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Geochemical characteristics of oil sands fluid petroleum coke☆

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ABSTRACT

The geochemical characteristics of fluid petroleum coke from the Athabasca Oil Sands Region (AOSR) of northern Alberta, Canada were investigated. Continuous core samples were collected to 8 m below surface at several locations ($n = 12$) from three coke deposits at an active oil sands mine. Bulk elemental analyses revealed the coke composition was dominated by C (84.2 ± 2.3 wt%) and S (6.99 ± 0.26 wt%). Silicon (9210 ± 3000 mg kg^{-1}), Al (5980 ± 1200 mg kg^{-1}), Fe (4760 ± 1200 mg kg^{-1}), and Ti (1380 ± 430 mg kg^{-1}) were present in lesser amounts. Vanadium (1280 ± 120 mg kg^{-1}) and Ni (230 ± 80 mg kg^{-1}) exhibited the highest concentrations among potentially-hazardous minor and trace elements. Sequential extractions revealed potential for release of these metals under field-relevant conditions. Synchrotron powder X-ray diffraction revealed the presence of Si and Ti oxides, organically-complexed V and hydrated Ni sulfate, and provided information about the asphaltenic carbon matrix. X-ray absorption near edge structure (XANES) spectroscopy at the V and Ni K-edges revealed that these metals were largely hosted in porphyrins and similar organic complexes throughout coke grains. Minor differences among measured V and Ni K-edge spectra were largely attributed to slight variations in local coordination of V(IV) and Ni(II) within these organic compounds. However, linear combination fits were improved by including reference spectra for inorganic phases with octahedrally-coordinated V(III) and Ni(II). Sulfur and Fe K-edge XANES confirmed that thiophenic coordination and pyritic-ilmenitic coordination are predominant, respectively. These results provide new information on the geochemical and mineralogical composition of oil sands fluid petroleum coke and improve understanding of potential controls on associated water chemistry.

1. Introduction

Large volumes of petroleum coke are generated during upgrading of oil sands bitumen to synthetic crude oil. This coking byproduct is produced during thermal conversion of the non-distillable bitumen fraction to lighter hydrocarbon fractions. Over 125 kg of petroleum coke are generated per m^3 of synthetic crude oil. Approximately 20% is used as fuel at on-site upgrading facilities, while the remainder is stored in on-site deposits (AER, 2015). The total coke inventory reached 100 million tonnes in 2015 in the Athabasca Oil Sands Region (AOSR) of northern Alberta, Canada, doubling over the preceding eight years (AER, 2015). Mine closure landscapes are expected to contain greater than 1 billion tonnes of coke once oil sands mining and upgrading activities conclude (Fedorak and Coy, 2006).

Oil sands petroleum coke has potential for negative environmental impacts within mine closure landscapes. Coke has been linked to metal accumulation in plants and invertebrates (Nakata et al., 2011; Baker et al., 2012; Jensen-Fontaine et al., 2014), toxic effects on plants and invertebrates (Puttaswamy et al., 2010; Nakata et al., 2011; Puttaswamy and Liber, 2011, 2012), and alter microbial communities (Fedorak and Coy, 2006) within these landscapes. Previous research has largely focused on petroleum coke contained within oil sands mine closure landscapes; however, aeolian transport and deposition has been linked to widespread distribution of polycyclic aromatic hydrocarbons in the AOSR (Zhang et al., 2016).

Oil sands petroleum coke is derived from bitumen and, therefore, is dominated by asphaltenic, aromatic and amorphous C compounds plus substantial S and N contents. Several major (e.g., Si, Al, Fe, Ca, K, Na, Mg) and minor to trace elements (e.g., Ti, V, Ni, Mn, Cu, Mo, Zn) are typically present (Jack et al., 1979a; Anthony,

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1995; Zubot et al., 2012). Vanadium and Ni have previously been identified as principal sources of toxicity in coke leachates (Puttaswamy et al., 2010; Nakata et al., 2011; Puttaswamy and Liber, 2011, 2012). Microbial cycling of coke-derived S may also suppress methanogenesis (Fedorak and Coy, 2006), which is an important hydrocarbon degrading process in oil sands mine closure landscapes (Fedorak et al., 2003; Siddique et al., 2006, 2007, 2011; Stasik et al., 2014; Stasik and Wendt-Potthoff, 2014).

Vanadium and Ni are among the most abundant trace metals in petroleum deposits derived from organic-rich marine sediments (Lewan and Maynard, 1982). These metals are generally hosted in porphyrins to metallated asphaltenic molecular aggregates in oil sands bitumen. Coking segregates these large, complex asphaltenic molecules from lighter C compounds, producing coke characterized by elevated V and Ni contents (Anthony, 1995; Dechaine and Gray, 2010; Zubot et al., 2012). Vanadium and Ni complexes and binding sites in many petroleum systems, including crude oil and oil sands bitumen, have previously been studied (Saraceno et al., 1961; Millson et al., 1966; Jacobs et al., 1984; Fish et al., 1986; Reynolds et al., 1987; Pearson and Green, 1993; Miller and Fisher, 1999; Caumette et al., 2009). However, the fate of these metals during coking and following deposition remains poorly understood.

