Structure of Glassy Rare-Earth Alumino-Silicates: an NMR Point of View

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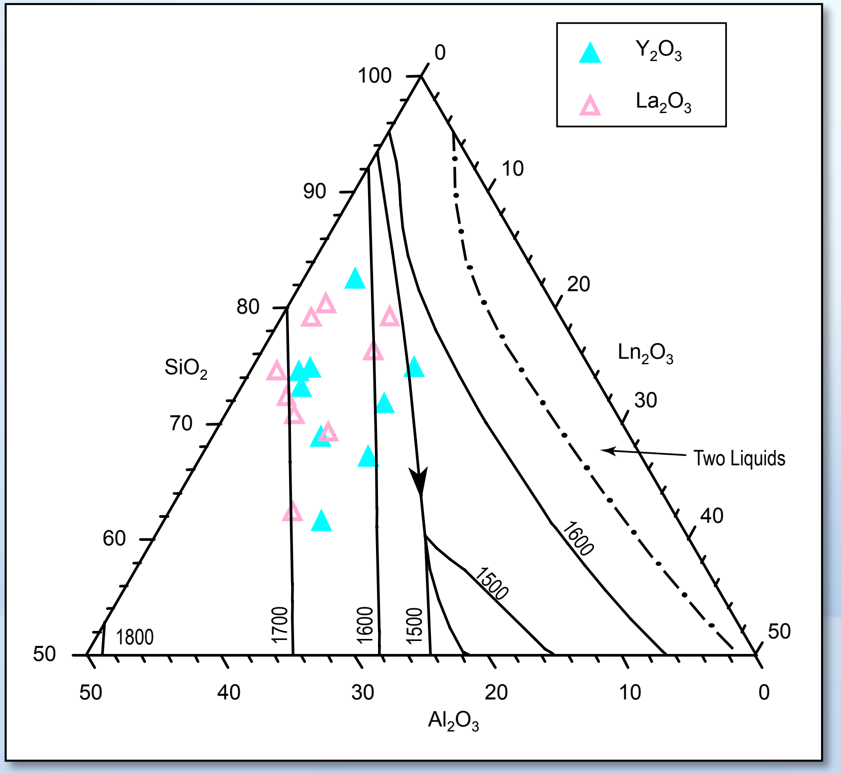
The RE_2O_3-Al_2O_3-SiO_2 ternary system



Mechanical properties:
- High T_g (~900°C)
- High Hardness (~8 GPa)
- High Elastic Moduly (~100 GPa)

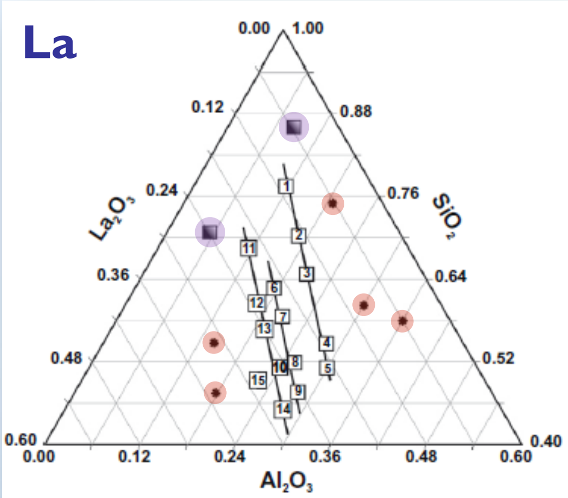
→ Corrosion resistant

Usable for:
- Nuclear waste holder
- Binding agent for SiN ceramics
- Microspheric glasses for radiotherapy
- Laser (e.g. optical device) matrices

^{27}Al NMR: Kohli *et al.*, *Phys. Chem. Glasses* **33** 73-78 (1992)
Clayden *et al.*, *J. Non Cryst. Solids* **258** 11-19 (1999)
Sen *et al.*, *J. Phys. Chem. B* **108** 7557-7564 (2004)
Marchi *et al.*, *J. Non Cryst. Solids* **351** 863-868 (2005)
Florian *et al.*, *J. Phys. Chem. B* **111** 9747-9757 (2007)
Iftekhar *et al.*, *J. Phys. Chem. C* (2012) **asap**

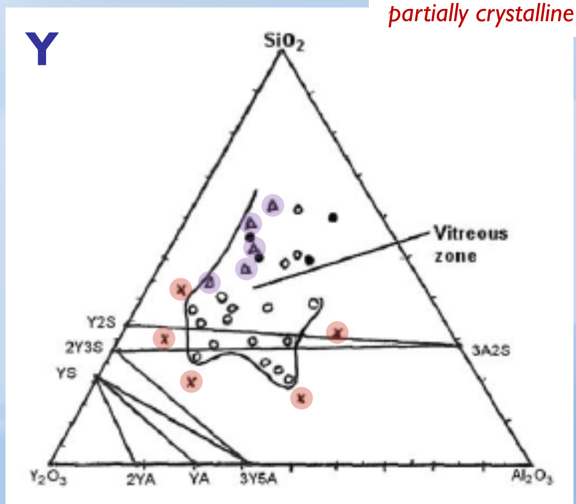
NMR Point of vue:
- ☞ **no paramagnetism**
- ☞ **no radioactivity**

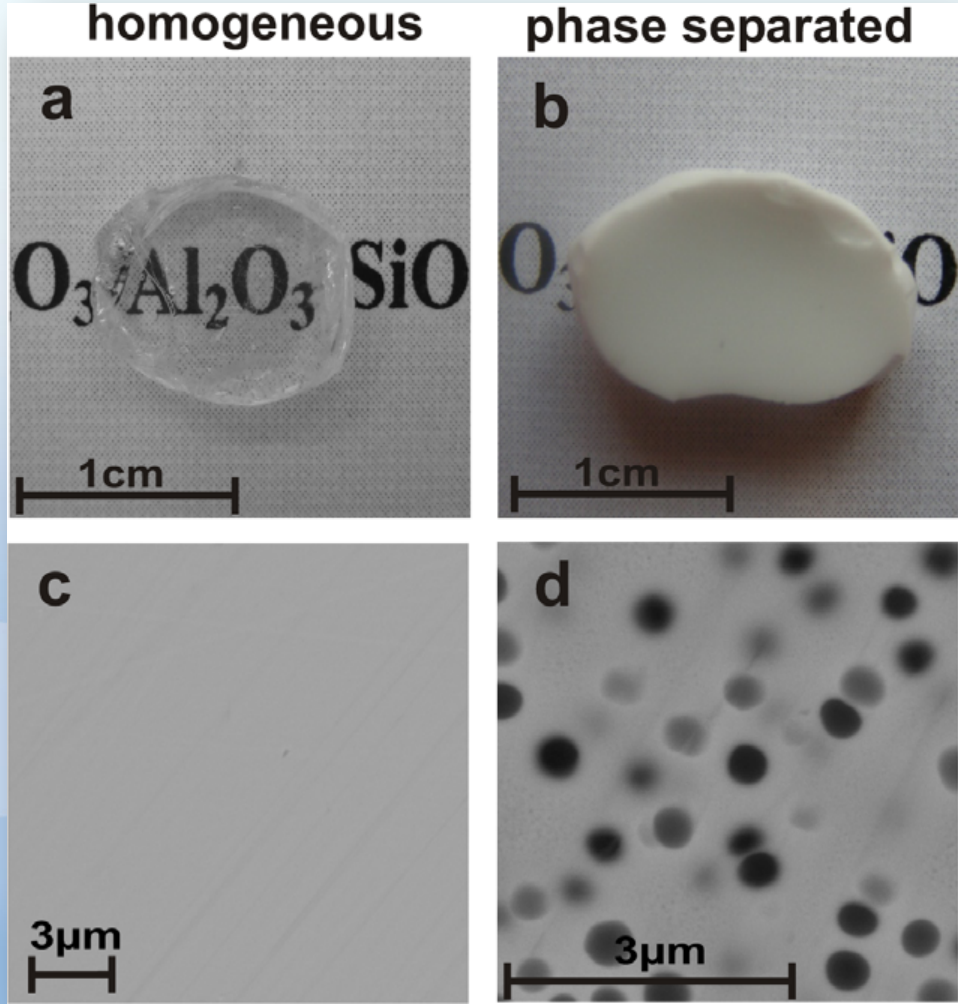
The RE_2O_3-Al_2O_3-SiO_2 ternary system



phase separated

partially crystalline





Iftekhar et al., J. Non Cryst. Solids ***356*** *1043 (2010)*
Sadiki et al., J. Nucl. Mat. ***348*** *70 (2006)*

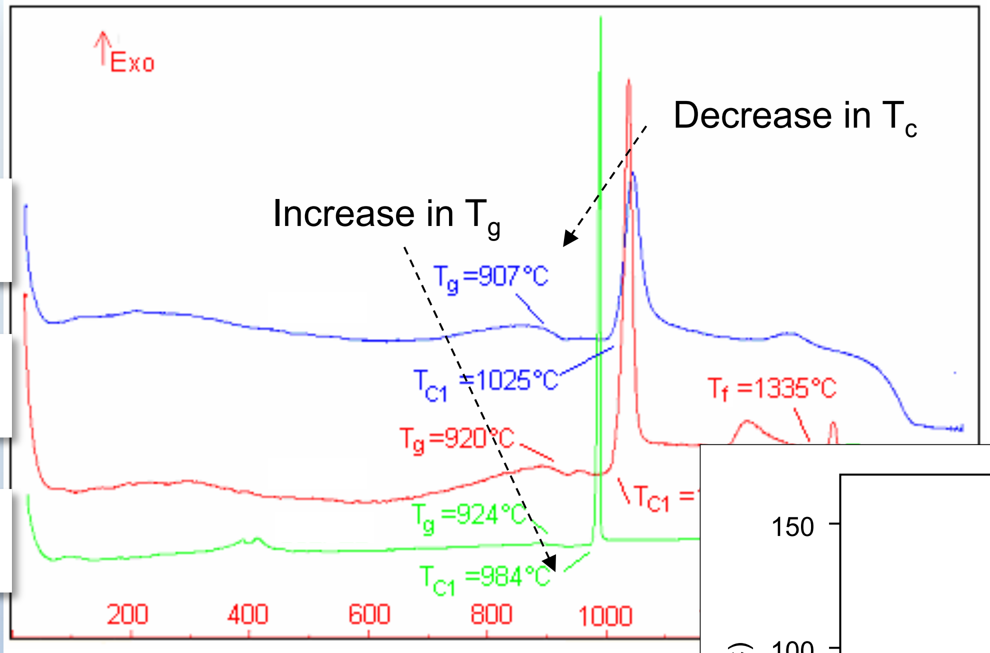
DTA in 2 RE_2O_3 – 22 Al_2O_3 – 76 SiO_2

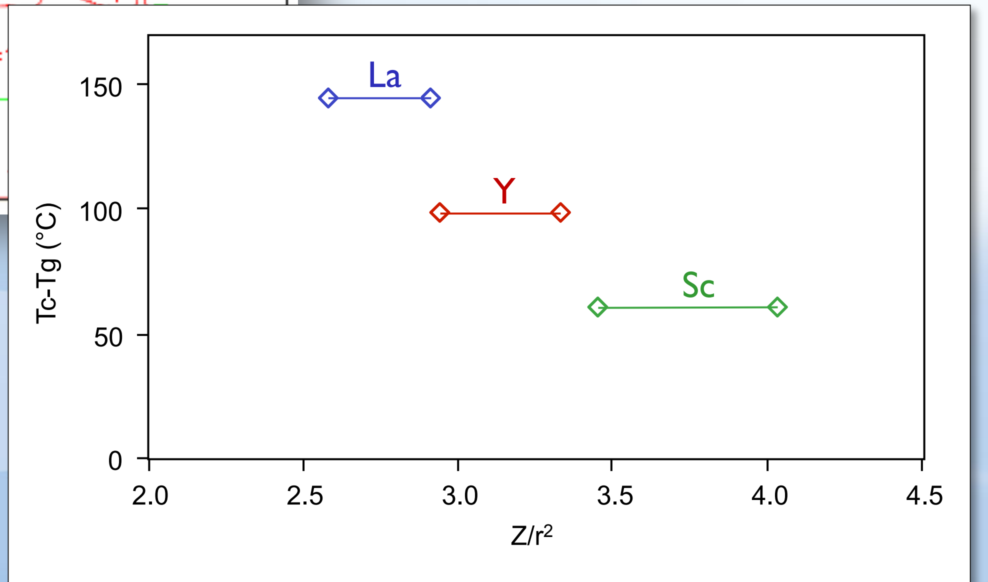
Z/r^2

La
2.91-2.58

Y
3.33-2.94

Sc
4.03-3.45





Nature of Rear-Earth impacts Thermodynamics of the Glasses
Cation Field Strengths Z/r^2 increases → $\Delta(T_c-T_g)$ decreases

