Microanalysis of barkinite from Chinese coals of high volatile bituminous rank

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Abstract

Permian high volatile bituminous barkinite-rich coal from China has been evaluated petrographically and analyzed by electron microprobe and micro-FTIR techniques. The analyzed samples varied in vitrinite reflectance from 0.65 to 0.73%, and corresponding reflectance of barkinite ranged from 0.19 to 0.23%. Compared to the associated vitrinite, barkinite had a higher carbon and lower oxygen content in all samples. It had stronger aliphatic CH_x absorbance at 2800-3000 and 1450-1460 cm⁻¹, and less intense both aromatic C=C ring stretching vibration at ~1600 cm⁻¹ and aromatic CH_x out-of-plane deformation at 700–900 cm⁻¹. Micro-FTIR revealed large variations in the aliphatic group intensities within barkinite, suggesting its varying oil generation potential. Air-oxidation of barkinite over a 6-month-period resulted in rapid consumption of aliphatic groups and the formation of oxygenated functional groups.

Keywords: coal, barkinite, vitrinite, FTIR

1.0 Introduction

Barkinite-rich coals from Permian coal basins in China have been a subject of research for many years (e.g., Hsieh, 1933; Yan and Li, 1958; Han et al., 1983; Sun and Horsfield, 2005; Tang et al., 2008) and the origin and properties of barkinite have been the most common issues addressed for these coals. Barkinite is a hydrogen-rich organic component thought to derive from *Psaronius* or *Lepidodendron* and to form in a marine-influenced peat-forming environment (Zhong and Smyth, 1997). Because *Lepidodendron*, extinct in Laurasia by Stephanian time, may not have survived in China until the late Permian (H. Pfferkorn, 2001 personal communication to Hower), *Psaronius* is the more likely source plant, as also suggested by Zhong and Smyth (1997). Barkinite has not been established as a distinct maceral (Querol et al., 2001; Hower et al., 2007; Sun, 2010), despite claims by some authors (Zhong and Smyth, 1997; Sun and Wang, 2000; Sun, 2001, 2002, 2003, 2005; Sun et al., 2002; Sun, 2010). As a component of the liptinite group, “barkinite” has features reminiscent of resinite, cutinite, and/or suberinite (Hower et al., 2007). Sun (2005) attempted to prove its distinct character compared to other liptinite macerals or to vitrinite. In that study, however, he did not compare the “barkinite” to other macerals of the same rank and age. Therefore, its different character could also result from changes in maceral chemistry associated with both metamorphism and the evolution in plant communities with time (Hower et al., 2007).

Although barkinite has been described as minor components from Triassic and Neogene coals (Sun et al., 2010), barkinite-rich coals with barkinite content at places exceeding 80% by volume are restricted to Late Permian coals in China, suggesting that the unique flora in combination with a marine-influenced depositional environment contributed to the accumulation and preservation of this component (Zhong and Smyth, 1997).

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4 In this study, we compare vitrinite and barkinite within Chinese coals across the high
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6 volatile B bituminous to high volatile A bituminous rank range using fresh as well as air-
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8 oxidized samples. Barkinite have been considered an excellent source of oil (Chen et al., 1989),
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10 and the main purpose of this study is to investigate variability in its chemical properties,
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12 including its susceptibility to oxidation.
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19 2.0 Methods

