Elucidating glass (and alteration gel) structure with a combined MD and NMR approach boosted by Machine Learning

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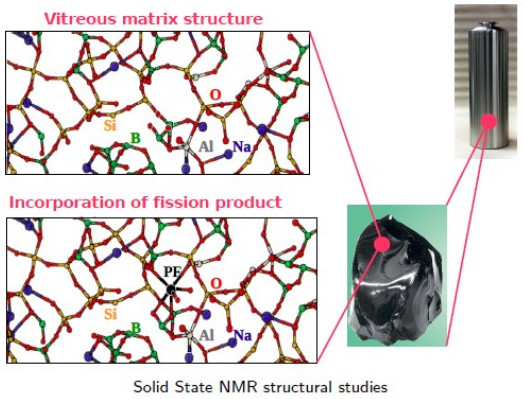
Overview

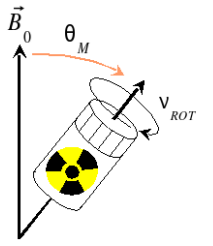
DRF/IRAMIS/NIMBE - LSDRM - Laboratory of Structure et Dynamics by Magnetic Resonance

Nuclear Waste Materials



Solid State NMR structural studies

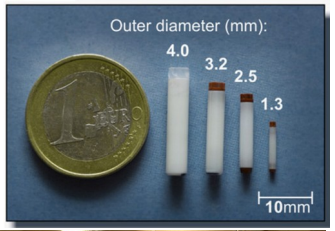
Long Term Behavior



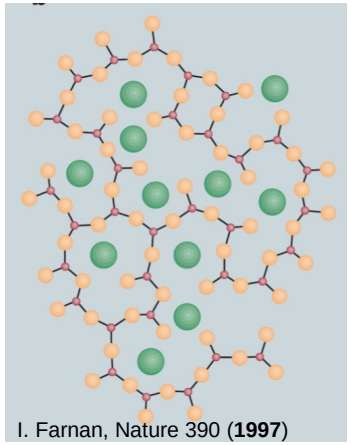
Magic Angle Spinning

Radiological and Tritium MAS NMR

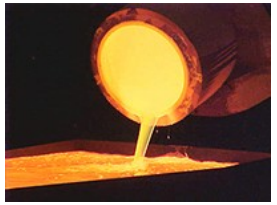
MAS NMR & Theory



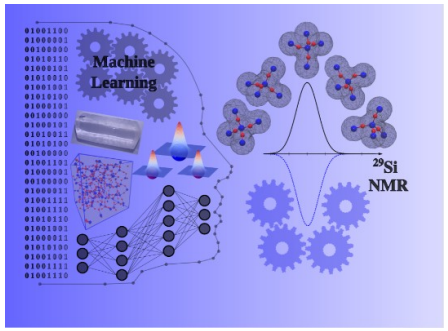
MAS NMR of Glass & Disordered Materials

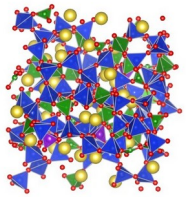


I. Farnan, Nature 390 (**1997**)



First-Principles NMR & Machine Learning





MAS NMR of (French) Nuclear Waste Glass

R7T7: A borosilicate glass comprising more than 30 oxides

	% (w)
$^{29}SiO_2$	45.12
$^{27}Al_2O_3$	4.87
$^{11}B_2O_3$	13.92
$^{6,7}Li_2O$	1.97
$^{23}Na_2O$	9.78
^{43}CaO	4.01
ZrO_2	0.99
ZnO	2.48
Fe_2O_3	2.89
P_2O_5	0.28
NiO	0.41
Cr_2O_3	0.50
Fission Products	10.35
⇒Mo, REE (La, Nd, Ce, ...)	
Actinides	0.89
Platinoides	1.54

For solid-state NMR investigations:
Representative simplified (3-8 oxides) compositions from the main oxides contained in nuclear glass

Many NMR Probes !

Network former cations

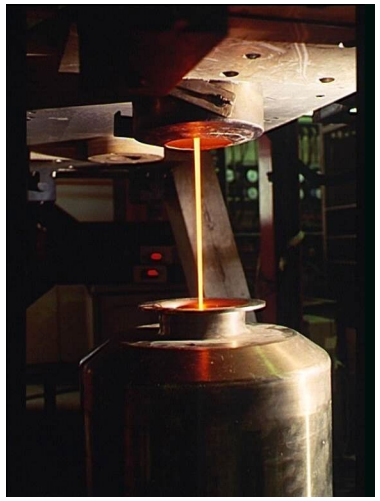
^{11}B (I=3/2) ^{27}Al (I=5/2)
^{29}Si (I=1/2)

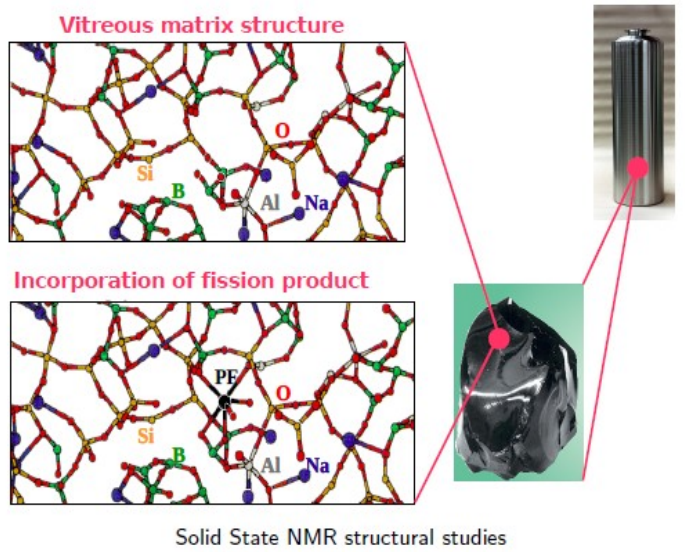
Network modifier / Charge compensator cations

^{23}Na (I=3/2) ^{43}Ca (I=7/2)
^{7}Li (I=3/2) ^{6}Li (I=1)

Central probe of bindings

^{17}O (I=5/2)





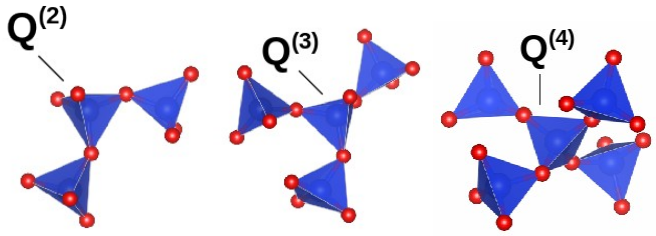
Solid State NMR structural studies

MAS NMR in Oxide Glasses

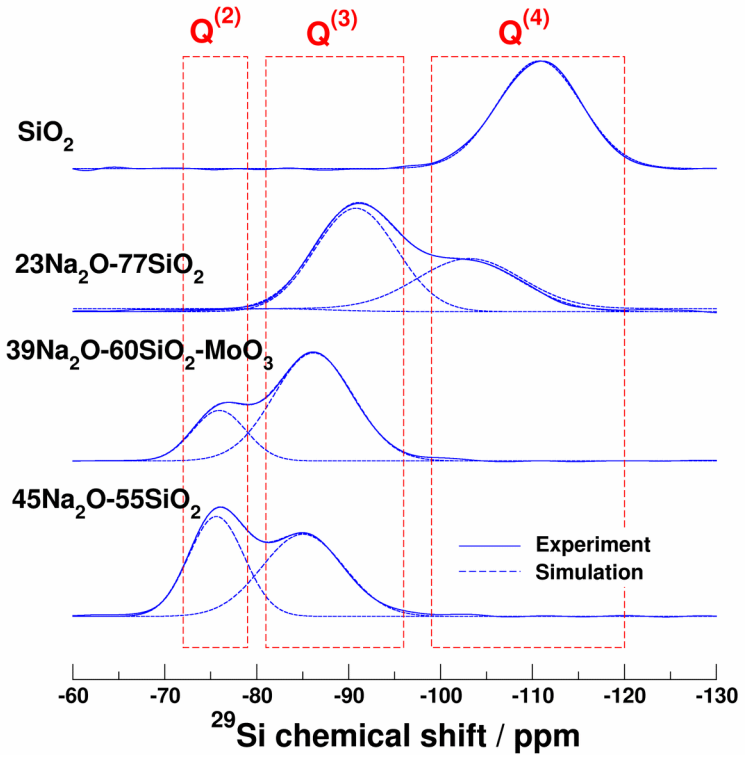
Deciphering the short-range order (**SRO**) – MAS NMR

^{29}Si

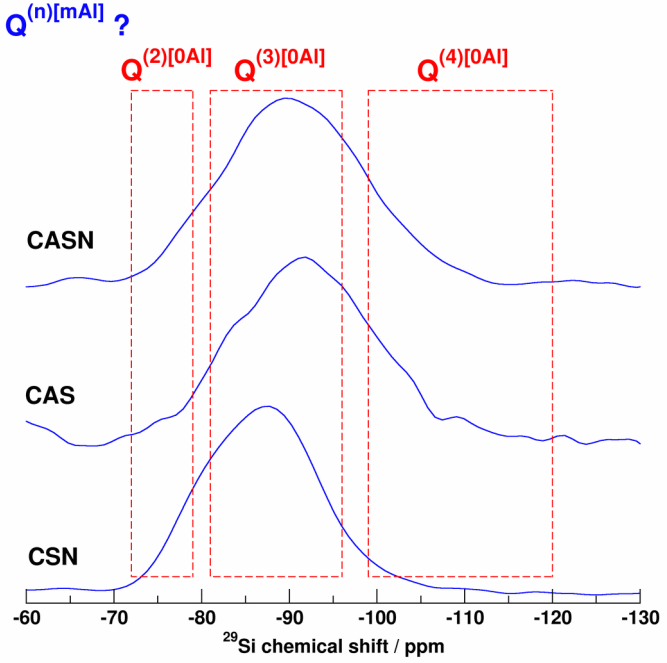
$I=1/2$



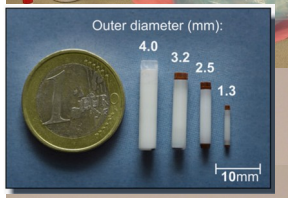
Silicon-29 MAS NMR can resolve $Q^{(n)}$ units in simple glass, revealing the polymerization degree.
But loss of resolution for more complex composition because of Next Nearest Neighbor (NNN) impact such as $Q^{(n)}(mAl)$, $Q^{(n)}(mB)$, … Computations are the needed.



SiO_2-Na_2O



SiO_2-Al_2O_3-Na_2O-CaO

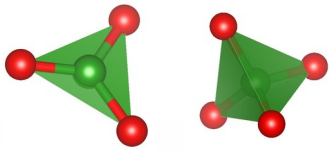


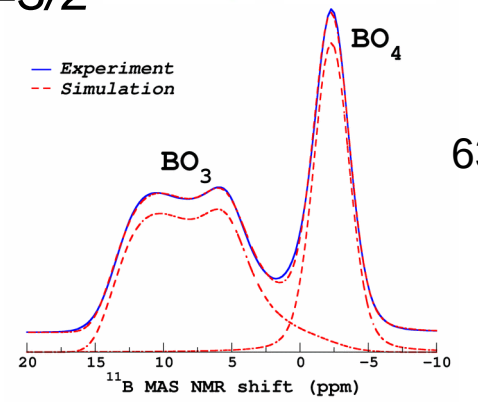
Angeli et al. Geochimica et Comoschimica Acta, 75 **2011**, *Gambuzzi et al. Geochimica et Comoschimica Acta 125* **2014**

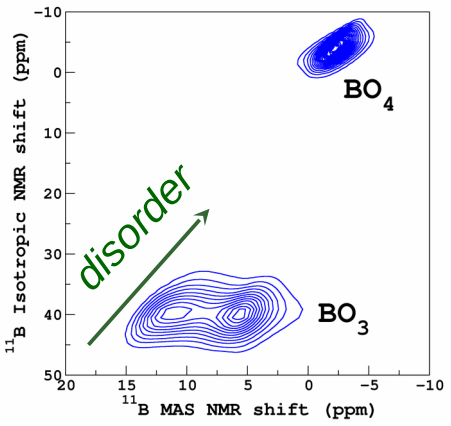
MAS NMR in Oxide Glasses

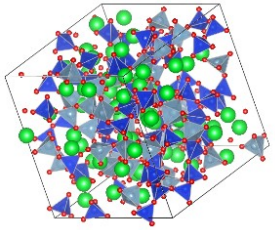
Deciphering the short-range order (**SRO**) – 2D MQMAS NMR

^{11}B $I=3/2$









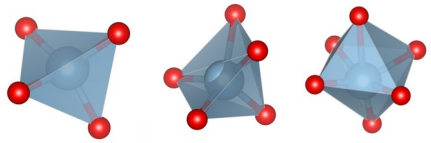
Aluminoborate glass
63 B_2O_3-21 La_2O_3 -16 Al_2O_3

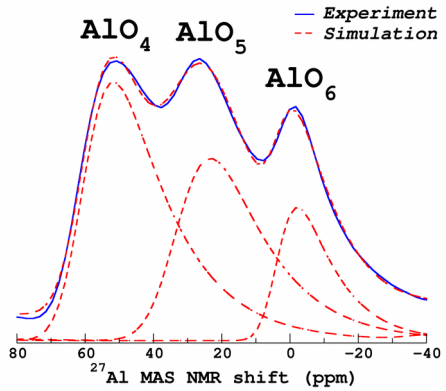
1D NMR

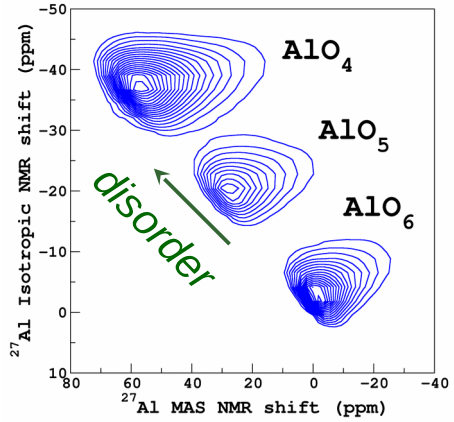
Gain in resolution with 2D NMR

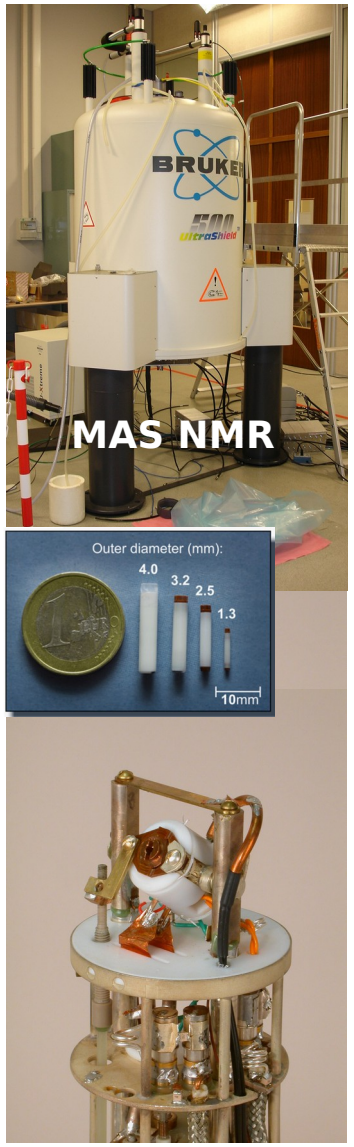
2D MQMAS NMR
(Triple Quantum MAS)

^{27}Al $I=5/2$







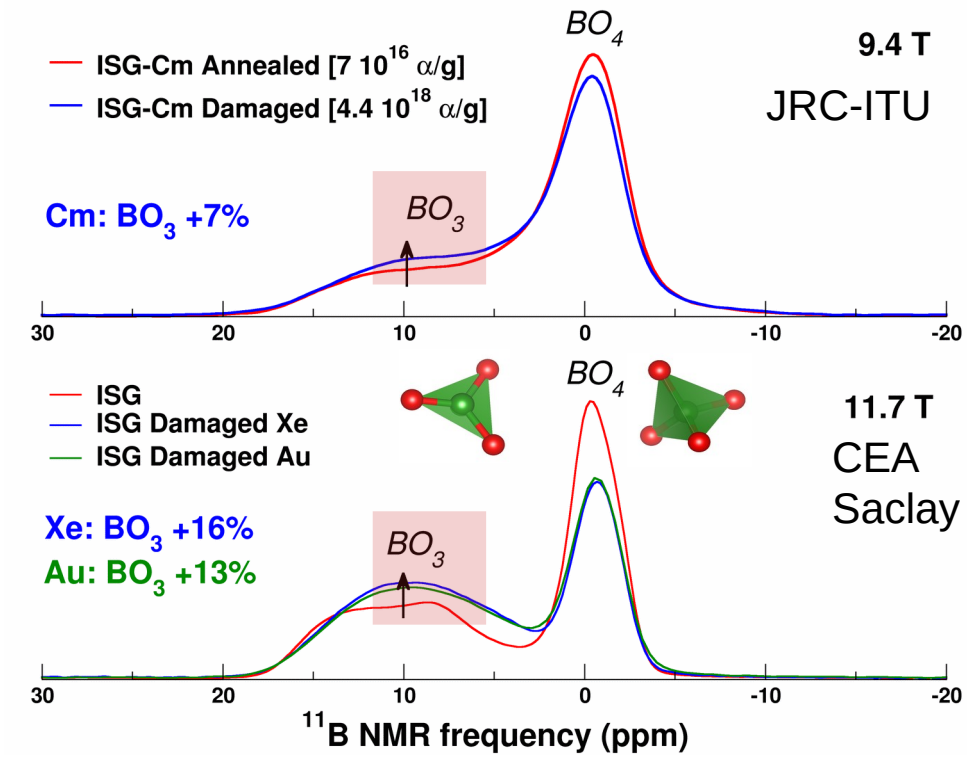


High-resolution MAS NMR reveals the structural motifs (network formers) building the glass network. NMR lineshapes are reflective of the local disorder and the underlying distribution of NMR parameters.

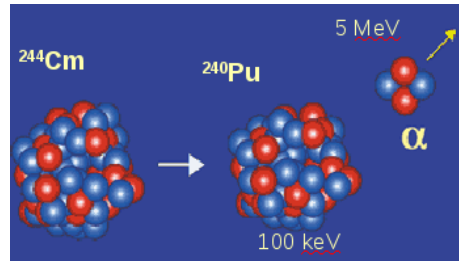
E. Chesneau, D Caurant, T. Charpentier, in preparation.

