Brant Walkley

The University of Sheffield

Materials for a Sustainable Future

Composition-'local-structure'-property relationships in sustainable cements

Brant Walkley

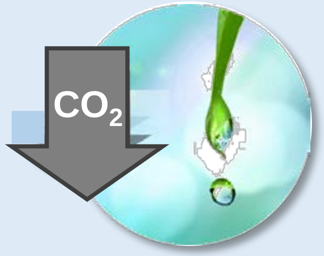
The University of Sheffield, UK

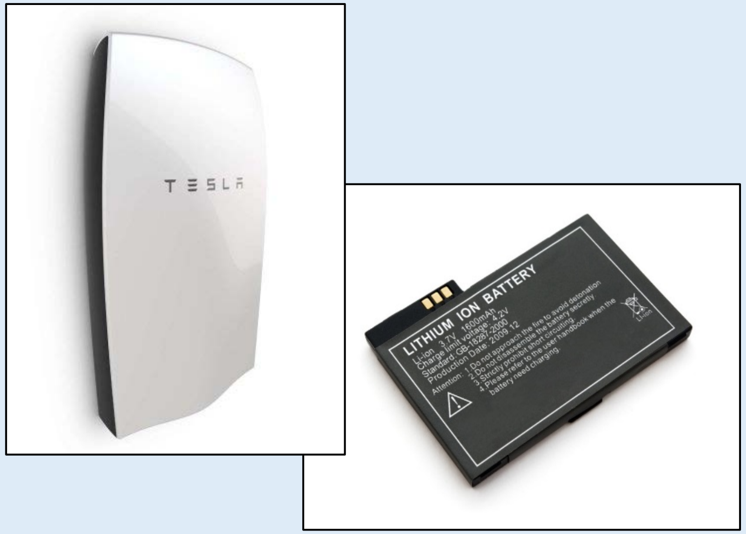
The University of Melbourne, Australia

Research Vision

Improve the well-being of society and environment by driving new advances in sustainable materials for

- **Infrastructure**
- **Environmental remediation**
- **Energy and electronics**

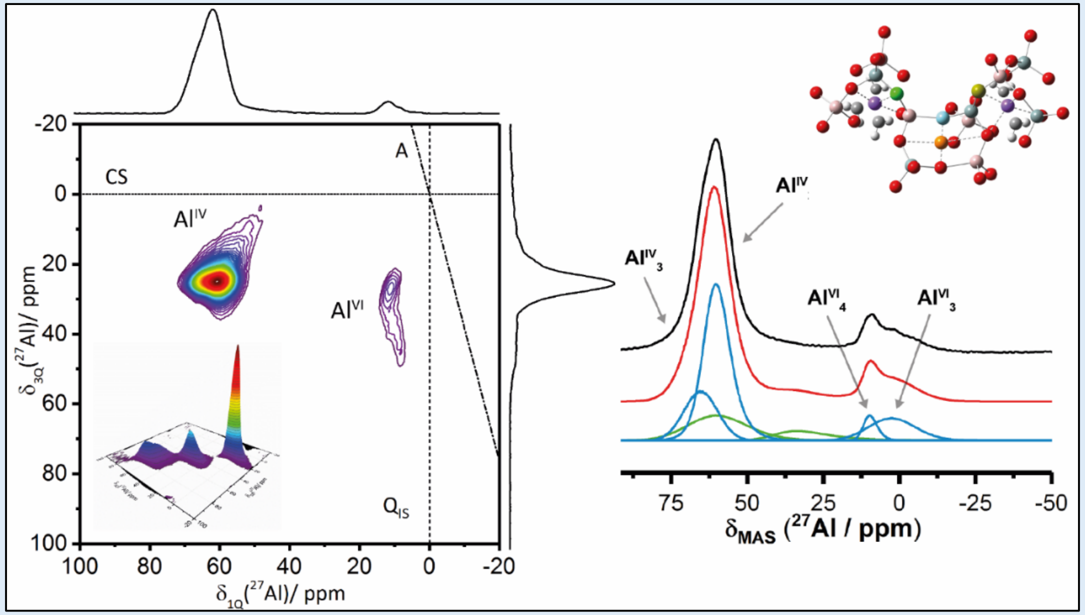


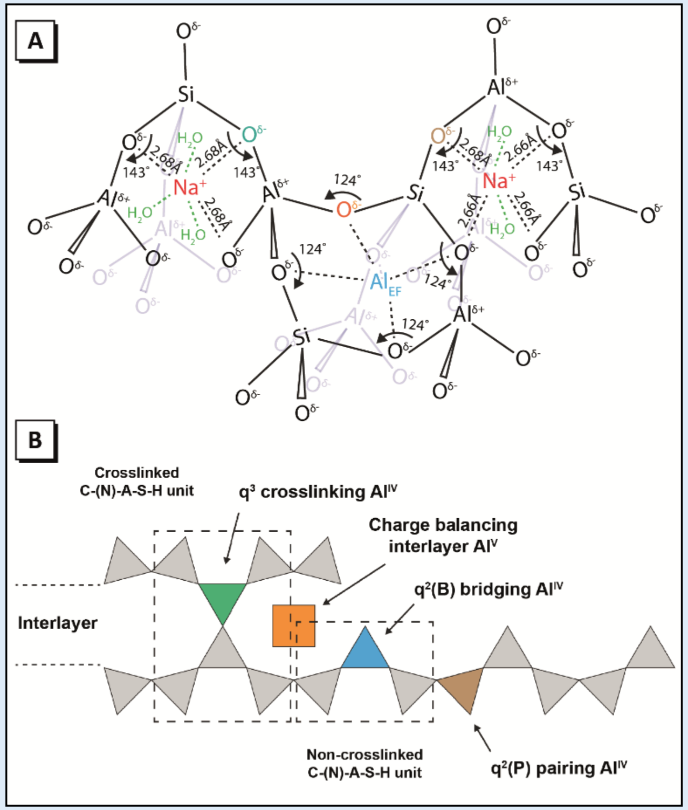


Research Vision

Optimise material synthesis, processing and properties by exploiting cutting-edge characterisation techniques to probe

- **composition-‘local-structure’-property relationships**
- **reaction mechanisms**
- **kinetics**

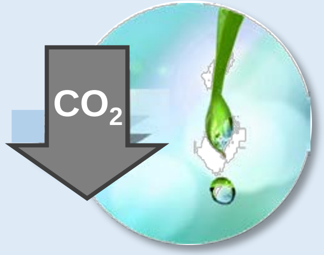


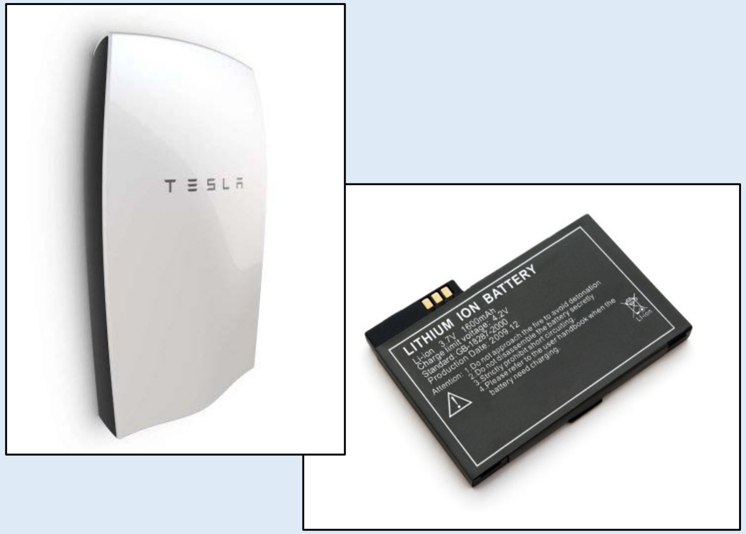


Research Vision

Improve the well-being of society and environment by driving new advances in sustainable materials for

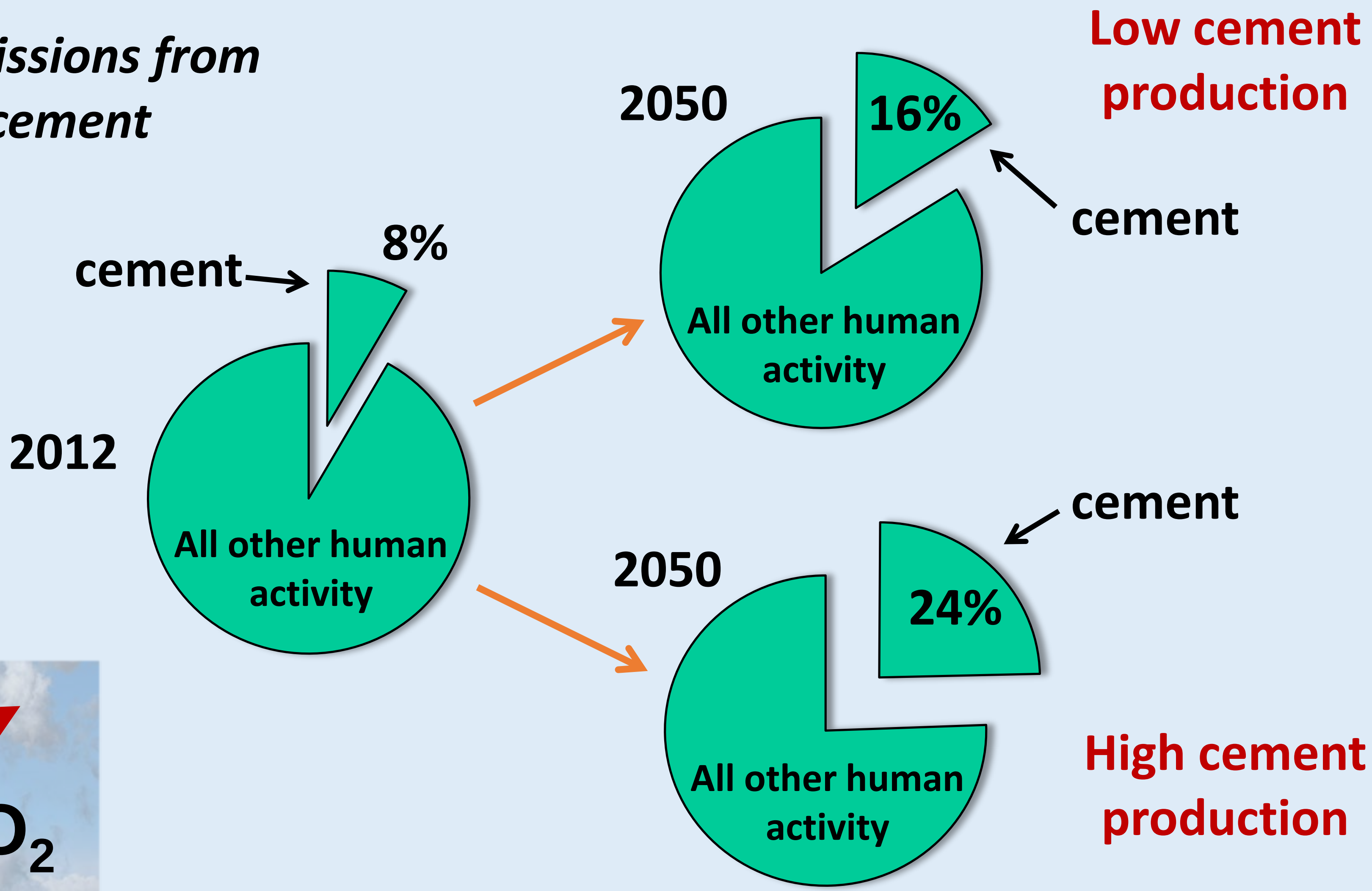
- Infrastructure
- Environmental remediation
- Energy and electronics

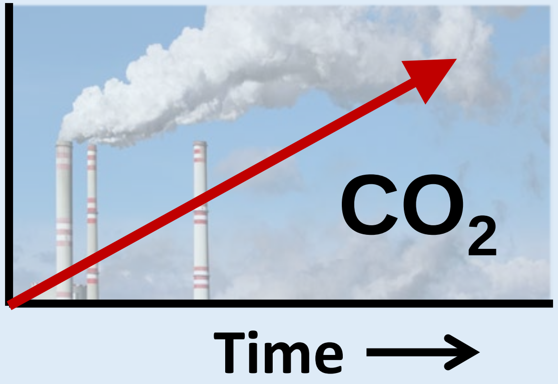




Environmental impact of cement

Global CO_2 emissions from Portland cement





Innovative, sustainable cements

Innovative, sustainable cements are crucial for

- Sustainable infrastructure
- Immobilisation of nuclear waste
- Advanced performance
- Contribute over £110 bn pa (7% GDP)

Innovative, sustainable cements

Innovative, sustainable cements are crucial for

- **Sustainable infrastructure**
- **Immobilisation of nuclear waste**
- **Advanced performance**
- **Contribute over £110 bn pa (7% GDP)**

There are many types of sustainable cements

- **Supplementary cementitious materials (limestone, slag, fly ash, calcined clays)**
- **Calcium aluminate cements**
- **Calcium sulfoaluminate cements**
- **Alkali-activated cements**

Innovative, sustainable cements

Innovative, sustainable cements are crucial for

- Sustainable infrastructure
- Immobilisation of nuclear waste
- Advanced performance
- Contribute over £110 bn pa (7% GDP)

There are many types of sustainable cements

- Supplementary cementitious materials (limestone, slag, fly ash, calcined clays)
- Calcium aluminate cements
- Calcium sulfoaluminate cements
- Alkali-activated cements

Alkali-activated cements

- **Low-CO_2 emissions**
- **Excellent mechanical properties and durability**
- **Waste valorisation**
- **Waste immobilisation**
- ***Industrial use still low***

Uni of QLD, Australia

Source of precursor materials

Alkali-activated cements in use

Alkali-activated cements

- Low-CO_2 emissions
- Excellent mechanical properties and durability
- Waste valorisation
- Waste immobilisation
- *Industrial use still low*
- ***Limited understanding of composition-structure-property relationships***

