Skoltech
Skolkovo Institute of Science and Technology

Linking mineral and material worlds: defects genealogy in olivine-type cathode materials

DR. STANISLAV S. FEDOTOV

ICYS-2019, Vozdvizhenskoe, September 16th, 2019

Outline

I. Olivine mineral group: variety and structure

II. Defects: brief introduction, classification, examples

III. Parallels between minerals and electrode materials:

“Learning from Nature” strategy

IV. Newly discovered old defects

V. Conclusions

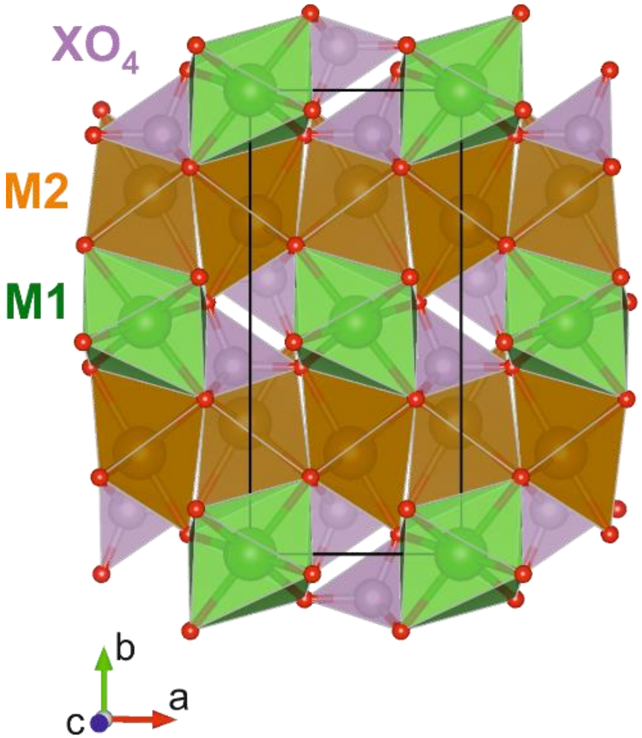
Olivine mineral $(Mg,Fe)_2SiO_4$

Papakolea beach in Hawaii

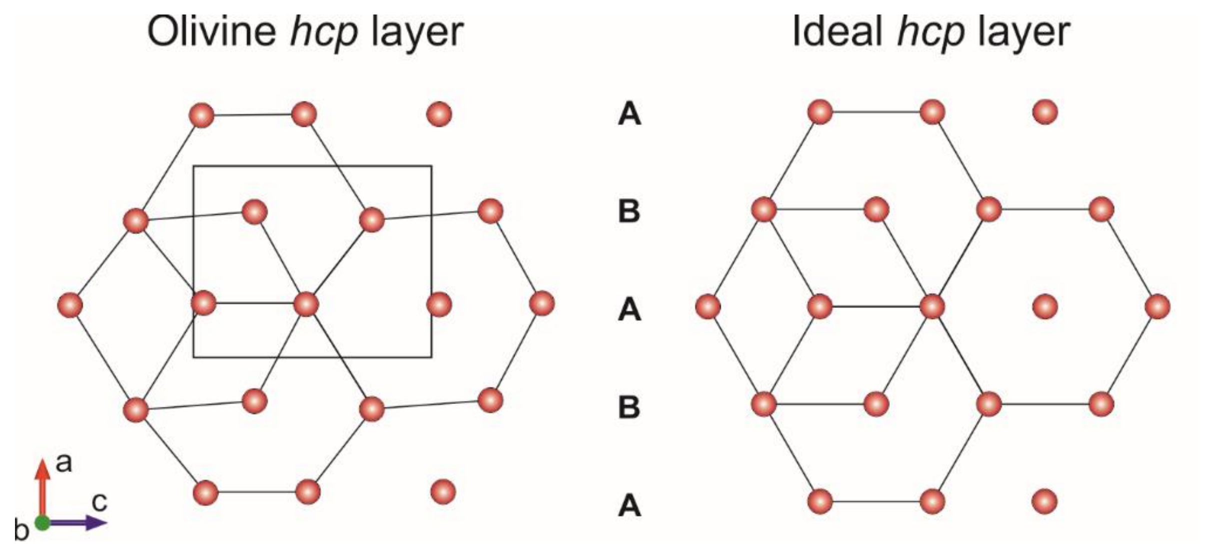
"Hawaiian diamond"

also known as **Green Sand Beach** or **Mahana Beach**

Olivine crystal structure



Distorted hcp of O atoms



Orthorhombic unit cell

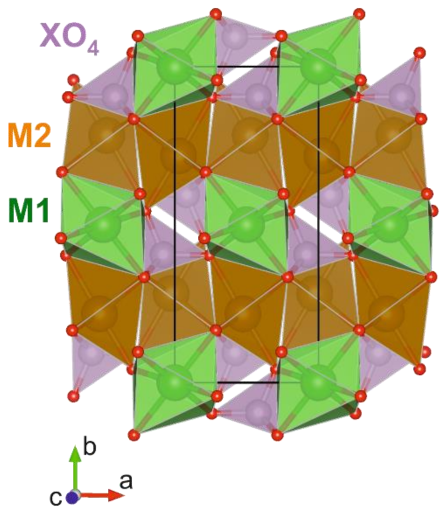
M_2XO_4 Olivine

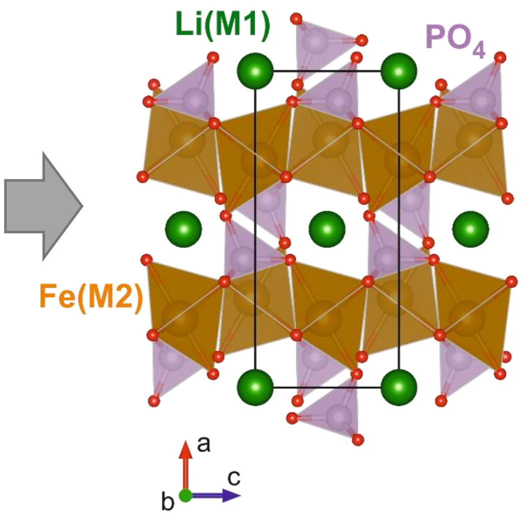
$(Mg,Fe)_2SiO_4$

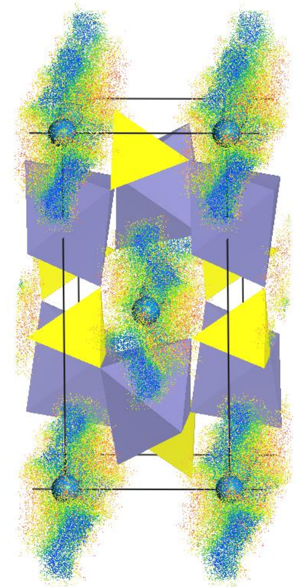
Two M sites

One X site edge-shared with M2

$LiFePO_4$ – triphylite (olivine-group mineral)



