Structural evolution of Tungsten Oxide Network during $WO_3.H_2O$ formation

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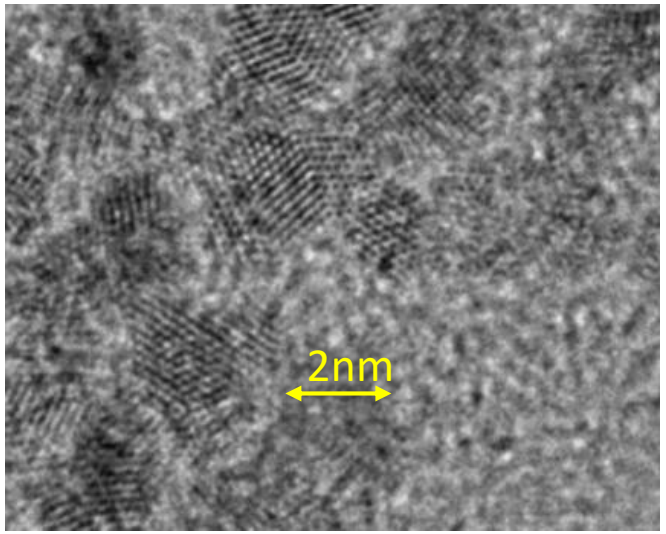
ADD 2026 Grenoble

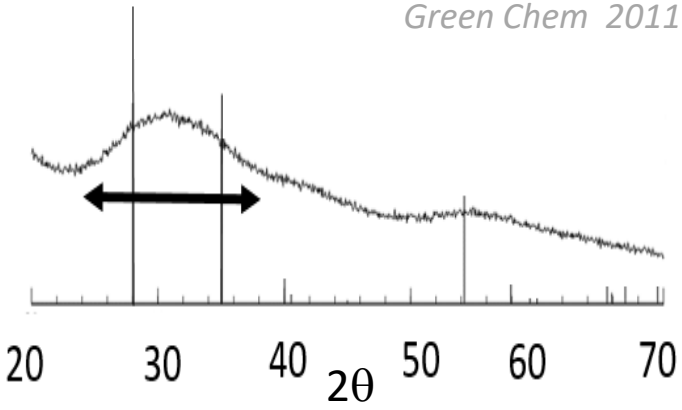
14th January 2026

Chemist background….

Nanoparticles Sol-Gel synthesis – Energy and catalysis
X-Ray Diffraction to identify structures
Shape and widening of the peaks to determine crystal size or anisotropy

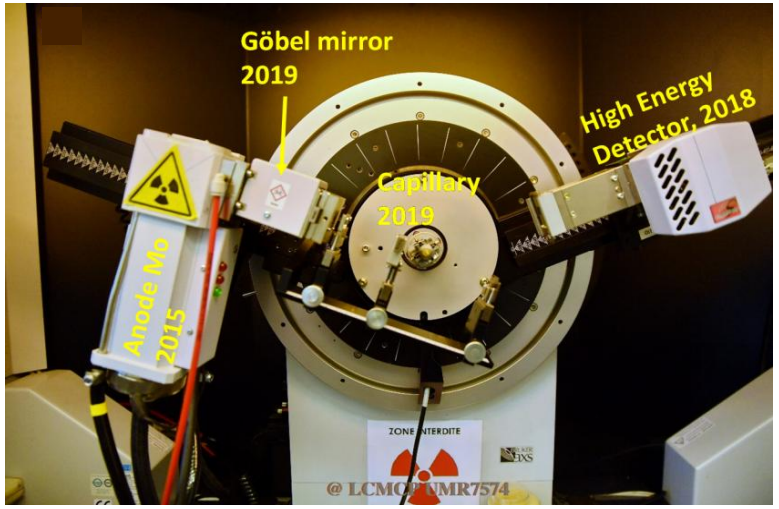


Green Chem 2011

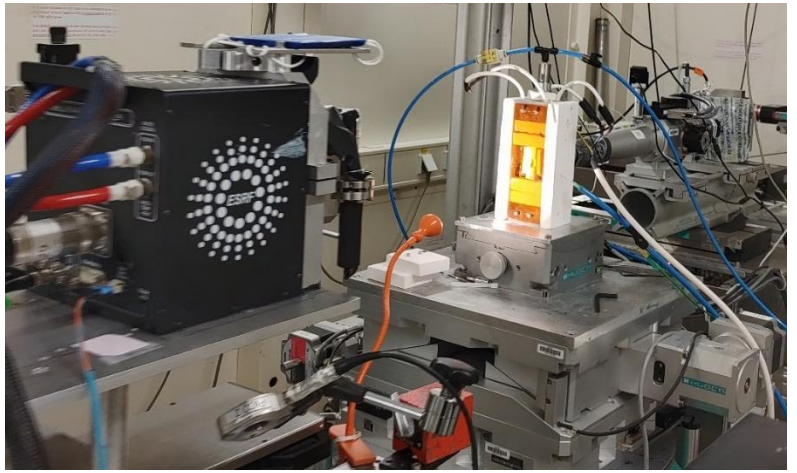


Tool to identify / describe the structure?

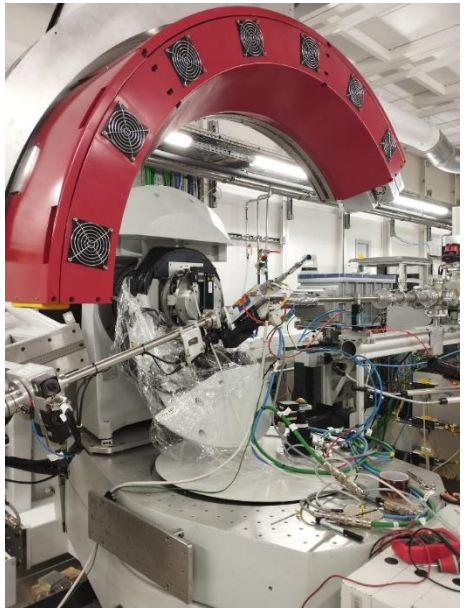
➡ **Pair Distribution Function Analysis**



D8 Advance : autonomy
Acquisition time : ~48h
try more experiments
prepare synchrotron beam time



ID11, ESRF
Acquisition time = few seconds



Diffabs, SOLEIL
Acquisition time = few minutes

When do we need Pair Distribution Function?

When XRD is insufficient to describe solid structure and explain/understand material properties

In our team, NANO (Novel Advanced Nano Objects) various solids - https://lcmcp.science/nano/

Among them….

Ultra small NP that are too small to diffract

Ni/NiO species on SiO_2 support for catalysis
Appl. Catal. B 2021, doi.org/10.1016/j.apcatb.2020.119417
ChemCatChem 2023, doi.org/10.1002/cctc.202300948

PDF

Well defined species

- Whose symmetry and organization is incompatible with its surrounding
- Rh MOP inside polymer matrix

(Cp*Rh, PW_{12})@UiO-67 for CO_2 photoreduction
J. Am. Chem. Soc. 2020, doi.org/10.1021/jacs.0c02425
Rh MOP
J. Am. Chem. Soc. 2022, doi.org/10.1021/jacs.1c12631

Phase purity / detection of non-crystallized impurities

SiCo nanoparticles
J. Am. Chem. Soc. 2023, doi.org/10.1021/jacs.3c01110
$Zn_4Si_2O_7Cl_2$
Angew. Chem. Int. Ed 2023, doi.org/10.1002/anie.202303487

Defects on the surface or core of crystalline NP

BP nanoparticles
see Clara Doisneau's poster N°1

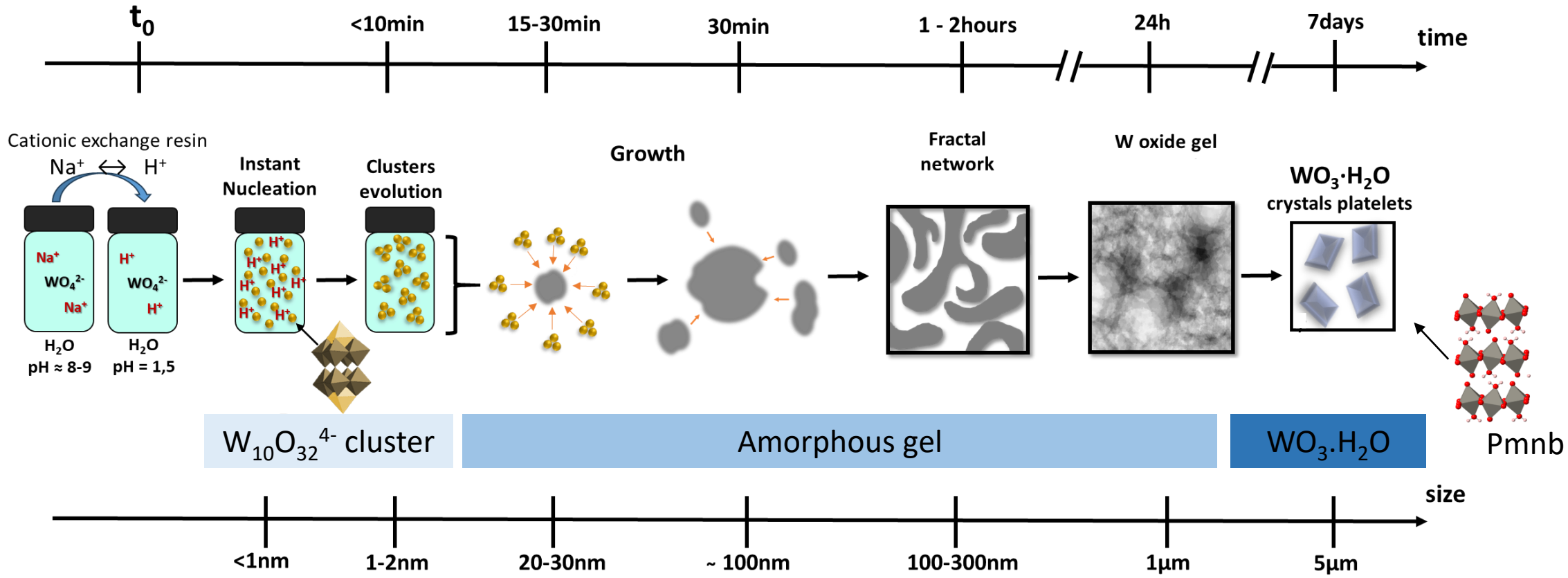
The $WO_3.H_2O$ case

Local order in amorphous materials

Short and long range order in crystalline material

WO_3 powders

WO_x for photo/electro-catalysis, electrochromism, energy storage…



Charles Sidhoum s' thesis – 2023 : Synthesis, **in situ liquid TEM**, DLS, SAXS, NMR

Morphological & kinetic evolution

Chem. Mater 2025, doi.org/10.1021/acs.chemmater.4c03003

Questions

Julien TREBOSC
Centre RMN haut Champs
(Université de Lille)

About the amorphous gels:

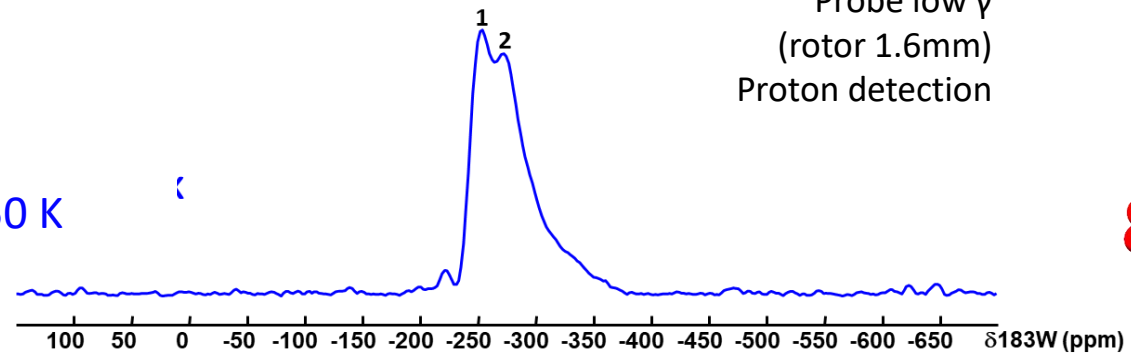
- Why 2 behaviours between hours and days samples?
- Can we describe the amorphous structure?
- Is it a progressive crystallisation or does intermediate phases exist?

