Solvent co-intercalation and mobility bottlenecks in Mg-intercalation cathodes

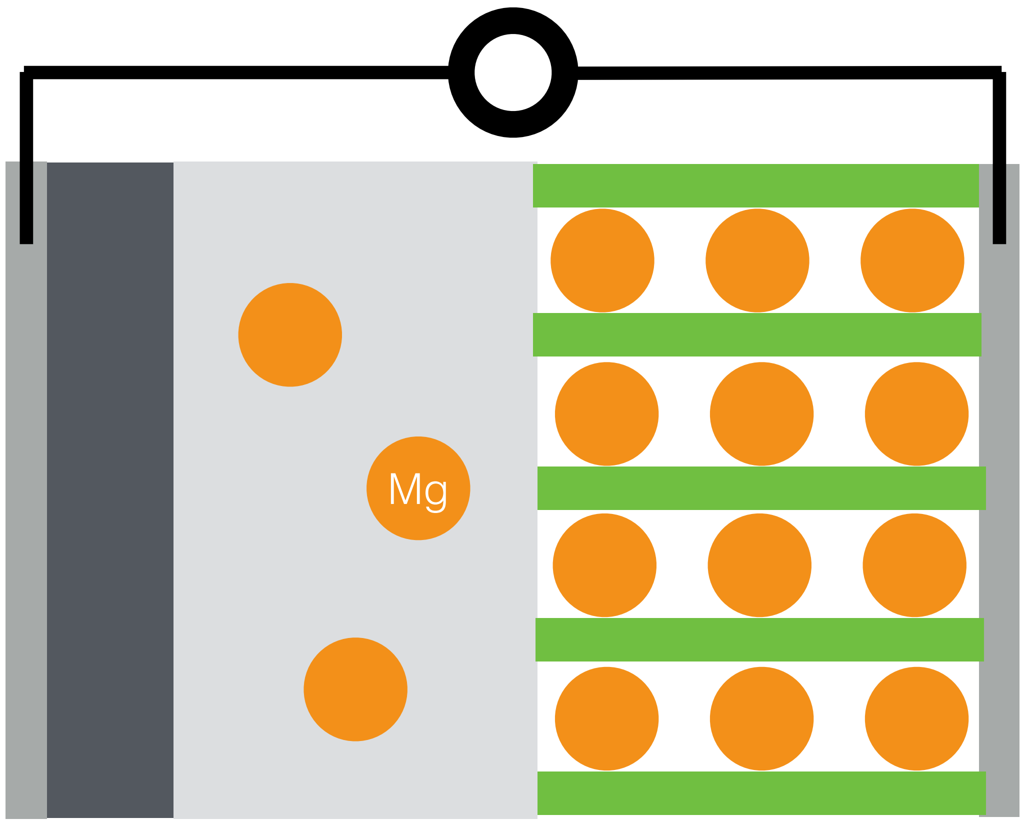
Sai Gautam Gopalakrishnan, Gerbrand Ceder

gautam91@mit.edu
gautam91@lbl.gov

ECS Prime 2016, Honolulu, HI
October 4, 2016
Slides available at http://ceder.berkeley.edu

Cathode design is critical to Mg (or multivalent) batteries

- Why Mg (or Multi-valent, MV)?
  - Next generation of electric devices will benefit from higher energy density storage systems
  - Superior volumetric capacity for Mg metal as anode (~3833 mAh/cm^3) vs. Li metal (~2046) or Li in graphite (~800)



- New chemistry: Cathode design challenge
  - High Voltage, High Capacity, High Mobility
- Possible oxide cathodes?
  - Sulfides are good: Mo_3S_4[1], Ti_2S_4[2]
  - V_2O_5 and MoO_3 have shown reversible Mg intercalation[3]
    - V- and Mo-based oxides possess multiple polymorphs: potential cathode space

1. Aurbach *et al.*, Nature, 2000
2. Sun *et al.*, Energy Environ. Sci., 2016

3. Gershinsky *et al.*, Langmuir, 2013

Solvent co-intercalation:
Mg in Xerogel V_2O_5

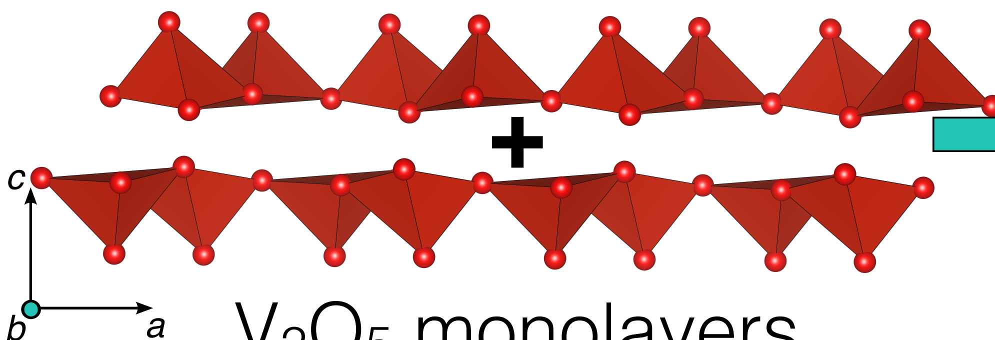
G. S. Gautam, P. Canepa, W. D. Richards, R. Malik and G. Ceder,
"Role of structural H_2O in intercalation electrodes: the case of Mg in nano crystalline Xerogel-V_2O_5",
Nano Lett. 16, **2016**, 2426-2431

Xerogel-V_2O_5 is a hydrated structure

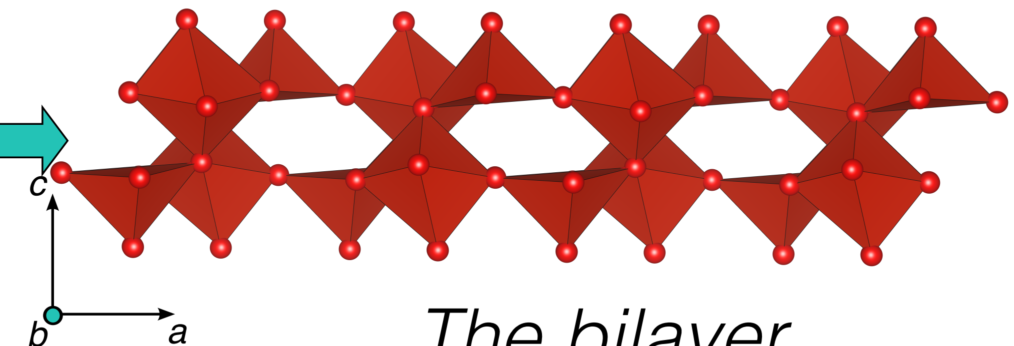
Does H_2O "shuttle" with Mg?

Hydrated version of V_2O_5
Better *mobility* of Mg
Possesses a "bilayer" structure

Xerogel —573 K, $-H_2O$→ Orthorhombic

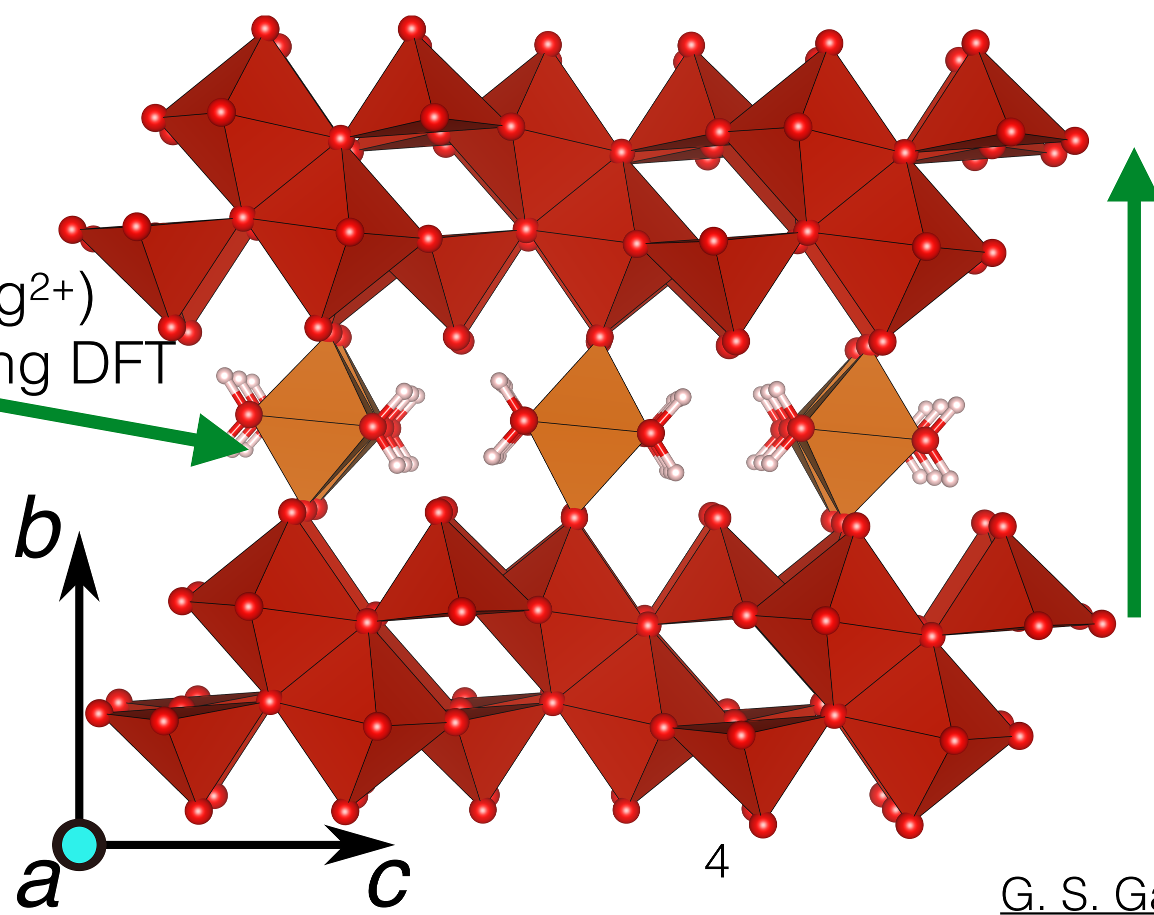


V_2O_5 monolayers



The bilayer

H_2O + Intercalant ion (Mg^{2+})
H-positions resolved using DFT



Large inter-bilayer spacing
~10-13Å

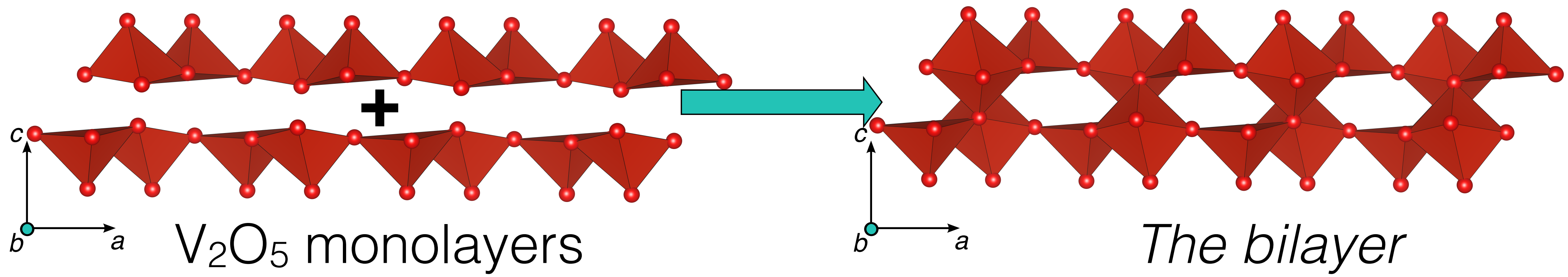
G. S. Gautam *et al.*, **Nano Lett.** 16, **2016**, 2426-2431

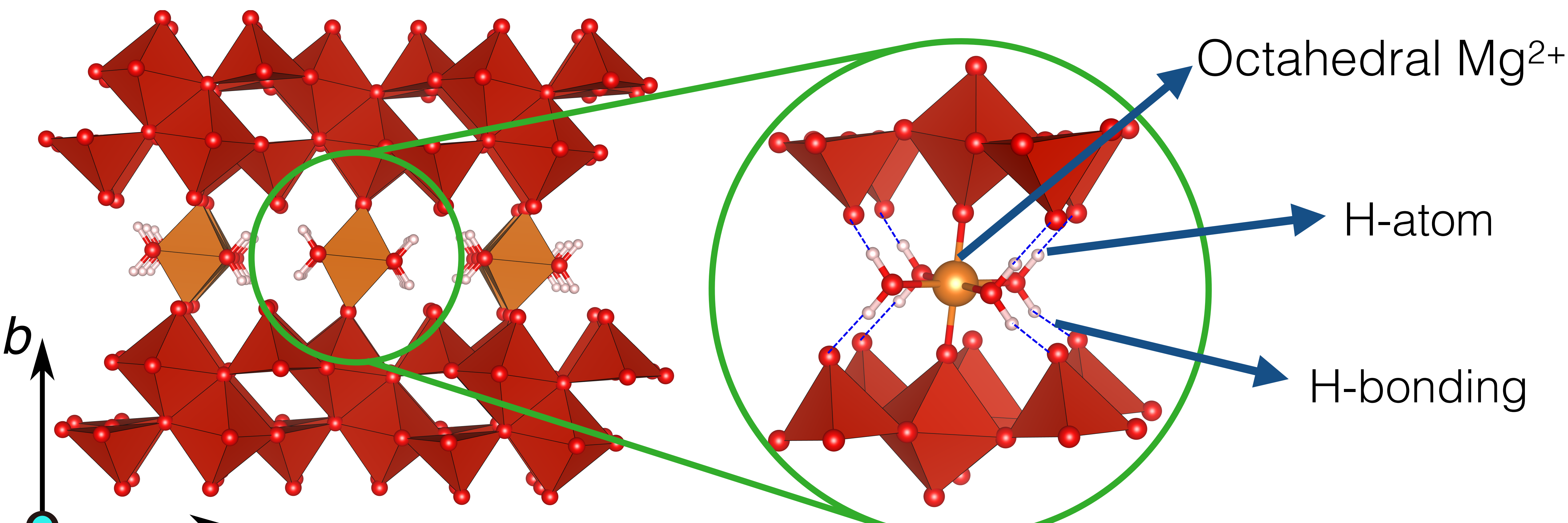
Xerogel-V_2O_5 is a hydrated structure

Does H_2O "shuttle" with Mg?

Hydrated version of V_2O_5
Better *mobility* of Mg
Possesses a "bilayer" structure

Xerogel $\xrightarrow[-H_2O]{573\ K}$ Orthorhombic





G. S. Gautam *et al.*, **Nano Lett.** 16, **2016**, 2426-2431

Methods detour: how do we calculate grand-potential phase diagrams?

