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# Latest Permian chars may derive from wildfires not coal combustion

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## ABSTRACT

The Permian-Triassic extinction event was the largest biocrisis of the Phanerozoic. One of the principle triggers for the 'big dying' is thought to be greenhouse warming resulting from the release of $CH_4$ from basalt-coal interaction during the extensive Siberian Trap eruptions. Observations of organic matter interpreted to be coal combustion products (fly ash) in latest Permian marine sediments have been used to support this hypothesis. However, this interpretation is dependent upon vesicular chars being fly ash (coal combustion-derived) and not formed by alternative mechanisms. Here we present reflectance microscopy images of vesicular chars from Russian Permian coals, as well as chars from modern tundra, peatland and boreal forest fires, to demonstrate that despite a difference in precursor fuels, wildfires are capable of generating vesicular chars that are morphologically comparable to end Permian 'fly ash'. These observations, coupled with extensive global evidence of wildfires during this time interval calls into question the contribution of coal combustion to the end Permian extinction event.

## INTRODUCTION

The Permian-Triassic boundary event decimated 80-96% of marine and 70% of terrestrial life and is marked in the geological record by a significant 2–8‰ negative organic and carbonate

$\delta^{13}C$ excursion (Chen and Benton, 2012). One suggestion is that massive greenhouse warming (Erwin, 1994) led to the most significant mass extinction event ever to occur on our planet. One of the greenhouse contributors is thought to have been extensive $CH_4$ release from the combustion of coals and organic-rich shales, during the emplacement of shallow intrusions, as part of the Siberian Trap eruptions (Retallack and Jahren, 2008; Grasby et al., 2011; Ogden and Sleep, 2012).

In modern coal-fired power stations char is produced during high temperature combustion of pulverized coal. The coals undergo complex physical and chemical transformations, giving off volatiles and producing solid residues (char). The resulting char (termed ‘coal fly ash’ in Grasby et al. (2011)) is highly variable depending on the organic constituents of the precursor coal (Bailey et al., 1990; Yu et al., 2007; Lester et al., 2010), and the morphology of the char ranges from solid to vesicular. Vesicular chars in particular, in Late Permian sediments from Lake Buchanan in Arctic Canada have been interpreted as definitive evidence of coal combustion. These chars represent the only physical indicator of coal combustion outside of Siberia and have been used extensively as evidence for global dispersal of coal fly ash at the end Permian extinction event (Grasby et al., 2011; Ogden and Sleep, 2012; Sanei et al., 2012; Knies et al., 2013; Kerr, 2013). In order to transport these coal combustion chars 20,000 km from the Siberian Trap source, models imply that explosive interactions of coal and magma would be required to propel coal-char-basalt mixtures into the stratosphere, thus enabling global distribution of the resulting coal fly ash (Ogden and Sleep, 2012). Yet the lack of documented coal fly ash elsewhere casts doubt on this transport mechanism. Until now, coal combustion has been the only considered mechanism for char formation; however, vesicular chars can also form naturally during modern wildfires (e.g. Fig. 1 E-J). Further, much of the "coal fly ash" (illustrated in Grasby et al. (2011)) is described as deriving from inertinite precursors. Inertinite is a coal petrography term for fossil charcoal (Glasspool and Scott, 2010). Therefore, it should be evaluated whether these Late Permian chars in fact represent small fragments of fossil charcoal produced in contemporaneous Late Permian wildfires (compare figure 2 in Grasby et al. (2011) with images of inertinite in Fig. S1). Typically, inertinite is described as having cellular structure (e.g., Figure 1B; Fig. S1G,I-J; ICCP, 2001), but inertinite morphology can be highly variable (e.g., Fig. S1; Fig. S2A-C; ICCP, 2001), and charcoal only represents one component in a continuum of products produced by wildfires (Masiello, 2004) (Fig. 1). Wildfire-derived char can have a variety of morphologies (Fig. 1) and in this study we will focus on one of these char products that we call vesicular char (otherwise referred to as natural char in the coal literature e.g., Petersen (1998) and Kwiecińska and Petersen (2004)). Vesicular chars have been documented previously in coals and carbonaceous mudstones of Carboniferous, Permian, Jurassic, Cretaceous and Tertiary age (Kwiecińska and Petersen, 2004). Here we document vesicular char from wildfire-derived charcoal assemblages, in modern ecosystems as well as in Late Permian coals (Fig. 1; Figs. S1-S2) in order to demonstrate that wildfires can produce vesicular char that is morphologically comparable to chars interpreted by Grasby et al. (2011) to be coal fly ash from the Permian-Triassic event.

