





## Environmentally persistent free radicals are ubiquitous in wildfire charcoals and remain stable for years

Gabriel Sigmund <sup>1</sup>, Cristina Santín <sup>2,3</sup>, Marc Pignitter <sup>4</sup>, Nathalie Tepe<sup>1</sup>, Stefan H. Doerr <sup>5</sup> & Thilo Hofmann <sup>1</sup>✉

Globally landscape fires produce about 256 Tg of pyrogenic carbon or charcoal each year. The role of charcoal as a source of environmentally persistent free radicals, which are precursors of potentially harmful reactive oxygen species, is poorly constrained. Here, we analyse 60 charcoal samples collected from 10 wildfires, that include crown as well as surface fires in forest, shrubland and grassland spanning different boreal, temperate, subtropical and tropical climate. Using electron spin resonance spectroscopy, we measure high concentrations of environmentally persistent free radicals in charcoal samples, much higher than those found in soils. Concentrations increased with degree of carbonization and woody fuels favoured higher concentrations. Moreover, environmentally persistent free radicals remained stable for an unexpectedly long time of at least 5 years. We suggest that wildfire charcoal is an important global source of environmentally persistent free radicals, and therefore potentially of harmful reactive oxygen species.

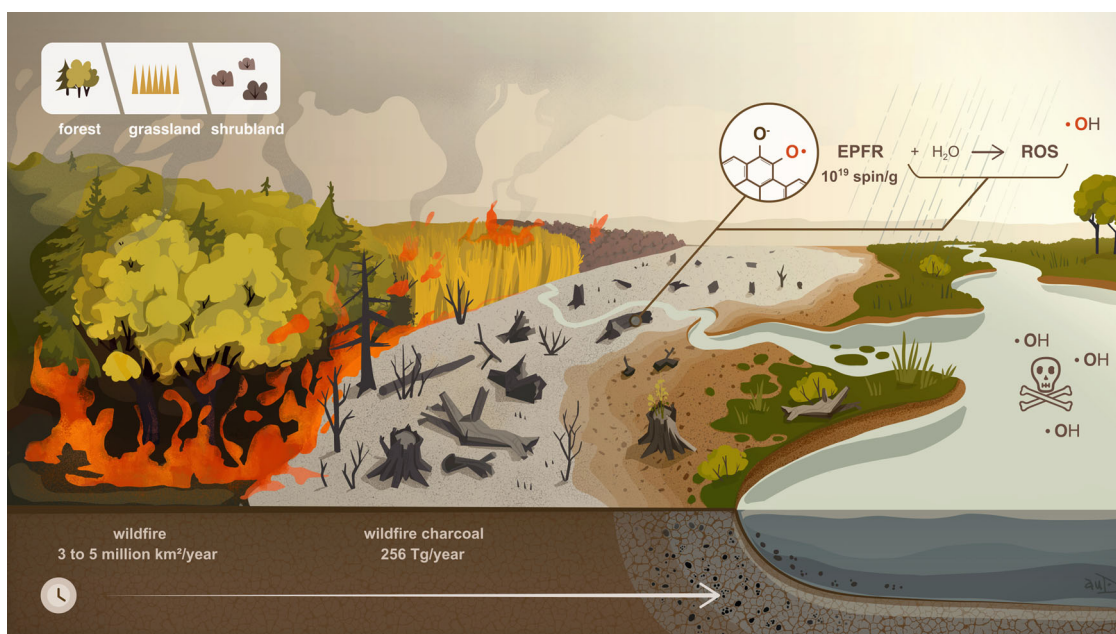
<sup>1</sup>Environmental Geosciences, Centre for Microbiology and Environmental Systems Science, University of Vienna, Wien, Austria. <sup>2</sup>Department of Biosciences, Swansea University, Swansea, UK. <sup>3</sup>Research Unit of Biodiversity (CSIC, UO, PA), Spanish National Research Council, Mieres, Spain. <sup>4</sup>Faculty of Chemistry, Department of Physiological Chemistry, University of Vienna, Wien, Austria. <sup>5</sup>Department of Geography, Swansea University, Swansea, UK. ✉email: [thilo.hofmann@univie.ac.at](mailto:thilo.hofmann@univie.ac.at)

