

Facile, Room-Temperature ^{17}O Enrichment of Zeolite Frameworks Revealed by Solid-State NMR Spectroscopy

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S1. Additional experimental NMR parameters

Table S1.1. Experimental NMR parameters used for the acquisition of ^{17}O MQMAS NMR spectra.

Sample	Time / days	ν_R / kHz	t_1 increment / μs	Number of increments	Number of transients
H-MOR					
slurry	2	10	100.00	28	2048
	16	10	100.00	33	2048
	31	10	100.00	42	1680
	141	14	71.43	48	768
	220	14	71.43	48	1156
gas		14	71.43	53	4128
Na-MOR					
slurry	25	14	71.43	34	1536
gas		14	71.43	38	1152
H-FER					
slurry	2	14	71.43	60	1056
	8	14	71.43	60	1056
	15	14	71.43	60	1056
	100	14	71.43	60	1200
gas		14	71.43	90	1056

S2. Extraction of ^{17}O NMR parameters from MQMAS spectra

It is possible to extract NMR parameters from MQMAS NMR spectra from either (i) the position of the centre of gravity of the resonance (which gives the isotropic chemical shift, δ_{iso} , and the quadrupolar product, $P_Q (= C_Q(1 + \eta_Q^2/3)^{1/2})$, or (ii) by analytical fitting of a cross section, extracted parallel to δ_2 (which gives information on C_Q and η_Q directly). Strictly, the disorder present in the hydrated forms of H-MOR (resulting both from the presence of Al substitution into the framework and the presence of H_2O within the pores) results in the determination only of average values of the NMR parameters (*i.e.*, $\langle\delta_{\text{iso}}\rangle$, $\langle P_Q\rangle$, $\langle C_Q\rangle$ and $\langle\eta_Q\rangle$) only. However, these appear very similar for the formally crystallographically distinct O species. Spectral fitting was carried out using the SOLA software available within the Bruker Topspin package

Table S2.1 gives the NMR parameters extracted from the MQMAS spectrum shown in Figure 2b of the main text (for H-MOR/ $\text{H}_2^{17}\text{O}(\text{l})$ slurried for 2 days). Examples of the fitting of the quadrupolar lineshapes in the cross sections extracted parallel to δ_2 are shown in Figure S2.1.

Table S2.1. Average ^{17}O NMR parameters, including δ_1 and δ_2 positions, isotropic chemical shift (δ_{iso}), quadrupolar product (P_Q), and the magnitude (C_Q) and asymmetry (η_Q) of the quadrupolar interaction, extracted from the MQMAS NMR spectrum in Figure 2b of the main text.

Species	$\langle\delta_1\rangle$ (ppm)	$\langle\delta_2\rangle$ (ppm)	$\langle\delta_{\text{iso}}\rangle$ (ppm)	$\langle P_Q\rangle /$ MHz	$\langle C_Q\rangle /$ MHz	$\langle\eta_Q\rangle$
Si- ^{17}O -Al	22.4(5)	19.3(5)	33(1)	3.9(5)	3.8(5)	0.3(1)
Si- ^{17}O -Si	31.7(5)	18.4(5)	43(1)	5.2(5)	5.0(5)	0.2(1)

