



Carbon isotope analysis of whole-coal and vitrinite from intruded coals from the Illinois Basin: No isotopic evidence for thermogenic methane generation



Mohammad W. Rahman^{a,1}, Susan M. Rimmer^{a,*}, Harold D. Rowe^b, William W. Huggett^a

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

^b Bureau of Economic Geology, University of Texas at Austin, Austin, TX 78713, USA

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ABSTRACT

Igneous intrusions into coals and organic-rich rocks may have contributed to global warming in the geologic past through the release of greenhouse gases. Evidence for a large release of thermogenic CH₄ from the organics would include significant δ¹³C_{org} enrichment in the residual organic matter (OM). However, δ¹³C_{org} values of thermally altered OM in coals and shales adjacent to intrusions often show negative trends or, in some cases, ambiguous or positive trends. Previous studies have evaluated the δ¹³C_{org} of whole-coal samples rather than that of individual organic components, or macerals. As different macerals have different isotopic compositions, maceral-specific trends may be masked by variations in maceral composition of the bulk samples. This study evaluates the hypothesis that, if a large-scale release of ¹³C-depleted thermogenic CH₄ resulted from intrusion of the coal, then it should have produced ¹³C-enriched coal residuum and, specifically, vitrinite (the most abundant component of the coal) adjacent to the intrusion. This study reports geochemical and petrographic data for whole-coal samples and vitrinite macerals (separated via density-gradient centrifugation, DGC) from a transect of thermally altered Springfield (No. 5) Coal (Pennsylvanian) in the Illinois Basin.

Approaching the dike contact, mean vitrinite reflectance (R_r) increases from background levels of 0.55% up to ~4.8% and liptinites become indistinguishable from vitrinite. Isotropic and fine-grained circular mosaic coke is observed in samples within ~1.3 m of the coal/intrusion contact. Approaching the intrusion, volatile matter (VM) decreases and fixed carbon (FC) and %C increase, whereas %H decreases. Total organic carbon (TOC) for whole coal decreases from 77% to 34%, whereas TOC for separated vitrinite fractions increases from ~66% to 93% toward the coal/intrusion contact. Density of DGC-separated vitrinites ranges from 1.27 g/mL in the unaltered coal to 1.52 g/mL in the sample adjacent to the coal/intrusion contact. Vitrinite density increases with increased R_r and %C, and decreases with increased %H and H/C.

Despite these marked geochemical and petrographic changes, no significant changes in δ¹³C_{org} values of the whole coal (−25.3‰ to −24.9‰) or the separated vitrinites (−25.3‰ to −25.0‰) occur proximal to the intrusion. Changes in the isotopic signatures are not of a magnitude that would be expected if significant quantities of isotopically depleted thermogenic CH₄ had been generated by the intrusive event. Moreover, no petrographic evidence supports the occurrence of condensed or immobilized thermal products due to rapid pyrolysis (such as ¹²C-rich pyrolytic carbon) close to the intrusion that could have moderated any changes in δ¹³C_{org}. Geochemical and petrographic results suggest that only minimal loss of CH₄ was associated with the rapid heating of the Springfield (No. 5) Coal by the intrusion. These findings have significant implications for models linking past global warming to the intrusion of coals and carbonaceous shales.

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1. Introduction

It has been hypothesized that the rapid release of greenhouse gases (e.g., ¹³C-depleted CH₄) from coals and other organic-rich strata during

intrusion may have resulted in global warming, and ultimately, may have led to several mass extinction events in geologic time (Svensen et al., 2004, 2007, 2009; McElwain et al., 2005; Retallack and Jahren, 2008; Ogden and Sleep, 2012). This release of ¹³C-depleted CH₄ is inferred from negative excursions in δ¹³C records (e.g., McElwain et al., 2005; Svensen et al., 2007; Retallack and Jahren, 2008). In addition, organic matter (OM) that has been identified tentatively as coal fly ash, produced by the combustion of intruded coals, has been linked to the

* Corresponding author.

