

MASS SPECTRAL RECOGNITION OF NOVEL HIGHLY BRANCHED ALKANES IN ROCK EXTRACTS FROM THE OFFICER BASIN

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A series of branched alkanes have been recognised in the extractable material (bitumen) from sedimentary rocks of the Neoproterozoic Ungoolya Group in the Officer Basin (~570Ma). These hydrocarbons were significantly more abundant than neighbouring *n*-alkanes, which is very unusual for a bitumen or petroleum. The branched alkane abundances were also highest at locations in the core coinciding with fossil microbial mats, a well known biological source of this general class of aliphatic compound.

Branched alkanes were recognised on the basis of their 70 eV mass spectra which reflect many similarities to the corresponding *n*-alkanes such as the same molecular ions and a similar series of even electron fragment ions (m/z 85, 99, 113, 127 etc). In contrast to the *n*-alkanes the fragment ion series have an uneven distribution caused by preferential cleavages at branch points. Characterisation of these products as branched alkanes was also supported by relative retention factors (RRF). Several of the alkane series showed RRF values in the range -1 to -6 which represent some of the lowest known values for naturally occurring hydrocarbons and suggests extensive branching. Petroleum derived branched alkanes generally reflect low levels of branching with mono methyl and dimethyl alkanes being most common and having RRFs of typically < -1 . The more highly branched acyclic isoprenoids, such as pristane and phytane, have RRFs of ~ -2 .

The relative abundance of the fragment ions can often help decipher the molecular structure of branched hydrocarbon products. Daughter scan analysis, in which the daughter ions from a selected parent ion are detected as their first field free region metastable ions, can similarly provide useful structural information on branched alkanes. However, with very high levels of branching much of the classical and daughter scan mass spectral is insufficient for the identification of the precise location of alkyl groups. The difficulty in identifying the molecular structure of highly branched alkanes from mass spectral data alone will be demonstrated.

Summation and subtraction of selected ion chromatograms is an effective way to highlight specific products or product classes from complex mixtures. In the Officer Basin samples selected ion chromatograms such as m/z 127-113 and m/z 141-127 highlight homologous series of 3,7-dimethylalkanes and 3-ethyl, 7-methylalkanes, respectively. The latter series has to our knowledge not previously been reported in geological samples although our identification on the basis of the MS data remains tentative until it can be compared (along with GC elution data) to synthetic analogues.
