

Notes on the origin of copromacrinite based on nitrogen functionalities and $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ determined on samples from the Peach Orchard coal bed, southern Magoffin County, Kentucky



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ABSTRACT

This paper represents the first attempt to show, by means other than just petrographic ones, that one type of macrinite, herein designated copromacrinite, may result from macrofauna feces. For that purpose a combination of coal petrography, X-ray photoelectron spectroscopy, and elemental-analysis continuous-flow isotope ratio mass spectrometry methods were used to determine nitrogen functionalities and $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ compositions in 1) vitrinite-rich, 2) fusinite + semifusinite-rich, and 3) macrinite-rich (with a possible coprolitic origin) samples of the high volatile A bituminous Peach Orchard coal (Bolsovian; Middle Pennsylvanian) from Magoffin County, Kentucky. There were no significant differences between pyridinic-N and quaternary-N abundance in the three samples, however, pyrrolic-N was higher (~54%) in the macrinite-rich sample than in the other two samples (~38%). The data suggest that pyridinic-N and quaternary-N are independent of maceral group composition and that pyrrolic-N is dependent on maceral composition (fusinite + semifusinite versus macrinite). $\delta^{13}\text{C}$ values obtained for bulk and demineralized coal of the vitrinite- and fusinite + semifusinite-rich samples are similar with $\delta^{13}\text{C}$ values of $-24.80 \pm 0.01\%$ VPDB and $-24.61 \pm 0.09\%$ VPDB for bulk samples and $-24.81 \pm 0.07\%$ VPDB and $-24.52 \pm 0.04\%$ VPDB for demineralized samples. These values are within the expected range for vitrinite-rich samples and the slightly higher $\delta^{13}\text{C}$ value of the fusinite + semifusinite-rich sample is expected as $\delta^{13}\text{C}$ values for inertinite are higher than for vitrinite. However, there was a significant shift to a lower $\delta^{13}\text{C}$ value ($-26.80 \pm 0.01\%$ VPDB for the bulk sample value) for the macrinite-rich sample. Because the samples are basically isorank, and $\delta^{13}\text{C}$ (and $\delta^{15}\text{N}$) shifts do not occur during maturation until anthracite rank, the difference may be related to the presence or composition of the macrinite within the sample which lacks heat-effect indicators, such as devolatilization vacuoles and distorted pores. $\delta^{15}\text{N}$ values are also similar for bulk and demineralized coal of the vitrinite- and fusinite + semifusinite-rich samples, and the bulk values were heavier in this samples ($3.07 \pm 0.03\%$ Air and $2.92 \pm 0.10\%$ Air, respectively), and much lighter ($-2.83 \pm 0.09\%$ Air) for the macrinite-rich sample.

The study of Peach Orchard coal samples using reflected-light microscopy, isotopic composition, and nitrogen-forms analyses revealed that the macrinite-rich sample contains macrinite with coprolitic features (e.g. oxidation rind, mix of undigested palynomorphs, frequent and randomly located funginite, agglutination pulp of semifusinite reflectance, internal lack of bedding fabric, and suggestion of structures resulting from intestines and stomach walls), more pyrrolic-N (~16%), and lower $\delta^{13}\text{C}$ (~2‰ VPDB) and $\delta^{15}\text{N}$ (~4‰ Air) values than the vitrinite and semifusinite + fusinite rich samples. These findings suggest that the maceral macrinite has multiple origins based on petrography and measurable chemical differences between the macrinite, vitrinite, and semifusinite + fusinite fractions within the coal. Assuming that copromacrinite observed is an excretion then the anomalies observed may result from the symbiotic relations between the macrofauna (e.g. cockroaches) and microbiota during the digestive processes, and the nitrogen balance mechanisms inside macrofauna body.

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1. Introduction

Is it possible a coal maceral can form from the feces of arthropods, earthworms, and other macrofauna? If so, that maceral should be called

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copromacrinite. Stach et al. (1982) and ICCP (International Committee for Coal and Organic Petrology) (2001) stated that “isolated aggregates may originate from coprolites”, and a coprolitic origin was established for Miocene coals from the Navaky and Handlova mining districts in Slovakia based on its petrographic structure (O’Keefe et al., 2011). Macrinite of coprolitic origin was also described in Hower et al. (2011, 2013b) and Dai et al. (2015). However, because detritory, coprophagy, and herbivory digestion evolved over geologic time, establishing a copromacrinite origin for coals across geologic time scales is not straightforward.

The isotope composition of coal is largely influenced by environmental conditions at the time of formation. Fossil plant matter ranges between -23% and -27% , averaging approximately -24% (Gröcke, 1998). For bulk coal samples, carbon isotope ratios are limited to a range of about 5% between $\delta^{13}\text{C} = -27\%$ VPDB and -22% VPDB (Whiticar, 1996; and references therein). These isotopic values are similar to those of modern terrestrial land plants (Whiticar, 1996; Gröcke, 1998). C_3 land plants (RuBP carboxylase photosynthesis) have a $\delta^{13}\text{C}_{\text{org}}$ range of -33% VPDB to -22% VPDB (mean $\delta^{13}\text{C}_{\text{org}}$ ca. -27% VPDB), whereas C_4 land plants (PEP carboxylase photosynthesis) values range from $\delta^{13}\text{C}_{\text{org}} = -18\%$ VPDB to -8% VPDB (mean $\delta^{13}\text{C}_{\text{org}}$ ca. -13% VPDB) (Whiticar, 1996; and references therein).

In modern soils, Cerling and Quade (1993) found that the $\delta^{13}\text{C}$ values of organic matter derived from C_3 plants range between -25.7% VPDB and -20.1% VPDB, and the respective soil carbonate $\delta^{13}\text{C}$ values range between -10.0% VPDB and 4.2% VPDB. The $\delta^{13}\text{C}$ values of organic matter derived from C_4 plants range between -20.7% VPDB and -10.5% VPDB, and the respective soil carbonate between -7.5% VPDB and 4.9% VPDB. The carbon isotopic composition of soil carbonate is essentially constant at depth, and if a significant variation in the isotopic composition of pedogenic carbonate is apparent from a single soil, then a complex vegetation history is implied (Cerling and Quade, 1993).

