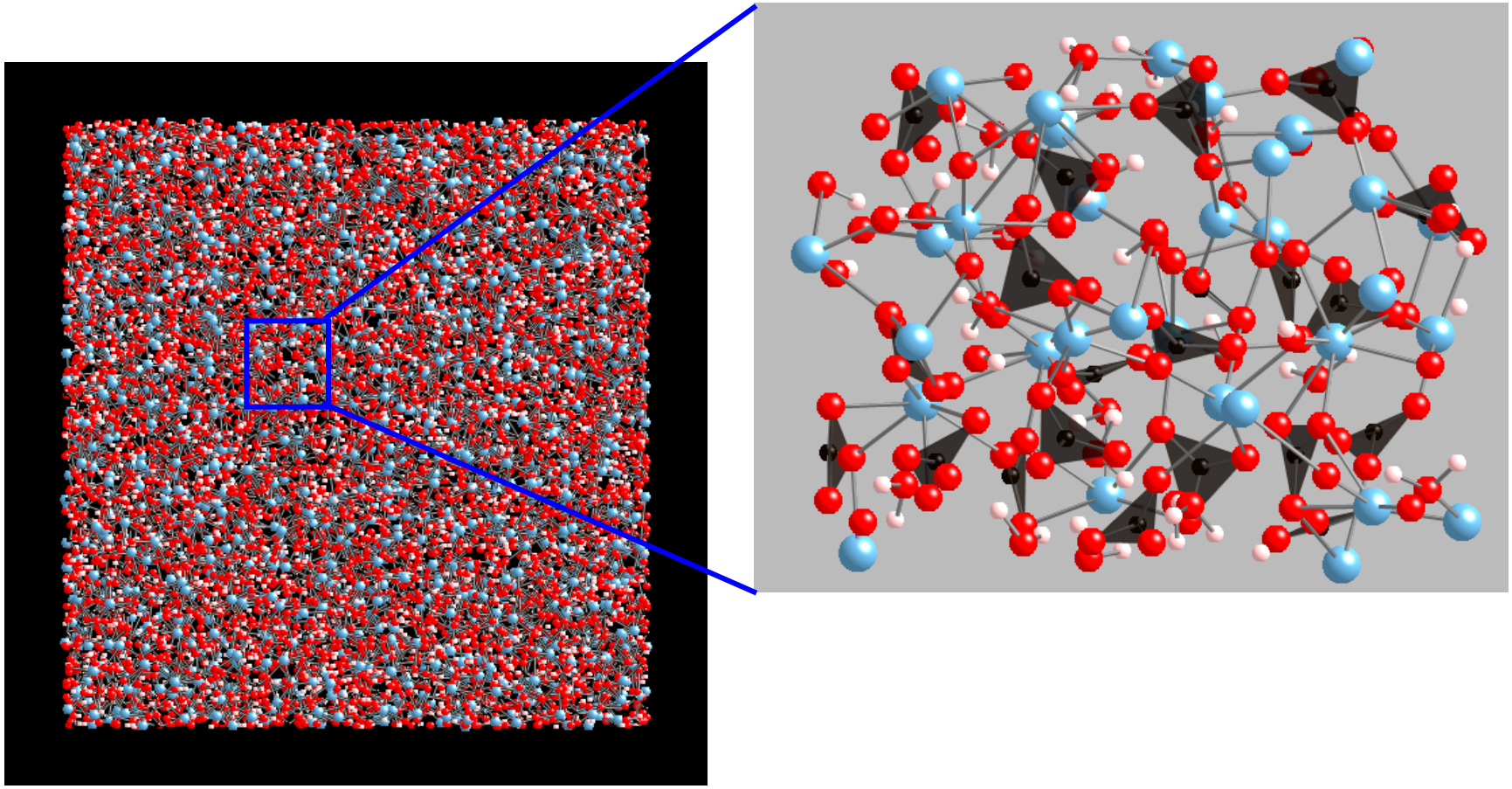




Goodwin et al., *Chem. Mater.*, 22, 3197 (2010)

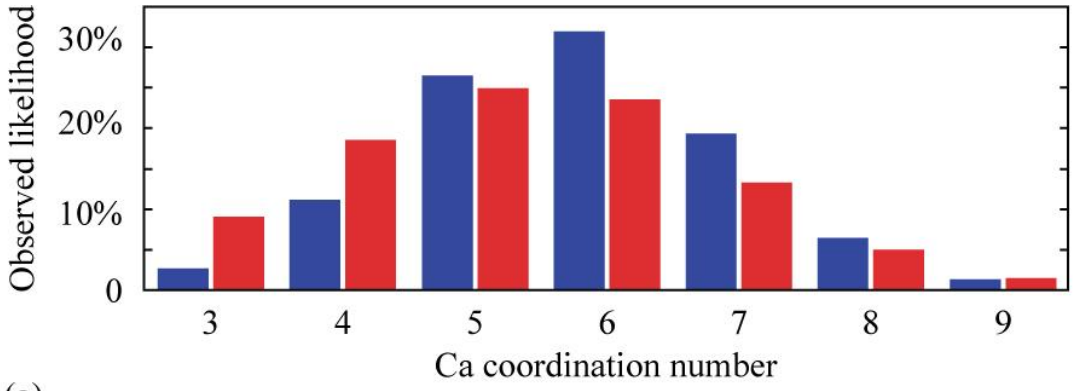
Reverse Monte Carlo Refinement

- Configurations are not unique
- Identify patterns of coordination
- RMC gives most disordered configuration consistent with data
- Protons accounted for indirectly

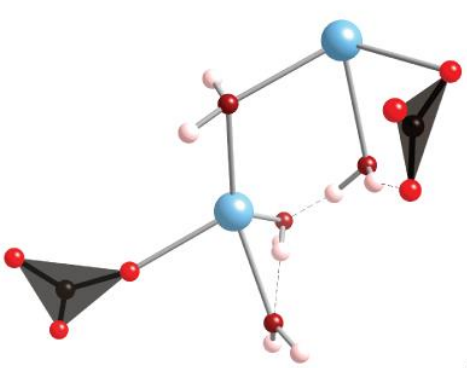


Goodwin et al., *Chem. Mater.*, 22, 3197 (2010)

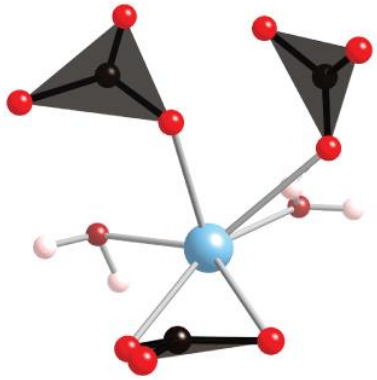
Ca coordination



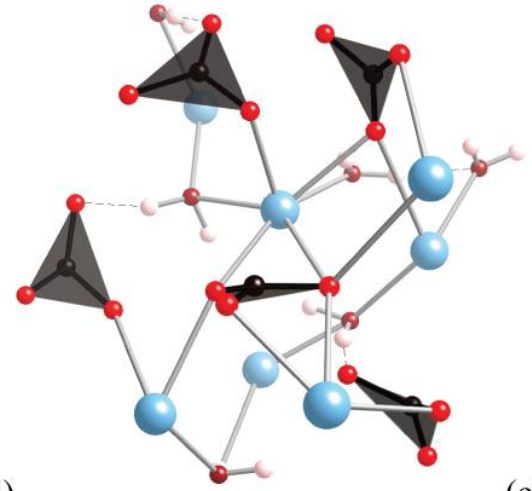
(a)



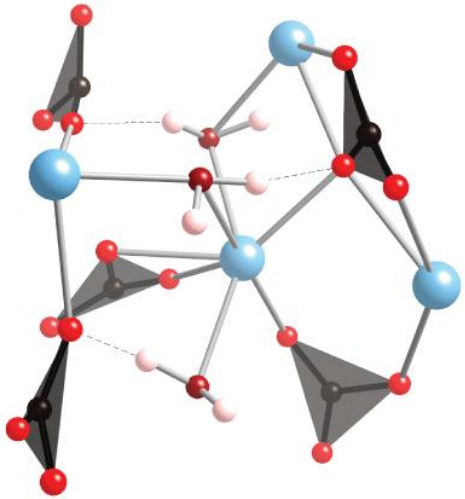
(b)



(c)



(d)



(e)

