Geochemical characteristics of oil sands fluid petroleum coke

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ABSTRACT

The geochemical characteristics of fluid petroleum coke from an oil sands mine in 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 \((84.2 \pm 2.3\ \text{wt.}\ %)\) and S \((6.99 \pm 0.26\ \text{wt.}\ %)\). Silicon \((9210 \pm 3000\ \text{mg}\ \text{kg}^{-1})\), Al \((5980 \pm 1200\ \text{mg}\ \text{kg}^{-1})\), Fe \((4760 \pm 1200\ \text{mg}\ \text{kg}^{-1})\), and Ti \((1380 \pm 430\ \text{mg}\ \text{kg}^{-1})\) were present in lesser amounts. Vanadium \((1280 \pm 120\ \text{mg}\ \text{kg}^{-1})\) and Ni \((230 \pm 80\ \text{mg}\ \text{kg}^{-1})\) occurred at the highest concentrations among potentially-hazardous minor and trace elements. Sequential extractions revealed potential for release of these elements 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 aromatic 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. Slight variations among 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 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, of which total production exceeded 56 million m$^3$ in 2015 (AER, 2015). Approximately 20% of this coke 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 at the conclusion of oil sands mining and upgrading activities (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; Puttaswamy and Liber, 2012), and suppression of methanogenic 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,
Vanadium and Ni are present (Jack et al., 1979b; Anthony, 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; Puttaswamy and Liber, 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 and Bachelor, 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 complexes 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 of make-up coke 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.
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).

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). Core samples were collected using an amphibious track-mounted sonic drill rig. Four sequential 2 m long cores were collected to 8 m total depth at 12 locations CB ($n = 6$), CW ($n = 3$), and CC5 ($n = 3$). Sub-samples collected from the cores at 0.5 m depth intervals were transferred into 1 L high-density polyethylene (HDPE) bottles. These bottles were sealed, transported on ice to the University of Saskatchewan, and stored at −18°C. Prior to analysis, the frozen samples were transferred into an anoxic chamber ($\leq 5$ vol. % $\text{H}_2$, balance $\text{N}_2$) where they
were thawed and vacuum-filtered. Sub-samples were collected into 40 mL amber glass vials, which were sealed and stored at −18°C. Once frozen, the samples were freeze-dried and then stored in an anoxic chamber (≤ 4 vol. % H₂, balance N₂), where all subsequent sample preparation occurred. Samples for optical and spectroscopic analyses were prepared as thin sections by embedding coke samples in spectrally-transparent epoxy (EPO-TEK 301, Epoxy Technology Inc., USA), mounting off-cuts to quartz glass slides using ethyl cyanoacrylate adhesive, and lapping and polishing to a final thickness of 30 μm without water.

3.2. Optical Microscopy and Surface Area Analysis

Optical examination of coke samples in thin section was performed using a reflected-light petrographic microscope (Eclipse LV100POL, Nikon Instruments, Japan). Brunauer-Emmett-Teller (BET) N₂ adsorption isotherms (Brunauer et al., 1938) were measured (Nova 2200e, Quantachrome Instruments, USA) to determine specific surface area of freeze-dried samples from the three coke deposits.

3.3. Elemental Analyses

Bulk elemental analyses were performed for samples from a range of depths and locations at CB (n = 17), CW (n = 3), and CC5 (n = 8). Following pulverizing and digestion by Li-borate fusion, major (Si, Al, Fe, Ti, Ca, K, Na, Mg, P, Mn, Cr) and trace element (V, Ni, Zr, Sr, Ba, Ce, La, Nd, Co, Y) contents were determined using inductively coupled plasma optical-emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS), respectively. Modified aqua regia (i.e., 1:1:1 HNO₃:HCl:deionized H₂O) digestion for 1 hour at 80°C followed by ICP-MS detection was employed for select elements (Mo, Cu, Zn, Pb). Total C and S contents were determined by combustion and infrared detection of evolved CO₂ and SO₂ (CS230 Carbon/Sulfur Determinator, Leco Corporation, USA). A centered log ratio
transformation was performed prior to statistical analysis using the Pearson product-moment correlation. Individual element concentrations for a given sample were divided by the geometric mean of all element concentrations for the sample. The $\log_{10}$ of the resulting quotient was calculated to generate an open dataset with the sum of all elemental values equaling zero. All statistical results are reported for the same sample size ($n = 28$) and a 5% significance level (i.e., $p = 0.05$).

