54%

46%

Aug 2013

Ceder Group, Oct 2013

Aug 2015

Apr 2017

"The ~~two coast~~ MIT PhD"

Thermodynamics and kinetics of Mg intercalation for multivalent cathode applications

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Thesis advisor: Prof. Gerbrand Ceder

Defense: April 25, 2017

Berkeley

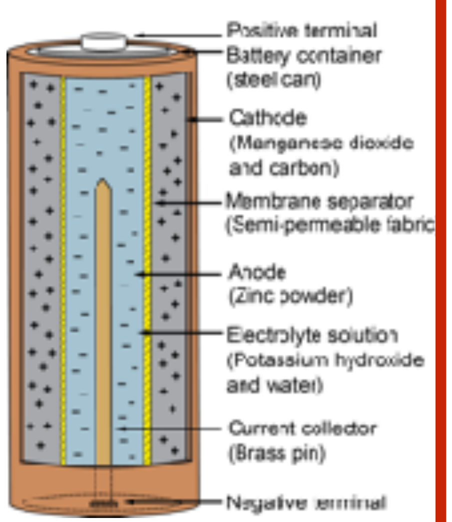
UNIVERSITY OF CALIFORNIA

Types of modern batteries

Primary:
"Use once"

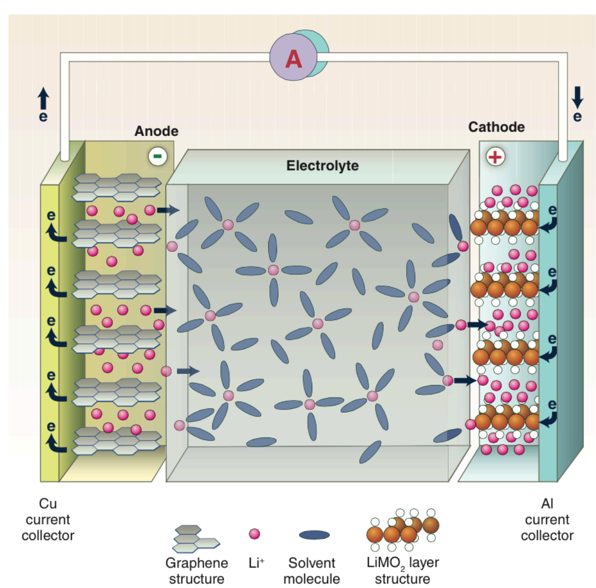
Secondary:
"Rechargeable"

Solid-liquid-solid



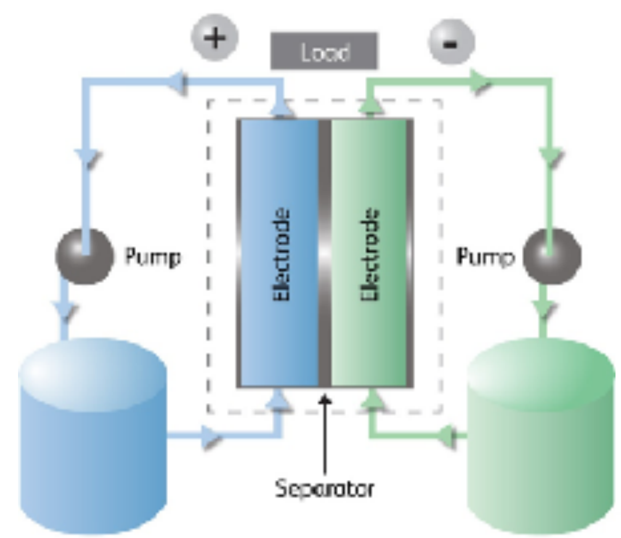
Alkaline

Intercalation-liquid-Intercalation



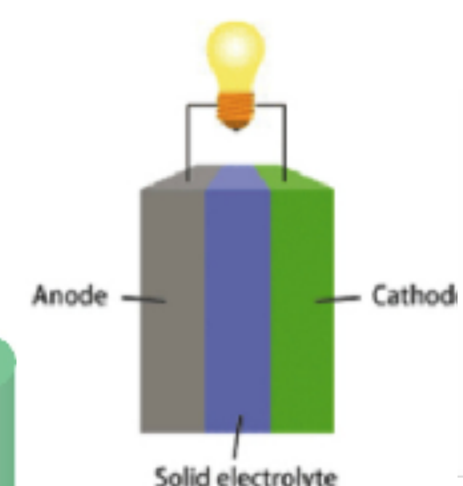
Li-ion

Liquid-Solid-Liquid



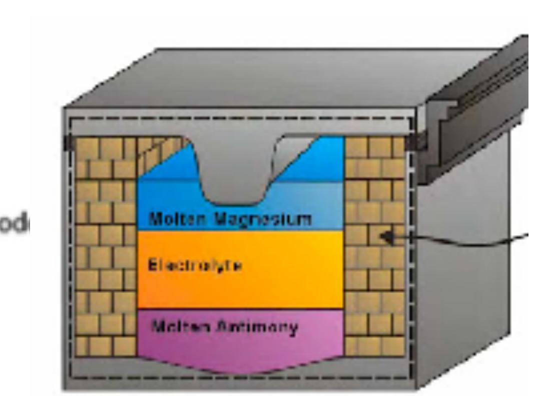
Flow

Solid-solid-solid



All-solid-state

Liquid-liquid-liquid



Liquid metal

Batteries 101:
How do modern Li-ion batteries work?

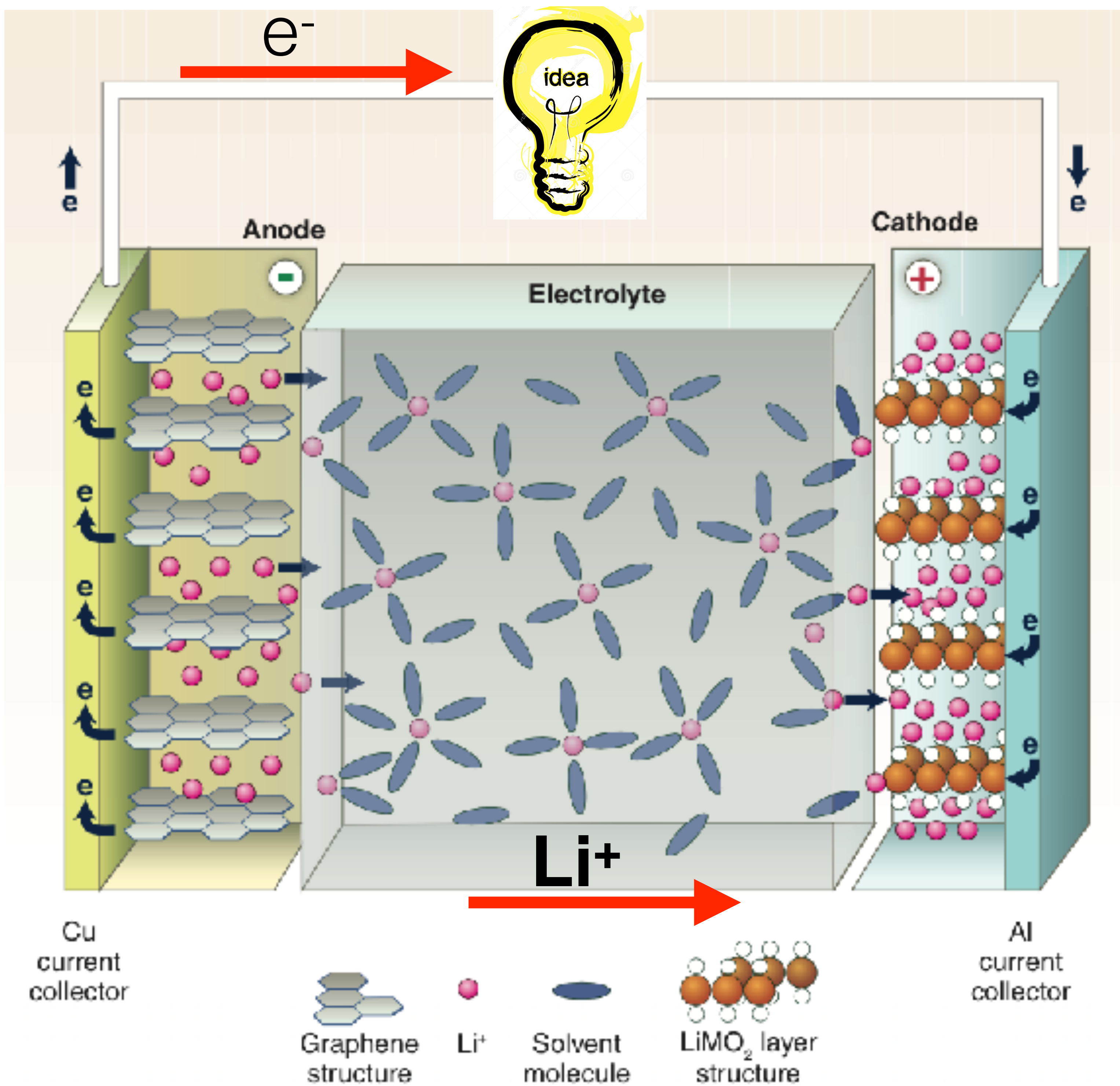


Image adopted from B. Dunn et al., Science 2011

Batteries 101:
How do modern Li-ion batteries work?

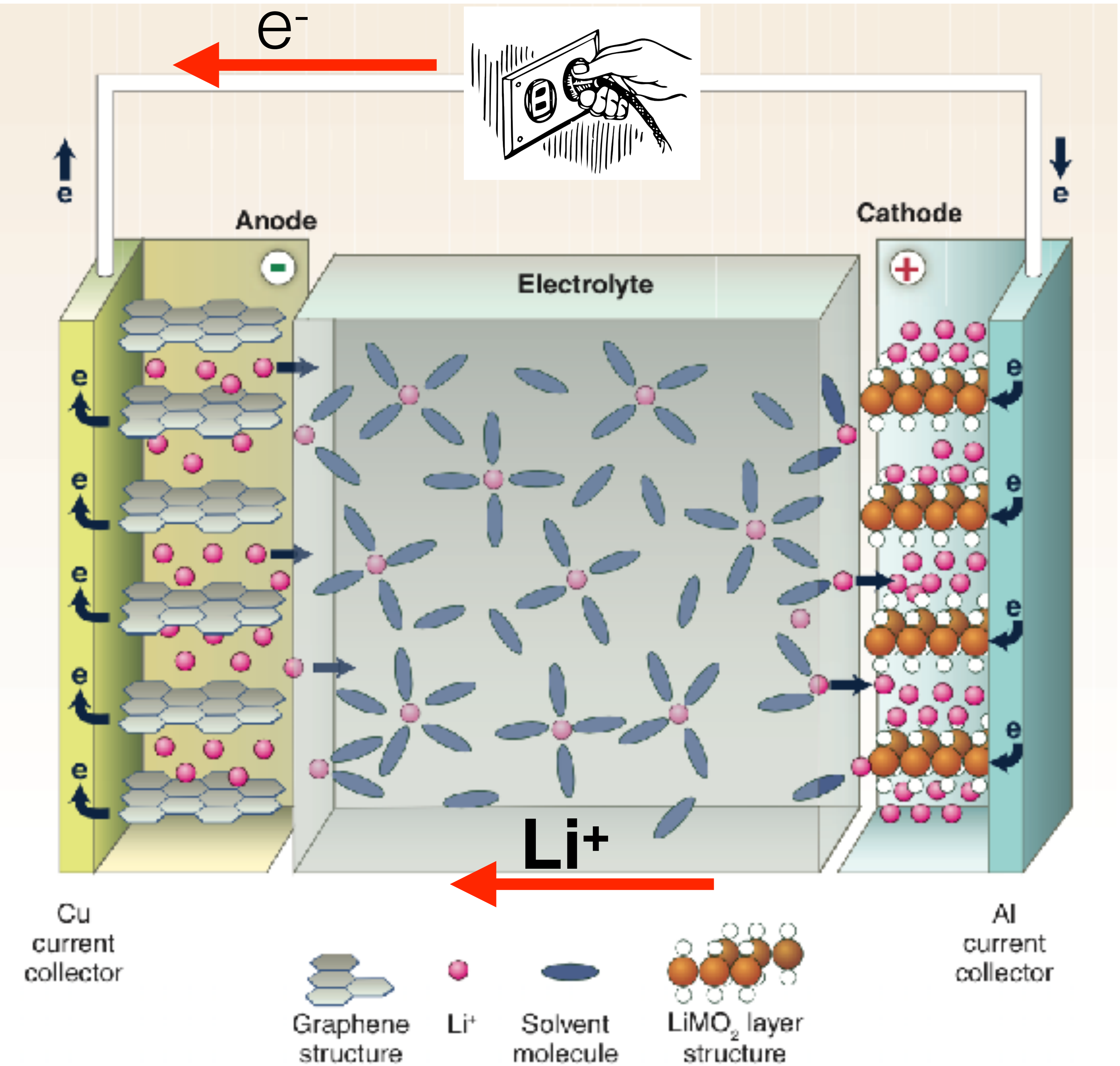


Image adopted from B. Dunn et al., Science 2011

Batteries 101: How do modern Li-ion batteries work?

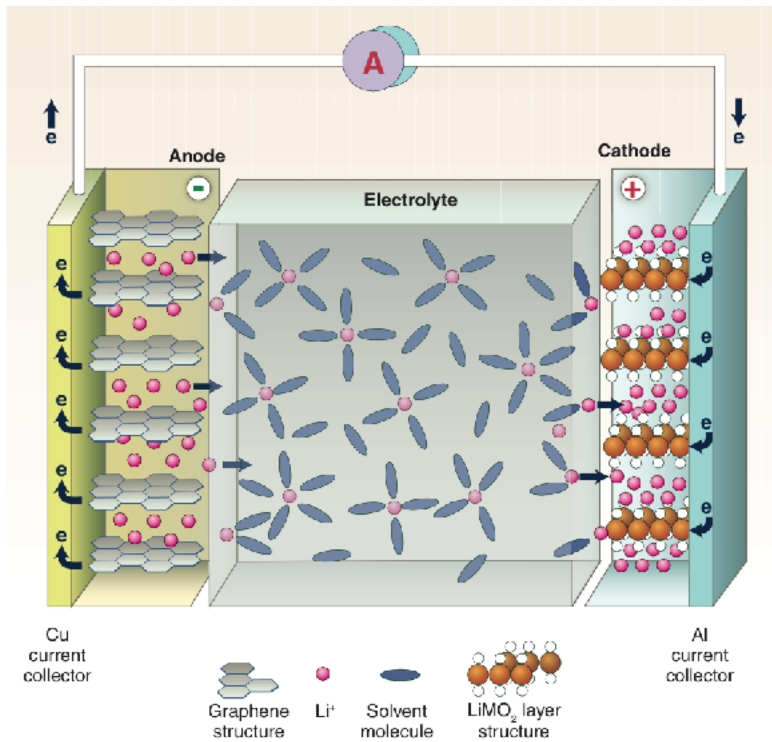
Voltage (V) : Potential to do work, $\propto(-\nabla\mu_{Li})$

Capacity (mAh/g) : Amount of charge stored (per electrode)

Energy stored (Wh) : Voltage x Capacity x Mass of cell

Gravimetric Energy density (Wh/kg) : Energy stored per weight of cell

Volumetric Energy density (Wh/l) : Energy stored per volume of cell



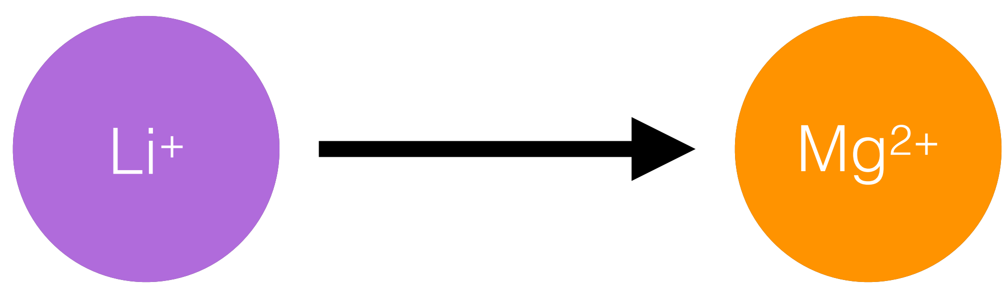
Rate: How fast can you (dis)charge?
Depends on ionic “mobility”

Electrochemical cycle : Charge + Discharge

Image adopted from B. Dunn et al., Science 2011

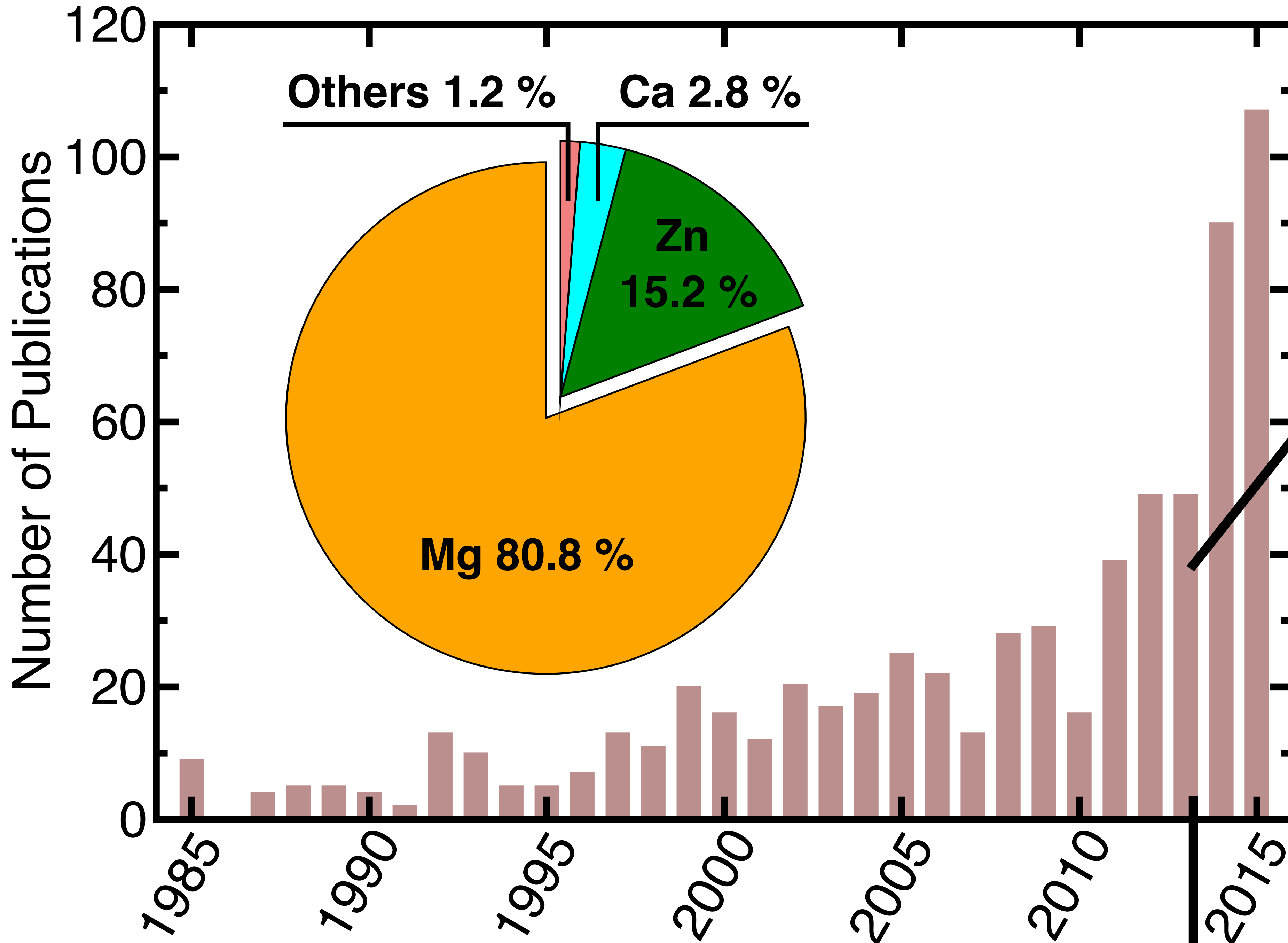
Why Multi-valent (MV) batteries?

- Next generation of electric devices will benefit from higher energy density storage systems
  - ✦ Multi-valent == More electrons (Mg^{2+}, Ca^{2+}, Al^{3+}, etc.)
  - ✦ Li-ion technology approaching fundamental limits
  - ✦ Smaller batteries useful for portable electronics
  - ✦ Lighter batteries favorable for electric vehicles



- Why Mg?
  - ✦ Superior volumetric capacity for Mg metal as anode (~3833 mAh/cm^3) vs. Li metal (~2046) or Li in graphite (~800)
  - ✦ Mg is safer than Li
  - ✦ Mg is “geopolitically” cheaper than Li

Increasing focus on MV technology

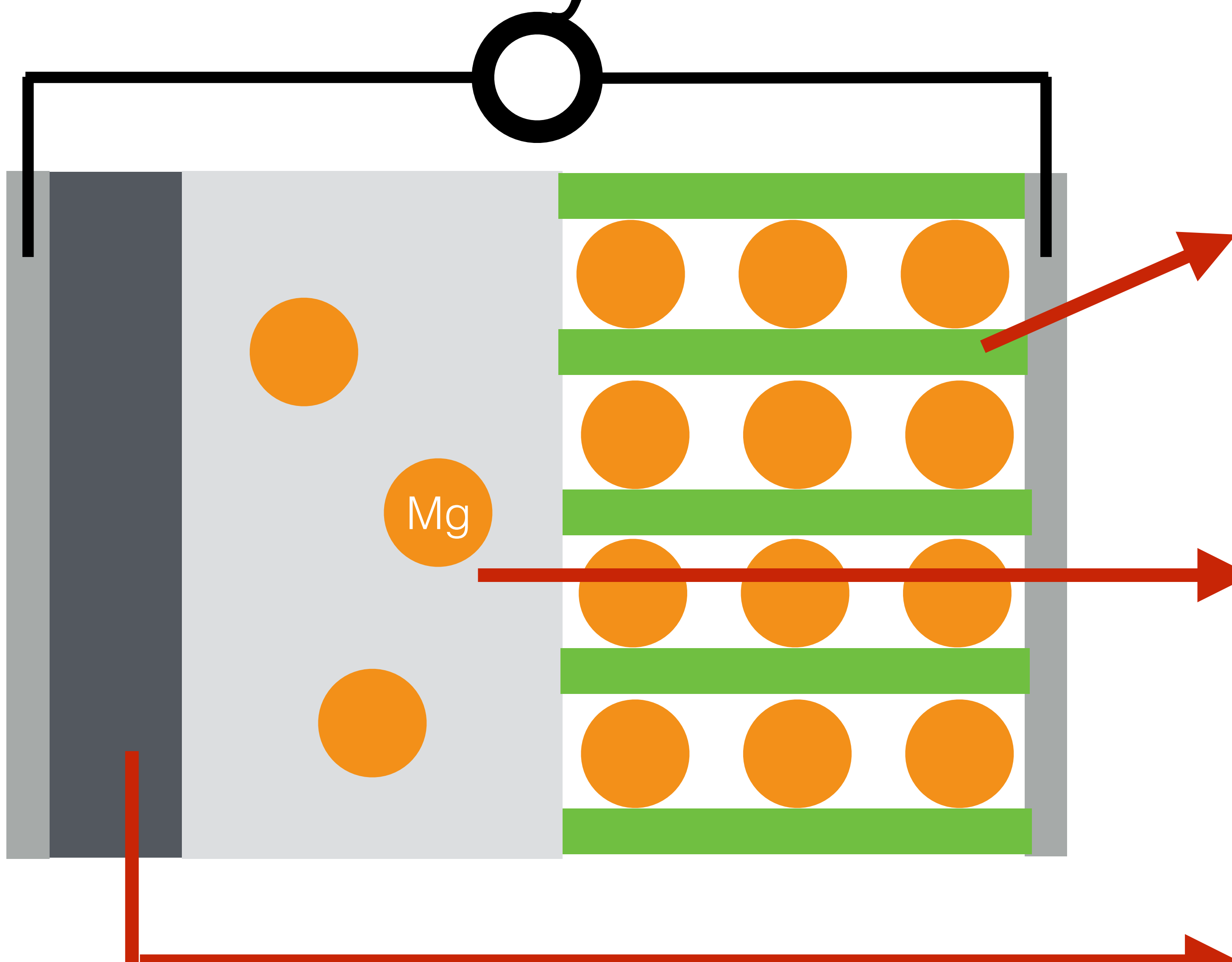


joins Ceder group!

