Electronic Supplementary Information

Protecting white Carrara marble with organophosphorus salts: case study of ammonium hydrogen phenylphosphonate

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Table S1. Methodology adopted for the synthesis and characterization of compounds **1** and **2**, the preparation and treatments on Carrara marble samples, and the characterization of treated mock-ups.

1. Synthesis and Characterization	2. Reactivity Towards $CaCO_3$ Powder	3. Assays with white Carrara marble Fragments		
Synthesis of compound 1 2 $PhPO_3H_2$ + $(NH_4)_2CO_3$ → 2 $(NH_4)(PhPO_3H)$ + CO_2 + H_2O	Synthesis of compound 2 (Compound 1 + $CaCO_3$ powder)	Thermal Weathering →	Application of Ammonium Hydrogen Phenylphosphonate 5%w/w (0.3 mol L^{-1})	➔ Immersion treat. ➔ Spraying treat. ➔ Brushing treat.
Fourier Transform Infrared Spectroscopy (FT-IR)	Fourier Transform Infrared Spectroscopy (FT-IR)	Grazing Incidence X-ray Diffraction (GID-XRD)	Colorimetry	Capillary Test Uptake
Nuclear Magnetic Resonance (NMR) in a solution and solid state	Nuclear Magnetic Resonance (NMR) in solid state	Water Saturation Measurements (including under pressure)	Ultrasonic Propagation	Determination of Drying Properties
UV-Vis Spectroscopy and Solubility Determination	Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)	Scanning Electron Microscopy (SEM)	Helium Picnometry	Mercury Intrusion Porosimetry
3D Electron Diffraction (3D ED)	Powder X-ray Diffraction (PXRD)	Optical Microscopy (OM)	Vapour Water Permeability	Shore Scale Hardness (C and D)
Elemental Analysis	Melting Point	Surface Roughness Determination	Liquid Water Permeability	Pull-off Test

Table S2. Selected crystal data and structure refinement for compound **2**.

CCDC deposition number	2473954
Empirical formula	$C_6H_9CaO_5P$
Formula weight	232.18
Temperature/K	175(5)
Crystal system	orthorhombic
Space group	*Pbca*
a/Å	29.5555(17)
b/Å	10.9536(4)
c/Å	5.6509(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1829.42(16)
Z	8
ρ_{calc}g/cm^3	1.686
Radiation	electron (λ = 0.0251)
2Θ range for data collection/°	0.164 to 1.8
Reflections collected	6985
Independent reflections	1686 [R_{int} = 0.1236, R_{sigma} = 0.1129]
Data/restraints/parameters	1686/143/122
Goodness-of-fit on F^2	1.288
Final R indexes [I ≥ 2σ (I)]	R_1 = 0.1861, wR_2 = 0.4445
Final R indexes [all data]	R_1 = 0.2042, wR_2 = 0.4528
Largest diff. peak/hole / e·Å^{-3}	0.42/−0.30

Table S3: Young elastic module determined for white Carrara marble stone mock–ups exposed to T–S and F–T cycles as pristine, thermally weathered, and immersion-, brushing-, and spraying-treated with a 5.0% w/w solution of compound **1**, along with relative variations (Δ% loss) compared to the values before the treatments.

Treatment		Young elastic module ($MN \cdot m^{-2}$)	$\Delta\%_{loss}$
T–S	Pristine	11.8 ± 0.4	**–16**
	Thermally weathered	1.0 ± 0.1	**–58**
	Immersion TR	7.3 ± 0.2	–5
	Brushing TR	14.8 ± 0.5	–6
	Spraying TR	10.4 ± 0.3	–10
F–T	Pristine	10.9 ± 0.3	**–27**
	Thermally weathered	2.5 ± 0.1	–4
	Immersion TR	7.7 ± 0.2	–8
	Brushing TR	14.9 ± 0.5	**–17**
	Spraying TR	8.4 ± 0.2	–8

Table S4: Physical characterisation of white Carrara marble stone mock–ups as pristine, thermally weathered, and immersion-, brushing-, and spraying-treated with a 5.0% w/w solution of compound **1** before and after the acidic attack.

	Treatment	Rz (µm)	ΔE CIELAB2000	WI CIELAB2000	v_{uts} (km·s^{-1})	Ed (MN·m^{-2})	HD
Before Acid attack	Pristine	45(5)	–	85.05	2.8 ± 0.2	14.1 ± 0.5	87(1)
	Thermally weathered	61(6)	–	79.41	1.2 ± 0.1	2.41 ± 0.04	75(1)
	Immersion TR	48(3)	–	85.23	2.1 ± 0.1	7.7 ± 0.2	86(2)
	Brushing TR	47(4)	–	72.75	3.1 ± 0.2	16.5 ± 0.6	90(2)
	Spraying TR	40(5)	–	84.12	2.2 ± 0.2	8.2 ± 0.2	92.3(8)
After Acid attack	Pristine	**26(6)**	2.05	**73.02**	2.7 ± 0.2	12.8 ± 0.4	88.3(7)
	Thermally weathered	54(11)	3.20	**67.72**	1.1 ± 0.1	2.0 ± 0.03	74(6)
	Immersion TR	**63(11)**	1.56	**76.42**	1.9 ± 0.1	6.1 ± 0.2	87.7(2)
	Brushing TR	49(9)	0.61	75.00	3.4 ± 0.2	20.3 ± 0.9	90.2(7)
	Spraying TR	42(3)	2.18	**72.32**	2.3 ± 0.2	9.4 ± 0.3	92(1)

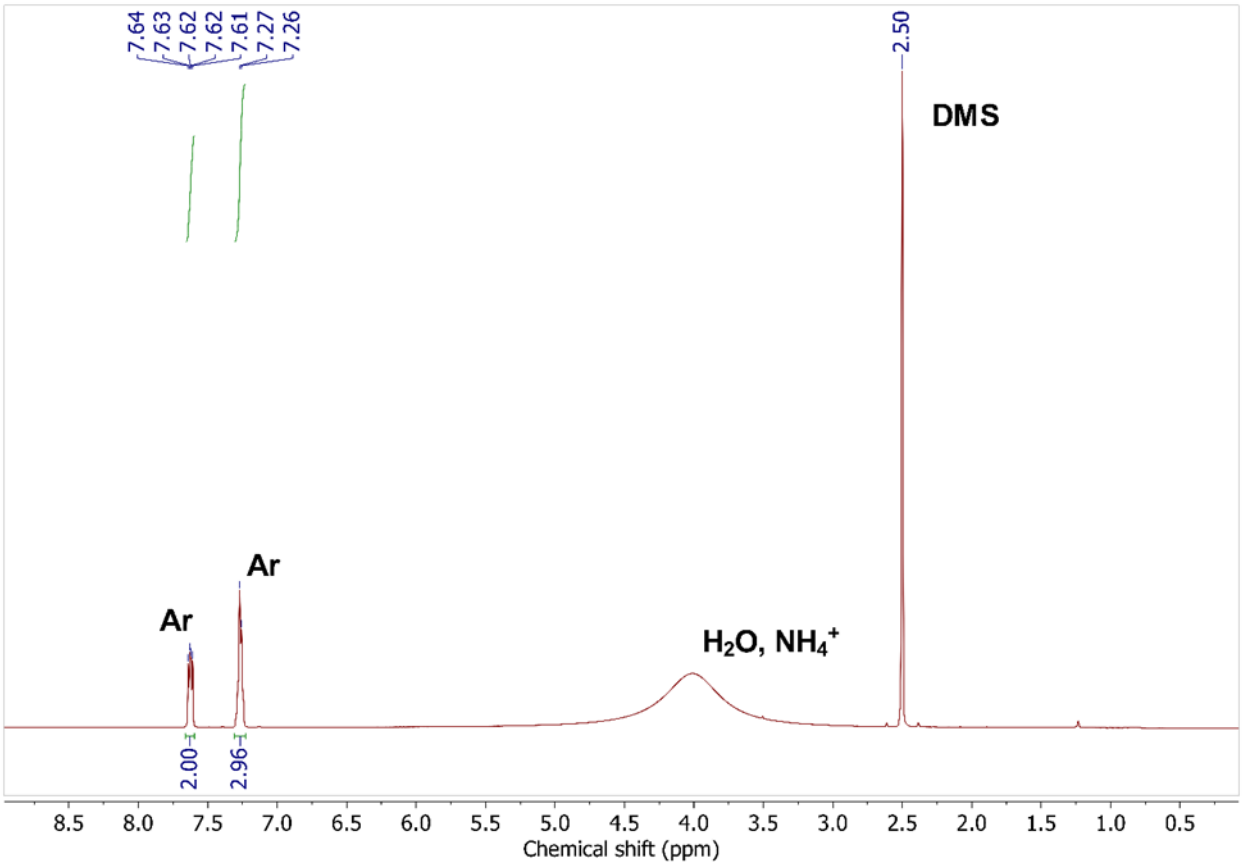


Figure S1. ^{1}H-NMR spectrum recorded for compound **1** in DMSO-d_6 solution. Marked signals are attributed as labelled.

