**Appendix**

Appendix Table 1: Overview on individual split 1 and 2 data of bicarbonate procedural standards with Fm and mass.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **NaHCO3** |  | Split 1 | | Split 2 | |
| Type | Mass (µg) | Fm | Mass (µg) | Fm |
| Fm = 1.0354±0.0021 (n = 6) | Sequence blank\* | 31.9 | 1.0300±0.0055 | 148.0 | 1.0150±0.0024 |
| Replicate 1 | 69.1 | 1.0204±0.0032 | 195.6 | 1.0180±0.0023 |
| Replicate 2 | 76.1 | 1.0193±0.0029 | 225.6 | 1.0140±0.0021 |
|  |  |  |  |  |  |
| Fm = 0.0119±0.0013 (n = 5) | Sequence blank\* | 189.0 | 0.0128±0.0009 | 190.1 | 0.0170±0.0009 |
| Replicate 1 | 214.8 | 0.0162±0.0016 | 182.4 | 0.0297±0.0017 |
| Replicate 2 | 213.6 | 0.0085±0.0012 | 184.8 | 0.0165±0.0014 |
| \*this data was produced during the experiment on the exact same column as all samples. The other data were added to support the reproducibility of the blank and have no further use in the study | | | | | |
|  |

Appendix Table : Comparison of mass-balance calculated bulk Fm of splits and bulk Fm data for the five environmental samples.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sample** | **Fm bulk (reconstructed)\*** | **Fm bulk (literature)** | **Fm difference** | **Literature** | **Detail** |
| NIST SRM 1649a Urban Dust | 0.5102 | 0.5090 | -0.0012 | Hanke et al 2017 | n/a |
| Nantucket Mud Patch | 0.8520 | 0.8434 | 0.0086 | Bao et al 2018 | Acid-rinsed |
| Gulf of Terror and Erebus Antarctic Sediment KC-5 | 0.0896 | 0.0975 | -0.0079 | Rosenheim et al 2008 | Acid-rinsed |
| Sierra Leone Rise | 0.1344 | 0.1619 | -0.0275 | Bao et al 2018 | Acid-fumigated |
| Wild Harbor Salt Marsh WH19 | 0.9762 | 0.9691 | 0.0071 | This study | Acid-rinsed |

\*mass-balance calculated 14C (Fm) values from total number of splits per sample

A comparative study of oxidation-RPO and FOX combustion mode with open-split interfaced residual gas analyzer

The aim of this experiment was to trace the gas compositions from thermal sequential mineralization of organic matter in a suite of samples (Table S1), some of them with critical amounts of sulfur or chlorine. We used almost identical sample weights for both reactor types (within about 1 %) to enable a direct comparison for each sample type.

Table S: Overview on samples used in this study. The result plots only show ID # that are specified in the first column

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **ID** | **Specifications** | | | | | |
| Sample name | Abbreviation | Feature | OC % | Flow rate  (mL min-1) | He : O2 |
| 1 | Nantucket Mud Patch | NMP | In-house standard | 1.2 | 35.0 | 90 : 10 |
| 2 | Nantucket Mud Patch | NMP | In-house standard | 1.2 | 17.5 | 90 : 10 |
| 3 | Nantucket Mud Patch | NMP fumig | Acid fumigated | 1.2 | 17.5 | 90 : 10 |
| 4 | Sierra Leone Rise | SLR fumig | Acid fumigated | 0.7 | 17.5 | 90 : 10 |
| 5 | Wild Harbor Marsh | WH19 | High sulfur = 3.4 % | 14.0 | 17.5 | 90 : 10 |
| 6 | Florida Bog | S1bog | Suspected high C volatility | 50.0 | 17.5 | 90 : 10 |
| 7 | Gulf of Terror and Erebus Antarctic Sed. | KC-5 | Original sample | 0.35 | 17.5 | 90 : 10 |

The analytical setup consists of sample oven (25 to 1000 °C with 5 °C min-1 ramp rate) above a combustion oven (800 °C) separated by a ceramic insolating plate and a carrier gas inflow from top to bottom (see manuscript Figure 1 for details). The combustion columns and chemicals are the same used in the main manuscript.

