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Petrographic and Chemical Properties of Carboniferous Resinite from the Herrin No. 6 Coal Seam

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Abstract

Resinite is a naturally occurring substance found in coal and derived from original plant resins. It is ubiquitous in North American coals and comprises 1 to 4% by volume of most Illinois coals. It has been commercially exploited in the western USA for use in adhesives, varnishes and thermal-setting inks. The major objectives of this study were: (1) to separate resinite macerals from the Herrin No. 6 coal seam and to carefully verify, by petrographic and fluorescence microspectrophotometric methods, that the separated material was indeed resinite; (2) to characterize the chemical composition of the separated resinite by Py–GC–MS techniques; and (3) to confirm the earlier results that show that this Carboniferous resinite was a much different chemical substance than the Cretaceous and younger resinites. An additional objective was to compare the separated resinite to the resinite being commercially exploited in the western USA. High purity fractions of resinite concentrates were separated from the Herrin No. 6 coal by a combination of density gradient separation and sink–float techniques. The chemical structure of the resinite concentrate indicated by the Py–GC–MS analysis is that of a straight chain aliphatic polymer much like common polyethylene. This result confirms the earlier work of Nip et al. [Nip, M. de Leeuw, J.W., Crelling, J.C., 1992. Chemical structure of bituminous coal and its constituent maceral fractions as revealed by flash pyrolysis, Energy Fuels 6, 125–136.]. The assumption that the resinites in the Illinois basin were similar in nature to the commercial resinites of the younger coals of the western USA appears invalid in the case of the resinite in the Herrin No. 6 coal. Although the botanical function of the Carboniferous resinite is at present unclear, it is clear that the cutinite and resinite precursors had not yet evolved to the point where they had differentiated into significantly different chemical compounds.

Keywords: coal; macerals; density gradient centrifugation; resinite; pyrolysis

1. Introduction and background

Resinite is a naturally occurring substance found in coal and is derived from resins in the original plants that were the precursors of the coal. Resinite is ubiquitous in North American coals. It is particularly abundant in some western USA coals; consequently, much of the published literature deals with these western resinites. Resinite in Utah coals has been reported by White (1914), Spieker and Baker (1928), Tomlinson (1932), Selvig (1945) and Buranek and Crawford (1952). The latter authors noted concentrations of resinite varying from trace amounts to 14.9% by volume. It has been frequently observed that the resinite in the western coals of Cretaceous and Tertiary age tends to commonly occur in cleats and fissures where it is observable megascopically (Buranek and Crawford, 1952; Crelling, 1995). Cleat and fissure-filling resinite in coals from England has been reported by Jones and

Murchison (1963) and by Murchison and Jones (1964). They conclude that the increased temperature and pressure of coalification in the bituminous range was sufficient to gently mobilize some of the resinite macerals to coalesce into globules and veins without increasing the reflectance or causing vesiculation of the resinite. On the basis of infrared spectral properties and carbonization behavior, Murchison (1966) was able to divide the resinite macerals into two types—one type occurring only in coals of sub-bituminous rank or lower and the other type occurring in bituminous coals. Murchison (1976) also noted that much of the resinite in bituminous coals occurred as interconnected globules and veins and he concluded that this was of secondary origin. Other petrographic work on resinites of the western USA has been reported by Crelling (1982), Crelling et al. (1982) and Teerman et al. (1987). Fusinized or charred resinites observed petrographically in a rod-like form (rodlets) have been reported in Illinois coals by Kosanke and Harrison (1957) and elsewhere by Lyons et al. (1984).

When resinite occurs as megascopic lumps suitable for jewelry, it is called amber (Anderson, 1996), and good summaries of the occurrence, botany, and chemistry of amber are found in Langenheim (1969, 1990). Recent work on the chemistry of resinites has been reported by Brackman et al. (1984), Simoneit et al. (1985), Crelling et al. (1991), Meuzelaar et al. (1991), Anderson (1995) and Anderson and Crelling (1995). This latter work gives a comprehensive chemical classification of resinites.

The availability of maceral group fractions and single maceral fractions has led to a rapid and broad expansion of our knowledge of maceral properties. The first elemental analyses of high quality DGC maceral group and single vitrinite maceral fractions were reported by Dyrkacz et al. (1984a,b,c) and additional analyses were also reported by Karas et al. (1985. and Winans et al. (1986). In general, this work has shown that there are distinct chemical differences between the maceral groups and the individual macerals, as well as a corresponding change with density. For example, in macerals from the same coal sample, the liptinite macerals have the highest hydrogen contents and the inertinite macerals the lowest; both groups have high carbon contents, while vitrinite has the lowest carbon; both H and H/C decrease with density. Separated macerals and maceral groups have been analyzed with a variety of analytical techniques, especially FTIR, gas chromatography, mass spectrometry, gas chromatography–mass spectrometry and ^{13}C NMR spectroscopy. In a study on liptinite macerals by Crelling (1987), resinite from an Illinois basin coal, the Brazil Block seam, showed that resinite could be concentrated by density gradient centrifugation methods. It had an apparent density in aqueous CsCl of 1.11 g/ml which was between cutinite (1.08) and sporinite (1.17). The petrographic properties and bulk (elemental) chemistry were also intermediate between those of cutinite and sporinite. Analyses of hundreds of coal samples from all parts of the Illinois basin (Harvey et al., 1979) showed a resinite content from less than 1% to more than 4% by volume.