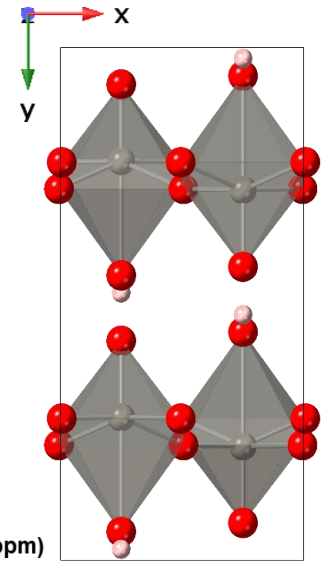
About the final $WO_3.H_2O$ structure:

^{183}W MAS NMR spectrum

B_0 19,04 T (800MHz)
ν_{rot} 35kHz
Probe low γ
(rotor 1.6mm)
Proton detection

T = 250 K



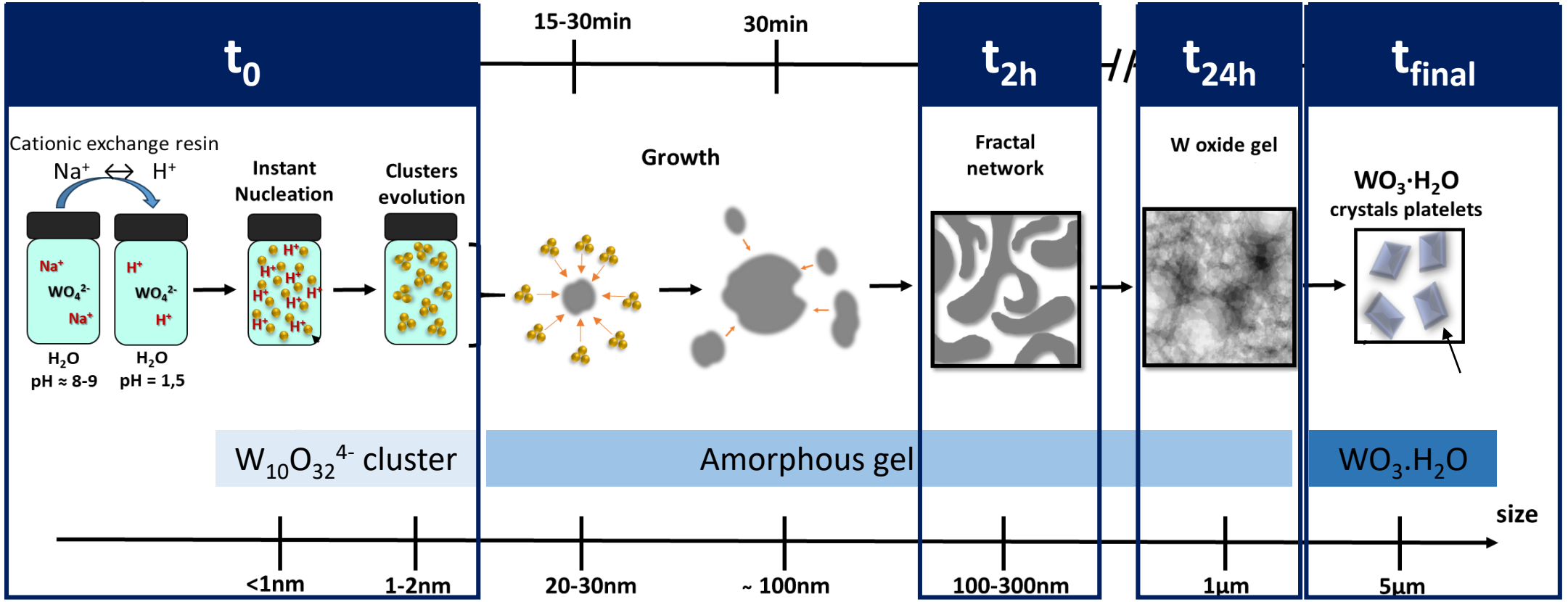


Presence of more than 1 W site ,
Whereas the crystallography indicates only one W

- Two phases?
- Local distortion?

Selected WO_3 powders

from Freeze drying at specific time

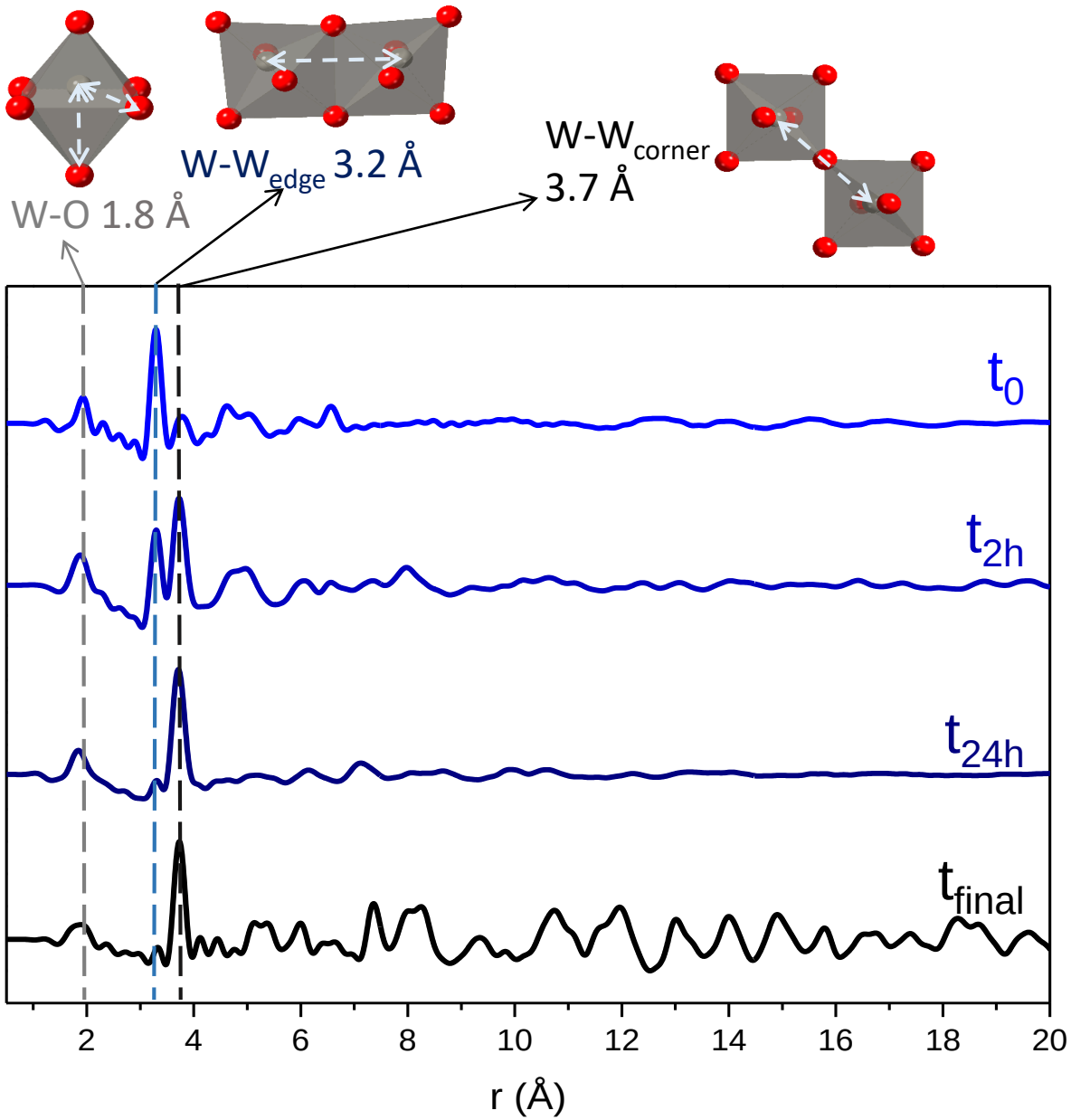


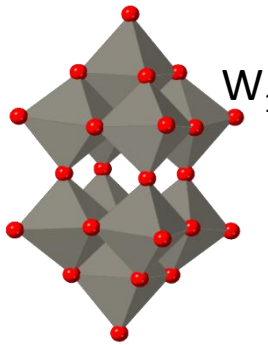
already prepared
$W_{10}O_{32}^{4-}$ cluster

