Durabilité aqueuse des verres de phosphates
Concepts et applications

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Phosphate glasses: applications

- Water softening (Calgon)

- biomaterials

- sealing glasses

- Photonic glasses, laser glasses

- Electrolyte glass

- Anti-oxidation coatings

- Nuclear waste vitrification

Biomaterials

Sealing glasses

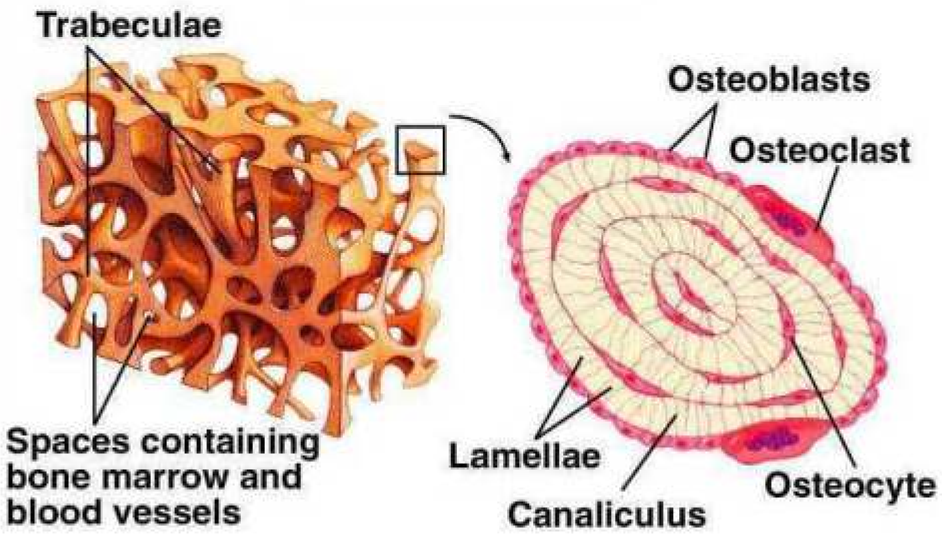
Laser glasses

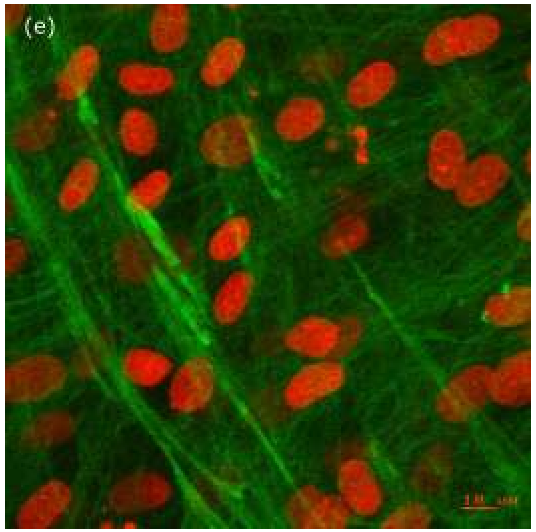
Waste storage

Anti-oxidation coating

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



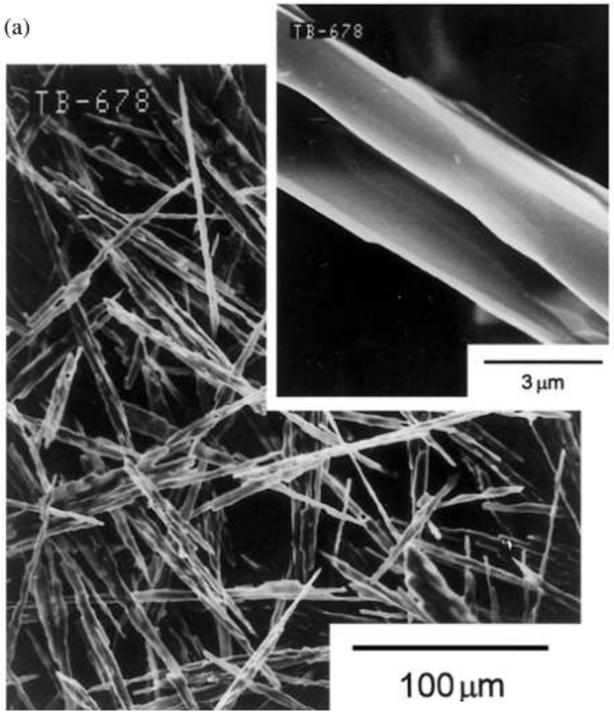


Knowles Acta Biomaterialia (2012)

Phosphate glass-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)



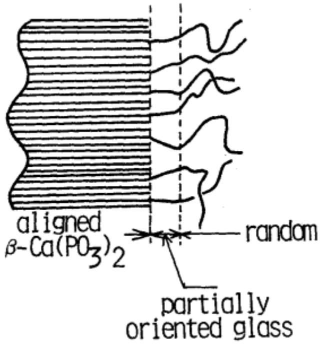


Figure 1 Schematic presentation of extended-chain crystallization model for $Ca(PO_3)_2$ glass (– indicates molecular chain of condensed phosphate).

Abe et al Nature (1989)

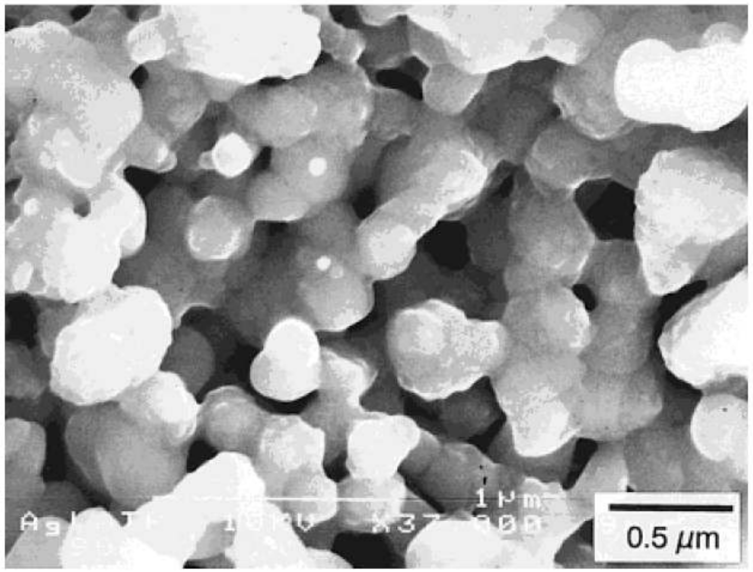


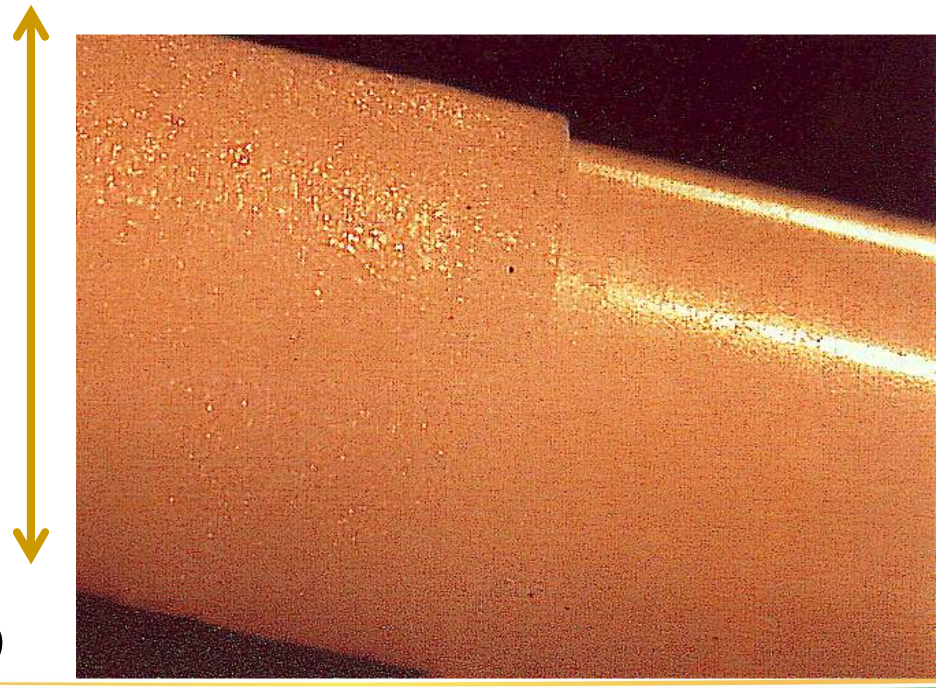
Fig. 5. SEM photos of porous glass-ceramic Ag-LATP heated at 900°C.

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

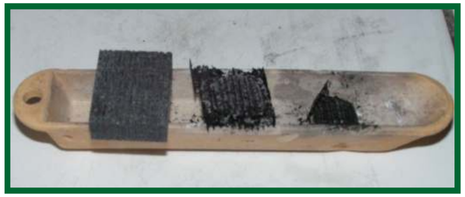
Ivandelko Völkenrode (2007)

Phosphates for aeronautic applications

- Alumino-phosphates as antioxydation coatings of C/C composites.

  E. Creton PhD Snecma (2009)

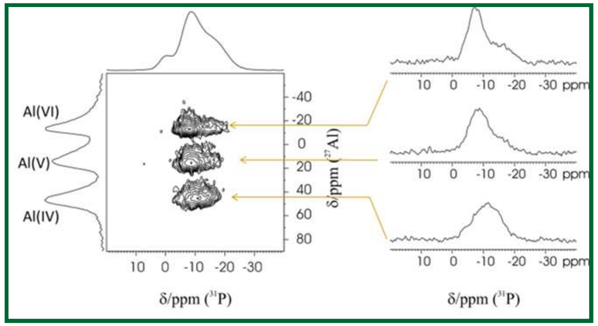
  A. Gatoux PhD Snecma (2013)



- Formulation of cosmetic enamels.

