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COMPARATIVE ORGANIC GEOCHEMISTRY OF SOME EUROPEAN OIL SHALES

By

A. G. Douglas and P. B. Hall  
Organic Geochemistry Unit, Geology Department, The University,  
Newcastle upon Tyne, England, NE1 7RU  
and  
H. Solli  
Continental Shelf Institute, Hakon Magnussons Gt.1B, 7001 Trondheim, Norway

The distribution, and geology, of oil shales occurring in Western Europe was described in a substantial paper by Bitterli (1) and briefly in a later paper by Schlatter (2). The interest of the former author was principally the location, depositional environments, mineralogy and organic carbon content of a very large number of bituminous sediments, and he proposed a classification which divided the bituminous rocks into seven categories. Although, in this work, we have followed Bitterli to some extent in the locations from which our samples were collected we have, for convenience, considered Duncan's (3) classification of three main oil shale lithologies. Although there were two major periods of European oil shale formation, namely deposits of Permo-Carboniferous age which are associated, in part, with coal sequences, and Jurassic deposits often of marine origin, the work undertaken in this laboratory has covered eighty samples from twenty deposits ranging in age from Cambrian to Oligocene. These may be divided, using Duncan's classification into a) those believed to have been deposited in shallow marine basins (Cambrian, Sweden; Permian, England; Lower, middle and upper Jurassic, Scotland/England; Oligocene, France), b) those deposited in large Lacustrine basins (Devonian, Scotland; Carboniferous, Scotland; Permian, France), and c) those deposited in small lagoonal basins, often associated with coal swamp environments (Carboniferous, Scotland; middle Jurassic, Scotland; Tertiary, Germany).

The types of analyses of these oil shales, which have been carried out by us include, *inter alia*, microscopical observation and maceral point count, vitrinite reflectance and spore fluorescence, oil assay using a simple mini Fischer-type retort followed by chromatographic analyses of some of the shale-oils, Rock Eval pyrolysis, organic carbon content, extractable bitumens and analyses of the contained hydrocarbons. Elemental analyses, pyrolysis gas chromatography and pyrolysis gas chromatography-mass spectrometry was achieved on some isolated kerogens.

This overview, which will hopefully provide some ground work for further investigations, has given some of the results which follow. Total organic carbon values varied widely: for instance, Devonian shales from N. Scotland had a maximum of 5% whereas in the Carboniferous shales of the Midland valley (Scotland) they ranged to 25% and to very high values in the torbanite-rich shales. The values for organic carbon in the Permian (Autun) samples ranged from 7-18%, lower and middle Jurassic figures ranged from 2% to 15% with the Brora Parrot Shale having the exceptionally high value of 32%. Upper Jurassic (Kimmeridgian) values ranged from 7% to 38%. Soluble bitumens were extracted from the rocks giving values ranging from traces to 3% with aliphatic/aromatic ratios varying from 0.06 to 3.90: in some instances unsaturated hydrocarbons formed the major fraction of the aliphatic fraction. Analysis of the saturated hydrocarbons by molecular sieve separation followed by GC and GC-MS indicate wide variations in distributions, and types, of compounds. Normal alkane distributions vary, as reflected in carbon preference indices, which range from less than 1.0 to 2.5 (exceptionally 6.0) with maxima indicating algal and higher plant contributions to the sediment. Steranes and triterpanes are ubiquitous with the former appearing to be more abundant in marine deposits and the latter in lake basin deposits. In certain of the samples from Autun (France) and Caithness (Scotland), which represent large lacustrine deposits, carotane and C<sub>13</sub> to C<sub>24</sub> alkyl substituted trimethylcyclohexanes, which are possibly degradation products of carotenoids, were identified by Hall and Douglas (4). Kovats retention indices for almost 70 cyclic compounds including the above, together with hopanes, diasteranes, and regular and nuclear methylated steranes were measured in many of the samples and provide useful data to help in identifications.

Oil assays were obtained using small samples in a simple laboratory-constructed apparatus and indicated that shale oil yields ranging from 2 to 300 liters/tonne could be expected. Twelve of the shale oils were then separated to provide trans- and terminal alkene fractions, together with

saturated hydrocarbons. Yields of saturated hydrocarbons varied from 3% to 23%, of terminal alkenes from 4% to 21% and possibly trans-alkenes from 2% to 16%. In all of the oils there was a large fraction (from 35% to 85%) which was more polar than the terminal alkenes on Ag<sup>+</sup> thin layer chromatography and presumably represented aromatic, heterocyclic and other polar compounds. Gas chromatographic analyses revealed principally homologies of the aliphatic hydrocarbons noted above: few firm conclusions can be drawn from these analysis although in general it appeared that marine sediments provided mainly normal hydrocarbon homologies superposed on a large unresolved 'hump', whereas non-marine sediments produced extended homologies on a less pronounced 'hump' of unresolved material.

Pyrolysis gas chromatography (and gas chromatography-mass spectrometry) indicates that oil shale kerogens can produce fingerprints that allows some measure of 'typing' the oil shales (5). Algal kerogens, with a substantial contribution from *Botryococcus braunii*, provided easily recognized programs in which the predominant feature is a homology of alkanes, -enes and -dienes: in some marine kerogens the triplet homology is much less predominant than are aromatic molecules. An attempt to use aliphatic/aromatic ratios in typing kerogens has already been made (6).

#### LITERATURE CITED

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