

1 Evidence of Wildfires and Elevated Atmospheric Oxygen at
2 the Frasnian–Famennian Boundary in New York (USA):
3 Implications for the Late Devonian Mass Extinction

4 **Zeyang Liu¹, David Selby^{1,4}, Paul C. Hackley², and D. Jeffrey³**

5 *¹Department of Earth Sciences, University of Durham, Durham DH1 3LE, UK*

6 *²U.S. Geological Survey, MS 956 National Center, Reston, VA 20192, USA*

7 *³Department of Geological Sciences, SUNY College at Geneseo, Geneseo, NY 14454, USA*

8 *⁴State Key Laboratory of Geological Processes and Mineral Resources, School of Earth
9 Resources, China University of Geosciences, Wuhan, 430074, Hubei, China*

10 Corresponding author: Zeyang Liu (geozy.liu@outlook.com)

11 **ABSTRACT**

12 The Devonian Period experienced significant fluctuations of atmospheric oxygen (O₂)
13 levels (~25 – 13%), for which the extent and timing are debated. Also characteristic of the
14 Devonian Period, at the Frasnian–Famennian (F–F) boundary, is one of the ‘big five’ mass
15 extinction events of the Phanerozoic. Fossilized charcoal (inertinite) provides a record of
16 wildfire events, which in turn can provide insight into the evolution of terrestrial ecosystems
17 and the atmospheric composition. Here, we report organic petrology, programmed pyrolysis
18 analysis, major and trace element analyses and initial osmium isotope (Os_i) stratigraphy from
19 five sections of Upper Devonian (F–F interval) from western New York, USA. These data are
20 discussed to infer evidence of a wildfire event at the Frasnian–Famennian boundary. Based
21 on the evidence for a wildfire at the F–F we also provide an estimate of atmospheric O₂ level
22 of ~23 – 25% at this interval, which is in agreement with the models that predict elevated *p*O₂ levels
23 during the Late Devonian. This, coupled with our Os isotope records, support the currently
24 published Os_i data that lacks any evidence for an extra-terrestrial impact or volcanic event at
25 the F-F interval, and therefore to act as a trigger for the F–F mass extinction. The elevated O₂
26 level at the F-F inferred from this study supports the hypothesis that *p*CO₂ drawdown and
27 associated climate cooling may have acted as a driving mechanism of the F–F mass
28 extinction.

29 INTRODUCTION

30 During the Devonian Period, the level of atmospheric O₂ is suggested to have
31 significantly fluctuated in response to the diversification and radiation of terrestrial plant life,
32 and to have driven the size increase in fauna (Dahl et al., 2010). Currently debated is the timing
33 and amount of O₂ change throughout the Devonian into the Carboniferous. For example, O₂
34 levels are estimated to have dropped from ~25 % to ~13 % during the Devonian, with levels
35 rising steadily to present day atmospheric levels (21 %) by the mid-Mississippian Epoch
36 (Berner, 2006; Rimmer et al., 2015; Scott and Glasspool, 2006). In contrast, O₂ levels are also
37 suggested to have dropped from ~25 % during the Early Devonian to ~17 % in the early Late
38 Devonian, and then increased to ~22 % during Late Devonian (Berner et al., 2003; Berner,
39 2009). In addition to the atmospheric O₂ response related to the evolution of flora and fauna,
40 a positive feedback between atmospheric O₂ and episodes of wildfire has been proposed,
41 whereby higher O₂ concentrations are related to higher frequencies of fire events that result in
42 charcoal production and burial (Berner et al., 2003). This burial of black carbon leads to
43 *p*CO₂ drawdown that, in turn, creates a further increase in atmospheric O₂ (Berner et al.,
44 2003). Inertinite macerals, the by-product of wildfires, provide a record of wildfire events and
45 inertinite presence in the sedimentary record has been used to infer ancient atmospheric O₂
46 levels (Scott and Glasspool, 2007; Glasspool and Scott, 2010).

47 In addition to fluctuations in atmospheric O₂, the Devonian Period also witnessed the
48 Frasnian–Famennian (F–F) mass extinction, which is one of the ‘big five’ mass extinction
49 events of the Phanerozoic (Stanley, 2016). Proposed extinction mechanisms for this
50 Devonian extinction include ocean anoxic or euxinic conditions (Bond et al., 2004), climate
51 cooling (Huang et al., 2018; Joachimski and Buggisch, 2002; Joachimski et al., 2009), sea-
52 level change (Johnson et al., 1985; Bond and Wignall, 2008), bolide impact (Claeys et al.,
53 1992), and volcanism (Racki et al., 2018).

54 This paper presents new organic petrology, programmed pyrolysis analysis, major and
55 trace element analyses, and initial osmium isotope ($^{187}\text{Os}/^{188}\text{Os}_i$, Os_i) stratigraphy, of samples
56 from five Upper Devonian (F–F interval) sections from western New York, USA, and
57 discusses the evidence for wildfire events at the F–F boundary and, by inference, the level of
58 atmospheric O_2 (and implied $p\text{CO}_2$ levels) and the possible mechanisms (e.g., wildfire,
59 volcanism, climate change, etc.) that led to the F–F mass extinction.

60 **GEOLOGICAL BACKGROUND**

61 In western New York State (USA), the sedimentary record of the F–F interval consists
62 of siliciclastic mudstones and sandstones that are interpreted as slope to basin deposits of the
63 northern Appalachian foreland basin (Fig. 1; Sageman et al., 2003; Over, 1997). This study
64 focuses on five measured sections (Fig. 1), four of which are from outcrops (Irish Gulf, IG;
65 Beaver Meadow Creek, BMC; Walnut Creek Bank, WCB; and Joint Creek, JC) and one from
66 a drill core (West Valley, WV). These sections are interpreted as proximal to distal deposits
67 (JC, BMC, WV, IG and WCB, respectively; Fig. 1).

68 In all sections, the Frasnian–Famennian (F–F) interval is mapped as Late Frasnian and
69 earliest Famennian Hanover Formation and the Early Famennian Dunkirk Formation (Over,
70 2002). The Hanover Formation comprises light gray, silty shale and interbedded black silty
71 shale that is rich in organic matter (~0.5–5 wt. % TOC), which is of low thermal maturity
72 (% $\text{BR}_o \sim 0.6$, solid bitumen reflectance). The BR_o values are used here as a proxy for thermal
73 maturity which are equivalent to or slightly less than the VR_o at this thermal maturity (Wei et
74 al., 2016; Hackley and Lewan, 2018). The gray shale is intensively bioturbated and contains
75 poorly preserved brachiopods and bivalves. The black shale is pyrite-rich, finely laminated
76 (except the basal parts where bioturbation is observed) and is interpreted as having
77 accumulated in anoxic/dysoxic conditions (Over, 2002). The Hanover Formation is overlain

78 by the Dunkirk Formation, which contains distinctive beds of black shale. In all sections, the
79 F–F boundary is defined by the first occurrence of the conodont *Palmatolepis triangularis*
80 (Fig. 2; Klapper et al., 1993; Over, 1997, 2002), and this boundary occurs in a regionally
81 continuous bed of black shale that is correlated with the upper Kellwasser Horizon.

82 **METHODS**

83 Across the F–F boundary interval black shale beds were sampled at 2 – 5 cm
84 stratigraphic resolution. Above and below the F–F boundary the black shale units were
85 sampled at a lower resolution of approximately 5 – 10 cm.

86 **Organic Petrology, Programmed Pyrolysis, and Total Organic Carbon Analysis**

87 Eighty-seven samples were prepared by ASTM D2797 for petrographic analyses at
88 the U.S. Geological Survey (USGS) in Reston, Virginia, using a thermoset plastic briquette
89 mount, which was ground and polished with successively finer abrasives until a 0.05-
90 micrometer (μm) finishing stage. Solid bitumen reflectance analyses (BR_o , %) were collected
91 according to ASTM D7708. Generally, at least 20 measurements of solid bitumen reflectance
92 were collected for each sample, with only 1 measurement per individual rock fragment.
93 Sample briquettes were imaged under oil immersion on a Zeiss AxioImager microscope in
94 white and blue incident light at 500x magnification. A Leica DM4000 microscope equipped
95 with LED illumination and monochrome camera detection was used for solid bitumen
96 reflectance analysis with the computer program DISKUS-FOSSIL by Hilgers Technisches
97 Buero. A YAG calibration standard (0.908% R_o) from Klein and Becker was used. Inertinite
98 reflectance (IR_o , %) was measured with the same method as solid bitumen. Samples were
99 point-counted (300 – 500 points per sample) to determine relative abundances of mineral
100 matter and macerals, which are inertinite, solid bitumen and telalginite (*Tasmanites*) that
101 presented in our sample sets. Bulk geochemical analyses were determined on the powdered

102 samples after crushing with a shatterbox. Bulk analyses included total organic carbon (TOC)
103 content by LECO carbon analyzer and hydrocarbon analyzer with kinetics (HAWK)
104 programmed pyrolysis (analyzed at the USGS in Denver, Colorado) using methods outlined
105 in Espitalié et al. (1985).

106 **Re–Os Analysis**

107 Rhenium-osmium (Re-Os) analysis was undertaken at the Laboratory for Sulphide
108 and Source Rock Geochronology and Geochemistry of Durham University (UK). Samples
109 were polished to remove any potential weathered surface and drilling marks. All samples
110 were powdered in a Zirconium dish using a shatterbox. Powdered sample (~1 g) and a known
111 amount of spike (mixed $^{185}\text{Re} + ^{190}\text{Os}$) were digested in a Carius tube with 8 ml of 0.25 g/g
112 CrO_3 in 4 N H_2SO_4 at 220 °C for 48 h. Rhenium was isolated using NaOH–acetone extraction
113 and anion chromatography. Osmium was isolated by solvent (chloroform) extraction and
114 purified by micro–distillation. The purified Re and Os fractions were analysed via negative
115 thermal ionization mass spectrometry using a Thermo Finnigan TRITON mass spectrometer
116 in the Arthur Holmes Laboratory at Durham University via static Faraday cup for Re and
117 secondary electron multiplier for Os. Total procedural blanks during this study were $12.5 \pm$
118 4.5 pg and 0.12 ± 0.06 pg (1σ S.D., $n = 3$) for Re and Os, respectively, with an average
119 $^{187}\text{Os}/^{188}\text{Os}$ value of 0.34 ± 0.20 ($n = 3$). The initial $^{187}\text{Os}/^{188}\text{Os}$ values were calculated using
120 the following equation:

$$121 \quad ^{187}\text{Os}/^{188}\text{Os}_{\text{initial}} = ^{187}\text{Os}/^{188}\text{Os}_{\text{measured}} - (^{187}\text{Re}/^{188}\text{Os}_{\text{measured}} * (\text{EXP}(\lambda * t) - 1))$$

122 where λ is ^{187}Re decay constant $1.666\text{e}^{-11} \text{ a}^{-1}$ (Smoliar et al., 1996), and t is the F–F boundary
123 age (371.93 Ma; Percival et al., 2018).

124 **Major and Trace Element Analysis**

125 Aliquots of the sample powder prepared for Re–Os analysis were also used for major
126 and trace element analysis. Major and trace element abundances were determined using a
127 Panalytical Zetium X–ray fluorescence (XRF) spectrometer at Department of Geography at
128 Durham University. Major and trace elements were analyzed with fused bead and pressed
129 pellet, respectively. For the former, 0.6 g of sample powder and 6 g of flux were used to fuse
130 the bead. The pressed pellet was prepared with 12 g of sample and 3 g of binder.
131 Reproducibility and precision were demonstrated through the repeated analysis of standards
132 (USGS SBC–1, USGS SDO–1). Uncertainty is less than 1 % for major elements (Si, Al and
133 Ti), less than 10 % for trace elements (Mn, V and Ni), and 20 % for Mo.

134 **RESULTS**

135 **Results of Organic Petrology and Pyrolysis Data**

136 Three types of macerals (inertinite, alginite, and solid bitumen) were identified in the
137 samples (Fig. 3). Pyrolysis data suggests the dominance of marine organic matter in the
138 samples (Fig. 4). Inertinite is observed in all studied sections (Fig. 2). Traces of inertinite are identified
139 in samples from the JC section below and above the F–F boundary, however, none were counted due to
140 the low abundance (lower than 0.2 %, volume percent of whole rock, here and after). In the BMC
141 section that represents the second-most proximal paleo-setting in the Appalachian Basin studied herein,
142 the first occurrence of inertinite is within Upper Frasnian strata (0.6 %) and continued upward, reaching
143 a maximum (2.2 %) just below the F–F boundary, after which the inertinite concentration decreased to
144 0.2 % above the F–F boundary. For the remaining WV, WCB, IG sections that represent a more
145 basinward depositional environment, the first occurrence of inertinite is within the lowest
146 Famennian strata. Inertinite abundance in the WV, IG, and WCB section is 0.2 to 0.4 %, 0.2 to 1 % and
147 0.2 to 1.2 %, respectively.