When the rate of organic material deposition is sufficiently rapid in soils, oxygen and sulphate are consumed by bacteria and organic matter is fermented by methanogens to bacterial CH_4 , which has a $\delta^{13}\text{C}$ value ranging between ca. -112% to -50% (Whiticar et al., 1986).

Although coalification may cause a slight enrichment in ^{13}C (Jones and Chaloner, 1991; Robinson and Hesselbo, 2004; Rimmer et al., 2006), the isotope ratios are not significantly affected by coalification

below the meta-anthracite rank (Whiticar, 1996; Boudou et al., 2008). However, different plant assemblages and peat preservation conditions may lead to variability in $\delta^{13}\text{C}$ for peats and resultant coals (Holmes et al., 1991; Rimmer et al., 2006; Bechtel et al., 2008). The $\delta^{13}\text{C}$ variation between the maceral groups, for example, as determined for 44 high volatile bituminous Ruhr coals (Schwartzkopf, 1984; Schwartzkopf and Schoell, 1985), is very small, ranging between -23.0% VPDB and -23.9% VPDB (lignite $\delta^{13}\text{C} = -23.9\%$, vitrinite $\delta^{13}\text{C} = -23.7\%$ and inertinite $\delta^{13}\text{C} = -23.0\%$) (Whiticar, 1996).

Nitrogen in coal is mostly of organic origin although clays in high-rank coals can retain NH_4^+ in interlayers or adsorbed on the clay surfaces (Dai et al., 2012a; Juster et al., 1987; Liu et al., 1996; Liang et al., 2005; Zheng et al., 2016). Nitrogen occurs within the carbon matrix mainly as pyrrolic, pyridinic, and quaternary nitrogen functional groups (Boudou et al., 2008; Gammon et al., 2003; Kelemen et al., 1994; Kelemen et al., 2007; Pels et al., 1995), and the relative amounts of these functionalities vary with coal rank (Mittra-Kirtley et al., 1993; Thomas, 1997). However, over a wide coal rank range (carbon 65–95 wt%, daf), the nitrogen functional forms are generally composed of 50–80% pyrrolic-N (N-5), 20–40% pyridinic-N (N-6), and 0–20% quaternary-N (N-Q). Small amounts ($<10\%$) of amino groups may be present in low-rank coals (Molina et al., 2000; Boudou et al., 2008).

There have been a limited number of studies on the influence of the type of fossil organic matter on the amounts of the functional forms of nitrogen. However, some trends were found: vitrinite in British coal with C contents (dry ash free basis) between 80–90% has more pyridinic-N than inertinite (from 10% in vitrinite to 5.8% in inertinite) (Burchill and Welch, 1989), and type-II kerogen has more pyrrolic-N and quaternary-N and less pyridine-N than type-III kerogen (Boudou et al., 2008).

In studies utilizing bulk coal samples up to the anthracite rank it was found that the $\delta^{15}\text{N}$ increases with rank, and the isotopic range of published $\delta^{15}\text{N}$ values for coals range between $\sim 0\%$ Air to $+5\%$ Air (Boudou et al., 1984; Rigby and Batts, 1986; Burchill and Welch, 1989; Whiticar, 1996; Ader et al., 1998; Rimmer et al., 2006; Boudou et al., 2008).

As outlined above, neither $\delta^{13}\text{C}$ nor $\delta^{15}\text{N}$ express strong shifts with increasing rank up to anthracite rank (Galimov, 1980; Lewan, 1986; Rigby and Batts, 1986; Whiticar, 1996; Boudou et al., 2008). However, the N and C isotopic composition of coal is dependent on the kerogen

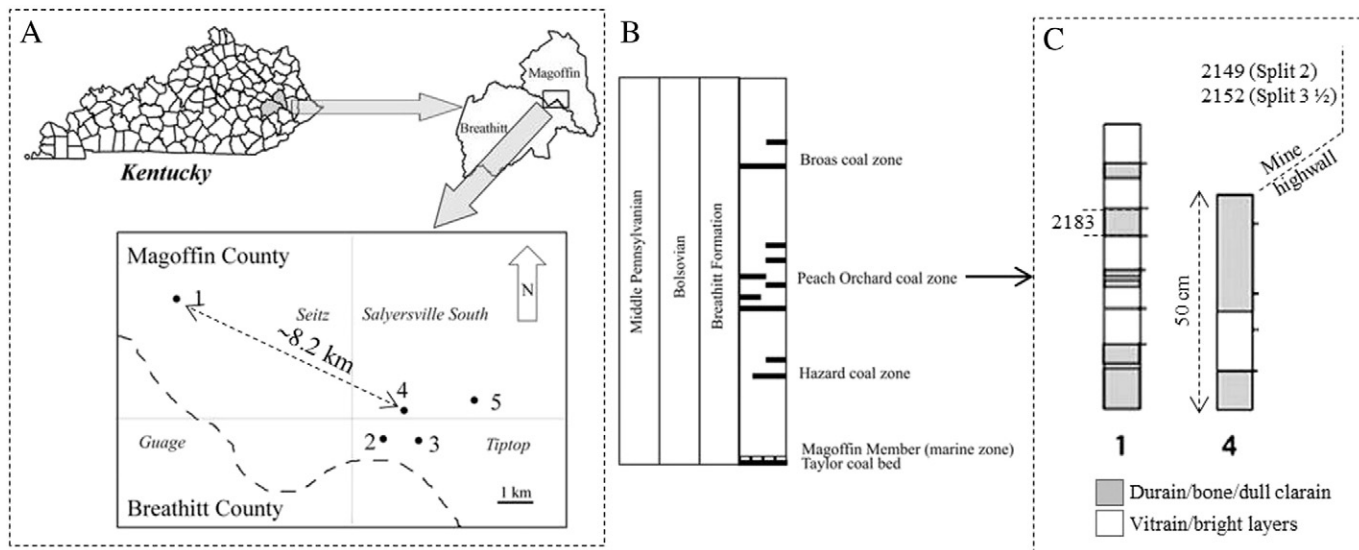


Fig. 1. Generalized locations of the five Peach Orchard coal mine sites in the Seitz and Salyersville South Quadrangles, Magoffin County, eastern Kentucky. The Guage and Tiptop Quadrangles, Breathitt County, are also shown. Sample 2183 was collected at site 1 (No. 3 Split), and samples 2149 (No. 2 Split) and 2152 (No. 3.5 Split) were collected at site 4.

type and the maceral composition. Type I and type II kerogen and liptinite have lower $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ than type-III kerogen and vitrinite, and $\delta^{15}\text{N}$ values of type-II kerogen range between -3‰ Air and $+2\text{‰}$ Air (Boudou et al., 2008; and references therein).

