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Supporting Information for:

A New Structural Model of Sodium Aluminosilicate Gels and the Role of Charge Balancing Extra-Framework Al

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Appendix A: Precursor synthesis and characterisation

A 5 wt. % polyvinyl alcohol (PVA) solution was made by adding 98-99% hydrolysed PVA (Sigma Aldrich, molecular weight 31-50 kDa) to distilled water in small increments over heat, with the resulting solution stirred at 60 °C for 1 h. Aluminium nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$ (Sigma Aldrich 98.5 wt. %) was added to distilled water to produce a 40 wt. % solution, which was then added to the 5 wt. % PVA solution and stirred at 60 °C for 1 h before addition of colloidal silica (Sigma Aldrich Ludox HS-40 colloidal silica (SiO_2), 40 wt. % in water). The stoichiometry was designed to achieve the elemental ratios of Si/Al = 1 and 0.5 for sample A ($2SiO_2 \cdot Al_2O_3$) and B ($4SiO_2 \cdot Al_2O_3$), respectively, as well as ensuring that the number of metal cations (M^{x+}) in solution was significantly more than the number that the PVA could chemically bind through its OH groups (M^{x+}/OH=4). Water was evaporated from the resulting solution by stirring over heat at 80 °C, to form a viscous aerated gel. The dry aerated gel was calcined by heating at 3 °C/min to 550 °C in a laboratory muffle furnace, with a 1 h hold time at 550 °C and then cooling in air, to produce a fine white powder which was subsequently ground by hand before characterisation. X-ray diffraction (XRD) data (Figure S1) were obtained using a Bruker D8 Advance instrument with Ni-filtered Cu Kα radiation, a step size of 0.020°, dwell time of 3 s and a 2θ range of 3–70°.

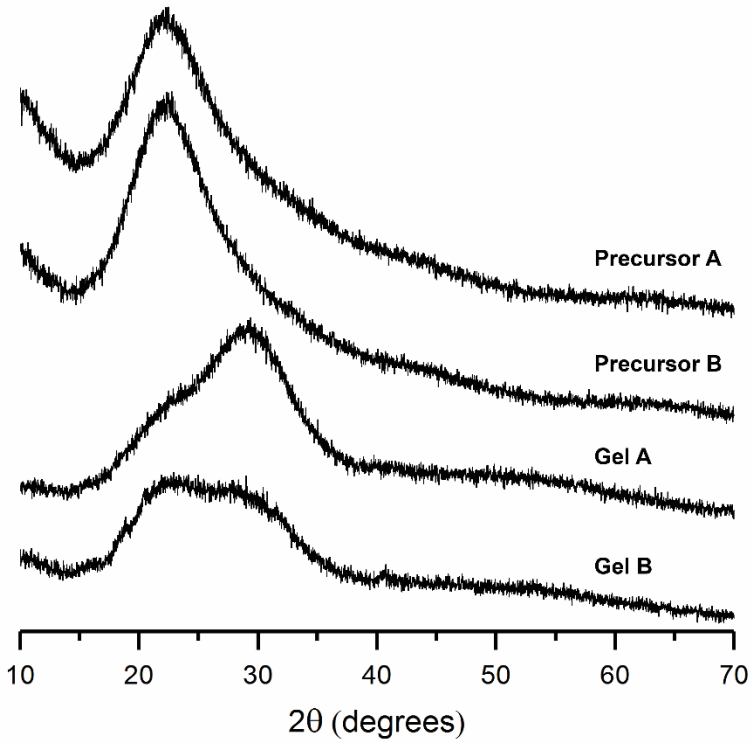

Figure S1: X-ray diffraction data for the precursor and gel for samples A and B as marked

