Verres et vitrocéramiques de phosphates

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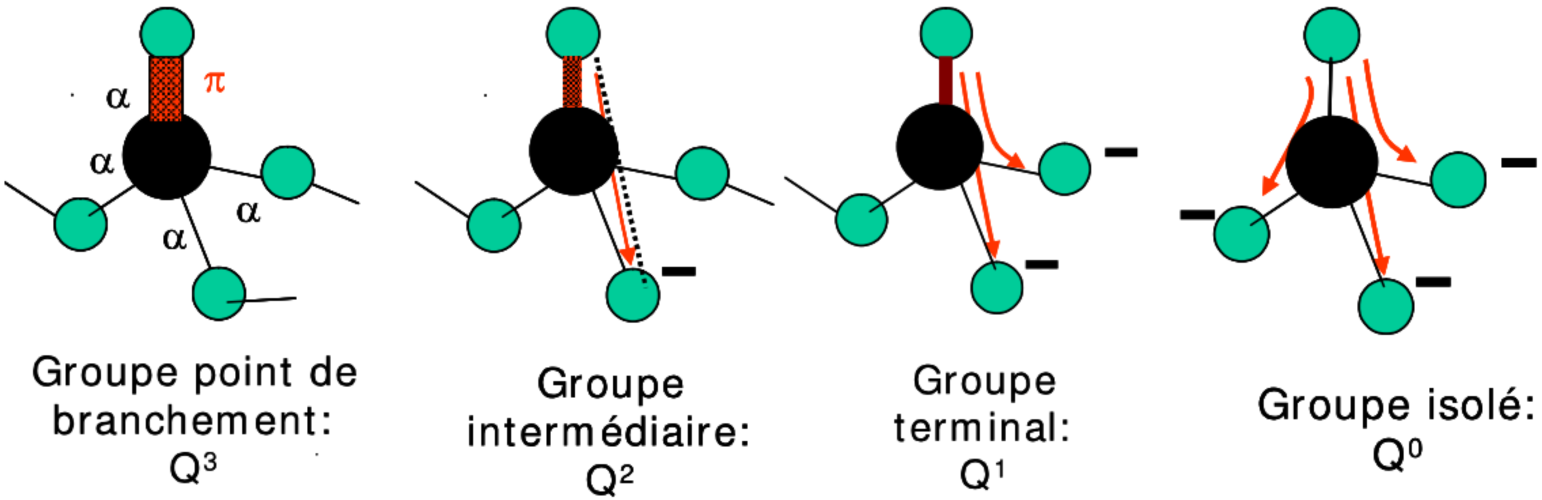
Equipe Verres et RMN
Université de Lille

- Verres de phosphates ?
- Applications des verres et vitrocéramiques de phosphates : bilbiographie (et contributions de l’UCCS)
  - Verres pour l’optique
  - Verres de confinement de déchets nucléaires
  - Verres pour applications biologiques

Verres de phosphates: caractéristiques structurales

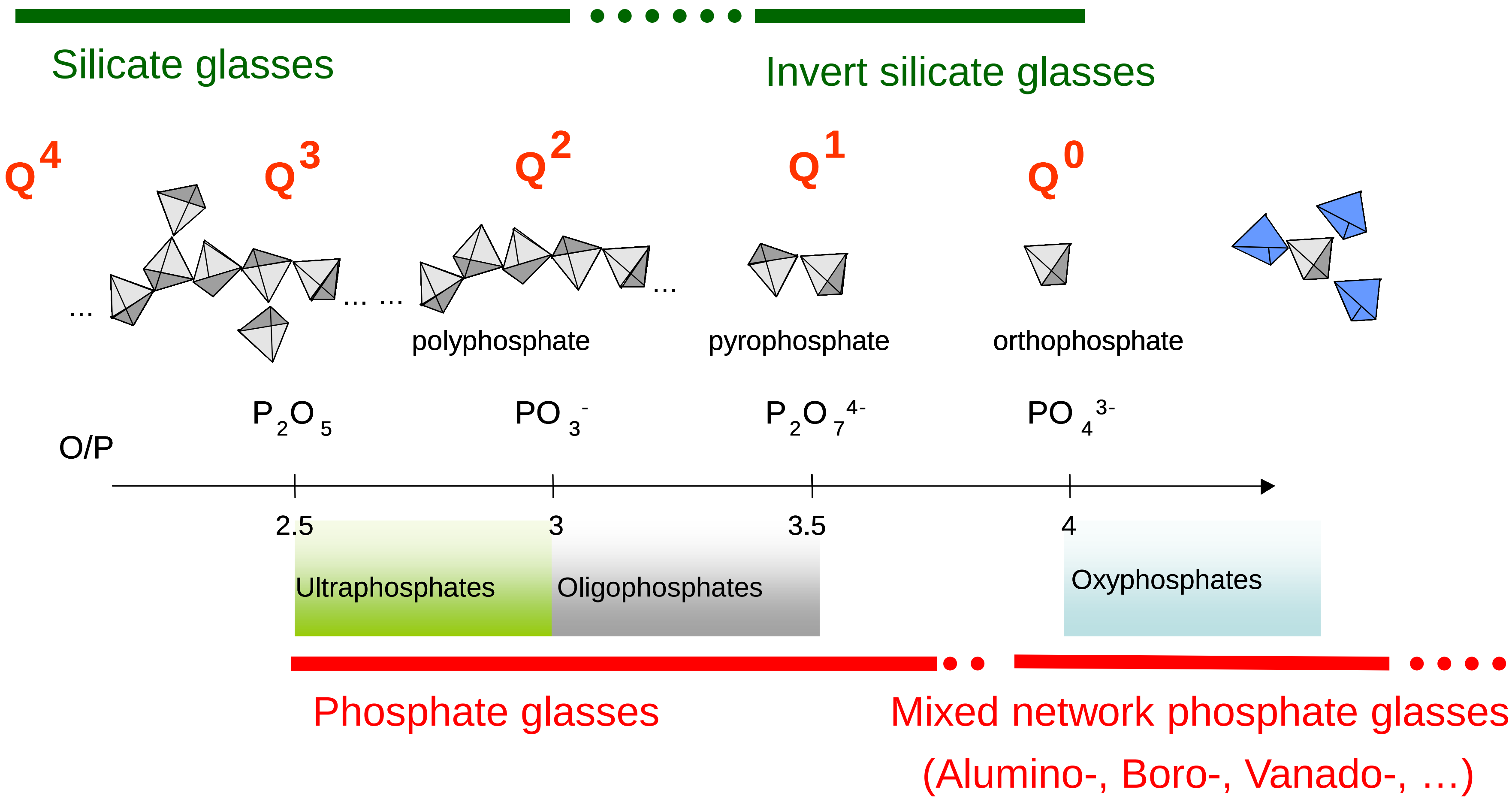
- P [Ne] $3s^2\ 3p^3$ => hydridation sp^3
- P^{5+}, Si^{4+}, B^{3+}
- Coordinence tétraèdrique : présence d'électrons π
- P=O d=0,145nm, P-O-P d=0,15 à 0,16 nm
- Délocalisation des électron π
- Conséquence structurale :
  - silicates : Q^0 à Q^4, phosphates Q^0 à Q^3
  - P^{5+} très peu compatible avec Si^{4+}, mais très compatible avec Al^{3+} ou B^{3+}

=> Verres de phosphates « à réseaux mixtes »



Videau, Le Flem (2010)

Phosphate glasses: compositions



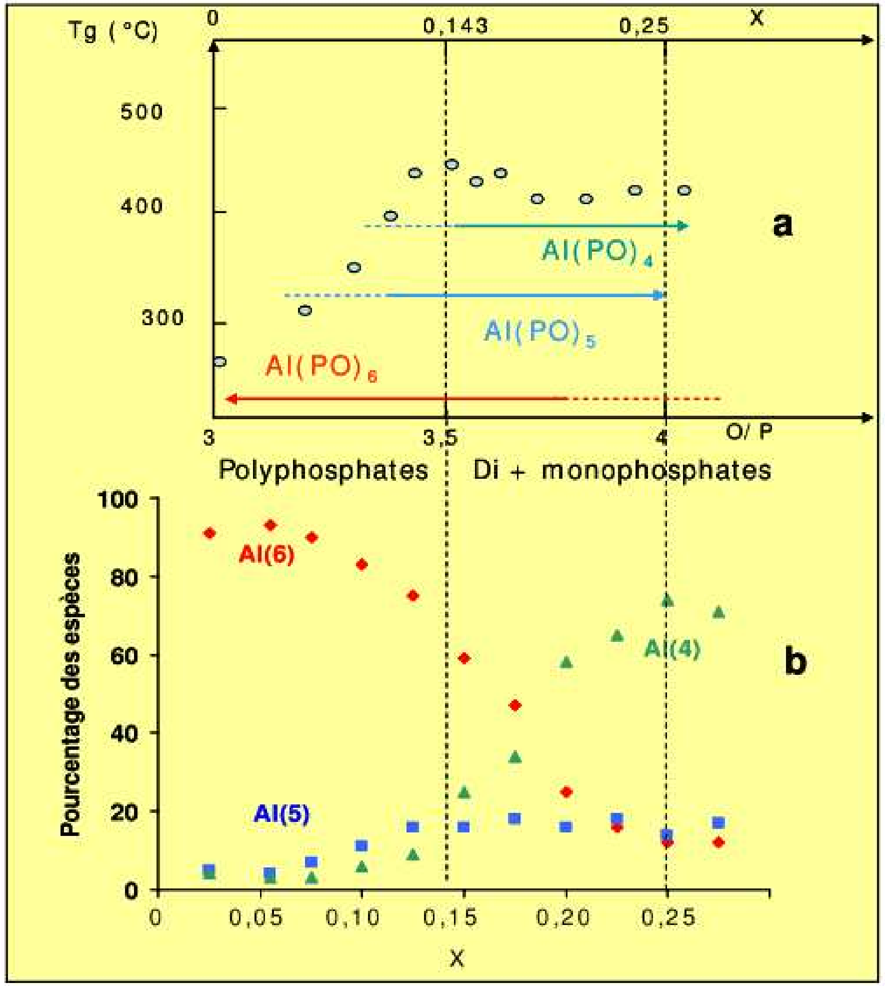
Conséquences sur les propriétés

- Q^0 à Q^3 => Réseau moins polymérisé que silicates
- Liaisons P-O-M labiles
  - => Tg basse
    - Valeur typique 300 à 400°C
  - => Coefficients de dilatation élevés (10 à $25.10^{-6}K^{-1}$)
  - => faible durabilité chimique

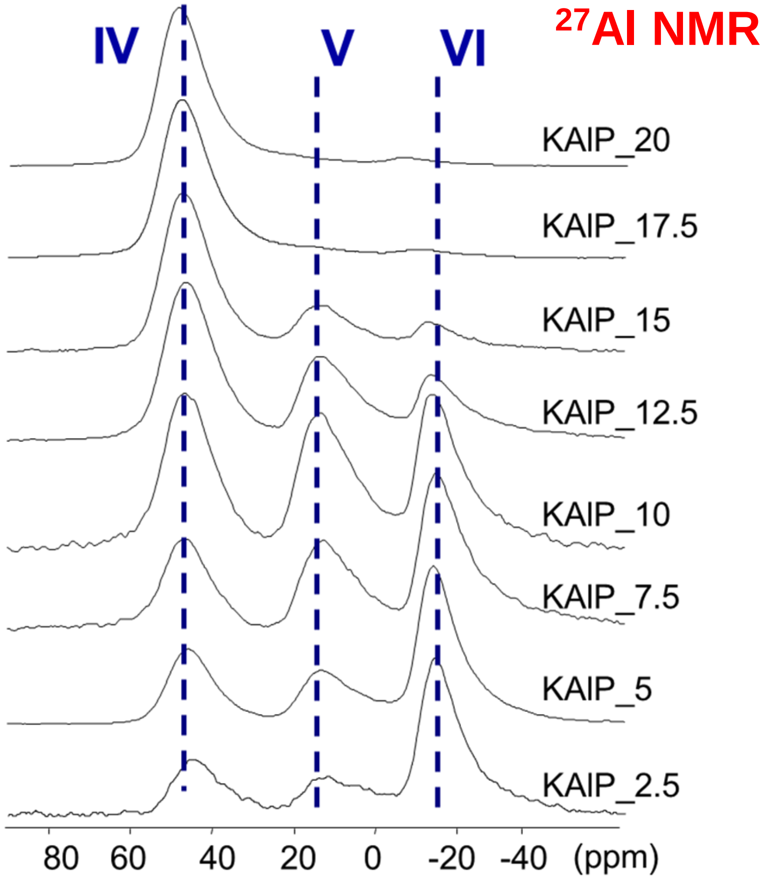
Verres de phosphates: caractéristiques chimiques

- Conséquence chimique : z/a^2 très élevé, donc oxyde très acide
  - P : $2{,}16.10^{20}$ m^{-2}
  - Si: $1{,}54.10^{20}$ m^{-2}
  - B: $1{,}39.10^{20}$ m^{-2}
  - $P_2O_5 + O^{2-} \Leftrightarrow 2PO_3^-$
  - Très fort pouvoir dissociant (perles de fluoX)
  - Accepte quasiment tous les oxydes, en grande quantité : zones de vitrifications très étendues (verres à réseaux mixtes)
  - Verres « réducteurs » (cas du Cr uniquement en Cr^{3+})

Verres à réseau mixte: aluminophosphates

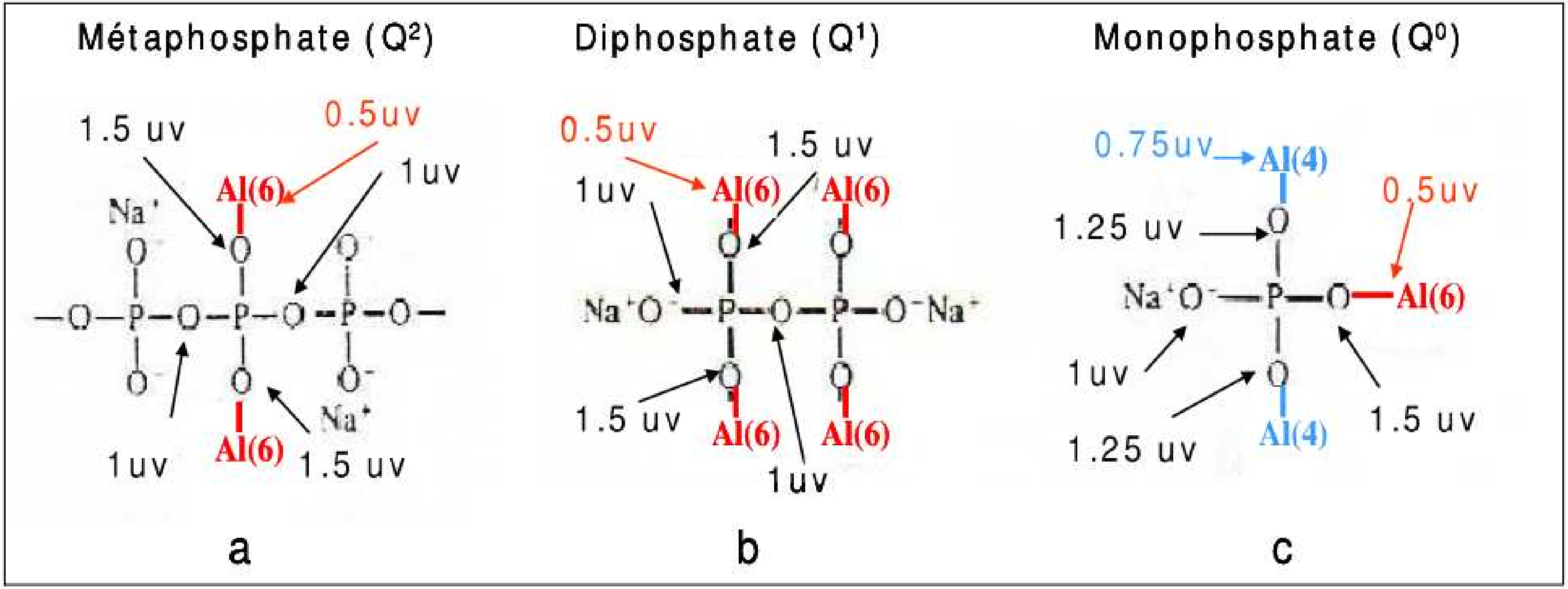


Brow JNCS (1990)



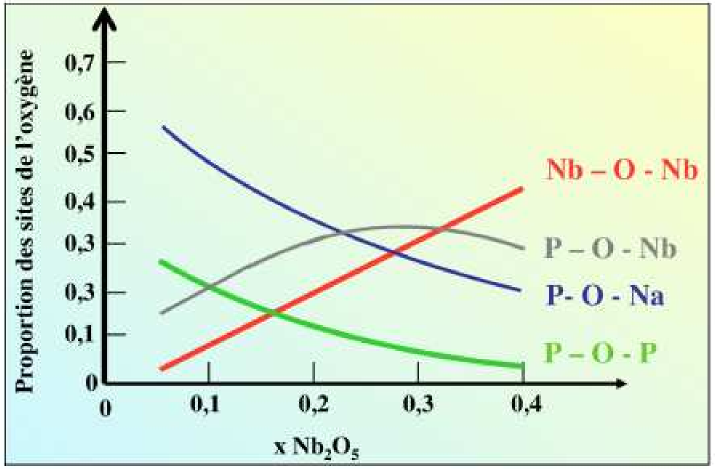
Van Wullen ss-nmr (2007)

Al(4) modificateur et Al(6) formateur ?

