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A systematic description of apatite frameworks

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A Systematic Description of Apatite Frameworks

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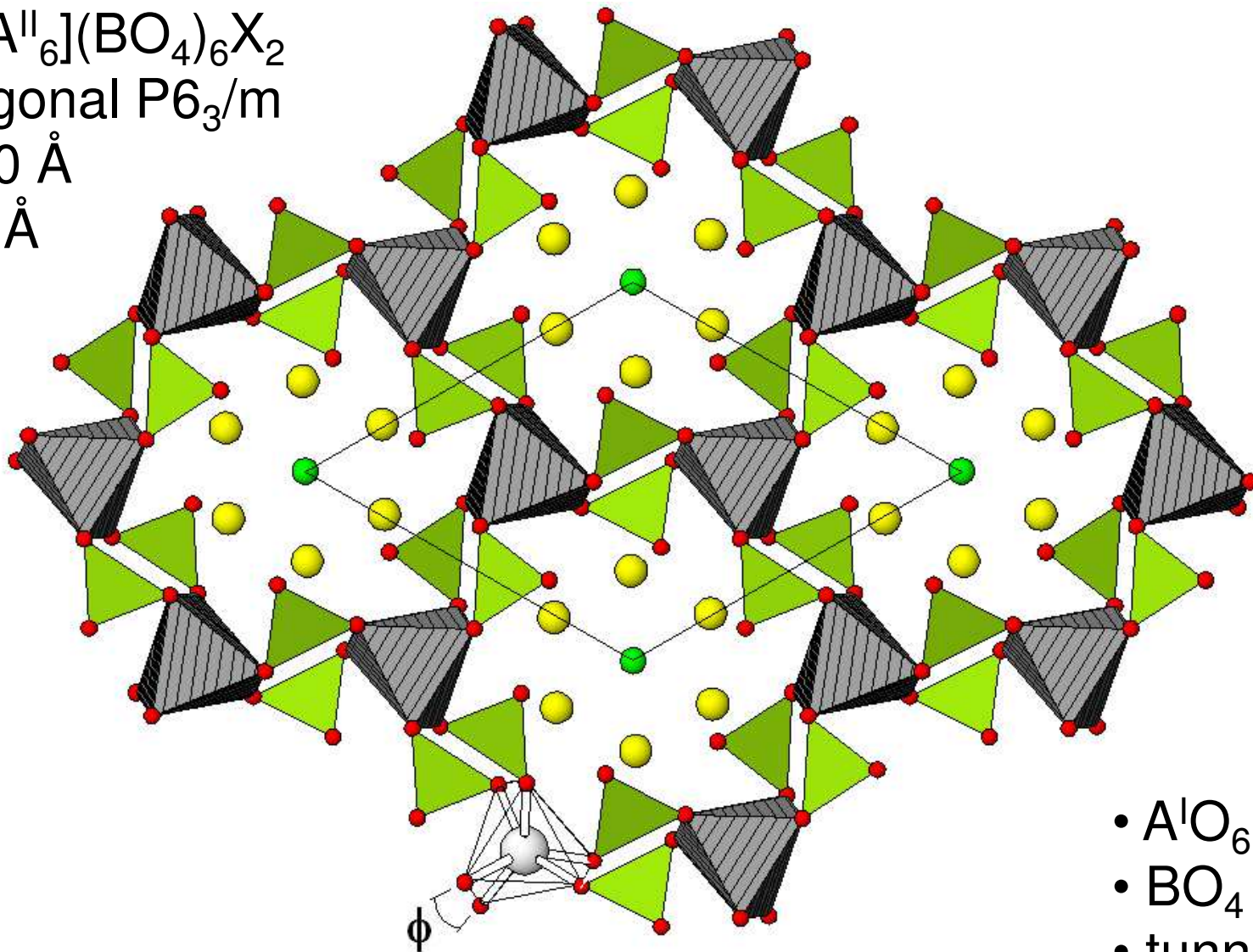
Patrick Mercier, Pam Whitefield, Lyndon Mitchell & Yvon Le Page

Ottawa

Dana Symposium - Baltimore 24 May 2006

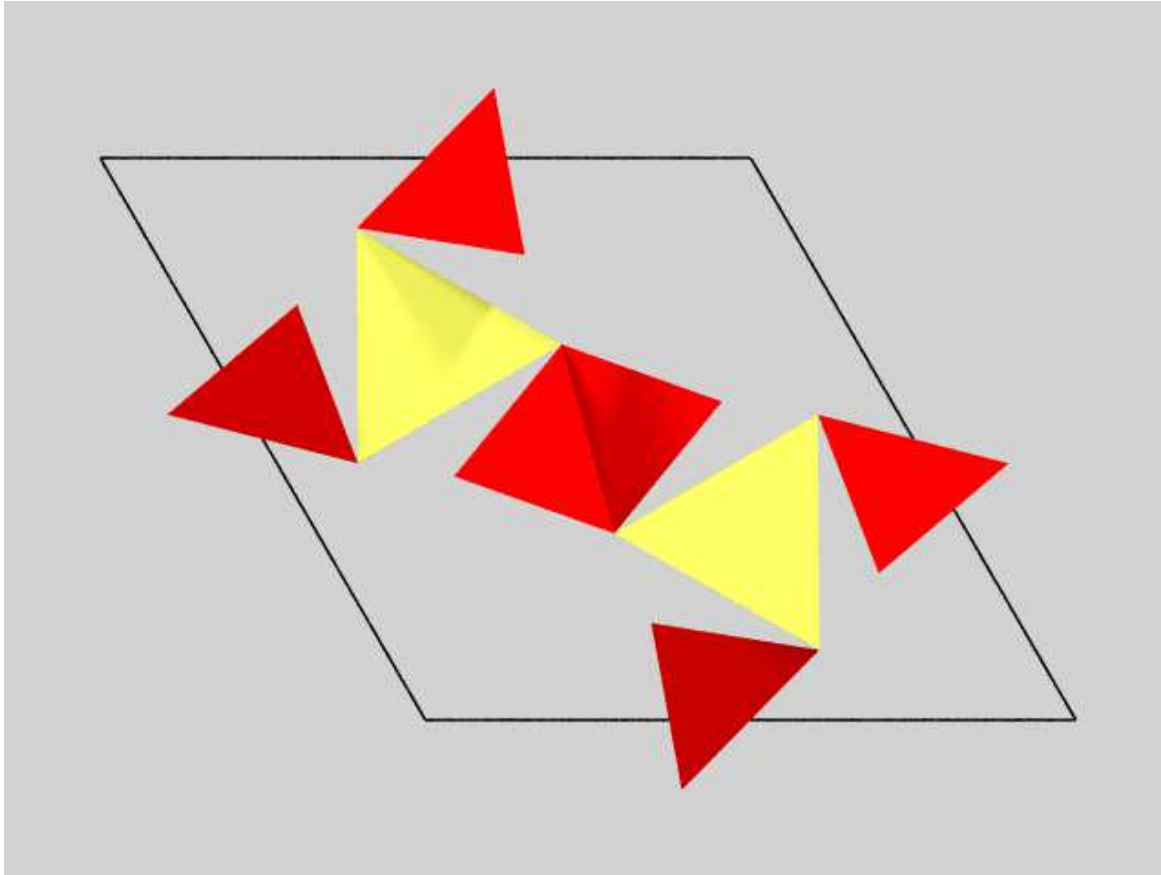
Apatite As a Microporous Structure

- $[A^I_4][A^{II}_6](BO_4)_6X_2$
- hexagonal $P6_3/m$
- $a \sim 10 \text{ \AA}$
- $c \sim 7 \text{ \AA}$



- AlO_6 metaprisms
- BO_4 tetrahedra
- tunnel structure

Apatite as an Adaptive Framework Structure



Two aristotypes are defined:

Type 1:

$$\phi = 0^\circ$$

$A^I O_6$ trigonal prism

tunnel maximally expanded

Type 2:

