Oxamate salts as novel agents for the restoration of marble and limestone substrates: case study of ammonium *N*-phenyloxamate

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Table S1. Crystal data and details of the structure determination for AmPhOxam.

Formula				C8 H10 N2 O3
Formula Weight				182.18
Crystal System				Monoclinic
Space group			P21/c	(No. 14)
a, b, c [Angstrom]		18.927(6)	6.364(2)	7.380(3)
alpha, beta, gamma [deg]		90	93.784(8)	90
V [Ang**3]				887.0(5)
Z				4
D(calc) [g/cm**3]				1.364
Mu(CuKa) [/mm]				0.897
F(000)				384
Crystal Size [mm]			0.01 x	0.10 x 0.15
		Data Collection		
Temperature (K)				125
Radiation [Angstrom]			CuKa	1.54187
Theta Min-Max [Deg]				4.7, 68.8
Dataset			-22: 22 ; -7: 7 ;	-8: 8
Tot.,Uniq. Data, R(int)			8449, 1596,	0.167
Observed data [I > 0.0 sigma(I)]				1290
		Refinement		
Nref, Npar				1596, 138
R, wR2, S			0.1491,	0.4063, 1.26
Max. and Av. Shift/Error				0.00, 0.00
Min. and Max.Resd. Dens. [e/Ang^3]				-0.42, 0.63

w = \S^2^(FO^2^)+(0.1775P)^2^+4.1276P], where P=(FO^2^+2FC^2^)/3'

Table S2. Final coordinates and equivalent isotropic displacement parameters of the non-hydrogen atoms for AmPhOxam.

Atom	x	y	z	U(eq) [Ang^2]
O1	0.4413(3)	0.3112(8)	0.5628(7)	0.0425(17)
O2	0.3361(3)	0.5728(7)	0.4267(7)	0.0401(17)
O10	0.3730(3)	0.0357(7)	0.4750(7)	0.0381(17)
N3	0.2724(3)	0.2855(9)	0.3257(8)	0.0335(17)
C1	0.3866(3)	0.2274(10)	0.4892(8)	0.0303(19)
C2	0.3295(4)	0.3821(10)	0.4093(9)	0.0304(19)
C4	0.2107(4)	0.3917(11)	0.2527(8)	0.033(2)
C5	0.2153(4)	0.5838(11)	0.1611(9)	0.034(2)
C6	0.1535(4)	0.6813(12)	0.0947(9)	0.040(2)
C7	0.0882(4)	0.5947(14)	0.1194(10)	0.046(3)
C8	0.0840(4)	0.4035(15)	0.2075(11)	0.049(3)
C9	0.1451(4)	0.3027(12)	0.2740(10)	0.041(2)
N1	0.4373(3)	-0.2769(8)	0.7047(7)	0.0271(16)

U(eq) = 1/3 of the trace of the orthogonalized U Tensor

Table S3. Hydrogen atom positions and isotropic displacement parameters for AmPhOxam.

Atom	x	y	z	U(iso) [Ang^2]
H3	0.274(4)	0.1319(16)	0.318(13)	0.05(2)
H5	0.26009	0.64593	0.14481	0.0412
H6	0.15622	0.81045	0.03097	0.0484
H7	0.04630	0.66572	0.07615	0.0548
H8	0.03909	0.34150	0.22243	0.0584
H9	0.14196	0.17161	0.33451	0.0485
H1A	0.419(5)	-0.161(11)	0.629(13)	0.07(3)
H1B	0.403(3)	-0.308(15)	0.793(9)	0.06(3)
H1C	0.436(5)	-0.387(11)	0.612(10)	0.06(3)
H1D	0.4870(14)	-0.263(13)	0.750(11)	0.04(2)

The Temperature Factor has the Form of Exp(-T) Where T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms

Table S4. (An)isotropic displacement parameters for AmPhOxam.

