International Journal of Coal Geology 141–142 (2015) 103–108

Contents lists available at ScienceDirect

International Journal of Coal Geology

journal homepage: www.elsevier.com/locate/ijcoalgeo

Microanalysis of barkinite from Chinese coals of high volatile bituminous rank

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ARTICLE INFO

Article history:
Received 15 December 2014
Received in revised form 4 March 2015
Accepted 5 March 2015
Available online 14 March 2015

Keywords:
Coal
Barkinite
Vitrinite
FTIR

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 the 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.

1. Introduction

Barkinite-rich coals from Permian coal basins in China have been a subject of research for many years (e.g., Han et al., 1983; Hsieh, 1933; Sun and Horsfield, 2005; Tang et al., 2008; Yan and Li, 1958), 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 (Hower et al., 2007; Querol et al., 2001; Sun, 2010), despite claims by some authors (Sun, 2001, 2002, 2003, 2005, 2010; Sun and Wang, 2000; Sun et al., 2002; Zhong and Smyth, 1997). 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).

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

2. Methods

Sample KCER-8014 was donated to the University of Kentucky Center for Applied Energy Research by Zhicong Gong in 1979. The other coal samples were part of the study by Querol et al. (2001). The latter authors provided details about the depositional setting and sampling methods employed. Reflectances of vitrinite and barkinite were determined on epoxy-bound particulate pellets prepared to a 0.05-μm alumina final polish using a Leica DM 2500P microscope with TIDAS PMT IV system and 50×, oil immersion, reflected-light optics.

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http://dx.doi.org/10.1016/j.coal.2015.03.004
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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.

	C13-2(2)		KCER 8014		C13-2(1)	
Element	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

Three barkinite-rich samples, C13 2(2), KCER 8014, and C13 2(1), were selected for petrographic analysis, electron microprobe, and FTIR evaluation. Samples for all these analyses were prepared as polished blocks according to standard coal petrographic procedures (ICCP, 1963). Fresh surfaces of the samples were investigated with organic petrography and micro-FTIR within a few days after polishing. These three samples were then left exposed at ambient conditions for 6 months. The half-year-exposed surfaces were subsequently re-analyzed with the same techniques to evaluate the effect of oxidation of barkinite and vitrinite at these conditions.

Micro-FTIR measurements were performed using a Nicolet 6700 spectrometer connected to a Nicolet Continuμm microscope operated in reflectance mode. The microscope was equipped with a video camera to display images and a computer-controlled mapping stage and was linked to a liquid nitrogen cooled-mercury cadmium telluride (MCT) detector (Nicolet Instrumentations Inc., Madison, WI, USA). Micro-FTIR spectra were obtained at a resolution of 4 cm^{-1}, using a gold plate as background. The OMNIC program was used for spectral deconvolution, curve-fitting, and determination of peak integration areas. The microscope software Atlus in OMNIC controlled the motorized stage, micro-FTIR mapping data collection, and data processing. Reflectance micro-FTIR spectra were subjected to Kramers–Kronig transformation. This transformation corrects for transflectance and shifts bands to the positions comparable to those in KBr pellet spectra (Kramers, 1927; Kronig, 1926) and needs to be used in reflectance micro-FTIR analysis on polished blocks of coal (Mastalerz and Bustin, 1996). Peak assignments of spectra were based on Painter et al. (1981, 1985) and Wang and Griffiths (1985). For micro-FTIR mapping, a step size of 15 μm was used. Currently, the smallest aperture size used for the analysis is 20 × 20 μm because using a smaller aperture size would result in spectra of poor quality due to deteriorating signal-to-noise ratios. Further details about instrumentation and micro-FTIR mapping were presented by Chen et al. (2012, 2013).

The same three samples were also analyzed using electron microprobe technique (Table 1). For electron microprobe analysis, the

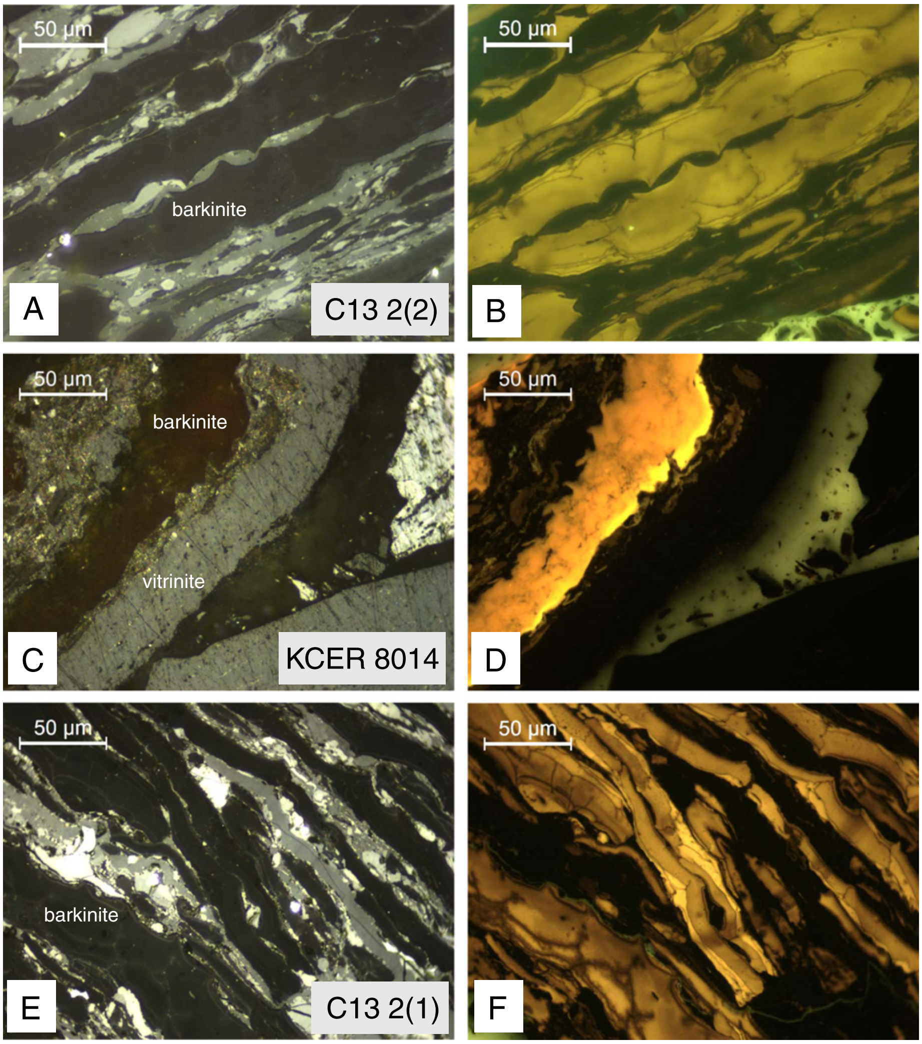

Fig. 1. Photomicrographs of barkinite in the samples studied. A, C, E—reflected light, oil immersion; B, D, F—the same field of view as A, C, E but in fluorescent light.