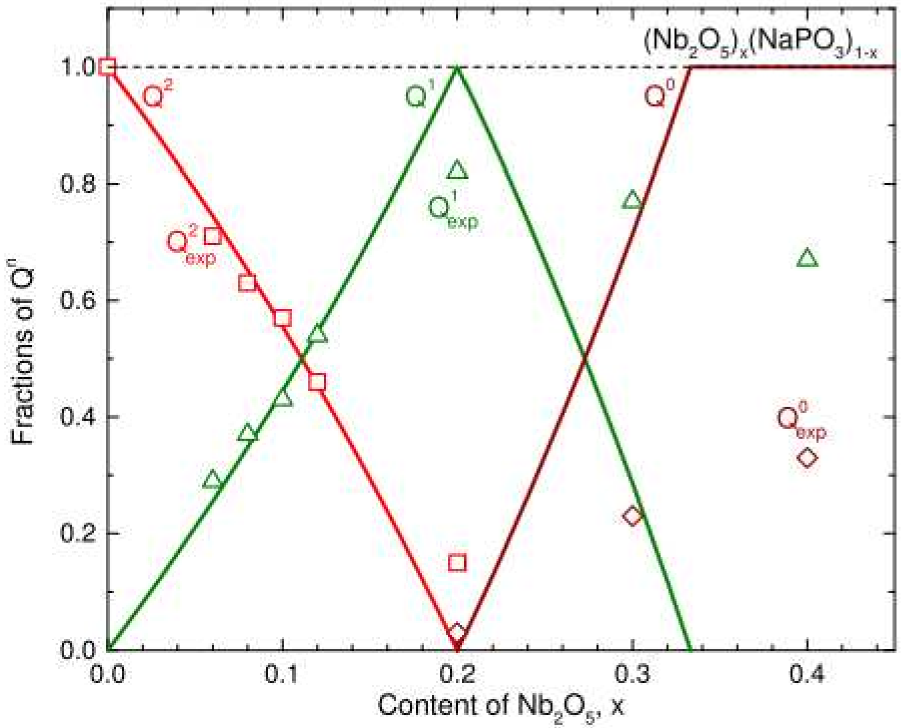


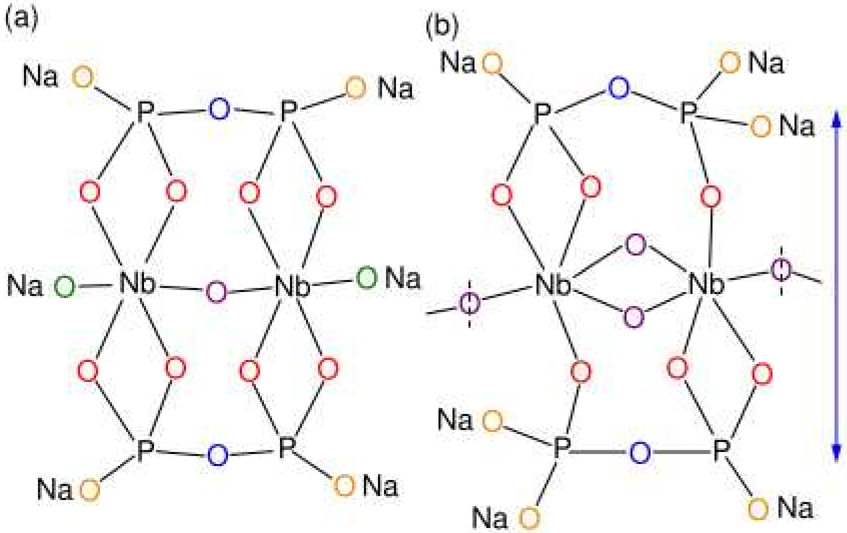
UCCS

Les niobiophosphates



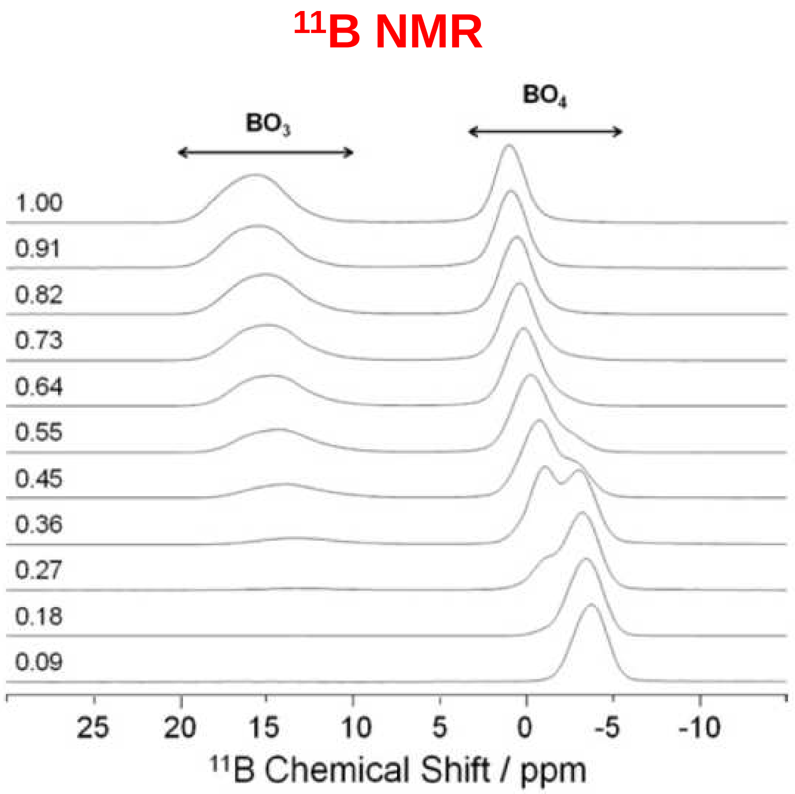
Flambard JNCS (2008)



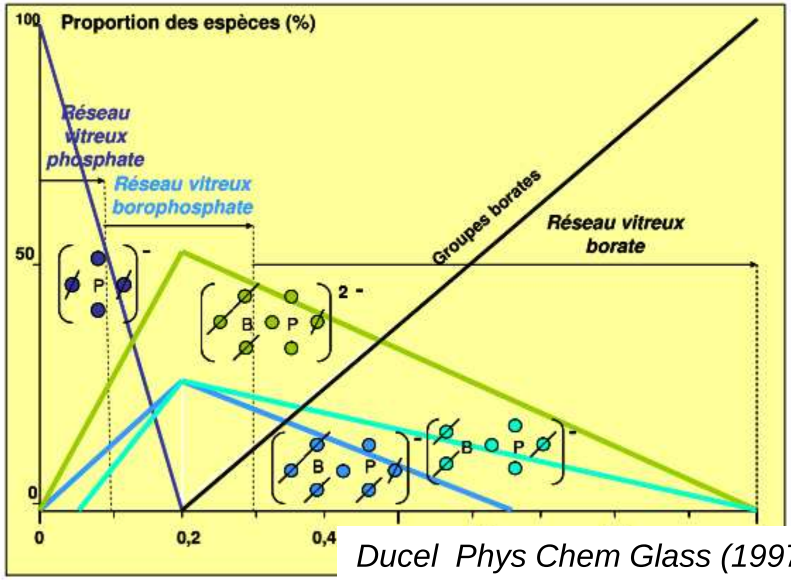


Hoppe PCCP (submitted)

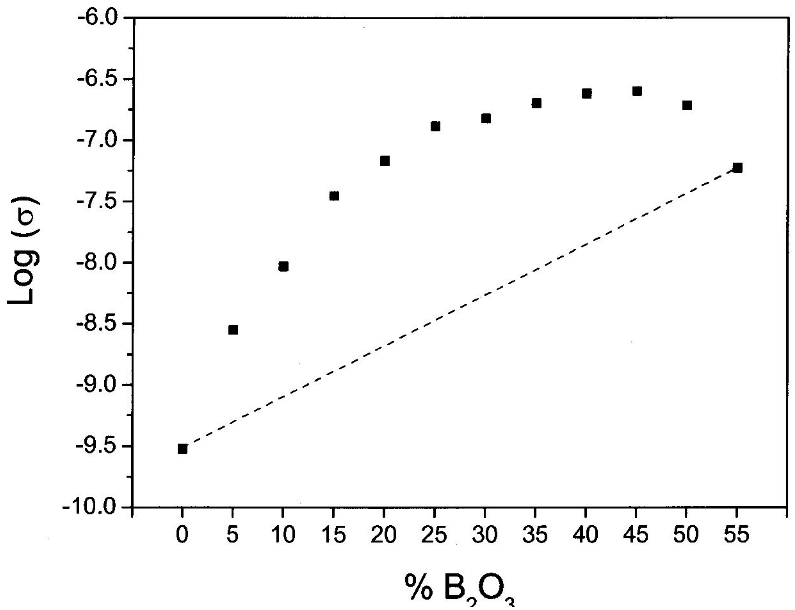
Les borophosphates



Raguenet SSI (2012)



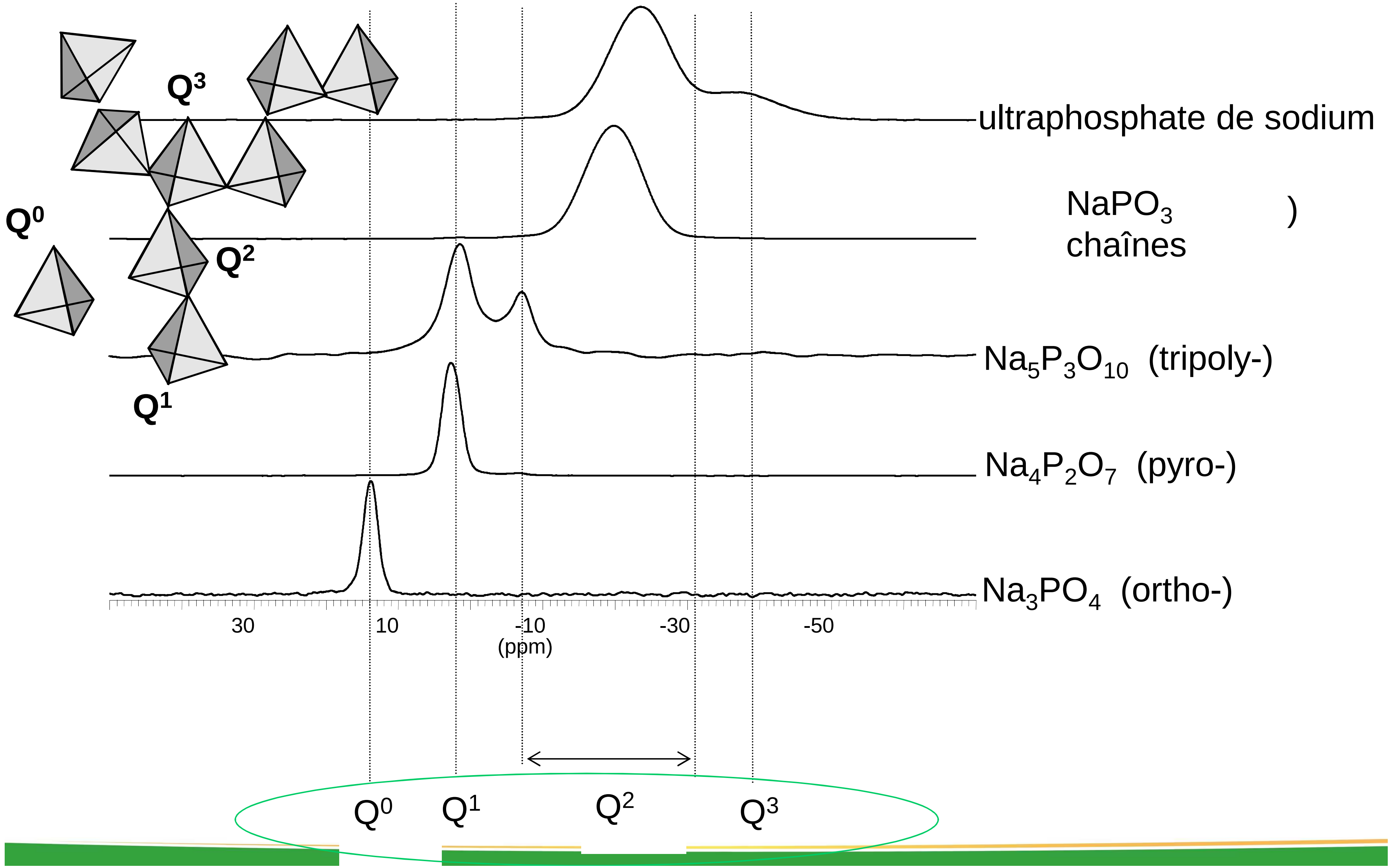
Ducel Phys Chem Glass (1997)



Et aussi…

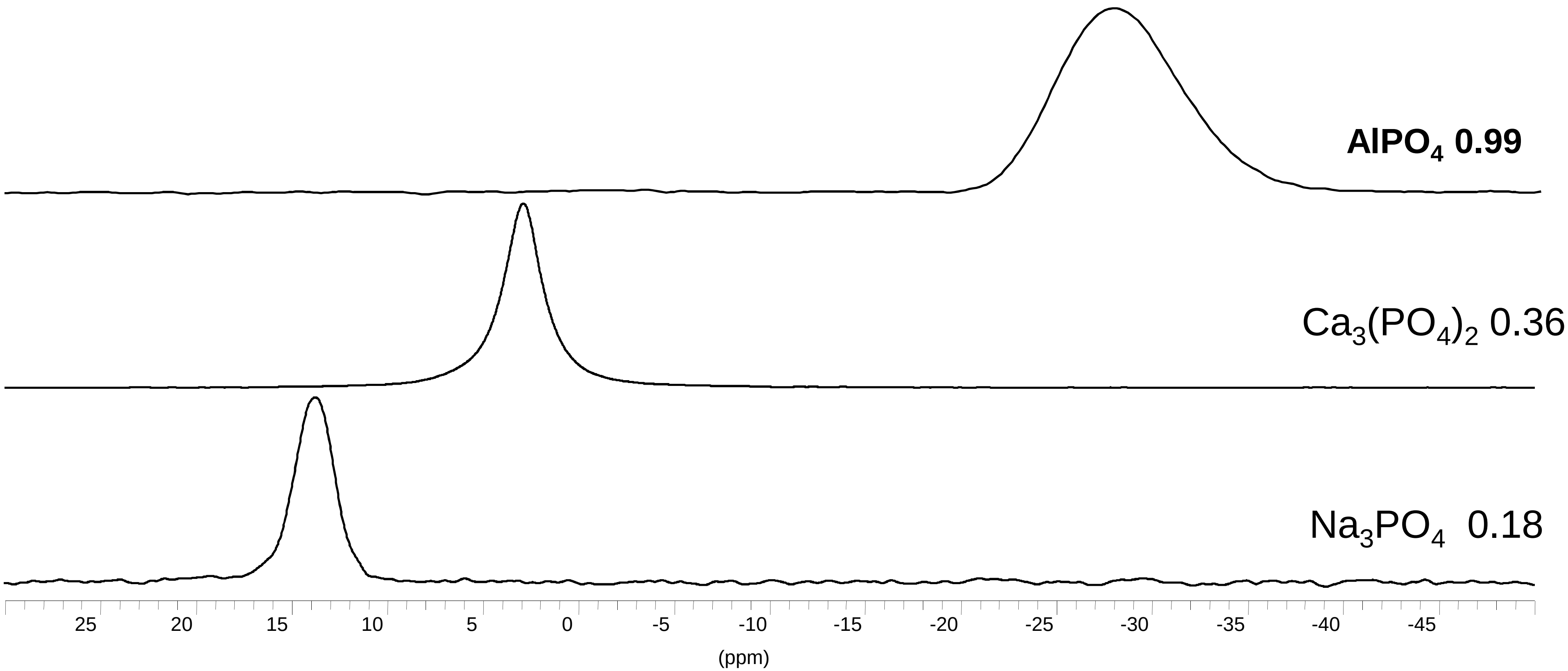
- Les vanadophosphates (Tricot 2011)
- Les phosphates de Zinc ? Ex: verre $2ZnO$-P_2O_5
- Les silicophosphates ?
  - Si(VI) modificateur (si faible qq de SiO_2 dans un verre de phosphate)
  - Incompatibilité due à l'instabilité de la liaison P-O-Si
  - Séparations de phase, ségrégation des cations autour des phosphates
  - Compatibilité si présence de Al_2O_3 et/ou B_2O_3
    - Connexions via P-O-Al ou P-O-B

^{31}P NMR: Q^n sites



^{31}P NMR: second neighbors

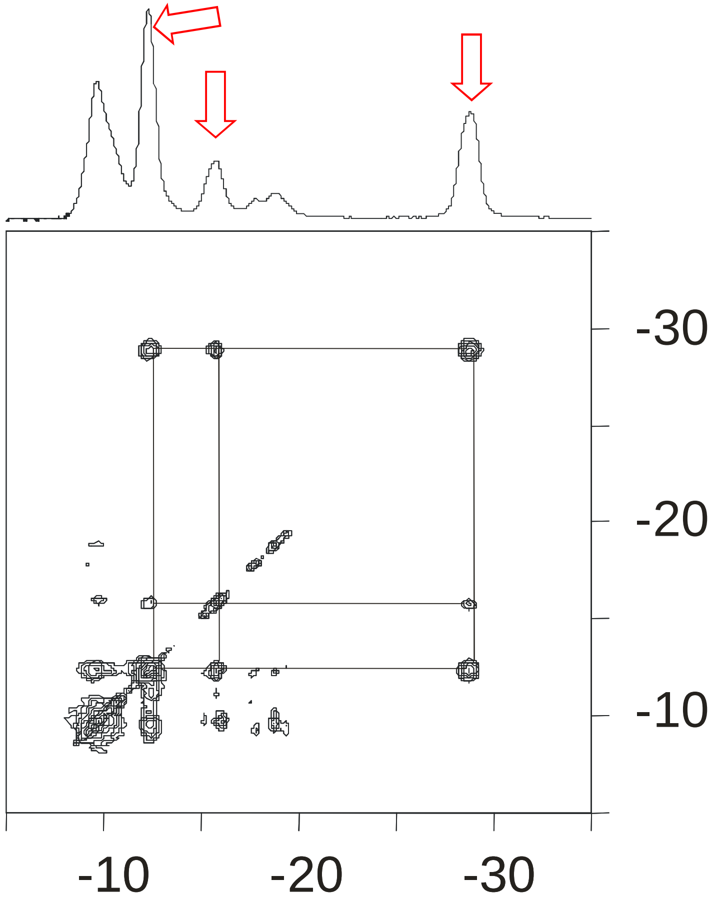
Q^n sites: chemical shifts depends on efs (z/a^2)



2D homo-nuclear connectivity (^{31}P/ ^{31}P)

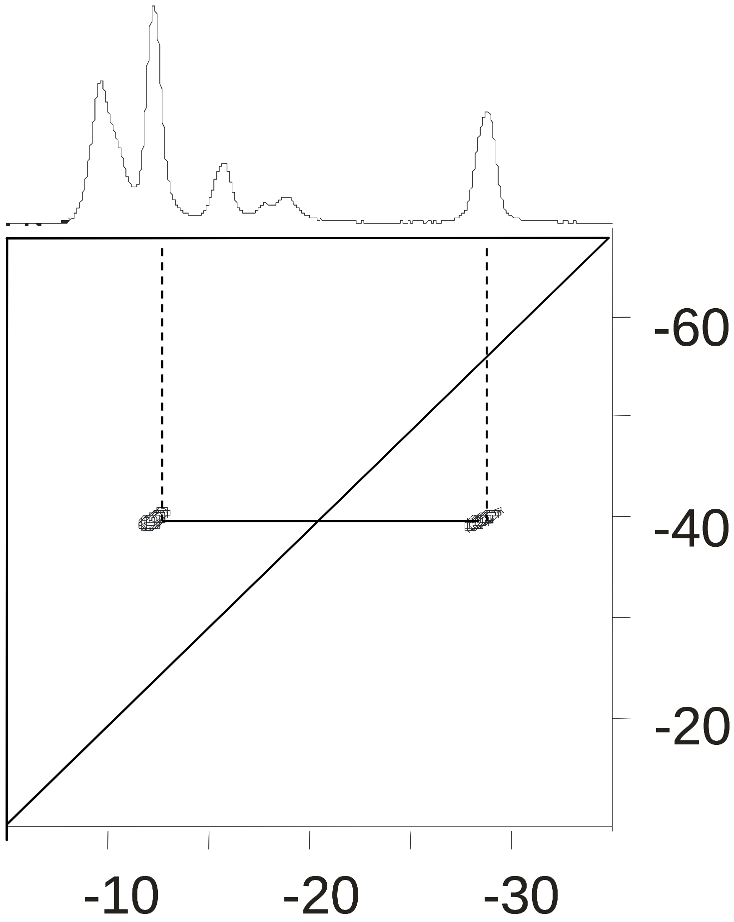
Devitrified Na_2O-Al_2O_3-P_2O_5 glass

- Through space (RFDR)



- 4 phases
- 1 of the phases, « Y » contains 3 sites

- Through bonds (INADEQUATE)