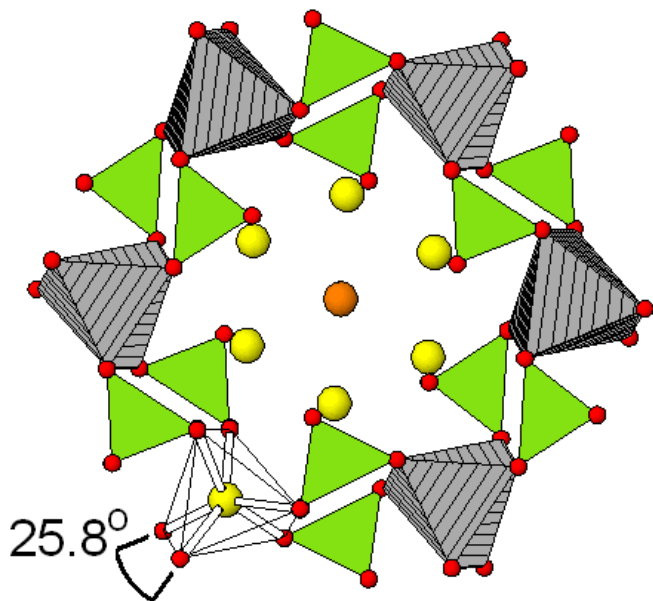
$$\phi = 60^\circ$$

$A^I O_6$ octahedron

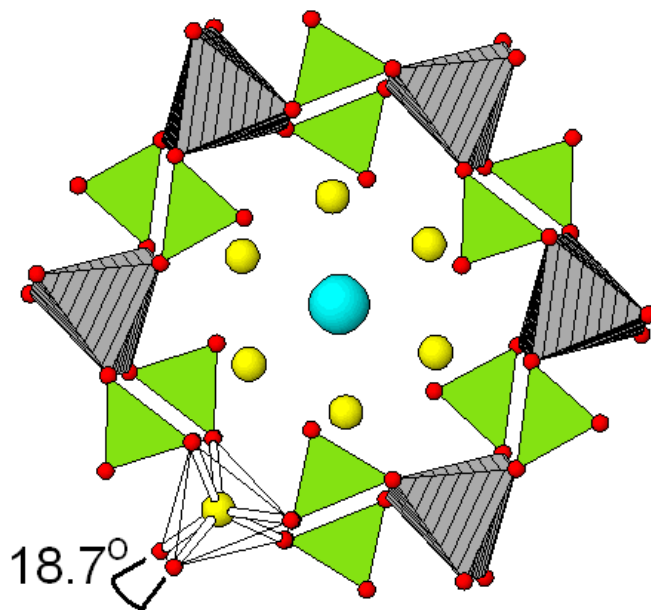
tunnel completely contracted

In practice: $\sim 5^\circ < \phi < \sim 26^\circ$

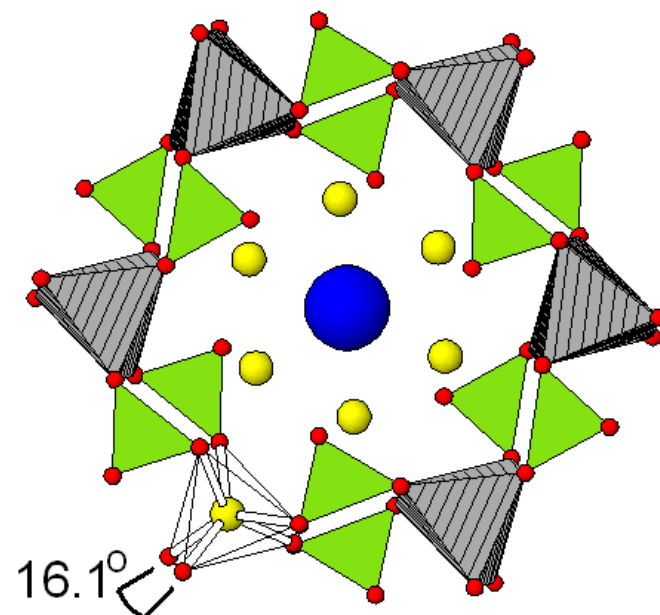
Metaprism Twist Angle And Tunnel Content



OH^- 1.40Å



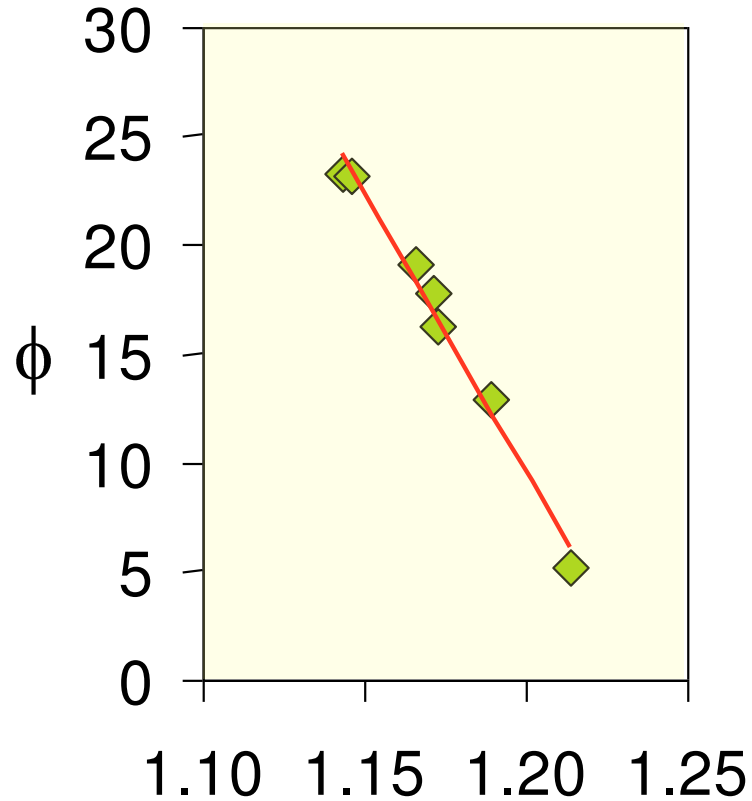
Cl^- 1.81Å



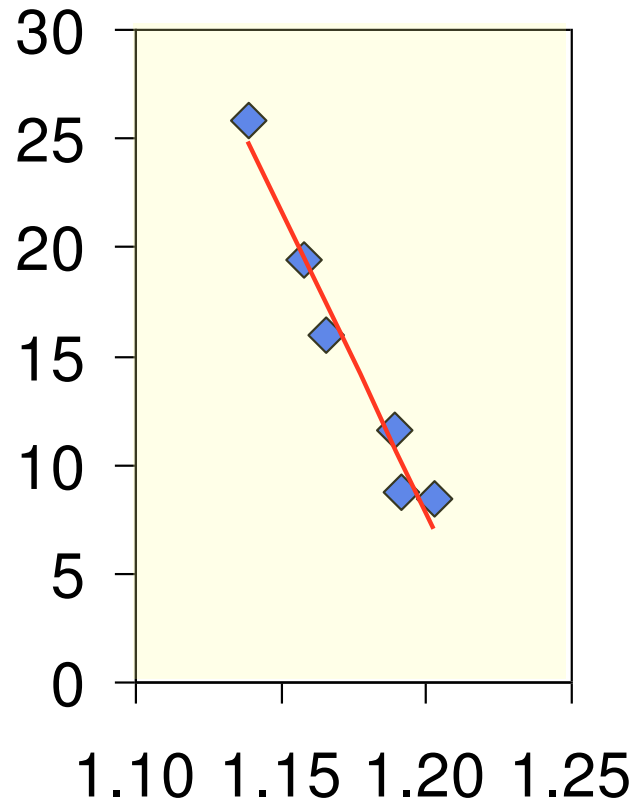
Br^- 1.96Å

A' Metaprism Twist Angle (ϕ) vs Average Crystal Radii

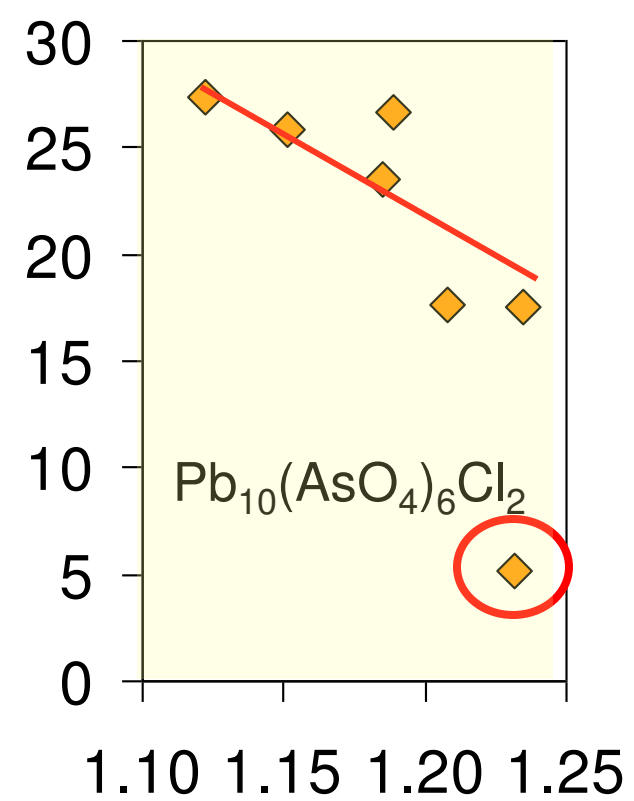
Calcium Apatites
 $\text{Ca}_{10}(\text{BO}_4)_6\text{X}_2$



