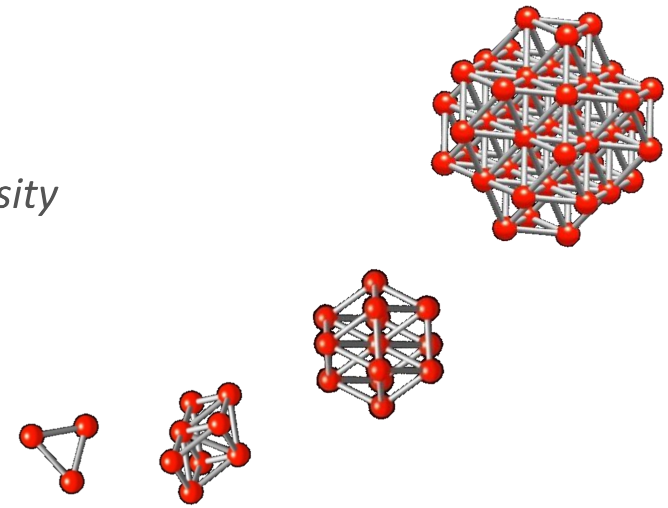
How *in situ* Characterization during Reactions Can Accelerate Materials Synthesis

Karena W. Chapman

Endowed Chair in Materials Chemistry
Department of Chemistry, Stony Brook University



Stony Brook University

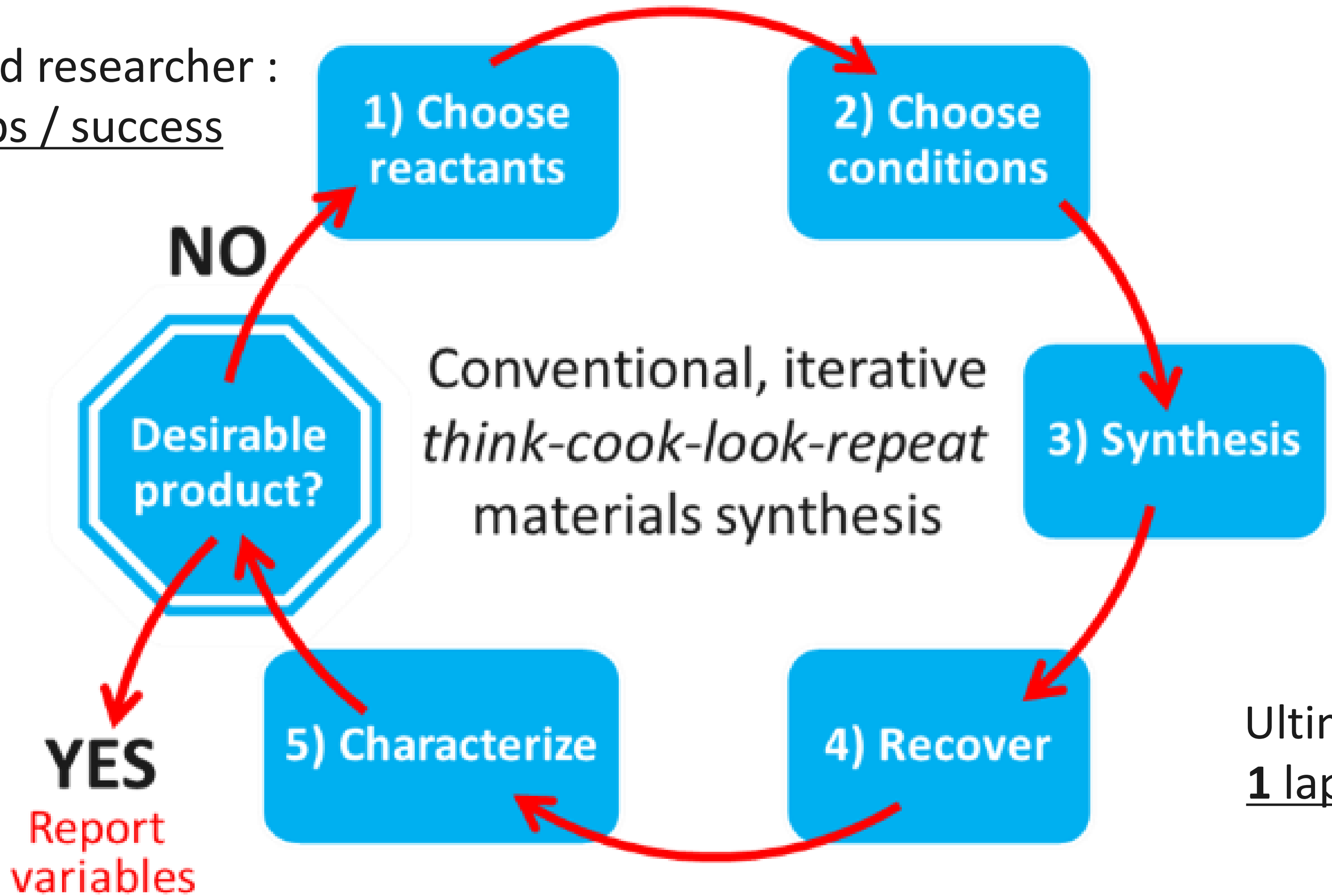
We can predict next generation materials…

How do we close the gap between
***synthesizable** and **synthesized**?*

Conventional materials synthesis is Edisonian

New grad student :
<u>**100** laps / success</u>

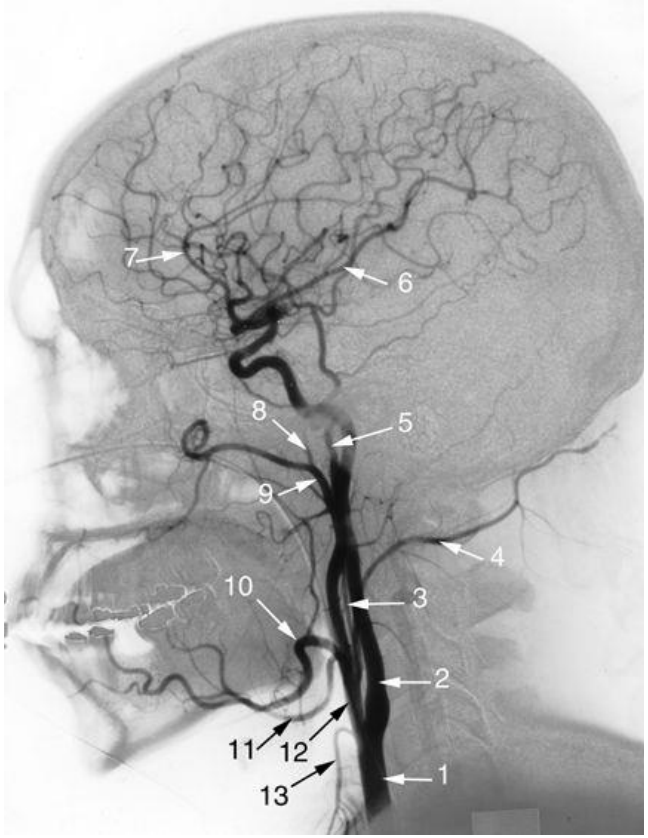
Seasoned researcher :
<u>**10** laps / success</u>

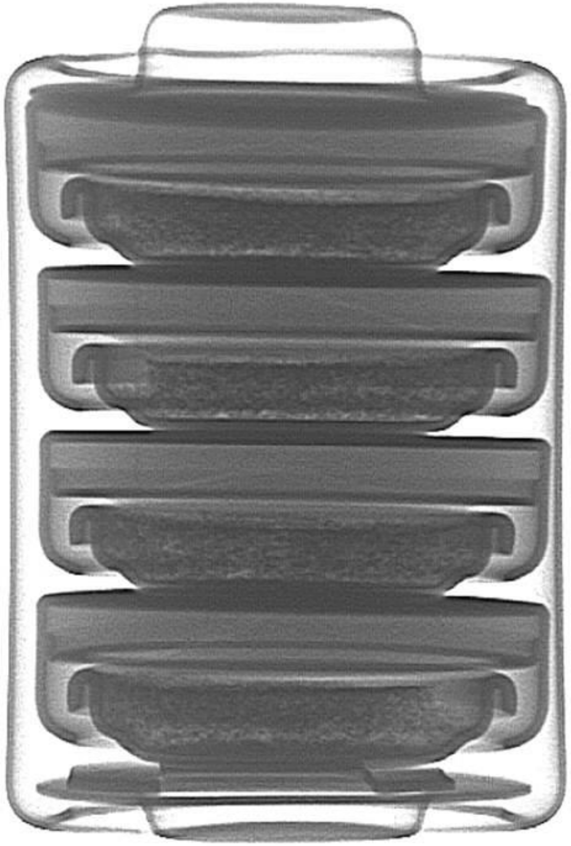


Ultimate goal :
<u>**1** lap / success</u>

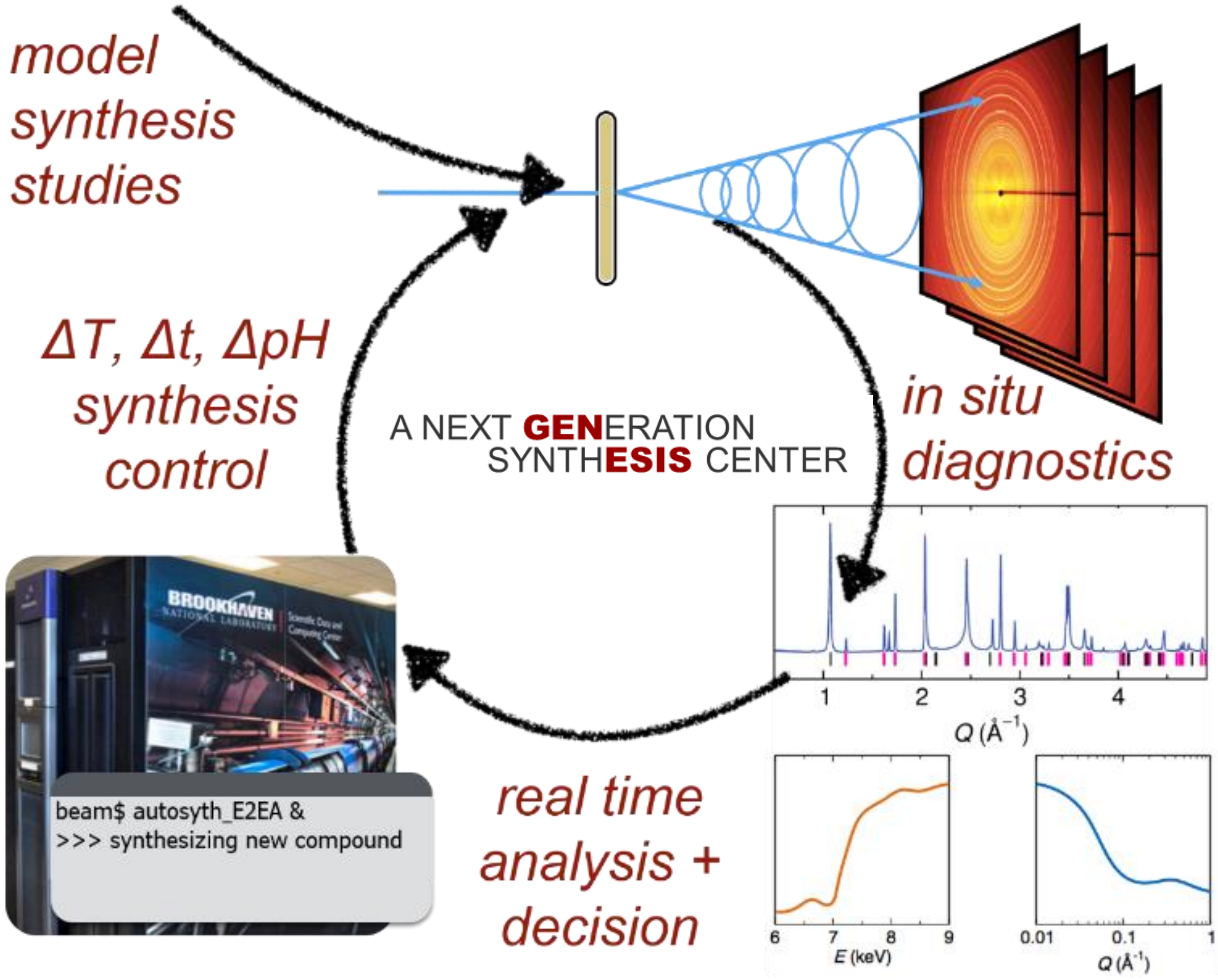
X-rays illuminate reaction pathway and products

X-rays can penetrate reactive systems without damage,
to allow us to probe the mechanism and limitations



