Supporting Information

Model structures of molten salt-promoted MgO to probe the mechanism of $MgCO_3$ formation during CO_2 capture at a solid-liquid interface.

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Table S1. Depth of grooves in the laser ablated samples MgO_A and MgO_B determined by SEM using mechanically cleaved cross sections and optical profilometry, respectively. Note optical profilometry was only possible in MgO_B. In sample MgO_A the width of all grooves at the top was 100 µm and in MgO_B 200 µm.

Groove No.	MgO_A Depth (µm)	MgO_B Depth (µm)
1	8	6
2	28	11
3	61	11
4	107	22
5	172	44
6	238	84
7		122
8		155
9		180

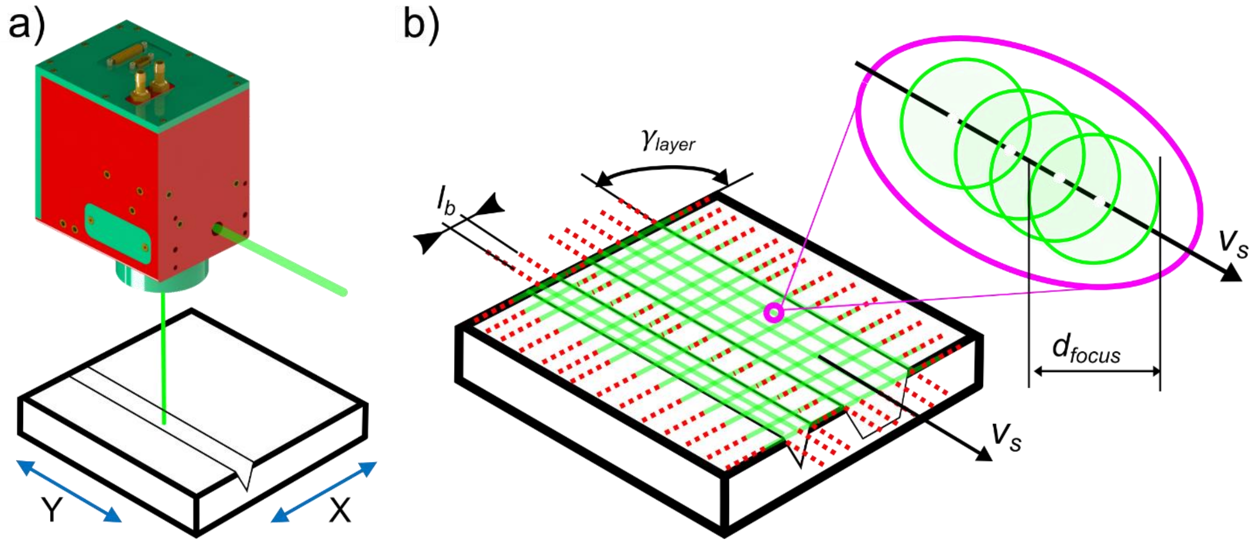

Figure S1. Illustration of the ultra-short pulse (USP) laser setup and ablation process. a) An USP laser source is guided to a Galvo-scanner head (red and green box) and focused onto the MgO crystal placed onto a xyz-stage. b) 2.5D volume ablation, i.e. layer-by-layer removal with cross-hatching. The laser beam (focal diameter d_{focus}) scans the surface with a certain scan speed (v_s) and a laser pulse repetition rate (f_{rep}). Within one layer, the laser scans the surface line by line with a specified line distance (l_b). For each subsequent layer, the sample is rotated by an angle of γ_{layer} yielding a cross-hatched pattern.