Grand-potential phase diagrams are used to study open systems

$$\Phi = G_{\mathrm{MgV_2O_5 \cdot \mathit{n}H_2O}} - n_{\mathrm{H_2O}} \cdot \mu_{\mathrm{H_2O}}$$

Grand-potential (Φ)
Governing thermodynamic potential
Minimize this to get stable phases

Gibbs energy (*G*)
Xerogel Mg-V_2O_5 with H_2O
Computed with DFT

Number of moles of H_2O (*n*)
In a given Xerogel structure

Chemical potential of H_2O (*μ*)
External to the Xerogel (electrolyte)
Can be expressed in activities

$$\mu_{\mathrm{H_2O}} = \mu^0_{\mathrm{H_2O}} - RT \ln a_{\mathrm{H_2O}}$$

Computed with DFT (Vapor)
Corrected with experimental values

Set manually based on wet, dry and superdry conditions

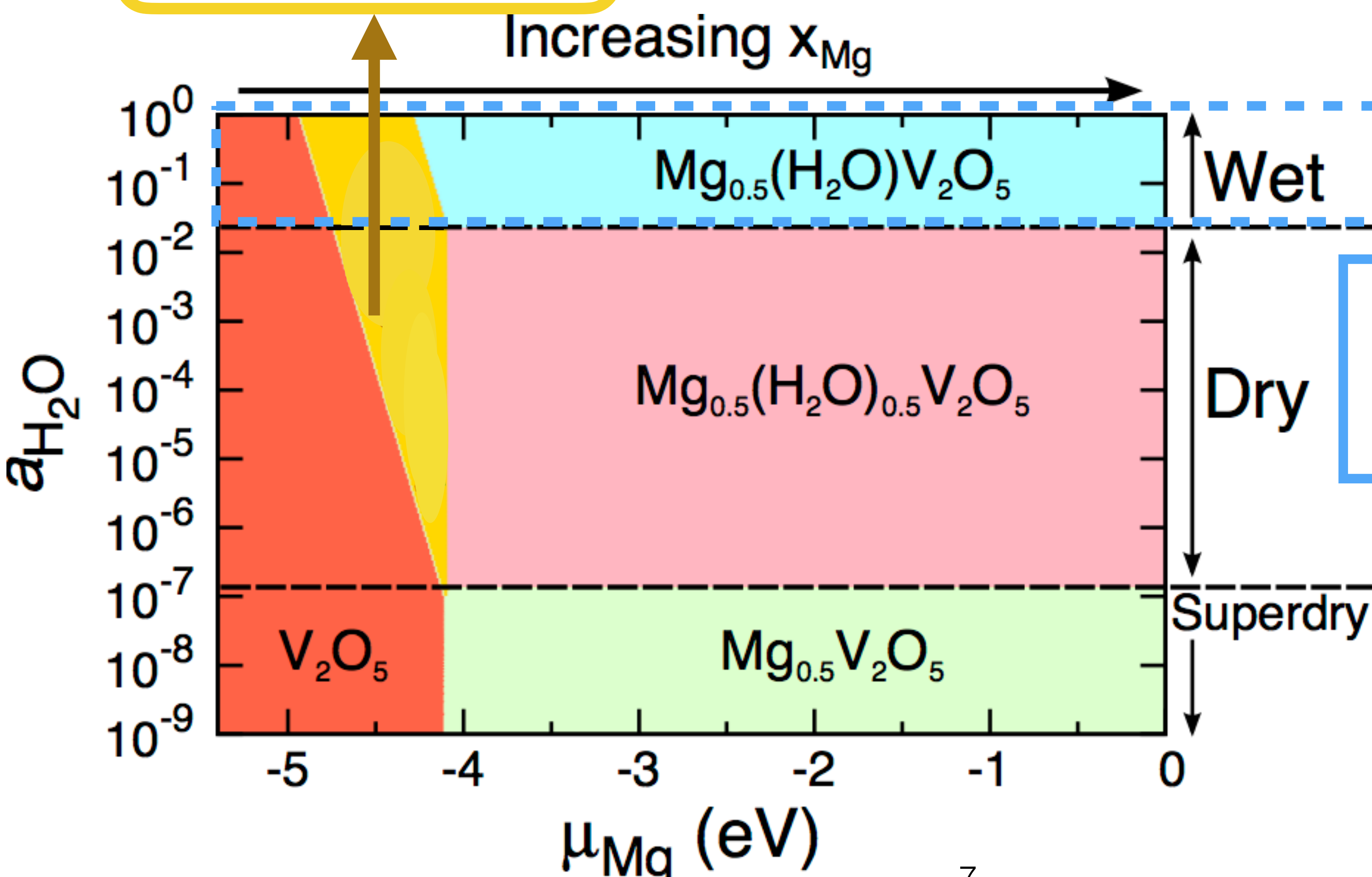
Grand-potential phase diagram

Electrolyte-dependent H_2O shuttling

$$\Phi = G_{\mathrm{MgV_2O_5} \cdot n\mathrm{H_2O}} - n_{\mathrm{H_2O}} \cdot \mu_{\mathrm{H_2O}} - x_{\mathrm{Mg}} \cdot \mu_{\mathrm{Mg}}$$

Activity **Voltage**

$Mg_{0.25}(H_2O)_{0.5}V_2O_5$



H_2O content changes with Mg content

H_2O shuttles with Mg

G. S. Gautam *et al.*, **Nano Lett.** 16**, 2016**, 2426-2431

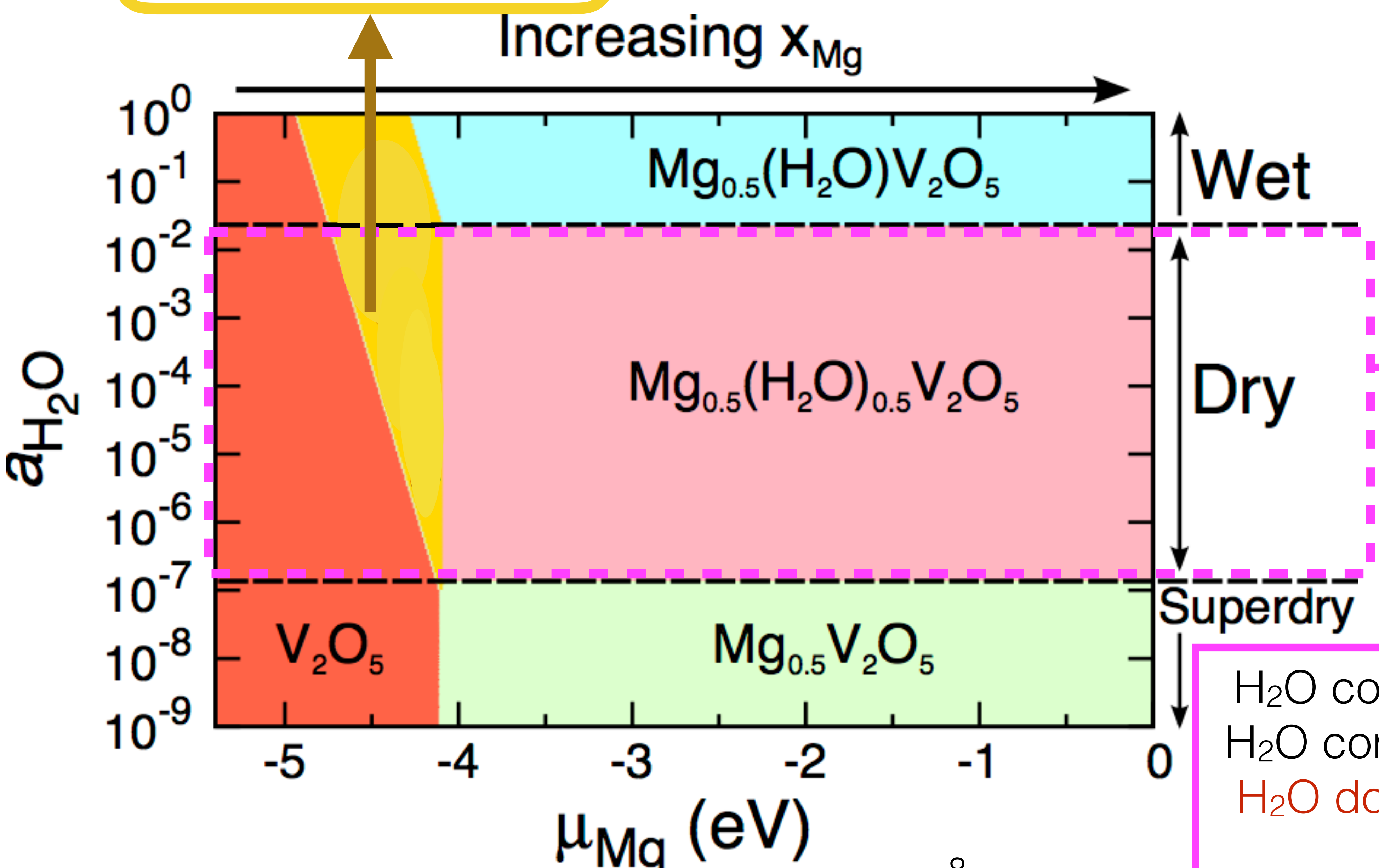
Grand-potential phase diagram

Electrolyte-dependent H_2O shuttling

$$\Phi = G_{\mathrm{MgV_2O_5 \cdot} n\mathrm{H_2O}} - n_{\mathrm{H_2O}} \cdot \mu_{\mathrm{H_2O}} - x_{\mathrm{Mg}} \cdot \mu_{\mathrm{Mg}}$$

Activity **Voltage**

$Mg_{0.25}(H_2O)_{0.5}V_2O_5$



H_2O content changes at low x_{Mg}
H_2O content constant at high x_{Mg}
H_2O does not shuttle with Mg at high x_{Mg}

G. S. Gautam *et al.*, **Nano Lett.** 16, **2016**, 2426-2431

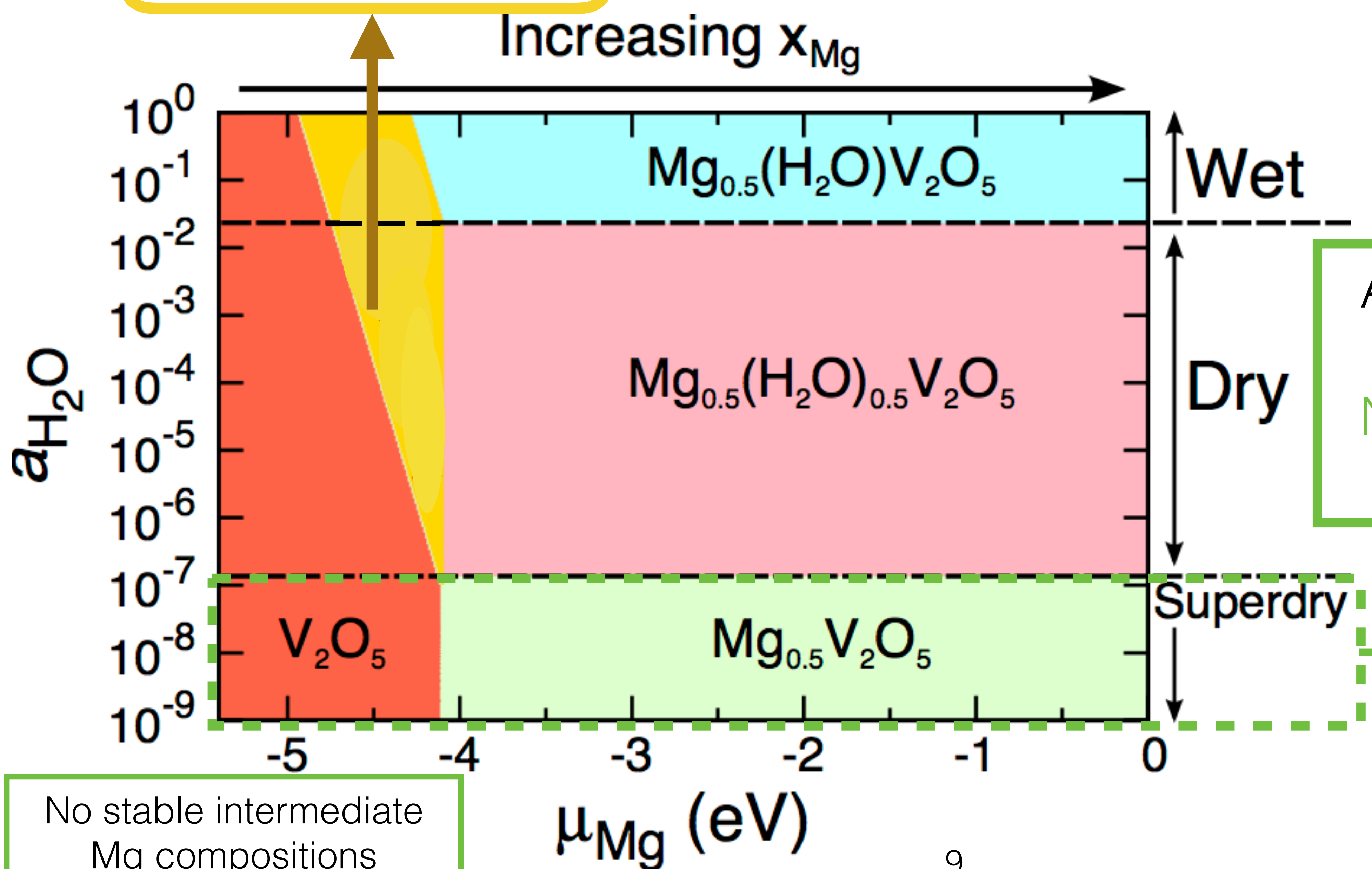
Grand-potential phase diagram

Electrolyte-dependent H_2O shuttling

$$\Phi = G_{\mathrm{MgV_2O_5 \cdot nH_2O}} - n_{\mathrm{H_2O}} \cdot \mu_{\mathrm{H_2O}} - x_{\mathrm{Mg}} \cdot \mu_{\mathrm{Mg}}$$