Appendix B: Anisotropic slices of iso-sheared ^{27}Al 3QMAS NMR spectra

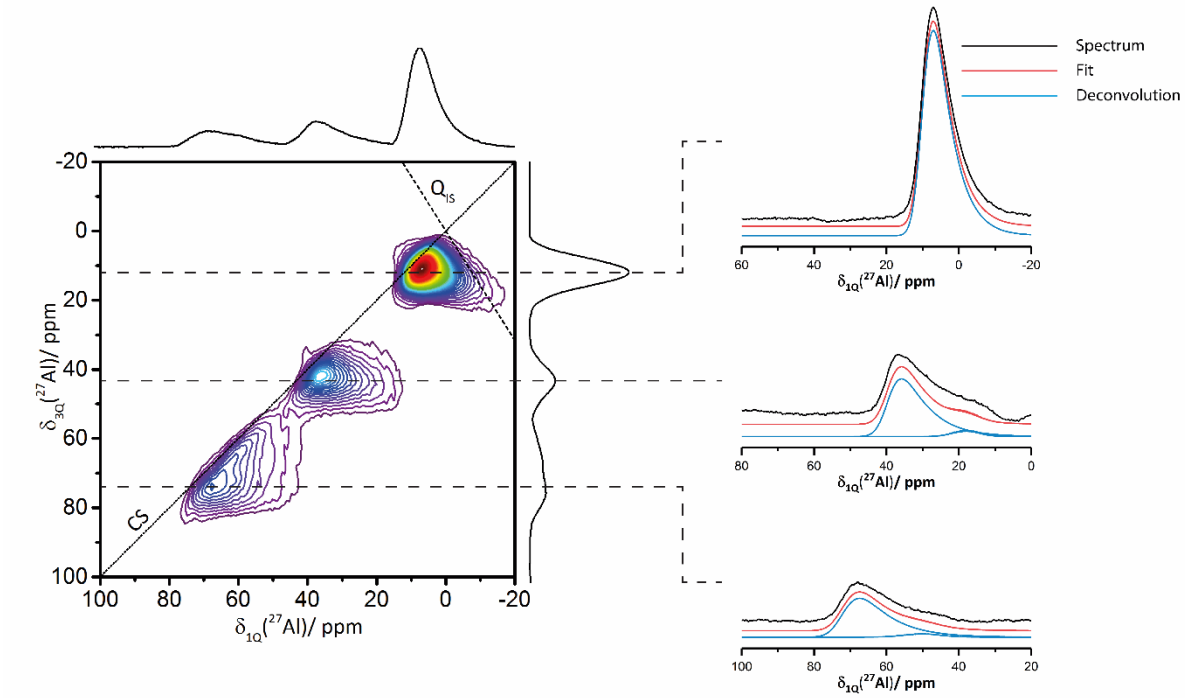

Figure S2: ^{27}Al 3QMAS NMR iso-sheared spectra of the precursor for sample A and associated deconvolutions of anisotropic slices.

