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An occurrence of coked bitumen, Raton Formation, Purgatoire River Valley, Colorado, U.S.A.

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ABSTRACT

Numerous examples of coke produced by igneous intrusion into coal have been reported in the Spanish Peaks region of south central Colorado. However, in a recent study of an intruded section of the Raton Formation (Upper Cretaceous-Paleocene) along the Purgatoire River near Medina Plaza, CO, coked bitumen has been observed. This material occurs in "fingers" (hexagonally jointed bodies) in a shaley xenolith within a lamprophyre sill and in carbonaceous Type III shale directly below the sill. The coke fingers are characterized by a remarkable flow mosaic texture, high vitrinite/coke reflectance (average random reflectance between 8% and 9%, but with maximum readings around 14–15%), high anisotropy, abundant devolatilization vacuoles, and an absence of inertinite inclusions. Within the underlying shales, the coked bitumen occurs as pore, void, and fracture linings and fillings. Geochemically, the coke in the fingers has low S_1 and S_2 values (<0.2 and <3 mg HC/g, respectively), and low HI and OI values (<6 mg HC/g TOC and <3 mg CO_2/g TOC, respectively). Within the fingers, there is evidence for multiple stages of accumulation, including coarse-grained circular or ribbon coke frequently containing pores edged by vapor-deposited carbon (pyrolytic carbon), layers of pyrolytic carbon, clusters of spherulitic pyrolytic carbon, and layers of highly porous coke. This coked bitumen is quite different from coked coal from the same locality. The coked coal has a medium-grained circular mosaic texture that is consistent with the high volatile bituminous rank of unaltered coal in the area. The coal-derived coke has similar devolatilization vacuoles but also has numerous inclusions of inertinite macerals such as fusinite and secretinite. A previously reported coal "dike" that had flowed through a sill in the same area also showed circular mosaic texture.

These observations suggest that the coke found in this study was not formed by the direct coking of coal, but from a mobile phase (bitumen or pitch) that was subsequently coked by the intrusion. This bitumen was either derived from the abundant coal within the section above the sill, or from the organic matter contained within the Type III carbonaceous shales, or both. Unaltered Type III shale sampled at this site has a HI of ~350 mg HC/g TOC suggesting some, albeit limited, capacity to generate petroleum. We suggest that bitumen was generated prior to or during the time of intrusion and was subsequently coked by the high temperatures of the emplaced sill. As the bitumen pooled adjacent to the sill, rapid heating led to the development of mesophase, resulting in a highly anisotropic ribbon mosaic texture on cooling, and vaporization of gases that subsequently condensed along pores, vacuoles, and fractures as pyrolytic carbon and spherulitic pyrolytic carbon. Bitumen within the underlying silty shales was also coked, but to a lesser degree. The texture of this coked bitumen looks very much like commercially produced petroleum coke. This coked bitumen differs from other reports of coked bitumen in its mode of occurrence (coke fingers in a xenolith), ribbon mosaic structure, and extremely high anisotropy and reflectance.

1. Introduction

Natural coke may be formed by the intrusion of igneous rocks (as dikes and sills) into coals and carbonaceous shales. The extreme heat associated with the intrusive rocks significantly alters the chemical and physical properties of the coal as reviewed in Rimmer et al. (2009). Intrusion of the coal typically leads to an increase in vitrinite reflectance (R_r), fixed carbon (FC), and ash content, a decrease in volatile matter (VM), and loss of visually-identifiable liptinite macerals (e.g., Clegg, 1955; Cooper et al., 2007; Crelling and Dutcher, 1968; Dutcher et al., 1966; Fredericks et al., 1985; Ghosh, 1967; Rahman and Rimmer, 2014; Rimmer et al., 2009; Saghafi et al., 2008; Stewart et al., 2005). Depending on the rank of the coal at the time of intrusion, various coke textures may result, including mosaic structure, along with fracturing, vesiculation, and an increase in density (Clegg, 1955; Crelling and Dutcher, 1968; Finkelman et al., 1998; Goodarzi and Cameron, 1989; Kisch, 1966; Kisch and Taylor, 1966; Rahman and Rimmer, 2014; Rimmer et al., 2009; Varga and Horvath, 1986). Mosaic structures form in coals that are bituminous in rank at the time of

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intrusion, but not in coals that are either very low rank (e.g., lignite) or very high rank (e.g., semi-anthracite) (Kisch, 1966). Pyrolytic carbon is derived from gases produced by high-temperature coking of the coal by an intrusion (Taylor et al., 1998). This vapor-derived carbon can subsequently be deposited along cracks and fractures (Gurba and Weber, 2001; Kisch and Taylor, 1966). In addition, liquid hydrocarbons can be generated that migrate through the coal, natural coke, or adjacent sediments and solidify into coke masses showing mosaic structure (Kisch and Taylor, 1966).

In the present study, we report on the occurrence and origin of two forms of coke produced by the intrusion of coal and carbonaceous shales of the Raton Formation (Upper Cretaceous-Paleocene) in south central Colorado; one that is formed directly by coking the coal, and one that results from coking of a liquid phase that was possibly generated prior to or during the early stages of the intrusive event (herein referred to as coked bitumen or cata-impsonite). Potential origins of this coke are considered, specifically whether it was derived from coal or from bitumen that had migrated within the carbonaceous shales or coals.

