

surface, particle degradation rates, and physical mixing processes. In addition to particulate removal and regeneration, selenium can also undergo oxidation-reduction reactions, which transform it from one dissolved species to another or to insoluble forms such as elemental selenium or metal selenides (this may be the mechanism that removes selenate and selenite from the anoxic zone).

The data in Fig. 2 provide insight into the particulate and species interconversion processes affecting the distributions of selenium species. These data are from an experiment on the regeneration of selenium from two types of marine particulate matter, zooplankton and source term material (fresh biogenic particles produced by these zooplankton). The collection and handling procedures for both the zooplankton and source term material have been detailed in (13). Organic selenide is rapidly and primarily released during biodegradation, selenite begins to increase during the time of the experiment, and no selenate is produced during this time (Fig. 2).

These data suggest that at least some of the selenium in biogenic matter undergoes a multistep regeneration. The significance of this idea for the Saanich Inlet data is that each of the species produced has its own thermodynamic and kinetic stability. Dissolved organic selenide would be most stable under anoxic conditions, and perhaps the regeneration would only proceed to this step. Correspondingly, the production of selenite and selenate by the oxidation of organic selenide might be the final regeneration step in oxic waters. This scenario would also necessitate that selenium's uptake into biological particulate material include an oxidation state change (that is, reductive incorporation). The exact nature of the biogeochemical cycle of selenium, and the determination of whether the cycle includes some of these features, remains to be elucidated.

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Organic Matter in a Coal Ball: Peat or Coal?

Abstract. *Chemical analyses of morphologically preserved organic matter in a Carboniferous coal ball reveal that the material is coalified to a rank approximately equal to that of the surrounding coal. Hence, the plant tissues in the coal ball were chemically altered by coalification processes and were not preserved as peat.*

During the Carboniferous and Permian periods, extensive deposits of peat accumulated and were later transformed to coal. Early in their development, some of these peat deposits were impregnated with pore fluids from which primarily calcium carbonate was precipitated. The calcium carbonate permineralized some of the peat, leading to the formation of the carbonate nodules now known as carbonate coal balls. The mineral also preserved the morphological characteristics of some of the plant remains, providing paleobotanists with an insight into the anatomy of vascular plants in the late Paleozoic (1).

Most carbonate coal balls contain 1 to 5 percent organic matter (1) which has a brownish, cellular appearance similar to that of some Holocene peat. Consequently, this organic matter commonly has been called "fossil peat" (2). Although the organic matter in coal balls generally is thought to have been altered chemically (3), some have argued that the material was preserved as peat and is, therefore, lignocellulosic in nature (4). Baxter (5) claimed to have identified microscopic "starch grains" in a coal ball, implying that the starch was chemi-

cally preserved even though chemical tests for starch were negative.

Clearly, the chemical character of organic matter in coal balls has not been resolved, and uncertainty exists as to whether this material is peat or coal. We now report the results of an investigation that conclusively identifies the chemical composition of organic matter entombed in a carbonate coal ball. In our study we also examined the relation between the organic constituents of the coal ball and the coal from which it was taken.

We selected the petrified stem of a medullosan seed fern in a coal ball from the Herrin (No. 6) Coal Member of the Carbondale Formation (Middle Pennsylvanian) in Illinois (6). Xylem, sclerenchyma, resin rodlets associated with sclerenchyma, and parenchymal tissues were isolated from residue that remained after the stem was treated with 2*N* aqueous hydrochloric acid to remove the carbonate matrix. These and small fragments of the coal attached to the outer rim of the coal ball were subjected to petrographic, elemental (C, H, N, and O), and solid-state ¹³C nuclear magnetic resonance (NMR) analyses.

A small fraction that settled rapidly in the aqueous acidic medium consisted mostly of pyrite grains and woody splinters—mainly xylem tissue—impregnated with pyrite. The amount of organic matter recovered in this fraction was insufficient for complete chemical analysis; therefore, its chemical composition is not addressed. Much of the residue from the acid treatment was flocculent and settled more slowly. This fraction, hereafter termed the fine cellular fraction, consisted of parenchyma, xylem, and unidentified organic matter. A few fragments of brownish thick-walled tissue with a honeycomb appearance (probably sclerenchyma), brownish angular fragments derived from the stem, and unidentified sporelike bodies were present

Table 1. Elemental composition of each sample on a dry, ash-free basis. Compositions were determined with a Carlo Erba C, H, N, O, and S analyzer.

