The Electrical Chemistry of Historical Oil Paintings

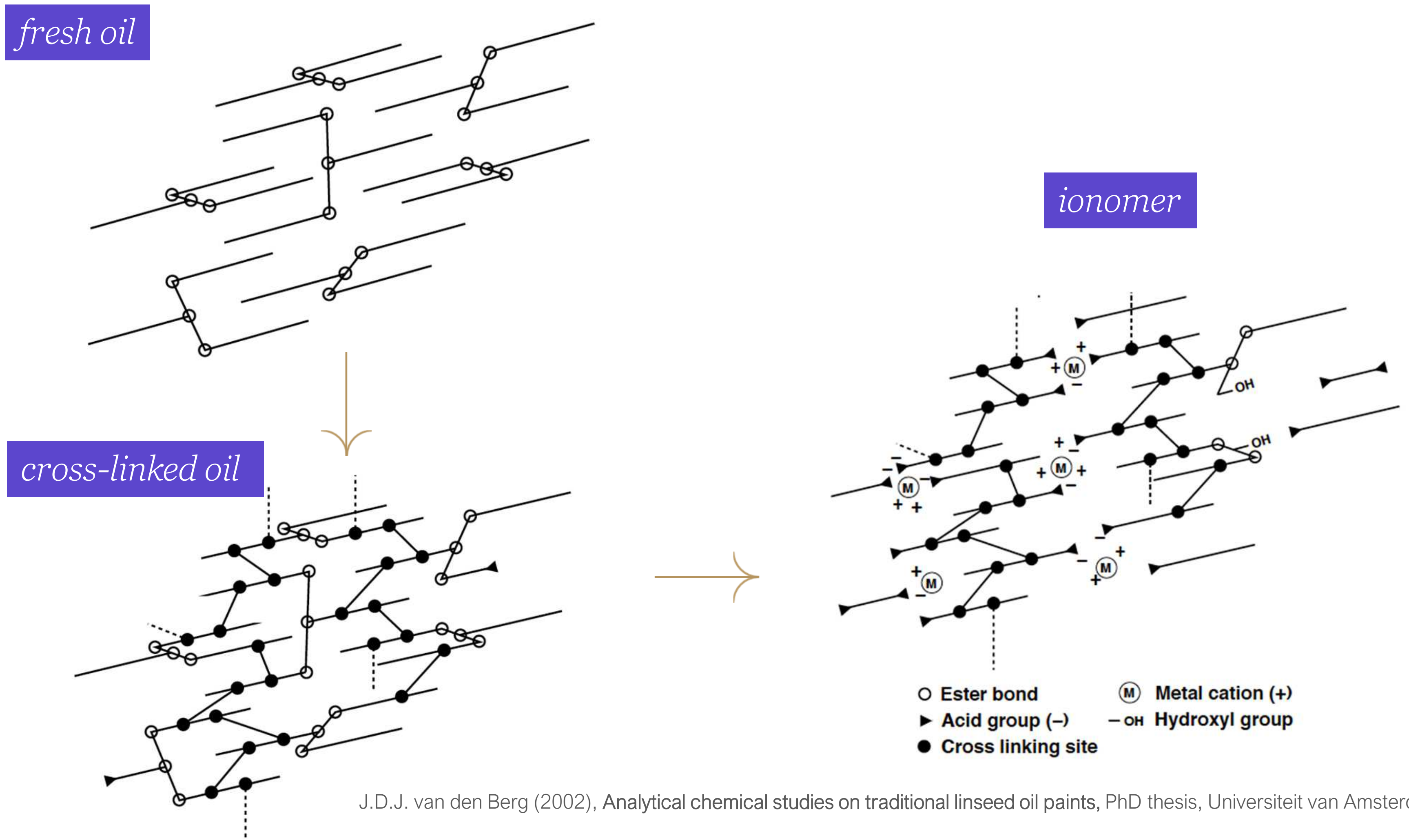
Dielectric properties** of aging **oil binders**, the role of **water**, and potential links to degradation compound **ionic exchange** and **migration

Beatrice Boracchi, Angelos Gkogkos,
Evgeniia Grzheshchuk, Samuel Bertolini Da Silva O.,
Prof. Isabelle Huynen, Prof. Arnaud Delcorte,
Dr. Francisco Mederos-Henry

Scientific Methods in Cultural Heritage Research
Gordon Research Conference
July 14 2026 - Les Diablerets Conference Center

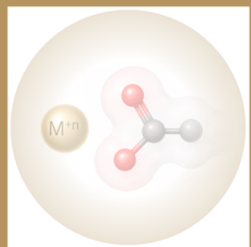
Royal Institute for Cultural Heritage
UNIVERSITÉ LIBRE DE BRUXELLES
UCLouvain

From a fresh siccative oil to an ionomeric paint film…



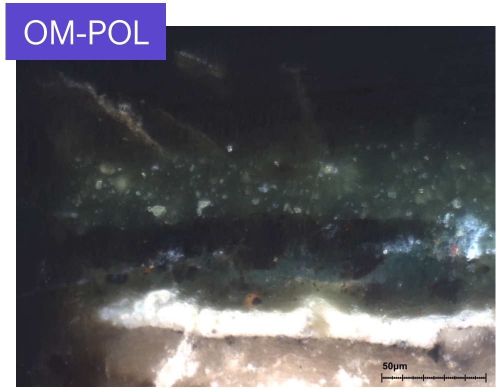
J.D.J. van den Berg (2002), Analytical chemical studies on traditional linseed oil paints, PhD thesis, Universiteit van Amsterdam

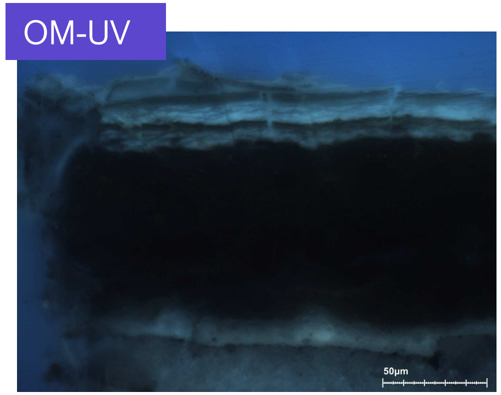
Evidence of ionic exchange & migration in oil paint films



Ionic migration within oil paint films

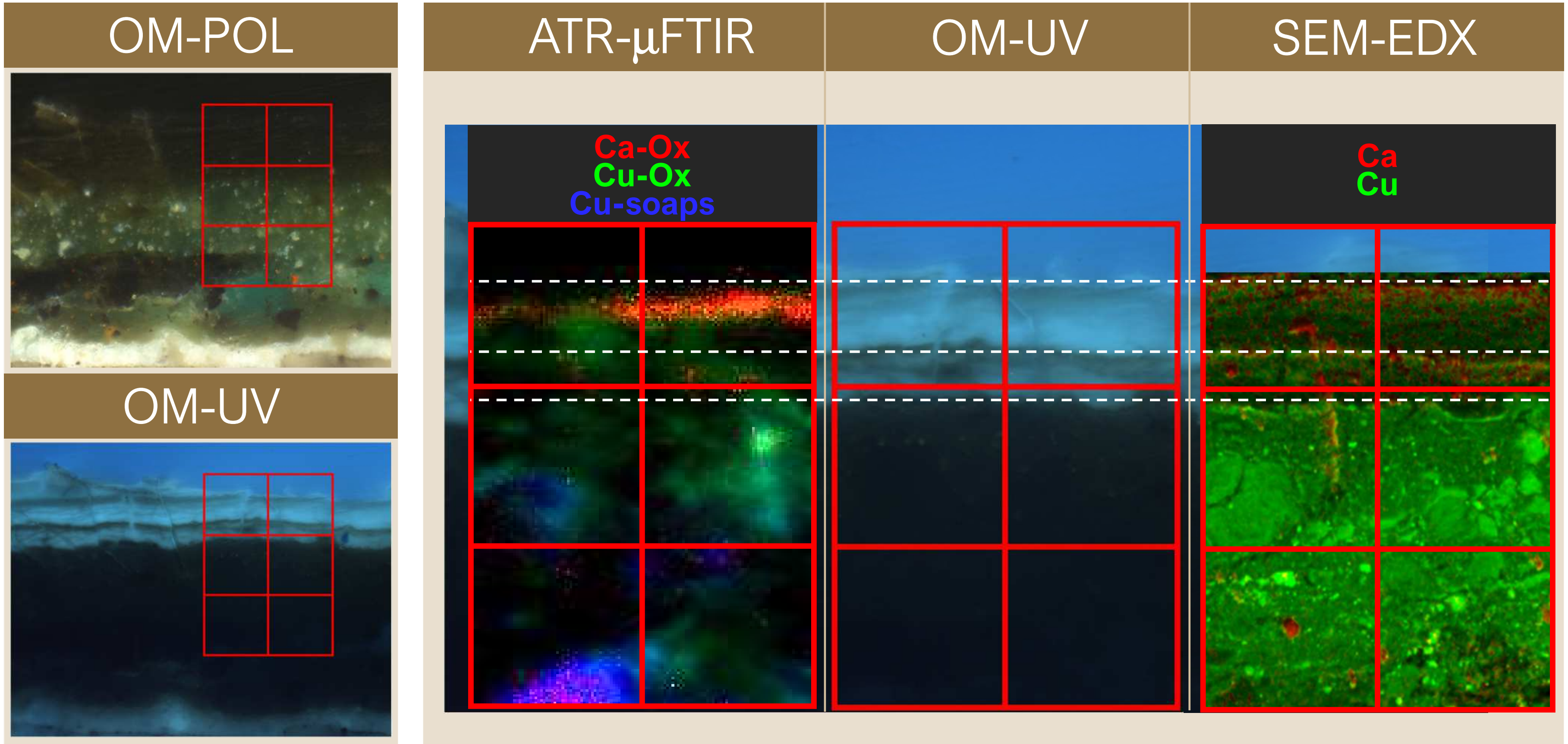
Petrus Christus (1455-1460), ‘The Lamentation’ (*Pietà*), Oil on wooden panel, 98 x 188 cm, Royal Museum of Fine Arts of Belgium





MetOx

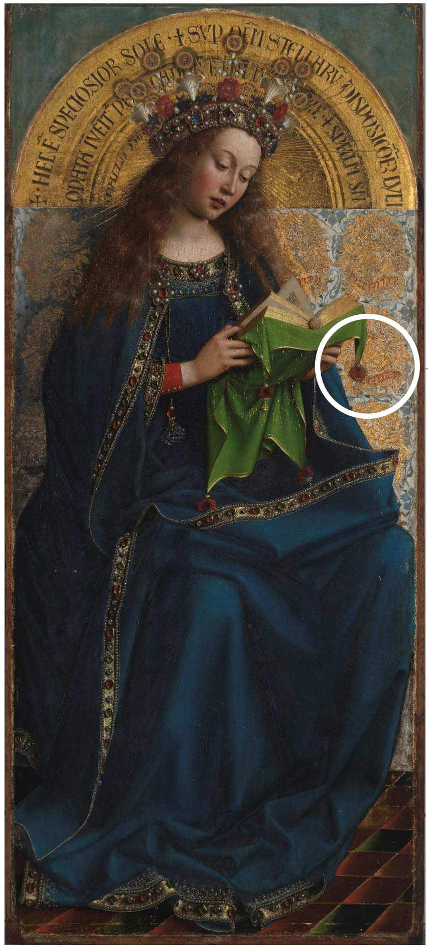
Ionic migration within oil paint films > Cu^{+2} enriched varnishes

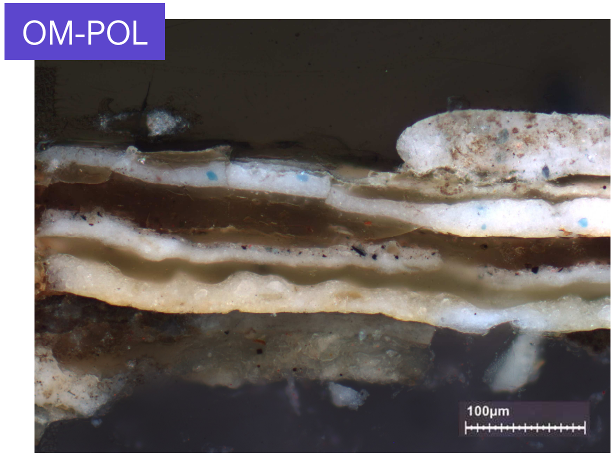


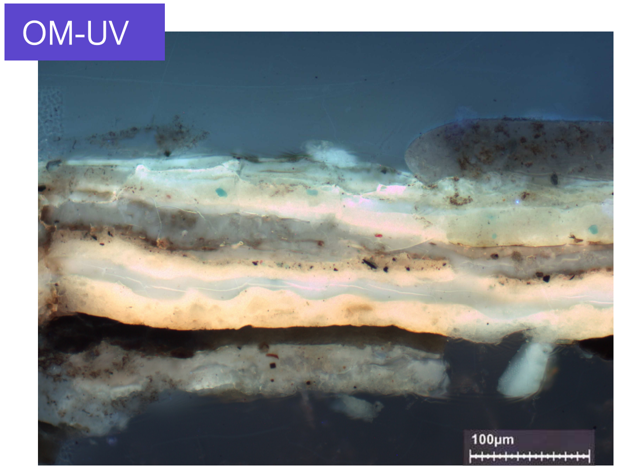
Ionic migration within oil paint films

Jan & Hubert van Eyck (1432), 'The Adoration of the Mystic Lamb', Oil on wooden panel, 520 x 1375 cm

Ionic migration within oil paint films





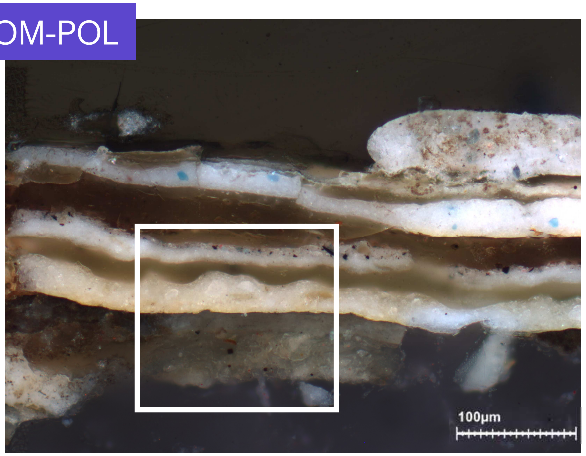


P033_058 / C007_017

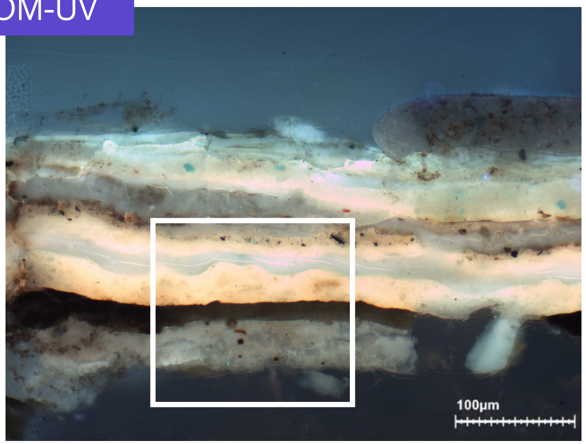
Jan & Hubert van Eyck (1432), '3. Virgin Enthroned', Oil on wooden panel, 168.7 x 74.9 cm

Ionic migration within oil paint films > Sn^{+x} enriched fillers

OM-POL

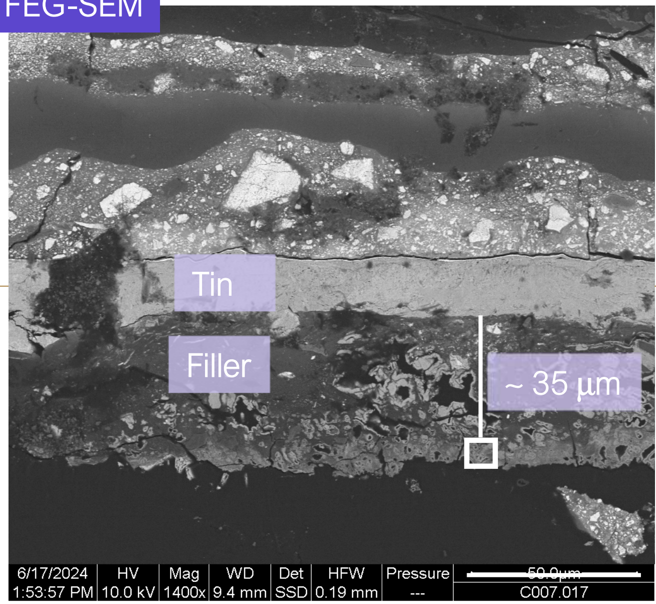


OM-UV



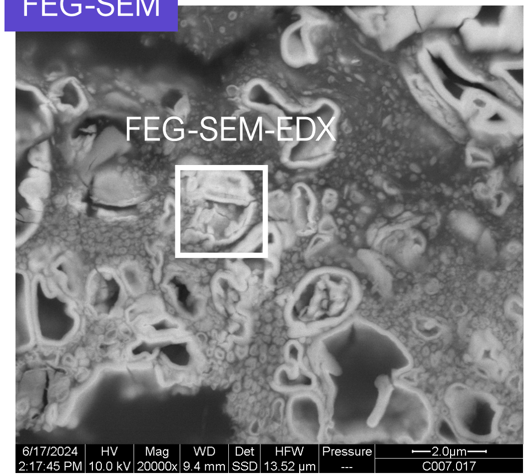
P033_058 / C007_017 © KIK-IRPA

FEG-SEM

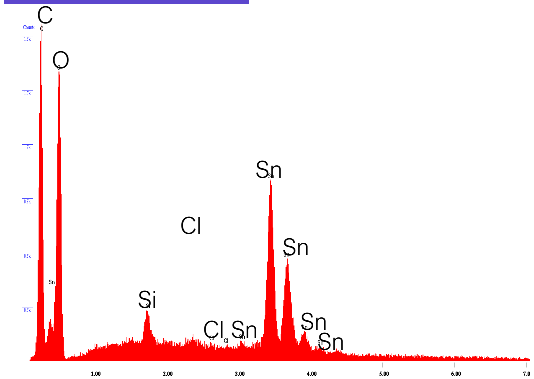


S. Kirkpatrick *et al.* (2026)
https://doi.org/10.21203/rs.3.rs-9941906/v1

FEG-SEM



FEG-SEM-EDX

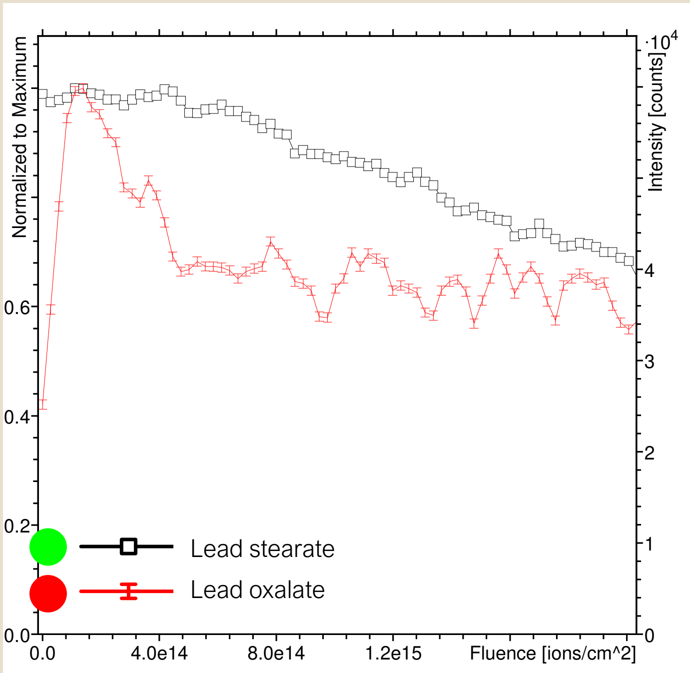


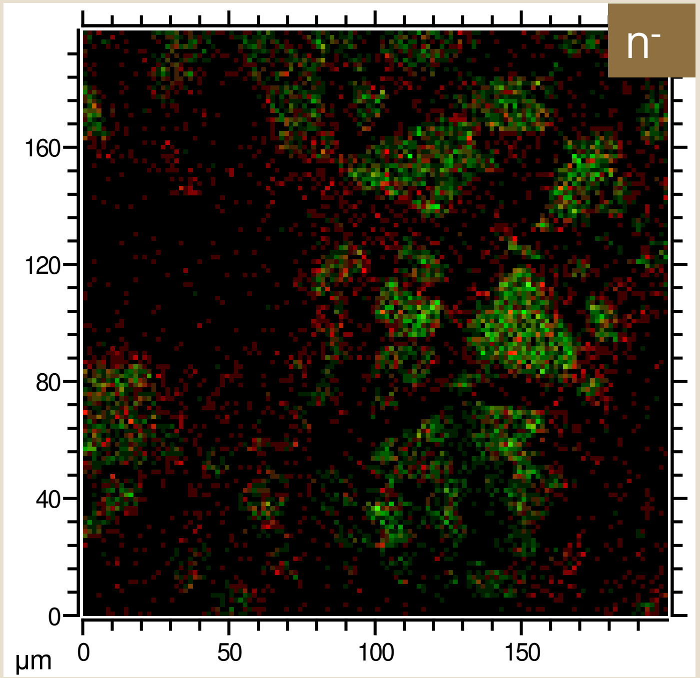
MetOx

Ionic exchange within oil paint films > metal oxalates speciation

Lead stearate @ linseed stand oil

ToF-SIMS





MetOx

Ionic exchange within oil paint films > metal oxalates speciation

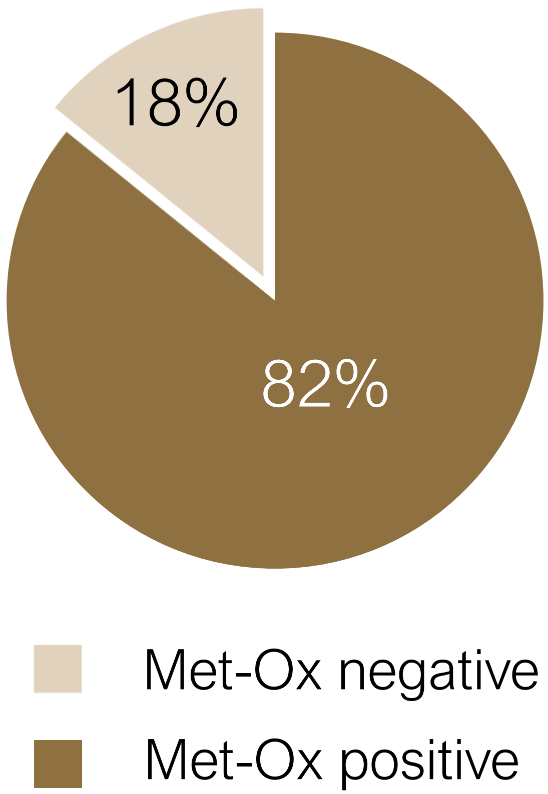
99 cross sections

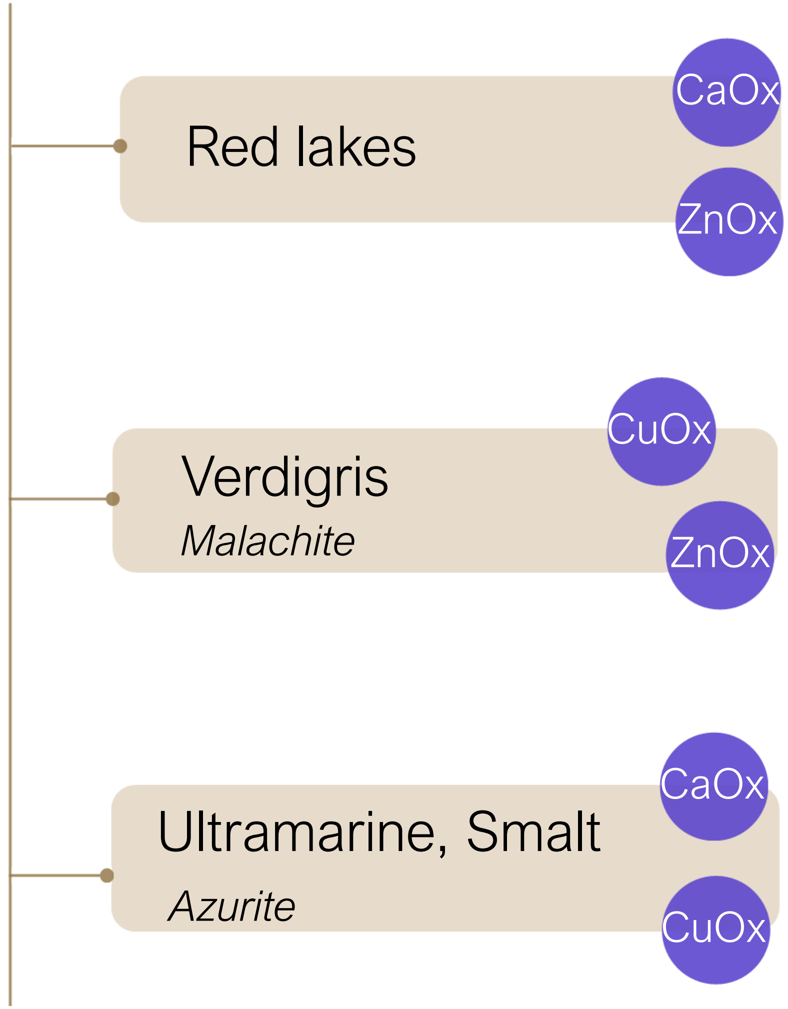
48 paintings

32 painters

15th-17th c.

