Synthesis, Isotopic Enrichment and Solid-State NMR Characterization of Zeolites Derived from the Assembly, Disassembly, Organization, Reassembly Process

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S1. Synthesis and diffraction

Ge-UTL (Si/Ge = 4.4) was prepared by the solid-state reaction of GeO$_2$, SiO$_2$ and (6R,10S)-6,10-dimethyl-5-azoniaspiro[4,5]decane hydroxide as the structure directing agent (SDA), in the quantities given in Table S1.1, under static heating for 7 days at 175 °C.$^1$ To prepare $^{29}$Si-enriched Ge-UTL a similar procedure was followed using a mix of 99% $^{29}$Si-enriched Si(OEt)$_4$ (TEOS) (1.6 mmol) and unenriched TEOS (10.1 mmol) as the silicon source, to give a total $^{29}$Si enrichment level of ~18% for TEOS, as summarized in Table S1.2. The reaction mixture was then heated for 14 days at 175 °C.

Table S1.1. Quantities of reagents used in the synthesis of natural abundance Ge-UTL.

|            | GeO$_2$ | SiO$_2$ | SDA  |
|------------|---------|---------|------|
| Quantity/mmol | 88.6    | 178.1   | 81.8 |
| Molar ratio  | 0.5     | 1       | 0.5  |
| Amount       | 9.3 g   | 10.7 g  | 150 ml of 0.55 M sol. |

Table S1.2. Quantities of reagents used in the synthesis of $^{29}$Si-enriched Ge-UTL.

|            | GeO$_2$ | Si(OEt)$_4$ | SDA |
|------------|---------|-------------|-----|
| Quantity/mmol | 5.8     | 1.6 (99% $^{29}$Si) + 10.1 (n. a. $^{29}$Si) | 5.8 |
| Molar ratio  | 0.5     | 1           | 0.5 |
| Amount       | 0.609 g | 0.333 g + 2.094 g | 10 ml of 0.58 M sol. |
The PXRD pattern for the as-made $^{29}$Si-enriched Ge-UTL (acquired as described in the main text) is shown in Figure S1.1. Figure S1.2 shows the PXRD pattern for the Ge-UTL (natural abundance) after calcination, along with the simulated pattern for a typical UTL framework from the IZA database.\textsuperscript{52}

![Figure S1.1](image1.png)

**Figure S1.1.** PXRD pattern for as-made $^{29}$Si-enriched Ge-UTL.

![Figure S1.2](image2.png)

**Figure S1.2.** PXRD pattern for calcined (unenriched) Ge-UTL (black) and a pattern simulated for the UTL framework from the IZA database (red).

To minimize the amount of $^{17}$O-enriched water that would ultimately be required, the hydrolysis reaction had to be scaled down, and was carried out (initially with natural-abundance zeolite and H$_2$O) using the conditions given in Table S1.3, resulting in a total acid concentration of 6 M, for reaction times between 4 and 48 h. Reactions were carried out using a 10 ml round-bottomed flask topped with a condensing tube in refluxing conditions at 95 °C. The amount of washing water was also minimized in an attempt to...
avoid possible loss of $^{17}$O. Calcination of the hydrolysed products was carried out to remove any remaining water, and to allow the condensation of the framework. Typically, the zeolite was heated to 575 °C at a rate of 1 °C / min, held for 6 hours and cooled to room temperature at a rate of 2 °C / min under an atmosphere of air.

**Table S1.3.** Quantities used for the scaled-down ADOR hydrolysis of Ge-UTL.

| Reactant                              | Quantity  |
|---------------------------------------|-----------|
| H$_2$O (or H$_2^{17}$O)              | 1.2 ml    |
| 12 M HCl                              | 1.2 ml    |
| Ge-UTL (or $^{29}$Si-enriched Ge-UTL) | 300 mg    |
| washing water                         | 2.4 ml    |
Figure S1.3 shows PXRD patterns (expanded to show only the region corresponding to the 200 peak) of unenriched Ge-UTL zeolites after hydrolysis using H₂O for varying reaction times. Corresponding d spacings (d_{200}) are given in Table S1.4. Calcination of the hydrolysed products was carried out to remove any remaining water from hydrolysis, and to allow the condensation of the framework. PXRD patterns (expanded to show only the region corresponding to the 200 peak) of the calcined hydrolysed materials are shown in Figure S1.4, with the d spacings (d_{200}) given in Table S1.4.

