Supplementary Information

Mineral-mediated carbohydrate synthesis by mechanical forces in a primordial geochemical setting

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Minerals

Supplementary Table 1: *Source and origin of tested minerals.*

Mineral	Class	Source	Origin (if known)
Fuchsite $(K,Cr)Al_2[AlSi_3O_{10}(OH)_2]$	mica	Mineralienhandel Dipl. Geol. A. Spinn, Erlangen, Germany	Brazil
Calcite $Ca[CO_3]$	carbonate	Mineralienhandel Dipl. Geol. A. Spinn, Erlangen, Germany	-
Muskovite $KAl_2[AlSi_3O_{10}(OH)_2]$	mica	Mineralienhandel Dipl. Geol. A. Spinn, Erlangen, Germany	Brazil
Analcime $Na_2[Al_2Si_4O_{12}]\cdot 2H_2O$	zeolite	Alfa Aesar, Haverhill, USA	-
Colemanite $Ca[B_3O_4(OH)_3]\cdot H_2O$	borate	Seltene Mineralien, Gunnar Färber, Samswegen, Germany	USA, California, Borax Mine
Anhydrite $Ca[SO_4]$	sulphate	Seltene Mineralien, Gunnar Färber, Samswegen, Germany	Germany, Kohnstedt Steinbruch
Apatite $Ca_5[(OH)(PO_4)_3]$	phosphate	abcr, Karlsruhe, Germany	-
Quartz SiO_2	silicate	Seltene Mineralien, Gunnar Färber, Samswegen, Germany	-
Magnesite $Mg[CO_3]$	carbonate	Mineralienhandel Dipl. Geol. A. Spinn, Erlangen, Germany	-
Portlandite $Ca(OH)_2$	hydroxide	Seltene Mineralien, Gunnar Färber, Samswegen, Germany	Germany, Caspar Steinbruch
Brucite $Mg(OH)_2$	hydroxide	Seltene Mineralien, Gunnar Färber, Samswegen, Germany	Pakistan, Kharan
Diaspore $AlO(OH)$	hydroxide	Seltene Mineralien, Gunnar Färber, Samswegen, Germany	Turkey, Selcuk
Peridot $(Mg,Fe)_2SiO_4$	olivine	Seltene Mineralien, Gunnar Färber, Samswegen, Germany	Pakistan, Sapat Gali
Montmorillonite 1 $(Na,Ca)_{0,3}[(Al,Mg)_2Si_4O_{10}(OH)_2]\cdot nH_2O$	clay	Alfa Aesar, Haverhill, USA	-
Montmorillonite 2 $(Na,Ca)_{0,3}[(Al,Mg)_2Si_4O_{10}(OH)_2]\cdot nH_2O$	clay	abcr, Karlsruhe, Germany	-
Talc $Mg_3[(OH)_2Si_4O_{10}]$	silicate	Lithos, Ennsdorf, Austria	Afghanistan, Khugiani
Basalt (pyroxene, plagioclase, olivine)	volcanic rock	Bettina Scheu, LMU Munich	Iceland, Krafla
Clinoptilolite 1 $(K,Na,Ca)_6[Si_{30}Al_6O_{72}]\cdot nH_2O$	zeolite	Zeocem, Bystré, Slovakia	Slovakia, Nižný Hrabovec
Clinoptilolite 2 $(K,Na,Ca)_6[Si_{30}Al_6O_{72}]\cdot nH_2O$	zeolite	Lithos, Ennsdorf, Austria	Romania, Zalau
Chabazite $(Ca,K,Mg,Na)_2[Al_4Si_8O_{24}]\cdot nH_2O$	zeolite	St. Cloud Mining, Tucson, USA	USA, Arizona, Bowie
Schreibersite $(Fe,Ni,Co)_3P$	phosphide	Sigma Aldrich, St. Louis, USA	synthetic

Supplementary Table 2: Weighted sample masses for the mineral-catalysed aldol reaction starting from glycolaldehyde-dimer (GA-D) and 20 mol% catalyst.

Mineral	**M_{Min} [g/mol]**	**m_{Min} [mg]**	**$m_{GA\text{-}D}$ [mg]**
Fuchsite $(K,Cr)Al_2[AlSi_3O_{10}(OH)_2]$	404.8	84.3	66.0
Calcite $Ca[CO_3]$	100.1	38.3	115.0
Muskovite $KAl_2[AlSi_3O_{10}(OH)_2]$	397.8	86.2	65.0
Analcime $Na_2[Al_2Si_4O_{12}]\cdot 2H_2O$	440.3	89.0	60.0
Colemanite $Ca[B_3O_4(OH)_3]\cdot H_2O$	205.5	61.6	90.0
Anhydrite $Ca[SO_4]$	136.1	47.6	105.0
Apatite $Ca_5[(OH)(PO_4)_3]$	502.3	92.0	55.0
Quartz SiO_2	60.1	25.0	125.0
Magnesite $Mg[CO_3]$	84.3	33.7	120.0
Portlandite $Ca(OH)_2$	74.1	30.8	125.0
Brucite $Mg(OH)_2$	58.3	24.3	125.0
Diaspore $AlO(OH)$	60.0	25.0	125.0
Peridot Mg_2SiO_4	140.7	49.2	105.0
Montmorillonite 1 $Na_{0,3}[(Al,Mg)_2Si_4O_{10}(OH)_2]\cdot H_2O$	385.9	90.0	70.0
Montmorillonite 2 $Na_{0,3}[(Al,Mg)_2Si_4O_{10}(OH)_2]\cdot H_2O$	385.9	90.0	70.0
Talc $Mg_3[Si_4O_{10}(OH)_2]$	379.3	88.4	70.0
Basalt (pyroxene, plagioclase, olivine)	*	75.0	75.0
Clinoptilolite 1 $Na_6[AlSi_5O_{12}]\cdot H_2O$		75.0	75.0
Clinoptilolite 2 $(K,Na,Ca)_6[Si_{30}Al_6O_{72}]\cdot nH_2O$		75.0	75.0
Chabazite $Ca_2[Al_4Si_8O_{24}]\cdot 13H_2O$		75.0	75.0
Schreibersite Fe_3P	198.5	59.5	90.0

*as the volcanic rock persists of several components, no molar mass was estimated

Supplementary Table 3: Elemental analysis results of the mineral catalysts.