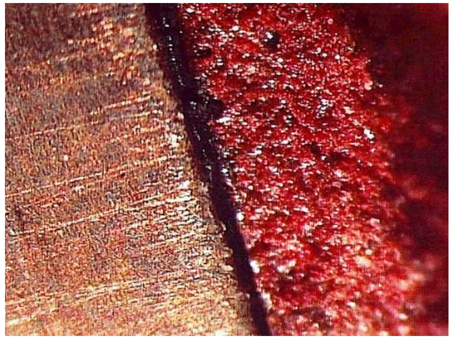
  S. Perez, Pdoc Snecma (2009-2011)

- Low Tg durable glasses : investigation of phosphate glass network through advanced NMR methods
  - P. Rajbandhari, PhD (2013)

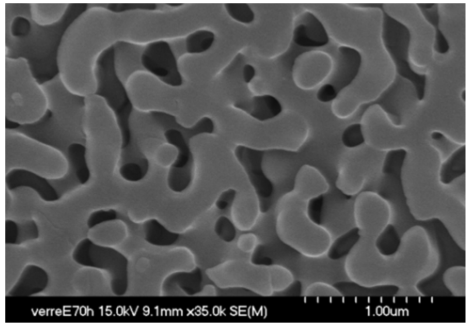


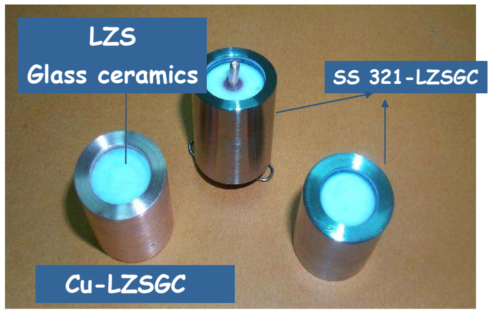
Sealing glasses for SOFC

- **Sealing of BiMeVOx to Stainless steel**
  - CTE#16-17.10^{-6}ppm.K^{-1}
  - Bi_2O_3 highly reactive
  - Formulation of Bi_2O_3-V_2O_5-P_2O_5 glass



- **P_2O_5-doped LZS, BAS, BCAS glass-ceramics**
  - G.P. Kothyial, (BARC, Mumbai) CEFIPRA (2009-2012)
  - NMR study of glass-ceramics



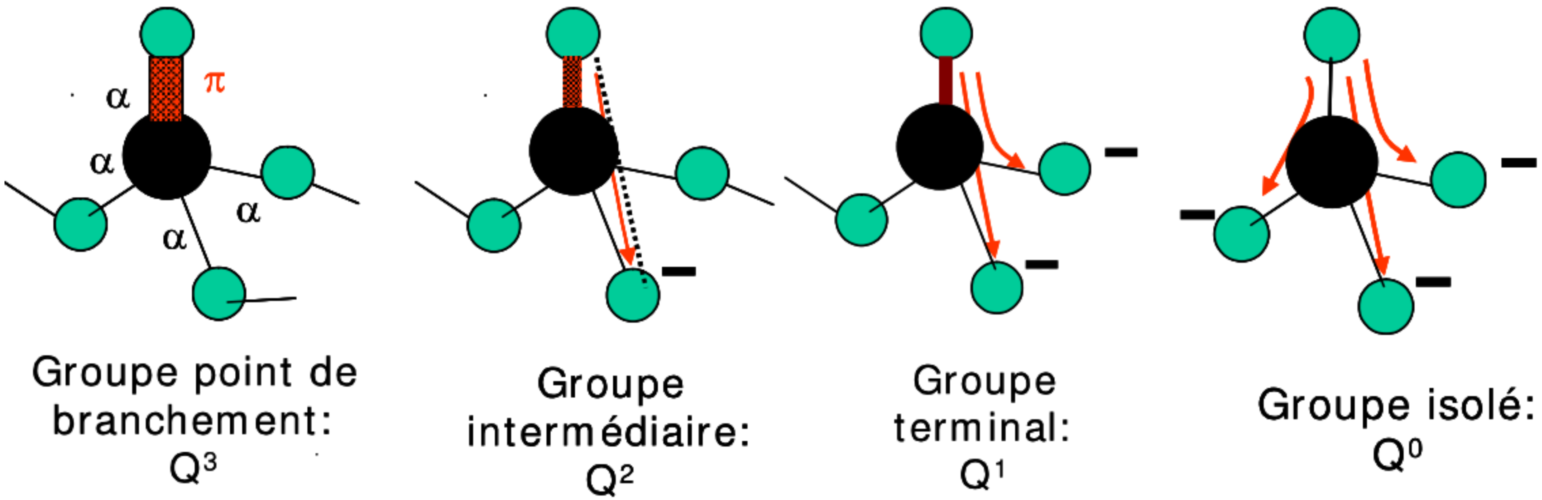


Verres de phosphates : quelques généralités

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 »

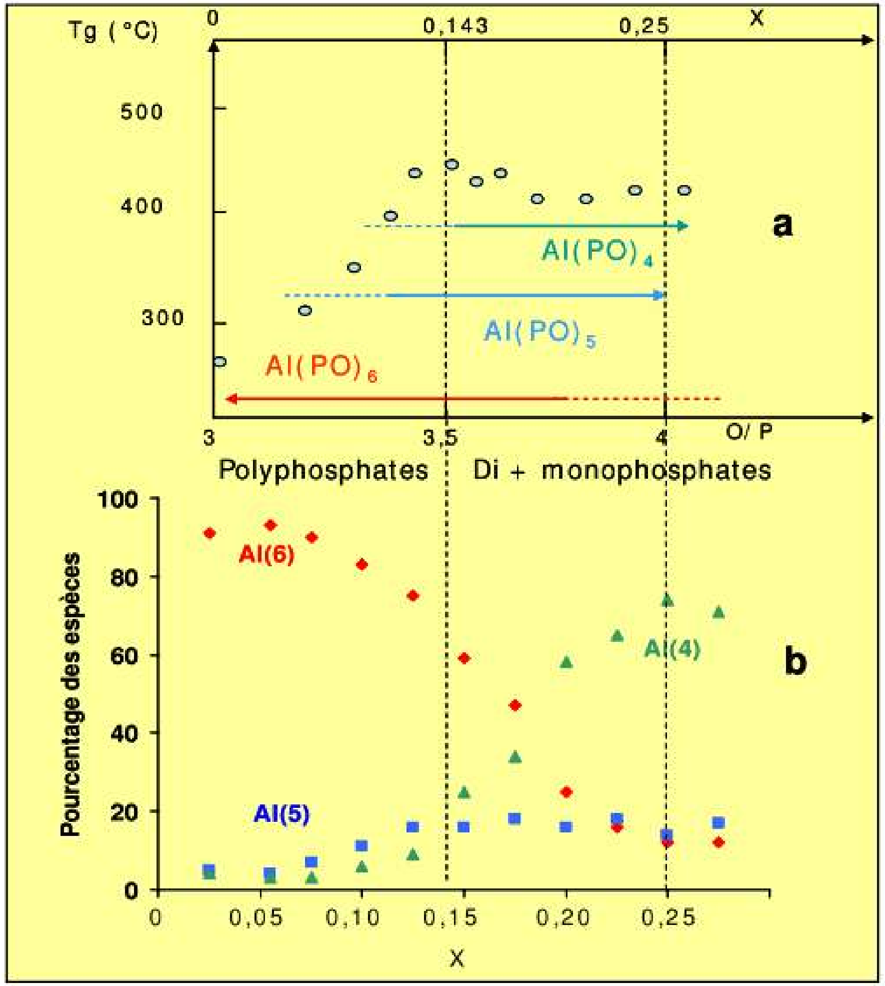


Videau, Le Flem (2010)

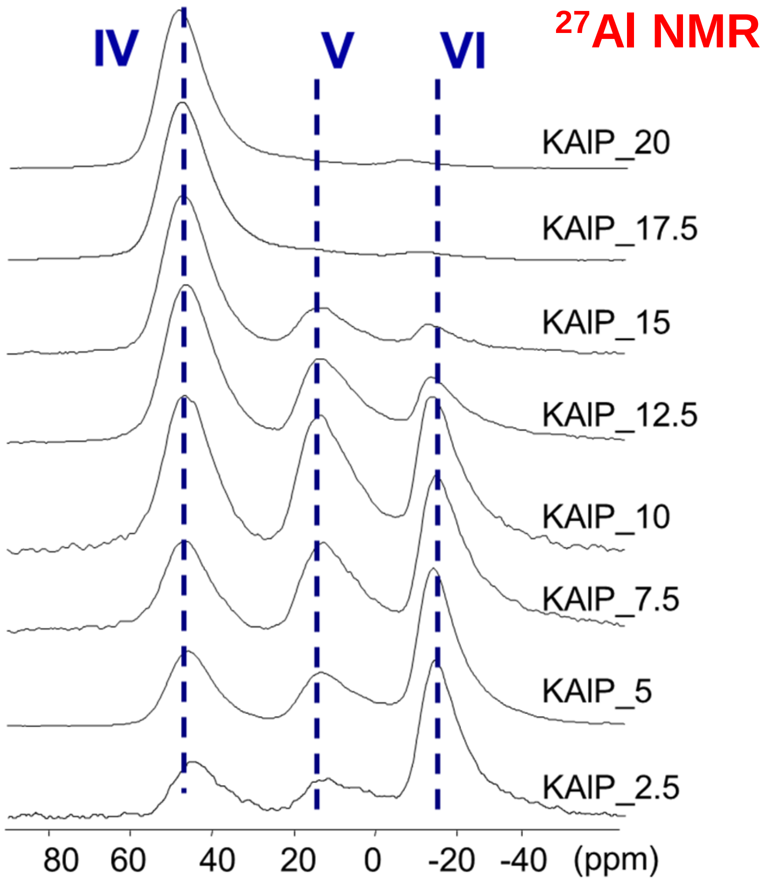
Verres de phosphates: caractéristiques chimiques

- 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

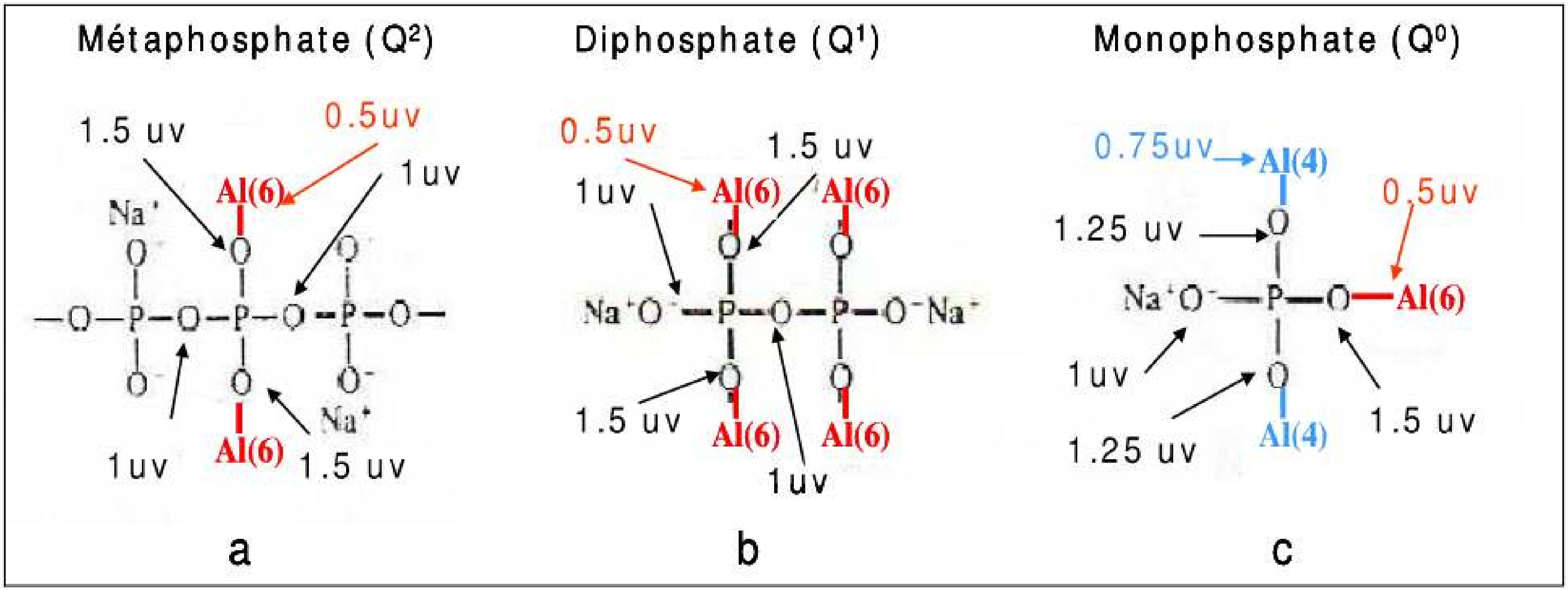


Brow JNCS (1990)



Van Wullen ss-nmr (2007)

