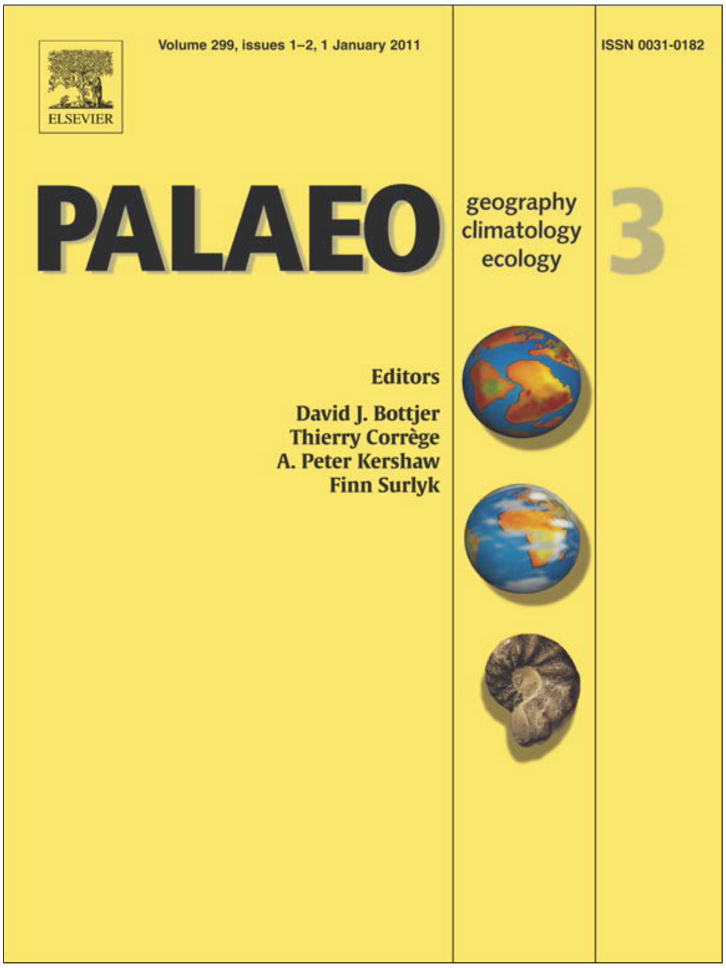

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First multi-proxy record of Jurassic wildfires from Gondwana: Evidence from the Middle Jurassic of the Neuquén Basin, Argentina

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ABSTRACT

Wildfires play a crucial role in recent and ancient ecosystem modeling but their detailed history on the Earth is still not well recorded or understood. The co-occurrence of charcoal and pyrolytic polycyclic aromatic hydrocarbons (PAHs) is used for the recognition of wildfires in geological record that may have implications for the analysis of the terrestrial environment, ecosystems, climate and the level of atmospheric oxygen. Here we present the first multi-proxy evidence of wildfires on the Gondwana continent during the Jurassic, based on the occurrence of charcoal and pyrolytic PAHs in the Middle Jurassic of the Neuquén Basin, Argentina. This is the first evidence of wildfire in the Aalenian, the lowest stage of the Middle Jurassic, and one of the few records of wildfires in the Bathonian. Temperature interpretations, derived from charcoal reflectance data, show that charcoals formed in low temperature surface fires that only sporadically reached the higher temperatures, possibly related to crown fires. The occurrence of charcoals in the Middle Jurassic deposits confirms recent results that the atmospheric oxygen level reached at least 15% during the Middle Jurassic times.

1. Introduction

Fire is an important element today in a range of terrestrial ecosystems (Bowman et al., 2009) and has been since soon after the appearance of plant life on land (Glasspool et al., 2004, 2006; Scott, 2000, 2009, 2010; Scott and Glasspool, 2006). By the Late Devonian wildfires are increasing in frequency and distribution as oxygen levels rose (Cressler, 2001; Fairon-Demaret and Hartkopf-Fröder, 2004; Marynowski and Filipiak, 2007; Marynowski et al., 2010; Prestianni et al., 2010; Rimmer and Scott, 2006; Rowe and Jones, 2000; Scott and Glasspool, 2006). Evidence of wildfire in the Triassic and Jurassic is much scarcer (Jones, 1997; Jones et al., 2002; Scott, 2000, 2009; Uhl et al., 2008) and this has been interpreted as a result of low levels of atmospheric oxygen (Berner, 2006; see Glasspool and Scott, 2010; Scott, 2010). However recent experimental data suggests that fires should occur when there is more than 15% atmospheric oxygen (Belcher and McElwain, 2008). A lack of records of wildfire at this time is not so much related to the atmospheric oxygen level but either a lack of recognition (Scott, 2010) or from other factors such as aridity and scarcity of available fuel (Scott, 2010; Uhl et al., 2008).

Evidence of wildfires in the Middle Jurassic is relatively scarce. Charcoal from sedimentary sequences has, until now, only been reported from Euramerican sites (e.g. Nielsen et al., 2010). Upper Bajocian–Bathonian charcoal has been reported from England (Cope, 1993; Harris, 1958; Morgans et al., 1999; Scott, 2010; Scott and Collinson, 1978). Moreover, some Bathonian–Callovian coals contain low inertinite contents (representing charcoal, Diessel, 2010; Glasspool and Scott, 2010; Scott, 2010; Scott and Glasspool, 2007) indicating relatively infrequent wildfires.

Multi-proxy evidence of wildfire occurrence is particularly significant whereby evidence is derived from a combination of charcoal occurrence and geochemical evidence from pyrolitic polycyclic aromatic hydrocarbons (PAHs) (Finklestein et al., 2005; Killops and Massoud, 1992; Marynowski and Simoneit, 2009; Scott et al., 2010).