The reactors were connected to the Infrared CO2 gas analyzer (IRGA) through a copper tubing (177 cm), from which another copper line (120 cm) was used to for open-split interface. Gas was supplied with passive flow to the residual gas analyser (RGA; Inficon Transpector MPS with Edwards vacuum pump XDD1 < 2mbar) through a capillary (0.5 mm ID and 245 cm length) with an approximated flow rate of about 100 µL min-1. We used the instrument in emission mode without an electron multiplier and recorded data at an acquisition rate of 9 seconds. Compared to high resolution mass spectrometry, quadrupole data only show integer values and thus individual masses comprise different possible molecular/fragment ions. For instance, 44 amu bins the parent molecules carbon dioxide and propane yet can also include additional fragments of higher mass parent molecules.

Our study objectives were (I) to trace magnitudes of molecular abundances of atomic masses between 2 and 50 amu; (II) to compare results of the two combustion columns; (III) to identify gas species that compromise graphitization or potentially promote corrosion of interface equipment.

Magnitude (∆Torr)

Figure S1: panel plot of RGA profiles showing time elapsed (x-axis) and pressure in Torr (y-axis)

Oven temperature and IRGA data were recorded in LabView and RGA data were recorded in FabGuard (Inficon software). We measured our in-house RPO standard Nantucket Mud Patch in the routine setting (35 mL min-1) as reference to then compare the results with data obtained at a modified flow rate (17.5 mL min-1). We chose to reduce to flow rate to increase the concentrations of sample gases aiming at a better signal intensity. The baseline data for Helium and Oxygen for both reactor types is included in table S2.

Exemplary evolution profiles of chemical elements during an analysis are shown in Figure S1. The results of maximum magnitude (∆Torr) are illustrated in Figures S2 to S18 for molecular or fragment masses (12, 14, 15, 16, 18, 26, 27, 28, 29, 30, 32, 33, 34 ,44, 45, 46, 48 amu) as specified in each plot. The x-axes of column plots list sample ID’s: 1 to 7 (table S2). Y-axes show magnitude of signal intensity (Torr difference between baseline and maximum change of pressure during the CO2 evolution profile). The bright yellow column bars (always in the left) shows results for ramped pyrolysis/oxidation mode (oxidation-RPO) and dark sand brown (always on the right) shows results for pure oxidation mode (FOX). Data are reported for each sample only when change in pressure is about twice the noise level. To record the native combustion gas, no calibration gas was used. So this data is exclusively qualitative and only presents relative differences between reactor types and to some extent between sample types. It, however, allows to address our study objectives of tracing gas abundance, comparing reactor types and investigating the abundance of potential corrosive gas species.

Table S: Baseline pressure (Torr) for the carrier gases Helium and Oxygen showing an experimental reproducibility of better than 2.21E-11 Torr for He and 7.70E-10 Torr for O2

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **ID** | **Sample specs** | **He** | | **O2** | |
| **Ox-RPO** | **FOX** | **Ox-RPO** | **FOX** |
| 1 | NMP 35 mL min-1 | 4.84E-11 | 4.90E-11 | 3.74E-09 | 3.86E-09 |
| 2 | NMP 17.5 mL min-1 | 4.85E-11 | 3.28E-11 | 3.88E-09 | 4.63E-09 |
| 3 | NMP fumig 17.5 mL min-1 | 3.89E-11 | 3.65E-11 | 4.10E-09 | 3.95E-09 |
| 4 | SLR fumig 17.5 mL min-1 | 3.50E-11 | 3.66E-11 | 4.28E-09 | 3.95E-09 |
| 5 | WH19 17.5 mL min-1 | 2.95E-11 | 4.50E-11 | 3.80E-09 | 4.20E-09 |
| 6 | S1bog 17.5 mL min-1 | 2.94E-11 | 3.05E-11 | 3.78E-09 | 4.05E-09 |
| 7 | KC-5 17.5 mL min-1 | 2.64E-11 | 3.25E-11 | 3.82E-09 | 3.96E-09 |