199 analysis zones





COMMSOP

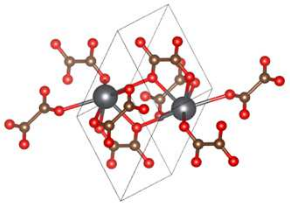
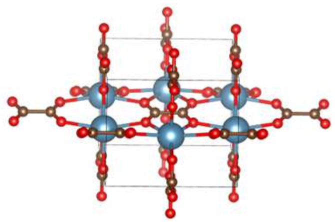
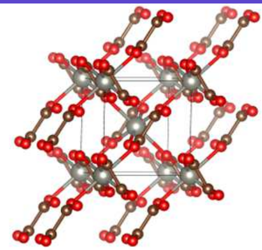
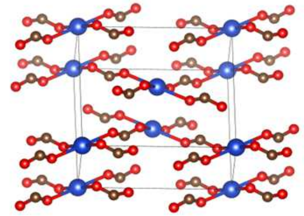
Ionic exchange within oil paint films > metal oxalates speciation

COMMSOP

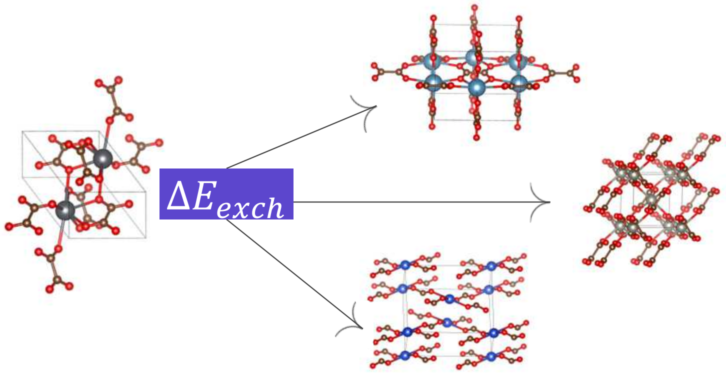
Ionic exchange within oil paint films > metal oxalates speciation

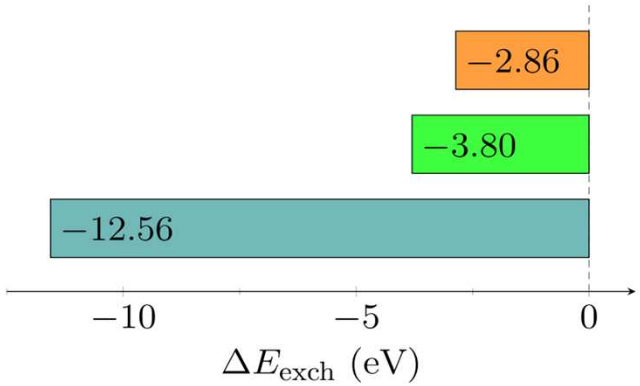
Angelos
GKOGKOS

Density functional theory (DFT) calculations of lattice enthalpies

PbC_2O_4	CaC_2O_4	ZnC_2O_4	CuC_2O_4
			
-52.2 eV	-103.4 eV	-56.2 eV	-204.0 eV

Density functional theory (DFT) calculations of ionic exchange enthalpies



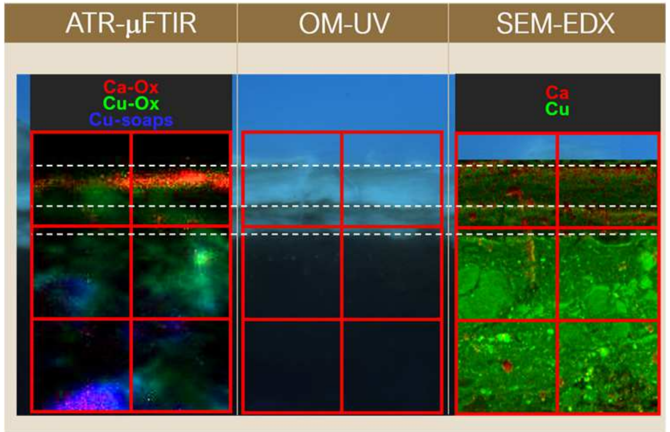


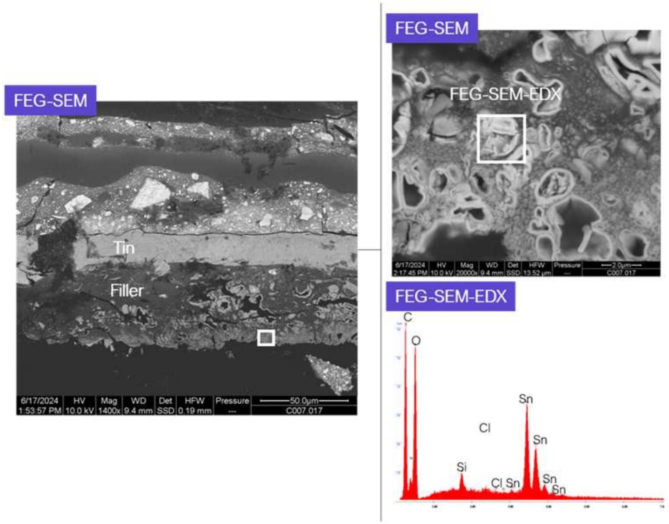
$PbC_2O_4 + Ca^{+2} \rightleftharpoons CaC_2O_4 + Pb^{+2}$

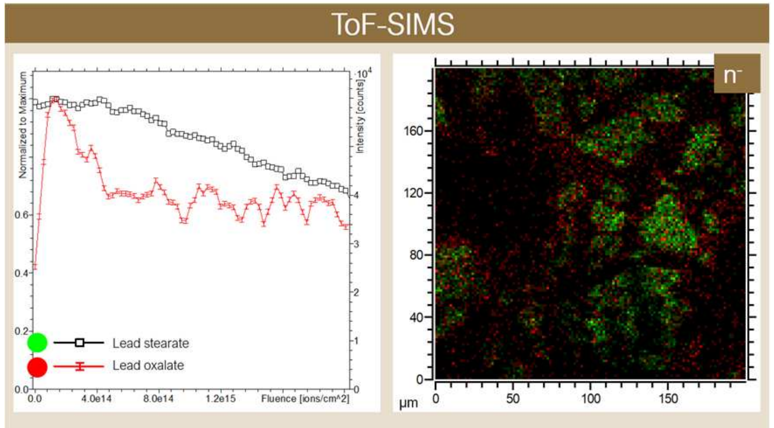
$PbC_2O_4 + Zn^{+2} \rightleftharpoons ZnC_2O_4 + Pb^{+2}$

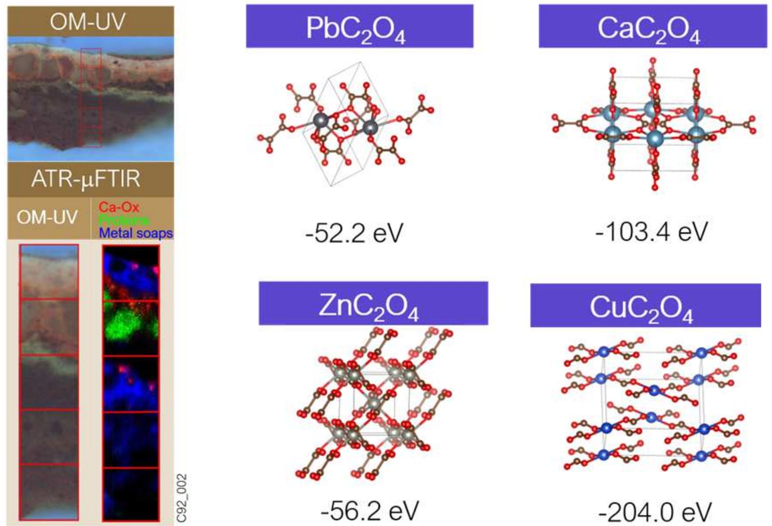
$PbC_2O_4 + Cu^{+2} \rightleftharpoons CuC_2O_4 + Pb^{+2}$

Ionic migration & exchange in oil paint films evidence



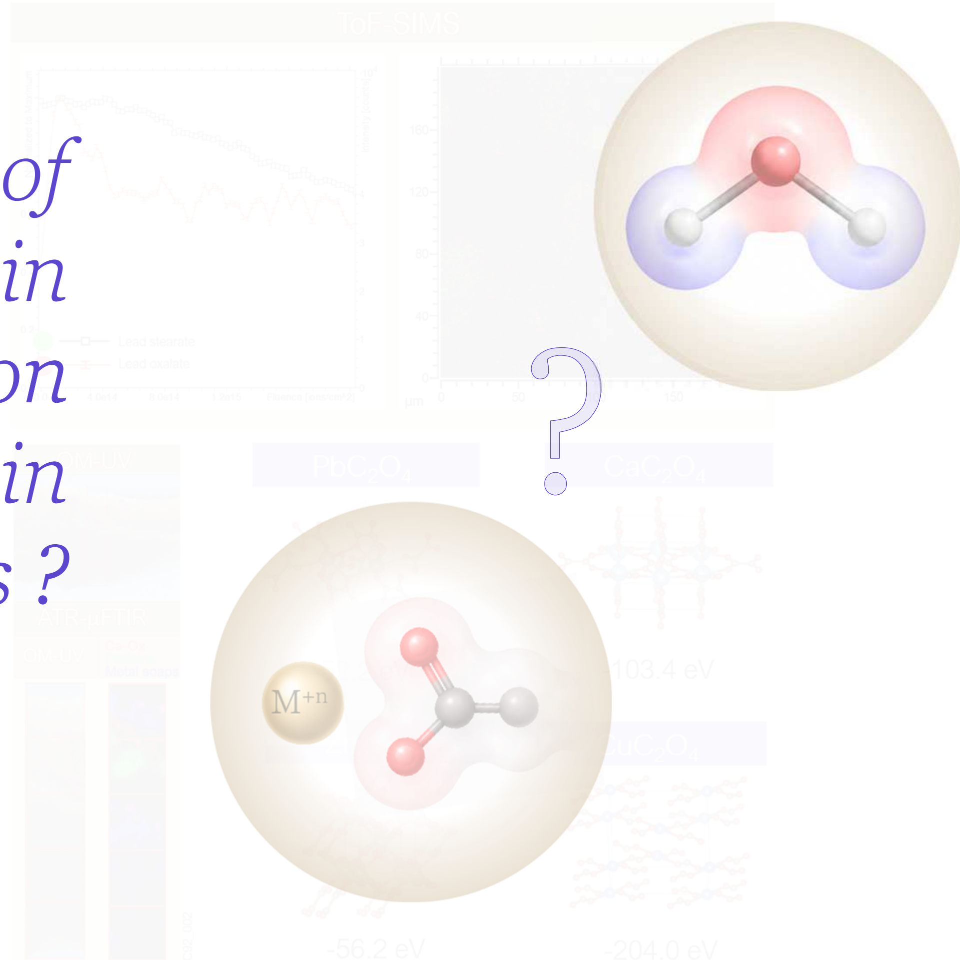




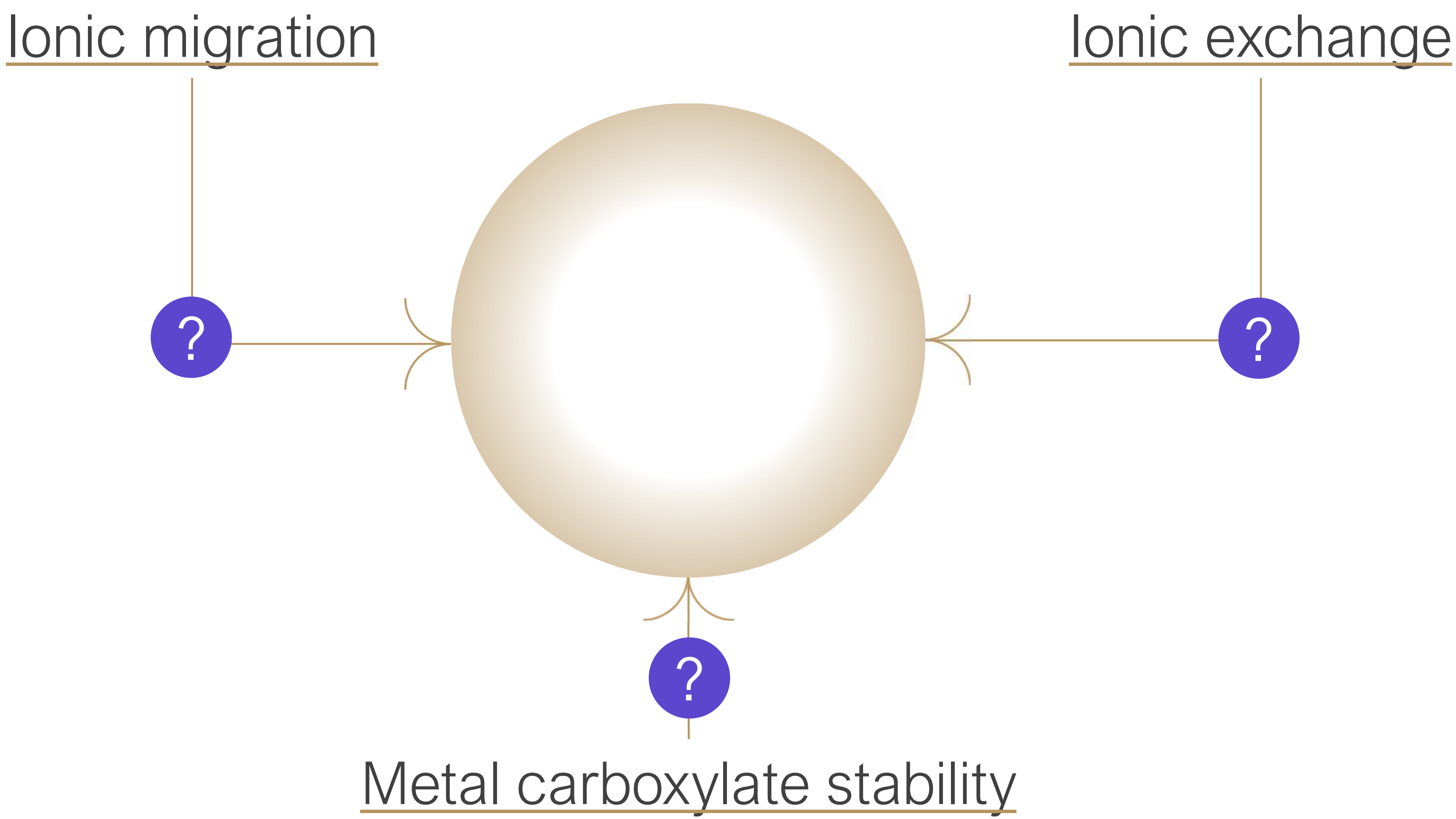


Ionic migration & exchange in oil paint films

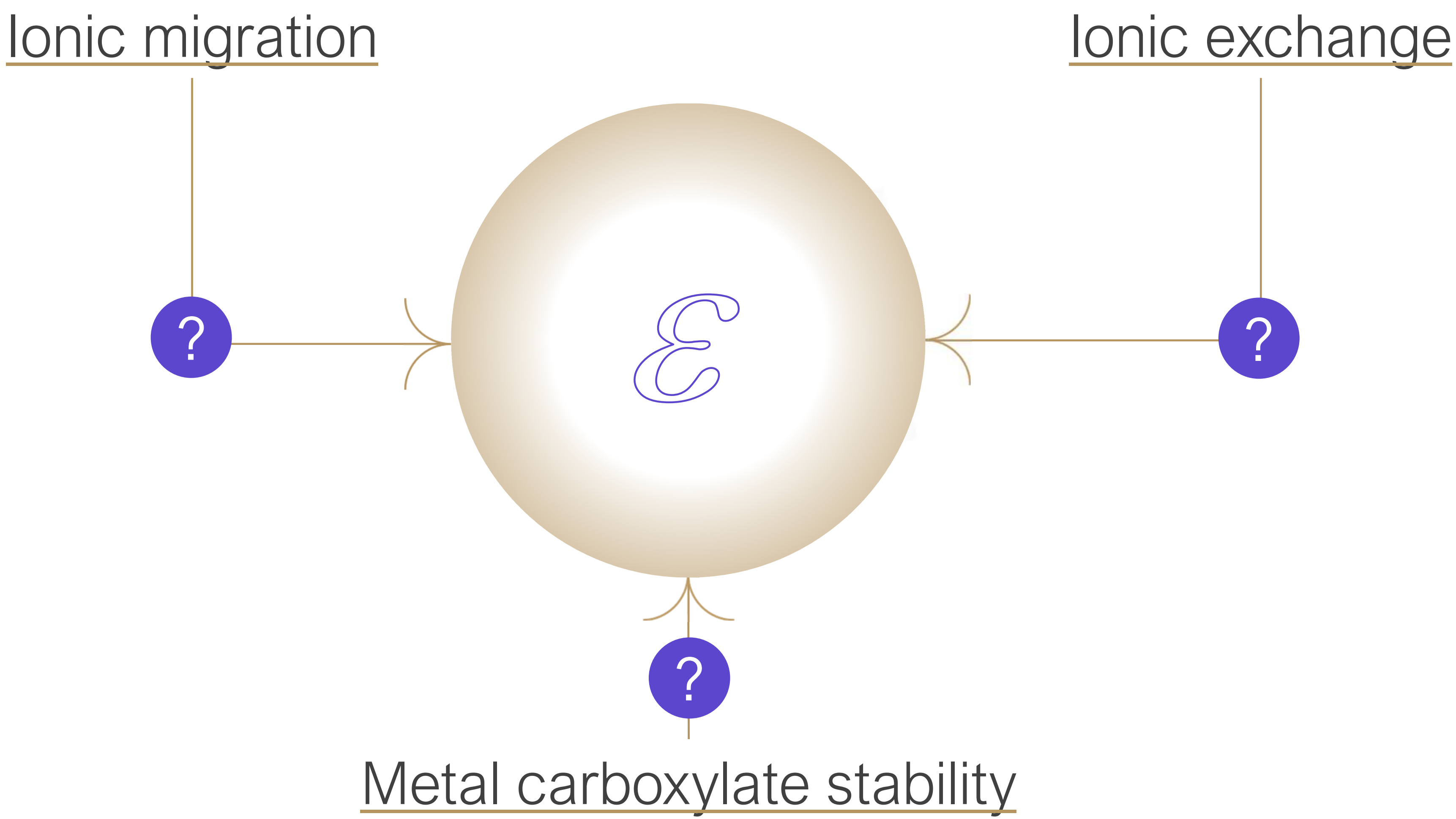
What's the role of carboxylate species & water in ionic exchange & migration processes happening in historical oil paintings ?



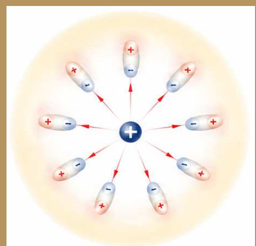
Fundamental questions...



