



## **Supplementary Materials**

**Table S1.** Properties of the employed solvent.

Solvent	Properties						
Solvent	Chemical Formula	<b>Boling Point (°C)</b>	REL (ppm)	Solubility in Water (wt %)*			
Ethanol	C <sub>2</sub> H <sub>6</sub> O	78.4	1000	∞			
Butanol	$C_4H_{10}O$	100	100	44.1			
n-butylacetate	C6H12O2	127	150	1.86			

REL: Recommended Exposure Limits, the concentration not to be exceed, mediated in a 40-h working week (US legislation). \* These values are reported in percentage and are expressed in weight (g/g): g of solvent in 100 g of water. The symbol  $\infty$  indicates that the solvent is completely miscible.

**Table S2.** Summary of coating results of all products, for all RH% conditions and all time intervals.

	Phase Identified with XRD/μFT-IR Analyses							
Sample	Portlandite	Vaterite	Calcite	Aragonite	Amorphous Calcium Carbonate			
2BU50 2W	_	✓	_	_	_			
2BU90 2W	_	✓	✓	_	_			
2BU50 1M	_	$\checkmark$	_	_	_			
2BU90 1M	_	✓	✓	_	_			
2BU50 3M	_	✓	_	_	_			
2BU90 3M	_	✓	✓	_	_			
NBU50 2W	_	_	_	_	✓			
NBU90 2W	_	✓	✓	_	_			
NBU50 1M	_	_	_	_	✓			
NBU90 1M	_	✓	_	_	_			
NBU50 3M	_	✓	_	_	_			
NBU90 3M	_	✓	_	_	_			
ETA50 2W	✓	✓	_	_	_			
ETA90 2W	✓	✓	✓	_	_			
ETA50 1M	_	✓	_	_	_			
ETA90 1M	_	✓	✓	_	_			
ETA50 3M	_	✓	_	_	_			
ETA90 3M	_	✓	✓	_	_			
CAL50 2W	_	_	_	✓	_			
CAL90 2W	_	✓	✓		_			
CAL50 1M	_	_		$\checkmark$	_			
CAL90 1M	_	✓	✓	_	_			
CAL503M	_	_	_	$\checkmark$	_			
CAL90 3M	_	✓	✓	_	_			

2BU: Ca(OEt)<sup>2</sup> diluted in 2-butanol; NBU: Ca(OEt)<sup>2</sup> diluted in n-butylacetate; ETA: Ca(OEt)<sup>2</sup> diluted in ethanol; CAL: CaLoSil. 2W: two weeks; 1M: one month; 3M: three months. 50: 50% RH; 90: 90% RH.

**Table S3.** Summary of the main vibrational bands associated to calcium carbonate polymorphs identified in this study by  $\mu$ FT-IR. Spectral range 700-1100 cm<sup>-1</sup>.

	Calcium Carbonate Polymorphs				
Spectral Band (cm <sup>-1</sup> )	Calcite	Vaterite	Amorphous Calcium Carbonate		
712	✓	-	_		
741/744/747	-	$\checkmark$	_		
864	-	-	✓		
876	$\checkmark$	-	_		
873/877	_	$\checkmark$	_		
1070	-	-	✓		
1088/1089	-	$\checkmark$	_		

**Table S4.** Amount of dry matter retained after one month for all stones treated with both application procedures and all products.

Amuliantion	Quantity of Dry Matter Retained (kg/m²)						
Application	ETA	2BU	NBU	CAL			
Lecce_AP1	0.063-0.067	0.046-0.056	0.077-0.085	0.010-0.014			
Lecce_AP2	0.067	0.034	0.097	0.086			
Noto_AP1	0.009 - 0.079	<0.010 *	0.008 - 0.136	$0.065 \pm 0.103$			
Noto_AP2	0.107	0.478	0.235	0.138			
Vicenza_AP1	00.010-0.014	0.034 - 0.068	0.062 - 0.090	0.170 – 0.240			
Vicenza_AP2	0.230	0.357	0.463	0.154			

AP1: brush till saturation; AP2: absorption by capillarity. \* For this sample, the quantity of product was very low to be measured with the available scale.