- Broad distribution of Ca coordination number

- Mixture of monodentate and bidentate CO_3 linkage

- Ca coordination environments of all crystalline polymorphs present

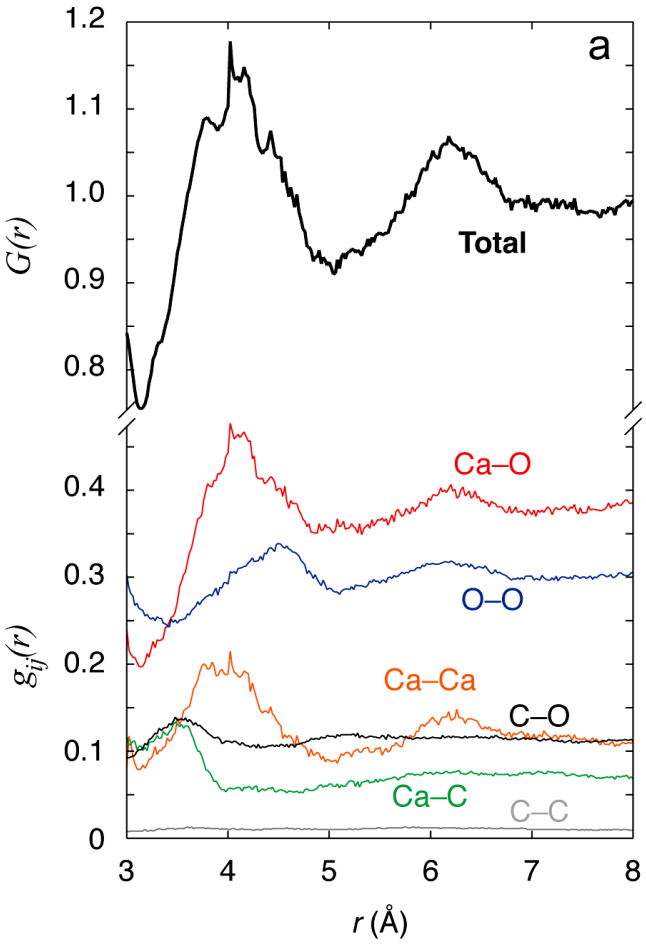
- Exclusively monodentate 6-fold environment of calcite is rare

- Hydrogen atoms/bonds added post-RMC

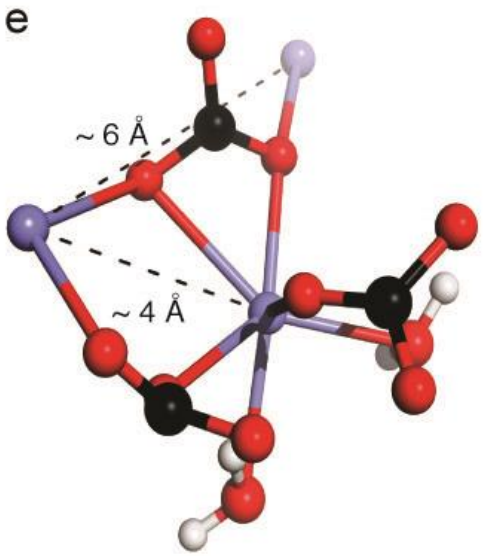
Goodwin et al., *Chem. Mater.*, 22, 3197 (2010)

Medium-range Order

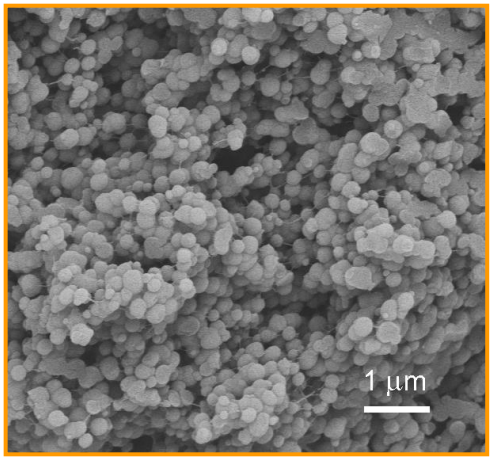
Partials



- Main contributions from Ca-Ca and Ca-O pairs

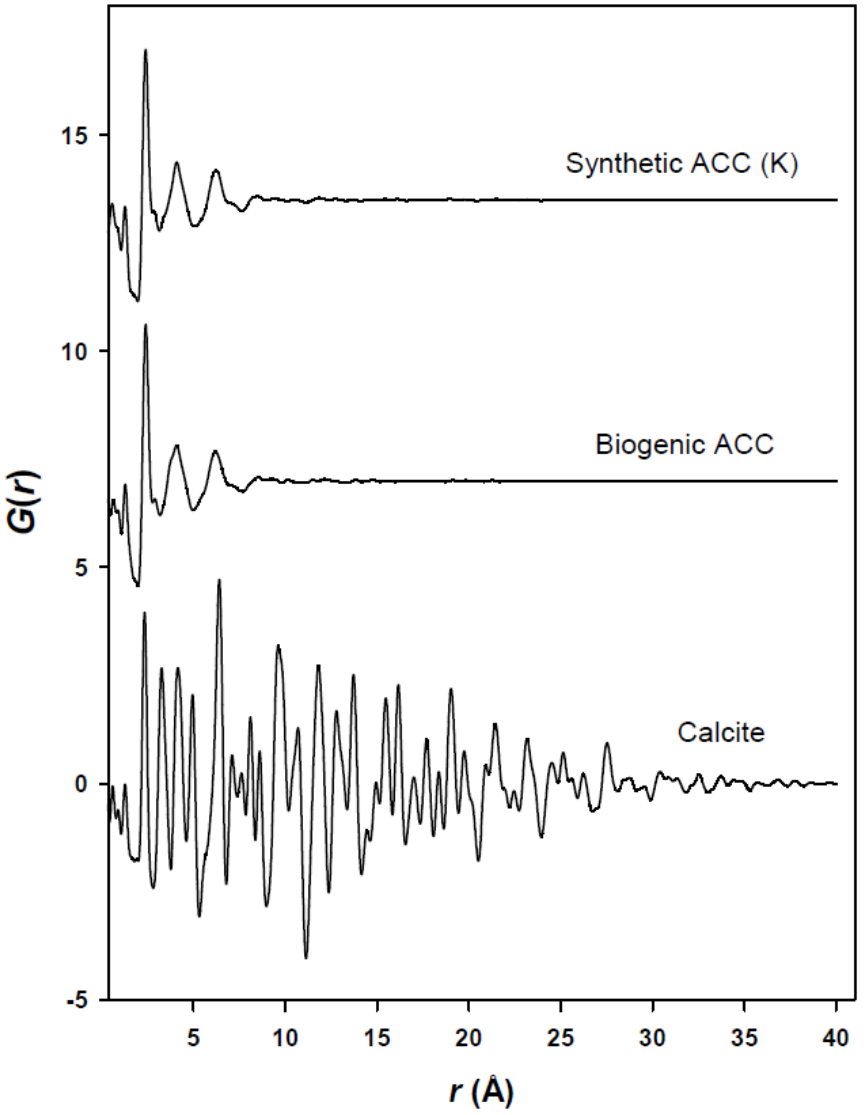


Goodwin et al., *Chem. Mater.*, 22, 3197 (2010)