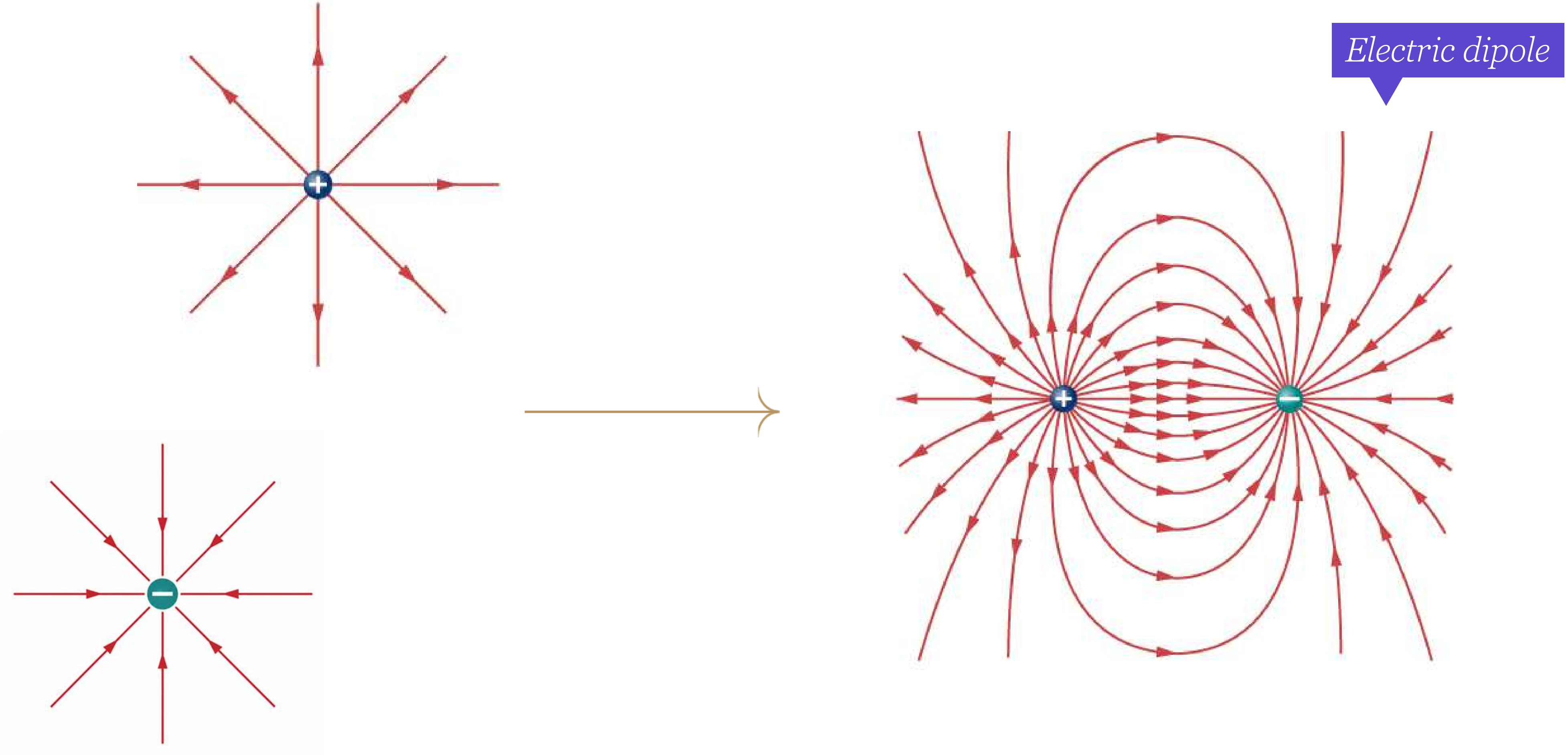
… require going back to the fundamental properties of matter



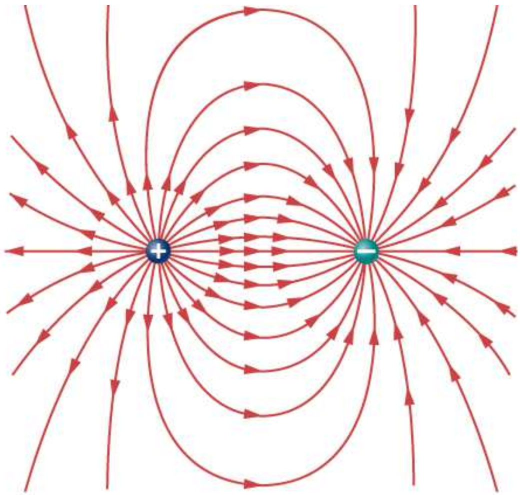
From electric fields to the dielectric spectroscopy of oil binders



Electric fields & electrostatic interactions



Coulomb's law



Coulomb force

How **strongly charges pull/push** *each other*

$$F_e = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0\varepsilon_r r^2}$$

Coulomb potential energy

Energy stored *in the charge configuration*

$$E_p(r) = -\int_{\infty}^{r} F_e(x)dx$$

Amount of charge

z_1, z_2

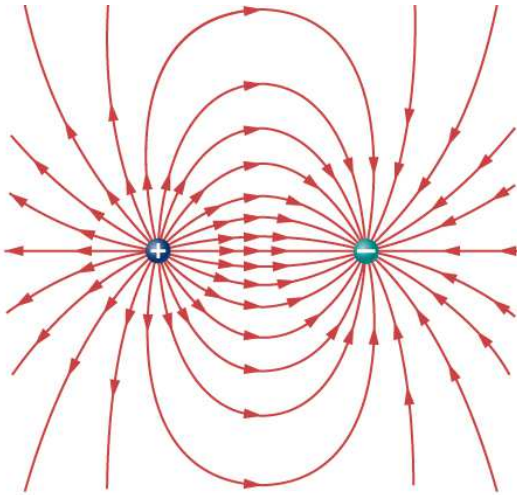
Distance between charges

r

The medium's electric permittivity

ε_r

Coulomb's law



Coulomb force

*How **strongly charges pull/push** each other*

$$F_e = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0\varepsilon_r r^2}$$

Coulomb potential energy

***Energy stored** in the charge configuration*

$$E_p(r) = -\int_{\infty}^{r} F_e(x)dx$$

Amount of charge

z_1, z_2

Distance between charges

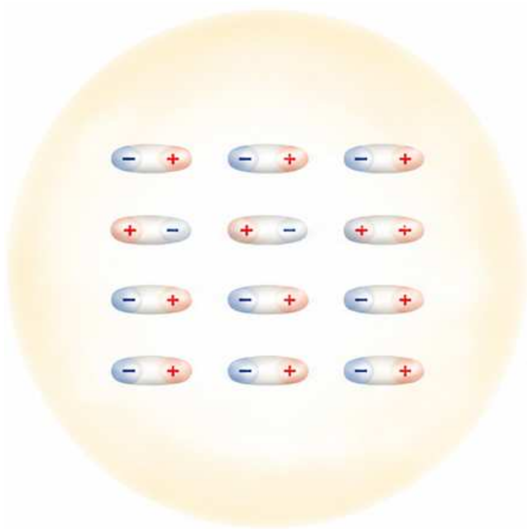
r

The medium's electric permittivity

ε_r

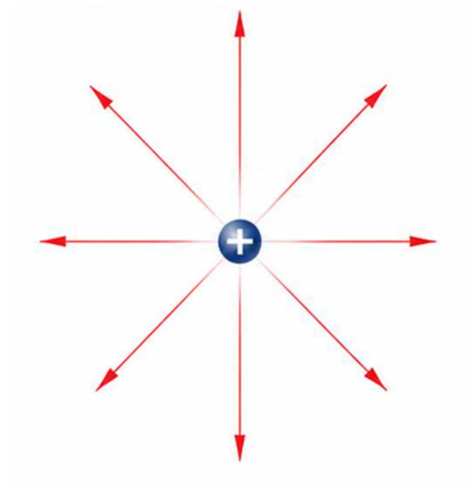
The medium's electric permittivity

Dielectric medium

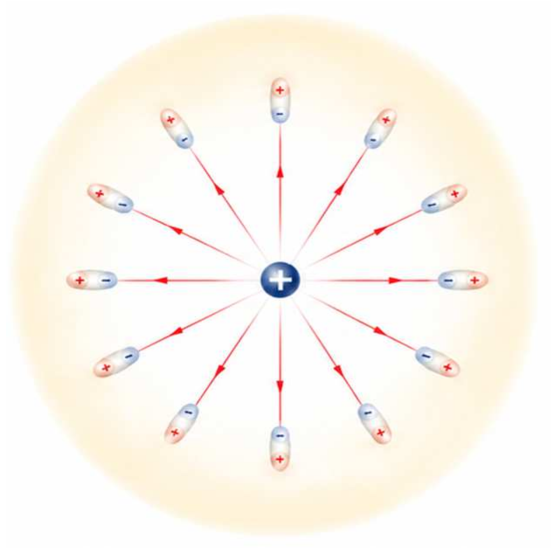


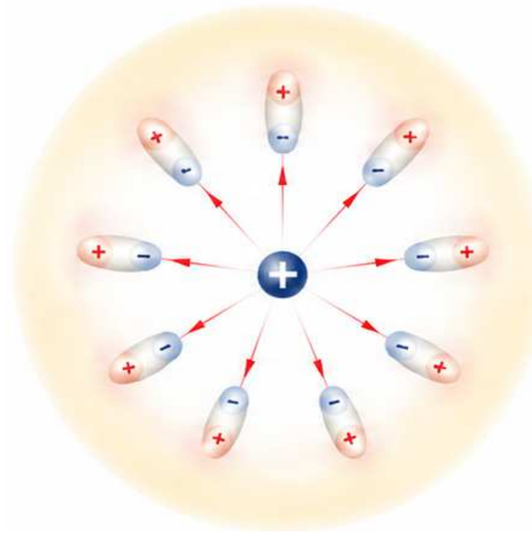
$\varepsilon_{r,1}$

Charge in vacuum



Charge in a dielectric medium





$\varepsilon_0 < \varepsilon_{r,1} < \varepsilon_{r,2}$

The medium's impact on electric permittivity

↑ ε_r

$$F_e = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0\varepsilon_r r^2}$$

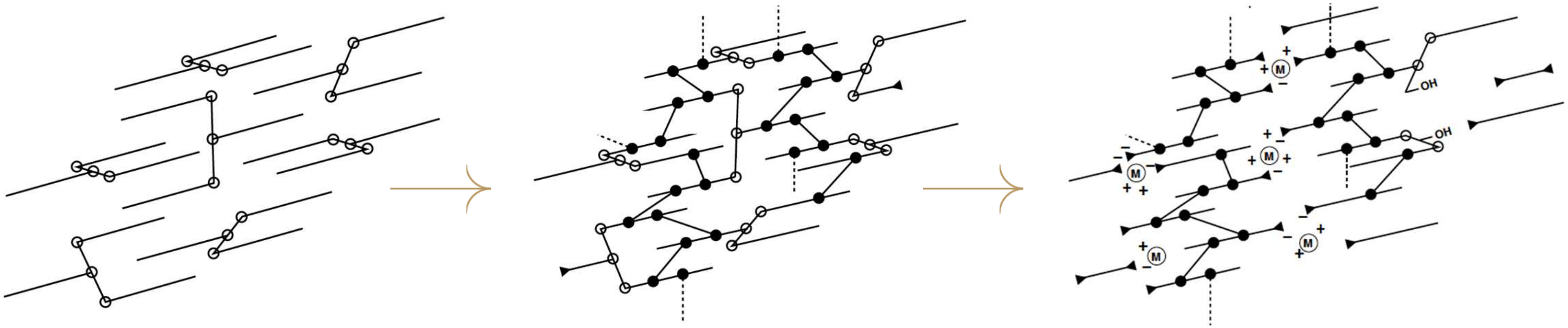
↑ *Dielectric screening*

↓ *Coulombic interactions*

- *Weaker ion pairing*
- *Favored ionic dissociation*
- *Enhanced* ion migration & exchange*
  - *Chemical bonding & ligand coordination*
  - *Oil matrix mobility*

Tracking electrical permittivity changes in oil paint binders

fresh oil | *oxidised oil* | *ionomeric oil*



$\varepsilon_{r,1}$ < $\varepsilon_{r,2}$ < $\varepsilon_{r,3}$

Dielectric spectroscopy applied to the study of vegetable oils

1931

THE ELECTRIC MOMENTS OF THE FIXED VEGETABLE OILS*

BY W. N. STOOPS

933 documents @ Scopus

2008

ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Journal of Food Engineering 88 (2008) 151–158

JOURNAL OF FOOD ENGINEERING

www.elsevier.com/locate/jfoodeng

Dielectric properties of edible oils and fatty acids as a function of frequency, temperature, moisture and composition

Hu Lizhi[a], K. Toyoda[b,*], I. Ihara[b]

88%

2025

Foods 2025 Conference

The 6th International Electronic Conference on Foods

28–30 October 2025 | Online

MDPI

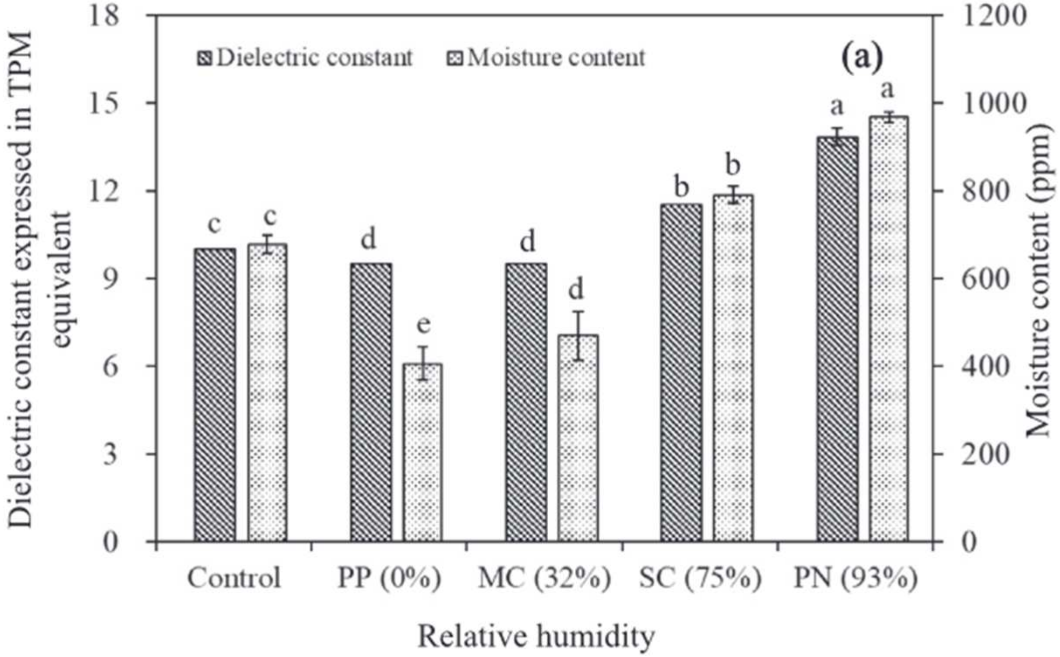
Dielectric Measurements for Monitoring the Storage of Vegetable Oils

Sándor Beszédes[1], Zoltán Jákói[1], Balázs Lemmer[2]

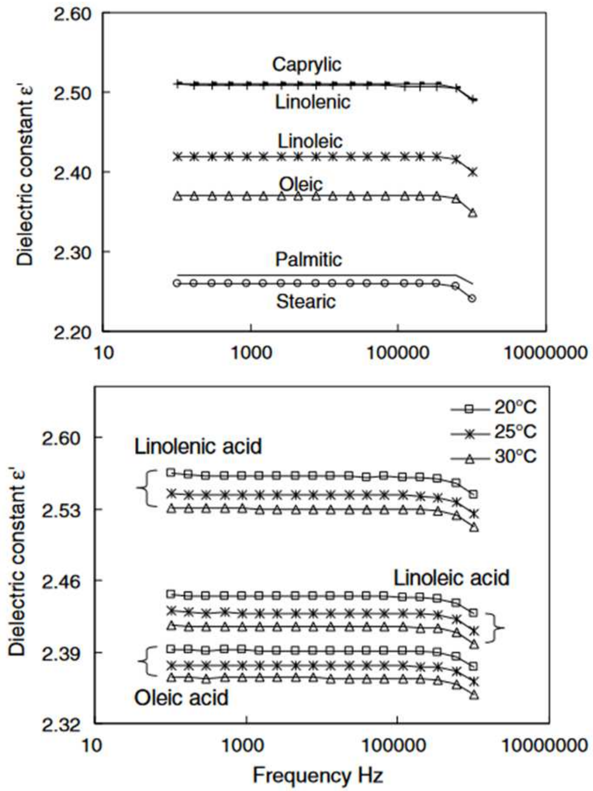
Department of Biosystems Engineering, Faculty of Engineering, University of Szeged, Szeged, HU-6725, Hungary[1]
Department of Food Engineering, Faculty of Engineering, University of Szeged, Szeged, HU-6725, Hungary[2]

Dielectric spectroscopy applied to the study of vegetable oils

ε_r → *composition, temperature & moisture-dependent*



YS. Woo, M-J Kim & JH Lee (2019) Prediction of oxidative stability in bulk oils using dielectric constant changes, *Food Chem., 279,* 216-222



H. Lizhi, K. Toyoda & I. Ihara (2008) Dielectric properties of edible oils and fatty acids as a function of frequency, temperature, moisture and composition, *J. Food Eng., 88,* 151-158

Dielectric spectroscop(y/ies) : probing diverse molecular dynamics

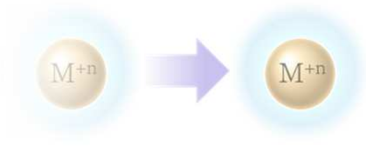
Low-frequency / impedance

Broadband

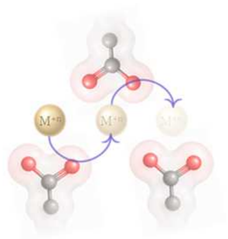
Microwave

10^{-3} 10^{0} 10^{3} 10^{6} 10^{9} 10^{12}

Frequency (Hz)

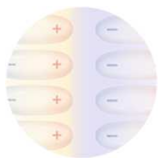


Long-range ionic transport ?



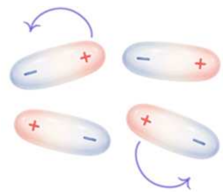
Ionomeric domain(s) dynamics ?

Short-range carboxylate hopping ?



Charge build-up @ interphases ?*

** oil/ionic/ water-rich*



Polar domains dynamics ?

Water confinement ?

Dielectric spectroscopy & complex electric permittivity (ε^*)

Ability to store electric energy

Polarizability

$$\varepsilon^*(f) = \varepsilon'(f) + i\varepsilon''(f)$$

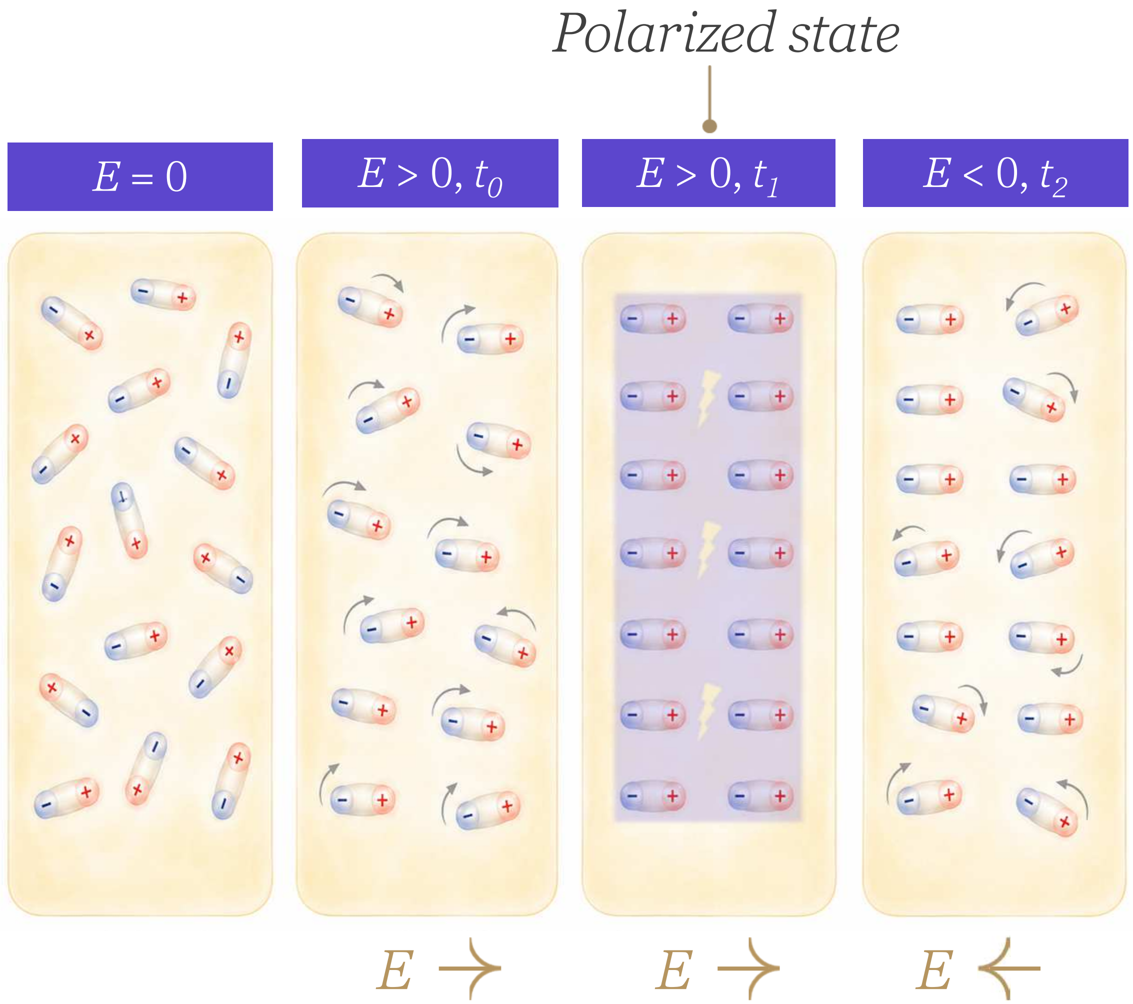
Frequency-dependent

Ability to dissipate electric energy

Conductivity

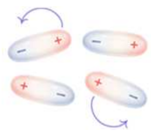
the energy storage component (ε') > polarizability

Ability to store

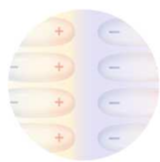


the lossy component (ε'') > conductivity

$$\sigma'(f) = 2\pi f \varepsilon_o \varepsilon''(f)$$

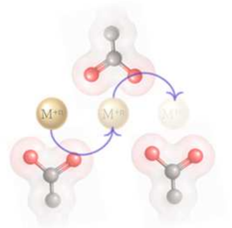


Dipolar relaxation losses

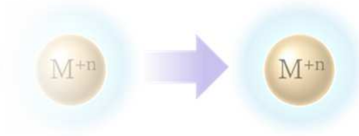


Interfacial charge accumulation

Maxwell–Wagner–Sillars polarization



Local ion hopping between carboxylate sites



Long-range ionic migration

EEHOP

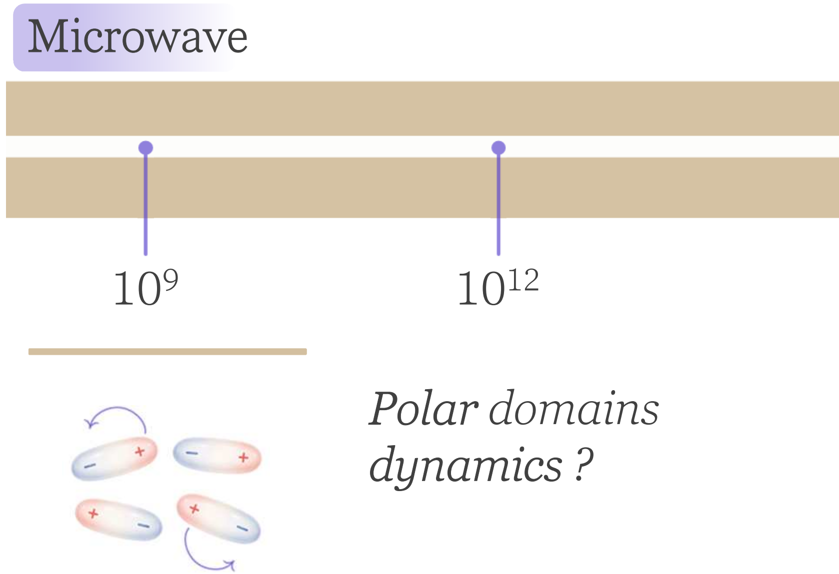
Electromagnetic exploration of historical oil paintings

LA LIBERTÉ DE CHERCHER
PDR T.0159.24

EEHOP

Correlating oil binders' chemical composition with ε' & ε''

Beatrice
BORACCHI



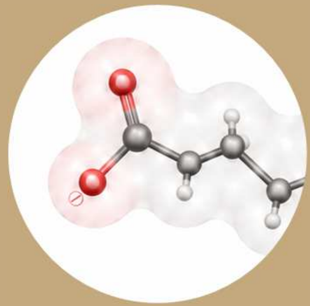
Polar domains dynamics ?