**Table S5.** Ultrasound pulse velocity values obtained from Lecce stone before and after treatment. The depth profile is expressed from treated (5 mm) to not treated surface (45 mm).

Don'th (mm)	Values of Ultrasound Pulse Velocity (m/s)							
Depth (mm)	NT	NBU_AP1	NT	NBU_AP2				
5	$3613.3 \pm 55.1$	$3710 \pm 17.3$	$3636.7 \pm 68.1$	$3693.3 \pm 28.9$				
10	$3546.7 \pm 11.5$	$3700 \pm 17.3$	$3713.3 \pm 25.2$	$3706.7 \pm 56.9$				
15	$3590 \pm 0$	$3673.3 \pm 56.9$	$3633.3 \pm 68.1$	$3713.3 \pm 25.2$				
20	$3563.3 \pm 25.1$	$3683.3 \pm 11.5$	$3670 \pm 96.4$	$3786.7 \pm 28.9$				
25	$3546.7 \pm 40.4$	$3646.7 \pm 63.5$	$3643.3 \pm 76.4$	$3723.3 \pm 41.6$				
30	$3580.0 \pm 36.1$	$3636.7 \pm 46.2$	$3626.7 \pm 28.8$	$3676.7 \pm 85.1$				
35	$3546.7 \pm 51.3$	$3580 \pm 17.3$	$3643.3 \pm 98.7$	$3720 \pm 17.3$				
40	$3570 \pm 36.1$	$3543.3 \pm 28.9$	$3633.3 \pm 25.2$	$3706.7 \pm 85.1$				
45	$3590.0 \pm 0$	$3616.7 \pm 92.9$	$3713.3 \pm 25.2$	$3780 \pm 36.6$				

NT: untreated stone; NBU: Ca(OEt)2 diluted in n-butylacetate; AP1: brushing till saturation; AP2: absorption by capillarity.

**Table S6.** Chromatic variation after both types of application procedures, for all stones treated with all products.

Amuliantion	$\Delta E^*$						
Application	ETA	2BU	NBU	CAL			
Lecce_AP1	$2.8 \pm 0.8$	$7.1 \pm 0.5$	$6.1 \pm 0.5$	$12.4 \pm 0.2$			
Lecce_AP2	$11.2 \pm 0.3$	$15.3 \pm 0.2$	$7.7 \pm 0.3$	$8.5 \pm 0.4$			
Noto_AP1	$4.9 \pm 0.5$	$8.7 \pm 0.4$	$5.3 \pm 0.4$	$16.6 \pm 0.2$			
Noto_AP2	$9.9 \pm 0.2$	$13.9 \pm 0.3$	$6.5 \pm 0.4$	$11.4 \pm 0.2$			
Vicenza_AP1	$2.1 \pm 1.3$	$1.1\pm0.5$	$3.3 \pm 1.9$	$6.9 \pm 0.3$			
Vicenza_AP2	$1.9 \pm 0.9$	$0.6 \pm 2.1$	$1.0 \pm 1.6$	$7.2 \pm 0.3$			

AP1: brush till saturation; AP2: absorption by capillarity.

**Table S7.** Ultrasound pulse velocity values obtained from Noto stone before and after treatment. The depth profile is expressed from treated (5 mm) to not treated surface (45 mm).