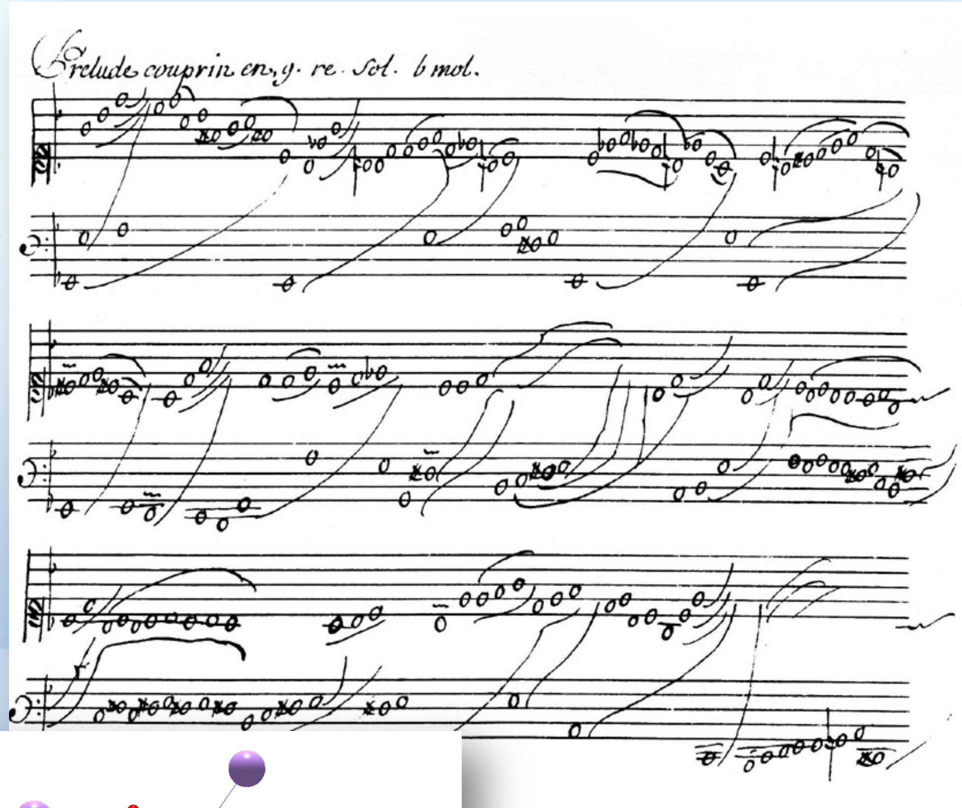
Sadiki et al., J. Nucl. Mat. ***348*** *70 (2006); Matériaux & Technique 2011*

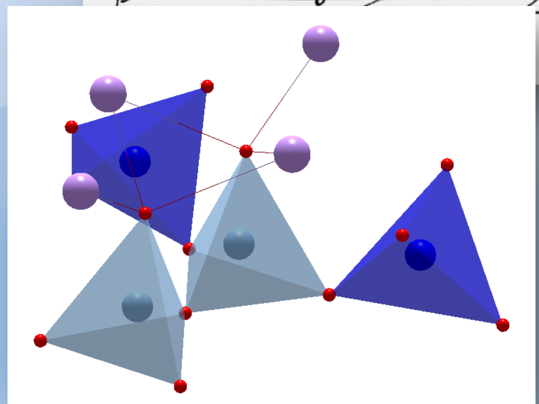
The Glassy State: Order & Disorder

“Order”

J.S. Bach, 1st prelude from “well tempered clavier”

“Disorder”

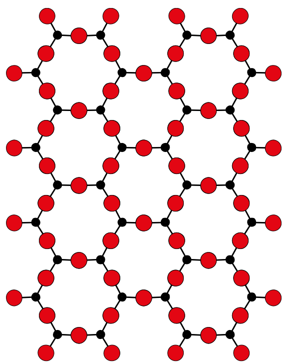




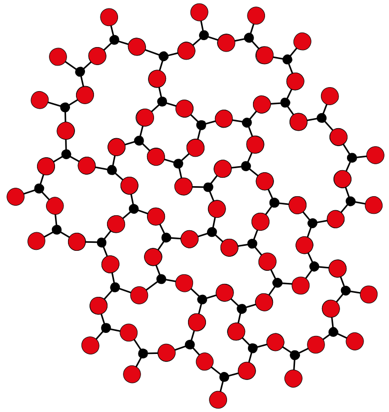
F. Couperin
“non measured” prelude

The Glassy State: Structure(s)

The Continuous Random Network



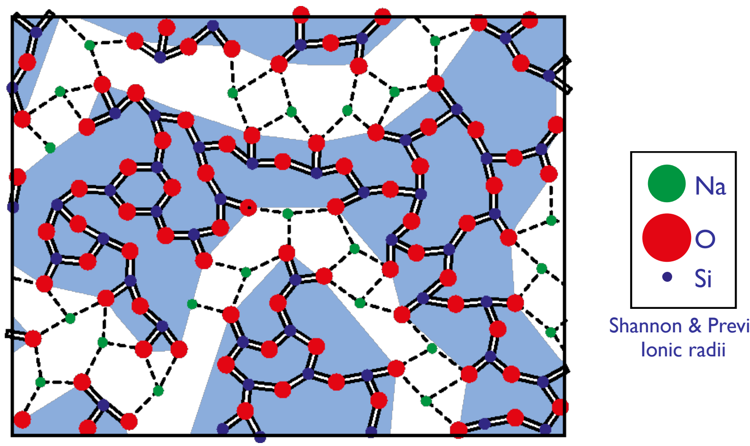
Crystalline A_2O_3



Glassy A_2O_3

after Zachariasen & Warren (1930's)

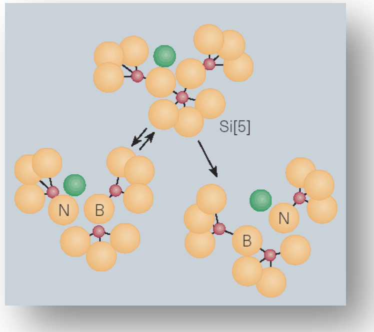
Proposed Structure of Alkali Silicate Glass



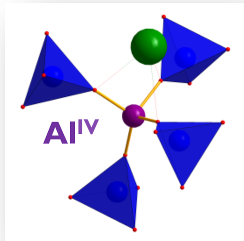
Shannon & Previtt
Ionic radii

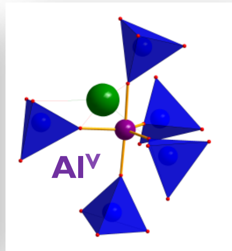
after Greaves, J. Non-Cryst. Solids 71 203 (1985)
after Warren & Biscoe (1930's)

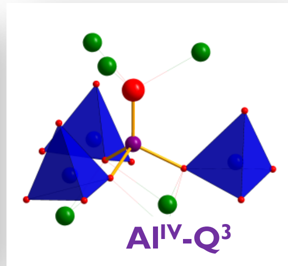
The (Complex) Reality…

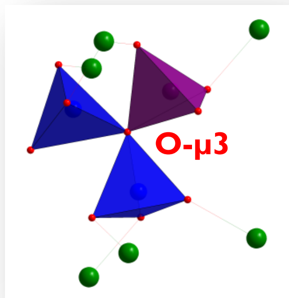


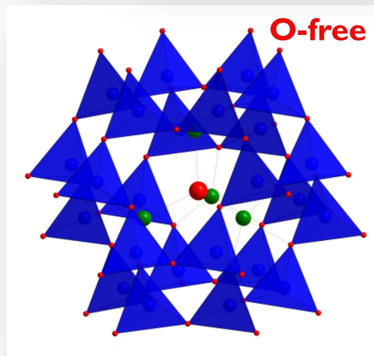
Farnan et al., J. Am. Chem. Soc. 112 32 (1990)