Figure S1.3. PXRD pattern (expanded to show the 200 peak) of unenriched Ge-UTL hydrolysed for varying reaction times.
Table S1.4. Values of the d_{200} spacing, extracted from the PXRD patterns in Figures S1.3 and S1.4, for Ge-UTL zeolites after hydrolysis, and after subsequent calcination.

| Hydrolysis time / h | d_{200} spacing / Å |
|---------------------|---------------------|
|                     | hydrolysed | calcined |
| 4                   | 12.0       | 12.0     |
| 8                   | 12.0       | 11.9     |
| 12                  | 12.2       | 11.8     |
| 16                  | 12.0       | 11.7     |
| 24                  | 11.9       | 11.7     |
| 48                  | 11.7       | 11.5     |

Figure S1.4. PXRD pattern (expanded to show the 200 peak) of unenriched Ge-UTL hydrolysed for varying reaction times and then calcined.
The repeatability of the results obtained from the small volume ADOR hydrolysis reactions was tested by carrying out a second hydrolysis for 16 h. The Q⁴/Q³ ratio of the hydrolysed material determined from the ²⁹Si MAS NMR spectrum (as described in the main text) was 5.7 for the second sample, in good agreement with the 5.4 obtained previously. Good agreement was also obtained for calcined samples, where this ratio was 5.8. The PXRD data showed consistent d₂₀₀ spacings for the two samples (12.0 Å and 11.9 Å, for the first and second as made samples, respectively, and 11.7 Å and 11.8 Å for the calcined materials).

For the calcined samples the average micropore volume was 0.18 ± 0.02 cm³ g⁻¹, characteristic of the IPC-2 structure. A typical adsorption isotherm is shown in Figure S1.5. To determine whether the small amount of washing water had an effect on the final porosity of the structures, the 16 h ADOR hydrolysis was repeated using 40 ml of washing water. The d₂₀₀ spacing observed for this sample in its hydrolysed form was 12.0 Å, and the micropore volume 0.17 cm³ g⁻¹. These values are in good agreement with those obtained previously.
Figure S1.5. 77 K N\textsubscript{2} adsorption isotherm (for the Ge-UTL sample hydrolysed for 4 h and subsequently calcined).

Hydrolysis using (41\% enriched) H\textsubscript{2}\textsuperscript{17}O was carried out on natural-abundance Ge-UTL and \textsuperscript{29}Si-enriched Ge-UTL for 16 h using 6 M HCl (as shown in Table S1.3). PXRD patterns (for experiments carried out in capillary mode, as described in the main text), of the resultant hydrolysed \textsuperscript{17}O-enriched and doubly \textsuperscript{17}O- and \textsuperscript{29}Si-enriched products are shown in Figures S1.6 and S1.7, respectively. The d\textsubscript{200} spacings observed for these two samples are 11.9 Å and 11.8 Å, in good agreement with the data given in Table S1.4.
Figure S1.6. Capillary PXRD pattern of the as-made $^{17}$O-enriched zeolite hydrolysed for 16 h, using the conditions given in Table S1.3. Reflection positions match that for IPC-2P.

Figure S1.7. Capillary PXRD pattern of the as-made doubly $^{17}$O- and $^{29}$Si-enriched zeolite hydrolysed for 16 h, using the conditions given in Table S1.3. Reflection positions match that for IPC-2P.
S2. Variable-field $^{17}$O MAS and MQMAS spectra