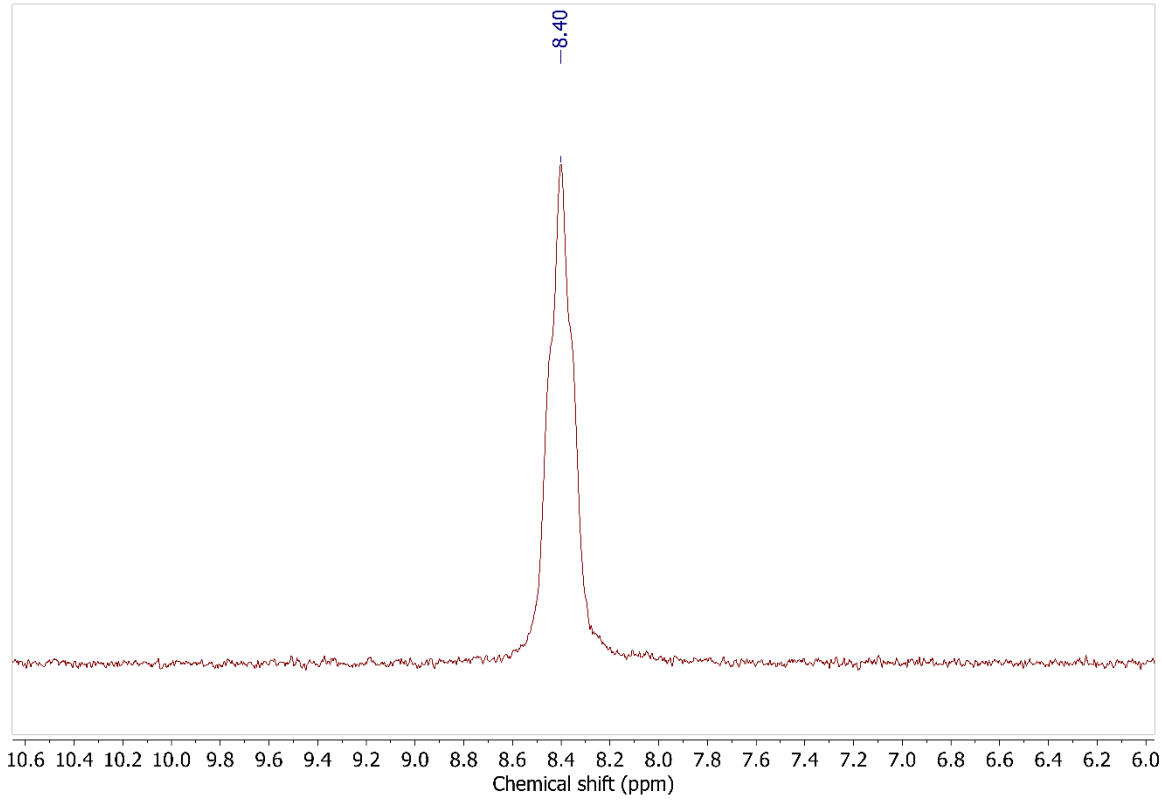


Figure S2. ^{31}P-NMR spectrum recorded for compound **1** in DMSO-d_6 solution.

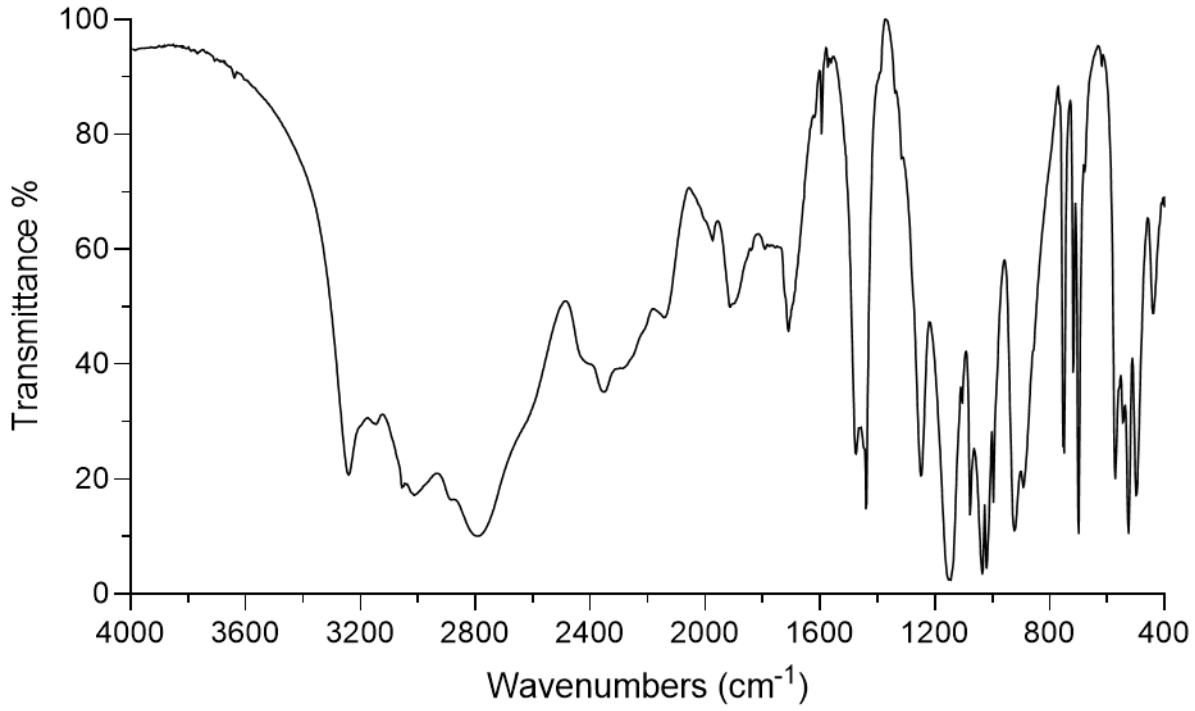


Figure S3. Solid state FT-IR spectrum (4000–400 cm^{-1}) for compound **1** in KBr pellets.

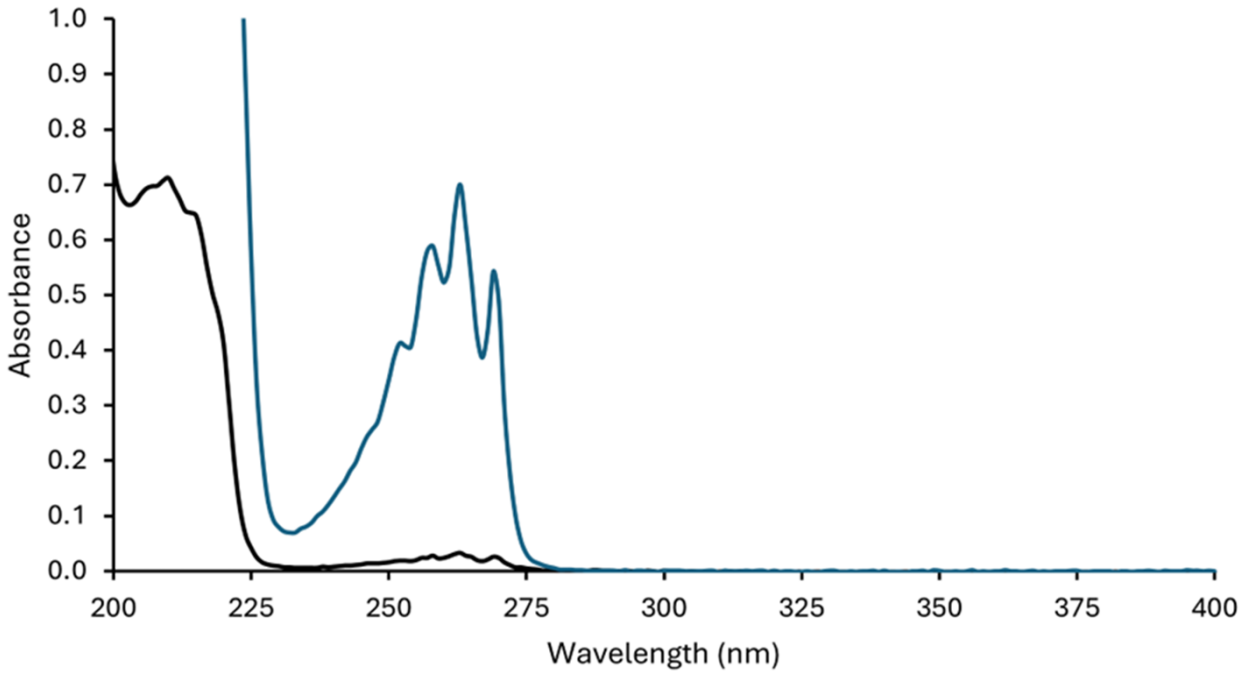


Figure S4. UV-Vis spectrum (200–400 nm) recorded for two water solutions of compound **1** with different concentration: $4.8 \cdot 10^{-5}$ mol L^{-1} (black line) and $1.0 \cdot 10^{-3}$ mol L^{-1} (blue line).

