

Electronic Supplementary Information

for the paper

Calcite-aragonite transformation in eggshell: A crucial role of organics and assessment of the impact of milling conditions on its extent using Taguchi design

Kairat Kenges^{a,b}, Stephanos Karafiludis^c, Róbert Džunda^d, Imelda Octa Tampubolon^a, Bagdat Satybaldiev^b, Franziska Emmerling^c, Matej Baláž^{a*}

^{a.} Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 04001 Košice, Slovakia; kenges.qayrat@gmail.com (K.K.); balazm@saske.sk (M.B.)

^{b.} Center of Physical-Chemical Methods of Research and Analysis, Al-Farabi Kazakh National University, Tole bi 96A, 050012, Almaty, Kazakhstan; bagdat.satybaldiev@gmail.com (B.S.)

^{c.} Federal Research Institute for Materials Testing, Richard- Wiltstätter Strasse 11, 12489 Berlin, Germany; stefanos.karafiludis@bam.de (S.K.); franziska.emmerling@bam.de (F.E.)

^{d.} Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 04001 Košice, Slovakia; rdzunda@saske.sk (R.DŽ.);

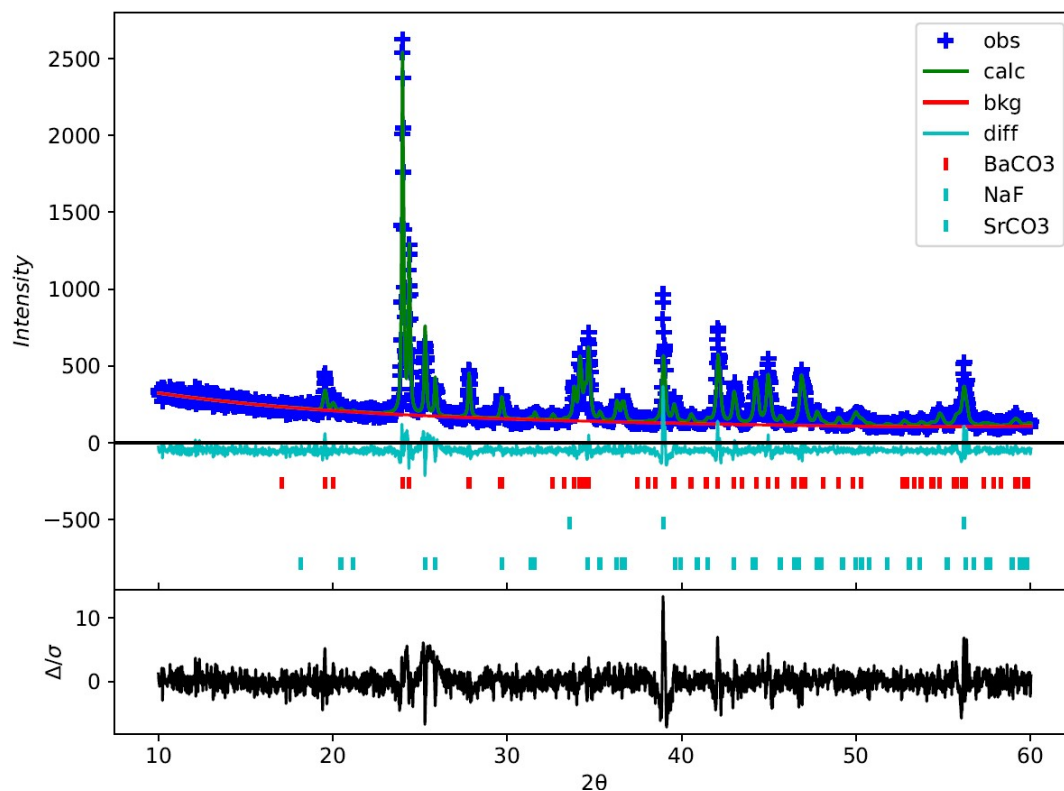


Fig S1. XRD patterns of the prepared mixture (0.50 BaCO₃- 0.25 NaF- 0.25 SrCO₃) along with the Le Bail refined data shown as solid lines. Estimated mass fraction of mixture minerals by the Le-Bail refinement was 0.499 for BaCO₃, 0.251 for NaF for 0.250.

