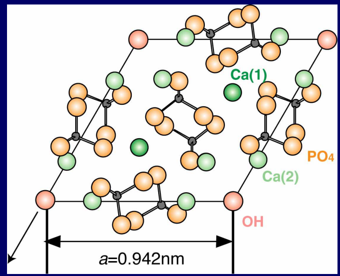
Sol Gel Derived Materials and Biocompatible Structures: the Solid State NMR Point of View !



C. Bonhomme, C. Gervais, C. Coelho, F. Pourpoint, G. Gasquères , F. Babonneau, T. Azaïs, G. Laurent, B. Alonso and F. Mauri

Laboratoire de Chimie de la Matière Condensée de Paris

Laboratoire de Minéralogie-Cristallographie

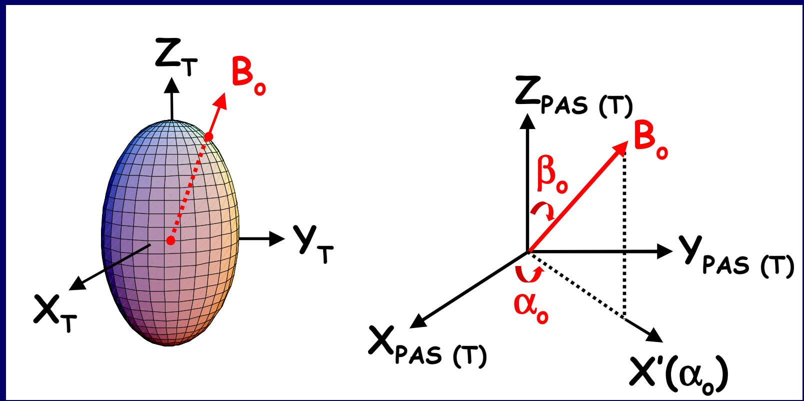
Université P. et M. Curie – Paris 6, France

GERM NMR school – march 2008

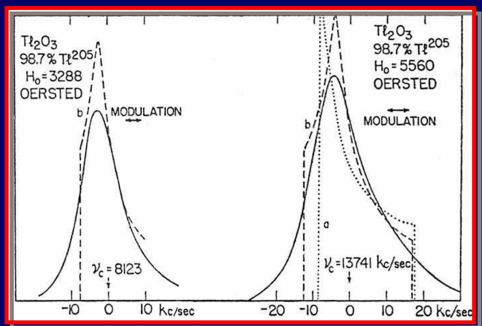
NMR interactions

a tensorial approach of nuclei by local probes:

the NMR interactions (CSA, J, quadrupolar, dipolar)

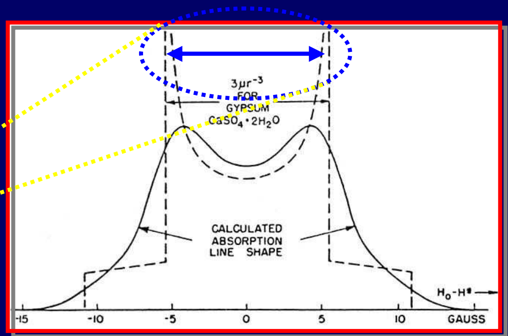


anisotropy: highly informative shapes

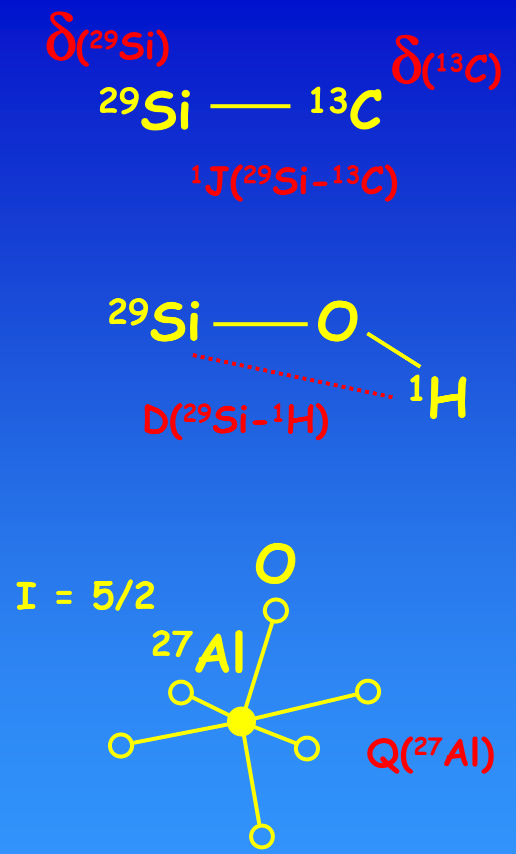


CSA

dipolar D

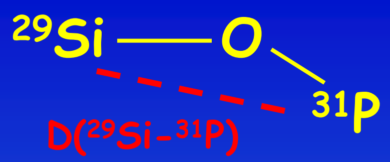


$D \propto 1/r^3$



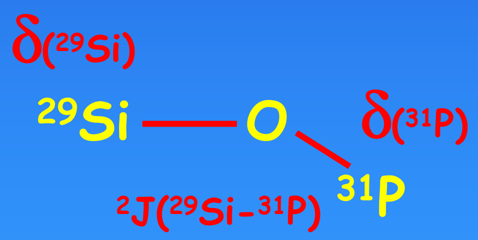
...quantum physics

High resolution in solid state NMR

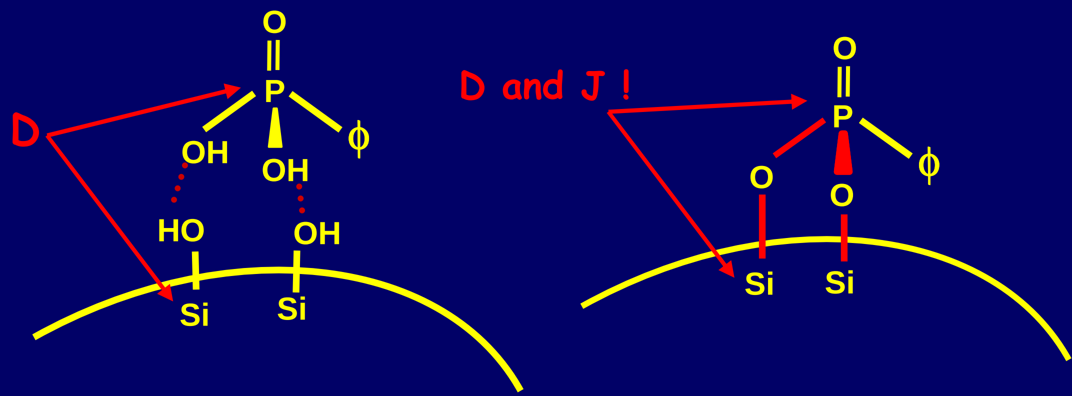


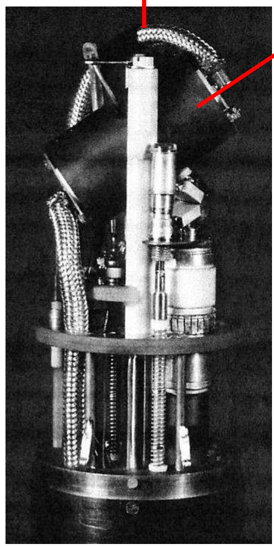
Cross Polarization

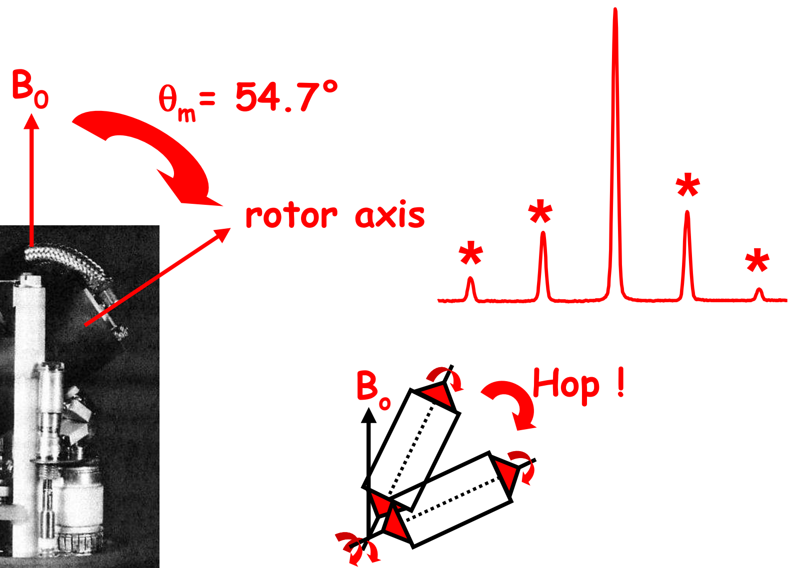
recoupling under high resolution conditions !



solid state J-INEPT,HMQC



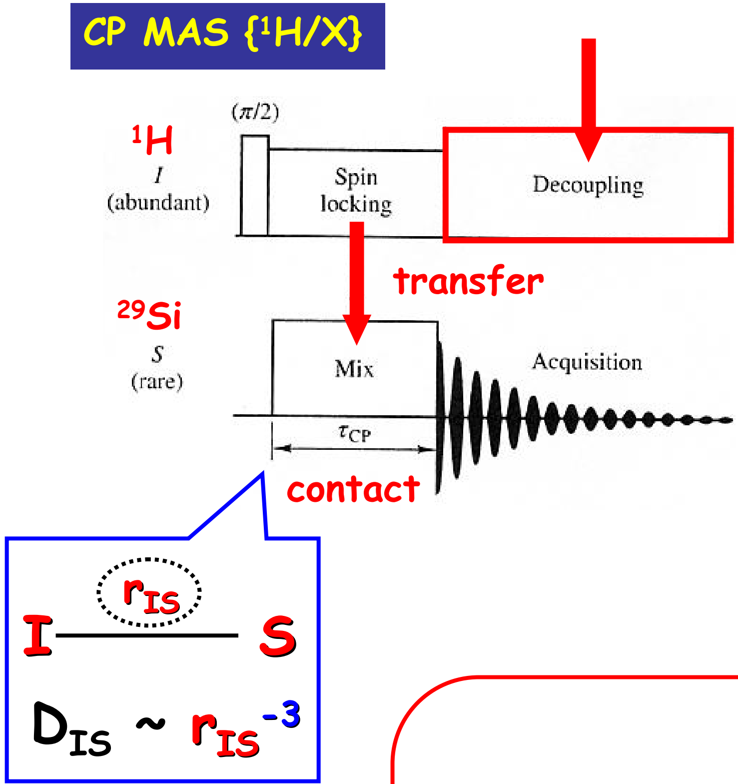


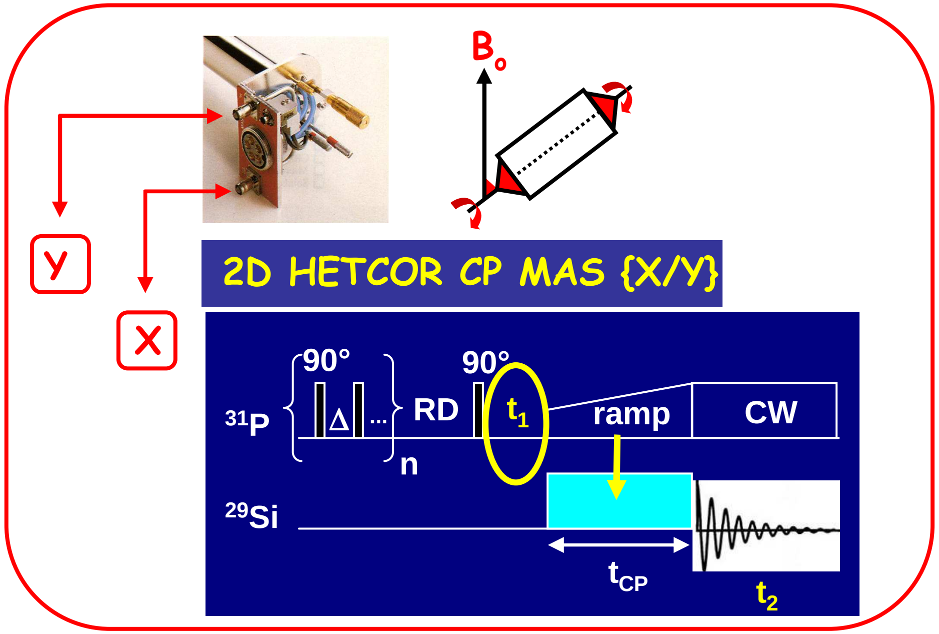


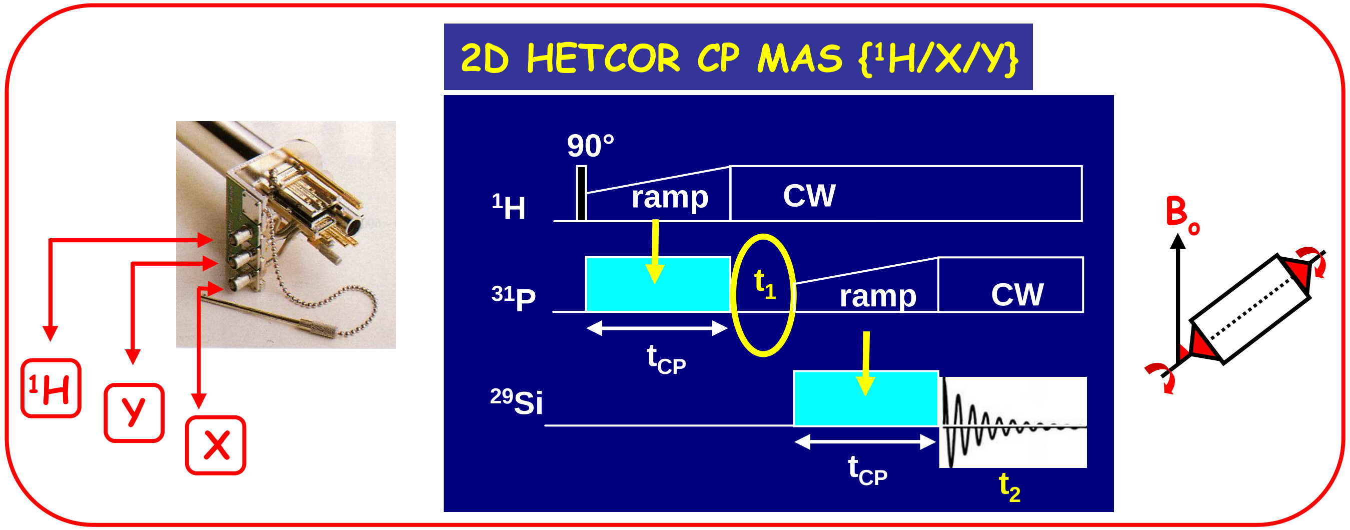
Dynamic Angle Spinning (DAS) I > 1/2

or MQ-MAS I > 1/2

Cross Polarization experiments (under MAS)

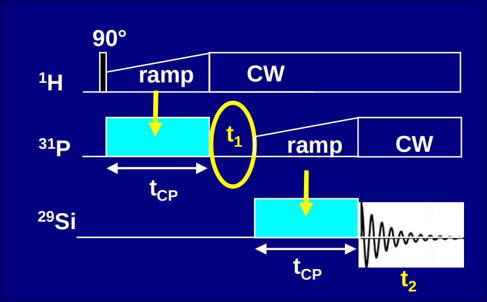




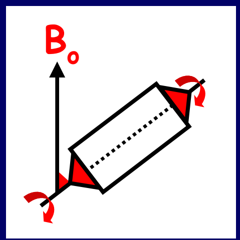


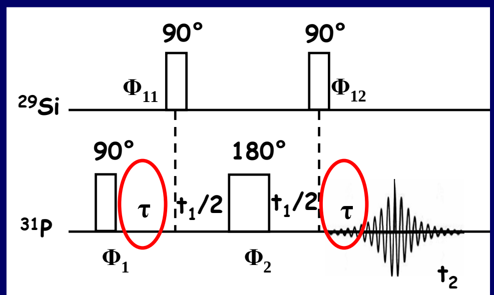
Methods: solid state NMR, first principles calculations, models

■ *D* and *J*-derived solid state NMR



2D triple res. CP MAS





2D MAS-*J*-HMQC

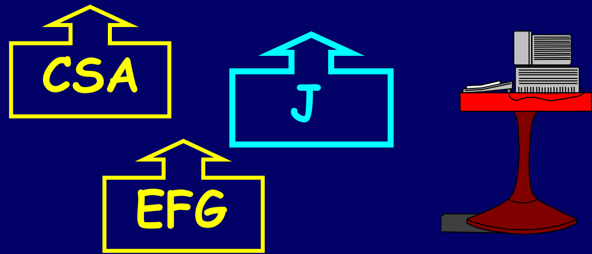
Sol Gel chemistry

Chimie Douce...