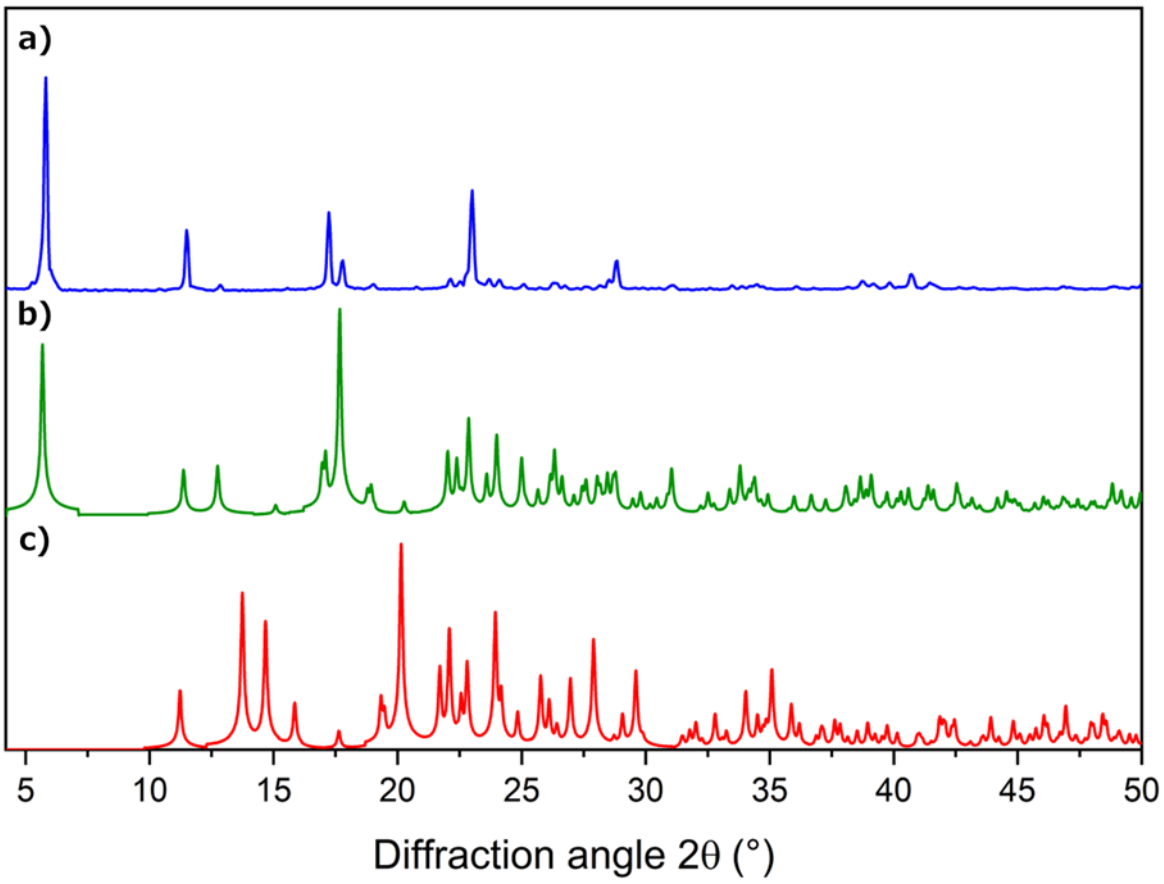


Figure S5. PXRD diffractograms recorded for compound **1** (a) and calculated from single-crystal XRD analysis of ammonium hydrogen phenylphosphonate (b; CSD entry YODNAH) and phenylphosphonic acid (c; CSD entry BZPHOT).

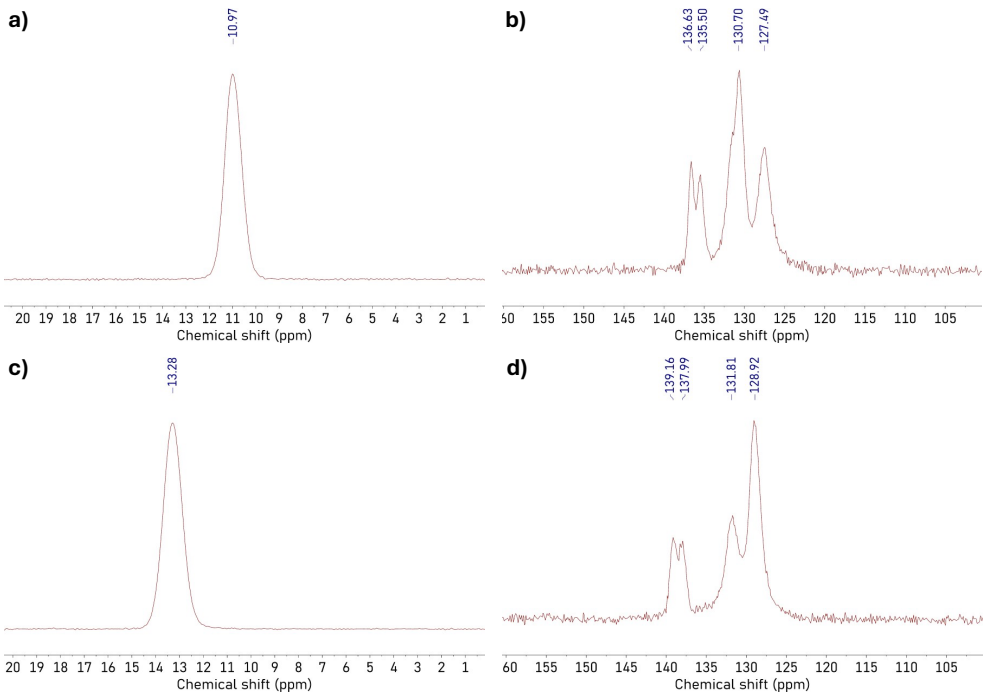


Figure S6. CP-MAS ^{31}P-NMR and ^{13}C-NMR spectrum recorded for 0.4 g of a powder of compound **1** (a and b) and compound **2** (c and d).

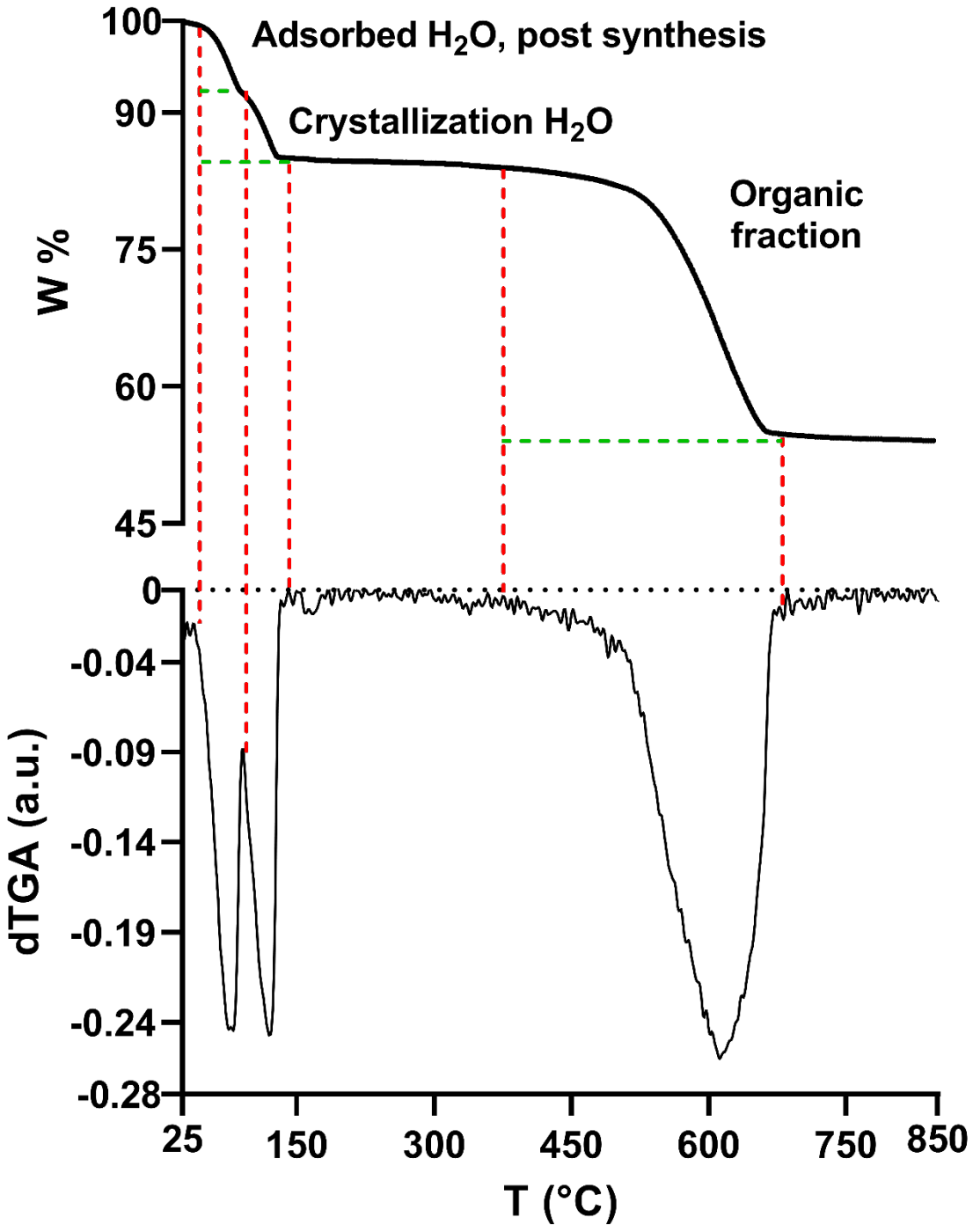


Figure S7. Thermogravimetric analysis (TGA) under N_2 flow for compound **2**.

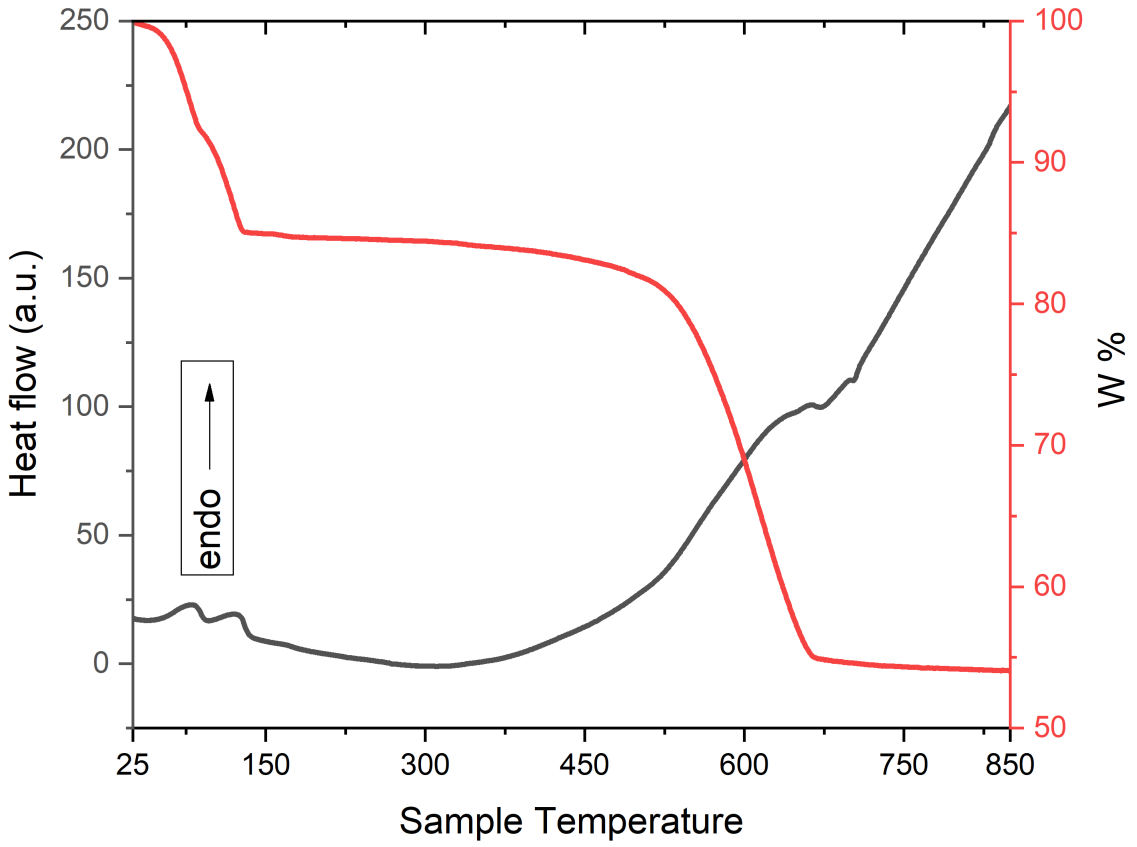


Figure S8. Differential Scanning Calorimetry (DSC) recorded during a TGA under N_2 flow for compound **2**.