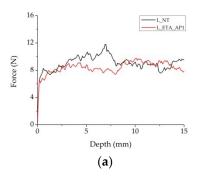
Depth		Values of Ultrasound Pulse Velocity (m/s)						
(mm)	NT	NBU_AP1	NT	NBU_AP2	NT	2BU_AP2	NT	ETA_AP2
5	3016.7 ±	3033.3 ±	3080 ±	3303.3 ±	2020 + 0	3033.3 ±	3253.3 ±	3286.7 ±
5	25.2	41.6	20	58.6	$3020 \pm 0$	30.5	23.1	30.5
10	$2980 \pm$	2042 + 47.2	$3120 \pm$	$3336.7 \pm$	$3033.3 \pm$	3063.3	2240 + 0	2220 + 24 6
10	26.5	$3043 \pm 47.3$	20	47.3	23.1	± 25.2	$3240 \pm 0$	$3220 \pm 34.6$
15	2050 + 0	2953.3 ±	$3033.3 \pm$	3313.3 ±	$3033.3 \pm$	$3063.3 \pm$	$3166.7 \pm$	$3186.7 \pm$
15	$2950 \pm 0$	90.7	11.5	11.5	23.1	25.2	11.5	11.5
20	2906.7 ±	$3026.7 \pm$	3033.3 ±	2220 . 0	$3053.3 \pm$	2040 - 20	3100 ±	$3093.3 \pm$
20	11.5	30.5	23.1	$3220 \pm 0$	11.5	$3040 \pm 20$	34.6	46.2
25	2900 ±	2040 - 70.2	3013.3	$3266.7 \pm$	3033.3 ±	$3043.3 \pm$	3133 ±	$3146.7 \pm$
25	52.9	$2940 \pm 79.3$	±25.2	30.5	23.1	25.2	23.1	61.1
20	2906.7 ±	2963.3 ±	2953.3 ±	$3266.7 \pm$	2996.7 ±	2000 - 17.2	$3166.3 \pm$	$3126.7 \pm$
30	11.5	11.5	15.3	11.5	37.9	$2990 \pm 17.3$	30.5	23.1
25	2936.7 ±	2000 + 247	$2956.7 \pm$	$3146.7 \pm$	2990 ±	$3033.3 \pm$	$3146.7 \pm$	$3153.3 \pm$
35	5.3	$2980 \pm 34.6$	11.5	80.8	26.5	11.5	30.5	41.6
40	2936.7 ±	2000 264	$2986.7 \pm$	$3146.7 \pm$	$3026.7 \pm$	$3070 \pm 36.1$	3120 ±	$3126.7 \pm$
40	28.9	$2990 \pm 36.1$	35.1	41.6	11.5		52.9	57.7
45	$2920 \pm 0$ $2980 \pm 26.5$	$3016.7 \pm$	$3073.3 \pm$	$3070 \pm$	3093.3 ±	$3180 \pm$	3226.7 ±	
45		2980 ± 26.5	5.7	61.1	36.1	47.3	34.6	30.5

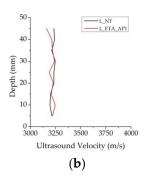
NT: untreated stone; NBU: Ca(OEt)<sub>2</sub> diluted in n-butylacetate; 2BU: Ca(OEt)<sub>2</sub> diluted in 2-butanol; ETA: Ca(OEt)<sub>2</sub> diluted in ethanol. AP1: brushing till saturation; AP2: absorption by capillarity.

**Table S8.** Ultrasound pulse velocity values obtained from Vicenza stone before and after treatment. The depth profile is expressed from treated (5 mm) to not treated surface (45 mm).

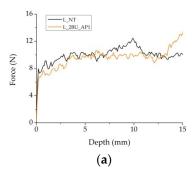
Donth (mm)	Values of Ultrasound Pulse Velocity (m/s)						
Depth (mm)	NT	2BU_AP1	NT	NBU_AP2			
5	$3293.3 \pm 45.1$	$3380 \pm 20$	$3053.3 \pm 23.1$	$3280 \pm 52.9$			
10	$3256.7 \pm 23.1$	$3276.7 \pm 11.5$	$3053.3 \pm 41.6$	$3316.7 \pm 42.3$			
15	$3263.3 \pm 23.1$	$3210 \pm 34.6$	$3086.7 \pm 30.5$	$3293.3 \pm 11.5$			
20	$3196.7 \pm 30.5$	$3223.3 \pm 11.5$	$3023.3 \pm 15.3$	$3190 \pm 0$			
25	$3210 \pm 34.6$	$3243.3 \pm 11.5$	$3046.7 \pm 11.5$	$3246.7 \pm 30.6$			
30	$3230 \pm 20$	$3250 \pm 20$	$3086.7 \pm 80.8$	$3246.7 \pm 11.5$			
35	$3210 \pm 20$	$3256.7 \pm 23.1$	$3026.7 \pm 80.8$	$3123.3 \pm 76.3$			
40	$3256.7 \pm 11.5$	$3183.3 \pm 11.5$	$3033.3 \pm 41.6$	$3126.7 \pm 41.6$			
45	$3236.7 \pm 11.5$	$3230 \pm 20$	$3073.3 \pm 50.3$	$3053.3 \pm 61.1$			