JCESR begins

P. Canepa, G.S. Gautam *et al.*, **Chem. Rev.** 117, **2017**, 4287-4341

Challenges of using a MV chemistry

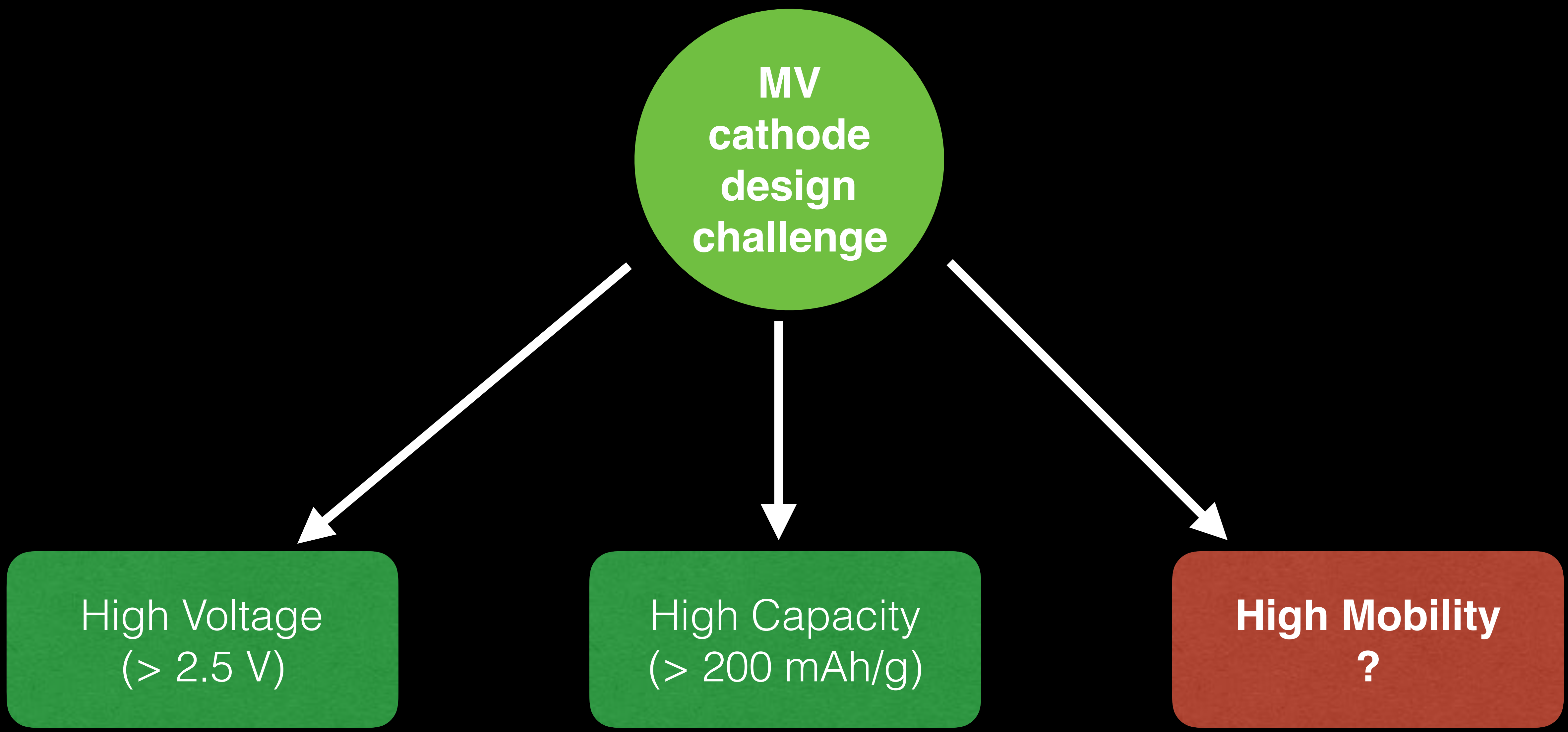


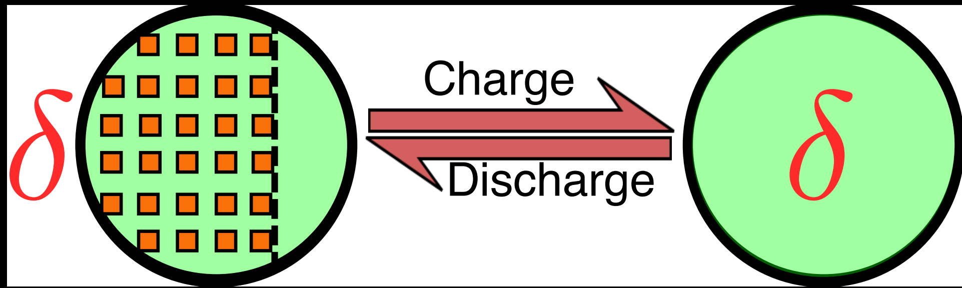
Intercalation Cathode:
High Voltage
High Capacity
High Mobility

Electrolyte:
Stable electrolyte (at both electrodes) with good conductivity

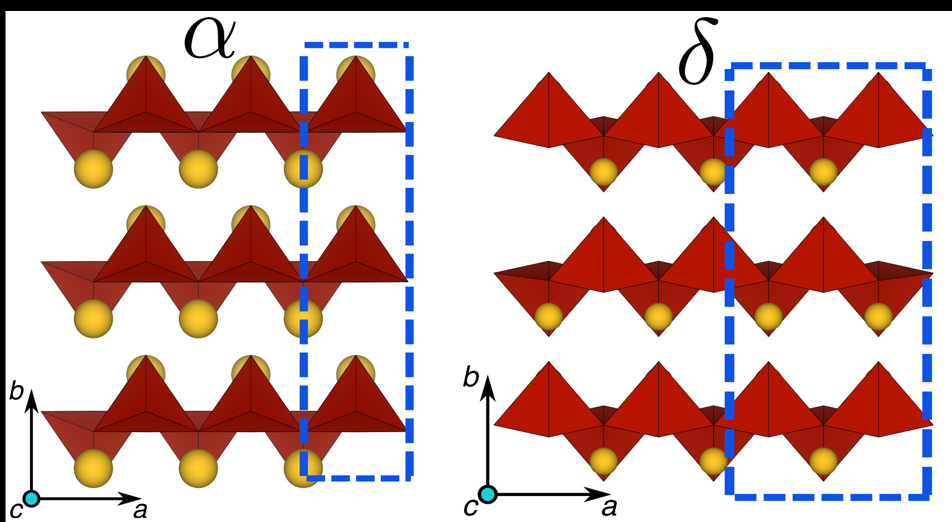
Metal Anode:
Understand plating and stripping in organic electrolytes

1. Find new high voltage cathodes with high MV mobility
2. Understand MV intercalation mechanisms in existing cathodes

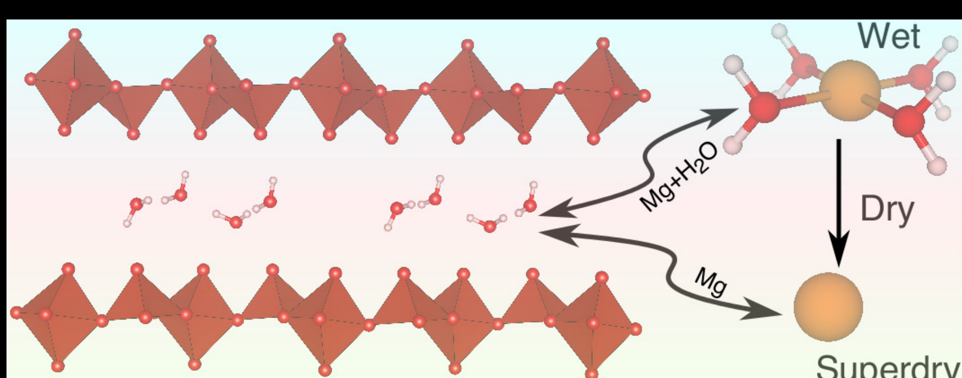

MV cathode design challenge
High Voltage (> 2.5 V)
High Capacity (> 200 mAh/g)
High Mobility ?



“The intercalation phase diagram of Mg in V_2O_5 from First-principles”, G.S. Gautam et al., **Chem. Mater.** 27, **2015**, 3733-3742

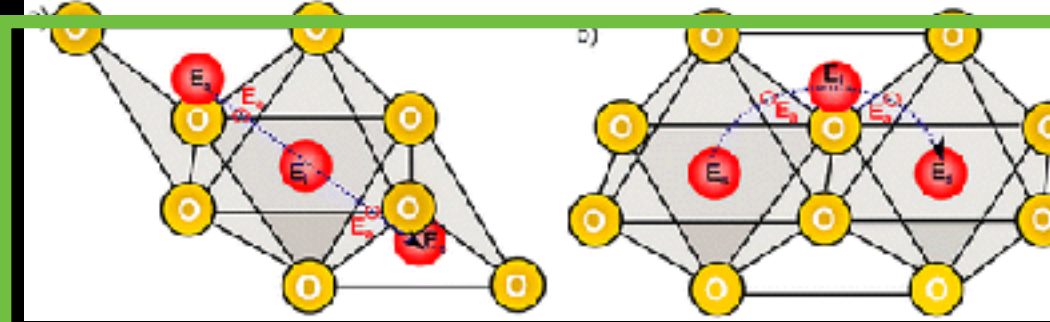


“First-principles evaluation of multi-valent cation insertion into orthorhombic V_2O_5”, G.S. Gautam et al., **Chem. Commun.** 51, **2015**, 13619-13622

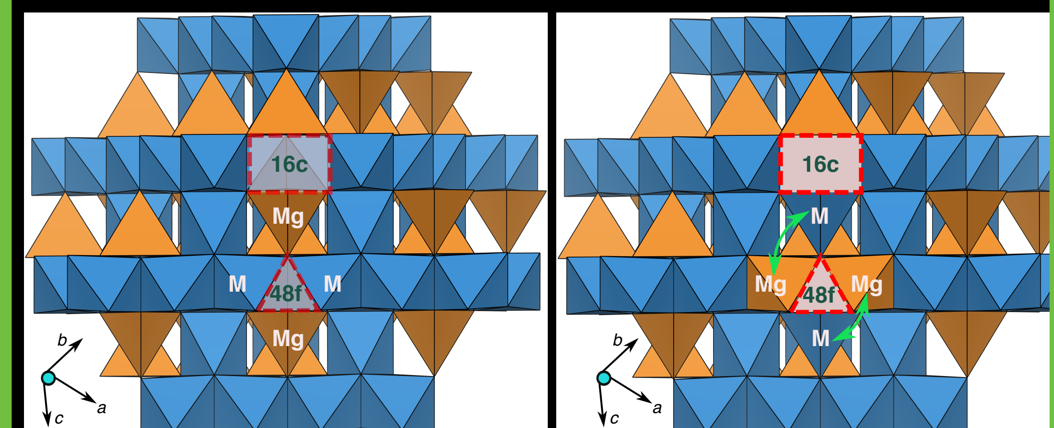


“Role of structural H_2O in intercalation electrodes: the case of Mg in nano crystalline Xerogel-V_2O_5”, G.S. Gautam et al., **Nano Lett.** 16, **2016**, 2426-2431

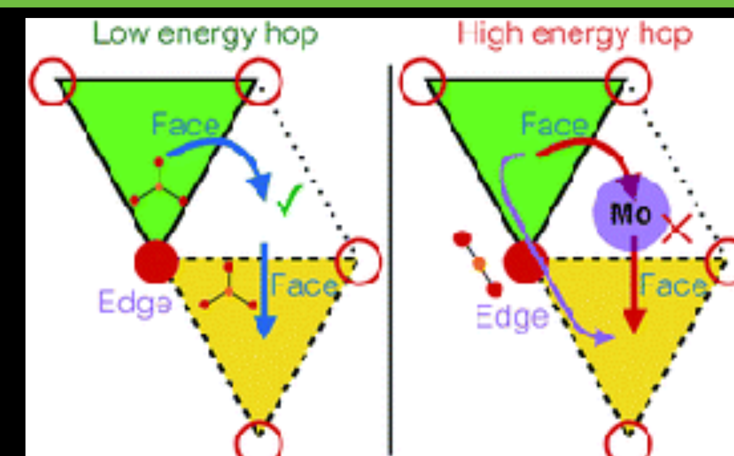
MV cathode design challenge



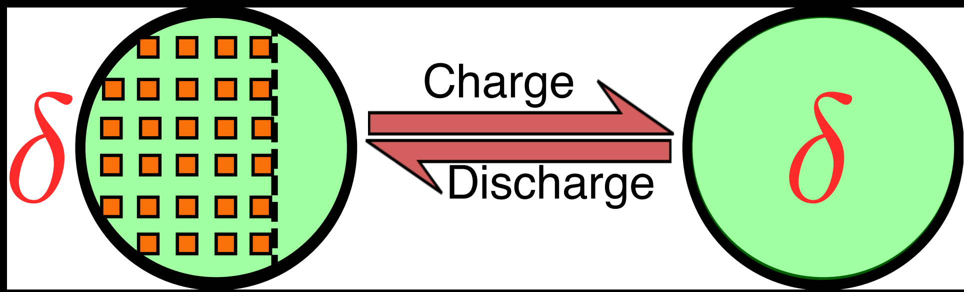
“Materials Design Rules for Multivalent Ion Mobility in Intercalation Structures”, Z. Rong, R. Malik, P.Canepa, G.S. Gautam et al., **Chem. Mater.** 27, **2015**, 6016-6021



“Influence of inversion on Mg mobility and electrochemistry in spinels”, G.S. Gautam et al., **under review**



“Impact of intermediate sites on bulk diffusion barriers: Mg intercalation in $Mg_2Mo_3O_8$”, G.S. Gautam et al., **J. Mater. Chem. A** 4, **2016**, 17643-17648



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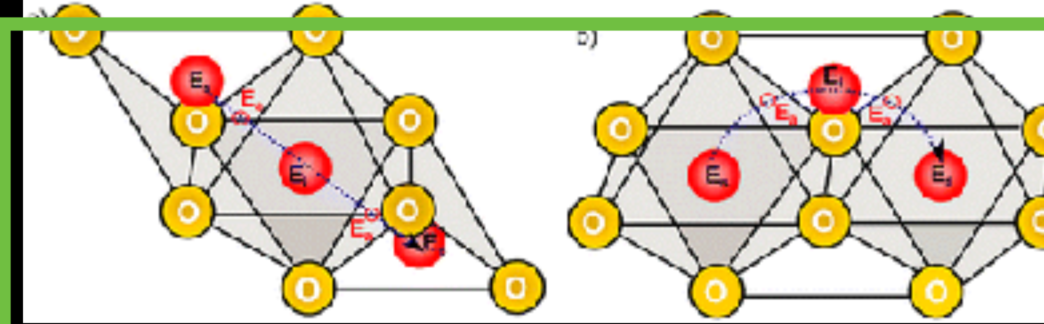

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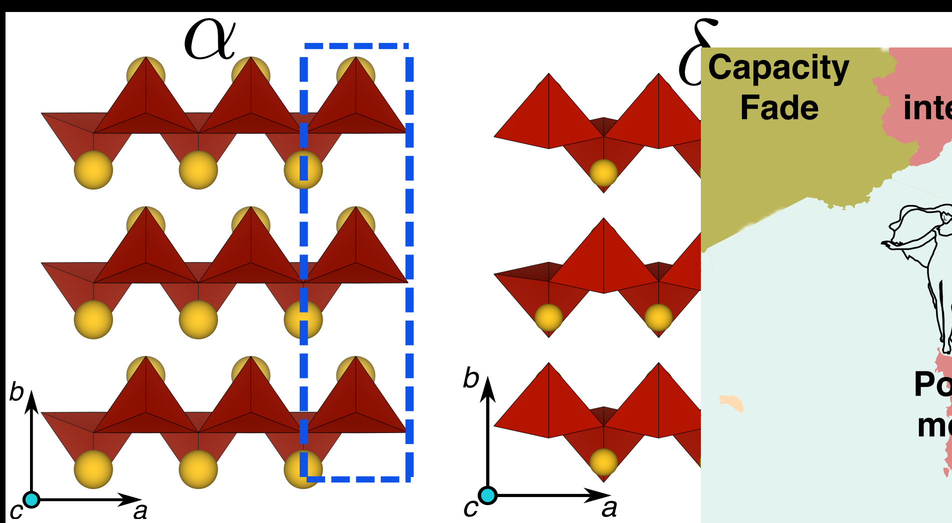
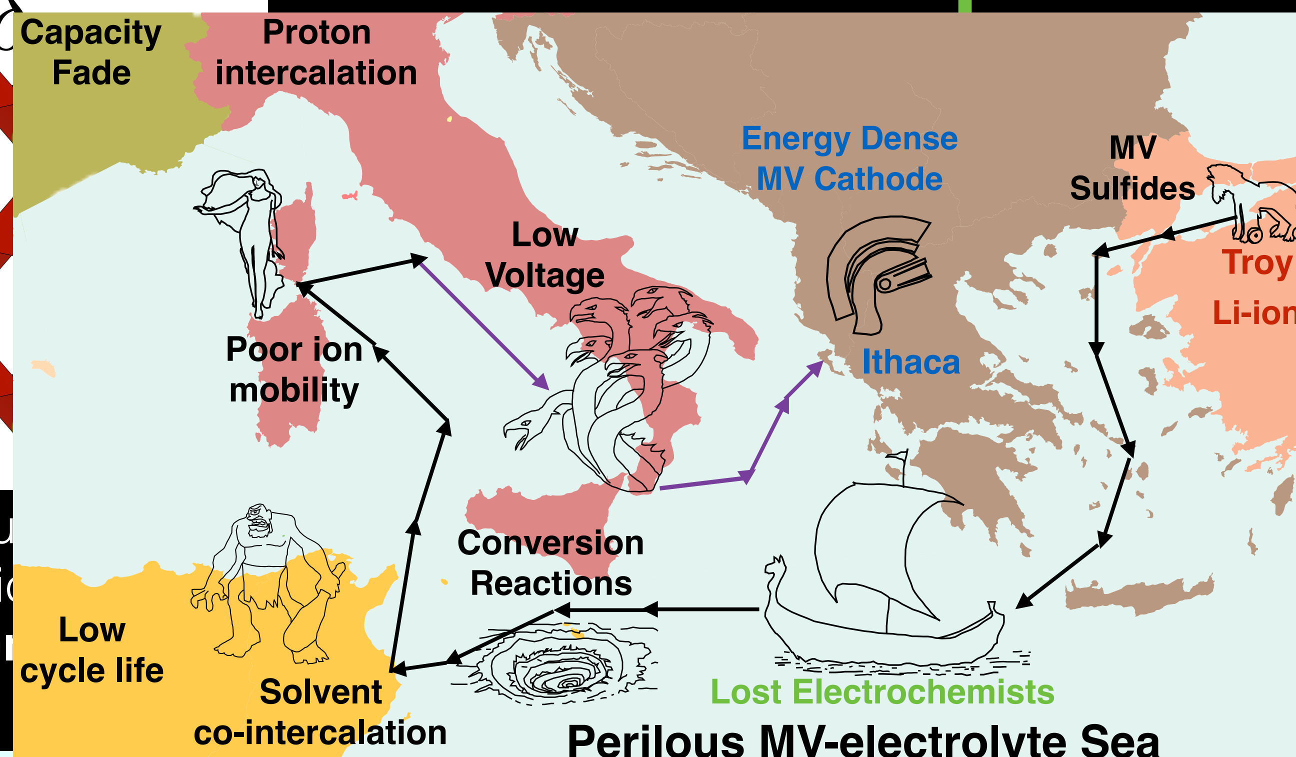
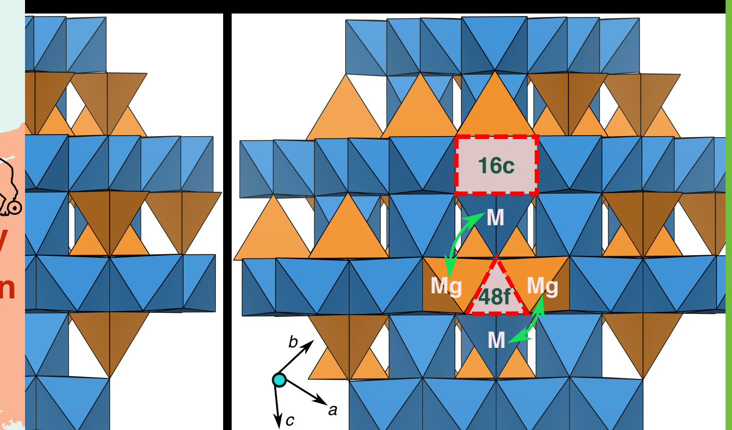
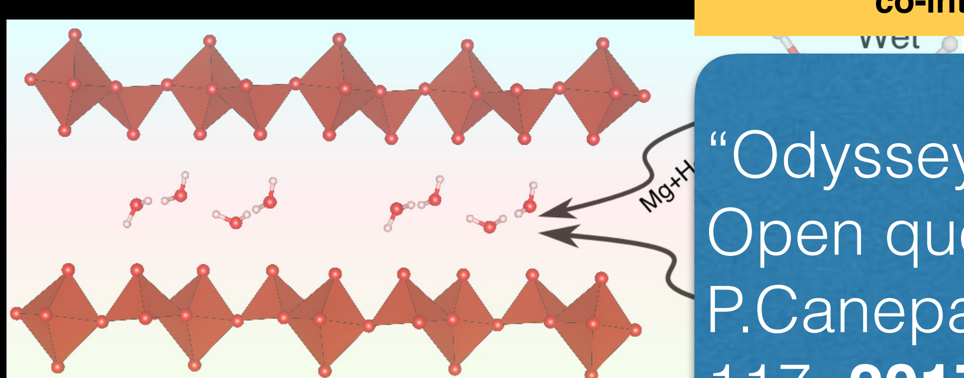


"First-principles evaluation of mu… cation insertion into orthorhombi… G.S. Gautam et al., **Chem. Com…** **2015**, 13619-13622





…version on Mg mobility and …ry in spinels", …t al., **under review**



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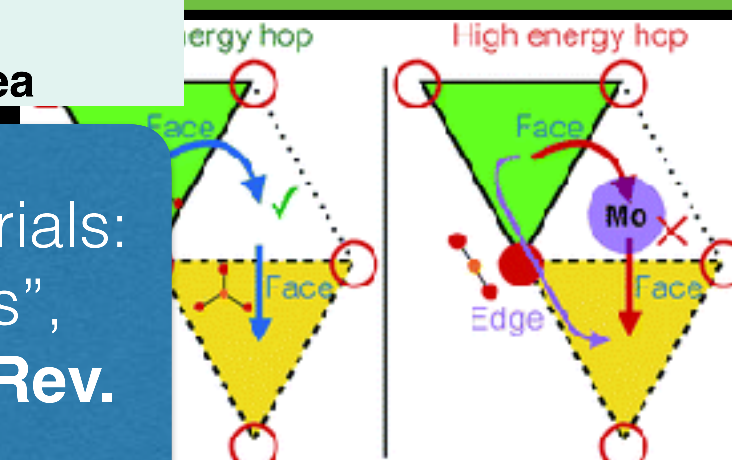
"Odyssey of Multivalent Cathode Materials: Open questions and Future Challenges", P.Canepa, G.S. Gautam et al., **Chem. Rev.** 117, **2017**, 4287-4341

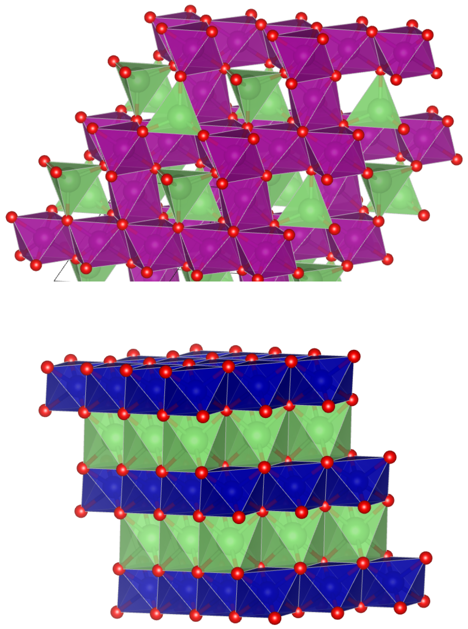


…termediate sites on bulk diffusion barriers: Mg intercalation in $Mg_2Mo_3O_8$", G.S. Gautam et al., **J. Mater. Chem. A** 4, **2016**, 17643-17648

Methods detour

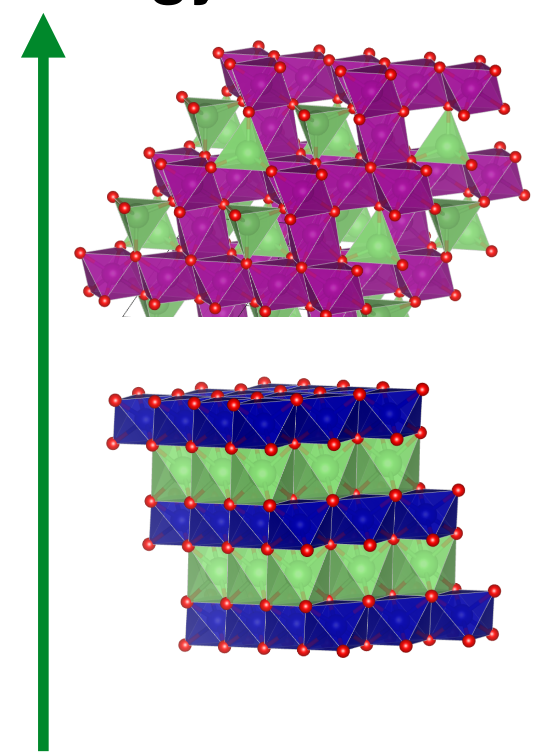
How to calculate material properties?

Thermodynamics: Voltages



$$H\psi = E\psi$$

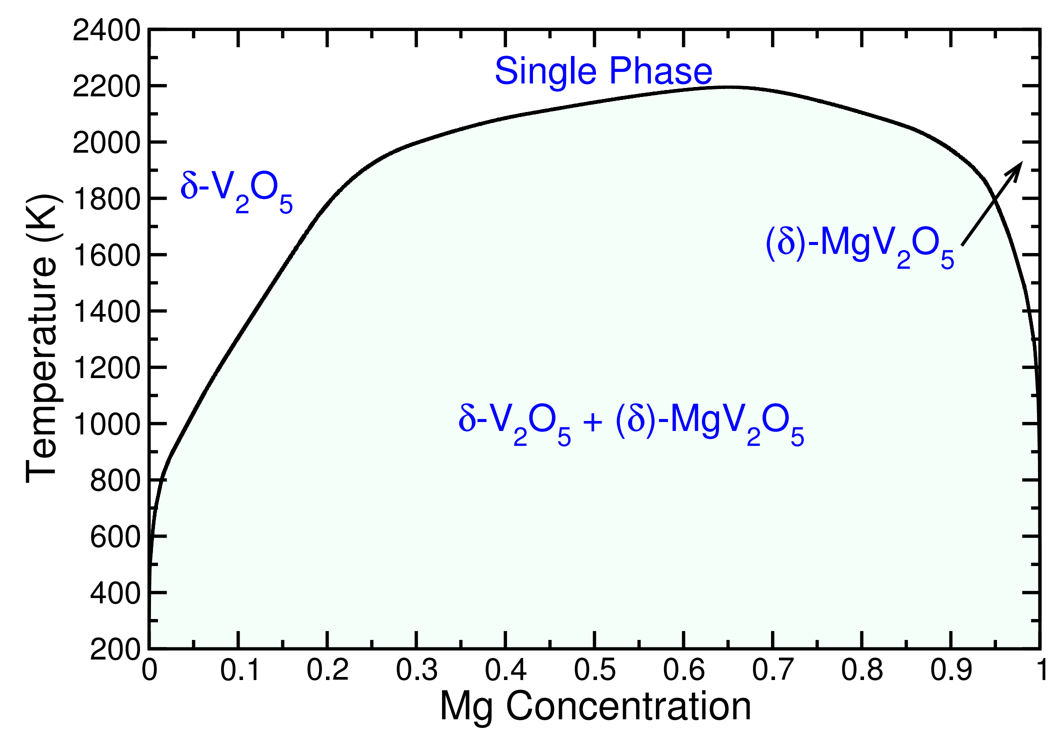
Free energy



DFT+
lattice models

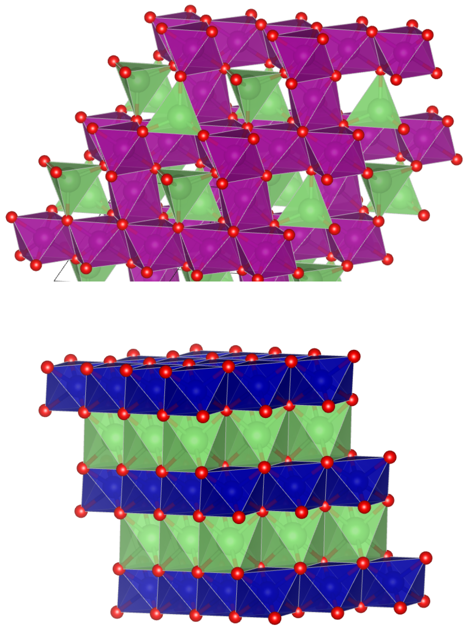
x, T, p

Density Functional Theory (DFT)[1-5]



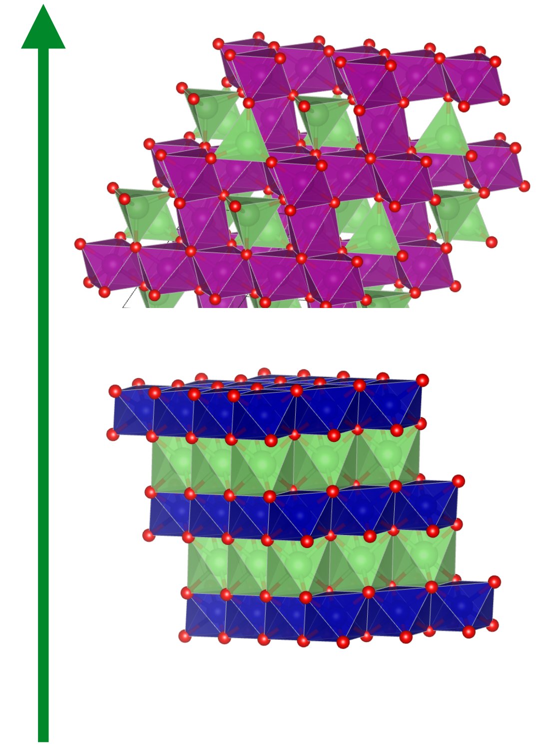
1. Kresse et al., Phys. Rev. B 1993
2. Kresse et al., Phys. Rev. B 1996
3. Perdew et al., Phys. Rev. Lett. 1996
4. Zhou et al., Phys. Rev. B 2004
5. Jain et al., Phys. Rev. B 2011