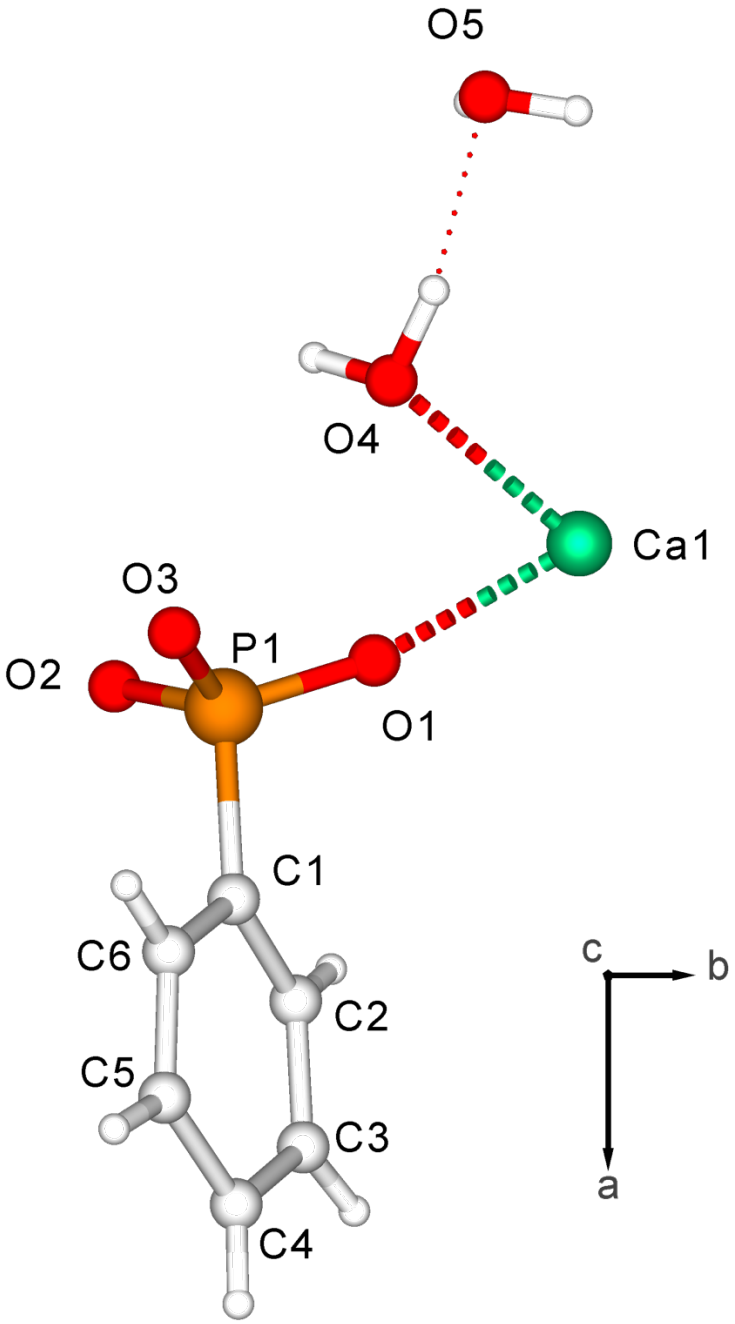


Figure S9. Structure and atom labelling scheme of compound **2** determined by 3D ED analysis.

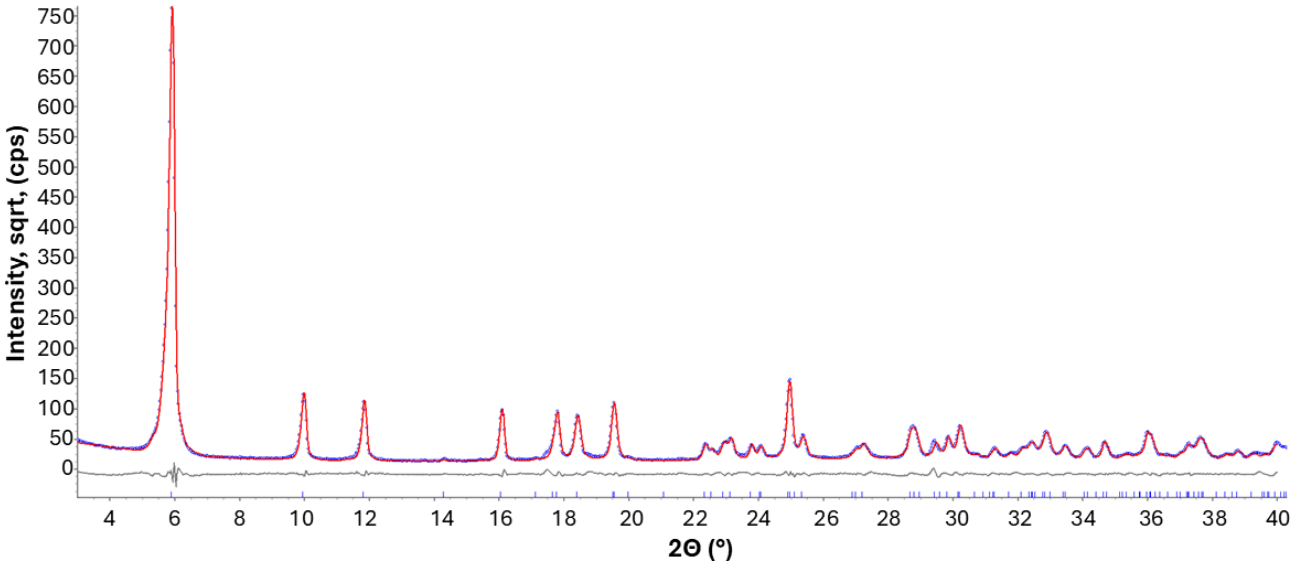


Figure S10. Rietveld refinement of the experimental PXRD data using the structural model derived from 3D ED data of compound **2**. The observed diffraction pattern is represented by blue dots, while the calculated and difference curves are shown in red and grey, respectively. Bragg reflections positions are marked by vertical blue ticks.

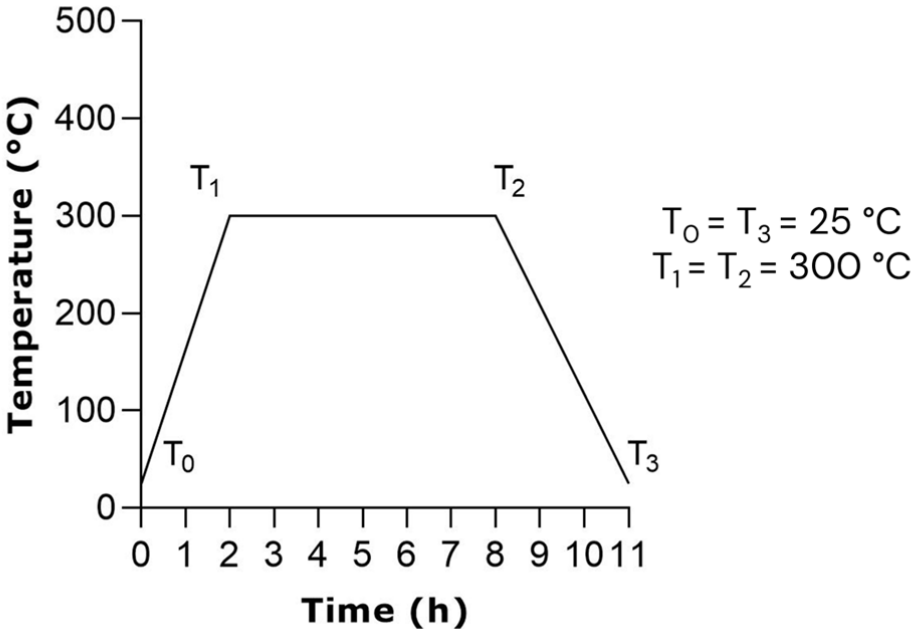


Figure S11. Thermal treatment diagram for the artificial weathering of Carrara Marble.