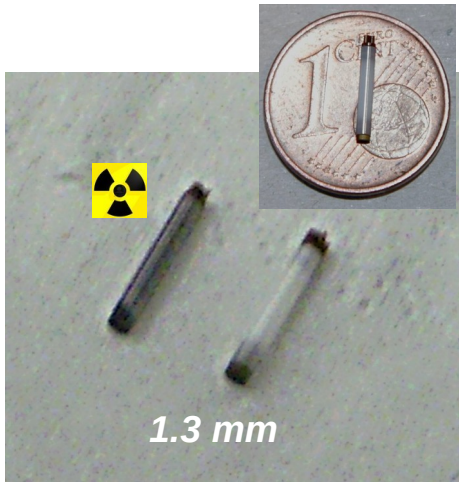
Self-Irradiation Damages: Radiological NMR

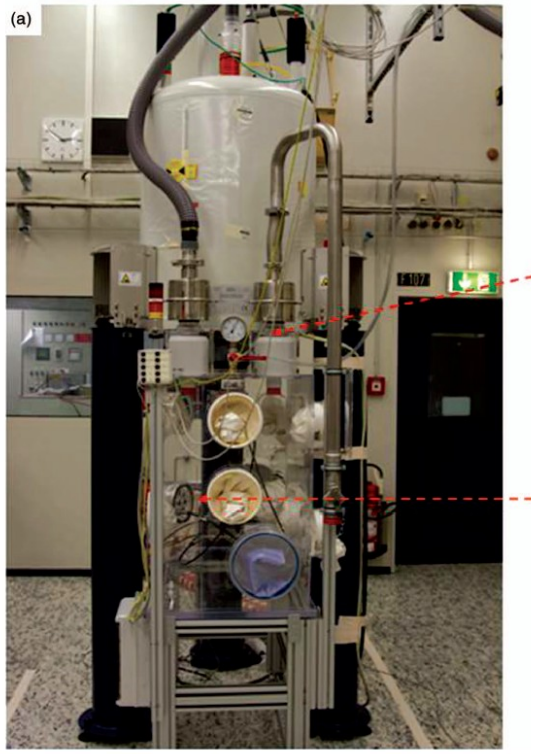
Radiological MAS NMR : examination of self-irradiated glasses (0.1% mol ^{244}Cm) and comparison with heavy ions external irradiations



BO_4 to BO_3 conversion and other structural modifications ***are lower*** in alpha-decays damaged glass than in heavy ions irradiated samples (Self-Healing Effects)







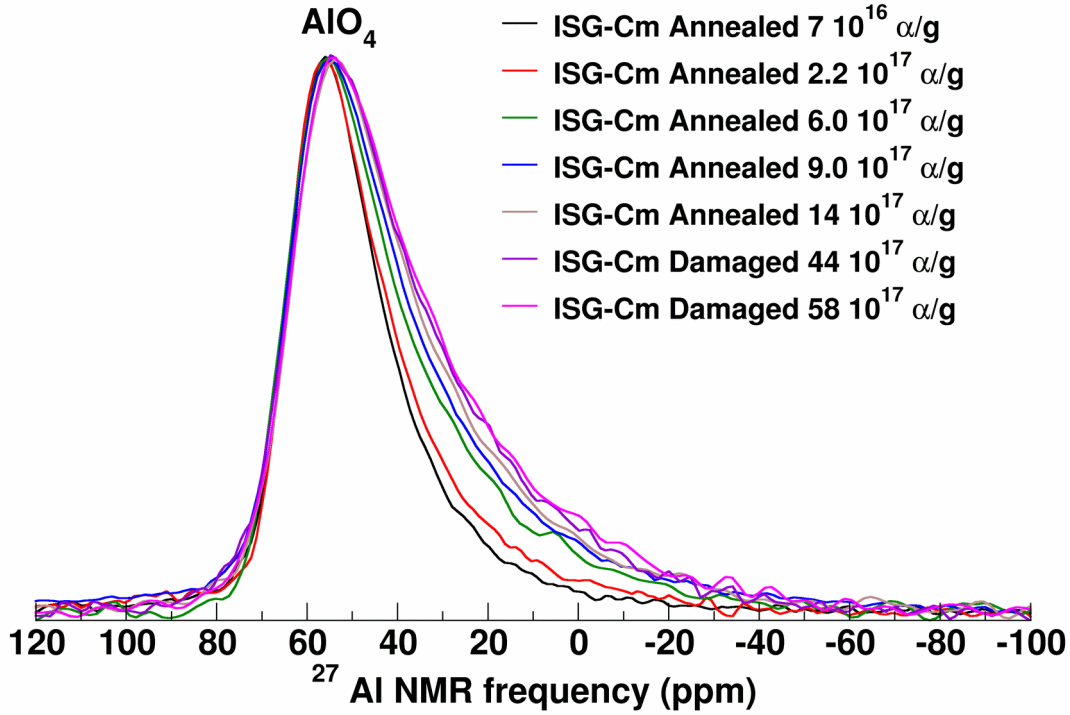
Nuclearized NMR (9.4T) @JRC in Karlsruhe

T. Charpentier et al., Scientific Reports 6 (**2016**).

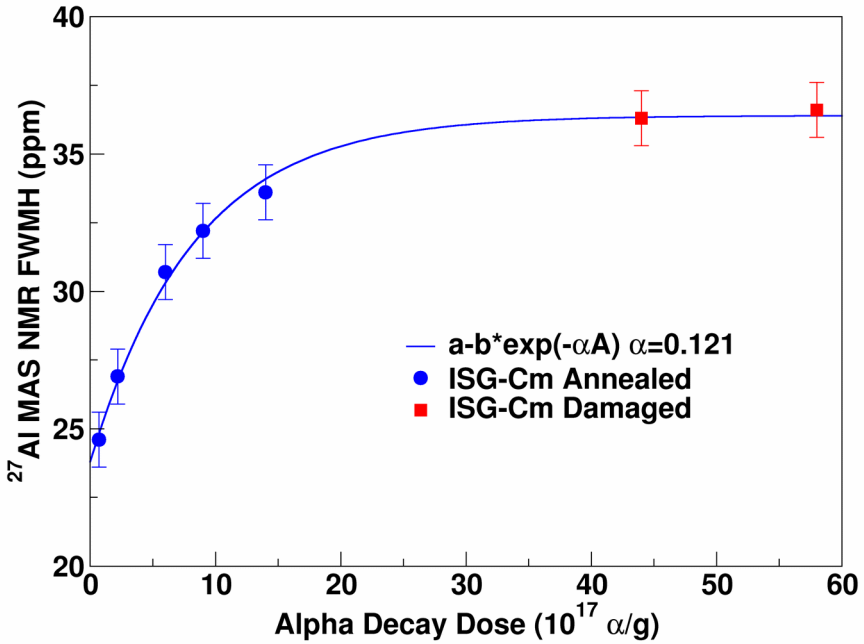
T. Charpentier, S. Peuget, EURACT-NMR Grant RP02/05 *Radiation damage in nuclear glass*.

Self-Irradiation Damages : Radiological NMR

Radiological MAS NMR : examination of self-irradiated glasses (0.1% mol ^{244}Cm)



The variations suggest a change from AlO_4 (Na^+) to AlO_4(Na^+,Ca^{++}). No AlO_5 is formed I contrast to external irradiation*.



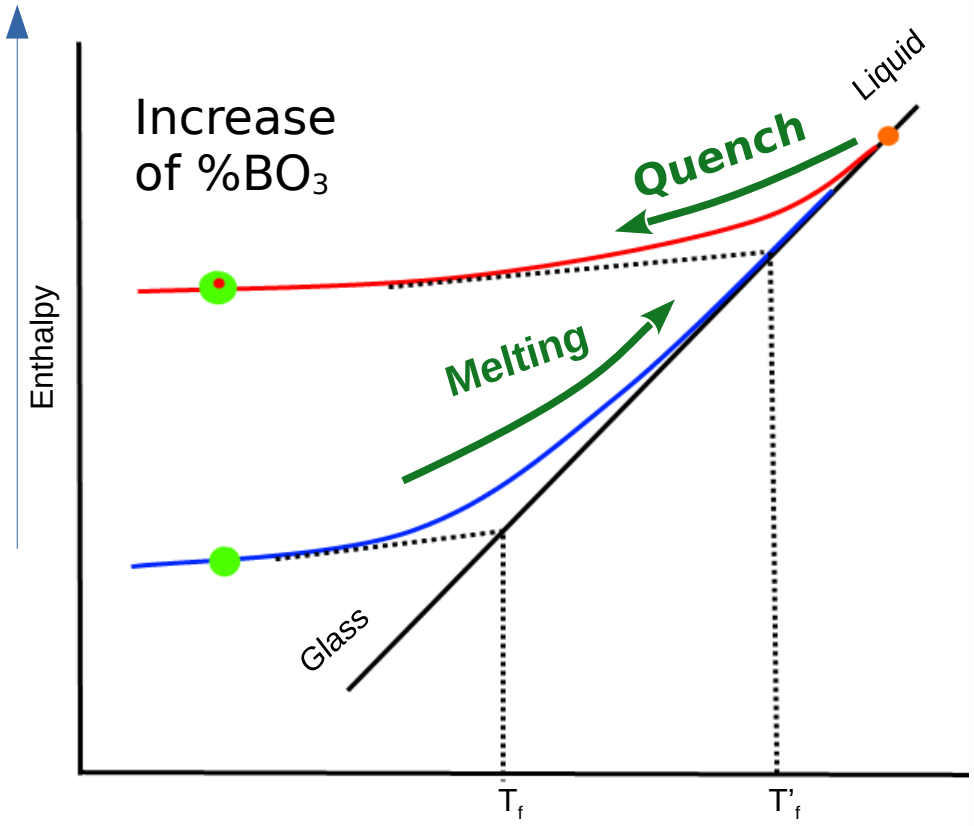
^{27}Al MAS NMR evolution is well described by a *single impact model*.
The damaged volume per event is estimated as 480 nm^3, comparable to the value obtained on macroscopic properties (300nm^3).*

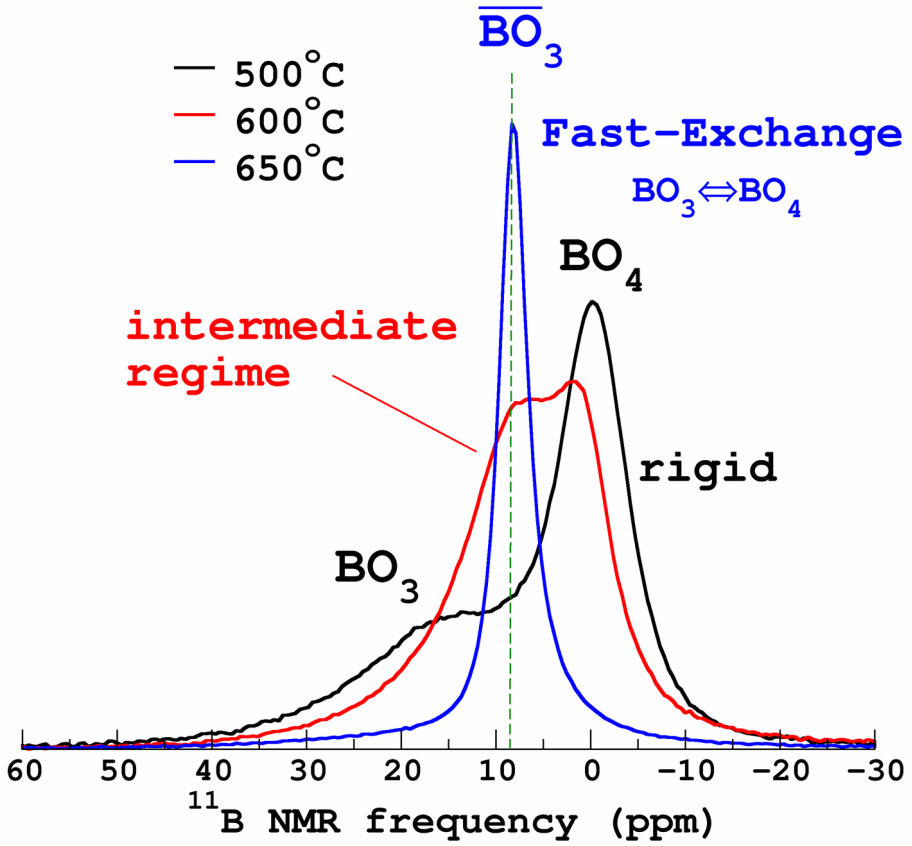
T. Charpentier et al., Scientific Reports 6 (**2016**) ; E.A. Maugeri et al., J. Am. Ceram. Soc, 95 (**2012**)

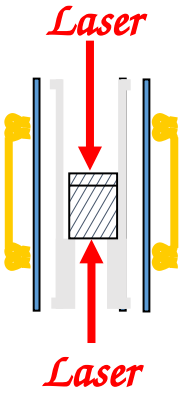
S. Peuget et al. J. Nucl. Mat. 354 (**2006**) ; *C. Mendoza et al. Nucl. Inst. and Meth. Phys. Res. Sect. B 325 (**2014**)

Boron speciation in the melt

High-Temperature NMR (CNRS CEMTHI, ORLEANS)







*Incident Beam creates a local heating (thermal spike) leading to a "localized" ultra-fast Melt/Quench event : **the supervitrification***

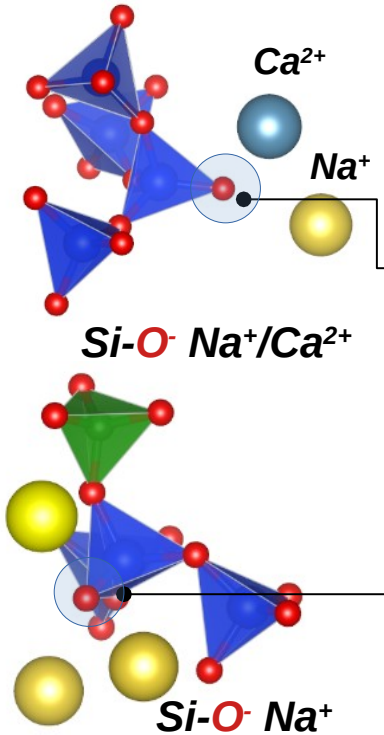
C. Mendoza et al., JNCS **2014**, S. Peuget et al. JNCS **2013**

Massiot et al., Solid State Ion. **1990** *37* 223-229
Bonafous et al., J. Chim. Phys. **1995** 92 1867-1870
Lacassagne et al., J. Phys. Chem. B **2002** 106 1862

MAS NMR in Oxide Glasses

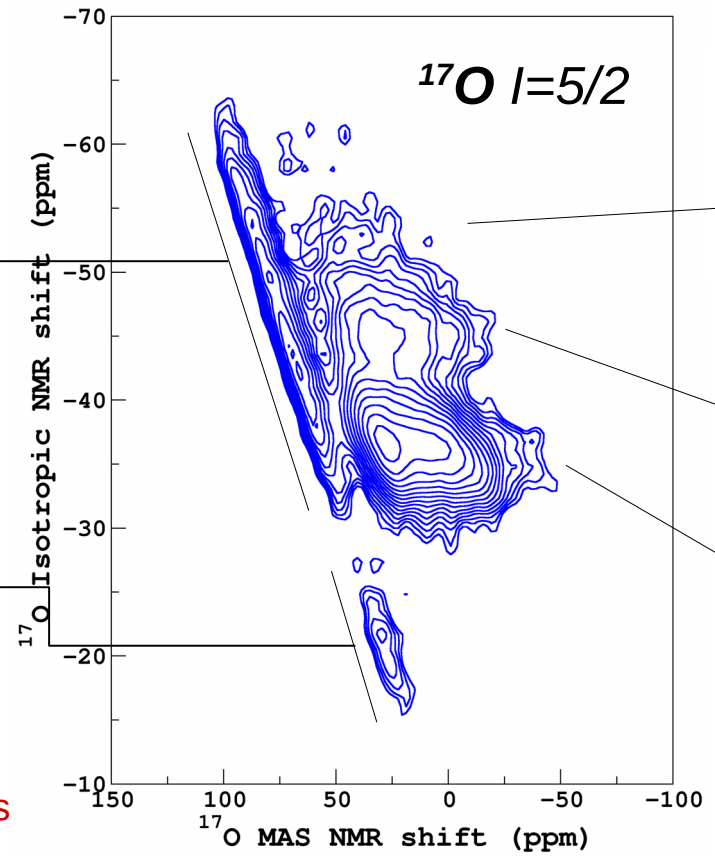
Deciphering the Intermediate Range Order (**IRO**) : ^{17}O 2D MQMAS NMR

Cation Mixing

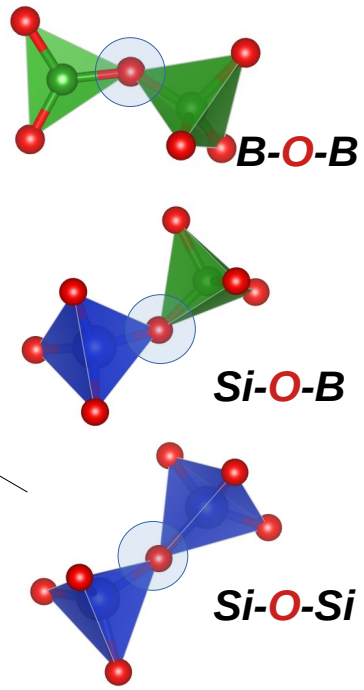


Non-Bridging-Oxygens

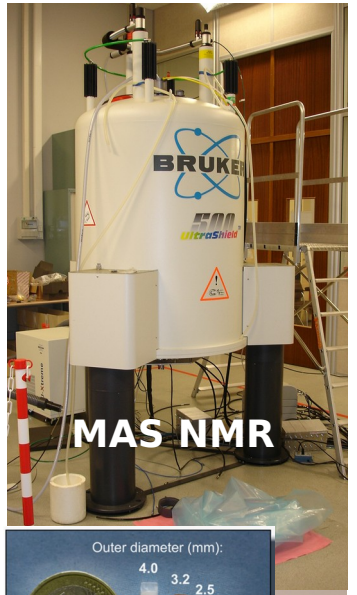
Analysis of a
soda-lime borosilicate glass