Atom	U(1,1) or U	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
O1	0.050(3)	0.035(3)	0.041(3)	-0.001(2)	-0.009(2)	0.002(2)
O2	0.058(3)	0.022(3)	0.039(3)	0.003(2)	-0.007(2)	-0.003(2)
O10	0.057(3)	0.022(3)	0.035(3)	0.0032(19)	0.001(2)	0.003(2)
N3	0.047(3)	0.025(3)	0.028(3)	0.001(2)	-0.002(2)	-0.002(2)
C1	0.046(4)	0.026(3)	0.019(3)	0.002(2)	0.002(3)	0.002(3)
C2	0.047(4)	0.024(3)	0.020(3)	0.003(2)	0.001(3)	-0.001(3)
C4	0.047(4)	0.032(4)	0.018(3)	-0.004(2)	-0.001(3)	0.002(3)
C5	0.052(4)	0.030(4)	0.021(3)	-0.003(3)	0.002(3)	0.000(3)
C6	0.059(4)	0.036(4)	0.025(3)	-0.001(3)	-0.003(3)	0.007(3)
C7	0.053(4)	0.057(5)	0.027(4)	-0.004(3)	-0.001(3)	0.013(4)
C8	0.045(4)	0.065(6)	0.036(4)	0.004(4)	0.004(3)	-0.006(4)
C9	0.054(4)	0.041(4)	0.026(3)	0.003(3)	-0.001(3)	-0.005(3)
N1	0.039(3)	0.022(3)	0.020(2)	0.002(2)	0.000(2)	-0.001(2)

The Temperature Factor has the Form of Exp(-T) Where T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms, T = 2*(Pi**2)*Sumij(h(i)*h(j)*U(i,j)*Astar(i)*Astar(j)), for Anisotropic Atoms. Astar(i) are Reciprocal Axial Lengths and h(i) are the Reflection Indices.

Table S5. Bond distances (Angstrom) for AmPhOxam.

O1	-C1	1.256(8)	C4	-C5	1.403(10)
O2	-C2	1.226(8)	C4	-C9	1.383(11)
O10	-C1	1.250(8)	C5	-C6	1.385(11)
N3	-C2	1.356(9)	C6	-C7	1.376(11)
N3	-C4	1.424(9)	C7	-C8	1.384(13)
N3	-H3	0.980(13)	C8	-C9	1.384(11)
N1	-H1D	0.98(4)	C5	-H5	0.9500
N1	-H1B	0.97(6)	C6	-H6	0.9500
N1	-H1A	0.98(8)	C7	-H7	0.9500
N1	-H1C	0.98(7)	C8	-H8	0.9500
C1	-C2	1.550(9)	C9	-H9	0.9500

Table S6. Bond angles (Degrees) for AmPhOxam.

C2	-N3	-C4	124.5(6)	C5	-C4	-C9	119.8(7)
C4	-N3	-H3	119(5)	C4	-C5	-C6	118.9(7)
C2	-N3	-H3	117(5)	C5	-C6	-C7	121.2(7)
H1B	-N1	-H1D	117(6)	C6	-C7	-C8	119.6(7)
H1A	-N1	-H1D	115(7)	C7	-C8	-C9	120.1(7)
H1C	-N1	-H1D	106(7)	C4	-C9	-C8	120.4(7)
H1A	-N1	-H1C	99(7)	C4	-C5	-H5	121.00
H1A	-N1	-H1B	108(8)	C6	-C5	-H5	121.00
H1B	-N1	-H1C	110(7)	C5	-C6	-H6	119.00
O10	-C1	-C2	117.0(5)	C7	-C6	-H6	119.00
O1	-C1	-C2	115.4(6)	C8	-C7	-H7	120.00
O1	-C1	-O10	127.6(6)	C6	-C7	-H7	120.00
O2	-C2	-C1	121.7(6)	C7	-C8	-H8	120.00
O2	-C2	-N3	124.7(7)	C9	-C8	-H8	120.00
N3	-C2	-C1	113.6(5)	C8	-C9	-H9	120.00
N3	-C4	-C5	121.4(7)	C4	-C9	-H9	120.00
N3	-C4	-C9	118.9(6)				

Table S7. Torsion angles (Degrees) for AmPhOxam.