Table 1. Sequential extraction protocol used to assess element release under different conditions.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Reagents</th>
<th>pH</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1: water soluble</td>
<td>deionized H$_2$O</td>
<td>7.5</td>
<td>0.6 h</td>
</tr>
<tr>
<td>F2: exchangeable</td>
<td>0.58 M Na$_2$HPO$_4$·7H$_2$O  0.42 M NaH$_2$PO$_4$·H$_2$O</td>
<td>6.7</td>
<td>16 h</td>
</tr>
<tr>
<td>F3: reducible</td>
<td>0.12 M Na-ascorbate  0.6 M Na-bicarbonate  0.17 M Na-citrate</td>
<td>8.0</td>
<td>24 h</td>
</tr>
</tbody>
</table>

3.4. **Selective Extractions**

Selective extractions were performed to examine element release under relevant field conditions. The protocol was developed based upon previous research (Jack, et al., 1979; Blackmore, et al., 1996; Kessler and Hendry, 2006; Zubot, et al., 2012) and targeted three fractions: (F1) water soluble; (F2) exchangeable; and (F3) reducible (Table 1). Coke samples ($n = 20$) were thawed, vacuum-filtered, freeze-dried and stored under anoxic conditions. These samples were not ground to avoid altering specific surface area and artificially enhancing element release. Extractions were performed in triplicate by combining 1.0 g of sample with 40 mL of extractant solution in 50 mL PE centrifuge tubes. The tubes were placed on a rotary shaker, which was operated at $6 \times g$ (180 rpm) for a predetermined time (Table 1). Samples were then centrifuged at $2934 \times g$ (4000 rpm) for 40 min in the dark and the supernatant was passed through 0.1 μm polyethersulfone (PES) filter membranes and acidified to pH < 2 with
concentrated trace-metal grade HNO$_3$ (OmniTrace Ultra, Millipore). Samples from 90% of triplicate extractions were pooled prior to analysis by ICP-MS and ICP-OES. Non-zero concentrations of elements for blank extractant solutions were subtracted from sample extraction concentrations.

3.5. X-Ray Diffraction

Synchrotron-based powder XRD was performed on beamline 08-B1-1 (CMCF-BM) at the Canadian Light Source. Samples were pulverized to less than 0.1 µm and loaded into 0.8 mm diameter polyimide capillary tubes and sealed with ethyl cyanoacrylate adhesive. Samples were mounted on a goniometer and continuously rotated around the longitudinal axis during 90-second exposures to an 18 keV ($\lambda = 0.68879$) X-ray beam with a 200 µm spot size. Two-dimensional diffraction patterns were collected using a high-resolution back-illuminated charge-coupled device (CCD) area detector (Rayonix MX300-HE) positioned approximately 0.25 m behind the sample. Data reduction was performed using GSAS-II crystallography data analysis software (Toby and Von Dreele, 2013). The detector geometry was calibrated using a lanthanum hexaboride standard. The capillary tube background pattern was subtracted and resulting patterns were radially integrated using a 2θ resolution of 0.005°. Phase identification was performed using Match! (Version 3.1.0, Crystal Impact GbR, Germany) and the Crystallography Open Database (Gražulis et al., 2009).

3.6. Electron Microanalysis

Scanning electron microscopy (SEM; Phenom G2 Pure, Phenom-World B.V., The Netherlands) was used to examine the external morphology and internal structure of coke particles. Bulk freeze-dried samples were mounted on carbon tape and examined without coating using a 5 kV acceleration voltage and backscattered electron detector. Electron microprobe
analysis (EMPA; JXA-8600 Superprobe, JEOL Ltd., Japan) was used to examine the chemical composition of discrete particles hosted within coke prepared as thin sections. These sections were coated with a 200 Å thick carbon layer prior to EMPA analysis.

3.7. **X-ray Absorption Spectroscopy**

Bulk X-ray absorption near edge structure (XANES) spectroscopy was performed at the Canadian Light Source (CLS) synchrotron. Vanadium and Ni K-edge XANES spectra were collected on beamline 06-ID-1 (HXMA), whereas Fe and S K-edge XANES spectra were obtained on beamline 06-B1-1 (SXRMB). For both beamlines, the incident X-ray energy was selected using a monochromator fitted with paired Si(111) crystals and the beam spot size was focused to 1 mm (vertical) by 3 mm (horizontal).

Samples for V and Ni K-edge XANES analyses were prepared by packing freeze-dried, ground coke into polytetrafluoroethylene sample holders (20 mm × 4 mm × 0.5 mm thick) between two layers of 25.4 μm thick polyimide tape. Samples were stored under anoxic conditions and transported to the CLS in an anoxic vacuum container. Replicate spectra ($n = 4$) for samples were collected in fluorescence mode using a 32-element Ge detector (Canberra Industries Inc., USA) at HXMA for V and Ni data. Energy calibration utilized transmission spectra obtained for V and Ni foils positioned between two ion chambers downstream of the samples. Duplicate spectra for reference compounds (Sigma-Aldrich, MO) including vanadyl octaethyl porphyrin (VOOEP), vanadyl tetraphenyl porphyrin (VOTPP), Ni octaethyl porphyrin (NiOEP), and Ni tetraphenyl porphyrin (NiTPP) were also obtained.

Samples for Fe and S K-edge XANES measurements were ground using an agate mortar and pestle, and mounted to a Cu plate with carbon tape. The mounted samples were transported to the CLS under an anoxic atmosphere in vacuum desiccator. The sample holders were
transferred into the end station, which was operated under high vacuum ($-5 \times 10^{-8}$ Torr).

