DNP/NMR @ LCMCP: instrumentation, beyond standard GIPAW and applications to biomaterials: Part I

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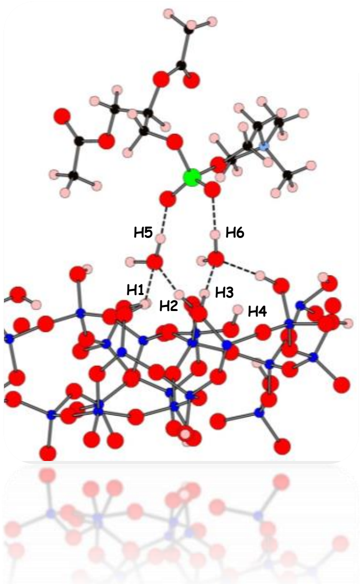
Sorbonne Universités



4th sino-french workshop 2017

Laboratoire de Chimie de la Matière Condensée de Paris (LCMCP), France

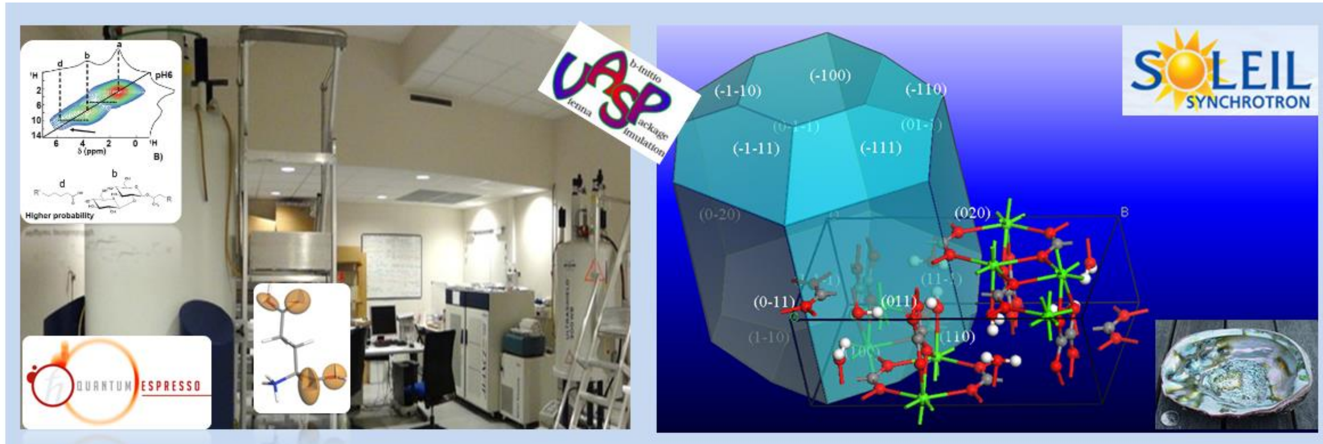
UPMC
SORBONNE UNIVERSITÉS

SMiLES group @LCMCP

SMiLES

Spectroscopy, **M**odelling, **i**nterfaces for natura**L** **E**nvironment and health topic**S**.

Spectroscopic and numerical approaches for synthetic and natural materials.

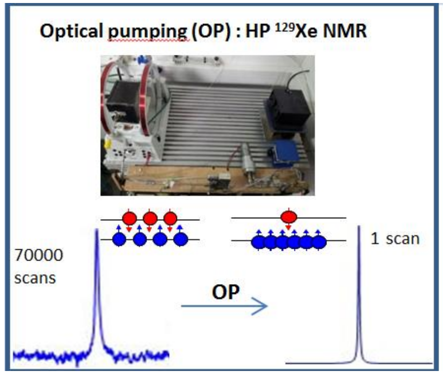


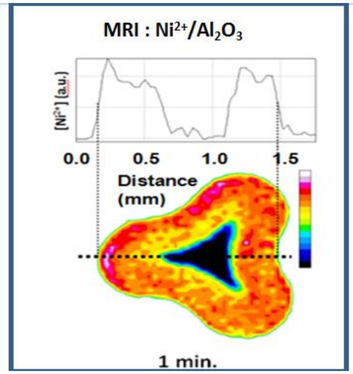
SMiLES group @LCMCP

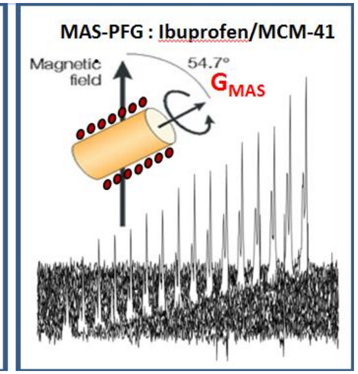
hyperpolarization

Diffusion by MAS-PFG NMR, MRI, hyperpolarized ^{129}Xe NMR : applications to porous materials.

Coll.: IFPEN.



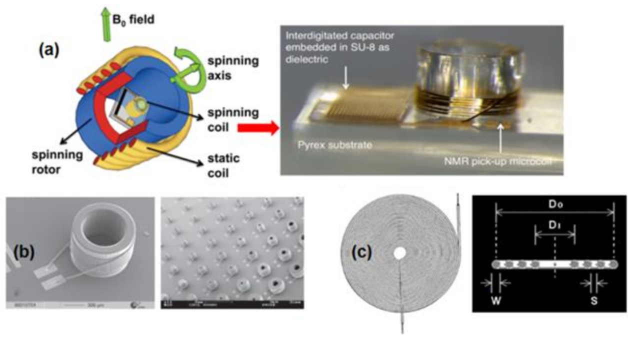


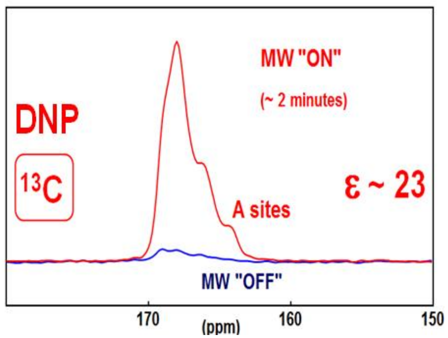


instrumentation

Instrumentation and methodology in solid state NMR: towards a net increase in *sensitivity*!

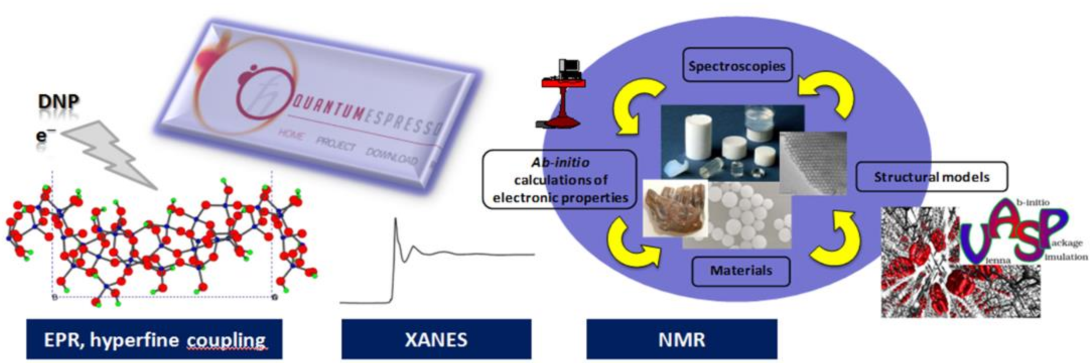
Coll.: D. Sakellariou (CEA, Saclay), V. Badilita (Freiburg), F. Aussenac (Bruker, Wissembourg).





first-principles calculations

The combined approach: "advanced NMR / *ab initio* calculations of NMR parameters" ; modeling of hybrid interfaces.



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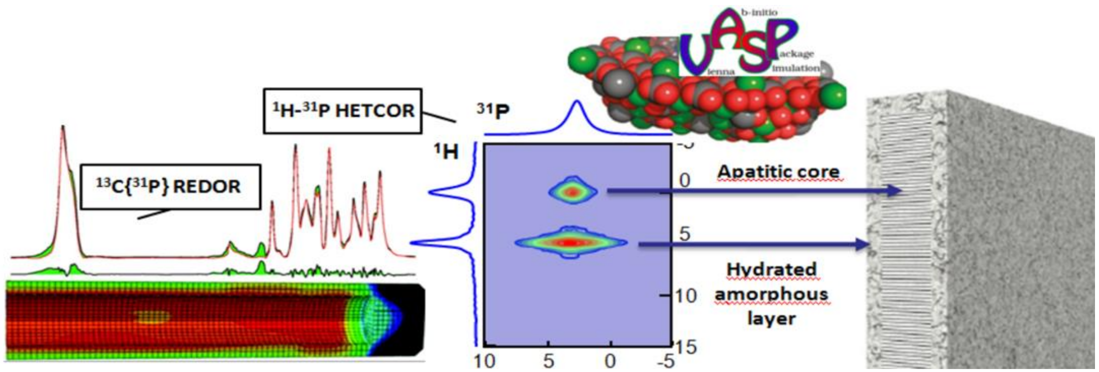
biomineralization
pathological calcifications

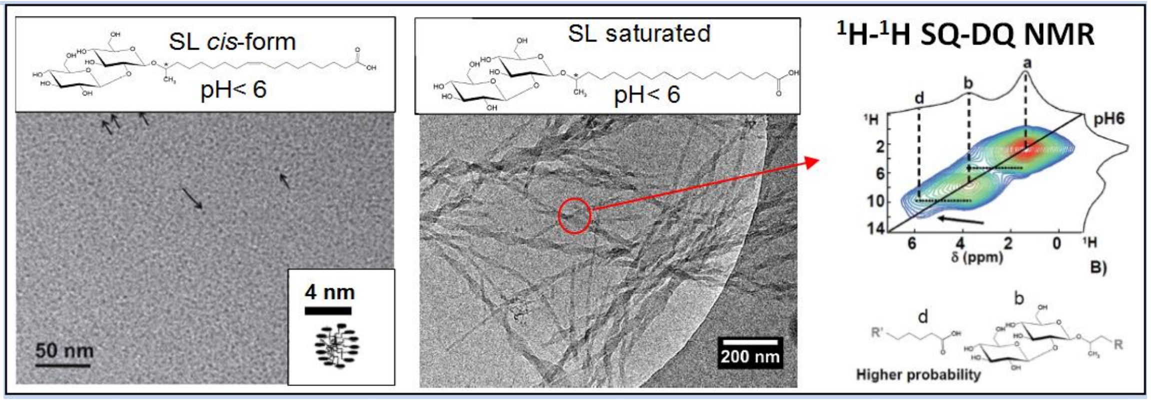
Two dimensional NMR and modeling: new tools for the characterization of hybrid interfaces in biological materials (bones, teeth…).



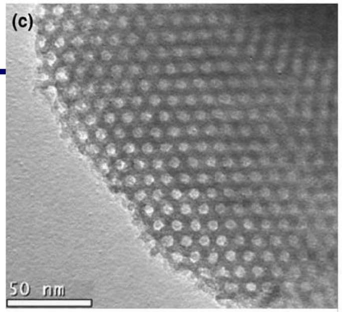
soft matter

Stimuli-responsive self-assembly of microbial glycolipids from biomass

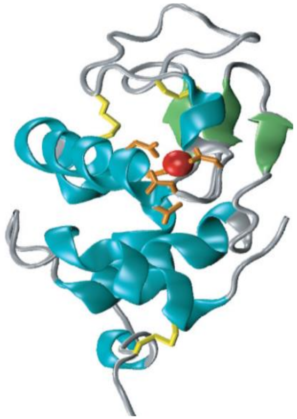
Coll.: University of Gent, Belgium.



Solid state NMR in materials science

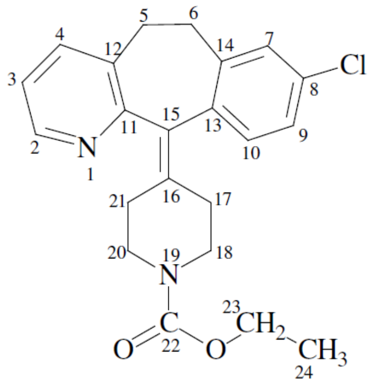


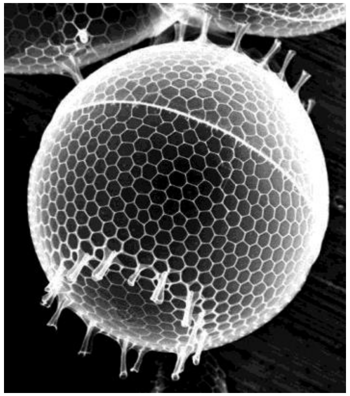
Bio-solids



Nanomaterials

Polymorphism





Biological materials

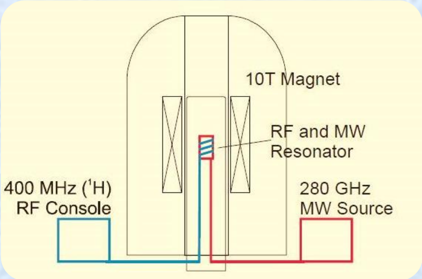
Hybrid materials

Outline

- **Sensitivity issues: DNP MAS**

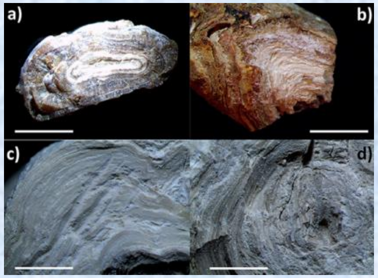
  HP ^{129}Xe

  micro-coils, micro-resonators

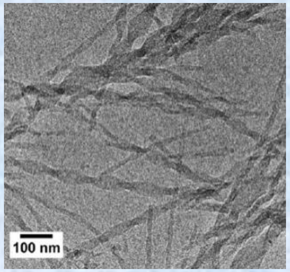


- ***Ab initio* calculations of NMR parameters**
- **New trends in GIPAW**

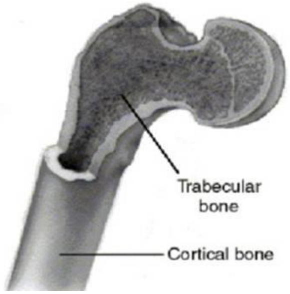
- **Biomineralization**
- **Pathological calcifications**



- **Soft Matter**



Context: biological hydroxyapatites (HAp)



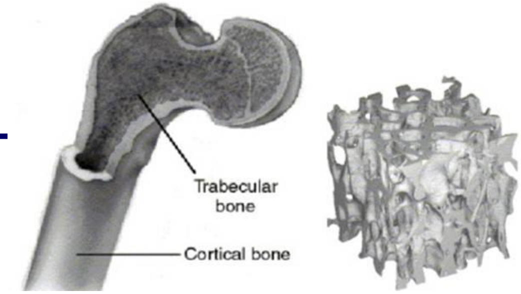
- **Sensitivity issues: DNP MAS**

F. Babonneau

C. Coelho

L. Bonhomme-Coury

Context: biological hydroxyapatites (HAp)

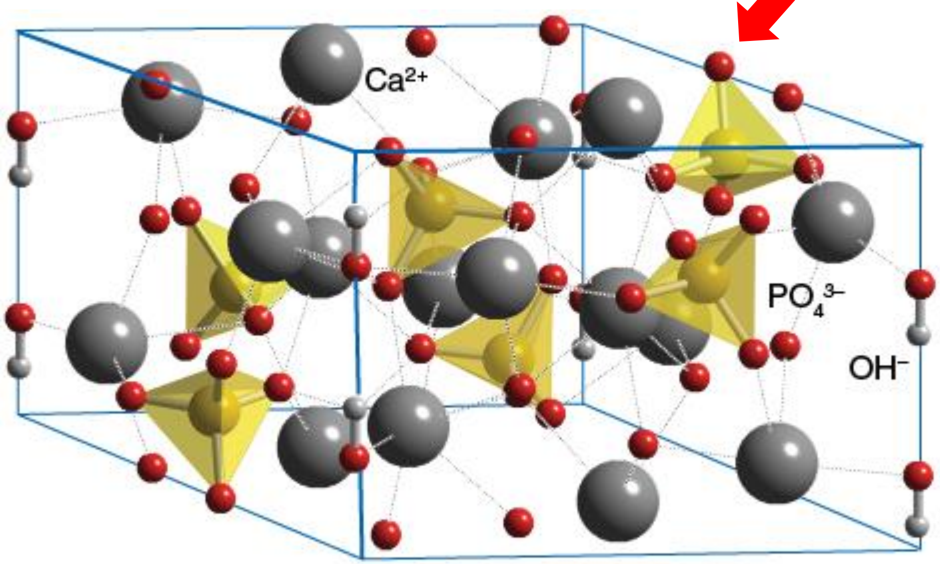


→ $Ca_{10}(PO_4)_6(OH)_2$ + substitutions (C$^+$ and A$^-$)

Na^+, K^+, Mg^{2+}, Zn^{2+}, Sr^{2+} …

F^-, Cl^-, CO_3^{2-}, SiO_4^{4-} …

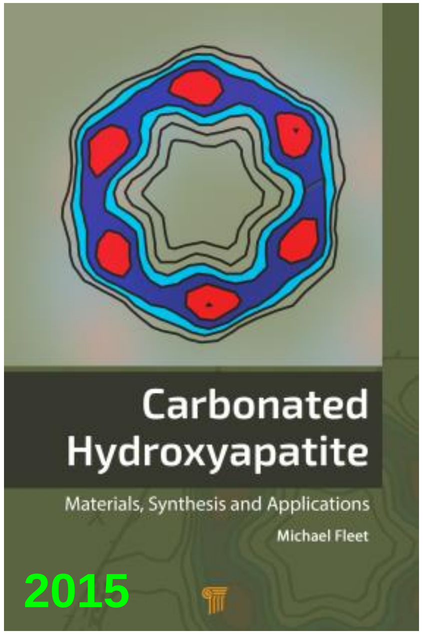
B site



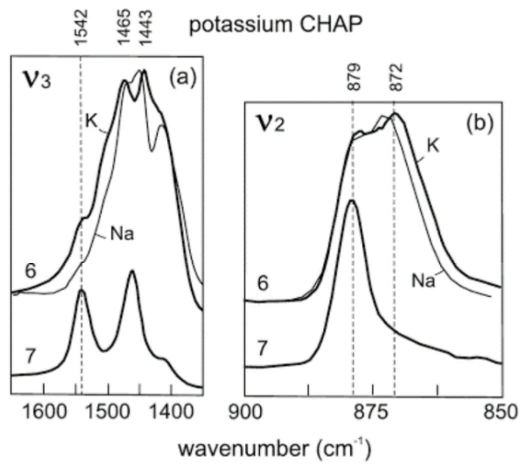
A site

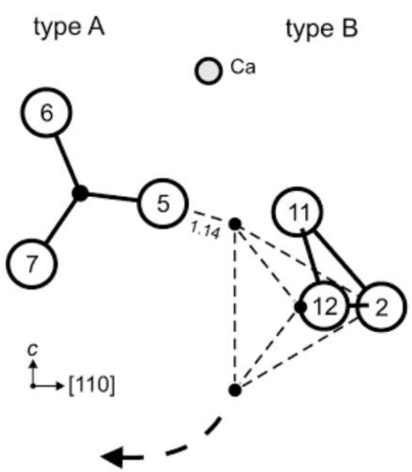
- ► ^{43}Ca: low γ and N.A. ~ 0.14%
- ► low wt% for all C$^+$ and A$^-$

