Fluoride Frameworks as Potential Calcium Battery Cathodes

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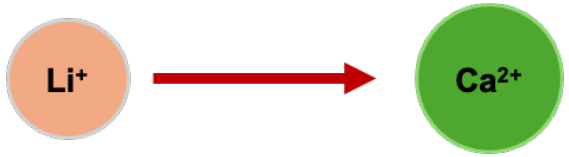
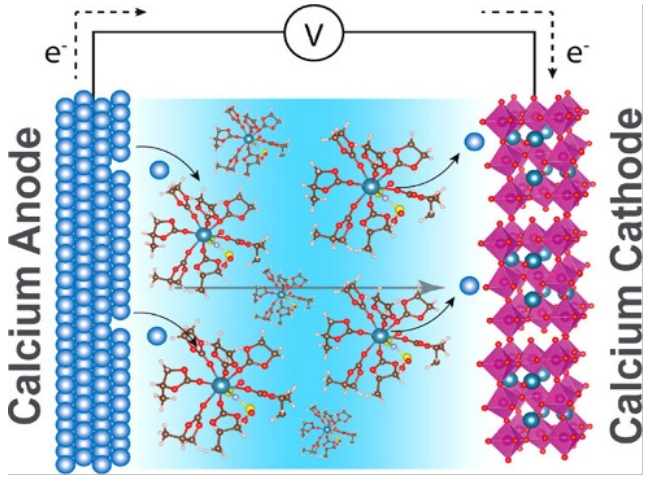
July 18, 2024

Calcium battery (CB): as alternative to Li-ion battery





Hosein, ACS Energy Lett. 2021

Why CB?

- Comparable standard reduction potential (**–2.87 V** vs SHE) with that of Li (**-3.04 V**)
- Ca^{2+}: exchanges **$2e^-$** at a time instead of **$1e^-$** for Li^+ case
- Use of **Ca metal anodes**: offer high energy density
- Ca is most abundant (**~ 4.15%**) than Li (**~ 0.002%**)[1]

1. https://en.wikipedia.org/wiki/Abundance_of_elements_in_Earth%27s_crust

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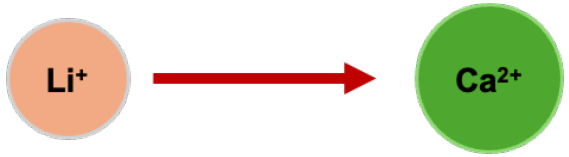

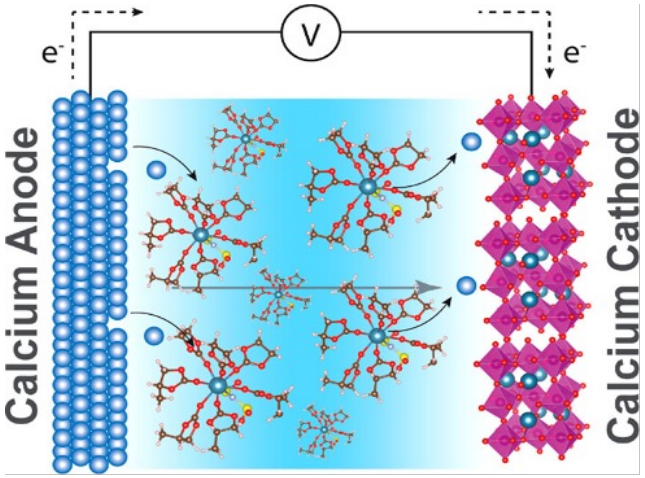

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The development of CB is challenged by the lack of suitable cathodes exhibiting:

- Thermodynamic and cyclic stability
- Reasonable energy density
- Facile ionic mobility

Hence, it is crucial to design a better Ca-cathodes that address these challenges

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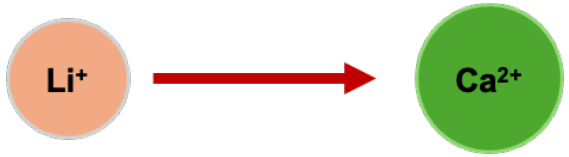

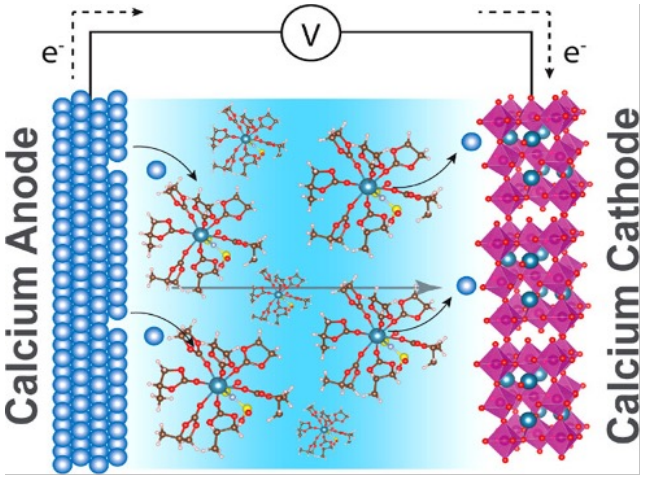

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Important battery metrics:

- Energy density(Wh/Kg) = Voltage(V)x Capacity(mAh/g)
- Power density (C-rate): migration barrier

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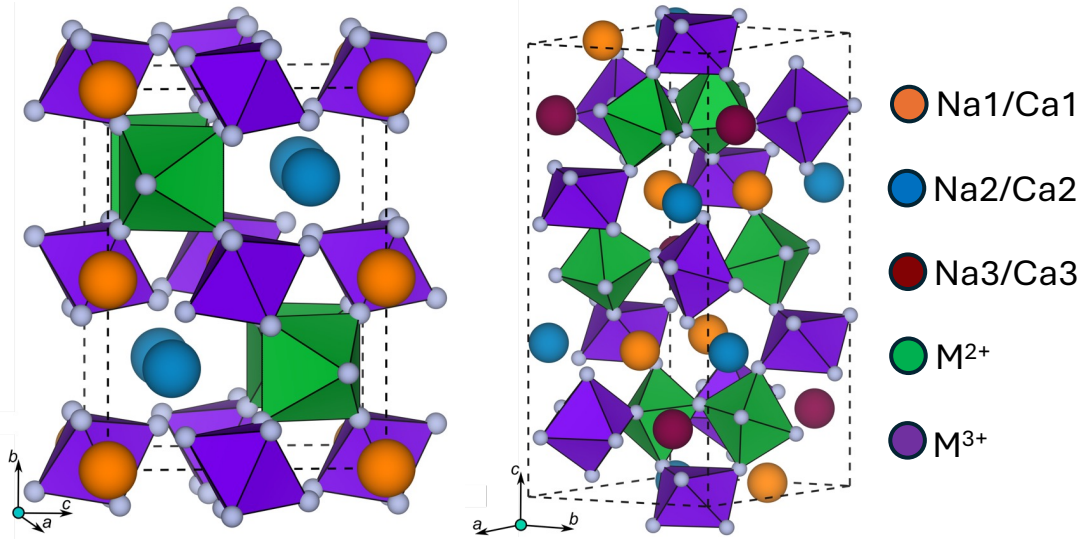
Fluoride frameworks as intercalation positive electrodes

- Role of fluorine (F) in fluoride positive electrodes
  - Fluorine's high electronegativity triggers inductive effect
  - Fluorine's lower molar mass compared to polyanions
- Weberites[1,2] and perovskites[3] fluorides – explored as sodium ion battery cathodes
  - Three dimensional frameworks–exhibit high structural stability
  - Can be easily synthesized using topochemical synthesis method at low temperature

Weberites

Orthorhombic ($Imma$)

Trigonal ($P3_121$)



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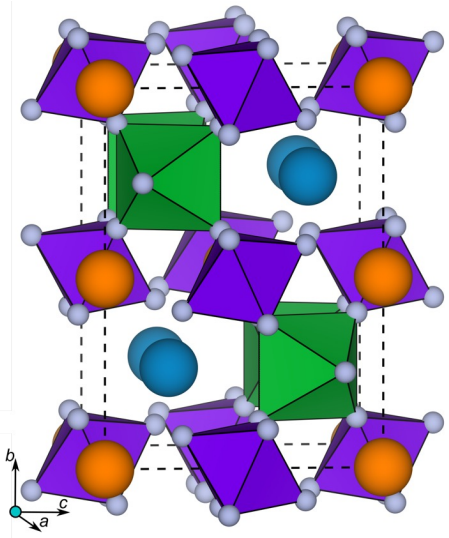

