The A-Lab:
Automating materials synthesis with robotics, DFT, and machine learning

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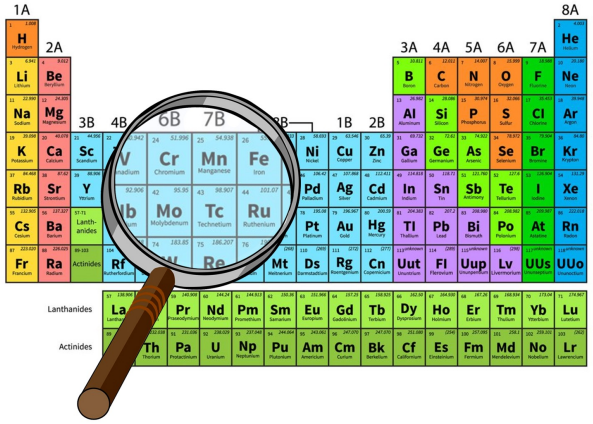
CEDER Group at UC Berkeley
Future Labs Workshop, UCSB
11/02/2023

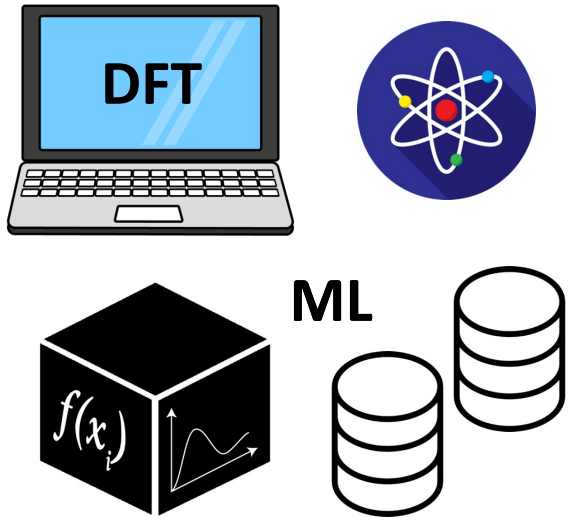
Berkeley
UNIVERSITY OF CALIFORNIA

BERKELEY LAB
Lawrence Berkeley National Laboratory

The problem: synthesizing novel inorganic materials

What compounds to make?





MP

146,000 compounds

> 1,000,000 compounds!

Google DeepMind

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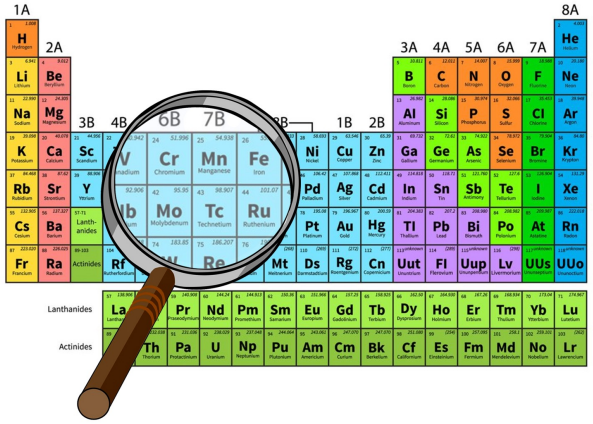

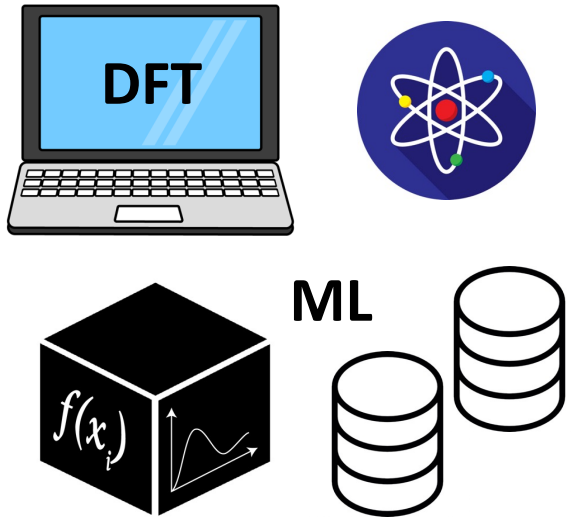

MP

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For comparison: the ICSD (an **experimental database**) contains only about **50,000 entries** whose structures match those in MP

→ **Many hypothetical structures have yet to be synthesized!**

The method: solid-state synthesis from inorganic powders

Target

$LiMnTiO_4$

Synthesis recipe

- ☑ 50 mg Li_2CO_3
- ☑ 80 mg MnO
- ☑ 20 mg TiO_2
- ☑ 800 °C (air)
- ☑ 24 hours

50 mg

20 mg

80 mg

Shake
'n bake

800 °C, 24 hours

Final product!

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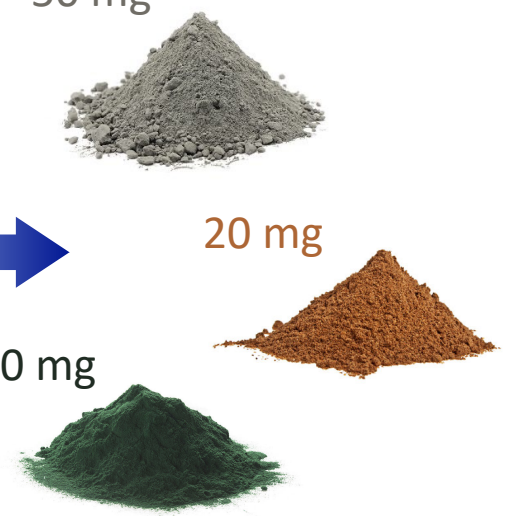


Shake
'n bake

800 °C, 24 hours

Final product!

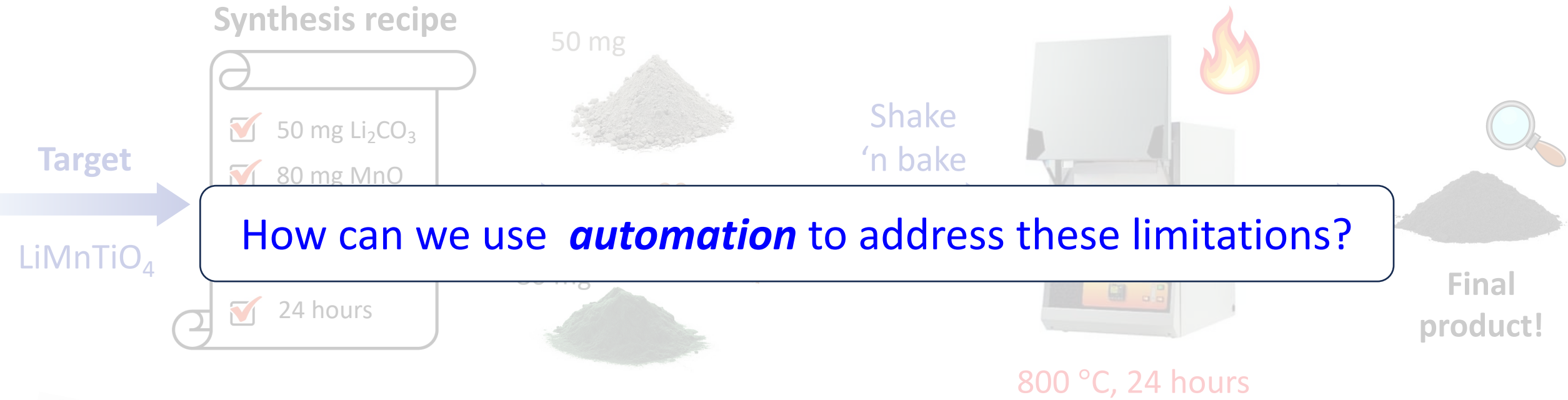
😢

There are no well-defined rules for choosing the most effective precursors and conditions

Experimental issues like precursor volatility or reactivity with the container

Initial experiments often give **zero target yield.** What to do next?

The method: solid-state synthesis from inorganic powders



How can we use ***automation*** to address these limitations?

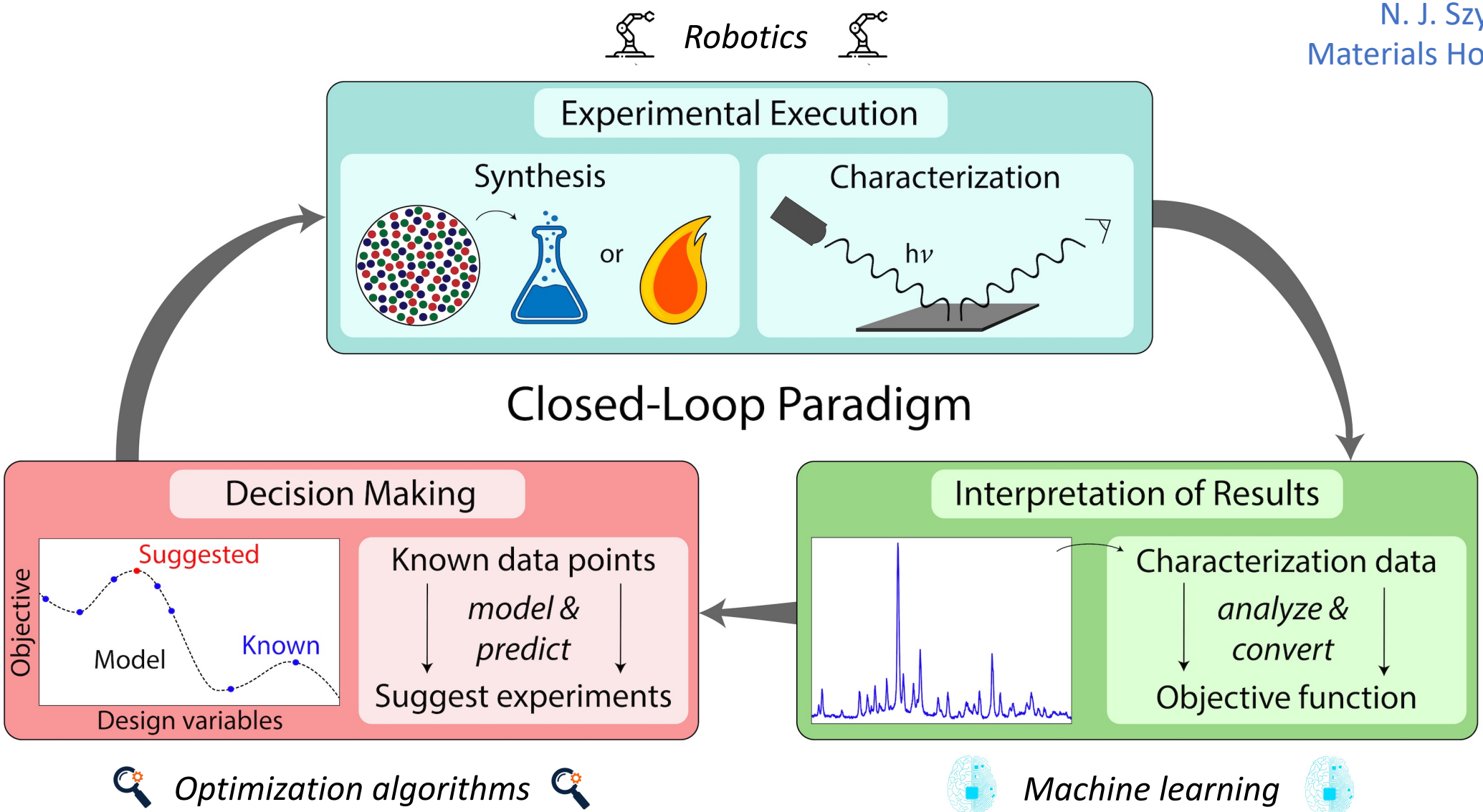
There are no well-defined rules for choosing the most effective precursors and conditions