Landscape fires (i.e., wildfires, land management fires, and agricultural burns) affect 3–5 million km<sup>2</sup> annually around the world, burning ~4% of Earth's vegetated land surface<sup>1</sup>. As a result of incomplete combustion, part of the biomass burnt during fire is transformed into charcoal (also known as pyrogenic carbon)<sup>2</sup>. The proportion of burnt biomass converted into charcoal is highly variable, and ranges from negligible up to 30%, depending on the characteristics of the vegetation and the fire itself<sup>3</sup>. Landscape fires have recently been estimated to produce about 256 Tg/year of charcoal globally, equivalent to 12% of the total carbon released by these fires<sup>4</sup>. Charcoal is more resistant to degradation than unburned biomass and can be preserved in soils, waters, and sediments for centuries to millennia<sup>2</sup>. About 200 Pg of charcoal is estimated to be stored globally in surface soils<sup>5</sup> and 480–1440 Pg in marine sediments<sup>6</sup>.

Wildfire charcoal is ubiquitous in many landscapes around the world and a comprehensive understanding of its effects on the climate system, ecosystem function, and environmental health is therefore fundamental. The impacts of charcoal on carbon and nutrient cycles have been widely investigated<sup>7</sup>, as well as its role as a source of pollutants such as polycyclic aromatic hydrocarbons<sup>8</sup>. There is, however, no information available to date concerning its potential as a source of environmentally persistent free radicals (EPFRs). In contrast to other free radicals with lifetimes in the range of microseconds to milliseconds, EPFRs can remain stable for prolonged periods of time (typically days to months) and are bound to particle surfaces. This makes them highly susceptible to redistribution within, and having impacts on, the natural environment<sup>9–11</sup>. EPFRs have recently been proposed as a new class of contaminant<sup>12</sup> because they can undergo a variety of reactions with water to form reactive oxygen species (ROS)<sup>13,14</sup>, which can have detrimental effects on ecosystem functions (see Fig. 1). EPFRs containing particles have thus been linked to adverse impacts on biological systems, including inhibition of plant germination<sup>15,16</sup>, reduced enzymatic activity<sup>17</sup>, cytotoxicity to single cells<sup>18</sup>, toxic effects on both bacteria<sup>19</sup>, and aquatic invertebrates<sup>20,21</sup>. Therefore, the presence

of EPFRs in charcoal and the subsequent formation of ROS may lead to yet unexplored effects on ecosystem functions and human health. For example, in the context of post-fire erosion and transport of wildfire charcoal into water bodies<sup>22</sup>.

No measurements of EPFRs have been reported from wildfire charcoals to date, but high EPFR concentrations have previously been reported in human-derived pyrogenic products; for example, in particulate matter (PM) from fossil fuel combustion<sup>23</sup> and biochar<sup>14</sup>, a man-made product of pyrolysis with some similarities to charcoal but produced under industrial conditions<sup>24,25</sup>. There is currently no information available concerning the stability of charcoal-bound EPFR in natural environments but, under laboratory conditions, EPFRs in biochars were shown to remain stable for months<sup>10,12</sup>. Based on these observations, we hypothesized that EPFRs would also be present in wildfire charcoal, with EPFR concentration being affected by fire conditions, type of fuel, and time since fire. To test this hypothesis across a variety of charcoal types, we analysed the EPFR content of 60 charcoal samples collected in different regions of the world from ten wildfires (crown fires and surface fires) in a range of ecosystems (forest, shrubland, and grassland) and climatic regions (boreal, temperate, tropical, and subtropical). In addition, different sized charcoal particles were also analysed, as well as charcoal derived from different types of feedstocks (e.g., wood, leaf litter, grass). Furthermore, to assess the stability of charcoal EPFRs in natural environments, we also included samples collected at different times after fire (aged 0–5 years) (Tables 1 and S1). We found that all charcoals analysed via electron spin resonance (ESR) spectroscopy have high concentrations of EPFRs (10<sup>18</sup> to 10<sup>19</sup> spin/g; every spin/g corresponds to a free electron/g), orders of magnitude higher than those previously reported for soils and airborne PM<sup>12</sup>. EPFR concentrations were related to charcoal carbonization degree, which in turn is determined largely by the type of fuel material (feedstock) and charring conditions. We also observe that EPFR concentrations in charcoal remained stable for an unexpectedly long time of at least 5 years.