Synthetic vs biogenic ACC

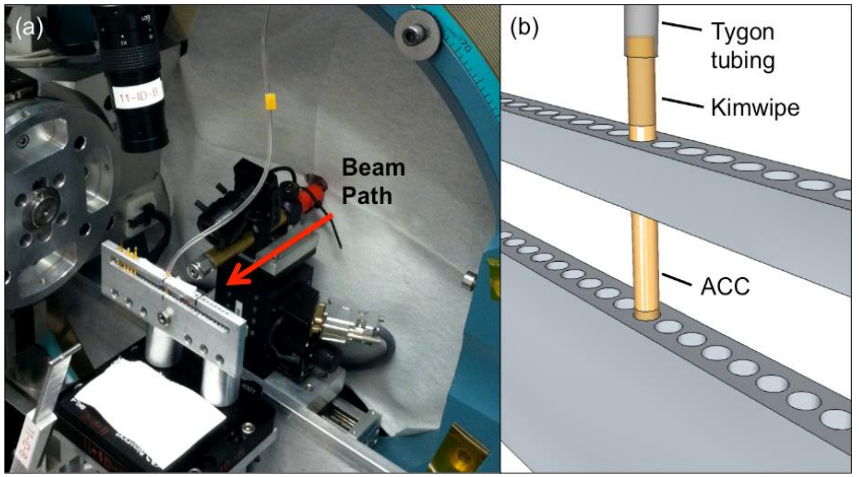
Lobster gastroliths

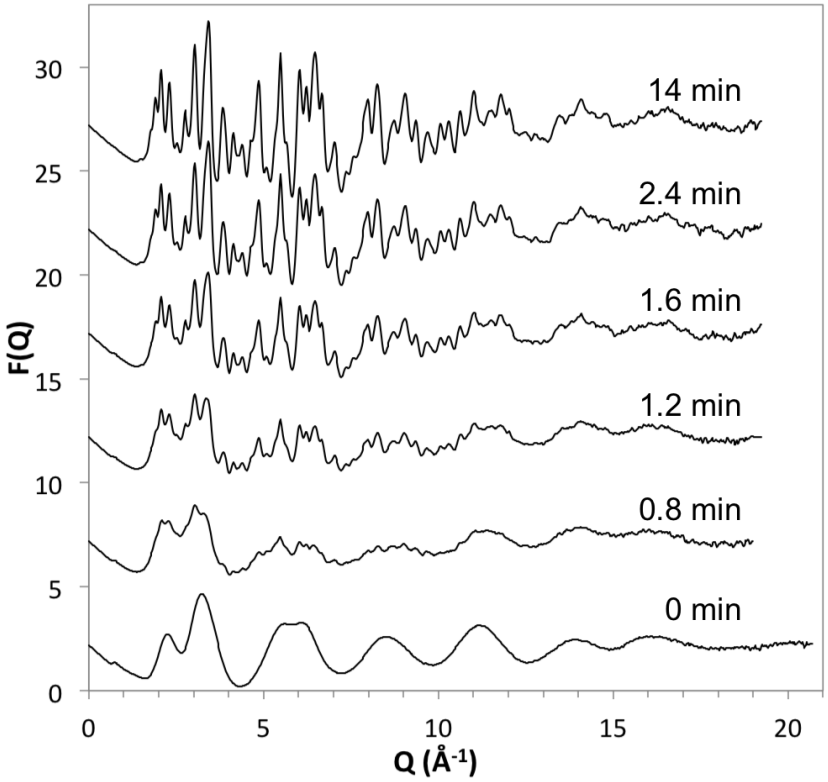


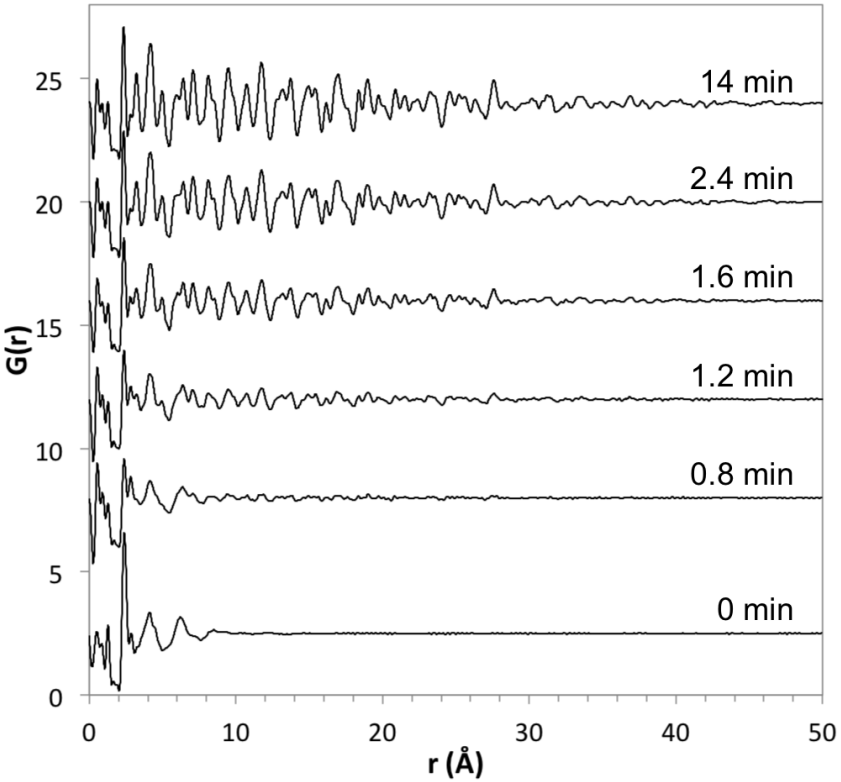
Reeder et al., *Cryst. Growth Design*, 13, 1905−1914 (2013)

In situ kinetic studies using total scattering

- Rapid data acquisition
  - 12 sec spectrum
- Reaction cell in beam path
  - Static cell
  - Flow-through cell





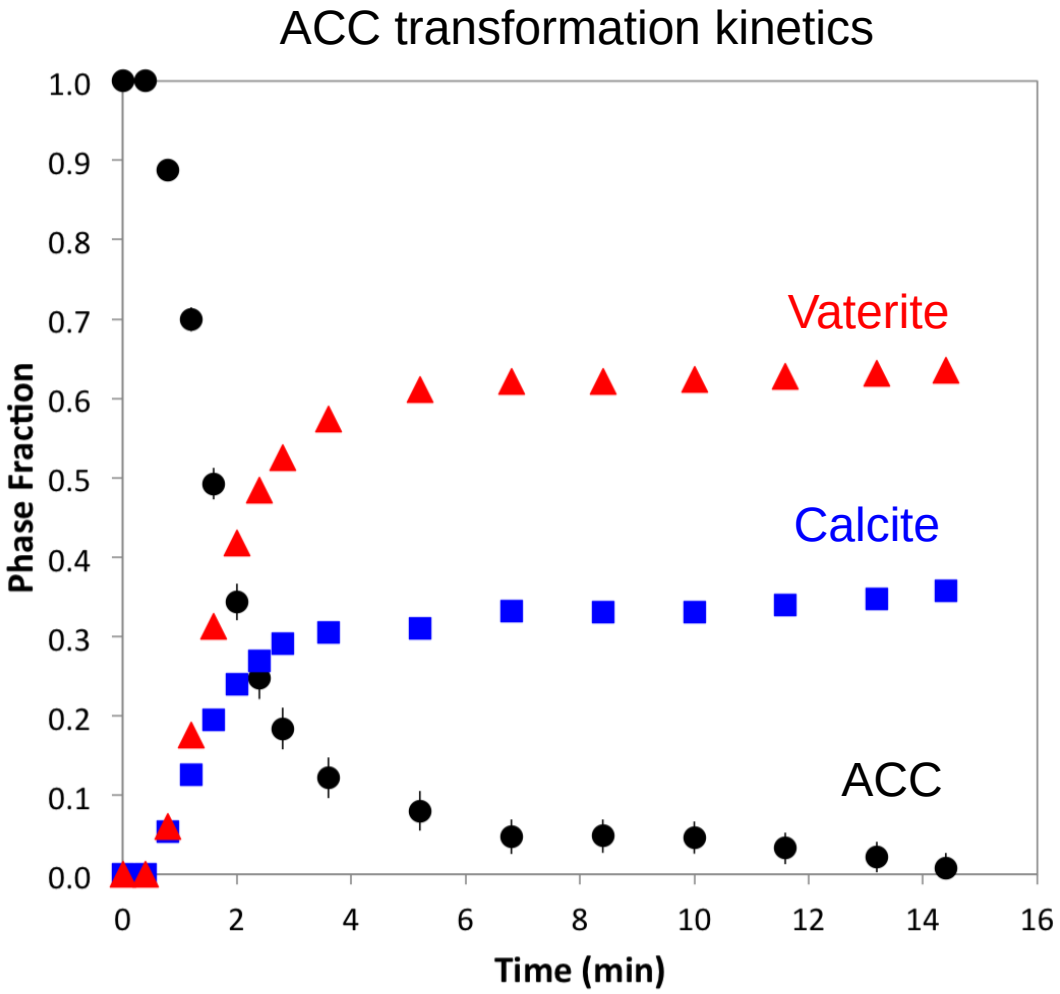


In situ kinetic studies using total scattering

Reactant and product fractions determined using linear combination fitting

Reference spectra:

- ACC
- Calcite
- Vaterite
- Aragonite
- Water

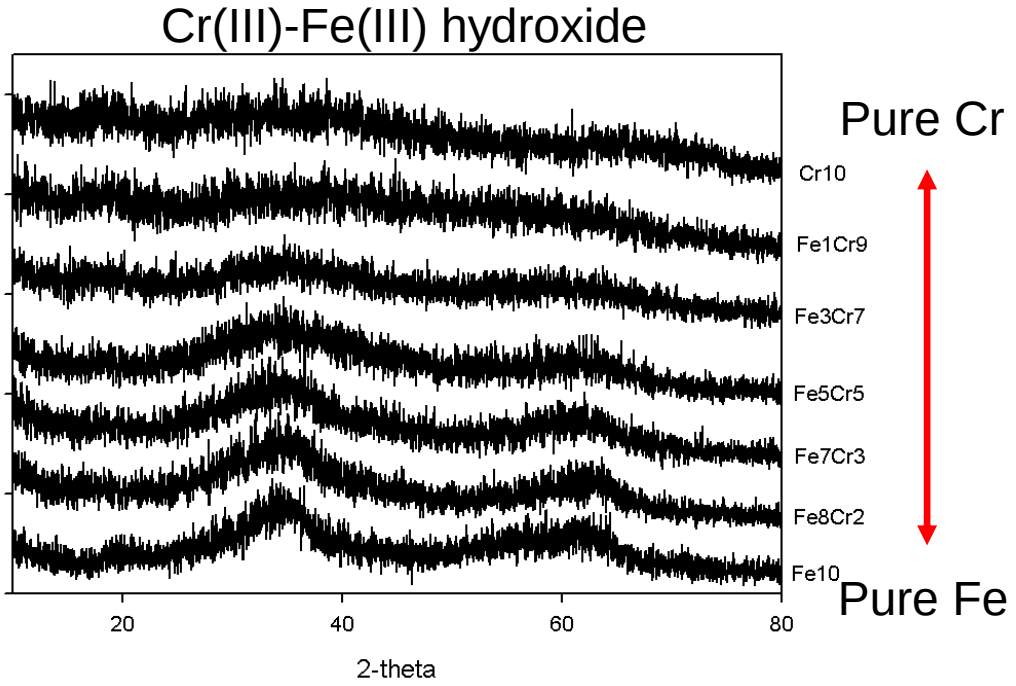


Schmidt et al. (in review)