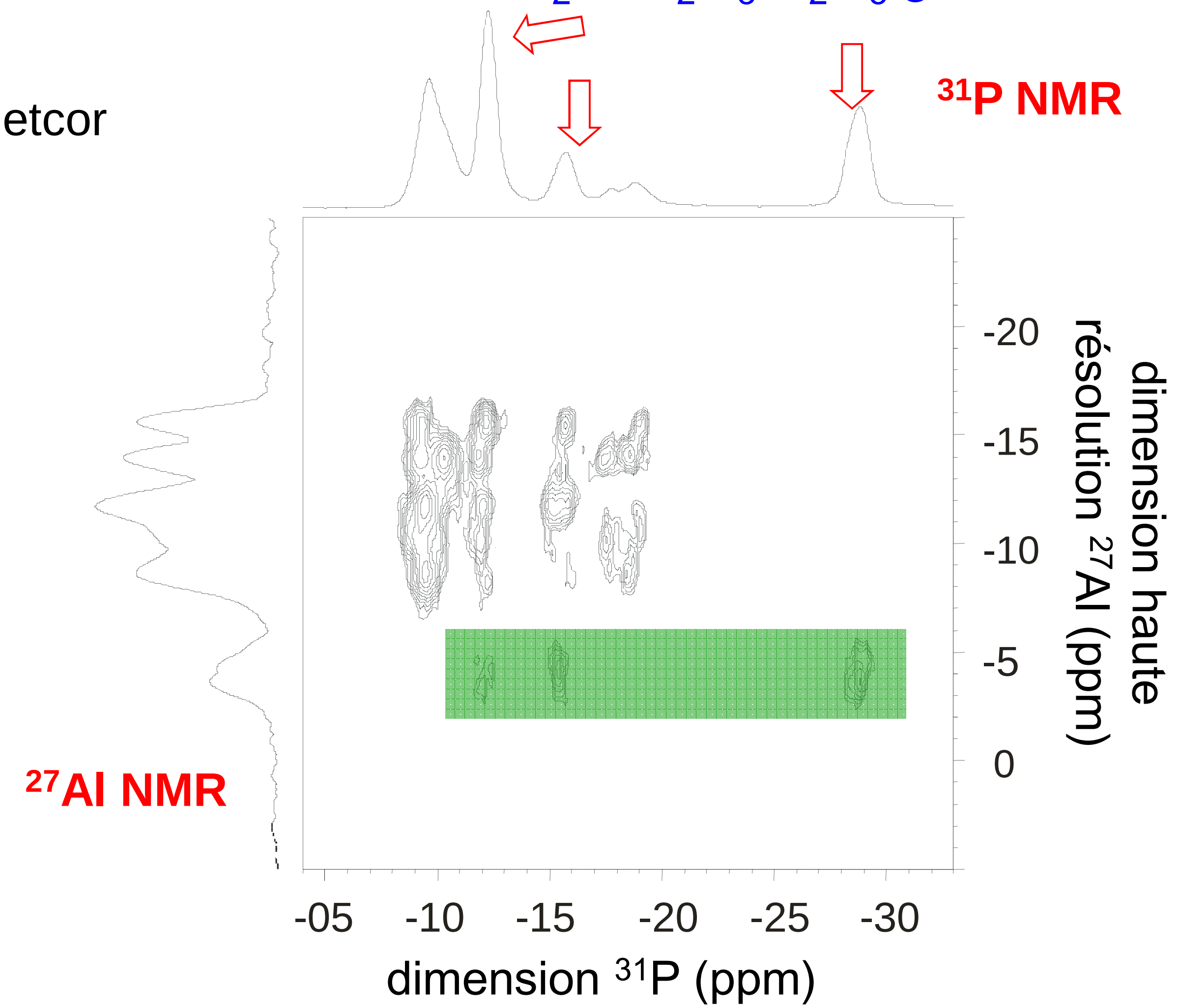


- This « Y »phase contains P-O-P

2D hetero-nuclear connectivity (^{31}P/ ^{27}Al)

Devitrified Na_2O-Al_2O_3-P_2O_5 glass

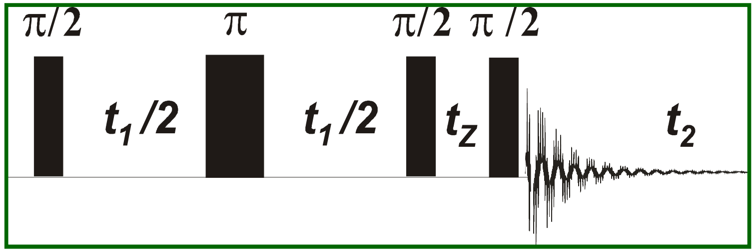
MQ-CP-Hetcor



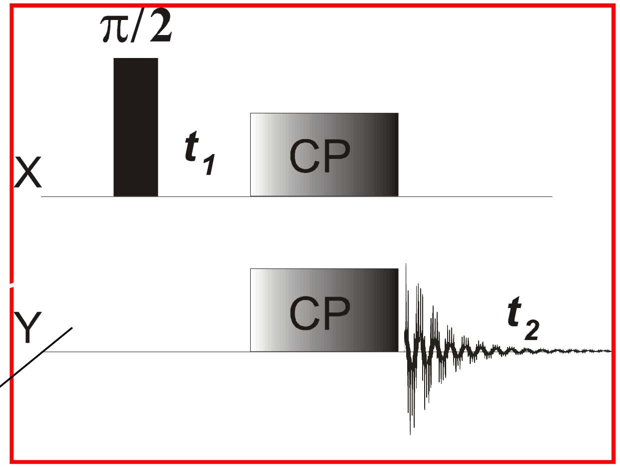
⇒ Several aluminophosphate phases

⇒The phase « Y » contains P-O-Al bonds

2D NMR « strategy »



^{31}P J-RESolved

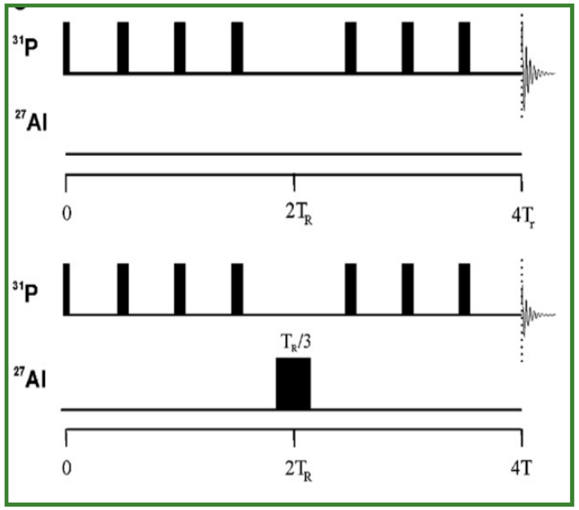


^{31}P {^{27}Al} CP-HETCOR

(c)

(a)

$$Q^{n}_{m,\ AlOx}$$



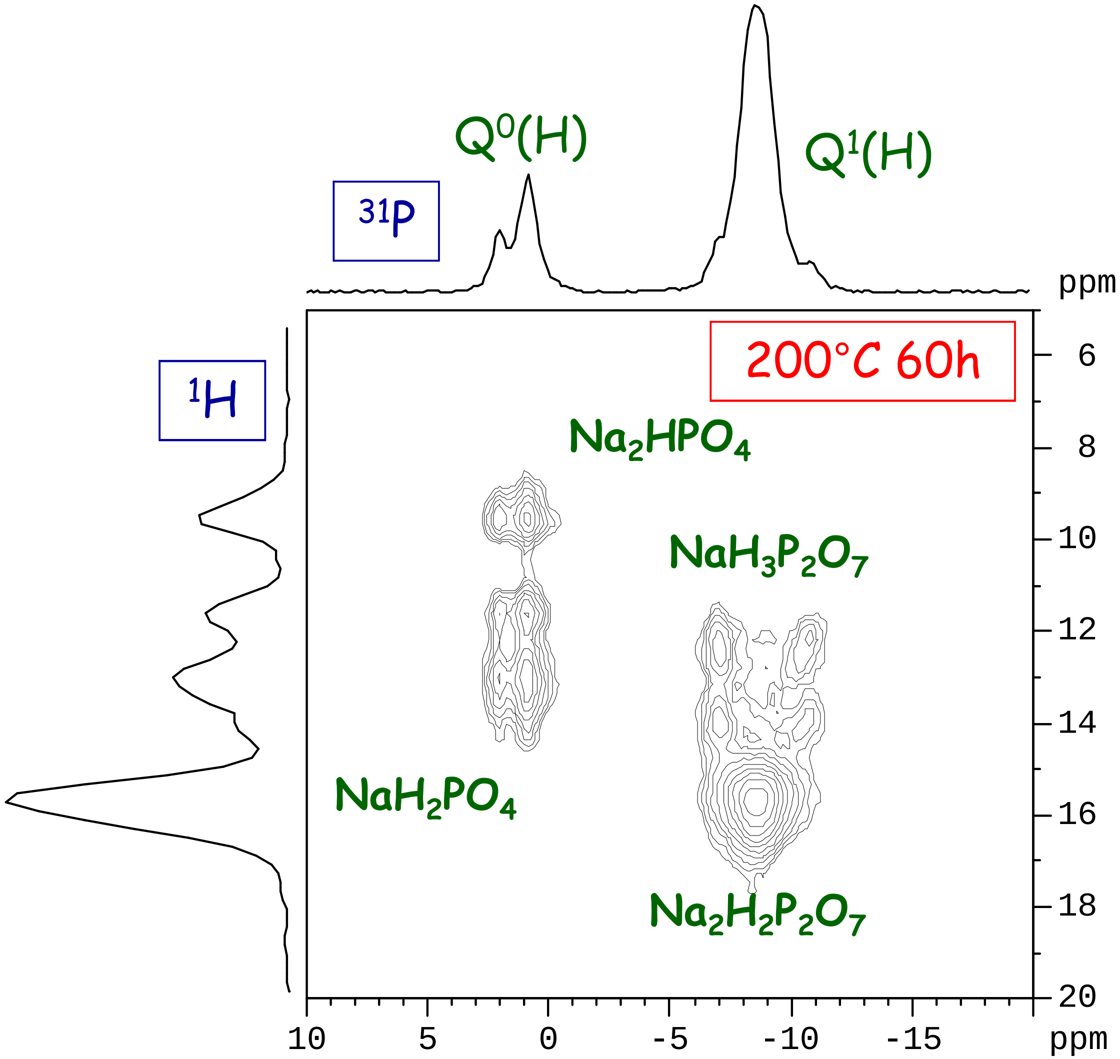
^{31}P {^{27}Al} REAPDOR

(b)

KAlP_10

2D hetero-nuclear connectivity (^{31}P/ ^{1}H)

^{1}H-^{31}P HETCOR (18.8T)



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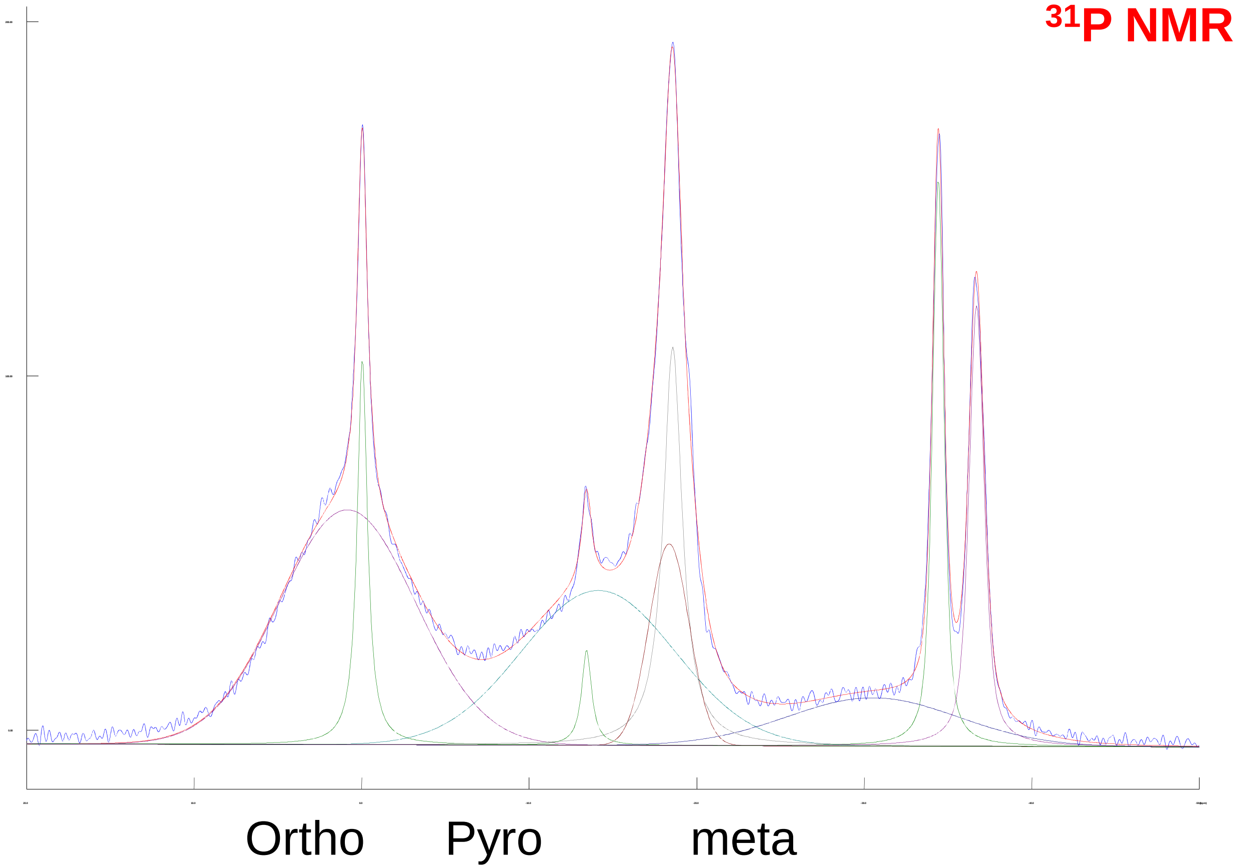
- 4-5 phases, assigned to hydrogen phosphates.
- XRD indicated only the presence of NaH_2PO_4.
- Study of glass alteration mechanism

^{31}P MAS-NMR of Mg phosphates



HT NMR of phosphate glasses: in situ study of crystallization, dynamics

^{31}P NMR

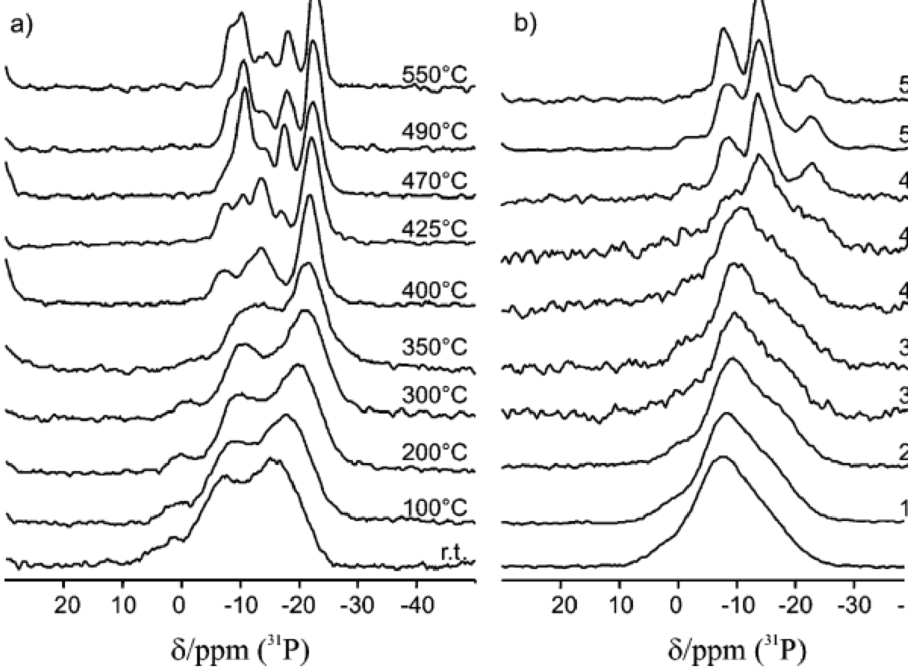
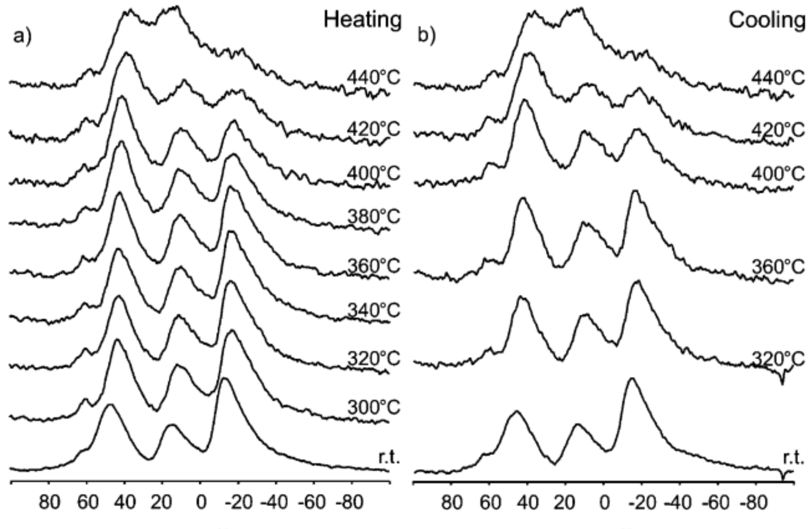
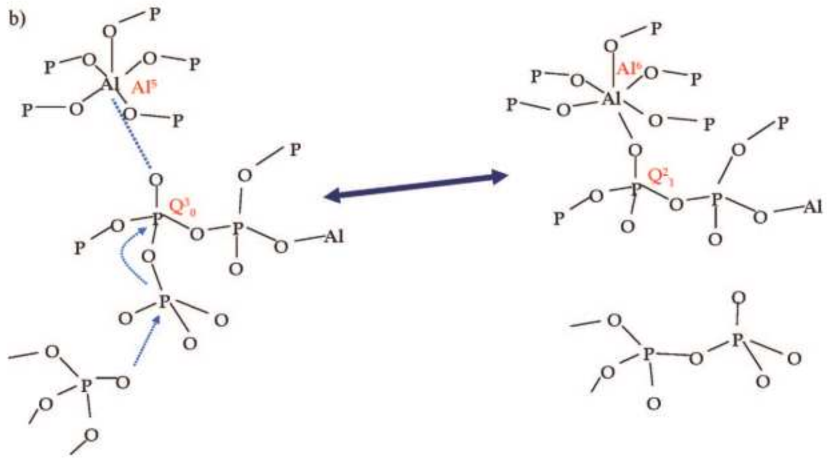


Figure 1. In situ high-temperature ^{31}P-MAS NMR spectra (at 4
for samples KAlP_5 (T_g = 303 °C, T_c = 410 °C) (a) and KAlP_1
= 349 °C, T_c = 467 °C) (b) for the indicated temperatures.