Experimental PDF analysis

ID11
Pierre-Olivier AUTRAN
ESRF The European Synchrotron

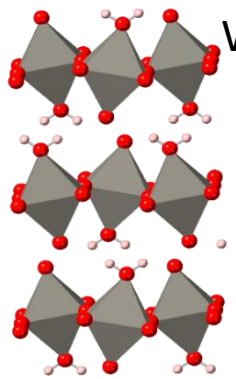
Qmax = 22 Å^{-1}





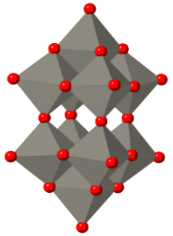
W-W$_{edge}$ + W-W$_{corner}$

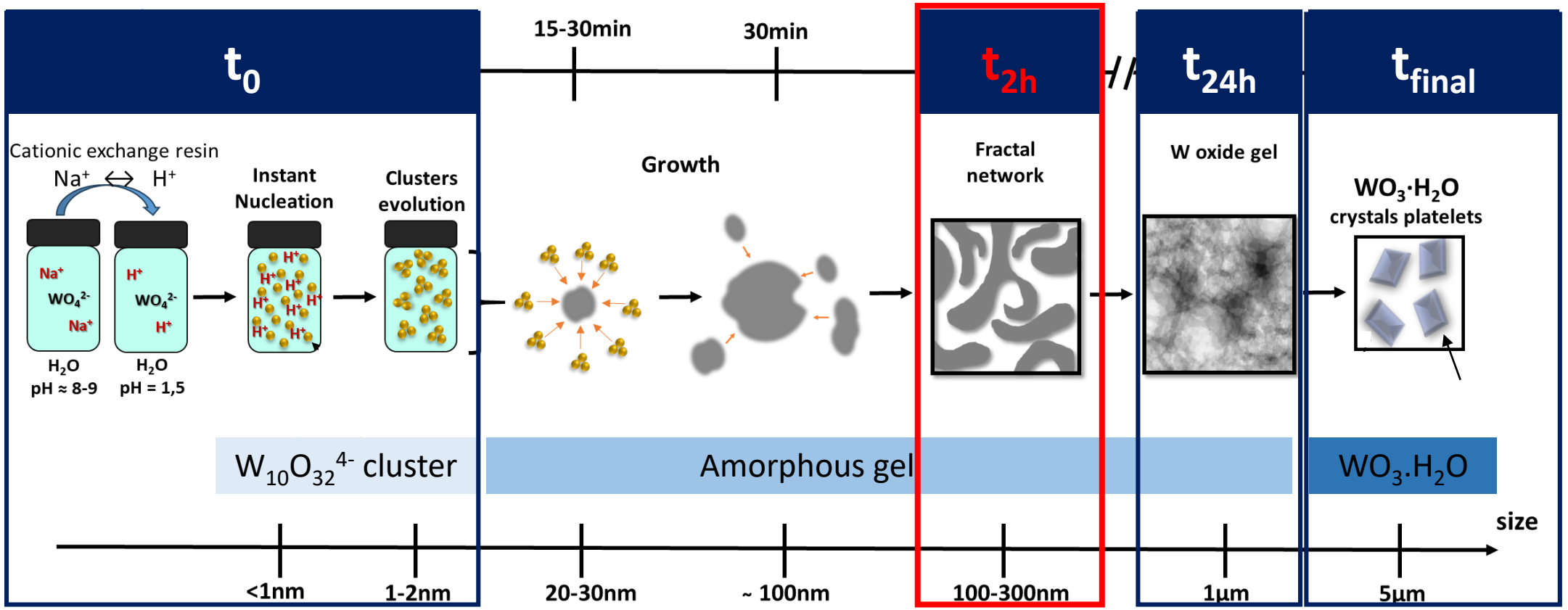
W-W edge-sharing ↘
W-W corner-sharing ↗



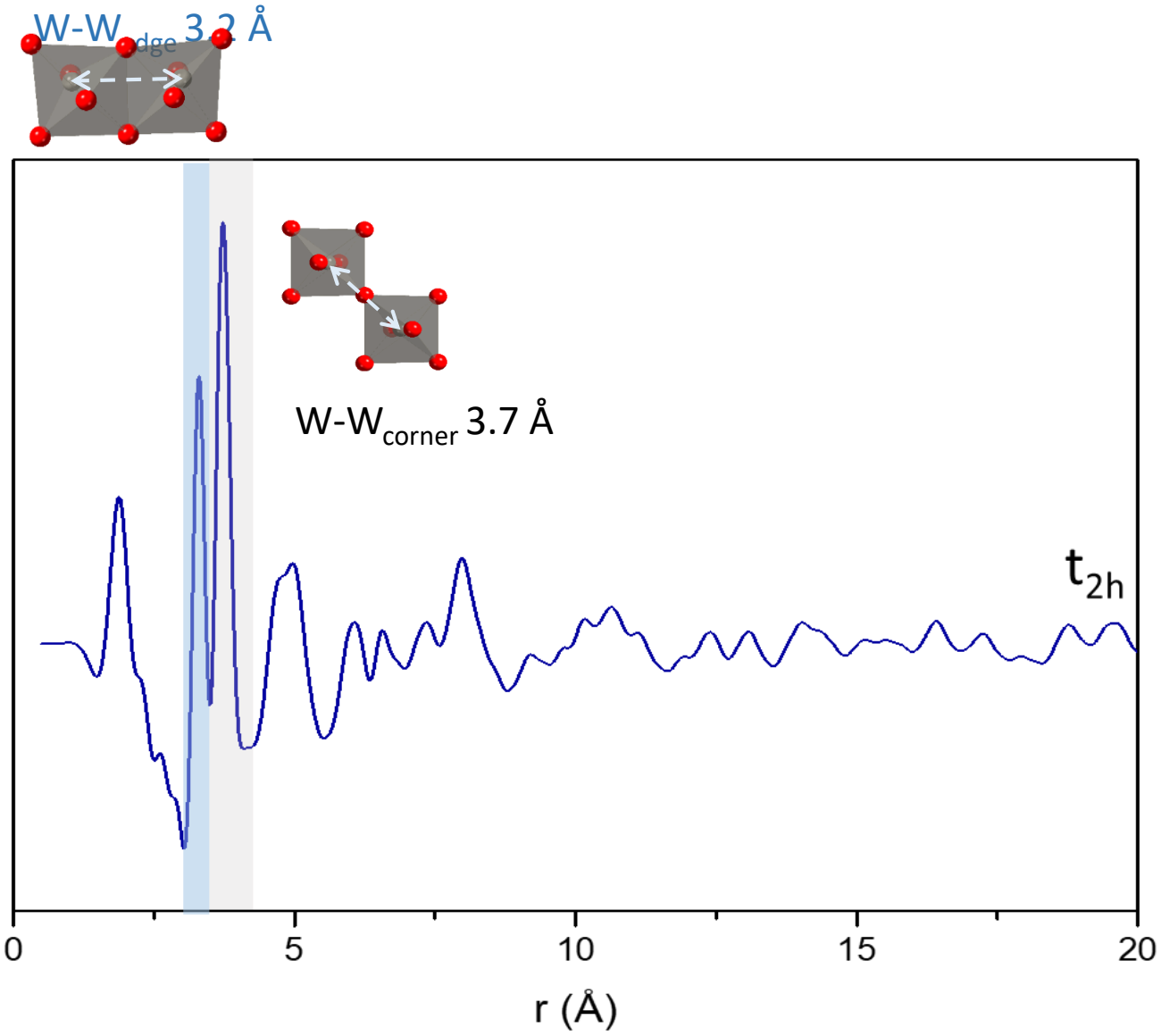
Only W-W$_{corner}$

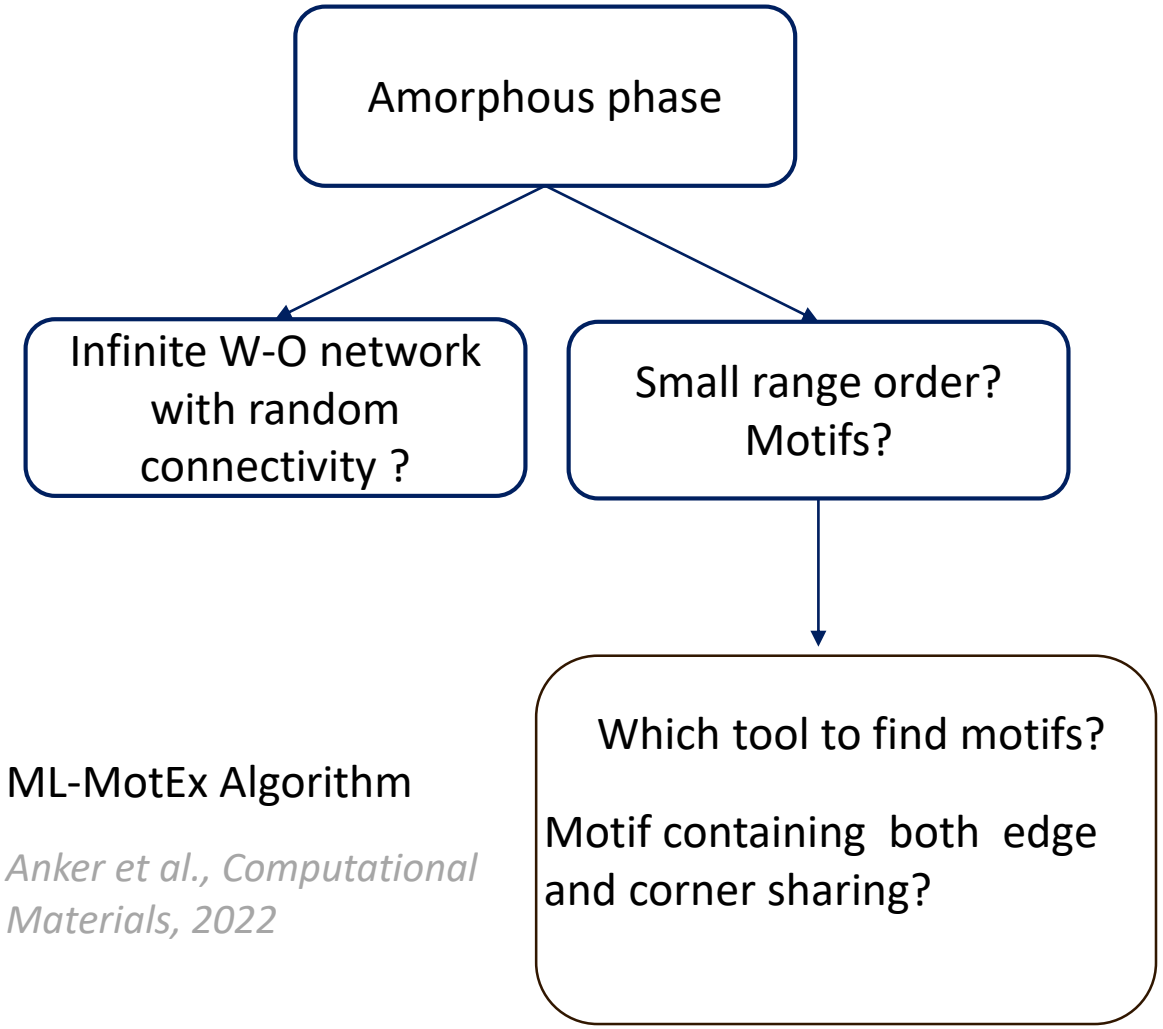
T_{2h} amorphous gel





T_{2h} amorphous gel



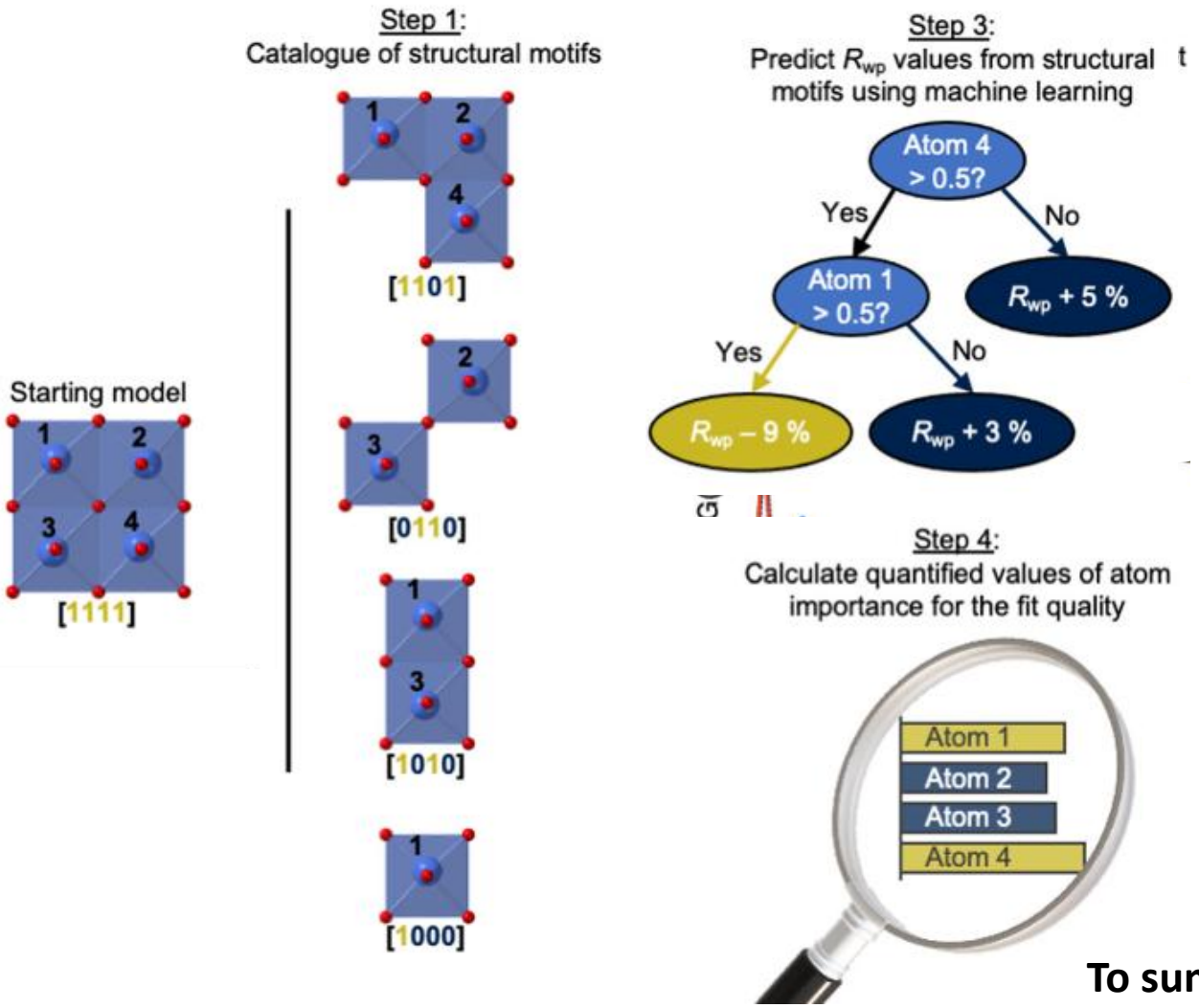


ML-MotEx Algorithm

Anker et al., Computational Materials, 2022

ML-MotEx: Machine Learning-Motif Extractor

Anker et al., Computational Materials, 2022



Step 1

- Produce a catalogue of structure motifs (From starting model)

Step 2

- Fit each structure => R_w value

Step 3