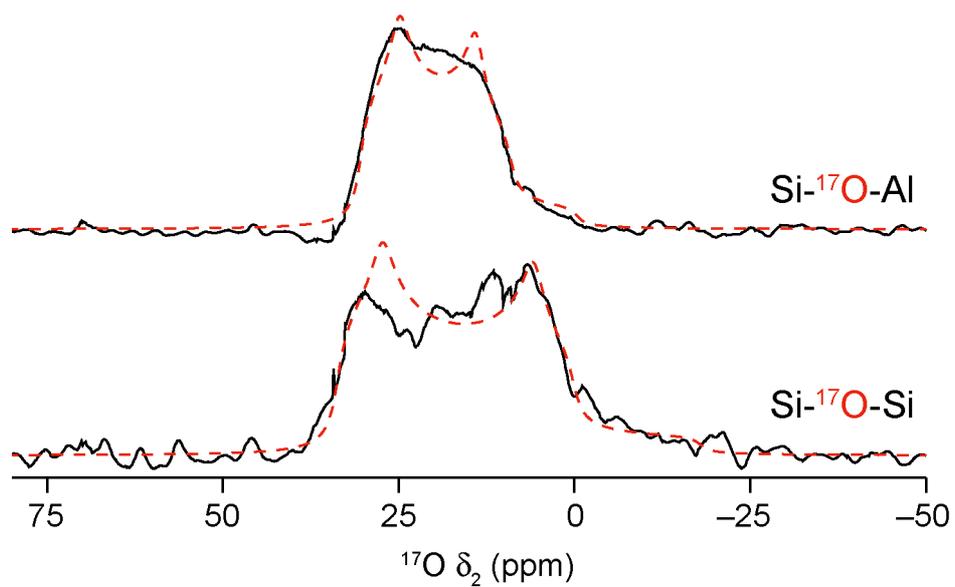


Figure S2.1. Cross sections, extracted parallel to δ_2 extracted (at $\delta_1 = 31.7$ and 22.4 ppm) from the ^{17}O MQMAS spectrum shown in Figure 2b of the main text, and corresponding fits (using the $\langle C_Q \rangle$ and $\langle \eta_Q \rangle$ values given in Table S2.1).

S3. Comparison of ^{17}O MQMAS spectra of enriched H-MOR

Figure S3.1 compares ^{17}O MQMAS NMR spectra (and their corresponding isotropic projections) of H-MOR enriched (i) by room temperature hydration with $\text{H}_2^{17}\text{O}(\text{l})$ for 220 days and (ii) post synthesis by high-temperature exchange with $^{17}\text{O}_2(\text{g})$.

