Using thermodynamics to predict the first product formed in solid-state reactions

Design of Materials on Computers
DMC LAB
Bartel Research Group

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Chemical Engineering & Materials Science
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Inorganic materials are often made by solid-state synthesis

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Target

$LiMn_xTi_yO_zF_{1-z}$

Synthesis recipe

- ☑ 50 mg Li_2CO_3
- ☑ 60 mg TiO_2
- ☑ 30 mg MnF_2
- ☑ 800 °C (air)
- ☑ 24 hours

50 mg

60 mg

30 mg

Shake
'n bake

800 °C, 24 hours

Final product!

But experimental synthesis attempts often fail

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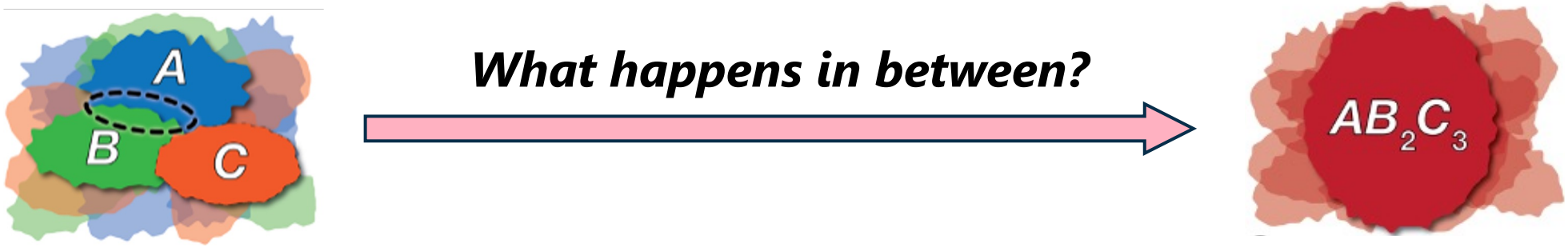
Final product!

😢

$Li_2CO_3|MnF_2 \rightarrow$ **LiF + MnO**

- Precursors may react to form **unreactive intermediates**, restricting target growth
- If we could **predict** these reactions beforehand, we could **plan better syntheses**

Solid-state reactions tend to occur in pairs



Precursors

Target

Figure adapted from: A. Muira, **C. J. Bartel**, …, G. Ceder, *Adv. Mater.* (2021).

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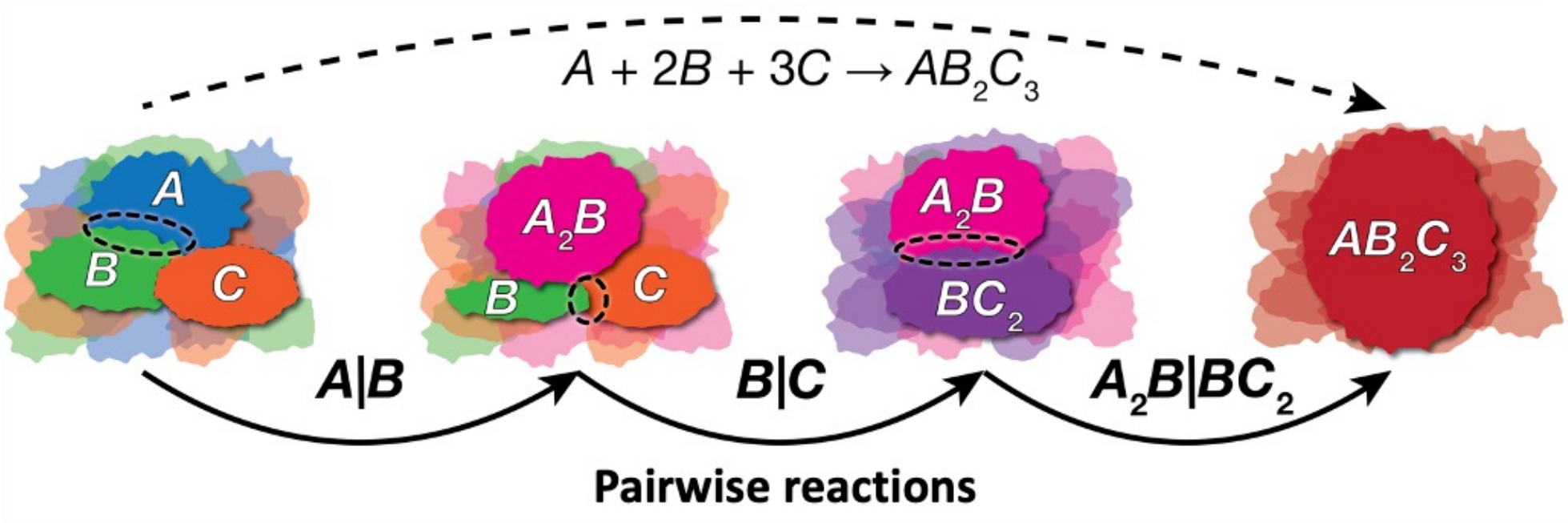