EEHOP

Correlating oil binders' chemical composition with ε' & ε"

Beatrice
BORACCHI

Liquid linseed oil (LO) systems in different chemical states



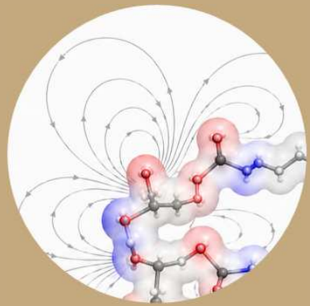
Characterization of chemical composition

GC-MS

t-μFTIR

AV

+



Characterization of dielectric behavior

VNA
0.5 – 20 GHz

Havriliak-Negami (HN) model fitting

EEHOP

Characterization of the chemical composition of the oil binders

Beatrice
BORACCHI

- F — Fresh, cold-pressed LO
- A — Naturally aged (~7 yr), cold-pressed LO
- PbO — Cold-pressed LO, boiled w/ 2% m/m PbO + H_2O, naturally aged for ~7 yr

EEHOP

Characterization of the chemical composition of the oil binders

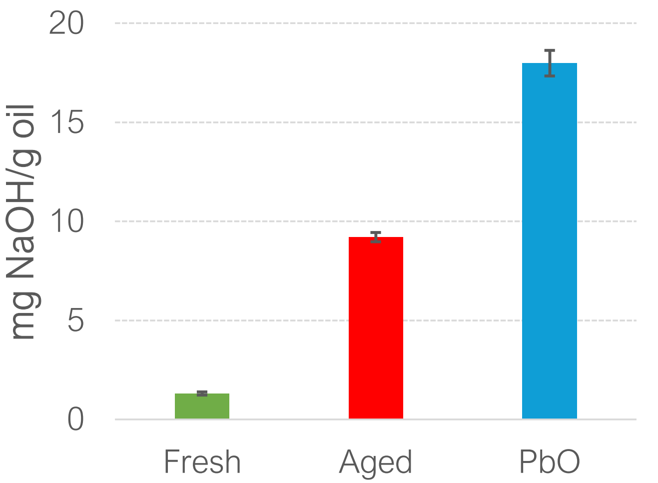
Beatrice
BORACCHI

F — Fresh, cold-pressed LO

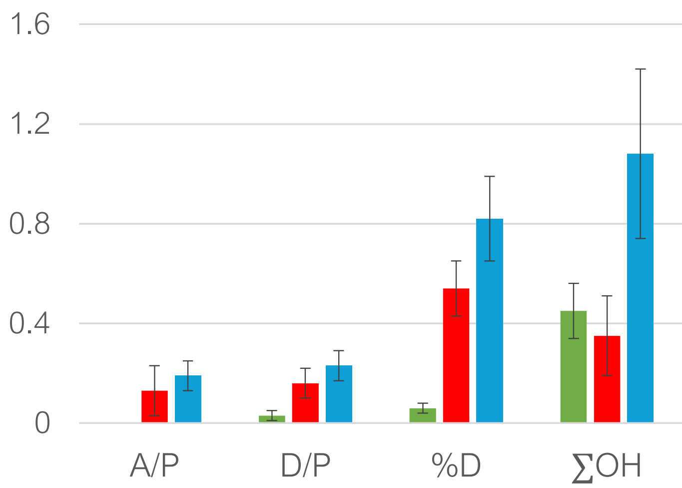
A — Naturally aged (~7 yr), cold-pressed LO

PbO — Cold-pressed LO, boiled w/ 2% m/m PbO + H_2O, naturally aged for ~7 yr

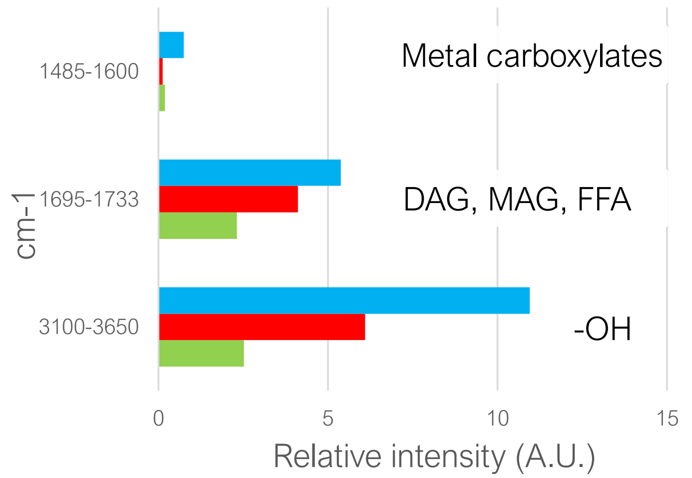
AV



GC-MS



t-µFTIR

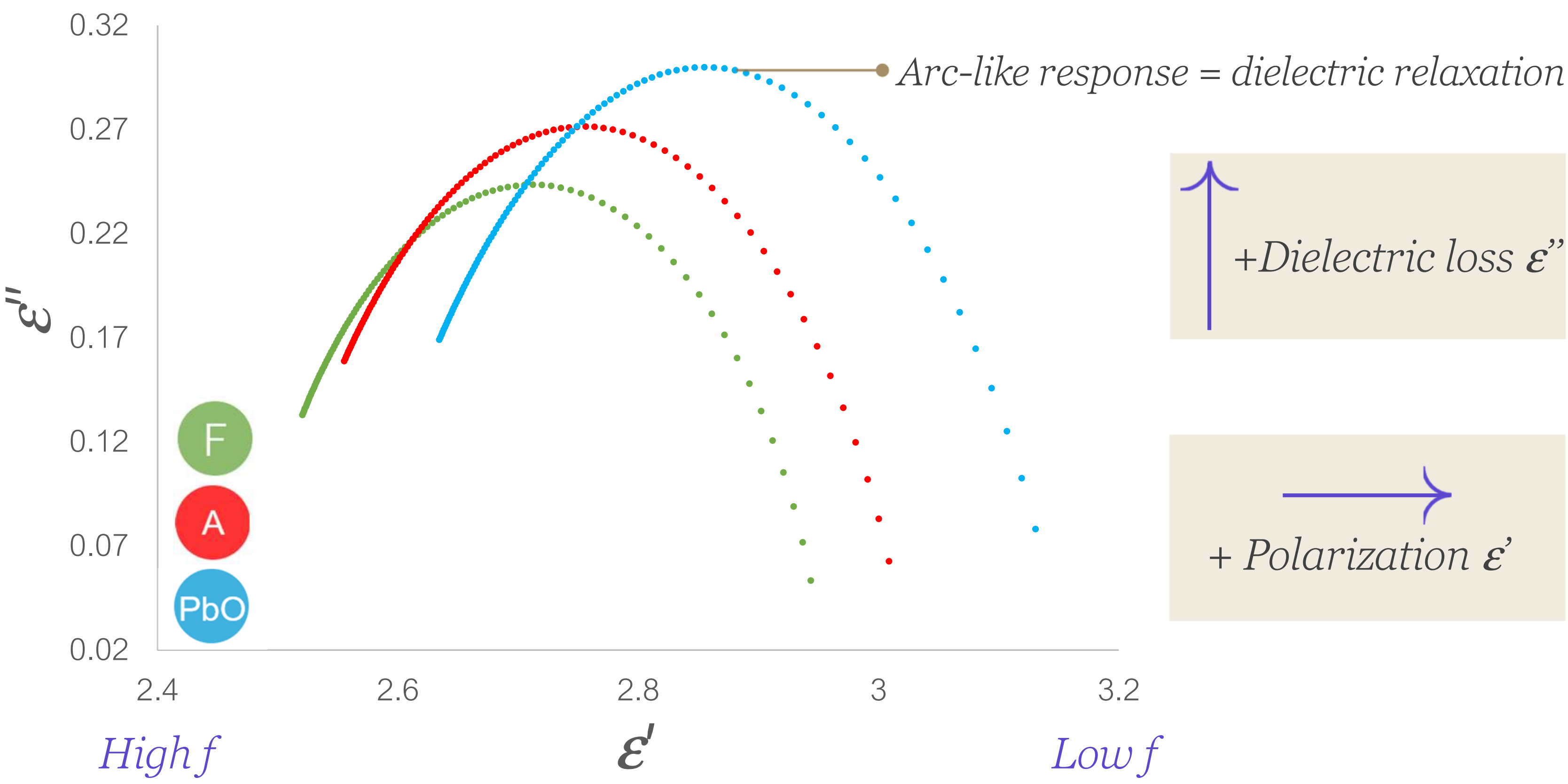


EEHOP

Characterization of the dielectric behavior of the oil binders

Beatrice
BORACCHI

Cole-Cole plot (HN model fit)

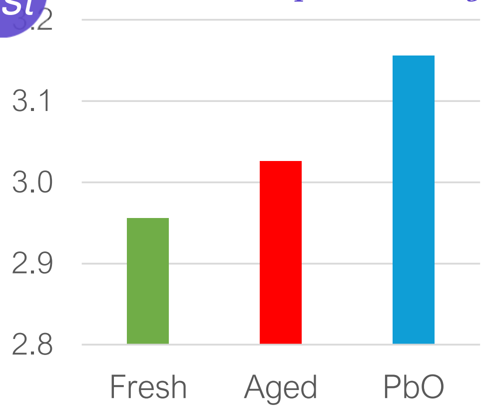


EEHOP

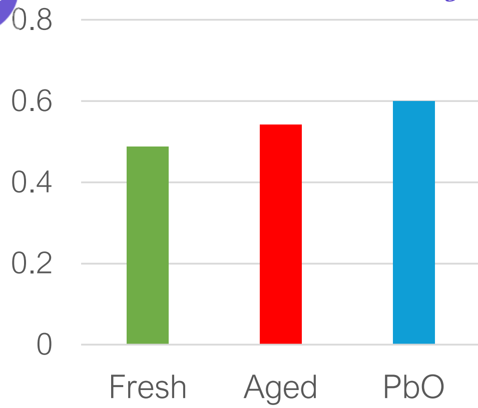
Extracting meaningful “molecular pictures” from dielectric spectroscopy

Beatrice
BORACCHI

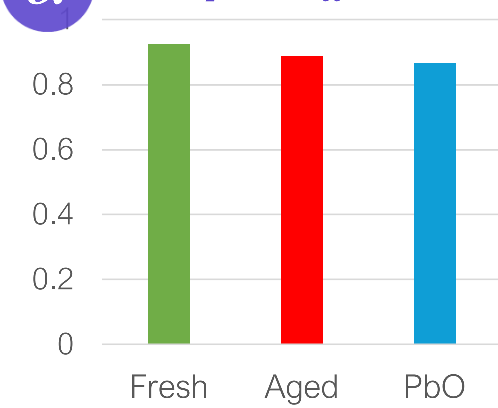
ε_{st} *Static electric permittivity*



$\Delta\varepsilon$ *Dielectric relaxation strength*



α *Alpha coefficient*



↑ Oxidised moieties
Metal carboxylates
Ion-pair or ionic-cluster domains (nm?)

- Higher low-frequency polarizability
- Stronger dipolar response

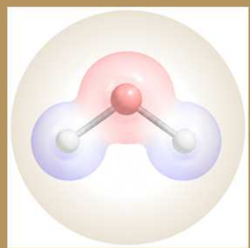
↑ ε_{st} $\Delta\varepsilon$

↑ Chemical heterogeneity
Diversity of polar/ionic domains (nm?)

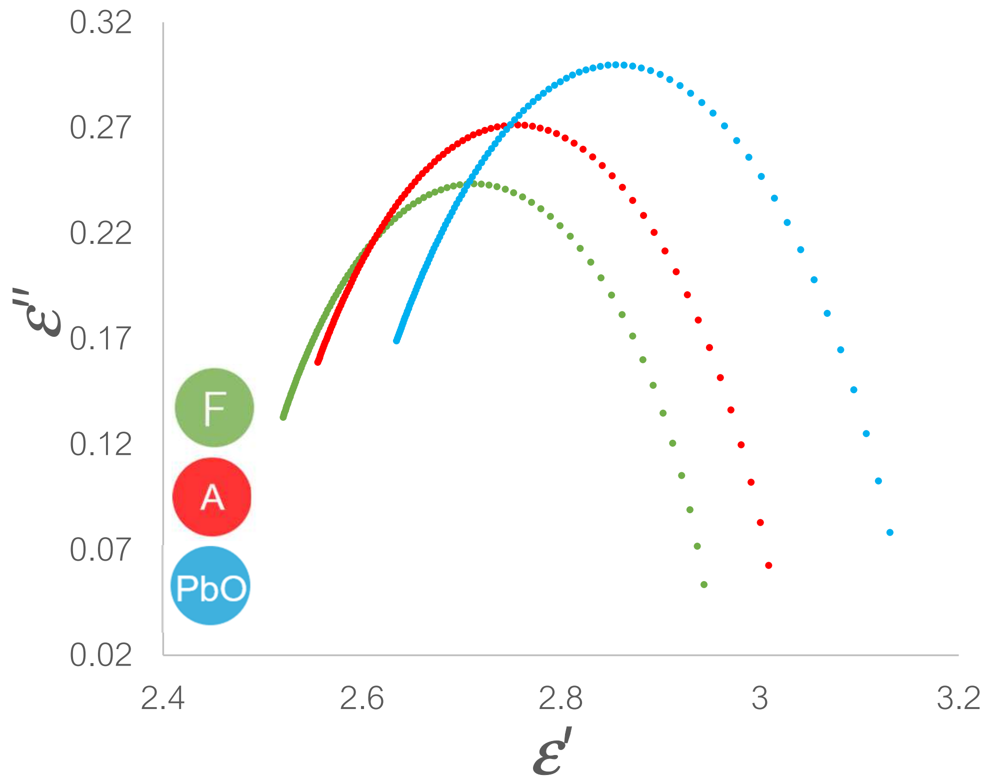
- Broader relaxation time distribution

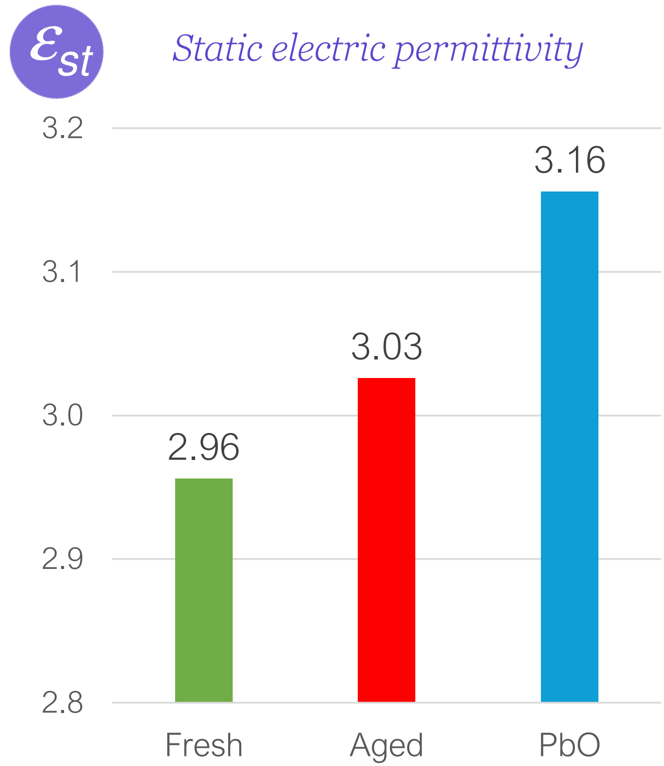
↓ α

The role of water

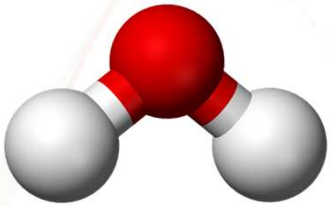


How can ionic migration & exchange occur in oily dielectrics?

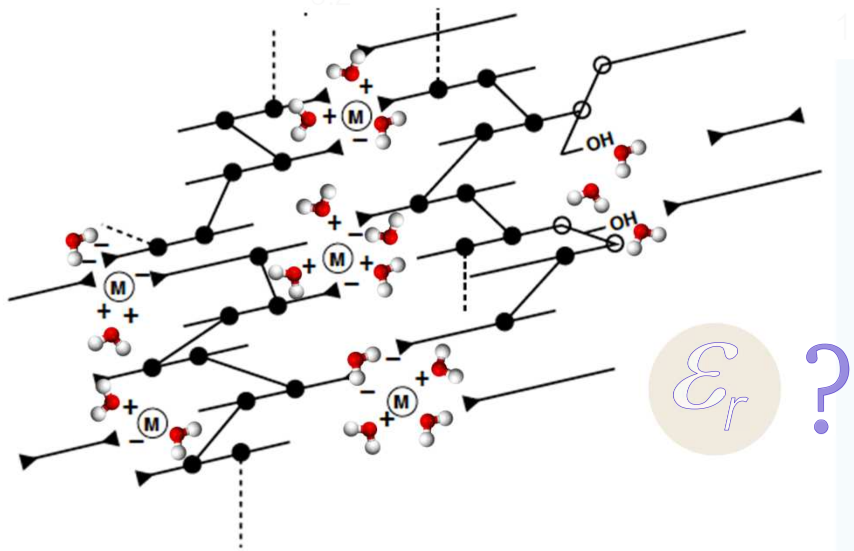




How can ionic migration & exchange occur in oily dielectrics?