We report here for the first time multi-proxy evidence of Late Aalenian/Early Bajocian to Bathonian wildfires from the Neuquén province, Argentina, based on both the identification of charcoal and the distribution of pyrolitic PAHs. This is the first multi-proxy evidence of Jurassic wildfire from the Gondwana continent and one of a very few records of wildfire in Gondwana during the Mesozoic (Bond and Scott, 2010; Eklund, 2003; Eklund et al., 2004; Pole and Douglas, 1999).

2. Geological background and samples provenance

The sampled sites are located in the Neuquén Province, western Argentina (Fig. 1A–B). Paleogeographically, the area studied is

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confined to the Neuquén Basin, the infilling of which consists of 6000 to 7000 m of Upper Triassic to Eocene marine and continental deposits, representing several cycles of marine transgressions that, since the Early Jurassic to Early Cretaceous, encroached from the Pacific Ocean (Gulisano and Gutiérrez Pleimling, 1995; Legarreta and Gulisano, 1989). The Cuyo Group (Lower to Middle Jurassic) represents the first widespread marine depositional event in the Neuquén Basin (Zavala and González, 2001). In the southern part of the basin, the Cuyo Group is composed by approximately 1400 m thick of a prograding clastic succession of off-shore shales and turbidites (Los Molles Formation), passing gradationally to sandy and gravelly, shelf and deltaic-fluvial deposits (Lajas and Challacó formations) (Leanza, 1990; Leanza and Hugo, 1997) (Fig. 1C).

During the Jurassic, the Neuquén Basin changed its palaeogeographic position from the most southward (c. 50°S) in Sinemurian to the nearly present-day location (c. 30°S) in the Middle and Late Jurassic (Llanos et al., 2006). Such palaeogeographic shift caused changes in palaeoclimatic regimes as well, what is correlated with a shift of some Jurassic floras (Volkheimer et al., 2008). It is considered that during the earliest Early Jurassic a cool climate prevailed in the Neuquén Basin, as evidenced from a lower (less than 60%) content of *Classopolis* (Cheirolepidiacean coniferous gymnosperms), but during the Pliensbachian–Toarcian its content was as high as 91%, indicating the onset of warm and arid climate (see Volkheimer et al., 2008). Later on, during the middle and late Early Jurassic the climate was moist in the basin, as evidenced form the presence of coal and well-preserved floras. On the basis of dominant floral assemblages (the conifer families Cheirolepidiaceae, Araucariaceae and Podocarpaceae), the climate in the Neuquén Basin during the Middle Jurassic is considered as warm to temperate with variable precipitation rates. During the Late Jurassic, the climate shifted to extremely arid conditions, as evidenced from eolian sandstones, thick gypsum and anhydrite deposits (see Volkheimer et al., 2008).

The charcoal-bearing samples have been collected in three localities: Portada Covunco, Picún Leufú and Rincón del Águila (Fig. 1B). The samples from Portada Covunco (38°48′10″S and 70°12′12″W) come from the upper part of the Lajas Formation attributed to the Lower Bathonian (Fig. 1C) by Leanza and Hugo (1997). The samples from Picún Leufú (39°12′17″S and 70°03′46″W) come from the uppermost section of the Lajas Formation, which may be attributed to the Upper Bathonian (Fig. 1C) according to Leanza (1990) and Leanza and Hugo (1997). The Challacó Formation, which overlies the Lajas Formation, is overlain by the Lotena Fm. which contains a well defined early Late Callovian ammonite fauna of the Pataginiense Zone (Parent, 2006). Thus, the Challacó Formation should be older than Late Callovian supporting the Late Bathonian age assumed for the samples from the Picún Leufú section.

Finally, the samples from Rincón del Águila (39°08′02″S and 69°37′54″W) come from the lowermost part of the Lajas Formation, representing Upper Aalenian–Lower Bajocian as indicated by the occurrence of the ammonites *Fontannesia* cf. *austroamericana* Jaworski, 1926 and *Eudmetoceras* sp. (H.P., pers. observ.) a few metres above the sampled section (Fig. 1C).

3. Methods

Observations on the charcoal were carried out using a Philips XL30 ESEM/TMP environmental scanning electron microscope. Samples, taken from the sandstones and mudstones in a form of small chips, were polished, coated with carbon and investigated using the ESEM. Additionally, macroscopically visible charcoal fragments were separated from mineral matrix and also analyzed using the ESEM. The observations were undertaken in the back-scattered (BSE) and secondary electron (SE) modes.

For the vitrinite and fusinite reflectance analysis, freshly polished rock fragments were used. Random reflectance was measured using an AXIOPLAN II microscope using 156 nm light and oil of 1.546 RI using a total magnification of 500×. The standards used were 0.42%, 0.898% and 1.42% reflectance (R_o). The total organic carbon (TOC)

