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How well does ramped thermal oxidation quantify the age distribution of soil carbon? Assessing thermal stability of physically and chemically fractionated soil organic matter

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Supplemental Text 1: Method testing and quality assurance

ST 1.1 Reproducibility of the thermograms

An artificial soil standard containing calcium carbonate was repeatedly analyzed (*n* = 6) to determine consistency and reproducibility of thermograms on commercially available equipment (Fig. S1). The bulk soil and fractions analyzed experimentally here released >99% of C below 600˚C. In the critical CO_2 collection range between 100 and 600˚C the average standard deviation of C released at a given temperature was +/- 2.2% of the mean C released within that range. The standard deviation between repeated standard soil samples over the entire temperature range, including the calcium carbonate peak between 650 and 800°C, averaged +/- 2.9%.

We also compared the bulk soil thermograms with the summed thermograms of component density fractions (see Figure 1b). The general agreement of bulk and summed thermograms suggest that there is no significant alteration of SOM thermal stability during fractionation and that density fractions may be compared to bulk soil.

ST 1.2 Accuracy of radiocarbon analyses

We analyzed ^{14}C standards with known isotopic composition to assess the degree to which extraneous C was added in our combustion and trapping procedures that could change the isotope signatures of analyzed samples. To assess how much extraneous C with low amounts of ^{14}C ('dead' C) was added, we analyzed a standard with ^{14}C values containing mostly 'bomb' C (Chinese Sugar Char, diluted with pre-combusted sand to 2% C by mass, UC Irvine Consensus measurement Fm 1.353 +/- 0.003, *n* = 55) and achieved final values of 1.355 +/- 0.009 (*n*=3). Not included in this average are many analyses made while refining the overall method that tended to be lower (up to Fm 0.034 below accepted values). However, in the configuration used for the soil analyses presented here, values were within Fm 0.007 of the known values. To assess whether extraneous modern C was added, we analyzed coal with zero ^{14}C, diluted with pre-combusted sand. The Fm averaged 0.006 +/- 0.001. The amount of 'extraneous' C was also assessed by analyzing only pre-combusted sand that should contain no C, and measuring the amount of CO_2 trapped after the full combustion procedure. Across the whole temperature range, this measured 0.026 mg C with average Fm 0.9766 (*n*=6), representing in most cases 0.5% (for 5 mg total C collected) of the total combusted sample. Such "blank" values were applied for correcting ^{14}C values reported here, and the blank C and ^{14}C was distributed across all thermal fractions proportionally based on temperature range.

ST 1.3 Mass balance of thermal fractions

Finally, our confidence that the method produces reliable and repeatable measurements of C content and isotopic composition was evaluated through successful mass and isotope balance. The amount and isotopic signatures of C estimated by summing the various fractions compared well with the bulk soil measurements (Figure 1b, Appendix tables 1 and 2). For example, summing C-weighted Fm ^{14}C from the three density fractions (FPOM, OPOM, MOM) for the 30-50 cm depth interval yielded 'bulk' Fm of 0.815, slightly below the measured bulk soil value of 0.824. Replicate analysis of bulk soil from 30-50 cm yielded Fm values of 0.819 and 0.815, and 0.812 from seven thermal fraction measurements including high temperature tail fractions.