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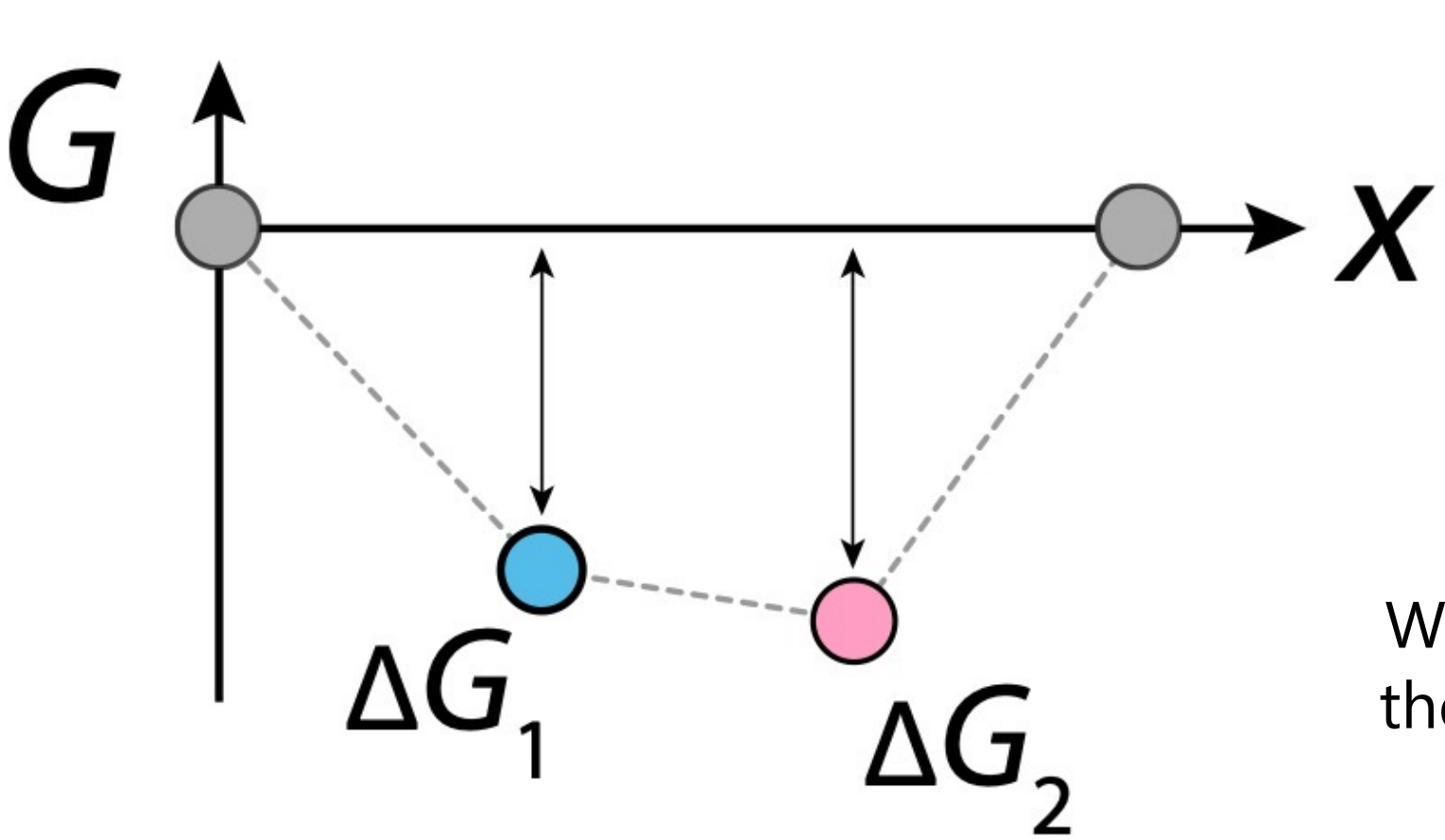
Each pair can be described using a binary convex hull

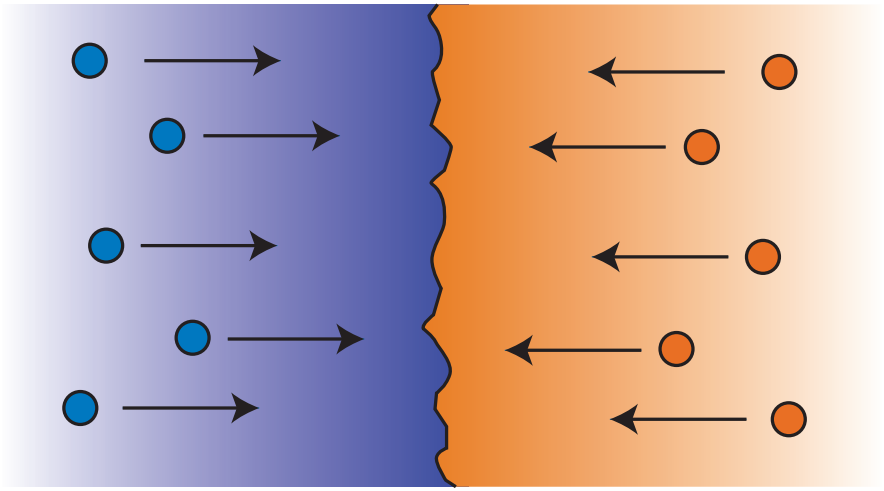


Precursors

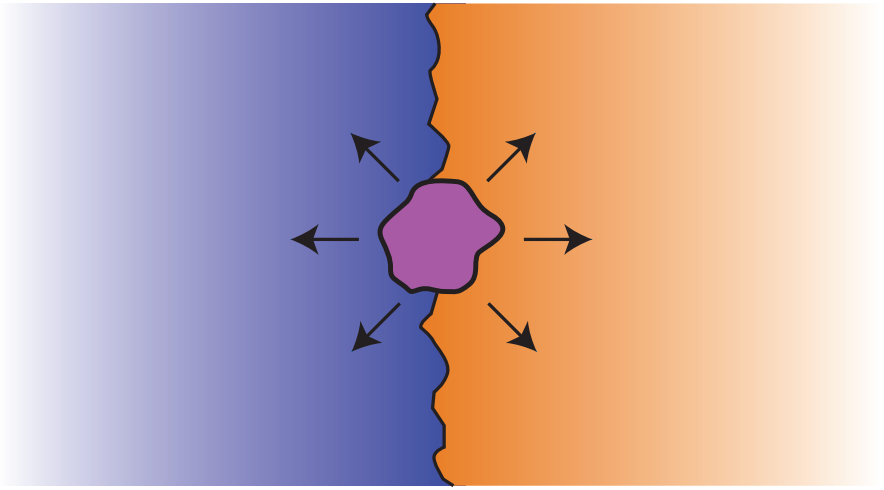
We can model the reaction thermodynamics (ΔG_i)…But does this tell us which product will form?

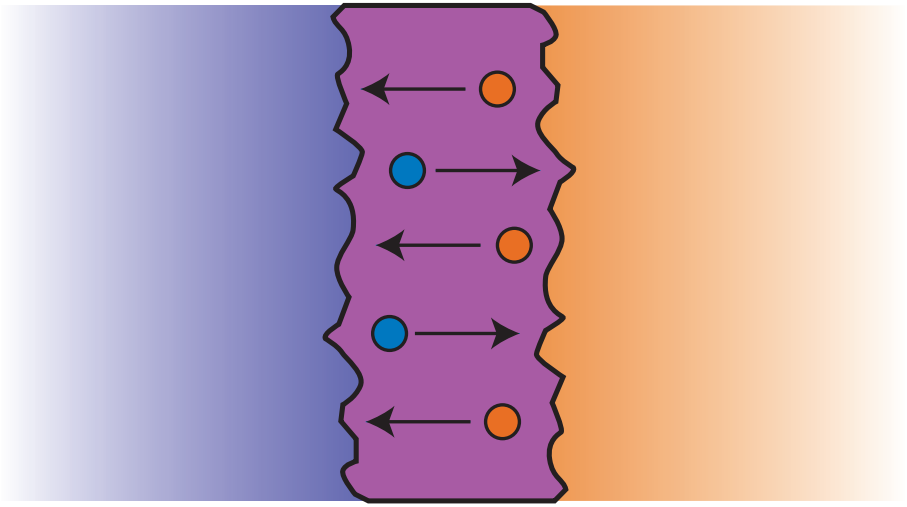
Diffusion and *nucleation* both dictate what product forms

Ions need to **diffuse** to the interface



A product needs to **nucleate**





That product needs to grow *via* interdiffusion

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Ions need to **diffuse** to the interface