C4	-N3	-C2	-O2	-2.7(11)
C4	-N3	-C2	-C1	175.4(6)
C2	-N3	-C4	-C5	39.4(10)
C2	-N3	-C4	-C9	-140.3(7)
O1	-C1	-C2	-O2	-4.0(9)
O1	-C1	-C2	-N3	177.9(6)
O10	-C1	-C2	-O2	175.4(6)
O10	-C1	-C2	-N3	-2.8(8)
N3	-C4	-C5	-C6	-179.3(6)
C9	-C4	-C5	-C6	0.4(10)
N3	-C4	-C9	-C8	178.9(7)
C5	-C4	-C9	-C8	-0.8(11)
C4	-C5	-C6	-C7	1.0(10)
C5	-C6	-C7	-C8	-1.9(11)
C6	-C7	-C8	-C9	1.5(12)
C7	-C8	-C9	-C4	-0.1(12)

Table S8. Contact distances (Angstrom) for AmPhOxam.

O1	.O2	2.735(8)	O10	.H5_d	2.8000
O1	.N1_a	2.826(7)	N1	.O1_o	3.134(8)
O1	.N1_c	3.134(8)	N1	.O2_d	2.908(8)
O1	.N1_b	2.832(8)	N1	.O10_p	2.914(7)
O1	.C1_d	3.386(8)	N1	.O1_h	2.826(7)
O2	.N1_a	2.877(8)	N1	.O2_h	2.877(8)
O2	.N1_f	2.908(8)	N1	.O10	2.836(7)
O2	.O10_e	3.043(7)	N1	.O1_n	2.832(8)
O2	.O1	2.735(8)	N3	.O10	2.663(8)
O2	.C5	2.913(9)	N3	.C1_j	3.399(8)
O10	.N3	2.663(8)	C1	.N3_d	3.399(8)
O10	.N1_i	2.914(7)	C1	.C2_d	3.422(9)
O10	.N1	2.836(7)	C1	.O1_j	3.386(8)
O10	.O2_h	3.043(7)	C2	.C1_j	3.422(9)
O10	.C2_d	3.402(9)	C2	.O10_j	3.402(9)
O1	.H1C_c	2.77(9)	C5	.O2	2.913(9)
O1	.H1D_c	2.77(7)	C1	.H1D_c	3.07(5)
O1	.H1D_b	1.93(6)	C1	.H1B_i	3.06(9)
O1	.H1C_a	1.96(7)	C1	.H1D_b	2.97(6)
O2	.H1A_f	2.84(9)	C1	.H1A	2.73(8)
O2	.H1A_a	2.69(9)	C1	.H1C_a	2.76(7)
O2	.H1C_a	2.27(9)	C2	.H1C_a	2.84(8)
O2	.H5	2.4900	C2	.H5	2.8300
O2	.H5_g	2.8600	C4	.H6_g	3.0300
O2	.H1B_f	2.23(8)	C5	.H6_g	3.0900
O10	.H3	2.22(8)	C6	.H9_j	2.9500
O10	.H1A	1.87(9)	C7	.H9_j	2.9300
O10	.H1B_i	2.08(8)	C8	.H9_j	3.0700
H1A	.O2_h	2.69(9)	H1D	.C1_n	2.97(6)
H1A	.C1	2.73(8)	H1D	.C1_o	3.07(5)
H1A	.O2_d	2.84(9)	H3	.O10	2.22(8)
H1A	.H1B_i	2.49(12)	H3	.H9	2.5200
H1A	.O10	1.87(9)	H5	.C2	2.8300
H1B	.O10_p	2.08(8)	H5	.O2_k	2.8600
H1B	.C1_p	3.06(9)	H5	.O2	2.4900
H1B	.O2_d	2.23(8)	H5	.O10_j	2.8000
H1B	.H1A_q	2.49(12)	H6	.C4_k	3.0300
H1C	.C1_h	2.76(7)	H6	.C5_k	3.0900
H1C	.C2_h	2.84(8)	H7	.H8_l	2.5300
H1C	.O1_o	2.77(9)	H8	.H7_m	2.5300
H1C	.O2_h	2.27(9)	H9	.H3	2.5200
H1C	.O1_h	1.96(7)	H9	.C6_d	2.9500
H1D	.O1_o	2.77(7)	H9	.C7_d	2.9300
H1D	.O1_n	1.93(6)	H9	.C8_d	3.0700

Table S9. Hydrogen bonds (Angstrom, Deg) for AmPhOxam.