Sample	Composition (percentage by weight)			
	C	H	N	O
Cellulose	44.4	6.2		49.4
Cypress log (Holocene)	50.2	6.1	0.17	43.5
Periodate lignin	63.0	6.1		30.9
Lignitic log (Oligocene)	70.0	4.3	0.34	28.3
Fine cellular fraction	75.3	5.5	1.2	18.1
Herrin coal	76.4	5.1	1.4	15.5

in the fine cellular fraction. In transmitted-light microscopy this fraction was brown to dark brown and resembled degraded and partly degraded fragments of plant debris commonly observed in peat. Such observations were reported by Schopf (4), who assumed that the material was chemically similar to peat.

Reflected-light microscopy of the individual plant parts in thin section and in polished blocks revealed that the mean random reflectance of the woody splinters ranged from 0.44 to 0.58 percent; the resin rodlets had reflectances from 0.50 to 0.65 percent and the strands of sclerenchyma had reflectances from 0.35 to 0.74 percent. The reflectance of a vitrinite grain isolated from the stem was 0.70 percent. This value is directly comparable to a reflectance of 0.66 percent for vitrinite in coal attached to the outer rim of the coal ball. These vitrinite reflectances are similar to those of a high volatile C bituminous coal. Teichmüller (3) noted that coal balls from Carboniferous coal in Germany contain vitrinite with a mean average reflectance comparable to that of vitrinite in the surrounding coal. This suggests that some of the organic matter in her coal balls was coalified. Teichmüller's observations and the common presence of fusinitized woody splinters in American coal and coal balls indicate that some of the organic matter in coal balls is coalified; however, we are unaware of any direct chemical evidence that conclusively shows that all the coal ball material is coal rather than peat.

Elemental analyses have been used for many years to differentiate coal from peat (7). Recently, ^{13}C NMR for solids was successfully applied to the study of coal and the coalification process, and this technique is capable of clearly distinguishing peat from coal (8). Theoretical considerations and numerous analyses show that coal has a chemical composition different from that of its precursors, namely, the remains of vascular plants in peat. These analyses show that vascular plants and peat contain significant quantities of carbohydrates (principally cellulose) and lignin, both of which are highly oxygenated organic compounds that impart a relatively high proportion of elemental oxygen or functionalized carbons to peat (7). The analyses also show that, in most cases, coal is devoid of carbohydrates and lignin, presumably because these substances do not survive the diagenetic transformations that peat undergoes to form coal.

Figure 1 shows the elemental compositions and ^{13}C NMR spectra for cellulose, periodate lignin, a cypress log that was

buried in peat in the Okefenokee Swamp, a lignitic log from Hungary, the fine cellular fraction from the medullosan stem, and a sample of coal (Herrin No. 6) that was attached to the coal ball in the immediate vicinity of the stem. The NMR spectrum for the fine cellular fraction is characterized by two major broad peaks, one centered at 130 ppm and the other at 37 ppm. The peak spanning the region 100 to 160 ppm represents aromatic carbons and the peak spanning 0 to 50 ppm represents paraffinic carbons. Such broad unresolved spectra, especially those which have a predominantly aromatic component, are characteristic of most banded coals having a rank higher than that of lignite (8). The spectrum for the sample from the

Herrin Coal Member (Fig. 1f) is nearly identical to that for the fine cellular fraction.

The spectrum for cellulose (Fig. 1a) has peaks at 65, 72, 85, and 106 ppm that identify the oxygen-substituted carbons of cellulose (9). The spectrum for the cypress log from the Okefenokee Swamp (Fig. 1b) has peaks indicating that this log is composed primarily of cellulose and of other carbohydrates that would also show peaks in this region of the spectrum. The spectrum for lignin (Fig. 1c) is characterized by peaks for aromatic carbons (120, 130, and 150 ppm) and an intense peak at 57 ppm for methoxyl carbons (10). There are similar peaks in the spectrum for the cypress log (Fig. 1b). The NMR spectra for logs coalified to lignite, subbituminous coal, and bituminous coal show the complete loss of peaks for cellulose (8). Lignin, the precursor of aromatic carbons in coalified logs, is also altered significantly, losing the peaks at 150 and 57 ppm that are characteristic of oxygenated carbons. Such changes in the lignin occur gradually, as evidenced by wood coalified to the rank of high volatile C bituminous coal. This coalified wood shows minor shoulders instead of peaks at 150 and 57 ppm in the NMR spectra. The spectra for the fine cellular fraction from the coal ball stem and for the coal attached to the coal ball show that the material in the coal ball contains no cellulose or lignin.

