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**PYROGENIC POLYCYCLIC AROMATIC HYDROCARBONS FROM
CARBONIFEROUS, TRIASSIC, AND MODERN CHARS: POTENTIAL
RELATIONS TO PALEOATMOSPHERIC OXYGEN CONTENT**

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DEDICATION

This thesis is dedicated to my family: John, Pyong Sun, Thomas, Daniel, and Julie, and foremost, to Tabbatha Cavendish.

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ABSTRACT

Atmospheric oxygen concentrations may have dramatically fluctuated throughout the Phanerozoic. Because oxygen is critical to fire, major oxygen fluctuations may have significantly affected biomass burning occurrences, suggesting that wildfires would have been more prevalent at times of elevated oxygen. Fossil charcoal abundances in the geologic record qualitatively reflect this relationship. Land plants evolved by the late Silurian, and the earliest true forests evolved by the mid-Devonian, while oxygen levels were still low. Fuel accumulations and oxygen content probably did not reach sufficient levels to sustain burning until the late-Devonian. There are only one or two isolated examples of fossil charcoal of this age. Oxygen levels rose to ~35% in the Carboniferous, and fossil charcoal of this age is globally abundant. During the Triassic, oxygen levels fell to ~15%, and fossil charcoal is nearly absent from the rock record. Based on the empirical association between modeled oxygen and charcoal abundance, an implicit relationship between biomass burning and oxygen level exists. By targeting a set of combustion-derived organic compounds, polycyclic aromatic hydrocarbons (PAH), the qualitative nature of this relationship can be approached quantitatively. During times of elevated oxygen level, biomass burning events are facilitated, and therefore, a greater proportion of PAH are expected to be produced and preserved in the geologic record.

To test the hypothetical relationship between atmospheric oxygen level and PAH production, charcoals were collected from Carboniferous- and Triassic-age rocks, which relate to the purportedly highest (~35%) and lowest (~15%) levels of atmospheric oxygen (Berner, 2001). To isolate the role of atmospheric oxygen in the development of PAH, sampling localities were chosen based upon their similarities to the most-probable vegetation source for charcoals, in the context of the ancient depositional environment. The occurrence and abundance of 16 PAH species extracted from these samples suggest that a relationship exists between atmospheric oxygen level and PAH content, but undoubtedly, a larger empirical data set, in conjunction with combustion experiments to produce PAH under controlled oxygen levels, are necessary to fully delineate the role of oxygen relative to other parameters such as humidity, fuel moisture, length of burn, combustion temperatures, and fuel geometry.

PREFACE

The goal of this study was to determine if a relationship exists between atmospheric oxygen content and the concentration of fire-derived organic compounds within wildfire products. Such a correlation would provide an independent means of assessing fluctuations in post-Devonian atmospheric oxygen content, providing a longer-term record of atmospheric change than is commonly used to assess anthropogenic impacts on the global environment.

TABLE OF CONTENTS

CHAPTER	PAGE
1. INTRODUCTION	1
1.1. Hypothesis	1
1.2. Significance	2
1.3. Background	5
1.3.1. Phanerozoic Atmospheric Oxygen Models	6
1.3.2. Combustion	11
1.3.3. Fire Types	13
1.3.4. Fire History	13
1.3.5. Fire Products	17
1.3.6. PAH Synthesis	18
1.3.7. PAH Utility	21
2. SAMPLE COLLECTION	23
2.1. Carboniferous Samples	24
2.2. Triassic Samples	26
2.3. Modern Samples	27
3. METHODS	29
3.1. Contamination Controls	29
3.2. Accelerated Solvent Extraction	30
3.3. Liquid Chromatography	31
3.4. Gas Chromatography – Mass Spectrometry	32
4. RESULTS AND DISCUSSION	35
4.1. Complete Empirical Data Set	36
4.1.1. Statistical Analysis of PAH Distributions	37
4.1.1.1. Kruskal-Wallis Test	37
4.1.1.2. Binomial Probabilities	39
4.1.2. Relative Proportions of PAH by Ring Number	39
4.1.3. PAH Isomer Source Ratios	41
4.1.4. Relations between Atmospheric Oxygen Content and PAH Concentrations	42
4.2. PAH Species Exhibiting a Positive Relation to Atmospheric Oxygen Content	43
5. CONCLUSIONS	44

REFERENCES CITED	46
APPENDICES	64
Appendix 1. Tables	65
Appendix 2. Figures	78
VITA	90

LIST OF TABLES

TABLE	PAGE
1. PAH Retention Times and Qualifying Ions	66
2. PAH Concentrations in ppm from Carboniferous, Triassic, and Modern Charcoals	67
3. Average PAH Concentrations (ppm), Standard Deviations (SD), and Numbers (<i>n</i>) from Carboniferous, Triassic, and Modern Charcoals	69
4. Statistical Analysis of PAH Distributions	70
5. Average Concentrations of PAH (ppm) and Proportion of the Total Mass of PAH by Ring Number and Period for Carboniferous, Triassic, and Modern Samples	72
6. PAH Isomer Ratios	73
7. Simple Statistics for the Sum of PAH Species by Period	77

LIST OF FIGURES

FIGURE	PAGE
1. Phanerozoic Record of Oxygen	79
2. Combustion Essentials	80
3. PAH Synthesis Scheme	81
4. Joggins Field Locality	82
5. Sample JFC-1 from the Joggins Formation (Carboniferous)	83
6. Petrified Forest Field Locality	84
7. Sample TP from the Chinle Formation (Triassic)	85
8. Zion Field Locality	86
9. Average PAH Species Concentrations by Period	87
10. Target PAH Species	88
11. Total mean [PAH] vs. Oxygen Level	89

1. INTRODUCTION

The geologic record of atmospheric oxygen content is based on a complex set of dynamic associations and suggests that significant fluctuations have occurred throughout the Phanerozoic (Berner and Canfield, 1989; Chaloner, 1989; Beerling and Berner, 2000; Berner et al., 2003). These complex associations rely on the long-term carbon and sulfur mass balance cycles (Berner et al., 2003), which incorporate global data sets for all of Phanerozoic time. Modeled atmospheric oxygen values are approximate because many of the input parameters are themselves derived and have high amounts of error (Figure 1; all tables and figures in appendix)). This study addresses the potential for a new, independent method of assessing atmospheric oxygen fluctuations for the post-Devonian Phanerozoic record. The relationships established by this research are not wholly conclusive, but provide the foundation for future experimental and improved empirical research.

1.1. Hypothesis

Wildfires develop in response to three parameters: sufficient atmospheric oxygen, fuel, and heat. During a wildfire event, vegetation acts as a fuel and is thermally altered in the combustion process. Polycyclic aromatic hydrocarbons, or PAH, are one class of organic compounds that form during this process. At elevated levels of oxygen, fires burn more efficiently; at diminished O₂ levels,

fires burn less efficiently. Based on this relationship, the production of fire-derived organic compounds should also relate to oxygen levels. At times of relatively low atmospheric oxygen content in Earth history, combustion efficiency is diminished, and it is hypothesized that PAH will also be decreased in their production. Based on this hypothesis, the PAH content extracted from Carboniferous charcoals, which developed in an enriched atmosphere with regard to oxygen (~35% O₂) (Berner et al., 2003), should be higher relative to other times in Earth history, such as the Triassic or Modern, when oxygen levels were lower (Figure 1).

This study tests the hypothesized relationship between PAH and atmospheric oxygen content by (1) targeting a spectrum of PAH species extracted from wildfire-produced chars of Carboniferous, Triassic and Modern ages, (2) isolating individual PAH species that exhibit a relationship to atmospheric oxygen content, and (3) describing the relationships in terms of closeness-of-fit (r^2) to linear, exponential, or logarithmic functions.

1.2. Significance

The goal of this research, to determine if a correlation exists between atmospheric oxygen content and PAH concentrations, is significant for several aspects of the geological sciences, including sedimentology, modern and ancient soil sciences, biological evolution, and climate change. Like most aspects of

geology, these are closely-associated dynamic systems, to which atmospheric and global modelers can attest (*e.g.* Berner, R.A.). Although it is beyond the goals of the present study, the ultimate aim of this type of research is to add precision and accuracy to the record of Phanerozoic atmospheric oxygen fluctuations. Only with an accurate and precise record can anthropogenic versus natural variations in atmospheric oxygen be delineated.

Fires affect not only the plant community, but also the associated animals, soil and water chemistry, and therefore, the erosion-depositional system (Swanson, 1981; Pyne et al., 1996; Scott, 2000). Biomass burning releases nutrients into the soil and significantly affects its geochemical character (Cerida et al., 1995). The organic-rich layer may be completely destroyed, and the death of binding roots may lead to substantial soil erosion (Swanson, 1981). Fires in mire or marsh-type systems may alter the hydrologic system by lowering the topography of the peat, allowing flooding and the arrival of sediments via stream crevassing, producing depositional phenomena called fire splays (Cohen, 1974). In sub-boreal forest soils, fire has been shown to raise pH, increase exchangeable Ca, Mg, K, and Na base saturation, and reduce the amount of expanding clays in Ae and Bm horizons (Arocena and Opio, 2003). Fire may also be responsible for the development of cracking patterns in soil aggregates and the sand fraction of sub-boreal soils, which would increase weathering rates (Arocena and Opio, 2003).

Wildfires clear significant amounts of debris from forest floors, facilitating erosion immediately after the event, and vegetative and habitat colonization soon thereafter. Fire splays are relatively common sedimentological phenomena that result from the rapid erosion of pediments directly after a fire event. Paleopedological studies may need to account for the occurrence of fossil charcoal (fusain) in soil profiles if geochemical trends are studied. For instance, if a ground or surface fire occurs within a humus layer or soil organic horizon, the charcoals that develop will likely affect a great percentage of the elements that exist in or illuviate through the organic layer. The resultant charcoals may preserve the geochemical character of an organic-rich layer that no longer exists in the soil profile. It may also elucidate the soil stratigraphy (i.e., differentiation of otherwise non-distinct horizons based on a missing organic layer, represented by a fossilized charcoal, or fusain, horizon). Considering the fusain as a chemical filter that concentrates mobile elements during pedogenesis and diagenesis may also provide explanation for otherwise inconclusive geochemical studies of ionic mobility during pedogenesis.

Atmospheric oxygen is undoubtedly a significant factor in biological evolution. It is no surprise that the dramatic rise in oxygen during the Devonian (Figure 1) is accompanied by the development of insect gigantism during the Carboniferous and Permian (Graham et al., 1995). The evolution of flapping flight, even, may have developed in conjunction with this atmospheric oxygen

maximum, which would have also increased the total pressure of O₂, making air denser and flight easier (Graham et al., 1995). Of course, this relies on the assumption that the Earth's absolute atmospheric pressure has remained constant throughout the Phanerozoic (Chaloner, 1989).

The idea of atmospheric uniformitarianism is relatively unstudied (Chaloner, 1989). Lyell addresses this question of constancy in global atmospheric pressures throughout the Phanerozoic. He uses Carboniferous raindrop casts to illustrate the point that they “resemble in their average size those which now fall from the clouds. From such data we may presume that the atmosphere of the Carboniferous Period corresponded in density with that now investing the globe” (Lyell, 1885, p. 389).

1.3. Background

Scientific and societal interests in climatic and biospheric evolution, at various temporal and spatial scales, has catalyzed a general interest in biomass burning as it relates to geological, atmospheric, pedological, and ecological changes (Goldammer and Crutzen, 1993; O'Hanlon, 1995; Parfit, 1996; McInnis, 1997; Scott, 2000). Globally, carbon emissions from biomass burning in wildfire settings approximately equal those produced by fossil fuel combustion (e.g., automobile exhausts) (Crutzen and Andreae, 1990; Andreae, 1991; O'Malley et al. 1997).

Biomass combustion has both instantaneous and long-term effects on the production of atmospheric gases (Levine et al., 1995; Ballentine et al., 1996). Pyrogenic aerosols affect the radiation balance of the earth, depending on their size, chemical composition, and the mixing state of single particles (Silva et al., 1999). Wildfires, aerosols, related climate regimes, and their resultant atmospheric conditions are relatively short in duration.

Wildfires can be devastating to the terrestrial environment, as well, by destroying habitats and increasing erosion, but may be equally necessary for the re-growth of specialized vegetation types (Crutzen and Goldammer, 1993; Pyne et al., 1996; Scott, 2000). Biomass burning is now recognized as a significant source of carbon emissions that have the potential to influence climate-biosphere interactions by altering biogeochemical cycles (Andreae, 1991; Goldammer, 1991; Levine et al., 1995; O'Malley et al., 1997).

1.3.1. Phanerozoic Atmospheric Oxygen Models

On a geologic timeframe, atmospheric levels of O₂ are the result of global sedimentation rates, carbonate- and silicate-rock weathering, and the thermal breakdown of carbonate rocks through metamorphism and volcanism (Berner, 1991, 2001; Berner and Canfield, 1989; Berner et al., 2000). Ultimately, changes in plate tectonic motions drive each of these processes. Tectonic influences on carbon and oxygen cycling exert considerable control on atmospheric

concentrations of O₂ over geologic time scales. Temporal resolution is a critical parameter in the assessment of global influences on atmospheric concentrations of O₂ because of significant differences in particular reservoir sizes and residence times.