Network Former Mixing



Bridging-Oxygens

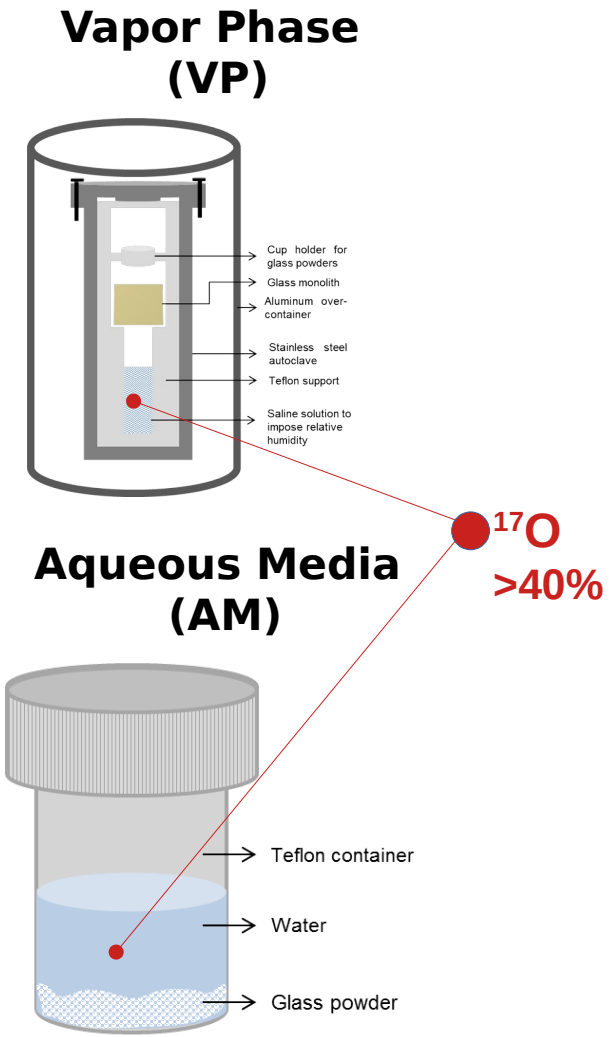


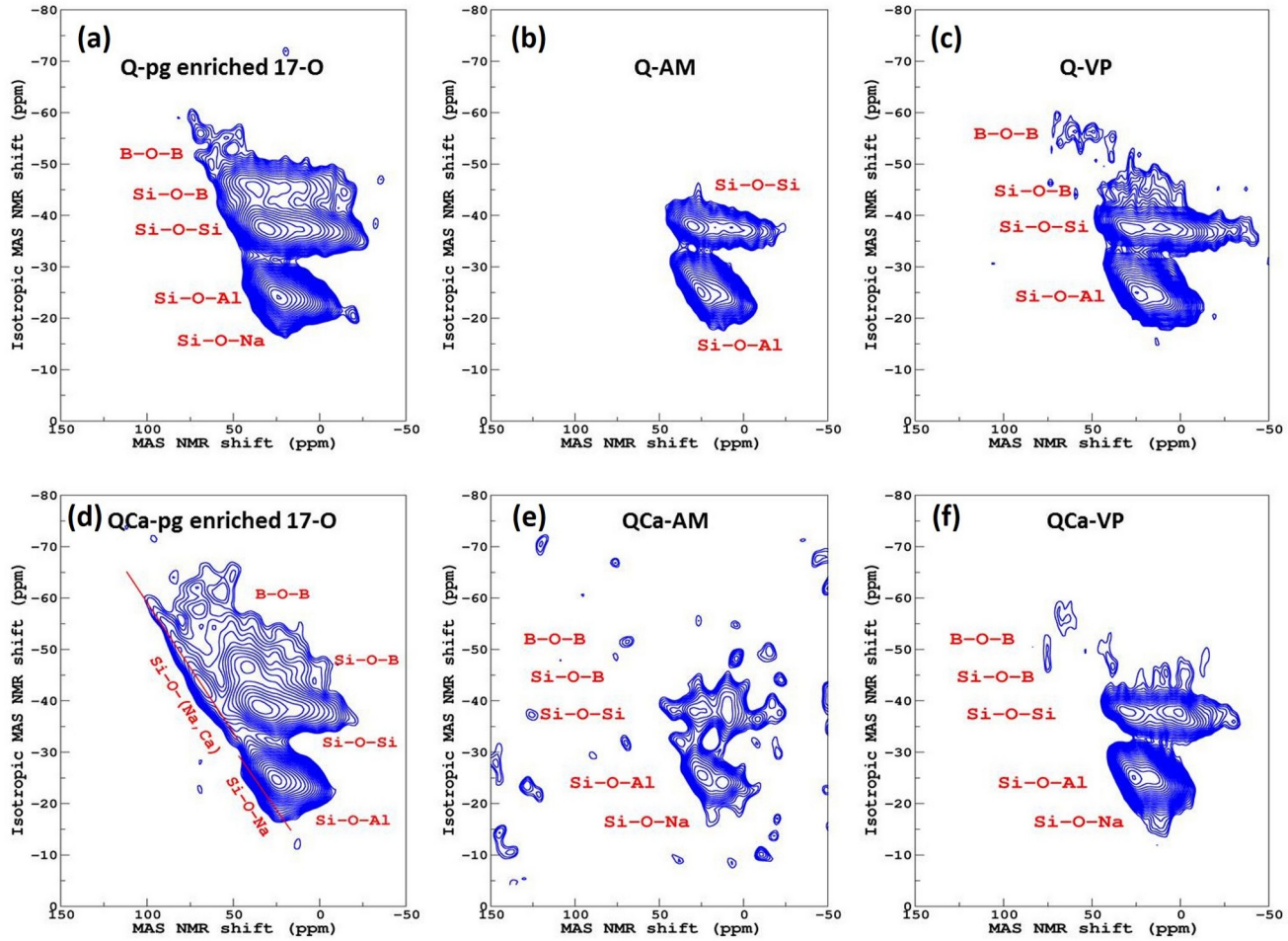
^{17}O MQMAS NMR reveals the structural motifs at a **molecular** level:
Accessing the **intermediate** range order (**IRO**)
NMR offers other (many) possibilities based on through-space (J) and –bond (D) interactions (but they are complex experiment for quadrupolar nuclei …)
^{17}O enrichment must be ≳40 %

NMR of altered Glasses: scrutating the altered layer

The oxygen-17 NMR approach

S. Narayanasami et al., npj Mat. Deg. 6 (**2022**)



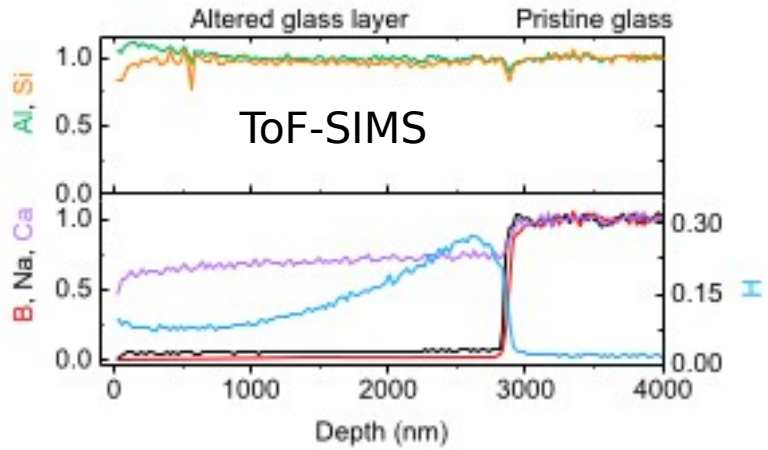


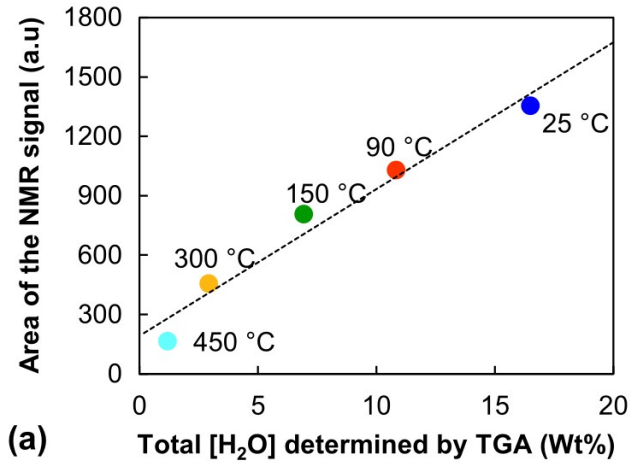
- Dominant Si-O-Si and Si-O-Al peaks (as expected…) in altered layer (depleted in boron and sodium)
- Confirmation of B-O-B and Si-O-B formation in VP altered samples only
- Weaker signal in QCa
- Note: ^{17}O MQMAS filters out the (Si-)-O-H signals

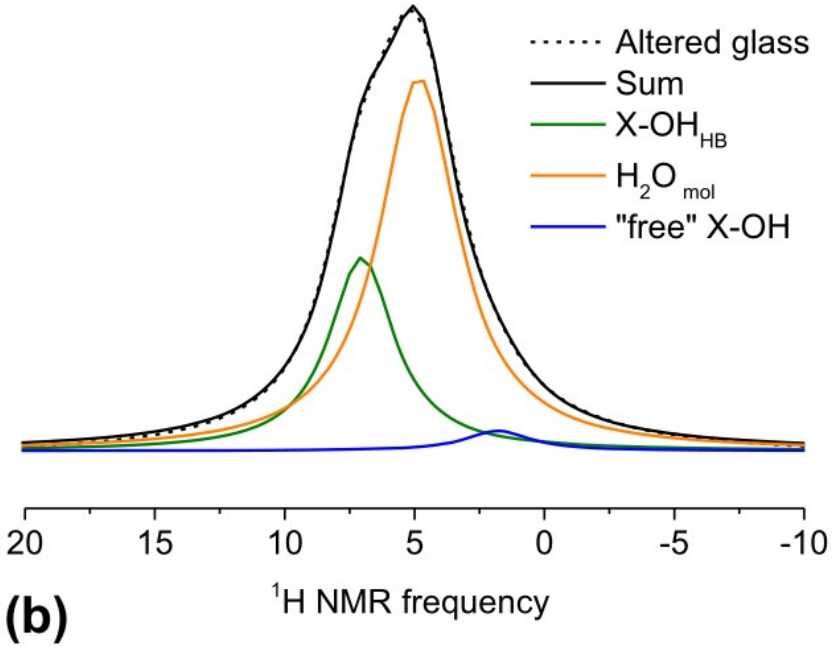
NMR of altered Glasses: scrutating the altered layer

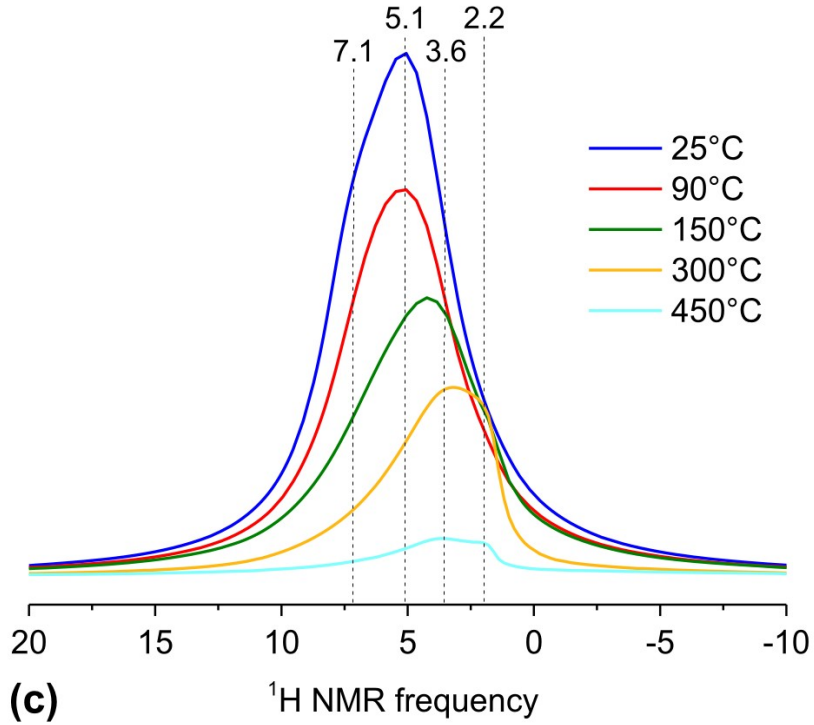
^{1}H MAS NMR – accurate quantification of molecular water content

M. Collin et al., npj Mat. Deg. 4 (**2018**)









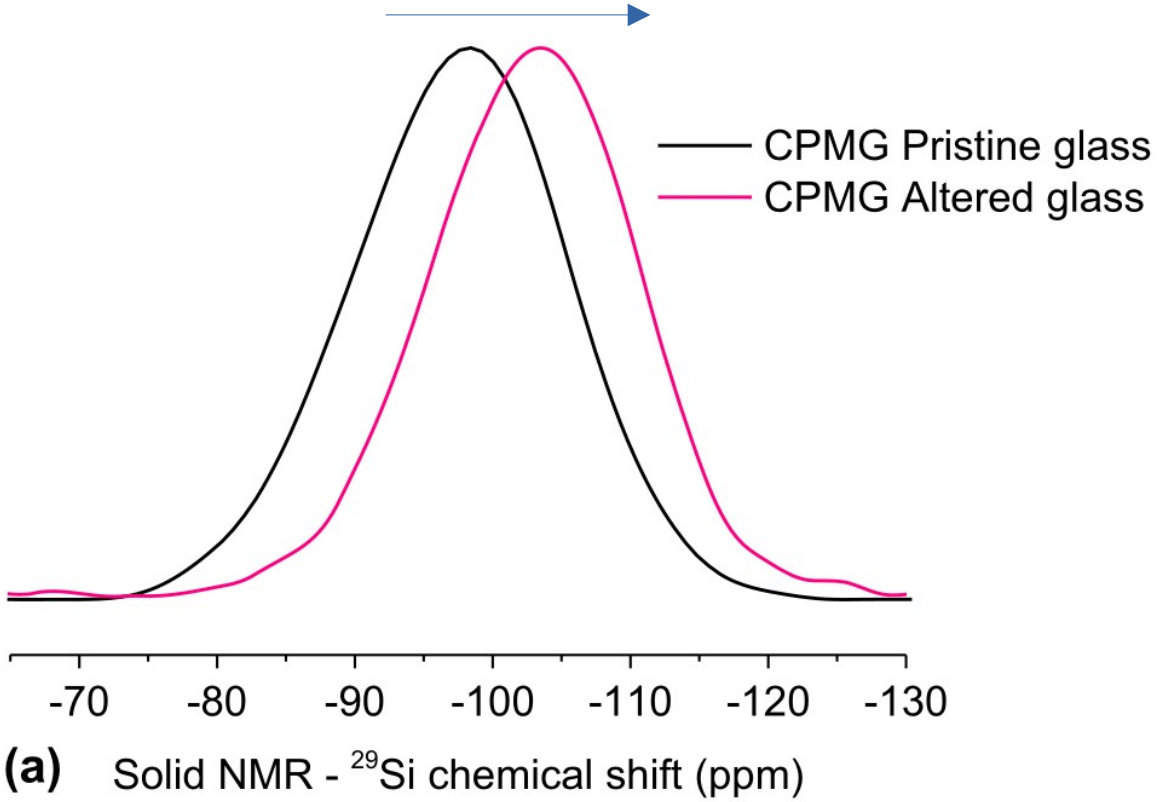
With molecular water removal, hydrogen bonds disappear, causing
A decrease of the ^{1}H shift of the Si-OH line (free Si-OH at ~ 2 ppm)

Alteration at pH(90°C)=7 in a solution saturated with amorphous silica (no silicate network dissolution)
Glass alteration is therefore driven only by the transport of water. See M. Collin, npj Mat. Deg. 4 (2018)

NMR of altered Glasses: scrutating the altered layer

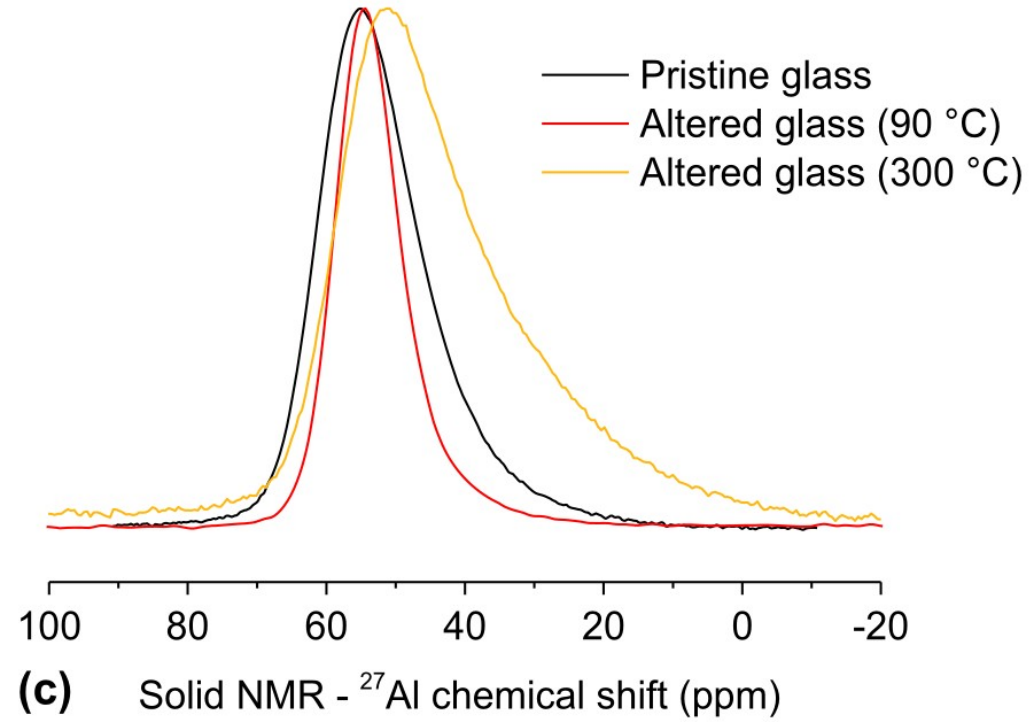
MAS NMR – modification of the network

M. Collin et al., npj Mat. Deg. 4 (**2018**)



(a) Solid NMR - ^{29}Si chemical shift (ppm)

Variation due to a change in polymerization but also as a result of the **boron depletion.**



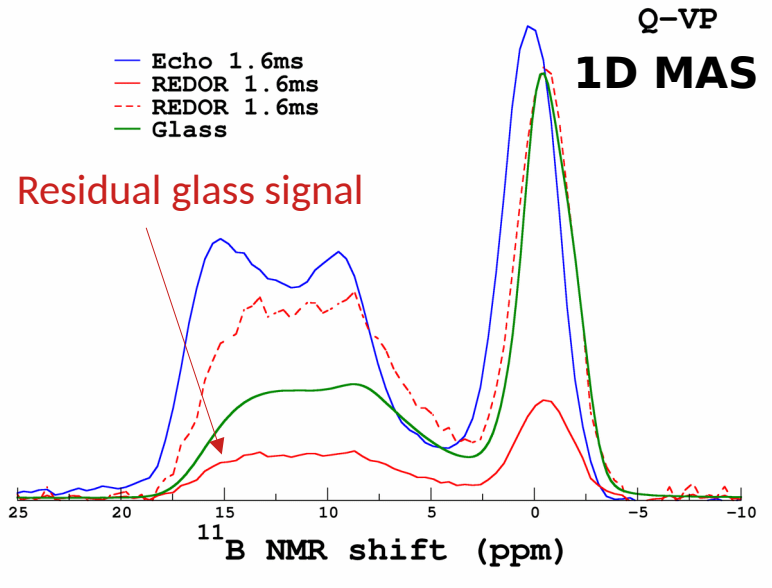
(c) Solid NMR - ^{27}Al chemical shift (ppm)

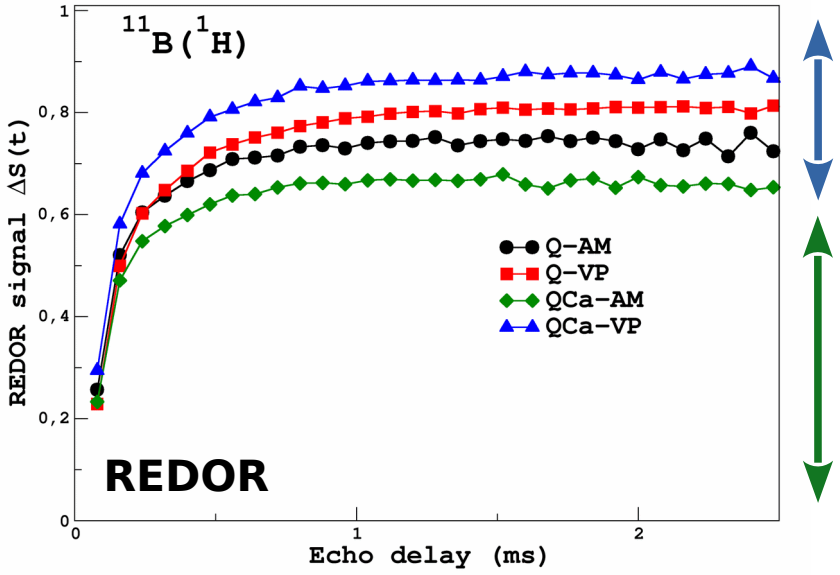
In gel, AlO_4 linewidth reduction due to coordination by H_2O water molecules. Removing molecular water, coordination by Ca^{2+}. Ca^{2+} is « solvated ».