Activity **Voltage**

$Mg_{0.25}(H_2O)_{0.5}V_2O_5$



All H_2O exits from the Xerogel structure
No H_2O shuttling with Mg

No stable intermediate Mg compositions

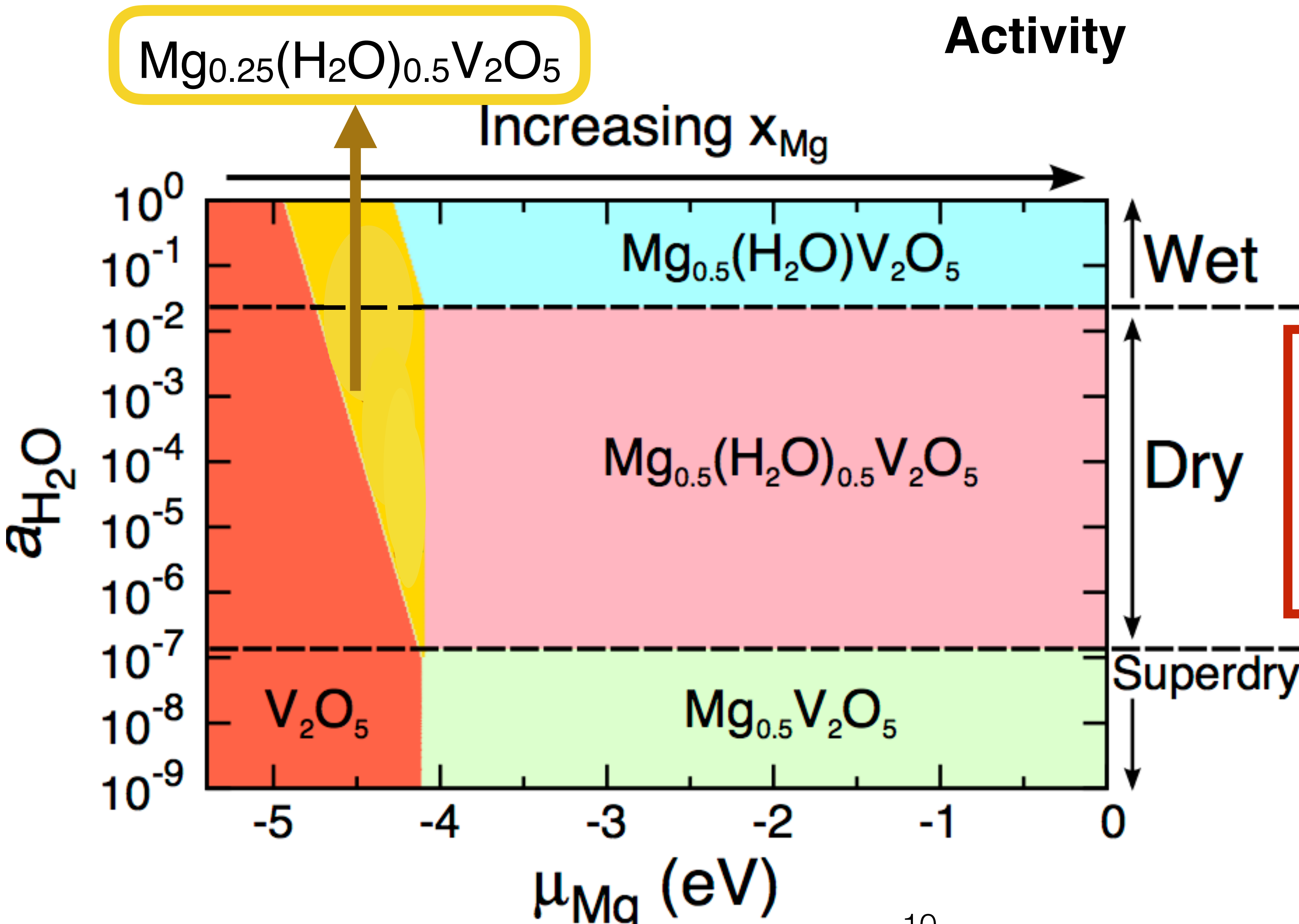
G. S. Gautam *et al.*, **Nano Lett.** 16**, 2016**, 2426-2431

Grand-potential phase diagram

Electrolyte-dependent H_2O shuttling

$$\Phi = G_{\mathrm{MgV_2O_5} \cdot n\mathrm{H_2O}} - n_{\mathrm{H_2O}} \cdot \mu_{\mathrm{H_2O}} - x_{\mathrm{Mg}} \cdot \mu_{\mathrm{Mg}}$$

Activity **Voltage**

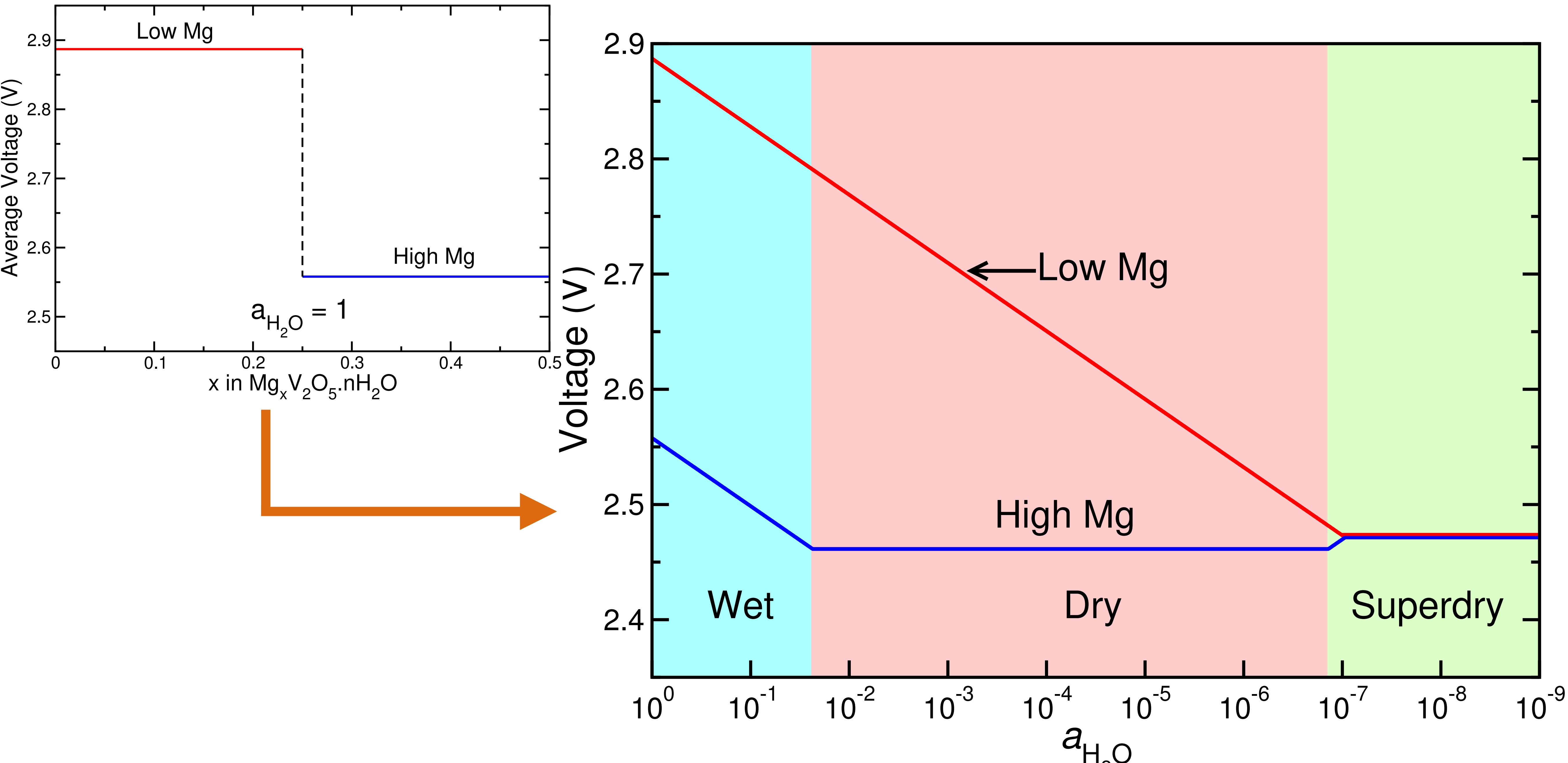


Water+Mg co-intercalation depends on electrolyte conditions

G. S. Gautam *et al.*, **Nano Lett.** 16**, 2016**, 2426-2431

Voltage vs. Water content

Electrolyte-dependent voltages could be important



G. S. Gautam *et al.*, **Nano Lett.** 16, **2016**, 2426-2431

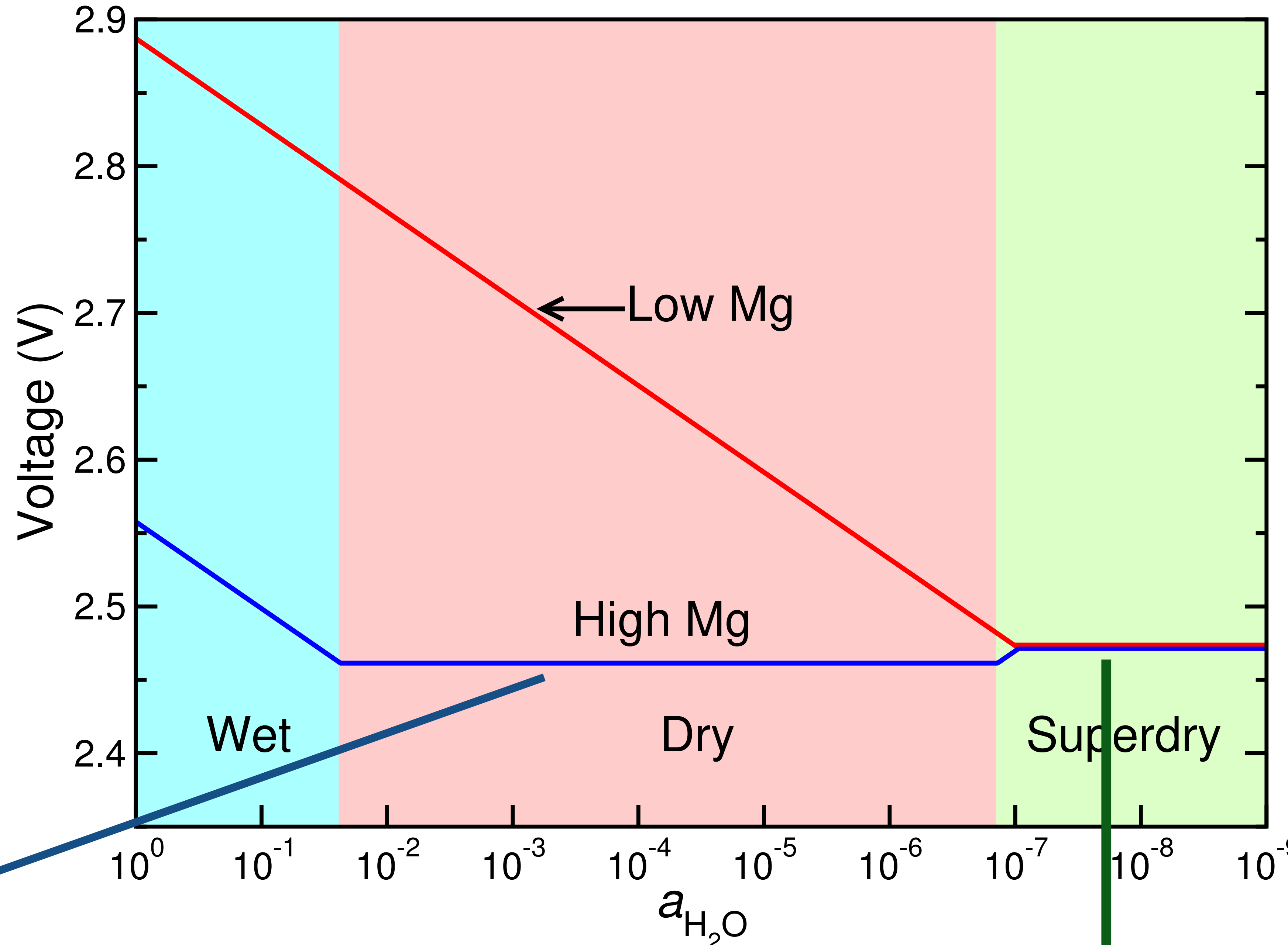
Voltage vs. Water content

Electrolyte-dependent voltages could be important

Normally, V $\propto(-\nabla\mu_{Mg})$

When H_2O co-intercalates with Mg, V $\propto(-\nabla\mu_{Mg},-\nabla\mu_{H_2O})$

Voltage in wet > dry



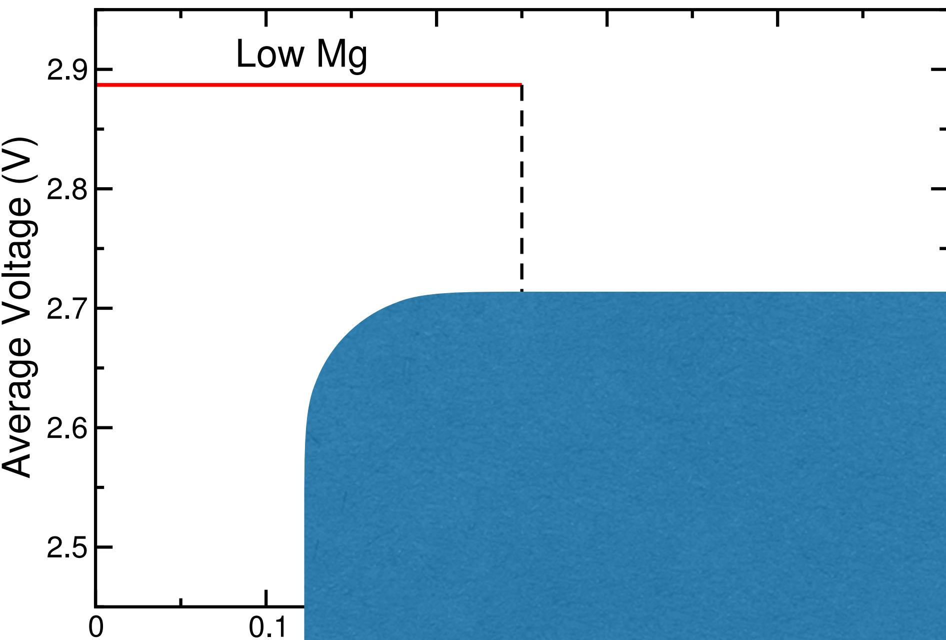
No water shuttling with Mg

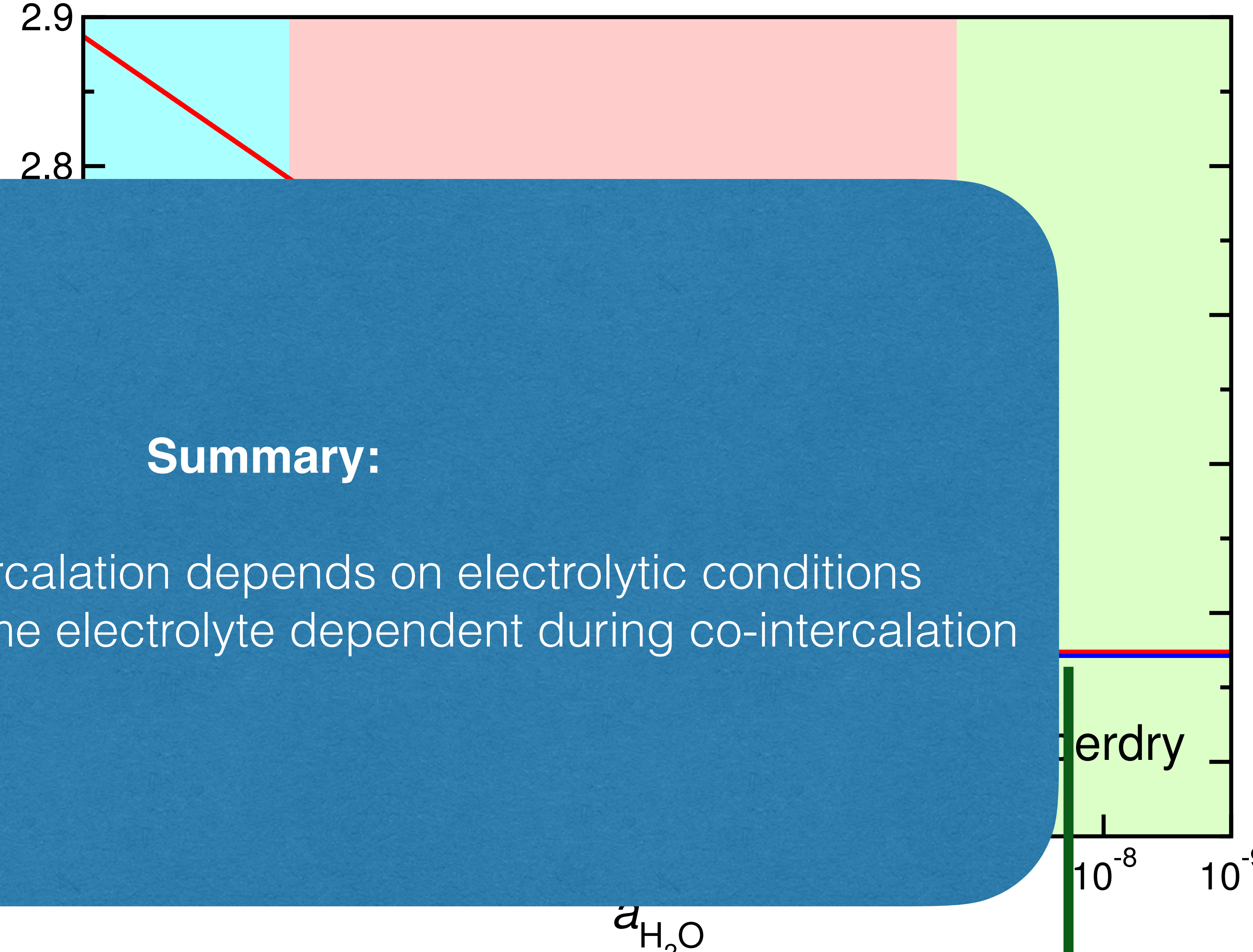
No stable intermediate Mg compositions

G. S. Gautam *et al.*, **Nano Lett.** 16, **2016**, 2426-2431

Voltage vs. Water content

Electrolyte-dependent voltages could be important





Summary:

1. Solvent co-intercalation depends on electrolytic conditions
2. Voltages can become electrolyte dependent during co-intercalation

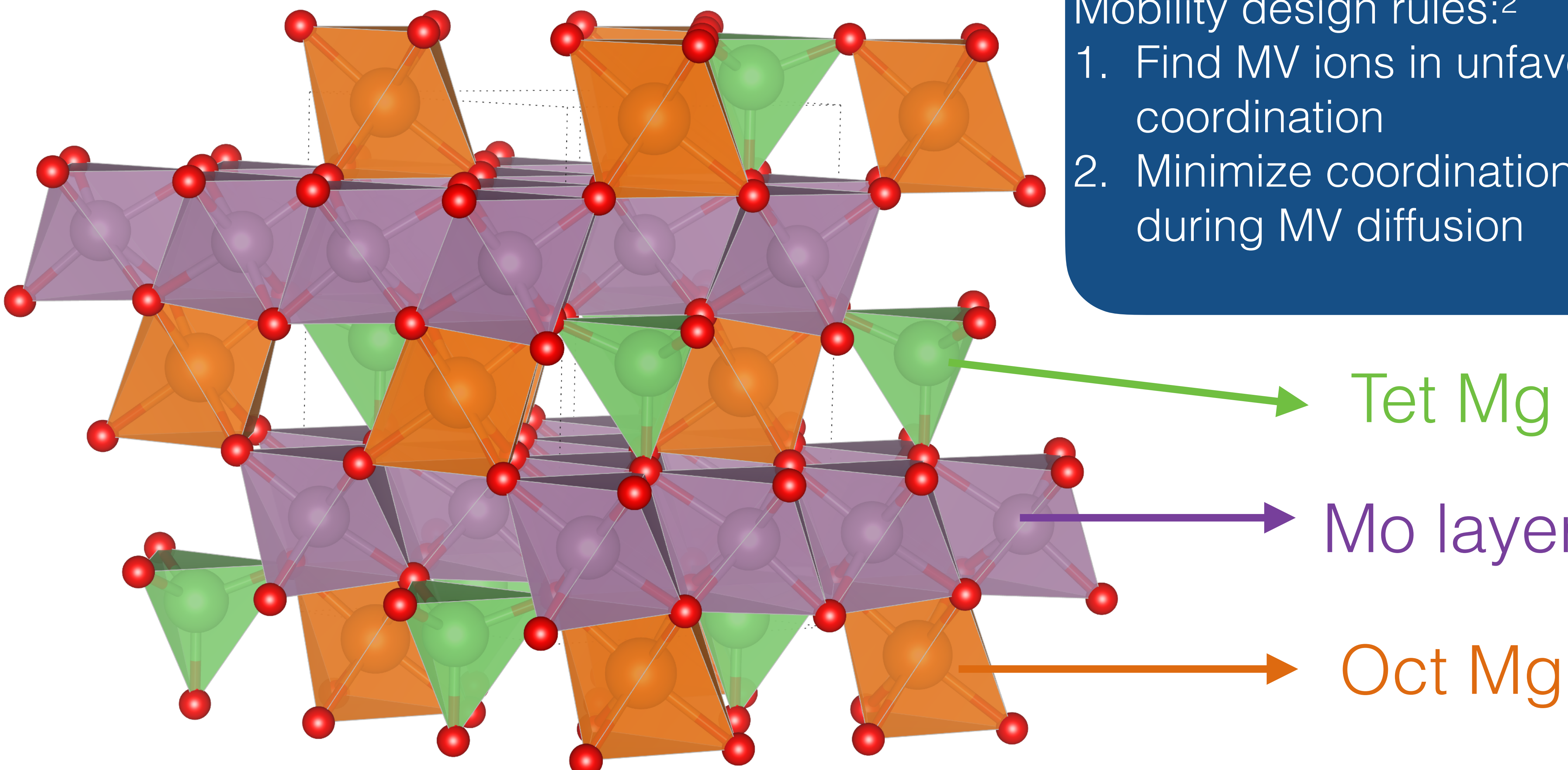
No water shuttling with Mg

No stable intermediate Mg compositions

Mobility bottlenecks:
Mg (de)intercalation in $Mg_2Mo_3O_8$

G. S. Gautam, X.Sun, V. Duffort, L.F. Nazar and G. Ceder,
“Impact of intermediate sites on bulk diffusion barriers: Mg intercalation in $Mg_2Mo_3O_8$”, **submitted**

Mo_3O_8: Layered structure
Mg found in tet and oct sites



$Mg_2Mo_3O_8$

Mobility design rules:[2]

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

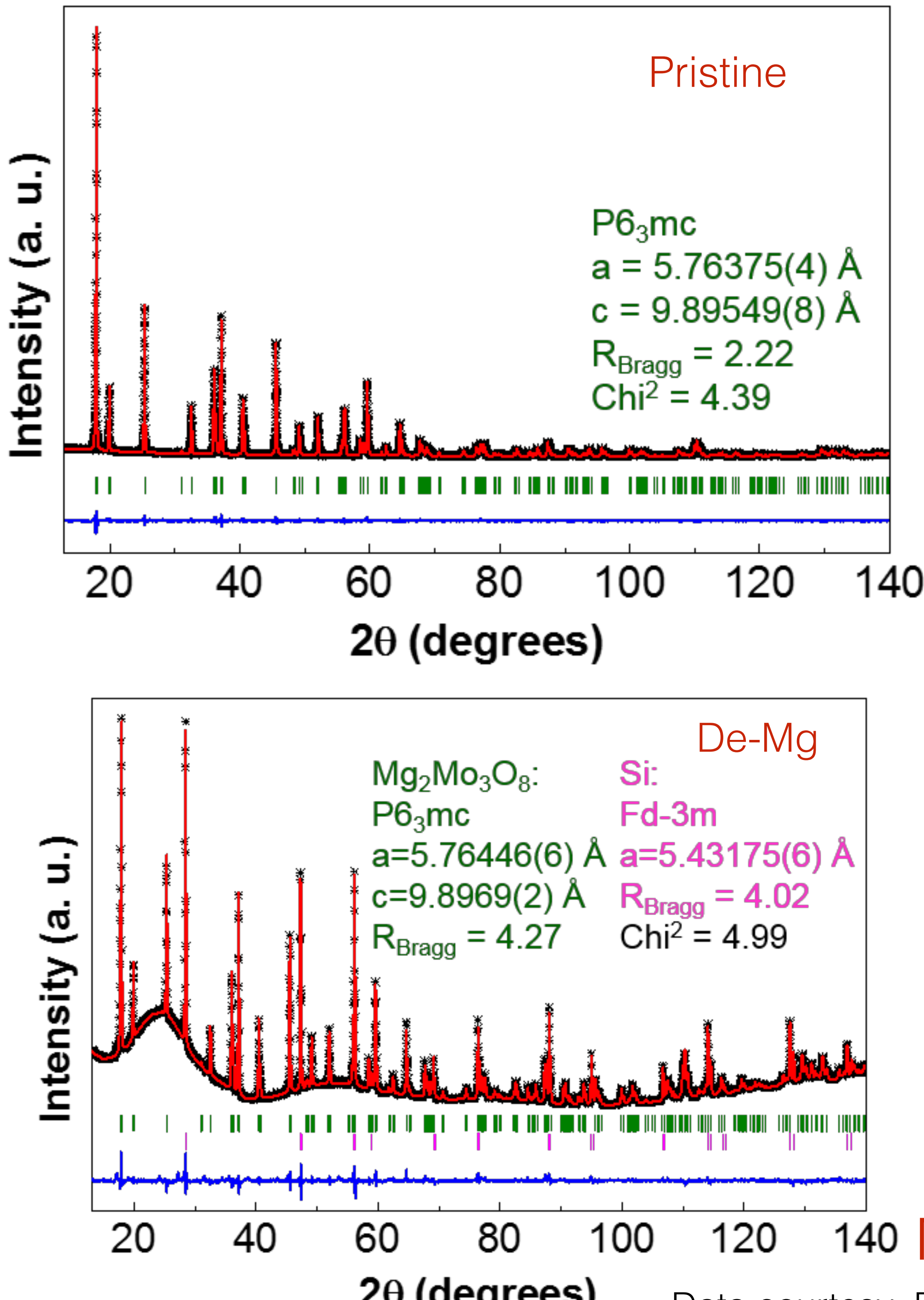
Li can be (de)intercalated from $Li_4Mo_3O_8$
(US Patent 6,908,710)

Can Mg be cycled?

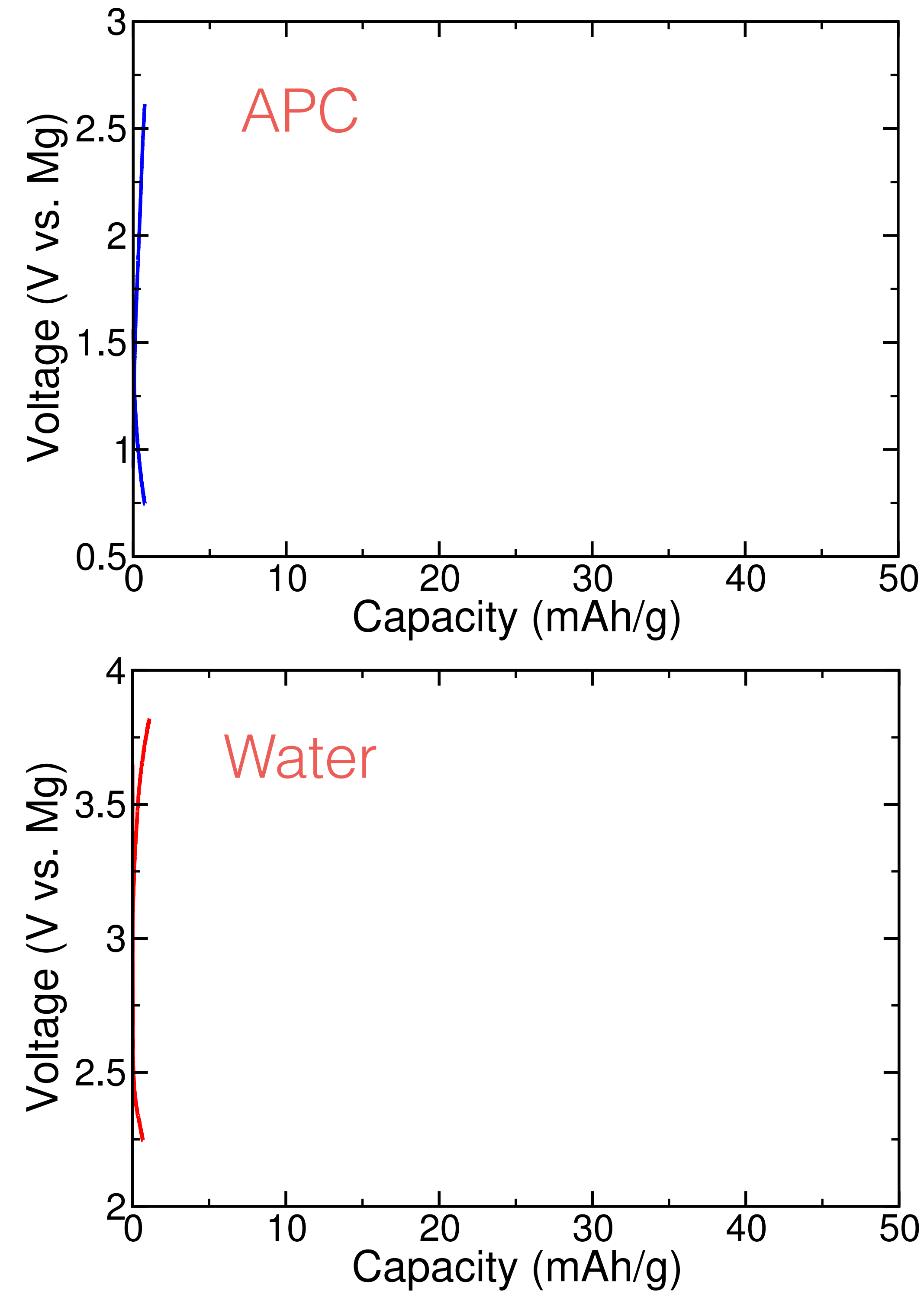
2. Rong *et al.*, Chem. Mater. 2015
G. S. Gautam, *et al.*, **submitted**

