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Structural characterization of gilsonite bitumen by advanced nuclear magnetic resonance spectroscopy and ultrahigh resolution mass spectrometry revealing pyrrolic and aromatic rings substituted with aliphatic chains

John R. Helms [a], Xueqian Kong [b], Elodie Salmon [a], Patrick G. Hatcher [a], Klaus Schmidt-Rohr [b,*], Jingdong Mao [a,*]

[a] *Old Dominion University, Department of Chemistry and Biochemistry, 4541 Hampton Blvd., Norfolk, VA 23529, United States*
[b] *Iowa State University, Department of Chemistry, Gilman Hall, Ames, IA 50011, United States*

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ABSTRACT

Gilsonite, a naturally occurring asphaltite bitumen, consists of a complex mixture of organic compounds. In the present study, advanced one and two dimensional solid state and solution ^{1}H, ^{13}C and ^{15}N nuclear magnetic resonance (NMR) and electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR-MS) were employed to investigate its composition and structure. ^{13}C NMR yielded a carbon aromaticity of 27%. Aromatic moieties in gilsonite were primarily single rings or small clusters of fused rings. Half of the aromatic carbons of gilsonite can be accounted for by pyrroles. ^{15}N and ^{13}C cross polarization-magic angle spinning (CP-MAS) NMR showed that most nitrogen in gilsonite was pyrrolic. The aromatic rings were heavily substituted with alkyl chains, as evidenced by ^{1}H—^{13}C correlation spectra. Advanced solid state NMR spectral editing techniques clearly identified specific functional groups such as CCH_3, CCH_2, and $C{=}CH_2$ (exomethylene). ^{1}H—^{13}C wideline separation (WISE) NMR helped identify mobile and non-protonated alkyl carbons. FT-ICR-MS indicated that ~64% of calculated formulae generated by ESI were aliphatic, while only about 0.8–2.5% of formulae contained possible aromatic rings. All of the assigned formulae contained at least one heteroatom (N, O or S), indicating that ionization by ESI was selective for the polar fraction of gilsonite and potentially less reflective of the overall chemical character of gilsonite than NMR spectroscopy. By combining the information obtained from advanced NMR and ultrahigh resolution MS we propose a structural model for gilsonite as a mixture of many pyrrolic and a few fused aromatic rings highly substituted with and connected by mobile aliphatic chains.

1. Introduction

Bitumen refers to solid or liquid hydrocarbon deposits soluble in organic solvents (Killops and Killops, 2005). Gilsonite is a naturally occurring bituminous asphalt and formally classified as an asphaltite bitumen (Abraham, 1945). It occurs primarily along the Colorado–Utah border and was found in the early 1860s in the Uinta Basin in northeastern Utah (Bell and Hunt, 1963). Gilsonite has been widely used in mining and industry and sold all over the world. For example, it has been used as an additive in oil drilling fluids and for oil well cementing and has a long history of use as both a pigment and binding agent in paints, enamels and inks (Tripp and White, 2006). Natural bitumens are also under investigation as exploitable petroleum fuels (Meyer et al., 2007). Furthermore, gilsonite and other natural bitumens are important intermediates and/or byproducts in the geological formation of crude oils that can be analyzed to improve our understanding of petroleum geochemistry (Bell and Hunt, 1963; Killops and Killops, 2005).

Abbreviations: AI, aromatic index; AI_{mod}, modified aromatic index; BC, black carbon; CARS, condensed aromatic ring structures; CP, cross polarization; COSY, correlation spectroscopy (2D-NMR); CSA, chemical shift anisotropy; DBE, double bond equivalents; DEPT, distortionless enhancement by polarization transfer; DP, direct polarization; DPEP, deoxyphylloerythroetioporphyrin ; EA, elemental analysis; ESCA, electron spectroscopy for chemical applications (X-ray photoelectron spectroscopy or XPS); ESI, electrospray ionization; FT, Fourier transform; HETCOR, heteronuclear correlation (2D-NMR); HH-CP, Hartmann–Hahn cross polarization; HMQC, heteronuclear multi-quantum correlation (2D-NMR); ICR, ion cyclotron resonance; KMDA, Kendrick mass defect analysis; LG-CP, Lee-Goldburg cross polarization; MAS, magic angle spinning; MS, mass spectrometry; MREV-8, Mansfield, Rhim, Elleman and Vaughn's 8 pulse line narrowing sequence; NMR, nuclear magnetic resonance spectroscopy; NOM, natural organic matter; ppm, parts per million units of frequency variation from a standard; T_1, spin–lattice relaxation time; TOCSY, total correlation spectroscopy (2D-NMR); TOSS, total sideband suppression; TPPM, two-pulse phase modulated decoupling; WISE NMR, wideline separation nuclear magnetic resonance.