Alteration : at pH(90°C)=7 in a solution saturated with amorphous silica (no silicate network dissolution) Glass alteration is therefore driven only by the transport of water. See Ref. M. Collin et al. npj Mat. Deg. 4 (2018)

NMR of altered Glasses: scrutating the altered layer

^{11}B MAS NMR – Probong the partial retention of B in the gel



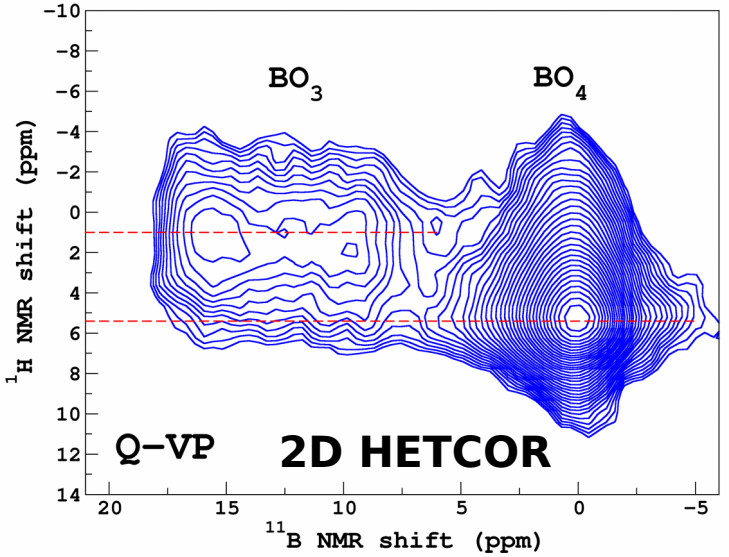


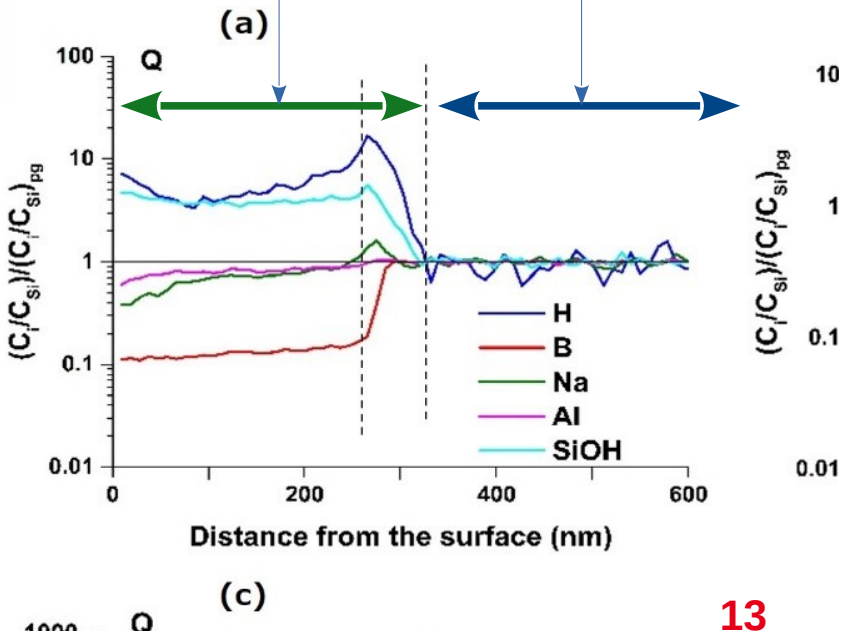
~ non-hydrated Boron
(core glass)

~ hydrated Boron
(altered glass)

NMR offers techniques that can select to the boron in the hydrated with ^{1}H-^{11}B Cross-Polarisation experiment (CPMAS) or REDOR, based on a transfer of magnetization between the two nuclei.

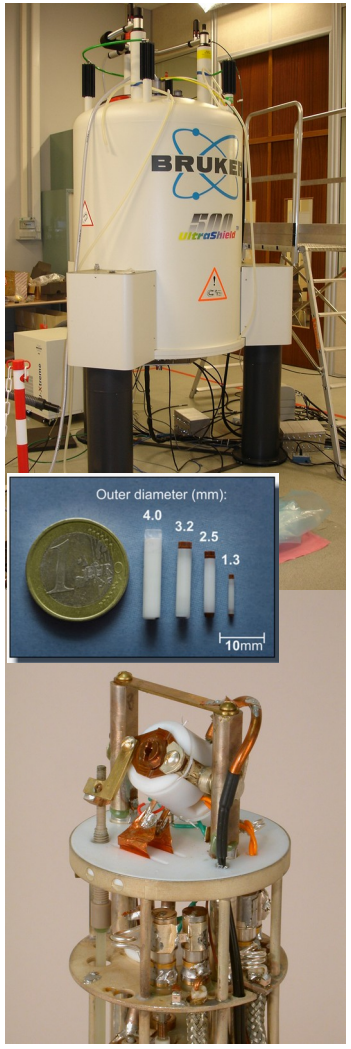
S. Narayanasami et al., npj Mat. Deg. 6 (**2022**)



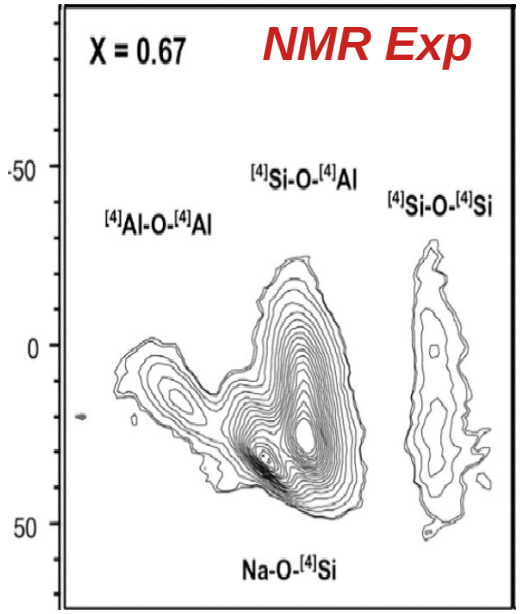


The MD-GIPAW Approach

Computing NMR experiments from First-Principles

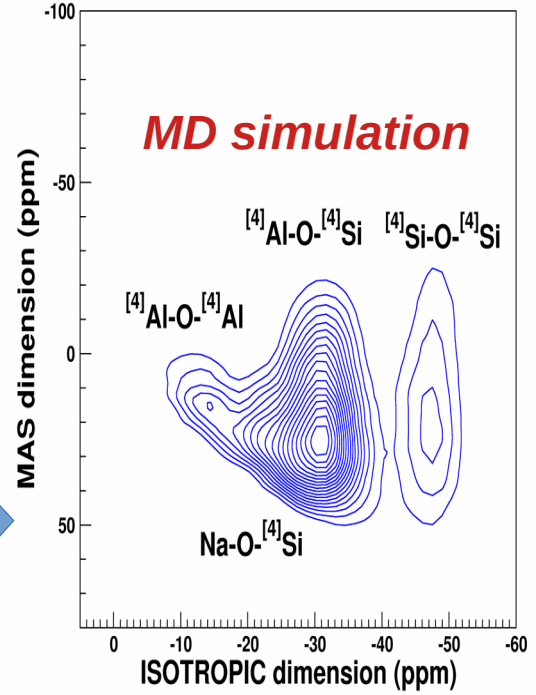


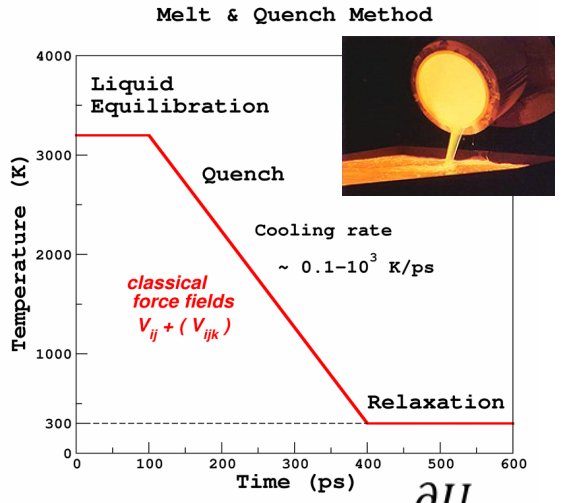
^{17}O MQMAS, 11.7 T ~1 to 5 days



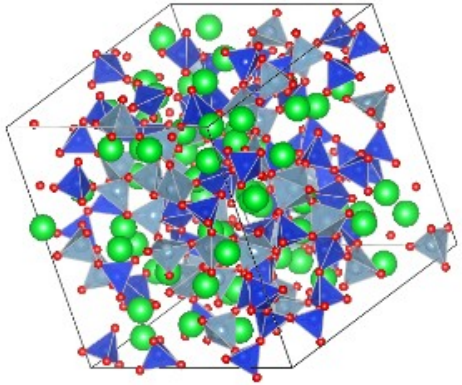
Experiment Interpretation

MD assessment





$$m_i \ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i = -\frac{\partial U}{\partial \boldsymbol{r}_i}$$

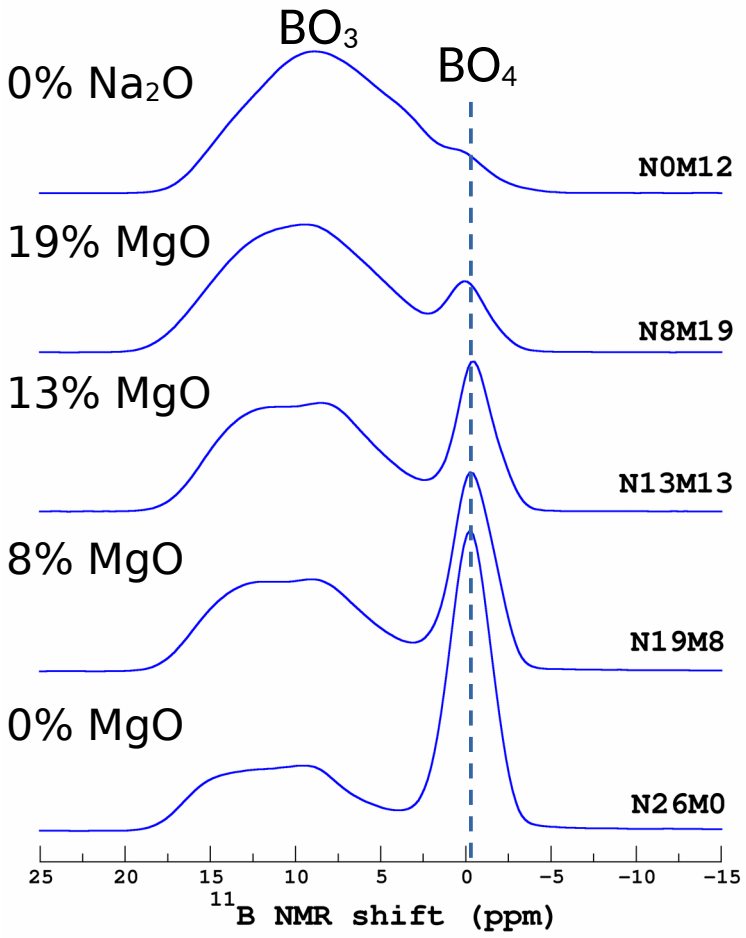


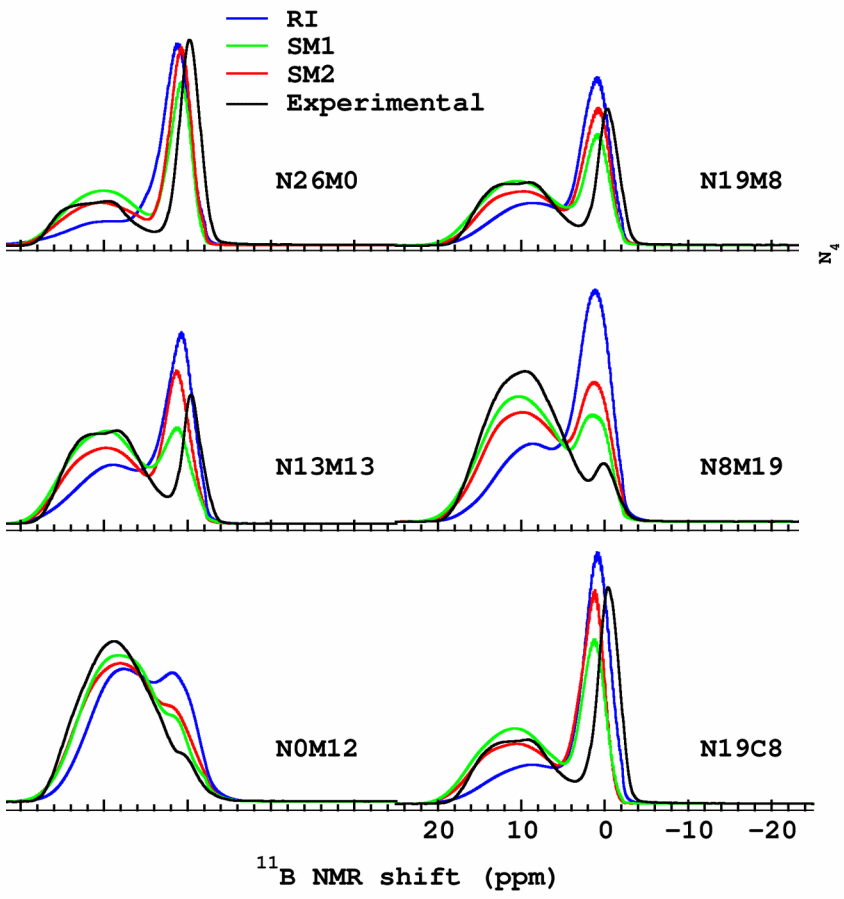
VASP-GIPAW, 400-800 atoms
~ 4-8h, 48-96 procs

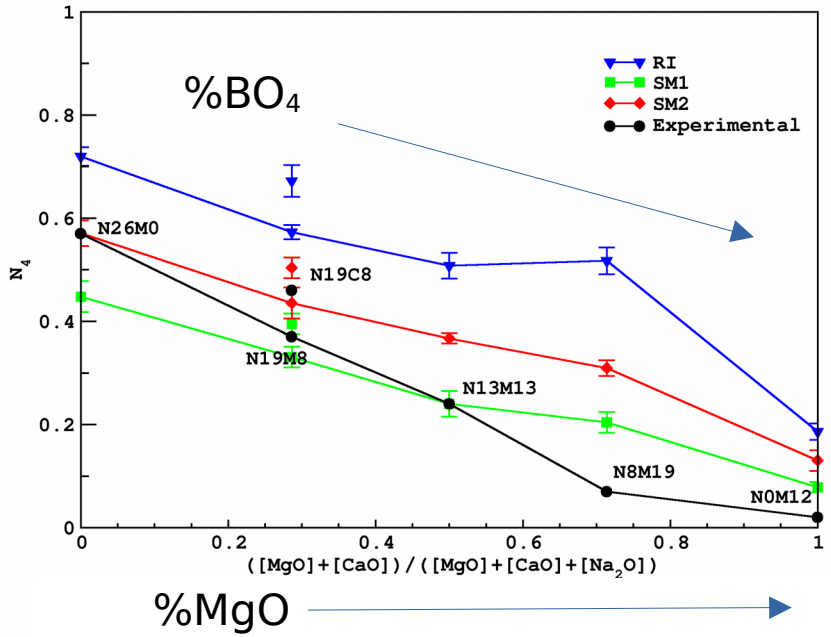
T. Charpentier et al., *Computational simulations of solid state NMR spectra: a new era in structure determination of oxide glasses* ; RSC Adv. 3, 10550–10578 (**2013**).

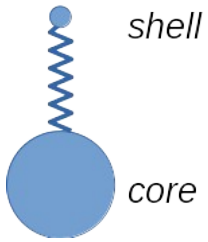
Impact of Magnesium on NW glasses

Effects of Magnesium on the Structure of Aluminoborosilicate Glasses: **NMR Assessment of Interatomic Potentials Models** for Molecular Dynamics









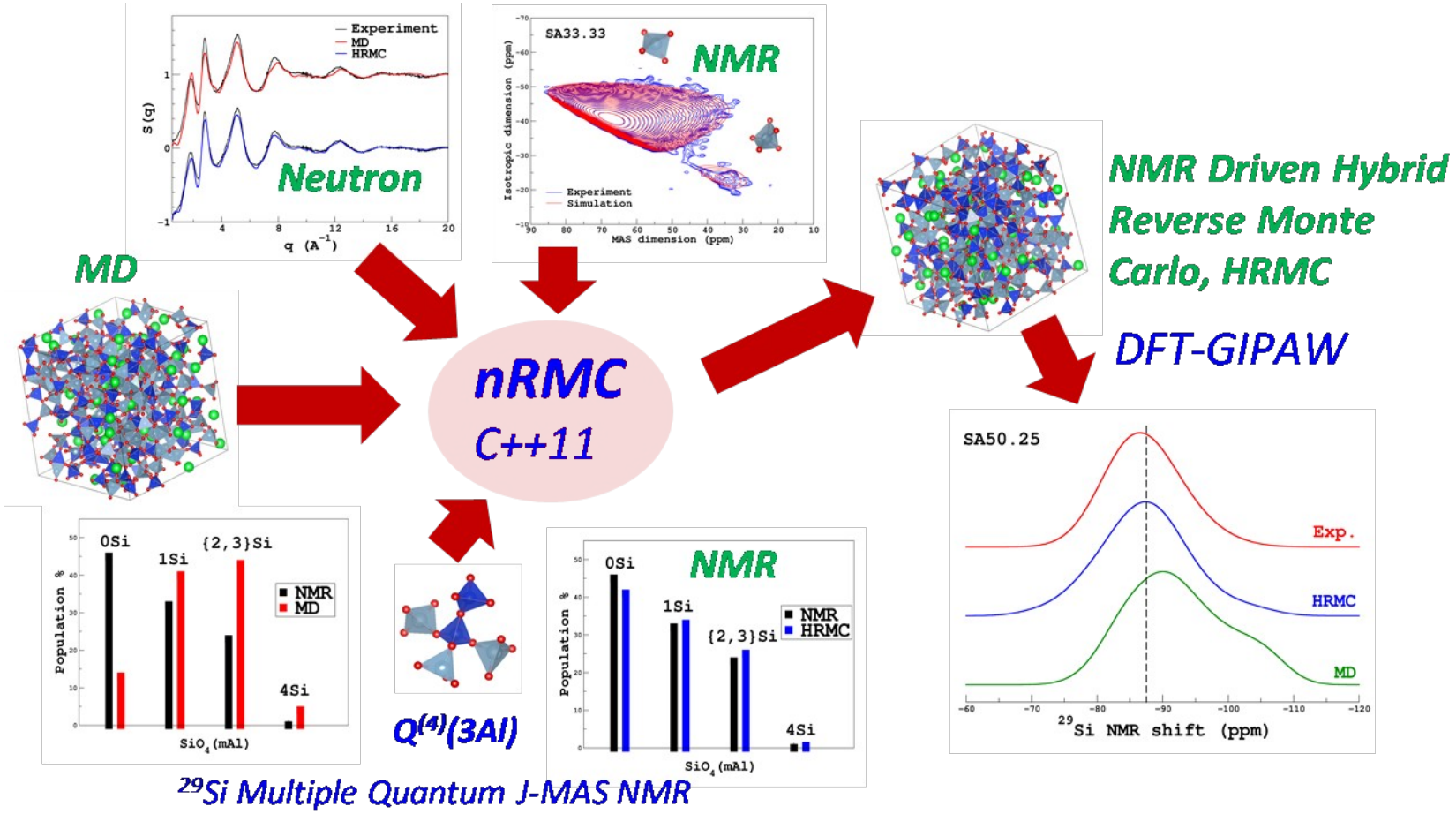
Drude Polarizable Oxygen Model

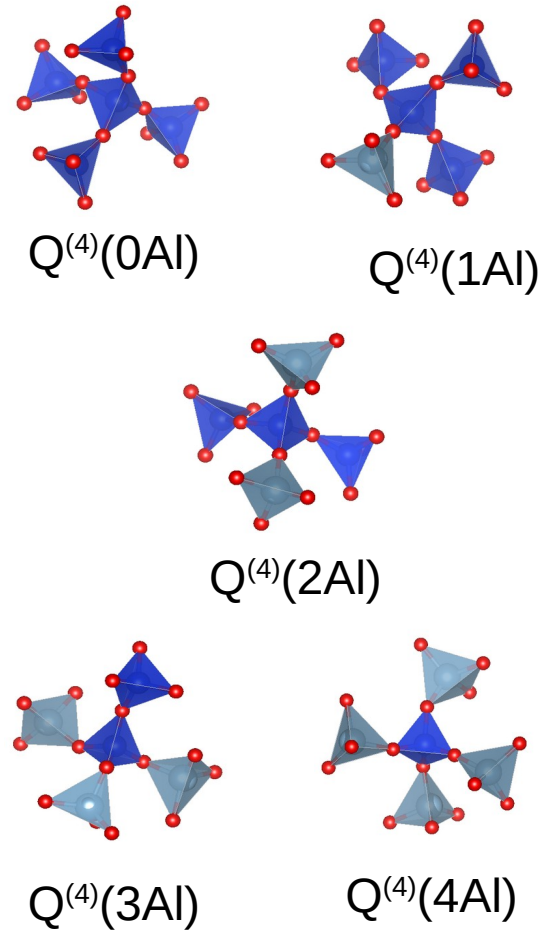
Shell Model (polarizable oxygen atoms) performs much better than Rigid Ion Model (RI) to reproduce NMR features

