

^{PS} **Mud Volcanoes of Azerbaijan - Windows to the Subsurface***

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Abstract

Mud volcanoes are prominent geological features of Azerbaijan. Tectonic stresses control their occurrences in regions with over-pressured subsurface sediments, as mud volcanoes are closely linked to fault systems. The mud from the volcano cones contains numerous ejected rock fragments, which we use to identify the depths from which the mud has been transported.

Organic geochemical, organic petrographical and micropalaeontological investigations have been performed on selected samples of 19 mud volcanoes. The amounts of extractable hydrocarbons in relation to organic carbon contents indicate that most of the sediment samples are impregnated by migrated hydrocarbons. Hydrogen and oxygen indices derived from RockEval pyrolyses indicate that the organic matter of the sediments consist mostly of mixtures of Type II and III kerogens.

All extracted hydrocarbons have been affected by secondary alterations that most likely involved biodegradation, as the normal alkanes have been removed to a large extend. Despite biodegradation, environmental and maturity sensitive biomarkers could be identified. C27- to C29-sterane isomers suggest a dominance of aquatic organic matter. An influence of diatoms on the sterane distribution seems plausible, although an admixture of land plant material can also not be excluded. Homohopane isomerization ratios as well as the ratio of trisnorhopane over trisnorhopane suggest that the extracted hydrocarbons come from a coalification range which spreads from immature to mature, although maximum maturity does not reach the peak of oil generation. C29-sterane isomerisation ratios support this finding.

Vitrinite reflectance measurements on the rock ejecta indicate a similar range of maturities as suggested from biomarker analyses. However, the data indicate again that most of the investigated rocks have been impregnated by allochthonous hydrocarbons, as biomarker maturities may slightly depart from the measured reflectance values.

We estimated from published maturity/depth conversion that the mud volcanoes along a SSW-NNE transect from the Kura Basin to the Apsheron Peninsula produce their mud from a depth range between 4000 and 5500 m corresponding to a maturity range of 0.5 to 0.65% vitrinite reflectance. However, no specific regional maturity or depth trends could be identified.

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Introduction

The South Caspian Basin of Azerbaijan is known to be one of the oldest petroleum producing regions in the world (Abrams and Narimanov, 1997). It has since the earliest 20th century a leading role in the oil production of the Central Asian region, and hence oil and gas exploration is at a level of high activity.

In this context numerous studies on the organic geochemistry of source and reservoir rocks as well as of hydrocarbon surface seepages have been conducted in the past. Abrams and Narimanov (1997), Nadirov et al. (1997) and Feyzullayev et al. (2001) for example summarized results of these investigations. Tagiyev et al. (1997) provide expertise on detailed hydrocarbon generation histories and Inan et al. (1998) have extended these investigations with additional information on basin modeling. Findings like Shakh Deniz (Gürgey, 2003) have significantly contributed to the petroleum reserves of Azerbaijan and Bagirov and Lerche (1998) suggested that a high percentage of the more than 360 known structures of Azerbaijan have a potential to contain petroleum bearing horizons. Hudson et al. (2008) provide a facies related overview on the paleogeographic development of a possible source rock of the Caspian Depression, which suggests that the Oligocene–Miocene Maikop Series are at least partly a favorable hydrocarbon source.



Fig. 1

Locations of investigated mud volcano sites of Azerbaijan (maps courtesy Google Earth 2009).

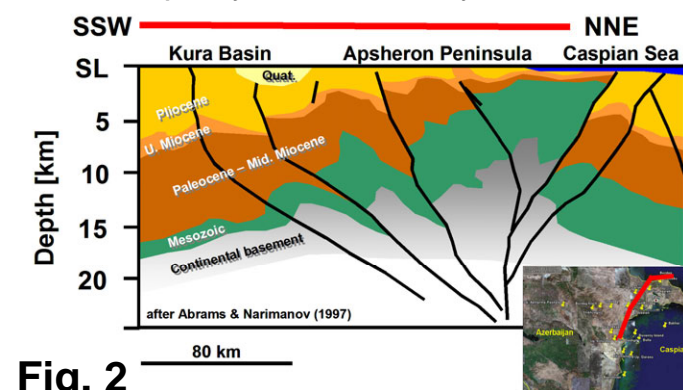


Fig. 2

Tectonic and stratigraphic sketch across Kura Basin and Apsheron Peninsula (Azerbaijan).