Cadmium Apatites
 $\text{Cd}_{10}(\text{BO}_4)_6\text{X}_2$



Lead Apatites
 $\text{Pb}_{10}(\text{BO}_4)_6\text{X}_2$



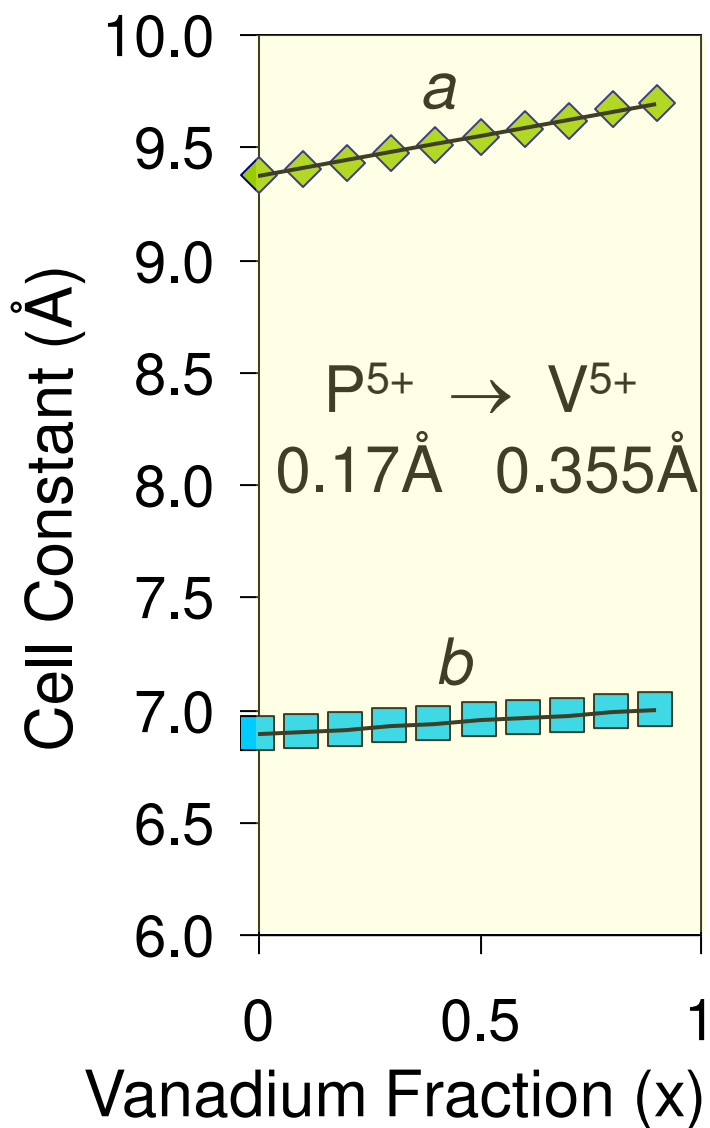
Average Crystal Radii for Total Unit Cell Content

Extracting Accurate Metaprism Twist Angles

Can the twist angle be derived with sufficient accuracy to be useful?

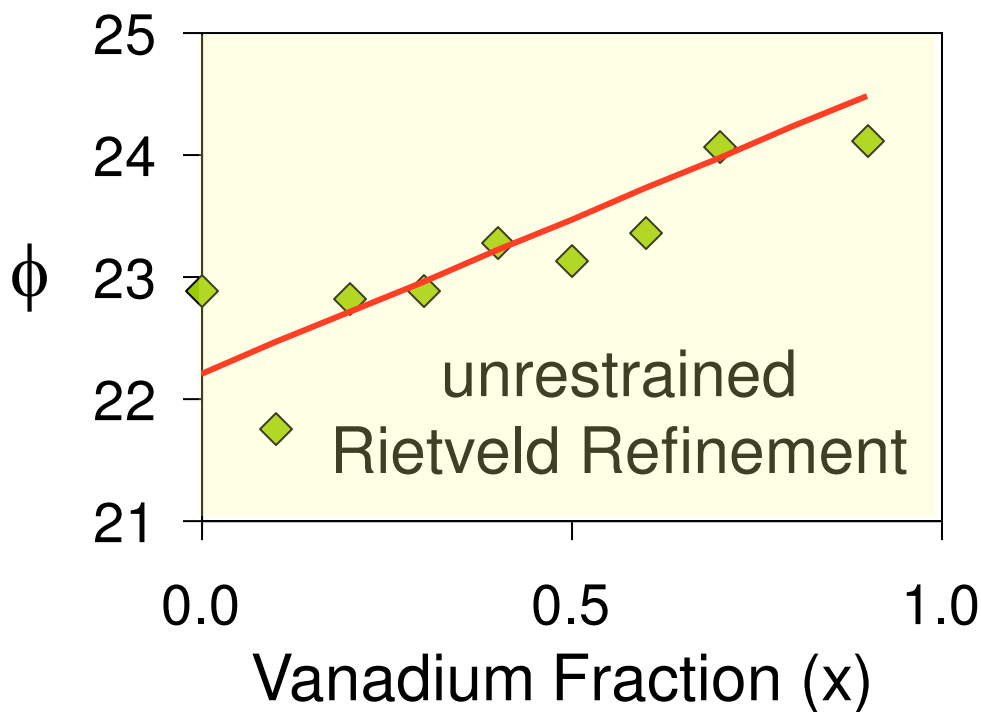
- The chemistry of an apatite might not be well known - or at least not verified through analysis independent of the crystal structure determination/refinement.
- It is particularly difficult to obtain reliable Rietveld refinements of apatites without constraints - usually of the tetrahedral site.
- The esds of the fractional co-ordinates of the oxygen atoms are large for X-ray determinations.
- Twist angle will adjust when different species are distributed over the A^I and A^{II} large cation sites.

Rietveld Analysis of Fluorovanadinates $\text{Ca}_{10}(\text{V}_x\text{P}_{1-x}\text{O}_4)_6\text{F}_2$



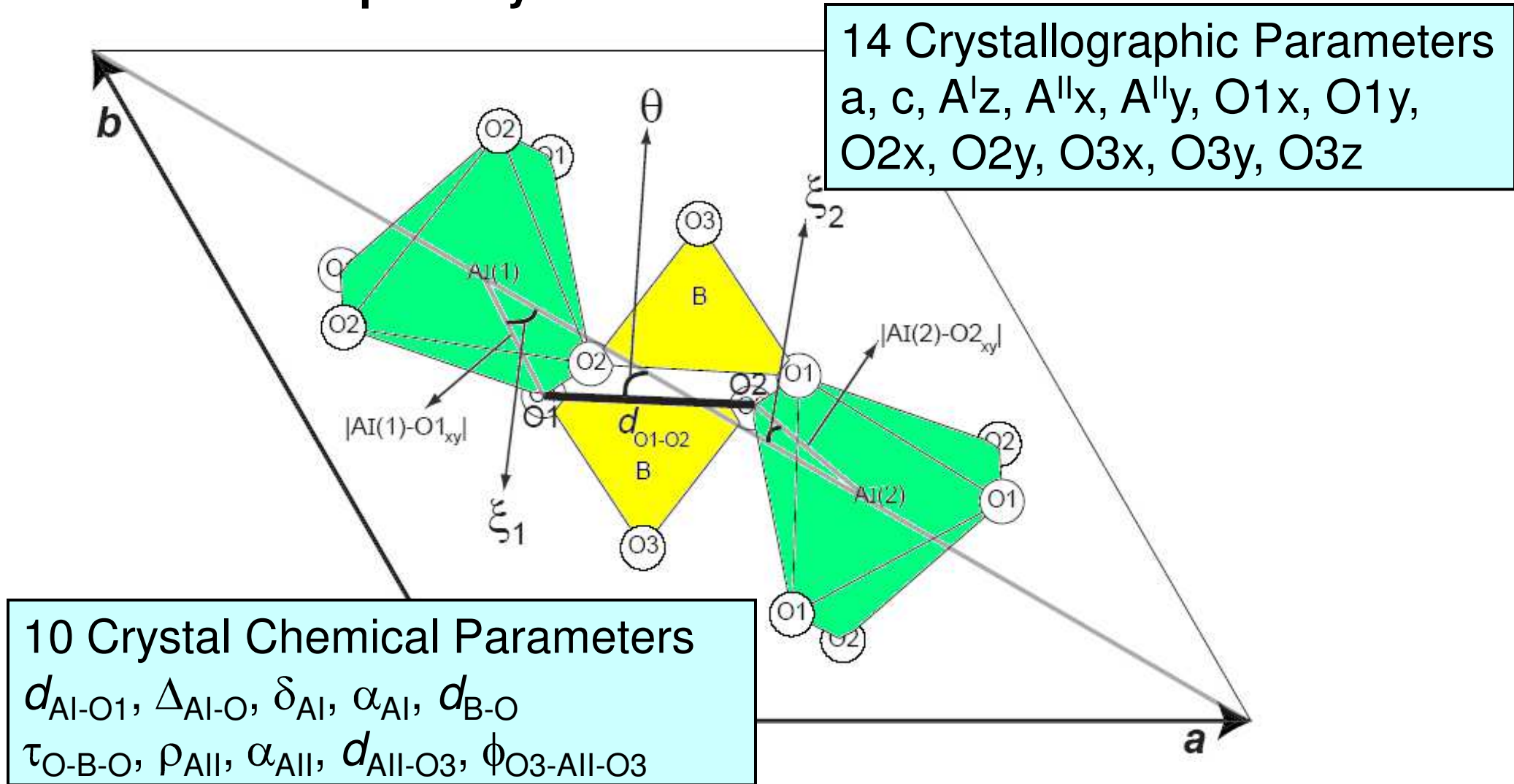
Prediction: Smaller ϕ with higher V^{5+}
Because: Average crystal radius increases from 1.143 to 1.169
Tunnel expansion reduces ϕ

