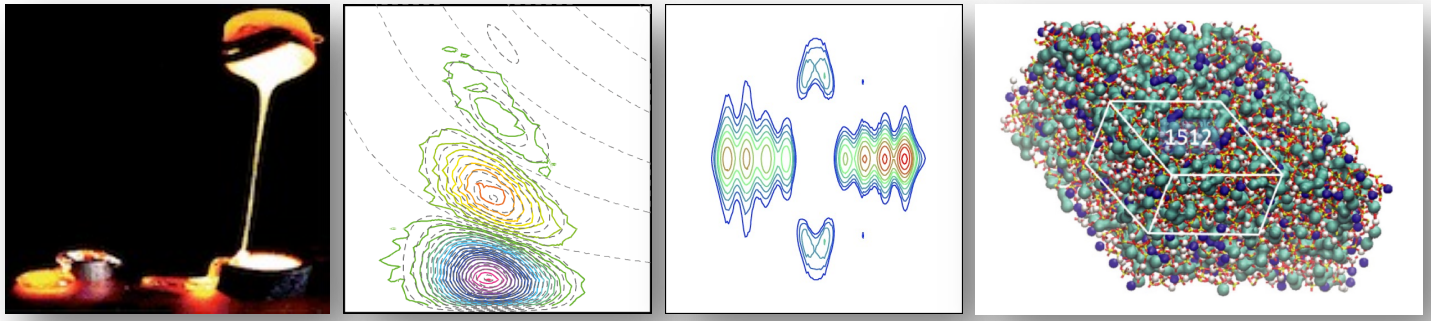
Ordre dans le désordre
apports de la RMN du solide

Dominique Massiot

CEMHTI-CNRS UPR3079 Orléans

http://www.cemhti.cnrs-orleans.fr/?nom=massiot



Google *dmfit nmr*

RESEARCH INFRASTRUCTURE
Magnetic Nuclear Resonance, Very High Fields
FR3050 CNRS

NOBEL PRIZES 2021

The Nobel Prize in Physics 2021

Syukuro Manabe

"for the physical modelling of Earth's climate, quantifying variability and reliably predicting global warming"

Klaus Hasselmann

"for the physical modelling of Earth's climate, quantifying variability and reliably predicting global warming"

Giorgio Parisi

"for the discovery of the interplay of disorder and fluctuations in physical systems from atomic to planetary scales"

NOBEL PRIZES 2021

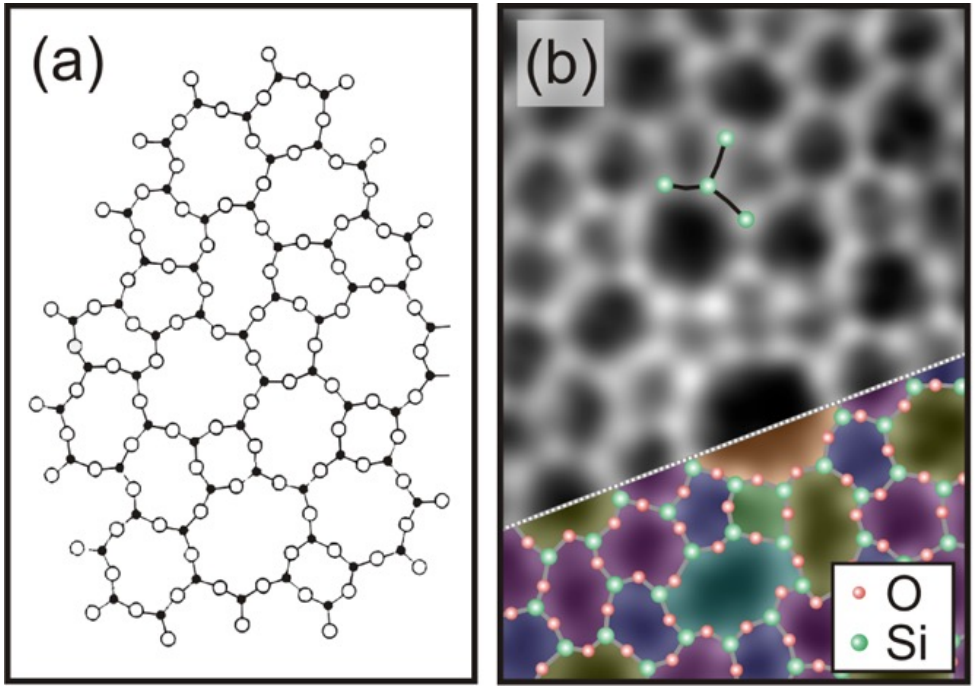
Amorphous materials: Order within disorder
Philip S. Salmon
Nature Material **1**, 87 - 88 (2002)
doi:10.1038/nmat737

Giorgio Parisi

"for the discovery of the interplay of disorder and fluctuations in physical systems from atomic to planetary scales"

Geometrical [Topological] & Chemical Order

Geometrical disorder / Topology



THE JOURNAL OF PHYSICAL CHEMISTRY C
Article
pubs.acs.org/JPCC

Atomic Arrangement in Two-Dimensional Silica: From Crystalline to Vitreous Structures

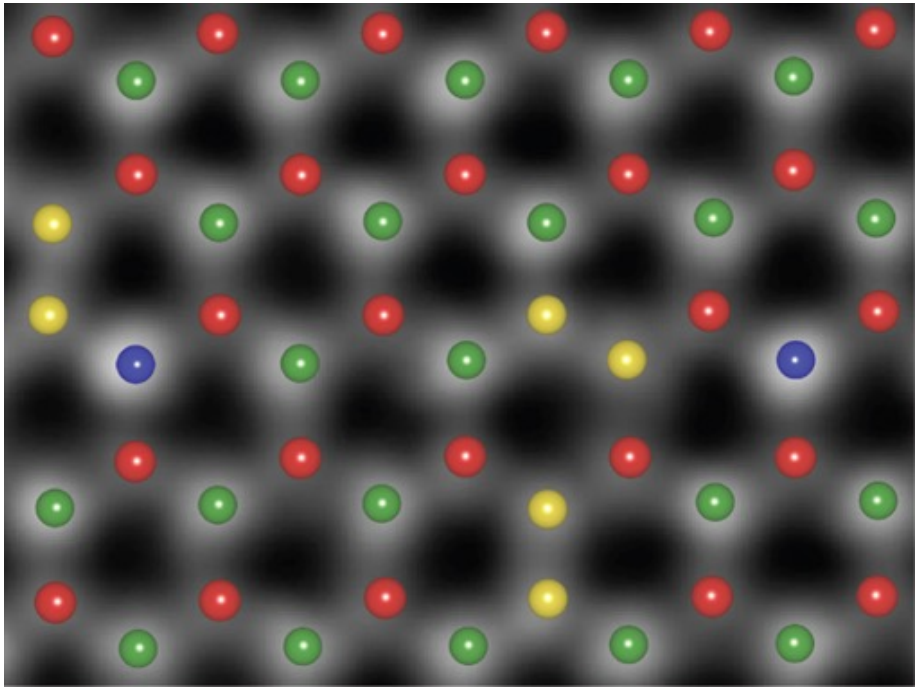
Leonid Lichtenstein, Markus Heyde,* and Hans-Joachim Freund

NANO LETTERS
Letter
pubs.acs.org/NanoLett

Direct Imaging of a Two-Dimensional Silica Glass on Graphene

Pinshane Y. Huang,[†,■] Simon Kurasch,[‡,■] Anchal Srivastava,[§,○] Viera Skakalova,[§,∥] Jani Kotakoski,[∥,⊥] Arkady V. Krasheninnikov,[⊥,¶] Robert Hovden,[†] Qingyun Mao,[†] Jannik C. Meyer,[‡,∥] Jurgen Smet,[§] David A. Muller,[*,†,□] and Ute Kaiser[*,‡]

Chemical disorder



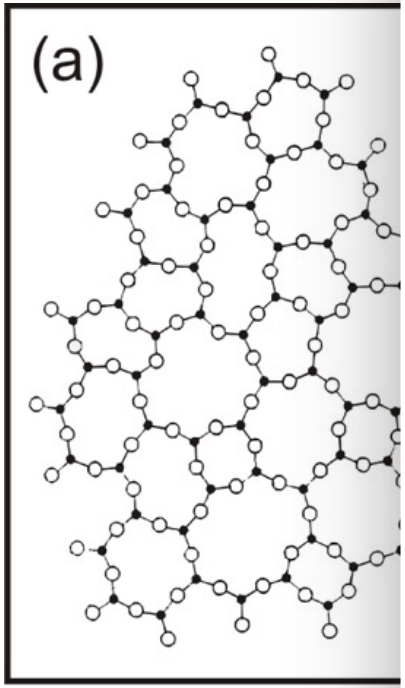
Vol 464|25 March 2010|doi:10.1038/nature08879
nature
nature
LETTERS

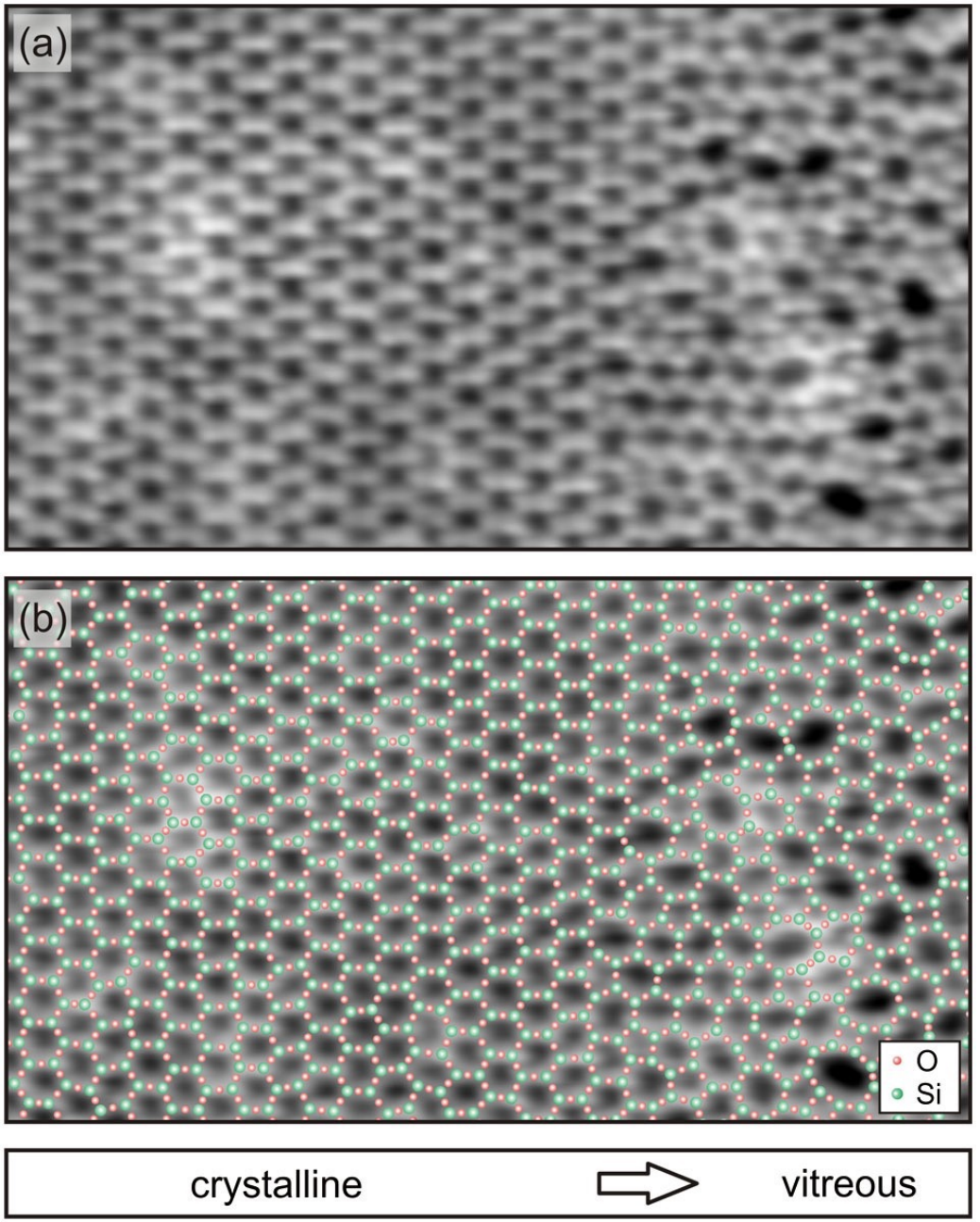
Atom-by-atom structural and chemical analysis by annular dark-field electron microscopy