Thermodynamics: Voltages



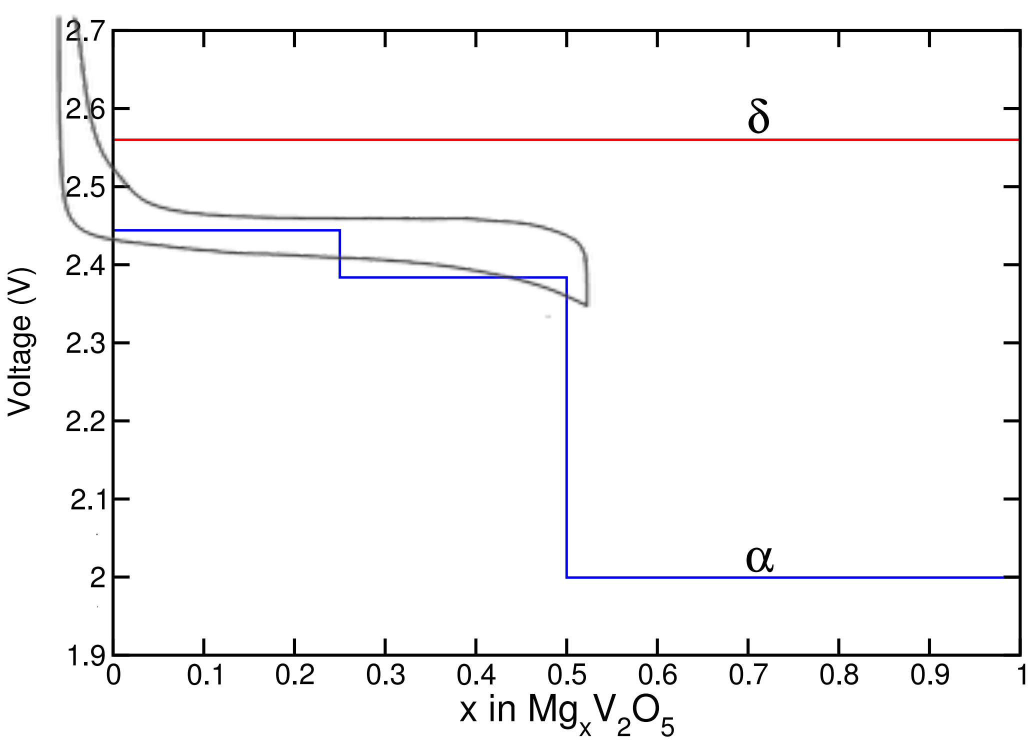
$$H\psi = E\psi$$

Free energy



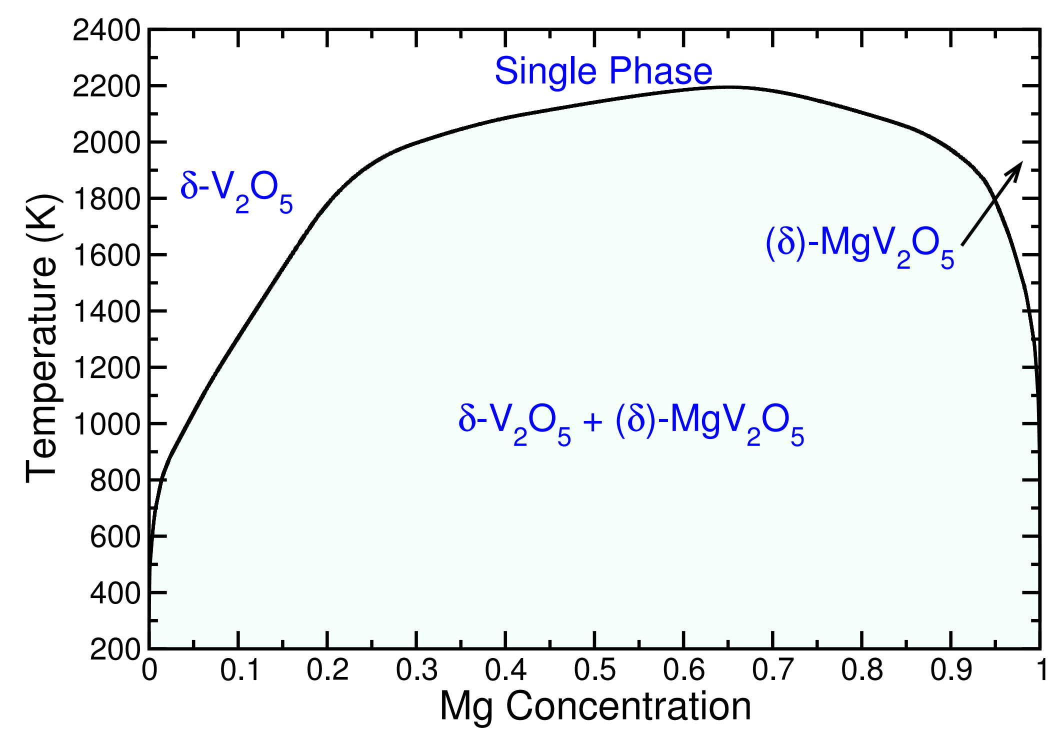
DFT+
lattice models

x, T, p

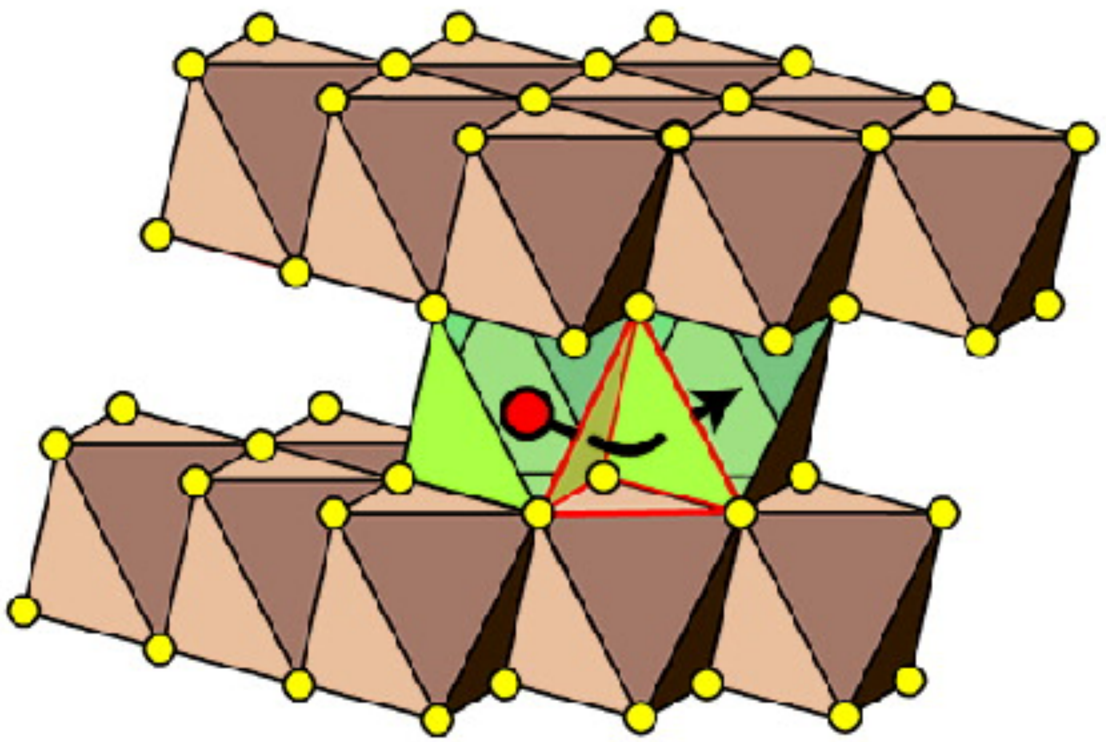


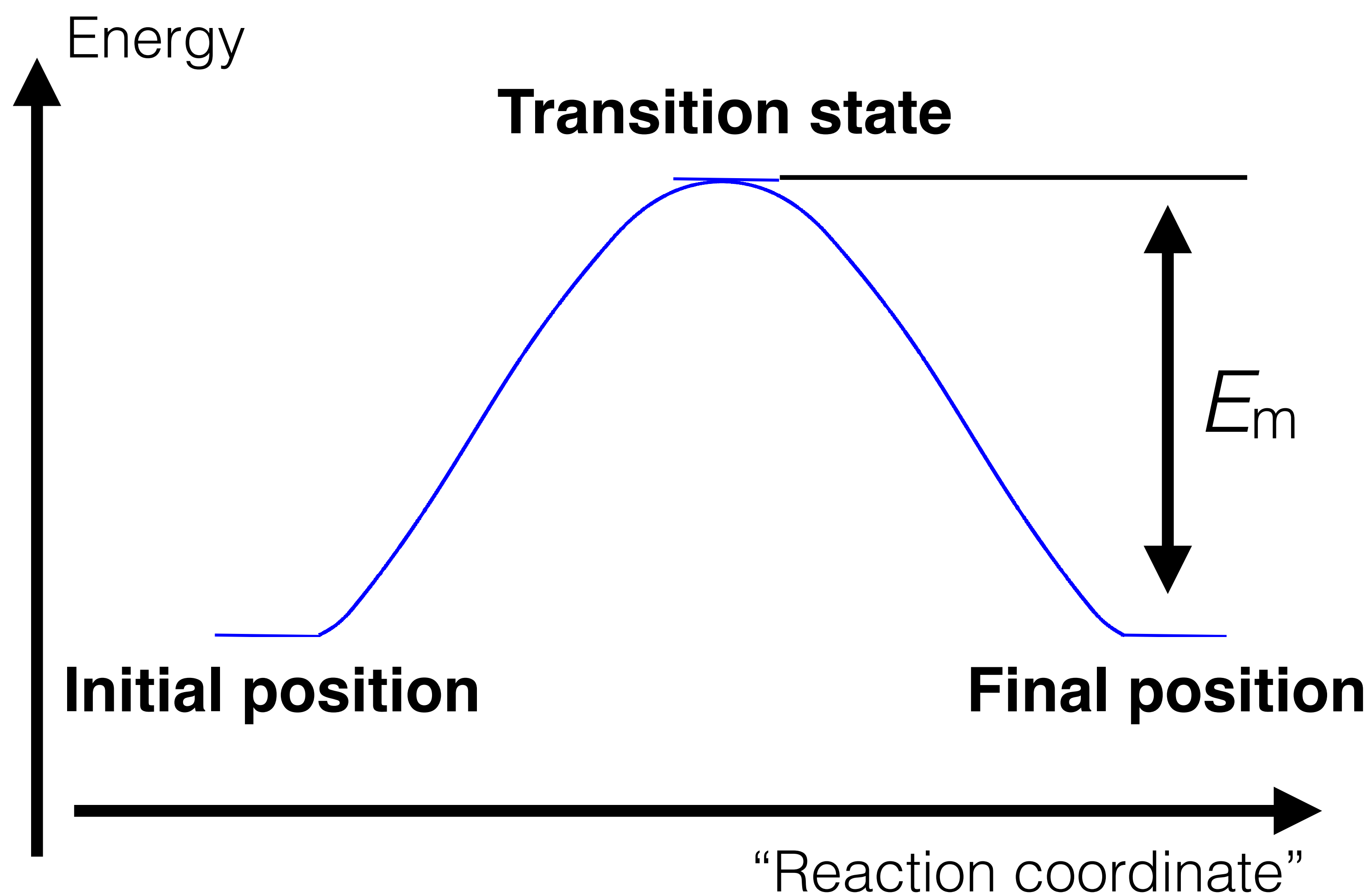
$$\Delta V = -\frac{\Delta G}{nF}$$

Nernst equation



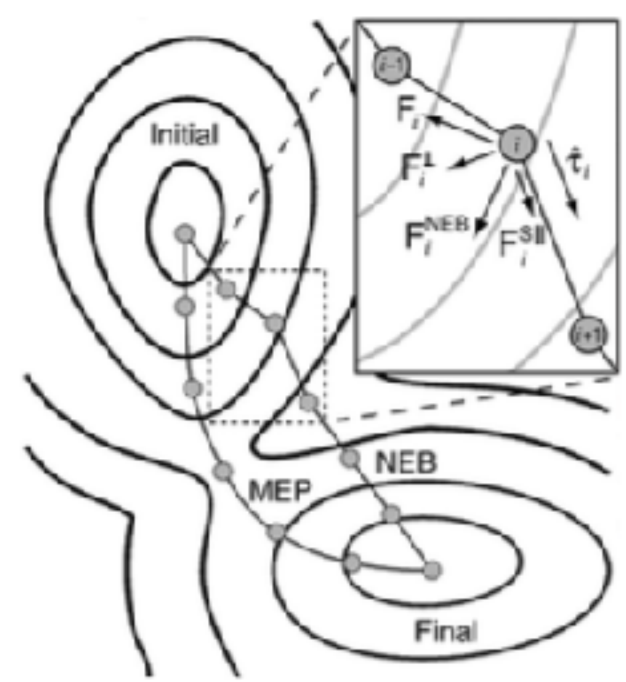
Kinetics: Mobility





$$D \propto \exp(-\frac{E_m}{kT})$$

Diffusivity - Mobility - Flux - Conductivity



Nudged Elastic Band (NEB) method + DFT = E_m

A. Van der ven *et al.*, Acc. Chem. Res. 2013

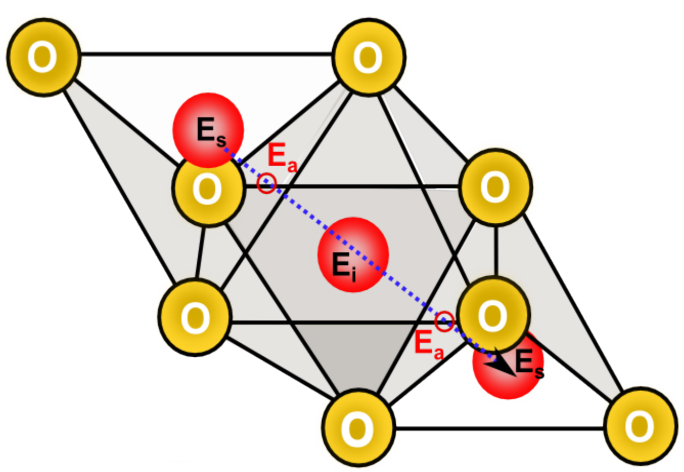
Sheppard et al., J. Chem. Phys. 2008

Cathode search

Z.Rong, R. Malik, P. Canepa, G.S. Gautam, *et al.*,
"Materials Design rules for multivalent ion mobility in intercalation structures",
Chem. Mater. 27, **2015**, 6016-6021

Understanding MV mobility: Requirements

Order of magnitude estimates indicate a migration barrier requirement in the range of 500 — 700 meV range



3 Å = 3 x 10^{-8} cm

$$D = \nu . a^2 . \exp(-\frac{E_m}{kT})$$

10^{12} s^{-1}

E_m ~ 525 meV
(for 1 μm particle)

E_m ~ 650 meV in 100 nm

E_m ~ 750 meV in 100 nm particles @ 60°C

$$D = \frac{x^2}{t}$$

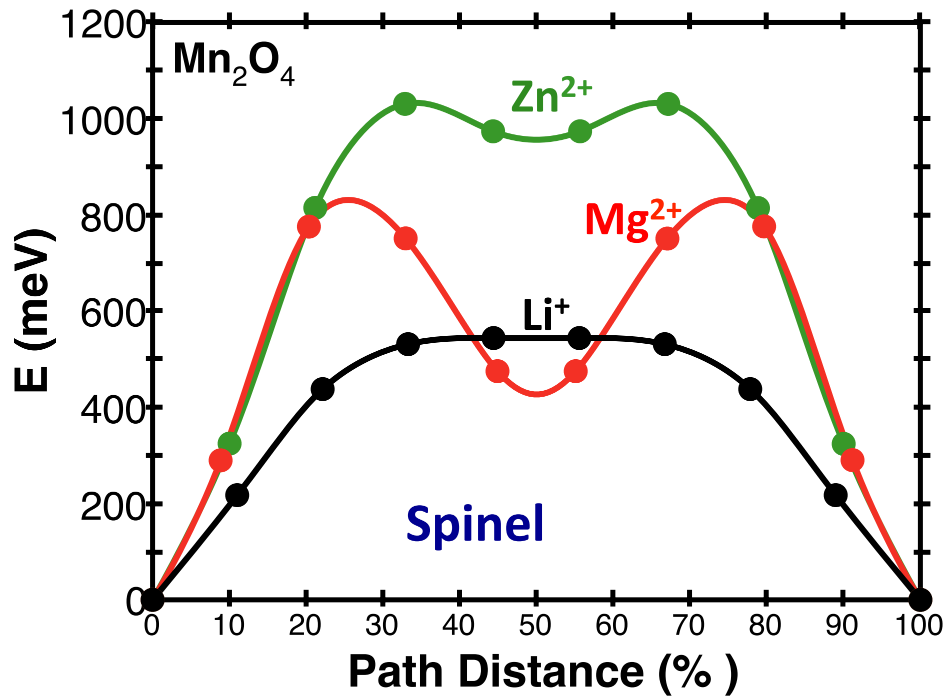
x^2 → Particle size; 10^{-4} cm (1 μm)

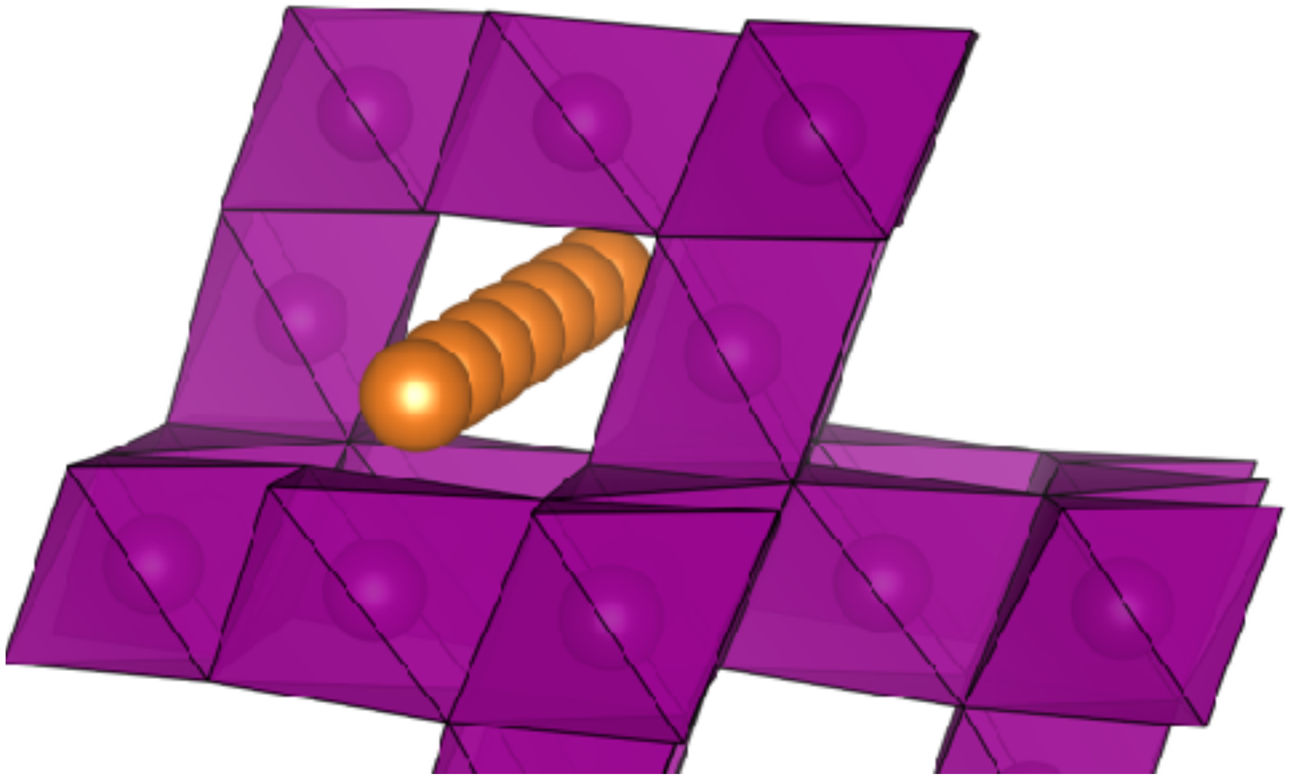
t → Charge rate; C/2 = 7200 s

D → ~10^{-12} cm^2/s

Rong *et al*., **Chem. Mater.** 27, **2015**, 6016-6021

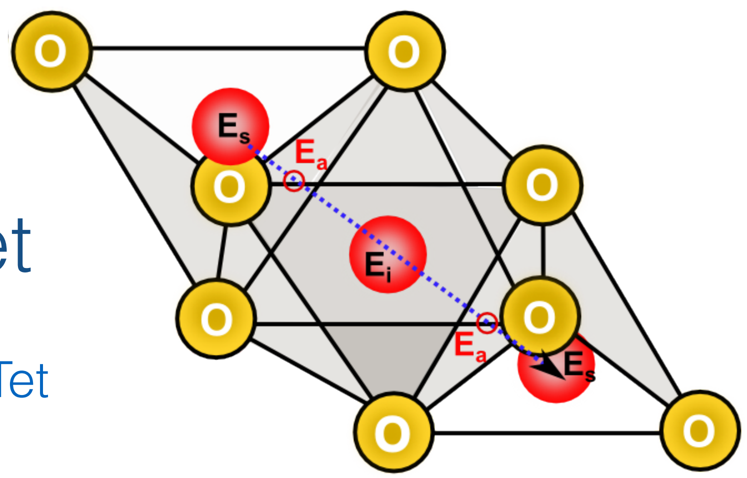
Trends differ with diffusion topology



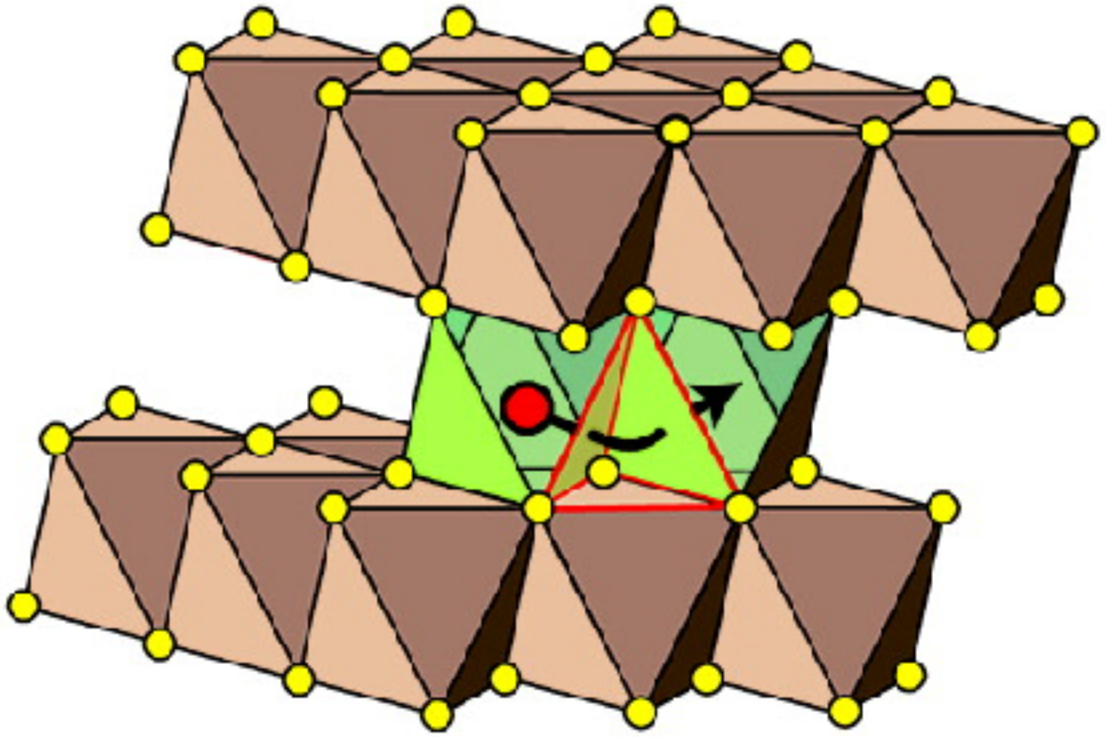


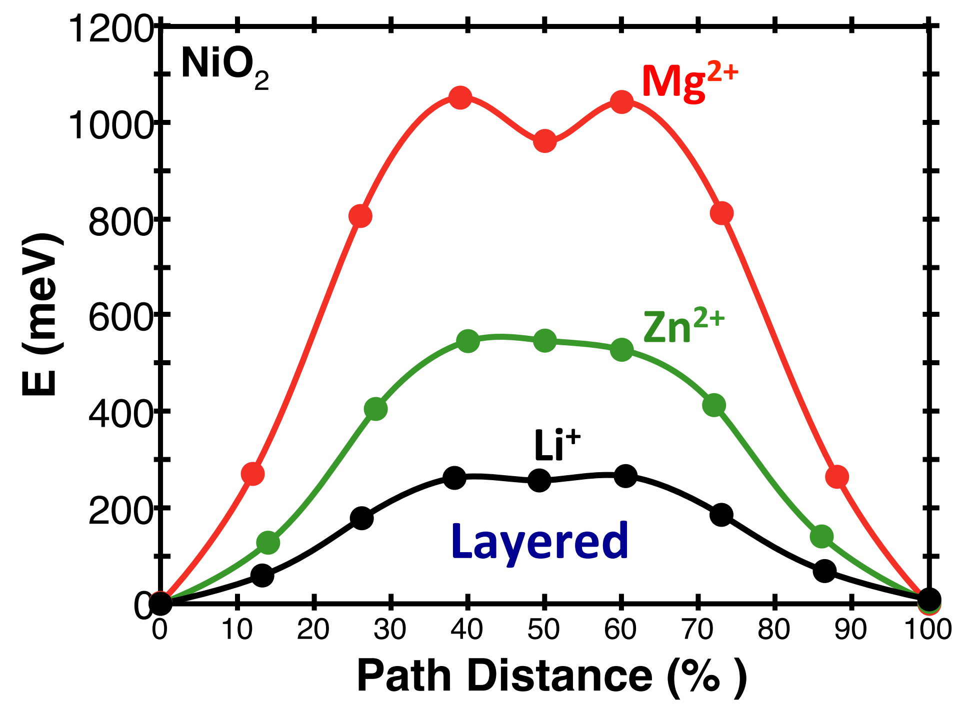
Tet - Oct - Tet

$E_{site} = E_{Oct} - E_{Tet}$



Trends differ with diffusion topology





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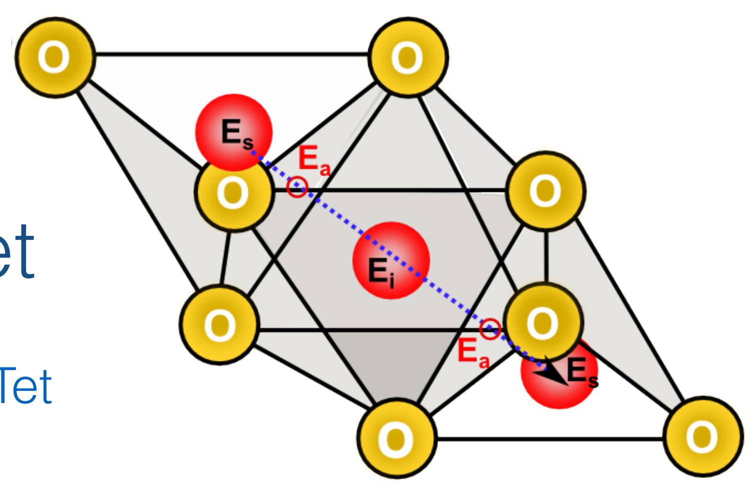
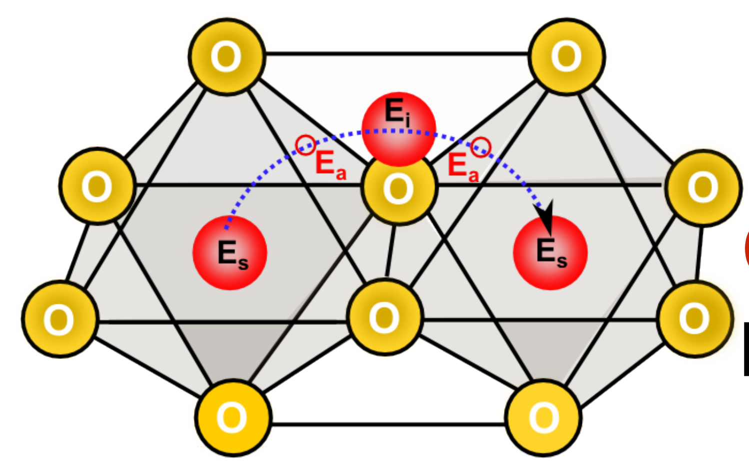