But... Wrong Direction!



How Can Errors in Rietveld Analysis be Reduced?

Step 1: Crystal Chemical Parameterization



How Can Errors in Rietveld Analysis be Reduced?

Step 2: Singular Value Decomposition (SVD)

SVD ranks anomalously high esds that are propagated due to round-off error and truncation errors.

SVD diagnosis found values of the crystal chemical parameters $\tau_{\text{O-B-O}}$ and $\phi_{\text{O3-Al-O3}}$ possessed especially high esds; many values are OK!!

What can be done?

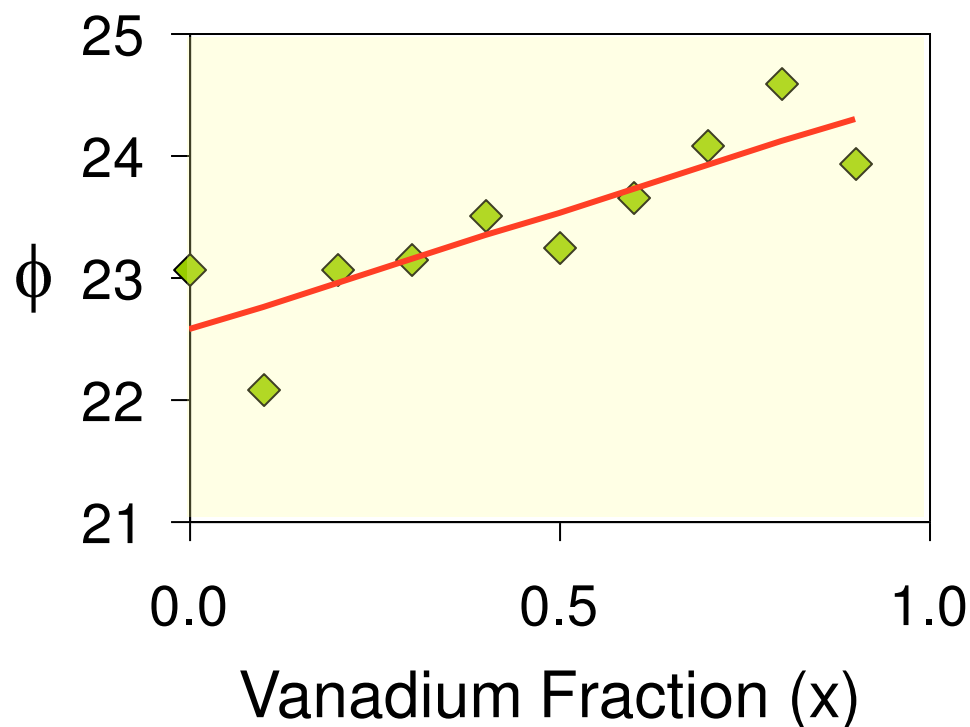
Step 3: *Ab Initio* Energy Minimization

VASP (Vienna Ab Initio Simulation Package) can perform an energy minimization starting with a P1 symmetry model of $P6_3/m$ vanadinites.

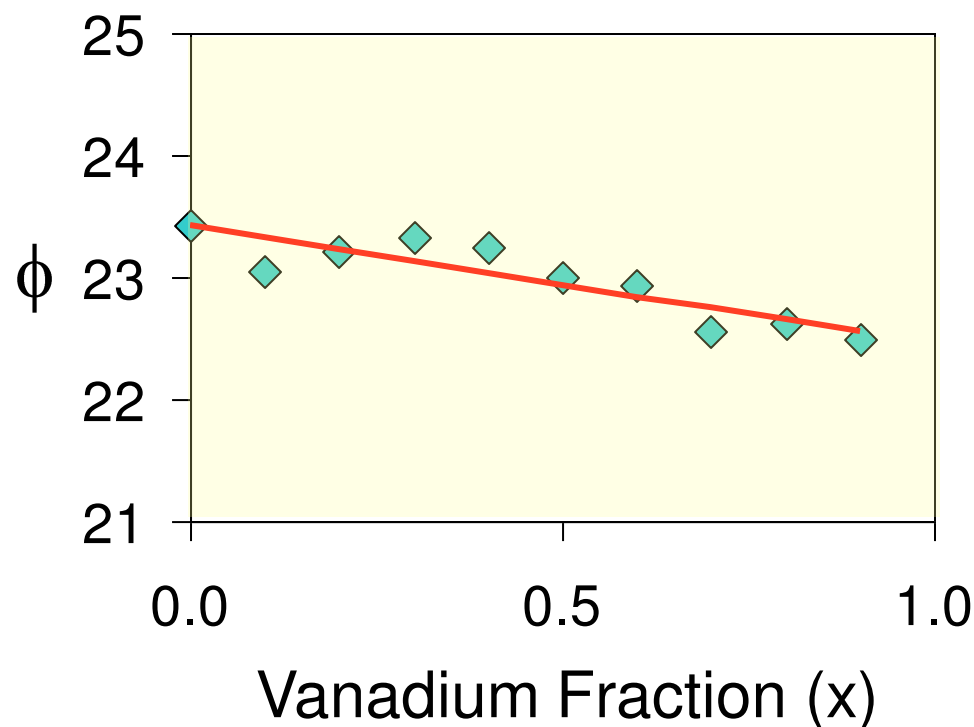
Energy minimized values of $\tau_{\text{O-B-O}}$ and $\phi_{\text{O3-Al-O3}}$ for each V/P composition were imposed during crystal chemical Reitveld analysis.

Crystal Chemical Rietveld Analysis of $\text{Ca}_{10}(\text{V}_x\text{P}_{1-x}\text{O}_4)_6\text{F}_2$