Nevertheless, there are some exceptions: in a study of $\delta^{15}\text{N}$ in bulk coals and vitrinite macerals of various British Columbia and Alberta coals, Whiticar (1996) observed that two vitrinite samples had very low $\delta^{15}\text{N}$ values (approximately -2‰ Air and -3‰ Air) while their respective bulk coal samples values were approximately 0‰ Air and $+1\text{‰}$ Air.

Coal samples from the Peach Orchard coal bed, collected from closely-spaced, active coal mines in eastern Kentucky, were shown to have major differences in maceral composition (Hower and Ruppert, 2011). We used representative subsplits of three samples to obtain additional information about the coal macerals, particularly macrinite, within the Peach Orchard coal. Coal petrography and elemental analyses were used to identify individual macerals. We determined $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ and assigned nitrogen organic functional groups using elemental analysis continuous flow isotope ratio mass spectrometry (EA-CF-IRMS) analysis and X-ray photoelectron spectroscopy (XPS), respectively, to compare samples rich in copromacrinite-type macrinite (Hower et al., 2011), fusinite and semifusinite, and vitrinite macerals to evaluate macrinite genesis.

Table 1
Geochemical, isotopic, and petrographic data for Peach Orchard coal samples.

Sample	2149	2152	2183	2180 ^a
Site	4	4	1	
Split	2	3 1/2	3	
Ash (wt%, d)	8.87	22.28	25.81	
S _t (wt%, d)	1.70	2.26	0.38	
Al ₂ O ₃	35.79	26.62	21.19	
SiO ₂	45.29	54.53	74.70	
CaO	0.29	0.16	0.40	
K ₂ O	1.45	2.36	0.13	
TiO ₂	0.77	1.45	3.13	
Fe ₂ O ₃	13.87	12.83	0.40	
MgO	0.43	0.80	0.00	
Na ₂ O	0.00	0.00	0.00	
P ₂ O ₅	0.08	0.08	0.13	
SO ₃	0.27	0.13	0.00	
<i>Isotopes - bulk samples</i>				
$\delta^{13}\text{C}$ (‰)	-24.80 ± 0.01	-24.61 ± 0.09	-26.80 ± 0.01	
C (‰)	68.38 ± 0.05	61.88 ± 0.24	65.86 ± 0.26	
$\delta^{15}\text{N}$ (‰)	3.07 ± 0.03	2.92 ± 0.10	-2.83 ± 0.09	
N (‰)	1.60 ± 0.08	1.64 ± 0.07	1.61 ± 0.02	
<i>Isotopes - demineralized samples</i>				
$\delta^{13}\text{C}$ (‰)	-24.81 ± 0.07	-24.52 ± 0.04	n.a.	
C (‰)	71.93 ± 1.47	61.81 ± 1.86	n.a.	
$\delta^{15}\text{N}$ (‰)	3.11 ± 0.10	3.06 ± 0.11	n.a.	
N (‰)	1.54 ± 0.02	1.18 ± 0.04	n.a.	
<i>Petrography</i>				
R _{max} (%)	0.79	0.71		0.73
St dev	0.03	0.03		0.05
R _t (%)	0.73	0.66		0.68
St dev	0.06	0.05		0.04
Vitrinite (vol%, mmf)	92.3	61.4	14.9	
Fusinite (vol%, mmf)	1.4	10.4	3.1	
Semifusinite (vol%, mmf)	1.0	14.4	5.3	
Fus + Sfus (vol%, mmf)	2.4	24.8	8.4	
Macrinite (vol%, mmf)	0.0	0.1	63.2	
Micrinite (vol%, mmf)	0.9	1.9	0.2	
Liptinite (vol%, mmf)	4.4	11.9	13.3	

d - dry basis; mmf - mineral matter free basis.

n.a. - sample not available; St dev - standard deviation.

^a Whole channel associated with 2183.

2. Materials and methods

2.1. Samples, ultimate, proximate and major oxides analyses and petrography

The coal lithotype samples studied were collected by the University of Kentucky Center for Applied Energy Research (CAER) in closely-spaced mines (~ 8.2 km distant from each other) of the Peach Orchard coal bed (Bolsopian; Middle Pennsylvanian) in southern Magoffin County, Kentucky (Fig. 1). This coal bed is characterized by the abundance of dull lithologies (durain, dull clarain, and bone) (Hower and Ruppert, 2011). Three samples were selected for this study because they represented extremes in the maceral composition, and one is rich in macrinite of possible fecal origin (copromacrinite) (Table 1). A fourth whole channel sample was also used for reflectance measurements. Samples were collected from 1986 to 1991 and stored in plastic jars under ambient conditions.

Petrographic analyses were performed at the CAER on epoxy-bound particulate pellets, polished to a $0.05\text{-}\mu\text{m}$ alumina final polish, and examined using reflected white-light, oil-immersion optics at a final magnification of $\times 500$. Maceral analyses are reported on a mineral-free basis. Proximate and ultimate analyses of the coal were conducted at the CAER following ASTM standard procedures. Major oxides were determined on a Phillips AXS2 X-ray fluorescence unit at the CAER following procedures outlined by Hower and Bland (1989).

2.2. X-ray photoelectron spectroscopy (XPS)

Prior to XPS analysis, a fraction of each of the coal samples was manually ground with an agate mortar in order to expose new and fresh coal surfaces.