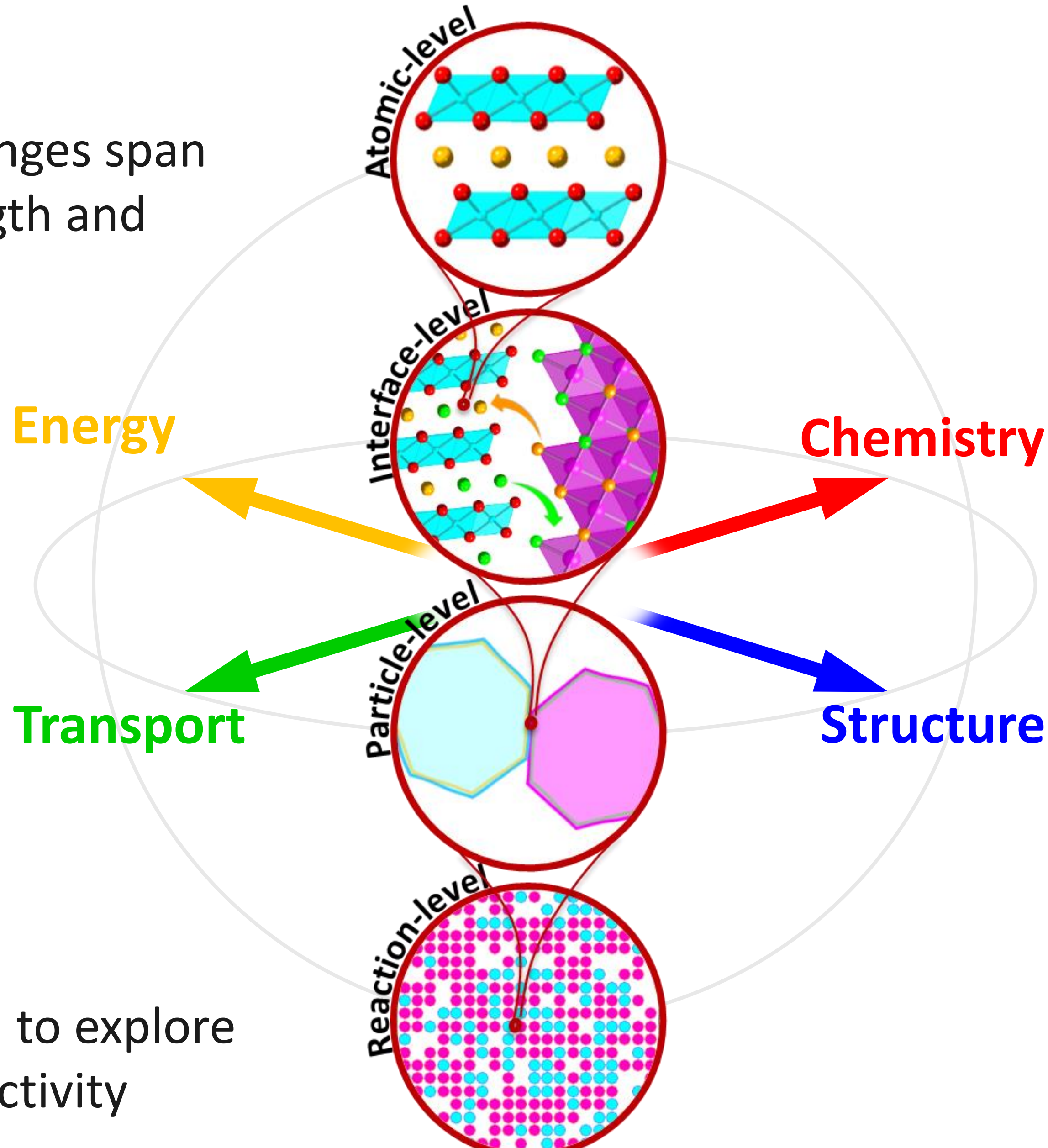


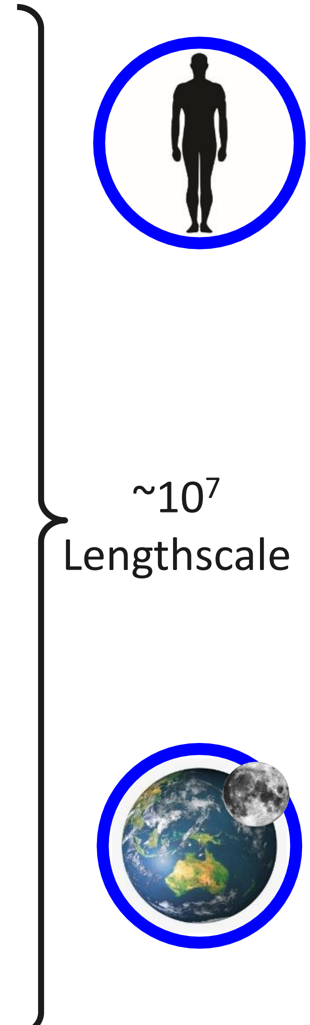
Controlling synthesis to access revolutionary materials



What are the key experimental controls?

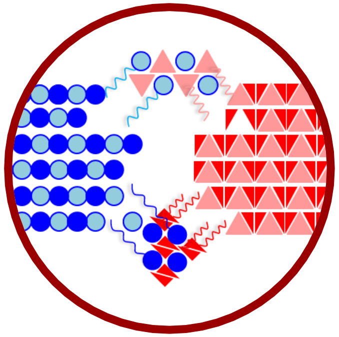
Coupled changes span multiple length and time scales





Operando experiments are essential to explore dynamic reactivity

The challenge of targeting products in the solid-state



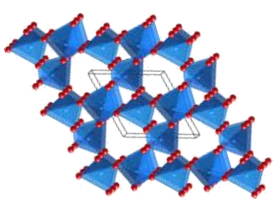
Solid-state reactions are transport-limited.

High temperatures facilitate transport, however,
high temperatures favor the thermodynamic product

Facilitates transport

High Reaction Temperature

Favors thermodynamic product

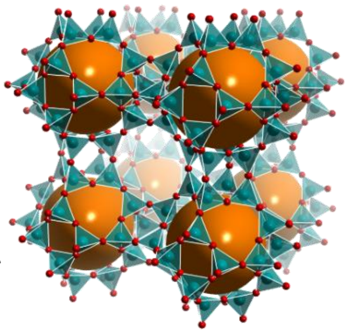


quartz

How can we access the rich variety of metastable phases?