ε_{r_st} (25ºC) = 88

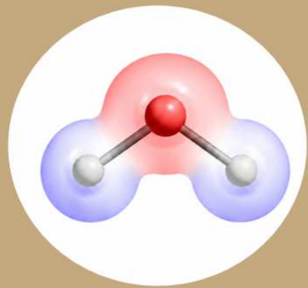


EEHOP

Correlating oil binders' water-related behavior with ε' & ε''

Beatrice
BORACCHI

Liquid linseed oil (LO) systems in different chemical states conditioned @ 100% RH

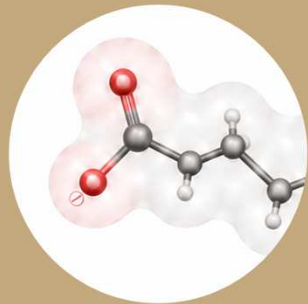


Characterization of "water-related" behavior

DVS

t-µFTIR

+



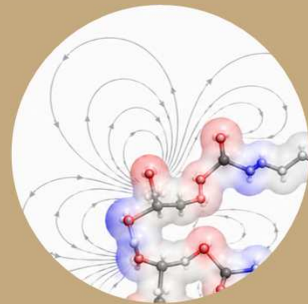
Characterization of chemical composition

GC-MS

t-µFTIR

AV

+



Characterization of dielectric behavior

VNA
0.5 – 20 GHz

Havriliak-Negami (HN) model fitting

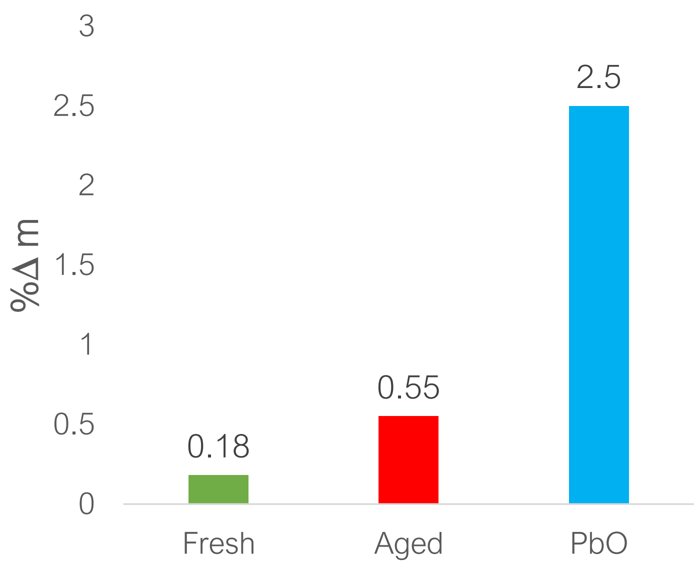
EEHOP

Correlating oil binders’ water-related behavior with ε’ & ε”

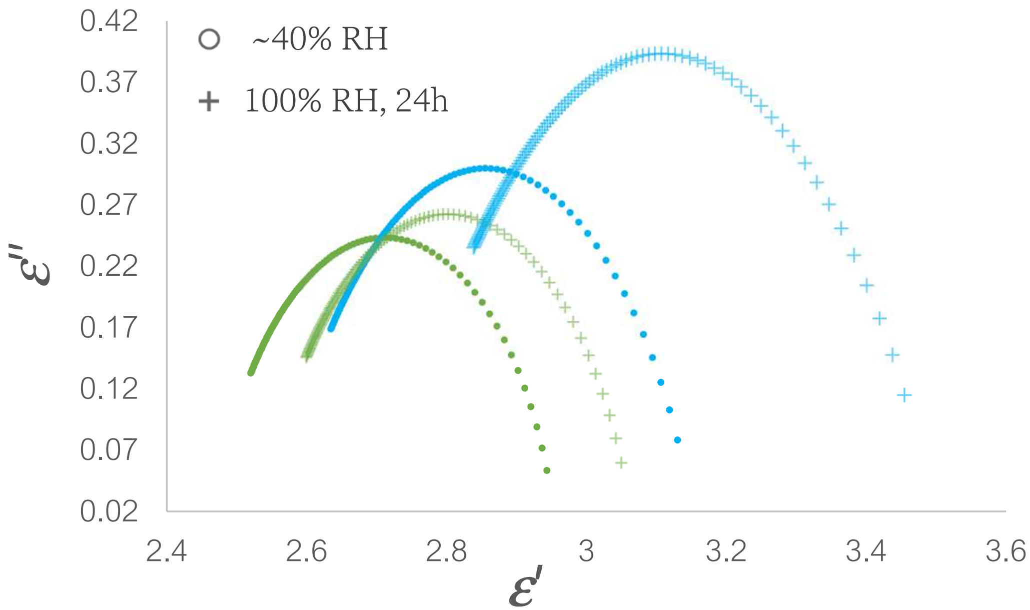
Beatrice
BORACCHI

F
A
PbO

Dynamic vapor sorption (DVS)



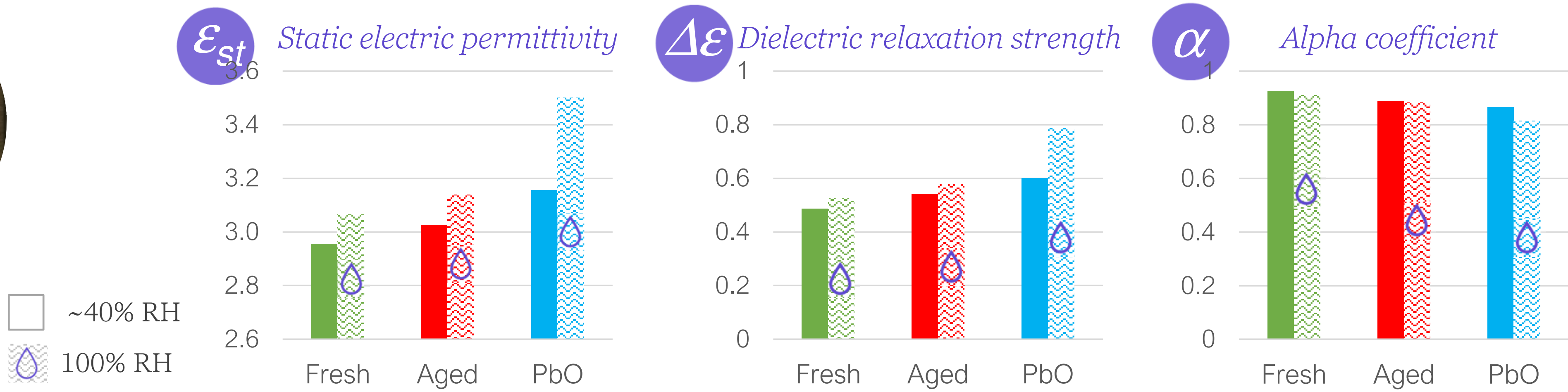
Cole-Cole plot (HN model fit)



EEHOP

Correlating oil binders’ water-related behavior with ε’ & ε”

Beatrice
BORACCHI



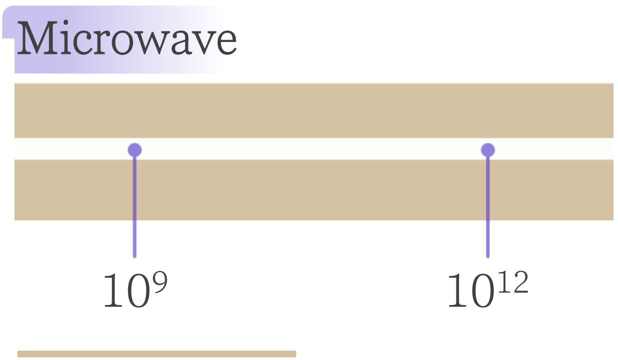
- Added water polarization
- “Plasticization” effect increasing mobility
- Chemical heterogeneity
  Diversity of polar/ionic domains (nm?)

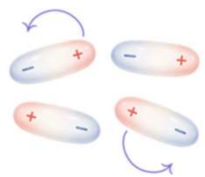
- Higher low-frequency polarizability
- Stronger dipolar response
- Broader relaxation time distribution

↑ ε_{st} $\Delta\varepsilon$

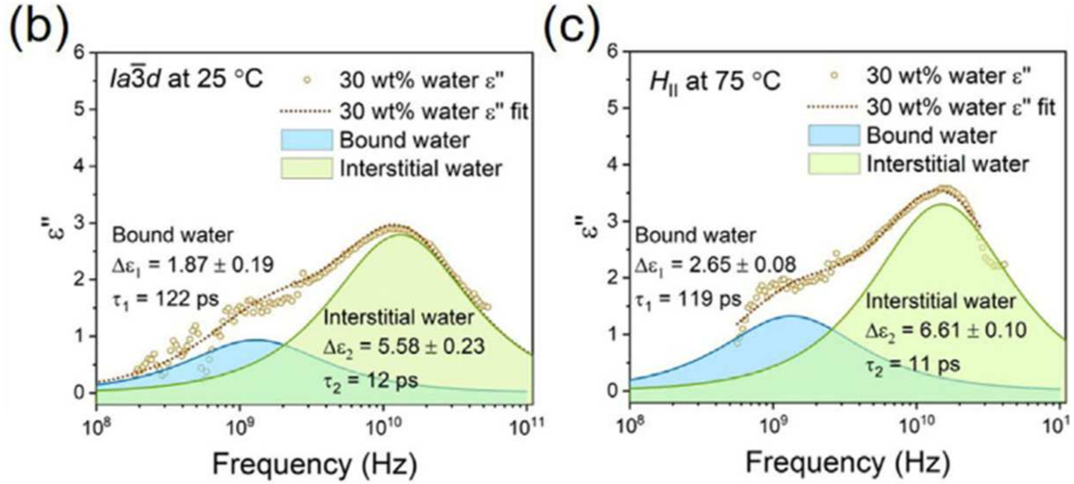
↓ α

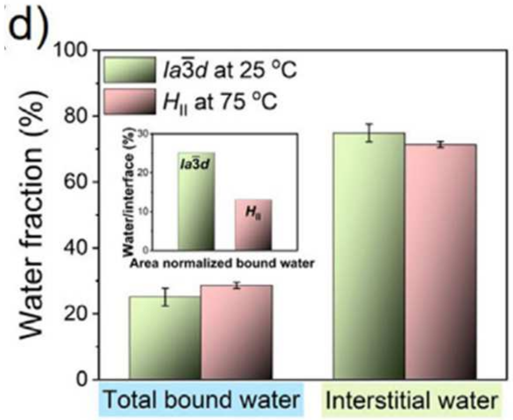
Probing water rotational dynamics with microwave dielectric spectroscopy





Water confinement ?

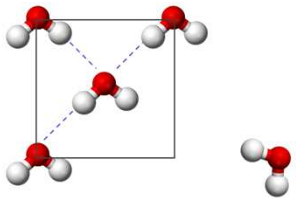




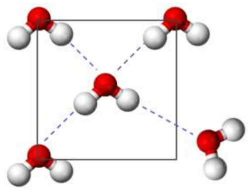
Y. Yao, S. Catalini, P. Foggi, and R. Mezzenga, ‘Probing Water State during Lipidic Mesophases Phase Transitions’, *Angew. Chem. Int. Ed.* 2021, 60, 1 – 8
doi: 10.1002/anie.202110975

Probing water confinement with t-μFTIR

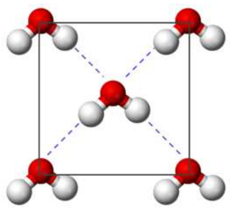
WBW Weakly bonded

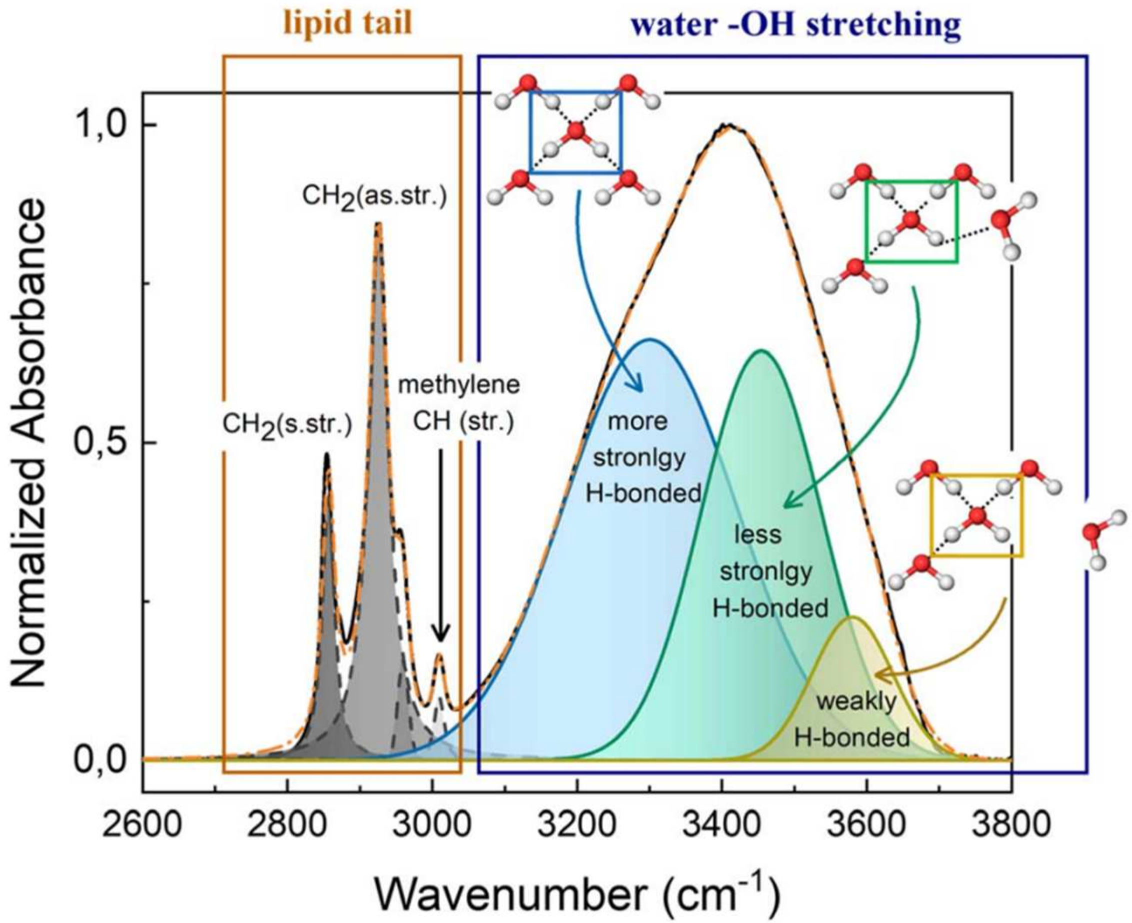


LSBW Less-strongly bonded



SBW Strongly bonded





Y. Yao, S. Catalini, P. Foggi, and R. Mezzenga, 'Water-Lipid Interface in Lipidic Mesophases with Excess Water', *Faraday Discuss.*, vol. 249, no. 10, Oct. 2023, doi: 10.1039/D3FD00118K.

EEHOP

Probing water environments with t-μFTIR

Evgeniia
GRZHESHCHUK

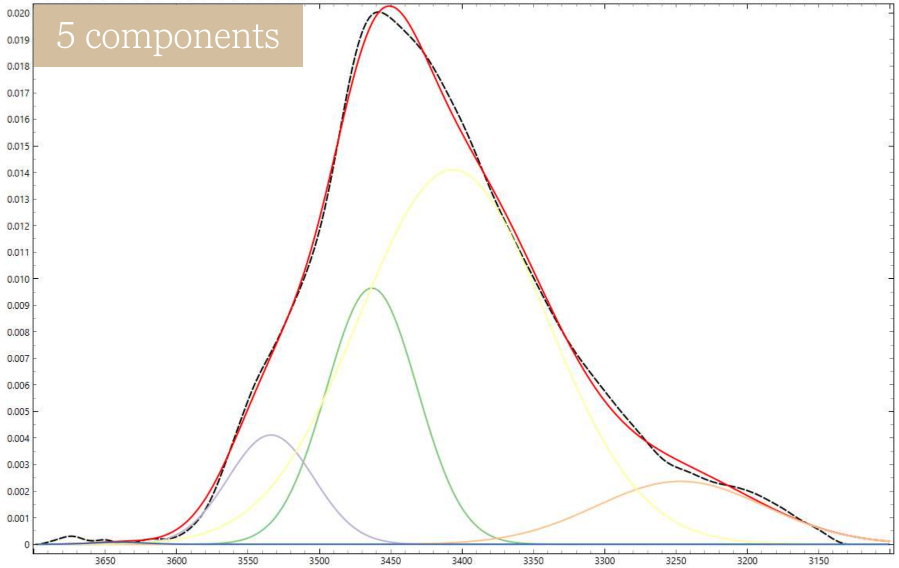
150 μm-thick film
@CaF_2 window

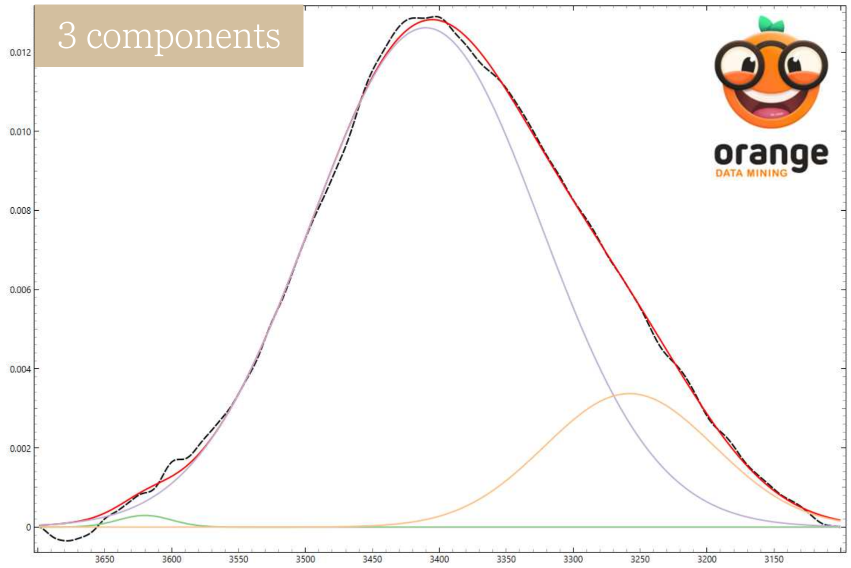
F
A
PbO

100% RH

0% RH

O-H stretching (3650-3100 cm^{-1}) peak deconvolution





Free water	3630 cm^{-1}
Oil-related –OH's stretching	3535 cm^{-1}
Oil-related C=O ester overtone	3473 cm^{-1}
Partially bonded water	3415 cm^{-1}
Strongly bonded water	3242 cm^{-1}

100% RH –0% RH

Free water	3630 cm^{-1}
Partially bonded water	3415 cm^{-1}
Strongly bonded water	3242 cm^{-1}

EEHOP

Probing water environments with t-μFTIR

Evgeniia
GRZHESHCHUK

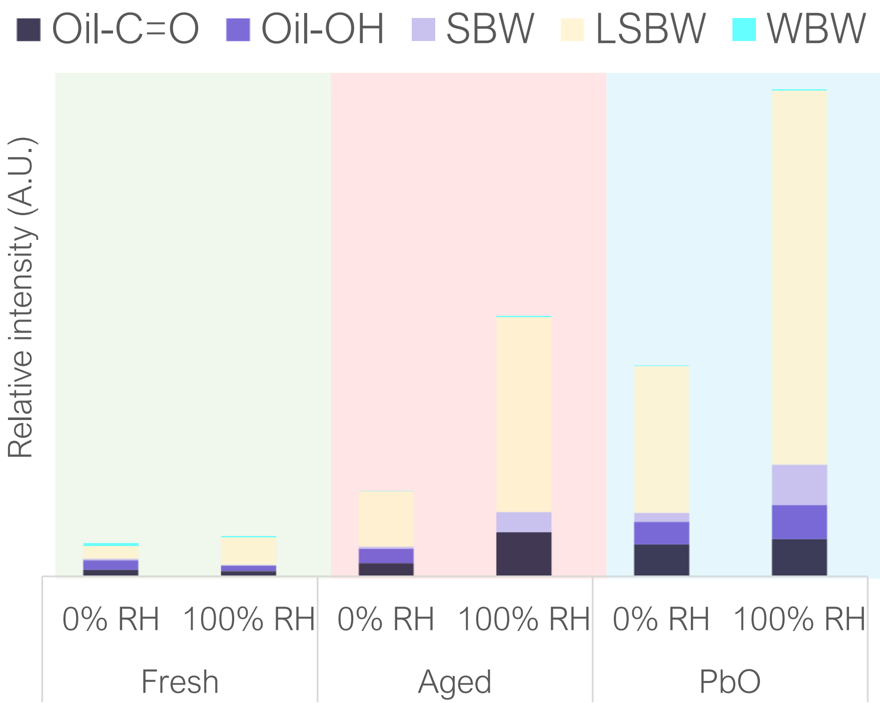
150 μm-thick film
@CaF_2 window

F

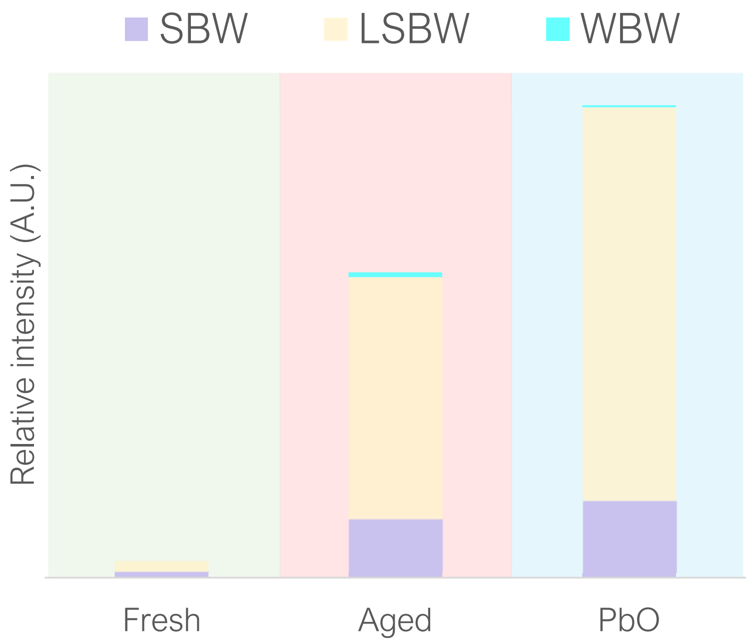
A

PbO

5 peaks



3 peaks



Conclusions

Dielectric spectroscop(y/ies) : probing diverse molecular dynamics

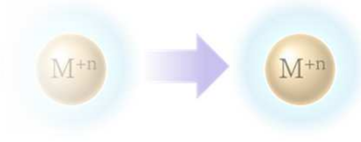
Low-frequency / impedance

Broadband

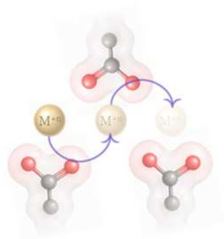
Microwave

10^{-3} 10^{0} 10^{3} 10^{6} 10^{9} 10^{12}

Frequency (Hz)

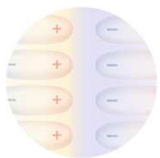


Long-range ionic transport ?



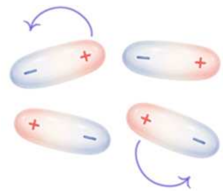
Ionomeric domain(s) dynamics ?

Short-range carboxylate hopping ?



Charge build-up @ interphases ?*

** oil/ionic/ water-rich*



Polar domains dynamics ?

Water confinement ?

Dielectric spectroscop(y/ies) : probing diverse molecular dynamics

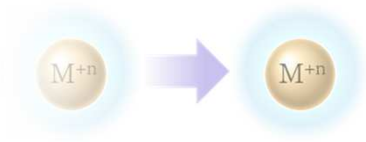
Low-frequency / impedance

Broadband

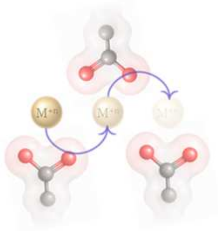
Microwave

10^{-3} 10^{0} 10^{3} 10^{6} 10^{9} 10^{12}

Frequency (Hz)

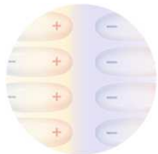


Long-range ionic transport ?



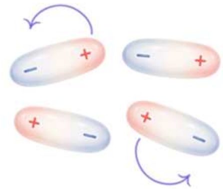
Ionomeric domain(s) dynamics ?

Short-range carboxylate hopping ?