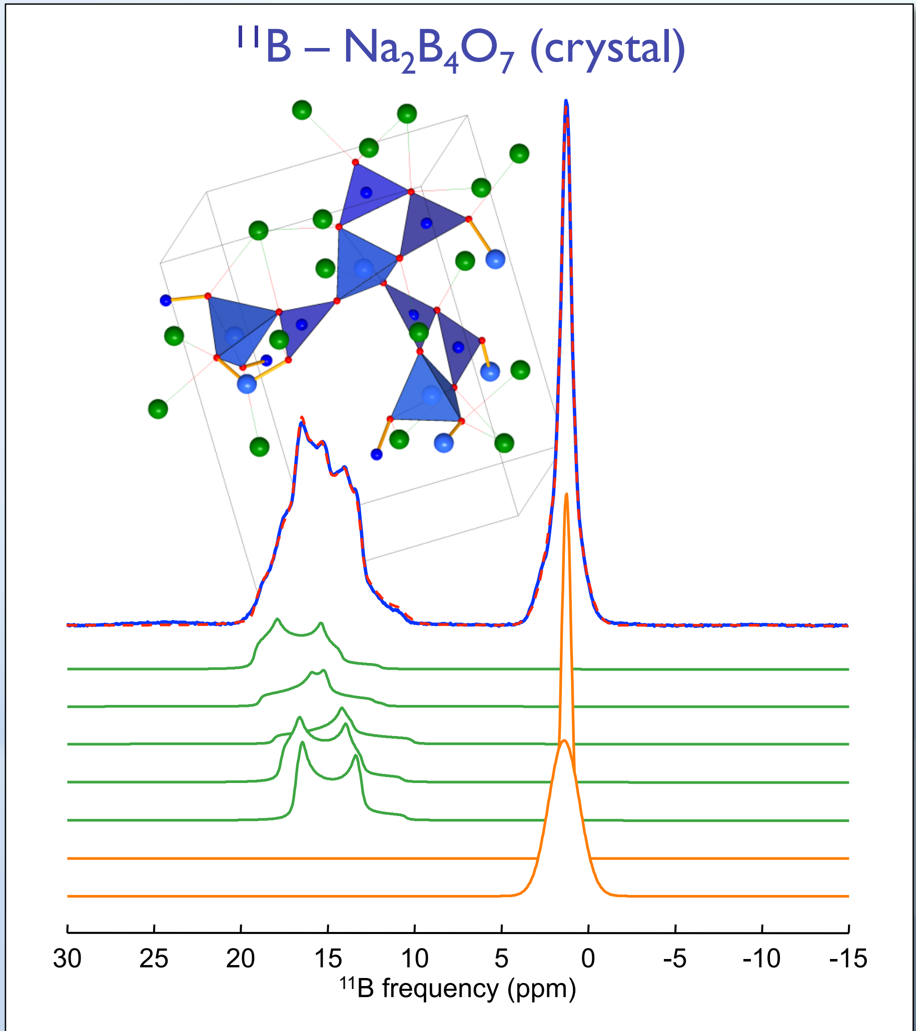


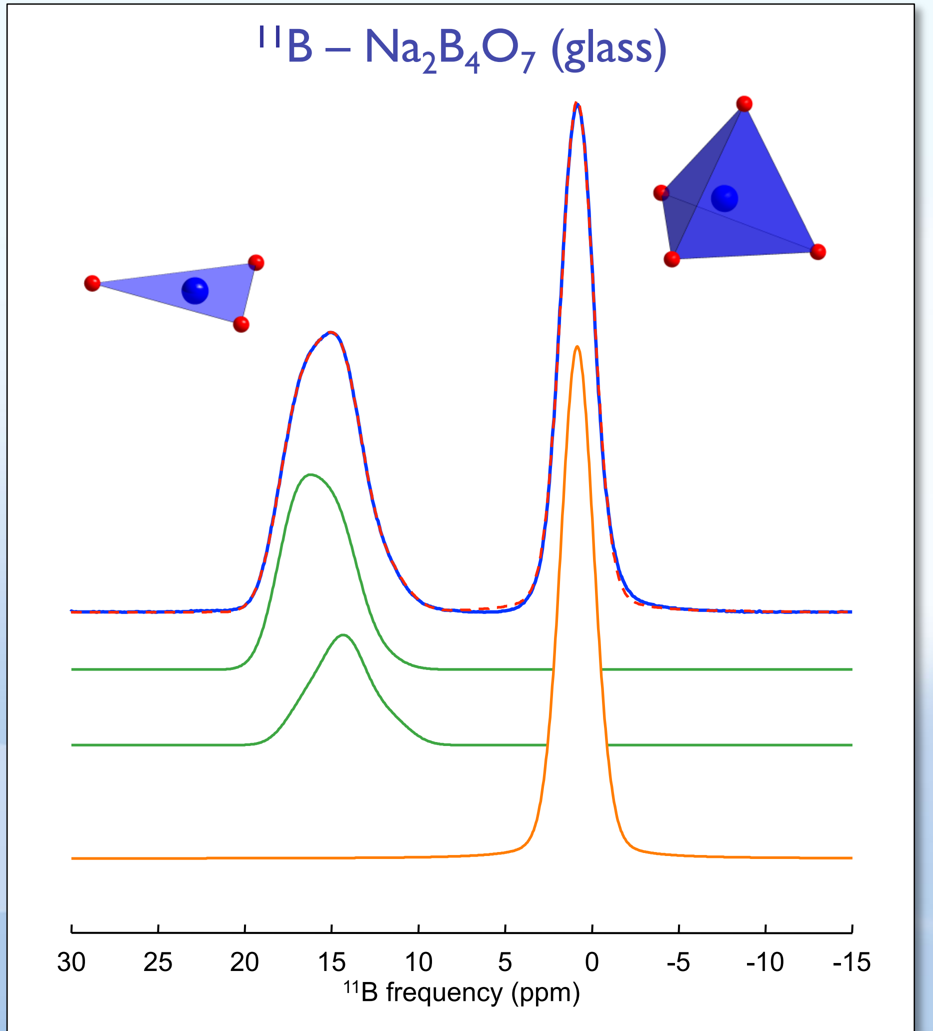




Courtesy of P. J. Grandinetti, Ohio State University, USA

Solid-State Nuclear Magnetic Resonance





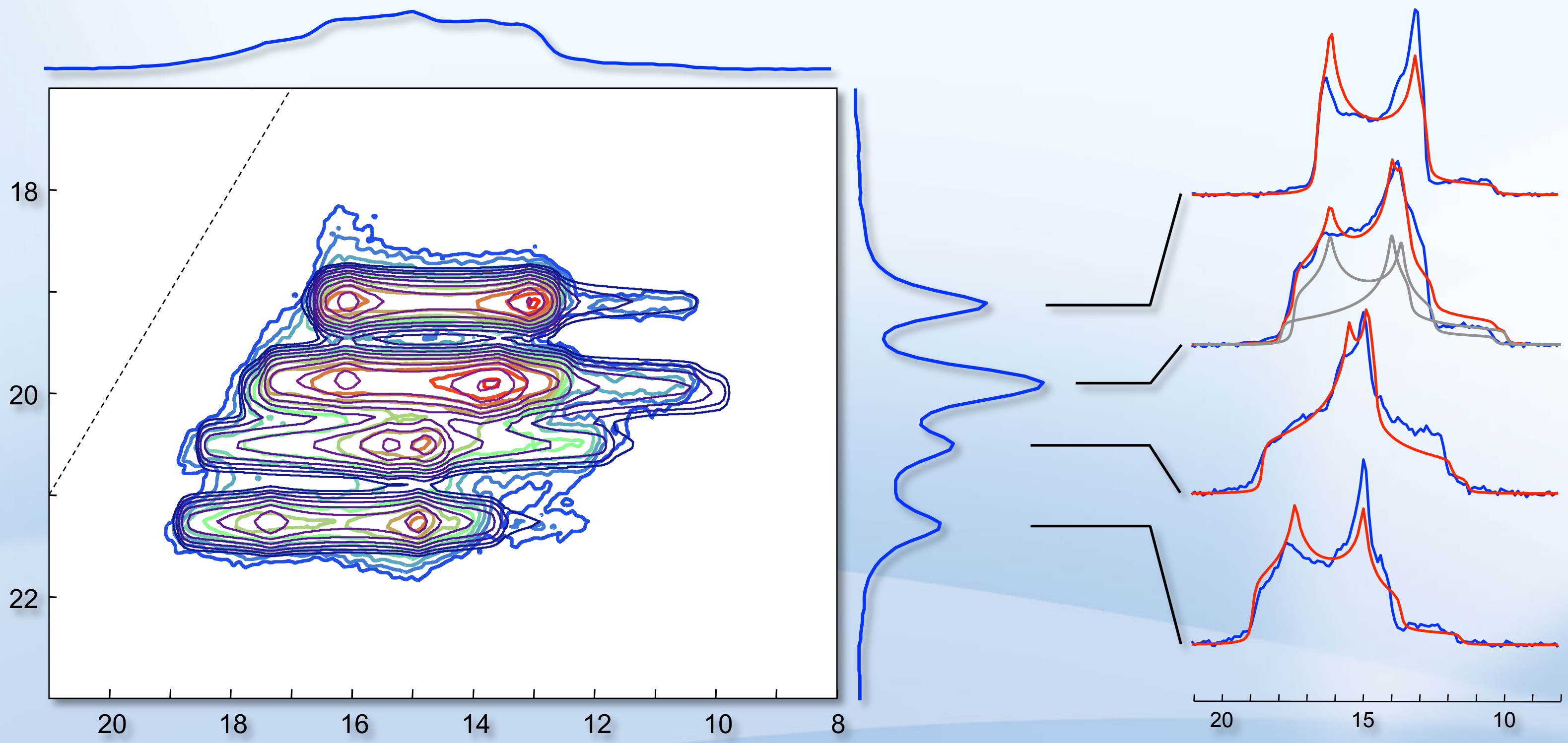
NMR is an atom-specific local probe

☞ distinguish between chemical environments

☞ quantitative

Two-dimensional SSNMR

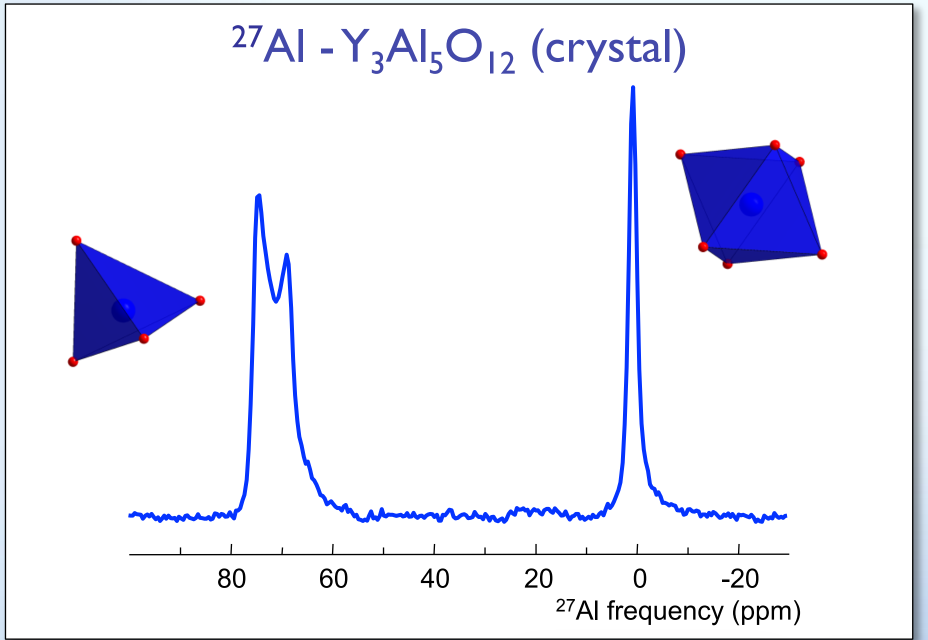
^{11}B MQMAS – $Na_2B_4O_7$ (crystal)

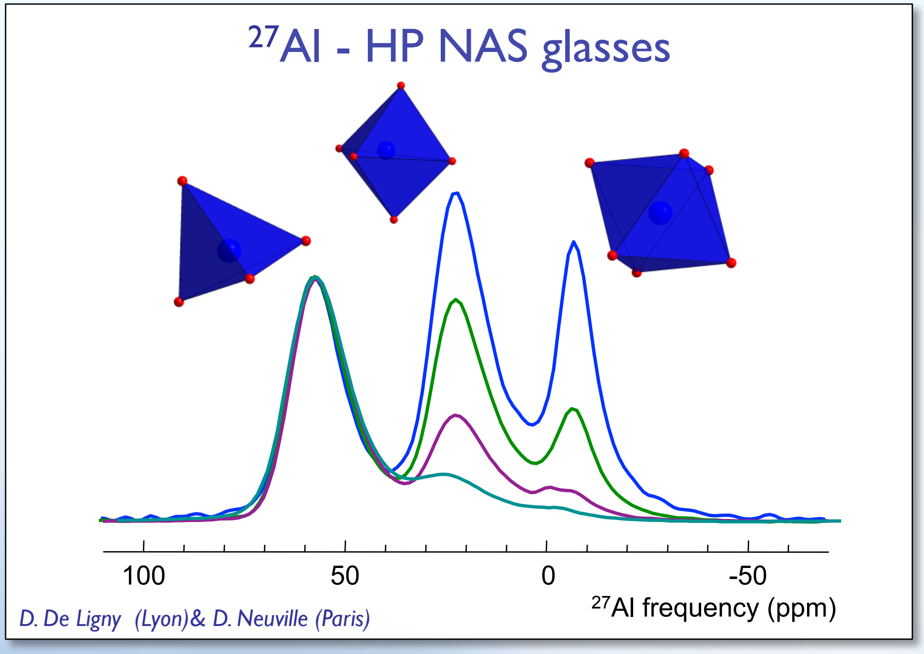


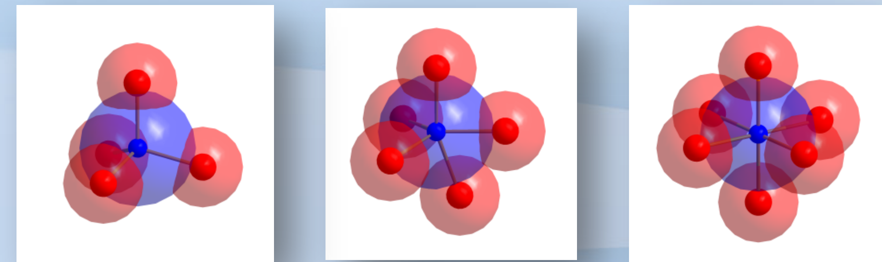
Information spread in a second dimension

☞ increase in resolution

^{27}Al Solid-State Nuclear Magnetic Resonance







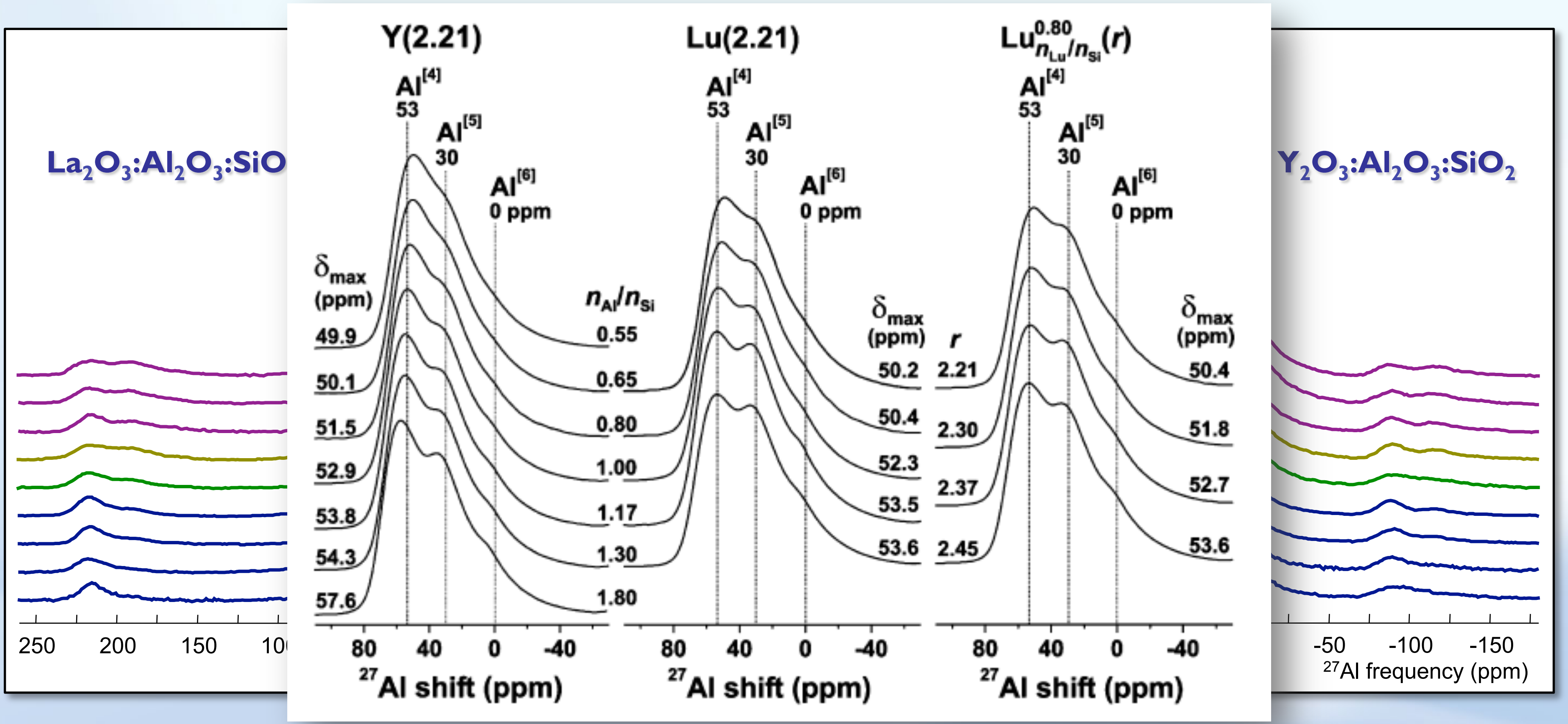
Position
(*chemical shift*, magnetic shielding):

- ☞ coordination number
- ☞ 2nd coordination sphere neighbors
- ☞ local geometry

Width & shape
(*quadrupolar coupling*, EFG):

- ☞ (*p*-) orbital population unbalance
- ☞ local polyhedra distortion
- ☞ possibly long-range effect

