

NORTH VIKING GRABEN
GEOCHEMICAL STUDY

GC-MS ANALYSIS

Well no. 30/6-4 NOCS

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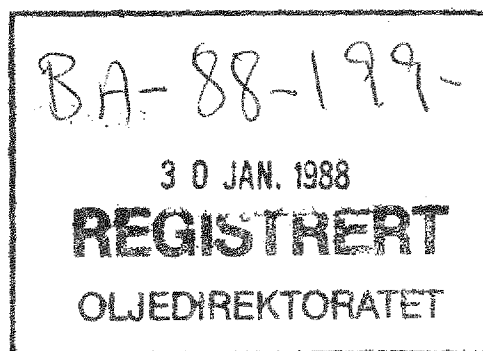
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RESULTS AND DISCUSSION

A total of nine samples, two from the Draupne Fm. (2417 - 2420 m and 2424 - 2429 m), three from the Heather Fm. (2432 - 2441 m, 2480 - 2492 m and 2531 - 2534 m) and four samples from the Dunlin Gr. (2771 - 2780 m, 2789 - 2813 m, 2813 - 2834 m and 2894 - 2927 m) in this well was analysed by GC - MS.

DRAUPNE FORMATION

Saturated Fraction

Terpanes:

The M/Z 163 fragmentograms of the two samples from the Draupne Fm. vary at first glance. The main variation is, however, the large peak found in the sample from 2429 m that is not found in the sample from 2420 m. This peak is a contaminant from the septa on the sample bottles (see discussion on well 30/6-3). When this peak is excluded, the two fragmentograms are similar.

The M/Z 177 fragmentograms of the two samples show that the steranes are very abundant, being the largest peaks in these fragmentograms. Some of the triterpanes are easily identified, especially $\alpha\beta$ and $\beta\alpha$ norhopane and $\alpha\beta$ hopane. There is no indication of any of these two samples containing demethylated triterpanes.

The M/Z 191 fragmentograms of the two samples show only minor differences apart from the contaminant eluting together with the C₂₅ tricyclic terpane. None of the samples have any significant amount of tricyclic and tetracyclic

equal amount, possibly with slightly more rearranged steranes than regular steranes. This is verified by the fragmentograms of the molecular ions.

Bicyclanes:

The M/Z 123, 179 and 193 fragmentograms show the different bicyclanes. The two samples from the Draupne Fm. show very similar pattern for all three fragmentograms. The M/Z 123 fragmentograms show the C₁₆ compounds to be most abundant.

Aromatic Fraction

Thiophenes:

The M/Z 84 fragmentograms for the two samples, appear at first, to be different. As with other fragmentograms, this is due to the normalization of the largest compound at the front end of the fragmentogram. This compound is thiophene. The series of peaks at higher retention times were not identified. They have an almost identical pattern for the two samples and might be useful compounds for correlation purposes.

The M/Z 98 fragmentograms, showing methyl-substituted thiophenes, also contain higher molecular weight compounds. The pattern of these are almost identical for the two samples and might be useful for correlation purposes.

The M/Z 112 fragmentograms also have higher molecular weight compounds. These show some variation between the two samples, but without knowing the identification of these samples, further discussion will not be undertaken.

The M/Z 126 fragmentograms of the two samples vary

significantly. The sample from 2420 m does not contain any light molecular weight material. This might be due to loss during the work up process. There are also variations in the higher molecular range. These compounds were not identified and further discussion will not be undertaken.

The M/Z 140 fragmentograms of the two samples, which should normally represent the C₄-thiophenes, show the same feature as the other fragmentograms representing alkyl-substituted thiophenes, i.e. higher molecular weight compounds are also present in the fragmentograms. The sample from 2420 m has lost a large proportion of the light molecular weight compounds, but there are also significant differences in the high molecular weight compounds as well. Without knowing the identity of these compounds, further discussion will not be undertaken.

Alkyl-substituted Benzenes:

The M/Z 106 fragmentograms, which mainly represent the C₂-substituted benzenes, show some minor differences between the two samples. This is in the front end of the fragmentogram, basically due to a loss of low molecular weight material for the sample from 2420 m. Apart from this, the two fragmentograms are almost identical. A similar situation is also found for the M/Z 134 and 148 fragmentograms representing C₄- and C₅-substituted benzenes, respectively.

Naphthalenes:

The M/Z 142 fragmentograms show, at first glance, a large difference between the two samples. This is, however, due to a loss of low molecular weight material from the sample from 2420 m, reducing the typical doublet for the methyl-substituted naphthalenes to almost zero.

The M/Z 156 fragmentograms representing the C₂-substituted naphthalenes are almost identical for the two samples, which is also the situation for the M/Z 170 fragmentograms, representing the C₃-substituted naphthalenes.

Benzothiophenes and Dibenzothiophenes:

The M/Z 162 fragmentograms for the two samples, representing C₂-substituted benzothiophenes, show large variations between the two samples. This is due to the loss of the light weight material showing a large proportion of high molecular weight compounds, that were not identified, in the sample from 2420 m. When the loss of the low molecular weight material from the sample from 2420 m is taken into consideration, then the two samples show a similar distribution in the M/Z 162 fragmentograms. A similar situation is also found for the M/Z 176 representing the C₃-benzothiophenes. The M/Z 184 fragmentograms show only the single peak for dibenzothiophenes for both samples, while the typical triplet is seen for the methylsubstituted dibenzothiophenes in the M/Z 190 fragmentograms. 1-methyldibenzothiophene is the largest compound which shows that the samples are of low maturity.

The M/Z 212 fragmentograms for the C₂-substituted dibenzothiophenes show the normal complex pattern for both samples. The pattern is similar for the two samples.

Phenanthrenes:

The M/Z 178 fragmentograms show only the single peak for phenanthrene for both samples, while the M/Z 192 fragmentograms show the two doublets representing the methylphenanthrenes. The second doublet (9-methyl- and 1-methylphenanthrenes) is the largest in both samples, which have almost identical patterns.

The M/Z 206 fragmentograms for the C₂-phenanthrene show an almost identical pattern for the two samples. This is also the situation for the M/Z 220 fragmentograms representing the C₃-phenanthrenes.

Aromatic Steranes:

The M/Z 253 fragmentograms show almost identical pattern for the monoaromatic steranes in the two samples. The C₂₁ and C₂₂ compounds are relatively small compared to the C₂₇ - C₂₉ compounds, indicating that the two samples are of low maturity. As with the monoaromatic steranes, the triaromatic steranes are found to be abundant in these two samples as seen by the M/Z 231 fragmentograms, and have very similar patterns.