Van Wüllen J. Phys Chem (2007)

^{27}Al NMR





Wegner J. Phys Chem (2009)

Quelques exemples d'applications

Phosphate glasses: applications

Phosphate glasses

Mixed network phosphate glasses

- Water softening (Calgon)
- biomaterials
- sealing glasses
- Photonic glasses, laser glasses
- Electrolyte glass
- Anti-oxidation coatings
- Nuclear waste vitrification

Water softening

Biomaterials

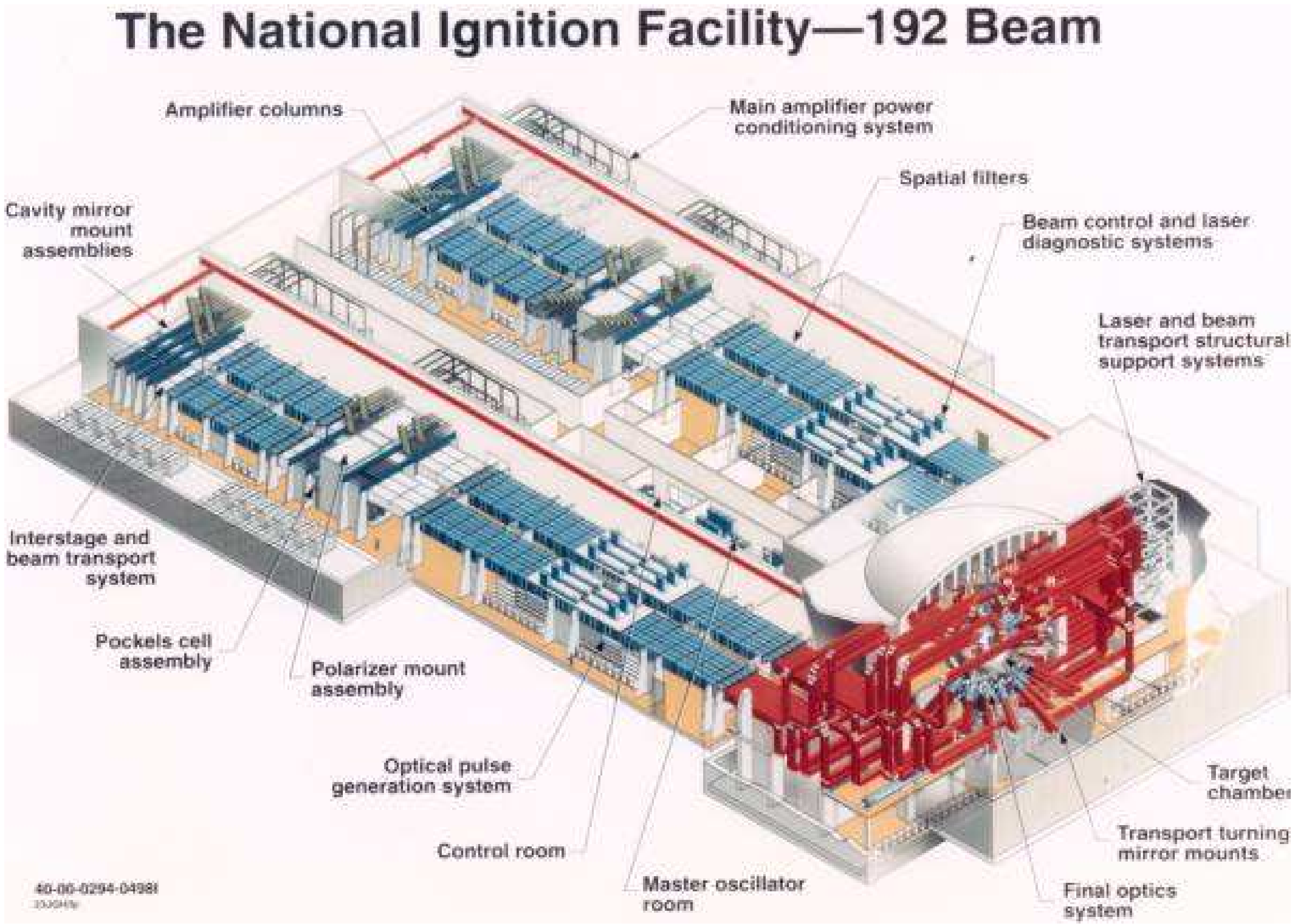
Sealing glasses

Laser glasses

Waste storage

Anti-oxidation coating

Development of continuous melting of phosphate laser glass

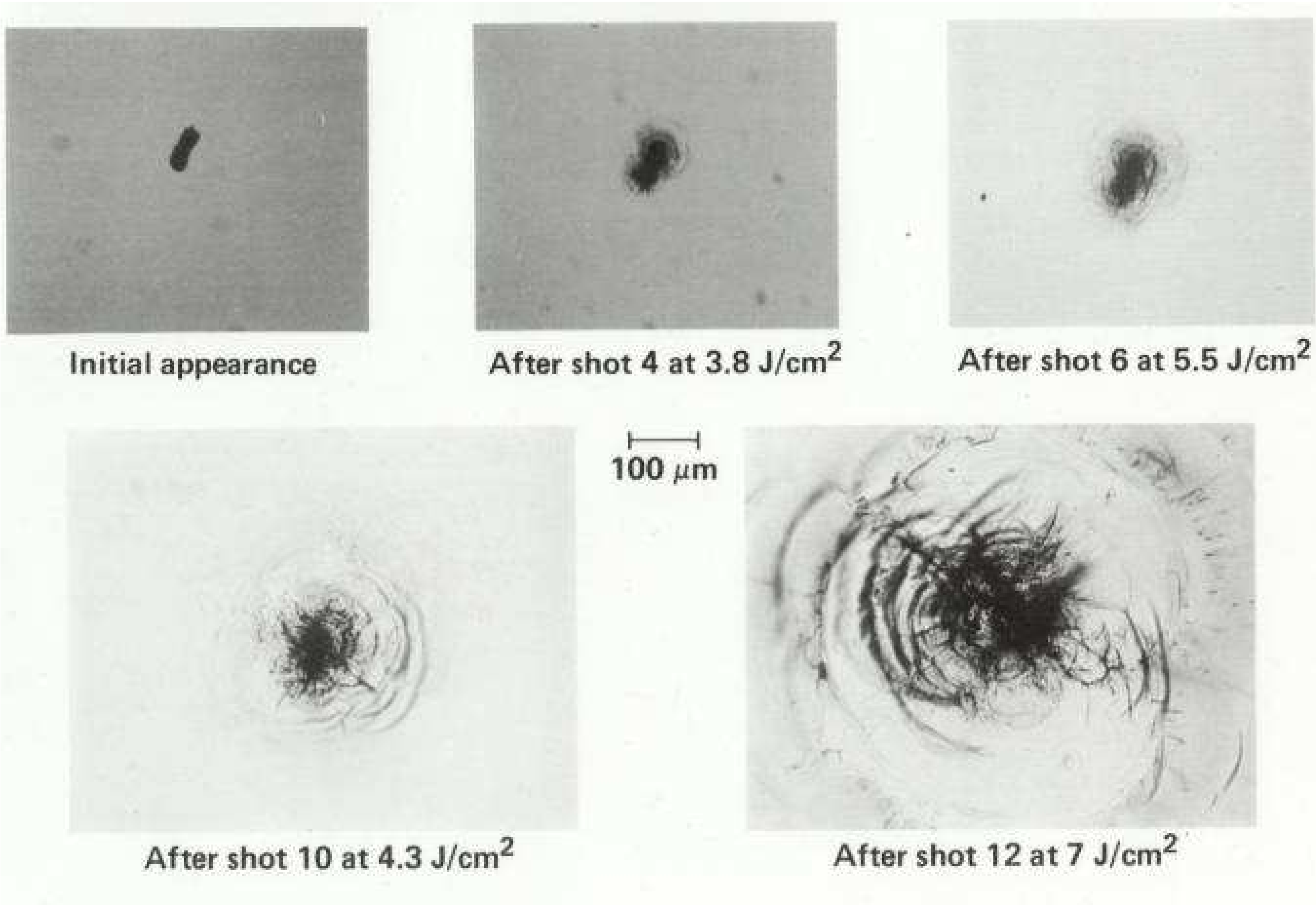


Artist Rendition of National Ignition Facility (NIF) Laser

- The NIF laser alone required 3000 slabs (150 metric ton) with the following specifications:
  - Index uniformity to <±0.000001
  - Free of inclusions and bubbles larger than 100um
  - Residual hydroxyl content <100ppmw
  - Platinum particle free
  - Free of all detectable striae
  - Low 1054nm absorption of <.19% per cm thickness

Beamlet eighteen liter rare earth doped phosphate glass amplifier slab

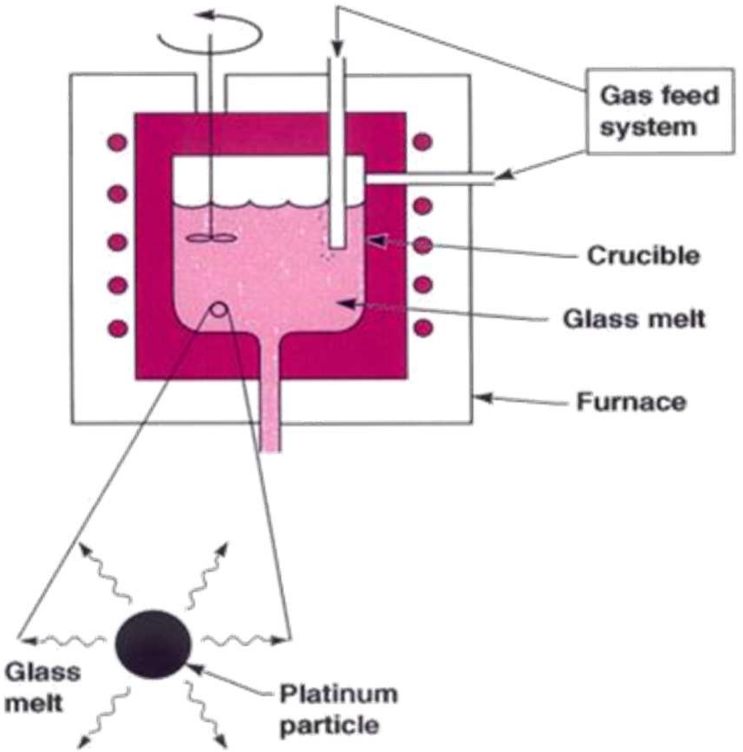
Damage grows with successive shots above the damage threshold



- Redeposited platinum vapor of spatial size >0.3µm can damage on the next shot
- Below 0.3µm, the heat is conducted into the glass
- Laser glass parts became unusable after only a few high power shots

SCHOTT
glass made of ideas

The key to solving the Pt particle problem was to dissolve the particles into the glass structure as ionic Pt^{4+}

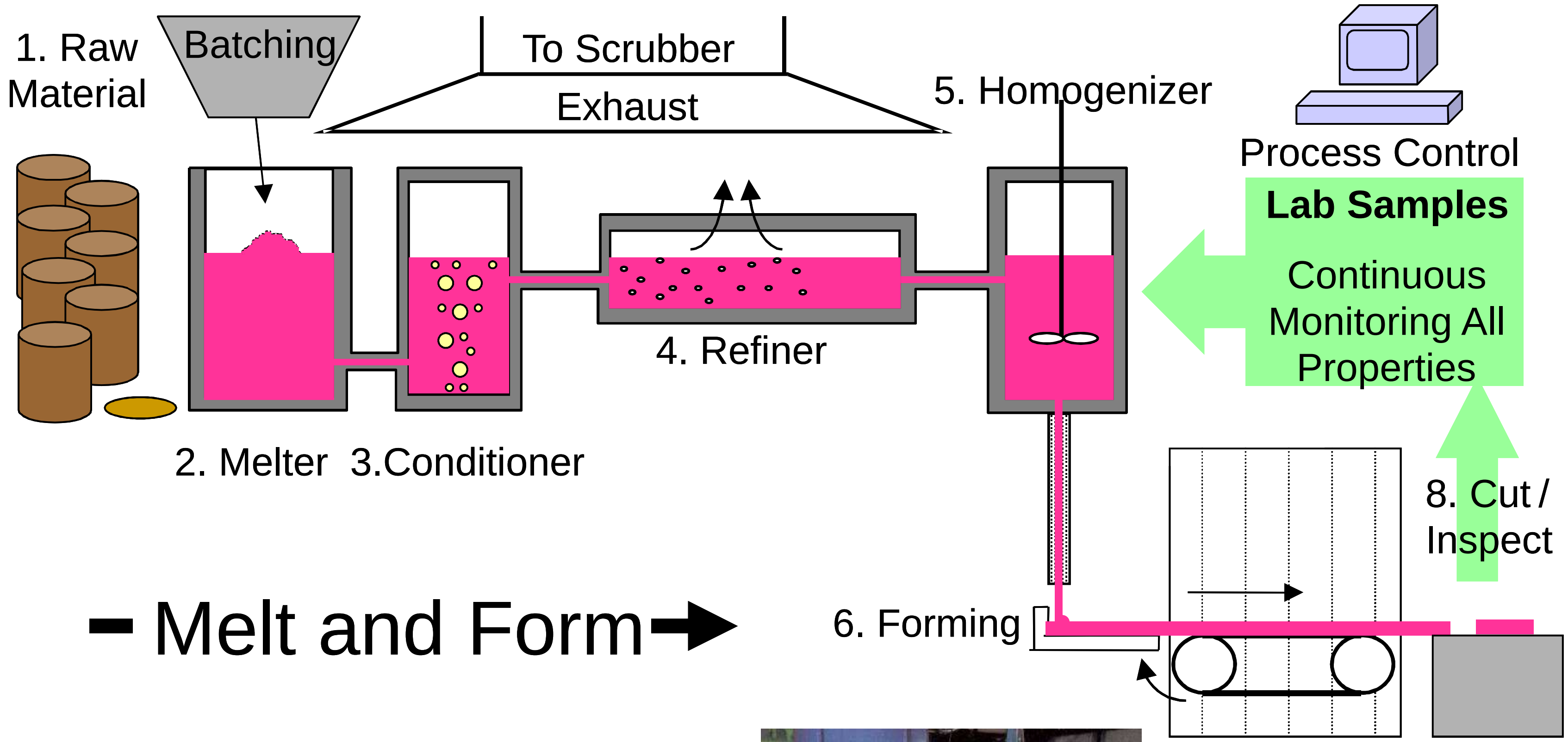


- Dissolve inclusions under oxidizing conditions ($Pt + n/4\ O^{2} \rightleftharpoons Pt^{n+} + n/2\ O^{2-}$)
- Minimize thermal gradients to reduce vapor transport $Pt^{o} + O_2 \rightleftharpoons PtO_2$ (g)

- Platinum particles appear to be created at the start of the melt cycle
- Dissolution is limited by diffusion of platinum away from the particle surface
- Care must be taken to avoid the late arrival of Pt particles into the melt from condensed vapors

SCHOTT
glass made of ideas

Meeting the laser glass requirements in terms of cost, quality, and rate of delivery for NIF



Over 1400 laser slabs were first produced by the new continuous melting process

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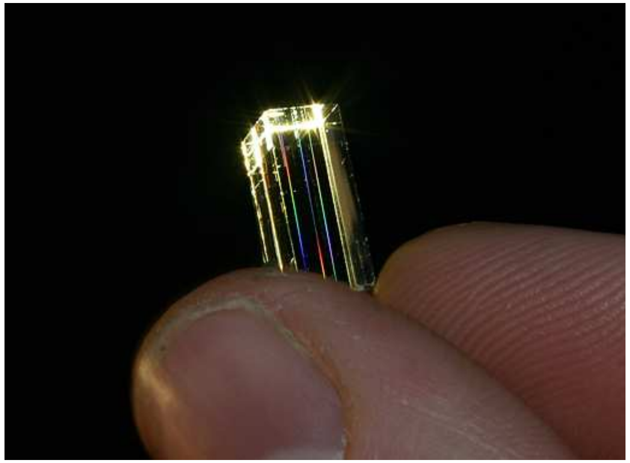
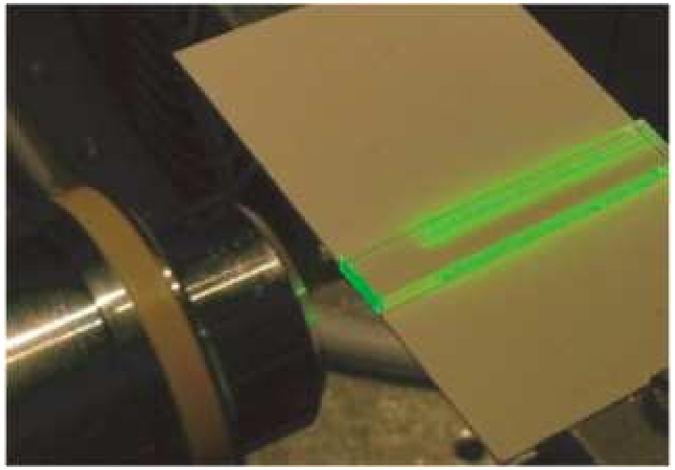
glass made of ideas

Laser phosphate glasses

High power lasers: >3000 neodynium-doped phosphate glass slabs (NIF LLNL USA, Megajoule Bordeaux, HPL Indore India)

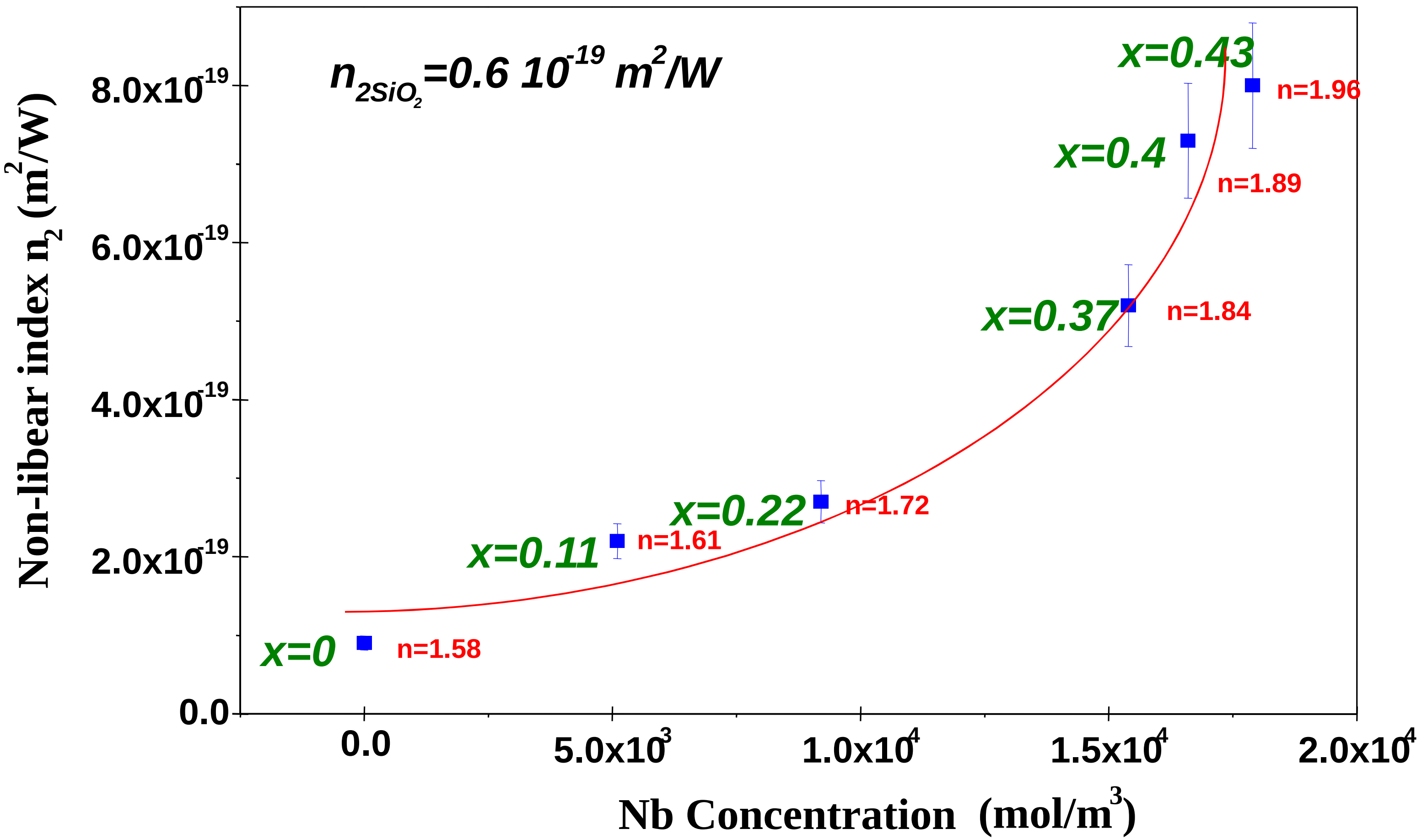




Second harmonic generation: optical switchs

Niobiophosphate glasses show large increase of n_2 index with Nb_2O_5 content

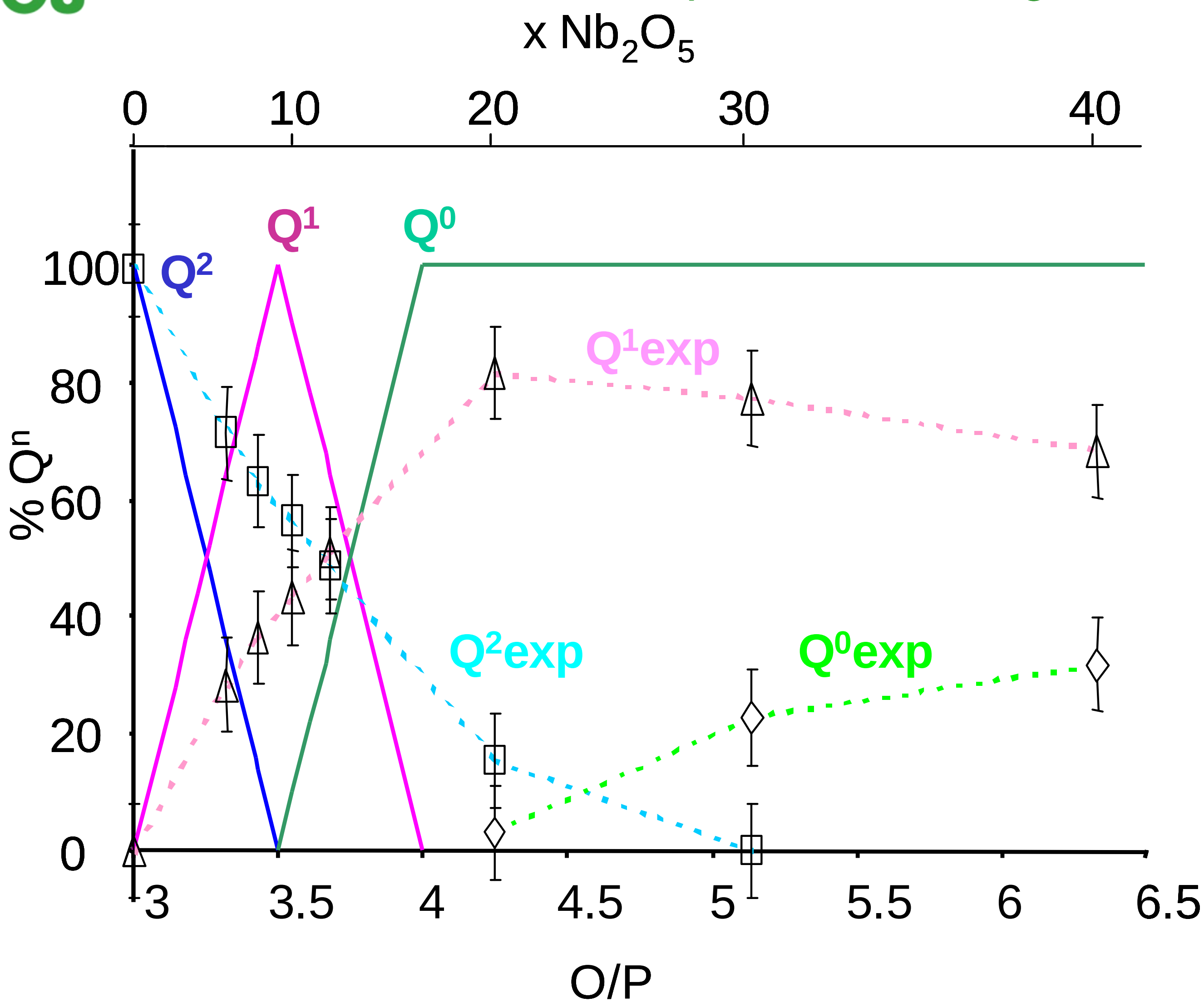
Glass compositions: xNb_2O_5-(100-x)(95$NaPO_3$-5$Na_2B_4O_7$)



