Supporting Information

Correlation of Magnetic Resonance (EPR, ssNMR) Parameters and Crystal-Microstrain in Marbles as a Tool to Probe their Provenance

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Supplementary Figures

Supplementary Figure 1

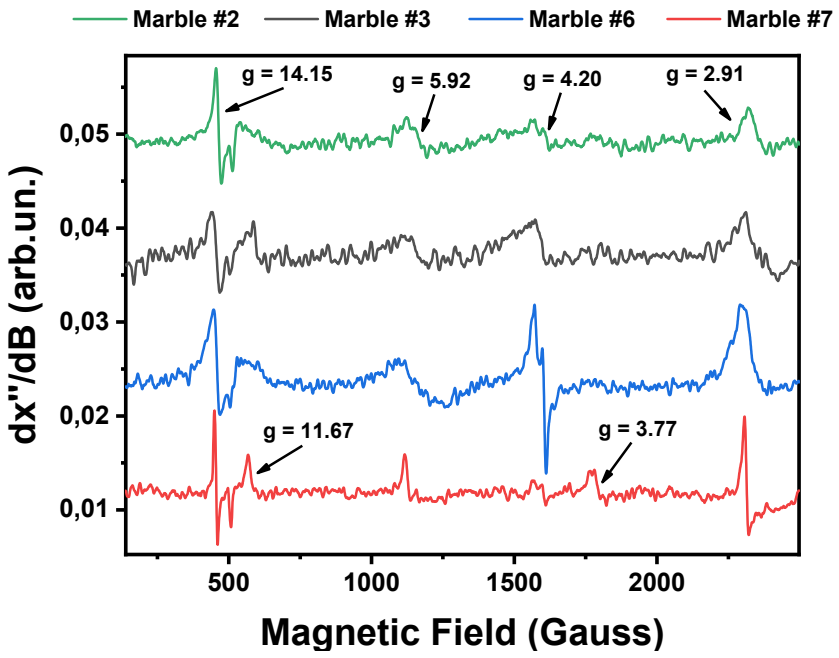
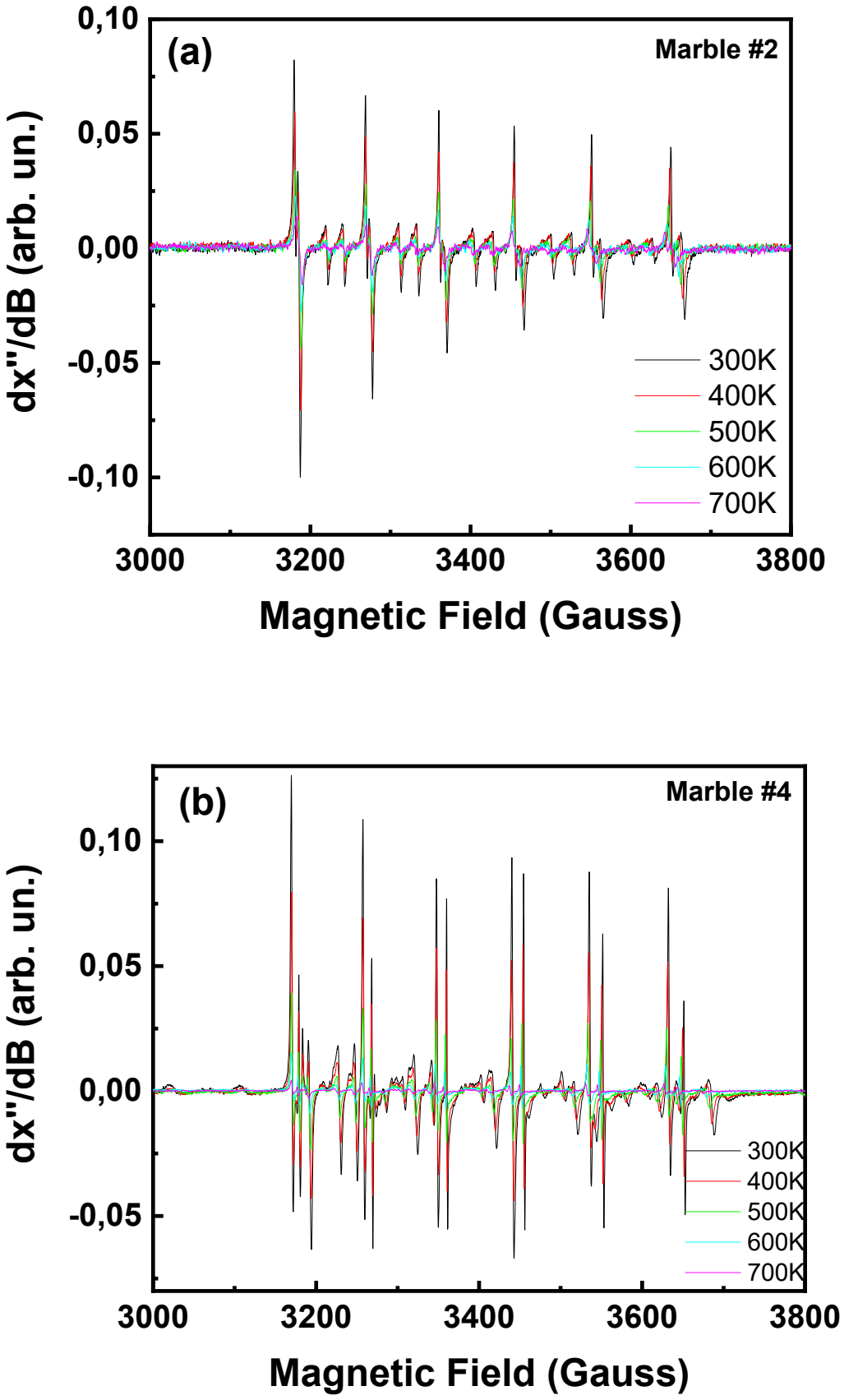