Mineral	Method	Result
Fuchsite	ICP-OES	Al: 122.47 mg/g, Ca: 0.18 mg/g, Cr: 7.67 mg/g, Fe: 2.98 mg/g, K: 41.42 mg/g, Mg: 1.44 mg/g, Mn: 0.02 mg/g, Na: 0.79 mg/g, Si: 181.05 mg/g
Calcite	ICP-OES	B: 0.11 mg/g, Ca: 395.65 mg/g, Fe: 0.01 mg/g, K: 0.32 mg/g, Mg: 2.50 mg/g, Mn: 0.15 mg/g, Na: 0.08 mg/g, S: 0.84 mg/g, Si: 0.99 mg/g
Muscovite	ICP-OES	Al: 74.73 mg/g, Fe: 1.36 mg/g, K: 27.60 mg/g, Mg: 0.07 mg/g, Mn: 0.07 mg/g, Na: 4.82 mg/g, Si:92.47 mg/g
Analcime	ICP-OES	Al: 115.80 mg/g, Ca: 0.60 mg/g, K: 4.10 mg/g, Mg: 0.59 mg/g, Mn: 4.84 mg/g, Na: 72.96 mg/g, Si: 244.11 mg/g
Colemanite	ICP-OES	Al: 5.28 mg/g, B: 141.59 mg/g, Ca: 198.12 mg/g, Fe: 1.90 mg/g, K: 2.44 mg/g, Mg: 2.49 mg/g, Mn: 0.71 mg/g, Na: 1.18 mg/g, S: 4.15 mg/g, Si: 16.31 mg/g
Anhydrite	ICP-OES	B: 0.34 mg/g, Ca: 292.25 mg/g, K: 0.57 mg/g, Mg: 2.08 mg/g, Na: 0.17 mg/g, S: 233.89 mg/g, Si: 0.91 mg/g
Apatite	ICP-OES	Ca: 380.41 mg/g, Mg: 0.30 mg/g, Mn: 0.10 mg/g, Na: 0.98 mg/g, P:185.85 mg/g
Quartz	ICP-OES	Si: 273.46 mg/g
Magnesite	ICP-OES	B: 0.07 mg/g, Ca: 4.72 mg/g, Fe: 0.07 mg/g, K: 0.35 mg/g, Mg: 289.00 mg/g, Mn: 0.07 mg/g, Na: 0.08 mg/g, S: 0.35 mg/g, Si: 4.60 mg/g
Portlandite	ICP-OES	B: 0.07 mg/g, Ca: 514.18 mg/g, Fe: 1.73 mg/g
Brucite	ICP-OES	B: 0.15 mg/g, Fe: 2.20 mg/g, Mg 433.99 mg/g
Diaspore	SEM-EDX	Al: 34%, O: 66%
Peridot	ICP-OES	Cr: 0.08 mg/g, Fe: 12.25 mg/g, Mg: 114.36 mg/g, Mn: 1.05 mg/g, Si: 178.48 mg/g
Montmorillonite 1	ICP-OES	Al: 88.71 mg/g, Ca: 7.63 mg/g, Fe: 24.38 mg/g, K: 1.09 mg/g, Mg: 13.84 mg/g, Mn: 0.22 mg/g, Na: 9.83 mg/g, Si: 260.00 mg/g
Montmorillonite 2	ICP-OES	Al: 82.73 mg/g, Ca: 11.44 mg/g, Fe: 22.02 mg/g, K 2.01 mg/g, Mg: 29.93 mg/g, Na: 21.00 mg/g, Si: 244.01 mg/g, Ti: 1.37 mg/g
Talc	ICP-OES	Al: 3.41 mg/g, Ca: 5.02 mg/g, Fe: 3.97 mg/g, Mg 200.00 mg/g, Si: 281.31 mg/g
Basalt	ICP-OES	Al: 67.53 mg/g, Ca: 71.99 mg/g, Fe: 114.91 mg/g, K: 2.57 mg/g, Mg: 35.62 mg/g, Mn: 1.93 mg/g, Na: 12.79 mg/g, Si: 228.79 mg/g, Sr: 0.16 mg/g, Ti: 12.13 mg/g, B: 0.09 mg/g, Cr: 0.13 mg/g, P: 0.88 mg/g, S: 1.63 mg/g
Clinoptilolite 1	ICP-OES	Al: 62.80 mg/g, Ca: 20.80 mg/g, Fe: 8.51 mg/g, K: 28.06 mg/g, Mg: 4.29 mg/g, Na: 3.51 mg/g, Si: 212.10 mg/g, Sr: 0.21 mg/g, Ti: 0.80 mg/g
Clinoptilolite 2	ICP-OES	Al: 60.97 mg/g, Ca: 22.60 mg/g, Fe: 10.00 mg/g, 24.56 mg/g, Mg: 6.01 mg/g, Mn: 0.24 mg/g, Na: 9.87 mg/g, Si: 302.39 mg/g, Sr: 0.41 mg/g, Ti: 0.73 mg/g
Chabazite	ICP-OES	Al: 69.90 mg/g, Ca: 13.53 mg/g, Fe: 21.13 mg/g, K: 9.17 mg/g, Mg: 11.74 mg/g, Mn: 0.16 mg/g, Na: 26.06 mg/g, Si: 253.93 mg/g, Sr: 1.30 mg/g, Ti: 1.08 mg/g
Schreibersite	SEM-EDX	synthetic material, characterisation see New J. Phys. 2018, 20, 055003.