- Train the algorithm to predict the R_w value based on the structure catalogue
  80% as training, 20% as validation of the data

Step 4

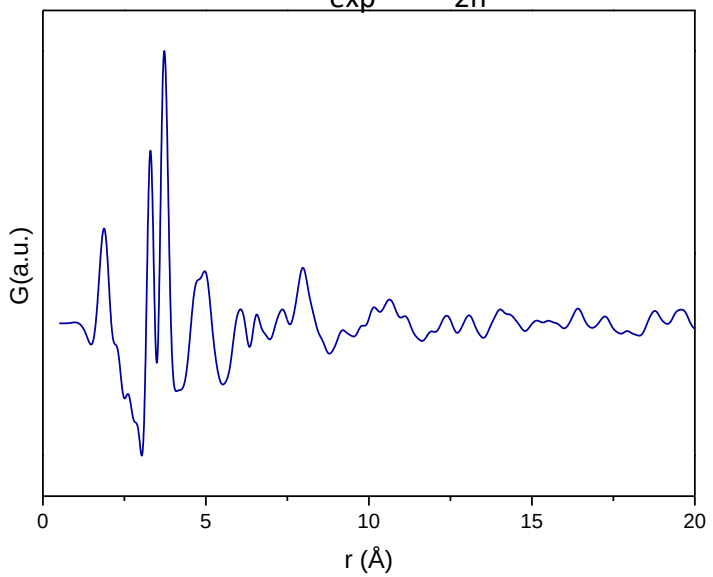
- Calculate SHAP values for all features
- Gives all the atom contribution values

To summarize, ML-MotEx tells us if an atom should be kept or not in the final motif

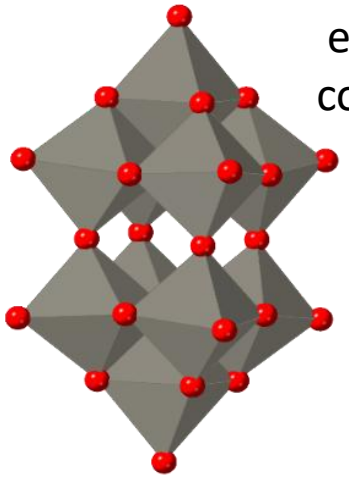
T_{2h} ML-MotEx

input

PDF$_{exp}$ of t_{2h}

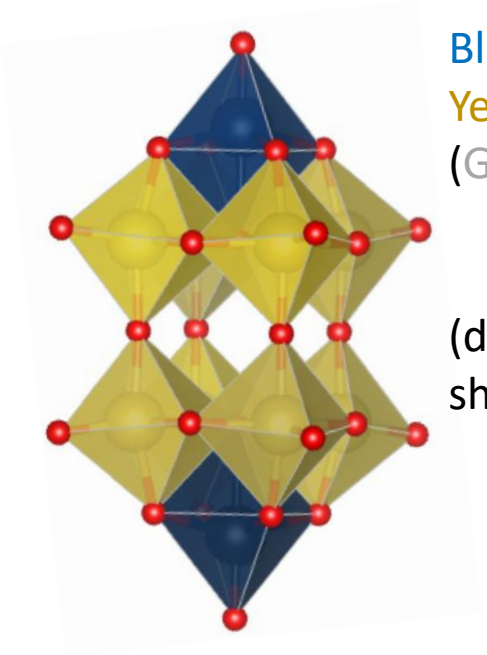


Starting model $W_{10}O_{32}^{4-}$ (t_0)



edge and corner sharing

ML-MotEx



Blue atoms: to remove
Yellow atoms: to keep
(Grey atoms: neutral)

(decrease the number of edge sharing octahedra)

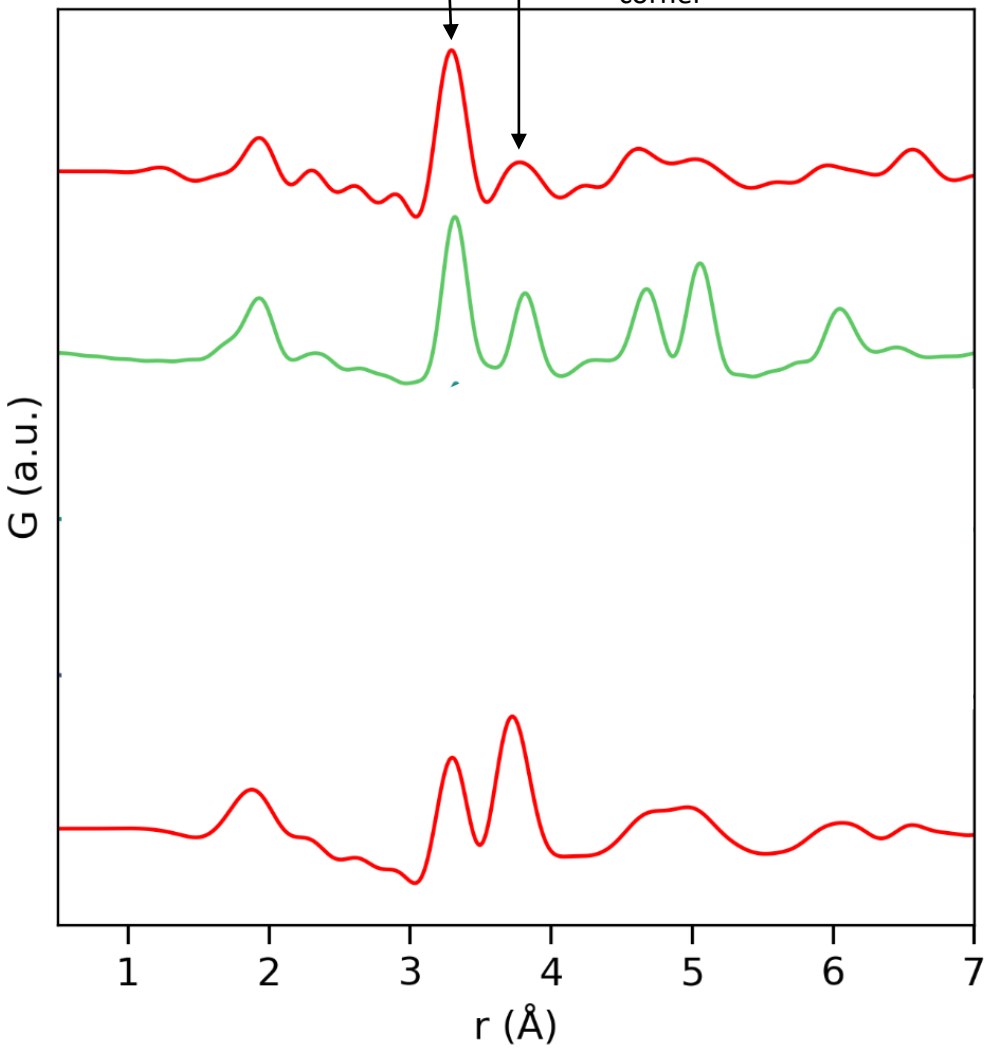
Preliminary test - successful

W_8O_{30} motif

T_{2h} : can we go further?