Experimental issues like precursor volatility or reactivity with the container

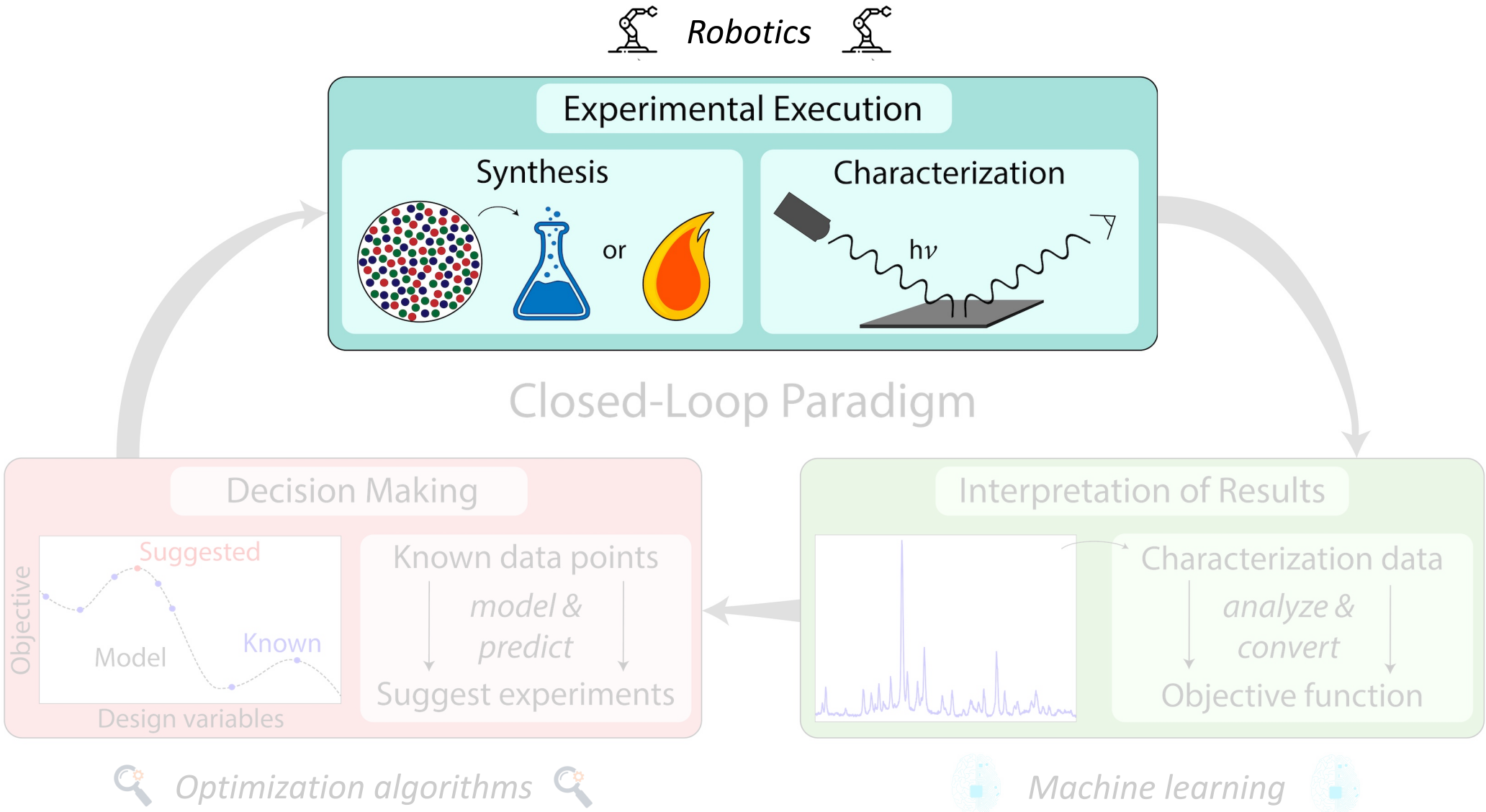
Initial experiments often give **zero target yield.** What to do next?

Closing the loop for autonomous materials synthesis

N. J. Szymanski *et al.*, Materials Horizons (2021).



First step: automating the experiments with robotics



The A-Lab: three robotic stations work together

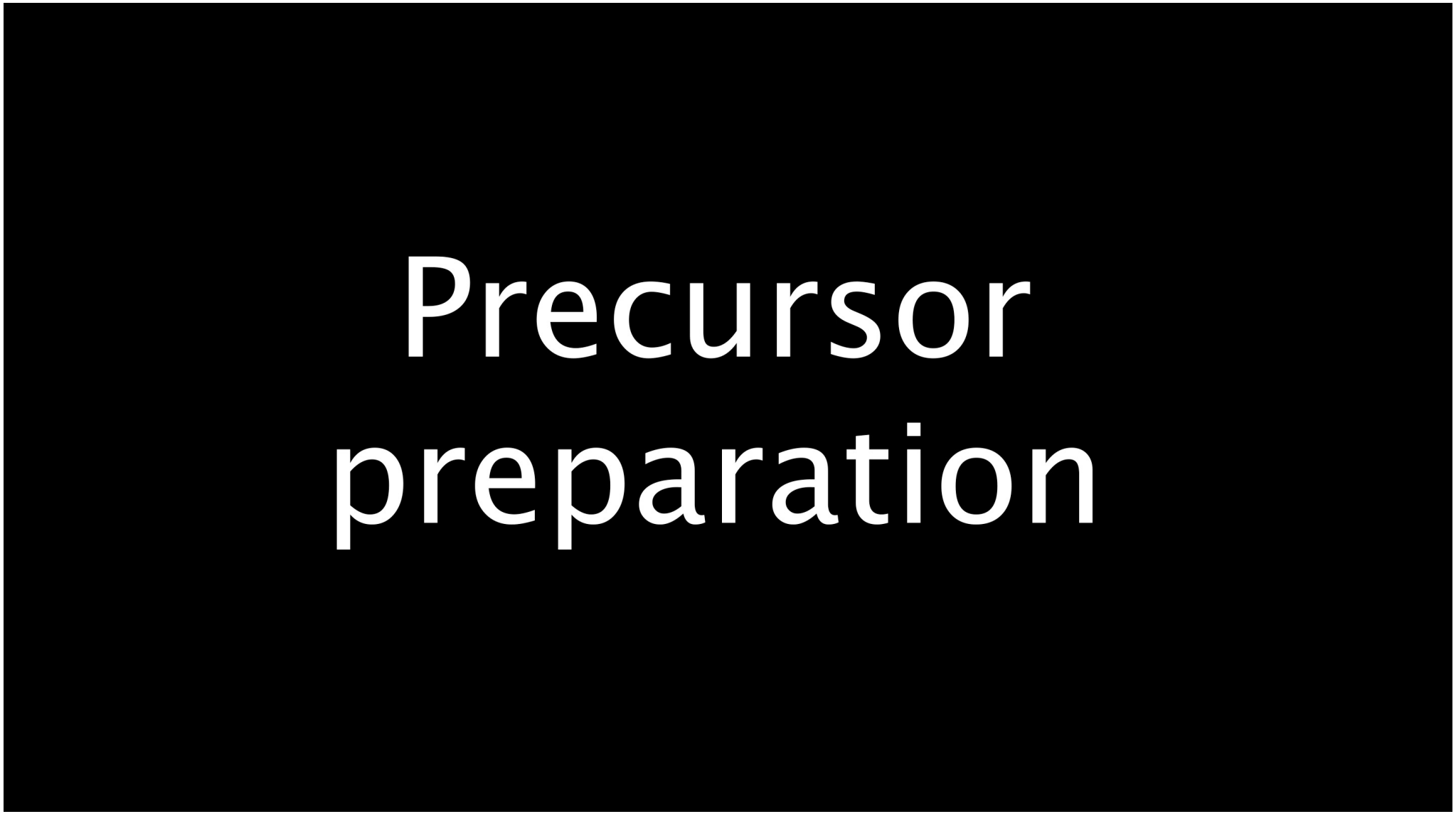
Precursor preparation:
Gravimetric dispenser works with a robot arm to weigh and mix powders

The hardware team

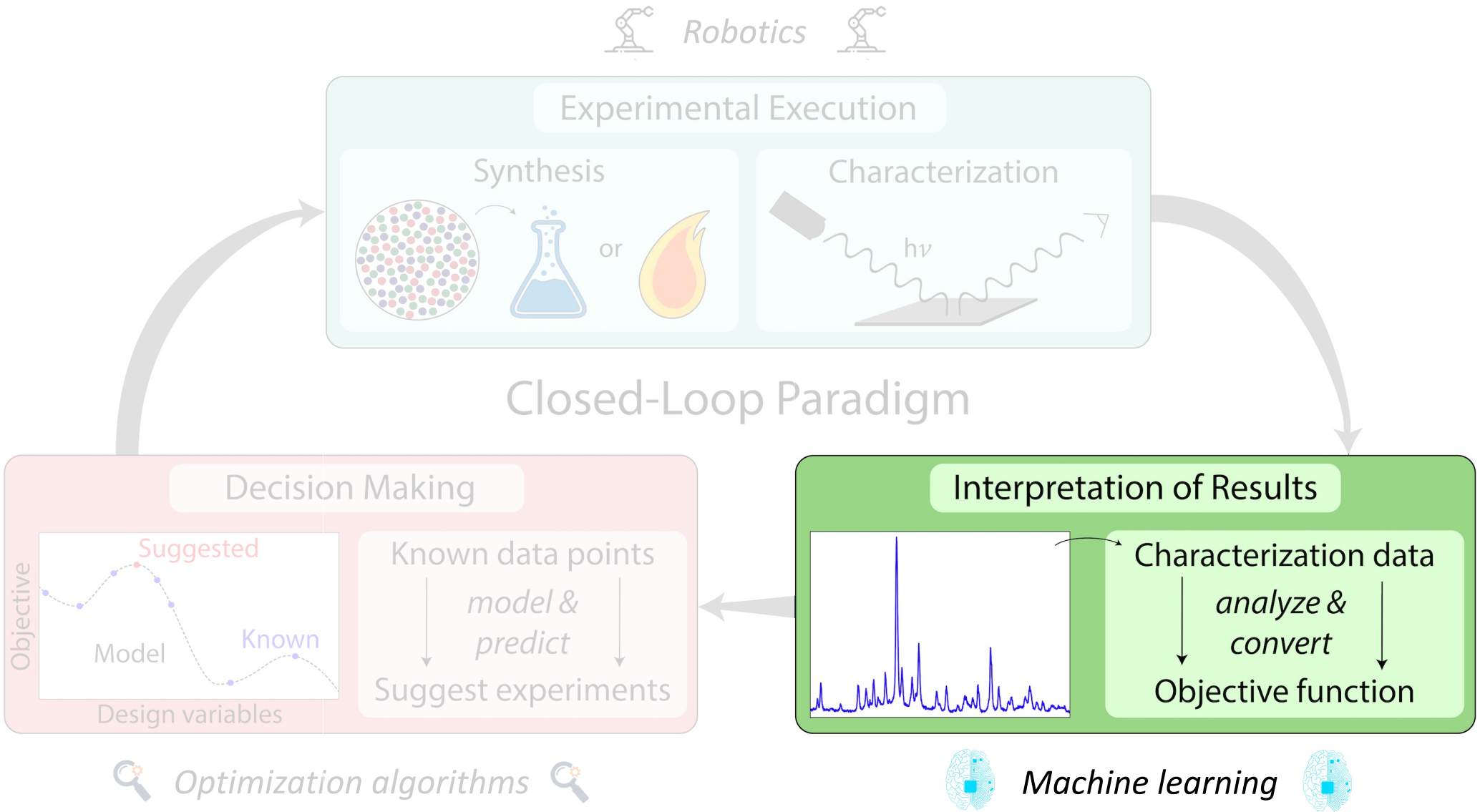
Heating station:
A second robot arm operates on a rail, transferring samples to and from box furnaces

Characterization:
A third robot arm extracts the synthesis products and prepares them for X-ray diffraction

A video demo of the A-lab



Experiments produce **XRD patterns**…How to interpret?