The degree of coalification of the stem can be determined by comparing its NMR spectrum with spectra for coalified logs. The spectrum for the lignitic log (Fig. 1d) is characteristic of coalified wood intermediate in rank between the cypress log (Fig. 1b) and the logs of high volatile bituminous rank. Note the presence of peaks at 150 and 57 ppm. Such peaks, which are typical of lignin, are not present in the spectrum for the fine cellular fraction, suggesting that the stem was coalified to a rank greater than that of lignite. The NMR spectra of coalified logs of subbituminous rank also show a peak at 150 ppm that disappears in coalified logs of bituminous rank (8). Thus, the absence of this peak in the spectrum for the fine cellular fraction indicates that the stem was coalified beyond the rank of subbituminous coal.

The elemental composition of the fine cellular fraction substantiates conclusions drawn from the NMR data, as it is similar to the elemental composition of the coal attached to the coal ball (Table 1). The carbon content of the fine cellular fraction (75.3 percent) is as high as that of the Herrin coal. The hydrogen content (5.5 percent) and the oxygen

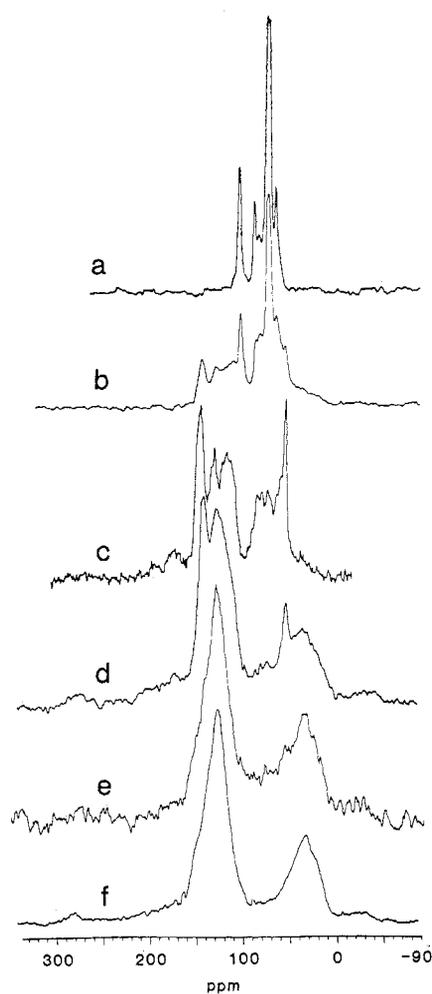


Fig. 1. Solid-state ^{13}C NMR spectra and elemental compositions of (a) cellulose; (b) a cypress log buried in the Okefenokee Swamp (collected by C. B. Cecil); (c) periodate spruce lignin (10); (d) a coalified log, lignite in rank, from the Bakony Mountains, Hungary (collected by P. Zubovic); (e) the fine cellular fraction recovered from the medullosan stem in the coal ball; and (f) the Herrin (No. 6) coal attached to the coal ball. All NMR spectra were obtained at a field strength of 1.4 T by the technique of cross-polarization and magic angle spinning (8). W. L. Earl provided the spectra in (a) and (c).

content (18.1 percent) of the cellular fraction are as low as those of the Herrin coal but lower than the hydrogen and oxygen contents of cellulose, the cypress log, and lignin. Even though the hydrogen content of the lignitic log is similar to that of the fine cellular fraction from the medullosan stem, the lower carbon content (70.0 percent) and higher oxygen content (28.3 percent) of the log clearly indicate that it is not as coalified. The elemental composition of the coal ball fraction indicates that the stem has approximately the same rank as a high volatile C bituminous coal, or the same rank as the Herrin coal from the area where the coal ball was collected (11).