W-W_{edge}

W-W_{corner}



t_0 exp

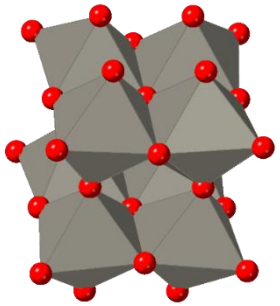
W_8O_{30}

5 W_8O_{30}

W_8O_{30} + 8 octahedra

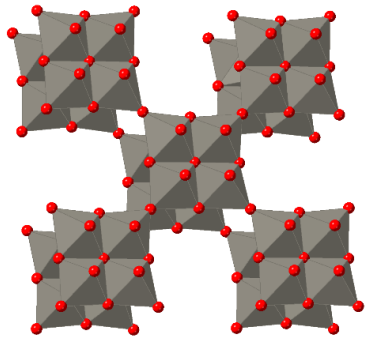
t_{2h} exp

W_8O_{30}

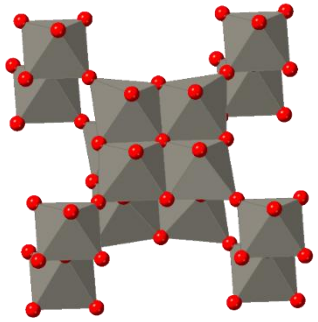


Lack of W-W corner sharing octahedra in the model

5 W_8O_{30}



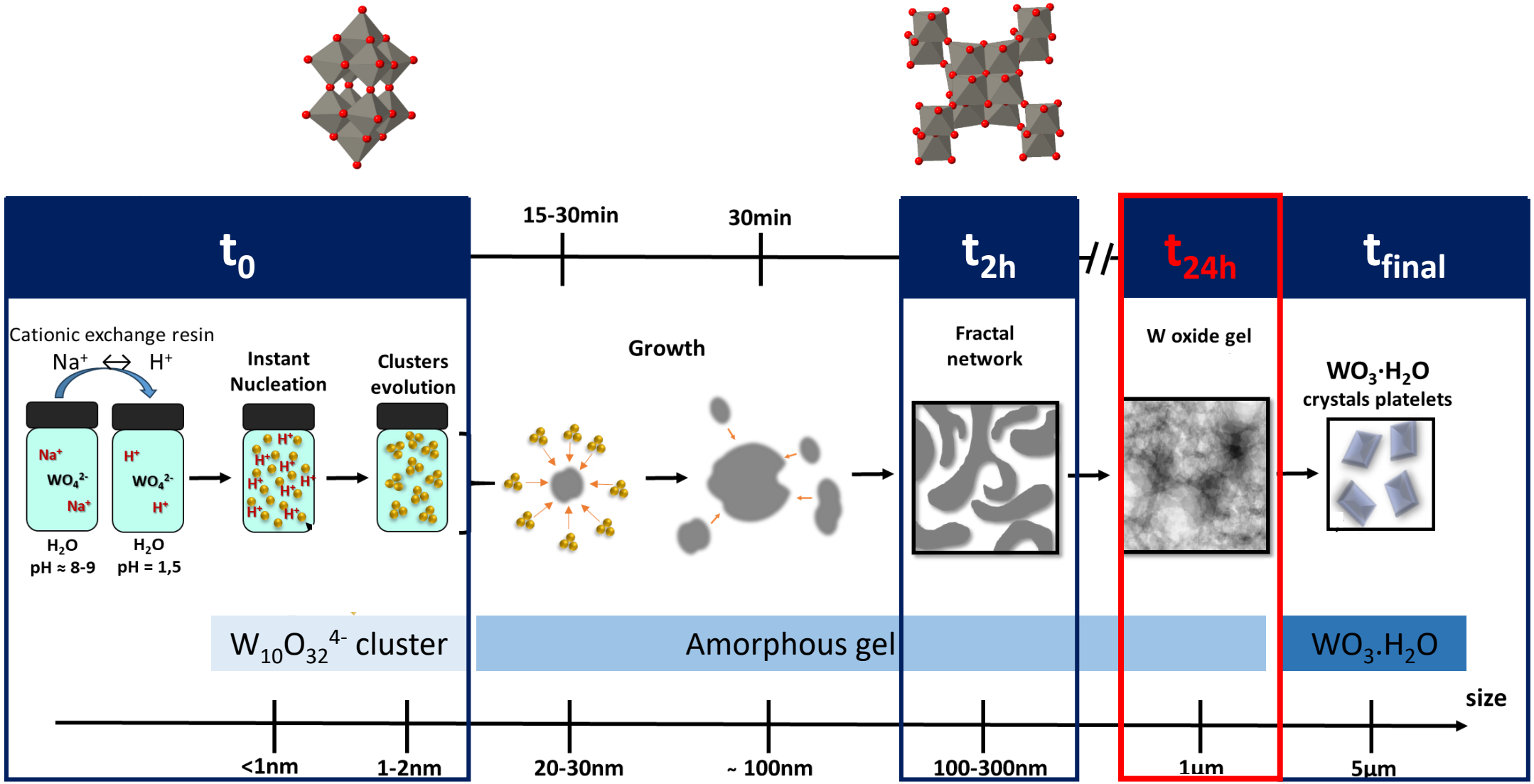
W_8O_{30} + 8 octahedra



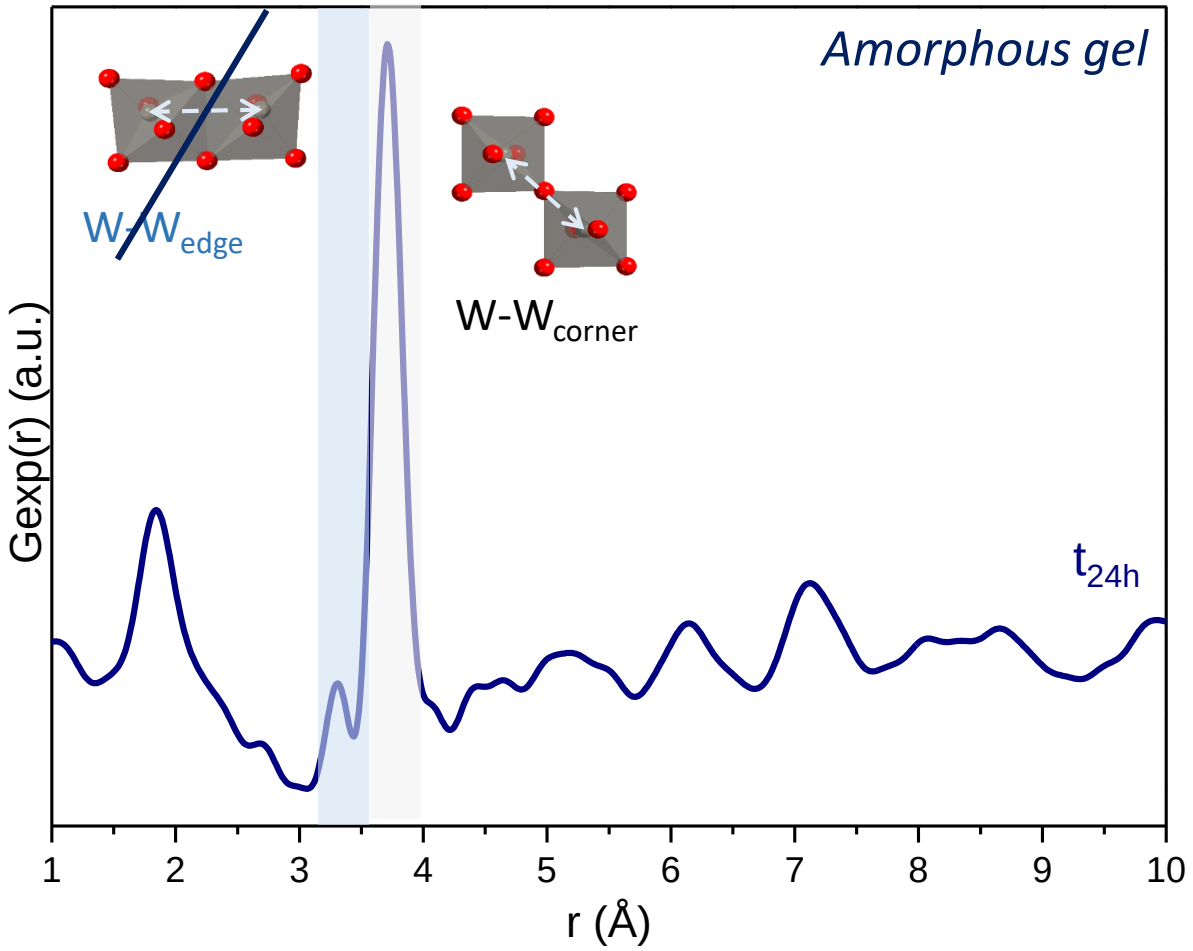
After 2h, W_8O_{30} surrounded by octahedra motif

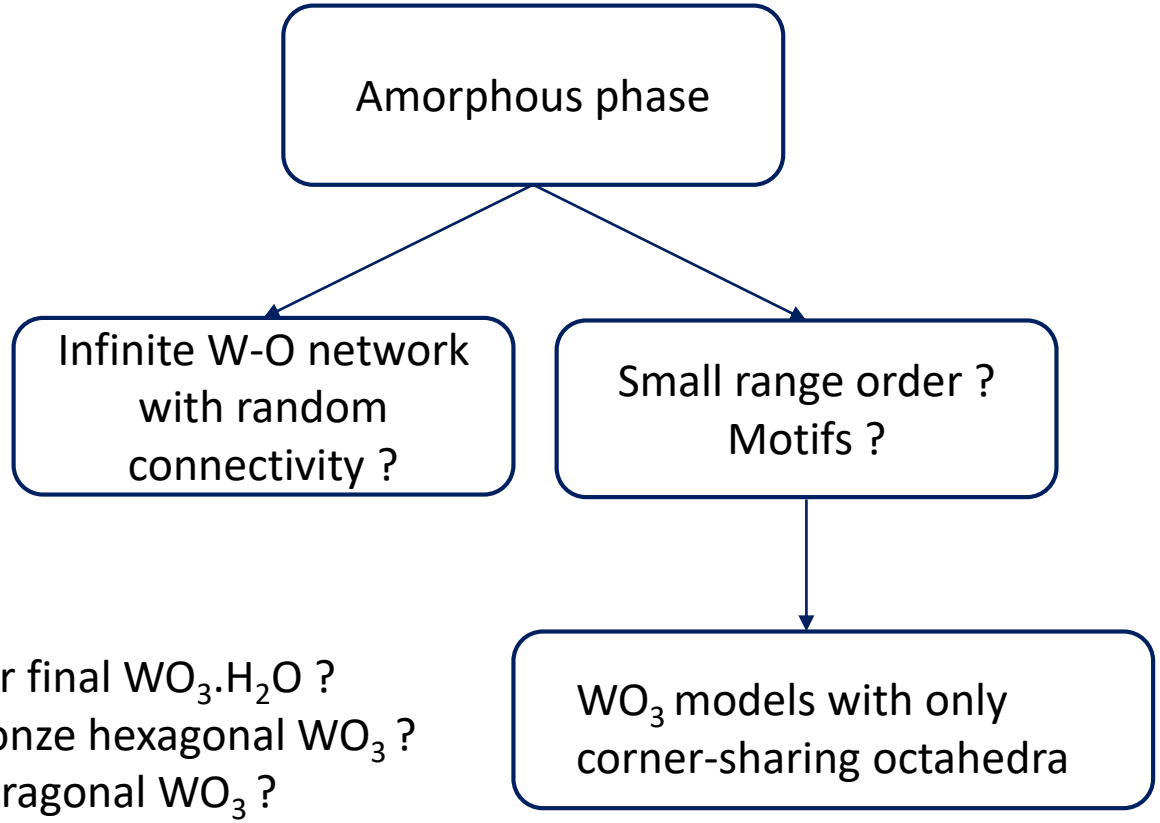
(in accordance with the fractal aspect in TEM and SAXS)

