Geochemical and petrographic alteration of rapidly heated coals from the Herrin (No. 6) Coal Seam, Illinois Basin

Severin M. Presswood, Susan M. Rimmer *, Ken B. Anderson, Justin Filiberto

Department of Geology, Southern Illinois University Carbondale, Carbondale, IL, 62901, USA

ABSTRACT

Coals altered by rapid heating events (i.e., those intruded by dikes and sills) are thought to follow a different geochemical maturation pathway than coals altered through diagenesis. If an igneous intrusion alters the petrographic and geochemical properties of a coal, the effect should also be observable in the coal's molecular structure. In this study, we evaluate whether coals altered by rapid heating follow distinct maturation trends from coals that were altered by slower heating (burial maturation). Petrographic, geochemical, and micro-FTIR analyses were performed on a series of Pennsylvanian Illinois Basin coal samples, collected at various distances from a Permian igneous dike. Standard coal characterization techniques including vitrinite reflectance and proximate and ultimate analyses provide valuable insights on the maturation pathways experienced by rapidly heated coals. These techniques were coupled with reflectance micro-FTIR to provide a better understanding of the molecular changes that occur in the coal structure during relatively short-lived, intensive heating events.

With decreasing distance to the intrusion, coals have higher mean random vitrinite reflectance values (R_r) within the dike alteration zone. Coking textures similar to those observed in industrial cokes are observed within 2 m of the intrusion. Geochemical data for HCl-treated coals indicate an overall loss of H, O, and N and an increase in C approaching the dike. Intruded coals have higher volatile matter (VM) yields at high rank than coals of similar rank that result from normal burial maturation. When plotted on a van Krevelen diagram or Seyler chart, intruded coals follow different coalification trends than coals matured through normal burial diagenesis.

Reflectance micro-FTIR analysis of collotelinite shows increased aromaticity with rank: both the ratio of the aromatic CH stretching band at ~3100–3000 cm^{-1} versus the aliphatic CH$_x$ stretching bands between 3000 and 2800 cm^{-1} (AR1), and the ratio of the aromatic out-of-plane deformation bands between ~900–700 cm^{-1} versus the aliphatic CH$_x$ band (AR2) increase with increasing R_r. Within the 3000–2800 cm^{-1} region, there is an increase in the area under the asymmetric CH$_3$ peak at ~2960 cm^{-1} relative to the asymmetric CH$_2$ peak at ~2920 cm^{-1} with increased rank. Within the 900–700 cm^{-1} region, the overall intensity of the ~750 cm^{-1} peak (aromatic rings with four adjacent H atoms) relative to the ~870 cm^{-1} peak (aromatic rings with one isolated H atom) increases up to 2.5% R_r, likely reflecting a lower degree of substitution (DOS) of alkyl groups on aromatic ring sites. The prevalence of the 750 cm^{-1} peak at high rank may represent a lower degree of condensation of aromatic rings in the structure of intruded coals compared to normally matured coals.

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1. Introduction

The effects of igneous intrusions on the geochemical, mineralogical, and petrographic composition of bulk coals and the microscopically distinguishable components of coals (macerals) have received considerable attention (Clayton and Bostick, 1985; Dai and Ren, 2007; Finkelman et al., 1998; Golab and Carr, 2003; Murchison, 2004, 2006; Murchison and Raymond, 1989; Raymond and Murchison, 1992; Rimmer et al., 2009, 2015; Stewart et al., 2005; Yoksoulian et al., 2016). Coals that have been heated rapidly by intruding dikes and sills have been shown to follow different coalification trends than those

altered under normal diagenetic conditions (Murchison, 2004, 2006; Murchison and Raymond, 1989; Rahman and Rimmer, 2014; Raymond and Murchison, 1992; Rimmer et al., 2009). When data for coals altered by igneous intrusion are plotted on a van Krevelen diagram, they have lower H/C ratios at given O/C values in comparison to coals matured through burial diagenesis (Rimmer et al., 2009; van Krevelen, 1993). Coals altered by igneous intrusions have higher volatile matter (VM) contents when compared to coals altered by diagenesis (Rahman and Rimmer, 2014; Rimmer et al., 2009). Only limited research has focused on the molecular trends coals experience through interaction with magmatic bodies (Amijaya and Littke, 2006; Dun et al., 2013). This study presents reflectance micro-FTIR spectra of vitrinite macerals from coal samples collected along a transect adjacent to an igneous dike.

