Determination of the Geological Age of Oil Using Diamondoids

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Abstract. Based on the study of a large number of Western and Eastern Siberia oils, it was shown that adamantanes can be used as a means of correlation in oils of different genotypes and ages. Based on the relative distribution of mono-, di-, and trialkyl-substituted \( C_{11}–C_{13} \) adamantanes marine and terristerial oils and Cenozoic and Proterozoic oils were distinguished. This approach could be used when there are no generally recognized biomarker hydrocarbons or indicators based on them are uninformative. We found that Jurassic and Cretaceous oils of Kalmykia can be distinguished by the distribution of methyl- and dimethyldiamantanes. It was concluded that the distributions of alkyl substituted diamantanes could also be applied for the differentiation of oils of different ages.

1. Introduction
Taxonomic indication or, in other words, the determination of the geological age of initial bioorganic molecules (the age of oil) is one of the most interesting tasks of petroleum geochemistry. It is much more complicated to determine the age than the geochemical (genetic) types of oils. Nevertheless it is very important as this parameter is associated with the distribution of organic compounds in the living organisms of the modern era and the distant past.

The age of oil is related to the age of the oil source strata that generated it. Since oil is migratory, it can be generated in ancient sediments and, as a result of migration, end up in younger reservoirs. Therefore, identifying the source of generation of hydrocarbons and their migration paths is of great applied importance in the search and exploration of oil fields. It is needed to build correlations in oil-oil, oil-organic matter of rocks (EOM) systems.

The most commonly used indicator of the age of oils or organic matter of rocks is the ratio of regular \( C_{28}/C_{29} \) steranes [1]. It was shown that with the decrease of geological age of organic matter there is an increase in the relative concentration of \( C_{28} \) steranes and an increase in \( C_{28}/C_{29} \) ratio. Hence this parameter has limitation as it cannot be used in case of oils of terrestrial genesis. These oils are initially characterized by a high relative concentration of \( C_{29} \) sterane. The use of sterane and terpane indicators is impossible in the case of light oils due to the absence of high molecular weight fractions and highly mature oils due to cracking of these hydrocarbons.

Indicators of the age may also be some biomarkers specific to certain geological era. The example is 12- and 13-methylalkanes which mark Precambrian oils [2,3]. On the basis of detailed studies of oils from the Timan-Pechora oil and gas province, it was found that the relative content of biomarker hydrocarbons such as pregnanes and cheilanthanes also changes with geological age of oil [4,5].

Diamondoids are not biomarkers, but they can also be useful in geochemical studies [6–15]. They are applied in the geochemical correlations of biodegraded oils and gas condensates, when bacterial
activity changes the relative content of biomarkers [16,17]. We have shown that diamondoids are omnipresent and are found in oils and organic matter of both clay and carbonate strata, in organic matter of various maturities. In this paper we propose to correlate the age and the genotype of organic matter of rocks and oils using adamantanes.

2. Adamantanes as a mean of correlation of oils of different age and genotype

Figure 1a shows typical mass chromatograms with characteristic ions of steranes and terpanes of highly mature oil. It can be seen that steranes and terpanes are practically absent, which is associated with their cracking in the occurrence conditions. At the same time from mass chromatograms on figure 1b one can see adamantanes of the same oil. These hydrocarbons were not cracked due to thermal stability and can be used for geochemical studies.

![Figure 1. Mass chromatograms of steranes, terpanes and adamantanes of highly mature oil. Steranes and terpanes are practically absent and uninformative, while adamantanes can be used in geochemical studies.](image)

In order to prove that adamantanes can be used to differentiate the age of oil, we studied the correlation of sterane and adamantane indicators in a large number of oils of different age and genotypes in Western and Eastern Siberia.