Tabulated data

Supplementary Table 4: *Product distribution of mineral-catalysed mechanochemical monosaccharide formation starting from glycolaldehyde.*

Mineral	Apatite		Magnesite		Calcite		Anhydrite		Diaspore		Brucite		Portlandite	
Products [%]		±		±		±		±		±		±		±
Glycolaldehyde	92.38	0.31	99.03	0.09	96.86	1.19	100.00	0.00	99.89	0.01	92.73	0.99	44.93	1.33
Erythrose	3.19	0.14	0.39	0.04	1.27	0.50	0.00	0.00	0.05	0.01	2.71	0.37	15.79	0.42
Threose	3.69	0.13	0.42	0.05	1.44	0.59	0.00	0.00	0.06	0.01	3.80	0.52	21.71	0.44
Erythrulose	0.30	0.02	0.06	0.01	0.12	0.02	0.00	0.00	0.00	0.00	0.28	0.04	5.42	0.15
Hexoses	0.44	0.07	0.10	0.03	0.31	0.11	0.00	0.00	0.00	0.00	0.47	0.07	12.16	0.35
Conversion	14.51		2.02		6.36		0.00		0.22		13.93		73.13	

Mineral	Montmoril. 2		Montmoril. 1		Clinoptilolite 2		Clinoptilolite 1		Analcime		Chabazite		Schreibersite	
Products [%]		±		±		±		±		±		±		±
Glycolaldehyde	85.26	2.86	96.55	0.92	98.51	0.08	98.93	0.08	97.08	0.70	97.21	0.77	99.15	0.08
Erythrose	6.17	0.98	1.68	0.44	0.65	0.05	0.44	0.01	1.11	0.27	1.40	0.41	0.36	0.03
Threose	7.28	1.51	1.37	0.35	0.65	0.03	0.47	0.02	1.49	0.37	1.25	0.37	0.37	0.03
Erythrulose	0.74	0.19	0.24	0.10	0.13	0.03	0.12	0.02	0.17	0.04	0.05	0.01	0.03	0.02
Hexoses	0.55	0.19	0.16	0.06	0.05	0.02	0.04	0.04	0.15	0.05	0.09	0.03	0.09	0.03
Conversion	26.04		6.82		2.96		2.17		5.82		5.51		1.77	

Mineral	Basalt		Colemanite		Peridot		Talc		Quartz		Muskovite		Fuchsite	
Products [%]		±		±		±		±		±		±		±
Glycolaldehyde	99.03	0.17	100.00	0.00	99.05	0.17	84.55	4.40	99.89	0.02	98.38	0.23	96.69	1.73
Erythrose	0.33	0.05	0.00	0.00	0.38	0.05	7.04	2.01	0.05	0.01	0.70	0.09	1.40	0.76
Threose	0.41	0.06	0.00	0.00	0.44	0.08	6.93	1.91	0.05	0.01	0.72	0.10	1.38	0.68
Erythrulose	0.14	0.02	0.00	0.00	0.05	0.03	0.80	0.21	0.00	0.00	0.20	0.03	0.51	0.27
Hexoses	0.09	0.05	0.00	0.00	0.08	0.04	0.68	0.26	0.00	0.00	0.00	0.00	0.01	0.01
Conversion	2.00		0.00		1.95		27.19		0.21		3.20		6.41	

Supplementary Table 5: *Product distribution of mineral-catalysed mechanochemical monosaccharide formation starting from glycolaldehyde and adsorbed formaldehyde.*

Mineral	**Fuchsite**		**Montmorillonite 1**		**Chabazite**		**Clinoptilolite 1**		**Clinoptilolite 2**		**Analcime**	
Amount of ads. 1	1.1 wt.%		3.1 wt.%		10.8 wt.%		9.7 wt.%		8.6 wt.%		2.5 wt.%	
Products [%]		±		±		±		±		±		±
Glycolaldehyde	60.22	0.29	74.28	0.21	81.11	0.23	95.78	0.02	91.19	0.07	59.15	0.21
Glyceraldehyde	16.34	0.09	8.46	0.01	6.59	0.06	0.69	0.02	1.76	0.01	11.39	0.03
Dihydroxyacetone	15.78	0.08	8.82	0.15	1.82	0.03	0.15	0.01	0.40	0.01	0.83	0.00
Erythrose	2.63	0.02	2.41	0.02	4.03	0.06	1.47	0.01	2.77	0.02	11.38	0.07
Threose	1.63	0.01	2.27	0.03	3.40	0.05	1.36	0.02	2.54	0.03	14.39	0.08
Erythrulose	2.76	0.01	2.81	0.04	1.60	0.01	0.19	0.01	0.64	0.01	1.17	0.01
other Pentoses	0.54	0.06	0.80	0.03	0.99	0.02	0.19	0.01	0.42	0.01	1.16	0.02
Ribose	0.07	0.01	0.10	0.00	0.07	0.01	0.01	0.01	0.05	0.01	0.10	0.01
Hexoses	0.03	0.01	0.05	0.03	0.38	0.01	0.07	0.01	0.19	0.01	0.37	0.02
Heptoses	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.01	0.10	0.02	0.12	0.01