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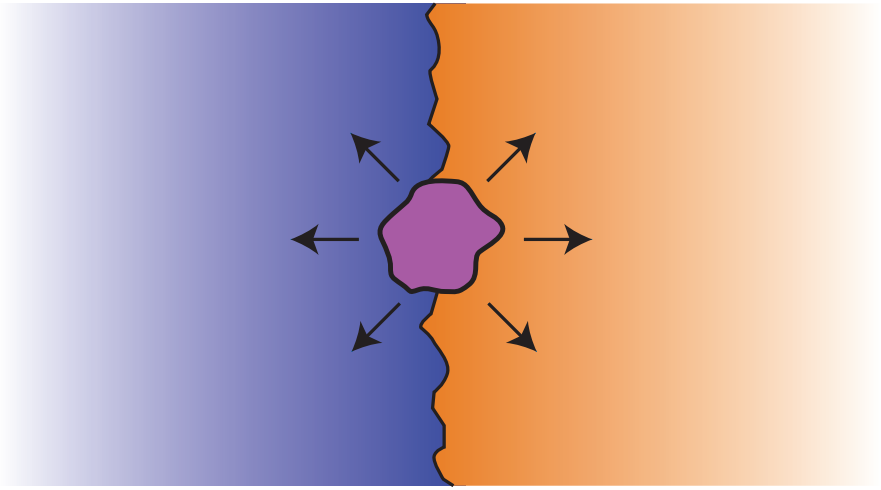

That product needs to grow *via* interdiffusion

Nucleation primarily depends on ΔG and σ

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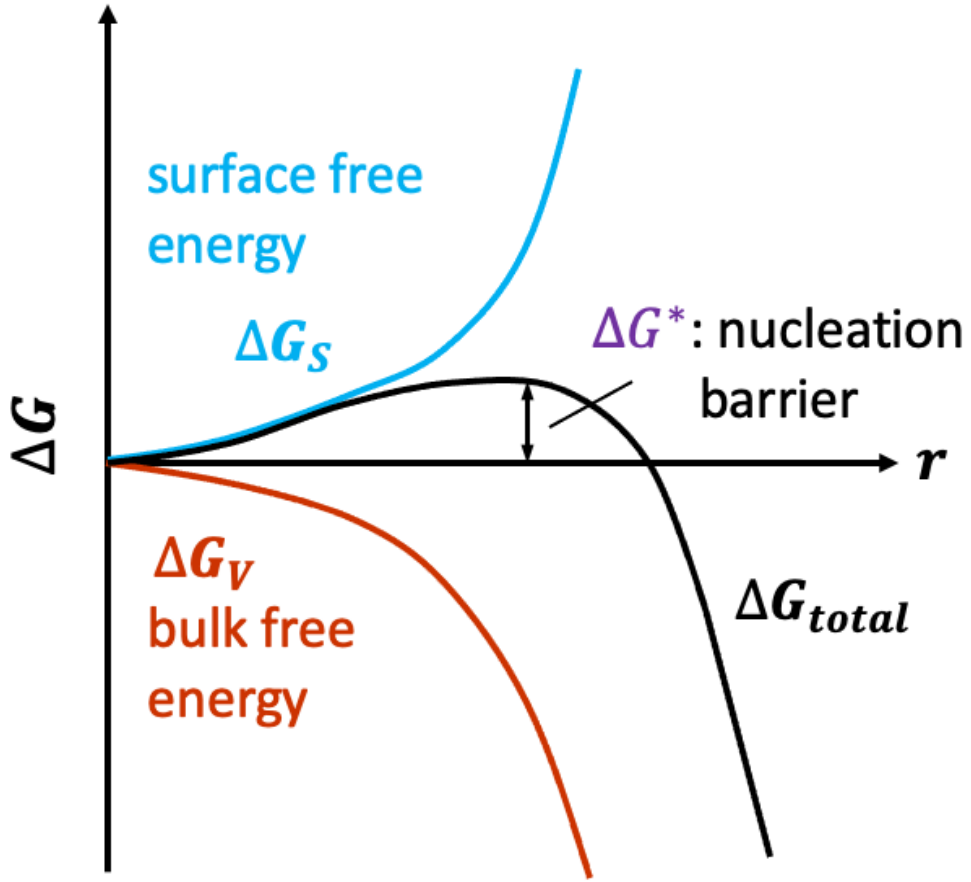
Classical nucleation theory



Nucleation rate:

$$Q = \mathrm{A}\exp\left(-\frac{\Delta G^*}{k_B T}\right)$$

Nucleation barrier:

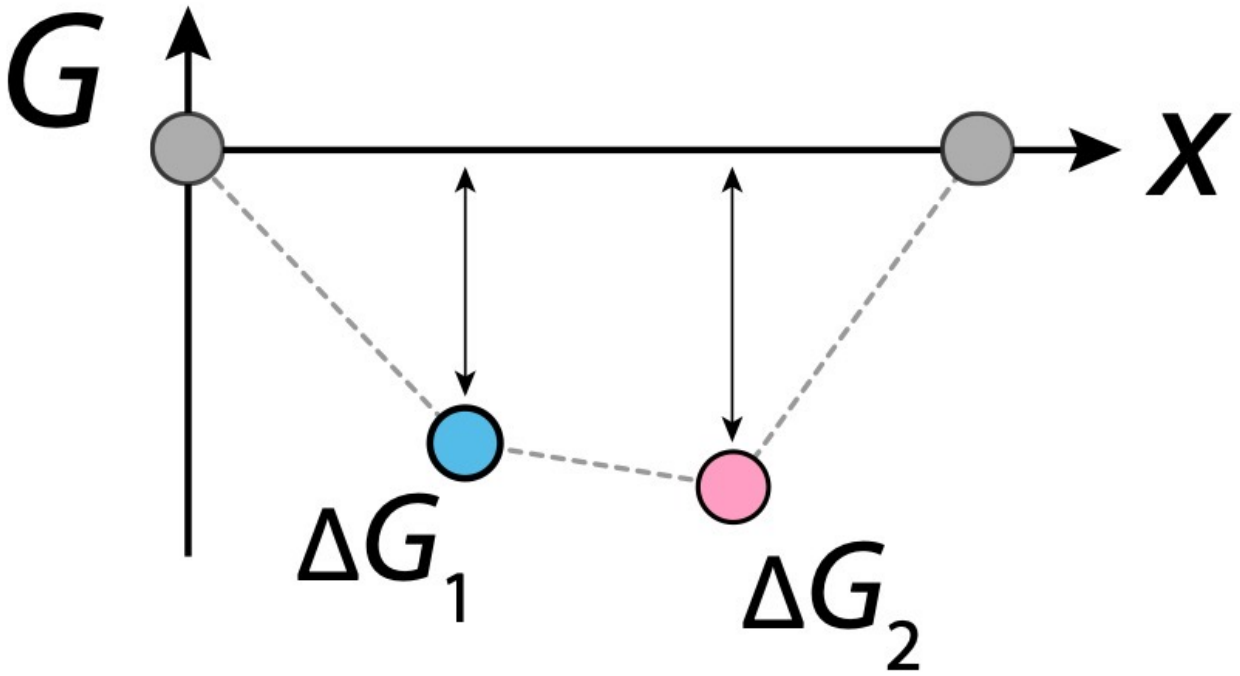
$$\Delta G^* = \frac{16\pi\sigma^3}{3(n\Delta G)^2}$$