Uni of QLD, Australia

Source of precursor materials

Alkali-activated cements in use

Key challenge

Key challenge is to understand **composition-'local-structure'-property relationships** of sustainable cements, and to use this knowledge to design tailored materials for demanding applications

Many techniques available

- Spectroscopic (solid state nuclear magnetic resonance, infrared, Raman etc.)
- Diffraction (X-ray, neutron, electron)
- Microscopic (transmission/scanning electron microscopy)

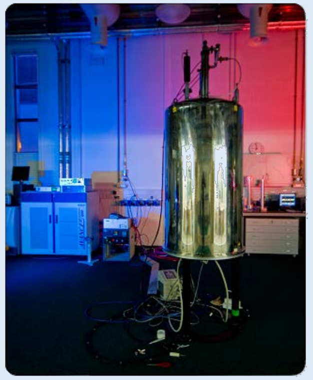
Key challenge

Key challenge is to understand composition-'local-structure'-property relationships of sustainable cements, and to use this knowledge to design tailored materials for demanding applications

Many techniques available

- Spectroscopic (solid state nuclear magnetic resonance, infrared, Raman etc.)
- Diffraction (X-ray, neutron, electron)
- Microscopic (transmission/scanning electron microscopy)





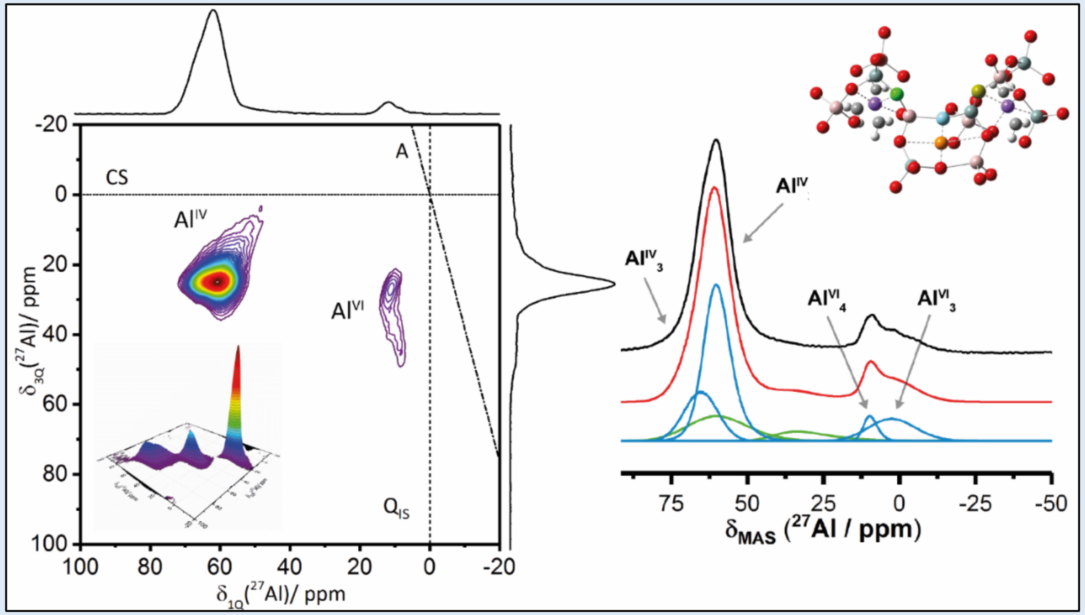
Solid state NMR spectroscopy

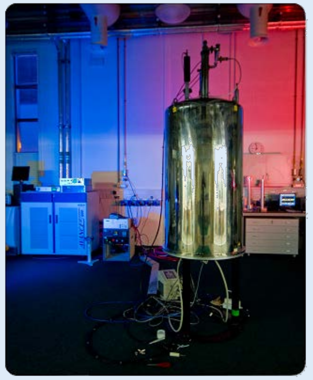
Provides information about

- Local (nano- or atomic-scale) structure
- Coordination spheres
- Electric field gradient (symmetry)

Probes specific nuclei

Very useful for disordered materials

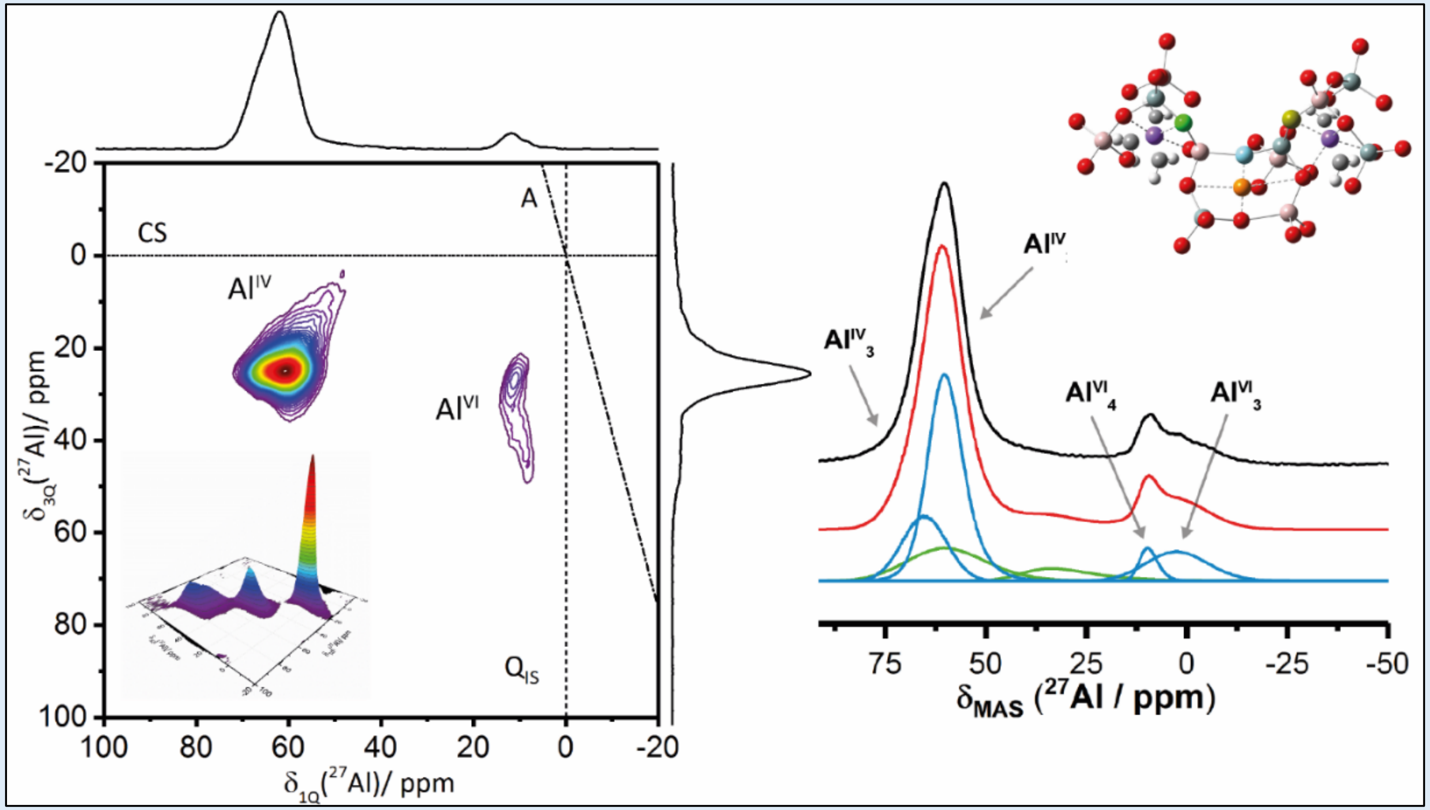


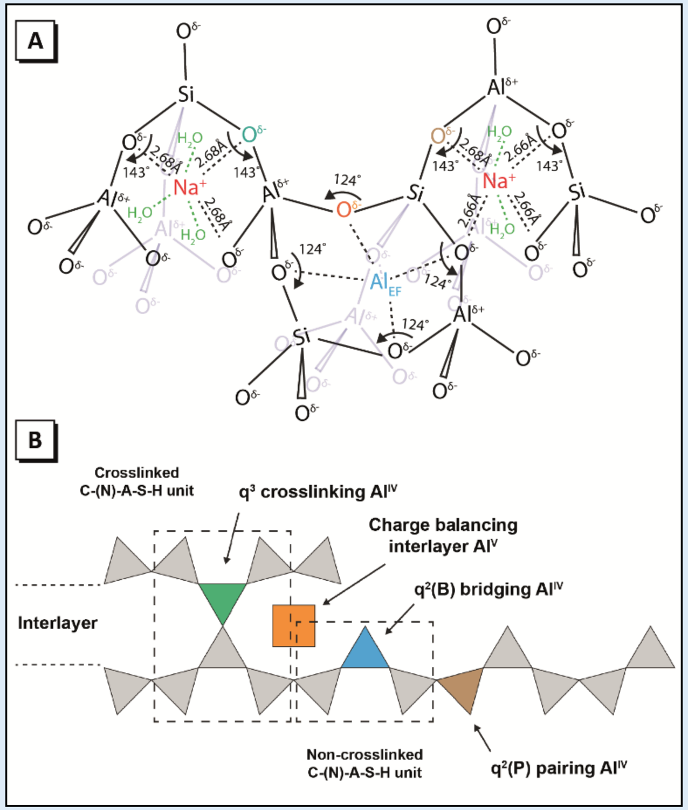


Alkali-activated cements

Case study

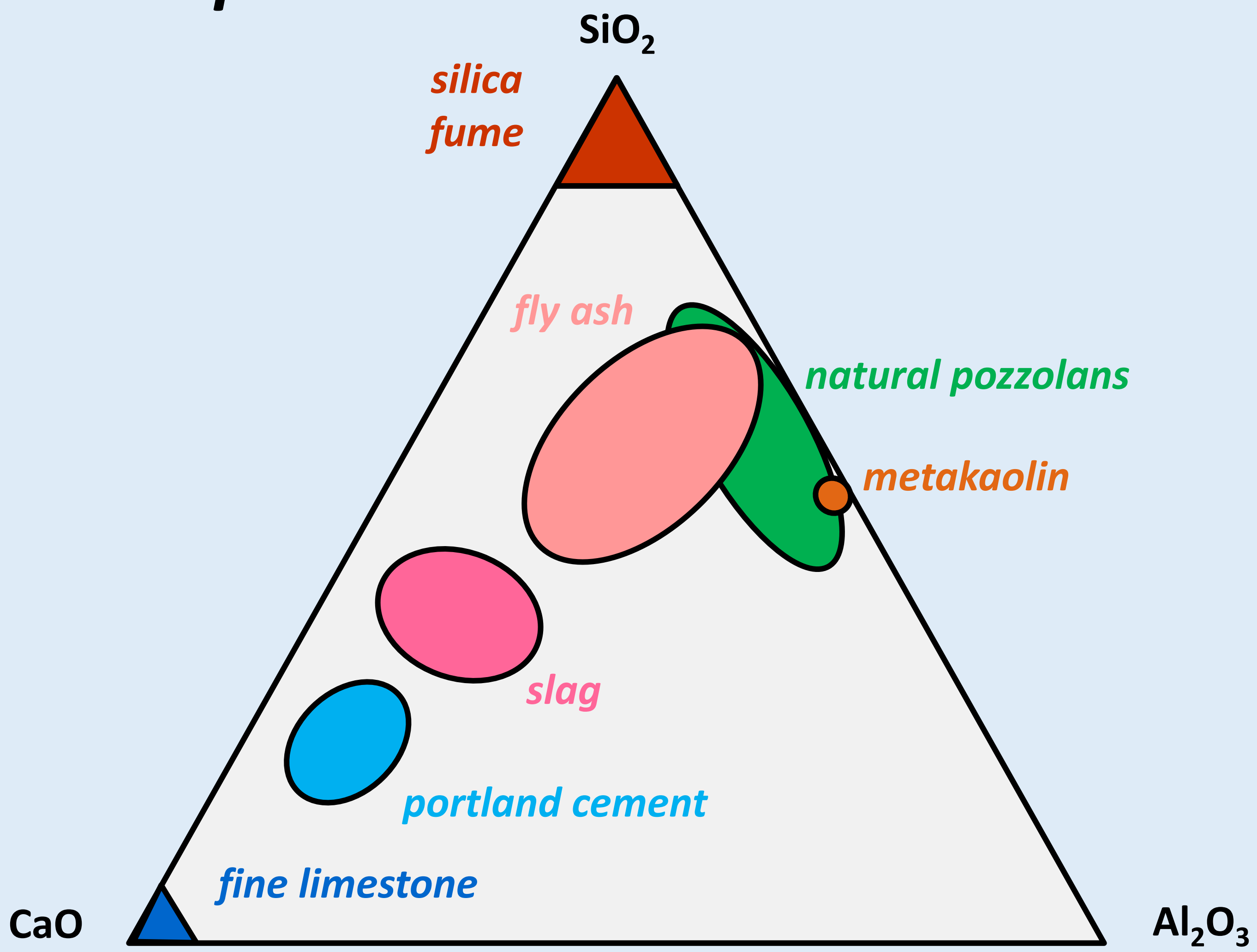
Understanding the nanostructure of synthetic alkali-activated cements





Alkali-activated cements

Why isn't use widespread?