HEATHER FORMATION

Saturated Fraction

Terpanes:

The M/Z 163 fragmentograms vary significantly for the three samples. The sample from 2432 - 2441 m (2441 m) shows an almost identical pattern to that found for the Draupne Fm. samples and could therefore represent caved material. The two other samples show the triterpanes to be far more abundant than the steranes, in direct opposition to the Draupne Fm. samples. The sample from 2480 - 2492 m (2492 m) was also found to contain a contaminant (from the septa on the sample flasks). Apart from this, the bisnorhopane is found to be the largest peak in the two samples from 2492 m and 2534 m. The pattern is almost identical for these two samples.

The M/Z 177 fragmentograms show a similar situation as found for the M/Z 163 fragmentograms. The sample from 2441 m has an identical distribution to the Draupne Fm. samples, while the samples from 2492 m and 2534 m show a different distribution with the triterpanes far more prominent than is found in the samples above. The most prominent peaks are bisnorhopane, $\alpha\beta$ norhopane and $\beta\alpha$ norhopane.

The M/Z 191 fragmentograms of the three samples show the same features as described for M/Z 163 and M/Z 177 fragmentograms, i.e. the samples from 2441 m shows the same pattern that was found for the Draupne Fm. samples, while the other two samples show a completely different pattern. The two samples have a similar distribution with bisnorhopane being the largest peak (except for the contaminant in the 2492 m sample) and almost equal amount of 17 α trisnorhopane, $\alpha\beta$ norhopane and $\alpha\beta$ hopane. This is

different from the Heather Fm. sample in well 30/6-3, where bisnorhopane was present, although it was not the largest compound. The large proportion of $\beta\alpha$ triterpanes and the high 22R/22S ratio show that the samples are of low maturity.

The M/Z 205 fragmentograms do not show any sign of the samples containing demethylated triterpanes. Again the sample from 2441 m shows an almost identical pattern with the samples from the Draupne Fm., while the two other samples are distinctly different. The fragmentograms of the molecular ions verify the different parts discussed above. The sample from 2441 m has almost identical patterns to that found for the Draupne Fm. samples, while the two other samples are distinctly different. The T_S/T_M ratio is very much lower for the Heather Fm. samples, clearly showing that there are differences in the organic material.

Steranes:

The M/Z 149 fragmentograms agree very well with the conclusions drawn from the terpanes, i.e. the sample from 2441 m has an almost identical pattern to the Draupne Fm. shales, while the two other Heather Fm. samples show completely different patterns. The latter two samples show a large peak of low molecular weight to which the rest of the peaks are normalized. This makes the sterane peaks rather small and therefore difficult to interpret. The two samples have, however, similar patterns.

The M/Z 189 and 259 fragmentograms, representing the rearranged steranes, show similar distributions to the Draupne Fm. samples. The only difference is an increase in the C_{29} compounds compared with the C_{27} compounds with increasing depth. This suggests an increase in the input of terrestrial plant material with increasing depth. The M/Z 217 and 218 fragmentograms show similar variations to

the terpanes, i.e. the sample from 2441 m shows patterns similar to the samples from the Draupne Fm., while the two other samples have different patterns. This is mainly due to a drastic reduction in the abundance of regular steranes compared to the rearranged steranes, clearly showing the changes in organic material and environment of deposition. This is also clearly seen in the fragmentograms of the molecular ions.

Bicyclanes:

The M/Z 123, 179 and 193 fragmentograms of the bicyclanes show similar features which were recorded for the terpanes and the steranes. The sample from 2441 m has similar distributions as the Draupne Fm. samples, while the samples from 2492 m and 2534 m are completely different. Some of this might be due to a loss of low molecular weight material, but the main difference is due to a change in the organic matter. The main difference in the fragmentograms is a reduction of the C₁₅ isomers relative to the C₁₆ compounds for the samples from the Heather Fm. compared with the samples from the Draupne Fm.

Aromatic Fraction

Thiophenes:

The M/Z 84 fragmentograms of the three samples vary significantly. This is mainly due to the variable abundance of thiophene, resulting in considerable variation of the peak heights of the higher molecular weight compounds also found in these fragmentograms. Apart from this, the main difference is found in the abundance of the peak at approximately 27 min. This is far larger in the samples from 2492 m and 2534 m than in the sample from 2441 m. This could

be due to a change in organic matter and environment of deposition.

The M/Z 98 fragmentograms, representing the methyl-substituted thiophenes show marked differences in the three samples. The sample from 2441 m shows mainly one peak, similar to the large peak found in the sample from 2429 m in the Draupne Fm. The other two samples show a series of high molecular weight compounds. The pattern of these compounds show many similarities between the two samples.

The M/Z 112 fragmentograms representing the C₂-thiophenes show marked differences between the three samples. The sample from 2441 m shows the same pattern as the samples from the Draupne Fm., while the samples from 2492 m and 2534 m are completely different, but they are very similar to each other. None of the compounds found in the M/Z 112 fragmentograms for these two samples are C₂-thiophenes.

The M/Z 126 fragmentograms for the C₃-substituted thiophenes and the M/Z 140 fragmentograms for the C₄-substituted thiophenes show similar features (i.e. the sample from 2441 m shows some resemblance to the samples from the Draupne Fm., while the samples from 2492 m and 2534 m are completely different, probably due to a change in the organic matter).

Alkyl-substituted Benzenes:

The M/Z 106, 134 and 148 for various alkyl-substituted benzenes, basically show the same features as discussed above.

Naphthalenes:

The M/Z 142 fragmentograms show the typical doublet for the

methyl-substituted naphthalenes for the sample from 2441 m, while only higher molecular weight compounds were recorded in the samples from 2492 m and 2534 m. This is probably due to a loss of the lighter compounds during preparation of the aromatic fraction.

The M/Z 156 fragmentograms show, partly the same situation with the typical C₂-substituted naphthalenes distribution in the sample from 2441 m, which is missing for the sample from 2492 m (again, probably due to loss during work up). The C₂-substituted naphthalenes are, however, clearly seen for the sample from 2534 m. Here the largest peak is 1,4+2,3+1,5 dimethylnaphthalene, while the doublet with 1,3+1,7 and 1,6 dimethylnaphthalene show the largest peaks in the samples from the Draupne Fm. This could partly be an effect from the work up of the sample, but it is also partly due to a change in the organic matter. The M/Z 170 fragmentograms representing the C₃-substituted naphthalenes show the sample from 2441 m to be almost identical to the samples from the Draupne Fm., while the other two samples from the Heather Fm. show a loss of the compounds with shortest retention time compared with the samples from the Draupne Fm. This is most probably due to a change in the organic matter in the samples.