XPS analysis was performed at the CEMUP – Materials Centre of the University of Porto (Portugal) using an ESCALAB 200A instrument (VG Scientific, UK) with PISCES software for data acquisition and analysis. An achromatic Al ($K\alpha$) X-ray source operating at 15 kV (300 W) was used and the spectrometer was operated in the Constant Analyzer Energy (CAE) mode with 20 eV pass energy. Data acquisition was performed with a pressure $<1\text{ }\mu\text{Pa}$ and spectral analysis was performed using peak fitting with Gaussian-Lorentzian peak shape and Shirley-type background subtraction (Shirley, 1972). The aliphatic C 1s level binding energy (285 eV at the maximum of the principal C 1s component) was used to calibrate the binding energy scale. Binding energy values were not subject to charging effects, making it unnecessary to utilize the charge compensation system. To assess the relative amounts of the species constituting the N 1s photoelectron line, curve resolution followed the procedure of Kelemen et al. (1995). Least squares curve fitting of the spectra was performed using a Gaussian-Lorentzian (30%) function; FWHM (Full Width at Half Maximum) was fixed at 1.7 eV, and the N peaks were defined but not fixed. Three peaks in the XPS energies (eV) for nitrogen functionality in carbonaceous material were initially measured in the coals.

The peaks measured were 1) pyridinic N at $398.9 (\pm 0.3)$ eV; N-6; 2) pyrrolic/amine/pyridone at $400.6 (\pm 0.3)$ eV; N-5; following Pels et al. (1995); 3) quaternary N at $401.3 (\pm 0.3)$ eV; N-Q; 4) pyridinic N-oxide complexes between 402 and 405 eV; N-X; and 5) high binding energy nitro type complexes ($-\text{NO}_2$) found above 405 eV (Seno and Tsuchiya, 1976; Pels et al., 1995), 405 (± 0.5) eV (Suzuki et al., 1994), or $406.2 (\pm 0.1)$ eV (1-nitropyrene model compound; Bartle et al., 1987).

Statistical uncertainties of all of the peaks were taken into account. Pyridinic N measurements are effected by the presence of low levels of amine species with binding energy of 399.4 eV, which cannot be unequivocally distinguished from pyridinic forms (Kelemen et al., 1999). The pyrrolic, amide, amines, and pyridine peaks are not always resolvable using XPS data (Kelemen et al., 1999, 2006 and references therein; Zhu et al., 1997), hence this measurement will be referred to

as the pyrrolic peak. Statistical uncertainties are also high for quaternary N because ammonium salts (Gong et al., 1997) and protonated amino acids (Hansson et al., 2003; Boudou et al., 2008 and references therein) have very close binding energies to this form of N. Finally, pyridinic N-oxide broad zone was also attributed to nitrogen atoms substituting for inner C atoms on the graphene layers (a form of quaternary nitrogen), and ammonium fixed in clay (Boudou et al., 2008, and references therein).

2.3. Elemental analyses continuous flow isotope ratio mass spectrometry (EA-CF-IRMS)

Before entering into further details it is important to state that in the case of sample 2183 (macrinite-rich) only the bulk sample (less than 0.5 g) was analyzed, i.e. the sample was not demineralized as there is no additional archived sample available and the mines where the samples were collected are closed. The authors are aware that using bulk samples is generally avoided because of the potential influence of carbonates. However:

- (i) by taking numbers from Table 1: the average coal has 65.4 wt% total carbon, thus 1 g of coal has 654 mg total C. The ash from 1 g of coal weighs 200 mg and contains 7.6 mg of calcium, which had been calcium carbonate before combustion. The inorganic carbon content in carbonate in 1 g of coal was therefore only 1.63 mg. Assuming a $\delta^{13}\text{C}$ value of -25% for TOC and a $\delta^{13}\text{C}$ value of zero for carbonate carbon, a mass-balance calculation yields a $\delta^{13}\text{C}$ value of total C (which was measured in this study) of -24.94% . This is indeed very similar to -25% for TOC;
- (ii) the CaO content of the three samples is very low (0.16–0.40%, dry ash basis (Table 1), and the measured values are close and inside the range of $\delta^{13}\text{C}$ obtained by other authors for bulk, demineralized coal samples and maceral concentrations (Wickman, 1952; Compston, 1960; Redding, 1978; Schwartzkopf and Schoell, 1985; Holmes et al., 1991).

Nevertheless, there was enough material to demineralize samples 2149 and 2152 and comparisons between the demineralized and bulk results for these samples are similar (Table 1), which suggests that the results found for bulk sample 2183 are valid. In addition, the results obtained for sample 2183 are within “normal” ranges and may still be compared with Whiticar's (1996) work and references therein. Therefore, the results are considered useful in comparing sample composition, and they are a basis for further work if additional Peach Orchard samples are collected. The demineralization of 1 g of the samples 2149 and 2152 was preceded by mechanic milling to $<25\text{ }\mu\text{m}$ followed by HCl (37% m/m, from Sigma-Aldrich) leaching for 24 h at room temperature.

The influence of NH_4 -rich illite on the N results is not considered since the samples in this study are too low in rank for the formation of NH_4 -rich illite, which is a mineral related with high temperature and found in higher rank coals, or in coals associated with hydrothermal fluid events (Buckley et al., 1996; Daniels et al., 1994; Holloway and Dahlgren, 2002; Juster et al., 1987; Liang et al., 2005; Liu et al., 1996; Liu and Zhang, 1997).

In addition, the study of maceral concentrates is not suitable for copromacrinite since it is not a homogeneous material; instead it is a feces-like mixture of several organic coal components (Hower et al., 2011). Therefore, maceral concentrates were not considered for this study.

The isotopic ratios were determined at the Research Support Central Services SCAI of the University of Málaga (Spain), using the elemental analyzer Flash EA 1112, a thermal conductivity detector, provided with a MAS200R auto-sampler (Thermo Scientific, USA). This system

is joined to an IRMS Delta V Advantage spectrometer as a detection system by a ConFloIV interface (Thermo Scientific, USA). The solid samples, which were subjected to a previous lyophilisation and cryogenic milling at $-77\text{ }^\circ\text{C}$, were weighed and packed into tin capsules, and then combusted at $1020\text{ }^\circ\text{C}$ to transform the carbon and nitrogen into CO_2 and N_2 .