Although it is generally assumed that all macerals of the same type (for example, sporinite, vitrinite and fusinite) found in coals of the same rank are similar materials, there is some evidence that this assumption may not be valid in the case of resinites. Most of the published chemical studies of resinites mentioned above show them to have a terpenoid structure. However, the samples analyzed were all of Cretaceous age or younger. Two studies dealing with resinites separated from Carboniferous coals suggest that these macerals may indeed have a different chemical structure. Nip et al. (1992) studied the various macerals including resinite separated from an Upper Carboniferous coal from Parke County, Indiana, USA. The results of their Curie point pyrolysis–gas chromatography/mass spectrometry (Py–GC–MS) analysis on the separated resinite indicated a distribution of normal hydrocarbons much like that observed in the pyrolyzate of the cutinite separated from the same. Similarly, Collinson et al. (1994) found the pyrolyzate of a sample of resin rodlets of Upper

Carboniferous age from Indiana, USA to also contain a homologous series of *n*-alk-1-enes and *n*-alkanes. The resin rodlet pyrogram also showed an abundance of phenolic compounds that are consistent with the presence of admixed vitrinite, suggesting an incomplete separation of the resinite. However, the resinite concentrate sample of Nip et al. (1992., with the unexpected chemical composition, was prepared at the Maceral Separation Laboratory of Southern Illinois University by density gradient separation techniques and was petrographically verified as being resinite.

The major objectives of this study were: (1) to separate resinite macerals from the Herrin No. 6 coal seam and to carefully verify, by petrographic and fluorescence microspectrophotometric methods, that the separated material was indeed resinite; (2) to characterize the chemical composition of the separated resinite by Py–GC–MS techniques; and (3) to confirm the results of Nip et al. (1992) and, thus, test the hypothesis that this Carboniferous resinite was in fact a much different chemical substance than the Cretaceous and younger resinites. An additional objective was to compare the separated resinite to the resinite being commercially exploited in the western USA to evaluate its economic potential.

2. Experimental procedures

The main sample used in this study was from the Herrin No. 6 seam sample (101) from Illinois Basin Coal Sample Program (IBCSP), which had the highest resinite content (2.9% by volume) of all of the samples in the program's collection. The results of proximate analysis of this sample are: moisture = 14.1%, volatile matter = 44.1%, ash = 10.3% and fixed carbon = 45.6. The results of ultimate analysis of this sample are: carbon = 67.7%, hydrogen = 4.9%, nitrogen = 1.9%, sulfur = 4.3%, chlorine = 0.13% and oxygen = 11.6%. The results of the petrographic analysis of this sample are: vitrinite = 88.3%, sporinite + cutinite = 2.7%, resinite = 2.9%, micrinite = 1.1%, macrinite + sclerotinite = 0.4%, semifusinite = 2.1%, fusinite = 1.3% and inertodetrinite = 1.2%. The mean maximum reflectance (in oil) = 0.46%. All of these results are from Harvey and Kruse (1988).

2.1. Separation of resinite

Because macerals vary in their chemistry and structure, they also vary in their density, and it is this variation that allows them to be separated. However, normal sink–float techniques have had only limited success in separating single macerals. This is mainly because the small particle size (<10 μm) needed to liberate single macerals and minimize multi-maceral particles precludes efficient separation in the sink–float process. Centrifugation is needed and centrifugation at a large number of densities for a single sample is not practical. A solution to this problem is the use of density gradient centrifugation (DGC) in which a sample is centrifuged through a density continuum and then fractionated (Dyrkacz et al., 1981, 1984a,b,c, Dyrkacz and Horwitz, 1982).

In this study, the coal sample was reduced to micron size in a fluid energy mill and then demineralized with HF and HCl. Although the particle size distribution was not determined, the typical particle size observed during petrographic analysis was in the range of 2–5 μm. Many of the largest particles were, indeed, resinite macerals that were liberated from the coal matrix intact at a top size of 50 μm. Two g of the sample were sonicated and put into a 2-l titanium centrifuge vessel that was filled with a continuous aqueous CsCl density gradient ranging from 1.0 to 1.6 g/ml and centrifuged. Brij-35 was used as a wetting agent. After centrifugation, the resulting gradient was pumped through a density meter into a fractionator. The fractions were then washed in distilled water, filtered, dried and weighed.