Structure of Mixed Cr(III)-Fe(III) Hydroxide Phases

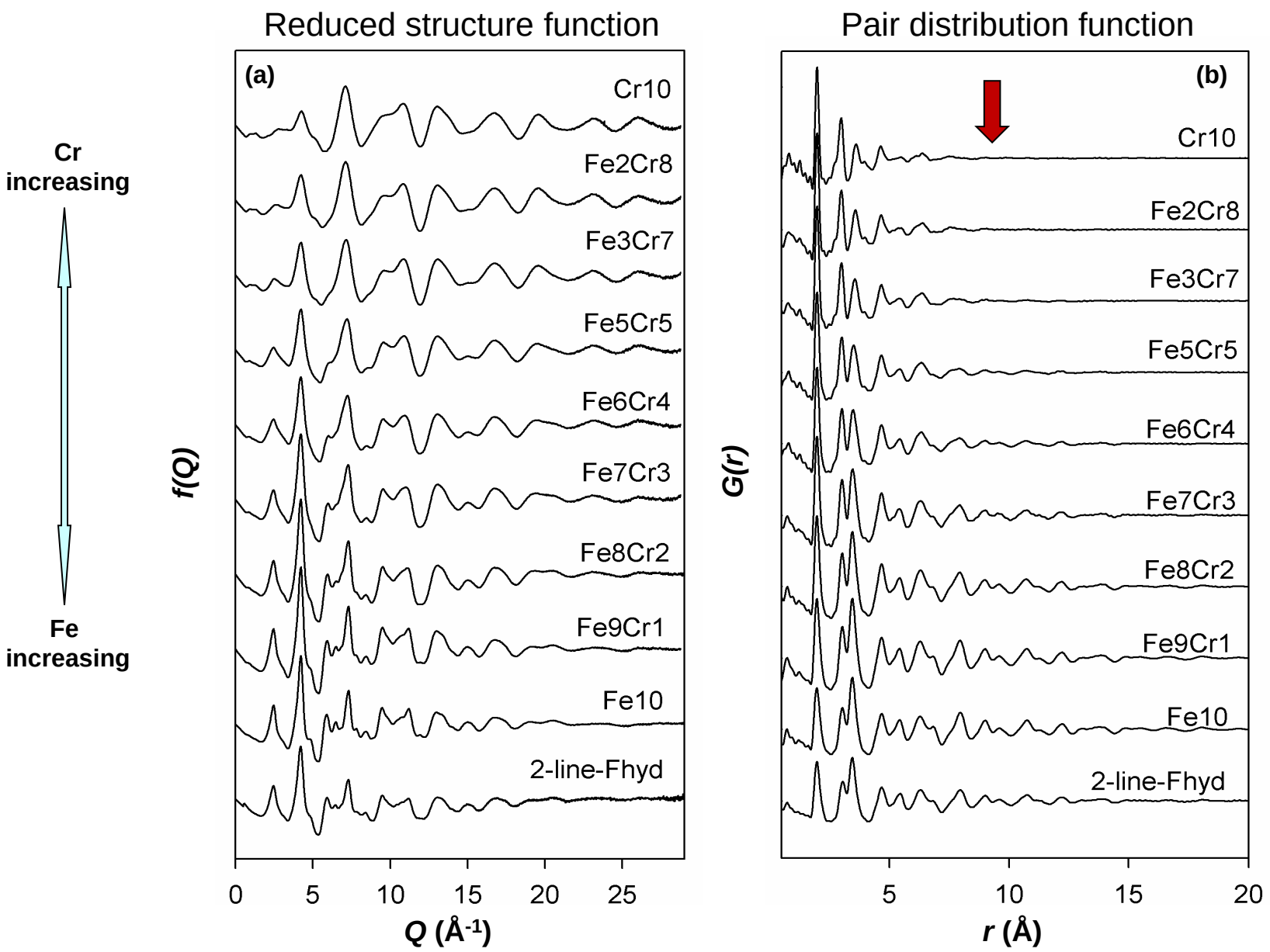
- Complete compositional series between Cr and Fe end members
- Solubility and FTIR studies suggest they behave as solid solution
- Mixed composition phases have lower solubility than the Cr end member (Sass and Rai, 1987; Rai et al., 1987)
- Important for environmental remediation via reduction of Cr(VI)

http://tarkine.org/mining/



Tang et al., *Chem. Mater.*, 22, 3589–3598 (2010)

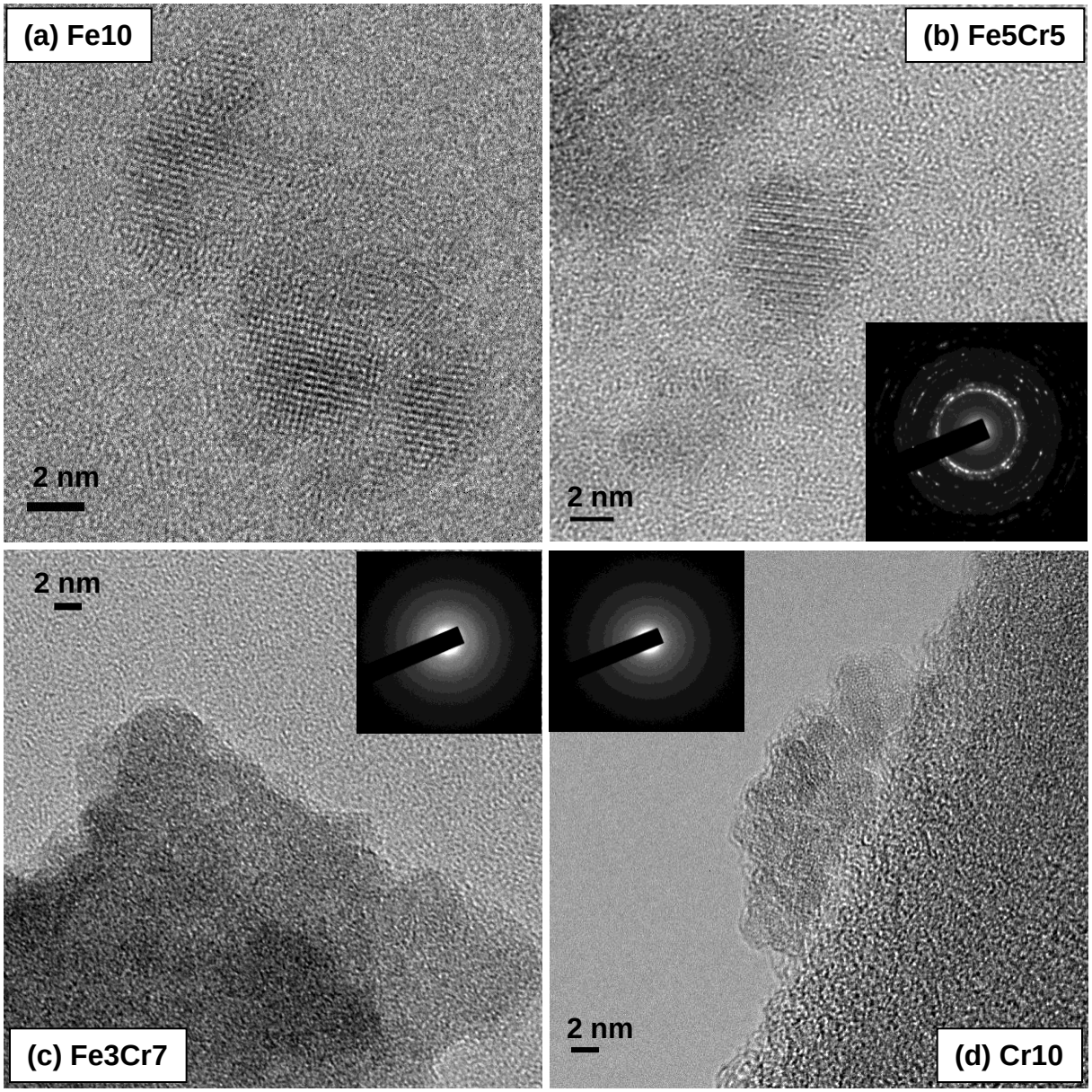
Pair distribution function analysis



Tang et al., *Chem. Mater.*, 22, 3589–3598 (2010)

