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Modern analogs reveal the origin of Carboniferous coal balls

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ABSTRACT

Coal balls are calcareous peats with cellular permineralization invaluable for understanding the anatomy of Pennsylvanian and Permian fossil plants. Two distinct kinds of coal balls are here recognized in both Holocene and Pennsylvanian calcareous Histosols. Respirogenic calcite coal balls have arrays of calcite $\delta^{18}O$ and $\delta^{13}C$ like those of desert soil calcic horizons reflecting isotopic composition of CO_2 gas from an aerobic microbiome. Methanogenic calcite coal balls in contrast have invariant $\delta^{18}O$ for a range of $\delta^{13}C$, and formed with anaerobic microbiomes in soil solutions with bicarbonate formed by methane oxidation and sugar fermentation. Respirogenic coal balls are described from Holocene peats in Eight Mile Creek South Australia, and noted from Carboniferous coals near Penistone, Yorkshire. Methanogenic coal balls are described from Carboniferous coals at Berryville (Illinois) and Steubenville (Ohio), Paleocene lignites of Sutton (Alaska), Eocene lignites of Axel Heiberg Island (Nunavut), Pleistocene peats of Konya (Turkey), and Holocene peats of Gramigne di Bando (Italy). Soils and paleosols with coal balls are neither common nor extinct, but were formed by two distinct soil microbiomes.

1. Introduction

Coal balls were best defined by Seward (1895, p. 85). "In the Coal Measures of England, especially in the neighbourhood of Halifax in Yorkshire, and in South Lancashire, the seams of coal occasionally contain calcareous nodules varying in size from a nut to a man's head, and consisting of about 70% of carbonate of calcium and magnesium, and 30% oxide of iron, sulphide of iron, etc. The nodules, often spoken of by English writers as 'coal balls', contain numerous fragments of plants in which the minute cellular structure is preserved with remarkable perfection." Subsequent paleobotanical studies have revealed that perfection, including details of stems and roots (Rothwell and Warner, 1984), vascular architecture (Long, 1979; Retallack and Dilcher, 1988), phloem (Smoot and Taylor, 1978), pollen tubes (Rothwell, 1972), starch granules (Baxter, 1964), and cell nuclei (Millay and Eggert, 1974). These fragile botanical microstructures were permineralized within days after death, before decay and compaction within peaty soils (Zodrow et al., 2002). Other coal balls show a spectrum of plant decay and differential organ preservation (Dimichele and Phillips, 1988; Raymond, 1988).

In soil taxonomy, peaty soils with abundant plant fiber are called Histosols, within the Suborder Fibrist (Soil Survey Staff, 2014). Calcareous peats may qualify as Ustifolists (Soil Survey Staff, 2014). Calcareous Histosols have also been considered an extinct soil type (Breecker and Royer, 2019). Although best known from Euramerican coal measures of Pennsylvanian age (Greb et al., 1999; Raymond et al., 2012, 2019), there are Cenozoic carbonate-permineralized plants in coal (Jahren et al., 2004; Williams et al., 2010). All these calcareous coals do not represent swamp or marsh vegetation, which are vegetation of acidic peats, but carr and fen vegetation (Retallack, 1992). A concise guide to recognizing these and other kinds of peat-forming vegetation in the fossil record is given in Table 1. Holocene calcareous peats are rare, but widely recognized (Stephens, 1943; Leng et al., 1999; Cremonini et al., 2008), and together with novel observations of classic Pennsylvanian coal ball localities, form the basis for this study of the origin of coal balls.

Plants also are cellularly permineralized in calcareous nodules within marine shales (Nishida, 1985) and sandstones (Stockey and Rothwell, 2004), and Holocene analogs of such marine-influenced permineralization are known (Chapman, 1906). Permineralized plants within pedogenic carbonate nodules of modern Aridosols (Klappa, 1978; Monger et al., 1991) are also widespread in the fossil record (Retallack and Dilcher, 1988; Bateman and Rothwell, 1990; Alonso-Zarza et al., 1998; Kabanov et al., 2008). Calcareous plant permineralization within clastic matrices is not strictly a coal ball, and not considered further here, only nodules and stumps permineralized within peat and coal.

The idea of calcite (generally alkaline) in peat (generally acidic) may seem an oxymoron, and explanations for coal balls have emphasized the

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Table 1
Soils and paleosols for different peat-forming vegetation types.

Ecosystem	Definition	Soil type	Paleosol plan language description
Marsh	Acidic herbaceous	Fibrist	Coal with herbaceous debris
Swamp	Acidic arboreal	Fibrist	Coal with woody debris
Bog	Acidic mossy	Sphagnofibrist	Coal with mossy debris
Salt marsh	Intertidal herbaceous	Sulfohemist	Coal with herbaceous debris and pyrite framboids or nodules
Mangal	Intertidal arboreal	Sulfohemist	Coal with woody debris and pyrite framboids or nodules
Fen	Alkaline herbaceous	Ustifolist	Coal with herbaceous debris and siderite, dolomite, or calcite nodules
Carr	Alkaline arboreal	Ustifolist	Coal with woody debris and siderite, dolomite or calcite nodules

Note: sources: Retallack (1992), Soil Survey Staff (2014).

pH problem with a variety of theories. One of the earliest theories is intrusion of marine-influenced water delivering carbonate cement into coastal peat swamps (Stopes and Watson, 1909; Evans and Amos, 1961; DeMaris et al., 1983). Coal balls have also been considered blocks of marine limestone physically thrown into coastal swamps by large storms (Mamay and Yochelson, 1962). Successive distinct hydrological regimes have also been proposed: flushing with carbonate-bearing meteoric water after peat accumulation (Anderson et al., 1980), or the reverse, sinking of meteoric ombrotrophic peats into saline and alkaline groundwater intrusion (Spicer, 1989). Calcite precipitation in peats has also been attributed to channels for soil CO_2 escape provided by the unique hollow roots of some Pennsylvanian swamp plants (Breecker and Royer, 2019). These various theories partly based on stable isotopic data of $\delta^{18}O$ and $\delta^{13}C$ are here reassessed from three case studies, as well as other examples, and new isotopic studies to refine microbiological explanations for the origin of coal balls.

2. Materials and methods

Geological sections and panel diagrams to scale were measured in the field at three locations: (1) Eight Mile Creek Swamp, South Australia; (2) Berryville coal ball locality, Illinois, and (3) Steubenville coal ball locality, Ohio (Fig. 1). Thin sections were prepared from coals and associated sediments. Stable isotopic compositions $\delta^{18}O$ and $\delta^{13}C$ were measured by J.G. Wynn in the Stable Isotope Laboratory of the Earth Environmental Group at the Australian National University, in Canberra, Australia, using a Finnigan MAT-251 attached to a Kiel-1 automatic carbonate reaction device, and NBS-19 and NBS-18 standards of Vienna Peedee belemnite. Reproducibility of $\delta^{13}C$ determined by replicate analyses is within 0.05‰ per specimen (Table 2). Fossils and rock specimens from each of the three localities are curated in the Condon Collection of the Museum of Natural and Cultural History, at the University of Oregon (online portal at https://mnch.uoregon.edu/collections/paleontology-collections/paleo.uoregon.edu).

3. Holocene coal balls of Eight Mile Creek, South Australia

Calcareous nodules in peat were examined in a summer-dry drainage-ditch in Eight Mile Creek Swamp, east of the sealed road 12 km east of Port Macdonnell, and 400 m north of the beach (Fig. 2), south

Table 2
Carbonate carbon and oxygen isotopes of Hitchcox and Berryville coal balls.