Ondrej L. Krivanek[1], Matthew F. Chisholm[2], Valeria Nicolosi[3], Timothy J. Pennycook[2,4], George J. Corbin[1], Niklas Dellby[1], Matthew F. Murfitt[1], Christopher S. Own[1], Zoltan S. Szilagyi[1], Mark P. Oxley[2,4], Sokrates T. Pantelides[2,4] & Stephen J. Pennycook[2,4]

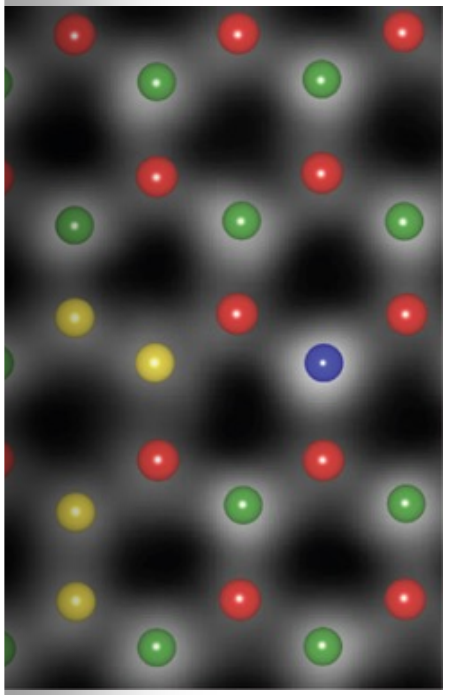
Geometrical [Topological] & Chemical Order

Geometrical





disorder



THE JOURNAL OF PHYSICAL CHEMISTRY C

Atomic Arrangement in Tw
Vitreous Structures

Leonid Lichtenstein, Markus Heyde,* an

NANO LETTERS

Direct Imaging of a Two-D

Pinshane Y. Huang,[†,■] Simon Kurasch,[‡]
Arkady V. Krasheninnikov,[⊥,¶] Robert Ho
David A. Muller,[*,†,□] and Ute Kaiser[*,‡]

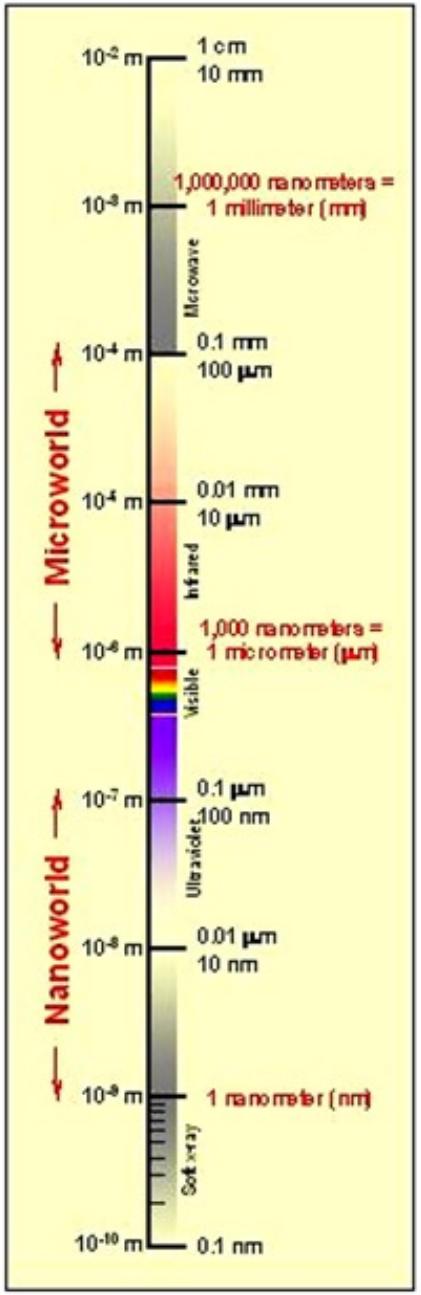
nature

LETTERS

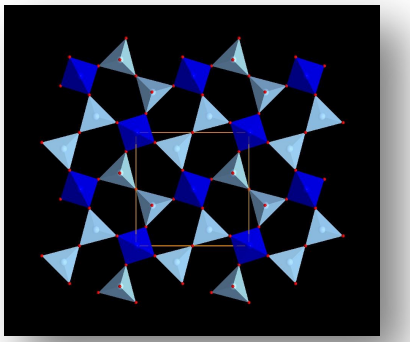
nd chemical analysis by
microscopy

si[3], Timothy J. Pennycook[2,4], George J. Corbin[1],
Zoltan S. Szilagyi[1], Mark P. Oxley[2,4],