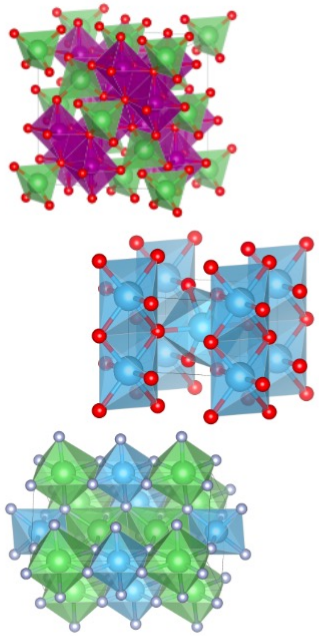
Phase analysis performed by **neural networks**

Previously reported structures

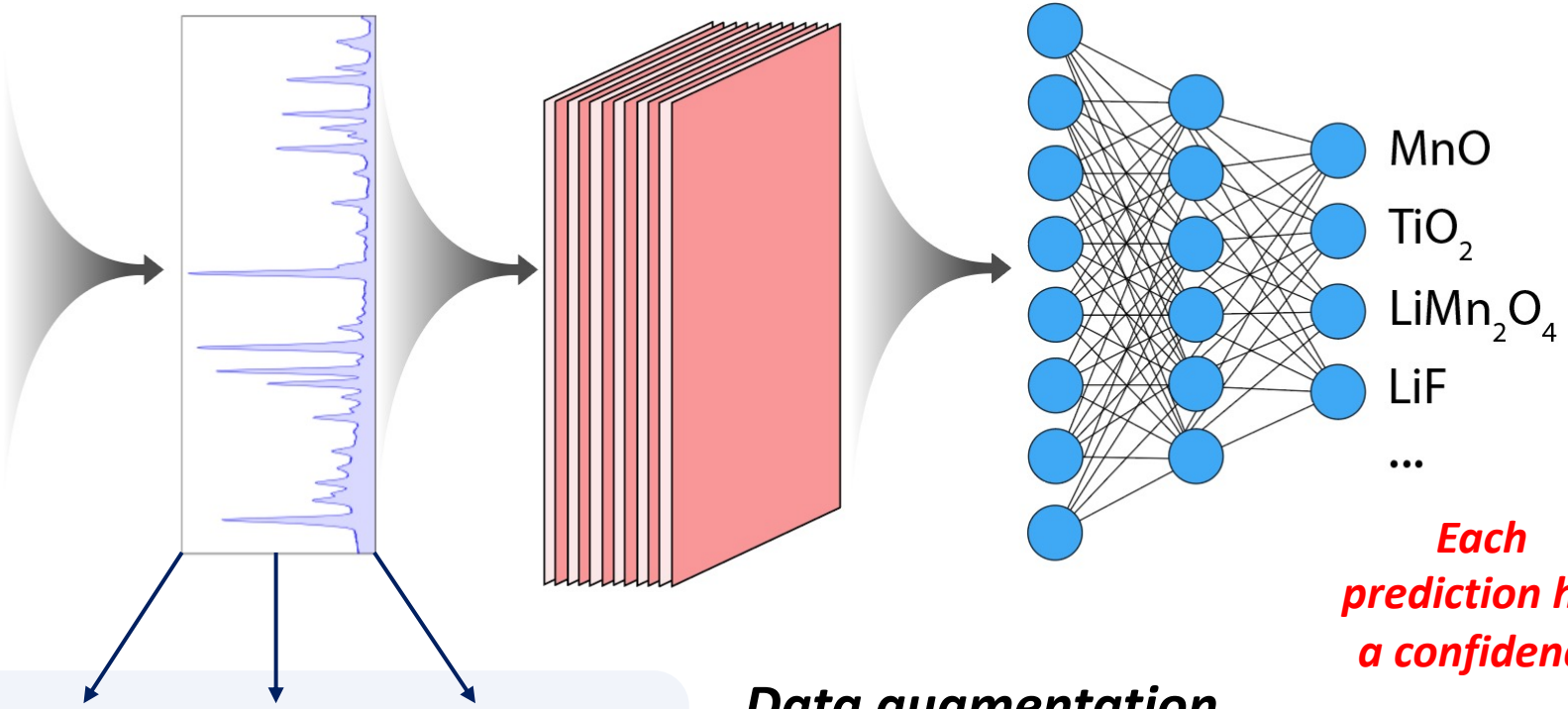
Simulated patterns

Convolutional neural network

ICSD
FIZ Karlsruhe



Materials Project



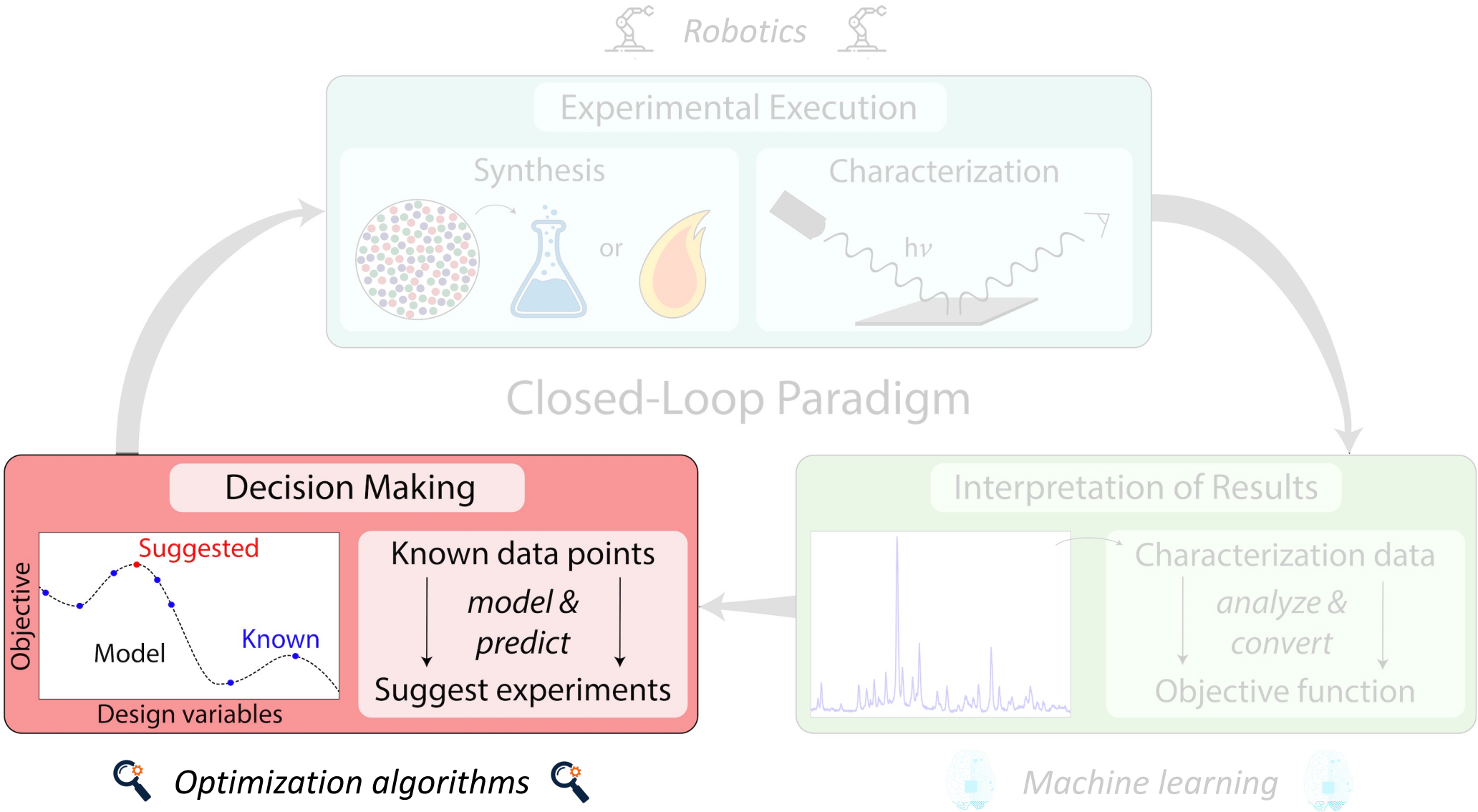
Shifts in 2θ | Intensity changes | Broad peaks

Each prediction has a confidence

Data augmentation from strain, texture, and poor crystallinity

N. J. Szymanski *et al.*, Chem. Mater (2021).

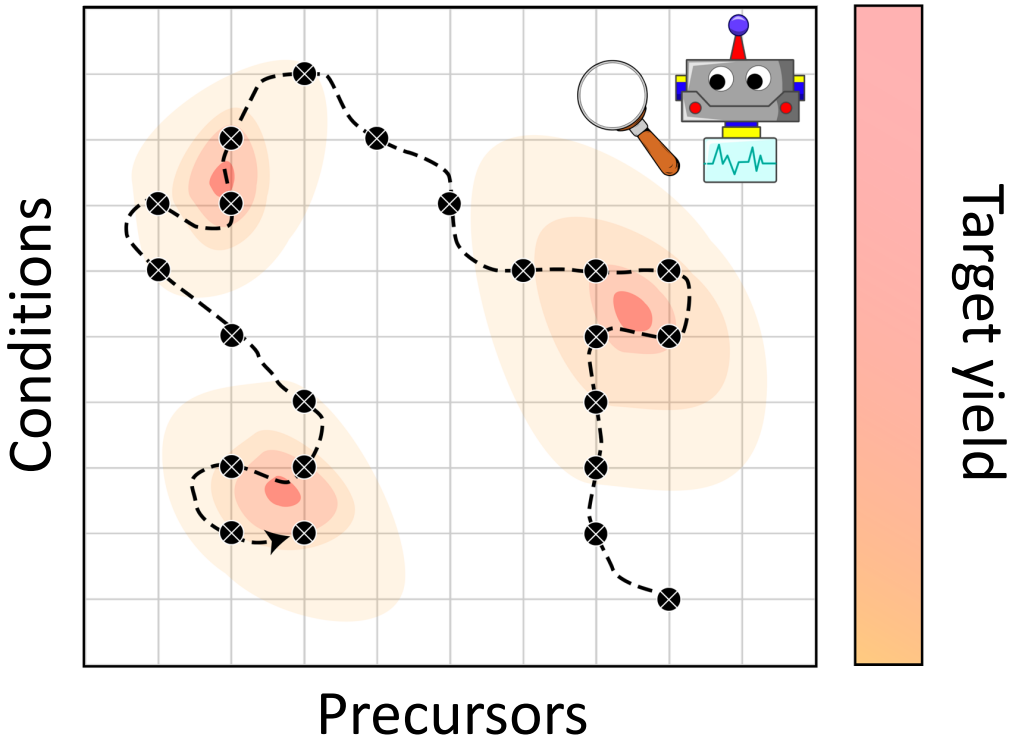
If the experiment failed, **what should the lab do next?**