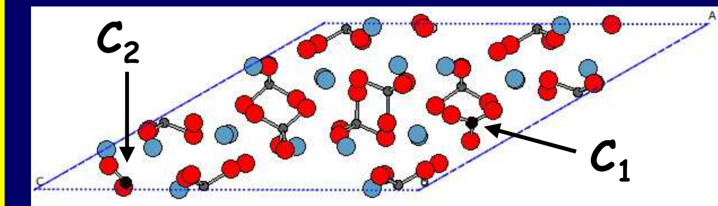
■ *ab initio* calculations

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

PAW, GIPAW methods



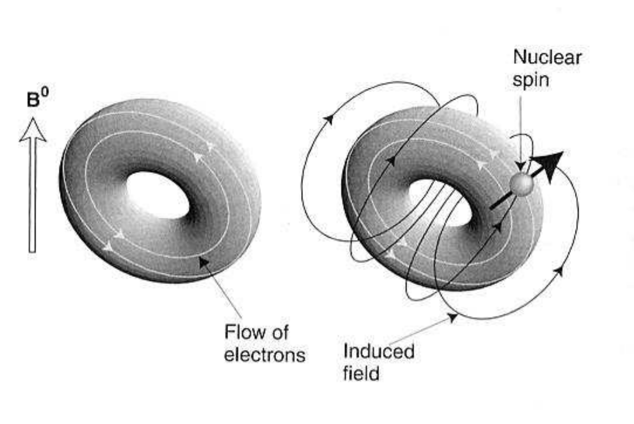
■ DFT models



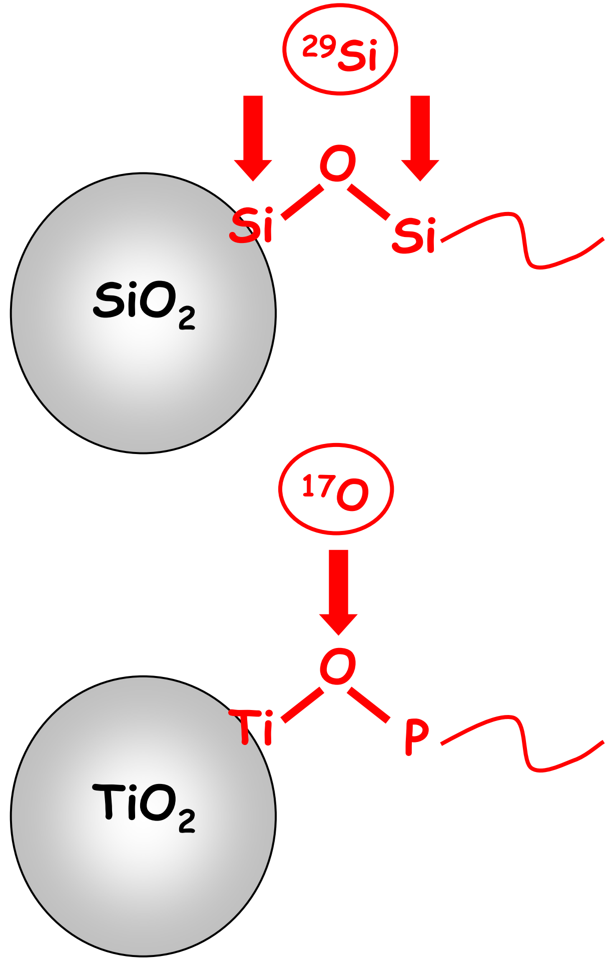
Astala *et al.*, *Chem. Mater.* 2005

Peroos *et al.*, *Biomaterials* 2006

♦ CHEMICAL SHIFT δ



in: Levitt, spin dynamics, 2002

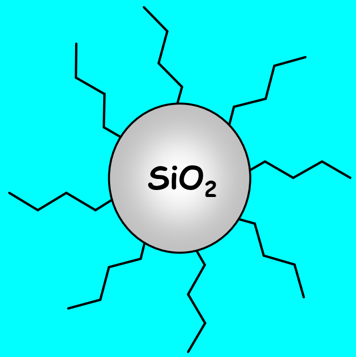


- covalent grafting
- oxide nanoparticles

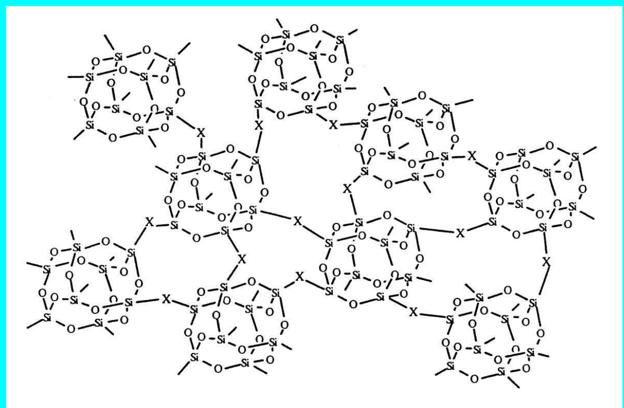
C. Gervais *et al.*, *Chem. Mater.* 15 (2003) 4098.

C. Bonhomme *et al.*, MRS Proceedings (2007) E-paper.

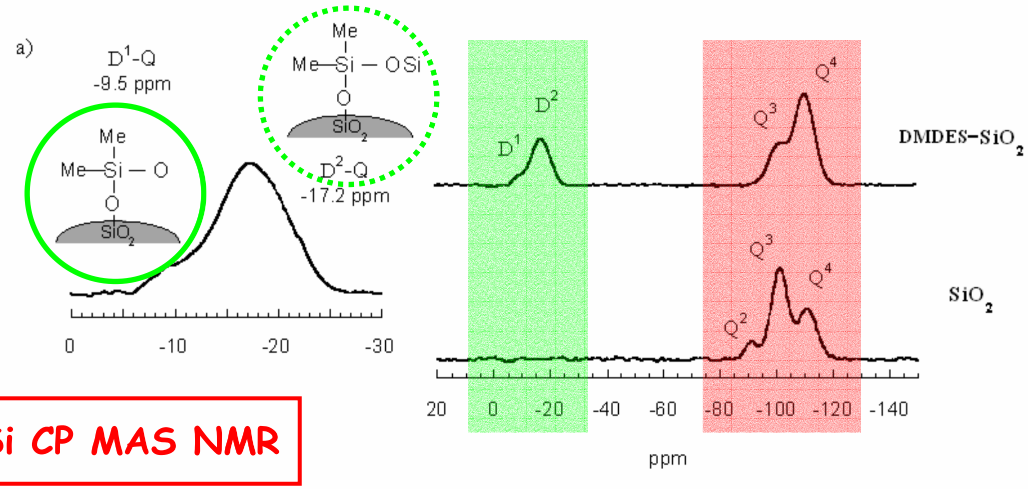
Covalent grafting on silica nanoparticles



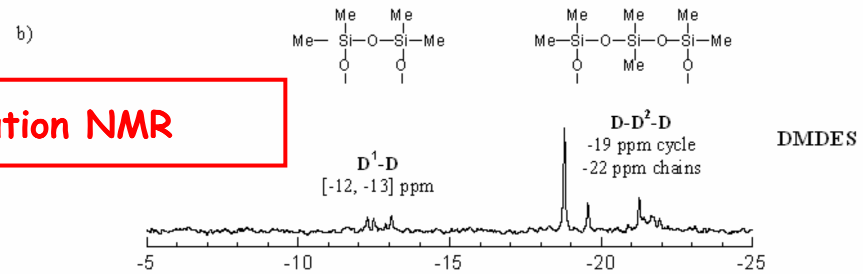
cluster integrity



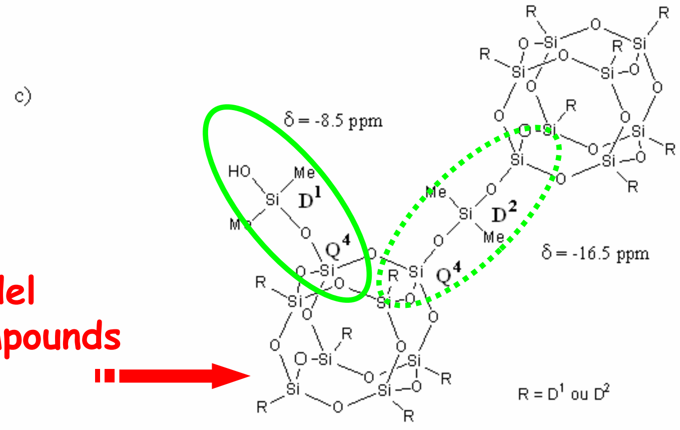
local dynamics reactivity



^{29}Si CP MAS NMR



solution NMR



model compounds

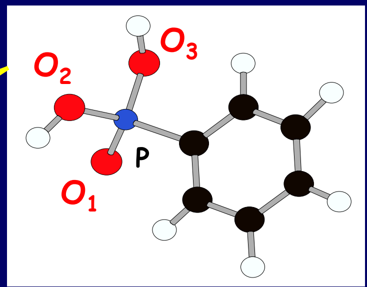
S. de Monredon (PhD)
Coll. : A. Pottier (Rhodia)

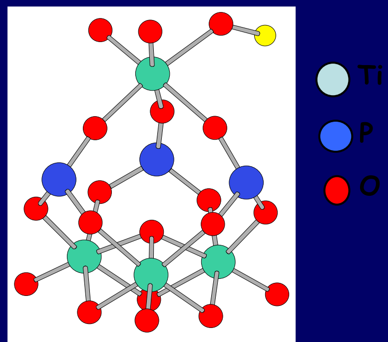
Covalent grafting on TiO_2 nanoparticles

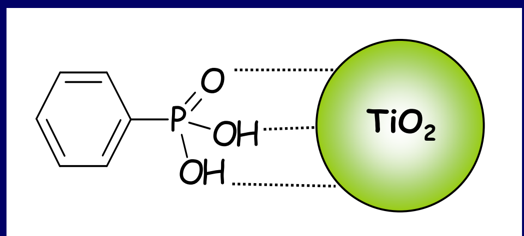
a particular probe: ^{17}O I = 5/2

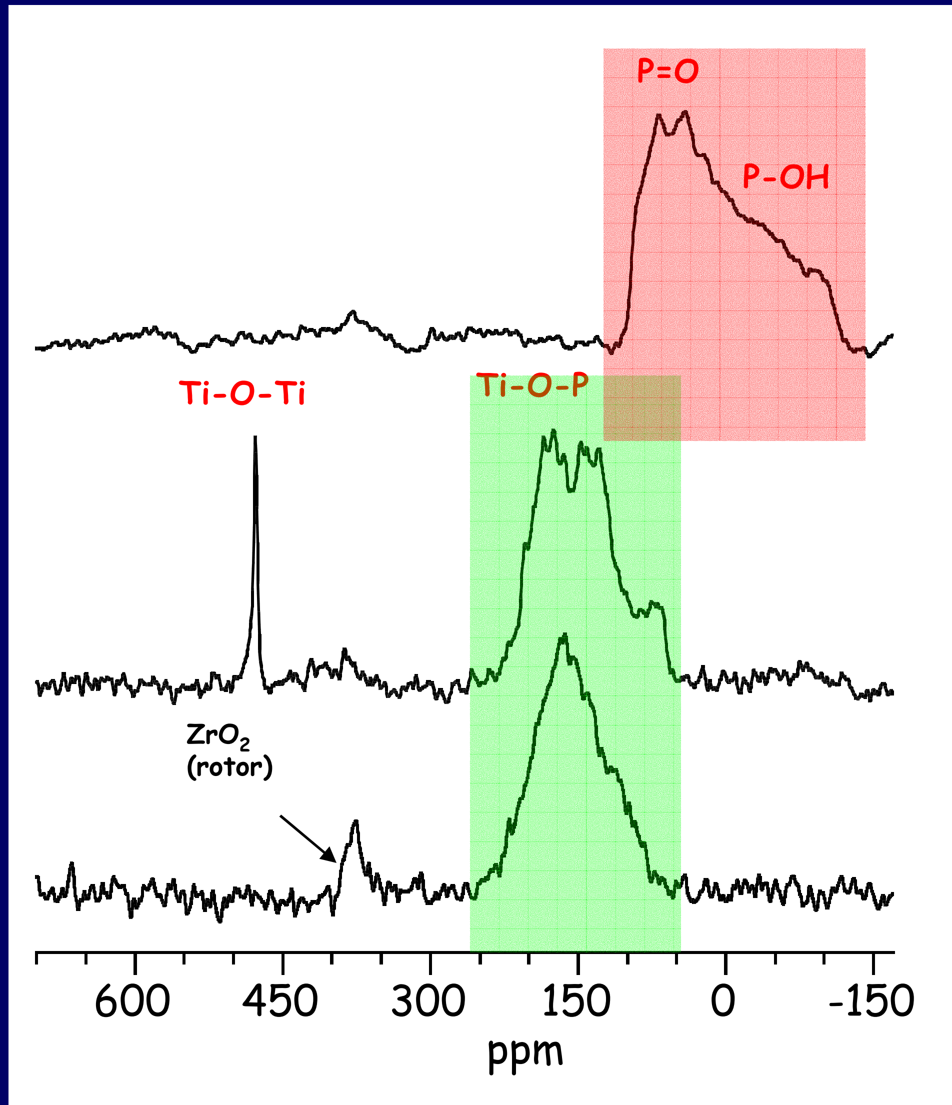
second-order quadrupolar broadening

^{17}O







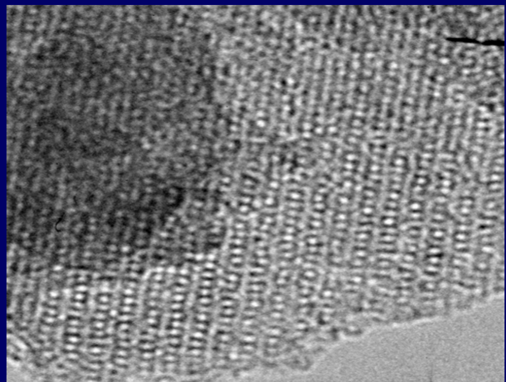


Coll. : H. Mutin (Montpellier)

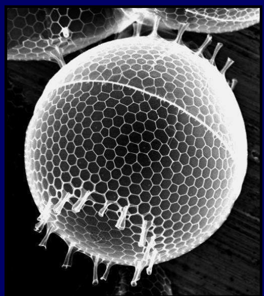
Sol Gel materials: questions ?

sol gel oxide glasses

hybrid materials

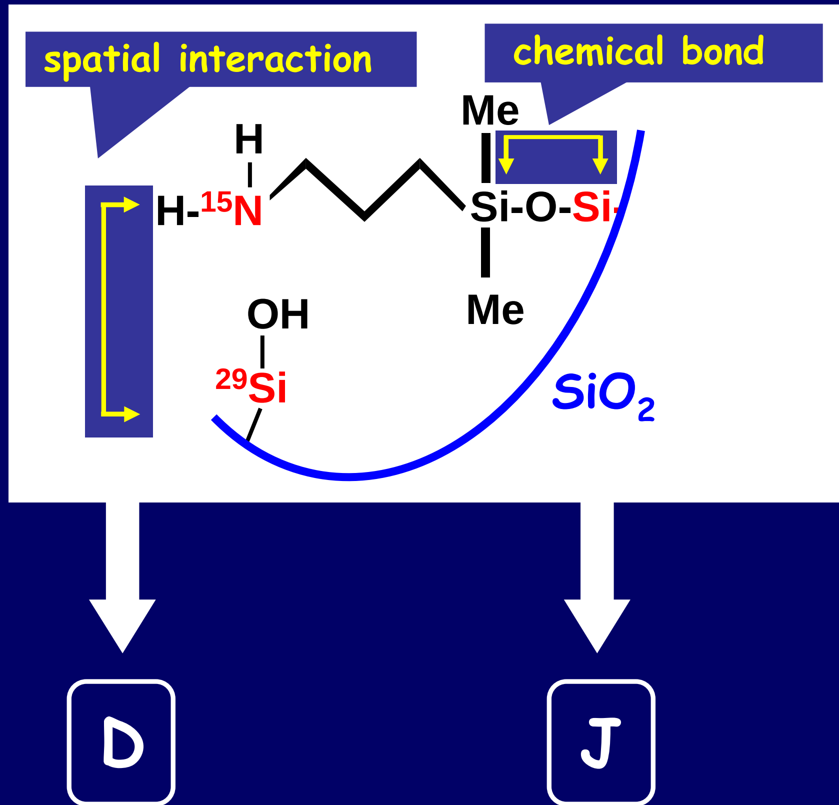


mesoporous materials



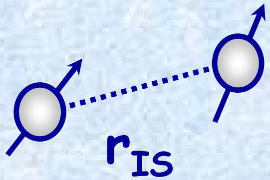
biogenic silica (diatoms)

«playing» with the dipolar *D* and scalar *J* interactions...

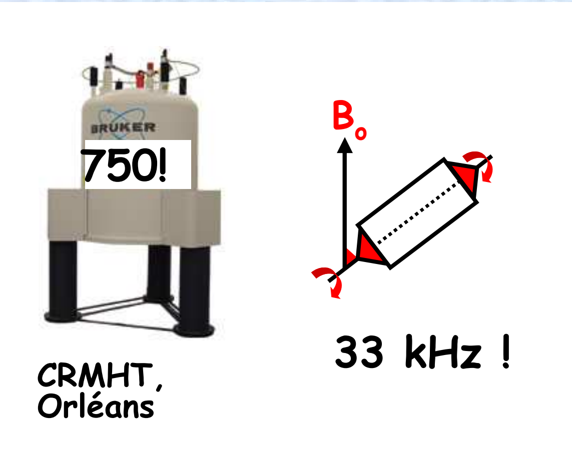


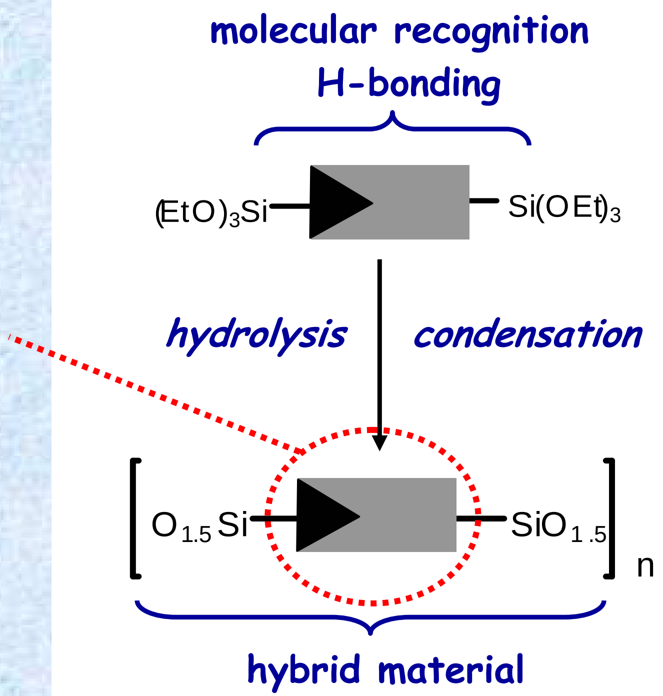
- connectivities in hybrids
- organic/inorganic interactions
- ...