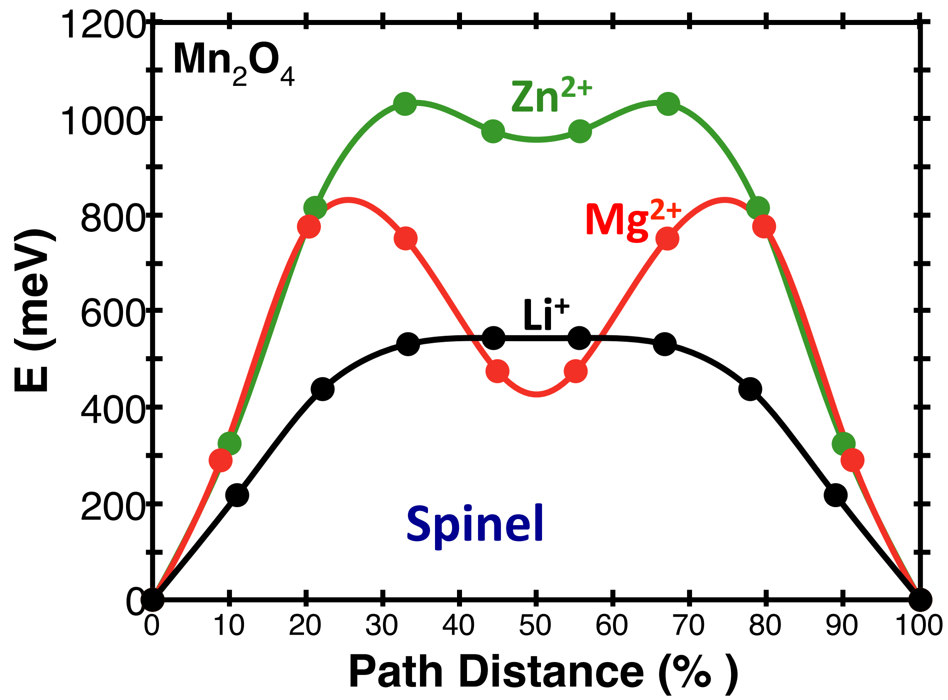
Oct - Tet - Oct

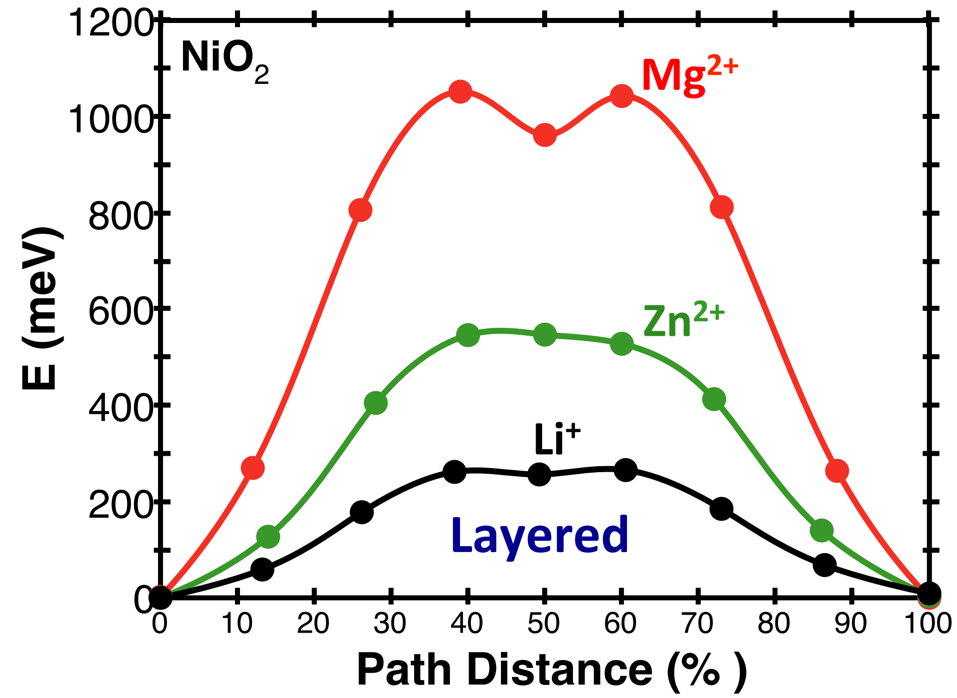
$E_{site} = E_{Tet} - E_{Oct}$

Rong *et al.*, **Chem. Mater.** 27, **2015**, 6016-6021
A. Van der ven *et al.*, Acc. Chem. Res. 2013

Liu *et al.*, **Energy Environ. Sci.** 8, **2015**, 964-974

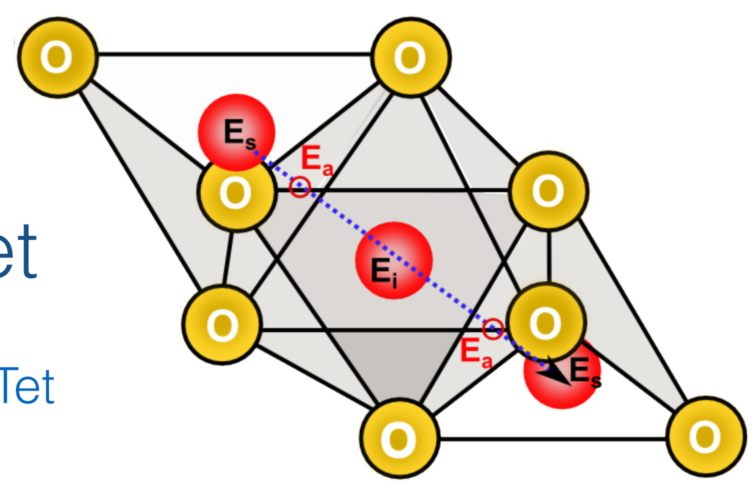
Trends differ with diffusion topology

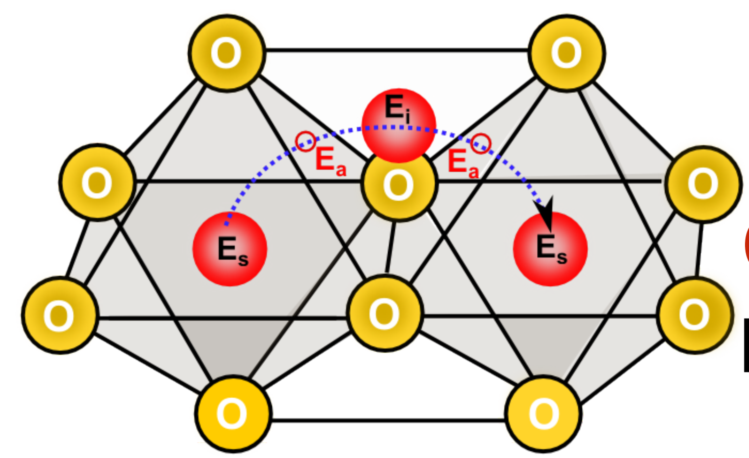




Tet - Oct - Tet

$E_{site} = E_{Oct} - E_{Tet}$





Oct - Tet - Oct

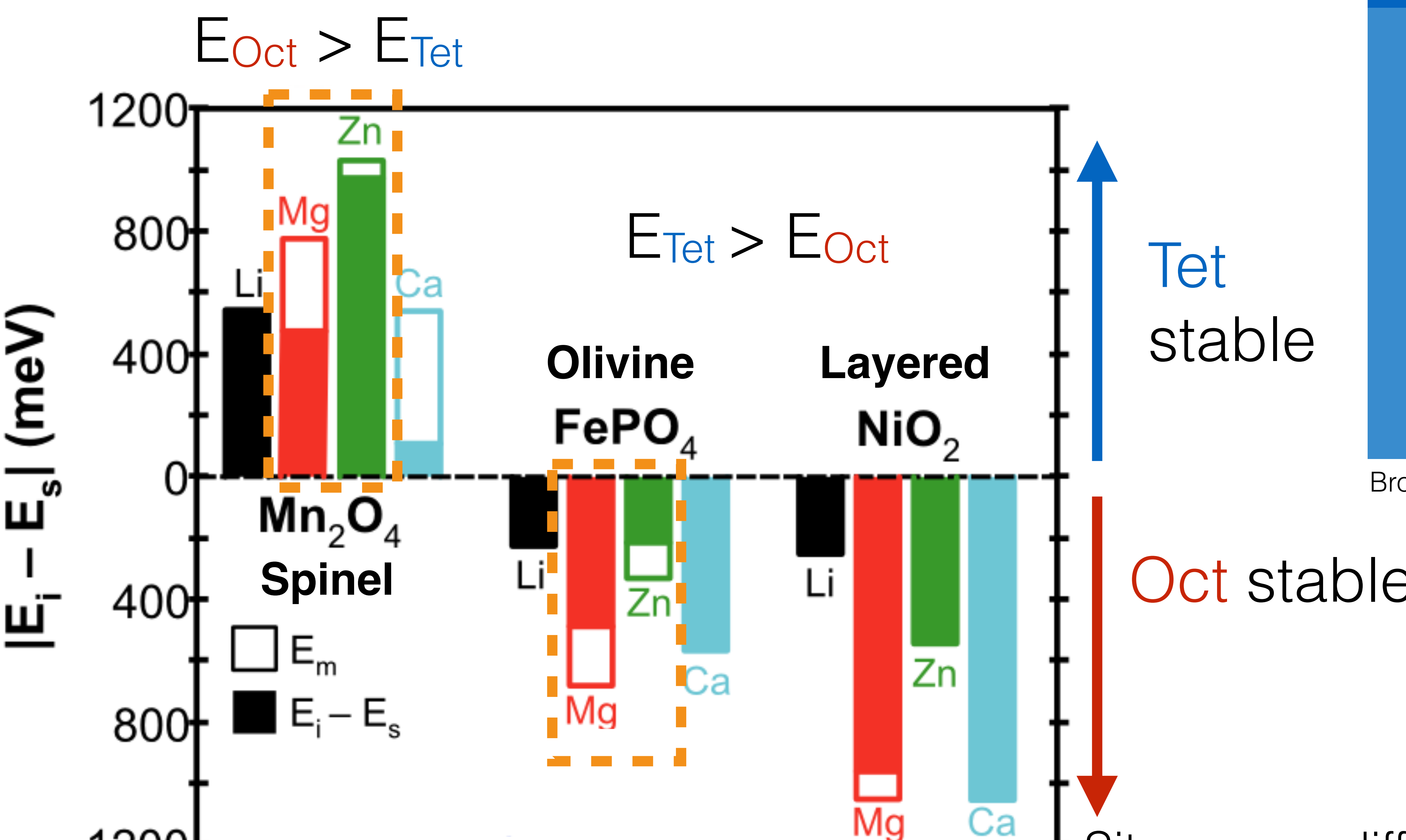
$E_{site} = E_{Tet} - E_{Oct}$

- General trend in E_m : $3^+ > 2^+ > 1^+$
- No universal trend in 2^+ (e.g., $Mg^{2+} > Zn^{2+}$)

Rong *et al.*, **Chem. Mater.** 27, **2015**, 6016-6021

Liu *et al.*, **Energy Environ. Sci.** 8, **2015**, 964-974

Coordination of the MV ion can be used as a screening criterion



Ion	Coord. pref.
Mg	6
Zn	4
Li	4-6
Ca	6-8

Brown, Acta Cryst. (1988)

Site energy difference is a good proxy to actual barrier

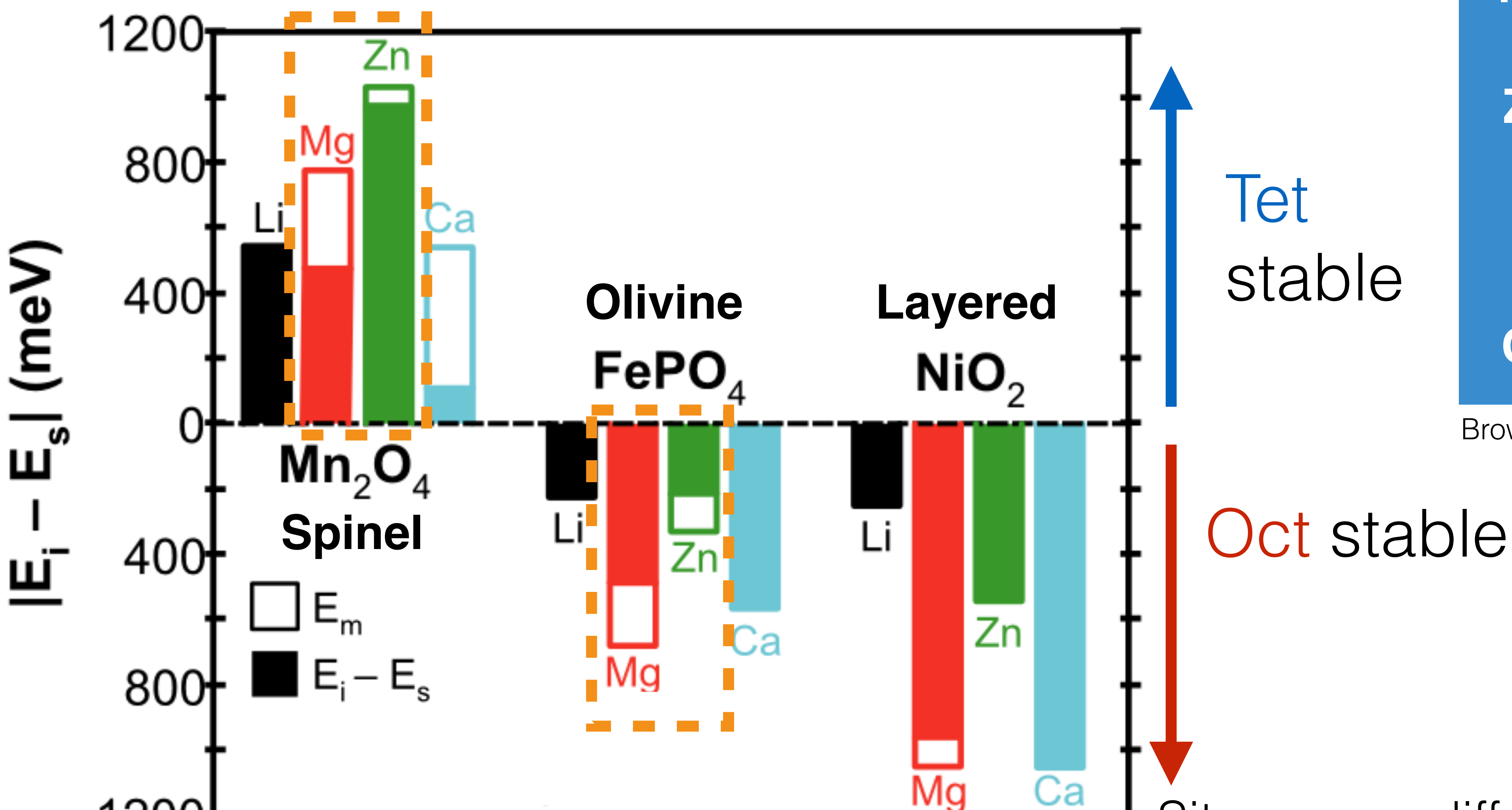
Rong *et al.*, **Chem. Mater.** 27, **2015**, 6016-6021

Coordination of the MV ion can be used as a screening criterion

MV ion-host pairs where MV ion resides in "**un-preferred**" coordination will have higher mobility

Ion	Coord. pref.
Mg	6
Zn	4
Li	4-6
Ca	6-8

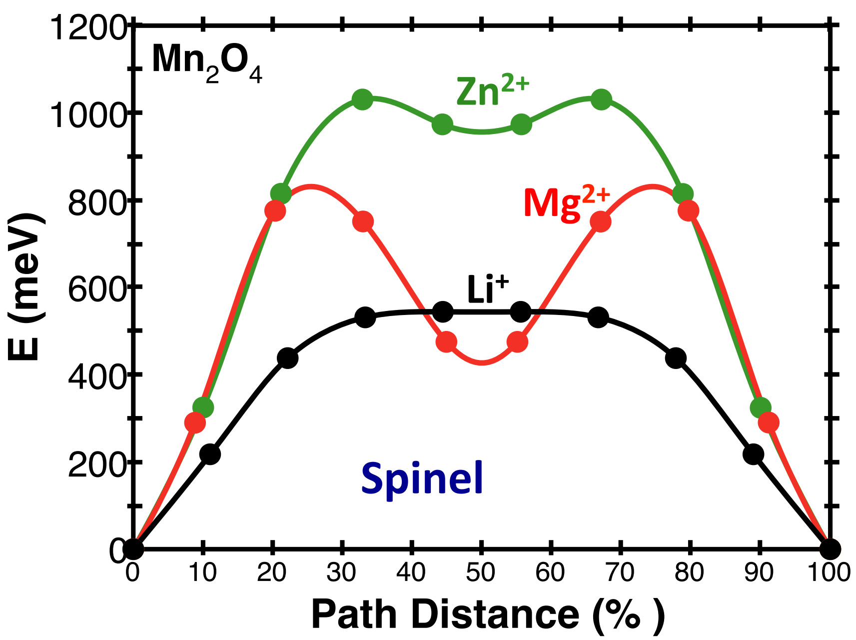
Brown, Acta Cryst. (1988)



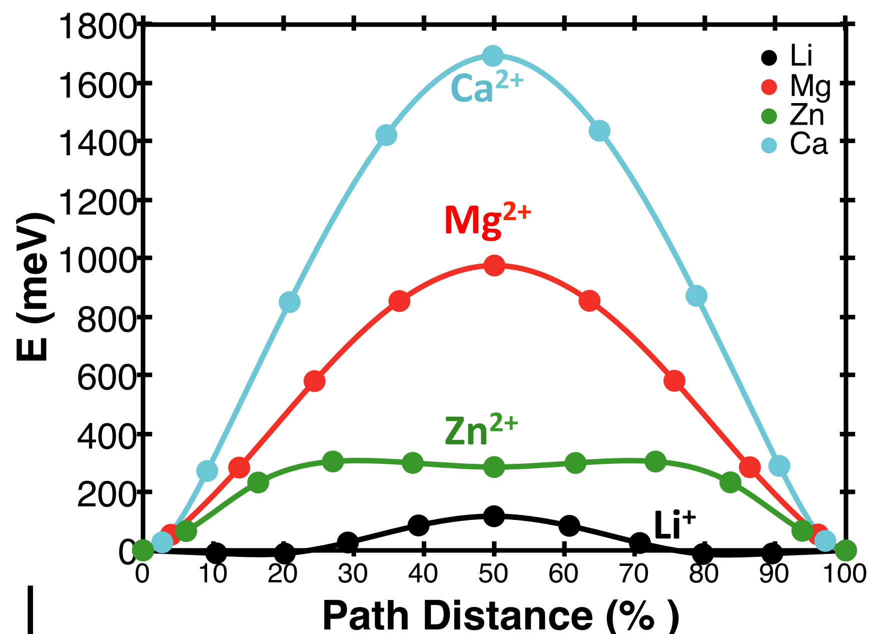
Site energy difference is a good proxy to actual barrier

Rong *et al.*, **Chem. Mater.** 27, **2015**, 6016-6021

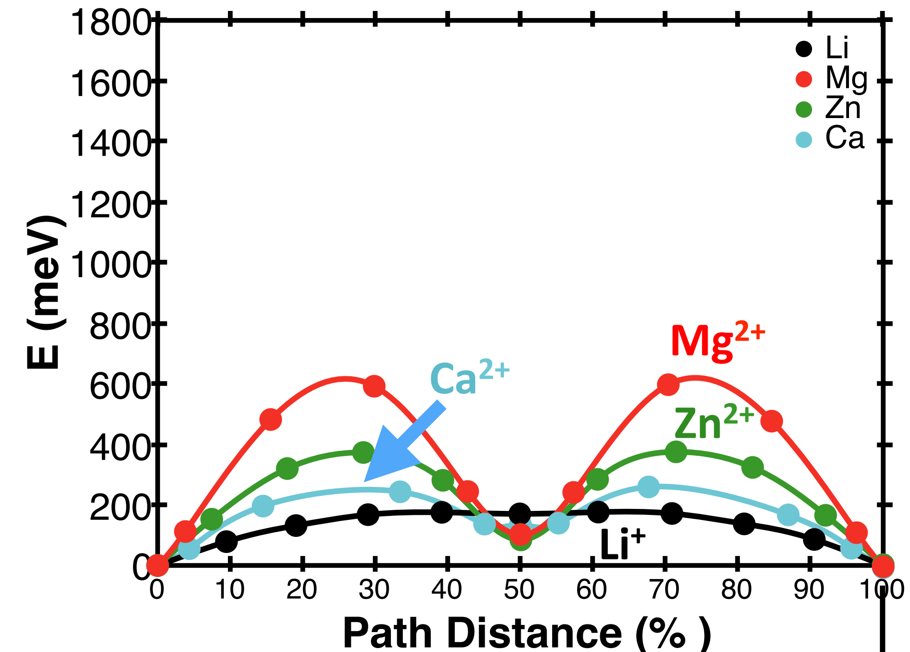
"Smaller" Δ(Coordination) is also important



Spinel Mn_2O_4



α



δ

Orthorhombic V_2O_5

Coordination change:

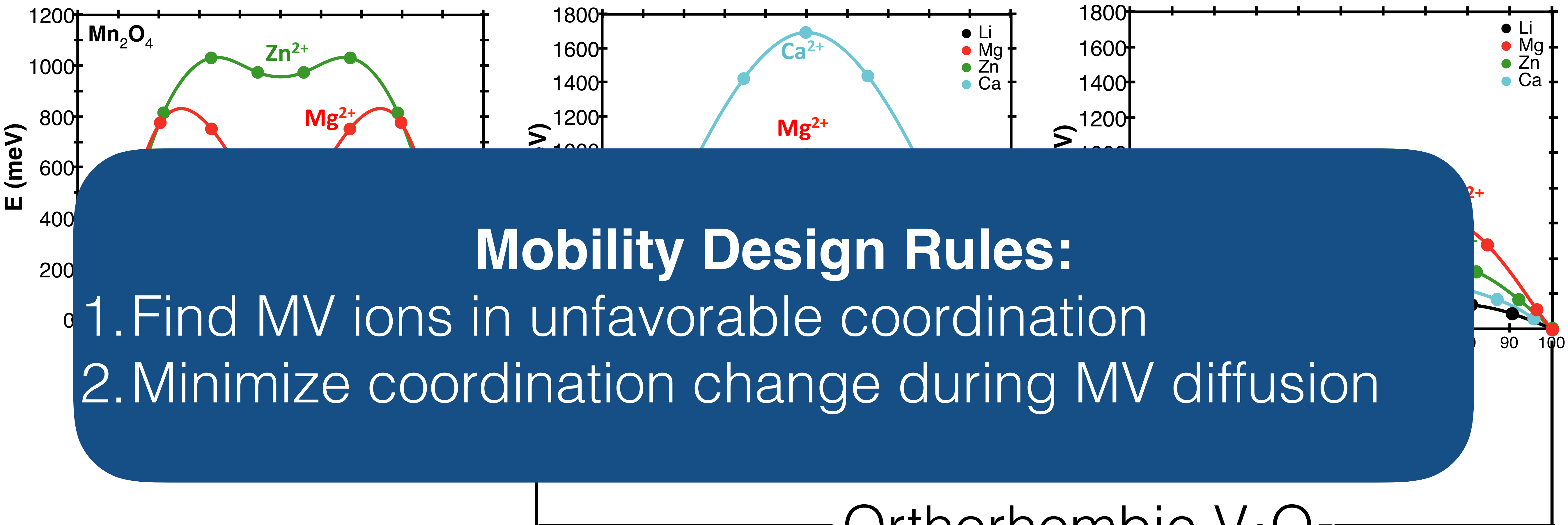
4-6-4 | 8-3-8 | 6-5-6

Host structures with "**smaller**" coordination change will have better MV mobility

More on spinels shortly…

Rong *et al.*, **Chem. Mater.** 27, **2015**, 6016-6021

"Smaller" Δ(Coordination) is also important



Mobility Design Rules:

1. Find MV ions in unfavorable coordination
2. Minimize coordination change during MV diffusion

Coordination change:

4-6-4 8-3-8 6-5-6

Host structures with "**smaller**" coordination change will have better MV mobility

More on spinels shortly…

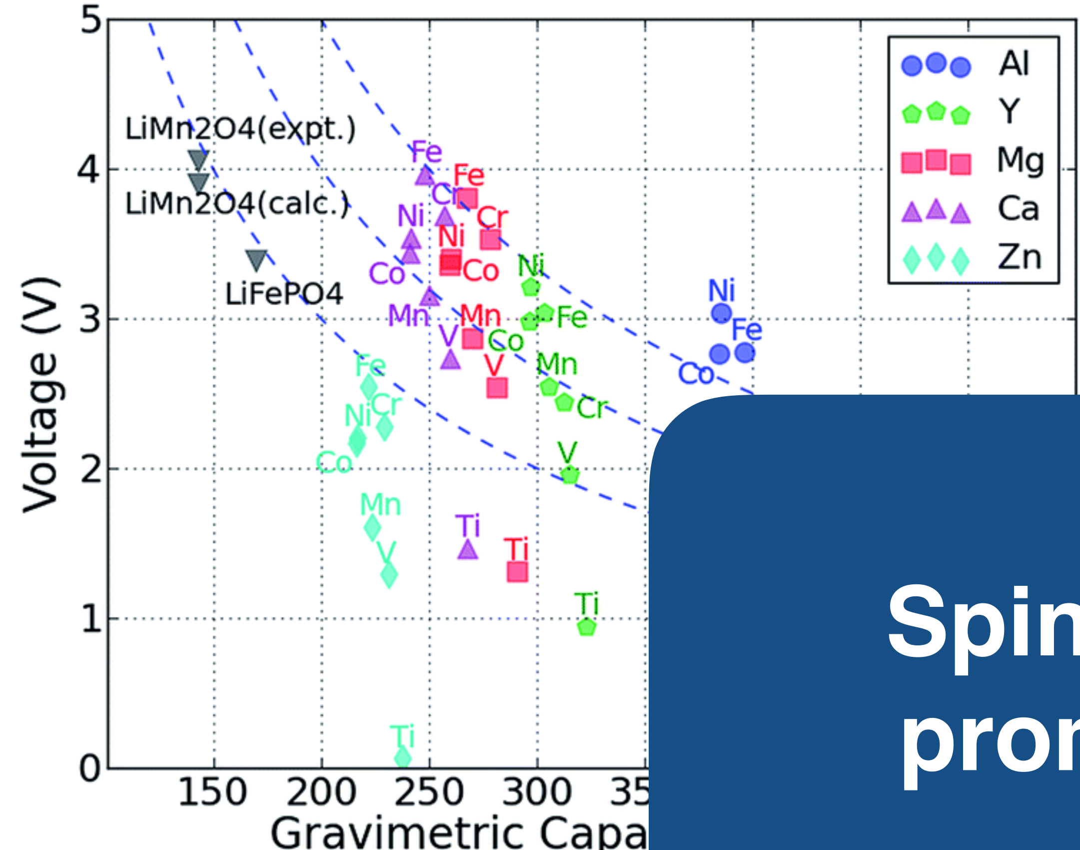
Rong *et al.*, **Chem. Mater.** 27, **2015**, 6016-6021

Spinels in MV batteries

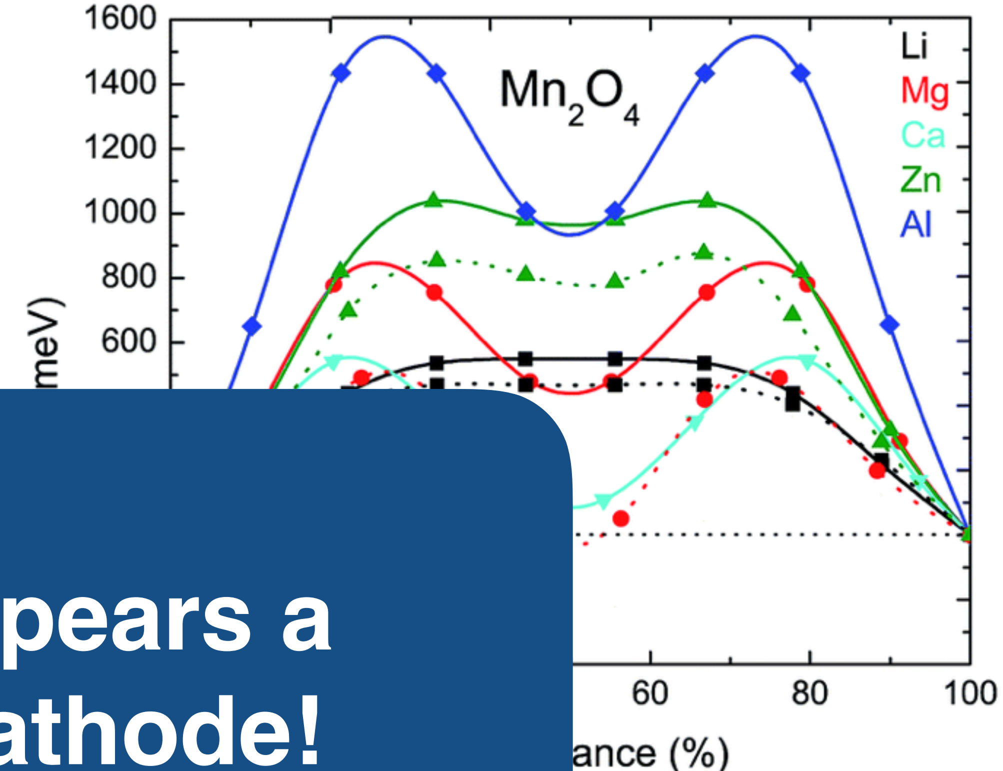
Inversion in $MgMn_2O_4$

G.S. Gautam *et al.*, “Influence of spinel inversion on Mg mobility and electrochemistry in spinels”, under review