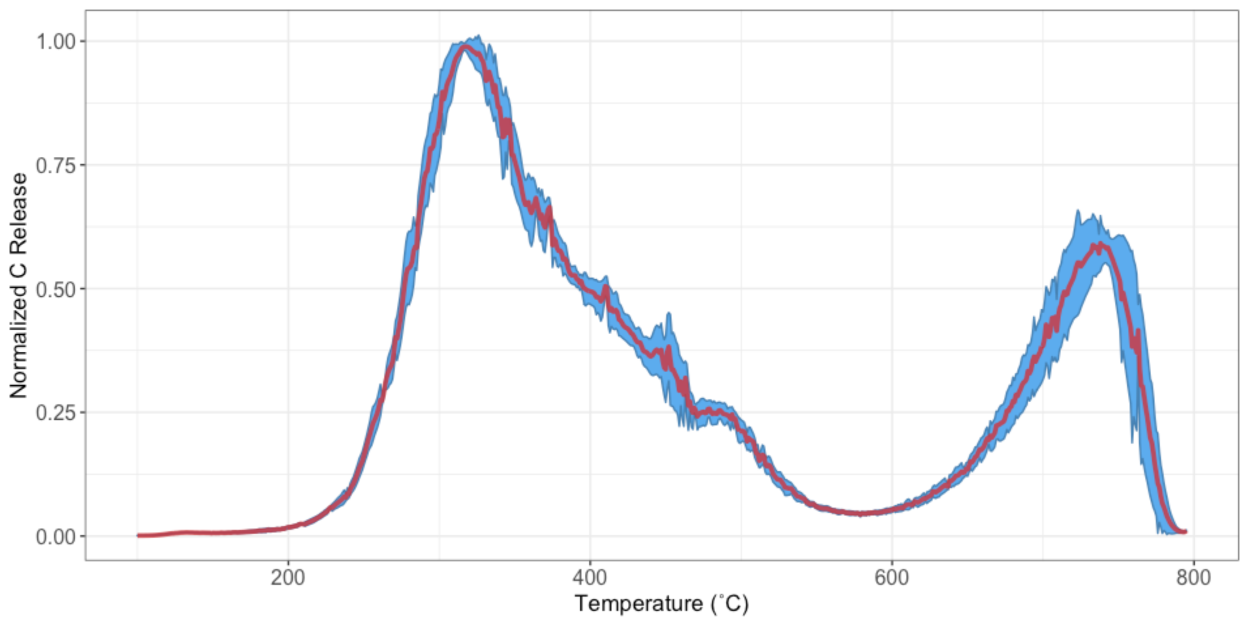

Figure S1: Repeatability of standard soil thermogram (n = 6). Red line represents the mean normalized C release at each temperature, and the blue area represents the mean +/- one standard deviation. Y-axis represents the relative magnitude of C release after all thermograms are normalized to a maximum value of 1.