148 Solid bitumen reflectance (BR_o , %) and T_{max} data suggest that the samples record a

149 low thermal maturity ($\%BR_o \sim 0.6$, $T_{max} \sim 445$ °C; **Table S7 and S8**). Inertinite reflectance
150 (IR_o) values range from 1.74 – 3.16 % (**Table S3**). In hydrogen and oxygen index space
151 (pseudo Van Krevelen plot; **Fig. 4**), the majority of samples are characterized by Type II-III
152 kerogen.

153 **Results of Major and Trace Element Analyses**

154 Trace element abundances and ratios can be reliable proxies for paleo-redox environment (e.g.,
155 Mn, Mo, and $V/[V+Ni]$). The Mn values of all of the samples range from 210 to 630 ppm with a mean
156 value of 322 ppm. The majority of the samples have Mn values ranging from 200 to 400 ppm (**Fig. 5**).
157 The Mo/Al ratio ($2.53 - 34.09 \times 10^{-4}$) exceeds the average shale value (0.32×10^{-4} ; Wedepohl, 1971),
158 suggesting authigenic enrichment. Average V/Al ratio (14.41×10^{-4}) and Ni/Al (7.78×10^{-4}) ratios are
159 comparable to those of average shale (14.62×10^{-4} and 7.65×10^{-4} respectively; Wedepohl, 1971). Only
160 a few samples from the F–F interval of BMC and WV sections have Mn values between 400 – 630
161 ppm, indicating decreased anoxia for the F–F interval relative to the other intervals. The Mo abundance
162 values (4 to 42 ppm, average 18 ppm) represent a non-euxinic to euxinic depositional environment (**Fig.**
163 **5**; Scott and Lyons, 2012). The Mo values for the F–F interval were typically less than 15 ppm,
164 suggesting a non-euxinic environment. The $V/(V+Ni)$ values range from 0.50 to 0.74, indicating
165 dysoxic to anoxic conditions (**Fig. 5**; Hatch and Leventhal, 1992). The Mo abundance (4 to 42 ppm,
166 average 18 ppm) across the F–F section coupled to the $V/(V+Ni)$ values of 0.50 to 0.74 and intervals of
167 elevated Mn (400 – 630 ppm) are suggestive of decreased anoxia (**Fig. 5**; Hatch and Leventhal, 1992;
168 Scott and Lyons, 2012).

169 **Results of Re–Os Analysis**

170 The Re and Os (^{192}Os) abundances, and $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ isotopic
171 compositions, range from 0.9 to 32 ppb and 48 to 460 ppt (18 to 145 ppt), and 97.46 to 658
172 and 0.80 to 4.85, respectively, across all the sections (Table S4). Stratigraphically, no

173 relationships are observed between trace metal redox proxies, Re and Os abundances, $^{187}\text{Re}/^{188}\text{Os}$ and
174 initial $^{187}\text{Os}/^{188}\text{Os}$ ratios, and TOC values (Fig. 5). Further, there is no apparent correlation
175 between Re and Os abundances and TOC values (Fig. 6). Initial $^{187}\text{Os}/^{188}\text{Os}$ (Os_i)
176 compositions (calculated at 371.93 Ma; Percival *et al.*, 2018) are broadly the same across the
177 F–F boundary (Fig. 7).

178 Samples with similar TOC possess significant variation in their Re and Os
179 abundances (up to 30 times for Re and 6 times for Os). At the F–F boundary, the $^{192}\text{Os}/\text{TOC}$
180 ratios for each section are generally identical, but the Re/TOC ratios vary greatly. Overall, no
181 linear relationship exists for Re/TOC and $^{192}\text{Os}/\text{TOC}$. The West Valley 777 unit (F–F
182 boundary) exhibits very limited range in its $^{187}\text{Re}/^{188}\text{Os}$ compositions (Re/Os fractionation,
183 ~20), whereas the other three units above and below the F–F boundary in the West Valley
184 section and other F–F sections exhibit a relatively large range in $^{187}\text{Re}/^{188}\text{Os}$ values (200–
185 400). In terms of organic matter composition, the 777 unit is dominated by solid bitumen
186 (~90 %) and has the most limited spread in the HI–OI index plot compared with the other
187 sections (Figs. 4 and 8). The other sections have more variable organic matter composition,
188 especially the JC section (the most proximal section), which shows the largest $^{187}\text{Re}/^{188}\text{Os}$
189 fractionation. Elevated Re and ^{192}Os abundances are present only in strata that are interpreted
190 as having accumulated in a highly reduced environment, based on the redox proxies of Mn
191 and V(V+Ni) (Fig. 5). However, samples that are interpreted as having accumulated in
192 reduced environments also have low Re and Os abundances (Fig. 5). The $^{187}\text{Re}/^{188}\text{Os}$ values
193 are variable across one redox environment, with the $^{187}\text{Re}/^{188}\text{Os}$ values and their variability
194 being lower with an increase in oxygen in the water column (Fig. 5). The OI values are
195 predominantly below 20 and show no specific relationship with $^{187}\text{Re}/^{188}\text{Os}$ within or across
196 the studied locations (Fig. 8). There is no correlation between Re and ^{192}Os abundances and
197 Mo concentration (Fig. 5). The overall $^{187}\text{Re}/^{188}\text{Os}$ values show no clear correlation with the

198 clastic input proxies (Si/Al and Ti/Al). Individually, each F–F section shows a negative
199 correlation between $^{187}\text{Re}/^{188}\text{Os}$ values and the clastic input proxies. The samples with more
200 clastic input correlate with lower $^{187}\text{Re}/^{188}\text{Os}$ values in that section (Fig. 9).

201 **DISCUSSION**

202 **Wildfire and Fire Type**

203 Inertinite as a record of wildfire events can provide vital estimates for the level of atmospheric
204 oxygen and thus implications for the evolution of Earth systems (Glasspool and Scott, 2010; Scott and
205 Glasspool, 2006). Although inertinite may originate from processes (e.g., organic matter
206 degradation by bacterial and fungal activity) other than a wildfire (Hunt and Smyth, 1989;
207 Moore et al., 1996; Taylor et al., 1989), it is unlikely that these processes are the sole cause of all
208 the inertinite observed in this study (Scott and Glasspool, 2007; Glasspool and Scott, 2010 and
209 references therein). The stratigraphic occurrence and relative enrichment of inertinite within each
210 section could be controlled by the proximity of the depositional site to a terrigenous source. Inertinite
211 abundances have been shown to increase with increased proximity to the paleoshoreline, probably due
212 to increased water-borne inertinite contribution (Herring, 1985). A fall in sea level would move the
213 paleoshoreline closer to the sample sites and increase the terrestrial input. The proximal sections of this
214 study have increased inertinite abundance relative to the distal sections. As such, this may be caused by
215 increased detrital input and/or wind-borne origin of inertinite. However, no obvious relationship is
216 observed between inertinite abundance and clastic input proxies (e.g., Ti/Al, Si/Al; Fig. 2). Regional
217 climate also can have an important effect on the wildfire events and thus the inertinite record. Paleomap
218 reconstruction suggests that the source area was located at southern mid-latitudes (Fig. 1), which may
219 have been associated with a subtropical climate. Given the limited stratigraphic interval during which
220 inertinite abundance increase is observed, plate tectonic motion to latitudes associated with a dryer
221 climate is unlikely. Further, the F-F interval records a period of climate cooling of $\sim 6^\circ\text{C}$ (Huang et al.,

222 2018). Studies of wildfire events since the Last Glaciation Maximum suggest that a cooler climate
223 would lead to less frequent fire events with less charcoal preservation in the geological record (Power et
224 al., 2008; Daniau, 2010). Thus, the climate cooling at the F-F boundary would likely result in a
225 reduction of inertinite abundance rather than an increase. However, the expansion of land plants
226 throughout the Devonian, specifically trees during the Late Devonian as a result of the development of
227 root systems, resulted in a diverse forest community (Scheckler, 2001; Stein et al., 2012). As such, by
228 the Late Devonian, the dominance of tree *Archaeopteris*, herbaceous ferns (Rhacophyton) and tree
229 lycopsids (Scheckler, 1986) led to the appearance and increased abundance of inertinite potentially as a
230 result of plants expanding to drier environments that would allow wildfire events to occur. The inertinite
231 abundance therefore is interpreted to suggest increased frequency of wildfire events surrounding the
232 paleosource region of the studied sites during the Frasnian–Famennian interval (Glasspool and Scott,
233 2010).

234 Wildfires can be divided into the following three groups: 1) ground fire 2) surface fire; and 3)
235 crown fire; with different burning material and different burning temperatures. Inertinite reflectance is
236 related to the burning temperature as shown by experimental analysis (Scott, 2000; Scott and Glasspool,
237 2005; Scott and Glasspool, 2007). Based on experimental data, the inertinite reflectance values reported
238 here (1.74 – 3.16 %) correlate to burning temperatures between 400 – 500 °C (Scott and Glasspool,
239 2007). Although it is known that the temperature provided by reflectance data on wildfire
240 charcoals is a minimum fire temperature (McParland et al., 2009; Scott, 2010) and that the use
241 of such data to determine the nature of wildfires is still at an early stage (Belcher and Hudspith,
242 2016; Belcher et al., 2018; Roos and Scott, 2018), the temperature range of 400 – 500 °C is indicative
243 of a surface fire, suggesting that the fuel type across the F–F boundary interval would have mainly been
244 herbaceous and shrubby plants, which is consistent with paleo-botanical observations during the Late
245 Devonian (Cressler, 2001; Hudspith et al., 2014; Scheckler, 1986).

246 **Implications for the Rise in Atmospheric O₂ Levels during the early Late Devonian**

247 A wildfire event depends on the combination of fuel and O₂ and the heat source. Throughout geological
248 time, lightning is considered to be the most common source of heat for ignition (Scott and Glasspool,
249 2006). However, the correlation of mercury data (mercury abundance and mercury/TOC ratios) with
250 inertinite abundance within the F–F interval may suggest that volcanism could have acted as a source of
251 ignition (Racki et al., 2018). The expansion of terrestrial vegetation to develop forests in the Middle
252 Devonian gave rise to a potential ready supply of fuel that could be ignited (Kenrick and Crane, 1997;
253 Stein et al., 2012). However, the hitherto absence of evidence of a fossilized charcoal record, specifically
254 during the Late Frasnian to Early Famennian, has resulted in the prediction of low levels of atmospheric
255 O₂ (17 %) during this time interval (Berner et al., 2003; Rimmer et al., 2015; Scott and Glasspool, 2006).
256 In contrast, the presence of abundant inertinite (average 11.9 %, volume percentage on a mineral-free
257 basis; this study), provides evidence for wildfires and may suggest higher atmospheric O₂ levels during
258 the Latest Frasnian. The presence of inertinite is proposed to indicate that the atmospheric O₂ level had
259 at least reached the fire window of 15 % (Belcher and McElwain, 2008).

260 To date, an equation is only available to estimate the pO_2 level based on the inertinite abundance
261 data of coal/peat (Glasspool and Scott, 2010). This approach utilized maceral data for coals and
262 modern-day peats, and used inertinite abundance data to estimate paleo atmospheric O₂ levels.
263 Here we use inertinite data for Devonian marine shales but apply the same equation. Firstly,
264 there would be a difference between the amount of inertinite preserved in-situ in a mire/peat
265 swamp versus the amount of inertinite that would be found in a marine shale. The inertinite
266 that makes it into the marine shales probably did not originate in a peat swamp but would
267 represent fire events across drier environments where charcoal could move into bodies of
268 water following fire events, either by water or wind transport as discussed above. Therefore,
269 it would not be representative of charcoal occurrences in coeval peats. The relative amounts
270 of organics from a terrestrial environment that can make it into a marine setting differ, and
271 therefore the inertinite abundance may be enhanced on a relative basis given that inertinite is

272 more recalcitrant than vitrinite (woody tissue) or liptinite (spores, pollen, algae) and thus has
273 an increased chance of surviving water or air transportation (Taylor et al., 1989). Further, this
274 terrestrial component would be diluted by marine organic matter, the amount being
275 dependent on paleoproductivity and preservation rates. The sedimentation rates vary from
276 different sections measured. Secondly, the relative amount of inertinite in the shales is a
277 volumetric estimate, thus additions or losses of other components will influence the reported
278 amount of inertinite. Solid bitumen is a secondary maceral that forms during hydrocarbon
279 generation. Therefore, the compositions reported may not reflect the initial kerogen
280 composition for the shale. Nevertheless, it is reasonable to assume that the inertinite
281 abundance is volumetrically close to the original, as the solid bitumen is replacing the
282 bituminite (Hackley and Cardott, 2016).