Figure S1: EPR spectra of Fe^{3+} ions (S = 5/2) in Greek marbles #2, #3, #6 and #7. g-values for the Fe^{3+} species are indexed.

Supplementary Figure 2
High Temperature EPR spectra 300 K up to 700 K.



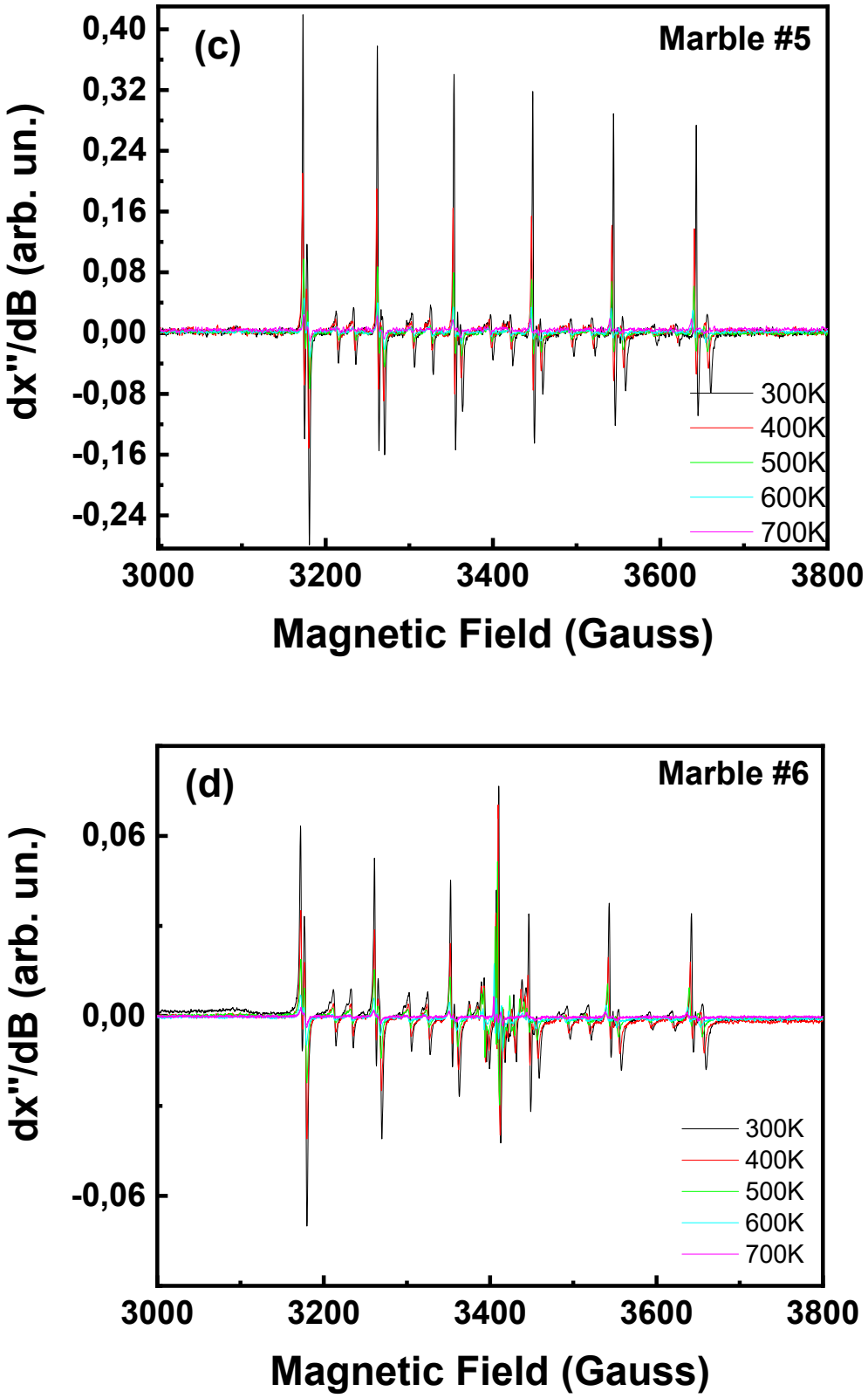
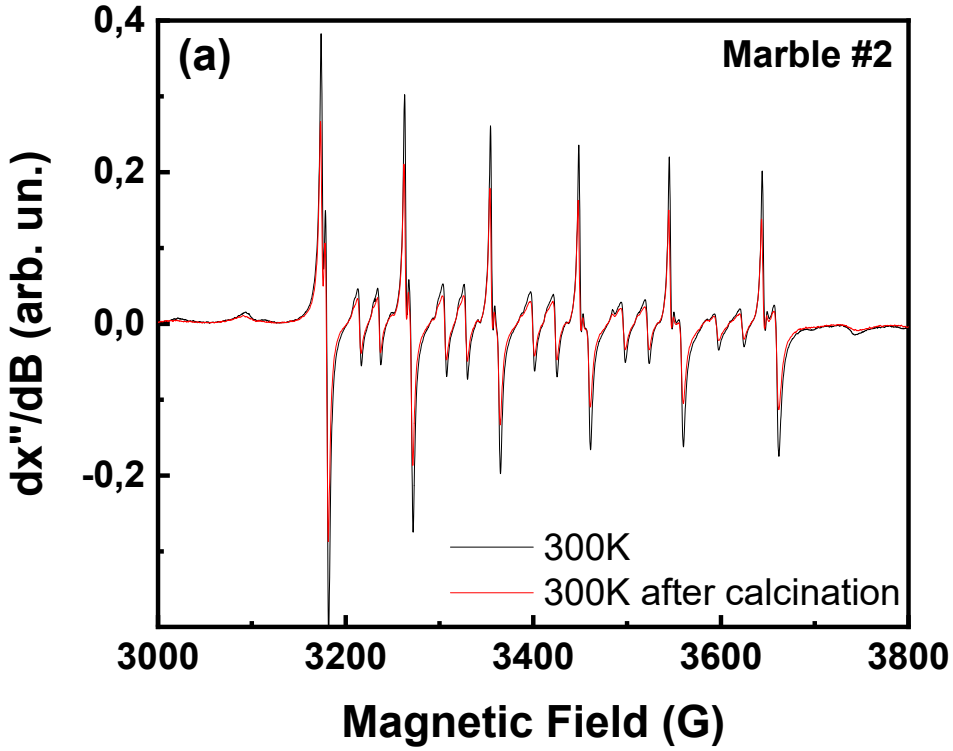
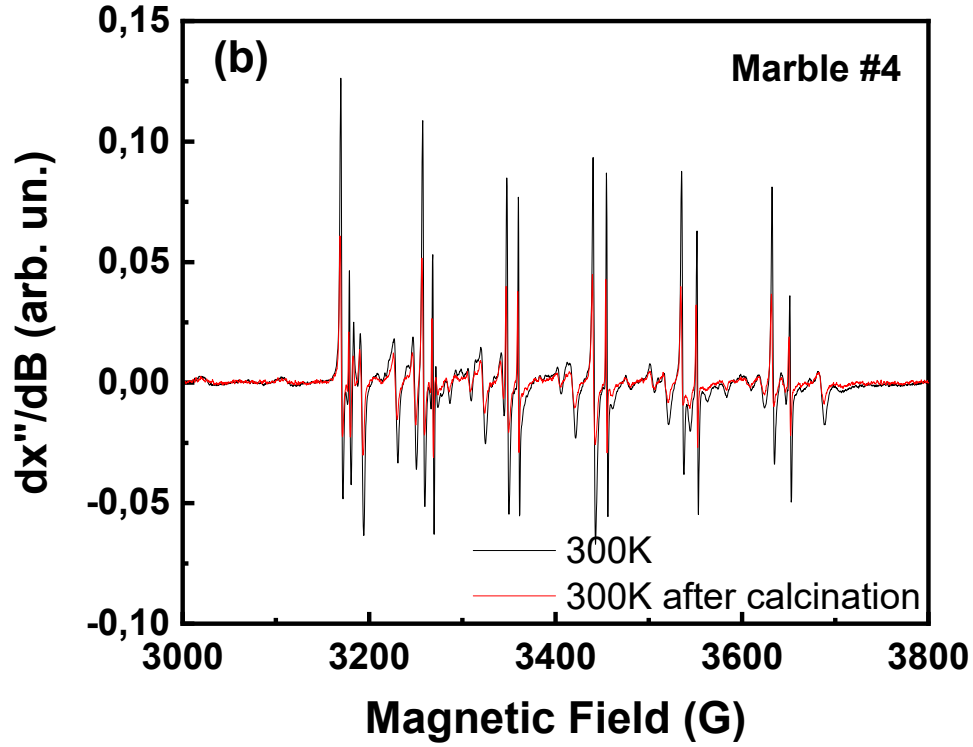