Sample	$d^{13}C$	$d^{18}O$	Description
Be1	−8.13	−8	Berryville Pennsylvanian marine limestone
Be2	−13.47	−8.1	Berryville Pennsylvanian marine limestone
Be3	−11.64	−7.91	Berryville Pennsylvanian coal ball
Be5	−19.08	−8.18	Berryville Pennsylvanian coal ball
Be7	−20.13	−7.46	Berryville Pennsylvanian coal ball
R312	−18.94	−12.01	Hitchcox Holocene coal ball
R313	−20.79	−13.5	Hitchcox Holocene coal ball
R313A	−19.7	−12.09	Hitchcox Holocene coal ball
R313B	−20.1	−12.96	Hitchcox Holocene coal ball
R313C	−20.9	−14.03	Hitchcox Holocene coal ball
R313D	−20.3	−13.35	Hitchcox Holocene coal ball
R313E	−16.7	−12.48	Hitchcox Holocene coal ball
R312A	−11.1	−2.10	Hitchcox Holocene coal ball
R312B	−9.9	−0.16	Hitchcox Holocene coal ball
R312C	−9.9	−1.51	Hitchcox Holocene coal ball
R312D	−11.1	−3.36	Hitchcox Holocene coal ball
R309	−2.1	−0.18	Hitchcox Miocene marl
R310	−5.4	−0.6	Hitchcox Miocene marl
R311	−3.52	0.03	Hitchcox Miocene marl
R314	−7.38	−3.96	Hitchcox Miocene limestone
R315	−7.7	−3.89	Hitchcox Miocene limestone
R316	−6.84	−3.49	Hitchcox Miocene limestone

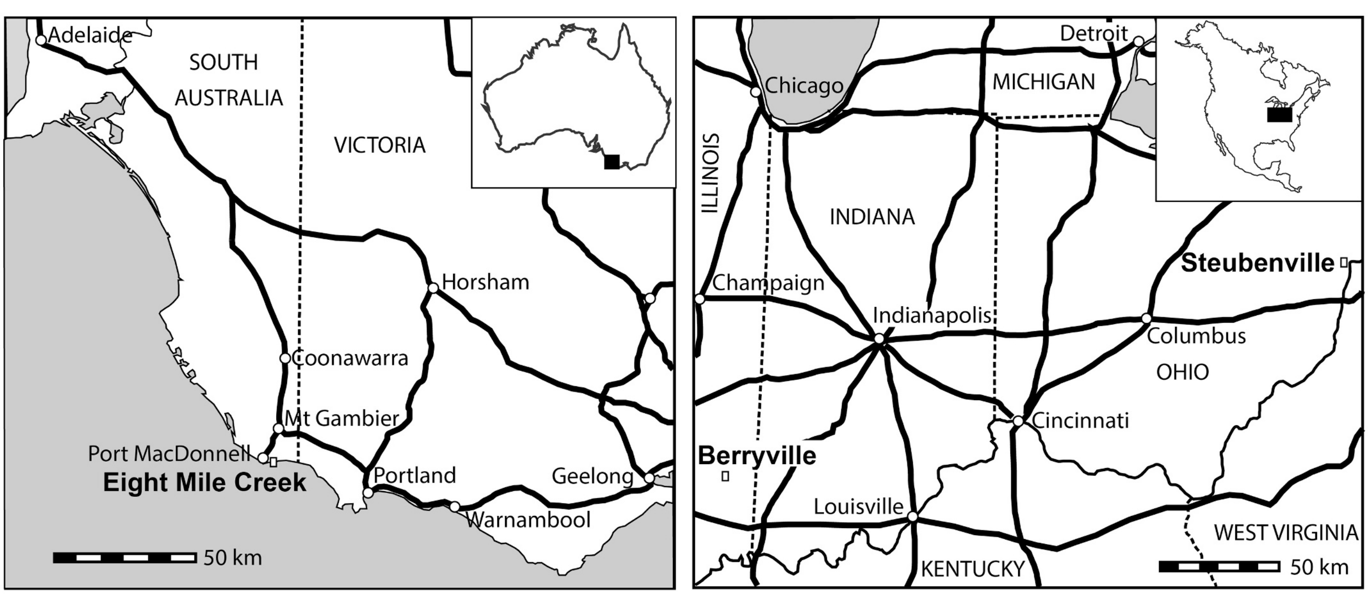

Fig. 1. Locations of Holocene coal balls at Eight Mile Creek, South Australia, and Pennsylvanian coal balls near Berryville, Illinois, and Steubenville, Ohio.

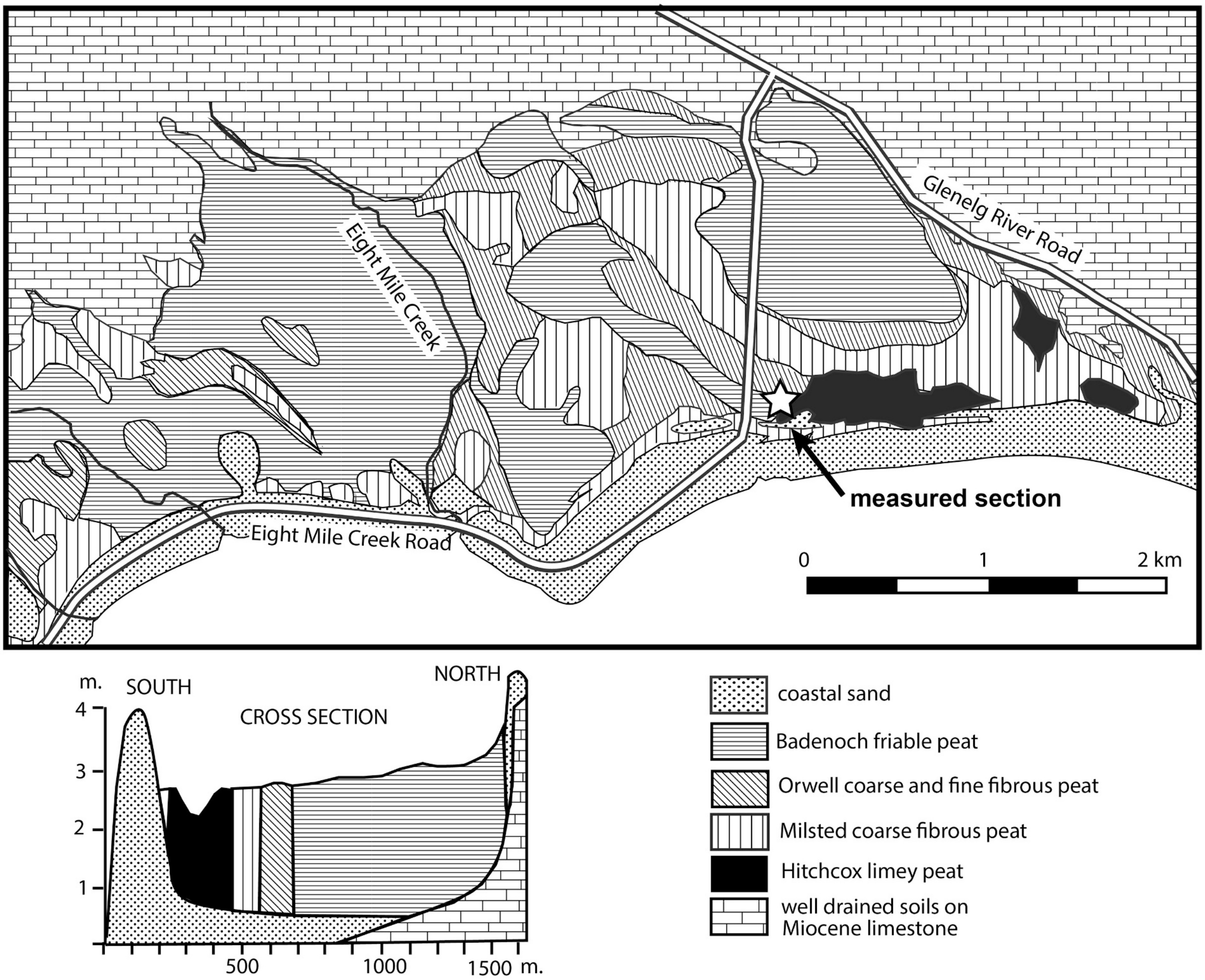

Fig. 2. Soil map and cross section of Hitchcox lime peat soil in Eight Mile Creek Swamp, South Australia (after Stephens, 1943).

eastern South Australia at S38.037146° W140.840141° and 5 m elevation. The Hitchcox limey peat soil with a pH of 7.9 to 8.4 supports sedges greener than in other areas (Eardley, 1943), mapped within a limited area of extensive non-calcareous and acidic peat (Fig. 2). The Hitchcox limey peat supports the grass *Triglochin procera* and the alga *Chara globularis*, not found in surrounding non-calcareous peats dominated by sedges *Cladium junceum* and *C. glomeratum* (Eardley, 1943; García, 1999). Calcareous peats with herbaceous vegetation support fen, not marsh vegetation (Eardley, 1943; Stephens, 1943). The calcareous fen is impounded by coastal dunes and eolianite of the Bridgewater

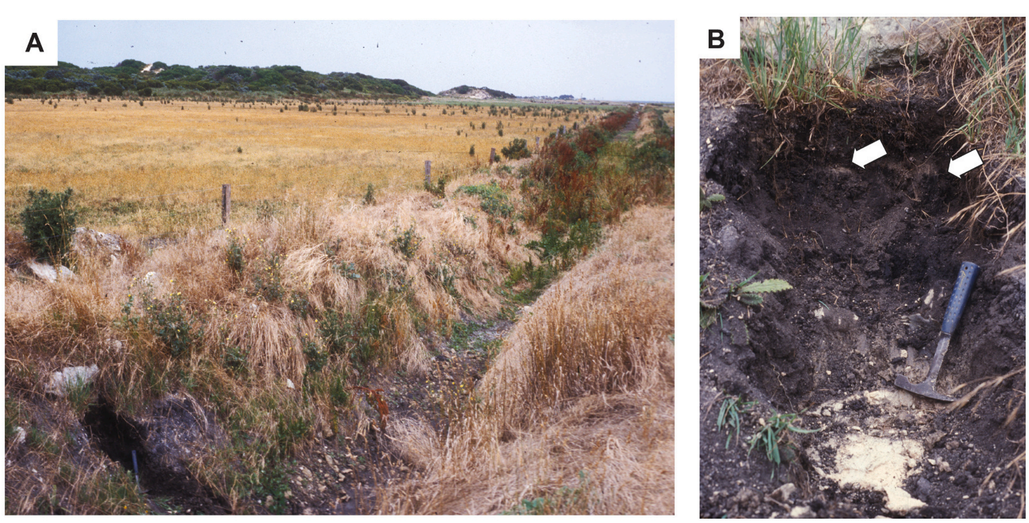

Fig. 3. Field photographs of the Hitchcox limey peat soil: A, measured section (lower left) in summer dry (January 1, 1986) drainage ditch within Eight Mile Creek Swamp looking northeast: B, excavated section of Hitchcox limey peat soil showing light gray nodules (at arrows) and Miocene limestone bedrock. Hammer for scale.