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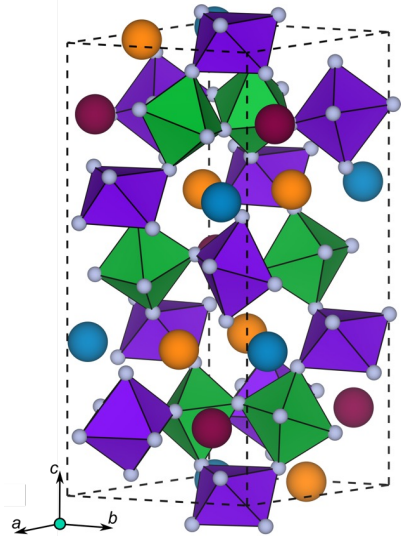
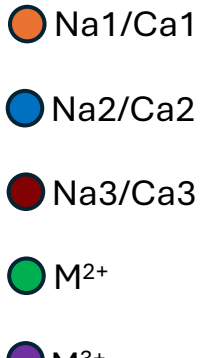
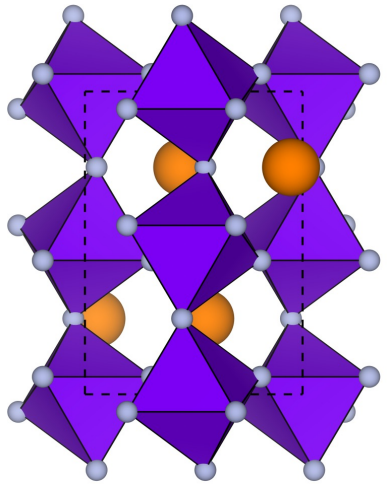


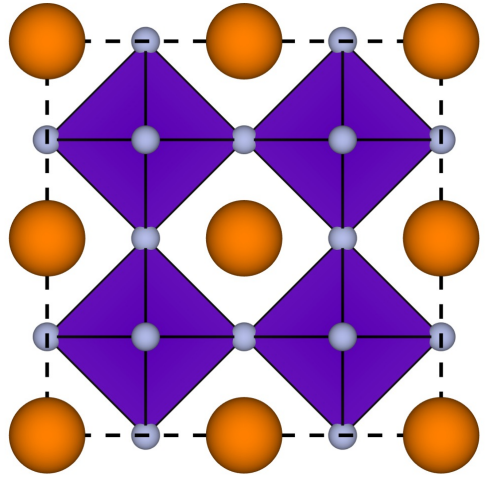


Perovskites

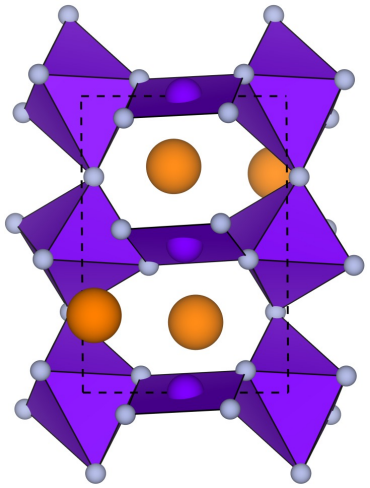
Orthorhombic (*Pnma*)



Cubic ($Pm\bar{3}m$)



Triclinic ($P\bar{1}$)



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  - Fluorine's high electronegativity triggers inductive effect
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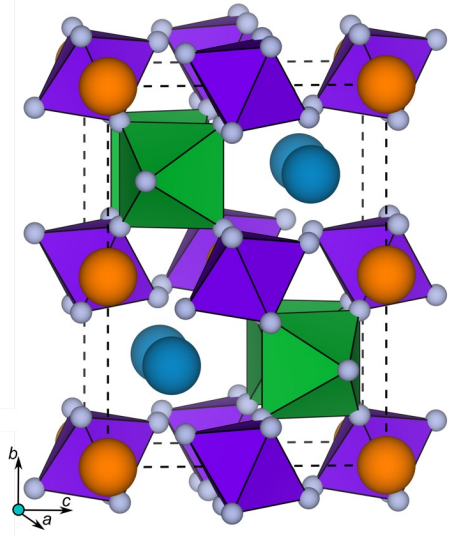
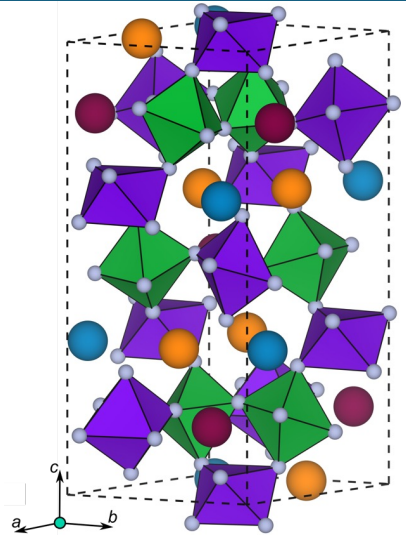
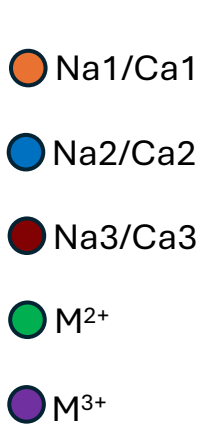
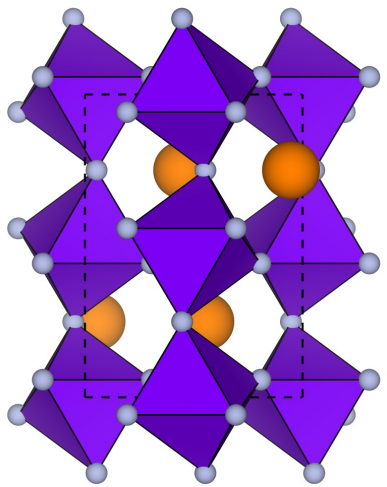
Given the ionic size similarity between **Na^+** (~1.02 Å) and **Ca^{2+}** (~1.00 Å), **weberite** and **perovskite-**based fluorides could be a potential **Ca-cathode**

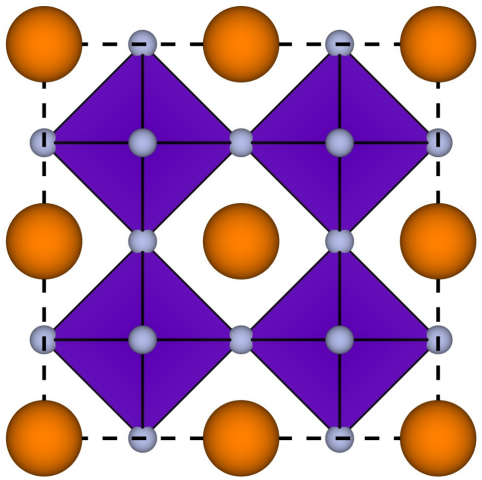
$Ca_xM_2F_7$ & **Ca_xMF_3,** where M = Ti, V, Cr, Mn, Fe, Co, or Ni

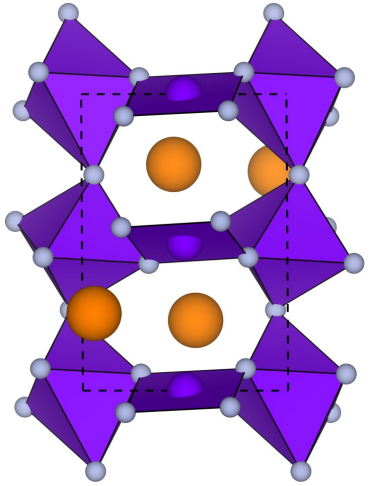












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Ca-cathode design: charge neutrality constraint

- Charge-neutrality (“*zero charge*”) is maintained for Ca content of:
  - **0≤x≤1.5** in $\mathbf{Ca_xM_2F_7}$ — Weberites ($M^{2+}\leftrightarrow M^{3.5+}$)
    - Charged: $Ca_x^{2+}M_2^{3.5+}F_7^{1-}$ → $2*x + 3.5*2 - 1*7 = 0$ → **x = 0** → $\mathbf{Ca_0M_2F_7}$
    - Discharged: $Ca_x^{2+}M_2^{2+}F_7^{1-}$ → $2*x + 2*2 - 1*7 = 0$ → **x = 1.5** → $\mathbf{Ca_{1.5}M_2F_7}$
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- Theoretical capacity (mAh/g): weberites (**320-351**)>perovskites (**231-255**)

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  - **$Na_2Fe_2F_7$** for trigonal and **Na_2NiFeF_7** for orthorhombic weberites
  - Na-based perovskites structures are considered for Ca-perovskites

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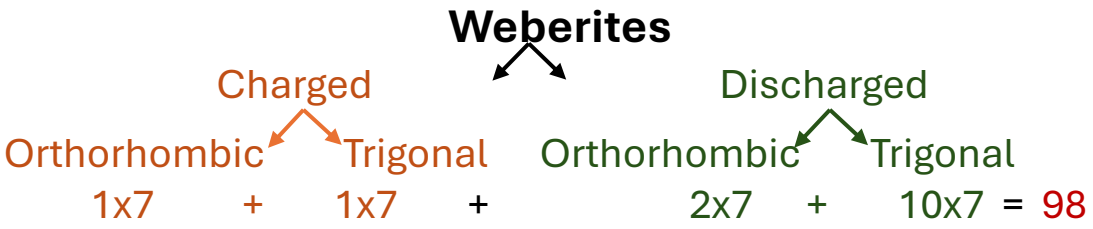