Charge build-up @ interphases ?*

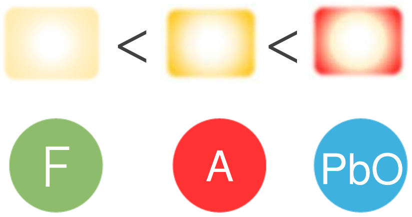
** oil/ionic/ water-rich*



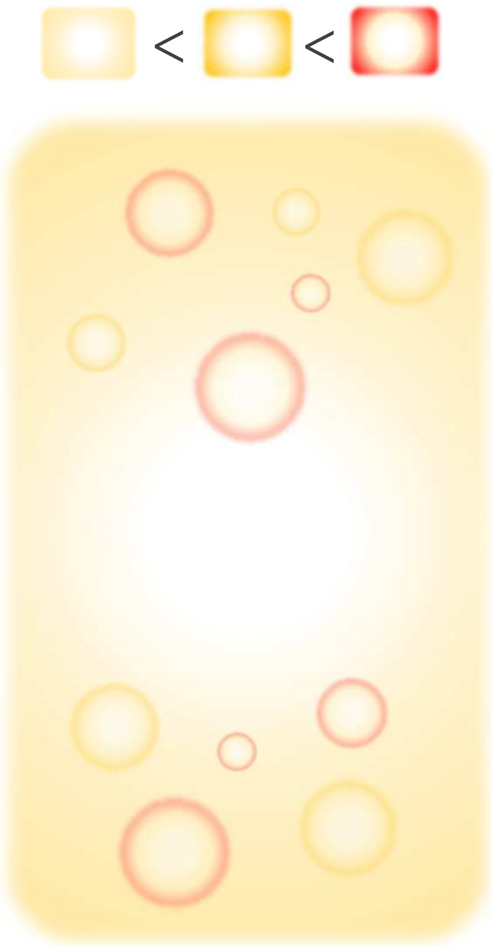
***Polar** domains **dynamics** ?*

Water confinement ?

Emerging molecular “dielectric snapshots” of the water@oil system

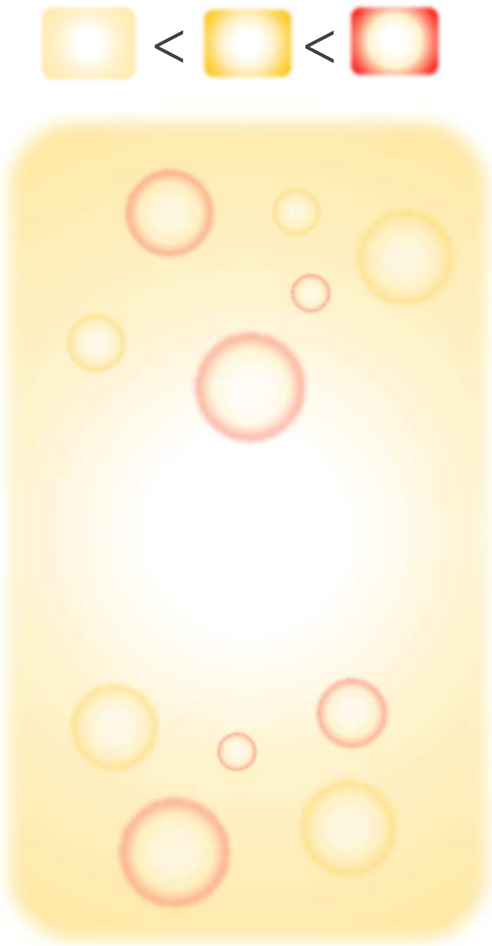


Emerging molecular "dielectric snapshots" of the water@oil system

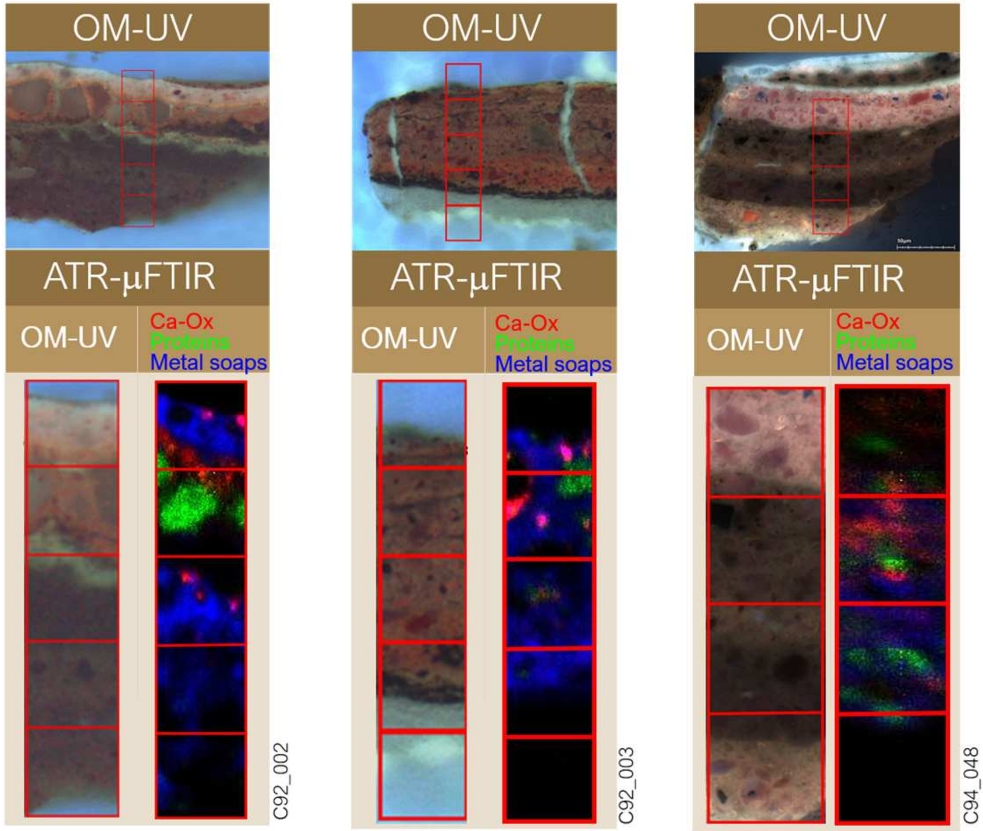


... the oil binder phase is a heterogeneous dielectric domain landscape... ?

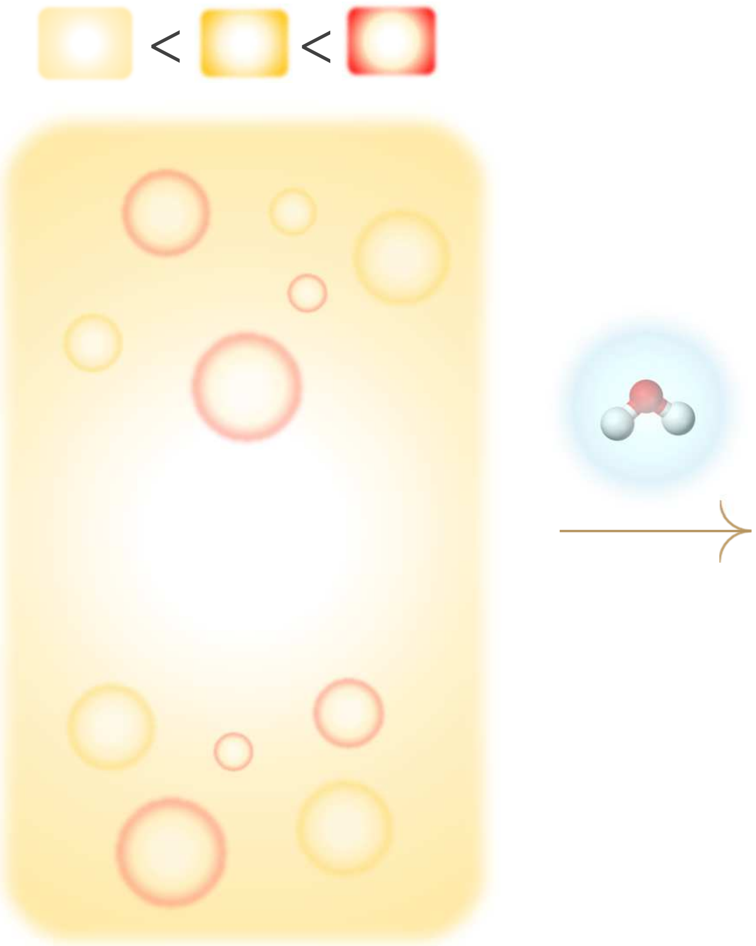
Emerging molecular "dielectric snapshots" of the water@oil system



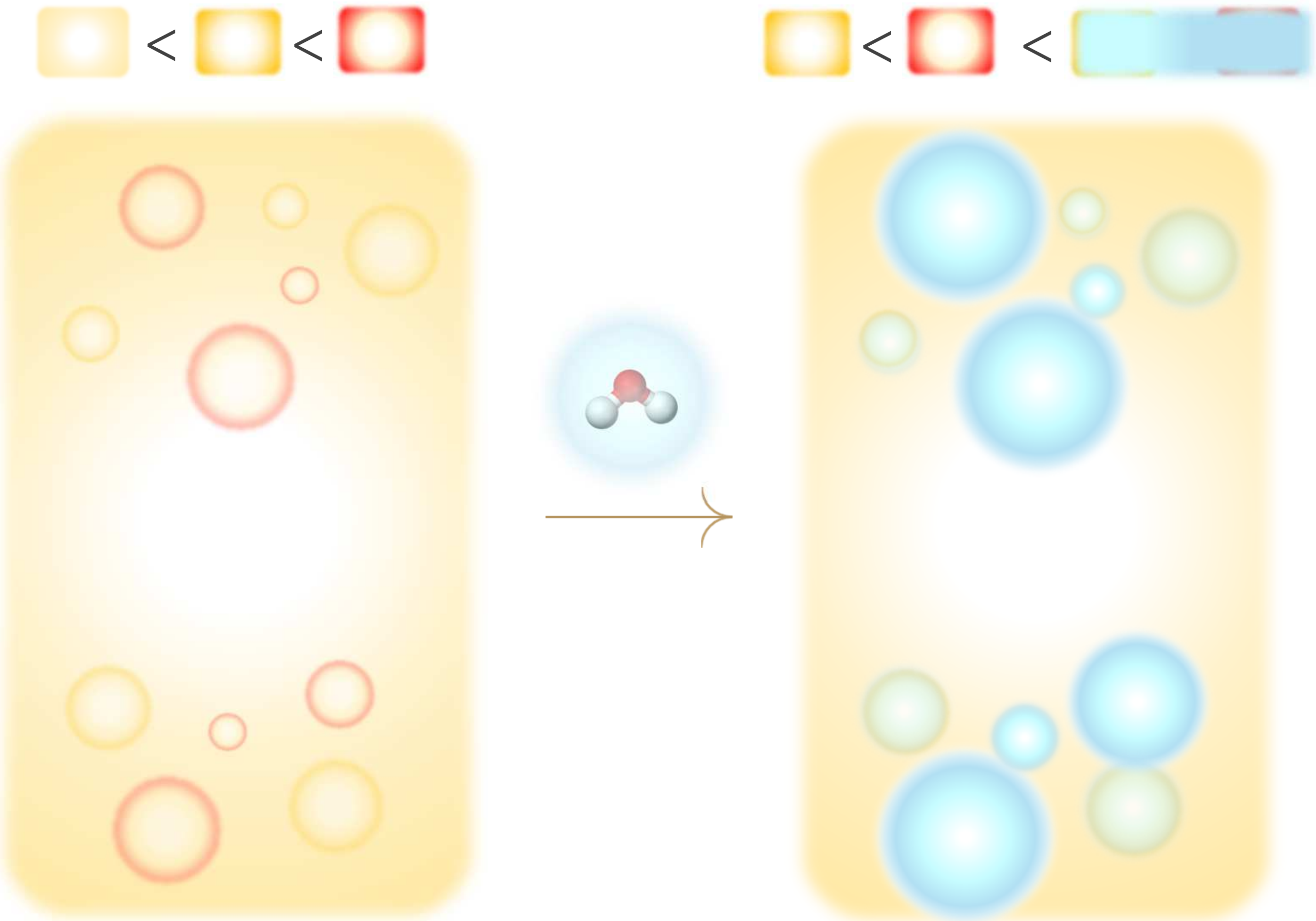
« Clustering » of high(er)
ε_r environments



Emerging molecular "dielectric snapshots" of the water@oil system

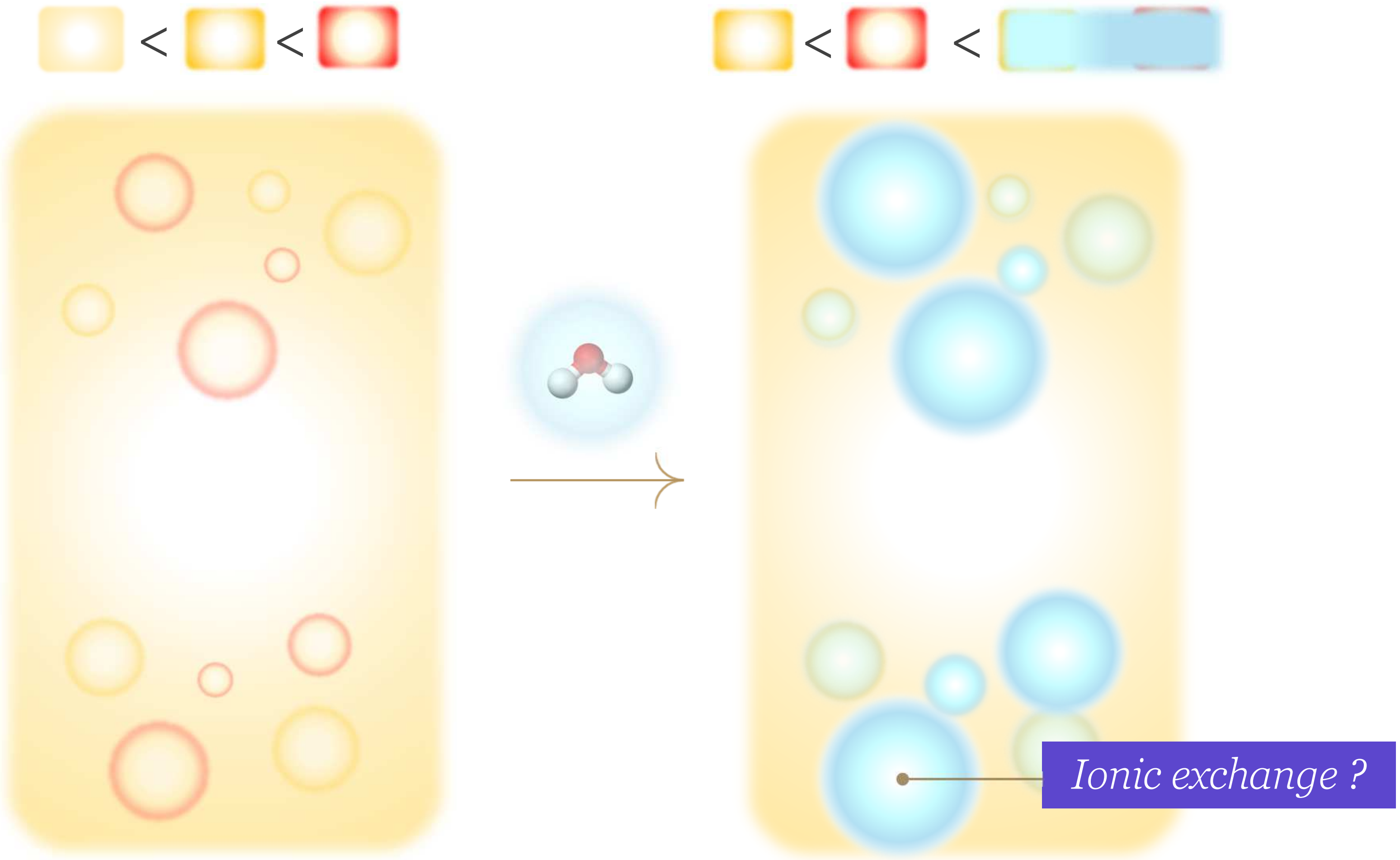


Emerging molecular “dielectric snapshots” of the water@oil system

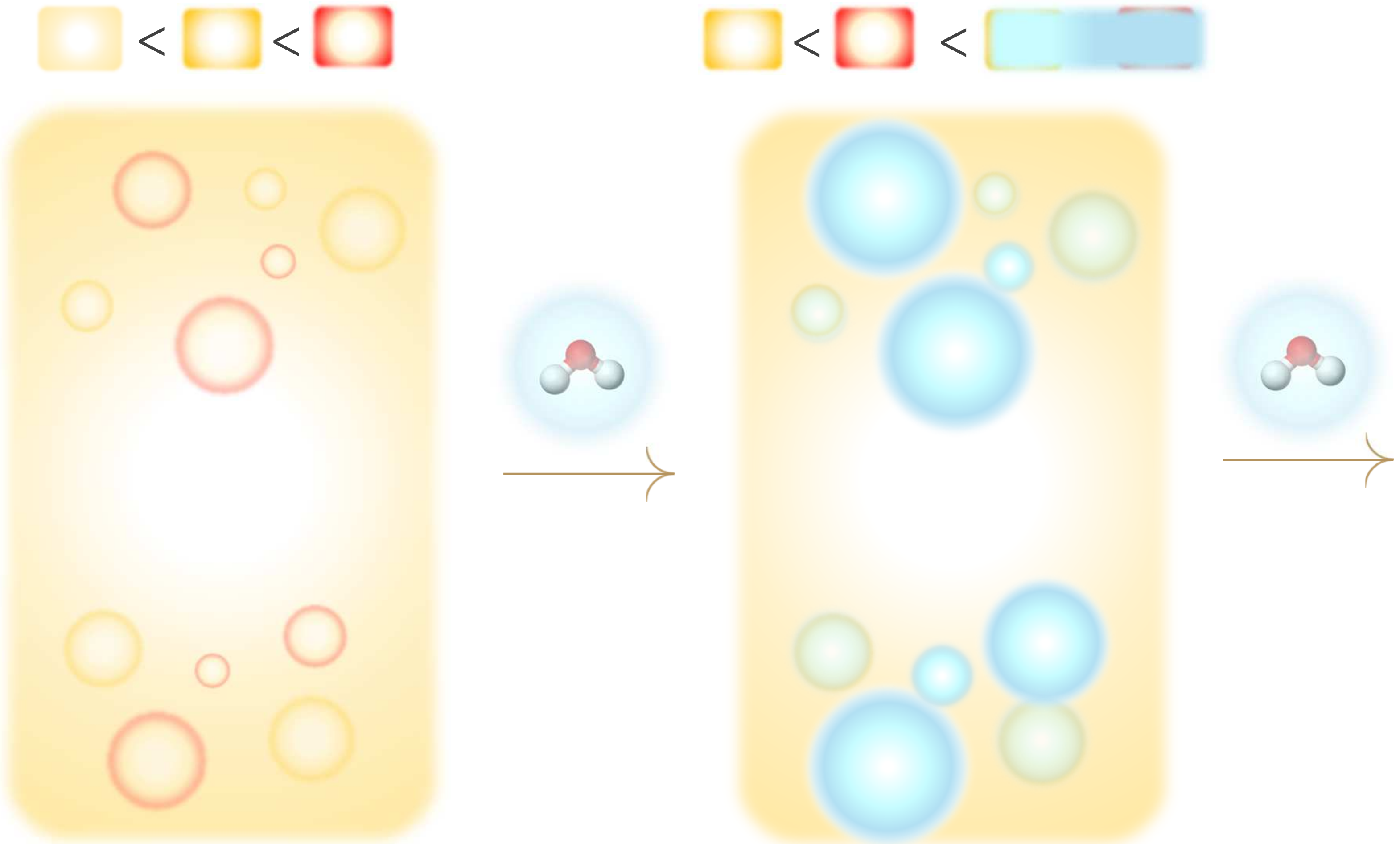


... oil binder ageing creates “water-friendly” dielectric domains with differential water sorption regimes... ?

