**Supporting Information**

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Figure S1. 13C{1H} rotational echo double resonance (REDOR) dephasing for the 13C-labelled 0.55K2CO3.0.45MgCO3 glass obtained from the intensities of the spin echo (S0) and dephased (S) spectra. The data were acquired at 125.68 MHz (11.7 T) and a spinning rate of 8.0 kHz. The 13C spin echoes were obtained by direct excitation pulses of 4 and 8 μs (90°/180°). 1H dephasing employed 10μs 180° pulses every one-half rotor period.

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Figure S2. Comparison of 13C MAS-NMR and 13C{1H} rotational echo double resonance (REDOR) spectra of 13C-labelled 0.55K2CO3.0.45MgCO3 glass acquired at 125.68 MHz (11.7 T) and spinning rate of 1.95 kHz. (a) acquired by direct 13C excitation (DE) with 4 μs pulses separated by a 30 s relaxation delay; (b) REDOR dephased spectrum (S) at 77% dephasing (6 ms), emphasizing 13C weakly coupled to 1H; (c) REDOR difference spectrum (ΔS = S0 – S) at 30% dephasing (1 ms), emphasizing 13C more strongly coupled to 1H. Center band is denoted by triangle symbol; all other peaks are spinning sidebands. Analysis of these spinning sideband intensities for all three spectra yields chemical shift tensor values that are within uncertainty.

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Figure S3. 13C-detected 1H MAS-NMR spectra of 13C-labelled 0.55K2CO3.0.45MgCO3 glass acquired at 399.97 MHz (9.4 T) and a spinning rate of 8.0 kHz. Spectra correspond to 1-dimensional cross-sections from 2-dimensional CP-heteronuclear correlation data, taken at 13C chemical shifts corresponding to the main carbonate peak (a), and a minor hydrogen carbonate signal (b). The CP contact time was 2 ms. Center bands are denoted by symbols, including hydrogen carbonate (●; 12.5 ppm), rigid structural water (▼; 5.5 ppm), and hydroxyl (■; 1.1 ppm). All other peaks are spinning sidebands arising dominantly from the structural water.