283 Given the above, we use the available equation as an approximation to estimate the Devonian
284 pO_2 , although there is different enrichment mechanism of inertinite between coal and shale samples (e.g.,
285 preservation, post depositional processes, Taylor et al., 1989). The average inertinite volume percentage
286 amount (12%) of this study estimates the pO_2 level for the F–F boundary interval to be 25 % (24–27 %,
287 see supplementary material). The lower value (24 %) is still considerably higher than the estimated pO_2
288 value of Early Devonian (~18 %), indicating a rapid rise of pO_2 level. The higher value (~27 %) is
289 comparable to those estimated for Early Carboniferous, suggesting the pO_2 might have reached ~27 %
290 much earlier than previously thought. As discussed above, inertinite in a marine environment could also
291 result from organic matter degradation by bacterial and fungal activity (Hunt and Smyth, 1989;
292 Moore et al., 1996; Taylor et al., 1989). However, such processes result in minimal addition to
293 the inertinite budget (Scott and Glasspool, 2007; Diessel, 2010). It is hard to estimate the
294 maximum amount of non-fire origin inertinite, but even if it is considered that only 50% of
295 the inertinite is a product of fossilized charcoal, the conservatively estimated O_2 level would still
296 be elevated (23 %). Although we emphasize that the inertinite data here used are from marine shale

297 samples and that different inertinite enrichment mechanisms exist between coal and shale deposition, we
298 consider that our data provide an approximation for the pO_2 level at the F–F. Even though this pO_2 level
299 might be an overestimate, because not every inertinite may represent fossilized charcoal (Hunt and
300 Smyth, 1989; Moore et al., 1996; Taylor et al., 1989), our estimated pO_2 value is in agreement with the
301 proposed higher estimated pO_2 value (Glasspool and Scott, 2010) (Fig. 10). The fact that our estimation
302 agrees with Glasspool and Scott (2010) highlights a potential wider application of this model to new
303 samples and localities. Interestingly, our estimation is also in agreement with the GEOCARBSULF
304 model (24 – 25 %; Schachat et al., 2018). Additional models yield lower pO_2 estimations (~17 % from
305 GEOCARBSULFOR and ~20 % from COPSE reload; Krause et al., 2018; Lenton et al., 2018).
306 Previously, models with lower pO_2 levels are preferred as a result of lacking an inertinite record for the
307 F-F interval - the ‘charcoal gap’ (Scott and Glasspool, 2006). Our finding of inertinite thus provides
308 evidence that supports higher pO_2 levels during this interval. Despite the different estimation of pO_2 , all
309 models seem to predict a dramatic rise in pO_2 for the Late Devonian, which correlates with increased
310 inertinite stratigraphically above the F–F boundary as reported from this study and previous work (Fig. 2;
311 Rimmer et al., 2015). As such the atmospheric O_2 level may have reached the present level (21 %) by
312 the Latest Frasnian - Early Famennian (Berner et al., 2003; Berner, 2009), rather than during the Early
313 Mississippian as predicted by previous models (Berner, 2006; Berner, 2009).

314 Additionally, during the F–F interval the atmospheric O_2 level may have been affected by
315 enhanced orogeny activity coupled with sea-level fall that caused increased continental weathering and
316 organic carbon burial (Averbuch et al., 2005; Berner et al., 2003; Bond and Wignall, 2008; Johnson et
317 al., 1985). A radiogenic shift of Os isotopes has been detected immediately before the F-F boundary,
318 indicating enhanced weathering of the continents (Percival et al., 2019). The enhanced weathering, in
319 turn, could have driven an increased nutrition flux to the oceans that would have boosted marine
320 productivity, and led to elevated carbon burial and pCO_2 drawdown (Berner et al., 2003; Huang et al.,
321 2018). All these factors together may have resulted in elevation of the atmospheric O_2 level (Berner et

322 al., 2003; Huang et al., 2018). Interestingly, the timing of higher O₂ levels within the F–F interval
323 correlates with the radiation of vascular plants and evolution of large animals with a higher O₂ demand
324 (Dahl et al., 2010).

325 **Implications for the Frasnian–Famennian Mass Extinction**

326 The F–F mass extinction has been proposed to have been triggered by an impact and
327 (or) volcanism (Claeys and Casier, 1994; Racki et al., 2018). Volcanism interpreted from Hg data
328 (Racki et al., 2018) and associated weathering of mafic material would have resulted in the
329 delivery of unradiogenic osmium to the ocean that would have caused an unradiogenic
330 excursion in the marine osmium isotope record (Peucker-Ehrenbrink and Ravizza, 2000).
331 However, Os-isotope data (Harris et al., 2013; Gordon et al., 2009; Percival et al., 2019; Turgeon et
332 al., 2007; this study) show no evidence of an unradiogenic osmium isotope excursion (Fig. 7).
333 A possible scenario is that the Hg was not injected into the atmosphere directly from volcanic
334 degassing, but derived from the thermal alteration of organic rich layers during magma
335 emplacement (Svensen et al., 2004). Further, as previously stated (Harris et al., 2013; Gordon et
336 al., 2009; Percival et al., 2019; Turgeon et al., 2007) our Os isotope records do not support an
337 impact scenario, as an impact body would also result in an unradiogenic Os excursion of the
338 marine osmium isotope record (Peucker-Ehrenbrink and Ravizza, 2000). Nevertheless, it is not
339 possible to rule out the scenario of a comet impactor with a very limited meteoritic dust
340 budget that left no elemental spike in the geological record (Jansa, 1993). To date, evidence
341 for a wildfire during the F–F interval is supported by organic geochemistry proxy data
342 [coronene, benzo(ghi)perylene and benzo(e)pyrene] from two sections in Belgium that
343 represent deposition in an epicontinental setting on the southern periphery of the Laurussian
344 continent (Fig.1, Kaiho et al., 2013). This wildfire scenario is questioned by possible
345 secondary processes (such as weathering, diagenetic and oxidative processes) causing the
346 maxima of the combustion proxies and the discrepancy between the lack of a charcoal record

347 and high combustion proxies (Marynowski and Racki, 2015). However, this argument has been
348 considered unlikely as samples with high and low values have the same lithology and are
349 both well preserved (Kaiho, 2015). Therefore, the inertinite data from the New York sections
350 (this study), and potentially the coronene, benzo(ghi)perylene and benzo(e)pyrene data from
351 Belgium (Kaiho et al., 2013) suggest a potential wildfire event across the F–F boundary
352 interval.

353 Wildfire has been proposed to destroy plant root systems and lead to enhanced
354 weathering, generate soot and aerosol, and affect the carbon cycle and climate, which then are
355 ultimately linked with major anoxia or extinction events (e.g. Baker et al., 2017; Archibald et
356 al., 2018). However, to determine the scale at which the proposed F–F wildfire burned and to
357 what extent it contributed to the F–F biotic crisis requires further research. Nonetheless, our
358 evidence of elevated O₂ level supports the hypothesis of enhanced mountain-building and
359 continent-weathering that, in turn, may have led to increased marine productivity and carbon
360 burial that resulted in the drawdown of *p*CO₂ (Averbuch et al., 2005; Berner et al., 2003,
361 Percival et al., 2019). In turn, the *p*CO₂ drawdown and associated climate cooling may have
362 caused the F–F biotic crisis (Averbuch et al., 2005; Berner et al., 2003; Huang et al., 2018).

363 **Further Insights to ¹⁸⁷Re/¹⁸⁸Os Fractionation in Organic-rich Sedimentary Rocks**

364 In addition to the evaluation and implications of O₂ levels throughout the F–F
365 interval, the organic petrology and geochemistry, coupled with the major and trace element
366 abundances, provide further insight to the fractionation of Re and Os in organic-rich
367 sedimentary rocks. Our data suggest that Re and Os fractionation has no relationship with a
368 redox/euxinic environment (Figs. 5 and 6) and thus excludes deposition under reduced oxygen
369 conditions as the principal controlling factor of Re and Os fractionation (Selby et al., 2009;
370 Harris et al., 2013). The correlation of ¹⁸⁷Re/¹⁸⁸Os ratios with the terrestrial input proxies

371 (Si/Al and Ti/Al) in each section suggests that a more variable depositional environment is
372 likely to yield more variable Re and Os fractionation (Fig. 9). Samples with homogeneous
373 organic matter composition have relatively limited Re and Os fractionation (Figs. 4 and 9). In
374 contrast, the other samples sets that have more variable organic matter composition have
375 larger Re and Os fractionations (Figs. 4 and 9). This suggest that the organic matter
376 composition/type and its variability may be the mechanism that controls Re and Os
377 fractionation. These findings concur with the findings that a variable depositional
378 environment together with heteorgenous organic matter composition may control Re and Os
379 fractionation (Cumming et al., 2012; Harris et al., 2013).

380 CONCLUSIONS

381 The presence of inertinite in Upper Devonian strata within the F–F boundary interval
382 suggests a wildfire event occurred in western New York at this time. The inertinite data also
383 suggest a possibly high atmospheric O₂ level (~ 23 %). Additionally, the Os isotope records
384 do not provide any evidence of an extraterrestrial impact event or volcanic activity as a
385 trigger for the F–F mass extinction. However, the extent of the wildfire event and its possible
386 link with the F–F mass extinction requires further research. Our estimated high O₂ level
387 supports the hypothesis that *p*CO₂ drawdown and associated climate cooling may have played
388 an important role in the F–F biotic crisis.

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631 236.

632 FIGURE CAPTIONS

633 Figure 1. Inset map showing present day sample locations – 1: Walnut Creek Bank, 2: Irish
634 Gulf, 3: West Valley, 4: Beaver Meadow Creek, 5: Joint Creek. Paleogeography map after
635 Joachimski et al. (2009) showing location of the Appalachian Basin in North America, and
636 the Belgium Frasnian–Famennian (F–F) sections where organic geochemistry is used to infer
637 a wildfire event at F–F boundary (black square; Kaiho et al., 2013).

638 Figure 2. Inertinite abundance (black circles) and clastic input proxies (Si/Al, open square; Ti/Al, open
639 diamonds). Inertinite abundance is calculated as volume percent of whole rock basis. H: Hanover
640 Formation, D: Dunkirk Formation; Stratigraphic sections are presented in order of proximity to the
641 paleoshoreline = JC: Joint Creek, BMC: Beaver Meadow Creek, WCB: Walnut Creek Bank, IG: Irish
642 Gulf, WV: West Valley; from proximal to distal: JC, BMC, WV, IG, WCB. Gray bars in the Joint
643 Creek section represent samples that contain inertinite, but the inertinite abundance is too low to be
644 counted. The upper top axes are for inertinite abundance. The lower top axes are for Si/Al. The
645 bottom axes are for Ti/Al.

646 Figure 3. Microscopic petrography of macerals through oil immersion. All images, except B
647 and D, are under white light. Images B and D are under blue light. T: telalginite, S: Solid
648 Bitumen, I: Inertinite.

649 Figure 4. Pseudo-Van Krevelen plot (hydrogen index vs. oxygen index) showing kerogen
650 types. Note that for the majority of the samples, the dominant organic matter is solid bitumen,
651 which is a secondary product (not a kerogen) residual from thermal conversion of oil-prone
652 sedimentary organic matter.

653 Figure 5. Stratigraphical plots of TOC, Re, ^{192}Os , $^{187}\text{Re}/^{188}\text{Os}$, Mo, Mn, and V/(V+Ni). Red
654 line indicates the F–F boundary. No relationships are observed between trace metal redox proxies,
655 Re and ^{192}Os abundances, $^{187}\text{Re}/^{188}\text{Os}$, and TOC values.

656 Figure 6. Plots of Re, ^{192}Os and $^{187}\text{Re}/^{188}\text{Os}$ versus Mn, Mo, and V/(V+Ni) for the JC: Joint
657 Creek, BMC: Beaver Meadow Creek, WCB: Walnut Creek Bank, IG: Irish Gulf, and WV: West
658 Valley sections.

659 Figure 7. Initial $^{187}\text{Os}/^{188}\text{Os}$ isotope stratigraphy for the Frasnian–Famennian interval in New
660 York. Sections are presented in order of proximity to the paleoshoreline = JC: Joint Creek, BMC:
661 Beaver Meadow Creek, WCB: Walnut Creek Bank, IG: Irish Gulf, WV: West Valley; from proximal to

662 distal: JC, BMC, WV, IG, WCB. Biostratigraphy constraints are from Klapper et al. (1993) and
663 Over (1997, 2002). Initial $^{187}\text{Os}/^{188}\text{Os}$ isotope values calculated at 371.93 Ma (Percival et al.,
664 2018). Uncertainties of the initial $^{187}\text{Os}/^{188}\text{Os}$ isotope values were determined by error
665 propagation of uncertainties in Re and Os mass spectrometer measurements, blank
666 abundances and isotopic compositions, spike calibrations and reproducibility of standard Re
667 and Os isotopic values. Typically, the range of uncertainty (2σ) of the initial $^{187}\text{Os}/^{188}\text{Os}$ is
668 smaller than the symbol size.