Materials structure at different scales

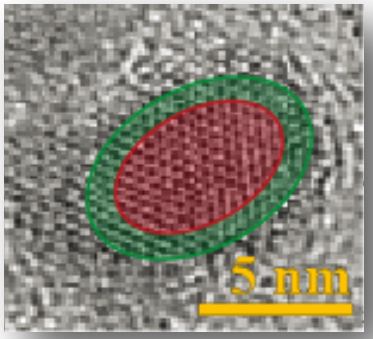


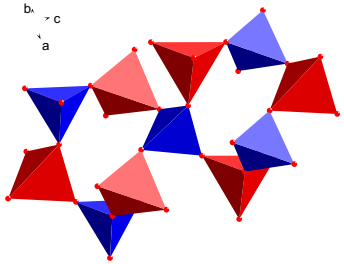
Diffraction X-Rays Neutrons e⁻

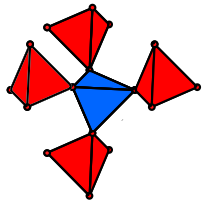


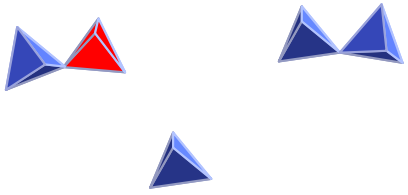
Order

Disorder









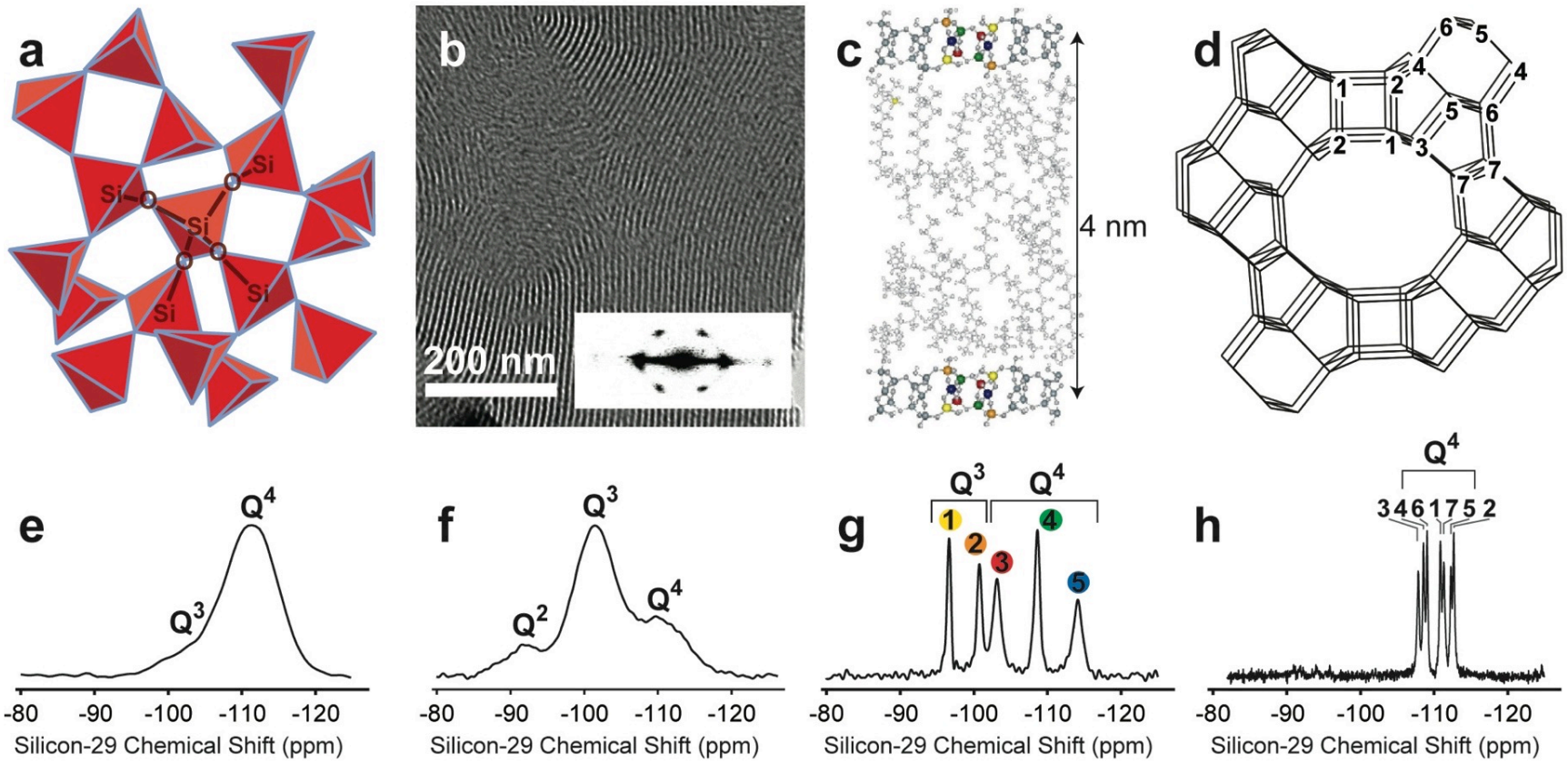
nm

Å

Local Order

NMR XAS Raman / IR

^{29}Si - Silica based materials



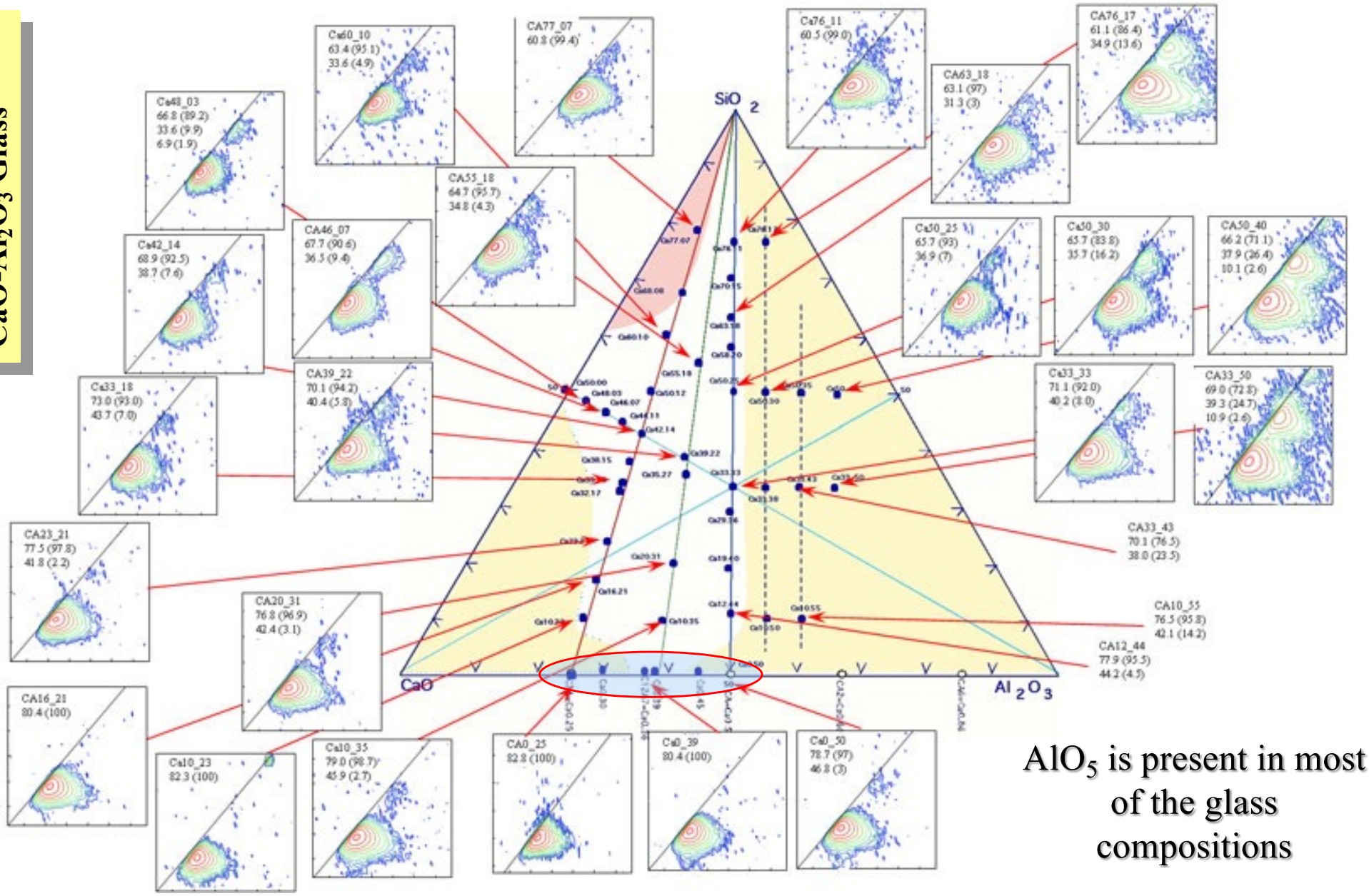
Glass | Mesoporous Silica | SiO_2-surfactant Mesophase | Zeolite

Resolution is gained by averaging out anisotropic signatures
Magic Angle Spinning MAS

D.Massiot, R.J.Messinger, S.Cadars, M.Deschamps, V.Montouillout, N.Pellerin, E.Veron, M.Allix, P.Florian, F.Fayon
Accounts Chem. Res. 46 1975–1984 2013

^{27}Al AlO_5 - Locally Favored Structures

CaO-Al_2O_3 Glass

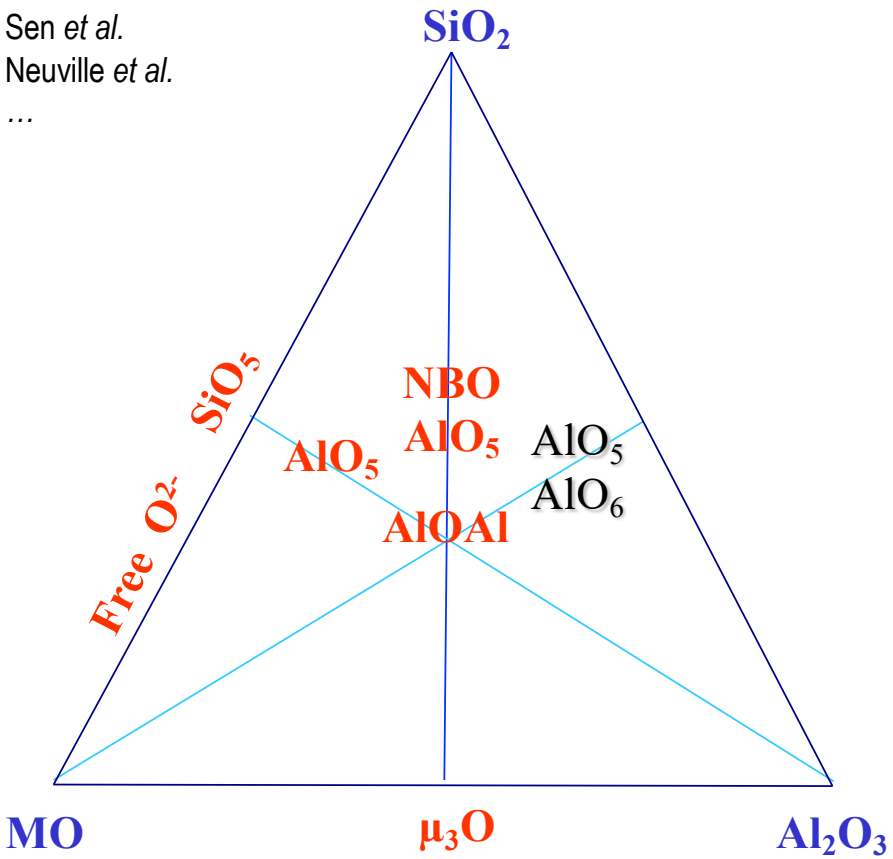


AlO_5 is present in most of the glass compositions

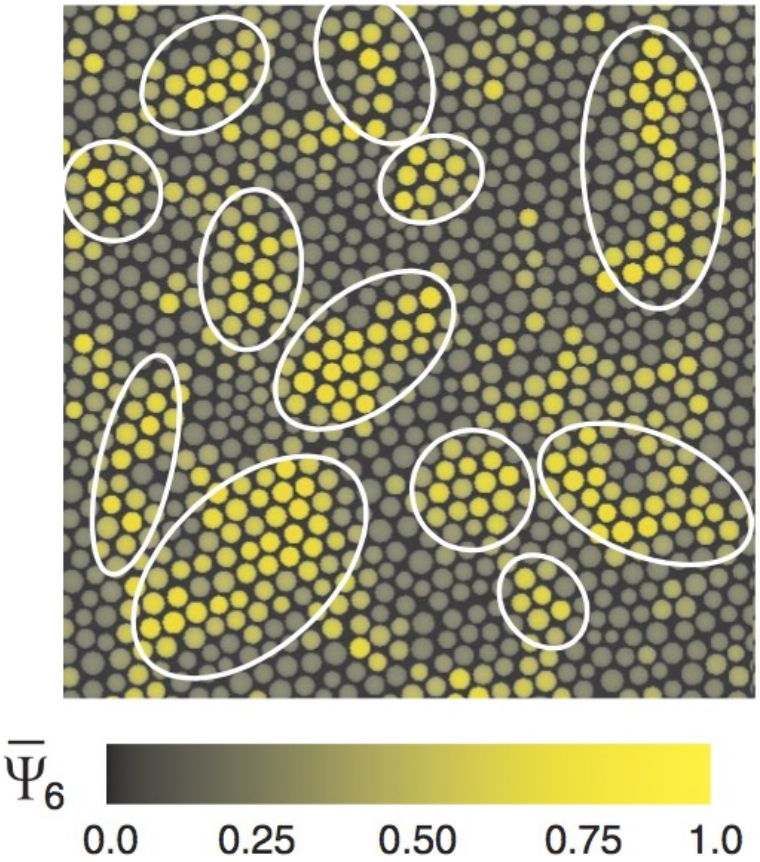
D.R.Neuville, L.Cormier, D.Massiot '*Al coordination and speciation in calcium aluminosilicate glasses : effects of composition determined by 27Al MQ-MAS NMR and Raman spectrocospy*' Chem. Geol. 229 173-185 (2006)

Unexpected local structures in Glasses

Stebbins *et al.*
Mc Millan *et al.*
Sen *et al.*
Neuville *et al.*
…



defects, chemical, geometrical and topological order / disorder



Locally Favored Structures LFS

Takeshi Kawasaki, Takeaki Araki, and Hajime Tanaka
PRL 99, 215701 (2007)

D.Massiot, R.J.Messinger, S.Cadars, M.Deschamps, V.Montouillout, N.Pellerin, E.Veron, M.Allix, P.Florian, F.Fayon
Accounts Chem. Res. 46 1975–1984 2013

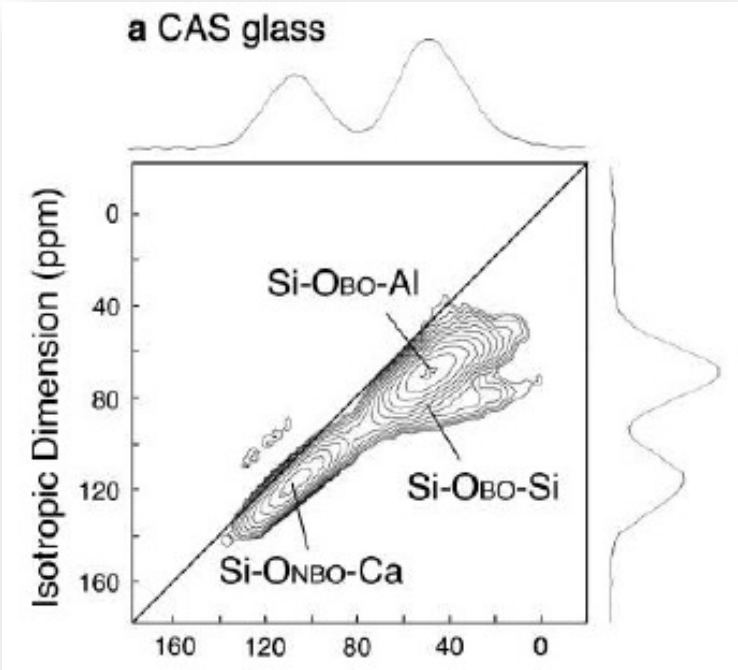
Selective observation – spectral edition

THE JOURNAL OF PHYSICAL CHEMISTRY Letters
Letter
pubs.acs.org/JPCL

Oxygen Speciation in Multicomponent Silicate Glasses Using Through Bond Double Resonance NMR Spectroscopy