The density and weight of each fraction was measured and plotted. The resulting density profile accurately reflects the maceral composition of the sample.

Even though the petrographic analysis indicated that the resinite content of the IBCSP 101 sample from the Herrin No. 6 seam was over 2.9% by volume, the resinite proved to be extremely difficult to separate from the original coal. Fig. 1 shows the density profile of the original 2-g sample. Note that the bulk of the sample is at a density greater than 1.20 g/ml which is the density boundary between the lighter liptinite macerals and the heavier vitrinite and inertinite macerals. The initial effort was to concentrate the liptinite maceral fraction from the whole coal sample. This was done in two different ways (Crelling, 1994). One way was to centrifuge 1 g of raw coal sample in a 50-ml tube to float the target liptinite macerals at a density of 1.2 g/ml. Six tubes could be processed with each centrifuge run. The other technique was to use a semi-continuous centrifuge that was capable of handling larger quantities of sample, but at a lower separation efficiency. By the end of these experiments, about 2 kg of the sample had been processed.

The 1.20 g/ml float was then separated in a 2-g DGC run as described above. The resulting fractions were analyzed petrographically. The results of this analysis showed that the resinite occurred in the density range of 1.065–1.165 g/ml with sporinite occurring above 1.165 g/m and cutinite occurring below 1.065 g/ml. Therefore, the 1.20 g/ml float was refloated in a CsCl solution at 1.165 g/ml and the resulting float was floated at 1.065 g/ml. The resulting sample was separated in another DGC run and the petrographic analysis of these DGC fractions showed that the fractions with the highest resinite content were in the density range 1.08–1.14 g/ml (see Fig. 2). The average resinite content, determined by point count methods, in this range was over 90% with the richest fraction containing 98% resinite (see Table 1). This petrographic analysis was done in blue light, under which the fluorescence of the various macerals was used to help with the identification.

2.2.   Characterization of resinite

The separated resinite was characterized with white light and blue light petrographic, fluorescence spectral and Py–GC–MS analyses. The separated concentrates were examined in white light illumination with a Leitz MPV II microscope with an Orthomat W camera. This same microscope was adapted for fluorescence spectral analysis with a 100-W Hg lamp with a BG23 heat filter, a BG 12 Blue excitation filter, a TK 400 dichroic mirror and a K 530 barrier filter. For fluorescence spectral analysis, a UG1 excitation filter and a K 430 barrier filter were used, along with a diode array detector.

Py–GC–MS analyses of the separated macerals were performed using a CDS 120 Pyroprobe, coupled to an HP 5890 gas chromatograph with an HP 5970 mass selective detector and a 50-m HP-1 column (i.d. = 0.2 mm, film thickness = 0.33 μm). A measured amount of dry, powdered maceral concentrate (<0.5 mg) was pyrolyzed in a flow of helium for 20 s in a platinum coil at 610°C, as measured by a thermocouple in the sample holder. The GC oven was operated under the following program: isothermal for 5 min. at 40°C; temperature programmed at 5°C/min to 300°C and then isothermal for 20 min. The MS was operated in full scan mode (50–550 Da, 0.86 scans/s, 70 eV ionization voltage). Compounds were identified based on mass spectra and GC retention indices, with reference to the Wiley and US National Bureau of Standards computerized mass spectral libraries and the literature (Anderson and Winans, 1991; Nip et al., 1992; Stankiewicz et al., 1994; Kruge and Bensley, 1994; Han et al., 1995).

3. Results and discussion

3.1. Petrographic characterization

Extensive petrographic analysis of the separated fractions revealed that the majority of the material in the resinite density range had the structureless ovoid form characteristic of resinite (see Fig. 3). In Fig. 3, photomicrographs of three in situ resinite occurrences are shown in both white light and in blue light (fluorescence mode) illumination. Below each pair of photomicrographs is a photomicrograph of the separated resinite. The similarity of the separated material to the in situ resinite is clear and supports the conclusion that the separated material is resinite. It should be noted that under petrographic examination, sporinite was characterized by its bilateral symmetry and ornamentation and cutinite occurred as linear fragments usually with one flat side and one crenulated side. None of these features were seen in the separated resinite.

To further support the conclusion that the separated material was indeed resinite, fluorescence spectra of both the resinite macerals in the whole coal and the separated material were collected and compared (Table 2). The fluorescence parameters used are the peak (the wavelength of maximum intensity) and Q (the red/green quotient—the intensity at 650 nm / the intensity at 500 nm) and cx and cy (international chromaticity indices). The averages of the spectral parameters from the two sets of samples (Table 3) show that the two sets of samples are very similar indicating that they are from the same maceral, resinite. It is well established that the other liptinite macerals (cutinite and sporinite) in the Herrin No. 6 coal have significantly different spectral parameters (Crelling, 1982). In summary, both the petrographic and fluorescence spectral analysis confirm that the separated material is resinite.