N. Bisbrouck et al., J. Am. Ceram. Soc. 104, (**2021**), M. Bertani et al. J. Am. Ceram. Soc. 106 (**2023**)

NMR-Driven Reverse Monte Carlo

Including NMR constraints (& shifts?) in RMC Modelling



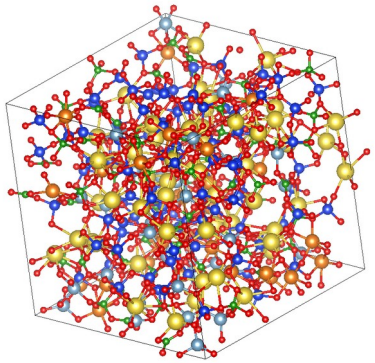


Using a **RMC approach including IRO constraints** (here Q$^{(n)}$(mAl) units) in the modelling significantly **improves the NMR simulations** (here ^{29}Si MAS NMR spectra) and macroscopic properties (such as density)

T. Charpentier et al. , in preparation

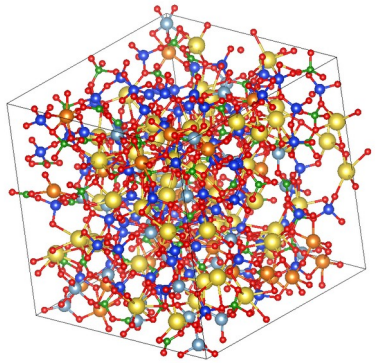
The MD-GIPAW workflow

MD or MC simulations

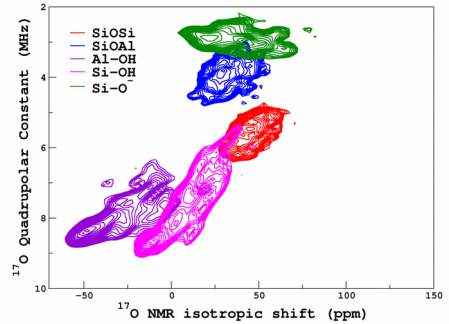


DFT optimization (VASP/CP2K)

DFT Optimized (0K) structure



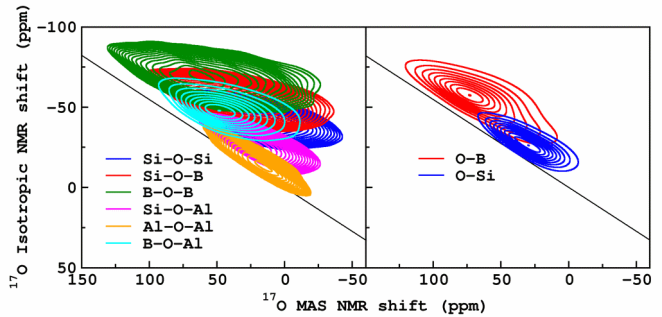
DFT GIPAW (VASP)



Magnetic shielding and EFG tensors for all atoms

fpNMR (Th.C)

NMR experiments



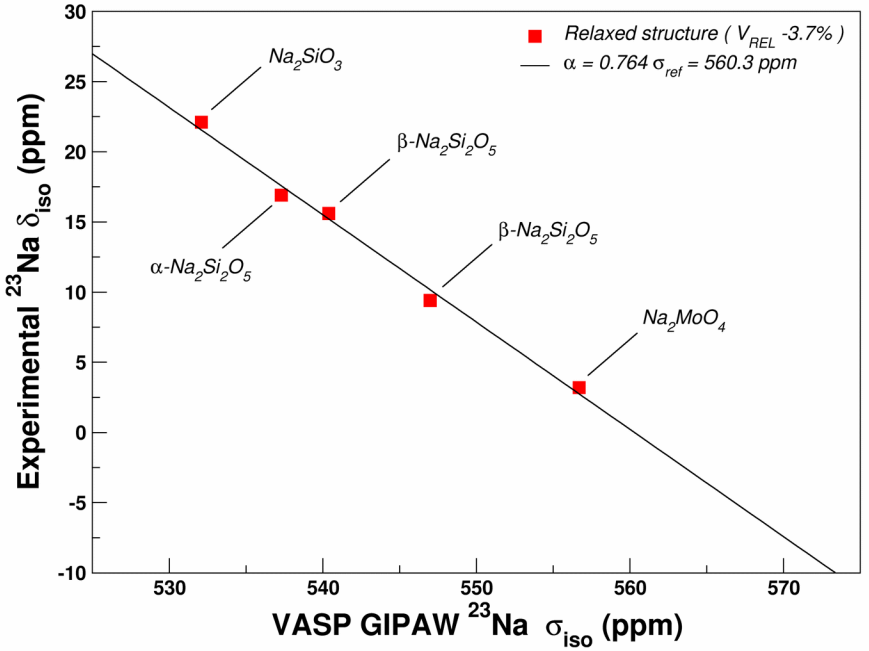
Current limitations in size due to the high cost of DFT computations
CP2K / VASP ~ 1000 atoms.

MD-GIPAW Modelling is limited to **frozen structures** : vibrations and local mobilities are not accounted for that can impact the experimental NMR spectrum (motional narrowing effects).

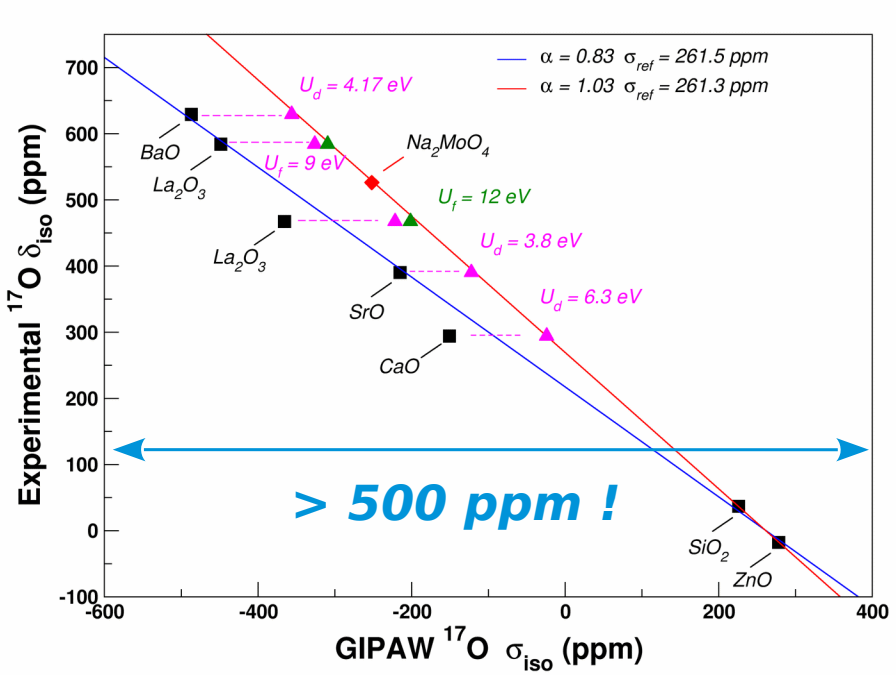
Solution : use **Machine Learning** !

The DFT GIPAW method

Computing NMR properties in periodic solids : *C.J. Pickard, F. Mauri, Phys. Rev.*



- Plane Wave Pseudopotential Method
- Outstanding accuracy (~ experimental accuracy)
- CASTEP, Quantum Espresso, VASP, (CP2K)
- Up to 1000 atoms systems (VASP)
- Typically ~ 5h/48 procs for 400 atoms
- DFT+U required for (d,f) empty orbitals



GIPAW REVIEWS :

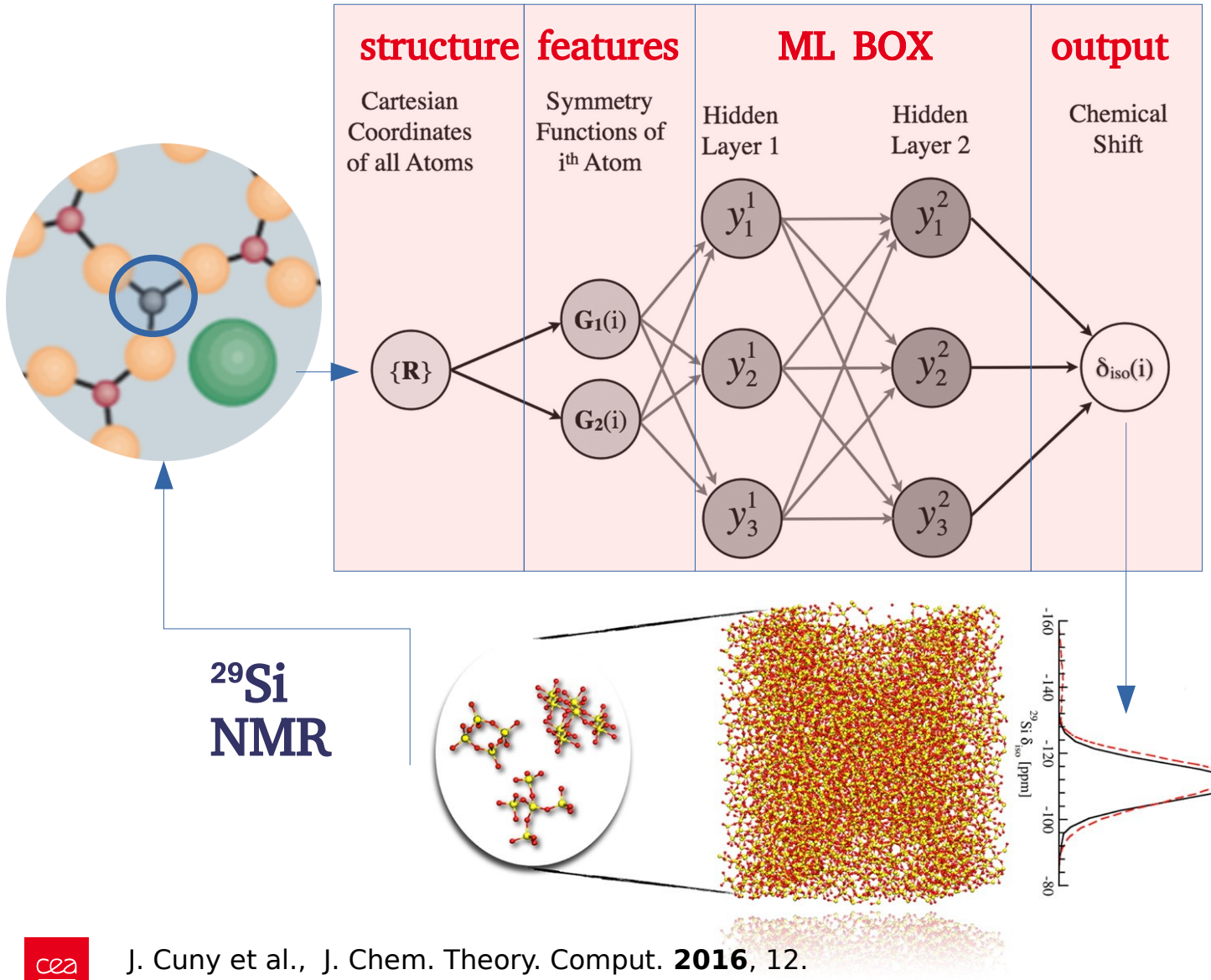
T. Charpentier, *The PAW/GIPAW approach for computing NMR parameters: A new dimension added to NMR study of solids*, Solid State Nucl. Magn. Reson., **2011**, 40, 1–20.

C. Bonhomme et al., *First-Principles Calculation of NMR Parameters Using the Gauge Including Projector Augmented Wave Method: A Chemist's Point of View, Chem. Rev.*, **2012**, 112, 5733–5779.

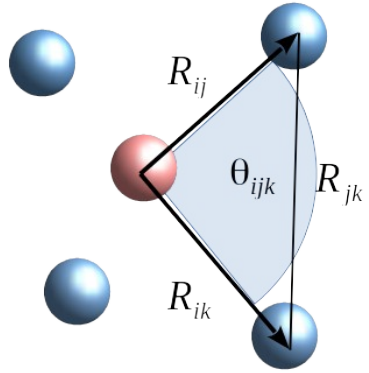
T. Charpentier, A. Pedone, A.C. Menziani, *Computational simulations of solid state NMR spectra: a new era in structure determination of oxide glasses* ; RSC Adv. **2013**, 3, 10550–10578.

NMR shifts by Machine Learning

A case of study : Vitreous Silica SiO_2



Atomic Descriptors (or features)



Radial descriptors

$$G_i^{(1)}(\eta, R_s) = \sum_{j \neq i} e^{-\eta\left(R_{ij}-R_s\right)^2} f_c\left(R_{ij}\right)$$

Angular descriptors

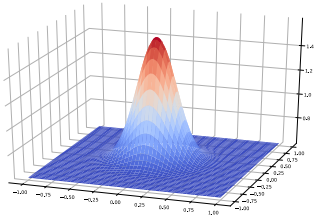
$$G_i^{(2)}(\eta, \lambda, \xi) = 2^{1-\xi} \sum_{j,k \neq i} \left(1+\lambda \cos\theta_{ijk}\right) \times e^{-\eta\left(R_{ij}^2+R_{ik}^2+R_{jk}^2\right)} f_c\left(R_{ij}\right) f_c\left(R_{ik}\right) f_c\left(R_{jk}\right)$$

J. Cuny et al., J. Chem. Theory. Comput. **2016**, 12.
J. Behler, M. Parrinello, Phys. Rev. Lett. **2007**, 98.

The SOAP descriptors

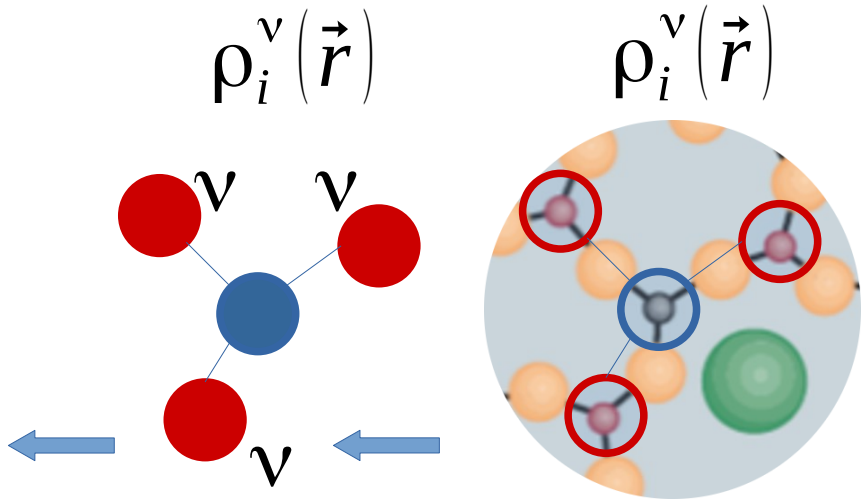
Smooth expansion of the atomic density with a radial cutoff function

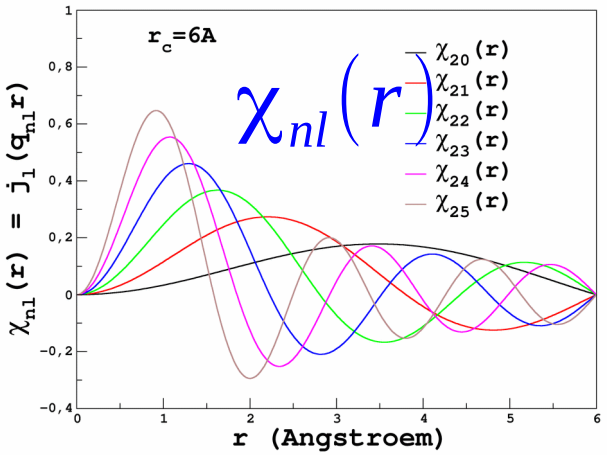
$$\rho_i^{\nu}(\vec{r}) = \sum_{j \in N_i^{\nu}} G_{\sigma}(\vec{r} - \vec{r}_{ij}) f_c(r_{ij})$$



Spherical Harmonics & radial basis expansion

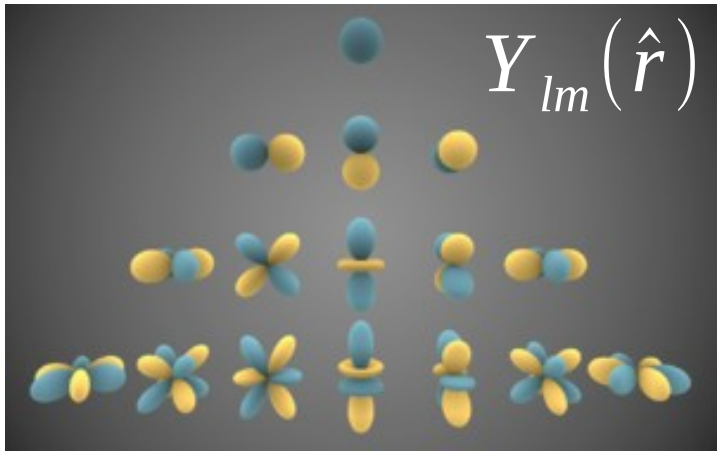
$$\rho_i^{\nu}(\vec{r}) = \sum_{nlm} c_{nlm}^{\nu} \chi_{nl}(r) Y_{lm}(\hat{r})$$





We found the spherical Bessel functions to be superior to other functions for the Radial Basis Expansion.

They form a natural orthonormal basis on the segment [0,r_c].