Large increase of n_2 : Nb-O-P, Nb-O-Nb ? => ^{31}P, ^{93}Nb, ^{17}O NMR

M. Dussauze, E. Fargin, J. Phys. Chem. (2007)
C. Rivero, E. Fargin, T. Cardinal, Ceram. Transaction (2006)

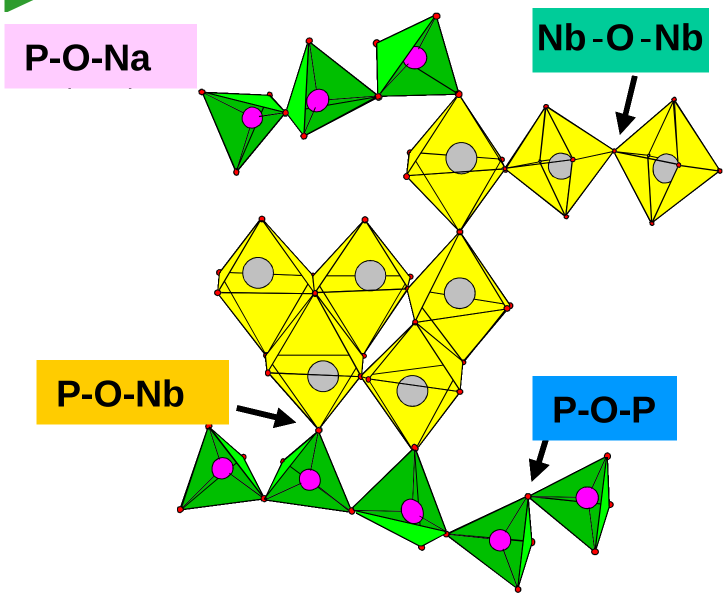
^{31}P NMR: Q^n site quantification in glasses



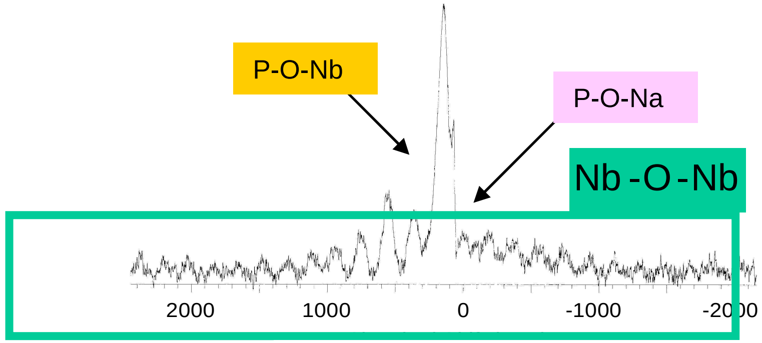
Nb_2O_5 dissociation is not complete: assumes Nb-O-Nb bonds

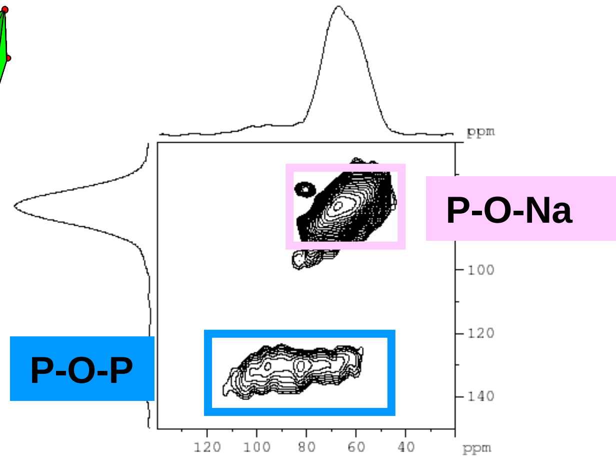
A. Flambard, L. Montagne, L. Delevoye, G. Palavit, J.P Amoureux, J.J. Videau JNCS (2004)

^{17}O NMR: chemical shift assignments

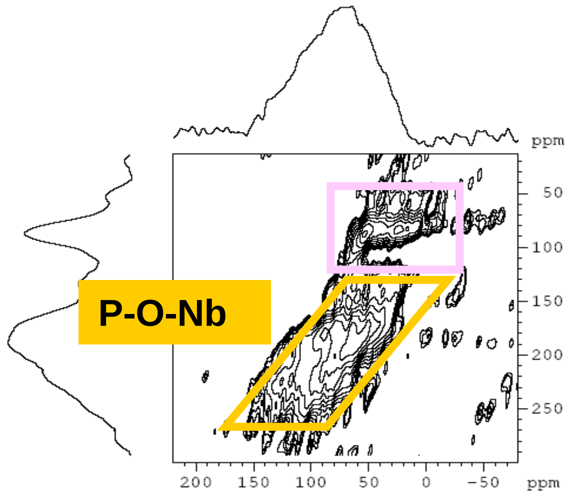


$40Nb_2O_5$-$60NaPO_3$ (18.8T)

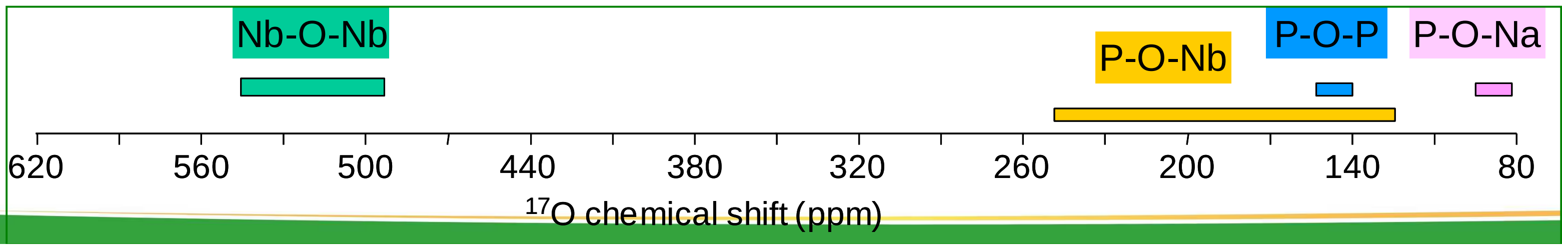




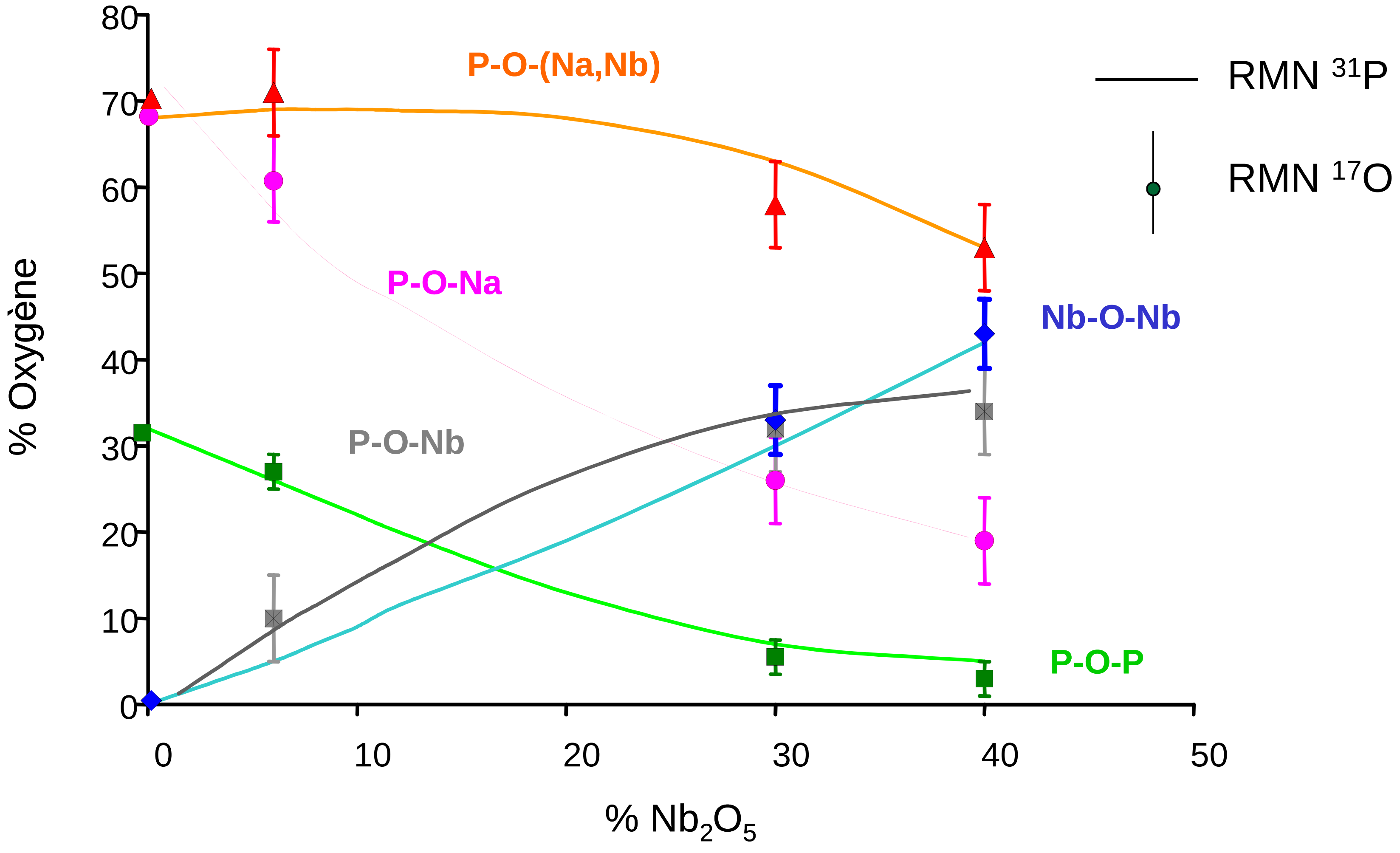
$6Nb_2O_5$-$94NaPO_3$



$40Nb_2O_5$-$60NaPO_3$ (9.4T)

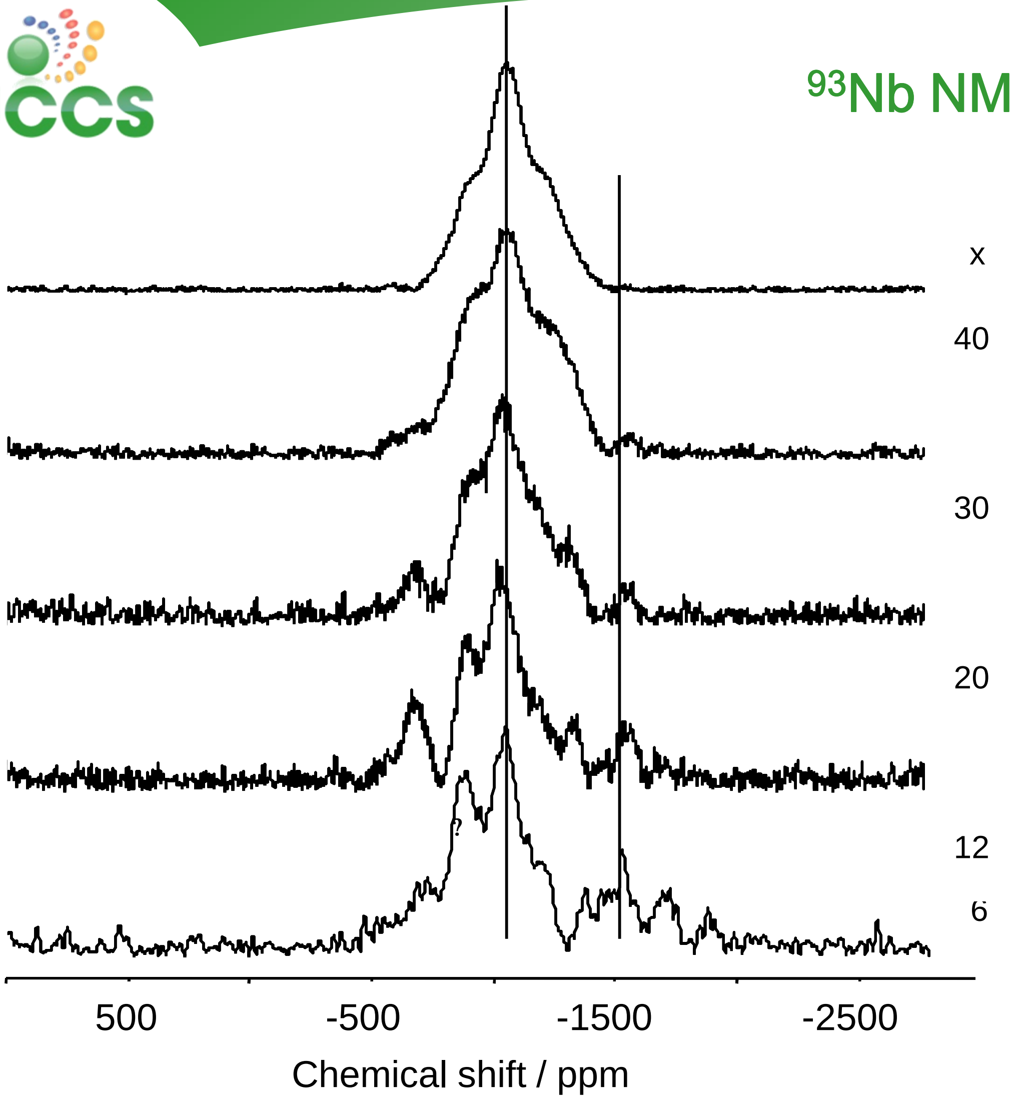


Oxygen sites in niobiophosphate glasses



Nb-O-Nb are confirmed by ^{17}O NMR

^{93}Nb NMR

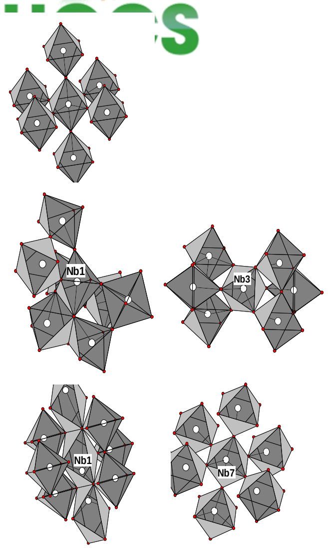


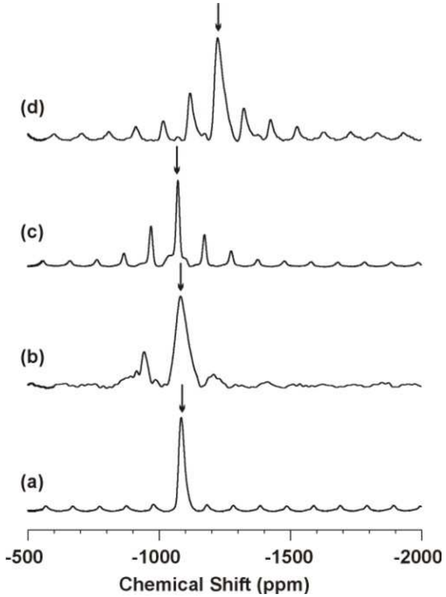
18.8T – 33KHz

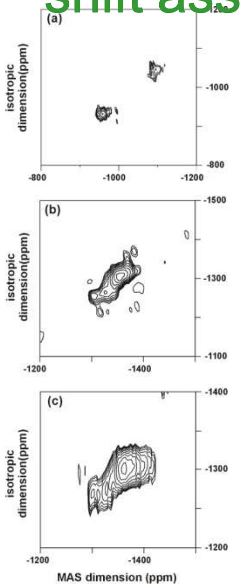
I=9/2:
High-field NMR reduces Quadrupolar broadening

^{93}Nb chemical shift assignment ?
We need crystalline reference compounds

Crystalline references for ^{93}Nb chemical shift assignment







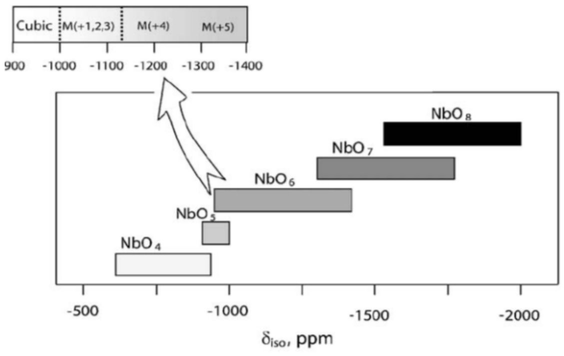
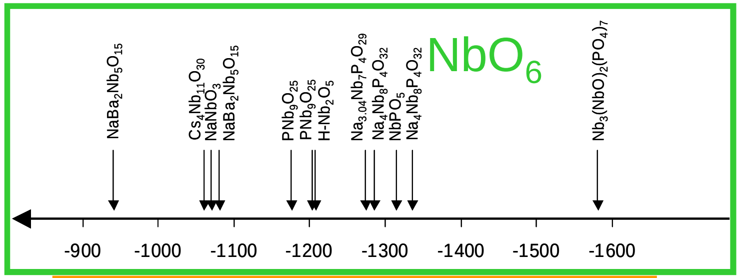
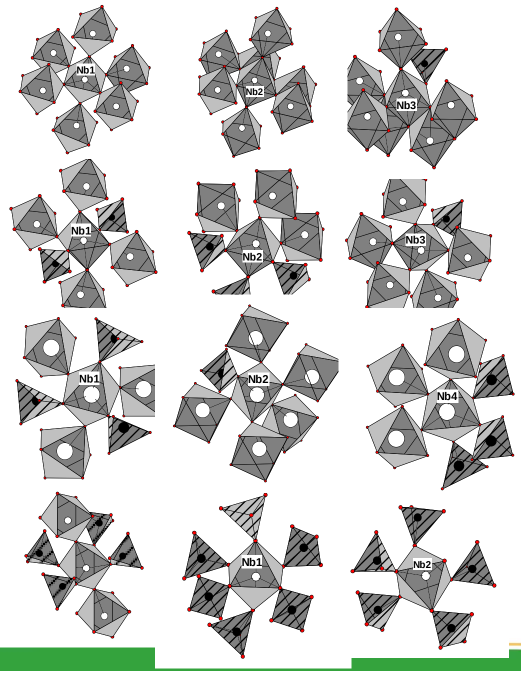
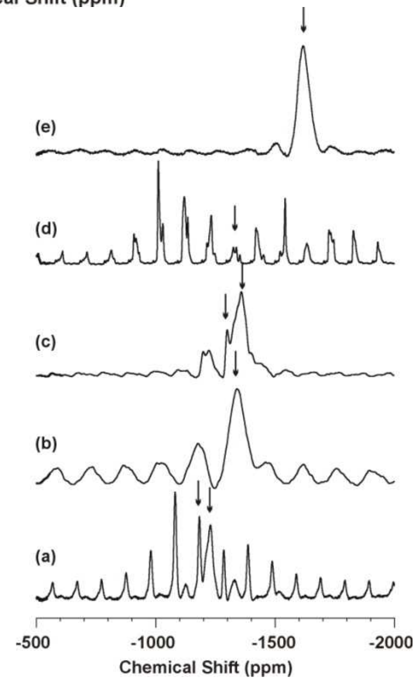


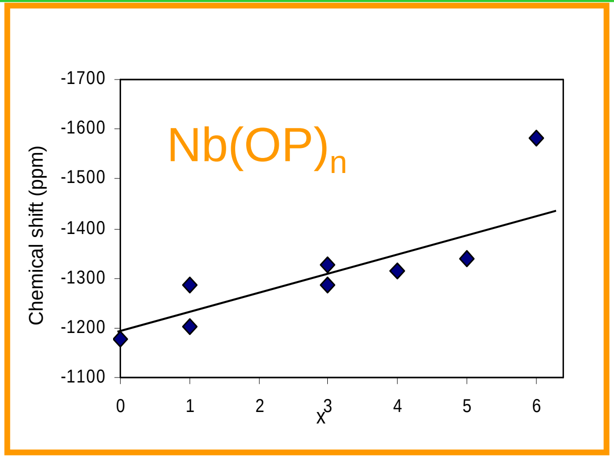
Fig. 24. ^{93}Nb NMR chemical shift scale for NbO_x polyhedra.