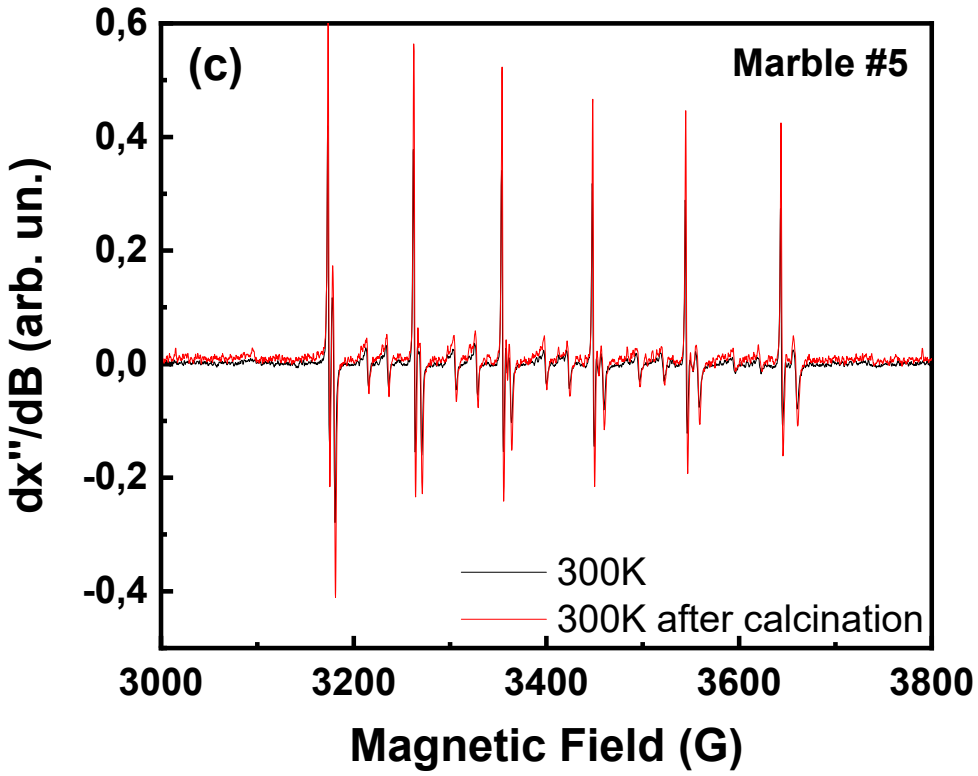
Figure S2: High Temperature EPR spectra for selected Greek Marbles according to their phase composition. (a) Marble #2-Ioannina, (b) Marble #4-Thassos, (c) Marble #5-Kavala and (d) Marble #6-Chios.

Supplementary Figure 3

In Figure S.3 a-d we present the EPR spectra of each selected marble at 300K before calcination (black line) and at 300K after calcined up to 700K (4 hours rest at 700K).




(b)
Marble #4
0,15
0,10
0,05
0,00
-0,05
-0,10
dx''/dB (arb. un.)
300K
300K after calcination
3000
3200
3400
3600
3800
Magnetic Field (G)


(c)
Marble #5
0,6
0,4
0,2
0,0
-0,2
-0,4
dx''/dB (arb. un.)
300K
300K after calcination
3000
3200
3400
3600
3800
Magnetic Field (G)