Surface energy

Atomic density

Bulk reaction energy

At some point, ΔG should dominate the initial product



If the difference between ΔG_1 and ΔG_2 is sufficiently large, it outweighs any difference between σ_1 and σ_2

$$\ln(\boldsymbol{Q_1}/\boldsymbol{Q_2}) = \frac{16\pi}{3n^2 k_B T}\left(\frac{(\sigma_1)^3}{(\Delta G_1)^2} - \frac{(\sigma_2)^3}{(\Delta G_2)^2}\right)$$

$\longrightarrow$ Surface energy

$\longrightarrow$ Bulk reaction energy

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How large is "sufficiently large"

If the difference between ΔG_1 and ΔG_2 is **sufficiently large**, it outweighs any difference between σ_1 and σ_2

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$\longrightarrow$ Surface energy

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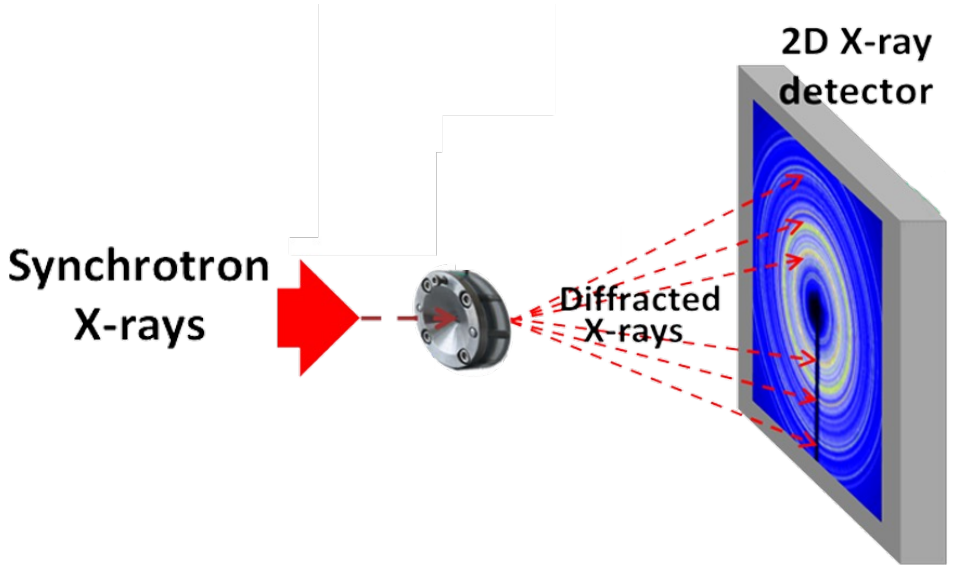
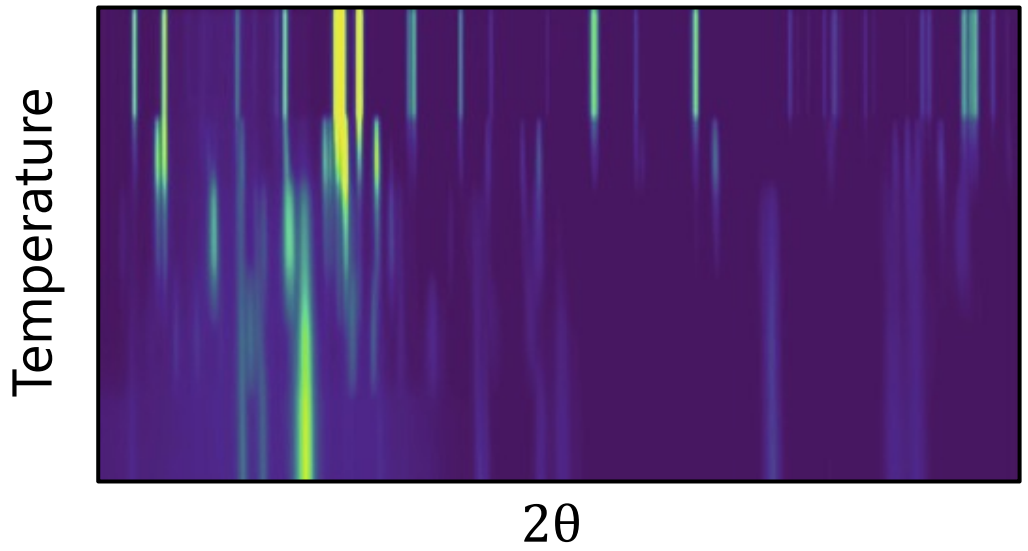
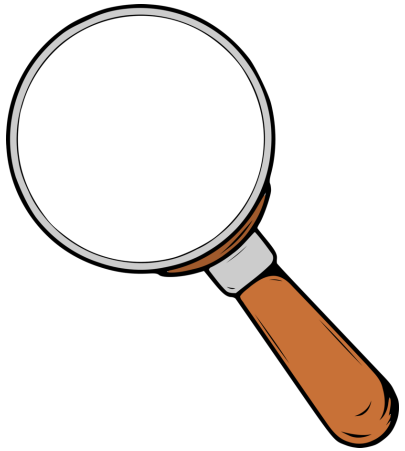
In situ X-ray diffraction (XRD) for experimental calibration





Given a pair of solid reactants, what is the **first product** that forms during heating?