**Fig. 1 Schematic overview on wildfire-produced charcoal and the related distribution of environmentally persistent free radicals (EPFRs).** Wildfires, including forest-, grassland-, and shrubland fires, globally form 256 Tg of wildfire charcoal every year<sup>4</sup>. Wildfire charcoal contains environmentally persistent free radicals, which can lead to the formation of reactive oxygen species (ROS), such as hydroxyl radicals (•OH) when in contact with water, where ROS may induce adverse effects.

**Table 1 Wildfire charcoal samples investigated.**

Fire ID	Sample type	Climatic region	Location	Ecosystem	Vegetation (feedstock)	Fire type	$T_{max}$ (°C)	Charring duration (s)
1	Woody	Boreal	NW Canada	Forest	Pine wood	Crown fire	1002	80–570
2 <sup>48</sup>	Woody	Humid temperate	SE Australia	Forest	Eucalypt wood	Crown fire	*800	*80–160
3 <sup>49</sup>	Woody	Humid temperate	SE Australia	Forest	Eucalypt wood	Crown fire	*850	*80–160
4 <sup>26</sup>	Woody	Humid temperate	SE Australia	Forest	Eucalypt wood	Surface fire	803	80–160
5 <sup>48</sup>	Woody	Humid temperate	SE Australia	Forest	Eucalypt wood	Surface fire	*700	*80–160
6	Woody	Subtropical	NE South Africa	Grassland	Clusterleaf wood	Surface fire	851	7200
7	Woody	Mediterranean	W Australia	Forest	Eucalypt wood	Surface fire	851	>7200
8	Woody	Boreal	Central Sweden	Forest	Pine wood	Surface fire	*800	*200
1	Fines	Boreal	NW Canada	Forest	Litter	Crown fire	976	65–364
4 <sup>26</sup>	Fines	Humid temperate	SE Australia	Forest	Litter	Surface fire	889	40–680
6	Fines	Subtropical	NE South Africa	Grassland	Grass	Surface fire	918	19–139
9	Fines	Mediterranean	NW Spain	Shrubland	Gorse/heath	Shrub fire	920	100–410
10	Fines	Humid temperate	NE England	Shrubland	Heath	Shrub fire	*900	*100–400

Woody = woody charcoal; fines = fine-size charcoal. Where previous work on a fire is published, this is indicated next to the relevant Fire ID. Maximum temperature recorded ( $T_{max}$ ) and charring duration (duration of temperature >300 °C). Values with an asterisk are estimates because no direct measurements were available; in this case, measured values from the most similar experimental fires were given. More information regarding charcoal formation conditions (location, vegetation, fire characteristics, sampling time, temperature measurement, etc.) can be found in Table S1.

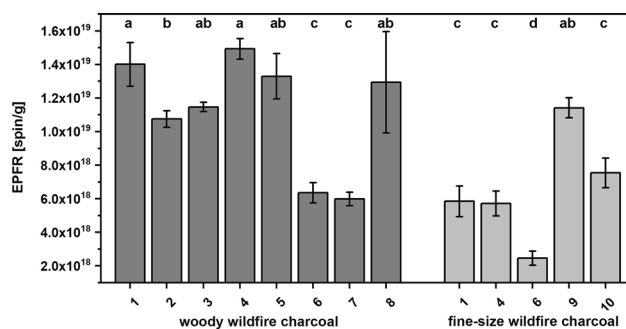
## Results and discussion

**High concentrations of EPFRs in wildfire charcoals.** All samples analysed contained notable EPFR concentrations (ranging from  $2.46 \times 10^{18}$  to  $1.49 \times 10^{19}$  spin/g, Fig. 2) that were orders of magnitude higher than those previously reported for soils and airborne PM ( $\sim 10^{16}$  to  $10^{17}$  spin/g)<sup>12</sup>. Concentrations in woody charcoal were generally at the upper end of the range of EPFR concentrations reported for woody biochars<sup>10,26,27</sup>.