♦ DIPOLAR INTERACTION *D*



$$D \propto \frac{1}{r_{IS}^{3}}$$



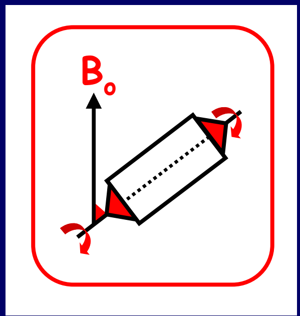


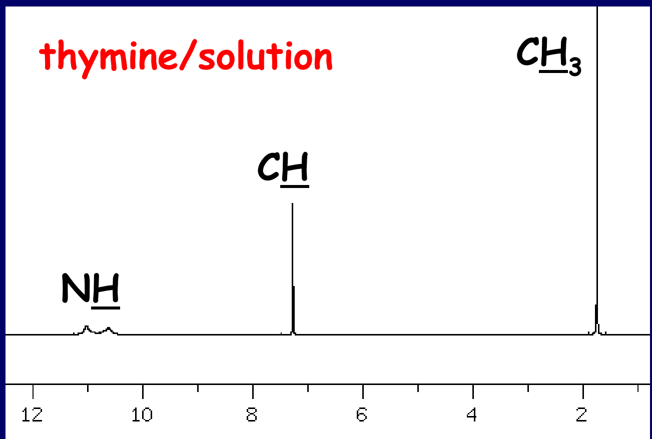
- ^1H-^1H dipolar interaction
- ureidopyrimidinone models
- bio-inspired materials

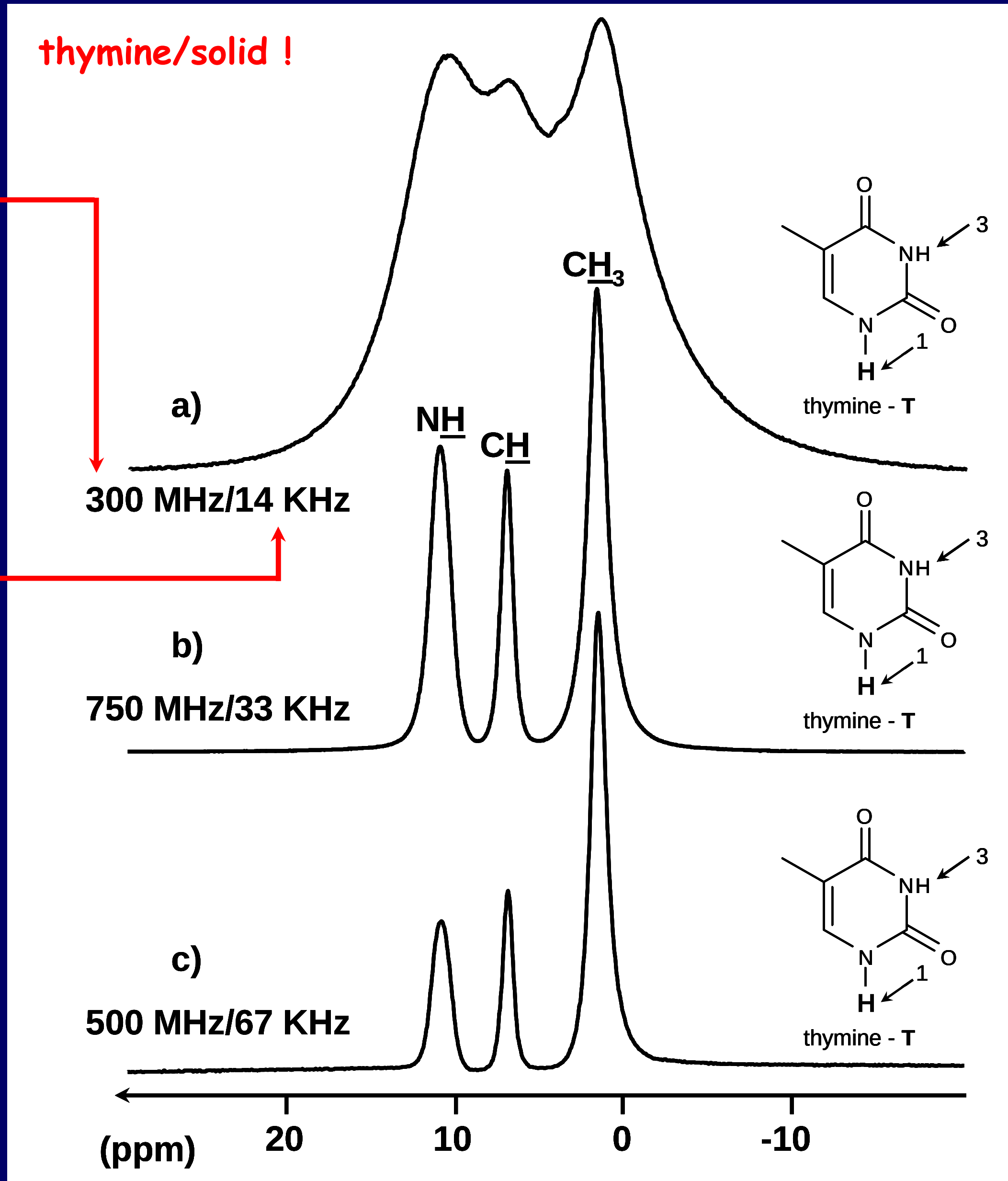
M. Wong Chi Man *et al.*, *Angew. Chem.* 43 (2004) 203.

M. Wong Chi Man *et al.*, *New. J. Chem.* 29 (2005) 653.

^{1}H high resolution solid state NMR. A major problem...

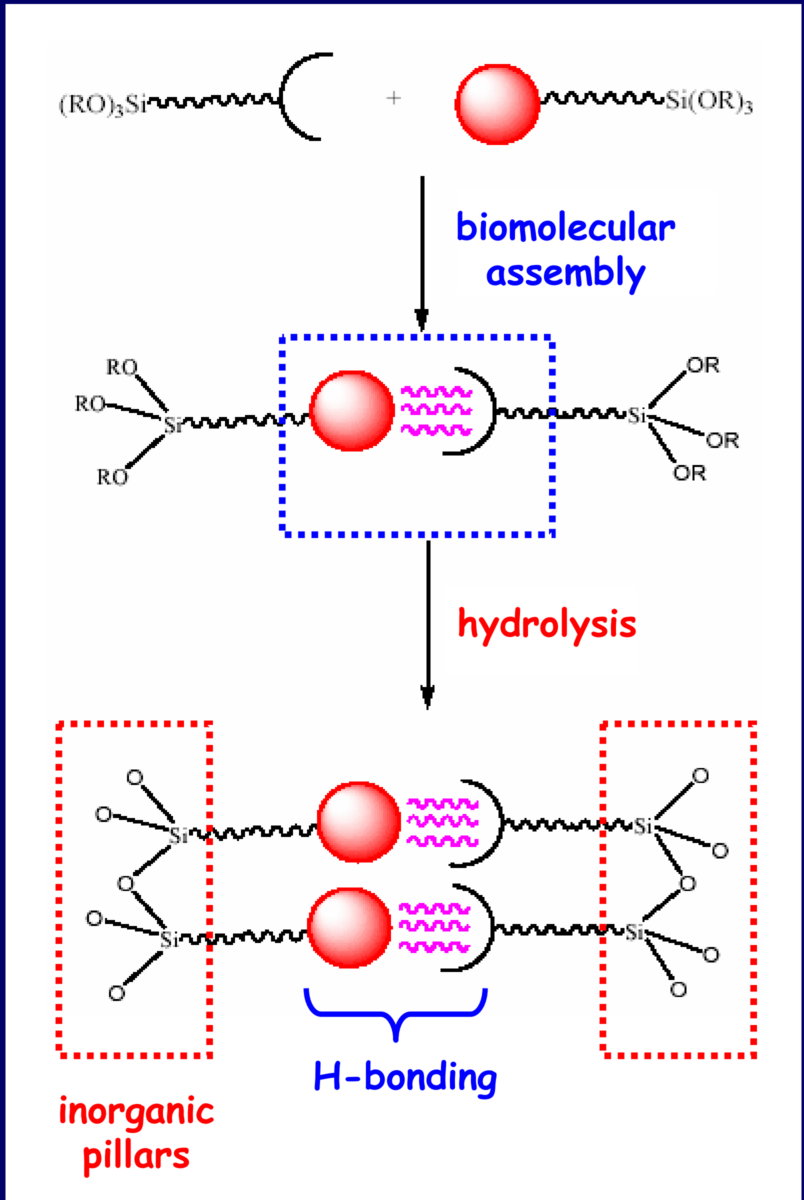


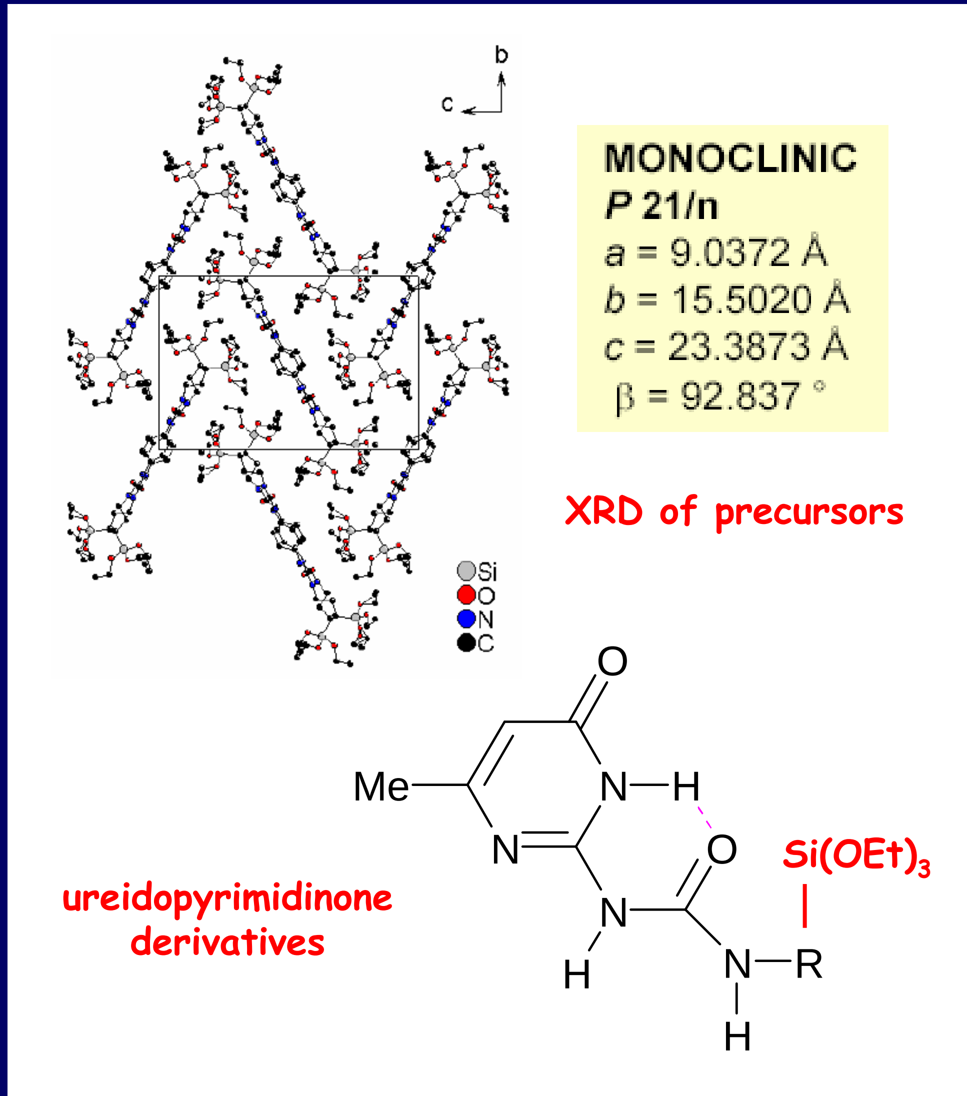




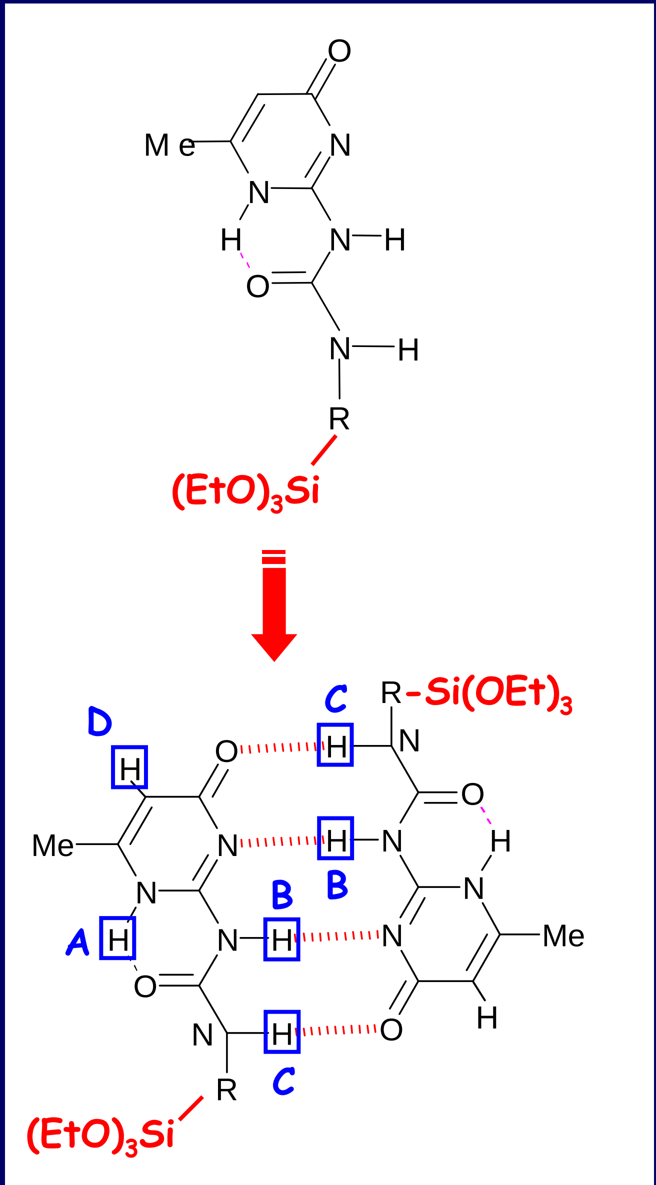
G. Arrachart et al., J. Mater. Chem. 18 (2008) 392-399.

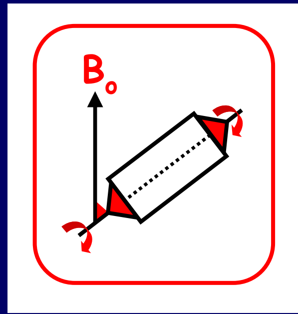
Ureidopyrimidinone based systems

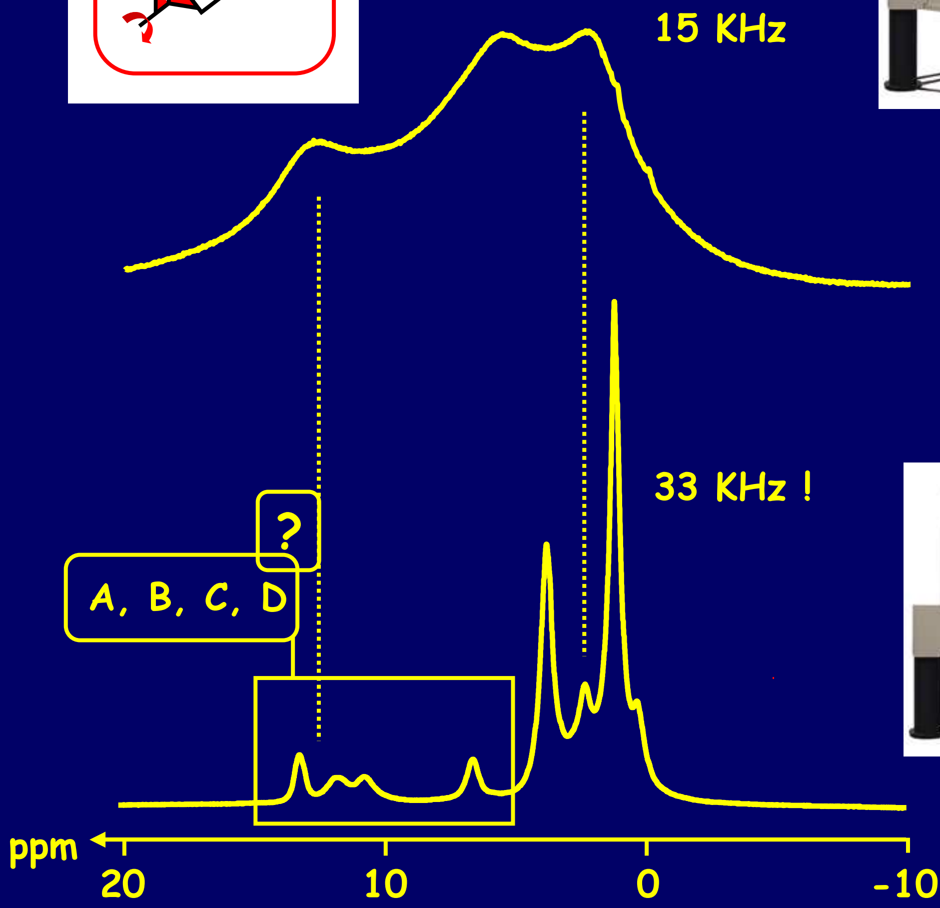




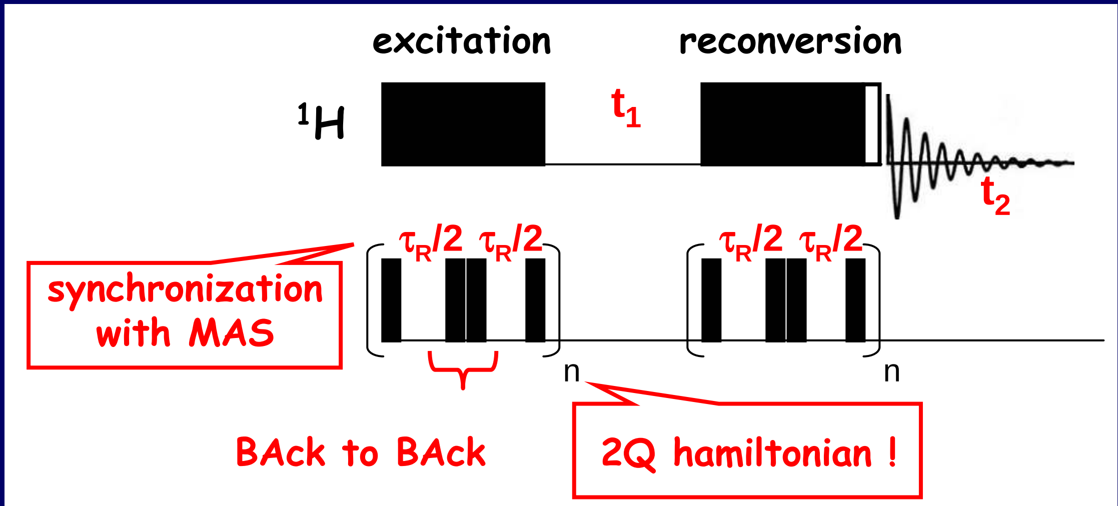
Ureidopyrimidinones: ^{1}H high resolution solid state NMR







Spatial connectivities: DQ ^{1}H fast MAS spectroscopy

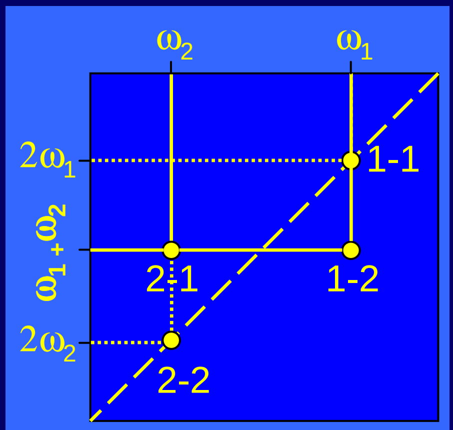


$D_{HH} \propto 1/r^3$

^{1}H .... ^{1}H
r

I=1/2 I=1/2

DQ
<++| ⇔ |-->



1—2
| |
1—2

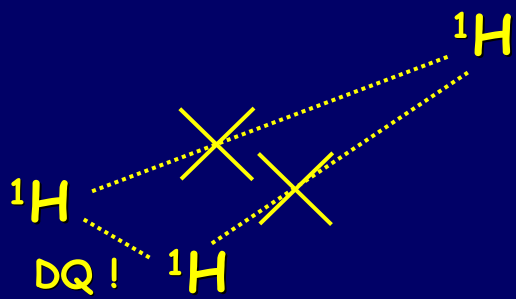
dipolar «links»

DQ dim.