^{27}Al MAS NMR of RE_2O_3-Al_2O_3-SiO_2



Presence of various AlO_n units

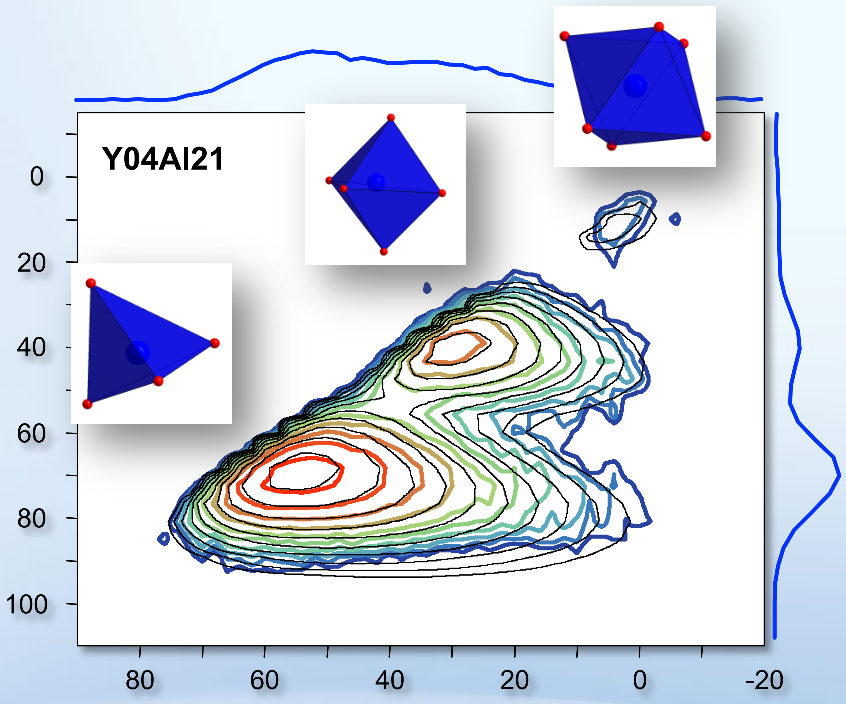
☞ amplitudes are a strong function of the composition

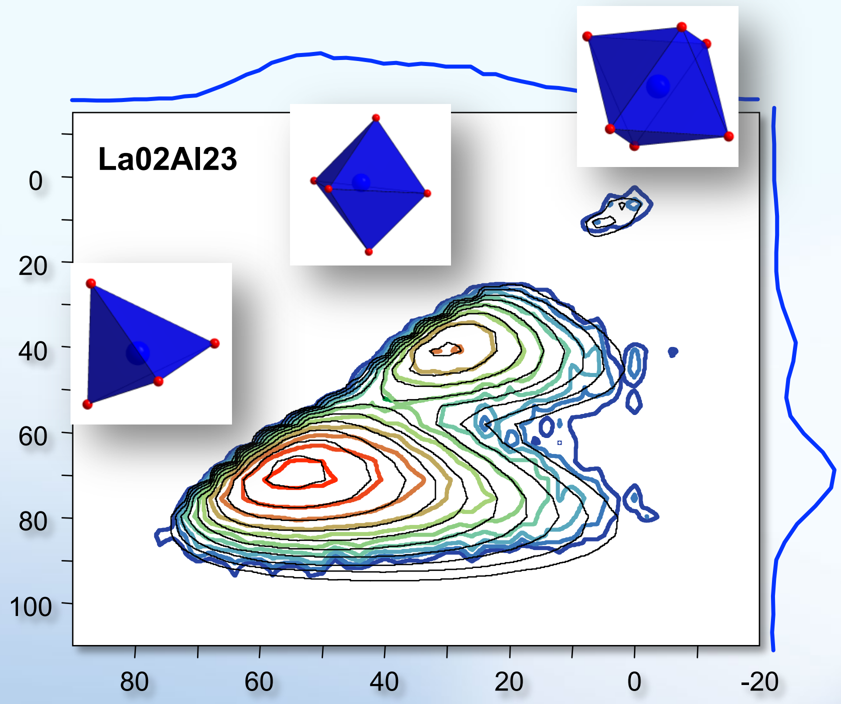
☞ width is a function of RE nature

Iftekhar et al., J. Phys. Chem. C 2012 asap

Florian et al., J. Phys. Chem. B 11 9747 (2007)

^{27}Al MQMAS NMR of RE_2O_3-Al_2O_3-SiO_2





$63.8 \leq {}^{IV}\delta_{iso} \leq 65.4$ ppm	$9.9 \leq {}^{IV}C_Q \leq 11.4$ MHz
$32.9 \leq {}^{V}\delta_{iso} \leq 37.4$ ppm	$6.1 \leq {}^{V}C_Q \leq 7.4$ MHz

$63.8 \leq {}^{IV}\delta_{iso} \leq 65.4$ ppm	$8.5 \leq {}^{IV}C_Q \leq 11.2$ MHz
$34.4 \leq {}^{V}\delta_{iso} \leq 37.2$ ppm	$6.9 \leq {}^{V}C_Q \leq 7.4$ MHz

Unambiguous presence of Al^{IV}, Al^{V} and Al^{VI},
experiencing a strong Electric Field Gradient on Al^{IV} with EFG(Y) > EFG(La)
→ preferential localization of RE ?

Florian et al., J. Phys. Chem. B ***111*** *9747 (2007)*
Massiot et al., Magn. Reson. Chem ***40*** *70 (2002)*
Neuville et al., Geochim. Cosmochim. Acta ***68*** *5071 (2004)*

Al Coordination: X-Ray & Neutron Diffraction

Interatomic distances and coordination numbers derived from the Gaussian fits of the X-ray (X) and neutron (N) data

		r (Å) Si–O	Al–O	La–O/Y–O	O–O	CN C Si–O	Al–O
Sum of ionic radii		~1.62	Al_{IV} 1.76 Al_{V} 1.84 Al_{IV} 1.9	2.39/2.26	2.72		
Errors		±0.03	±0.03	±0.05	±0.1	±0.5	±0.5
LAS1	X	1.62	1.82	2.34	2.70	4.1	4.5
	N	1.62	1.84	2.36	2.70	4.2	4.6
LAS3	X	1.62	1.82	2.36	2.66	4.0	4.4
	N	1.62	1.82	2.36	2.66	4.1	4.5
YAS1	X	1.60	1.80	2.26	2.62	3.9	4.5
	N	1.60	1.80	2.22	2.64	4.0	4.5
YAS3	X	1.62	1.82	2.24	2.62	4.0	4.6
	N	1.62	1.82	2.20	2.64	4.0	4.4

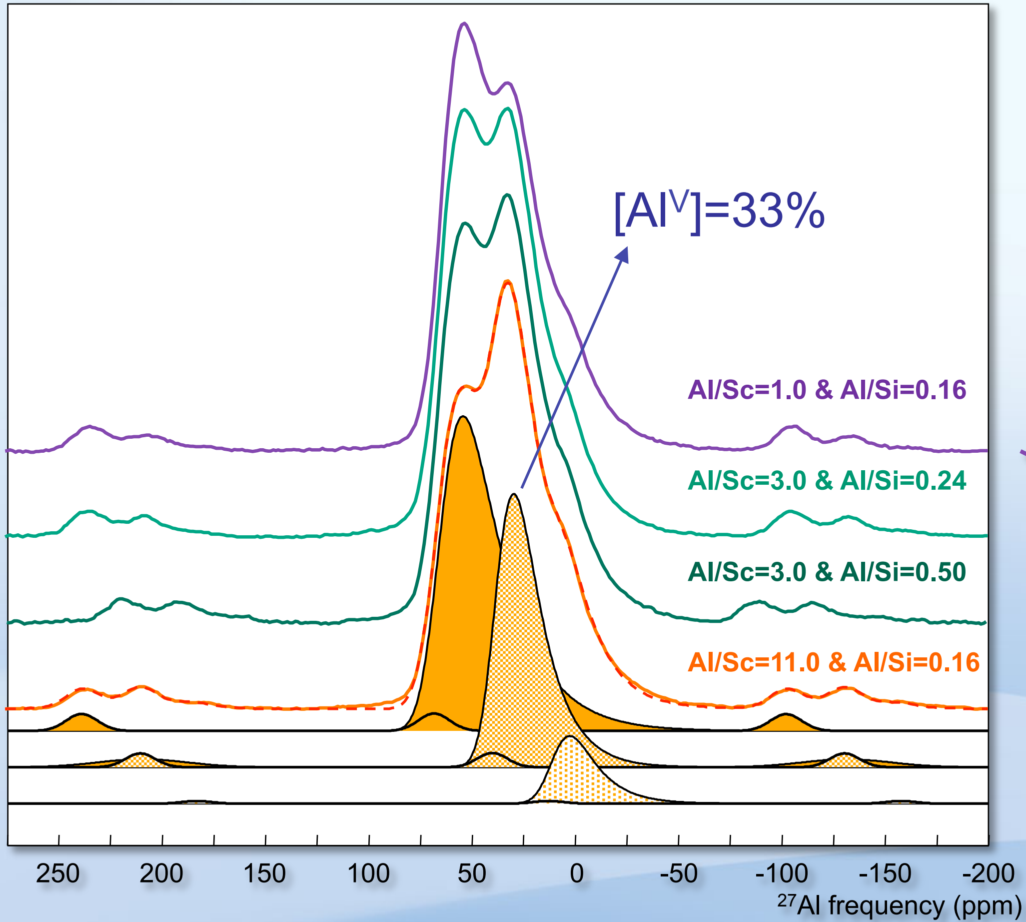
Compositions and densities of the glasses studied [22]

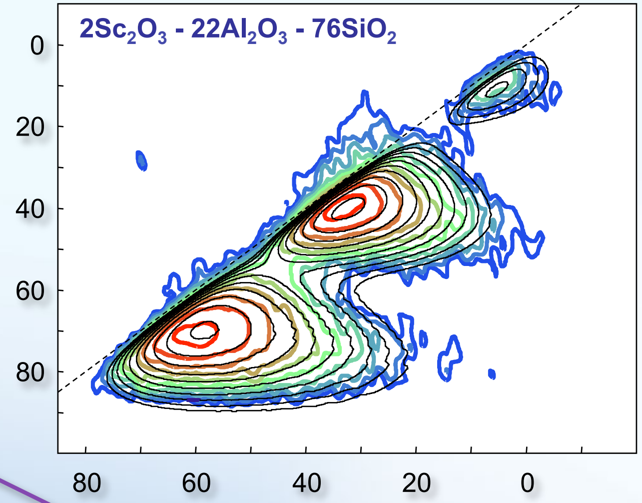
Sample	Composition (wt%)			Composition (mol%)			Al/Si	Al/Ln	Density, (g/cm^3) from Ref. [22]
	Ln_2O_3	Al_2O_3	SiO_2	La_2O_3	Al_2O_3	SiO_2			
LAS1	30	20	50	8.22	17.50	74.29	0.202	1.86	3.702
LAS3	10	30	60	2.32	22.23	75.45	0.314	12.3	2.851
YAS1	30	20	50	11.43	16.89	71.67	0.236	1.49	3.042
YAS3	10	30	60	3.31	22.00	74.69	0.279	4.86	2.769

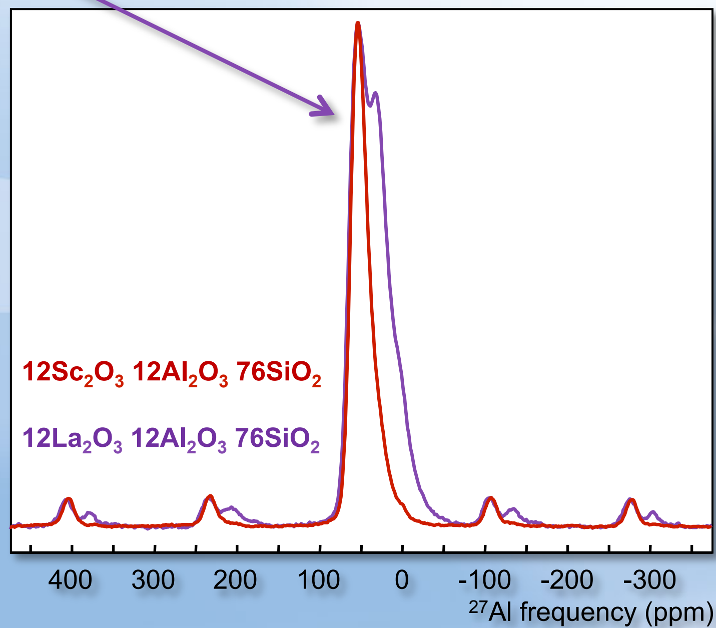
☞ No evolution of distances with composition
☞ Al coordination > 4