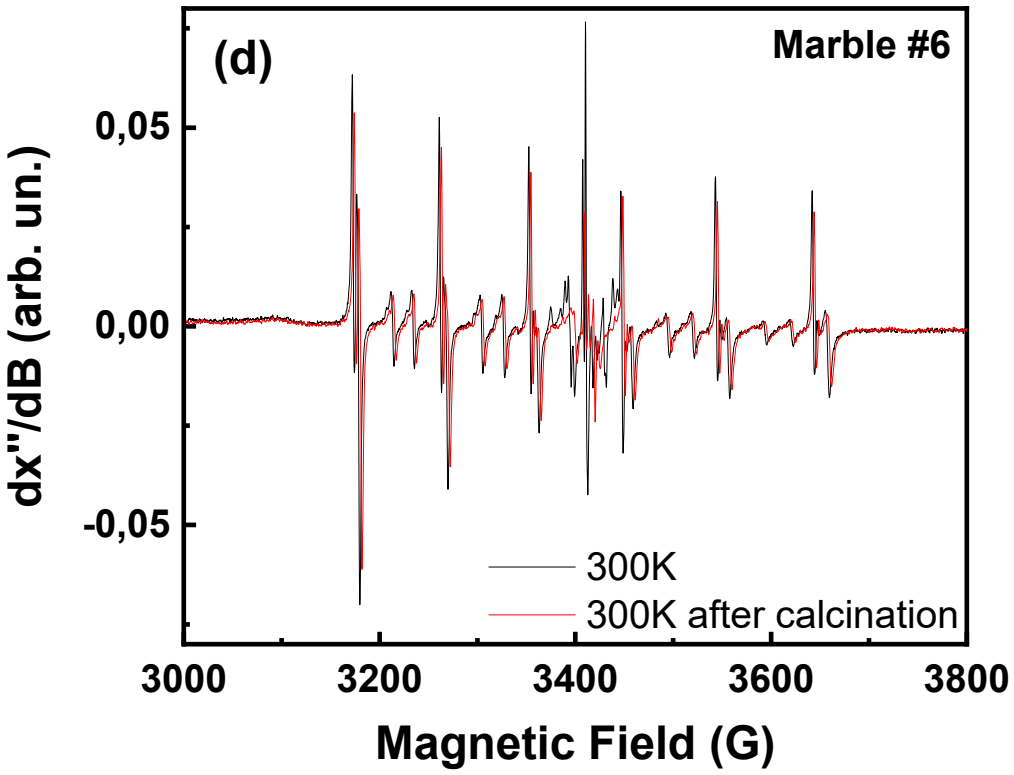
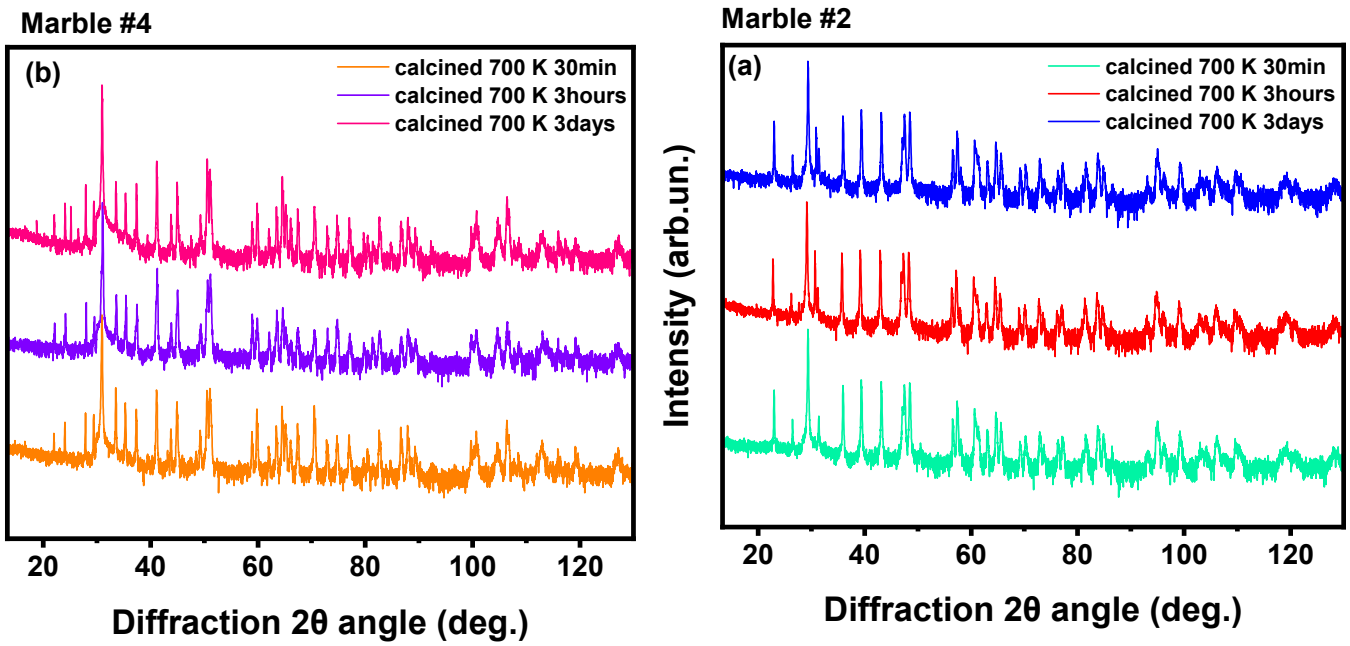


Figure S3: High Temperature EPR spectra from selected Greek Marbles before and after calcination. (a) Marble #2, (b) Marble #4, (c) Marble #5 and (d) Marble #6.