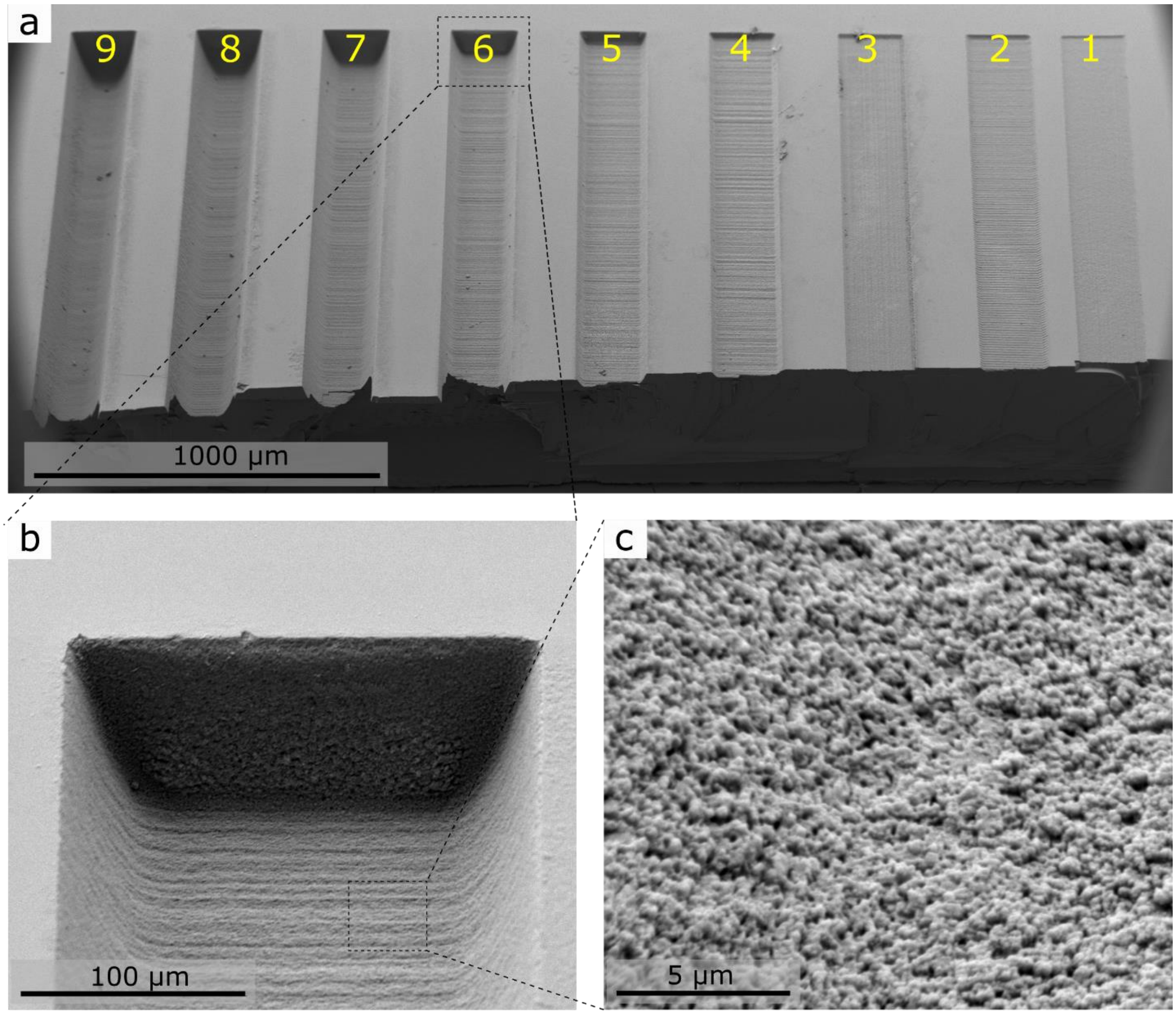

Figure S2. SEM images of the mechanically cleaved MgO_B sample. a) Tilted view of MgO_B showing grooves 9-1 (numbers in yellow font). b) Magnified tilted view of groove 6 in a). c) Top view of groove 6 showing the surface roughness of MgO at the bottom of the groove.