HRTEM

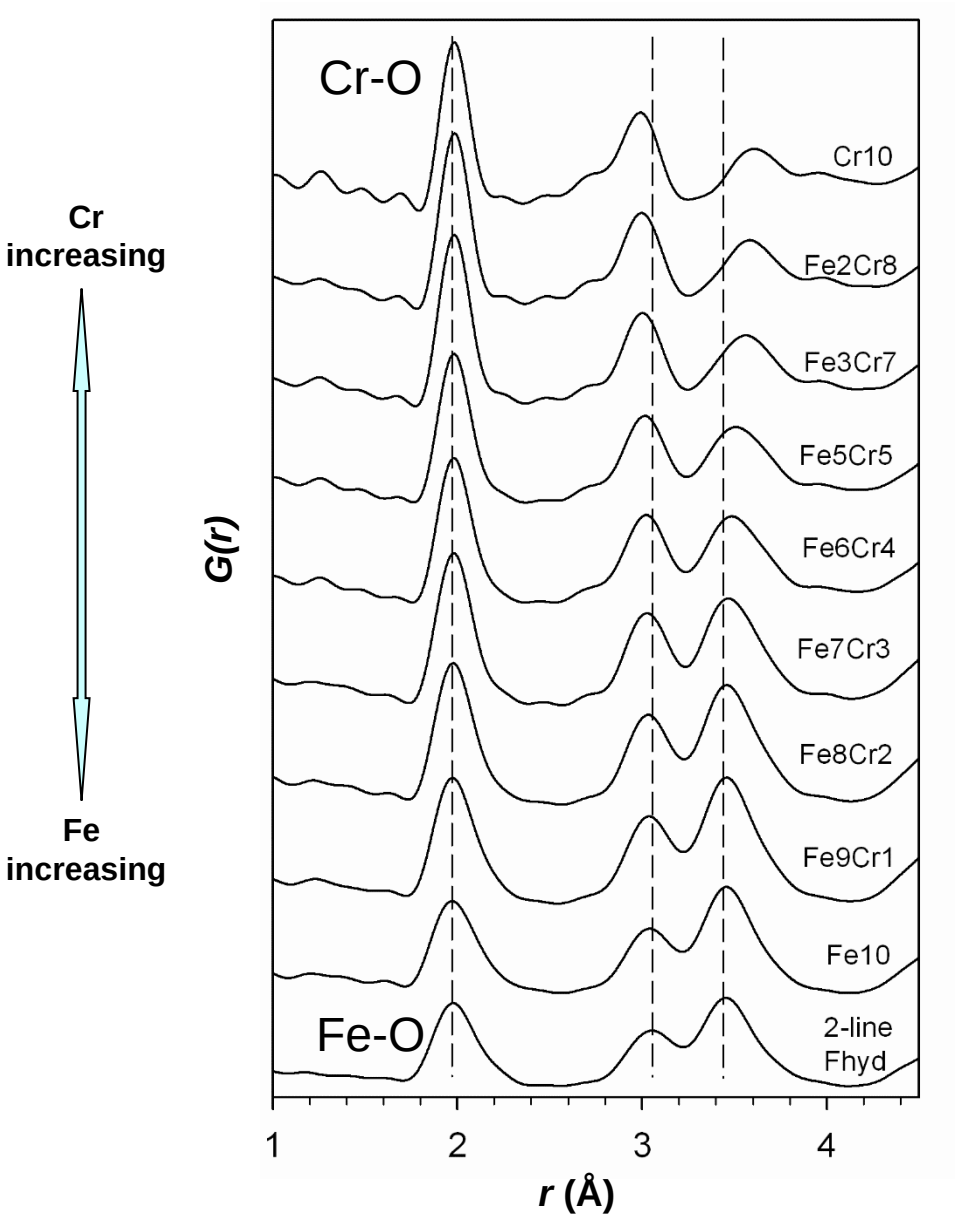
Pure Fe



Pure Cr

Tang et al., *Chem. Mater.*, 22, 3589–3598 (2010)