Intrinsically distributed materials



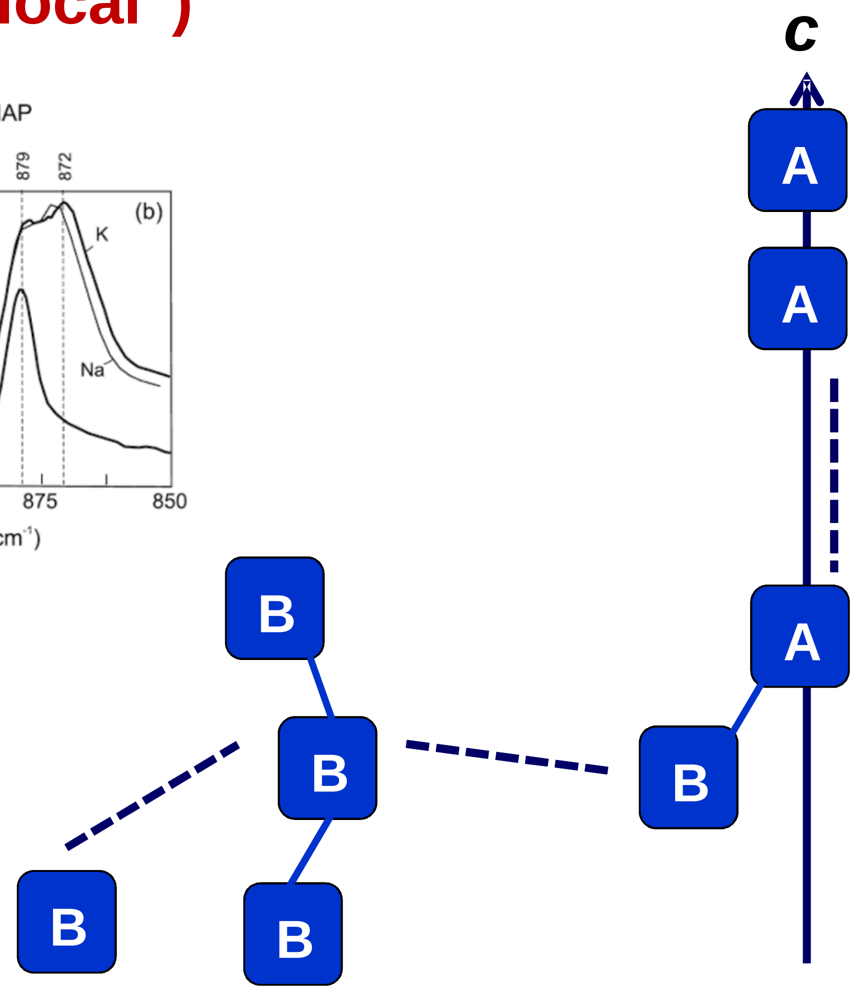
FTIR ("too local")



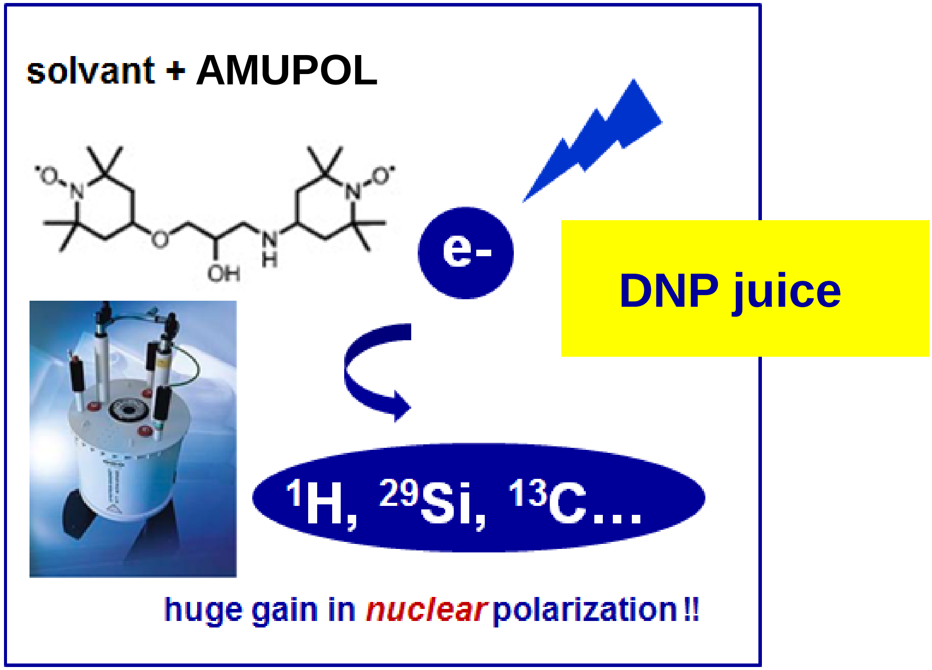


PXRD

("average")



Dynamic Nuclear Polarization (DNP) MAS



- **SENSITIVITY**

"impossible experiments"

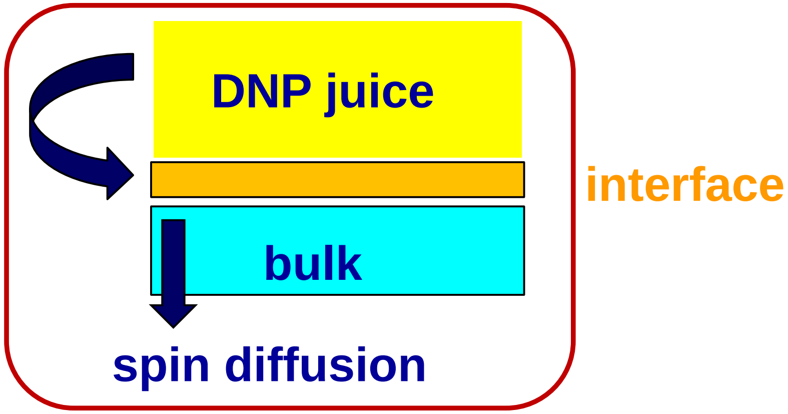
- **LOW TEMPERATURE & MAS**

(~ 100 K or lower…)

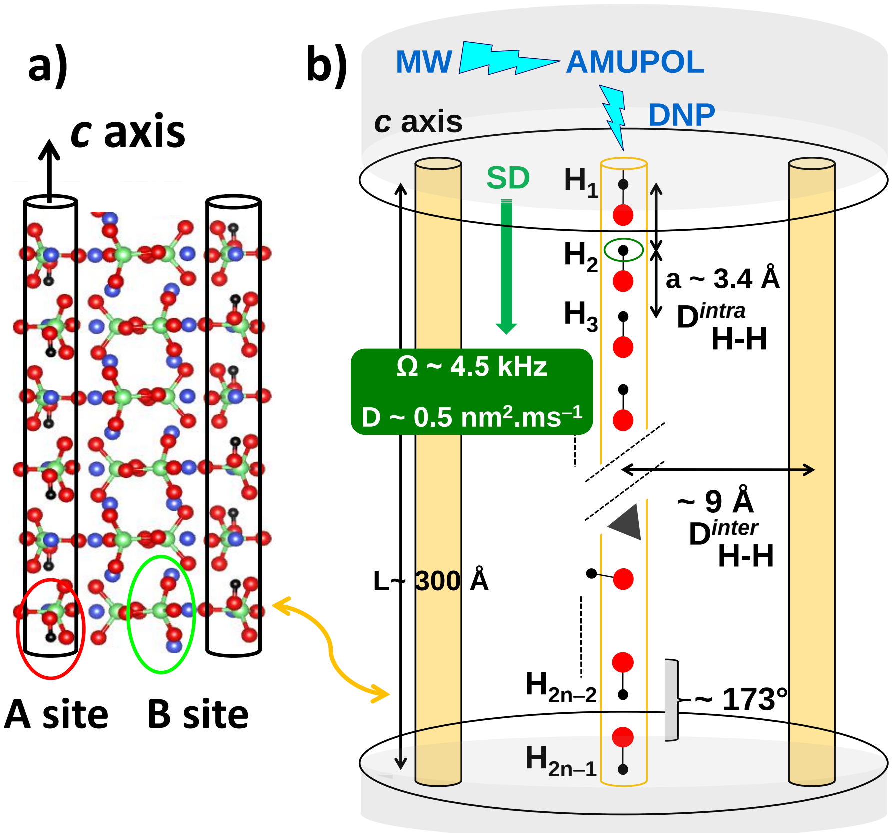
depending on the sample…

- **enhanced spin locking during CP**
- **better homonuclear decoupling**
- **…**

- **but: questions …**



The HAp structure (hexagonal)



channels of OH⁻ groups

$D_{H\text{-}H}$inter << $D_{H\text{-}H}^{intra}$

A site substitutions (▲)

orientation of OH⁻

$$\frac{\partial P}{\partial t} = D\,\frac{\partial^2 P}{\partial z^2} - \frac{P}{T_{1n}}$$

$$D = \Omega\, a^2$$

$$\varepsilon = \varepsilon_{1H}^{0}\,\frac{2\sqrt{DT_{1n}}}{L}\,tanh\left(\frac{L}{2\sqrt{DT_{1n}}}\right)$$

P.C.A. van der Wel *et al., J. Am. Chem. Soc.*, 2006

analytical chemistry — Article — pubs.acs.org/ac

Hydroxyapatites: Key Structural Questions and Answers from Dynamic Nuclear Polarization

César Leroy,[†] Fabien Aussenac,[‡] Laure Bonhomme-Coury,[†] Akiyoshi Osaka,[§] Satoshi Hayakawa,[§] Florence Babonneau,[†] Cristina Coelho-Diogo,[∥] and Christian Bonhomme*,[†]

[†]Sorbonne Universités, UPMC Université Paris 06, CNRS, Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris (LCMCP) UMR 7574, 4 Place Jussieu, 75252 Paris Cedex 05, France

[‡]Bruker France, 34, rue de l'Industrie, 67166 Wissembourg, France

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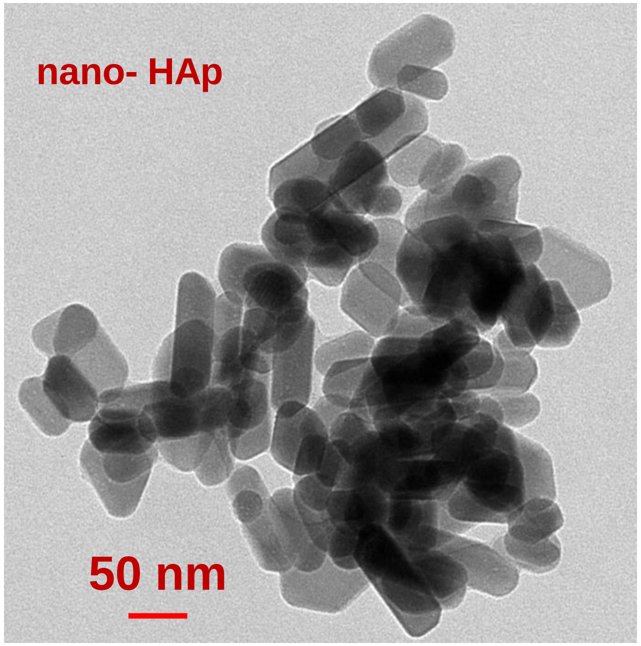
[∥]Sorbonne Universités, UPMC Université Paris 06, CNRS, Institut des Matériaux de Paris Centre (IMPC-UPMC-FR2482), 75252 Paris, Cedex 05, France

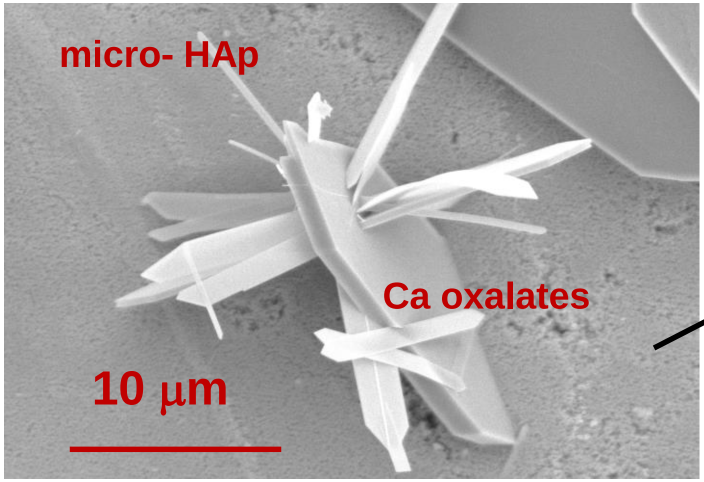
Hydroxyapatite (HAp) materials

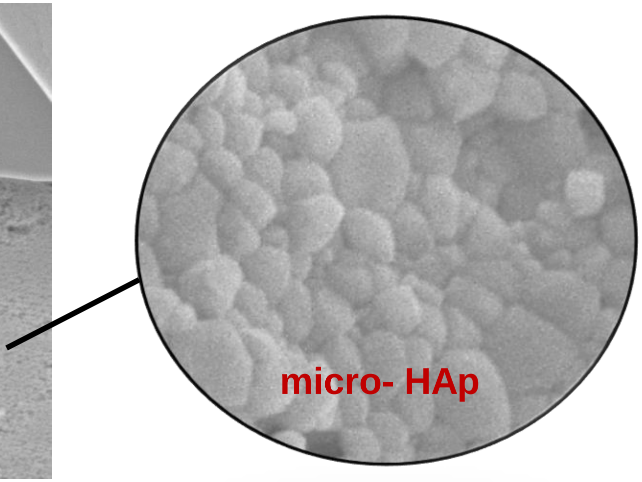
In vitro



tunability in:

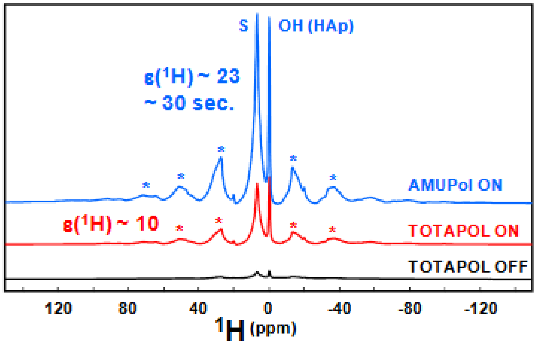
- ► size
- ► morphology
- ► crystallinity
- ► chemical composition (C^+, A^-)

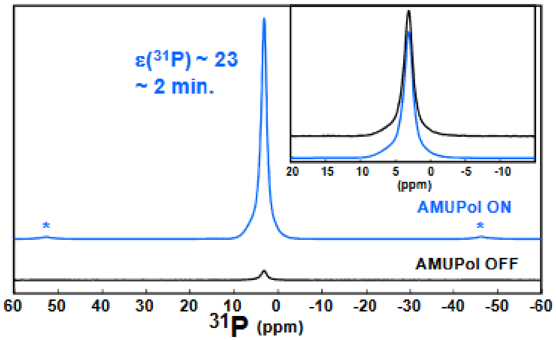


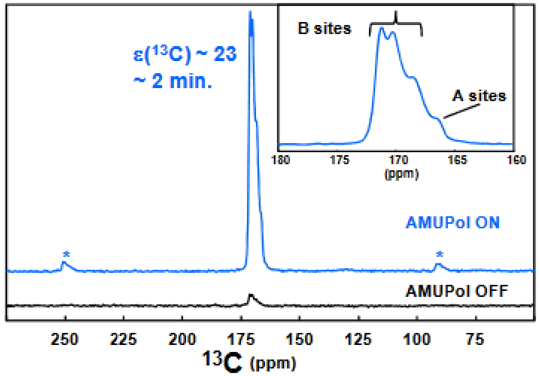


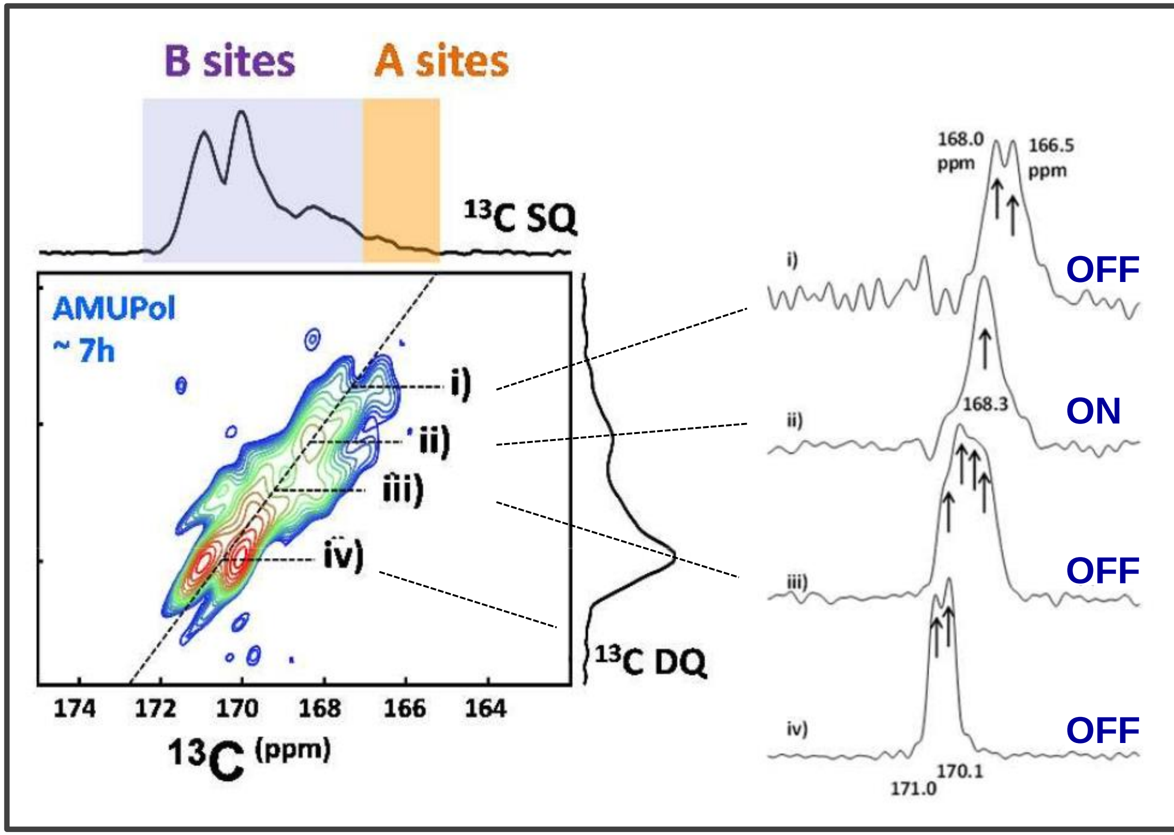
Synthetic carbonated nanosized HAp

- ► synthetic HAp, ~ 1 wt % in C, labeled in ^{13}C
- ► 1D, 2D, double– and triple resonance CP, SQ-DQ experiments