O.B. Lapina ss-nmr 28 (2005) 204–224

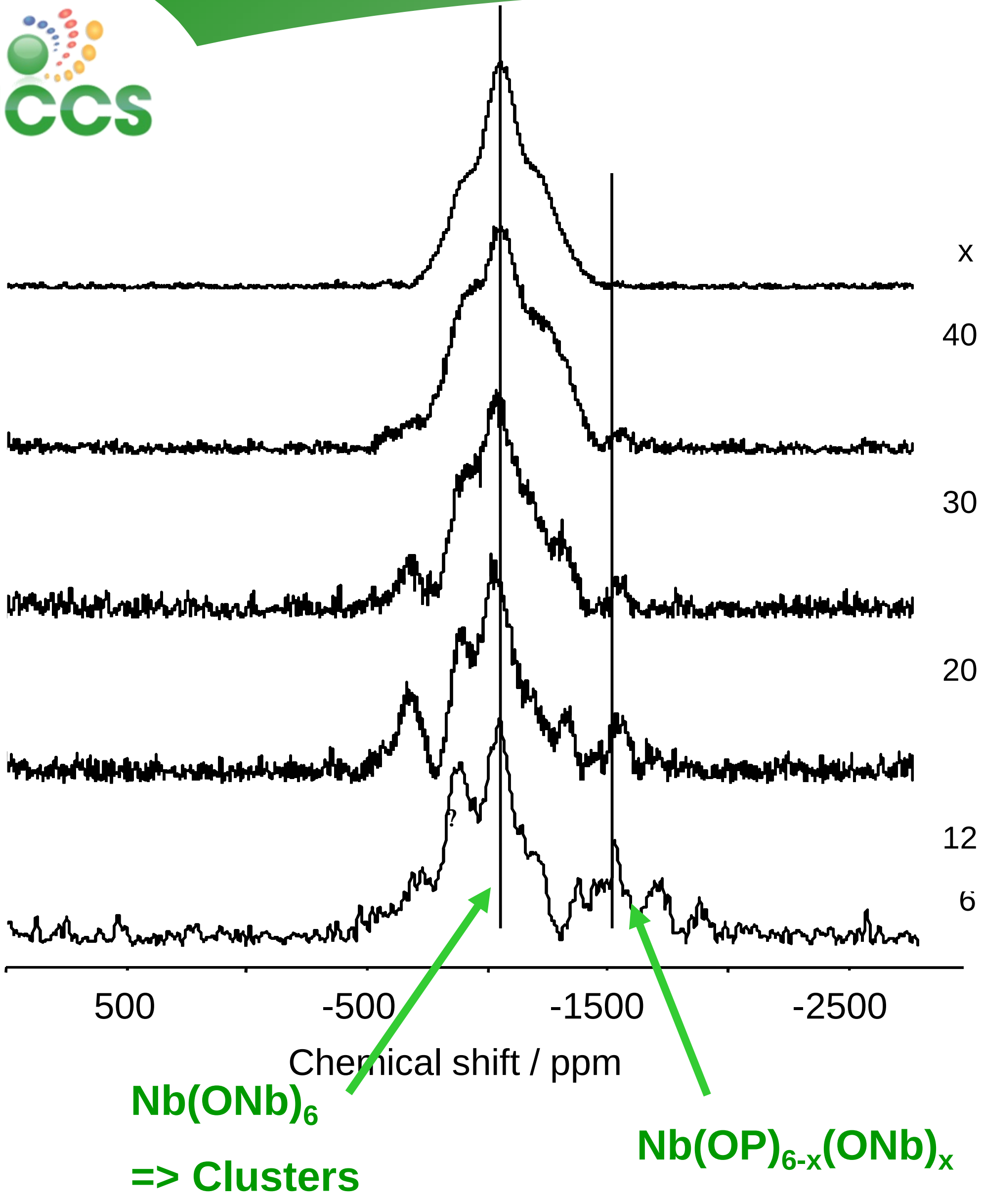








A. Flambard, L. Montagne, L. Delevoye, S. Steuernagel Solid-State NMR (2007)



I=9/2:
High-field NMR reduces
Quadrupolar broadening

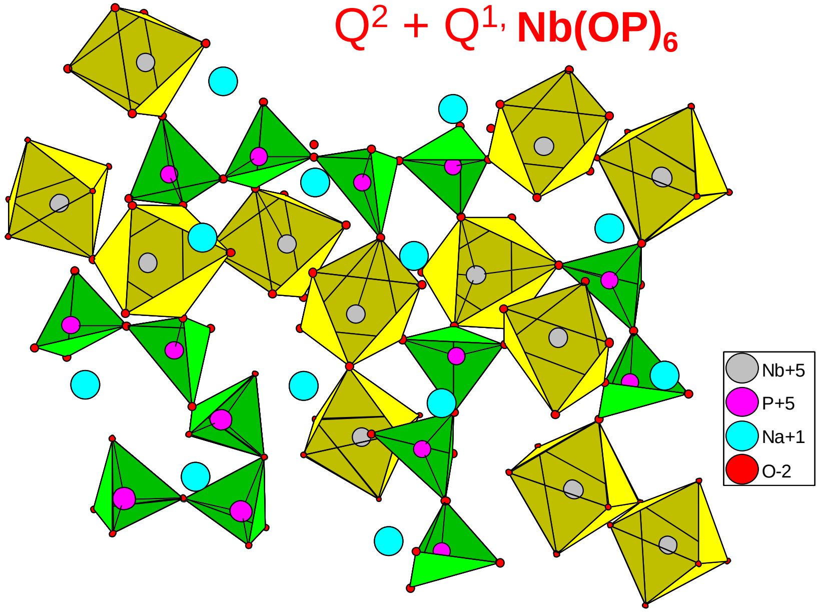
[93]Nb sites are assigned from crystalline references, but uncertainty remains,

→ DFT calculations are needed.

Property vs. structure

$0 < x < 20$

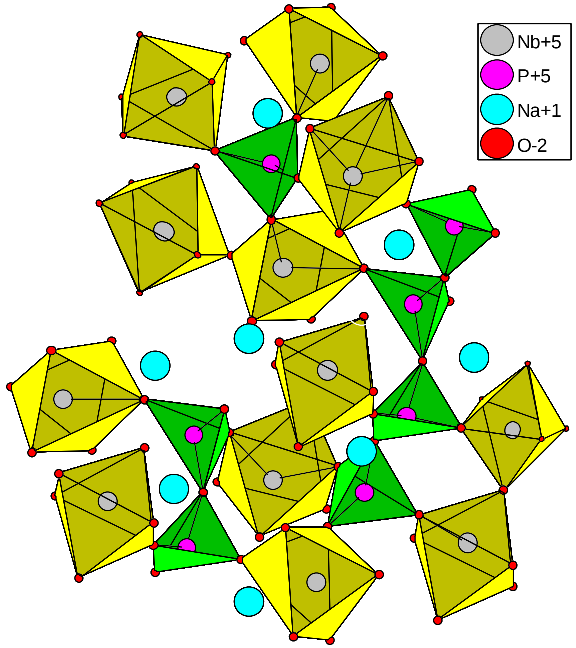
$Q^2 + Q^1$, **$Nb(OP)_6$**

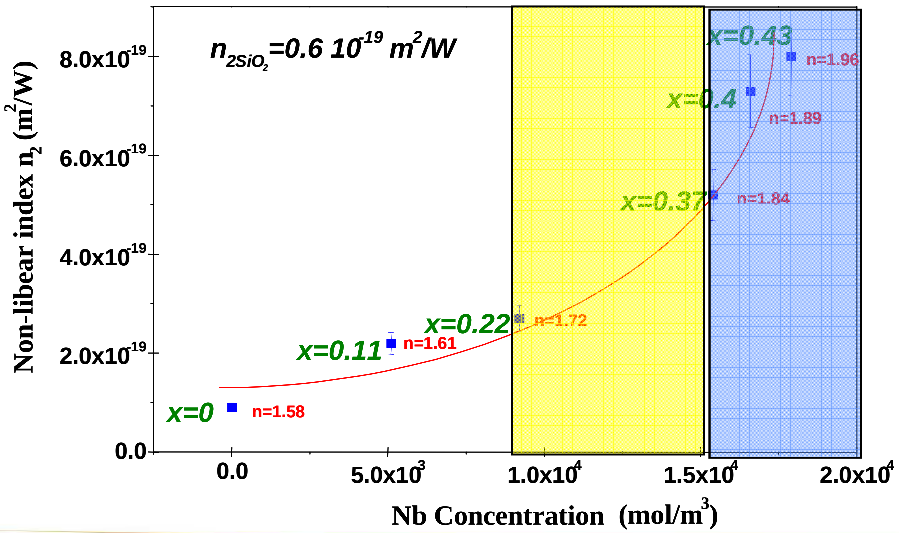


$20 \leq x < 30$

Q^2, $Q^1 + Q^0$

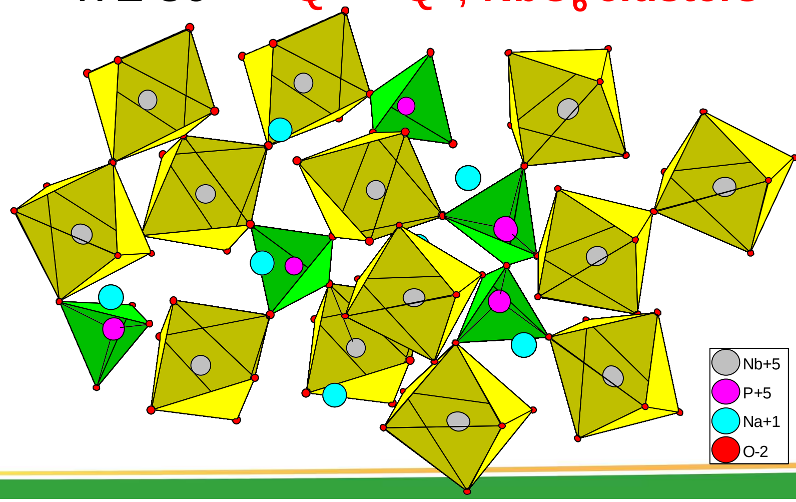
$Nb(OP)_{6-x}(ONb)_x$





$x \geq 30$

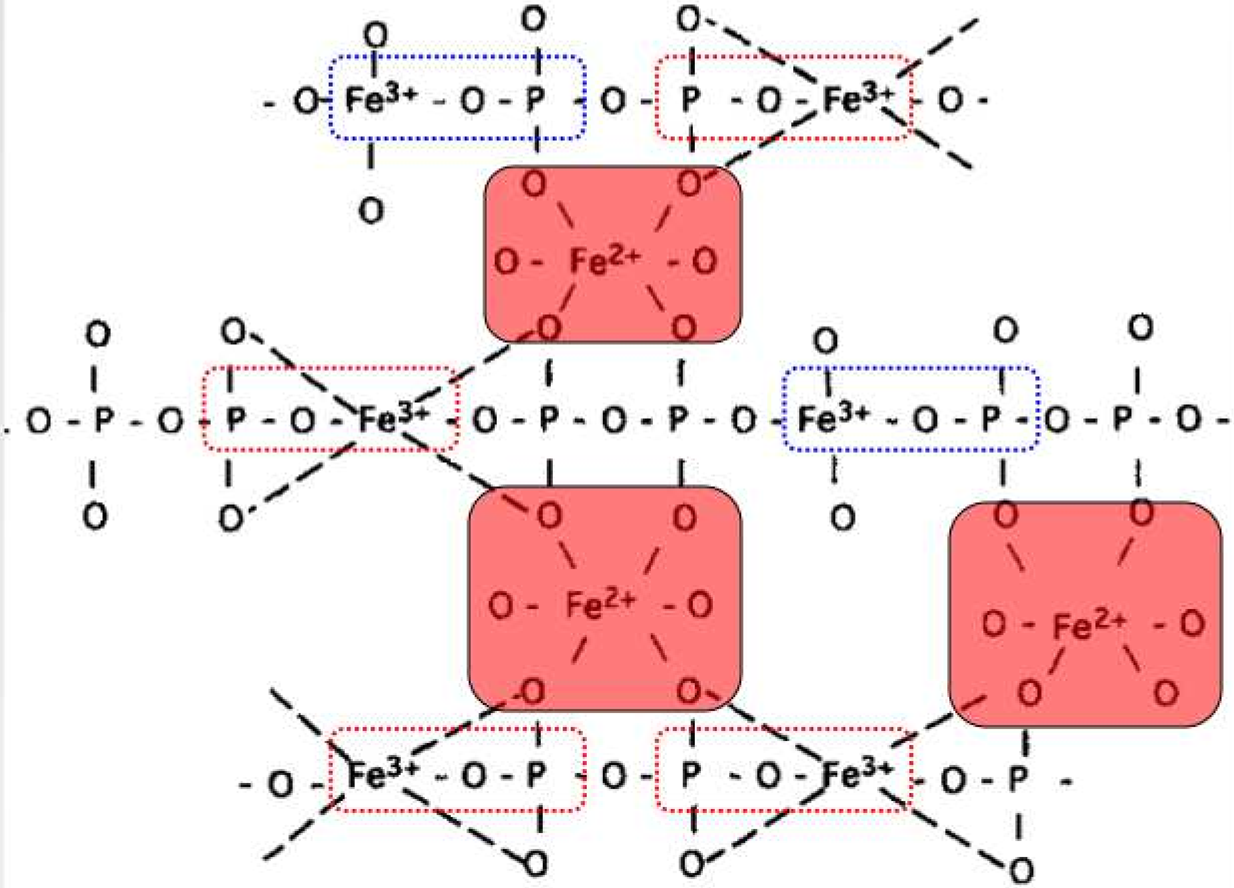
$Q^1 + Q^0$, **NbO_6 clusters**



Phosphate glasses and nuclear waste vitrification

Phosphate glasses and nuclear waste vitrification

- Alternative solution to borosilicate glasses for special wastes
  - High load
  - Larger solubility of chromium, molybdenum
  - Lower melting T : less volatilization of sulfur, iodine
- 70’ : USSR: Mamoshin: aluminophosphate glasses
- 80’: USA: Sales and Boatner : Pb-Fe phosphate glasses
- 90’: USA: Day : Fe phosphate glasses

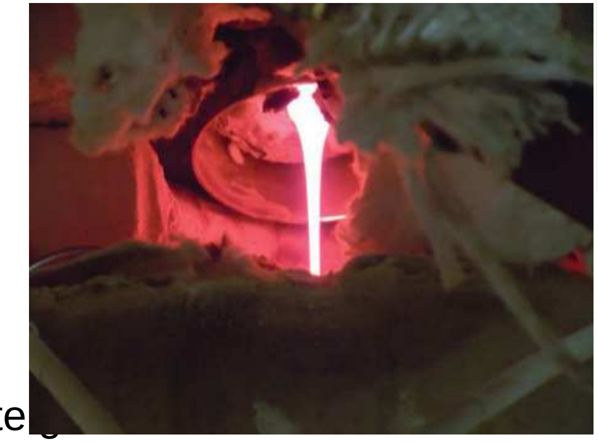


1) Low melting T: ~900-1100 ℃; 2) High waste loading;

3) Chemically durable P-O-Fe bonds in glass structure.

X. Yu *et al.*, *J. Non-Cryst. Solids* 215, (1997) 21.

iron phosphate glass



C.-W. Kim, D.E. Day JNCS (2010)

- Contains 26 wt% of the Hanford AZ-102 LAW
  - Targets high sulfate (4.3 wt%) and high Na_2O (20 wt%)
  - Approximately 3x greater waste loading than typical borosilicate
- Recommended processing temperature of 1000 - 1050°C
- High retention of Cs, Re, and SO_3 in laboratory melts
- Meets PCT and VHT durability requirements for Hanford L disposal (regardless of thermal history)
- Melt viscosity and electrical conductivity within acceptable for JHM and CCIM processing
- Compatible with Inconel 693/690 and K-3 refractory

Simulated waste glass cylinder, 8 liters, melted at 1200°C (Brow, personnal communication)

Open questions:

Chemical durability (long term)
Devitrification resistance
Corrosiveness

Immobilization of Radioactive iodine in phosphate glasses

T. Lemesle[1,2], F.O. Méar[1], L. Campayo[2], O. Pinet[2], L. Montagne[1]

[1] Unité de Catalyse et Chimie du Solide - UMR-CNRS 8181 - Université Lille Nord de France, F-59652 Villeneuve d'Ascq, France

[2]DEN/DTCD/SECM/LDMC, CEA Marcoule, BP 17171, 30207 Bagnols sur Cèze, France

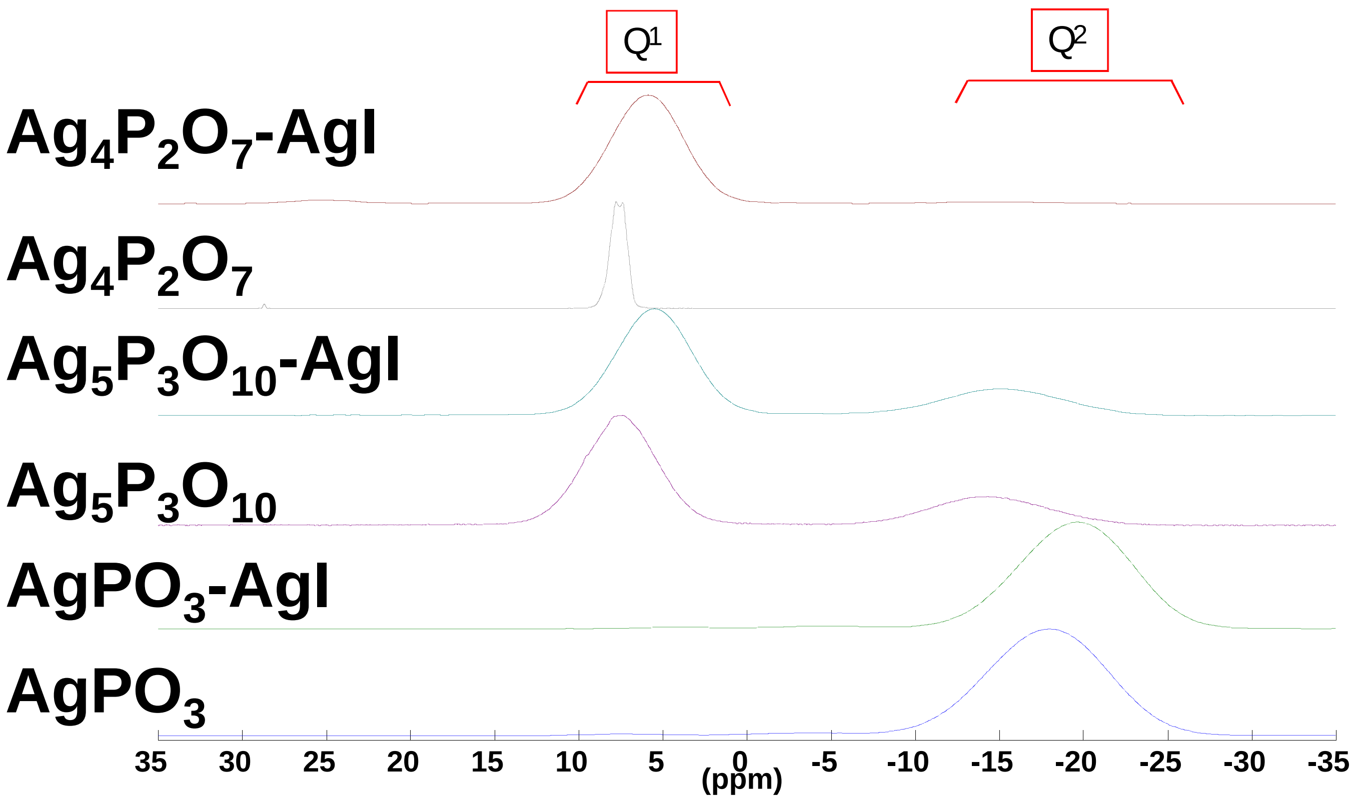
Why Iodine?