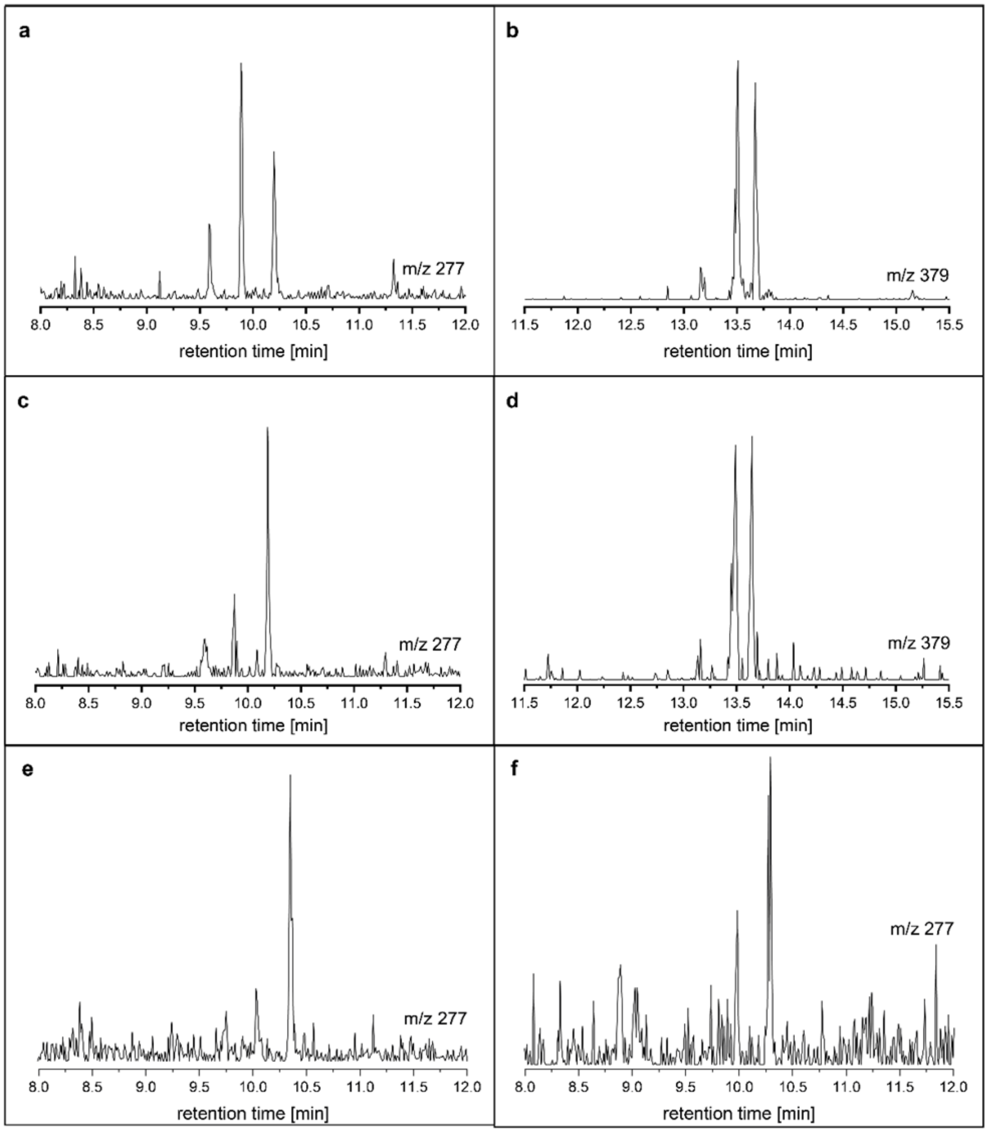
Supplementary Table 6: *Product distribution of mechanochemical monosaccharide formation starting from glycolaldehyde and calcium hydroxide under different atmospheres.*

Atmosphere	**Nitrogen**		**Carbon Dioxide**		**Air**		**Methane**	
Products [%]		±		±		±		±
Glycolaldehyde	30.24	0.59	75.66	3.28	28.00	0.99	29.41	0.97
Erythrose	18.08	0.20	9.21	1.14	17.67	0.15	17.76	0.14
Threose	25.63	0.14	11.77	1.53	25.27	0.12	25.42	0.17
Erythrulose	7.20	0.43	0.90	0.15	7.30	0.17	7.76	0.10
Hexoses	17.47	0.54	2.40	0.42	19.39	0.80	18.18	0.93
Heptoses	0.45	0.05	0.04	0.04	0.67	0.04	0.57	0.03
Octoses	0.93	0.07	0.02	0.02	1.69	0.24	0.91	0.04

Supplementary Table 7*: Particle size of each mineral before and after the ball mill reaction determined by optical microscopy.*

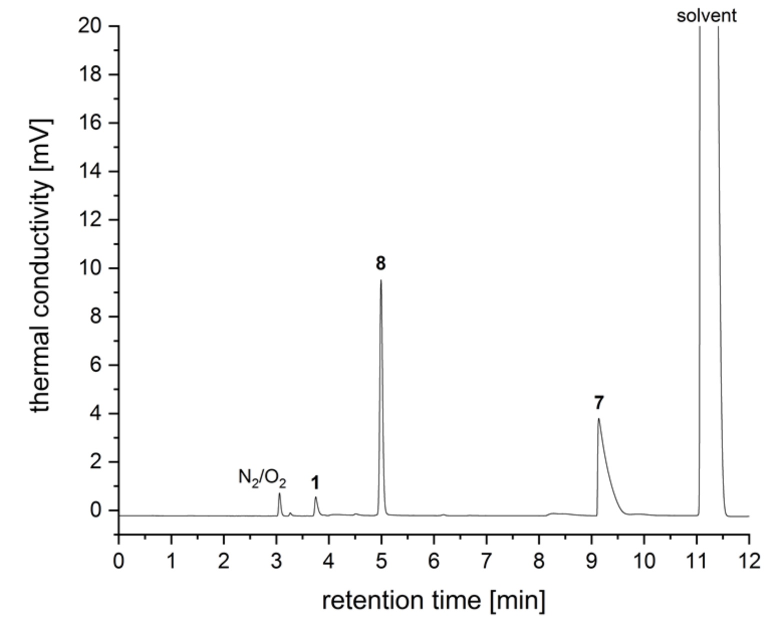
Mineral	**Particle Size [µm]**
Fuchsite	15-50
Calcite	50-110
Muscovite	15-50
Analcime	50-150
Colemanite	30-110
Anhydrite	80-190
Apatite	15-110
Quartz	15-80
Magnesite	15-80
Portlandite	30-110
Brucite	50-175
Diaspore	80-150
Peridot	30-110
Montmorillonite 1	15-80
Montmorillonite 2	15-50
Talc	8-15
Basalt	350-500
Clinoptilolite 1	80-250
Clinoptilolite 2	15-50
Chabazite	15-50
Schreibersite	50-400
All after milling	5-30