Rietveld Analysis
with Geometrical Parameterization



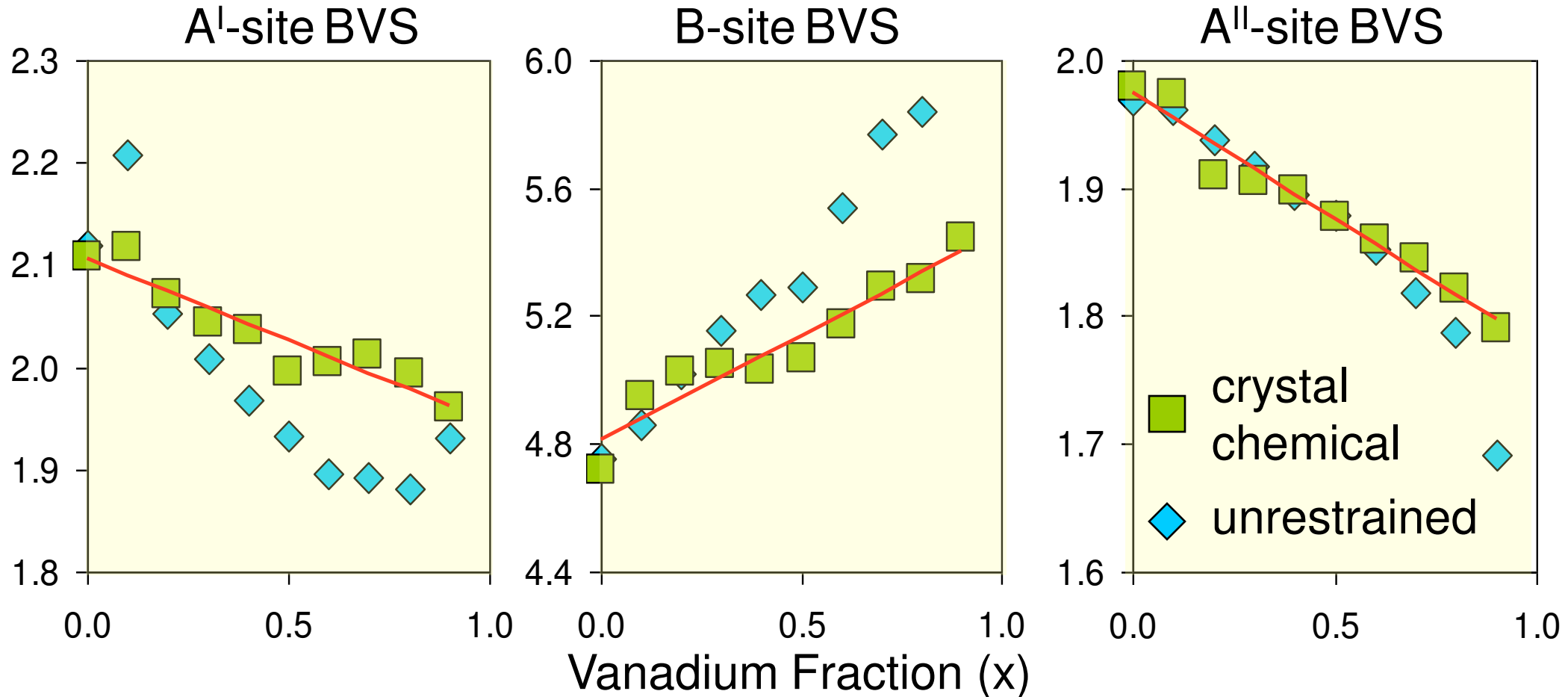
Geometrical Parameterization
and Energy Minimization



By combining Geometrical Parameterization and Energy Minimization:

- the spread of metaprism twist angles is reduced; and
- the trend as function of composition is as expected for tunnel expansion.

Bond Valence Considerations in $\text{Ca}_{10}(\text{V}_x\text{P}_{1-x}\text{O}_4)_6\text{F}_2$

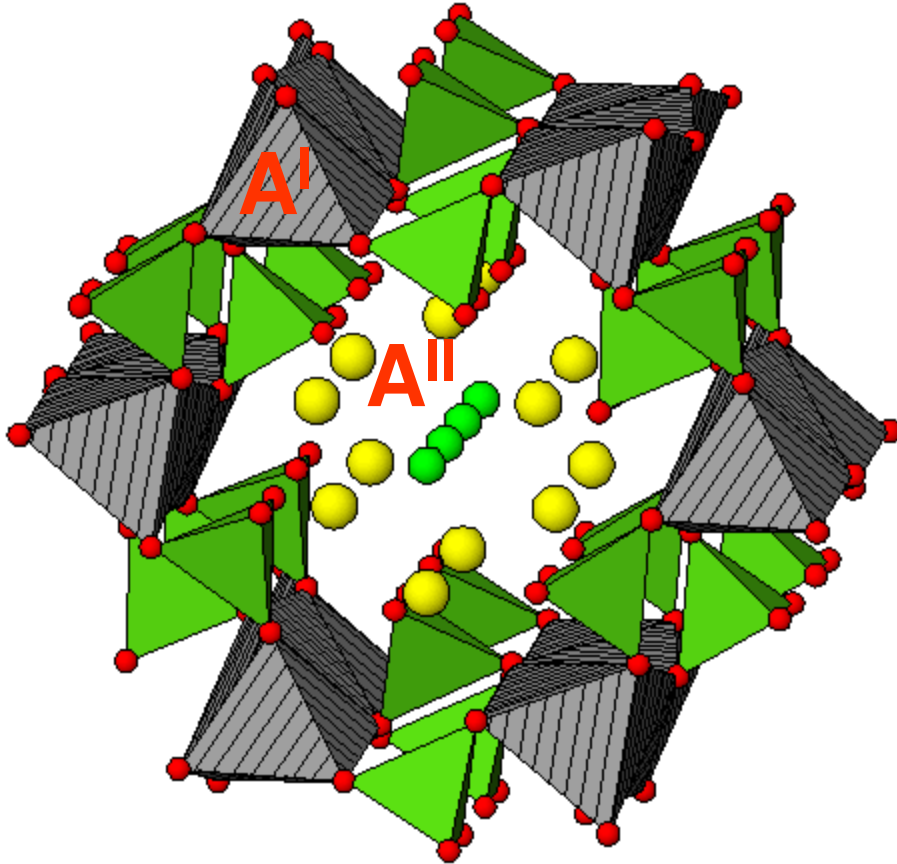


Extreme departures from formal valence are avoided by applying crystal chemical constraints.

Cation Partitioning Between A^I and A^{II}

Partitioning is controlled by size & charge

Consider: $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$
 $\text{Ca}_{10-x}\text{Na}_x(\text{P}_{1-x}\text{S}_x\text{O}_4)_6\text{F}_2$
 $\text{Ca}_{10-x}\text{Nd}_x(\text{P}_{1-x}\text{Si}_x\text{O}_4)_6\text{F}_2$