Pozdnyakova et al., JNCS ***354*** *2034 (2008)*

^{27}Al NMR in Sc_2O_3-Al_2O_3-SiO_2

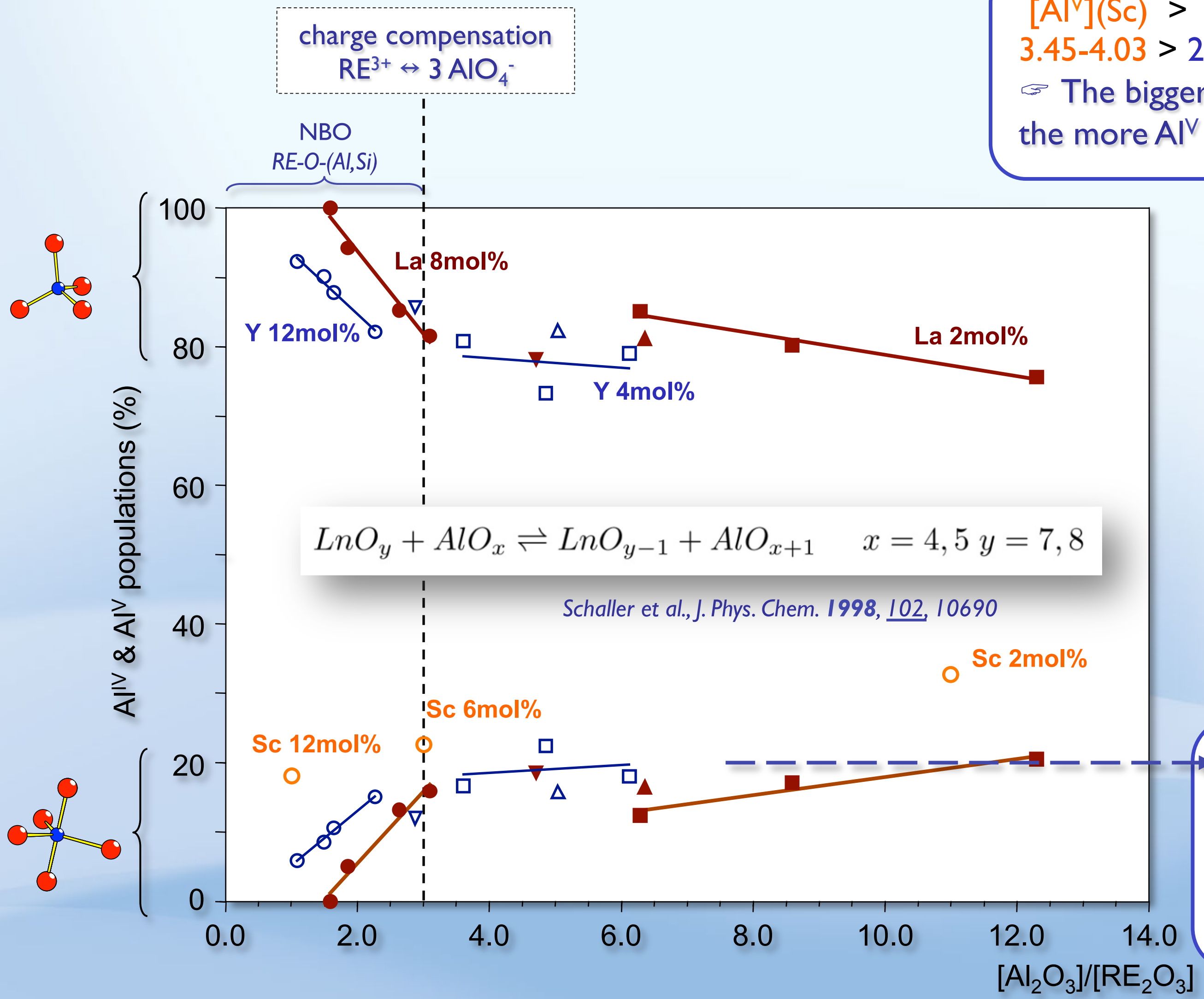






☞ % AlO_n units is a strong function of <u>both</u> composition and RE nature

Composition & Al^{IV} / Al^{V} populations

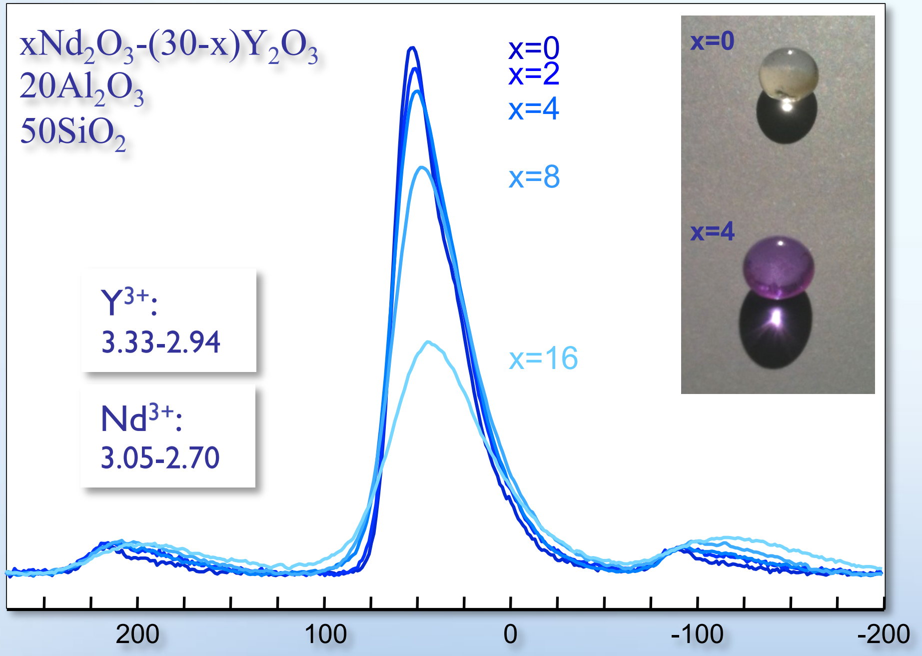


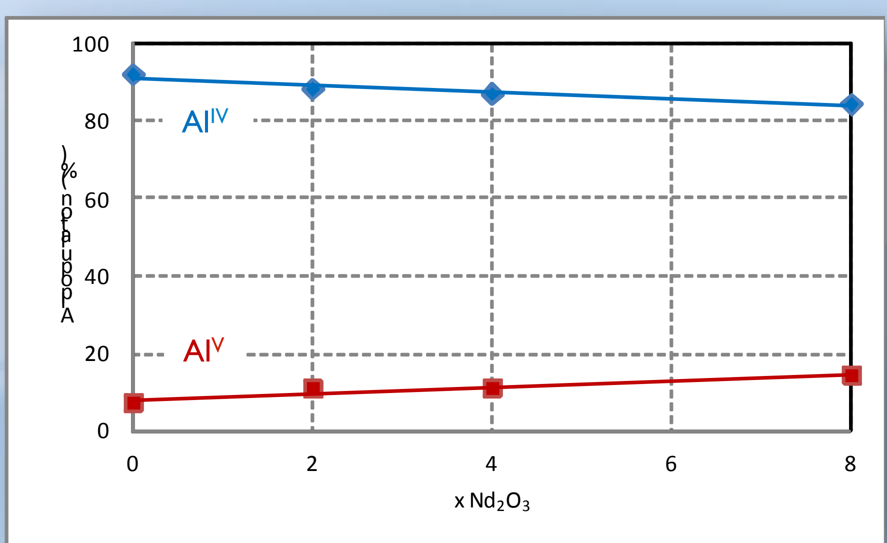
$[Al^V](Sc)$ > $[Al^V](Y)$ > $[Al^V](La)$
3.45-4.03 > 2.94-3.33 > 2.58-2.91
☞ The bigger the cation field strength, the more Al^V formed.

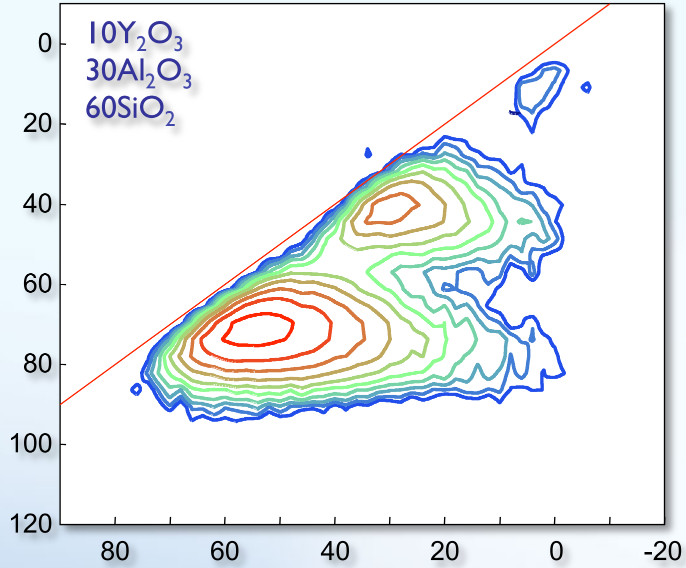
Stabilization at ~ 20%
<< Al_2O_3-SiO_2
presence of tri-cluster (AlO_3)-O-$(SiO_3)_2$ or RE coordination change ?

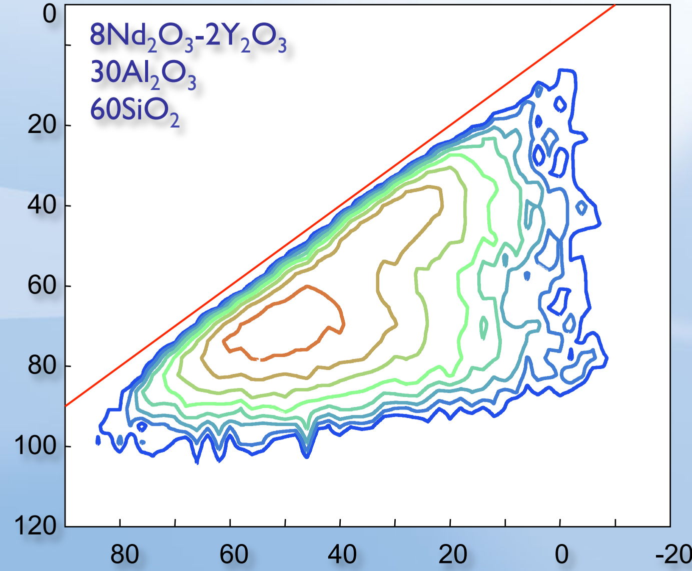
Florian et al., J. Phys. Chem. B **111** 9747 (2007)

^{27}Al NMR in $(Nd_xY_{1-x})_2O_3$-Al_2O_3-SiO_2





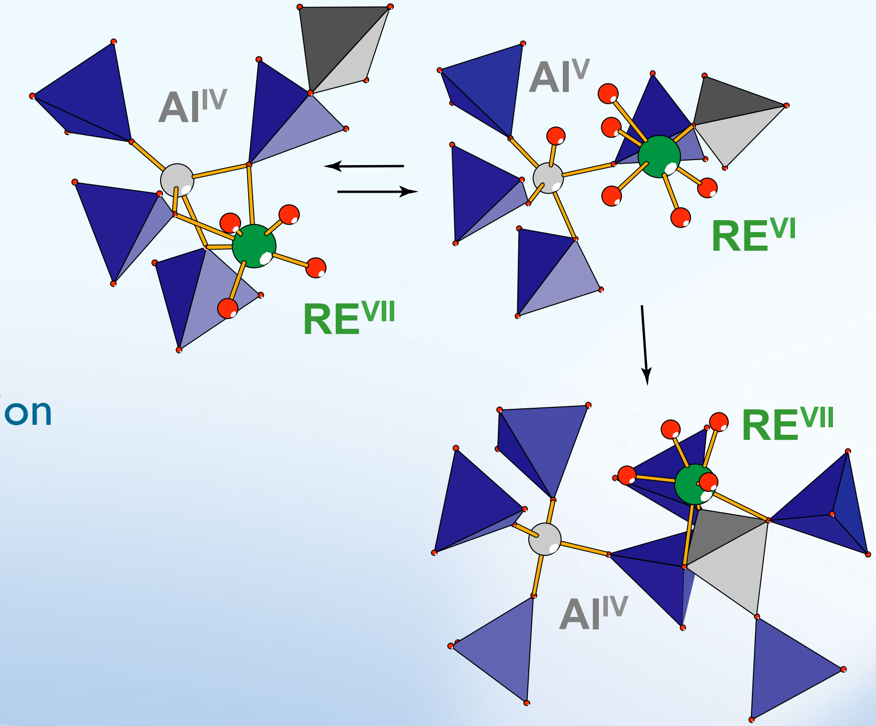




NMR still possible, but loss of resolution

^{27}Al NMR: what have we learned ?

- Presence of Al^{V} :
  up to 20% (Y, La) or more (Sc)
  for $[Al_2O_3]/[RE_2O_3] \geq 3$
  favored at high temperature

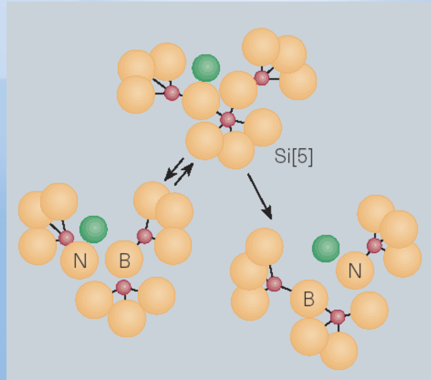


- Stabilization of Al^{IV} in the per-aluminous region
  → presence of tricluster (AlO_3)-O-$(SiO_3)_2$?
  → change of the RE^{3+} coordination state ?