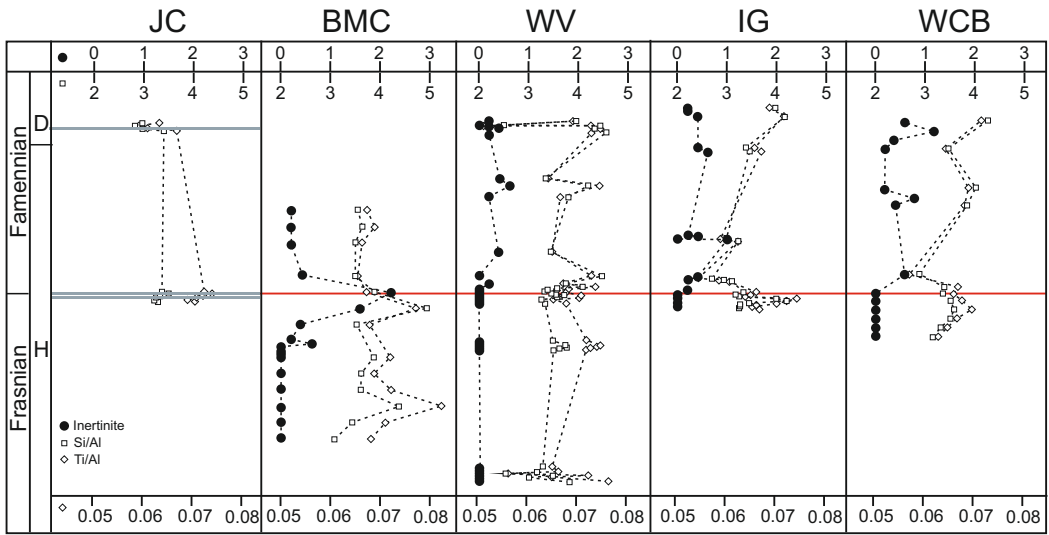
669 Figure 8. Plots of total organic carbon (TOC) versus Re (A) and ^{192}Os (B), and plots of
670 oxygen index (OI) versus Re (C), ^{192}Os (D), and $^{187}\text{Re}/^{188}\text{Os}$ (E) for the JC: Joint Creek, BMC:
671 Beaver Meadow Creek, WCB: Walnut Creek Bank, IG: Irish Gulf, and WV: West Valley sections.

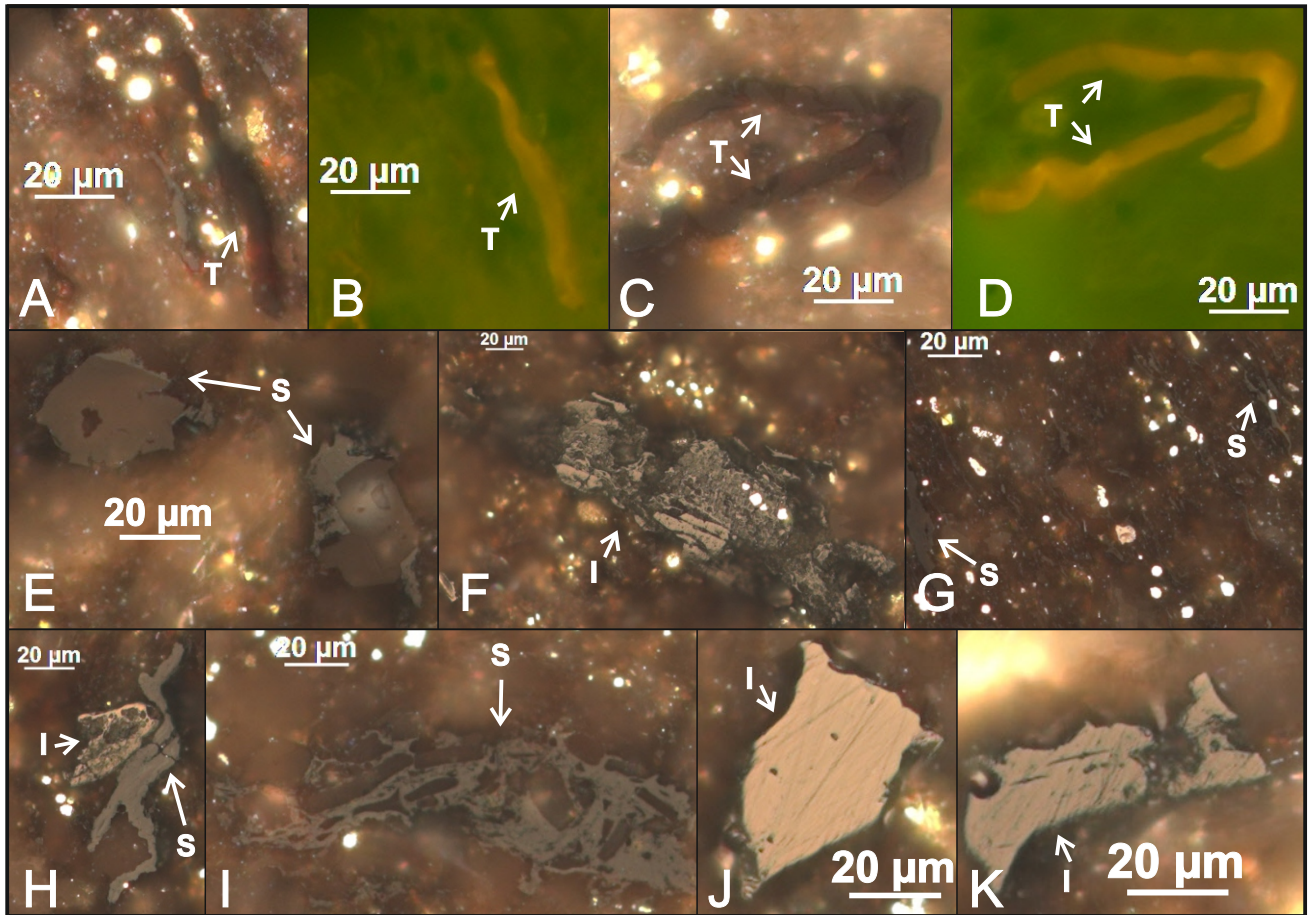
672 Figure 9. Summary of results from organic matter (OM) analysis, Re/TOC ratios, and clastic
673 input proxies (Ti/Al and Si/Al). OM color represents organic matter types. Green: telalginite,
674 black: Solid bitumen, gray: Inertinite. Red bar represents the Frasnian–Famennian boundary.
675 Lines represent the broad trend of the data points.

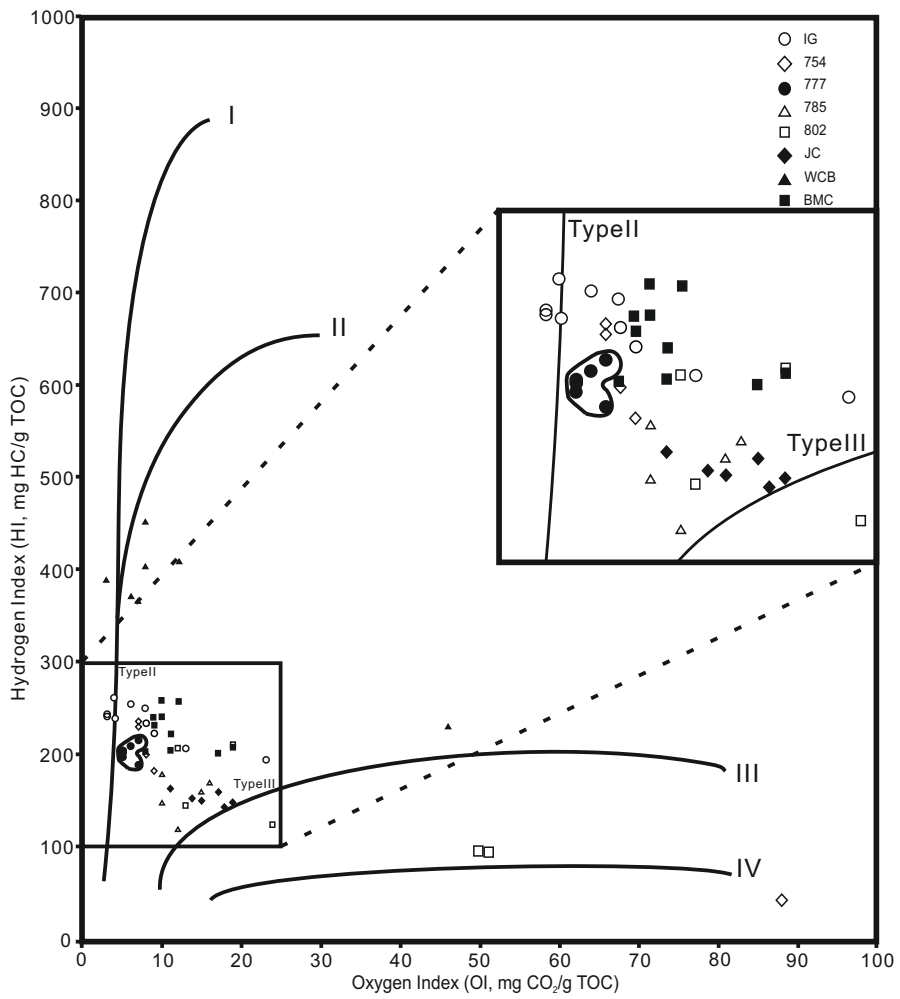
676 Figure 10. Modelled $p\text{O}_2$ level from inertinite abundance modified after Glasspool and Scott (2010). See
677 text for discussion. Line; best estimate on the basis of late Palaeozoic $p\text{O}_2$ maxima of 30%. Ranges of
678 uncertainty (“error bars”) are 1 standard deviation (s.d.) from mean. Shaded area; estimate of maximum
679 uncertainty (“error”) assuming Phanerozoic $p\text{O}_2$ maxima of 35 % + 1 s.d. (upper margin) and 25 % - 1
680 s.d. (lower margin).

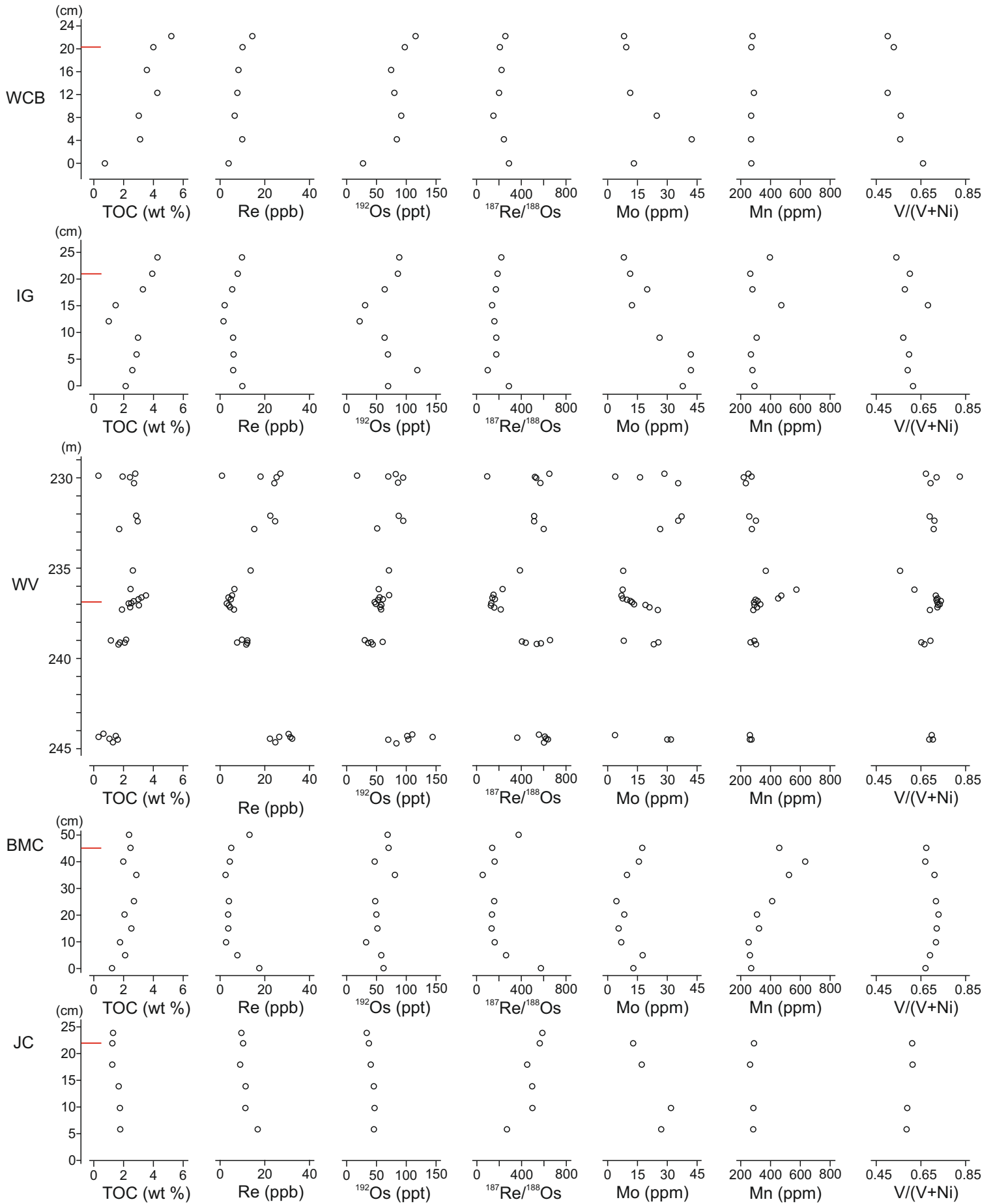
681 ¹GSA Data Repository item 201Xxxx, [\[\[one supplementary text and one data set\]\]](#), is
682 available online at www.geosociety.org/pubs/ft20XX.htm, or on request from
683 editing@geosociety.org.