## METHODS

Polished blocks containing Permian, modern tundra, modern peatland and Holocene Alaskan boreal forest vesicular chars (see supplementary material for detailed sampling information) were studied under oil using reflected-light microscopy. The peatland and Holocene samples were studied using a Leica DM2500P reflectance microscope at × 200 and × 500 magnifications, at Southern Illinois University Carbondale, USA. Images were taken using a

Leica DFC 400 digital camera and Leica Application Suite imaging software. The Permian coal and tundra samples were analyzed at Royal Holloway University of London, UK, using a Leica DM2500P reflectance microscope at × 200 magnification. Representative color photomicrographs (2560 × 1920 pixel resolution) were taken using a 5-megapixel camera attached to the reflectance microscope and Prog-Res Capture Pro 2.7 software.

**RESULTS**

Vesicular char is thought to form from the burning of gelified plant material during ground or surface fires in ancient mire environments (Petersen, 1998). The Permian chars in this study originate from a peat-forming environment in the Kuznetsk Basin, Siberia (Fig. 1A-D; Fig. S1), supporting the formation of vesicular chars in mire ground/surface fires. However, we further document the occurrence of vesicular chars in charcoal assemblages from Holocene boreal forest (Fig. 1E-F), and modern tundra (Fig. 1G-H) ecosystems in Alaska, as well as a modern peat bog in Ireland (Fig. 1I-J), thus demonstrating that vesicular char can form irrespective of fuel or ecosystem type, and emphasizing that the mechanisms of char formation are still not fully understood. This might explain why vesicular chars, despite their common occurrence in coals and carbonaceous mudstones, are an often overlooked signature of wildfires. These wildfire-derived vesicular chars vary in morphology as the plant material undergoes a plastic deformation phase when rapidly heated; losing cellular structure and generating tar (Cetin et al., 2005). The volatile matter becomes trapped during combustion and produces bubbles, which then form irregularly distributed vesicles after devolatilization (Petersen, 1998) (Fig. 1; Fig. S2). The Late Permian (Fig. 1A-D; Fig. S1), and modern tundra (Fig. 1G-H) vesicular chars are dense and contain fewer vesicles, possibly indicative of slower volatile release caused by longer heating durations or lower maximum temperatures reached. Whereas, the boreal forest

(Fig. 1F) and modern peatland (Fig. 1I-J; Fig. S2I-K) vesicular chars are highly vesiculated, suggestive of rapid heating, or higher temperatures reached during char formation. Vesicles have also been observed in low reflecting, hence low temperature chars (Jones et al., 1991), in modern tundra, peatland and experimentally charred inner bark (Fig. 1G-H; Fig. S2D,E,H) suggesting that processes other than formation temperature may influence char morphology. For instance, vesicles observed in charred degraded inner bark (Fig. S2D-G), and charred degraded plant material from a modern peat bog (Fig. S2J-K), suggest that the type and degree of degradation may influence the resulting char morphology. The degree of degradation that the original plant material has undergone prior to charring also prevents determining the original botanical affinity of these vesicular chars, which may further limit their identification in the fossil record. These results indicate that vesicular chars may be products of wildfire, irrespective of geological time interval, vegetation, ecosystem type, or fire behavior. It is likely that differences in morphology can be attributed to variations in heating temperature and duration, the precursor fuels, and degree of degradation prior to charring.

## DISCUSSION

Late Permian peat-forming environments covered large swathes of Pangaea (now coal deposits in modern day southeastern Africa, India, Australia, China, Antarctica, South America, and Russia). Wildfire was a frequent disturbance in these ancient peat-forming environments, as is evidenced in the fossil record by coeval high fossil charcoal (inertinite) contents (mean 38.9 vol. %) observed in Late Permian coals, compared to modern peats (mean 4.3 vol. %) (Glasspool and Scott, 2010). The ignition potential of the Permian peat would have been greatly enhanced due to elevated atmospheric oxygen levels at the time (Belcher et al., 2010; Glasspool and Scott, 2010), resulting in higher temperature fires with more rapid spread rates (Belcher et al., 2010;

Hadden et al., 2013), beyond those seen in modern peat fires. These factors may explain why coals with high inertinite contents, such as those from the Late Permian, contain more vesicular char (Kwiecińska and Petersen, 2004).