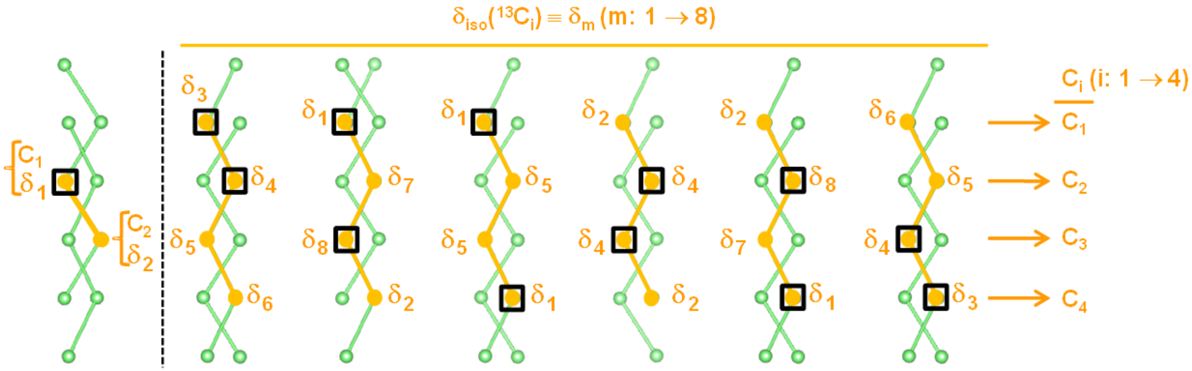


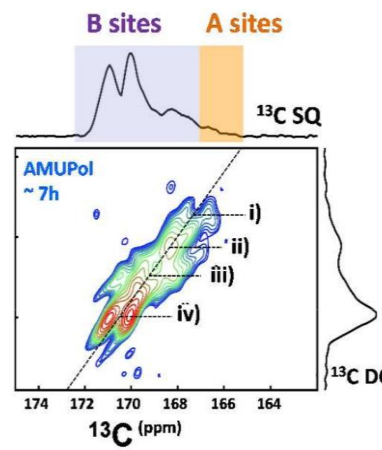


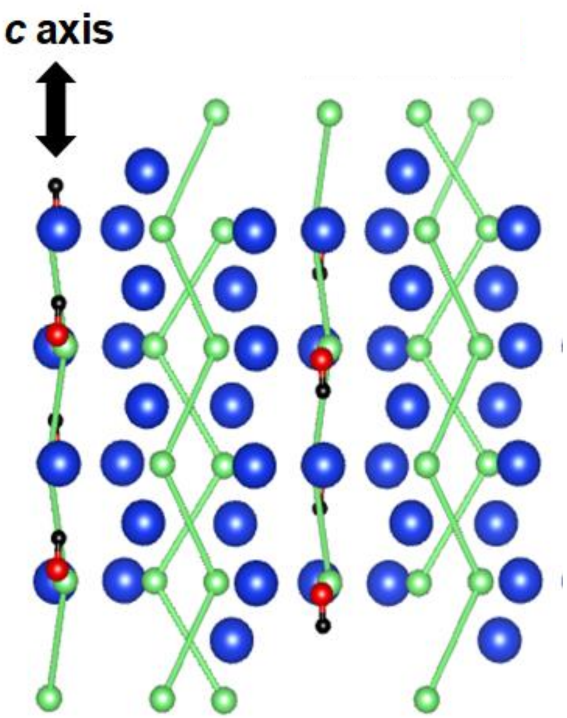


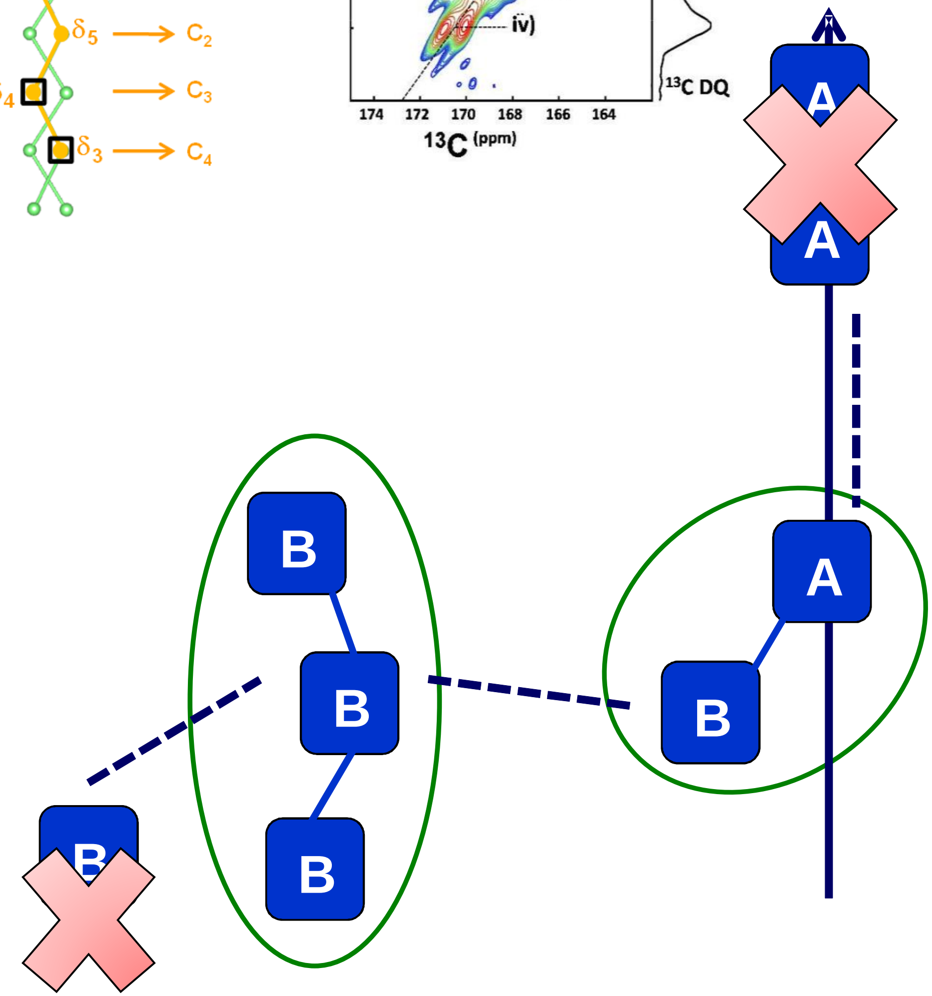


Towards structural models







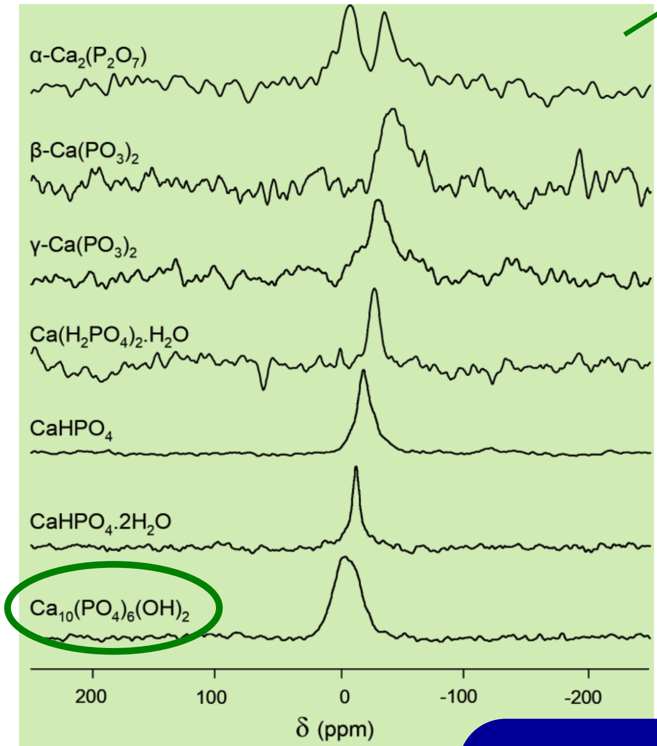


Options for ^{43}Ca solid state NMR

low γ N.A. ~ 0.14 %

► **natural abundance**: large volume rotor, highest magnetic field, moderate MAS

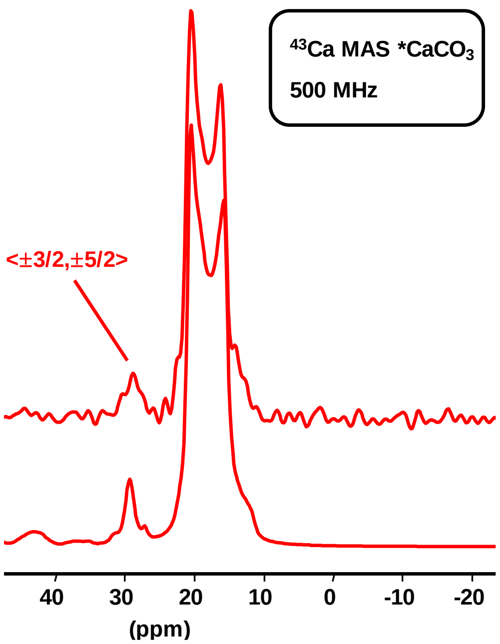
^{43}Ca MAS



- 7mm, 850 MHz, 5 kHz, ~ 10 hours
- No 2D

► **labeled samples**: 60% labeled *$CaCO_3$ (calcite)

- fast… and 2D
- but costs !!



many thanks to:

D. Laurencin, D. Lee, G. De Paëpe, F. Aussenac

Natural abundance ^{43}Ca DNP spectroscopy

$\nu_0(^{43}Ca)$ = 26,94 MHz, 100 K, DNP juice: glycerol-$d_8/D_2O/H_2O$ (60/30/10; v/v/v) + AMUPol,

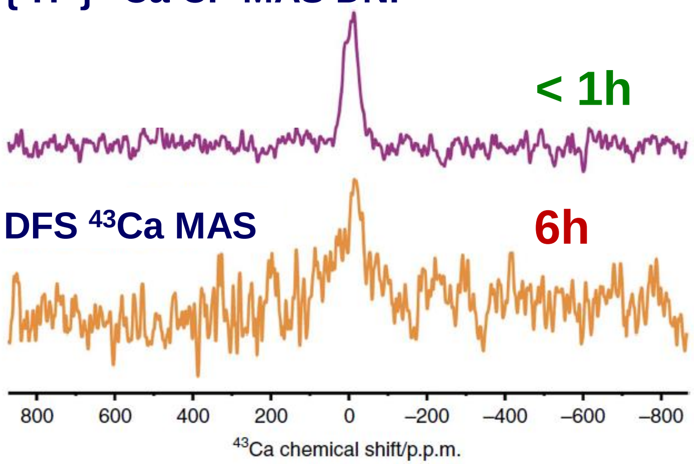
sample: ~ 20 mg

$\{^1H–\}^{43}$Ca CP MAS DNP

< 1h

DFS ^{43}Ca MAS

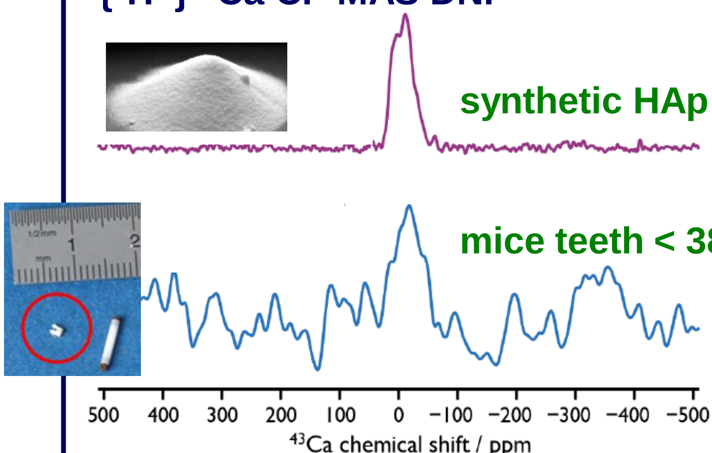
6h



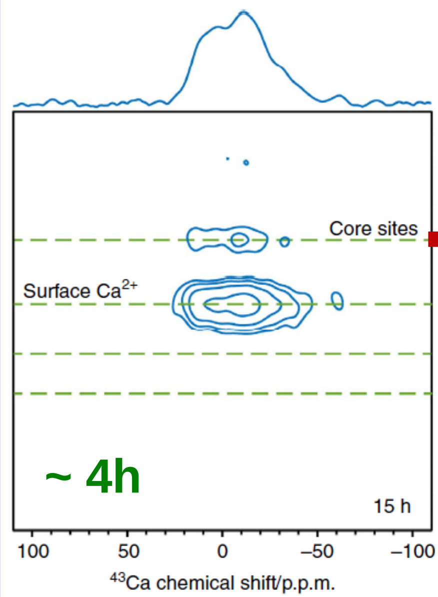
$\{^1H–\}^{43}$Ca CP MAS DNP

synthetic HAp < 1h

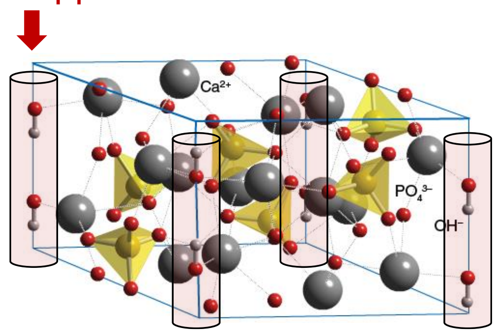
mice teeth < 38h



N.A. 2D $\{^1H–\}^{43}$Ca HETCOR CP MAS DNP



0 ppm



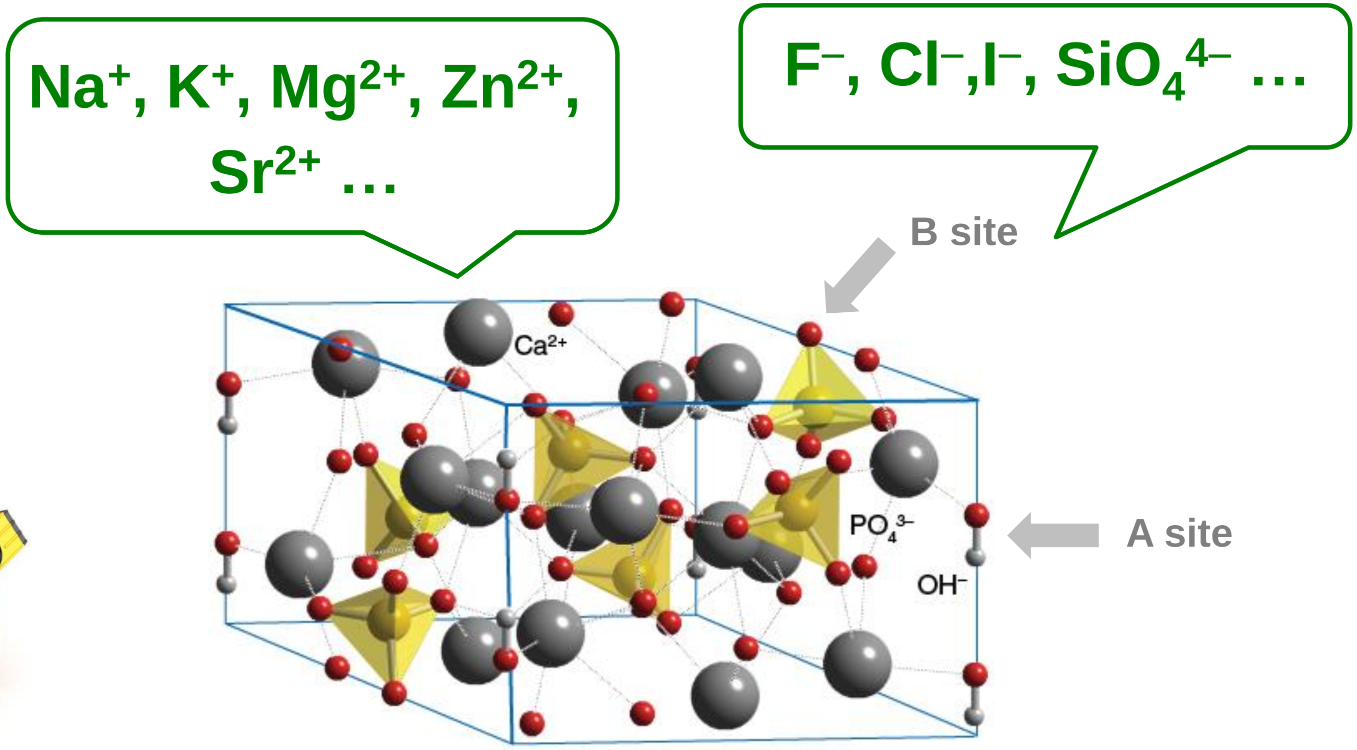
nature COMMUNICATIONS

Interfacial Ca^{2+} environments in nanocrystalline apatites revealed by dynamic nuclear polarization enhanced ^{43}Ca NMR spectroscopy

Daniel Lee, César Leroy, Charlène Crevant, Laure Bonhomme-Coury, Florence Babonneau, Danielle Laurencin, Christian Bonhomme & Gaël De Paëpe

Future experiments

- elements with low wt % in calcium phosphates (including HAp)
- surface modifications of HAp
- … extension to (human) biological sample → see Part II (kidney stones)



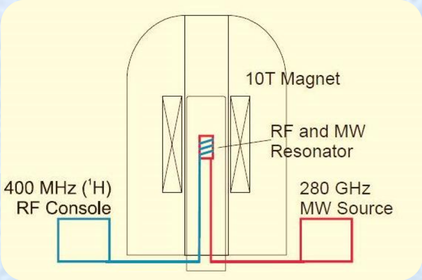
DFS, (Q)CPMG, WURST, BRAIN CP, SOSO,… (Kentgens, … Schurko … ***et al*****.)**

Outline

- **Sensitivity issues:** DNP MAS

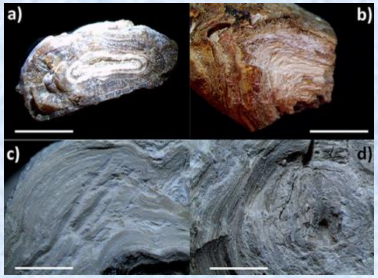
  HP ^{129}Xe

  micro-coils, micro-resonators

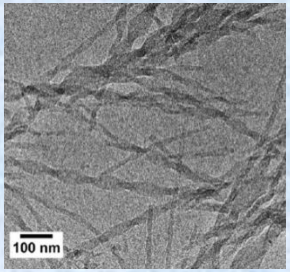


- *Ab initio* calculations of NMR parameters
- New trends in GIPAW

- Biomineralization
- Pathological calcifications



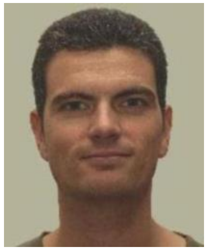
- Soft Matter



Context: Morphology and dynamics of zeolite nucleation

M.-A. Springuel-Huet

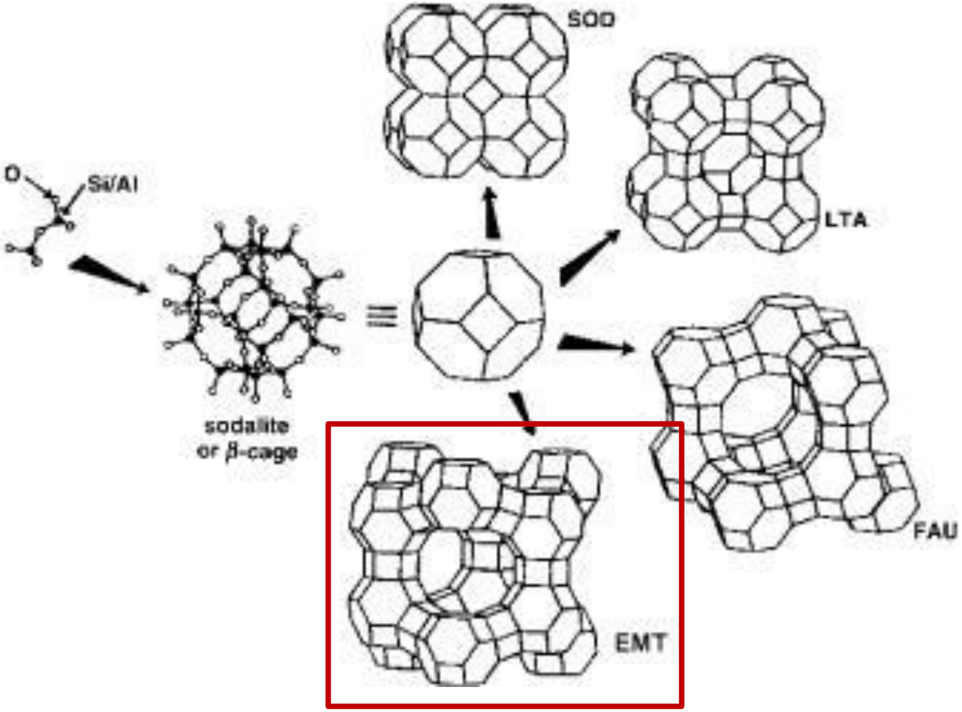
A. Nossov



F. Guenneau

A. Gédéon

- Sensitivity issues: HP ^{129}Xe



catalysis, molecular sieves

EMT-like zeolites

Hyperpolarized ^{129}Xe

CHEMISTRY
A European Journal

Crystal Growth | *Hot Paper* |

3D Study of the Morphology and Dynamics of Zeolite Nucleation

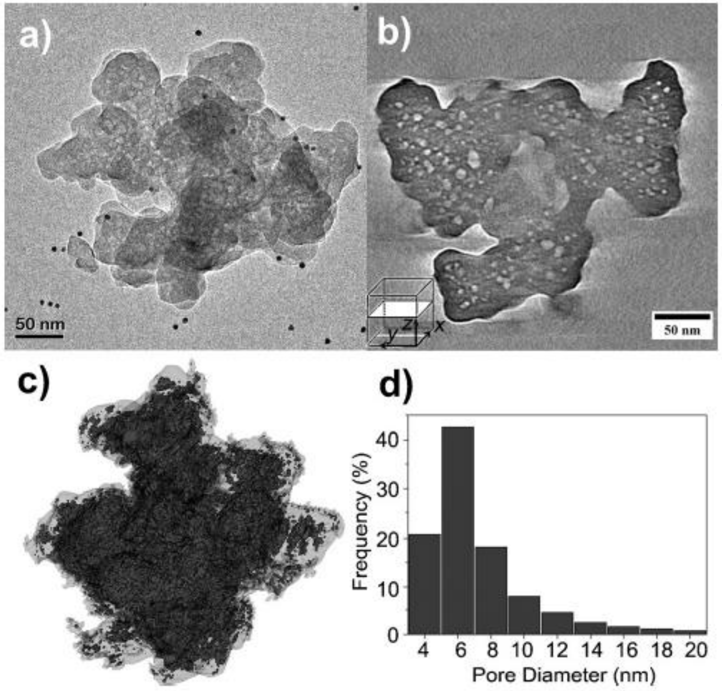
Georgian Melinte,[a] Veselina Georgieva,[b] Marie-Anne Springuel-Huet,[c] Andreï Nossov,[c] Ovidiu Ersen,[a] Flavien Guenneau,[c] Antoine Gedeon,[c] Ana Palčić,[b] Krassimir N. Bozhilov,[d] Cuong Pham-Huu,[e] Shilun Qiu,[f] Svetlana Mintova,[b] and Valentin Valtchev*[b]