Formation, dated by OSL at 53 ± 4 ka nearby at Port MacDonnell (Blakemore et al., 2014, 2015), but the peat largely accumulated during post-glacial marine transgression, which reached the current location by 7 ka (Murray-Wallace et al., 1999). The basement rock is Miocene (22 Ma), Gambier Limestone dipping seaward (Li et al., 2000), and forming a ridgeline to the north (Fig. 3A). The dip has been produced by continuing uplift of this region at a rate of 0.13 mm yr^{-1}, stranding successively older Pleistocene beach ridges to the north (Sprigg, 1979; Blakemore et al., 2015). The disconformity between Quaternary peat and calcarenite is marked regionally by karst weathering (James and Bone, 1989). The unconfined aquifer of Miocene limestone is fed by gravity flow from Mt. Gambier (Grimes, 1994), and prone to subsurface seawater intrusion for 15 km inland, with a volume of sea water when recharge is zero of 400,000 m^3/m, and a mixed convection ratio of 0.51 (Werner et al., 2012; Morgan and Werner, 2015). Climate of this locality inferred from nearby Mt. Gambier is warm-temperate, summer-dry, subhumid: 13.6 °C mean annual temperature, 714 mm mean annual precipitation, and 75 mm mean annual range of precipitation difference between wettest and driest month mean (Bureau of Meteorology, 2019).

An irrigation ditch wall was excavated for a measured section (Fig. 3–4), supplemented with compositional data from Stephens (1943). Thin sections revealed cellular permineralization within the nodules (Fig. 5), and stable isotopic analysis showed a strong correlation between $\delta^{18}O$ and $\delta^{13}C$ of the carbonate (Fig. 6A). As a soil, the Hitchcox limey peat consists of a histic epipedon of 22 cm of fibrous peat enclosing light-gray, rounded nodules of massive carbonate, above 30 cm of clayey peat with tabular light gray calcite nodules, and a paleokarst with 8 cm of local relief on Miocene bryozoan limestone (Condon locality OU 11106). Partial permineralization of sedges is found in nodules near the surface (Fig. 5A–B), and permineralization of tabular root systems is found in the nodules lower in the profile (Fig. 5C–D). Ostracods, snails (Fig. 5F) and charophytes (Fig. 5E) are found within the calcareous nodules. The snails are freshwater pond species, *Glyptophysa novaehollandiae* (Planorbidae, Smith and Kershaw, 1979) and *Austropyrgus tumidus* (Hydrobiidae, Clark et al., 2003). Also found at the surface was a large living population of the European invasive land snail *Theba pisana* (Helicidae: Baker and Vogelzang, 1988). These modern species of freshwater snails in the nodules are completely enclosed in peat and thus distinguish Holocene micritic nodules from Miocene karsted Gambier Limestone, which is a grainstone packed with marine bryozoans and large foraminifera (James and Bone, 1989).

The stable isotopic composition of both the Miocene limestone and Holocene soil calcite shows a pronounced correlation between $\delta^{18}O$ and $\delta^{13}C$ (Fig. 6A). This pattern is comparable with correlations seen in pedogenic carbonate of Aridisols (Fig. 6C: Knauth et al., 2003; Huang et al., 2005), and in marine limestone altered by meteoric weathering (Fig. 6D; Lohmann, 1988; Melim et al., 2004), and unlike the scattered distribution of marine limestone (Fig. 6E; Surge et al., 1997; Veizer et al., 1999) and low $\delta^{13}C$ but $\delta^{18}O$-invariant methane seeps (Fig. 6F; Aiello et al., 2001; Martin et al., 2007). Some of these $\delta^{13}C$ values are unusually low for pedogenic nodules (Table 2), perhaps due to methanogenesis low in the Hitchcox limey peat. While it is true that peats and Histosols are found mainly in humid climates, they also form in climates with as little as 400 mm mean annual precipitation (Parrish, 1998). Nor is a high stagnant water table necessary for peat accumulation, because the soil suborder Folist is defined as "saturated with water for less than 30 cumulative days during normal years (and not artificially drained)" by Soil Survey Staff (2014). Although best known in Aridisols, the highly correlated pattern of $\delta^{18}O$ and $\delta^{13}C$ reflects an aerobic soil microbiome of seasonally low water tables (Retallack, 2016).

4. Pennsylvanian coal balls of Berryville, Illinois

This famous coal ball locality is 1.5 miles northeast of Berryville, a

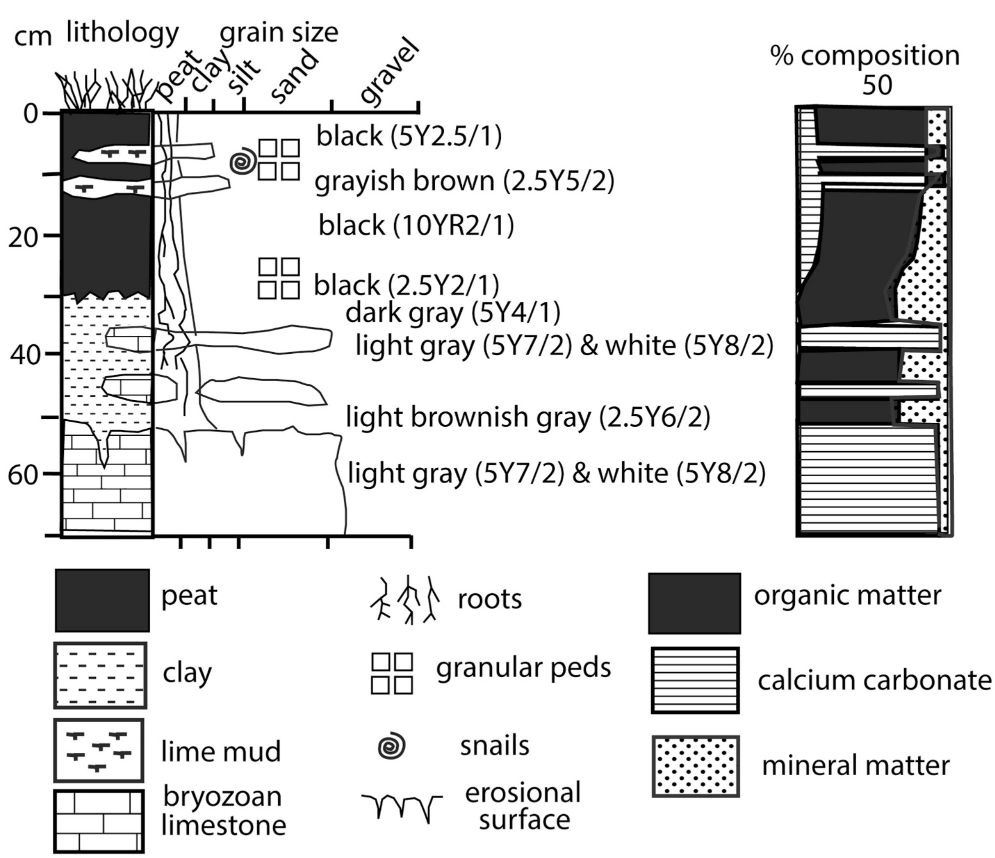

Fig. 4. Geological section of the Hitchcox limey peat soil.