Figure S2.1 shows $^{17}$O MAS and MQMAS spectra of $^{17}$O-enriched hydrolysed UTL zeolite acquired at $B_0$ fields of 14.1 T and 20.0 T. MQMAS spectra were acquired using a triple-quantum z-filtered pulse sequence, and are shown after a shearing transformation. The indirect dimension is scaled and referenced according to the convention described in Ref. S4. The sharp peak at $\delta \approx -5.1$ ppm is only resolved in the $^{17}$O MAS spectrum acquired at 20.0 T, and does not appear in the corresponding MQMAS spectrum. $^{17}$O MAS NMR spectra (acquired for another sample that was prepared in the same way) shown in Figure S2.2 reveal this peak exhibits little field dependence, suggesting it has a negligible $C_Q$ and confirming it can be attributed to $H_2O$. Average NMR parameters $<P_Q>$ and $<\delta_{iso}>$, extracted from the position of the centre of gravity of the lineshape seen in the MQMAS spectra, are given in Table S2.1. This resonance can be assigned to Si-O-Si species, expected to be found primarily in the bulk of the zeolitic layers. The Si-OH signal is not observed in MQMAS spectra unless $^1H$ decoupling is applied.

Note that $P_Q$ is a combined quadrupolar parameter that depends on both the magnitude and asymmetry of the quadrupolar interaction, with $P_Q = C_Q \left(1 + \eta_Q^2/3\right)^{1/2}$. This parameter can be determined from the position of the centre of gravity of the lineshapes within an MQMAS spectrum, whilst the determination of $C_Q$ and $\eta_Q$ individually requires the fitting of cross sections through the lineshapes. This latter process can be difficult for disordered materials and $P_Q$ (and $<P_Q>$) is often used in preference.
Figure S2.1. $^{17}$O MAS and triple-quantum MAS spectra of an $^{17}$O-enriched hydrolysed UTL zeolite (shown after a shearing transformation), acquired at a $B_0$ field strength of (a) 14.1 T and (b) 20.0 T, and with a MAS rate of 20 kHz. Cross sections of the Si-O-Si lineshape from the MQMAS spectra in (a) and (b) are shown in (c) and (d), respectively, along with (from the top) the overall fit (blue), and the individual contributions from Si-O-Si and Si-OH (red).
**Table S2.1.** Average $^{17}$O NMR parameters (for the Si-O-Si species) extracted from the MQMAS NMR spectra shown in Figure S2.1.

| $B_0$/T | $\delta_1$/ppm | $<\delta_{iso}>$/ppm | $<P_q>/MHz$ |
|---------|----------------|----------------------|----------------|
| 14.1    | 28.1           | 37.9                 | 5.0            |
| 20.0    | 25.6           | 39.3                 | 5.3            |
Table S2. \(^{17}\)O NMR parameters determined from the fitted cross sections for the Si-O-Si lineshapes shown in red in Figure S2.1 (c) and (d).

| B. / T | \(\delta_{\text{iso}}\) (ppm) | C\(_z\) / MHz |
|--------|-------------------------------|--------------|
| 14.1   | 38.0                          | 5.2          |
| 20.0   | 38.8                          | 5.2          |
S3. Synthesis and NMR characterization of $^{17}$O-enriched amorphous silica

$^{17}$O-enriched amorphous SiO$_2$ was synthesized following a scaled-down version of the procedure reported in Ref. S5, using the reagents given in Table S3.1. The reaction proceeds according to Eqn. S3.1 and, unless any isotopic scrambling with the reaction solvent occurs, the final enrichment level should be consistent with that of the initial $^{17}$O-enriched water.

$$\text{SiCl}_4(\text{l}) + 2\text{H}_2^{17}\text{O}(\text{l}) \xrightarrow{\text{Ar atm, } 0^\circ\text{C}, \text{Et}_2\text{O}} \text{Si}^{17}\text{O}_2(\text{s}) + 4\text{HCl}(\text{g})$$  (S3.1)

Table S3.1. Quantities of reagents used in the synthesis of $^{17}$O-enriched SiO$_2$.

|            | SiCl$_4$ | $^{17}$H$_2$O (35%) | Et$_2$O |
|------------|----------|---------------------|---------|
| Quantity / mmol | 8.7      | 17.4                |         |
| Amount      | 1 ml     | 313 µl              | 12.5 ml |