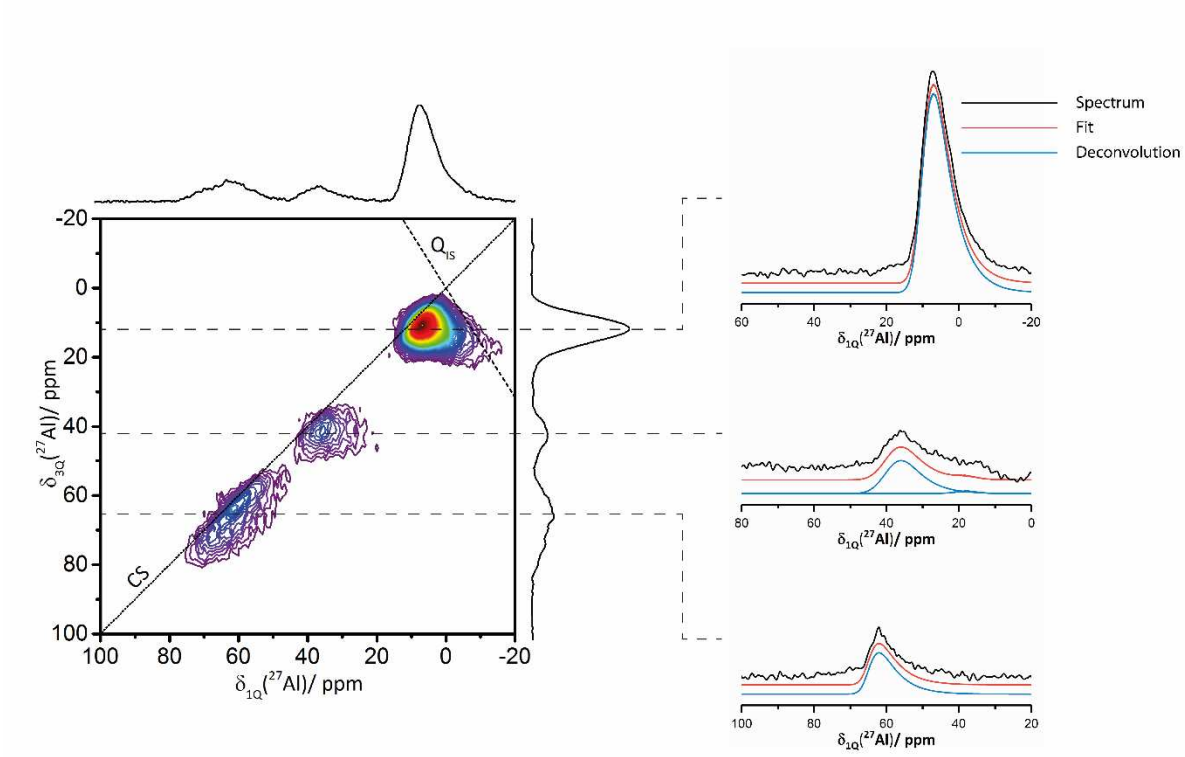

Figure S3: ^{27}Al 3QMAS NMR iso-sheared spectra of the precursor for sample B and associated deconvolutions of anisotropic slices.

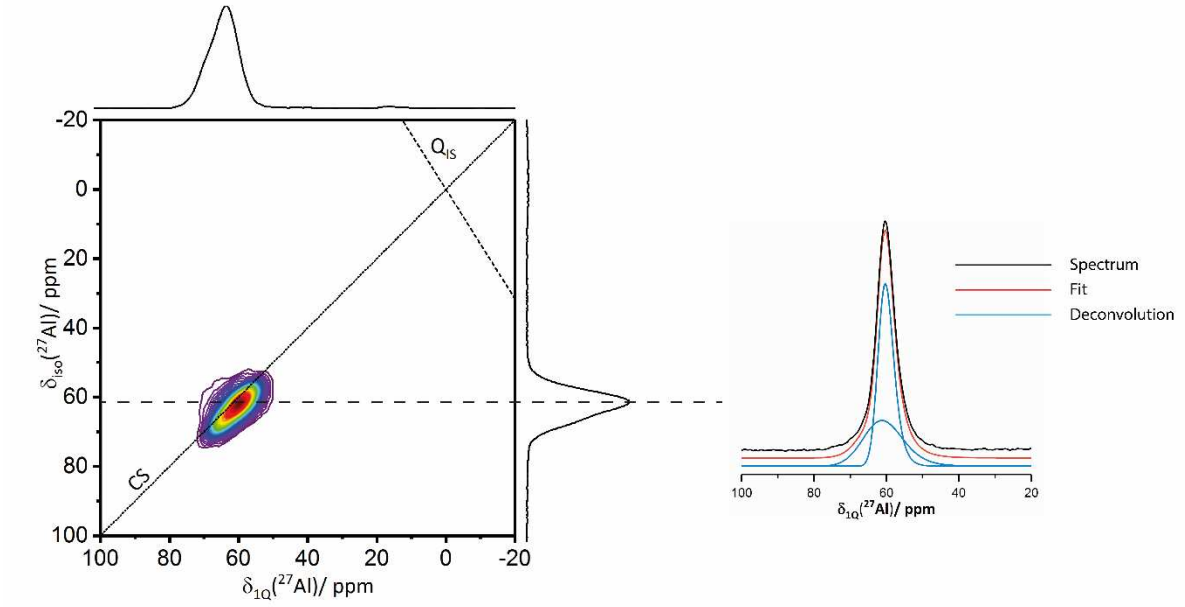

Figure S4: ^{27}Al 3QMAS NMR iso-sheared spectra of the alkali aluminosilicate gel for sample A and associated deconvolutions of anisotropic slices