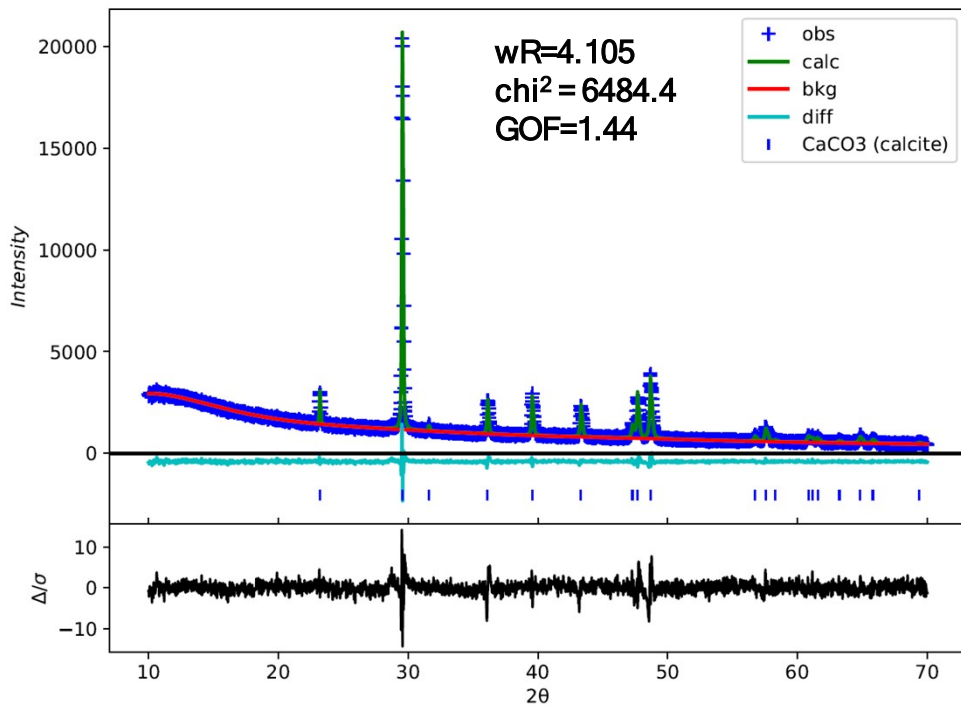
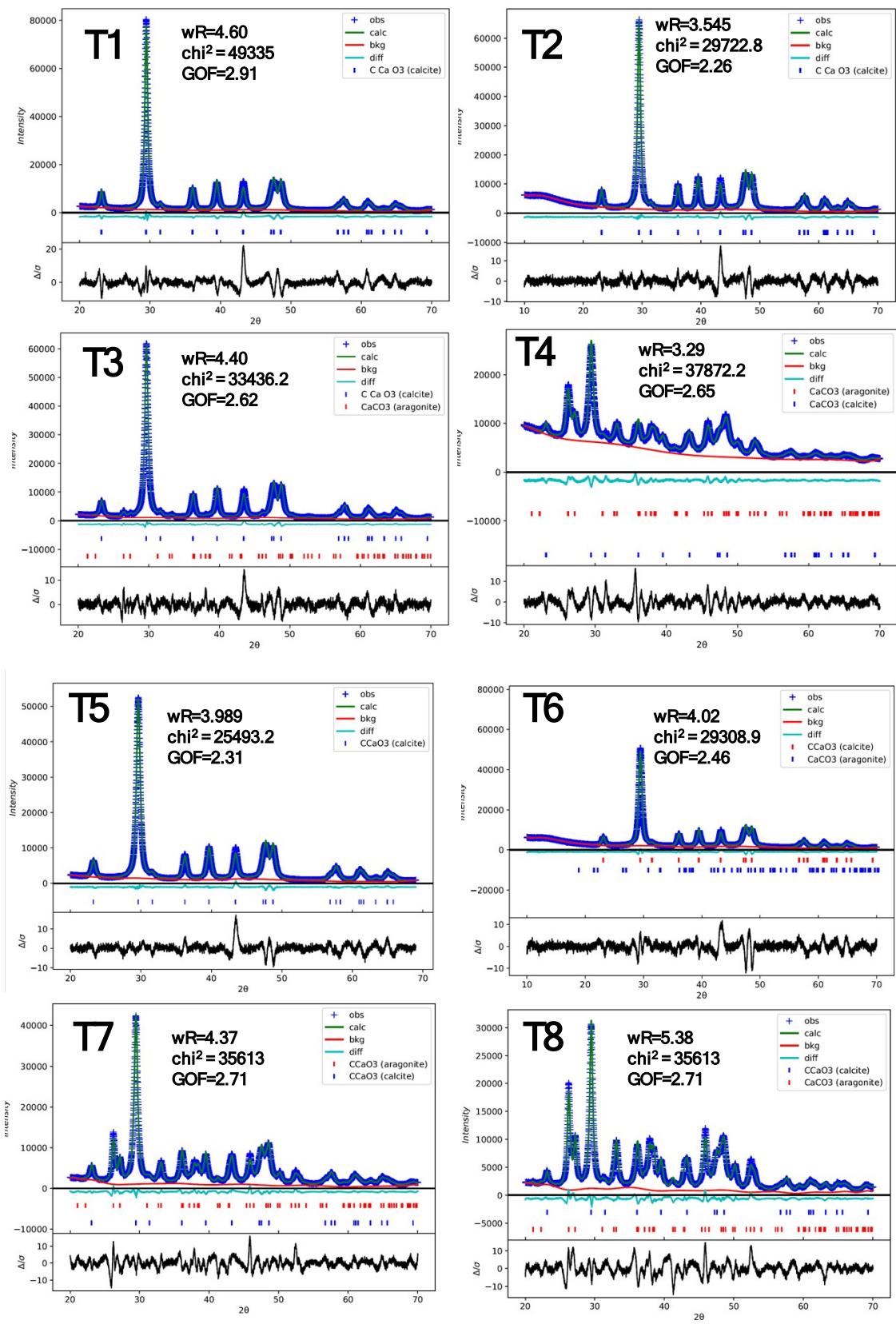
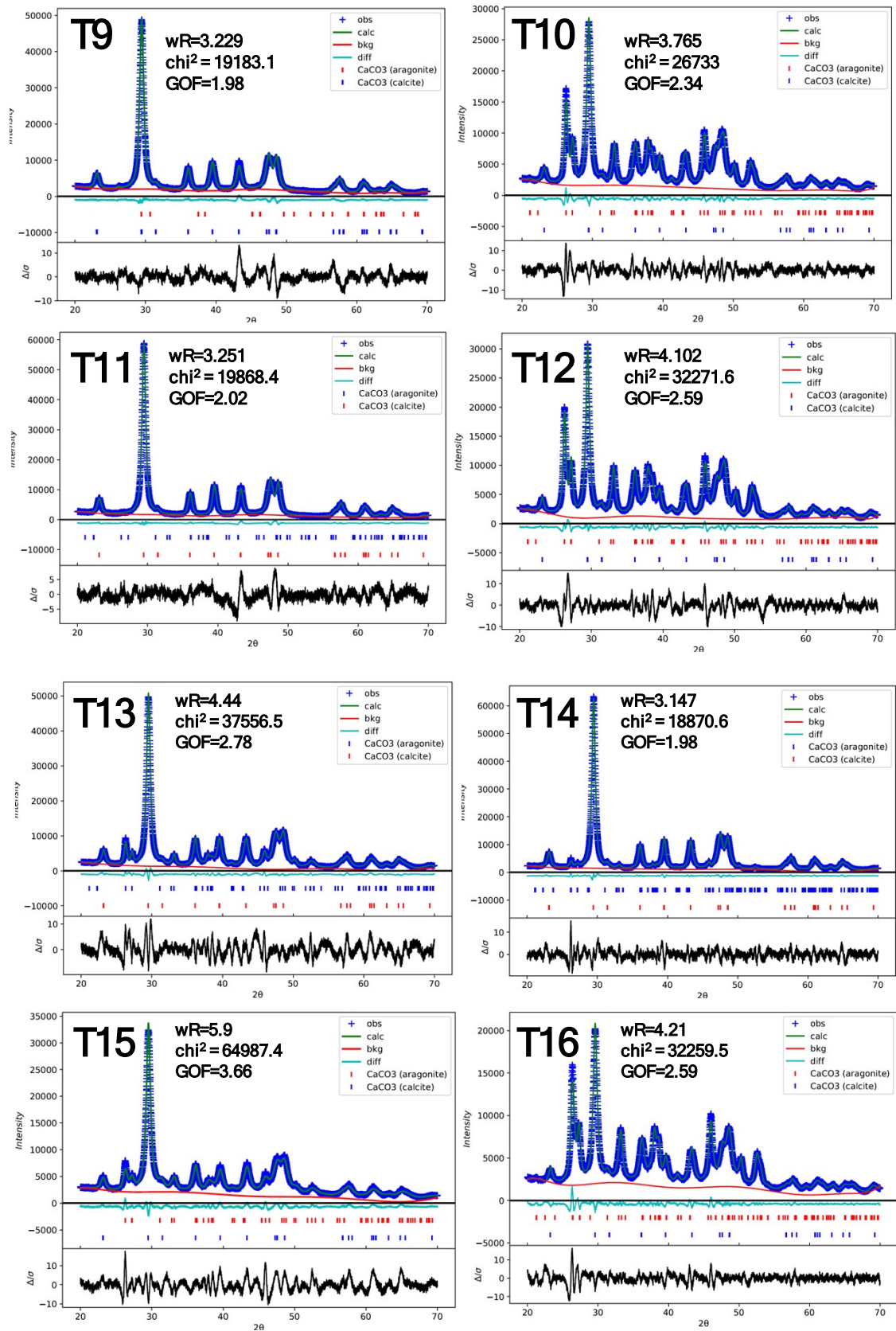