Electrochemical experiments show no activity

Chemical demagnesiation possible with NO_2BF_4



No significant capacity with aqueous/non-aqueous systems

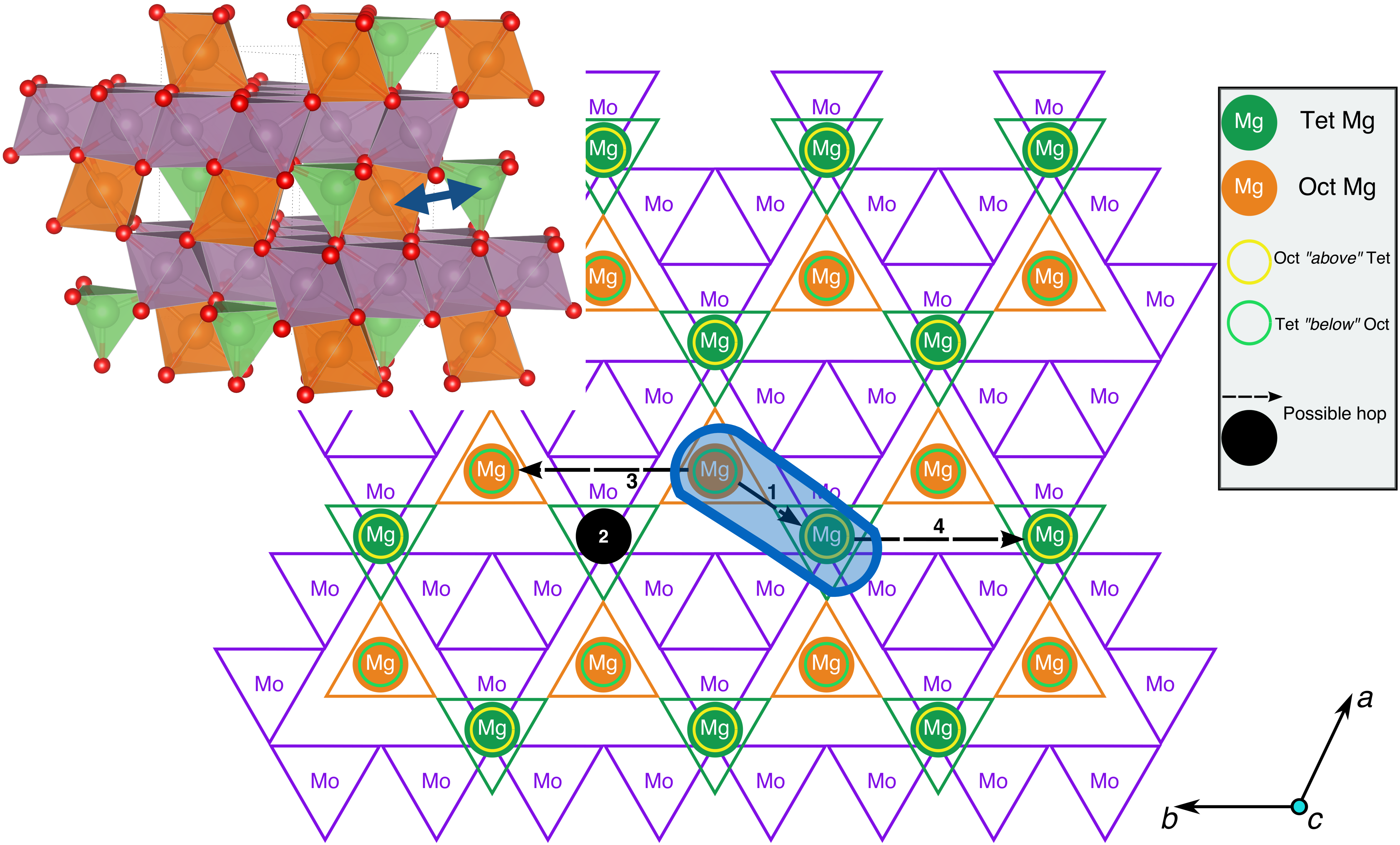


Mg extraction limited by high migration barriers?

Data courtesy: Prof. Nazar's group, University of Waterloo G. S. Gautam, *et al.*, **submitted**