These gases are separated via an isothermal packed column at $45\text{ }^\circ\text{C}$ using a He flow at 100 ml/min. Certified reference materials were used to normalize the raw data for the instrument to the international reference scale: IAEA-N-1 ammonium sulphate [$\delta^{15}\text{N} = +0.4\%$], IAEA-N-2 ammonium sulphate [$\delta^{15}\text{N} = +20.3\%$], USGS 34 potassium nitrate [$\delta^{15}\text{N} = -1.8\%$], USGS 35 sodium nitrate [$\delta^{15}\text{N} = +2.7\%$], USGS40 L-glutamic acid [$\delta^{15}\text{N} = -4.52\%$; $\delta^{13}\text{C} = -26.39\%$], USGS41 L-glutamic acid [$\delta^{15}\text{N} = +47.57\%$; $\delta^{13}\text{C} = +37.63\%$], IAEA-CH-6 sucrose acid [$\delta^{13}\text{C} = -10.8\%$], NBS 22 oil acid [$\delta^{13}\text{C} = -30.03\%$] purchased from International Atomic Energy Agency (IAEA), Vienna, Austria.

The results are reported in δ notation (Coplen, 2011):

$$\delta^{13}\text{C} = \left(\frac{{}^{13}\text{C}/({}^{12}\text{C})}_{\text{P}}}{({}^{13}\text{C}/({}^{12}\text{C}))_{\text{Std}}} - 1 \right) \quad (1)$$

$$\delta^{15}\text{N} = \left(\frac{{}^{15}\text{N}/({}^{14}\text{N})}_{\text{P}}}{({}^{15}\text{N}/({}^{14}\text{N}))_{\text{Std}}} - 1 \right) \quad (2)$$

The reported values of the relative difference of isotopes ratios ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) were carried out based on isotopic reference materials, expressed in terms of the conventional δ giving the per mil (‰) deviation of the isotope ratio of a sample P from the standards, and representing the arithmetic means of three duplicate analysis where the variations were generally less than 0.5‰.

3. Results

3.1. Petrography

The Peach Orchard coal samples are high volatile A bituminous (ASTM D388-12, 2012), medium rank C or bituminous C in rank after ISO 11760 (2005), with slight vitrinite reflectance variations (Table 1). However, they have very different maceral compositions: sample 2149 is vitrinite-rich, sample 2152 has a significant amount of fusinite + semifusinite, and sample 2183 is macrinite-rich (Table 1). The macrinite in sample 2183 (Fig. 2) is copromacrinite as it resembles micro-coprolite (Hower et al., 2011, 2013b; also this article, the “Discussion” section).

3.2. Coal nitrogen functionalities (XPS)

The results suggest that the long storage time did not significantly affect the nitrogen functionalities of samples 2152 and 2183 but had some influence on the vitrinite-rich sample 2149. In all of the samples, the values of oxidized-N and Quaternary-N at 401.6 eV (N-Q1) are higher in the unground sub-sample, and the pyridinic-N and the quaternary-N at 402.7 (N-Q2) values are lower. The pyrrolic-N functionality of all samples studied seems only slightly affected by oxidation during storage, since variations in the ground and unground sub-samples are less than 2% (Table 2; Fig. 2). There are pyridinic-N variations between the samples that may or may not be attributed to oxidation during storage as the pyridine-N is lower in the respective unground samples 2149 and 2183, and higher in the unground sample 2152. However, the XPS data of samples 2149 and 2152 are similar, except for the Q-N values where differences are probably due to the conversion of N-Q2 to N-X during storage (Table 2; Fig. 3).

There is a marked difference between the amount of pyrrolic-N in samples 2149 and 2152 and the macrinite-rich sample 2183. The pyrrolic-N values are consistently higher (ca. 14–15% higher) for the ground and unground samples of sample 2183 (Table 2; Fig. 3).

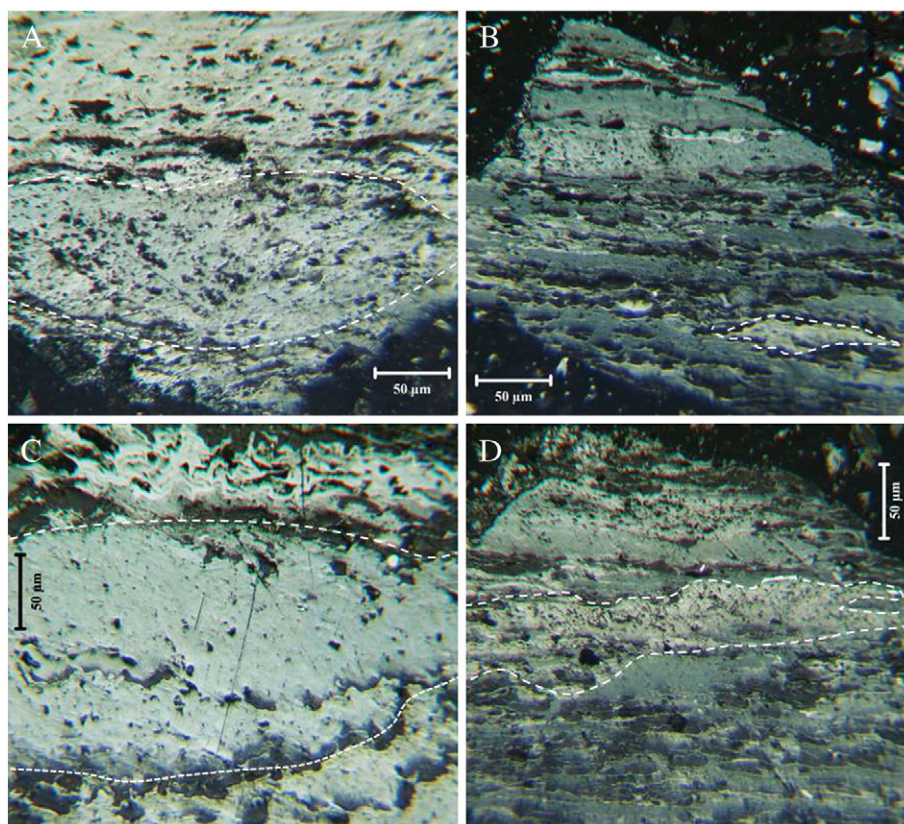


Fig. 2. Peach Orchard coal bed (sample 2183): A to D) macrinite examples (optical microscopy reflected white light).

