Supporting Information

Structural Characterization of Mg-Stabilized Amorphous Calcium Carbonate by Mg-25 Solid-State NMR Spectroscopy

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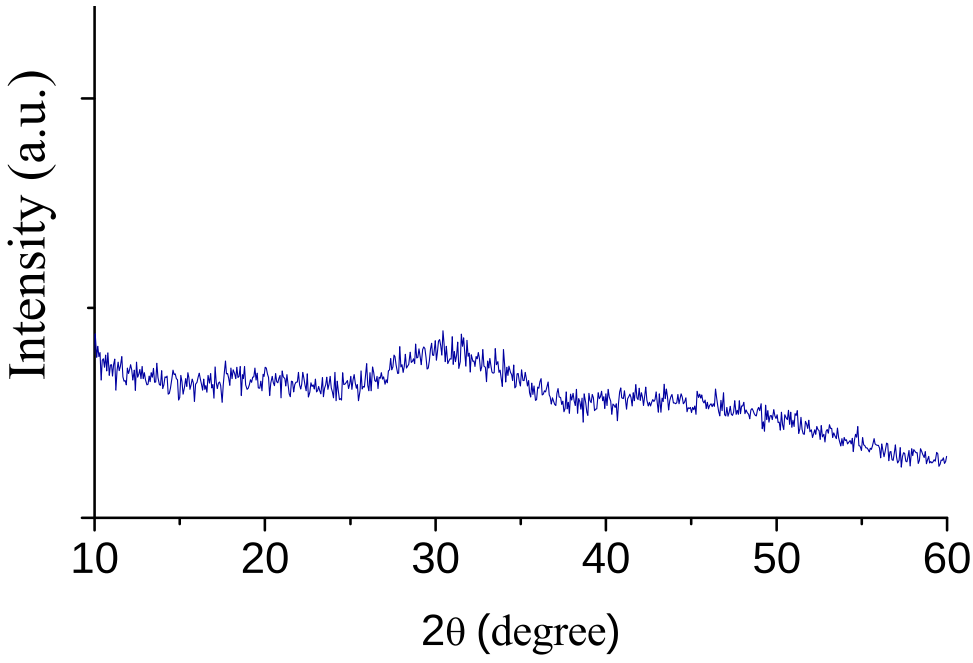

Figure S1. Typical XRD pattern measured for the Mg*X*ACC samples.

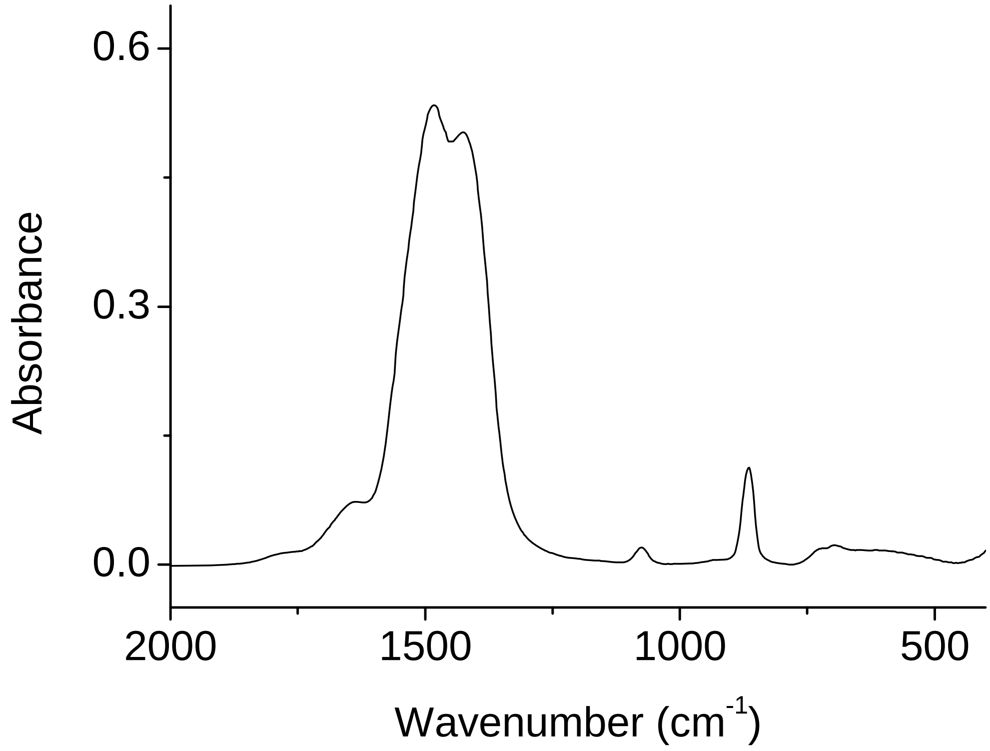

Figure S2. Typical FT-IR spectrum measured for Mg*X*ACC samples. The absorption peak at 865 cm^{-1} is the characteristic spectral feature of ACC.

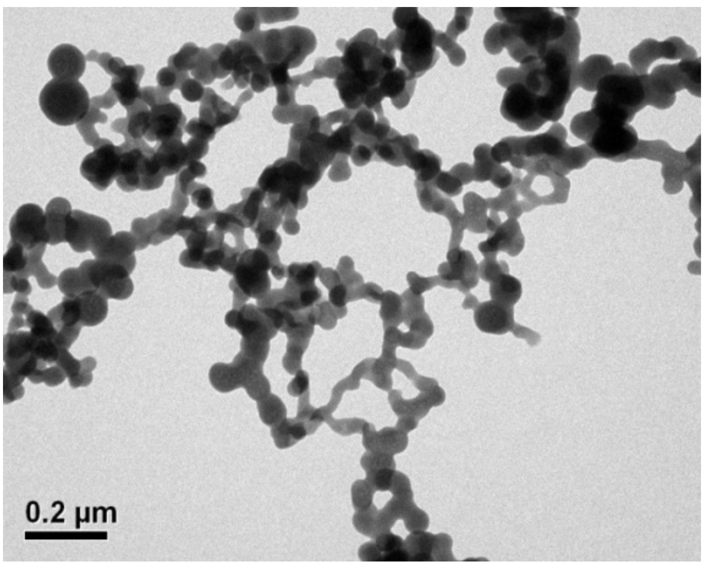

Figure S3. Typical TEM image obtained for Mg*X*ACC samples.

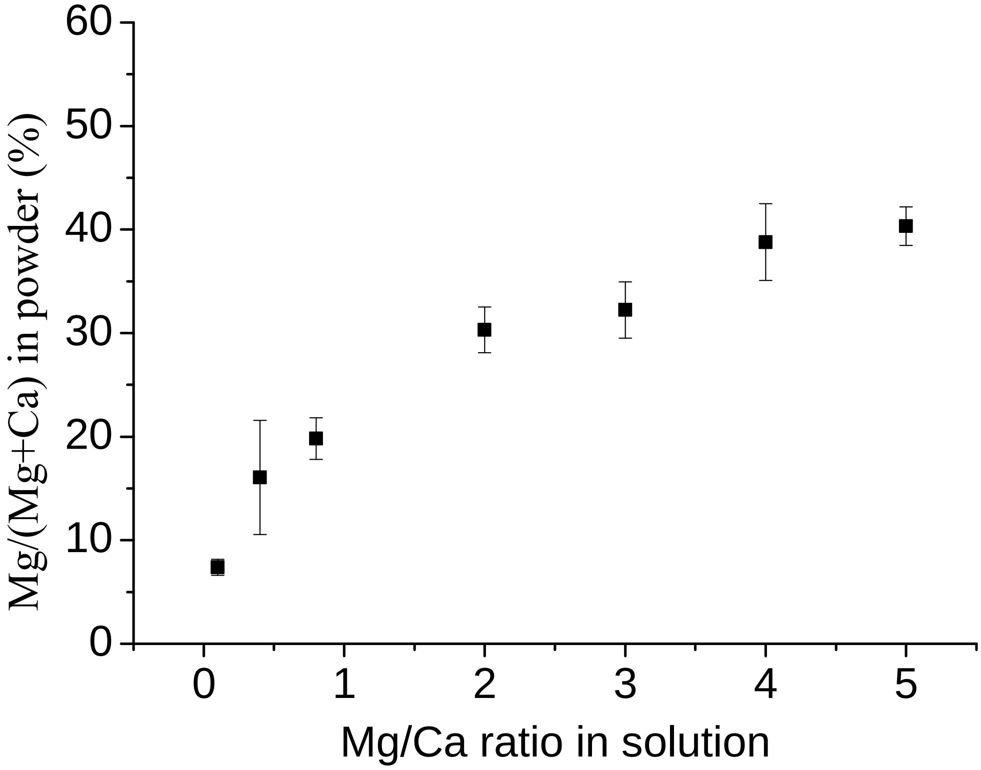

Figure S4. Plot of the Mg content of the Mg*X*ACC determined by SEM-EDX.