Spinels have promising energy densities and Mg^{2+} mobility

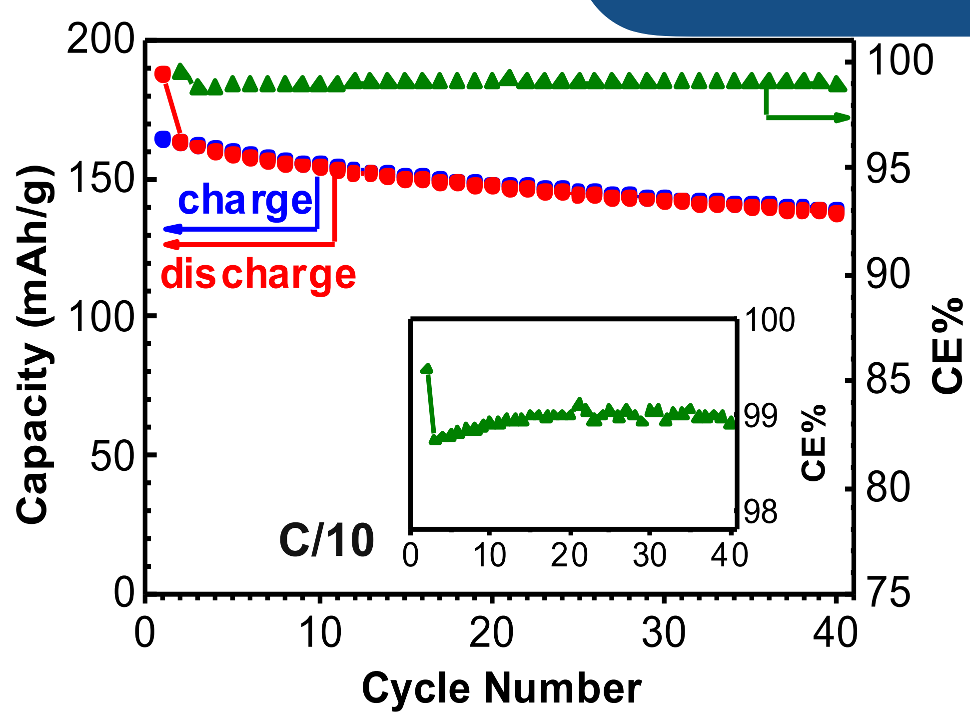


Liu *et al.*, **Energy Environ. Sc**

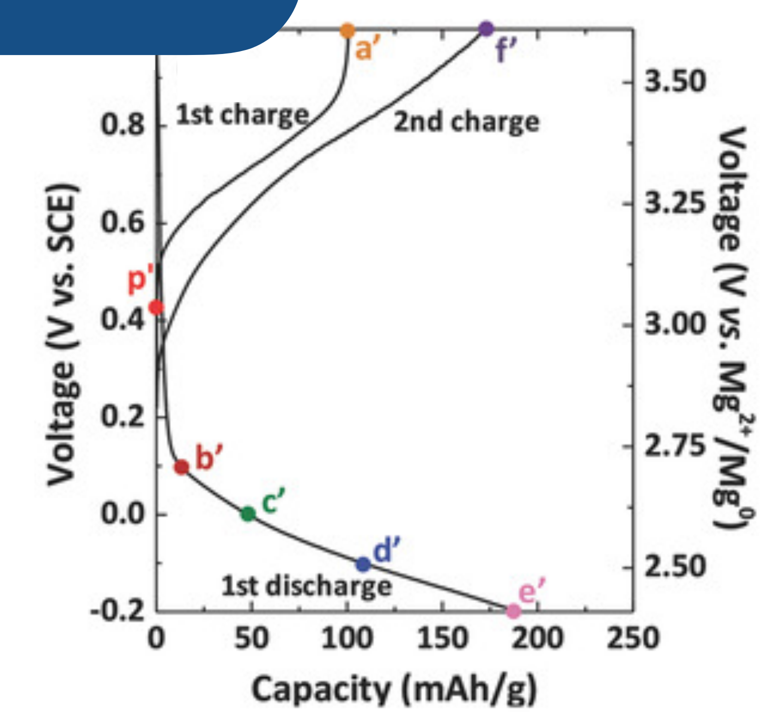


r. 27, **2015**, 6016-6021

Spinel-Mn_2O_4 appears a promising Mg cathode!



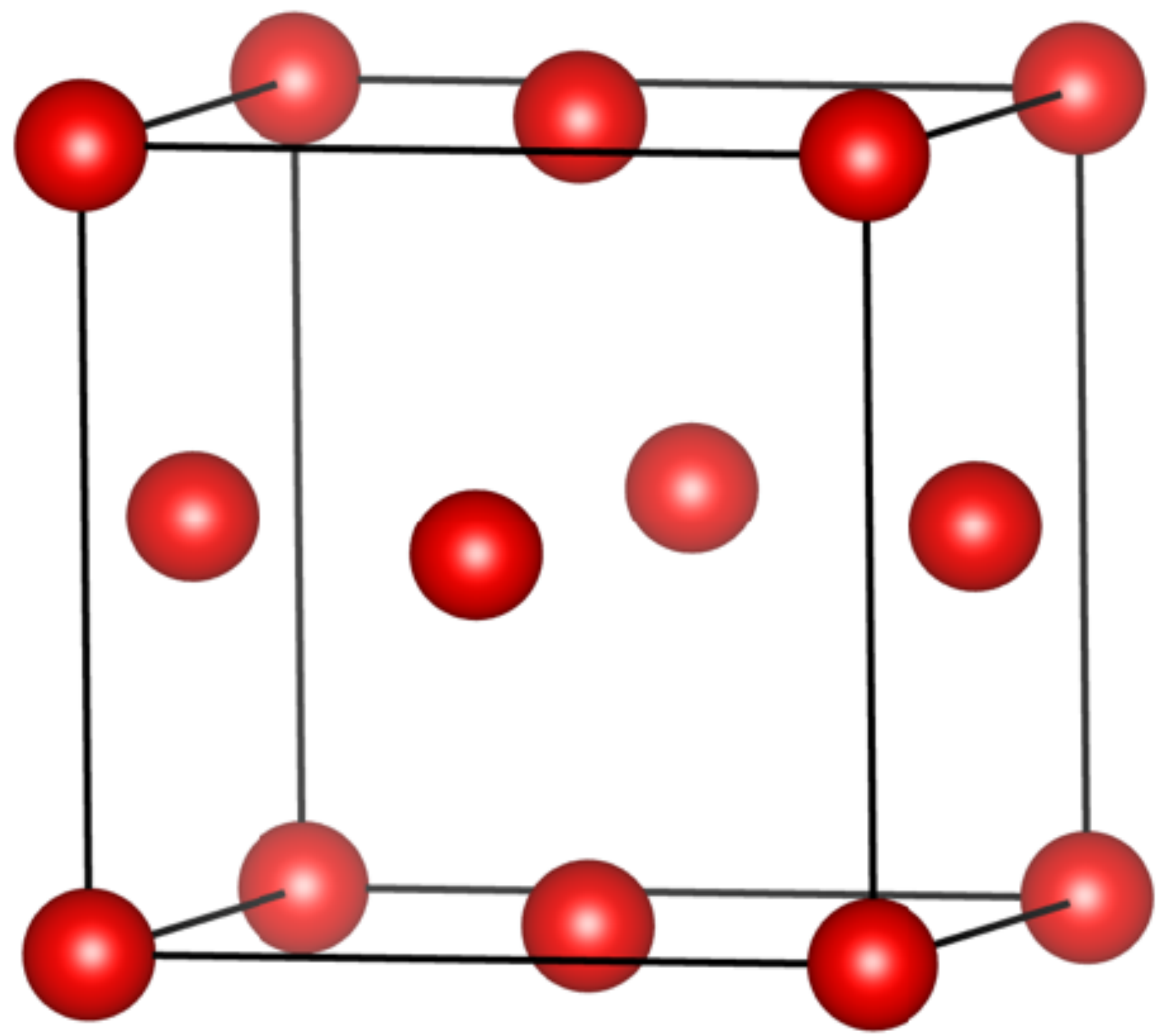
Sun *et al.*, **Energy Environ. Sci.** 9, **2016**, 2273-2277



Kim *et al.*, **Adv. Mater.** 27, **2015**, 3377-3384

Normal spinel structure: AM_2X_4

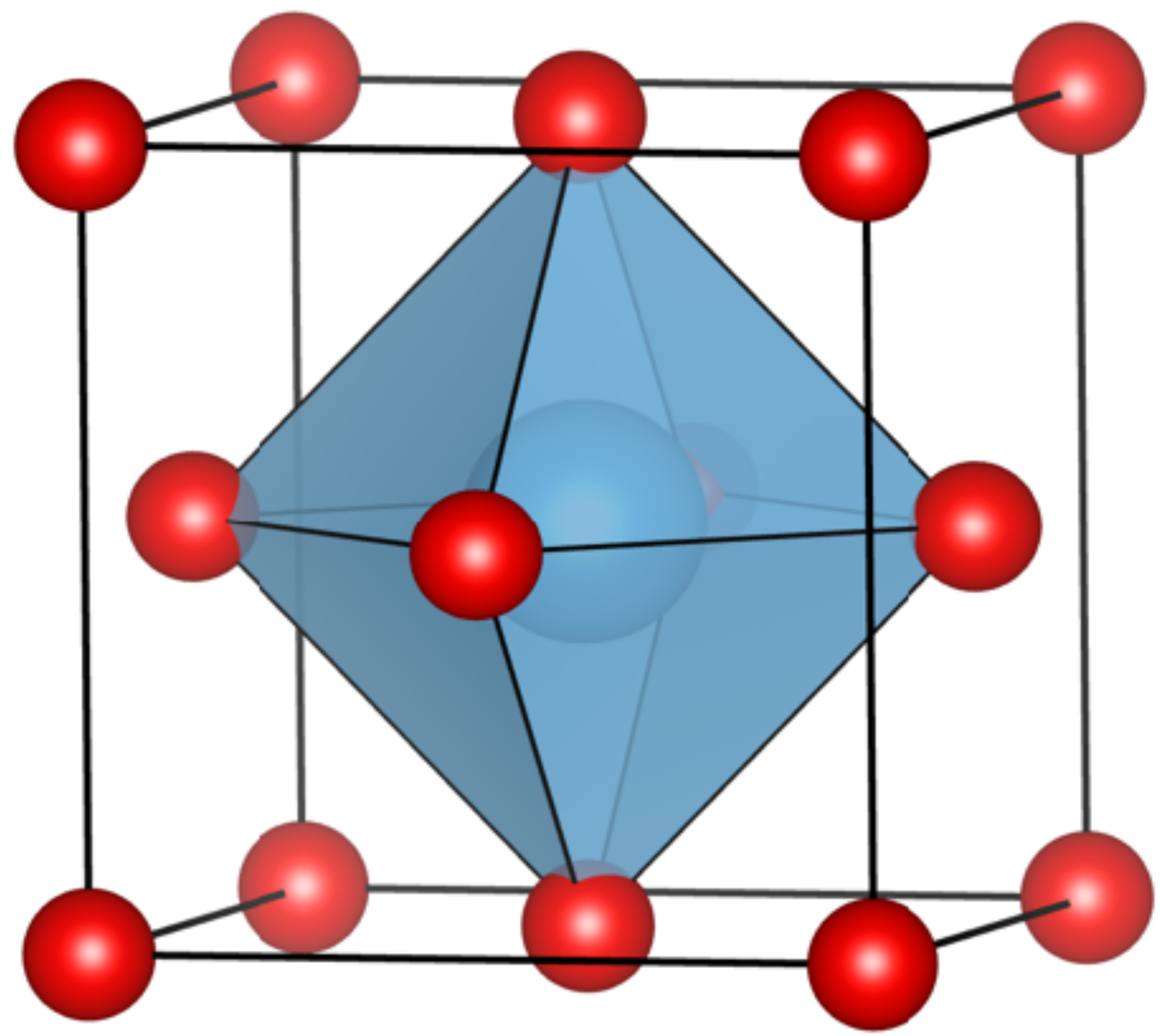
A = Mg M = Mn X = O Vac = Vacancy



Anions

Normal spinel structure: AM_2X_4

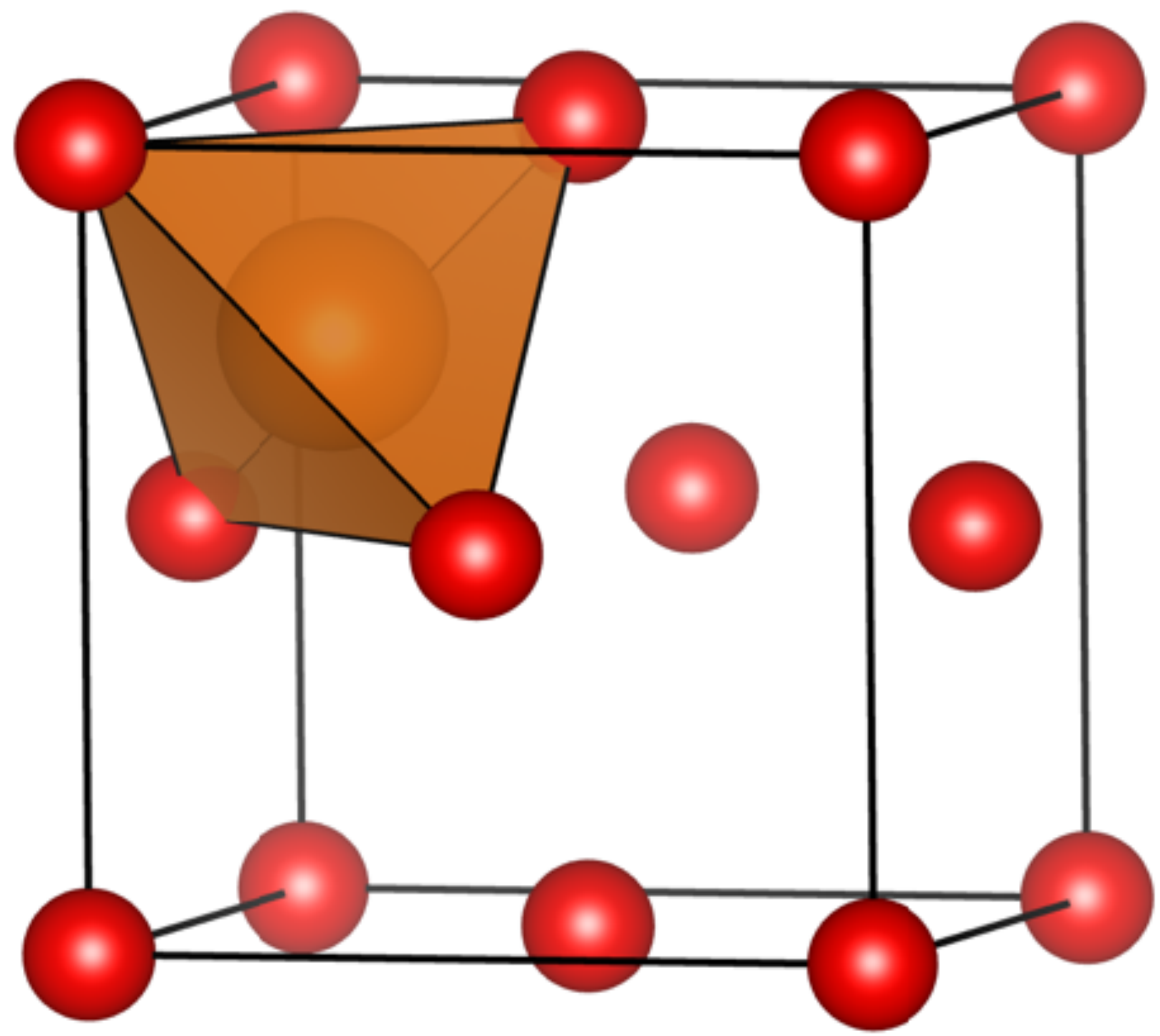
A = Mg M = Mn X = O Vac = Vacancy



= (# Anions)

Normal spinel structure: AM_2X_4

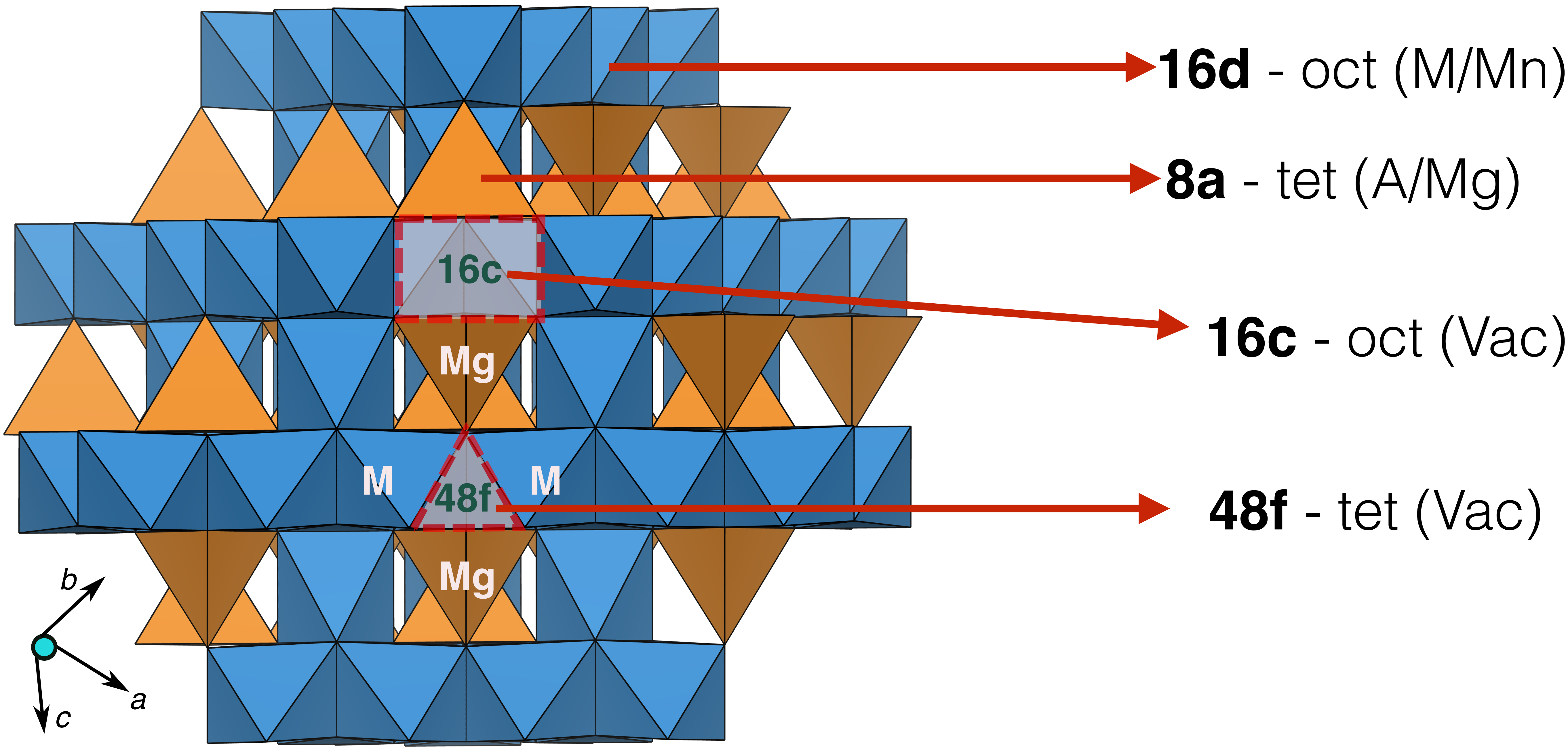
A = Mg M = Mn X = O Vac = Vacancy



= 2*(# Anions)

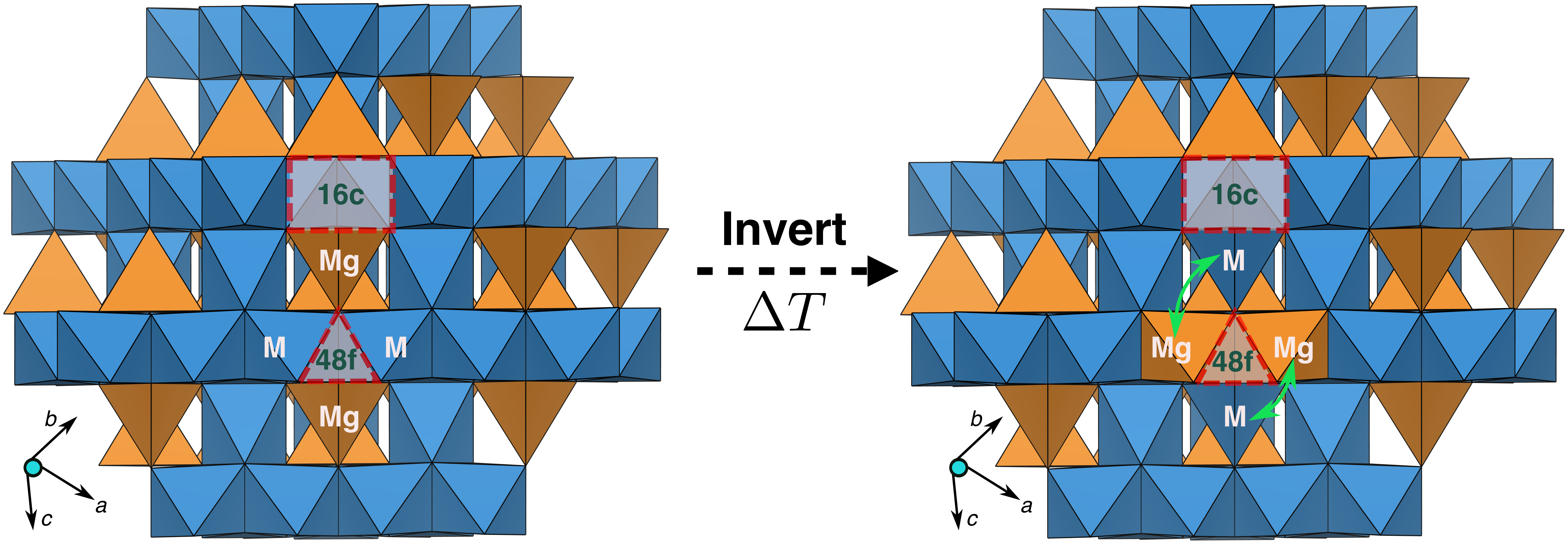
Normal spinel structure: AM_2X_4

A = Mg M = Mn X = O Vac = Vacancy



$MgMn_2O_4$ spinel afflicted by inversion

Inversion: Exchange of A and M sites in AM_2X_4



Degree of inversion (*i*): Fraction of 8a (tet) sites occupied by M

$i \sim 0.2 — 0.6$[6,7] in $MgMn_2O_4$

6. Irani *et al.*, **J. Phys. Chem. Solids** 23, **1962**, 711-727
7. Malavasi *et al.*, **J. Solid State Chem.** 166, **2002**, 171-176

$MgMn_2O_4$ spinel afflicted by inversion

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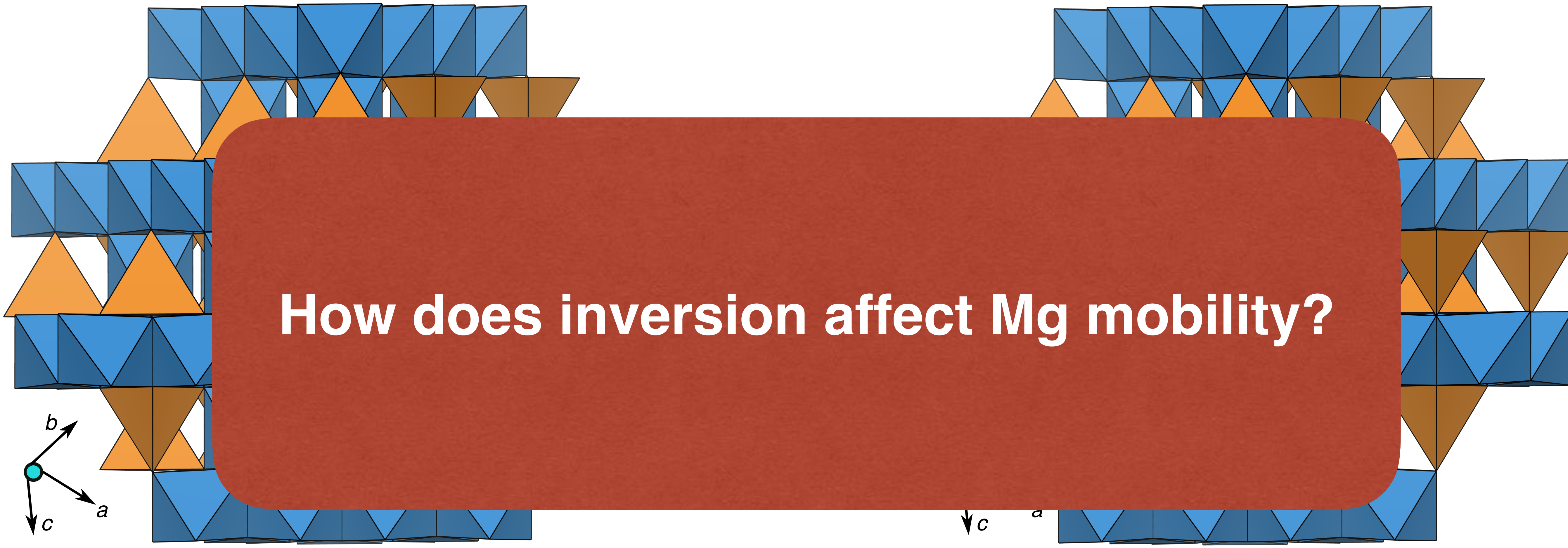


How does inversion affect Mg mobility?

