***Supplementary materials***



**Figure S1.** Fm values comparisons between calculated (from RPO isotopic mass balance) and measured bulk values under the Rinse*HCl* (A) and Fume*HCl* (B). ∆Fm (offset between calculated and measured Fm values) against measured bulk values under the Rinse*HCl* (C) and Fume*HCl* (D).

A blank assessment was performed on the RPO system using methodologies detailed in Hemingway et al. (2017a). For the samples analyzed here, applying the blank correction shifts resulting isotope values by < 0.001 for Fm and < 0.1 ‰ for δ13C, within analytical uncertainty. Calculated bulk Fm values, reconstructed using Fm values of thermal windows and their mass percentages, are compared with measured bulk Fm values in Figure S1. The calculated Fm values are indistinguishable from measured bulk values for both Rinse*HCl* and Fume*HCl*. However, calculated δ13C values are displaced from the 1:1 line (Supplementary Fig. 3). According to Hemingway et al. (2017a) and Rosenheim et al. (2013), stable carbon isotopic fractionation on the order of ~1–2 ‰ may occur during the reaction of OM in the RPO (without Chemical Oven). Nevertheless, this does not affect 14C results since Fm values are corrected for isotope fractionation (Stuiver and Polach 1977; Rosenheim et al. 2013; Longworth et al. 2015).

 A complicating factor is whether the acid treatments redistribute OM into pools of carbon with different thermal stability. If OC were redistributed dramatically, we would expect the isotopic compositions to change as well. For example, moving thermally labile, and young, carbon to a more thermally stable portion of the thermogram should reduce the age of the higher temperature portions of the thermogram. We don’t observe this (Table 2). Our results thus suggest that there is no marked redistribution of OC with the removal of IC.



**Figure S2.** δ13C values comparisons between calculated (from RPO isotopic mass balance) and measured bulk values under the Rinse*HCl* (a) and Fume*HCl* (b). ∆ δ13C (offset between calculated and measured Fm values) against measured bulk values under the Rinse*HCl* (c) and Fume*HCl* (d).

***Assessment of chemical oven:***

 In order to minimize the influence of HCl remained in fumigated sample during experimental operation, we developed an external oven (so-called: Chemical Oven) at ~520 oC. It contains a glass tube with a few grams CuO, Ag, and Mn (Froelich, 1980) which was connected with reactor and CO2 analyzer to purify the gases. Residual gas analyzer (RGA) detected a sharp decrease of chlorine concentration (signal) of the gaseous impurities from the reactor when connected to this Chemical Oven (no shown).

 In addition, a comparison of released CO2 amounts before and after connection with chemical oven was examined. In Figure S3, the thermograms show similar patterns of normalized CO2 concentration at a range of reactor temperature, suggesting that there is no marked alteration when the chemical oven is connected for removing impurities.



**Figure S3.** Comparison of CO2 thermograms before (blue) and after (green) connection with Chemical Oven. Both mass recovery rates are similar, ~98 %.

 Furthermore, a stable carbon isotopic mass balance was conducted to test the occurrence of carbon isotopic fractionation in the Chemical Oven. Here, we present the stable carbon isotopic mass balances on raw sample standard (from Nantucket mud) for three measurements: **a**) non-connection with chemical oven but reactor with catalyze wire; **b**) connection with Chemical Oven but reactor without catalyze wire; **c**) connection with chemical oven and reactor with catalyze wire. The offsets between calculated and measured δ13C values are similar: -1.6 ‰, -2.0 ‰, -1.2 ‰ with 0.5 ‰ error, respectively (Table S1). Considering the isotopic fraction (~1-2 ‰) in the reactor (Hemingway et al., 2017a), our assessment suggests that there is no marked isotopic excursion (fractionation) occurred in the Chemical Oven.