E-mail address: srimmer@siu.edu (S.M. Rimmer).

¹ Current affiliation: Devon Energy Corporation, Oklahoma City, OK, USA.

end-Permian mass extinction event (Grasby et al., 2011). However, Hudspeth et al. (2014, 2015) have questioned the origin of this OM, suggesting that the “fly ash” is in fact vesicular char that was likely produced by wildfires. Because of the interest in the potential role of intrusion of organic-rich strata and coal in global warming episodes, it is important to understand the geochemistry of thermally altered coals and the changes that result from intrusion events. Intruded coals are thought to release gases including CH₄ and CO₂ (McElwain et al., 2005; Svensen et al., 2007; Retallack and Jahren, 2008; Ogden and Sleep, 2012) but it is debatable how much of these greenhouse gases may have been produced, and what effect they may have had in the geologic record (Gröcke et al., 2009).

Numerous studies have documented the effects of igneous intrusion on the organic fraction of coal (Clegg, 1955; Crelling and Dutcher, 1968; Stewart et al., 2005; Cooper et al., 2007; Mastalerz et al., 2009; Rimmer et al., 2009, 2015; Schimmelmann et al., 2009; Rahman and Rimmer, 2014; Presswood et al., 2016) and organic-rich sedimentary rocks (Simoneit et al., 1981; Dennis et al., 1985; Clayton and Bostick, 1986; Saxby and Stephenson, 1987; Aarnes et al., 2011; Rimmer et al., 2015). Most of these studies have concentrated on petrographic analyses, vitrinite reflectance, and bulk geochemical analyses such as proximate and ultimate analyses. In addition, carbon isotopic compositions of thermally altered coal and sedimentary rocks have been studied in many parts of the world (Baker and Claypool, 1970; Simoneit et al., 1981; Clayton and Bostick, 1986; Saxby and Stephenson, 1987; Meyers and Simoneit, 1999; Cooper et al., 2007; Gröcke et al., 2009; Yoksoulia et al., 2016; among others). Previous work has shown that intruded coals and sediments can show ambiguous, uniform, or decreasing trends in $\delta^{13}\text{C}_{\text{org}}$ (Clayton and Bostick, 1986; Meyers and Simoneit, 1999; Cooper et al., 2007; Gröcke et al., 2009; Schimmelmann et al., 2009; Yoksoulia et al., 2010; Yoksoulia et al., 2016) or increasing trends in $\delta^{13}\text{C}_{\text{org}}$ approaching intrusions (Simoneit et al., 1981; Saxby and Stephenson, 1987; Conkright and Sackett, 1992; Cooper et al., 2007) (Fig. 1).

Results that indicate depleted $\delta^{13}\text{C}_{\text{org}}$ values in thermally altered coal and shales that are closest to an intrusion (Saxby and Stephenson, 1987; Meyers and Simoneit, 1999; Cooper et al., 2007; Schimmelmann et al., 2009) are unanticipated, as enriched $\delta^{13}\text{C}_{\text{org}}$ values would be expected toward the intrusion because contact metamorphism of OM should result in the release of gases enriched in ¹²C (e.g., Cooper et al., 2007; Gröcke et al., 2009). Whiticar (1996) reported that $\delta^{13}\text{C}_{\text{org}}$ signatures

of liptinites and vitrinites become 1‰ heavier (i.e., more enriched in ¹³C) with increased vitrinite reflectance, probably due to loss of volatile matter (VM) (Gröcke et al., 2009). More negative $\delta^{13}\text{C}_{\text{org}}$ values observed near an intrusion may result from rapid pyrolysis of coal that produces volatiles, which are subsequently re-deposited in the coal in the form of pyrolytic carbon (Meyers and Simoneit, 1999).