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21 Sample KCER-8014 was donated to the University of Kentucky Center for Applied
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23 Energy Research by Zhicong Gong in 1979. The other coal samples were part of the study by
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25 Querol et al. (2001). The latter authors provided details about the depositional setting and
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27 sampling methods employed. Reflectances of vitrinite and barkinite were determined on epoxy-
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29 bound particulate pellets prepared to a 0.05- μm alumina final polish using a Leica DM 2500P
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31 microscope with TIDAS PMT IV system and 50x, oil-immersion, reflected-light optics.
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36 Three barkinite-rich samples: C13 2(2), KCER 8014, and C13 2(1) were selected for
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38 petrographic analysis, electron microprobe, and FTIR evaluation. Samples for all these analyses
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40 were prepared as polished blocks according to standard coal petrographic procedures (ICCP,
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42 1963). Fresh surfaces of the samples were investigated with organic petrography and micro-
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44 FTIR within a few days after polishing. These three samples were then left exposed at ambient
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46 conditions for six months. The half-year-exposed surfaces were subsequently re-analyzed with
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48 the same techniques to evaluate the effect of oxidation of barkinite and vitrinite at these
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55 Micro-FTIR measurements were performed using a Nicolet 6700 spectrometer connected
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57 to a Nicolet Continuum microscope operated in reflectance mode. The microscope was equipped
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4 with a video camera to display images and a computer-controlled mapping stage, and was linked
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7 to a liquid nitrogen cooled-mercury cadmium telluride (MCT) detector (Nicolet Instrumentations
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9 Inc., Madison, WI, USA). Micro-FTIR spectra were obtained at a resolution of 4 cm^{-1} , using a
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11 gold plate as background. The OMNIC program was used for spectral de-convolution, curve-
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13 fitting, and determination of peak integration areas. The microscope software Atlus in OMNIC
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15 controlled the motorized stage, micro-FTIR mapping data collection, and data processing.
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17 Reflectance micro-FTIR spectra were subjected to Kramers-Kronig transformation. This
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19 transformation corrects for transmittance and shifts bands to the positions comparable to those in
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21 KBr pellet spectra (Kronig, 1926; Kramers, 1927), and needs to be used in reflectance micro-
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23 FTIR analysis on polished blocks of coal (Mastalerz and Bustin, 1996). Peak assignments of
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25 spectra were based on Painter et al. (1981, 1985) and Wang and Griffiths (1985). For micro-
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27 FTIR mapping, a step size of $20\text{ }\mu\text{m}$ was used. Currently, the smallest aperture size used for the
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29 analysis is $25\times 25\text{ }\mu\text{m}$, because using a smaller aperture size would result in spectra of poor
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31 quality due to deteriorating signal-to-noise ratios. Further details about instrumentation and
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33 micro-FTIR mapping were presented by Chen et al. (2012, 2013).
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Figure 1. Photomicrographs of barkinite in the samples studied. A, C, E – reflected light, oil immersion, B, D, F – the same field of view as A, C, E but in fluorescent light

The same three samples were also analyzed using electron microprobe technique (Table 1). For electron microprobe analysis, the polished samples were sputter-coated with carbon for

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4 use in the microprobe. The samples were analyzed for the abundances of carbon, oxygen,
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6 nitrogen, sulfur, silicon, iron, and calcium using a Cameca SX-100 electron microprobe equipped
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8 with four wavelength-dispersive spectrometers. The microprobe provides compositional data in
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10 weight percent for each element, based on the total number of elements analyzed. A PC2 crystal
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12 was used to measure carbon and oxygen; a PET crystal for sulfur, calcium, and silicon; PC0 for
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14 nitrogen; and an LiF crystal for Fe. Ten-second beam count times were used for C, O, and S, and
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16 20 seconds for N. Detailed procedures for light element determination are found in Bustin et al.
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18 (1993) and Mastalerz and Gurba (2001). Beam conditions included a beam size of 20 μm , a
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20 current of 20 nA, and an accelerating voltage of 10 kV. The average elemental compositions for
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22 both vitrinite and barkinite are based on 10 individual analyses.
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31 3.0 Results and Discussion

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33 The coal samples have vitrinite reflectance of 0.65% for sample C13 2(2), 0.69% for
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35 sample KCER 8014, and 0.73% for sample C13 2(1). Corresponding reflectances of barkinite
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37 were 0.19, 0.21, and 0.23%. In freshly polished samples, barkinite was distinctly fluorescent
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39 (Fig. 1).
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43 Comparison of the elemental composition of barkinite with that of vitrinite shows
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45 consistently higher carbon content and lower oxygen content in barkinite (Table 1). Barkinite,
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47 whether or not it can be considered to be a distinct maceral, has affinities to the liptinite group,
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49 and these differences would be expected based on previous microprobe studies of coals (for
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51 example, Walker and Mastalerz, 2004). These observations, however, contradict some previous
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53 results on barkinite-rich coal (Sun 2002) that showed carbon content to be higher in vitrinite than
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55 in barkinite. Sun (2002) used density fractions to study elemental composition whereas this
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study generated in-situ elemental analyses. Both techniques provide reliable results, and this difference in carbon content of barkinite relative to vitrinite may reflect a variable degree of oxidation of barkinite and correspondingly variable carbon content. As we document below, barkinite is much more susceptible to oxidation than vitrinite. Sample C13 2(1) has higher carbon and lower oxygen content than KCER 8014 and C13-2(2), consistent with a slightly higher maturity in the former (R_o 0.73% compared to 0.69% and 0.65% in the other two samples (Table 1).