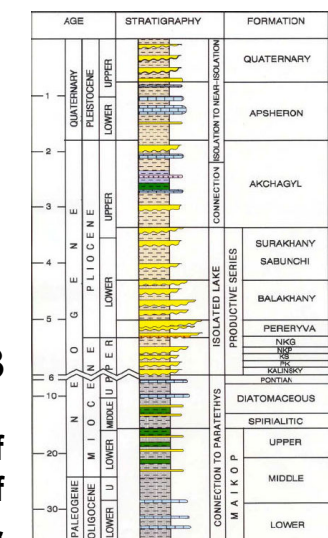


Fig. 3

Idealized geological profile of the Cenozoic succession of Azerbaijan (after Abrams & Narimanov, 1997)

Mud volcanoes are prominent geological features of Azerbaijan. Their occurrence is suggested to be controlled by tectonic forces in regions containing overpressured subsurface sediments. Mud volcanoes are closely linked to faults, which may partly be detached at the basement level. As mud volcano activity is not related to distinct subsurface horizons the mud of the volcano cones contains numerous ejected rocks, which can be used to identify the sediments from, which the mud has been transported to the surface.

The South Caspian Basin is characterized by extreme sedimentation rates, which lead to the accumulation of large volumes of Mesozoic and Cenozoic sediments. These mostly unconsolidated strata reach thicknesses of up to more than 15 km and overlay onshore a continental basement (Fig. 2). Figure 3 gives an generalized overview on the sedimentary successions of Azerbaijan (Abrams and Narimanov, 1997).

Geological overview

Mesozoic deposits of Upper Cretaceous age occur within the Shamakha-Gobustan and the Pri-Caspian-Guba regions and represent flysch type sedimentary alternations. The onset of Cenozoic sedimentation in the Caspian Basin consists mainly of reddish to brownish Paleocene clays intersected with conglomerates and sand deposits. The Lower Eocene comprises marls, clays and sandstones whereas the Middle Eocene already contains a higher portion of organic material represented through dark-brown clays, bituminous marls and slates intercalated with sandstones. Marls and sandstones represent the Upper Eocene. The organic rich sediments of Oligocene to Miocene ages are commonly named Maikop Suite and represent the major hydrocarbon source rock of this region. This suite of sediments comprises clays and fine-grained sand deposits. Sediments of the Middle Miocene contain marls, clays and sandstones. The sandstones of the Pri-Caspian-Guba and Gobustan regions and partially on the Absheron Peninsula are important hydrocarbon reservoirs. Upper Miocene sediments comprise clays, limestones and conglomerates. The Lower Pliocene sediments contain clays intercalated by limestones and sandy-argillaceous rocks with good reservoir quality. The sand deposits of Middle Pliocene are preferred reservoir targets whereas Upper Pliocene deposits consist of clays, sandstones and limestones. Intercalated volcanic ashes indicated increased Upper Pliocene backarc volcanic activities. Quaternary sediments are mainly deposited under continental conditions.

Undercompaction of the unconsolidated sediments of Cenozoic age leads to extremely high pore pressures, which together with a high variability of Cenozoic rock/facies types may lead to vertical and lateral rock density variations. This variability together with tectonically induced stress fields of the convergent margins of the Caspian region are the basic conditions that mud volcanism has developed over large areas of Azerbaijan. Light hydrocarbons i.e. methane generated through microbial or thermogenic processes contribute as well to these high-pressure conditions of the sediments, which can be released through tectonically induced earthquakes and result in blowouts of mixtures of gas, water and mud at the surface. Mud volcanoes are therefore one possible surface expression of vertical hydrocarbon migration and may give chance to investigate the subsurface by means of ejected rock transported to the surface.

Analytical methods

Forty-nine samples of nineteen mud volcanoes have been analyzed by organic petrographical and organic geochemical methods. The samples have been crushed and ground for the subsequent investigations.