Fig. S2: XRD patterns of the initial ES+ESM sample along with the Le-Bail refined data shown as solid lines. The black solid lines at the bottom represent the difference between the recorded and the refined XRD data.



a

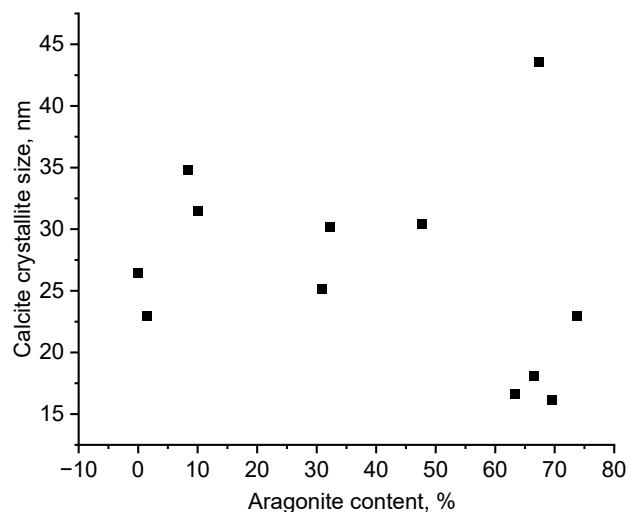
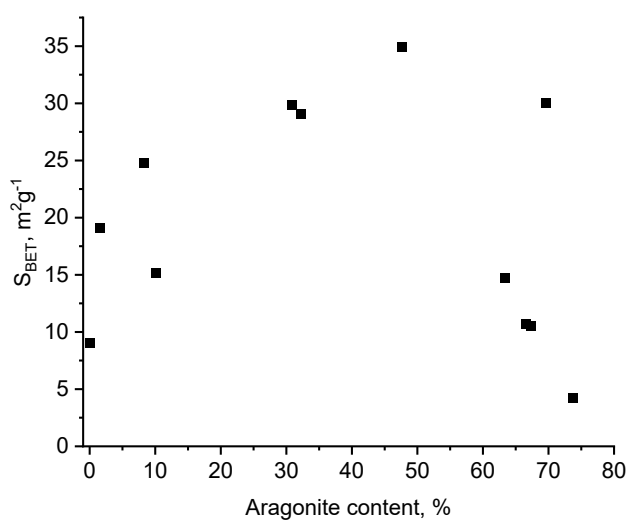


b

Fig. S3: XRD patterns of ES-EISM samples, (a) T1-T8, (b) T9-T16 samples along with the Le Bail refined data shown as solid lines. The black solid lines at the bottom represent the difference between the recorded and the refined XRD data.