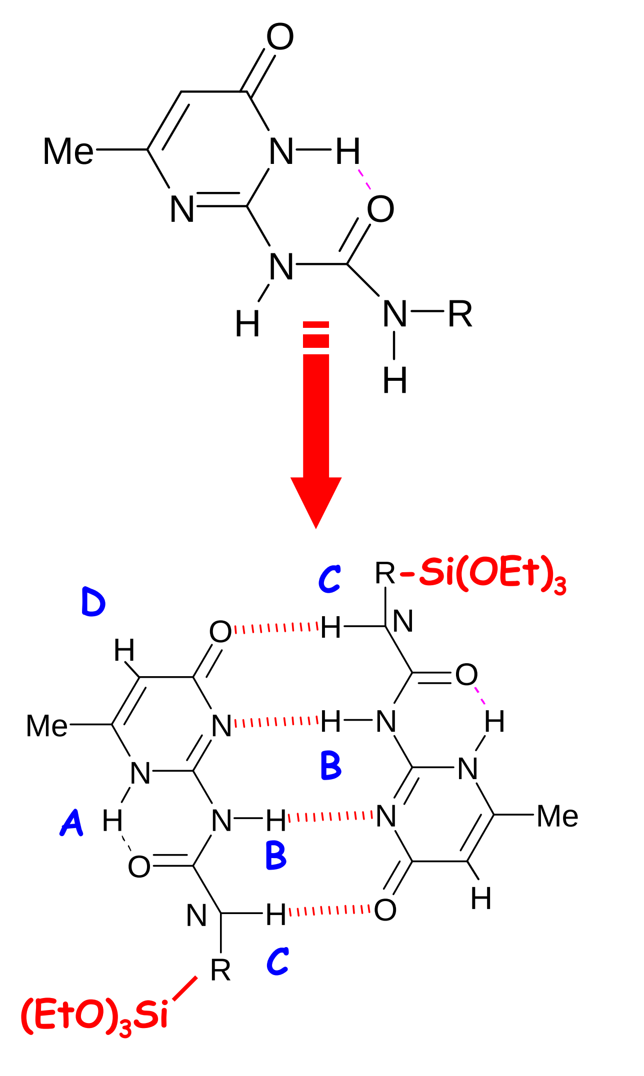
SQ dim.

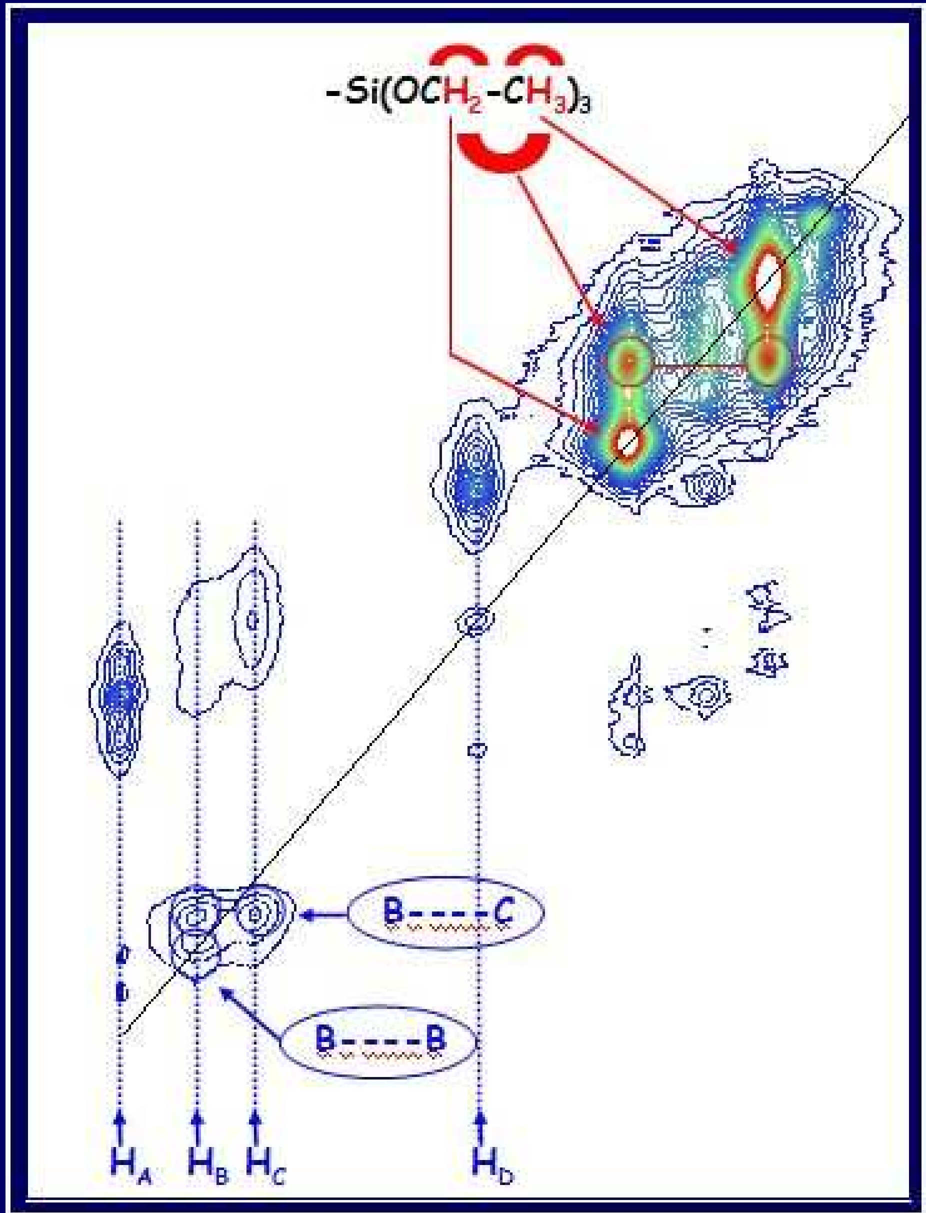
$\delta_{iso.}$: very fast MAS, very high B_0!

selectivity

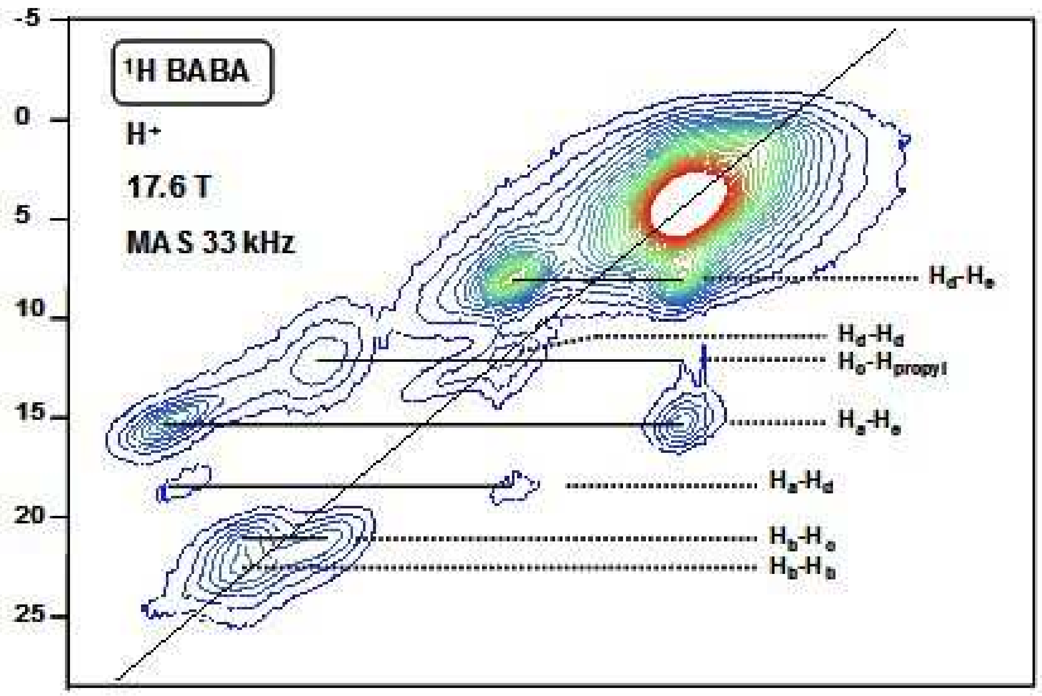


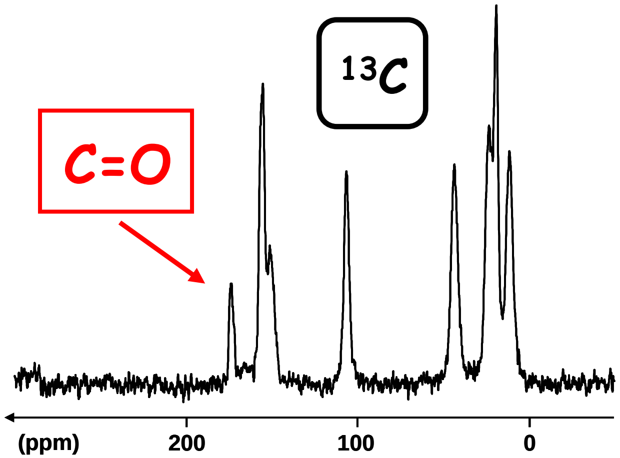
Application to ureidopyrimidinone precursors



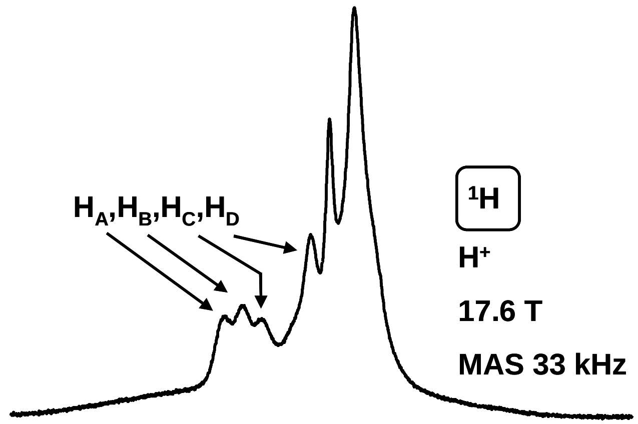


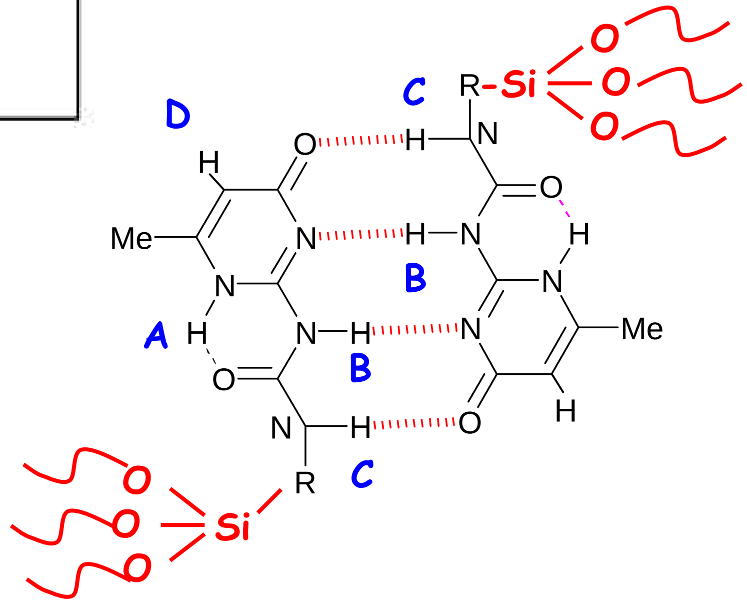
Application to ureidopyrimidinone derived materials: hybrid silica





hydrolysis-condensation

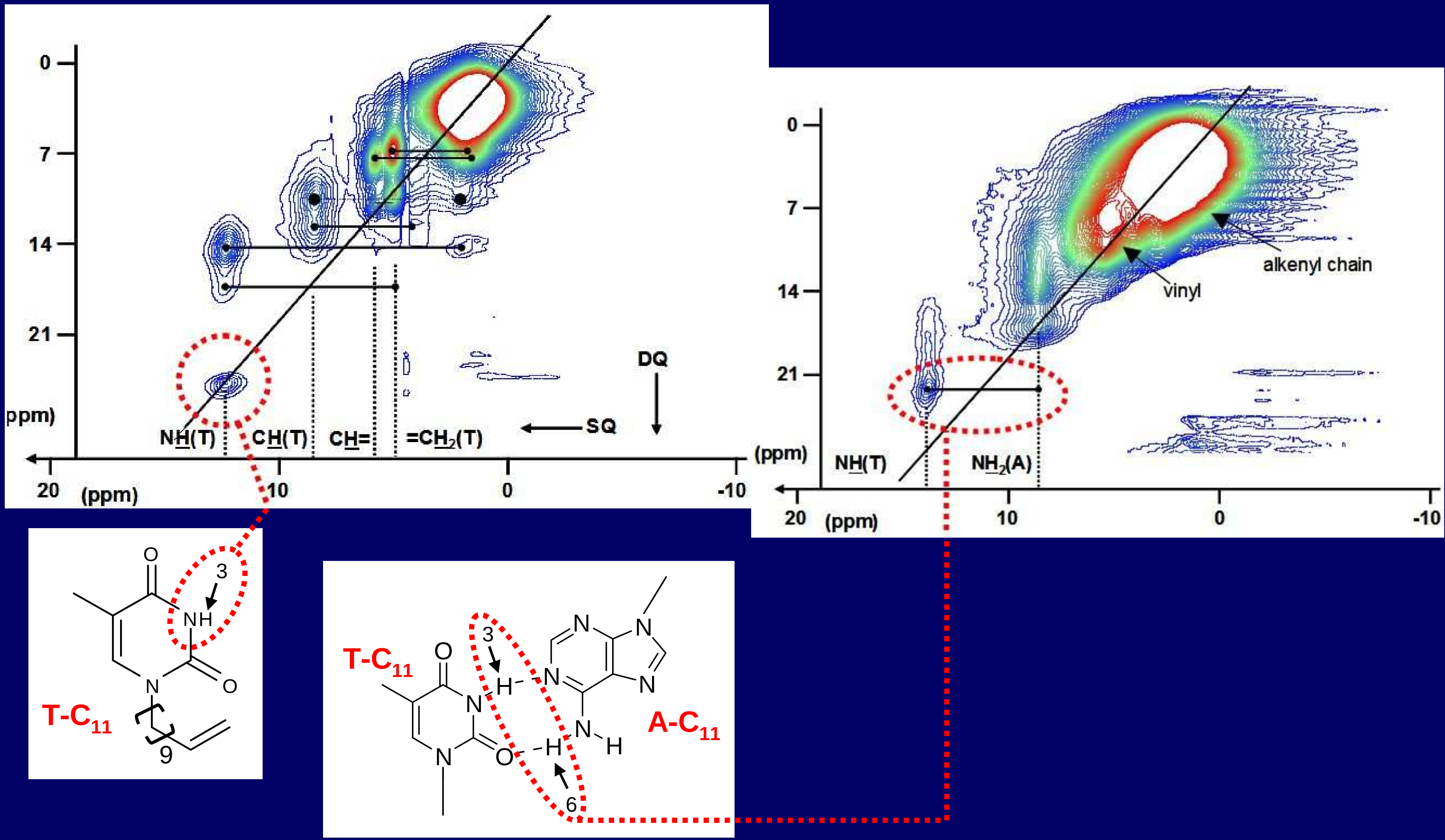




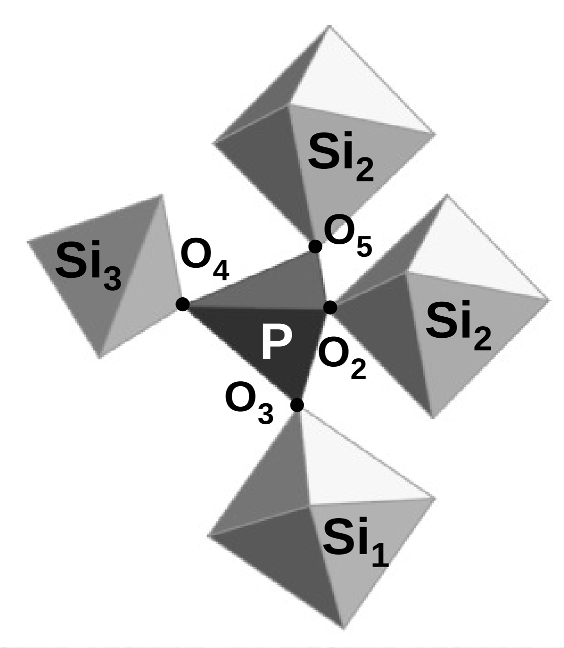
Towards bio-inspired materials: adenine (A) and thymine (T) derivatives