Organic petrographical preparations and analyses have been conducted according to German DIN 22020. Measurements were carried out on a Leica DMR microscope, which was coupled to a MPV-Compact-2 photometer (for a description of the methods also compare Stach et al., 1982).

We measured total sedimentary sulphur (TS) and total organic carbon (TOC) on a LECO CS-200 with standard methods (Peters et al., 2005). RockEval pyrolyses were carried out according standard procedures described by Behar et al. (2001) on a Delsi RockEval-6, and resulting parameters S1, S2, S3 and Tmax have been used to calculate hydrogen, oxygen and production indices.

The ratios of stable carbon isotopes of the sedimentary bulk organic matter have been analyzed according to the methods given in Brand (1998). We used a system of an elemental analyzer (Carlo Erba CHN1100) coupled to an isotope-ratio mass-spectrometer (Finnigan DeltaPlus). Carbon isotope ratios are reported as delta values with reference to the international standard PDB (Brand, 1998).

Depending on the amount of organic matter we extracted 10 to 30 g of selected samples (see below) with dichlorid methanol using a Dionex ASE-200. We removed elemental sulphur from the hydrocarbon extract by treatment with activated copper granular, and also separated the asphaltenes by a treatment with dichloride methanol and an addition of petroleum benzene. The residual fraction of maltenes and resins has been separated into aliphatic and aromatic fractions as well as into hetero-compounds by mid-pressure liquid chromatography using a BESTA-MPLC with different organic solvents. Gas chromatographic analyzes on the aliphatic fraction provided a typecast of the fraction and an estimation of biomarker concentrations using an Agilent 6890 GC-FID-system equipped with a 50 m UltraII column. Single biomarker compounds have been determined by a gas chromatographic separation of the aliphatic fraction and a subsequent mass spectrometric determination on a coupled system of an Agilent 6890 GC and a Finnigan MAT95S mass spectrometer (compare Wehner et al., 2008).

Organic-petrographical characterization

The lithologies of the ejected rocks vary unsystematically between the different locations and contain clastics as well as carbonate sediments. Based on the calcareous nannoplankton the investigated sediments are of Late Cretaceous to Palaeogene ages. We give here only a gross overview on the analyzed lithologies. Generally, we observe one dominant lithology and up to three minor lithologies within the ejected material. Vitrinite reflectance values have been determined on all lithologies and show that up to six distinct vitrinite populations can be determined on one sample. However, for correlation purposes with biomarker-derived maturities, we will refer in the organic geochemistry chapter (s. below) to the maturities of the dominant lithologies.

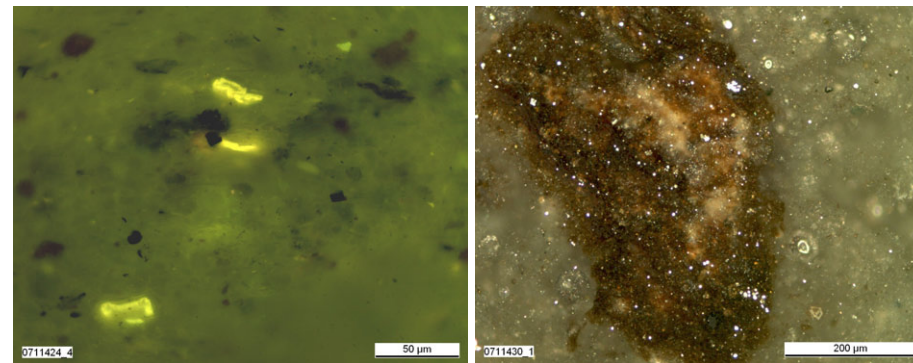


Fig. 4

Left: #0711424 (fluorescing light); yellow fluorescing spores of sediments of Kirmaku (Apsheeron); right #0711430 (normal light): bitumen in sediment matrix at Bozdag (Apsheeron).

