



The impact of thermal maturity level on the composition of crude oils, assessed using ultra-high resolution mass spectrometry



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ABSTRACT

We have examined, using a 12 Tesla FTICR-MS instrument, the impact of varying thermal maturity level on a suite of 9 related crude oils charged from source rocks covering most of the liquid petroleum generating portion of the oil window (0.68–1.11% vitrinite reflectance equivalent (%Re)). The sample suite was analyzed as whole oils under three different conditions, electrospray ionization (ESI) in positive and negative ion mode to analyze basic and acidic components, respectively, and atmospheric pressure photoionization (APPI) in positive ion mode, for sulfur and hydrocarbon species.

Increasing oil maturity level had a strong influence on the composition of all compound classes in the oils with several major observations evident:

The relative apparent abundances of all heteroatom containing compound classes detected in this study, using all ionization modes, decrease systematically with increasing oil maturation levels. Both aromatic hydrocarbons, detectable in APPI mode, and NSO compound classes (detectable in both ESI and APPI modes), as broad classes, are becoming more aromatic (shift to a greater predominance of higher DBE group members) and dealkylated (decreasing average molecular mass of individual compound groups), with increasing maturation level in the oil suite. Several putative oil maturity level dependent, molecular ratios were identified in the study. Of particular note, the relative abundance ratios of heteroatom compound classes tentatively identified as alkylated carbazoles, quinolines and benzothiophenes, compared to their benzannulated homologues are very sensitive to maturation level. Several groups of compounds show interesting and specific carbon number distributions, suggesting there may be hints of specific molecular markers in the FTICR-MS data. One observation of note is the strong increase in the relative abundance of protonated hydrocarbon components with DBE 5. We speculate this might reflect the presence of previously unreported higher molecular weight diamondoid (diamantane) species in oils with up to 40 carbon atoms or more, at advanced maturity levels. Such species may prove very valuable as molecular markers in highly mature fluids, such as those currently being produced from some shale reservoirs. Covariation of quantitative GC-MS data for alkylated hetero aromatic sulfur and nitrogen compounds in this oil suite, together with the corresponding FTICR-MS data from compounds believed to be, based on accurate mass, alkylated sulfur and alkylated nitrogen compounds, suggests that FTICR-MS already has some very rudimentary quantitation capabilities.

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1. Introduction

Crude oils and extractable (solvent soluble) organic matter (EOM) fractions of source rocks are complex mixtures of chemical species derived from once living organisms and catagenetic

products of kerogen maturation. Although crude oils are derived from source rock bitumens, their physical properties and chemical composition can differ significantly due to fractionations related to expulsion from the source rock (Pepper et al., 1995), secondary migration and in-reservoir processes. Advances in gas chromatography in the 1960s, and gas chromatography–mass spectrometry in the 1970s led to a quantum leap in molecular organic geochemistry. Due to their relatively high abundance in oil and their ease of analysis, the saturated and aromatic hydrocarbon fractions were the main focus of early organic geochemistry studies, with a major focus on biomarker alkanes and related aromatic compounds. As the biological markers occurred in both source rock bitumens

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and oils, they provided a tool for oil-source rock correlation, facies and maturity assessments and improved our understanding of reservoirs and petroleum migration pathways. The applications are numerous and classical petroleum geochemistry can be considered a mainstream discipline today. There remain, however, many issues, including the notion that any given petroleum in a reservoir represents not a single material derived from a single source rock at a single level of maturity, but that it is a complex integrated package of fluids contributed from multiple source rocks at multiple levels of maturity over long periods of geological time. This, together with orders of magnitude variations in crude oil component concentrations through the maturity window, inverse component concentration and maturity relationships for most biomarker species, and the ubiquitous nature of petroleum fluid mixing, means that traditional maturity and organic facies parameters are heavily compromised in many common settings (Wilhelms and Larter, 1994). New approaches are needed and with the advent of FTICR-MS (Marshall and Rodgers, 2004), it is now possible to try and extend the petroleum geochemical revolution of the late 20th century into the non-hydrocarbon species that are ubiquitously present in crude oils and in some cases, such as in an severely biodegraded oils, may be the dominant molecular species present.