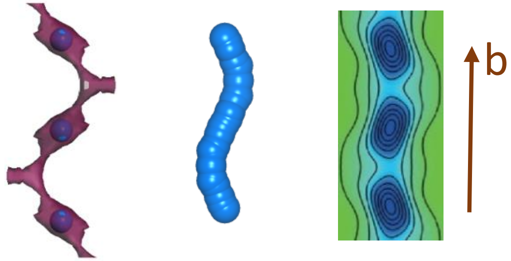




M_2XO_4 Olivine

$(Mg,Fe)_2SiO_4$

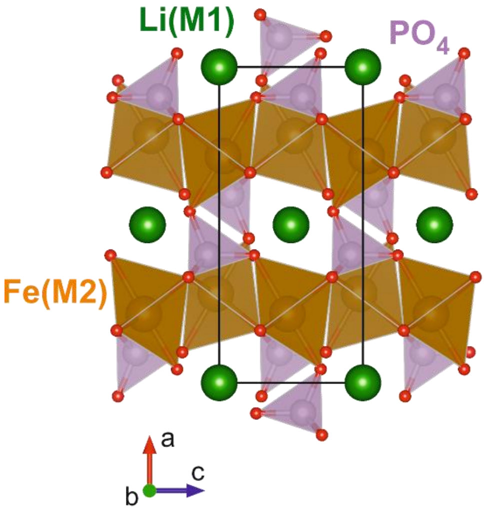
$LiFePO_4$ Triphylite



BVEL DFT MEM

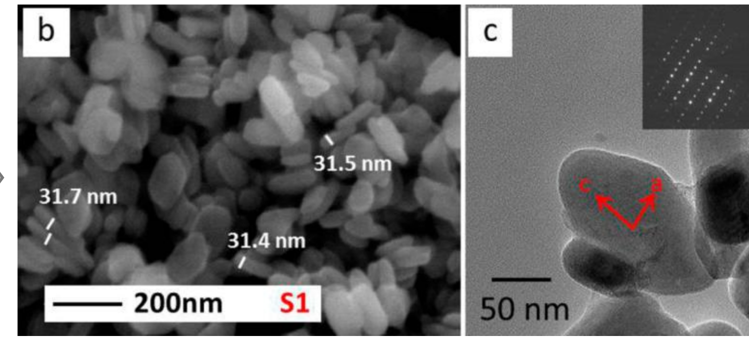
1D Li^+ migration

$LiFePO_4$ – triphylite (olivine-group mineral)



Triphylite

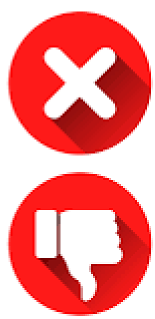
Nanosizing + Carbon-coating



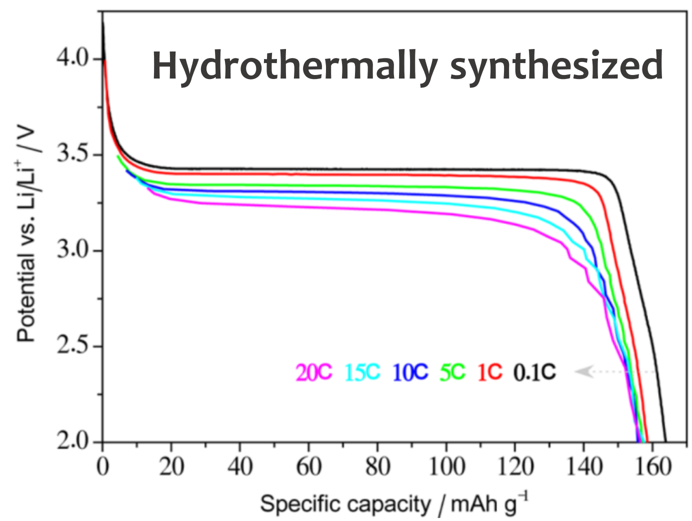
$LiFePO_4$/C cathode material

1D Li^+ migration

- Low conductivity
- Slow diffusion



No properties

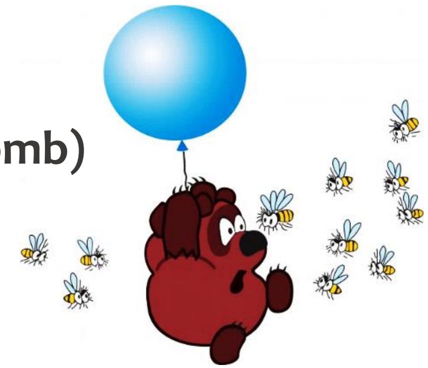


Wang, L. et al, *Nano Lett., 2012, 12(11), 5632*

Defects make it unique…

Australian bee hive (honeycomb)

1D defects



“Odd bees” ©

Vinnie-Pooh

Ruby gemstone

Point defects (0D)

Spider in Amber

3D defects

Damascus steel

2D defects

Terminology

Defects

Point defects (0D):
- Vacancies
- Interstitials
- Substitutions
- Their combinations

Linear defects (1D):
- Dislocations

Planar defects (2D):
- Antiphase boundaries
- Deformation bands
- Stacking faults
- Crystallographic shears
- ...

Bulk defects (3D):
- Inclusions

Types of point defects: Kröger-Vink notation

A_B^C

A – atom or vacancy

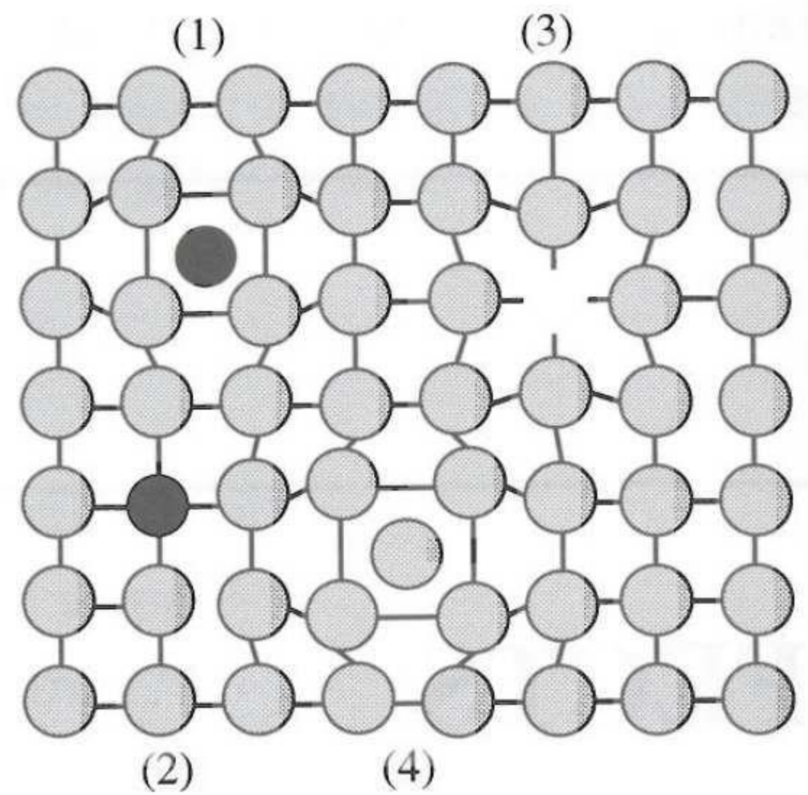
B – position (site or interstitial)