3.3. Major oxides, elemental, and isotopic composition of Peach Orchard coal samples

The ash concentration of the coal samples ranges between 8.87 and 25.81 (wt%), and the total sulfur concentration is low and varies between 0.38 wt% for sample 2183 and 2.26 wt% for sample 2152. The major oxides values are similar for samples 2149 and 2152 while sample 2183 has higher concentrations of SiO_2 , TiO_2 , and P_2O_5 , and much lower of Fe_2O_3 . All samples have low-CaO content. The C concentration reflected the coal rank and is higher for sample 2149 (0.79% R_{max}) and lowest for sample 2152 (0.71% R_{max}). The N concentration is similar for all samples studied, and shows the expected high concentration relative to the accumulation of coal nitrogen for the coal rank range considered (0.71–0.79% R_{max}) (Boudou and Espitalié, 1995; and references therein).

The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of the bulk and demineralized samples are similar (Table 1). Concerning just the bulk samples, the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values are lower for sample 2183, and are similar for samples 2149 and 2152, ranging between -26.8% VPDB and -24.6% VPDB for $\delta^{13}\text{C}$, and between -2.8% Air and $+3.1\%$ Air for $\delta^{15}\text{N}$. Taking into account the maceral composition of these samples, the $\delta^{13}\text{N}$ value is highest for the vitrinite-rich sample (2149) and lowest for the macrinite-rich sample (2183) (Table 1).

4. Discussion

The samples examined in this study are of the same age, rank (high volatile bituminous A), and burial depth, were subjected to the same thermal history, and the nitrogen cycle are presumed to be similar as they come from closely-spaced areas (Evans, 2001; Robinson, 2001).

Table 2

Results from XPS carbon (1s), nitrogen (1s), and oxygen (1s) spectra of coal samples: element C, N, O (in atom%) and coal nitrogen functionalities (in %).

Sample	2149		2152		2183	
	Ground	Unground	Ground	Unground	Ground	Unground
Element						
C 1s (atom%)	69.27	64.93	56.01	63.04	74.51	80.65
N 1s (atom%)	1.41	1.46	1.29	1.25	1.35	1.59
O 1s (atom%)	29.32	33.61	42.7	35.71	24.14	17.76
N-form	Binding energy (eV)					
Pyridinic (N-6)	398.8	19.65	15.71	18.31	20.48	17.49
Pyrrrolic (N-5)	400.6	38.67	39.88	37.81	54.7	54.11
Quaternary (N-Q1)	401.6	22.21	18.95	21.66	14.72	21.19
Quaternary (N-Q2)	402.7	10.49	18.03	15.13	6.39	4.68
Oxidized nitrogen (N-X)	403.6	6.79	5.23	5.98	1.2	2.53
Nitro	>405	2.19	2.19	1.1	2.5	0

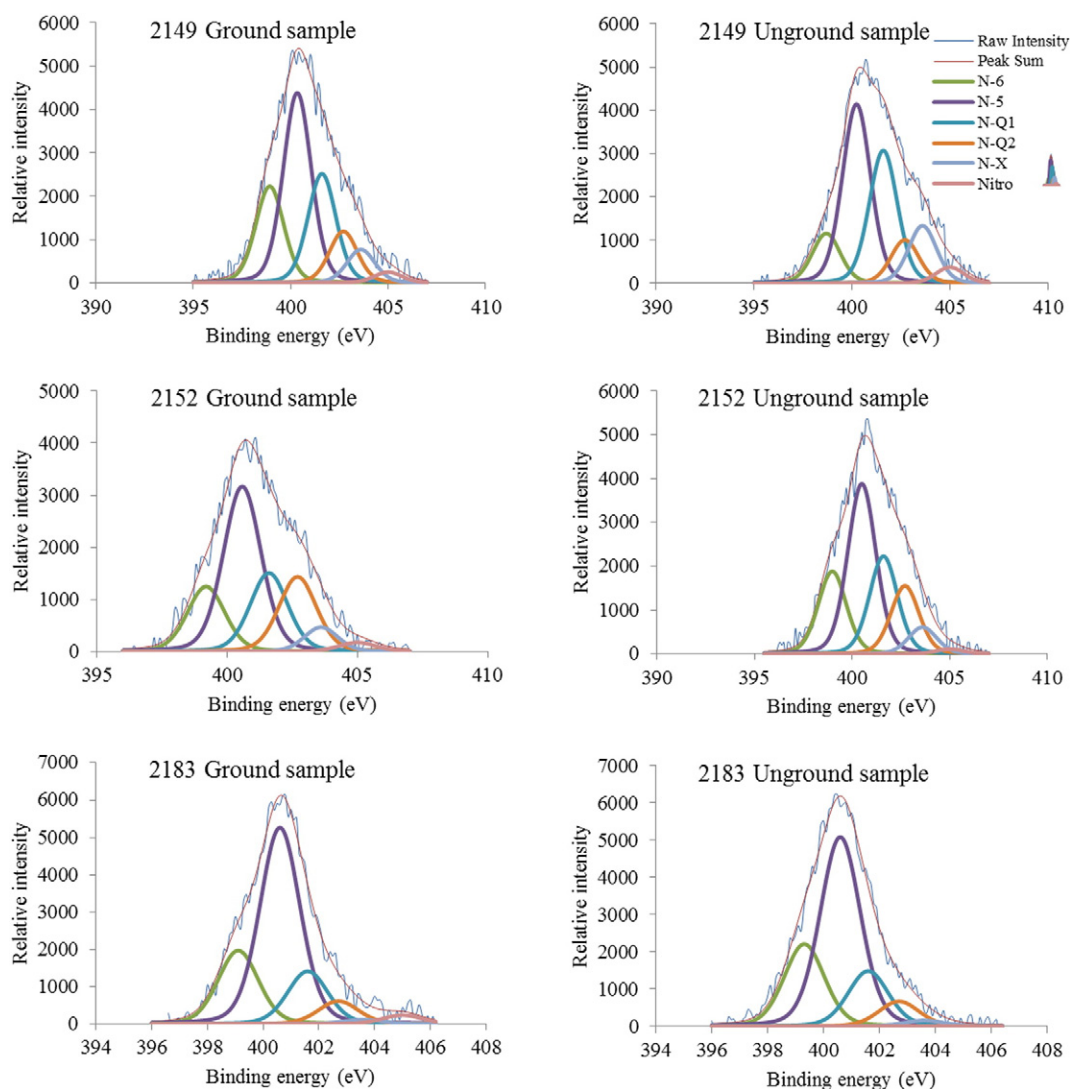


Fig. 3. N 1s core level spectra of the coal samples studied (ground samples on left and unground ones at right) showing pyrrolic-N, pyridinic-N, quaternary (Q1 and Q2) nitrogen, oxidized nitrogen and nitro sub-peaks.