Supplementary Figure 4



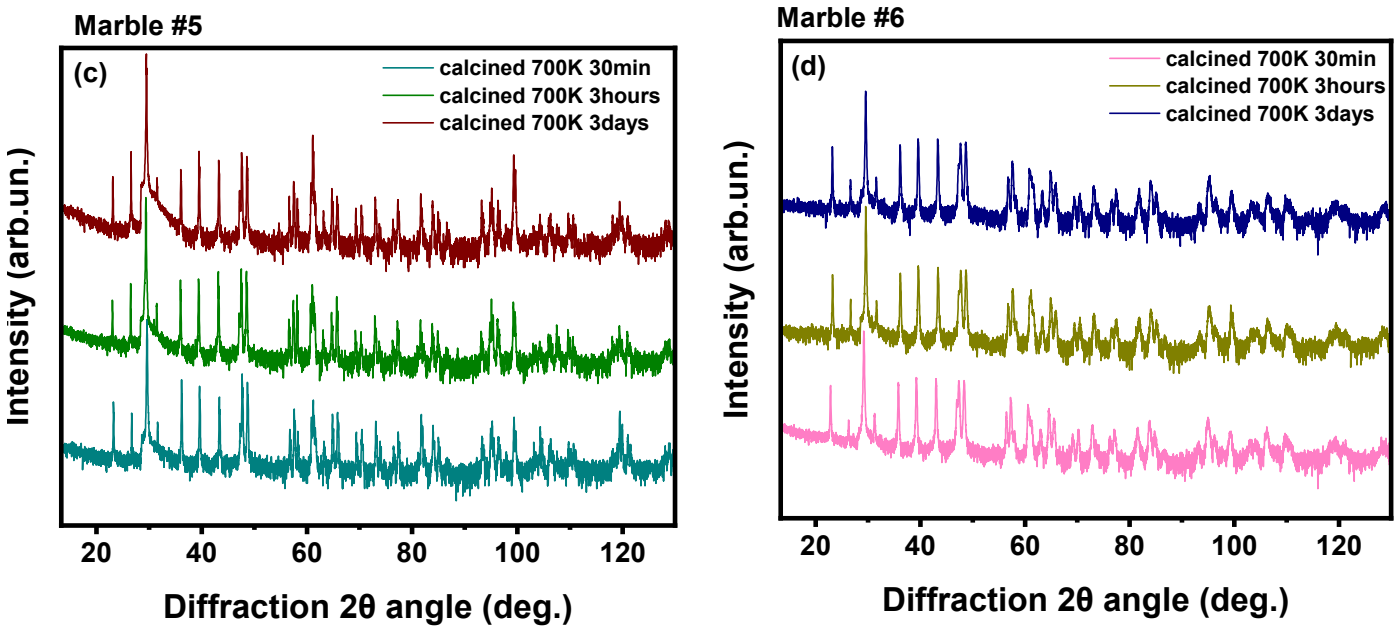
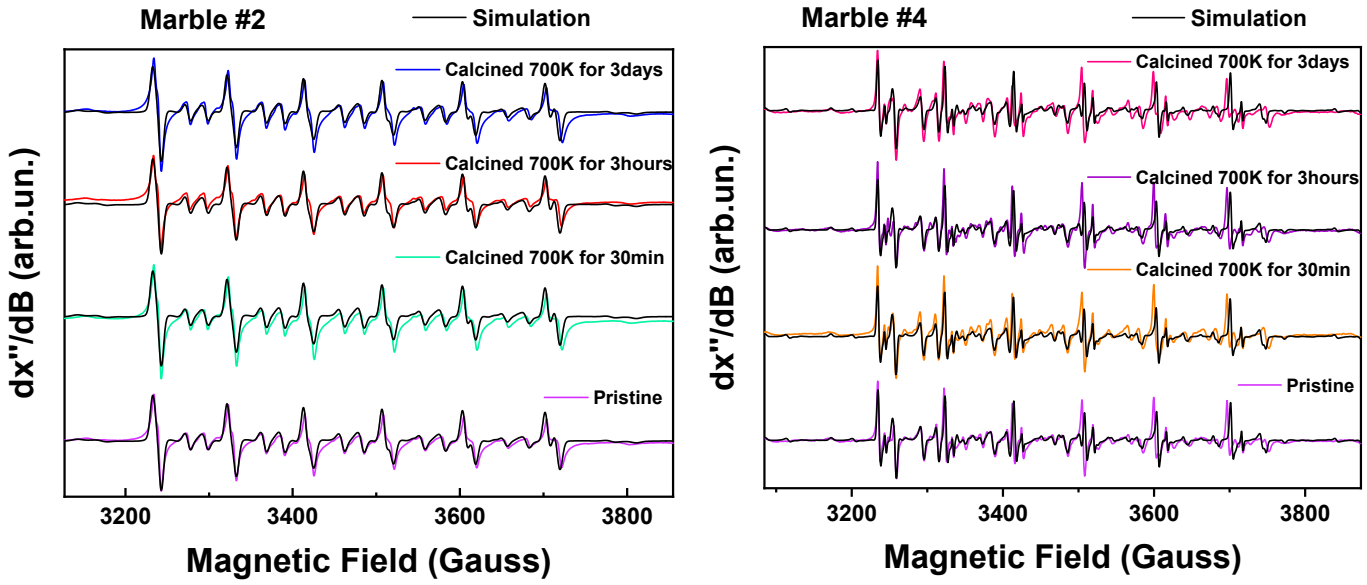


Figure S4: XRD patterns of the selected Greek marbles (a) #2, (b) #4, (c) #5, (d) #6 with a calcination treatment of 700 K for 30 min, 3 hours and 3 days.