- **to explore the nucleation process in an hydrogel system**
- **HP ^{129}Xe: to determine the *first formed zeolite cages* (EMT-like ; Si/Al = 1.2)**

conventional TEM →

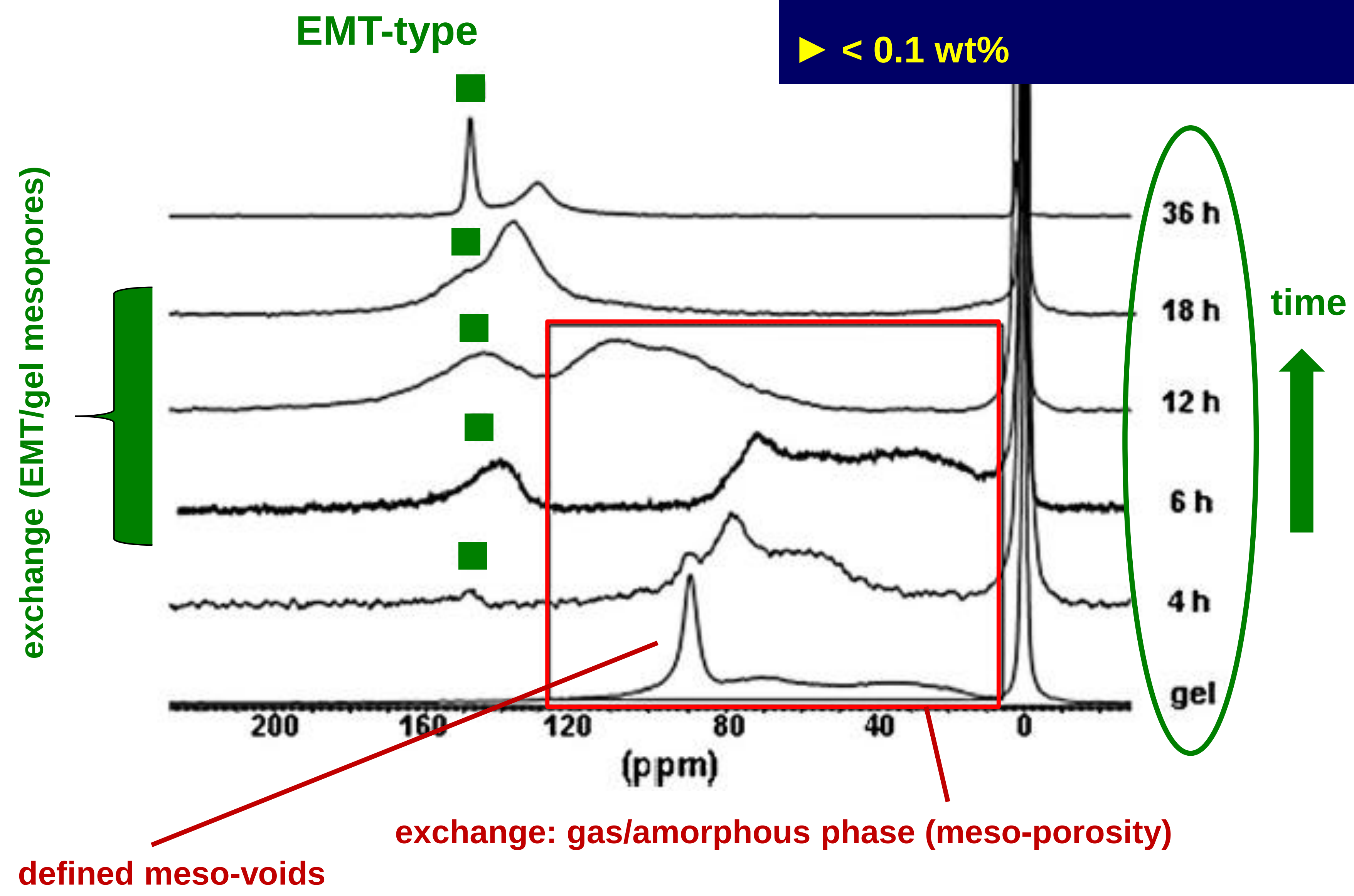
← **cryo-tomogram**

reconstruction of the gel particle (pores: dark grey) →



First stages (*in time*) explored by HP ^{129}Xe NMR

- ► early detection of EMT cages
- ► < 0.1 wt%



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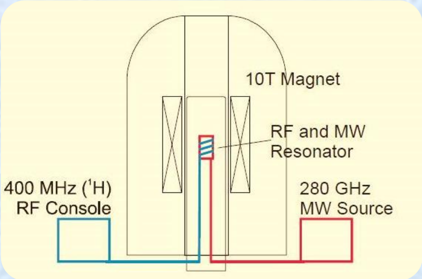

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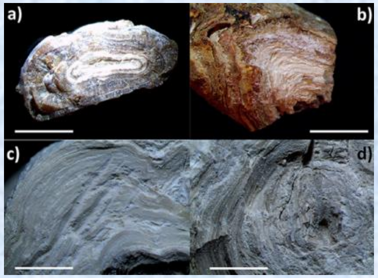
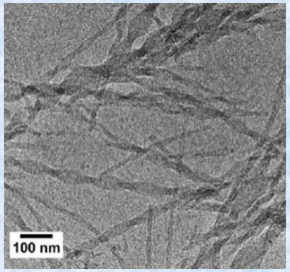
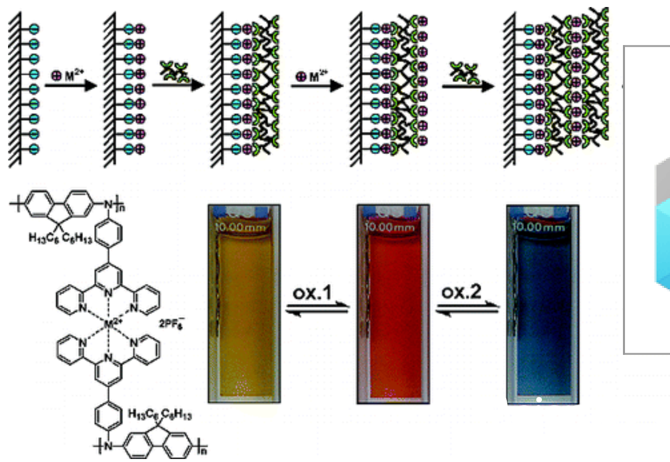
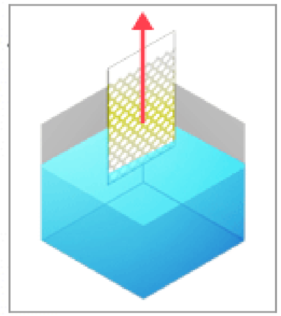


- Soft Matter



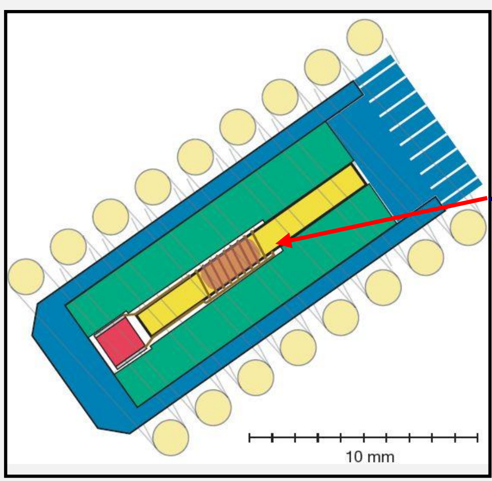
NMR of hybrid mesoporous thin films: a "naive" question





G. Laurent

Magic Angle Coil Spinning



rotor at θ_m

μ-coil

Static coil

D. Sakellariou et al., Nature, 447, 2007.

Potential applications:

- films

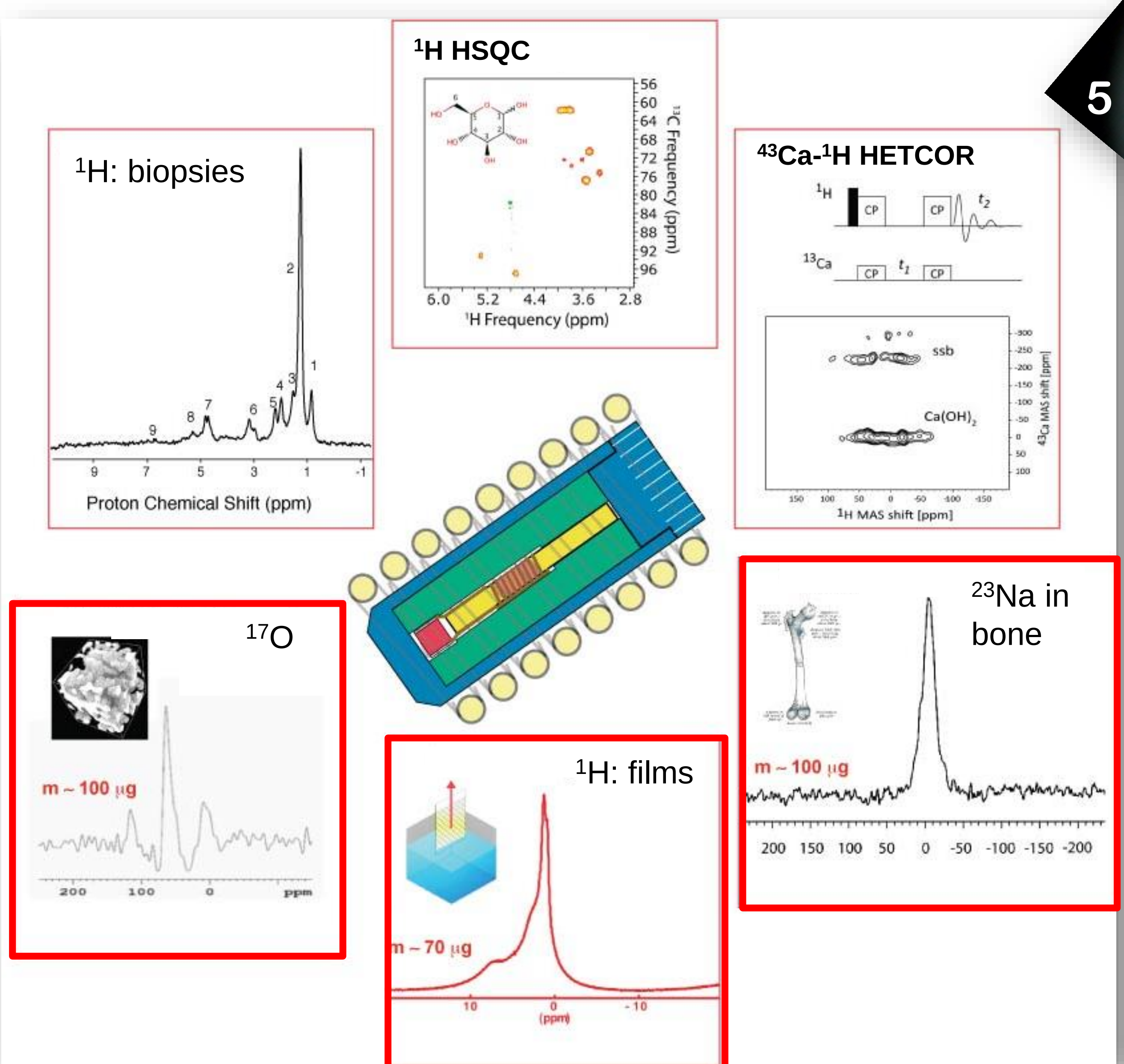
$S \sim 2\ cm^2$

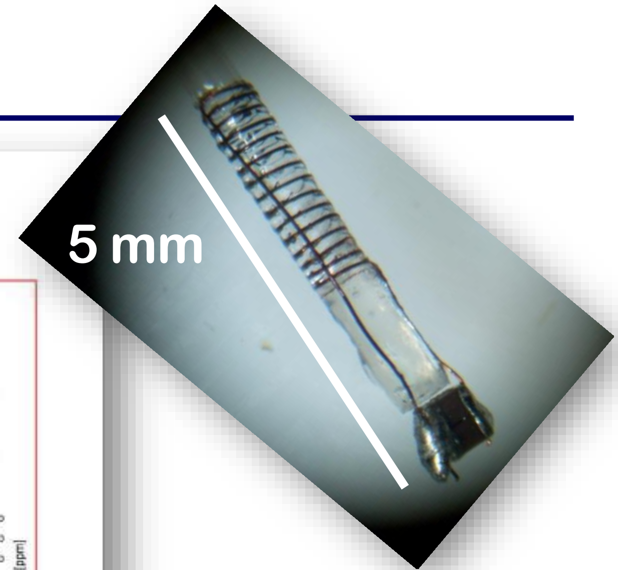
$h \sim 300\ nm$

$m \sim 100\ \mu g$

^{1}H … ^{29}Si, ^{13}C, $^{47/49}Ti$, …

MACS experiments





"hand made" micro-coils

↓

100 µg

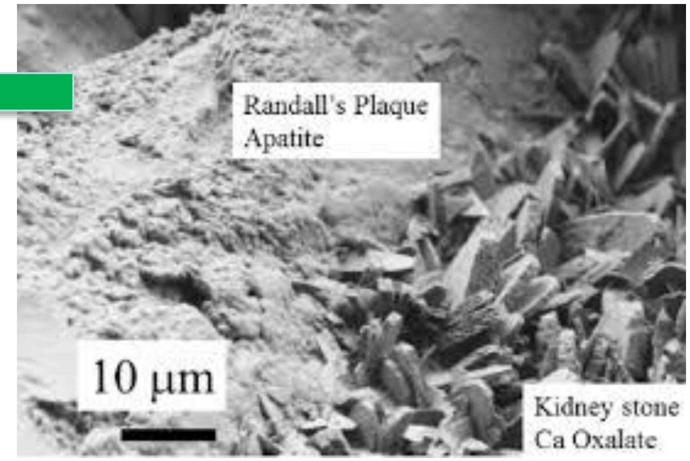
↓

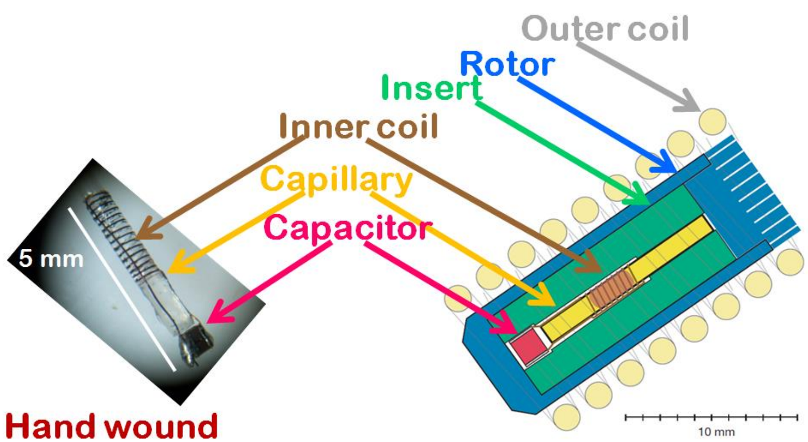
70 µg

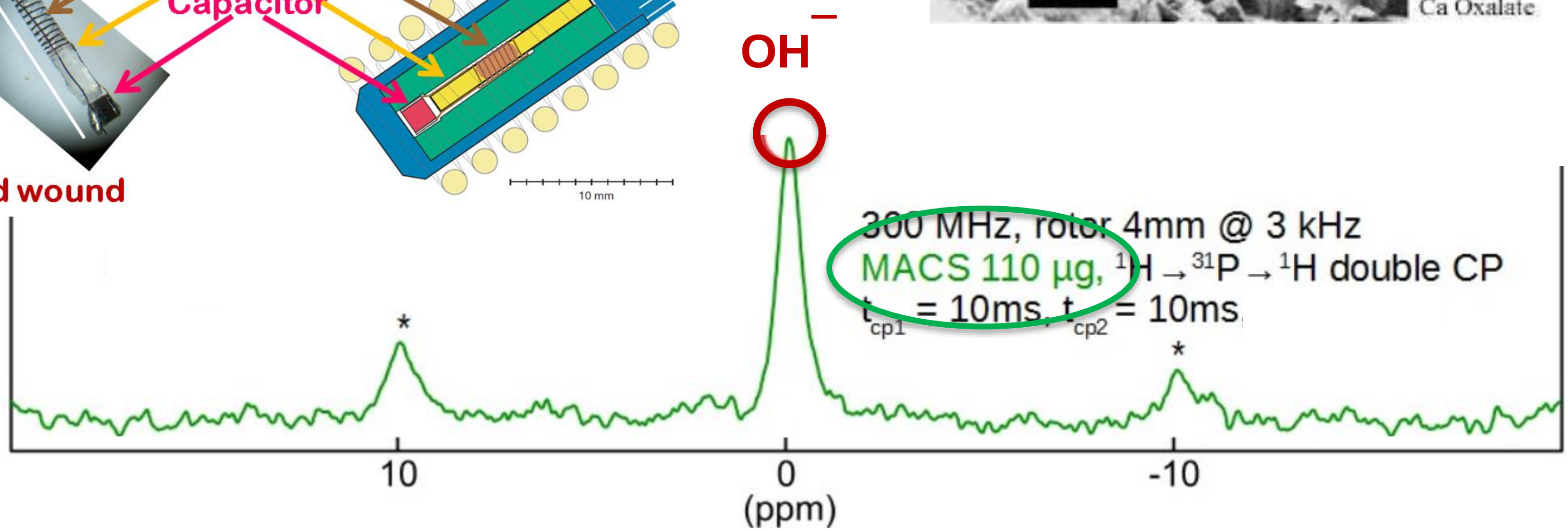
Hydroxyapatite as a model compound

→ see Part II (kidney stones)