The $^{29}$Si MAS NMR spectrum of the synthesized $^{17}$O-enriched amorphous SiO$_2$, shown in Figure S3.1a (black line) indicates the presence of a distribution of Q sites with approximate intensity ratios of 0.05% : 2.92% : 73.5% : 23.53% for Q$^1$ : Q$^2$ : Q$^3$ : Q$^4$ species. This distribution is confirmed by the $^1$H-$^{29}$Si CP MAS spectrum shown in Figure S3.1a (red line) and appears to show a greater proportion of Q$^3$ than spectra reported for other amorphous silica samples obtained using a similar synthetic procedure.$^{55}$ Figure S3.1b shows the $^1$H MAS NMR spectrum recorded 10 days after synthesis, where a broad line is observed, indicating the presence not only of isolated and hydrogen-bonded silanols, but also of physisorbed water with varying degrees of hydrogen bond strengths (signals in the range 3-8 ppm).$^{56}$ The $^{17}$O MAS NMR spectrum is shown in Figure S3.1c. The average quadrupolar parameters of $<C_Q>$ ≈ 5.3 MHz, $<\eta_Q>$ ≈ 0.2 and $<\delta_{iso}>$ ≈ 42.3 ppm were obtained from an $^{17}$O MQMAS spectrum (not shown), and are good in agreement with previously reported values for bulk Si-O-Si units.$^{57}$ While it is not possible to resolve S14
directly resonances from Si-O-Si and Si-OH species in the $^{17}$O MAS NMR spectrum, $T_1$ inversion recovery measurements indicate that the signal centered around 0 ppm exhibits faster relaxation (by a factor of ~3) than that centered around 30 ppm, suggesting the presence of faster relaxing silanol species in the spectrum, as previously reported.$^{37}$

Figure S3.1. (a) $^{29}$Si, (b) $^1$H and (c) $^{17}$O (14.1 T, 20 kHz MAS) MAS NMR spectra of amorphous $^{17}$O-enriched SiO$_2$. In (a), the $^1$H-$^{29}$Si CP MAS NMR spectrum, recorded with a contact time of 5 ms, is shown in red.

Figure S3.2 plots the signal intensity obtained from $^{17}$O spin-locking experiments for Si$^{17}$O$_2$, carried out at $B_0 = 14.1$ T and at 20.0 kHz MAS. In each case, transverse magnetization was generated using a rf pulse with $\nu_1 = 50$ kHz, before a spin-locking pulse was applied, with $\nu_1 = 8$ kHz or 45 kHz in Figures S3.2a and S3.2b, respectively. In Figure S3.2a, after a sharp drop in signal intensity (owing to initial dephasing of terms that do not commute with the spin-locking Hamiltonian, as described in Ref. S8) a reasonable spin lock is observed. The behaviour seen is characteristic of the sudden limit and the adiabaticity parameter, $\alpha (= \nu_1^2 / 2\nu_Q^{PAS} 2\nu_R)$ is $4.3 \times 10^{-3}$. When the spin lock is applied with a higher rf field, the drop in signal intensity is more significant and a pronounced oscillation with the rotor period confirms the system is between the intermediate and adiabatic regimes ($\alpha \approx 0.127$).
Figure S3.2. Plot showing (normalized) $^{17}$O (14.1 T, 20 kHz) spin-locking signal intensity for amorphous $^{17}$O-enriched SiO$_2$ as a function of spin-lock duration, for spin-lock pulses applied with $\nu_1$ of (a) 8 kHz and (b) 45 kHz.
Figure S3.3 shows $^{17}$O (14.1 T, 20 kHz) CP MAS NMR spectra of $^{17}$O-enriched SiO$_2$, acquired with a cross-polarization rf field strength, $\nu_1 = 10$ kHz, and contact times of 100 µs (blue line) and 500 µs (red line). The $^{17}$O MAS NMR spectrum is also shown for comparison (black line). It can be seen that the signal from the Si-O-Si is almost entirely removed in the CP spectra.

