CO₂-induced biochemical changes in leaf volatiles decreased fire-intensity in the run-up to the Triassic–Jurassic boundary

Sarah J. Baker¹*, Rebecca A. Dewhirst¹*, Jennifer C. McElwain², Matthew Haworth³ and Claire M. Belcher¹

¹wildFIRE Lab, University of Exeter, Exeter, EX4 4PS, UK; ²Botany Department, School of Natural Sciences, Trinity College Dublin, Dublin, D02 PN40, Ireland; ³Institute for Sustainable Plant Protection, National Research Council (CNR-IPSP), Via Madonna del Piano 10 Sesto Fiorentino, Florence, Firenze 50019, Italy

Author for correspondence:
Sarah J. Baker
Email: sarahbaker189@gmail.com

Received: 2 December 2021
Accepted: 22 April 2022

New Phytologist (2022) 235: 1442–1454
doi: 10.1111/nph.18299

Key words: CO₂-induced biochemical changes, fire behaviour, fire intensity, leaf volatiles, lignin content, Triassic–Jurassic transition.

Summary

- The Triassic–Jurassic boundary marks the third largest mass extinction event in the Phanerozoic, characterized by a rise in CO₂-concentrations from c. 600 ppm to c. 2100–2400 ppm, coupled with a c. 3.0–4.0°C temperature rise. This is hypothesized to have induced major floral turnover, altering vegetation structure, composition and leaf morphology, which in turn are hypothesized to have driven changes in wildfire. However, the effects of elevated CO₂ on fuel properties, such as chemical composition of leaves, are also important in influencing fire behaviour, but yet have not been considered.
- We test this by selecting three Triassic analogue species grown experimentally in different atmospheric compositions, and analyse variations in leaf chemistry, and leaf level flammability. These data were used to inform a fire behaviour model.
- We find that all three species tested showed a reduction in their volatile component, leading to lower flammability. Accounting for these variations in a model, our results suggest that leaf intrinsic flammability has a measurable impact on modelled fire behaviour.
- If scaled up to ecosystem level, periods of elevated CO₂ may therefore be capable of inducing both biochemical and morphological changes in fuel properties, and thus may be capable of influencing fire behaviour.

Introduction

The Triassic–Jurassic boundary transition (TJT) marks one of the largest mass extinction events in the Phanerozoic (Fowell & Olsen, 1993; McElwain et al., 1999; Ward et al., 2001). At Aastarkelk, East Greenland, stomatal pCO₂ proxy analysis of macrofossil leaves preserved, suggest CO₂ concentrations rose from c. 600 ppm to c. 2100–2400 ppm, where CO₂ concentrations rose gradually during the Rhaetian, before doubling at/ slightly after the boundary (McElwain et al., 1999; Steinhorsdot-tir et al., 2011), driving a c. 3.0–4.0°C temperature rise across the TJT (McElwain et al., 1999). In East Greenland, modelled local summer temperatures are estimated to have risen to 36°C (Huynh & Poulsen, 2005; Sellwood & Valdes, 2006).

These CO₂-climate driven changes are hypothesized to have induced major floral turnover, altering vegetation structure, composition and leaf morphology (e.g. McElwain et al., 2007; Belcher et al., 2010). This, coupled with an increased probability of ignition through increased lightning strikes under higher atmospheric CO₂ conditions are hypothesized to have driven changes in wildfire activity and behaviour across the TJT (Belcher et al., 2010; Peterson & Linström, 2012; Belcher, 2016). Here, evidence of wildfire in the form of fossil charcoal and polycyclic aromatic hydrocarbons (PAHs) have been well documented from numerous locations (e.g. Harris, 1957, 1958; Marynowski & Simonite, 2009; Peterson & Linström, 2012; Song et al., 2020).

However, records of fossil charcoal and other combustion residues are difficult to interpret in deep time because these signatures rarely represent individual fire events, but rather overall rises in fire activity during long periods of time. Moreover, fires themselves create varied abundances of these products depending on the nature of combustion. Recent research has indicated for example, that the abundance of charcoal produced by fires varies according to plant species, which is related to the intrinsic physical and chemical properties of the fuel that leads to different fire behaviours (Hudsphith et al., 2017). This means that not only will different fires produce different amounts and sizes of char ( Crawford & Belcher, 2016; Hudsphith et al., 2017) but that also certain taxa will be over represented in fossil charcoal assemblages and some indeed not preserved at all (Hudsphith et al., 2017; Hudsphith & Belcher, 2017).

Perhaps more importantly fire frequency is only one aspect of fire regime that determines the effects of fire on vegetation shifts and its ecological impact. More significant is that of the fire behaviour and fire severity, hence estimates of palaeofire behaviour are required for the ancient past if we are to

*These authors contributed equally to this work.
understand the impacts of significant shifts in fire regime on ecosystems. A shift in fire regime has previously been suggested across the TJT at Astartekløft, where prior to the rise in CO2 ecosystems are hypothesized to have experienced infrequent but intense fires. Then as CO2 concentrations rose fires are hypothesized to have become more frequent but of lower intensity (Belcher et al., 2010; Belcher, 2016). These changes were inferred by coupling variations in the abundance of fossil charcoal with flammability metrics derived from laboratory experiments linked to changes in the leaf morphology of dominant species across the TJT. Here we expand this approach by modelling fire behaviour across the TJT by constructing fuel models based on the shifts in plant dominance observed at Astartekløft (McElwain et al., 2007; Belcher et al., 2010). We utilize the model BEHAVEPLUS (Andrews, 2010) which requires the heat content of the fuel components. To gather this information we have undertaken unique plant growth experiments to explore the effect of changing atmosphere CO2 on the volatile components of plants, which are known to be important in influencing fire behaviour (Belcher, 2013; Hudspith et al., 2017; Dewhirst et al., 2020). For example, an astounding array of secondary metabolites including thousands of volatile compounds play a range of roles including herbivory defence, signalling, and immunity in plants. Some of these compounds, such as terpenoids (specifically monoterpene and sesquiterpenes) also contribute to leaf flammability due to their low flash points (e.g. Owens et al., 1998; Pausas et al., 2016; Dewhirst et al., 2020).

Changes in temperature, atmospheric CO2 levels, aridity, and drought, can influence changes in leaf morphology and chemistry, as well as bark traits which in turn affect fire behaviour (Popović et al., 2021; Scalon et al., 2021). Warming leads to a decline in photosynthetic rate, as Rubisco favours oxygenation rather than carboxylation at higher temperatures (Berry & Björkman, 1980), leading to lower carbon fixation (Haworth et al., 2018). Increased CO2 however provides more substrate for photosynthesis and so increases carbon assimilation (Berry & Björkman, 1980). As such plants grown under elevated CO2 have been hypothesized to accumulate greater levels of carbon-based secondary metabolites (Peñuelas et al., 1997). This is further supported by an observed increase in community weighted leaf mass per area across the TJT, which based on leaf economic spectrum (Wright et al., 2004) supports greater levels of carbon-based secondary metabolites in the earliest Jurassic and TJT leaves (Soh et al., 2017). However, the observed response to elevated CO2 in various experimental trials has been varied.

Warming and elevated CO2 have been reported to have contrasting effects on secondary metabolites, including terpenes (Valor et al., 2017) and reviewed in Holopainen et al. (2018) and Feng et al. (2019). In gymnosperms, foliar terpenes increased with warming (Zvereva & Kozlov, 2005), whereas they decreased with elevated CO2 in Pinus sylvestris and Picea abies (Sallas et al., 2003). Monoterpene production was downregulated under elevated CO2 resulting in a decrease in monoterpenes in terpenestoring conifers (De Lillos et al., 2009).

Different compound types respond in different ways to elevated CO2; for instance, phenolic compounds tend to increase under elevated CO2 (e.g. Peltonen et al., 2005) whereas terpenoid compounds tend to decrease (Holopainen et al., 2018). The opposite is true for elevated temperature, under which phenolics decreased and terpenes increased. Under elevated CO2 phenolic compounds in Salix myrsinifolia were found to increase, but decrease under elevated temperatures. The combination of elevated CO2 and temperature resulted in no change in total shoot phenolics, but a decrease in the total phenolic concentration (Veteli et al., 2002).