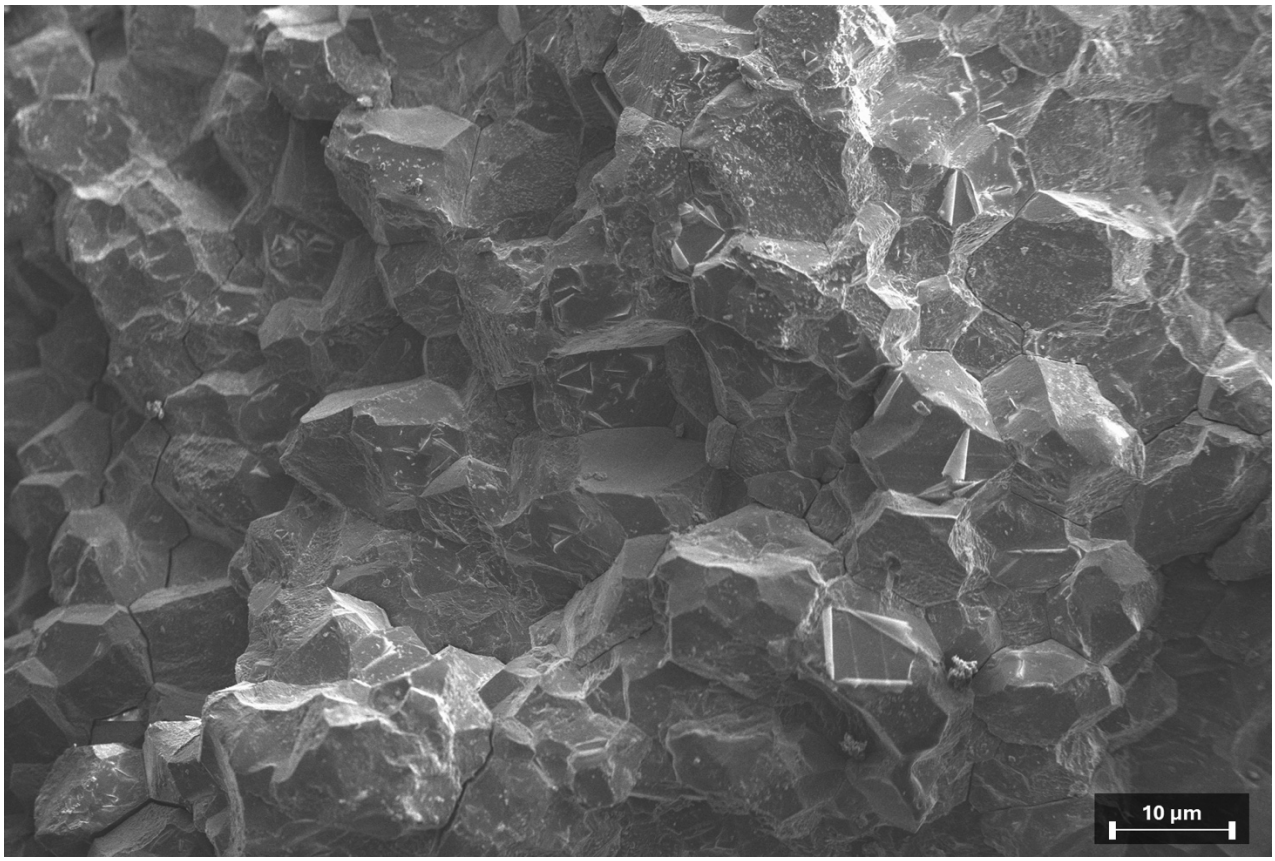


Figure S12. SEM Image of the white Carrara marble stone surface after the thermal weathering process.

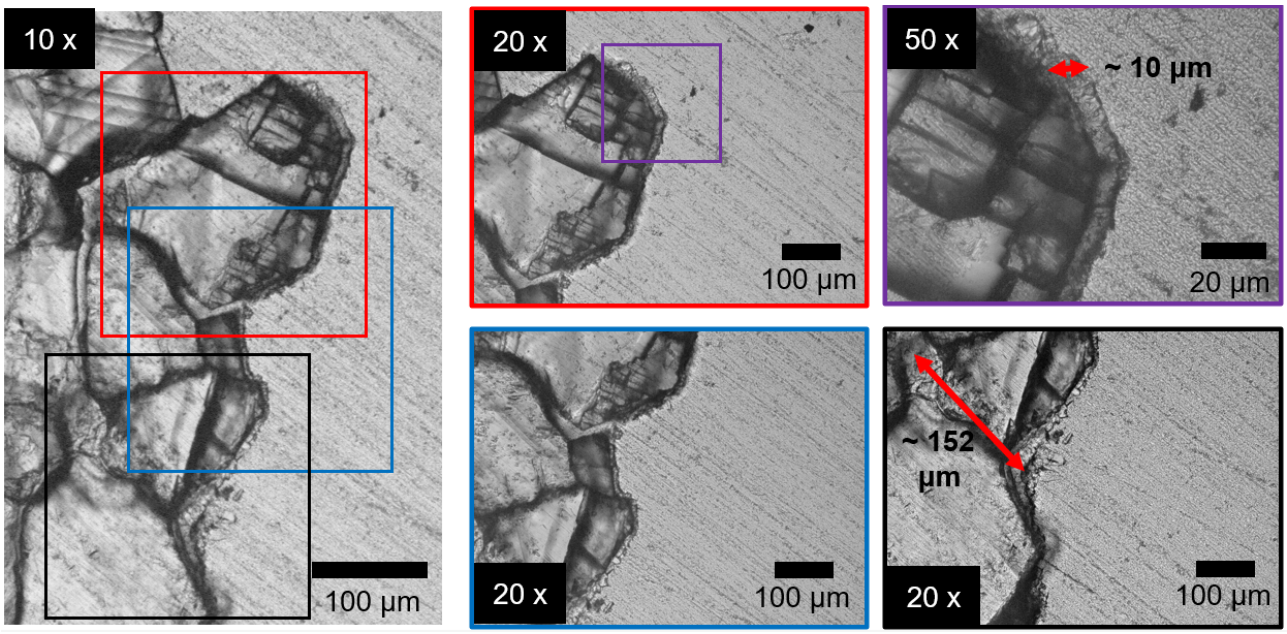


Figure S13. Optical microscopy images of a cross-section of white Carrara marble treated with an immersion in a 5% w/w solution of compound **1**. Coloured squares show the sites where the pictures with higher magnification were acquired.

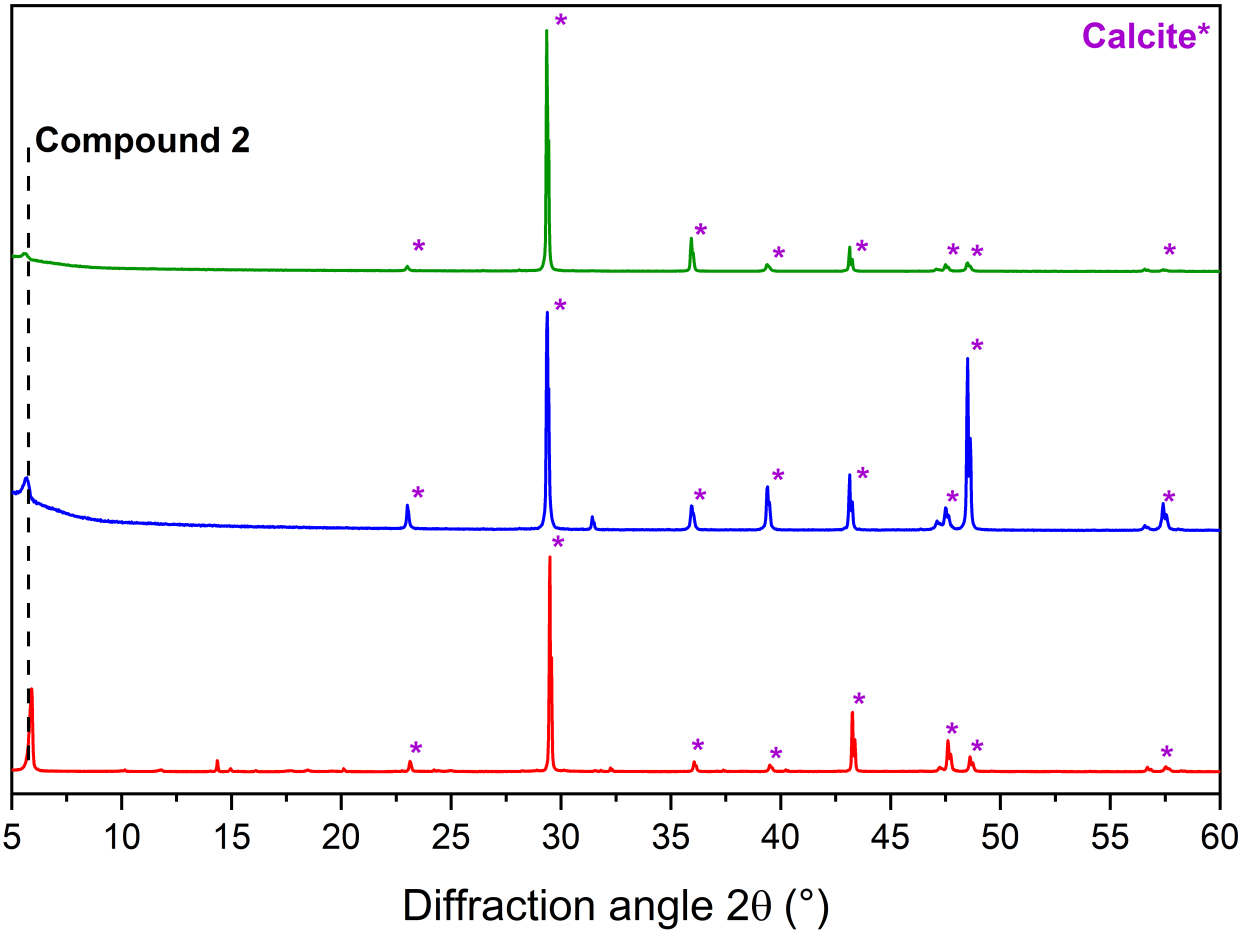


Figure S14. PXRD patterns of white Carrara marble mock-ups treated with a 5% w/w solution of compound **1** by immersion (red), brushing (blue), and spraying (green).