Replicate fluorescence spectra for samples ($n = 3$) and reference compounds ($n = 2$) were obtained using a four-element Si drift detector (XFlash 4040, Bruker Corporation, USA). Reference compounds included elemental S, gypsum [CaSO$_4$$\cdot$2H$_2$O], pyrite [FeS$_2$], magnetite [Fe$_3$O$_4$], and Fe$_3$(SO$_4$)$_2$. Reference spectra for additional organic and inorganic S compounds were obtained from the European Synchrotron Research Facility XANES database. Spectra for ilmenite (FeTiO$_3$), akaganeite (β-FeOOH), and lepidocrocite (γ-FeOOH) were obtained from the Advanced Light Source beamline 10.3.2 X-ray absorption spectroscopy (XAS) database.

Data processing and analysis was performed using the Athena (Version 0.9.21) module of the Demeter software package (Ravel and Newville, 2005). Energy calibration, pre-edge background subtraction and post-edge normalization were performed prior to linear combination fitting (LCF). A fitting range of -25 eV to +60 eV relative to the theoretical K-edge energy was employed. Individual component weights and the sum of weights were not constrained during fitting. The R-factor was used for primary goodness of fit assessment, while component weights, weighting sums, and fit residuals were also considered. Finite difference modelling of the near-edge structure (FDMNES) (Bunau and Joly, 2009) of the V and Ni porphyrin molecules were performed to assess impacts of distortions in metallated porphyrin cores on K-edge XANES spectra. Porphyrin molecular structures proposed by Molinaro and Ibers (1976), Meyer (1972) and Maclean et al. (1996) were used as base cases for this modelling (Supporting Information, Tables S6–S8).
4. Results and Discussion

4.1. Physical Characteristics

The mean specific surface area $4.5 \pm 2.8 \text{ m}^2 \text{ g}^{-1} (n = 20)$ was generally consistent with values of $10 \text{ m}^2 \text{ g}^{-1}$ (Har, 1981), $11 \text{ m}^2 \text{ g}^{-1}$ (Fedorak and Coy, 2006), $6 \text{ m}^2 \text{ g}^{-1}$ (Zubot, 2010), and $8 \text{ m}^2 \text{ g}^{-1}$ (Pourrezaei et al., 2014) previously reported for fluid petroleum coke generated at the study site. Micro-pores are assumed negligible in fluid coke (Har, 1981; Pourrezaei et al., 2014) and measured surface areas are, therefore, attributed to primary surfaces. The low surface area of fluid petroleum coke (i.e., $< 10 \text{ m}^2 \text{ g}^{-1}$), as compared to that of most activated carbon materials (i.e., $> 750 \text{ m}^2 \text{ g}^{-1}$), is attributed to the low porosity (Pourrezaei et al., 2014). Pores measuring between 2 and 40 nm (mesopores) dominate surface porosity of coke and are therefore important for adsorption reactions (Pourrezaei et al., 2014). Thin-section analysis by SEM revealed successive concentric sub-spherical layers within fluid coke samples from this study (Fig. 2a). Micro-structures perpendicular to concentric layers (Fig. 2b) likely formed during rapid heating and cooling cycles during residual bitumen layer addition within the coker.

Fig. 2. (a) Optical reflected light image of coke particle section showing visible concentric ring micro-structure. (b) Back-scattered electron micrograph of interior of fractured coke particle showing perpendicularly-radiating micro-structures. Scale bars represent 50 µm.
4.2. Chemical Characteristics

Coke was largely composed of C (84.2 ± 2.3 wt. %) and contained S (6.99 ± 0.26 wt. %) at approximately 12 times lower concentration (Fig. 3). 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 the next most abundant elements. Remaining elements with mean concentrations greater than 10\(^2\) mg kg\(^{-1}\) followed the general order: V > Ca > K > Na > Mg > Ni > P > Mn (Fig. 3). Several potentially-hazardous elements including Mo, Cu, Zn, and Pb exhibited mean concentrations less than 10\(^2\) mg kg\(^{-1}\) (Supporting Information, Table S2). Volatile elements lost on ignition including H (1.50 to 1.67 wt. %), N (1.3 to 1.6 wt. %), and O (2.3 to 2.5 wt. %) are also major components of fluid petroleum coke (Har, 1981; Chung et al., 1996; Kessler and Hendry 2006).

![Fig. 3. Results of bulk elemental analyses for samples (\(n = 28\)) from CB, CW and CC5. Boxes define 25\(^{th}\), 50\(^{th}\), and 75\(^{th}\) percentile concentrations, while lower and upper whiskers denote 10\(^{th}\) and 90\(^{th}\) percentile concentrations and open circles signify outliers. Values for elements with mean concentrations below 10 mg kg\(^{-1}\) are not shown.](https://doi.org/10.1016/j.apgeochem.2016.11.023)
Elemental concentrations were generally consistent with values reported in previous studies (Table 1). However, measured Ni concentrations were approximately one half of previously-published values except for those reported by Zubot et al. (2012). These previous studies have commonly analyzed fresh coke sampled directly from the coker (Jack et al., 1979; Har, 1981; Zubot et al., 2012). Kessler and Hendry (2006) and Chung et al. (1996) examined a limited sample size from a single coke deposit and suggested that weathering and aging did not alter the overall chemistry of coke. However, it is possible that certain elements are more readily leachable from the coke matrix. It is unclear whether variability among studies is due to sampling source or bitumen feedstock, or whether differences in sample size and analytical methods may also produce some variability.