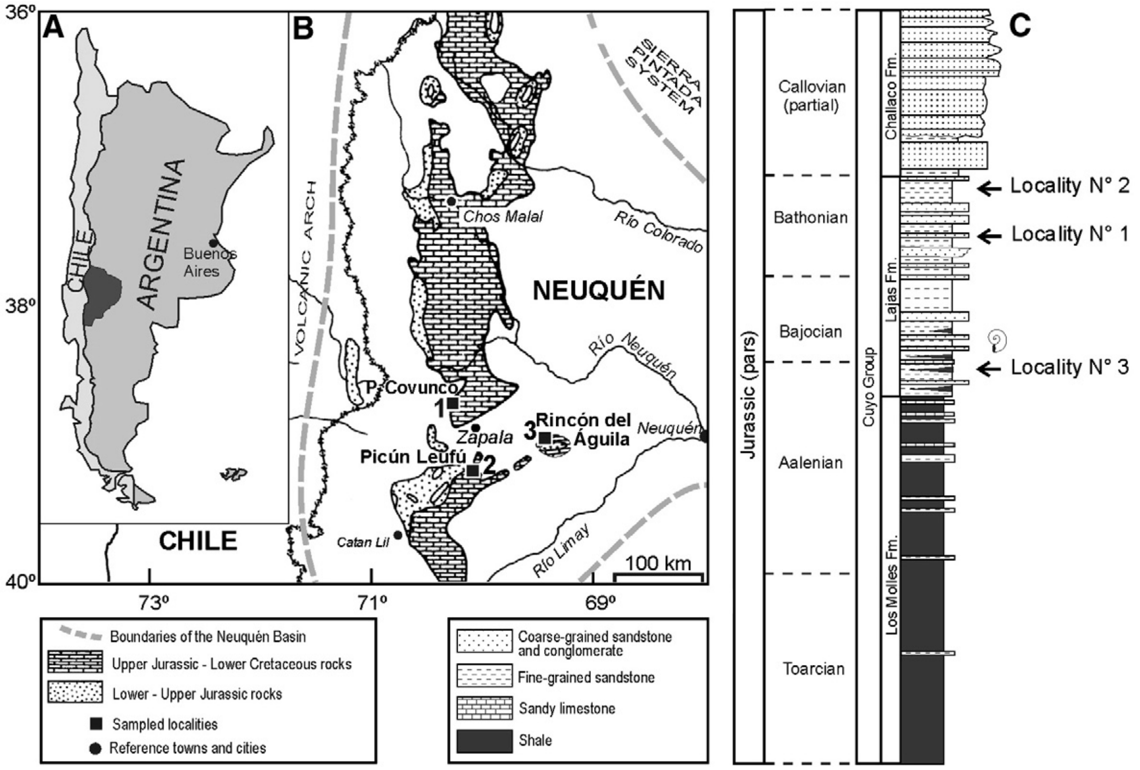

Fig. 1. Localities and general section investigated. A. A map of Argentina showing the location of the Neuquén Province (shaded) B. Location map C. Generalized log-section of the Cuyo Group in the studied area, with an indication of the stratigraphic position of the collected samples.

content was determined using an Eltra Elemental Analyzer model CS530.

For charcoal quantification 10 g of samples from Rincón del Águila and Picún Leufú sections were demineralized using cold 37.7% hydrochloric acid for 72 h and cold 38% hydrofluoric acid for further 72 h. The process was completed with a final treatment in cold 37.7% hydrochloric acid for 24 h in order to avoid a calcium fluoride precipitation. The samples then were rinsed with water until a neutral pH was achieved. The remaining organic material was sieved through a 125 μm mesh and both fractions were collected. The >125 μm residues of the samples was examined using a low-power binocular microscope and all the charcoal particles observed were counted. The data was expressed per gram of the rock analyzed (see Belcher et al., 2010).

Cleaned and powdered samples were extracted with dichloromethane/methanol (9:1) by using Soxhlet extraction techniques for 48 h. Extracts were further separated using pre-washed TLC plates coated with silica gel (Merck, 20×20×0.25 cm). The aliphatic and aromatic fractions of all samples were analyzed in further detail by gas chromatography–mass spectrometry (GC-MS). The GC-MS analyses were performed with an Agilent 6890 Series Gas Chromatograph interfaced to an Agilent 5973 Network Mass Selective Detector and Agilent 7683 Series Injector (Agilent Technologies, Palo Alto, CA). A 0.5 μl sample was introduced into the cool on-column injector under electronic pressure control. Helium (6.0 Grade, Linde, Kraków) was used as the carrier gas at a constant flow rate of 2.6 ml/min. The GC separation was on either of two fused-silica capillary columns: J&W HP5-MS (60 m×0.32 mm i.d., 0.25 μm film thickness) coated with a chemically bonded phase (95% polydimethylsiloxane, 5% diphenylsiloxane) and J&W DB35-MS (60 m×0.25 mm i.d., 0.25 μm film thickness) coated with a chemically bonded phase (35% phenyl-methylpolysiloxane). The GC oven temperature was programmed from 50 °C (isothermal for 1 min) to 120 °C at a rate of 20 °C/min, then to 300 °C at a rate of 3 °C/min. The final temperature was held for 45 min. For more details see Marynowski and Simoneit (2009).

4. Charcoal characteristics and taphonomy

Charcoals were found in lithologically different sedimentary rocks including siliciclastics (sandstone and mudstone) and carbonates (limestone). In the most of the samples, charcoals were macroscopically identified as black, splintery and lustrous fragments (see Scott, 2010) that were abundant in most of the samples (Fig. 2). Microscopic observations revealed that the samples collected contain charcoal (Fig. 2) and that the particles from sandstones are much better preserved than those from mudstones and limestones. Similar conditions were found in the Lower Jurassic terrestrial sequences of Poland (Marynowski and Simoneit, 2009) and Middle Jurassic Papilė Formation (Lower Callovian) from Lithuania (Marynowski and Zatoń, 2010), and in the all cases it is connected with compaction effect which influenced the charcoal structure much more intensely in fine grained sediments than in sandstones. In both the Picún Leufú and Rincón del Águila sections, the assemblages of charcoals comprised a variety of sizes, including large parts of macroscopic fragments (>1 mm, up to 5–6 cm), as well as meso- (180 μm–1 mm) and microscopic charcoal fragments (<180 μm). These features, together with not rounded shape imply minimal transport of charcoals that may indicate local fires (see Scott, 2010). It is clear, however, that as the assemblage comprises mainly wood fragments and not leaves or other organs then there is likely to have been some pre-burial sedimentary sorting (Nichols et al., 2000; Scott, 2010; Scott et al., 2000).