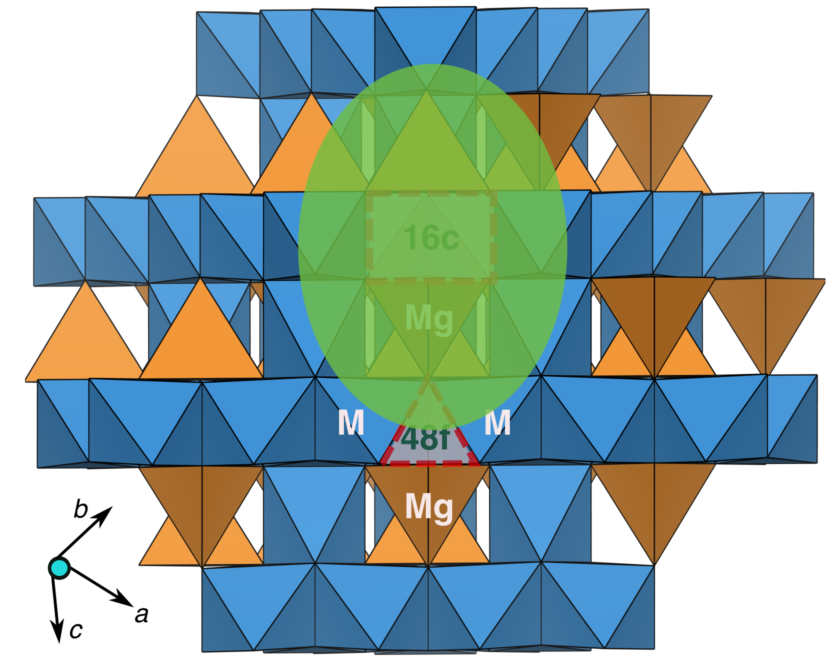
Degree of inversion (*i*): Fraction of 8a (tet) sites occupied by M

$i \sim 0.2 — 0.6$[6,7] in $MgMn_2O_4$

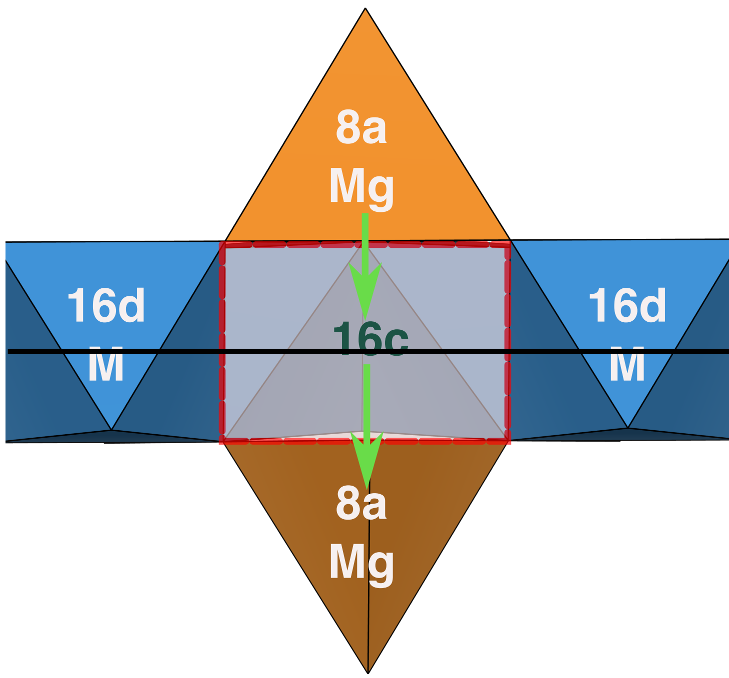
6. Irani *et al.*, **J. Phys. Chem. Solids** 23, **1962**, 711-727
7. Malavasi *et al.*, **J. Solid State Chem.** 166, **2002**, 171-176

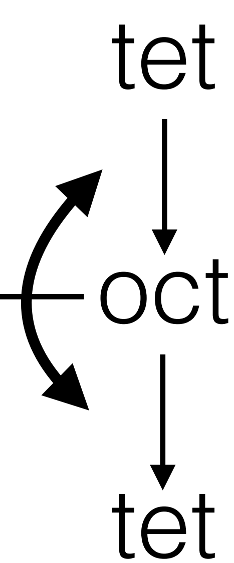
Inversion: distinct local cation decorations

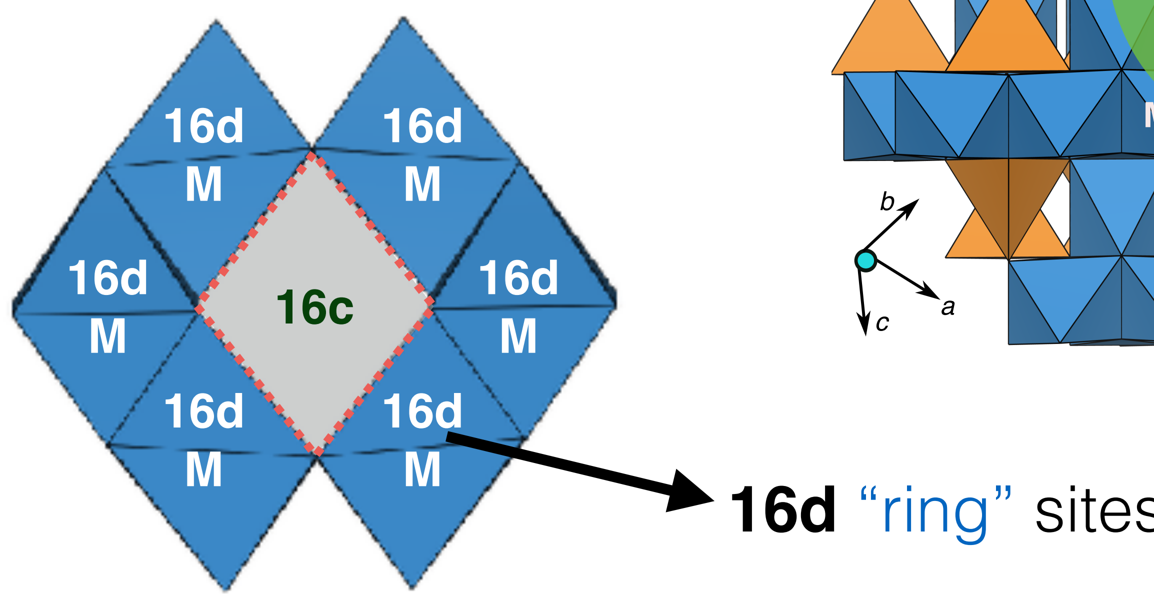
tet —> tet hops

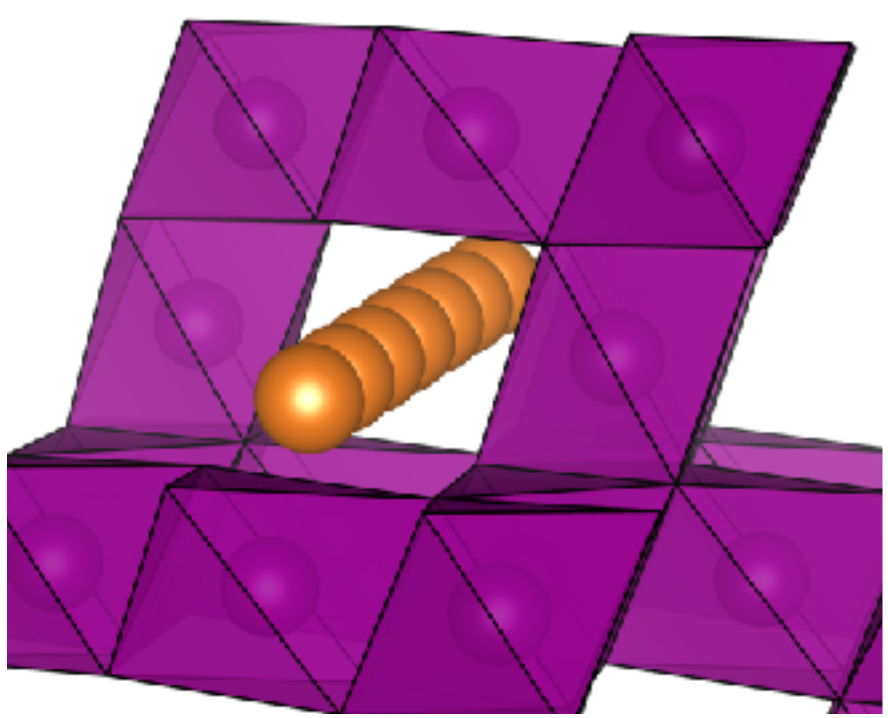


Hop 1



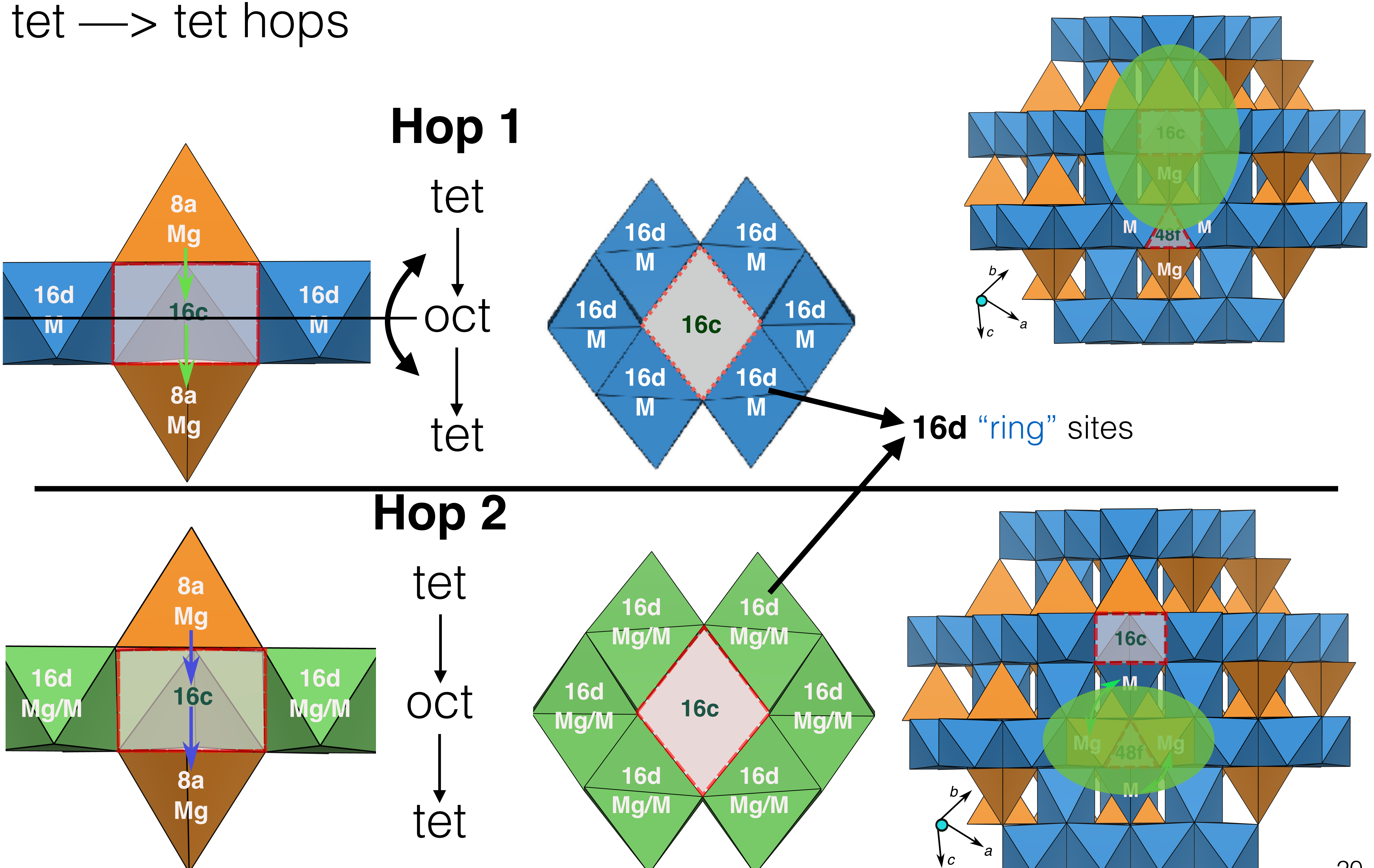






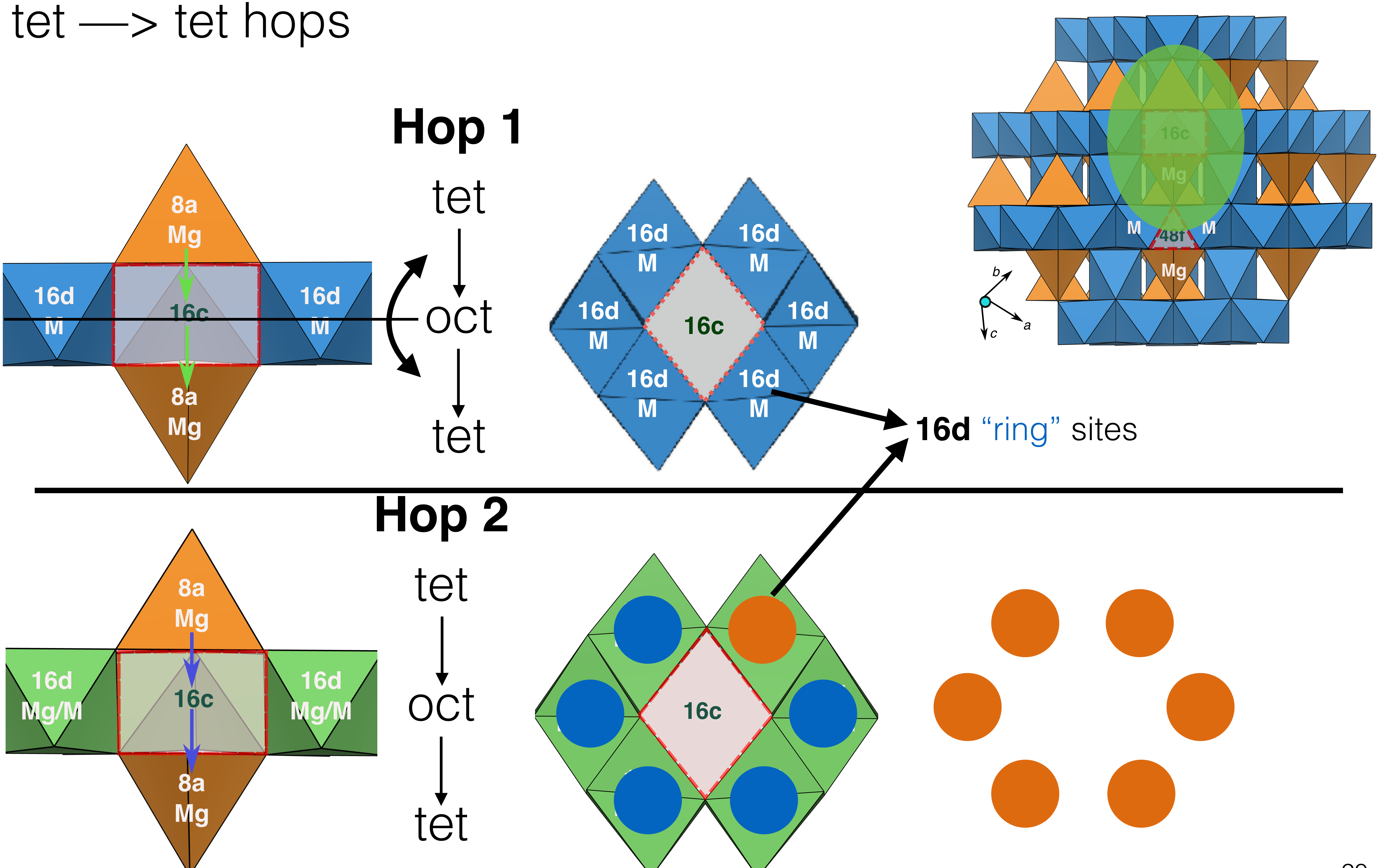
Inversion: distinct local cation decorations

tet —> tet hops



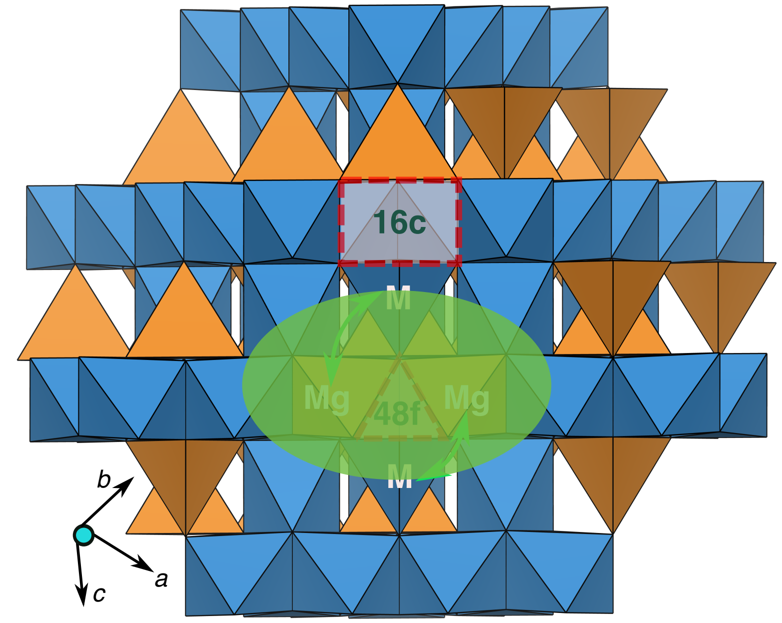
Inversion: distinct local cation decorations

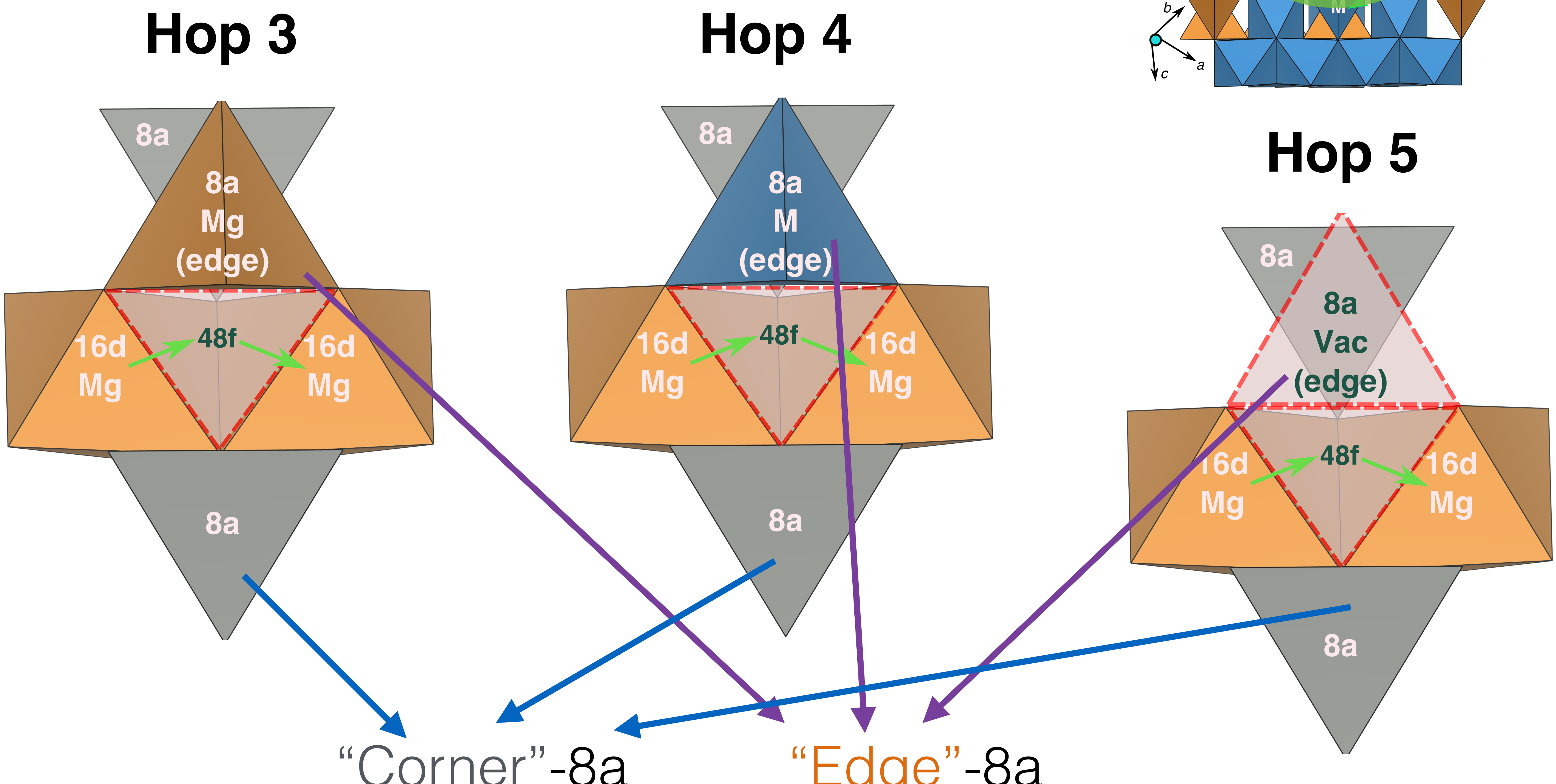
tet —> tet hops



Inversion: distinct local cation decorations

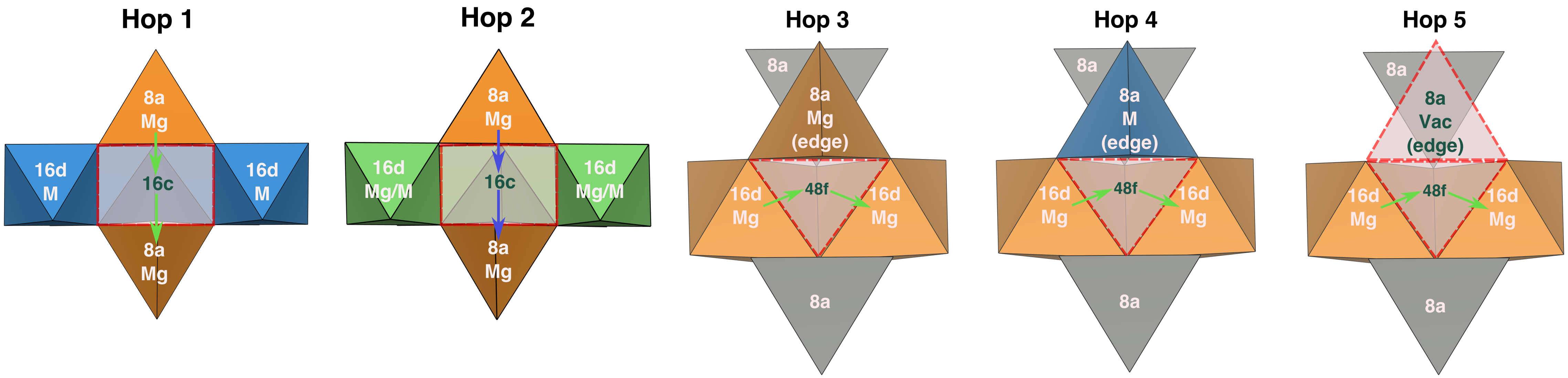
oct —> oct hops





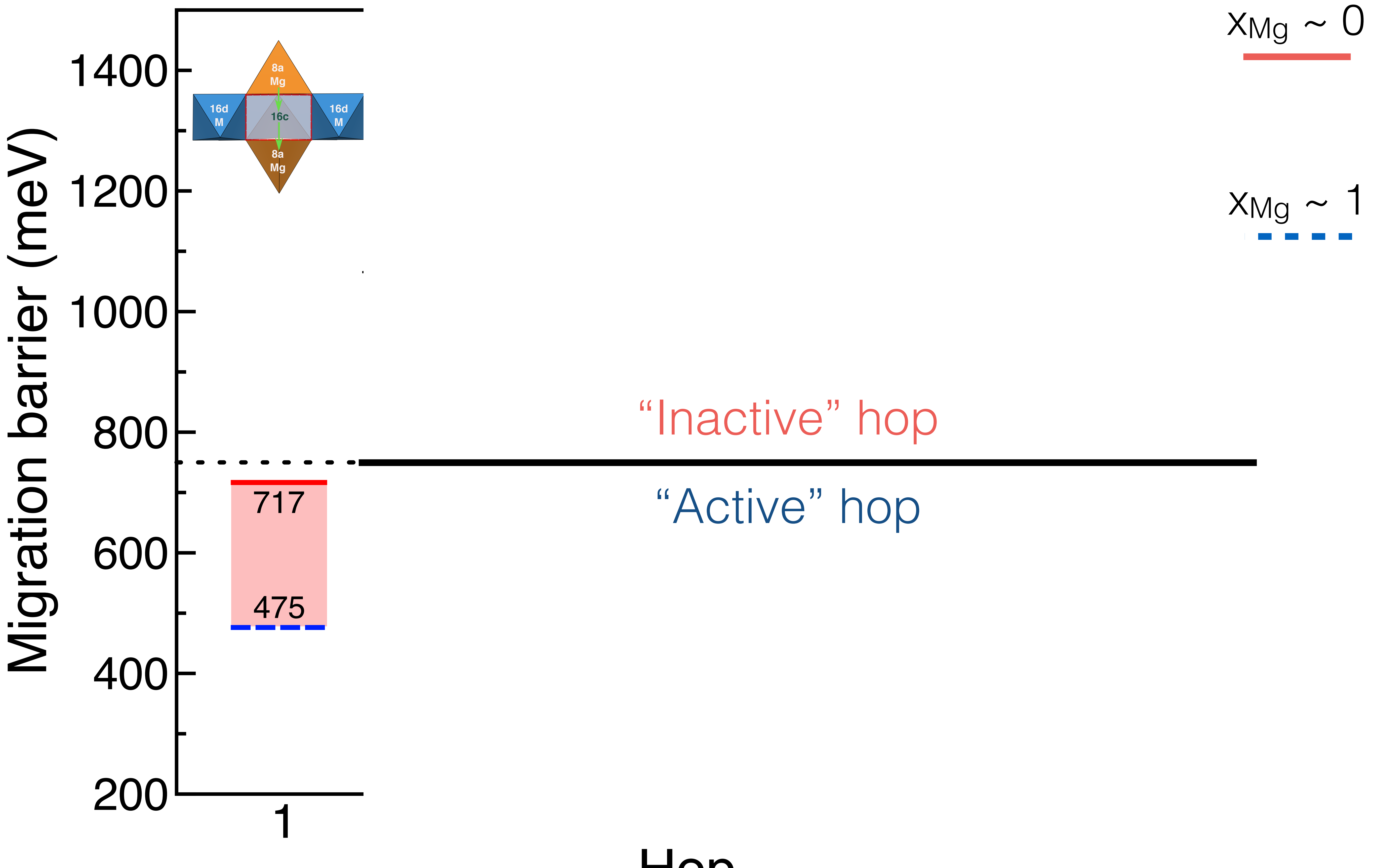
oct —> tet —> oct

Notations Summary

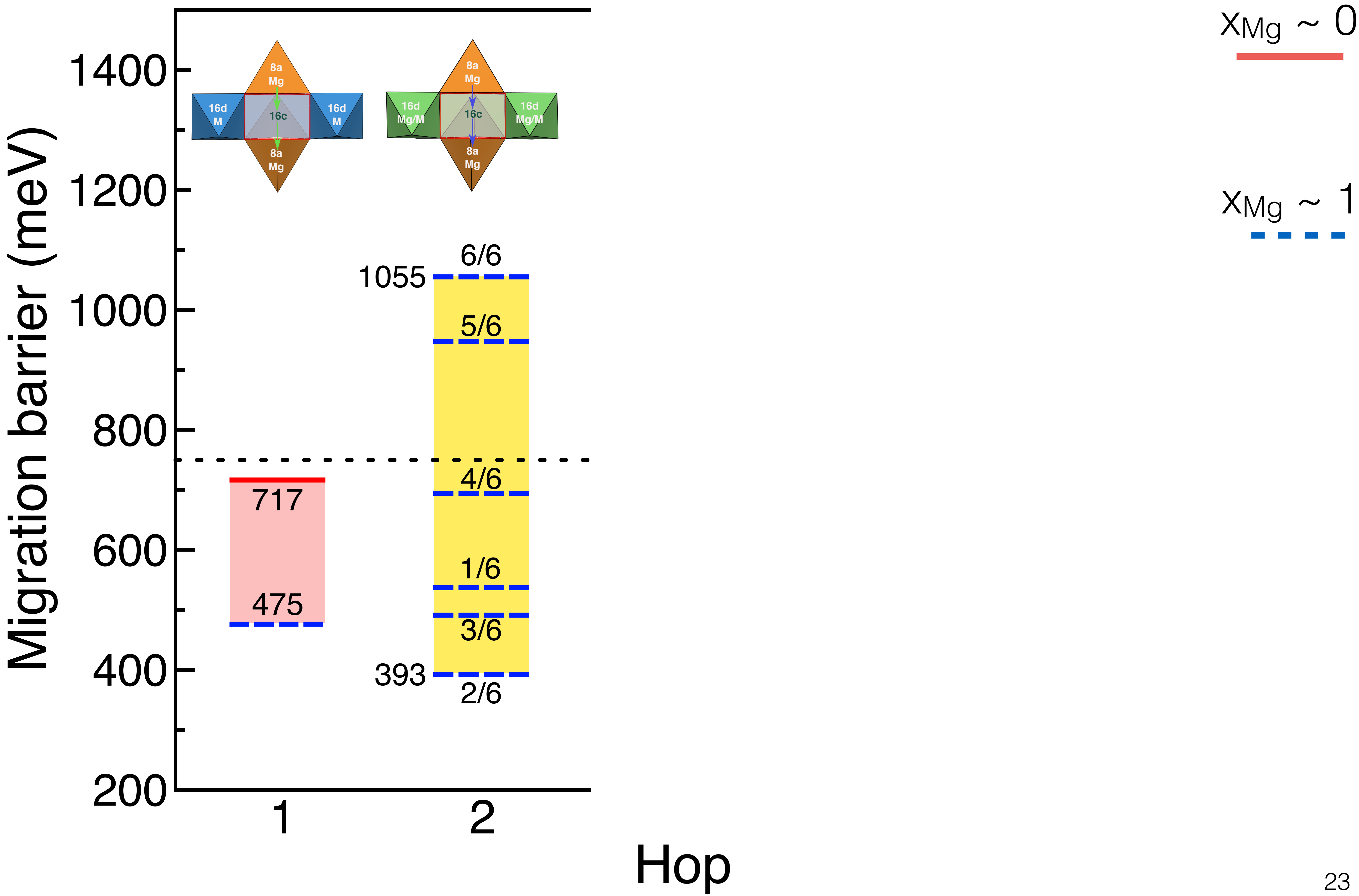


Topology	**tet-oct-tet**	**tet-oct-tet**	**oct-tet-oct**	**oct-tet-oct**	**oct-tet-oct**
Stable site	8a	8a	16d	16d	16d
Intermediate site	16c	16c	48f	48f	48f
Edge neighbors	“Ring” 16d (Mn)	“Ring” 16d (Mg/Mn)	“Edge” 8a (Mg)	“Edge” 8a (Mn)	“Edge” 8a (Vac)
Corner neighbors	—	—	“Corner” 8a (Mg/Mn/Vac)	“Corner” 8a (Mg/Mn/Vac)	“Corner” 8a (Mg/Mn/Vac)