**Table S1.** The stable carbon isotopic mass balances among the uses of chemical oven and catalyze wire.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Chemical Oven | 1 fraction | 2 fraction | 3 fraction | 4 fraction  | 5 fraction | Mass balanced bulk (‰) | Combusted bulk (‰) (n = 1) | Offset(‰) |
| **Non-connection, reactor with catalyze wire****Measured** δ13C (‰) | -24.3 | -21.2 | -19.9 | -18.3 | -22.3 |  |  |  |
| Mass% | 0.25 | 0.26 | 0.26 | 0.17 | 0.06 |  |  |  |
| Stable carbon isotopic balance | -6.1 | -5.6 | -5.1 | -3.1 | -1.3 | -21.2±0.5 | -19.6±0.2 | -1.6±0.5 |
| **Connection, reactor without catalyze wire****Measured** δ13C (‰) | -26.1 | -25.1 | -21.9 | -19.0 | -22.3 |  |  |  |
| Mass% | 0.03 | 0.18 | 0.37 | 0.36 | 0.06 |  |  |  |
| Stable carbon isotopic balance | -0.9 | -4.6 | -8.1 | -6.8 | -1.3 | -21.6±0.5 | -19.6±0.2 | -2.0±0.5 |
| **Connection, reactor with catalyze wire****Measured** δ13C (‰) | -25.6 | -23.8 | -21.0 | -18.4 | -21.9 |  |  |  |
| Mass% | 0.02 | 0.21 | 0.36 | 0.35 | 0.06 |  |  |  |
| Stable carbon isotopic balance | -0.6 | -5.0 | -7.5 | -6.4 | -1.4 | -20.8±0.5 | -19.6±0.2 | -1.2±0.5 |

*Note:* The first fraction was trapped at ~125oC, the fifth fraction was stopped at ~900 oC. The error is ±2σ.