- Cation field strength Z/r^2 influences $[Al^{V}]$

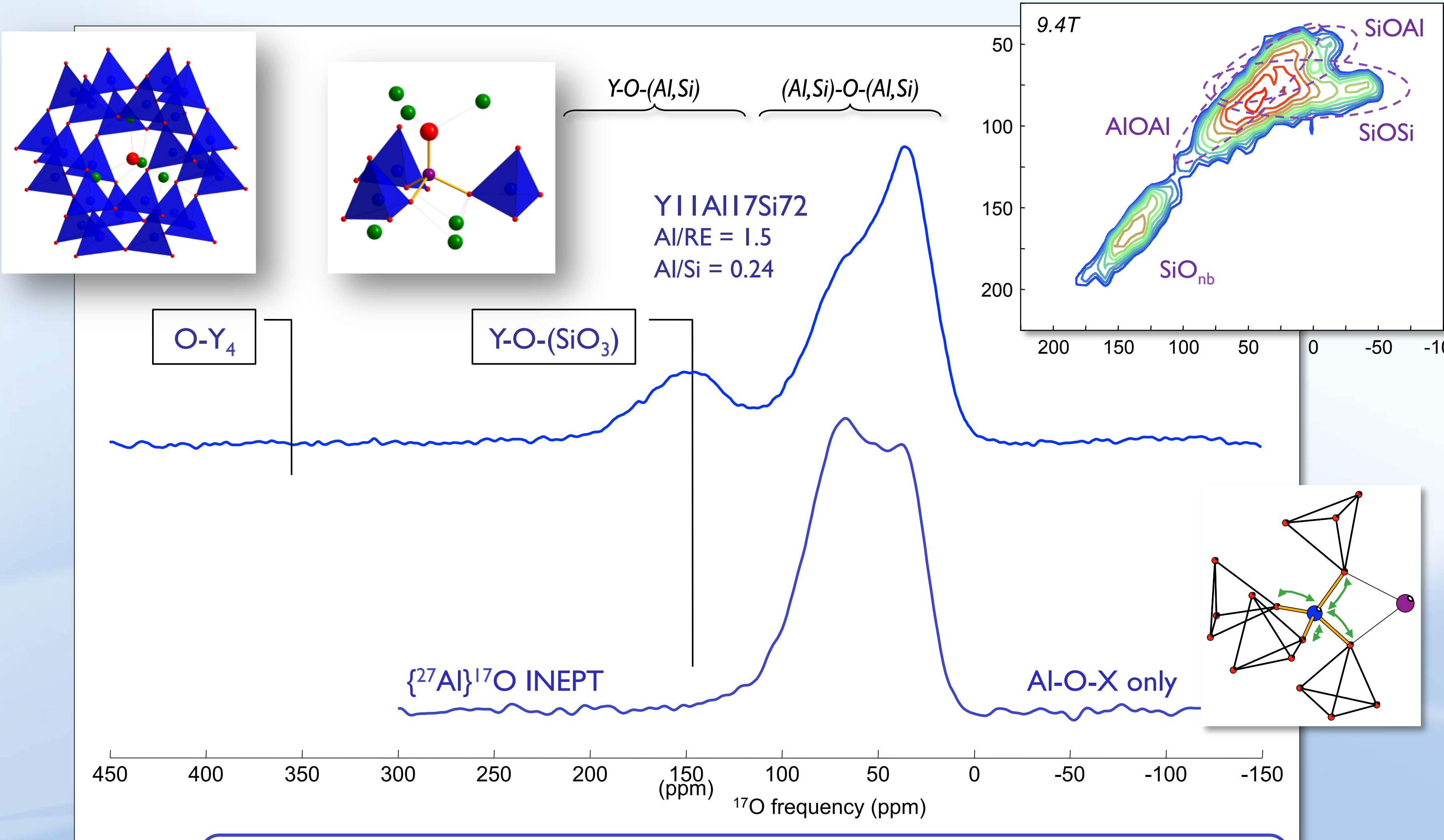
- Preferential localization of RE^{3+} near Al^{IV} ?

- Where are the Non-Bridging Oxygens ?



Farnan et al., J. Am. Chem. Soc. ***112*** *32 (1990)*

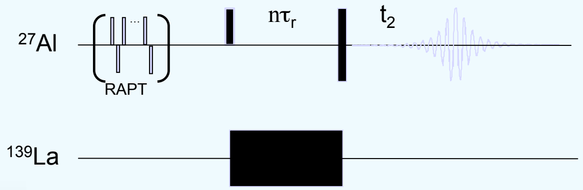
Oxygen free & NBOs ...

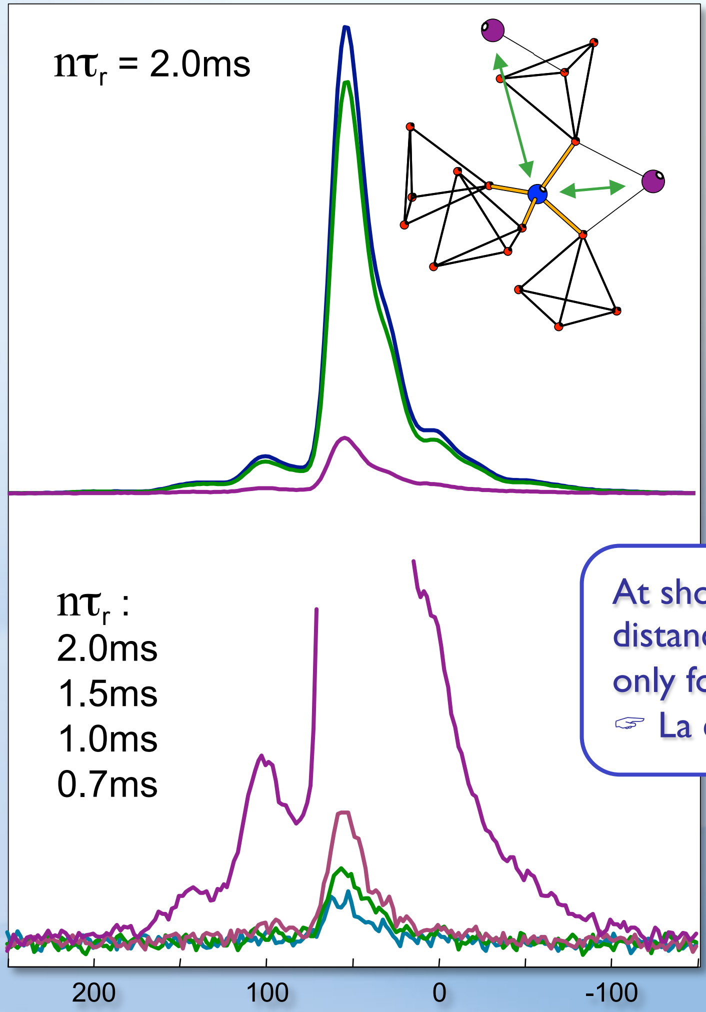


☞ **Unambiguous presence of Y-O-(SiO_3) in the peralkaline region but no obvious signs of Y-O-(AlO_3) nor OY_4**

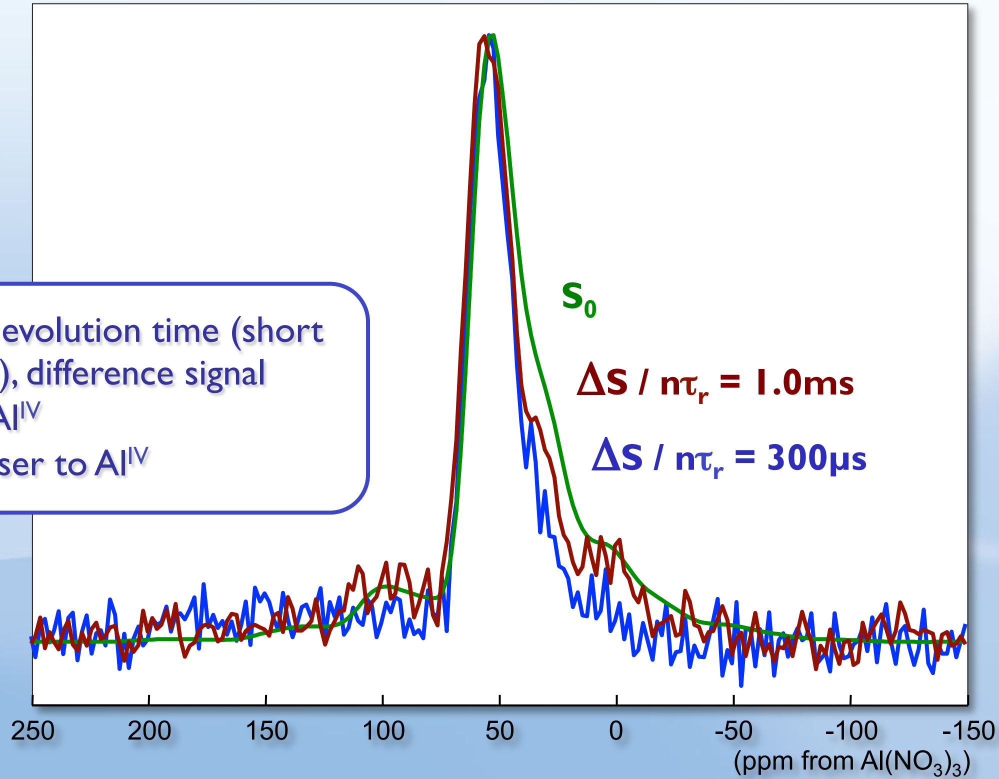
Lee et al., Chem. Geol. ***256*** *326 (2008) & Geochim. Cosmochim. Acta* ***70*** *4275 (2006)*

Checking La^{3+} / Al proximity: TRAPDOR





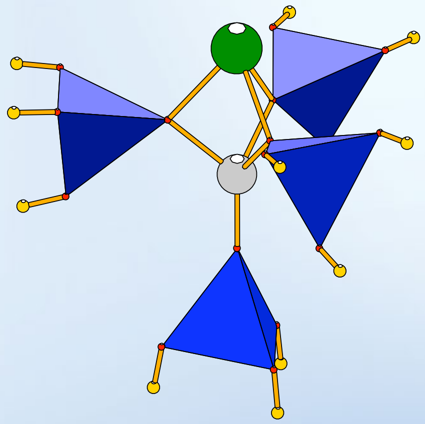
At short evolution time (short distances), difference signal only for Al^{IV}
☞ La closer to Al^{IV}