Meta-analysis revealed that ‘leaf toughness’ increased under elevated CO2 (Zvereva & Kozlov, 2005; Stiling & Cornelissen, 2007; Robinson et al., 2012). Leaf toughness is potentially linked to lignin, as lignin is an important structural component of plants. Lignin is one of the most recalcitrant plant compounds and lignin-rich leaf litter has a slower rate of decomposition than lignin-poor litter (Wedderburn & Carter, 1999). This has an impact on the accumulation of fuels required for surface fires; high-lignin litter will accumulate to greater amounts than easily decomposed low-lignin litter and so increase the probability of a surface fire occurring.

Hence, we hypothesize that CO2-driven climate changes in the run-up to the TJT may have been capable of not only inducing changes in leaf morphological fuel properties (Belcher et al., 2010; Belcher, 2016), but also variations in biochemical properties, which together alter wildfire behaviour (Dewhirst et al., 2020). We selected three species with ancient evolutionary origins (the gymnosperms Agathis australis, Ginkgo biloba and the fern Dicksonia antartica) that correspond to morphotypes of the dominant litter-forming vegetation observed at the Astartekløft site (McElwain et al., 2007; Belcher, 2016). We grew these species in current ambient and elevated CO2 (Triassic–Jurassic) atmospheric conditions for 18 months and analysed variations in the chemistry of the leaves (terpene and lignin content), using gas chromatography–mass spectrometry (GC–MS), and aspects of their leaf level flammability using micro-calorimetry. These data were used to inform a fire behaviour model (BEHAVEPLUS; Andrews, 2010) to produce estimates in variations in surface fire rate of spread, fireline intensity and canopy scorch height based on the increase in [CO2] and global temperatures in the run-up to the TJT and the floral changes observed in plant macrofossils at Astartekløft, East Greenland (McElwain et al., 2007; Belcher, 2016).

Materials and Methods

Study site

The site at Astartekløft comprises eight sedimentary rock horizons, termed ‘plant beds’, that span the TJT and contain an abundance of well-preserved macrofossils (Harris, 1935; McElwain et al., 2007) (>3000 census collected fossil leaves), thus enabling the reconstruction of surface litter and surface fuel for fire reconstructions (Belcher, 2016). Here, the Triassic comprises plant beds 1, 1.5, 2, 3, 4, and 5 where plant bed 5 is split into 5A and 5B that represents the shift in leaf morphology, during the Triassic–Jurassic transition (Belcher et al., 2010). The
increase in charcoal abundance has been observed in plant bed 5B.

Plant growth experiments

Volatile content and flammability Plants were grown in Conviron BDW-40 walk-in growth chambers at University College Dublin, Ireland, at ambient (380 μmol mol⁻¹) and elevated (1500 μmol mol⁻¹) [CO₂]. All other growth conditions remained constant between [CO₂] treatments: 600 μmol m⁻² s⁻¹ photosynthetically active radiation for 16 h d⁻¹ with 1 h simulated dawn : dusk, day : night time temperature regime of 28°C : 18°C, relative humidity of 80% and irrigation with 60 ml of water per day. Leaves were fully expanded and from the top of the canopy receiving full illumination. Only leaves that had formed during the chambers after 18 months were used, and were collected at the same time to eliminate reactions to herbivory. Leaves were then placed in paper envelopes and allowed to dry.

Volatile compound analysis Volatiles were extracted from dried leaves (two leaves per plant from two plants, see Supporting Information Tables S1, S2) ground in glass pestle and mortar under liquid nitrogen in n-hexane (0.01 g (dry weight) in 1 ml hexane) with 10 μM butylated hydroxytoluene (BHT; as an internal standard) by sonication and subsequent overnight incubation. Samples were analysed using an Agilent 7200 series accurate mass quadrupole time-of-flight (Q-TOF) mass spectrometer coupled to a 7890A GC system (Agilent Technologies, Santa Clara, CA, USA), equipped with an EI (electron ionization) ion source. Briefly, 5 μl of each sample was injected into a nondeactivated, baffled glass liner with a 12:1 split ratio (14.448 ml min⁻¹ split flow) and the inlet temperature was maintained at 250°C. A Zebron semi-volatiles (Phenomenex, Torrance, CA, USA) column (30 m × 250 μm × 0.25 μm) coupled with a 10 m guard column, was maintained at a constant helium flow of 1.2 ml min⁻¹. The temperature of the column was ramped up at a rate of 15°C min⁻¹, from 70°C to 310°C over 16 min, and then held at 310°C for a further 6 min. The EI source emission current and voltage were held at 35 μA and 70 eV, respectively. The mass range was set from 50 to 600 m/z, with an acquisition rate of 5 spectra s⁻¹, and a solvent delay of 4 min. Data were analysed using AGILENT MASSHUNTER QUALITATIVE ANALYSIS software (v.B.07.00) and compounds identified where possible by comparison with standards and National Institute of Standards and Technology (NIST 11 Mass Spectral Library) and Golm libraries (Hummel et al., 2007). See Figs S1–S3 for replicate GC profiles.

Lignin analysis Protein-free cell wall preparations were obtained for two leaves per plant from two plants by sequential washing in pH 7 potassium phosphate buffer (0.1 M), 1 M sodium chloride (NaCl) solution, 1% (v/v) Triton-X100 and acetone. Acid-soluble lignin was assayed using the acetyl bromide method (Moreira-Vilar et al., 2014), and the absorbance measured at 280 nm.

Leaf-level flammability analysis The intrinsic flammability of the leaves was measured using a Federal Aviation Administration (FAA) microcalorimeter (Fire Testing Technology, East Grinstead, UK) that was developed to allow direct measurements of heat release rate in respect to material properties and chemical composition of materials. The FAA microcalorimeter is a pyrolysis combustion flow calorimeter and was used to reproduce the solid-state and gas phase processes of flaming combustion by heating 10–15 mg samples of each leaf type in an inert gas stream (nitrogen gas) where the volatile gases are driven off and oxidized at high-temperature in excess oxygen. The microcalorimeter then measures the rate of heat release based on the oxygen consumption history of the fuel. The samples were exposed to a heating programme that ramped up to 750°C at a rate of 3°C s⁻¹. Two leaves per plant from two plants were analysed each in duplicate. The peak heat release rate (pHRR: the most intense flux of heat during the combustion of the leaf material, indicates the maximum decomposition rate of the leaves which is related to the volatile gas flux of the material), heat capacity (HRC: the maximum capability of the leaf material to release combustion heat per degree of temperature during pyrolysis; this measure provides an indication of the resistance of the leaves to thermal degradation) and total heat release (THR: the total energy released by the leaf during combustion) was determined for each leaf on a per gram dry mass basis. The THR was used to inform the heat content aspect of the fuel models run in BEHAVEPLUS for each fuel type.

Estimating changes in fire behaviour in the run-up to the TJT We utilized the BEHAVEPLUS modelling system (Andrews, 2010) to estimate alterations in fire behaviour across the TJT. BEHAVEPLUS is used in predicting fire behaviour in modern US ecosystems and has also been used to estimate changes in Cretaceous fire behaviour (Belcher & Hudspith, 2017). BEHAVEPLUS consists of a set of mathematical models and requires simple input parameters that detail fuel characteristics and environmental conditions, such as dead and live fuel loads, fuel bed depth, moisture of extinction and live heat contents (see Notes S1 for full details). Here, calculations are included for surface fire rate of spread, fireline intensity and flame length, reaction intensity and heat per unit area, intermediate values of heat source, heat sink, dead fuel moisture and many more (see Andrews, 2014). We modelled the behaviour of surface fires and their ability to scorch the canopy. We did not predict crown fire behaviour because the information that is required (for example, surface fuel moisture and canopy base height) is currently beyond the state-of-the-art for palaeontological observations. Hence, we have modelled interactions between dead litter fuel, surface level fuels (such as ferns) and the reach of the effects of the surface fires on the canopy.