This study was focused on the geochemical characteristics of fluid petroleum coke produced during oil sands bitumen upgrading. Chemical and mineralogical analyses were performed on coke samples obtained from multiple deposits at an oil sands mine in the AOSR. Forms of V, Ni, S and Fe present within coke were also examined. Results from this study provide insight into the chemical composition and potential behavior of oil sands petroleum coke within mine closure landscapes.

2. Study site

The Mildred Lake mine is located approximately 35 km north of Fort McMurray, Alberta, Canada (Fig. 1). Bitumen upgrading at this open pit oil sands mine utilizes fluid coking, which involves cycling coke particles between a burner vessel and a coker vessel. Bitumen is sprayed onto coke particles heated to between 480 and 565 °C to convert non-distillable fractions to volatile compounds. Successive fluid coking cycles add layers to these coke particles, which increase in size until they exceed approximately 0.3 mm in diameter and are excluded from the coker. The resulting fluid petroleum coke is combined with oil sands process water to form a slurry, which is hydrotransported and discharged into large sub-aerial deposits at the land surface. This coke generally exhibits a uniform, fine sand texture characterized by sub-spherical particles typically ranging from 0.08 to 0.3 mm, though particles exceeding 1 mm in diameter are common (Furimsky, 1998; Kessler and Hendry, 2006).

This study was focused on three production-scale fluid coke deposits (Fig. 1): Coke Beach (CB) is an active sub-aerial deposit covering 1.5 km^2 at the western margin of Mildred Lake Settling Basin (MLSB); Coke Watershed (CW) is a 0.28 km^2 inactive deposit in MLSB with an established reclamation cover; and Coke Cell 5 (CC5) is an inactive deposit adjacent to Base Mine Lake (BML) covering 0.90 km^2 also reclaimed with an established reclamation cover. Coke deposition at CB has been ongoing since 2000, whereas CW was formed in 2003 and CC5 was formed between 1985 and 1999. Consequently, fluid petroleum coke stored within these deposits has been subjected to varied weathering intervals under different geochemical conditions.

3. Materials and methods

3.1. Sample collection and preparation

Core samples were collected along transects of the three coke deposits, with specific locations selected to capture spatial variability in geochemical conditions and weathering duration (Fig. 1).

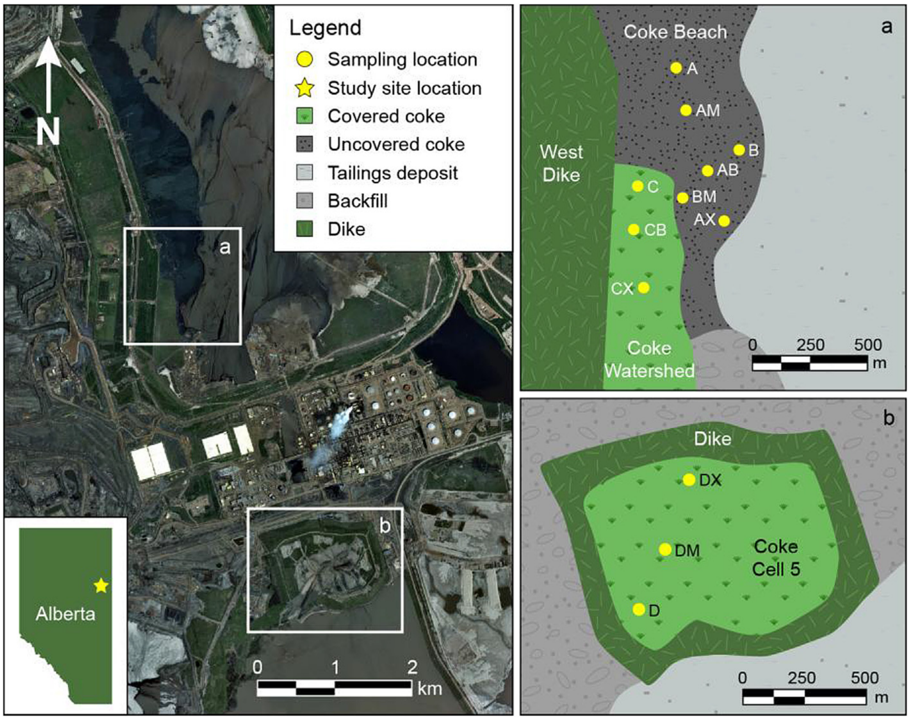

Fig. 1. Aerial photograph of the Mildred Lake mine (left) showing approximate location in Alberta, Canada (inset). Core sampling locations shown in plan views of Coke Beach and Coke Watershed (**a**), and Coke Cell 5 (**b**).