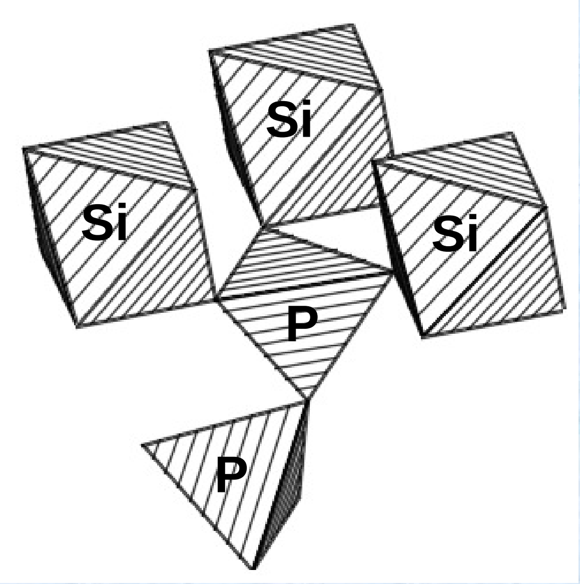
^{1}H BABA NMR

750 MHz/33 KHz

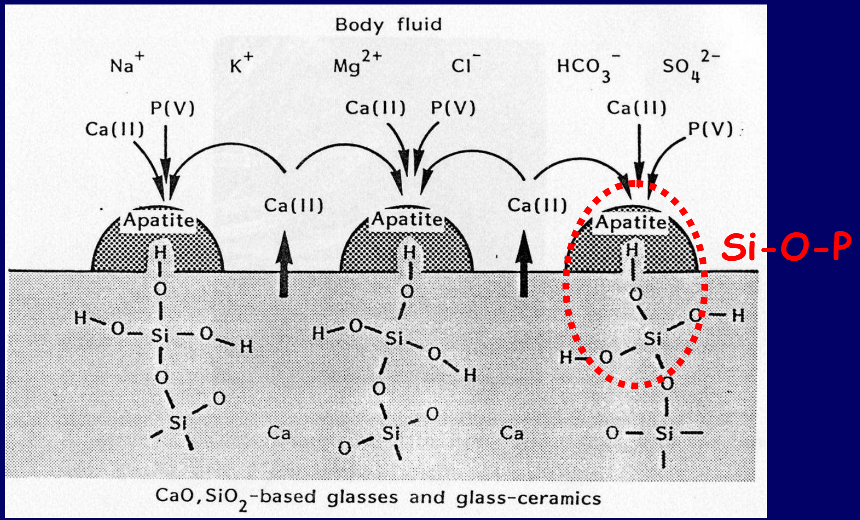


♦ silicophosphates

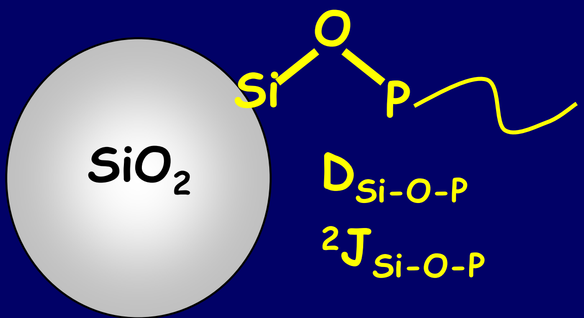




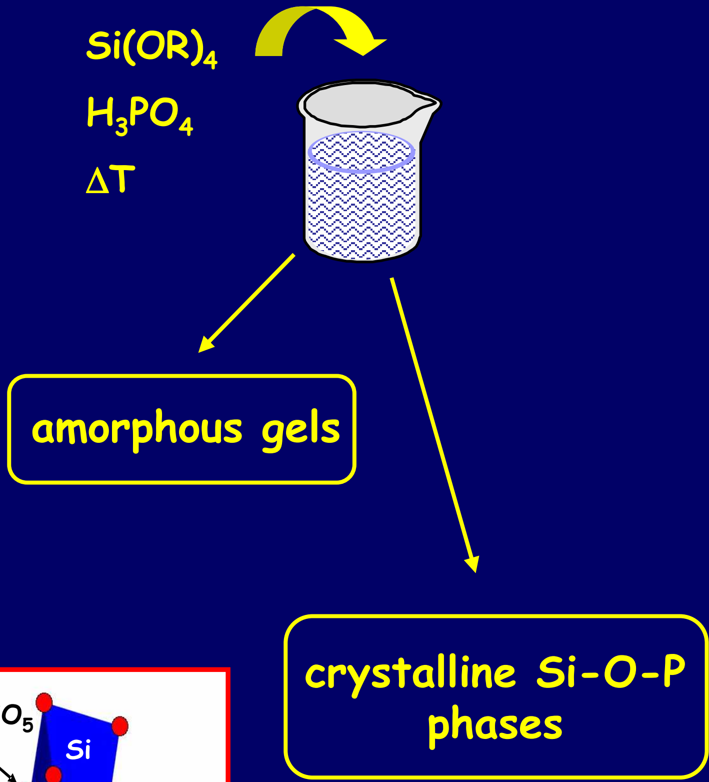
Silicophosphates and Si-O-P systems

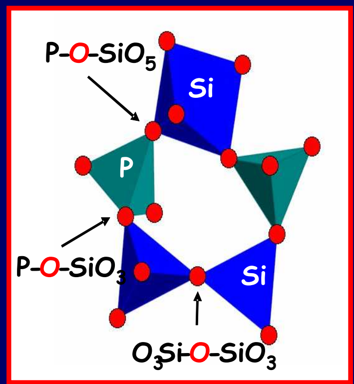


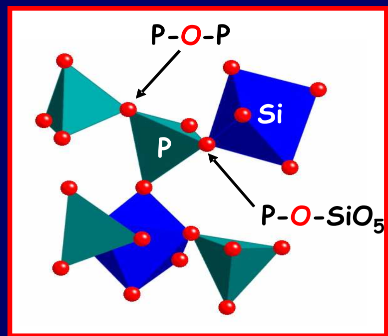
■ biocompatible materials



■ grafting on nanoparticles

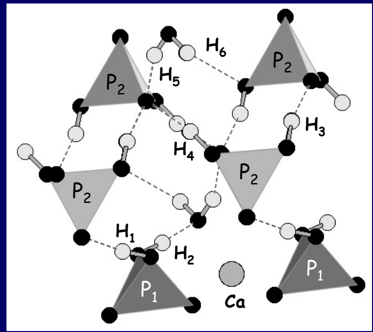




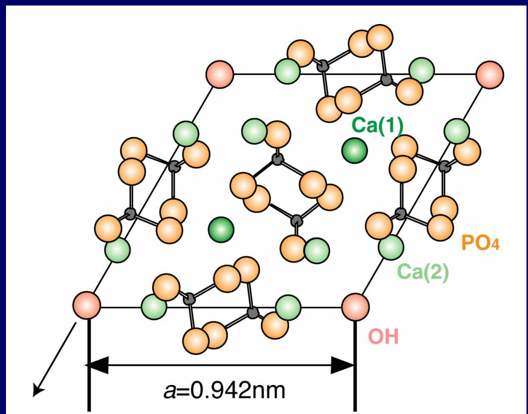


Calcium phosphates and substituted hydroxyapatite (HAp)

Brushite, $CaHPO_4.2H_2O$
MCPM, $Ca(H_2PO_4)_2.H_2O$
β- and γ-$Ca(PO_3)_2$
$Ca_4P_2O_9$
...

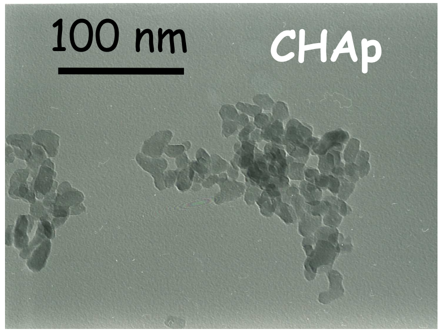


■ calcium phosphates

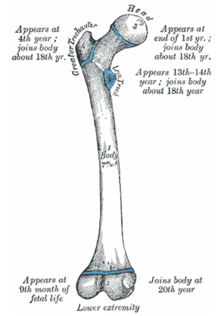


$Ca_{10}(PO_4)_6(OH)_2$

■ hydroxyapatite (HAp)



nano-crystalline CHAp



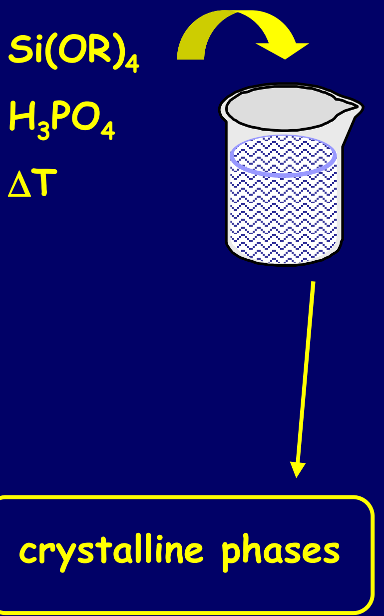
bone

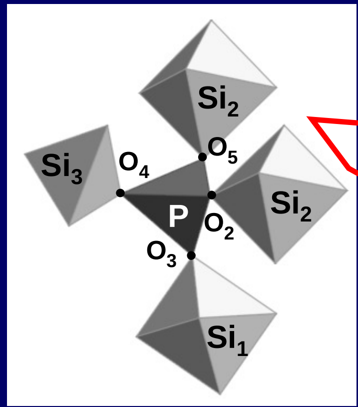
$Ca_{10-x/2}[(PO_4)_{6-x}(CO_3)_x]\ [(OH)_{2-2y}(CO_3)_y]$

carbonated hydroxyapatite $x \neq 0$

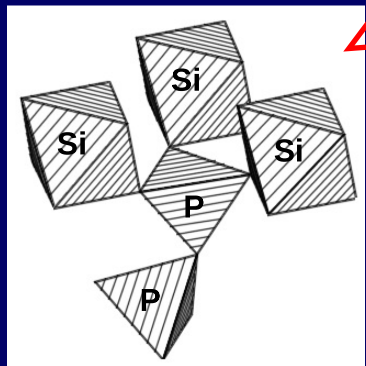
Coll. : S. Hayakawa, A. Osaka, Okayama, Japan.

Crystalline silicophosphates: $Si_5O(PO_4)_6$ and SiP_2O_7 polymorphs



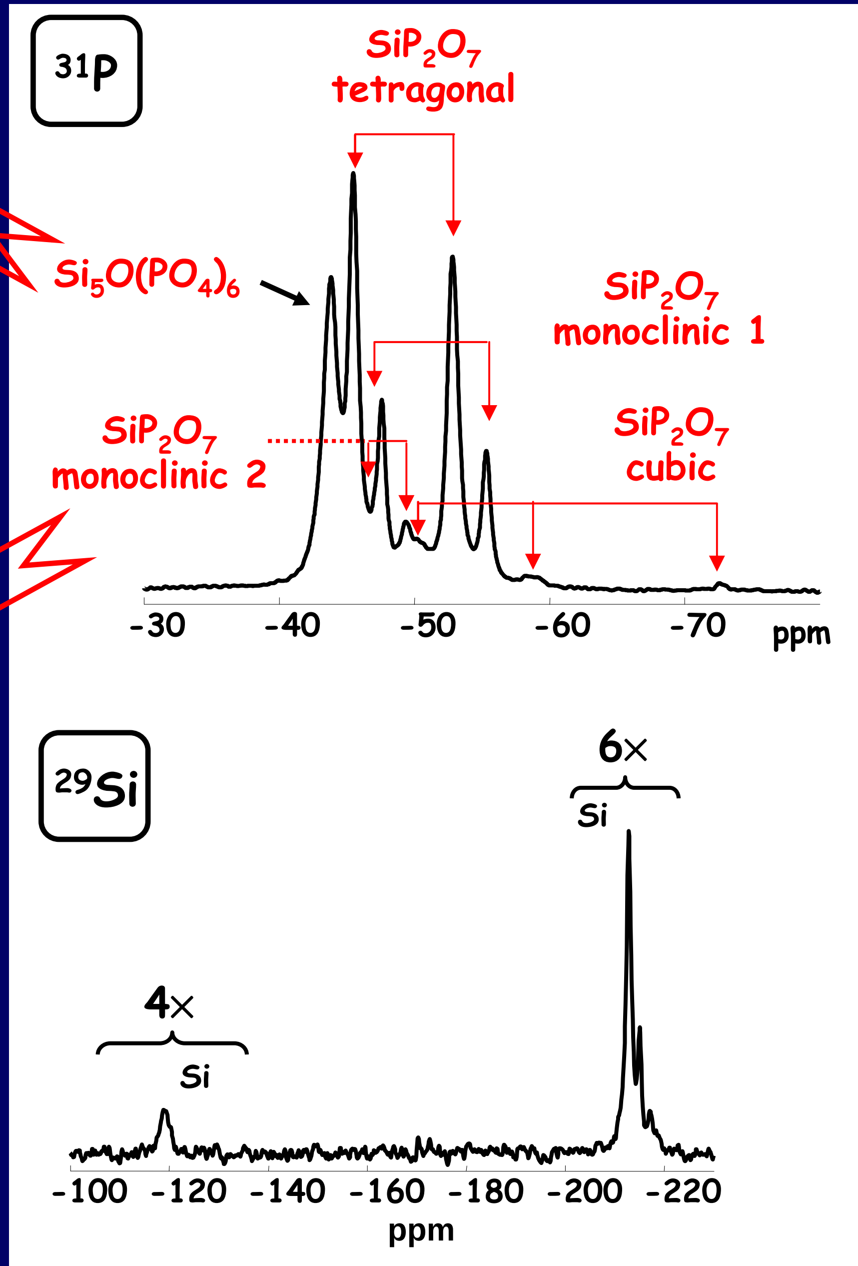


Si_5P_6

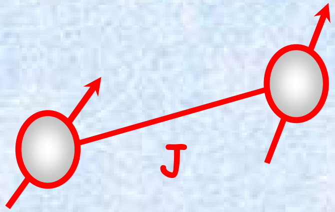


SiP_2O_7

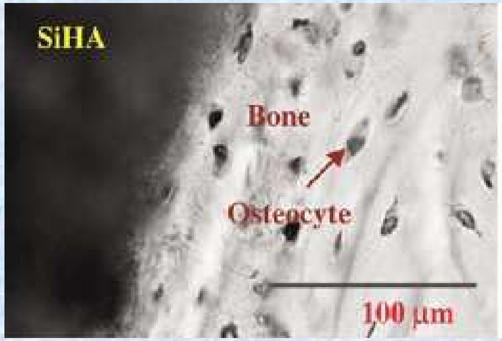
- SiP_2O_7-monoclinic 1
- SiP_2O_7-monoclinic 2
- SiP_2O_7-tetragonal
- SiP_2O_7-cubic
- $Si_5O(PO_4)_6$
- $Si(HPO_4)_2.H_2O$
- ?...



♦ SCALAR INTERACTION *J*



chemical bonding

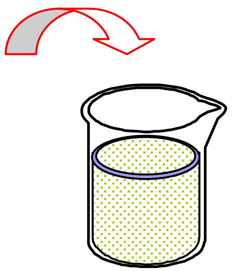


Coelho *et al.*, *J. Sol Gel Sc. Technol.* 40 (2006) 181.

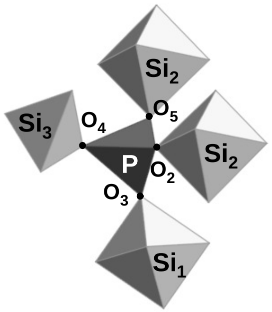
Coelho *et al.*, *J. Magn. Reson.* 179 (2006) 106.

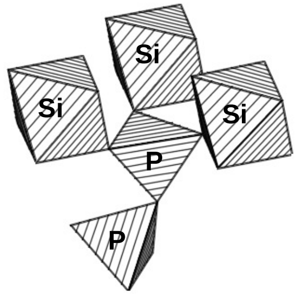
Coelho *et al.*, *Inorg. Chem.* 46 (2007) 1379.

$Si(OCH_2CH_3)_4$
EtOH
H_3PO_4
$NiCl_2.6H_2O$



gel
135°C





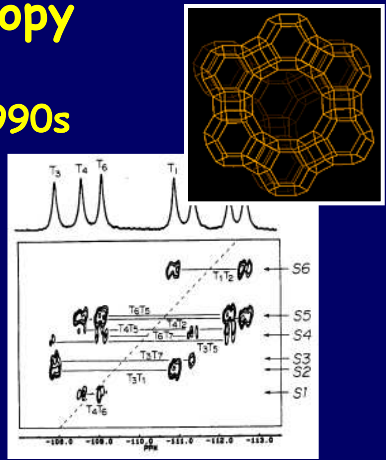
- $^2J_{P-O-Si}$ couplings
- silicophosphates
- biocompatible Si-O-P gels