The size of vesicular chars is highly variable and can range from 30 - 900µm (Kwiecińska and Petersen, 2004), unlike the typical 50µm size observed in Grasby et al. (2011). Numerous charcoal taphonomy studies have demonstrated that charcoal particle size distribution can indicate the distance to source; with the microscopic fraction (particles 20–50µm in size) typically being windborne over long distances (Clark, 1988; Patterson et al., 1987). Moreover, during periods of enhanced fire activity and/or exceptional fire weather, intense convection from modern wildfires can transport smoke plumes (particulates and gaseous emissions) to the stratosphere (Fromm et al., 2000), thus enabling global dispersal of microscopic wildfire-derived particulates (Fromm et al., 2000); however, these high elevation smoke plumes are typically latitudinally restricted (Siddaway and Petelina, 2011). If vesicular chars were indeed produced in Permian peatland wildfires, and assuming that transport behavior of Permian smoke plumes was analogous to that seen today, in order to transport the char to the Buchanan Lake site the fires would need to be at a comparable paleolatitude. The predominant Permian paleowind direction was thought to be Westerly (e.g., Gibbs et al., 2002). This means that paleowildfires occurring in the extensive peat-forming environments of Angara and Cathaysia could represent viable sources of this vesicular char.

Our interpretation of vesicular char production in Late Permian wildfires, and the global transport of wildfire-derived products in high elevation smoke plumes, is further supported by the occurrence of high concentrations of wildfire-derived black carbon (including charcoal and soot), and biomass burning-derived polycyclic aromatic hydrocarbons (PAHs), observed in numerous Northern Hemisphere Permian-Triassic boundary sections across Meishan, China, E. Greenland and the Peace River Basin, Canada (Nabbefeld et al., 2010; Shen et al., 2011). The latter is ~3000km distant from the documented occurrence of char in the Sverdrup Basin, Canada (Fig. 1 in Beatty et al. (2008)). These combined lines of evidence suggest that chars observed in Grasby et al. (2011) could have formed in latest Permian wildfires.

In addition to char occurrence, other chemical signatures have also been associated with ‘fly ash loading events’ (Grasby et al., 2011), such as anomalously high mercury levels (Sanei et al., 2012). Volcanic emissions account for the majority of modern perturbations in the mercury cycle and high mercury levels at the Permian-Triassic are likely explained by Siberian Trap volcanism (Sanei et al., 2012). In addition, vegetation, and peat in particular, have been shown to strongly bond mercury, causing peat-forming environments to become syngenetically enriched in mercury (Yudovich and Ketris, 2005). Peak accumulation rates of mercury have also been directly correlated with volcanic events (Roos-Barraclough et al., 2002). Modern forest fires are capable of re-emitting substantial quantities of atmospherically deposited mercury to the atmosphere (Friedli et al., 2009). Within the timeframe of the Permian-Triassic extinction interval (60 ± 48 ka) (Burgess et al., 2014) it is feasible that volcanic-derived heavy metals and mercury became sequestered by plants and peat, which then could have been remobilized to the atmosphere in smoke plumes during subsequent wildfires.

The compelling evidence for widespread wildfire activity throughout the Permian and leading up to the extinction event, suggest that wildfires may have also contributed a minor amount to the greenhouse crisis; sustained peat combustion has been shown to increase $CO_2$ emissions significantly enough to generate a pronounced negative $\delta^{13}C$ excursion (Finkelstein et al., 2006), and negative $\delta^{13}C$ shifts are noted after each ‘fly ash loading event’ (Grasby et al., 2011). In order generate the negative $\delta^{13}C$ isotope excursion by coal combustion alone modeling suggests that all of the carbon in 1000 $km^3$ of coal would need to be extracted (Ogden and Sleep, 2012). The extent of coal-magma interaction cannot be verified due to the lack of metamorphosed coal exposures at the surface therefore we reason that latest Permian chars were more likely produced by wildfires, and do not represent conclusive evidence for 'fly ash' (in Grasby et al. (2011)). Further, recent work has suggested that methane release from microbial metabolic activity alone could have generated the $\delta^{13}C$ excursion (Rothman et al., 2014). This combined with the wildfire-derived char evidence casts doubt on the fly ash hypothesis, and therefore the contribution of coal combustion to the greenhouse crisis at the end Permian extinction event.