Extracted ion chromatograms

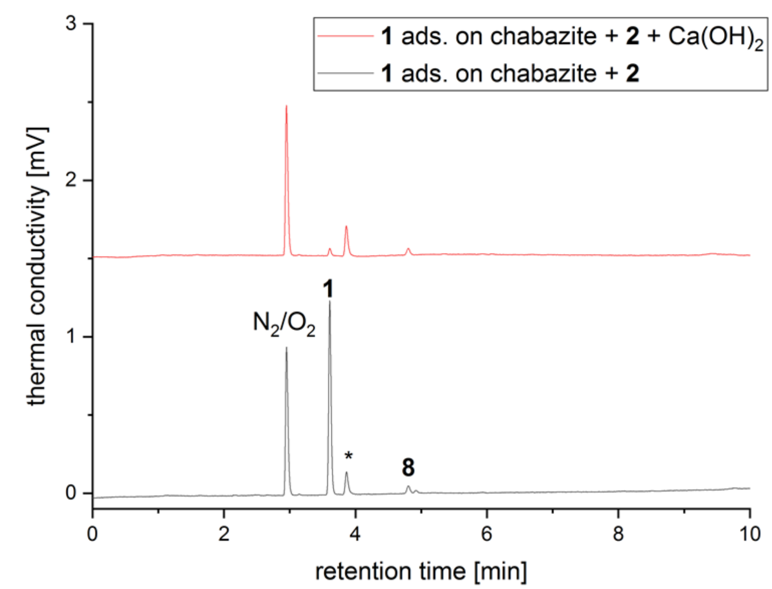


Supplementary Figure 1: *Extracted ion chromatograms of derivatized sugar samples of the mechanochemical reaction starting from formaldehyde adsorbed on molecular sieves, calcium hydroxide and* ***a/b*** *2-hydroxy-1-phenylethan-1-on,* ***c/d*** *3-ethylthiazoliumbromide,* ***e*** *3-ethylbenzothiazoliumbromide or* ***f*** *3-methylbenzothiazoliumiodide.* ***a/c/e/f*** *m/z 277 corresponds to trioses,* ***b/d*** *m/z 379 corresponds to tetroses.*

GC-TCD Chromatograms

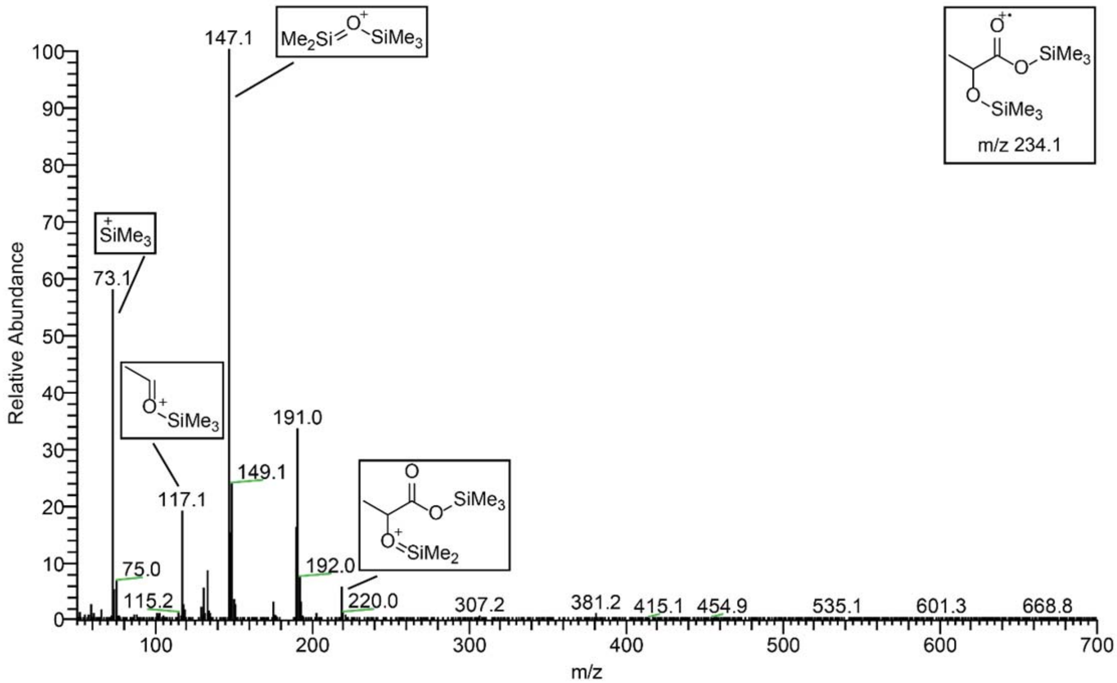


Supplementary Figure 2: *Gas chromatogram of reference compounds using a CP-Sil 5CP column (L = 50 m, ID = 320 µm, FT = 5 µm) at 50°C and 2 mL/min helium.* ***1*** *formaldehyde,* ***7*** *formic acid,* ***8*** *methanol.*