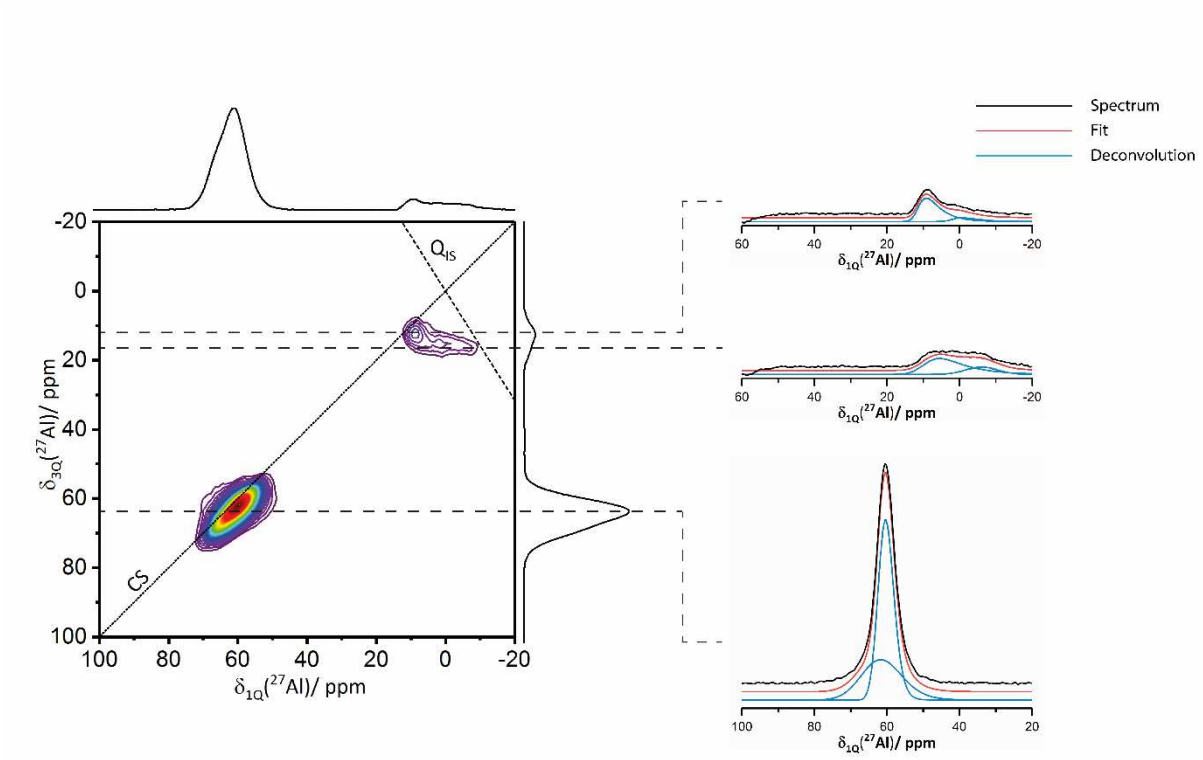

Figure S5: ^{27}Al 3QMAS NMR iso-sheared spectra of the alkali aluminosilicate gel for sample B and associated deconvolutions of anisotropic slices

Appendix C: Iso-sheared ^{23}Na 3QMAS NMR spectra and associated anisotropic slices

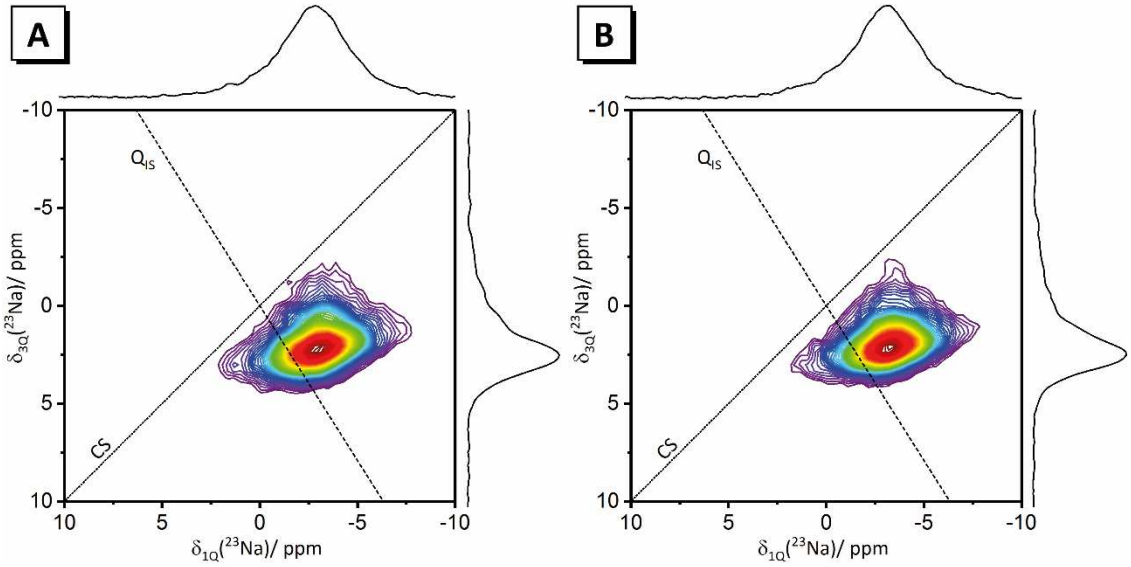

Figure S6: ^{23}Na 3QMAS NMR spectra of the alkali aluminosilicate gels A and B as marked. Spectra are sheared using conventional single axial iso-shearing in the δ_{3Q}, δ_{1Q} axes by factors of (-7/9, 0), respectively, to give an isotropic component in the δ_{3Q} (F1) dimension and an anisotropic component in the δ_{1Q} (F2) dimension. The chemical shift (CS) and quadrupolar induced shift (Q_{IS}) axes are indicated by dotted and dashed lines, respectively.