vs

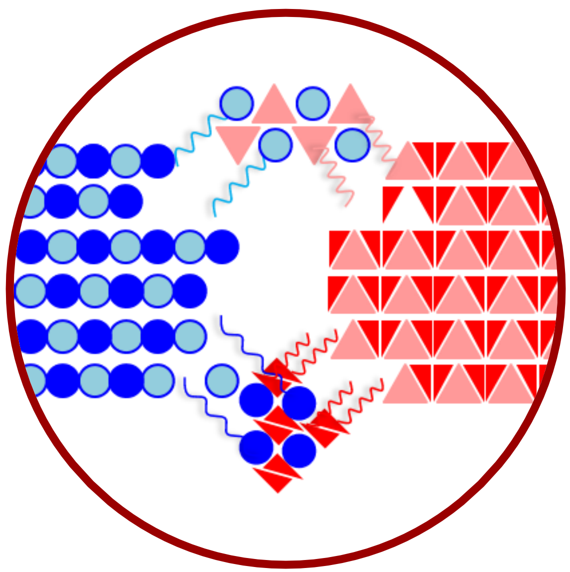
LTA

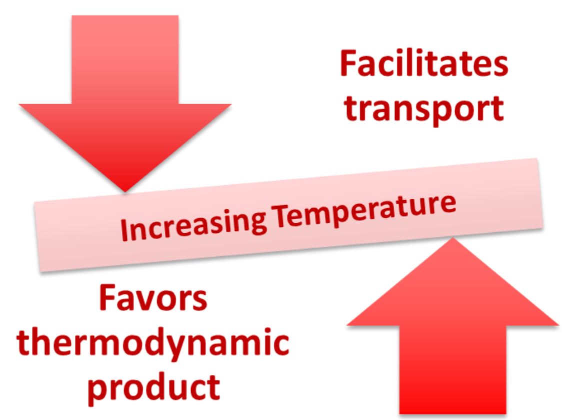


Mechanism of solid-state reactions

AB + CD → AD + BC

Break → **Move** → **Make**
Bonds Atoms/Energy Bonds

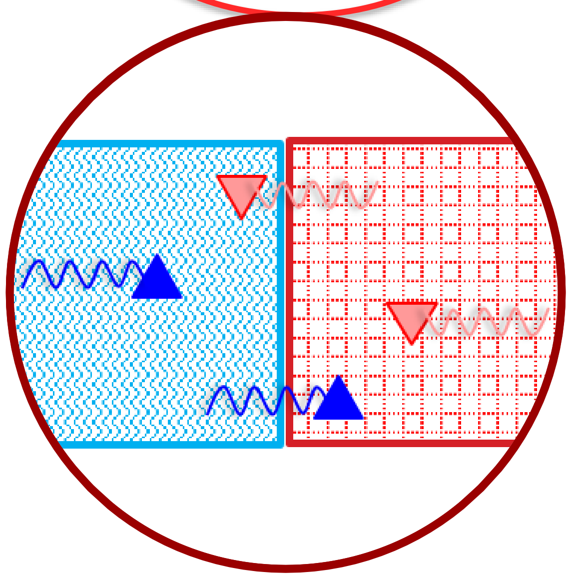


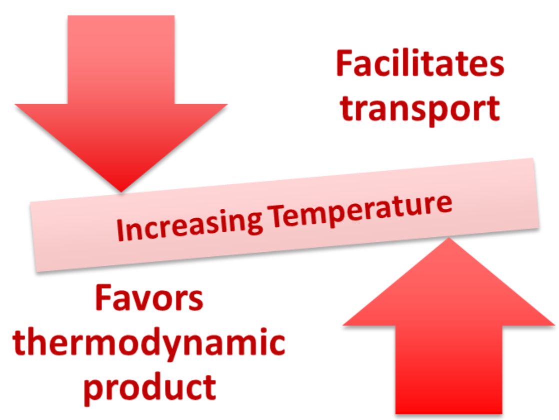


Ion-exchange as a probe of transport limitations

AB + CD → AD + BC

Break Bonds → Move Atoms/Energy → Make Bonds

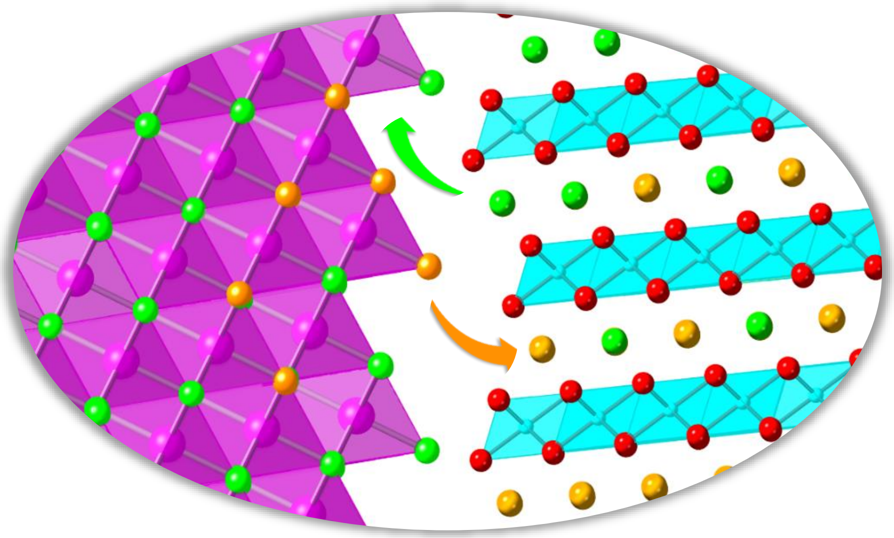




Ion-exchange as a probe of transport limitations

$$LiBr + NaFeO_2 \rightarrow NaBr + LiFeO_2$$

Break Bonds → **Move** Atoms/Energy → **Make** Bonds

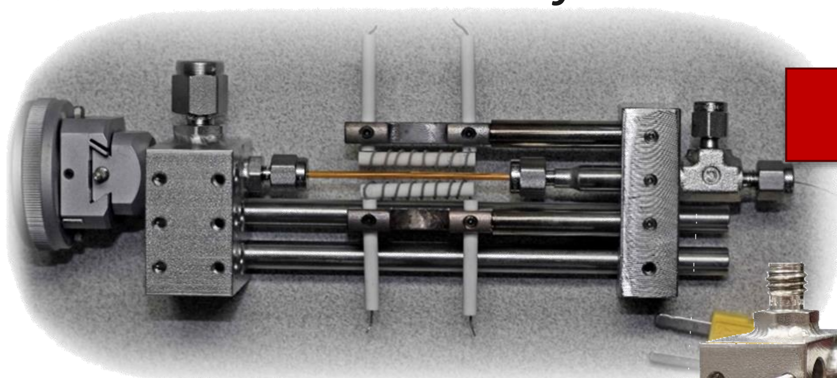


Cooking while looking

To track reaction kinetics

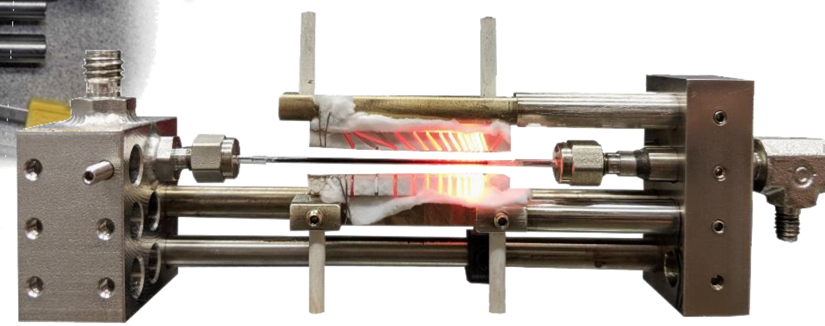
Cook then look
No kinetics

Cook while looking
Kinetic info



J. Appl. Cryst. **2008** 41, 822-824

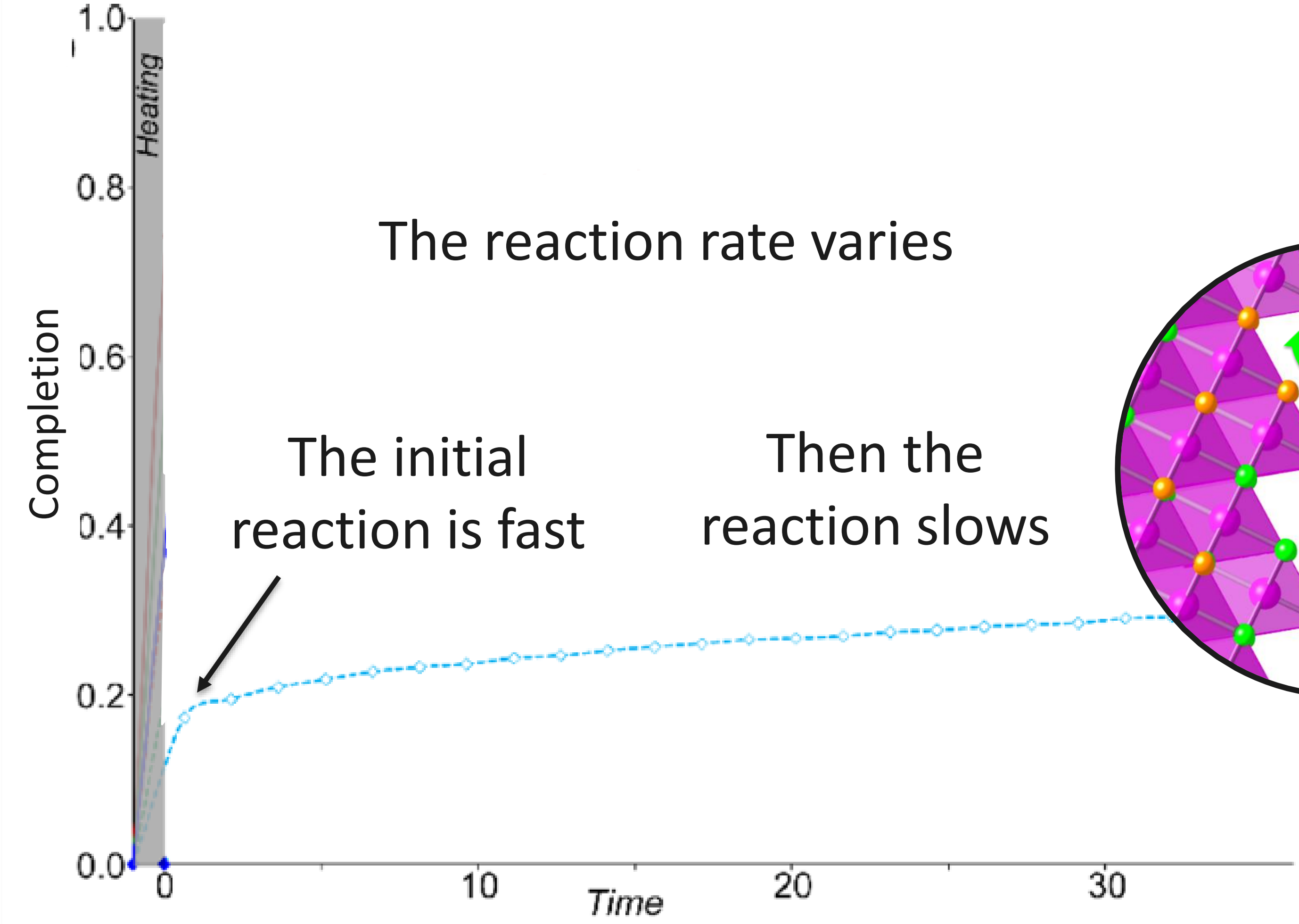
Cook while looking
w T-dependence

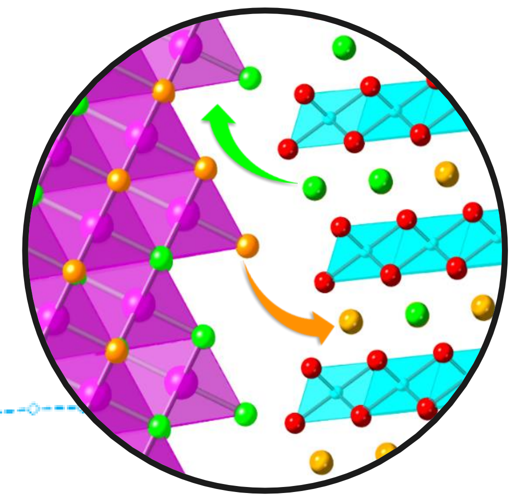


J. Appl. Cryst. **2020**. 53, 662-670

Initial reaction is not rate-limited

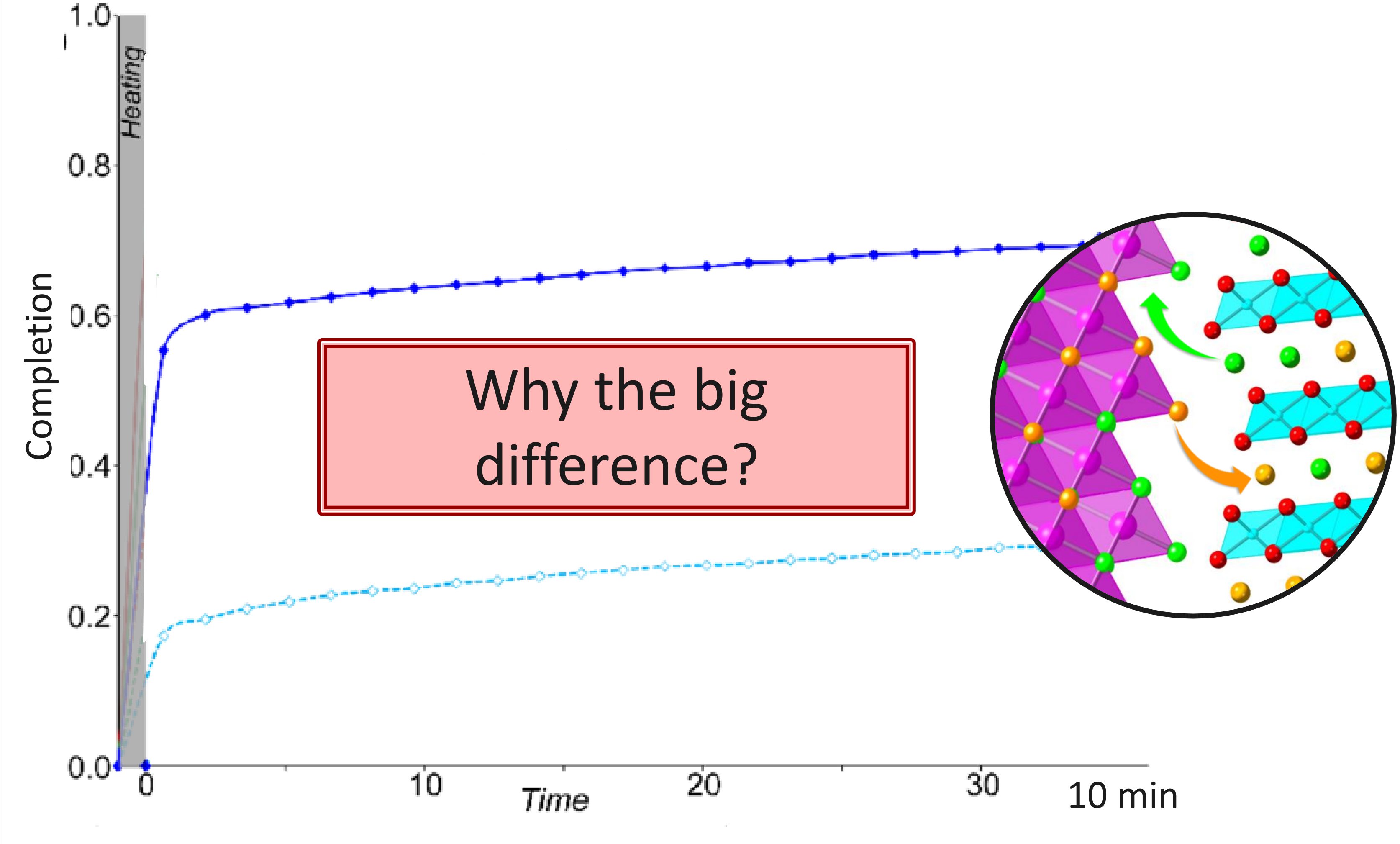
$LiBr + NaFeO_2 \rightarrow NaBr + LiFeO_2$





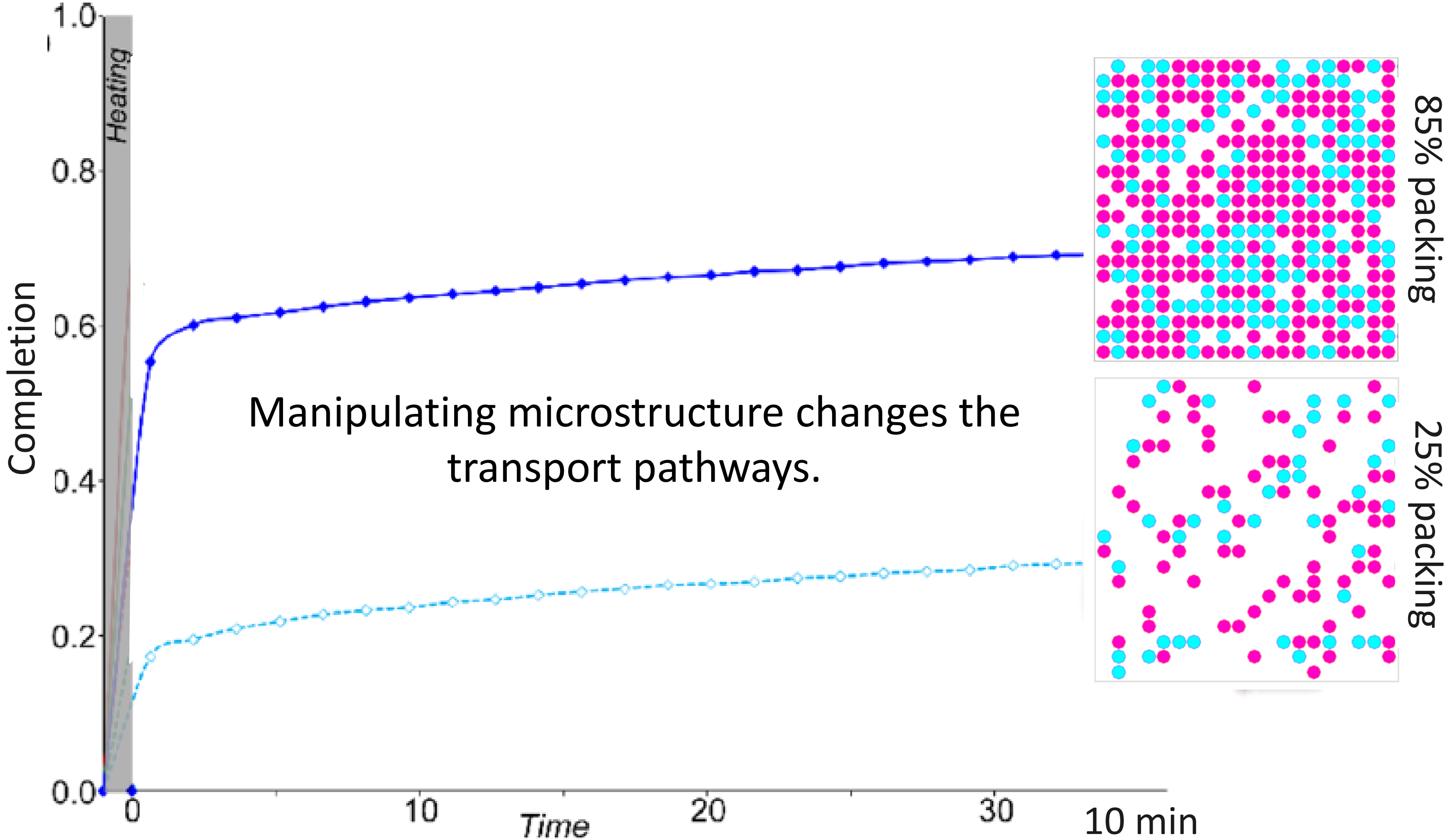
Exploring transport limits using ion-exchange models

$LiBr + NaFeO_2 \rightarrow NaBr + LiFeO_2$



Exploring transport limits using ion-exchange models

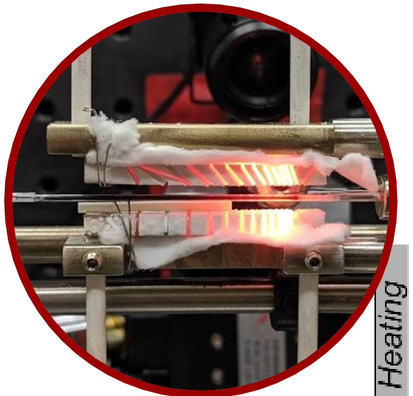
$$LiBr + NaFeO_2 \rightarrow NaBr + LiFeO_2$$



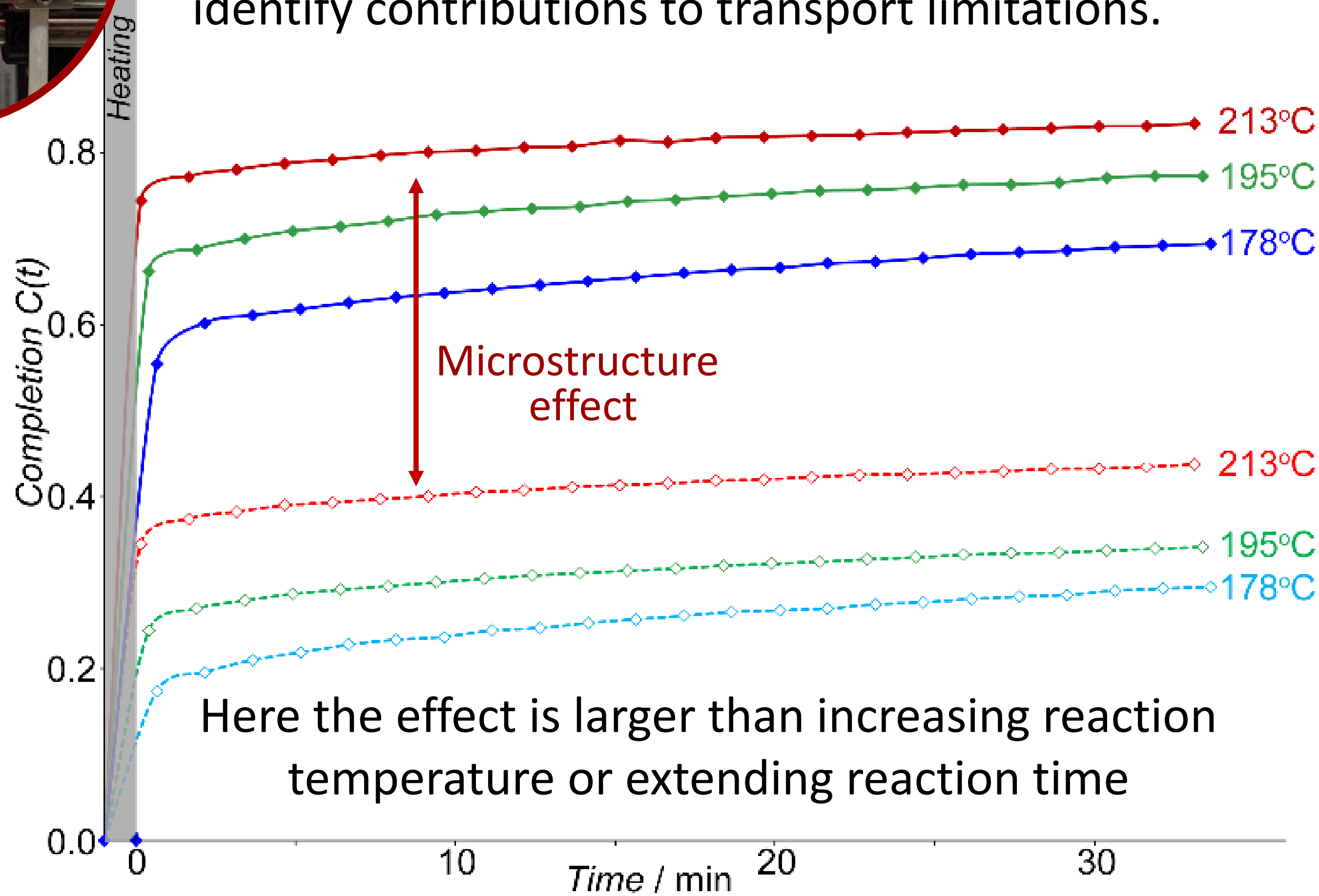
Manipulating microstructure changes the transport pathways.

