

Santos et al. Radiocarbon step-combustion oxidation method and FTIR analysis of Trondheim CaCO₃ precipitates of atmospheric CO₂ samples: further investigations and insights

Supplementary Material

Table S1: Radiocarbon results as F¹⁴C and uncertainty values from both 1963 and 1980 samples from CaCO₃ precipitates stored at NTNU are displayed. Just four samples from the 1963 series (UCIAMS#s) were run in duplicates. Overall graphite sizes ranged between 0.38 to 0.97 mg C, reflecting the combination of differences on CaCO₃ mass loaded in quartz tubes (before step-combustion) and incomplete combustion at lower temperatures and durations, as indicated.

NTNU series	Identifier	Sample ID	Sample weight (mg)	Combustion temp./duration	Target size (mgC)	F ¹⁴ C	± 1σ
1963	UCIAMS260778	L-22-B	11.9	1000°C/6hours	0.75	1.7032	0.0028
	UCIAMS260779		-	1000°C/6hours	0.45	1.7140	0.0029
	TRa-16393		-	-	-	1.7125	0.003
	Nydal's		-	-	-	1.804	0.01
	UCIAMS260780	L-24	12.0	1000°C/6hours	0.92	1.8286	0.0030
	UCIAMS260783		10.4	1000°C/6hours	0.38	1.8410	0.0031
	TRa-16395		-	-	-	1.8346	0.0018
	Nydal's		-	-	-	1.896	0.012
	UCIAMS260781	L-26	12.2	1000°C/6hours	0.75	1.8398	0.0032
	UCIAMS260784		10.0	1000°C/6hours	0.53	1.8436	0.0037
	TRa-16397		-	-	-	1.8465	0.0018
	Nydal's		-	-	-	1.925	0.012
	UCIAMS260782	L-28	12.0	1000°C/6hours	0.97	1.8415	0.0035
	UCIAMS260785		10.1	1000°C/6hours	0.45	1.8622	0.0033
	TRa-16399		-	-	-	1.8575	0.0029
	Nydal's		-	-	-	1.964	0.012
1980 Spring/Fall	UCIAMS263930	L-358	11.0	900°C/3hours	0.68	1.2867	0.0021
	TRa-16401		-	-	-	1.2783	0.0016
	UCIAMS263931	L-359	10.0	900°C/3hours	0.43	1.2764	0.0021
	TRa-16402		-	-	-	1.2773	0.0015
	UCIAMS263934	L-360	10.1	900°C/3hours	0.48	1.2866	0.0023
	TRa-16403		-	-	-	1.2837	0.0014
	UCIAMS263935	L-361	10.0	900°C/3hours	0.38	1.2782	0.0021
	TRa-16404		-	-	-	1.2733	0.0017

NTNU TRa values used for comparisons are those of chemically untreated CaCO₃ powders subjected to combustion using an elemental analyzer (see Seiler et al. 2023); Nydal's reference source numbers in parenthesis refers to the time period of ambient-CO₂ adsorption into the NaOH solution. Their associated F¹⁴C and uncertainties were extracted from (Seiler et al. 2023). Weight of one of the L22B samples run at UCI was not recorded.

Table S2: Radiocarbon results as $F^{14}C$ and/or ^{14}C age BP of reference materials of carbonates and organics are shown followed by uncertainties. Graphite target sizes ranged between 0.22 to 0.52 mg C for carbonates, and 0.40 to 0.95 mg C for organics. Blank results variability is associated with sample masses as graphite in mg C. Results shown here were compared with consensus values reported in the literature, and are discussed in main text (section 2.1)

Reference materials	UCIAMS #	Sample ID	Sample weight (mg)	Combustion temp./duration	Target size (mgC)	$F^{14}C$	$\pm 1\sigma$	^{14}C age BP	\pm
CaCO ₃ samples	260790	CAL	8.0	1000°C/6hours	0.22	0.0050	0.0001	42590	150
	260791		8.0	1000°C/6hours	0.36	0.0028	0.0001	47220	270
	260792	CST	8.1	1000°C/6hours	0.36	0.9435	0.0015	465	15
	260793	FRC	8.0	1000°C/6hours	0.52	0.1020	0.0008	18340	70
	260794		8.0	1000°C/6hours	0.50	0.1010	0.0008	18420	70
Organics	260749	USGS Coal	1.1	1000°C/6hours	0.87	0.0016	0.0001	51870	330
	260786		1.0	1000°C/6hours	0.52	0.0020	0.0001	49890	420
	260787		n/a	n/a	0.65	0.0016	0.0001	51820	270
	263963		1.1	900°C/3hours	0.95	0.0019	0.0001	50130	220
	263964		0.6	900°C/3hours	0.40	0.0034	0.0001	45620	160
	260788	Rice Char	6.3	1000°C/6hours	0.73	1.0643	0.0018	n/a	
	260789		6.6	1000°C/6hours	0.67	1.0634	0.0019		
	263932		6.4	900°C/3hours	0.69	1.0674	0.0018		
	263933		6.5	900°C/3hours	0.69	1.0669	0.0018		