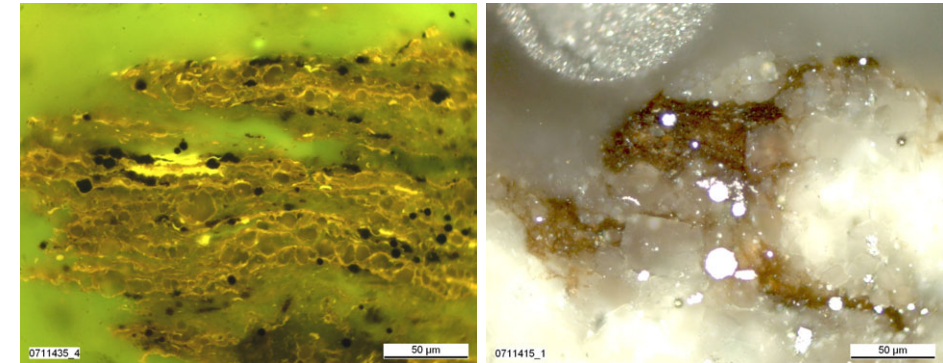


Fig. 5

Left: #0711435 (fluorescing light): alginites and bitumen of sediments of Shikhzairli (Sheakha-Kobystan); right #0711415 (normal light): amorphous bitumen within sediments of Bozdag Klych (Sheakha-Kobystan).

Average thermal maturities of silt sediments of the Apsheeron area vary between 0.49 – 0.54% Rr (random vitrinite reflectance). Exceptions are samples from Otman Bozdag (#0711416) and Up. Saryndja (#0711417) with maturities of 0.62 and 0.65 % Rr, respectively. In nearly all samples, we observe in addition to the major sediment component clastics as well as carbonate sediments with higher thermal maturities. The values cluster around 0.74 – 0.89 %, 1.04 – 1.07 %, 1.12 – 1.18 % and 1.24 – 1.34 % Rr.

Average vitrinite reflectance values of the major clastic sediment population of the Sheakha-Kobystan Region vary between 0.65 and 0.69% Rm. One exception is sample Ayrantekyan (#0711437) with 0.57% Rr. Sediments of Ayrantekyan (#0711437) and Dashgil (#0711446) contain material which show reflectance values of 0.45 and 0.57% Rr, respectively. The observed low mature particles may be explained as particles dragged along from younger sediments during mud extrusion. Within a few other samples we also observe vitrinite populations of minor clastic and carbonate sediment components, which indicate higher maturities clustering around 0.80 – 0.87%, 0.95 – 0.97%, 1.07 %, 1.12 % and 1.32 %.

Sediment samples of mud volcanoes from the landward areas of the Kura Basin, Up. Akhtrama-Pashaly and Khamamdad show main vitrinite populations between 0.58 and 0.60% Rr. The ejected sediments of Up. Akhtrama-Pashaly (#0711449) and Khamamdad (#0711428) contain also sediments with vitrinite populations around 0.42 and 0.47% Rr. The observed low mature particles may be explained as particles dragged along from younger sediments during mud extrusion.

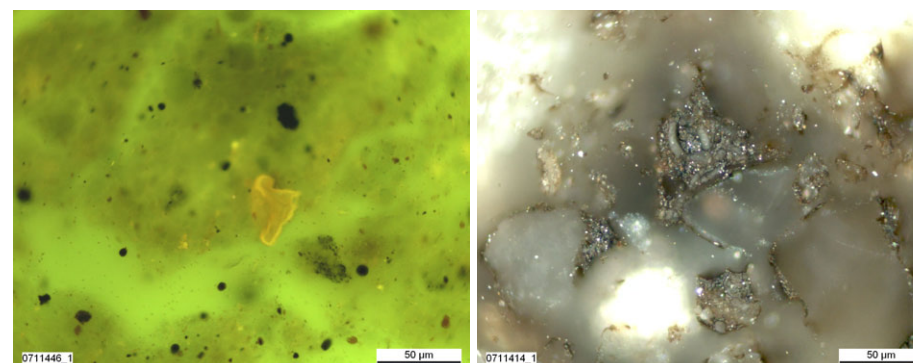


Fig. 6

Left: #0711446 (fluorescing light); yellow fluorescing pollen of sediments of Dashgil (Kura Basin); right #0711414 (normal light); porous and pyrite containing humodetrinite of sediments of Duvanny Island (Kura Basin).