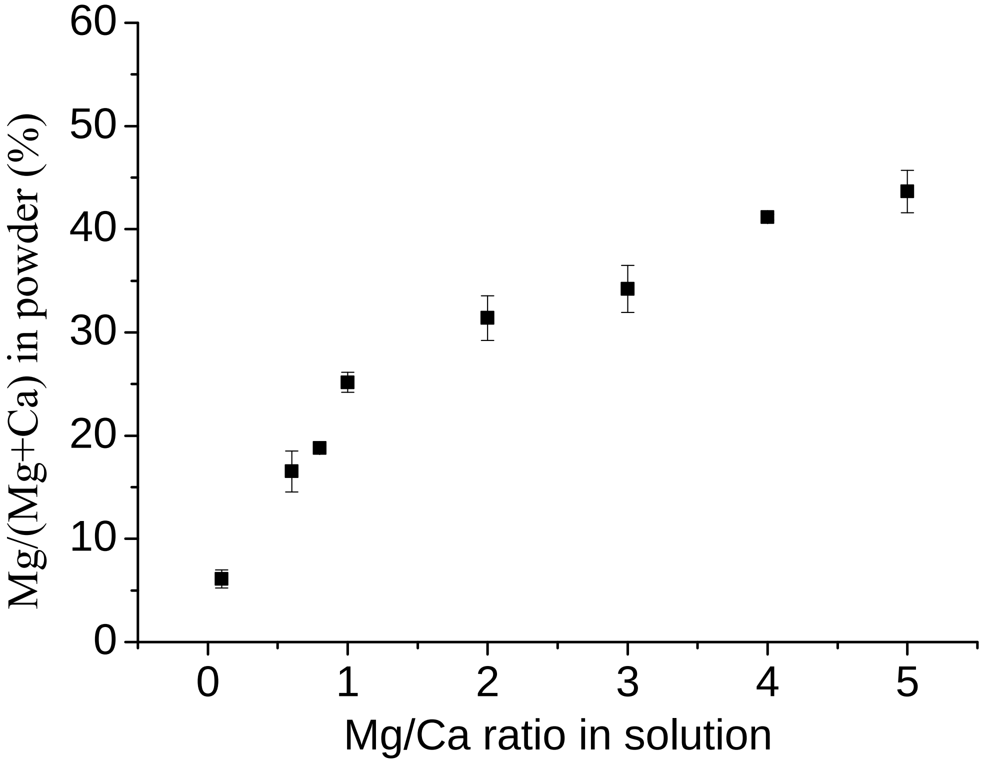

Figure S5. Plot of the Mg content of the Mg*X*ACC determined by ICPMS.

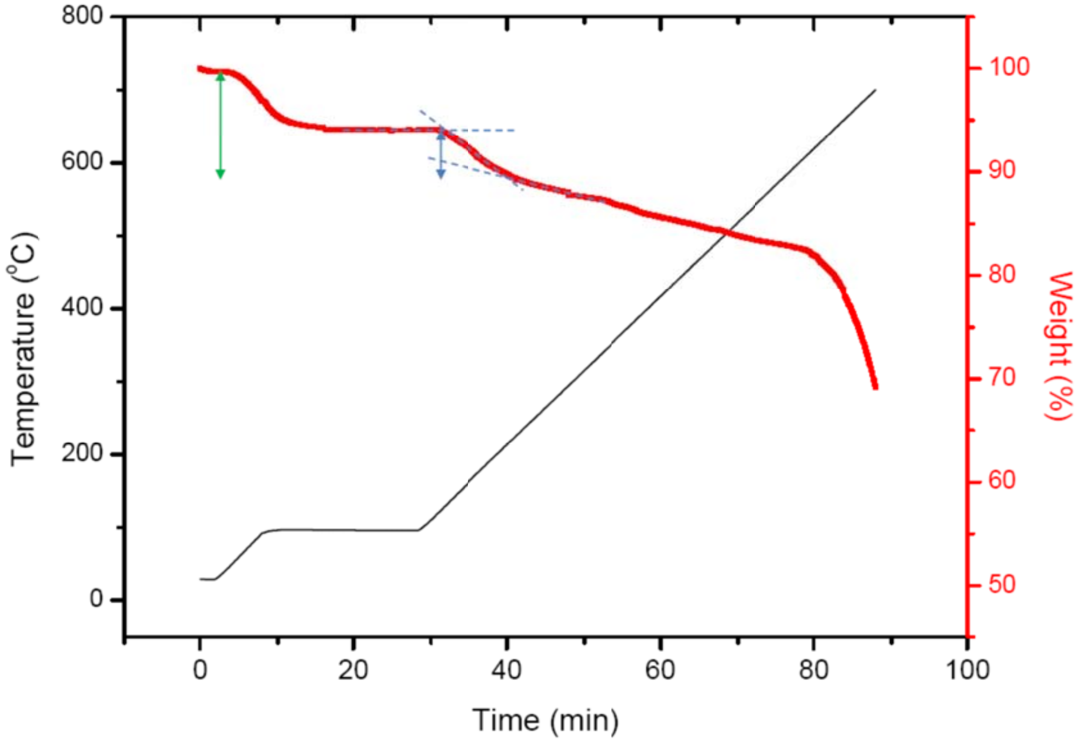

Figure S6. TGA results obtained for Mg0.6ACC. The longer arrow indicates the weight loss due to the total water content and the shorter arrow denotes the loss due to the tightly bound water.

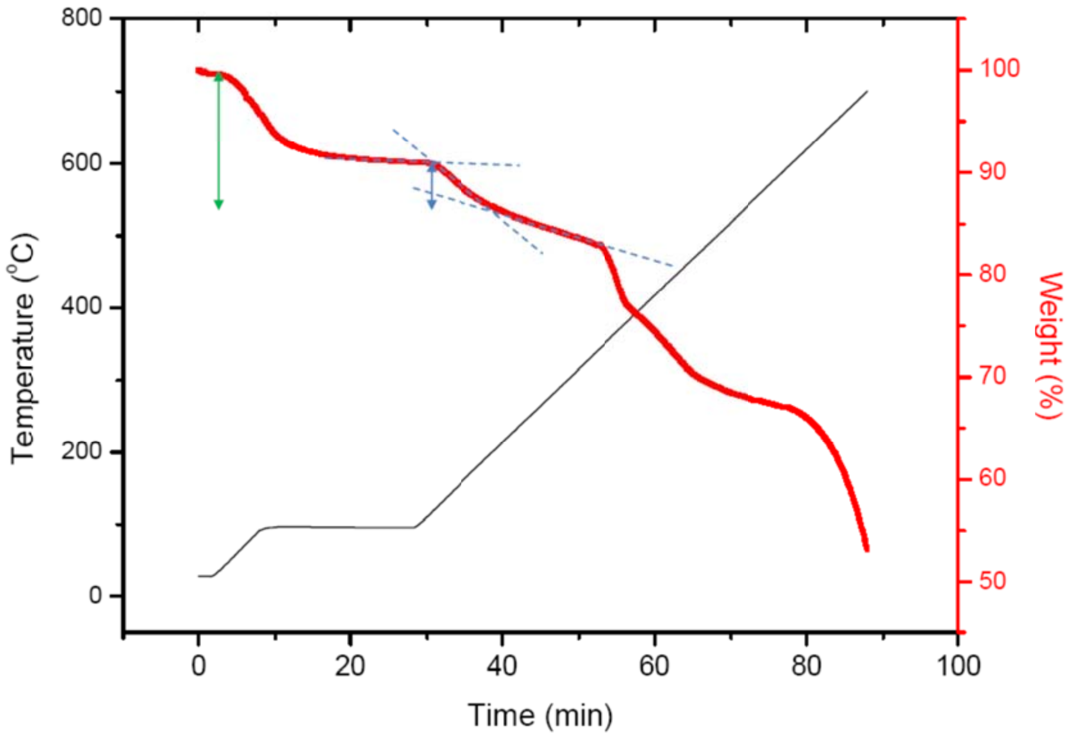

Figure S7. TGA results obtained for Mg5ACC.