A.P. Bartok et al. (**2013**) *On representing chemical environments*, Phys. Rev. B

E. Kocer et al. (**2020**) *Continuous and optimally complete description of chemical environments using Spherical Bessel descriptors*, AIP Advances 10, 015021

The SOAP descriptors

Atomic local environment: $$\rho_i^{\nu}(\vec{r}) = \sum_{nlm} c^{\nu}_{nlm}\, \chi_{nl}(r)\, Y_{lm}(\theta,\phi)$$

Rotational invariant (isotropic shift) descriptors are

$$c^{\nu}_{n00}$$ **2-body terms**

To get more descriptors, one option is to couple channels in such a way that they form **rotational invariants**:

$$c^{\nu}_{nl+m} \times c^{\mu}_{n'l-m}$$

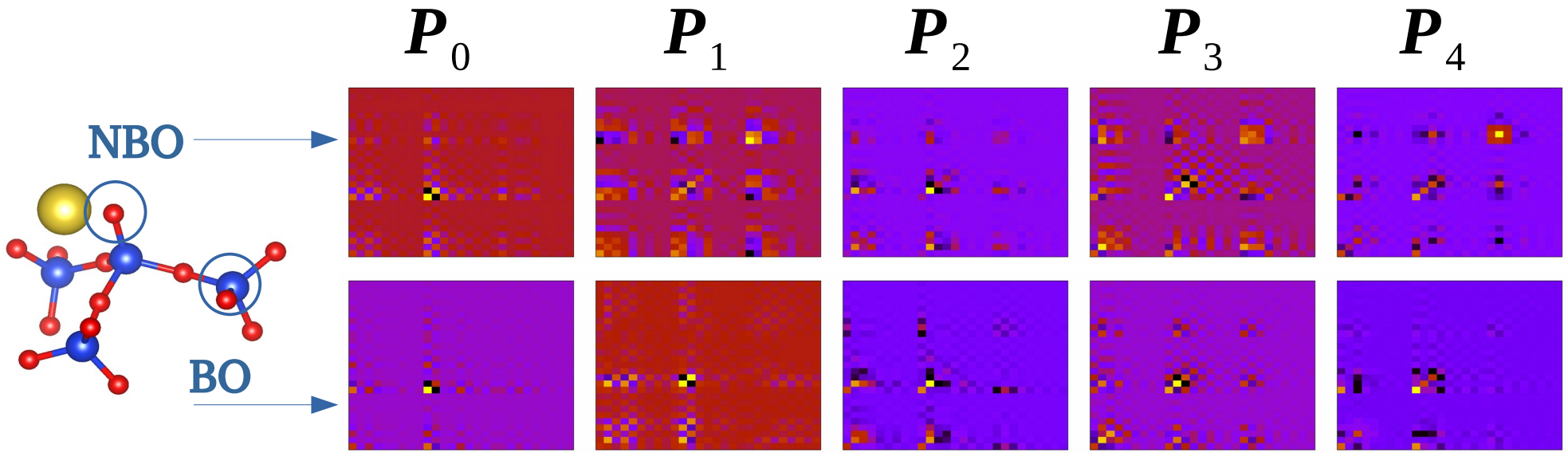
This is the so-called **SOAP** powerspectrum

$$p^{\nu\mu}_{nn'l} = \sum_{m} c^{\nu}_{nl+m} \times c^{\mu}_{n'l-m}$$ **3-body terms**

We can go farther… with the bispectrum

$$b^{\lambda\nu\mu}_{nn_1n_2ll_1l_2} = \sum c^{\lambda}_{n_1l_1m_1} c^{\nu}_{n_2l_2m_2} c^{\mu}_{nlm} C^{lm}_{l_1m_1l_2m_2}$$ **4-body terms**

The SOAP descriptors



n.b. The powerspectrum can be seen efficiently stored using a Gram matrix product

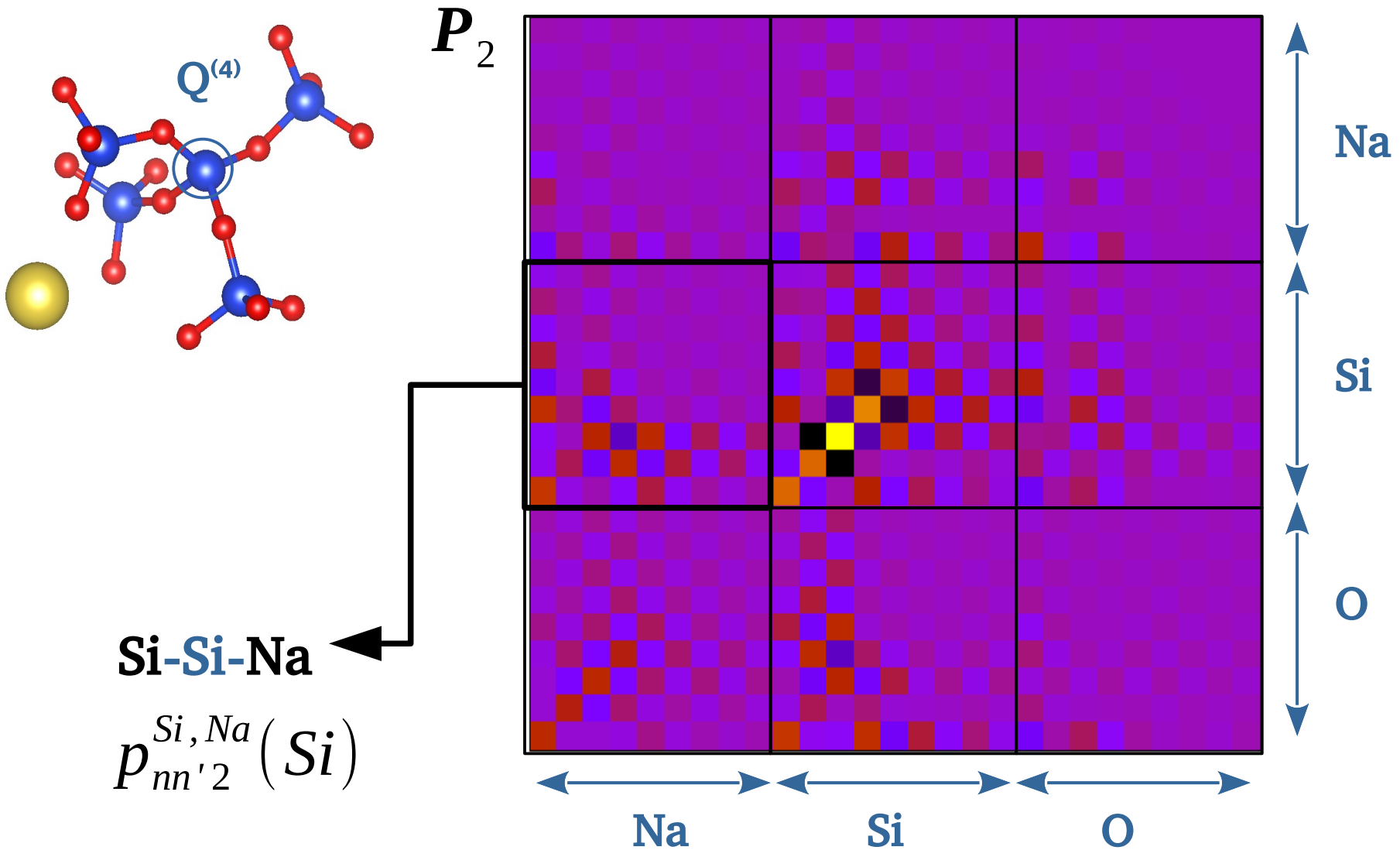
$$c^{\mu}_{n,l} = \begin{pmatrix} c^{\mu}_{n,l,-l} \\ \vdots \\ c^{\mu}_{n,l,+l} \end{pmatrix}$$

$$\{p^{\nu\mu}_{nn'l}\} = \boldsymbol{P}_l = \boldsymbol{X}_l^t \cdot \boldsymbol{X}_l \text{ with } \boldsymbol{X}_l = \left(c^{\mu}_{1,l} c^{\mu}_{2,l} \ldots c^{\mu}_{N,l} c^{\nu}_{1,l} \ldots c^{S}_{N,l} \right)$$

J.P. Darby et al. (2022) Compressing local atomic neighbourhood descriptors, npj Comp. Mat.

The SOAP descriptors

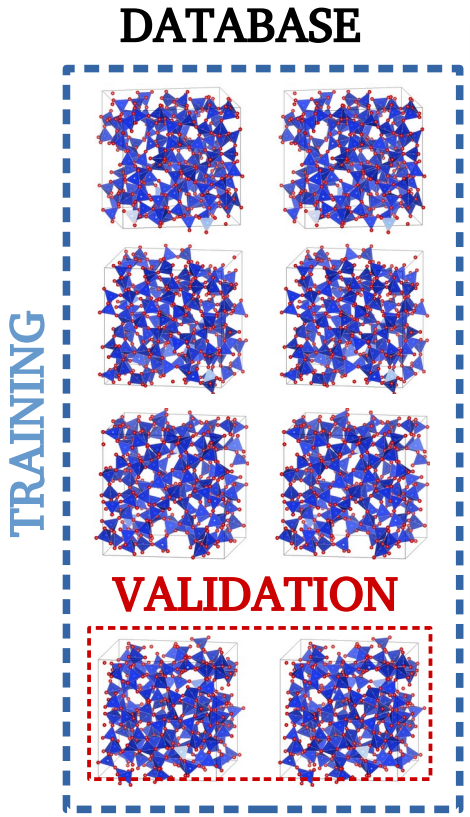
In binary Na_2O-SiO_2 glasses



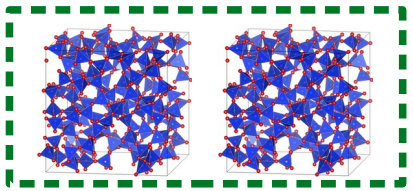
J.P. Darby et al. (2022) Compressing local atomic neighbourhood descriptors, npj Comp. Mat.

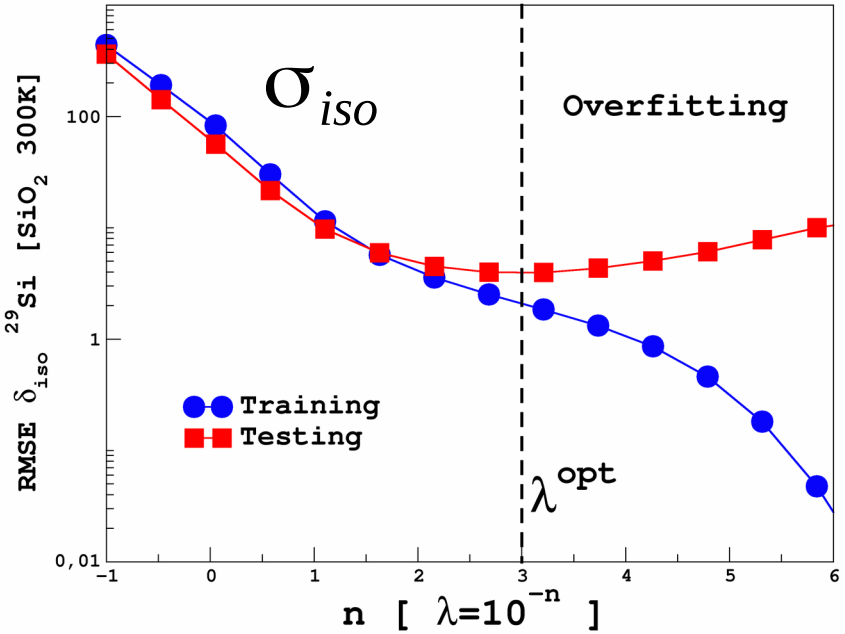
NMR shifts by Machine Learning

The Training Procedure : k-fold Cross-Validation



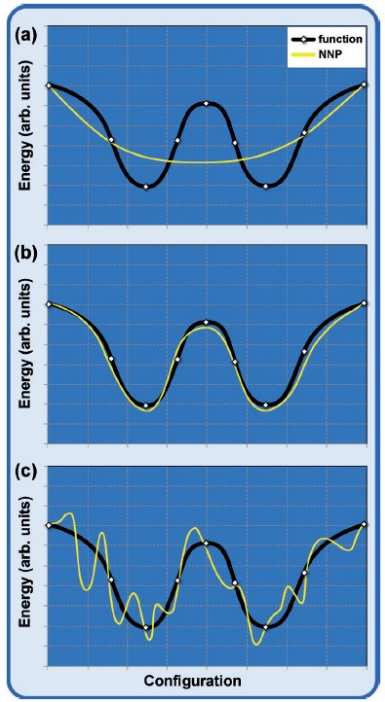
λ and κ are optimized on a validation set before testing.





$$\alpha = \left(K_G^{train} + \lambda I \right)^{-1} \delta^{train}$$

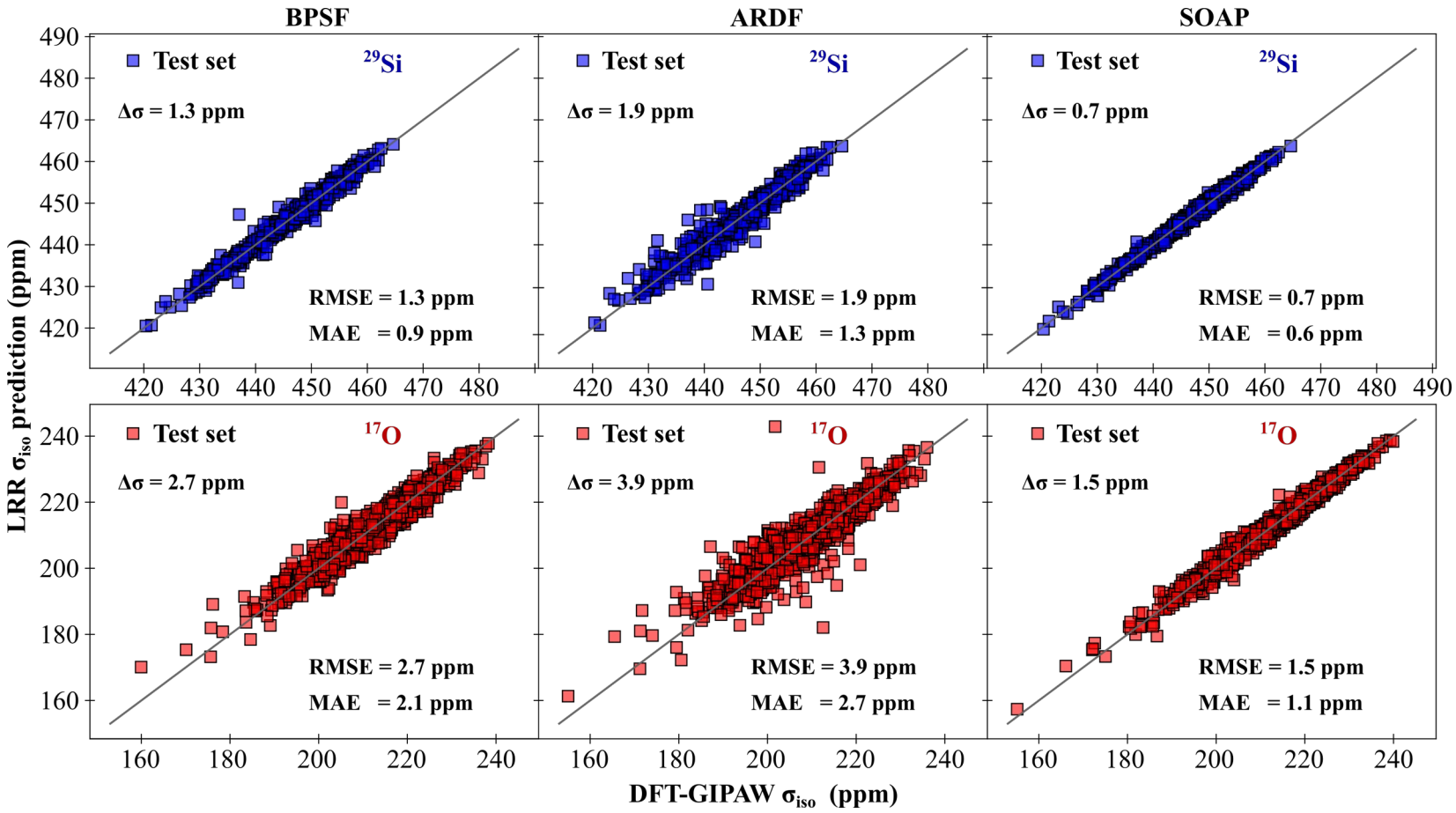
J. Behler et al. Angewandte Chemie 2017

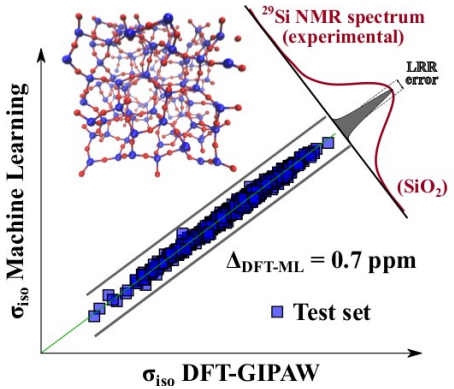


k-fold Cross Validation

NMR shifts by Machine Learning

Aluminosilicate Glasses : Comparison of Descriptors





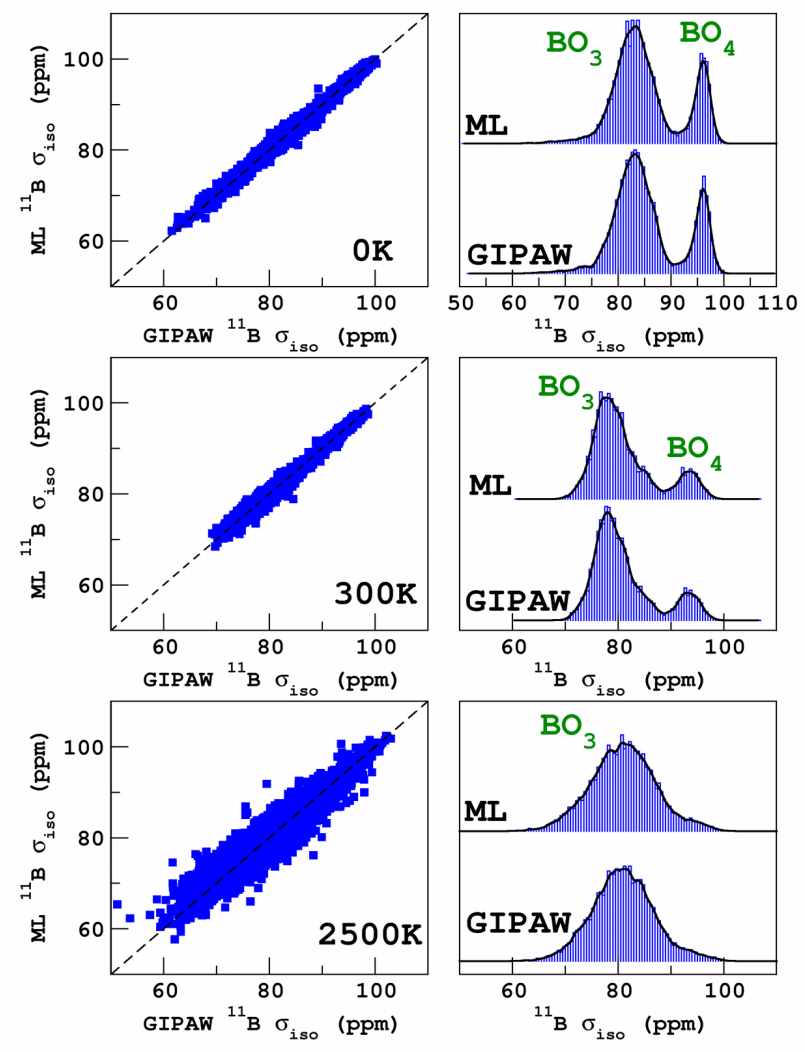
☞ SOAP (Smoth Overlap of Atomic Positions)