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

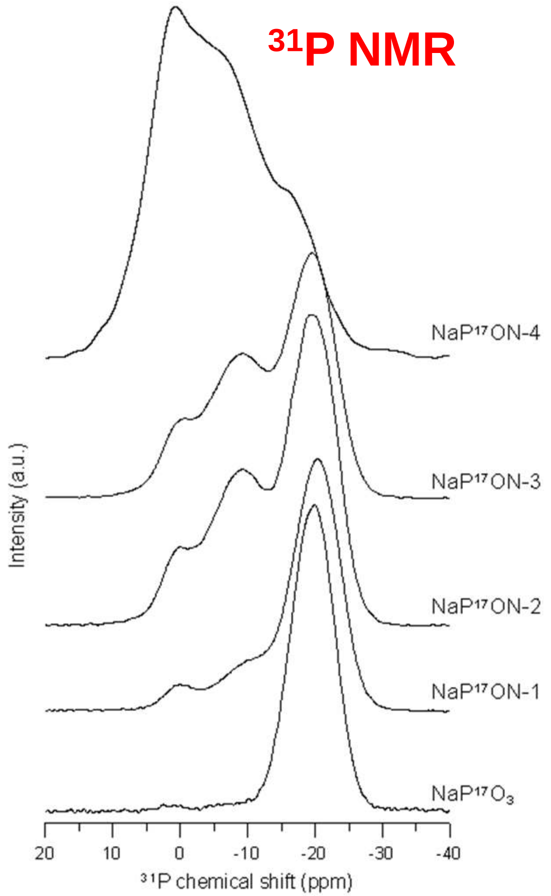


Phosphates à réseaux mixtes

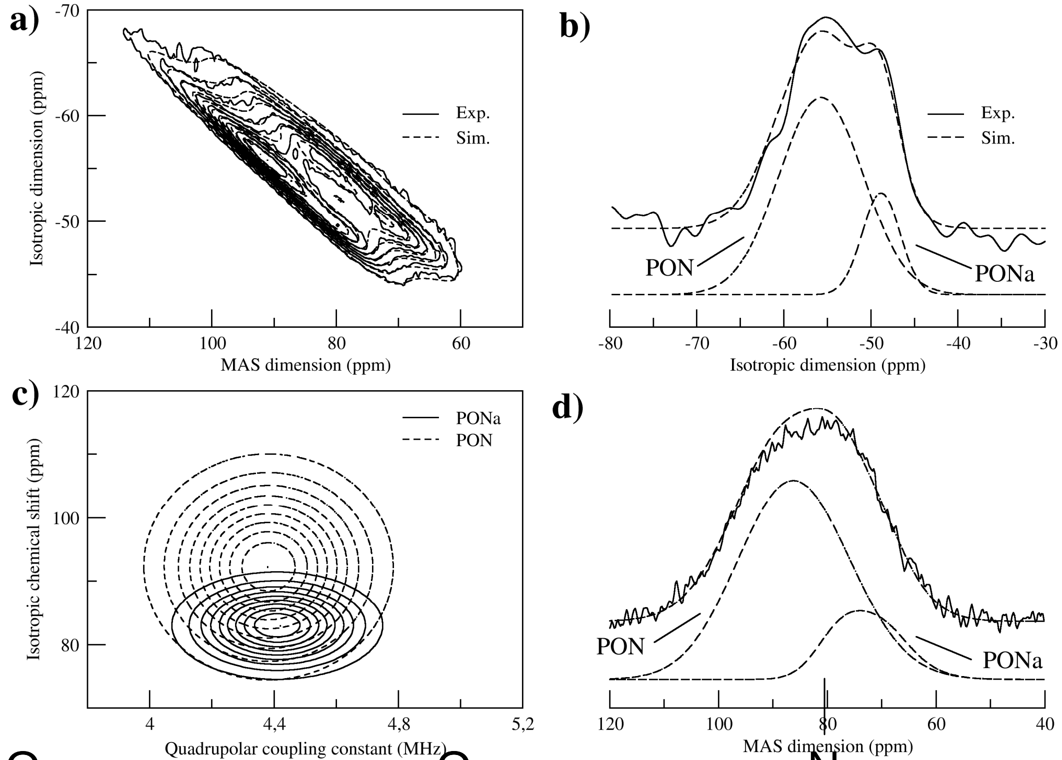
- Aluminophosphates
  - Scellement, anti-oxydation
- Borophosphates
  - Électrolytes batteries
- Niobiophosphates
  - Optique non-linéaire
- Vanadophosphates
  - électrolytes
- Phosphates de Zinc/Etain
  - Scellement, composites polymères
- Silicophosphates
  - Biomatériaux

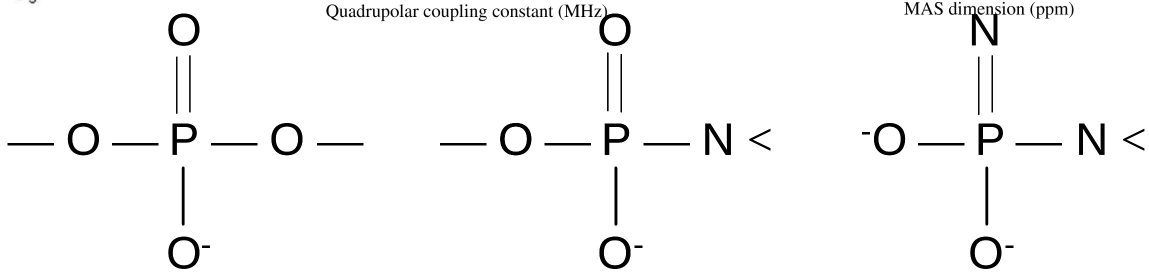
Oxynitride phosphate glasses: mixed anions glasses

^{31}P NMR



^{17}O NMR





PO_4 (Q^2)
BO/NBO = 0.5

PO_3N
BO/NBO = 0.25

PO_2N_2
BO/NBO = 0

Munoz JNCS (2013)

Improving chemical durability of phosphate glasses : increase of connectivity through N incorporation

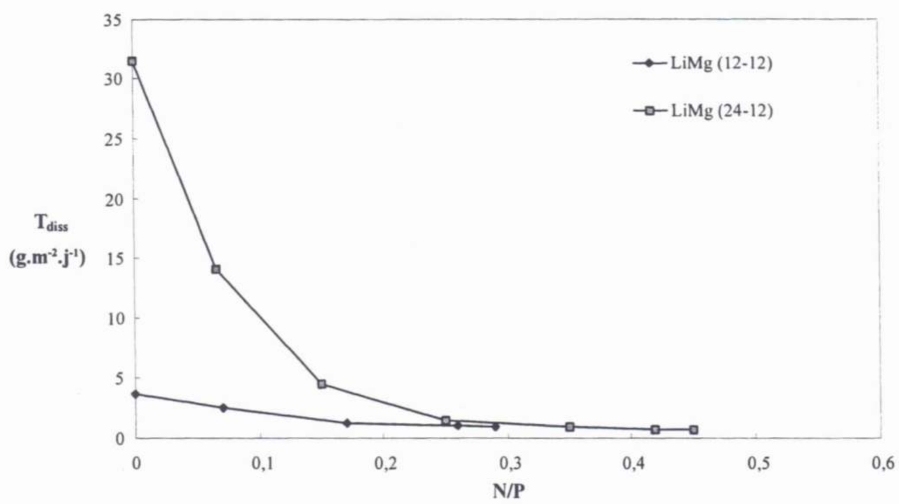


Figure III.23 : *évolution des taux de dissolution en soxhlet eau/100°C des verres issus de la nitruration sous ammoniac à 800°C des compositions oxydes LiMg(24-12) et LiMg(12-12)*

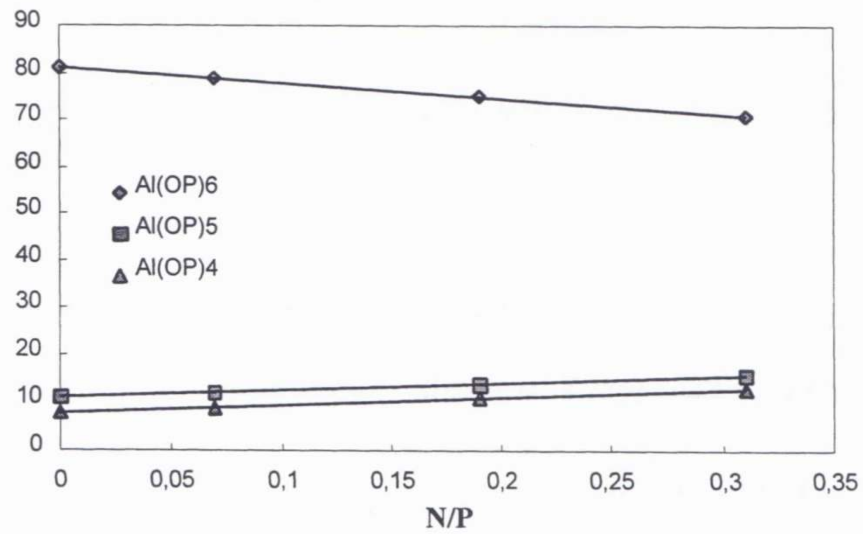


Figure III.19. : *évolution des proportions relatives des atomes d'aluminium en sites $Al(OP)_4$, $Al(OP)_5$ et $Al(OP)_6$ avec le rapport N/P*

G. Le Sauze, R. Marchand, ISCRennes

Improving chemical durability of phosphate glasses : increase of connectivity through N incorporation