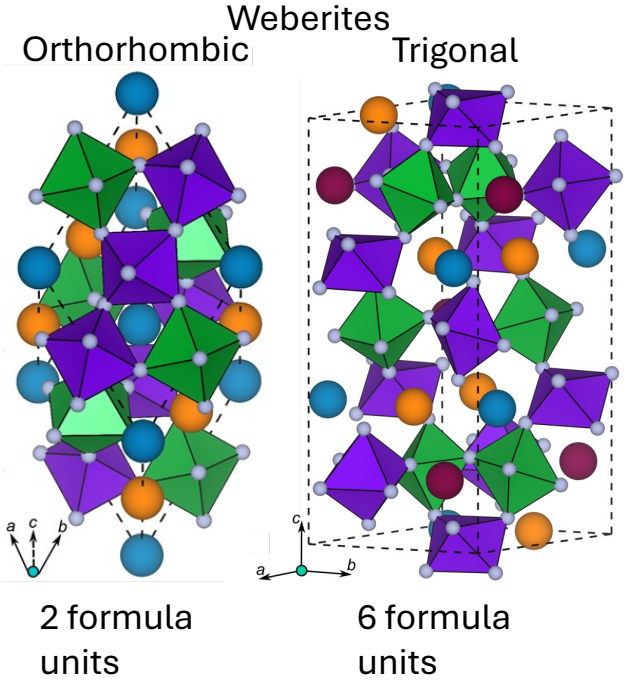

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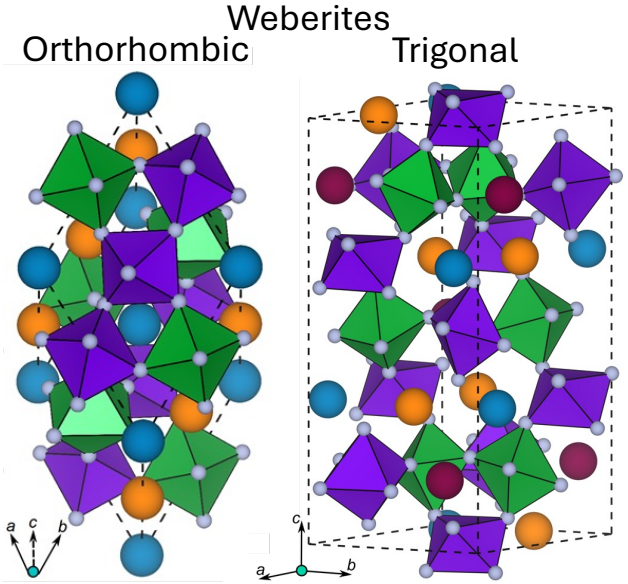

Weberites

Charged: Orthorhombic 1x7 + Trigonal 1x7 +

Discharged: Orthorhombic 2x7 + Trigonal 10x7 = 98

Perovskites

Charged: Orthorhombic, Cubic, Triclinic 1x7

Discharged: Orthorhombic 13(Ti)+3x4(Mn-Ni) + Cubic 6(V) + Triclinic 4(Cr) = 35

- Perform a SCAN+U[2,3] calculations for 98+42=140 configurations to identify the ground state structure

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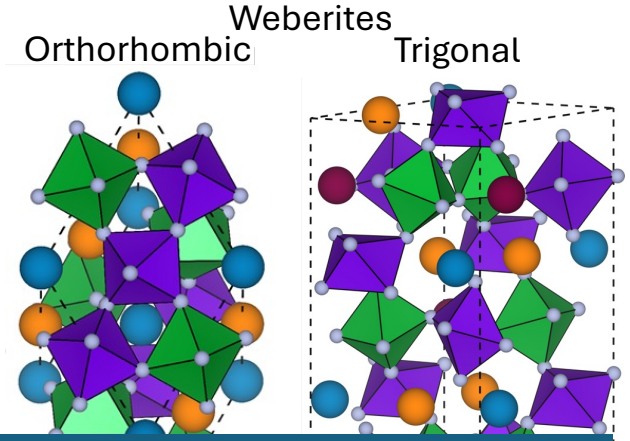

28 (weberite + perovskite) ground state structures are identified for further study as potential Ca-cathodes

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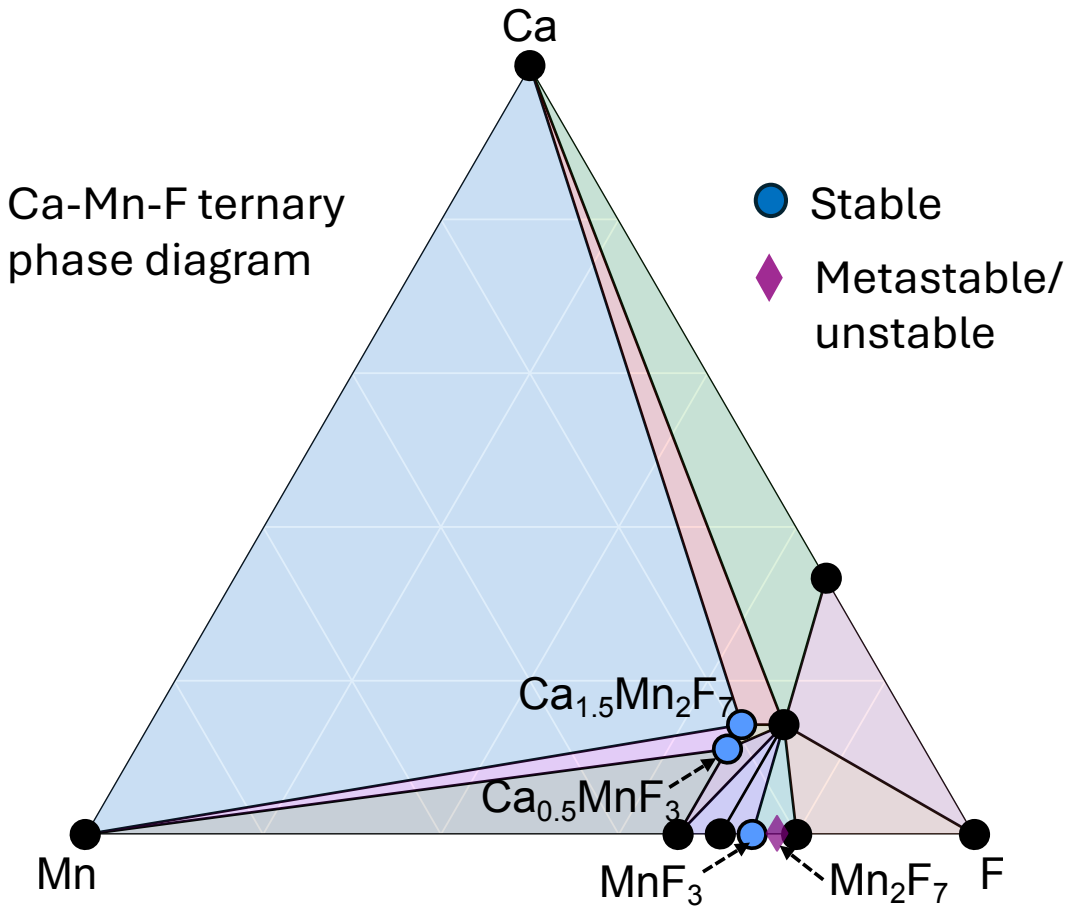
Several weberites & perovskites are stable/metastable

- Potential cathodes should have thermodynamically stable or metastable charged and discharged phases
- Stability is evaluated against the ground state energy of calculated **elemental**, **binary**, and **ternary** phases by quantifying energy above/bellow convex hull ($\mathbf{E^{Hull}}$) using pymatgen[1]