Benzothiophenes and Dibenzothiophenes:

The M/Z 162 fragmentograms show the C₂-substituted benzothiophenes in the sample from 2441 m are similar to the samples from the Draupne Fm. They are not recorded in the sample from 2492 m, probably due to a loss during work up. The compounds were recorded in the sample from 2534 m, but they are completely different to that for the Draupne Fm. samples.

The M/Z 176 fragmentograms, representing the C₃-substituted benzothiophenes show clearly that the sample from 2441 m is

similar to the Draupne Fm. samples, while the two other Heather Fm. samples show only one peak for this fragmentogram. This peak is also present in the samples from the Draupne Fm., but is not as dominant as in the Heather Fm. samples. This is similar to that found for most of the samples from well 30/6-3.

The M/Z 184 fragmentograms show only the single peak for dibenzothiophene for all the samples, while the M/Z 198 show the triplet for methyl-substituted dibenzothiophene together with a single peak at a lower retention time. This is only 40 % of the largest methyl-dibenzothiophene for the sample from 2441 m, but it is the largest peak in the fragmentograms for the sample from 2492 m. The other major difference between the three samples is in the distribution of the methyl-dibenzothiophenes. 1-methyl-dibenzothiophene is the largest peak in the sample from 2441 m as in the sample from the Draupne Fm. It is still the largest peak in the samples from 2492 m and 2534 m, but the difference between this and the two other peaks is considerably reduced. This pattern, as seen for the Heather Fm. samples, was also found for the Heather Fm. samples in well 30/6-3.

The M/Z 212 fragmentograms, which represent the C₂-dibenzothiophenes, show that the sample from 2441 m has a similar pattern to that found for the samples from the Draupne Fm., while this is clearly different from the samples from 2492 m and 2534 m, due, most probably, to the changes in the organic matter.

Phenanthrenes:

The M/Z 178 fragmentograms show the single peak for the phenanthrenes to be similar to that found for the Draupne Fm., while the samples from 2492 m and 2534 m also show the small peak from anthracene, similar to that found for the Heather Fm. samples in well 30/6-3.

The M/Z 192 fragmentograms for the methyl-substituted phenanthrenes are similar for all three samples, which is also the situation for the M/Z 206 fragmentograms for the C₂-substituted phenanthrenes.

The M/Z 220 fragmentograms for the C₃-substituted phenanthrenes show the sample from 2441 m to have a similar pattern to that found for the Draupne Fm. samples. The samples from 2492 m and 2534 m show significant differences, especially for the doublet with the highest retention time. The internal peak height in this doublet is reversed as compared with the samples above. This is probably due to the change in organic matter.

Aromatic Steranes:

The M/Z 253 fragmentograms for the monoaromatic steranes show the sample from 2441 m has a similar distribution to that found for the Draupne Fm. samples. The distribution changes for the samples from 2492 m and 2534 m, in particular the abundance of the C₂₉ monoaromatic steranes, which increases relative to the C₂₇ and C₂₈ monoaromatic steranes. This is clearly due to a change in the organic matter.

The M/Z 231 fragmentograms, representing the triaromatic steranes, show only minor differences between the three samples. The sample from 2441 m has a pattern similar to that found for the Draupne Fm. samples, while the samples from 2492 m and 2534 m show an increase in the abundance of the 20S C₂₈ peak compared to the rest of the triaromatic sterane peaks.

DUNLIN GROUP

Saturated Fraction

Terpanes:

The M/Z 163 fragmentograms of the four samples from the Dunlin Gr. seem to vary somewhat from sample to sample. They are all clearly different from both the Draupne Fm. and the Heather Fm. samples. The rearranged steranes seem to be dominant in all the samples, and the C₂₇ and C₂₉ rearranged steranes are particularly prominent in the sample from 2813 - 2834 m (2834 m) and 2894 - 2927 m (2927 m). It is difficult to evaluate the samples from 2771 - 2780 m (2780 m) and 2789 - 2813 m (2813 m) due firstly to the sample from 2780 m which has a large unresolved envelope which partly distorts the distribution and secondly to the sample from 2813 m which has a very prominent peak of low molecular weight which dominates the steranes/triterpanes pattern so much that the typical sterane/terpane pattern is lost. This peak is registered in all the Dunlin Gr. samples, but is not recorded in the Draupne Fm. or Heather Fm. samples. It is not recorded in any of the Dunlin Gr. samples from well 30/6-3.

The M/Z 177 fragmentograms show some variation for the four samples. The sample from 2780 m still shows the bisnorhopane to be the major peak and the triterpanes are completely dominant over the steranes. This is changed for the three remaining samples, which do not show any peak where bisnorhopane will elute. $\alpha\beta$ norhopane is the dominating peak with $\beta\alpha$ norhopane as the second largest peak. These three samples show similar patterns.

The M/Z 191 fragmentograms for the Dunlin Gr. samples are quite different from the samples from the Draupne Fm. and

the Heather Fm. The bisnorhopane peak is only present as a minor peak in the sample from 2780 m, while it is absent in the rest of the samples. The sample from 2780 m also has a large abundance of tri- and tetracyclic terpanes, while these are absent in the samples from higher up in the well. The tri- and tetracyclic terpanes are also clearly present in the other three samples from the Dunlin Gr., but not in the same magnitude as the sample from 2780 m. This sample also differs in other ways from the rest of the Dunlin Gr. samples in that $\alpha\beta$ norhopane is the largest triterpane peak, while $\alpha\beta$ hopane is the largest triterpane peak for the other three samples. There is also a significant variation in the T_S/T_M ratio. This is far larger in the sample from 2780 m than in the rest of the Dunlin Gr. samples. This would all indicate a slight difference in the organic matter or deposition of environment for the analysed Dunlin Gr. samples. This is also very different to that found for the Draupne Fm. and Heather Fm. samples.

The M/Z 205 fragmentograms show a variation for the Dunlin Group samples. The sample from 2780 m has a large unresolved envelope which distorts the results. This is also partly present in the other samples as well. The relative ratios of the various triterpanes is similar for the Dunlin Gr. samples, but different to that found for the Draupne Fm. and Heather Fm. samples. The fragmentograms of the various molecular ions verify what has been discussed above for the triterpanes.