The lab's **decision-making agent**: ARROWS^3

ARROWS^3

Autonomous Reaction Route Optimization
With Solid-State Synthesis

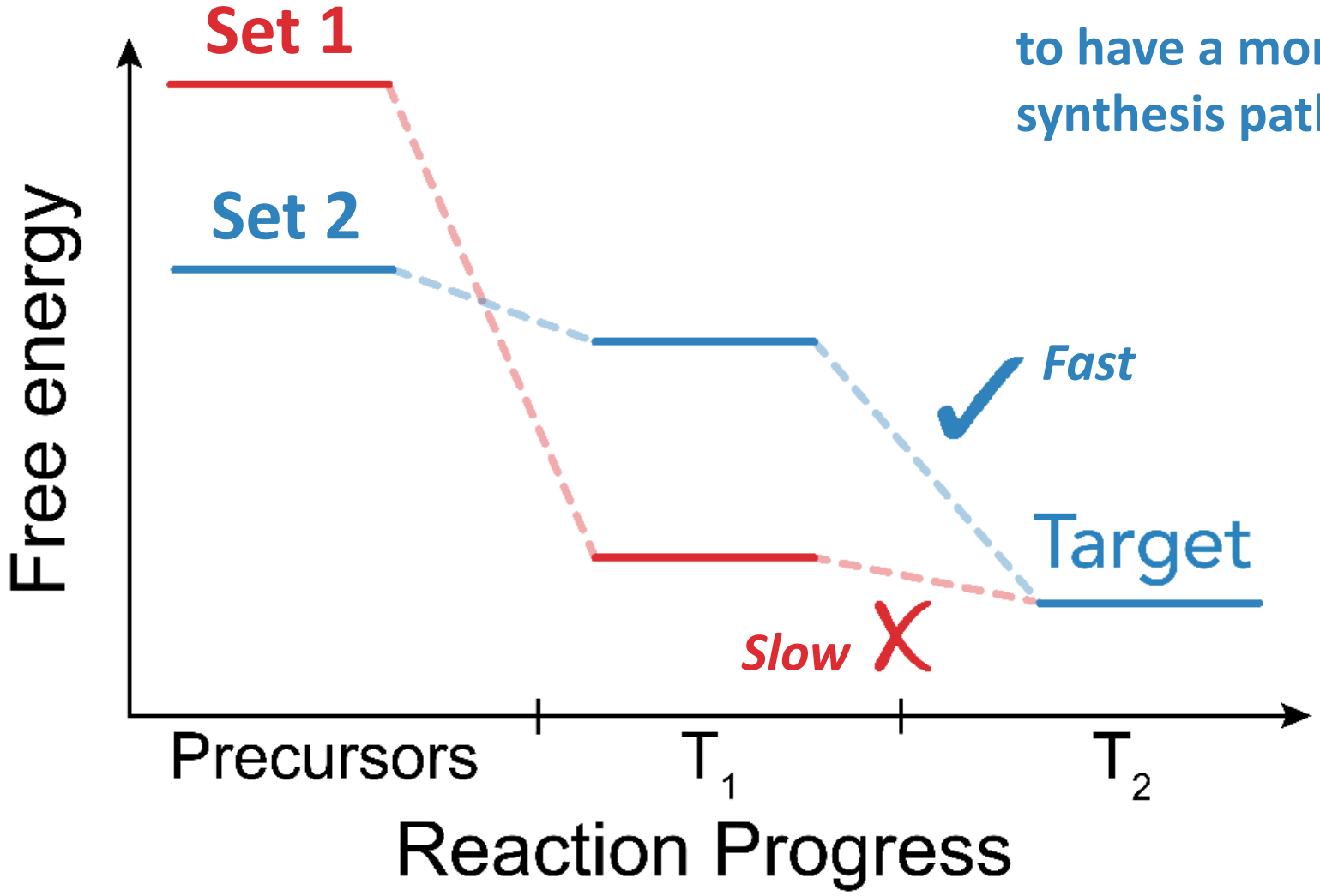


- ARROWS^3 is designed to **optimize the selection of precursors** while requiring **few experimental iterations**

It combines ab-initio (DFT) computed data with experimental observations to **maximize the driving force at the target-forming step** in the reaction pathway

N. J. Szymanski *et al.*, *Nature Commun.* (2023).

Large driving force (ΔG) enables faster reactions



Precursor set 2 is expected to have a more effective synthesis pathway

ARROWS iteratively learns to prioritize max-ΔG pathways

MATERIALS PROJECT

DFT-calculated energetics

ΔG = driving force to form target phase

Prioritize precursor sets with **large ΔG**

Precursors

ΔG

Target

Predict reaction outcomes of new precursor sets

Perform experiments using suggested precursors

ARROWS iteratively learns to prioritize max-ΔG pathways

MATERIALS PROJECT

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Precursors → Target (ΔG)

Predict reaction outcomes of new precursor sets

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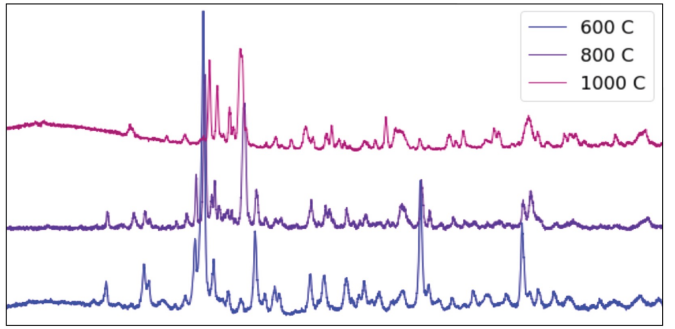

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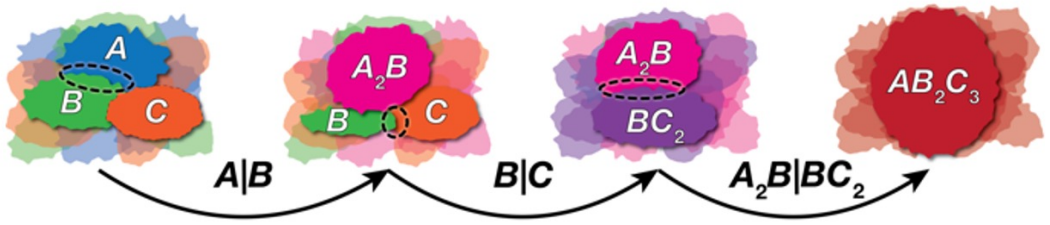
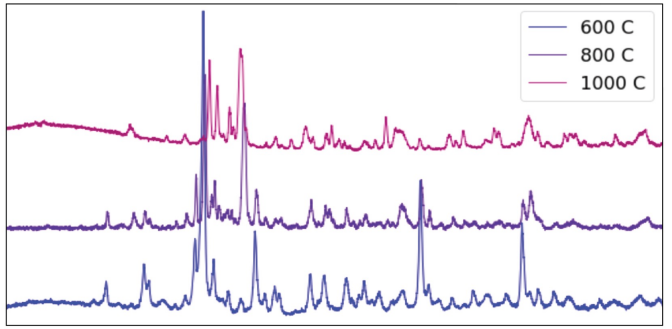


Learn which reactions consume ΔG

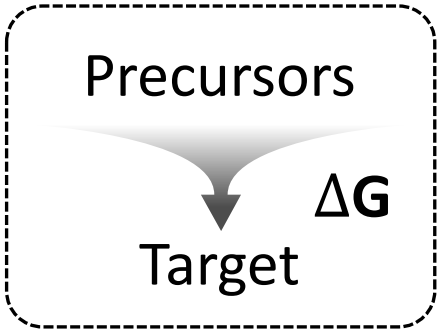


ARROWS iteratively learns to prioritize max-ΔG pathways

Avoid cmpds that form impurities

ΔG = driving force to form target phase

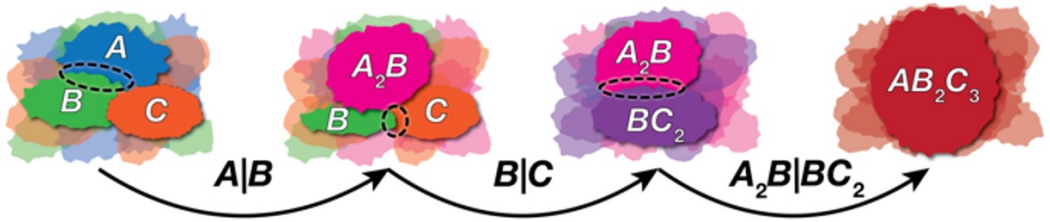
Prioritize precursor sets that ***retain*** **large ΔG**



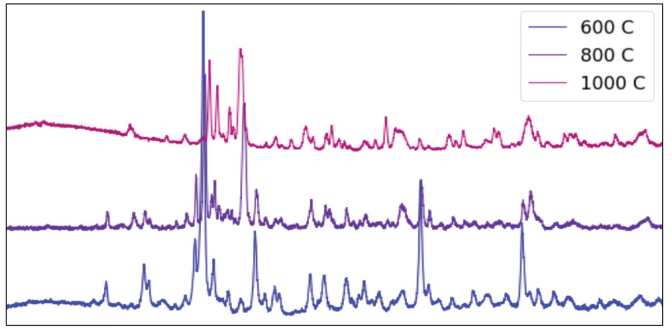
Update ranking

Predict reaction outcomes of new precursor sets

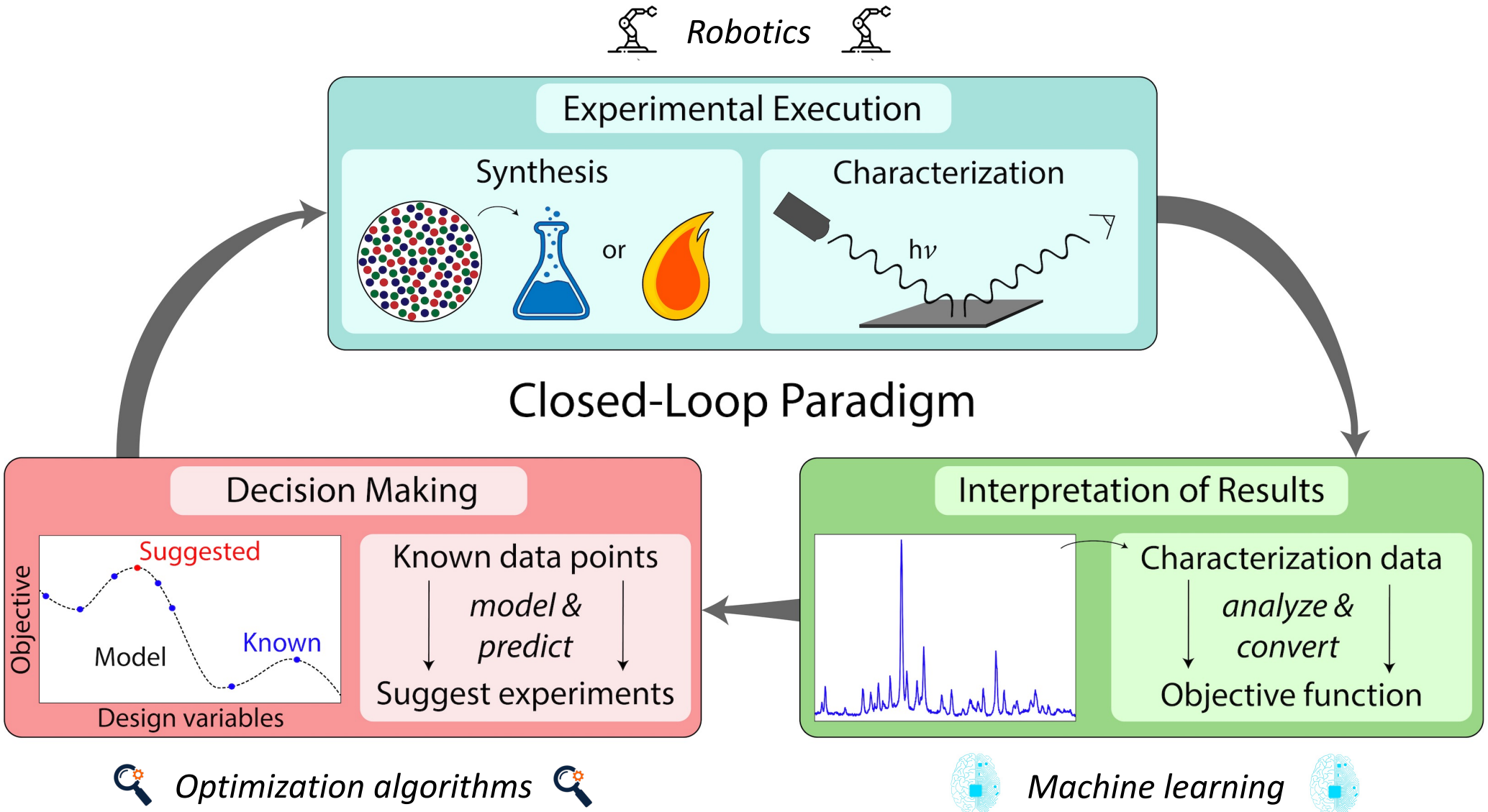
Perform experiments using suggested precursors