Charcoals from the Picún Leufú section were partially mineralized by jarosite (Fig. 3). In the charcoals from the both localities, however, cell walls are homogenized (Fig. 3), suggesting temperatures of fires greater than 350 °C (to be discussed in the later part, see also Scott, 2000, 2010).

In contrast, charcoal fragments from the Portada Covunco section are of moderate size (not exceeding 1 cm) and slightly rounded that suggests that they were transported some way before being deposited and incorporated into sediments (Scott, 2010). Their preservation is generally poor. In many fragments open cellular spaces are completely filled with clay minerals (Fig. 3) but the overall anatomical structure is still preserved.

In the case of the all sections studied here, the plant fossils commonly consist almost exclusively of charcoal fragments. On one hand, it is possible that early diagenetic degradation processes removed most of the less-resistant higher plant remains, leaving the more resistant charcoal (Ascough et al., 2010; Jones et al., 2002). On the other hand, all sections studied are natural exposures affected by weathering processes for a considerable time, that potentially may have led to degradation of less resistant fossil wood fragments.

5. Types of wildfires

The average vitrinite reflectance values are similar for the all samples reaching ~0.7% (Table 1) with one exception for PLEU3 sample, were R_r value is 0.51% (Table 1). It suggests that maturity level of the sequences studied corresponds to lower stage of oil window (Hunt, 1995).

Fusain fragments (= fossil charcoal, Scott, 1989, 2010) showed a wide range of reflectance values, and the values obtained differ for different samples from the same section (Table 1). Calculated minimum fire temperatures were calculated using the experimentally produced curve from Scott (2010). The temperatures must be considered as minimum fire temperatures as the time of heat exposure is not known (McParland et al., 2009). The temperatures ranged from approximately 360 to 425 °C for the Rincón del Águila section and from 360 to 370 °C for the Picún Leufú samples. The lowest average minimum fire temperatures reached 350 °C were calculated for the Covunco sample. The calculations shown previously suggest that the charcoal formed in lower temperature surface fires (McParland et al., 2009; Scott, 2010), possibly sporadically reaching the crowns (highest values for sample RDAG5; Table 1). Similarly, such as in the case of the Lower Jurassic of Poland (Marynowski and Simoneit, 2009), the highest temperatures noted for the RDAG5 sample correlate with the highest PAH concentrations (Fig. 5; Table 2).

6. Bulk geochemical data and pyrogenic polycyclic aromatic compounds

6.1. Bulk data

The samples contain different amounts of total organic carbon (TOC), depending on lithological differences, charcoal amount and weathering (Table 2).

In the distribution of *n*-alkanes, short-chain *n*-alkanes predominate in most of the samples. Despite this, between long-chain *n*-alkanes, those with an odd carbon number significantly predominate (especially n-C_{27}, n-C_{29}, and n-C_{31}) indicating higher plant input (e.g. Eglinton and Hamilton, 1967). Moreover, the analyzed sections are characterized by the presence of compounds that originated from terrestrial higher plants like cadalene and retene, described also as biomass burning indicators (Simoneit, 2002). Thermally less stable terrestrial biomarkers like simmonelite or dehydroabietane were not found. Moreover, the samples contain thermally more stable $\alpha\beta$- and $\beta\alpha$-hopanes and in some cases traces of regular steranes. Thermally less stable $\beta\beta$-hopanes, hopenes, sterenes and diasterenes were not found.

6.2. Polycyclic aromatic hydrocarbons (PAHs) and other aromatic compounds

Unsubstituted PAHs were extensively applied as vegetation fire indicators in the reconstruction of ancient palaeoenvironments due to