**Supplementary Table S2.** Calculation of RPO mass isotopic balance.

|  |  |  |  |
| --- | --- | --- | --- |
|   | Sample |   | Fm |
| Low-carbonate | Nan |   | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  | RPO balance | Bulk measurement | Offset |
| Rinse*HCl* |  | Mass % | 0.22 | 0.23 | 0.24 | 0.24 | 0.07 |  |  |  |  |
|  |  | Measurement | 0.8970 | 0.8725 | 0.8611 | 0.7581 | 0.3854 |  |  |  |  |
|  |  | ∑ | 0.1995 | 0.1985 | 0.2076 | 0.1823 | 0.0264 |  | 0.8143 | 0.8236 | -0.0093 |
|  | Buzz |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
|  |  | Mass % | 0.19 | 0.20 | 0.29 | 0.24 | 0.08 |  |  |  |  |
|  |  | Measurement | 1.0162 | 0.9796 | 0.9399 | 0.8293 | 0.3565 |  |  |  |  |
|  |  | ∑ | 0.1975 | 0.1925 | 0.2695 | 0.2026 | 0.0278 |  | 0.8899 | 0.9121 | -0.0222 |
|  | Taun |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction | 6 Fraction |  |  |  |
|  |  | Mass % | 0.10 | 0.23 | 0.31 | 0.19 | 0.09 | 0.07 |  |  |  |
|  |  | Measurement | 0.9197 | 0.9007 | 0.7689 | 0.3950 | 0.1154 | 0.0337 |  |  |  |
|  |  | ∑ | 0.0956 | 0.2047 | 0.2376 | 0.0770 | 0.0104 | 0.0025 | 0.6279 | 0.6519 | -0.0240 |
| Fume*HCl* | Nan |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
|  |  | Mass % | 0.37 | 0.27 | 0.22 | 0.11 | 0.03 |  |  |  |  |
|  |  | Measurement | 0.9098 | 0.8943 | 0.8395 | 0.6753 | 0.2327 |  |  |  |  |
|  |  | ∑ | 0.3404 | 0.2384 | 0.1829 | 0.0768 | 0.0064 |  | 0.8449 | 0.8324 | 0.0125 |
|  | Buzz |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
|  |  | Mass % | 0.40 | 0.22 | 0.23 | 0.11 | 0.04 |  |  |  |  |
|  |  | Measurement | 1.0398 | 1.0048 | 0.8767 | 0.5800 | 0.1779 |  |  |  |  |
|  |  | ∑ | 0.4146 | 0.2173 | 0.2009 | 0.0646 | 0.0079 |  | 0.9053 | 0.9073 | -0.0020 |
|  | Taun |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction | 6 Fraction |  |  |  |
|  |  | Mass % | 0.16 | 0.24 | 0.28 | 0.17 | 0.07 | 0.08 |  |  |  |
|  |  | Measurement | 0.9381 | 0.8508 | 0.6566 | 0.4673 | 0.1230 | 0.1064 |  |  |  |
|  |  | ∑ | 0.1533 | 0.2014 | 0.1813 | 0.0791 | 0.0090 | 0.6241 | 0.7133 | 0.7133 | 0.0000 |
| High-carbonate | Berm |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
| Rinse*HCl* |  | Mass % | 0.25 | 0.24 | 0.26 | 0.17 | 0.08 |  |  |  |  |
|  |  | Measurement | 0.6282 | 0.5865 | 0.5160 | 0.3637 | 0.2544 |  |  |  |  |
|  |  | ∑ | 0.1574 | 0.1398 | 0.1327 | 0.0633 | 0.0203 |  | 0.5135 | 0.5072 | 0.0063 |
|  | Ceara |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
|  |  | Mass % | 0.16 | 0.24 | 0.27 | 0.28 | 0.05 |  |  |  |  |
|  |  | Measurement | 0.8147 | 0.7986 | 0.8097 | 0.8231 | 0.4209 |  |  |  |  |
|  |  | ∑ | 0.1279 | 0.1929 | 0.2192 | 0.2306 | 0.0213 |  | 0.7919 | 0.7874 | 0.0045 |
|  | Serria |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
|  |  | Mass % | 0.19 | 0.30 | 0.30 | 0.17 | 0.03 |  |  |  |  |
|  |  | Measurement | 0.1672 | 0.1465 | 0.1589 | 0.1775 | 0.1007 |  |  |  |  |
|  |  | ∑ | 0.0322 | 0.0440 | 0.0483 | 0.0308 | 0.0030 |  | 0.1583 | 0.1563 | 0.0020 |
| Fume*HCl* | Berm |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
|  |  | Mass % | 0.16 | 0.27 | 0.31 | 0.20 | 0.06 |  |  |  |  |
|  |  | Measurement | 0.6281 | 0.5865 | 0.5169 | 0.3637 | 0.2544 |  |  |  |  |
|  |  | ∑ | 0.1010 | 0.1571 | 0.1627 | 0.0725 | 0.0145 |  | 0.5079 | 0.5284 | -0.0205 |
|  | Ceara |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
|  |  | Mass % | 0.16 | 0.22 | 0.32 | 0.27 | 0.03 |  |  |  |  |
|  |  | Measurement | 0.5653 | 0.7934 | 0.7864 | 0.7557 | 0.5086 |  |  |  |  |
|  |  | ∑ | 0.0926 | 0.1753 | 0.2505 | 0.2012 | 0.01553 |  | 0.7351 | 0.7756 | -0.0405 |
|  | Serria |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
|  |  | Mass % | 0.20 | 0.18 | 0.16 | 0.16 | 0.16 |  |  |  |  |
|  |  | Measurement | 0.2048 | 0.1778 | 0.1589 | 0.1562 | 0.1615 |  |  |  |  |
|   |   | ∑ | 0.0072 | 0.0219 | 0.0578 | 0.0668 | 0.0082 |  | 0.1618 | 0.1619 | -0.0001 |