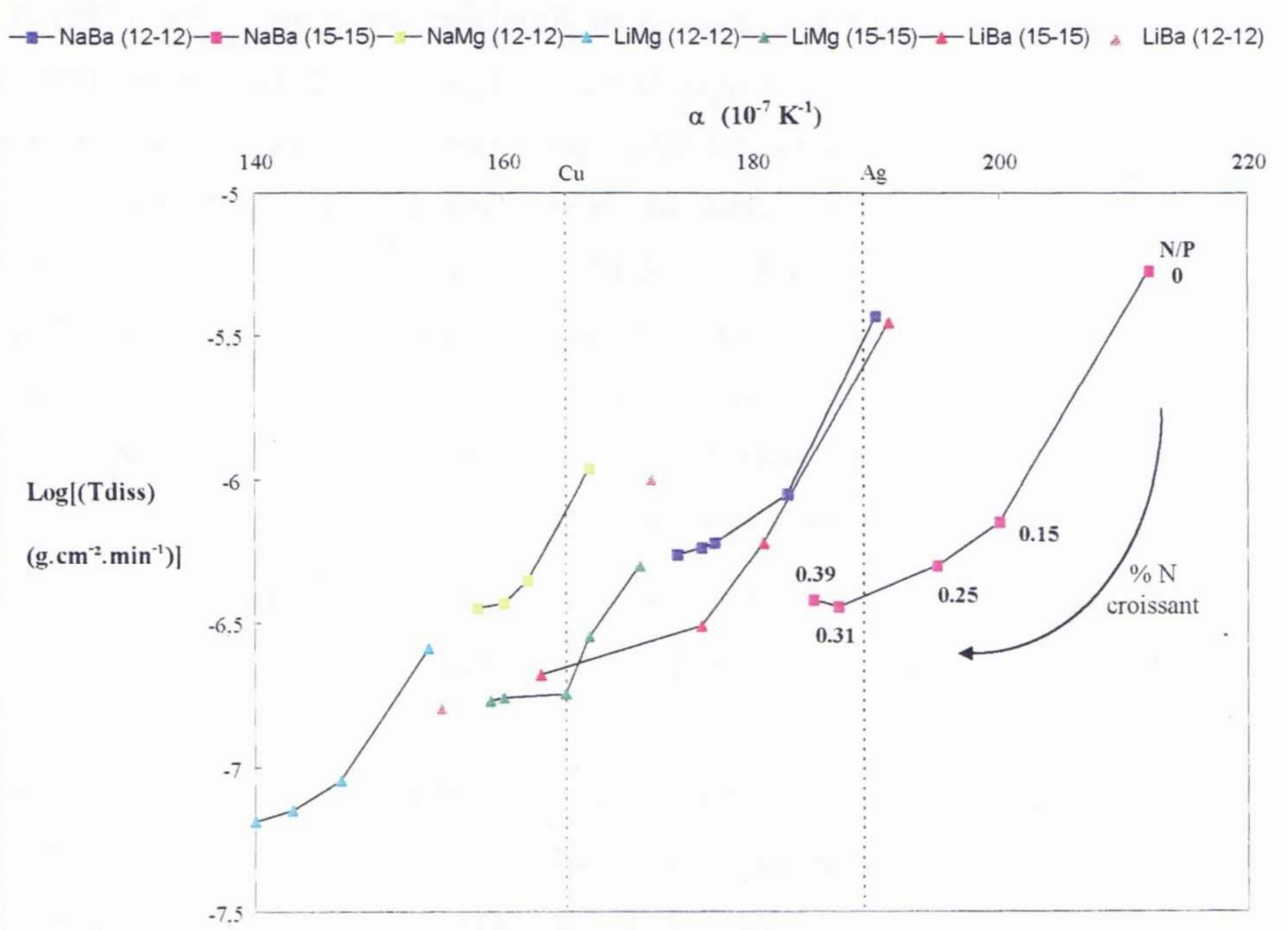


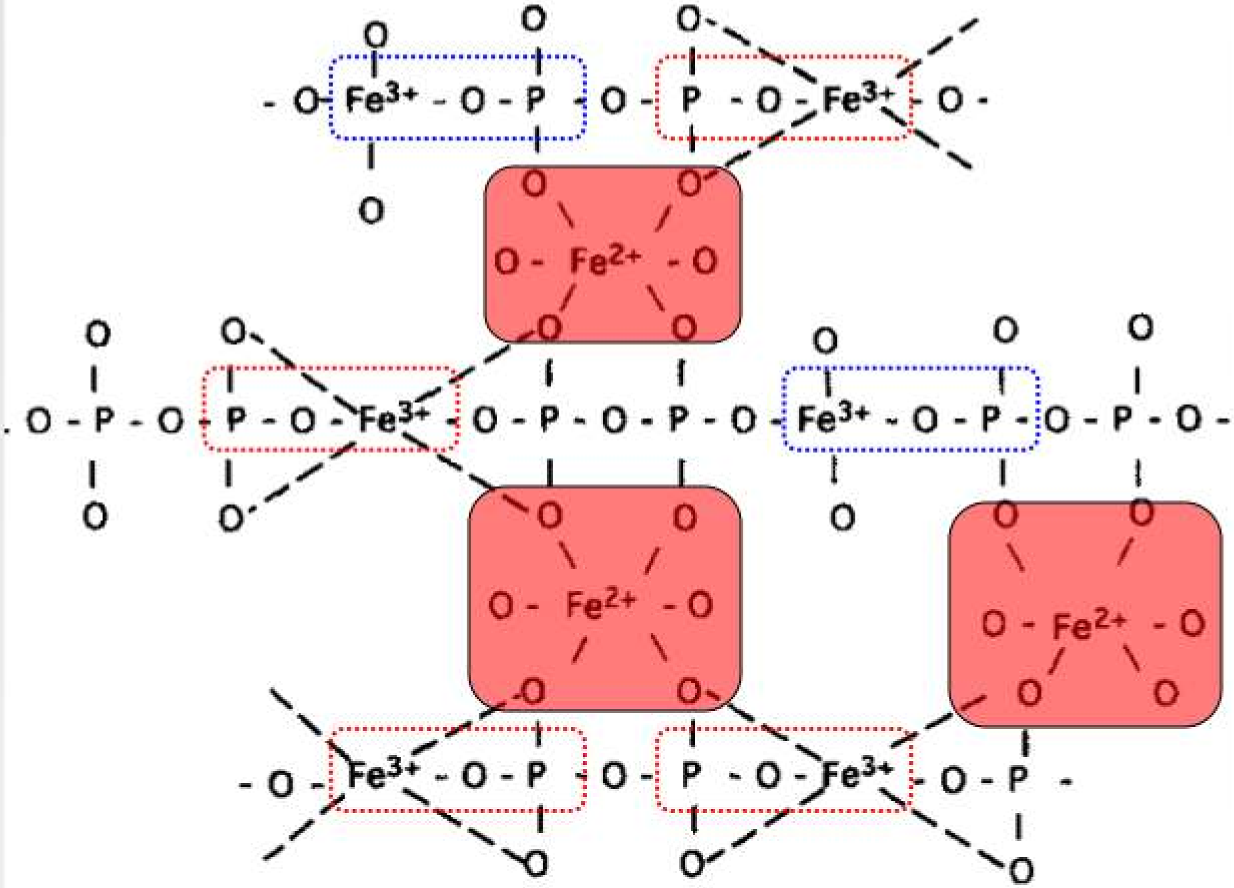
***Figure III.9.** : évolution du taux de dissolution (Tdiss) en fonction du coefficient de dilatation thermique (α) pour des verres azotés de phosphates issus de la nitruration sous ammoniac de précurseurs oxydes du type R_2O - K_2O - $R'O$ - Al_2O_3 - P_2O_5.*

G. Le Sauze,
R. Marchand,
ISCRennes

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

Iron increases Network connectivity



1) Low melting *T*: ~900-1100 °C; 2) High waste loading;

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

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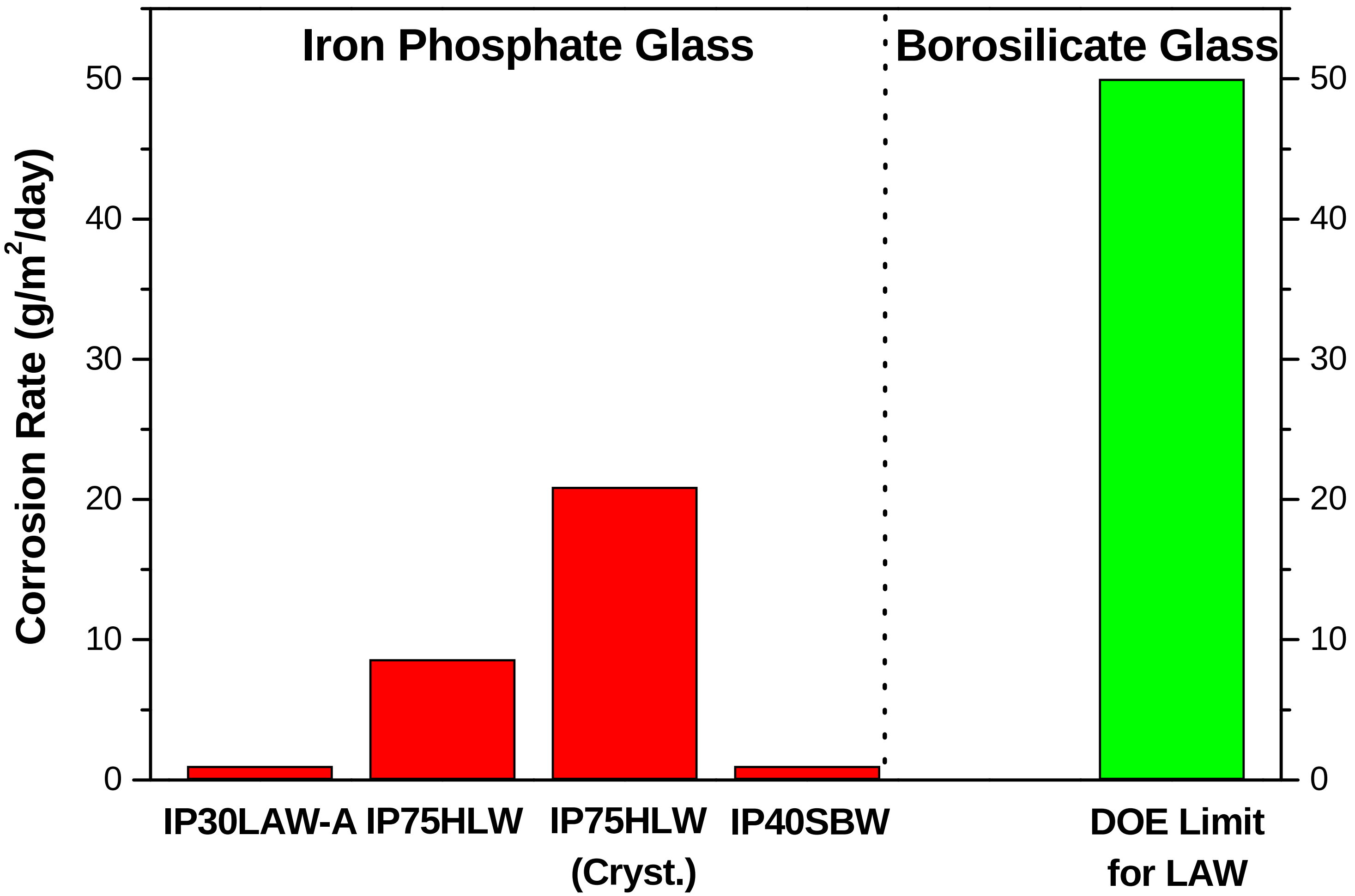
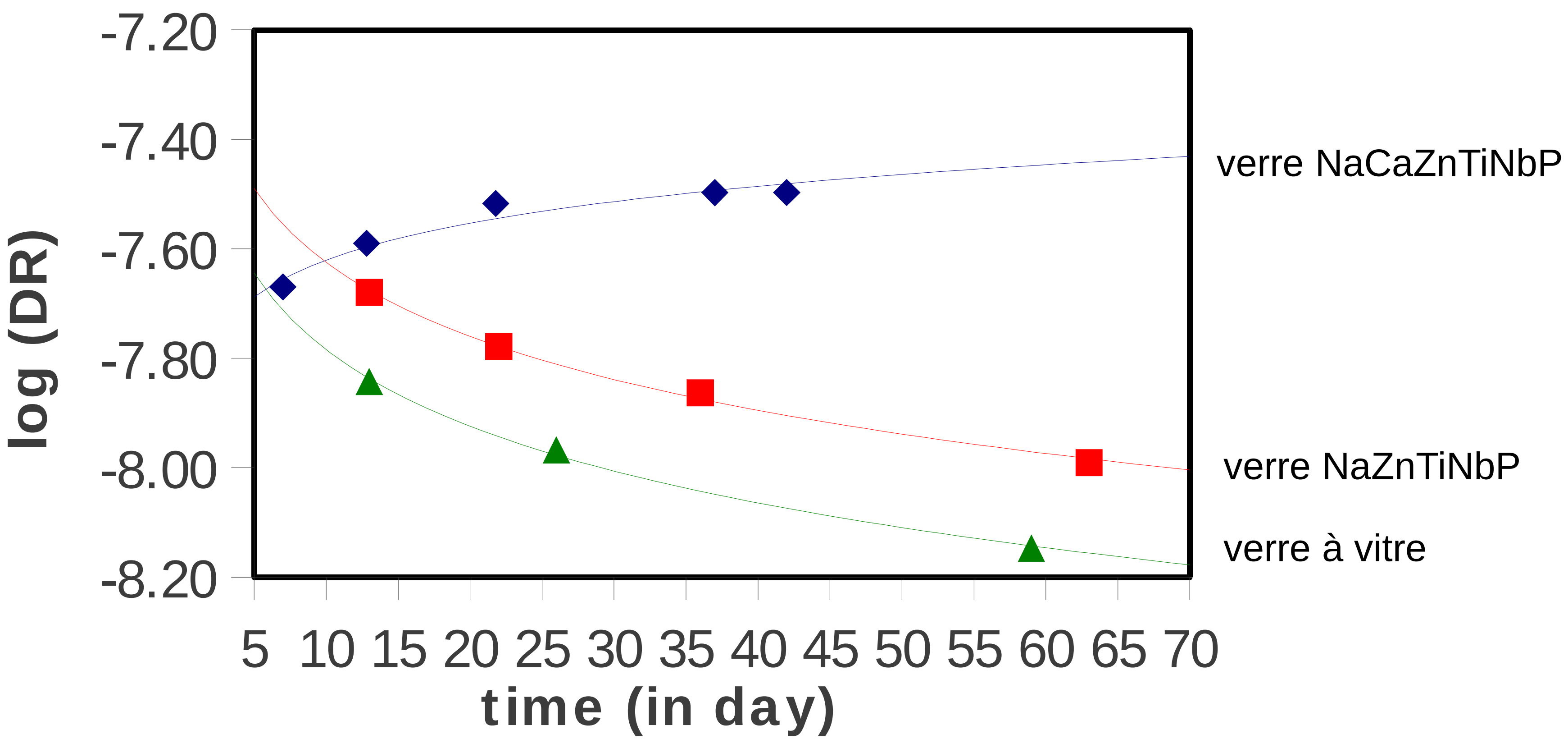
X. Yu *et al.*, *J. Non-Cryst. Solids* 215, (1997) 21.