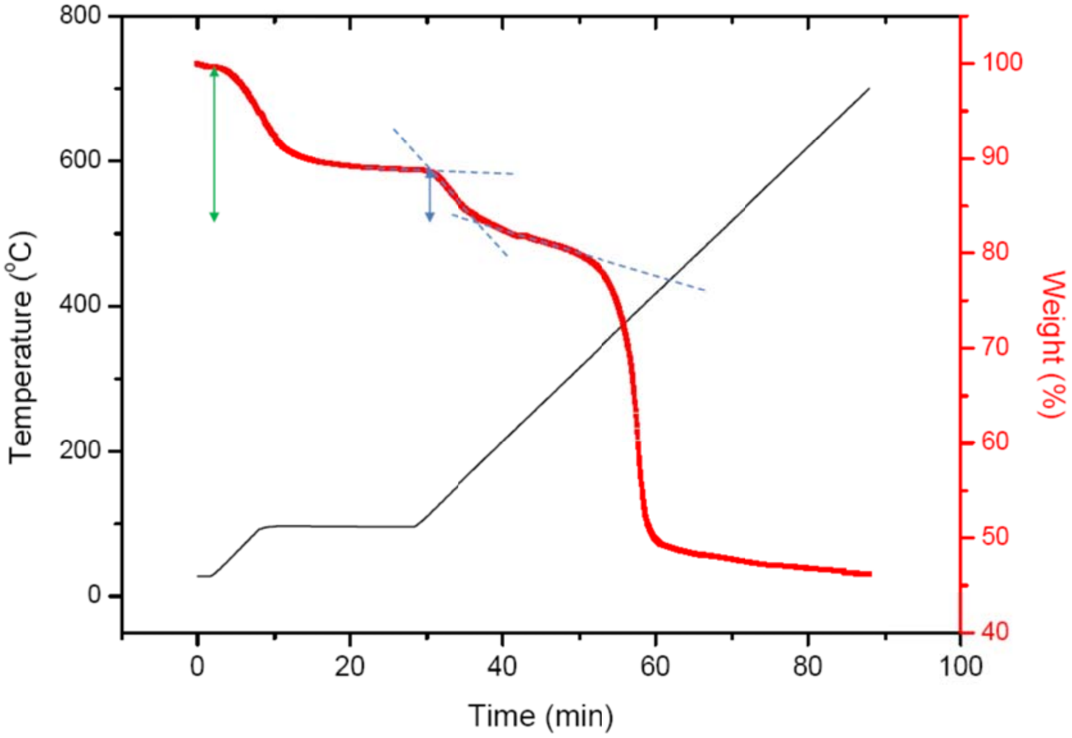

Figure S8. TGA results obtained for AMC.

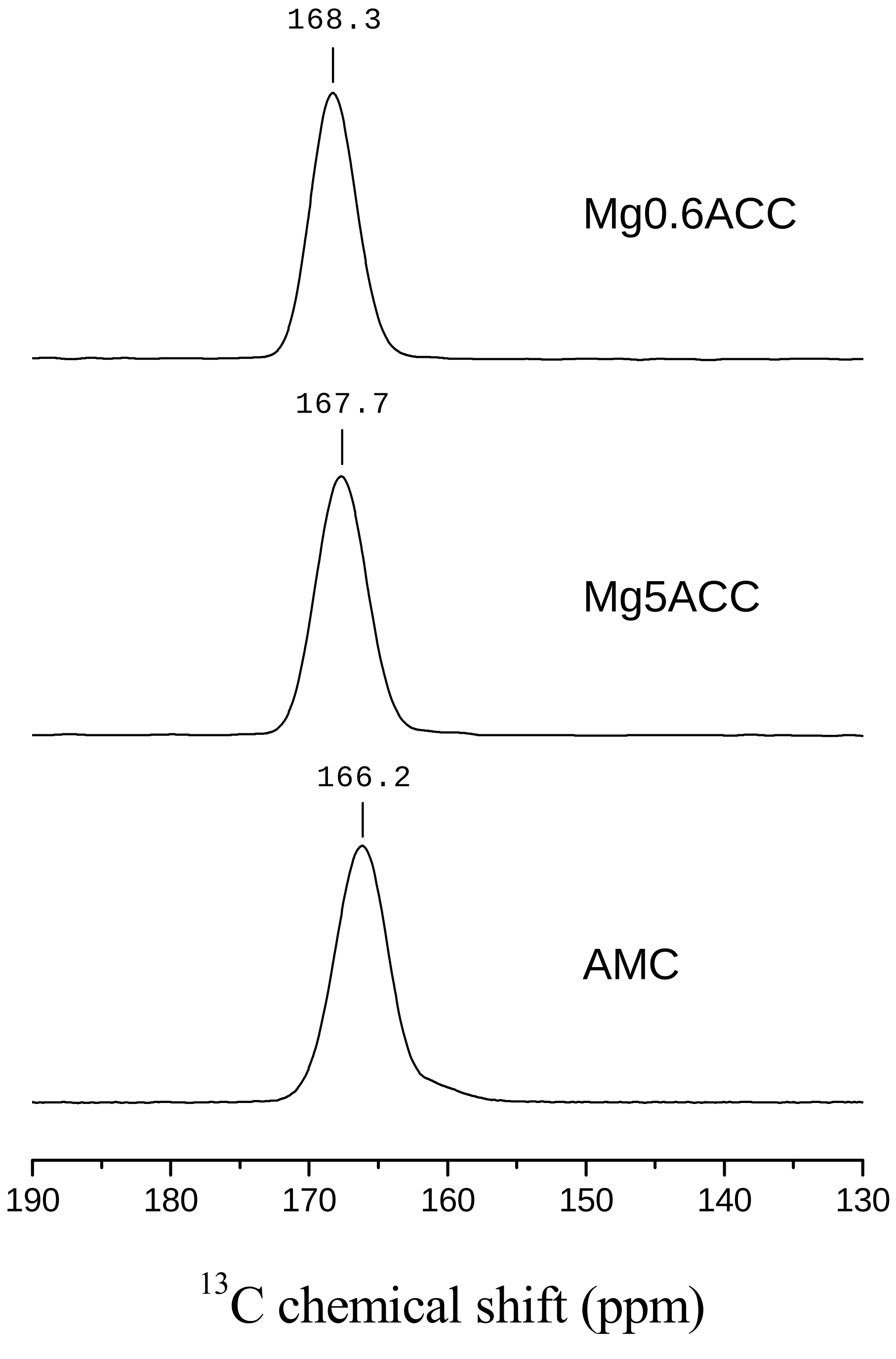

Figure S9. $^{13}C\{^{1}H\}$ CPMAS spectra obtained under the spin rate of 12.5 kHz. The chemical shifts were referenced to TMS using adamantine as the secondary standard. The ^{13}C Bloch decay spectra of Mg5ACC and Mg0.6ACC gave exactly the same results.