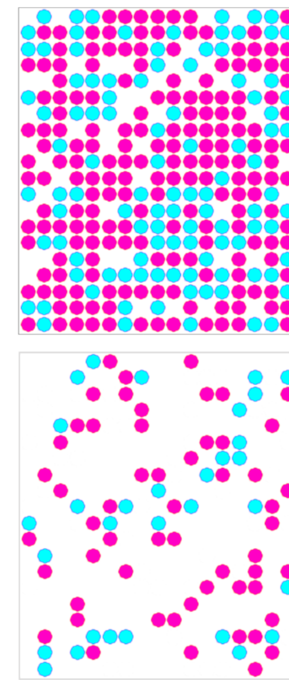
J. Am. Chem. Soc. **2022**, 144, 27, 11975–11979

The Role of Architecture in Controlling Reactivity



We manipulate microstructure to change the transport pathways on different length scales to identify contributions to transport limitations.

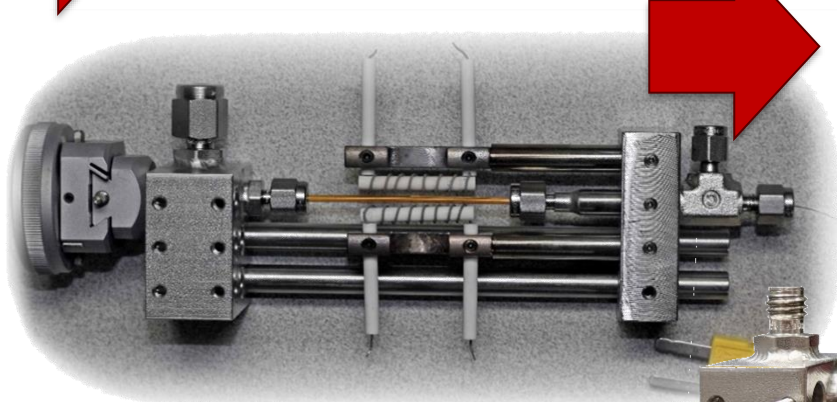




Here the effect is larger than increasing reaction temperature or extending reaction time

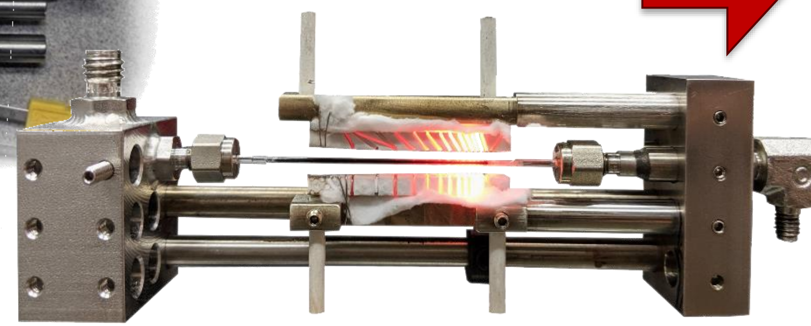
What if the system evolves too fast?

For thermally driven reactions, rapid initiation of the reaction through rapid heating is required to capture the earliest reaction kinetics



J. Appl. Cryst. **2008** 41, 822-824

Heating rate is limited in conventional cells



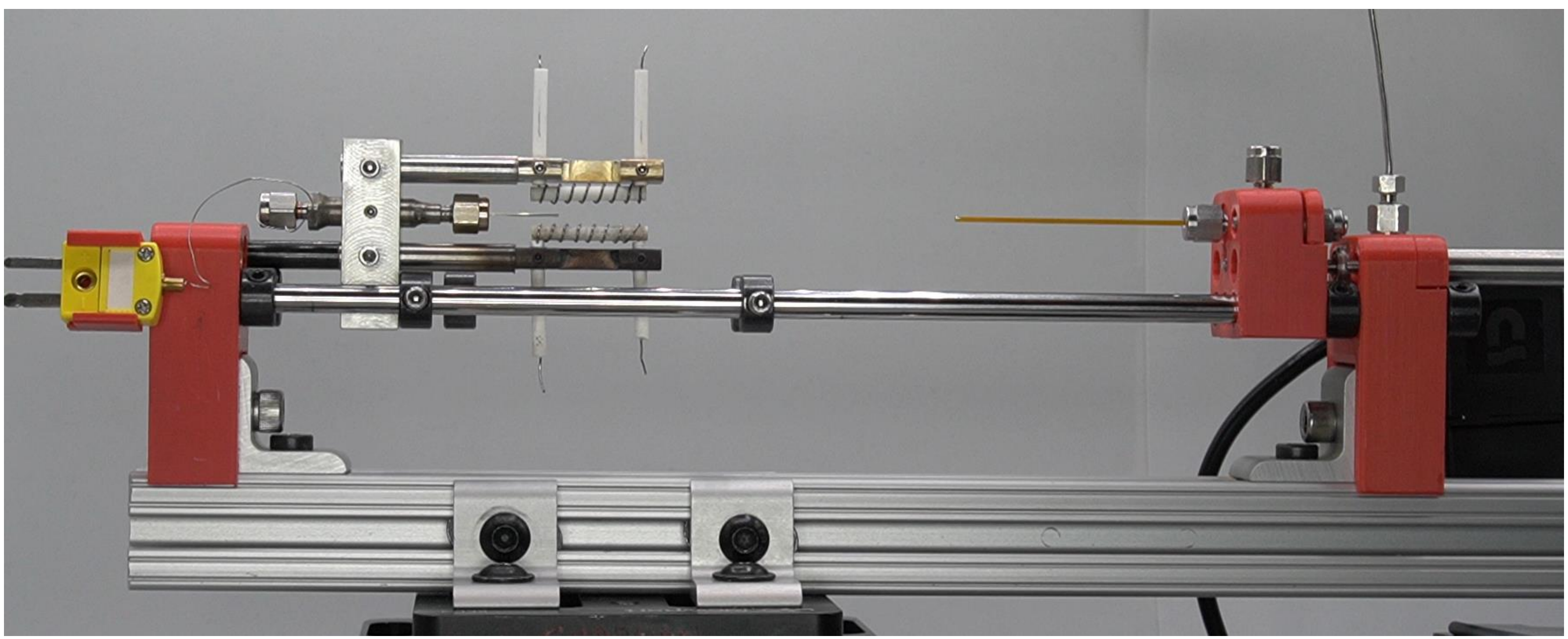
J. Appl. Cryst. **2020**. 53, 662-670

Rapid-Actuating Pneumatic Thermal Reactor - RAPTR

The RAPTR quickly heats and cools samples by translating them into and out of a pre-heated hot zone.

So the heating is only limited by the thermal mass of the sample itself

It adapts the resistive heating elements from the original or thermal gradient heater.

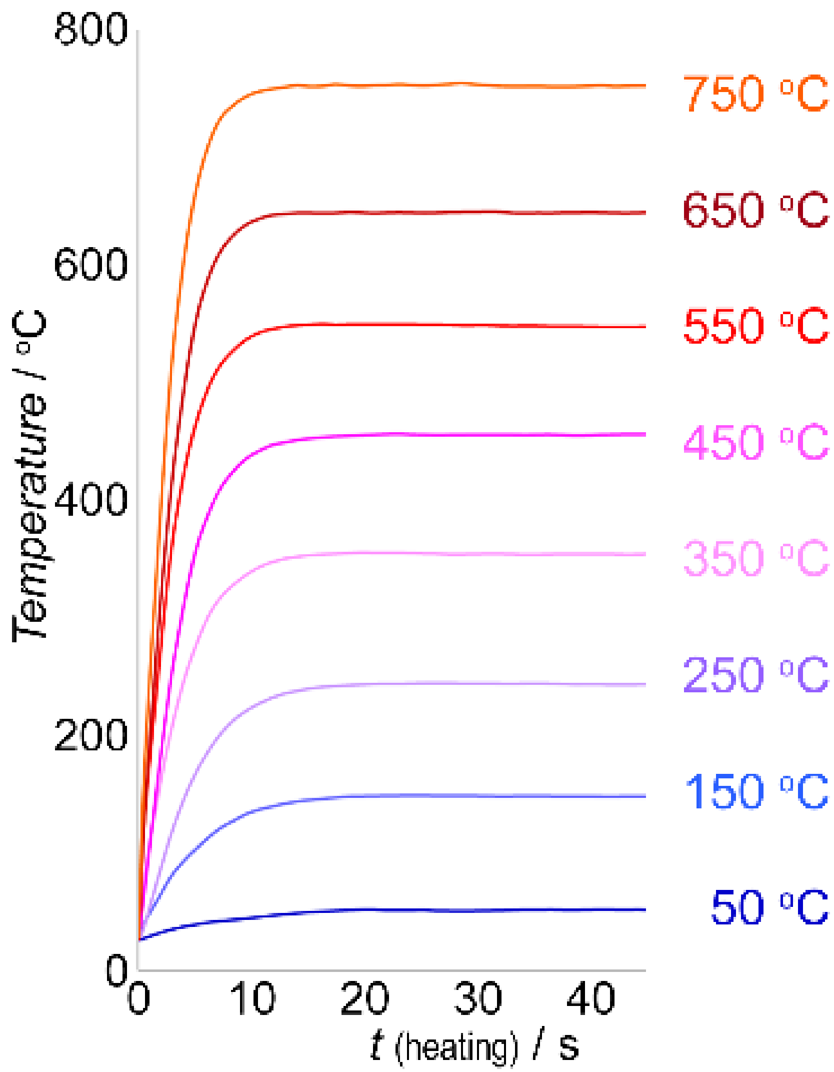


J. Appl. Crystallogr. **2024** 88-93

Fast heating performance

From diffraction thermometry we see the sample reaches the target temperature within 10s.

This means we can explore the fast kinetics in the early stages of the reaction using the RAPTR

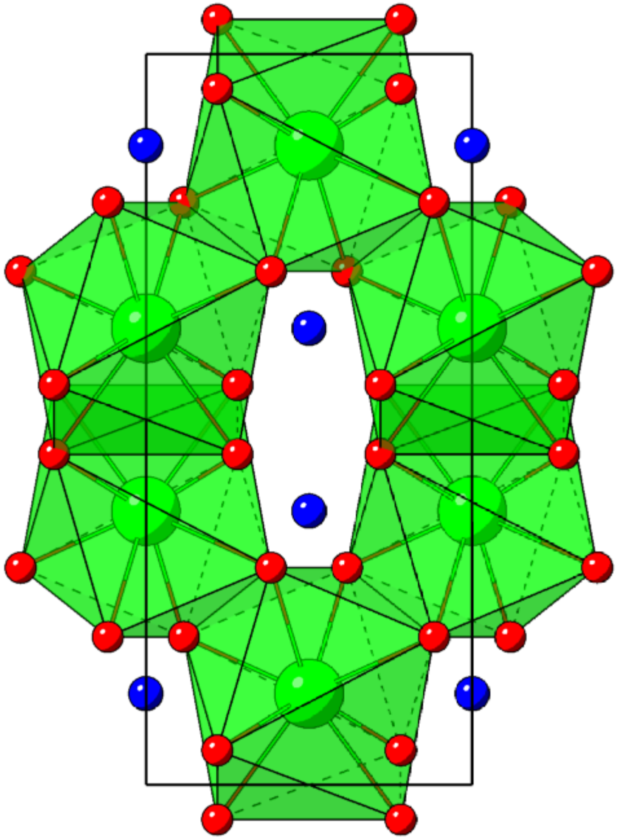


J. Appl. Crystallogr. **2024** 88-93

Test reaction: Scheelite, $PbWO_4$

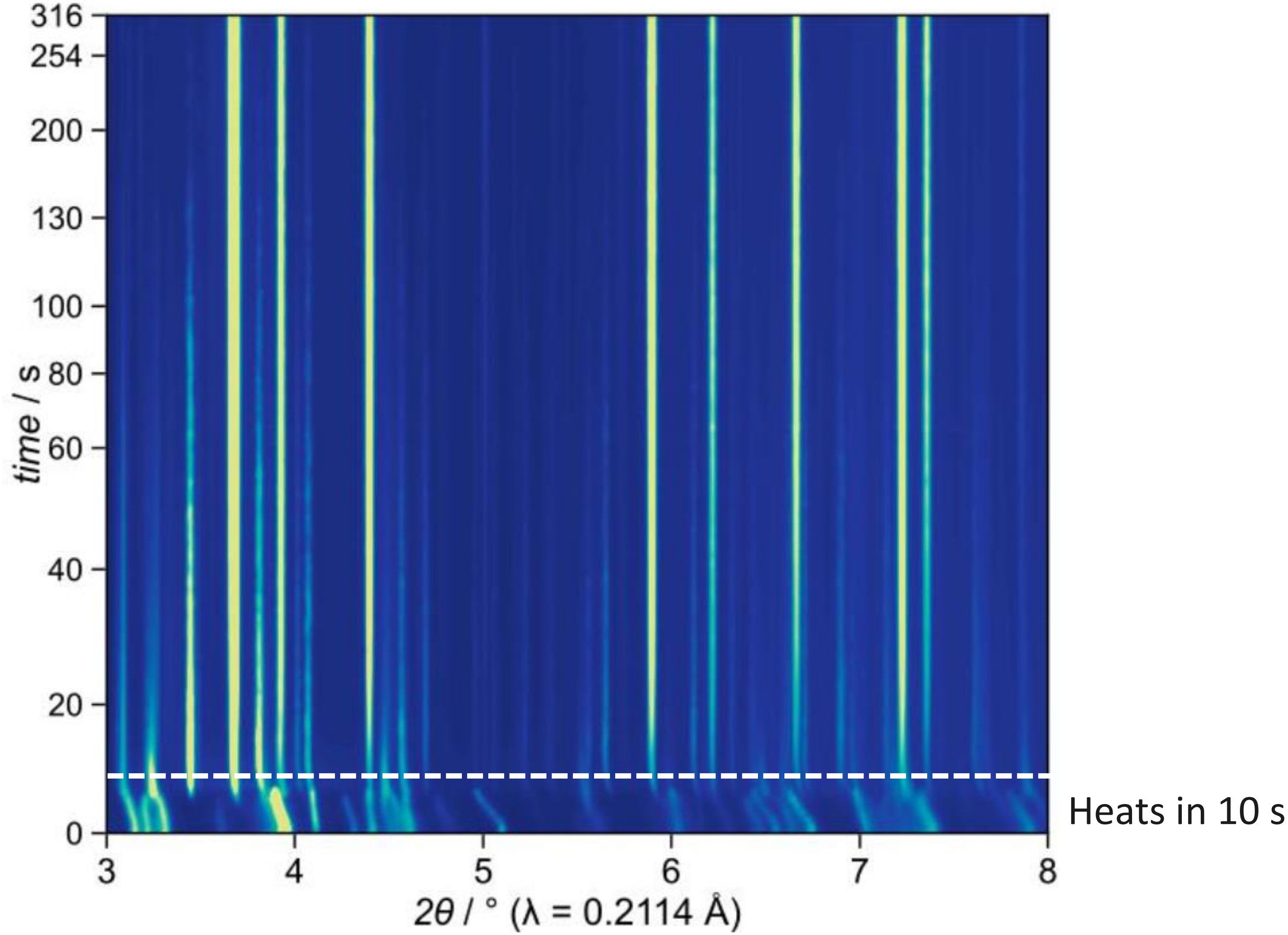
Scheelite-type oxides are synthesized via conventional solid-state synthesis routes, heating in air at high temperatures (700-900 ^{o}C) for hours

