Supplementary Material

**1 Statistical Analyses**

* 1. **Distribution and Normality**

Individual assessments of normality for laboratory-acquired and natural wildfire charcoals, respectively, indicate mild differences in the distribution of each dataset, highlighted by Shapiro-Wilk analysis (*see* Suppl. Table 1 and 2). Whilst experimental pyrolysis samples present only two instances in which normality may be assumed – associated with RBS – this is somewhat contrasted by three occasions of normality in wildfire charcoals. The key difference here, however, remains the parameters in which normality is associated. For wildfire charcoals, a normal distribution may be assumed in R1 and AD/AG. It must, however, be considered that the comparison of distribution shown here is generalized and may not be directly compared between differing charcoal sources, due to differences in recorded formation temperature (or maximum fire temperature). These results may be a product of innate differences in distribution associated with variable temperatures presented in the laboratory and natural conditions. Nonetheless, both sources present a statistical difference in the distribution of data, and considerable predisposition toward non-normality.

**Supplementary Table 1.**Table indicating results for the investigation of statistical normality, via the Shapiro-Wilk test, for charcoals derived from tube furnace pyrolysis. This has been completed for each formation temperature across all six Raman parameters in use. Number of data points utilized in each test is denoted by *N.*Values labelled *W* that exceed 1 indicate data that does not correspond to the null hypothesis, further supported by *p*(normal). Below a0.05, a *p*(normal) value indicates that the reliable rejection of the null hypothesis is permitted, and a non-normal distribution may be attributed to the dataset in question.

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| Parameter | Tube Furnace Charcoal |
| °C | *N* | *W* | *p*(normal) |
| D-FWHM | 400  | 150 | 0.813 | <.001 |
| 600  | 150 | 0.964 | <.01 |
| 800  | 150 | 0.894 | <.001 |
| 1000  | 150 | 0.940 | <.001 |
| G-FWHM | 400  | 150 | 0.780 | <.001 |
| 600  | 150 | 0.947 | <.001 |
| 800  | 150 | 0.979 | <.05 |
| 1000  | 150 | 0.929 | <.001 |
| R1 | 400  | 150 | 0.774 | <.001 |
| 600  | 150 | 0.962 | <.001 |
| 800 1000  | 150150 | 0.9590.951 | <.001<.001 |
|
| RBS | 400  | 150 | 0.969 | <.01 |
| 600  | 150 | 0.989 | *Not Significant* |
| 800  | 150 | 0.987 | *Not Significant* |
| 1000  | 150 | 0.957 | <.001 |
| AD/AG | 400  | 150 | 0.735 | <.001 |
| 600  | 150 | 0.981 | <.05 |
| 800  | 150 | 0.868 | <.001 |
| 1000  | 150 | 0.973 | <.01 |
| FWHMRa | 400  | 150 | 0.920 | <.001 |
| 600  | 150 | 0.919 | <.001 |
| 800  | 150 | 0.941 | <.001 |
| 1000  | 150 | 0.977 | <.05 |

**Supplementary Table 2,**Table indicating results for the investigation of statistical normality, via the Shapiro-Wilk test, for charcoals collected from the prescribed *Calluna* fire. This has been completed for each formation temperature across all six Raman parameters in use. Number of data points utilized in each test is denoted by *N.*Values labelled *W* that exceed 1 indicate data that does not correspond to the null hypothesis, further supported by *p*(normal). Below a0.05, a *p*(normal) value indicates that the reliable rejection of the null hypothesis is permitted, and a non-normal distribution may be attributed to the dataset in question.

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| Parameter | Prescribed *Calluna* Burn Charcoal |
| °C | *N* | *W* | *p*(normal) |
| D-FWHM | 466  | 150 | 0.781 | <.001 |
| 592 | 150 | 0.852 | <.001 |
| 705  | 150 | 0.806 | <.001 |
| 803  | 150 | 0.862 | <.001 |
| G-FWHM | 466  | 150 | 0.914 | <.001 |
| 592 | 150 | 0.917 | <.001 |
| 705  | 150 | 0.939 | <.001 |
| 803  | 150 | 0.894 | <.001 |
| R1 | 466  | 150 | 0.720 | <.001 |
| 592 | 150 | 0.991 | *Not Significant* |
| 705  | 150 | 0.711 | <.001 |
| 803  | 150 | 0.990 | *Not Significant* |
| RBS | 466  | 150 | 0.856 | <.001 |
| 592 | 150 | 0.889 | <.001 |
| 705  | 150 | 0.816 | <.001 |
| 803  | 150 | 0.883 | <.001 |
| AD/AG | 466  | 150 | 0.630 | <.001 |
| 592 | 150 | 0.980 | <.05 |
| 705  | 150 | 0.603 | <.001 |
| 803  | 150 | 0.984 | *Not Significant* |
| FWHMRa | 466  | 150 | 0.788 | <.001 |
| 592 | 150 | 0.874 | <.001 |
| 705  | 150 | 0.815 | <.001 |
| 803  | 150 | 0.929 | <.001 |