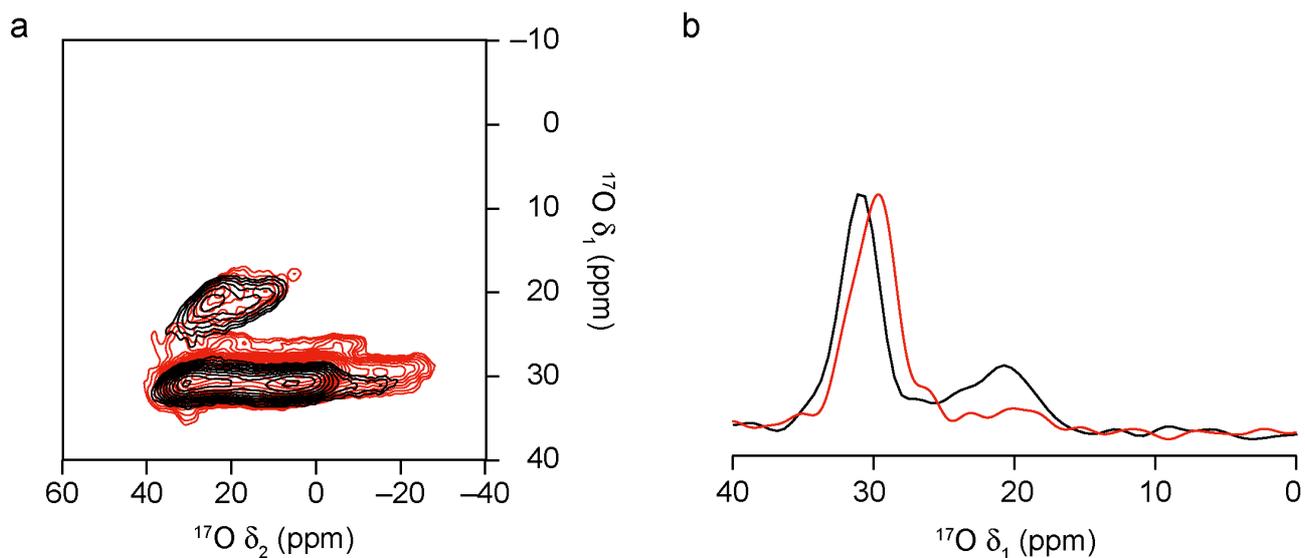


Figure S3.1. ^{17}O (14.1 T, 14 kHz) (a) MQMAS NMR spectra and (b) corresponding isotropic projections of H-MOR enriched by room temperature hydration with $\text{H}_2^{17}\text{O}(\text{l})$ for 220 days (black) and post synthesis by high-temperature exchange with $^{17}\text{O}_2(\text{g})$ (red).

S4. NMR spectra of H-FER

Figure S4.1 compares ^{17}O MAS spectra and isotropic projections of ^{17}O MQMAS NMR spectra of H-FER/ $\text{H}_2^{17}\text{O}(\text{l})$ slurries, with spectra for a sample enriched by post-synthetic exchange with $^{17}\text{O}_2(\text{g})$. Preferential enrichment of Si-O-Al species is seen at the shorter hydration time, but there is a small increase in Si- ^{17}O -Si at the longer duration. The additional Si- ^{17}O -Si signal that appears with increasing hydration time suggests that some framework oxygens enrich much more slowly under these conditions. The ratio of Si- ^{17}O -Al:Si- ^{17}O -Si signals is much lower for the gas-exchanged sample, suggesting that the overall level of enrichment in the H-FER slurry may be limited by the initial volume of $\text{H}_2^{17}\text{O}(\text{l})$ used in the reaction.

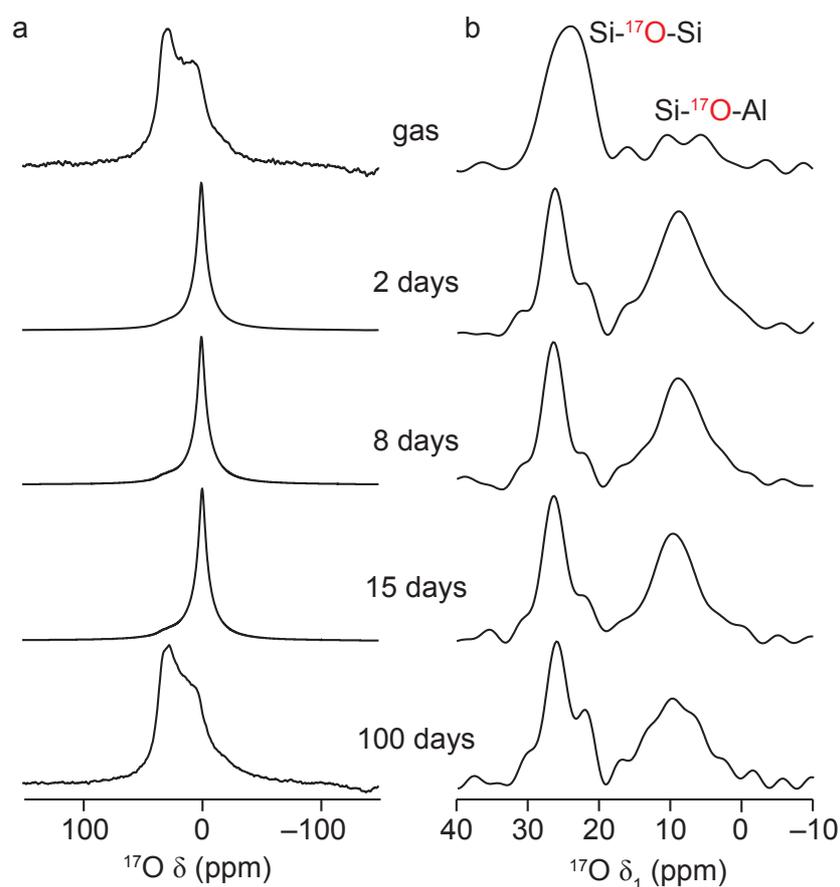


Figure S4.1. ^{17}O (14.1 T) (a) MAS and (b) isotropic projections of MQMAS NMR spectra of a 50 $\mu\text{l}/50$ mg slurry of H-FER/ $\text{H}_2^{17}\text{O}(\text{l})$ after varying times. Spectra are shown normalized. Also shown for comparison are the corresponding spectra of H-FER enriched by post-synthetic gas exchange.