MAS-*J* derived experiments

MAS-*J* spectroscopy

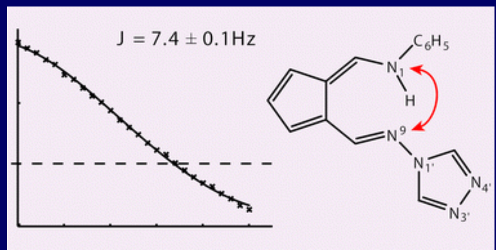
C. Fyfe, H. Eckert 1990s

$^{29}Si/^{29}Si$



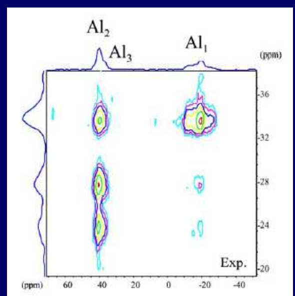
L. Emsley, S. Brown 1998

$^{15}N/^{15}N$



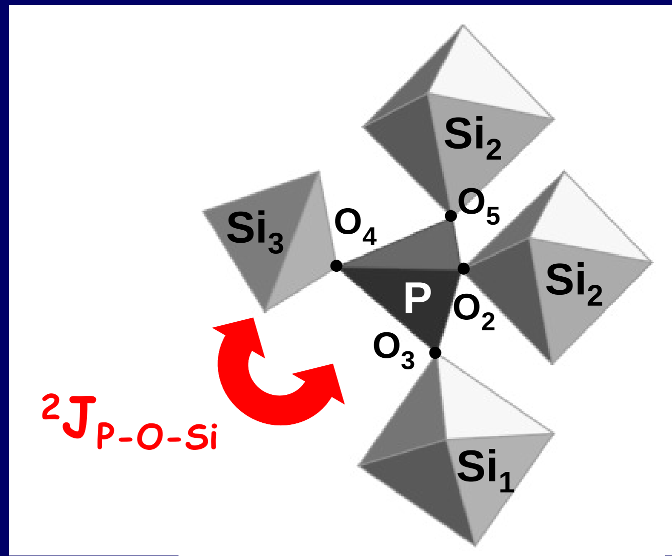
D. Massiot, J. P. Amoureux 2003

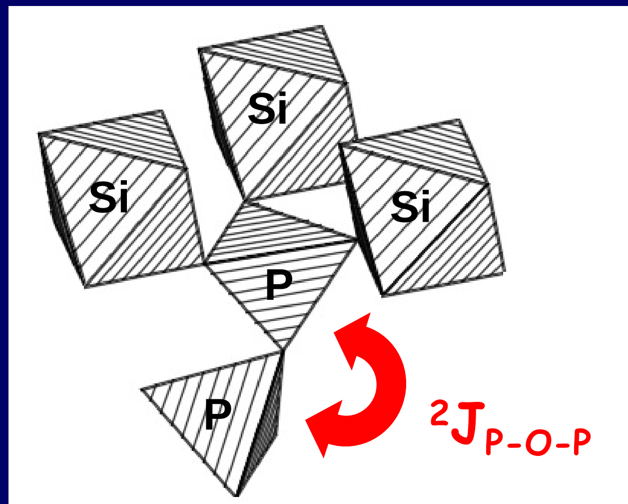
$^{27}Al/^{31}P$



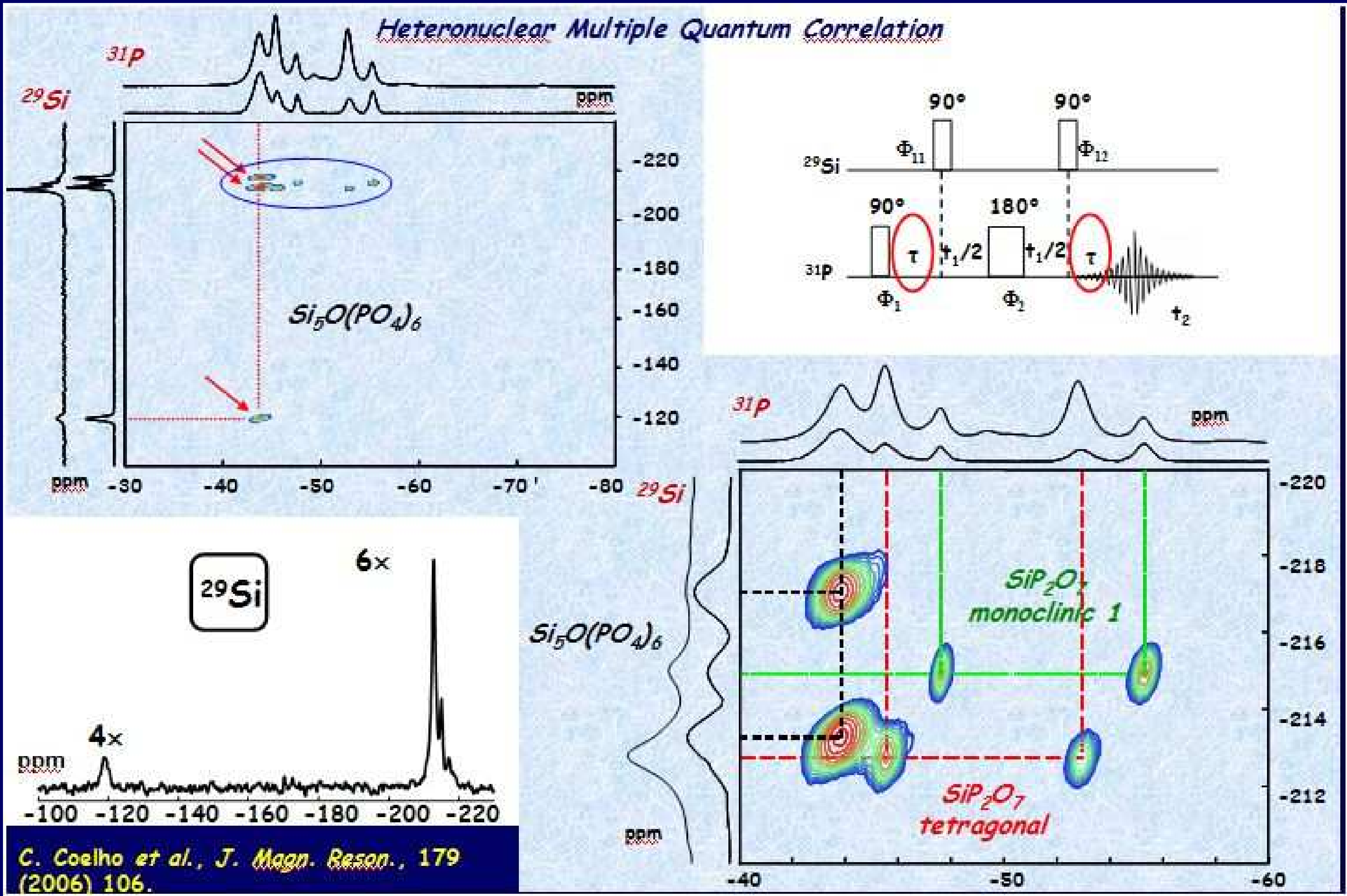
...

homonuclear and heteronuclear correlations





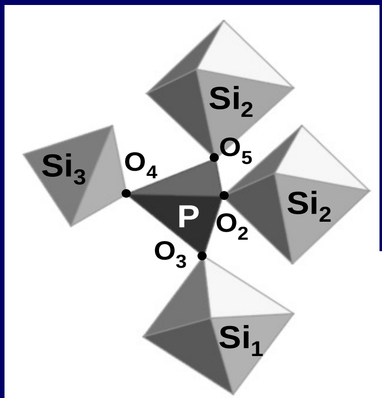
Heteronuclear *J* correlations: $^{31}P/^{29}Si$ MAS-*J*-HMQC



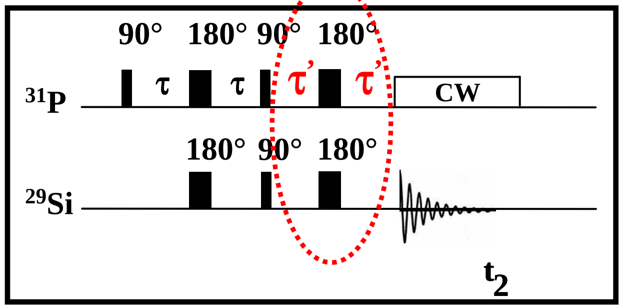
C. Coelho *et al.*, *J. Magn. Reson.*, 179 (2006) 106.

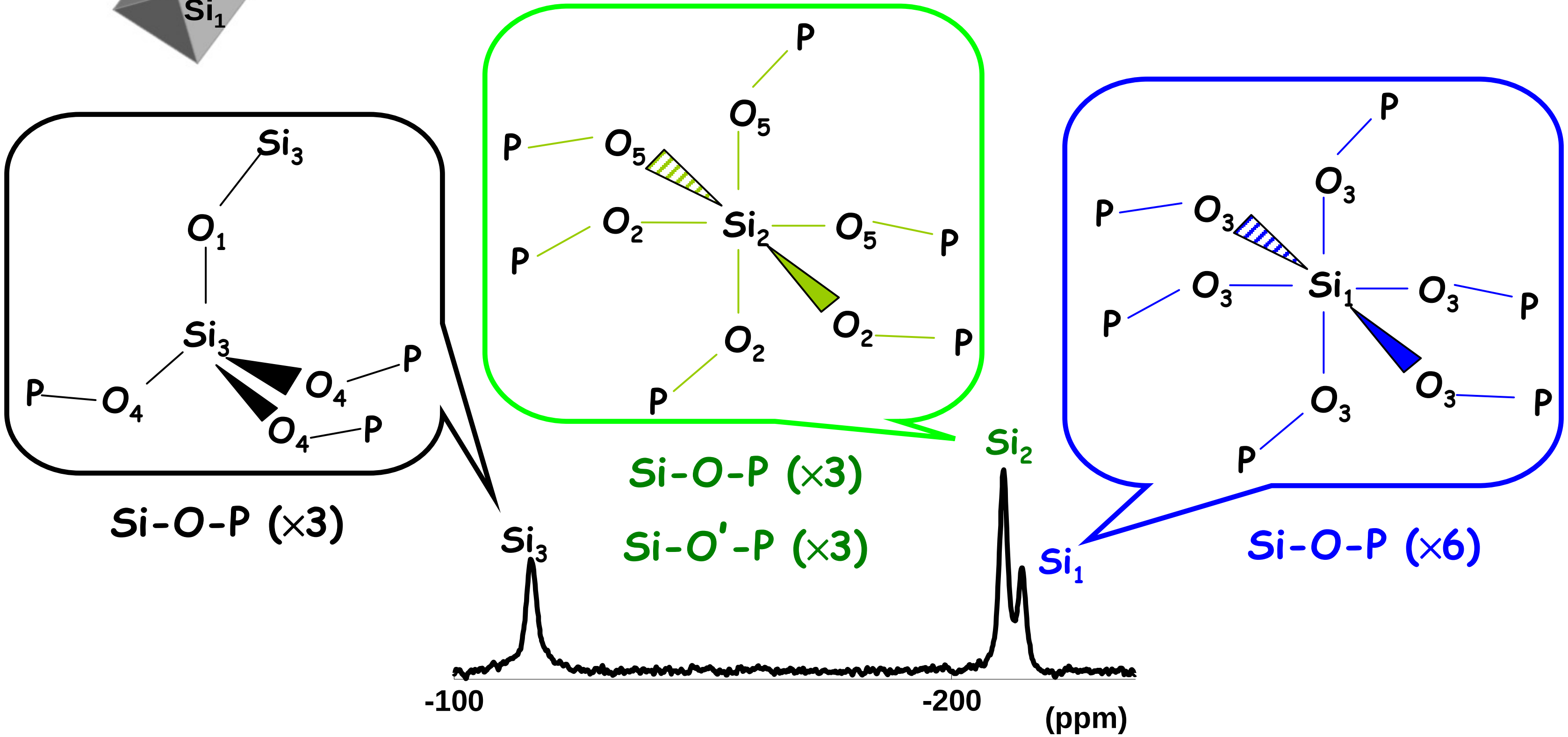
Heteronuclear *J* correlations: $^{31}P \rightarrow {}^{29}Si$ MAS-*J*-INEPT -1

Insensitive Nuclei Enhanced by Polarization Transfer



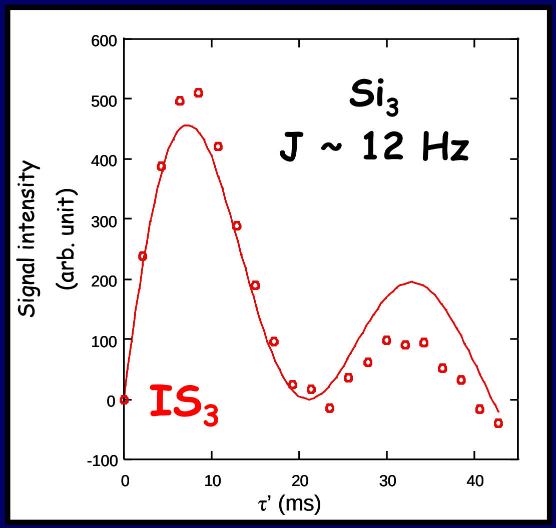
INEPT gain
~ $|\gamma_S/\gamma_I|$

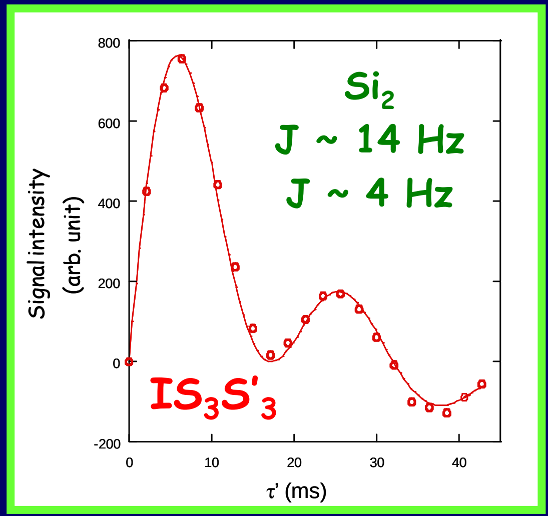


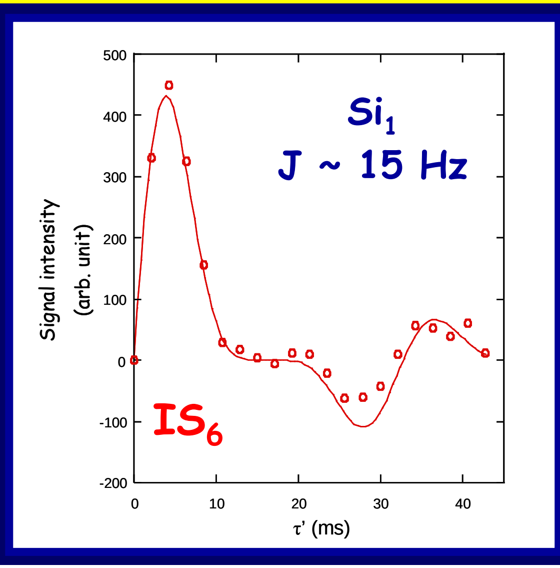


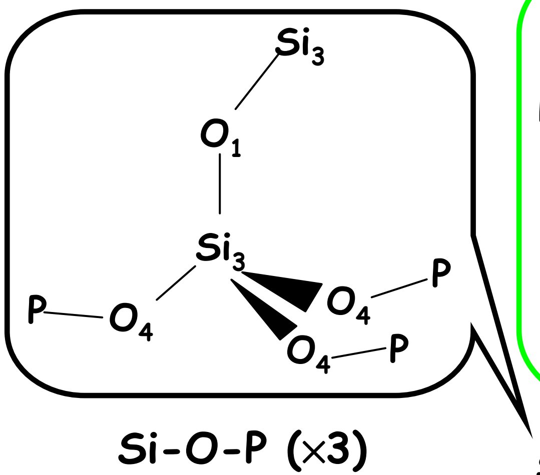
Coelho et al., Inorg. Chem. 46 (2007) 1379.

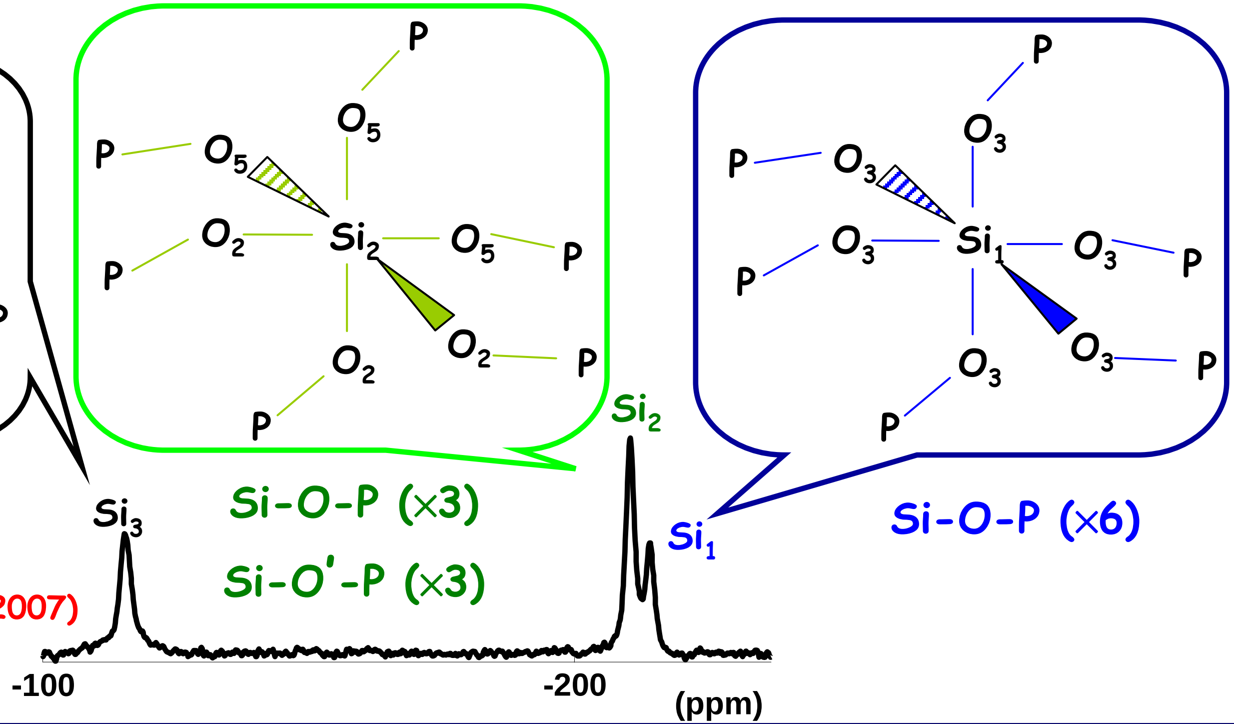
Heteronuclear *J* correlations: $^{31}P \rightarrow {}^{29}Si$ MAS-*J*-INEPT -2











Coelho *et al.*, *Inorg. Chem.* 46 (2007) 1379.

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

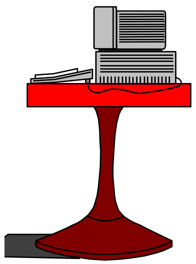
$$B_{in}^{(1)}(r) = 1/c \int d^3r'\, j^{(1)}(r') \times \frac{r-r'}{|r-r'|^3}$$

CSA

$$E(r) = \int d^3r'\, n(r') \times \frac{r-r'}{|r-r'|^3}$$

EFG

! J !



IDRIS

Gervais et al., Magn. Reson. Chem. 42 (2004) 445.

Gervais et al., J. Phys. Chem. A 109 (2005) 6960.

Gervais et al., J. Magn. Reson. 187 (2007) 181.

M. Profeta, C. J. Pickard, F. Mauri *et al.*

T. Charpentier *et al.*

R. Dupree *et al.*

R. K. Harris *et al.*

I. Farnan *et al.*

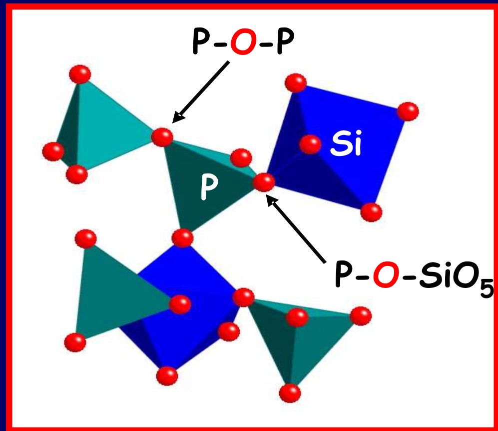
S. Ashbrook *et al.*

J. W. Zwanziger *et al.*

F. Boucher *et al.*

...

inorganic *and* organic derivatives...