Literature that focuses on fluctuations in O₂ inevitably cite long-term carbon or sulfur mass balance models (e.g., GEOCARB I, II, and III; GEOCARBSULF) produced by Berner and others since 1989 (Berner and Canfield, 1989; Berner, 1991; Berner and Kothavala, 2001; Berner et al., 2003; Berner 2006b). These models provide qualitative assessments of atmospheric change based on available data sets of geochemical reservoir abundances and inferred or assumed interactions between model parameters. Berner's models are mathematical calculations based on a set of geochemical relationships first established by J.J. Ebelmen in 1845, with sensitivity tests for error calculations. Investigators other than Berner, who in general rely on sample collection (e.g., pedogenic carbonates) to infer paleoatmospheric compositions, do not readily have samples from the entire Phanerozoic, and for that reason, are unable to discuss atmospheric change for the entire Phanerozoic. Rather, these values are plotted against the record set by Berner and others, sometimes exhibiting flaws in the record set by Berner and others.

The overall control on atmospheric oxygen concentration depends on the balance of productive and consumptive fluxes. According to Berner and others

(Berner and Canfield, 1989; Berner et al., 2003; Berner, 2006) the most important factors affecting atmospheric oxygen content over the Phanerozoic are the burial and weathering of organic matter in sediments, the burial and weathering of sedimentary pyrite, oxidation and reduction of iron (in minerals other than pyrite) and manganese, and oxidation of reduced volcanically and metamorphically derived gases. Lasaga and Ohmoto (2002) propose that the dynamics of atmospheric oxygen are affected dominantly by the composition and flux of volcanic gases, the level of atmospheric CO₂, total area of soil formation, average soil depth, and average rate of physical erosion of soils, which is linked to the average rate of accumulation of clastic sediments in oceans.

In Berner and Canfield's (1989) model for Phanerozoic atmospheric oxygen, variations in burial and weathering rates of both organic matter and pyrite are assumed to be likely, and because atmospheric O₂ turnover is relatively short, on the order of 5 to 10 million years, changes in O₂ level should result. Burial rates for terrigenous sediments, which are the major source of both organic matter and pyrite, are calculated from an assumed constant global clastic sedimentation rate and the relative abundances (and carbon and sulfur contents) of three main rock types – marine sandstone and shale, coal basin sediments, and other non-marine clastic sediments – which account for about 80% of all preserved sedimentary rocks and more than 80% of all surface organic matter and pyrite (Berner and Canfield, 1989). Proportions of each rock type are calculated from rock

abundance data (Berner and Canfield, 1989) and mass-balance calculations based on C and S isotopic compositions of the oceans, as recorded in sedimentary rocks (Berner et al., 2003). Increases in global burial of organic matter and pyrite, and concomitant oxygen production, are accompanied by a corresponding increase in erosion and increased oxidation of organic carbon and pyrite. The dominant factor, then, is redistribution of sediment between the three rock type parameters and not weathering.

In Lasaga and Ohmoto's (2002) model for atmospheric oxygen, oxygen accumulations in the atmosphere are the net effects of production from organic matter burial, and consumption from oxidation of reduced volcanic gases and reduced compounds in pedogenically active soils. The expulsion of reduced volcanic gases, and resulting drawdown in atmospheric O₂, is independent of oxygen levels; however, the rate of weathering and soil formation are strongly dependent on oxygen levels. Based on the average contents of reducing compounds in upper crustal rocks, Lasaga and Ohmoto (2002) estimate that 60% of oxygen consumption by soils during weathering may be carried out by organic carbon. This major assumption relies on oxygen being able to reach reduced compounds, which is where the role of vascular land plants is established.

Vascular land plants, which produce microbially-resistant lignin, facilitate soil respiration and weathering. The evolution of vascular land plants allowed for more organic carbon to be buried, which increased O₂ levels (Berner and

Canfield, 1989; Lasaga and Ohmoto, 2002; Berner et al., 2003), while facilitating higher rates of soil respiration, which decreased O₂ levels (Lasaga and Ohmoto, 2002). The dominant effect is not addressed, but must be significantly influenced by the development of microbial and fungal communities capable of degrading such organic matter (Robinson, 1990).

In the modeled record of atmospheric oxygen by Berner et al. (2003), the most prominent feature is the large and rapid rise in oxygen during the Late Devonian and rapid decline at the end of the Permian (Figure 1). The increase is likely due to enhanced burial and sequestration of organic carbon accompanying the evolution and establishment of vascular land plants. An additional cause for the increase could have been the abundance of lowland swamps during the Carboniferous, which may have resulted from climatic conditions and/or the emergent nature of Pangea. The rapid decrease of oxygen levels early in the Permian is attributed to two events. A pronounced drop in sea level occurred at the end of the Permian, exposing Carboniferous and Permian coals to enhanced erosion and weathering. The climate may have also shifted to more arid conditions, shifting from organic-rich deposition in coal swamps to deposition in well-drained regions, resulting in the rapid oxidation of organic matter and the formation of red beds and shales essentially free of reduced carbon and sulfur.

1.3.2. Combustion

Combustion occurs at a critical balance between free atmospheric oxygen, fuel, and heat (Figure 2). Combustion of plant materials as fuels consumes oxygen and releases carbon dioxide, carbon monoxide, methane, hydrogen gas, water and heat. In addition, solid organic particulates and aerosols are produced. Atmospheric levels of oxygen necessary to sustain combustion (i.e., the fire window; Figure 1) have been estimated at 7-13% as the lower limit (Coward and Jones, 1952; Cope and Chaloner, 1980; Chaloner, 1989) and 25-35% as the upper limit (Scott, 2000). Beyond 25-35%, it has been shown experimentally that land plants would spontaneously combust (Scott, 2000), but there is no evidence for this in the geologic record.

There are four phases of combustion: pre-ignition, ignition, combustion, and extinction (Pyne et al., 1996). During the pre-ignition phase, the fuel temperature is raised by sunlight and microbially-mediated endothermic reactions that evaporate water and release volatile gases, which are produced by pyrolysis and volatilization of organic compounds, including plant waxes and oils. Pyrolysis also generates tars, carbonaceous char, ash (Pyne et al., 1996), and PAH (Zepp and Macko, 1997). The ignition phase is a transition from the pre-ignition state to the combustion state that only occurs with a substantial supply of free oxygen, producing a strong, self-sustaining exothermic reaction around 325° C (Pyne et al., 1996). Oxygen is essential for the initiation of combustion, which exists in

two forms, the proportions of which vary throughout the life of a fire. Flaming is one form of combustion in which volatile gases reach temperatures above 425° - 480° C. Common flaming temperatures are 700° - 980° C, but can reach 2200° C. Such high temperatures are not commonly sustained for more than a few minutes as fuels are quickly consumed. The smoldering or glowing form of combustion occurs, generally, within surface litter layers at temperatures near 300° C, although temperatures may reach 600° C and remain relatively high for several hours. Beyond the general availability of free oxygen ($O_{2\text{ gas}}$), the extinction phase of combustion is a function of heat, fuel quantity, and moisture. Extinction occurs when the fuel is exhausted or heat is reduced, dependent mainly on moisture content.

In temperate climates, most natural fuels are about 10% water by mass before a wildfire event (Watson et al., 1978). Experimentally, Watson et al. (1978), found a 60% increase in fire probability associated with only a 1% increase in atmospheric oxygen content. At 25% O_2 , Watson et al. (1978) conclude that water-saturated fuels would burn even in a rainstorm. This implies that at elevated atmospheric oxygen levels (e.g., > 25%), the importance of fuel moisture as a fire suppressant is effectively nil; however, at diminished atmospheric oxygen levels, the importance of fuel moisture may be the dominant control on fire extinction, and possibly, PAH production and distribution.

1.3.3. Fire Types

Wildfires may burn fuels from living plants, recently dead plants, or decayed plant accumulations. Based on fuel type, there are three classifications of fire: surface, crown, and ground fires. Surface fires exist at the soil-atmosphere interface, burn only recent litter accumulations, are low temperature ($<350^{\circ}\text{C}$), and produce high amounts of charcoal (Albini, 1993; Scott, 2000; Stocks and Kauffman, 1997). Crown fires exist above the ground in the upper portions of standing trees and predominantly burn living twigs and needles (Stocks and Kauffman, 1997), tend to be hotter, and are often ignited by surface fires through ladder fuels (Van Wagner, 1977). Ground fires exist within the upper layer of soils, in the humus and peat accumulation. These fires are generally low temperature ($<350^{\circ}\text{C}$) and can last up to years, depending on the burn conditions (Scott, 2000).

1.3.4. Fire History

Fire ecology since the Late Devonian, when evidence of fire is well established (Cressler, 2001), is relatively unstudied, techniques are poorly developed, and interpretations uncertain (Clark and Robinson, 1993). The recognition of fire in the rock record is mainly based on the occurrence of fossil charcoal, or fusain (Harris, 1958; Komarek, 1973; Cope and Chaloner, 1985; Moore, 1989; Scott, 1989, 2000; Scott and Jones, 1991). The identity of fusain as

fossil charcoal has been established beyond reasonable doubt (Cope, 1980, 1981, 1984; Scott, 1989, 2000, 2001; Jones, 1993). Macroscopically, fusain occurs as wedges or cubes of fibrous black and opaque material showing the cellular structure of wood with the cell lumina being generally empty (Stopes, 1919; Scott, 2000). Charcoal is found in a wide range of facies, from peats to lake sediments, alluvial fan deposits, fluvial and floodplain deposits and marine sediments (Scott, 2000 and references therein). Deeper marine sediments yield very small particles that are likely wind-derived from large fires (Scott, 2000 and references therein) or possibly through mechanisms similar to turbidites, where sediments may be transported very rapidly between provenance and final depositional environment.

Throughout most of earth history, wildfires were most commonly ignited by lightning strikes, with fewer generated from volcanic activity, rock-fall sparks, spontaneous combustion (Batchelder, 1967), or bolide impacts. Lightning strikes, and resulting wildfires, occur in a wide range of vegetation types, including deciduous and semi-deciduous forest biomes, as well as in rainforest settings (Goldammer, 1993). They are even known currently from such ever-wet places as the Everglades in Florida. Human interventions are an obvious modern ignition source, but would not have affected the ancient (Carboniferous and Triassic) samples presented here. The role of specific ignition sources should be relatively

minor to PAH production, whereas post-ignition combustion efficiency is most-likely the dominant control.

Through the past 400 Ma, there have been major changes in atmospheric oxygen levels that have affected fire intensity and frequency (Figure 1) (Scott, 2000). Although the first land plants developed by late Silurian time, sufficient fuels to sustain extensive wildfires probably did not exist until the mid-late Devonian. The evolution of terrestrial vegetation and the development of extensive forests with crowned foliage likely played a significant role in fuel accumulation by Late Devonian time (Meyer-Berthand et al., 1999; Scott, 2000). Not until the Devonian did both oxygen levels and fuel sources rise to sufficient levels to sustain wildfires (Berner and Canfield, 1989).

The earliest record of fusain is from the Late Devonian of the Catskill Delta in Pennsylvania (Cressler, 2001), providing evidence that atmospheric oxygen and fuel levels were sufficient to sustain wildfires at least by this time. Since the Late Devonian, fossil charcoals are relatively common, except from the Permo-Triassic (Tappan, 1968; Scott, 2000; Jones et al., 2002).

Very few records exist that focus on Triassic-aged fire history (Scott, 2000). This absence is notable given the abundance of fusain from Carboniferous, Jurassic, and Cretaceous sediments (Scott, 2000; Jones et al., 2002). It has even been suggested that the Permian through early Jurassic was essentially fire-free because fluctuations in photosynthetic oxygen production by phytoplankton

caused the atmospheric oxygen level to drop below the ~13% threshold for wildfire occurrence (Tappan, 1968).

The Carboniferous environment is modeled with extensive coal-forming vegetation and swamp fires; wildfires sweeping through extensive conifer forests of the Jurassic and Cretaceous; and an arid, relatively fire-free Permo-Triassic (Scott, 2000; Jones et al., 2002). According to Berner and Canfield (1989), the Triassic initiated and ended with a relatively low level of atmospheric oxygen, approximately 13% - 15%. In the mid-Triassic, however, oxygen levels were nearly equivalent to the present value of 20.9% at ~20% (Berner and Canfield, 1989). In contrast to the Triassic, there is no shortage of evidence for both abundant vegetation and atmospheric oxygen from the Carboniferous (Berner and Canfield, 1989; Arens, 1991; Chandler, 1998; Falcon-Lang, 1999, 2000; Scott, 2000). The Joggins Formation (Carboniferous, Nova Scotia) epitomizes the Carboniferous ecosystem of a warm, humid tropical wetland with groves of lycophytes and an understory of tree ferns and pteridosperms in ever-wet, poorly-drained soils (Arens, 1991). Included in its diverse floral assemblage is an abundance of fusain in channel and overbank sands interbedded with stacked immature paleosols (Arens, 1991).

The Carboniferous was a period of high atmospheric oxygen concentration (Berner and Canfield, 1989), and combustion efficiency would have been heightened during this regime. There is also a global abundance of fusain and

coals from the Carboniferous (Scott, 2000). In such an oxygen-enriched atmosphere, fires were likely high-temperature surface and crown fires. A major decrease in atmospheric oxygen levels during the Permian and Triassic suggest that fires were not nearly as extensive as in the Carboniferous, and were likely low-temperature surface and ground fires (Scott, 2000). Triassic occurrences of fusain are rare globally, though well-preserved samples from the Petrified Forest National Park have been studied (Jones et al., 2002). Since Jurassic and Cretaceous time, fusain occurrences are widespread, suggesting an intimate relationship between early Angiosperms and wildfire occurrences. Particular attention has been paid to fires at the Cretaceous-Tertiary boundary because of the possibility that impact-related events may have lead to global fires (Jones and Lim, 2000). Convincing evidence of this has yet to be presented.