1.1. Previous FTIR studies of coal rank

Reflectance micro-FTIR can provide information on changes in the relative abundances of some specific molecular substructures, and it has been demonstrated as a viable tool for the characterization of coal macerals (Chen et al., 2012; Mastalerz and Bustin, 1993a, 1993b, 1995, 1996). This approach allows in-situ characterization of individual macerals, and provides greater detail on the heterogeneity of coals (Chen et al., 2012; Mastalerz and Bustin, 1993a, 1993b, 1995, 1996). Sample preparation for reflectance micro-FTIR is identical to that for vitrinite reflectance analysis, allowing for detailed comparisons between petrographic and molecular features (Mastalerz and Bustin, 1995). The reflectance micro-FTIR process is non-destructive, is very reproducible when the same area on a maceral is measured (Mastalerz and Bustin, 1996), and does not require separation techniques such as density-gradient centrifugation (Dyrkacz and Horwitz, 1982) in order to analyze individual macerals (Mastalerz and Bustin, 1995).

Much of the fundamental work, including the assignment of specific bands within the spectra (Painter et al., 1981, 1982, 1985; Wang and Griffiths, 1985), and the overall applications of FTIR to the characterization of the complex structure of coal and kerogen (Painter et al., 1982; Solomon et al., 1982) were discussed extensively in the 1980's. Several advances have been made recently in the FTIR characterization of coals (Chen et al., 2012; Dun et al., 2013; Li et al., 2007; Petersen et al., 2007), facilitated by enhanced signal processing techniques and detector capabilities, as well as advanced software capable of rapid spectral deconvolution (Chen et al., 2012; Dun et al., 2013; Li et al., 2007; Petersen et al., 2007).

Several studies have used FTIR data to characterize the distributions of chemical functional groups within coals of different ranks (Amijaya and Littke, 2006; Chen et al., 2012; Dun et al., 2013). Previous FTIR studies of coals have found aromaticity, condensation of aromatic rings, and out-of-plane aromatic C—H responses increase with increasing coal rank (Chen et al., 2012). Aliphatic chain length, as well as the absorbance of aromatic C=C ring stretch, decreases with increasing rank (Amijaya and Littke, 2006).

FTIR studies on intruded coals have generally been conducted using KBr-FTIR techniques (Amijaya and Littke, 2006; Dun et al., 2013; Saikia et al., 2007) and are therefore representations of bulk molecular trends. Reflectance micro-FTIR is capable of rapid data collection on individual macerals in-situ (Mastalerz and Bustin, 1993a, 1993b, 1995, 1996), and could be used to complement bulk geochemical data and vitrinite reflectance trends that have been identified in rapidly heated coals.

1.2. Characteristic IR absorption bands in the FTIR spectra of coal

Several mid-infrared absorption bands are commonly used for coal studies (Chen et al., 2012; Mastalerz and Bustin, 1995). Typically, these are selected on the basis of being well resolved (i.e., occurring in regions of the spectrum where there are relatively few overlapping absorbances) and useful for investigation of specific structural characteristics of interest (i.e., they correspond to specific, well defined, molecular sub-structures). Among the most useful absorption bands in the micro-FTIR spectra are: (1) the 3100–3000 cm^{-1} region, representing aromatic C—H stretching bands; (2) the 3000–2800 cm^{-1} region, representing aliphatic C—H stretching; and (3) the 900–700 cm^{-1} bandwidth, representing aromatic out-of-plane deformation modes. These absorptions can provide semi-quantitative information regarding the evolution of aromatic and aliphatic structures with increased coal rank (Chen et al., 2012; Li et al., 2007).