A set of fuel models that numerically describe the Triassic and transitional surface fuels based on the major canopy- and litter-forming morphotypes, coupled with the change in vegetation documented within each plant bed, were constructed (McElwain et al., 2007; Belcher, 2016). The descriptions were made using details of the litter forming fuel types present, as outlined in the
genus-level relative abundance of the plant fossils found at Astarkloft used in Belcher et al. (2010) (see their SI 41561_2010_BFngeo871_MoSem293_ESM.xls), and their morphology (Belcher, 2016). The relative percentages for each ecosystem element’s influence on each fuel model is indicated in Table S3 and the numeric descriptors of all the fuel models used are shown in Table S4.

Vegetation Phase 1 (plant beds 1, 1.5 and 2 Triassic age) In these plant beds the canopy and main litter forming species consisted of broad-leaved fuels of Ginkgos and the conifer Podozamites, whilst the sub-canopy likely consisted of ferns, cycads and bennettites (with ferns as the dominant) (McElwain et al., 2007; Belcher et al., 2010; Belcher, 2016) (Table S3). During Vegetation Phase 2 (plant beds 3, 4 and 5A Triassic to latest Triassic age), the sub-canopy habitat is diminished, with the loss of cycads and bennettites. Ginkgos are also lost and osmundaceous ferns replace dipterid ferns (McElwain et al., 2007; Belcher, 2016). During this phase, interpreted litter fuels remain dominated by broad-leaved conifer leaf-shed litter of Podozamites (Belcher, 2016) (Table S3). The fuel models for all plant beds 1 through to 5A are based on a Timber-Litter fuel model – TU5 of Scott & Burgan (2005) (Table S4). TU5 is a timber understory fuel model and representative of broad-leaved fuel, to represent the broad-leaved surface litter likely, from a canopy of Ginkgo and Podozamites (making up the dead litter fuel class), coupled with the sub-canopy of ferns, cycads and bennettites (dominating the live surface fuel load).

Vegetation Phase 3 In plant bed 5B, narrow-leaved shoot-shedding conifers are hypothesized to become dominant (Stachyoxus), and abundances of ferns, cycads and bennettites become limited (McElwain et al., 2007; Belcher et al., 2010; Belcher, 2016). To account for this switch in inferred dominance from broad-leaved to narrow-leaved litter species, a different fuel model is used which is based on a Timber-Litter fuel model – TL8 of Scott & Burgan (2005) (Table S4). TL8 is a timber understory fuel model and representative of broad-leaved fuel, to represent the broad-leaved surface litter likely, from a canopy of Ginkgo and Podozamites (making up the dead litter fuel class), coupled with the sub-canopy of Ginkgo and Podozamites (making up the dead litter fuel class), coupled with the sub-canopy of ferns, cycads and bennettites (dominating the live surface fuel load).

Table 1 Summary of volatile compound peaks from gas chromatography–mass spectrometry (GC–MS) for each species.

| Compound class       | Dicksonia | Ginkgo   | Agathis |
|----------------------|-----------|----------|---------|
| Monoterpenes         |           | —        | 40, 41, 42, 43, 44 |
| Sesquiterpenes       | —         | —        | 45, 46, 47, 48, 49 |
| Diterpenes           | 2, 3      | 3, 19, 22, 23, 25 | 2, 3, 19, 22, 23, 25, 50, 51 |
| Fatty acid           |           | 13, 14, 20, 21, 26 | 13, 20 |
| Fatty alcohol        |           | 12, 38   | 38 |
| Long-chain hydrocarbon| 5, 6, 7, 8, 9, 10 | 15, 16, 29, 35, 36 | 15, 29, 35, 36, 53, 54 |
| Phenolic             | 28        | 1        | 1 |
| Isoprenoid ketone    | 1         | 11, 17, 24, 27, 30, 31, 32, 33, 34, 37, 39 | 17, 54 |
| Unknown              | 4         | 11, 17 | — |

Because our plant growth experiments indicated differences in heat content between species and a clear decrease in the heat content (THR) between leaves grown under control and high CO2 conditions (Table 1), we altered the heat content in each fuel model according to shifts in plant dominance and environmental changes. The heat content for each of the plant beds fuel model were informed using values from modern day morphotypes or nearest living relatives from published data taken from Belcher (2016) and Belcher & Hudspith (2017). The dead fuel (litter) heat content for each palaeo-fuel model was then established by weighting according to the dominance of the major litter-forming fossil genera represented in each plant bed from Belcher (2016) and by adjusting this according to the proportion of change we observed between control and high CO2 (see Table S3). As an example, in plant bed 1, Ginkgo makes up 38% of the dominant litter morphotype, and Podozamites makes up 62% (Belcher et al., 2010; Belcher, 2016), hence a weighting of 62% was assigned to the dead fuel heat content of Agathis (a nearest living morphotype) and 38% weighted from the heat content of Ginkgo (the nearest living relative) (see Table S3). This approach was used for all plant beds (see Tables S3, S4).

For the TJJ beds 5A and 5B, heat content was further adjusted accordingly for the effects of elevated [CO2] based on the plant biochemistry and the resultant flammability using the findings of our plant growth experiments. For example, A. australis saw a 35% reduction in dead fuel heat content under elevated [CO2] (Tables 1, S3, S4). For the TJJ beds, a range of scenarios were run to allow us to consider how changes in: (a) fuel alone, (b) fuel and increasing [CO2], (c) fuel, increasing [CO2] plus and an assumed 4°C rise in global temperature (McElwain et al., 1999) and (d) fuel, [CO2] plus and an assumed 11°C rise in regional summertime peak temperature (Huynh & Poulsen, 2005) would alter the fire behaviour (see Table 2). All live fuel heat contents, i.e. that of the understory/sub-canopy were derived from D. antarctica as a nearest living morphotype where the data was taken from Belcher & Hudspith (2017) and adjusted as noted earlier.

Two further changes were made. (1) To represent the loss in sub-canopy of cycads and bennettites in Vegetation Phase 2 (plant beds 3, 4 and 5A), the live herbaceous fuel load was halved...
and further adjustments in this fuel category were made for bed 5B (see Table S4 for information on changes to the live herbaceous fuel load). (2) To represent the debate surrounding changes in leaf litter fuel load across the TJT, we ran two options for beds 5A and 5B. The first assumed that a 25% decrease in lignin content would lead to a lower load of 1 h fuel and a second with a high fuel based on the increase in leaf mass per area across the TJT (Soh et al., 2017). Hence, we ran one set of options with a lower 1 h fuel load and another set assuming the standard fuel load of the TLI fuel.

Each fuel model created was added as a custom fuel model into the BEHAVEPLUS fire behaviour modelling program (Andrews, 2010). We modelled outputs of surface spread rate, surface fireline intensity and scorch height for fires carried in the understory fuels only. Surface spread rate refers to the speed at which a fire travels through the surface fuels. Fireline intensity refers to the amount of energy released per unit of time per unit length of the fire front, whilst scorch height is the height at which the surface fire will begin to dry and scorch canopy fuels. Higher output values for each of these parameters allows for better preheating and drying of fuels ahead of a fire, thus enabling the fire to propagate more easily. For example, increased scorch height and fireline intensity (which also relates to flame length) allow for heating and scorching of canopy fuels, increasing the probability that a surface fire will transition into a crown fire. The parameters required to produce these estimates are: Fuel model (described in Tables S2, S3), dead surface fuel moisture (set at 8% in all runs), live surface fuel moisture (set at 100% in all runs), slope angle (set at 30% for all runs) and temperature. These choices are explained in Notes S1. We ran two alternatives for mid-flame wind speed, of 5.6 km h⁻¹ and 11.2 km h⁻¹, where mid-flame wind speed describes the wind speed at eye height, beneath a forest canopy. We selected relatively low mid-flame wind speeds, because the vegetation at Astartekloft is believed to be considered to have been a relatively dense subtropical forest (McElwain et al., 2007).