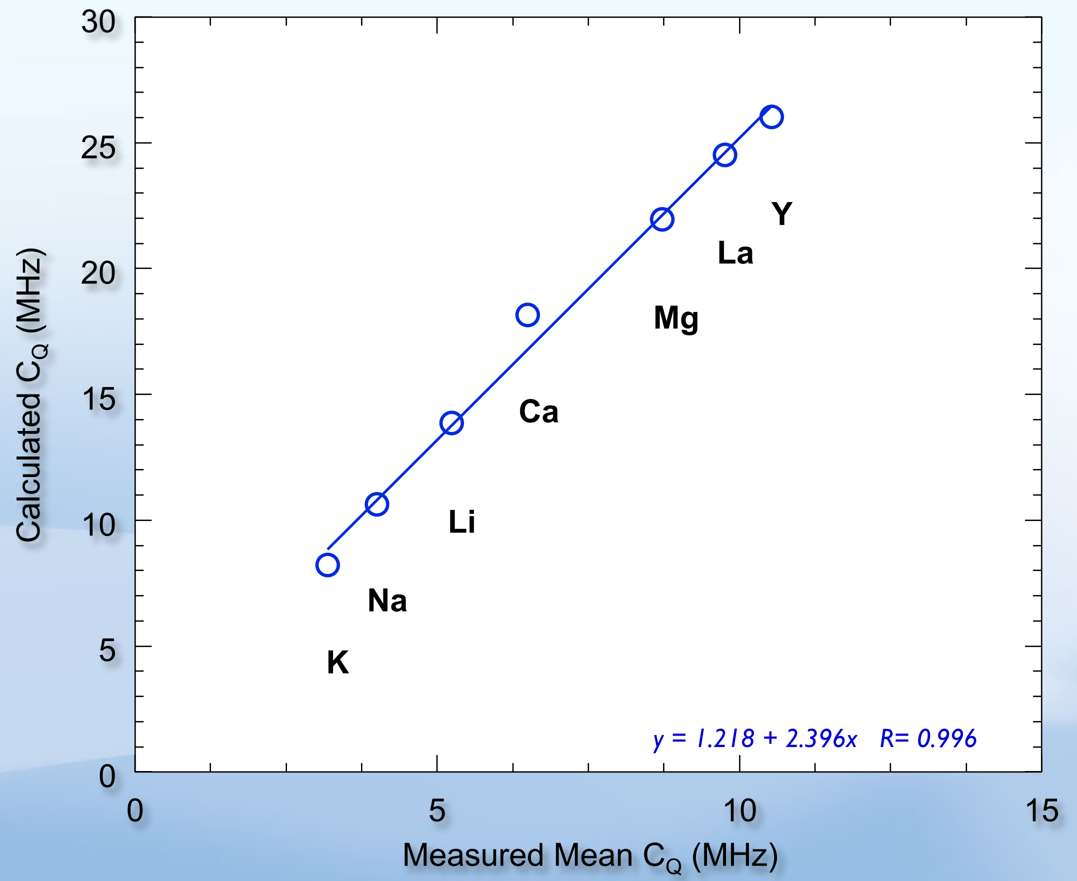


$9La_2O_3$-$28Al_2O_3$-$63SiO_2$

Cation / AlO_4 proximity: ab-initio calculations

Al, Si, O, H : 6-311+G(d)
Li -> Ca : 3-21G
Y, La : LanL2DZ

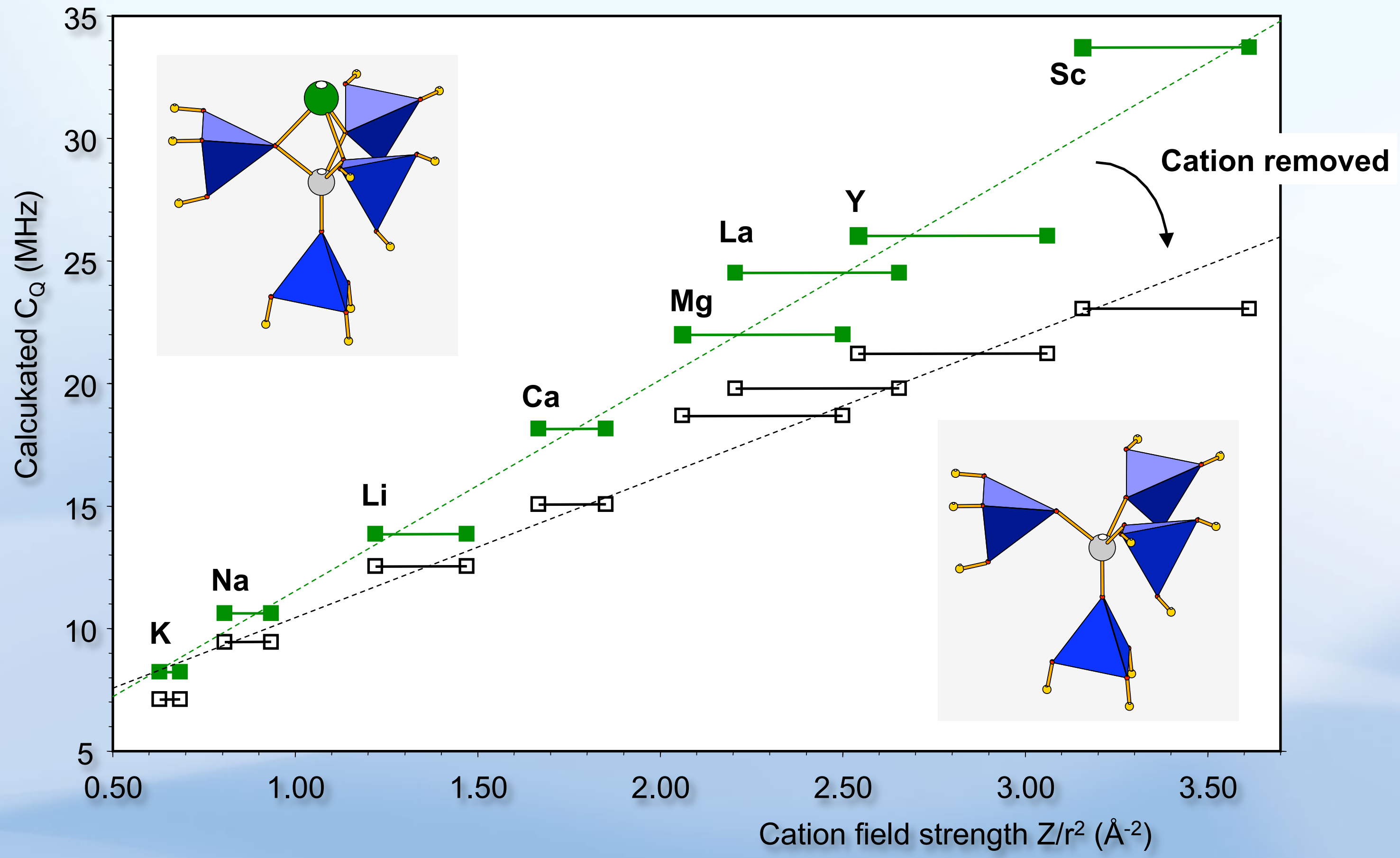




Neuville et al., Chem. Geol. ***213*** *153 (2004), Am. Mineral.* ***93*** *1721 (2008)*
Florian et al., J. Phys. Chem. B ***111*** *9747 (2007)*
Neuville, private communication

Cation / AlO_4 proximity: calculations

Al, Si, O, H : 6-311+G(d)
Li -> Ca : 3-21G
Y, La : LanL2DZ

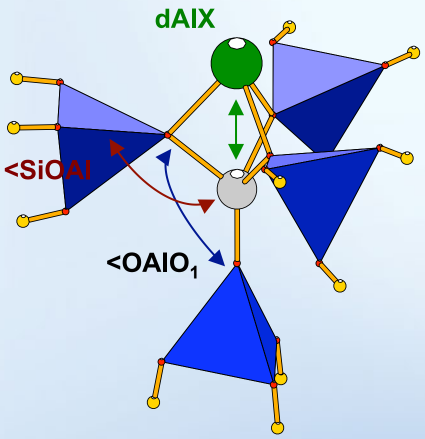


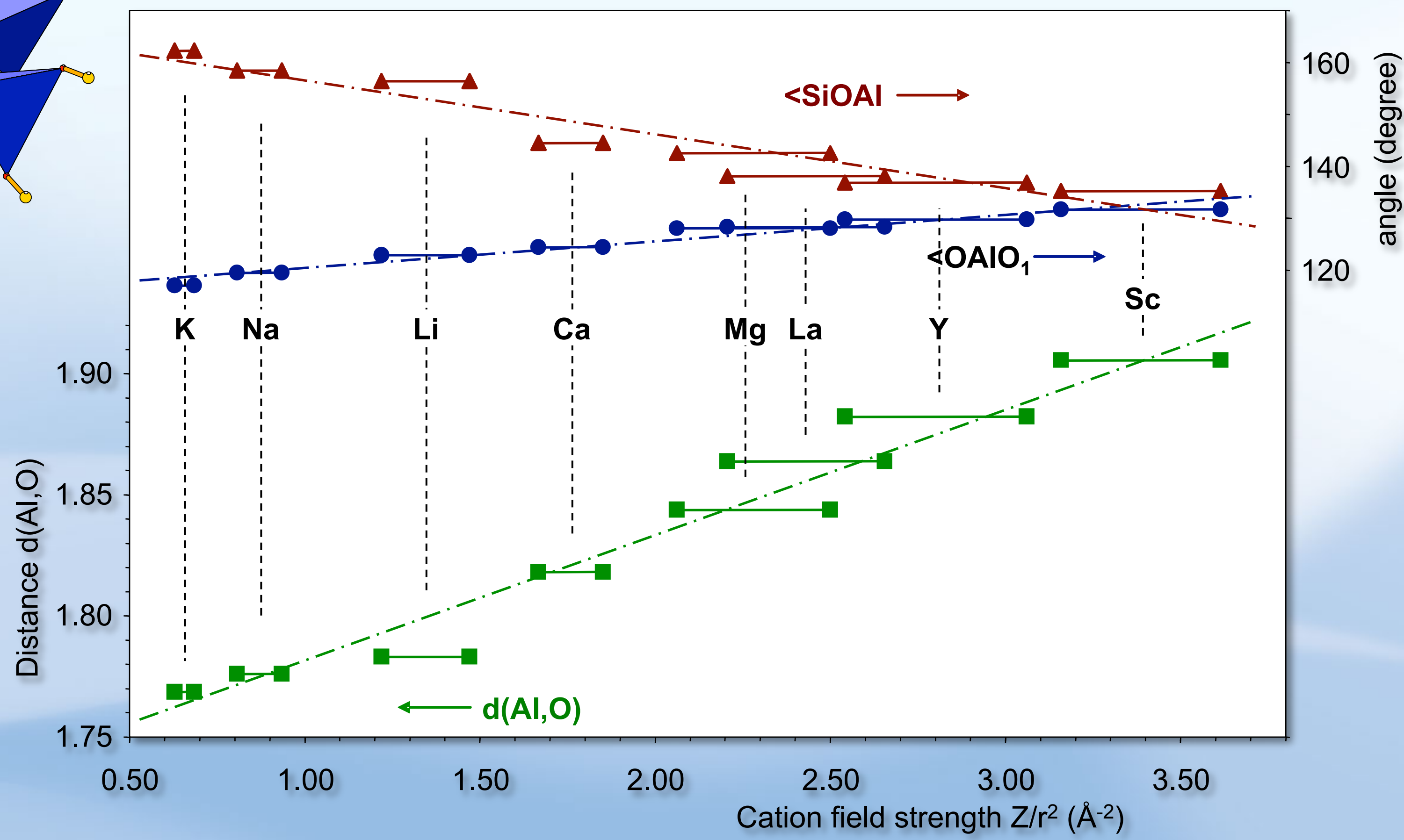
☞ EFG is primarily a measure of the AlO_4 tetrahedra distortion
Increase of EFG with Z/r^2 observed experimentally → cations are close to Al^{IV}

Cation / AlO_4 proximity: calculations

Whittaker & Muntus, *Ionic radii for use in geochemistry, Geochim. Cosmocchim. Acta*, 1970, **34**, 945-956

Al, Si, O, H : 6-31G
Li –> Ca : 3-21G
Y, La, Sc : LanL2DZ

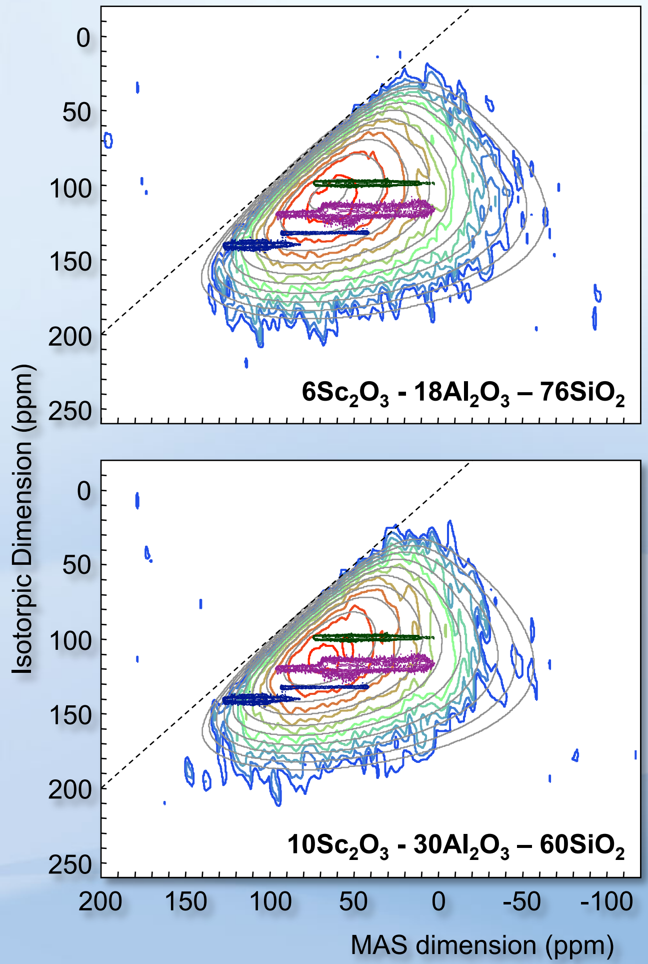


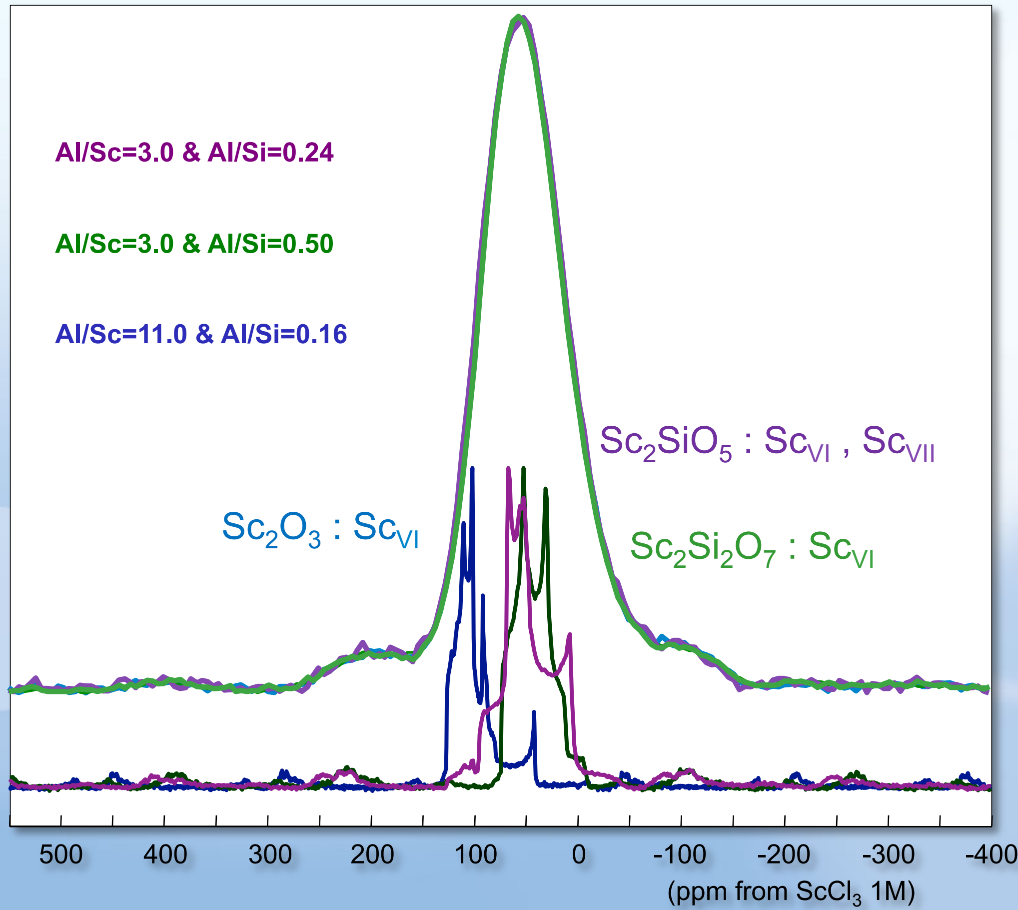


☞ Ab-initio calculations on model molecule: AlO_4 distortions are a function of Z/r^2