Table 2. Comparison of select element contents for samples of oil sands fluid petroleum coke from the Mildred Lake mine.

<table>
<thead>
<tr>
<th>Source</th>
<th>n</th>
<th>C (wt. %)</th>
<th>S (wt. %)</th>
<th>Fe (mg kg⁻¹)</th>
<th>V (mg kg⁻¹)</th>
<th>Ni (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>coker</td>
<td>1</td>
<td>82</td>
<td>3.3</td>
<td>2600</td>
<td>1600</td>
<td>660</td>
</tr>
<tr>
<td>coker</td>
<td>10</td>
<td>79−82</td>
<td>5.8−7.1</td>
<td>4100−6200</td>
<td>1500−1900</td>
<td>550−710</td>
</tr>
<tr>
<td>deposit</td>
<td>5</td>
<td>81−84</td>
<td>6.2−6.8</td>
<td>3500−6700</td>
<td>1600−1800</td>
<td>480−520</td>
</tr>
<tr>
<td>deposit</td>
<td>3</td>
<td>78−84</td>
<td>7.0−8.1</td>
<td>3000−8700</td>
<td>1100−1500</td>
<td>470−590</td>
</tr>
<tr>
<td>coker</td>
<td>29</td>
<td>75−89</td>
<td>5.6−7.2</td>
<td>4500−8400</td>
<td>1000−1400</td>
<td>35−68</td>
</tr>
<tr>
<td>deposit</td>
<td>28</td>
<td>80−89</td>
<td>6.4−7.6</td>
<td>3200−7600</td>
<td>1100−1500</td>
<td>140−460</td>
</tr>
</tbody>
</table>

a) Jack et al. (1979a)
b) Har (1981)
c) Chung et al. (1996)
d) Kessler and Hendry (2006)
e) Zubot et al. (2012)
f) this study
Bulk C and S concentrations exhibited strong positive correlation \((R = 0.96)\). All elements that were negatively correlated with C, including Fe, Ti, P, Zr, Ce, Nd and Y, were also negatively correlated with S at similar \(R\) values. Vanadium was very strongly correlated with both C \((R = 0.83)\) and S \((R = 0.89)\), whereas Ni was not correlated to either C \((R = 0.17)\) or S \((R = -0.20)\). Vanadium exhibited moderate negative correlations with Ti \((R = -0.71)\) or Fe \((R = -0.45)\) and sequential extractions revealed that V was associated with the exchangeable and water soluble fractions. Bulk elemental correlations between Ni and other major and minor elements were generally weak and less significant compared to V. Conversely, sequential extraction results suggested that Ni was predominantly associated with the exchangeable fraction (Fig. 4). These findings indicate that V could be mobilized by infiltrating precipitation, whereas both V and Ni may be mobilized in the presence of exchangeable ions (e.g., \(\text{Na}^+\), \(\text{HCO}_3^-\), \(\text{SO}_4^{2-}\)) commonly present at elevated concentrations in oil sands process-affected water (Allen, 2008).

Iron and Ti exhibited strong correlations \((R = 0.80)\), which is indicative of their association with oxide phases. Iron association with the reducible fraction during sequential extractions (Fig. 4) was also indicative of Fe-containing oxide phases within coke grains. Discrete Ti crystals were observed with EMPA throughout the coke matrix (Supporting Information, Fig. S2). However, distinct regions within analyzed coke grains exhibited a higher concentration of collocated sub-micron sized Fe and Ti particles. Correlations between bulk Si, Al, K, and Mg \((R = 0.49–0.67)\) were attributed to their co-occurrence in aluminosilicate and clay minerals contained within coke grains. This interpretation was supported by EMPA analyses, which revealed the presence of distinct Si-bearing particles and sub-micron sized particles containing Al, K, Mg, and Si (Supporting Information, Fig. S2). Weak but significant correlation of P with the rare earth elements (REEs) Ce \((R = 0.38)\), Nd \((R = 0.41)\) was attributed to the presence of
monazite, which was corroborated by EMPA results that revealed co-occurrence of La, Ce, Nd, and Y in discrete P-bearing particles. Elements commonly found in monazite (i.e., Ce, La, Nd, Y) also exhibited strong correlations with bulk Ti, Fe, and Zr contents. These correlations are likely due to association of Fe- and Ti-bearing phases with monazite particles in the bitumen ore. Correlation between Sr and Ca ($R = 0.50$) was indicative of the presence of carbonate minerals, which were previously reported (Kessler and Hendry, 2006).

![Graph](https://example.com/graph.png)

**Fig. 4.** Box and whisker plots of sequential extraction results ($n = 20$) for V, Ni and Fe in water soluble (F1), exchangeable (F2), and reducible (F3) fractions. Boxes span interquartile range (i.e., 25th to 75th percentile) and include median values (horizontal line). Whisker caps represent the 10th and 90th percentile values and outliers are open circles.