Nitrogen content is lower in barkinite compared to vitrinite. There is no consistent difference between vitrinite and barkinite in the concentrations of other elements studied - S, Cl, Ca, and Fe. Surprisingly S content in barkinite in the samples studied is low and comparable to vitrinite. Compared to two other samples, the higher sulfur content in barkinite of sample C13-2(1) is accompanied by higher S content in vitrinite. Barkinite-rich coals have often high sulfur content and are believed to form in a strongly marine-influenced peat-forming environment (e.g., Han et al., 1983; Zhong and Smyth, 1997).

Table 1. Elemental composition (weight %) and vitrinite reflectance (R_o , %) of vitrinite and barkinite of the samples studied. Each element content is the average value calculated from 10 measurements obtained using the electron microprobe technique

Element	C13-2(2)		KCER 8014		C13-2(1)	
	vitrinite	barkinite	vitrinite	barkinite	vitrinite	barkinite
C	74.25	80.63	75.79	80.63	78.78	82.77
N	1.37	1.08	1.35	1.08	1.78	1.28
O	20.15	14.11	19.41	14.11	15.65	11.56
S	0.25	0.24	0.26	0.24	0.81	0.91
Cl	0.45	0.39	0.46	0.39	0.44	0.39
Ca	0.03	0.06	0.04	0.06	0.02	0.03
Fe	0.02	0.08	0.02	0.08	0.00	0.04
R_o	0.65	0.20	0.69	0.21	0.73	0.23

With respect to the functional group distribution, in comparison with the micro-FTIR spectra of vitrinite, either on fresh or oxidized surfaces, the spectra of barkinite are characterized by strong aliphatic CH_x absorbance at 3000–2800 and 1460–1450 cm^{-1} , less intense aromatic C=C ring stretching vibration at $\sim 1600 \text{ cm}^{-1}$, and aromatic CH_x out-of-plane deformation at 700–900 cm^{-1} , as exemplified for the least mature sample C13-2(2) (Fig. 2). These observations support previous FTIR studies of barkinite from Chinese coals (Guo et al., 1996). CH_2/CH_3 ratios calculated after self-deconvolution of 2800–3000 cm^{-1} aliphatic stretching region ranged from 7.4 to 4.2 for barkinite and 1.2 to 1.4 for vitrinite. These ratios for vitrinite are similar to those of vitrinite of high volatile bituminous coals of other areas (Walker and Mastalerz, 2004), whereas those for barkinite are most similar to those of cutinite (Mastalerz et al., 2013). Differences between integrated areas of selected functional groups of vitrinite and barkinite for all three samples are listed in Table 2. Absorbance of C=O groups at $\sim 1700 \text{ cm}^{-1}$ are comparable for barkinite and vitrinite on fresh surfaces of all the samples (Table 2).

Exposure to air increased the intensity of C=O absorbance of vitrinite, and this oxidation phenomenon is even more remarkable in barkinite (Table 2, Fig. 3). Oxidation indices, defined as the ratios of integrated area of C=O over that of aliphatic CH_x peak areas at 3000–2800 cm^{-1} (Ox1), were quadrupled and doubled for barkinite and vitrinite, respectively, both in samples C13-2(2) and C13-2(1). We interpret that room-temperature oxidation resulted in consumption of aliphatic C-H compounds and generation of oxygenated functional groups. The elevation in oxidation indices after ambient air exposure of barkinite and vitrinite is even more dramatic in sample KCER-8014, however, high standard deviations associated with the calculations of oxidation indices of this sample (Table 2) make this comparison of lower confidence.