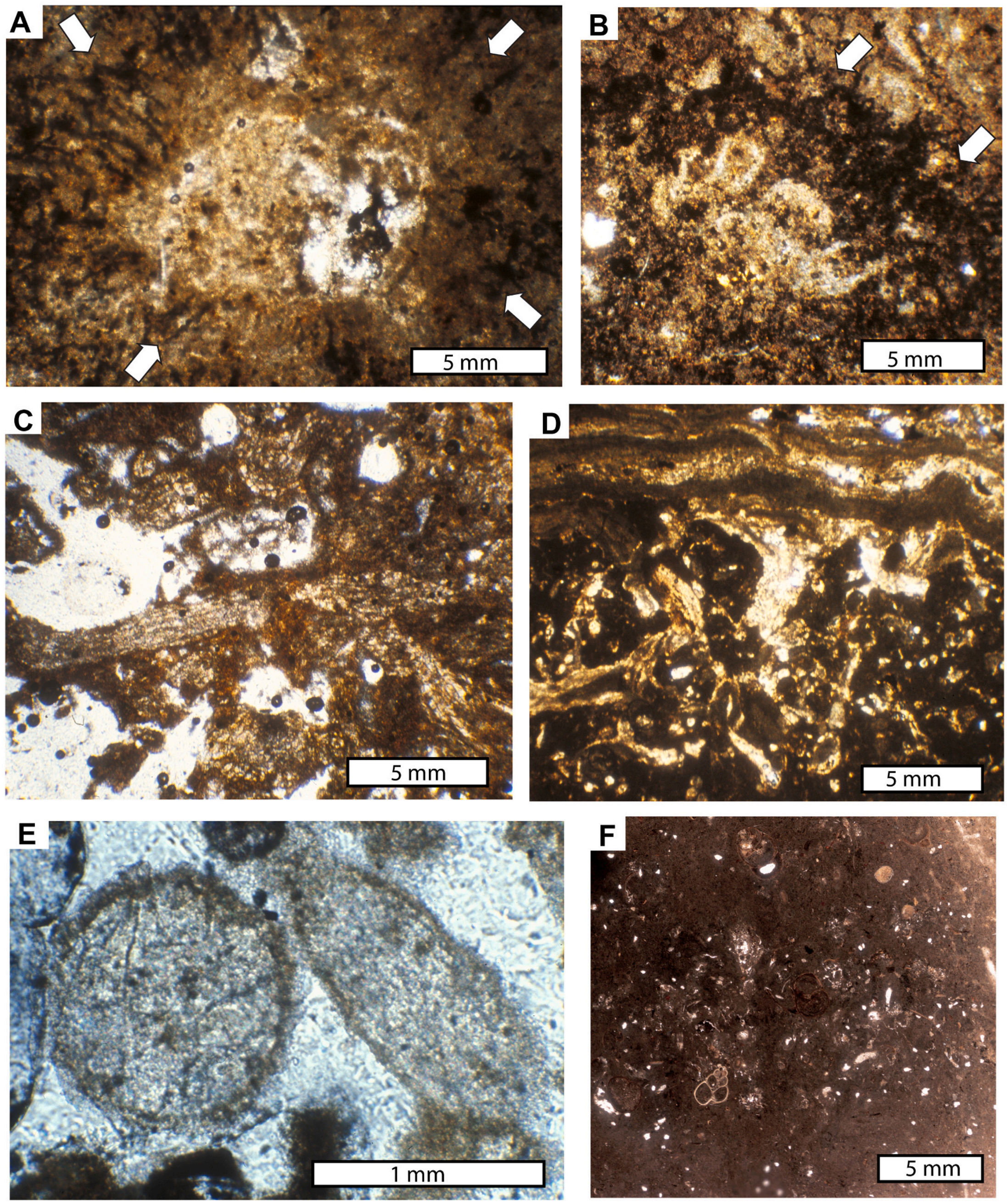

Fig. 5. Petrographic thin sections of carbonate of the Hitchcox limey peat soil: A–B, partial cellular permineralization of sedges with hollow culm and radiating sclereid bands (at arrows) from nodules within peat; C–D., permineralized root traces from carbonate crust in base of profile; E, permineralized oogonium and stem of *Chara globularis* in marl of lower part of profile; F, cross sections of snail (*Austropyrgus tumidus*) and ostracods in nodule within peat.

hamlet in Richland County (Retallack and Dilcher, 1988; Willard et al., 2007). Coal balls are abundant on the south bank of Sugar Creek, just across the county line in Lawrence County, at N38.625696° W87.90184° elevation 178 m. Only 1.6 m of vertical section and 8 m along strike is exposed above creek level (Figs. 1, 7A, 8A), showing coal with massive coal balls, many of them including marine fossils. This coal is the Calhoun Coal of the Mattoon Formation of Late Pennsylvanian (Missourian) age (Phillips et al., 1985), or about 303 Ma (Ogg et al., 2016). The coal is black and high-volatile bituminous in rank (Korose and Elrick, 2010), and like nearby coal balls near Harrisburg, carbon within the coal balls is of rank comparable with the noncalcareous coal (Hatcher et al., 1982).

The outcrop is a dramatic demonstration of the lack of compaction of coal balls, because the coal seam thins by a half only 2 m to the east (Fig. 7C). The seam is directly overlain by marine limestone, and 5 cm diameter burrows filled with fossiliferous limestone penetrate down into the coal (Fig. 8A). This bedded limestone has large corals (*Neozaphrentis* sp), brachiopods (*Linoproductus cora*, *Antiquatonia portlockiana*, *Orthotetes kaskaskiensis*, *Phricodothyris perplexa*, *Composita subtilita*), and gastropods (*Trepospira sphaerulatus*: Condon Collection locality UO11278). A variety of small marine fossils were collected from burrows filled with skeletal debris up to 30 cm below the top of the seam, including brachiopods (*Hystriculina wabashensis*, *Neochonetes granuilfer*, *Rhipodomella carbonaria*, *Composita subtilita*), pelecypods (*Aviculopecten* sp.), trilobites (*Ditomopyge scitula*), and crinoid columnals. Megascopic plant remains are abundant in the coal balls, and can be exposed in plan by parting along bedding planes (Stidd, 1988), or peeled and thin-sectioned in cross section (Willard et al., 2007). The plants include mainly seed fern remains (*Alethopteris lesquereuxii*, *Pachytesta illinoensis*, *Bernaultia formosa*,

