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Full Length Article

Selenium and sulphur in Athabasca bituminous sands mineral and bitumen fractions

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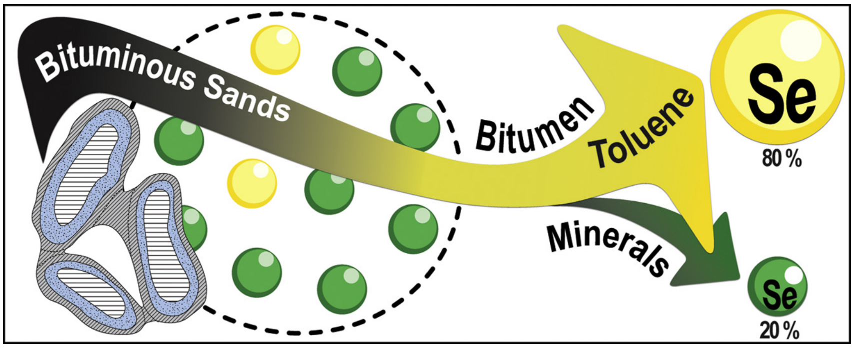
GRAPHICAL ABSTRACT



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ABSTRACT

There is increasing environmental concern regarding the emission of selenium (Se) from mining and upgrading of bitumen extracted from the Athabasca bituminous sands (ABS) in northern Alberta, Canada. However, there remains a lack of high quality analytical data for Se in this massive hydrocarbon reserve. Accurate analytical determinations of Se in bitumen from ABS are an important first step toward understanding its potential to be emitted to the environment. This has been a challenge due to the low abundance of Se combined with the preponderance of entrained mineral material (sand, clay) and the generally inadequate sensitivity of analytical methods used in the past. To overcome these issues, samples of ABS ores (McMurray Formation) underwent a toluene extraction procedure under ultra-clean lab conditions to separate bitumen from mineral particles. Separated bitumen, residual mineral material, and bulk ores were then subjected to acid-digestion and analysis using inductively coupled plasma sector-field mass spectrometry (ICP-SFMS) as well as hydride generation atomic fluorescence spectroscopy (HG-AFS). Unlike many other potentially toxic trace elements (Ag, As, Be, Cd, Cu, Pb, Sb, Tl and Zn) which exist almost exclusively in the mineral fraction, Se was found primarily (ca. 80%) in the organic (bitumen) fraction. Sulphur was determined in the same acid digests using both ICP-SFMS and inductively coupled plasma-optical emission spectroscopy (ICP-OES) and it too, was found almost exclusively in the bitumen fraction. Despite the limited number of samples available to our study, the positive, linear correlation between Se and S concentrations in bitumen suggests that S concentrations can be used as a guide to estimate their Se content. Given that Se is found mainly in the organic fraction of the ABS, there is considerable potential for mobilization of this element during upgrading and refining. The analytical methods successfully employed here have sufficient sensitivity to support studies of Se contamination of environmental media in the ABS region.

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1. Introduction

Bituminous sands are hydrocarbon reserves consisting of mixtures of sand, clay, water and bitumen – a heavily biodegraded crude oil [1]. The largest known group of bitumen deposits is the Lower Cretaceous Mannville group (Athabasca-Wabasca, Peace River, Cold Lake) in Alberta, Canada [2], which together contains an estimated 165.4×10^9 barrels of (remaining) established reserves [3]. Of this group, the Athabasca bituminous sands (ABS) region is the largest deposit [2] (initial established reserve = $6.16 \times 10^9\,m^3$) and contains an estimated 32.09×10^9 barrels remaining established reserves [3]. The Athabasca deposit is also well known for its shallow (average) pay-zone (~30 m deep) accessible by surface mining [4]. Geochemical characterization of bitumen from the ABS region was a priority during the early stages of development (ca. 1950–1985). This included determining the trace element content to provide information on the type of petroleum (i.e., origin, geological formation, maturation, etc.) as well as the abundance of elements known to be problematic during the bitumen upgrading processes [5]. Much of the trace element research at that time was focused on vanadium (V) and nickel (Ni) due to their enrichment in bitumen as metal-porphyrin complexes and ability to cause significant corrosion of equipment and impair the catalytic cracking process [6,7]. Atmospheric emissions of trace elements to the environment were also of interest, with monitoring efforts concentrated on V as an indicator of ABS mining and upgrading emissions [8,9].

Aside from V and Ni, there have been very few published studies examining the trace element content of bitumen in the ABS region since the pioneering work over 30 years ago [5,10–13]. This is despite: i) considerable improvements in relevant analytical techniques ii) extremely rapid industrial growth and iii) growing concerns in regard to contamination of potentially toxic trace elements such as Ag, As, Be, Cd, Cr, Cu, Ni, Hg, Pb, Sb, Se, Tl and Zn [14–16]; for these reasons, a contemporary investigation of the trace element content in bitumen from the ABS was undertaken [17]. In that study [17], bitumen and mineral phases were separated under ultra-clean lab conditions using toluene, then digested and analyzed using inductively coupled plasma sector-field mass spectrometry (ICP-SFMS). The results confirmed the enrichment of V, Ni and Mo in bitumen, which is consistent with the historical work by Goldschmidt [18]. Rhenium (Re) was also found to be hosted predominantly in the bitumen fraction, in agreement with the more recent work on Re-Os dating by Creaser and Selby [19]. In contrast to V, Ni, Mo and Re, potentially toxic trace elements such as Ag, As, Be, Bi, Cd, Cu, Pb, Sb, Tl and Zn were found almost exclusively in the mineral fraction [17]. Unfortunately, the work by Bicalho et al. [17] provided no information about selenium (Se), a non-metallic trace element with properties chemically analogous to sulphur (S) [20].