The major vitrinite components at Duvanny (#0711414) and Bulla Islands (#0711411) of 0.49 and 0.61 % Rr, respectively, indicate sediments which have reached oil window maturities. We observe in both sediments low mature vitrinite particles, which may be explained as particles dragged along from younger sediments during mud extrusion. However, either re-deposition of organic particles or admixtures of sediments, which were transported from greater depths and higher maturities, can explain the high mature vitrinite population at Bulla Island (#0711411) of about 0.98 %.

Organic-geochemical characterization

Based on total sulphur and total organic carbon contents most of the sediments can be classified as anoxic marine deposits whereas only few are sediments of a lacustrine environment (Berner & Raiswell, 1983). Hydrogen and oxygen indices derived from RockEval pyrolyses suggest that the organic matter of the sediments consist mostly of mixtures of Type II and III kerogens (Espitalié et al., 1977; Lafargue et al., 1998).

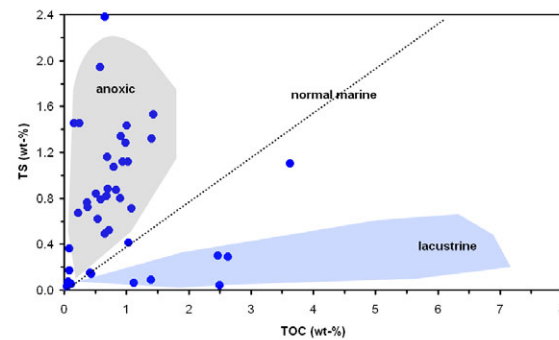


Fig. 7

Total sulfur (TS) and total organic carbon (TOC) in samples of mud volcanoes of Azerbaijan (classification after Berner & Raiswell, 1983).

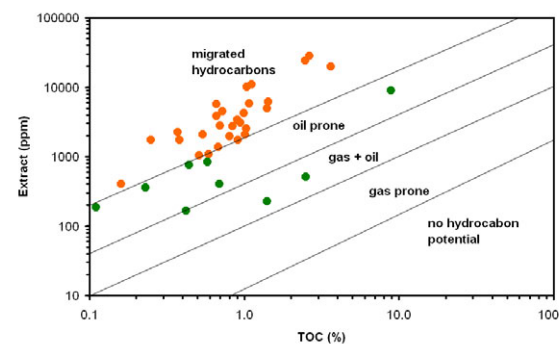


Fig. 9

Total organic carbon (TOC) and amounts of extractable hydrocarbons (ppm related to sediment weight) of samples of mud volcanoes of Azerbaijan (orange: impregnated).

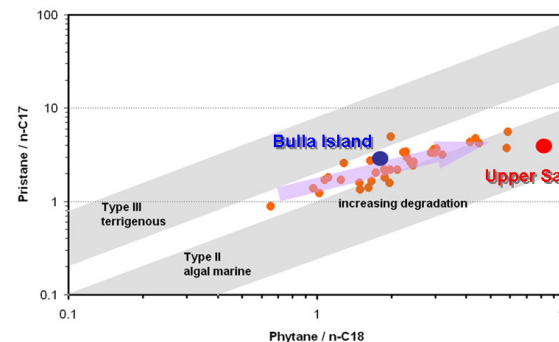


Fig. 10

Ratios of phytane over n-C18 and pristane over n-C17 of samples of mud volcanoes of Azerbaijan (classification after Peters et al., 2005).