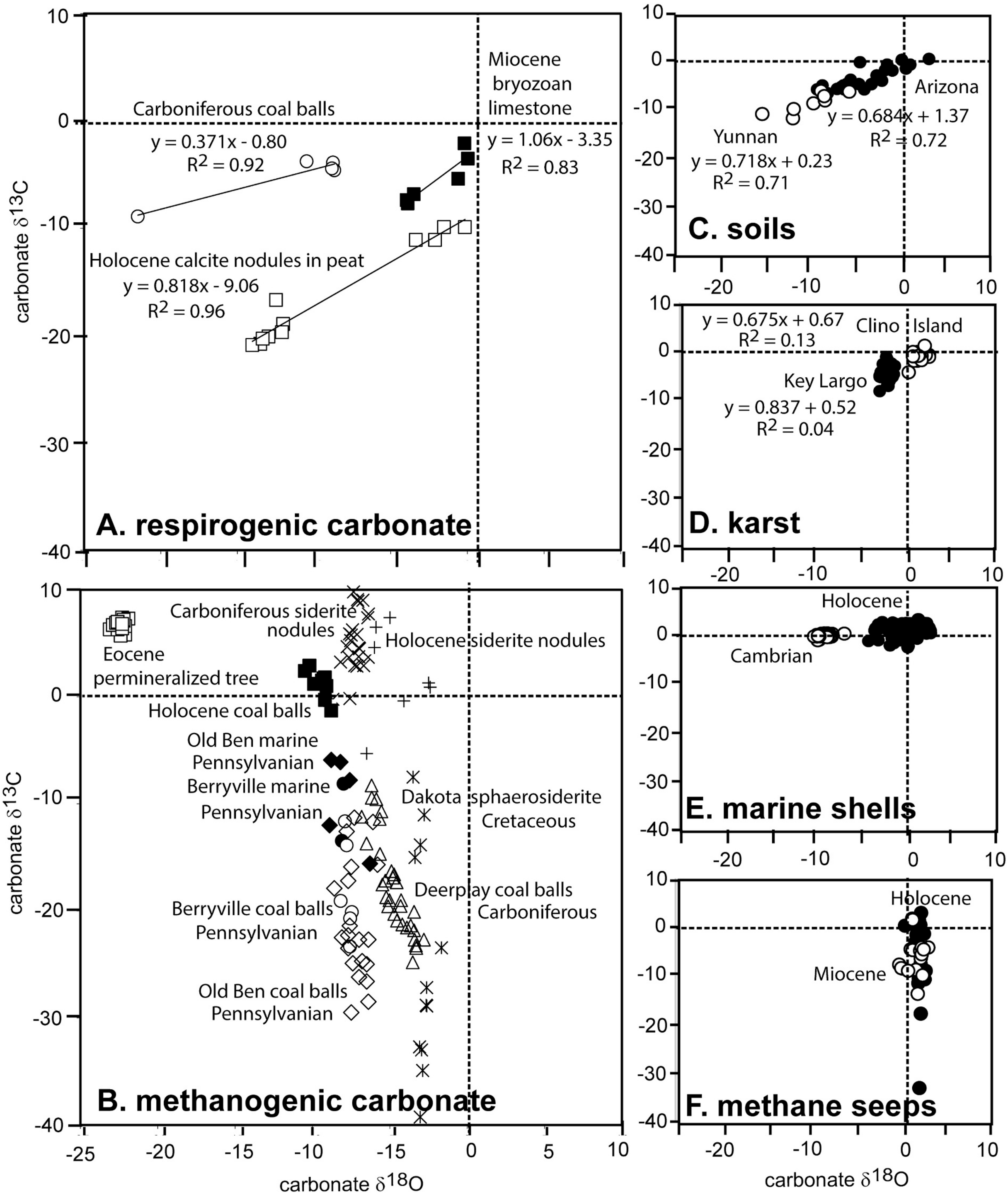

Fig. 6. Stable isotopic systematics of A, respirogenic calcite nodules in peat (Table 1; Weber and Keith, 1962; Curtis et al., 1986); B, methanogenic calcite in Histosols and siderite in Gleysols (DeMaris et al., 1983; Curtis et al., 1986; Scott et al., 1996, 1997; Moore et al., 1992; Leng et al., 1999), and in comparable other environments including C, soils (Knauth et al., 2003; Huang et al., 2005; D, karst (Lohmann, 1988; Melim et al., 2004), E., marine shells (Surge et al., 1997; Veizer et al., 1999), and F., methane seeps (Aiello et al., 2001; Martin et al., 2007).

Medullosa noei) as well as tree ferns (*Psaronius blicklei*) and lycopsids (*Stigmaria ficoides*). This locality is best known for the seed fern *Pachytesta illinoensis* (Retallack and Dilcher, 1988), but has yielded 62 different species, although most of these are form species for different plant parts of fewer biological species (Phillips, 1981). In a reconstruction of the fossil flora of the Calhoun coal bed, "The forest is dominated by a framework of *Psaronius* canopy trees with patches of *Medullosa* [=*Pachytesta*] and *Sigillaria* dominance" (Willard et al., 2007, p. 43). Although such communities have been mislabelled ancient "swamps", such calcareous substrates including sea shells and woody remains mark them as carr vegetation (Table 1), like the willow carr of modern East Anglia (Retallack, 1992). No marine fossils, but more plants were found below 45 cm from the surface. The base of the coal histic epipedon is a carbonaceous siltstone A horizon with carbonaceous gymnosperm (not stigmarian) root traces (Fig. 8A). Below that again is bedded gray shale, as a parent material to an Entisol (Fluvent of Soil Survey Staff, 2014).

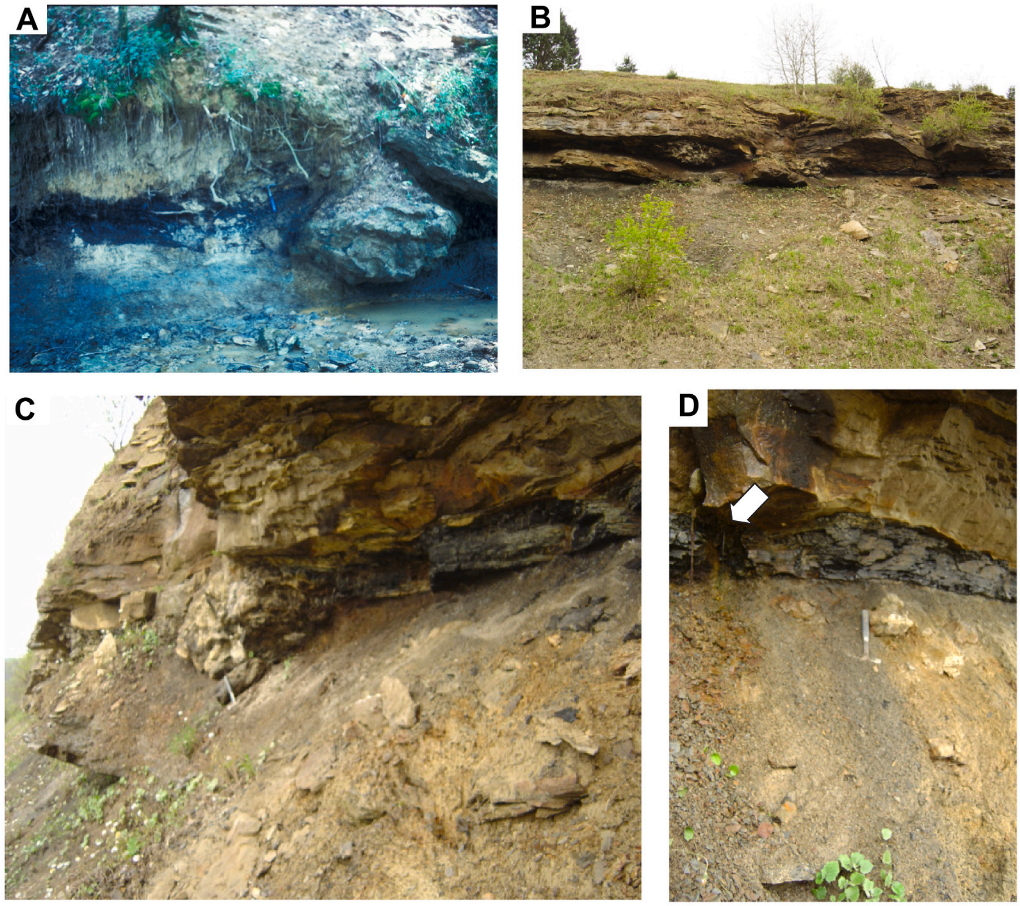

Fig. 7. Field photographs of the Pennsylvanian coal balls in the Calhoun Coal of the Mattoon Formation, near Berryville, Illinois on July 14, 1994 (A), and Duquesne Coal of the Glenshaw Formation, near Steubenville, Ohio, on May 10, 2007 (B–D); showing lateral variation in thickness of coal ball zone (A–B), pinchout (at hammer) of coal (C), and pull-apart of coal injected by underclay (at arrow), and horizonation of underclay paleosol (D).

There are several lines of evidence for syndepositional carbonate precipitation at Berryville. Fossil nuclei and other structures that decay within days are preserved in some prepollen (Retallack and Dilcher, 1988). Ledges of coal ball are interleaved with plies of the coal, and slope downward on either side. Coal to the side of the big carbonate mass is strongly compacted as if carbonate is preserving the original peat thickness (Fig. 7A). Finally, carbonate cement held open tubular burrows into the coal, into which marine shells fell from above after marine transgression.

Isotopic studies of Berryville coal balls and marine limestone (Weber and Keith, 1962; Table 2) show a distinctive pattern of δ^{18}O-invariance (Fig. 6B), like methane seeps (Fig. 6F). The carbon isotopic composition of the overlying marine limestone and burrows varies from −8.13 to −13.47‰, and the plant bearing coal ball carbonate from −11.64 to −23.35‰. This δ^{18}O-invariant pattern is also seen in other coal balls and in pedogenic sphaerosiderite of gleyed clayey paleosols (Fig. 6B), and represents an anaerobic soil microbiome of a waterlogged soil. These waterlogged Histosols of subhumid to humid paleoclimates alternate within Illinois cyclothems with calcareous Aridisol paleosols (Schutter and Heckel, 1985; de Wet et al., 1997).

5. Pennsylvanian coal balls of Steubenville, Ohio

Coal balls are well exposed in road cuts on both sides of Ohio highway 22, 5 miles west of Steubenville, and 0.5 miles east of exit 22A to Wintersville, Jefferson County (Fig. 1), at N40.393152° W80.720224° and 345 m elevation (Rothwell, 1988). These exposures are remarkable for showing lateral variation in thickness of the coal ball hummocks over a distance of 135 m between the outcrop edge and the point where the coal is erosionally truncated by a sandstone paleochannel (Fig. 7C, 8B), This outcrop thus reveals with more completely hummocks of coal balls like those exposed at Berryville (Fig. 7A) and Harrisburg, Illinois (Evans and Amos, 1961). The upper seam with coal balls at Steubenville is the high volatile bituminous rank Duquesne Coal of the Glenshaw Formation of the Late Pennsylvanian Missourian stage (Phillips et al., 1985; Rothwell, 1988; Ruppert et al., 2010), thus 304 Ma (Ogg et al., 2016).

The coal-ball bed at Steubenville is overlain sharply and laterally truncated by paleochannel sandstone, with coal ball clasts in its erosional base (Fig. 9). The coal balls themselves are much less compacted than the coal, so that the underlying claystones are deformed into broad depressions (Fig. 7B–C). Each of the coal balls is more or less rounded, and 15–30 cm in diameter, but they aggregate into hummocks 2–3 m wide, with varying lateral spacing. Seams and tubes of coal branching vertically, penetrate downward from the summit of the hummocks like the root traces of *Pennsylvanioxylon nauertianum* permineralized in this part of the hummock (Rothwell and Warner, 1984; DiMichele and Phillips, 1994). In another telling detail the coal is locally cracked and separated by as much as 9 cm, and the clayey underlying seat earth is injected upward though the entire seam, to be truncated by the overlying sandstone (Fig. 9). This is evidence of tension gashes in lithified coal due to compactional deformation.