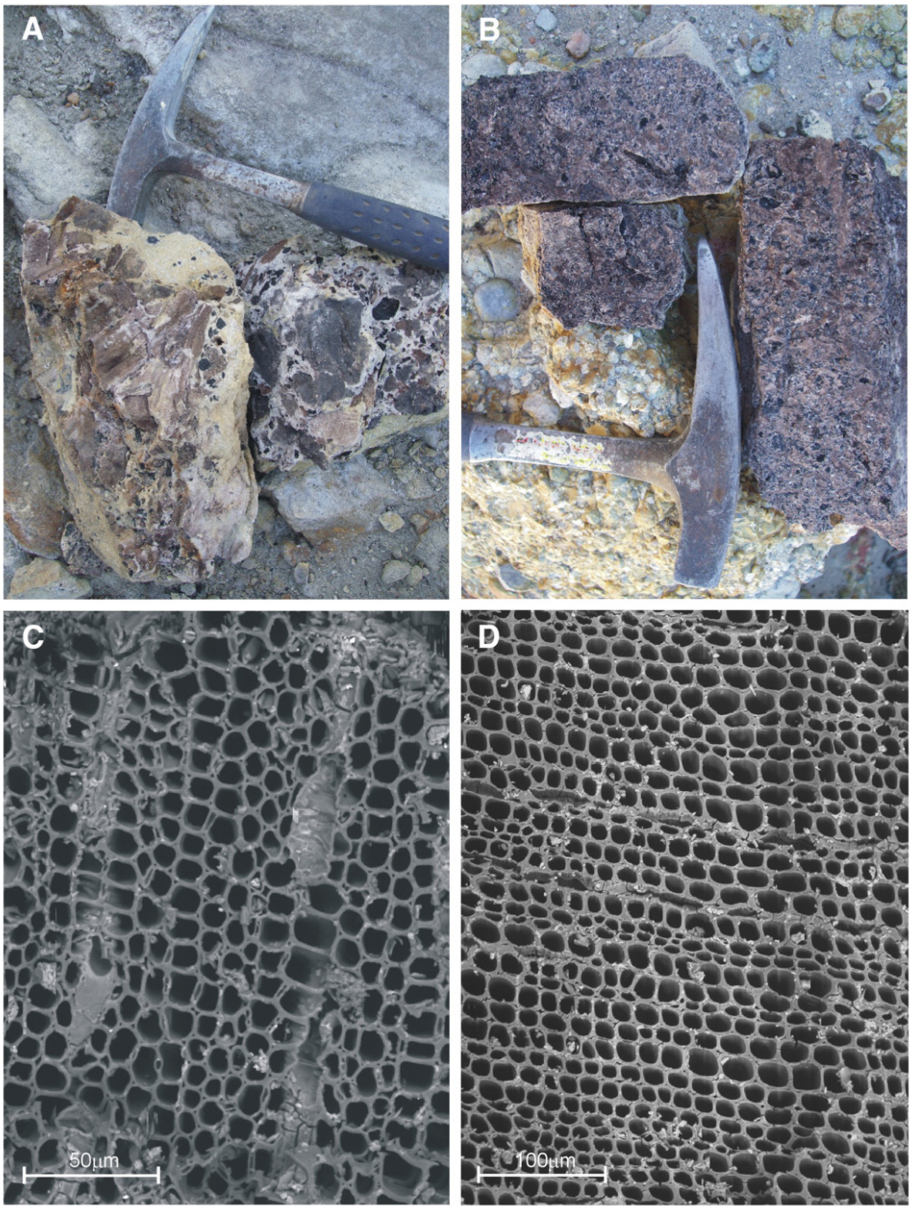

Fig. 2. Large, macroscopically visible charcoals preserved in sandstones of (A) Picún Leufú (sample PLEU0) and (B) Rincón del Águila (sample RDAG4) sections, as well as scanning electron photomicrographs of (C) Tangential section of well-preserved charcoal from the Picún Leufú exposure (sample PLEU0) and (D) Tangential section of charcoal from the Rincón del Águila exposure (sample RDAG4).

their pyrolitic origin (e.g. Finklestein et al., 2005; Jiang et al., 1998; Killops and Massoud, 1992; Marynowski and Simoneit, 2009; Scott et al., 2010; Venkatesan and Dahl, 1989). Despite the fact that PAHs may also form in other geological and extraterrestrial conditions (e.g. Grice et al., 2007; Sephton et al., 2005; Simoneit and Fetzer, 1996), the co-occurrence of charcoal fragments and high concentrations of unsubstituted PAHs are unquestionably connected with wildfires (Finklestein et al., 2005; Marynowski and Simoneit, 2009; Scott et al., 2010).

The typical distribution of PAHs in the Argentinean samples is presented in Fig. 4. In the both sections phenanthrene, fluoranthene, chrysene and benzo[*b*]fluoranthene are the major compounds (Fig. 4), while the second quantitatively important group of PAHs are: 2-phenylnaphthalene, pyrene, benzo[*ghi*]fluoranthene, triphenylene, benzo[*e*]pyrene and benzo[*ghi*]perylene (Fig. 4). Moreover, phenyl derivatives of PAHs including phenylnaphthalenes, phenylphenanthrenes and binaphthyls (Rospondek et al., 2009) were found (Fig. 4), with distribution suggesting their pyrolytic origin (see Marynowski and Simoneit, 2009).

Beside the PAHs, another widespread group of aromatic compounds in most of the samples are oxygen-containing aromatic compounds. This group of compounds includes: benzonaphthofurans, dinaphthofurans, phenyldibenzofurans and benzobisbenzofurans and such oxygenated polycyclic aromatic hydrocarbons (Oxy-PAHs) as: fluoren-9-one, xanthone, benzophenone, three isomers of benzofluorenones and 1,9-benzoanthrone (Fig. 4). Oxy-PAHs are typical products of incomplete OM (organic matter) combustion (del Rosario Sienra, 2006), although some of these compounds were also reported from sedimentary organic matter (Wilkes et al., 1998). Other, low molecular weight compounds as dibenzofuran and its alkyl-derivatives are absent in the analyzed samples, most probably due to post-diagenetic weathering processes (to be discussed in the later part).

The concentrations of individual compounds vary between the samples, but are generally low in comparison to those from the Lower Jurassic of Poland (Marynowski and Simoneit, 2009). For example, the maximum concentrations of phenanthrene in Argentinean samples reached 2.5 to 3.8 μg/g TOC (Table 2), while in the lowermost