* ^{14}C -free calcite (CAL) and USGS coal materials were used for procedural blank evaluations (Fig. S1), and therefore their ^{14}C results have not been background corrected by any means. For data display consistency, individual uncertainties associated to $F^{14}C$ values of those blanks have been truncated to ten-thousandths place after decimal point, and therefore do not quite reflect the ^{14}C -age uncertainties displayed in the last column. Other abbreviations used are: CST = coral standard and FRC = FIRI-C.

Figure S1: Ratio to OX-I of ^{14}C -free targets of calcites (n=2) and USGS coal (n=5) treated by step-combustion oxidation method, and normalized to HOx-I standards of approximately 1 mg C, plotted in relation to target mass (in mg C). Radiocarbon results from two pairs of coal samples measured on separate days overlapped each other. Our measured ratio to OX-I values showed clear mass-dependence, where smaller graphite sizes yielded higher ratio to OX-I than larger sizes. Nonetheless, both calcites and coals fell on the same constant-mass line of $1\mu\text{g C}$, except for one coal target, the largest. Mass-balance subtraction of a constant-mass of $1\mu\text{g C}$ blank has been employed to correct ^{14}C results in this study, using the formulation shown in Santos et al. 2007. The associated uncertainty was propagated accordingly.

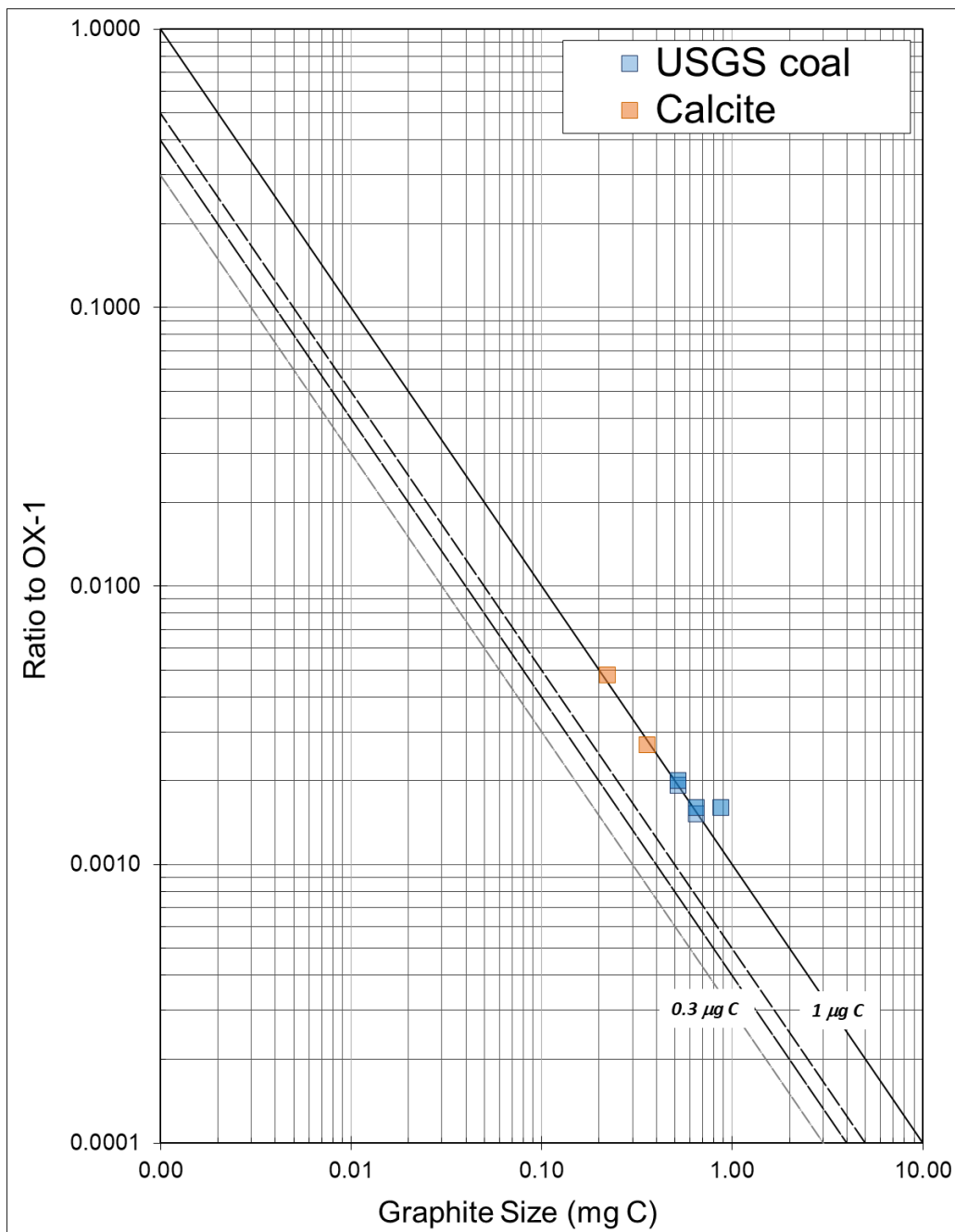
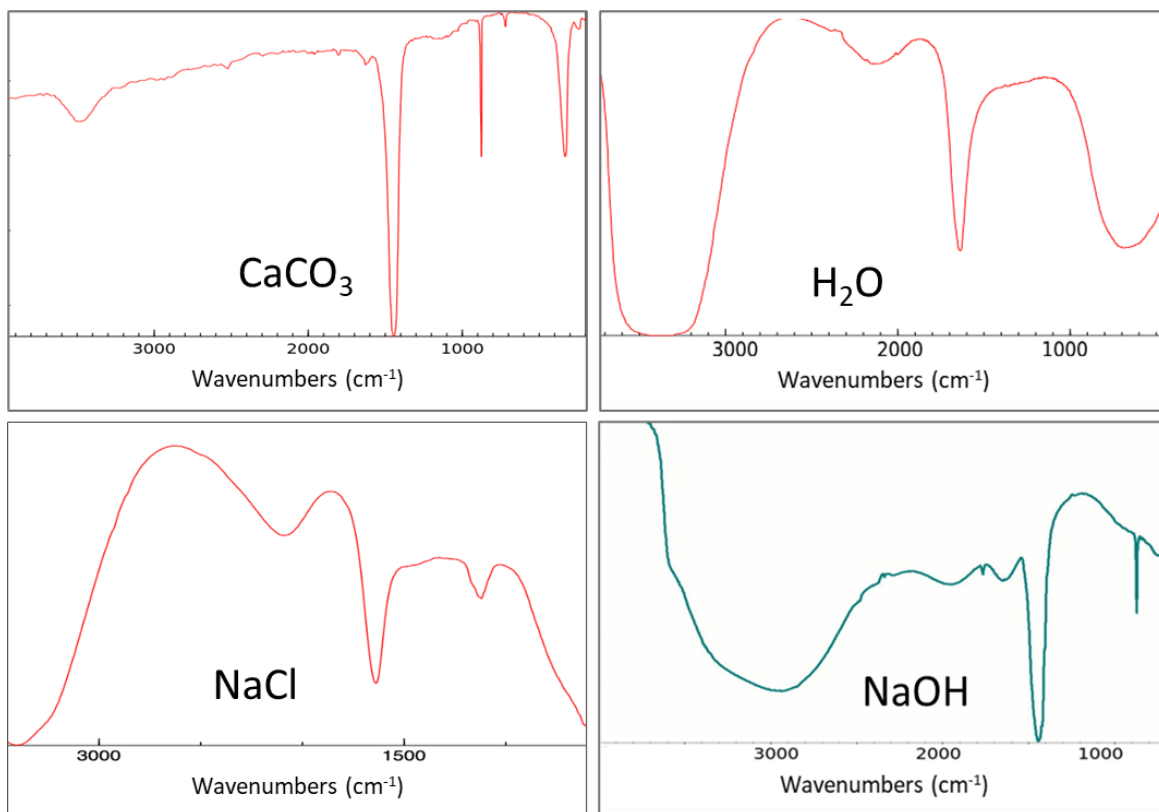


Figure S2: Transmittance profiles of calcium carbonate (CaCO_3), water (H_2O), sodium hydroxide (NaOH) and sodium chloride (NaCl) by Fourier-transform infrared spectroscopy (FTIR) analysis are displayed. They were reproduced from NIST webbook (<https://webbook.nist.gov/>) and Cameo Materials Database (https://cameo.mfa.org/wiki/Sodium_hydroxide). Transmittance regions of interest are i) the peak profiles of CaCO_3 between 2000 and 300 cm^{-1} and ii) the broad peaks between 4000 to 2500 cm^{-1} (all panels).



References

Cameo Materials Database, https://cameo.mfa.org/wiki/Sodium_hydroxide

NIST webbook, <https://webbook.nist.gov/>

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