Pryor (1996) listed 75 fossil plant form species from these coal balls, and notes local dominance of "*Cordaitoxylon dumusum*" wood (Rothwell and Warner, 1984; Rothwell, 1993), now referred to *Pennsylvanioxylon nauertianum* (Dimichele and Phillips, 1994). The cordaitean wood *P. nauertianum* was a member of a seral community that contained the

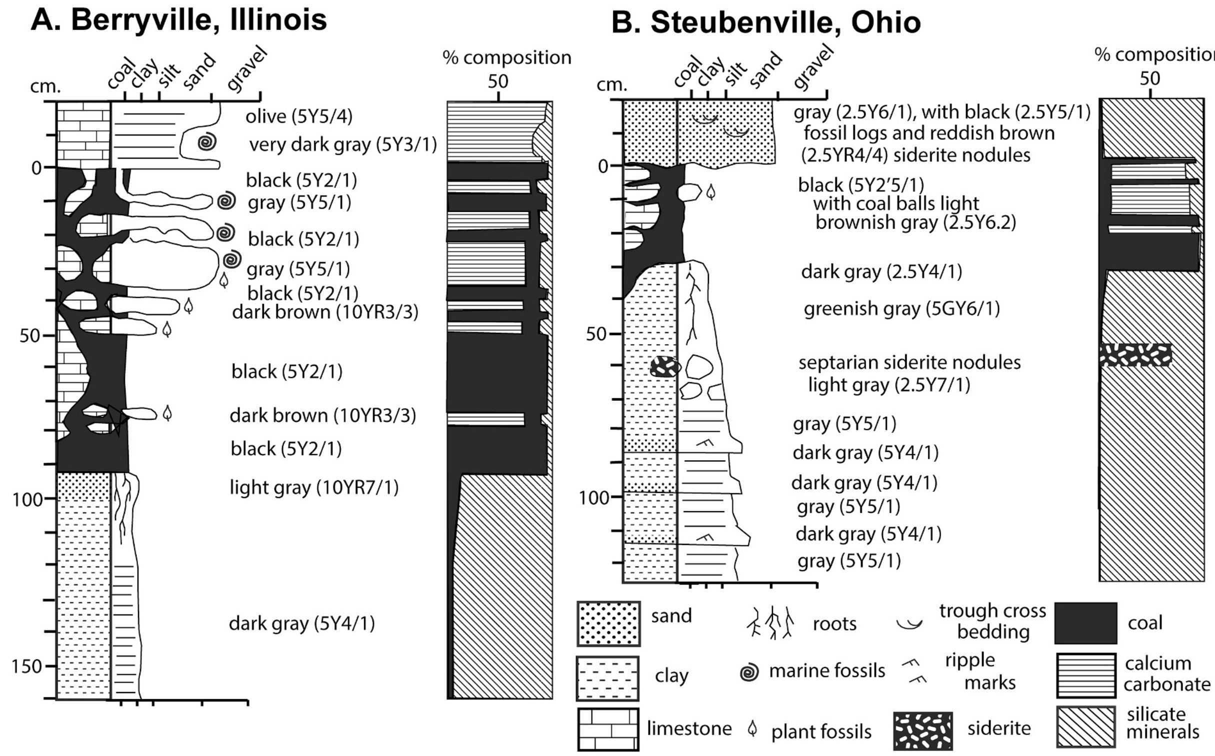

Fig. 8. Geological sections of coal balls near Berryville, Illinois, and Steubenville, Ohio.

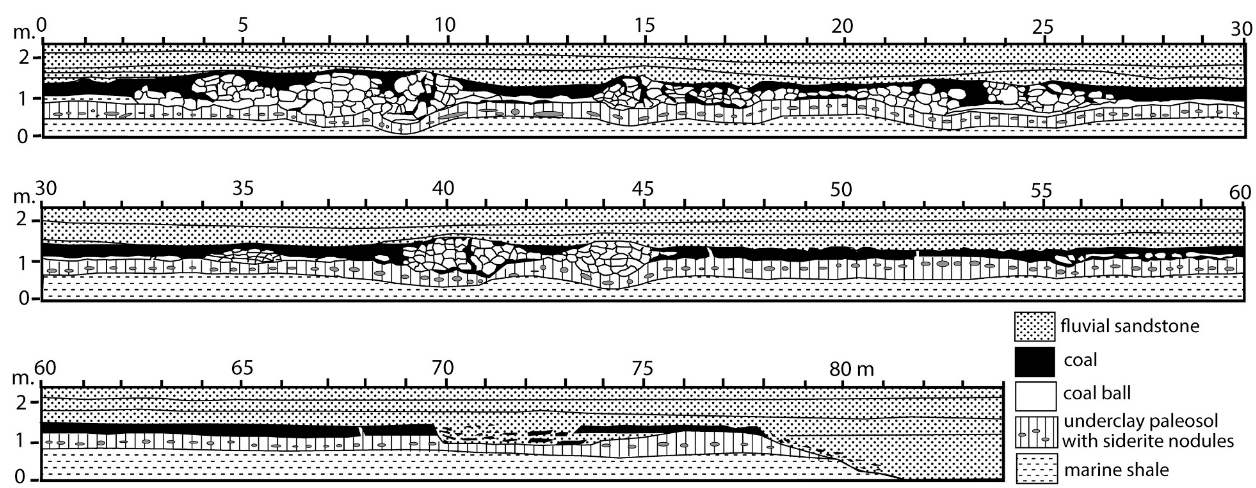

Fig. 9. Panel sections true to scale of lateral variations in coal balls near Steubenville, Ohio.

greatest species diversity of this vegetation (Fig. 10). *Pennsylvanioxylon* carr vegetation succeeded nearly monotypic stands of *Chaloneria cormosa* (Pigg and Rothwell, 1983), which was a colonizing fen over debris from swamp margin vegetation. *Psaronius* swamp created coal both before and after the *Pennsylvanioxylon* hummock phase (Rothwell, 1993). Other taxa found near the base of the coal were *Mesoxylon priapi*, *Calamites*, and *Sigillaria* (Trivett and Rothwell, 1985; Pryor, 1996).

Three lines of evidence suggest that carbonate formed during accumulation of the peat. First is preservation of haustorial pollen tubes and nuclei within cells that have seen very little decay (Rothwell, 1972). Second is evidence from deformation around the coal balls that they preserve original peat thickness (Fig. 9, 10), before natural peat settling within the living swamp and then subsequent cover by overburden. Third is clasts of coal ball in the erosional base of the overlying paleochannel sandstone (Fig. 9).

The coaly histic epipedon with coal balls, or O horizon, of this paleosol is 38 cm thick, and overlies a clayey seat earth, with clayey blocky structured surface (A) horizon over a subsurface gleyed (Bg) horizon of large siderite nodules. The surface of this paleosol included rare stigmarian roots. The parent material to this paleosol was a ripple marked siltstone some 3 m thick, above Ames Limestone, which includes the following marine fossils at the base of the roadcut: bryozoan (*Rhombopora*), brachiopods (*Neospirifer dunbari*, *Punctospirifer transversus*, *Linoproductus prattenianus*, *Dictyoclostus portlockianus*, *Mesolobus mesolobus*, *Chonetes granulifer*, *Derbyia crassa*, *Composita subtilita*), gastropods (*Straparollus plummeri*), and nautilid (*Metacoceras cavatiforme*: Condon Collection locality UO12482). The Ames coal beneath the limestone was not exposed during this fieldwork on May 10, 2007. Limestone and coal (Histosols) represent the humid paleoclimate part of cyclothems in rocks of comparable age in Ohio, and are interbedded