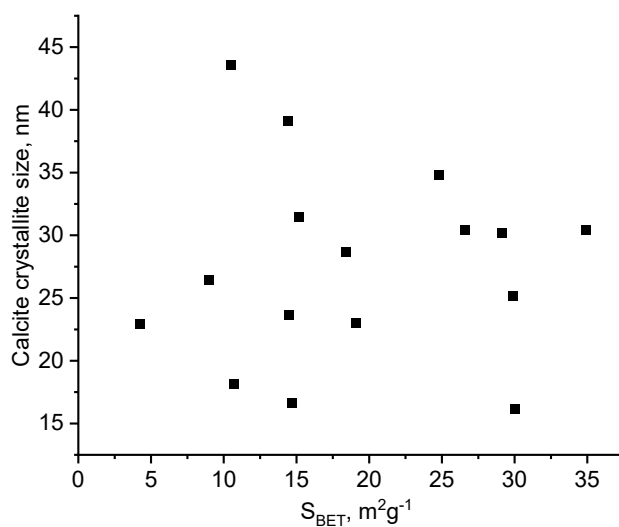
Table S1: Aragonite crystallite size in the samples according to the Le-Bail refinement

Sample	Aragonite crystallite size (nm)
T1	not detected
T2	not detected
T3	33.8±3.4
T4	15.0±1.5
T5	not detected
T6	not detected
T7	32.6±2.0
T8	30.4±1.6
T9	not detected
T10	20.4±0.5
T11	not detected
T12	22.6±2.9
T13	41.0±4.3
T14	27.6±6.3
T15	20.2±2.8
T16	21.5±1.6



a

b



c

Fig. S4: The relationships between different properties of ES+ESM-T1-T16 sample: (a) aragonite content vs. S_{BET} value, (b) aragonite content vs. calcite crystallite size, (c) S_{BET} value vs. calcite crystallite size

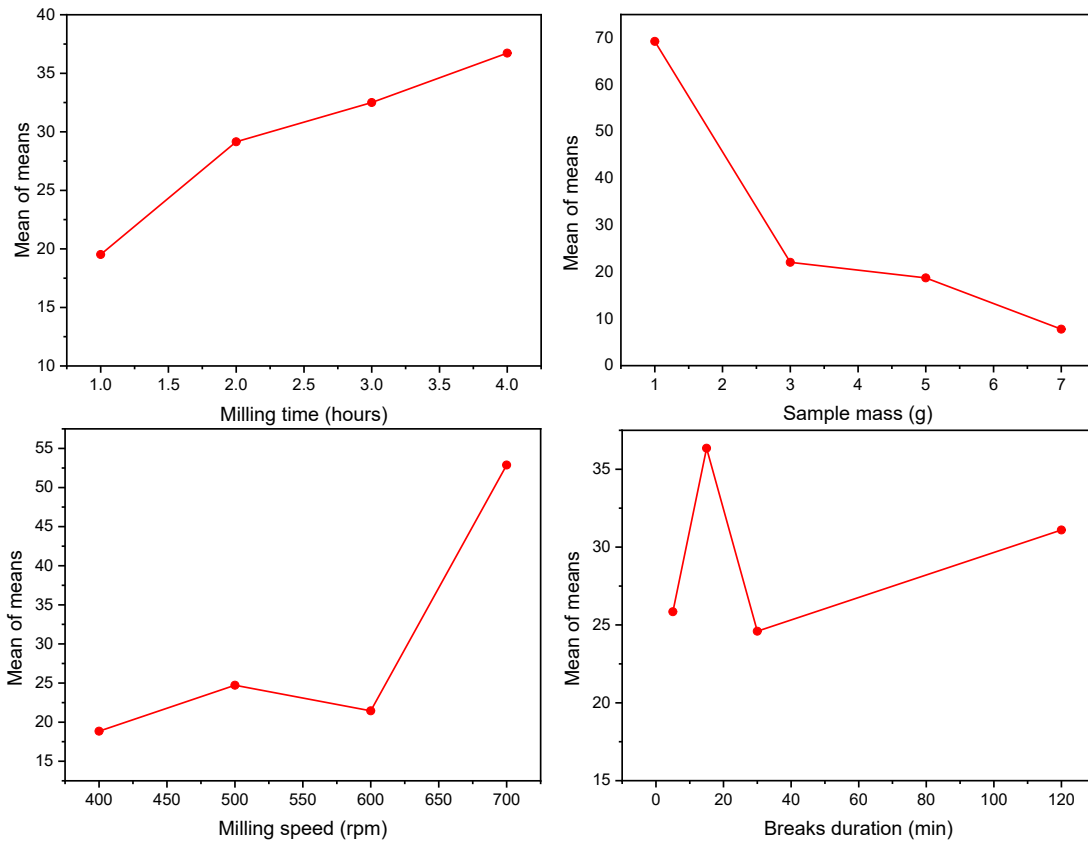


Fig. S5: Results of Taguchi calculations in Minitab (mean values) for the maximum content of aragonite

Table S2: Regression analysis: Equations calculated by the MINITAB14 software. Variables abbreviations: MT- milling time, SM- sample mass, MS- milling speed, BD- breaks duration.