## Results

### Changes in leaf biochemistry

Representative GC–MS profiles for each species are shown in Fig. 1 with each producing distinct volatile compounds. *Dicksonia antarctica* had the lowest abundance of compounds, and *A. australis* had the highest (Fig. 1). *Dicksonia antarctica* predominately contains long-chain alkane hydrocarbons whilst, *A. australis* is the only species to contain monoterpenes. *Ginkgo biloba* and *A. australis* both contain sesquiterpenes, to varying degrees, and all three species contain at least two diterpenes (Table 1). There were two compounds common to all species; an isoprenoid ketone (trimethyl pentadecanone) and a diterpene (kaur-16-ene). In addition to kaur-16-ene, *D. antarctica* predominantly contained long-chain alkane hydrocarbons, whilst *A. australis* extracts contained a significant proportion of terpenes, including monoterpenes, sesquiterpenes and diterpenes, along with some long-chain hydrocarbons. *Ginkgo biloba* contained several isoprenoid-related compounds, including several diterpenes and a sesquiterpene.

Both *A. australis* and *G. biloba* showed a decrease in volatile compounds (as detected on GC–MS) following 18 months of growth and development under elevated CO₂ (Figs 1, 2). *Agathis australis* leaves grown in elevated CO₂ showed a decrease in monoterpenes, which is consistent with observations for *Pinus sylvestris* leaves (Kainulainen et al., 1998). Similarly, *G. biloba* grown under elevated CO₂ also showed a reduction in early-eluting compounds (generally short-chain fatty acids and alcohols rather than monoterpenes in *G. biloba*) compared to control atmosphere grown plants. The early-eluting compounds represent the most volatile compounds, so a loss of these compounds may have an impact on leaf-level flammability, by influencing the ease of ignition.

The three species all revealed lower leaf-level flammability under elevated CO₂ conditions, when measured using a microcalorimeter (see Fig. 2; Table 2). This trend was most apparent in *A. australis*, where the pHRR (peak intensity of flame) under elevated CO₂ was around half that of the control (126.0 J g⁻¹ K⁻¹ compared to 234.1 J g⁻¹ K⁻¹ in the control (P < 0.001)). Similar, but less extreme differences were seen in *D. antarctica* (P < 0.01) and *G. biloba* (P < 0.01). The THR describes the total energy release during combustion. The THR in all species and tests was higher in the control than under elevated CO₂, with the exception of one test for *Dicksonia* where the THR was lower in the control compared to under elevated CO₂ (P < 0.001 for *Agathis* and *Gingko*, and *Dicksonia* P > 0.05 at 0.176). The HRC (that indicates the resistance of the leaves to thermal degradation, where lower values of this measure report enhanced fire resistance), was also lower in elevated CO₂.

### Table 2

| Vegetation type | Mean total heat release control conditions (kJ g⁻¹) | Mean total heat release under elevated CO₂ (kJ g⁻¹) | Percentage change in mean total heat release between control and elevated CO₂ (%) | Mean heat release capacity control conditions (g⁻¹ K⁻¹) | Mean heat release capacity under elevated CO₂ (g⁻¹ K⁻¹) | Percentage change in mean heat release capacity between control and elevated CO₂ (%) |
|-----------------|-----------------------------------------------|-----------------------------------------------|-------------------------------------------------|-----------------------------------------------|-----------------------------------------------|-------------------------------------------------|
| Dicksonia       | 7.65 (±0.15)                                  | 7.35 (±0.17)                                  | 4                                               | 58 (±2.26)                                    | 50.5 (±0.58)                                  | 13                                              |
| Ginkgo          | 9.5 (±0.25)                                   | 7.38 (±0.34)                                  | 22                                              | 58 (±4.69)                                    | 42.75 (±2.92)                                  | 26                                              |
| Agathis         | 11.37 (±0.24)                                 | 7.35 (±0.03)                                  | 35                                              | 84.75 (±1.66)                                 | 45.75 (±0.55)                                  | 46                                              |

n = 4 in each case, two leaves per plant from two plants were analysed. The standard error for each measurement is indicated in parentheses.
Fig. 1 Volatile compound representative profiles of *Dicksonia*, *Ginkgo* and *Agathis*. Volatile compounds were extracted from dried samples of *Dicksonia* (a), *Ginkgo* (b) and *Agathis* (c) in hexane with an internal standard of butylated hydroxytoluene, and analysed by gas chromatography–mass spectrometry. Peaks representing individual compounds are numbered. Where possible peaks were identified to compounds class level, as in Table 1. More detailed information for individual compounds can be found in Supporting Information Figs S1–S3. Representative profiles selected out of three replicates.
Fig. 2 Flammability and chemistry of species under elevated CO2. Intrinsic flammability of *Dicksonia*, *Agathis* and *Ginkgo* was measured using a microcalorimeter. Heat release capacity (HRC; a), peak heat release rate (pHRR; b), total heat release (THR; c) and temperature of maximum decomposition (temp; d) were recorded. Lignin (e) was measured using the acetyl-bromide method and volatile compounds (f) were measured using gas chromatography–mass spectrometry.
compared to the controls in all tests for each species (P-value of < 0.01 for all species) (see Fig. 2; Table 2).

We found that the abundance of lignin in the leaves declined when grown under elevated CO₂ conditions (Fig. 2e; Table S1). Here, the abundance of lignin decreased by 21% in Dicksonia, declining from a mean of 286.82 mg g⁻¹ to 227.11 mg g⁻¹ under elevated CO₂; 19% in Ginkgo, decreasing from a mean of 300.40 mg g⁻¹ to 242.93 mg g⁻¹, and 25% in Agathis declining from a mean of 147.68 mg g⁻¹ to 111.45 mg g⁻¹. Interestingly however, a P-test and Kruskal–Wallis test confirm that the lignin levels in all species showed no significant difference (P = 0.682 across all species, Kruskal–Wallis test, n = 26) between the two different atmospheric conditions.

Changes in fire behaviour across the Triassic–Jurassic transition

The fuel models and environmental conditions inferred for Triassic plant beds 1 to 4 suggest that the surface rate of spread ranges between 4.1 m min⁻¹ to 5.0 m min⁻¹. Modelled fireline intensity ranges between 1583 kW m⁻¹ to 2016 kW m⁻¹ leading to scorch heights of between 17.0 m and 21.0 m (Table 3). The variations in fire behaviour estimated for these plant beds (Table 3) are driven by changes in inferred dominance of different leaf types in the litter (reflecting the composition of the overstory) and changes in the interpreted abundance of understory live fuels (in this case D. antarctica). This variation of surface fuel types influences the energy that the fuel can give to the fire (its heat content) which together account for the small changes in modelled fire behaviour between plant beds 1 through to 4. For example, Plant bed 1 contains fossil leaves of Podozamites and Ginkgo. Plant bed 2 similarly contains remains of Podozamites and Ginkgo as well as Elatocladus. Plant beds 3 and 4 contain remnants of Podozamites, but are missing Elatocladus and Ginkgo. The modern analogue for Podozamites (A. australis) has a higher heat of combustion (HoC) value than Ginkgo and Elatocladus. This is reflected in the modelled fire behaviour outputs, which yield slightly higher rates of surface fire spread, greater scorch heights and increased fireline intensity within plant beds 3 and 4 when compared to plant beds containing litter fuels with lower HoC values, such as beds 1, 1.5 and 2.