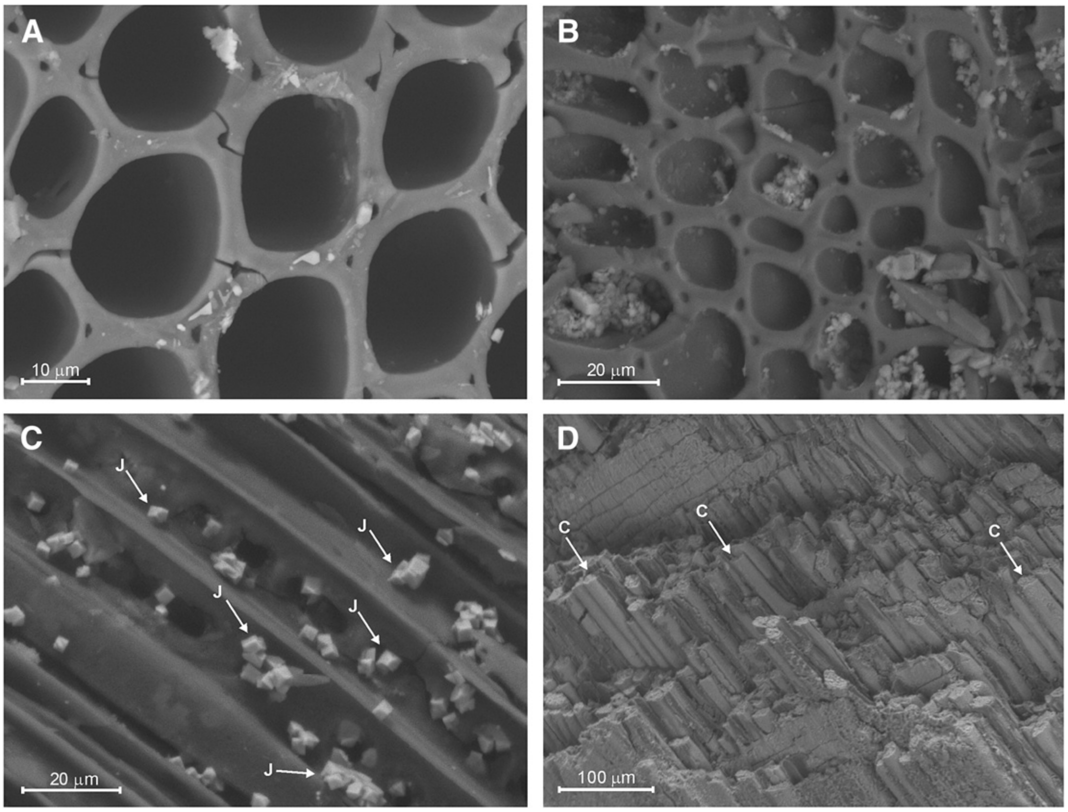

Fig. 3. Scanning electron photomicrographs of: (A) Partial jarosite mineralization of the charcoal walls (Picún Leufú, sample PLEU1) (B) Homogenized cell walls (Picún Leufú, sample PLEU0) and (C) Rincón del Águila (sample RDAG5) (D) Radial section of the specimen with overall cellular structure preserved almost completely replaced by clay minerals (Portada Covunco, sample RCOR). J - jarosite, C - clay minerals.

Hettangian section of Poland its maximum concentration is between 130 and 450 μg/g TOC (Marynowski and Simoneit, 2009). Other dominant compounds also characterized by low concentrations, reaching in case of fluoranthene, 0.02 to 0.85 μg/g TOC, chrysene + triphenylene, 0.07 to 1.91 μg/g TOC and benzo[*b*]fluoranthene, 0.12 to 1.97 μg/g TOC (Table 2). These low PAHs concentrations together with high amount of macroscopically identifiable charcoal particles (Fig. 2) may be explained as post-diagenetic weathering of the analyzed material.

Besides the concentrations of individual PAHs (Table 2), we summed the amounts of some most characteristic pyrolytic aromatic hydrocarbons based on formulas of Marynowski and Simoneit (2009) and Finklestein et al. (2005) (Table 2). What is interesting, despite of dissolution/oxidation and migration of the large part of PAHs by meteoric waters, the curves of TOC amount and sum of pyrolytic PAH compound concentrations (Fig. 5; Table 2) are very similar for both sections that suggest that the major part of the OM present in the rocks is genetically connected with a pyrogenic processes such as wildfire, and that charcoals are major OM components (compare to Marynowski and Simoneit, 2009). In case of the Picún Leufú section, TOC amount and pyrolytic PAH concentrations correlate with the number of charcoal particles (Fig. 5). On the other hand, in Rincón del Águila section such correlation is not so clear (Fig. 5) and may be connected with oxidative weathering processes which preferentially degraded the PAHs and less resistant non-charred OM, especially in coarse grained sandstones (Fig 5).

The obtained low concentrations of PAHs1 and PAHs2 parameters for Argentinean samples, which are undoubtedly connected with wildfires, led us to make a re-evaluation of the proposed minimum concentration values of both parameters equaling <3 μg/g TOC and <4 μg/g TOC, respectively (Marynowski and Simoneit, 2009). These data show that this is not possible to fix the minimum limit of the PAH parameter concentrations for wildfire origin, and that the crucial factor of the PAH source is their distribution and connections with other sedimentological and geochemical factors.

Table 1
Vitrinite and inertinite reflectance values and interpreted minimum fire temperatures.

Location	Vitrinite reflectance (%)					Inertinite reflectance (Rro%)					Combustion temp. (°C)*		
	Mean	SD	Min	Max	n	Mean	SD	Min	Max	n	Mean	Min	Max
RDAG 1	0.70	0.10	0.43	0.83	90	1.17	0.51	0.68	2.89	140	360	325	490
RDAG 5	0.73	0.13	0.51	0.90	50	2.04	1.18	0.78	4.63	110	425	330	580
PLEU 2	n.f.	n.f.	n.f.	n.f.	n.f.	1.34	0.55	0.66	2.74	130	370	325	470
PLEU 3	0.51	0.11	0.25	0.66	60	1.14	0.60	0.61	2.50	90	360	325	450
RCOR 3	0.75	0.09	0.44	0.86	60	0.98	0.18	0.71	1.36	130	350	330	370

SD, standard deviation; Min, minimum; Max, maximum; n, number of measurements; n.f., not found.
* Calculated from data presented in Scott (2010).

Table 2
Total organic carbon (TOC) content and concentrations of the selected pyrolytic aromatic hydrocarbons. Ph; phenanthrene, Fl; fluoranthene, Py; pyrene, BaA; benzo[*a*]anthracene, Chr; chrysene, Triph; triphenylene, BeP; benzo[*e*]pyrene, BbFl; benzo[*b*]fluoranthene, BaP; benzo[*a*]pyrene, B[*ghi*]Pe; benzo[*ghi*]perylene, Cor; coronene, PAHs1 = BaA + BbFl + BeP + BaP + Cor (Marynowski and Simoneit, 2009), PAHs2 = Fl + Py + BbFl + BaP + B[*ghi*]P + Cor (Finklestein et al., 2005).