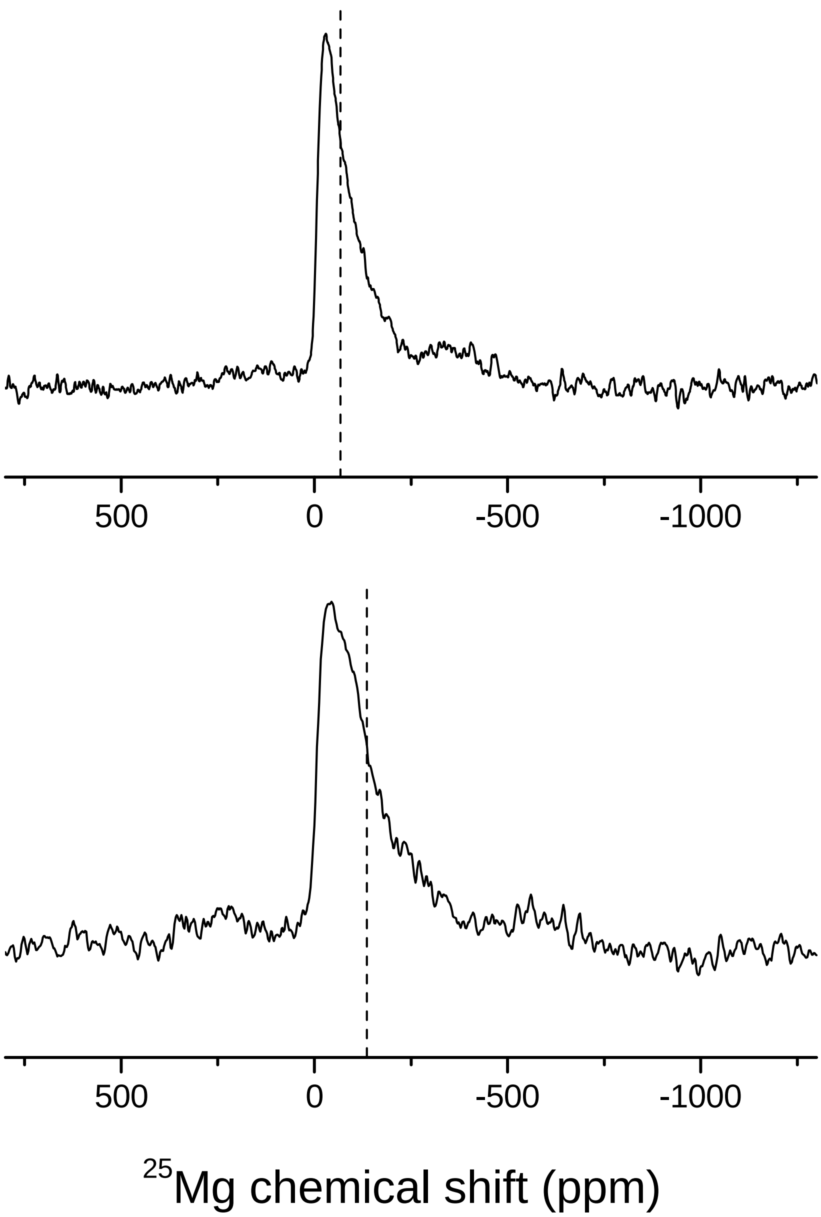

Figure S10. ^{25}Mg MAS spectra of the Mg5ACC sample acquired at 9.4 T (lower trace) and 14.1 T (upper trace). The corresponding spectra of Mg0.6ACC and AMC look very similar. The dashed lines indicate the positions of the spectral center of gravity. The procedure to obtain χ_Q and chemical shifts is given in Table S1.

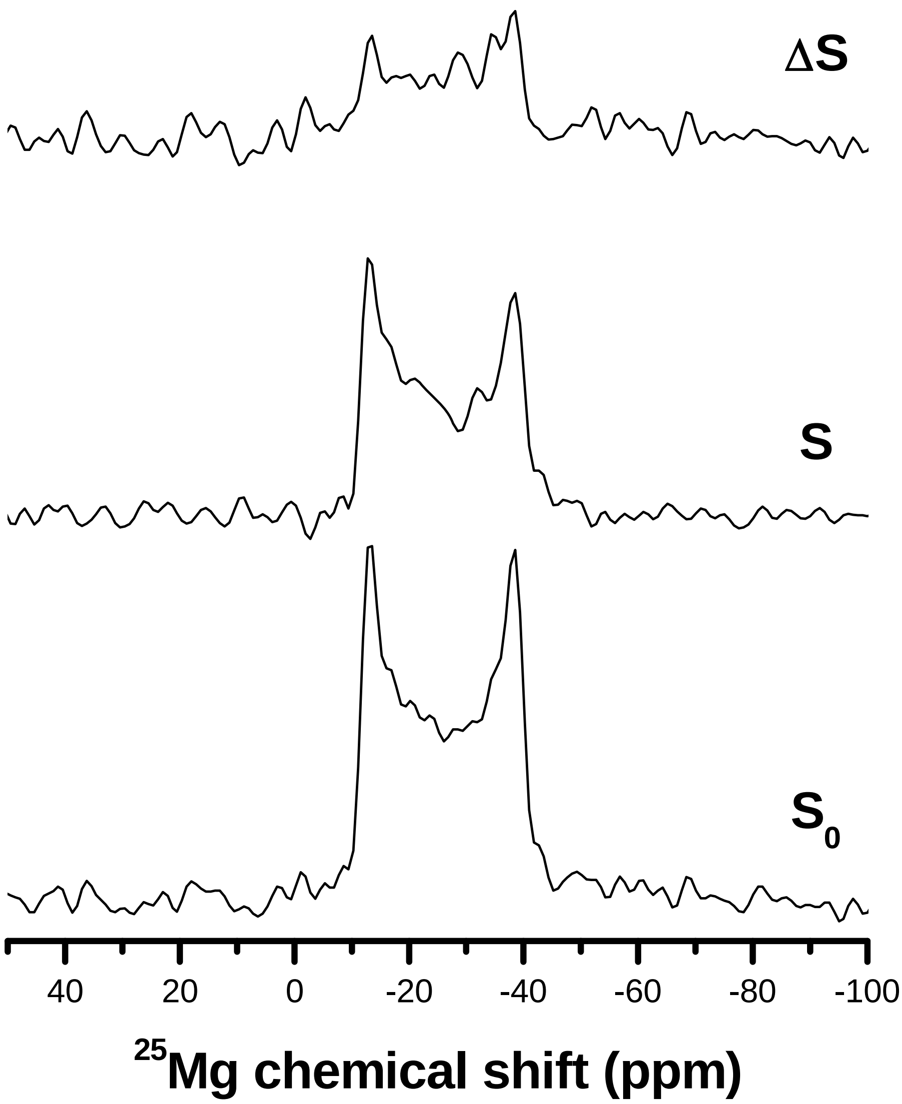

Figure S11. $^{25}Mg\{^{13}C\}$ REDOR spectra acquired for magnesite (^{25}Mg in natural abundance and 100% ^{13}C labeled) at a dephasing time of 4 ms. Sample mass was 19.3 mg and the number of transients accumulated for each spectrum is 2048. Exponential window function of line broadening equal to 40 Hz was applied before Fourier transformation.