Figure S4.2 shows ^{27}Al and ^{29}Si MAS NMR spectra of H-FER prior to enrichment and post enrichment. Both sets of spectra are very similar, confirming no breakdown of the zeolite framework has occurred.

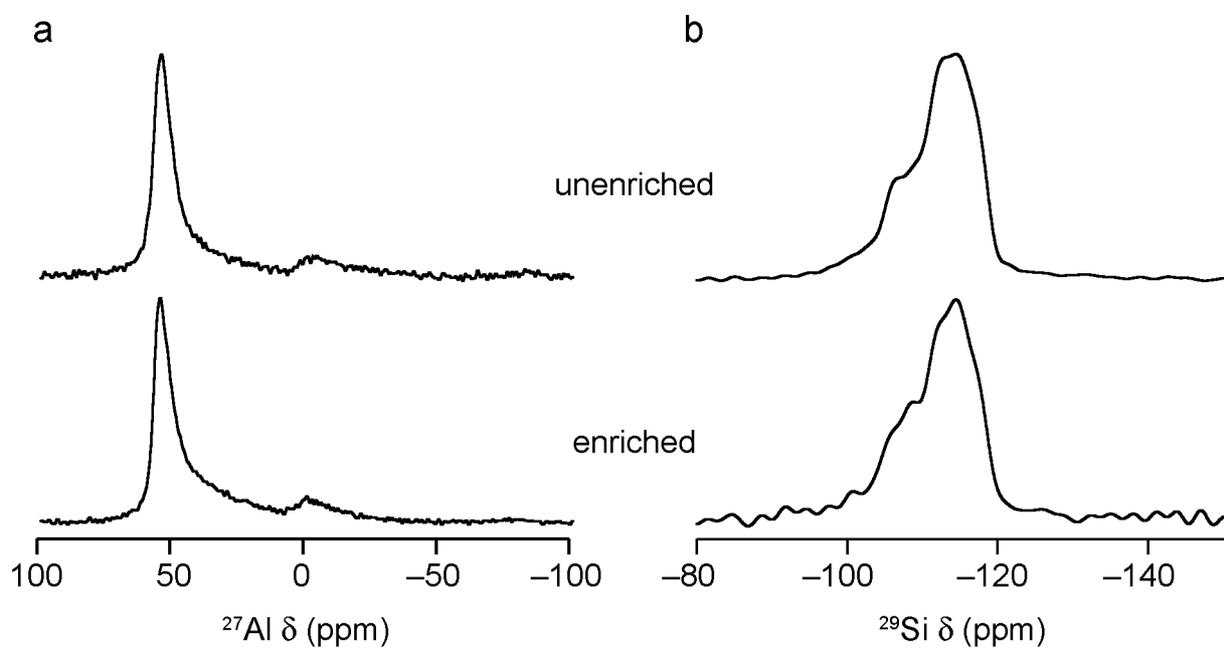


Figure S4.2. (a) ^{27}Al (14.1 T, 14 kHz) and (b) ^{29}Si (9.4 T, 14 kHz) MAS NMR spectra of H-FER prior to enrichment and of a H-FER/ $\text{H}_2^{17}\text{O(l)}$ slurry after (a) 128 days.