C – charge:

- $\cdot$ - positive
- $'$ - negative
- $\times$ - neutral

e' – electron

$h^{\cdot}$ – hole



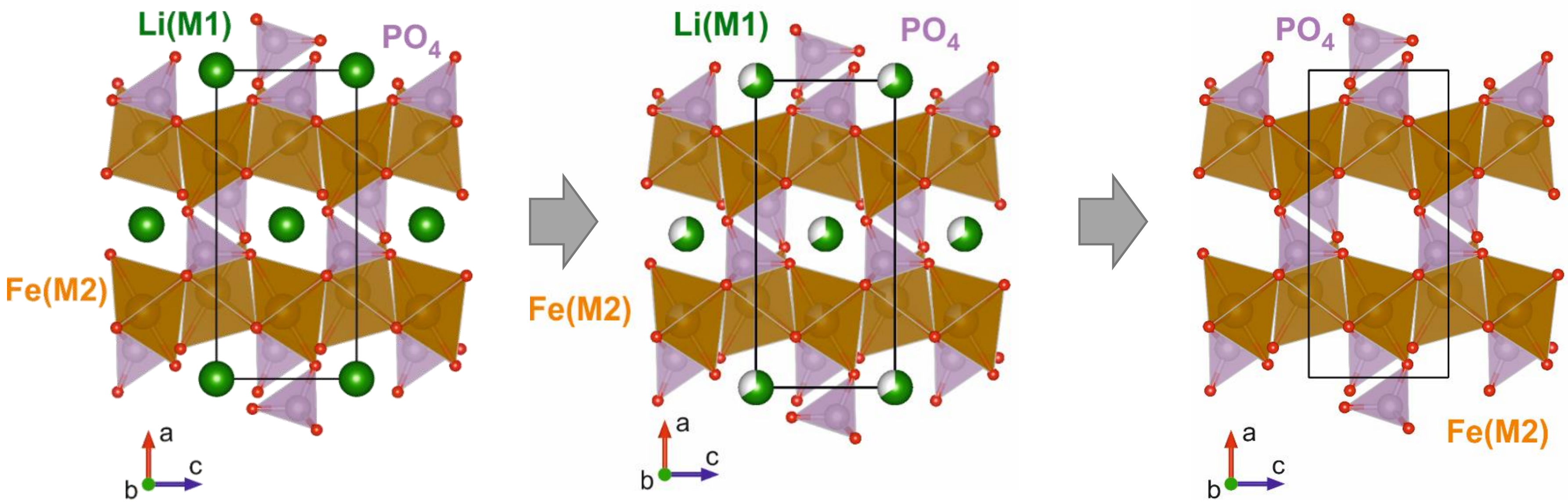
X_2Y_3 stoichiometry

$X_i^{\cdot\cdot}$	Y_X'	$V_Y^{\cdot\cdot\cdot}$
X interstitial	Y at X site	Vacancy in Y

$LiFePO_4$ defects – vacancies

$Li_{Li}^{\times} - Fe_{Fe}^{\times}$

$V_{Li}' - Fe_{Fe}^{\cdot}$



$LiFePO_4$ Triphylite

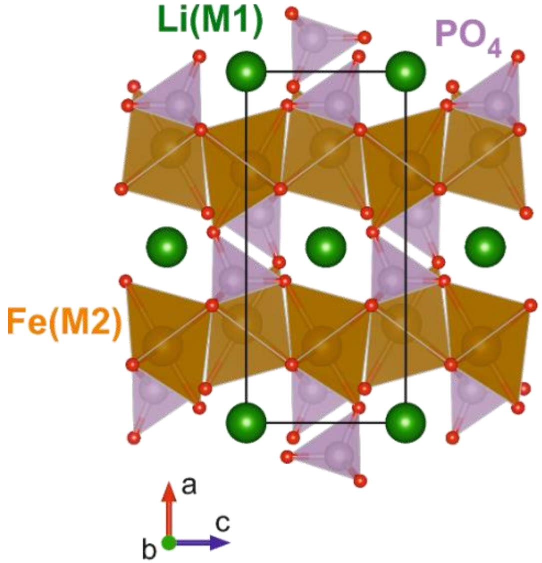
Li_xFePO_4 Ferrisicklerite

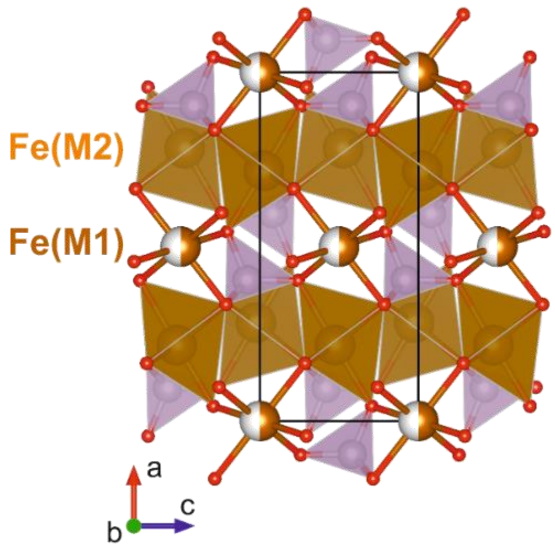
$FePO_4$ Heterosite

$LiFePO_4$ defects

$Li_{Li}^{\times} - Fe_{Fe}^{\times}$

$Fe_{Li}^{\cdot} - V_{Li}'$





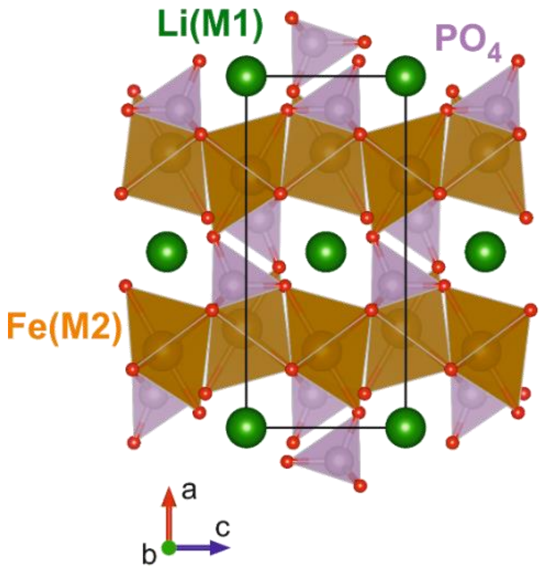
Li⁺ diffusion is blocked!