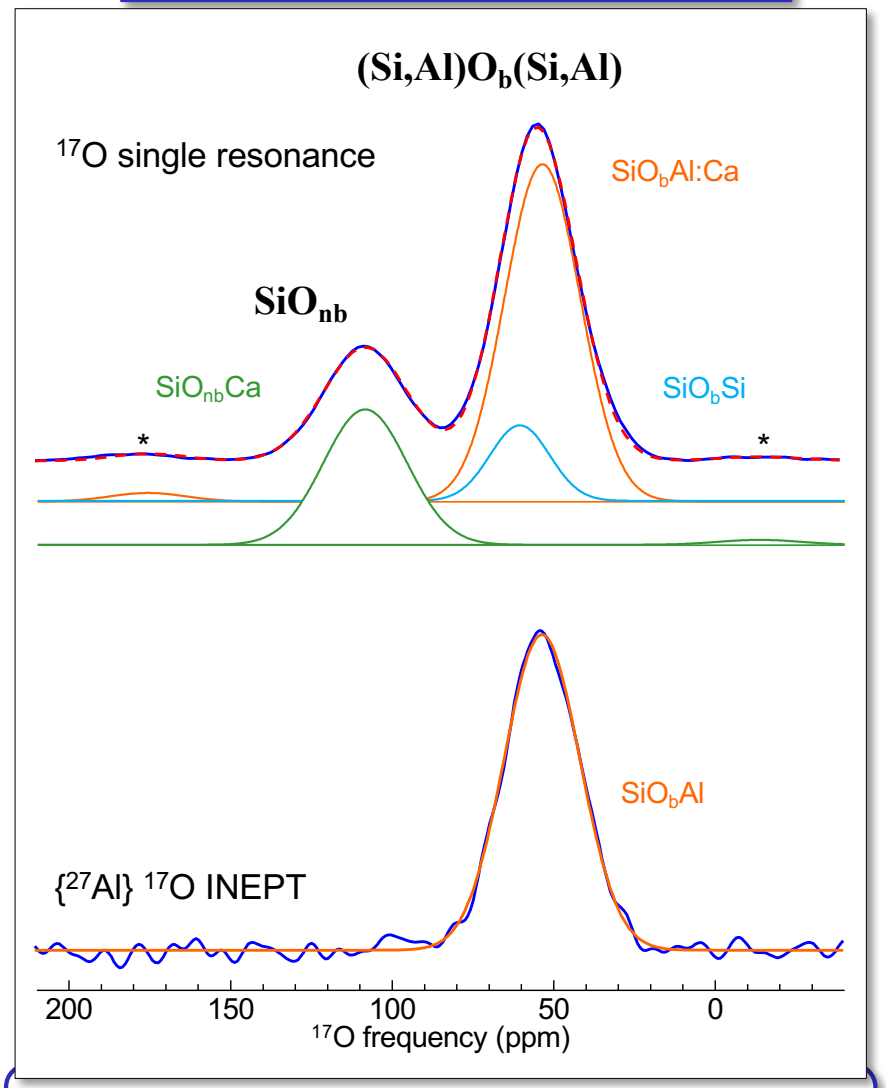
Sohei Sukenaga,*,† Pierre Florian,*,‡ Koji Kanehashi,§ Hiroyuki Shibata,† Noritaka Saito,‖ Kunihiko Nakashima,‖ and Dominique Massiot‡

$CaO\text{-}Al_2O_3\text{-}SiO_2$ the ^{17}O viewpoint



Lee et al., Geochim. Cosmochim. Acta ***70*** *4275-4286 (2006)*

36.5 CaO – 51 SiO_2 – 12.5 Al_2O_3



- Ca close to Si-Onb (modifier)
- Ca close to Si-O-Al (charge compensator)

S.Sukenaga, P.Florian, K.Kanehashi, H.Shibata, N.Saito, K.Nakashima, D.Massiot – J.Phys.Chem. Lett. 8, 2274, **2017**

Percolation Channels

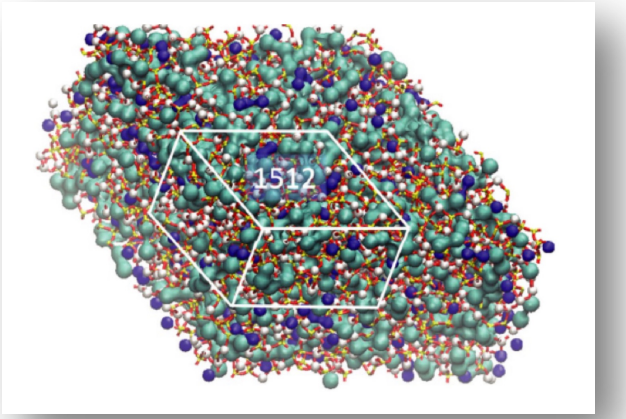
SCIENTIFIC REPORTS

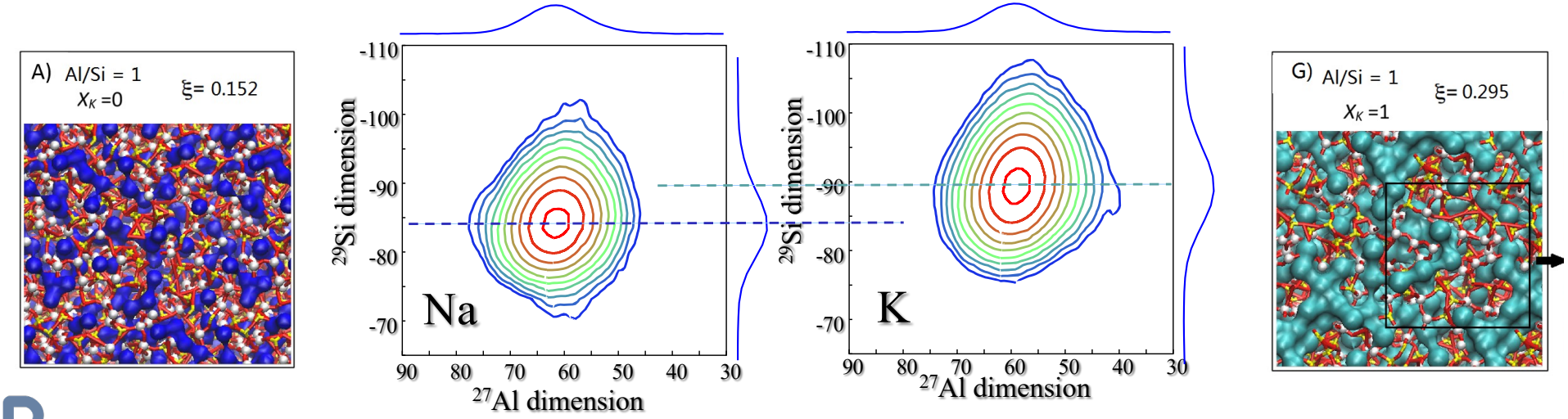
OPEN

Percolation channels: a universal idea to describe the atomic structure and dynamics of glasses and melts

Received: 17 August 2017
Accepted: 15 November 2017
Published online: 28 November 2017

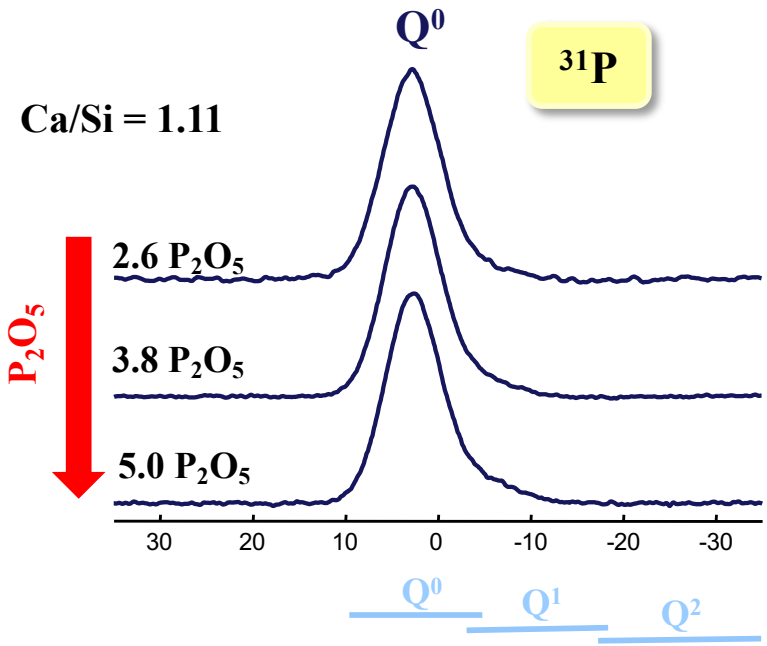
Charles Le Losq[1,2], Daniel R. Neuville[1], Wenlin Chen[3], Pierre Florian[4], Dominique Massiot[4], Zhongfu Zhou[3] & George N. Greaves[3,5,6]

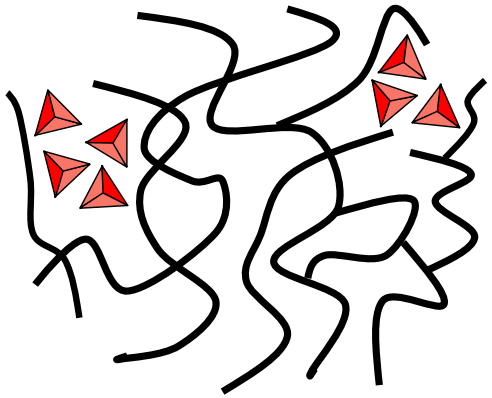




Ch. Le Losq, D.R.Neuville, W.Chen, P.Florian, D.Massiot, Z.Zou, G.N.Greaves, Scientific Reports | 7: 16490 **2017**

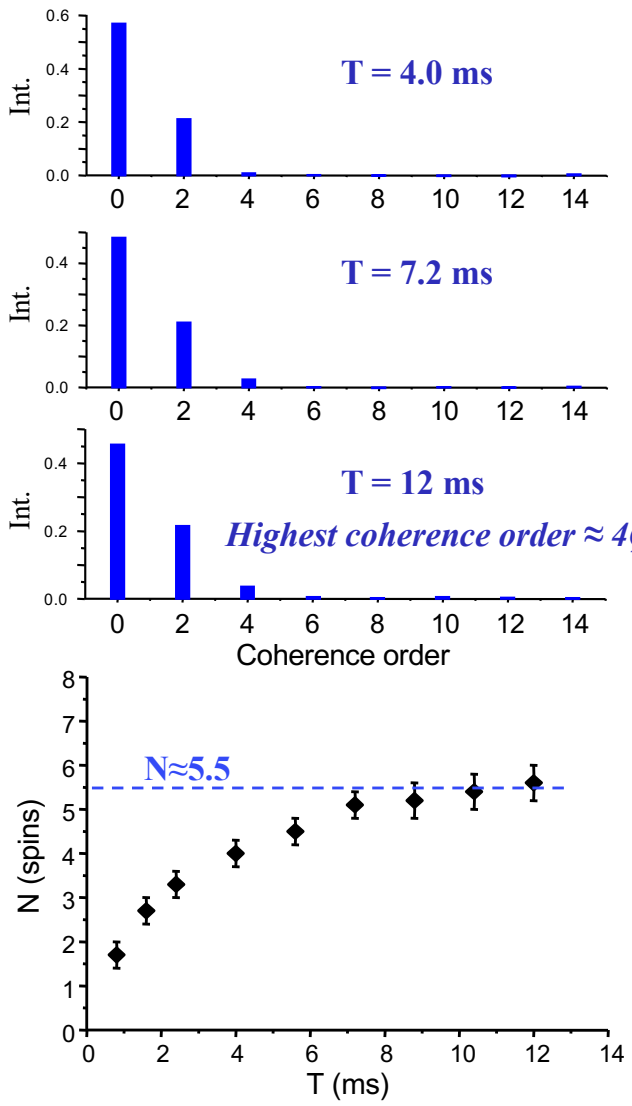
PO_4^{3-} clustering in bioactive glasses





Silicate chains

Q^0 (PO_4^{3-})