Supplementary Figure 5



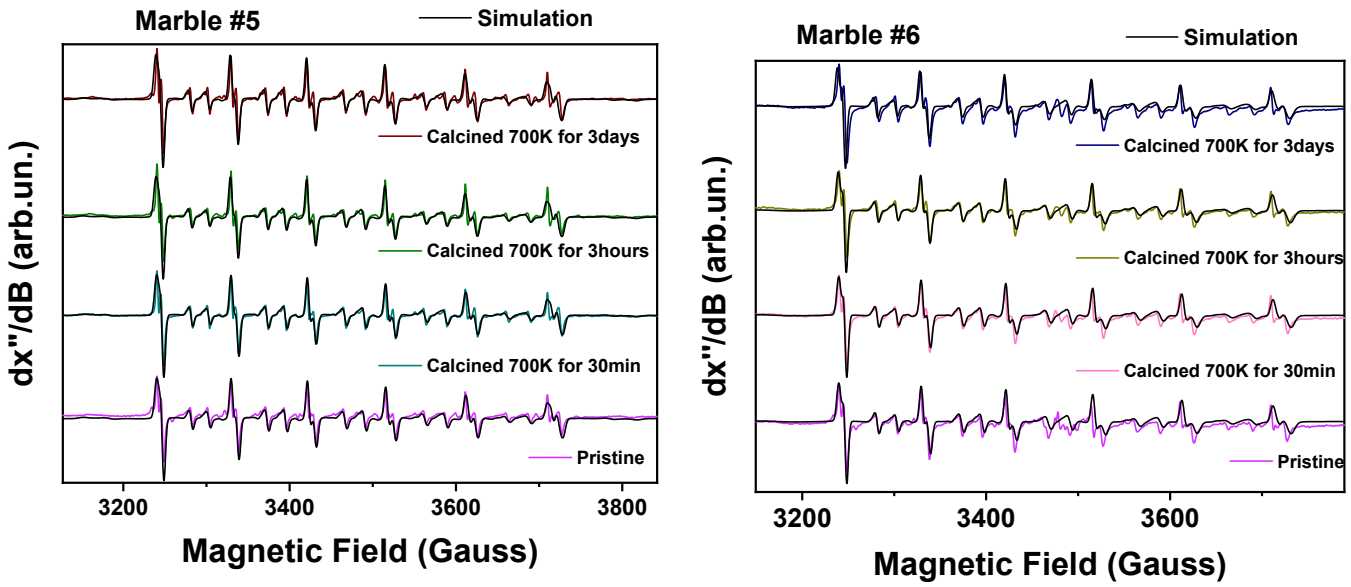


Figure S5: EPR spectra of selected Greek marbles (#2, #4, #5, #6) calcined at 700 K for different time periods.

Supplementary Figure 6

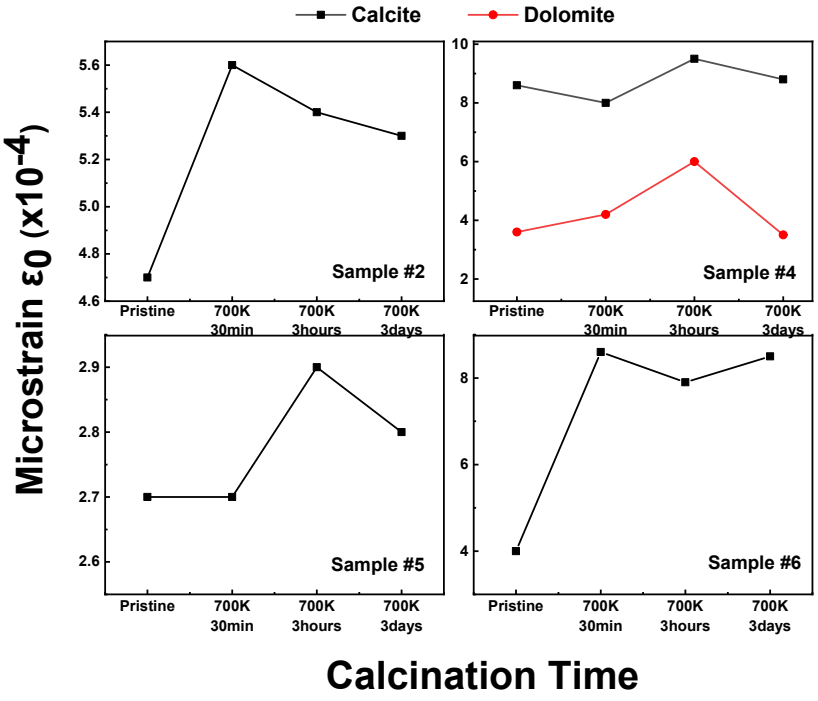


Figure S6: Microstrain vs calcination time for the temperature of 700 K.

Supplementary Figure 7

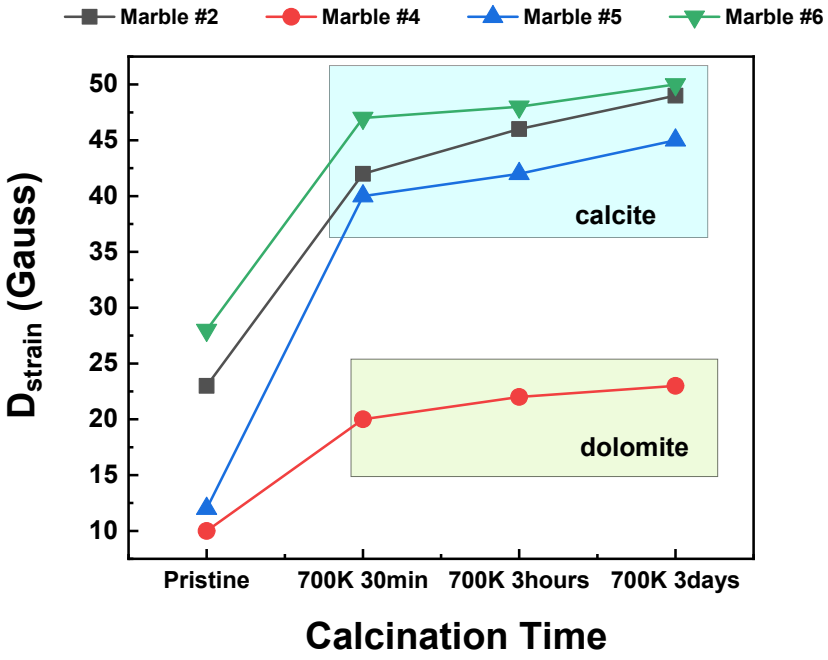


Figure S7: D_{strain} versus calcination time of the selected Greek marbles (#2, #4, #5, #6). We acknowledge that calcitic marbles have large D_{strain} = 35-50 G over time, whilst dolomitic have low D_{strain} = 15-20 G.