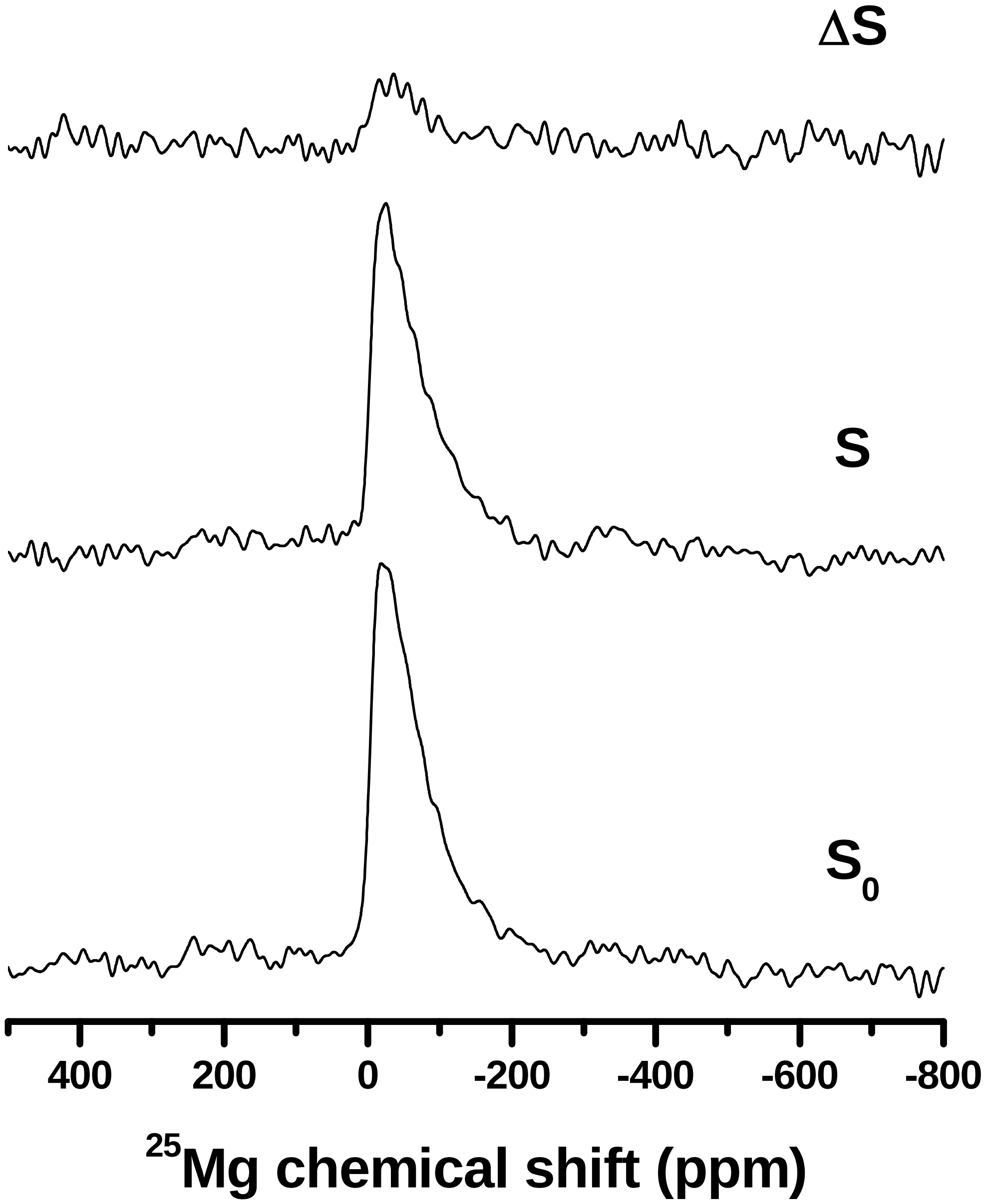

Figure S12. $^{25}Mg\{^{13}C\}$ REDOR spectra acquired for Mg0.6ACC (Mg/Ca = 0.20, 100% ^{25}Mg and ^{13}C labeled) at a dephasing time of 4 ms. Sample mass was 19.5 mg and the number of transients accumulated for each spectrum is 81960. Exponential window function of line broadening equal to 500 Hz was applied before Fourier transformation.

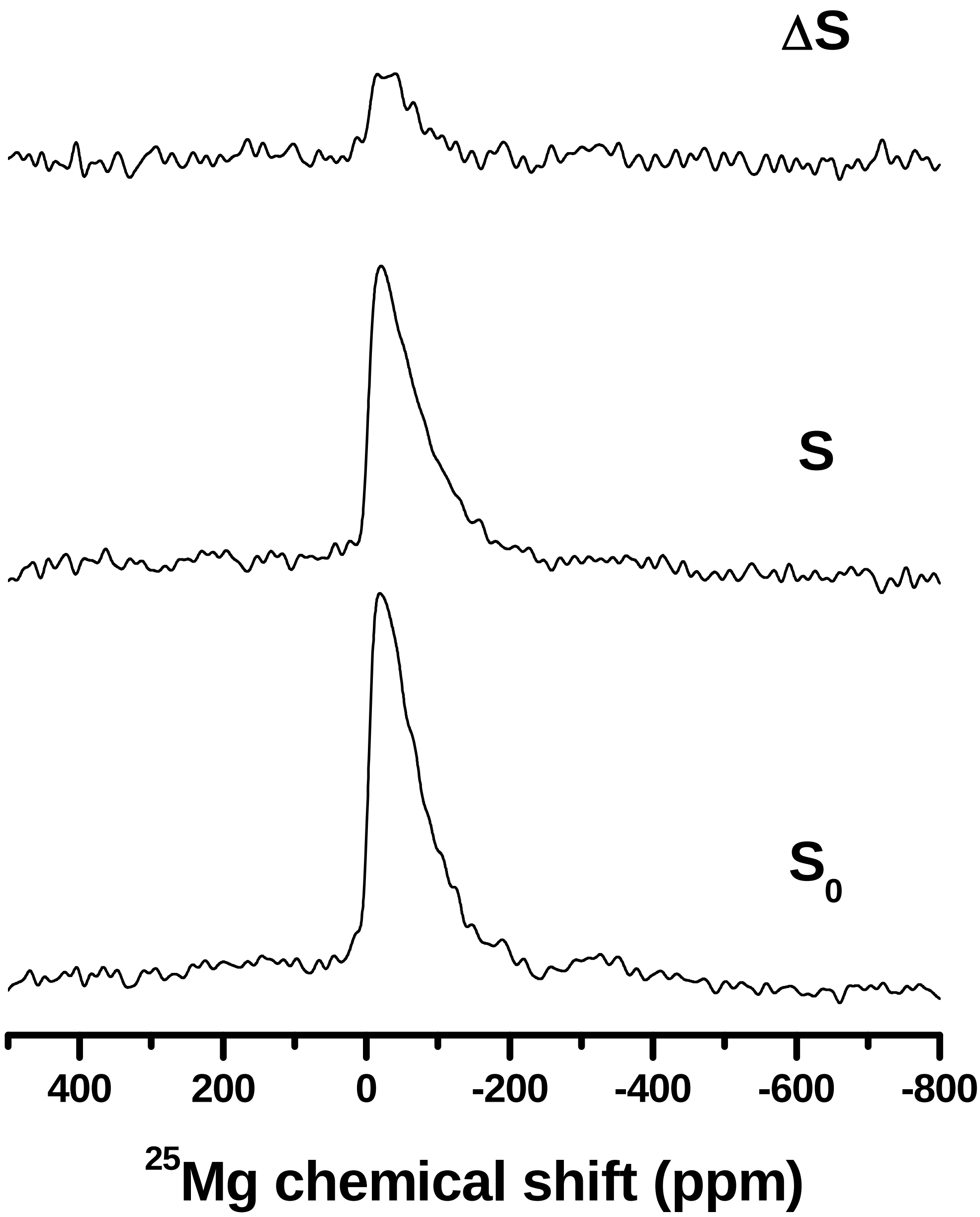

Figure S13. $^{25}Mg\{^{13}C\}$ REDOR spectra acquired for Mg5ACC (Mg/Ca = 0.79, 55% ^{25}Mg and 100% ^{13}C labeled) at a dephasing time of 4 ms. Sample mass was 21.4 mg and the number of transients accumulated for each spectrum is 81960. Exponential window function of line broadening equal to 500 Hz was applied before Fourier transformation.