The magnitude of the difference in aliphatic C-H functional groups between vitrinite and barkinite changes with coal rank. For fresh surfaces of sample C13-2(2) (R_o 0.65 %), average aliphatic CH_x groups are 8.2 and 3.4 in barkinite and vitrinite, respectively, amounting to a difference of 4.80 (Table 2). The aliphatic peak area difference decreases to 4.5 in sample C13-2(1) (R_o 0.73 %) with aliphatic $C-H_x$ of 7.7 in barkinite and 3.2 in vitrinite. The difference of aliphatic C-H between barkinite and vitrinite also holds true for oxidized samples, declining from 2.5 for C13-2(2) to 2.2 for C13-2(1). Sample KCER-8014, with intermediate vitrinite reflectance (0.69%), does not follow the same trend, however. No consistent relationships were found between the difference of the integrated areas of other investigated functional groups and coal rank as expressed by vitrinite reflectance.

Figure 2. Comparison between the spectra of barkinite and vitrinite in sample C13-2(2). Relative integrated areas of aliphatic CH_x peaks at 3000-2800 cm^{-1} are 11.6 and 2.4 in barkinite and vitrinite, respectively. Vitrinite shows distinct aromatic CH_x peaks at 900-700 cm^{-1} . For this pair of spectra, CH_2/CH_3 ratio calculated after self-deconvolution of 2800-3000 cm^{-1} aliphatic stretching region equals 7.4 for barkinite and 1.2 for vitrinite.

Table 2. Comparison of integrated areas of selected functional groups in vitrinite and barkinite for all three samples (IR absorbance is given in arbitrary absorbance units). These values were obtained based on 10 spectra of barkinite and vitrinite in each sample; each spectrum was collected on a different area of each maceral.

	Fresh surface					Oxidized surface				
	Aliphatic CH _x	C=O	Aromatic C=C	Aromatic CH	Oxidation index (Ox1)	Aliphatic CH _x	C=O	Aromatic C=C	Aromatic CH	Oxidation index (Ox1)
C-13-2(2) R₀ 0.65%										
Barkinite average	8.2	3.4	5.6	1.3	0.4	5.2	7.2	2.7	0.3	1.6
Std	0.6	0.6	0.5	0.3	0.1	1.7	0.8	0.2	0.1	0.8
Vitrinite average	3.4	3.5	7.5	1.4	1.1	2.7	4.7	4.9	1.4	1.7
Std	0.4	0.3	0.5	0.3	0.2	0.7	2.5	2.8	1.1	0.6
Diff	4.80	0.2	1.9	0.1	0.7	2.5	2.6	2.2	1.1	0.0
KCER 8014 R₀ 0.69%										
Barkinite average	6.1	1.1	3.6	0.8	0.2	4.6	8.3	2.7	0.2	2.0
Std	1.2	0.8	0.8	0.2	0.2	1.5	0.9	0.2	0.0	0.8
Vitrinite average	2.6	0.6	4.9	2.6	0.2	1.8	2.1	3.3	0.6	1.2
Std	0.2	0.8	1.2	0.5	0.3	0.4	1.3	0.2	0.3	0.6
Diff	3.5	0.6	1.4	1.8	0.0	2.8	6.2	0.6	0.4	0.8
C13-2(1) R₀ 0.73%										
Barkinite average	7.7	3.4	4.7	1.0	0.4	4.9	7.9	1.9	0.4	1.7
Std	0.4	0.7	0.3	0.1	0.1	1.1	0.8	0.5	0.2	0.4
Vitrinite average	3.2	3.4	7.1	1.1	1.1	2.8	5.5	2.4	1.0	2.0
Std	0.3	0.2	0.5	0.1	0.1	0.8	3.8	1.0	0.7	1.4
Diff	4.5	0.0	2.4	0.6	0.6	2.2	2.4	0.4	0.5	0.3

Note: Oxidation index (Ox1) is calculated here as the ratio of integrated area of C=O at ~1700 cm⁻¹ over that of aliphatic CH_x at 3000-2800 cm⁻¹; average - average peak areas of selected functional groups of barkinite and vitrinite for each sample; Std - standard deviation of integrated peak area of selected functional groups of barkinite and vitrinite for each sample; Diff - absolute differences between the average peak areas of selected functional groups of barkinite and vitrinite.

Fig. 3. Comparison of FTIR spectrum of fresh and oxidized barkinite. Note an increase in 1707 cm^{-1} band (carboxyl/carbonyl) in the oxidized barkinite at the expense of aliphatic CH_x stretching bands in the 2800-3000 cm^{-1} region.