We used 37 ternary metal oxides (*A*-*M*-O) as a test case

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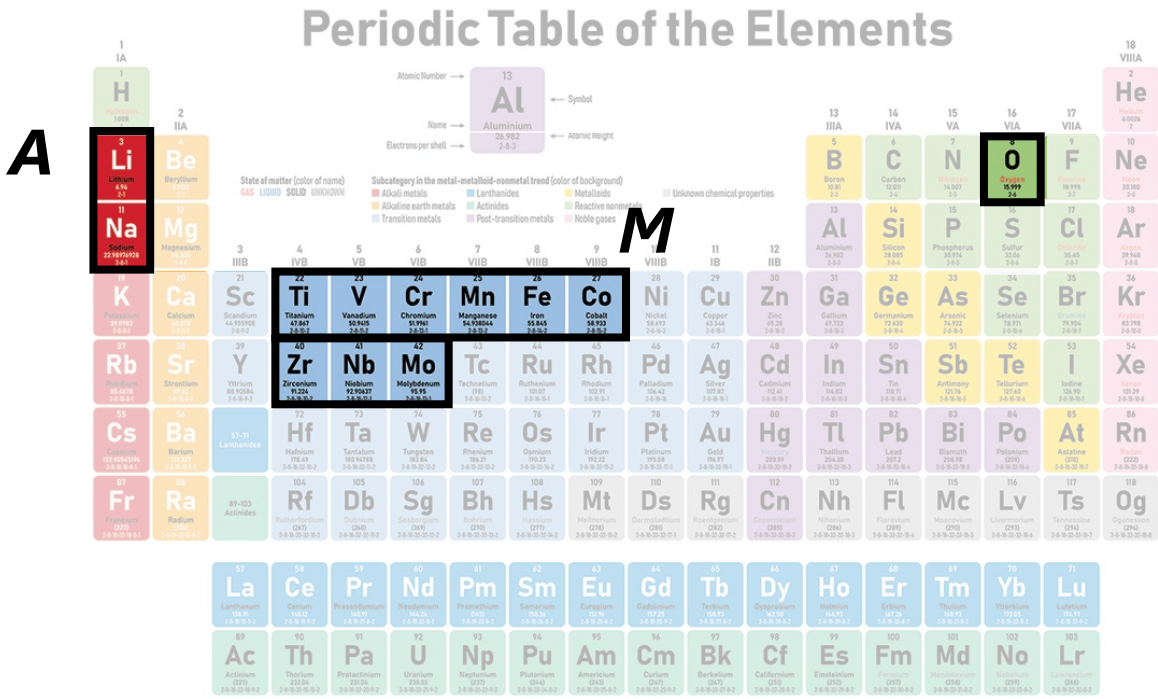
We took **alkali (*A*) precursors**:

Li_2CO_3, LiOH, Li_2O, $NaNO_3$, …

Mixed them with **metal (*M*) precursors**:

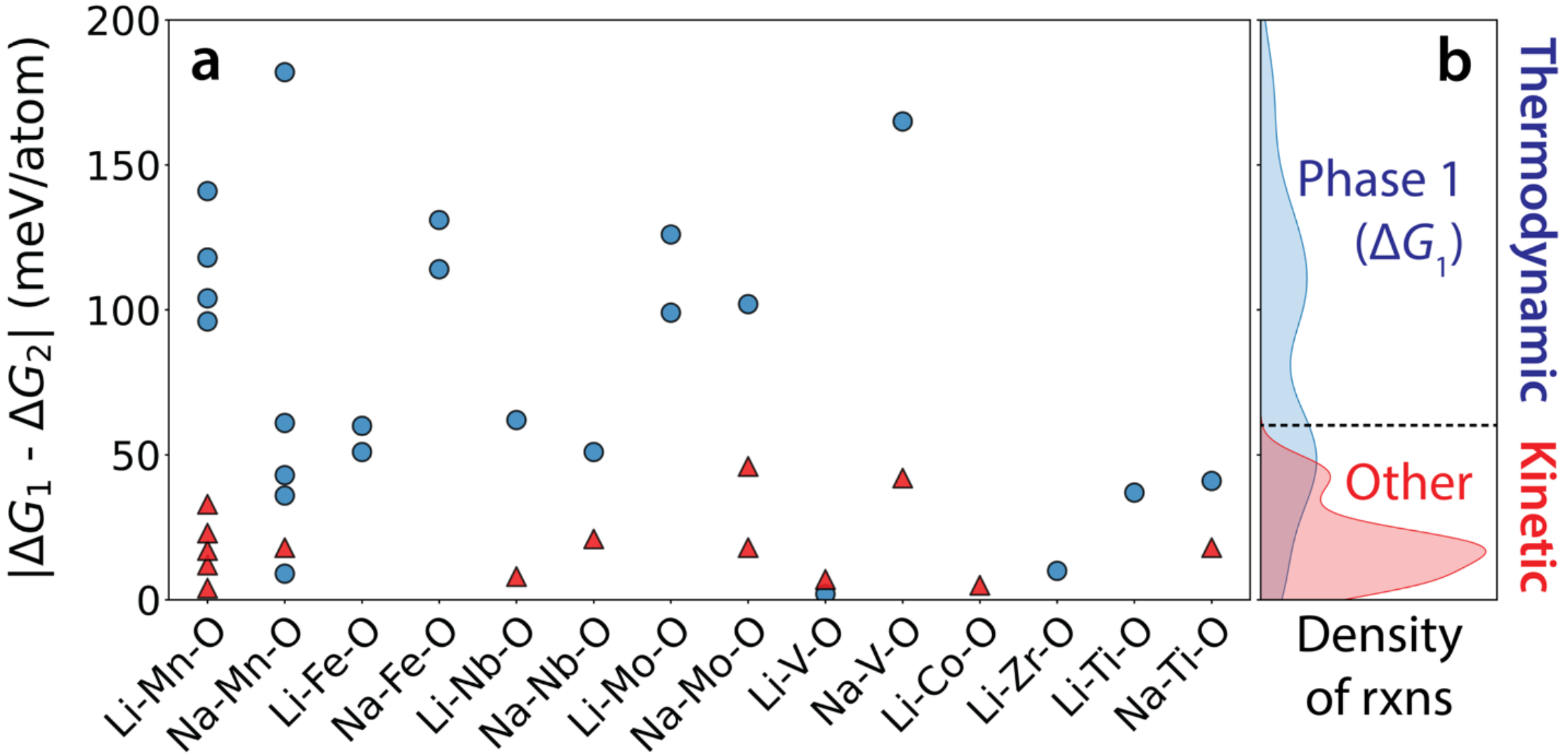
MnO, Mn_3O_4, MnO_2, Cr_2O_3, …

In a **1:1 ratio of *A*:*M*** for each sample, which was then **heated to 600 °C** while XRD scans were performed.



Szymanski *et al.*, Science Advances (2024).