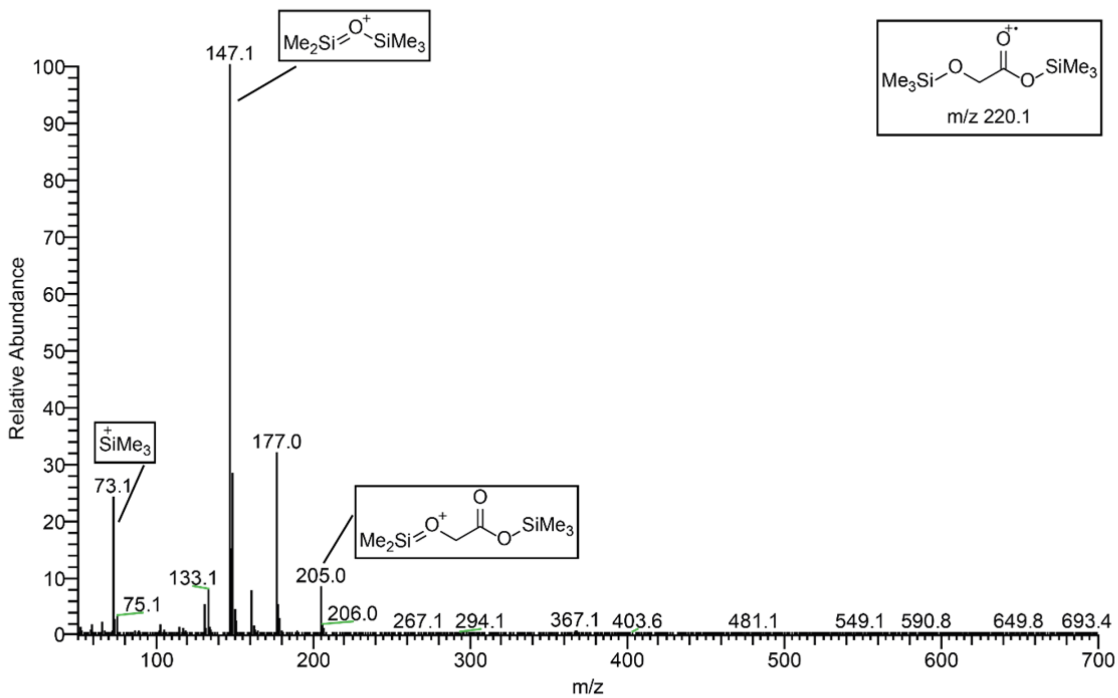


Supplementary Figure 3: *Gas chromatogram of mechanochemical reaction of* ***1*** *adsorbed on chabazite and* ***2*** *with and without additional calcium hydroxide catalyst forming* ***8*** *(*unidentified impurity from solvent).*