Figure 4. Chemistry maps of aliphatic C-H in sample C13-2(2) (panels **A**, **B**, and **C**) with the 3000-2800 cm^{-1} aliphatic peak area ($\text{Al}_{\text{stretch}}$) range of 3.2-36; in sample C13-2(1) (panels **D**, **E**, and **F**) having an $\text{Al}_{\text{stretch}}$ range of 3.5-38, and sample KCER (panels **G**, **H**, and **I**) with an $\text{Al}_{\text{stretch}}$ range of 3.1-7.1. For mapping, aperture size was 50×50 μm for samples C13-2(2) and C13-2(1), and 20×20 μm for KCER-8014. Step size was 15 μm .

Microscopic regions from coal samples C13-2(2), C13-2(1), and KCER featured multiple barkinite bands adjacent to vitrinite (Fig. 1) and they were micro-FTIR mapped for distribution of functional groups in order to see how chemistry of barkinite contrasts with that of the adjacent vitrinite (Fig. 4). **In particular, mapping** of the integrated areas of aliphatic CH_x stretching (3000–2800 cm^{-1}) yielded a good match with the petrography of the same area (Fig. 4**C**, **F**, and **I**), showing a clear differentiation between highly aliphatic barkinite and less aliphatic vitrinite. The signal intensities of aliphatic CH_x stretching at 3000–2800 cm^{-1} were much higher in barkinite

(i.e. red and yellow colors in Fig. 4B, E, and H) than in vitrinite. Moreover, this mapping revealed that within barkinite itself, there is a large variation in the aliphatic group intensities (Fig. 4).

Barkinite is considered to be an excellent source of oil; it is hydrogen-rich, has high tar yields upon pyrolysis and high hydrocarbon generation potential (Cheng et al., 1989; Chen and Chen, 1996, Sun, 2002). Sun (2002) showed that barkinite could generate large quantities of hydrocarbons upon pyrolysis and that its pyrolysis products include light oil, followed by wet gas, heavy oil, and methane. He also showed that those hydrocarbons can be generated over wide temperature range and suggested that barkinite is a good source of oil even at the late oil generation stage. However, the oil potential of barkinite can vary significantly, as suggested by the variations in the aliphatic group intensities. This, together with extensive oxidation over a relatively short experimental time period, necessitates caution in interpreting its hydrocarbon generation potential.

4.0 Conclusions

Freshly polished and ambient-air oxidized (six month exposure) surfaces of vitrinite and barkinite were analyzed by micro-FTIR and a wavelength-dispersive electron microprobe. The vitrinite reflectance varied from 0.65% R_o (high volatile B bituminous) to 0.73% R_o (high volatile A bituminous). The barkinite in the same samples varied in R_o from 0.19-0.23%.

For the samples studied, barkinite has a higher C and lower O content than the corresponding vitrinite. It exhibits strong aliphatic CH_x absorbance at 2800-3000 and 1450–1460 cm^{-1} , albeit with significant variations in intensity, and less intense aromatic C=C ring stretching vibration at ~1600 cm^{-1} and aromatic CH_x out-of-plane deformation at 700–900 cm^{-1} . Vitrinite shows a more significant aromatic CH_x out-of-plane deformation in the 700–900 cm^{-1}

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4 range. All these observations point to much higher aliphatic character of barkinite compared to
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7 vitrinite, consistent with properties of liptinite group macerals.
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9 This study shows that barkinite is much more prone to oxidation than vitrinite. The
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11 **extent** of oxidation was shown by a dramatic increase in the intensity of the oxygenated groups at
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13 ~1700 cm⁻¹ and especially by increase in the ratio of C=O to the aliphatic CH_x peak at 2800-
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15 3000 cm⁻¹, an indication of the oxidative consumption of aliphatic groups and the formation of
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17 oxygenated functional groups.
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21 Micro-FTIR mapping confirmed much more aliphatic character of barkinite compared to
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23 vitrinite, and also revealed large variations in the aliphatic group intensities within barkinite
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25 itself. These variations together with our experimental evidence for fast oxidation of barkinite
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27 suggest that oil generation potential of this **organic constituent, which has** traditionally **been**
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29 considered an excellent oil source, needs to be evaluated carefully because it may show
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31 significant **variability**.
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