Equation No.	Variables				Equation
	MT	SM	MS	BD	
1		X			Aragonite = 67,0 - 9,40 Sample mass (g)
2			X		Aragonite = - 25,0 + 0,0990 Milling speed (rpm)
3	X				Aragonite = 15,7 + 5,51 Milling time (hours)
4				X	Aragonite = 28,8 + 0,016 Breaks duration (min)
5		X	X		Aragonite = 12,6 - 9,40 Sample mass (g) + 0,0990 Milling speed (rpm)
6	X	X			Aragonite = 53,3 + 5,51 Milling time (hours) - 9,40 Sample mass (g)
7		X		X	Aragonite = 66,4 - 9,40 Sample mass (g) + 0,016 Breaks duration (min)
8	X		X		Aragonite = - 38,8 + 5,51 Milling time (hours) + 0,0990 Milling speed (rpm)
9			X	X	Aragonite = - 25,7 + 0,0990 Milling speed (rpm) + 0,016 Breaks duration (min)
10	X	X	X		Aragonite = - 1,2 + 5,51 Milling time (hours) - 9,40 Sample mass (g) + 0,0990 Milling speed (rpm)
11		X	X	X	Aragonite = 11,9 - 9,40 Sample mass (g) + 0,0990 Milling speed (rpm) + 0,016 Breaks duration (min)
12	X	X		X	Aragonite = 52,6 + 5,51 Milling time (hours) - 9,40 Sample mass (g) + 0,016 Breaks duration (min)
13	X		X	X	Aragonite = - 39,4 + 5,51 Milling time (hours) + 0,0990 Milling speed (rpm) + 0,016 Breaks duration (min)
14	X	X	X	X	Aragonite = - 1,9 + 5,51 Milling time (hours) - 9,40 Sample mass (g) + 0,0990 Milling speed (rpm) + 0,016 Breaks duration (min)
15	X				Aragonite = 8,96 + 12,23 Milling time (hours) - 1,344 Milling time (hours)**2
16		X			Aragonite = 91,94 - 27,51 Sample mass (g) + 2,264 Sample mass (g)**2
17			X		Aragonite = 160,4 - 0,6043 Milling speed (rpm) + 0,000639 Milling speed (rpm)**2
18				X	Aragonite = 30,37 - 0,108 Breaks duration (min) + 0,000940 Breaks duration (min)**2
19	x				Aragonite = - 3,8 + 32,5 Milling time (hours) - 10,44 Milling time (hours)**2 + 1,21 Milling time (hours)**3
20		x			Aragonite = 125,5 - 70,28 Sample mass (g) + 15,16 Sample mass (g)**2 - 1,074 Sample mass (g)**3
21			x		Aragonite = - 972 + 5,874 Milling speed (rpm) - 0,01141 Milling speed (rpm)**2 + 0,000007 Milling speed (rpm)**3
22				x	Aragonite = 13,47 + 2,997 Breaks duration (min) - 0,1089 Breaks duration (min)**2 + 0,000709 Breaks duration (min)**3