A positive relationship has been reported between the concentration of transition metal oxides in biochar and EPFRs formation, with a charge transfer between the aromatic structures of biochars and transition metal oxides identified as an important mechanism in EPFRs formation<sup>14,28–30</sup>. We found no such correlation in our data between transition metal content and EPFRs formation (Fig. S1, Electronic Supplementary Material), which may be due to the different formation conditions of charcoal and biochar, as discussed in the next section. Therefore, other factors such as the charring duration and fuel/feedstock properties also need to be considered to better understand EPFRs formation in wildfire charcoal.

**EPFR abundance depends on carbonization.** A positive relationship was found between the EPFR abundance in wildfire charcoal samples and their carbon content (Fig. 3a, Pearson's  $R = 0.83$ ,  $p < 0.05$ ), and a negative relationship with their molar O/C ratio (Fig. 3b, Pearson's  $R = -0.80$ ,  $p < 0.05$ ). These two parameters are indicators of the degree of carbonization, with the degree of carbonization increasing with higher carbon contents and lower molar O/C ratios<sup>31</sup>. This indicates that the degree of carbonization is a determining factor for the different EPFR concentrations observed in wildfire charcoal samples. The degree of carbonization is a function of both the properties of the original fuel material (i.e. feedstock), and formation conditions (i.e., temperature, duration, and oxygen availability)<sup>32</sup>.

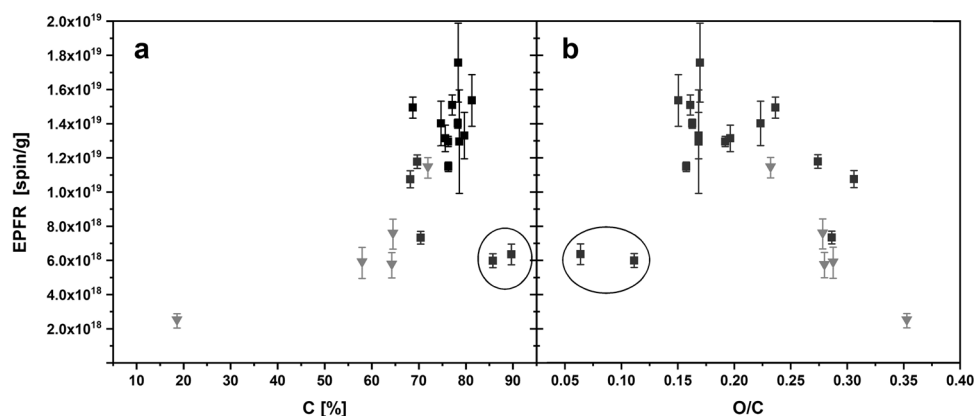
Regarding type of original fuel material, carbonization during wildfires is generally higher for woody fuels than for fine materials such as leaves or plant litter, which usually burn more completely because of their larger surface area per unit volume<sup>3,33</sup>. In addition, the high lignin content of woody materials also leads to them experiencing less complete combustion during charring<sup>34</sup>. Furthermore, the pyrolysis of lignin is reported to result in a higher concentration of EPFRs than the pyrolysis of cellulose<sup>10</sup>. All these factors have probably contributed to the higher EPFR concentrations observed in woody



**Fig. 2 Distribution of environmentally persistent free radicals in charcoal samples.** Environmentally persistent free radical concentrations (spin/g) in woody wildfire charcoal (dark grey) and fine-size wildfire charcoal (light grey) collected within the first year after a fire. Error bars represent standard deviation. Different lower-case letters at the top of the bars indicate statistical differences, with  $p < 0.05$ . All samples were analysed in triplicate. Numbers along the X-axis refer to the fire IDs in Table 1.

charcoals than in fine-size charcoal for the range of samples measured in this study (Fig. 2). Both the degree of carbonization as well as the aromaticity of the original fuel material (e.g., linked to lignin content) can be linked to the size of aromatic clusters within the wildfire charcoal. These aromatic clusters are likely responsible for the stability of EPFRs<sup>26</sup>.