Synthetic alkali-activated cements

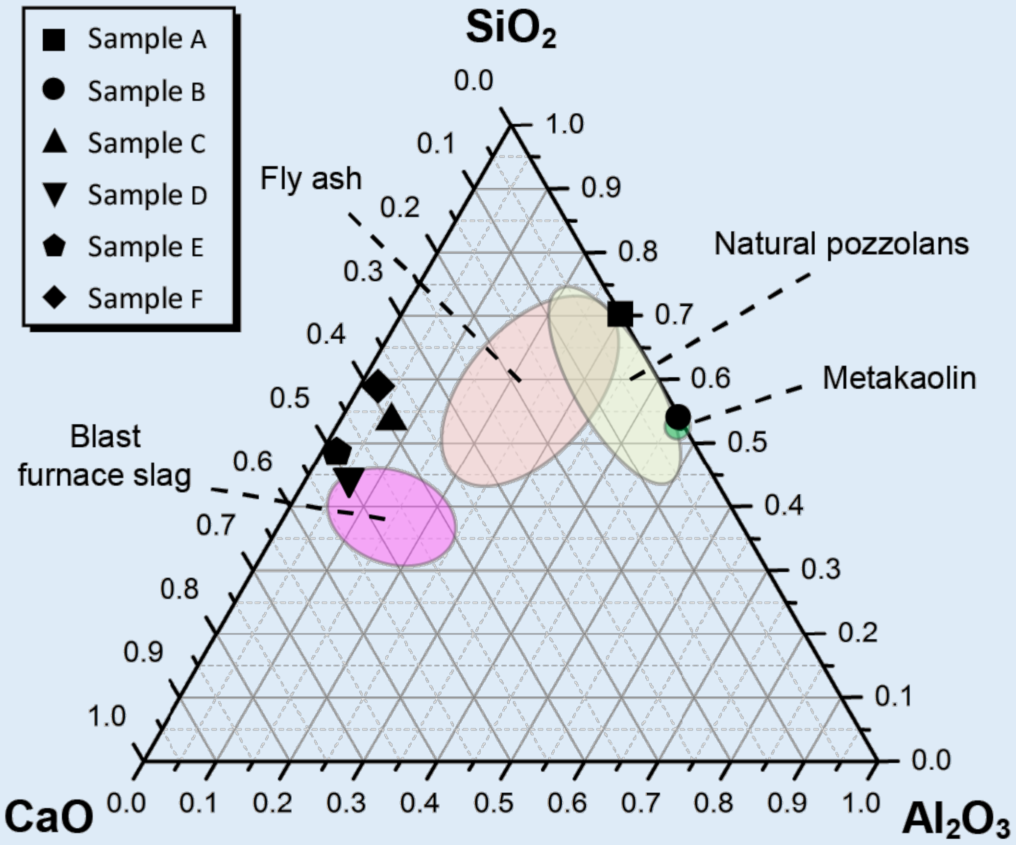
Organic steric entrapment method

Aqueous precursors
& polymer carrier

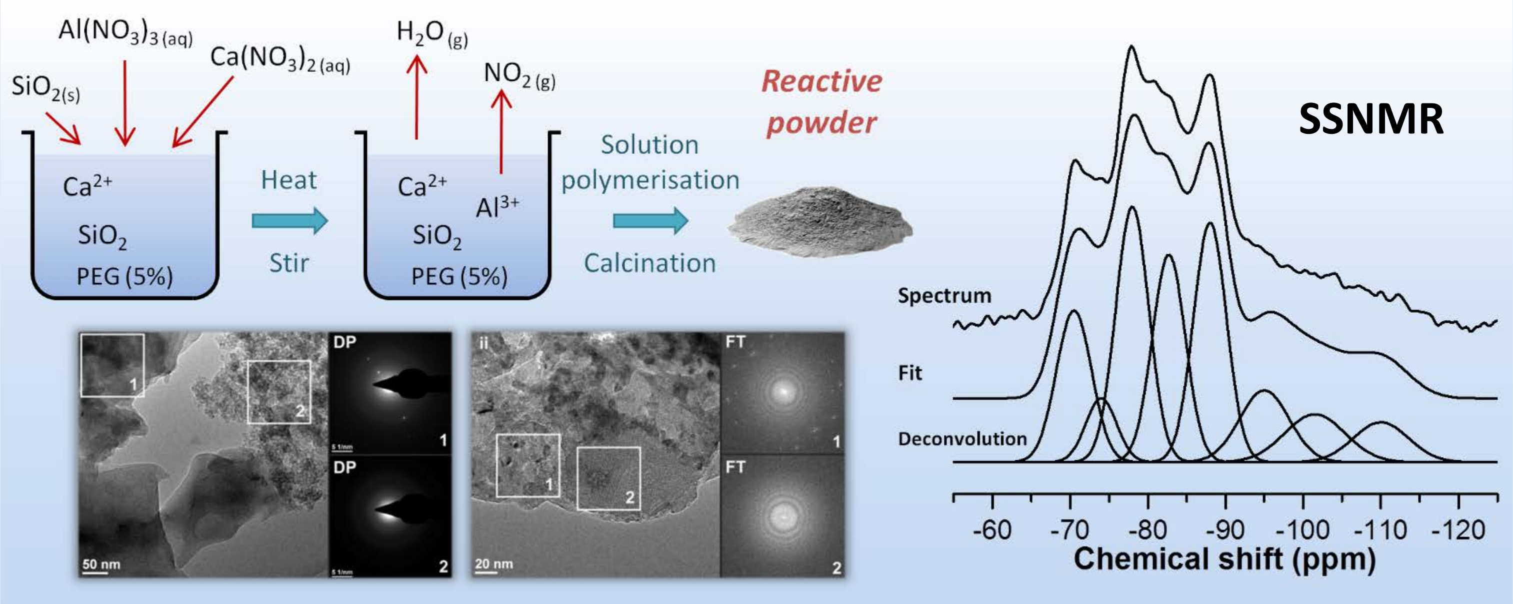
Reactive powder

Synthetic AAC

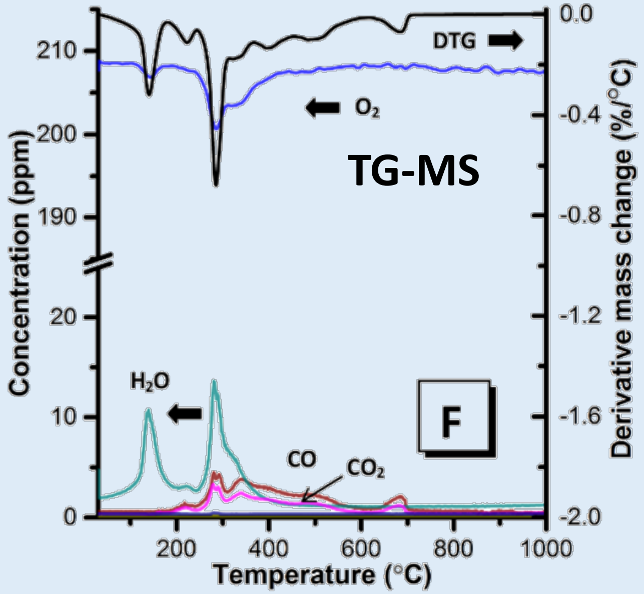
Precursor synthesis



Precursor characterisation



TEM-EDX



Characteristics similar to commercial precursors, but with controlled composition, high purity and no minor constituents (e.g. Fe, Mg, K)

Alkali-activation

Precursor

Sodium silicate solution

SiO_2/Na_2O = 1
pH >13

Alkali-activated cement

Sealed in tubes and cured at ambient temperature (~23°C)

Alkali-activation

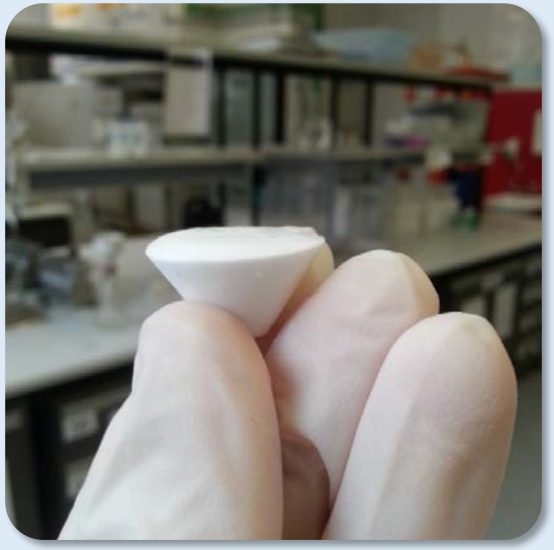
Precursor

Sodium silicate solution

$SiO_2/Na_2O = 1$
pH >13

Alkali-activated cement

Sealed in tubes and cured at ambient temperature (~23°C)



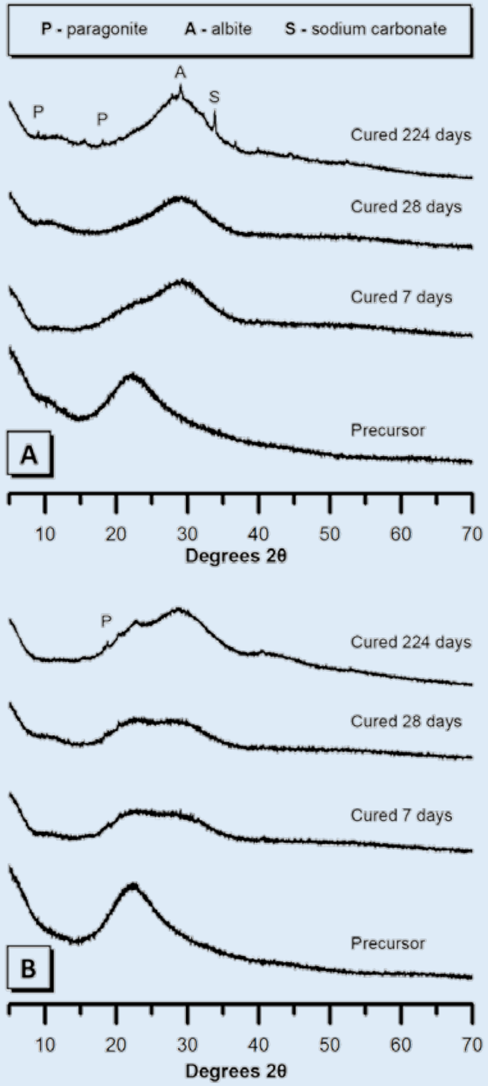
Microstructural analysis

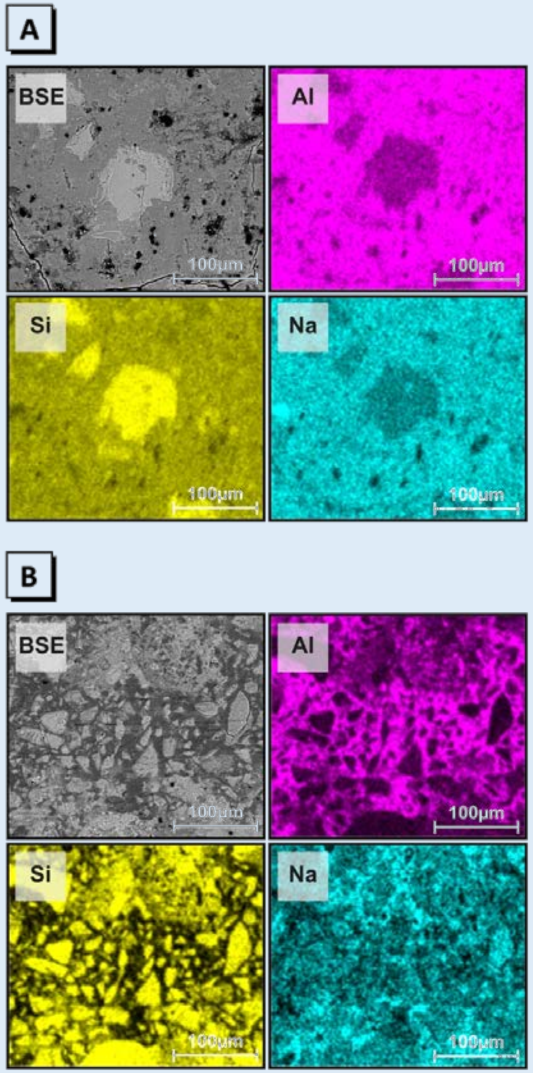
X-ray diffraction

SEM-EDX

Al/Si = 1

Al/Si = 0.5

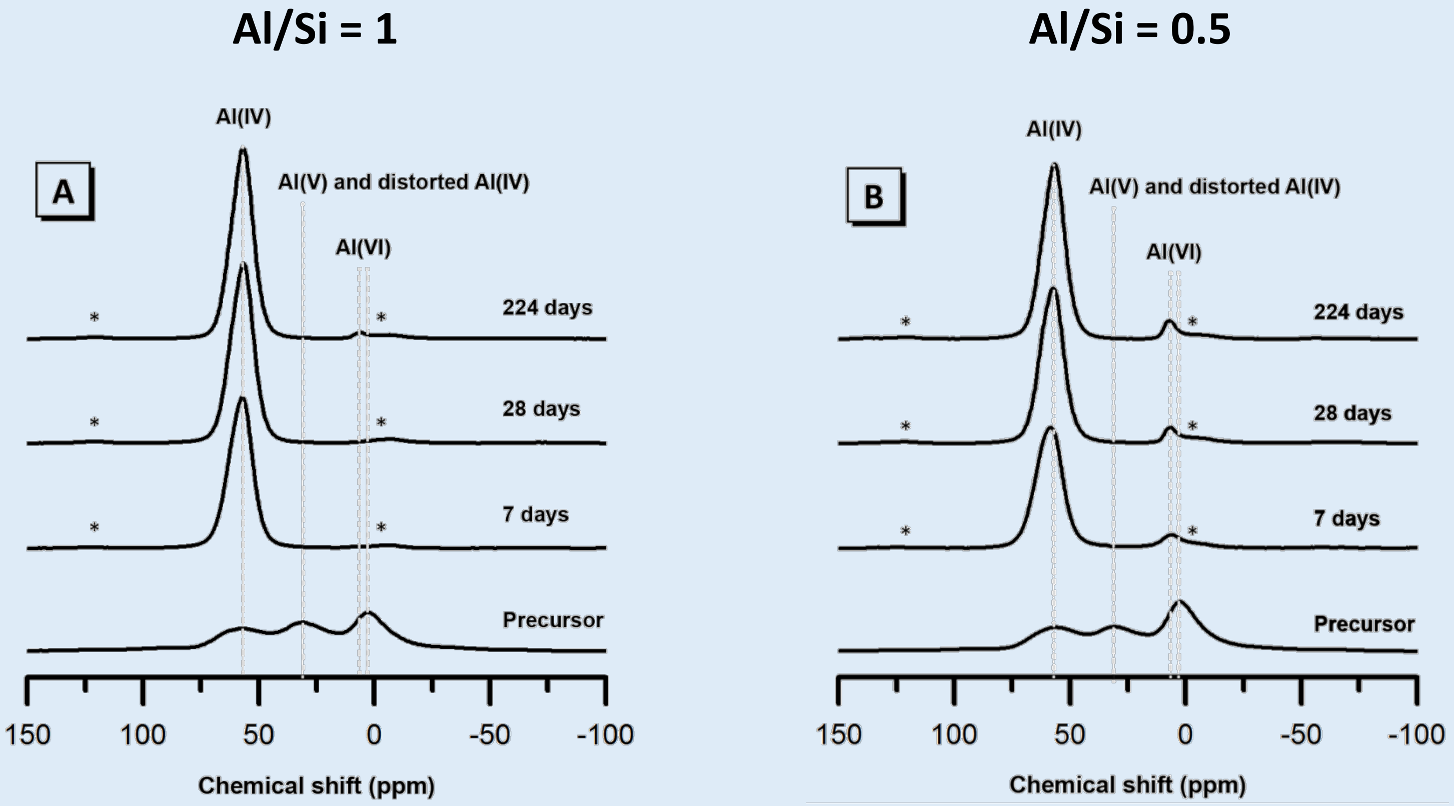




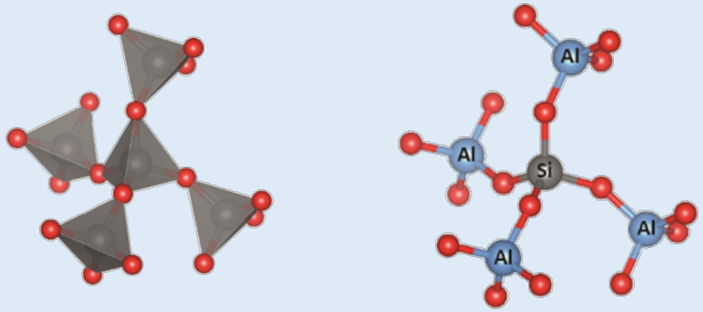
Solid state NMR analysis

^{27}Al solid state MAS NMR

- Al in binder is predominantly tetrahedral
- Nanostructural development occurs in first 7 days