$PbO + WO_3 \rightarrow PbWO_4$ <u>overnight</u> @ 750oC



Scheelite $PbWO_4$ has applications as a scintillator material, photocatalyst, and potential <u>solid electrolyte</u> for solid-oxide fuel cells

Scheelite, $PbWO_3$: The first 5 min



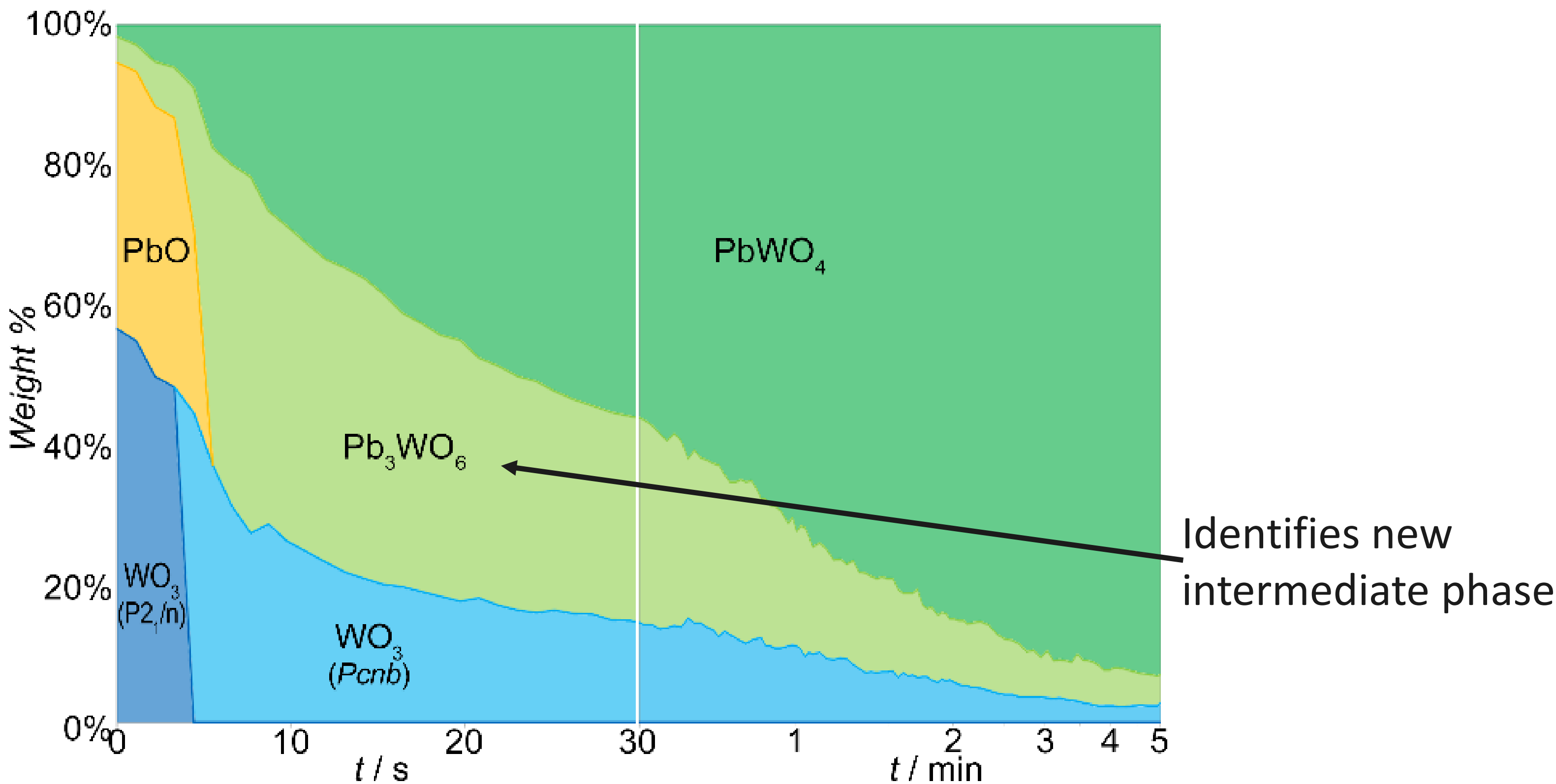
J. Appl. Crystallogr. **2024** 88-93

Scheelite, $PbWO_3$: The first 5 min

$PbO + WO_3 \rightarrow$ Pb-rich $PbO\text{-}WO_3$ melt $+ WO_3$ (1)

Pb-rich $PbO\text{-}WO_3$ melt $+ WO_3 \rightarrow \frac{1}{3}Pb_3WO_6 + \frac{2}{3}WO_3$ (2)

$\frac{1}{3}Pb_3WO_6 + \frac{2}{3}WO_3 \rightarrow PbWO_4$ (3)



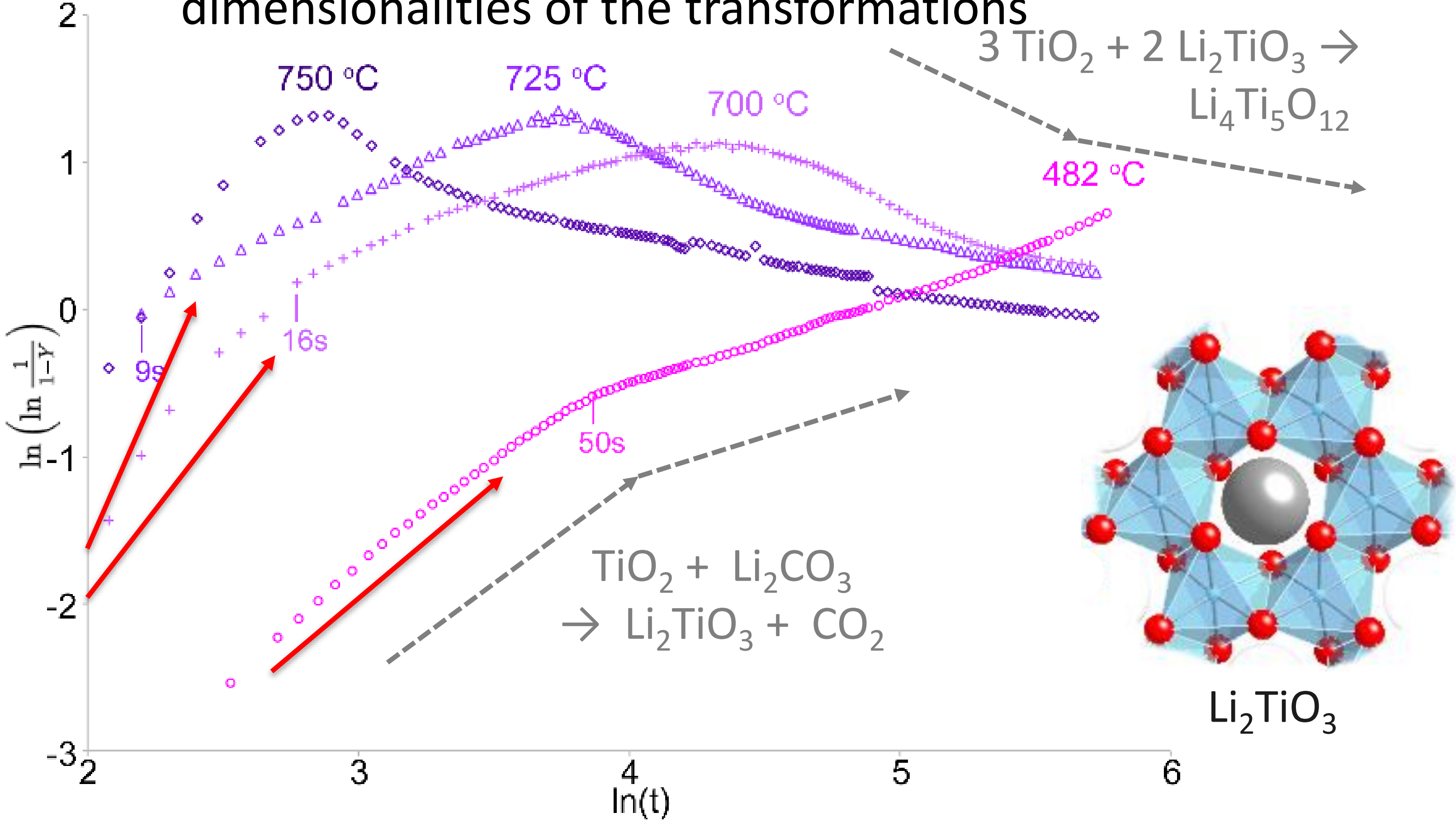
J. Appl. Crystallogr. **2024** 88-93

J. Am. Chem. Soc. **2023** 26545–26549

Fast kinetics are common - Avrami analysis

There are dual kinetic regimes (fast then slower), with a well-defined transition between these.

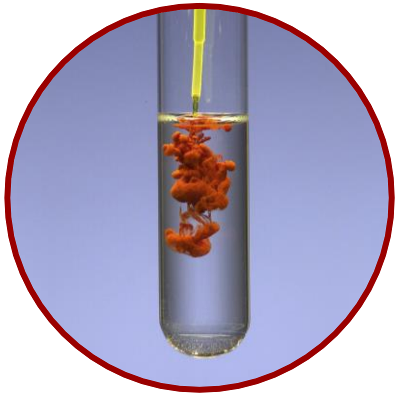
The common slopes of the plot suggest characteristic dimensionalities of the transformations

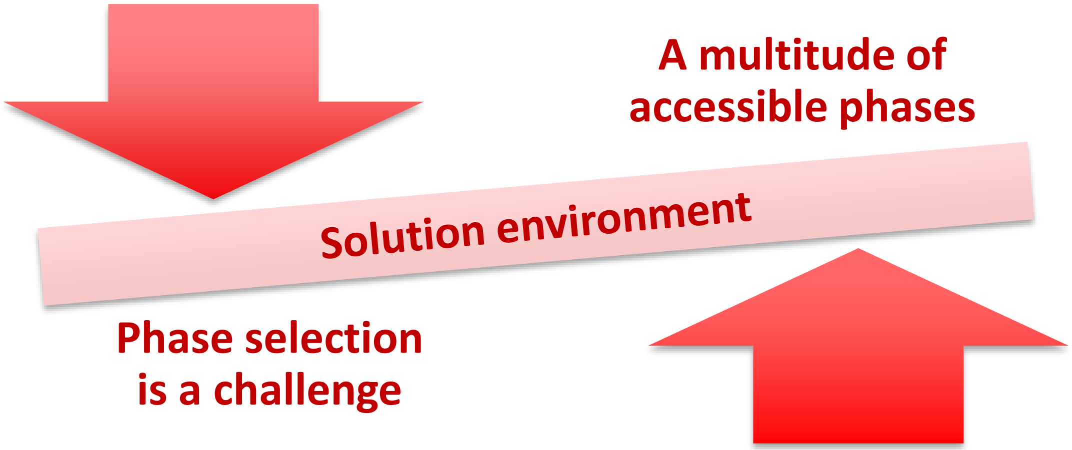


The challenge of targeting products in solution

Solution-phase reactions are dynamic but dilute.

The solution environment mediates transport
but also influences the reaction outcome.
Reactive species are a minor component





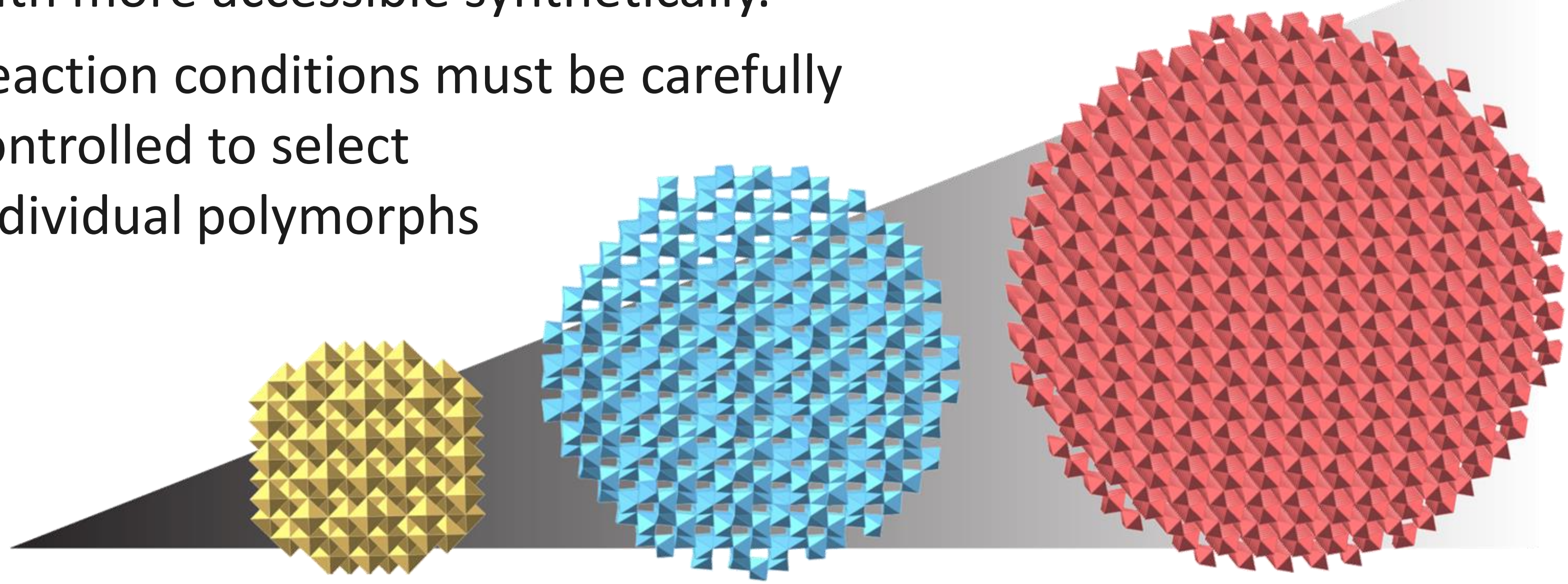
How can we control reaction to target specific metastable phases?

TiO_2 is highly polymorphic

absorbing light *reflecting light* *photocatalysis*

There are 3 naturally occurring polymorphs with more accessible synthetically.