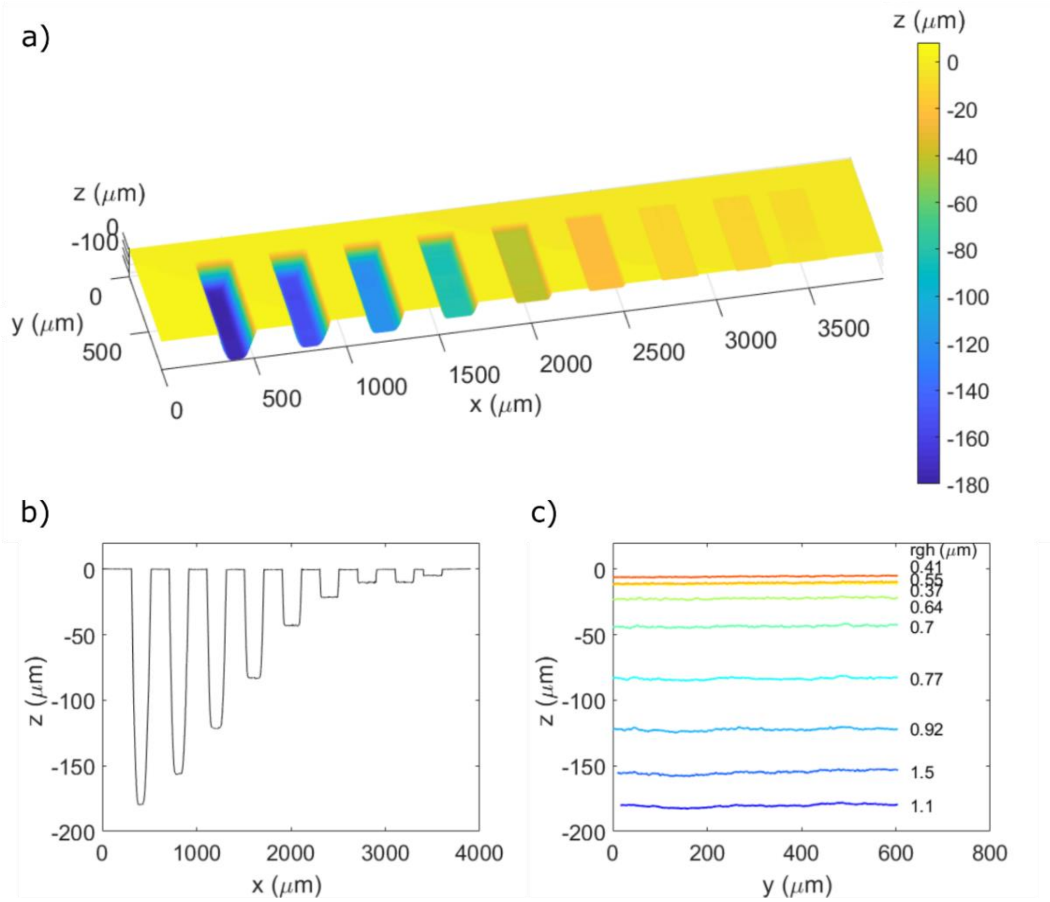

Figure S3. Optical profilometry measurements of MgO_B. a) Tilted 3D view of MgO-B showing grooves 9-1 from left to right. b) cross-section (x-direction) showing the depths of the grooves of sample given in a). c) line-plot along the length (y-direction) of all 9 grooves with the average roughness (rgh) given in µm. The average roughness (rgh) is calculated as the standard deviation from the mean *z* position along the length of the groove measured over a 600 µm window in the y-direction.

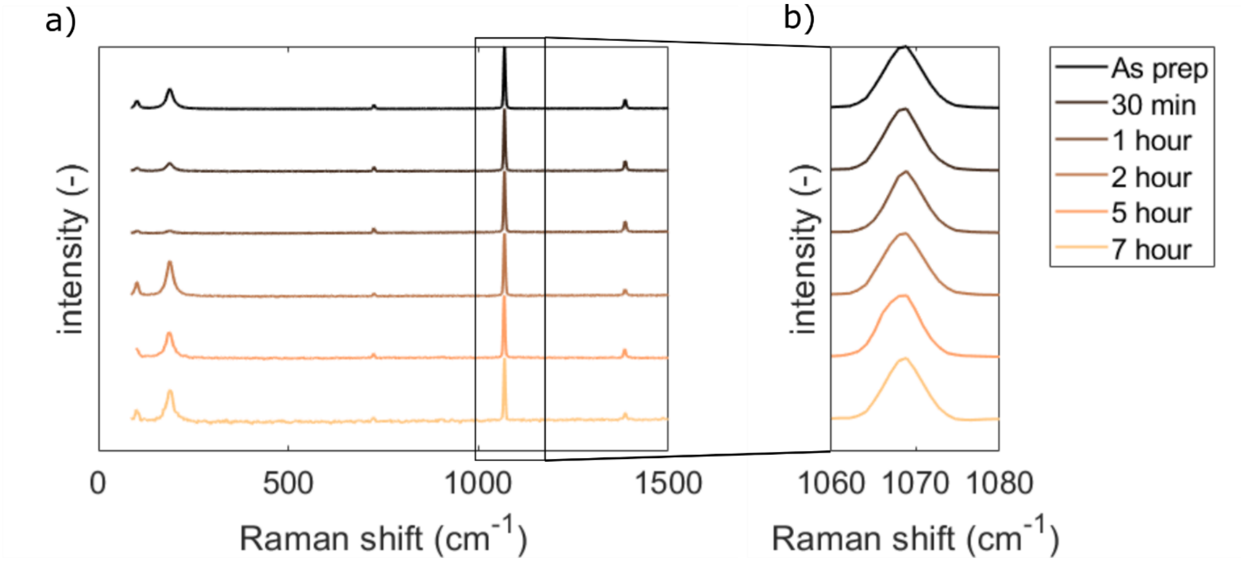

Figure S4. Ex situ time-dependent Raman spectroscopy of $NaNO_3$ in $NaNO_3$-MgO_B for the as-prepared sample and after exposure to CO_2 capture conditions (carbonation time ranging from 30 min to 7 hours). a) Full spectra and b) zoom of the most intense peak at 1067 cm^{-1}.

