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Signatures of Geo-steroids in InfraCambrain Crude oils from Western India

Abstract

The Neoproterozoic-Early Cambrian Bikaner Nagaur Basin in western India had housed a huge spectrum of eukaryotic life and is an excellent provenience to study steroid biomarkers. The present study with GC×GC-TOFMS demonstrates an improved distribution of the fossil steroids in the terminal Proterozoic crude oils. A variety of steroids biomarkers that could not be identified with GC-MS analysis was noticeable in this analysis. Substantial resolution was achieved between steranes and triterpanes, which intensely co-elute, in the saturated hydrocarbon fraction. Compounds particularly modified androstane (19C isomer), short-chain C_{21} and C_{22} steranes and lanostanes are favorably produced in high-salinity depositional environment. These indicate the predominance of halotolerant organisms and a very high rate of evaporitic sedimentation. Basal metazoan input (sponge) was confirmed by the presence of 24-isopropylcholestane. Regular steranes and 24-n-propylcholestane suggest the terminal Proterozoic oceans were inhabited by algae and 24-n-propylcholestane, which happened to be the fundamental primary producers during the time frame. Very low abundance of 4α-methyl sterane and 3β-Alkyl steranes could be recorded which predominate and a distinctive feature of the terminal Proterozoic time frame. These and 2α-methyl steranes are plausibly sedimentary methylation products, whereas the secosteranes detected could have formed by diagenetic cleaving.

Introduction

Biomarkers are fossil organic molecules which provide information of biodiversity and depositional environment in deep time (Brocks and Summons, 2003). Additionally, these data can provide information about thermal maturity and degree of biodegradation essential for the reconstruction of past geological processes. Biomarkers are particularly important for the biotic reconstruction of deep time in the Earth history such as the Precambrian Eon wherein the signature of fossil record is meagre. The steroid biomarkers are instrumental in understanding the chronology of eukaryotic evolution. The biosynthesis of eukaryotic membrane lipids or steroids is oxygen-dependent and these are derived from squalene precursors (Summons et al., 2006). The precursor sterol compounds undergo various stereochemical reactions involving oxidation, dehydration of hydroxyl groups thus forming sterenes, isomerization of double bonds in sterenes and reduction of the double bonds to form steranes during the journey from biosphere to geosphere (Amo et al., 2007 and references therein). Examination of biomarkers in natural samples like crude oil and rock extracts has been a well-established technique to understand Earth processes. Gas chromatography mass spectrometry (GC-MS) has been a longstanding technique used to study chemical compounds in geological and biological samples (Kałużna-Czaplińska and Jóźwik, 2014 and references therein). However, due to the presence of a plethora of peaks and co-elution effect, a large number of compounds go unnoticed in conventional gas chromatography mass spectrometry and a lot of valuable information remains obscure. The investigation of stereoisomers becomes particularly difficult with GCMS since on many occasions the peaks are not well-resolved. Ongoing research work demonstrate the fact that application of GC×GC-TOFMS could be a windfall to the building of a precise global dataset of biomarkers spanning an impressive range in the geological time scale (Ventura et al., 2008; Silva et al., 2011; Eiserbeck et al., 2012; Oliveira et al., 2012). Hence, the development of GC×GC, which provides an additional dimension of separation, was a necessary step forward which is especially suitable for analysis of increasingly complex mixtures like crude oil and source rock extracts. It utilizes two columns serially coupled utilizing the orthogonal principle of different column selectivity. A cryogenic modulator is connected which decreases the peak width thereby producing peaks with greater sensitivity and these are re-injected into the second column for further separation to produce peaks with high signal-to-noise ratio. This strategy can satisfactorily unwind huge measure of data thus depicting geochemically significant eukaryotic molecular fossils, many of which were not recorded in previous analyses with one dimensional GC-MS and metastable reaction monitoring (MRM) transitions (Peters et al., 1995; Dutta et al., 2013; Bhattacharya and Dutta, 2015)

Here, we report steroid biomarkers present in InfraCambrian crude oil recovered from the Marwar Supergroup, employing excellent capabilities of the two-dimensional gas chromatography coupled to time-of-flight mass spectrometer.

Samples and Method

Nine oil samples extracted from cores belonging to the Marwar Supergroup from four distinct wells in the Bikaner-Nagaur Basin, western India were presently examined.

The sample preparation technique is described in Dutta et al. (2013) and Bhattacharya and Dutta (2015). For the present study, the saturated fractions were analyzed in two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC×GC-TOFMS).