Phase 2 (Triassic plant beds 3, 4 and 5A) (Belcher, 2016) is characterized by a hypothesized plant species richness decline when compared to those of Phase 1. Plant beds 3 and 4 being dominated by Podozamites, and bed 5A Podozamites and Stachyotaxis. Within this phase, there is also a hypothesized loss of the mid-canopy and understory (McElwain et al., 2007; Belcher, 2016), represented by a halving of the live herbaceous fuel load in the fuel models for this phase (see the Materials and Methods section and Table S4 for information). Interestingly, this halving of the live herbaceous fuel load (in the fuel model) appears to have little impact on the modelled fire behaviour outputs, with surface spread rate, fireline intensity and scorch height remaining within a similar range to the phase 1 beds (Fig. 3). Between plant beds 3, 4 and 5A ‘control’, only fuel type is influencing the changes in fire behaviour modelled.

| Vegetation-fire phase (Belcher, 2016) | Plant bed number | Surface spread rate (m min⁻¹) | Fireline intensity (kW m⁻¹) | Scorch height (m) |
|---------------------------------------|------------------|-------------------------------|-----------------------------|--------------------|
| Phase 1                               | Plant bed 1      | 4.4                           | 1816                        | 19.0               |
| Phase 1                               | Plant bed 1.5    | 4.1                           | 1583                        | 17.0               |
| Phase 1                               | Plant bed 2      | 4.4                           | 1819                        | 19.0               |
| Phase 2                               | Plant beds 3 and 4 | 5.0                      | 2016                        | 21.0               |
| Phase 2                               | Plant bed 5A     | 5.2                           | 2206                        | 22.0               |
| Phase 3 (plant bed 5B)                | Scenario (a) ‘Control’ |                          | 3.5 (±4.3)                  | 1003 (±1469) 12.0 (±16.0) |
| Phase 3 (plant bed 5B)                | Scenario (b) [CO₂] effects on heat of combustion (HoC) + lignin only | 3.5 (±4.3)                  | 1003 (±1469) 14.0 (±19.0) |
| Phase 3 (plant bed 5B)                | Scenario (c) [CO₂] effects on HoC, lignin + 4°C increase | 3.5 (±4.3)                  | 1003 (±1469) 18.0 (±24.0) |
| Phase 3 (plant bed 5B)                | Scenario (d) [CO₂] effects on HoC, lignin + 11°C increase | 1.2                         | 158               3.0                |
| Phase 3 (plant bed 5B)                | Scenario (b) [CO₂] effects on HoC + lignin only | 0.9 (±0.9)                   | 98 (±96)                 2.0 (±2.0) |
| Phase 3 (plant bed 5B)                | Scenario (c) [CO₂] effects on HoC, lignin + 4°C increase | 0.9 (±0.9)                   | 98 (±96)                 2.2 (±2.2) |
| Phase 3 (plant bed 5B)                | Scenario (d) [CO₂] effects on HoC, lignin + 11°C increase | 0.9 (±0.9)                   | 98 (±96)                 3.0 (±3.0) |

*The same run but assuming no decrease in lignin content (following Soh et al., 2017). Plant beds 1, 1.5, 2, 3, 4 and 5A model run using a broad-leaved fuel model, that includes an understory TU5, where TU is a Timber Understory fuel model (see Scott & Burgan, 2005). Plant bed 5B run using narrow, needle leaf fuel model TL8, where TL is a timber litter fuel model (see Scott & Burgan, 2005) to capture changes in fuel morphology (Belcher et al., 2010; Belcher, 2016). Plant bed 5A and 5B model runs were conducted under four scenarios: (a) ‘Control’ conditions with no [CO₂] or temperature change effects, only fuel changes; (b) increased [CO₂] effects on heat of combustion (HoC) and lignin content only; (c) increased [CO₂] effects on HoC, lignin content and a 4°C global temperature rise; (d) increased [CO₂] effects on HoC, lignin content and an 11°C local summer temperature rise. For comparison, model run results where no increased [CO₂] effects on lignin content, and therefore no change in decomposition rates (Soh et al., 2017) are also given for plant beds 5A and 5B and are denoted by (*number).
Plant bed 5A ‘control’ is modelled to have the fastest spread rate of 5.2 m min\(^{-1}\), as well as the highest fireline intensity of 2206 kW m\(^{-1}\) and scorch height of 22.0 m, whilst plant bed 5B ‘control’, which accounts for a change in leaf morphology only, is modelled to have the lowest spread rate of 1.2 m min\(^{-1}\); fireline intensity of 158 kW m\(^{-1}\) and scorch height of 3.0 m. By incorporating effects of increased CO\(_2\) on the HoC and lignin content into the models for plant beds 5A and 5B, spread rates, fireline intensity and scorch heights decrease, from 5.2 m min\(^{-1}\) to 3.5 m min\(^{-1}\); 2206 kW m\(^{-1}\) to 1003 kW m\(^{-1}\) and from 22.0 m to 12.0 m in plant bed 5A, respectively, and from 1.2 m min\(^{-1}\) to 0.9 m min\(^{-1}\); 158 kW m\(^{-1}\) to 98 kW m and from 3.0 m to 2.0 m in plant bed 5B, respectively. By increasing the air temperature for beds 5A and 5B, only scorch height is affected, increasing to 18.0 m for bed 5A and 3.0 m for bed 5B with an 11°C increase in air temperature. Removing the effects of lignin content (*number, Table 3), results in slightly higher spread rates, fireline intensity and scorch heights for bed 5A, whilst for bed 5B has no effect on spread rate or scorch height, but decreases the fireline intensity by 2 kW m\(^{-1}\) (Fig. 3). Here, \(P\)-values of < 0.05 (largest being 0.01) confirm that model scenario’s (b), (c) and (d) run for plant bed 5A and scenario’s (a), (b), (c) and (d) for plant bed 5B are statistically significant when compared to the previous modelled fire behaviour for plants beds 1–4.

All results are shown in Table 3 and an example for an increased mid-flame wind speed to 11.2 km h\(^{-1}\) in Table S5.

**Discussion**

**Changes in leaf biochemistry**

The evolution of secretory structures which contain terpenoid compounds is thought to have occurred in gymnosperms (Lange, 2015). Ferns have been documented to contain larger terpenoids (triterpenes and larger), but do not generally produce monoterpenes or sesquiterpenes (Lange, 2015). As such, *D. antarctica* was not found to contain many smaller volatile compounds in either atmospheric treatment (Figs 1, 2). In contrast to the gymnosperm species, *D. antarctica* leaves contained greater levels of long-chain hydrocarbons under elevated CO\(_2\).*
Agathis australis showed a marked decrease in flammability under elevated CO₂. It has been suggested that volatile terpenoid compounds contribute to plant flammability (Varner et al., 2015; Dewhirst et al., 2020); however, lignin levels have been reported to increase under elevated CO₂ (Lindroth, 2010). This was not replicated in the species in this study, which showed no significant difference in lignin levels between the two different atmospheric conditions. Therefore, the major decrease in flammability in A. australis is likely to be driven by a decrease in volatile compounds rather than lignin. As such, we hypothesize that the decrease in volatile compounds, particularly monoterpenes, in A. australis plays a role in the decrease in heat release. While the relatively short duration of this study may represent acclimation rather than adaptation of leaf biochemistry to elevated CO₂, it is reasonable to assume that the adaptive response would be similar to the acclimation response. We found that the abundance of lignin in the leaves declined when grown in elevated CO₂ (Fig. 2e; Table S1). Here, the abundance of lignin decreased by 21% in Dicksonia, 19% in Ginkgo and 25% in Agathis. Lignin content has been reported to have a variable response to elevated CO₂: leaves of Pinus sylvestris (Overdieck & Fenselau, 2009) and Betula pendula Roth (Kostiainen et al., 2006) had decreased lignin content, whereas poplar (Luo & Polle, 2009), Pinus densiflora and Quercus (Park et al., 2018) foliage showed an increase in lignin. It may be that there are different responses between gymnosperms and angiosperms in regard to biochemical variations in response to elevated CO₂. It has been shown that leaf litters containing leaves with lower lignin contents have a faster rate of decomposition than those with higher lignin contents (Wedderburn & Carter, 1999). We would therefore predict that as an example, Podozamites, one of the inferred dominant litter formers in the section, that continues to be present across the TJT, may have seen an increase in its ease of decomposition owing to a likely decrease in lignin due to rising CO₂. Similarly, enhanced temperatures, when in conjunction with a rise in moisture, tend to speed up chemical reactions such that both would tend to lead to lower litter abundances being available to carry surface fires. We note however, that Soh et al. (2017) predicted greater leaf fuel on the ground, based on their estimates of an increase in leaf mass per area across the TJT at Astartekloft.