N1	-- H1A	.. O10	0.98(8)	1.87(9)	2.836(7)	172(9)	.
N1	-- H1B	.. O2	0.97(6)	2.23(8)	2.908(8)	126(7)	4_555
N1	-- H1B	.. O10	0.97(6)	2.08(8)	2.914(7)	143(7)	4_545
N1	-- H1C	.. O1	0.98(7)	1.96(7)	2.826(7)	146(6)	1_545
N1	-- H1C	.. O2	0.98(7)	2.27(9)	2.877(8)	119(7)	1_545
N1	-- H1D	.. O1	0.98(4)	1.93(6)	2.832(8)	152(6)	2_646
N3	-- H3	.. O10	0.980(13)	2.22(8)	2.663(8)	106(5)	.
C5	-- H5	.. O2	0.9500	2.4900	2.913(9)	107.00	.

Table S10. Translation of symmetry code to equiv. pos for AmPhOxam.

```
a =[  1565.00] = [  1_565] = x,1+y,z
b =[  2656.00] = [  2_656] = 1-x,1/2+y,3/2-z
c =[  3656.00] = [  3_656] = 1-x,-y,1-z
d =[  4555.00] = [  4_555] = x,1/2-y,1/2+z
e =[  1565.00] = [  1_565] = x,1+y,z
f =[  4554.00] = [  4_554] = x,1/2-y,-1/2+z
g =[  4565.00] = [  4_565] = x,3/2-y,1/2+z
h =[  1545.00] = [  1_545] = x,-1+y,z
i =[  4544.00] = [  4_544] = x,-1/2-y,-1/2+z
j =[  4554.00] = [  4_554] = x,1/2-y,-1/2+z
k =[  4564.00] = [  4_564] = x,3/2-y,-1/2+z
l =[  2555.00] = [  2_555] = -x,1/2+y,1/2-z
m =[  2545.00] = [  2_545] = -x,-1/2+y,1/2-z
n =[  2646.00] = [  2_646] = 1-x,-1/2+y,3/2-z
o =[  3656.00] = [  3_656] = 1-x,-y,1-z
p =[  4545.00] = [  4_545] = x,-1/2-y,1/2+z
```

Table S11. Colorimetric measurements (average values of lightness L^*, chromaticity coordinates a^* and b^*, and color difference ΔE) determined for Carrara marble and biomicritic limestone before and after treatment with AmPhOxam.

White Carrara marble				
	L^*	a^*	b^*	ΔE
Untreated	85.52(±0.62)	1.38(±0.19)	15.26(±0.56)	3.763(±0.42)
AmPhOxam 2.50% w/w	82.12(±0.39)	2.13(±0.13)	16.65(±0.68)	
Biomicritic limestone				
Untreated	89.37(±1.04)	-0.07(±0.12)	4.33(±0.80)	2.79(±0.49)
AmPhOxam 2.50% w/w	91.65(±1.05)	-0.50(±0.22)	4.37(±1.56)	