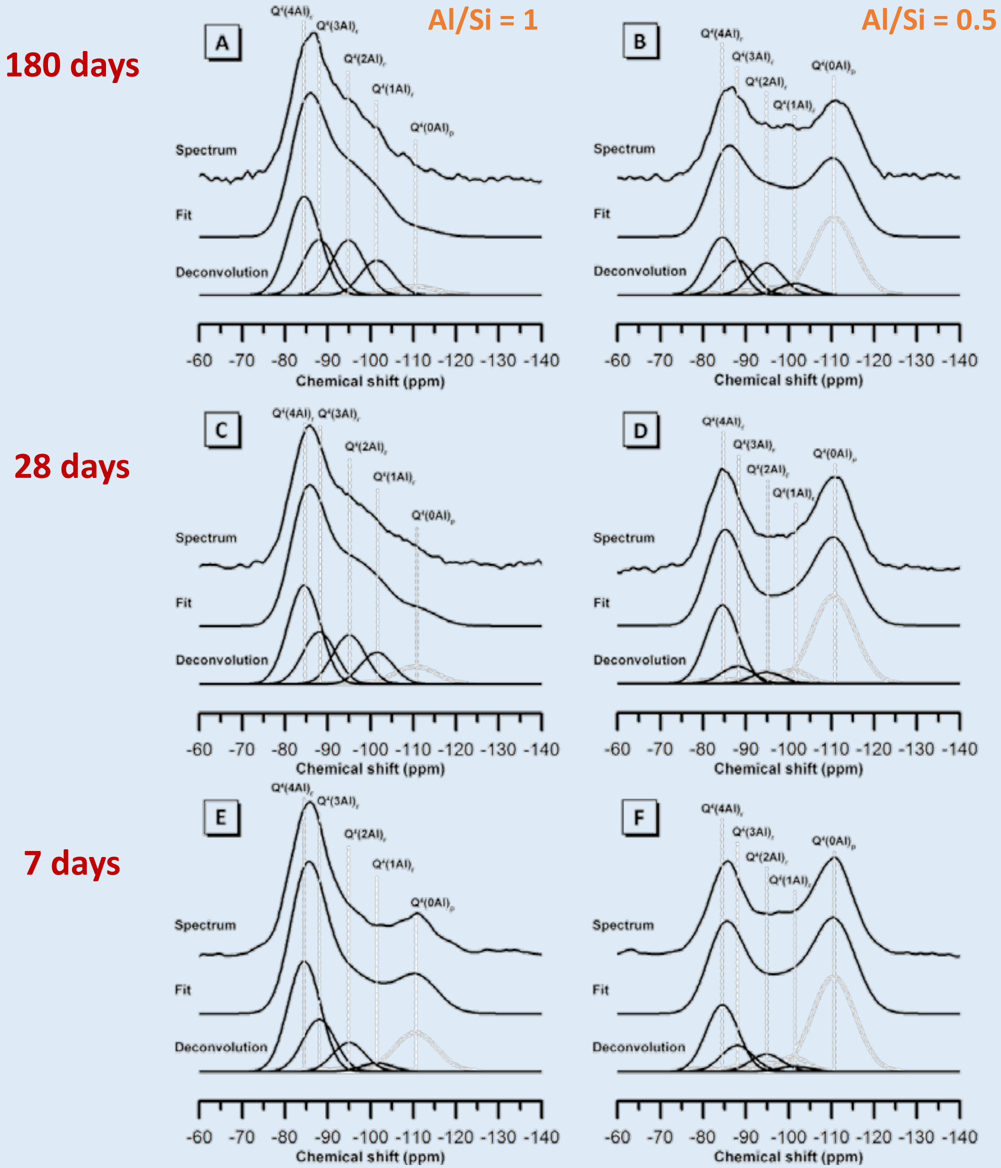
Solid state NMR analysis



Q^4 $Q^4(4Al)$

^{29}Si solid state MAS NMR w/ Gaussian peak deconvolution

- **Predominantly $Q^4(4Al)$ sites $(Si\text{-}(O\text{-}Al)_4)$ at early ages**
- **Increase in $Q^4(3Al)$, $Q^4(2Al)$ and $Q^4(1Al)$ sites at later ages**
- **Nanostructural development continues at later ages**



Multiple-quantum SS MAS NMR

^{27}Al, ^{23}Na and ^{17}O are quadrupolar nuclei

MAS NMR spectra of quadrupolar nuclei are difficult to deconvolute due to quadrupolar interactions

Quadrupolar interaction is between the quadrupole moment and electric field gradient of the nucleus – related to symmetry

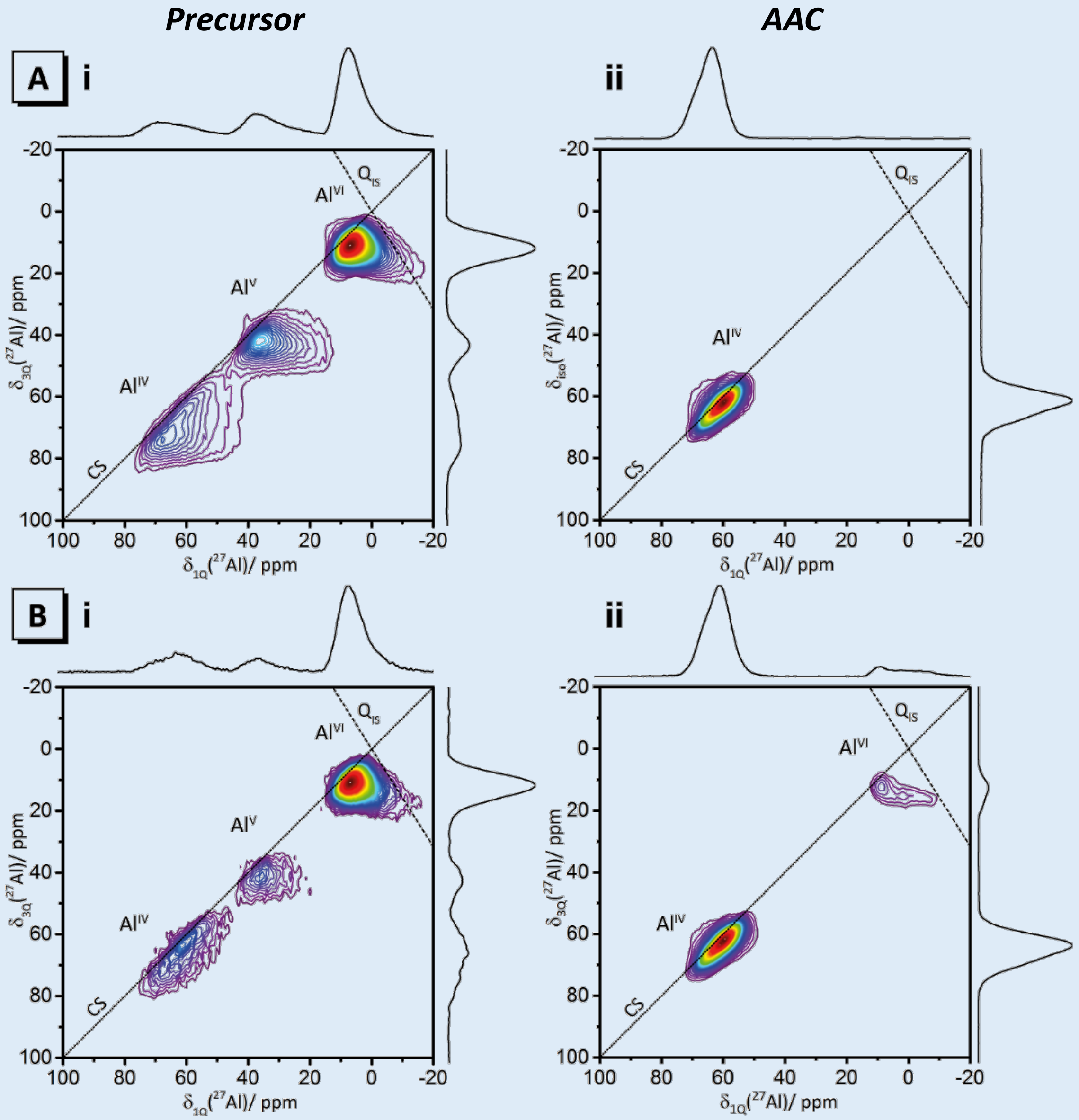
This means quadrupolar parameters must be determined first to enable accurate deconvolution and identification of chemical environment