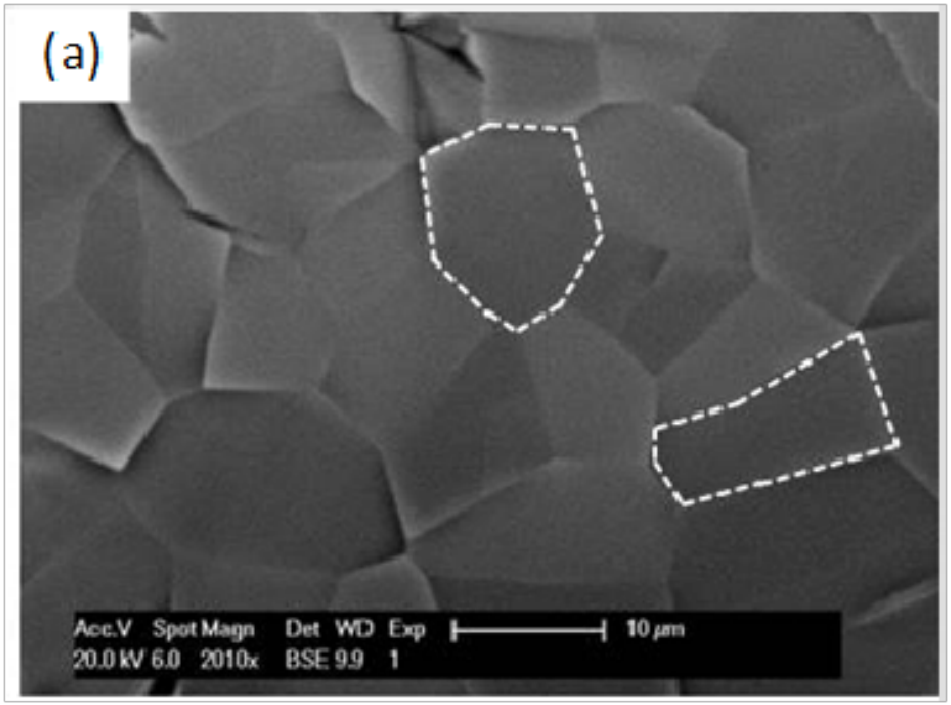


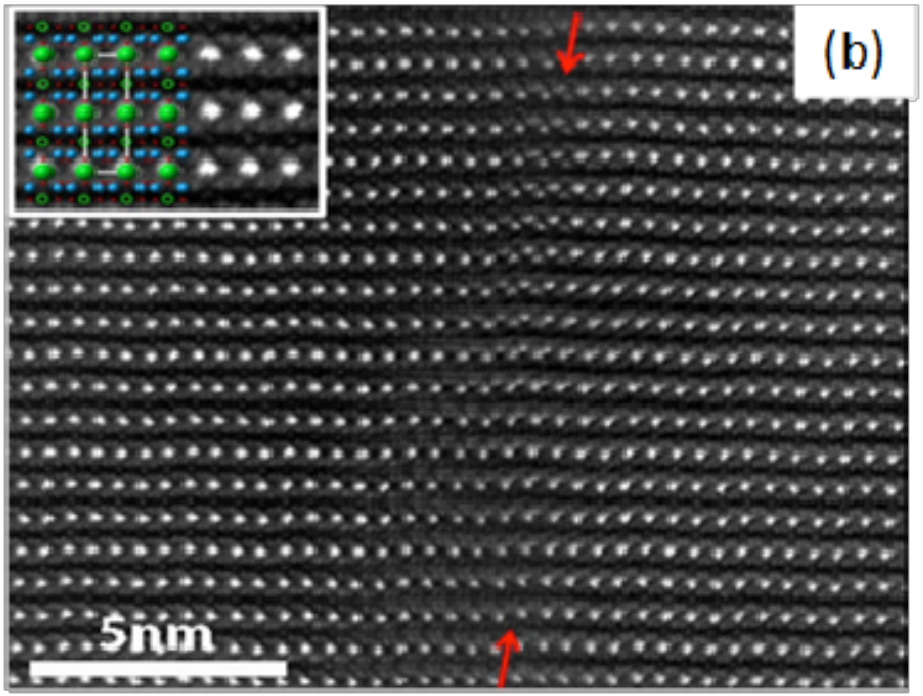
BioGlass – 2.6%P_2O_5

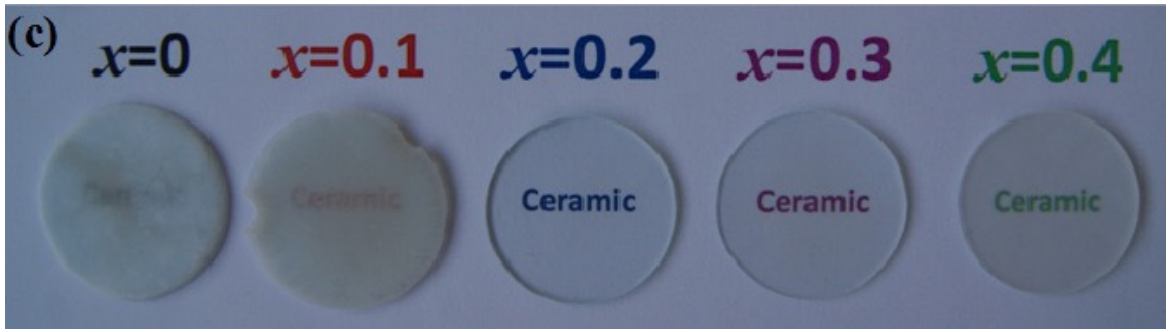
F.Fayon, C.Duée, T.Poumeyrol, M.Allix, D.Massiot, J. Phys. Chem. 117 2283-2288 **2013**

Reaching Maximal transmission from disorder in ceramics

⇒ New phases within the $SrAl_2Si_2O_8$ - $SrAl_2O_4$ binary system ⇒ $Sr_{1+x/2}Al_{2+x}Si_{2-x}O_8$



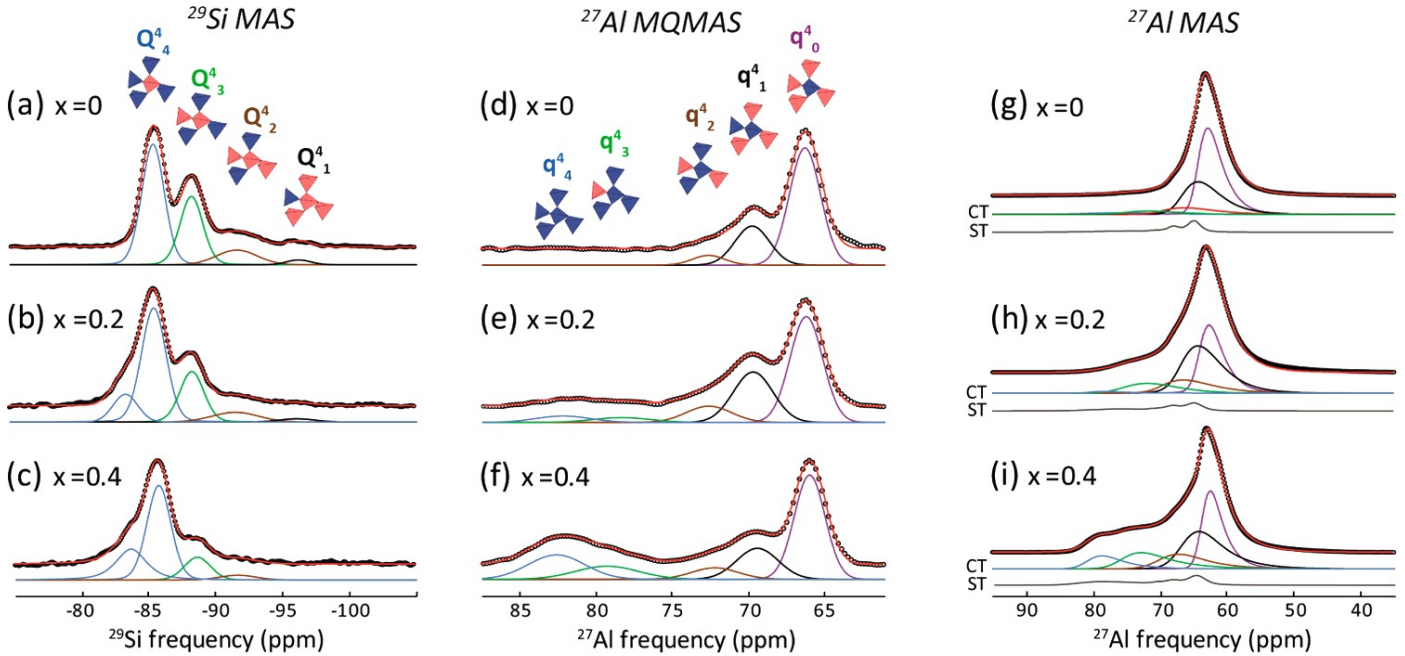




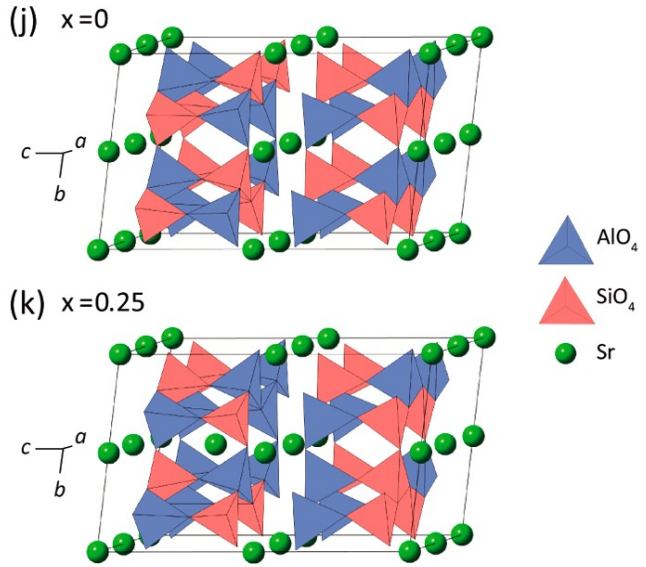
K.Al Saghir, S.Chenu, E.Veron, F.Fayon, M.Suchomel, C.Genevois, F.Porcher, G.Matzen, D.Massiot and M.Allix
Chem. Mater. 27 508-514 (2015)

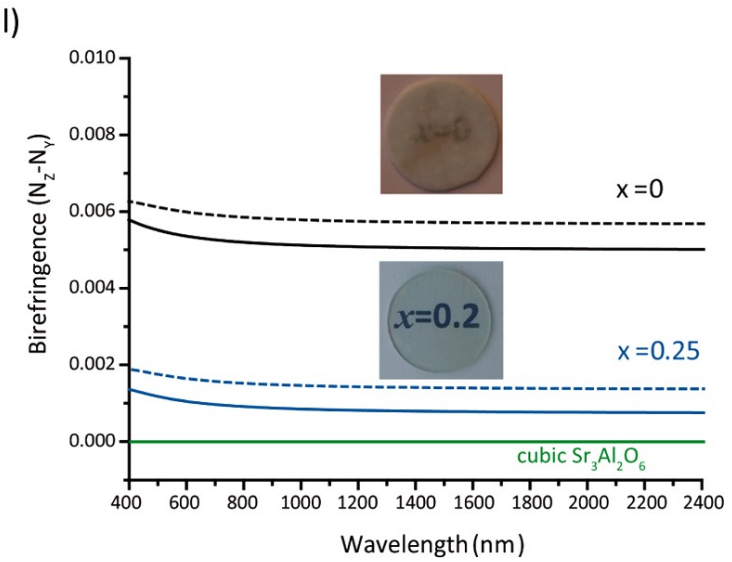
Reaching Maximal transmission from disorder in ceramics

MAS NMR



DFT Comp.