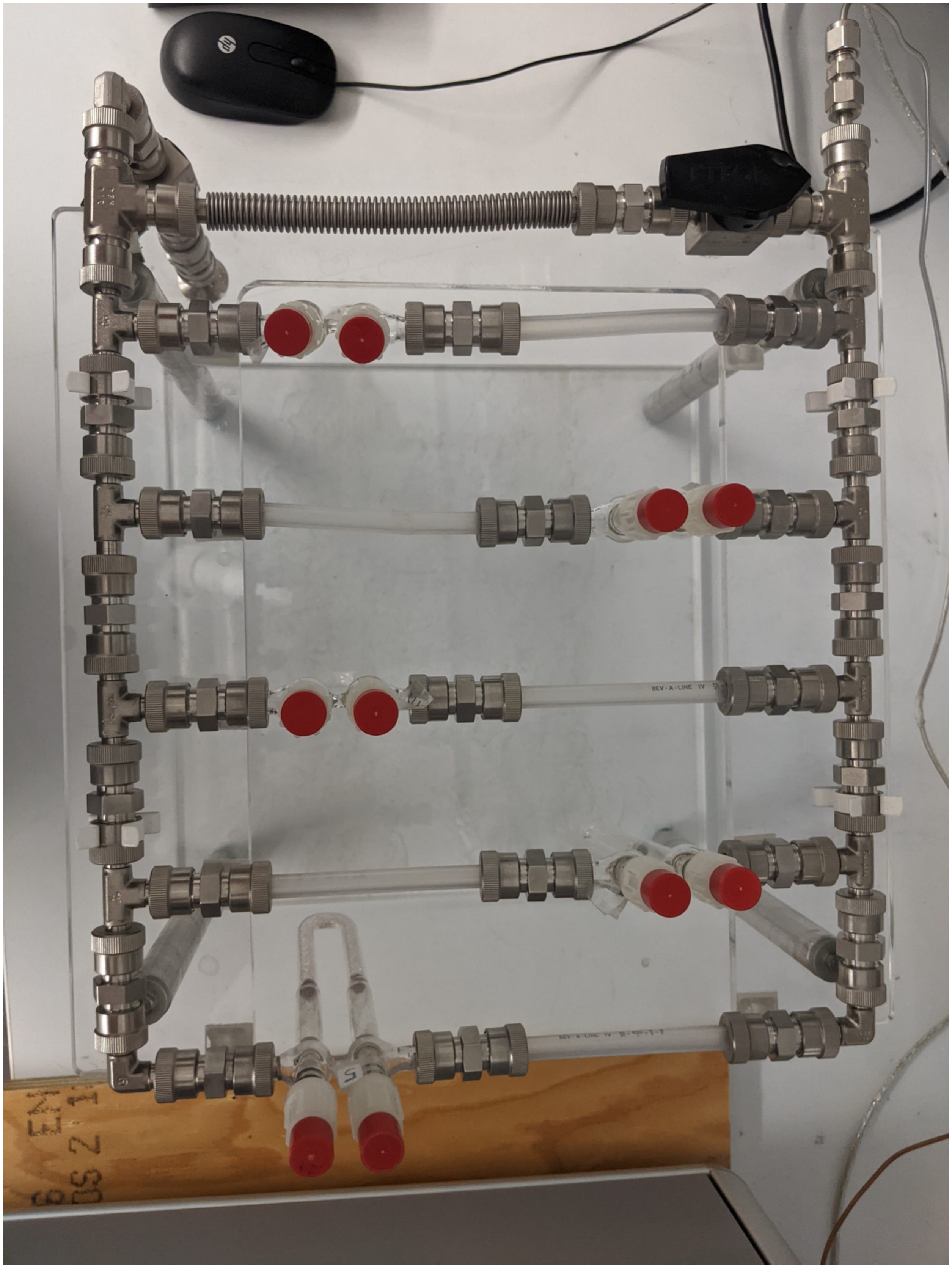

Figure S2

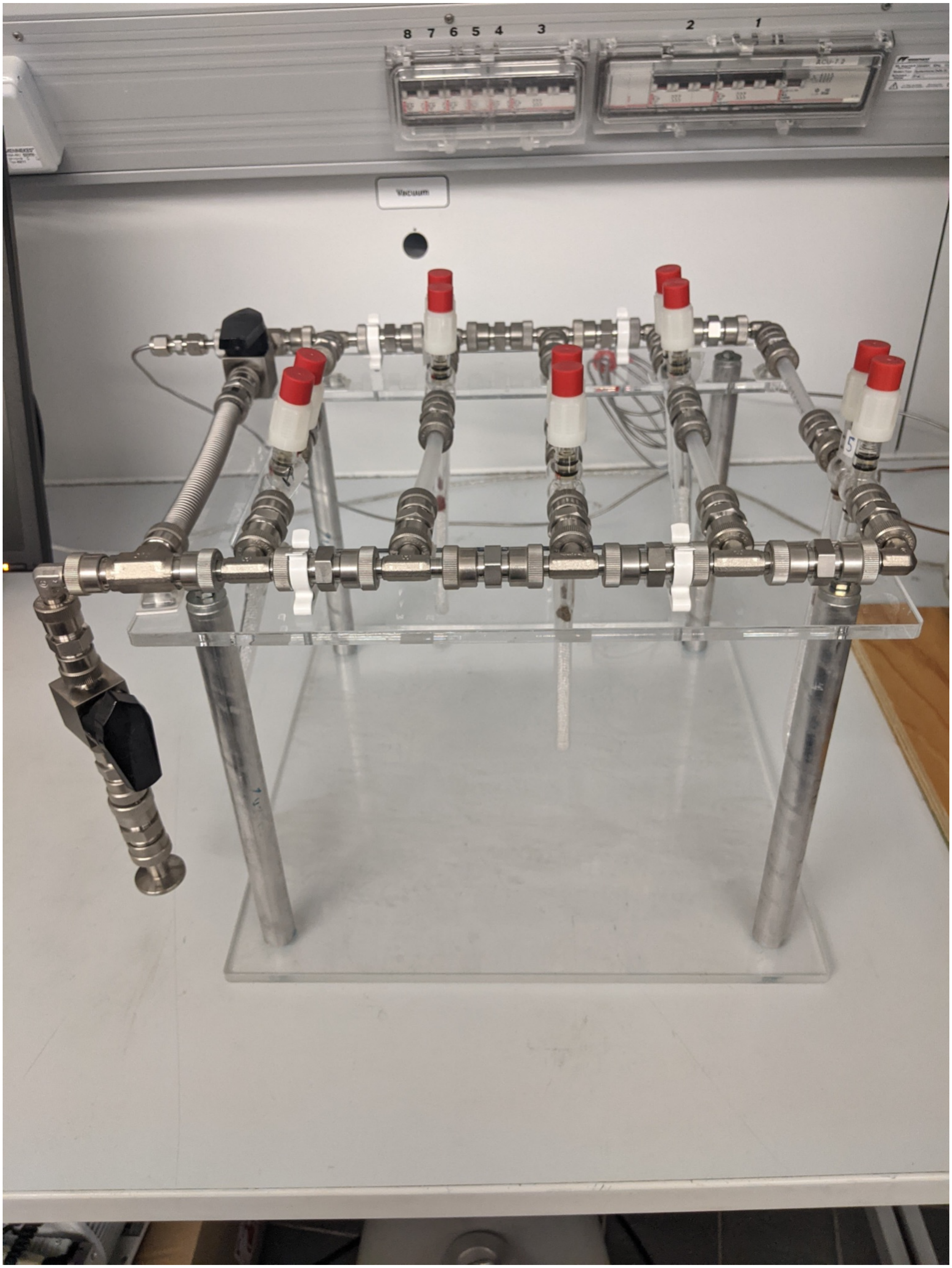

Figure S3

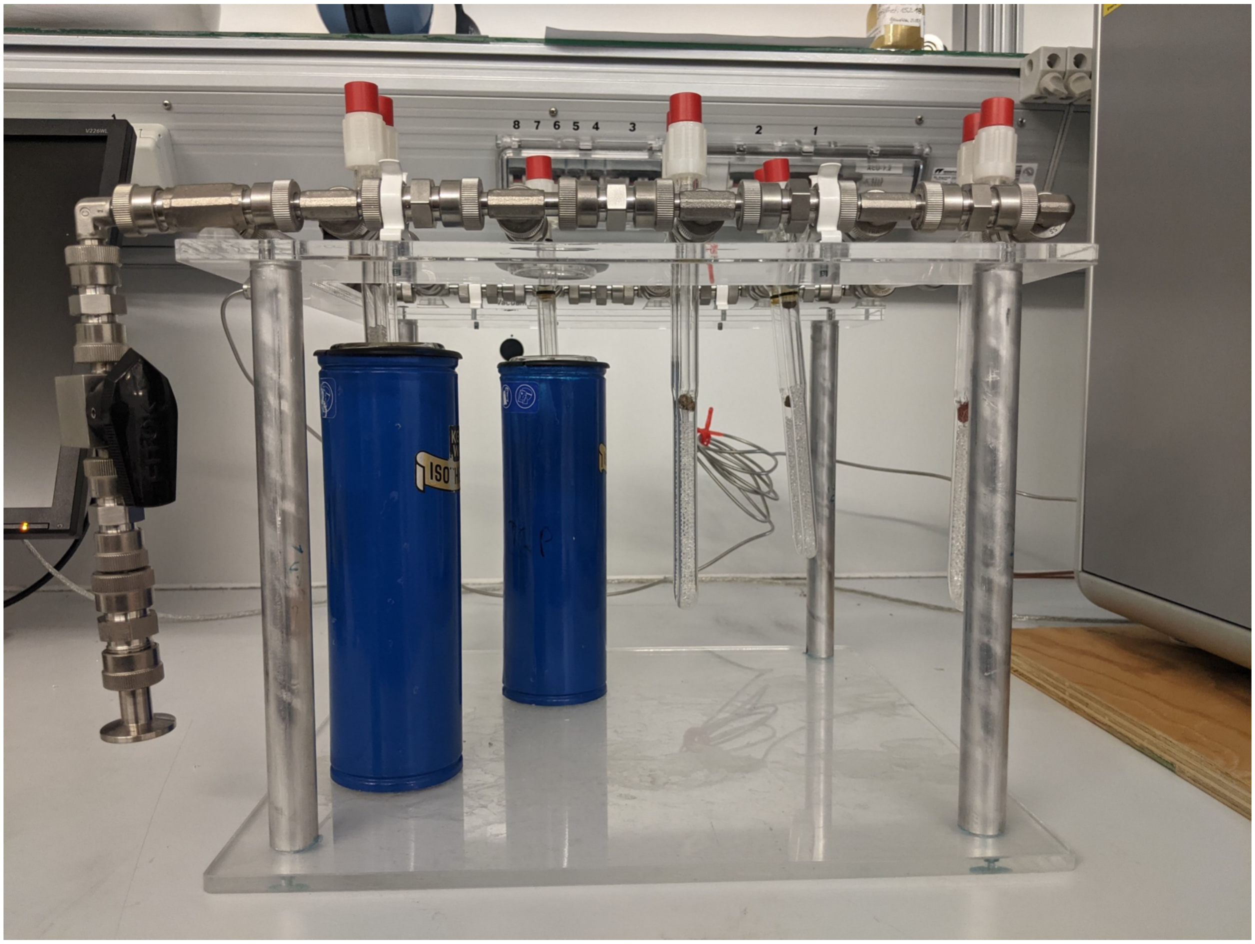

Figure S4: Photos of CO_2 collection manifold. Five glass traps filled with glass beads are attached in parallel. Manifold is constructed from Swagelok fittings and tubing. A vacuum pump is attached to the valve pictured in the lower left corner of the center and bottom photos. A bypass valve is included before the traps to evacuate manifold and to avoid pressure buildup in instrument when sample gas is not being collected.