- ^{129}I : radioactive isotope extracted during the processing of the nuclear fuel
- **MAVL's waste** (Medium activity waste with a long life).

  - High mobility in the geologic environment
  - Strong tendency to volatilization (600°C)

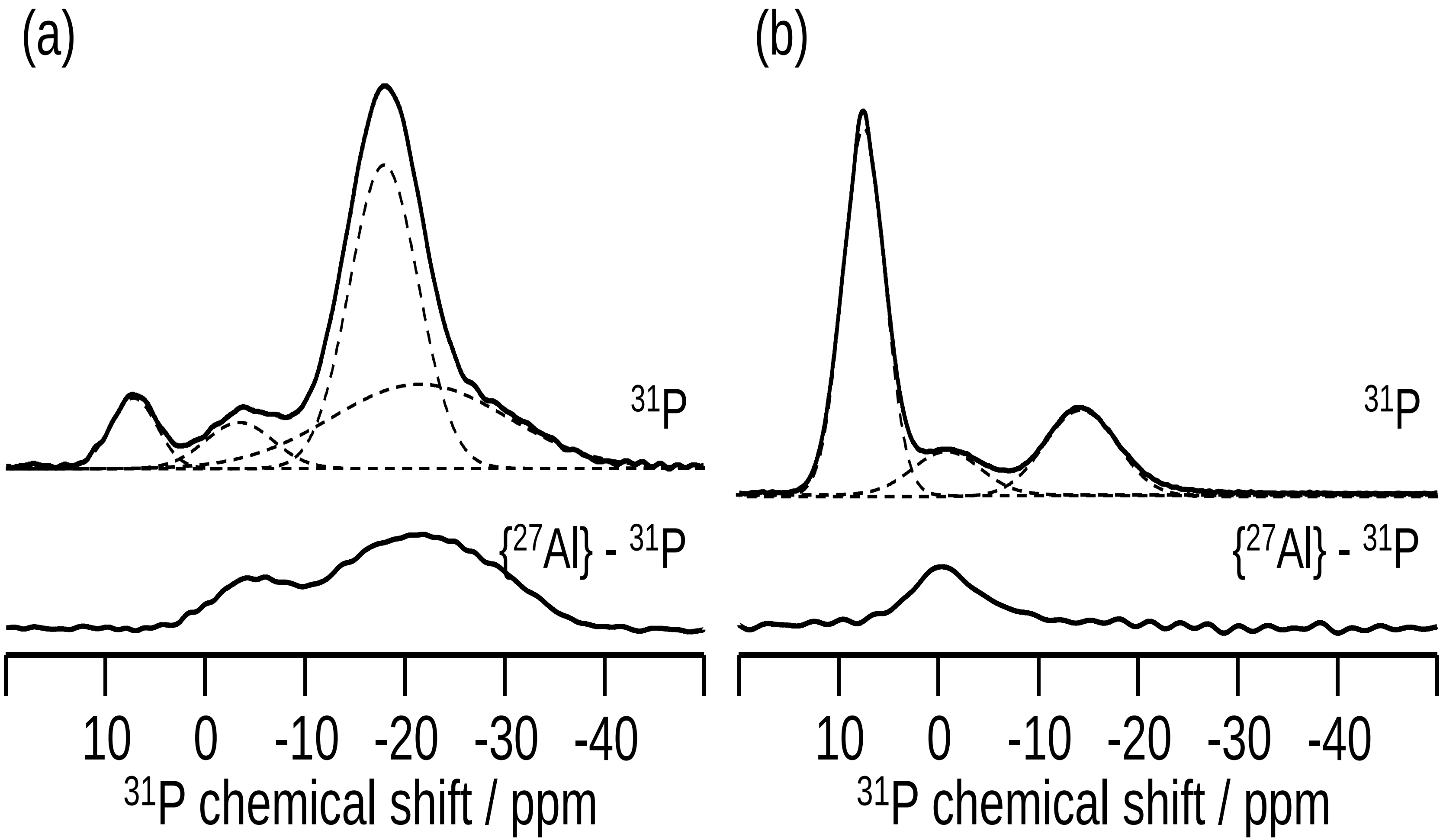
- Silver phosphate glasses
  - Low melting T
  - High incorporation rate for I

Influence of the incorporation of AgI on the structure as a function of Ag/P by ^{31}P NMR



Addition of AgI for different ratios of Ag/P changes the chemical shift: modification of angles and bond length in phosphate network

Ajout de Al_2O_3 : réseau aluminophosphate



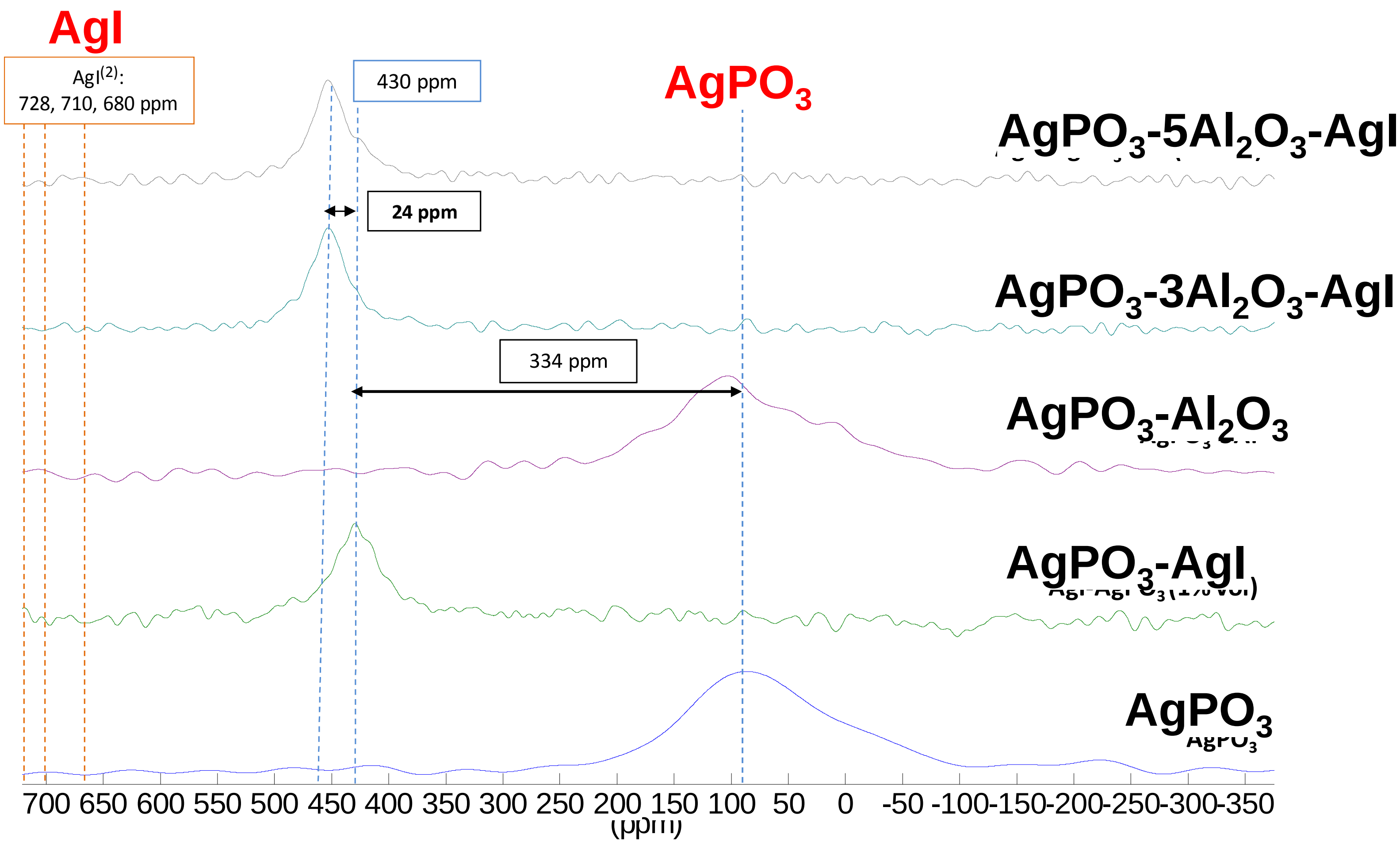
^{109}Ag NMR

[1]Multi-nuclear, Solid Stz Nuclear Magnetic Resonance, KK Olsen, 123-132 (1995)

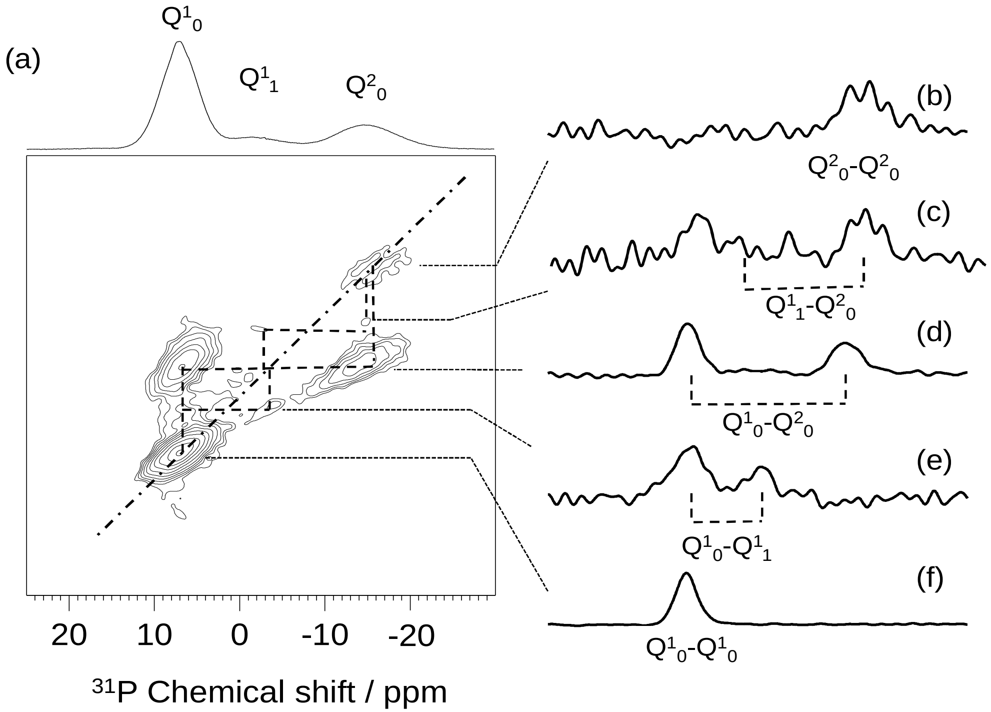
[2]Mustarelli et al., 1998

[3]Kawamura and al., 2002

[4]Kawamura and al., 2002



- Broad signal of P-O-Ag : distribution of ionic bonds
- No signal of AgI : no cluster
- Average signal of silver in AgI-$AgPO_3$-Al_2O_3 glasses : confirms no clustering since all Ag+ are bonded both to Iodine and phosphates



Without AgI

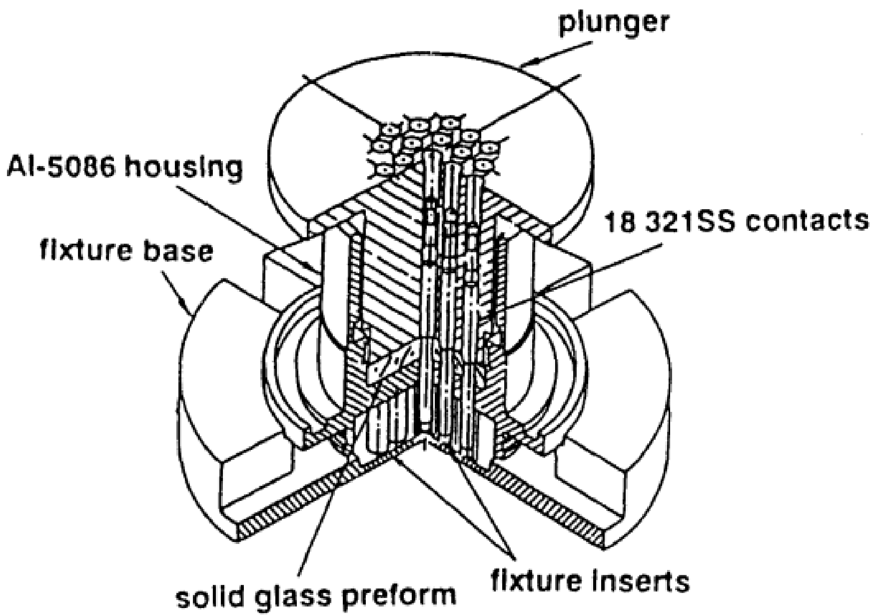
^{31}P-^{1}P DQ-NMR

With AgI

Sealing glasses

- Wilder et al.
- Brow et al. (Sandia)
- Morena et al. (Corning)
- Low Tg
- High CTE for sealing to Al alloys
- Sn phosphate glass
- Zn phosphate glass
- F phosphate glass : extension to Glass-polymer blends (Tischendorf)

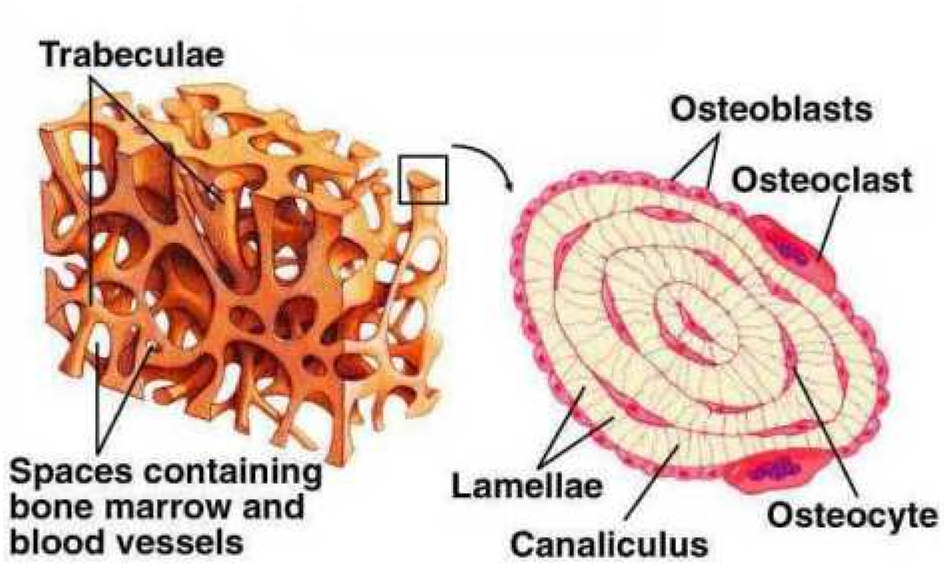
Figure 1. Aluminum LAC Fixture Assembly

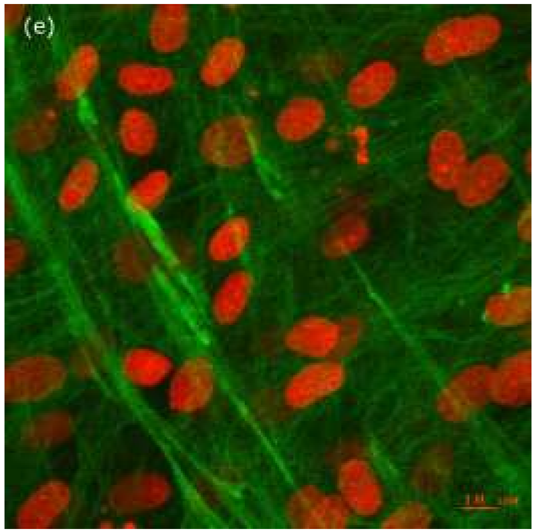


Phosphate glasses as biomaterials

Phosphate glasses as biomaterials

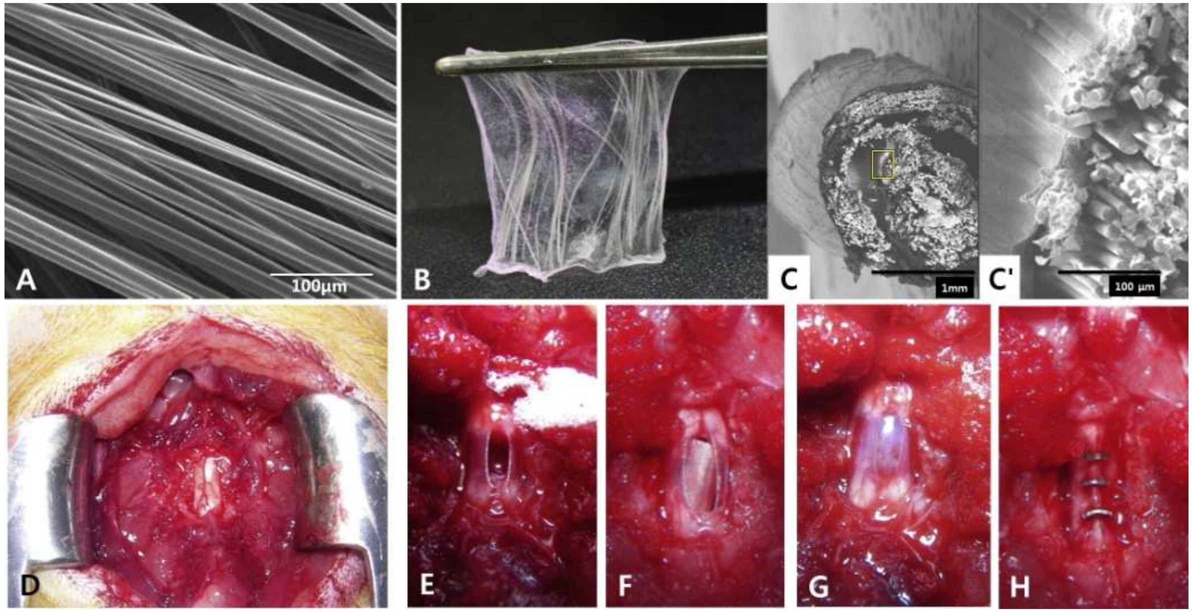
- Bone : apatite = calcium phosphate
- Hench's bioglasses : silicophosphates
- Vogel et al : Ca, Fe, Na phosphate glass-ceramics (machineable)
- Knowles : Na, Ca, Ti phosphate
- Good biocompatibility
- Control of dissolution rate is a key issue