PDF

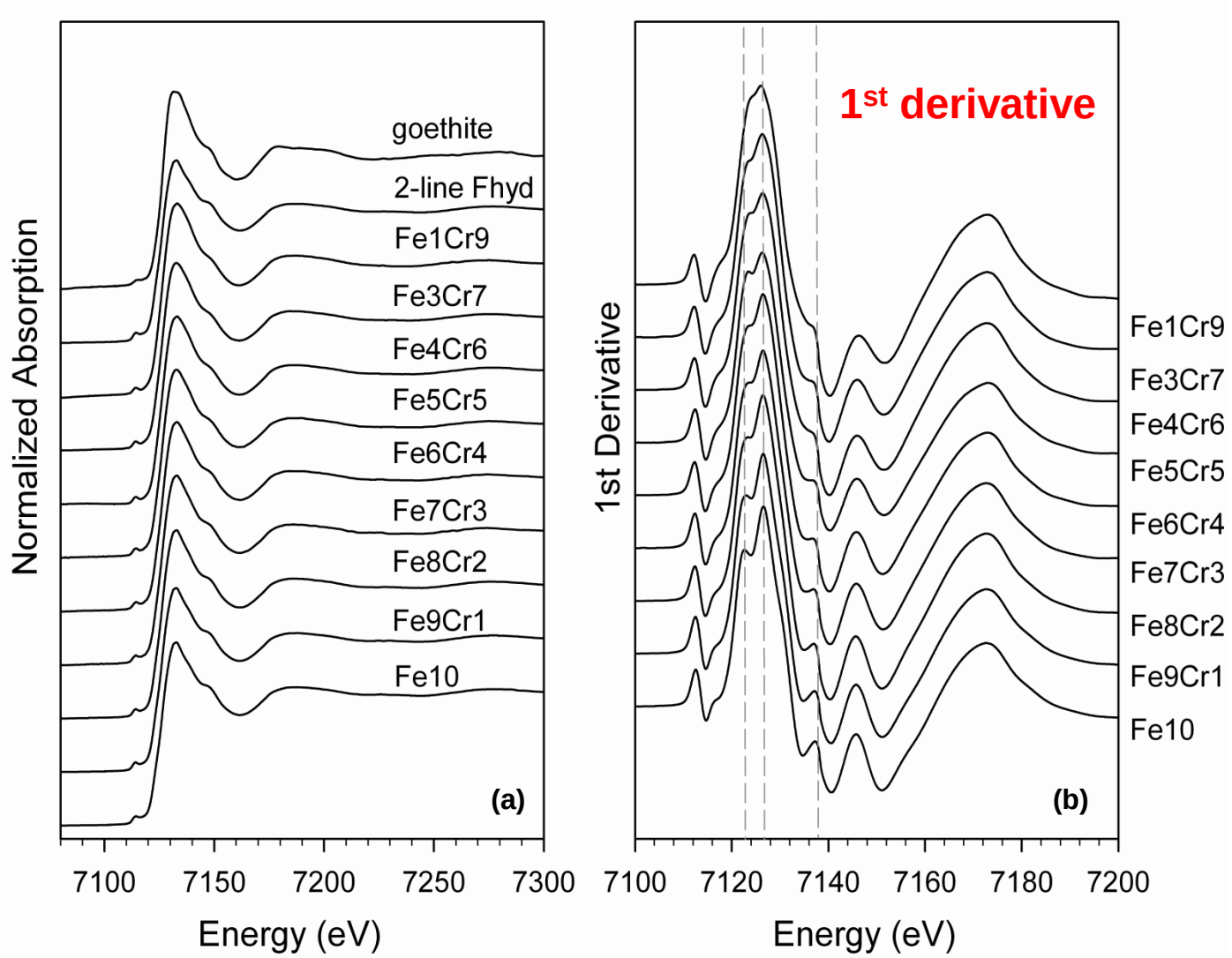


Pair correlations average over all atoms

Not element specific

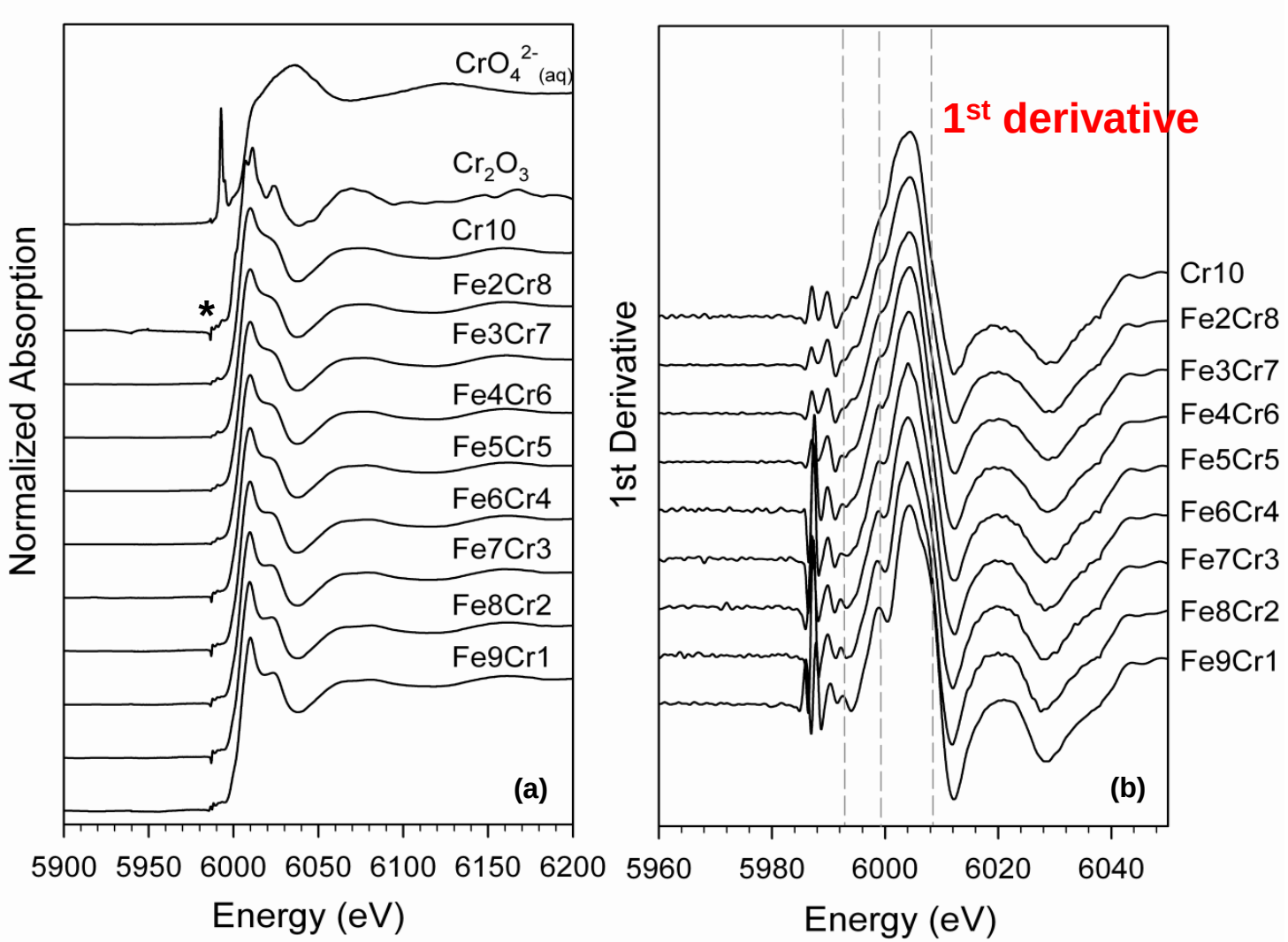
Tang et al., *Chem. Mater*., 22, 3589–3598 (2010)

Fe K-edge XANES



- Position of edge and pre-edge feature indicate all Fe^{3+}
- Edge structure changes with composition as seen in 1st deriv

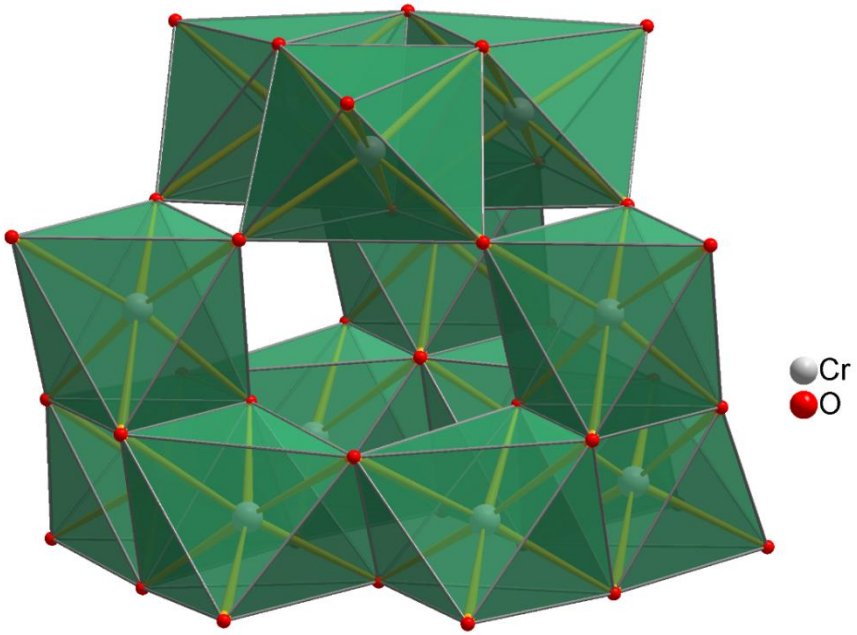
Cr K-edge XANES



- Absence of pre-edge peak indicates all Cr^{3+}
- Edge structure changes with composition (1st deriv)

What can we do with this?

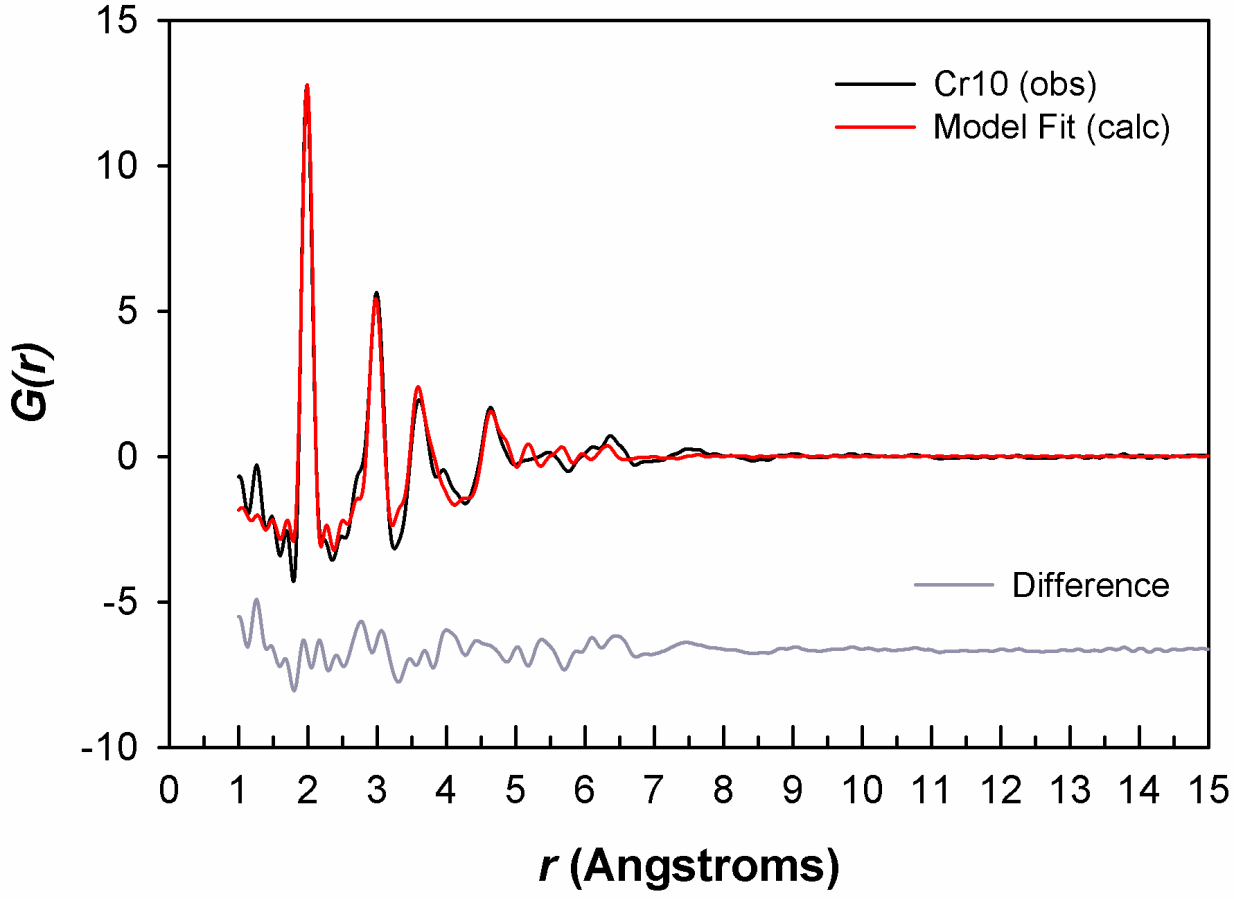
- Previous studies suggest small oligomers are produced as a result of polymerization during Cr(III) hydrolysis



Edge- and corner-sharing of Cr(III) octahedra

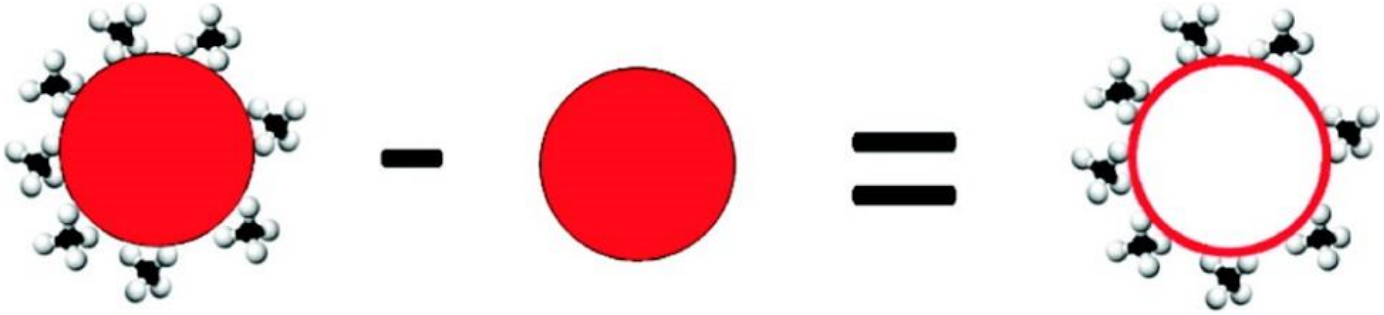
Conceptual view of a possible cluster (oligomer?) without protons shown