IP glasses exhibit outstanding durabilities

Vapor Hydration Test (VHT)



Augmentation de la connectivité par Nb^{5+} et Ti^{4+}



J. Rocherulle, ISC-Rennes

Immobilization of Radioactive iodine in phosphate glasses

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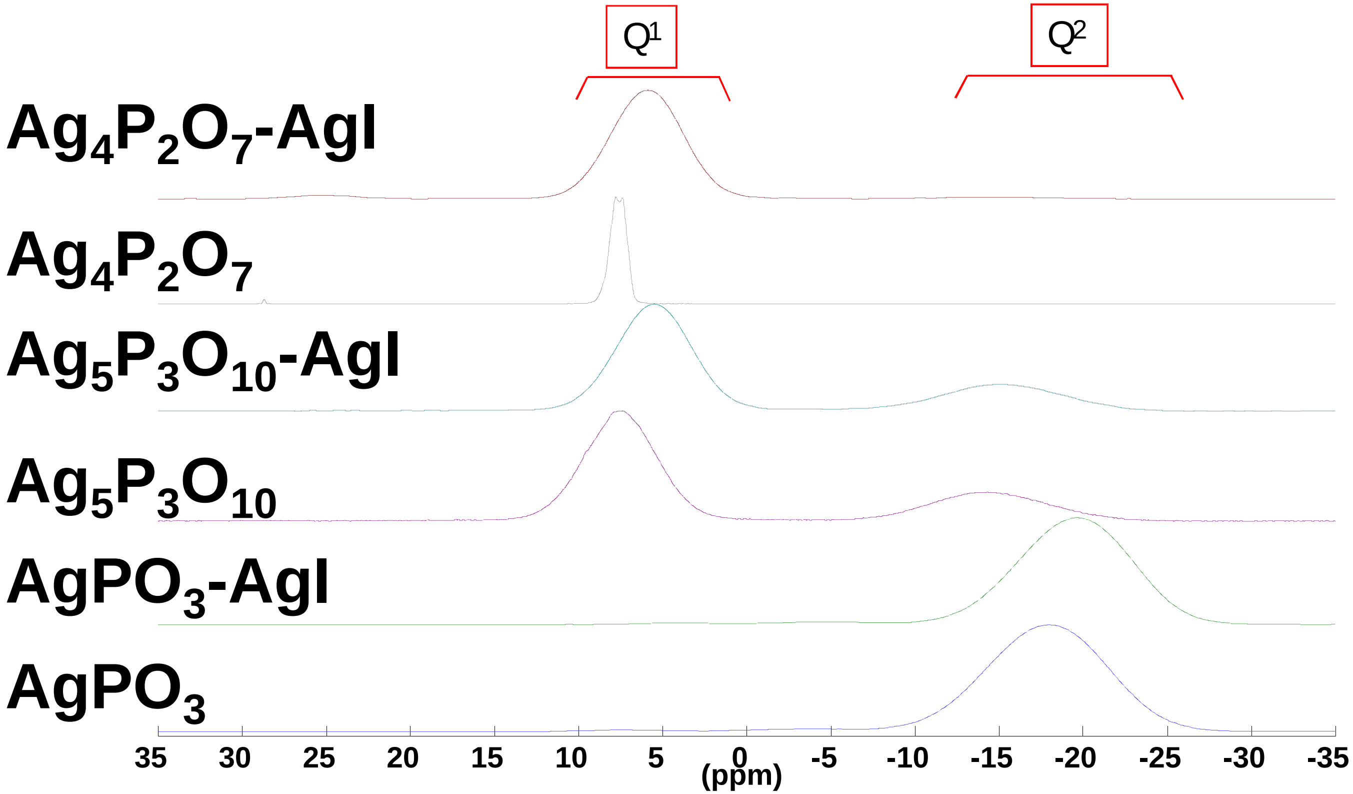
30207 Bagnols sur Cèze, France

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)

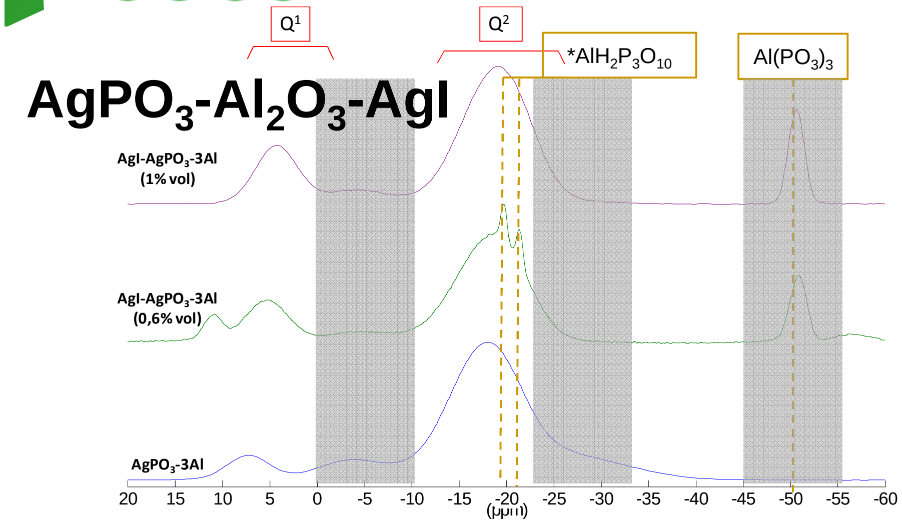
- Silver phosphate glasses
  - Low melting T
  - High incorporation rate for I

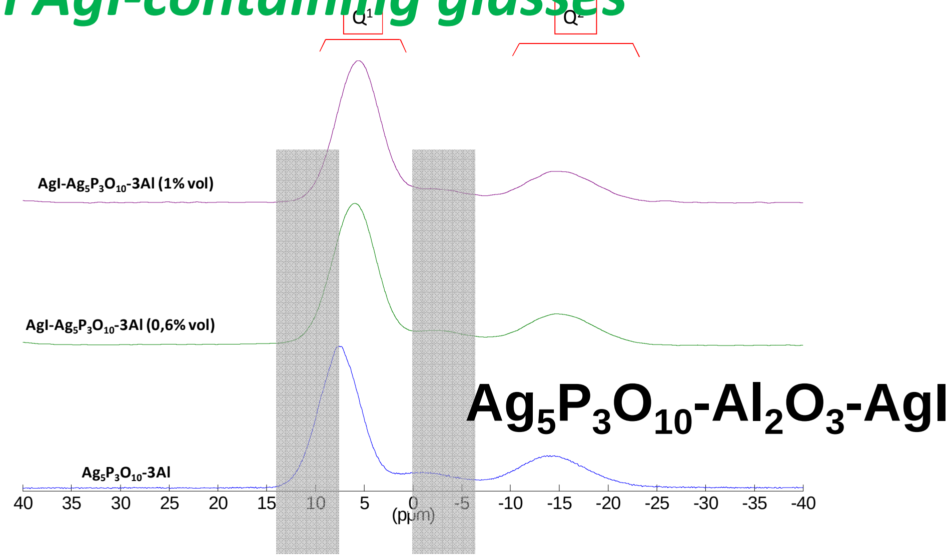
Influence of the incorporation of AgI on the structure as a function of Ag/P by ^{31}P NMR

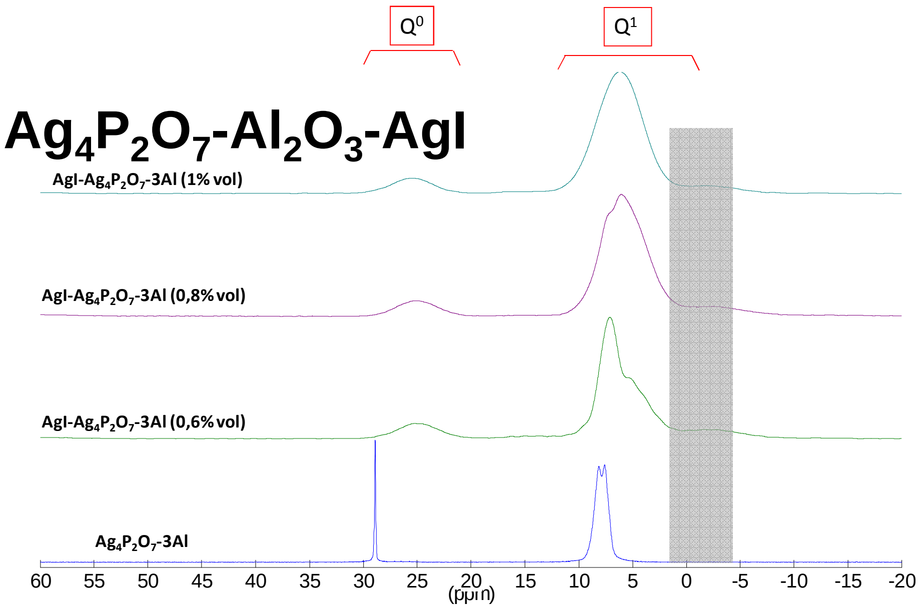


Addition of AgI for different ratios of Ag/P changes the chemical shift: modification of angles and bond length in phosphate network

Influence of Al_2O_3 on AgI-containing glasses







^{31}P NMR:

- $AgPO_3$: formation of $Al(PO_3)_3$ crystals
- $Ag_5P_3O_{10}$: larger compatibility
- $Ag_4P_2O_7$: increase of vitrification range