For most samples, produced under flaming conditions, the charring duration (i.e. the time above 300 °C)<sup>34</sup> was relatively short, ranging between 80 and 680 s. For these samples, the trends described above were consistently observed when applying ESR spectroscopy to quantify EPFRs. This measurement also included the determination of  $g$ -factors. The  $g$ -factor is a characteristic value for the EPFR paramagnetic centre's electronic structure. It can thus be used to characterize the neighbouring chemical structure of the EPFR. All measured samples had a  $g$ -factor value of  $2.0032 \pm 0.0003$ , which indicates that the EPFRs were associated with oxygen-containing functional groups ( $n = 57$ , Table S2 and Fig. S2 in the Supplementary Material). Oxygen-centred EPFRs are stable in the air, whereas carbon-centred EPFRs are not<sup>26</sup>, which may explain why only oxygen-centred EPFRs were measured in all samples. It is possible that C-centred EPFRs indirectly formed O-centred EPFRs during their degradation. However, we have not identified any evidence that would confirm

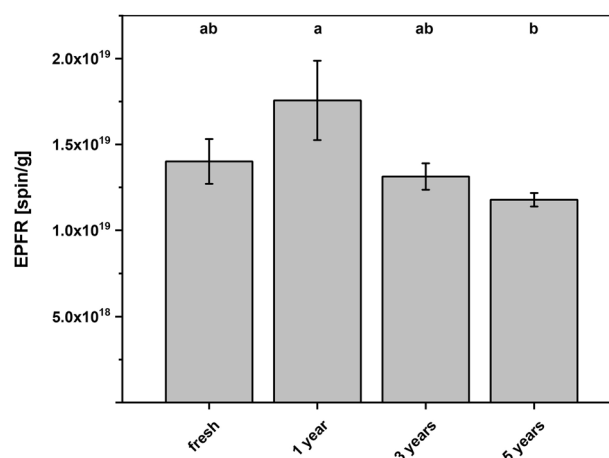


**Fig. 3 The degree of carbonization is related to measured concentrations of environmentally persistent free radicals.** The abundance of environmentally persistent free radicals increased with increasing carbon content (**a**, Pearson's  $R = 0.83$ ,  $p < 0.05$ ) and decreased with increasing molar oxygen to carbon ratios (**b**, Pearson's  $R = -0.80$ ,  $p < 0.05$ ), both of which are proxies for the degree of carbonization. Black blocks (■) represent woody charcoal, grey triangles (▼) represent fine-size wildfire charcoal. Woody charcoal samples 6 and 7 (circled) were excluded from the correlation analysis because of the distinctive formation conditions for these two samples (smouldering for prolonged periods of time rather than flaming combustion, see Table S1). Error bars represent standard deviation.

this hypothesis. Two samples were obtained from burnt logs after smouldering combustion instead of flaming combustion (Table S1). For these two samples, the charring duration was more than 7200 s (Table S1). As shown in Fig. 2, they report some of the lowest EPFR concentrations despite having the highest degrees of carbonization (i.e. highest C% and lowest O/C; Fig. 3). We hypothesize the prolonged exposure to high temperatures caused an extremely high degree of carbonization and loss of oxygen surface functional groups, which in turn decreased the EPFR concentrations. This is in good agreement with previous studies on biochars<sup>35</sup> and PM including soot<sup>36</sup>, which report reduced EPFR concentrations at very high degrees of carbonization. These results suggest that EPFR formation during both wildfires and biochar production can be expressed as a bell-shaped curve, with EPFR concentrations first increasing with the degree of carbonization (as most charcoal samples here), but subsequently decreasing following further carbonization, as reported for highly carbonized biochars<sup>29,35,37</sup> and the two smouldering charcoal samples here. It is worth highlighting that, of all samples examined in our study, these latter two charcoal samples are the most similar to biochar, in terms of the prolonged heating times compared to wildfire charcoal<sup>24</sup>.

In addition, to assess if the degree of carbonization depends on the particle size of the feedstock, we analysed woody charcoal particles in four different sizes classes (i.e., 0.5–1.0, 1.5–2.0, 2.5–3.0, and >5 cm) produced from the same original feedstock material (*Pinus sylvestris*) in the same fire (Swedish boreal forest fire: Fire ID 8 in Table 1). The EPFR concentrations tended to increase with increasing particle size, but the differences between the samples were small ( $p = 0.10$ , Fig. S3 in the Supplementary Material). Larger particles were very probably derived from larger pieces of wood, which in turn are likely to burn for longer periods of time and hence would be more highly carbonized, as indicated by a slight decrease in the molar O/C ratios from  $0.19 \pm 0.01$  for pieces in the 0.5–1.0 cm size range to  $0.16 \pm 0.01$  for pieces >5 cm.