Outcomes show a regime of thermodynamic (ΔG) control



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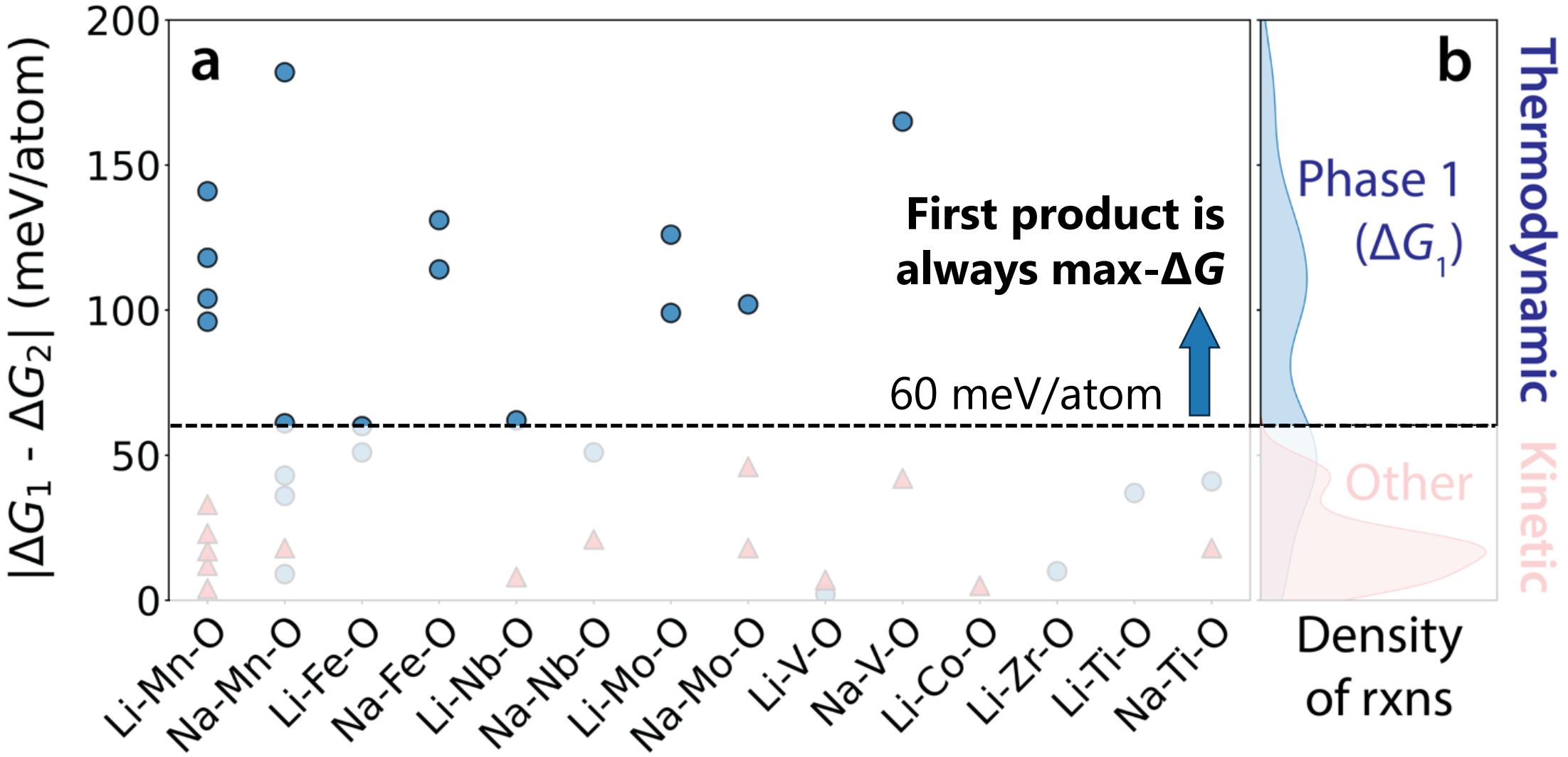

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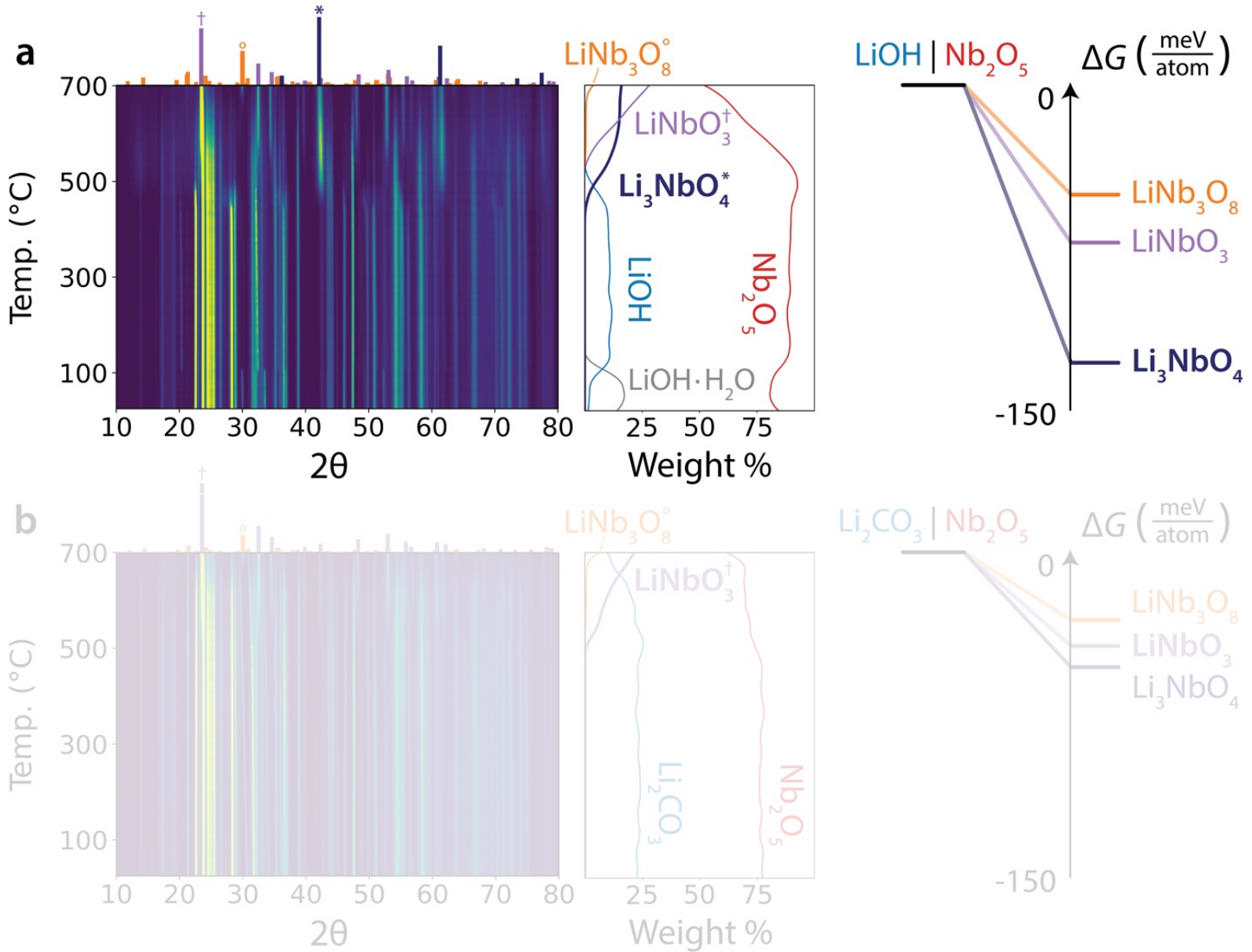
An example: precursors influence the first Li-Nb-O product