**1.2 Statistical Significance and Parameter Datasets**

By conducting and comparing the significance of variation across mean values - associated with both charcoal sources - the legitimacy of experimentally derived trends and their relation to a natural counterpart dataset may be examined. Via the application of one-way ANOVA (Suppl. Table 3) testing to all parameters across both datasets, independent of one another, we have shown that all mean values are statistically significant in variability to those in the same sample set. Whilst this test refers to the variance between mean values, its robustness to non-normality assures that it is also applicable to median values, as reported. As with Shapiro-Wilk testing, values below 0.05 indicate statistical significance and the rejection of the null hypothesis. In this case, we may reliably accept the notion of significant variation between mean values at each tested temperature within our parameters.

Implementation of Levene’s test of variance for mean and median values (Suppl. Table 3) indicates heterogenous variance across almost all parameters in both datasets, via the presentation of statistically significant *p*-values. The exception to this may be found with R1 from naturally derived wildfire charcoals (*p*-values exceeding 0.05). As a result, *p*-values derived from a Welch’s test of unequal variance may be used in lieu of those attained in one-way ANOVA testing for all parameters, except R1. Welch’s *p*-values below a0.05, as shown in Table 3, corroborate our earlier conclusion of significance in variation across all mean parameter values. The permitted application of ANOVA *p*-values continues to indicate statistically significant variations between mean values in R1 from natural charcoals.

**Supplementary Table 3**, Table indicating the statistical significance of variation in mean values across all parameters, shown by Welch’s *p*-values below 0.05, for both tube furnace pyrolysis and naturally sourced charcoals, respectively. Application of Welch’s *p*-values is permissible under an assessment of heterogenous variance (Levene’s *p*<0.05) and preceding one-way ANOVA testing. Here, *dfB* and *dfT* refer to *df* values derived from between groups and the total dataset, respectively. *N.S.* = Not significant.

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| Sample Source | Parameter | One-way ANOVA | Levene’s Variance Test | Modified Levene’s Test | Welch’s Unequal-VarianceTest |
| *F* | *(dfB, dfT)* | *p* | *p*(mean) | *p*(median) | *F* | *(df1, df2)* | *p* |
| Tube Furnace Pyrolysis | D-FWHM | 220.254 | (3,599) | <.001 | <.001 | <.001 | 300.248 | (3,273.614) | <.001 |
| G-FWHM | 76.747 | (3,599) | <.001 | <.001 | <.001 | 48.605 | (3,318.083) | <.001 |
| R1 | 51.410 | (3,599) | <.001 | <.001 | <.001 | 168.444 | (3,313.740) | <.001 |
| RBS | 56.739 | (3,599) | <.001 | <.001 | <.001 | 135.602 | (3,309.266) | <.001 |
| AD/AG | 25.786 | (3,599) | <.001 | <.001 | <.001 | 30.989 | (3,302.748) | <.001 |
| FWHMRa | 155.989 | (3,599) | <.001 | <.001 | <.001 | 229.448 | (3,292.665) | <.001 |
| 2021 Prescribed *Calluna* Burn | D-FWHM | 13.866 | (5, 899) | <.001 | <.001 | <.001 | 13.183 | (5, 409.197) | <.001 |
| G-FWHM | 27.111 | (5, 899) | <.001 | <.001 | <.001 | 22.368 | (5, 413.562) | <.001 |
| R1 | 2.448 | (5, 899) | <.05 | *N.S.* | *N.S.* | N/A | N/A | N/A |
| RBS | 10.155 | (5, 899) | <.001 | <.001 | <.001 | 8.729 | (5, 411.997) | <.001 |
| AD/AG | 7.612 | (5, 899) | <.001 | <.001 | <.01 | 7.714 | (5, 408.547) | <.001 |
| FWHMRa | 8.445 | (5, 899) | <.001 | <.001 | <.001 | 10.873 | (5, 410.144) | <.001 |