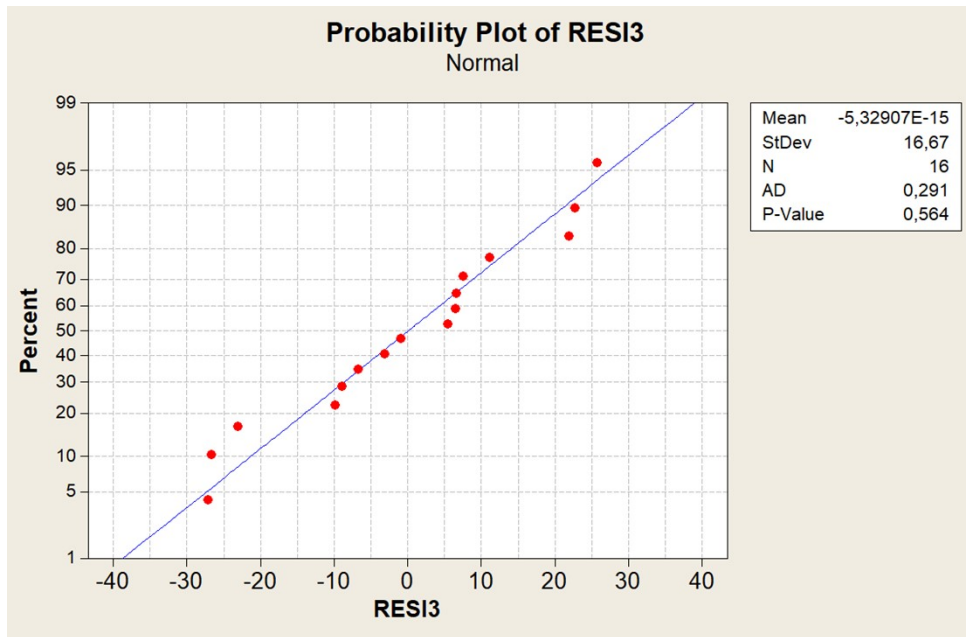


Fig. S6: The normality test of the residuals for equations

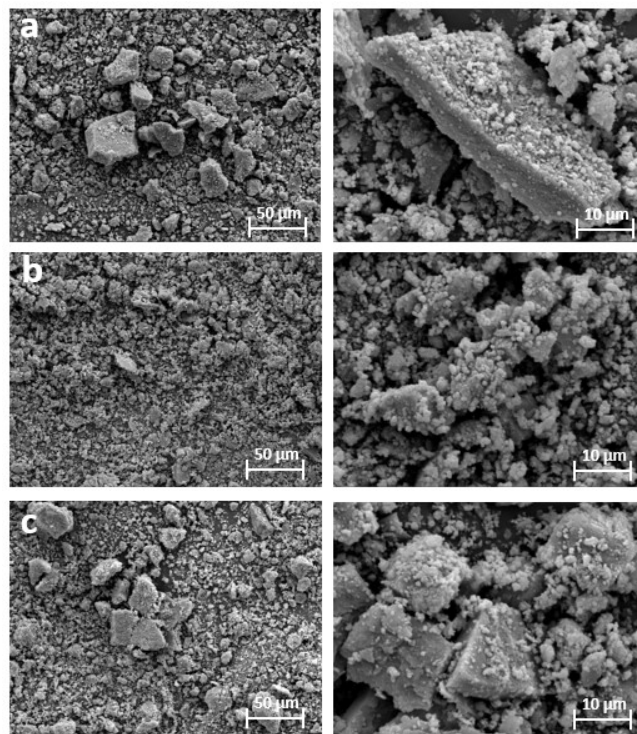


Fig. S7: Scanning electron micrographs (SEM) of mechanically activated material under T4 conditions: (a) ES, (b) ES+ESM, (c) ES+CYS

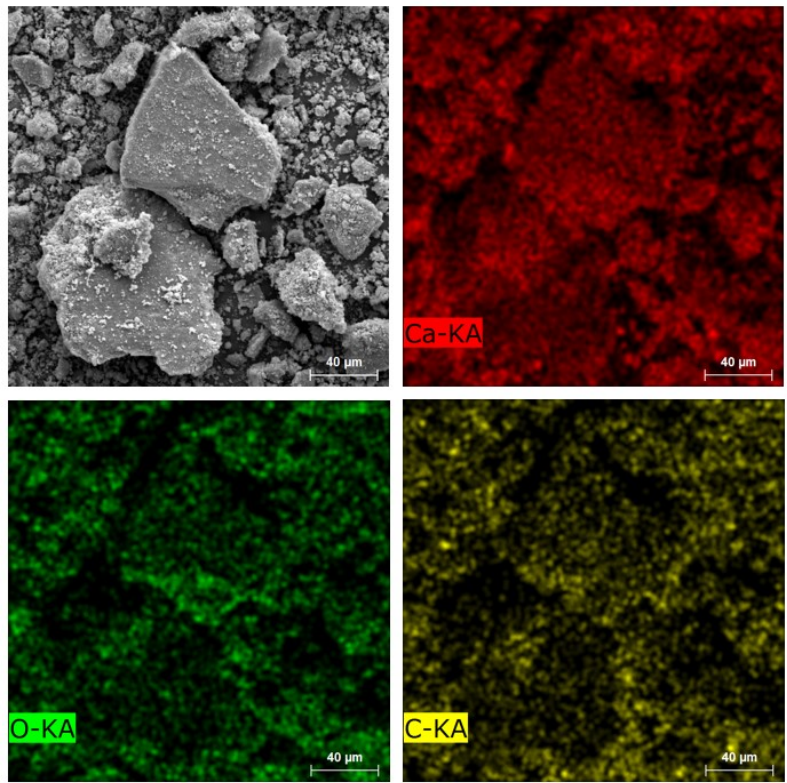


Fig. S8: Scanning electron micrographs (SEM) and mapping of mechanically activated ES under T4 conditions

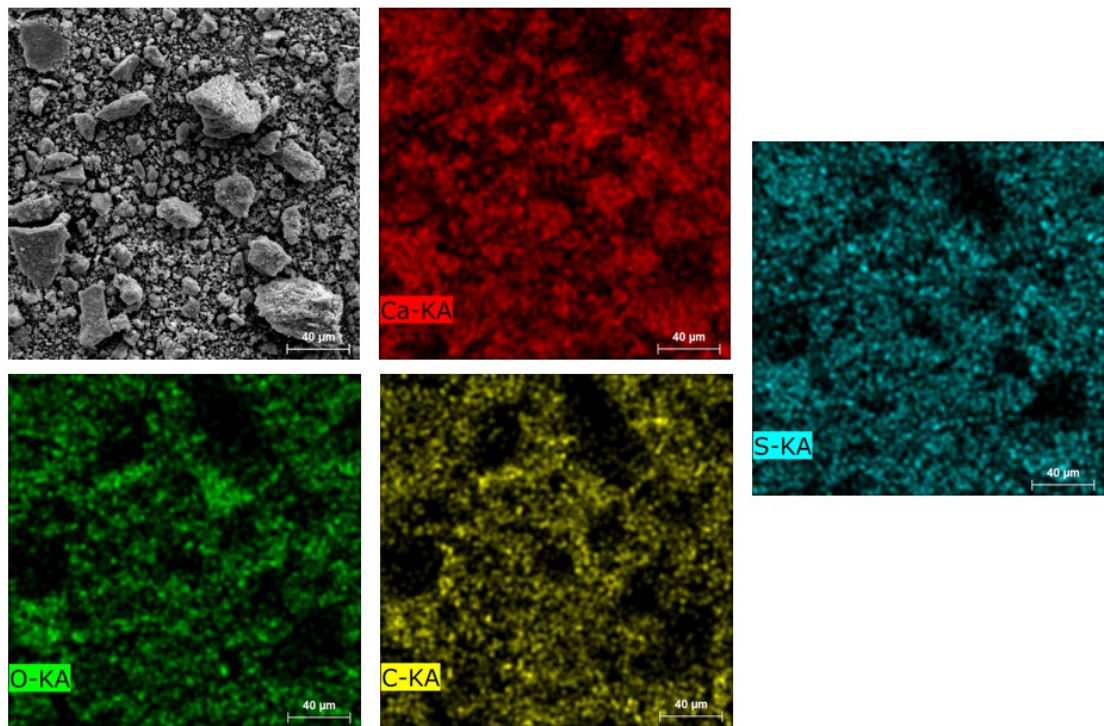


Fig. S9: Scanning electron micrographs (SEM) and mapping of mechanically activated ES+CYS under T4 conditions ES+ESM