* Corresponding authors. Tel.: +1 515 294 6105; fax: +1 515 294 0105 (K. Schmidt-Rohr), tel.: +1 757 683 6874; fax: +1 757 683 4628 (J. Mao).

E-mail addresses: srohr@iastate.edu (K. Schmidt-Rohr), jmao@odu.edu (J. Mao).

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Despite the widespread industrial use and petrochemical potential of gilsonite, its molecular structure has not been well characterized due to its complexity and heterogeneity. Past studies have primarily focused on the investigations of biomarkers such as petroporphyrins (Treibs, 1934, 1936; Sugihara and McGee, 1957; Corwin, 1959; Quirke and Maxwell, 1980; Quirke et al., 1980a, 1980b; Hajibrahim et al., 1981; Gill et al., 1985), hopanes, steranes and carotenoids (Ruble et al., 1994; Schoell et al., 1994). Quirke et al. (1980b) found that the aetio-type porphyrins and deoxyphylloerythroetioporphyrin (DPEP) were products of reductive degradation of chlorophylls. The porphyrins present in gilsonite were most likely formed from naturally occurring chlorophylls through this degradation (Quirke and Maxwell, 1980; Quirke et al., 1980b; Hajibrahim et al., 1981). Compound specific isotopic analysis of carotenoids indicated a strong algal or cyanobacterial source for the diagenetic starting material for gilsonite (Ruble et al., 1994; Schoell et al., 1994). Additionally, isotopic values for hopanes (pentacyclic membrane lipids) and moretanes suggested the influence of mid-water bacteria and potentially some methanotrophs (Schoell et al., 1994).

However, biomarkers such as the porphyrin compounds only account for a minor fraction of gilsonite (Treibs, 1936). The bulk of the gilsonite consists of aliphatic and aromatic hydrocarbons with few olefinic groups, as indicated by the iodine number (Baker et al., 1967; Quirke and Maxwell, 1980). Its bulk chemical characteristics have been investigated using electron spectroscopy for chemical applications (ESCA; usually referred to as X-ray photoelectron spectroscopy or XPS), infrared spectroscopy, X-ray diffraction spectroscopy, and ^{1}H and ^{13}C solution NMR analysis. ESCA provided verification of elemental analysis results. ESCA also indicated that carbon was mainly present as aliphatic hydrocarbons, that nitrogen–carbon bonding environments such as aliphatic and aromatic amines as well as nitrogen heterocycles such as pyrrole were present, that C—O bonding environments were present and that a very small amount of sulfur was present as organic sulfides or heterocycles such as thiophenes (Clark et al., 1983). Infrared spectroscopy showed that C—H (~88% of IR signal) and C—O (~10% of IR signal) were the dominant vibrational modes present in gilsonite with acids and esters each representing <1% of the vibrational signal (Clark et al., 1983). Organic acids were present in gilsonite in trace amounts (Grantham and Douglas, 1977; Clark et al., 1983).

Yen et al. (1961) used X-ray diffraction to estimate the aromaticity of gilsonite as well as several petroleum asphaltenes. They reported a much lower aromaticity for gilsonite (~14%) than for petroleum asphaltenes (22–53%). However, Bell and Hunt (1963) described gilsonite as "predominantly aromatic" based on liquid chromatography, elemental analysis and infrared measurements. Wen et al. (1978) report the aromaticity of gilsonite asphaltene, which is the pentane insoluble, benzene soluble fraction, as 38% based on ^{1}H solution NMR. Yet the perception of gilsonite as a "predominantly aromatic substance" (North, 1985) persisted until Clark et al. (1983) applied solution ^{1}H and ^{13}C NMR to gilsonite samples and showed a variety of aliphatic carbon environments and a single broad aromatic peak. They reported an aromatic:aliphatic carbon ratio of 1:4 for a gilsonite sample with limited atmospheric exposure, which was more in line with the X-ray diffraction results (Yen et al., 1961) and the absence of a 'shake-up satellite' peak, indicative of conjugated systems, in the ESCA spectrum (Clark et al., 1983). To resolve this controversy, reliable quantification of aromaticity is required. Direct polarization ^{13}C NMR, after a sufficiently long relaxation delay (Mao et al., 2000; Mao and Schmidt-Rohr, 2004a), provides accurate aromaticity values. Gilsonite has often been described as containing condensed polyaromatic 'sheets' or 'asphaltene sheets' (Yen et al., 1961; Bell and Hunt, 1963; Wen et al., 1978; Yen, 2000) based on its high carbon content and its high refractive index, but little direct evidence has supported this. Solid state NMR can address this question by estimating the size of clusters of fused aromatic rings, by long range C—H dipolar dephasing and quantification of the ring edge carbon fractions (Brewer et al., 2009; Mao et al., 2010b).