- $\mathbf{E^{Hull} > 0}$: largest energy release upon decomposition

- $\mathbf{E^{Hull} \leq 0}$: lowest energy release upon formation

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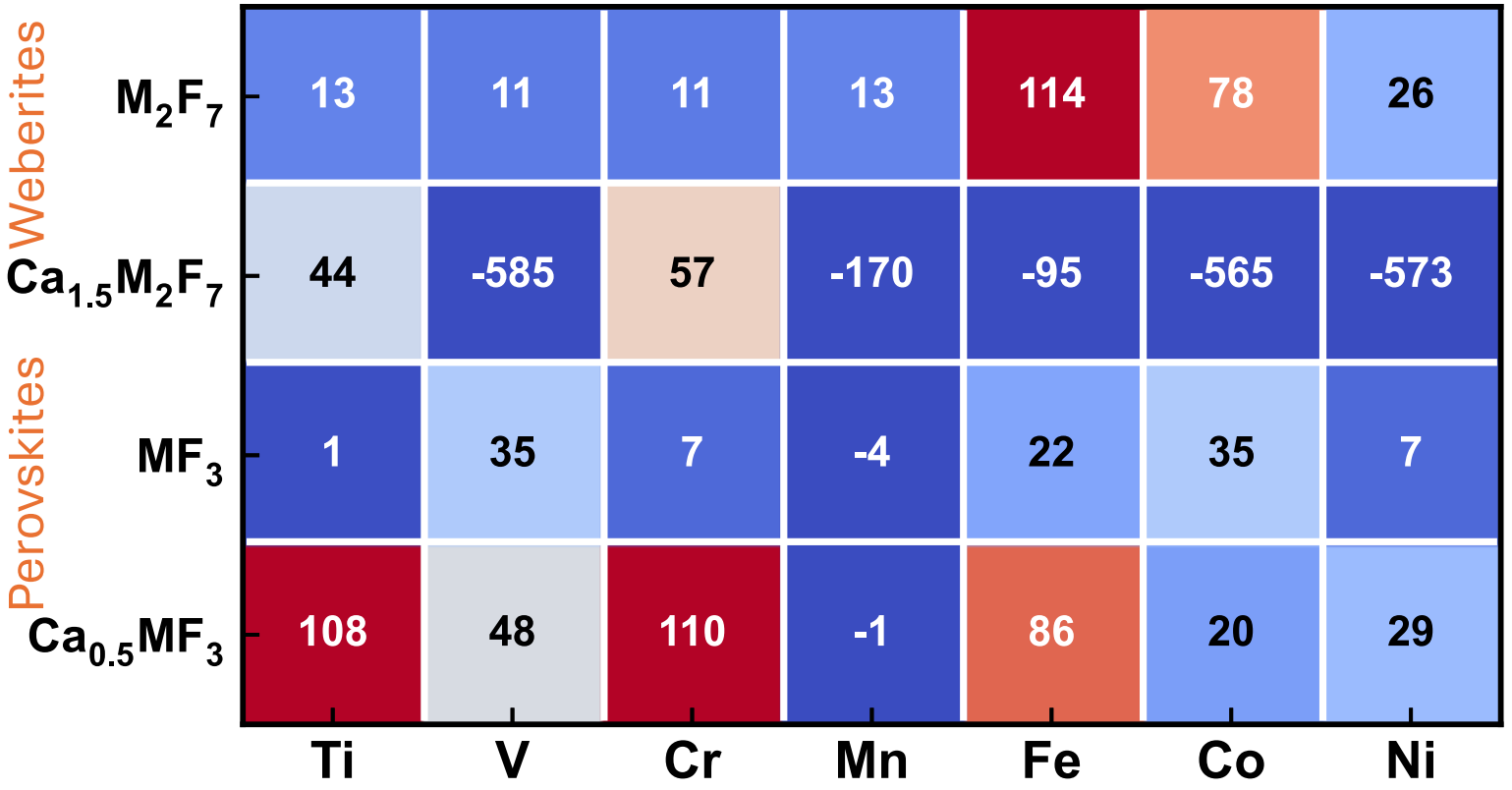

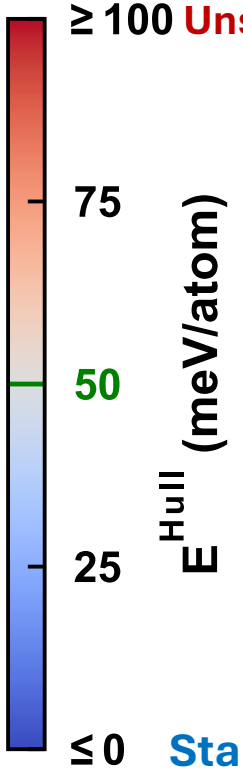

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Threshold for synthesizability[2]

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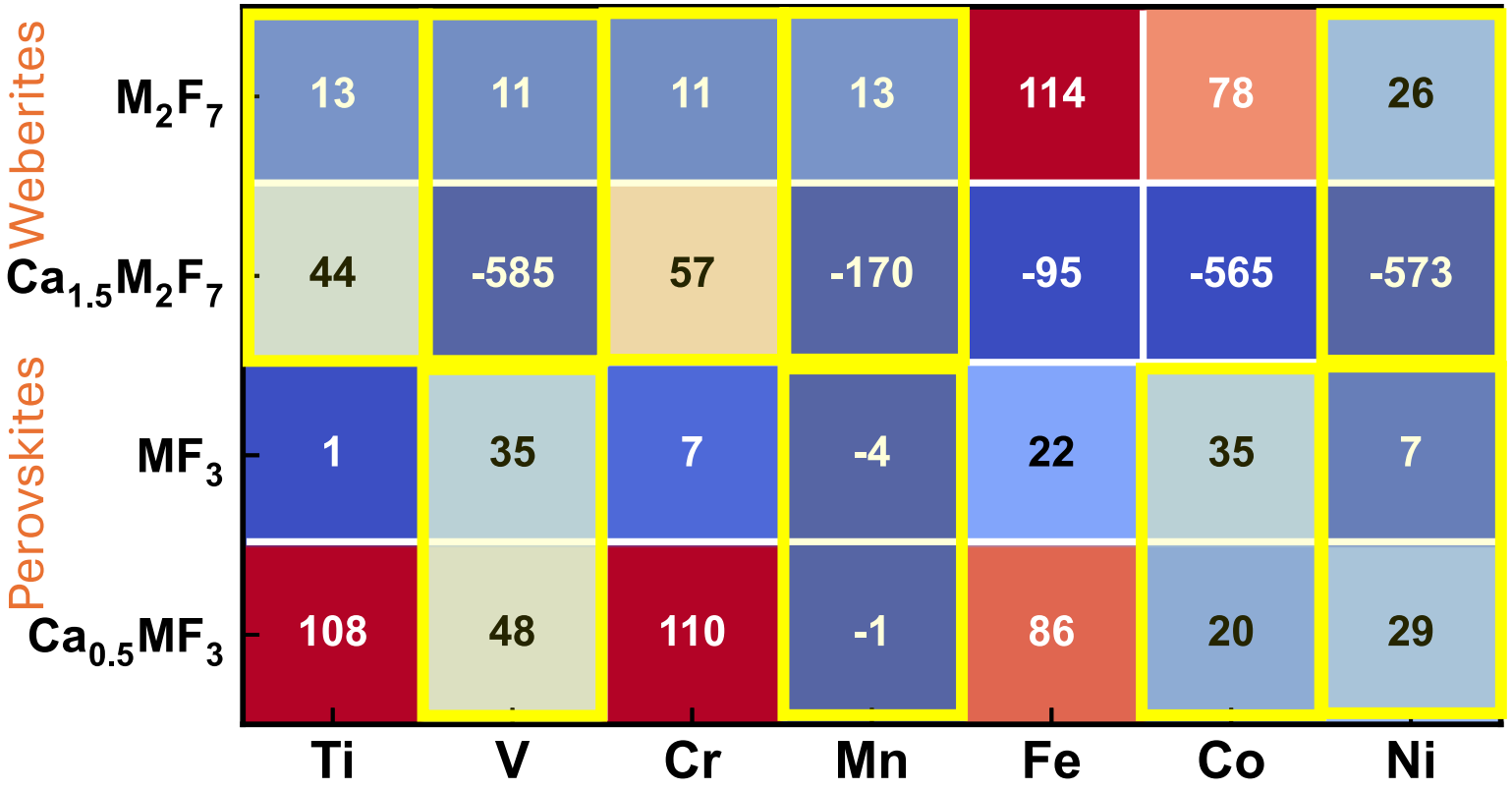
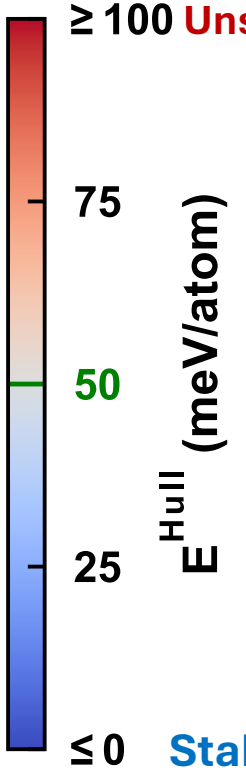
Ti, V, Cr, Mn, Ni-weberites and **V, Mn, Co, Ni-perovskites** are identified as candidate based on thermodynamic stability