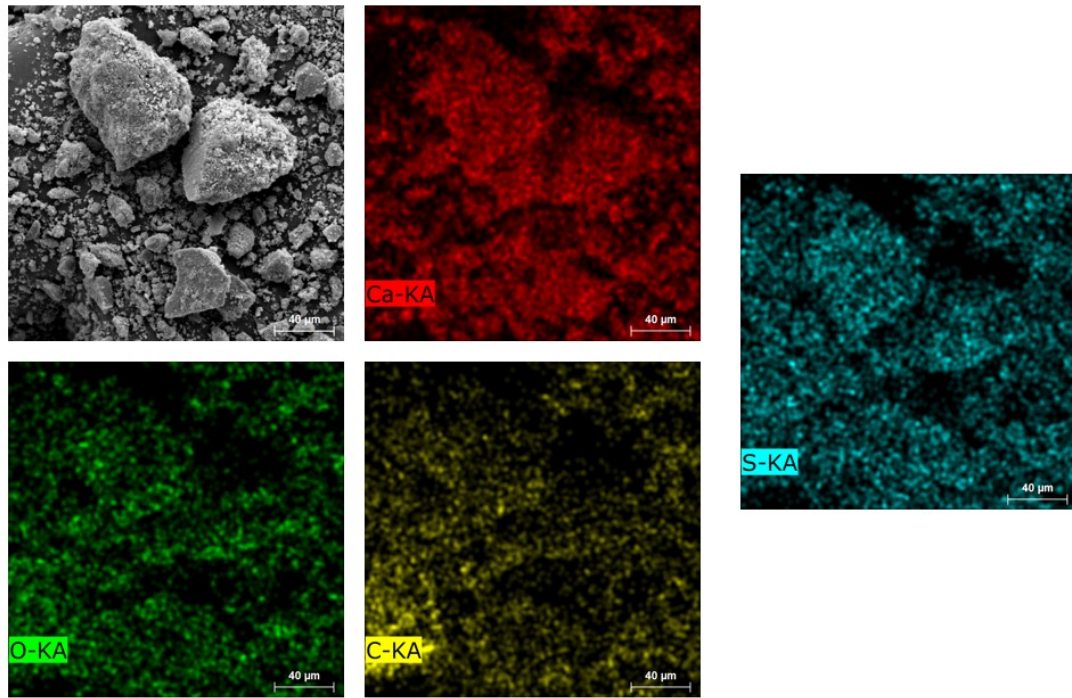


Fig. S10: Scanning electron micrographs (SEM) and mapping of mechanically activated ES+ESM under T4 conditions

Table S3: EDS chemical composition of samples according to area EDS analysis from the three distinct areas for ES, ES+CYS, ES+ESM milled at T4 conditions and initial ES+ESM

ES (T4)			
Area	Ca	O	S
1	21.03	78.97	-
2	21.11	78.89	-
3	20.86	79.14	-
Average	21	79	
ES+CYS (T4)			
Area	Ca	O	S
1	20.30	78.70	1.00
2	21.04	78.09	0.87
3	20.40	78.79	0.81
Average	20.58	78.53	0.89
ES+ESM (initial)			
Area	Ca	O	S
1	25.58	73.73	0.69
2	25.70	73.49	0.81
3	25.92	73.41	0.67
Average	25.73	73.54	0.72
ES+ESM (T4)			
Area	Ca	O	S
1	22.82	76.42	0.76
2	21.50	77.79	0.71
3	20.91	78.34	0.75
Average	21.74	77.52	0.74

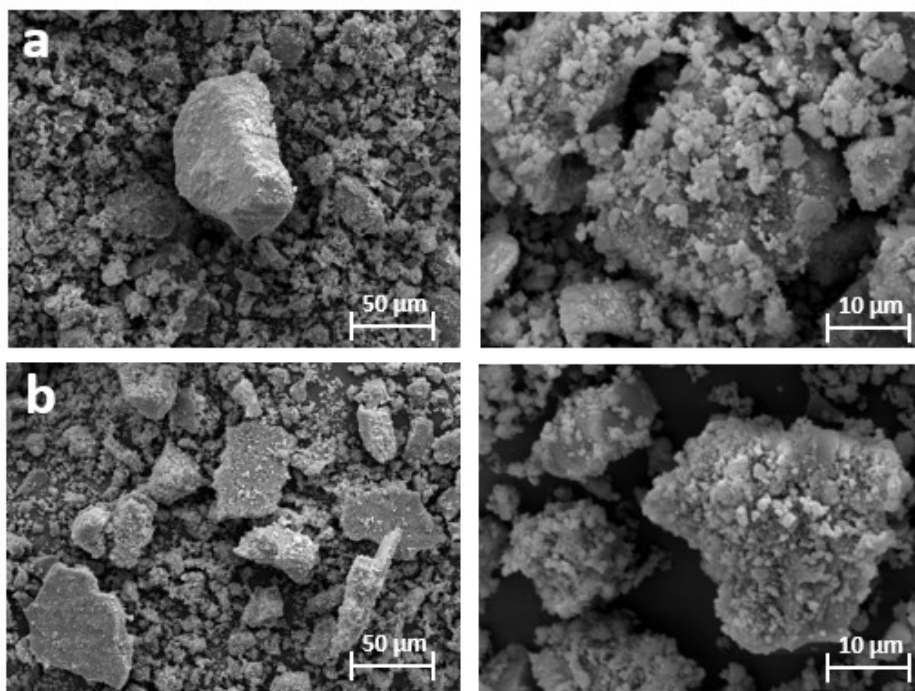


Fig. S11: Scanning electron micrographs (SEM) of commercial calcite (CC) (a) and CC with 5% L-cysteine (b) treated under T4 conditions.