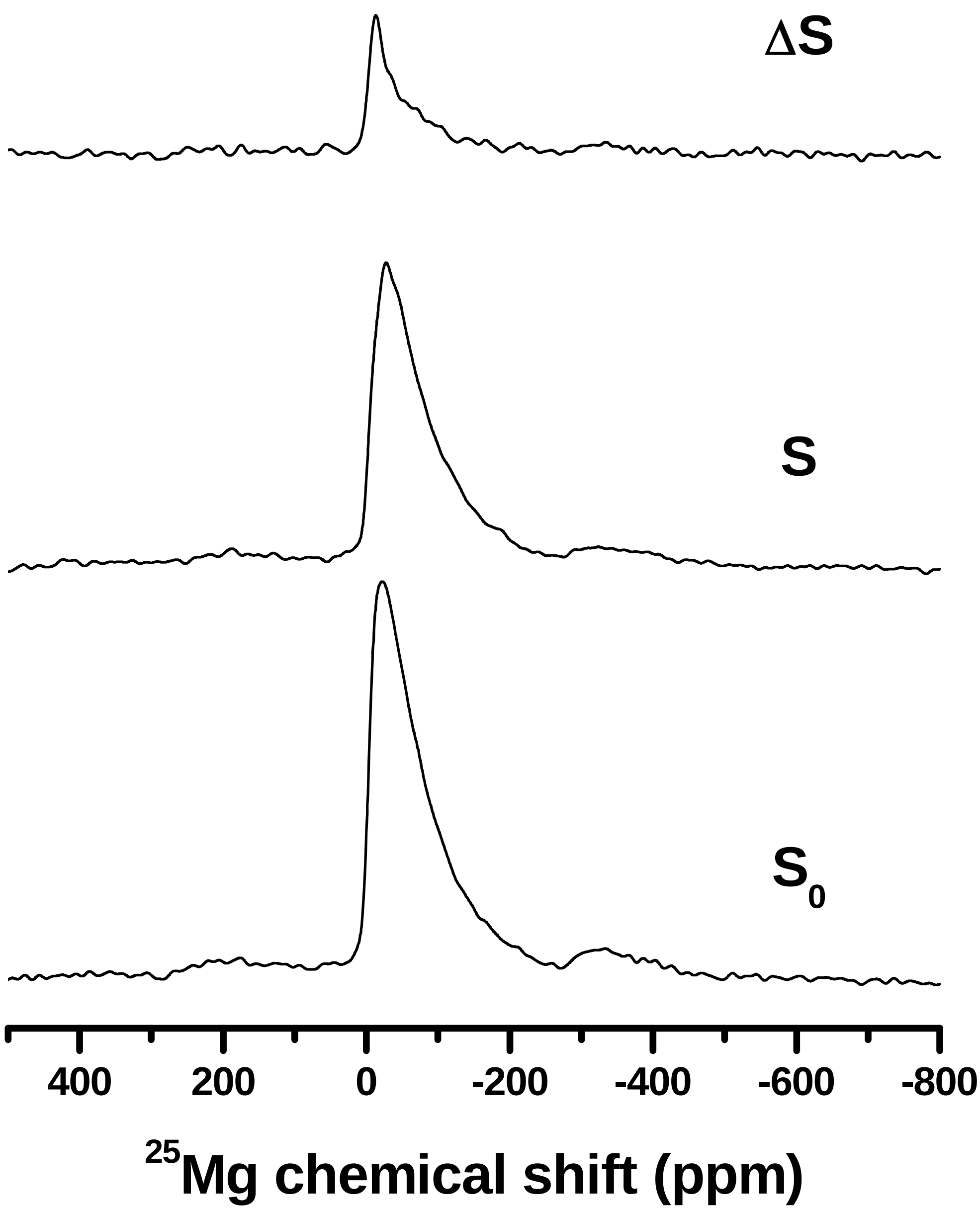

Figure S14. $^{25}Mg\{^{13}C\}$ REDOR spectra acquired for AMC (100% ^{25}Mg and ^{13}C labeled) at a dephasing time of 4 ms. Sample mass was 14.9 mg and the number of transients accumulated for each spectrum is 32768. Exponential window function of line broadening equal to 500 Hz was applied before Fourier transformation.

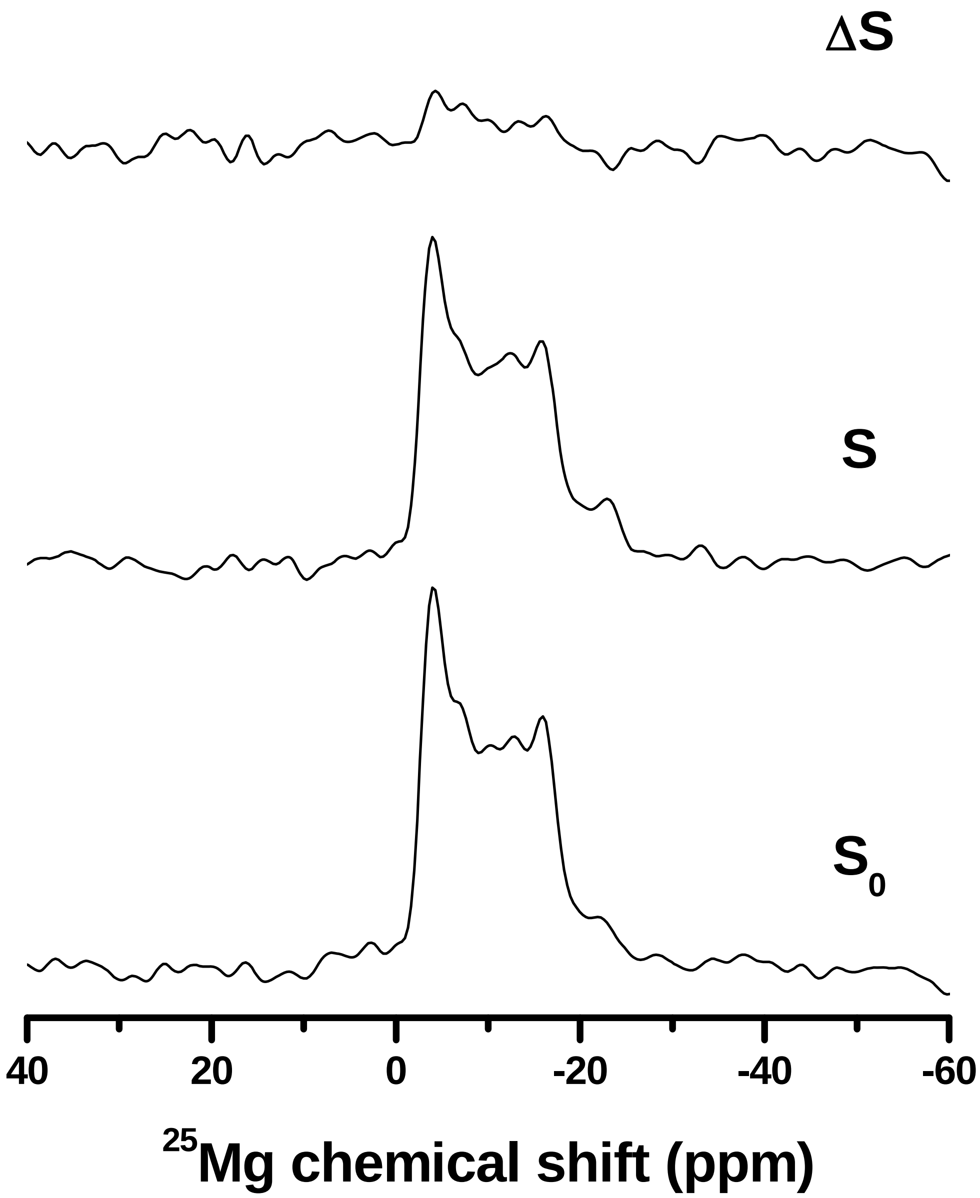

Figure S15. $^{25}Mg\{^{1}H\}$ C-REDOR spectra acquired for $Mg(NO_3)_2{\cdot}6H_2O$ in natural abundance at a dephasing time of 0.6 ms. Sample mass was 11.7 mg and the number of transients accumulated for each spectrum is 30720. Exponential window function of line broadening equal to 50 Hz was applied before Fourier transformation.