$LiFePO_4$ Triphylite

$Fe_{0.5}FePO_4$ Sarcopside
or $Fe_3(PO_4)_2$

$LiFePO_4$ – antisites

$$Li_{Li}^{\times} - Fe_{Fe}^{\times}$$



$LiFePO_4$ Triphylite

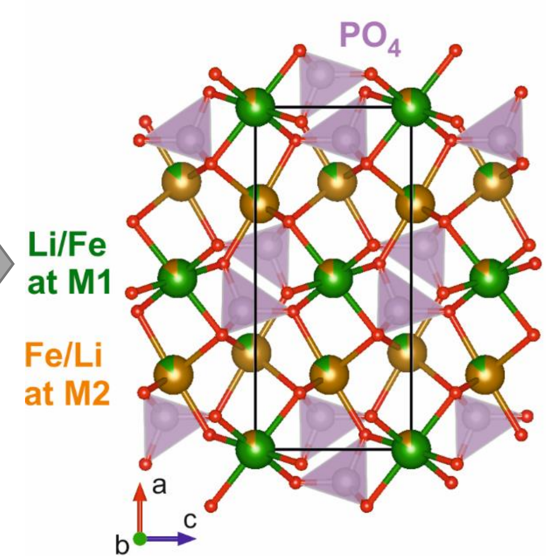
Li^{+} (r = 0.76Å)
Fe^{2+} (r = 0.78 Å)

$$Fe_{Mg}^{\times} - Mg_{Fe}^{\times}$$

Mg-Fe interdiffusion

Continuous solid-solution:
Fe_2SiO_4 Fayalite – Mg_2SiO_4 Forsterite

$$Fe_{Li}^{\cdot} - Li_{Fe}'$$



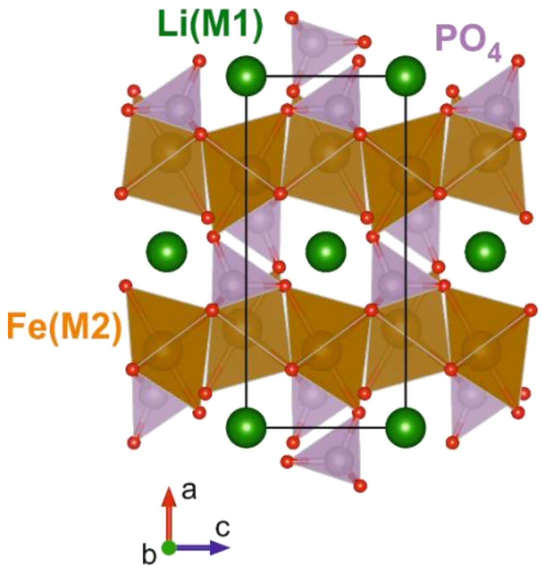
$(Li_{1-x}Fe_x)_{M1}(Fe_{1-x}Li_x)_{M2}PO_4$

Antisite defects

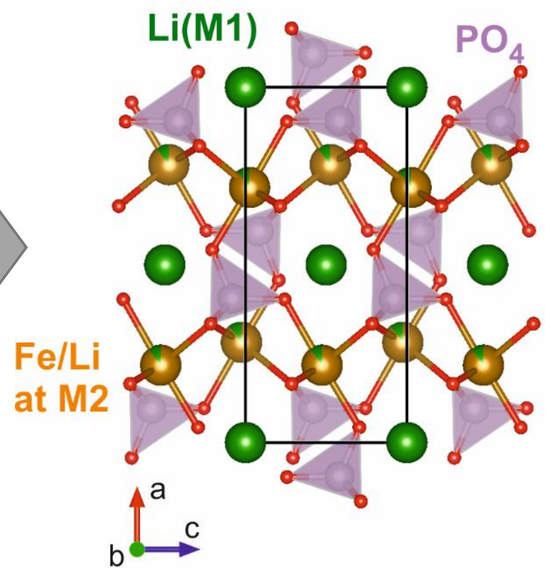
$LiFePO_4$ – Li-rich

$$Li_{Li}^{\times} - Fe_{Fe}^{\times}$$

$$Li_{Fe}' - Fe_{Fe}^{\cdot}$$



$LiFePO_4$ Triphylite



$Li_{1+x}Fe_{1-x}PO_4$

"Li-rich"

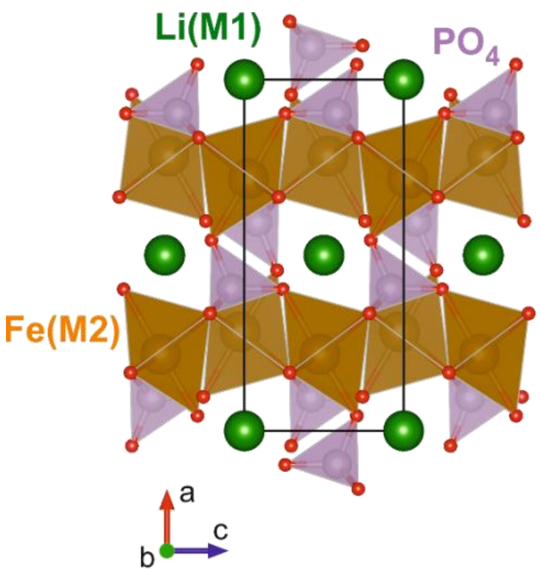
2D Li^+ transport

Not known in minerals (yet?)

What about electrode materials?

Poster on Li-rich $LiMPO_4$ by A. Grebenschikova

$LiFePO_4$ – defects in anion sublattice



$LiFePO_4$ Triphylite

Amisse, R.
Chem. Mater.
2015, **27**, 4261–4270

What about anions?

Any defects in anionic sublattice?

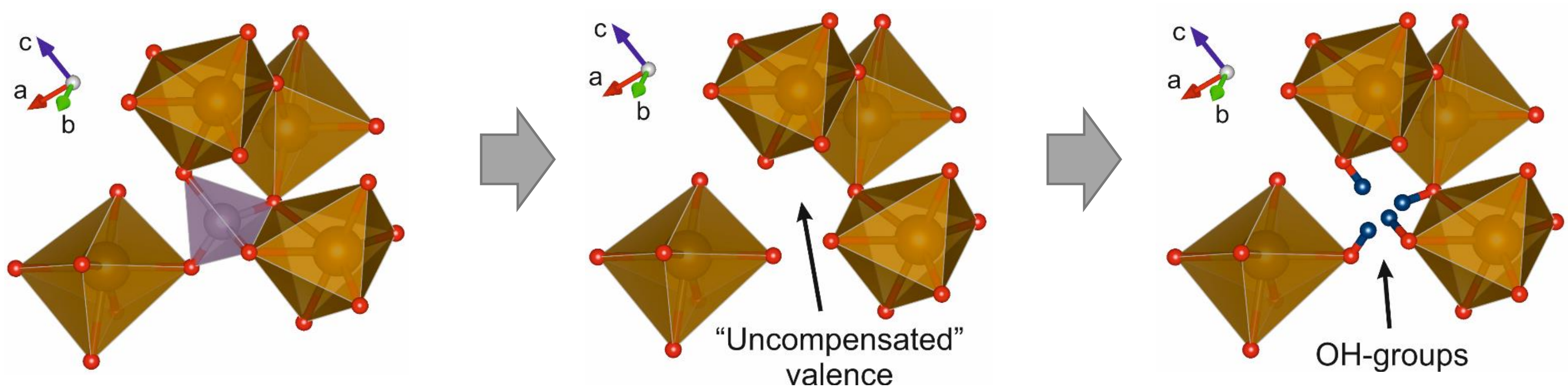
$V_P^{'''''}$ DFT: 3.56 eV – "highly unlikely"