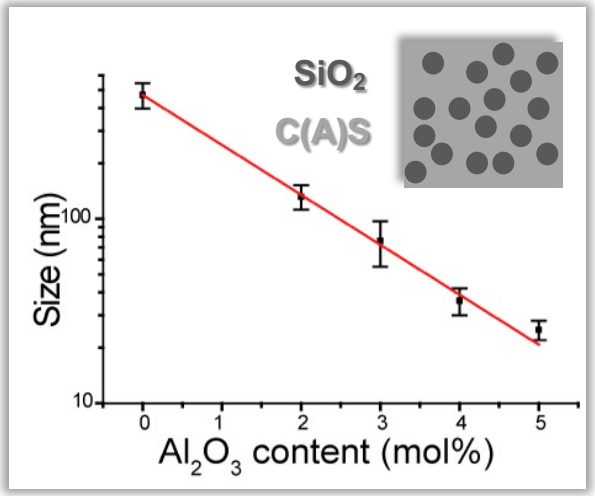


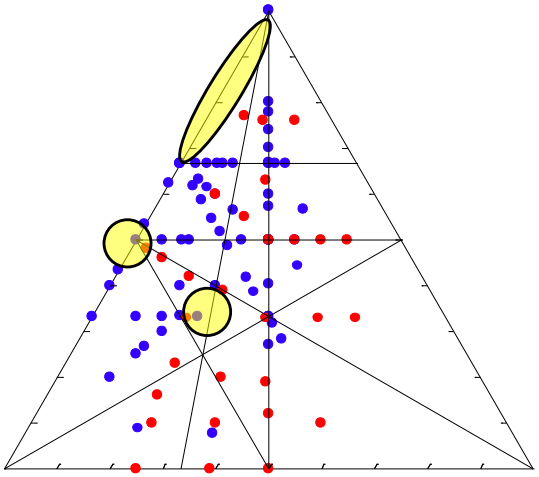


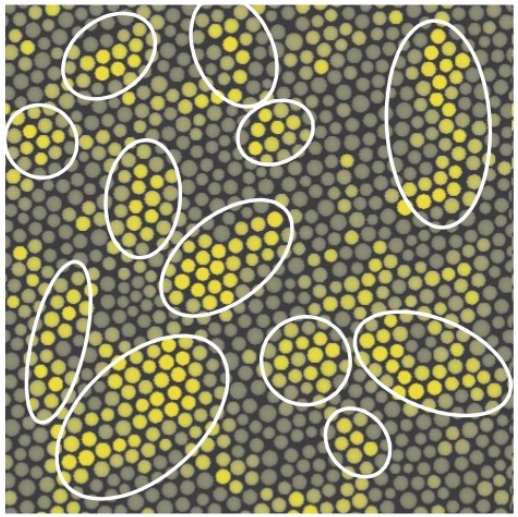
Δn

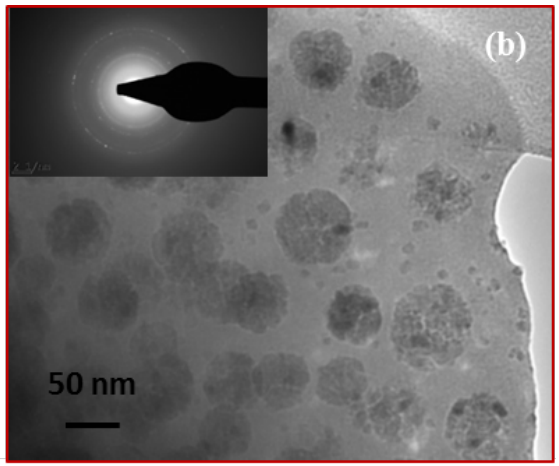
K.Al Saghir, S.Chenu, E.Veron, F.Fayon, M.Suchomel, C.Genevois, F.Porcher, G.Matzen, D.Massiot and M.Allix
Chem. Mater. 27 508-514 (2015)

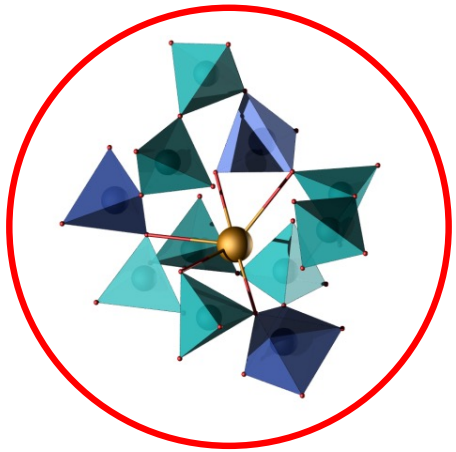
From fluctuations to phase separation



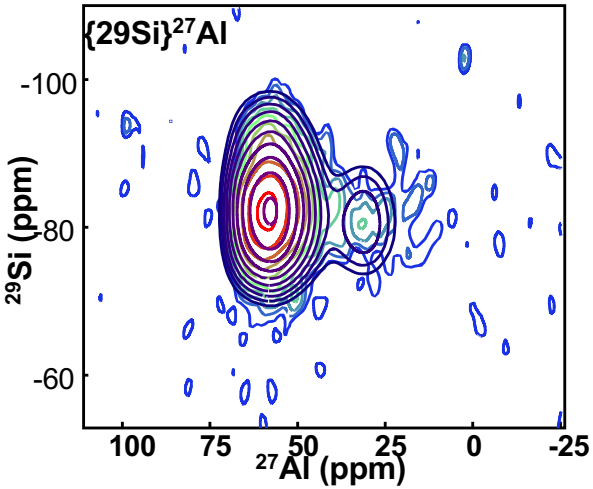






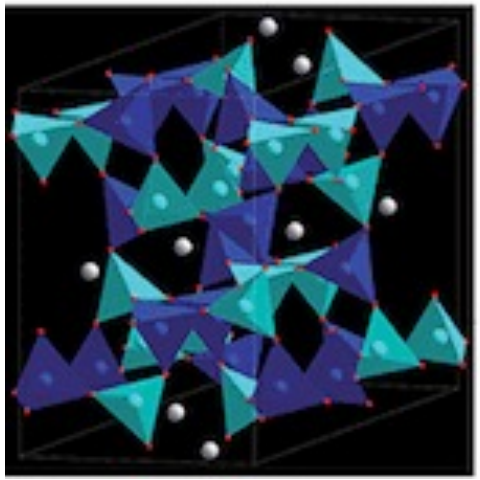


Network Topology and Chemistry



Phase separation

Local structures



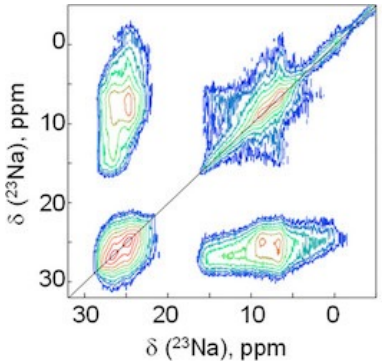
ACCOUNTS
of chemical research

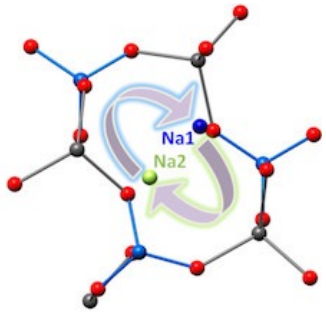
Topological, Geometric, and Chemical Order in Materials: Insights from Solid-State NMR

DOMINIQUE MASSIOT,* ROBERT J. MESSINGER,
SYLVIAN CADARS, MICHAËL DESCHAMPS,
VALERIE MONTOUILLOUT, NADIA PELLERIN,
EMMANUEL VERON, MATHIEU ALLIX, PIERRE FLORIAN, AND
FRANCK FAYON

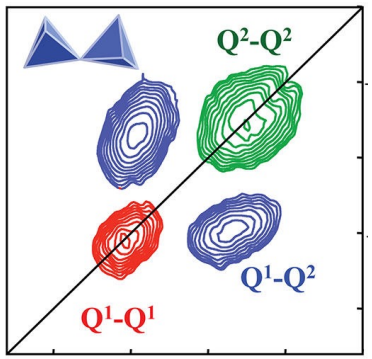
Accounts Chem. Res. **46** 1975–1984 (2013)

Correlation spectroscopy





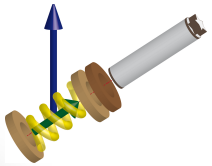
Chemical Exchange



Chemical bond or spatial proximity

Dmfit ~8000 reg. users ~3000 citations

^{23}Na Chemical Exchange - Na_2MgSiO_4



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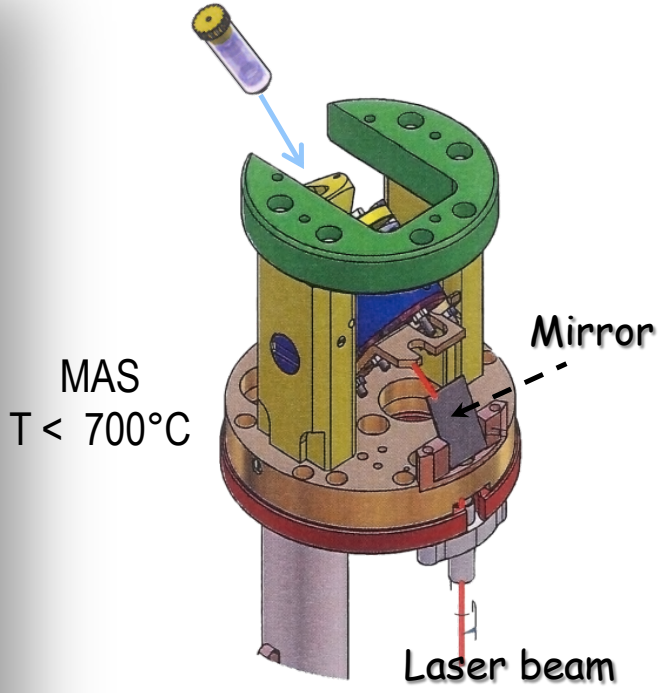

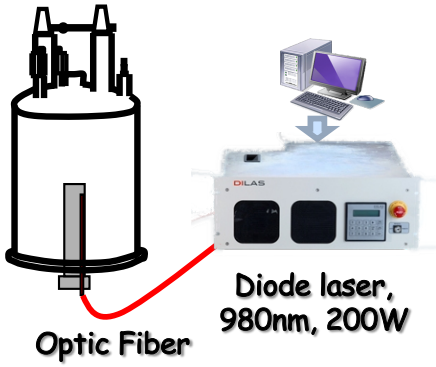

Inorganic Chemistry

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Sodium Site Exchange and Migration in a Polar Stuffed-Cristobalite Framework Structure

Alberto J. Fernández-Carrión, Aydar Rakhmatullin, Li Yang, Michael J. Pitcher, Dominique Massiot, Florence Porcher, Mathieu Allix, and Xiaojun Kuang*

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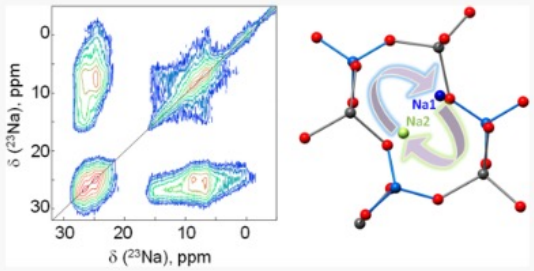
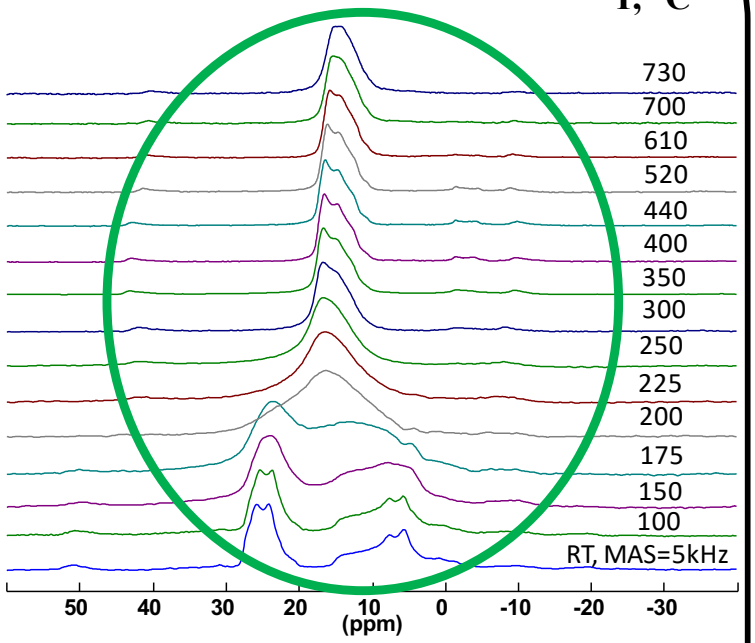
ABSTRACT: The study of ionic dynamics in solids is essential to understanding and developing modern energy technologies. Here we study the ionic dynamics of orthorhombic Na_2MgSiO_4, an interesting case of a polar stuffed-cristobalite-type structure that contains two inequivalent Na sites within the channels of the magnesium silicate tetrahedral framework. Its preparation by a solid-state reaction method favors the presence of ~2% of Na vacancies, converting it into a pure Na ionic conductor with an optimized ionic conductivity of $\sim 10^{-5}$ S cm^{-1} at 200 °C. The macroscopic migration has been characterized through impedance spectroscopy and molecular dynamics simulation, which proves the pure Na ionic character of the compound through hopping between Na1 and Na2 sites, forming three-dimensional migration zigzag-shaped paths. High-resolution solid-state ^{23}Na magic-angle-spinning (MAS) NMR spectroscopy is employed to characterize the local structure and microscopic dynamics of Na-ion transport in Na_2MgSiO_4. Remarkably, variable-temperature ^{23}Na MAS NMR and two-dimensional exchange spectroscopy evidence for the first time a Na site exchange phenomenon at room temperature, which further triggers Na ionic conduction at elevated temperatures.