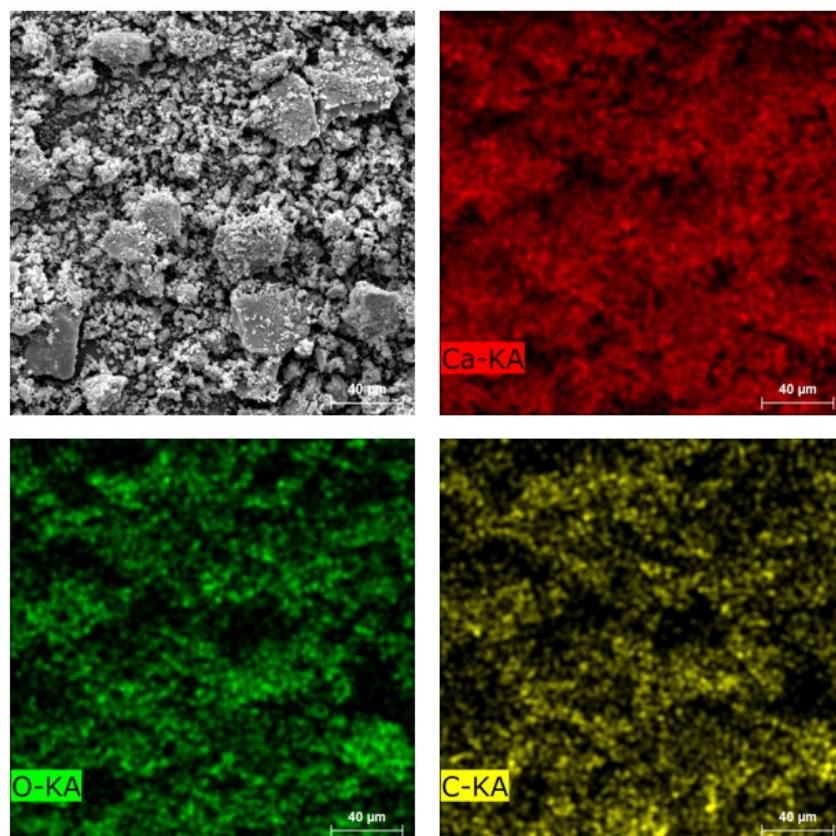


Fig. S12: Scanning electron micrographs (SEM) and mapping of mechanically activated CC under T4 conditions

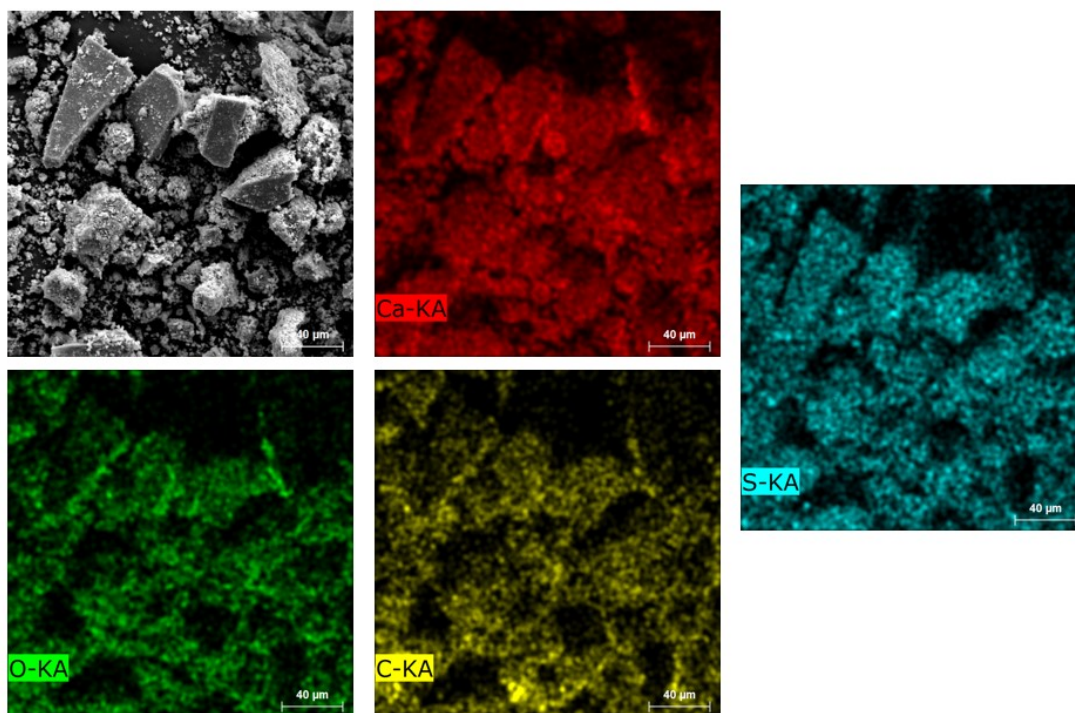


Fig. S13: Scanning electron micrographs (SEM) and mapping of mechanically activated CC with 5% L-cysteine under T4 conditions
