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Biomarker Signatures of Eocene Oils from Cambay Basin Using Two-Dimensional Gas Chromatography Coupled to Time of Flight Mass Spectrometry

Abstract

Eocene crude oil samples from Cambay Basin has been analyzed using comprehensive two-dimensional gas chromatography with time of flight mass spectrometry (GCXGC-TOFMS) overcomes the challenges faced by traditional GCMS where resolving a large number of compounds is hard to comprehend. This will give a precise assessment of mass spectra of compounds for their appropriate identification and/or quantification. The oils are dominated with *n*-alkanes and acyclic isoprenoids in the saturated fractions. The other isoprenoids detected in saturated fractions are bicyclic sesquiterpenoids, steranes (regular and rearranged) and triterpenoids with three, four and five rings. The aromatic fractions are dominated by naphthalenes and phenanthrenes and PAH. The biomarker distribution includes Eudesmane, oleananes, bicadinanes, hopanes and steranes including their isomers and secobicadinanes and oleanane derived PAH (2,2,3-trimethyl-1,2,3,4-tetrahydropicene, 7-methyl-1'-ethyl-1,2-cyclopentanochoyrene, lenosta(eupha) hexaene and 8,14-seco-oleanane). A high Pristane/Phytane ratio and the abundance of diagnostic biomarkers bicadinane and oleanane recognized in the oil fractions showing a significant contribution of terrestrial plants of angiosperm families to the source, which was deposited in a sub-oxic environment. Parameters calculated based on biomarkers indicates that shale as the source rock. The efficiency of GCXGC manages to improve in better understanding on biotic contribution and palaeodepositional environment of the Cambay Basin.

Introduction

Biomarkers are the complex molecule or chemical fossils whose carbon structure, or skeleton, are produced by living organisms and are adequately stable to be recognized in crude oil or in the organic matter of ancient sediments (Hunt, 1996). Normally biomarkers, are used to link some of the specific group of bacteria, plants and animals from which they had originated. Its distributions provide a method to address the origin of petroleum, mapping petroleum systems, source to oil and oil to oil correlation, to interpret the characteristics of petroleum source rocks even when only oil samples or source rocks are available. Biomarkers studies enabled an understanding about the nature of the organic matter in the source rock, the type of kerogen, and environmental condition during its deposition and burial history and the degree of biodegradation. Biomarkers are also used to encode thermal history which enables us to estimate the maturity of organic matter in the source rock.

The biological markers present in both crude oil and extract of source rock successfully used by many geochemists to study the biotic evolution and its relation to the ecosystem and also to understand past Earth processes. Organic matter consists of various a class of organic compounds with an isomeric complexity, which is difficult to separate using conventional gas chromatography. In addition, due to a low resolving capability of GC-MS, many compounds that usually occur in low concentration are remained undetected and much useful information remain inaccessible.

Comprehensive two-dimensional gas chromatography (GCXGC) coupled to time of flight mass spectrometry (TOFMS), presently one of the most powerful analytical tool in the field of gas chromatography. With an additional dimension of separation in GCXGC-TOFMS, it surprisingly overcomes the challenges faced by traditional gas chromatography such as resolving of an unresolved complex mixture (UCM) and co-elution problem. This will help to provide an accurate assessment of mass spectra of compounds for their proper identification and/or quantification. (Ventura et al., 2008, Ávila et al., 2010, Eiserbeck et al., 2012).

In the present study, an advance analytical instrument has been used to separate complex mixtures of crude oil from Cambay Basin, at a higher resolution in order to provide more detail geochemical characterization of the Cambay oil of Eocene age. A special focus is given on the isomers of pentacyclic triterpenoids and steroids and in both the saturated and aromatics fractions.

Samples and Method

The Cambay Basin is a pericratonic rift basin which is located on the Western Onshore part of India. It is one of the major oil producing fields of India. Raju (1969) and Biswas (1987) has provided the detailed geology of the basin. In order to study the detail molecular composition, Eocene age crude oils were selected from the Tarapur field (Cambay-Tarapur Block) of Cambay Basin.