|  |  |  |  |  |  |  |  |  |  |  |  |
|  |  |  | δ13C |
| Low-carbonate | Nan |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  | RPO balance | Bulk measurement | Offset |
| Rinse*HCl* |  | Mass % | 0.22 | 0.23 | 0.24 | 0.24 | 0.07 |  |  |  |  |
|  |  | Measurement | -22.30 | -21.60 | -21.20 | -22.80 | -23.80 |  |  |  |  |
|  |  | ∑ | -4.96 | -4.91 | -5.11 | -5.48 | -1.63 |  | -22.10 | -21.30 | -0.80 |
|  | Buzz |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
|  |  | Mass % | 0.19 | 0.20 | 0.29 | 0.24 | 0.08 |  |  |  |  |
|  |  | Measurement | -21.50 | -20.80 | -21.20 | -22.20 | -23.70 |  |  |  |  |
|  |  | ∑ | -4.18 | -4.09 | -6.08 | -5.42 | -1.85 |  | -21.62 | -21.10 | -0.52 |
|  | Taun |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction | 6 Fraction |  |  |  |
|  |  | Mass % | 0.10 | 0.23 | 0.31 | 0.19 | 0.09 | 0.07 |  |  |  |
|  |  | Measurement | -30.90 | -30.80 | -29.20 | -28.10 | -26.30 | -25.40 |  |  |  |
|  |  | ∑ | -3.21 | -7.00 | -9.02 | -5.48 | -2.37 | -1.90 | -28.98 | -27.40 | -1.58 |
| Fume*HCl* | Nan |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
|  |  | Mass % | 0.37 | 0.27 | 0.22 | 0.11 | 0.03 |  |  |  |  |
|  |  | Measurement | -23.20 | -20.50 | -22.20 | -26.10 | -23.40 |  |  |  |  |
|  |  | ∑ | -8.68 | -5.46 | -4.84 | -2.97 | -0.65 |  | -22.60 | -20.90 | -1.70 |
|  | Buzz |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
|  |  | Mass % | 0.40 | 0.22 | 0.23 | 0.11 | 0.04 |  |  |  |  |
|  |  | Measurement | -22.50 | -20.10 | -21.90 | -25.70 | -24.80 |  |  |  |  |
|  |  | ∑ | -8.97 | -4.35 | -5.02 | -2.86 | -1.10 |  | -22.30 | -20.90 | -1.40 |
|  | Taun |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction | 6 Fraction |  |  |  |
|  |  | Mass % | 0.16 | 0.24 | 0.28 | 0.17 | 0.07 | 0.08 |  |  |  |
|  |  | Measurement | -31.80 | -31.30 | -32.00 | -27.60 | -24.70 | -24.10 |  |  |  |
|  |  | ∑ | -5.20 | -7.41 | -8.84 | -4.67 | -1.81 | -1.95 | -29.88 | -27.50 | -2.38 |
| High-carbonate | Berm |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
| Rinse*HCl* |  | Mass % | 0.25 | 0.24 | 0.26 | 0.17 | 0.08 |  |  |  |  |
|  |  | Measurement | -21.90 | -21.10 | -21.80 | -23.80 | -26.40 |  |  |  |  |
|  |  | ∑ | -5.49 | -5.03 | -5.61 | -4.14 | -2.11 |  | -22.37 | -21.50 | -0.87 |
|  | Ceara |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
|  |  | Mass % | 0.16 | 0.24 | 0.27 | 0.28 | 0.05 |  |  |  |  |
|  |  | Measurement | -21.40 | -20.10 | -19.40 | -20.40 | -22.30 |  |  |  |  |
|  |  | ∑ | -3.36 | -4.85 | -5.25 | -5.71 | -1.13 |  | -20.31 | -19.50 | -0.81 |
|  | Serria |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
|  |  | Mass % | 0.19 | 0.30 | 0.30 | 0.17 | 0.03 |  |  |  |  |
|  |  | Measurement | -21.60 | -17.10 | -16.50 | -16.90 | -22.70 |  |  |  |  |
|  |  | ∑ | -4.16 | -5.14 | -5.01 | -2.94 | -0.67 |  | -17.91 | -16.60 | -1.31 |
| Fume*HCl* | Berm |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
|  |  | Mass % | 0.16 | 0.27 | 0.31 | 0.20 | 0.06 |  |  |  |  |
|  |  | Measurement | -23.20 | -24.20 | -21.50 | -31.50 | -27.80 |  |  |  |  |
|  |  | ∑ | -3.73 | -6.48 | -6.77 | -6.28 | -1.58 |  | -24.85 | -20.70 | -4.15 |
|  | Ceara |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
|  |  | Mass % | 0.16 | 0.22 | 0.32 | 0.27 | 0.03 |  |  |  |  |
|  |  | Measurement | -24.4 | -23.0 | -21.3 | -29.2 | - |  |  |  |  |
|  |  | ∑ | -3.904 | -5.06 | -6.816 | -7.884 | - |  | -24.45±0.5 | -19.50 | -4.95 |
|  | Serria |  | 1 Fraction | 2 Fraction | 3 Fraction | 4 Fraction | 5 Fraction |  |  |  |  |
|  |  | Mass % | 0.20 | 0.18 | 0.16 | 0.16 | 0.16 |  |  |  |  |
|  |  | Measurement | -22.4 | -21.4 | -17.2 | -18.2 | -26.1 |  |  |  |  |
|   |   | ∑ | -4.48 | -3.852 | -2.752 | -2.912 | -4.176 |  | -18.8 | -17.60 | -1.20 |

n

 Note: - indicates that the 13C composition of the 5th fraction was not measured. ∑ indicated mass % multiplied by measured isotopic values.