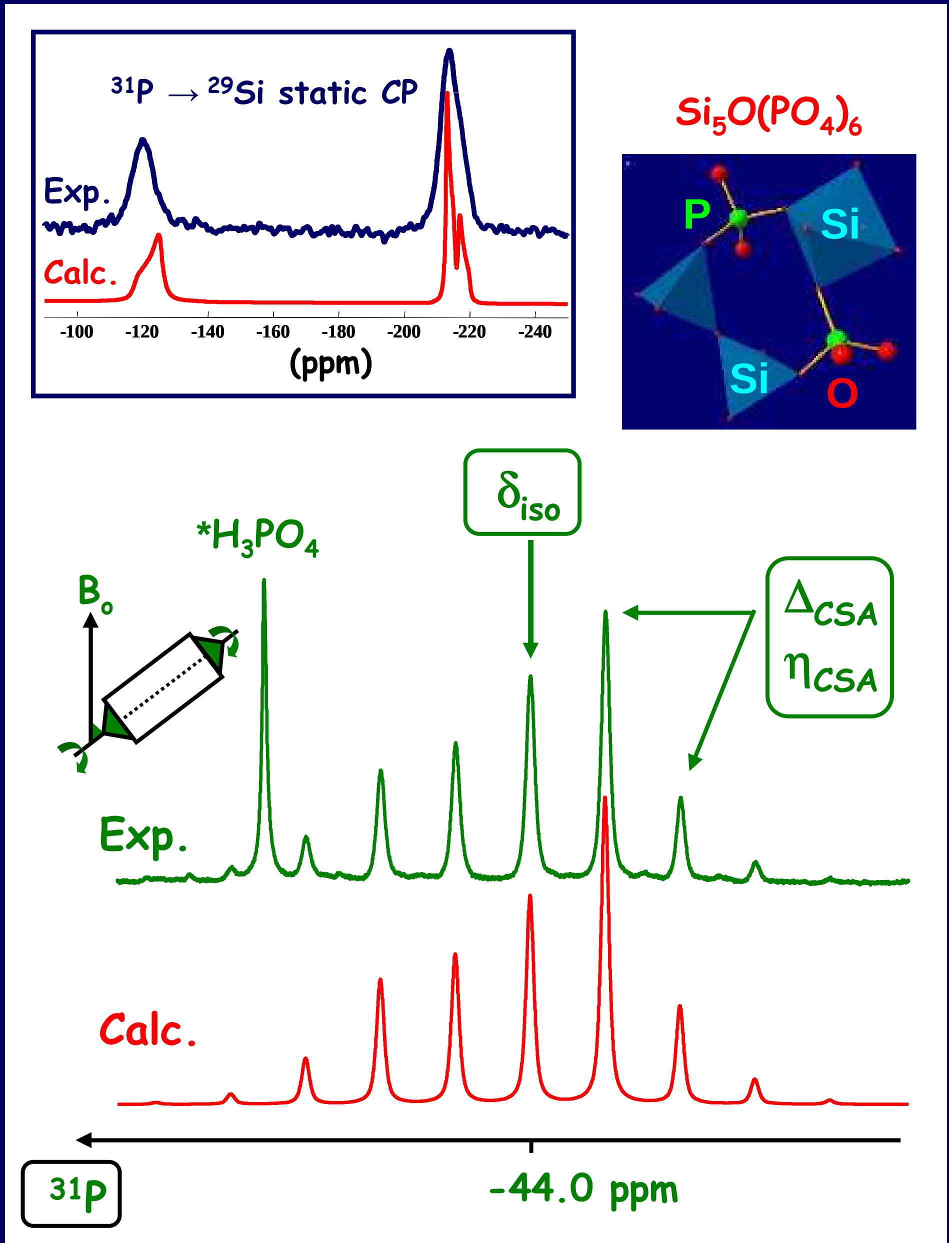


^{29}Si, ^{31}P, ^{17}O

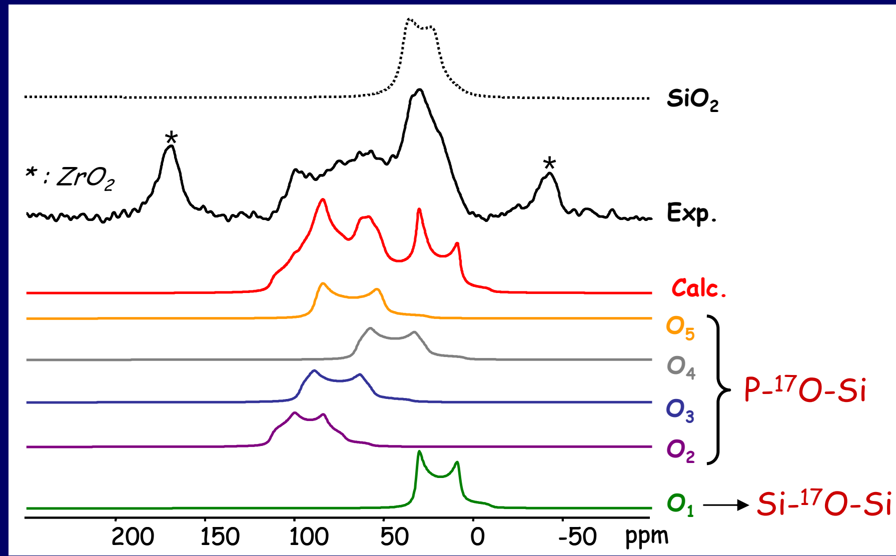
δ, Q

$^2J_{P-O-Si}$, $^2J_{P-O-P}$, $^1J_{P-O}$

^{29}Si, ^{31}P and ^{17}O CSA and Q parameters: $Si_5O(PO_4)_6$ and SiP_2O_7



N.A. ^{17}O MAS experiment



Collab. L. Montagne, G. Tricot,

L. Delevoye, Lille, France

800 MHz spectrometer

Towards first principles calculations of *J* coupling constants

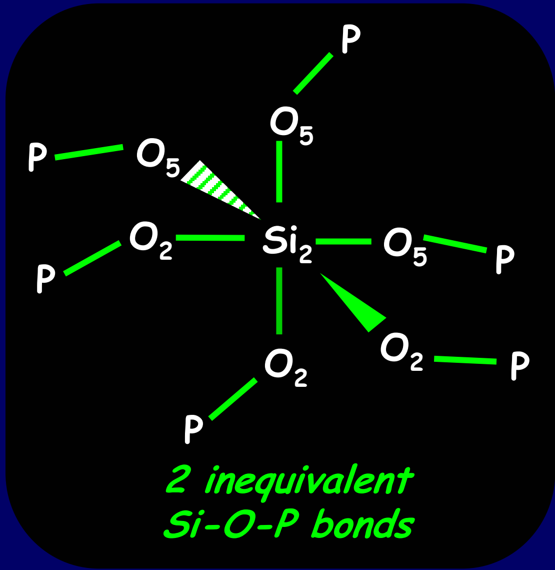
the case study of $Si_5O(PO_4)_6$

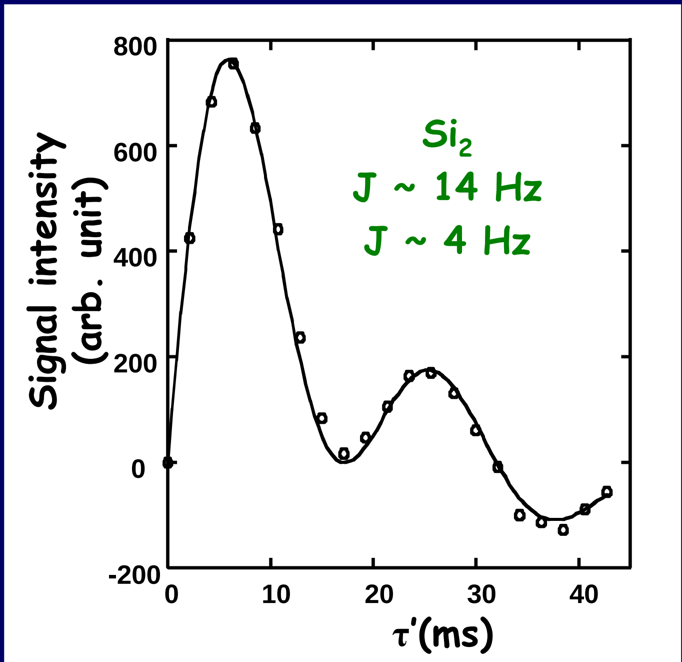
INEPT data: J ~ [4 Hz – 15 Hz]

Coelho *et al.*, *Inorg. Chem.* 46 (2007) 1379.

		$^2J_{P-O-Si}$ (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

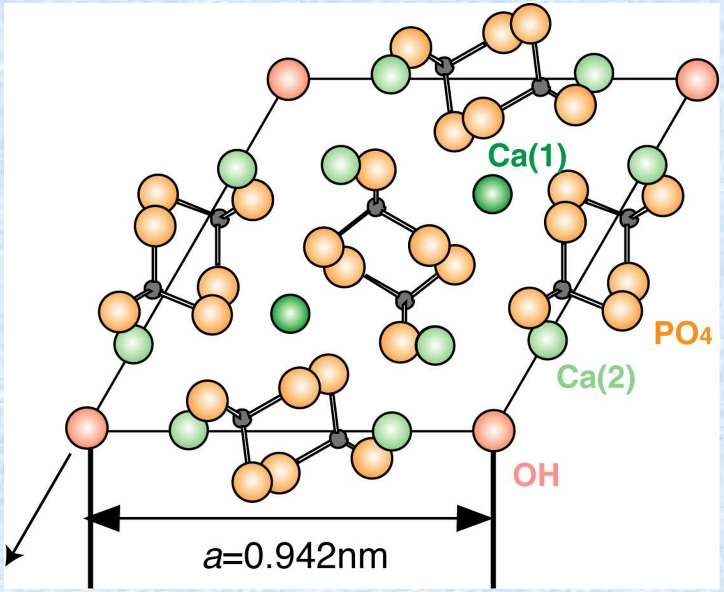
	calc. (Hz)
$^1J_{P-O3}$	61.49
$^1J_{P-O5}$	103.73
...	

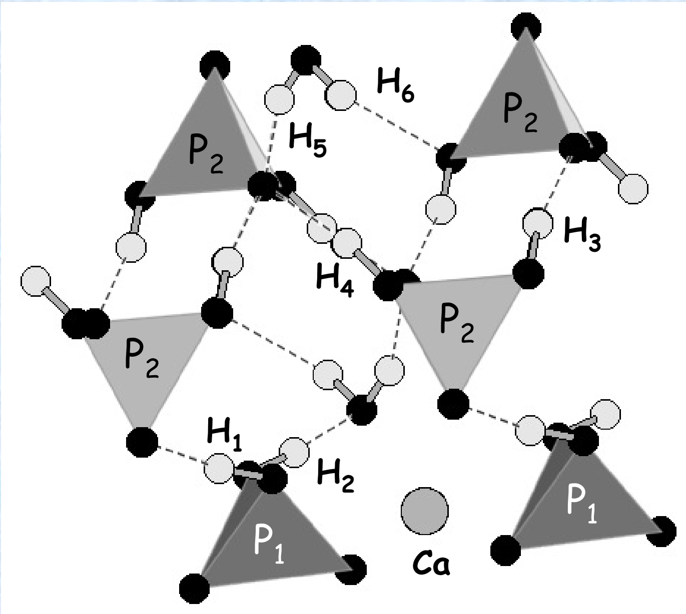




by courtesy of S. Joyce, J. Yates, C. J. Pickard and F. Mauri (http://arxiv.org/abs/0708.3589) and J. Chem. Phys. 2007

♦ Calcium phosphates and HAp structures



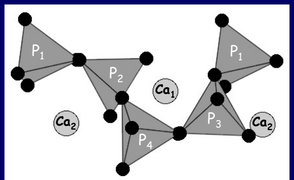


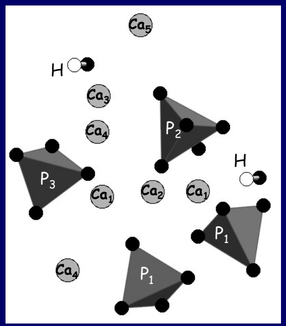
Biocompatible calcium phosphates

Brushite, $CaHPO_4.2H_2O$
MCPM, $Ca(H_2PO_4)_2.H_2O$
β- and γ-$Ca(PO_3)_2$
$Ca_4P_2O_9$

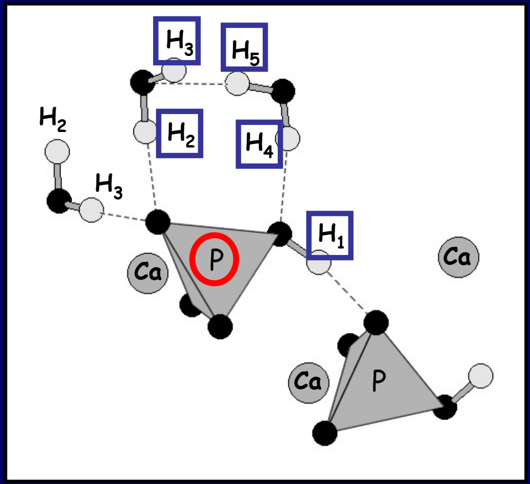
$Ca_{10}(PO_4)_6(OH)_2$ (HAp)
...

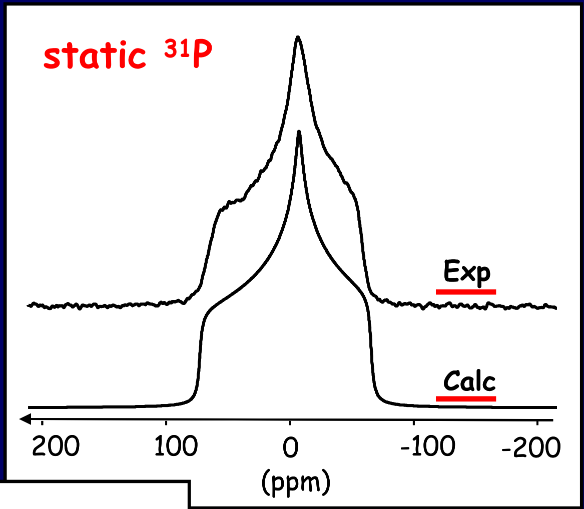
hydrated, dehydrated, and hydroxylated structures

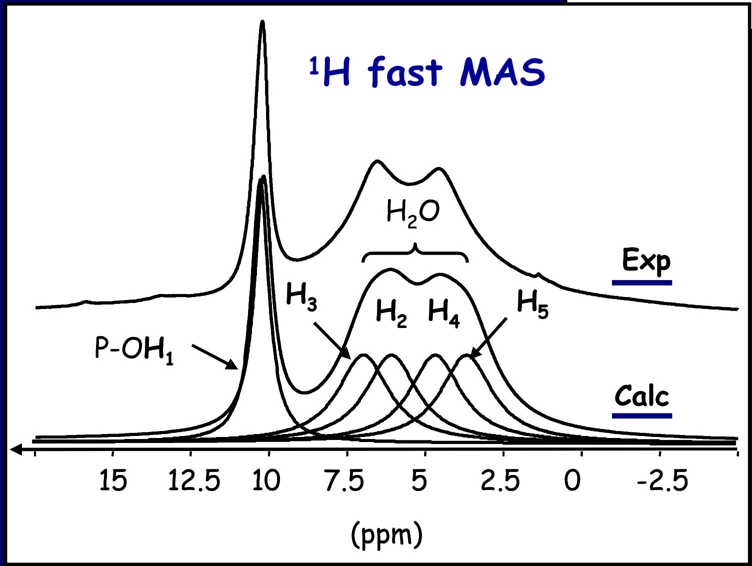




Brushite: the GIPAW approach (^{31}P, ^{1}H)





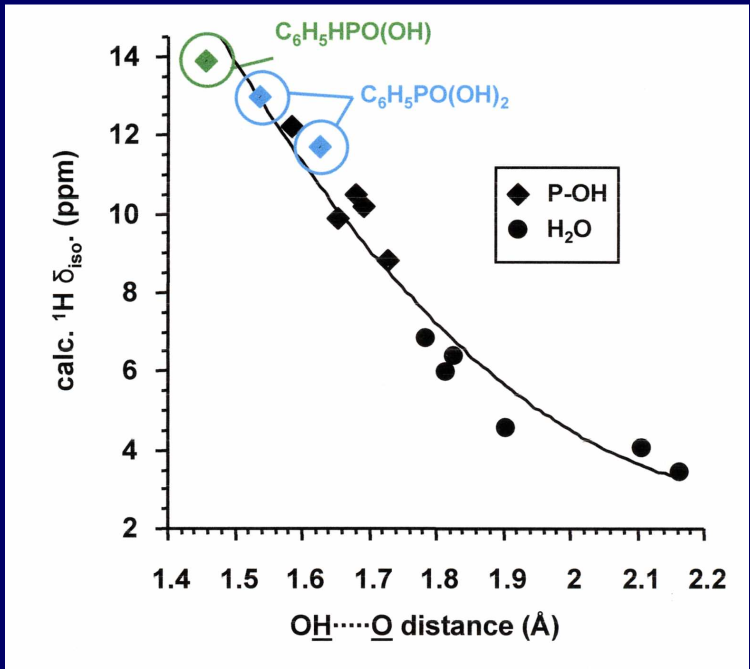


Collab. B. Alonso, D. Massiot, CRMHT, Orléans, France

Pourpoint *et al.*, *Appl. Magn. Reson.* (2008), *in the press*.

More from ^1H GIPAW data: H-bonding and CSA tensors

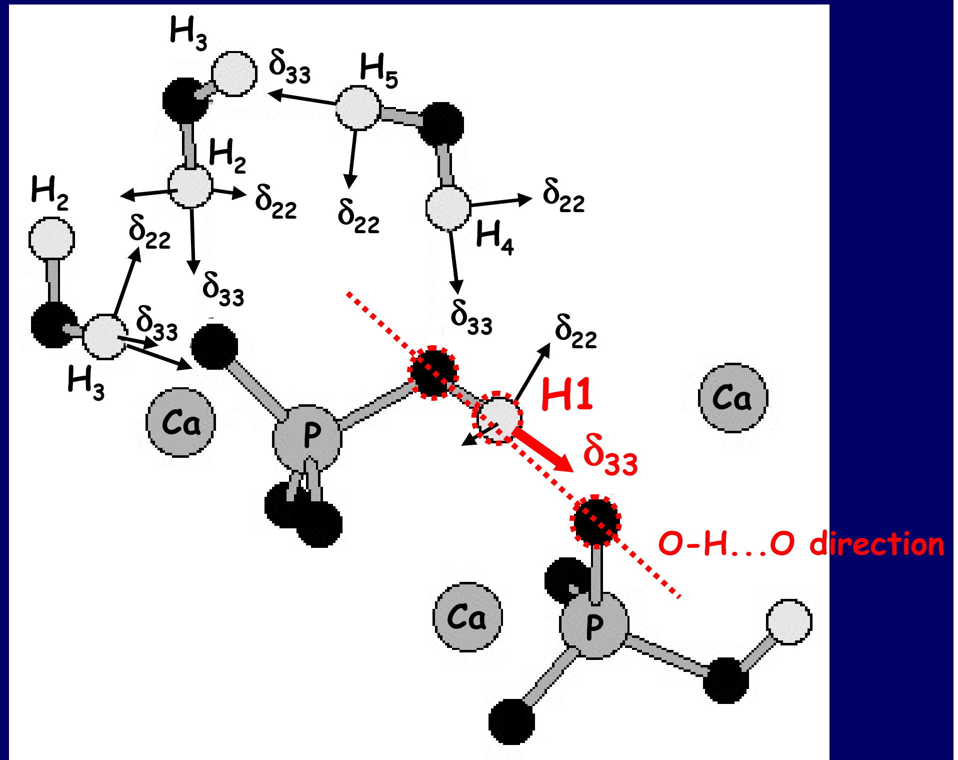
^1H *isotropic* chemical shifts



H-bonding in calcium phosphates
and phosphonic acids

Gervais et al., J. Magn. Reson. 187 (2007) 181.