The elemental composition of coke was generally consistent among and within the three coke deposits. While mean elemental concentrations were similar (within 1 σ) among deposits, some spatial trends were observed. The mean Fe and Ti concentrations in coke samples obtained from CB are higher, by 1.3 and 1.5 times, respectively, compared with the other two deposits. These higher concentrations likely corresponded to variations in ore composition or, potentially, fine-grained inorganic mineral particulate contributed by fluid fine tailings stored in MLSB. The
presence of Fe and Ti is geochemically relevant as oxide particles hosted in coke may act as adsorption sites for aqueous trace metals (Blackmore et al., 1996; Zubot et al., 2012).

Fig. 5. Synchrotron powder X-ray diffraction patterns for select fluid coke samples.

4.3. Mineralogical Characteristics

X-ray diffraction patterns for all samples were dominated by the aromatic, asphaltenic molecules that comprise the bulk of the coke matrix (Fig. 5). Both the inorganic, crystalline mineralogical phases and the organic, amorphous and aromatic asphaltenic carbon matrix were investigated. Synchrotron PXRD revealed more information about both the structure of the carbonaceous component in coke and the crystalline phases hosted therein. Synchrotron PXRD facilitated the detection of several crystalline phases within the asphaltenic matrix that were not discernible using a conventional Cu Kα source XRD due to poor 2θ resolution (Supporting Information, Fig. S1). While XRD is well suited to, and more commonly used in, the

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identification of crystalline phases, the technique also provided detailed structural information about the volumetrically-larger non-crystalline component.

4.3.1. **Inorganic components**

The crystalline fraction contained crystalline aromatic C, SiO$_2$, TiO$_2$, a hydrated Ni sulfate phase (Angel and Finger, 1988), and an organically-complexed V phase (Miyoshi et al., 2012) (Supporting Information, Table S3). Muscovite or a similar phyllosilicate phase was detected in several samples, whereas pyrite [FeS$_2$] and calcite [CaCO$_3$], which have previously been reported in oil sands petroleum coke (Kessler and Hendry, 2006), were not detected.

The ash (non-carbonaceous) content of fluid coke typically ranges from 4 to 7 wt. % due to clay particles in the bitumen ore (Jack et al., 1979a; Chung et al., 1996). Har (1981) reported that the ash content of fluid coke from the study site ranged from 7 to 8.5 wt. %. Previous XRD analysis revealed that the fluid petroleum coke ash content is dominated by quartz, kaolinite, illite, feldspars, anhydrite, and hematite are the dominant crystalline phases (Jang and Etsell, 2006).

Disseminated Ti- and Fe-bearing phases and aluminosilicates were detected by EMPA within most coke particles. Discrete quartz, calcite, dolomite, and Fe-sulfide (e.g., pyrite) particles were detected within some coke particles using this technique. Monazite (La, Ce) crystals were less frequently observed during EMPA analysis of these samples. Since these phases were observed as inclusions within coke particles – occasionally forming the particle core – they were most likely derived from the ore rather than being formed during coking or introduced post-deposition. This interpretation is consistent with previous observations that showed that Ti- and Zr-bearing minerals present in oil sands ore are concentrated in the froth during bitumen recovery (Kaminsky, et al., 2008). These and other minerals – including Ti
oxides, Fe sulfides, Fe carbonates, Fe-Ti oxides, and REE oxides – were often observed as intergrowths with silicates in bitumen ore (Kaminsky et al., 2008).

4.3.2. Organic components

Diffraction patterns for samples from all deposits and depths were similar with respect to the carbonaceous matrix. These patterns are consistent with those reported for coal by Lu et al. (2001) suggesting that the structural forms of carbon are comparable between these two materials. Coal contains short-range, localized, crystalline, graphitic structures, but also contains a large proportion of disorganized, amorphous carbon (Lu et al., 2001). This variety gave rise to three main amorphous carbon diffraction peaks, matching those observed for coke samples (Fig. 5). These peaks loosely approximated the locations of equivalent reflections in pure, crystalline graphite, but were far broader due to the amorphous content. The peaks were located at ~11.04°, ~19.34°, and ~34.06° in units of 2θ, or 0.140, 0.244, and 0.425 in units of [sinθ / λ]. The first corresponds to the (002) band which arises from the interlayer spacing (Lu, et al., 2001). The last two correspond to the (10) and (11) bands which arise from the hexagonal aromatic ring structure (Yen et al., 1961; Lu et al., 2001).