Steranes:

The M/Z 149 fragmentograms show some differences between the four samples. The main difference is between the sample from 2780 m and the rest. This could partly be due to the unresolved envelope found for this sample, which is not present to the same degree in the other samples.

The M/Z 189 and 259 show the C₂₇ and C₂₉ rearranged steranes to be of approximately equal height, which shows there is an increase in the C₂₉ compounds for these samples compared with the Draupne Fm. and the Heather Fm. samples. This is similar to the pattern found for the Dunlin Gr. samples in well 30/6-3. The M/Z 217 and 218 fragmentograms show the regular steranes to be quite abundant in these samples and the pattern is significantly different from what is seen for the Draupne Fm. and the Heather Fm. samples. The fragmentograms of the molecular ions show that the abundance of C₂₇ regular steranes is lower than C₂₇ rearranged steranes in the Dunlin Gr. samples compared with the Draupne Fm. samples.

The M/Z 372 fragmentograms have a similar pattern to that found for the Heather Fm. samples. This is also partly the situation for the C₂₈ compounds as seen in the M/Z 386 fragmentograms and the C₂₉ compounds as seen by the M/Z 400 fragmentograms.

Bicyclanes:

The M/Z 123, 179 and 193 fragmentograms show some variation between the different samples. The main variation is seen for the M/Z 179 fragmentograms and could partly be due to the work up of the samples. On the whole, there is only a minor variation between the various samples, especially for the M/Z 123 fragmentograms. There is, however, a significant variation between these samples and the samples from the Draupne Fm.

Aromatic Fraction

Thiophenes:

The M/Z 84 fragmentograms clearly show the thiophene in all the samples. The group of compounds with a retention time between 22 and 27 minutes that is prominent in the Draupne Fm. samples was only recorded in the sample from 2780 m. The rest of the samples show only the thiophene peak, and a few peaks (of high molecular weight compounds).

The M/Z 98 fragmentograms show a series of peaks with retention time between 25 and 35 minutes. These peaks are clearly present in all the samples, also those from Draupne Fm. and Heather Fm.

The M/Z 112 fragmentograms show relatively strong variation between the samples. It is, however, impossible to discuss this variation further since the various peaks were not identified. A similar situation was also found for the M/Z 126 and 140 fragmentograms.

Alkyl-substituted Benzenes:

The M/Z 106, 134 and 148 fragmentograms for the different substituted benzenes show some variations. The M/Z 106 fragmentograms show that the samples are very similar. There are minor differences between these Dunlin Gr. samples and samples higher up in the well.

The M/Z 134 fragmentograms, however, show a marked difference between the Dunlin Gr. samples and those from higher up in the well. The largest difference is in the compounds with shortest retention time. The sample from 2780 m resembles the pattern seen for the lowermost analysed sample in the Heather Fm., while this changes drastically in

the sample from 2813 m, and shows a similar pattern to that found for the Dunlin Gr. samples in well 30/6-3. Some of the lower molecular weight compounds disappear in the samples from 2834 and 2927 m. This could be due to the work up process of the sample. The large variation for C₄-alkyl-benzenes could make these compounds useful for correlation purposes.

The M/Z 148 fragmentograms for the Dunlin Gr. samples are found to be different to those from samples higher up in the well. The distinct peaks have disappeared for these samples and show only a large unresolved envelope.

Naphthalenes:

The typical doublet in the M/Z 142 fragmentograms for the methylnaphthalenes is only present in one of the samples from the Dunlin Gr. probably due to loss in the work up process for the other samples, and will therefore not be discussed further. The typical pattern of peaks in the M/Z 156 fragmentogram for the C₂-substituted naphthalenes is only found in two of the samples, probably also due to loss during work up of the samples and the results therefore are not discussed any further.

The M/Z 170 fragmentograms representing the C₃-substituted naphthalenes show the typical pattern which is similar to that found for the Heather Fm. samples.

Benzothiophenes and Dibenzothiophenes:

The M/Z 162 fragmentograms, which mainly represent the C₂-substituted benzothiophenes, show that there is some variation between the four samples. The main difference is found for the sample from 2780 m compared to the rest, especially in the abundance of one peak. This is also found

for the sample from 2813 m, which has a peak which is not recorded in any of the other samples. With this exception, the four samples show a similar pattern which is completely different from that found for the Draupne Fm. and Heather Fm. samples.

The M/Z 176 fragmentograms, which normally represent the C₃-substituted benzothiophenes, show, as for the Heather Fm. samples, only one peak.

The M/Z 184 fragmentograms show the dibenzothiophene as the major peak, while the M/Z 198 fragmentograms show the typical triplet for the methyl-substituted dibenzothiophenes. 4-methyldibenzothiophene is now the largest peak in the samples, and the 3+2-methyl- and 1-methyldibenzothiophene peaks are approximately the same height. This is different from the Dunlin Gr. samples in well 30/6-3, which showed the 1-methyldibenzothiophene peak to be smaller than the 3+2-methyldibenzothiophene peak.

The M/Z 212 fragmentograms show the normal pattern for the C₂-substituted dibenzothiophenes. The pattern is similar for the four samples, but differs clearly from that found for the samples higher up in the well. The pattern is similar to that found for the Dunlin Gr. samples in well 30/6-3.

Phenanthrenes:

The M/Z 178 fragmentograms show only the single peak for phenanthrene, while the M/Z 192 fragmentogram show the typical quartet for the methyl-substituted phenanthrenes. The abundance of 3-methyl- and 2-methylphenanthrenes relative to the 9-methyl- and 1-methylphenanthrenes in the Dunlin Gr. samples is greater than in the Draupne Fm. and Heather Fm. samples. This could be a combination of increased maturity and changes in the organic matter.

The C₂-substituted phenanthrenes, represented by the M/Z 206 fragmentograms, show only one minor difference between the Dunlin Gr. samples and the Heather Fm. samples. A similar observation can be made for the M/Z 220 fragmentograms which represent the C₃-substituted phenanthrenes.

Aromatic Steranes:

The increase in the C₂₉ monoaromatic steranes relative to the C₂₇ and C₂₈ compounds recorded in the M/Z 253 fragmentograms for the Heather Fm. samples compared with the Draupne Fm. samples, is even now masked in the Dunlin Gr. samples and is probably due to a change in the environment of deposition/organic matter.

The M/Z 231 fragmentograms also show variation compared to the samples from younger sequences. The main change is the increase in the abundance of the 20S C₂₈ peak compared with the rest. This was first noted for the Heather Fm. samples compared with the Draupne Fm. samples and is strengthened further for the Dunlin Gr. samples.

