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Notes on the origin of copromacrinite based on nitrogen functionalities and $\delta^{13}C$ and $\delta^{15}N$ 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 $\delta^{13}C$ and $\delta^{15}N$ 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). $\delta^{13}C$ values obtained for bulk and demineralized coal of the vitrinite- and fusinite + semifusinite-rich samples are similar with $\delta^{13}C$ 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 $\delta^{13}C$ value of the fusinite + semifusinite-rich sample is expected as $\delta^{13}C$ values for inertinite are higher than for vitrinite. However, there was a significant shift to a lower $\delta^{13}C$ value ($-26.80 \pm 0.01‰$ VPDB for the bulk sample value) for the macrinite-rich sample. Because the samples are basically isorank, and $\delta^{13}C$ (and $\delta^{15}N$) 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. $\delta^{15}N$ 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 ± 0.03‰ Air and 2.92 ± 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 $\delta^{13}C$ (~2‰ VPDB) and $\delta^{15}N$ (~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 detrivory, 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 $\delta^{13}C$ −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 $\delta^{13}C_{org}$ range of −33‰ VPDB to −22‰ VPDB (mean $\delta^{13}C_{org}$ ca. −27‰ VPDB), whereas C$_4$ land plants (PEP carboxylase photosynthesis) values range from $\delta^{13}C_{org}$ −18‰ VPDB to −8‰ VPDB (mean $\delta^{13}C_{org}$ ca. −13‰ VPDB) (Whiticar, 1996; and references therein).

In modern soils, Cerling and Quade (1993) found that the $\delta^{13}C$ values of organic matter derived from C$_3$ plants range between −25.7‰ VPDB and −20.1‰ VPDB, and the respective soil carbonate $\delta^{13}C$ values range between −10.0‰ VPDB and 4.2‰ VPDB. The $\delta^{13}C$ 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 $\delta^{13}C$ 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 $\delta^{13}C$ for peats and resultant coals (Holmes et al., 1991; Rimmer et al., 2006; Bechtel et al., 2008). The $\delta^{13}C$ 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 (liptinite $\delta^{13}C$ = −23.9‰, vitrinite $\delta^{13}C$ = −23.7‰ and inertinite $\delta^{13}C$ = −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 absorbed 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 (Mitra-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 $\delta^{15}N$ increases with rank, and the isotopic range of published $\delta^{15}N$ values for coals range between ~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 $\delta^{13}C$ nor $\delta^{15}N$ 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
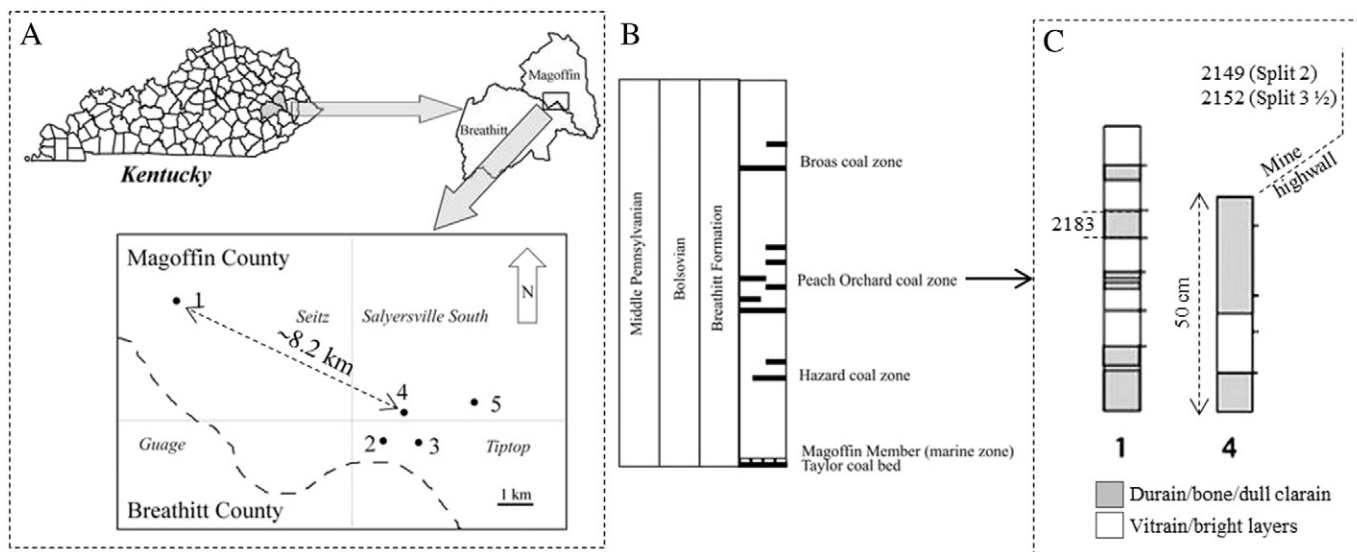

Fig. 1. Generalized locations of the five Peach Orchard coal mine sites in the Seitz and Salyersville South Quadrangles, Magoffin County, eastern Kentucky. The Guage and Tiptop Quadrangles, Breathitt County, are also shown. Sample 2183 was collected at site 1 (No. 3 Split), and samples 2149 (No. 2 Split)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