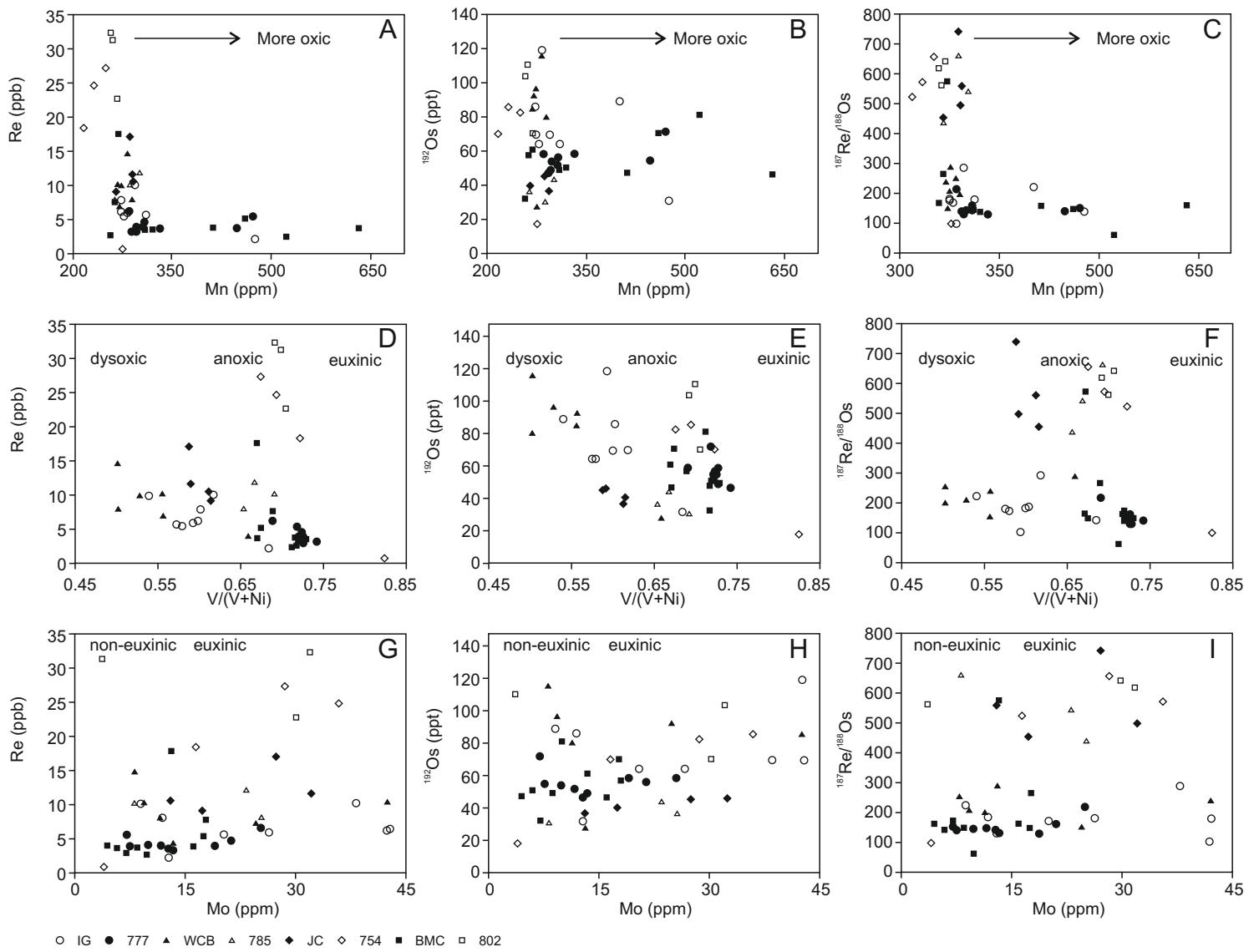




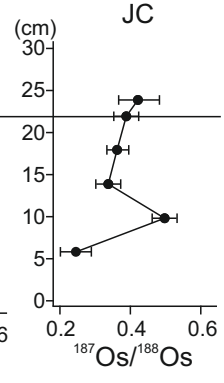
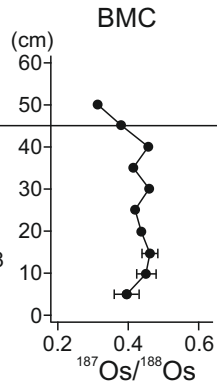
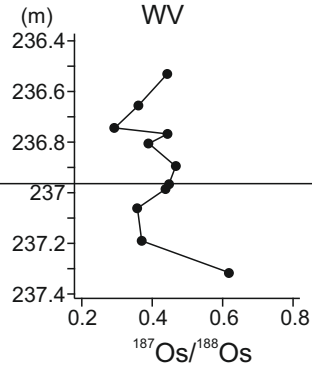
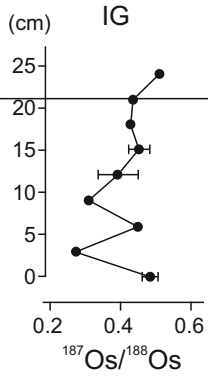
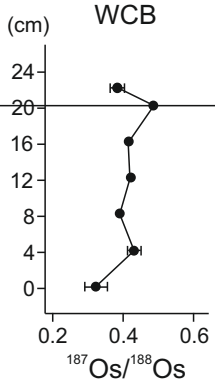


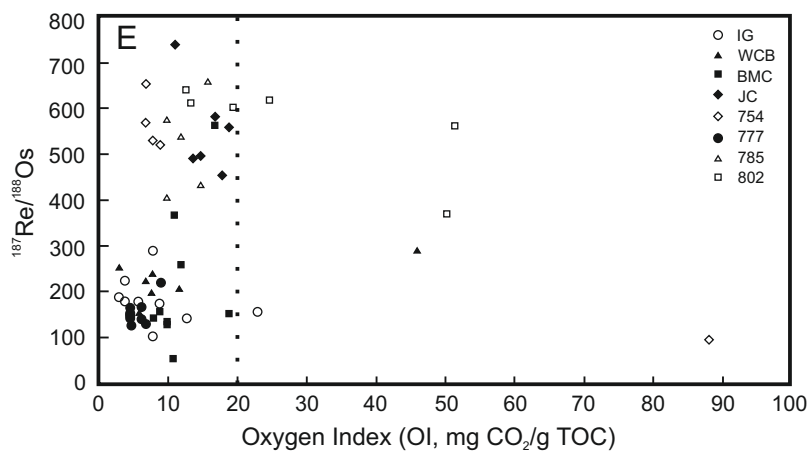
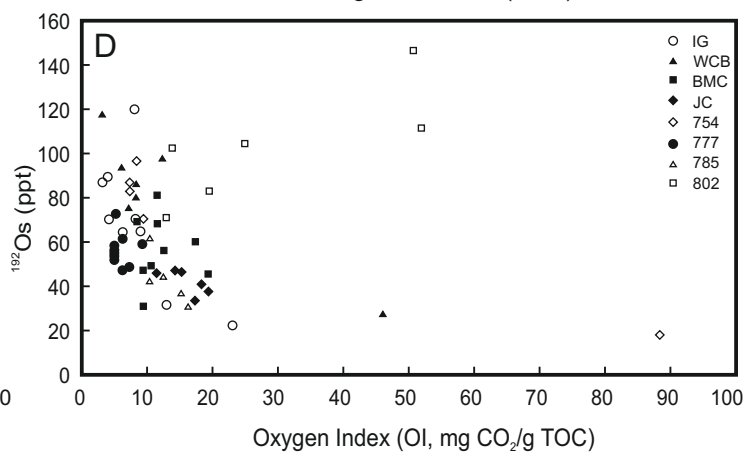
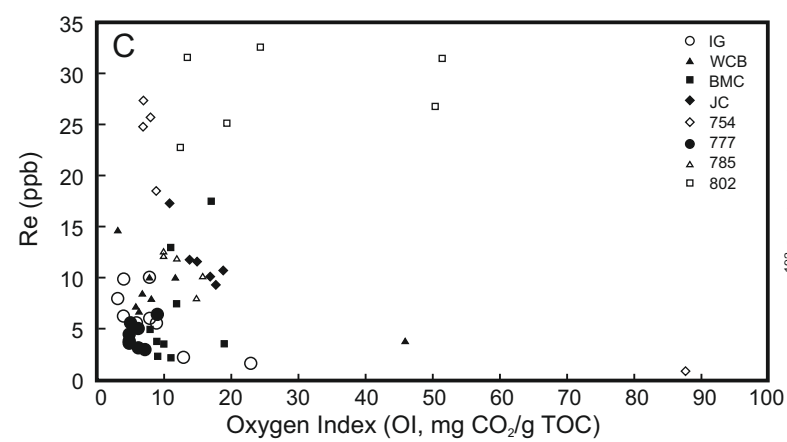
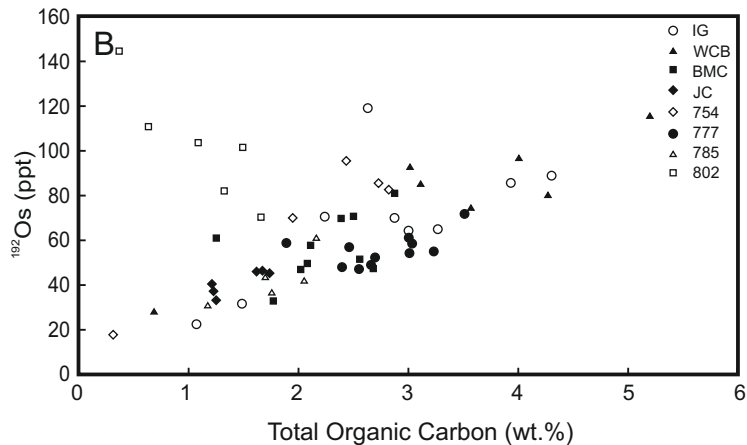
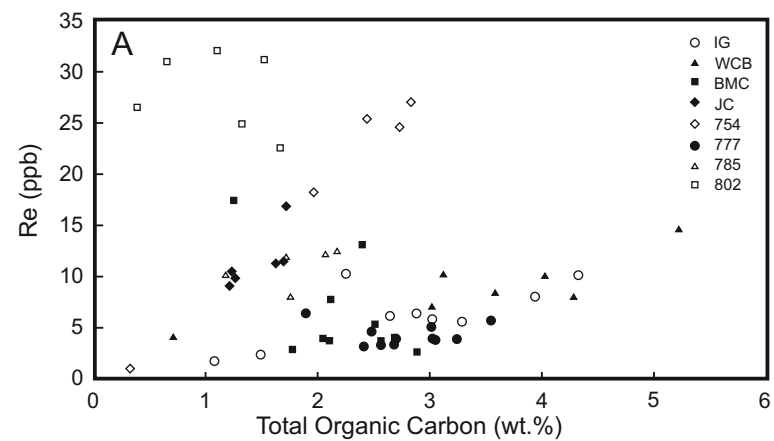