Experimental, combined gas chromatography - mass spectrometry (GC-MS)

The GC-MS analyses were performed on a VG TS250 system interfaced to a Hewlett Packard 5890 gas chromatograph. The GC was fitted with a fused silica OV-1 capillary column (25m x 0.22 mm i.d.) directly into the ion source. Helium (10psi) was used as carrier gas and the injections were performed in splittless mode. The GC oven was programmed from 50°C to 150°C at 35°C/min. at which point the programme rate was 4°C/min up to 280° where the column was held isothermally for 37 min. For the aromatic hydrocarbons, the GC oven was programmed from 50oC to 280°C at 5°C/min. and held isothermally at 280_oC for 22 min. The mass spectrometer was operated in electron impact (EI) mode at 70 eV electron energy, a trap current of 500 uA and a source temperature of 220°C. The instrument resolution was 2500 (10% valley) for most of the samples, but had to be decreased to 1000 for some samples to improve the sensitivity of some mass fragmentograms.

The datasystem used was a VG PDP11/73 system. The samples were analysed in multiple ion detection mode (MID) at a scan cycle time of approximately 1,8 sec.

Calculation of peak ratios was done from peak height in the appropriate mass fragmentograms.

In the discussion of the GC-MS data, the results will be discussed by area. The wells within an area will be discussed separately. In the discussion, samples within one formation are discussed together. The discussion is further divided into types of compounds as follows:

Saturated Fractions:

Terpanes:

The most commonly used fragmentions for detection of terpanes are M/Z 163 for detection of 25,28,30 trisnor-moretane or 25,28,30 trisnorhopane, M/Z 177 for detection of demethylated hopanes or moretanes, M/Z 191 for detection of tricyclic, tetracyclic- and pentacyclic terpanes and M/Z 205 for methylated hopanes or moretanes. The molecular ions M/Z 370, 384, 398, 412 and 426 are also recorded for identification of C₂₇, C₂₈, C₂₉, C₃₀ and C₃₁ triterpanes respectively.

Steranes:

The most commonly used fragmentions for detection of steranes are M/Z 149 to distinguish between 5 α and 5 β steranes, M/Z 189 and 259 for detection of rearranged steranes, M/Z 217 for detection of rearranged and normal steranes and M/Z 218 for detection of 14 β (H), 17 β (H) steranes. The molecular ions M/Z 372, 386, 400 and 414 are also recorded for identification of C₂₇, C₂₈, C₂₉ and C₃₀ steranes respectively.

Bicyclanes:

The fragmentions M/Z 123, 179 and 193 are normally used for

the detection of the bicyclanes (sesquiterpanes and diterpanes). M/Z 123 will detect all bicyclanes while M/Z 179 and 193 will show the C₁₄ and C₁₅ bicyclanes respectively.

Aromatic Fractions:

Alkyl-substituted Benzenes:

The M/Z 106 fragmentation is often used to detect the alkyl-substituted benzenes. It is especially useful for the detection of di-substituted benzenes. M/Z 134 can also be used for the detection of C₄-alkylbenzenes, but benzothiophene will also give a signal with this fragmentation. M/Z 148 can be used for the detection of C₅-alkylbenzenes, but will also give signals for methyl-substituted benzothiophenes.

Naphthalenes:

Methylnaphthalenes are normally detected by the M/Z 142 fragmentation while C₂-naphthalenes are detected by M/Z 156 and C₃-naphthalenes by M/Z 170.

Benzothiophenes and Dibenzothiophenes:

Benzothiophene can be detected, as mentioned above, by M/Z 134. The M/Z 198 and M/Z 212 fragmentations are used for methyl-substituted dibenzothiophenes and dimethyl-substituted dibenzothiophenes respectively.

Phenanthrenes:

Phenanthrene is detected using the M/Z 178 fragmentation. Anthracene will, if present also give a signal in the M/Z 178 fragmentation. Methyl-substituted phenanthrenes give signals in the M/Z 192 fragmentation while the M/Z 206 fragmentation shows the dimethyl-substituted phenanthrenes.

Aromatic Steranes:

Monoaromatic steranes are detected using the M/Z 253 fragmentation while the triaromatic steranes are detected using the M/Z 231 fragmentation.

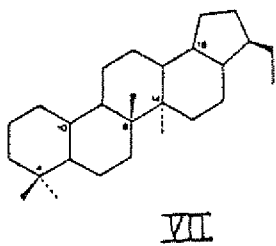
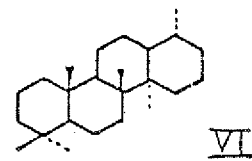
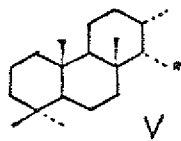
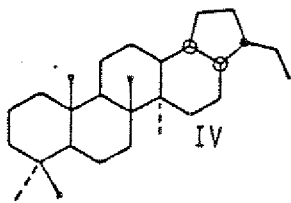
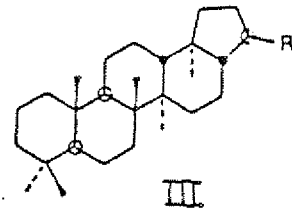
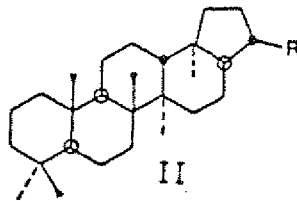
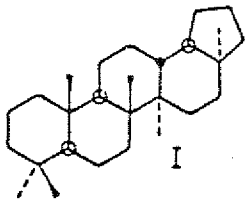
2a. Mass Fragmentograms representing Terpanes

(M/Z 163, 177, 191, 205, 370, 384, 398, 412 and 426)

Peak identification. (α and β refer to hydrogen atoms at C-17 and C-21 respectively unless indicated otherwise).