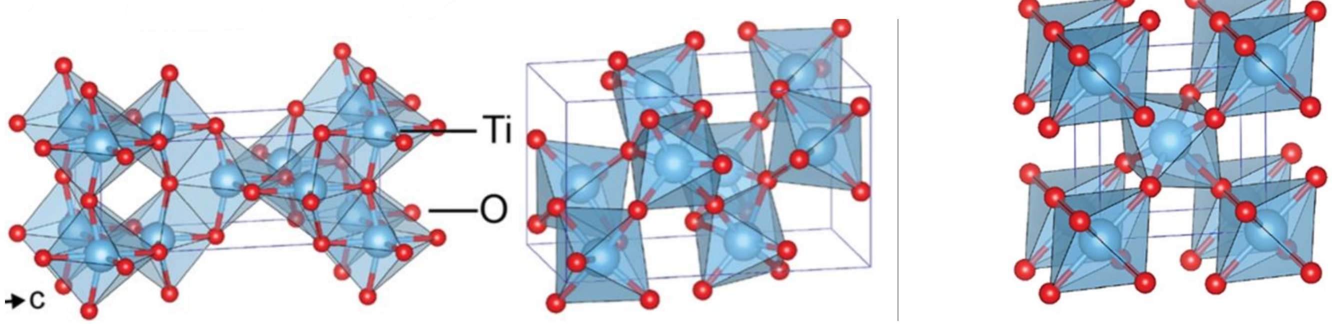
Reaction conditions must be carefully controlled to select individual polymorphs



Anatase
(Metastable)

Brookite
(Metastable)

Rutile

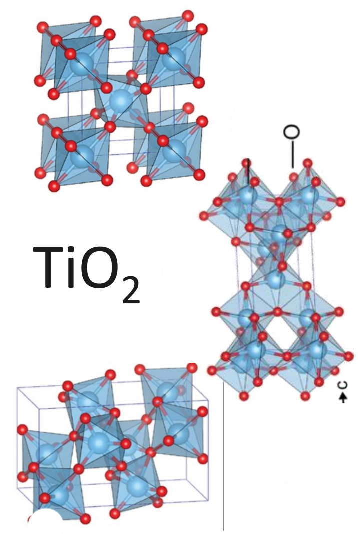


Opening the hydrothermal black box

$TiCl_4$
+
H_2O →

...and then some
CHEMISTRY
happens →

TiO_2



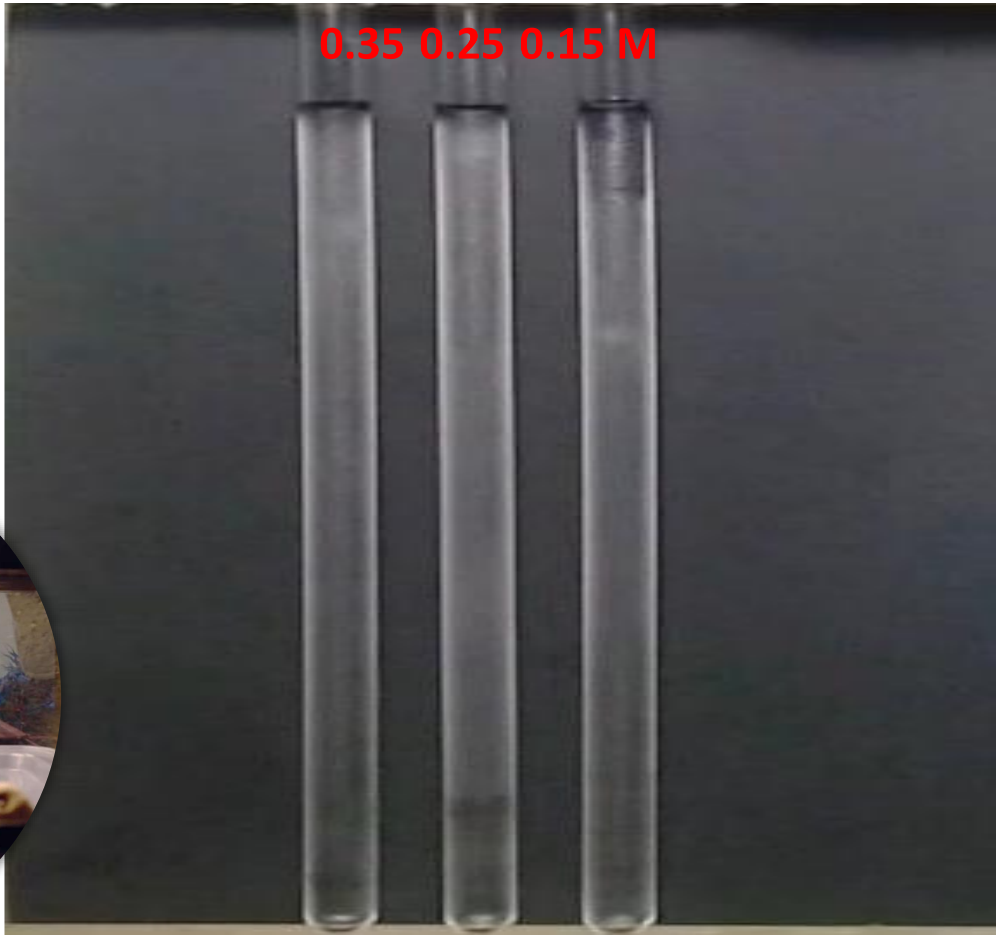
An alternative reaction environment

Hydrothermal reactors that are widely used to synthesize functional inorganic materials are not X-ray friendly.

NMR tubes are suitable for X-ray solution scattering measurements and can withstand hydrothermal pressures

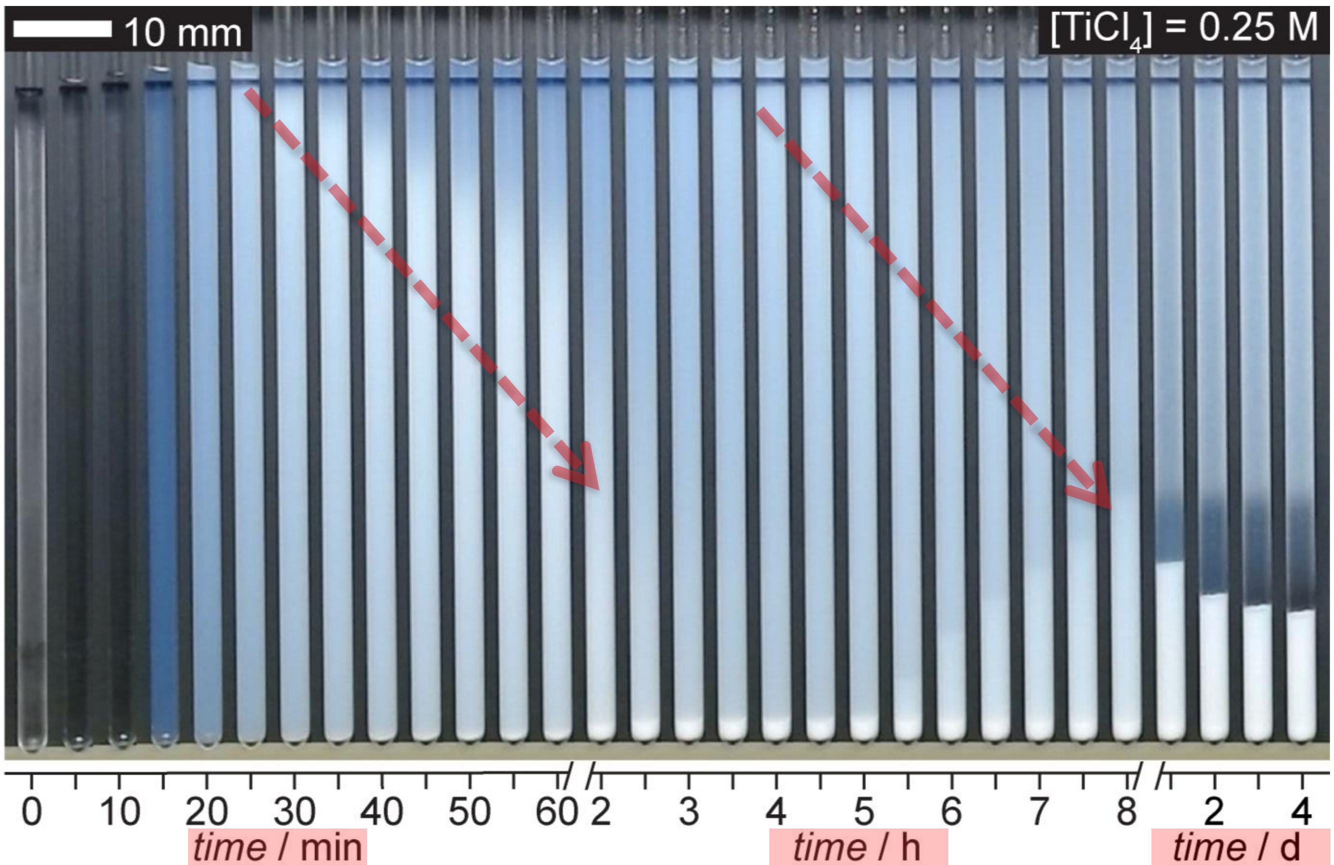
Then we pointed a camera at the oven…

$$TiCl_{4\,(aq)} + 2H_2O_{(l)} \rightarrow TiO_{2\,(s)} + 4H^+_{(aq)} + 4Cl^-_{(aq)}$$



Watching the reaction evolve

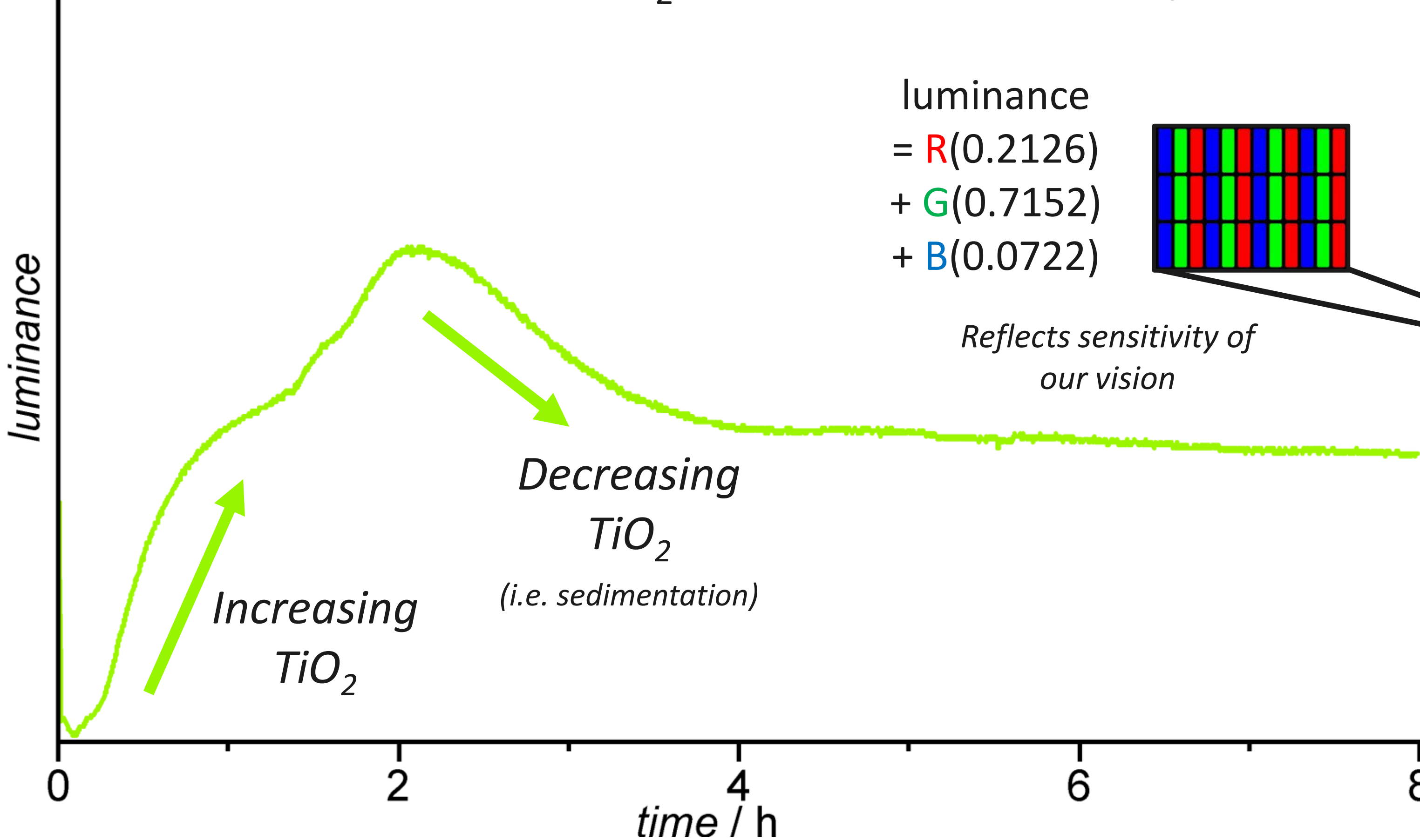
We see <u>2 distinct cycles</u> of TiO_2 formation and sedimentation.