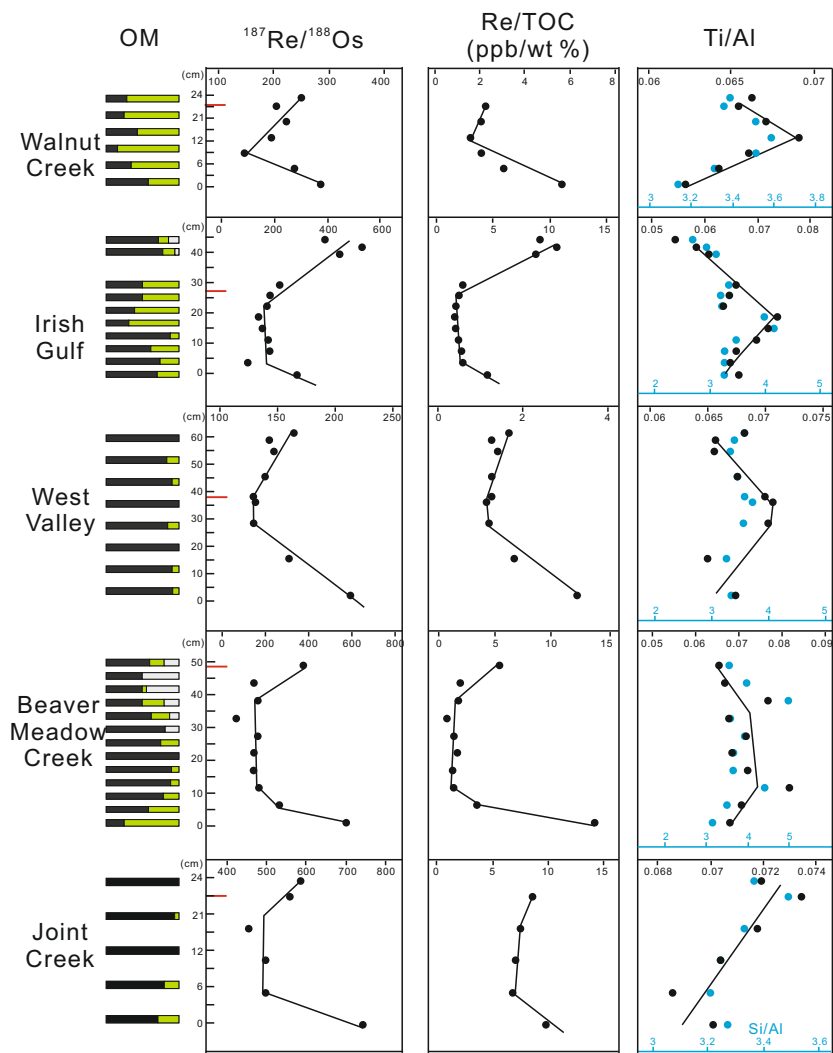




Frasnian	Famennian
<i>linguiformis</i> biozone	<i>triangularis</i> biozone







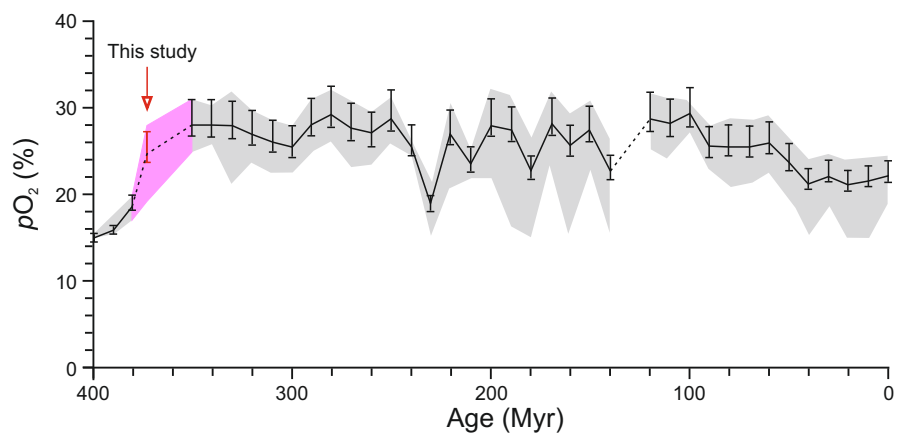


Table S1. Organic petrology data.

Sample ID	Depth (cm)	Mineral	Solid Bitumen	Tasmanites	Inertinites
B1-03	70	486	11	2	1
B1-02	65	487	11	1	1
B1-01	60	488	10	1	1
BMC_1_02	50	490	6	2	2
BMC_5	45	478	11	0	11
BMC_10	40	482	9	1	8
BMC_15	35	490	5	3	2
BMC_20	30	492	5	2	1
BMC_21	29	484	13	0	3
BMC_22	28	492	6	2	0
BMC_23	27	493	6	1	0
BMC_24	26	490	10	0	0
BMC_25	25	492	8	0	0
BMC_30	20	490	9	1	0
BMC_35	15	491	8	1	0
BMC_40	10	486	11	3	0
BMC_45	5	488	7	5	0
BMC_51	0	496	1	3	0
754	22982	490	5	4	1
754_4	22992	498	1	1	0
754_6	22997	486	8	5	1
754_8	23002	485	13	0	2
755_8	23033	486	11	2	1
761_6	23214	475	20	3	2
762_6	23241	482	8	7	3
764	23287	490	6	3	1
771_6	23515	493	5	0	2
774_10.5	23618	494	6	0	0
776	23652	464	35	0	1
776_9.5	23677	487	13	0	0
776_11	23680	488	10	2	0
777_2.5	23689	489	10	1	0
777_5.3	23696	487	13	0	0
777_6	23698	487	11	2	0
777_9	23706	270	8	0	0
778_2	23719	479	19	2	0
778_7	23731	488	11	1	0
784_1.5	23900	458	0	42	0
784_5.5	23910	483	17	0	0
784_6.5	23913	403	2	1	0
784_8	23917	495	0	5	0
784_10	23922	491	9	0	0
801_3	24422	488	0	12	0
801_7	24432	336	5	11	0

801_9	24437	422	5	2	0
802	24445	425	2	16	0
802_1.5	24449	487	1	12	0
802_9	24468	493	2	5	0
ZL-16-01	313	478	13	8	1
ZL-15-03	308	478	15	6	1
ZL_15_01	300	472	14	12	2
ZL_13_01	250	468	15	15	2
ZL_12-01	245	464	26	7	3
ZL_06_06	110.25	469	18	12	1
ZL_06_04	107.75	456	24	18	2
ZL_06_03	106.5	453	35	12	0
ZL_06_02	105.25	463	14	18	5
ZL-01-03	45	486	10	2	2
ZL-01-02	43	485	14	3	1
ZLV_01	24	485	14	3	1
ZLV_02	21	314	4	4	0
ZLV_04	15	314	4	4	0
ZLV_07	6	472	11	17	0
ZLV_09	0	484	5	11	0
WCB_B3_02	96	474	8	15	3
WCB_B3_04	92	472	7	15	6
WCB_B3_06	88	474	4	20	2
WCB_B3_08	84	466	15	18	1
WCB_B2_01	66	469	11	19	1
WCB_B2_07	62	459	10	27	4
WCB_B2_09	59	472	9	17	2
WCB_B1_02	28	461	23	13	3
WCB_FF_02	20	460	11	29	0
WCB_FF_04	16	470	7	23	0
WCB_FF_06	12	461	8	31	0
WCB_FF_08	8	479	7	14	0
WCB_FF_10	4	471	4	25	0
WCB_FF_12	0	468	14	18	0
JPC_D8	360	494	3	3	0
JPC_D6	355	492	4	4	0
JPC_D3	350	489	8	3	0
JPC_D1	345	494	4	2	0
JPC_FF_02	22	493	5	2	0
JPC_FF_04	18	495	4	1	0
JPC_FF_06	14	489	11	0	0
JPC_FF_08	10	482	17	1	0
JPC_FF_10	6	493	7	0	0

Inertinite abundance data is calculated as volume percent on a whole rock bas

Table S2. Inertinite abundance data calculated as volume per

Sample ID	Mineral	Solid Bitumen	Tasmanites	Inertinite
B1-03	486	11	2	1
B1-02	487	11	1	1
B1-01	488	10	1	1
BMC_1_02	490	6	2	2
BMC_5	478	11	0	11
BMC_10	482	9	1	8
BMC_15	490	5	3	2
BMC_20	492	5	2	1
BMC_21	484	13	0	3
754	490	5	4	1
754_6	486	8	5	1
754_8	485	13	0	2
755_8	486	11	2	1
761_6	475	20	3	2
762_6	482	8	7	3
764	490	6	3	1
771_6	493	5	0	2
776	464	35	0	1
ZL-16-01	478	13	8	1
ZL-15-03	478	15	6	1
ZL_15_01	472	14	12	2
ZL_13_01	468	15	15	2
ZL_12-01	464	26	7	3
ZL_06_06	469	18	12	1
ZL_06_04	456	24	18	2
ZL_06_02	463	14	18	5
ZL-01-03	486	10	2	2
ZL-01-01	485	14	3	1
ZLV_01	485	14	3	1
WCB_B3_02	474	8	15	3
WCB_B3_04	472	7	15	6
WCB_B3_06	474	4	20	2
WCB_B3_08	465	15	18	1
WCB_B2_01	469	11	19	1
WCB_B2_07	459	10	27	4
WCB_B2_09	472	9	17	2
WCB_B1_02	461	23	13	3

average
s.d.

value used for pO_2 %

	calculation	pO_2 %	formular
average	11.90	24.8	(1)
average	11.90	27.1	(2)

average	11.90	23.8	(3)
average-s.d.	1.52	19.4	(4)
average+s.d.	22.34	28.0	(5)

percent on mineral-free basis.

**Inertinite abundance-
mineral free (%)**

7.1
7.7
8.3
20.0
50.0
44.4
20.0
12.5
18.8
10.0
7.1
13.3
7.1
8.0
16.7
10.0
28.6
2.8
4.5
4.5
7.1
6.3
8.3
3.2
4.5
13.5
14.3
5.6
5.6
11.5
21.4
7.7
2.9
3.2
9.8
7.1
7.7

11.9
10.4

shaded area
shaded area

Table S3. Inertinite reflectance data.

Sample ID	Inertinite reflectance (%)	No. of measurements	s.d.
B1-03	1.98	101	0.93
B1-02	1.94	32	0.63
B1-01	1.74	100	0.93
BMC_1_02	1.91	100	0.63
BMC_5	3.17	100	1.35
BMC_10	2.64	100	1.1
BMC_15	2.05	100	1.04
BMC_20	1.86	100	0.99
BMC_21	2.08	100	1.27
754_6	2.85	104	0.9
754_8	2.78	100	0.78
755_8	2.25	100	0.71
761_6	2.89	100	1
762_6	3.16	100	1.11
764	2.83	100	1.27
771_6	2.26	100	0.86
ZL-16-01	2.07	101	0.88
ZL-15-03	2.14	100	0.68
ZL_15_01	2.36	100	0.71
ZL_13_01	2.93	100	1.06
ZL_12-01	2.31	100	0.85
ZL_06_02	2.95	100	0.87
WCB_B3_02	2.69	100	1.09
WCB_B3_04	2.72	100	0.82
WCB_B3_06	2.19	100	1.09
WCB_B3_08	2.55	100	0.88
WCB_B2_01	2.54	100	1.09
WCB_B2_07	2.11	100	0.92
WCB_B2_09	2.90	100	1.27
WCB_B1_02	2.42	100	0.77

Table S4. Re–Os abundance and isotope data.

Sample ID	Re (ppb)	±	Os (ppt)	±	¹⁹² Os (ppt)	±	¹⁸⁷ Re/ ¹⁸⁸ Os	±
WCB-FF-01	14.57	0.04	345.93	1.94	115.36	0.57	251.34	1.38
WCB-FF-02	9.95	0.06	283.33	1.41	96.36	0.41	205.36	1.55
WCB_FF_04	8.32	0.02	219.24	1.11	74.25	0.31	222.83	1.10
WCB_FF_06	7.90	0.03	232.14	1.16	80.00	0.35	196.40	1.08
WCB_FF_08	6.95	0.02	258.94	1.22	92.47	0.42	149.51	0.80
WCB_FF_10	10.10	0.03	253.18	1.32	84.84	0.37	236.75	1.19
WCB-FF-12	3.97	0.02	84.01	0.55	27.56	0.17	286.58	2.11
BMC_1_02	13.16	0.03	223.71	1.22	69.43	0.27	377.08	1.75
BMC_5	5.23	0.01	197.32	1.10	70.70	0.43	147.05	0.97
BMC_10	3.82	0.01	133.33	0.77	46.87	0.29	162.09	1.09
BMC_15	2.55	0.01	214.31	1.02	81.30	0.49	62.40	0.41
BMC_25	3.88	0.01	136.11	0.79	47.85	0.29	161.30	1.07
BMC_30	3.64	0.01	139.15	0.81	49.68	0.32	145.86	1.02
BMC_35	3.59	0.01	142.35	0.80	50.92	0.31	140.36	0.93
BMC_40	2.77	0.01	93.25	0.55	32.61	0.20	169.07	1.13
BMC_45	7.69	0.02	175.21	1.13	57.51	0.35	265.88	1.75
BMC_51	17.59	0.04	221.66	1.33	61.01	0.23	573.67	2.58
JPC_FF_01	9.98	0.02	124.39	0.99	33.92	0.21	585.35	3.93
JPC_FF_02	10.59	0.03	135.55	0.87	37.59	0.16	560.15	2.82
JPC_FF_04	9.25	0.02	137.11	0.84	40.42	0.17	455.17	2.28
JPC_FF_06	11.53	0.03	159.81	0.99	46.09	0.20	497.82	2.49
JPC_FF_08	11.72	0.03	165.02	1.01	46.94	0.19	496.54	2.51
JPC_FF_10	17.16	0.04	180.39	1.15	46.08	0.18	740.68	3.41
776.00	5.47	0.01	202.30	1.05	71.76	0.37	151.52	0.87
776_5	3.86	0.01	152.03	1.04	54.87	0.48	139.99	1.27
776_8.5	5.09	0.01	171.26	1.09	61.20	0.46	165.38	1.31
776_9.5	3.92	0.01	152.08	0.90	54.25	0.36	143.63	1.02
776_11	3.86	0.01	145.36	0.86	52.03	0.35	147.53	1.06
777_2.5	3.30	0.01	131.82	0.92	47.04	0.41	139.39	1.27
777_5.3	3.10	0.01	132.57	0.91	47.76	0.42	129.09	1.18
777_6	3.23	0.01	136.38	0.93	49.10	0.43	131.07	1.19
777_9	3.81	0.01	160.69	1.08	58.45	0.51	129.67	1.17
778_2	4.55	0.01	158.88	0.95	56.48	0.38	160.24	1.14
778_7	6.32	0.02	175.69	0.97	58.57	0.28	214.64	1.15
ZLV_01	9.96	0.02	265.64	1.36	89.10	0.38	222.43	1.09
ZLV_02	7.95	0.02	247.83	1.25	86.00	0.40	183.92	0.96
ZLV_03	5.56	0.01	184.27	1.02	64.53	0.36	171.53	1.05
ZLV_04	2.25	0.01	89.05	0.71	31.76	0.34	141.22	1.56
ZLV_05	1.71	0.00	61.33	0.76	21.80	0.44	156.10	3.21
ZLV_06	5.79	0.01	182.11	1.04	64.31	0.39	179.15	1.17
ZLV_07	6.30	0.02	200.60	1.07	69.65	0.35	179.95	1.02
ZLV_08	6.04	0.01	317.75	1.50	119.12	0.67	100.95	0.62
ZLV_09	10.11	0.02	216.87	1.18	69.95	0.30	287.53	1.41
754.00	27.16	0.07	312.74	1.95	82.56	0.32	654.41	2.96
754_4	0.87	0.00	48.54	0.71	17.84	0.48	97.46	2.66