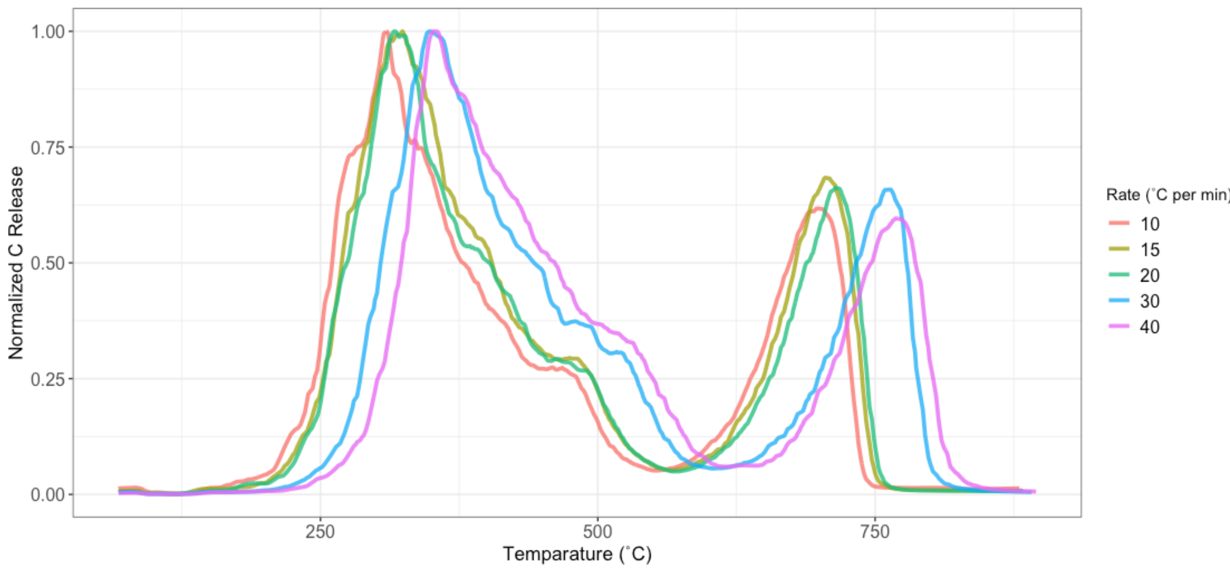

Figure S5: Effects of heating rate on thermogram shift during sample collection. A standard soil with carbonate was analyzed to determine the effects of heating rate on the reported temperature of the oven and the actual release of C. It was determined that thermograms produced with heating rates of 10, 15, and 20˚C min^{-1} did not differ significantly ($p = 0.67$). Heating rate of 15˚C was used in this analysis.