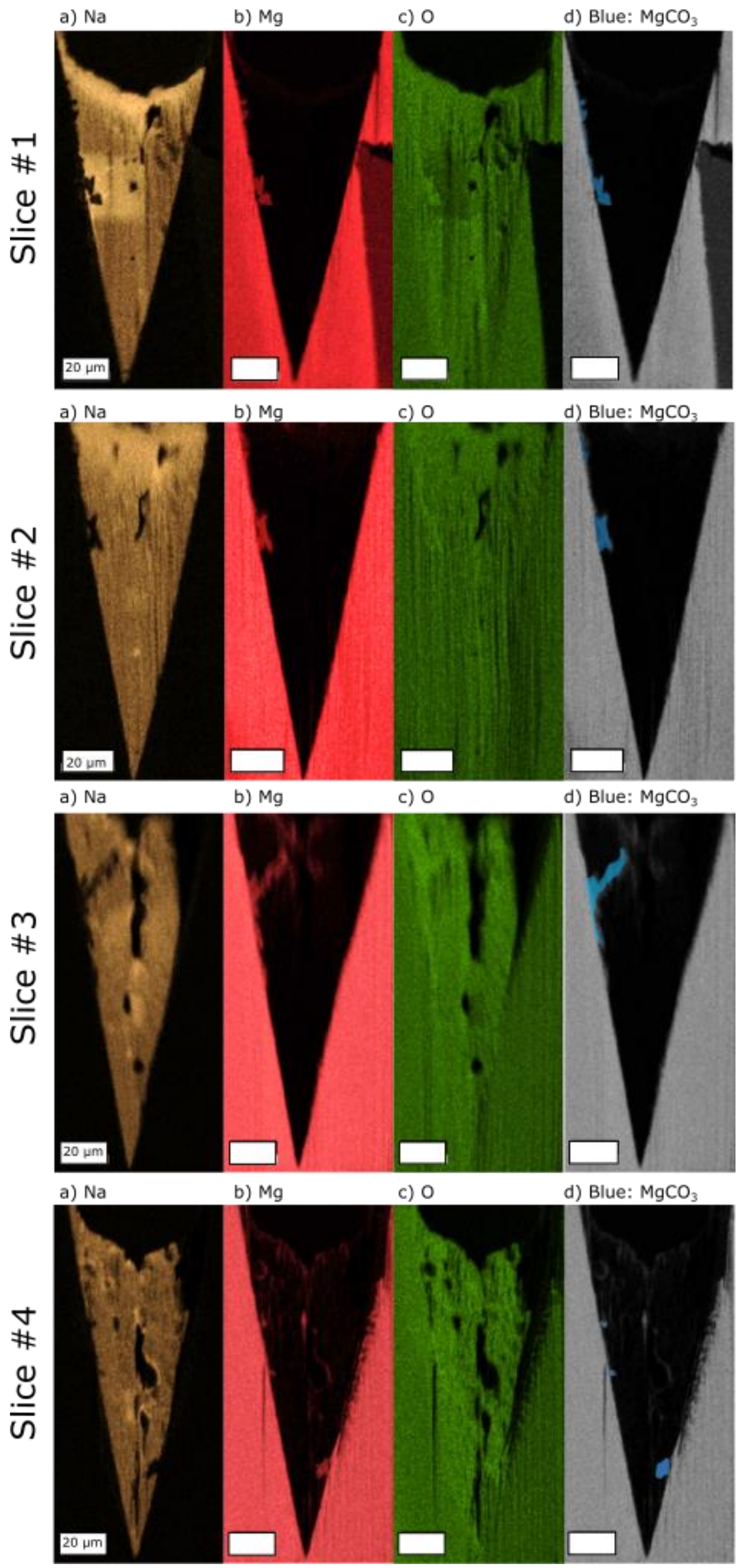

Figure S5. Plasma FIB SEM EDX at four different locations (Slice #1-4) along the length of the groove (y-direction) of $NaNO_3$-MgO_A$_{5\ hours\text{-}CO2}$. a)-c) SEM EDX elemental maps, d) SEM EDX Mg map in grey with blue overlay to highlight $MgCO_3$ particles as identified by the presence of Mg and absence of Na in EDX. Scalebar is 20 µm.