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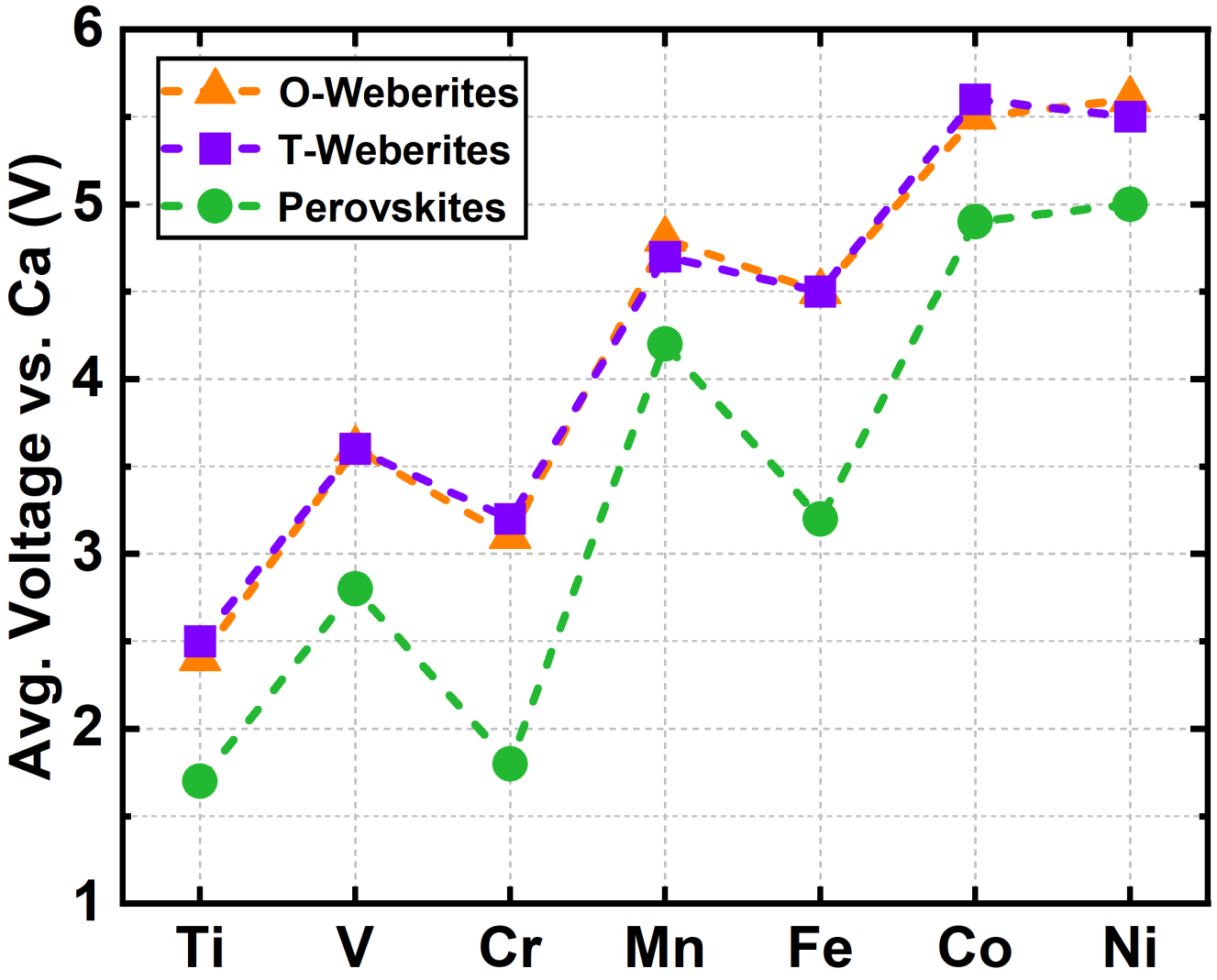

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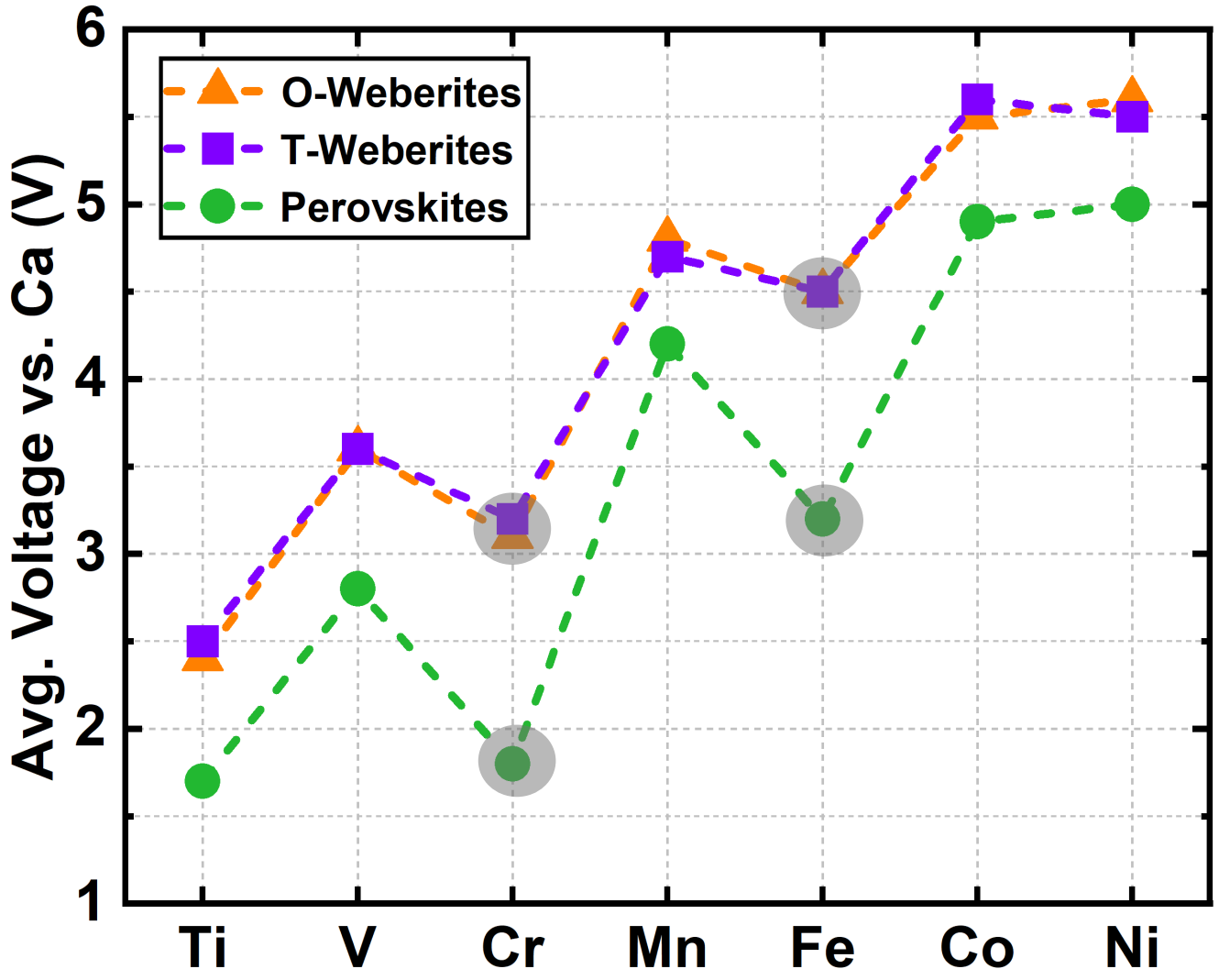
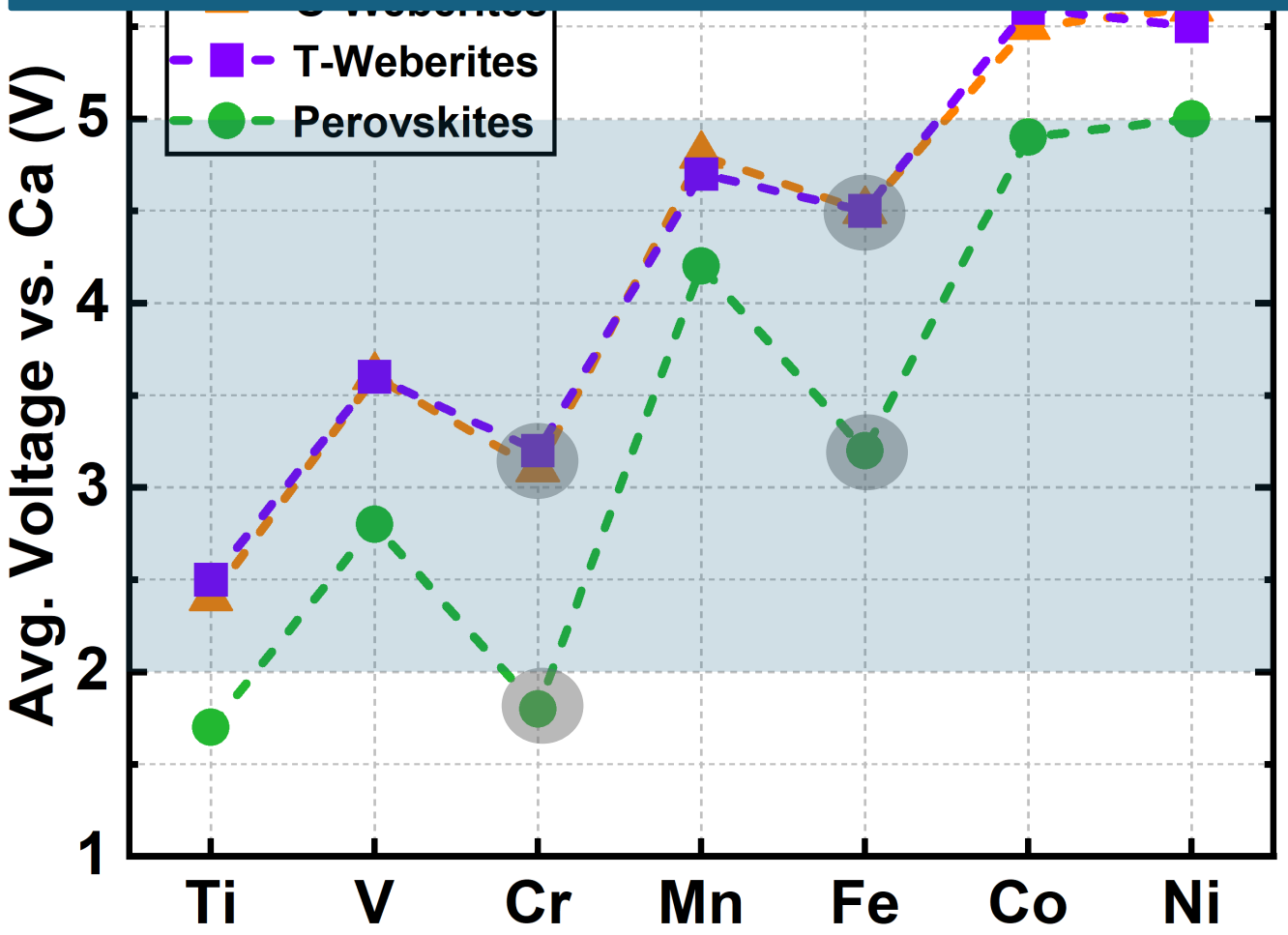