Figure S3.3. $^{17}$O (14.1 T, 20 kHz MAS) CP NMR spectra of amorphous $^{17}$O-enriched SiO$_2$, acquired with a CP rf field strength, $\nu_1 = 10$ kHz, and contact times of 100 µs (blue) and 500 µs (red). The $^{17}$O MAS NMR spectrum is also shown for comparison (black).
S4. T$_p$ measurements and spin-locking behaviour

Figure S4.1 shows the intensity resulting from a $^1$H spin-lock experiment (or T$_{1p}$ measurement) for a hydrolysed Ge-UTL zeolite. Only a small drop in intensity is observed over a spin-lock duration of 1 ms, demonstrating that rapid $^1$H T$_{1p}$ relaxation is not responsible for the poor $^1$H-$^{17}$O CP efficiency observed in Figure 6 of the main text. Figure S4.2 shows $^{17}$O MAS NMR spectra for a hydrolysed Ge-UTL zeolite, acquired using a spin-lock experiment, with different values of the spin-lock duration. When a short duration is used signals from the Si-O-Si, Si-O-H and H$_2$O oxygen species can clearly be seen. However, as the duration increases the signal from H$_2$O is lost. At longer durations signal from the Si-O-H species is primarily observed, again confirming that poor $^{17}$O spin-lock efficiency or inherently fast T$_{1p}$ relaxation does not appear to be responsible for the poor CP efficiency observed.

![Graph showing intensity of $^1$H spin-lock experiment](image)

Figure S4.1. Intensity of $^1$H (14.1 T, 20 kHz MAS) spin-lock experiment (i.e., T$_{1p}$ measurement) for a hydrolysed Ge-UTL zeolite, with a spin-lock rf field strength, $\nu_r$, of 75 kHz.
Figure S4.2. $^{17}$O (14.1 T, 20 kHz MAS) NMR spectra of a hydrolysed Ge-UTL zeolite, acquired using a spin-lock experiment, with a spin-lock rf field strength, $v_L$, of 8 kHz at varying spin-lock durations of (a) 50 µs, (b) 100 µs and (c) 3000 µs.
Three different approaches were tested (using unenriched material) for the deuteration of zeolites; (i) post-synthetic exchange with D$_2$O vapour over 42 days, (ii) stirring of the hydrolysed zeolite in D$_2$O for 24 h at room temperature and (iii) in-situ hydrolysis using D$_2$O and DCl. Only the first of these methods was carried out on $^{17}$O- and doubly $^{17}$O- and $^{29}$Si-enriched zeolites to avoid the possible loss of $^{17}$O or $^{29}$Si by exchange or significant hydrolysis when large amounts of D$_2$O were used. Deuterated enriched samples were dried under Ar flow prior to spectral acquisition in an attempt to remove any excess D$_2$O.

Figure S5.1 compares $^{17}$O (20.0 T, 20 kHz) MAS NMR spectra of an $^{17}$O-enriched hydrolysed Ge-UTL zeolite, prior to and post deuteration. The signal attributed to water between −4 and −5 ppm is removed upon deuteration, owing to exchange with both D$_2$O and atmospheric H$_2$O (both containing $^{17}$O at natural abundance). However, there is also a loss of total $^{17}$O signal (from both Si-O-Si and Si-O-H sites), suggesting that the deuteration process triggers further hydrolytic rearrangement. As already shown in Figure 4 (main text), the $^{17}$O spectra and, therefore the layered structure, evolve with time when stored at room temperature in air. However, the saturated D$_2$O vapour used for deuteration creates a more favorable environment for further hydrolysis and, hence, back exchange of $^{17}$O with natural abundance (for $^{17}$O) D$_2$O to occur. Comparison of the $^{29}$Si Q$^4$/Q$^3$ ratios for the enriched sample before and after deuteration confirms this is the case, with a lower ratio, by a factor of ~1.4, for the deuterated sample. This rapid $^2$H back exchange, and $^{17}$O loss during the deuteration process, hindered the acquisition of high-resolution $^{17}$O NMR spectra for the deuterated compounds.
Figure S5.1. $^{17}$O (20.0 T, 20 kHz) MAS NMR spectra of $^{17}$O-enriched hydrolysed Ge-UTL zeolite prior to (black) and post (red) exchange with D$_2$O vapour.