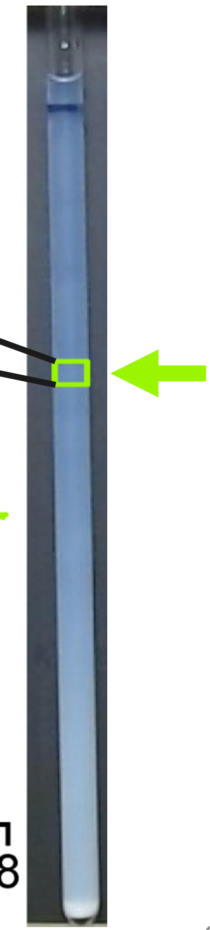


J. Am. Chem. Soc. 2024, 10745–10752

Quantifying product concentration with luminance

The luminance of pixels (i.e., brightness / whiteness) is correlated to TiO_2 concentration at that point

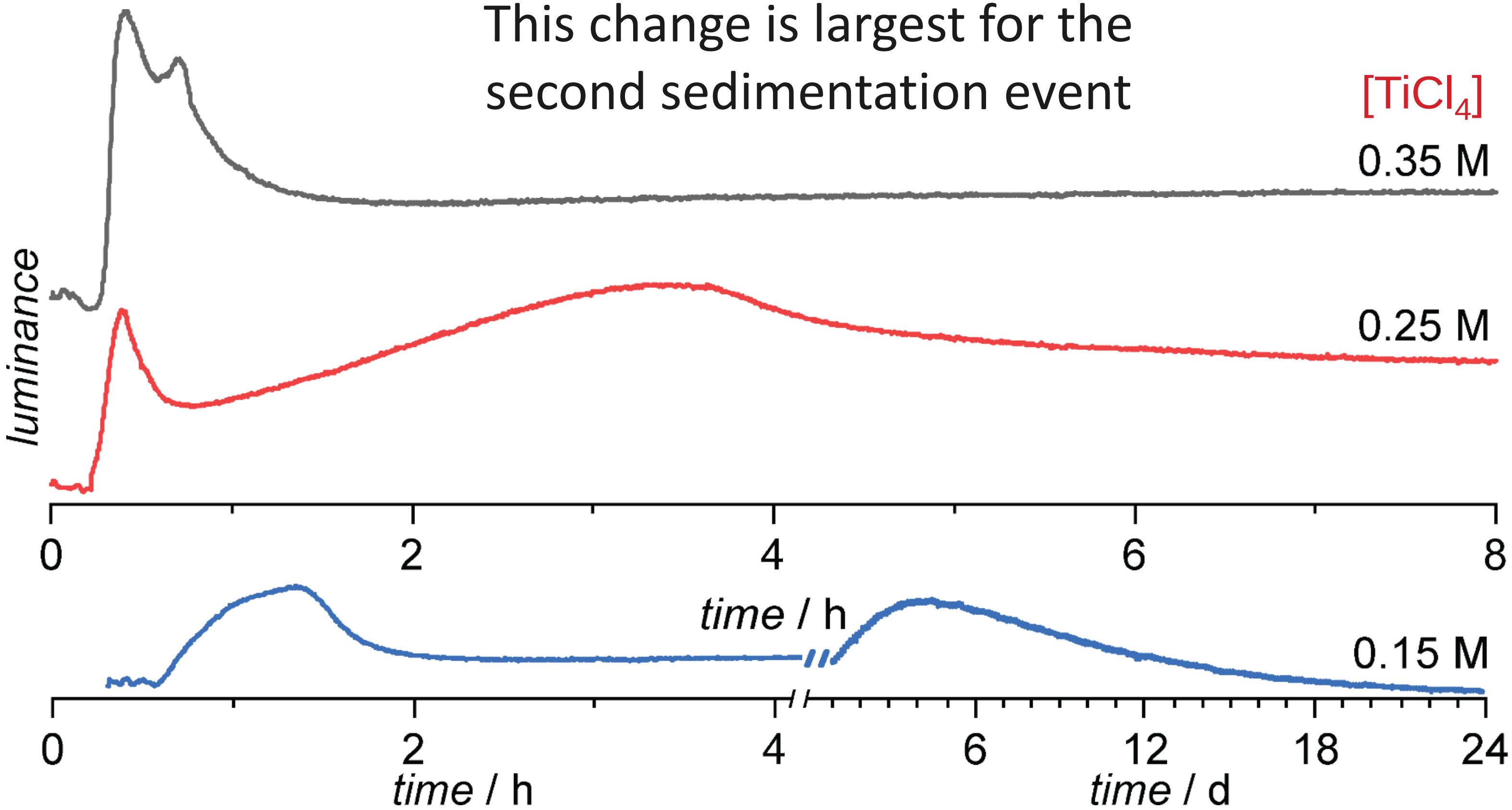




Reaction kinetics over weeks

Lower concentrations of the $TiCl_4$ reaction leads to *slower* TiO_2 formation and sedimentation.

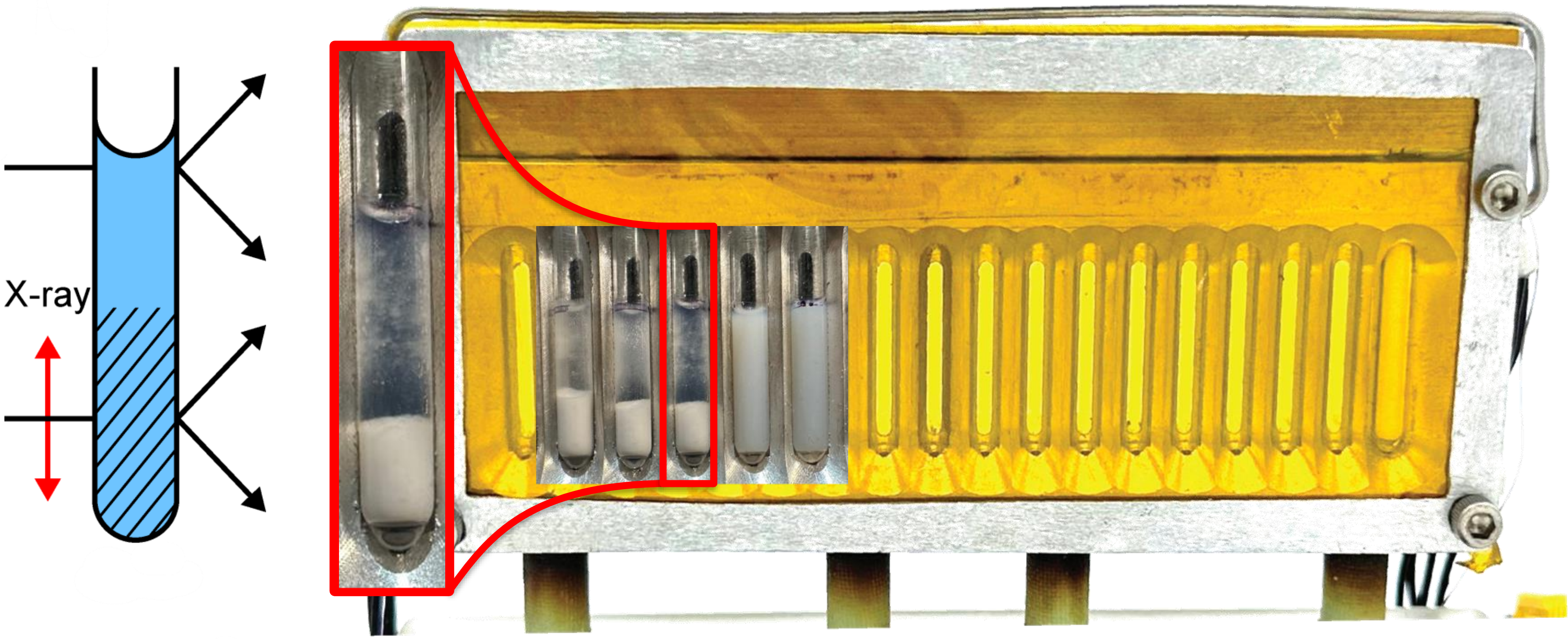
This change is largest for the second sedimentation event



Resolving the atomic structure with X-rays

We use our custom heated sample changer to probe multiple samples, in parallel, for spatially resolved *in situ* X-ray scattering experiments

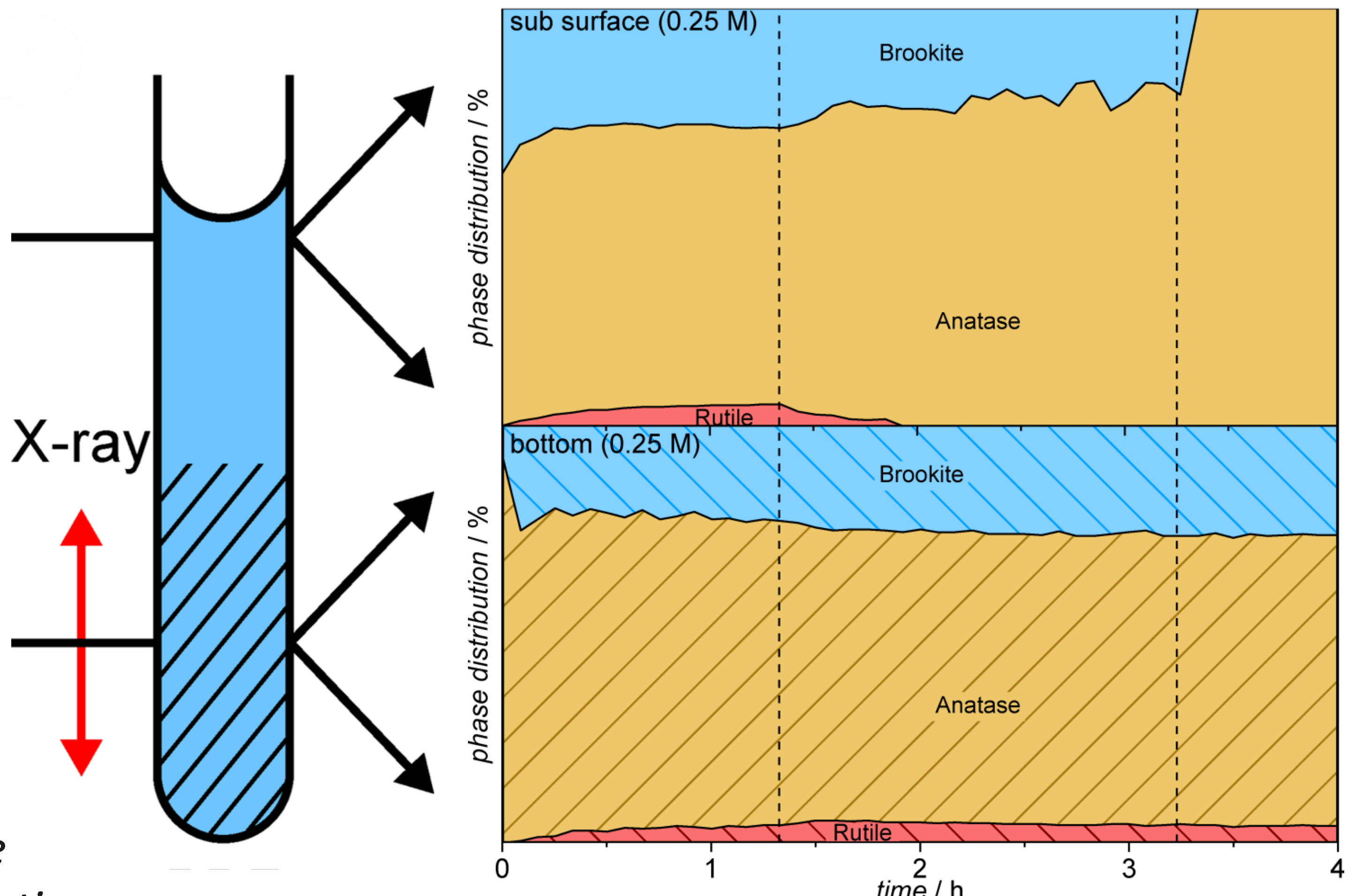
J. Appl. Crystallogr. **2023**, 1732-1738



J. Am. Chem. Soc. 2024, 10745–10752

Rutile only forms during the first cycle

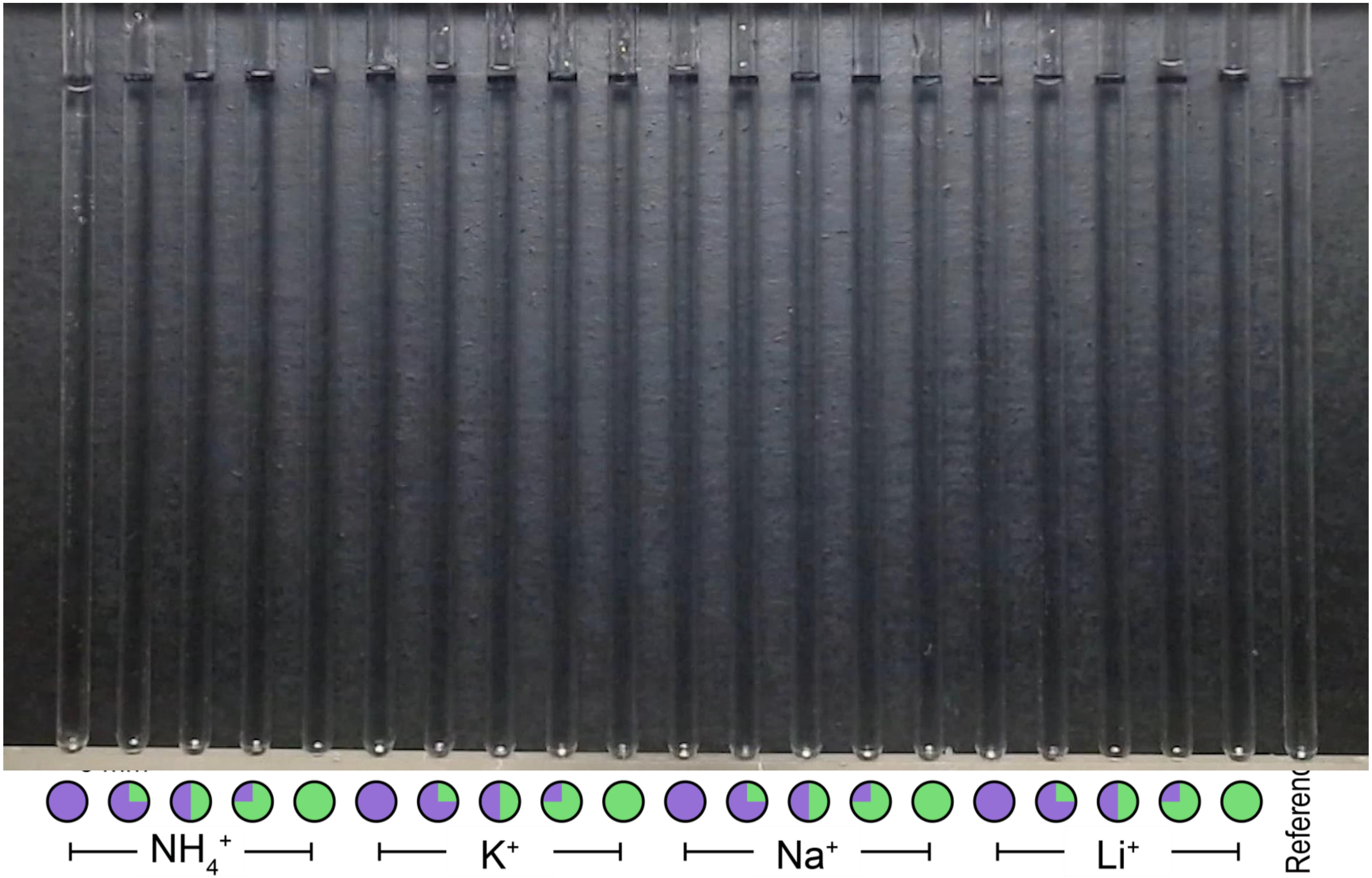
Anatase is the dominant product, with
less of brookite, and a minor component of rutile



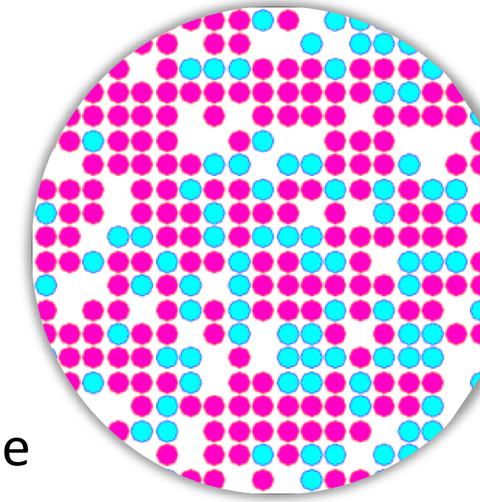
Beware homogenization

Look at a wide array of samples simultaneously

The way chemistry impacts the kinetics tells us about rate limiting steps.