Low-temperature co-precipitation:

$$[Li_{0.85}Fe^{3+}_{0.15}]_{M1}[Fe^{2+}_{0.72}Fe^{3+}_{0.19}Li_{0.09}]_{M2}P_{0.92}O_4$$

$V_P^{'''''}$ 8% No explanation given…

$LiFePO_4$ – defects in anion sublattice



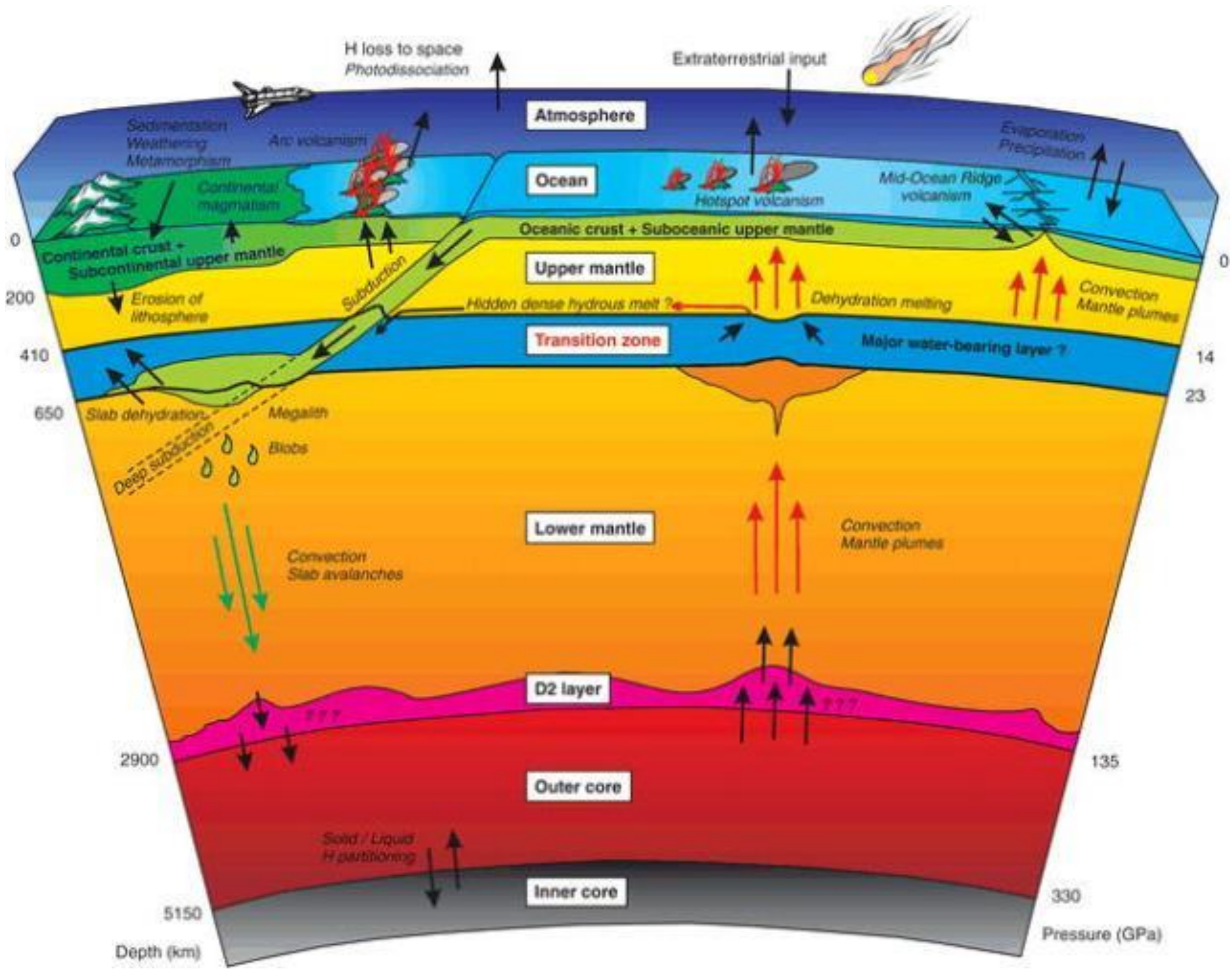
After several cycles of refinement the occupancy factors of the cation sites in the isotropic and anisotropic refinements agreed within the standard errors and were, for the anisotropic refinement, M(1) = 40·8 ± 2·2 %, M(2) = 98·6 ± 0·4 %, P = 95·8 ± 0·4 %. These results seem to indicate that the M(1) site is occupied only by Li. Moreover the partial occupancy of the P site (95·8 %) confirms the substitution of the PO_4 group by the $(OH)_4$ group as suggested by Fontan *et al.* (1976) and agrees satisfactorily with the calculated occupancy (93·9 %).

Albertia, A. (**1976**)
Acta Cryst. B, 32(10), 2761–2764.

Fontan, F., Huveun, P., Orliac, M. & Permingeat, F. (**1976**). Bull. Soc. Fr. Mindr. Crist. **In preparation.**

Never been published…

Water in the upper mantle and transition zone



Source: https://sureshemre.wordpress.com/2014/05/04/huge-amount-of-water-in-earths-mantle/

Hydrogen in natural $(Mg,Fe)_2SiO_4$ olivines

nature
International journal of science

Review Article | Published: 23 July 1992

Water in

Alan Bruce Thompso

Nature **358**, 295–302

Science Contents News Careers Journals

ARTICLES

Water i … hydrous
Mineral

DAVID R. BELL[1],
+ See all authors

Science 13 Mar
Vol. 255, Issue 50
DOI: 10.1126/sci

nature
International journal of science

Letter | Published: 25 June 1992

Substantia
olivine anc
storage in

Quan Bai & D. L. Kohlste

Nature **357**, 672–674 (19

ELSEVIER

Earth and Planetary Science Letters

Volume 144, Issues 1–2, October 1996, Pages 93-108

Water in th
implication
extraction a
lithosphere

Greg Hirth [a], David L.

nature
International journal of science

Letter | Published: 02 September 2010

Olivine water contents in the continental lithosphere and the longevity of cratons