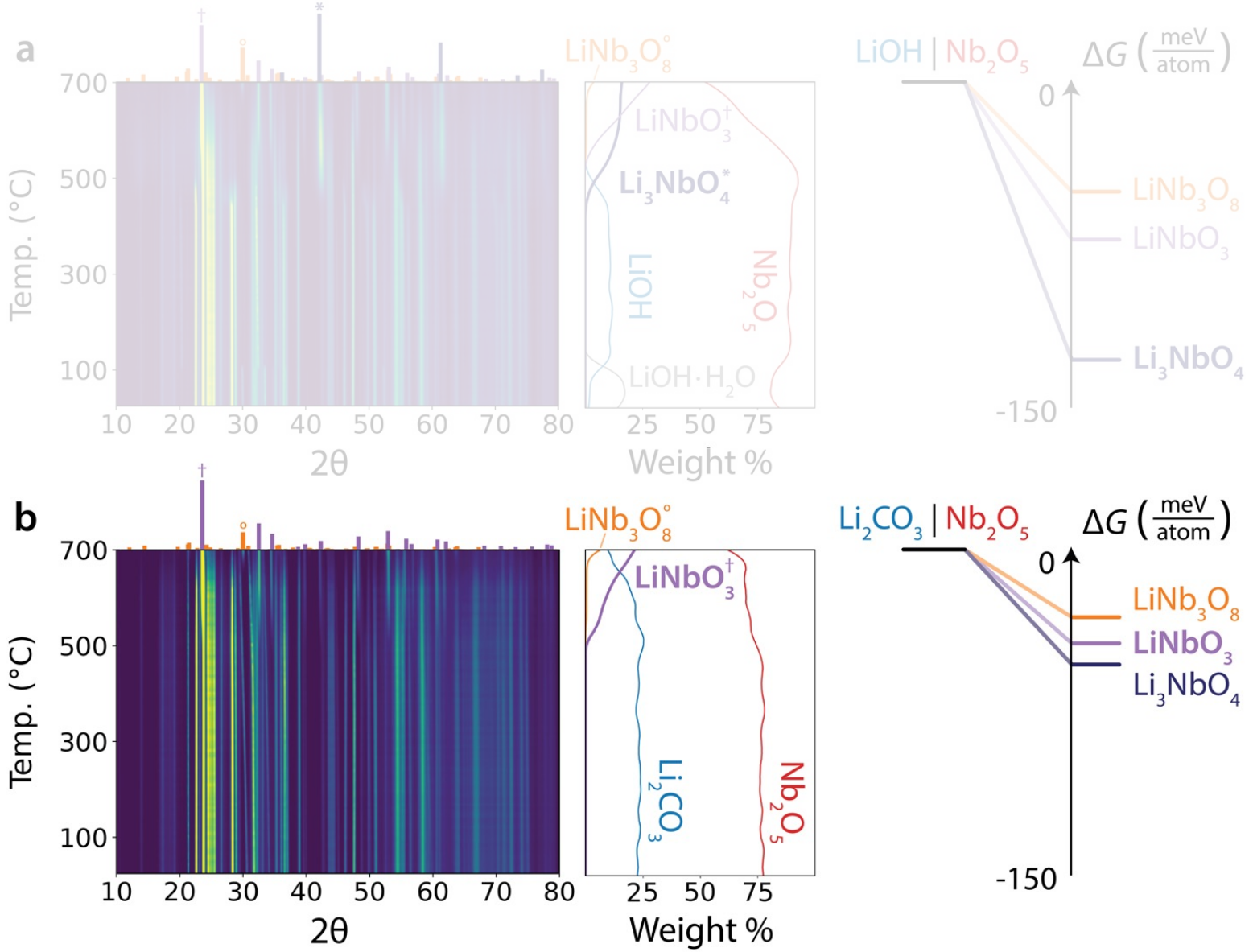
Case 1:

Strong thermodynamic preference for **Li_3NbO_4** allows it to form first

Case 2:

Weak thermodynamic preference leads to the formation of **$LiNbO_3$**, which matches the overall sample stoichiometry of 1:1 Li:Nb

An example: precursors influence the first Li-Nb-O product



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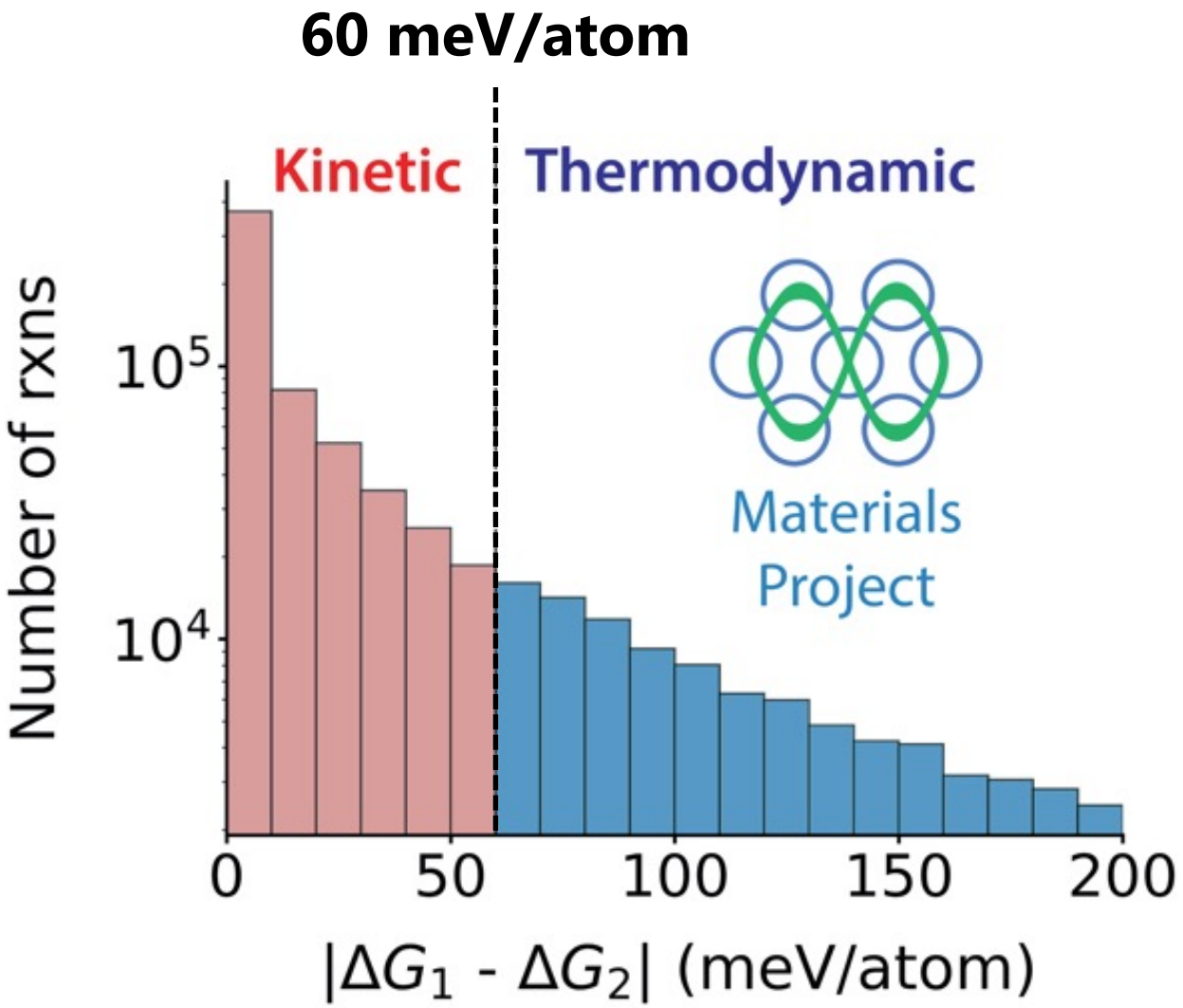
Analysis of reaction energy different in the Materials Project