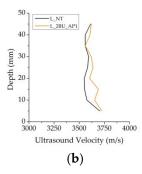
NT: untreated stone; 2BU: Ca(OEt)2 diluted in 2-butanol; NBU: Ca(OEt)2 diluted in n-butyalcetate; AP1: brushing till saturation; AP2: absorption by capillarity.



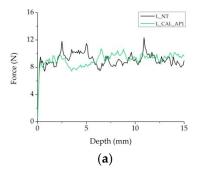


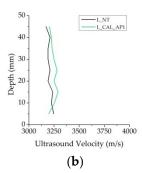
**Figure S1.** Lecce stone treated with ETA applied by brushing till saturation AP1 (L\_ETA\_AP1): (a) drilling resistance and (b) UPV profile. NT: untreated part of the stone for DRMS and untreated stone for UPV.



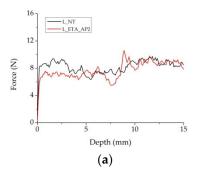


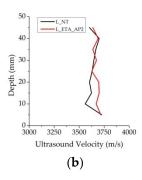
**Figure S2.** Lecce stone treated with 2BU applied by brushing till saturation AP1 (L\_2BU\_AP1): (a) drilling resistance and (b) UPV profile. NT: untreated part of the stone for DRMS and untreated stone for UPV.



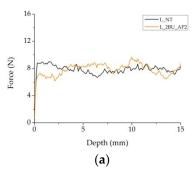


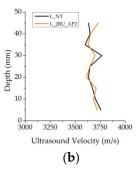
**Figure S3.** Lecce stone treated with CAL applied by brushing till saturation AP1 (L\_CAL\_AP1): (a) drilling resistance and (b) UPV profile. NT: untreated part of the stone for DRMS and untreated stone for UPV.



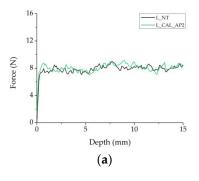


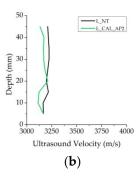
**Figure S4.** Lecce stone treated with ETA applied through absorption by capillarity AP2 (L\_ETA\_AP2): (a) drilling resistance and (b) UPV profile. NT: untreated part of the stone for DRMS and untreated stone for UPV.



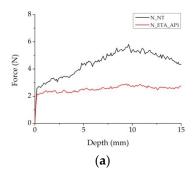


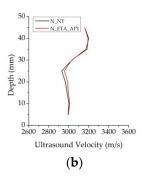
**Figure S5.** Lecce stone treated with 2BU applied through absorption by capillarity AP2 (L\_2BU\_AP2): (a) drilling resistance and (b) UPV profile. NT: untreated part of the stone for DRMS and untreated stone for UPV.



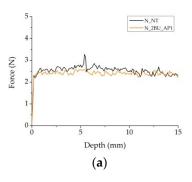


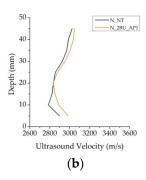
**Figure S6.** Lecce stone treated with CAL applied through absorption by capillarity AP2 (L\_CAL\_AP2): (a) drilling resistance and (b) UPV profile. NT: untreated part of the stone for DRMS and untreated stone for UPV.



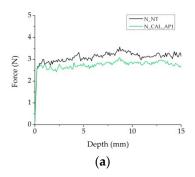


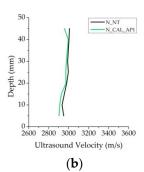
**Figure S7.** Noto stone treated with ETA applied by brushing till saturation AP1 (N\_ETA\_AP1): (a) drilling resistance and (b) UPV profile. NT: untreated part of the stone for DRMS and untreated stone for UPV.