The non-hydrocarbon fraction of crude oils (comprising nitrogen, sulfur and oxygen (NSO) containing organic compounds) can make up a significant proportion of petroleum. Although the importance of the heteroatom compounds has been recognized in many of the processes involved in the origin and alteration of petroleum (Tissot and Welte, 1984; Hunt, 1995), their geochemistry as a broad group, is poorly understood and few non-hydrocarbons have been used for process assessment proxies, with the exception of alkylated thioaromatics, which have been used as maturity assessment tools (Radke et al., 1982; Hughes, 1984; Radke et al., 1986; Leythaeuser et al., 1988; Radke and Willsch, 1991) and alkyl aromatic nitrogen compounds, which have been used as migration tracking tools under specific situations (Larter et al., 1996; Bechtel et al., 2013). The potential value of NSO species in migrated oils, for the definition and understanding of geochemical properties and processes such as organic facies assessment, migration, biodegradation and water washing, lies in the much greater range in physico-chemical properties exhibited by these compounds, compared to hydrocarbons and has prompted some limited research activity over the past two decades. However, these studies were restricted by the lack of suitable analytical tools (e.g., GC-MS), but recent advances, such as ultra-high resolution mass spectrometry (Fourier transform ion cyclotron resonance mass spectrometry (Marshall and Rodgers, 2004), now allow routine analysis of these often sorptive or low volatility species. While truly quantitative data are not yet available from such instruments, the instruments are sufficiently stable and data are sufficiently reproducible such that qualitative and semiquantitative analysis of processes is now possible. A first approach studying the influence of maturity on the composition of NSO heteroatom constituents of oils using FTICR-MS technology was carried out by Hughey et al. (2004). The authors compared an immature oil (0.7 %Re) (vitrinite reflectance equivalent) with a more mature oil (0.85 %Re) and observed a reduction in sulfur containing compound classes with increasing maturity. In addition, the authors suggested that thermal maturation promotes aromatization and condensation of acidic polar compounds and a decrease in the degree of alkylation. In this study, an oil suite derived from a common marine source facies with variable maturity was investigated for compositional changes in the heteroatom classes as a function of maturity level, using a 12 T ultra-high resolution mass spectrometer (FTICR-MS).

2. Samples and methods

2.1. Samples

The oil maturity suite consists of nine crude oils produced from the North Sea that belong to one single petroleum family generated predominantly in the Upper Jurassic Kimmeridge Clay Formation. As described in a previous study by Bennett et al. (2002), the maturity of these samples were defined according to proximal source kitchen temperatures and classical aliphatic and aromatic hydrocarbon maturity parameters as spanning the oil window from 0.68–1.11 %Re. Good correlations exist between the saturated and aromatic hydrocarbon and aromatic sulfur-containing species derived maturity parameters, such as $T_s/(T_s + T_m)$ and the 4-methyldibenzothiophene/dibenzothiophene ratio, with the maturities defined according to proximal source kitchen temperature (Fig. 1). The oils were selected from reservoirs located in close proximity (< 10 km) to the source rocks to limit compositional fractionation due to secondary migration and to minimize complexity with multiple charging source rocks.

2.2. Methods

All oil samples were analyzed without fractionation using a 12 Tesla Bruker Apex Fourier transform ion cyclotron resonance-mass spectrometer (FTICR-MS) located at the Tesla Petroleomics Centre in the University of Calgary. Samples were prepared by diluting whole oils to a final concentration of 0.25 mg/ml, in a solvent composed of equal parts of toluene and methanol. Just before analysis, the samples were spiked with 1 ppm of reserpine and 1% of ammonium hydroxide for analysis in negative ion electrospray ionization (ESI-N) or 1% formic acid for analysis in positive ion electrospray (ESI-P) and atmospheric pressure photoionization (APPI-P) using a krypton lamp at 10.6 eV. The samples were introduced into the mass spectrometer using a syringe pump set to deliver 240 μ l/h. The instrument was tuned and optimized using a set of standard compounds and oils and calibrated daily. Internal standards are included in each sample suite to ensure mass accuracy. Typically, for each sample, 200 scans are collected and summed to improve the experimental signal/noise ratio. For a typical crude oil sample the mass range of the instrument is set to between 165.88 Da and 1400.00 Da.

The resolving power at 400 Da is > 500,000 ($M/\Delta M_{fwhm}$). The mass accuracy is typically < 200 ppb.

The data were processed by recalibration with known oil constituents and each species assigned to chemical molecular formulae, mainly as $C_cH_hN_nS_sO_o$ compounds, using the Composer software (Sierra Analytics). Ragnarök (Aphorist Inc.), a data processing software tool for quantitation, visualization and interpretation of multidimensional and multi-sample FTICR-MS data was then used for the data analysis and visualization. Apart from the determination of molecular masses and double bond equivalents (DBE derived as $DBE(C_cH_hN_nS_sO_o) = c - h/2 + n/2 + 1$) of detectable individual species in whole oils or bitumen fractions (see the definitions below), we derived lumped abundances of whole heteroatom classes (a heteroatom class is a group of compounds with a uniform heteroatom population), DBE group distributions within a heteroatom class, carbon number distributions of an individual group of pseudohomolog compounds and also a variety of plots, including modified Kendrick plots and averaged molecular mass plots for related groups of compounds. The terminology we use in this paper is defined in the chart in Appendix A.

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