- Weberites voltage is higher than perovskites
- Both orthorhombic and trigonal weberites exhibit similar voltage profile
- From Ti-Ni voltage increment for both weberites and perovskites is *nonmonotonic*
  - "Local" minima at Cr & Fe, attributed to the stability of Cr^{3+} and Fe^{3+}
- Ti- and Cr-perovskites have low voltage
  - Could be a potential anode instead of Ca-cathode

Weberites consistently exhibits higher voltage

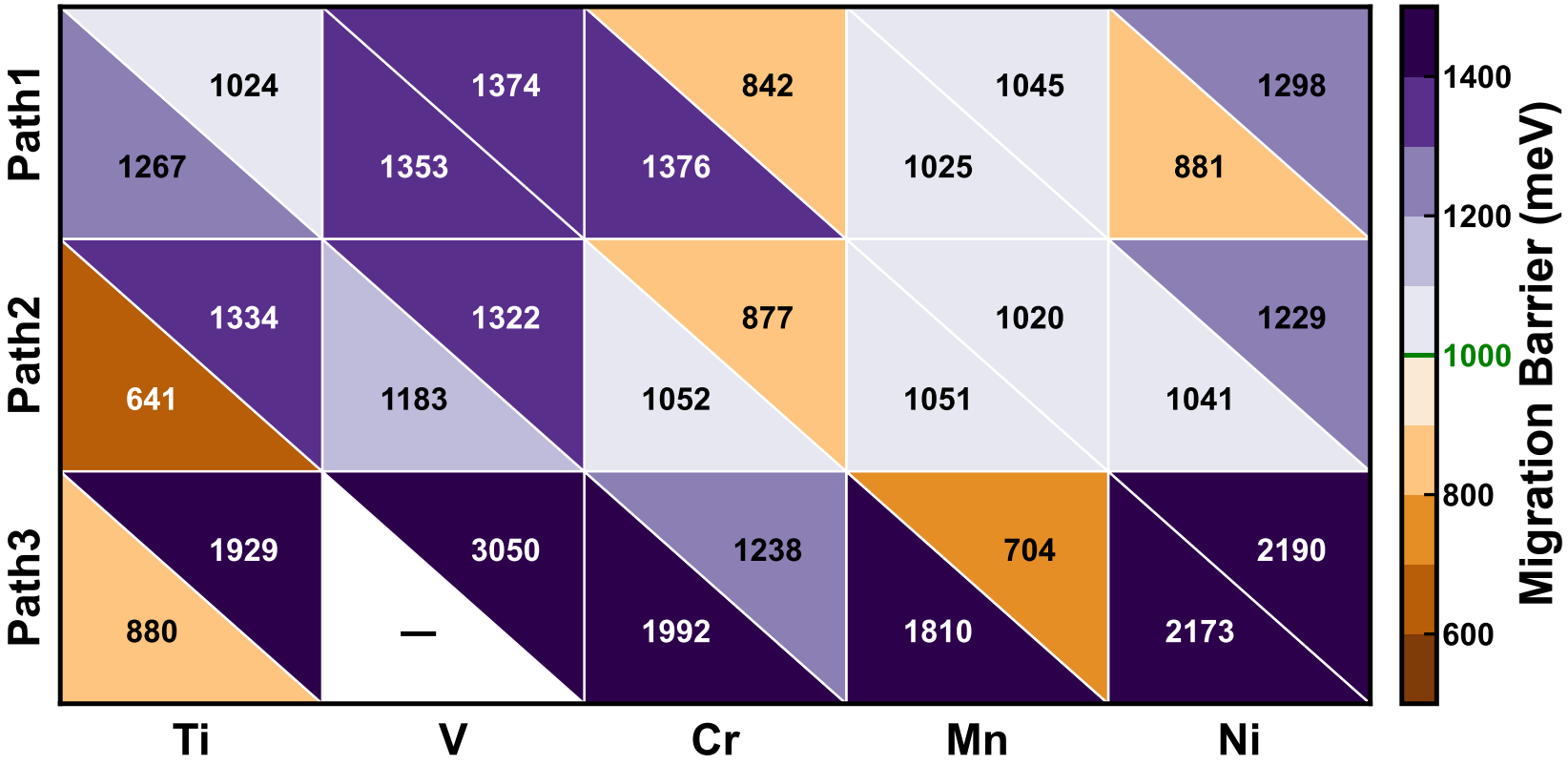
Ti, V, Cr, Mn, Ni-weberites and **V, Mn, Co, Ni-perovskites** are identified as candidate based on stability and voltage calculations

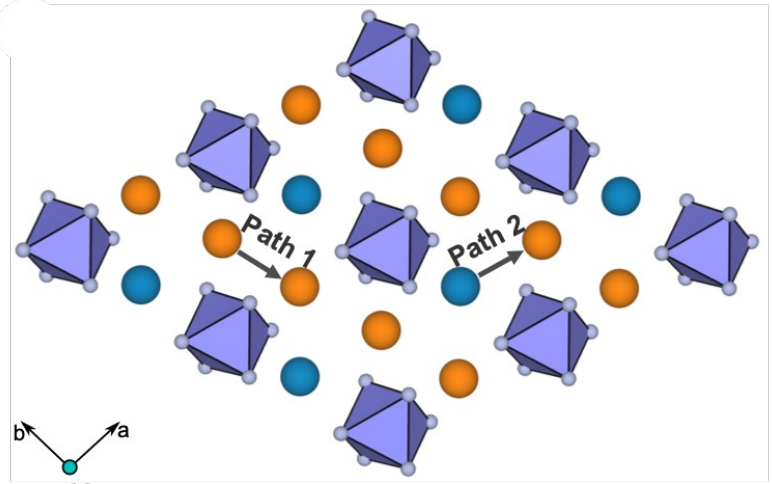


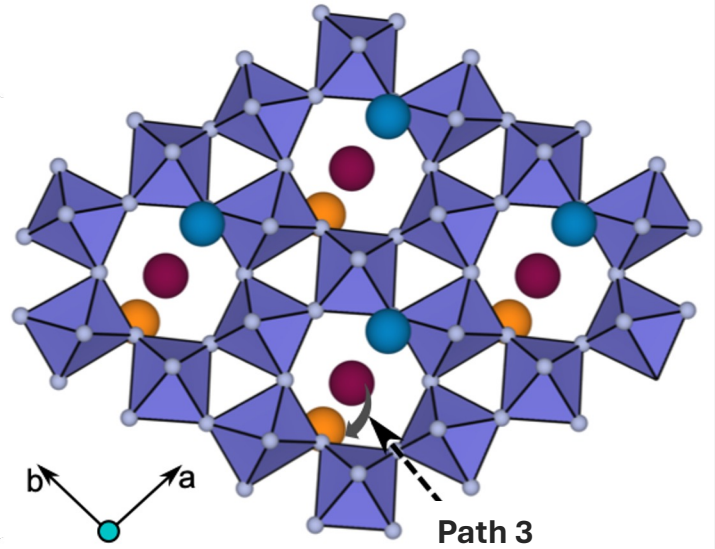
- Weberites voltage is higher than perovskites
- Both orthorhombic and trigonal weberites exhibit similar voltage profile
- From Ti-Ni voltage increment for both weberites and perovskites is *nonmonotonic*
  - "Local" minima at Cr & Fe, attributed to the stability of Cr^{3+} and Fe^{3+}
- Ti- and Cr-perovskites have low voltage
  - Could be a potential anode instead of Ca-cathode