Amorphous gel t_{24h}



Amorphous gel t_{24h}





Our final $WO_3.H_2O$?
Bronze hexagonal WO_3 ?
Tetragonal WO_3 ?

Build simple models first

Home made cluster models for t_{24h}

Hydrate Orthorombic WO_3 2D

Bronze Hexagonal WO_3 3D

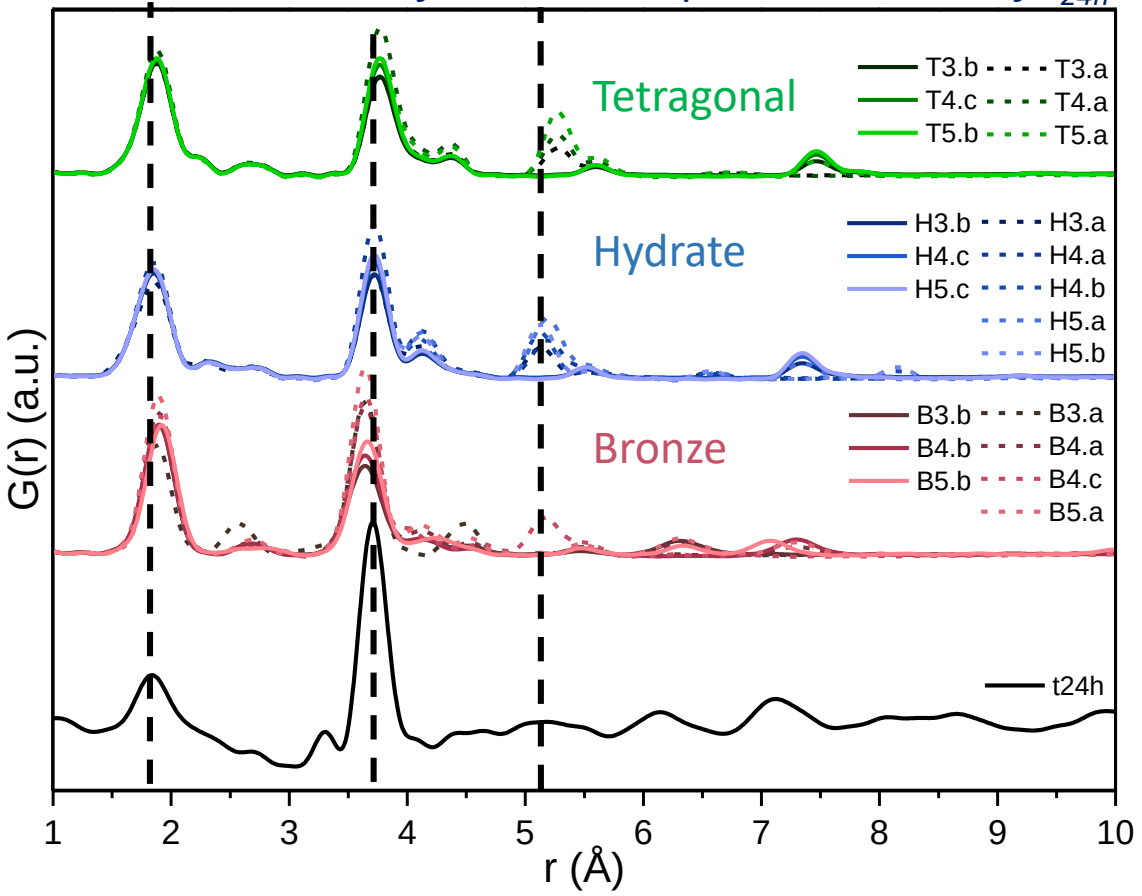
Tetragonal WO_3 3D

Compact / linear clusters

t_{24h} – Calculated vs experimentl PDF

Dashed line: compact clusters
Straight line: linear clusters

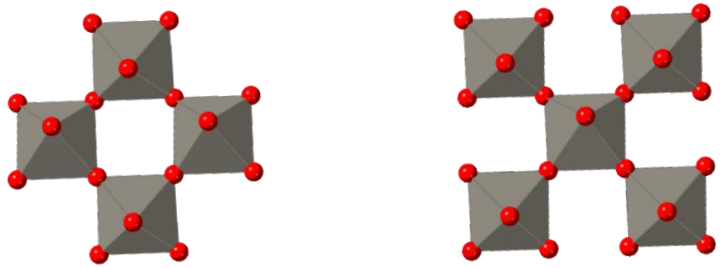
Calculated PDFs of clusters + Experimental PDF of t_{24h}



Hydrate Clusters

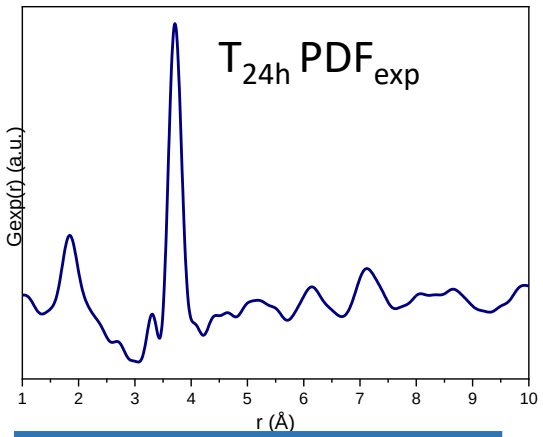
Compact clusters >> linear cluster

24h amorphous gel contains nuclei of $WO_3 \cdot H_2O$



t_{24h} ML-MotEx

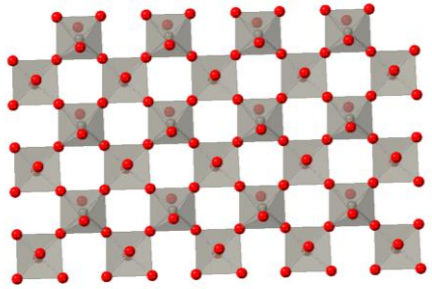
input



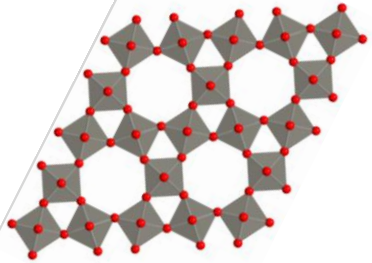
Larges slabs to observe the behavior

ML-MotEx

$WO_3.H_2O$ 2D

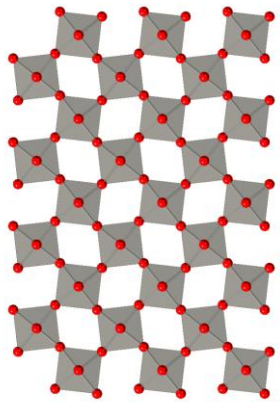


WO_3 Bronze 3D



Starting models

WO_3 Tetragonal 3D



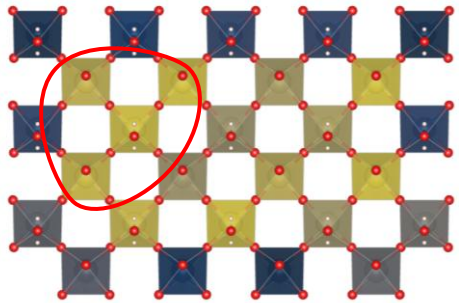
Hydrate structure: clear decrease of the chess board size.
Small yellow zone.

Bronze : no clusters!

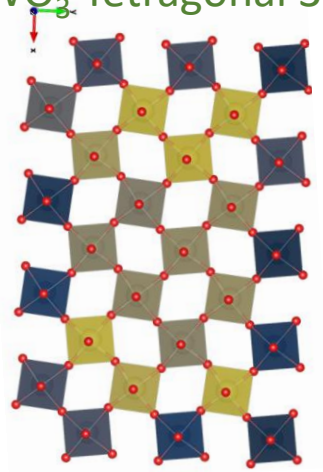
Tetragonal = reduction of the area. Less contrast in the center