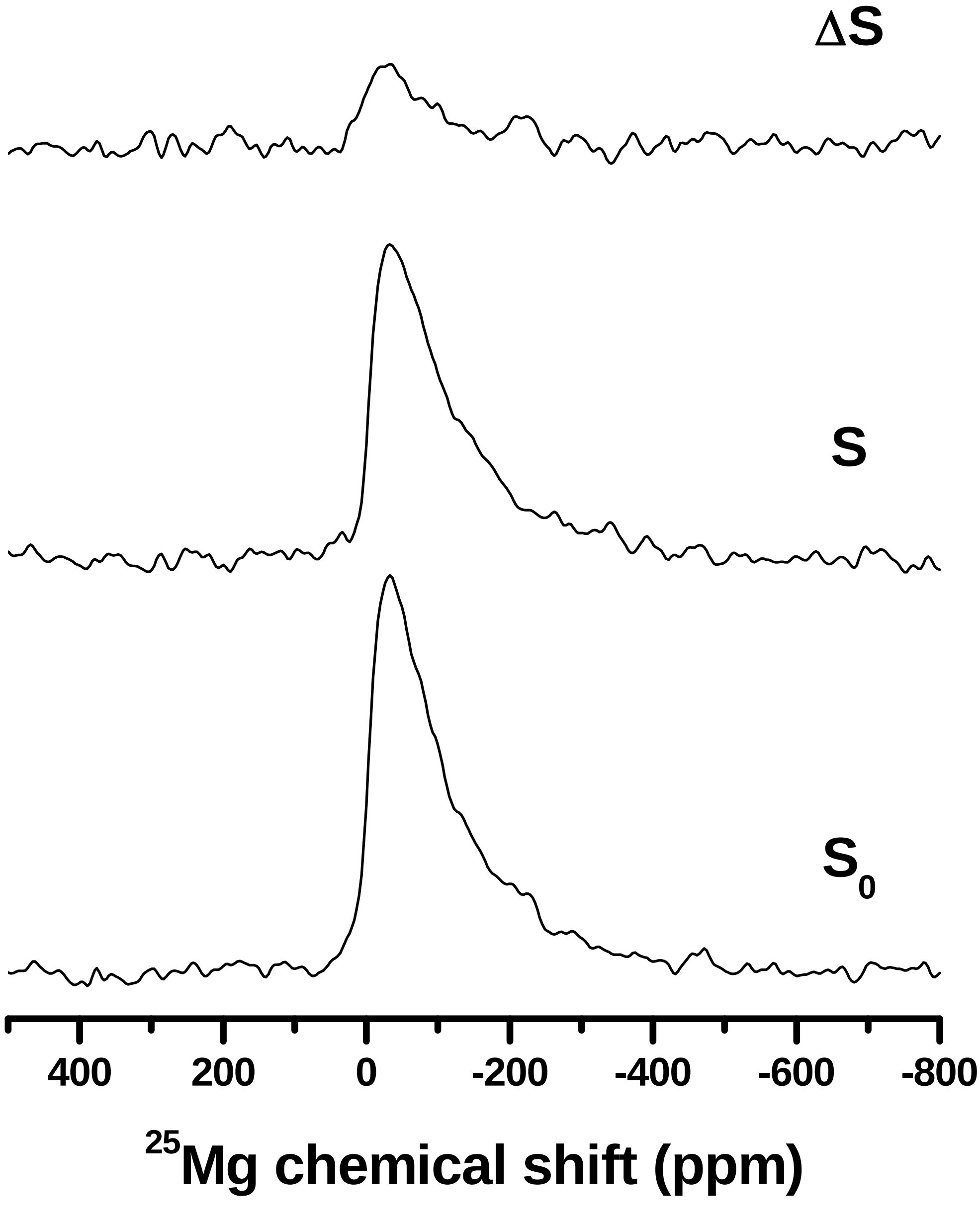

Figure S16. $^{25}Mg\{^{1}H\}$ C-REDOR spectra acquired for Mg0.6ACC at a dephasing time of 1.05 ms. Sample mass was 5.9 mg and the number of transients accumulated for each spectrum is 163840. Exponential window function of line broadening equal to 500 Hz was applied before Fourier transformation.

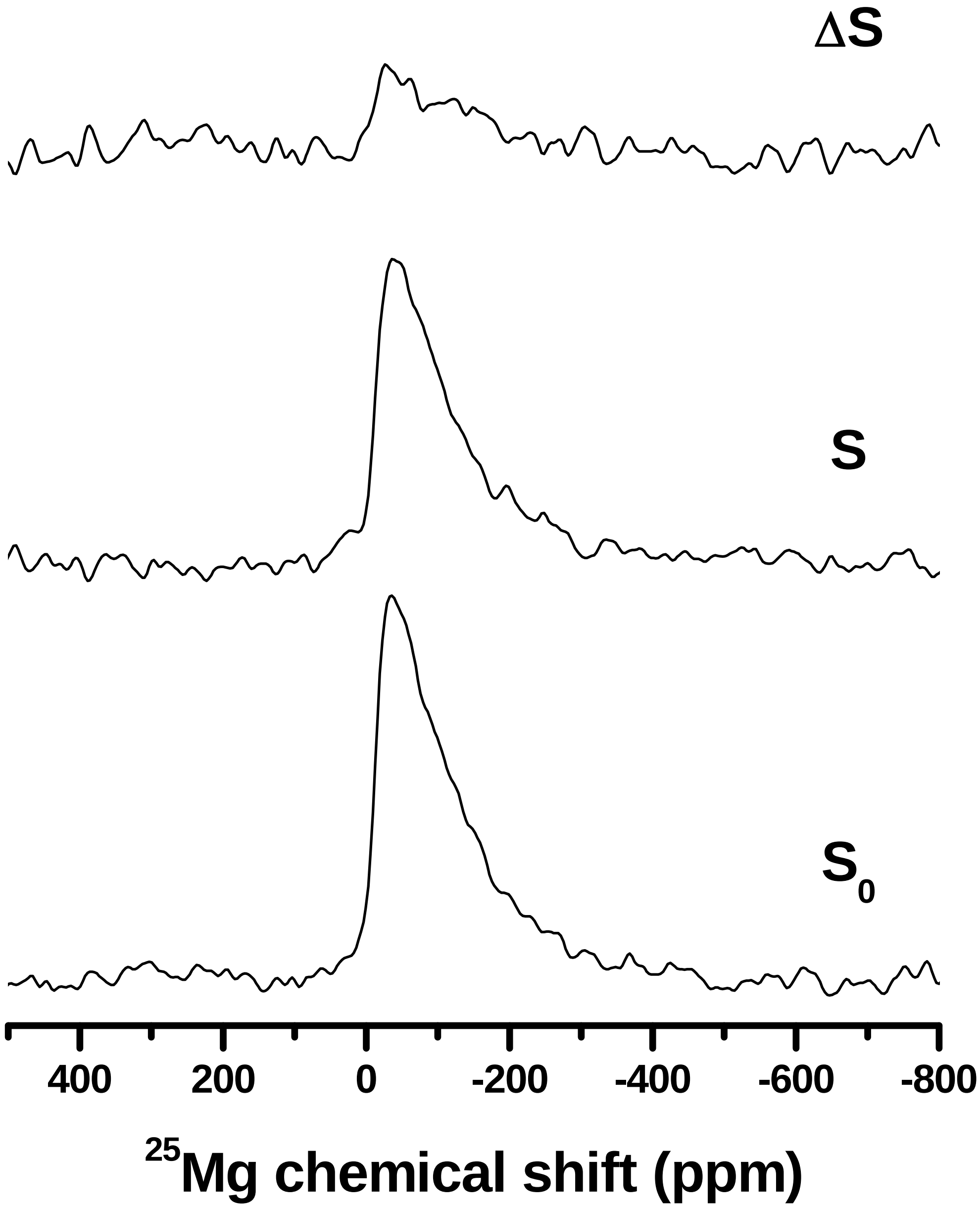

Figure S17. ^{25}Mg{^{1}H} C-REDOR spectra acquired for Mg5ACC at a dephasing time of 1.05 ms. Sample mass was 6.3 mg and the number of transients accumulated for each spectrum is 131072. Exponential window function of line broadening equal to 500 Hz was applied before Fourier transformation.