Figure 2 demonstrates the steranes and adamantanes ratios of oils of various genotypes – terrestrial and marine. Based on the distribution of regular C27–C29 steranes, it is easy to distinguish between marine and terrestrial oils (Figure 2a). Terrestrial oils have a significantly higher relative content of stigmastane C29 (more than 80%) compare to marine ones. The same oils differ well in the ratios of mono-, di-, and trialkyl-substituted adamantanes: C11/C13 (on average 0.3 for terrestrial oils and 1.0 for marine oils) and C12/C13 (0.8 for terrestrial and ~ 2.8 for marine oils) (figure 2b). Thus, we can talk about the good accordance of adamantane indicators with common sterane parameters for genetic correlations in oil–oil and oil–EOM.
We propose that the distribution of C\textsubscript{11}–C\textsubscript{13} mono-, di-, and trialkyl-substituted adamantanes can also be applied for differentiating young and ancient oils when the taxonomic Grantham coefficient is not applicable like in light oils, terrestrial oils and highly mature oils. On figure 3a it can be seen that according to the ratios of the regular steranes \( \frac{C_{27}}{C_{29}} \) and \( \frac{C_{28}}{C_{29}} \), the Cenozoic oils sharply differ from the oldest Proterozoic oils. If we consider the ratios of the adamantanes \( \frac{C_{11}}{C_{13}} \) and \( \frac{C_{12}}{C_{13}} \) used above (Figure 2b), we can conclude that they can also be used to differentiate these oils. Thus, it is seen that the \( \frac{C_{11}}{C_{13}} \) ratio of the adamantanes is on average 1.5 for the Cenozoic oils and 0.8 for the Proterozoic oils, while the \( \frac{C_{12}}{C_{13}} \) ratio is 3.2 for the Cenozoic and 2.5 for the Proterozoic ones.

**Figure 2.** Steranes (a) and adamantanes (b) in oils of various genotypes (an average data).

**Figure 3.** Steranes (a) and adamantanes (b) in oils of different ages (an average data).

### 3. Diamantanes as a mean of correlation of oils of different age

Another example of using adamantanoids distributions in oil-oil correlations is differentiation of oils of different age (the Jurassic and the Cretaceous) on the example of Kalmykia oils.

We studied the patterns of distribution of biomarkers and methyl- and dimethyldiamantanes in seven Jurassic (Bajocian) and fifteen Cretaceous (Aptian) oils of Kalmykia. It should be noted that according to the relative distribution of biomarkers – steranes – these oils are not possible to distinguish. Figure 4 presents a stellar diagram that shows the main sterane parameters, which are generally used in organic geochemistry. It can be seen that in both the Jurassic and the Cretaceous oils the values of these parameters are very close.
At the same time, we found that Jurassic and Cretaceous oils can be distinguished by the distribution of methyl- and dimethyl-diamantanes. Figure 5a shows a triangular diagram with the distribution of 1-, 3- and 4-methyl-diamantanes. It is clearly seen that oils of different ages fall into different areas of the diagram. A similar conclusion can be made based on the distribution of 3,4-, 4,8- and 4,9-dimethyl-diamantanes (Figure 5b), where oils of different ages also fall into different areas of the triangular diagram. It is interesting to note that oil from the Vostochno-Kamyshanskoye field, well 95, despite being selected from the Jurassic sediments corresponds to Cretaceous oils according to diamantanes distribution. It is possible that in this case there was an error in determining the geological age of the deposits.
Conclusion
On the example of oils of different genotypes (marine and terrestrial) and of different ages (Cenozoic and Proterozoic), we showed that characterization of oils can be carried out on the basis of the distribution of C_{11}–C_{13} adamantanes. Conclusion based on the distribution of adamantanes coincides with conclusion based on commonly used biomarkers – steranes. We propose that the distribution of C_{11}–C_{13} mono-, di-, and trialkyl-substituted adamantanes can be used for differentiating young and ancient oils when the taxonomic Grantham coefficient is not applicable. Mono- and dialkyl substituted diamantanes can also serve as a means of differentiating oils of different ages. As it was shown on the example of Jurassic and Cretaceous oils of Kalmykia. For this, triangular diagrams in the coordinates of 1-/3- / 4-methyldiamantanes and 3,4- / 4,8- / 4,9-dimethyldiamantanes can be used.

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