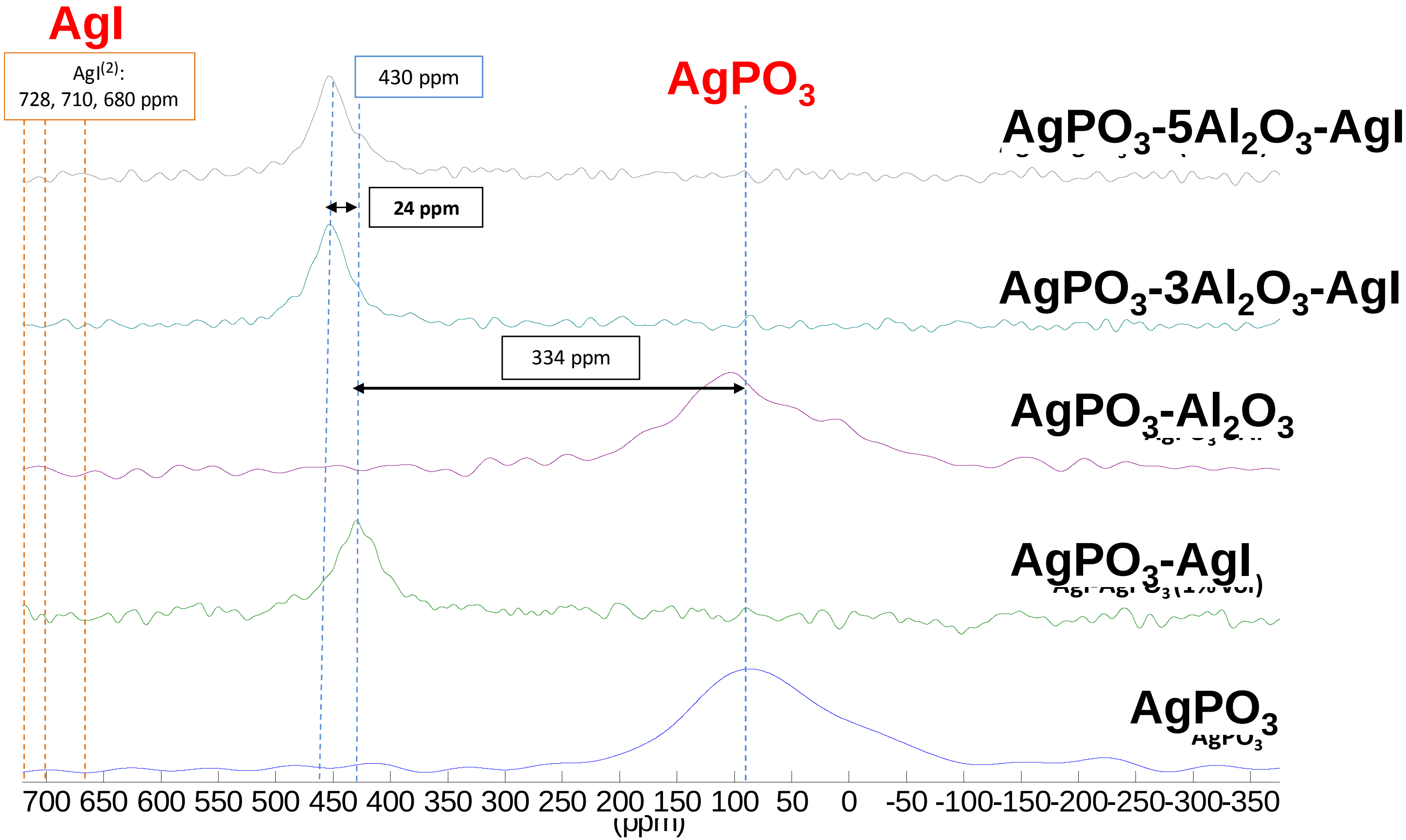
^{109}Ag NMR

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

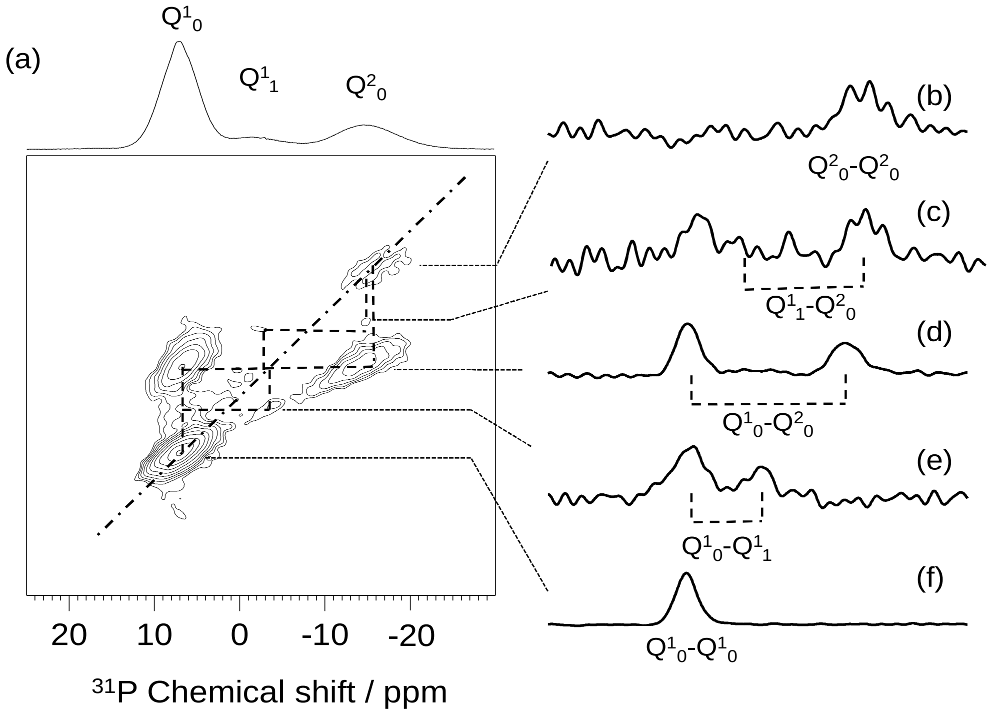
[2]Mustarelli et al., 1998

[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:
AgI does not modify network connectivity

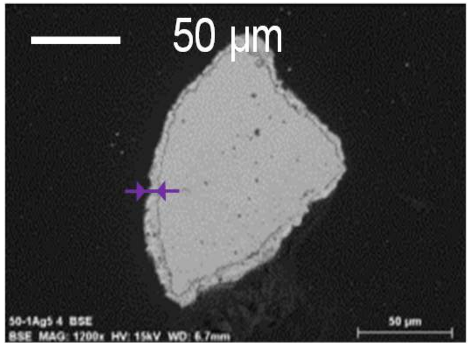
With AgI

Effet d'Al_2O_3

Durabilité

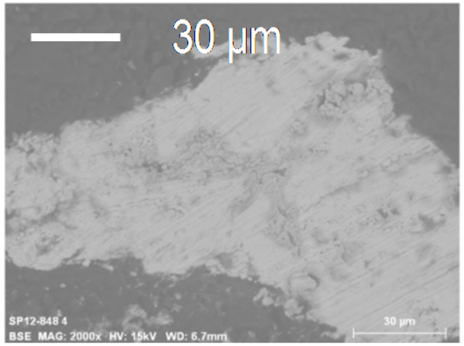
Statique	T=50℃	Eau pure

1I-$Ag_5P_3O_{10}$

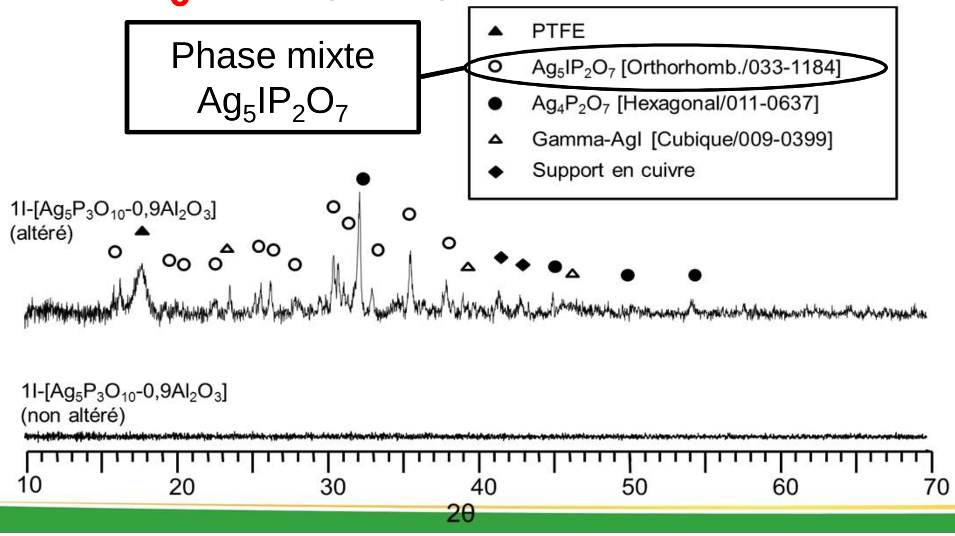


V_0 : 8,4 $g.m^{-2}.j^{-1}$

1I-[$Ag_5P_3O_{10}$-0,9Al_2O_3]



V_0 : 6,0 $g.m^{-2}.j^{-1}$



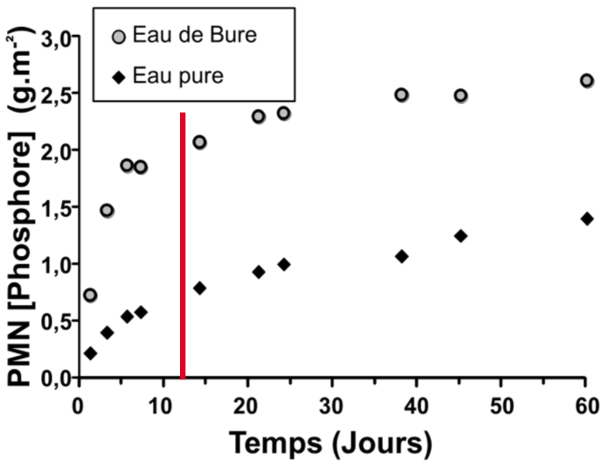
Avec Al_2O_3 :

Durabilité évolue peu

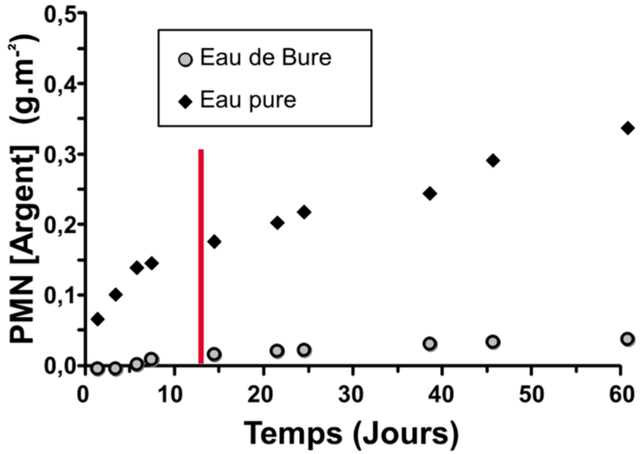
Verre $AgI\text{-}[Ag_5P_3O_{10}\text{-}0,9Al_2O_3]$: Test Statique-effets du milieu

