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Estimating Oil Thermal Maturity from Biomarkers and Alkyl Aromatics

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Summary

A number of terpane and sterane biomarker ratios are sensitive to changes in thermal maturity and likely record the maturity of the corresponding source rock at the time the oil was expelled (primary migration). These include C27 and C29 norhopanes, diahopanes, diasteranes, and triaromatic steranes as well as methyldibenzothiophenes. C29 sterane 20S & 20R isomer ratios are useful at lower maturities. Typically, biomarkers are measured using conventional GC-MS techniques (SIM mode) on saturate (or branched-cyclic) and aromatic hydrocarbon fractions derived from liquid chromatography. A combination of these biomarker ratios can be subjected to principal component analysis, and the resulting first or primary factor often carries over 75% of the total variation in the dataset. It is important to evaluate maturity in oils that belong to the same oil 'family' (i.e., oils from the same source facies) since some of these maturity ratios also have a significant genetic or source component. The principal component (Factor 1) calculated for each oil in each family can be converted to a 'vitrinite reflectance equivalent' value (VRE) in order to place each oil within the confines of the oil generation window (~0.6-1.2% Ro). By estimating a VRE for both the lowest and highest Factor 1 values, the oils with intermediate levels of maturity can be linearly extrapolated to give VREs for each oil. However, at advanced oil maturity levels that yield volatile oils or condensates (~1.0-1.3% Ro), terpane and sterane biomarkers are thermally degraded and are often insufficient in abundance to be useful. Also, these biomarker-derived maturity estimations reflect the maturity of the heavier-ends (C15+) of the oil; lighter components of the same oil may have been derived from more mature, biomarker deficient fluids expelled from the same source rock.

Since many of the fluids produced from unconventional lateral completions are light oils or condensates with minimal biomarker concentrations, or may have high maturity lighter-end components in addition to typical biomarker distributions, we have developed an oil maturity calculation based on known differences in thermal stability of alkyl-substituted benzenes, naphthalenes, and phenanthrenes. These compounds are present in all petroleum liquids regardless of the maturity rank. A GC-triple quadrupole mass spectrometer is used to determine the concentration of these compounds which allows the injection of whole crudes diluted with DCM solvent containing deuterated internal standards. Therefore, due to the specificity of the triple quadrupole instrument, it is not necessary to obtain liquid chromatographic fractions which can result in the loss of light-ends. In addition, during the same analysis, concentrations of volatile adamantane and diamantane diamondoid isomers are determined, another measure of the oil's maturity components. Also, terpane and sterane biomarkers at low concentrations can be determined during the same run with more specificity than is possible in the usual GC-MS biomarker analyses.

In order to derive VREQ values (vitrinite reflectance equivalent based on the triple quadrupole), a series of thirteen alkyl-substituted naphthalene and phenanthrene ratios are constructed such that they increase

with increasing maturity, with the more thermally stable isomer in the numerator. The percentages of all thirteen are simply added together with the higher total values corresponding to higher maturity levels. To calibrate the scale, the upper end of fluid maturity is fixed at 1.35% Ro and given to a number of clear condensates analyzed with the highest alkyl aromatic summations measured. Lower values are equated to oil standards of known or suspected maturities and, especially, source rock extracts. Source rocks, with measured Ro values as well as Tmax determinations from pyrolysis, are crushed but not powdered, and the DCM extract (never taken to dryness to minimize evaporation) is injected on the GC-triple quadrupole after deuterated internal standards are added. For example, six samples each from two Oklahoma Upper Devonian Woodford Shale cores from Kingfisher Co. (9,393-9,432 ft) and Canadian Co. (10,326-10,426 ft) were analyzed by Rock-Eval pyrolysis (after solvent extraction) and measured Ro determined (polished whole rock reflectance). The measured Ro values average 0.97% and 1.05% for the Kingfisher and Canadian Counties, respectively, consistent with the difference in burial depth. The standard error is 0.06% when considering all the multiple reflectance measurements on each of the six samples per core. The corresponding extracted Tmax values equate to 0.98% and 1.07% ±0.03% VRE for the six samples from each core. Extracted Tmax numbers are much more reproducible than unextracted Tmax values due to the lack of S1 interference with S2. The corresponding VREQ maturities calculated from the alkyl aromatics in the Woodford extracts are 1.02% and 1.09% ±0.02%. Considering the three very different maturity determination methods, the similarities are exceptional.

VRE and VREQ maturities were determined for a number of Alberta Basin oils generated from the UK Second White Specks Shale (as determined by characteristic biomarkers and carbon isotopes). Variations in maturity, both stratigraphically (e.g., in older Viking and younger Cardium reservoirs) and geographically are evident and help locate optimal regions for potential unconventional production of light oil.