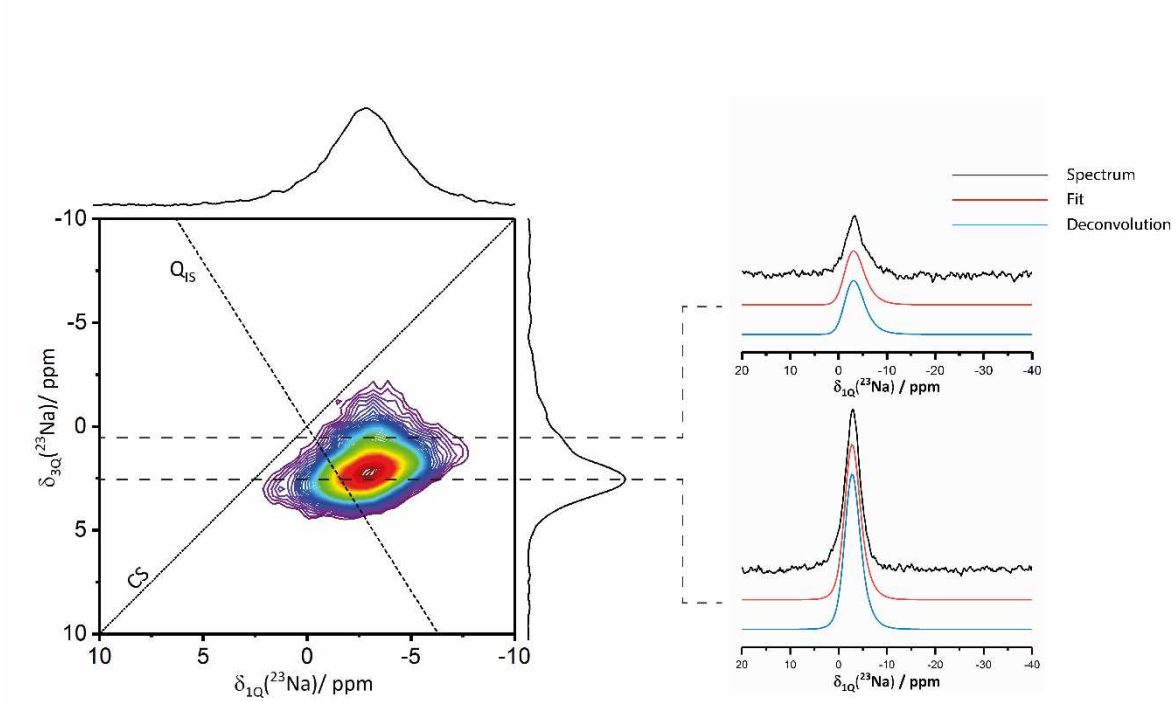

Figure S7: ^{23}Na 3QMAS NMR iso-sheared spectra of the alkali aluminosilicate gel for sample A and associated deconvolutions of anisotropic slices