The crude oils were treated initially with *n*-pentane for asphaltene separation. The remaining maltenes fractions were further fractionated into saturates and aromatics using column chromatography. The compositional analysis of the final fractions was studied using a Leco Pegasus 4D GCXGC (LECO Corporation, Saint Joseph, Michigan, USA) instrument, having a time-of-flight mass spectrometer (TOFMS) coupled with a Gas chromatograph (Agilent 7890B GC) having Gerstel multipurpose sampler (MPS). The GC oven was housed with a non-polar primary column (Rxi-5MS Silica column having length, 30 m, i.d. 0.18mm and film thickness 0.2 μ m) and a moderately polar secondary column (Rxi-17 having length 2.0 m, i.d. 0.10 mm and film thickness 0.1 μ m) 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 50°C isothermal for 2 min, heated to 120°C at a ramp rate of 10°C /min and kept isothermal for 1min. The oven temperature further rose to 300°C at a heating rate of 1.25°C /min and kept isothermal for 1 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 temperature 250°C; electron ionization at 70 eV; detector voltage 1600 V; spectra acquisition rate at 100 Hz.

Results and Discussions

The saturated fractions show aliphatic hydrocarbons which are dominated by *n*-alkanes (C₁₅ to C₃₉) as well as branched and cyclic isoprenoids. Pristane and phytane are the major isoprenoids are detected in the saturated fractions. The distribution of *n*-alkanes and acyclic isoprenoids are substantial for evaluating the origin and source of organic matter as they are widespread in the biosphere. The other isoprenoids identified are bicyclic sesquiterpenoids, steranes (regular and rearranged) and triterpenoids with three, four and five rings (Figure 1). The studied samples contain bacteria derived triterpenoids along with their methylated series in considerable amount. An extended series of tricyclic terpanes and steranes have also been identified. A predominance of C₂₉ regular sterane over C₂₇ and C₂₈ steranes indicates higher plant contribution to the organic matter. Angiosperm-derived triterpenoids (bacadinane, oleanane) have also been detected in the present study of GCXGC, which is hard to detect in Cambay oils by conventional 1D GC because of low abundance and occurrence of co-elutions.

Aromatic fractions are dominated with naphthalenes, phenanthrenes and its alkylated homologues, diaromatic tricyclic terpanes, triaromatic steranes, C₁₉, C₂₀ and C₂₁ benzohopanes, C₃₀ diaromatic secobicadinanes and many polyaromatic hydrocarbons (PAH) (Figure 2). Chaffee and Johns (1988) proposed that diagenetic products of oleanane-type triterpenoids, which is a constituent of angiosperms, can form 1,2,5- and 1,2,7- trimethylnaphthalenes (TMN). Cadalene has been proposed as a non-specific terrestrial marker and it present in vascular plants of various families (van Aarssen et al., 2000; Dutta et al., 2011). Diaromatic secobicadinane were detected in crude oils which are derived from polycadinene dammar resins, produced by the diterocarpaceae tree of a tropical angiosperm family (van Aarssen et al., 1990). The occurrence of diaromatic secobicadinanes is indicative that the organic matter falls into the early catagenetic zone (Chattopadhyay and Dutta, 2014). Many oleanane and lupane skeletons derived PAH including 2,2,3-trimethyl-1,2,3,4-tetrahydropicene, 7-methyl-1'-ethyl-1,2-cyclopentanochoyrene, lenosta(eupha) pentaene, lenosta(eupha) hexaene, 24,25,26-trisnor-lupa-1,3,5(10)-tetraene, des-A-26,27,28-trisnor-oleana-5,7,9,11,13,15,17-hepataene, 24,25,26,27-tetranor-lupa-1,3,5(10),6,11,13-heptaene and 8,14-seco-oleanane have been detected. These aromatic triterpenes considered to degradation products of micro-organism (Trendel et al., 1989).