754_6	18.37	0.04	250.37	1.60	70.12	0.31	521.07	2.61
754_8	25.52	0.06	345.66	2.34	95.38	0.45	532.30	2.81
755_8	24.61	0.06	309.52	1.88	85.82	0.34	570.55	2.64
761_6	22.63	0.06	307.89	1.76	87.43	0.31	514.99	2.23
762_6	24.74	0.06	332.76	1.89	95.26	0.34	516.64	2.24
764.00	15.61	0.04	190.26	1.19	51.37	0.20	604.46	2.81
771_6	13.84	0.03	233.03	1.32	71.07	0.28	387.27	1.81
774_10.5	6.43	0.02	164.82	0.96	54.85	0.29	233.27	1.34
784_1.5	10.08	0.02	115.92	1.52	30.49	0.42	658.01	9.24
784_5.5	12.49	0.03	199.73	1.96	60.94	0.64	407.86	4.43
784_6.5	7.97	0.02	126.69	1.55	36.40	0.50	435.69	6.12
784_8	12.11	0.03	152.31	1.65	41.75	0.44	577.17	6.28
784_10	11.83	0.03	156.47	1.67	43.56	0.46	540.43	5.88
801_3	31.14	0.08	394.47	3.74	110.60	0.96	560.20	5.06
801_7	31.37	0.08	375.73	3.65	101.90	0.89	612.41	5.53
801_9	26.64	0.06	459.79	3.89	144.51	1.26	366.72	3.32
802.00	32.21	0.08	384.99	2.29	103.89	0.37	616.85	2.70
802_1.5	22.63	0.09	262.63	1.59	70.34	0.26	640.07	3.41
802_9	24.90	0.06	303.64	3.31	82.55	0.87	600.19	6.52
ZL-01-04	10.56	0.03	175.16	1.13	53.05	0.27	396.21	2.24
ZL-01-03	25.81	0.06	340.74	1.96	95.24	0.34	539.13	2.32
ZL-01-02	22.38	0.05	336.27	1.84	99.29	0.35	448.42	1.94

^aOnly the samples close to the F-F interval were calculated for Os_i.
Initial Os isotope composition (Osi) is calculated at 371.93 Ma (Percival et al., 2018). All unce
the associated error correlation (Ludwig, 1980).

$^{187}\text{Os}/^{188}\text{Os}$	\pm	rho	Os_i^a	\pm
1.95	###	0.63	0.39	0.02
1.77	###	0.39	0.49	0.02
1.81	###	0.60	0.42	0.02
1.64	###	0.57	0.42	0.02
1.32	###	0.59	0.39	0.01
1.91	###	0.61	0.43	0.02
2.11	###	0.60	0.33	0.03
2.66	###	0.60	0.31	0.03
1.29	###	0.65	0.38	0.02
1.46	###	0.65	0.46	0.02
0.80	###	0.65	0.42	0.01
1.46	###	0.65	0.46	0.02
1.33	###	0.65	0.42	0.02
1.31	###	0.65	0.44	0.02
1.51	###	0.66	0.46	0.02
2.10	###	0.65	0.45	0.03
3.96	###	0.59	0.39	0.04
4.07	###	0.66	0.43	0.06
3.87	###	0.62	0.39	0.04
3.20	###	0.61	0.37	0.03
3.43	###	0.61	0.34	0.04
3.59	###	0.58	0.50	0.04
4.85	###	0.59	0.25	0.05
1.38	###	0.64	0.44	0.02
1.23	###	0.68	0.36	0.02
1.32	###	0.67	0.29	0.02
1.33	###	0.66	0.44	0.02
1.30	###	0.66	0.39	0.02
1.33	###	0.68	0.46	0.02
1.25	###	0.68	0.44	0.02
1.25	###	0.68	0.44	0.02
1.16	###	0.68	0.36	0.02
1.36	###	0.66	0.37	0.02
1.95	###	0.63	0.62	0.02
1.90	###	0.61	0.51	0.02
1.58	###	0.62	0.44	0.02
1.50	###	0.65	0.43	0.02
1.34	###	0.69	0.46	0.03
1.37	###	0.70	0.40	0.06
1.42	###	0.66	0.31	0.02
1.58	###	0.64	0.46	0.02
0.90	###	0.65	0.28	0.01
2.27	###	0.61	0.49	0.02
4.45	###	0.60		
1.07	###	0.70		

3.76	###	0.62
3.93	###	0.63
3.88	###	0.61
3.61	###	0.58
3.52	###	0.58
4.18	###	0.60
2.84	###	0.60
1.97	###	0.64
4.50	###	0.70
2.83	###	0.69
3.48	###	0.70
4.01	###	0.69
3.83	###	0.69
3.75	###	0.68
4.13	###	0.68
2.53	###	0.68
4.19	###	0.58
4.28	###	0.48
4.10	###	0.69
2.91	###	0.64
3.78	###	0.58
3.18	###	0.58

uncertainties are at 2σ level. Rho (ρ) is

Table S5. Major element data.

Sample ID	Al ₂ O ₃ %	SiO ₂ %	TiO ₂ %	Si %	Ti %	Al %	Si/Al
WCB B3-02	13.665	66.263	0.857	30.973	0.514	7.232	4.283
WCB B3-08	15.386	60.254	0.868	28.164	0.520	8.143	3.459
WCB 02-01	12.813	58.414	0.775	27.304	0.464	6.781	4.026
WCB B2-09	14.535	63.342	0.865	29.607	0.518	7.693	3.849
WCB 01-02	17.226	55.885	0.858	26.122	0.514	9.117	2.865
WCB-FF-01	15.288	58.642	0.893	27.366	0.535	8.087	3.384
WCB-FF-02	15.647	59.476	0.904	27.755	0.542	8.277	3.353
WCB_FF_04	15.402	61.266	0.912	28.591	0.547	8.148	3.509
WCB_FF_06	14.948	60.678	0.912	28.316	0.547	7.907	3.581
WCB_FF_08	15.550	61.949	0.907	28.910	0.544	8.226	3.514
WCB_FF_10	16.064	60.241	0.911	28.112	0.546	8.498	3.308
WCB-FF-12	17.036	60.367	0.937	28.171	0.562	9.012	3.126
BMC B1-03	15.46	62.857	0.919	29.381	0.551	8.182	3.591
BMC B1-02	15.223	63.683	0.928	29.767	0.556	8.057	3.695
BMC B1-01	15.636	62.791	0.916	29.350	0.549	8.275	3.547
BMC_1_02	14.722	59.209	0.853	27.631	0.511	7.788	3.548
BMC_5	13.807	61.615	0.820	28.754	0.491	7.304	3.937
BMC_10	11.374	64.052	0.774	29.891	0.464	6.017	4.968
BMC_15	14.406	58.430	0.864	27.267	0.518	7.621	3.578
BMC_25	14.297	63.597	0.908	29.679	0.544	7.563	3.924
BMC_30	15.275	63.269	0.928	29.526	0.556	8.080	3.654
BMC_35	15.205	63.029	0.969	29.414	0.581	8.043	3.657
BMC_40	13.603	68.075	0.987	31.768	0.592	7.196	4.415
BMC_45	15.804	62.663	0.992	29.243	0.595	8.360	3.498
BMC_51	16.888	60.082	1.017	28.038	0.610	8.934	3.138
JPC D8	18.129	60.901	1.009	28.466	0.605	9.595	2.967
JPC D6	18.621	59.361	0.972	27.747	0.583	9.855	2.815
JPC D3	17.849	59.961	0.956	28.027	0.573	9.447	2.967
JPC D-01	16.493	63.474	0.968	29.669	0.580	8.729	3.399
JPC_FF_01	16.343	62.322	1.038	29.084	0.622	8.645	3.364
JPC_FF_02	16.091	63.684	1.044	29.719	0.626	8.512	3.491
JPC_FF_04	16.701	63.095	1.057	29.444	0.633	8.835	3.333
JPC_FF_06	16.721	61.486	1.039	28.693	0.623	8.845	3.244
JPC_FF_08	16.950	61.687	1.026	28.787	0.615	8.967	3.211
JPC_FF_10	16.702	61.891	1.034	28.882	0.620	8.835	3.269
754	14.224	63.922	0.868	29.830	0.520	7.524	3.964
754_4	20.019	56.993	0.902	26.597	0.541	10.59	2.511
754_6	13.395	67.403	0.858	31.455	0.514	7.086	4.439
754_8	13.561	66.814	0.892	31.180	0.535	7.174	4.346
755_8	12.933	67.171	0.830	31.346	0.497	6.842	4.582
761_6	16.014	60.869	0.899	28.451	0.539	8.475	3.357
762_6	13.650	65.291	0.896	30.469	0.537	7.221	4.220
764	14.851	64.465	0.872	30.084	0.523	7.856	3.829
771_6	15.569	60.942	0.889	28.440	0.533	8.236	3.453
774_10.5	12.260	62.273	0.787	29.061	0.472	6.486	4.481
776	14.198	60.448	0.838	28.209	0.502	7.511	3.756

776_5	13.546	62.930	0.878	29.367	0.526	7.166	4.098
776_8.5	15.141	61.560	0.911	28.728	0.546	8.010	3.587
776_9.5	15.857	61.000	0.919	28.467	0.551	8.388	3.394
776_11	15.957	60.388	0.922	28.181	0.553	8.441	3.338
777_2.5	15.790	61.854	0.942	28.865	0.565	8.353	3.456
777_5.3	15.417	62.735	0.953	29.276	0.571	8.156	3.590
777_6	15.010	63.465	0.936	29.617	0.561	7.940	3.730
777_9	15.356	62.361	0.953	29.102	0.571	8.123	3.582
778_2	16.399	60.846	0.941	28.395	0.564	8.675	3.273
778_7	16.333	61.842	0.973	28.860	0.583	8.640	3.340
784_1.5	15.727	63.323	0.996	29.551	0.597	8.320	3.552
784_5.5	15.126	64.451	0.995	30.077	0.596	8.002	3.759
784_6.5	15.005	64.091	0.978	29.909	0.586	7.938	3.768
784_8	15.515	63.768	0.993	29.758	0.595	8.207	3.626
784_10	15.381	61.653	0.975	28.771	0.584	8.137	3.536
801_3	16.819	62.897	0.962	29.352	0.577	8.897	3.299
801_7	16.896	61.223	0.984	28.571	0.590	8.938	3.197
801_9	20.082	58.137	0.993	27.131	0.595	10.62	2.554
802	15.905	63.100	1.013	29.447	0.607	8.414	3.500
802_1.5	17.334	59.010	0.987	27.538	0.592	9.170	3.003
802_9	14.994	65.491	1.009	30.562	0.605	7.932	3.853
ZL-16-01	14.387	64.657	0.87	30.222	0.521	7.614	3.969
ZL-15-01	13.853	65.129	0.873	30.443	0.523	7.332	4.152
ZL-13-01	15.733	60.513	0.909	28.285	0.545	8.327	3.397
ZL-12-01	15.806	61.458	0.933	28.727	0.559	8.365	3.434
ZL-06-06	17.424	58.98	0.902	27.568	0.541	9.222	2.990
ZL-06-02	16.379	60.152	0.9	28.116	0.539	8.669	3.243
ZL-01-04	18.608	57.094	0.893	26.644	0.535	9.844	2.707
ZL-01-03	17.042	56.753	0.878	26.485	0.526	9.015	2.938
ZL-01-02	16.271	57.101	0.869	26.647	0.521	8.607	3.096
ZLV_01	15.061	57.064	0.876	26.630	0.525	7.967	3.342
ZLV_02	16.427	59.199	0.937	27.626	0.562	8.690	3.179
ZLV_03	15.849	58.010	0.888	27.071	0.532	8.384	3.229
ZLV_04	14.429	65.154	0.942	30.405	0.565	7.633	3.983
ZLV_05	14.275	67.898	0.908	31.686	0.544	7.551	4.196
ZLV_06	15.625	61.166	0.963	28.544	0.577	8.266	3.453
ZLV_07	16.414	60.910	0.954	28.425	0.572	8.683	3.274
ZLV_08	16.272	60.374	0.934	28.175	0.560	8.608	3.273
ZLV_09	16.590	61.240	0.973	28.579	0.583	8.776	3.256

Ti/Al

0.071
0.064
0.068
0.067
0.056
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0.072
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0.065
0.066

Table S6. Trace element data.