What has been lacking in this previous work is information on how the isotopic compositions of individual macerals change in response to an intrusion. As coal is very heterogeneous, bulk isotopic trends may be complicated by variations in inherent maceral composition as different macerals have different $\delta^{13}\text{C}_{\text{org}}$ values (Rimmer et al., 2006); for example, in-sample variability between macerals of high volatile bituminous coal is at least 2–3‰ (Rimmer et al., 2006). Geochemical analysis of individual macerals (i.e., vitrinites, liptinites, and inertinites) obtained via density-gradient centrifugation (DGC) can provide important insights to the changes produced by intrusion events, thus avoiding problems introduced by mixing varying amounts of macerals with different isotopic compositions. Thus, this study tested the hypothesis that the $\delta^{13}\text{C}_{\text{org}}$ of vitrinite macerals (preserved woody and bark tissue) becomes enriched in ¹³C with the increase in rank approaching a coal/intrusion contact due to the release of isotopically light gases. This study reports geochemical ($\delta^{13}\text{C}_{\text{org}}$, proximate, and ultimate analyses) and petrographic (maceral composition and vitrinite reflectance) data for whole coals, and $\delta^{13}\text{C}_{\text{org}}$ and total organic carbon (TOC) data for vitrinite concentrates separated by DGC for a suite of closely spaced intruded coal samples from the Pennsylvanian-age Springfield (No. 5) Coal seam from the Illinois Basin. Although not associated with a LIP or a negative carbon isotope excursion, the intruded coals of the southern part of the Illinois Basin can serve as a proxy for such occurrences.

2. Procedures

2.1. Sampling

Grab samples of thermally altered coal were collected from the Springfield (No. 5) Coal, a Pennsylvanian-age high volatile bituminous coal in the Carbondale Formation from a mine in southern Illinois, Illinois Basin (Fig. 2). At this location, the coal had been intruded by a Permian-age ultramafic peridotite dike (Fifarek et al., 2001; Stewart et al., 2005). Forty-four samples were collected at distances out to ~15 m

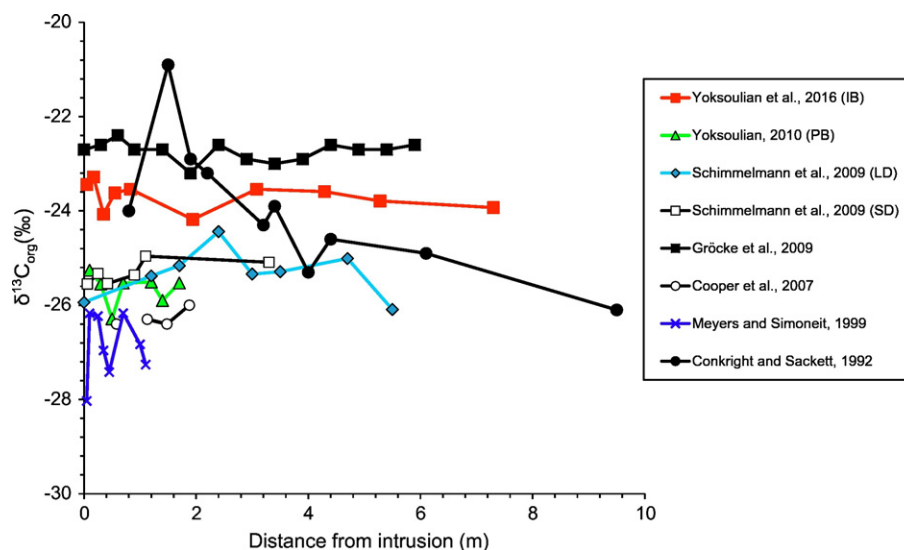


Fig. 1. Variation in carbon isotopic composition ($\delta^{13}\text{C}_{\text{org}}$) approaching an intrusion. Conkright and Sackett (1992) data are for altered sediments; remaining transects show data for intruded coals. (IB = Illinois Basin, PB = Piceance Basin, LD = large dike, and SD = small dike).

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