Can do this with multiple-quantum SS MAS NMR

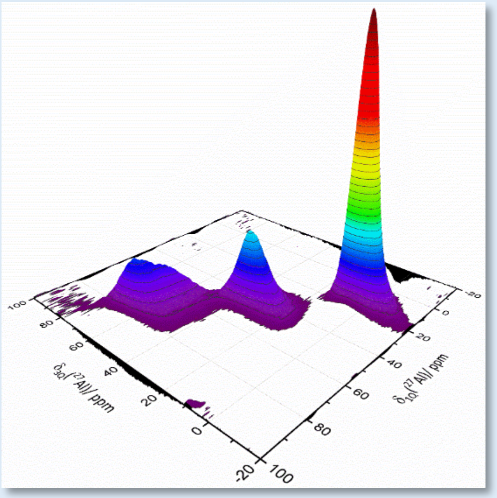
Multiple-quantum SS MAS NMR

Al/Si = 1

Al/Si = 0.5



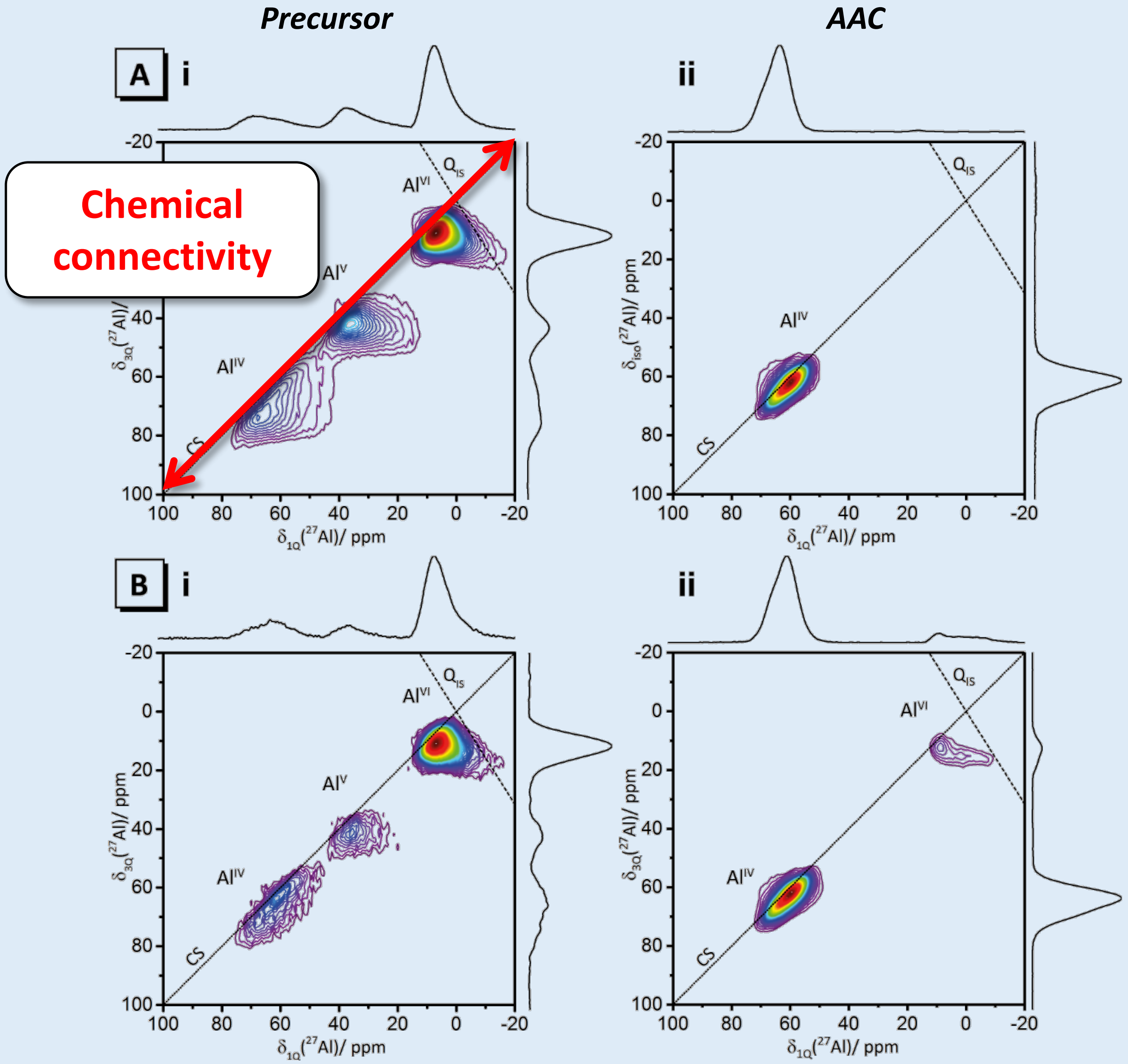
^{27}Al solid state 3QMAS NMR



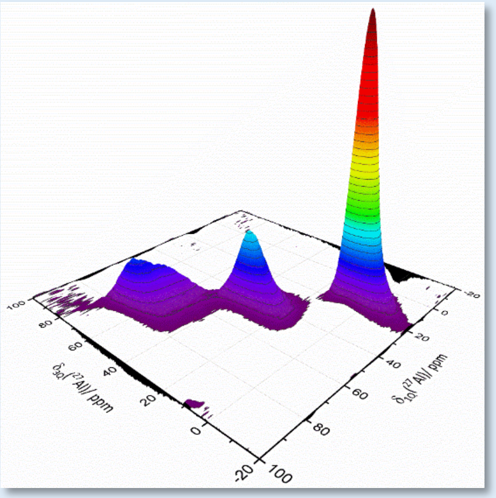
Multiple-quantum SS MAS NMR

Al/Si = 1

Al/Si = 0.5



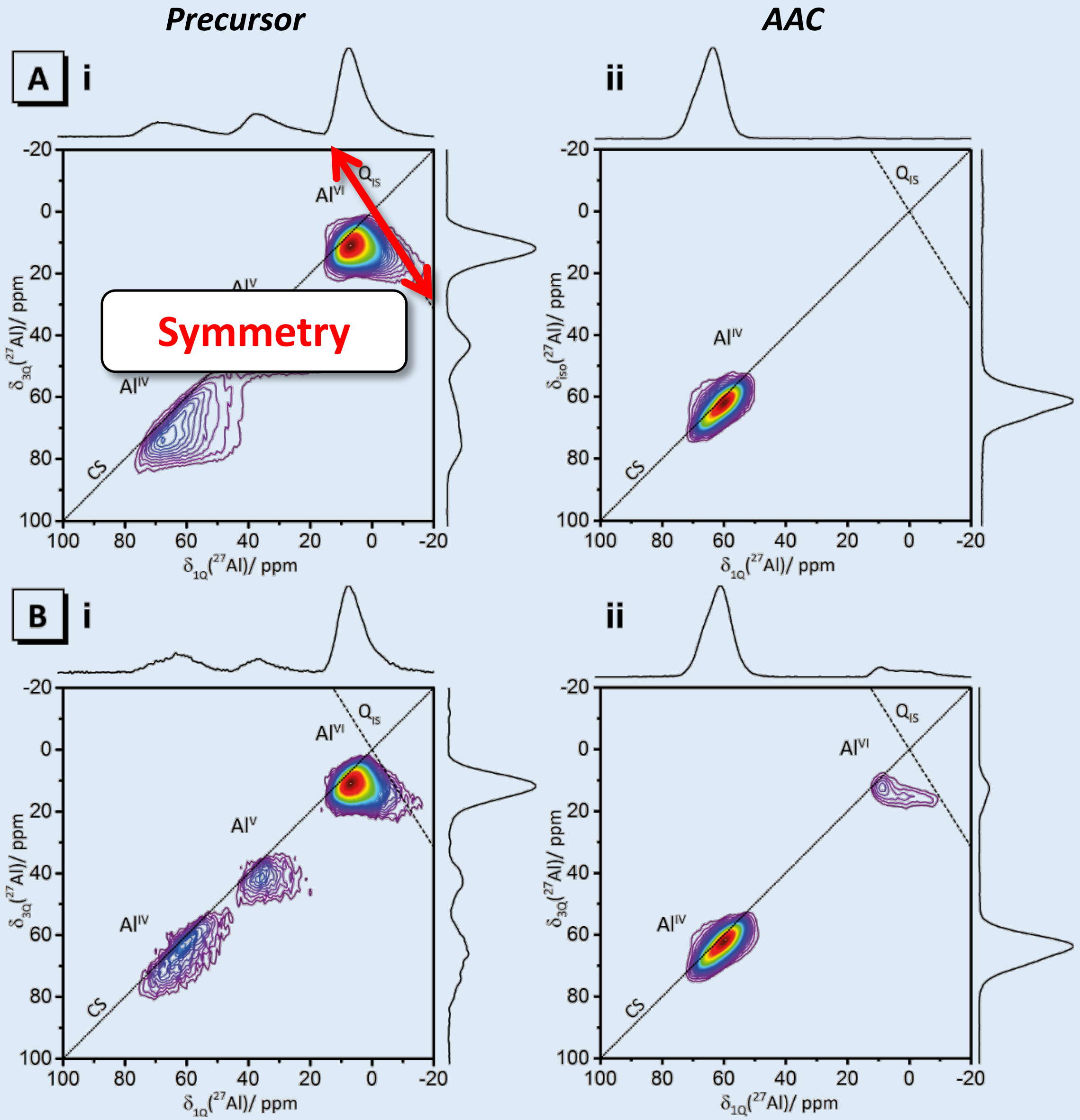
^{27}Al solid state 3QMAS NMR



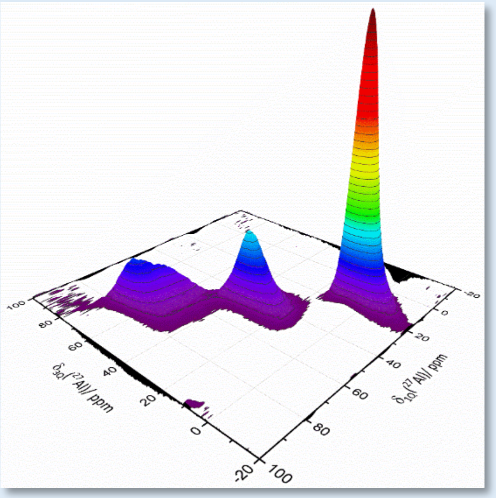
Multiple-quantum SS MAS NMR

Al/Si = 1

Al/Si = 0.5



^{27}Al solid state 3QMAS NMR



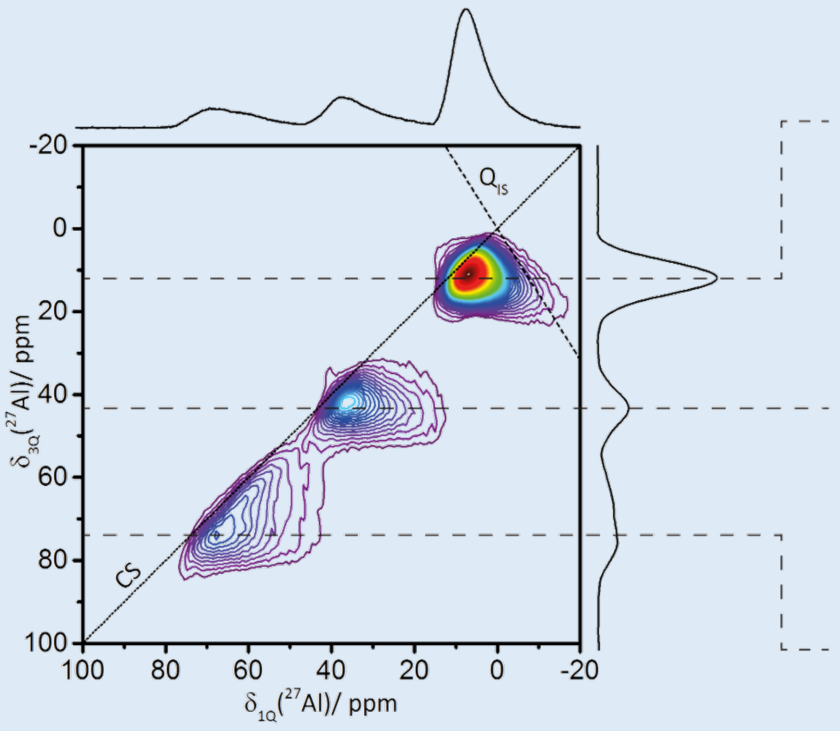
Multiple-quantum SS MAS NMR

Fit the anisotropic slice to determine initial estimates for NMR parameters of each site

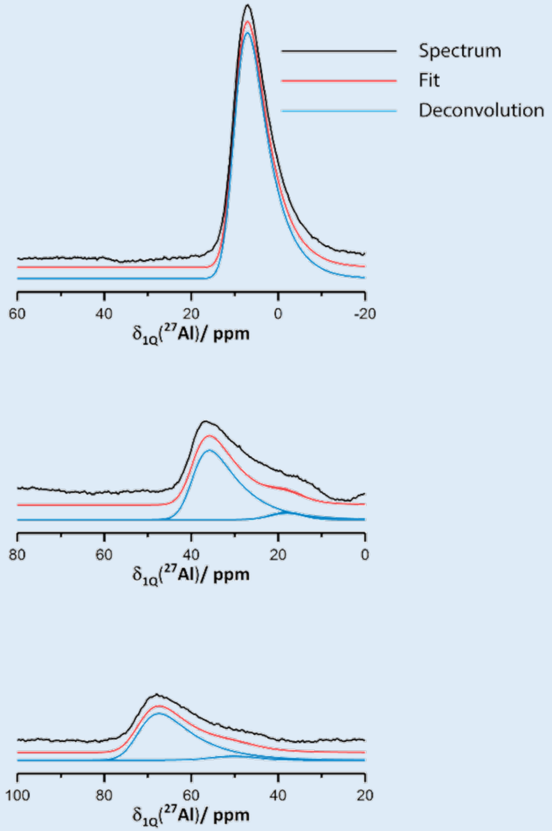
^{27}Al solid state 3QMAS NMR

Fit w/ *Czjezek Gaussian Isotropic Model*

Al/Si = 1



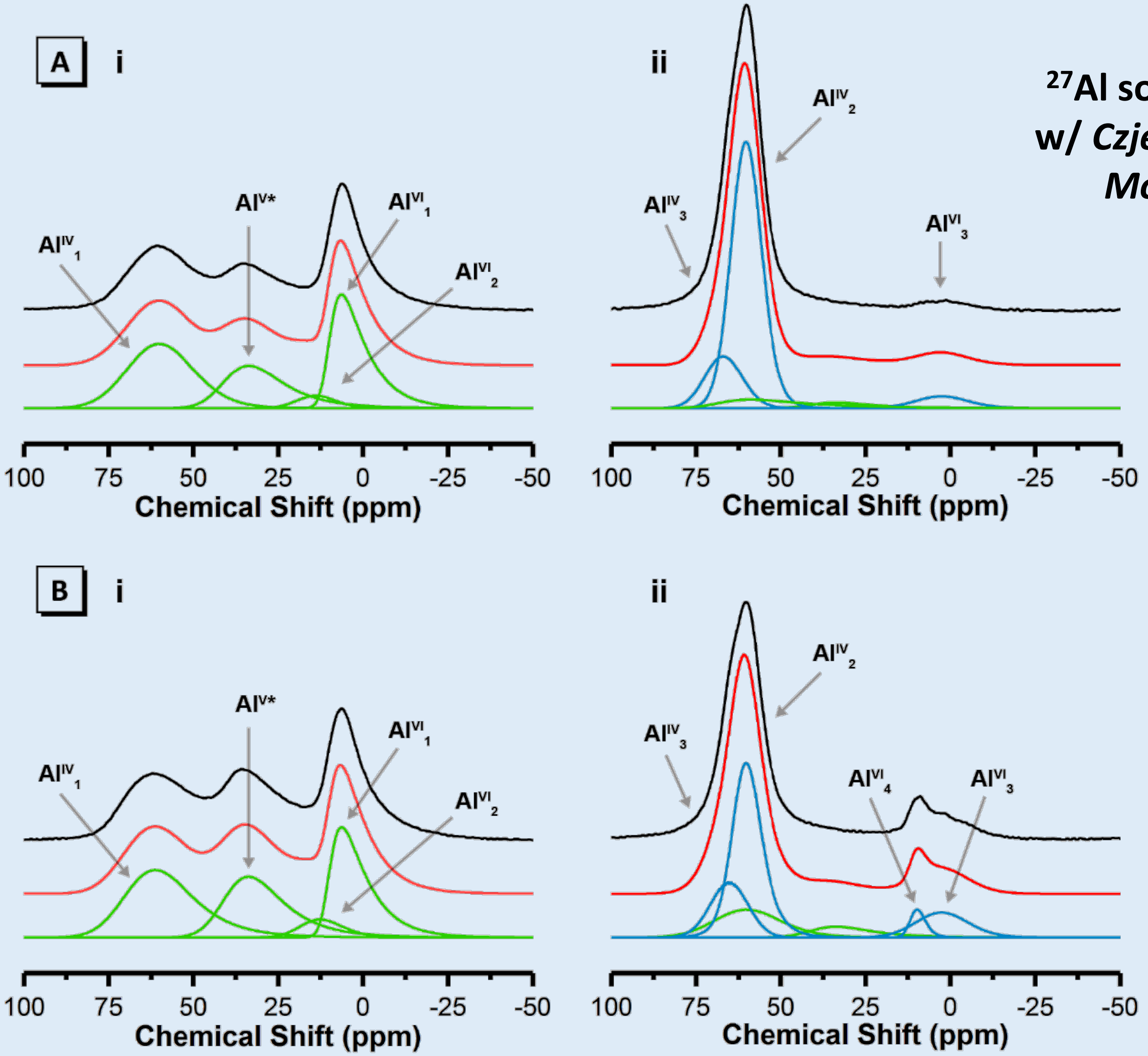
Precursor



Multiple-quantum SS MAS NMR

Use initial estimates to guide deconvolution of single pulse MAS NMR spectra

^{27}Al solid state 3QMAS NMR w/ *Czjezek Gaussian Isotropic Model* deconvolution