1.3.5. Fire Products

Wildfires produce particulate matter that consists largely of condensed hydrocarbons, which are emitted into the atmosphere as aerosols and deposited in sediments as charred residues (Ward and Radke, 1993; Lobert and Warnatz, 1993; Allen and Miguel, 1995; Kuhlbusch and Crutzen, 1996; O'Malley et al., 1997). Low temperature (smoldering) fires produce fatty acids, waxes, and alcohols and a range of chemically- and radiatively-important reduced trace gases, such as carbon monoxide and methane (O'Malley et al., 1997). Hotter fires, as a result of

higher air to fuel ratios, result in byproducts consisting of biogenic and combustion-derived compounds, such as polycyclic aromatic hydrocarbons (PAH), which form through the oxidation and thermal cracking of original plant material (O'Malley et al., 1997). It is important to note that PAH are not the result of complete combustion, which yields elemental carbon; rather, they are one group of organic compounds that result from the incomplete combustion of hydrocarbons.

1.3.6. PAH Synthesis

Polycyclic or polynuclear aromatic hydrocarbons (PAH) are widespread environmental pollutants that form in a variety of natural and anthropogenic combustion processes of carbonaceous materials at high temperature, including biomass burning (Laflamme and Hites, 1978; Baek, et al., 1991; Peltonen and Kuljukka, 1995; Ballentine et al., 1996)). These compounds are well recognized by the environmental consulting field and regulatory agencies because of their carcinogenic and mutagenic properties, endocrine disrupting effects, widespread dispersion, high environmental half-lives, hydrophobicity, and semivolatility (Ratola et al., 2006). Point sources for PAH include emissions from automobiles, industrial processes such as coal coking, domestic heating systems, waste incineration facilities, tobacco smoking, as well as natural sources that include volcanic eruptions and wildfires (Peltonen and Kuljukka, 1995). Combustion

sources are thought to account for greater than 90% of present-day environmental concentrations of polycyclic aromatic hydrocarbons (PAH) (Howsam and Jones, 1998).

Mechanisms of PAH synthesis are not well understood. Most proposed mechanisms of PAH formation involves polymerization reactions followed by cyclization, possibly involving dehydrogenation (Crittenden and Long, 1976) (Figure 3). The temperature range that is favorable for PAH production is 650° - 900° C during pyrolysis (Crittenden and Long, 1976), with more complex, larger-ring-number PAH forming at higher temperatures (Schmeltz and Hoffman, 1976).

Theoretically, PAH can be synthesized during combustion of any hydrocarbon of sufficient C and H number (Schmeltz and Hoffman, 1976). Principal mechanisms of PAH synthesis are thought to involve free radicals, but there is evidence for alternative modes of PAH formation involving dimerization of dienes and polymerization of acetylenic (C₂) intermediates (Harvey, 1997). There are generally two accepted thermal mechanisms to form PAH: pyrosynthesis from aliphatic hydrocarbon and aromatic species, and survival of PAH in starter fuels (Harvey, 1997). Survival simply means that a fuel started out with PAH, and those PAH remained throughout the combustion event. Other mechanisms of PAH formation are generally concerned with tobacco combustion, during which the synthesis of PAH is minimal, according to the work of McGrath and others (2001, 2003) at the Philip Morris Research Center.

One of only two mechanisms of PAH formation that does not rely on initial PAH to form additional PAH is proposed by Harvey (1997). Pyrogenic PAH is thought to be driven by recurring addition of C₂ (acetylene) and C₄ (1,3-butadiene) radicals, leading to the formation of C₆-C₂ and C₆-C₄ radicals that are the building blocks of the parent PAH. These high-energy radicals can be generated by the partial cracking of aliphatic species and/or complex organic molecules with the synthesis of parent PAH proceeding rapidly via the combination of these radicals. An additional pathway involves dehydration of benzene derivatives that then undergo transformation to PAH.

Simoneit (1998) provides an alternative explanation of PAH formation that does not involve initial PAH as a starting material. During combustion at high temperatures and relatively low oxygen content, organic matter is partially cracked into smaller molecular fragments, mostly free radicals, which recombine to form PAH by pyrosynthesis as the temperature decreases. Successive recombination of acetylene and 1,3-butadiene radicals yield the unsubstituted PAH series. Once formed, the relatively simple, low-molecular-weight PAH undergo further pyrosynthesis according to the “zigzag addition process”. This process is the most thermodynamically stable series proposed for higher-molecular-weight PAH synthesis. In the zigzag addition process, two different reactions create the fully alternate PAH, first by a two-carbon (acetylenic) addition to a three-sided bay region, and second by a four-carbon (1,3-butadienic)

addition to the ring position of highest Π -electron density. Alkyl-substituted PAH undergo direct nuclear condensation preferentially across the alkyl group with further cyclization.

1.3.7. PAH Utility

Charcoal, black carbon, and PAH are pyrogenic substances that are presently used as atmospheric and sedimentary tracers of past fire activity (Youngblood and Blumer, 1975; Griffen and Goldberg, 1981; Charles and Hites, 1987; Venkatesan and Dahl, 1989; Clark, 1990; Killops and Massoud, 1992; O'Malley et al., 1997). PAH distributions that result from both natural and anthropogenic combustion are generally similar and indistinct (Hites et al., 1980). PAH can also undergo weathering reactions when suspended in the atmosphere and water column, as well as during deposition at the sediment-water interface. These alterations and the non-unique character of potential sources have made it difficult to clearly identify the character of past fire events using PAH molecular signatures from environmental samples alone.

Although the utility of PAH signatures from environmental samples alone is limited, their distributions from within wildfire residues are unstudied and may prove useful in a similar manner to stable isotope analyses. Bulk and compound-specific H- and C-isotopic analyses of individual PAH that are isolated from various biomass combustion sources may provide independent constraints to

uniquely characterize atmospheric conditions during combustion. Carbon isotopic ratios ($\delta^{13}\text{C}$) have been used to distinguish marine and continental sources of sedimentary organic matter, and also to identify organic matter from different types of land plants (Meyers, 1997). The $\delta^{13}\text{C}$ of organic matter reflects the dynamics of carbon assimilation during primary production, the metabolic pathway utilized by the plant (*e.g.*, C_3 , C_4 , or CAM), and the carbon isotopic composition of the carbon source (Hayes, 1993). O'Malley (1994) has demonstrated that the $\delta^{13}\text{C}$ of individual PAH, particularly four- and five-ring compounds, are not significantly altered when exposed to volatilization, photolytic, and microbial degradation reactions, and therefore, offer the potential to serve as robust indicators of past fire activity. PAH have an extremely high potential for utility in paleoatmospheric studies of oxygen because of their low volatility and reactivity and the fact that they form as a result of direct oxidation (combustion) in the atmosphere.

2. SAMPLE COLLECTION

Charcoal macrofossils are readily identifiable and easily distinguished from carbonaceous material and true coals in the field (Cantrill, 1919; Scott, 1989; Jones and Chaloner, 1991). In sandstones and siltstones, they generally occur along bedding planes, while in massive mudstones, they generally occur in geographically-limited pockets. Each charcoal fragment is blocky and brittle, has a silky luster, leaves a black streak on paper, and easily crumbles.

In the lab, charcoals are also insoluble in oxidizing mixtures such as nitric acid plus potassium chlorate (Cantrill, 1919). Their cell lumina are generally empty and cell walls homogenized (Chaloner, 1989; Scott, 2000). Depending on the combustion efficiency, charcoals generally contain few volatile organic compounds (Chaloner, 1989).

Three periods in Earth history were identified to test the hypothesis of this study based on their modeled O_2 content: Carboniferous (35% O_2), Triassic (15%), and Modern (21%) (Figure 1). These times were selected based on their relative magnitudes of atmospheric oxygen difference, as well as for a modern comparison. The Carboniferous is modeled at 35% O_2 , the highest in Earth history; the Triassic is modeled at 15% O_2 , the lowest in the Phanerozoic; and modern samples reflecting a known atmospheric oxygen content of 20.9% O_2 .

Carboniferous charcoal samples were collected from the Joggins area of Nova Scotia, Canada (Figure 4); Triassic samples were collected from the Petrified

Forest National Park of Arizona, USA (Figure 6); and Modern samples were collected from Zion National Park, Utah, USA (Figure 8). To isolate the role of atmospheric oxygen on PAH development, sample localities were chosen based on similarities with respect to depositional environment and vegetation types for ancient samples, and similarity of vegetation to the modern.

All samples were collected in aluminum foil and placed on dry ice before shipment to The University of Tennessee, where each sample was cataloged and inspected for contamination before frozen-storage until analysis.

2.1. Carboniferous Samples

Carboniferous charcoals were collected from three areas along sea cliff exposures of the Bay of Fundy, Nova Scotia, Canada, from the Joggins, Springhill Mines, and Ragged Reef Formations (Figure 4) in 2003. The Joggins Fossil Cliffs site was brought to international attention by Lyell in 1843 who described it as “the finest example in the world of a Carboniferous exposure” (Lyell, 1843). During the Westphalian, the Joggins, Springhill Mines, and Ragged Reef Formations were deposited in the equatorial (Golonka et al., 1994), rapidly-subsiding Cumberland sub-basin of the Maritimes Basin, which developed in southeastern Laurasia following convergence with Gondwanaland (Calder, 1994; Gibling, 1995; Scotese and McKerrow, 1990; Pascucci et al., 2000). At the time of formation, the Joggins site was at least 1000 km inland from the nearest open-

marine region, but was connected to open-marine waters via a narrow strait during marine highstands (Falcon-Lang, 2003). There are three main depositional facies interpreted for the Joggins Formation (Davies and Gibling, 2003), which grade from an open-water brackish bay facies to a poorly-drained, coal-forming coastal-plain facies, and to a well-drained, pedogenic carbonate-bearing alluvial plain facies. Throughout deposition, the climate was likely ever-wet to possibly having a minor amount of seasonality, which is interpreted from the strata overlying the Joggins Formation (Falcon-Lang, 2003). The coastal plain facies exemplifies a typical Late Carboniferous tropical wetland assemblage, which is dominated by lycopsids (Lyell and Dawson, 1853; Scott, 1998; Falcon-Lang, 1999, 2003; Hower et al., 2000), while alluvial-plain facies include cordaites and araucarian-related conifers, pteridosperms, gymnosperms, sphenopsids, and lycopsids (Falcon-Lang, 2003). The charred remains of cordaites are common to fluvial channel and splay deposits (Falcon-Lang, 2003). Charcoals also co-occur commonly with true coals. A total of 8 samples were collected from the Joggins Fossil Cliffs; JFC-1 (Figure 5) through JFC-6 were collected from the Joggins Formation; MC-1 from the Springhill Mines Formation; and SC-1 from the Ragged Reef Formation (Figure 4). Sample JFC-6 was insufficient in mass for triplicate analysis and is, therefore, not included in the data set presented here.

2.2. Triassic Samples

Triassic charcoals were collected from the Chinle Formation (Triassic) at three locations within Petrified Forest National Park, Arizona, USA (Figure 6) in 2003. The Chinle Formation is a 550-m-thick continental succession that was deposited as fluvial, lacustrine, and floodplain sediments during the Late Triassic in a broad basin approximately 15° north of the paleoequator near the west coast of Pangea (Stewart et al., 1972; Jones et al., 2002). Sediments of the Chinle Formation were mostly deposited by meandering streams crossing a wide floodplain, with associated marshes, swamps, ponds, and lakes (Dubiel, 1994; Therrien and Fastovsky, 2000). During deposition, the climate was warm and moist, with a dense vegetation cover that included large araucarian conifers (Jones et al., 2002), which made excellent targets for lightning strikes, the most likely ignition source for wildfires. Charcoals that were known to exist prior to this study have been identified as secondary wood of araucarian conifer type (Jones et al., 2002). A total of 8 samples were collected from two distinct lithologies: samples AR1, AR2, TP1a, TP1b, and TP1c (Figure 7) were collected from a greenish mudstone facies in two different locations, Adamana Road and The Tepees, respectively (Figure 6); samples DW1, DW2, and DW3 were retrieved from a cross-bedded sandstone facies at the Dry Wash locality (Figure 6). Because the mass of collected sample from each locality was so small, samples AR1 and AR2 were combined into a single sample designated AR; TP1a, TP1b,

and TP1c were combined into TP; and samples DW1, DW2, and DW1 were combined into DW. This allowed for triplicate analysis for three (combined) samples.

2.3. Modern Samples

Modern samples were collected at Zion National Park, Utah, USA in 2002 from National Park Service prescribed pile burns that occurred during the 1999/2000 and 2001/2002 fire seasons (Figure 8) (Bastian, *personal communication*). Pile burns are accumulations of litter from a small ($< 200 \text{ m}^2$) area that is burned by National Park Service personnel. All samples were collected within 1 km^2 of each other near the Lava Point Fire Lookout station from silty- to sandy-loams within a mixed flora consisting dominantly of pine, with lesser amounts of sage, manzanita, grasses, and scrub brush. At this location in the Park, soil loams overlie Pleistocene basaltic bedrock (0.26 – 1.4 Ma) (Hamilton, 1987). Sample collection consisted of removing the top 5-7 cm of litter and soil within an approximately 20 cm x 20 cm area with a standard combination tool (shovel and maddox). A total of four samples were collected: LPA, a pile-burned sample that burned during the 2001/2002 fire season; LPB, a pile-burned sample that burned during the 1999/2000 fire season; LPC, a soil sample; and LTR, multiple samples of unburned litter consisting dominantly of pine needles. Pine needles are one of the most common matrices used to passively

monitor contaminants such as PAH (Ratola et al., 2006). Pine litter is an ideal passive sampler for PAH because of its lipid-rich cuticle, which is likely to accumulate lipophilic organic pollutants (Ratola et al., 2006).