Depending on its concentration and chemical form, Se may act either as an essential micro-nutrient [21,22] or environmental toxin [23]. The concentration range between toxic and beneficial can be relatively narrow, particularly for aquatic organisms such as fish [24–26] and waterfowl [27]. This highlights the importance of understanding human activities that could mobilize Se or change its speciation, thereby increasing the potential for bioaccumulation within the food chain [28]. Industrial combustion and roasting processes involving crude oil, coal and metal sulphide ores dominate anthropogenic Se emissions to the atmosphere [29–33]. Selenium emissions can be especially problematic during industrial processing of fossil fuels (particularly coal) due to its ability to form sub-micron or gaseous species which by-pass many engineered air pollution controls such as electrostatic precipitators and baghouse filters [34–36]. However, due to its chemical similarity to S, the use of modern wet-scrubber technologies (e.g., flue gas desulphurization; FGD) can be effective in reducing atmospheric Se emissions [37,38]. The impacts of atmospheric emissions can be assessed by determining Se concentrations in various environmental compartments (soil, water, plants, etc.), but even in polluted areas this can still be a challenge due to its low abundance and complexity of chemical transformations. The most common method of analysis currently used for Se determination is ICP-MS, however, accurate and precise measurements of Se are often hindered by its high ionization potential and a large number of molecular interferences for an array of stable isotopes (^{74}Se, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se) [39–42].

Early work on bitumen from the ABS region that examined a wide spectrum of trace elements either did not include Se in the list of elements studied [43], or reported inadequate limits of detection [44]. Previous studies were also limited to only one or two samples and therefore provided no information about possible relations between Se concentrations and ore quality. The analytical challenges and paucity of information on the abundance and forms of Se in ABS makes it difficult to fully evaluate the potential environmental impacts of resource development, from open pit mining to upgrading and eventually refining. Here we provide an accurate assessment of the distribution of Se between the mineral and bitumen fractions of the ABS. Due to the chemical similarities between Se and S, we also examined the abundance of S in the two fractions, with a view toward using it as a proxy for estimating the abundance of Se in bitumen.

2. Materials and methods

2.1. General

All experimental procedures were carried out within class 100, metal-free clean air cabinets. High-purity water (18 MΩ·cm, Q-Pod Element, Millipore) was used throughout the study. Laboratory soap (Versa-Clean, Fisherbrand) and trace grade acids (Fisherbrand HNO_3 and HCl) were used in material cleaning routines. Trace metal grade HNO_3 used for sample digestion and preparation of working solutions was purified twice by sub-boiling distillation and stored in cleaned polytetrafluoroethylene (PTFE) bottles. ACS certified toluene (> 99.5%, Fisher Scientific) was used for the bitumen extractions. Polypropylene (PP) syringes and filters (30 mm PTFE membrane, 0.45 µm, PP housing, Target-2, ThermoFisher) were cleaned by filtering 20 mL of 2% double-distilled HNO_3, water, toluene and methanol (LC-MS grade, Fisher Scientific). Chemical reductant solution for HG-AFS analysis consisted of NaOH (BioXtra, ≥98%) and $NaBH_4$ (98%) purchased from Sigma Aldrich; HCl used for sample acidification and preparing the reagent blank was trace metal grade (Fisherbrand).

2.2. Athabasca bituminous sands

Seven samples from the McMurray Formation of the ABS region were obtained for analysis. The bitumen content of the samples ranged from 8.0 to 15.6 wt%. This range is ideal for study, as ores are typically graded into three categories based on their bitumen content: rich (> 10 wt% bitumen), moderate (6–10 wt% bitumen), and lean (< 6 wt %) [45]; an ore containing less than 8 wt% bitumen is generally considered uneconomical and is not desirable for mining [46]. Depending on the amount of mineral material, a typical ore also contains ~3–5 wt % connate water present as an ultra-thin film (estimated ~10 nm) between mineral particles and the bitumen [45,47].

Each ore sample was separated into its bitumen and mineral fractions by extraction with toluene three times then twice using methanol [17]. Bulk ore samples and the extracted bitumen and minerals were digested in a mixture of HNO_3 and HBF_4 using a high pressure microwave (ULTRAclave, MLS, Leutkirch, Germany). The mineral phases were also digested using an HF-HNO_3 procedure. The extraction and digestion procedures are described in detail elsewhere [17]. We assume that any connate water present would end up in the organic fraction (bitumen) following the methanol wash. The potential significance of connate water is discussed in greater detail in the Results and Discussion. To calculate the mass balance for Se and S, the concentrations determined using ICP-SFMS and hydride generation atomic fluorescence spectroscopy (HG-AFS), for Se, and ICP-SFMS and inductively