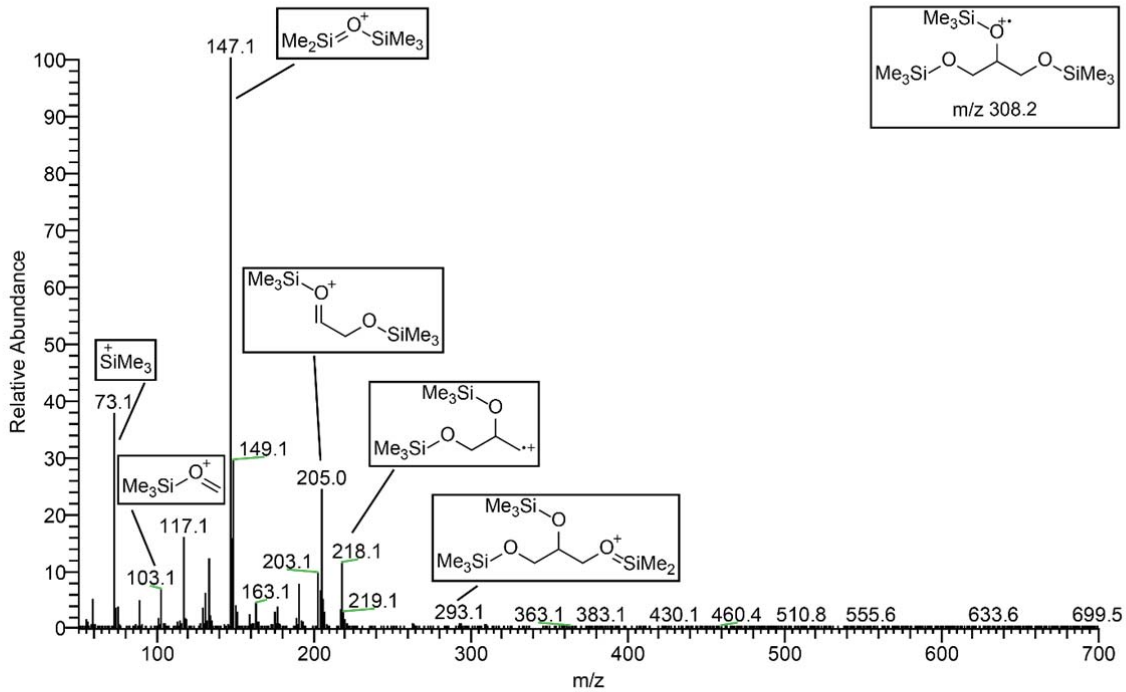
Mass spectra



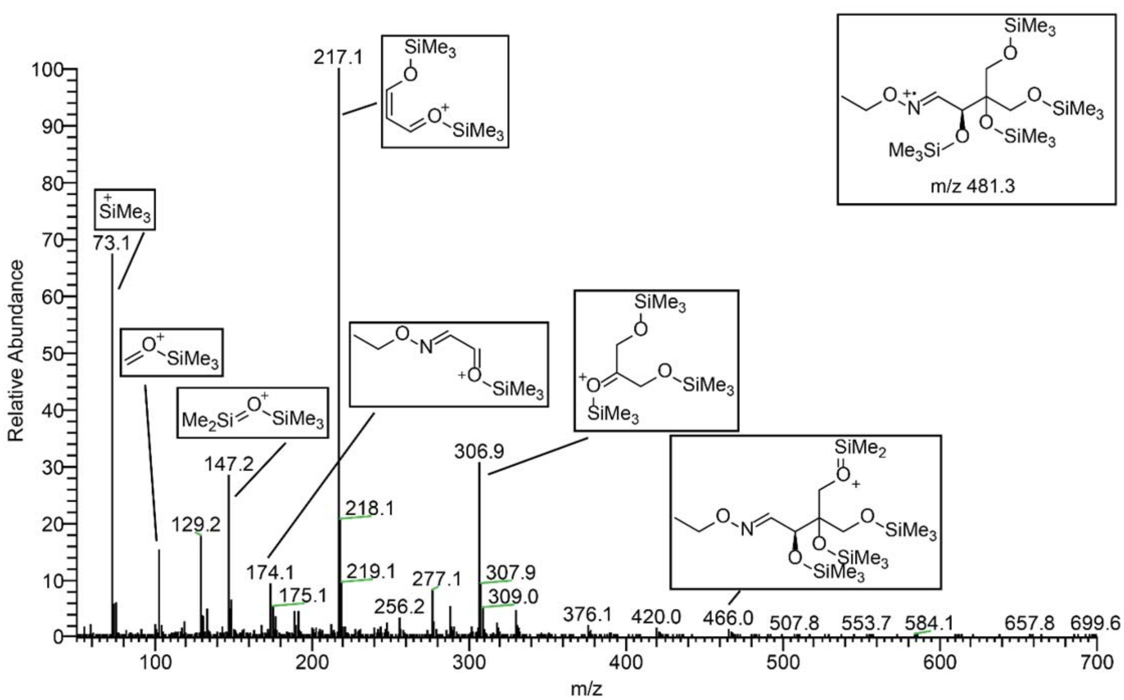
__Supplementary Figure 4:__ Reference mass spectrum for derivatized lactic acid __12__.



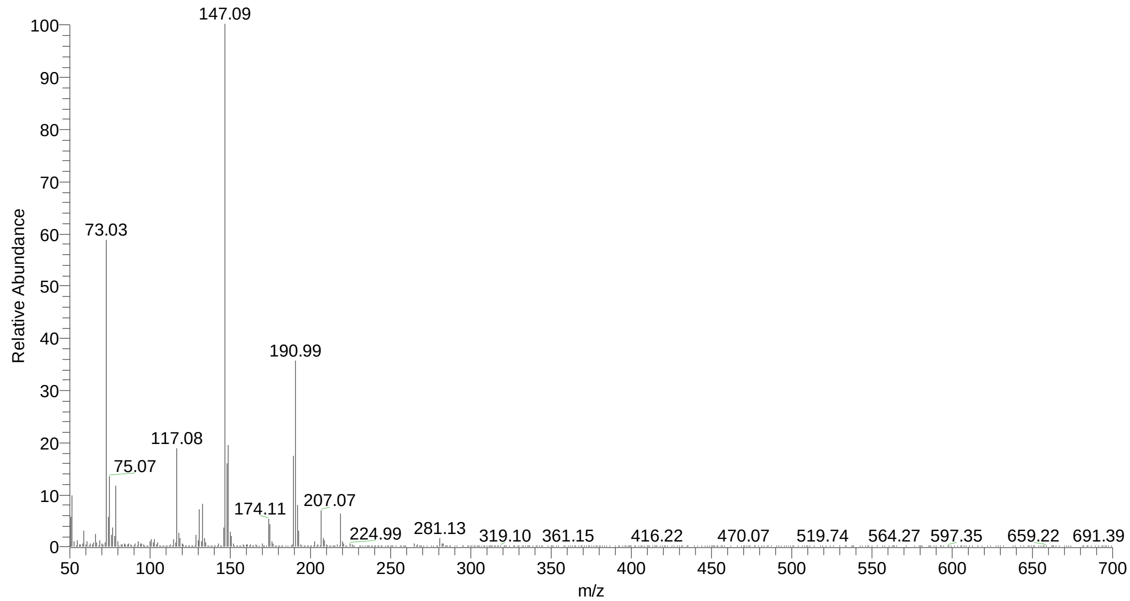
__Supplementary Figure 5:__ Reference mass spectrum for derivatized glycolic acid __9__.



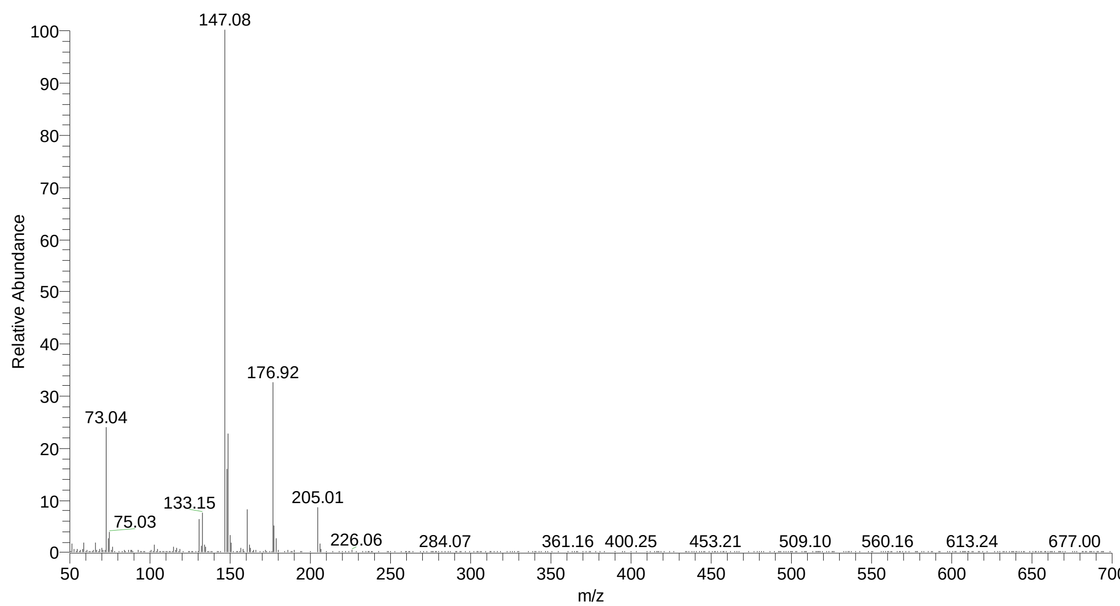
Supplementary Figure 6: *Reference mass spectrum of derivatized glycerol **15**.*