Supplementary Figure 8

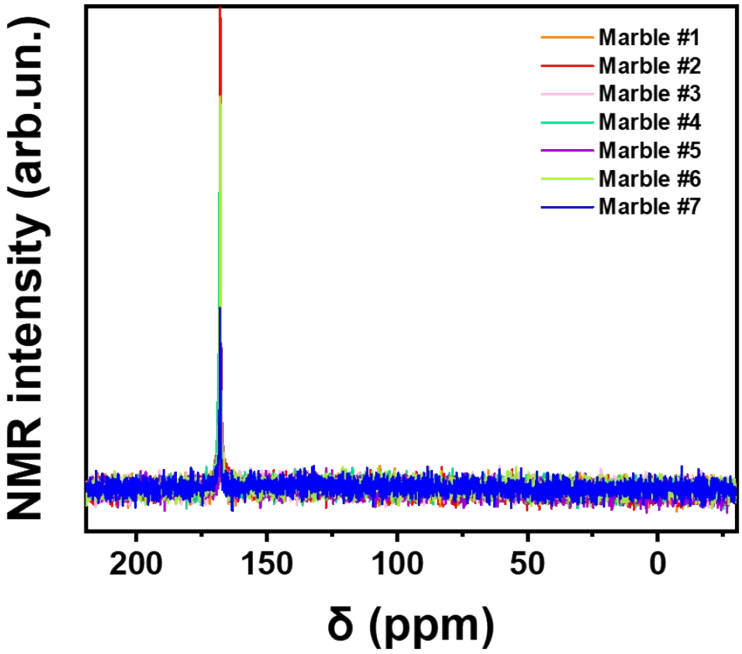


Figure S8: ^{13}C NMR spectra of marbles.

Supplementary Tables

Table S1: Microstain ε_0 values for the calcined Greek marbles (#2, #4, #5, #6) obtained from TOPAS analysis for the XRD data.

Calcination Time	Microstrain ε_0 ($\times$ 10^{-4})	
	Calcite $CaCO_3$	Dolomite $CaMg(CO_3)_2$
Marble #2		
700K for 30 min	5.6 $\pm$ 0.2	–
700K for 3 hours	5.4 $\pm$ 0.1	–
700K for 3 days	5.3 $\pm$ 0.1	–
Marble #4		
700K for 30 min	8.0 $\pm$ 0.7	4.2 $\pm$ 0.6
700K for 3 hours	9.5 $\pm$ 1.7	6.0 $\pm$ 0.6
700K for 3 days	8.8 $\pm$ 1.3	3.5 $\pm$ 0.7
Marble #5		
700K for 30 min	2.7 $\pm$ 0.2	–
700K for 3 hours	2.9 $\pm$ 0.4	–
700K for 3 days	2.8 $\pm$ 0.4	–
Marble #6		
700K for 30 min	8.6 $\pm$ 0.2	–
700K for 3 hours	7.9 $\pm$ 0.4	–
700K for 3 days	8.5 $\pm$ 0.4	–

Table S2: Spin Hamiltonian parameters for the calcined Greek marbles (#2, #4, #5, #6).

Calcination Time	A [A_x , A_y , A_z] (Gauss) (± 1)	[D, E] (Gauss) (± 0.5)	D_{strain} (Gauss) (± 1)	g (± 0.0001)
Marble #2				
700K for 30 min	[95, 94, 93]	[86.0, 4.3]	42	2.0005
700K for 3 hours	[95, 94, 93]	[86.4, 4.3]	46	2.0005
700K for 3 days	[95, 94, 93]	[85.2, 4.3]	49	2.0005
Marble #4				
700K for 30 min	[94, 95, 95]	[14.0, 0.5]	20	2.0005
700K for 3 hours	[95, 95, 95]	[14.5, 0.5]	22	2.0005
700K for 3 days	[95, 95, 95]	[14.9, 0.5]	23	2.0005
Marble #5				
700K for 30 min	[93, 96, 93]	[82.0, 4.6]	40	2.0005
700K for 3 hours	[93, 96, 93]	[90.3, 4.6]	42	2.0005
700K for 3 days	[93, 96, 93]	[83.3, 4.6]	45	2.0005
Marble #6				
700K for 30 min	[94, 96, 94]	[90.0, 3.6]	47	2.0005
700K for 3 hours	[94, 94, 93]	[89.8, 3.6]	48	2.0005
700K for 3 days	[94, 94, 93]	[85.3, 3.6]	50	2.0005

Table S3: Integrated areas of the ^{13}C solid state NMR spectra of Greek marbles.

Marble	Integrated area
#1	101613
#2	450926
#3	256272
#4	349316
#5	95384
#6	301752
#7	122979