These results suggest that, if scaled up to the ecosystem level, periods of elevated CO₂ and the resulting influence on heat release may be capable of altering fire behaviour. Hence, it could be hypothesized that CO₂-driven climate changes in the run-up to the TJT may have induced both biochemical (this study) and morphological changes in fuel properties observed across plant beds 5A and 5B (Belcher et al., 2010; Belcher, 2016) capable of influencing fire behaviour.

The TJT provides a good case study for plant responses to a period of warming. Under current climate model projections, rising anthropogenic CO₂ emissions are expected to increase annual temperatures by 3–6°C (Flato et al., 2013), similar to the estimated global average 3–4°C temperature rise across the TJT (McElwain et al., 1999). Hence plant responses during the TJT could provide a useful indicator to future changes in fire behaviour under a warming planet.

Changing surface fire behaviour in the run-up to the TJT

The fire behaviour estimates suggest that fire behaviour may have been more extreme prior to the increase in [CO₂] in the latest Triassic (Table 3). Interestingly, model runs where a decrease in lignin content was not included lead to a smaller decline in surface spread rates fireline intensity and scorch heights when compared to the 5A control run, bringing spread rates, fireline intensity and scorch height to similar levels to pre ‘elevated [CO₂]’ plant bed results. Here, surface spread rates declined by 17%, to 4.3 m min⁻¹, fireline intensity by 33% to 1469 KW m⁻¹ and scorch height by 27% to 16.0 m.

The latest Triassic plant bed 5B results run under ‘control’ conditions (scenario (a) – representing the change in observed leaf morphology to narrow leaved morphotypes and conifers, with limited understory only) show a marked decline in all parameters modelled compared to all previous ‘broad-leaved’ Triassic plant bed model runs (Table 3; Fig. 3). Here, the average surface rate of spread was reduced from 4.4 m min⁻¹ to 1.2 m min⁻¹; average fireline intensity from 1708 kW m⁻¹ to 158 kW m⁻¹ and scorch height from 18.17 m to 3.0 m when compared to plant beds 1 to 5A ‘scenario (b)’ (elevated CO₂ only). As shown in Belcher (2016), these results indicate that a change from broad-leaved fuels with the presence of a fern understory to a narrow-leaved conifer surface fuel with little understory has the ability to alter fire. Here, our results suggest a switch from a period of modelled fast-moving surface fires, with high scorch heights and fireline intensity for plant beds 1 to 5A, to a period of reduced fire spread rates, fireline intensity and scorch heights during the vegetation change in plant bed 5B.

Model runs for plant bed 5B in which the 1 h load was reduced to represent the decline in lignin content and where the heat content was lowered to represent the change in biochemical flammability observed under ‘elevated [CO₂]’ conditions (scenario (b)), results in a further observable decrease in all aspects of fire behaviour when compared to the bed 5B ‘control’ run. Here, the observed decrease in pHRR in all three species tested under elevated CO₂ conditions, is reflected by the further 38% decrease in fireline intensity, 25% decrease in spread rate and 33% decline in scorch height in the ‘elevated [CO₂]’ model run output compared to the control output. This decline in fireline intensity, coupled with a decline in surface fire spread and decline in scorch height observed within our ‘elevated [CO₂]’ fire behaviour output suggests a period of reduced fire spread rate, declining to 0.9 m min⁻¹; fireline intensity, declining to 98 KW m⁻¹ and scorch height, declining to 2.0 m.

Increased mean annual global air temperature of +4°C (McElwain et al., 1999), coupled with elevated [CO₂] influences on heat content and lignin content (scenario (c)), like that observed in plant bed 5A, increased the scorch height from 2.0 m to 2.2 m when compared to the elevated [CO₂] only run (scenario (b)). Interestingly, there is no change in fireline intensity nor the surface spread rate. Moreover, by increasing the temperature to the maximum modelled mean summer temperature of 36°C (Huynh & Poulsen, 2005) (scenario (d)), scorch height further increases to 3.0 m for bed 5B, owing to drier canopy fuels.
Interestingly, unlike in plant bed 5A, removing the effects of ‘elevated \([\text{CO}_2]\)’ on lignin contents has little effect on the modelled outputs, with no change in surface spread rate nor scorched height, and a decline of just 2 kW m\(^{-1}\) in fireline intensity throughout each of the ‘elevated \([\text{CO}_2]\)’ runs.

Our results show that the effects of increased \(\text{CO}_2\) on the heat of combustion and lignin content, appear to have a measurable influence on modelled fire behaviour; where with increasing atmospheric \(\text{CO}_2\), surface spread rate, fireline intensity and scorched height are reduced between 25–33\%, 38–55\% and 40–45\%, respectively, in both plant beds 5A and 5B. Whilst altering the chemical parameters in the model runs (control vs \([\text{CO}_2]\) scenarios for both plant beds) did induce additional reductions in modelled surface spread rate, fireline intensity and scorched height by 3\%, 3\% and 11\%, respectively, these shifts appear smaller than those induced by shifts in leaf morphology alone (control plant bed 5A vs control plant bed 5B) which displayed reductions of 77\%, 93\% and 86\%, respectively. These results highlight that changes in plant chemical composition may likely have an impact on fire behaviour under rising \(\text{CO}_2\) concentrations, even where leaf morphology does not change, although, changes in leaf morphology do appear to be the dominant driver in altering modelled fire behaviour.

Current predictions for changes in fire regime under a warming climate, primarily focus on three aspects; (1) changes in fuel conditions, such as warmer, drier weather reducing moisture content of fuels, (2) the volume, structure and type of fuel available to burn, and (3) ignitions (Hessl, 2011; Flannigan et al., 2013; Keeley & Syphard, 2016). Using these, our modelling study results predict a general increase in rate of modelled fire spread, fire intensity and a lengthening of the fire season under a 2 \(\times\) \(\text{CO}_2\) climate (Hessl, 2011), in Canadian boreal forests (de Groot et al., 2013), the Mediterranean (e.g. Mouillot et al., 2002), the western United States (Brown et al., 2004), Australia (Cary, 2002), and forest-tundra (Abbott et al., 2016). Additionally, model simulations predict increased fuel consumption in boreal regions under increased \(\text{CO}_2\)-driven climates, with higher forest floor and crown fuel consumption rates in both western Canada and central Russia, although Russia is expected to see a much smaller increase when compared with current day climate conditions (de Groot et al., 2013).

However, the relationship between global warming and shifts in fire regimes is not simple, and has been shown to vary at regional levels depending on vegetation type and ignition probability. For example, Keeley & Syphard (2016) highlight that landscapes at lower elevation and latitudes show no or very little increase in fire activity, despite projected warmer, drier conditions due to limited ignitions. Additionally, Pausas & Paula (2012) conclude that fuel structure is more relevant than climate conditions in driving fire activity changes under Mediterranean climate conditions. Girardin et al. (2013) and Foster et al. (2022) highlight that changes in climate driven plant composition may in fact mitigate against the increase in fire frequency driven by climate change.

Keeley & Syphard (2016) suggest that the effects of rising \(\text{CO}_2\) on plants can further complicate fire regime predictions. For example, plants shift their optimum temperature for photosynthesis under elevated \(\text{CO}_2\) conditions, thus increasing productivity (Pausas & Paula, 2012). Furthermore, elevated \(\text{CO}_2\) concentrations have been found to increase water use efficiency, helping to protect some plants from drought, and increasing effective precipitation (Charney et al., 2016). Equally, fire events themselves led to increased water use efficiency inPinus halepensis (Battipaglia et al., 2014), demonstrating a complex relationship between these factors.