Sample	Lithology	TOC [%]	Ph μg/TOC	Fl μg/TOC	Py μg/TOC	BaA μg/TOC	Chr & Triph μg/TOC	BeP μg/TOC	BbFl μg/TOC	BaP μg/TOC	B[*ghi*]Pe μg/TOC	Cor μg/TOC	PAHs1 μg/TOC	PAHs2 μg/TOC
Portada Covunco														
RCOR	Sandstone	0.54	0.55	0.26	0.15	0.06	0.40	0.28	0.48	0.02	0.13	0.07	0.91	1.10
Picún Leufú														
PLEUU	Sandstone	5.03	3.84	0.79	0.98	0.30	1.91	0.56	0.50	0.15	0.51	0.12	1.62	3.04
PLEU0	Sandstone	0.36	0.88	0.35	0.20	0.03	0.14	0.05	0.17	0.00	0.01	0.01	0.25	0.74
PLEU1	Sandstone	1.40	0.88	0.14	0.90	0.05	0.56	0.18	0.65	0.01	0.10	0.04	0.93	1.84
PLEU2	Mudstone	2.94	1.73	0.18	1.19	0.05	0.49	0.17	0.49	0.02	0.06	0.06	0.80	2.00
PLEU3	Sandstone	0.35	2.51	0.70	0.41	0.04	0.23	0.08	0.22	0.00	0.00	0.00	0.33	1.32
PLEU4	Sandstone	0.65	0.60	0.25	0.20	0.01	0.10	0.06	0.12	0.00	0.00	0.00	0.19	0.65
Rincón del Águila														
RDAG1	Siltstone	1.87	1.02	0.09	0.58	0.03	0.46	0.21	1.17	0.02	0.09	0.10	1.53	2.05
RDAG2	Sandstone	0.75	0.31	0.04	0.27	0.04	0.36	0.36	1.02	0.01	0.14	0.14	1.56	1.62
RDAG3	Sandstone	1.57	0.02	0.02	0.04	0.01	0.07	0.07	0.24	0.00	0.09	0.02	0.34	0.39
RDAG4	Sandstone	3.53	0.05	0.05	0.02	0.00	0.11	0.23	0.76	0.23	0.03	0.15	1.36	1.25
RDAG5	Sandy mudstone	0.98	0.79	0.07	0.64	0.06	0.66	0.33	1.97	0.02	0.37	0.25	2.63	3.32
RDAG6 bed 34	Limestone	0.21	0.58	0.85	0.64	0.28	0.58	0.32	1.40	0.09	0.55	0.27	2.35	3.80

7. Implications for the Mesozoic oxygen curve

It has been proposed by numerous geochemical modelers that oxygen level during Triassic and especially Jurassic was significantly lower than today (Berner, 2006, 2009). Such conclusions rely upon both: 1) low O_2 levels based on models that used isotopic data (Arvidson et al., 2006; Berner, 2006, 2009) and 2) scarce finds of wildfire evidence including charcoals and high pyrolytic PAH concentrations (Belcher and McElwain, 2008; Harris, 1958; Jones et al., 2002; Marynowski and Simoneit, 2009; Morgans et al., 1999; Scott and Collinson, 1978; Uhl et al., 2008; Zeigler et al., 2005). Earlier calculated oxygen levels for the Early and Middle Jurassic was calculated as low as 12% (Berner, 2006), the lowest oxygen level for the whole Mesozoic and Cenozoic. Recently, Belcher and McElwain (2008) undertook burn experiments that indicated that the lower O_2 limit for combustion in natural environments may be 15%. This implies that the paleoatmospheric O_2 levels for the Mesozoic using the curve of Berner (2006) needs to be reassessed. Newest modifications of the GEOCARBSULF model (Berner, 2009) show the Jurassic O_2 levels as low as 15%, but in some parts of the Jurassic even as low as 14%, including the Aalenian. In their oxygen proxy model using charcoal concentration in coal, Glasspool and Scott (2010) indicate rapid rises and falls through the Jurassic. Our charcoal finds confirmed the higher than previously assumed O_2 level for the Middle Jurassic and shows the occurrence of wildfires in the first stage of the Middle Jurassic–Aalenian. This is also the first multi-proxy documentation of wildfire evidence on Gondwana continent during the Mesozoic.

8. Conclusions

Based on microscopic and organic geochemical methods we document for the first time evidence of Jurassic wildfire from Gondwana. The data comes from three Middle Jurassic sections located in the Neuquén Basin, Argentina, where well-preserved charcoals and pyrolytic PAHs were recovered. Moreover, the charcoal and pyrolytic PAH discoveries are the first record of wildfires during Aalenian, the earliest stage of the Middle Jurassic. Charcoals formed in lower temperature surface fires, occasionally reaching higher temperatures, possibly from crown fires. The occurrence of charcoals in the Middle Jurassic sediments confirms the recent results about at least 15% atmospheric concentration of oxygen during the Jurassic time period.