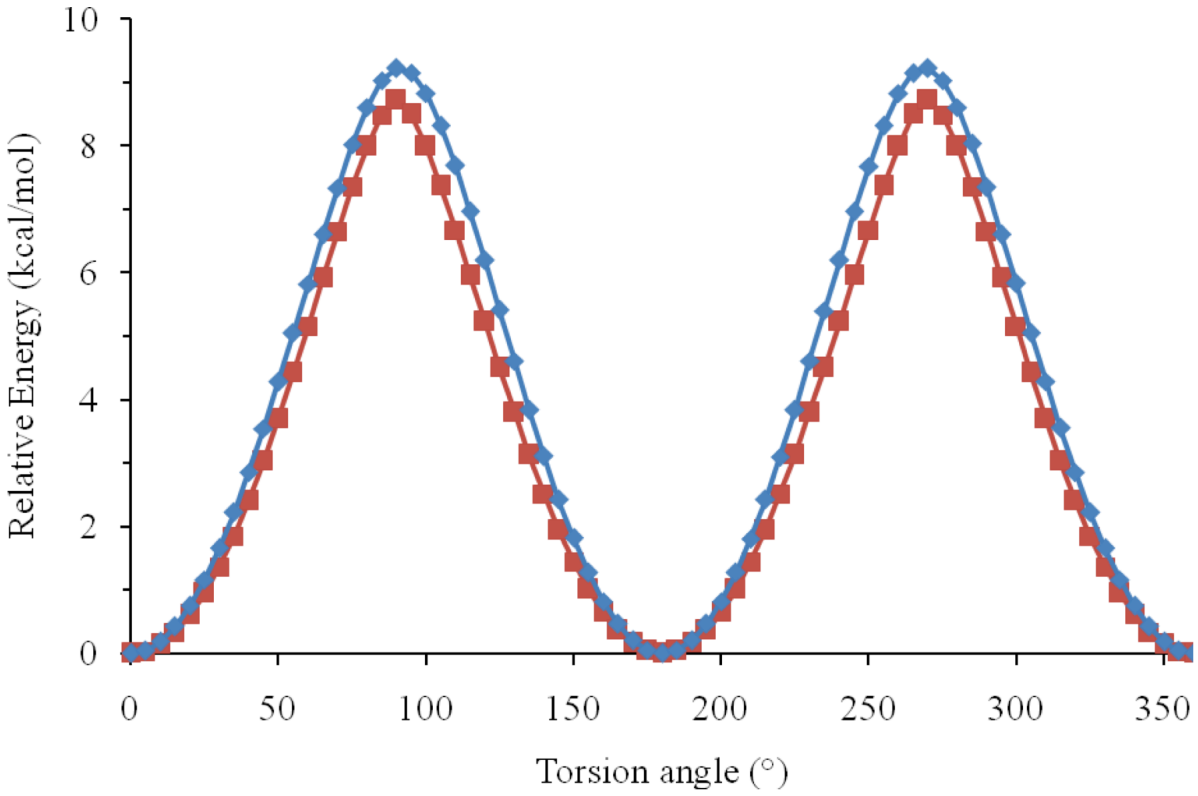

Figure S1. Relaxed PES diagrams reporting the relative energy variations calculated on rotating the $-COO^-$ (blue) and the phenyl ring (red) of the *N*-phenyloxamate anion.