The saturated fraction of crude oil was analyzed on Leco Pegasus 4D GCXGC (LECO Corporation, Saint Joseph, Michigan, USA) instrument, having a period of-flight mass spectrometer (TOFMS) coupled in a series with a Gas chromatograph (Agilent 7890B GC) having Gerstel multipurpose sampler (MPS). The GC oven was comprised of a non-polar primary column (Rxi-5MS) column having length, 2m, i.d. 0.18mm and film thickness 0.2 µm and a mid-polar secondary column (Rxi-17 having length 2.0 m, i.d. 0.10 mm and film thickness 0.1 µm) through a modulator (LECO Corporation, Saint Joseph, Michigan, USA). The secondary column was mounted in a separate oven inside the main GC oven. The injector temperature was kept at 290°C and the carrier gas used was Helium at a constant flow rate of 1.5 ml/min. The main GC oven temperature program kept was 60°C isothermal for 1 min, heated to 180°C at a ramp rate of 10°C /min. The oven temperature further rose to 270°C at a heating rate of 5°C /min. and the final temperature was reached at 310°C with a ramp of 10°C /min, maintained isothermally for 10 min. The secondary oven and the modulator temperatures were kept at an offset of 10°C and 15°C, respectively, higher than the primary GC oven. The modulation period was 5.5 sec with 0.9 sec hot pulse. The MS operating parameters were: transfer line temperature 280°C; ion source 250°C; electron ionization at 70 eV; detector voltage 1600 V; acquisition rate at 100 Hz.

Results

The present analysis of C_{27}-C_{29} steranes with GC×GC-TOFMS not just demonstrates the distribution of the regular steranes but also presents improved spectra devoid of the interfering masses from coelution. All the four stereoisomers (ααα**S**, αββ**R**, αββ**S**, ααα**R**) of regular steranes were recorded. These are clearly separated from triterpenoids. The other steranes identified were short chain steranes (prenanae and homoprenane). A series of compounds were observed to elute between 5α (H) pregnane and 5α(H) cholestanes visible in the extracted ion chromatograms at *m/z* 217 and *m/z* 218. The compounds are recognized as short-chain and medium-chain steranes ranging from

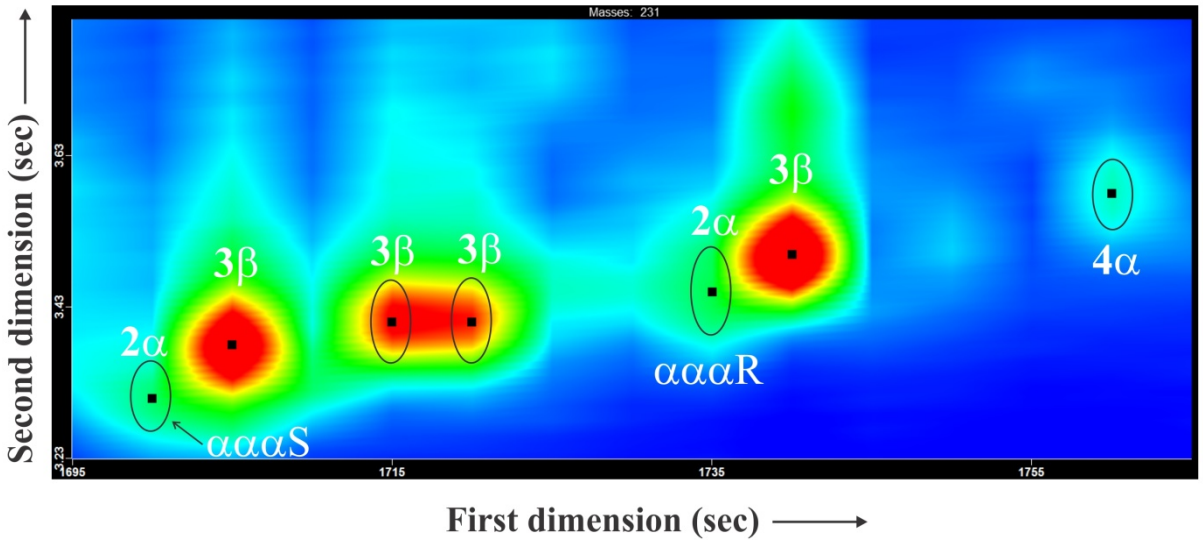
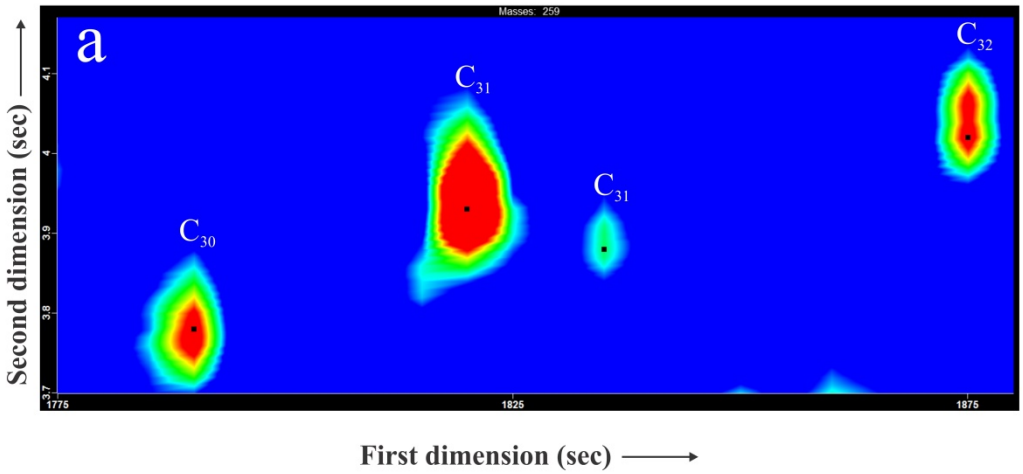


Figure 1 Extracted ion chromatogram (*m/z* 231) depicting the presence of 2α-methyl and 4α-methyl steranes in the saturated hydrocarbon fraction of Neoproterozoic-Early Cambrian crude oil sample from Bikaner-Nagaur Basin, western India. Two isomers were detected for the 2α-methyl steranes comprising ααα**S** and ααα**R**.