Multiple Mg hops possible

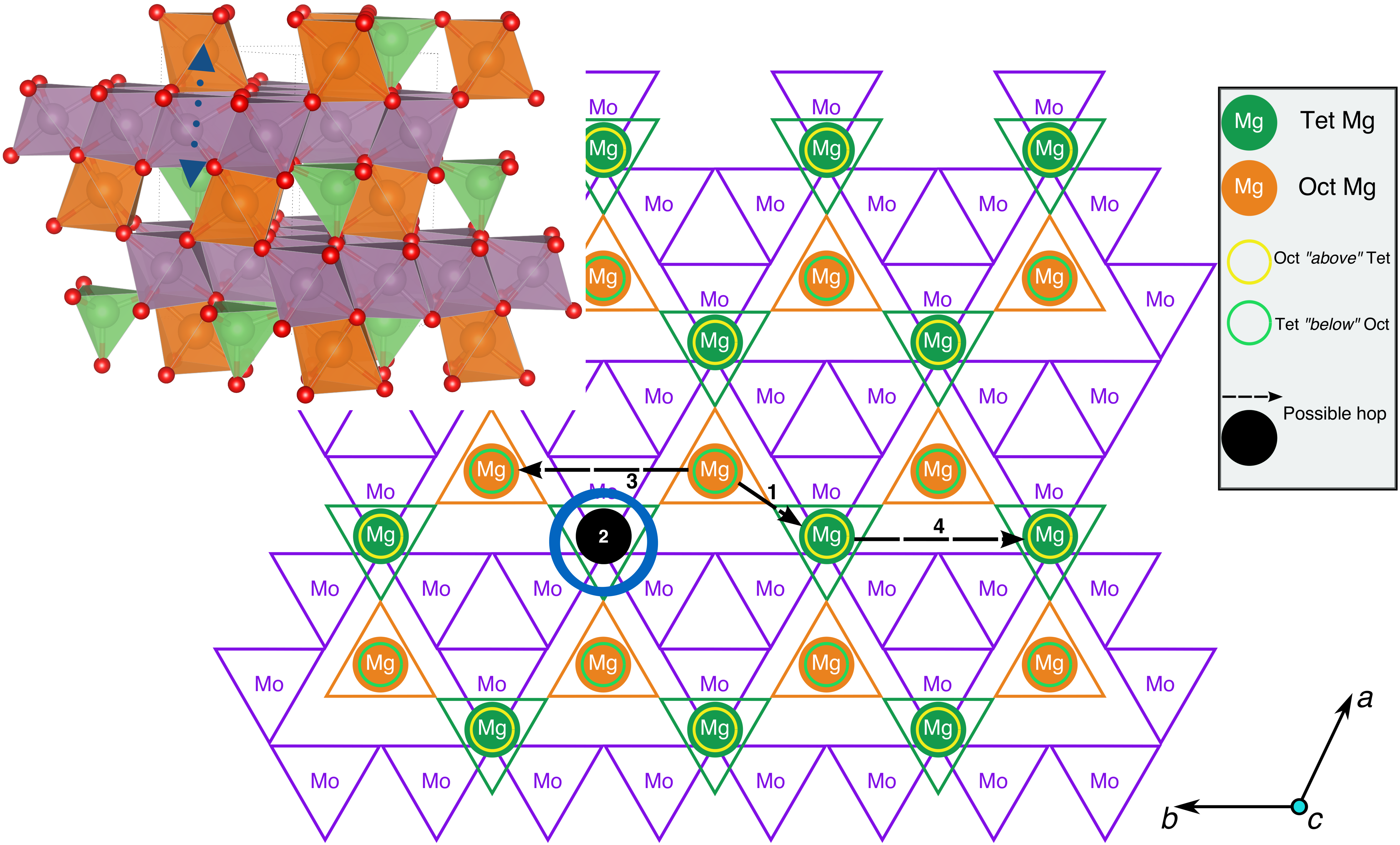
Hops 1 and 2 are relevant



G. S. Gautam, *et al.*, **submitted**

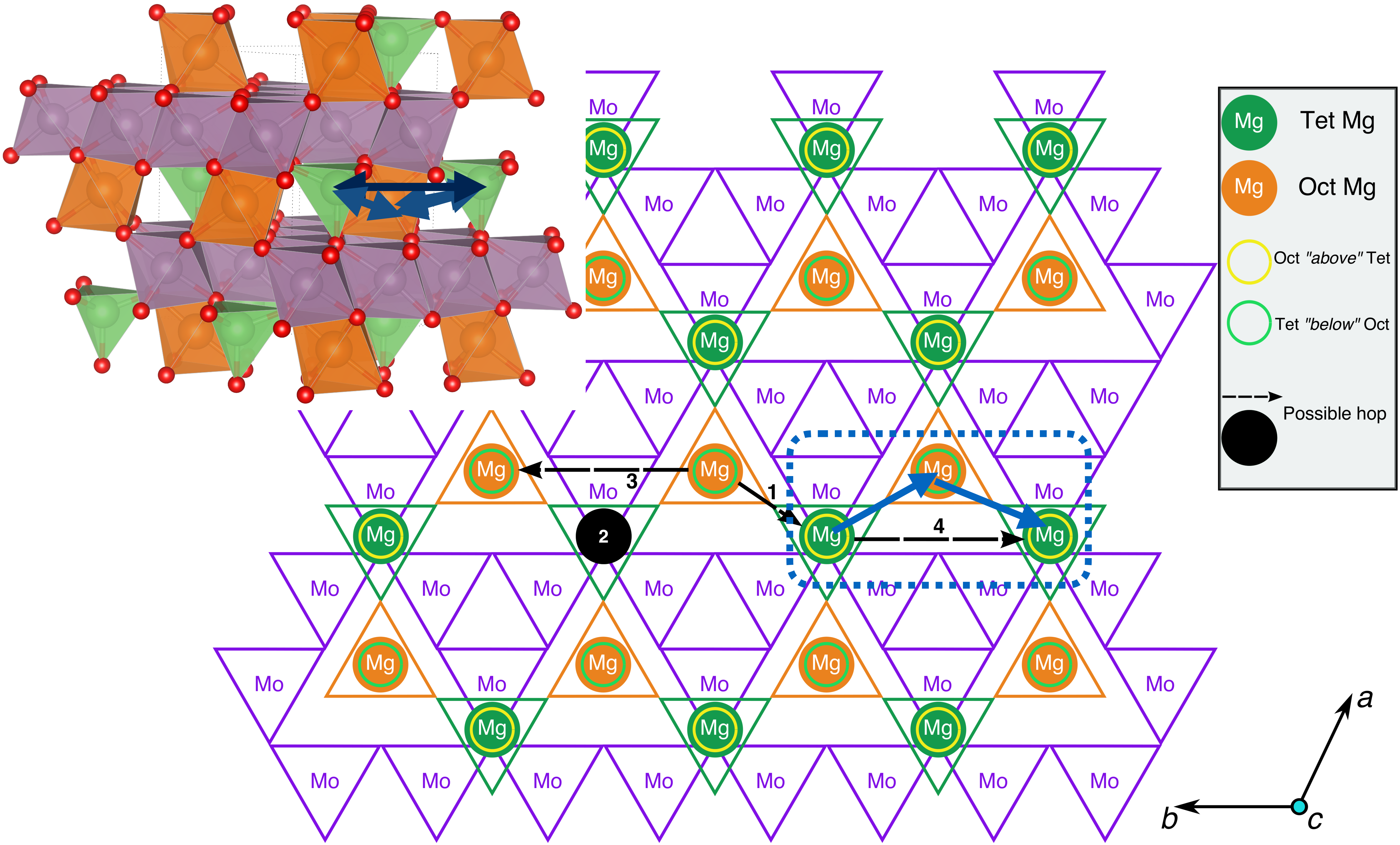
Multiple Mg hops possible

Hops 1 and 2 are relevant



Multiple Mg hops possible

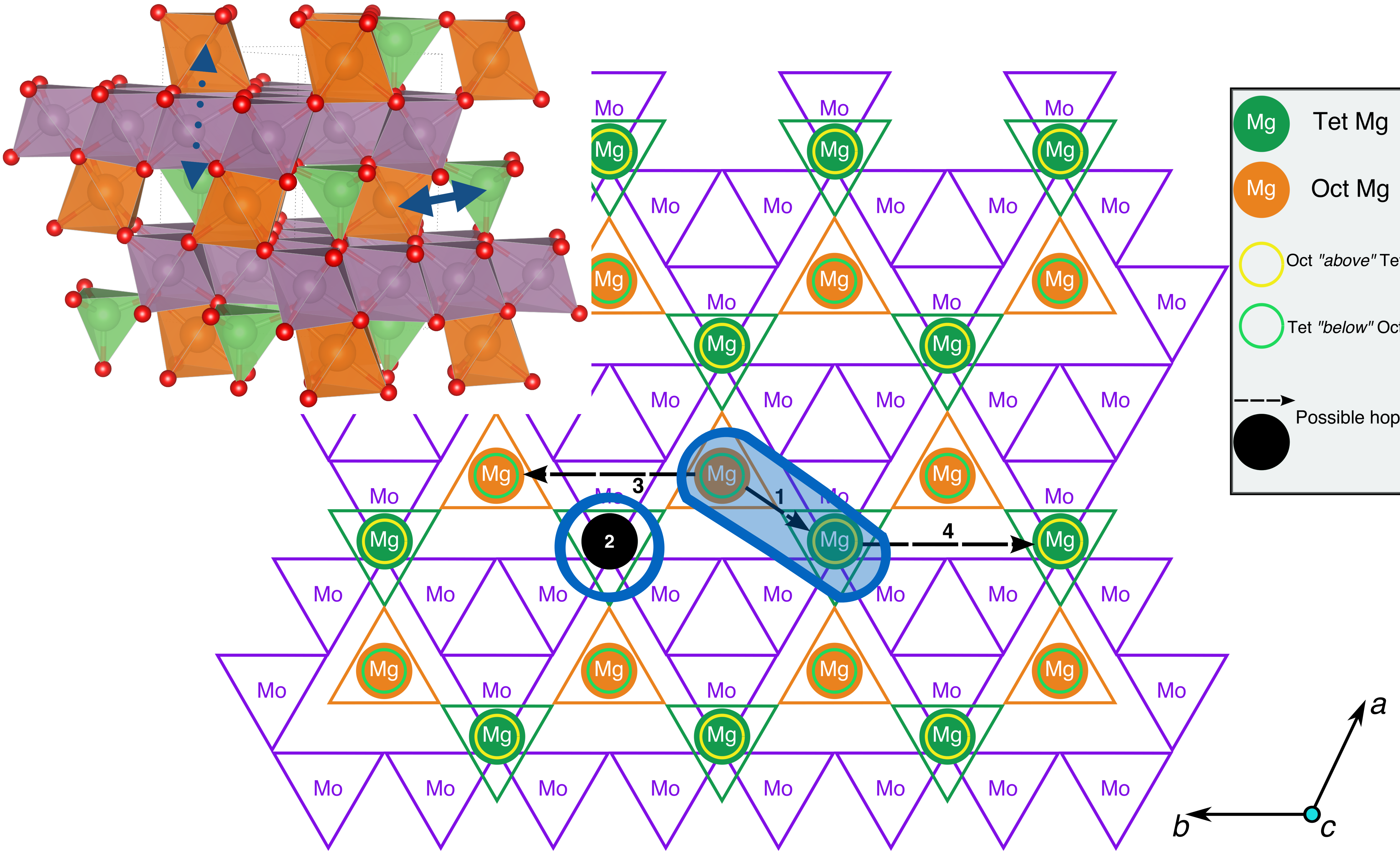
Hops 1 and 2 are relevant



G. S. Gautam, *et al.*, **submitted**

Multiple Mg hops possible

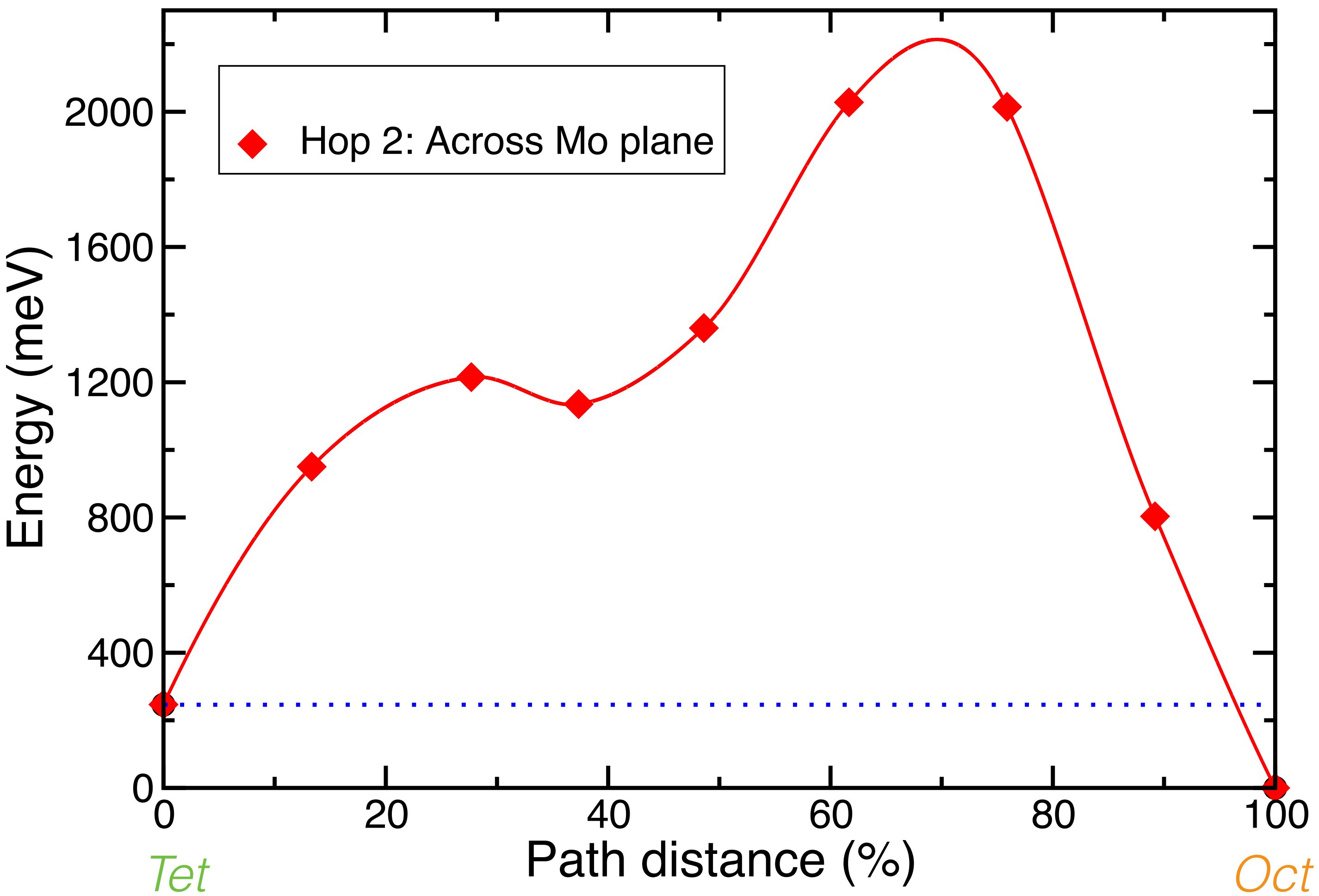
Hops 1 and 2 are relevant

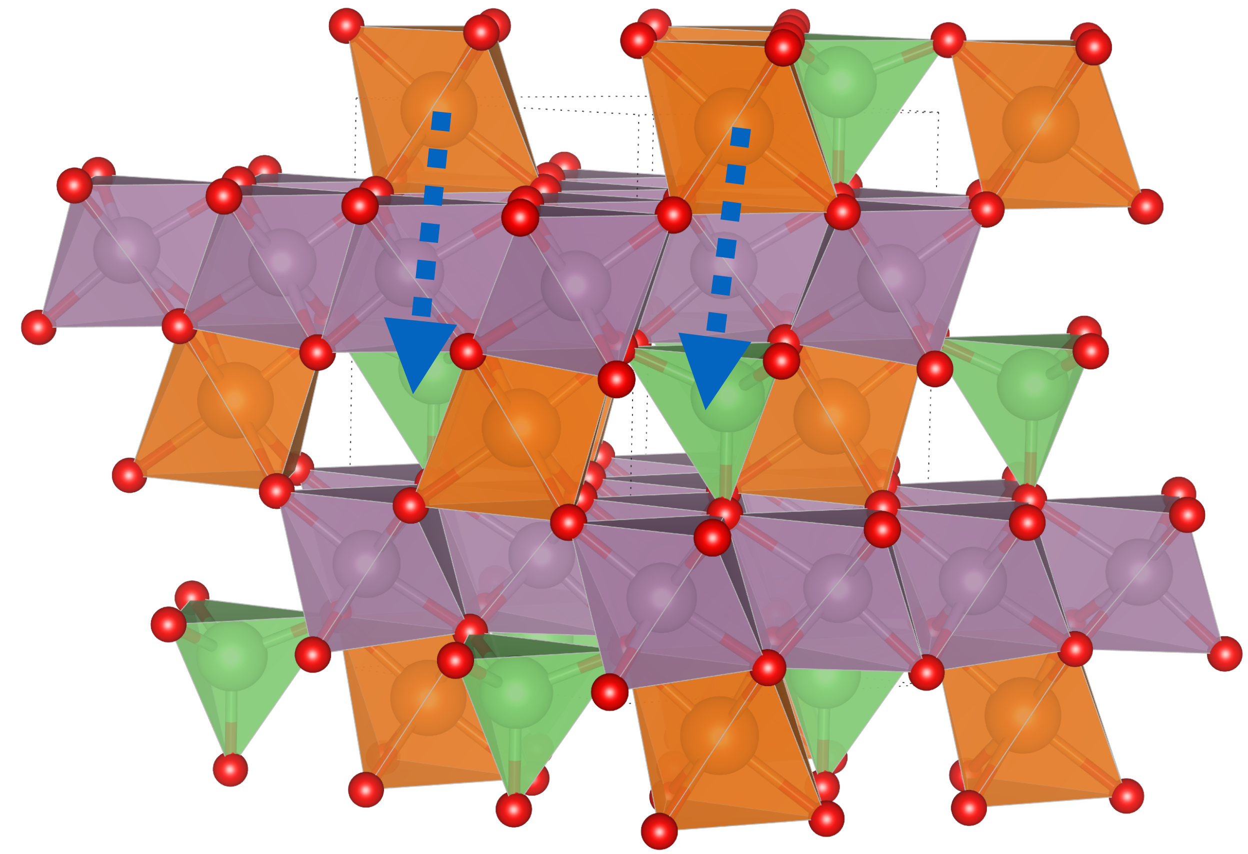


<u>G. S. Gautam,</u> *et al.*, **submitted**

Mg migration barriers