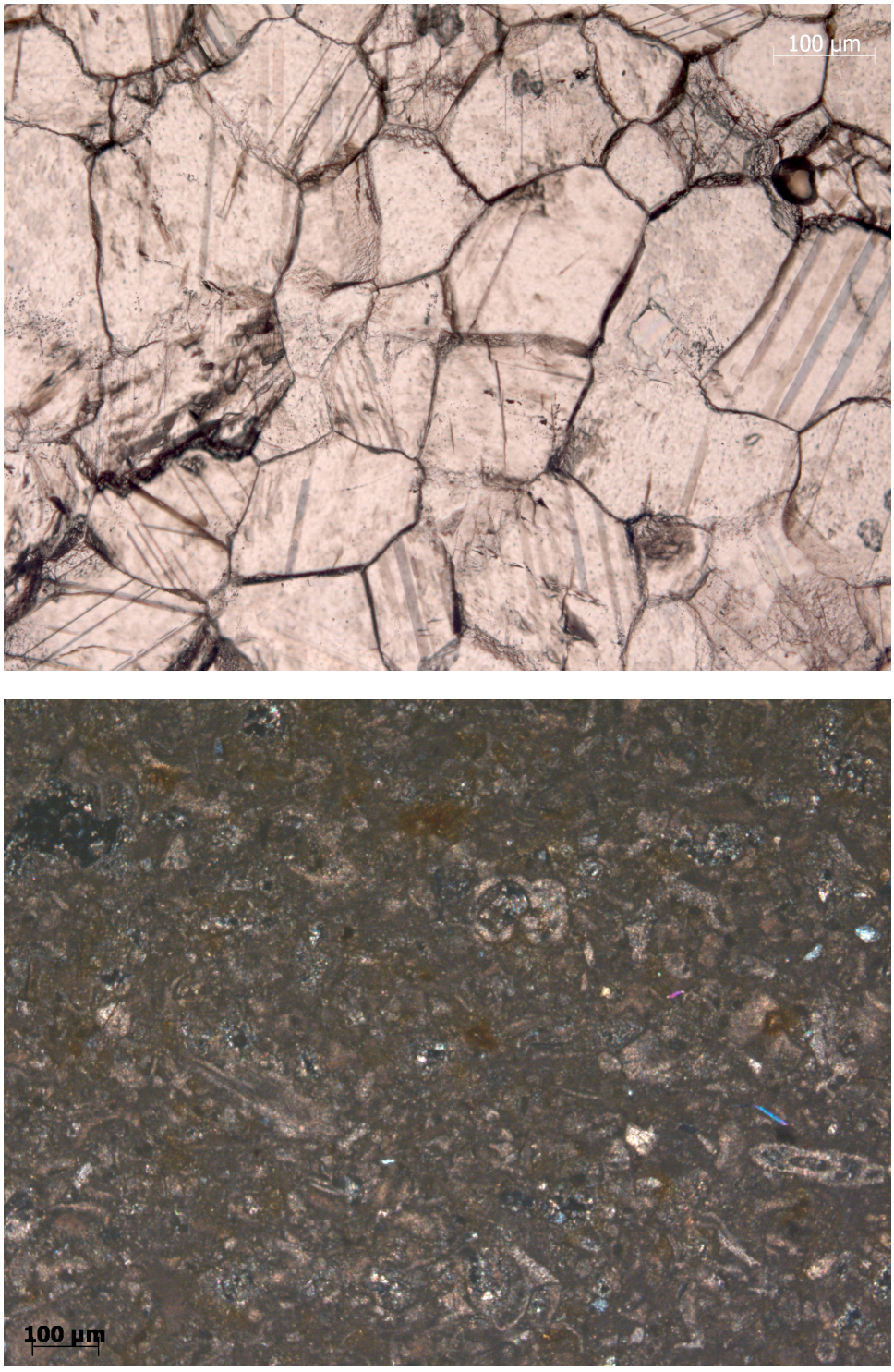

Figure S2. Thin sections photomicrographs of untreated Carrara marble (top) and biomicritic limestone (bottom) samples. Carrara marble (TPPL mode) shows a typical homeoblastic polygonal microstructure. The biomicritic limestone (bottom) reveals (CTPL mode) an abundant microfossilifer *fauna* embedded within a micritic matrix; the carbonatic cement is very scarce.