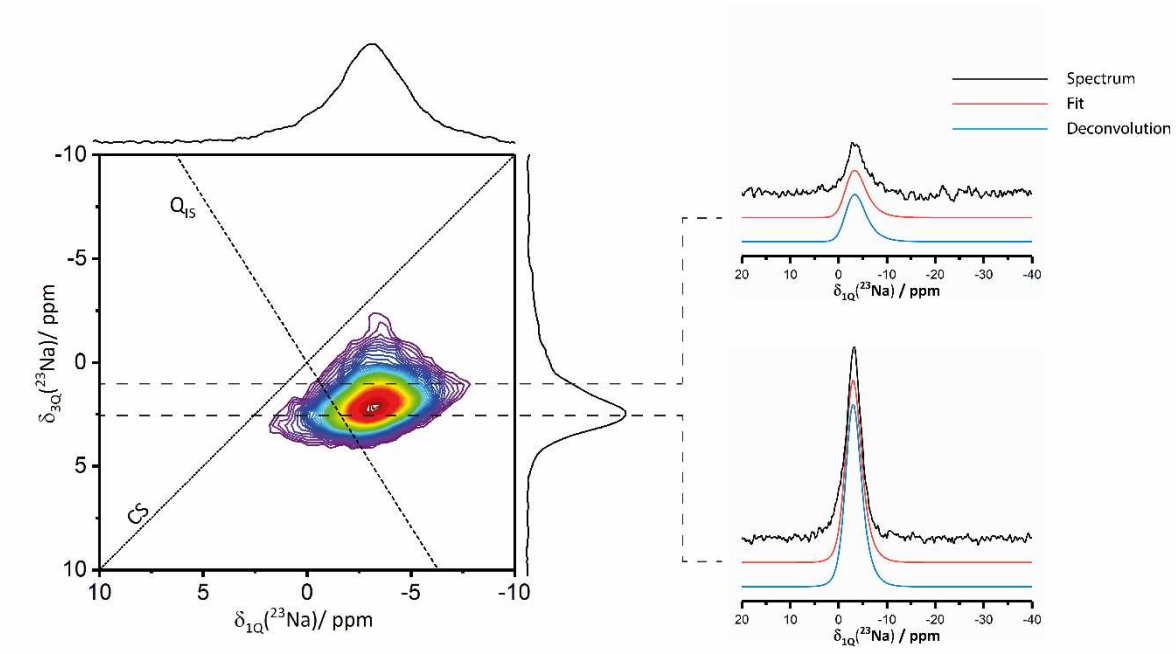

Figure S8: ^{23}Na 3QMAS NMR iso-sheared spectra of the alkali aluminosilicate gel for sample B and associated deconvolutions of anisotropic slices

Appendix D: Anisotropic slices of iso-sheared ^{17}O 3QMAS NMR spectra

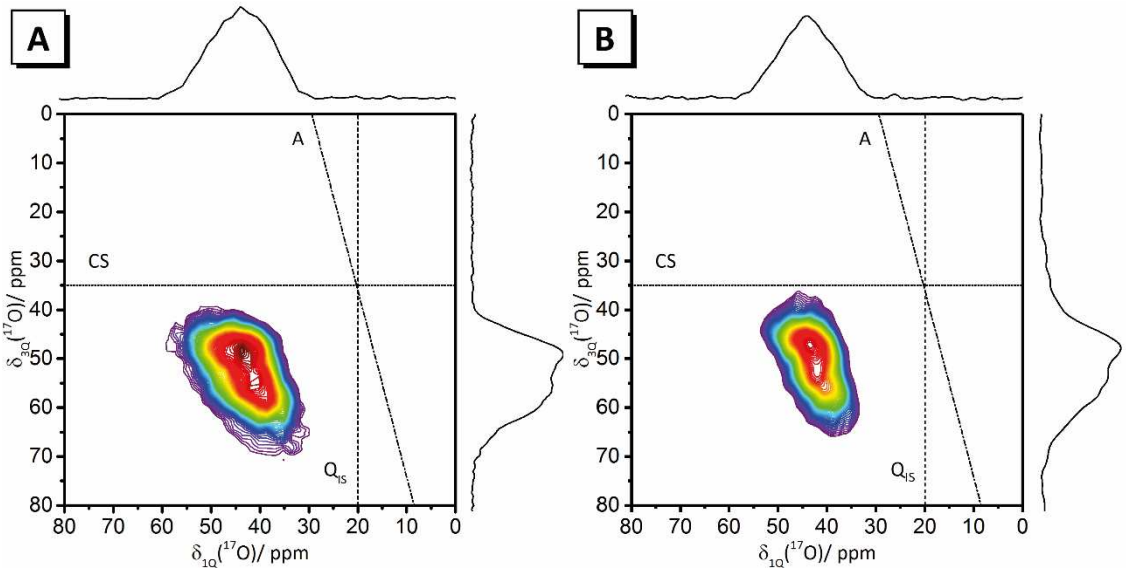

Figure S9: ^{17}O 3QMAS NMR spectra of the alkali aluminosilicate gels A and B, as marked. Spectra are sheared using biaxial Q-shearing in the δ_{3Q}, δ_{1Q} axes by a factor of 3, -4/9, respectively, so that the δ_{1Q} (F2) axis purely reflects the isotropic chemical shift and the quadrupolar parameters are separated in the δ_{3Q} (F1) axis. The chemical shift (CS), quadrupolar induced shift (Q_{IS}) and anisotropic (A) axes are indicated by dotted, dashed and combined dotted/dashed lines, respectively.