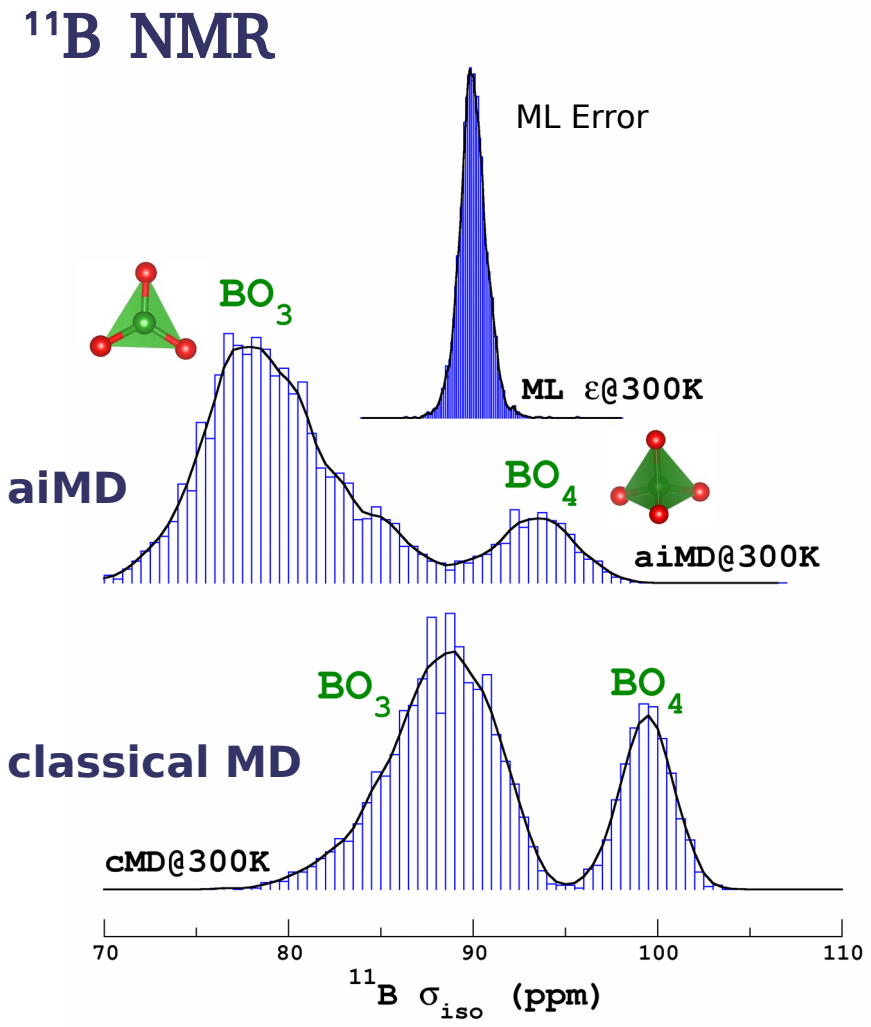
Z. Chaker et al. PCCP **2019**

*Symmetry Functions (**BPSF**) : J. Behler and M. Parrinello, Phys. Rev. Lett. 98, 146401 (2007)*
*Angular-Radial Distribution Functions (**ARDF**) : N. Artrith, A. Urban, and G. Ceder, PHYSICAL REVIEW B 96, 014112 (2017)*
Smooth Overlap of Atomic Positions (SOAP**) : Albert P. Bartók, Risi Kondor, and Gábor Csányi, Phys. Rev. B 87, 184115 (2013)*

Boosting DFT/NMR with Machine Learning

JSOAP descriptors and Least-Squares Support Vector Regression

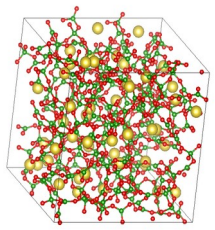




Prediction of ^{11}B magnetic shielding tensor (chemical shift) and Electric Field Gradient tensor (Quadrupolar Parameters)

Boosting DFT/NMR with Machine Learning

jSOAP descriptors and Least-Squares Support Vector Regression

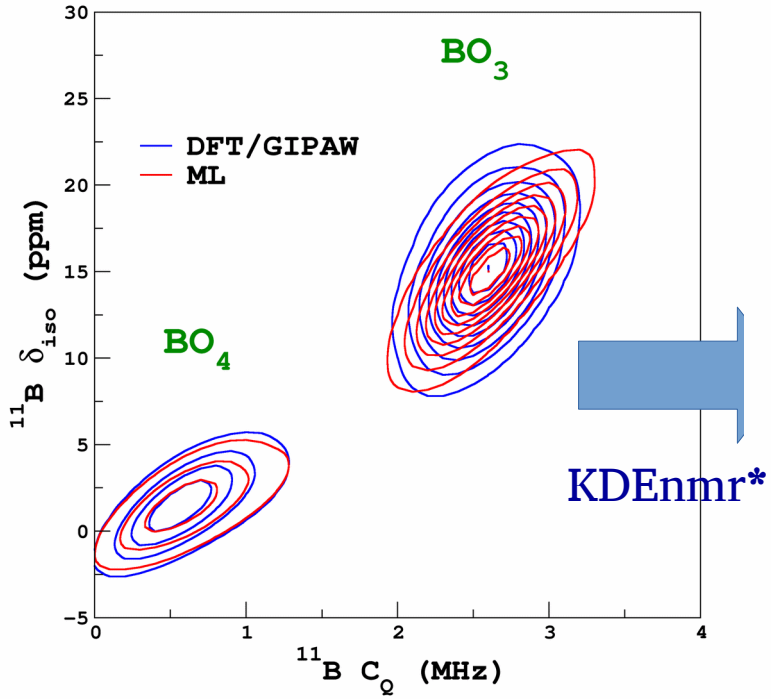


CPU for a single model of 800 atoms :

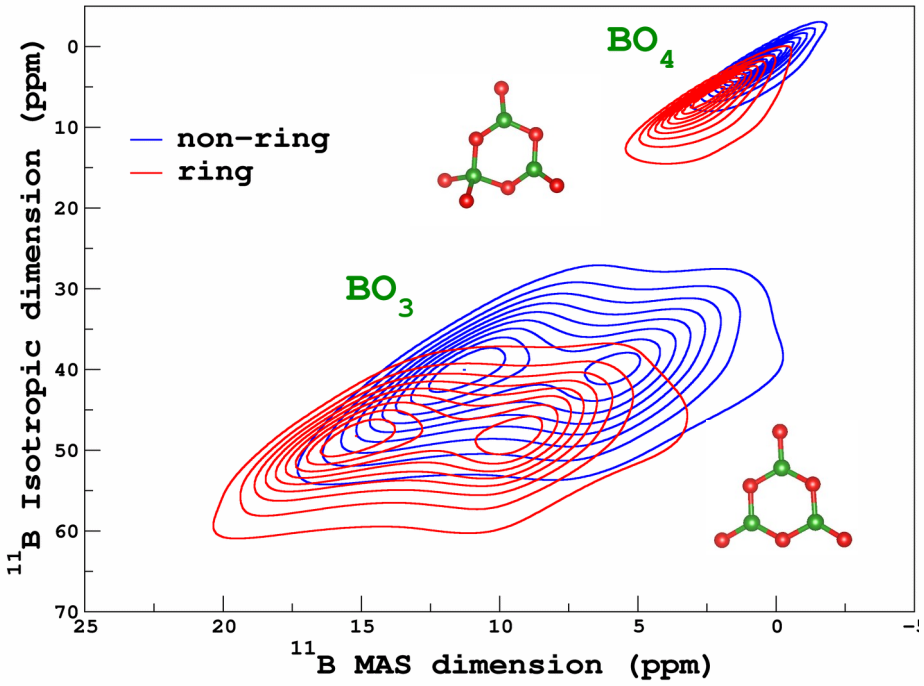
DFT ~ 96 (procs) *8h

☞ ML ~ 10s (1 proc)

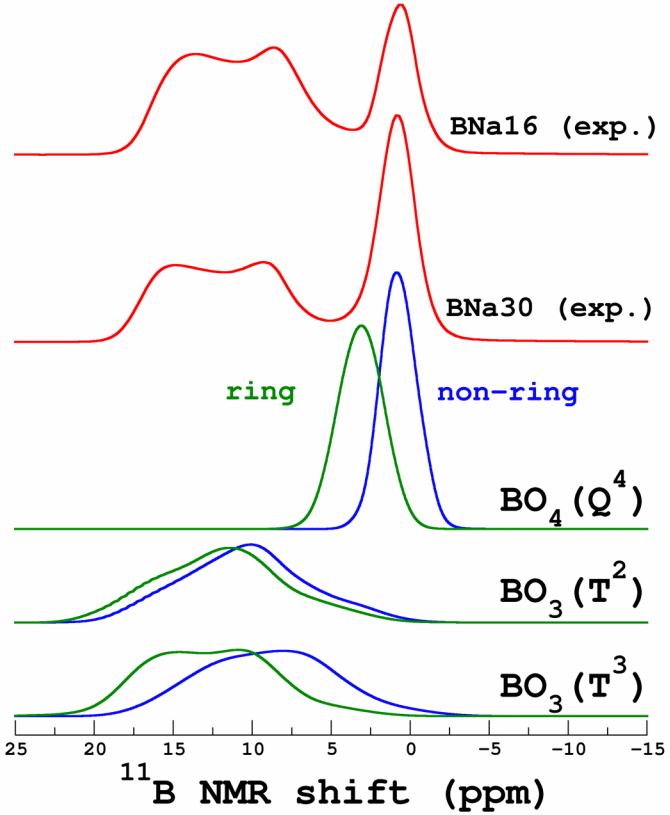
^{11}B NMR



NMR parameter distribution



^{11}B MQMAS NMR simulation



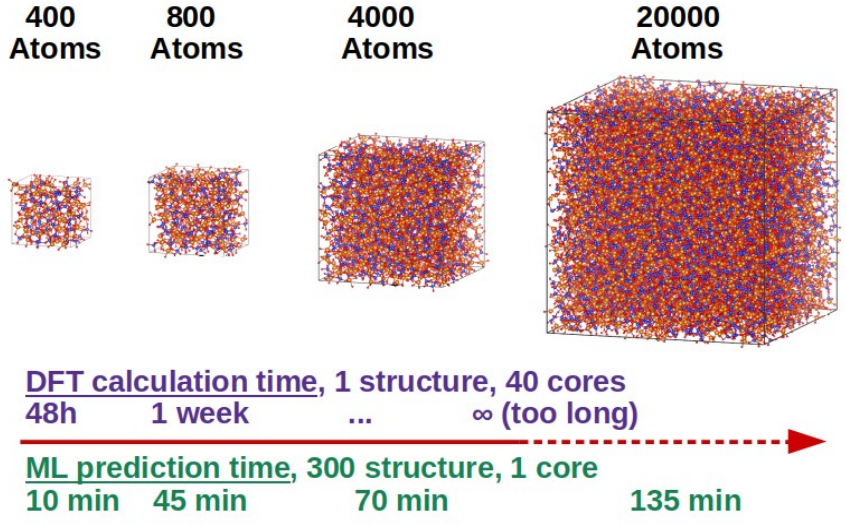
^{11}B NMR fingerprints
in Sodium Borate Glasses

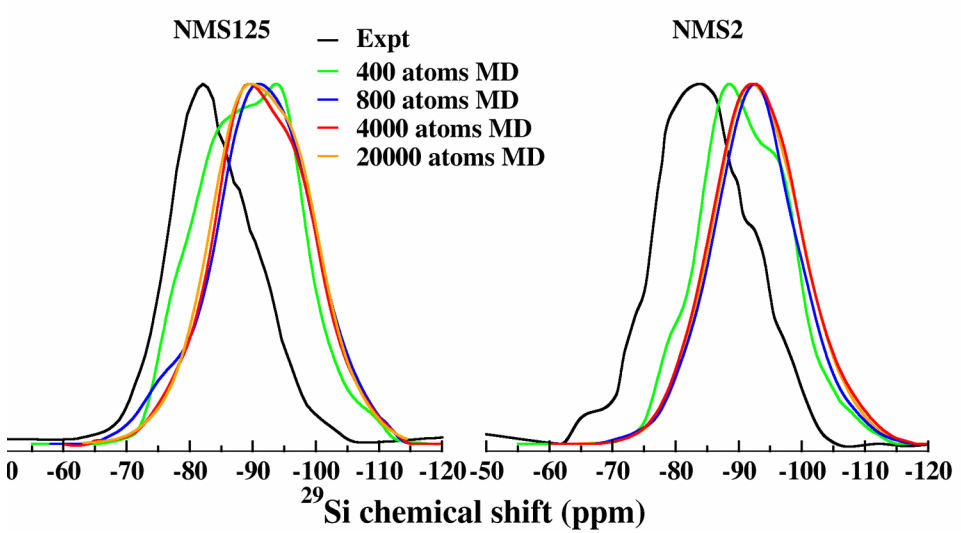
*Kernel Density Estimate of NMR parameter distribution

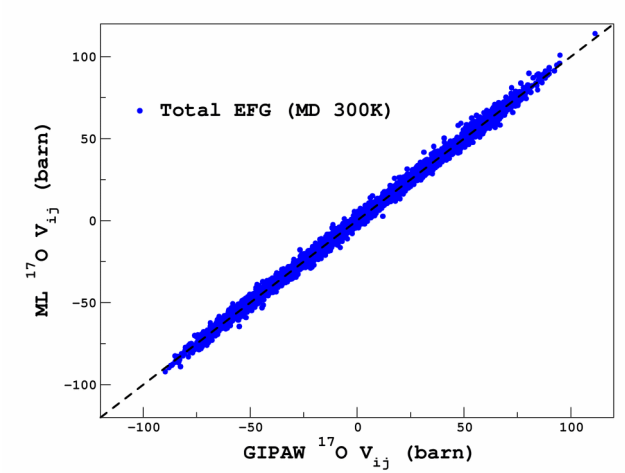
*T. Charpentier et al. *First-Principles Nuclear Magnetic Resonance Structural Analysis of Vitreous Silica,* The Journal of Physical Chemistry C 2009 113 (18), 7917-7929.

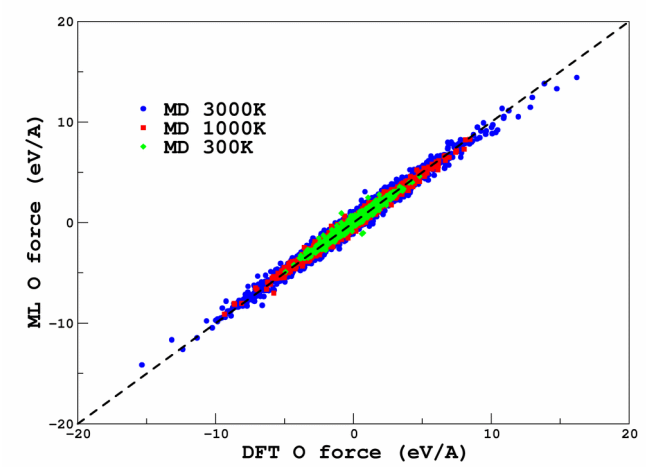
Boosting DFT/NMR with Machine Learning

JSOAP descriptors and Least-Squares Support Vector Regression







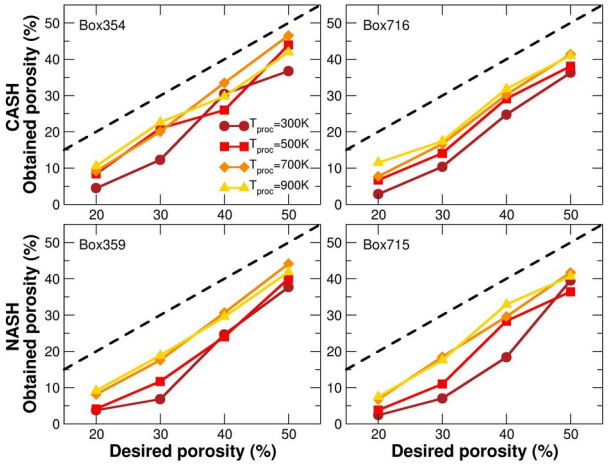


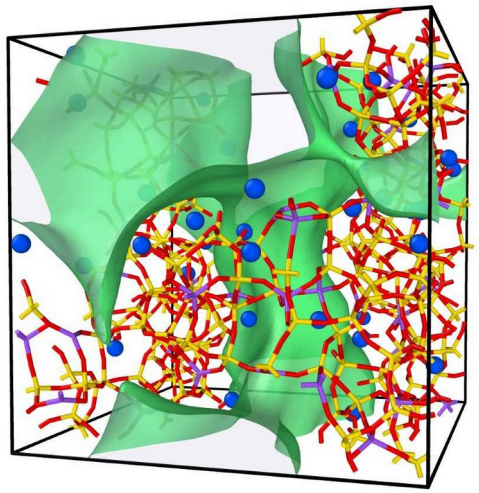
RAMAN example : Using Gaussian process regression to simulate the vibrational Raman spectra of molecular crystals, N. Raimbault, A. Grifasi, M. Ceriotti, M. Rossi September 2019 New Journal of Physics 21(10)

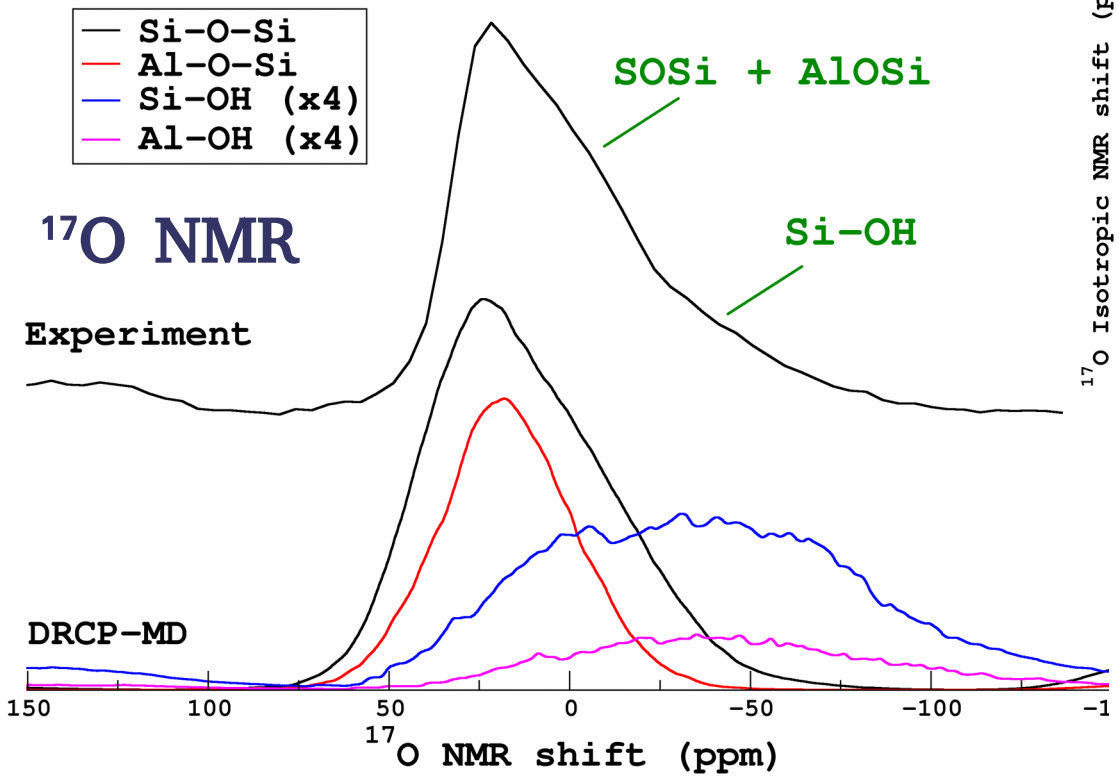
Modelling the alteration layer

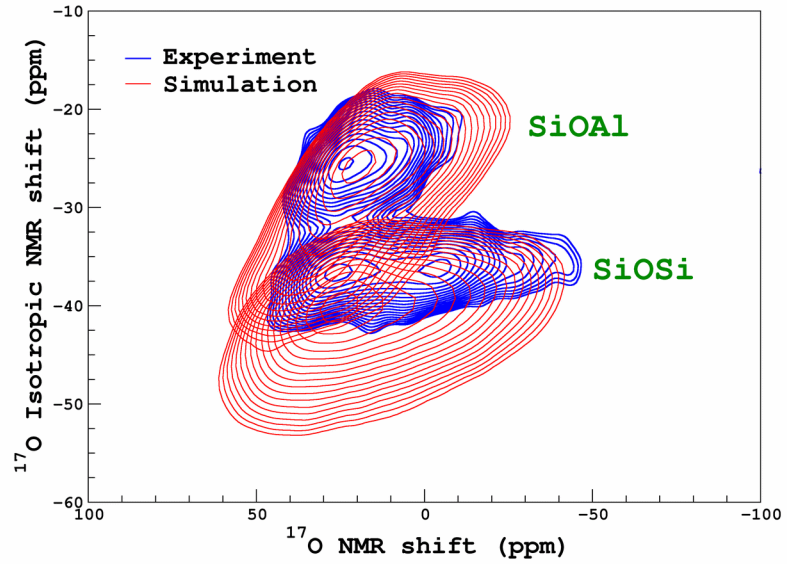
A nanoporous hydrated aluminosilicate structures