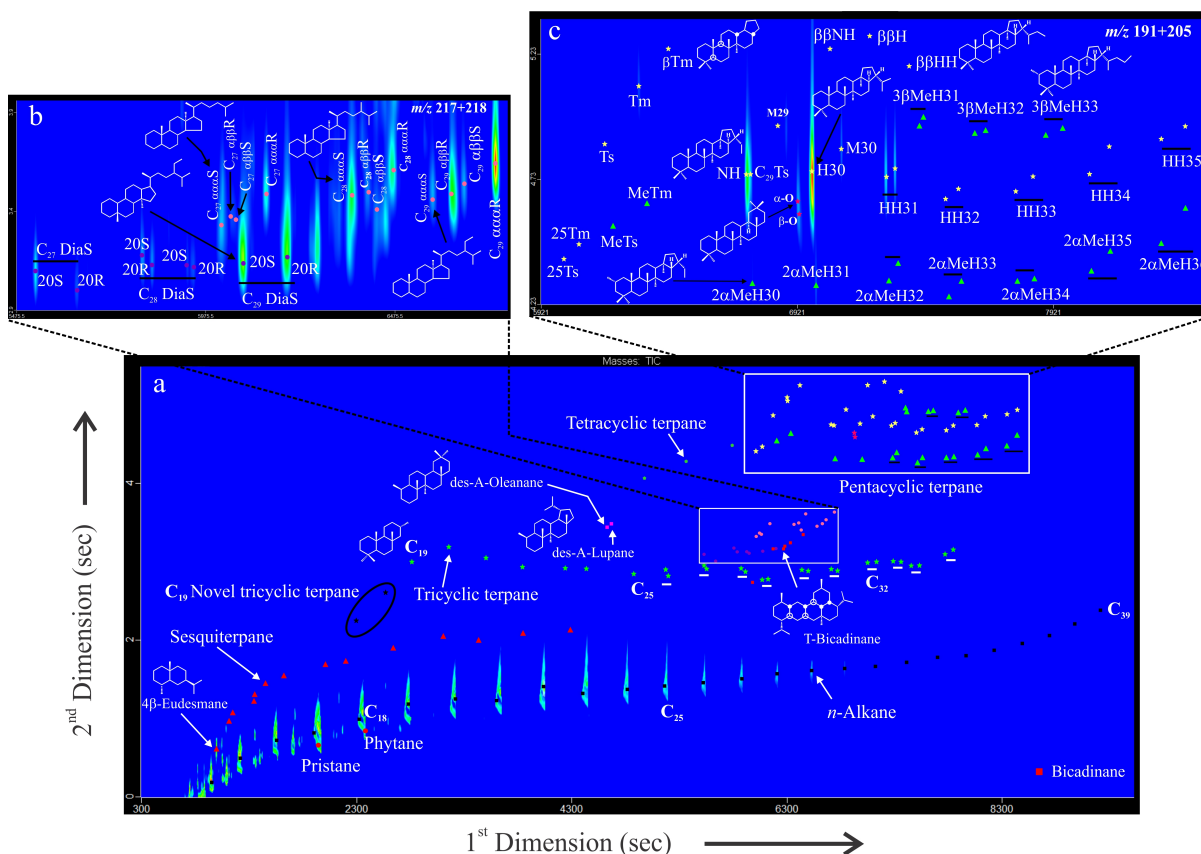


Figure 1: (a) TIC of saturated fraction T-5 crude oil from Cambay Basin; (b) selected ion chromatogram (m/z 217+218) showing distribution of steranes and diasteranes; (c) selected ion chromatogram (m/z 191+205) showing distribution of hopanes and methylated hopanes. Key: DiaS: diasteranes, H: hopanes; HH: homohopanes, M: moretanes; Ts: trisnorneohopane; Tm: trisnorhopanes; MeH: methylated hopanes; O: oleanane; MeTs: methyl trisnorneohopane; MeTm: methyl trisnorhopanes