Checking the cation environment: ^{45}Sc NMR

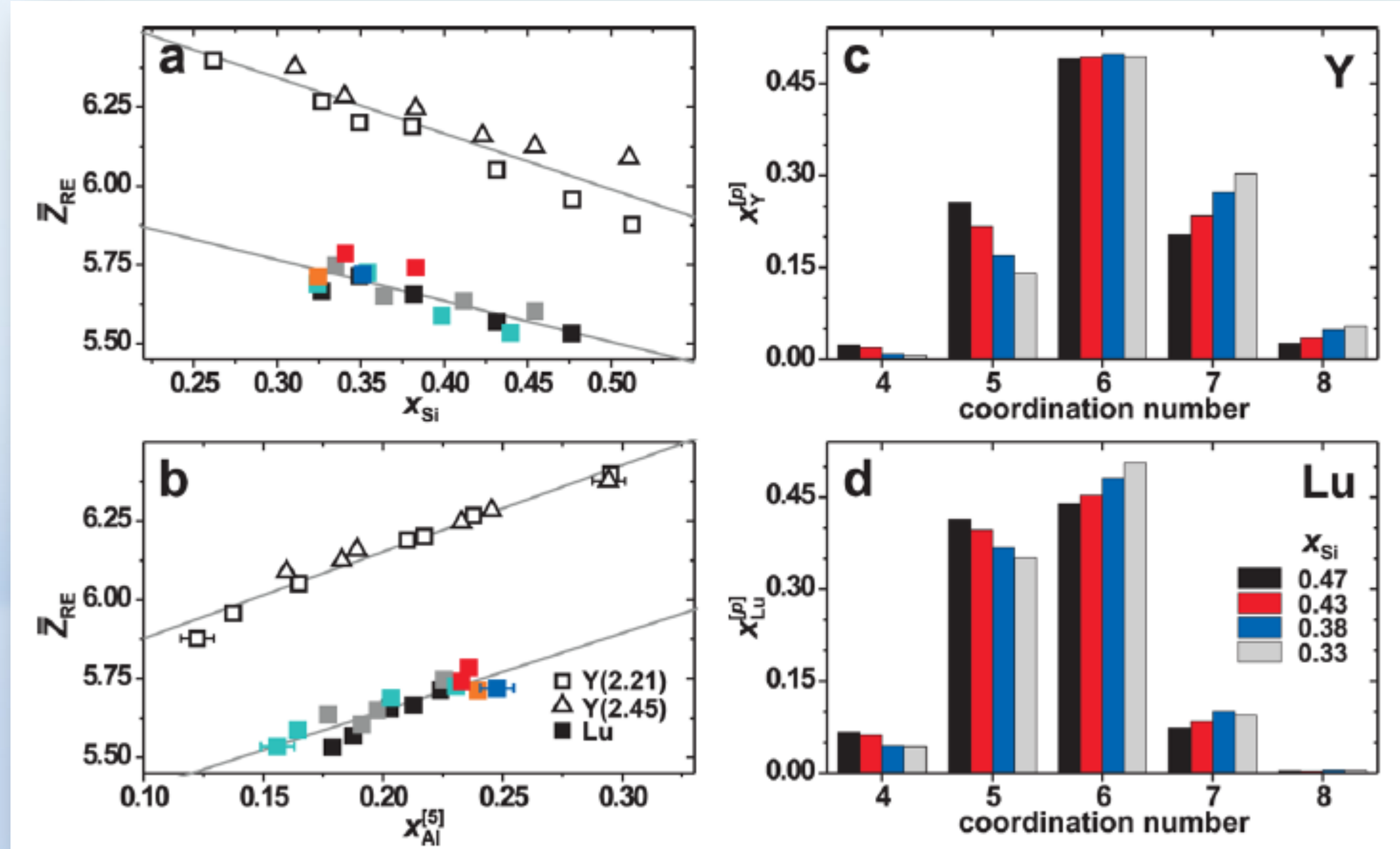
$LnO_y + AlO_x \rightleftharpoons LnO_{y-1} + AlO_{x+1} \quad x = 4,5 \; y = 7,8$





☞ No changes of the Sc environment with composition (mainly Sc^{VI})

RE coordination : Molecular Dynamics

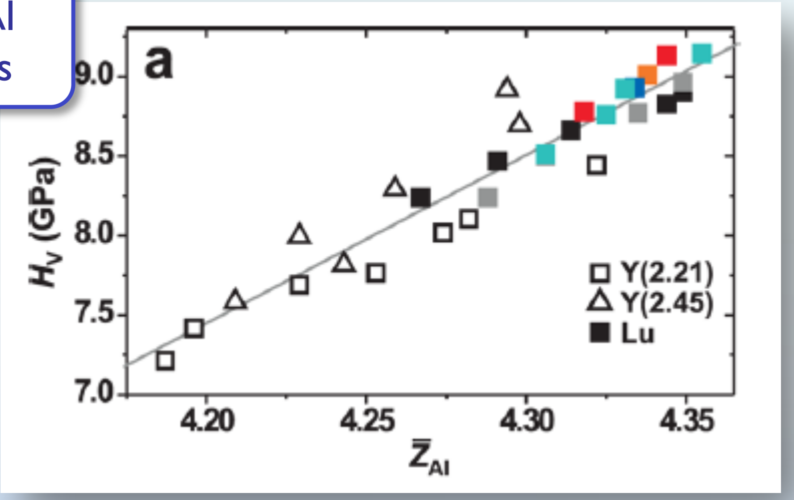


☞ Small evolution of the RE coordination state with composition

Iftekhar et al., J. Phys. Chem. C 2012 asap

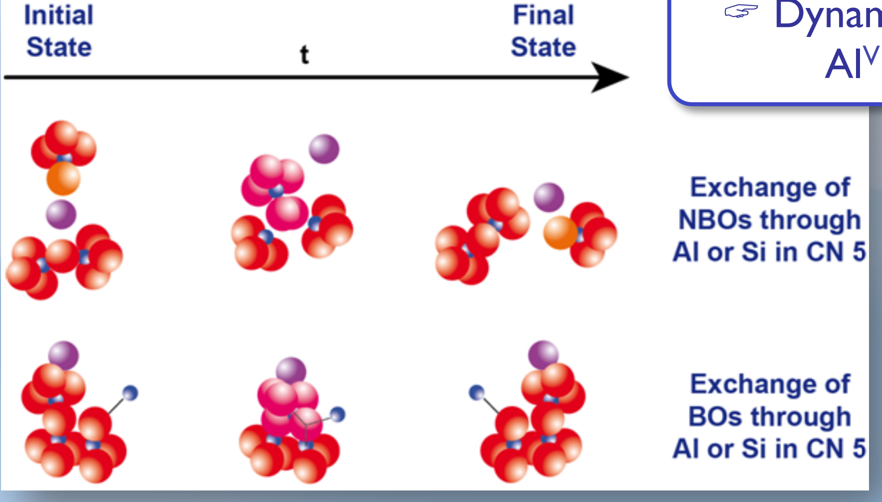
Structural Role of Al^{V}

☞ Correlation of average Al coordination with Hardness



Iftekhar et al., J. Phys. Chem. C 2012 asap

☞ Dynamics of Al in High-T Melts: Al^{V} decreases viscosity



Le Losq et al. Geochim. Cosmochim. Acta, submitted

Conclusions

- RE -with their high Z/r^2- favor high Al coordination states (i.e. presence of Al^{V})
- RE are localized nearby Al^{IV}, strongly distorting the Al tetrahedra
- No sign of changes in RE coordination with composition
- RE does not favor energetically "unstable" species (NBO, etc…)

TGIR RMN

http://www.tgir-rmn.org/

Gif
ICSN
800 SB liq.
950 SB SB liq.

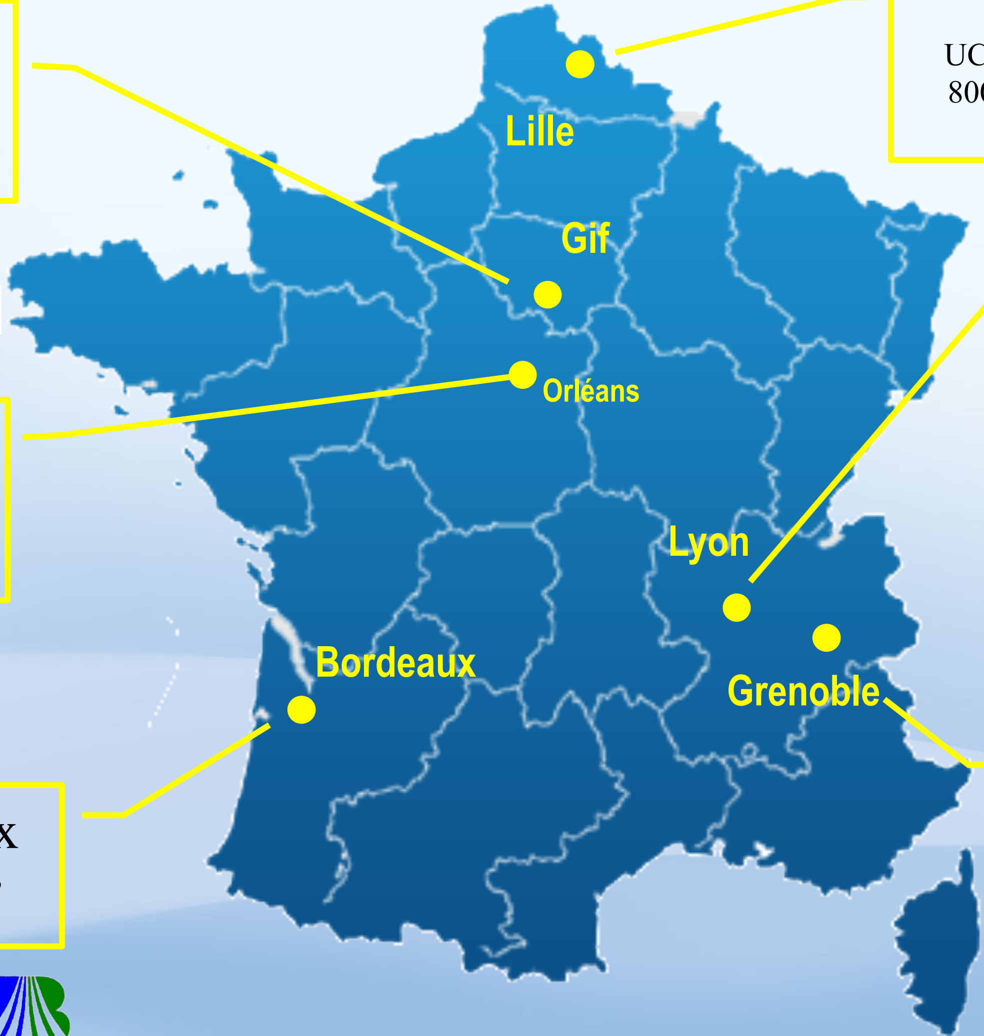
INC

Orléans
CEMHTI
750 WB sol/HT
850 WB (Oct. 2010)

INC

Bordeaux
CBMN IECB
800 SB

INC/INSB



Lille
UCCS / UGSF
800 SB sol/liq
900 SB

INC

Lyon
CRMN
*800 SB sol/liq**
1000 SB

INC

EU-NMR

Grenoble
IBS
800 SB liq

INSB