All the data on the coal ball stem indicate that the organic matter is coalified to a rank equivalent or nearly equivalent to that of coal outside the coal ball. This leads us to an important point concerning the effect of compactional pressure in coalification. In coal balls the organic matter was entombed at an early peat stage and generally is uncompressed (1). Furthermore, once entombed, such coal ball peat was protected from the effects of pressure; the surrounding peat underwent compaction in a manner characteristic of normal coalification. Thus this study suggests that compaction has little, if any, effect on the chemical processes involved in coalification of medullosan plant tissues up to the rank of high volatile C bituminous coal.

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Remote Acoustic Detection of a Turbidity Current Surge

Abstract. A turbidity current surge has been detected in a leveed submarine channel in Rupert Inlet, British Columbia, with the use of acoustic sounders operating at 42.5, 107, and 200 kilohertz.

It is generally believed that turbidity currents have been responsible for the formation of submarine canyons and their associated deep-sea fans and fan channels (1). Yet there have been very few real-time observations of turbidity current surges, and this has led Normark (2), among others, to point out the absence of empirical constraints on the existing theory. We report the detection of a surge-type turbidity current in water depths of 130 to 140 m, using acoustic sounders operating at 42.5, 107, and 200 kHz with transducers mounted in the hull of a surface vessel. The event was detected during a thesis study by one of us (A.E.H.) of turbidity currents and submarine channels resulting from the discharge of mine tailing into Rupert Inlet, British Columbia. To our knowledge, the results presented here are the first of their kind.

The bathymetry in Rupert Inlet in November 1976 is shown in Fig. 1. The leveed submarine channel is evident and is shown extending from the point of discharge (outfall) across- and then down-inlet. The channel exhibits in sequence a left-hooking upper reach, a meandering middle reach, and a relatively straight lower reach, as the axial slope decreases with increasing distance from the outfall. Also shown in Fig. 1 is the echo-sounding transect (line T-T') corresponding to the acoustic records in Fig. 2. These records were obtained with a 200-kHz Ross Laboratories model 200 fine-line recorder on the Canadian Survey Ship *Vector* on 26 August 1976 during four successive repetitions of the transect in opposite directions. The first and second transects were part of a bathymetric survey. Repeated crossings were made after the event was detected.

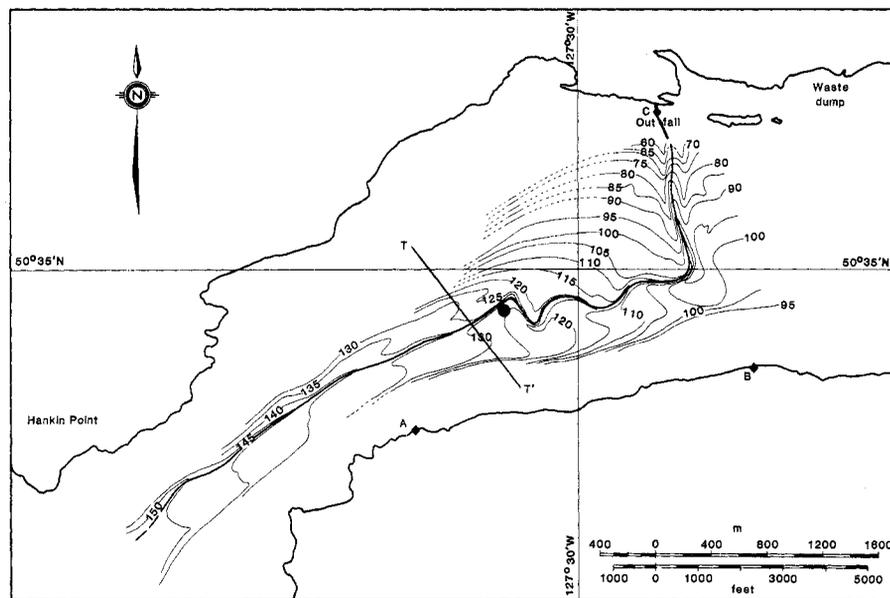


Fig. 1. Rupert Inlet bathymetry in November 1976. Contours are in meters. The circle indicates the approximate location of the August 1976 current meter mooring, and the line T-T' marks the position of the sounding transect corresponding to the records in Figs. 2 and 3; A, B, and C denote the locations of microwave positioning transponders.