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**FIGURE CAPTION**

Figure 1. Photomicrographs of vesicular chars. A-D Vesicular chars in Late Permian coals, Kuznetsk Basin, Siberia. E-F chars extracted from Holocene lake sediments, boreal forest, Yukon Flats, Alaska, G-H char from a modern tussock tundra fire, Alaska. I-J chars from a modern peatland fire, Ireland.

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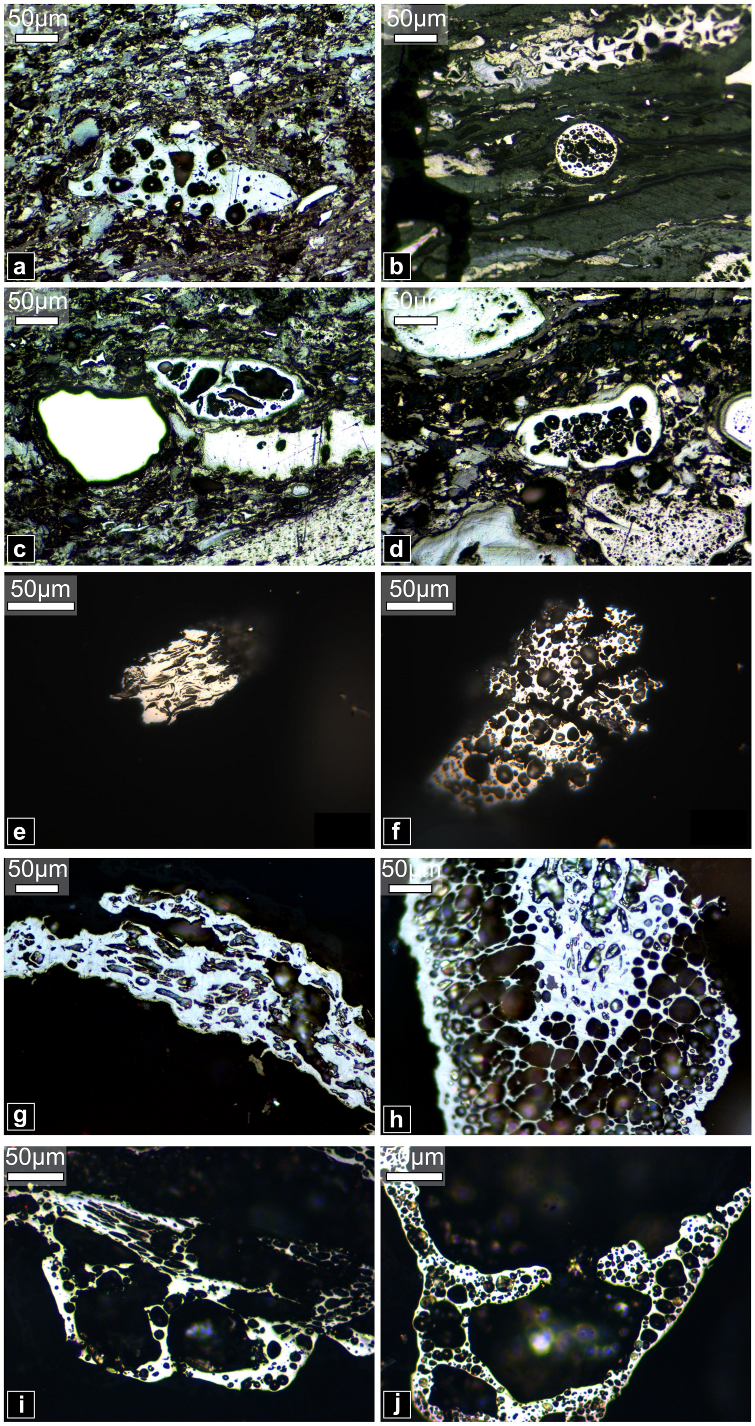


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