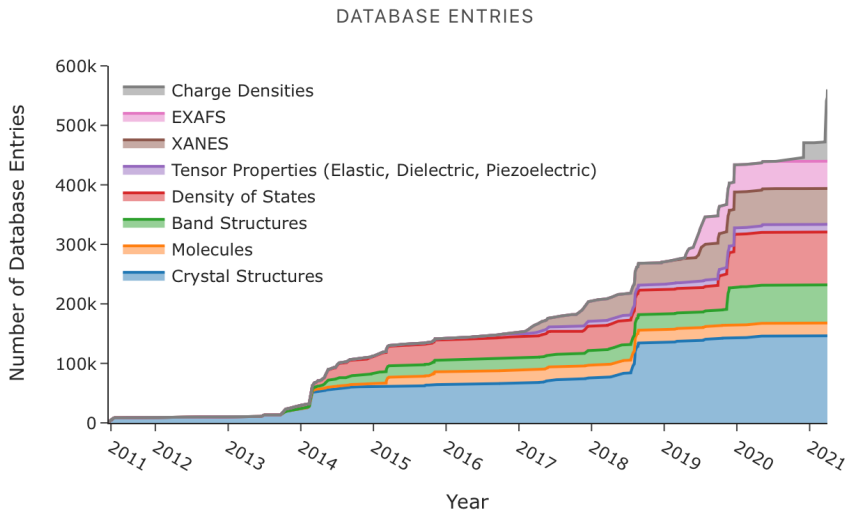
Learn which reactions consume ΔG



We have now **closed the loop!**



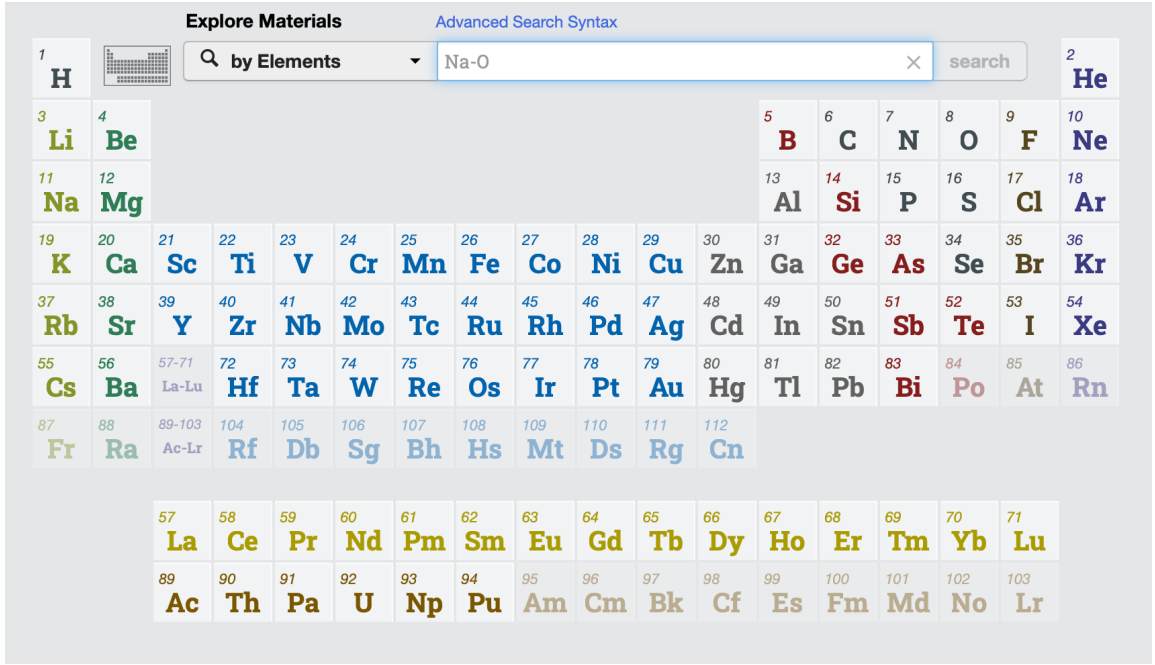
An application: synthesizing DFT-predicted compounds



MATERIALS

146,323

The Materials Project



42,000 thermodynamically stable cmpds

But only a fraction of these are experimentally reported

27,000 of the stable MP cmpds exist in the ICSD

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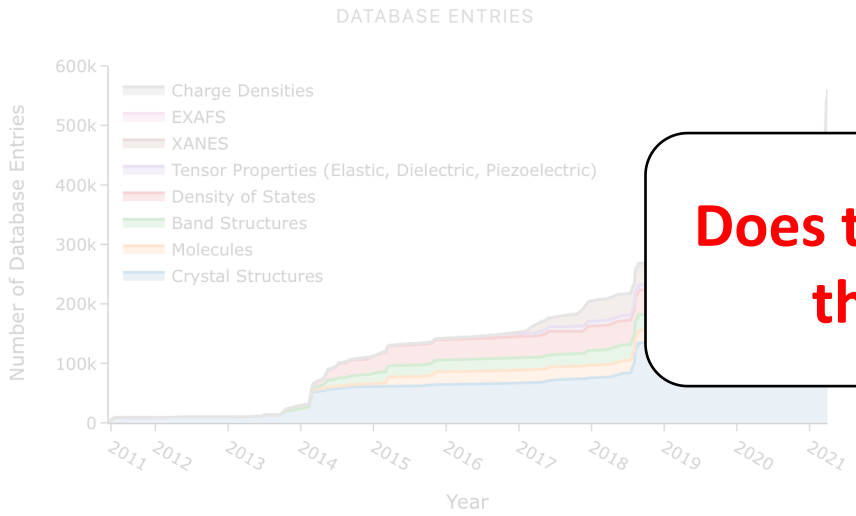
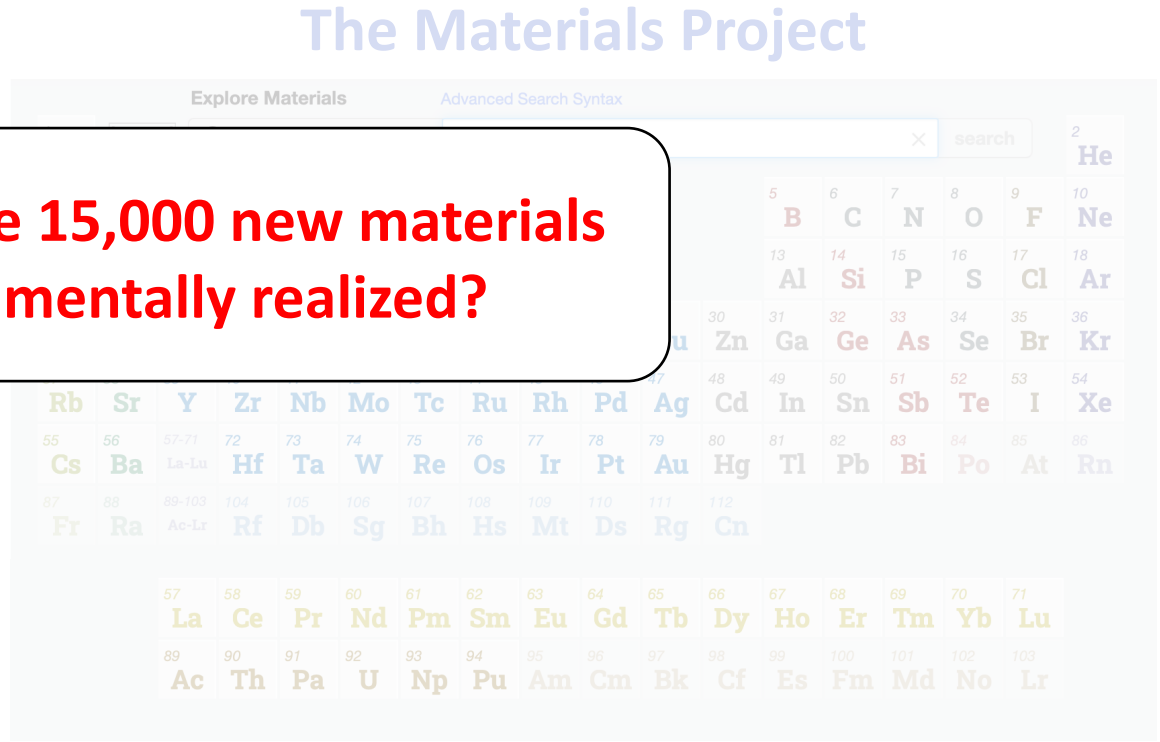


Does this mean there are 15,000 new materials that could be experimentally realized?



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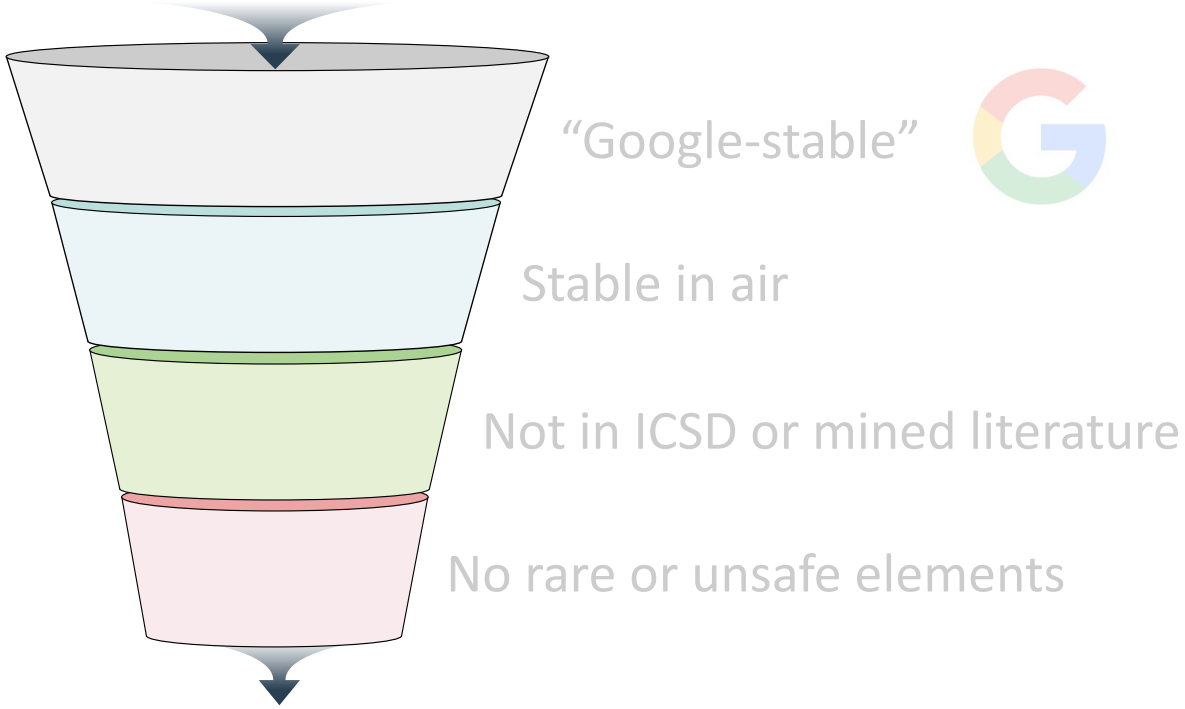
Targets filtered by novelty and air stability

42,000 stable cmpds



"Google-stable"

Stable in air

Not in ICSD or mined literature

No rare or unsafe elements

146 final cmpds

Let's validate whether a subset of these MP-stable materials can be synthesized!