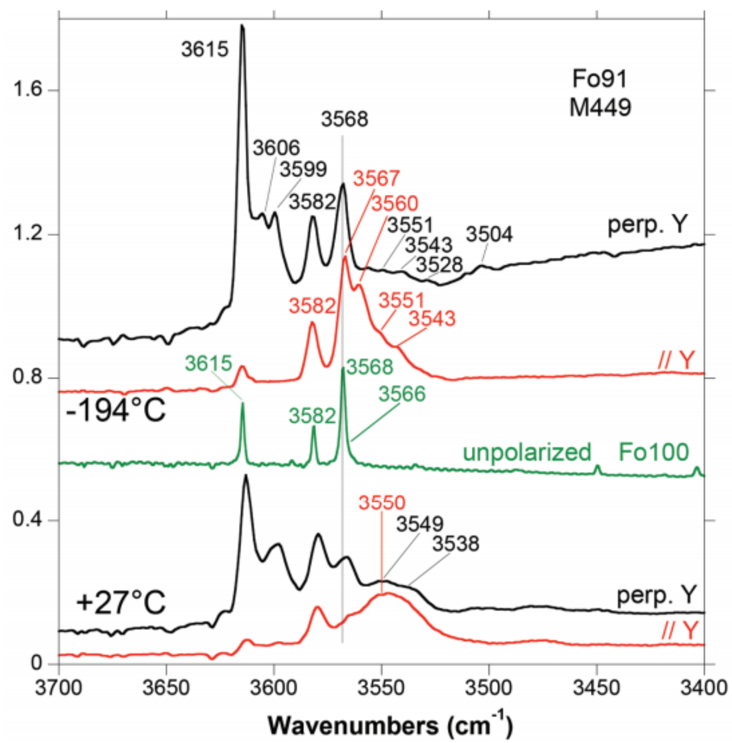
Anne H. Peslier, Alan B. Woodland, David R. Bell & Marina Lazarov

Nature **467**, 78–81 (02 September 2010) | Download Citation

What is the mechanism of water relocation in the upper mantle?

Hydroxyl defects in $(Mg,Fe)_2SiO_4$ olivines

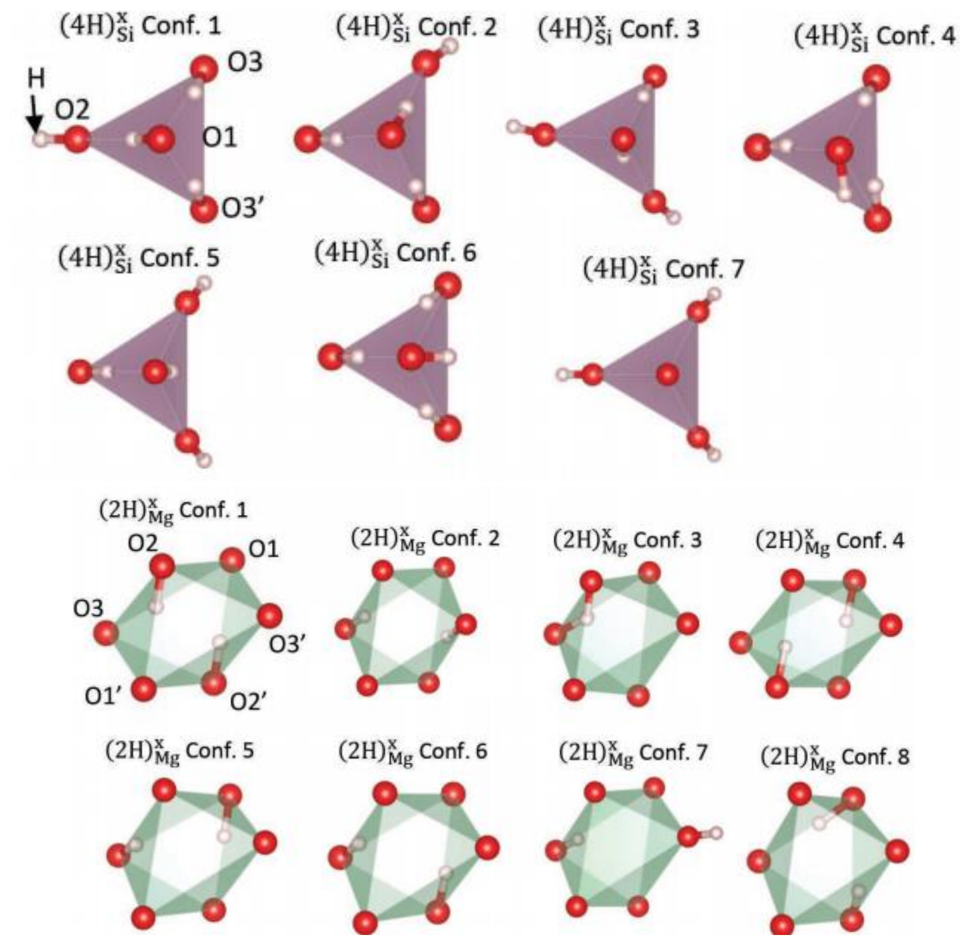
FTIR spectroscopy for Forsterite



Modeling of FTIR spectra

Blanchard, M. et al *American Mineralogist, 2017, 102(2), 302–311.*

DFT for OH groups in Si and Mg positions

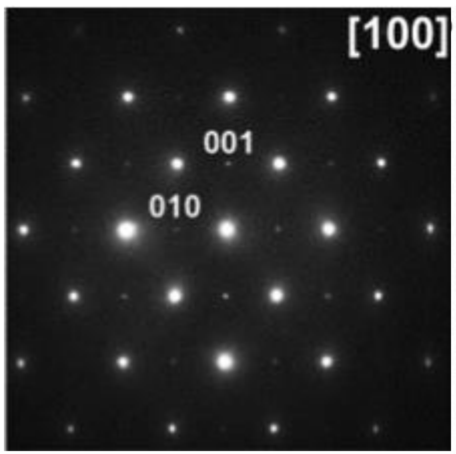


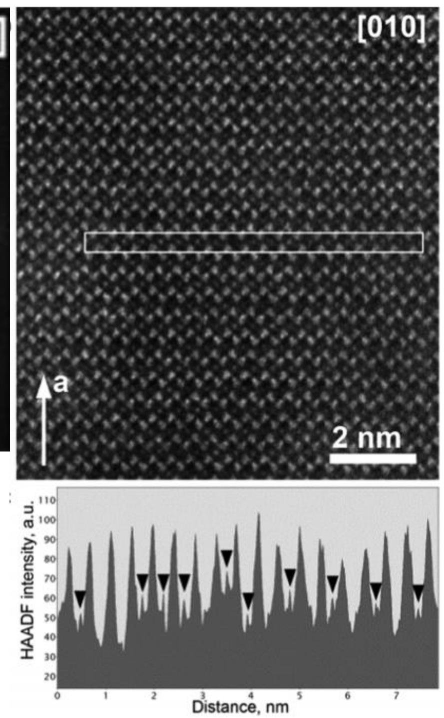
Qin, T. et al. American Mineralogist, 2018, 103(5), 692–699.