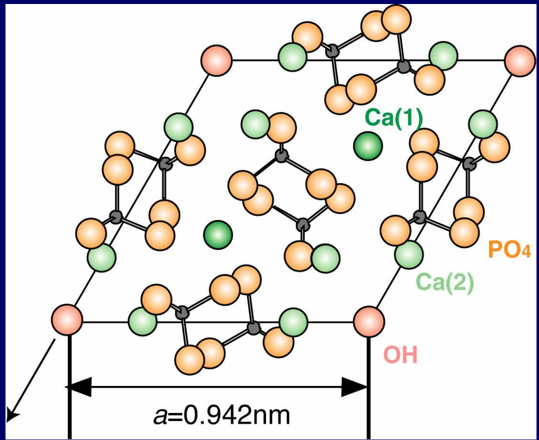
Brushite: $CaHPO_4.2H_2O$



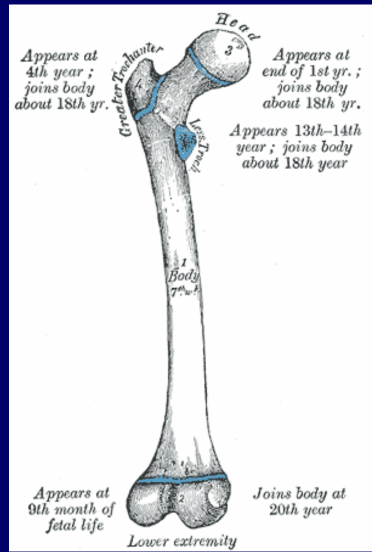
^1H CSA tensors and orientations

Pourpoint *et al., Appl. Magn. Reson.* (2008), *in the press.*

Substituted HAp structures



the fundamental role of substitutions...



$Ca_{10}(PO_4)_6(OH)_2$

Mg^{2+}, Zn^{2+}, Na^{+}, K^{+} ...

SO_4^{2-}, CO_3^{2-}...

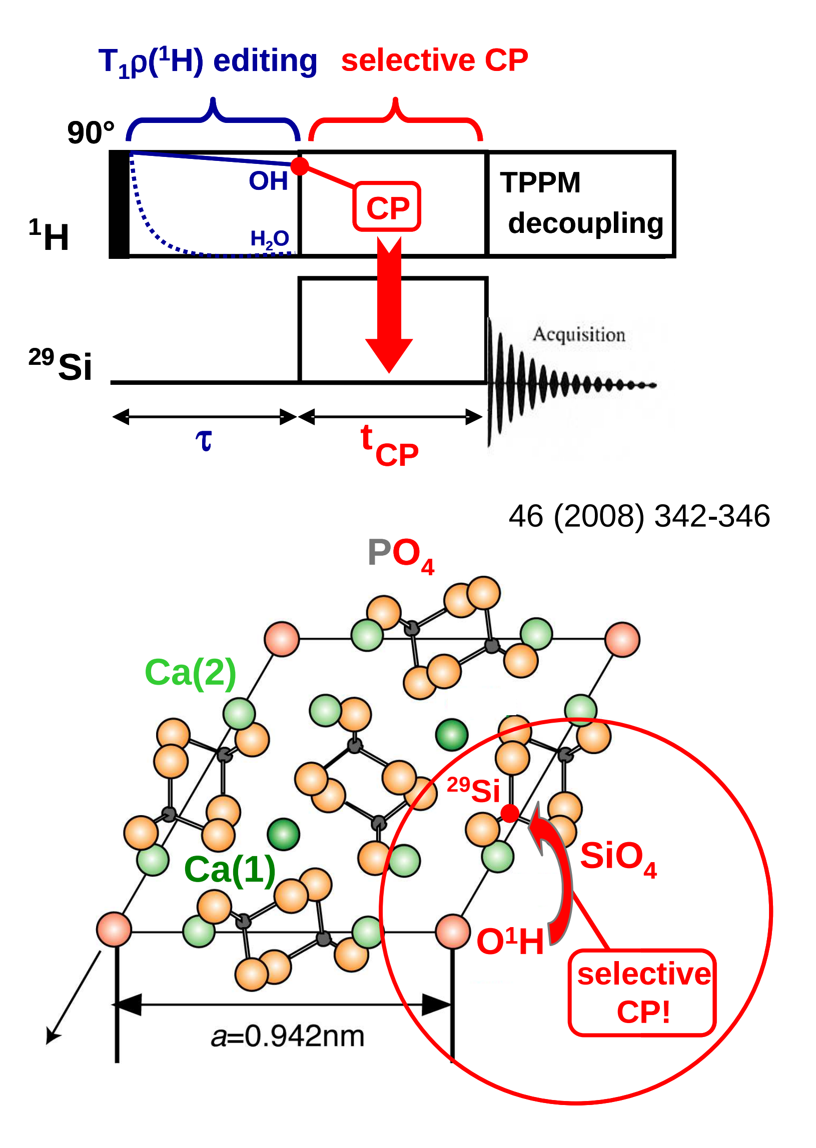
CO_3^{2-}, F^{-}, Cl^{-}...

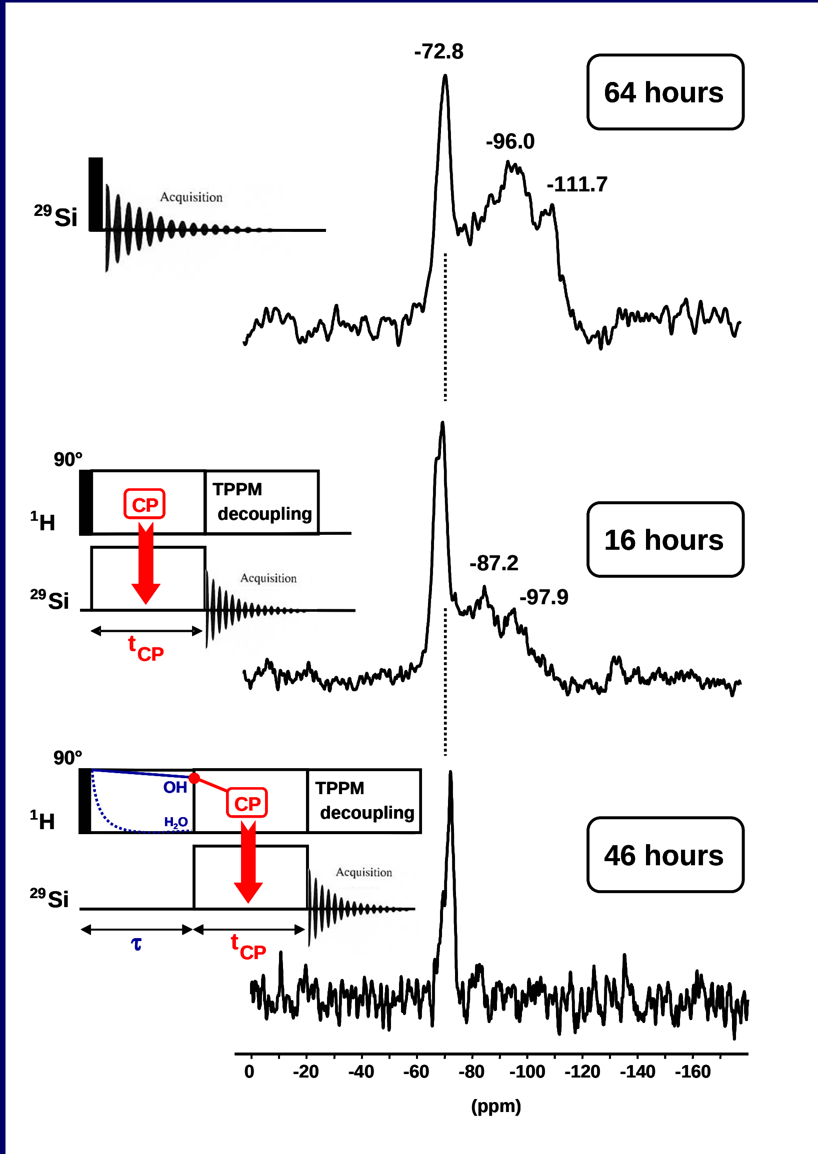
$Ca_{10}(PO_4)_6(OH)_2$

B A

SiO_4^{4-} or CO_3^{2-}

Silicate substituted HAp

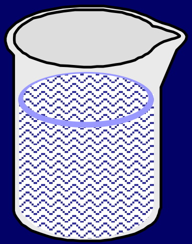




Gasquères et al., Magn. Reson. Chem., 46 (2008), 342-346.

Si: 4.6 wt %

Carbonated HAp



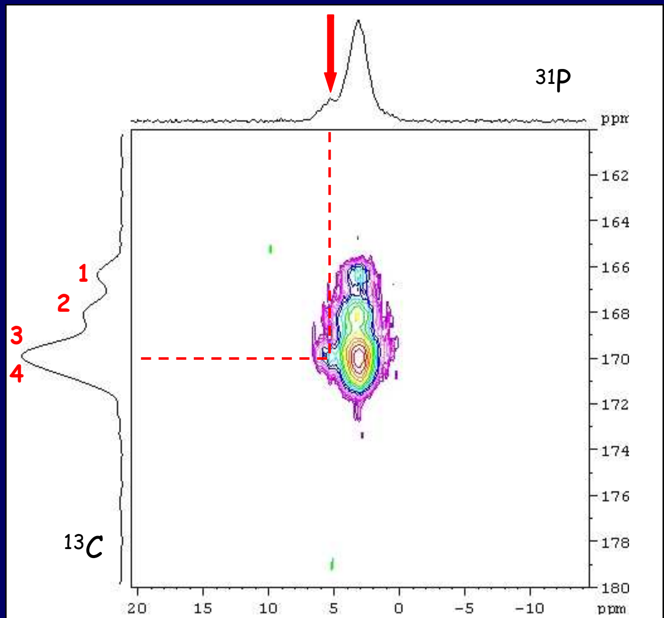
- pH = 10
- 0.3 M $(NH_4)_2HPO_4$
- 0.15 M $NaH^{13}CO_3$

^{13}C: 99 %

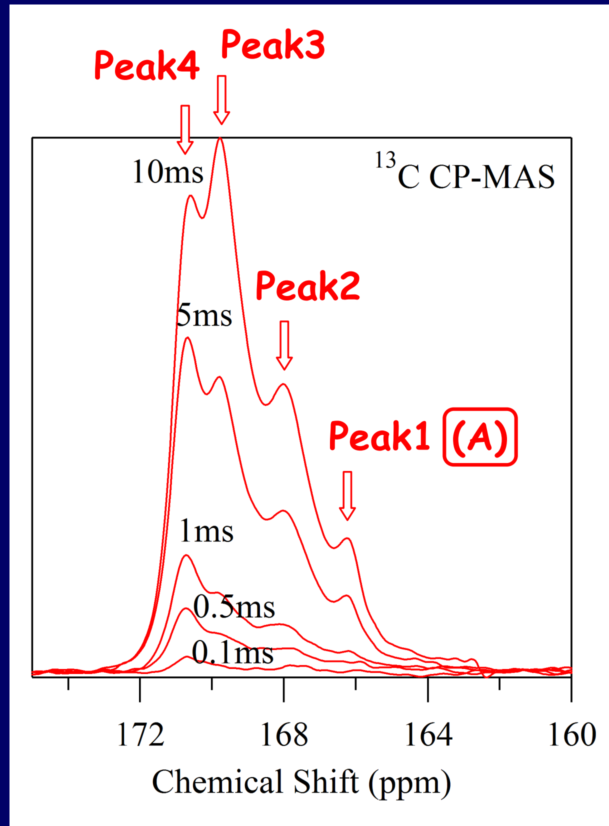
4.8 wt %

N_2

- 0.3 M $Ca(NO_3)_2.4H_2O$



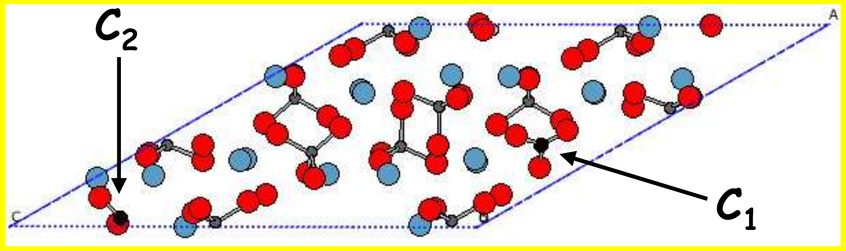
$^1H \rightarrow {}^{13}C \rightarrow {}^{31}P$ triple resonance exp. (CP MAS)



$^1H \rightarrow {}^{13}C$ CP MAS dynamics

distribution of carbonated sites...

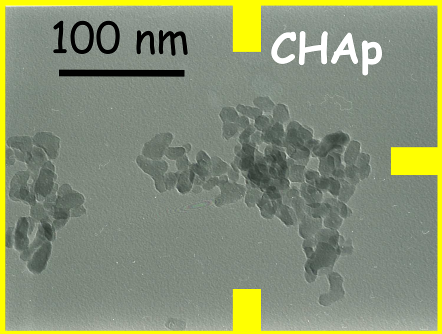
DFT models, 2D NMR, *ab initio* calculations: a combined approach

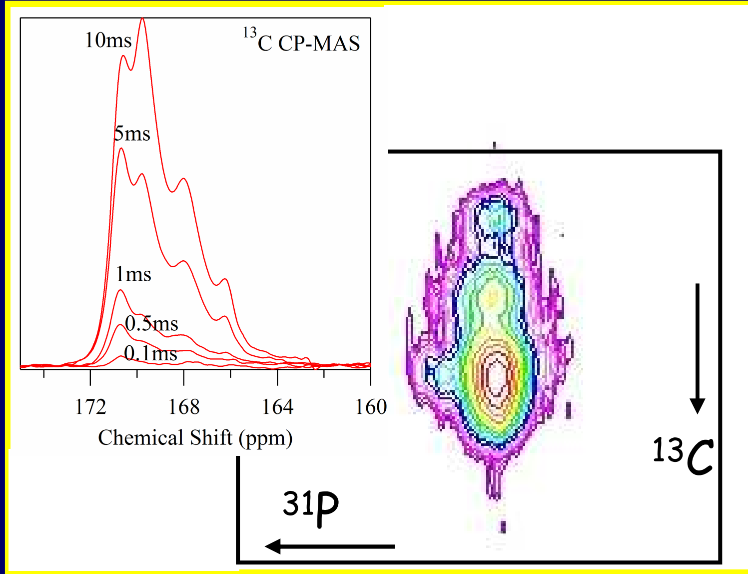


Astala *et al.*, *Chem. Mater.* 2005

Peroos *et al.*, *Biomat.* 2006

■ DFT models





■ 1D, 2D NMR experiments

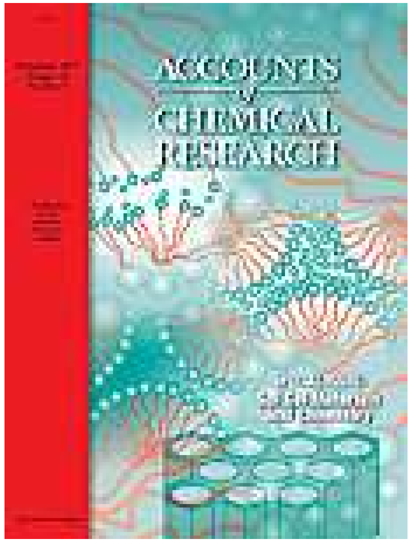
	δ (ppm)		δ (ppm)		δ (ppm)
P1	2.1	P7	1.9	C1	166.7
P2	0.1	P8	2.1	C2	165.7
P3	2.1	P9	1.8	H1	1.1
P4	3.3	P10	4.0	H2	1.1
P5	1.1	P11	3.3	H3	-0.7
P6	1.5				

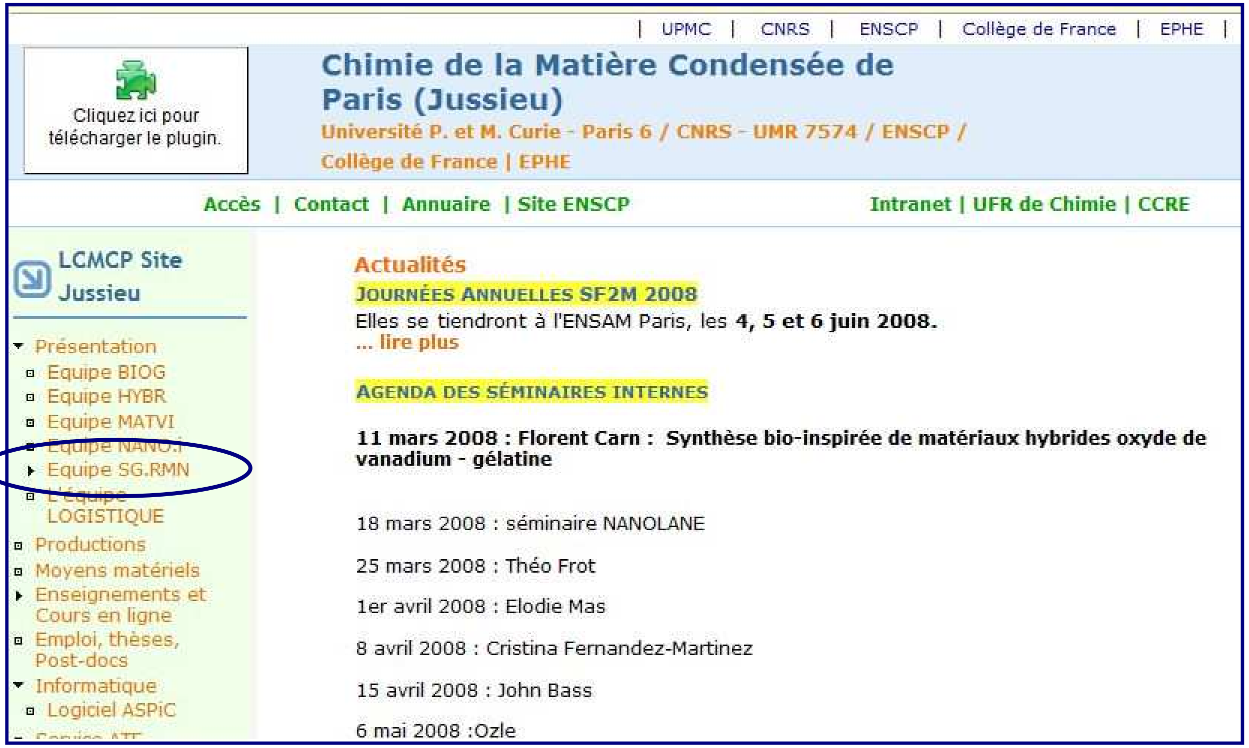
■ first principles calculations

distribution of A-, B- and A/B sites...

Further reading

Advanced solid state NMR techniques for the characterization of sol-gel-derived materials
Bonhomme C., Coelho C., Baccile N., Gervais C., Azaïs T., Babonneau F.
Acc. Chem. Res., Vol. 40, 2007, pp. 738-746





http://www.labos.upmc.fr/lcmcp/newsite/

Equipe "Matériaux Sol-Gel et RMN"