Targets filtered by novelty and air stability

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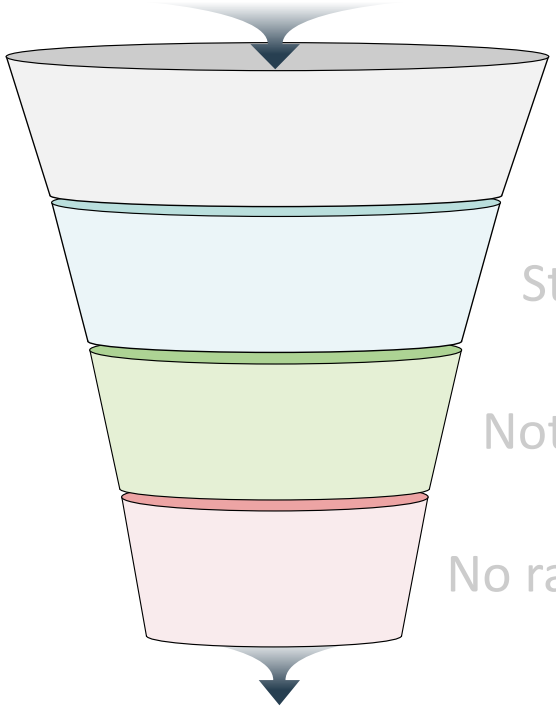

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Google DeepMind claims to have a database with > **1 million stable phases**

MP-stable cmpds were confirmed to be on or near the hull (< 10 meV/atom) in Google’s database

Targets filtered by novelty and air stability

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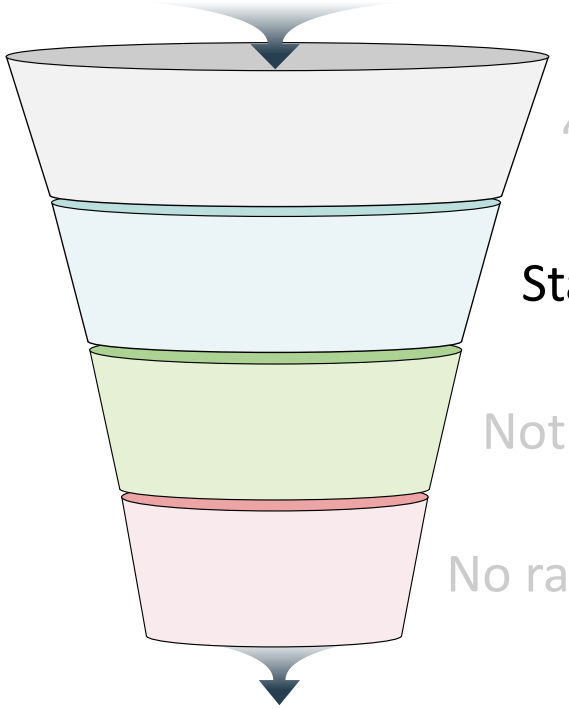

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Check 1: grand potential, open to O_2

$$\phi_{O_2} = G - \mu_{O_2} N_{O_2}$$

p_{O_2} = 21,220 Pa

T = 600-1000 °C

Check 2: reactivity with CO_2 and H_2O

$Li_2O|CO_2 \rightarrow Li_2CO_3$ ($\Delta G < 0$?)

$Li_2O|H_2O \rightarrow LiOH$ ($\Delta G < 0$?)

Targets filtered by novelty and air stability

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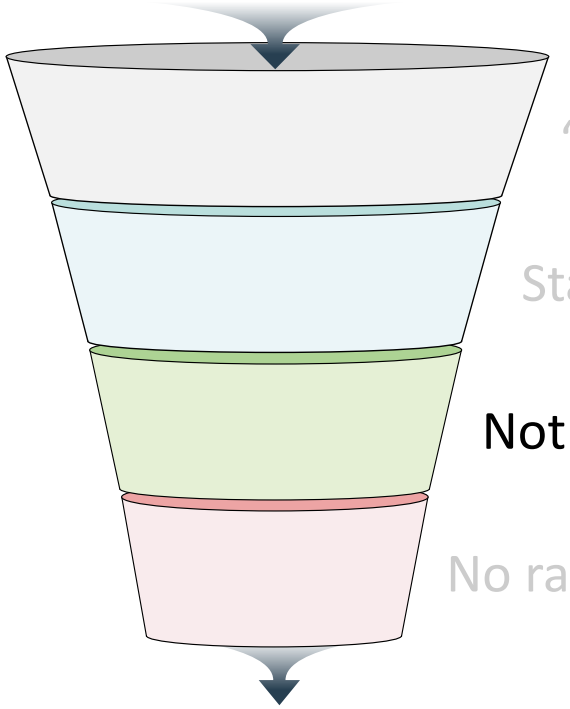

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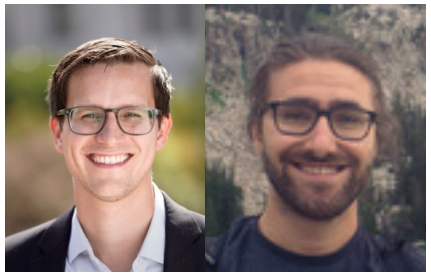
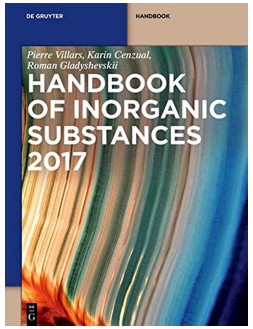
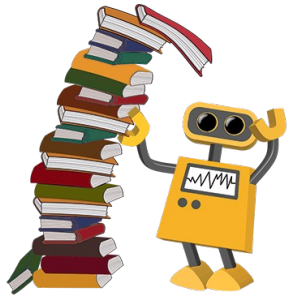


Matt & Max





NLP database

Targets filtered by novelty and air stability

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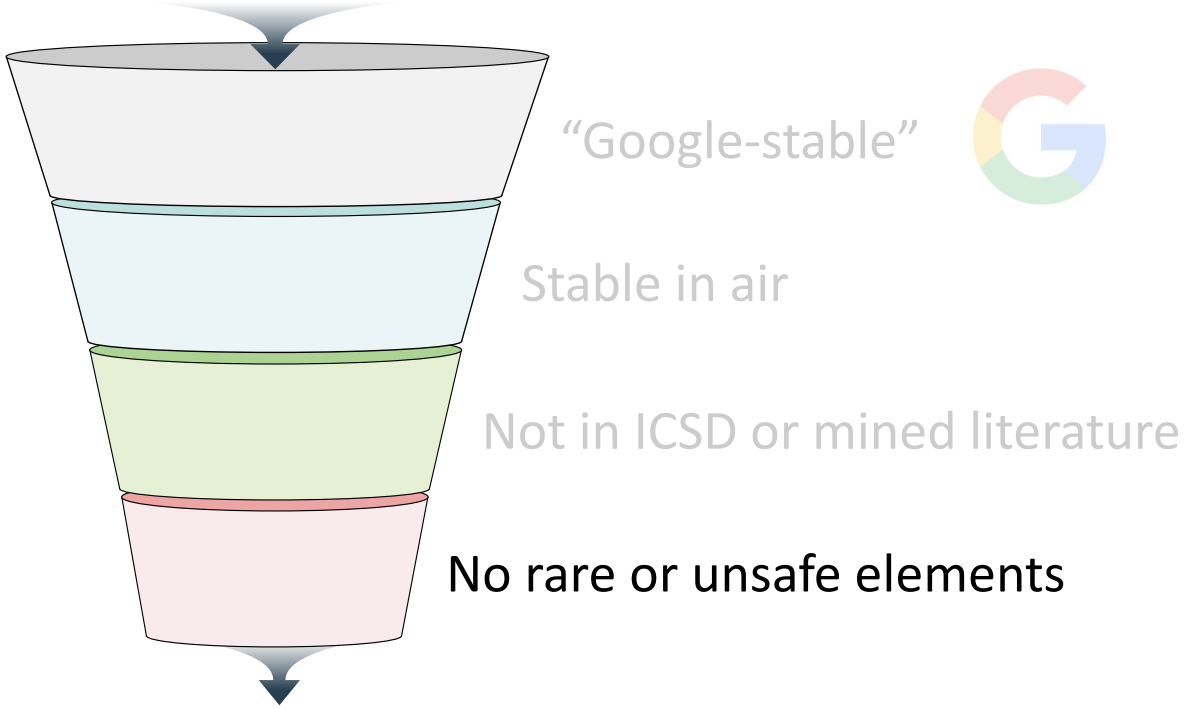

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Matt & Max

Radioactive:
Ac, Th, Pa, U, Np, Pu, Tc

Costly:
Pd, Pt, Rh, Ir, Au, Ru, Os, Re, Tl, Sc, Tm, Pm, Rb, Cs

Toxic:
Hg, As

Targets filtered by novelty and air stability

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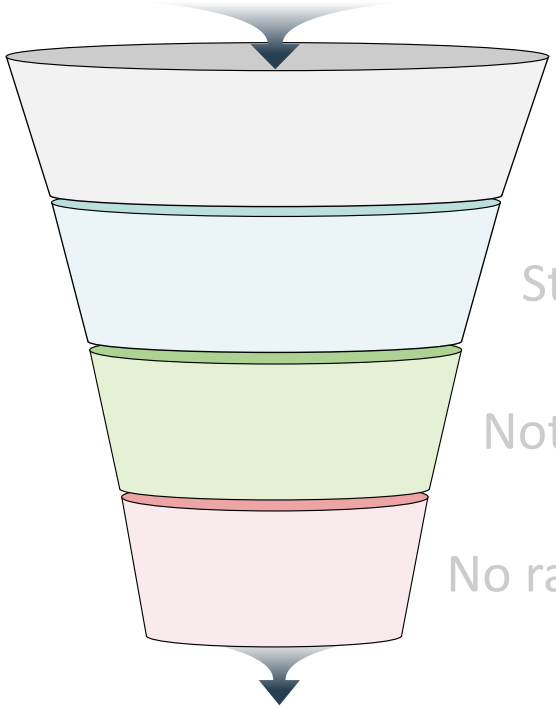

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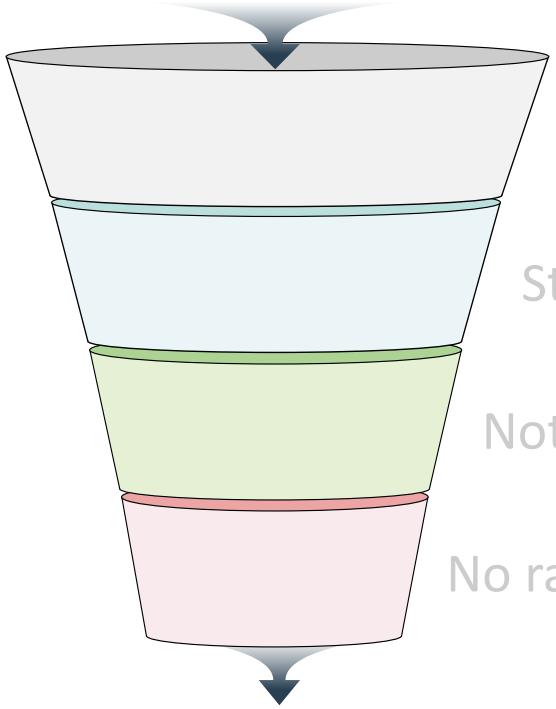

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146 final cmpds

Of these, we selected **58 cmpds** for which precursors were readily available

Let's validate whether a subset of these MP-stable materials can be synthesized!

Targets filtered by novelty and air stability

We tasked the A-Lab with synthesizing these 58 novel compounds and let it run for 3 weeks…How did it do?

Of these, we selected **58 cmpds** for which precursors were readily available

Results from the A-Lab syntheses: **41/58 targets made!**

71% success per target

37% success per recipe

A high success rate per target suggests that DFT-predicted stability is useful for finding new (synthesizable) materials ☺

A much lower success rate per recipe demonstrates how challenging synthesis can be… even for stable materials!