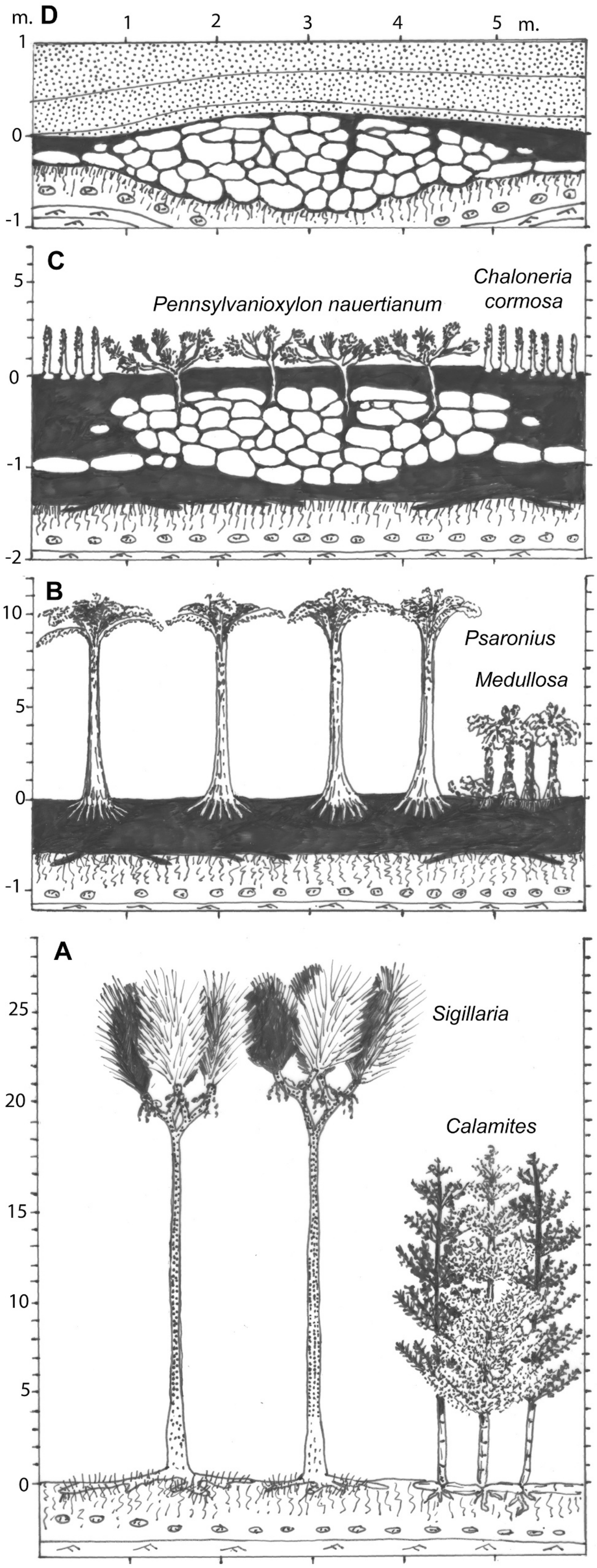

Fig. 10. Reconstructed changes in soils and vegetation during formation of the coal balls at Steubenville, Ohio. Successive stages are (A) *Sigillaria* forest on Aquept; (B) *Psaronius* swamp on Fibrist; (C) mosaic of *Pennsylvanioxylon* carr and *Chaloneria* fen on methanogenic Fibrist; (D) burial and compaction.

with drier-climate, calcareous Aridisols (Retallack, 1994; Martino, 2004).

6. Other coal ball occurrences

6.1. Carboniferous Penistone, Yorkshire

The Alton Coal of the Lower Coal Measures, in Bullhouse quarry, near Penistone, Yorkshire (Curtis et al., 1986), is Westphalian A in age (Percival, 1986) or about 317 Ma (Ogg et al., 2016). The coal is 1.5 m thick below the Alton marine band with the ammonoid *Gastrioceras listeri*, and contains dolomite and calcite coal balls rimmed by pyrite. The coal is underlain by the 1-m-thick Sheffield Blue Ganister, which is a paleosol albic A horizon, with well preserved carbonaceous stigmarian roots (Percival, 1986). There is clayey material below the ganister, but it is separated by a disconformity, so not part of an Ultisol paleosol. The $\delta^{18}O$ and $\delta^{13}C$ isotopic composition of the calcite and dolomite coal balls, as well as siderite nodules in overlying shales, were provided by Curtis et al. (1986), and show two distinct patterns (Fig. 6A–B). The calcite-dolomite shows a $\delta^{18}O$ and $\delta^{13}C$ correlation, with two distinct populations, like the Hitchcox limey peat (Fig. 6A), but the siderite shows $\delta^{18}O$-invariance, like modern siderite nodules (Moore et al., 1992). Dolomite rather than calcite is favored by anaerobic microbial consortia (Kenward et al., 2009). Galactose and rhamnose catalytic for dolomite are produced mainly by decay of extracellular polysaccharides of methanogens, fermenting bacteria and sulfur reducing bacteria, whereas glucose and mannose catalytic for calcite are produced as part of extracellular polysaccharides by cyanobacteria, among others (Zhang et al., 2012).

6.2. Paleocene, Sutton, Alaska

Fossil wood permineralized by carbonate has been reported from the Paleocene (54 Ma) Chickaloon Formation near Sutton, southeast Alaska (Williams et al., 2010). The wood consisted of prone logs and erect stumps in the base of coal seams of high volatile bituminous coal (Merritt, 1990). Despite this high coal rank, the histology of the wood is preserved by fully inflated cell lumens filled with calcite, ankerite, and siderite, allowing assignment to the conifer form genus *Taxodioxylon* (Williams et al., 2010). The stumps and logs retain bark on the outside, and are only partly rounded into nodules by carbonate overgrowth, so may not be true coal balls which preserve plant fragments of varied size.

6.3. Eocene Axel Heiberg Island, Nunavut

Fossil wood of *Metasequoia* permineralized by calcite has been found in lignites of the White Mountain locality of the Eocene (45 Ma) Buchanan Lake Formation of Axel Heiberg Island (Jahren, 2007). As for the permineralized wood from Sutton Alaska (Williams et al., 2010), these logs and stumps are not nodularized like coal balls. Their $\delta^{18}O$ and $\delta^{13}C$ isotopic composition is $\delta^{18}O$-invariant, but unusually heavy for $\delta^{13}C$ (+4.0 to +7.4‰: Fig. 6B) compatible with oxidation from methane (eq. 4) derived from acetoclastic methanogenesis (Jahren et al., 2004).

6.4. Pleistocene Konya, Turkey

Authigenic carbonate nodules and ostracods were found in peat at depths of 654–833 cm, dated at between 36 and 45 ka, in Pinarbaşi core, 55 km south east of Konya, within an intramontane lake basin (Leng et al., 1999). The studied core is on a low ridge between a spring-fed karstic lake, and a saline lake deeper within the intramontane basin. The dark brown humified peat overlies 43 cm of brown claystone (paleosol?), and has 50–80% calcite throughout, including authigenic micrite, aquatic molluscs (*Valvata* and *Gyraulus*) and ostracods (*Prionocypris*: Leng et al., 1999). Carbonate $\delta^{18}O$ and $\delta^{13}C$ isotopic composition within the peat is $\delta^{18}O$-invariant (Fig. 6B), as is common for coal balls (Scott et al., 1996, 1997).

6.5. Holocene Gramigne di Bando, Italy

A burning peat site on a reclaimed coastal lagoon 15 km west of the Adriatic Sea and 6 km north of Gramigne di Bando, is in an unusual geological situation, supplied by active faults tapping natural gas from Miocene rocks at depths of up to 4 km. The peat burned in classical times, and intermittently since, for example over an area of 8 ha for 3 months in 2006. The peat has been radiocarbon dated at increasing depths as 2045 ± 35 years, 3960 ± 40, and 10,800 ± 10 years, and the carbonate nodules within the peats at 7930 ± 55 years. The peats are up to 1 m thick, but calcite nodules 5–10 cm diameter in the upper 20 cm are clustered, and partly amalgamated, in areas 1–2 m wide. Some nodules have the odd shape of a mushroom, and also include tubes after freshwater reed stems (Cremonini et al., 2008).

7. Two microbiome models for coal balls

Precipitation of calcite in soils at thermodynamic equilibrium and pH less than 9 occurs when the activity of calcite (a_{CaCO3}) reaches 1 (Drever, 1982), from values as low as 0 (eq. 1).

$$a_{CaCO_3} = \frac{4(m_{Ca^{2+}})^3}{pCO_2}\lfloor\frac{K_2}{K_1 K_{cal} K_{CO_2}}\rfloor \quad (1)$$

Controls on calcite precipitation include concentration of calcium ions in aqueous solution ($m_{Ca^{2+}}$), partial pressure of CO_2 in soil gas (pCO_2), and temperature sensitive equilibrium constants for dissociation of carbonic acid (K_1), for dissociation of bicarbonate (K_2), for dissociation of calcite (K_{cal}), and for hydration of CO_2 (K_{CO_2}). The K terms increase with temperature, so that calcite more readily precipitates at higher temperatures, as well as with increase in the concentration of Ca^{2+} in soil solution, a decrease in pCO_2 of soil gas, or an increase in bicarbonate in soil solution. Soil water Ca^{2+} is usually low and invariant in peaty soils whose main source of it is dust (Le Roux et al., 2006), but coal balls are commonly associated with ostracods, snails, and marine carbonate storm debris, or underlying limestone (Rothwell, 1988; Scott et al., 1996). Temperature controls are responsible for late summer precipitation of calcite in aridland soils (Breecker et al., 2009), especially in summer dry (Mediterranean) climates, and waterlogged soils such as Histosols can also have significant temperature variation though the year (Bridgham et al., 1999). In both cases, average temperatures over the several thousands of years of Histosol and Aridosol formation are likely to have been similar for each particular paleosol.