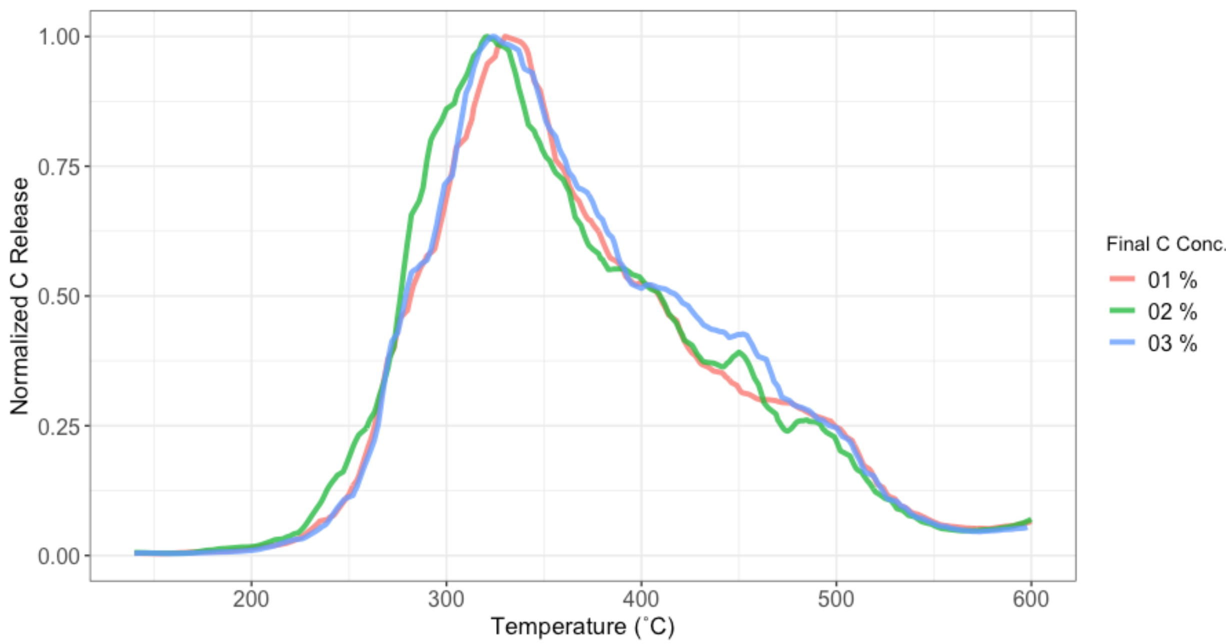

Figure S6: Effect of dilution with pre-combusted (carbon-free) sand on thermograms, heated at 15˚C min^{-1}. Standard soil analyzed here contained 3.249% C, including calcium carbonate (peak not shown). Dilution was determined to have no effect on thermogram distribution. Sand was added to dilute high-C samples in order to prevent combustion during heating. For this study, dilution to 2% C by mass was used.