15% of all pairwise reactions in the Materials Project fall above the proposed threshold of 60 meV/atom, and therefore have outcomes that *may* be predictable using DFT

These predictions can inform synthesis planning

Szymanski *et al.*, Science Advances (2024).

Some caveats and limitations

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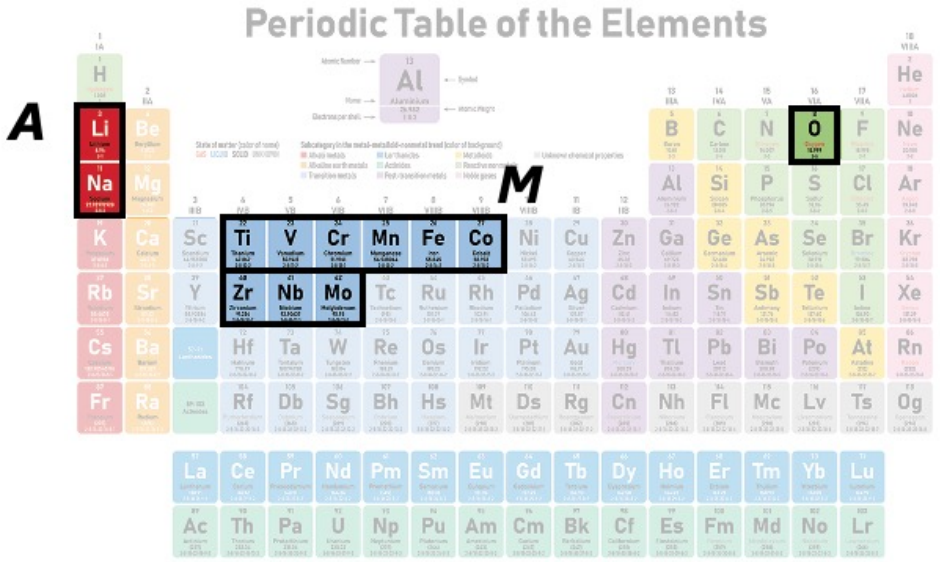
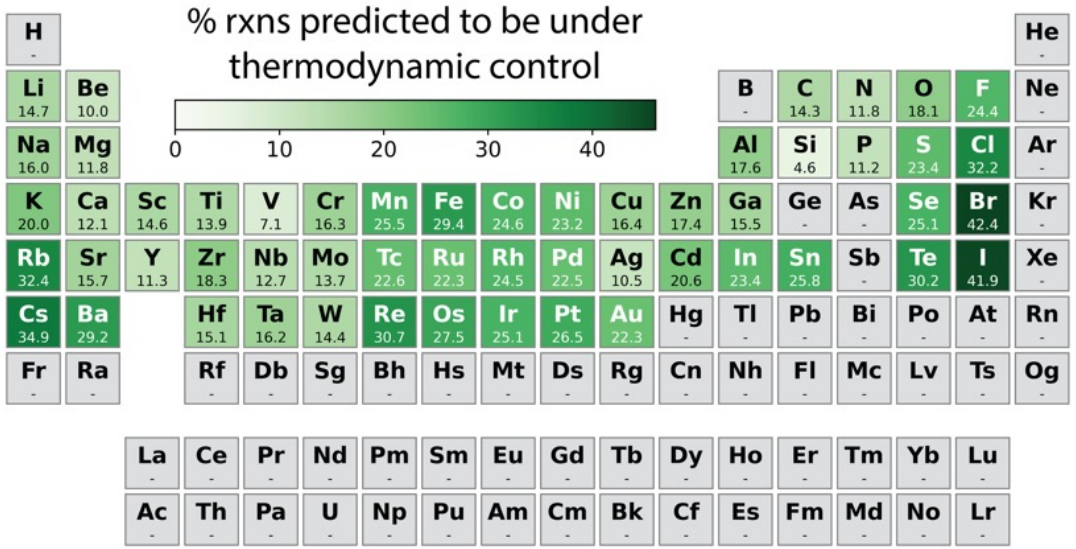
Our "training" set



Our "test" set



There is likely to be some **chemistry-dependence** of the proposed threshold

More work is needed on this front! **Collaboration between exp and theory is key**

Acknowledgements

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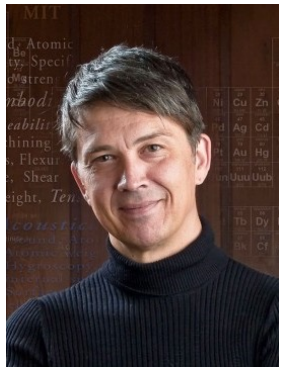




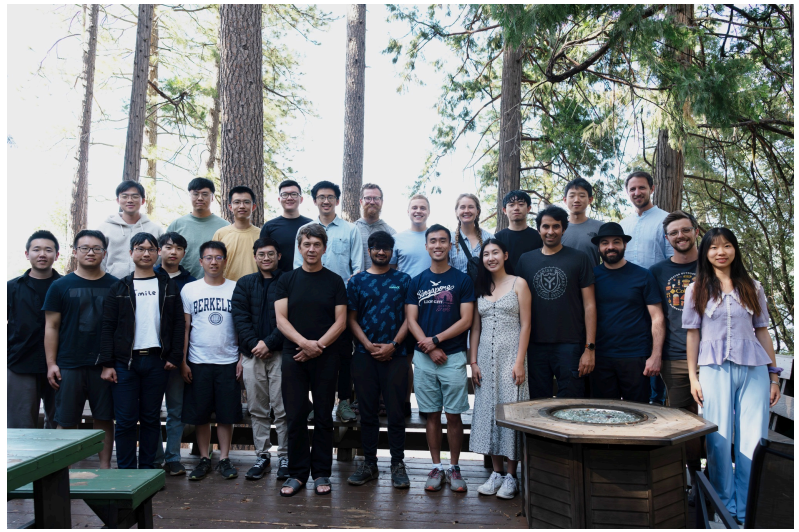

GRC

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