3. METHODS

Each step of the analytical procedures outlined in this research was developed to minimize contamination while maximizing data accuracy. Prior to analysis, samples were prepared by separation of charcoals from sediment matrices, powdering charcoals by hand in a mortar and pestle, accelerated solvent extraction of organic constituents, concentration under heat and N₂ by RapidVap, liquid-column chromatography, and a final concentration to dryness under a combination of RapidVap heat and N₂ as well as N₂ alone. Extracts were resuspended in a known volume of methylene chloride (dichloromethane) immediately prior to gas-chromatographic analysis.

3.1. Contamination Controls

All samples were kept frozen to minimize microbial alteration of samples until analysis at The University of Tennessee Department of Earth and Planetary Sciences Organic Geochemistry laboratory. All disposable glassware is ashed in a muffle furnace (Fisher Scientific, Fair Lawn, NJ) at 550° C for a minimum of 2.5 hours prior to use. All glassware that is repeatedly used is first washed with a non-organic detergent, then triple-rinsed with ultrapure (Milli-Q Gradient System) water, triple-rinsed with HPLC-Resolve acetone and methanol, triple-rinsed with ultrapure water again, and finally ashed at 550° C for a minimum of 2.5 hours. All solvents are at least HPLC-grade or GC-Resolve grade (Fisher Scientific). Ottawa

sand standard (20-30 mesh, Fisher Scientific) used in accelerated solvent extraction (ASE) is ashed at 550° C for a minimum of 2.5 hours prior to use. Each ASE cell is cleaned between samples with non-organic detergent, rinsed with methanol and acetone, sonicated in methanol for 15 minutes, and air dried prior to usage.

3.2. Accelerated Solvent Extraction

Because spiked artificial matrices do not generally behave in the same way as natural samples (Colmsjo, 1998), extraction methods were not developed and optimized specifically for this research; instead, accelerated solvent extraction was determined to be best suited to these samples over microwave assisted extraction, pure solvent extraction, soxhlet extraction, ultrasonic extraction, and solid phase extraction based on published literature (Dean, 1996; Colmsjo, 1998).

Organic extractions were conducted on a Dionex 300 accelerated solvent extractor to remove the solvent-extractable organic compounds from each charcoal sample. Accelerated solvent extraction (ASE) utilizes solvents of differing polarities at elevated temperatures and pressures to increase the solvating capacity of each solvent. Increased pressure increases the boiling point of each solvent, allowing their use at elevated temperatures while remaining in a liquid phase. Each powdered sample was loaded into an ASE cell, with a filter on both ends, and ashed quartz sand filled the remaining volume of the cell.

Extractions were conducted at 1500 psi, 100° C, with a heat-up time of 5 minutes, 10 minute stasis, 60% flush, and 100 second N₂ purge. Each extraction consisted of 2 cycles automatically conducted by the ASE. Solvents used were hexane (30%), methylene chloride (40%), and methanol (30%).

Eluants were concentrated to approximately 2 mL in a RapidVap (Labconco, Kansas City, MO). The RapidVap utilizes N₂, vortex motion, and heat to evaporate solvents. Eluants were placed in a RapidVap vessel, heated, and subjected to vortex motion, which allows a directed stream of N₂ to reduce the partial pressure directly over the liquid to speed evaporation and help drive concentration of the sample without alteration. Concentrated eluants were transferred to glass vials for final concentration to dryness, conducted with only a direct N₂ stream.

3.3. Liquid Chromatography

Liquid chromatography utilizes solvents of increasing polarities to separate a total organic extract into different polar fractions. PAH are mid-polarity compounds. The purpose of liquid chromatography is to separate compounds based on polarity to improve the resolution of future analyses, in this case, gas chromatography-mass spectrometry.

Each liquid chromatography column (30 cm x 2 cm) was loaded with 5% deactivated silica gel (70-230 mesh, Whatman, Clifton, NJ), and then conditioned

with methanol (5.1 polarity), methylene chloride (3.1), and hexane (0.0), respectively. A re-suspended sample was then loaded onto the column, and eluted with hexane, methylene chloride, and methanol, respectively. Each fraction was collected in separate vessels, and again concentrated to dryness.

3.4. Gas Chromatography-Mass Spectrometry

Analytical methods to quantify PAH concentrations ([PAH]) from charcoals needed to first be developed through the use of authentic reference standards (Polynuclear Aromatic Hydrocarbons Mix, 2000 µg/mL, 18 analytes, Supelco, Bellefonte, PA). Target analytes for this study consist of 16 U.S. Environmental Protection Agency (EPA) priority PAH: 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benz(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, and benzo(ghi)perylene. Gas chromatography-mass spectrometry (GC-MS) was conducted with an Agilent 6890 GC interfaced to a 5973N mass selective detector and a 7683 autosampler. Analyses were performed with a ZB-5ms column: 30 m x 0.25 mm i.d. x 0.25 µm film thickness (Phenomenex, Torrance, CA). This system is controlled by Agilent Enhanced Chemstation software G1701DA version D.00.01.27 and coupled to the National Institute of Standards and Testing (NIST) 1998 spectral library, in addition to

chemical-standard-derived compound databases for identification and quantification. Calibration standards were utilized to lock-in retention times of target compounds and build, within Chemstation, a database for the quantification of target species from samples. The quantitation database was refreshed with each batch of sample analysis, based on a 5-member calibration set. Calibration curves for each compound resulted in r^2 values of at least 0.95 for each analyte.

The initial GC-MS parameters for the analysis of PAH were those of the EPA (8270D). This method was optimized to provide greater spectral resolution and quantification accuracy, in addition to the potential for future compound-specific isotopic analysis, which requires more chromatographic separation than simple compound quantification. The optimal method to identify and quantify PAH from charcoals was determined to be the following: 1 μ L split injection at 250° C, oven initially at 70° C held isothermal for 2.00 minutes, then ramped to 110° C at 6.00°/minute and held isothermal for 2.00 minutes, then ramped to 170° C at 3.00°/minute and held isothermal for 2.00 minutes, then ramped to 300° C at 6.00°/minute and held isothermal for 15.00 minutes for a total run time of 69.33 minutes. The MS detector interface was set to 280° C. Ultrapure helium was employed as the carrier gas, and analyses were performed in electron impact ionization mode with an electron energy of 70 eV. Acquisition was performed under time scheduled selected ion monitoring (SIM) using the retention time

windows and qualifying ions for each compound separated into 9 groupings, as indicated in Table 1.

4. RESULTS AND DISCUSSION

The concentrations of 16 target PAH species were determined from Carboniferous, Triassic, and Modern samples by GC-MS after ASE extraction. Target PAH species are: 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, and benzo(ghi)perylene. Each of 14 samples was analyzed in triplicate and results are shown in Table 2. Average values and standard deviations of triplicate analyses by Period and PAH species are shown in Table 3. Time-averaged values for individual PAH species are presented in Figure 9. These values represent the species average values of all samples of the specified Period based on n observations, as indicated in Table 3. All concentrations are presented in parts per million, defined as μg of PAH species per gram of charcoal, except for samples LPC and LTR (Modern), which are not charcoal samples, but soil and litter samples, respectively. These samples were located directly adjacent to modern pile burns at Zion National Park, UT, and collected within one square kilometer of the charcoal samples, LPA and LP2. The units for non-charcoal samples (ppm) represent μg of PAH species per gram of soil (LPC) or litter (LTR). These samples, serving as passive samples, contain PAH as a result of airborne fallout (both particulate and aerosol) from surrounding fires.

Sixteen PAH species were selected as target analytes because (1) they represent a wide range (2 – 6 fused benzene rings, Figure 10) of compounds that develop during the combustion process (O'Malley et al., 1997), and (2) analytical standards are readily available and relatively inexpensive. Standard deviations (SD) are based on the relationship given by: $SD = \sqrt{\frac{n \sum x^2 - (\sum x)^2}{n^2}}$ where n is the number of PAH concentration values above detection, and x is the PAH concentration value. Concentrations below detection (nd) are ignored.

4.1. Complete Empirical Data Set

PAH concentrations determined for individual samples range from 0.09 to 63.58 ppm for all Periods (Table 2). For the Carboniferous samples, values range from 0.09 to 63.58 ppm with an average value of 3.53 ppm and standard deviation (SD) of 5.53; the most abundant species is phenanthrene (6.21 ppm average). Triassic values range from 0.29 to 4.26 ppm with an average of 2.66 and SD of 1.42; the most abundant species is indeno(1,2,3-cd)pyrene (3.04 ppm average). Modern values range from 0.36 to 6.98 ppm with an average of 3.12 ppm and SD of 1.18; the most abundant species is indeno(1,2,3-cd)pyrene (4.19 ppm average).

4.1.1. Statistical Analysis of PAH Distributions

The complete data set is presented in Table 2, and period-averaged values by PAH species are presented in Table 3. To examine nonrandom patterns in the data, two tests were performed. A Kruskal-Wallis test was performed to determine the significances of difference by species between the three periods. A binomial probabilities test was performed on the period-averaged concentrations of PAH species to compare the probabilities of potential relationships with observed relationships between the three groups.

4.1.1.1 Kruskal-Wallis Test

A non-parametric test was chosen to determine the statistical significance between data of different periods (Carboniferous, Triassic, and Modern) because the data are neither normally distributed nor of equal number per group. To determine the significance of differences between values, the data were subjected to Kruskal-Wallis tests, which are used to determine the variance between ranked data. This analysis produces a probability (p) value for the observed aggregate difference among the three periods. The Kruskal-Wallis H statistic is given by the equation

$$H = \frac{SS_{bg(R)}}{N(N+1)/12}$$

where, $SS_{bg(R)}$ is the between-period sum of squared deviate ranks, and N is the highest ranking. All of the data are ranked from lowest to highest concentration and then grouped by period and species. The sum and average rank value for each species by period is then determined. For each period, the number of observed measurements is multiplied by the squared difference between the period and total means for all three periods. The sum of these squared deviates gives the aggregate degree to which the groups differ ($SS_{bg(R)}$). To assess probability to this statistic, the sum of squared deviates is then divided by the mean of the sampling distribution of the $SS_{bg(R)}$ value. Treating the resultant H value as a chi-square with two degrees of freedom, the probability (p) can be assessed. The null hypothesis for this analysis is that the mean ranks of the three periods do not substantially differ.

The results of the Kruskal-Wallis analyses are presented in Table 4a. The null hypothesis is rejected in all cases except for 2-mtheylnaphthalene, acenaphthylene, acenaphthene, and fluorene. For these four compounds, which all correspond to 2-ring PAH species, the number of detectable observations in any period is less than five, the critical number of observations for statistical significance. Therefore, the significance of difference between these four compounds cannot be determined statistically. By the Kruskal-Wallis test, the aggregate difference among the three periods is significant to the p level given in Table 4a for 3- to 6-ring PAH species, phenanthrene through benzo(ghi)perylene.

4.1.1.2. Binomial Probabilities

Binomial probabilities (P) were calculated for the data in Table 3 using the following equation

$$P_{(k/n)} = \frac{n!}{k!(n-k)!} (p^k)(q^{n-k})$$

where, n is the total number of measured values; k is the number of times a binomial outcome is observed; p is the probability that the outcome will occur on any particular occasion; q is the complementary probability that the outcome will not occur on any particular occasion. The binomial probability (P) of any one period's PAH values being higher than either of the other Periods' PAH values is a test of the null hypothesis that there is no significant difference between samples. This hypothesis is rejected in all cases based on the P values presented in Table 4b.

4.1.2. Relative Proportions of PAH by Ring Number

Table 5 presents the relative proportions of PAH species by ring number and period. The 4-ring PAH species represent the largest proportion of species by average concentration for all periods. Two-ring PAH species have relatively low abundance in all periods, except for the modern, where they are ranked second-lowest to 3-ring species. This apparent lack of smaller-ring-number PAH may be

the result of microbial degradation, preferential loss to the atmosphere of the lower-molecular-weight compounds during the wildfire event, or combustion dynamics (e.g., the fire may have been hot enough to preferentially produce higher-ring-number PAH species).

PAH stability and hydrophobicity increase thermodynamically with ring number (Juhasz and Naidu, 2000; Yunker et al., 2002), and therefore, the higher molecular weight species should comprise the majority of PAH species present in any of the samples, especially the ancient samples, which have had more time for physical and chemical biotic and abiotic degradation. This assumes, of course, that the fire dynamics were such that higher ring number PAH species developed. The majority of PAH species in all samples are indeed of larger, 4- to 6-ring species; however, the Carboniferous samples are somewhat enigmatic for their relatively high proportion of 2- and 3-ring species (47.7% collectively). This may simply be due to excellent preservation where degradation is minimal, or may be due to the addition of PAH species from the substantial coal measures in the sub- and superjacent strata during diagenesis. The specific mechanism(s) responsible for this trend is (are) yet unknown, but will likely require experiments to determine the effects of each parameter on the resultant charcoals and PAH distributions.

4.1.3. PAH Isomer Source Ratios

PAH isomer ratios have been used to identify sources, such as distinguishing gasoline and diesel automobile emissions from coal combustion or wood combustion (Yunker et al., 2002). This technique derives from the thermodynamic stabilities of various PAH species, which tend to increase with ring number, and therefore, molecular mass (MM). For each of the ratios, different PAH species with the same MM are compared. For example, the PAH species anthracene and phenanthrene each have a MM of 178; the ratio of MM 178 therefore is determined by dividing the mass of anthracene by the combined masses of anthracene plus phenanthrene. The ratios are most definitive for MM 202 and MM 276, the PAH with the largest differences in thermodynamic stability between isomers (Yunker et al., 2002). The technique is generally only applied to PAH compositions from within sediments and accounts for PAH loss during transport. Although the samples utilized in the present study are not sediment samples (except LPC and LTR), in general, the ratios provide a secondary means of source assessment, that of combustion.