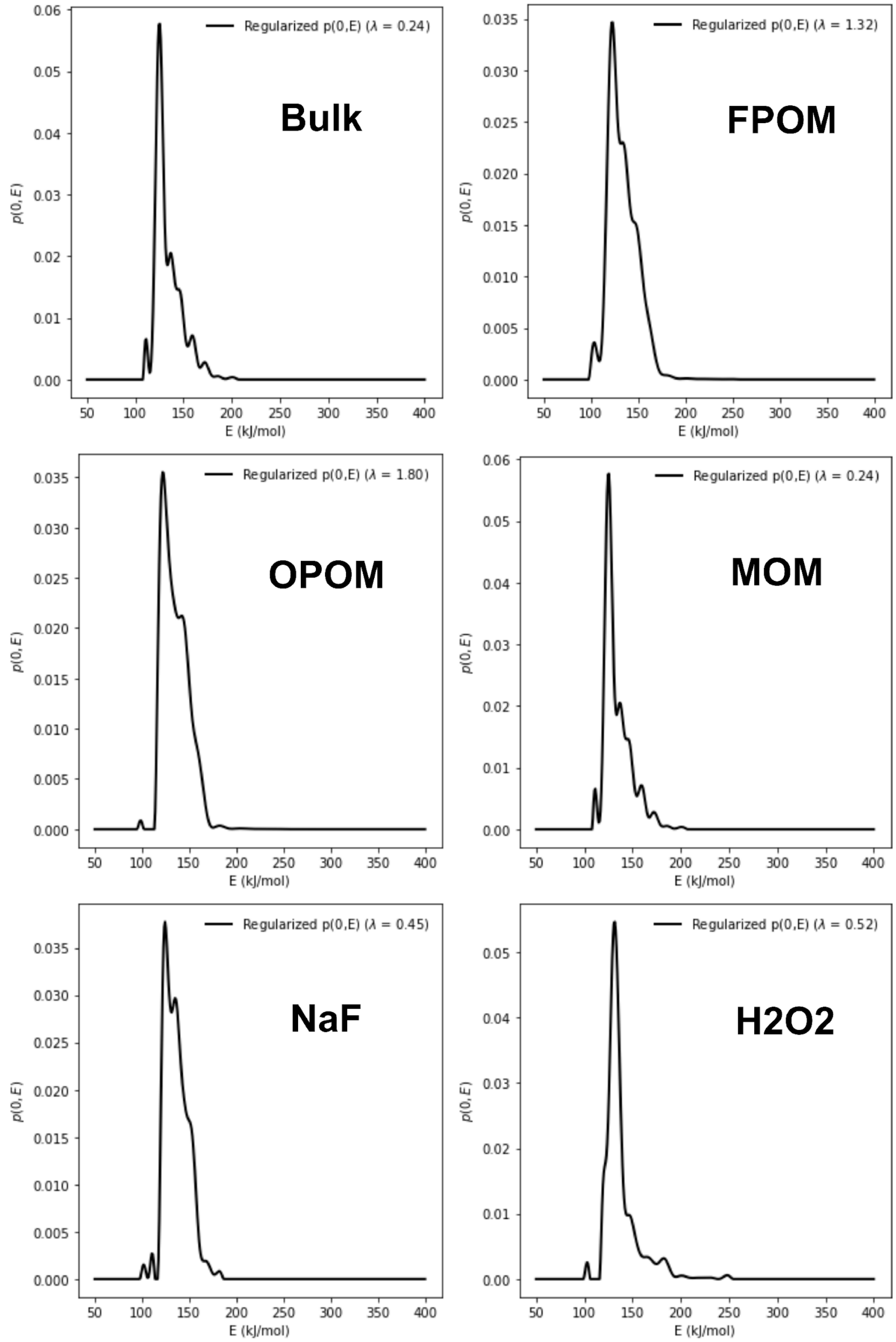

Figure S7: Activation energy density distributions of bulk surface soil and all fractions calculated using package 'rampedpyrox' (Hemingway et al., 2017). Distributions are regularized and smoothed using an automatically calculated λ value, reported in each panel.

