EVOLUTION OF THE UNRESOLVED COMPLEX MIXTURE AND ASSOCIATED BIOMARKERS IN BIODEGRADED PETROLEUM

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Introduction

The so called unresolved complex mixture (UCM), appearing as a big "hump" above the baseline in gas chromatograms (GC), is common and pronounced in biodegraded petroleum and seeps. In addition, it contains hundreds of thousands of unresolved compounds with similar low concentrations (Sutton et al., 2005). The UCM consists in part of simple aliphatic and aromatic hydrocarbons such as highly-branched alkanes, cycloalkyl systems comprised mainly of single ring units, substituted benzenoid structures, and alkylated tetralins or decalins (Gough and Rowland, 1990; Killops and Al-Juboori, 1990; Tran et al., 2010). Moreover, it has been proposed that the differences in UCM composition probably reflect differences in the kerogen from which the oils were derived (Gough and Rowland, 1990; Killops and Al-Juboori, 1990). Comprehensive two-dimensional gas chromatography, allowing the separation of complex mixtures using two capillary GC columns of different selectivity coupled by a modulator, when connected to a time-of-flight mass spectrometer (GC × GC-TOFMS) provides a powerful tool to characterize petroleum biomarkers, source rock extracts and UCM compositions.

Results

A set of biodegraded petroleums derived from distinct sedimentary basins, including northwestern Sichuan (Neoproterozoic, marine), Tarim (Early Paleozoic, marine), Bohai Bay (Eocene, saline/brackish), and Pearl River Mouth (Eocene, freshwater), were investigated by GC × GC-TOFMS in order to illustrate the occurrence and origin of the UCM. In general, hydrocarbons that constitute the UCM of petroleum saturate fractions can be divided into three zones as indicated in Figure 1, based on the elution of compounds in the first and second dimensions of GC×GC-TOFMS chromatograms equipped a P/NP column set. The hydrocarbon classes that fall into Zone 1 have higher 2nd dimensional retention times on the P/NP column set, showing weak or no polarity of the compounds. Apart from the normal, branched and isoprenoid alkanes, the other significant components of Zone 1 are mono- and bicyclic hydrocarbons (Fig. 1). Compounds falling into Zone 2 consist principally of bicyclic-to pentacyclic terpanes, such as sesquiterpanes, tricyclic terpanes, A-norsteranes, steranes, hopanes and 25-norhopanes, and all linked as biomarkers or molecular fossils across the geological record (Peters et al., 2005). The compounds falling into Zone 3 generally contain one aromatic ring in their structures, which increases the polarity of the hydrocarbons. It has been estimated that they can constitute 30% of the UCM components in petroleum (Killops and Al-Juboori, 1990). Tetralins and indanes, aryl isoprenoids, and ring-C monoaromatic steranes are major compound classes in Zone 3.

Conclusions

Based on the investigation of hydrocarbon compositions from a range of heavily biodegraded petroleums, the identification of compounds in the UCMs comprises mainly groups of tetralins and indanes, substituted xylenes and aryl isoprenoids, bicyclic to pentacyclic terpanes, and steranes and monoaromatic steranes. The biomarker compositions of the UCM depend primarily on source and organic input, and thus vary between petroleum groups. Although these constituents may also have resulted from hydrothermal alteration of organic matter, the UCM compositions will alter further with biodegradation, reducing or eliminating some hydrocarbon classes.
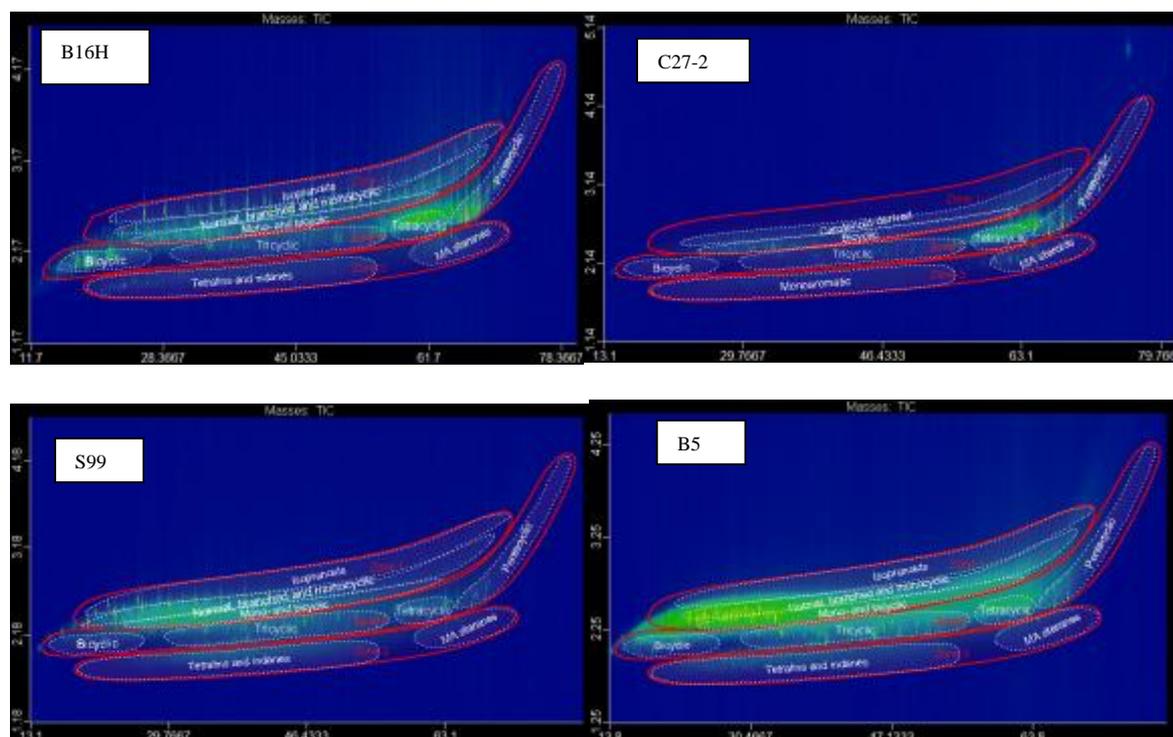
Figure 1 *GC×GC–TOFMS TIC plots for the saturate fractions of four biodegraded petroleums*

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