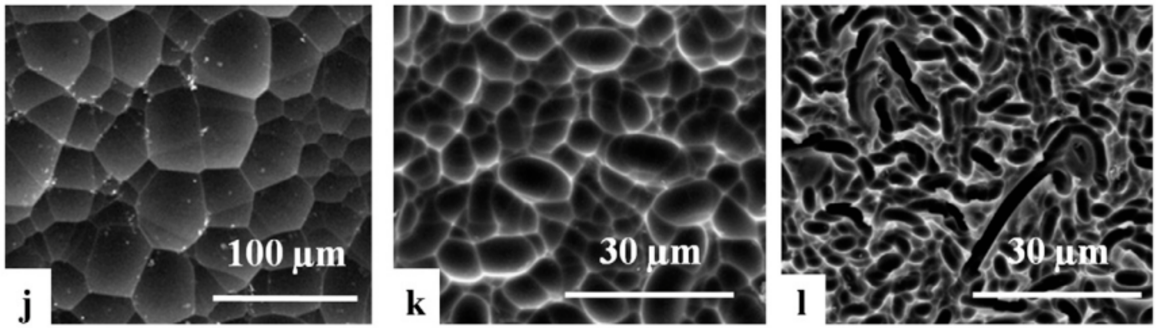


Knowles Acta Biomaterialia (2012)

Phosphate glass fibers as biomaterials



Glass	Glass composition (mol%)						
	P_2O_5	CaO	Na_2O	SiO_2	MgO	K_2O	TiO_2
$TiPS_0$	50	30	9	3	3	5	–
$TiPS_{2.5}$	50	30	9	3	3	2.5	2.5
$TiPS_5$	50	30	9	3	3	–	5



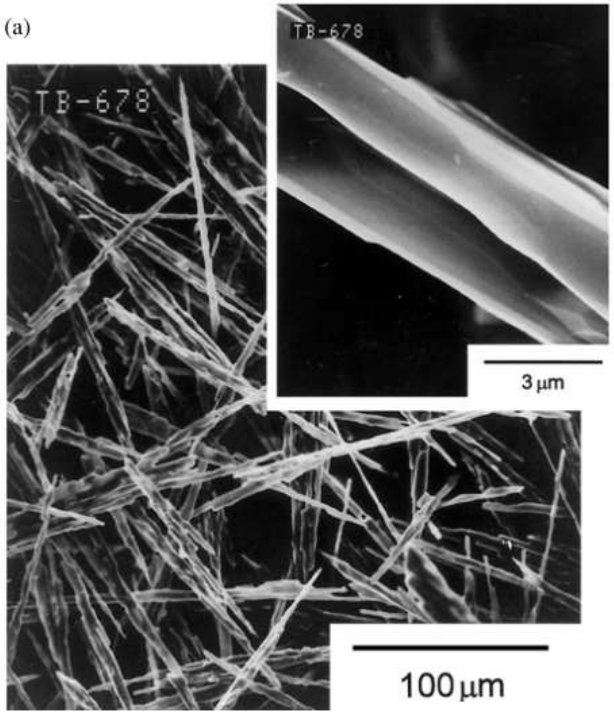
$TiPS_0$ $TiPS_{2.5}$ $TiPS_5$

C. Vitale Mat. Sc & Eng.(2011)

Phosphate glass-ceramics as biomaterials

- Abe et al. (Nagoya)
- $Ca(PO_3)_2$ sub-Tg crystallization
- $NaCaTi(PO_4)_2$ NASICON porous glass-ceramics impregnated with Ag^+ : bactericide bioceramics

(a)



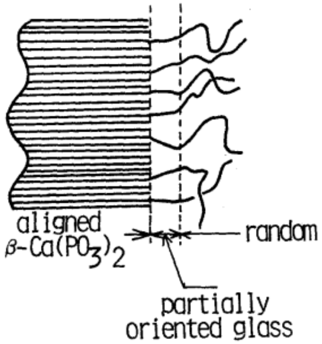


Figure 1 Schematic presentation of extended-chain crystallization model for $Ca(PO_3)_2$ glass (– indicates molecular chain of condensed phosphate).

Abe et al Nature (1989)

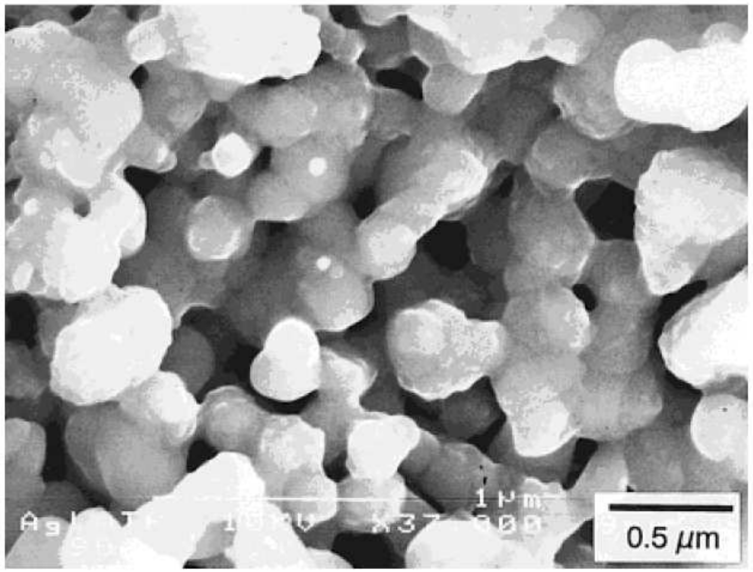


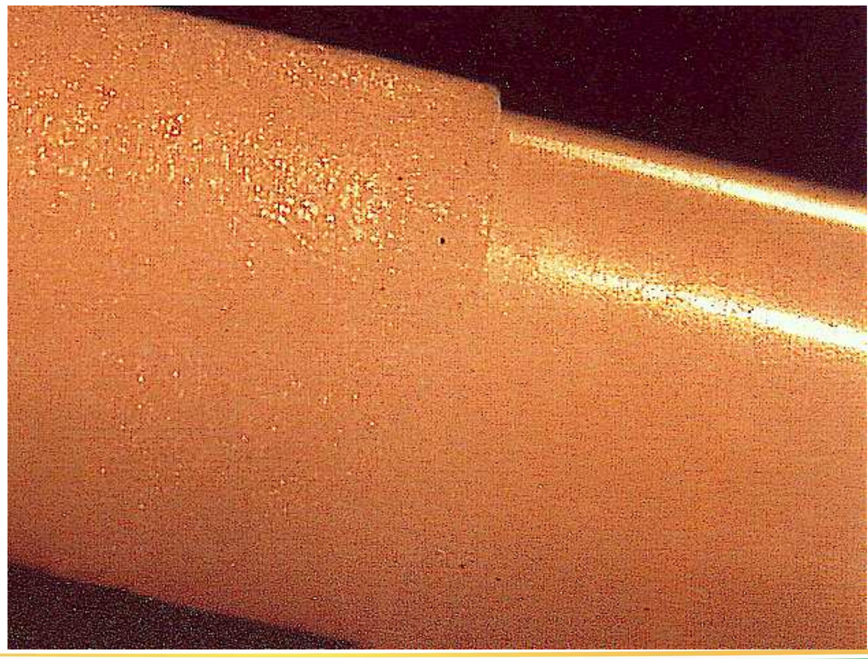
Fig. 5. SEM photos of porous glass-ceramic Ag-LATP heated at 900°C.

Kasuga ACERS (1997)

Phosphate glass bio-enamels

- Na,Ca, Fe phosphate glasses + TiO_2 (CTE matching)
- Enamels on Alumina hip prothesis cup
- In-vivo tests and push-out evaluation (Hopital Lariboisière Paris)
- Showed good bioactivity (apatite formation, osteocells)
- However, alumina diffusion through coating inhibited bone mineralization

4 mm



Montagne et al. GTB (1998)

Phosphate glass fertilizers

- Slow release of oligo-elements (Mn, Cu)

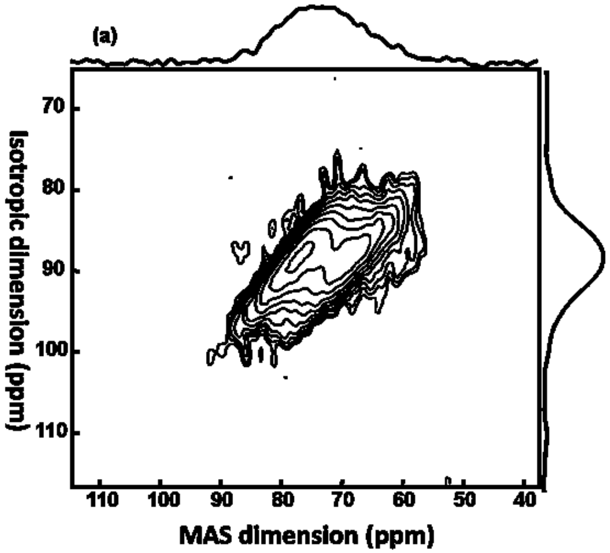
Glass code	Mol %			
	P_2O_5	K_2O	CaO	MgO
	Set B			
B-1	33.33	33.3	11.1	22.2
B-2	36.84	31.6	21.1	10.5
B-3	40.00	30.0	20.0	10.0
B-4	42.86	28.6	19.0	9.5

	CuO	MnO_2	MoO_3	Fe_2O_3	ZnO	CoO	S	B_2O_3
B-3M1	0.61	0.61	0.61	0.61	0.61	0	0	0
B-3M2	0.025	0.051	0.024	0.012	0.024	0.026	0.025	1.44

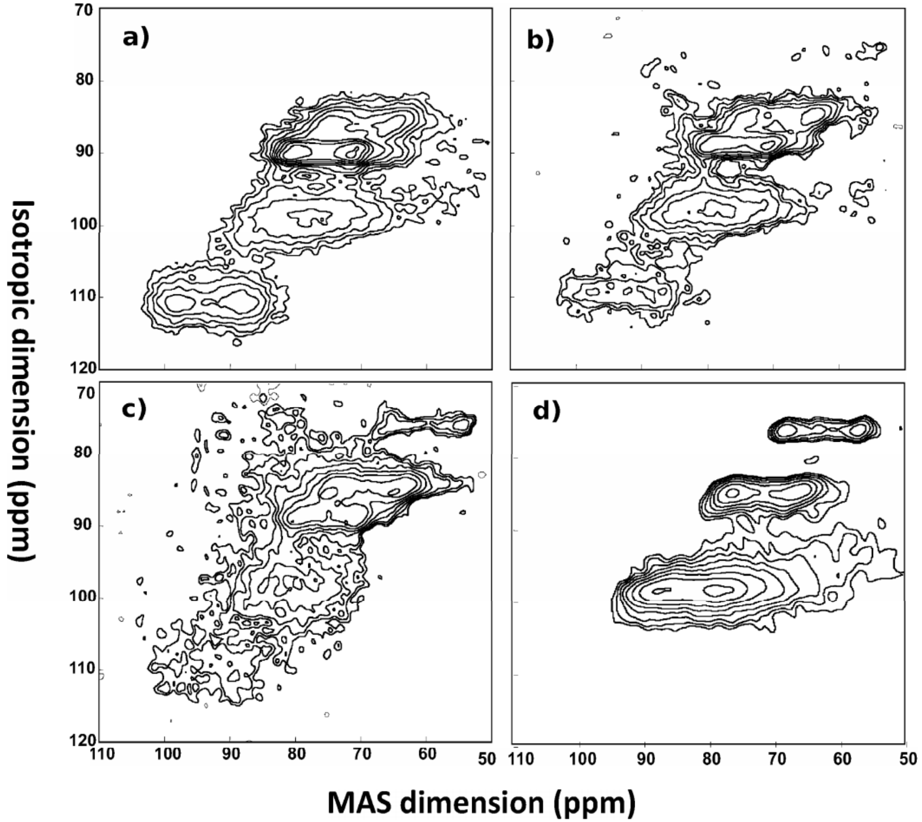
Ivandelko Völkenrode (2007)

$NaPO_3$ Hydration (Calgon)

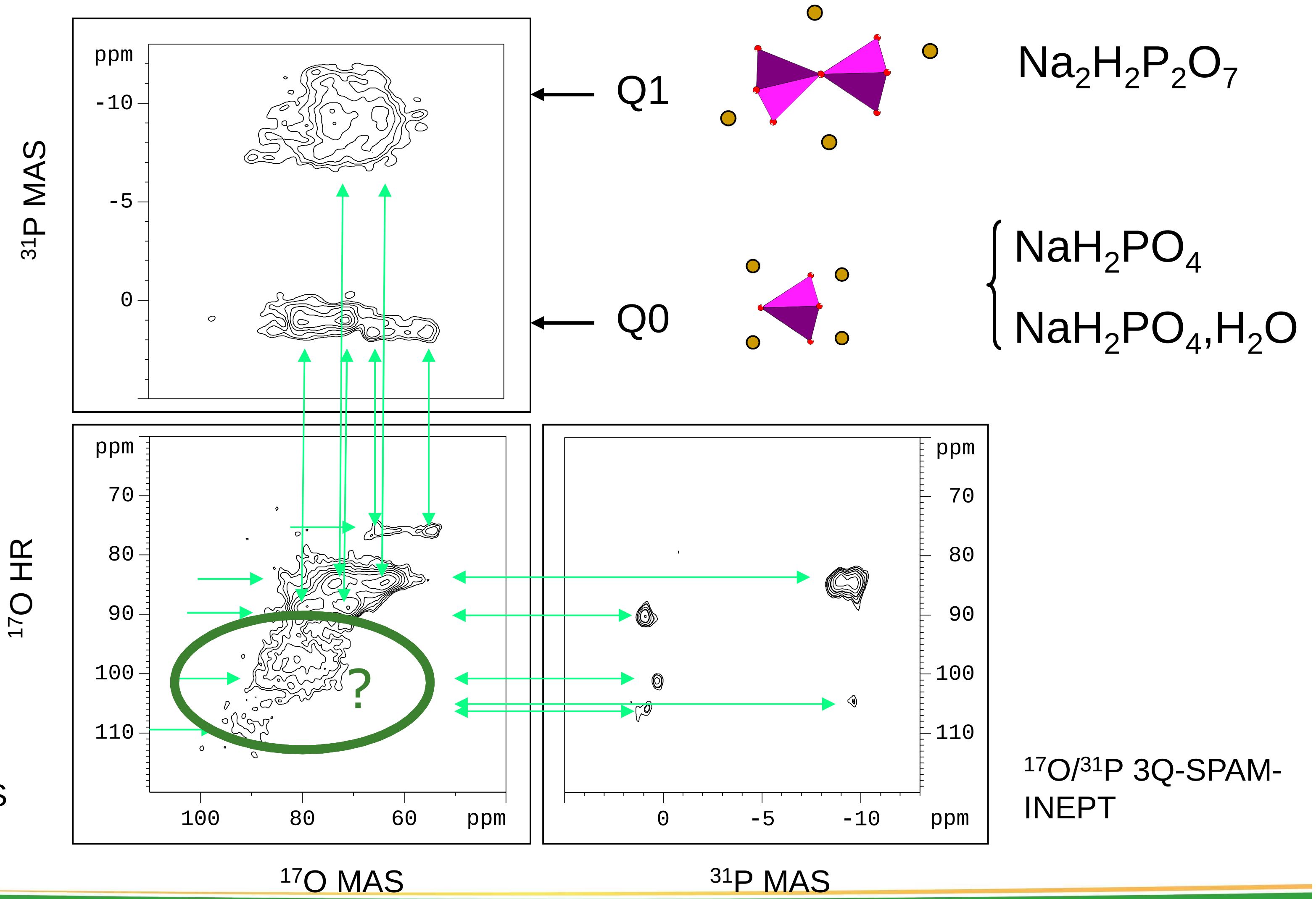
^{17}O NMR @18.8T



Hydration
=f(T, t, Rh)



^{17}O-^{31}P Heteronuclear correlations



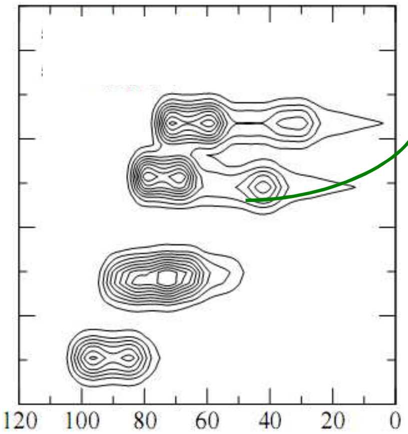
$^{31}P/^{17}O$ HMQC

^{17}O 3Q-SPAM-MAS

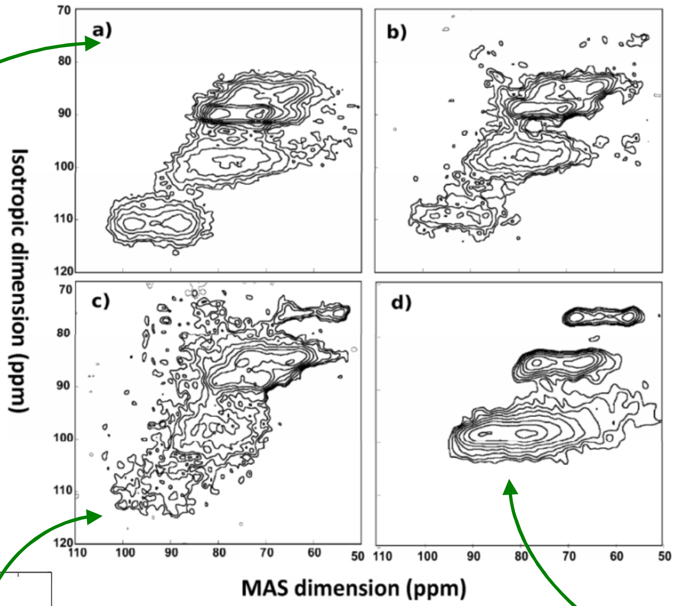
$^{17}O/^{31}P$ 3Q-SPAM-INEPT

Identification & Quantification of $NaPO_3$ hydration products through spectra simulations.

(Coll. T. Charpentier, CEA Saclay)

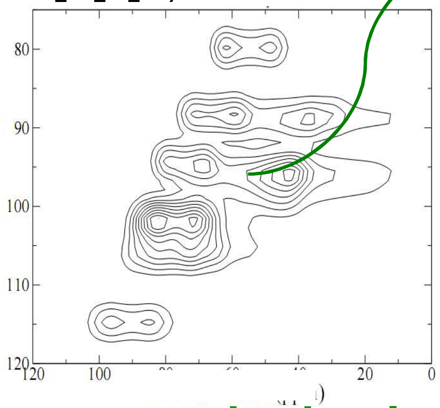


50 % NaH_2PO_4-H_2O
50 % $Na_2H_2P_2O_7$

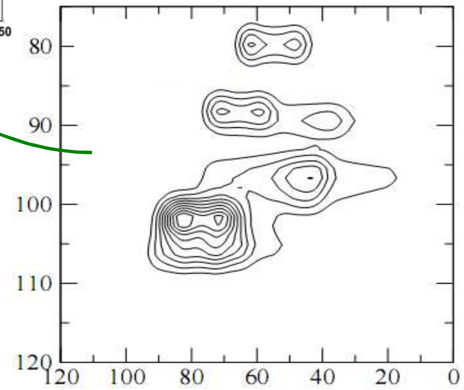


^{17}O 3QMAS NMR at 18.8T

50 % NaH_2PO_4
50 % $Na_2H_2P_2O_7$



33% NaH_2PO_4
33% NaH_2PO_4-H_2O
33% $Na_2H_2P_2O_7$



- Weathering leads to monomers and short phosphate chains.
- Modelisation enables quantification (kinetic study)

Phosphate glasses: applications

Phosphate glasses

Mixed network phosphate glasses

- *Water softening*
- *biomaterials*
- *sealing glasses*
- *Photonic glasses, laser glasses*
- *Electrolyte glass*
- *Anti-oxidation coatings*
- *Nuclear waste vitrification*

Water softening

Biomaterials

Sealing glasses

Laser glasses

Waste storage

Anti-oxidation coating


"To stop glasses becoming cloudy in the dishwasher, add glass."
Hard water in dishwashers can cause limescale build-up on glasses. This can be removed with salt and rinse-aid. Soft water can cause glass corrosion. This can't be removed but at least it can now be prevented.


Calgonit


Apart from water softness, glass corrosion depends on the glass, the temperature and cleanliness of the water, the length of the cycle and the type of dirt. Preventing further corrosion depends on us.

UCCS

Acknowledgements

EC and French institutions for NMR and projects fundings

F.E.D.E.R.

Région Nord-Pas de Calais

cnrs dépasser les frontières

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AGENCE NATIONALE DE LA RECHERCHE ANR

IFCPAR for project funding #4008-1

The glass & NMR group