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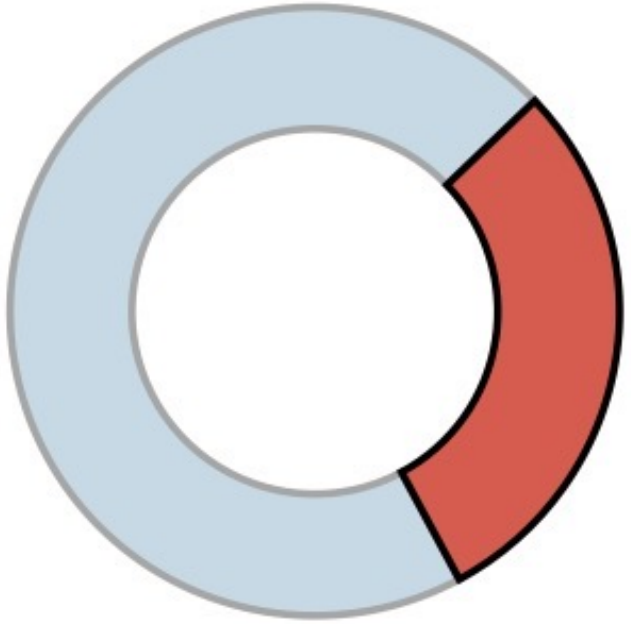
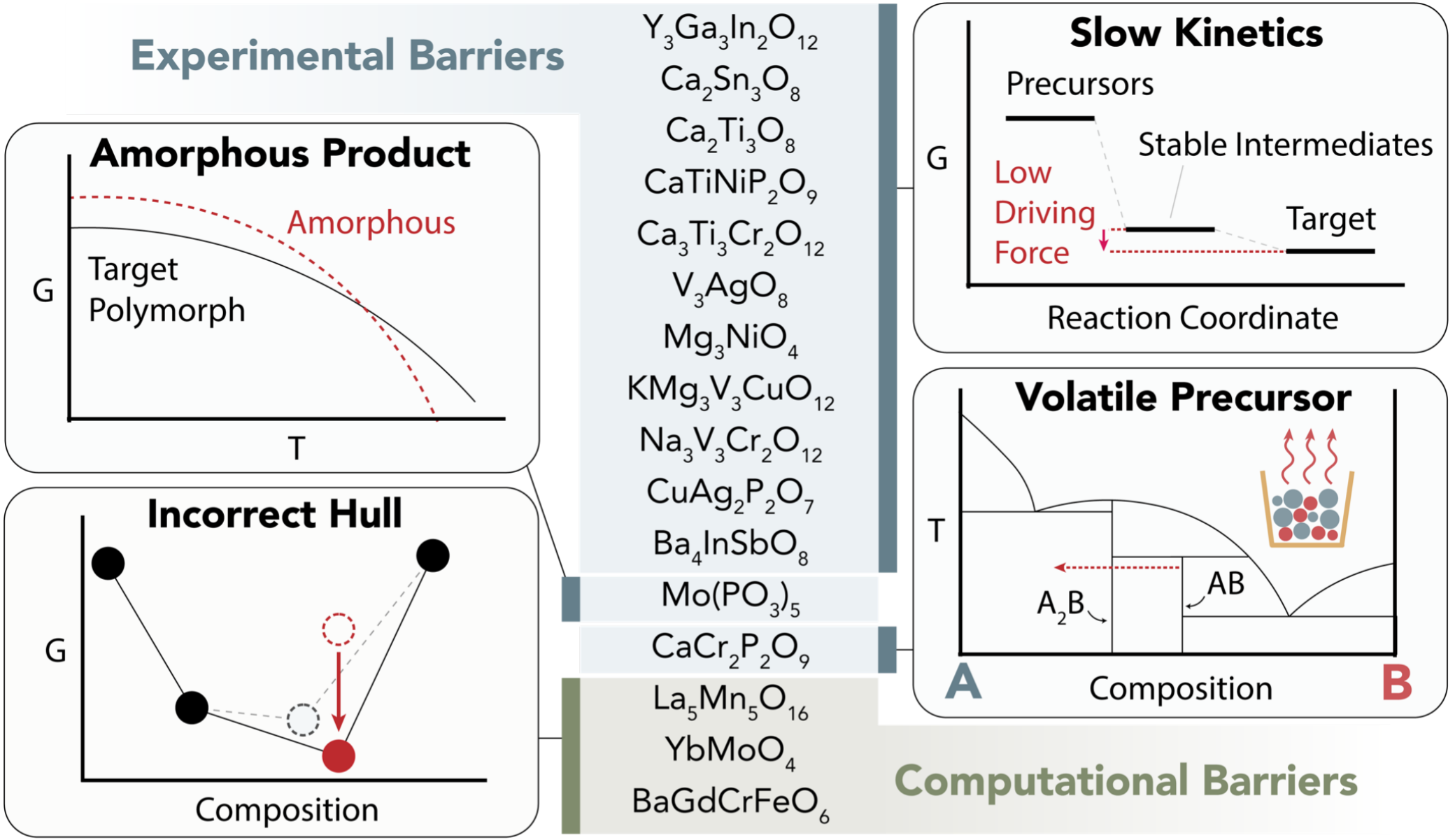
What about the materials that A-Lab could ***not*** make?

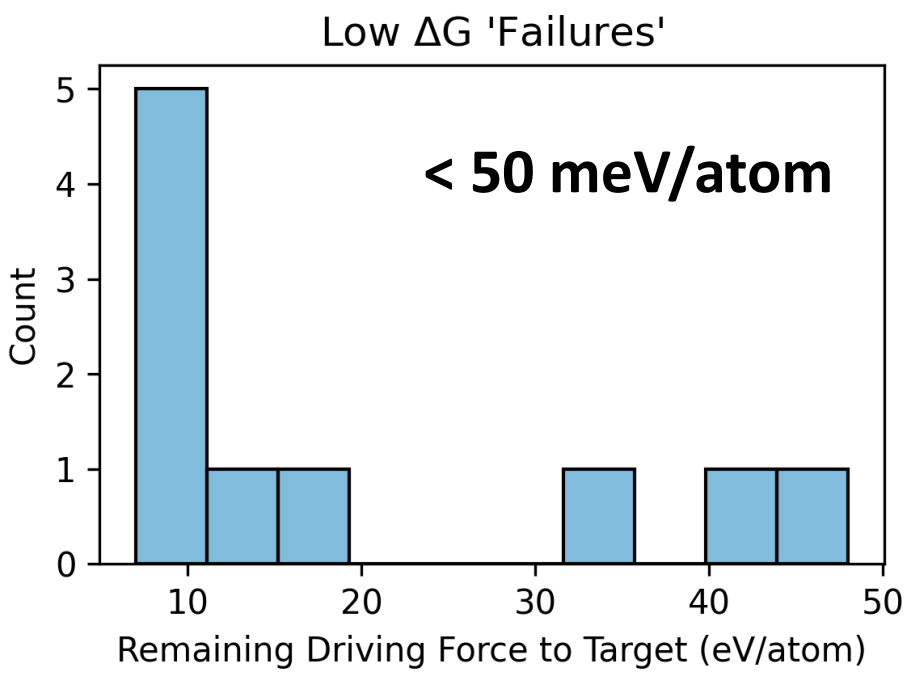


17 targets could not be made, even after optimization in the A-Lab

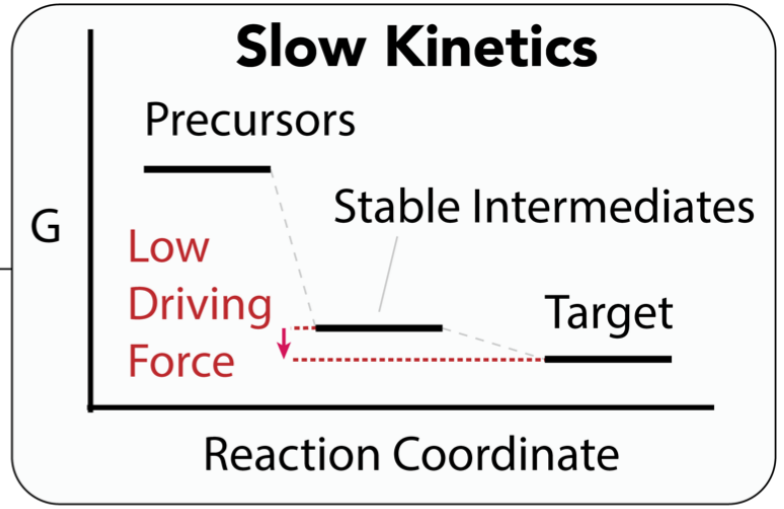
Four major failure modes



Four major failure modes: **Slow kinetics**



$Y_3Ga_3In_2O_{12}$
$Ca_2Sn_3O_8$
$Ca_2Ti_3O_8$
$CaTiNiP_2O_9$
$Ca_3Ti_3Cr_2O_{12}$
V_3AgO_8
Mg_3NiO_4
$KMg_3V_3CuO_{12}$
$Na_3V_3Cr_2O_{12}$
$CuAg_2P_2O_7$
Ba_4InSbO_8



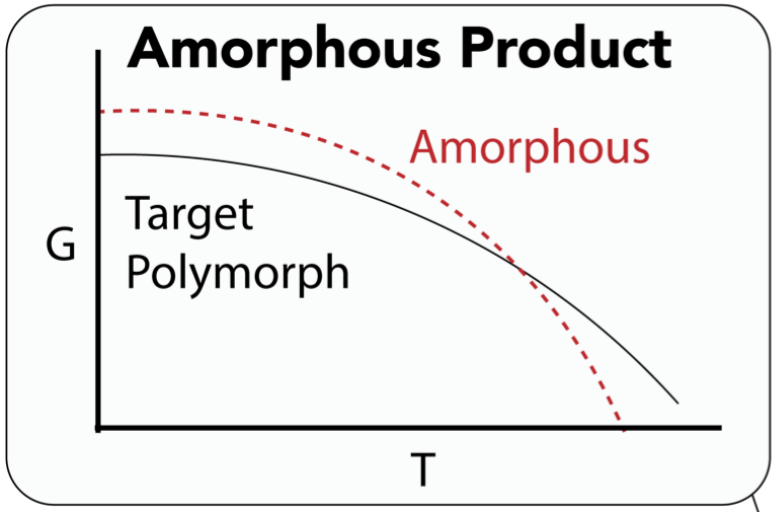
11 targets

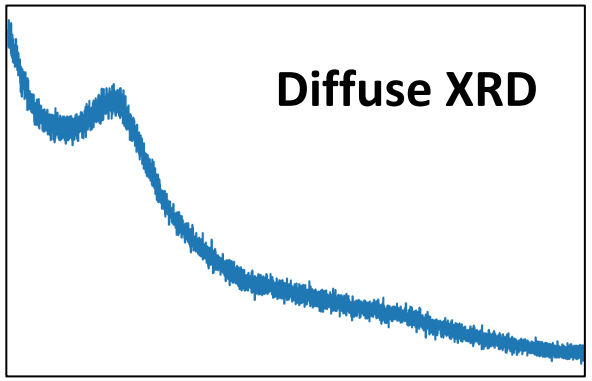
At least two of these targets can be obtained after the fact by:

1) Regrinding and reheating (Mg_3NiO_4)
2) Increased synthesis temperature ($Y_3Ga_3In_2O_{12}$)