Our results highlight that although climate and weather are known to play key roles in determining fire activity, and may increase modelled scorched heights under high \(\text{CO}_2\) conditions (e.g. our model scenario (c)); morphological and intrinsic fuel properties are equally important when considering the effects of rising \(\text{CO}_2\) on fire behaviour, and may actually lead to a reduction in fire spread rates and intensity in certain types of vegetation. Our results demonstrate that a coupled approach that incorporates variations in plant morphology and biochemistry, is essential if we are to predict both past and future shifts in fire regimes to changing climates and \(\text{CO}_2\) concentrations.

Conclusion

Our results show that although leaf morphology may likely be the primary driving force behind changes in fire behaviour, \(\text{CO}_2\)-driven changes in leaf intrinsic flammability has an additional measurable impact on modelled fire behaviour that may be capable of lowering scorched heights by up to 45\%. This coupled approach indicates that accounting for variations in plant morphological and chemical traits in models is essential when considering shifts in fire regimes. It is clear that interpretations based solely on the abundances of fossil charcoal will lead to errors in the understanding of palaeofire regimes and the palaeoecological impacts of fire. But this also indicates the importance of considering how current climatic change may influence the biochemical properties of plants that relate to flammability. Additional species and a range of plant groups should be assessed to determine whether or not \(\text{CO}_2\) enrichment has the possibility to alter biochemical plant traits and how this might impact on Earth’s future fire regimes.

Acknowledgements

CMB, RAD and SJB acknowledge funding via a European Research Council (ERC) Starter Grant (ERC-2013- StG-335891-ECOFIAML) awarded to CMB. CMB, MH, JCM, acknowledge funding through a European Union Marie Curie Excellence Grant (MEXT-CT-2006-042531), awarded to JCM. CMB acknowledges funding via the Natural Environment Research Council (NERC) (grant no. NE/N018508/1). Open access funding enabled and organized by ProjektDEAL.

Author contributions

CMB designed the research. JCM, MH, CMB and RAD carried out the data collection and analysis. RAD undertook the
chemical analyses. CMB undertook the flammability experiments. SJB undertook the fire behaviour modelling. SJB and RAD contributed equally to the writing of the manuscript and interpretation of the data. All authors contributed to writing and editing the manuscript.

ORCID
Sarah J. Baker https://orcid.org/0000-0002-9172-0729
Rebecca A. Dewhirst https://orcid.org/0000-0001-8651-2426
Matthew Haworth https://orcid.org/0000-0002-3225-6620
Jennifer C. McElwain https://orcid.org/0000-0002-1729-6755

Data availability
The data that support the findings of this study are openly available in Dryad, doi: 10.5061/dryad.tb2rbp033.

References
Abbott BW, Jones JB, Schuur EAG, Chapin FS III, Bowden WB, Bret-Harte MS, Epstein OE, Flannigan MD, Harms TK, Hollingsworth TN et al. 2016. Biomass offsets little or none of permafrost carbon release from soils, streams, and wildfire: an expert assessment. Environmental Research Letters 11: 34014.
Andrews PL. 2010. BehavePlus fire modelling system, v.5.0: variables. General technical report RMRS-GTR-213WWW. Fort Collins, CO, USA: USDA Forest Service, Rocky Mountain Research Station.
Andrews PL. 2014. Current status and future needs of the BehavePlus Fire Modeling System. International Journal of Wildland Fire 23: 21–33.
Battaglia G, De Micco V, Fournier T, Aronne G, Carcaillet C. 2014. Isotopic and anatomical signals for interpreting fire-related responses in Pinus halepensis. Trees – Structure and Function 28: 1095–1104.
Belcher CM. 2013. Fire phenomena and the earth system. West Sussex, UK: Wiley-Blackwell Press, 288–308.
Belcher CM. 2016. The influence of leaf morphology on litter flammability and its utility for interpreting palaeofire. Philosophical Transactions of the Royal Society of London. Series B: Biological Sciences 371: 20150163.
Belcher CM, Hudspith VA. 2017. Changes to Cretaceous surface fire behaviour influenced the spread of the early angiosperms. New Phytologist 213: 1521–1532.
Belcher CM, Mander I, Rein G, Jervis FX, Haworth M, Hessellbo SP, Glasspool JJ, McElwain JC. 2010. Increased fire activity at the Triassic/Jurassic boundary in Greenland due to climate-driven floral change. Nature Geoscience 3: 1–4.
Berry J, Bjorkman O. 1980. Photosynthetic response and adaptation to temperature in higher plants. Annual Review of Plant Physiology. 31: 491–543.
Brown TJ, Hall BL, Westerling AL. 2004. The impact of twenty-first century climate change on wildfire fire danger in the Western United States: an applications perspective. Climatic Change 62: 365–388.
Cary G. 2002. Importance of a changing climate for fire regimes in Australia. In: Bradstock RA, Williams JE, Gill MA, eds. Flammable Australia: the fire regimes and biodiversity of a continent. Cambridge, UK: Cambridge University Press, 26–46.
Charnzey ND, Babar F, Poulter B, Record S, Trouet VM, Frank D, Enquist BJ, Evans MEK. 2016. Observed forest sensitivity to climate implied large changes in 21st century North American forest growth. Ecology Letters 19: 1119–1128.
Crawford AJ, Belcher CM. 2016. Area–volume relationships for fossil charcoal and their relevance for fire history reconstruction. The Holocene 26: 822–826.
De Lillis M, Bianco PM, Loreto F. 2009. The influence of leaf water content and isoprenoids on flammability of some Mediterranean woody species. International Journal of Wildland Fire 18: 203–212.