S/V= 80 cm^{-1} | T= 50℃

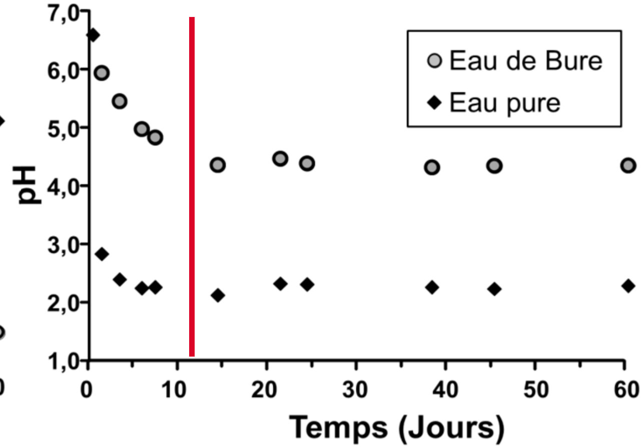
Phosphore



Argent



pH

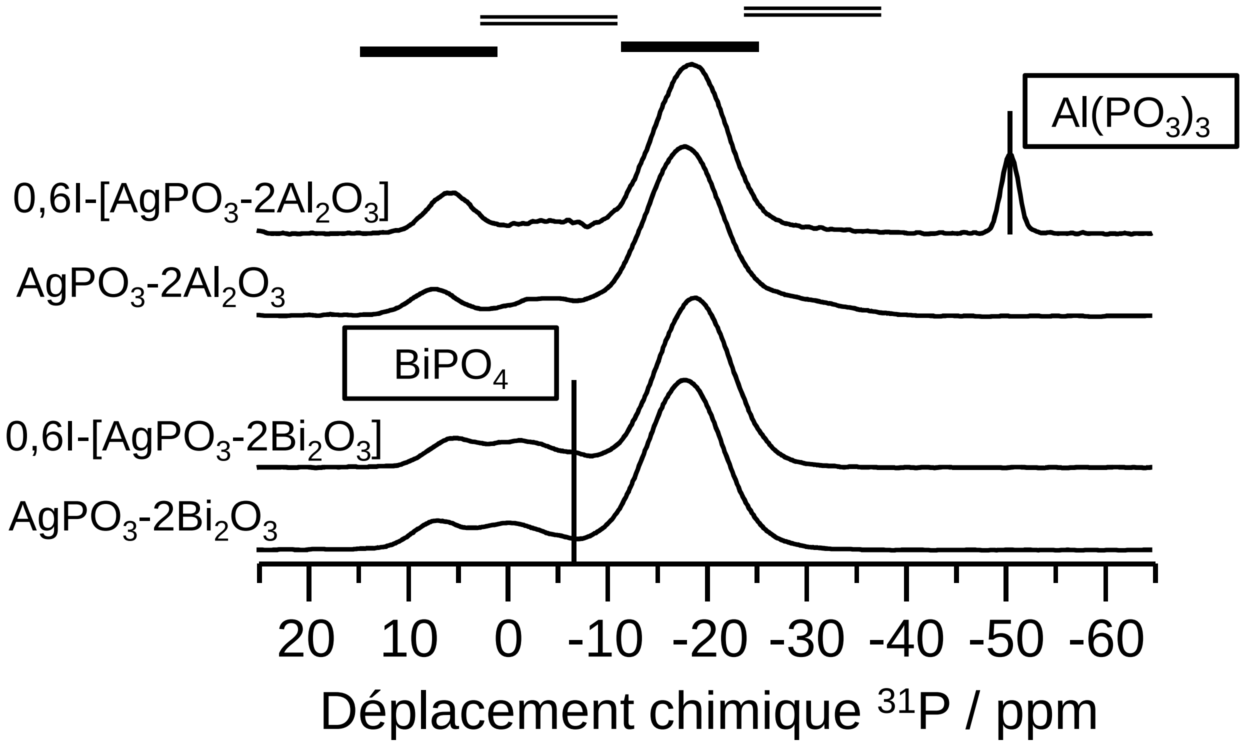


- Pénétration à cœur en 13 jours
- « Vitesse d'altération » du matériau néoformé : environ 10^{-2} $g.m^{-2}.j^{-1}$

		Pourcentage atomique élémentaire (% at.)				
		Ag	P	Al	I	O
Eau Pure	Avant	29,9	13,5	0,2	7,4	49,0
	Après	37,7	10,5	0,2	6,1	45,4
Eau de Bure	Avant	29,9	13,5	0,2	7,4	49,0
	Après	43,9	7,7	0,2	4,9	43,3

- Conservation de la majeure partie de l'iode au sein du matériau néoformé.
- Pas d'iode en solution
  - ← Acidité de la solution (eau pure)
  - ← *Rétention par des phases cristallisées (eau de Bure)*

Perspectives



Composition	T_g (°C)
1I-[$Ag_5P_3O_{10}$-Al_2O_3]	123
1I-[$Ag_5P_3O_{10}$-ZnO]	177

Verres de phosphates et d’aluminophosphates : mécanisme d’altération

$NaPO_3$ Hydration

^{17}O NMR @18.8T

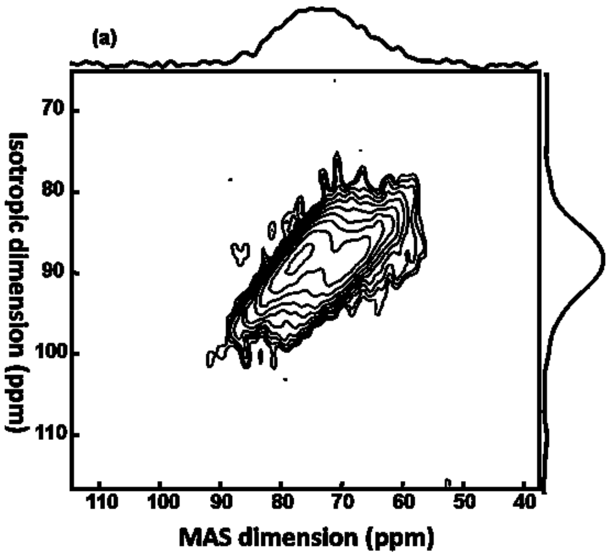
- **XRD** – 2 phases

NaH_2PO_4

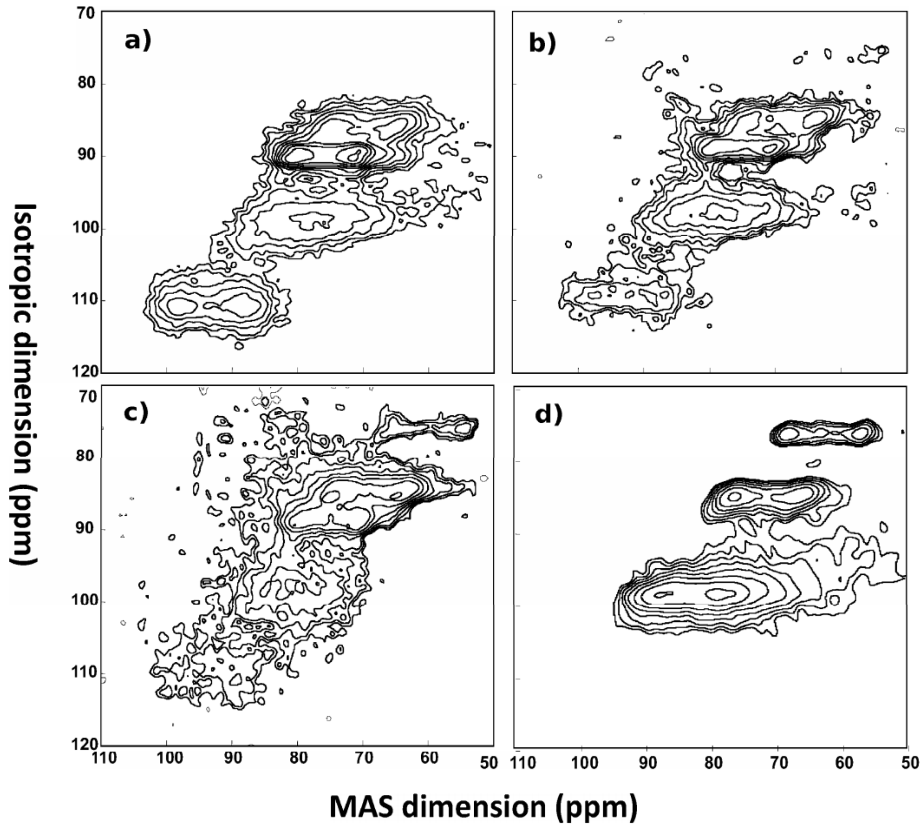
NaH_2PO_4-H_2O

- **^{31}P NMR**– 3 phases

$Na_2H_2P_2O_7$

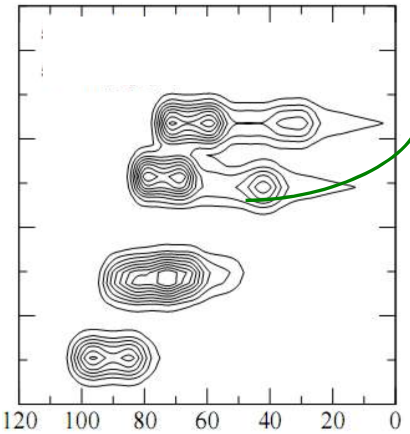


Hydration
=f(T, t, Rh)

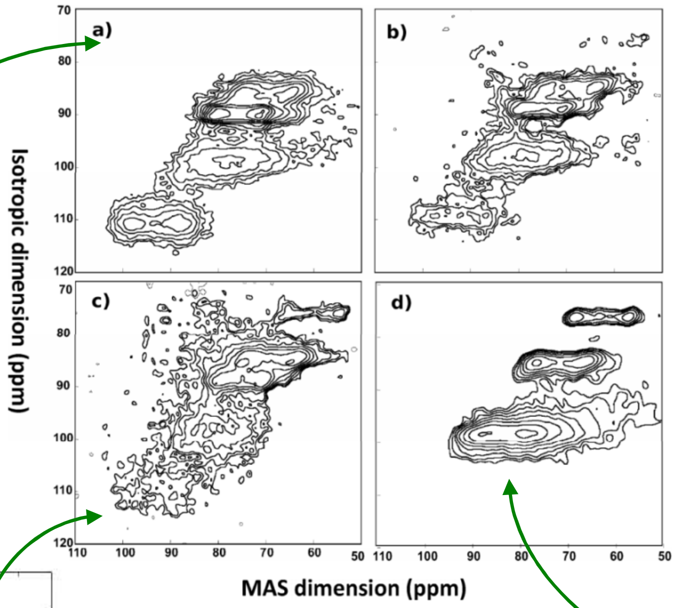


Identification & Quantification of $NaPO_3$ hydration products through spectra simulations.

(Coll. T. Charpentier, CEA Saclay)