The comparison between the maceral compositions of the Peach Orchard coal samples studied shows that there are major differences between the amounts of vitrinite in the samples but there are no significant differences between their pyridinic-N and Quaternary-N compositions. For the samples studied, pyridine-N is independent of the maceral composition. The percentage of pyrrolic-N of the samples 2149 (92 vol% vitrinite) and 2152 (61 vol% vitrinite and 24 vol% fusinite + semifusinite) is very similar. In these two samples, the proportion of pyrrolic-N is higher than pyridinic-N, but pyrrolic-N is not the predominant N form since the sum of the pyridinic-N and the quaternary-N forms is predominant. When compared with other authors' results, where the amount of pyrrolic-N is typically 50–80% (e.g. Kelly et al., 1991; Kambara et al., 1993; Mullins et al., 1993; Buckley, 1994; Wójtowicz et al., 1995; Thomas, 1997; Kelemen et al., 2006; Valentim et al., 2011a,b), the pyrrolic-N content of samples 2149 and 2152 is very low but it is not anomalous. However, in sample 2183, the pyrrolic-N form is clearly dominant, and anomalous for an inertinite-rich sample. The implication of this for the $\delta^{15}\text{N}$ depletion is unknown but could be associated with the original coal depositional conditions and with the high amount of macrinite in this sample.

The bulk and demineralized coal $\delta^{13}\text{C}$ values obtained for samples 2149 and 2152 are in the expected range for vitrinite-rich samples as they were derived from woody plants. C_3 -type plants have $\delta^{13}\text{C}$ values

ranging from -23% VPDB to -34% VPDB (Gröcke, 1998) and an average value of -27% VPDB (Whiticar, 1996). $\delta^{13}\text{C}$ values also fall in the range of values determined by Schwartzkopf (1984) for vitrinite. The higher bulk and demineralized coal $\delta^{13}\text{C}$ values of sample 2152 in relation to sample 2149 are probably associated with the higher amount of fusinite + semifusinite in sample 2152, in agreement with Whiticar's (1996) description of higher $\delta^{13}\text{C}$ values for inertinite. The results of samples 2149 and 2152 are also within the range of values determined by Rimmer et al. (2006) for parental coals and respective macerals concentrates.

Sample 2183 shows a lower $\delta^{13}\text{C}$ value (-26.8% VPDB), which could be associated with the higher volume of liptinite of this sample (13 vol%) in relation to the other two samples since the lipid-rich materials are inherently lighter $\delta^{13}\text{C}$ in than woody tissues (Rimmer et al., 2006). The low $\delta^{13}\text{C}$ value of sample 2183 may only in part be attributed to the liptinite content since it is $\sim 1\%$ lower than the value of a 74 vol% liptinite concentrate in Rimmer et al. (2006). However, Van de Wetering et al. (2013) suggested that lithotype and maceral groups vary independently from the $\delta^{13}\text{C}$ within seam, and $\delta^{13}\text{C}$ variations represent stratigraphic changes in climate and depositional regimes. For example, they found that the lowest $\delta^{13}\text{C}$ value (-26%) was on dull coal, a precursor to decreasing $\delta^{13}\text{C}$ values near the Permian–Triassic extinction 252.28 ± 0.08 Ma.

Therefore, if the anomalous $\delta^{13}\text{C}$ value of -26% was related by Van de Wetering et al. (2013) to an uncommon event, there is a possibility that the anomalous $\delta^{13}\text{C}$ value of sample 2183 is related also to unusual conditions, and not with variations in the swamp vegetation. The $\delta^{13}\text{C}$ values between the three samples is not rank related because the samples are basically isorank, maturation does not cause a $\delta^{13}\text{C}$ shift (Galimov, 1980; Lewan, 1986), and environmental factors, which may cause considerable $\delta^{13}\text{C}$ shifts (Gröcke, 1998), are absent as, the samples are of same stratigraphic age and are too closely-spaced to be differentially affected by seasonal changes of light and temperature. The $\delta^{13}\text{C}$ shift observed on sample 2183 could be due to an uncommon origin of the inertinite, and we propose that it is of copromacrinite of fecal origin and the associated metabolic processes of the macrofauna (e.g. cockroaches) and microbiota such as bacteria. Bacterial methyl-type fermentation has been shown to result in negative $\delta^{13}\text{C}$ shifts (Valiela, 1984; Benner et al., 1992; Gröcke, 1998). However, it cannot be discarded that $\delta^{13}\text{C}$ can also decrease if the carbonate anion in solid carbonates was derived from the anaerobic oxidation of methane.

The remarkably low $\delta^{15}\text{N}$ value of sample 2183 may also be explained by a fecal origin of copromacrinite and metabolic processes since the results of samples 2149 and 2152 are within the range of values determined by Rimmer et al. (2006), i.e. slightly enriched $\delta^{15}\text{N}$ values for vitrinite relative to inertinite while the $\delta^{15}\text{N}$ value of sample 2183 is much lower. There is a long-established degradational origin of macrinite (Waksman, 1930; Barghoorn, 1949, 1952; Duparque and Delattre, 1953a,b; Stach, 1956; Teichmüller, 1958; Beneš, 1959, 1960a, b, 1969; Beneš and Kraussová, 1964, 1965; Lapo and Malán, 1981; Cross and Phillips, 1990; Eble et al., 1994; Belkin et al., 2009, 2010; Pujana et al., 2009; Sweeney et al., 2009; Hower et al., 2010, 2011, 2013a; Taylor and Krings, 2010; Hower and Ruppert, 2011; O'Keefe and Hower, 2011; Dai et al., 2012b; O'Keefe et al., 2013) that can be preceded (Lavelle and Spain, 2001) or followed (Massee and Salmon, 1901, 1902; Page, 1939; Harper and Webster, 1964; Wicklow and Hirschfield, 1979; Kuthubutheen and Webster, 1986; Richardson, 2002; Greif and Currah, 2007) by fungal and bacterial attack (Hower et al., 2011, 2013b; O'Keefe et al., 2013).