Dewhirst RA, Smirnoff N, Belcher CM. 2020. Pine species that crown fire regimes have lower leaf-level terpene contents than those native to surface fire regimes. Fire 3: 17.
Feng Z, Yuan X, Fares S, Loreto F, Li P, Hoshika Y, Paolletti E. 2019. Isoprene is more affected by climate drivers than monoterpenes: a meta-analytic review on plant isoprenoid emissions. Plant, Cell & Environment 42: 1939–1949.
Flannigan M, Cantin AS, de Groot WJ, Wotton M, Newbery A, Gowman LM. 2013. Global wildland fire season severity in the 21st century. Forest Ecology and Management 294: 54–61.
Flato G, Marotzke J, Abiodun B, Braconnot P, Chou SC, Collins W, Cox PM, Driouech F, Emori S, Eyring V et al. 2013. Evaluation of climate models. Chapter 9 in climate change 2013: the physical science basis, evaluation of climate models. In: Climate Change 2013: the physical science basis. Contribution of working group I to the fifth assessment report of the Intergovernmental Panel on Climate Change. Cambridge, UK: Cambridge University Press, 741–866.
Foster AC, Shuman JK, Rogers BM, Walker XJ, Mack MC, Bourgeau-Chevey LL, Varavebeke S, Goetz SJ. 2022. Bottom-up drivers of future fire regimes in western boreal North America. Environmental Research Letters 17: 25006.
Fowell SJ, Olsen PE. 1993. Time calibration of Triassic/Jurassic microfossil turnover, eastern North America. Teichonophy 222: 361–369.
Girardin MP, Ali AA, Carcarillier C, Blarquez O, Hely C, Terrier A, Genries A, Bergeron Y. 2013. Vegetation limits the impact of a warm climate on boreal wildfires. New Phytologist 199: 1001–1011.
de Groot WJ, Flannigan MD, Cantin AS. 2013. Climate change impacts on future boreal fire regimes. Forest Ecology and Management 294: 35–44.
Harris TM. 1935. The fossil flora of Scrosby Sound, East Greenland, part 4. Ginkgales, Lycopodiales and isolated frutications. Meddeleler Om Gronland 112: 1–21.
Harris TM. 1957. A liasso-thaetie flora in South Wales. Proceedings of the Royal Society London. Series B: Biological Sciences 147: 289–308.
Harris TM. 1958. Forest fire in the Mesozoic. Journal of Ecology 46: 447–453.
Haworth M, Belcher CM, Kilili D, Dewhirst RA, Materassi A, Raschi A, Centritto M. 2018. Impaired photosynthesis and increased leaf construction costs may induce floral stress during episodes of global warming over macroevolutionary timescales. Scientific Reports 8: 1–14.
Head A. 2011. Pathways for climate change effects on fire: models, data, and uncertainties. Progress in Physical Geography: Earth and Environment 35: 393–407.
Holopainen JK, Virjamo V, Ghimire RP, Blande JD, Julkunen-Titro T, Kiviinpani M. 2018. Climate change effects on secondary compounds of forest trees in the Northern hemisphere. Frontiers in Plant Science 9: 1445.
Hudspith VA, Belcher CM. 2017. Fire biases the production of charred flowers: Implications for the Cretaceous fossil record. Geology 45: 727–730.
Hudspith VA, Hadden RM, Bartlett AI, Belcher CM. 2017. Does fuel type influence the amount of charcoal produced in wildfires? Implications for the fossil record. Palaeontology 61: 159–171.
Hummel J, Selbig J, Walther D, Kopka J. 2007. The Golm metabolome database: a database for GC-MS based metabolite profiling. Topics in Current Genetics 18: 75–95.
Huynh TT, Poulsen CJ. 2005. Rising atmospheric CO2 as a possible trigger for the end-Triassic mass extinction. Palaeogeography, Palaeoclimatology, Palaeoecology 217: 223–242.
Kainulainen P, Holopainen JK, Holopainen T. 1998. The influence of elevated CO2 and O3 concentrations on Scots pine needles: changes in starch and secondary metabolites over three exposure years. Oecologia 114: 455–460.
Keeley JE, Pyrath AD. 2016. Historical patterns of wildfire ignition sources in California ecosystems. International Journal of Wildland Fire 27: 781–799.
Kostainen K, Jalkanen H, Kaakinen S, Saranpää P, Vapaavuori E. 2006. Wood properties of two silver birch clones exposed to elevated CO2 and O3. Global Change Biology 12: 1230–1240.
Lange BM. 2015. The evolution of plant secretory structures and emergence of terpenoid chemical diversity. Annual Review of Plant Biology 66: 139–159.
Lindroth RL. 2010. Impacts of elevated atmospheric CO2 and O3 on forests: phytochemistry, trophic interactions and ecosystem dynamics. 2010. Journal of Chemical Ecology 36: 2–21.
Luo Z-B, Polle A. 2009. Wood composition and energy content in a poplar short rotation plantation on fertilized agricultural land in a future CO2 atmosphere. Global Change Biology 15: 38–47.
Marynowski L, Simonneit BR. 2009. Widespread Upper Triassic to Lower Jurassic wildfire records from Poland: evidence from charcoal and pyrolytic polycyclic aromatic hydrocarbons. Palaeontologia Polonica 24: 785–798.

McElwain JC, Beerling DJ, Woodward FI. 1999. Fossil plants and global warming at the Triassic–Jurassic boundary. Science 285: 1386–1390.

McElwain JC, Popa ME, Hesselbo SP, Haworth M, Suriłk F. 2007. Macroecological responses of terrestrial vegetation to climatic and atmospheric change across the Triassic/Jurassic boundary in East Greenland. Palaeobiology 33: 547–573.

Moreira-Vilar FC, de Cásia Siqueira-Soares R, Figueiro-Teixeira A, Matias de Oliveira D, Paula FA, Jackson da Rocha G, Ferrarese ML, Dantas dos Santos W, Ferrarese-Filho O. 2014. The acetyl bromide method is faster, simpler and presents best recovery of lignin in different herbaceous tissues than Klasson and thiglycolic acid methods. PLoS ONE 9: e100000.

Mouillot F, Rambal S, Joffre R. 2002. Simulating climate change impacts on fire frequency and vegetation dynamics in a Mediterranean-type ecosystem. Global Change Biology 8: 423–437.

Overdieck D, Fenselau K. 2009. Elevated CO2 concentration and temperature effects on the partitioning of chemical components along juvenile Scots pine stems (Pinus sylvestris L.). Trees 23: 771–786.

Owens MK, Lin CD, Taylor CA, Whisenant SG. 1998. Effect of elevated CO2 concentration and temperature on plant growth and herbivore defensive chemistry. Global Change Biology 4: 725–735.

Park HJ, Lim SS, Kwak JH, Yang HI, Lee KS, Lee YH, Kim HY, Choi WJ. 2018. Elevated CO2 concentration affected pine and oak litter chemistry and the respiration and microbial biomass of soils amended with these litters. Biology and Fertility of Soils 54: 583–594.

Pausas JG, Alessio GA, Moreira B, Segurra-Moragues JG. 2016. Secondary compounds enhance flammability in a Mediterranean plant. Oecologia 180: 103–110.

Pausas JG, Paula S. 2012. Fuel shapes the fire–climate relationship: evidence from Mediterranean ecosystems. Global Ecology and Biogeography 21: 1074–1082.

Peltonen PA, Vapaavuori E, Julkunen-titto R. 2005. Accumulation of phenolic compounds in birch leaves is changed by elevated carbon dioxide and ozone. Global Change Biology 11: 1305–1324.

Peñuelas J, Estiarte M, Lliusa J. 1997. Carbon-based secondary compounds at elevated CO2. Phytosymbiosis 2: 313–316.

Petersen HI, Linnström S. 2012. Synchronous wildfire activity rise and mire deforestation at the Triassic–Jurassic boundary. Palaeogeography, Palaeoclimatology, Palaeoecology 308: 418–432.

Stiling P, Cornelissen T. 2007. How does elevated carbon dioxide (CO2) affect plant-herbivore interactions? A field experiment and meta-analysis of CO2-mediated changes on plant chemistry and herbivore performance. Global Change Biology 13: 1823–1842.

Valer T, Ormeño E, Casals P. 2017. Temporal effects of prescribed burning on terpene production in Mediterranean pines. Tree Physiology 37: 1622–1636.

Varner JM, Kane JM, Kreye JK, Engber E. 2015. The flammability of forest and woodland litter: a synthesis. Current Forestry Reports 1: 91–99.

Veteli TO, Kuokkanen K, Julkunen-Titto R, Roininen H, Tavanaininen J. 2002. Effects of elevated CO2 and temperature on plant growth and herbivore defensive chemistry. Global Change Biology 8: 1240–1252.

Ward PD, Haggart JW, Carter ES, Willbur D, Tipper HW, Evans T. 2001. Sudden productivity collapse associated with the Triassic–Jurassic boundary mass extinction. Science 292: 1148–1151.

Wedderburn ME, Carter J. 1999. Litter decomposition by four functional tree types for use in silvopastoral systems. Soil Biology and Biochemistry 31: 455–461.

Wright IJ, Reich PB, Westoby M, Ackerly DD, Baruch Z, Bongers F, Cavender-Bares J, Chapin T, Cornelissen JHC, Diemer M et al. 2004. The worldwide leaf economics spectrum. Nature 428: 821–827.

Zvereva EL, Kodov MV. 2005. Consequences of simultaneous elevation of carbon dioxide and temperature for plant-herbivore interactions: a meta-analysis. Global Change Biology 12: 27–41.

Supporting Information

Additional Supporting Information may be found online in the Supporting Information section at the end of the article.

Fig. S1 Agathis replicate GC profiles.

Fig. S2 Dicksonia replicate GC profiles.

Fig. S3 Ginkgo replicate GC profiles.

Notes S1 Details of construction of fuel models for the TJT ecosystems at Astartekloft.

Table S1 Flammability test results.

Table S2 Volatile compound identification as detected by GC–MS.

Table S3 Number of dominant litter-forming conifer morphotypes within each plant bed.

Table S4 Numerical description of the fuel model and parameters used for each of the plant beds modelled.

Table S5 BEHAVEplus model run results adjusted for varying parameters.