C_{21} to C_{26} based on elution pattern and mass spectra of individual peaks. C_{30} Steranes with unusual methylation patterns in the side chain, 24-*n*-propylcholestane and 24-isopropylcholestane, are recognized at *m/z* 217, to following the C_{29} regular sterane isomers. Due to lower abundance these couldn't be identified in earlier investigation of oil and/or sediment. In the present analysis, two peaks could be clearly recognized as 24-*n*-propylcholestane and 24-isopropylcholestane. The molecular fossils depict biological input into an environment stressed by high salinity and anoxia. Compounds particularly modified androstane (19C isomer), short-chain C_{21} and C_{22} steranes and lanostanes which are favorably produced in high-salinity depositional environment are detected in the present study. These indicate the predominance of halotolerant organisms and a very high rate of evaporitic sedimentation. Observation of the relative abundances of the sterane compounds is suggestive of the fact that progenitors of desmethyl steranes were significant producers into the organic matter with fewer contributions from methylated steroid precursors. Very low abundance of 2α-methyl steranes and 4α-methyl sterane could be recorded, while 3β-Alkyl steranes are detected in significant abundance (Figure 1), which is a distinctive feature of the terminal Proterozoic time frame. These and 2α-methyl steranes are plausibly sedimentary methylation products, whereas the secosteranes detected could have formed by diagenetic cleaving. Lanostanes are clearly been detected in the studied samples (Figure 2). Sponges or dinoflagellates could be the likely precursors to these detected lanostanes, since their molecular markers have already been identified in the studies samples.



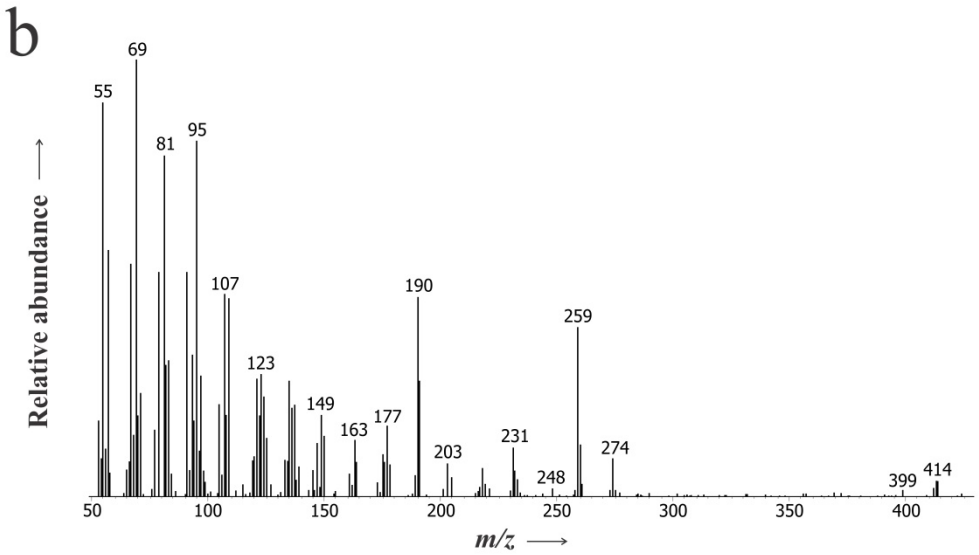


Figure 2 Well resolved peaks of lanostanes recorded by GC×GC-TOFMS (*m/z* 259) ranging from C_{30} to C_{32} in the saturated hydrocarbon fraction of Neoproterozoic-Early Cambrian crude oil sample from Bikaner-Nagaur Basin, western India. (b) Mass spectrum of C_{30} lanostane.

Conclusion

Excellent resolving power of GC×GC enabled the identification of a diverse range of eukaryotic-derived lipids in the form of the de-functionalized analogue of sterols in InfraCambrian crude oils from Neoproterozoic-Early Cambrian Marwar Supergroup, western India. The difficulty often encountered because of co-elution of the vital class of compounds like steranes and triterpanes could be improved with GC×GC-TOFMS, thus delineating unmistakably the range of steroidal peaks in the studied samples. Likewise, generation of clean mass spectra facilitated easier identification of peaks and more certainty while assigning the compound. Concisely, the astounding competency of GC×GC-TOFMS in deconvoluting co-eluting peaks could be promoted capitalized for studying complex natural constituents, especially Precambrian biomarkers thus supporting research on the incipient phases of evolution on the Earth.

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