Hydrothermally prepared $LiFePO_4$

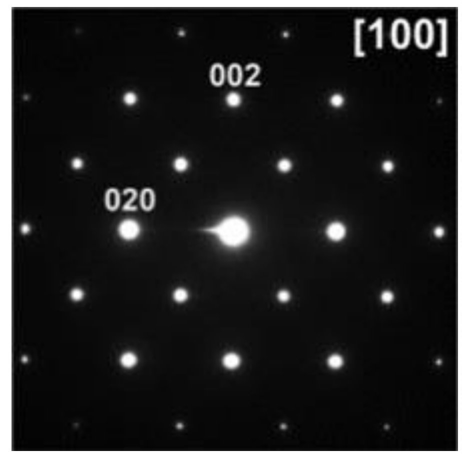
Hydrothermal synthesis: precursor concentration variation

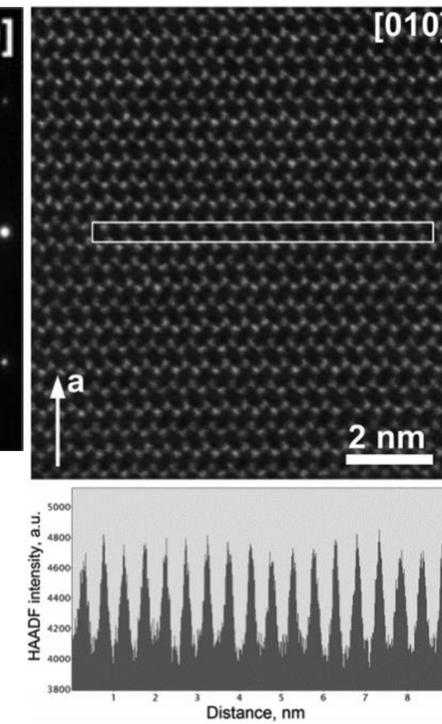
$Li_{0.93}Fe_{1.07}P_{\mathbf{0.84}}O_4$	**TEM-EDX**	$Li_{1.050}Fe_{0.950}P_{\mathbf{0.962}}O_4$
$P2_1ma$ V, Å^3 293.12(2)	**XRD**	$Pnma$ V, Å^3 290.431(9)





7% Fe
in M1 position
16% P-deficiency





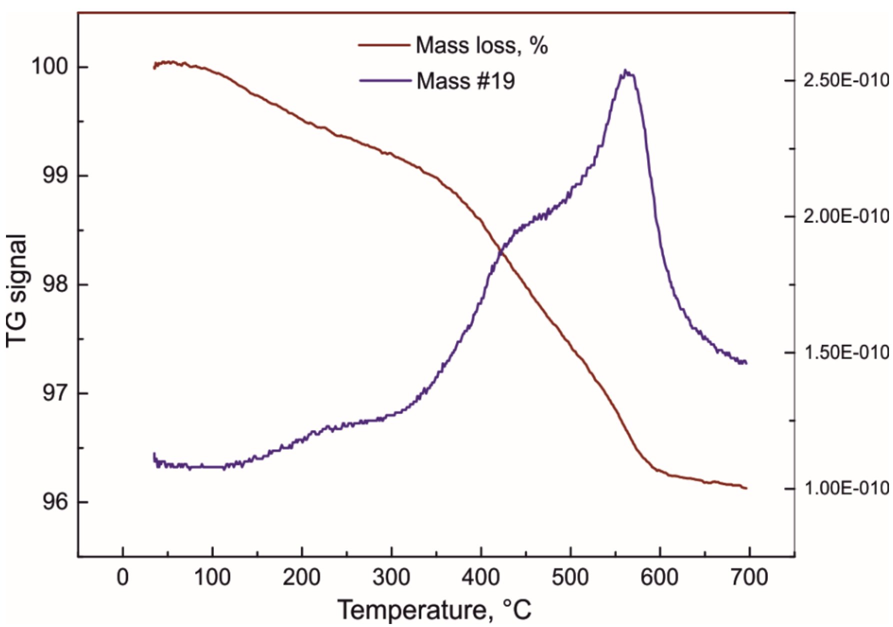
"Li-rich"
No Li-Fe anti-sites

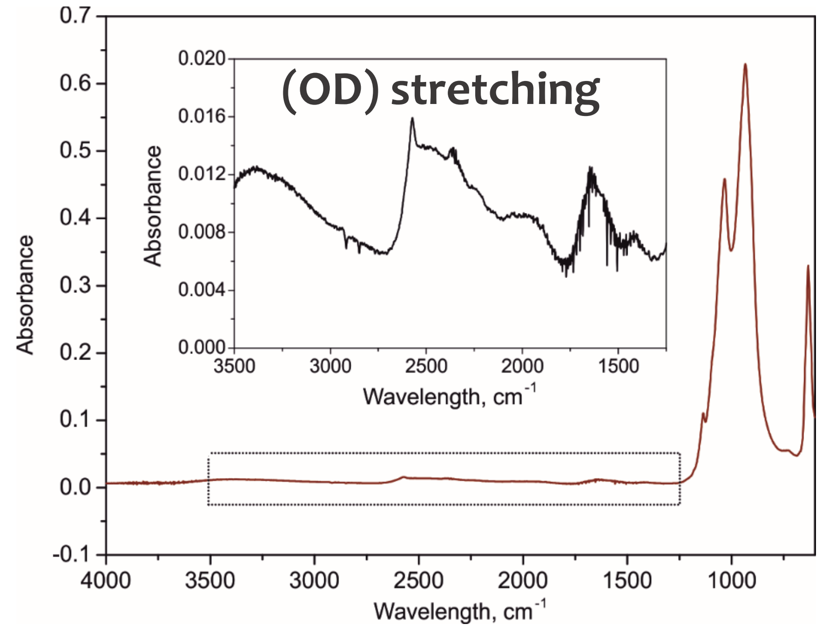
Sharikov, F. Yu et al, Cryst. Growth. Des., 2018

Sumanov, V. D. et al, Chem. Mater. 2019

OH-detecting: TG-MS + FTIR

Hydrothermal synthesis in D_2O





Total mass loss 3.9 %

D-shift, band at ~2600 cm^{-1}

–OD (cryst.) mass corresponds to y ≈ 0.17 in

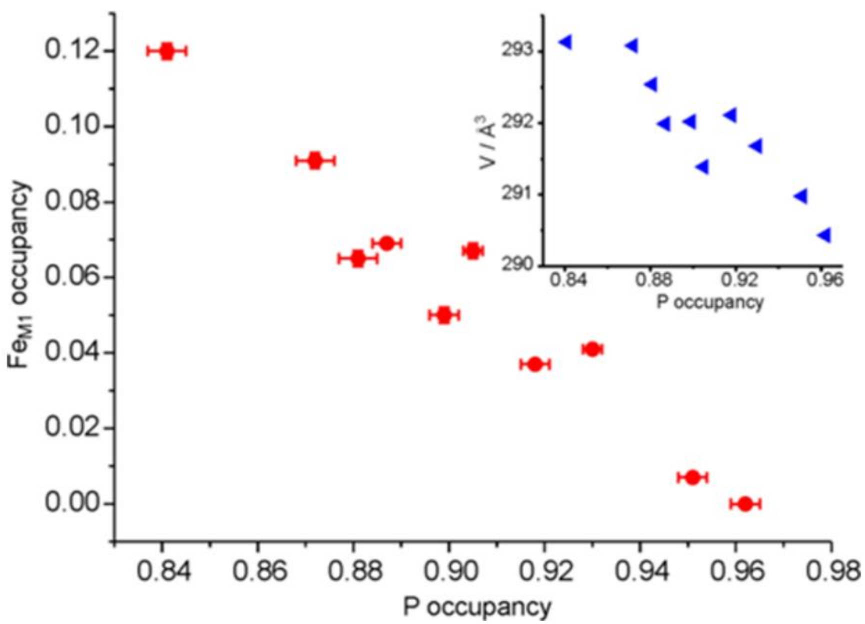
$$Li_{1-x}Fe_{1+x}(PO_4)_{1-y}(OD)_{4y}$$