3.2. Chemical characterization

Analysis of the Upper Carboniferous Herrin resinite concentrate by pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) revealed a predominantly aliphatic character. The pyrolyzate was composed almost entirely of straight-chain hydrocarbons, predominantly C_6–C_{31} n-alk-1-enes and n-alkanes, with secondary amounts of n-alk-α,ω-dienes (Fig. 4). Alkylbenzenes and (alkyl)phenols were present in very low relative concentrations. The Herrin resinite pyrolyzates bear a strong resemblance to those of other highly aliphatic macerals, such as cutinite and *Botryococcus*-related alginite and to artificial polyethylene (cf. Nip et al., 1988, 1992; Han et al., 1995). The pyrolysis evidence suggested that the Carboniferous resinite is a fossilized, cross-linked, aliphatic biogeopolymer.

Comparison with the other exinite macerals separated from the same Carboniferous coal sample is instructive. The Herrin cutinite concentrate also produced a predominance of C_6–C_{31} n-alk-1-enes and n-alkanes upon pyrolysis, again with relatively lesser quantities of n-alk-α,ω-dienes and negligible amounts of aromatic and phenolic compounds (Fig. 5), as previously noted for another sample of Carboniferous cutinite (Nip et al., 1989). It differed subtly from the resinite in the relative amounts of individual homologues in its pyrolyzate. For example, the cutinite pyrolyzate showed a slightly more pronounced bimodal distribution (Figs. 4 and 5). Such features imply differences in the structure of the two fossil biogeopolymers, consistent with their distinct petrographic and density characteristics.

The Herrin sporinite pyrolyzate, while still having abundant aliphatic hydrocarbons, had relatively high concentrations of (alkyl)benzenes and (alkyl)phenols (Fig. 6), as has been previously recognized (cf. Nip et al., 1988, 1992; Stankiewicz et al., 1994). This reflects the more aromatic and phenolic structure of the original sporopollenin (Nip et al), 1992. and contrasts markedly with the Herrin resinite and cutinite results (Figs. 4 and 5). Unlike the

resinite and cutinite, thiophenes were readily detectable in the sporinite pyrolyzate (Fig. 6). It was previously observed that of all the macerals in high-sulfur Illinois basin coals, sporinites had the highest absolute concentrations of organic sulfur, as well as the highest relative concentrations of thiophenic sulfur in pyrolyzates (Kruge et al., 1991). The complex structural characteristics of the sporopollenin made the peat component most susceptible to early diagenetic sulfurization.

For purposes of comparison, the resinite concentrate from a sample of the Cretaceous Hiawatha seam coal was also analyzed. Its pyrolyzate was predominantly composed of aromatized and unsaturated cadinanes, as well as cadinane dimers, smaller aromatic molecules and isoprenoid hydrocarbons (Fig. 7). Relatively small amounts of long-chain normal alkanes were detected, likely to be due to thermal desorption. These features are typical of the pyrolyzates of Cretaceous and Cenozoic resinites and are indicative of a polycadinane structure (e.g., van Aarssen et al., 1990, 1991, 1992, 1994). The Cretaceous resinite pyrolyzate stands in sharp contrast to the Carboniferous (Fig. 4). If the Carboniferous resinite and the Cretaceous resinite did indeed have some similarities in botanical function, we could speculate that the wound sealing capability of the two would have been very different. Like modern conifer resins, the Cretaceous resins would have cured to form a tough protective surface over a wound, while the more primitive aliphatic Carboniferous 'resin' would simply have left a waxy film. However, there is petrographic evidence of deformation around resinite bodies that suggests that the resinite was already a hard solid material at the time of its incorporation into the precursor peat.

3.3. Discussion

The separation and characterization research demonstrated that although the resinite in Illinois coals has the classic petrographic properties of resinite, it is not a typical Cretaceous or younger resinite in its chemistry. The chemical structure indicated by the Py–GC–MS analysis is that of a straight-chain aliphatic polymer much like common polyethylene. This work confirms the results of Nip et al. (1992. and Collinson et al. (1994). The assumption that the resinites in the Illinois basin were similar in nature to the commercial resinites of the younger coals of the western USA appears to be invalid in the case of the resinite in the Herrin No. 6 coal. The fact that the Herrin No.6 resinite does not share the chemistry of the western USA resinites also means that it does not share their commercial potential. However, a positive aspect to these results is that they are of considerable scientific interest. The petrographic results of this study and of Crelling (1995) show that the Carboniferous resinites and the primary Cretaceous resinites have the same mode of occurrence and petrographic properties, which suggests that they may also have had the same botanical functions as wound resins. If this assumption is valid, then, in the Carboniferous period, the material that apparently served the botanical functions of both plant cuticle and wound resins had not evolved to the point where they differentiated into significantly different chemical compounds.