A.	18 α trisnorneohopane (T_S)	$C_{27}H_{44}$	(I)
B.	17 α trisnorhopane (T_M)	$C_{27}H_{46}$	(II, R=H)
Z.	Bisnorhopane	$C_{28}H_{48}$	(IV)
C.	$\alpha\beta$ norhopane	$C_{29}H_{50}$	(II, R= C_2H_5)
D.	$\beta\alpha$ norhopane	$C_{29}H_{50}$	(III, R= C_2H_5)
E.	$\alpha\beta$ hopane	$C_{30}H_{52}$	(II, R=i- C_3H_7)
F.	$\beta\alpha$ hopane	$C_{30}H_{52}$	(III, R=i- C_3H_7)
G.	22S $\alpha\beta$ homohopane	$C_{31}H_{54}$	(II, R=i- C_4H_9)
H.	22R $\alpha\beta$ homohopane	$C_{31}H_{54}$	(II, R=i- C_4H_9)
I.	$\beta\alpha$ homomoretane	$C_{31}H_{54}$	(III, R=i- C_4H_9)
J.	22S $\alpha\beta$ bishomohopane	$C_{32}H_{56}$	(II, R=i- C_5H_{11})
	22R $\alpha\beta$ bishomohopane	$C_{32}H_{56}$	(II, R=i- C_5H_{11})
K.	22S $\alpha\beta$ trishomohopane	$C_{33}H_{58}$	(II, R=i- C_6H_{13})
	22R $\alpha\beta$ trishomohopane	$C_{33}H_{58}$	(II, R=i- C_6H_{13})
L.	22S $\alpha\beta$ tetrakishomohopane	$C_{34}H_{60}$	(II, R=i- C_7H_{15})
	22R $\alpha\beta$ tetrakishomohopane	$C_{34}H_{60}$	(II, R=i- C_7H_{15})
M.	22S $\alpha\beta$ pentakishomohopane	$C_{35}H_{62}$	(II, R=i- C_8H_{17})
	22R $\alpha\beta$ pentakishomohopane	$C_{35}H_{62}$	(II, R=i- C_8H_{17})
P.	Tricyclic terpene	$C_{23}H_{42}$	(V, R=i- C_4H_9)
Q.	Tricyclic terpene	$C_{24}H_{44}$	(V, R=i- C_5H_{11})
R.	Tricyclic terpene (17R, 17S)	$C_{25}H_{66}$	(V, R=i- C_6H_{13})
S.	Tetracyclic terpene	$C_{24}H_{42}$	(VI)
T.	Tricyclic terpene (17R, 17S)	$C_{26}H_{48}$	(V, R=i- C_7H_{15})
N.	Tricyclic terpene	$C_{21}H_{38}$	(V, R= C_2H_5)
O.	Tricyclic terpene	$C_{22}H_{40}$	(V, R= C_3H_7)
Y.	25,28,30 trisnorhopane/moretane	$C_{27}H_{46}$	(VII)
X.	Unknown triterpene	$C_{30}H_{52}$	

STRUCTURES REPRESENTING TERPANES



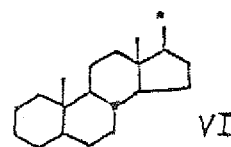
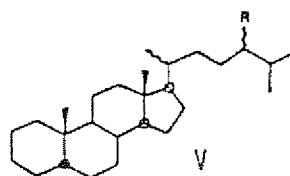
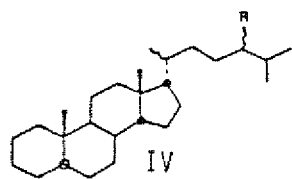
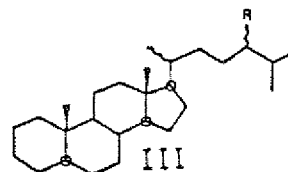
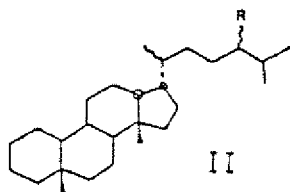
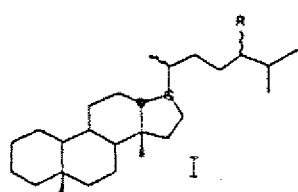
2b. Mass Fragmentograms representing Steranes

(M/Z 149, 189, 217, 218, 259, 372, 386, 400 and 414)

Peak identifications. (α and β refer to hydrogen atoms at C-5, C-14 and C-17 in regular steranes and at C-13 and C-17 in diasteranes).

a.	20S $\beta\alpha$ diacholestane	$C_{27}H_{48}$	(I, R=H)
b.	20R $\beta\alpha$ diacholestane	$C_{27}H_{48}$	(I, R=H)
c.	20S $\alpha\beta$ diacholestane	$C_{27}H_{48}$	(II, R=H)
d.	20R $\alpha\beta$ diacholestane	$C_{27}H_{48}$	(II, R=H)
e.	20S $\beta\alpha$ 24 methyl diacholestane	$C_{28}H_{50}$	(I, R=CH ₃)
f.	20R $\beta\alpha$ 24 methyl diacholestane	$C_{28}H_{50}$	(I, R=CH ₃)
g.	20S $\alpha\beta$ 24 methyl diacholestane	$C_{28}H_{50}$	(II, R=CH ₃)
	+ 20S $\alpha\alpha\alpha$ cholestane	$C_{27}H_{48}$	(III, R=H)
h.	20S $\beta\alpha$ 24 ethyl diacholestane	$C_{29}H_{52}$	(II, R=C ₂ H ₅)
	+ 20R $\alpha\beta\beta$ cholestane	$C_{27}H_{48}$	(IV, R=H)
i.	20S $\alpha\beta\beta$ cholestane	$C_{27}H_{48}$	(IV, R=H)
	+ 20R $\alpha\beta$ 24 methyl diacholestane	$C_{28}H_{50}$	(II, R=CH ₃)
j.	20R $\alpha\alpha\alpha$ cholestane	$C_{27}H_{48}$	(III, R=H)
k.	20R $\beta\alpha$ 24 ethyl diacholestane	$C_{29}H_{52}$	(I, R=C ₂ H ₅)
l.	20S $\alpha\beta$ 24 ethyl diacholestane	$C_{29}H_{52}$	(II, R=C ₂ H ₅)
m.	20S $\alpha\alpha\alpha$ 24 methyl cholestane	$C_{28}H_{50}$	(III, R=CH ₃)
n.	20R $\alpha\beta\beta$ 24 methyl cholestane	$C_{28}H_{50}$	(IV, R=CH ₃)
	+ 20R $\alpha\beta$ 24 ethyl diacholestane	$C_{29}H_{52}$	(II, R=C ₂ H ₅)
o.	20S $\alpha\beta\beta$ 24 methyl cholestane	$C_{28}H_{50}$	(IV, R=CH ₃)
p.	20R $\alpha\alpha\alpha$ 24 methyl cholestane	$C_{28}H_{50}$	(III, R=CH ₃)
q.	20S $\alpha\alpha\alpha$ 24 ethyl cholestane	$C_{29}H_{52}$	(III, R=C ₂ H ₅)
r.	20R $\alpha\beta\beta$ 24 ethyl cholestane	$C_{29}H_{52}$	(IV, R=C ₂ H ₅)
s.	20S $\alpha\beta\beta$ 24 ethyl cholestane	$C_{29}H_{52}$	(IV, R=C ₂ H ₅)
t.	20R $\alpha\alpha\alpha$ 24 ethyl cholestane	$C_{29}H_{52}$	(III, R=C ₂ H ₅)
u.	5 α sterane	$C_{21}H_{36}$	(VI, R=C ₂ H ₅)
v.	5 α sterane	$C_{22}H_{38}$	(VI, R=C ₃ H ₇)