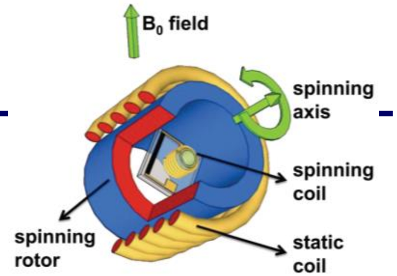
m ~ 250 µg



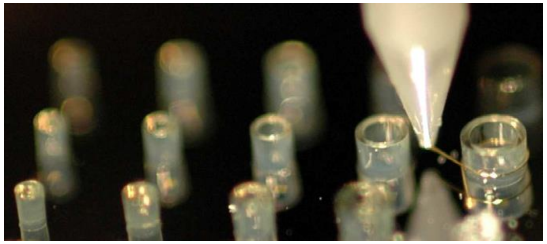


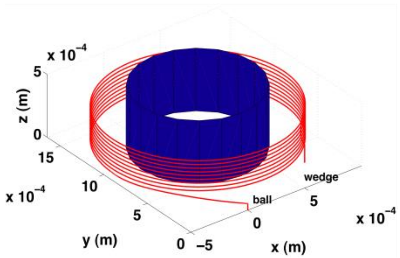


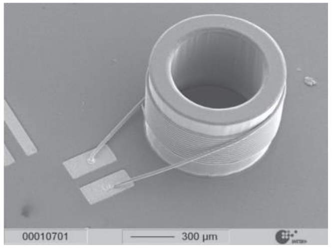
MEMS techniques applied to micro-coils



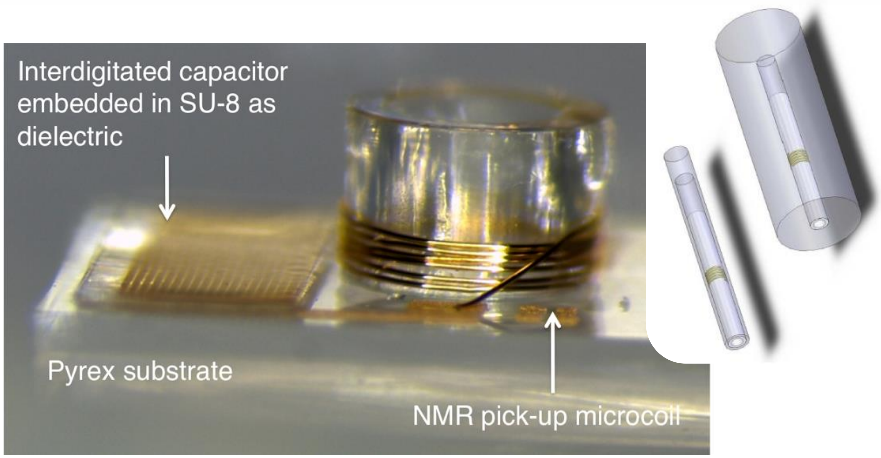
Coll. **: V. Badilita, U. Wallrabe, J. G. Korvink – IMTEK, Freiburg, Germany**

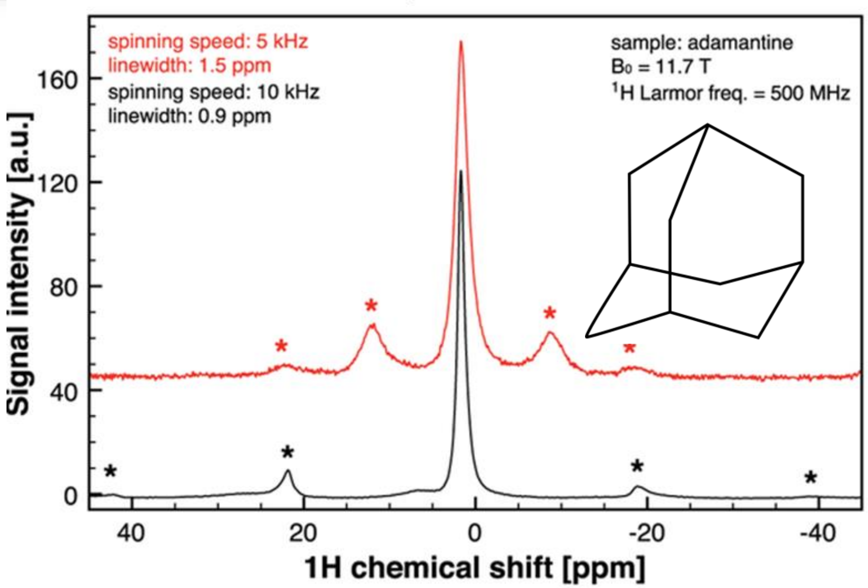






Microfabricated inserts for magic angle coil spinning (MACS) wireless NMR spectroscopy.
Badilita, V., B. Fassbender, K. Kratt, A. Wong, C. Bonhomme, D. Sakellariou, J. G. Korvink and U. Wallrabe
PloS one, Vol., 7(8), 2012, pp. e42848-e42848.





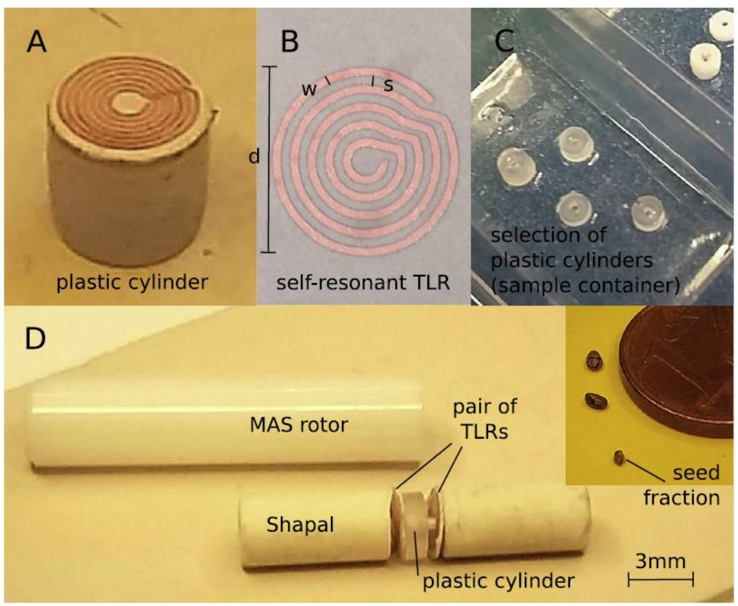
Monolithic micro-resonators

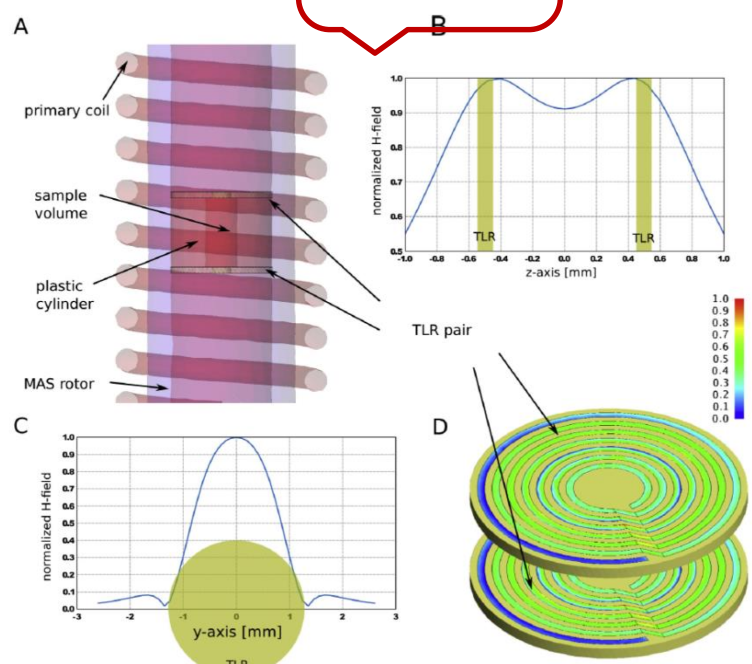
Monolithic MACS micro resonators

J.A. Lehmann-Horn [a], J.-F. Jacquinot [a], J.C. Ginefri [b], C. Bonhomme [c], D. Sakellariou [a,*]

[a] NIMBE, CEA-CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France
[b] Laboratoire d'Imagerie par Résonance Magnétique Médicale et Multi-Modalités (IR4M), UMR8081, CNRS, Université Paris-Sud, Université Paris Saclay, Orsay, France
[c] Sorbonne Universités, UPMC Université Paris 06, UMR CNRS 7574, Laboratoire de Chimie de la Matière Condensée de Paris, Collège de France, 4 place Jussieu, 75252 Paris Cedex 05, France

$B_1/\sqrt{P}$

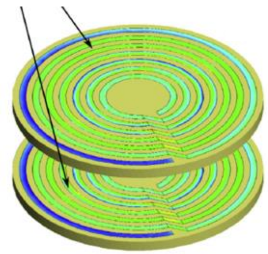




Application to thin hybrid membranes

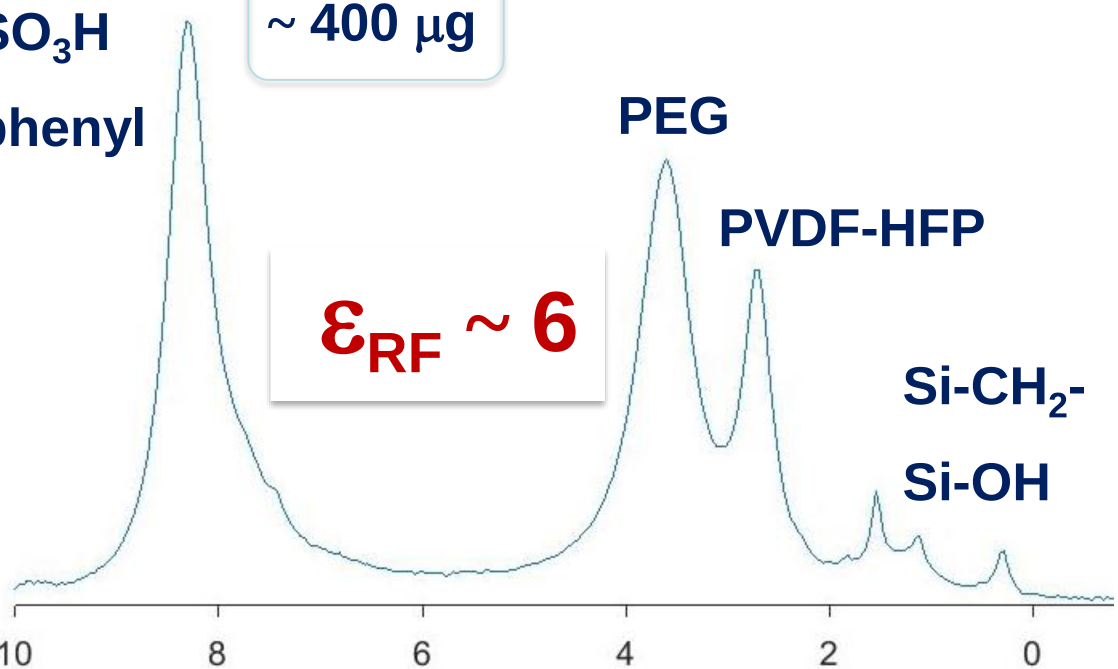
many thanks to:

D. Sakellariou

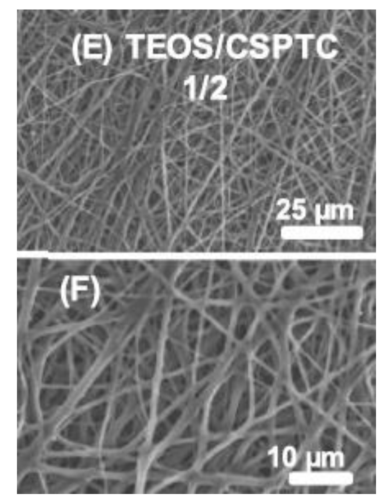


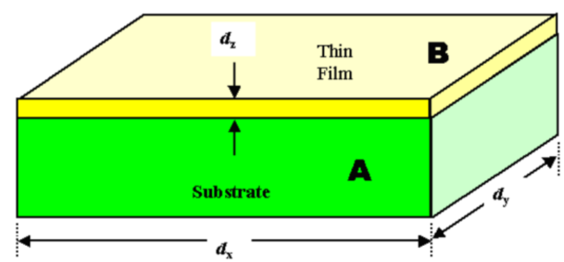
- no chip capacitor
- easy–to–handle
- cylindrical symmetry
- reduced Eddy currents

~ 400 μg



$\varepsilon_{RF} \sim 6$



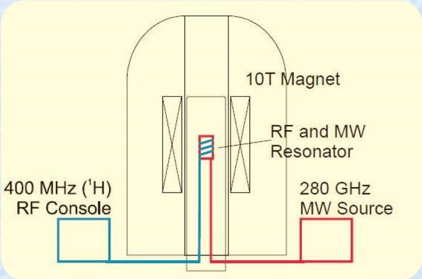


^{1}H (MAS) (5 kHz, 5 minutes, h ~ 30 μm)

Coll.: C. Laberty (LCMCP)

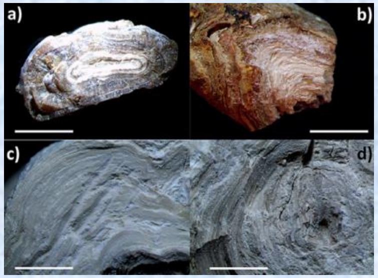
Outline

- Sensitivity issues: DNP MAS
  HP ^{129}Xe
  micro-coils, micro-resonators

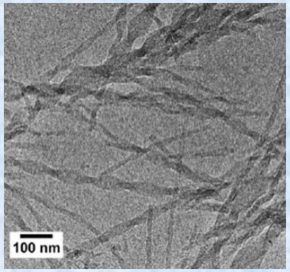


- ***Ab initio* calculations of NMR parameters**
- **New trends in GIPAW**

- Biomineralization
- Pathological calcifications



- Soft Matter



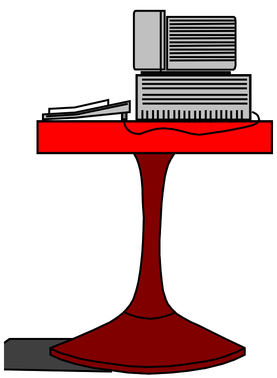
Modeling of materials and first principles calculations of NMR parameters

C. Gervais

QUANTUM ESPRESSO
HOME PROJECT DOWNLOAD

F. Tielens

VASP
Vienna Ab-initio Simulation Package



First principles calculations: the GIPAW approach

Pickard, Mauri, *Phys. Rev. B* (2001)

GIPAW

DFT

periodic systems

all-electron hamiltonians

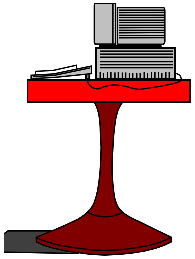
evaluation of $j^{(1)}(r')$ using pseudopotentials

$$B_{in}^{(1)}(r) = 1/c \int d^3r' \; j^{(1)}(r') \times \frac{r-r'}{|r-r'|^3}$$

CSA

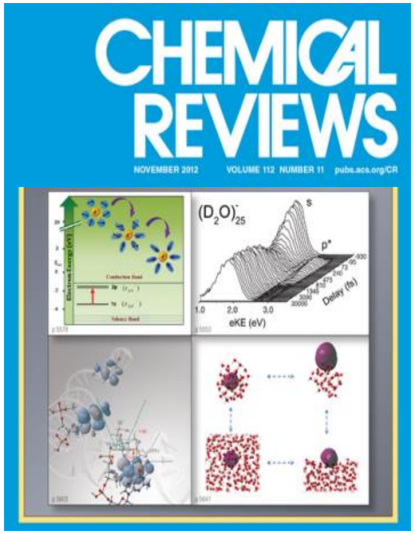
! J !