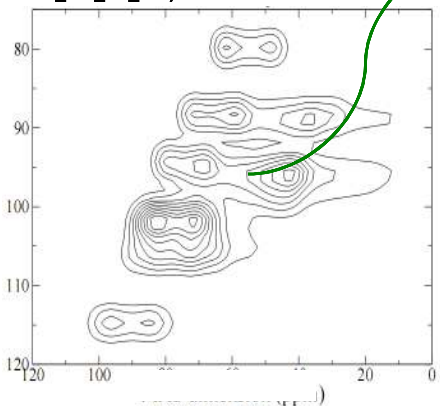


50 % NaH_2PO_4-H_2O
50 % $Na_2H_2P_2O_7$

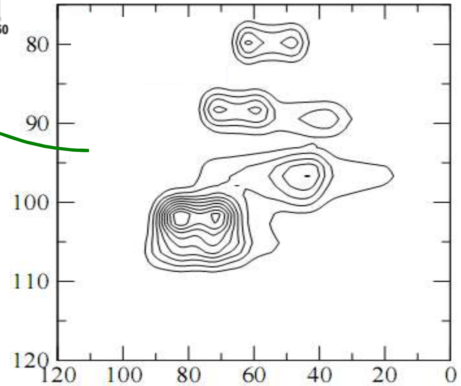


^{17}O 3QMAS NMR at 18.8T

50 % NaH_2PO_4
50 % $Na_2H_2P_2O_7$

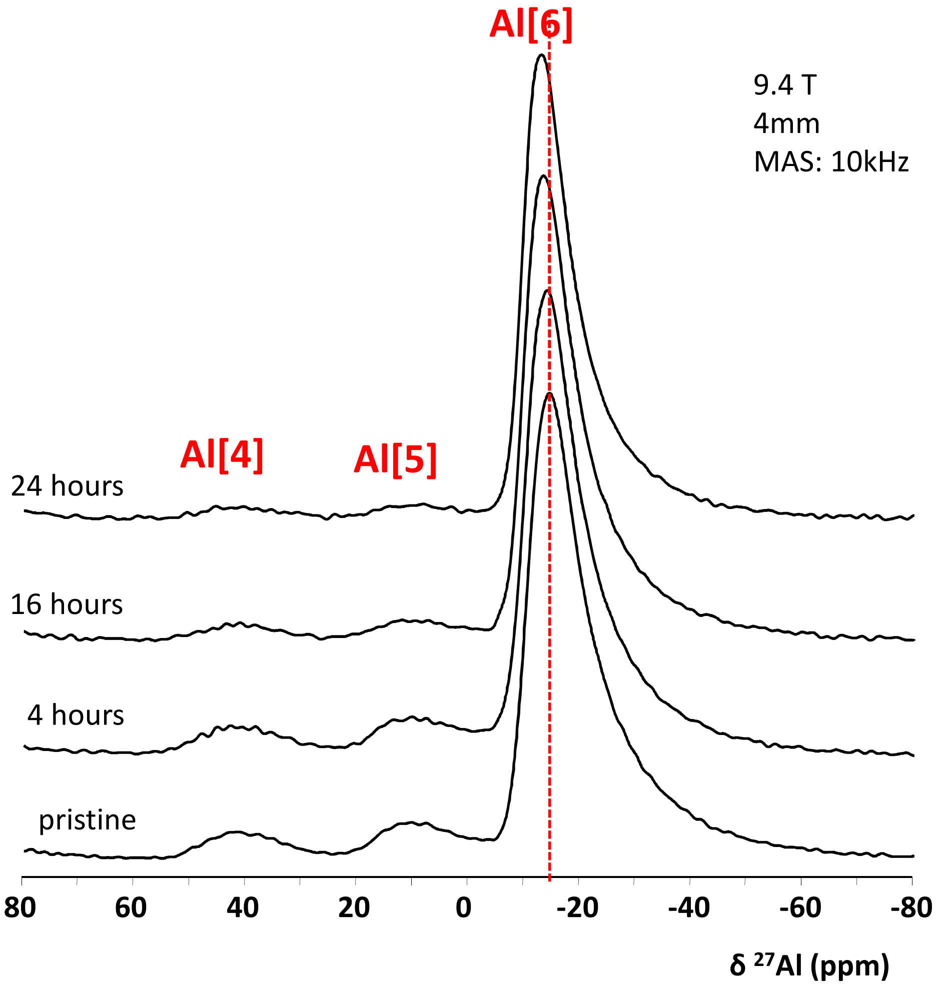


33% NaH_2PO_4
33% NaH_2PO_4-H_2O
33% $Na_2H_2P_2O_7$



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

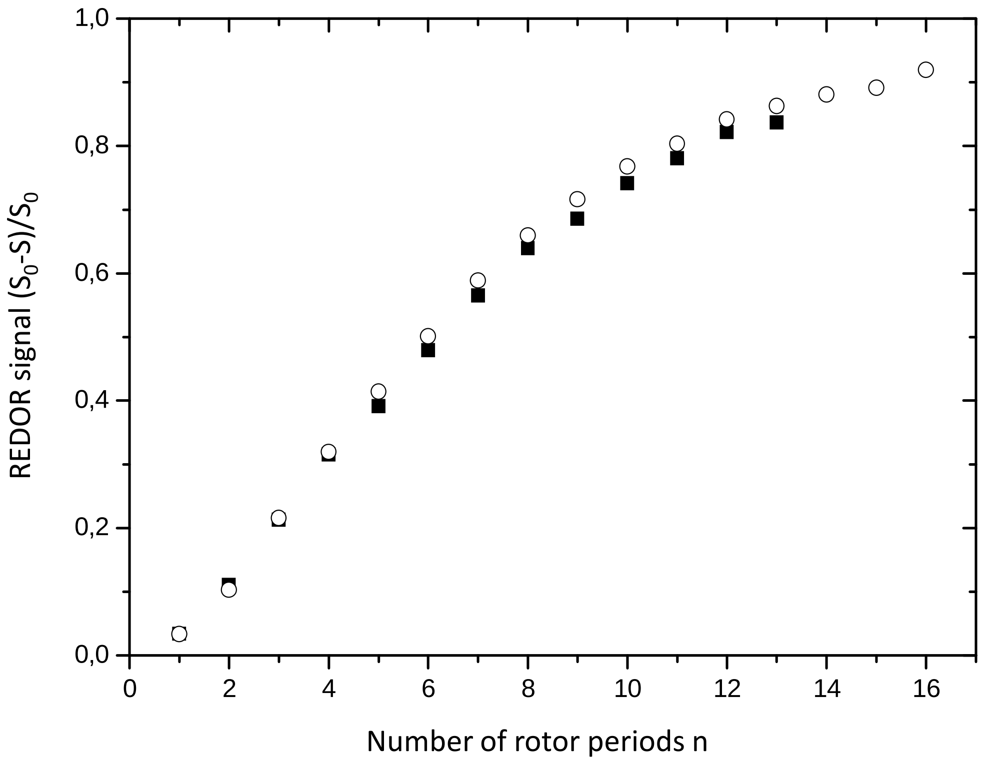
1D ^{27}Al NMR



➢ **With increasing weathering time, Al[6] fraction increases, Al[4] and Al[5] decrease.**

Probing spatial proximity between ^{31}P and ^{27}Al in weathered glass

^{27}Al-{^{31}P} REDOR evaluates the distance and the number of nearby nuclei between $^{27}Al(6)$ and ^{31}P by measuring the strength of dipolar coupling.

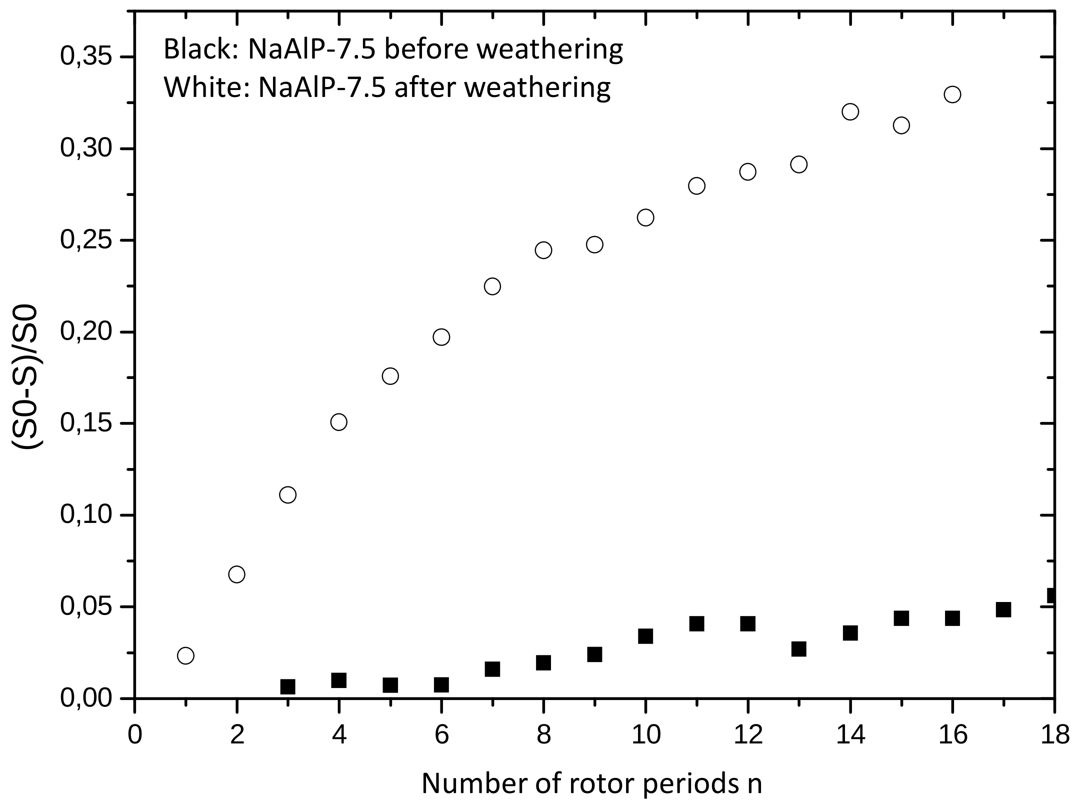


Black circles: before weathering, White circles: after 24h weathering

- **No decrease in Al(6)-O-P network polymerization in the glass throughout weathering.**

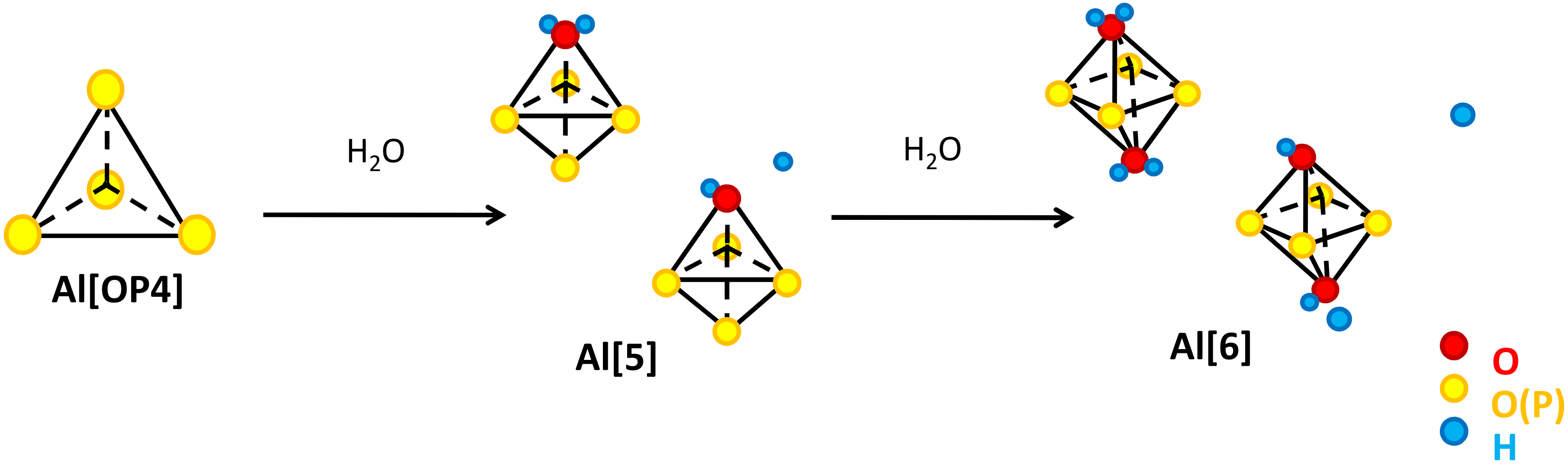
Al[6] fraction increase: ^{27}Al[6] REDOR curves

^{27}Al-{^{1}H} REDOR evaluates the distance and the number of nearby nuclei between ^{27}Al[6] and ^{1}H by measuring the strength of dipolar coupling.



- **Al[6] is strongly coupled to ^{1}H nuclei : hydration occurs on these sites**

Weathering mechanism of $Al(OP)_{4-6}$ sites



- Al[4] and Al[5] are transformed into Al[6] (1D ^{27}Al)
- Hydrated Al[6] sites are observed (^{1}H-^{27}Al HMQC)
- $Al(OP)_6$ connectivity is not modified (Redor)
- Formation of mixed $Al(OP)(OH)_6$ sites

Phosphate glasses: applications

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

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

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The glass & NMR group