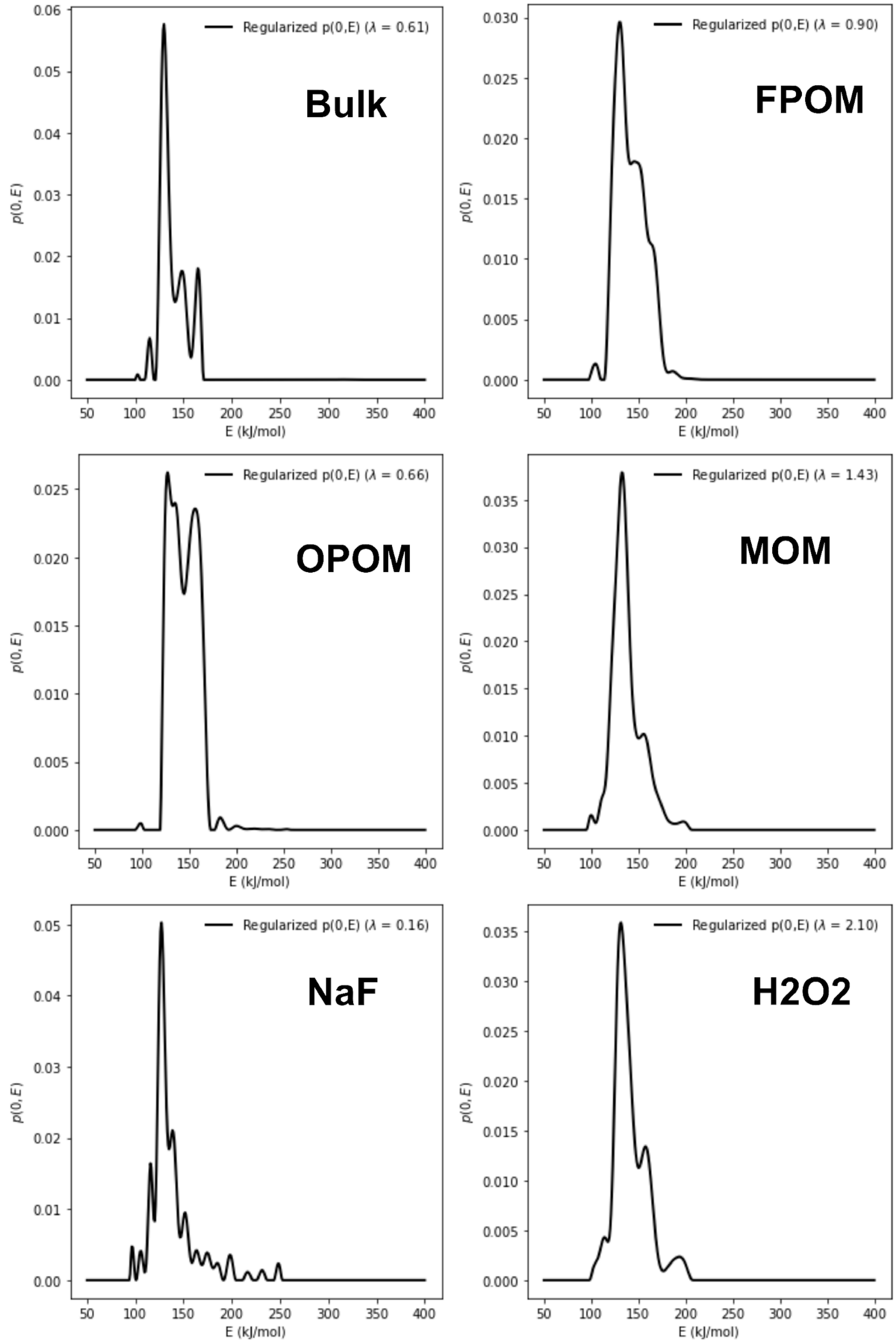

Figure S8: Activation energy density distributions of bulk subsoil and all fractions calculated using package 'rampedpyrox' (Hemingway et al., 2017). Distributions are regularized and smoothed using an automatically calculated ⎣ value, reported in each panel.

Table S1

Depth	Fraction	Fraction (F)	Min. Temp	Max. Temp	50th Temp	Prop. Mass	μE (kJ mol^{-1})	σE (kJ mol^{-1})	Fm	Fm error	$\delta^{13}C$ (‰)	$\delta^{13}C$ Error
0-10	Bulk Soil	1	140	205	188	0.041	116.49	6.31	1.045	0.003	-28	0.02
0-10	Bulk Soil	2	205	260	241	0.217	121.65	5.42	1.037	0.001	-27.87	0.01
0-10	Bulk Soil	3	260	310	286	0.389	126.56	4.80	1.003	0.001	-27.36	0.01
0-10	Bulk Soil	4	310	350	327	0.185	135.60	6.29	0.987	0.001	-26.44	0.01
0-10	Bulk Soil	5	350	380	363	0.073	144.06	5.62	0.965	0.001	-25.68	0.15
0-10	Bulk Soil	6	380	410	393	0.042	150.23	5.92	0.946	0.002	-25.32	0.15
0-10	Bulk Soil	7	410	450	426	0.027	158.00	6.14	0.907	0.002	-25.66	0.15
0-10	Bulk Soil	8	450	750	508	0.026	172.49	11.05	0.762	0.001	-25.18	0.15
0-10	FPOM	1	140	240	221	0.108	115.17	7.40	1.100	0.002	-28.03	0.01
0-10	FPOM	2	240	315	279	0.43	125.65	6.42	1.094	0.002	-26.46	0.01
0-10	FPOM	3	315	400	355	0.334	141.76	7.56	1.072	0.002	-26.47	0.01
0-10	FPOM	4	400	750	432	0.126	160.10	11.12	1.064	0.002	-26.08	0.01
0-10	OPOM	1	140	260	246	0.16	120.62	5.38	1.039	0.001	-28.626	0.01
0-10	OPOM	2	260	320	289	0.366	127.78	6.47	0.996	0.001	-27.9	0.15
0-10	OPOM	3	320	400	356	0.349	142.69	6.97	0.985	0.002	-27.55	0.01
0-10	OPOM	4	400	750	430	0.126	158.92	10.22	0.968	0.002	-26.50	0.01

0-10	MOM	1	140	250	229	0.182	121.15	6.38	1.037	0.002	-27.72	0.15
0-10	MOM	2	250	330	287	0.569	127.18	5.03	0.991	0.002	-26.95	0.15
0-10	MOM	3	335	370	347	0.135	140.06	6.53	0.963	0.002	-25.50	0.15
0-10	MOM	4	370	400	384	0.050	148.48	5.87	0.944	0.002	-25.11	0.15
0-10	MOM	5	400	450	418	0.039	155.80	5.25	0.901	0.002	-25.73	0.15
0-10	MOM	6	450	750	523	0.026	179.30	20.10	0.74	0.003	-25.05	0.15
0-10	NaF Res.	1	140	285	265	0.227	124.83	6.80	0.96	0.002	-29.94	0.15
0-10	NaF Res.	2	285	355	316	0.512	132.72	5.24	0.93	0.001	-27.96	0.15
0-10	NaF Res.	3	355	440	382	0.156	147.94	8.42	0.91	0.002	-25.23	0.15
0-10	NaF Res.	4	440	750	512	0.095	179.09	16.24	0.77	0.001	-24.89	0.15
0-10	H2O2 Res.	1	140	275	256	0.176	122.98	6.73	0.87	0.001	-30.67	0.15
0-10	H2O2 Res.	2	275	330	302	0.366	130.50	6.09	0.89	0.001	-30.32	0.15
0-10	H2O2 Res.	3	330	380	352	0.234	141.19	6.18	0.88	0.001	-27.44	0.15
0-10	H2O2 Res.	4	380	750	417	0.225	154.57	8.48	0.79	0.001	-25.89	0.15