2. Procedures

2.1. Sampling

The area where samples were collected is part of the Trinidad Coal Field in south central Colorado that includes coals of Upper Cretaceous and Tertiary age (Johnson, 1961). The coalfield lies in the northern part of the Raton Basin within Colorado, and covers approximately 2850 km^2 (1100 mi^2) of Huerfano and Las Animas counties (Lee, 1917) (Fig. 1). It is bounded on the west by the Sangre de Cristo Mountains and on the north by the Wet Mountains. Within the basin, two igneous stocks called the Middle Tertiary Spanish Peaks (East and West Spanish Peaks) intrude the sedimentary cover, and from these a series of radial and sub-parallel dikes (over 500) and sills intrude throughout the basin (Crelling and Dutcher, 1968; Johnson, 1961). Dikes in the Purgatoire River valley intrude coals exposed in outcrop along the river; these dikes are thought to be 25 my old (Carroll and Hoffman, 2013). Surficial coal rank for the Raton Basin is primarily high volatile bituminous with localized increases in rank due to contact alteration around dikes and sills; along the Purgatoire River, vitrinite reflectances (R_r) of the surface coals are approximately 0.7% to 0.8%, with a small area over 0.9% towards the eastern end of the valley (Close, 1988; Crelling, 1967; Nuccio et al., 2002) (Fig. 1). At depth, coal rank for the base of the underlying Vermejo Formation ranges from high volatile C and B along the margins of the basin, and increases towards the center of the basin where it is primarily medium volatile bituminous, with the highest ranks (a small area of low volatile bituminous) underlying the southwestern corner of Las Animas County, west of Trinidad (Flores and Bader, 1999). Regional coal rank increases are thought to be mostly due to burial metamorphism, although localized increases in rank resulted from contact metamorphism associated with the dikes and sills (Close, 1988; Close and Dutcher, 2002).

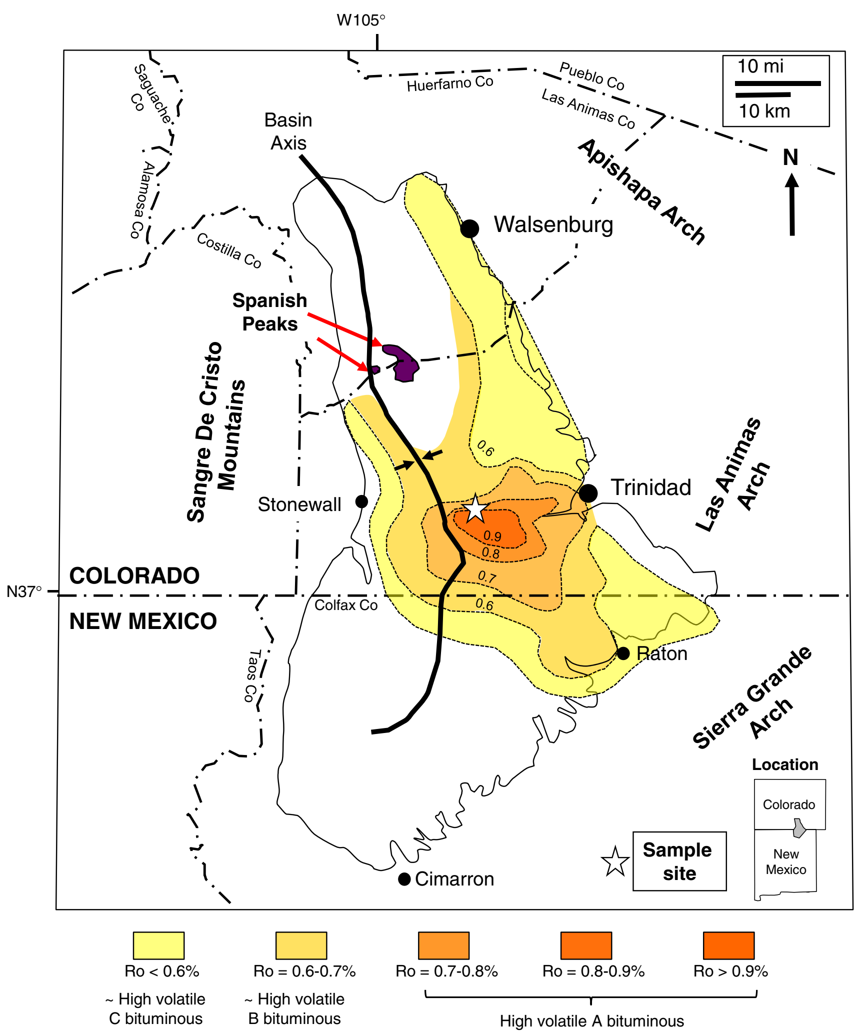

Fig. 1. Map showing regional geology of the Raton Basin and coal rank of surficial coals (adapted from Flores and Bader, 1999; coal rank distribution from Nuccio et al., 2002).