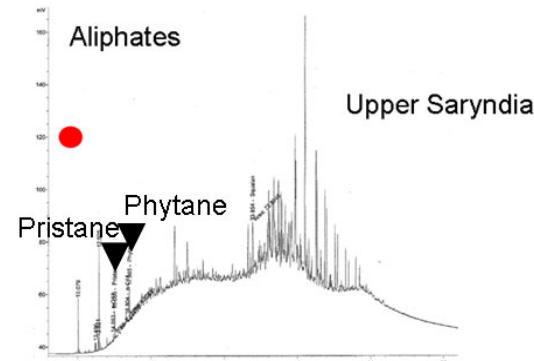
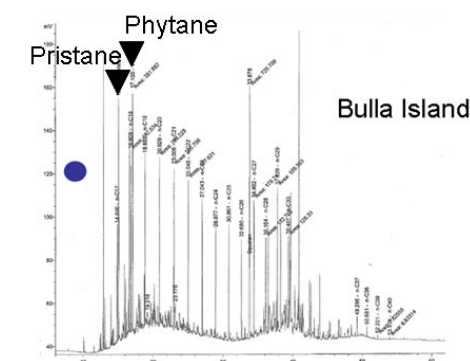
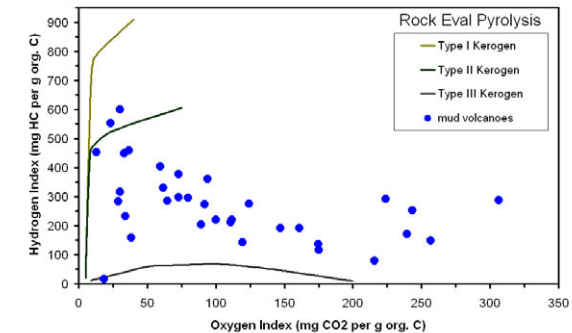


Fig. 11

Gas chromatographic traces of the aliphatic fraction of two samples of mud volcanoes of Azerbaijan – left: moderate biodegradation; right: severe biodegradation.

Fig. 8

Oxygen and hydrogen indices of samples of mud volcanoes of Azerbaijan (after Espitalié et al., 1977; Lafargue et al., 1998).



The amounts of extractable hydrocarbons in relation to total organic carbon show that rock samples have been impregnated by allochthonous hydrocarbons. This finding suggests that the type characterization derived from RockEval pyrolyses (s. above) must be treated with caution.

Phytane/n-C18 and pristane/n-C17 data support the previous interpretation of contributions from Type II and III kerogens to the extracted hydrocarbons, but also suggest that secondary processes have affected the aliphatic hydrocarbons. Biodegradation seems to be the likely process as can be seen from the chromatographic traces. Examples are given in Fig. 11, extracts of Bulla Island are less affected by biodegradation than is the extract of Up. Saryndja.

The aliphatic and aromatic extract fractions of all samples have been analyzed for stable carbon isotope ratios. The carbon isotopes clearly indicate a predominance of aquatic organic matter (Fig. 12). The isotope ratios of the aromatic fractions show similarities with published isotope ratios of source rock extracts of the Maikop Formation (Abrams and Narimanov, 1997), which suggests that the Maikop Fm. might be a likely source rock for the hydrocarbons of investigated samples.

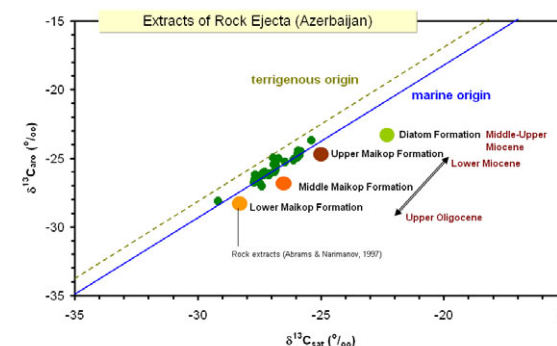


Fig. 12

Stable carbon isotope values of the aliphatic and aromatic extract fractions of two samples of mud volcanoes of Azerbaijan (classification after Sofer, 1984; source rock data after Abrams & Narimanov, 1997).

Mixing between different source types (different aquatic as well as terrestrial) seems likely based on iso-steranes C27 to C29 (Fig. 13). Sterane concentrations fall within the field of aquatic organic matter, and the amounts of C29 iso-steranes are comparatively low and tend towards the diatome-field, which suggest that the aquatic matter may be partly influenced by diatome organic matter. This interpretation compares well with carbon isotope ratios of the extracts (Fig. 12) and is plausible in the light of the geological observations, which show (Fig. 3) deposition of diatomitic sediments during Miocene (especially during lower Upper Miocene).