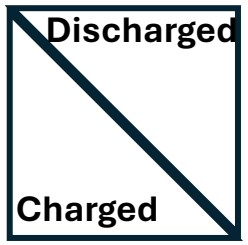
Migration barrier (E_m): weberites exhibit reasonable E_m

Weberites (Trigonal)









E_m is calculated using Nudged Elastic Band method[1] Green bar represent tolerance limit[2]

1. Henkelmann et al., J. Chem. Phys. 2000
2. D. B. Tekliye et al., Chem. Mater. 2022

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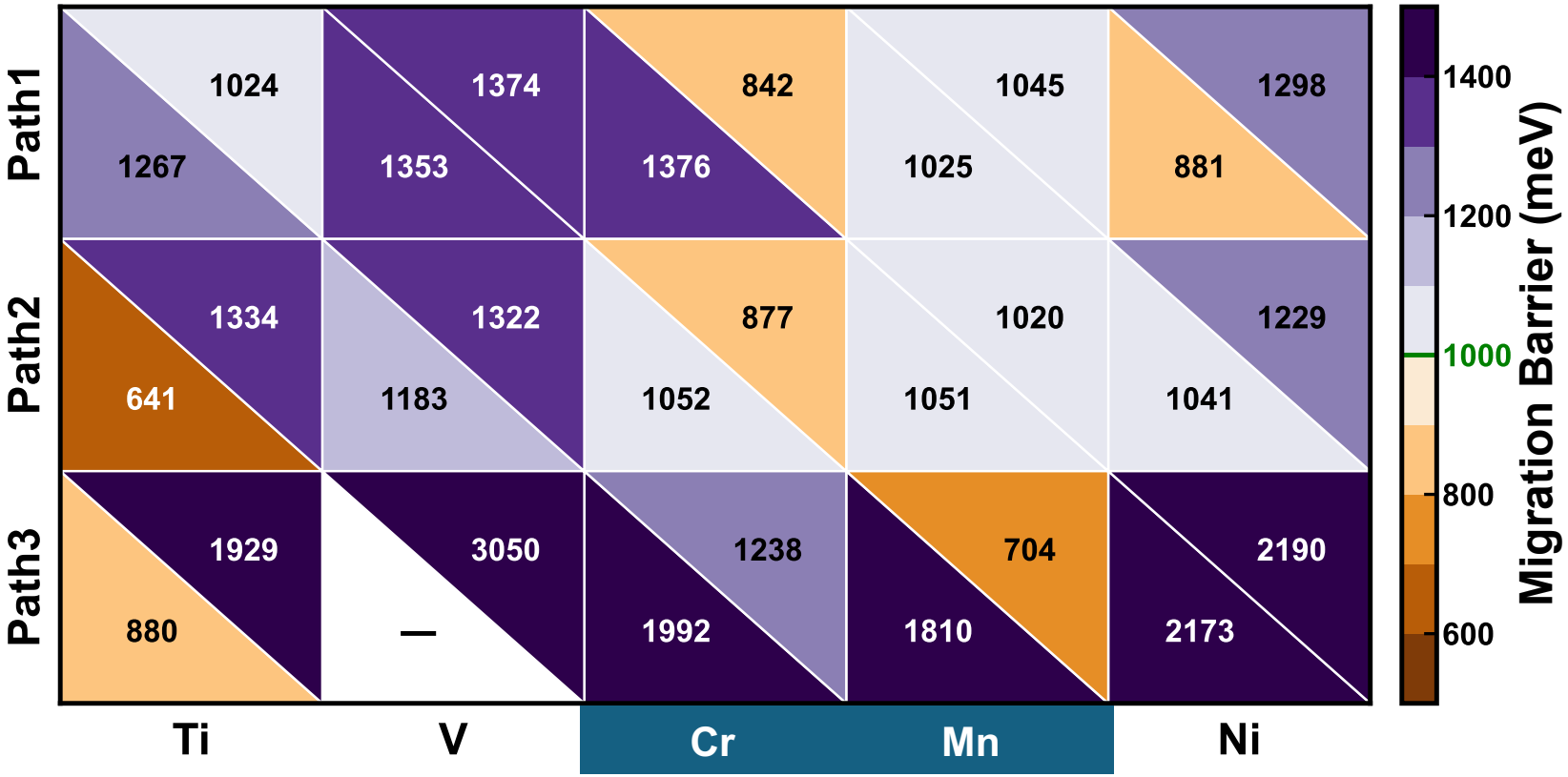

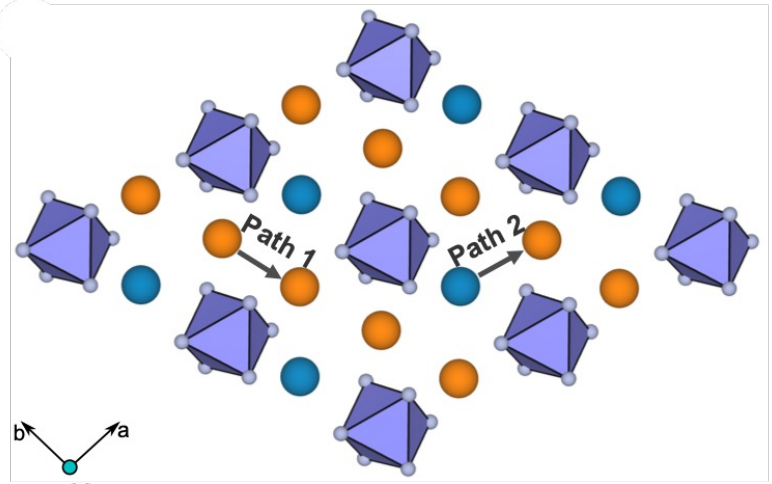

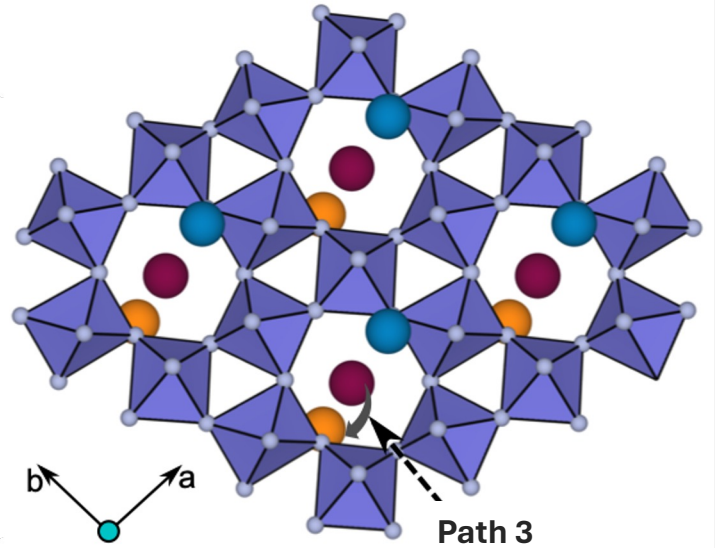

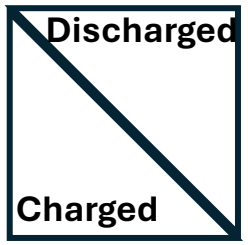

$Ca_xCr_2F_7$ and $Ca_xMn_2F_7$-weberites are promising Ca-cathodes due to their reasonable E_m