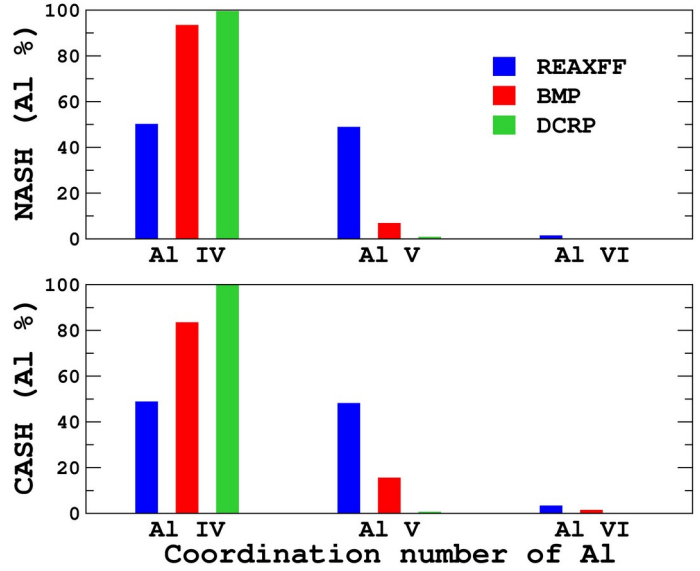
F. Lodesani et al. In preparation.











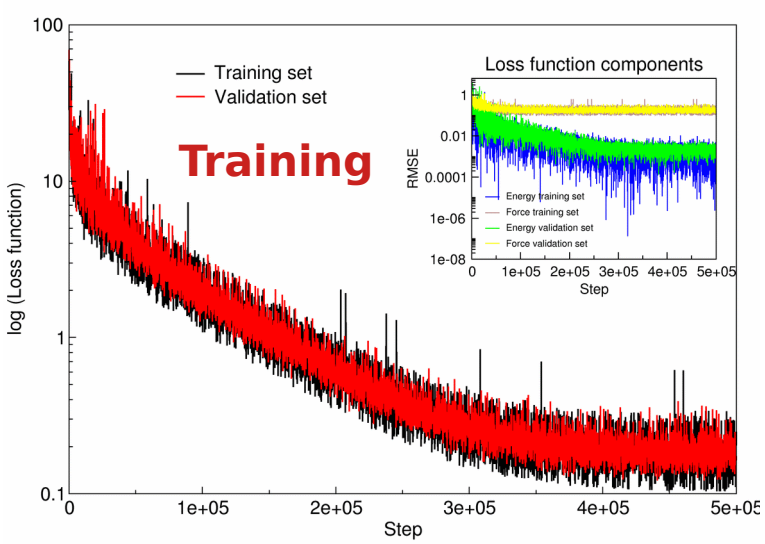
Porous structures are build with the Charge-Scaling (CS) and then filled with water molecules followed by MD (Diffuse Charge Reactive Pair potential)* relaxation.
DFT/DATABASE for ML in progress

DRCP:* S. Mahadevan, J. Du, J. Am. Ceram. Soc. 104 (**2021**), ☞ **see also Jinseng Du TALK.**

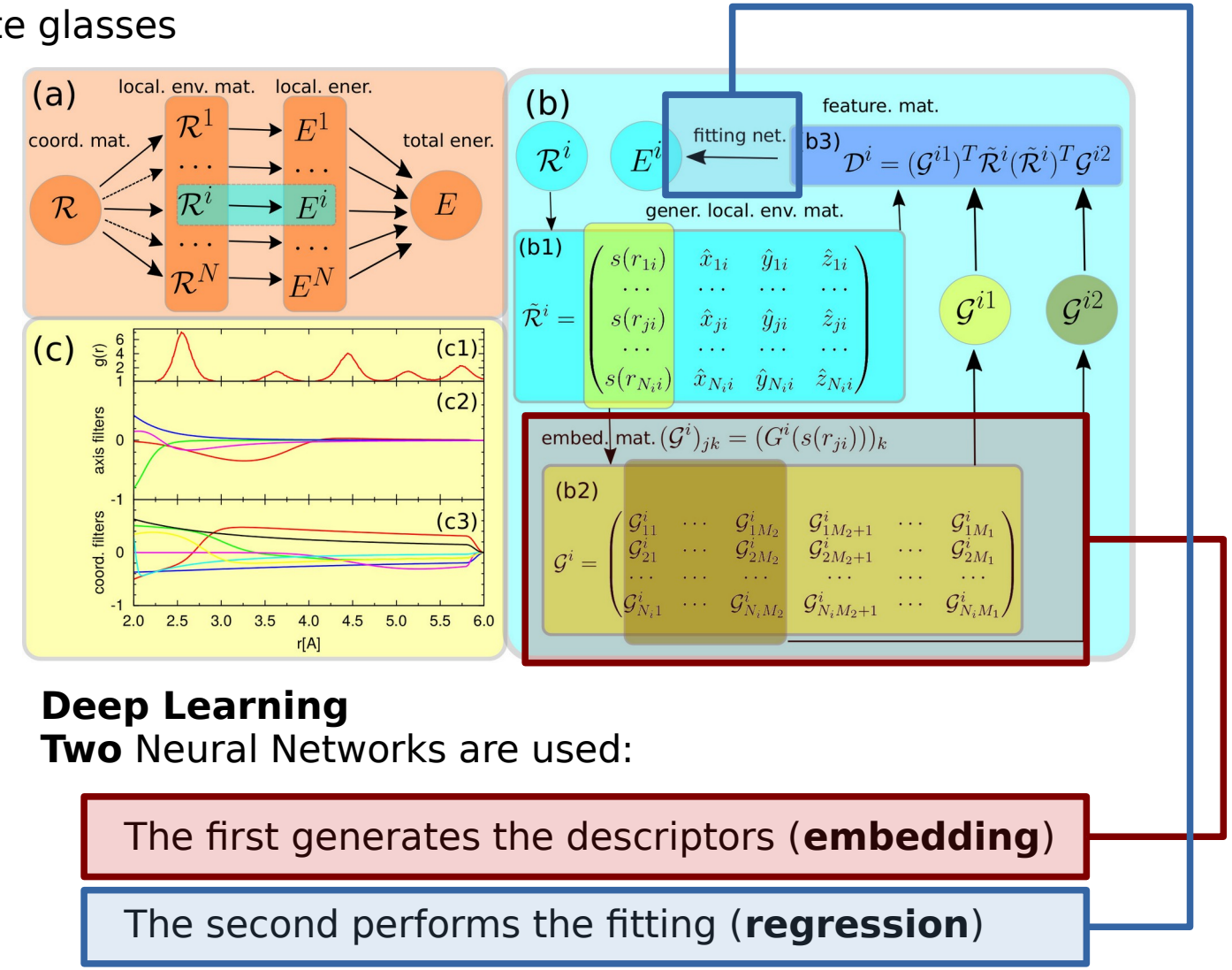
Machine Learning in MD : learning the descriptors

Deep Learning in MD simulations: the next generation of force-fields ?

Modelling (DeepMD-SE/LAMMPS) sodium-silicate glasses



The **training** is (very) time-consuming (GPU required).
Active-Learning approach is needed: faulty environments are predicted in production mode.
They must be reintroduced in the database for a new training ...



Deep Learning
Two Neural Networks are used:

The first generates the descriptors (**embedding**)

The second performs the fitting (**regression**)

M. Bertani et al.. *An Accurate and transferable Machine Learning potential for Molecular Dynamics simulation of sodium silicate glasses*, submitted. **DeepMD-SE:** * Zhang et al., *Phys. Rev. Lett. 120*, 143001 (**2018**).

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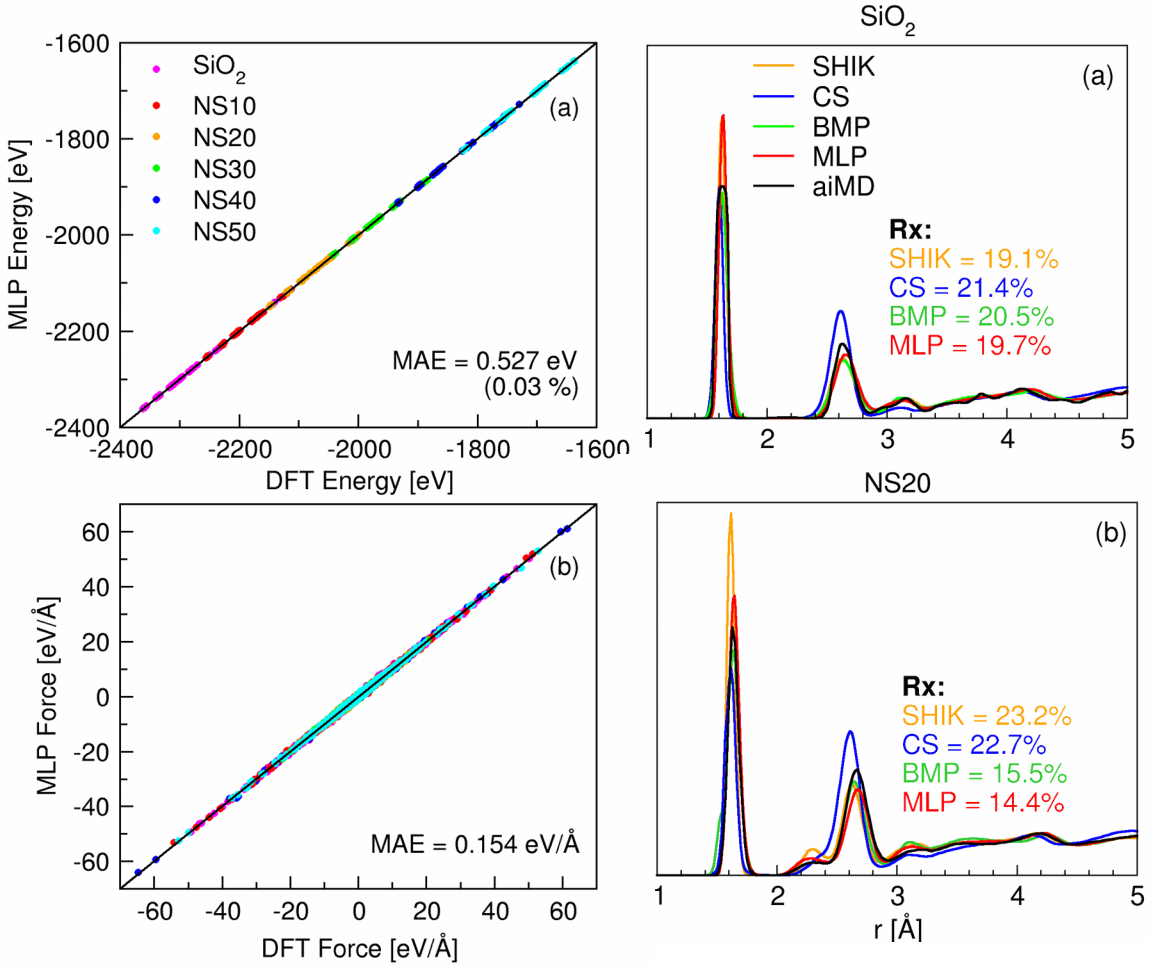
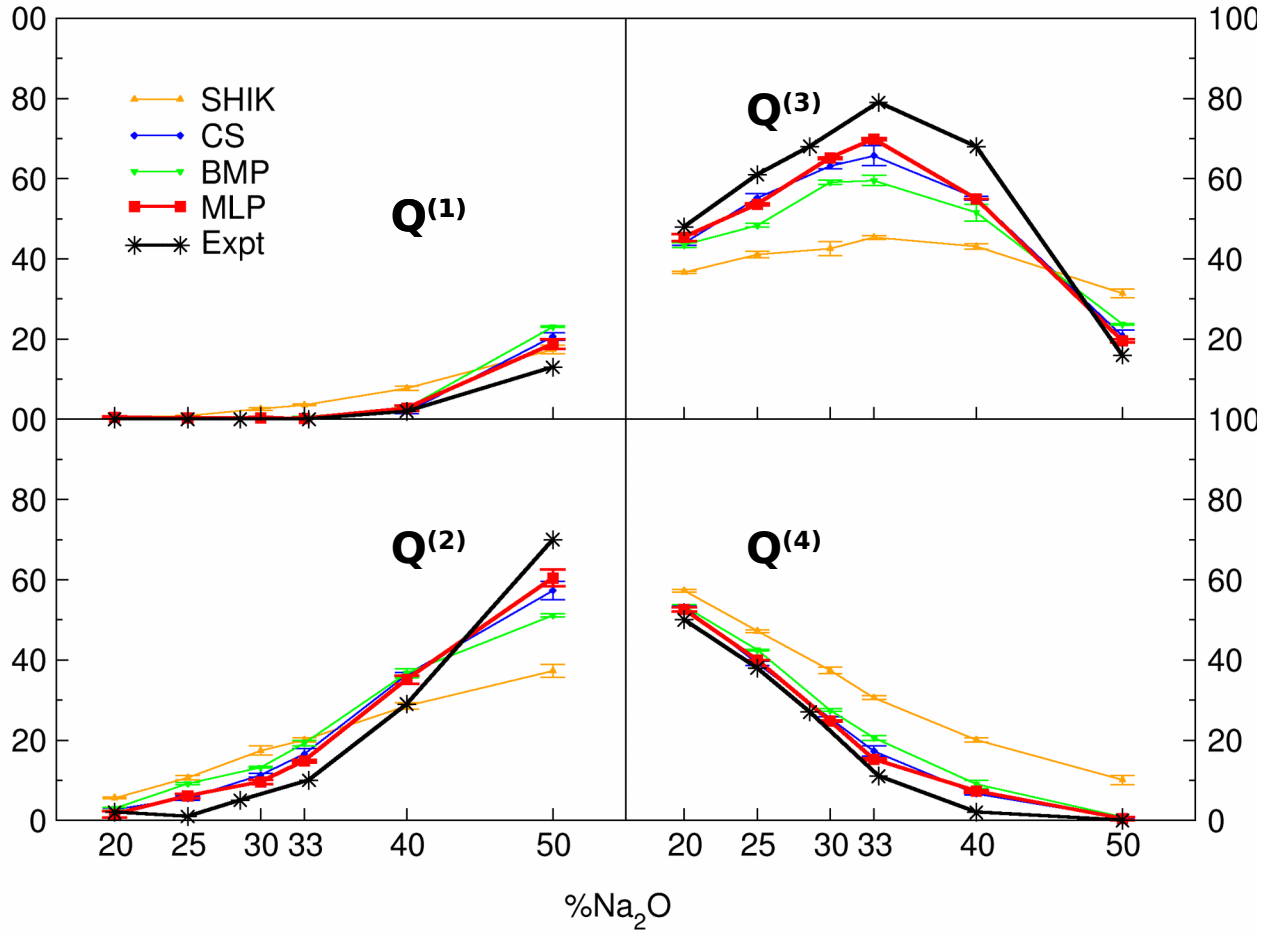


Si Q$^{(n)}$ speciations

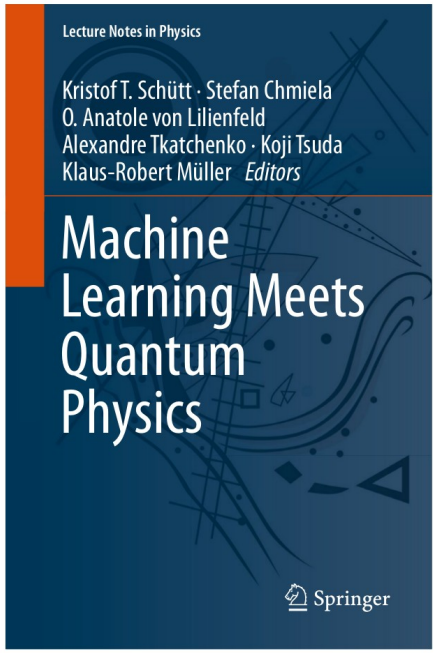


M. Bertani et al.. *An Accurate and transferable Machine Learning potential for Molecular Dynamics simulation of sodium silicate glasses*, submitted.

DeepMD-SE: * Zhang et al., Deep Potential Molecular Dynamics: A Scalable Model with the Accuracy of Quantum Mechanics. *Phys. Rev. Lett. 120*, 143001 (**2018**).

Conclusions and Perspectives

- NMR provides a wealth of techniques for studying oxide glasses and their alteration (in aqueous media or in vapor phase)
- NMR experiments can be simulated from MD simulations (with DFT/GIPAW)
- MD and DFT/NMR can be accelerated with Machine Learning
- ML-MD offers exciting perspective for modelling hydrated systems (H)
- Big Database need to be constructed : aiMD/DFT simulations are needed (in progress)
- *ML vibrational fingerprint (IR, RAMAN) in progress*



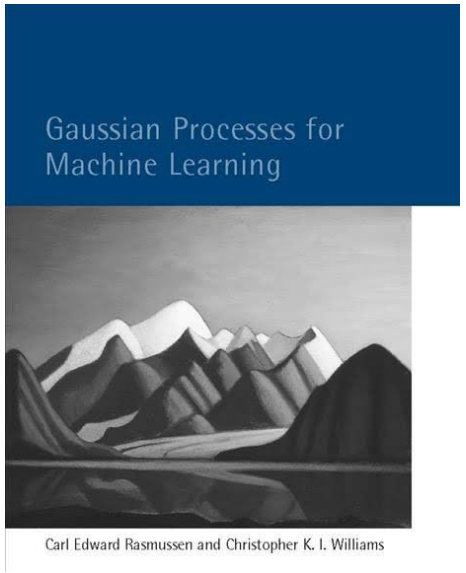


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Photo: https://www.patrimoine-environnement.fr/le-musee-de-la-romanite-a-nimes-a-ouvert-ses-portes/