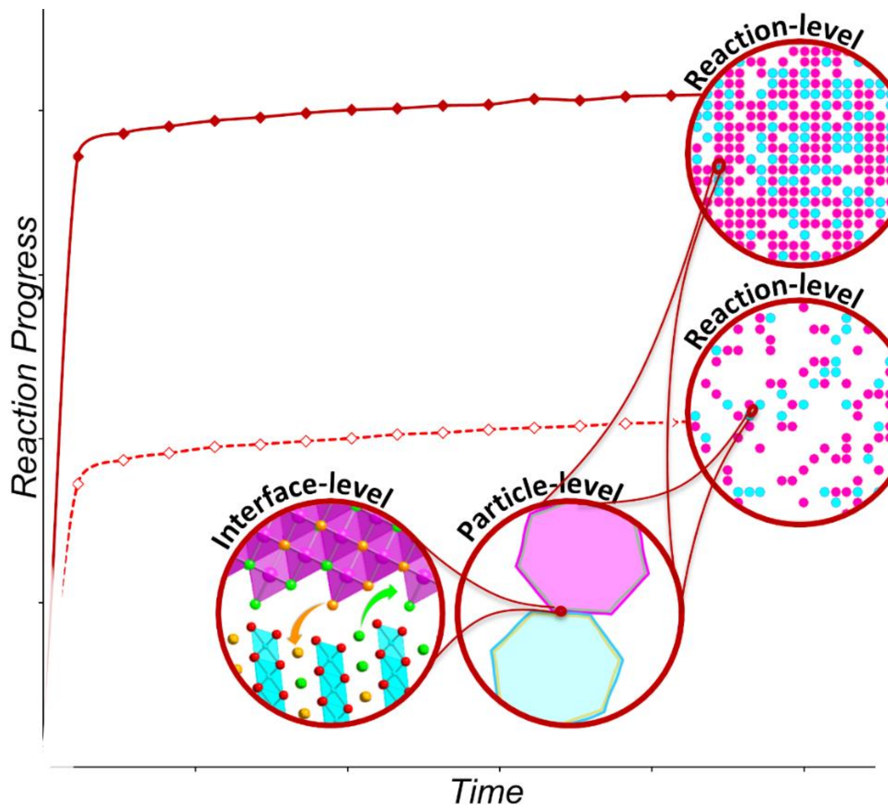


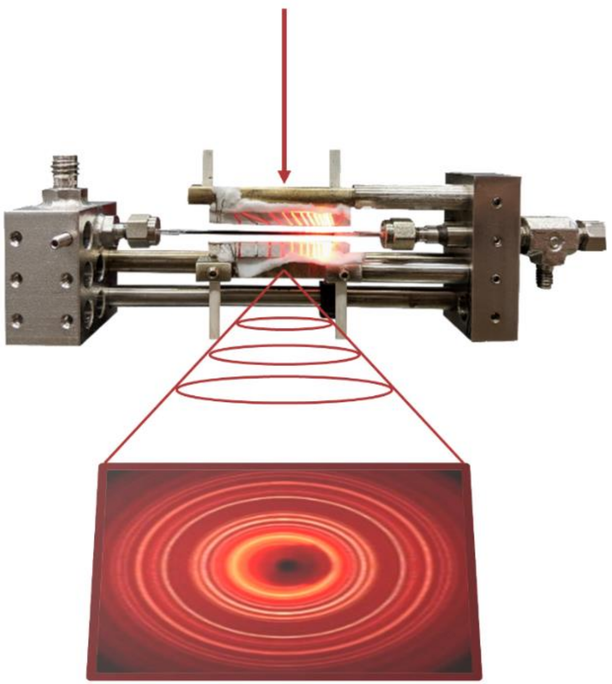
Some take aways



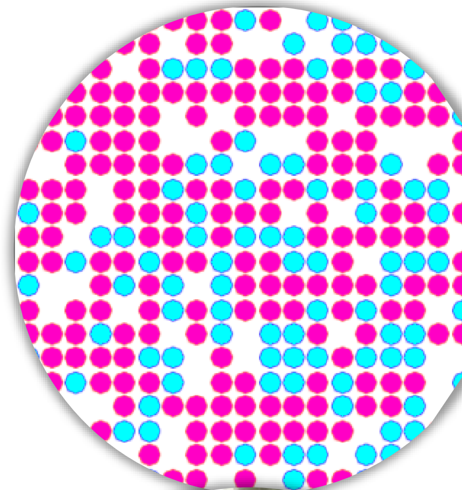
The critical phenomena can span multiple length scales

Concentration need to be defined on a specific lengthscale





Some take aways

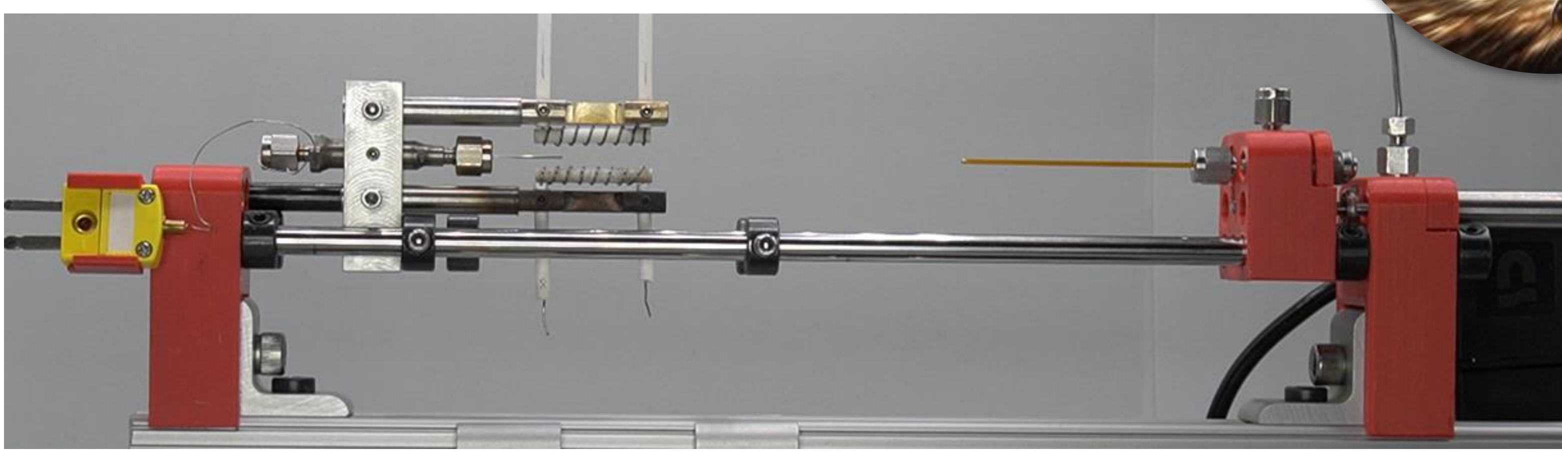


The critical phenomena can span multiple length scales

New sample environments are critical to accessing different reaction conditions and time-scales

Solid state reactions can be fast!

Just focusing on the final product can be misleading

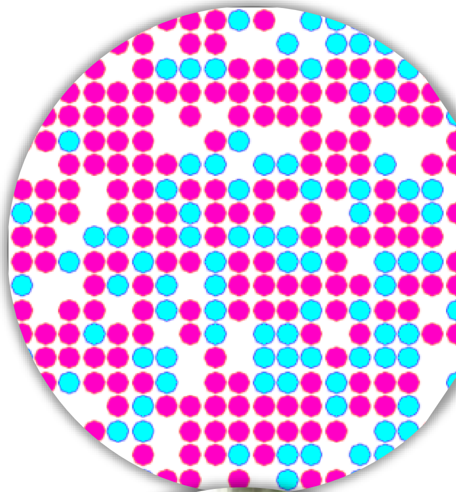


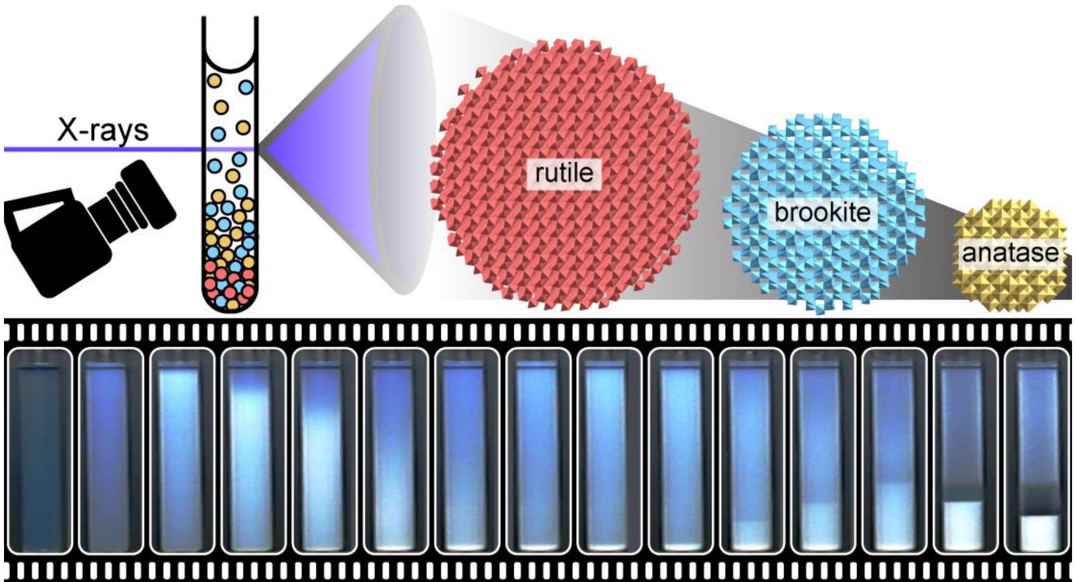
Some take aways

The critical phenomena can span multiple length scales

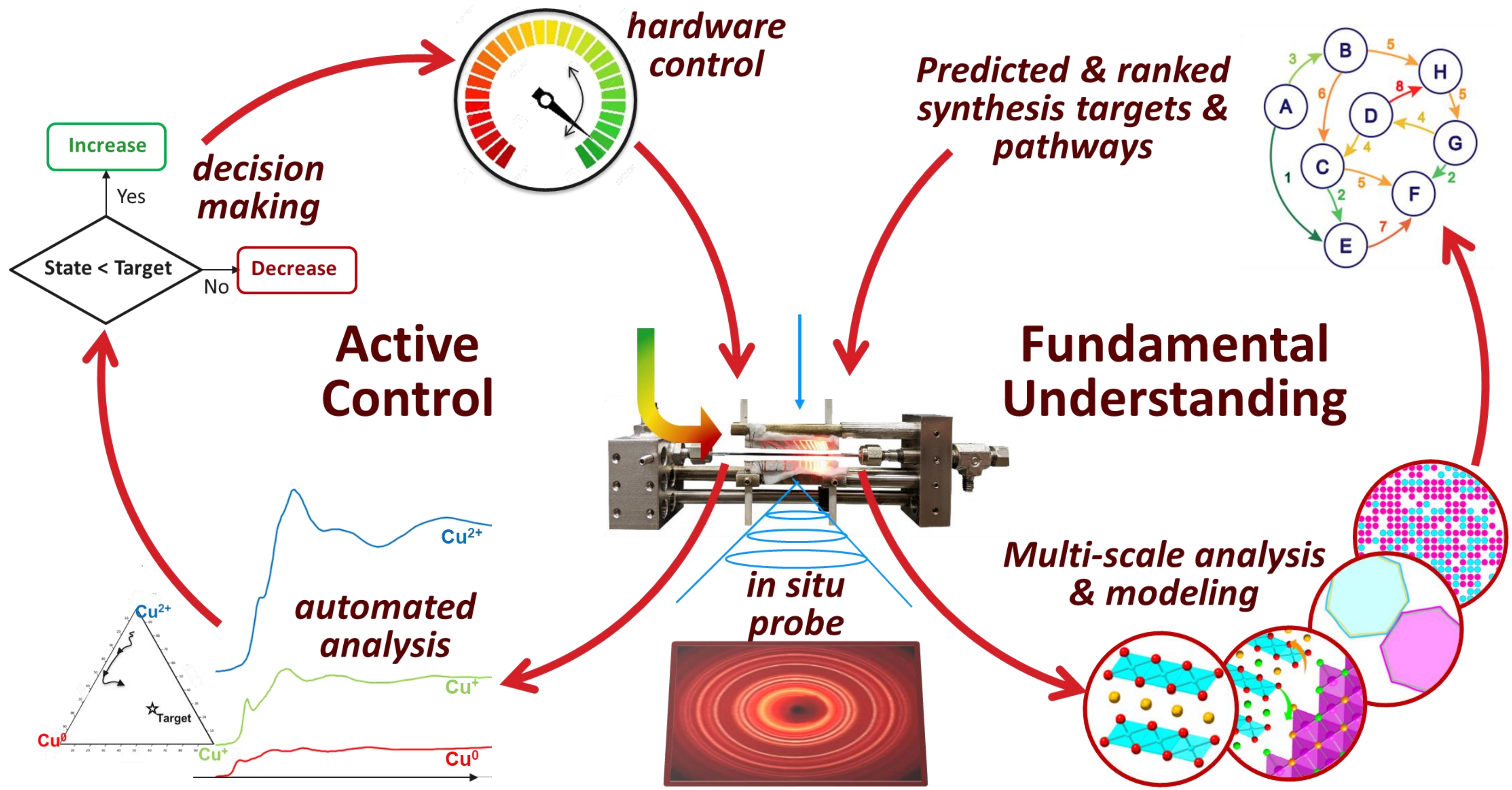
New sample environments are critical to accessing different reaction conditions and time-scales

High tech tools can provide valuable insights
Low tech, accessible tools should not be overlooked





If we can capture, understand, predict and control synthesis pathways, we will be able to discover new materials phases, to prepare known phases with narrowly controlled structure, morphology & defects, and identify energy- and atom-efficient synthetic routes.



A NEXT GENERATION SYNTHESIS CENTER

Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Argonne National Laboratory, were supported by the U.S. Department of Energy under Contract No. DE-AC02-06CH11357.

U.S. DEPARTMENT OF ENERGY | Office of Science