EFG



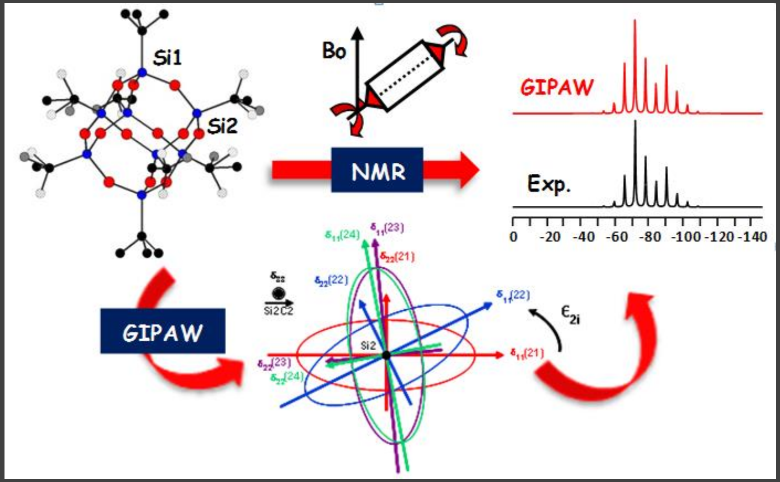
IDRIS

- **assignment**
- **dynamics**
- **amorphous samples**

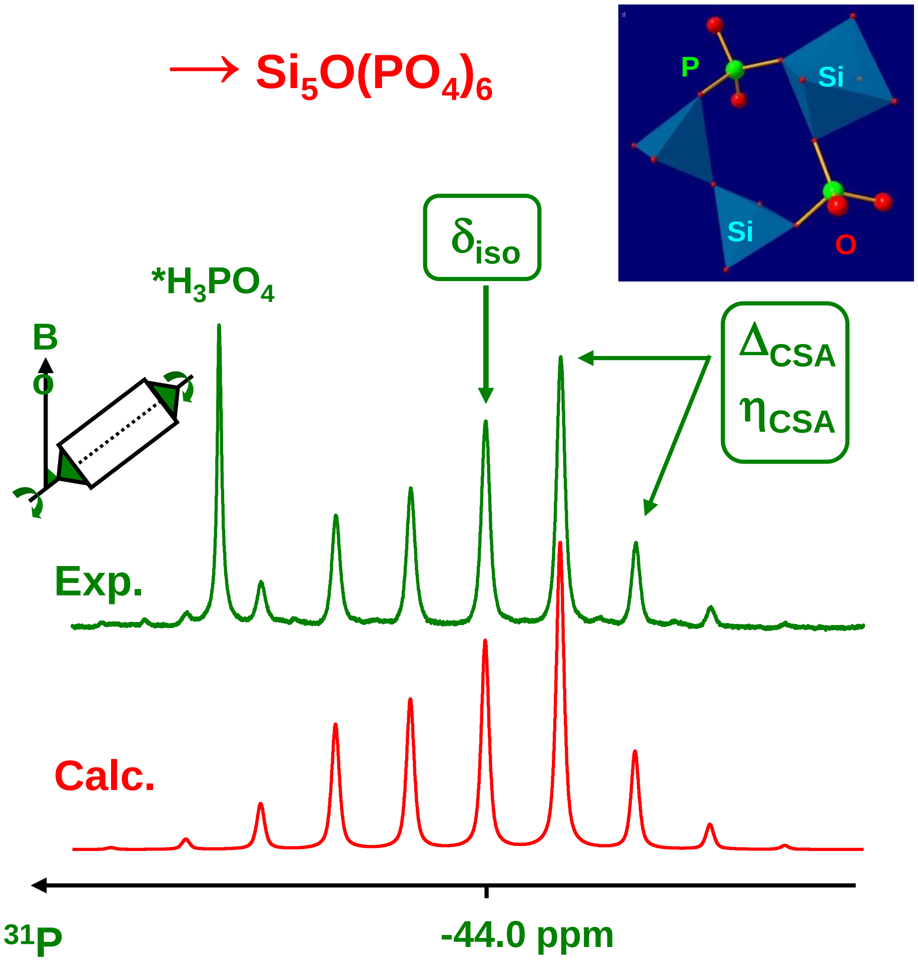


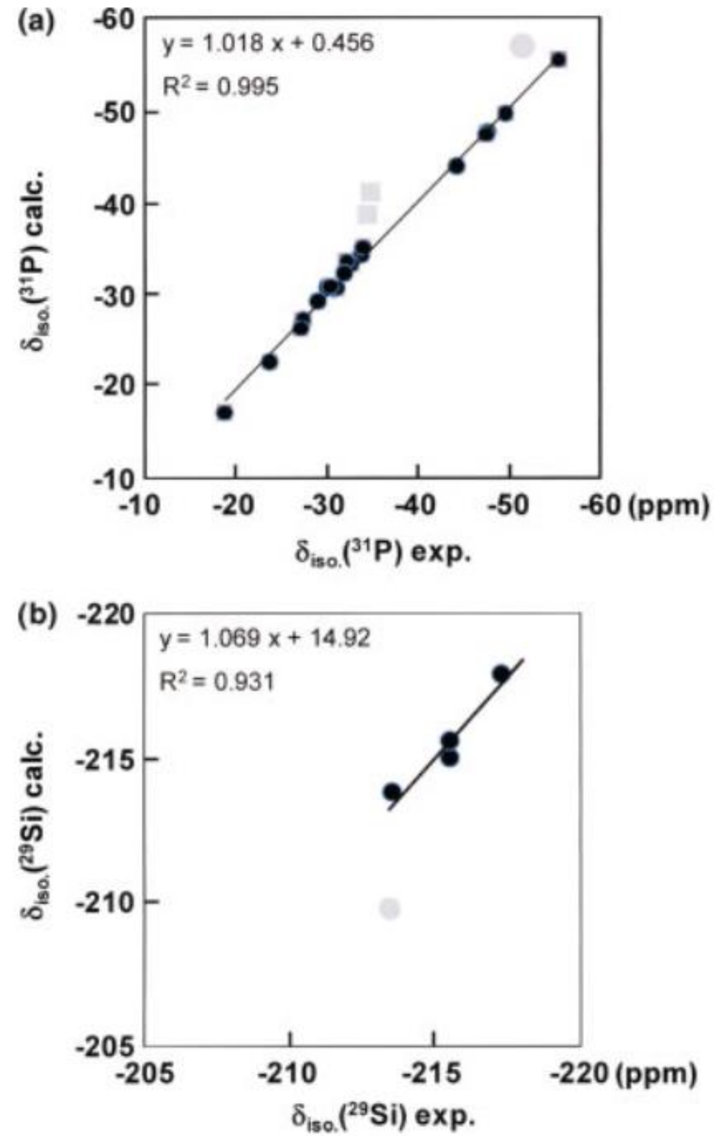
C. Bonhomme, C. Gervais, F. Babonneau *et al.*,

***Chemical Reviews*, 112, 5733, 2012.**



Validation of GIPAW: the example of ^{31}P





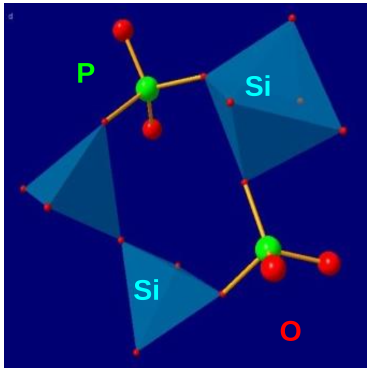
New perspectives in the PAW/GIPAW approach: $J_{P\text{-}O\text{-}Si}$ coupling constants, antisymmetric parts of shift tensors and NQR predictions (pages S86–S102)

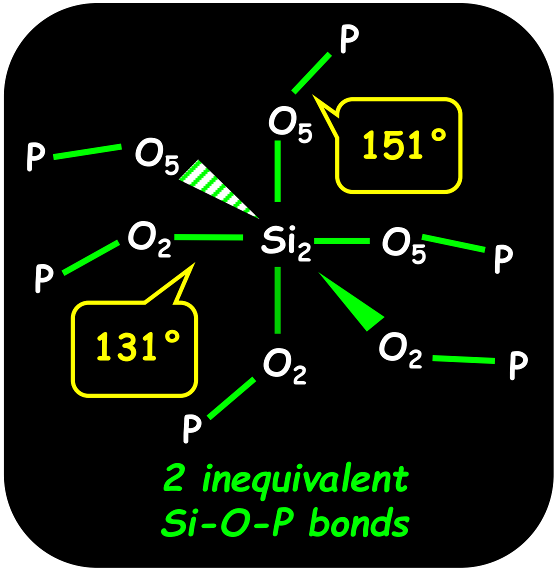
Christian Bonhomme, Christel Gervais, Cristina Coelho, Frédérique Pourpoint, Thierry Azaïs, Laure Bonhomme-Coury, Florence Babonneau, Guy Jacob, Maude Ferrari, Daniel Canet, Jonathan R. Yates, Chris J. Pickard, Siân A. Joyce, Francesco Mauri and Dominique Massiot

Article first published online: 29 JUN 2010 | DOI: 10.1002/mrc.2635

First principles calculations of *J* coupling constants: $Si_5O(PO_4)_6$

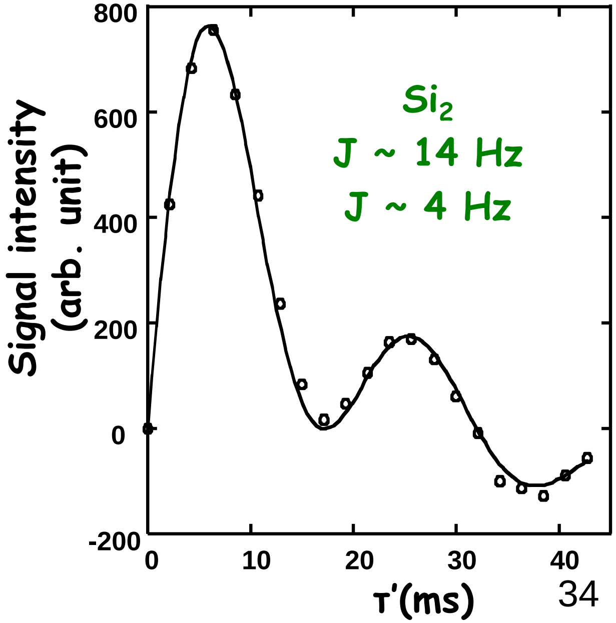
→ $Si_5O(PO_4)_6$





INEPT MAS data: J ~ [4 Hz – 15 Hz]

		$^2J_{P-O-Si}$ (Hz)	
Phase	Sites	exp	calc
$Si_5O(PO_4)_6$	Si(1)-O(3)-P	15 ± 2	-17,08
	Si(2)-O(2)-P	14 & 4 ± 2	-16,22
	Si(2)-O(5)-P		-1,17
	Si(3)-O(4)-P	12 ± 2	-14,18



New perspectives in the PAW/GIPAW approach: J_{P-O-Si} coupling constants, antisymmetric parts of shift tensors and NQR predictions (pages S86–S102)
Christian Bonhomme, Christel Gervais, Cristina Coelho, Frédérique Pourpoint, Thierry Azaïs, Laure Bonhomme-Coury, Florence Babonneau, Guy Jacob, Maude Ferrari, Daniel Canet, Jonathan R. Yates, Chris J. Pickard, Siân A. Joyce, Francesco Mauri and Dominique Massiot
Article first published online: 29 JUN 2010 | DOI: 10.1002/mrc.2635

Peptide-functionalized MOFs

CHEMISTRY
A European Journal

Functionalized Metal–Organic Frameworks |Hot Paper|

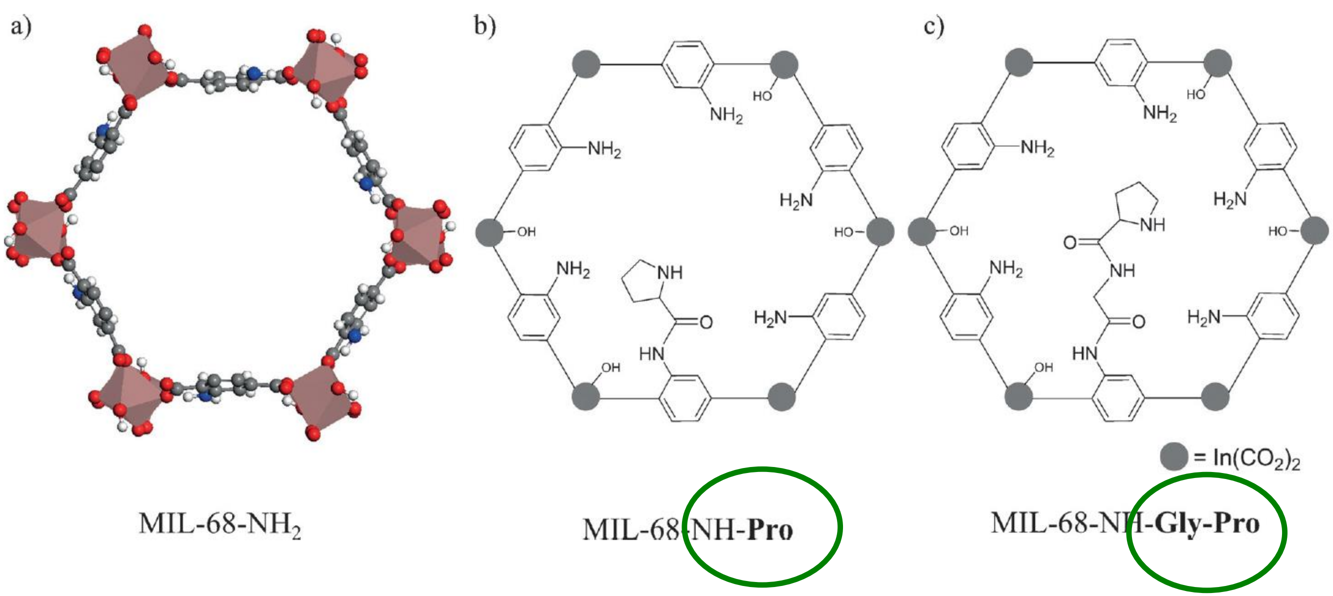
Molecular Level Characterization of the Structure and Interactions in Peptide-Functionalized Metal–Organic Frameworks

Tanya K. Todorova,[a] Xavier Rozanska,[b] Christel Gervais,[c] Alexandre Legrand,[d] Linh N. Ho,[d] Pierrick Berruyer,[e] Anne Lesage,[e] Lyndon Emsley,[f] David Farrusseng,[d] Jérôme Canivet,*[d] and Caroline Mellot-Draznieks*[a]

- ► peptide conformation in peptide-functionalized MOFs
- ► combination of DFT / MD / GIPAW / ^{15}N DNP MAS experiments

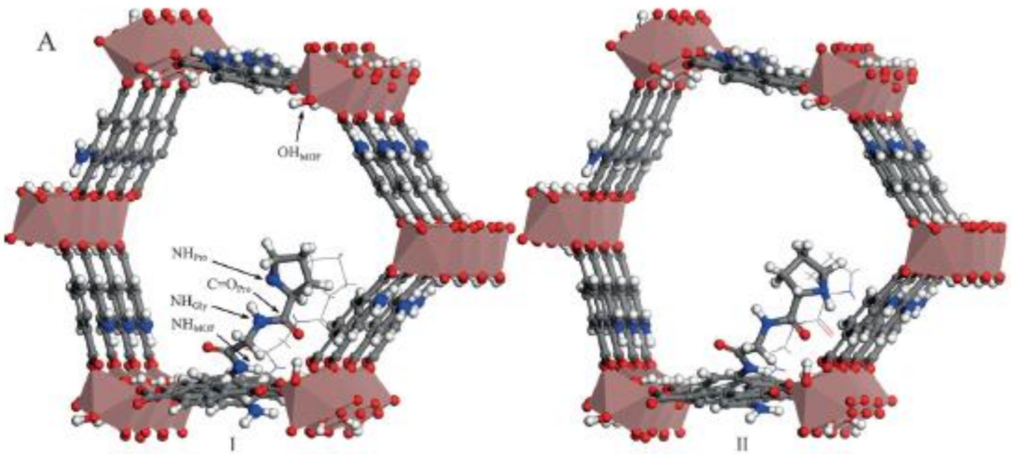
▼ NMR CRYSTALLOGRAPHY

MIL-68: *indium* derived MOF



Peptide-functionalized MOFs

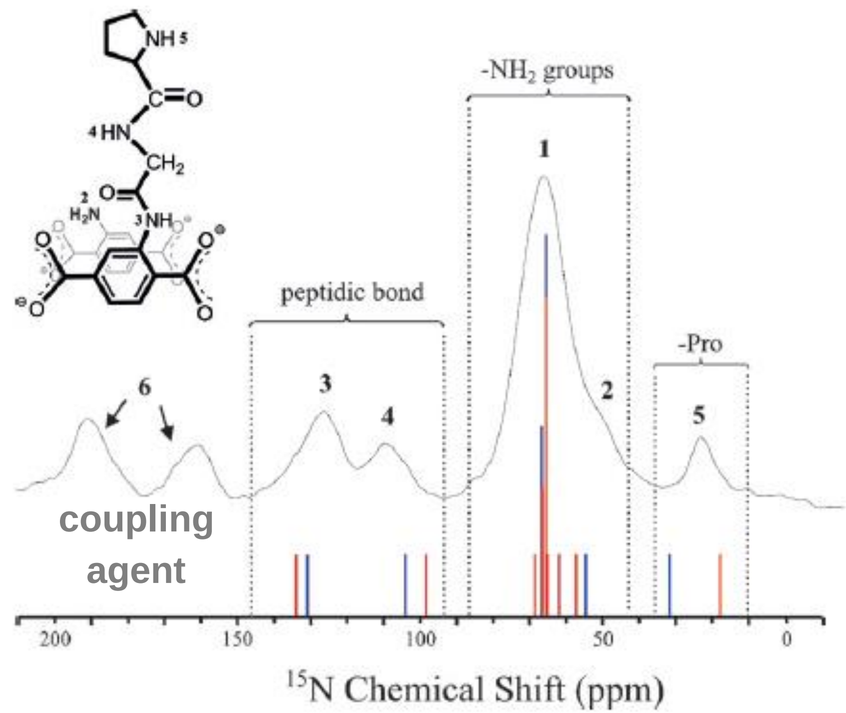
MIL-68-NH-*Gly-Pro*: low energy conformations



conformers I **conformers II**

^{15}N: low γ, *n.a.* = 0.37%

DNP MAS: TekPol/TCE, 100K



^{15}N GIPAW calculations

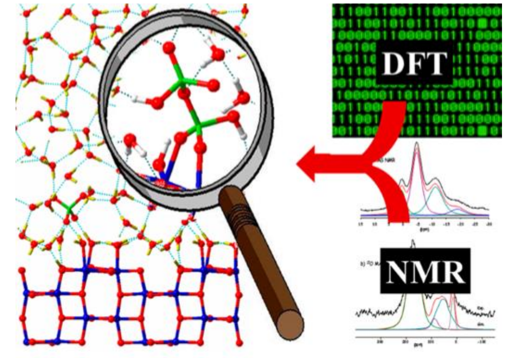
(H-bonding, Grimme DFT-D3

Phosphate species on hydrated anatase surfaces

LANGMUIR
Article
pubs.acs.org/Langmuir

Characterization of Phosphate Species on Hydrated Anatase TiO_2 Surfaces

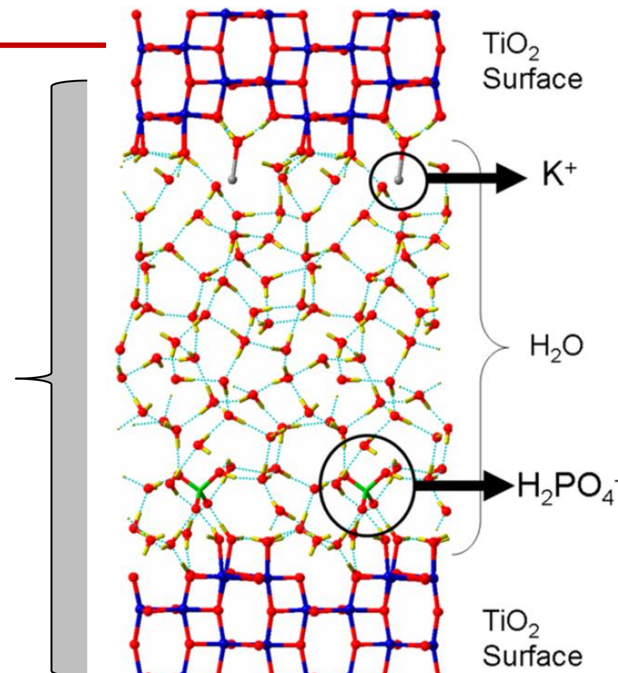
Frederik Tielens,*,† Christel Gervais,† Geraldine Deroy,‡ Maguy Jaber,§ Lorenzo Stievano,‖ Cristina Coelho Diogo,†,⊥ and Jean-François Lambert†



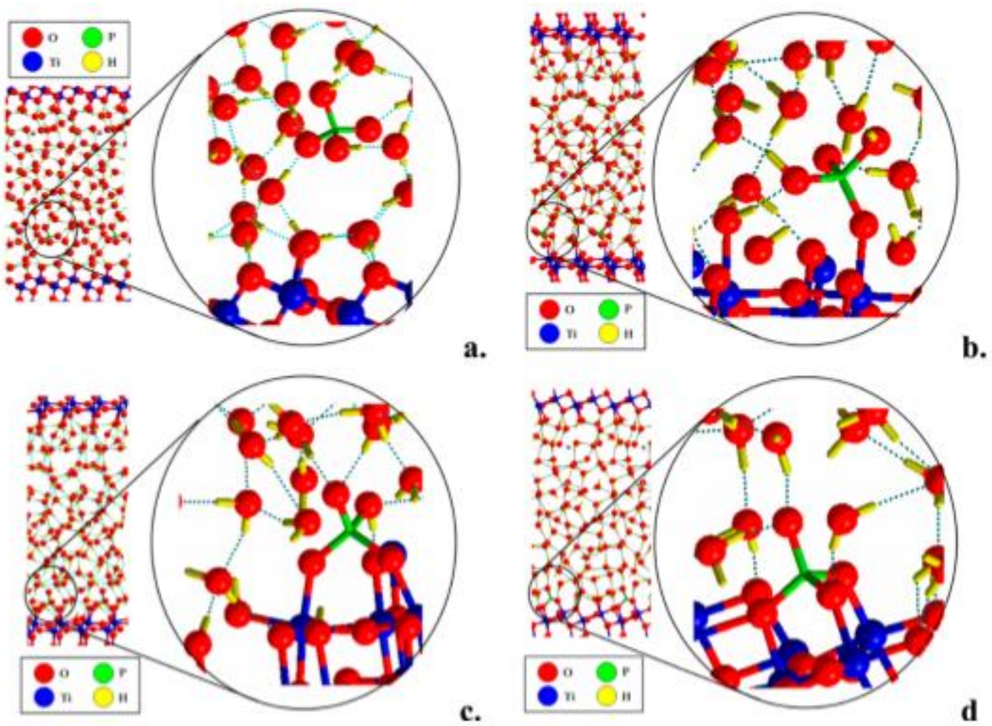
Phosphate Species on Hydrated Anatase TiO_2 Surfaces