Less conclusive
In accordance with of our previous home made models

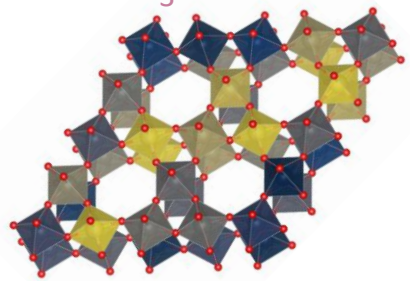
$WO_3.H_2O$ 2D



WO_3 Tetragonal 3D

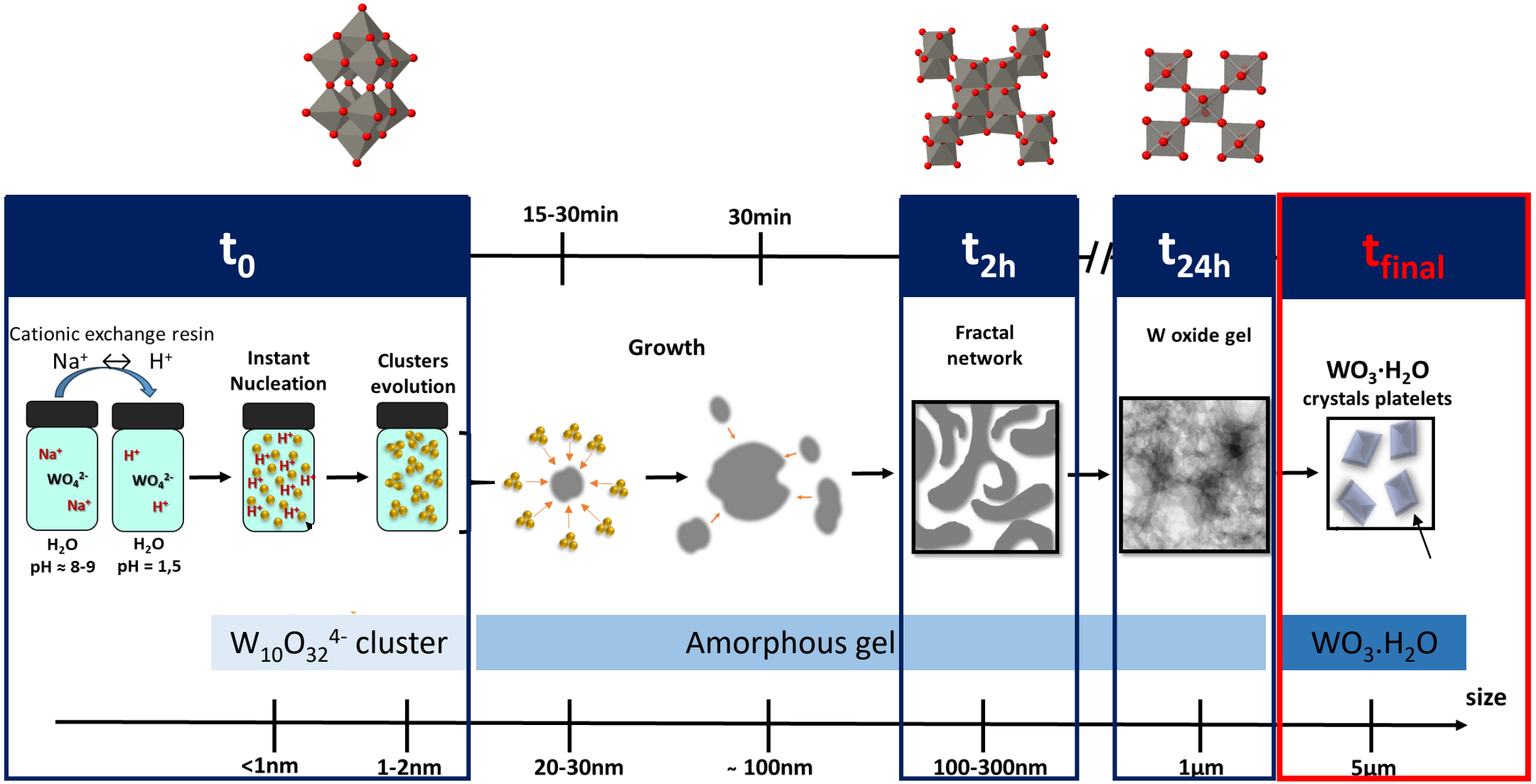


WO_3 Bronze 3D

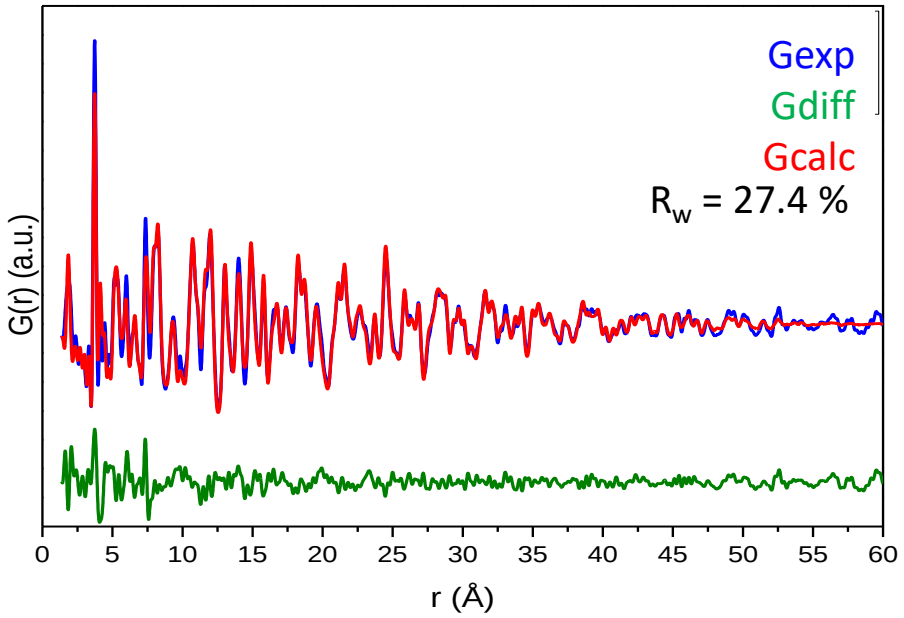


Blue atoms: to remove
Yellow atoms: to keep
(Grey atoms: neutral)

t_{final} crystalline powder



t_{final} pdf refinement



1.6 – 60 Å pdf refinement not good enough

- Middle range order (10-50 Å) fine
- Small (r<10 Å) and long (r>50 Å) range order not well described

2 phases?

$WO_3.H_2O$ crystalline

+

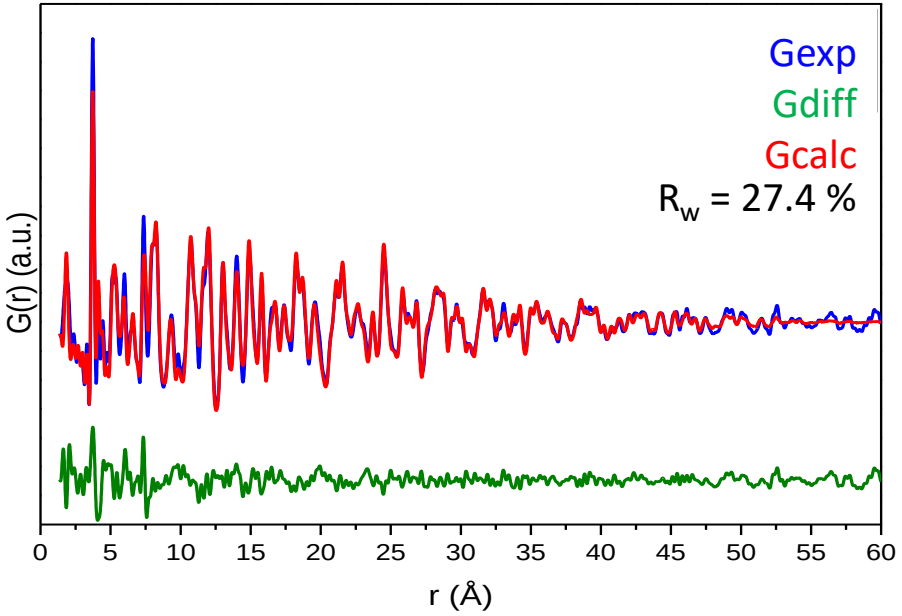
$WO_3.H_2O$ amorphous

1 phases with local distortion?

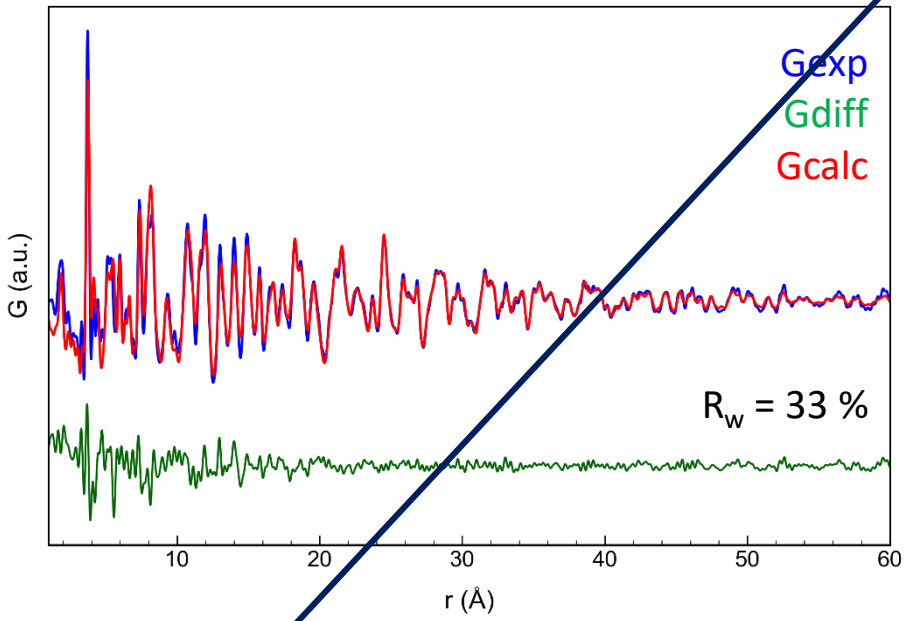
M. Juesholt et al. J. Phys. Chem. C 2019

M. Juesholt et al. Inorg. Chem. 2023

t_{final} pdf refinement - 2 phases hypothesis



1 phase refinement from 1.6 to 60Å
= reference

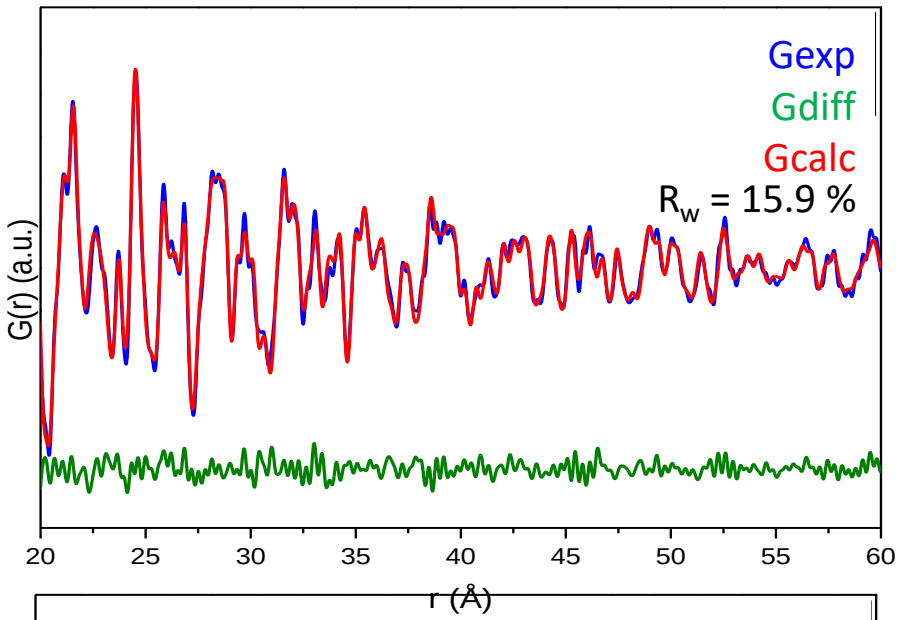


2 phases refinement 1.6-60 Å

56% crystalline $WO_3 \cdot H_2O$ (~90 Å)
44% "amorphous" $WO_3 \cdot H_2O$ (13 Å)