Sample ID	Mn (ppm)	V (ppm)	Ni (ppm)	Mo (ppm)	V/(V+Ni)
WCB-FF-01	283.24	127.71	126.42	8.04	0.50
WCB-FF-02	274.07	129.10	115.21	9.29	0.53
WCB_FF_06	289.53	118.66	117.48	11.37	0.50
WCB_FF_08	271.11	118.75	94.44	24.71	0.56
WCB_FF_10	269.39	120.04	95.65	42.35	0.56
WCB-FF-12	275.15	123.76	64.22	13.14	0.66
BMC_5	459.79	102.73	49.45	17.64	0.68
BMC_10	631.36	84.08	41.26	16.10	0.67
BMC_15	521.85	108.31	43.77	9.97	0.71
BMC_25	412.34	105.32	41.56	4.57	0.72
BMC_30	309.54	113.88	42.34	8.63	0.73
BMC_35	320.66	113.92	44.37	5.90	0.72
BMC_40	258.11	97.71	38.38	7.06	0.72
BMC_45	264.45	114.67	51.58	17.87	0.69
BMC_51	270.16	127.12	62.54	13.31	0.67
JPC_FF_02	292.84	115.94	73.46	13.10	0.61
JPC_FF_04	265.60	118.95	74.48	17.39	0.61
JPC_FF_08	290.42	125.78	87.17	32.17	0.59
JPC_FF_10	287.41	120.80	84.63	27.24	0.59
754.00	250.18	113.23	54.46	28.46	0.68
754_4	276.03	155.46	33.13	3.92	0.82
754_6	217.43	106.15	40.87	16.50	0.72
755_8	232.99	103.95	45.78	35.73	0.69
761_6	255.77	125.68	56.19	37.10	0.69
762_6	300.25	110.12	44.72	35.32	0.71
764.00	273.83	109.29	44.88	26.48	0.71
771_6	365.14	121.69	95.92	7.71	0.56
774_10.5	570.69	97.16	58.38	7.63	0.62
776.00	471.01	106.60	41.80	7.04	0.72
776_5	448.03	101.10	38.94	7.53	0.72
776_9.5	297.88	119.38	45.57	9.88	0.72
776_11	306.92	119.86	46.48	11.70	0.72
777_2.5	291.69	119.83	41.64	12.74	0.74
777_6	295.87	114.17	43.01	13.34	0.73
777_9	331.82	116.19	43.72	18.97	0.73
778_2	307.47	124.62	47.58	21.20	0.72
778_7	284.70	122.68	55.17	25.25	0.69
784_1.5	287.28	116.86	52.09	8.23	0.69
784_6.5	264.41	110.66	58.46	25.41	0.65
784_10	301.80	119.39	59.37	23.29	0.67
801_3	261.53	126.52	54.35	3.67	0.70
802.00	258.11	131.52	58.56	31.91	0.69
802_1.5	267.71	142.64	59.54	30.02	0.71
ZL-01-04	376.23	140.02	50.83	4.75	0.73
ZL-01-03	398.43	134.24	88.19	18.61	0.60
ZL-01-02	374.25	132.02	90.40	20.54	0.59

ZLV_01	399.97	117.50	100.41	8.77	0.54
ZLV_02	272.18	127.99	84.97	11.74	0.60
ZLV_03	277.22	122.85	89.63	20.04	0.58
ZLV_04	474.36	106.55	49.41	12.47	0.68
ZLV_06	309.82	117.03	87.30	26.29	0.57
ZLV_07	272.58	123.11	82.80	42.39	0.60
ZLV_08	282.15	121.04	83.50	42.08	0.59
ZLV_09	293.54	119.44	74.31	38.03	0.62

Table S7. Bitumen reflectance data.

Sample ID	BRO (%)	No. of measurements	s.d.
B1-03	0.56	50	0.073
B1-02	0.66	62	0.158
B1-01	0.53	51	0.084
BMC_1_02	0.66	50	0.158
BMC_5	0.64	50	0.167
BMC_10	0.73	50	0.083
BMC_15	0.56	50	0.076
BMC_20	0.60	51	0.098
BMC_21	0.56	70	0.016
BMC_22	0.65	50	0.115
BMC_25	0.55	50	0.080
BMC_30	0.56	100	0.112
BMC_35	0.54	50	0.106
BMC_40	0.60	53	0.118
BMC_45	0.59	50	0.106
BMC_51	0.57	33	0.076
754_6	0.60	25	0.163
755_8	0.62	27	0.146
761_6	0.61	81	0.086
762_6	0.61	25	0.146
771_6	0.66	25	0.141
776	0.58	25	0.078
776_9.5	0.68	30	0.118
776_11	0.60	26	0.104
777_2.5	0.64	26	0.099
777_5.3	0.58	25	0.070
777_6	0.56	26	0.066
777_9	0.56	26	0.096
778_7	0.60	25	0.125
784_1.5	0.63	25	0.106
784_5.5	0.66	30	0.072
784_8	0.61	26	0.113
801_7	0.64	28	0.160
801_9	0.63	23	0.180
802	0.63	20	0.140
802_9	0.53	14	0.139
ZL-16-01	0.73	25	0.220
ZL_06_04	0.70	25	0.165
ZL_06_02	0.62	25	0.167
ZL-01-03	0.67	50	0.104
ZL-01-02	0.65	50	0.090
ZLV_02	0.60	25	0.070
ZLV_04	0.63	25	0.127
WCB_B3_02	0.49	30	0.056
WCB_B3_04	0.46	50	0.058
WCB_B3_06	0.49	30	0.099

WCB_B3_08	0.62	50	0.091
WCB_B2_01	0.55	70	0.116
WCB_B2_07	0.48	50	0.092
WCB_B2_09	0.46	50	0.093
WCB_B1_02	0.57	30	0.090
WCB_FF_02	0.50	59	0.089
WCB_FF_06	0.59	30	0.096
WCB_FF_08	0.43	30	0.069
WCB_FF_10	0.50	30	0.107
WCB_FF_12	0.51	30	0.081
JPC_D8	0.67	50	0.142
JPC_D6	0.68	50	0.106
JPC_D3	0.57	30	0.137
JPC_D1	0.55	50	0.061
JPC_FF_02	0.69	50	0.087
JPC_FF_04	0.72	50	0.088
JPC_FF_06	0.69	52	0.109
JPC_FF_08	0.70	30	0.077
JPC_FF_10	0.67	50	0.082

Table S8. TOC and programmed pyrolysis data.

Sample ID	TOC	S1	S2	S3	Tmax (°C)	HI	OI
WCB-FF-01	5.23	2.09	20.21	0.16	442	388	3
WCB-FF-02	4.03	1.89	16.45	0.5	443	408	12
WCB_FF_04	3.59	1.75	13.19	0.24	443	367	7
WCB_FF_06	4.3	1.93	17.39	0.35	443	404	8
WCB_FF_08	3.03	1.44	11.23	0.19	443	371	6
WCB_FF_10	3.13	1.59	14.15	0.26	446	452	8
WCB-FF-12	0.69	1.03	1.57	0.32	442	228	46
BMC_1_02	2.4	1.28	4.94	0.27	440	206	11
BMC_5	2.51	1.25	5.11	0.21	442	204	8
BMC_10	2.05	1.11	4.28	0.39	442	209	19
BMC_15	2.89	1.5	6.45	0.33	442	223	11
BMC_25	2.69	1.73	6.28	0.24	444	233	9
BMC_30	2.09	1.44	5.03	0.21	442	241	10
BMC_35	2.57	1.8	6.65	0.25	442	259	10
BMC_40	1.78	1.16	4.29	0.16	441	241	9
BMC_45	2.13	1.36	5.48	0.26	442	257	12
BMC_51	1.27	0.73	2.55	0.22	443	201	17
JPC_FF_01	1.25	0.5	2.03	0.21	444	161	17
JPC_FF_02	1.23	0.52	1.84	0.23	443	150	19
JPC_FF_04	1.22	0.54	1.76	0.22	444	144	18
JPC_FF_06	1.63	0.64	2.48	0.24	442	152	15
JPC_FF_08	1.69	0.68	2.59	0.24	444	153	14
JPC_FF_10	1.74	0.68	2.85	0.2	444	164	11
754	2.83	1.25	6.66	0.19	446	235	7
754_4	0.32	0.08	0.13	0.28	437	41	88
754_6	1.96	0.9	3.57	0.17	444	182	9
754_8	2.44	1.18	4.87	0.19	446	200	8
755_8	2.74	1.22	6.34	0.18	444	231	7
761_6	2.86	1.33	6.71	0.25	443	235	9
762_6	3.01	1.3	7.32	0.17	446	243	6
764	1.72	0.83	3.25	0.2	445	189	12
771_6	2.65	0.99	4.35	0.22	445	164	8
774_10.5	2.48	0.97	4.22	0.24	444	170	10
776	3.53	1.58	7.16	0.19	447	203	5
776_5	3.25	1.68	7.52	0.17	445	231	5
776_8.5	3.02	1.61	6.53	0.17	442	216	6
776_9.5	3.03	1.47	5.99	0.15	444	198	5
776_11	2.71	1.43	5.50	0.14	445	203	5
777_2.5	2.57	1.37	5.38	0.15	444	209	6
777_5.3	2.41	1.30	4.52	0.18	443	188	7
777_6	2.68	1.41	5.77	0.18	445	215	7
777_9	3.05	1.65	6.17	0.15	444	202	5
778_2	2.48	1.34	5.54	0.12	444	223	5
778_7	1.9	1.27	3.77	0.17	445	198	9
784_1.5	1.18	0.55	1.98	0.19	446	168	16
784_5.5	2.17	1.15	3.85	0.21	445	177	10

784_6.5	1.76	0.85	2.8	0.27	442	159	15
784_8	2.06	0.87	3.02	0.21	443	147	10
784_10	1.71	0.75	2.02	0.2	445	118	12
801_3	0.65	0.22	0.61	0.33	442	94	51
801_7	1.51	0.62	2.17	0.2	443	144	13
801_9	0.38	0.14	0.36	0.19	439	95	50
802	1.1	0.41	1.35	0.26	443	123	24
802_1.5	1.67	0.74	3.46	0.2	445	207	12
802_9	1.33	0.61	2.79	0.25	445	210	19
ZL-01-04	1.16	0.49	1.8	0.18	445	155	16
ZL-01-03	2.44	1.16	4.91	0.15	444	201	6
ZL-01-02	2.54	1.22	5.17	0.12	445	204	5
ZLV_01	4.3	2.07	11.23	0.18	444	261	4
ZLV_02	3.92	1.62	9.51	0.13	448	243	3
ZLV_03	3.26	1.61	7.29	0.28	444	224	9
ZLV_04	1.46	0.89	3.01	0.19	444	206	13
ZLV_05	1.04	0.71	2.02	0.24	441	194	23
ZLV_06	2.99	1.68	7.64	0.18	446	256	6
ZLV_07	2.85	1.43	6.82	0.12	448	239	4
ZLV_08	2.62	1.37	6.57	0.2	446	251	8
ZLV_09	2.22	1.3	5.19	0.18	448	234	8

PI	S2/S3	S1/TOC*100
0.09	126	40
0.1	33	47
0.12	55	49
0.1	50	45
0.11	59	48
0.1	54	51
0.4	5	149
0.21	18	53
0.2	24	50
0.21	11	54
0.19	20	52
0.22	26	64
0.22	24	69
0.21	27	70
0.21	27	65
0.2	21	64
0.22	12	57
0.2	10	40
0.22	8	42
0.23	8	44
0.21	10	39
0.21	11	40
0.19	14	39
0.16	35	44
0.4	0.5	25
0.2	21	46
0.19	26	48
0.16	35	45
0.17	27	47
0.15	43	43
0.2	16	48
0.18	20	37
0.19	18	39
0.18	38	45
0.18	44	52
0.2	38	53
0.2	40	49
0.21	39	53
0.2	36	53
0.22	25	54
0.2	32	53
0.21	41	54
0.19	46	54
0.25	22	67
0.22	10	47
0.23	18	53

0.23	10	48
0.22	14	42
0.27	10	44
0.27	2	34
0.22	11	41
0.28	2	37
0.23	5	37
0.18	17	44
0.18	11	46
0.21	10	42
0.19	33	48
0.19	43	48
0.16	62	48
0.15	73	41
0.18	26	49
0.23	16	61
0.26	8	68
0.18	42	56
0.17	57	50
0.17	33	52
0.2	29	59