4. Conclusions

The major objectives of this study were: (1) to separate resinite macerals from the Herrin No. 6 coal seam and to carefully verify, by petrographic and fluorescence microspectrophotometric methods, that the separated material was indeed resinite; (2) to characterize the chemical composition of the separated resinite by Py–GC–MS techniques; and (3) to confirm the results of Nip et al. (1992) and Collinson et al. (1994), showing that this Carboniferous resinite was a much different chemical substance than the Cretaceous and

younger resinites. An additional objective was to compare the separated resinite to the resinite being commercially exploited in the western USA.

The following are the specific conclusions of this study. (1) High purity resinite concentrates were in fact separated from the Herrin No. 6 coal seam using a combination of DGC and sink–float techniques. (2) The identification of the separated fractions were confirmed as resinite by extensive petrographic analysis and fluorescence spectral analysis. (3) The chemical structure of the resinite concentrate indicated by the Py–GC– MS analysis is that of a straight-chain aliphatic polymer much like common polyethylene. This result confirms the work of Nip et al. (1992) and Collinson et al. (1994). The assumption that the resinites in the Illinois basin were similar in nature to the commercial resinites of the younger coals of the western U.S. appears to be invalid in the case of the resinite in the Herrin No. 6 coal. (4) The petrographic results of this study and of Crelling (1995) show that the Carboniferous resinites and the primary Cretaceous resinites have the same mode of occurrence and petrographic properties which suggest that they may also have had the same botanical functions as wound resins. If this assumption is valid, then, in the Carboniferous period, the material that apparently served the botanical functions of both plant cuticle and wound resins had not evolved to the point where they differentiated into significantly different chemical compounds.

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Table 1. Results of petrographic analysis of resinite-rich density fractions (JCF-Z run 2684).

Fraction	Density (g/ml)	Resinite (vol.%)	Vitrinite (vol.%)	Sporinite (vol.%)	Cutinite (vol.%)
2684-7	1.1553	53	4	18	25
2684-8	1.1474	58	5	14	23
2684-9	1.1386	65	8	10	17
2684-10	1.1298	95	1	3	1
2684-11	1.1220	76	2	5	17
2684-12	1.1133	93	1	3	3
2684-13	1.1057	93	1	3	4
2684-14	1.0969	85	4	3	9
2684-15	1.0876	93	1	2	4
2684-16	1.0781	98	1	1	0

Table 2. Results of fluorescence spectral analysis.

In situ resinite				Separated resinite			
Peak	Q	(CIE) cx	(CIE) cy	Peak	Q	(CIE) cx	(CIE) cy
520	0.61	0.434	0.455	520	0.60	0.433	0.456
520	0.62	0.437	0.451	520	0.57	0.435	0.456
520	0.60	0.432	0.452	520	0.58	0.435	0.455
520	0.59	0.433	0.454	520	0.58	0.433	0.454
530	0.58	0.432	0.453	520	0.60	0.439	0.452
530	0.58	0.429	0.456	520	0.60	0.437	0.454
530	0.60	0.432	0.456	520	0.57	0.435	0.453
520	0.55	0.429	0.455				
530	0.56	0.432	0.456				

Table 3. Average fluorescence parameters of in situ and separated resinite.

In situ resinite				Separated resinite			
Peak	Q	(CIE) cx	(CIE) cy	Peak	Q	(CIE) cx	(CIE) cy
524	0.59	0.432	0.454	520	0.59	0.435	0.454

Fig. 1. Density profile of a whole seam sample of the Herrin No. 6 seam (IBCSP 101).The large peak in the center represents the high vitrinite content of the coal.
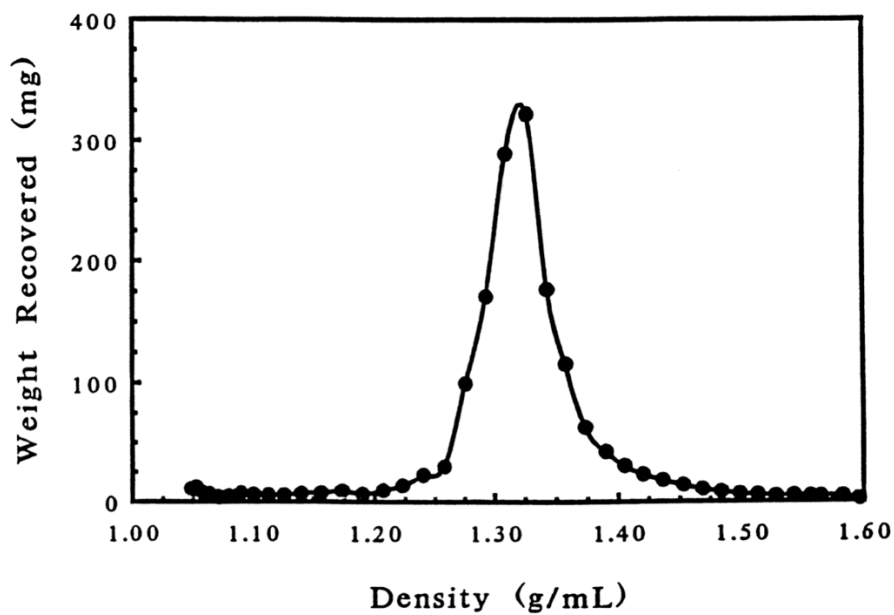