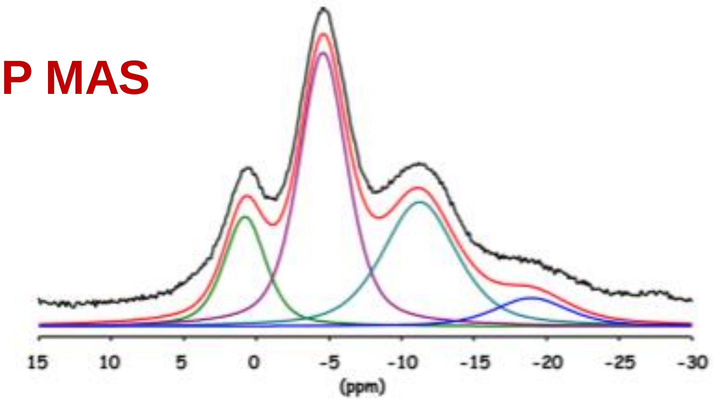
- ► adsorption / interaction of KH_2PO_4 with (100) / (101) TiO_2
- ► essential role of the solvent: here, H_2O

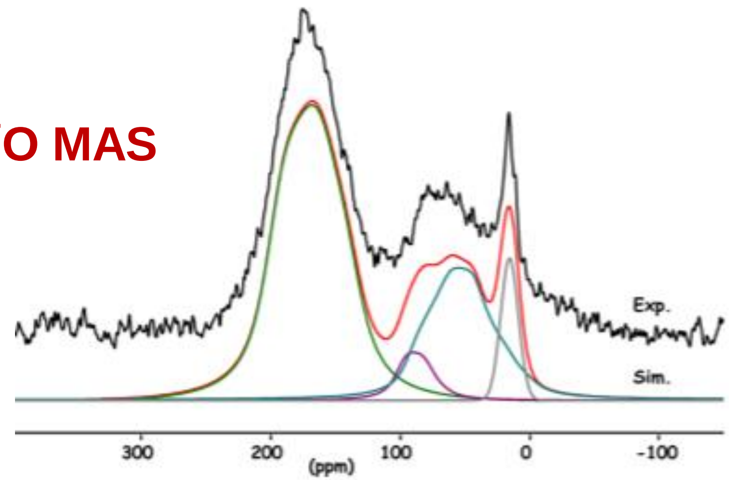
hydrated phosphate adsorption: a model



GIPAW and NMR crystallography







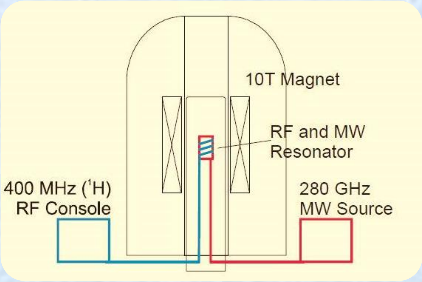
most favorable physisorption & chemisorption schemes for $H_2PO_4^-$ on (101) anatase surface

^{31}P		
δ_{iso} (ppm)	assignment	intensity (%)
0.8		16
−4.6		45
−11.2		32
−19.0		7

^{17}O				
δ_{iso} (ppm)	C_Q (MHz)	η	assignment	intensity (%)
180	4.7	0.3	P−O−Ti	60
105	5	0.3	P=O	6
90	7.5	0.6	P−O−H	27
15			H_2O	7

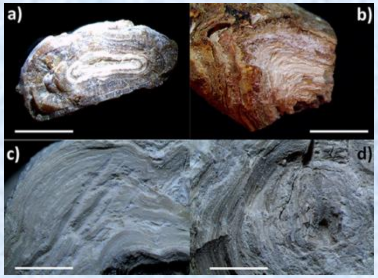
Outline

- Sensitivity issues: DNP MAS
  HP ^{129}Xe
  micro-coils, micro-resonators

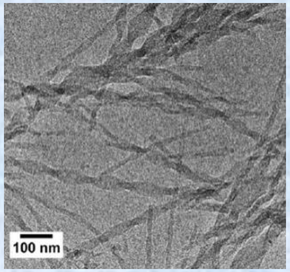


- *Ab initio* calculations of NMR parameters
- **New trends in GIPAW**

- Biomineralization
- Pathological calcifications



- Soft Matter



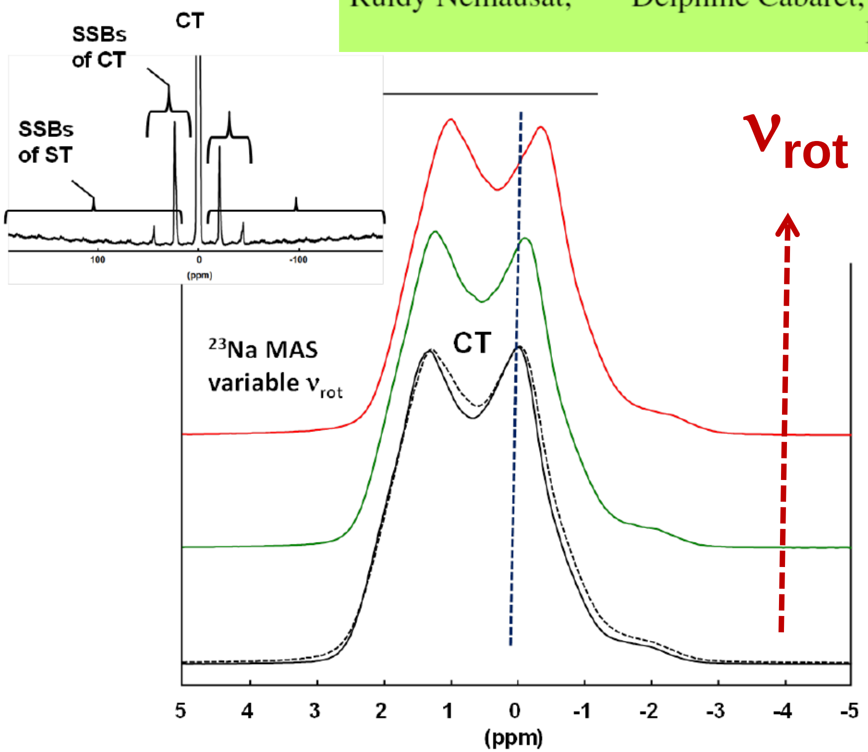
A recent trend: including temperature in GIPAW

^{23}Na

PHYSICAL REVIEW B **92**, 144310 (2015)

Phonon effects on x-ray absorption and nuclear magnetic resonance spectroscopies

Ruidy Nemausat,[1,2,*] Delphine Cabaret,[1] Christel Gervais,[2] Christian Brouder,[1] Nicolas Trcera,[3] Amélie Bordage
Ion Errea,[5,6] and Francesco Mauri[1]



$NaHC_2O_4$. H_2O

quantum thermal fluctuations

description of the effets of T

GIPAW

see also: MD, *ab initio* MD, Path Integral MD (J. N. Dumez, C. Pickard, J. Yates, P. Hodgkinson…)

<u>review</u>: S. Ashbrook, *Chem. Comm.* 2016

Temperature in GIPAW

Temperature dependence of X-ray absorption and nuclear magnetic resonance spectra: probing quantum vibrations of light elements in oxides†

Ruidy Nemausat,*[ab] Christel Gervais,[b] Christian Brouder,[a] Nicolas Trcera,[c] Amélie Bordage,[d] Cristina Coelho-Diogo,[e] Pierre Florian,[f] Aydar Rakhmatullin,[f] Ion Errea,[gh] Lorenzo Paulatto,[a] Michele Lazzeri[a] and Delphine Cabaret[a]

PCCP

ROYAL SOCIETY OF CHEMISTRY

- ► Temperature dependence of NMR (and XANES) spectra
- ► predictive calculations taking *quantum thermal vibrations* into account
- ► non-equilibrium configurations (finite T quantum statistics at the quasiharmonic level

Mineral (formula)	Sample type	Probed atom
Periclase (MgO)	Single crystal	Mg (6)
Spinel ($MgAl_2O_4$)	Powder	Mg (4), Al (6)
Corundum (α-Al_2O_3)	Single crystal	Al (6)
Berlinite (α-$AlPO_4$)	Powder	Al (4)
Stishovite (SiO_2)	Polycrystal	Si (6)
α-Quartz (SiO_2)	Single crystal	Si (4)

$C_Q(^{25}Mg, ^{27}Al, ^{17}O)$ *vs* temperature

theoretical ingredients

$$D_{IJ} = \frac{1}{\sqrt{M_I M_J}} \frac{\partial^2 E(\bar{\mathbf{R}})}{\partial u_I \partial u_J}\bigg|_{\mathbf{u}=0}$$

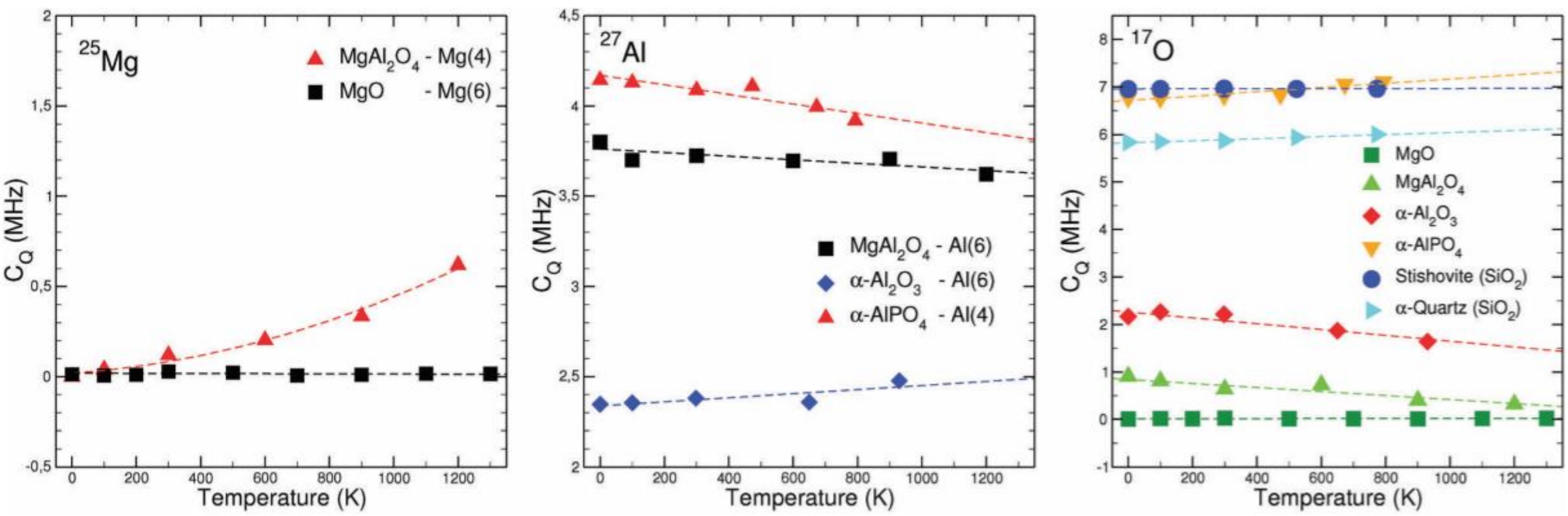
► **dynamical matrix**

$$\sum_{J=1}^{3N} D_{IJ} e_{J\mu} = \Omega_\mu{}^2 e_{I\mu}$$

► **phonon modes**

$$P(\bar{\mathbf{R}}) = A \exp\left[-\sum_\mu{}' \frac{\left(\sum_I \sqrt{M_I} e_{I\mu} u_I\right)^2}{2a_\mu}\right]$$

► **probability of the $\bar{\mathbf{R}}$ configuration**



► **for (any) observable *O*:**

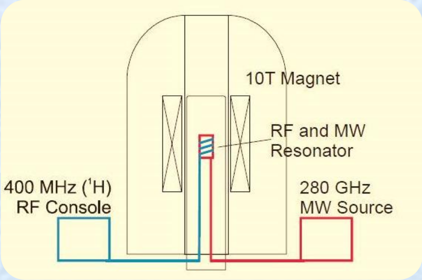
$$O(T) = \int \mathrm{d}\bar{\mathbf{R}}\, P(\bar{\mathbf{R}}) O(\bar{\mathbf{R}}) \simeq \frac{1}{N_c} \sum_{i=1}^{N_c} O(\bar{\mathbf{R}}^i)$$

Outline

- Sensitivity issues: DNP MAS

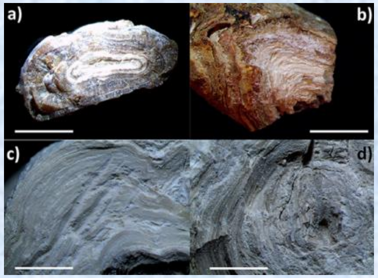
  HP ^{129}Xe

  micro-coils, micro-resonators

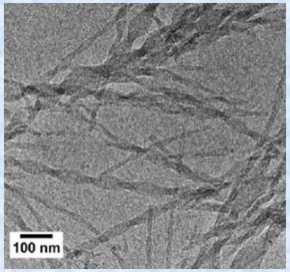


- *Ab initio* calculations of NMR parameters
- New trends in GIPAW

- **Biomineralization**
- **Pathological calcifications**



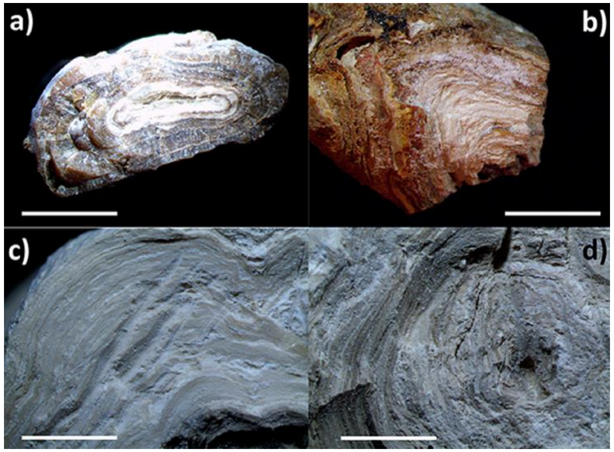
- Soft Matter



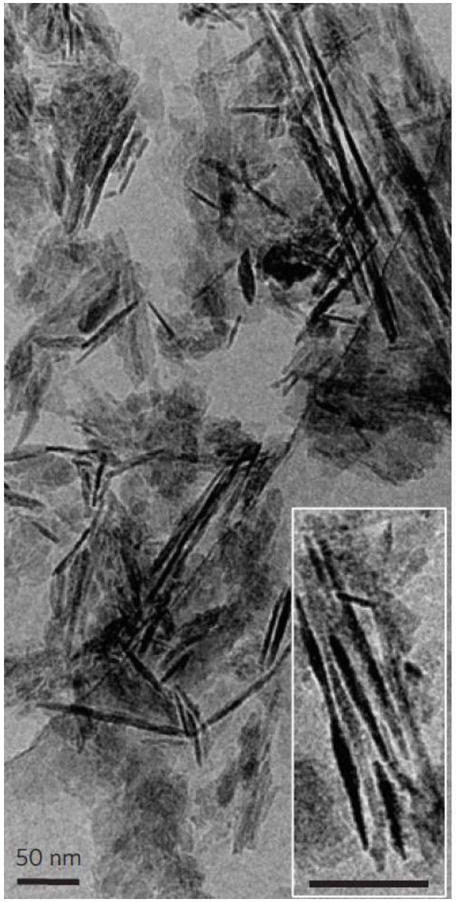
Biomineralization and pathological calcifications (kidney stones)

T. Azaïs (& N. Nassif)

D. Bazin



kidney stone macro-crystals



hydroxyapatite nano-crystals

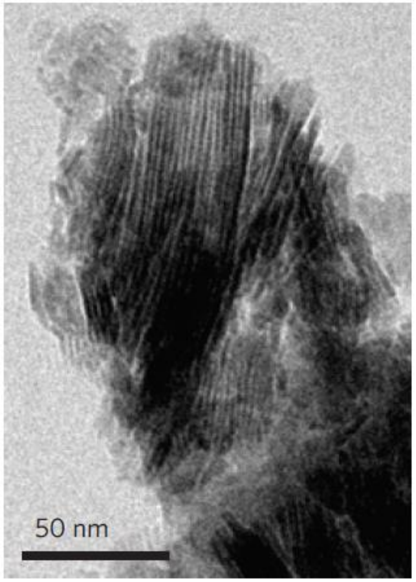
Biomineralization

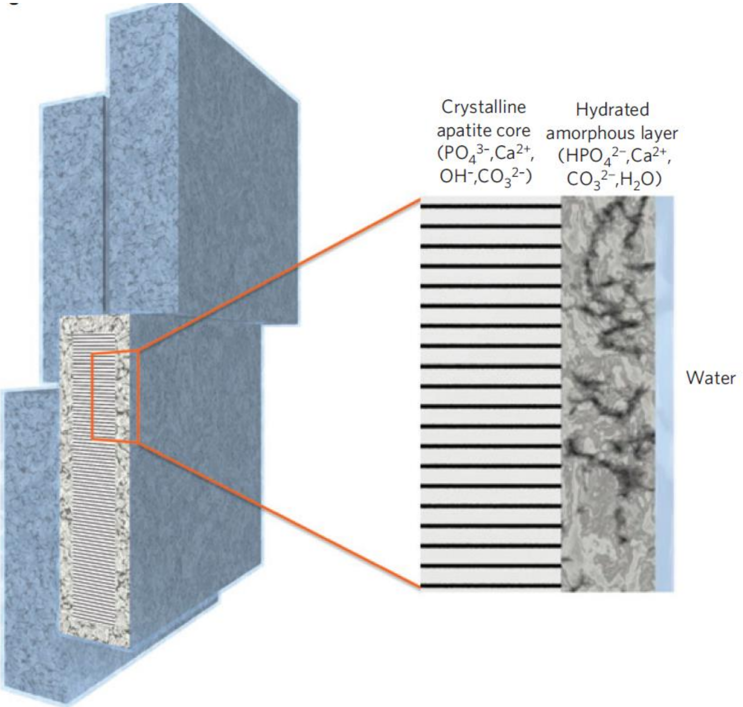
nature materials

Water-mediated structuring of bone apatite

Yan Wang[1†], Stanislas Von Euw[1†], Francisco M. Fernandes[1], Sophie Cassaignon[1], Mohamed Selmane[2], Guillaume Laurent[1], Gérard Pehau-Arnaudet[3], Cristina Coelho[2], Laure Bonhomme-Coury[1], Marie-Madeleine Giraud-Guille[1], Florence Babonneau[1], Thierry Azaïs[1*] and Nadine Nassif[1*]