S5. NMR spectra of Na-MOR

Figure S5.1 shows ^{17}O MQMAS spectrum of a 50 μl /50 mg slurry of Na-MOR/ $\text{H}_2^{17}\text{O}(\text{l})$ left for 2 days. This shows enrichment of the Si-O-Al species, but very little enrichment of Si-O-Si oxygens, suggesting that the overall rate of enrichment is slower than in H-MOR. Enrichment of Si-O-Al and Si-O-Si framework linkages is observed at 25 days (see Figure 7 in the main text). This suggests enrichment is slower for Na-MOR (likely due to the lack of the Brønsted acid H), but confirms room temperature lability of the framework occurs.

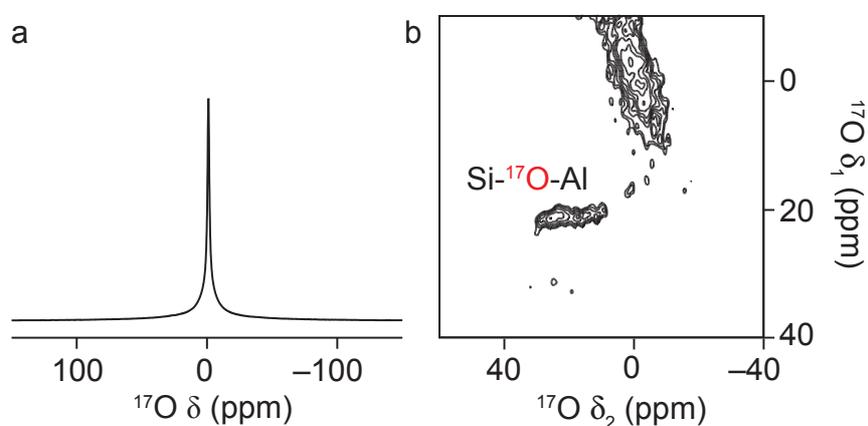


Figure S5.1. ^{17}O (14.1 T, 10 kHz) MAS and MQMAS spectra of a 50 μl /50 mg slurry of Na-MOR/ $\text{H}_2^{17}\text{O}(\text{l})$ left for 2 days.

Figure S5.2 shows ^{27}Al and ^{29}Si MAS NMR spectra of Na-MOR prior to enrichment and post (after 26 days) enrichment. Both sets of spectra are very similar, confirming no breakdown of the zeolite framework has occurred.