The concept of this comparative pre-study in the development of FOX was to compare the two types of combustion columns at minimal risk to compromise analytical instrumentation in particular the quadrupole detector. In consequence this limits the information content that could allow for robust interpretation, yet a few observations may be interesting.

1. Time series revealed a stable baseline after equilibration of carrier gases He, O2 with some (dissociated) H2O and only traces of N2 and CO2 as blank.
2. To increase the signal intensity, we reduced the flow rate. To ensure that we yield similar thermogram profiles and data, the in-house standard Nantucket Mud Patch (NMP) was analyzed with the oxidation-RPO at common 35 mL min-1 and reduced flow rate at 17.5 mL min-1 at almost identical sample weights. Results are about the same yet the increased concentrations facilitated a better signal-to-noise ratio.
3. The results for the different sample typesdiffer in magnitude and dynamics for even for common masses like C and CO2 that are evidently present in all samples. While the sample weight and its respective C content controls the total CO2 yield, the mineralization of organic matter differs among sample types due to its origin and composition. Homogenous portions of the organic matter can rapidly be oxidized with immediate effect on the detected magnitude.
4. Results for oxidation-RPO and FOX agree well for the most molecular or fragment masses for the illustrated maximum differences (Figure S2 to S18) and agree well for the time-series (not shown here). This further supports the good agreement and thus intercomparability of results for both combustion column types.
5. A complete combustion of hydrocarbons would only yield CO2 and H2O. Together with the molecular fragments C and O this yields four central data plots. Further nitrogen is a natural constituent of organic matter that can account for about 10 % of carbon content. Thus, nitrogen abundance would generally be of interest but as the experiment was carried out in open-split mode – adding a baseline of nitrogen – N dynamics are lower than ambient concentrations in this experiment. Further, the low mass resolution of the RGA limits the informative value for the expected molecular/fragment ion mass of 28 and 30 as various chemical configurations with similar molecular weights may be expected.
6. The sample sequence included two acid fumigated samples (3 and 4) that are known to be notorious for their chlorine contents with corrosive effects and formation of precipitants that can clog the lines. While we observed a distinct sanitizing smell of chlorine in the FOX as well as precipitants in the oxidation-RPO the RGA did not record any significant changes above the signal-to-noise level. We attribute this to the long transfer line (~3 m) between the reactor and the RGA and to the open-split setup. We infer the here the reduced flow rate obscured the chlorine front by lower mass helium.
7. An apparent sulfur dynamic was only found for the mass SO (48 amu) in the sulfur rich (3.4 %) Wild Harbor sediment. We observed a difference between the combustion columns. The oxidation-RPO showed some dynamic behavior while the FOX remained at the signal-to-noise level. Sulfur monoxide (SO) can act very well as a corrosive agent as it can be a further oxidized to sulfuric acid. Other than that, we observed only negative magnitudes for the reduced sulfur species (33 and 34 while the depression in mass 32 may record O2 consumption during the oxidation). We speculate that the formation of secondary electrons during comparative high abundance of other molecular or fragmented ions caused this systematic depression of reduced sulfur species.

This first test in the development of FOX provided indications for a CO2 purification capacity similar or better than the oxidation-RPO with similar thermogram behavior. There are certainly constraints in this experiment that limit a conclusive and robust interpretation, yet it gave confidence to succeed with FOX and investigate the direct combustion for isotope analysis. This open-split setup did not result in instrumental failure or breakdown of the quadrupole but facilitated tracing the comparability and record dynamics in low resolution.

