Mg mobility limited by O—Mg—O "edge" hop

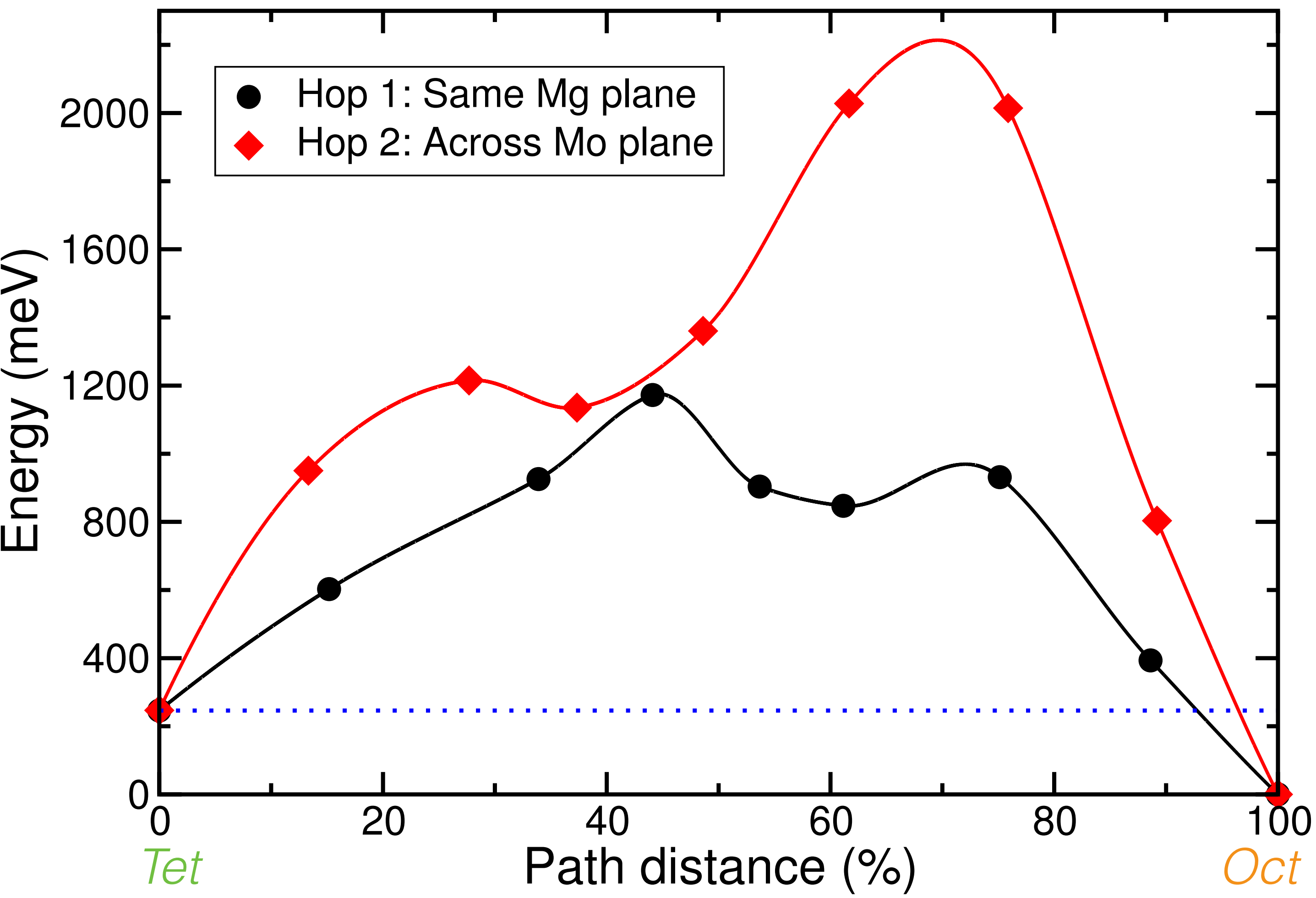


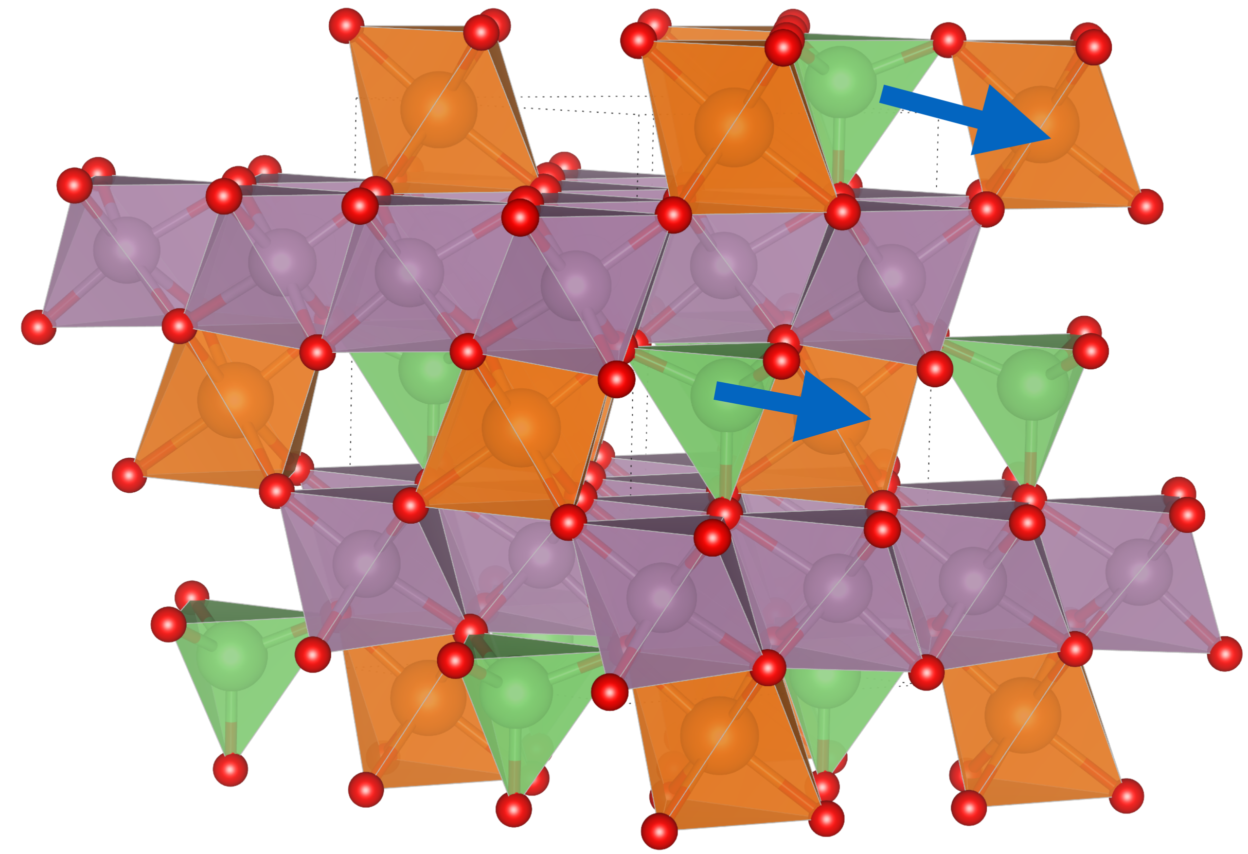


G. Sai Gautam *et al.*, **submitted**

Mg migration barriers

Mg mobility limited by O—Mg—O “edge” hop

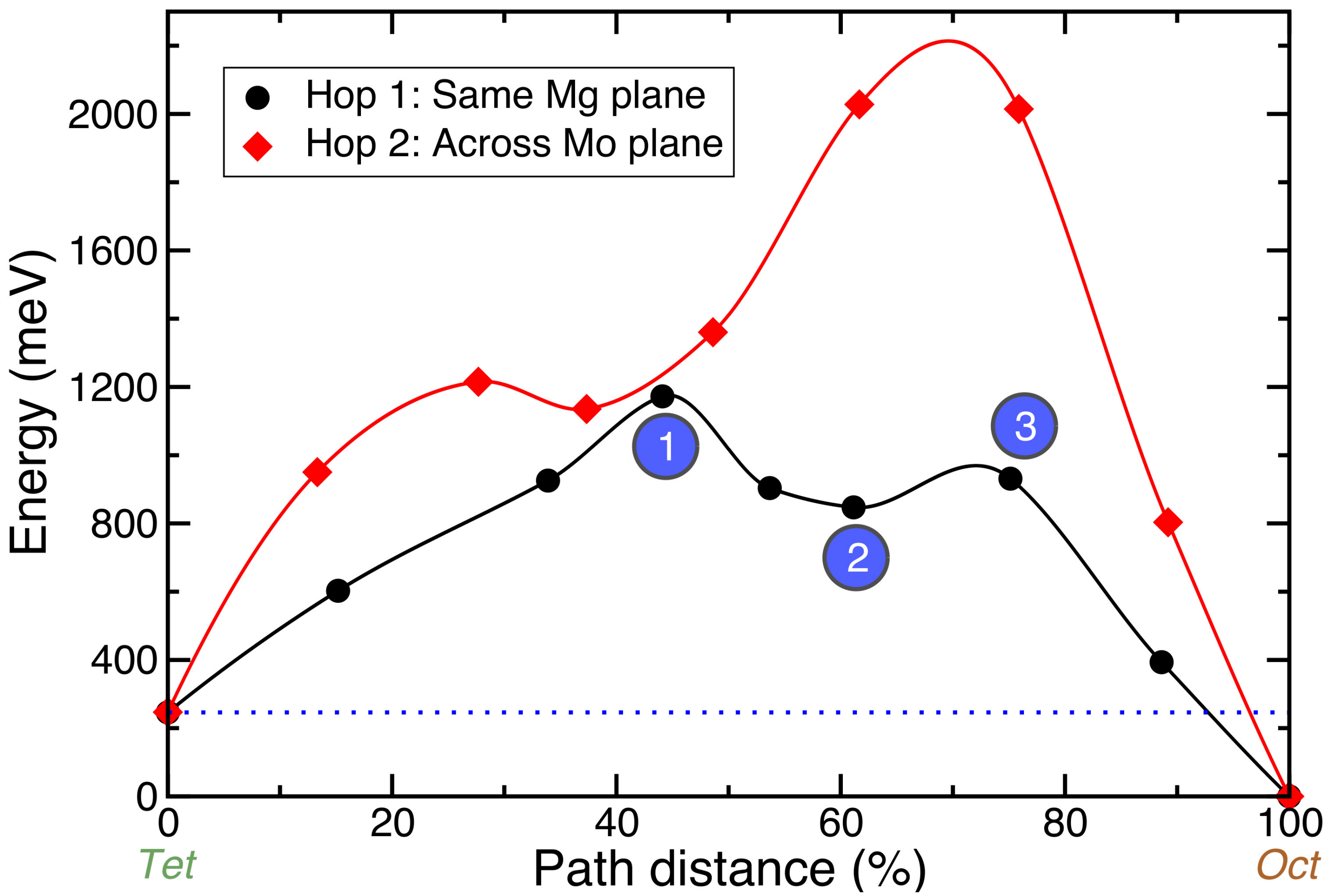


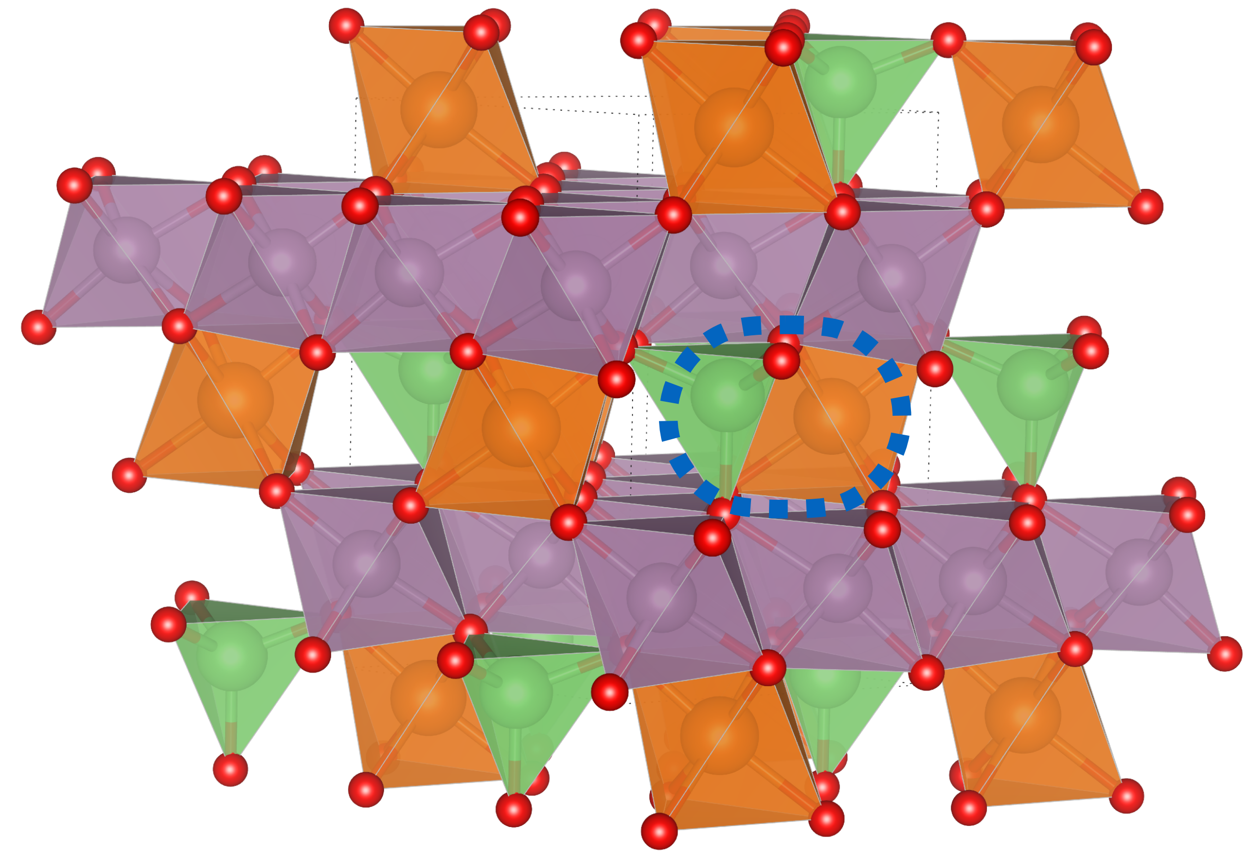


G. Sai Gautam *et al.*, **submitted**

Mg migration barriers

Mg mobility limited by O—Mg—O “edge” hop



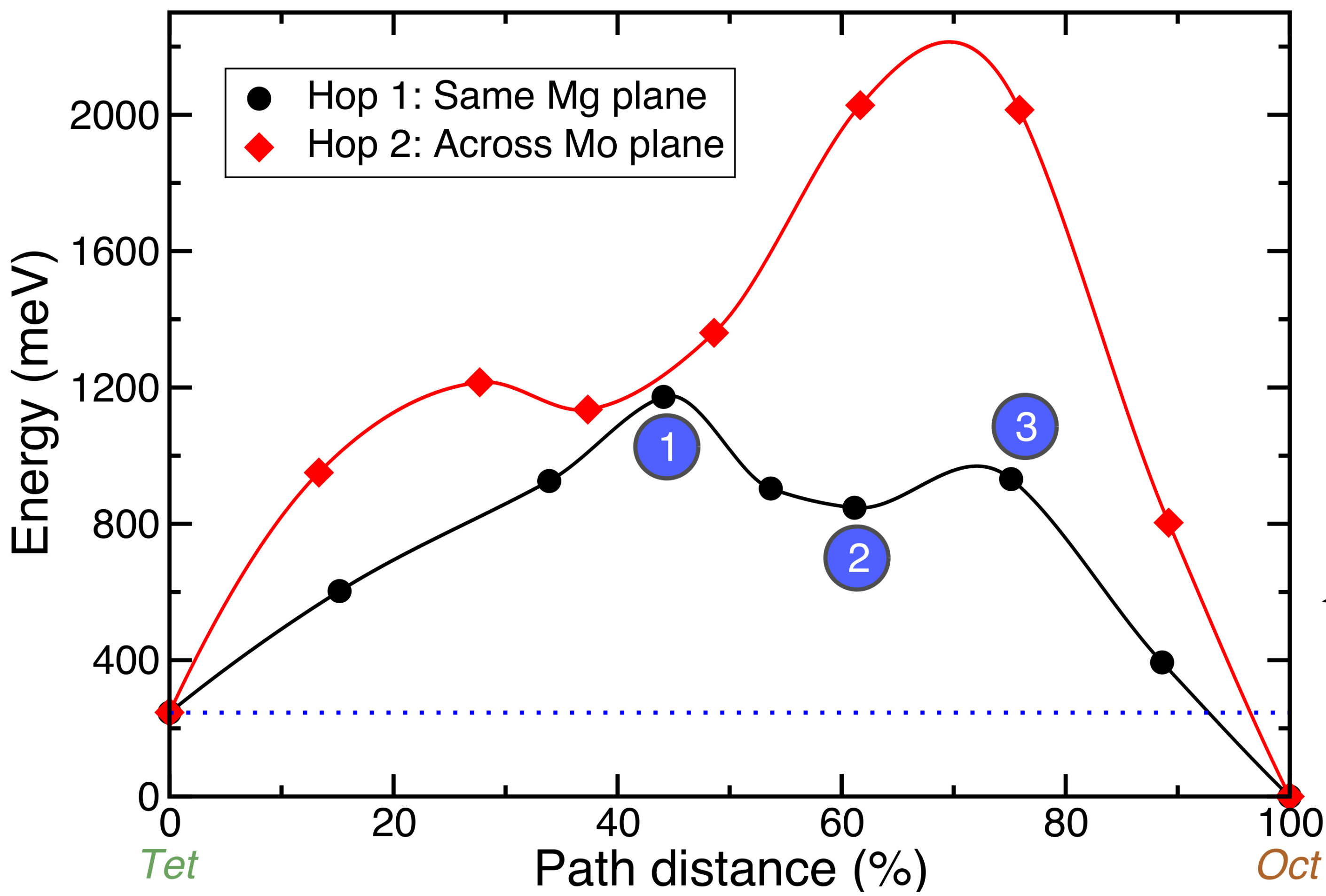


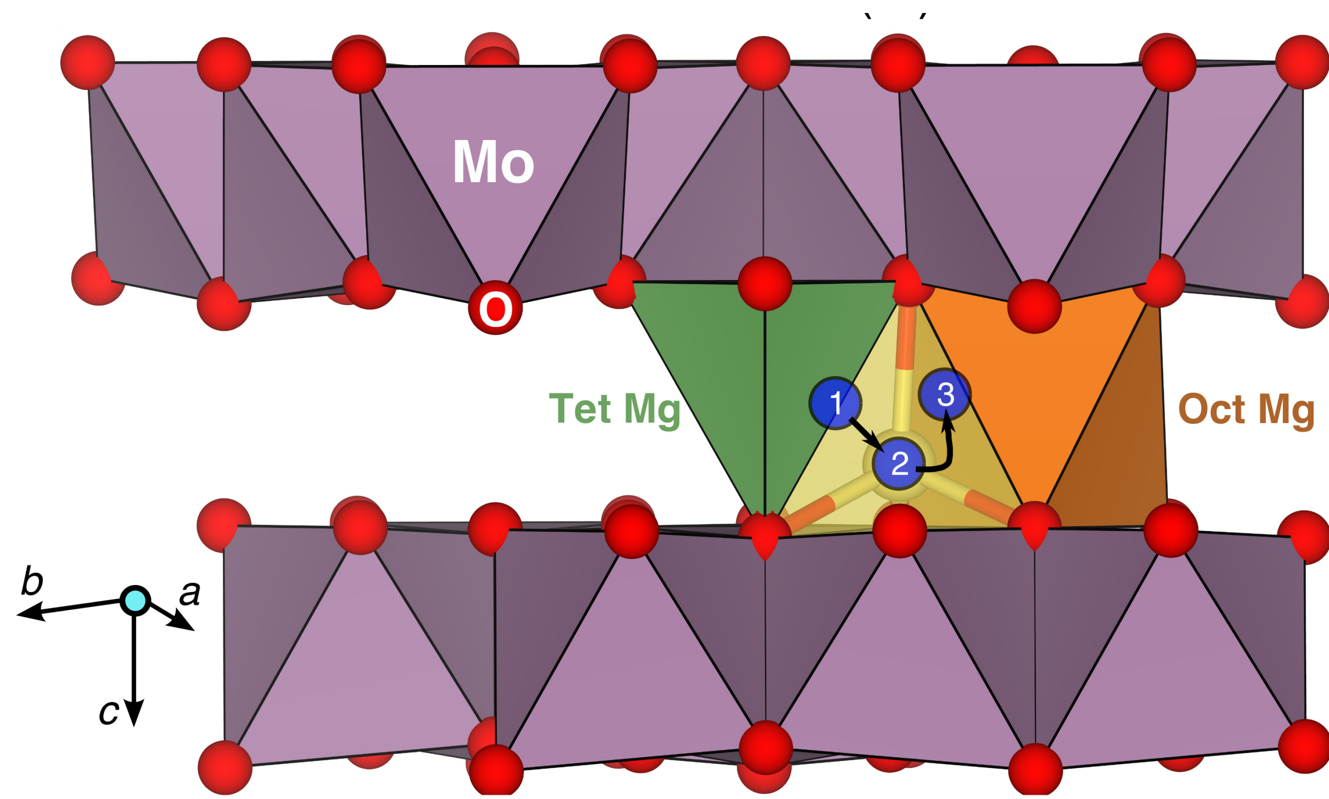
High Mg barrier (> 1 eV) caused by the O—Mg—O edge hop