Yuxing

Four major failure modes: **Amorphous product**

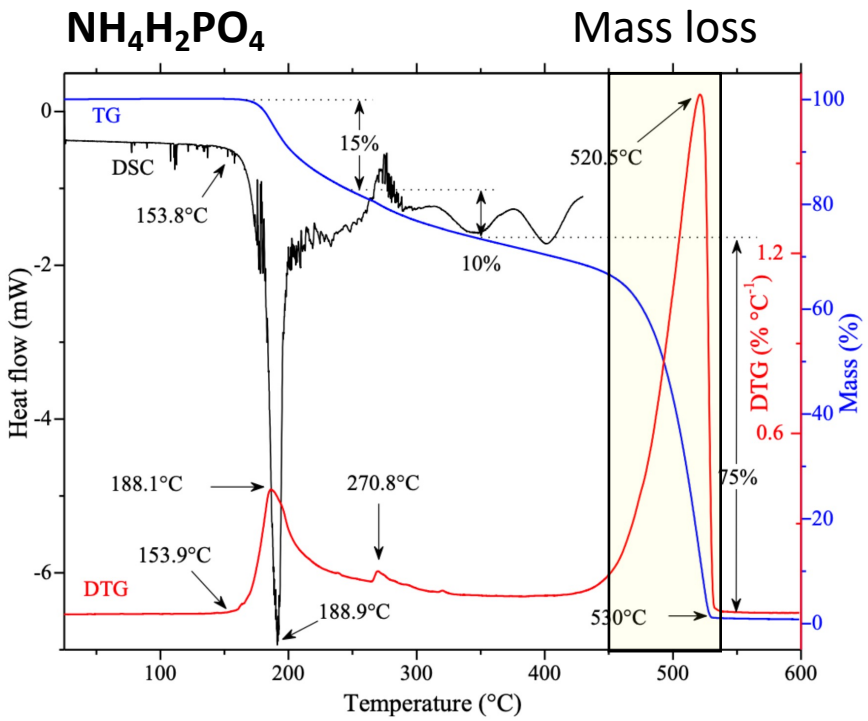




$Mo(PO_3)_5$

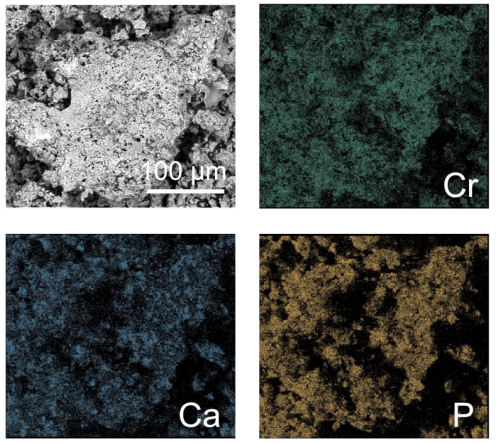
- Sample melts at high T and doesn't crystallize upon cooling → amorphous
- More prevalent in certain chemistries – *e.g.*, phosphate-rich compounds

Four major failure modes: **Precursor volatility**

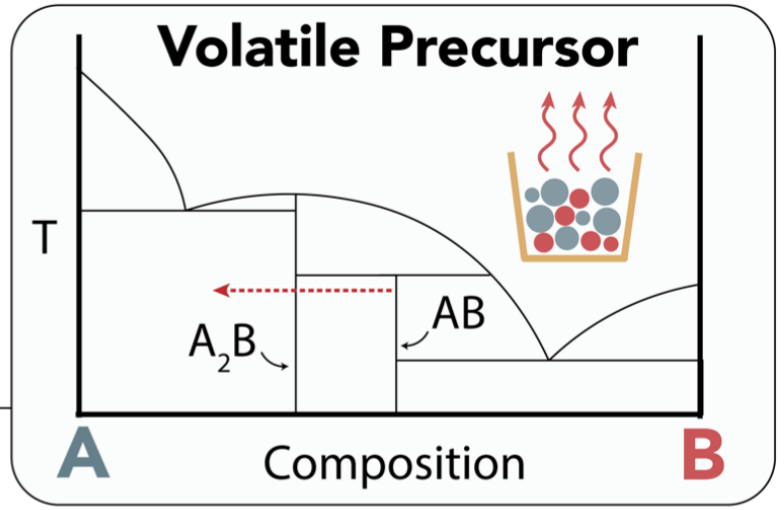


Ammonium phosphate precursors tend to evaporate above 450 °C

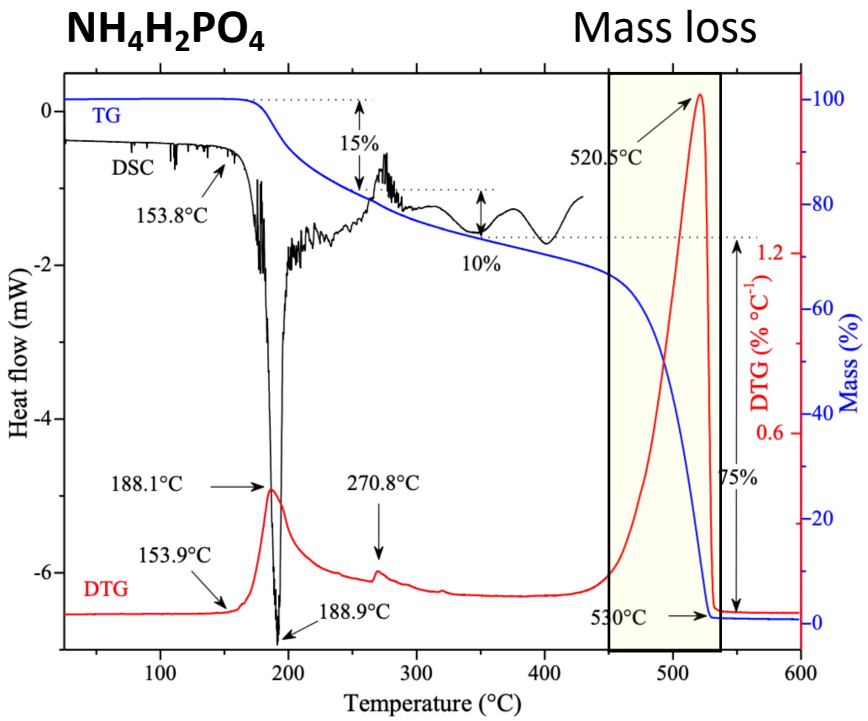
For all samples targeting $CaCr_2P_2O_9$, EDS shows a lower-than-expected amount of phosphorus



$CaCr_2P_2O_9$



Four major failure modes: **Precursor volatility**



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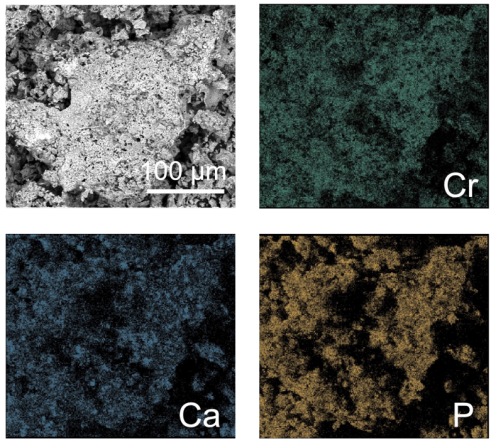
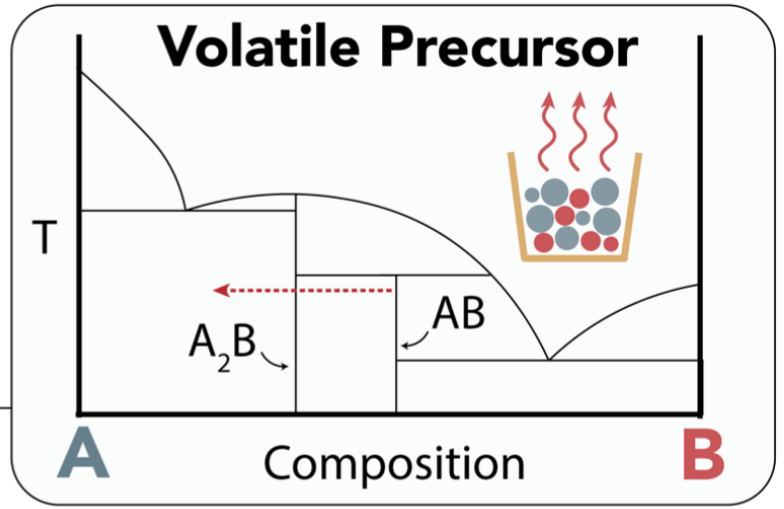
Ca|P ✓ Cr|P ✗



Some precursors react to lock in PO_4, others don't

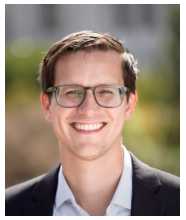


$CaCr_2P_2O_9$

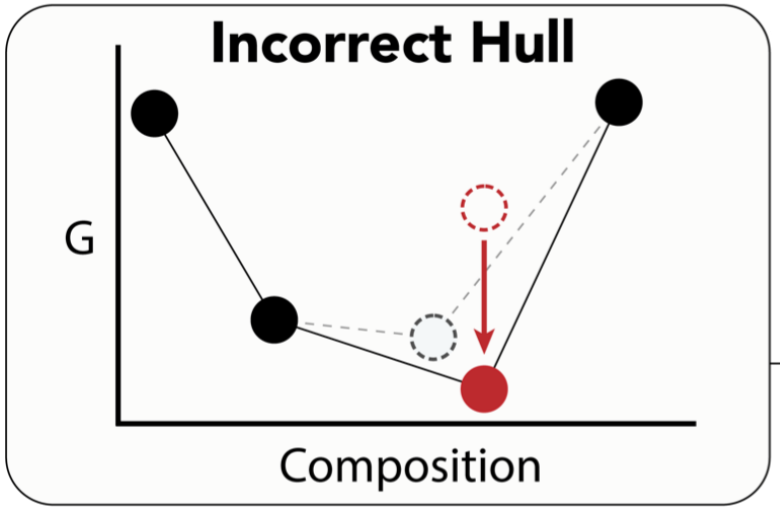
Four major failure modes: **Incorrect computed hull**

Occasional Materials Project errors

- Target: $YbMoO_4$
- Major products: Yb_2O_3 + MoO_3 (no reaction)
  - Upon further investigation, MP used Yb^{2+} pseudopotential but should have used Yb^{3+}
  - New calculations stabilize Yb_2O_3 and destabilize $YbMoO_4$ (+100 meV/atom)



Matt



$La_5Mn_5O_{16}$
$YbMoO_4$
$BaGdCrFeO_6$

Computational Barriers

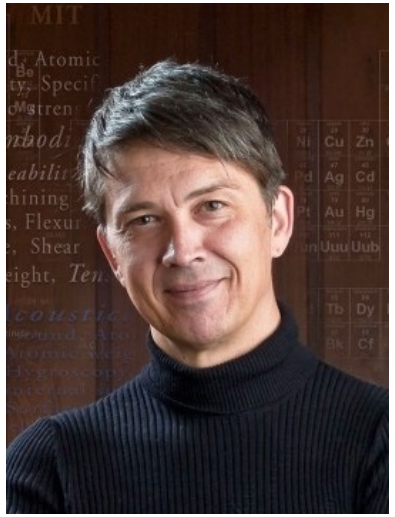
Conclusions

- 43/58 targets successfully made **(74% success rate) → DFT is effective**
- These materials were discovered from **< 3 weeks of experimentation**

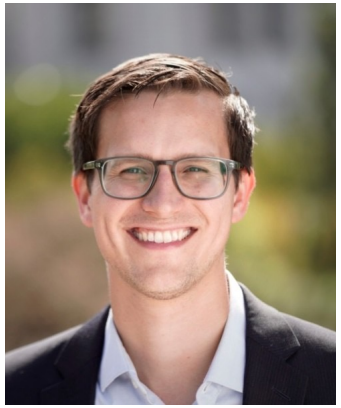
  → Automation enables **rapid discovery**; much more is possible!

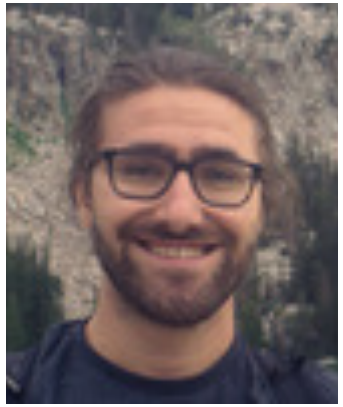
- But even with automation, it's **not easy…**
  - Manual effort needed to refill chemicals, clean the consumables, and take a closer look at the most difficult XRD patterns
  - Several failure modes still need to be overcome

Acknowledgements



A very large **team effort**! Some members of the “A-Team”





Persson group, UCB

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