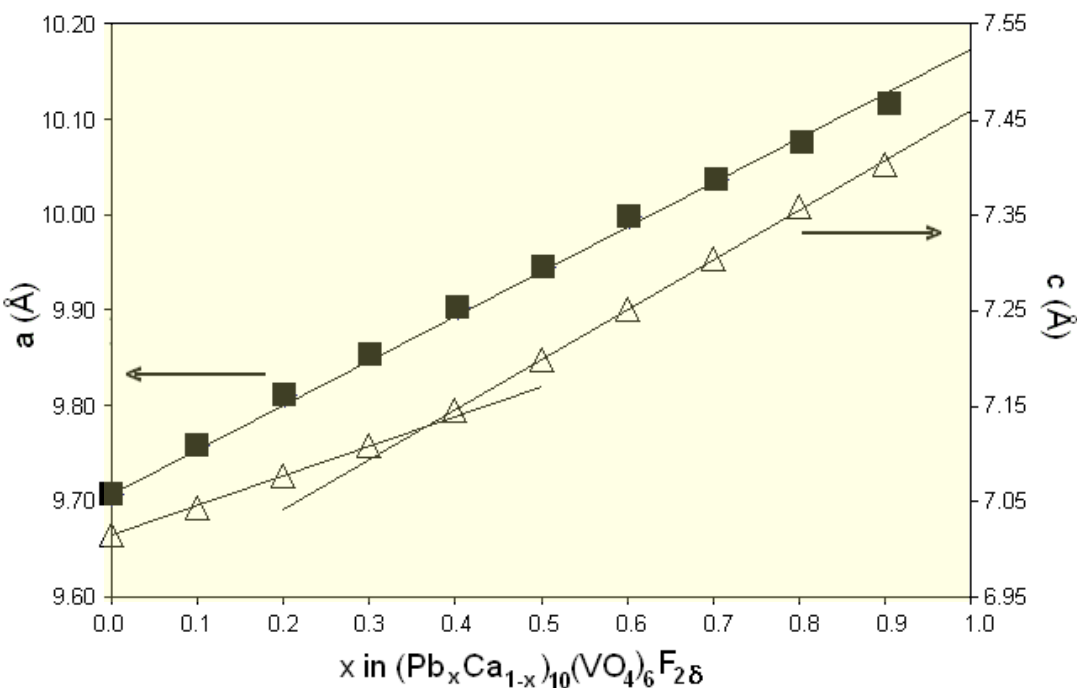


$$A^I < A^{II}$$

←	Ca^{2+}	1.00	→
←	Na^+	1.02	
	Nd^{3+}	0.983	→

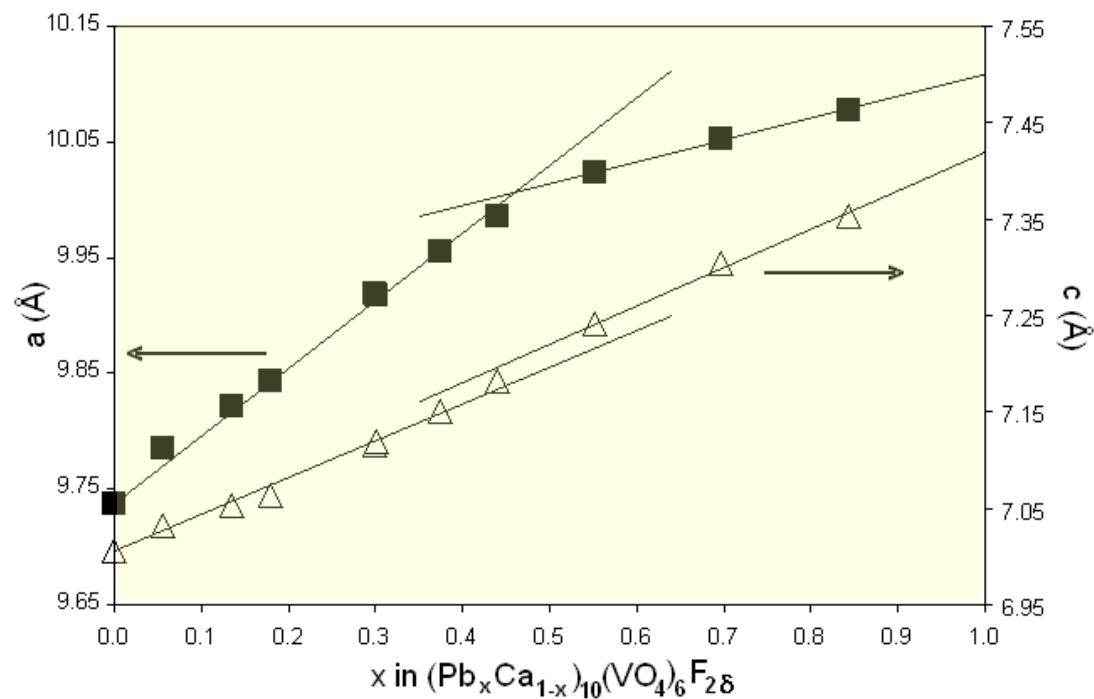
Charge always trumps size

Cation Partitioning in $(\text{Ca}_5\text{Pb}_5)(\text{VO}_4)_6\text{F}_{2-\delta}$



Non-equilibrated 10hr anneal

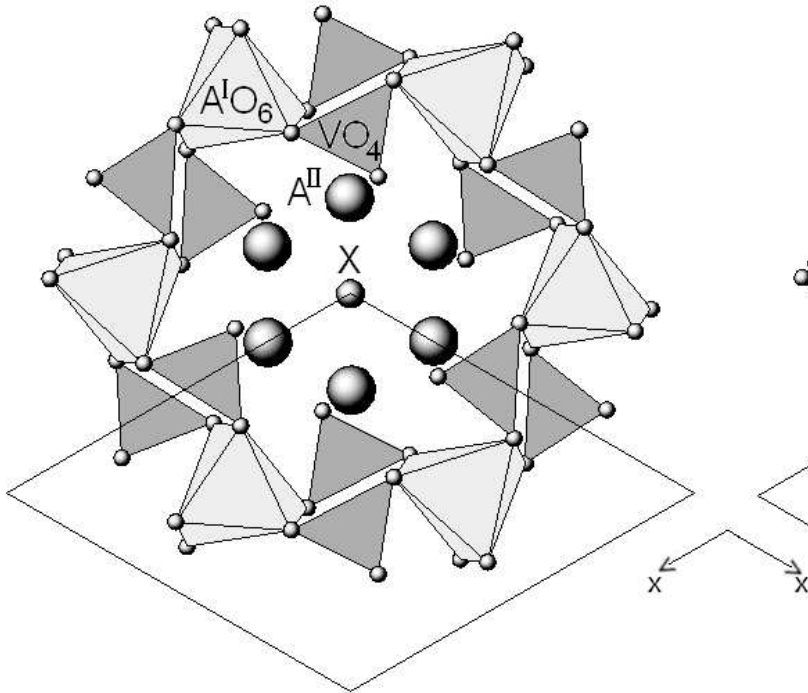
Equilibrated 4w anneal



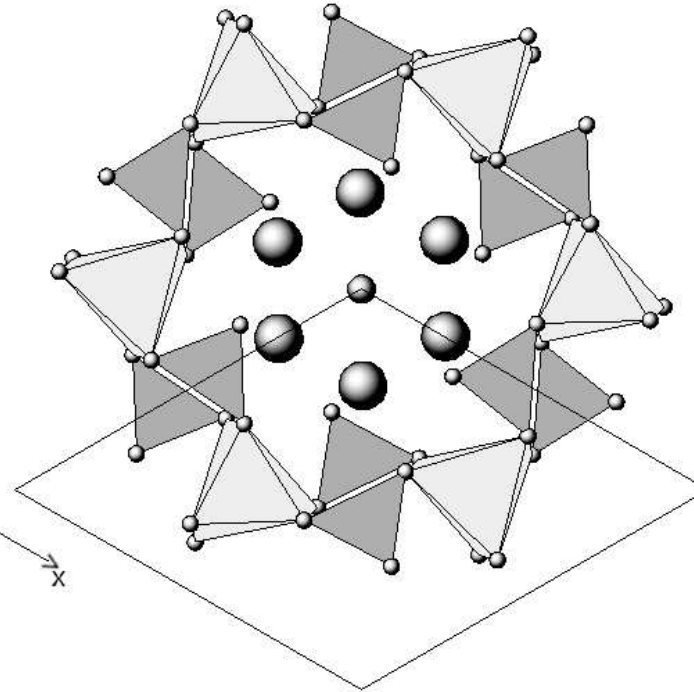
What is the origin of this behaviour?

Crystal Structure Refinement (Pb_5Ca_5)(VO_4) $_6\text{F}_{2-\delta}$

Non-equilibrated
10hr anneal

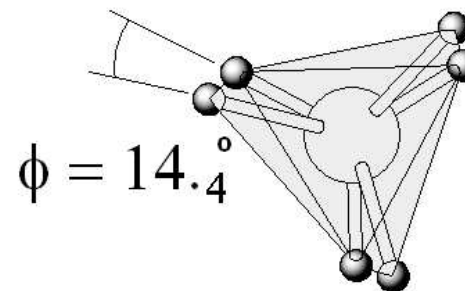
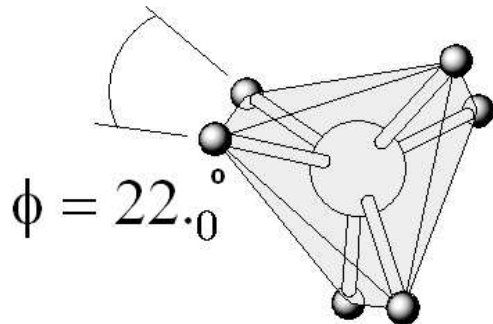