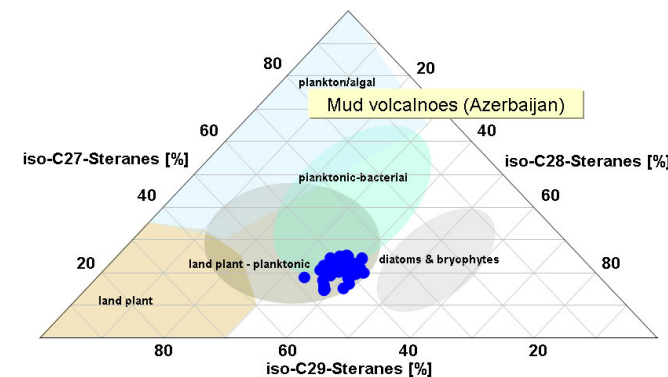
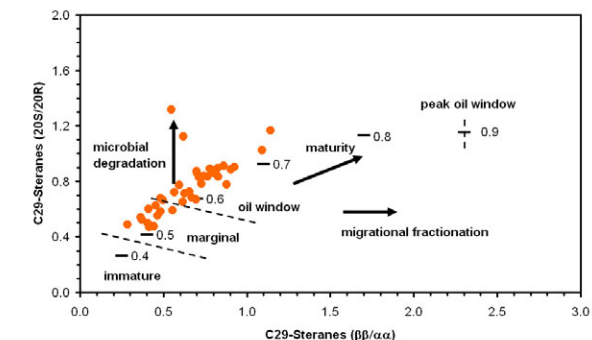


Fig. 13

Distribution of sterane isomers of samples of mud volcanoes of Azerbaijan (classification modified after Peters et al., 2005).

Ratios of sterane biomarkers of samples of mud volcanoes of Azerbaijan indicate varying maturities but also degradation effects on at least two samples (compare Peters et al., 2005).

Fig. 14



C29-sterane ratios (20S/20R as well as bb/aa) suggest that the extracted hydrocarbons come from a coalification range of the early oil window. Homohopane isomerization ratios as well as the ratio of trisnorhopane over trisnorhopane support this finding. The influence of microbial degradation is obvious on the 20S/20R ratios of two samples (Fig. 14).

However, vitrinite reflectance of the main sediment components of the rock ejecta indicate a similar range of maturities as suggested from biomarker analyses (Fig. 15). A direct comparison between vitrinite reflectance data and biomarker maturities shows again (compare Fig. 9) that most of the investigated rocks have been impregnated by allochthonous hydrocarbons as biomarker derived maturities may depart from the measured reflectance values (Fig. 15).

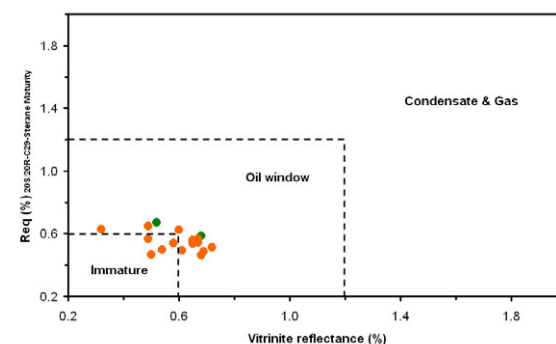
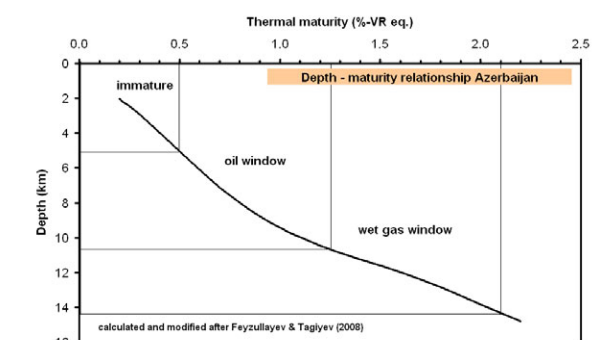


Fig. 15

Thermal maturities calculated from sterane biomarker ratios (%-Rr) of samples of mud volcanoes of Azerbaijan (orange: impregnated).

Relationship between sedimentary depth and thermal maturities (graph calculated from data of Feyzullayev & Tagiyev, 2008).