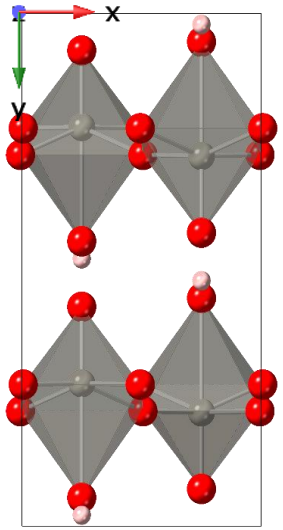
Not acceptable

t_{final} pdf refinement – 1 phase with local distortion

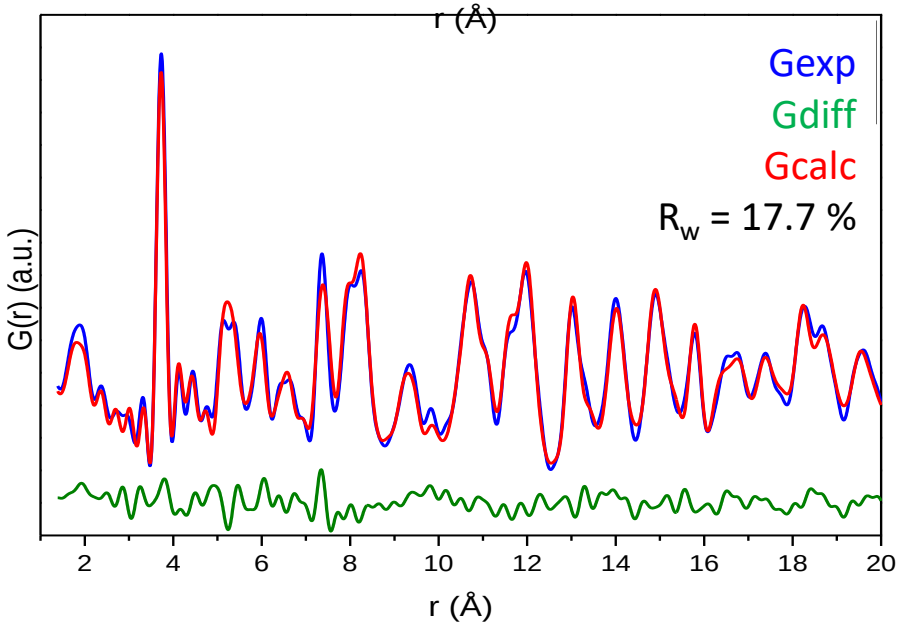


High range refinement
Pmnb
Allows W & O to move
in x & y

Close to the referenced structure :
4 identical distorted WO_6 octahedra
(W-O from 1.7Å to 2.2 Å)

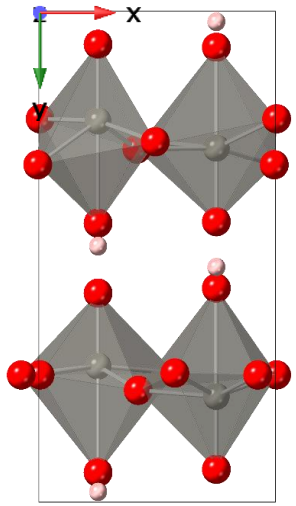


1 crystalline phase with local distortions



Low range refinement
P1
Allows W & O to move
in x & y

4 different and more distorted WO_6 octahedral (W-O between 1.6-2.4 Å)

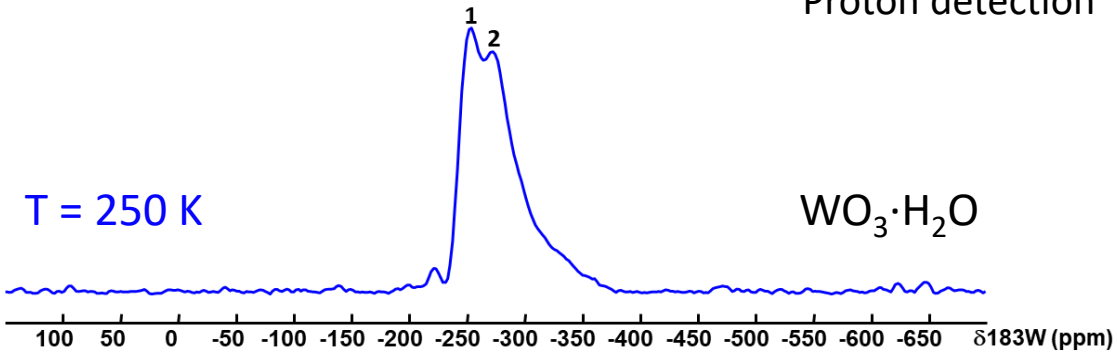


^{183}W NMR Confirmation

Julien TREBOSC
Centre RMN haut Champs
(Université de Lille)

^{183}W MAS NMR spectrum

B_0 19,04 T (800MHz)
ν_{rot} 35kHz
Probe low γ
(rotor 1.6mm)
Proton detection

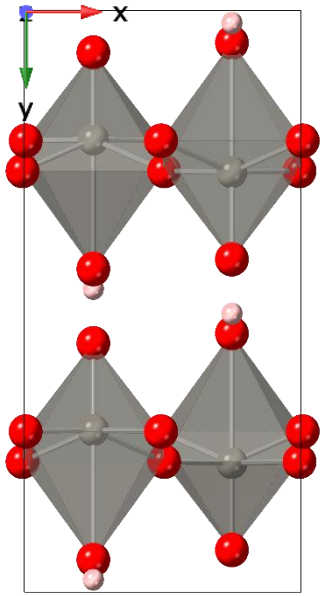


T = 250 K

$WO_3 \cdot H_2O$

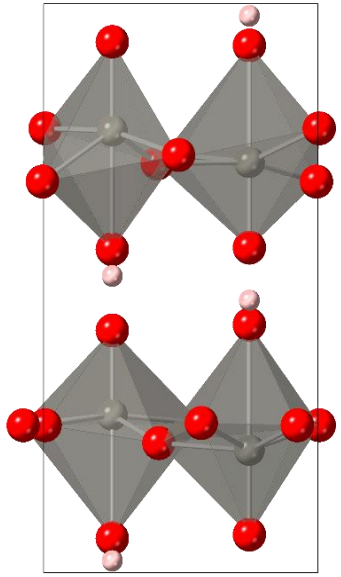
Presence of more than 1 site
Coherent with PDF results

Without distortion



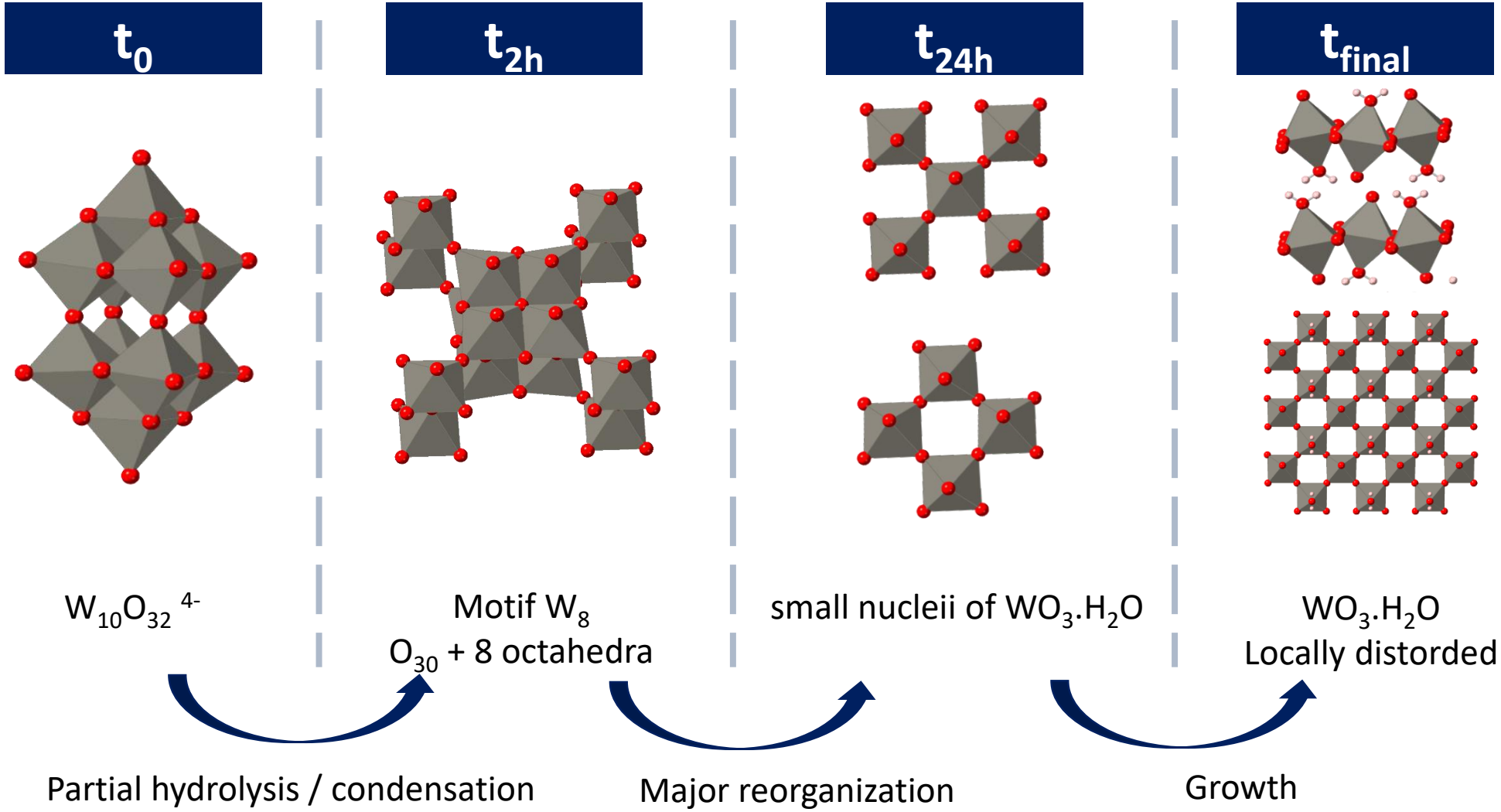
1 site of W

With distortion



4 different sites of W

Conclusion



Perspectives : Relaxation on the models – find other relevant tools for model - publication

Thanks to….

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Poster n°1