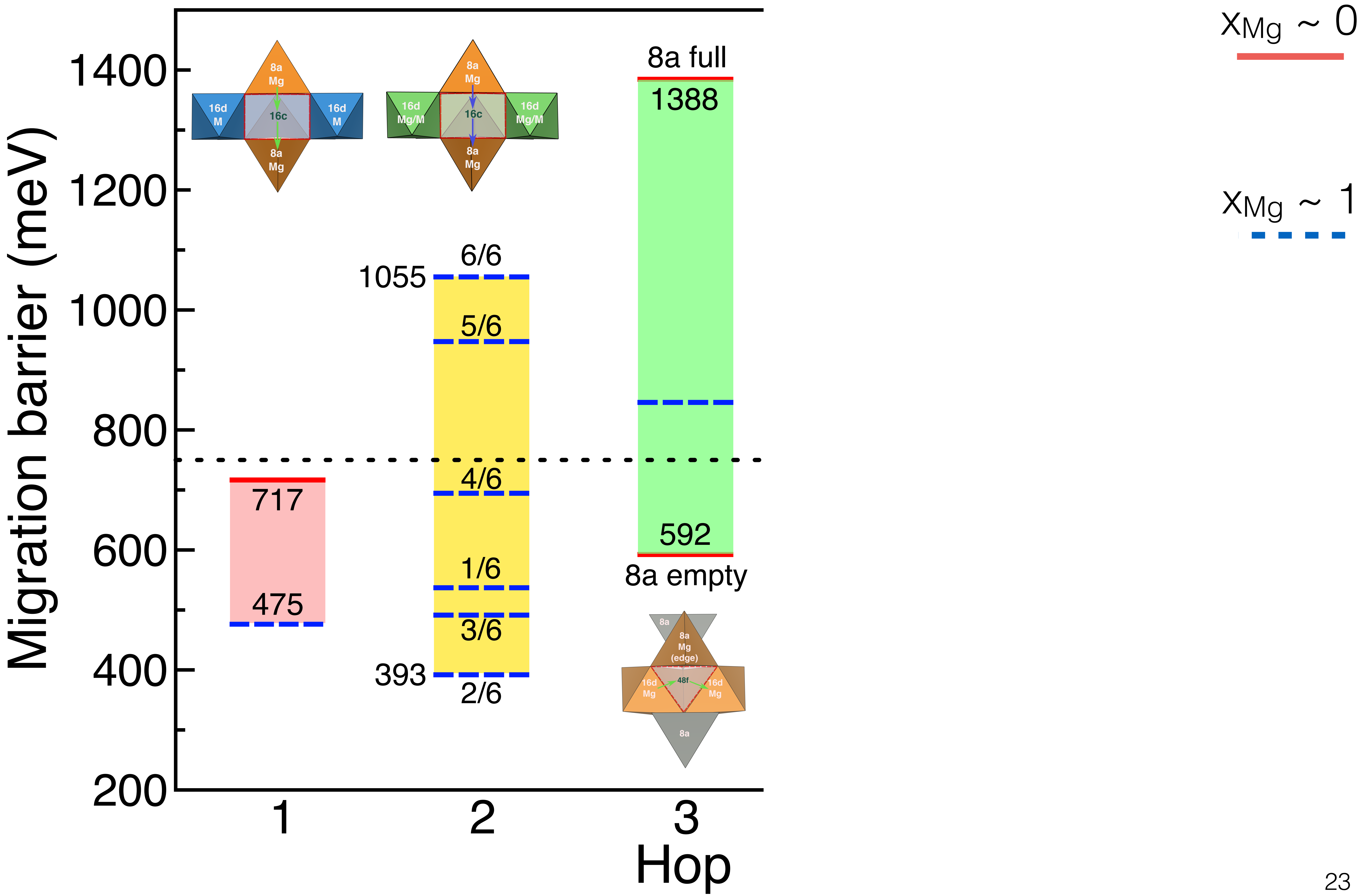
Barriers in $MgMn_2O_4$



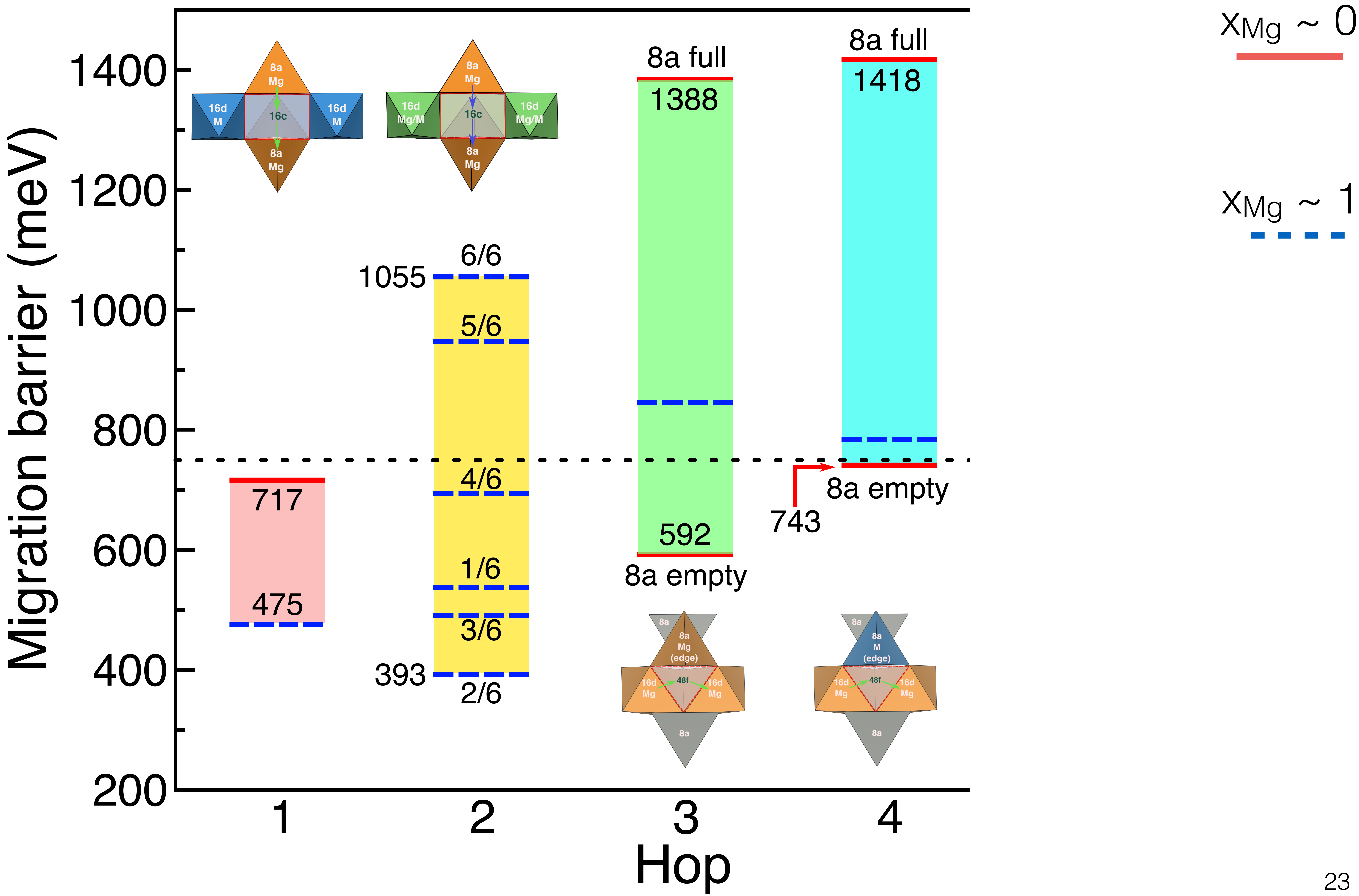
Barriers in $MgMn_2O_4$



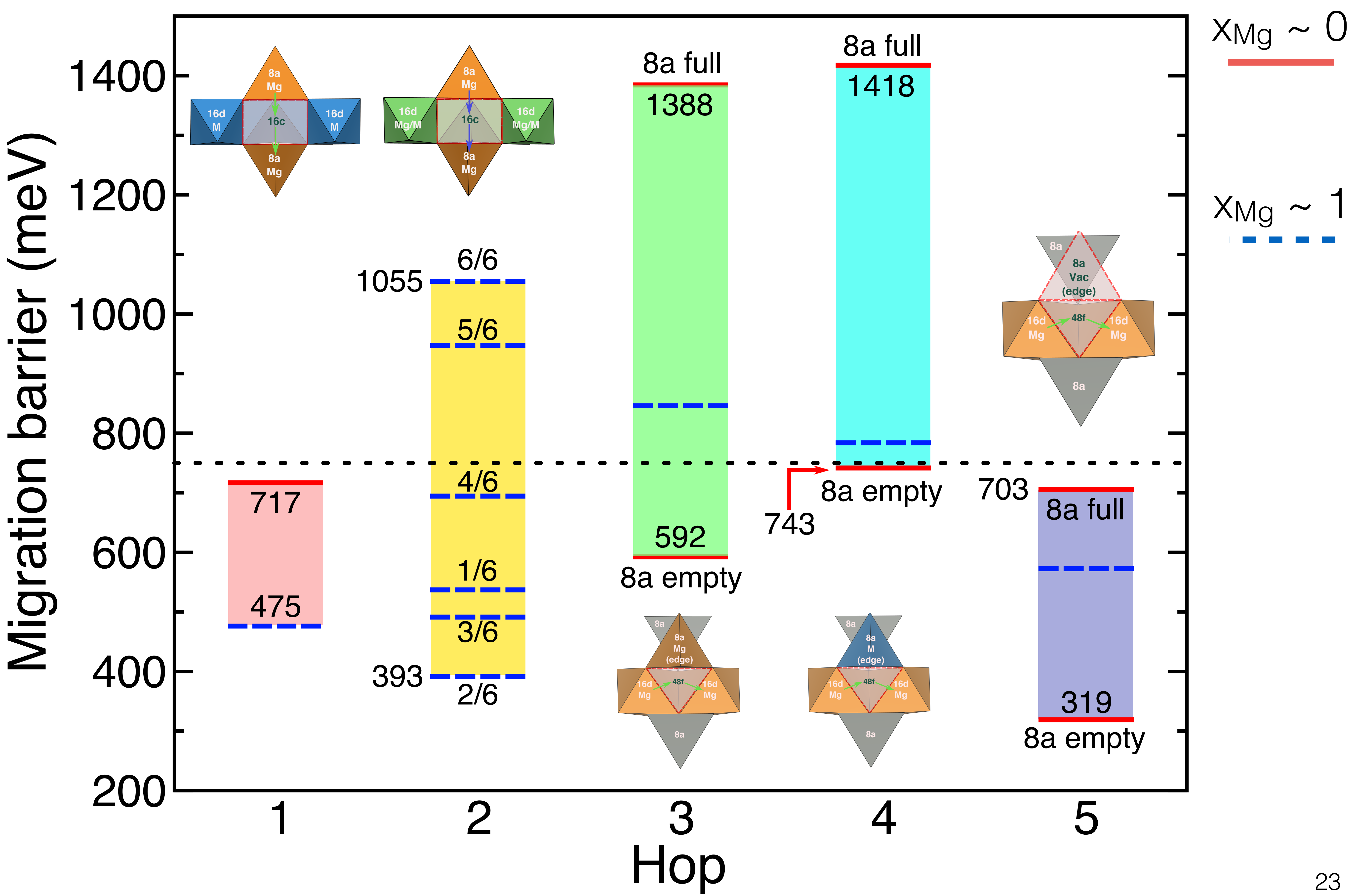
Barriers in $MgMn_2O_4$



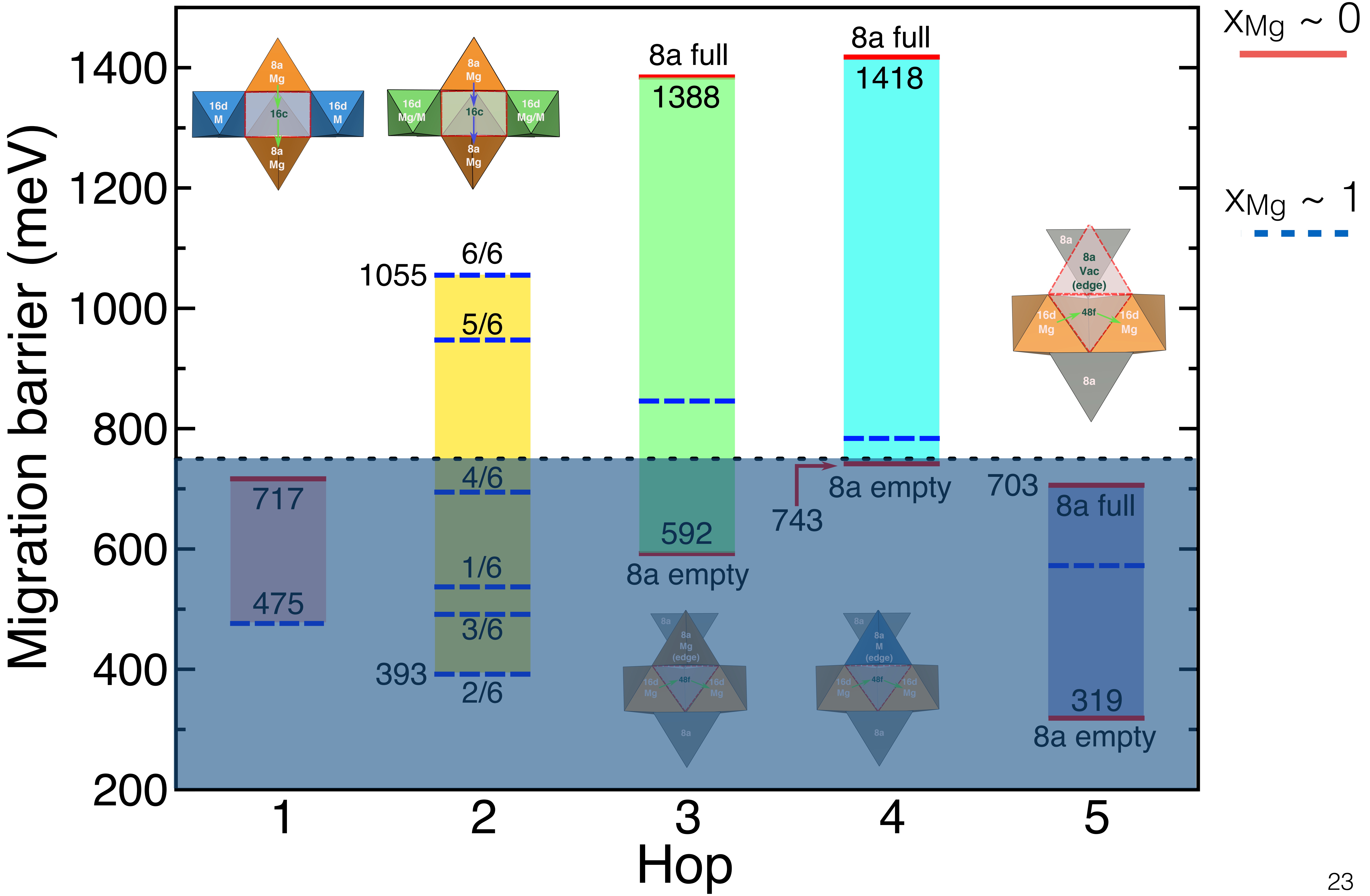
Barriers in $MgMn_2O_4$



Barriers in $MgMn_2O_4$



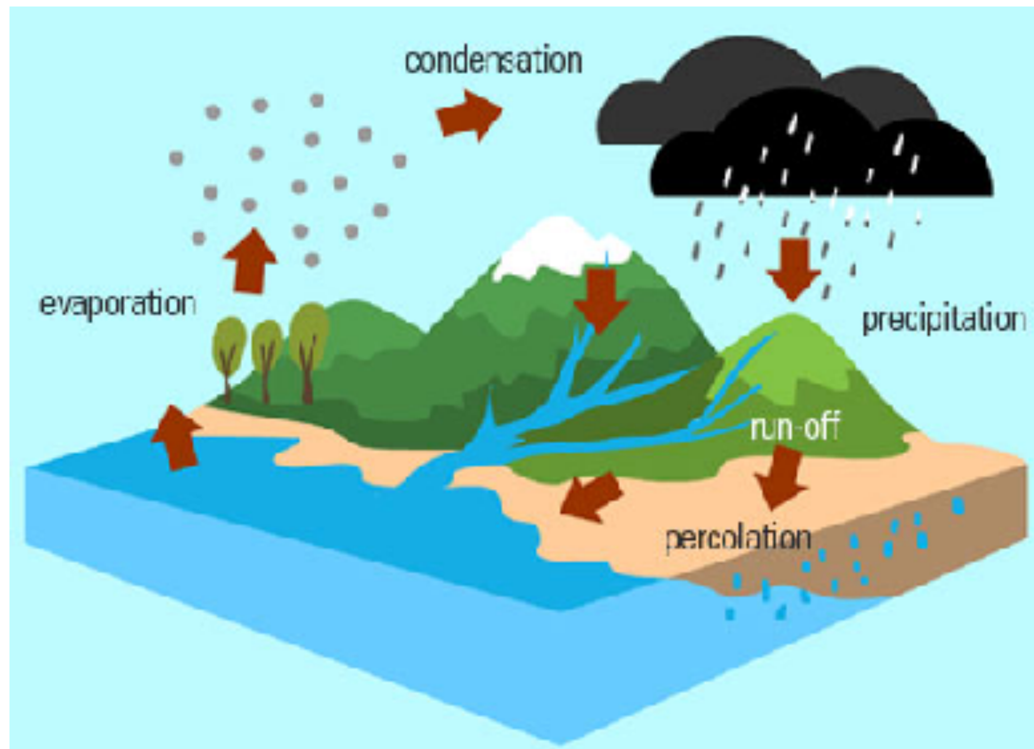
Barriers in $MgMn_2O_4$



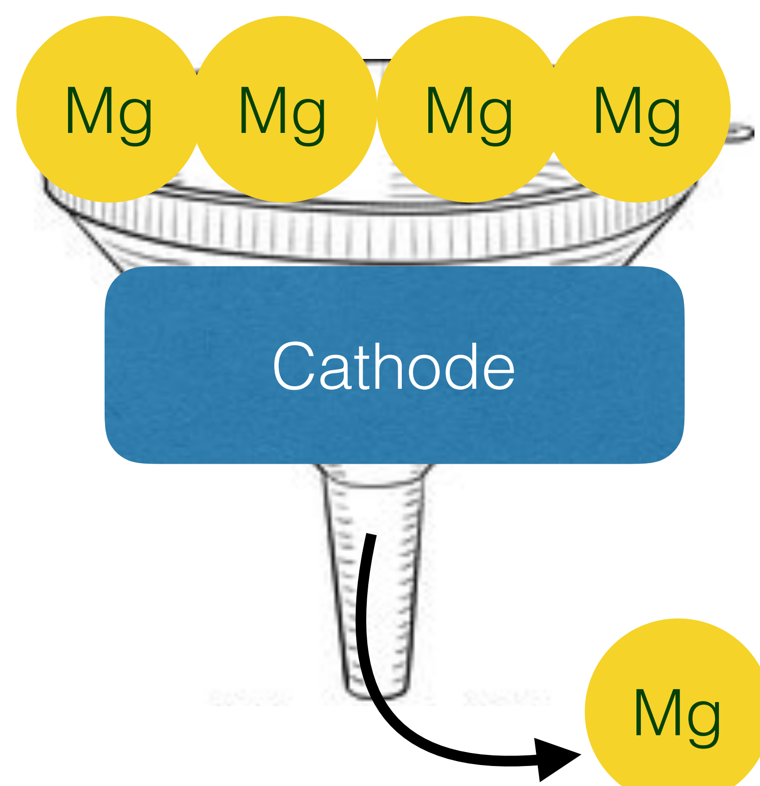
I understand barriers in local environments, but what happens to macroscopic Mg migration?

Percolation in nature

Ground water



Coffee



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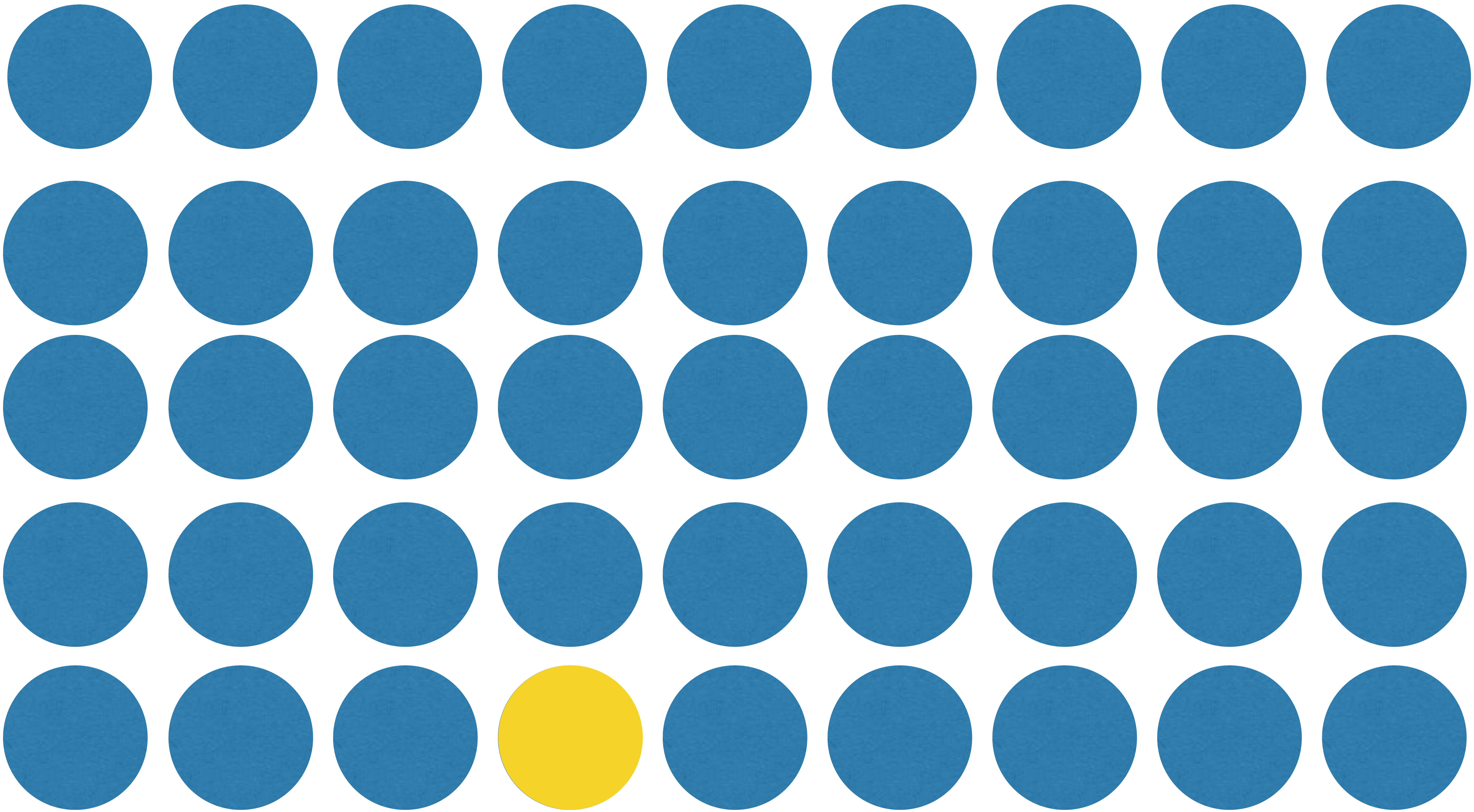

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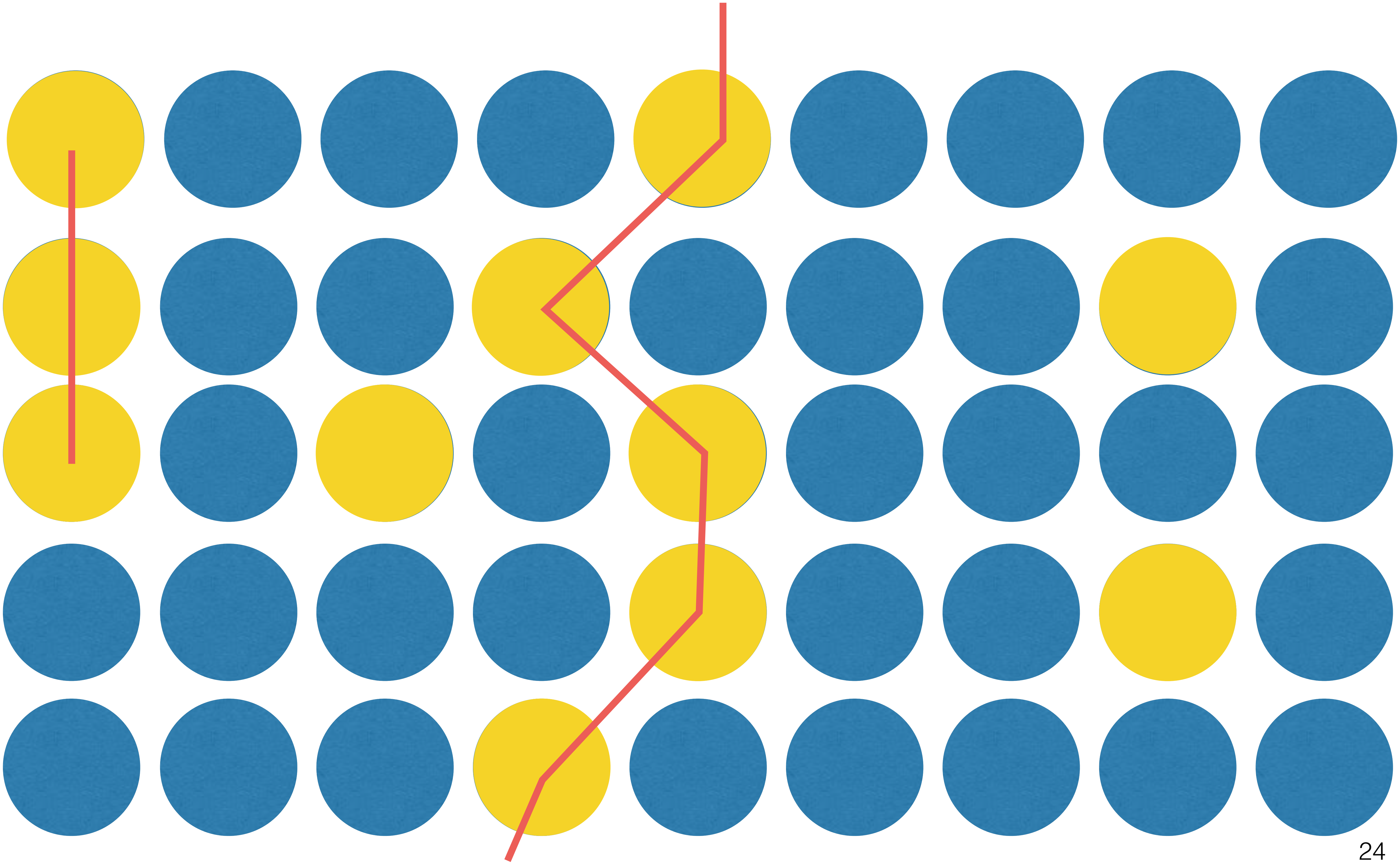