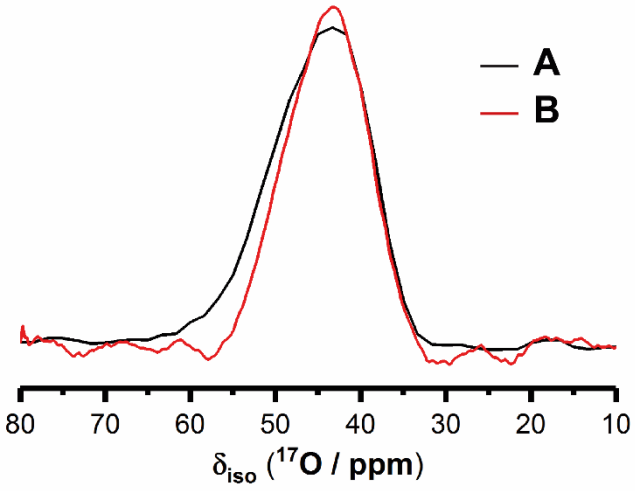

Figure S10: ^{17}O isotropic slices (taken through the centre of gravity of each resonance) extracted from the biaxial Q-sheared ^{17}O 3QMAS NMR spectra of the alkali aluminosilicate gels A and B as marked.

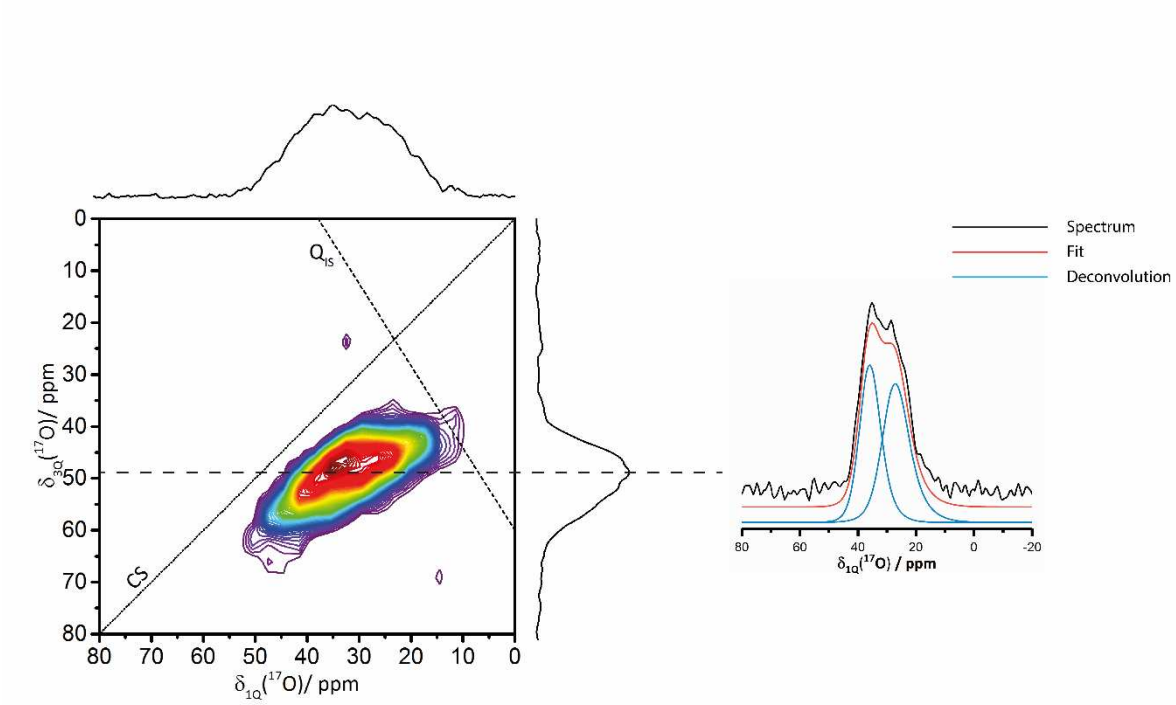

Figure S11: ^{17}O 3QMAS NMR iso-sheared spectra of alkali aluminosilicate gel A and associated deconvolutions of anisotropic slices