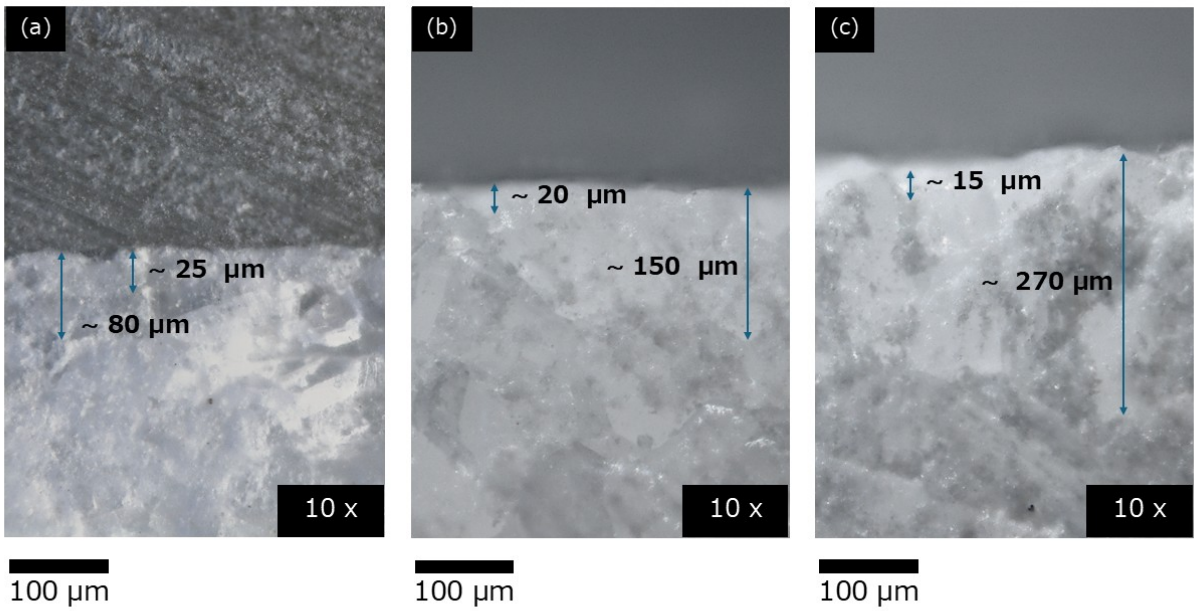
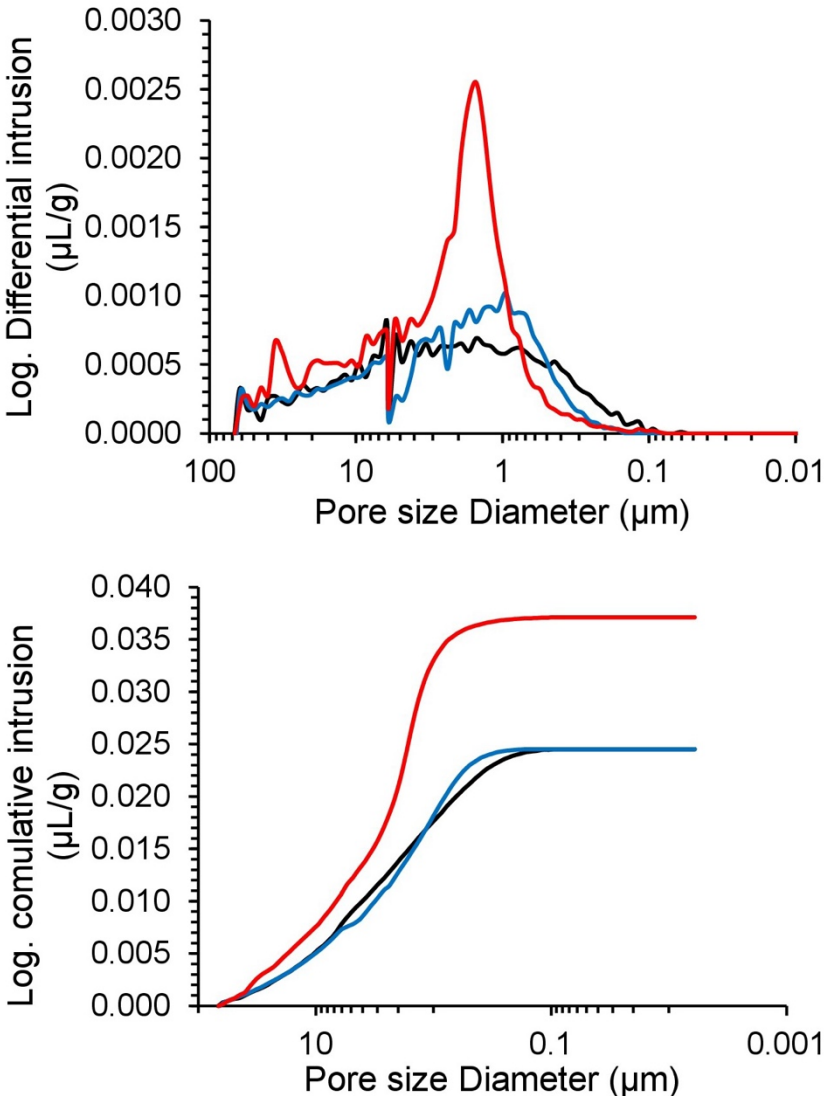


Figure S15. Optical microscopy images of a section of white Carrara marble treated with a 5% w/w solution of compound **1**, applied by immersion (a), brushing (b), and spraying (c).



Sample	Average pore size (µm)	Porosity, Φ_{Hg}%	Skeletal density, $\rho_{skeletal\ Hg}$ (g·cm^{-3})	Bulk density $\rho_{bulk\ Hg}$ (g·cm^{-3})
PR	0.9 (5)	1.7 (5)	2.7 (1)	2.6 (1)
TW	1.0 (5)	2.1 (2)	2.7 (1)	2.6 (1)
Imm. TR	0.8 (5)	2.7 (2)	2.7 (1)	2.7 (1)

Figure S16. Differential (top) and cumulative (bottom) intrusion of Hg, measured with Mercury Intrusion Porosimetry (MIP), on pristine (PR, black), thermally weathered (TW, blue) and treated by immersion with a 5% w/w solution of compound **1** (TR, red) white Carrara marble fragments (~1 cm^3). The structural parameters determined with the analysis are reported in the Table.

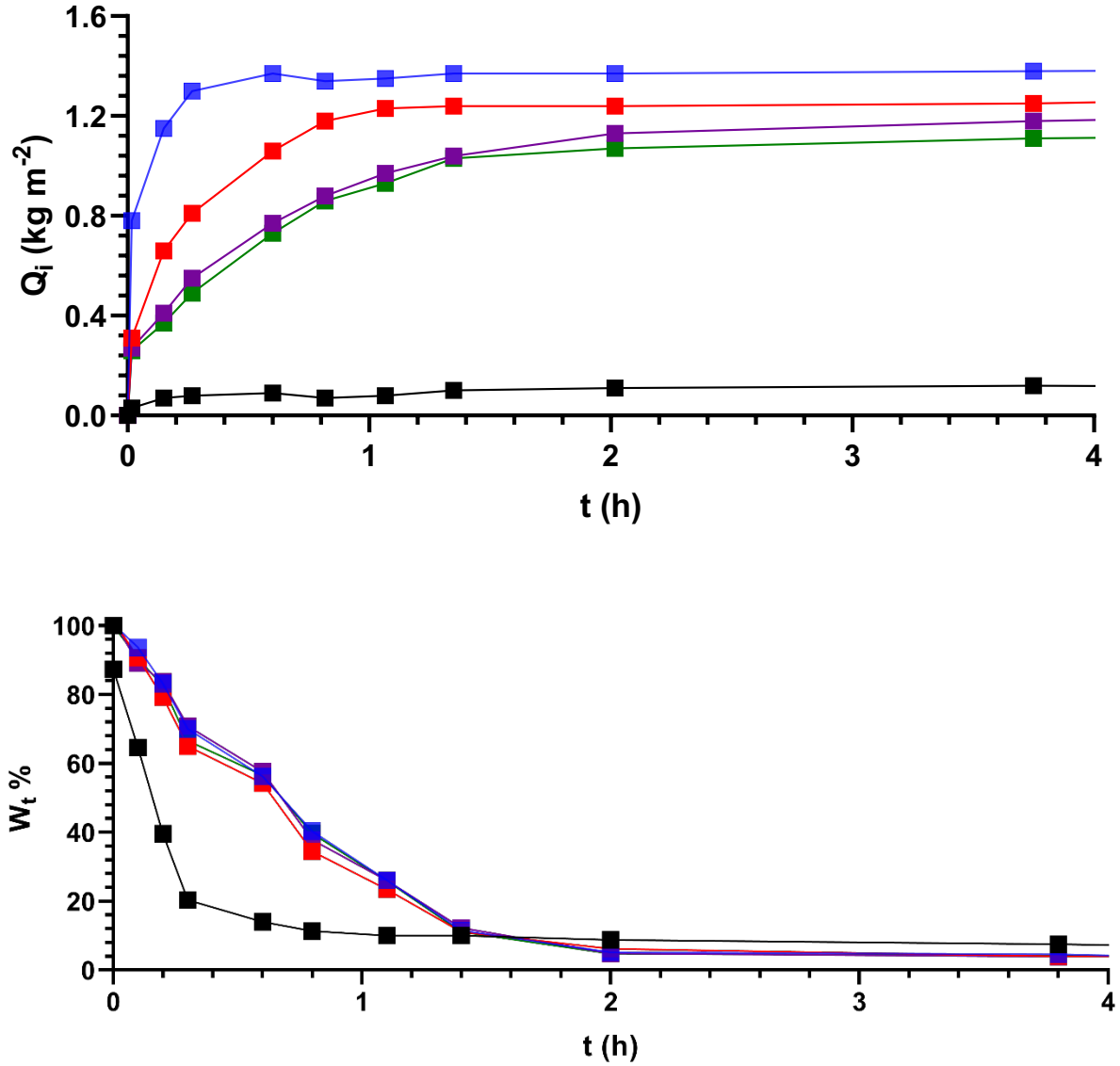


Figure S17. Water capillary absorption (top) and desorption (bottom) measured on white Carrara marble mock-ups: pristine (black), thermally weathered (blue), treated by immersion (red), brushing (purple), and spraying (green) with a 5% w/w solution of compound **1**.