Fig. 2. Density profile of the resinite-rich range of the Herrin No. 6 seam (IBCSP 101). See Table 1.
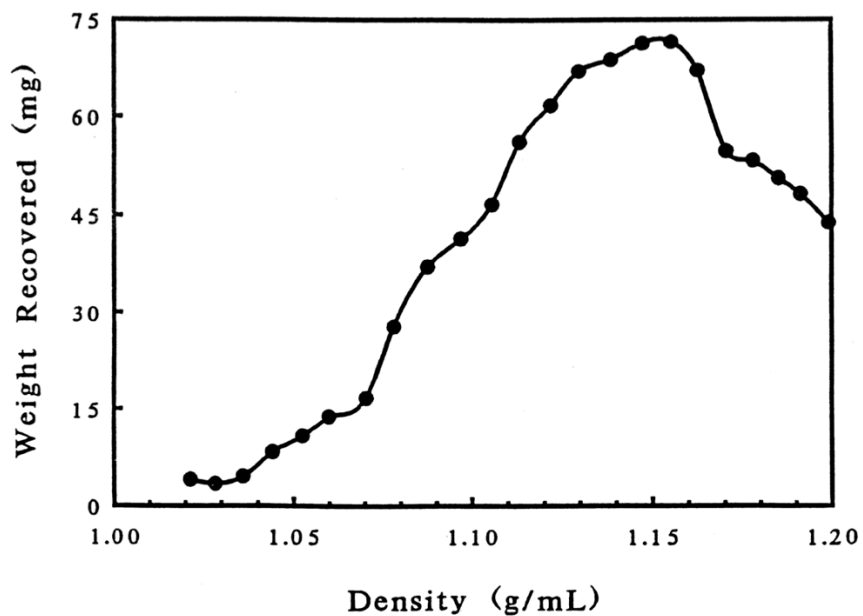
Fig. 3. Photomicrographs of three in situ resinite occurrences (left to right) are shown in both white light (top row) and in blue light (fluorescence) illumination (middle row). Below each pair of photomicrographs is a photomicrograph of a selected field of the separated resinite (bottom row). The similarity of the separated material to the in situ resinite is clear and supports the conclusion that the separated material is resinite.
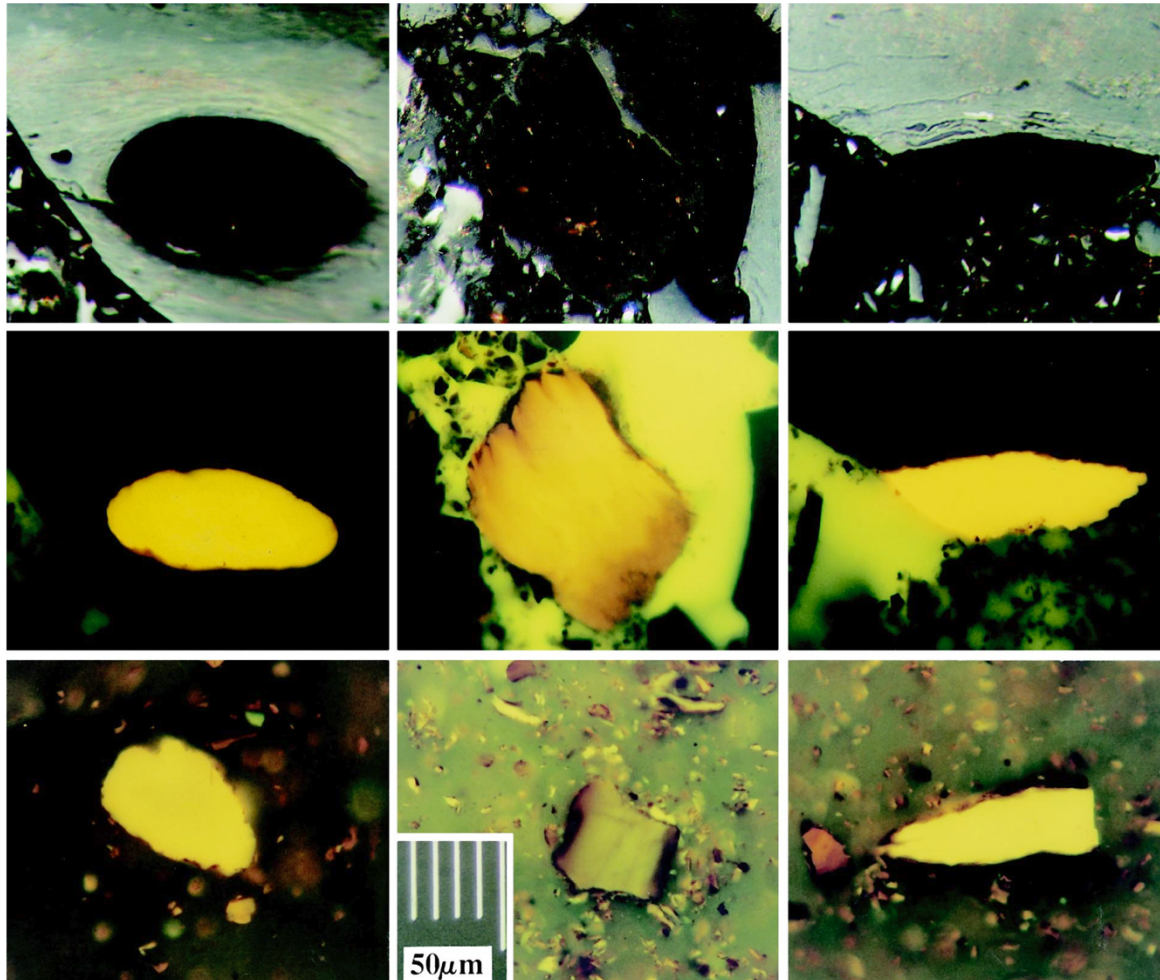