Due to the inherent bandwidth of most mid IR absorption bands and the structural complexity and heterogeneous nature of coal structure, coals express broad and overlapping peaks in their IR spectra. Most observed absorption bands are actually comprised of several individual bands (Painter et al., 1982). The most prominent issue in studying coals via FTIR techniques involves the separation of these overlapping absorptions into their individual components using deconvolution functions (Painter et al., 1982). Absorption observed in the 3000–2800 cm^{-1} range is composed of the symmetric and asymmetric stretching vibrations of aliphatic CH structures. Previous studies (Chen et al., 2012; Ibarra and Miranda, 1995) have attempted to use the ratio of the area under the asymmetric methyl peak (~2955 cm^{-1}) to the area under the asymmetric methylene peak (~2920 cm^{-1}) as a semi-quantitative measurement of aliphatic chain length (Ibarra and Miranda, 1995), although this is complicated by differences in the extinction coefficients associated with these discrete absorbances. Deconvolution of absorbances between 900 and 700 cm^{-1}, which largely correspond to out-of-plane deformations of aromatic C—H groups, can be used to measure the degree of substitution of aromatic sites with alkyl groups, through the comparison of the area under the 870 cm^{-1} peak (typically associated with deformation of isolated aromatic C—H structures) versus the area under the 750 cm^{-1} peak (typically associated with deformations of aromatic CH structures with 4 adjacent aromatic protons) (Chen et al., 2012; Iglesias et al., 1995).

The absorption from ~1800–1550 cm^{-1} represents both oxygenated (carbonyl/carboxyl) structures and ring-stretching modes of aromatic carbon groups. The prominent peak centered at ~1600 cm^{-1} is representative of aromatic ring stretching modes, but several challenges exist within the interpretation of this peak as a quantitative measurement of aromatic groups or oxygenated structures (Li et al., 2007; Painter et al., 1983, 1985). Water bands overlap within this region of the spectra. Water bands can significantly alter the results of deconvolution if precise atmospheric substitution is not achieved, or if the atmospheric conditions in the laboratory change during analysis (Venyaminov and Prendergast, 1997). The number of bands that makes up the 1800–1550 cm^{-1} region makes deconvolution very difficult (Li et al., 2007; Painter et al., 1983, 1985). The separation of this region differs considerably from author to author as well (Chen et al., 2012; Ibarra and Miranda, 1995). Regardless of the degree of separation of the 1800–1550 cm^{-1} bandwidth, there is still considerable overlap of the aromatic C=C band by highly conjugated C=O bands (Ibarra and Miranda, 1995; Painter et al., 1983, 1985). Similarly, there is overlap of absorption due to aromatic C=C structures by absorption due to carboxyl groups. This is especially significant in lower rank coals where COO^- groups are commonly prevalent (Li et al., 2007). It is therefore difficult to use the aromatic C=C band at ~1600 cm^{-1} as a quantitative indicator of aromaticity (Li et al., 2007).

2. Methods

2.1. Sampling

Thirty-six samples were collected along a transect of the Herrin (No. 6) Coal at various distances from a northwest-trending igneous intrusion from an underground mine in northern Saline County, Illinois (Fig. 1). Grab samples of approximately 200 g each were collected along the transect. NEM-1 was collected as close to the intrusion as possible. Samples NEM-2 through NEM-15 were collected in 3- to 10-cm intervals. 30- to 50-cm intervals were used for collection of NEM-16 through NEM-25. Beyond this range, the distance between sample points increased to 0.2 to 0.3 m to ensure sufficient collection of unaltered background coal. The sampling interval was more closely spaced near the intrusion due to exponential maturation reported by Rimmer et al. (2009) for another intruded coal seam in this region.

2.2. Sample preparation

Coals were processed to minus 20-mesh for petrographic and micro-FTIR analysis, and to minus 60-mesh for geochemical analysis according to ASTM standards (ASTM, 2011a). Ground coals were embedded in epoxy resin and polished to a final 0.06 μm colloidal silica polish by