Real-space fit of cluster model with Cr10 PDF



- Model fit shows some discrepancies
- Likely that multiple cluster (oligomer) types exist

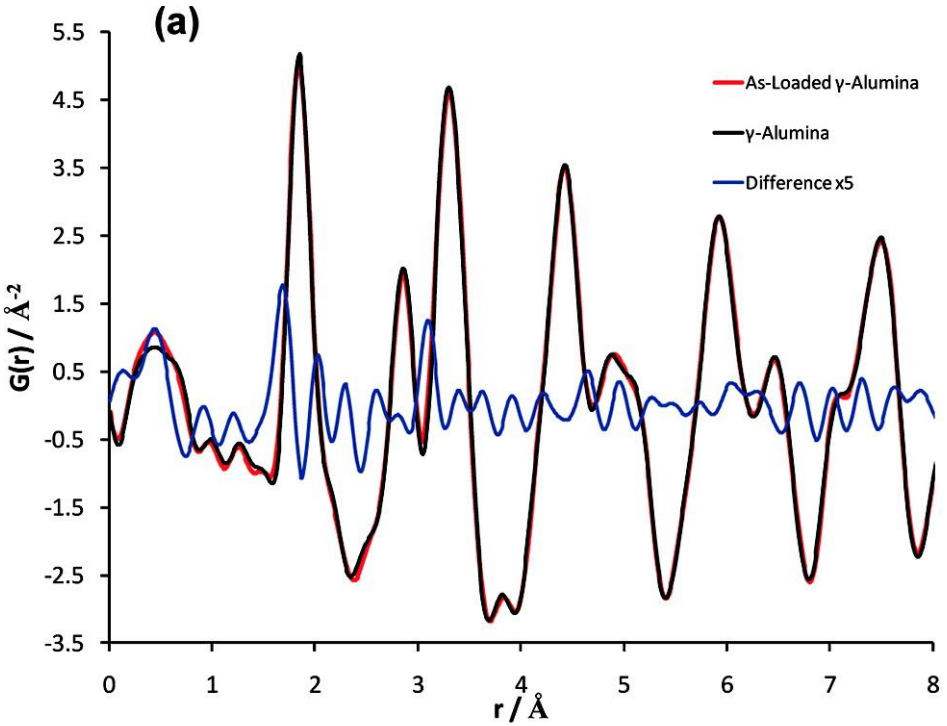
Using PDF to look at surface complexes – differential PDF



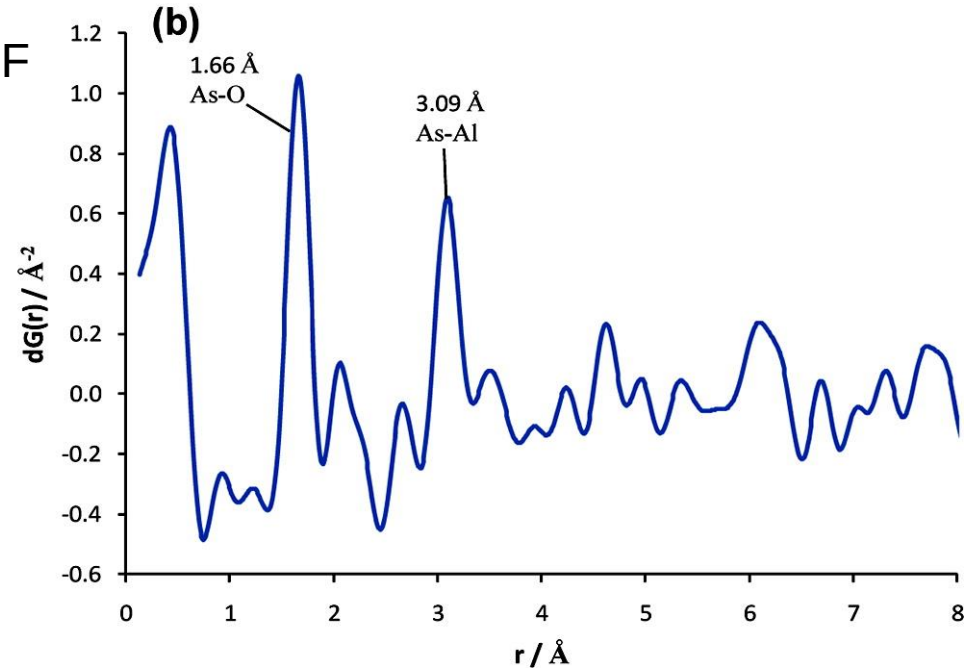
- Difference in scattering is due to adsorbate
- Very weak overall contribution
- Difference is very small; data quality must be very good
- Need strong scatterer in adsorbate molecule (heavy element)

Example: Arsenate sorbed onto alumina and ferrihydrite

PDF



d-PDF



AsO_4^{3-} sorbed onto alumina

As-alumina

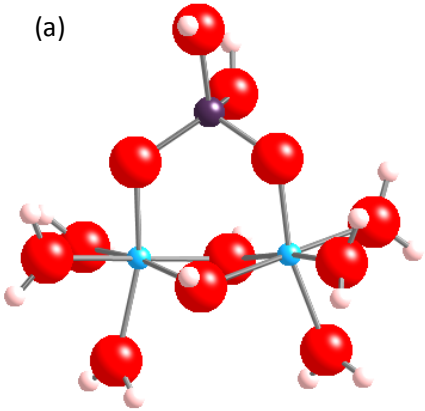
Alumina

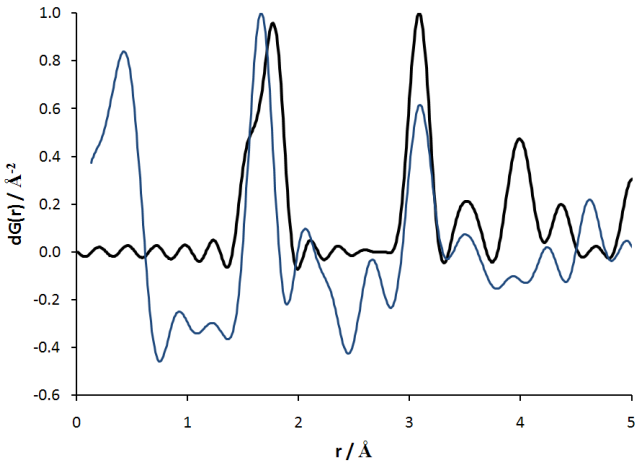
Difference (x5)

Li et al., *Environ. Sci. Technol.*, 45, 9687–9692 (2011)

AsO_4^{3-} sorbed onto alumina

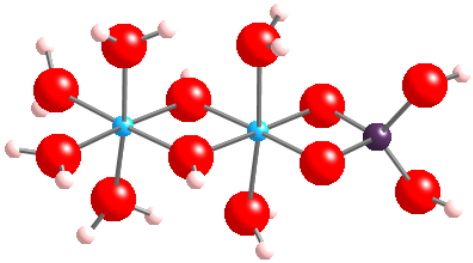
(a)

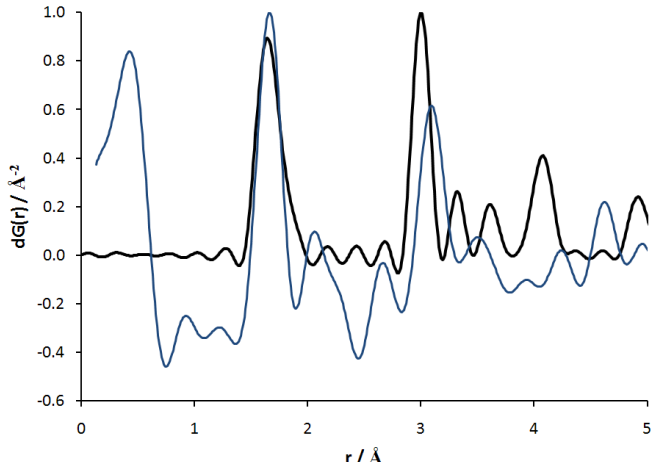




Bidentate, binuclear surface complex

(b)