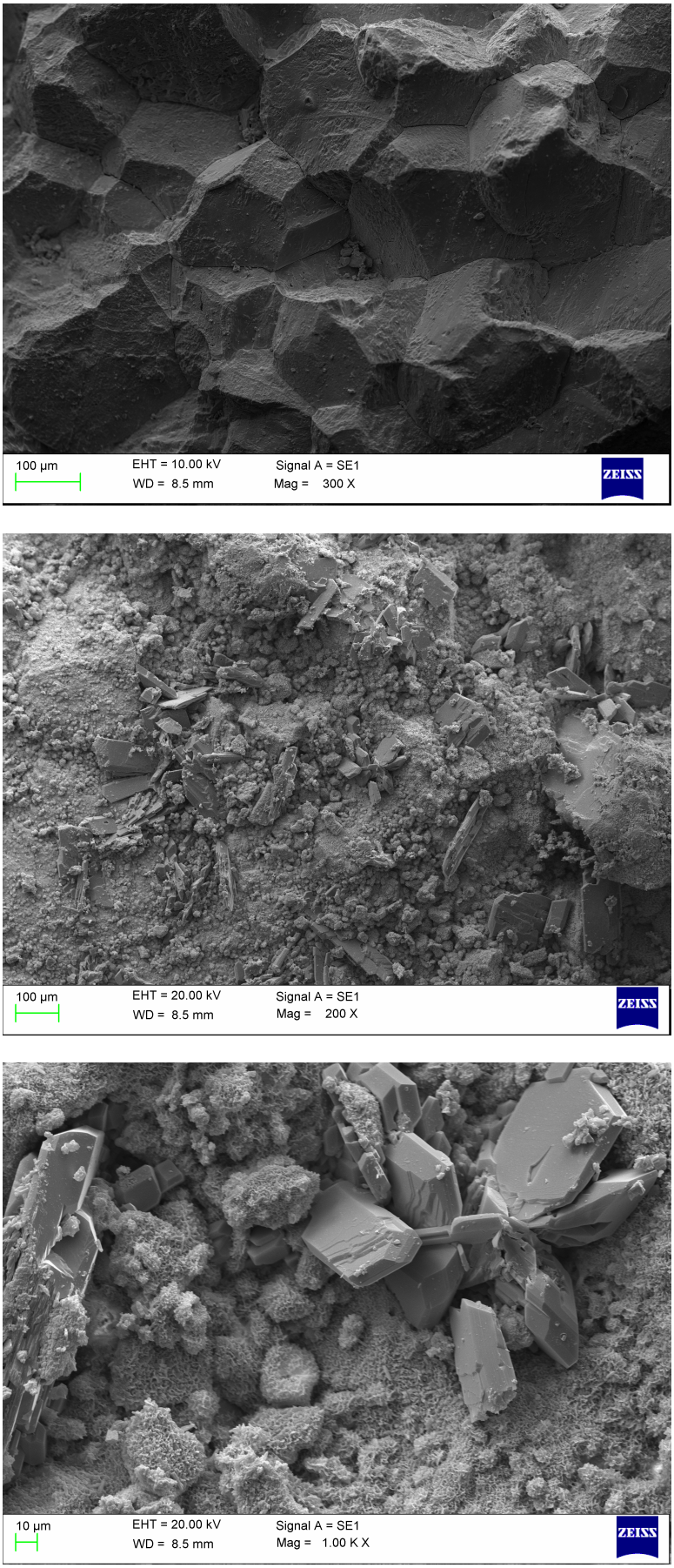

Figure S3. SEM images of Carrara marble. Untreated sample (top); overview of treated sample (middle); close-up of previous image showing the mineral coating (bottom).

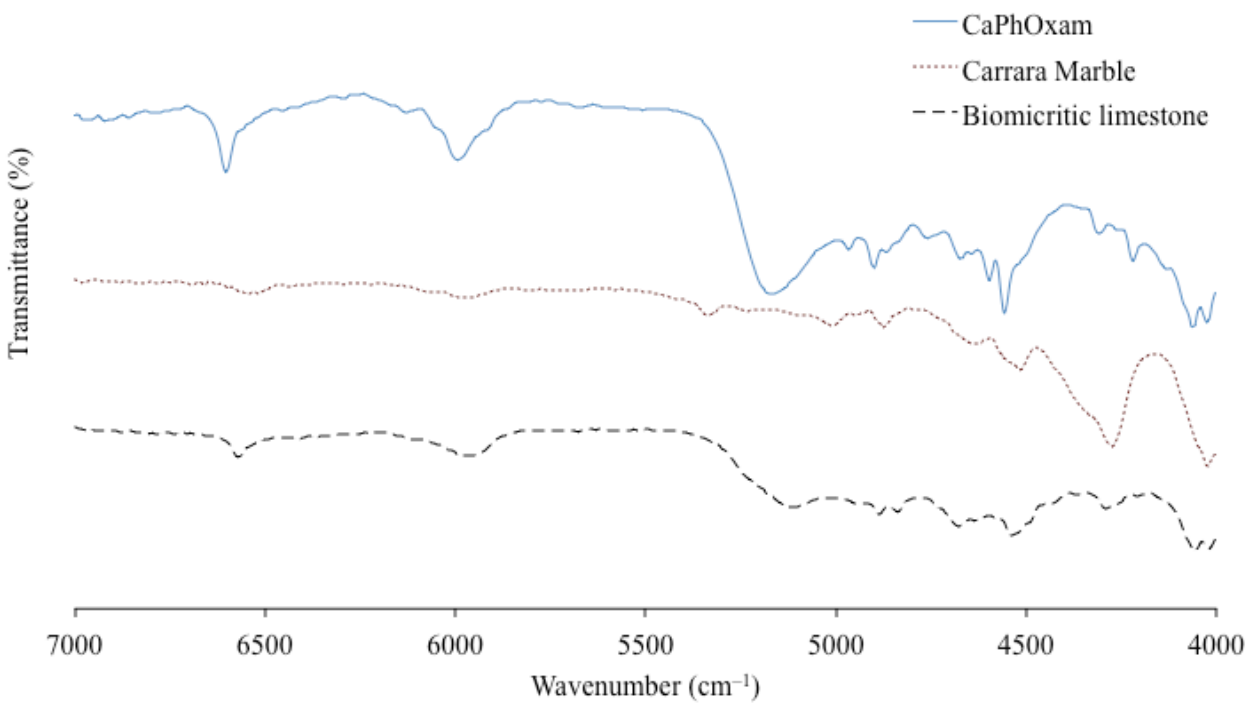

Figure S4. Superimposed FT-NIR spectra of CaPhOxam and treated samples of Carrara marble and biomicritic limestone.