**EPFRs in wildfire charcoal remain stable for years.** To explore the in situ stability of EPFRs in wildfire charcoal aged in natural environments, samples from the Canadian boreal forest fire (Fire ID 1, Table 1) were taken immediately after the fire, and also after 1 year, 3 years, and 5 years (Fig. 4 and Table S3). These samples



**Fig. 4 Environmentally persistent free radical concentrations in woody charcoal over time since fire.** Samples from Fire ID 1 (see Table 1), showing a high level of stability for EPFRs in a natural boreal conifer forest environment. Different lower-case letters at the top of the bars indicate statistical differences, with  $p < 0.05$ ; all samples were analysed in triplicate. Error bars represent standard deviation.

showed an initial slight increase in EPFRs after the first year, possibly due to the formation of secondary radicals during oxidative aging as previously described for pyrolysis of tobacco<sup>38</sup>. Over the subsequent four sampling years, the EPFR concentrations decreased only slightly, with the most pronounced reduction occurring in the fifth year (Fig. 4). Throughout the 5 years, the EPFR concentrations remained of the order of  $10^{19}$  spin/g, indicating a high level of stability in the natural environment. This may partially be explained by the occurrence of a catalytic EPFR cycle causing continuous re-generation of EPFRs, similar to that previously described by Khachatryan et al.<sup>39</sup>, and/or the structural enclosure of EPFRs within the charcoal which would make them not highly reactive.

**Environmental implications of EPFRs in wildfire charcoal.** The EPFR concentrations in the wide range of wildfire charcoals examined here ( $2.46 \times 10^{18}$  to  $1.49 \times 10^{19}$  spin/g) are orders of magnitude above those previously reported in soils and airborne

PM ( $\sim 10^{16}$  to  $10^{17}$  spin/g)<sup>12</sup>. Although the range of samples collected was limited to ten fires, the overall evidence of high EPFR concentrations in wildfire charcoals and their stability in the natural environment is strong. Since the most recent estimates put the global annual production of wildfire charcoal at 256 Tg<sup>4</sup>, wildfire charcoal may represent a substantial, as well as ubiquitous, global source of EPFRs. Charcoal is highly mobile in post-fire landscapes and substantial quantities eventually reach the hydrological network, in either particulate or dissolved form<sup>40,41</sup>. When in contact with water, be it in rivers, lakes, oceans, or soils, EPFRs can form various types of ROS such as, for example, hydroxyl radicals ( $\bullet\text{OH}$ )<sup>13,39</sup>. In laboratory-produced biochars, most of the ROS-forming reactions take place within the first few hours of water contact<sup>10</sup>. However, our results indicate that EPFR in wildfire charcoals can remain highly stable in natural environments over far longer periods of time. This suggests these long-lived EPFR may not be very reactive and/or undergo to date unexplored catalytic cycles similar to previously described mechanisms described by Khachatryan et al.<sup>39</sup>, including charge transfer reactions with transition metal oxides from the surrounding environment and/or the mineral fraction within the wildfire charcoals. In both cases, they may still produce some quantities of ROS when in contact with water. Whether EPFRs in wildfire charcoal do indeed pose an environmental risk remains unclear, and the rate of ROS production from EPFRs in field aged wildfire charcoal will be an important area for future research. Even at low concentrations, EPFR-derived ROS in environmental systems may influence ecosystem functions including organic matter transformation<sup>42</sup>, plant germination<sup>15,16</sup>, aquatic algal growth<sup>43</sup>, and enzymatic activity<sup>17</sup>, as well as having adverse effects on bacteria<sup>19</sup> and invertebrates<sup>20,21</sup>. Wildfires are a natural, necessary and frequent disturbance in many of the world's ecosystems<sup>44</sup>. However, fire frequency and severity are increasing in many regions due to human activity and a warming planet<sup>4,45</sup>. For example, the annual area burned in California has increased by over 400% over the last five decades and ecosystems that are less prone to wildfires, such as tropical rainforests or arctic tundra, are now suffering extensive fires<sup>45,46</sup>. In such regions, the increasing EPFR quantities, and possible ROS production, associated with higher wildfire charcoal production may be of concern and thus the potential environmental effects require further investigation.