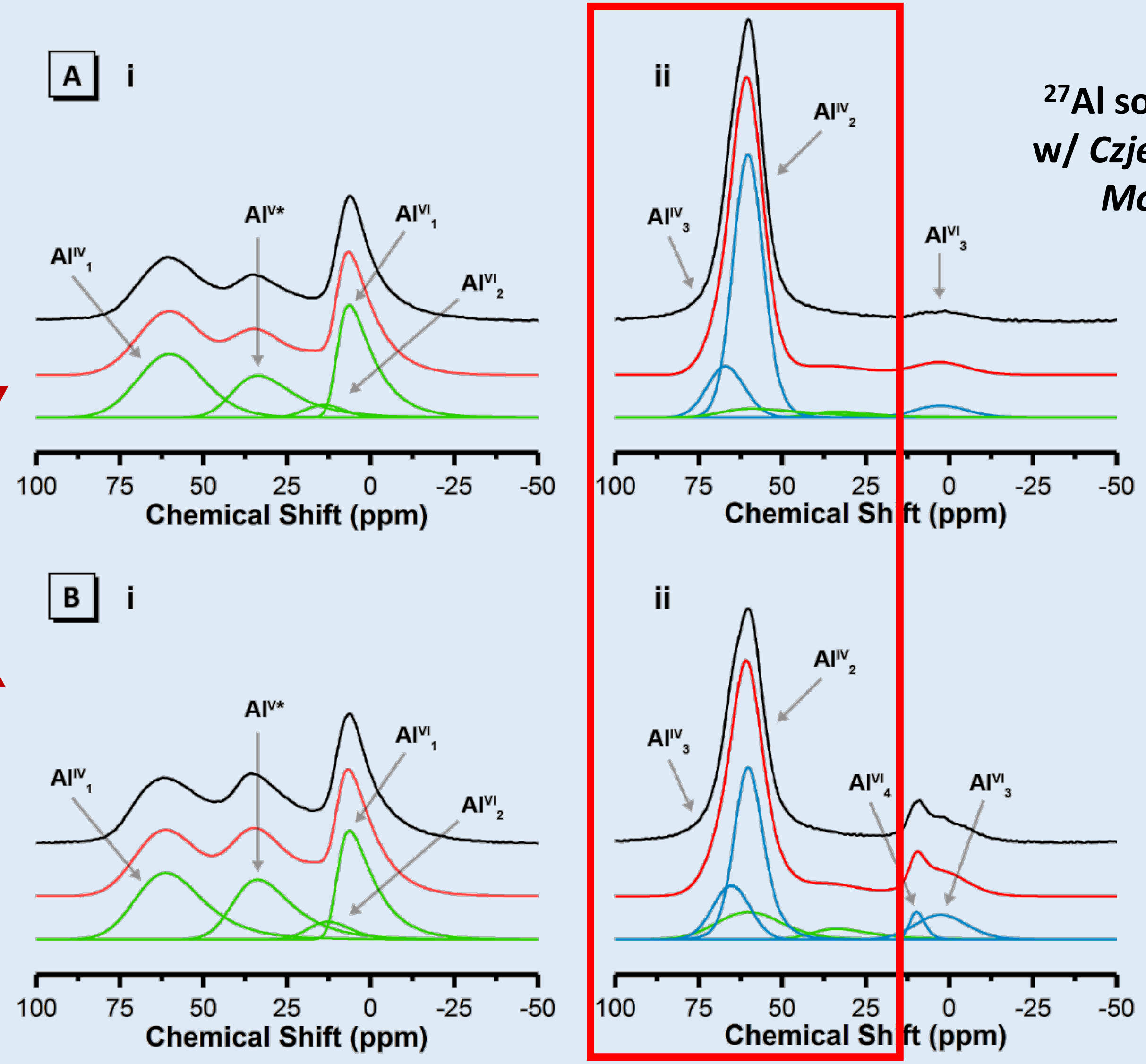


Precursors

Alkali-activated cement

Multiple-quantum SS MAS NMR

Use initial estimates to guide deconvolution of single pulse MAS NMR spectra



^{27}Al solid state 3QMAS NMR w/ *Czjezek Gaussian Isotropic Model* deconvolution

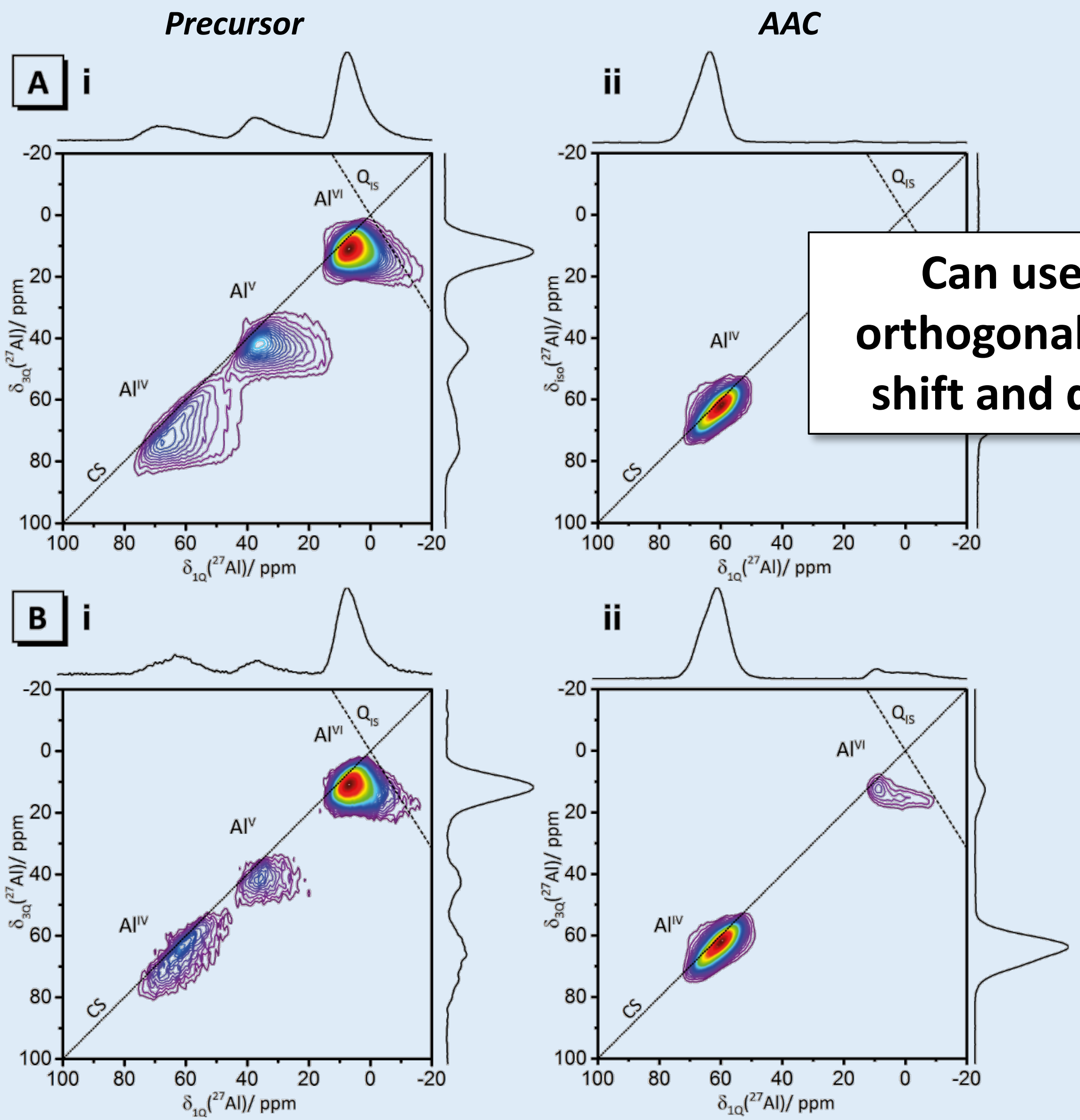
Precursors

Alkali-activated cement

Multiple-quantum SS MAS NMR

Al/Si = 1

Al/Si = 0.5

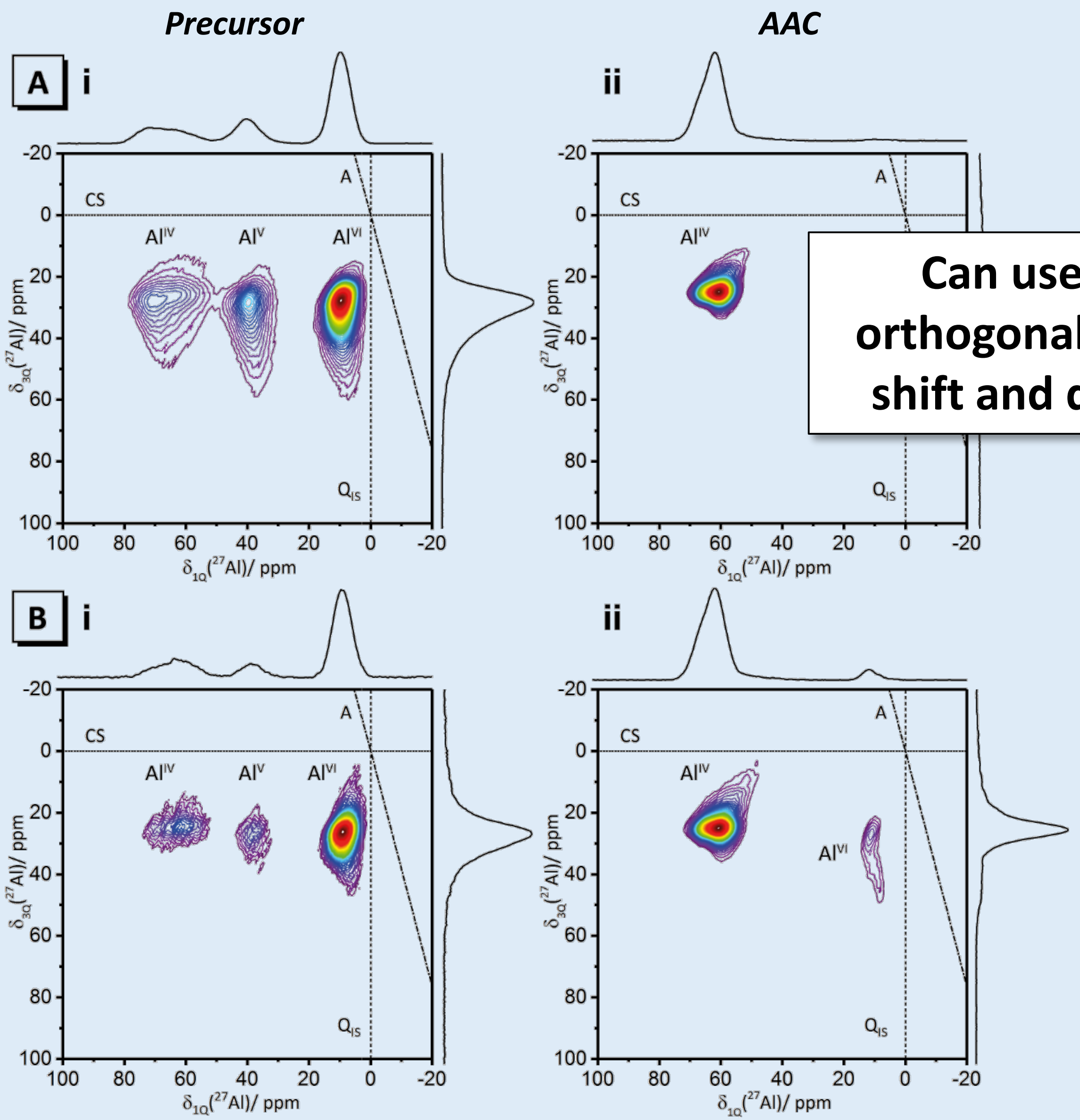


Can use biaxial Q-shearing to orthogonally separate the chemical shift and quadrupolar parameters