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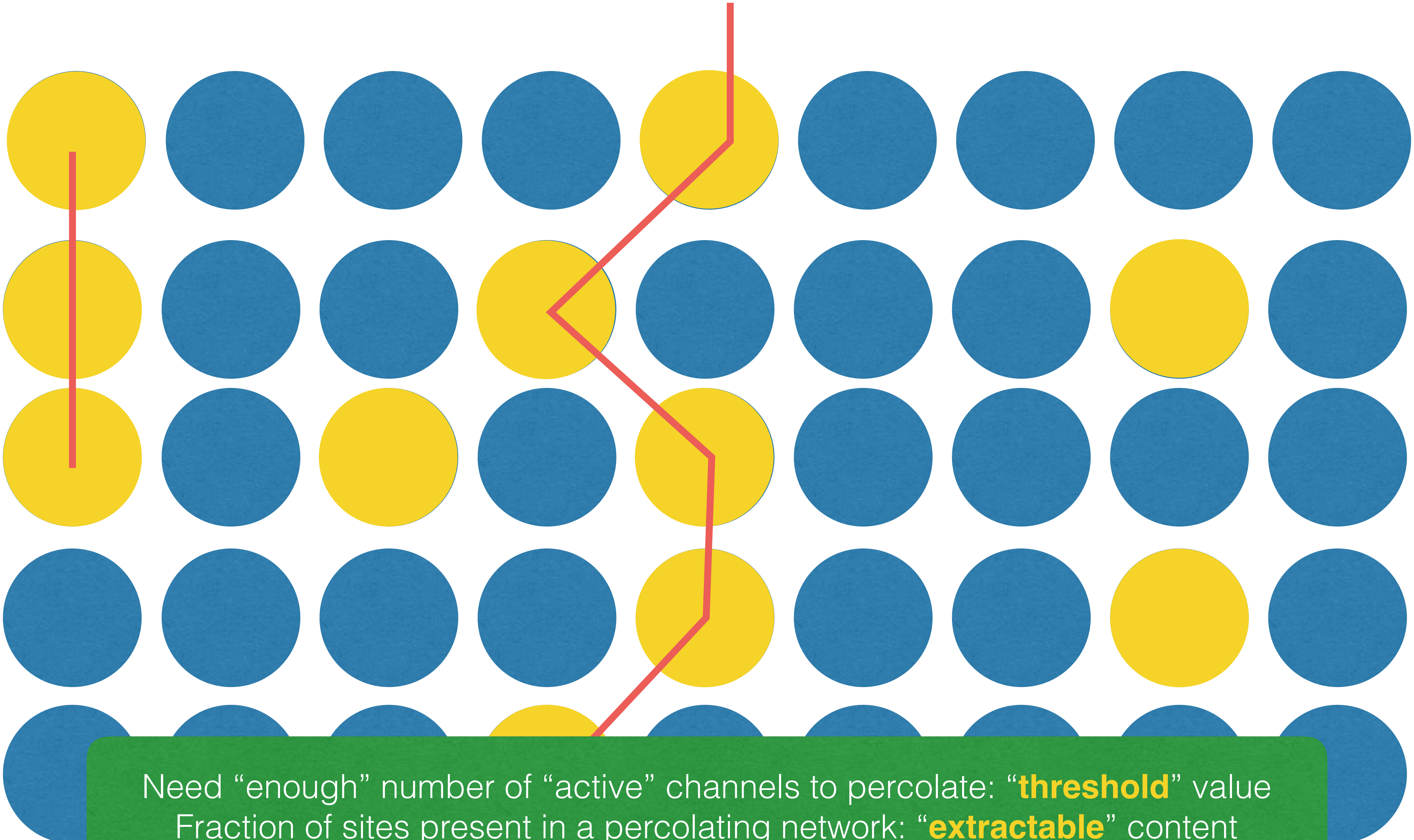
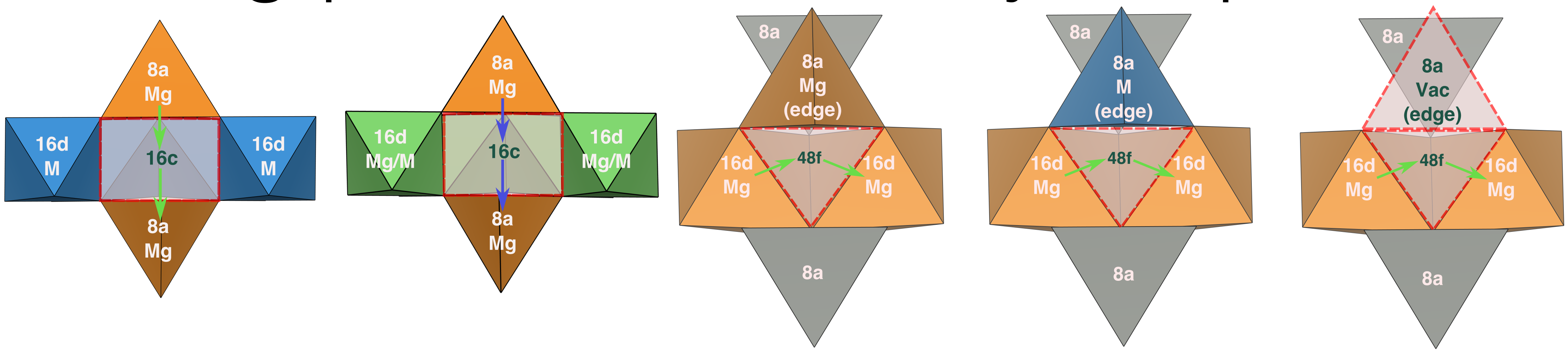


Need “enough” number of “active” channels to percolate: “**threshold**” value
Fraction of sites present in a percolating network: “**extractable**” content

Translating percolation theory to spinels

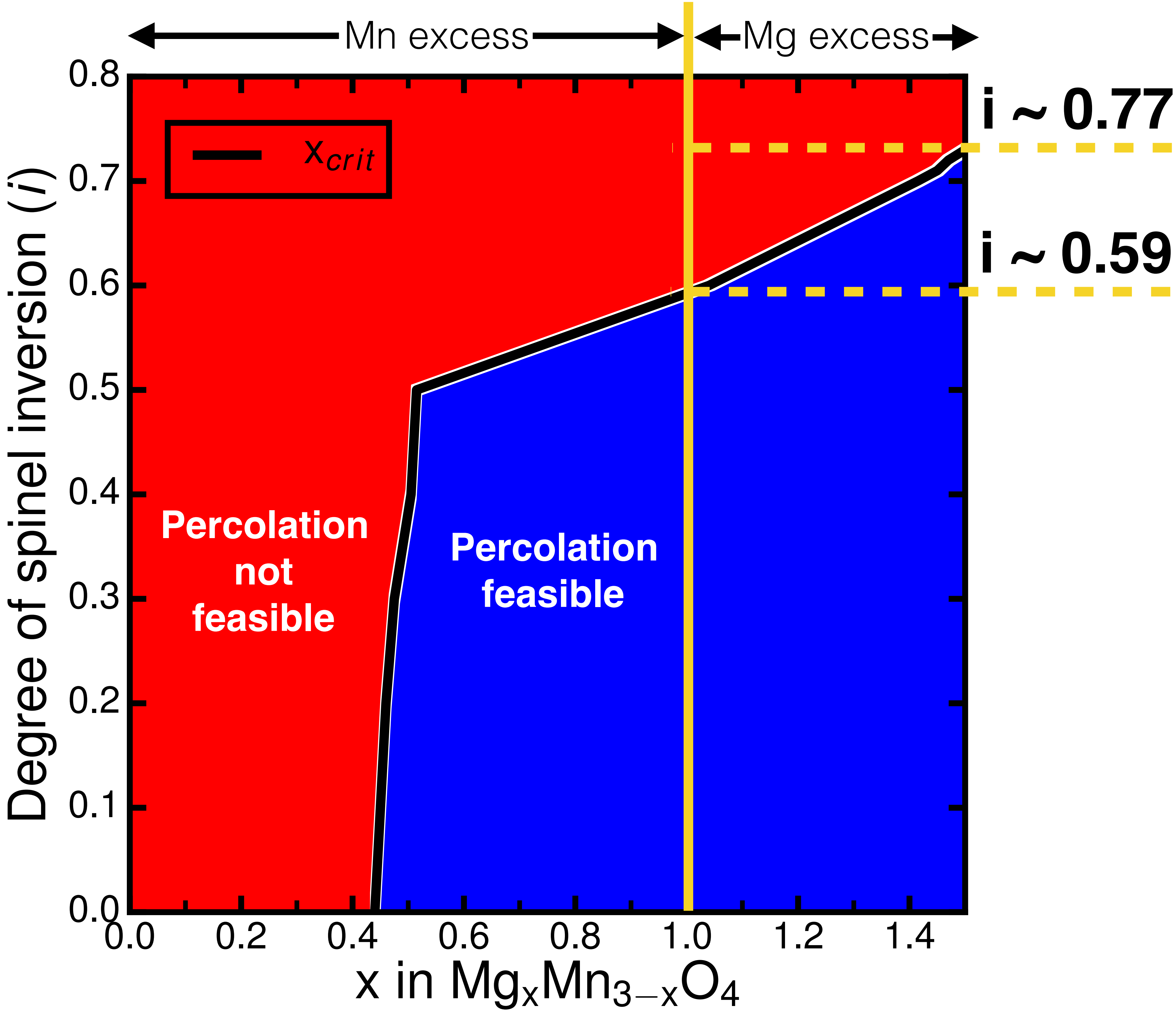


Hop	**1**	**2**	**3**	**4**	**5**
Topology	**tet-oct-tet**	**tet-oct-tet**	**oct-tet-oct**	**oct-tet-oct**	**oct-tet-oct**
Open under	Always open	Up to 4/6 Mg in ring	Corner 8a vacant	Closed	Always open

$MgMn_2O_4$: 750 meV

Perform Monte-Carlo simulations

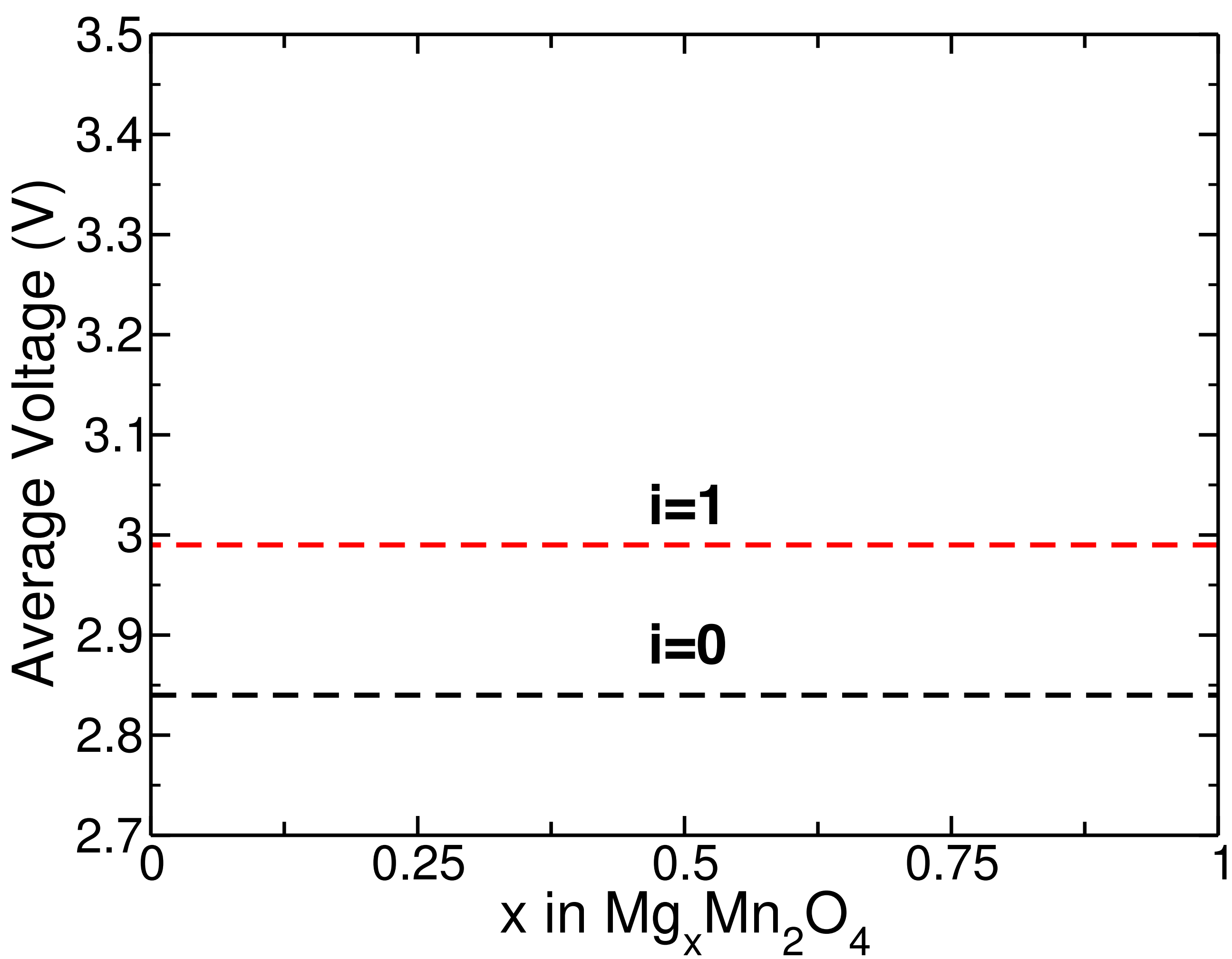
Stoichiometric $MgMn_2O_4$ should percolate up to ~59% inversion



Does inversion affect electrochemical properties?

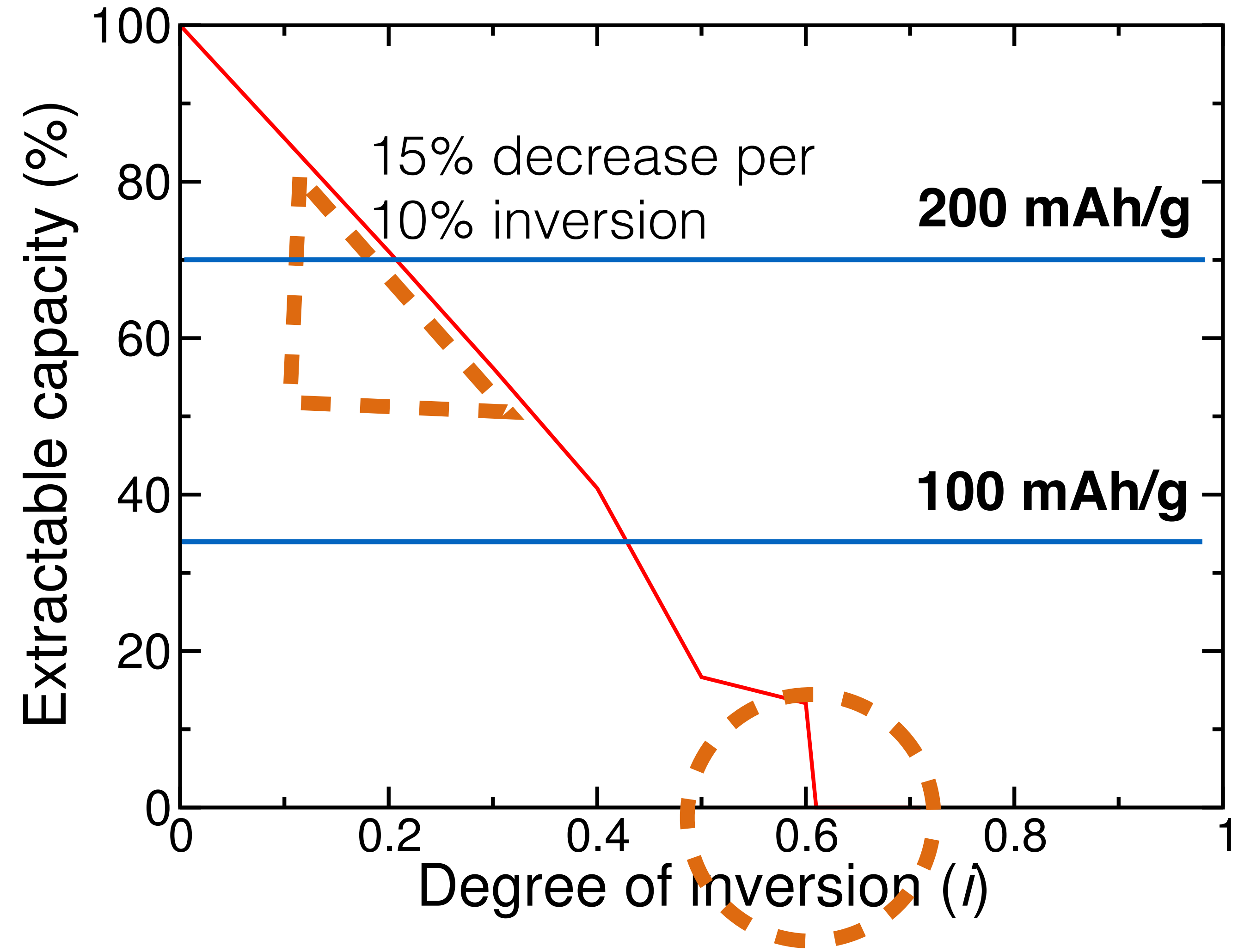
No inversion: 2.84 V

Fully inverted: 2.99 V



Inversion increases average voltage

Theoretical capacity for $MgMn_2O_4$: 270 mAh/g

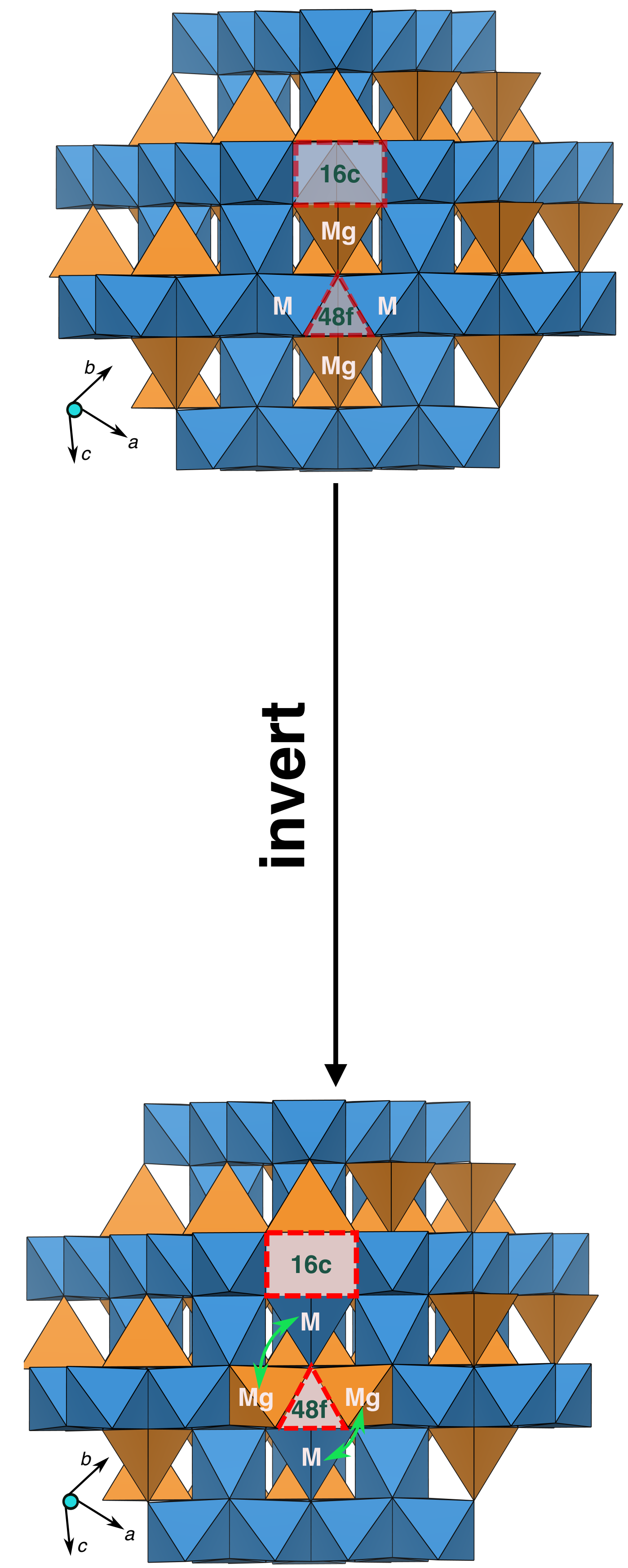


0 capacity at ~60% inversion

Inversion decreases extractable capacity significantly

Summary

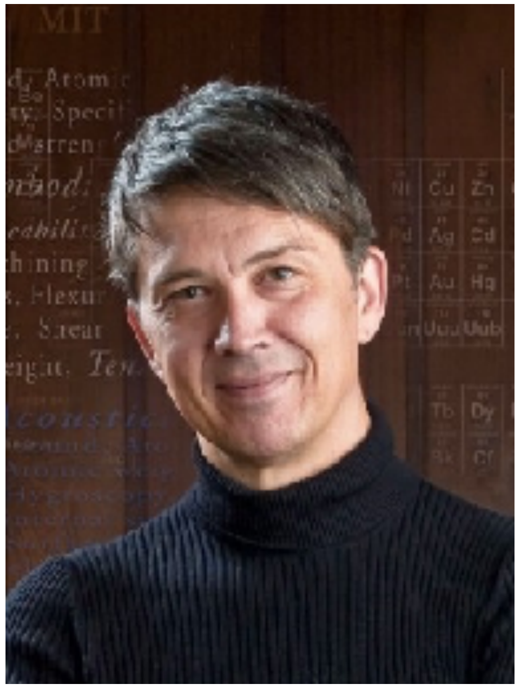
- $MgMn_2O_4$ (cathode) is susceptible to spinel inversion
- Several cation arrangements under inversion
- Inversion can open and close Mg diffusion channels
- Percolation simulations: stoichiometric $MgMn_2O_4$ should percolate Mg up to 59%
- Inversion raises the average voltage but detrimentally reduces extractable capacity

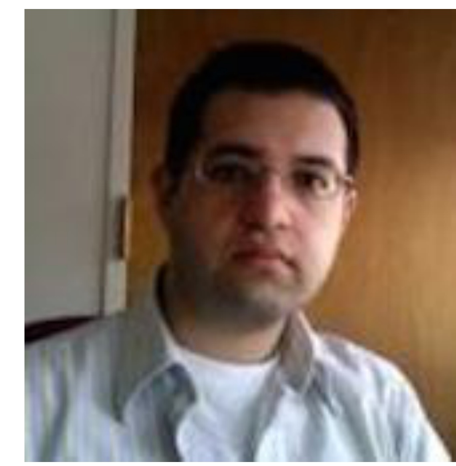


Conclusions

- Multivalent batteries have the potential to achieve high energy densities than current state-of-the-art Li-ion technology
  - But the development has been hindered by the **lack of energy-dense cathodes and efficient electrolytes**
- Cathode design challenge: design a high voltage, high capacity material with high Mg mobility
  - **Coordination preferences** can be a good guiding principle in finding fast diffusers
- Spinels are important in the Multivalent space, but may be prone to **inversion**
  - Spinels host Mg in an “un-preferred” tetrahedral environment
  - Inversion will affect both Mg mobility and electrochemical properties
- Develop more robust design rules/parameters to **identify frameworks with fast Mg mobility**
  - High-pressure, post-spinel phases hold the key?

Thanks!





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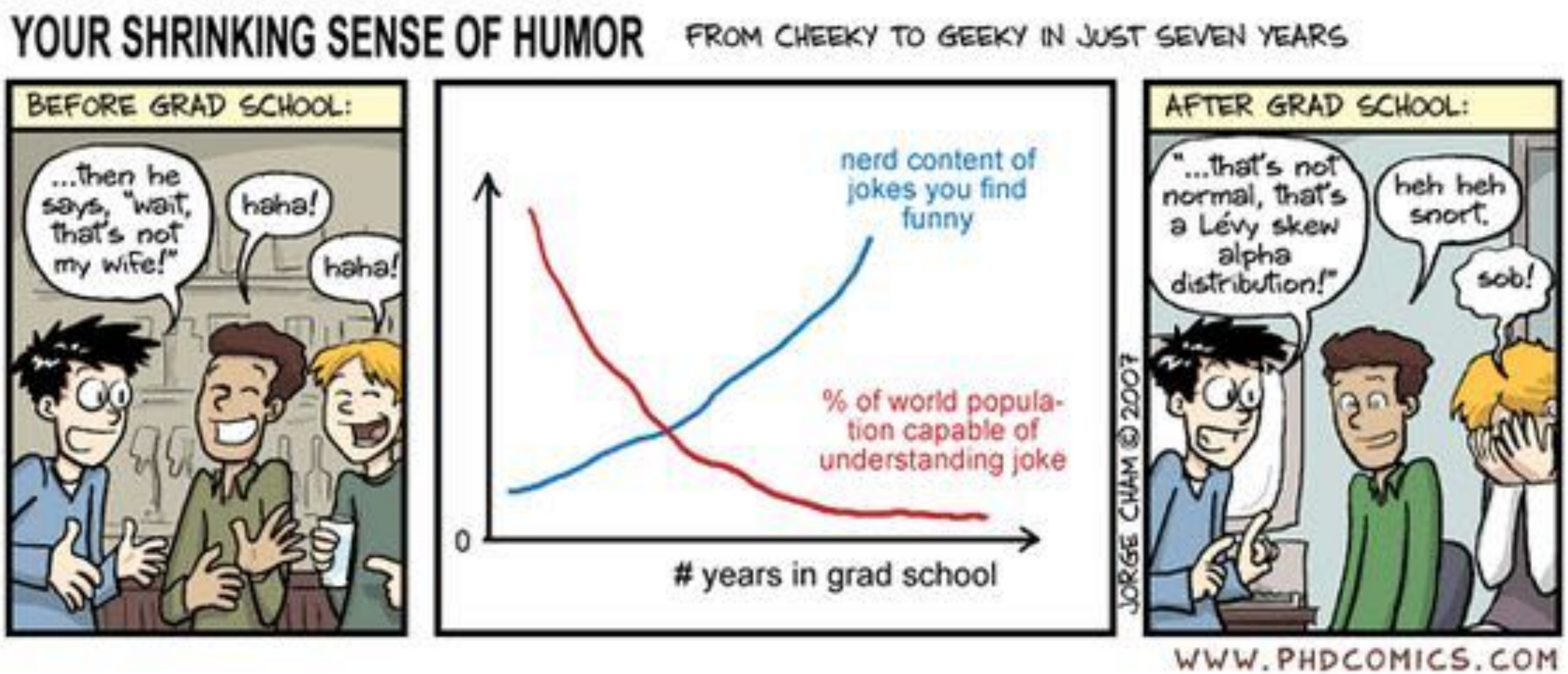
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