STRUCTURES REPRESENTING STERANES

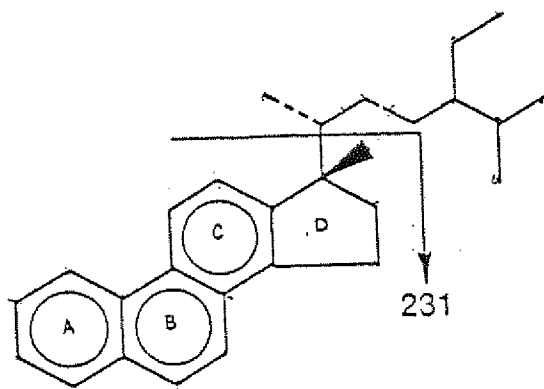


Mass Fragmentograms representing Triaromatic Steranes
 (M/Z 231)

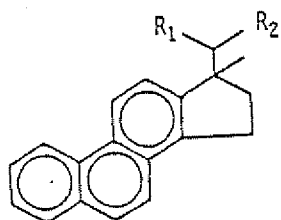
Description of ABC-ring triaromatic steroid hydrocarbons

Peak	Substituents		Abbreviation of Compound
	R ₁	R ₂	
a1	CH ₃	H	C ₂₀ TA
b1	CH ₃	CH ₃	C ₂₁ TA
c1	S(CH ₃)	C ₆ H ₁₃	SC ₂₆ TA
d1	R(CH ₃)	C ₆ H ₁₃	RC ₂₆ TA
	S(CH ₃)	C ₇ H ₁₅	SC ₂₇ TA
e1	S(CH ₃)	C ₈ H ₁₇	SC ₂₈ TA
f1	S(CH ₃)	C ₇ H ₁₅	RC ₂₇ TA
g1	R(CH ₃)	C ₈ H ₁₇	RC ₂₈ TA

STRUCTURES REPRESENTING TRIAROMATIC STERANES:



II



Mass Fragmentograms representing Monoaromatic Steranes
(M/Z 253)

Description of C-ring monoaromatic steroid hydrocarbons

Peak	Substituents				Abbreviation of Compound
	R ₁	R ₂	R ₃	R ₄	
A1					C ₂₁ MA
B1					C ₂₂ MA
C1	β(H)	CH ₃	S(CH ₃)	H	βSC ₂₇ MA
	CH ₃	H	S(CH ₃)	H	SC ₂₇ DMA
D1	β(H)	CH ₃	R(CH ₃)	H	βRC ₂₇ MA
	CH ₃	H	R(CH ₃)	H	RC ₂₇ DMA
	α(H)	CH ₃	S(CH ₃)	H	αSC ₂₇ MA
E1	β(H)	CH ₃	S(CH ₃)	CH ₃	βSC ₂₈ MA
	CH ₃	H	S(CH ₃)	CH ₃	SC ₂₈ DMA
F1	α(H)	CH ₃	R(CH ₃)	H	αRC ₂₇ MA
	α(H)	CH ₃	S(CH ₃)	CH ₃	αSC ₂₈ MA
	β(H)	CH ₃	R(CH ₃)	CH ₃	βRC ₂₈ MA
G1	CH ₃	H	R(CH ₃)	CH ₃	RC ₂₈ DMA
	β(H)	CH ₃	S(CH ₃)	C ₂ H ₅	βSC ₂₉ MA
	CH ₃	H	S(CH ₃)	C ₂ H ₅	SC ₂₉ DMA
H1	α(H)	CH ₃	R(CH ₃)	CH ₃	αRC ₂₈ MA
	β(H)	CH ₃	R(CH ₃)	C ₂ H ₅	βRC ₂₉ MA
	CH ₃	H	R(CH ₃)	C ₂ H ₅	RC ₂₉ DMA
I1	α(H)	CH ₃	R(CH ₃)	C ₂ H ₅	αRC ₂₉ MA

STRUCTURES REPRESENTING MONOAROMATIC STERANES:

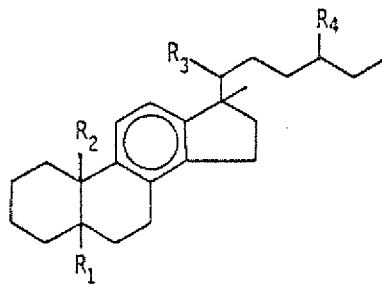
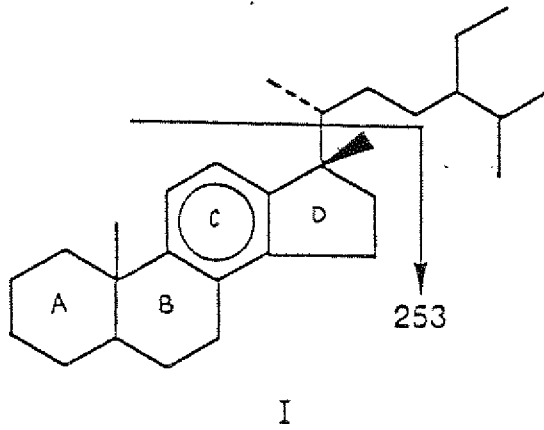