Table 6 presents four different PAH isomer ratios, those of MM 178 (Table 6a), 202 (Table 6b), 228 (Table 6c), and 276 (Table 6d). Three of these four ratios (MM 202, 228, and 276) generally indicate a wood combustion source, while the ratio for MM 178 does not. Phenanthrene and anthracene (MM 178), in addition to fluoranthene, are 3-ring PAH species, which constitute the lowest and

second-lowest proportion of PAH species for Modern and Triassic samples, respectively; however, the 3-ring PAH constitute the second-highest proportion of Carboniferous charcoal samples (Table 5). The input of modern automobile emissions may account for the Modern ratios, but cannot account for the ancient. These ratios have been developed for use in modern sediment samples and experimental work is needed to determine the utility of these ratios, or other yet unknown relationships, in purely fire-derived residues such as charcoal.

4.1.4. Relations between Atmospheric Oxygen Content and PAH Concentrations

Based on the total averages of PAH concentrations per period, a positive relationship exists between atmospheric oxygen level and total average concentration of the 16 PAH species (Table 7 and Figure 11). Total averages are calculated by taking the sum of all concentrations for all replicate samples and all PAH species by period, then dividing by the number of observations, n . In many instances, concentrations of target analytes are below detection (nd), and those statements are ignored.

In no instances is there an inverse relationship between modeled atmospheric oxygen content and either total mean PAH concentration or individual mean PAH concentration by time. There are no instances in which Carboniferous PAH concentrations are lower than Triassic values, as might be

expected if PAH were developing in greater abundances due to lower oxygen contents, as might be implied from Simoneit (1998). Therefore, it is not likely that PAH concentrations will have an inverse relationship with atmospheric oxygen content; rather, the data suggest, although primitively, that PAH concentrations are positively correlated to atmospheric oxygen.

4.2. PAH Species Exhibiting a Positive Relation to Atmospheric Oxygen Content

Of the 16 target analytes, 8 individual 2- to 4-ring PAH co-vary with modeled (Berner et al., 2003) atmospheric oxygen: 2-methylnaphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, and benzo(b)fluoranthene. These 8 compounds each have higher concentrations in samples that developed in higher atmospheric oxygen levels, according to modeled atmospheric oxygen contents (Berner et al., 2003). Each average PAH concentration by Period is calculated by taking the sum of the concentrations for each triplicate sample by Period and species, then dividing that sum by the total number of samples, n , for that Period and species. If any replicate sample did not have detectable amounts of the target analyte, the value (nd) is ignored.

5. CONCLUSIONS

This study is a first attempt at directly relating atmospheric oxygen level to the sum-average of PAH concentrations and individual-average PAH concentrations. Though the general relationships between combustion and gaseous O₂, and therefore wildfires and global oxygen content, are established beyond doubt (Scott, 2000), the role of atmospheric oxygen in the production of PAH and their retained geochemical signatures within wildfire residues (charcoals) are yet to be determined conclusively. The results presented here are clearly observational and first-order, yet they serve as a starting point for future study. The preliminary status of this study is underscored by (1) considerable imprecision in the Phanerozoic atmospheric oxygen model (Berner et al., 2003), which affects any quantitative mathematical relationship with PAH concentrations; (2) the limited time frame considered (three periods); and (3) the influence of many parameters that are beyond control, such as combustion efficiency, fuel geometry, and fuel moisture. Each of these drawbacks, however, may be addressed with future experimental designs that account for each of these parameters individually.

With those considerations in mind, several conclusions may be drawn regarding the wildfire-derived PAH concentrations from samples that developed in three significantly different atmospheric oxygen regimes. (1) Data for each period is significantly different from the other two. (2) The summed-averages of

PAH concentrations for each period - Carboniferous, Triassic, and Modern - correlate to modeled atmospheric oxygen levels (Berner et al., 2003). (3) Eight individual PAH species correlate to modeled atmospheric oxygen content: 2-methylnaphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, and benzo(b)fluoranthene. Although preliminary, the results of this study are an encouraging first step toward the development of an independent means to assess long-term, post-Devonian atmospheric oxygen change.

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APPENDICES

TABLES

TABLE 1. PAH Retention Times and Qualifying Ions

Elution Order	PAH Species	Retention Time (min)	Group	Start Time	Qualifying Ions (mass)
1	2-Methylnaphthalene	12.35	1	11.00	142, 141, 115
2	Acenaphthylene	17.75	2	15.00	152, 151, 150
3	Acenaphthene	18.98	3	18.40	153, 154, 152, 76
4	Fluorene	22.68	4	21.00	166, 165, 82, 163
5	Phenanthrene	29.61	5	29.00	178, 176, 179, 89, 76
6	Anthracene	29.99			
7	Fluoranthene	38.21	6	37.00	202, 200, 203, 101
8	Pyrene	39.33			
9	Benz(a)anthracene	45.11	7	42.00	228, 226, 229, 114
10	Chrysene	45.24			
11	Benzo(b)fluoranthene	49.26	8	48.00	252, 250, 253, 126
12	Benzo(k)fluoranthene	49.37			
13	Benzo(a)pyrene	50.34	9	53.00	276, 138, 277
14	Indeno(1,2,3-cd)pyrene	53.82			
15	Dibenz(a,h)anthracene	53.97			
16	Benzo(ghi)perylene	54.52			

Table 2. PAH concentrations in ppm from Carboniferous, Triassic, and Modern Charcoals

Period	Sample	Replicate	2-Methylnaphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benz(a)anthracene
Modern (21% α)	LPA	1	1.18	0.78	nd	0.49	1.63	0.68	2.38	nd	3.10
		2	3.40	3.71	nd	nd	3.43	3.40	3.87	3.59	4.03
		3	3.40	3.61	3.37	3.39	3.45	3.41	4.02	3.58	4.13
	LPB	1	nd	nd	nd	nd	1.58	0.67	nd	0.87	2.02
		2	nd	nd	nd	nd	3.38	3.35	3.57	3.56	nd
		3	nd	nd	3.34	nd	3.40	3.37	3.58	3.57	nd
	LPC	1	nd	nd	nd	nd	nd	nd	nd	nd	1.38
		2	nd	nd	nd	nd	nd	nd	3.57	3.57	nd
		3	nd	nd	nd	nd	nd	nd	3.54	3.53	nd
	LTR	1	1.03	nd	nd	0.36	1.20	0.49	1.06	0.98	1.75
		2	nd	nd	nd	nd	3.37	nd	nd	3.57	nd
		3	nd	3.55	nd	nd	3.64	3.57	3.62	3.59	4.02
Triassic (15% α)	DW	1	nd	nd	nd	nd	2.01	1.63	0.63	0.53	0.68
		2	nd	nd	nd	nd	3.41	3.39	3.56	3.55	3.99
		3	nd	nd	nd	nd	3.56	3.54	3.62	3.61	4.06
	AR	1	nd	nd	nd	nd	0.77	0.30	nd	0.38	0.84
		2	nd	nd	nd	nd	nd	nd	3.56	3.56	4.02
		3	nd	nd	nd	nd	nd	nd	3.57	nd	4.02
	TP	1	0.29	nd	nd	nd	1.06	0.72	0.38	0.36	0.54
		2	nd	nd	nd	nd	3.52	3.50	3.59	3.60	4.01
		3	nd	nd	nd	nd	3.43	3.41	3.57	3.57	4.00
Carboniferous (35% α)	JFC1	1	0.63	nd	0.09	0.13	0.39	0.24	0.14	0.13	0.24
		2	3.59	nd	3.35	3.42	3.77	3.74	3.60	3.61	4.00
		3	3.60	nd	3.34	3.42	3.71	3.69	3.58	3.59	3.97
	JFC2	1	1.30	nd	nd	0.26	0.77	0.56	0.23	0.23	0.32
		2	3.80	3.51	3.35	3.60	4.54	4.50	3.77	3.88	4.06
		3	3.39	nd	nd	3.58	5.03	5.01	3.84	3.98	4.07
	JFC3	1	0.39	nd	nd	0.12	0.69	0.52	0.29	0.29	0.31
		2	nd	nd	nd	nd	3.46	3.43	3.62	3.63	4.01
		3	nd	nd	nd	nd	3.47	3.45	3.62	3.63	4.00
	JFC4	1	0.24	nd	nd	nd	3.27	2.76	0.98	0.54	0.73
		2	nd	nd	nd	nd	3.38	3.36	3.63	3.59	4.00
		3	nd	nd	nd	nd	3.52	3.49	3.63	3.58	4.00
	JFC5	1	2.89	nd	nd	1.49	63.58	60.51	29.02	11.00	11.06
		2	nd	nd	nd	nd	4.46	4.43	4.46	3.89	4.05
		3	3.33	nd	nd	3.34	5.74	5.71	4.86	4.02	4.14
	MC1	1	0.99	0.31	0.20	1.01	3.67	0.78	1.76	1.54	1.53
		2	3.47	3.47	3.33	3.58	4.68	3.47	4.24	4.22	4.50
		3	3.64	3.54	3.38	3.69	4.92	3.55	4.39	4.31	4.62
	SCI	1	0.23	nd	nd	0.18	0.50	0.23	0.34	0.54	0.50
		2	3.39	nd	nd	3.37	3.39	3.36	3.62	3.83	3.98
		3	3.36	nd	nd	3.37	3.41	3.38	3.66	3.99	3.99

Table 2, continued.

Period	Sample	Replicate	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene	Dibenzo(a,h)anthracene	Benzo(ghi)perylene
Modern (21 % O ₂)	LPA	1	3.45	1.70	1.52	nd	2.07	2.56	nd
		2	3.27	4.20	3.48	4.12	4.52	3.78	3.74
		3	3.39	4.24	3.52	nd	4.29	3.79	3.40
	LPB	1	3.17	nd	nd	nd	nd	nd	2.55
		2	nd	nd	nd	nd	4.25	3.67	3.48
		3	nd	nd	nd	nd	4.24	3.60	3.45
	LPC	1	1.59	nd	nd	1.16	nd	2.09	nd
		2	nd	nd	nd	4.09	4.33	3.98	3.60
		3	nd	nd	3.44	nd	4.18	3.49	3.38
	LTR	1	6.98	1.78	1.60	1.43	nd	1.86	1.90
		2	nd	4.30	3.61	4.42	5.07	4.30	4.36
		3	3.26	4.21	3.48	4.17	4.76	3.94	3.97
Triassic (15 % O ₂)	DW	1	1.06	0.72	0.73	0.73	0.72	0.84	0.98
		2	3.25	4.17	3.45	4.08	4.15	3.40	3.35
		3	3.31	4.26	3.53	4.14	4.19	3.45	3.40
	AR	1	0.99	0.80	nd	0.78	0.97	1.26	nd
		2	3.27	4.21	3.48	4.10	4.17	3.40	3.36
		3	3.27	4.20	3.48	nd	4.18	3.39	3.36
	TP	1	0.65	0.53	0.52	0.54	0.66	0.83	0.87
		2	3.26	nd	3.48	4.11	4.18	3.39	3.36
		3	3.25	nd	3.46	4.10	4.17	3.36	3.35
Carboniferous (35 % O ₂)	JFC1	1	0.28	0.25	0.23	0.25	0.33	0.46	0.42
		2	3.27	4.20	3.48	4.10	4.16	3.37	3.36
		3	3.24	4.17	3.45	4.08	4.14	3.34	3.33
	JFC2	1	0.38	0.33	nd	0.32	0.40	0.54	0.54
		2	3.33	4.25	3.52	4.14	4.20	3.48	3.44
		3	3.35	4.25	3.53	4.14	4.19	3.46	3.45
	JFC3	1	0.35	0.39	0.35	0.32	0.34	0.42	0.47
		2	3.28	4.21	3.48	4.11	4.18	3.41	3.37
		3	3.27	4.23	3.51	4.11	4.17	3.40	3.37
	JFC4	1	0.88	0.78	0.69	0.70	0.87	1.13	1.16
		2	3.26	nd	nd	nd	nd	3.37	3.35
		3	3.25	nd	nd	nd	nd	nd	3.34
	JFC5	1	9.08	16.16	5.71	6.42	6.97	2.90	7.82
		2	3.60	4.93	3.66	4.27	4.58	4.87	3.79
		3	3.73	5.16	3.72	4.33	4.72	5.47	3.93
	MC1	1	1.46	1.14	0.82	1.03	0.80	0.87	1.03
		2	3.80	4.69	3.56	4.42	4.25	3.84	3.49
		3	3.91	4.82	3.61	4.54	4.29	3.90	3.57
	SC1	1	0.59	0.55	0.49	0.48	0.63	nd	0.79
		2	3.23	4.20	3.48	4.09	4.16	3.39	3.36
		3	3.22	4.21	3.49	4.10	4.16	3.42	3.37

Table 3. Average PAH Concentrations (ppm), Standard Deviations (SD), and Number (*n*) from Carboniferous, Triassic, and Modern Charcoals. Values represent the average or SD of all samples from that Period based on *n* observations.