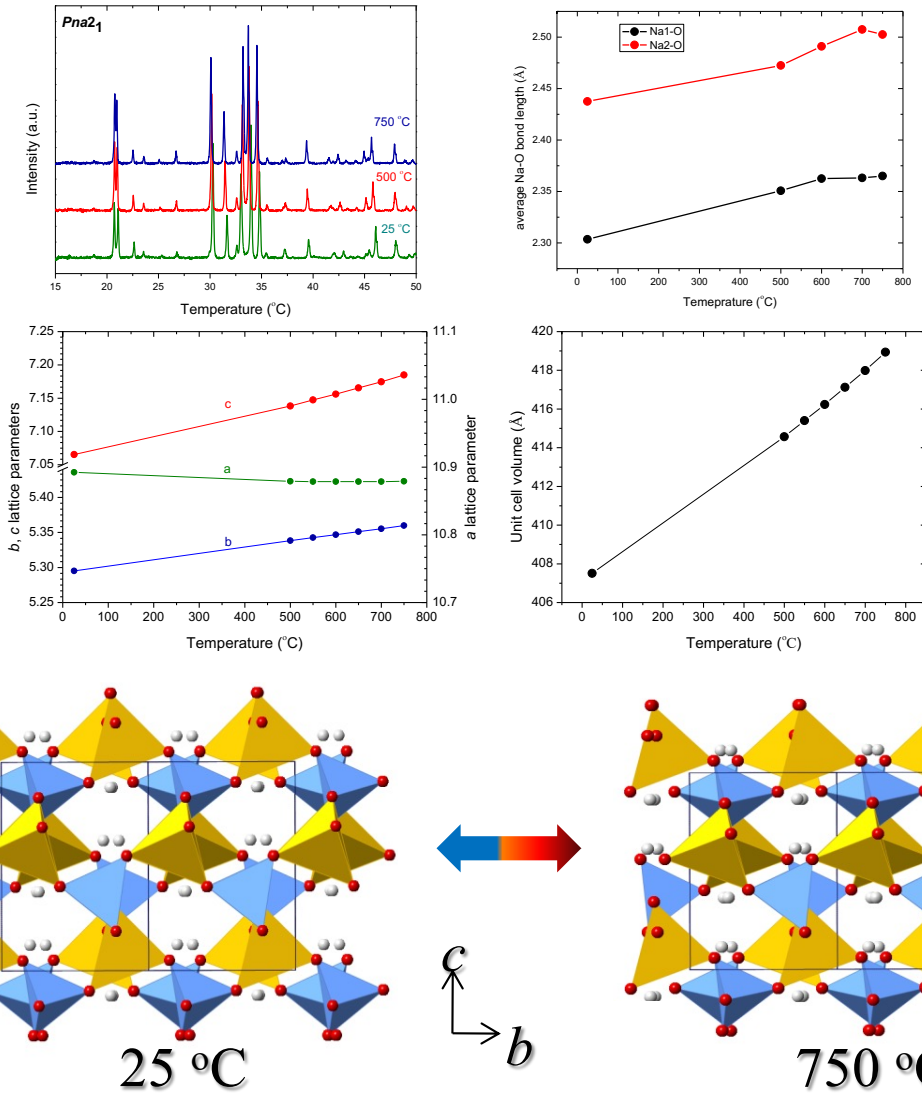


Na_2MgSiO_4 - NMR and XRD f(T)



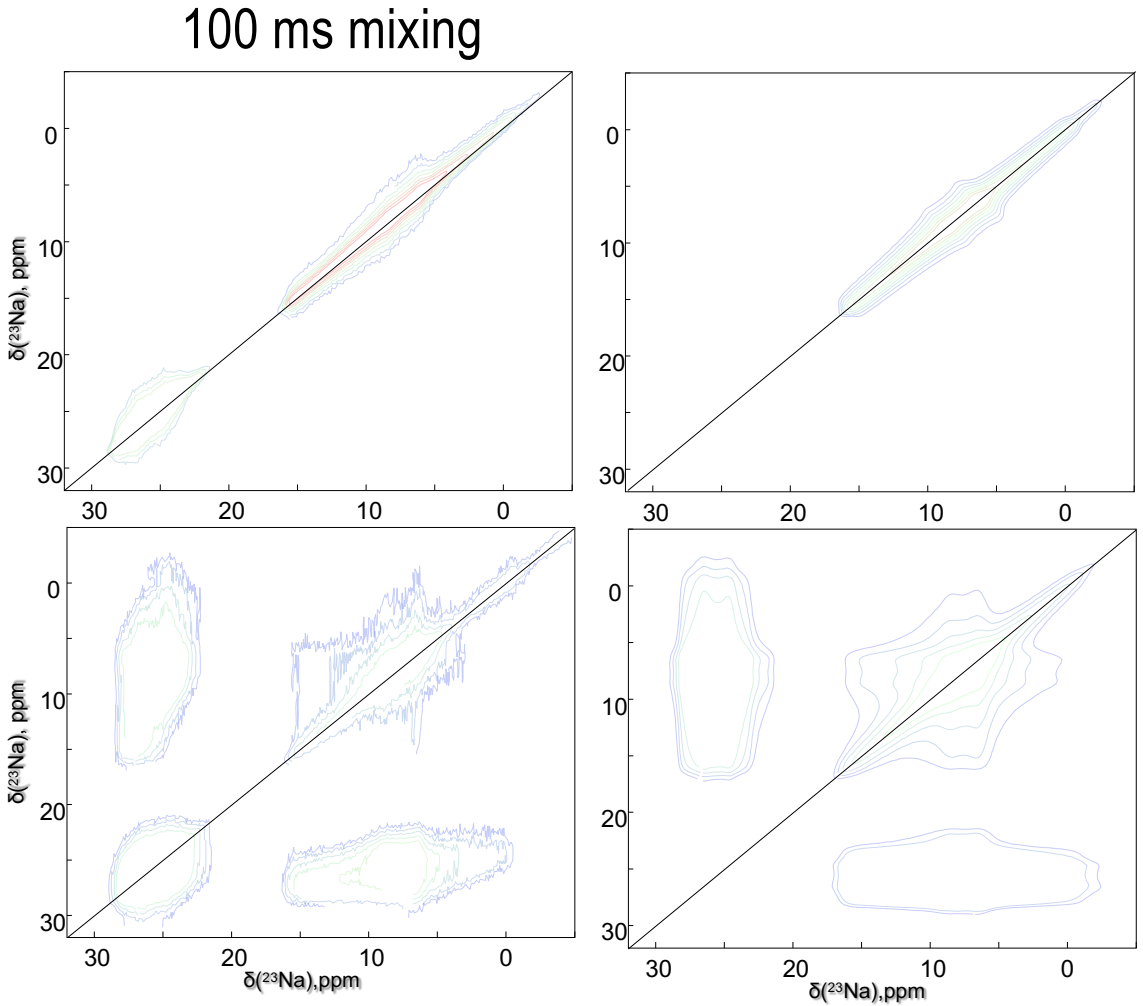
Sodium site exchange

VT-XRD

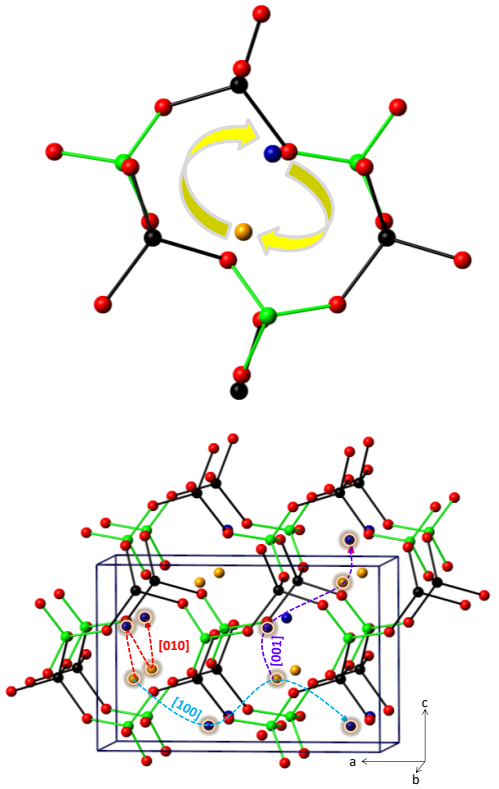


Fernández-Carrión, Rakhmatullin, Yang, Pitcher, Massiot, Porcher, Allix, Kuang,
'Sodium Site Exchange and Migration in a Polar Stuffed-Cristobalite Framework Structure', Inorg. Chem., 60 4322–4331 (2021)

^{23}Na 2D EXSY NMR



^{23}Na 2D EXSY NMR spectra and model
100 ms mixing time, at room temperature [RT] and 100 C



a) <010> view of the sodium site exchange at low temperatures. Si, Mg, Na1 and Na2 are represented as green, navy blue and yellow spheres, respectively.
b) <010> view refined structure emphasizing the voids along (010) direction.