The $^2$H MAS NMR spectrum of a deuterated $^{17}$O-enriched hydrolysed Ge-UTL zeolite shortly after its removal from the saturated D$_2$O vapor is shown in Figure S5.2 (and Figure 7 of the main text). The spectrum is dominated by a sharp, isotropic signal, resulting from rapidly reorienting D$_2$O within the interlayer region. A set of spinning sidebands is also seen, resulting from the much broader Si-O-D lineshape. From the width of this lineshape, $C_Q$ can be estimated as 80 - 100 kHz, but it should be noted that it is not possible to fit the spectral lineshape with a single quadrupolar lineshape, suggesting some motional averaging of this signal also.

Figure S5.2. $^2$H (9.4 T, 10 kHz) MAS NMR spectrum of a deuterated $^{17}$O-enriched hydrolysed Ge-UTL zeolite, with an expansion to show the broad spinning sideband manifold.

From the $^2$H MAS NMR spectrum in Figure S5.2, it can be estimated that the
intensity ratio of the Si-O-D: D$_2$O signal is ~1:4 (suggesting a 1:2 ratio of Si-O-H groups to molecular water in the interlayer spacing). It should be noted, however, that the level of water in the hydrolysed zeolites varies with hydrolysis duration and storage time and conditions. From samples studied in this work it is estimated that the ratio of Si-O-H groups to molecular water in the interlayer spacing ranges between 1:2 and 1:4.
S6. Analysis of the $^{17}$O MAS NMR spectrum

Figure S6.1a shows a $^{17}$O MAS NMR spectrum, acquired with a short flip angle to provide a quantitative result. Also shown (in Figure S6.1b) is the best fit (using the estimated average NMR parameters determined from MQMAS, CP and spin-lock experiments), along with lineshapes for the individual components (Figures S6.1c-e). Note that the amount of water present varies between samples hydrolysed for different durations, and those stored for different times under different conditions. Furthermore, it is not possible to determine accurate quadrupolar parameters for the Si-O-H species, owing to the more unusual (and distorted) lineshape observed in CP and spin-lock experiments, resulting in some uncertainty on the proportions obtained. From the fitting, the ratio of Si-O-Si : Si-O-H : H$_2$O species is 8 : 1 : 1.

Figure S6.1. (a) $^{17}$O (14.1 T, 20 kHz) MAS NMR short flip angle spectrum of $^{17}$O-enriched hydrolysed Ge-UTL zeolite. Also shown are (b) lineshape fitting and individual lineshapes for (c) Si-O-Si species, (d) water and (e) Si-OH species.

Similar fits were also carried out for the $^{17}$O MAS NMR spectra shown in Figure 4 of the main text. Although these spectra are not truly quantitative (as a short flip angle pulse was not used), the fits do provide insight into the changes in the lineshape observed over a
time period of 30 days. As shown in Figure S6.2 and Table S6.1, the relative proportion of the three components changes with time, with an increase in the proportion of Si-O-H groups and a relative decrease in Si-O-Si signal. This reflects a low level of ongoing hydrolysis, most likely as a result of small amount of acid remaining between the layers, owing to the reduced volume of (unenriched) washing water used.

![Figure S6.2.](image)

**Figure S6.2.**(a) $^{17}$O (14.1 T, 20 kHz) MAS NMR spectra of $^{17}$O-enriched Ge-UTL zeolite 2, 16 and 30 days after hydrolysis, reproduced from Figure 4 of the main text. Also shown are (b) lineshape fitting and individual lineshapes for (c) Si-O-Si species, (d) water and (e) Si-OH species.

**Table S6.1.** Integrated intensities (%) of the types of $^{17}$O species, extracted from the fits of the MAS NMR spectra in Figure S6.2 (and Figure 4 of the main text), collected 2, 16 and 30 days after hydrolysis. Errors are estimated as 0.5%.

|        | 2 days | 16 days | 30 days |
|--------|--------|---------|---------|
| Si-O-Si| 83.4   | 76.9    | 71.4    |
| Si-OH  | 8.3    | 15.4    | 21.5    |
| H$_2$O | 8.3    | 7.7     | 7.1     |
S7. References

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