We propose that the feces origin of copromacrinite, when associated with anomalously low $\delta^{15}\text{N}$ values, is related with the digestive mechanisms and nitrogen balance of some macrofauna. The paradigmatic example could be the cockroaches (and more recently termites):

- (i) Cockroaches have remained virtually unchanged since the Silurian (~350 million years ago): fossil cockroaches are found in large numbers from the Upper Carboniferous coal measures and are the predominant insect group in the Carboniferous deposits in Siberia and in the lower Permian coal measures of North America, Europe and the Urals (Blatchley, 1920; Carpenter, 1960; Grimaldi and Engel, 2005; Rust et al., 1995; Tillyard, 1917, 1937a,b; Wootton, 1981).
- (ii) Termite evolution in the Late Jurassic was marked by the acquisition of cellulolytic gut flagellates protists, which gave a presumably omnivorous, ancestral cockroach the capacity to digest wood (Bignell, 1994; Bignell et al., 2011; Brune, 2014; Lo and Eggleton, 2011). The ability of modern termites to degrade lignocellulose relies on their partnership with a diverse community of bacterial, archaeal and eukaryotic gut symbionts which break down plant fiber and ferment the products to acetate and variable amounts of methane. Both cockroaches and termites utilize a multi-step digestive process that includes the regulation or elimination of urate excretion, the intracellular integration of bacteroids, the evolution of urate and mycetocyte cells in the fat body, and the coordination of the intricate interplay between host and symbionts during transovarial transmission (Cochran, 1985).
- (iii) Some cockroaches living in the Carboniferous fed on the detritus from living organism which was colonized and altered by

microbial decomposers. The guts of termites and cockroaches house a diverse anaerobic microbiota, with methanogenic bacteria, ciliates, amoebae, flagellates, and prokaryotic assemblages. In the Carboniferous, as today, the bacteria and fungi responsible for decay predigest plant litter in a phenomenon known as the “external rumen” to remove or detoxify unpalatable chemicals, release carbon sources for assimilation, and physically soften the substrate. These changes improve the palatability of plant litter and increase both its water-holding capacity and its nutritional value. As a result, decay organisms can guide food choice in cockroaches, and some cockroaches species consume bacteria and fungal tissue (fungal hyphae and spores) along with larger amounts of the substrate on which the fungus is growing, but it is the fungi and microbial material, rather than the substrate, that may serve as the primary source of nutrients in some cockroaches species (and millipedes also) (Bell et al., 2007; and references therein), “like feeding on peanut butter spread on an indigestible biscuit” (Cummins, 1974).

- (iv) Meanwhile, the nitrogen excretion in cockroaches is a complex phenomenon that differs from the expected terrestrial insect pattern of producing and voiding uric acid, and the bacteroid-assisted ability of cockroaches to store, mobilize, and in some cases, transfer urates uniquely allows them to utilize nitrogen that is typically lost via excretion in the vast majority of insects (Cochran, 1985). Nevertheless, urate excretion cases found in the family Blattellidae include void urate-containing pellets, with urates constituting 0.5–3.0% of total excreta by weight (Cochran, 1981), and small amount of urates (2% by weight) mixed with fecal material, similar to that of other generalized orthopteroid insects (Bell et al., 2007; Cochran and Mullins, 1982; Cochran, 1985).

During the bibliographic research no references were found concerning the $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values in excretions of cockroaches, which seemed more appropriate than termite results since the gut microbiota of termites should be very different from that of the Carboniferous cockroaches. In addition, it is not clear why wide ranges of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ are observed in termites carcass and guts (Tayasu, 1998), and earthworms (Schmidt et al., 1997). However, the use of stable isotope ratios in the study of detritivorous animals has some potential for elucidating complex relationships occurring in the detritus food web (Tayasu, 1998), and are relevant for understanding the copromacrinite origin. For example, the excretion of low $\delta^{15}\text{N}$ as urea or ammonium seems to account for the ^{15}N -enriched nitrogen that is incorporated into animal tissues, presumably due to isotopic processes occurring during amino acid metabolism in the reaction of urea cycle, and the need for the animals to balance the concentration of ^{15}N in the body (Steele and Daniel, 1978; Minagawa and Wada, 1984). Therefore, anomalous low $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values associated with high copromacrinite volume may indicate ^{15}N depleted feces from cockroaches, or other macrofauna.

There are different pathways to the development of inertinite macerals, as indicated by the large variations in isotopic composition and nitrogen functionalities in the semifusinite + fusinite-rich sample 2152 and the macrinite-rich 2183 of the isorank Peach Orchard coal bed. We suggest that the origin of the macrinite in sample 2183 is coprolitic based on chemical composition, petrographic features, and the lack of heating effects. Additional studies of copromacrinite within other coals should be examined in greater detail focusing on textural relationships between macerals and mineral matter inclusions (clay and quartz), and the chemical composition of inorganic nutrients (P, Ca, and NH_4), organically combined C and N (e.g., Brauman et al., 2000), polyaromatic compounds and C—C linkages (e.g., Hopkins et al., 1998; Hyodo et al., 1999; Katsumata et al., 2007), carbon mineralization (e.g., Kuhnigk et al., 1994), and fecal hydrocarbons (e.g., Haverty et al., 2005).

5. Summary

We examined three isorank samples [vitrinite- and two different inertinite-rich samples (fusinite + semifusinite, and macrinite)] from the Peach Orchard coal bed using coal petrography, X-ray photoelectron spectroscopy, and elemental analysis continuous flow isotope ratio mass spectrometry methods to determine nitrogen functionalities and $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ composition in the samples. Results show that there were no significant differences between pyridinic-N and quaternary-N abundances. However, the macrinite-rich sample was richer in pyrrolic-N (~54%) and lower in $\delta^{13}\text{C}$ (−26.8‰ VPDB) and $\delta^{15}\text{N}$ (−2.8‰ Air) than the vitrinite-rich (~38%, −24.8‰ VPDB, and 3.1‰ Air, respectively) and semifusinite + fusinite rich (~38%, −24.6‰ VPDB, and 2.9‰ Air, respectively) samples. The results indicate that the composition and the origin of the macrinite are different than the composition and origin of vitrinite and fusinite + semifusinite. We attribute the macrinite to a coprolitic origin related to macrovertebrate digestion processes and nitrogen balance.

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Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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