PAH Species	Modern (21% O ₂)			Triassic (15% O ₂)			Carboniferous (35% O ₂)		
	Average	SD	<i>n</i>	Average	SD	<i>n</i>	Average	SD	<i>n</i>
2-Methylnaphthalene	2.26	1.15	4	0.29	0.00	1	2.39	1.40	16
Acenaphthylene	2.91	1.23	4	nd	nd	0	2.71	1.38	4
Acenaphthene	3.36	0.02	2	nd	nd	0	2.44	1.45	7
Fluorene	1.41	1.40	3	nd	nd	0	2.30	1.49	15
Phenanthrene	2.79	0.94	9	2.54	1.15	7	6.21	12.91	21
Anthracene	2.37	1.36	8	2.36	1.33	7	5.72	12.35	21
Fluoranthene	3.25	0.89	9	2.81	1.33	8	4.16	5.77	21
Pyrene	3.04	1.06	10	2.40	1.53	8	3.24	2.30	21
Benz(a)anthracene	2.92	1.10	7	2.90	1.57	9	3.43	2.33	21
Chrysene	3.59	1.51	7	2.48	1.12	9	2.89	1.87	21
Benzo(b)fluoranthene	3.41	1.18	6	2.70	1.75	7	3.84	3.42	19
Benzo(k)fluoranthene	2.95	0.88	7	2.77	1.24	8	2.82	1.52	18
Benzo(a)pyrene	3.23	1.38	6	2.82	1.66	8	3.15	1.87	19
Indeno(1,2,3-cd)pyrene	4.19	0.80	9	3.04	1.60	9	3.24	1.92	19
Dibenz(a,h)anthracene	3.37	0.77	11	2.59	1.15	9	2.90	1.44	19
Benzo(ghi)perylene	3.38	0.66	10	2.75	1.06	8	2.89	1.66	21

Table 4. Statistical Analysis of PAH Distributions

Table 4a. Kruskal-Wallis (*H*) Analysis. *n*, number of PAH concentration values from the specified Period; *df*, degrees of freedom; *p*, probability associated with *H*.

Period	2-Methylnaphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene
Modern <i>n</i>	4	4	2	3	9	8	9	10
Triassic <i>n</i>	1	0	0	0	7	7	8	8
Carboniferous <i>n</i>	16	4	7	15	21	21	21	21
<i>H</i>	1.75	Not Determined	Not Determined	Not Determined	3.74	2.33	3.19	5.4
<i>df</i>	2	2	2	2	2	2	2	2
<i>p</i> *	Not Determined	Not Determined	Not Determined	Not Determined	0.1541	0.3119	0.2029	0.0672
Period	Benz(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene	Dibenz(a,h)anthracene	Benzo(ghi)perylene
Modern <i>n</i>	7	7	6	7	6	9	11	10
Triassic <i>n</i>	9	9	7	8	8	9	9	8
Carboniferous <i>n</i>	21	21	19	18	19	19	19	21
<i>H</i>	0.1	1.58	1.2	1.08	1.07	7.69	5.24	5.6
<i>df</i>	2	2	2	2	2	2	2	2
<i>p</i> *	0.9512	0.4538	0.5488	0.5827	0.5857	0.0214	0.0728	0.0608

* If the size (*n*) of each sample is at least 5, the sampling distribution of *H* can be taken as a reasonably close approximation of the sampling distribution of chi-square with *df* = *k*−1. If any of the *n*'s are of a size smaller than 5, regard the calculated *p*-value as an imperfect approximation.

Table 4, continued.

Table 4b. Binomial Distribution Analysis.

Scenario	k	n	p	q	$P_{\text{exactly } k \text{ times}}$	$P_{\leq k \text{ times}}$	$P_{\geq k \text{ times}}$
Modern > Triassic	13	13	0.50	0.50	0.0001	1.0000	1.0000
Modern > Carboniferous	8	16	0.50	0.50	0.1964	0.5982	0.5982
Triassic > Carboniferous	0	13	0.50	0.50	0.0001	0.5982	0.5982

k , number of observed values in which the scenario is true; n , total number of possible scenarios; p , probability of the scenario being true; q , complement probability that the scenario is false; $P_{\text{exactly } k \text{ times}}$, probability associated with the null hypothesis being accepted exactly k times; $P_{\leq k}$, probability associated with the null hypothesis being accepted less times than k ; $P_{\geq k}$, probability associated with the null hypothesis being accepted more than k times.

Table 5. Average Concentrations of PAH (ppm) and Proportion of the Total Mass of PAH by Ring Number and Period for Carboniferous, Triassic, and Modern Samples.

PAH Species	Ring #	Modern (21% O ₂)		Triassic (15% O ₂)		Carboniferous (35% O ₂)	
		Average	Proportion	Average	Proportion	Average	Proportion
2-Methylnaphthalene	2	2.26	20.5%	0.29	0.9%	2.39	18.1%
Acenaphthylene		2.91		nd		2.71	
Acenaphthene		3.36		nd		2.44	
Fluorene		1.41		nd		2.30	
Phenanthrene	3	2.79	17.4%	2.54	23.7%	6.21	29.6%
Anthracene		2.37		2.36		5.72	
Fluoranthene		3.25		2.81		4.16	
Pyrene	4	3.04	32.9%	2.40	40.8%	3.24	29.9%
Benz(a)anthracene		2.92		2.90		3.43	
Chrysene		3.59		2.48		2.89	
Benzo(b)fluoranthene		3.41		2.70		3.84	
Benzo(k)fluoranthene		2.95		2.77		2.82	
Benzo(a)pyrene	5	3.23	29.3%	2.82	34.6%	3.15	22.4%
Indeno(1,2,3-cd)pyrene		4.19		3.04		3.24	
Dibenz(a,h)anthracene		3.37		2.59		2.90	
Benzo(ghi)perylene	6	3.38		2.75		2.89	

Table 6. PAH Isomer Ratios

Table 6a. Average Anthracene (An) and Phenanthrene (Ph) concentrations (ppm) and ratio An/(An + Ph); MM = 178

Period	Sample	Anthracene	Phenanthrene	An/(An+Ph)	Indicates
Modern (21% O ₂)	LPA	2.50	2.84	0.47	Non-combustion
	LPB	2.47	2.78	0.47	
	LPC	nd	nd	nd	
	LTR	2.03	2.74	0.43	
Triassic (15% O ₂)	DW	2.85	3.00	0.49	Non-combustion
	AR	0.30	0.77	0.28	
	TP	2.54	2.67	0.49	
Carboniferous (35% O ₂)	JFC1	2.56	2.62	0.49	Non-combustion
	JFC2	3.36	3.45	0.49	
	JFC3	2.47	2.54	0.49	
	JFC4	3.20	3.39	0.49	
	JFC5	23.55	24.59	0.49	
	MC1	2.60	4.42	0.37	
	SC1	2.32	2.43	0.49	

An/(An+Ph) < 0.10 indicates combustion (Yunker et al., 2002).

Table 6, continued.

Table 6b. Average Fluoranthene (Fl) and Pyrene (Py) concentrations (ppm) and ratio Fl/(Fl + Py); MM = 202

Period	Sample	Fluoranthene	Pyrene	Fl/(Fl+Py)	Indicates
Modern (21% O ₂)	LPA	3.42	3.58	0.49	Gasoline, diesel, and crude oil combustion
	LPB	3.58	2.67	0.57	Kerosene, grass, most coal and wood combustion, and cresote
	LPC	3.55	3.55	0.50	
	LTR	2.34	2.71	0.46	Gasoline, diesel, and crude oil combustion
Triassic (15% O ₂)	DW	2.60	2.57	0.50	Kerosene, grass, most coal and wood combustion, and cresote
	AR	3.56	1.97	0.64	
	TP	2.52	2.51	0.50	
Carboniferous (35% O ₂)	JFC1	2.44	2.44	0.50	Kerosene, grass, most coal and wood combustion, and cresote
	JFC2	2.61	2.70	0.49	Gasoline, diesel, and crude oil combustion
	JFC3	2.51	2.52	0.50	Kerosene, grass, most coal and wood combustion, and cresote
	JFC4	2.75	2.57	0.52	
	JFC5	12.78	6.30	0.67	
	MC1	3.46	3.35	0.51	Gasoline, diesel, and crude oil combustion
	SC1	2.54	2.79	0.48	

Fl/(Fl+Py) < 0.50 indicates gasoline, diesel, and crude oil combustion and emissions; > 0.50 indicates kerosene, grass, most coal and wood combustion and creosote (Yunker et al., 2002).

Table 6, continued.

Table 6c. Average Benz(a)anthracene (BaA) and Chrysene (Ch) concentrations (ppm) and ratio BaA/(BaA + Ch); MM = 228

Period	Sample	Benz(a)anthracene	Chrysene	BaA/(BaA+Ch)	Indicates
Modern (21% O ₂)	LPA	3.76	3.37	0.53	Combustion
	LPB	2.02	3.17	0.39	
	LPC	1.38	1.59	0.46	
	LTR	2.88	5.12	0.36	
Triassic (15% O ₂)	DW	2.91	2.54	0.53	Combustion
	AR	2.96	2.51	0.54	
	TP	2.85	2.39	0.54	
Carboniferous (35% O ₂)	JFC1	2.74	2.26	0.55	Combustion
	JFC2	2.82	2.35	0.54	
	JFC3	2.77	2.30	0.55	
	JFC4	2.91	2.46	0.54	
	JFC5	6.42	5.47	0.54	
	MC1	3.55	3.06	0.54	
	SC1	2.82	2.35	0.55	

BaA/(BaA+Ch) > 0.35 indicates combustion source (Yunker et al., 2002).

Table 6, continued.

Table 6d. Average Indeno(1,2,3-cd)pyrene (IP) and Benzo(ghi)perylene (Bghi) concentrations (ppm) and ratio IP/(IP + Bghi); MM = 276

Period	Sample	Indeno(1,2,3-cd)pyrene	Benzo(ghi)perylene	IP/(IP+Bghi)	Indicates
Modern (21% O ₂)	LPA	3.63	3.57	0.50	Grass, wood, or coal combustion
	LPB	4.24	3.16	0.57	
	LPC	4.25	3.49	0.55	
	LTR	4.92	3.41	0.59	
Triassic (15% O ₂)	DW	3.02	2.58	0.54	Grass, wood, or coal combustion
	AR	3.11	3.36	0.48	Liquid fossil fuel combustion
	TP	3.00	2.53	0.54	Grass, wood, or coal combustion
Carboniferous (35% O ₂)	JFC1	2.88	2.37	0.55	Grass, wood, or coal combustion
	JFC2	2.93	2.48	0.54	
	JFC3	2.90	2.41	0.55	
	JFC4	0.87	2.62	0.25	
	JFC5	5.43	5.18	0.51	
	MC1	3.11	2.70	0.54	
	SC1	2.98	2.51	0.54	

IP/(IP+Bghi) = 0.20 to 0.50 indicates liquid fossil fuel combustion; > 0.50 indicates grass, wood, and coal combustion sources (Yunker et al., 2002).

Table 7. Simple Statistics for the Sum of PAH Species by Period. Total mean [PAH] (ppm); standard deviation (SD); number of observations. O₂% from Berner et al. (2003)

	Carboniferous	Triassic	Modern
O ₂ %	35%	15%	21%
Mean	3.53	2.66	3.12
SD	5.53	1.42	1.18
<i>n</i>	283	98	112

FIGURES

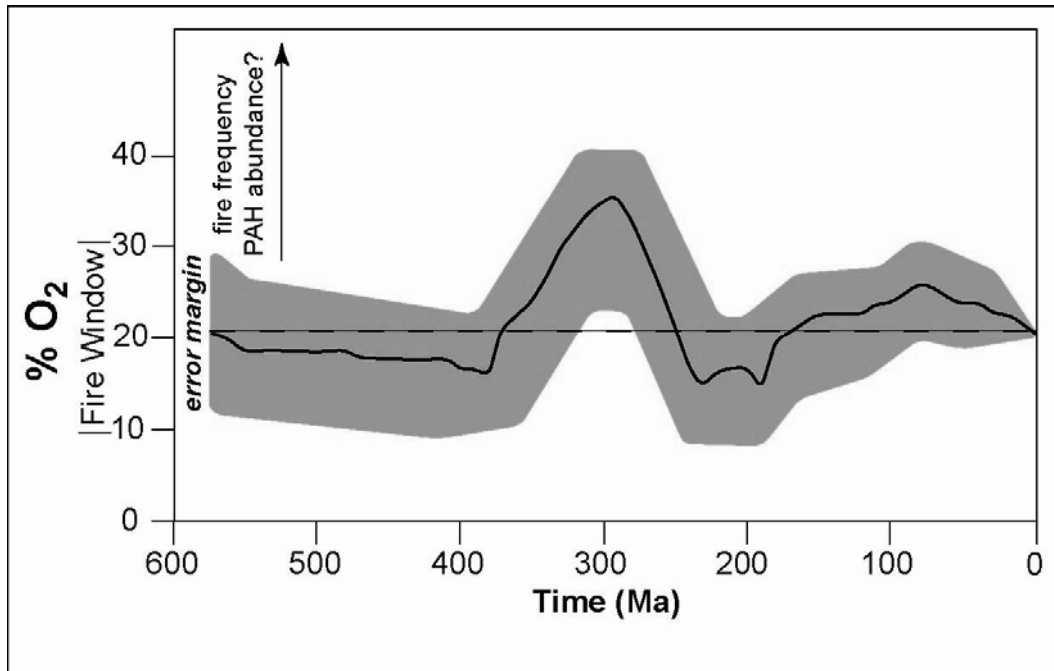


Figure 1. Phanerozoic Record of Oxygen. Model-derived Phanerozoic atmospheric oxygen concentrations, the fire window, and hypothesized relationship between fire frequency, PAH abundance, and oxygen level (modified from Berner et al., 2003 and Scott, 2000).