Table 1: Variation in Triterpane Distribution for Well NOCS 30/6-4

Depth unit of measure: m

Depth	Lithology	B/A	B/B+A	B		C/E	C/C+E	X/E	Z/E	Z/C	Z/Z+E	Q/E	E/E+F	C+D		J1		Sample
				B+E+F	C/E									C+D+E+F	D+F/C+E	J1+J2%		
2420.00	bulk	2.28	0.70	0.31	0.61	0.38	0.06	-	-	-	0.08	0.83	0.40	0.24	47.77	156-0		
2429.00	bulk	2.72	0.73	0.32	0.65	0.39	0.07	-	-	-	0.08	0.82	0.41	0.25	48.43	157-0		
2441.00	bulk	2.81	0.74	0.32	0.65	0.39	0.07	-	-	-	0.08	0.82	0.41	0.25	47.08	158-0		
2492.00	bulk	5.18	0.84	0.35	0.74	0.42	0.05	-	-	-	0.14	0.80	0.43	0.26	48.03	159-0		
2558.00	bulk	4.12	0.80	0.37	0.76	0.43	0.07	1.72	2.26	0.63	0.05	0.78	0.44	0.31	46.59	160-0		
2780.00	bulk	1.50	0.60	0.43	1.15	0.53	-	0.32	0.28	0.24	0.33	0.84	0.53	0.18	60.77	162-0		
2813.00	bulk	2.83	0.74	0.31	0.68	0.41	0.08	-	-	-	0.08	0.83	0.40	0.19	57.11	164-0		
2834.00	bulk	2.90	0.74	0.33	0.76	0.43	0.07	-	-	-	0.17	0.83	0.42	0.19	60.03	165-0		
2936.00	bulk	3.60	0.78	0.33	0.77	0.44	0.04	-	-	-	0.06	0.84	0.44	0.19	56.59	167-0		

Table 2: Variation in Sterane Distribution for Well NOCS 30/6-4

Depth unit of measure: m

<u>Depth</u>	<u>Lithology</u>	<u>Ratio1</u>	<u>Ratio2</u>	<u>Ratio3</u>	<u>Ratio4</u>	<u>Ratio5</u>	<u>Ratio6</u>	<u>Ratio7</u>	<u>Sample</u>
2420.00	bulk	0.42	22.35	54.55	1.30	0.73	0.18	0.14	156-0
2429.00	bulk	0.44	22.17	54.84	1.27	0.73	0.19	0.15	157-0
2441.00	bulk	0.41	22.45	54.80	1.15	0.73	0.21	0.17	158-0
2492.00	bulk	0.53	17.53	55.97	1.01	0.78	0.23	0.18	159-0
2558.00	bulk	0.52	23.23	57.09	0.89	0.74	0.16	0.12	160-0
2780.00	bulk	0.45	42.65	58.70	0.61	0.62	0.34	0.26	162-0
2813.00	bulk	0.50	36.53	51.88	0.87	0.60	0.16	0.13	164-0
2834.00	bulk	0.10	39.03	52.34	0.50	0.58	0.26	0.21	165-0
2936.00	bulk	0.43	26.34	51.34	1.04	0.67	0.19	0.16	167-0

Ratio1: $a / a + j$

Ratio2: $q / q + t * 100\%$

Ratio3: $2(r + s) / (q + t + 2(r + s)) * 100\%$

Ratio4: $a + b + c + d / h + k + l + n$

Ratio5: $r + s / r + s + q$

Ratio6: $u + v / u + v + q + r + s + t$

Ratio7: $u + v / u + v + i + m + n + q + r + s + t$

Table 3: Aromatisation of Steranes for Well NOCS 30/6-4

Depth unit of measure: m

<u>Depth</u>	<u>Lithology</u>	<u>Ratio1</u>	<u>Ratio2</u>	<u>Sample</u>
2420.00	bulk	0.63	0.46	156-0
2429.00	bulk	0.62	0.51	157-0
2441.00	bulk	0.63	0.49	158-0
2492.00	bulk	0.68	0.57	159-0
2558.00	bulk	0.63	0.61	160-0
2780.00	bulk	0.56	0.66	162-0
2813.00	bulk	0.54	0.75	164-0
2834.00	bulk	0.56	0.78	165-0
2936.00	bulk	0.58	0.76	167-0

$$\text{Ratio1: } \frac{\text{C1+D1+E1+F1+G1+H1+I1}}{\text{C1+D1+E1+F1+G1+H1+I1} + \text{c1+d1+e1+f1+g1}}$$

$$\text{Ratio2: } \text{g1} / \text{g1} + \text{I1}$$

Table 4: Variation in Triaromatic Sterane Distribution for Well NOCS 30/6-4

Depth unit of measure: m

<u>Depth</u>	<u>Lithology</u>	<u>Ratio1</u>	<u>Ratio2</u>	<u>Ratio3</u>	<u>Ratio4</u>	<u>Ratio5</u>	<u>Sample</u>
2420.00	bulk	0.91	0.41	0.47	0.69	0.65	156-0
2429.00	bulk	0.59	0.47	0.17	0.25	0.23	157-0
2441.00	bulk	0.57	0.45	0.16	0.23	0.21	158-0
2492.00	bulk	0.65	0.50	0.20	0.32	0.25	159-0
2558.00	bulk	0.56	0.46	0.16	0.23	0.21	160-0
2780.00	bulk	0.73	0.65	0.31	0.39	0.41	162-0
2813.00	bulk	0.56	0.51	0.24	0.28	0.34	164-0
2834.00	bulk	0.57	0.49	0.24	0.30	0.34	165-0
2936.00	bulk	0.70	0.62	0.32	0.41	0.41	167-0

Ratio1: a1 / a1 + g1

Ratio2: b1 / b1 + g1

Ratio3: a1 + b1 / a1 + b1 + c1 + d1 + e1 + f1 + g1

Ratio4: a1 / a1 + e1 + f1 + g1

Ratio5: a1 / a1 + d1

Table 5: Variation in Monoaromatic Sterane Distribution for Well NOCS 30/6-4

Depth unit of measure: m

<u>Depth</u>	<u>Lithology</u>	<u>Ratio1</u>	<u>Ratio2</u>	<u>Ratio3</u>	<u>Ratio4</u>	<u>Sample</u>
2420.00	bulk	0.20	0.18	0.12	0.11	156-0
2429.00	bulk	0.23	0.21	0.14	0.12	157-0
2441.00	bulk	0.23	0.23	0.13	0.13	158-0
2492.00	bulk	0.24	0.19	0.14	0.11	159-0
2558.00	bulk	0.22	0.16	0.12	0.09	160-0
2780.00	bulk	0.34	0.25	0.19	0.16	162-0
2813.00	bulk	0.33	0.24	0.17	0.13	164-0
2834.00	bulk	0.28	0.19	0.16	0.13	165-0
2936.00	bulk	0.30	0.19	0.16	0.13	167-0

Ratio1: A1 / A1 + E1
 Ratio2: B1 / B1 + E1

Ratio3: A1 / A1 + E1 + G1
 Ratio4: A1+B1 / A1+B1+C1+D1+E1+F1+G1+H1+I1