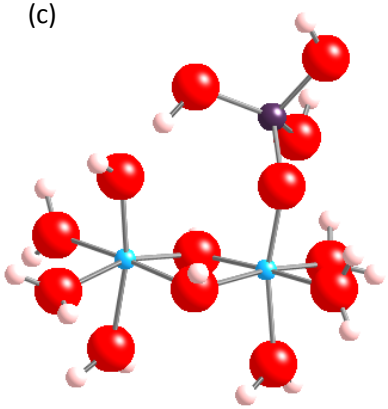


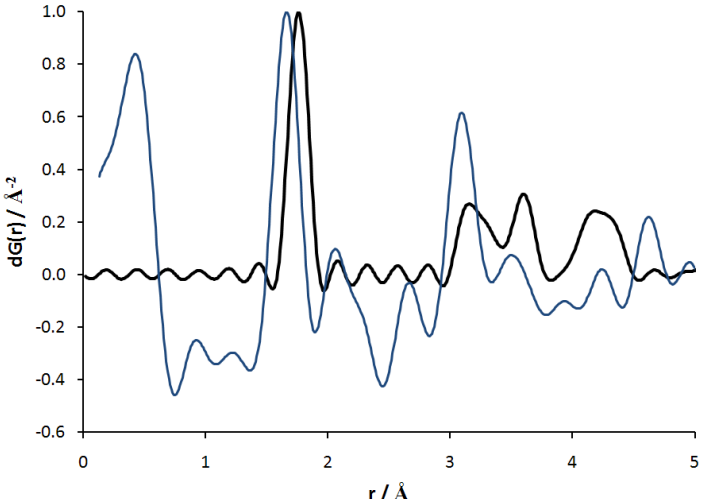


Bidentate, mononuclear surface complex

DFT-optimized

(c)

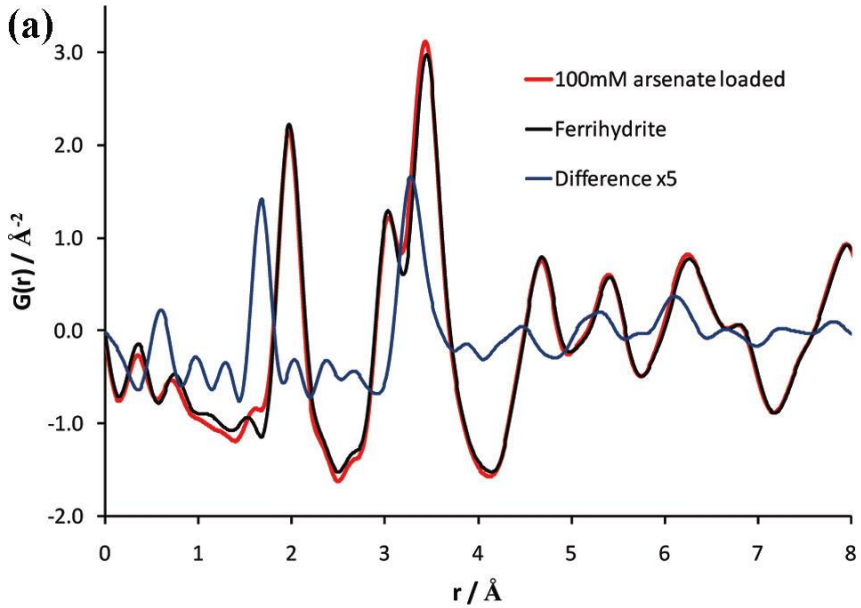


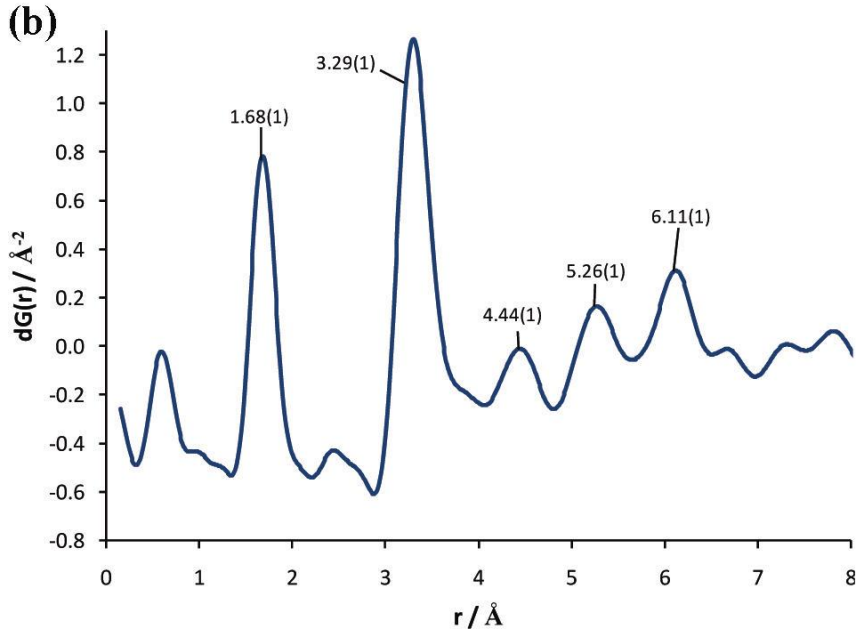


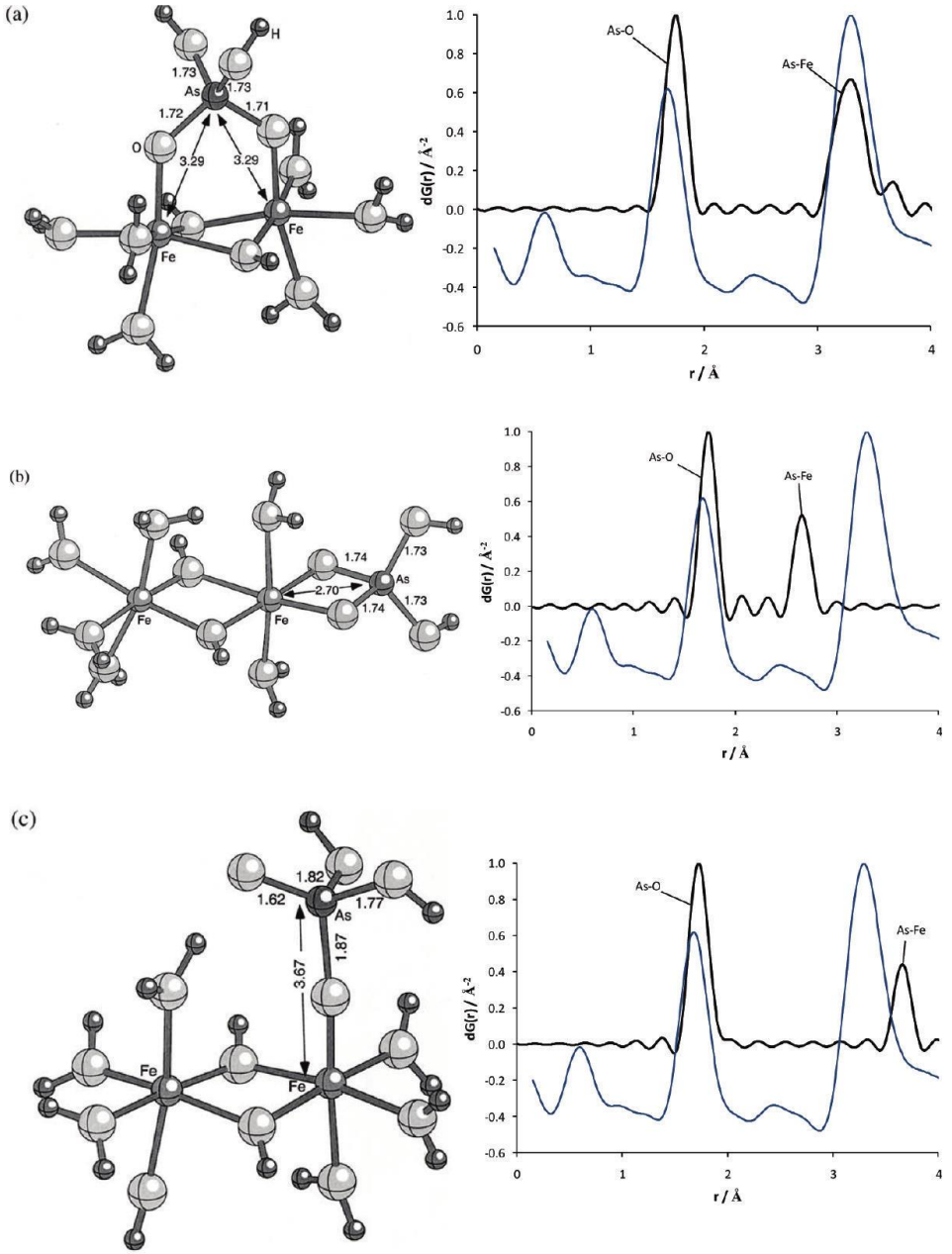
Monodentate surface complex

Li et al., *Environ. Sci. Technol.*, 45, 9687–9692 (2011)

d-PDF of arsenate sorbed onto ferrihydrite







Harrington et al., *Inorg. Chem.*, 49, 325–330 (2010)

Summary

- PDF analysis is complementary to EXAFS
- Not element specific; averages over all atoms
- Structure determination possible for amorphous and nanocrystalline phases
- More precise determination of distances than EXAFS
- Greater length scale accessible compared to EXAFS
- Poorly suited for dilute phase/species, except in optimal conditions
- X-ray scattering cross section for H atoms extremely small