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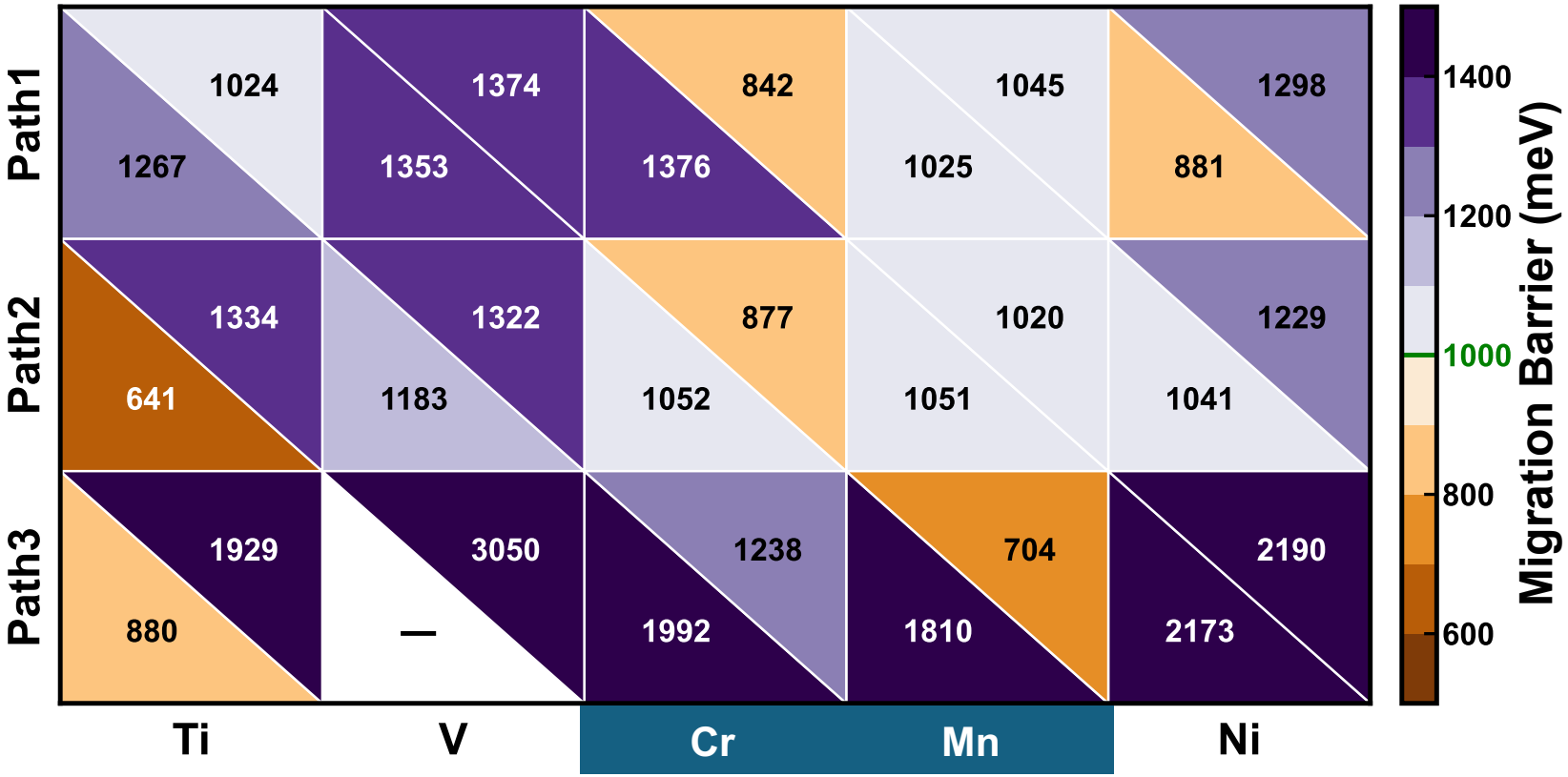

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Perovskites

Compounds	Migration Barrier (meV)	
	Charged	Discharged
Ca_xVF_3	2,875	1,832
Ca_xMnF_3	--	1,980
Ca_xCoF_3	1,666	--
Ca_xNiF_3	2,445	2,120

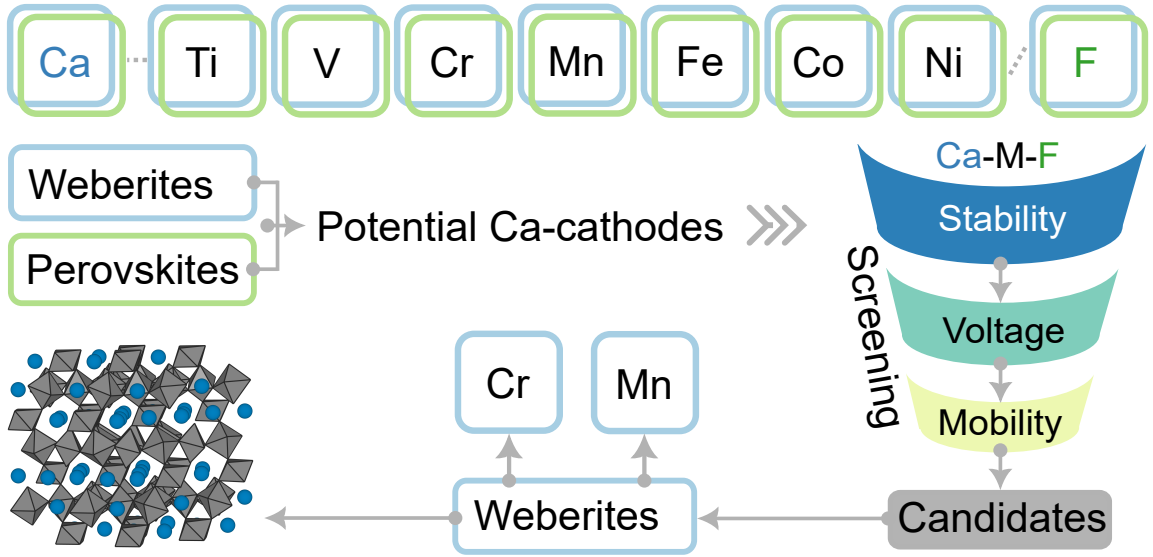
None of the perovskites are feasible as Ca-cathode due to their high E_m

E_m is calculated using Nudged Elastic Band method[1] Green bar represent tolerance limit[2]

1. Henkelmann et al., J. Chem. Phys. 2000
2. D. B. Tekliye et al., Chem. Mater. 2022

Conclusions and Acknowledgment

- Calcium batteries offer **high energy density** and **abundant Ca resources,** but lack suitable cathodes
- We explored the chemical space of **weberite** and **perovskite**-based transition metal fluorides as potential Ca-cathodes
- We identify **$Ca_xCr_2F_7$** and **$Ca_xMn_2F_7$ weberite**-based fluoride frameworks as promising Ca-cathodes



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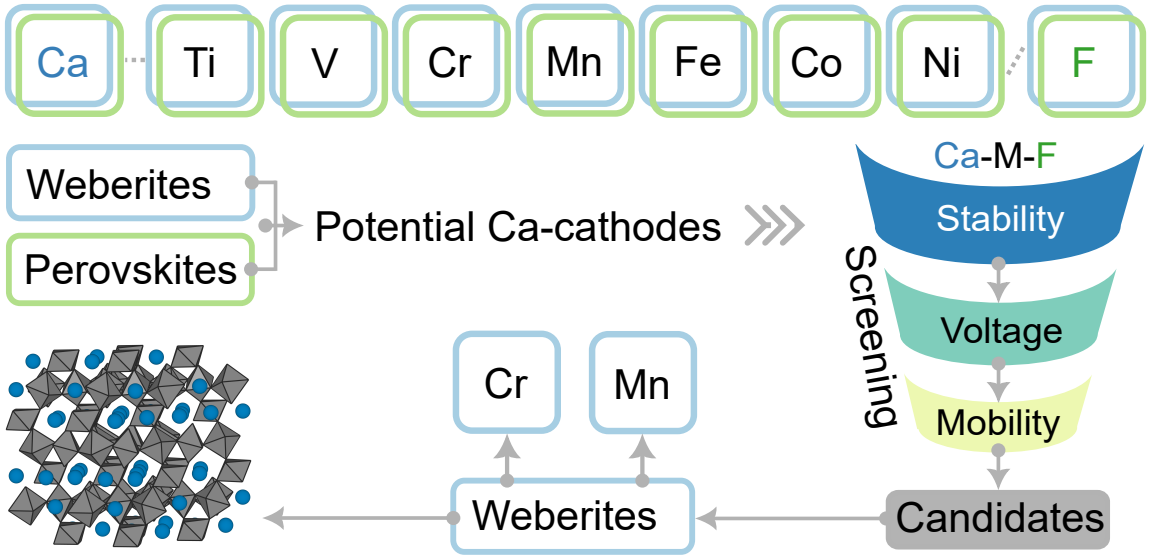

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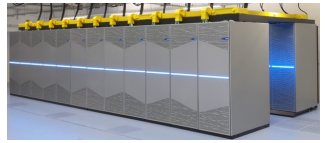

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