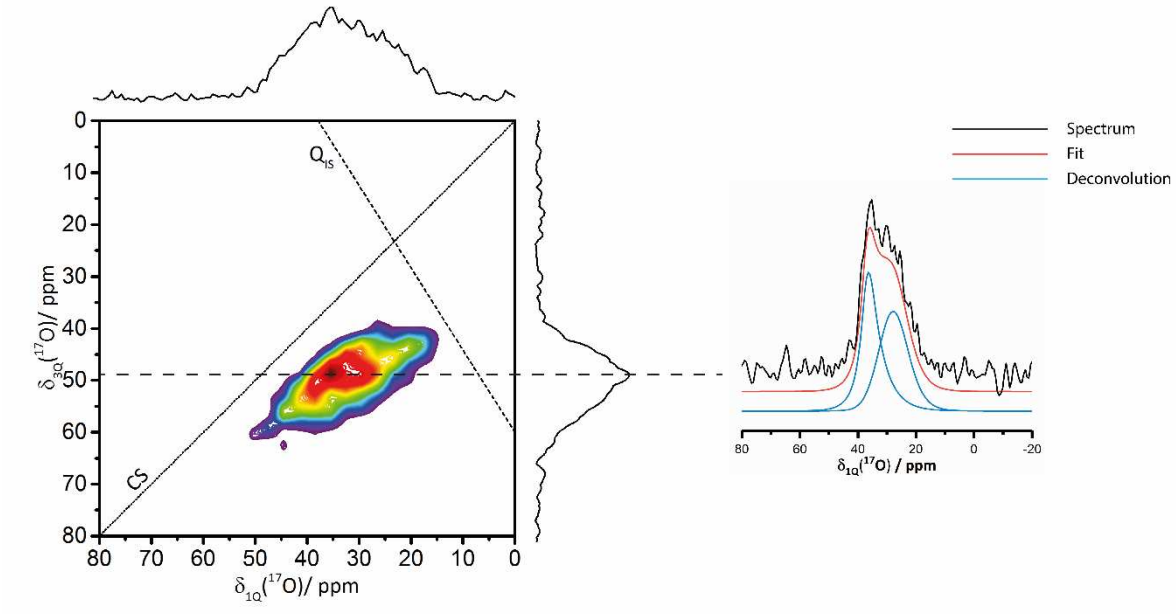

Figure S12: ^{17}O 3QMAS NMR iso-sheared spectra of alkali aluminosilicate gel B and associated deconvolutions of anisotropic slices

Appendix E: ^{29}Si MAS NMR spectra

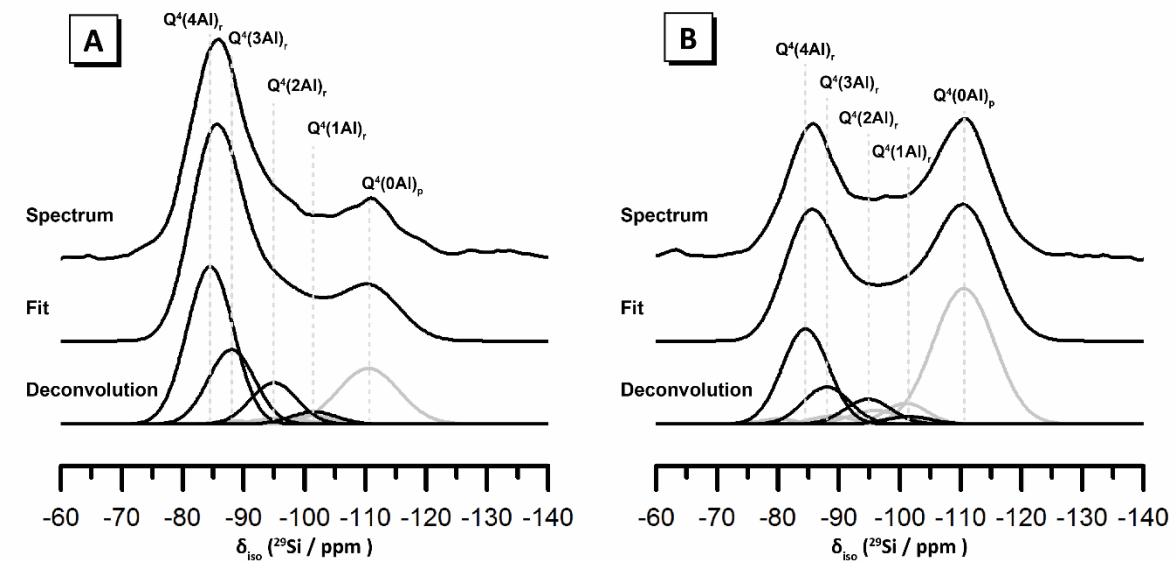

Figure S13: ^{29}Si MAS NMR data (B_0 = 14.1 T, v_R = 10 kHz) of alkali aluminosilicate gels A and B and associated deconvolutions. Deconvoluted peaks attributed to the alkali aluminosilicate gels are shown in black, while deconvoluted peaks attributed to the precursors are shown in grey.