## Methods

**Wildfire charcoal sample collection.** Samples were collected from areas burnt by either actual or experimental wildfires, between 1 day and a few months after the fire. The maximum temperatures ( $T_{\text{max}}$ ) and charring times for the experimental fires were recorded using K-type thermocouples ( $\leq 1$  mm diameter) that had been attached to the surfaces of the woody samples or were placed within the litter/grass fuel layer, and connected to data loggers (Lascar, Easylog). The loggers were buried in the adjacent soil to protect them from thermal exposure and recorded the temperature at the interface between the samples and the surface-flames at 1–10 s intervals during the fire (depending on the fire). Additional samples were collected at annual intervals following the Canadian boreal forest fire, for up to 5 years after the fire. Details concerning the sampling locations, the characteristics of the fires, and the ecosystems are provided in Table S1. Samples were either air-dried or dried in an oven at low temperature ( $<45$  °C,  $>48$  h), and then stored in airtight containers in the dark prior to analysis. Each sample was crushed with a ceramic mortar, sieved to  $<250$   $\mu\text{m}$ , and then dried overnight in a laboratory oven at 80 °C before taking any measurements.

**Physical and chemical characterization of wildfire charcoals.** Total C, H, and N concentrations were determined using an elemental analyser (Elementar VarioMacro) and O concentrations then calculated by mass balance:  $\text{O} = 100 - (\text{C} + \text{H} + \text{N} + \text{ash})$ . The mineral ash content was determined by weighing samples before and after heating at 750 °C for 6 h in a muffle furnace.

Fifteen to 25 mg of each homogenized wildfire charcoal sample weighed (Mettler Toledo AT201,  $d = 0.02$  mg) was digested using 65% nitric acid (suprapure  $\text{HNO}_3$ , Merck), 30% hydrochloric acid (suprapure  $\text{HCl}$ , Roth), 40%

hydrofluoric acid (suprapure  $\text{HF}$ , Merck), and hydrogen peroxide (suprapure  $\text{H}_2\text{O}_2$ , Merck) in a stepwise approach, as detailed in the Electronic Supplementary Material (Fig. S4). Transition metal analyses were quantified using an inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 5110) and a quadrupole inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7900).

**ESR spectroscopy.** Solid dry samples were analysed at room temperature using an X-band Bruker EleXsys-II E500 ESR spectrometer (Bruker Biospin GmbH), with a modulation frequency of 100 kHz and a microwave frequency of 9.8 GHz. The sweep width was 100 G, the sweep time 20 s, the modulation amplitude 1.00 G, the centre field 3508 G, the microwave power 0.16 mW, and the resolution along the X axes was 1024 points. ESR spectra were simulated and the area under the curve determined by double integration of the spectrum. A reference-free quantitation of the number of spins was performed, as has been described elsewhere<sup>47</sup>. The unit spin/g can be understood as “free radical/g”.

The  $g$ -factor was estimated using Bruker Win ESR Acquisition software. Measurements were performed using 100  $\mu\text{L}$  capillaries and a sample weight of 2–10 mg. All measurements were replicated using three subsamples and the results normalized to sample weight.

**Data analysis.** For the data analysis and production of figures, we used OriginPro 2018 software. Correlation analyses were performed using linear regressions and reporting Pearson's  $R$ . The two smouldering-produced charcoal samples 6 and 7 were excluded from our analysis of the relationships between carbon content, O/C ratios, and EPFR abundance because they strongly differed in their material properties compared to other charcoal samples. To compare multiple sample groups, the Tukey's post-hoc test was used for pairwise comparison following single factor ANOVA in OriginPro 2018.

## Data availability

The data generated during the current study are available at <https://doi.org/10.5281/zenodo.4564056>.

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### Author contributions

G.S. and C.S. developed the conceptual framework of the study. G.S., C.S., M.P., S.H.D., and T.H. critically discussed the approach and participated in developing the study. C.S. and S.H.D. collected the field samples and information on the fire conditions. M.P. performed all ESR measurements. Transition metal concentrations were measured by N.T.; all other measurements were made by G.S. The manuscript writing and editing was conceived and led by G.S. All authors carefully revised the manuscript and approved the submission.

### Competing interests

The authors declare no competing interests.

### Additional information

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**Correspondence** and requests for materials should be addressed to T.H.

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