Fig. 16

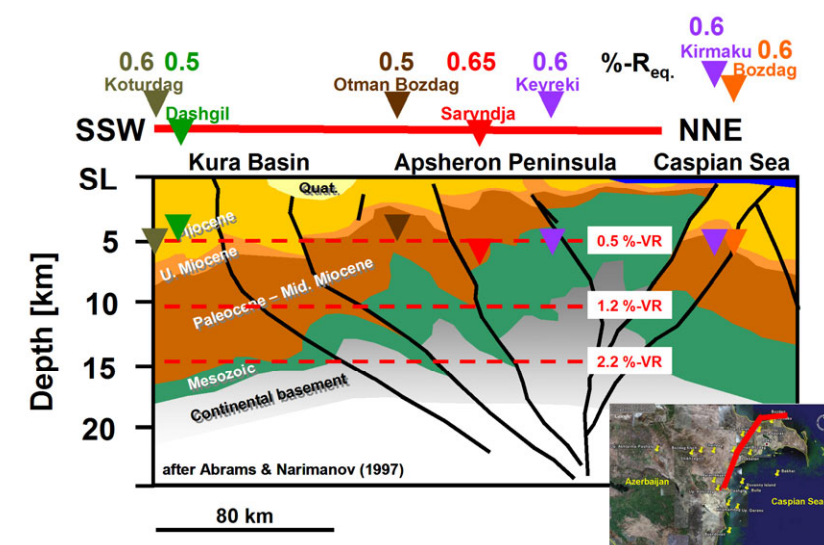


Published data of the South Caspian Basin suggests (Fig. 16) a nearly linear relationship between thermal maturity and sediment depth, however, a change of the trend is obvious at depths greater 9 km.

We have used biomarker maturities to calculate the possible depth ranges from which the hydrocarbons have been generated. Along the SSW – NNE profile we find that at Koturdag and Dashgill upper Lower Pliocene hydrocarbon sources are plausible, whereas at Otman Bozdog sediments of the Middle to Lower Maikop Fm. must be envisaged as likely sources. At Saryndia we suggest a Lower Maikop Fm. source and at Keyreki even Mesozoic sediments seem to be plausible hydrocarbon sources. At Kirmaku and Bozdog likely sources could be related to the Upper Maikop Fm.

Fig. 17

Thermal maturities (% vitrinite reflectance equivalent) calculated from sterane biomarker ratios of extracted hydrocarbons of ejected sediments of mud volcanoes of Azerbaijan.



Conclusions

Elemental analyses classify most of the sediments as anoxic marine deposits whereas only few are sediments of a lacustrine environment. Hydrogen and oxygen indices derived from RockEval pyrolyses indicate that the organic matter of the sediments consist mostly of mixtures of Type II and III kerogens. The amounts of extractable hydrocarbons in relation to organic carbon contents indicate that most of the sediment samples are impregnated by migrated hydrocarbons. The data also suggests that the hydrocarbon generation potential of autochthonous organic matter ranges from oil to oil/gas prone. All extracted hydrocarbons have been affected by secondary alterations that most likely involved biodegradation as the normal alkanes have partly been removed from the aliphatic fraction.

Despite of biodegradation, source and maturity sensitive biomarkers are present. Sterane isomers suggest a dominance of aquatic organic matter, supported by the carbon isotopic composition of aliphatic and aromatic extract fractions. C29-sterane ratios (20S/20R as well as bb/aa) suggest that the extracted hydrocarbons come from a coalification range, which covers the early oil window.

Vitrinite reflectance measurements on the ejected rocks indicate a similar range of maturities as suggested from biomarker analyses. However, the data indicate again that most of the investigated rocks have been impregnated by allochthonous hydrocarbons as biomarker maturities may slightly depart from the measured reflectance values.

We estimated from a maturity/depth conversion, using biomarkers as maturity indicators that the mud volcanoes along a SSW-NNE transect from the Kura Basin to the Apsheron Peninsula produce associated hydrocarbons from a depth range of 5 to 6.5 km. Likely hydrocarbon sources, which contributed to the extracts of the ejected rocks are of Mesozoic to Lower Pliocene age. However, presently, a basin modeling approach, incorporating additional data, is conducted in order to better describe hydrocarbon generation within the area of investigation.

Acknowledgements

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