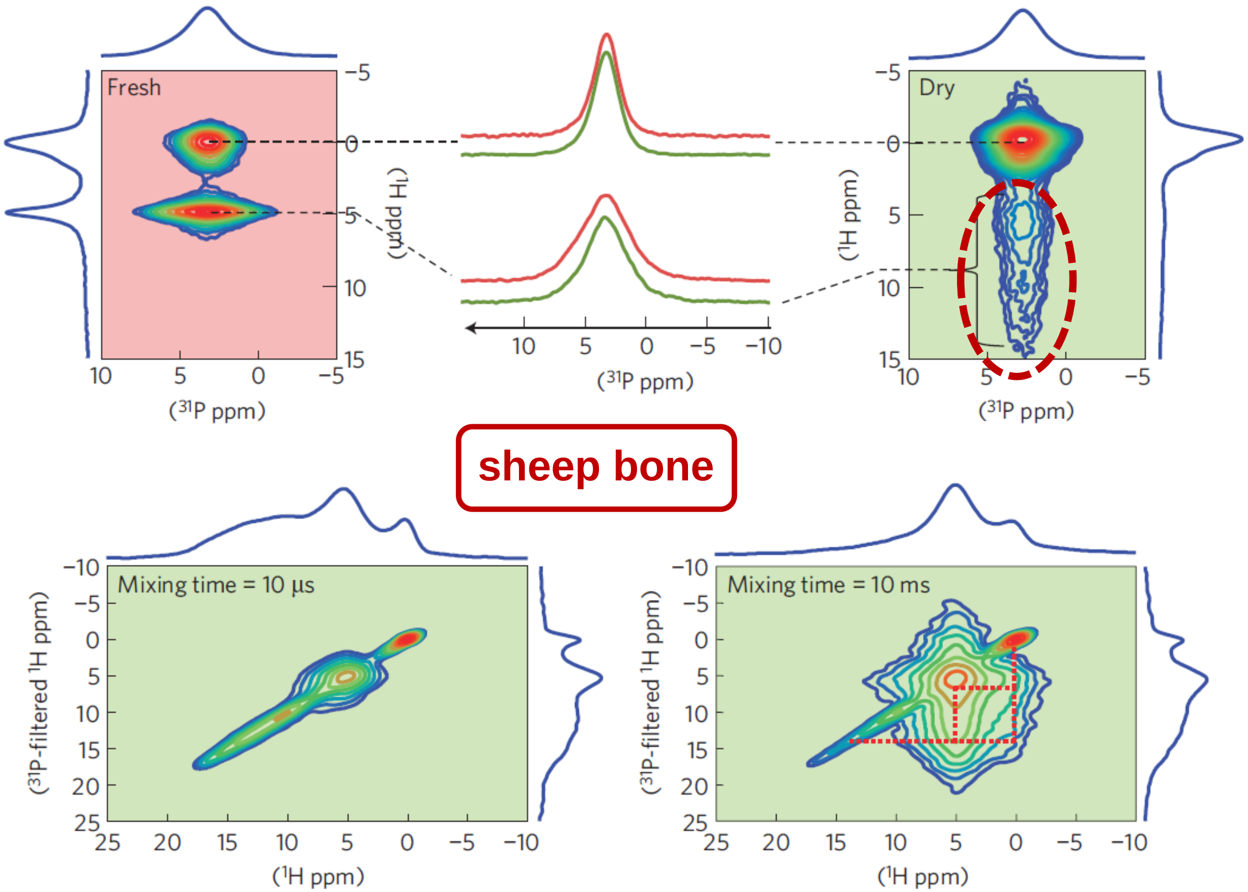
- ► **crystalline, biomimetic apatite nano-particles and intact bones**
- ► ***amorphous Ca-P layer* coating the crystalline HAp cores**





HETCOR and EXSY experiments

FRESH **DRY**

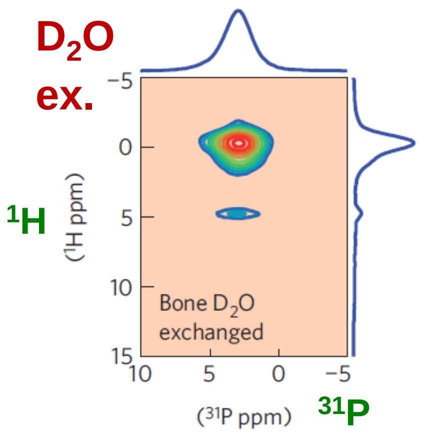


^{1}H–^{31}P HETCOR MAS

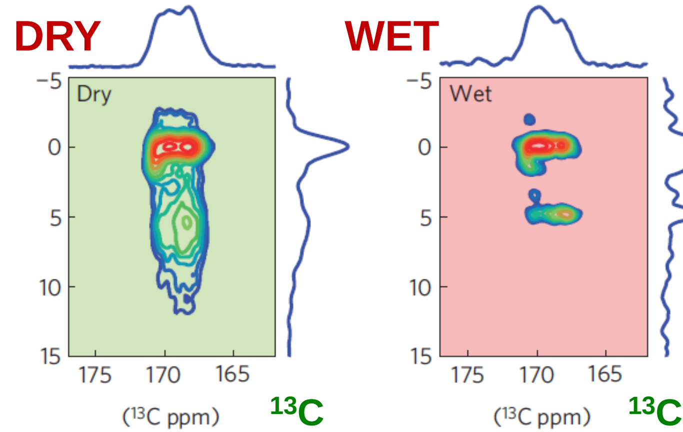
^{1}H–^{1}H EXSY MAS

^{31}P filtered

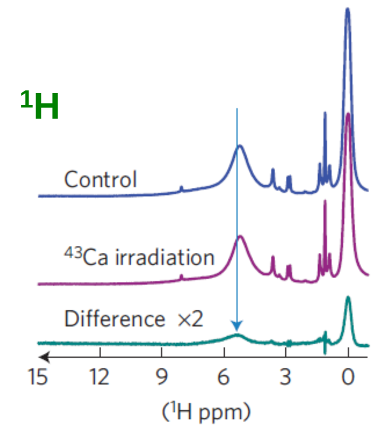
Chemical composition of the apatitic layer



sheep bone

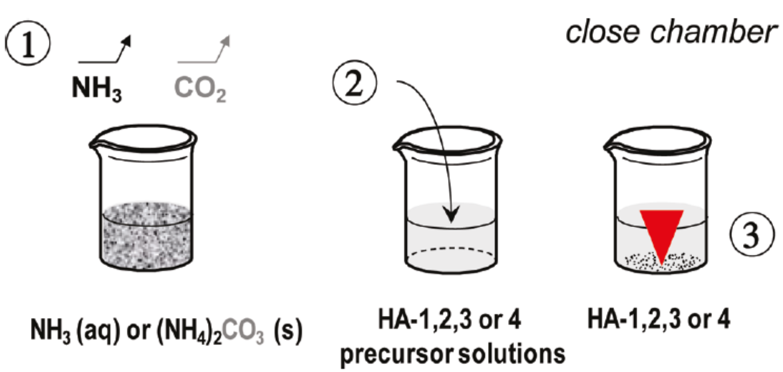


^{13}C HETCOR (labeled in ^{13}C)



^{43}Ca TRAPDOR (labeled in ^{43}Ca)

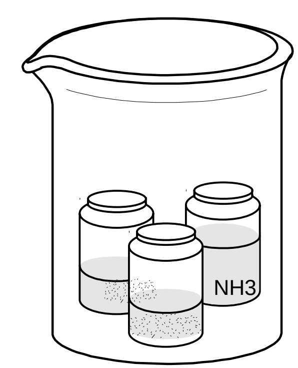
biomimetic (synthetic) apatites



$CaCl_2$, NaH_2PO_4, $NaHCO_3$

acidic medium

N. Nassif *et al. Chem .Mater*, 2010, 22, 3653.

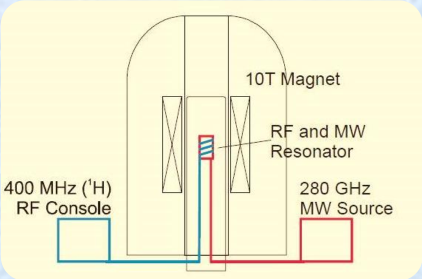


Outline

- Sensitivity issues: DNP MAS

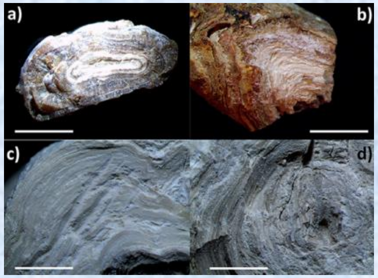
  HP ^{129}Xe

  micro-coils, micro-resonators



- *Ab initio* calculations of NMR parameters
- New trends in GIPAW

- Biomineralization
- **Pathological calcifications**



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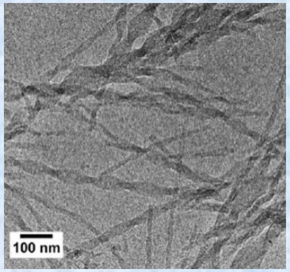


A first NMR approach of kidney stones (KS)

see also Part II

Full paper/Mémoire

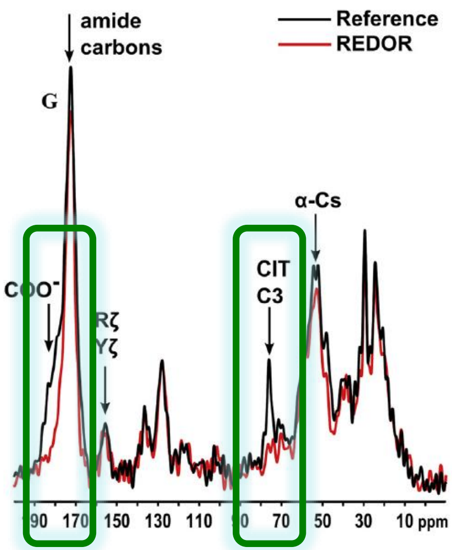
Solid state NMR of salivary calculi: Proline-rich salivary proteins, citrate, polysaccharides, lipids, and organic–mineral interactions

Yang Li [a], David G. Reid [a], Dominique Bazin [b, c], Michel Daudon [d], Melinda J. Duer [a, *]

Structural elucidation of silica present in kidney stones coming from Burkina Faso

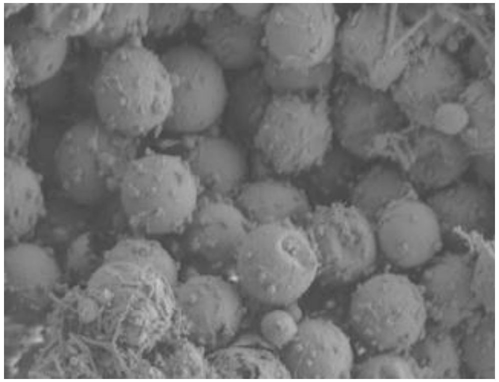
Élucidation structurale de la silice présente dans des calculs rénaux prélevés au Burkina Faso

Arnaud Dessombz [a, b, *], Gérard Coulibaly [c], Brahima Kirakoya [c], Richard W. Ouedraogo [c], Adama Lengani [c], Stéphan Rouziere [b], Raphael Weil [b], Lise Picaut [b], Christian Bonhomme [d], Florence Babonneau [d], Dominique Bazin [b, d], Michel Daudon [e]

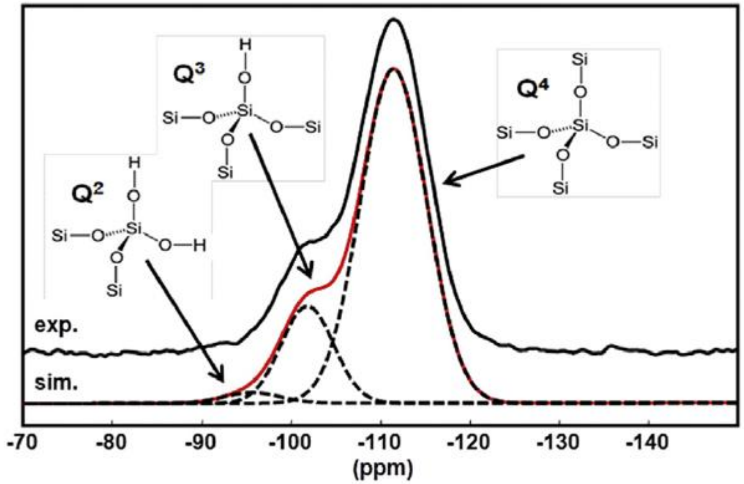


- apatite
- proteins
- lipids
- citrate
- polysaccharides
- …

$^{13}C\{^{31}P\}$ REDOR experiments



^{29}Si MAS



many thanks to:

M.J. Duer

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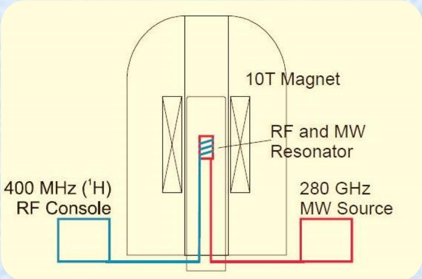

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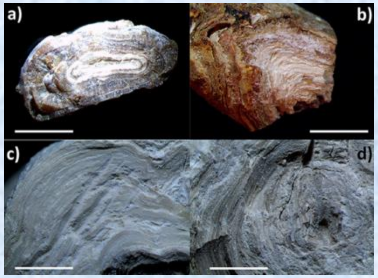

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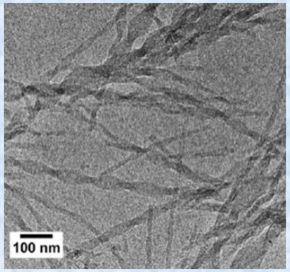
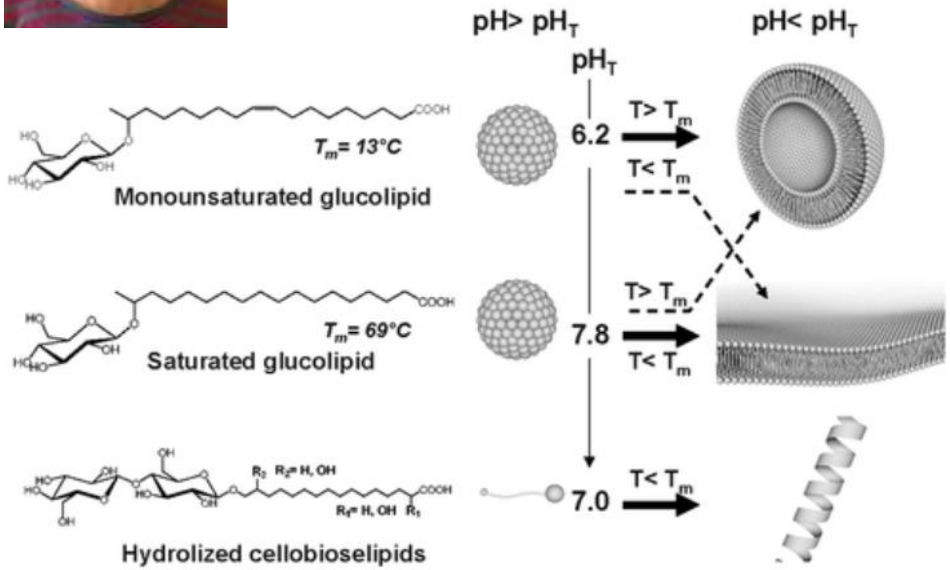
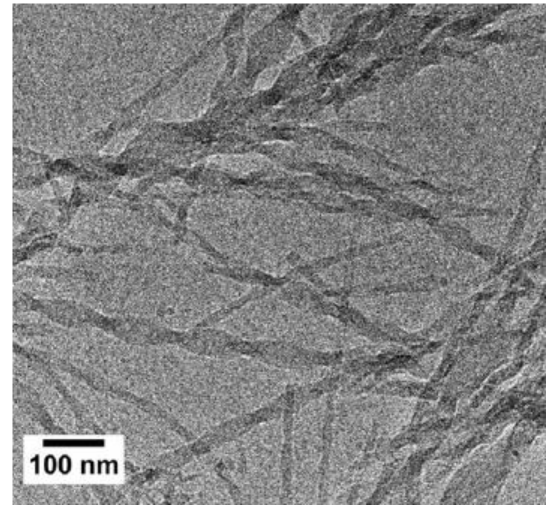


Applications of solid state NMR to soft matter

N. Baccile





- ► biocompatible, biodegradable, low toxicity bio-surfactants
- ► sophorolipids (glycolipids), starting from vegetal oil, glucose and yeast (fermentation)
- ► nanoscale chirality

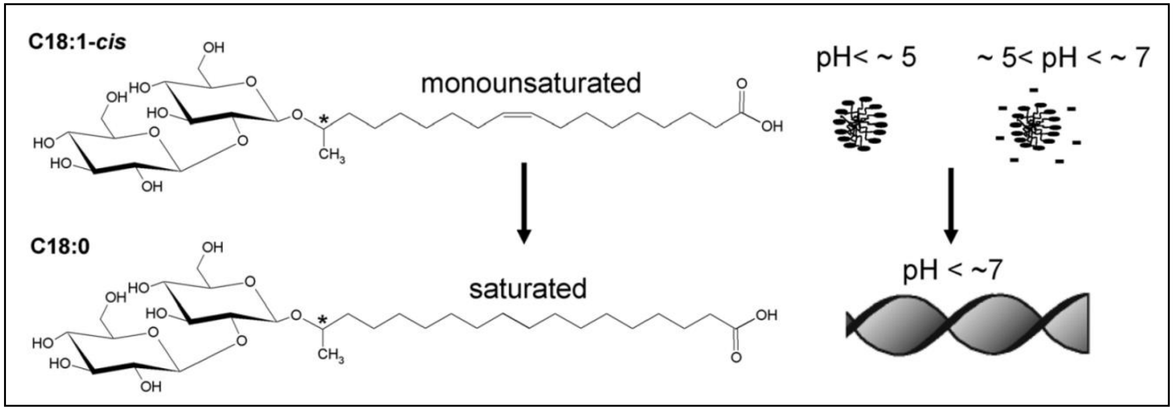
Sophorolipids

pH-triggered formation of nanoribbons from yeast-derived glycolipid biosurfactants†

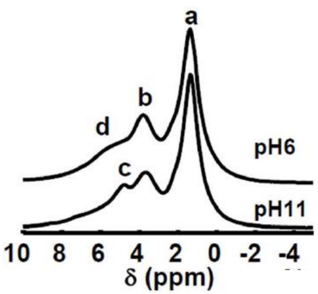
Anne-Sophie Cuvier,[abc] Jan Berton,[d] Christian V. Stevens,[d] Giulia C. Fadda,[e] Florence Babonneau,[abc] Inge N. A. Van Bogaert,[f] Wim Soetaert,[f] Gérard Pehau-Arnaudet[g] and Niki Baccile*[abc]

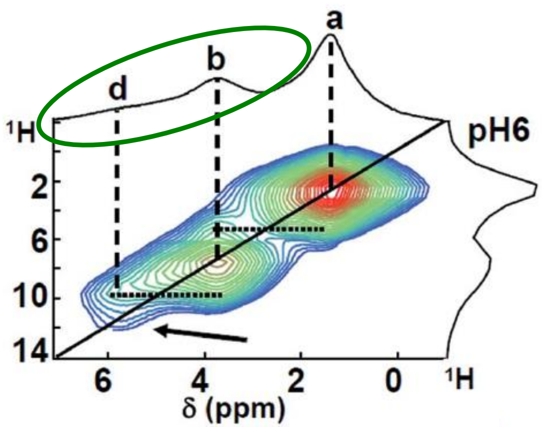
Soft Matter

ROYAL SOCIETY OF CHEMISTRY

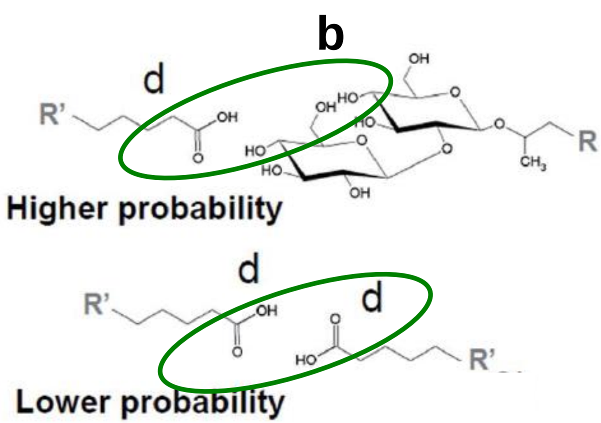


a	H in aliphatic chain
b	H in sophorose
c	H_2O
d	COOH





^{1}H DQ BABA



Hybrid materials and solid state NMR: a review

ELSEVIER

Progress in Nuclear Magnetic Resonance Spectroscopy

Volume 77, February 2014, Pages 1–48

Recent NMR developments applied to organic–inorganic materials

Christian Bonhomme[a], Christel Gervais[a], Danielle Laurencin[b]

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sensitivity issues

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