The mean layer distance (d_m) between aromatic sheets was determined to be 3.58 Å using the position of the (002) band. This distance is slightly larger than that obtained for electrode pitch binder cokes (3.47-3.52 Å) (Pollack and Alexander, 1960) and considerably larger than that of pure graphite (3.34 Å) (Yen et al., 1961). The interlayer distance between successive aromatic sheets is a function of sheet flatness, the presence of sheet imperfections, and the inclusion of heteroatoms like S or metals in the asphaltenic micelles. Clusters composed of fewer aromatic sheets can display larger interlayer spacing (Pollack and Alexander, 1960). Pure graphite is composed of flat aromatic sheets free from inclusions or imperfections. Bitumen-derived coke
may contain more impurities, and thus more asphaltenic sheet imperfections, than electrode binder pitch cokes. The small asymmetric shoulder on the left side of the (002) band was the $\gamma$ band (Fig. 5), which was found at $-8.93^{\circ}$ 2θ or 0.113 $\sin\theta / \lambda$. The distance between saturated portions of the molecules ($d_\gamma$) was calculated to be 5.53 Å which was slightly smaller than distances reported by Yen et al. (1961) for asphaltenes in bitumen (5.6–6.0 Å). This band arises from the presence of saturated aliphatic side chains attached to the edges of aromatic carbon crystallites (Lu et al., 2001). Asphaltene micelle breakage, subsequent hydrogenation, saturation, and addition of more aliphatic side chains during coking could explain the decrease in mean distance between saturated side chains.

4.4. **Bulk XANES Analyses**

4.4.1. **Vanadium and nickel**

Bulk V K-edge XANES spectra for all samples exhibited similar white-line shapes (Fig. 6a), characterized by a flattened, tilted, asymmetric white-line (features 2-3) centered at $\sim 5491$ eV and a pre-edge peak (feature 1) roughly 0.45 times the height of the absorption edge positioned at 5469 eV. These features are broadly consistent with organically-complexed V(IV). While vanadyl- (VO$^{2+}$) porphyrin complexes dominate V speciation in heavy oil and bituminous deposits (Lewan and Maynard, 1982), several differences between bulk coke and vanadyl-porphyrin reference spectra were noted. These differences included pre-edge peak splitting, pre-edge peak magnitude decrease, and flattening of the white-line. Consequently, model porphyrin reference compounds were poor models for measured bulk V K-edge spectra. Finite difference modelling of the near-edge structure (FDMNES) (Bunau and Joly, 2009) of model porphyrins (Molinaro and Ibers, 1976) revealed that the V pre-edge feature shape and magnitude were sensitive to small variations (i.e., $\pm 0.02$ Å) in first-shell interatomic distances (Supporting
Information, Fig. S3). This modelling demonstrated that the pre-edge peak-splitting results from either a slight decrease in V-O bond distance or a slight increase in V-N distance. However, neither of these distortion mechanisms flattened the near-edge region to the extent observed for the V K-edge spectra.

Vanadium K-edge XANES spectra of pre-coking asphaltene (Fig. 6a) exhibits considerable broadening of most near-edge features compared to pure porphyrins (Lytle, 1983). The high-temperature, oxidizing conditions present during fluid coking (Asaoka et al., 1983) may promote some replacement of N atoms by O atoms around the porphyrinic metal centre in asphaltene micelles. Therefore, square-pyramidal O coordination found in VOPBD (Hon et al., 1965) was also considered. A V K-edge XANES spectrum for VOPBD from Wong et al. (1984) was used as a proxy for this coordination type during LCF analysis (Fig. 6a). Conversion of porphyrinic V to octahedrally-coordinated V was previously noted by Miller and Fisher (1999) in association with thermal treatment of asphaltenes (hydrocracking). Vanadium (III) octahedrally coordinated to O atoms exhibits a small pre-edge peak shifted to slightly higher energy as compared with the porphyrinic pre-edge peak (Maylotte et al., 1981; Wong et al., 1984). An XANES spectrum for V(III) substituted into distorted octahedral sites in the phyllosilicate mineral roscelite (Maylotte et al., 1981; Wong et al., 1984) displayed two distinct, asymmetrical peaks at ~5486 and ~5499 eV (features 2 and 3), straddling the energy of the single rounded porphyrin peak at ~5491 eV. Octahedral coordination of V(III) with O can also occur in V$_2$O$_3$ and as V substituted in some spinels and ferro-titanian oxide minerals (Balan et al., 2006). However, the near-edge doublet peak feature in these compounds was not consistent with sample V K-edge spectra and, therefore, produced poor LCF results. Combining spectra for the square-pyramidal V(IV)-N, V(IV)-O, and octahedral V(III)-O coordination types flattened the XANES
line shape and better explained the pre-edge peak magnitude decrease and splitting in coke spectra (Fig. 6a). Fitting of bulk coke suggested that square-pyramidal N and O coordination dominated and that distorted octahedral V(III)-O coordination was a minor component. Including VOPBD-like coordination in fits decreased R-factors by roughly one-half and considerably minimized fitting residuals. Reference spectra for V$_2$O$_3$(s), V$_2$O$_4$(s), V$_2$O$_5$(s), V$_4$O$_7$(s), and metallic V$_3$(s) were initially included in LCF analysis; however, the V K-edge lineshapes for these reference compounds were inconsistent with sample spectra.