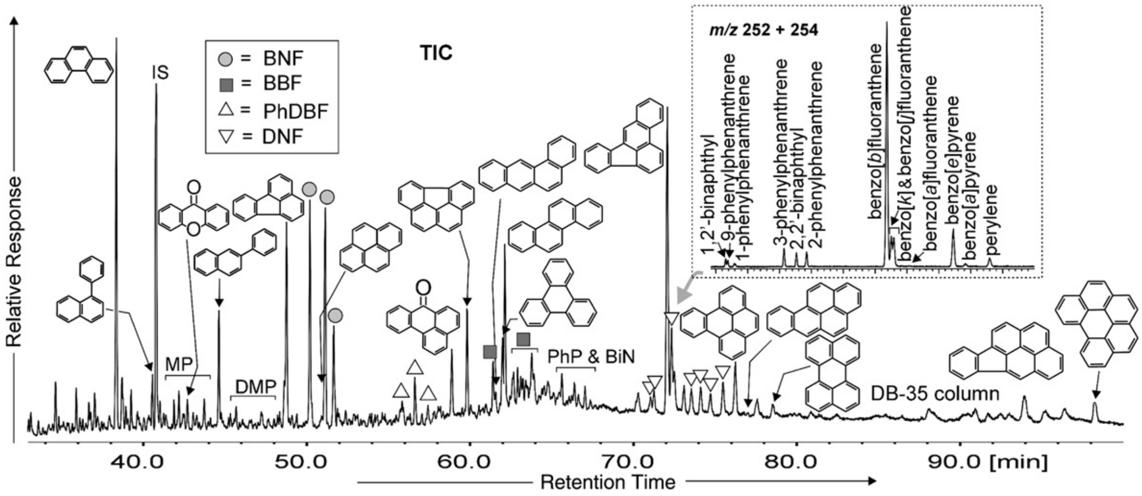

Fig. 4. Total ion chromatogram (TIC) trace of the aromatic fraction of the RDAG1 sample, showing the predominance of three to seven ring-containing PAH and relatively high amounts of oxygen-containing aromatic compounds. BNF—benzonaphthofuran isomers, BBF—benzobisbenzofuran isomers, PhDBF—phenyldibenzofuran isomers, DNF—dinaphthofuran isomers, MP—methylphenanthrenes, PhP—phenylphenanthrenes, BiN—binaphthyls, IS—internal standard.

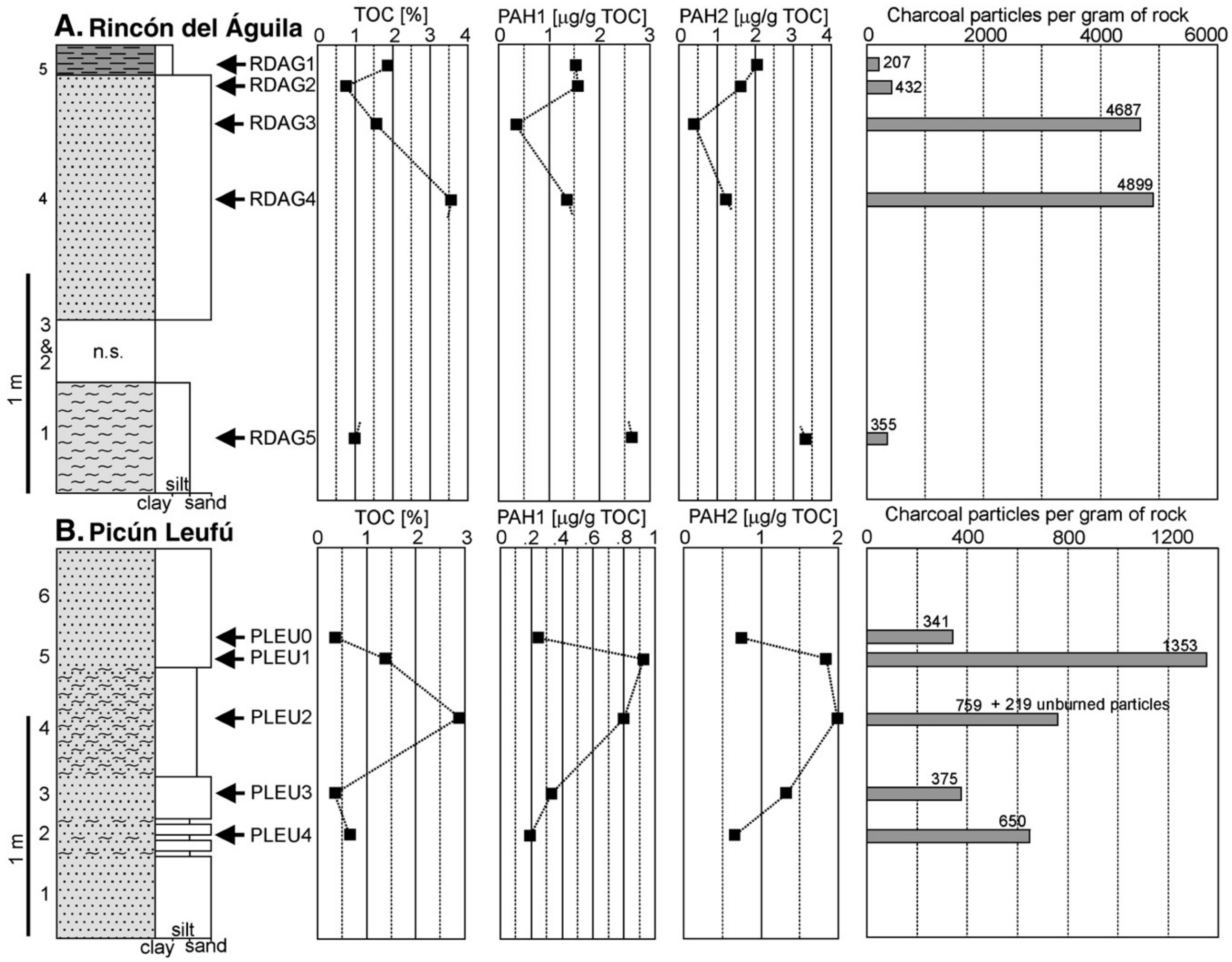

Fig. 5. Composite plots of the A. Rincón del Águila and B. Picún Leufú sampled parts of the sections showing the bulk TOC and PAHs data. n.s.—not sampled.

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