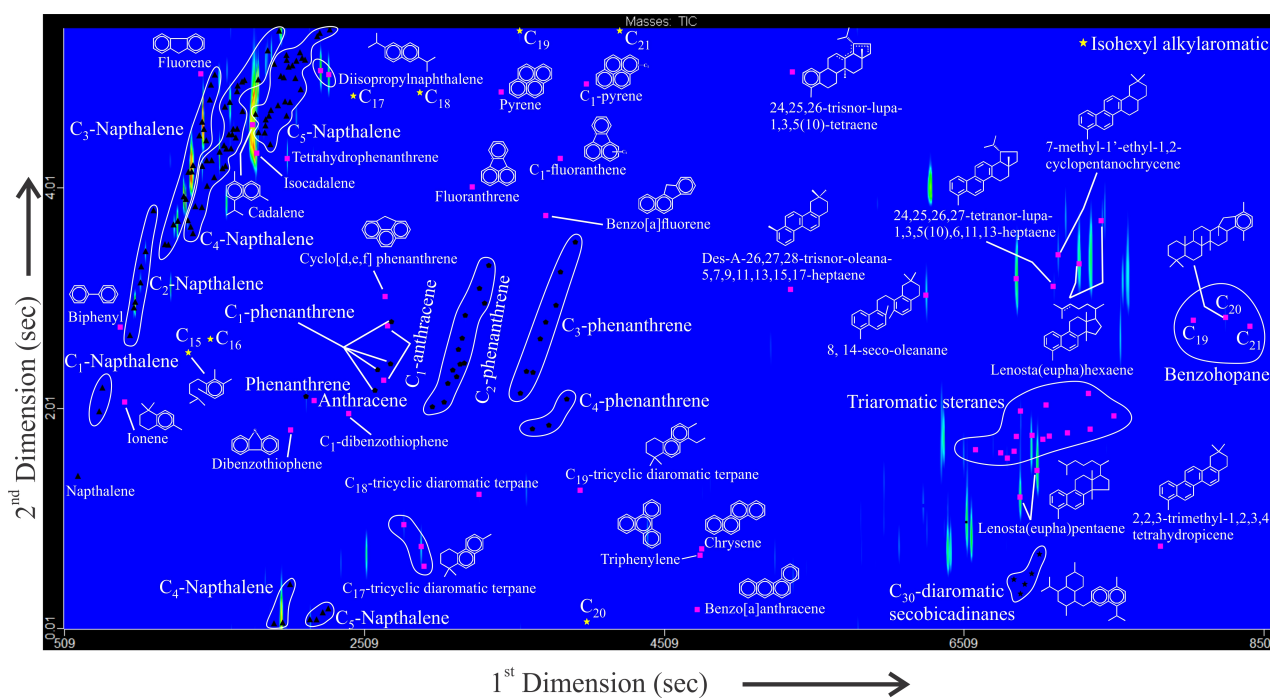


Figure 2: Total ion chromatogram of aromatic fraction of T-5 crude oil from Tarapur field, Cambay Basin

Summary

High Pristane/Phytane ratio and the abundance of diagnostic biomarkers like eudesmane, bicadinane, oleanane, ionene, cadalene and secobicadianane detected in the oil fractions indicating a significant contribution of terrestrial plants of angiosperm families to the source, which was deposited in a sub-oxic environment. Aromatic triterpenes detected in the aromatic fractions indicate that there is a significant contribution of micro-organism activity on organic matter. The presence of rearranged hopanes and steranes and calculated parameters based on certain biomarkers indicates shale as source rock. Various maturity parameters signify that the Cambay-Tarapur block oils have reached the initial catagenetic stage. The efficiency of GCXGC manages to improve in better understanding on biotic contribution and palaeodepositional environment of the Cambay Basin.

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