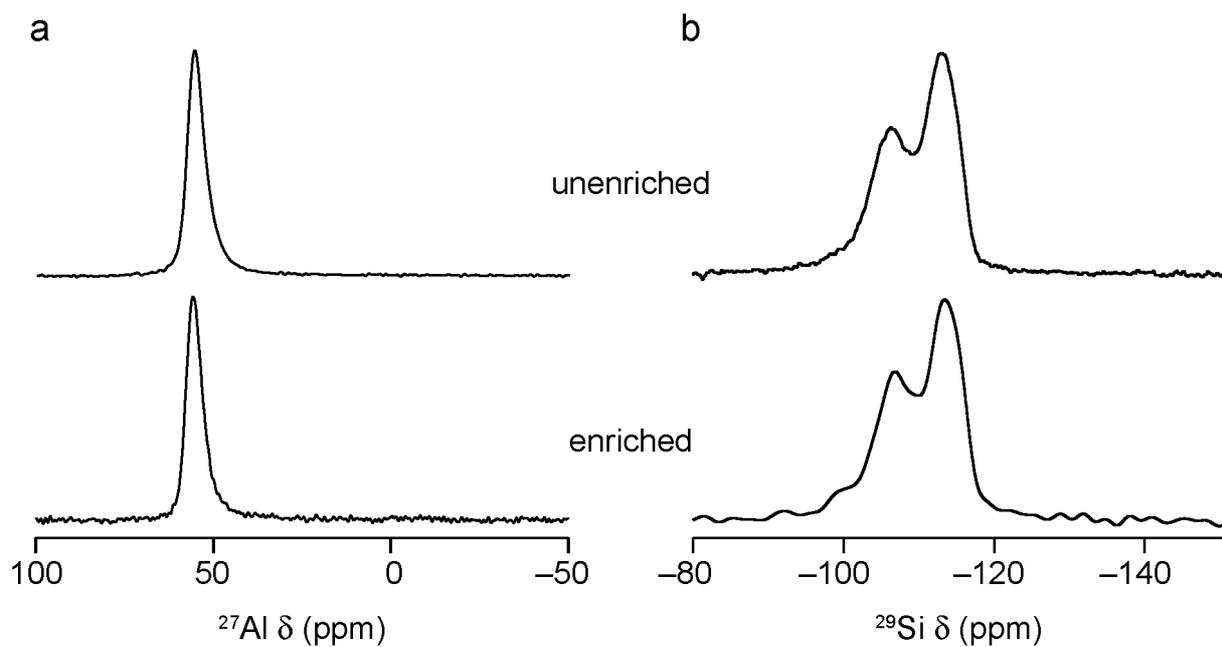


Figure S5.2. (a) ^{27}Al (14.1 T, 14 kHz) and (b) ^{29}Si (9.4 T, 14 kHz) MAS NMR spectra of Na-MOR prior to enrichment and of a Na-MOR/ $\text{H}_2^{17}\text{O(l)}$ slurry, after 26 days.

S6. ^{29}Si CP MAS NMR spectra of H-MOR

Figure S6.1 shows ^{29}Si cross polarization (CP) MAS NMR spectra of H-MOR prior to and post enrichment. CP spectra were acquired using a contact pulse of 0.5 ms (ramped from 90 to 100% for ^1H) and a recycle interval of 1 s. Spectra are the result of averaging 7218 and 57424 transients in Figures S6.1a and S6.1b, respectively. However, when the differences in mass of the two samples are also accounted for (77.2 and 17.2 mg) the expected difference in signal intensity is a factor of 1.75, as observed experimentally. This confirms that although both spectra show the presence of a small number of Q^3 species, the level of these does not change at all with hydration. (This is perhaps not unexpected as samples have been exposed to water previously in various ion exchange reactions). The absolute level of Q^3 species cannot be easily estimated using CP experiments (owing the inefficient magnetization transfer as a result of water dynamics), but from the ^{29}Si MAS NMR spectra (also shown in Figure S6.1 for comparison) these defects are at levels ($\sim 4\text{-}6\%$) consistent with typical zeolites.

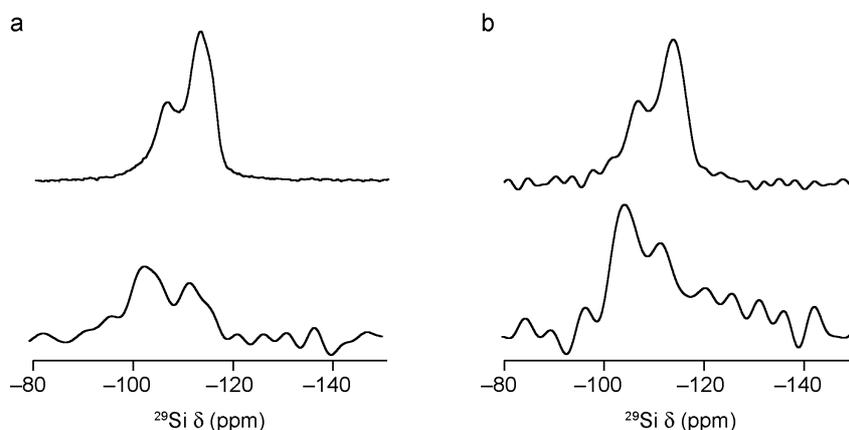


Figure S6.1. ^{29}Si (9.4 T, 14 kHz) MAS and CP MAS NMR spectra of (a) H-MOR prior to enrichment and (b) of a H-MOR/ $\text{H}_2^{17}\text{O}(\text{l})$ slurry, after 206 days.