The product asphaltenes in coke, which dominate the carbonaceous component of coke, retain metallo-porphyrins from the bitumen source (Asaoka et al., 1983; Bausell et al., 1992). However, the removal of vanadyl-porphyrin metal centers and the breakage of weak organic S bonds were found to be the main reactions leading to the breakdown of the irregular and structurally-weaker portions of asphaltenic micelles. The vanadyl ions released from these portions may remain loosely bound or may form complexes with non-asphaltenic or inorganic phases during coking. Zuliana et al. (2016) identified inorganic V-bearing nanoclusters in oil sands fluid petroleum coke, which supports the presence of a non-porphyrin fraction. Vanadium associated with this non-porphyrin fraction could be more labile and, therefore, more readily transferred to the aqueous phase during weathering. Nitrogen sites and organo-metallic Ni sites are less important in mediating cracking reactions and, therefore, remain more intact within asphaltenic micelles (Asaoka et al., 1983).

Bulk Ni K-edge XANES spectra for bulk coke were characterized by four main features (Fig. 6b). A small pre-edge feature at 8334 eV (feature 1) and shoulder at 8340 eV (feature 2) were generally consistent among all samples. Like V, porphyrins are also an important host for Ni in petroleum systems (Lewan and Maynard, 1982; Lewan, 1984). Two peaks at ~8352 eV
(feature 3) and ~8359 eV (feature 4) on the principal edge were generally consistent with Ni porphyrins including NiOEP and NiTPP. However, these peaks fluctuated in relative magnitude among bulk samples, indicating slight variations in the Ni coordination environment. The NiOEP standard produced the best fit to most sample Ni K-edge XANES spectra. Nickel-porphyrin references could not, however, be used to reproduce the sample spectra. This reference compound was an especially poor fit to the magnitude of the feature observed at ~8352 eV (feature 3).

Spectra reported by Lytle (1983) for asphaltenes appeared intermediary between the sample Ni K-edge XANES spectra and the NiOEP reference spectrum (Fig. 6b). The sharp shoulder at ~8340 eV (feature 2) was shifted to slightly higher energy from porphyrin to asphaltene to coke. This shoulder and the spectral lineshape after 8370 eV are consistent between the porphyrin standard and the asphaltene spectrum (Lytle, 1983), but both regions become broadened and smoothed in the sample spectra. Features 3 and 4 exhibited a larger difference in magnitude in the NiOEP reference compared to Ni K-edge spectra for the coke samples and the reference asphaltene spectrum. These spectral relationships support the conclusion that organo-metallic Ni sites show increasing distortion and variability as porphyrins are incorporated into asphaltenes, and then subsequently as asphaltenes undergo coking. Numerous variations in metal site coordination may have contributed to the broadening of spectral features in bulk XANES spectra. Modelling of the near-edge structure for the NiOEP and NiTPP reference compounds could not fully describe the experimental Ni K-edge XANES for these porphyrin standards. However, this XANES modelling showed that slightly increased interatomic distances between Ni and the surrounding N and C atoms increased the relative magnitude of the lower energy peak (feature 3) in the porphyrin spectra (Supporting Information, Fig. S4). Subtle variations in
asphaltene metal site chemistry may, therefore, contribute to observed fluctuations in the sample Ni K-edge XANES spectra (Fig. 6b).

**Fig. 6.** Comparison of bulk K-edge XANES spectra for V (a) and Ni (b), with spectra for asphaltene (Lytle, 1983), porphyrin-like standards (VOOEP, VOTPP, VOPBD, NiOEP, NiTPP), and inorganic standards (roscoelite, NiO). Solid lines represent measured spectra and open circles denote results of LCF analysis (Supporting Information, Tables S4, S5).

Inorganic Ni reference compounds including NiO, NiSO₄•6H₂O, Ni(OH)₂, NiCO₃•2Ni(OH)₂ exhibited a prominent, narrow white-line feature centered between 8349 and 8352 eV (Fig. 6b). An increase in magnitude of feature 3 relative to feature 4 observed in sample spectra could, therefore, indicate the presence of inorganic Ni compounds. Statistically strong...
LCF results (R-factor < 0.0060) for Ni K-edge XANES for coke samples were achieved by including the NiOEP, NiTPP, and NiO reference compounds. The Ni K-edge spectrum for NiO was consistent with octahedral Ni-O coordination, similar to measured V K-edge XANES results (Fig. 6) and to coordination proposed by Miller and Fisher (1999). Like V, non-porphyrin Ni may preferentially contribute Ni to the aqueous phase during weathering. However, XRD analysis (Fig. 5) suggested the presence of Ni-SO$_4$ rather than a Ni-O phase. Furthermore, Jack et al. (1979b) reported Ni and SO$_4$ leached at a 1:1 molar ratio from coke produced via flexicoking (Jack et al., 1979b). However, fitting of the measured coke Ni K-edge XANES with NiOEP, NiTPP, and NiSO$_4$•6H$_2$O standard spectra yielded statistically (R-factor ≈ 0.011) and larger residuals.