Equilibrated
7w anneal

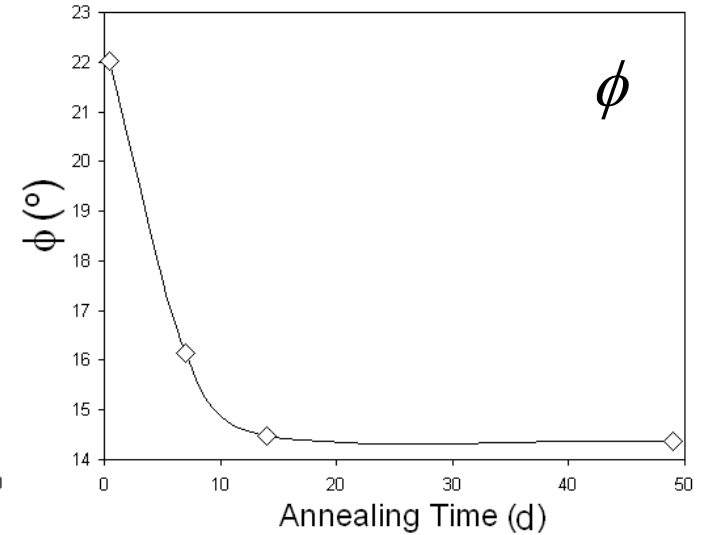
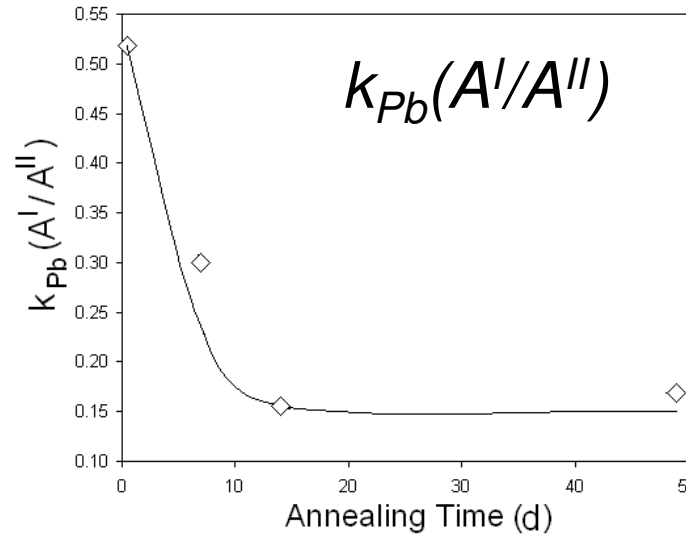
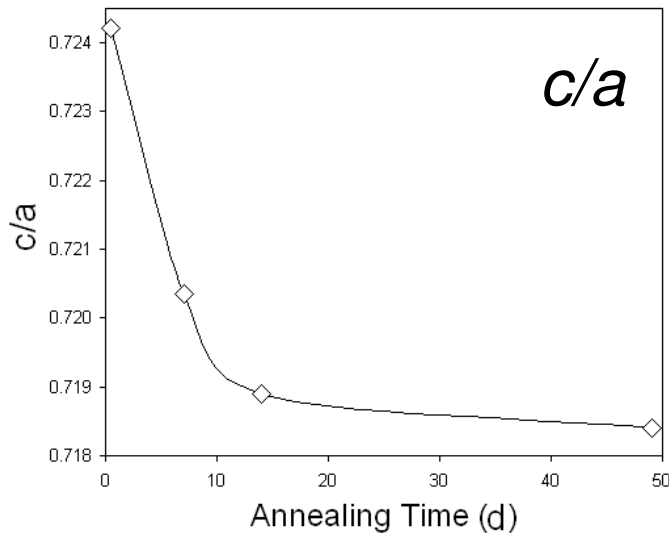


What's Happening

- $2\text{F}^- \leftrightarrow \text{O}^{2-}$
- Ca/Pb ordering
Pb A^{II} enrichment
- Tunnel expansion
- Twist angle reduced

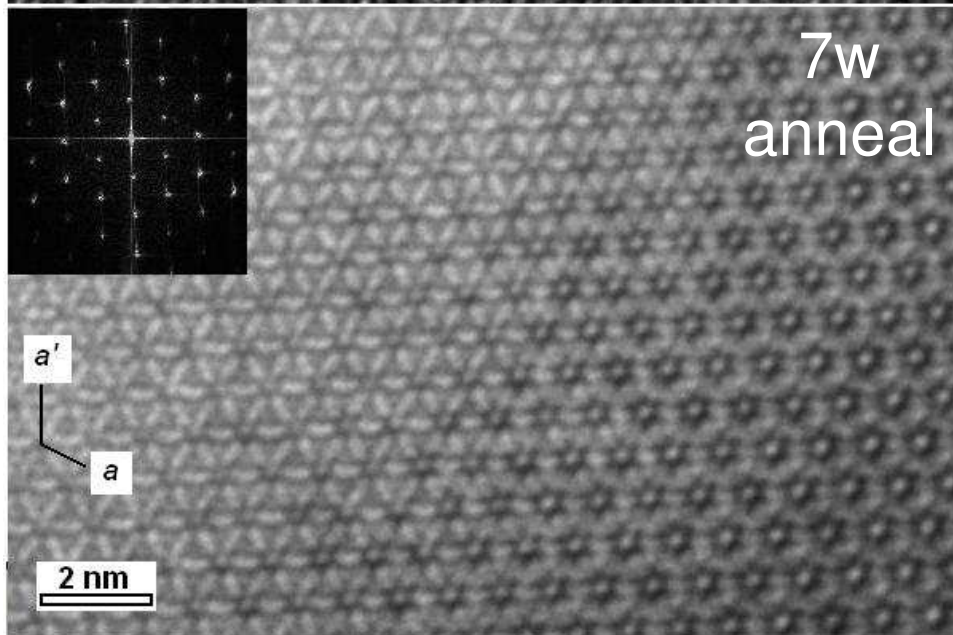
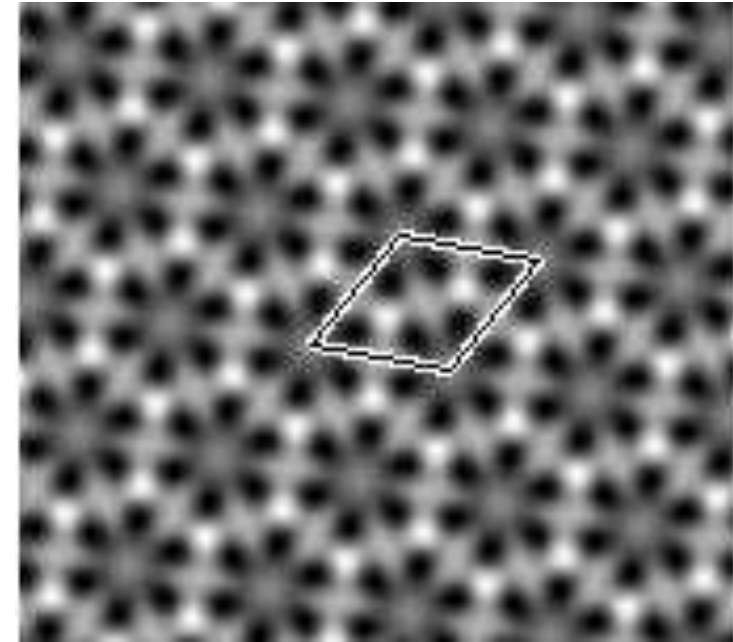
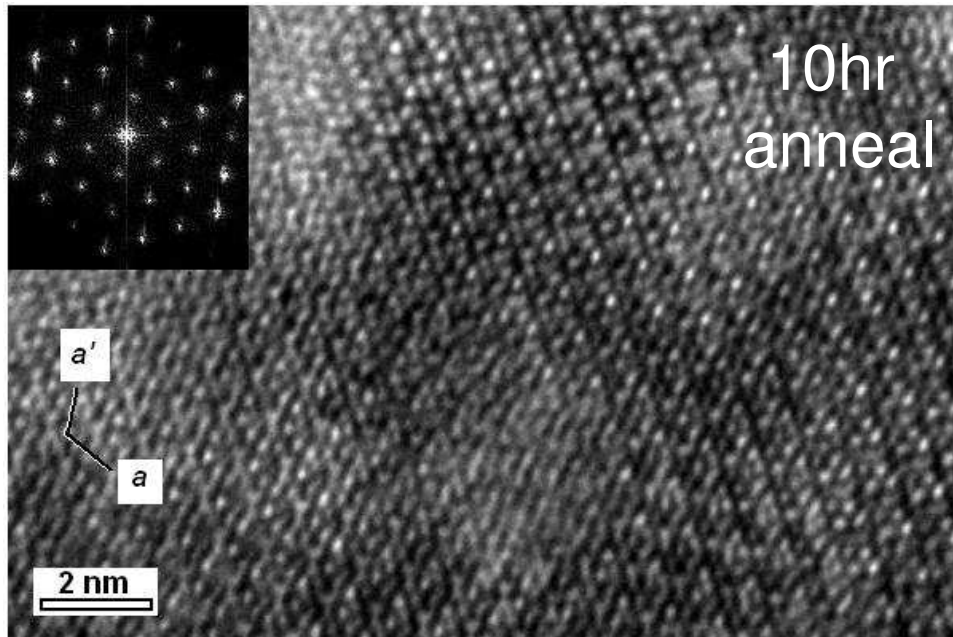


Long Terms Trends $(\text{Pb}_5\text{Ca}_5)(\text{VO}_4)_6\text{F}_{2\delta}$



Annealing Time	Refined Composition	Crystal Chemical Formula
10hr	$x = 4.6_2$	$[\text{Pb}_{1.56}\text{Ca}_{2.44}][\text{Pb}_{2.06}\text{Ca}_{2.94}](\text{VO}_4)_6\text{F}_2$
1 w	$x = 4.9_0$	$[\text{Pb}_{1.12}\text{Ca}_{2.88}][\text{Pb}_{3.78}\text{Ca}_{2.22}](\text{VO}_4)_6(\text{F}_{0.3}\text{O}_{0.7})$
2 w	$x = 4.7_8$	$[\text{Pb}_{0.64}\text{Ca}_{3.36}][\text{Pb}_{4.14}\text{Ca}_{1.96}](\text{VO}_4)_6(\text{F}_{0.25}\text{O}_{0.75})$
7 w	$x = 4.7_6$	$[\text{Pb}_{0.68}\text{Ca}_{3.32}][\text{Pb}_{4.08}\text{Ca}_{1.92}](\text{VO}_4)_6(\text{F}_{0.3}\text{O}_{0.7})$

What Happens at the Unit Cell Scale of $(\text{Pb}_5\text{Ca}_5)(\text{VO}_4)_6\text{F}_{2\delta}$?