Fedotov S. et al, in preparation, 2019

$Li_{1-x}Fe_{1+x}(PO_4)_{1-y}(OH)_{4y}$ "hydroxytriphylites"

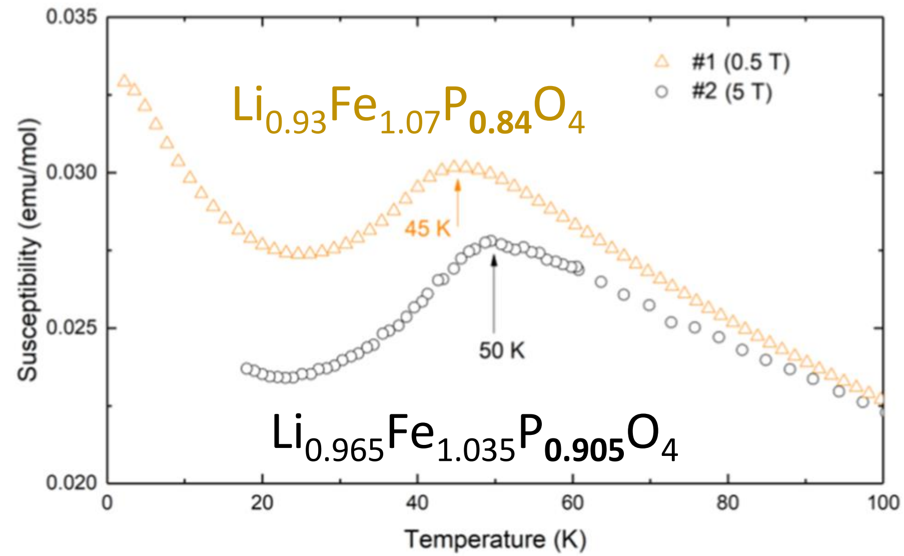
Hydrothermal synthesis: precursor concentration/temperature scans

P deficiency vs. Fe(M1) occupancy



Higher P deficiency – Larger cell volume

Magnetic behavior: T_N change

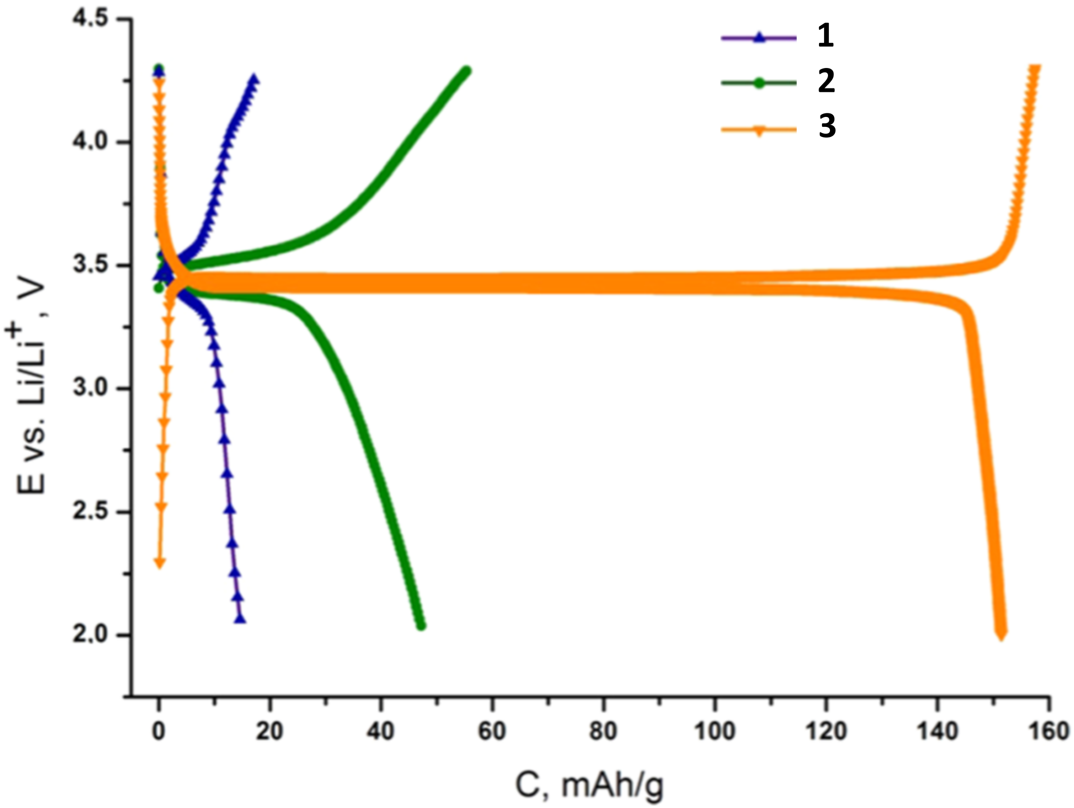


For stoichiometric $LiFePO_4$ T_N = 52 K

Higher P deficiency – Lower T_N

Sumanov, V. D. et al, Chem. Mater. 2019, accepted

$Li_{1-x}Fe_{1+x}(PO_4)_{1-y}(OH)_{4y}$ electrochemistry



1) $Li_{0.93}Fe_{1.07}P_{\mathbf{0.84}}O_4$

2) $Li_{0.965}Fe_{1.035}P_{\mathbf{0.905}}O_4$

3) $Li_{1.050}Fe_{0.950}P_{\mathbf{0.962}}O_4$

C/10 rate, $LiPF_6$ in 1M EC:DMC

Sumanov, V. D. et al, Chem. Mater. 2019, accepted

Conclusions

I. **Look for creativeness in minerals and Nature**

II. **Much richer defects chemistry of $LiFePO_4$: polyanion sublattice is not inert**

III. **Hydroxytriphylite solid solutions $Li_{1-x}Fe_{1+x}(PO_4)_{1-y}(OH)_{4y}$ inspired by minerals and Nature.**

Glass beach in Vladivostok

Acknowledgements

Skoltech

Dr. Dmitry Aksyonov

Dr. Alexandra Savina

Dr. Sergey Ryazantsev

Dr. Victoria Nikitina

Dr. Dmitry Rupasov

Mr. Anatoly Morozov

Ms. Polina Morozova

Prof. Keith Stevenson

Prof. Artem Abakumov

EMAT

Ms. Olesia M. Karakulina

Prof. Joke Hadermann

MSU

Mr. Vasily Sumanov

Mr. Nikita Luchinin

Dr. Oleg Drozhzhin

Dr. Andrey Mironov

Prof. Evgeny Antipov

RFBR grant #18-29-12097

Thank you for attention!