The structural characterization of gilsonite is critical for understanding its properties, its applications in industry, and its geological significance. Solid state NMR has been widely applied in the study of natural organic matter (NOM) such as coal, oil shale, humic materials and peats (Hatcher et al., 1981, 1983; Dennis et al., 1982; Miknis et al., 1982; Wilson, 1987; Solum et al., 1989; Anderson et al., 1992; Maciel et al., 1993; Wilson et al., 1993; Preston, 1996; Nanny et al., 1997; Clifford et al., 1999; Hu et al., 2000; Conte et al., 2004; Smernik et al., 2006). Advanced NMR techniques, especially spectral editing techniques, have increased the amount of information obtainable from NOM samples (Wu and Zilm, 1993; Wu et al., 1994; Hu et al., 2000; Keeler and Maciel, 2000). We have developed and applied many new, advanced solid state NMR techniques, especially spectral editing (Schmidt-Rohr and Mao, 2002; Mao and Schmidt-Rohr, 2003), for the investigations of NOM (Mao et al., 2007a, 2007c). While the broad and heavily overlapped bands of complex NOM allow traditional ^{13}C NMR to identify only about 10 types of chemical groups, our spectral editing techniques, which selectively retain peaks of certain types of functional groups, can identify more than two dozen different moieties (Mao et al., 2007a, 2007c). Moreover, two dimensional ^{1}H—^{13}C heteronuclear correlation (HETCOR) NMR is used to detect proximities and connectivities of different functional groups. ^{15}N CP-MAS NMR is applied to characterize forms of nitrogen in gilsonite and combined with recoupled dipolar dephasing to determine which resonances are from N bonded to hydrogen (Fang and Schmidt-Rohr, 2009).

Gilsonite is soluble in a range of organic solvents such as chloroform; therefore we have also studied it by solution NMR techniques. Solution ^{13}C NMR spectra appear well resolved; however, the signals of many components are broad and almost invisible due to low mobility of some components and resulting short spin–spin relaxation times (T_2). Thus, advanced solid state and solution NMR techniques provide complementary structural information.

Mass spectrometry is used to determine the molecular weight of ions. In organic chemistry, advanced solution NMR and mass spectrometry data have been routinely collected to elucidate the structures of organic compounds. However, the approach has not been frequently used to elucidate the structures of natural organic matter in organic geochemistry. Despite the availability of high resolution mass spectrometry for the analysis of fossil fuels for over two decades (Comisarow and Marshall, 1974; Grigsby, 1989; Hsu et al., 1994; Amster, 1996; Marshall et al., 1998), to date, there has been no detailed, comprehensive characterization of gilsonite using Fourier transform ion cyclotron mass spectrometry (FT-ICR-MS) reported in the literature. The high mass accuracy of FT-ICR-MS makes it possible to differentiate ions in complex mixtures without employing a separation method prior to infusion into the mass spectrometer (Klein et al., 2006).

Mass separation is only carried out on charged particles (ions) and therefore the quality of MS data strongly depends on the type of ionization used during sample introduction. Electrospray ionization (ESI) coupled with FT-ICR-MS yields a detailed mass spectrum of ionic organic molecules with highly accurate mass to charge (m/z) determination. Positive ionization and negative ionization modes are selective in favor of chemical moieties capable of bearing positive or negative formal charges, respectively. As anticipated, positive ionization exhibits higher selectivity/sensitivity for nitrogen containing molecules such as amines, amides and nitrogen heterocycles, while negative ionization shows higher selectivity/sensitivity to acidic moieties such as fatty acids and phenols.

Smith et al. (2008) used ESI-FT-ICR-MS to characterize heavy vacuum gas oil distillation cuts from Athabasca bitumen and found