Fig. 4. Py–GC–MS total ion current chromatogram of the Herrin No. 6 resinite concentrate (sample JCFZ2684, fraction 16, 1.13 g/ml). (+) *n*-Alkanes, (Δ) *n*-alk-1-enes, (o) *n*-alk-α,ω-dienes. Other major compounds identified by molecular structure diagrams. Insets show details of the *n*-C$_{10}$ and *n*-C$_{20}$ regions. (X) silane contaminants.
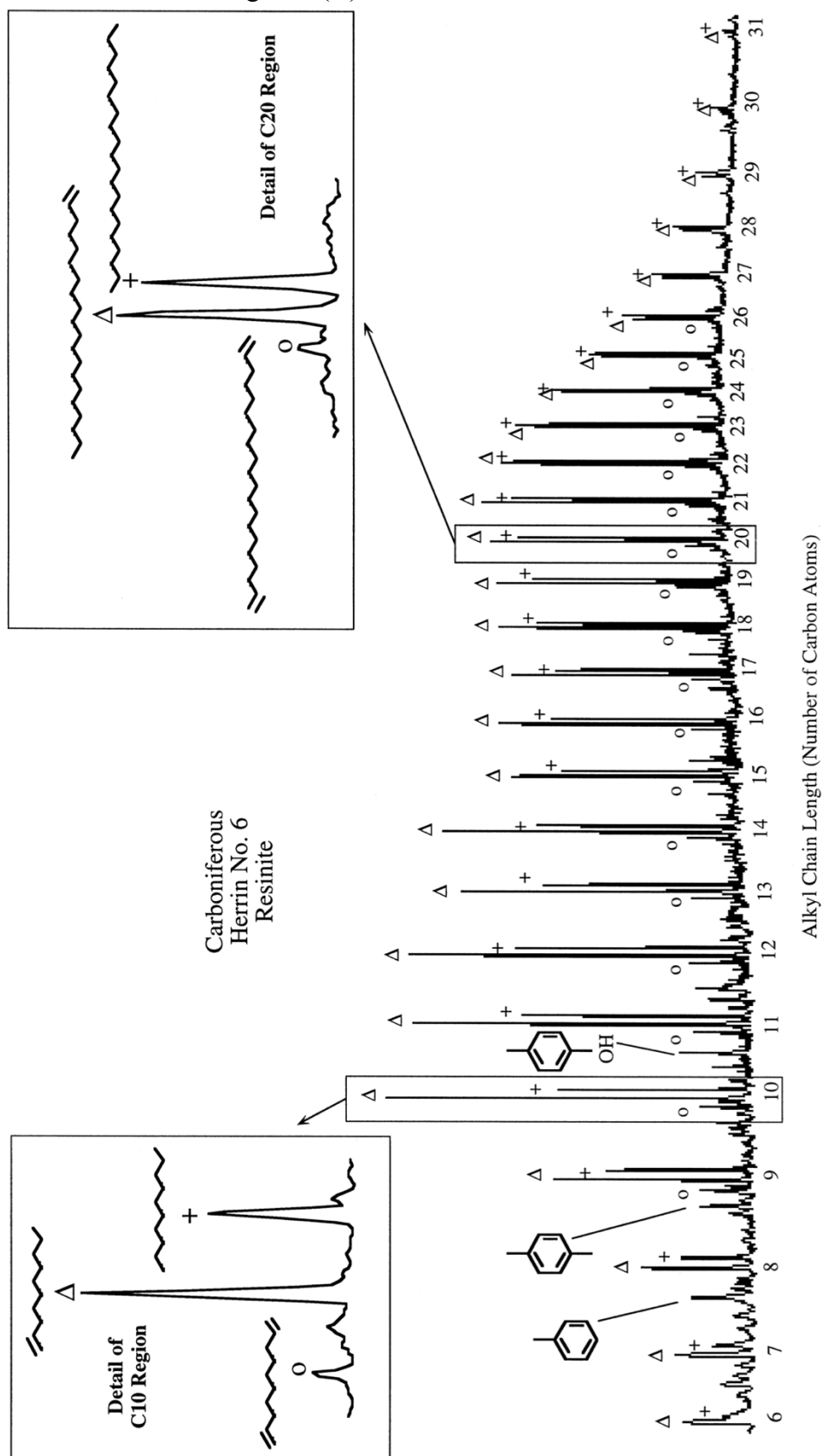
Fig. 5. Py–GC–MS total ion current chromatogram of the Herrin No. 6 cutinite concentrate (sample JCFZ2684, fraction 18, 1.060 g/ml). Compound identification as in Fig. 4.
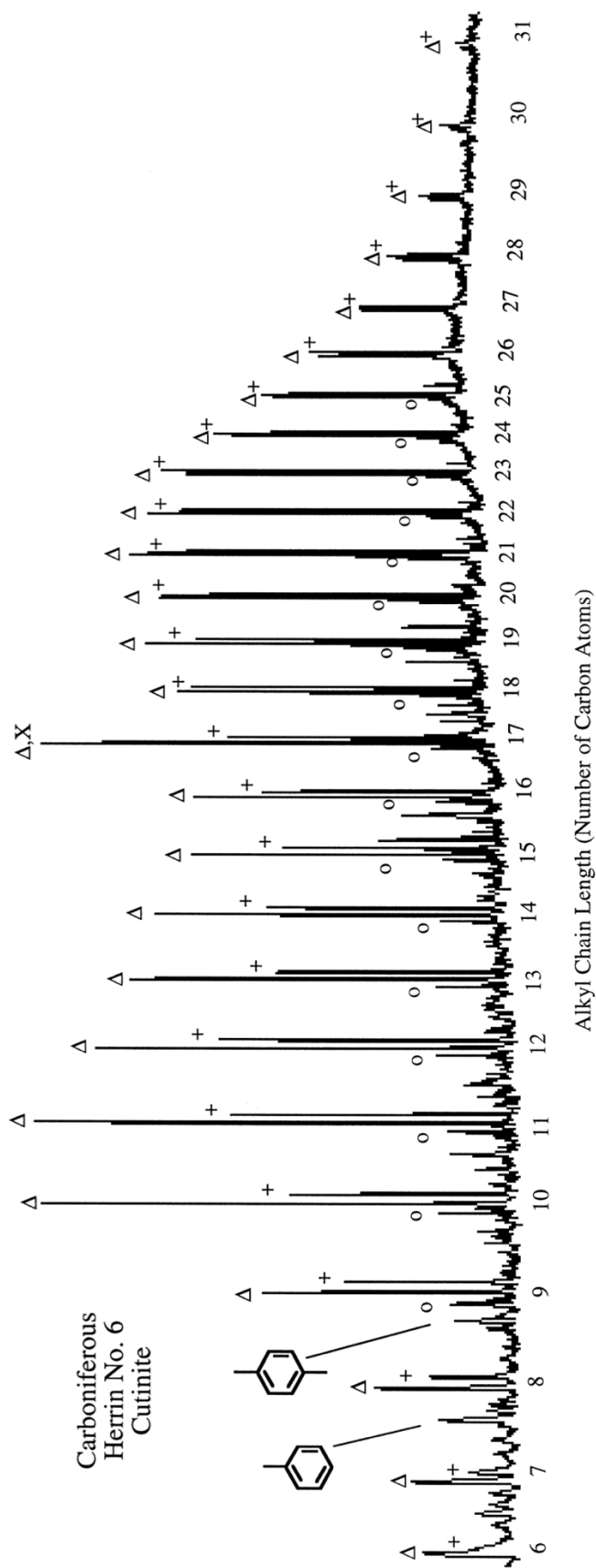
Fig. 6. Py–GC–MS total ion current chromatogram of the Herrin No. 6 sporinite concentrate (sample JCFZ2685, fraction 18, 1.179 g/ml). Compound identification as in Fig. 4.

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Fig. 7. Py–GC–MS total ion current chromatogram of the Hiawatha seam resinite concentrate (sample SIU561, fraction 16, 1.10 g/ml). Aromatized and unsaturated cadinanes identified by molecular weight (Da) and examples of structures. (+) *n*-Alkanes, (Δ) *n*-alk-1-enes, (o) *n*-alk-*α,ω*-dienes. Other major compounds identified by molecular structure diagrams.