This leaves two remaining controls of soil CO_2 gas and soil water bicarbonate that may explain the two distinct isotopic systems of coal balls (Fig. 9A–B). Calcite and dolomite can be precipitated from an increase in bicarbonate within soil water, which can be achieved through hydrolysis of minerals such as olivine (eq. 2; Köhler et al., 2010), fermentative respiration of sugar (eq. 3: Thauer et al., 1977), or anaerobic oxidation of methanogenic methane (eq. 4; Knittel and Boetius, 2009). Laboratory experiments demonstrate that carbonate precipitation in anaerobic communities of methanogens, archaea and bacteria are not merely due to inorganic solution chemistry, but enabled by binding to cell walls and extra-cellular polysaccharides (Roberts et al., 2004; Kenward et al., 2009).

$$Mg_2SiO_4 + 4CO_2 + 4H_2O \rightleftharpoons 2Mg^{2+} + 4HCO_3^- + H_4SiO_4 \quad (2)$$

$$C_6H_{12}O_6 + 4H_2O \rightarrow 2CH_3COO^- + 2HCO3^- + 4H+ + 4H_2 \quad (3)$$

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \quad (4)$$

These are all anaerobic mechanisms for bicarbonate production with potential for high fidelity preservation of organic cell structure (Retallack, 1984). Weatherable silicate minerals are uncommon in peats and coals (Le Roux et al., 2006), including all those considered here (Stephens, 1943; de Maris et al., 1983). However, plant-derived sugars fuel methane production by methanogens in peats (Bridgham et al., 1999). Methanogenic carbon is unusually isotopically light, ranging from −29 to −85‰ $\delta^{13}C$ (Schidlowski, 2001), and is very likely for coal balls with extremely negative $\delta^{13}C$ isotopic composition (Fig. 9B). Similar involvement of methanogens in precipitation of sphaerosiderite in waterlogged soils has also been proposed (Ludvigson et al., 2013). Unusually enriched $\delta^{13}C$ values of siderite nodules (Curtis et al., 1986; Moore et al., 1992), and calcite permineralized wood (Jahren et al., 2004), may also be due to such extreme fractionation of methanogens. In these anaerobic settings the carbon is biogenic, but the oxygen is controlled by local hydrological conditions, and so invariant within a single profile (Aiello et al., 2001). These vertical arrays in $\delta^{18}O$-$\delta^{13}C$ space (Fig. 9B), have long been used for inferring paleotemperatures from pedogenic sphaerosiderite of gleyed paleosols (Ludvigson et al., 2013). This $\delta^{18}O$ invariant isotopic system for carbonates in Histosols can thus be called methanogenic carbonate, formed by a microbiome emphasizing anaerobic fermentation (Thauer et al., 1977) and methanogenesis (Knittel and Boetius, 2009).

In contrast, calcite precipitation can also involve soil CO_2 gas derived from microbial aerobic respiration of organic matter, and this can be called respirogenic carbonate. Strong covariance of $\delta^{18}O$ and $\delta^{13}C$ in coal balls is like that found in well drained Aridosols (Retallack, 2016) and a few Histosols (Fig. 9A). These isotopes are not independent, but selected simultaneously from light isotopologues of CO_2 gas. These isotopologues are locked into carbonate when respired soil CO_2 drops at the onset of the unproductive winter season, and thus soil water acidity also drops (Breecker et al., 2009). Calcite can also be precipitated by soil CO_2 lowering as it escapes through hollow aerenchymatous roots (Breecker and Royer, 2019), but not all coal balls have large hollow roots, especially after the mid-Pennsylvanian replacement of swamp lycopsids with tree ferns (Phillips, 1981; Phillips et al., 1985), and swamp lycopsid extinction after the Late Permian mass extinction (Stephens, 1943; Retallack et al., 1996; Jahren et al., 2004). Strong covariance of $\delta^{18}O$ and $\delta^{13}C$ values is also found in cellulose and other organic matter fractionated by Rubisco or carbonic anhydrase enzymes and stomatal resistance acting on different isotopologues of gaseous CO_2 (Ehleringer and Cook, 1998; Ehleringer et al., 2000; Chen et al., 2018). Decay of this organic matter by aerobic microbial and microfaunal respiration (eq. 5: Kader and Saltveit, 2002) without significant isotopic fractionation gives soil CO_2 with highly correlated $\delta^{18}O$ and $\delta^{13}C$ fixed in pedogenic carbonate of well drained soils (Monger et al., 1991; Retallack, 2016). Aerobic, respiring, soil microbiomes of cyanobacteria, fungi and lichens also promote carbonate precipitation by binding to cell walls (Monger et al., 1991) and catalysis by calcium oxalate pruina of whewellite and weddellite (Verrecchia et al., 1993; Giordani et al., 2003; Vítek et al., 2013).

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \quad (5)$$

Atmospheric CO_2 gas also diffuses down into the soil to be incorporated in pedogenic carbonate (Breecker and Retallack, 2014), and this soil diffusion is the basis for a widely used CO_2 paleobarometer based on the isotopic composition of pedogenic carbonate (Cerling, 1991). The slope of the correlation in cellulose and pedogenic carbonate is known to be related to vapor pressure deficit during the dry season (Barbour and Farquhar, 2000; Barbour et al., 2002). This distinctive correlation is diagnostic of pedogenic, as opposed to marine carbonate (Fig. 9). A similar correlation, though less statistically significant, can be seen in marine carbonate altered by meteoric weathering. These karst carbonates can be deeply altered as demonstrated by marine limestones of tropical islands altered by weathering during sea level lowstands of the last glacial (Lohmann, 1988; Melim et al., 2004). The position in $\delta^{18}O$-$\delta^{13}C$ space of analyzed carbonates is determined by oxygen in local water, and particularly its temperature (Romanek et al., 1992), and by carbon from the proportion of C3, C4, or CAM plants (Cerling et al., 1989; Still et al., 2003). It is not the position within the crossplot that is at issue for Fig. 6, but the tightness of correlation of variance, if any, and whether it is vertical as in methanogenic carbonate or sloping as in respirogenic carbonate. Local water values vary due to adjustment with seasonal microbial production of aqueous HCO_3^- and gaseous CO_2.

8. Conclusions

The geological setting of Holocene coal balls of the Hitchcox limey peat soil, from Eight Mile Swamp of South Australia (Figs. 1–5) lends some support for all previous theories of coal ball formation: (1) intrusion of marine influenced water and carbonate cements into coastal peat swamps (Stopes and Watson, 1909; Evans and Amos, 1961; DeMaris et al., 1983); (2) physical transport of marine limestone into coastal swamps by large storms (Mamay and Yochelson, 1962), (3) flushing with meteoric water after peat accumulation (Anderson et al., 1980), or (4) sinking of meteoric ombrotophic peats into saline and alkaline groundwater intrusion (Spicer, 1989). For the Hitchcox limey peat soil acidity is limited by subhumid, summer-dry climate (Bureau of Meteorology, 2019), limestone bedrock (Stephens, 1943), hard water from an unconfined aquifer in limestone (Grimes, 1994), subsurface seawater intrusion (Morgan and Werner, 2015), and a low-phenol sedge-grass plant community (Eardley, 1943). These climatic and local factors also apply to many Pennsylvanian coal balls in cyclothems with alternating Histosols and Aridisols (Retallack, 1994; Schutter and Heckel, 1985; de Wet et al., 1997; Martino, 2004). Vegetation acidity may explain the rarity of post-Permian coal balls, because a long-term increase of insect-suppressant acidic phenols is also apparent from the fossil record of podzolization and Spodosols (Retallack, 1997).

While much attention has been paid to paleogeomorphic setting of coal balls, this study suggests a local role for the microbiome of peaty soils. Two distinct kinds of isotopic systems are seen in coal balls of Pennsylvanian to Holocene age and reflect two physiologically distinct soil microbiomes. Respirogenic coal ball paleosols have arrays of calcite $\delta^{18}O$ and $\delta^{13}C$ like those of desert soil calcic horizons reflecting isotopic composition of CO_2 gas from an aerobic microbiome in well drained soils. Methanogenic calcite coal balls in contrast have invariant $\delta^{18}O$ for a range of $\delta^{13}C$, and reflect anaerobic microbiomes creating bicarbonate in solution from anaerobic microbial methane oxidation and sugar fermentation.

Declaration of Competing Interest

This is to confirm that I, Gregory J. Retallack, have no conflict of interest in researching and publishing the attached research manuscript "Modern analogs reveal the origin of Carboniferous coal balls".

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