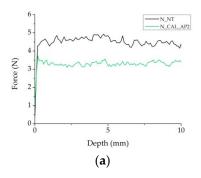


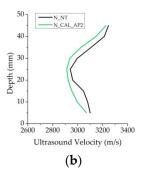
**Figure S8.** Noto stone treated with 2BU applied by brushing till saturation AP1 (N\_2BU\_AP1): (a) drilling resistance and (b) UPV profile. NT: untreated part of the stone for DRMS and untreated stone for UPV.



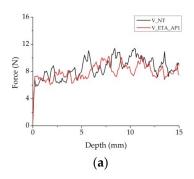


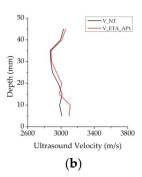
**Figure S9.** Noto stone treated with CAL applied by brushing till saturation AP1 (N\_CAL\_AP1): (a) drilling resistance and (b) UPV profile. NT: untreated part of the stone for DRMS and untreated stone for UPV.



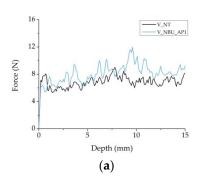


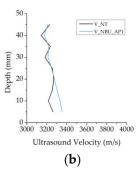
**Figure S10.** Noto stone treated with CAL applied through absorption by capillarity AP2 (N\_CAL\_AP2): (a) drilling resistance and (b) UPV profile NT: untreated part of the stone for DRMS and untreated stone for UPV.



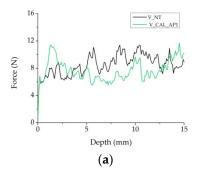


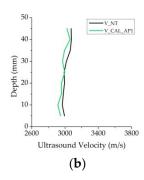
**Figure S11.** Vicenza stone treated with ETA applied by brushing till saturation AP1 (V\_ETA\_AP1): (a) drilling resistance and (b) UPV profile NT: untreated part of the stone for DRMS and untreated stone for UPV.



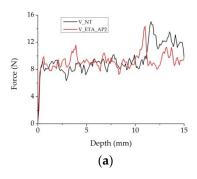


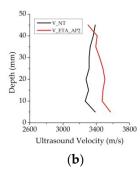
**Figure 12.** Vicenza stone treated with NBU applied by brushing till saturation AP1 (V\_NBU\_AP1): (a) drilling resistance and (b) UPV profile. NT: untreated part of the stone for DRMS and untreated stone for UPV.



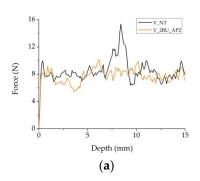


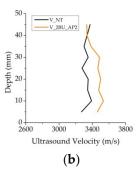
**Figure S13.** Vicenza stone treated with CAL applied by brushing till saturation AP1 (V\_CAL\_AP1): (a) drilling resistance and (b) UPV profile NT: untreated part of the stone for DRMS and untreated stone for UPV.



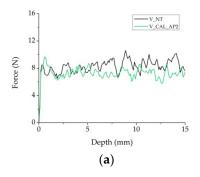


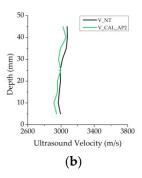
**Figure S14.** Vicenza stone treated with ETA applied through absorption by capillarity AP2 (V\_ETA\_AP2): (a) drilling resistance and (b) UPV profile. NT: untreated part of the stone for DRMS and untreated stone for UPV.





**Figure S15.** Vicenza stone treated with 2BU applied through absorption by capillarity AP2 (V\_2BU\_AP2): (a) drilling resistance and (b) UPV profile. NT: untreated part of the stone for DRMS and untreated stone for UPV.





**Figure S16.** Vicenza stone treated with CAL applied through absorption by capillarity AP2 (V\_CAL\_AP2): (a) drilling resistance and (b) UPV profile. NT: untreated part of the stone for DRMS and untreated stone for UPV.