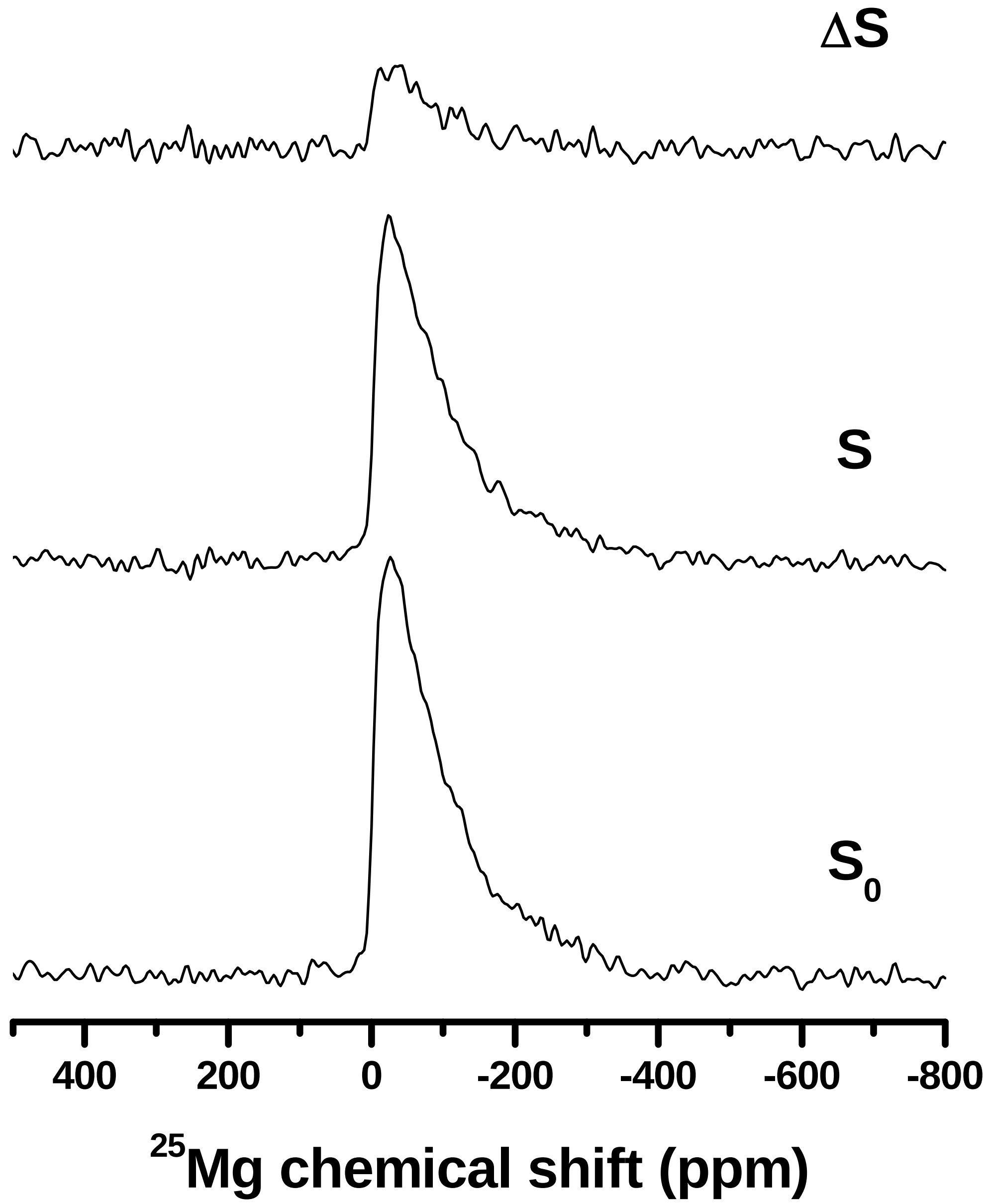

Figure S18. $^{25}Mg\{^{1}H\}$ C-REDOR spectra acquired for AMC at a dephasing time of 1.05 ms. Sample mass was 4.3 mg and the number of transients accumulated for each spectrum is 13768. Exponential window function of line broadening equal to 500 Hz was applied before Fourier transformation.

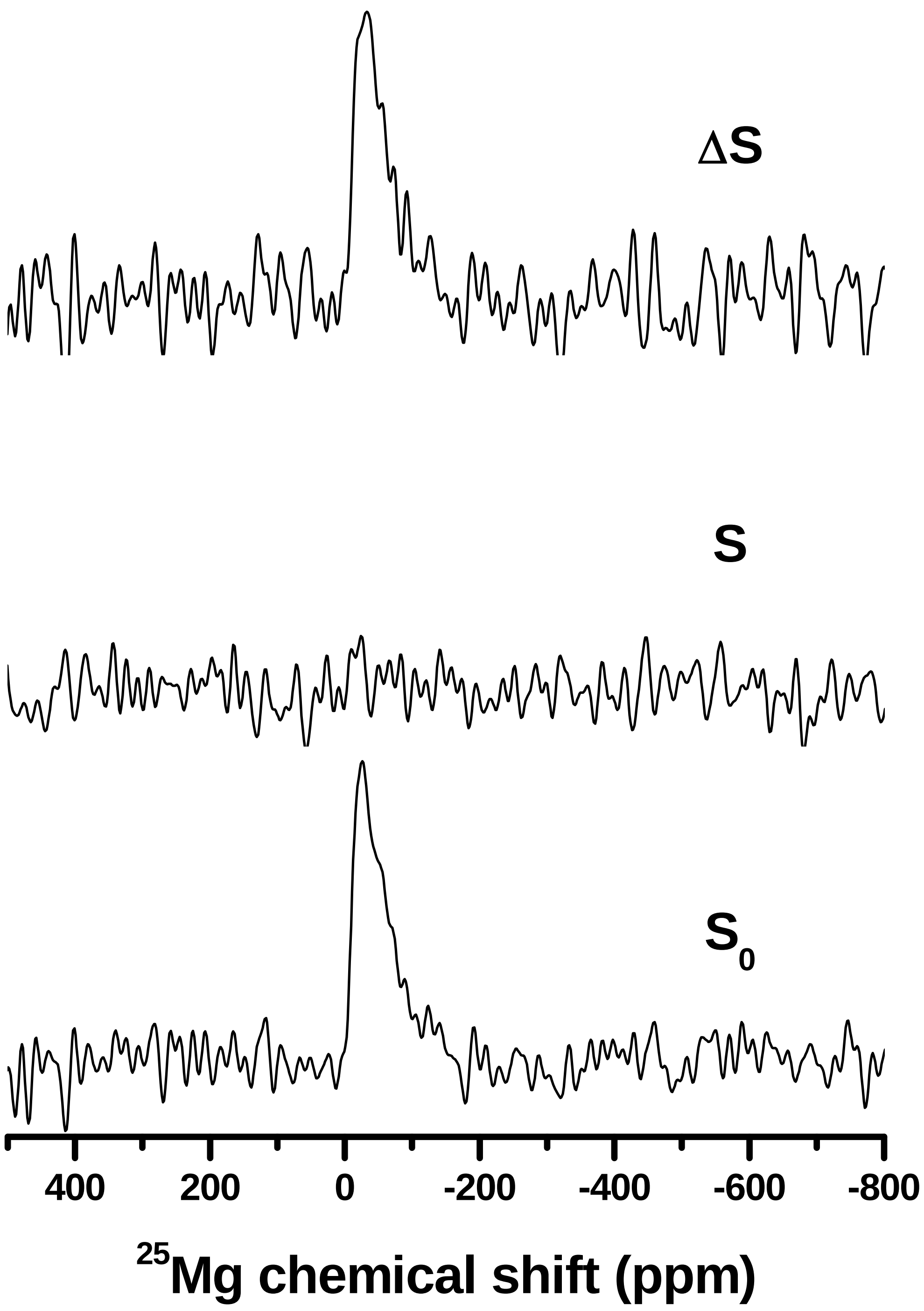

Figure S19. ^{25}Mg{^{1}H} C-REDOR spectra acquired for AMC at a dephasing time of 9.45 ms. The number of transients accumulated for each spectrum is 49152. Exponential window function of line broadening equal to 500 Hz was applied before Fourier transformation.

Table S1. Summary of the ^{25}Mg spectral center of gravity (δ_{cg}) obtained for the amorphous samples

Samples	δ_{cg} at 9.4 T (ppm)	δ_{cg} at 14.1 T (ppm)	χ_Q (MHz)	δ_{cs} (ppm)
Mg0.6ACC	−103.7 ± 0.5	−60.9 ± 0.5	2.8 ± 0.2	−26.9 ± 0.5
Mg5ACC	−105.0 ± 0.5	−63.0 ± 0.5	2.7 ± 0.2	−29.3 ± 0.5
AMC	−97.7 ± 0.5	−61.6 ± 0.5	2.5 ± 0.2	−32.6 ± 0.5

$$\delta_{cg} = \delta_{cs} + \delta^{QIS}_{-\frac{1}{2},\frac{1}{2}}$$

where

$$\delta^{QIS}_{-\frac{1}{2},\frac{1}{2}} = -\frac{3}{40\nu_0^2}\left[\frac{\chi_Q}{I(2I-1)}\right]^2\left[I(I+1)-\frac{3}{4}\right]$$

I = 5/2 for Mg and ν_0 is the Larmor frequency in MHz.