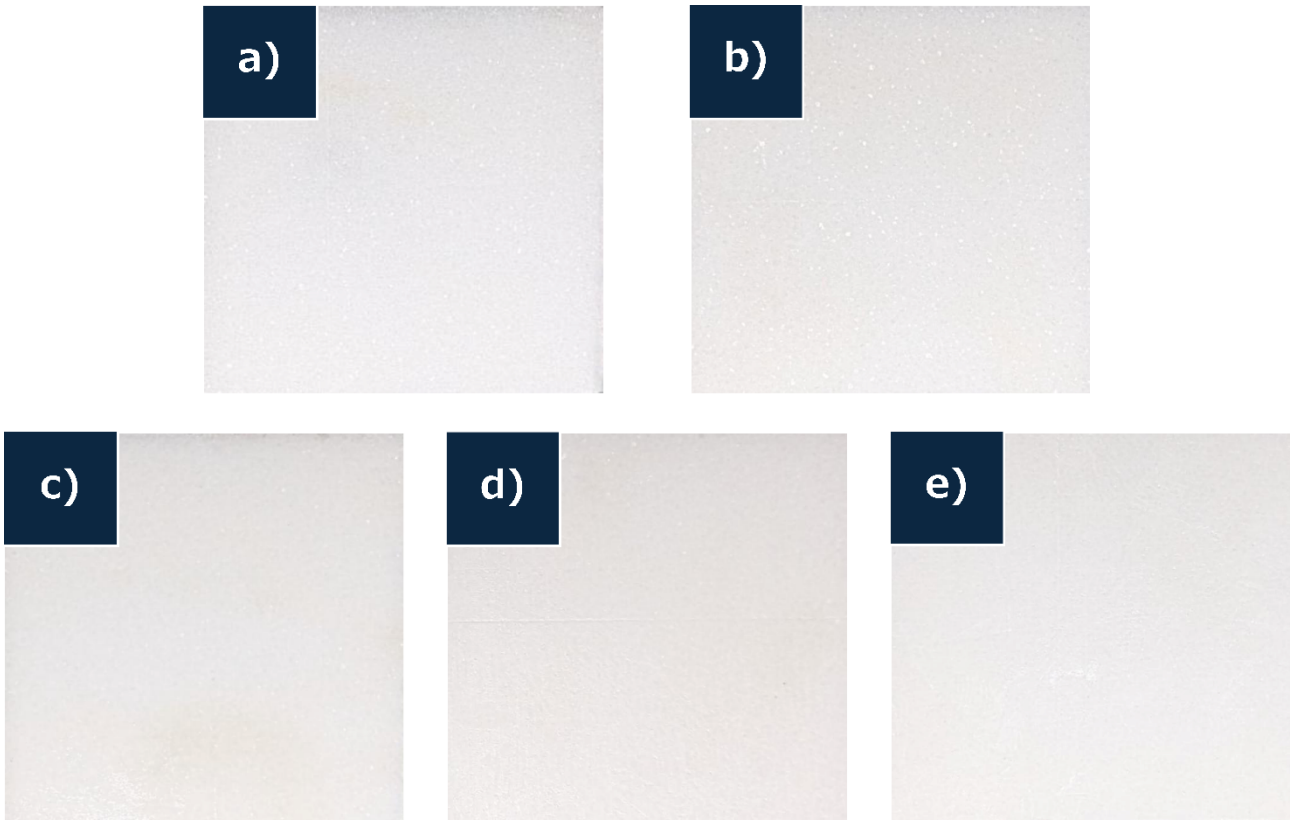


Figure S18. Photographs under a plain white led of 4.5 x 4.5 x 2.0 cm white Carrara marble mock-ups: pristine (a), thermally weathered (b), and treated by immersion (c), brushing (d), spraying (e) with a 5% w/w solution of compound **1**.

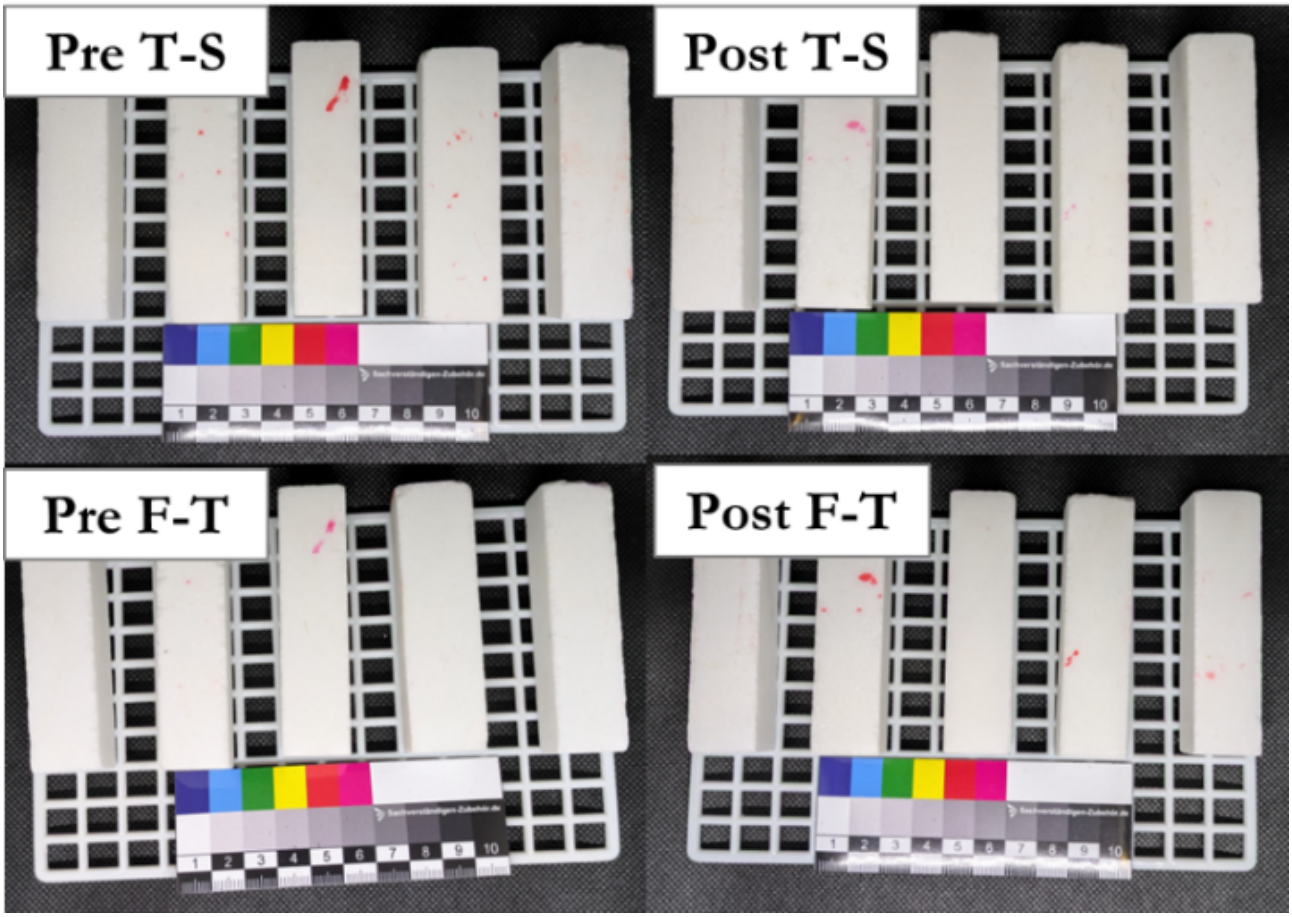


Figure S19: White Carrara marble stone mock–ups subjected to the T–S and F–T tests. From left to right: pristine, thermally weathered, immersion–, brushing–, and spraying–treated with a 5.0% w/w solution of compound **1**.

Figure S20: Experimental set–up for the acid attack resistance test.