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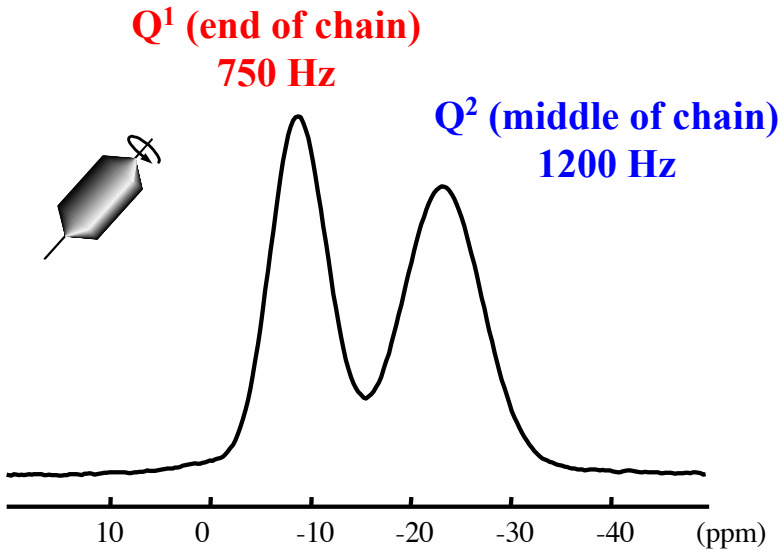
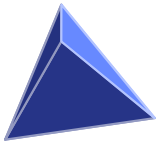
Phosphate Glasses : ^{31}P MAS NMR

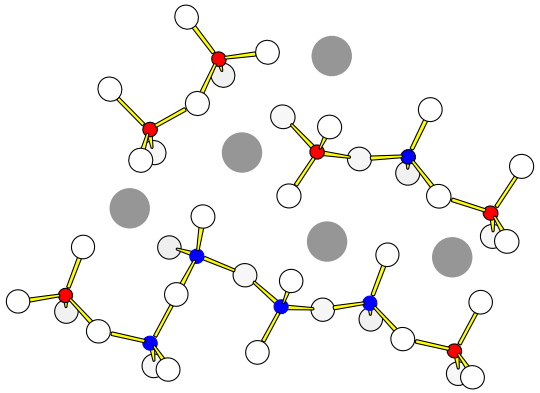
$(PbO)_{0.61}(P_2O_5)_{0.39}$ glass



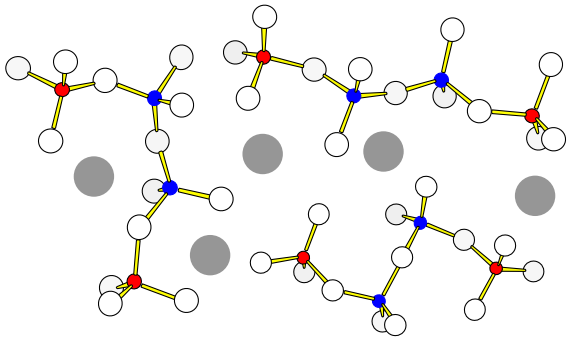


$[Q^1] = [Q^2]$

Average chain length
$N_{av.} \sim 4$



? Nature of disorder at the nanometric scale ?

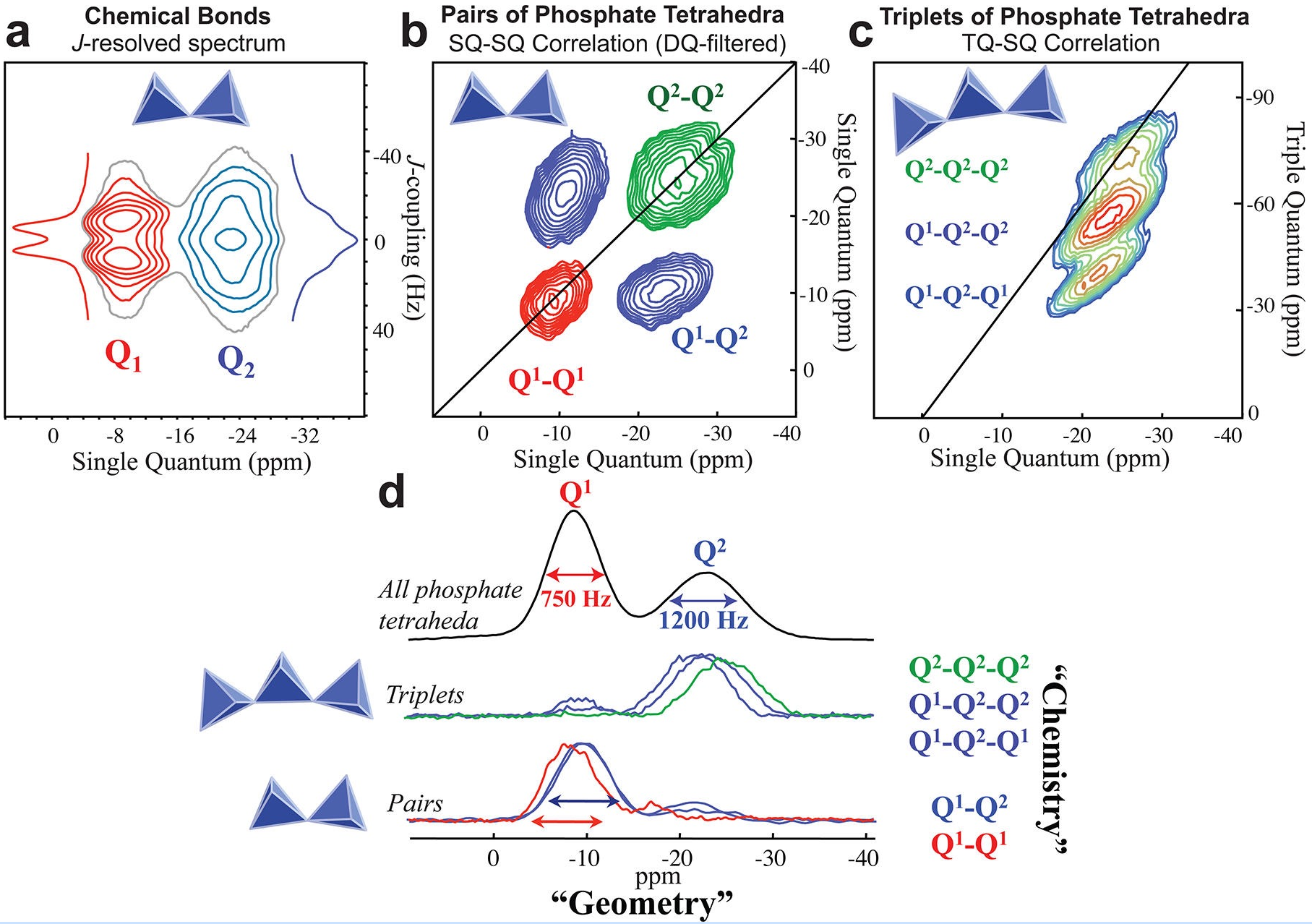


Chain length distribution?
Chemical disorder

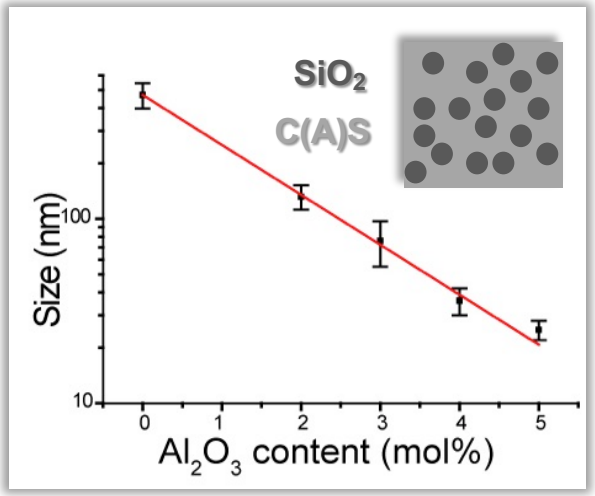
Chain geometries?
Topological or geometrical disorder

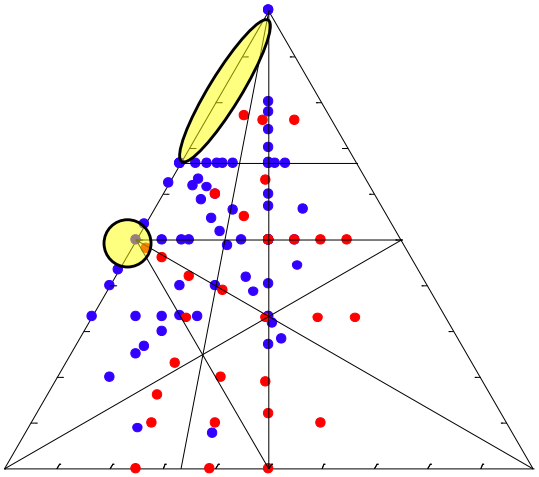
P-O-P chemical bonds can be viewed from J based P-P experiments

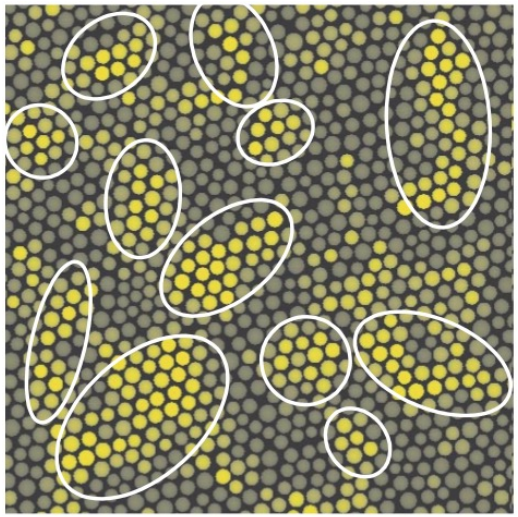
Chemical and Geometrical Disorder

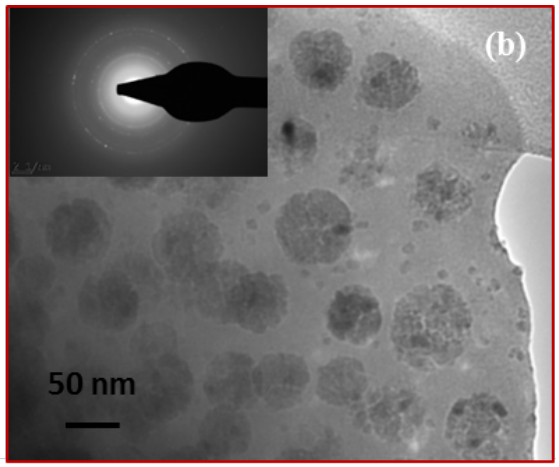


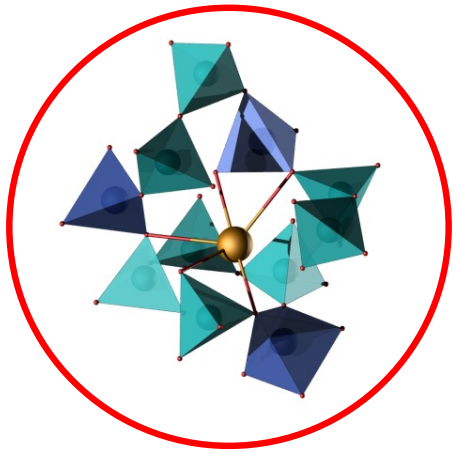
D.Massiot, R.J.Messinger, S.Cadars, M.Deschamps, V.Montouillout, N.Pellerin, E.Veron, M.Allix, P.Florian, F.Fayon, 'Topological, Geometric, and Chemical Order in Materials: Insights from Solid-State NMR', Accounts Chem. Res., 46 1975–1984 (2013)

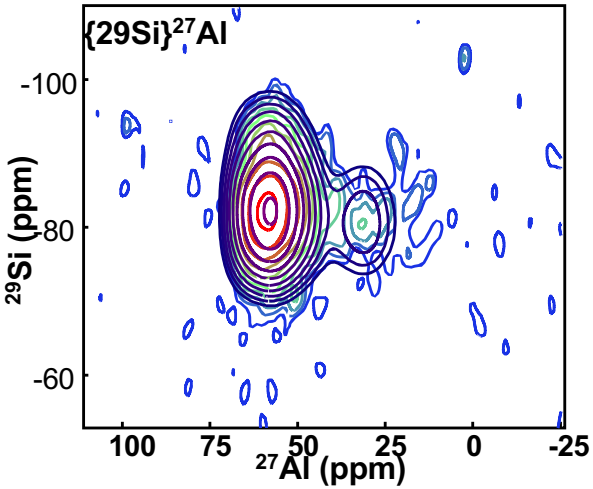












Phase separation

Network Topology and Chemistry

Local structures

Acknowledgements

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