Multiple-quantum SS MAS NMR

Al/Si = 1

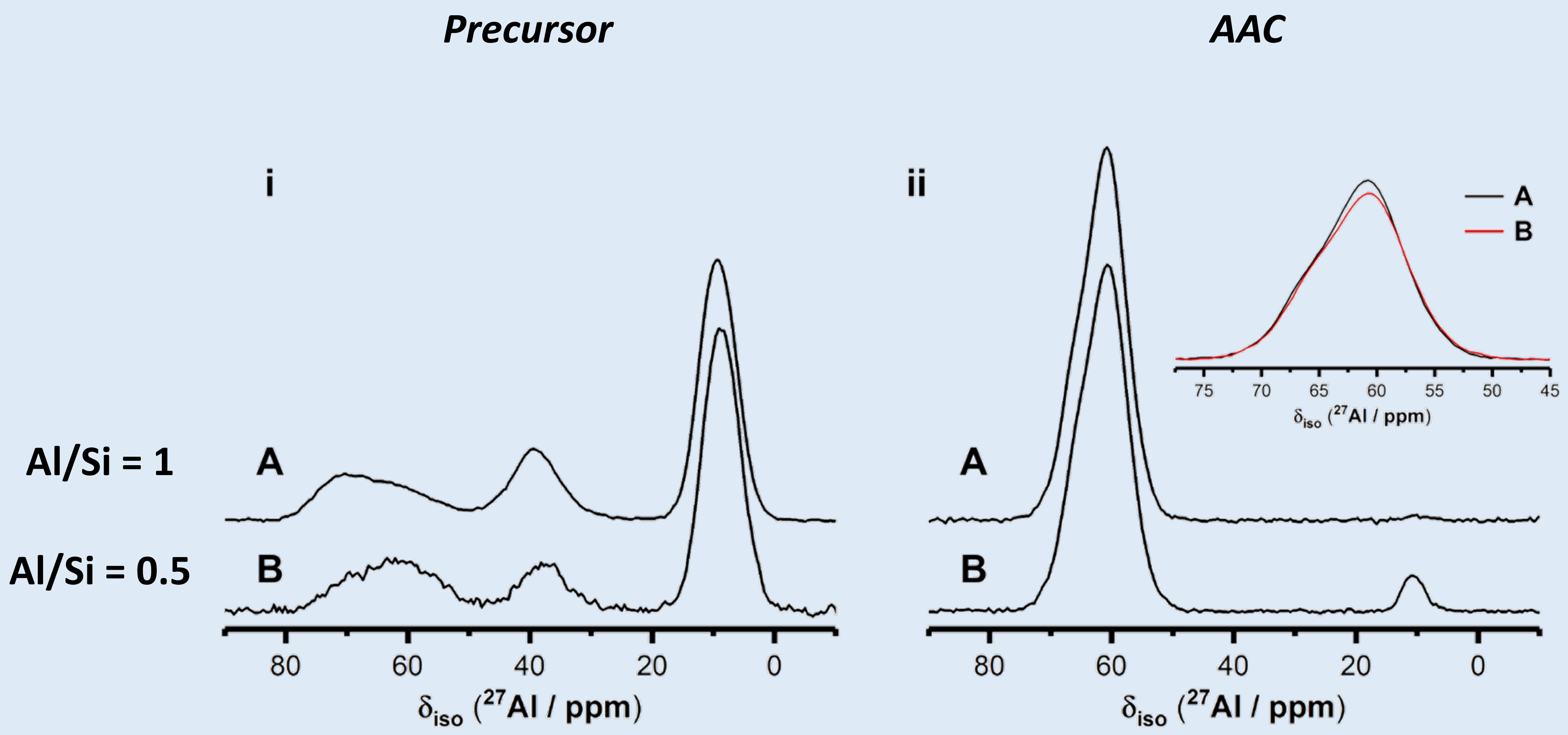
Al/Si = 0.5



Can use biaxial Q-shearing to orthogonally separate the chemical shift and quadrupolar parameters

Multiple-quantum SS MAS NMR

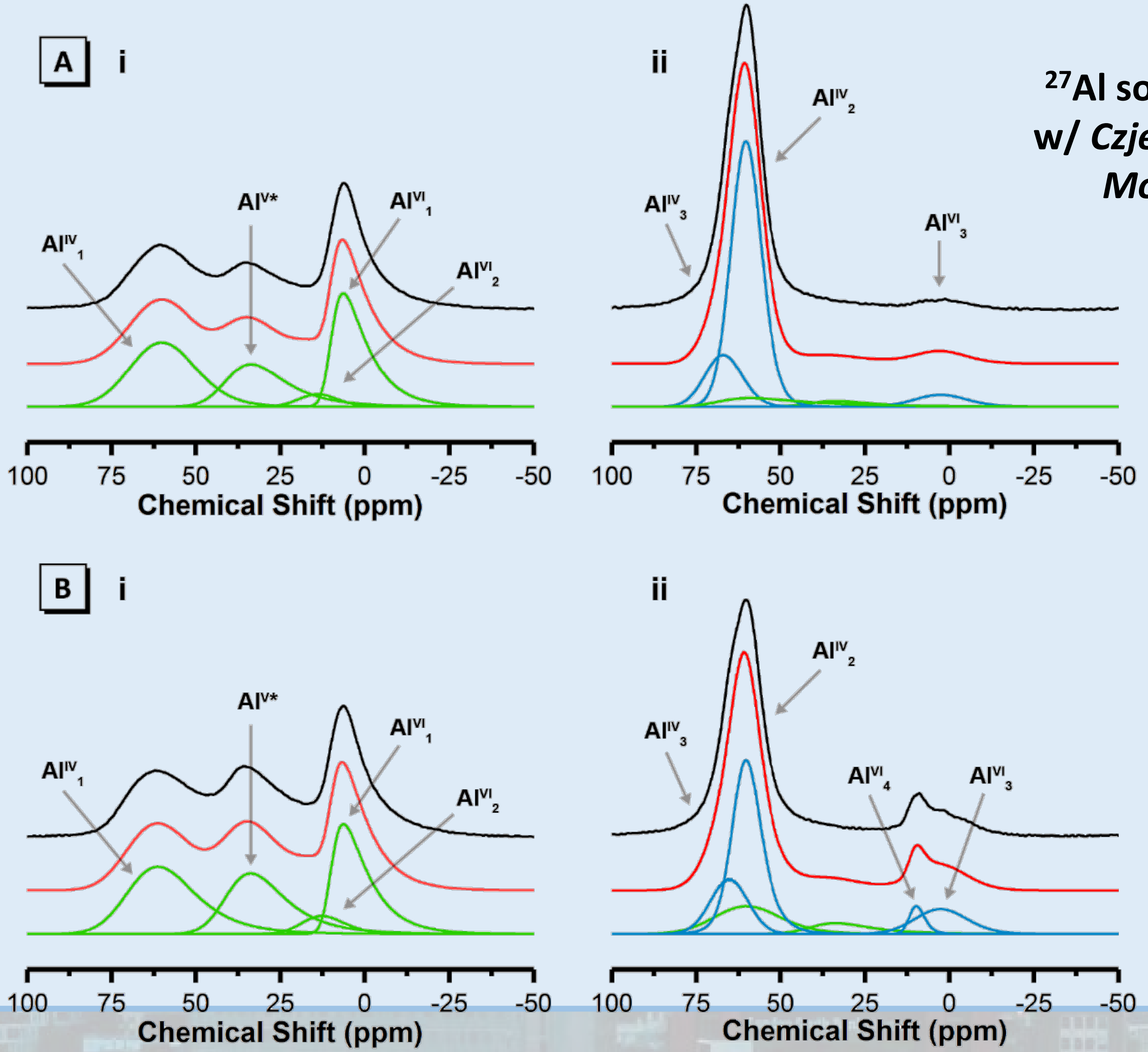
Biaxial Q-shearing



Multiple-quantum SS MAS NMR

Can use **biaxial Q-shearing** to prove existence of two Al distributions (i.e. two Al sites)

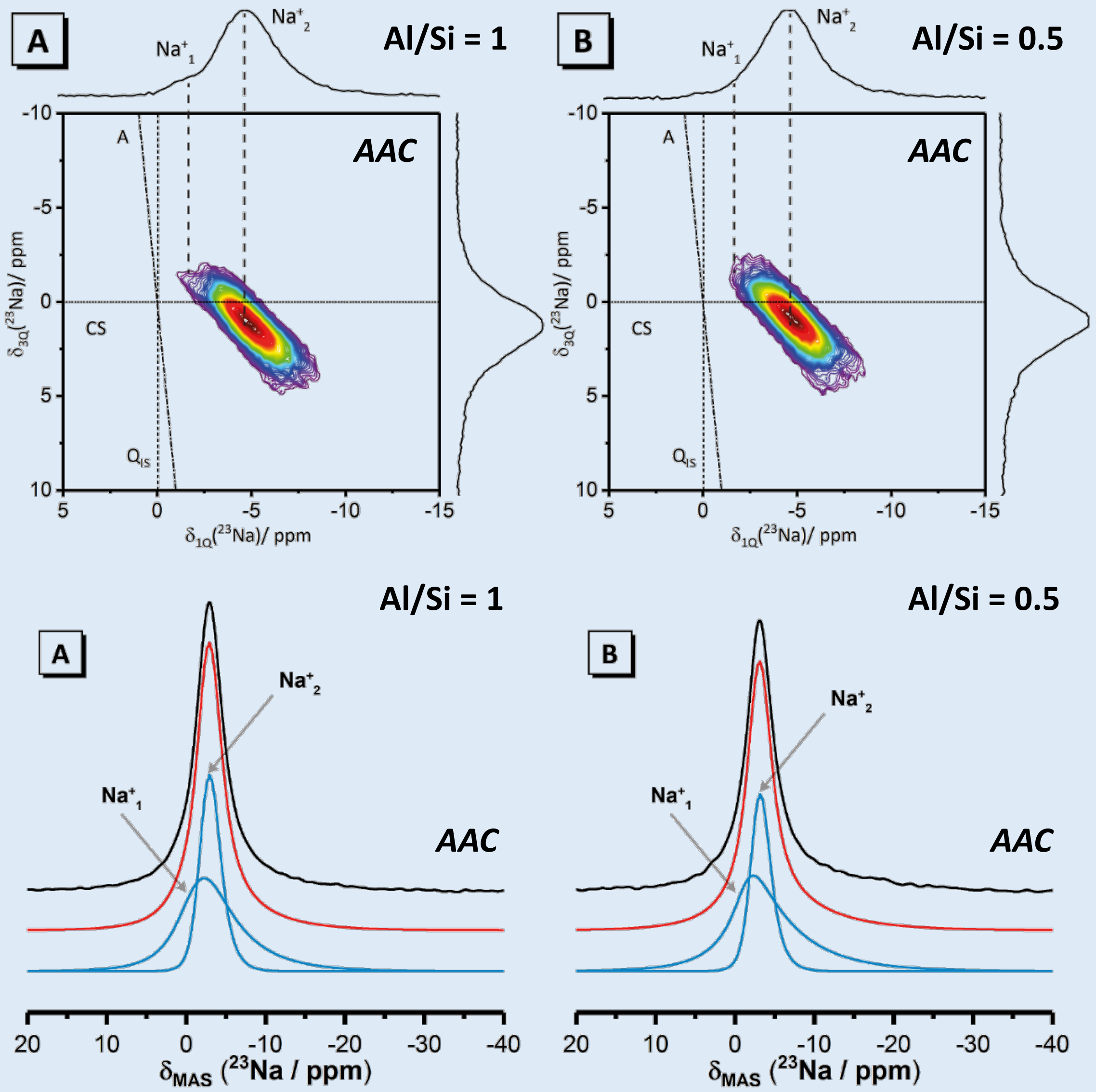
Precursors



Alkali-activated cement

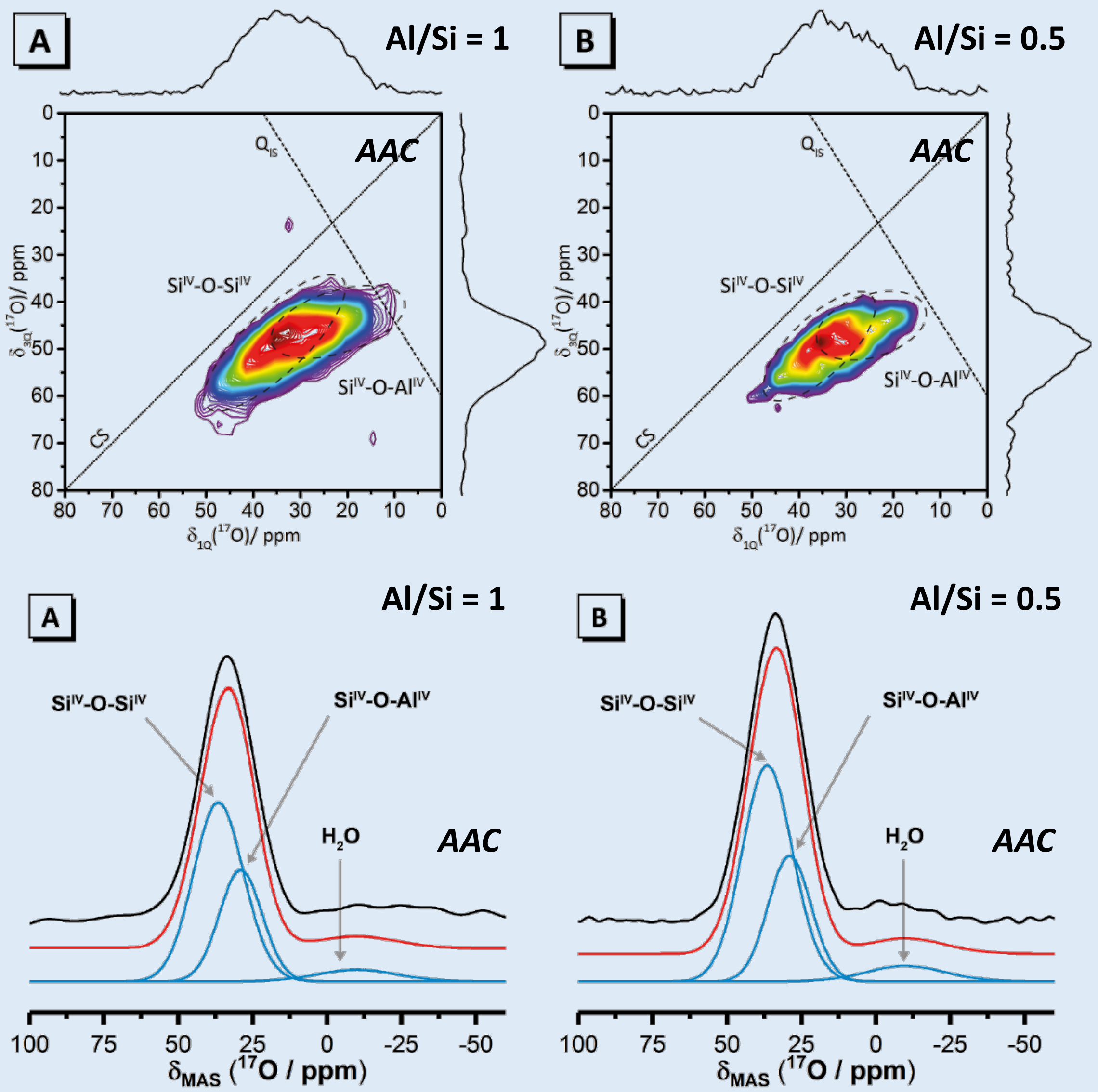
^{27}Al solid state 3QMAS NMR w/ *Czjezek Gaussian Isotropic Model* deconvolution

Multiple-quantum SS MAS NMR



^{23}Na solid state 3QMAS NMR w/ *Czjezek Gaussian Isotropic Model* deconvolution