Table S1: Data collected and calculated for surface soils (0-10 cm). All temperatures in ˚C. "50th Temp" indicates the temperature at which 50% of the C had been released within a given thermal fraction. "Prop. Mass" represents the proportion of the total Fraction represented by a given thermal fraction (sum of 1 per Fraction).

Table S2

Depth	Fraction	Fraction (F)	Min. Temp	Max. Temp	50th Temp	Prop. Mass	μE (kJ mol^{-1})	σE (kJ mol^{-1})	Fm	Fm error	$\delta^{13}C$ (‰)	$\delta^{13}C$ Error
30-50	Bulk Soil	1	140	280	260	0.16	125.44	6.86	0.83	0.00	-28.40	0.15
30-50	Bulk Soil	2	280	335	307	0.36	131.77	5.01	0.84	0.00	-26.30	0.15
30-50	Bulk Soil	3	335	375	353	0.15	141.87	6.87	0.85	0.00	-24.90	0.15
30-50	Bulk Soil	4	375	415	394	0.11	151.28	6.43	0.85	0.00	-25.40	0.15
30-50	Bulk Soil	5	415	455	425	0.09	160.67	5.68	0.83	0.00	-25.20	0.15
30-50	Bulk Soil	6	455	505	475	0.07	165.39	2.56	0.79	0.00	-24.70	0.15
30-50	Bulk Soil	7	505	750	552	0.05	167.78	1.63	0.34	0.00	-23.60	0.15
30-50	FPOM	1	140	290	267	0.21	125.57	6.84	1.06	0.00	-27.10	0.15
30-50	FPOM	2	290	350	320	0.33	136.05	6.91	1.09	0.00	-27.00	0.15
30-50	FPOM	3	350	400	374	0.20	149.06	6.74	1.08	0.00	-26.30	0.15
30-50	FPOM	4	400	750	443	0.26	163.69	9.09	1.06	0.00	-24.78	0.15
30-50	OPOM	1	140	285	269	0.13	126.50	6.03	0.85	0.00	-30.40	0.15
30-50	OPOM	2	285	370	326	0.43	136.58	8.15	0.87	0.00	-28.90	0.15
30-50	OPOM	3	370	435	402	0.29	153.47	6.34	0.82	0.00	-27.40	0.15
30-50	OPOM	4	435	750	459	0.15	164.81	11.08	0.84	0.00	-26.40	0.15

30-50	MOM	1	140	285	261	0.24	122.36	8.04	0.77	0.00	-26.05	0.15
30-50	MOM	2	285	345	314	0.37	132.91	5.69	0.79	0.00	-26.28	0.15
30-50	MOM	3	345	415	367	0.23	145.32	7.69	0.78	0.00	N.D.	N.D.
30-50	MOM	4	415	455	432	0.07	158.94	5.94	0.76 a	0.01 a	N.D.	N.D.
30-50	MOM	5	455	505	475	0.05	167.80	6.57	0.71 a	0.02 a	N.D.	N.D.
30-50	MOM	6	505	750	566	0.04	185.89	10.25	0.23 a	0.02 a	N.D.	N.D.
30-50	NaF Res.	1	140	270	244	0.24	118.10	8.86	0.80	0.00	N.D.	N.D.
30-50	NaF Res.	2	270	310	291	0.27	128.08	4.79	0.79	0.00	N.D.	N.D.
30-50	NaF Res.	3	310	360	331	0.22	135.94	6.00	0.76	0.00	N.D.	N.D.
30-50	NaF Res.	4	360	750	440	0.27	16z5.95	23.46	0.57	0.00	N.D.	N.D.
30-50	H2O2 Res.	1	140	302	274	0.28	125.90	8.24	0.69	0.00	N.D.	N.D.
30-50	H2O2 Res.	2	302	354	327	0.30	135.86	5.85	0.75	0.00	N.D.	N.D.
30-50	H2O2 Res.	3	354	402	375	0.18	146.86	7.05	0.73	0.00	N.D.	N.D.
30-50	H2O2 Res.	4	402	800	460	0.25	167.05	14.45	0.43	0.00	N.D.	N.D.

Table S2: Data collected and calculated for surface soils (0-10 cm). All temperatures in ˚C. "50th Temp" indicates the temperature at which 50% of the C had been released within a given thermal fraction. "Prop. Mass" represents the proportion of the total Fraction represented by a given thermal fraction (sum of 1 per Fraction).
a: Values estimated via mass balance.