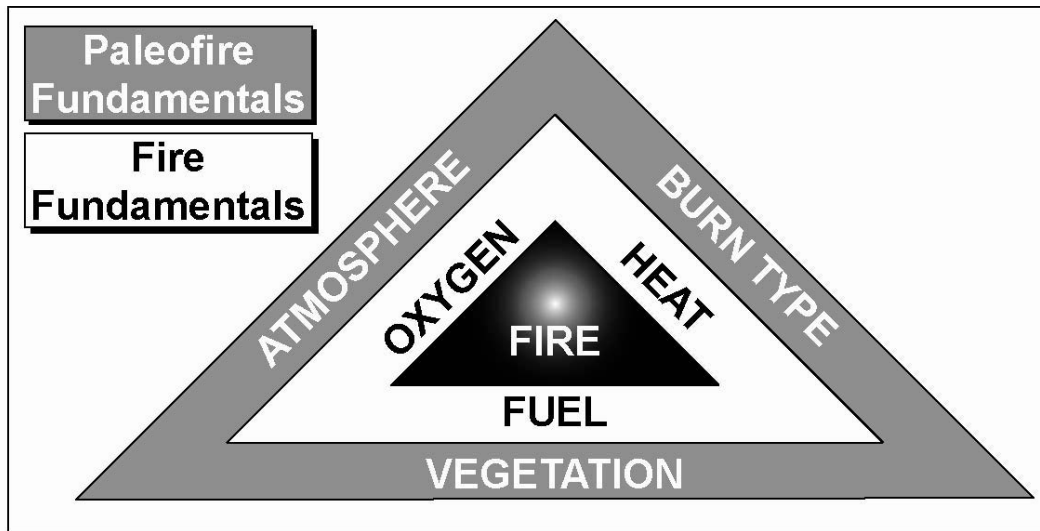


Figure 2. Combustion Essentials. Fire and paleofire triangles representing the main parameters controlling the combustion process in wildfires.

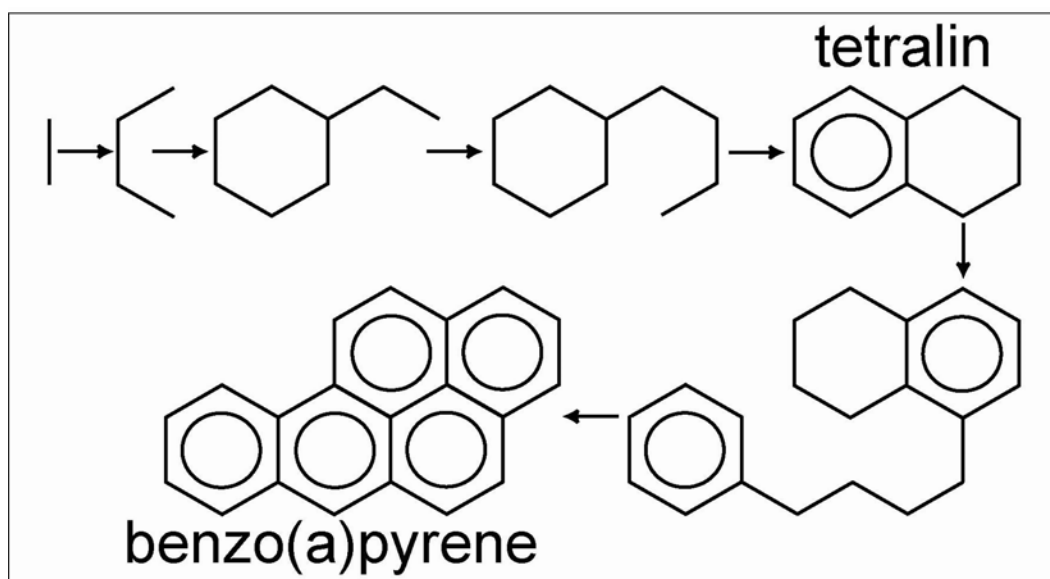


Figure 3. PAH Synthesis Scheme.

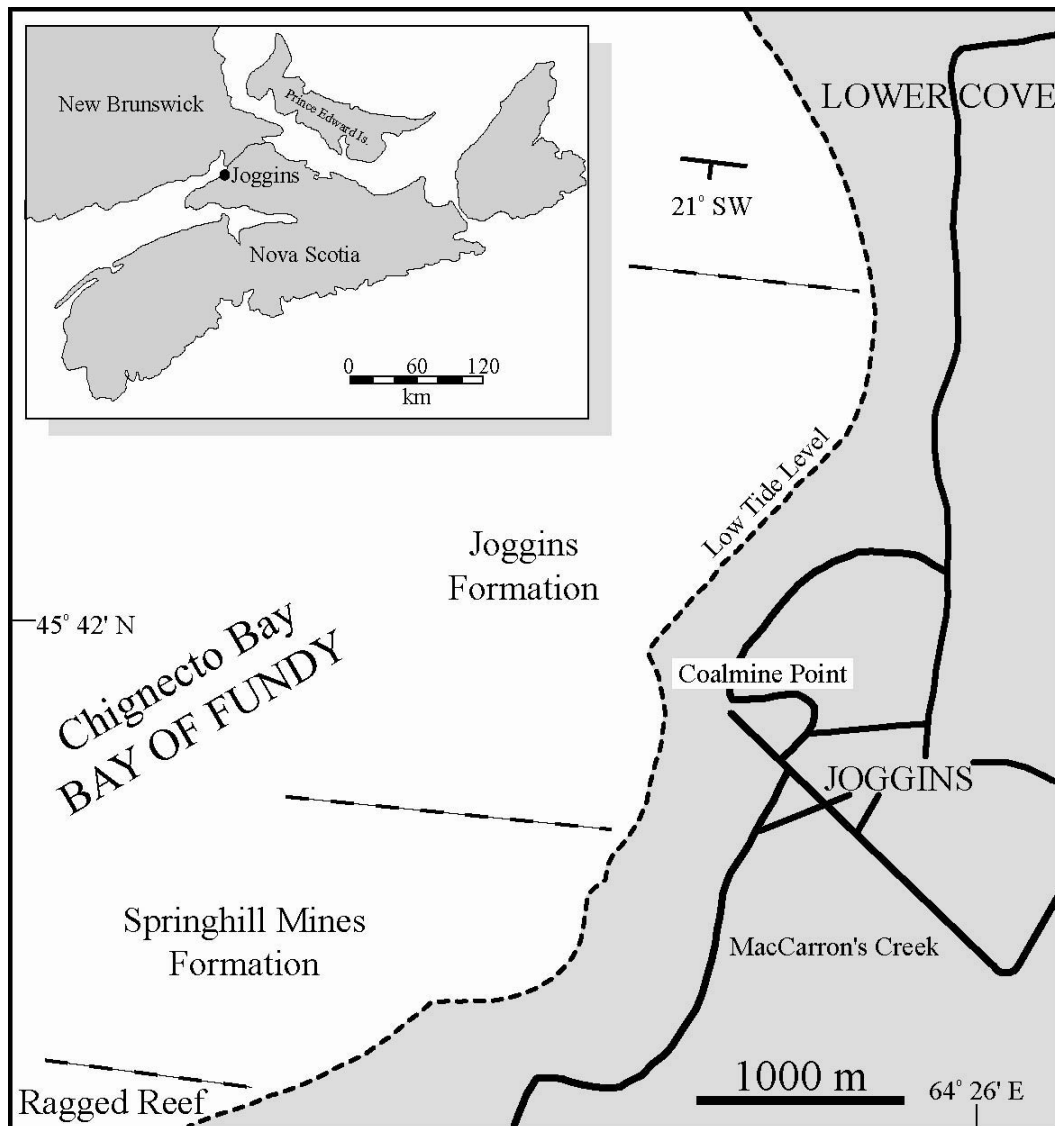


Figure 4. Joggins Field Locality. Location map of the eastern shore of Chignecto Bay showing the Joggins, Springhill Mines, and Ragged Reef Formations (modified from Arens, 1991 and Falcon-Lang, 1999).



Figure 5. Sample JFC-1 from the Joggins Formation (Carboniferous). Note the co-occurrence of fossil charcoal within a mass dominated by true coal.

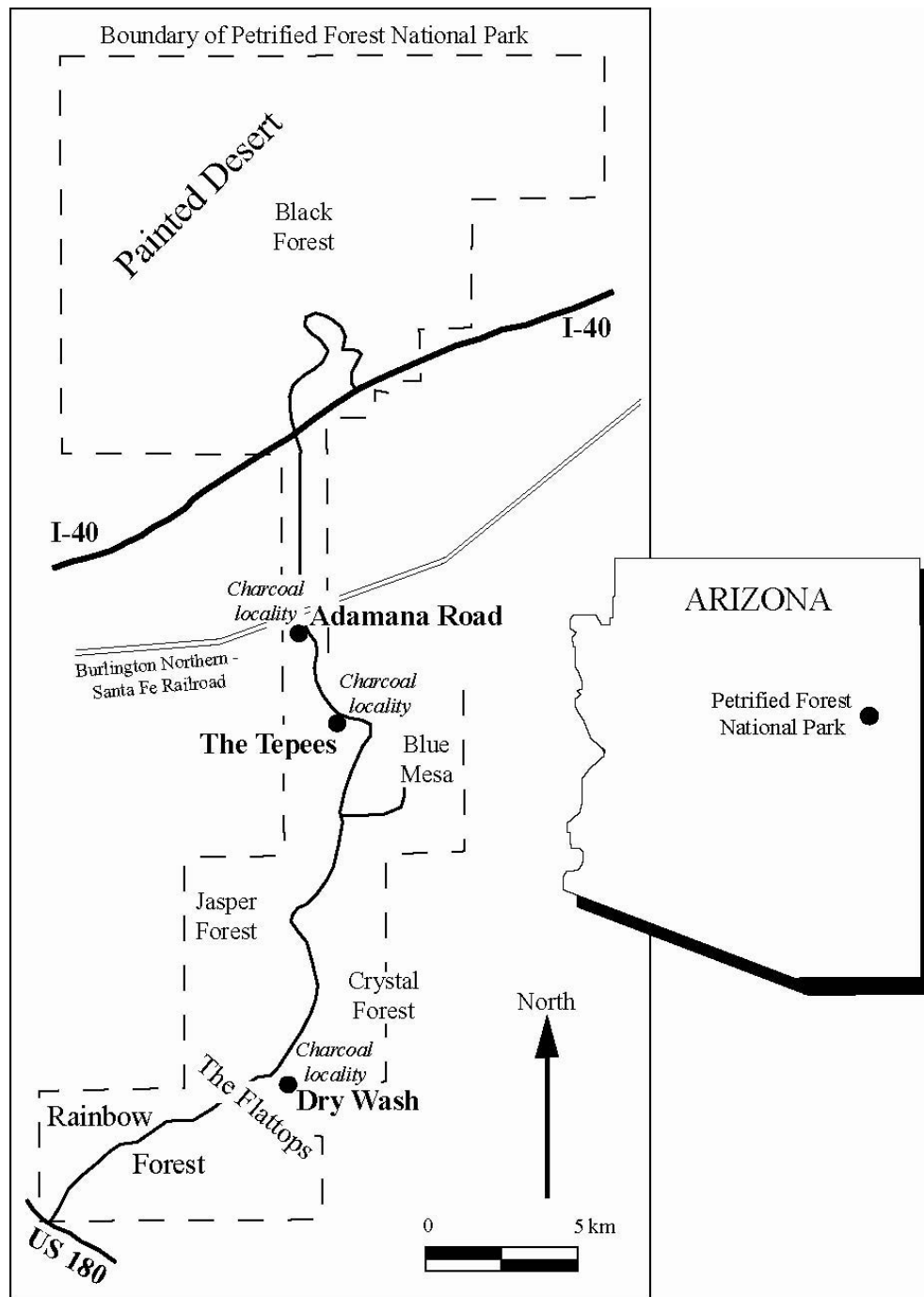


Figure 6. Petrified Forest Field Locality. Location map of Petrified Forest National Park, Arizona, USA (modified from Jones et al., 2002). Entire area is Chinle Formation (Triassic). Charcoal localities are labeled.



Figure 7. Sample TP from the Chinle Formation (Triassic). Note cuboidal morphology and silky luster of the fossilized charcoal.