G. Sai Gautam *et al.*, **submitted**

Mg migration barriers

Mg mobility limited by O—Mg—O “edge” hop



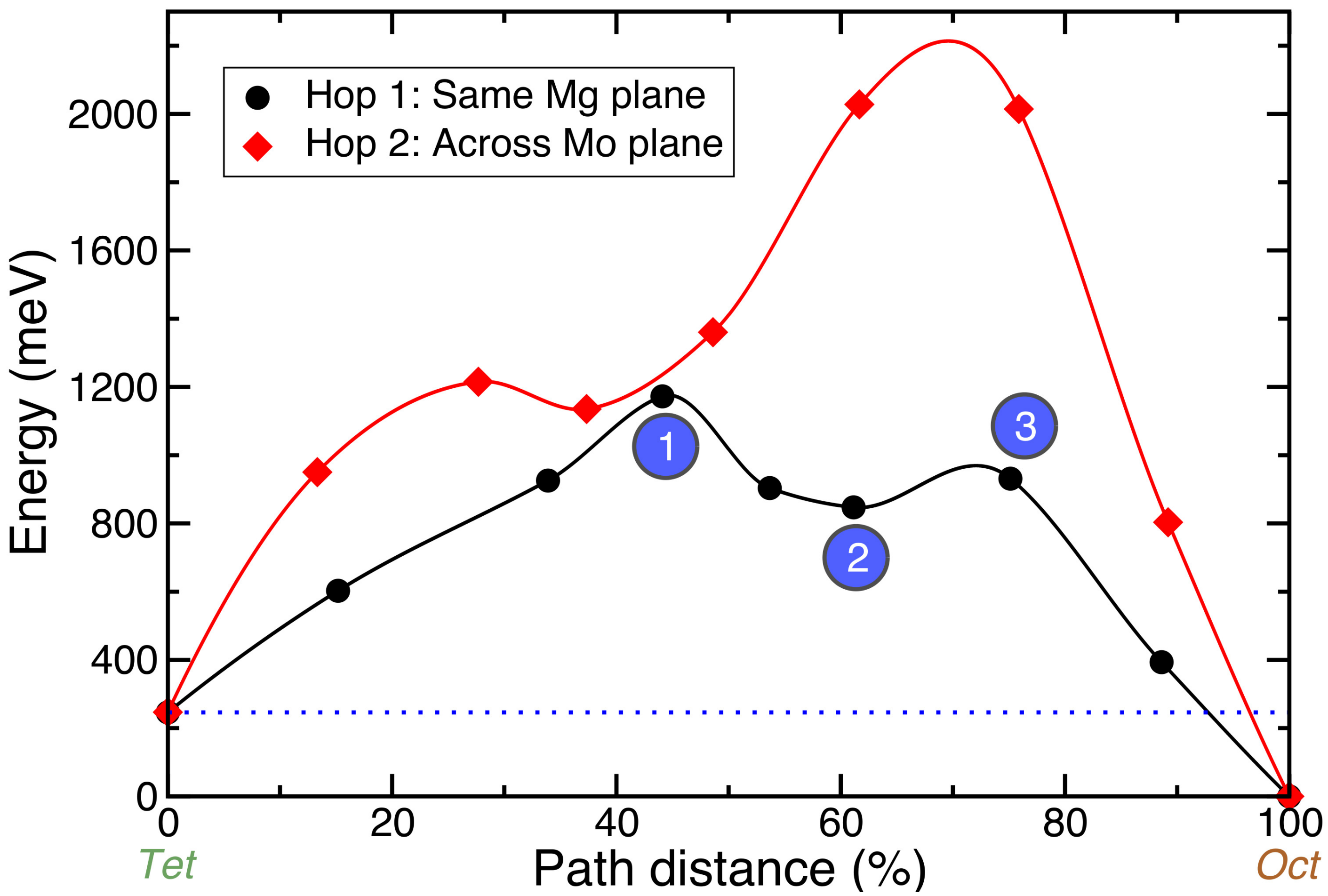


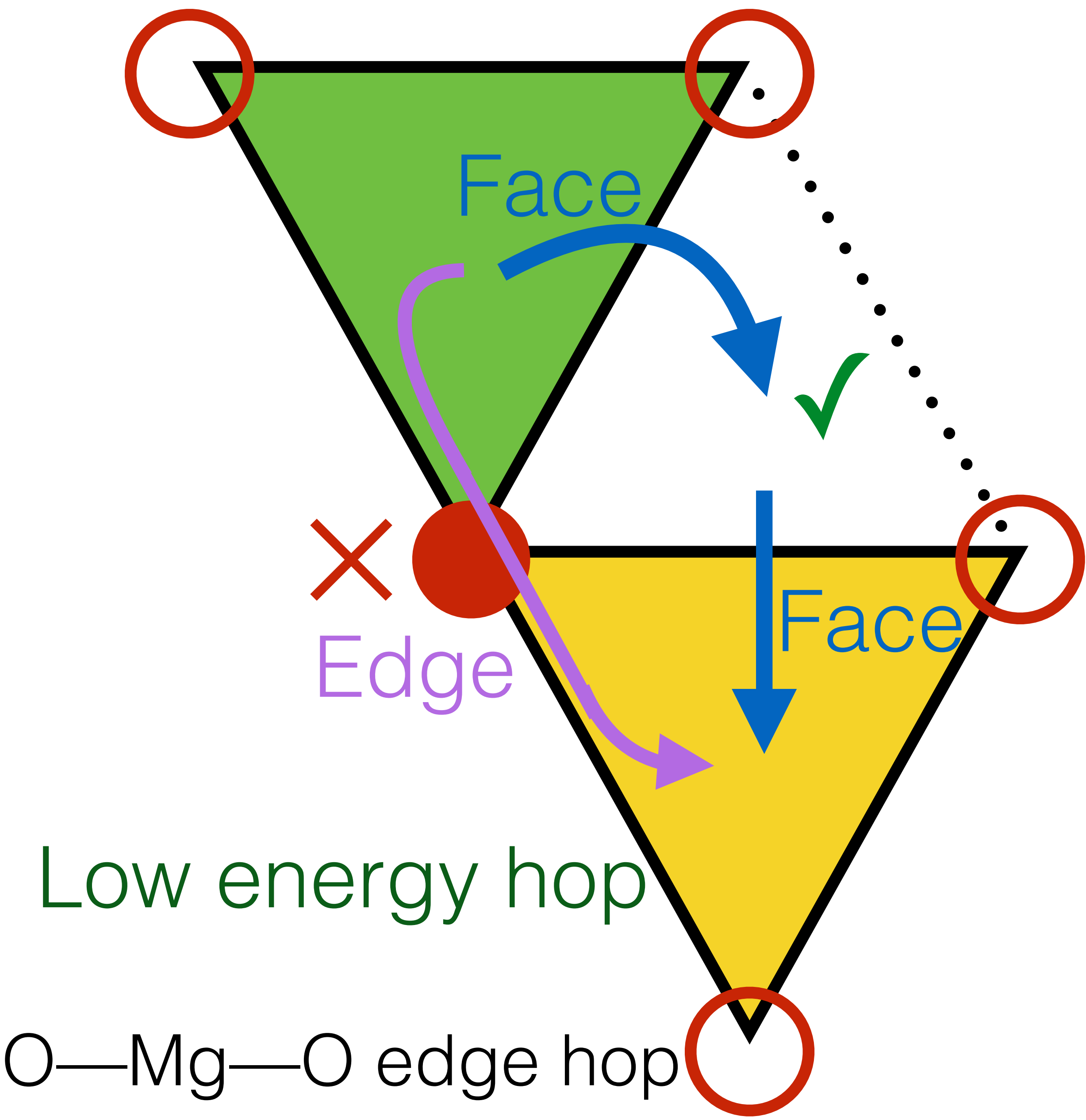
High Mg barrier (> 1 eV) caused by the O—Mg—O edge hop

G. Sai Gautam *et al.*, **submitted**

Mg migration barriers

Mg mobility limited by O—Mg—O “edge” hop



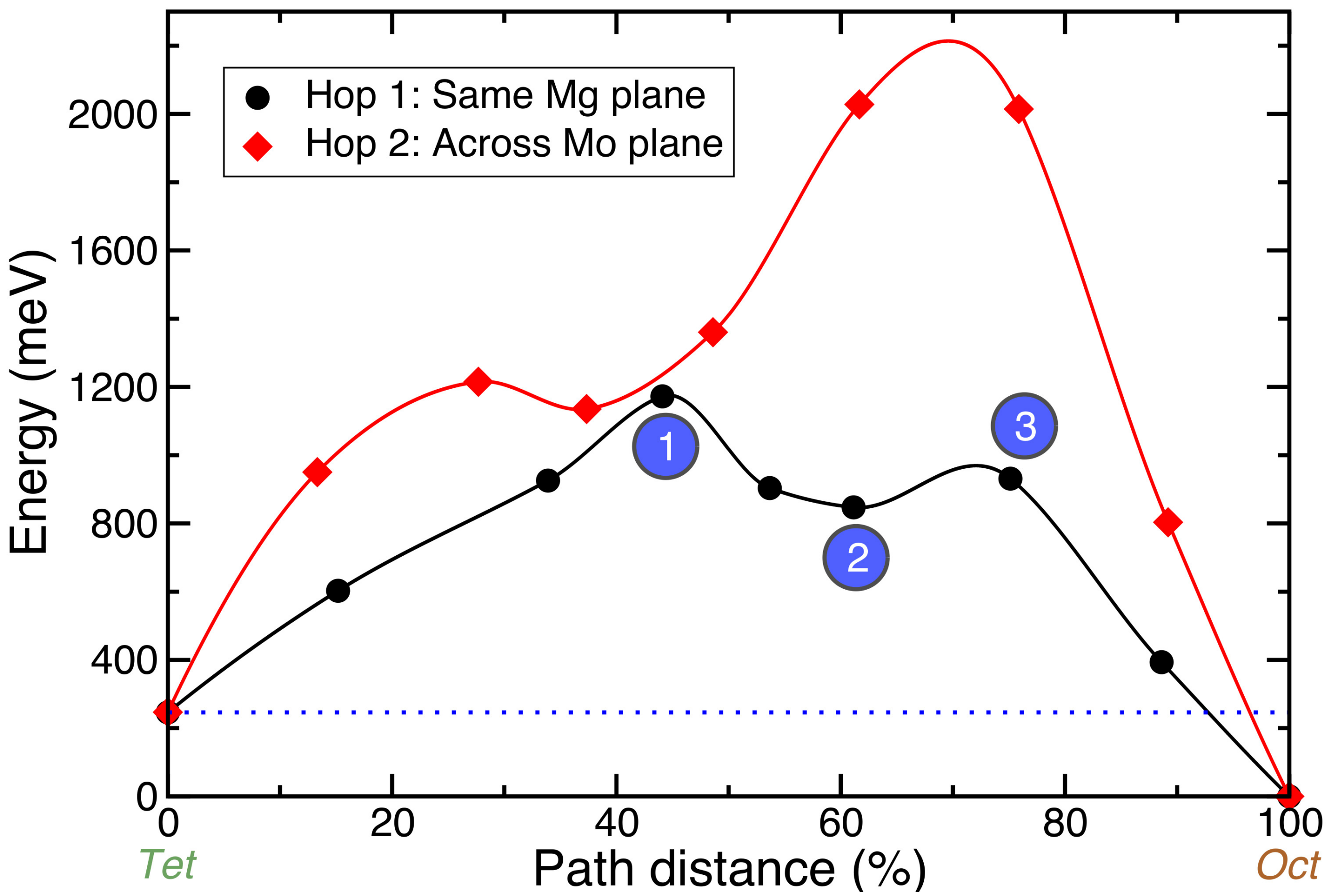


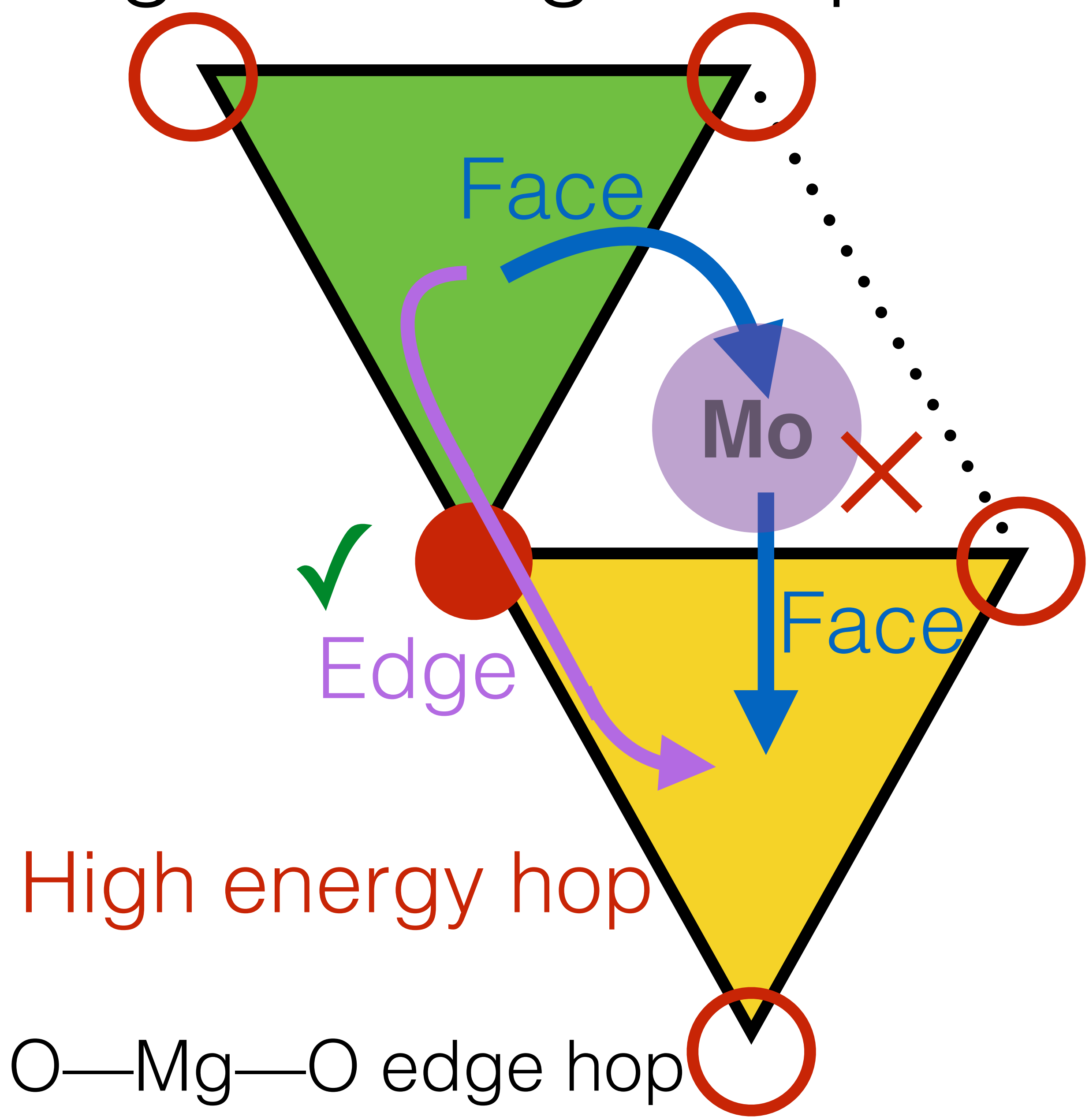
High Mg barrier (> 1 eV) caused by the O—Mg—O edge hop

G. Sai Gautam *et al.*, **submitted**

Mg migration barriers

Mg mobility limited by O—Mg—O “edge” hop





High Mg barrier (> 1 eV) caused by the O—Mg—O edge hop

Topology of sites, in addition to coordination changes, is important

G. Sai Gautam *et al.*, **submitted**

Summary

- Poor MV mobility is the pressing challenge in cathode search
- Solvent co-intercalation can mitigate poor MV mobility
  - Co-intercalation dependent on electrolyte conditions; can cause voltage change
- Although coordination is a good screening criterion for fast MV diffusers, mobility bottlenecks can exist
  - Topology of sites important; O—Mg—O edge state leads to high Mg migration barriers in $Mg_2Mo_3O_8$

1. G. S. Gautam *et al.*, "Role of structural H_2O in intercalation electrodes: the case of Mg in nano crystalline Xerogel-V_2O_5", **Nano Lett.** 16, **2016**, 2426-2431
2. G. S. Gautam *et al.*, "Impact of intermediate sites on bulk diffusion barriers: Mg intercalation in $Mg_2Mo_3O_8$", **under review**
3. P. Canepa, G. S. Gautam, D. C. Hannah *et al.*, "The odyssey of multivalent cathode materials: open questions and future challenges", **under review in Chem. Rev.**
4. G. S. Gautam *et al.*, **Chem. Mater.** 27, **2015**, 3733-3742
5. G. S. Gautam *et al.*, **Chem. Commun.** 51, **2015**, 13619-13622
6. Z. Rong *et al.*, **Chem. Mater.** 27, **2015**, 6016-6021