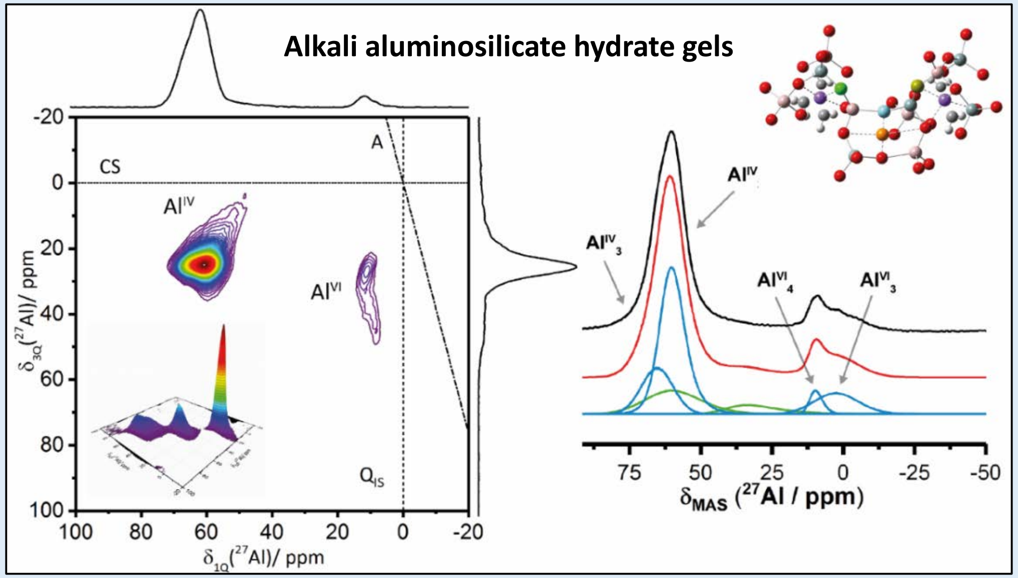
Multiple-quantum SS MAS NMR

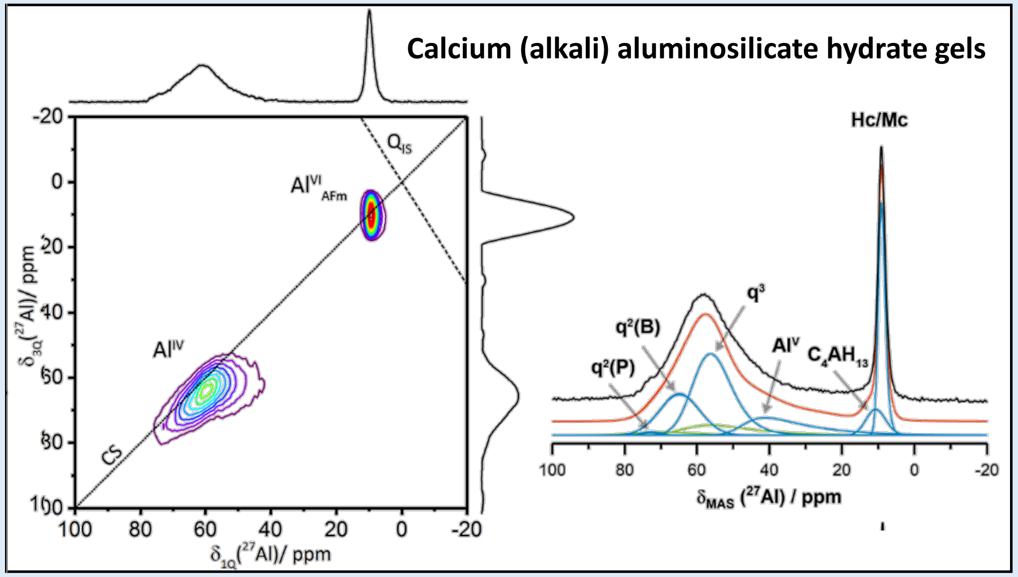


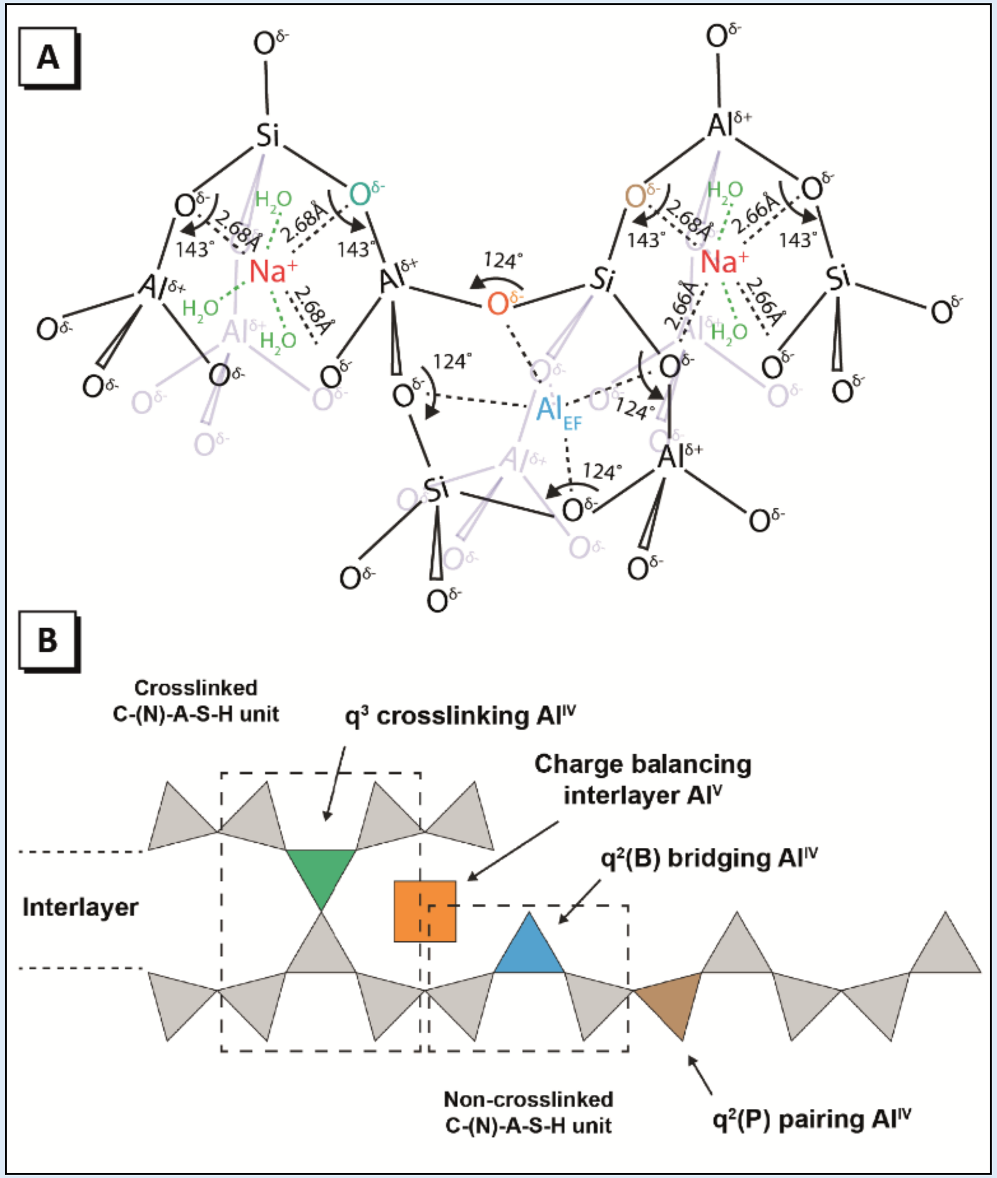
^{17}O natural abundance = 0.037%

^{17}O solid state 3QMAS NMR w/ *Czjezek Gaussian Isotropic Model* deconvolution

New structural models for AAC

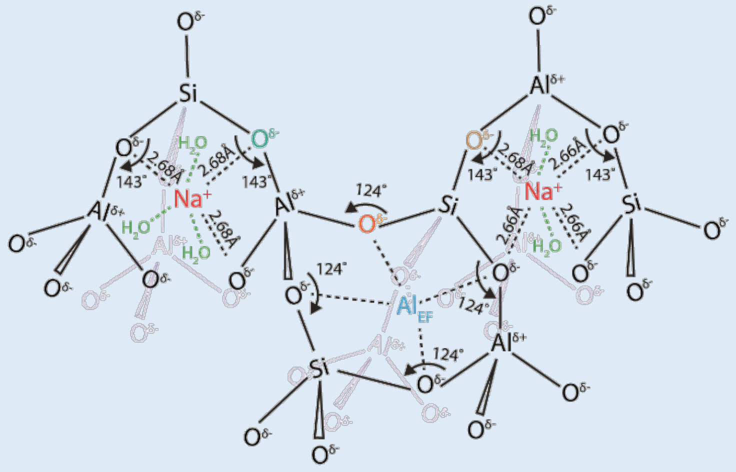


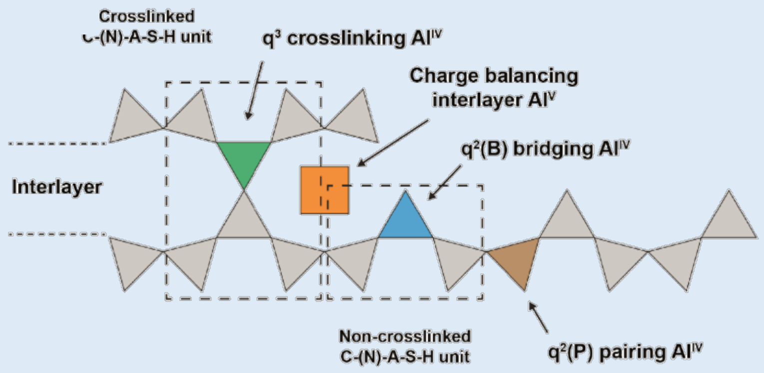




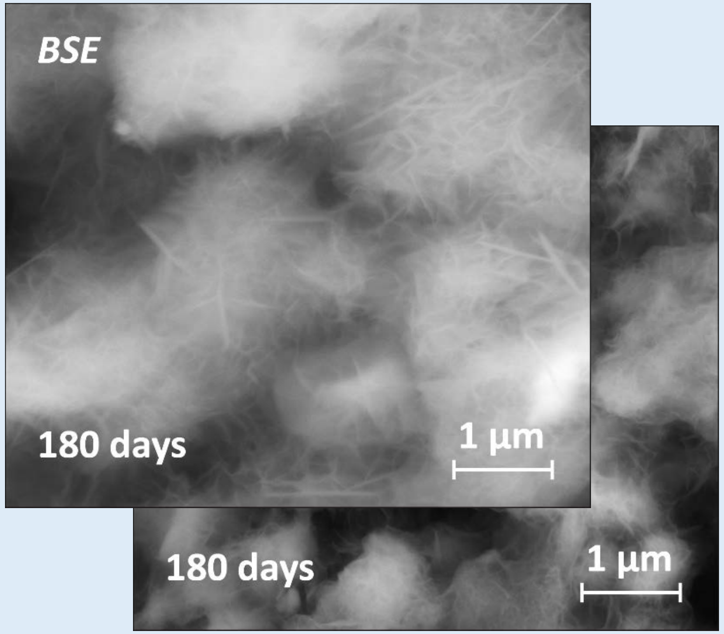
Conclusions

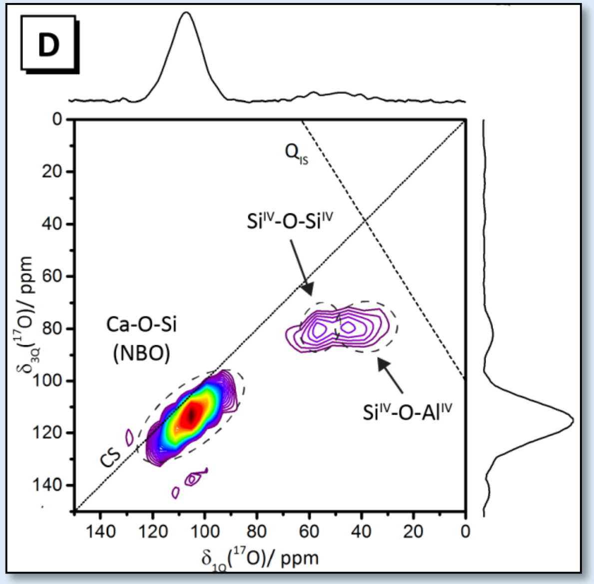
- Synthesised a **novel class of stoichiometrically controlled reactive precursor powders** via the organic steric entrapment method
- Produced a **novel class of stoichiometrically controlled alkali-activated materials** to study nanostructural development
- Applied **advanced characterisation techniques**, particularly solid state MAS and 3QMAS NMR spectroscopy
- Revealed new insight into **composition-'local-structure'-property relationships** in alkali activated cements
- Developed **new structural models for alkali aluminosilicate hydrate and calcium (alkali) aluminosilicate hydrate gels** – the key binding phases in alkali activated cements





Further information





- Walkley, B. et al. (2018), Journal of Physical Chemistry C, *122* (10) 5673-5685
- Walkley, B. et al. (2016), Dalton Transactions, *45*(13) 5521-5535.
- Walkley, B. et al. (2016), Cement and Concrete Research, *89* 120-135.

Acknowledgements

Dr Gregory Rees and Dr John Hanna, Department of Physics, The University of Warwick, UK

Dr Marc-Antoine Sani and **Dr John Gehman**, School of Chemistry, The University of Melbourne, Australia

Geopolymer & Minerals Processing Group, Department of Chemical & Biomolecular Engineering, The University of Melbourne, Australia

Cements@Sheffield Research Group, Department of Materials Science and Engineering, The University of Sheffield, UK

Cements@Sheffield, **Particulate Fluids Processing Centre** and **Melbourne Scholarships Office** and **Australian Research Council** for funding

This research was performed in part at the **MIDAS Facility**, University of Sheffield, which was established with support from the **Department of Energy and Climate Change**.