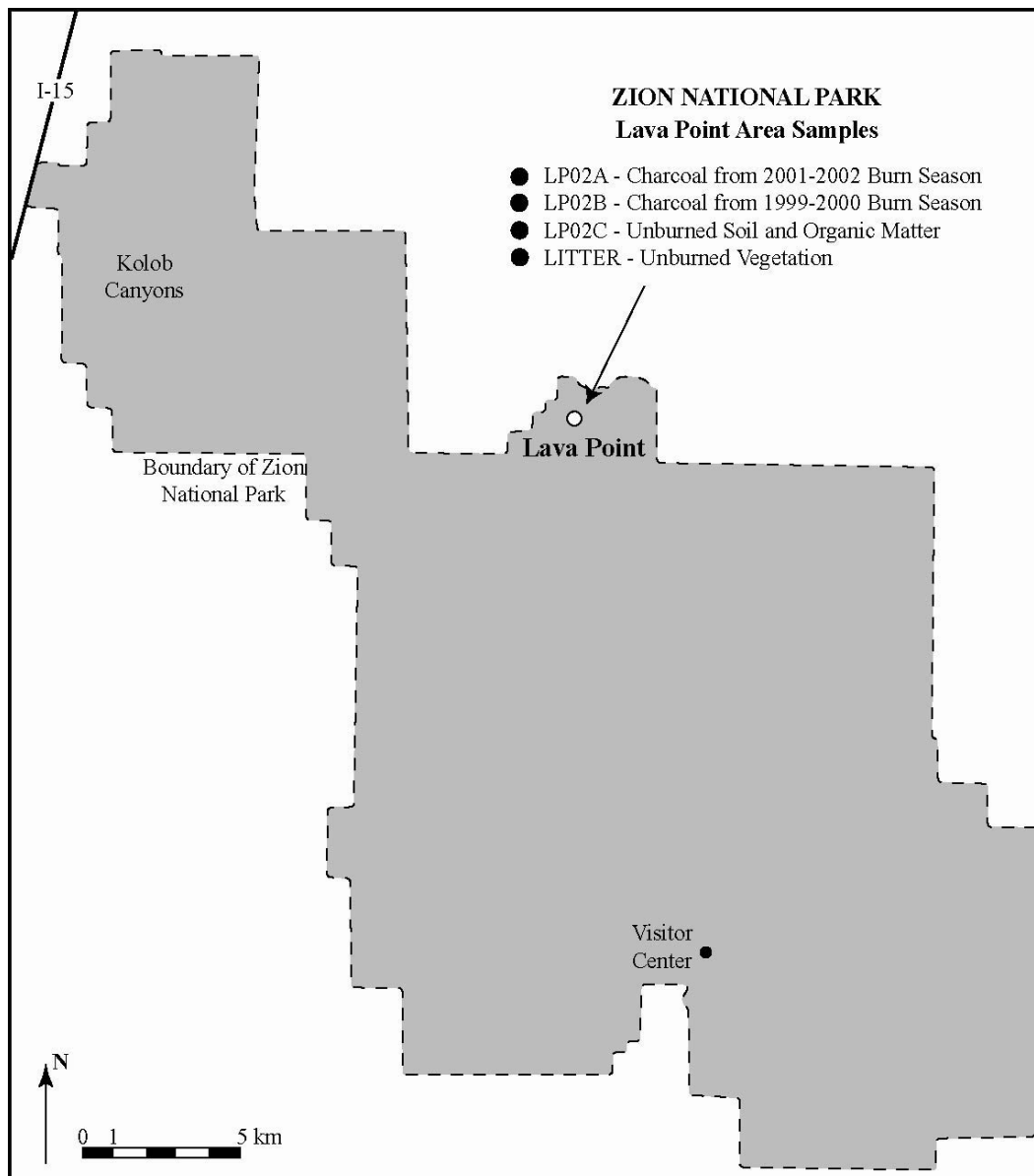


Figure 8. Zion Field Locality. Location map of Zion National Park, Utah, USA. All samples were collected from National Park Service prescribed pile burns within a square-mile of each other from the Lava Point Fire Lookout Station.

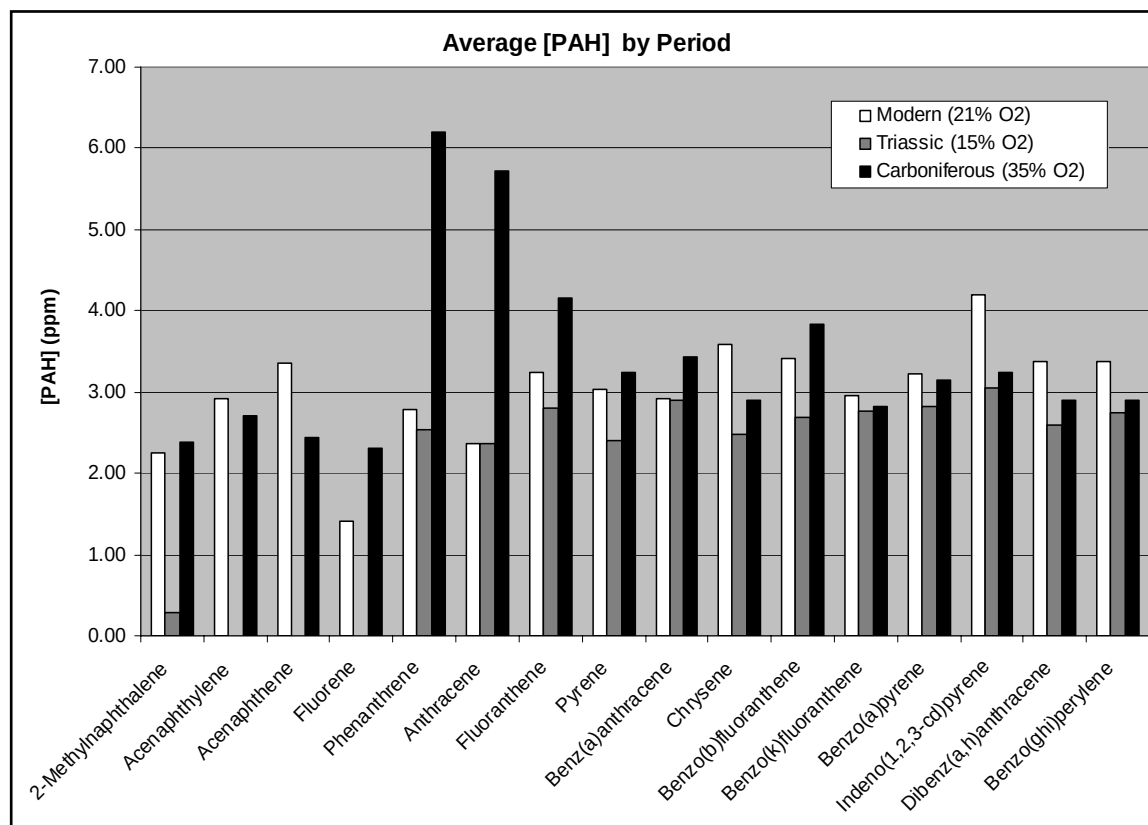


Figure 9. Average PAH Species Concentrations by Period. Values correspond to Table 3 and represent the average of all samples of the specified Period.

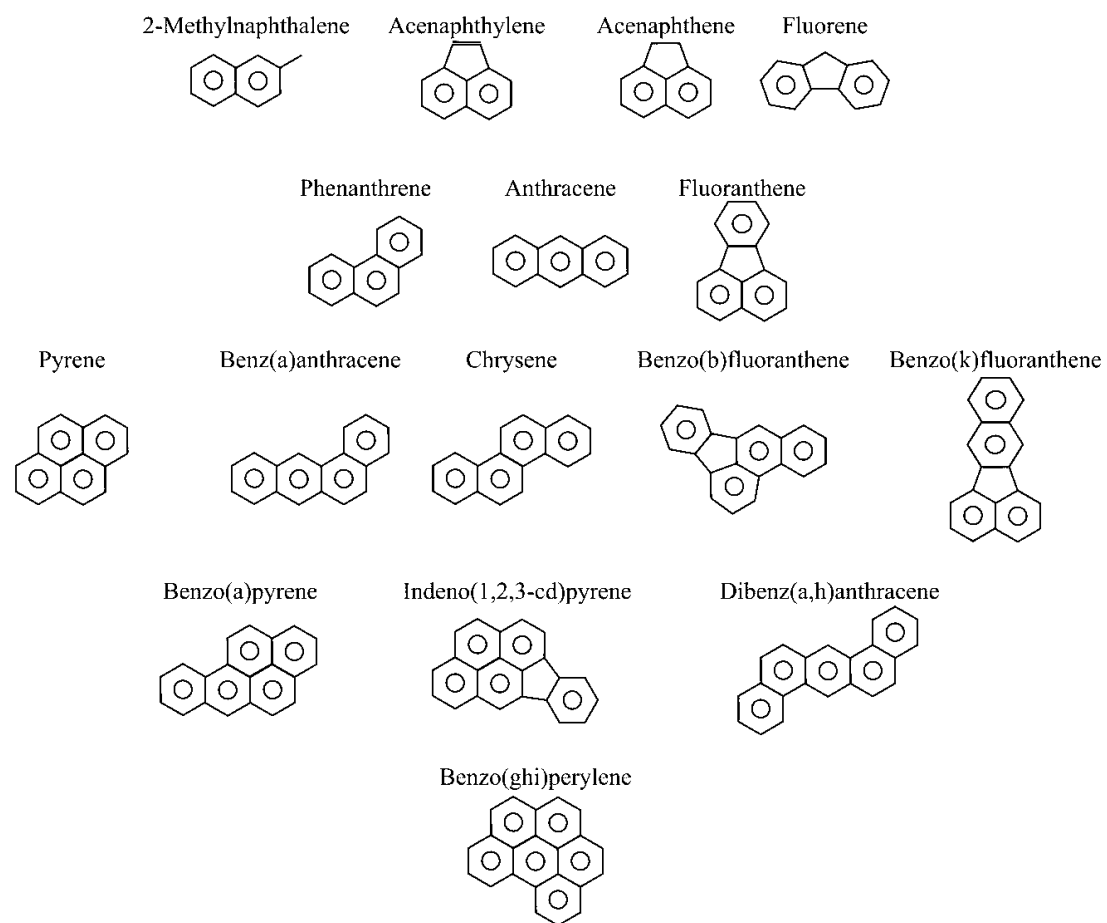


Figure 10. Target PAH species.

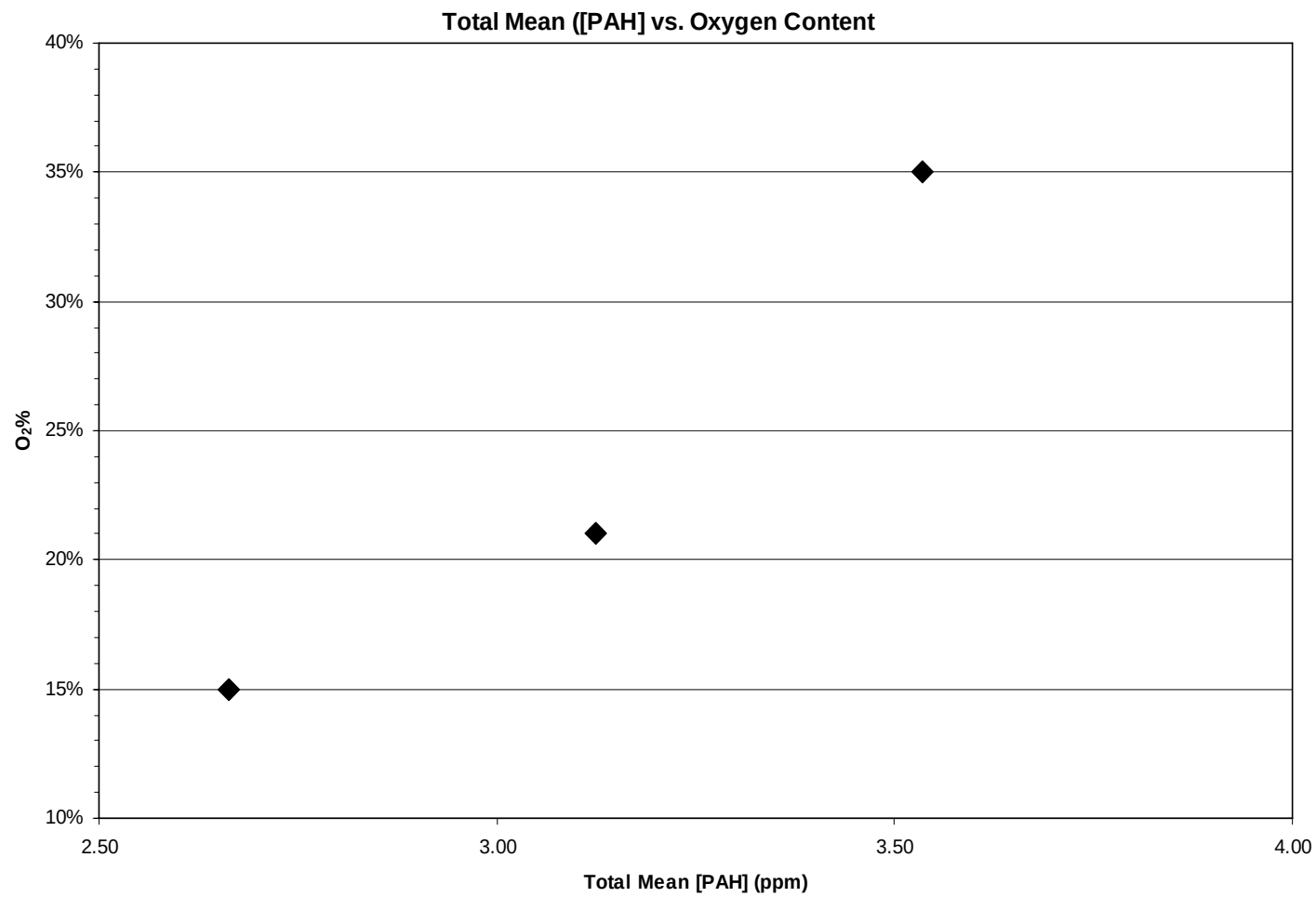


Figure 11. Total mean [PAH] vs. Oxygen Level. [PAH] based on all PAH species by Period, relating to atmospheric oxygen content.

VITA

Patrick J. Schuneman was born in Los Angeles County, California on November 14, 1977. He was raised in Cerritos and Anaheim, graduating from Servite High School in 1995. From there he went to California State University at Fullerton where he earned a Bachelor of Science in Geological Sciences in 2000. In August 2000, Patrick began pursuing a graduate degree at The University of Tennessee, Knoxville. In November 2004, Patrick accepted employment as a geologist with ExxonMobil Exploration Company, to follow successful completion of his graduate degree.