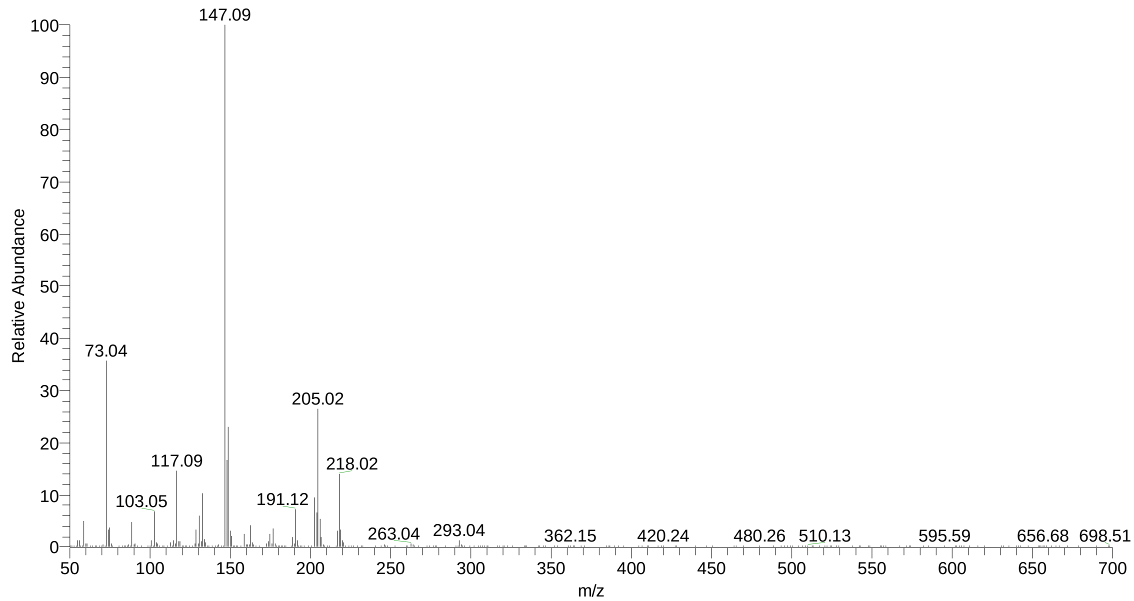
Supplementary Figure 7: *Reference mass spectrum of derivatized D-apiose **17**.*



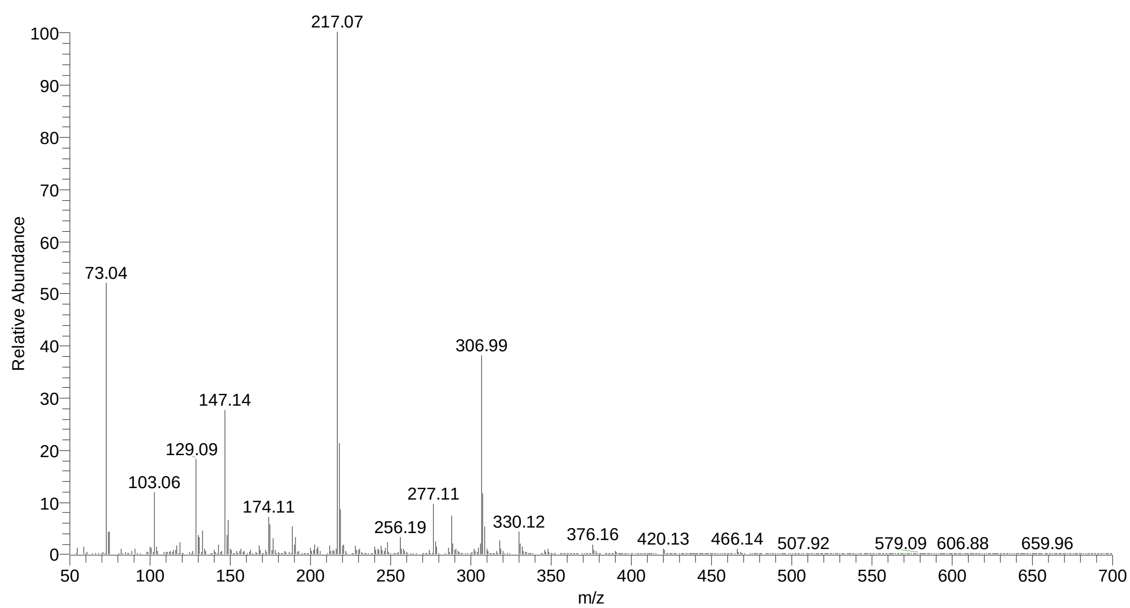
Supplementary Figure 8: *Mass spectrum of peak at t_{ret} = 6.4 min of mechanochemical reaction of adsorbed **1** on analcime + **2** + calcium hydroxide after derivatization as trimethylsilylated* O*-ethyloximes. This peak corresponds to lactic acid **12**.*



Supplementary Figure 9: *Mass spectrum of peak at t_{ret} = 6.6 min of mechanochemical reaction of adsorbed **1** on analcime + **2** + calcium hydroxide after derivatization as trimethylsilylated* O*-ethyloximes. This peak corresponds to glycolic acid **9**.*



Supplementary Figure 10: *Mass spectrum of peak at t_{ret} = 9.8 min of mechanochemical reaction of adsorbed **1** on analcime + **2** + calcium hydroxide after derivatization as trimethylsilylated* O*-ethyloximes. This peak corresponds to glycerol **15**.*



Supplementary Figure 11: *Mass spectrum of peak at t_{ret} = 16.8 min of mechanochemical reaction of adsorbed **1** on analcime + **2** + calcium hydroxide after derivatization as trimethylsilylated* O*-ethyloximes. This peak corresponds to apiose **17**.*