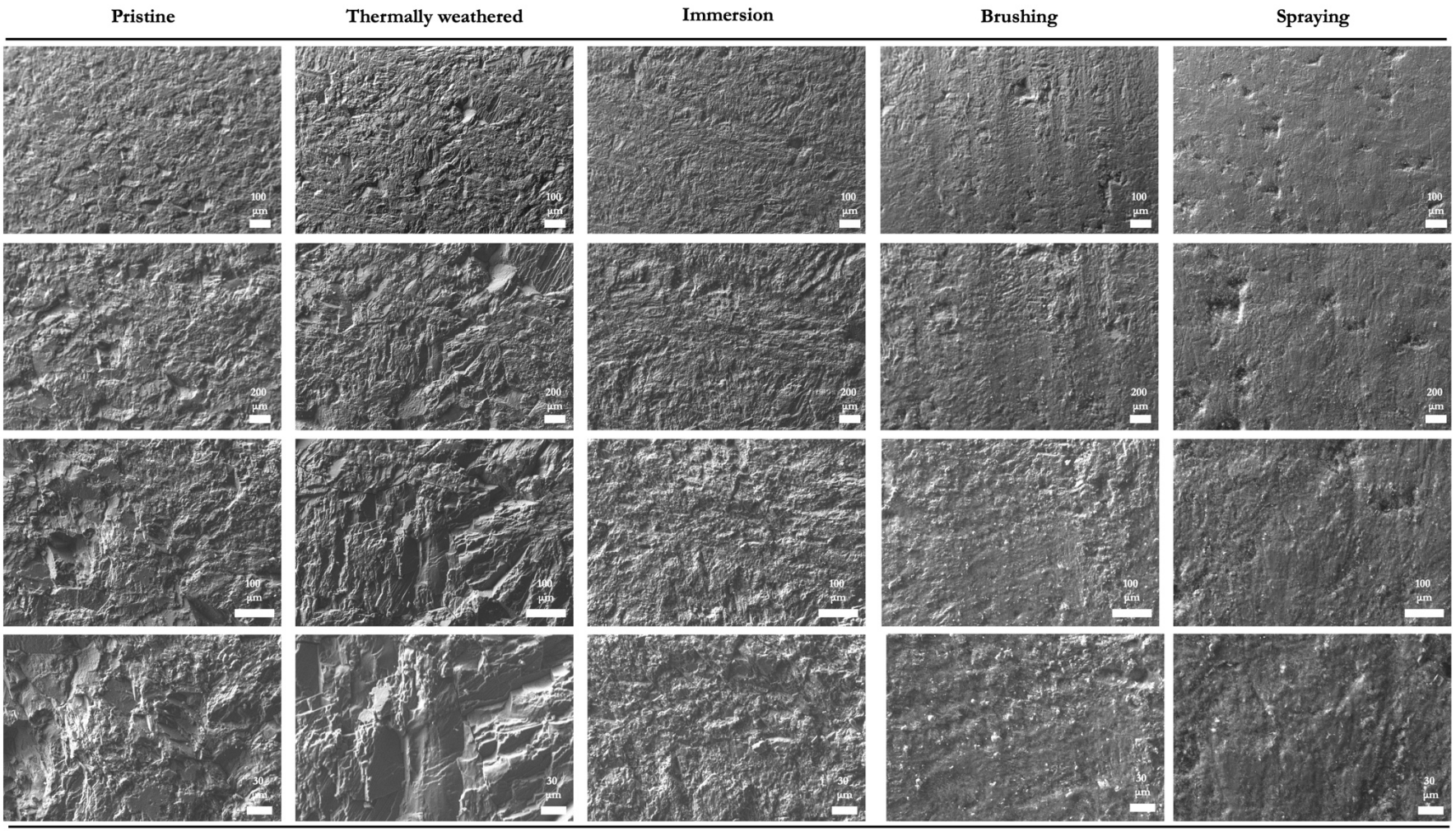


Figure S21: SEM images for white Carrara stone mock–ups surfaces before the acid attack experiment. Magnification increases from top to bottom.

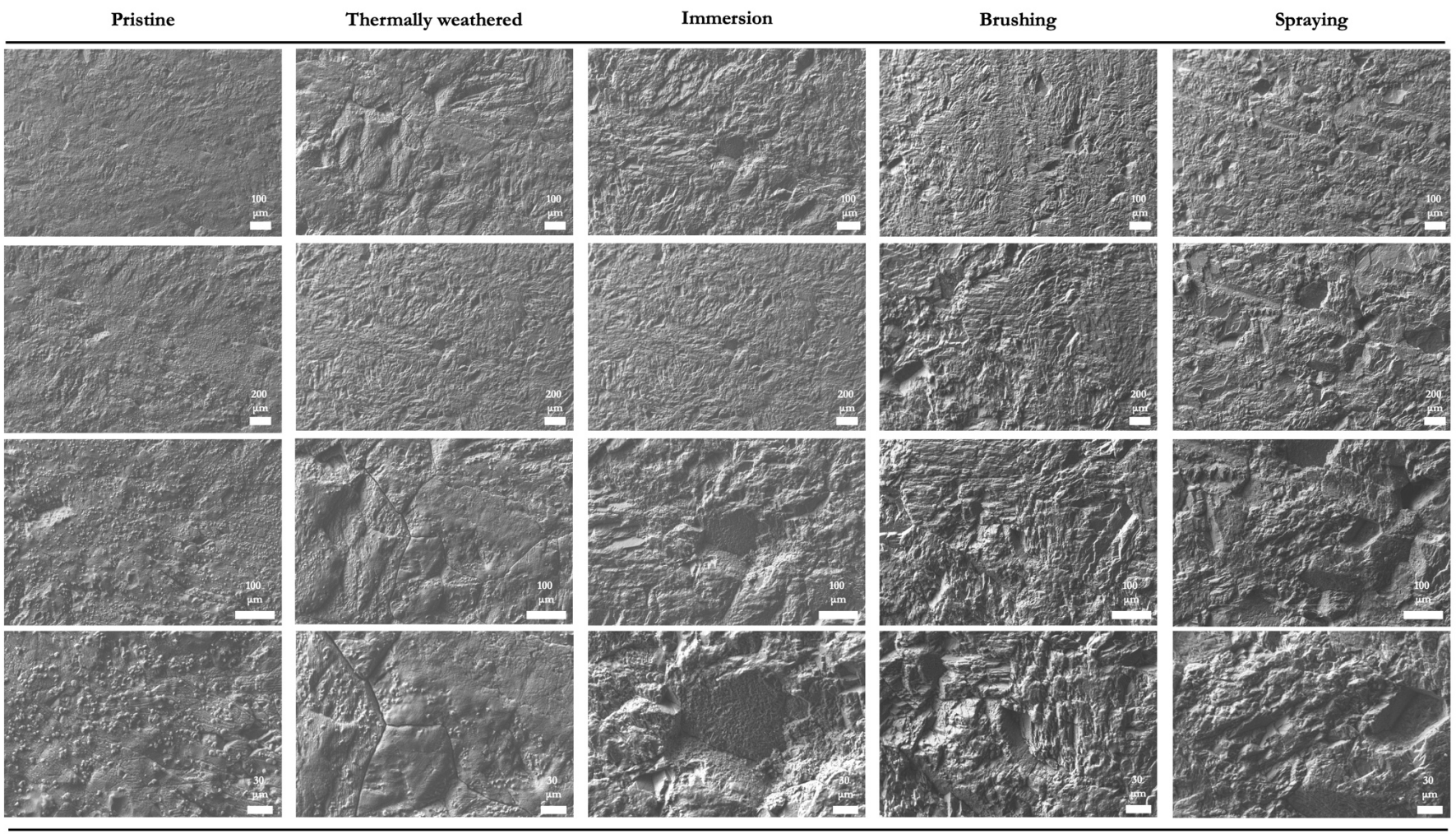


Figure S22: SEM images for white Carrara stone mock–ups surfaces after the acid attack experiment. Magnification increases from top to bottom.

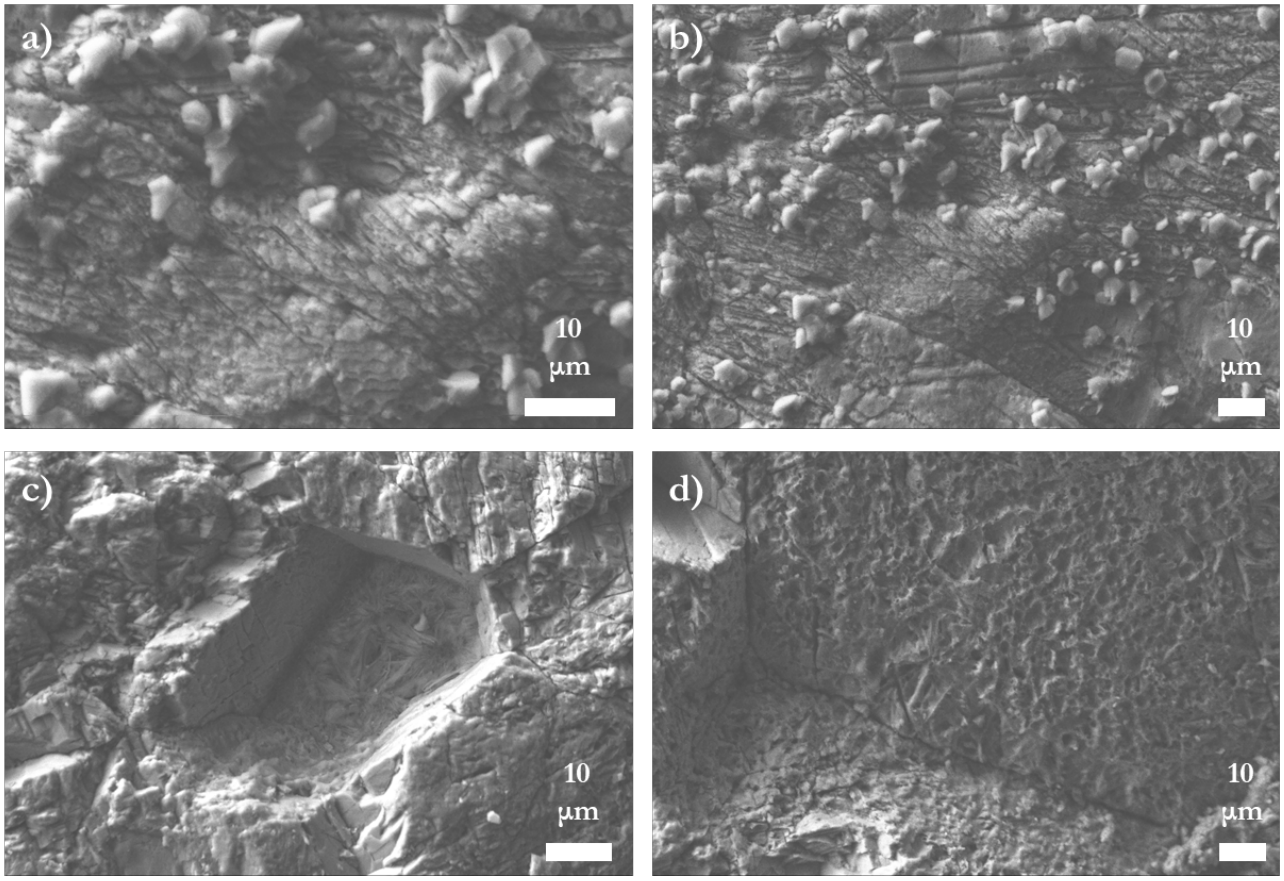


Figure S23: SEM images showing the effects of the acid attack on a pristine specimen (a and b); grain detachment over deposited compound **2** (c); effect of acid washing on calcite exposed after the removal of compound **2** (d).