- Nanodomains with different Ca/Pb ordering & twist angle
- XRD gives 'average' structure
- Local areas have $p6$ symmetry

Natural Apatites - Brazil Gem Grade Apatite



Nominally $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH},\text{F})$

$[\text{A}_4]$

$(\text{Ca}_{3.946}\text{Na}_{0.052}\text{Y}_{0.001})_{\Sigma=3.999}$

$[\text{A}_6]$

$(\text{Ca}_{5.995}\text{Sr}_{0.003}\text{Pb}_{0.001}\text{RE}^{3+}_{0.008}\text{Th}_{0.004})_{\Sigma=6.011}$

(BO_4)

$(\text{P}_{5.692}\text{Si}_{0.189}\text{S}_{0.132})_{\Sigma=6.013}$

X_2

$(\text{F}_{1.541}\text{Cl}_{0.122}\text{OH}_{0.337})_{\Sigma=2}$

Apatite Immiscibility

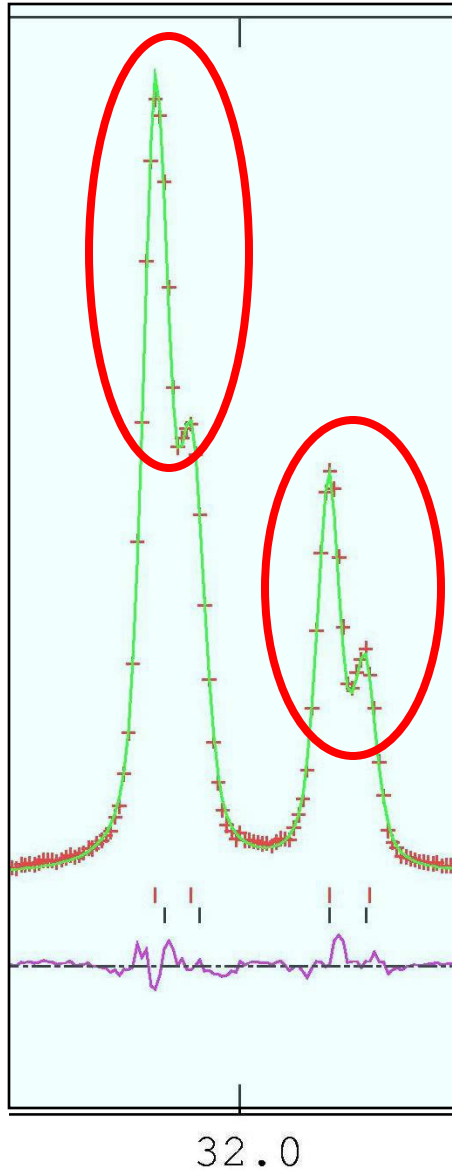
Powder X-ray diffraction showed peak splitting .

host-Ap (F-rich apatite)

$P6_3/m$ $a = 9.410\text{\AA}$ $c = 6.885\text{\AA}$ 71wt% 400 nm

guest-Ap (Cl-rich apatite)

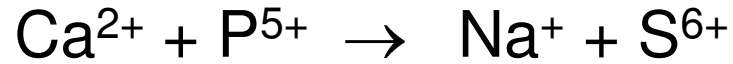
$P6_3/m$ $a = 9.401\text{\AA}$ $c = 6.889\text{\AA}$ 29wt% 250 nm



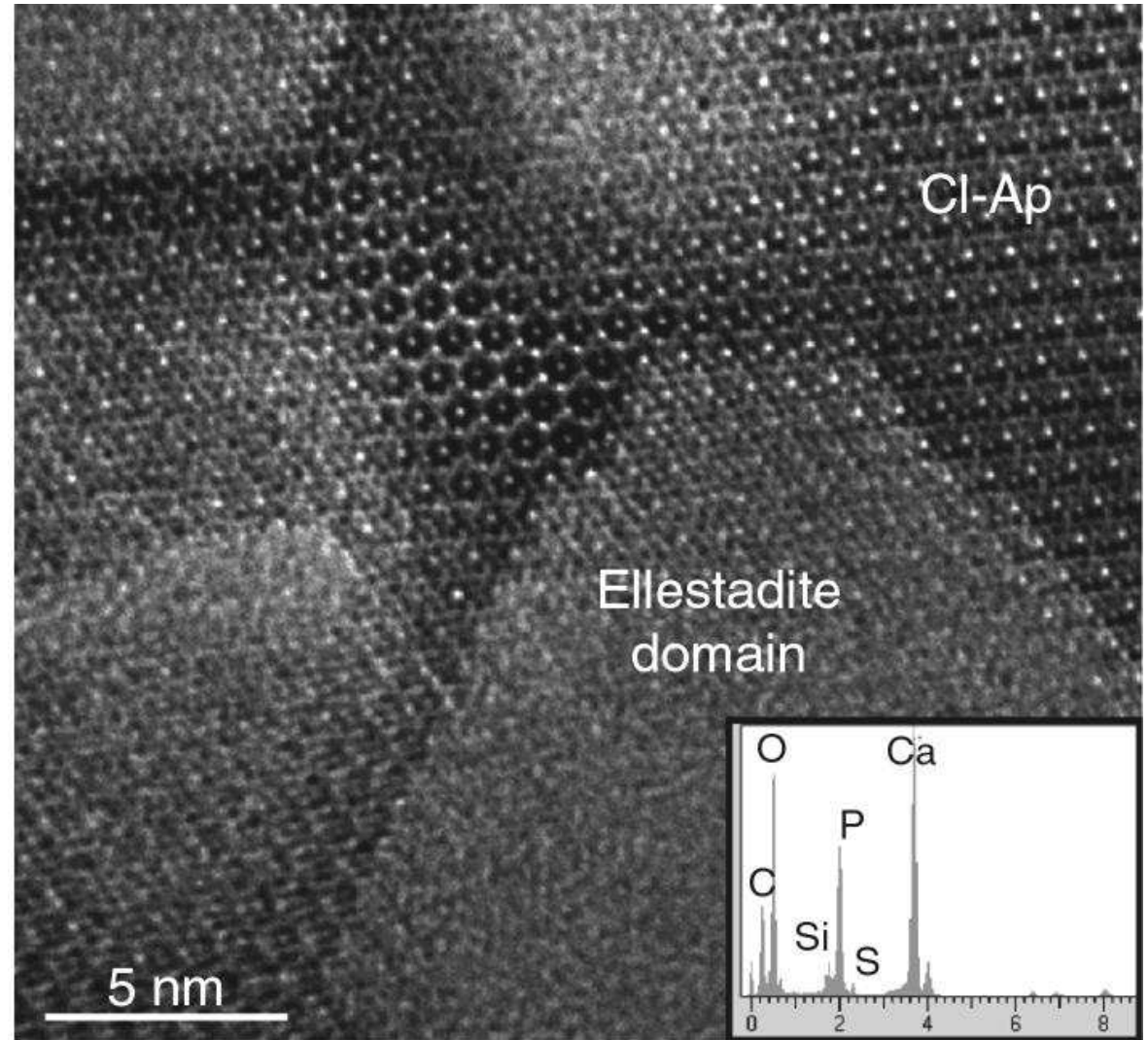
HRTEM-AEM reveal a complex nanostructure.

- At scales one order of magnitude apart
- two area-types were identified
- by their different contrast and beam sensitivity.

Encapsulation of Ellestadite Nanodomains



- Disequilibrium and/or immiscibility is present in both synthetic and natural apatites
- Chemically distinct nanodomains appear to be more common than previously thought
- Ab Initio energy minimization will possibly be useful to explain phase separation



Wrapping Up

- Apatites can be described as microporous frameworks.
- The metaprism twist angle (ϕ) is a highly sensitive probe for recognizing disequilibrium features and false minima in crystal structure refinements.
- Rietveld refinement of apatites appears to be problematic especially for X-rays.
- Restraining refinements using a combination of geometrical parameterization and *ab initio* energy minimization yield refined structures that are consistent with expected trends in twist angles.
- Bond valence sums (BVS) from *ab initio* constrained crystal chemical Rietveld refinements are superior.
- In both synthetic and natural apatites there is a tendency to phase separate into chemically distinct nanodomains.