4.4.2. Sulfur and iron

Sulfur K-edge XANES spectra for all samples (Fig. 7a) revealed a prominent white-line peak at 2473.8 eV (feature 1), a smaller secondary feature at 2475.8 eV (feature 2), and a broad plateau from 2480-2483 eV (feature 3). The peaks correspond well with values for thiophenic sulfur (Zeng et al., 2013). Discrepancies were apparent in the S K-edge XANES spectra lineshape compared to the dibenzothiophene standard (Bohic et al., 2008) at energies greater than 2478 eV. Features 1 and 2 in coke sample spectra were also dampened and broadened compared to the dibenzothiophene reference spectra. Sulfur K-edge XANES spectra obtained for coke samples were generally consistent with those for asphaltenes reported by George and Gorbaty (1989) and Pomerantz et al. (2014), which was attributed to the large asphaltene component of coke. George and Gorbaty (1989) concluded that S in asphaltenes is almost entirely thiophenic. Bejarano et al. (2003) came to a similar conclusion with X-ray photoelectron spectroscopic (XPS) analysis of fluid coke from the Mildred Lake mine. While the local atomic
interaction between S sites and the surrounding aromatic cycles are distinctly thiophenic, longer-range interactions into the asphaltene micelle structure do not possess the same pure thiophenic character found in reference compounds.

Iron K-edge XANES spectra exhibited greater variability among samples compared to other elements (Fig. 7b). The spectra were characterized by three main features: a broad low-magnitude pre-edge feature centred at 7113.5 eV (feature 1), and a rounded white-line feature centred at 7132 eV (feature 3), and a variable double-shoulder feature found between these two energies (feature 2). These spectra could not be fit using a single reference standard. Distinct Fe-S grains were observed in coke particles using EMPA. Both bulk-scale chemistry and microspatial spectroscopic relationships were observed between Fe and Ti, suggesting the presence of an ilmenite-like phase. Pyrite, ilmenite, magnetite, akaganeite, lepidocrocite, goethite, hematite, Fe(III) sulfate, jarosite, siderite, and ferrosmectite spectra were included in the fitting process. Combinatorial LCF of the near-edge spectra was performed, first by assessing all unique combinations of two of the eleven Fe standards, for each of the nine spectra. While the best of these combinations of two standards provided statistically acceptable fits (R-factor < 0.010), the residuals between fit and experimental spectra were large. Fitting was also performed using all unique combinations of three of the eleven Fe standards. The best of these fits were superior both statistically (R-factor < 0.005) and with respect to fitting residuals. The best fits for all spectra included pyrite (25-35 %), magnetite or ilmenite (40-60 %), with the balance comprising one of akaganeite, lepidocrocite, or Fe(III) sulfate (15-25 %).
**Fig. 7.** Comparison of bulk coke S (a) and Fe (b) XANES spectra with spectra for thiophene (Bohic et al., 2008), pyrite, ilmenite, magnetite, lepidocrocite, and iron(III) sulfate.

5. Conclusions

This study examined the linkage between the geochemical characteristics and the bulk form of trace elements in fluid petroleum coke deposits at an oil sands mine in northern Alberta, Canada. Relationships between changes in chemistry and trace element speciation were observed in bulk elemental and mineralogical analyses, though these fluctuations were generally small. Coke samples contained a variety of mineral phases as inclusions and as disseminated micron-scale particles. Mineralogy, bulk elemental composition, and bulk speciation of V and Ni
fluctuated only slightly among depths, deposits of different ages, and storage conditions. Weathering appeared to have limited influence on bulk coke chemistry.  

Linear combination fitting of bulk V K-edge XANES suggests that V is hosted in a range of different atomic coordination environments. Square-pyramidal VO$^{2+}$ coordination with N (porphyrinic) and O (dionatic/altered porphyrinic) dominated V comportment; however, distorted octahedral V(III) coordination with O – consistent with that observed in the phyllosilicate rosoelite – was present. Bulk Ni chemistry was characterized by porphyrinic species, with small deviations resulting either from asphaltenic metal site structural heterogeneity or inorganic coordination as an oxide or hydrated sulfate phase. The dominant form of S is thiophenic coordination, attributable to association with the asphaltenic coke matrix. Iron appears to be hosted in a combination of pyrite and ilmenite-like phases, with a tertiary component comprised of oxyhydroxides or sulfates.  

Although porphyrin complexes dominated bulk V and Ni speciation, the minor non-porphyrin V and Ni fractions are expected to be less stable and potentially more susceptible to weathering. Sequential extractions suggested that both V and Ni may be mobilized under field conditions. This finding is consistent with previous studies reporting elevated V and Ni concentrations in coke leachates under field conditions. Since metal porphyrin complexes are resistant to weathering, non-porphyrinic complexes could be an important source of dissolved V and Ni in coke leachates. Elevated concentrations of these metals in coke leachate have previously been linked to toxic effects on aquatic, benthic, and terrestrial organisms. Consequently, understanding V and Ni sources in oil sands petroleum coke is critical for predicting and managing water quality.
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7. References


Baker, L.F., Ciborowski, J.J.H., MacKinnon, M.D., 2012. Petroleum coke and soft tailings sediment in constructed wetlands may contribute to the uptake of trace metals by algae

https://doi.org/10.1016/j.apgeochem.2016.11.023


https://doi.org/10.1016/j.apgeochem.2016.11.023


https://doi.org/10.1016/j.apgeochem.2016.11.023
https://dx.doi.org/10.1107/S0021889813003531


https://dx.doi.org/10.1021/es303914q


https://dx.doi.org/10.1016/j.scitotenv.2012.04.024