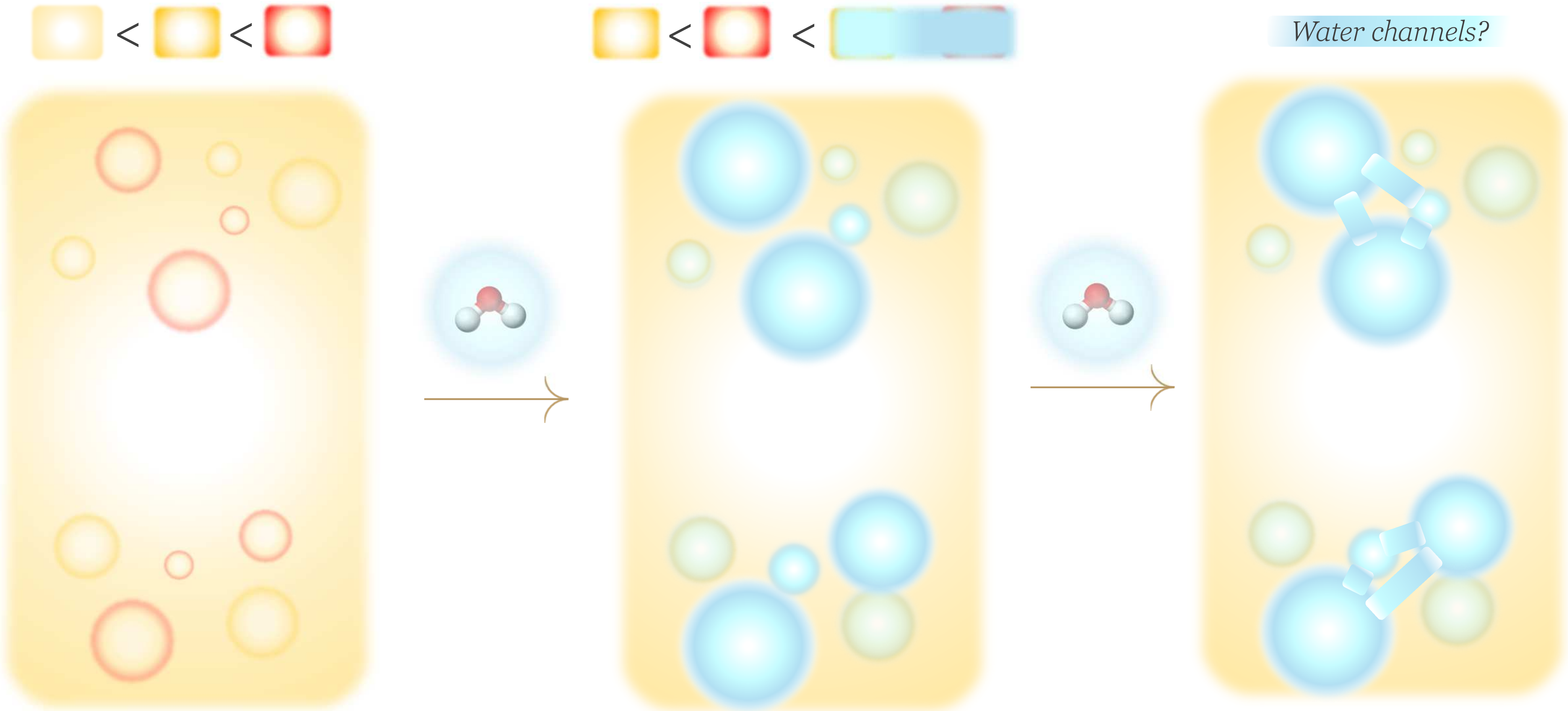
Emerging molecular “dielectric snapshots” of the water@oil system



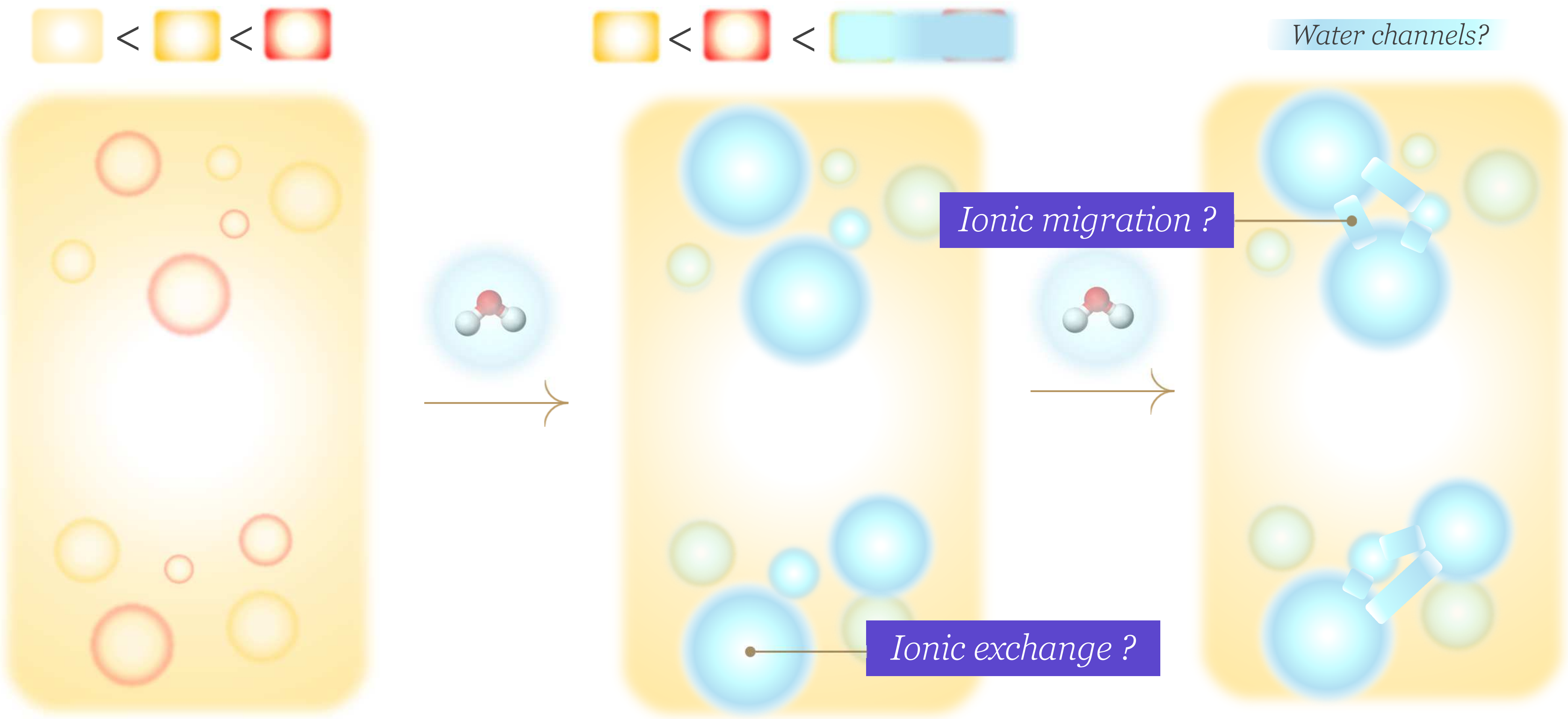
Emerging molecular “dielectric snapshots” of the water@oil system



Emerging molecular "dielectric snapshots" of the water@oil system



Emerging molecular “dielectric snapshots” of the water@oil system



Possible futures

Additional oil formulations

Cooked oils / dosed metal carboxylates

- Zn^{+2} & Cu^{+2}
- Stand-oil
- Gradients of $[M^{+n}]$

Further characterization

- Rheology
- Microwave DS (> 20-100 GHz)
- Broadband DS (10 Hz -40 MHz)

… then, repeat the experimental design using dried oil films and try…

Imaging the ε_r domains

- Impedance AFM (sMIM/LEIS)
- *Neutron radiography (@PSI!) ?*

Possible futures

Additional oil formulations

Cooked oils / dosed metal carboxylates

- Zn^{+2} & Cu^{+2}
- Stand oil
- Gradients of $[M^{+n}]$
- Rheology

Further characterization

- Microwave DS (> 20-100 GHz)
- Broadband DS (10 Hz -40 MHz)

… then, repeat the experimental design using dried oil films and try…

Imaging the ε_r domains

- Impedance AFM (sMIM/LEIS)
- *Neutron radiography (@PSI!) ?*

… Experimenting in the time of finitude…

?

... Experimenting in the time of finitude... ?

Defining, as a community, the "what" & the "what for" of dielectric spectroscopy applied to historical oil paintings degradation ...?

Possible futures

Additional oil formulations

Cooked oils / dosed metal carboxylates

Further characterization

... then, repeat the experimental design using dried oil films and try...

Imaging the ε_r domains

- Zn^{+2} & Cu^{+2}
- Stand oil
- Gradients of $[M^{+n}]$
- Rheology
- Microwave DS (> 20-100 GHz)
- Impedance AFM (sMIM/LEIS)
- *Neutron radiography (@PSI!) ?*

The Electrical Chemistry of Historical Oil Paintings

Dielectric properties *of aging* ***oil binders****, the role of* ***water****, and potential links to degradation compound* ***ionic exchange*** *and* ***migration***

Beatrice
BORACCHI

Angelos
GKOGKOS

Evgeniia
GRZHESHCHUK

Samuel
BERTOLINI DA SILVA OLIVEIRA

Prof. Isabelle
HUYNEN

Amandine
COLIGNON

Prof. Arnaud
DELCORTE

GRC

Scientific Methods in Cultural Heritage Research
Gordon Research Conference
July 12 - 17, 2026 - Les Diablerets Conference Center

fnrs

KIK IRPA Royal Institute for Cultural Heritage

ULB UNIVERSITÉ LIBRE DE BRUXELLES

UCLouvain

belspo .be

Dr. Francisco Mederos-Henry

francisco.mederos@kikirpa.be
francisco.mederos-henry@ulb.be

Materials science for conservation-restauration (MatCoRe) research unit

KIK IRPA Royal Institute for Cultural Heritage

ULB UNIVERSITÉ LIBRE DE BRUXELLES

The medium's impact on electric permittivity

↑ ε_r

$$F_e = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0\varepsilon_r r^2}$$

↑ *Dielectric screening*

↓ *Coulombic interactions*

Bjerrum length

$$l_B = \frac{|z_i z_j| e^2}{4\pi\varepsilon_0\varepsilon_r k_B T} \approx \frac{57|z_i z_j|}{\varepsilon_r} nm^{@20°C}$$

Weaker ion pairing

Favored ionic dissociation

Enhanced ion migration & exchange*

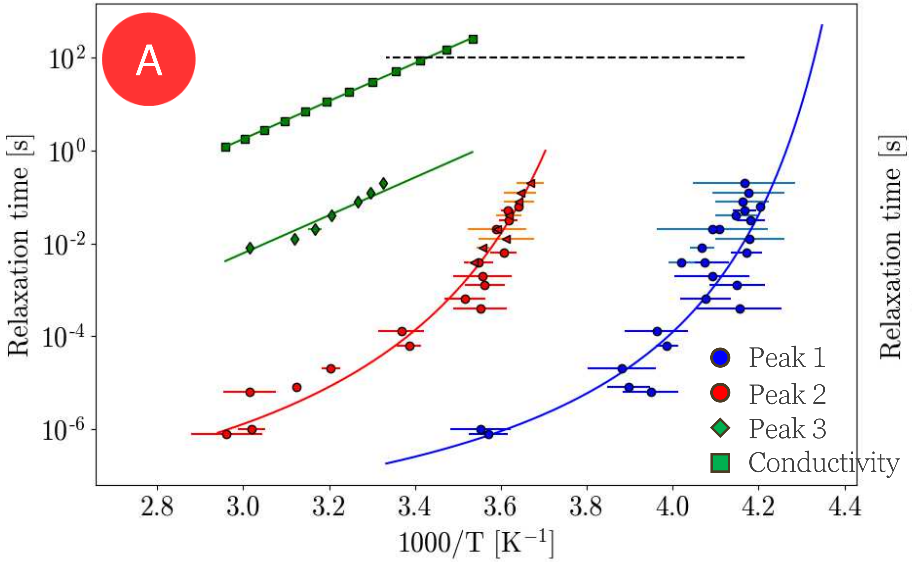
Chemical bonding & ligand coordination

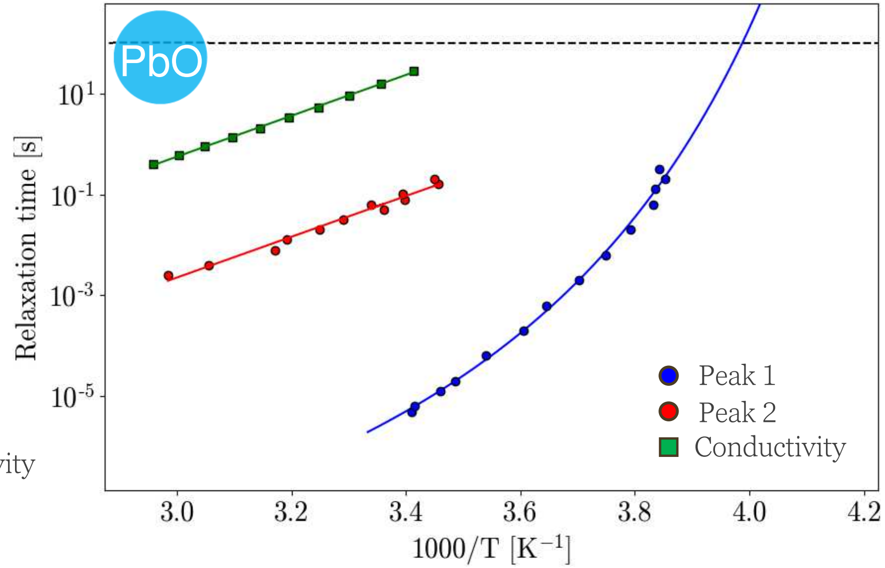
Oil matrix mobility

Broadband dielectric spectroscopy applied to oil films

Prof. Simone Simon
NAPOLITANO

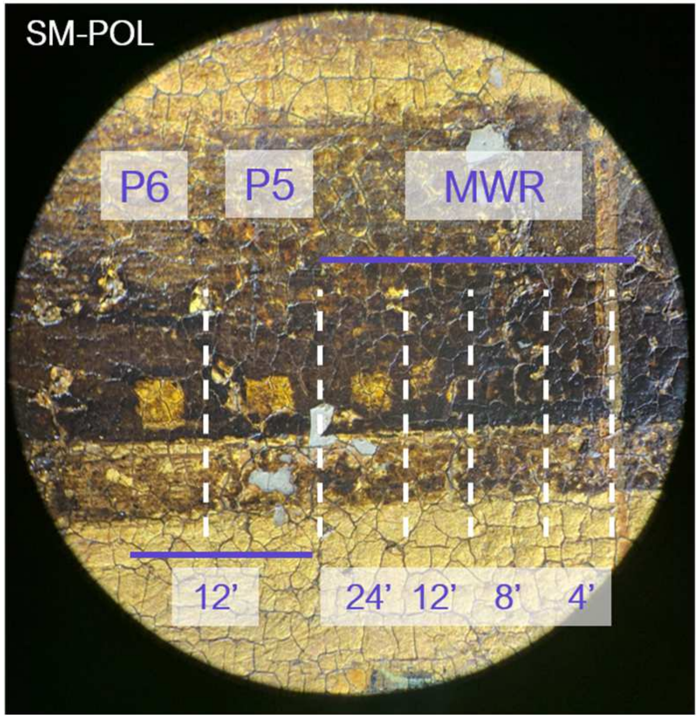
Temperature-dependent 10 Hz – 40 MHz





ULB UNIVERSITÉ LIBRE DE BRUXELLES

In the meanwhile...

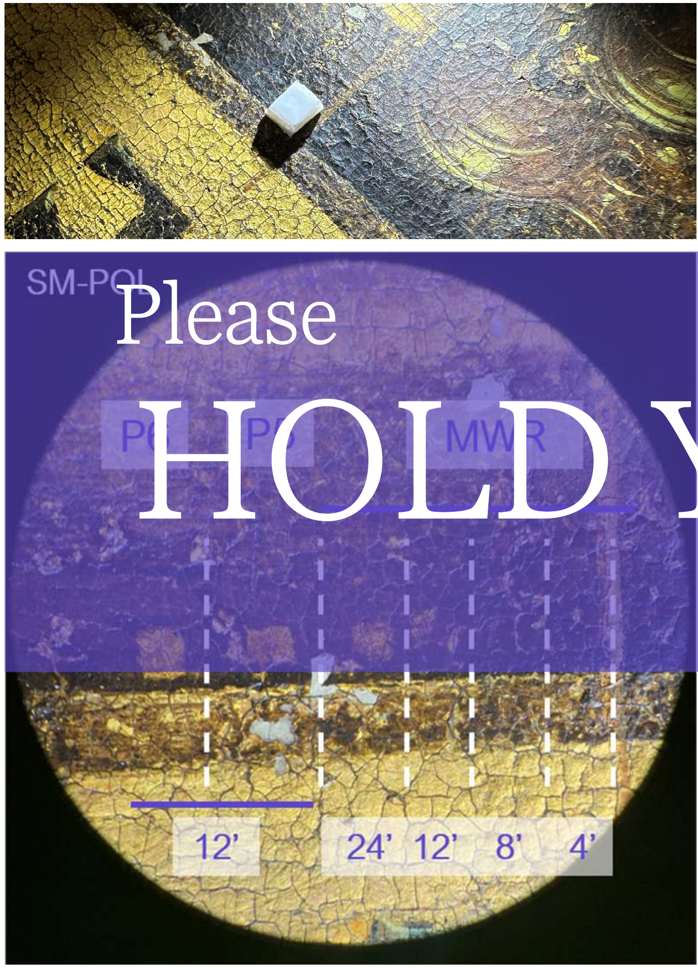


ASAP
Art Salinity and Acidity Project

CSGI

PÉRIER D'IETEREN

In the meanwhile…



Please

HOLD YOUR WATER !

ASAP
Art Salinity and Acidity Project

CSGI

PÉRIER D'IETEREN

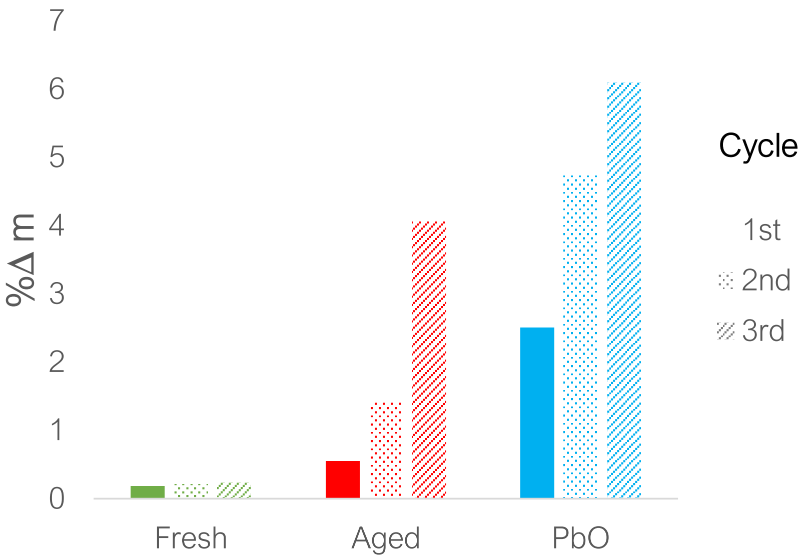
EEHOP

Correlating oil binders’ water-related behavior with ε’ & ε”

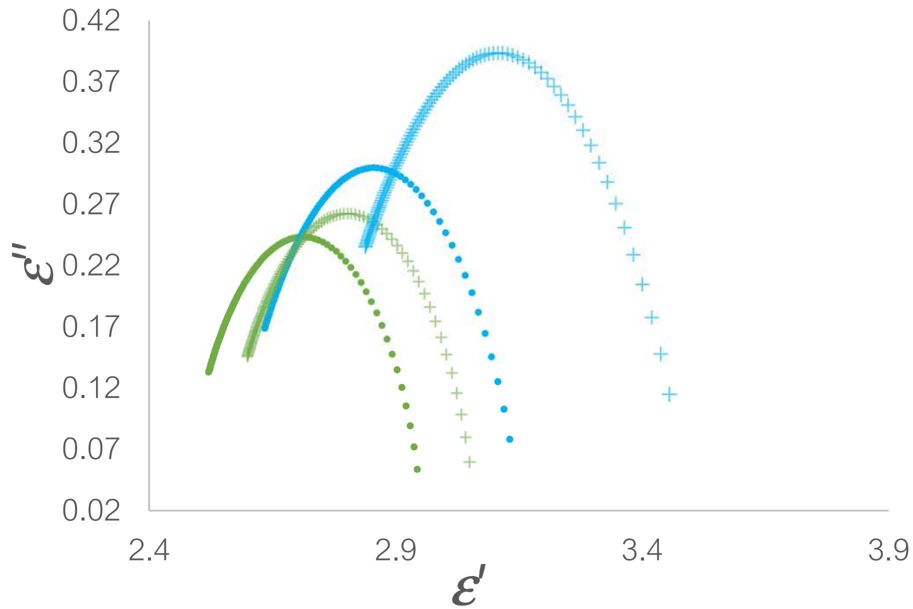
Beatrice
BORACCHI

F
A
PbO

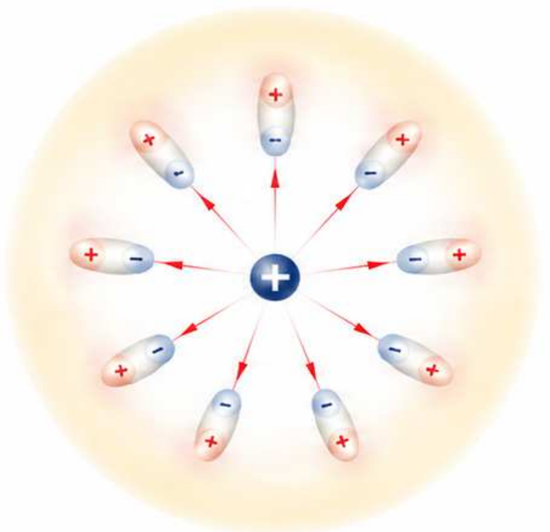
Dynamic vapor sorption (DVS)

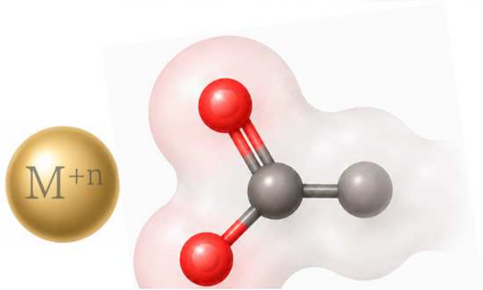


Cole-Cole plot (HN model fit)