Figure S6. SEM image of grooves 3-4 (top to bottom) after 5 hours of carbonation at 330°C, i.e. $NaNO_3$-$MgO\_B_{5\ hours\text{-}CO2}$. $NaNO_3$ has been removed by a rinse in water and the sample was coated with PtPD prior to SEM (secondary electron) imaging.

Figure S7. SEM image of grooves 7-9 (top to bottom) after 5 hours of exposure to CO_2 at 330°C, i.e. $NaNO_3$-MgO_B$_{5\ hours\text{-}CO2}$. $MgCO_3$ particles grow close and far away from the TPB (top of groove). $NaNO_3$ has been removed by a rinse in water and the sample was coated by PtPd prior to SEM (secondary electron) imaging.

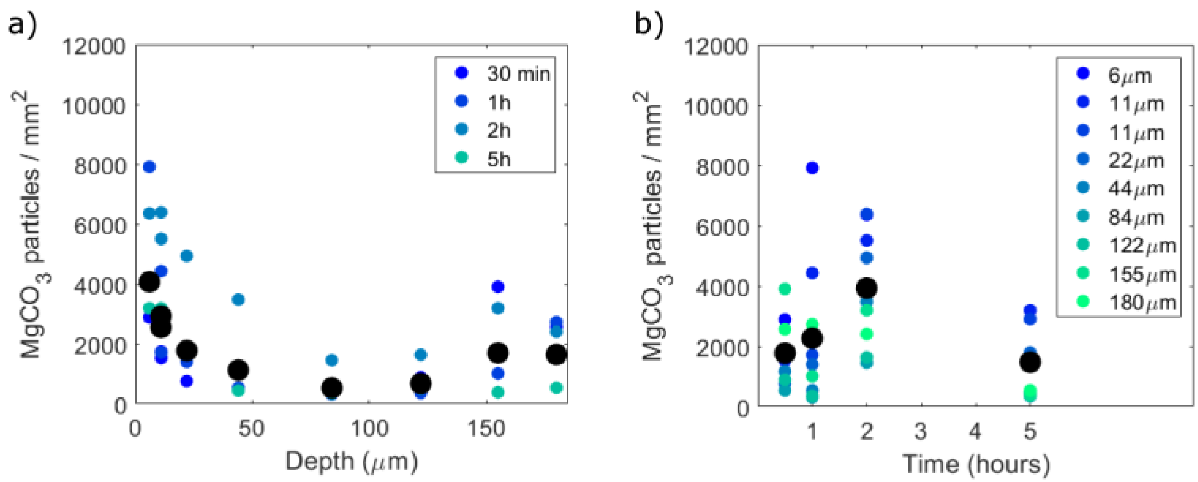

Figure S8. Number of $MgCO_3$ of particles per unit area at the bottom of the MgO grooves in MgO_B determined from SEM images using ImageJ. a) Number of $MgCO_3$ particles as a function of groove depth and b) number of $MgCO_3$ particles as function of carbonation time for the nine grooves studied (groove depth given in µm). The black data points correspond to the mean number of particles per unit area for a given groove depth (a) or a given carbonation time (b).

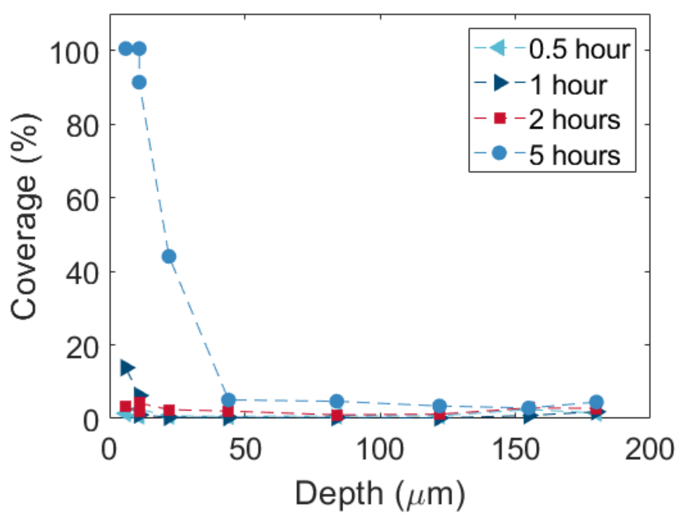

Figure S9. Coverage of the surface of MgO at the bottom of a groove as function of groove depth in MgO_B carbonated for 0.5, 1, 2, 5 hours. Coverage is defined as the area of $MgCO_3$ (top view) covering the surface of MgO divided by the total area of MgO at the bottom of a groove.