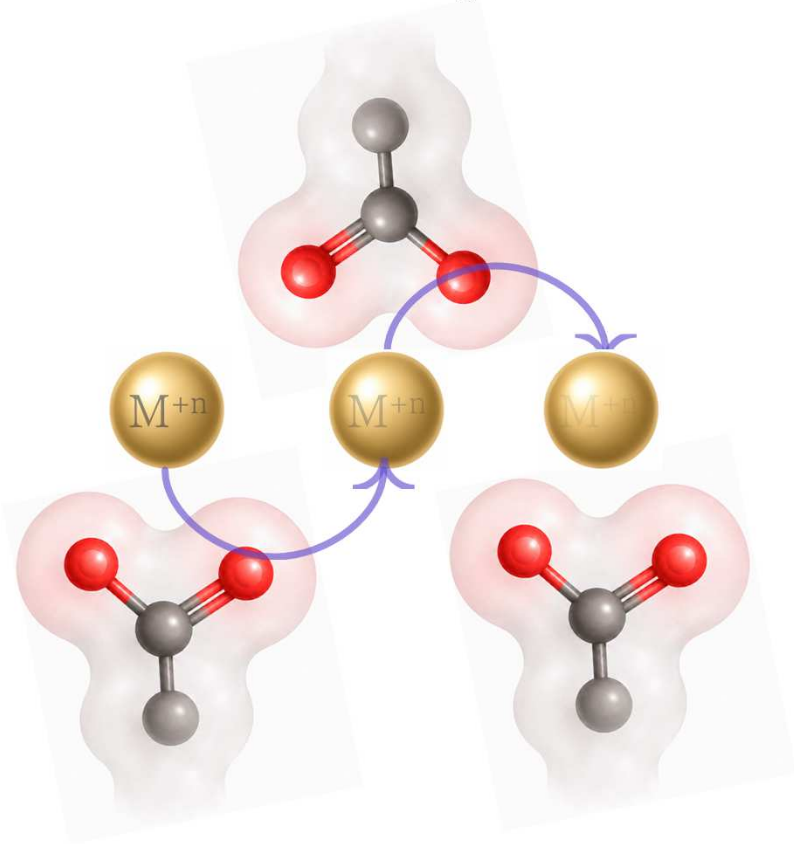


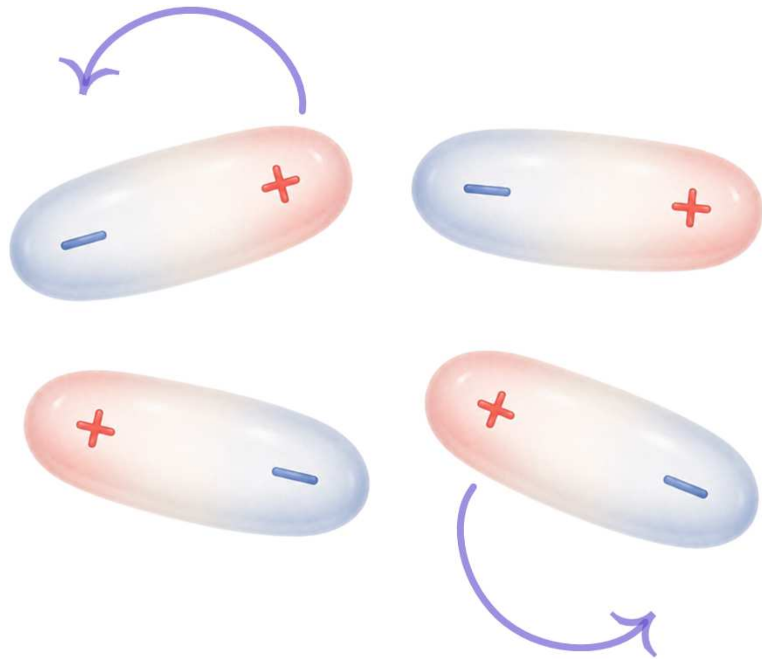
Fundamental questions…



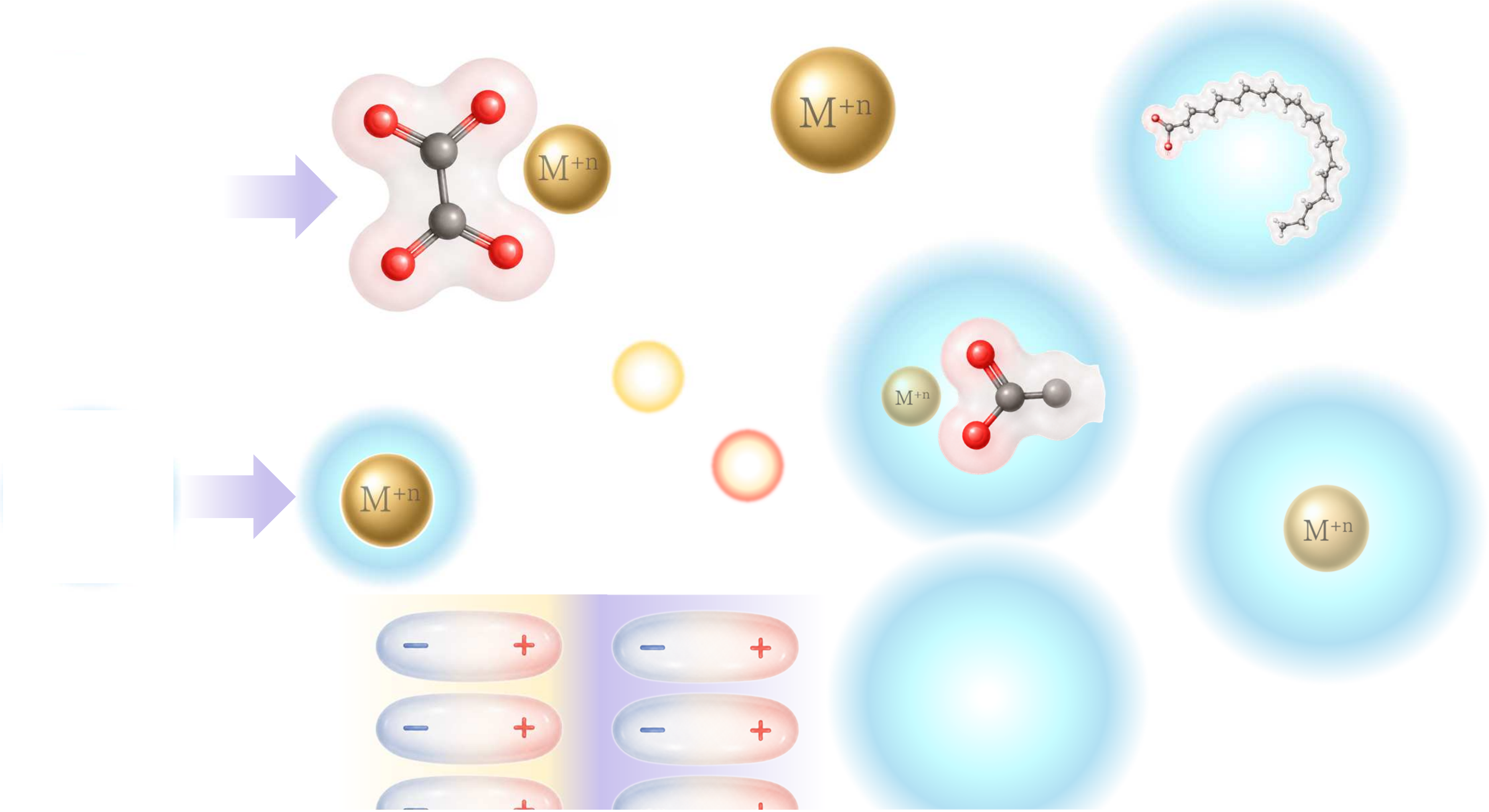


Fundamental questions...

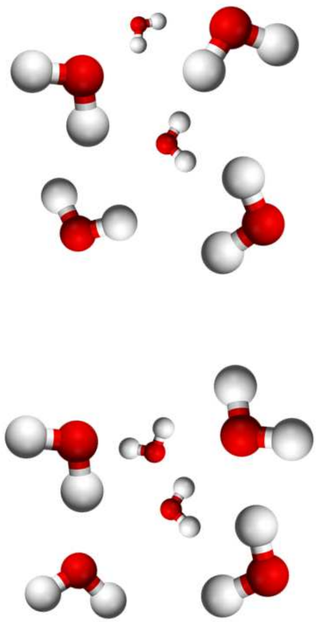


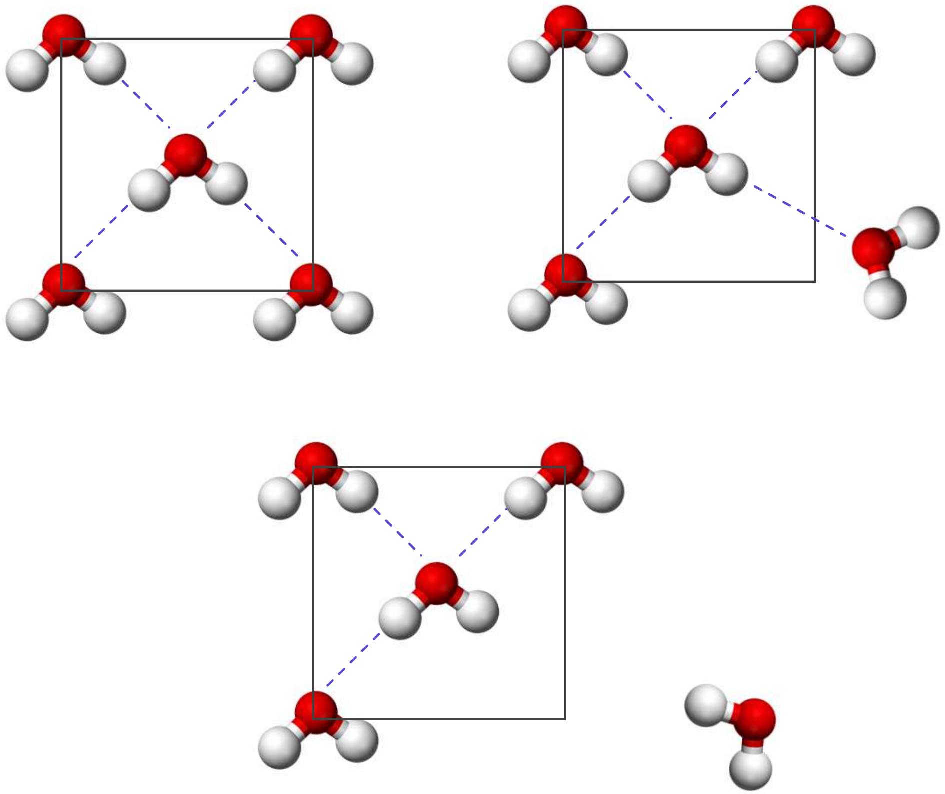


Fundamental questions...

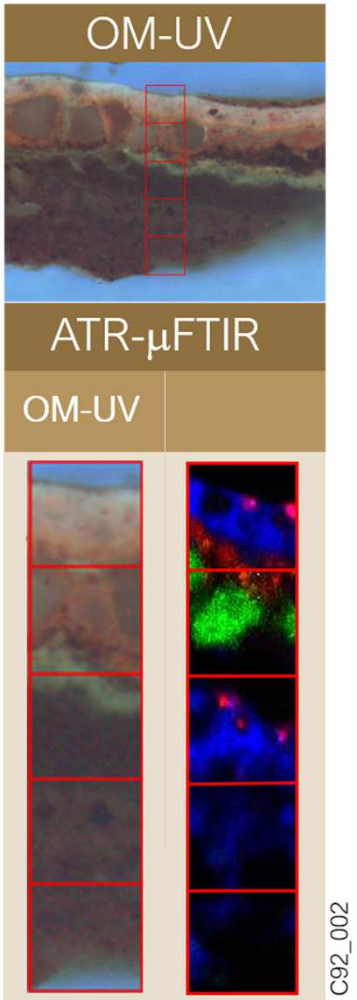


Fundamental questions…





Ionic exchange within oil paint films > metal oxalates speciation



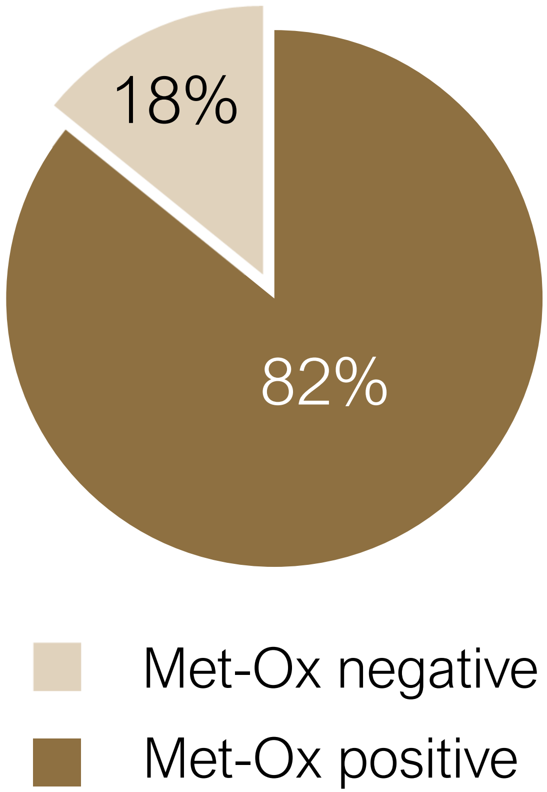
99 cross sections

48 paintings

32 painters

15th-17th c.

199 analysis zones



Red lakes

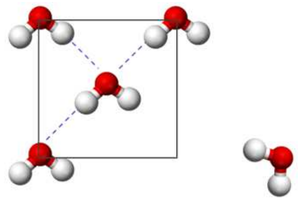
Verdigris
Malachite

Ultramarine
Azurite

Probing water environments with t-µFTIR

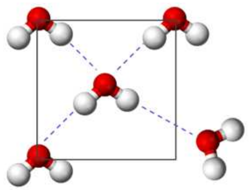
WBW Weakly bonded

3630 cm^{-1}



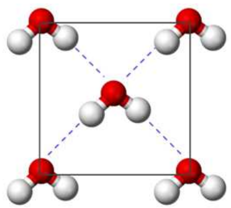
LSBW Less-strongly bonded

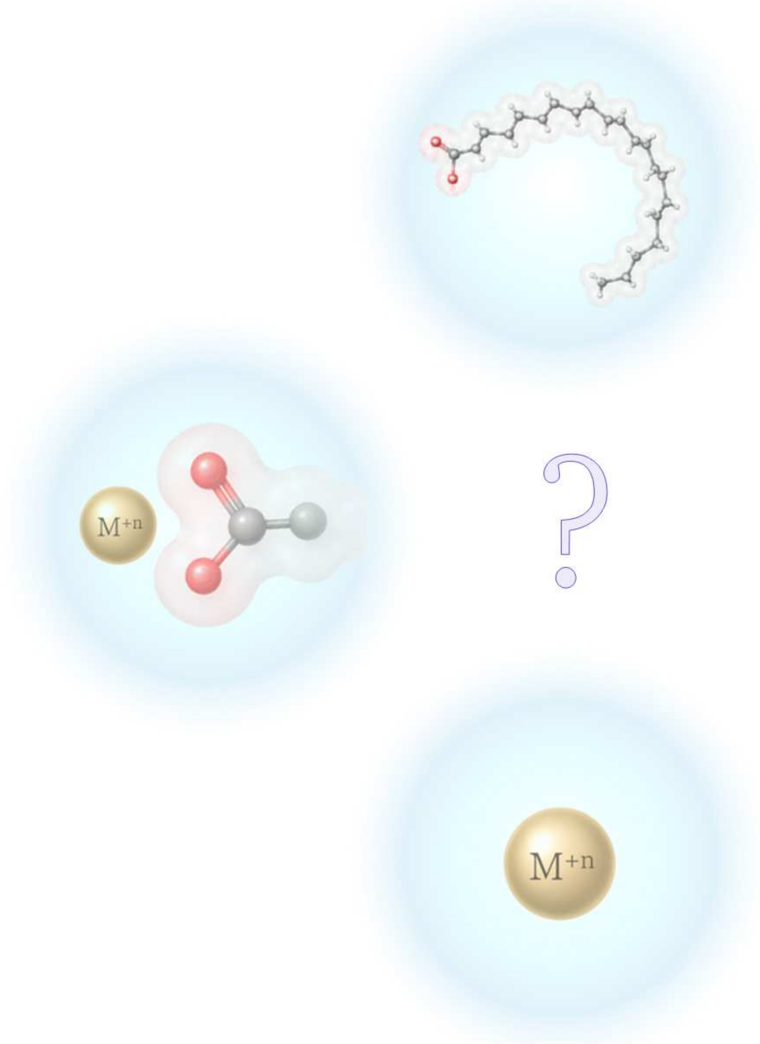
3415 cm^{-1}



SBW Strongly bonded

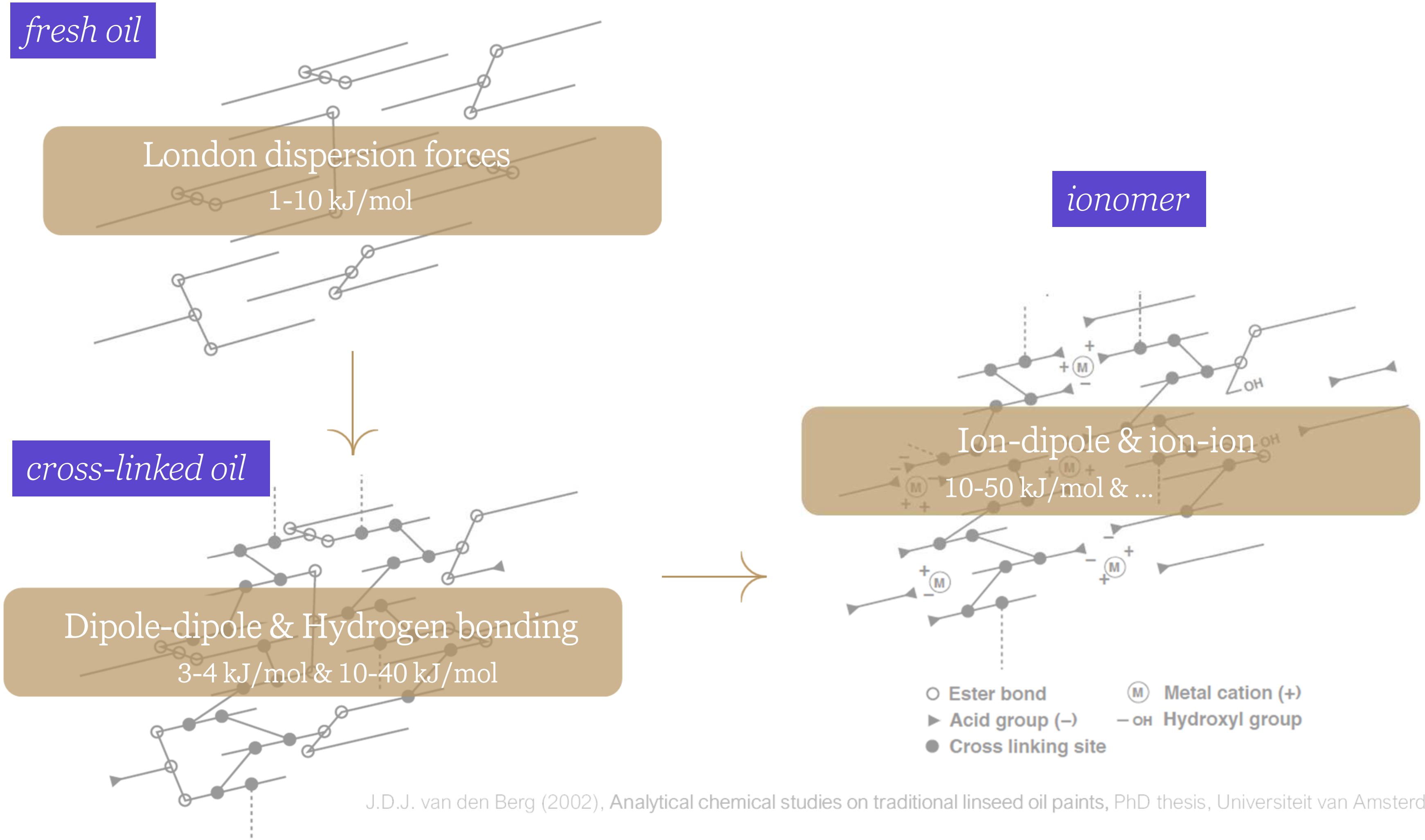
3242 cm^{-1}





Y. Yao, S. Catalini, P. Foggi, and R. Mezzenga, 'Water-Lipid Interface in Lipidic Mesophases with Excess Water', *Faraday Discuss.*, vol. 249, no. 10, Oct. 2023, doi: 10.1039/D3FD00118K.

Probing water environments with t-µFTIR



J.D.J. van den Berg (2002), Analytical chemical studies on traditional linseed oil paints, PhD thesis, Universiteit van Amsterdam

EEHOP

Probing water environments with t-μFTIR

Evgeniia
GRZHESHCHUK

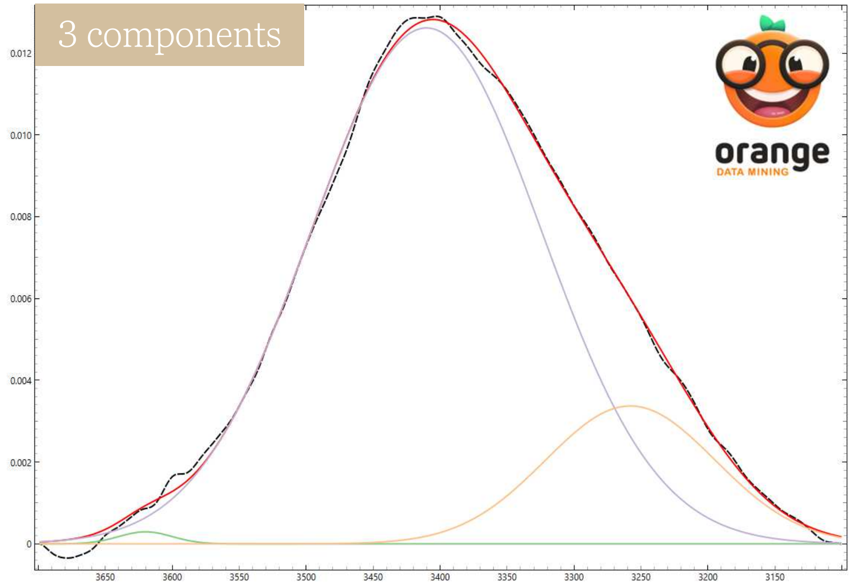
150 μm-thick film
@CaF_2 window

F
A
PbO

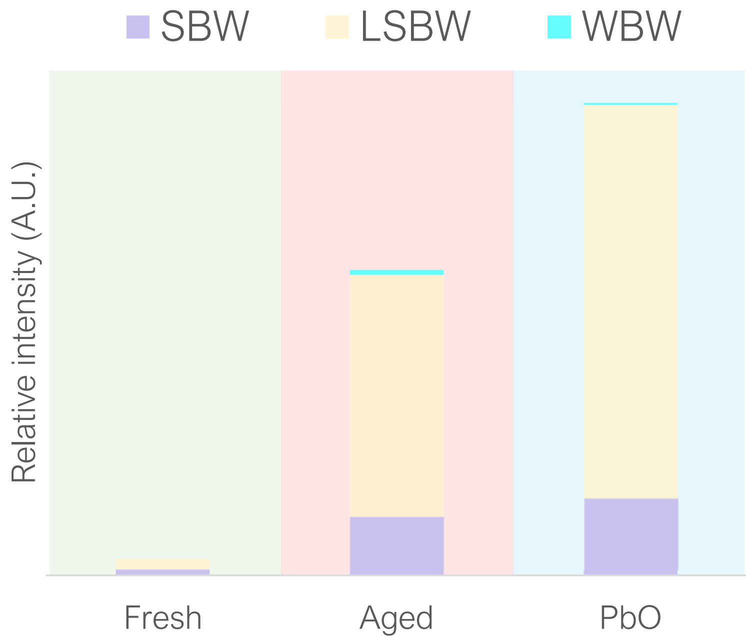
100% RH

0% RH

O-H stretching (3650-3100 cm^{-1}) peak deconvolution



100% RH –0% RH



Free water	3630 cm^{-1}
Partially bonded water	3415 cm^{-1}
Strongly bonded water	3242 cm^{-1}